Ferrocenephosphonates: Copper-Promoted Synthesis and Further Functionalization

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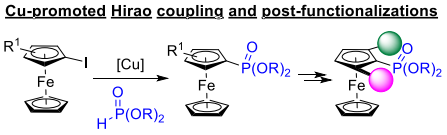


Abstract Ferrocenephosphonates are an important class of organometallic derivatives with a wide range of useful applications in organic synthesis and coordination chemistry. Here, an approach to ferrocenephosphonates based on a copper-promoted Hirao coupling is reported. Further functionalization based on regioselective deprotolithiation and both Negishi and Suzuki-Miyaura cross-coupling reactions is also described to reach original derivatives.

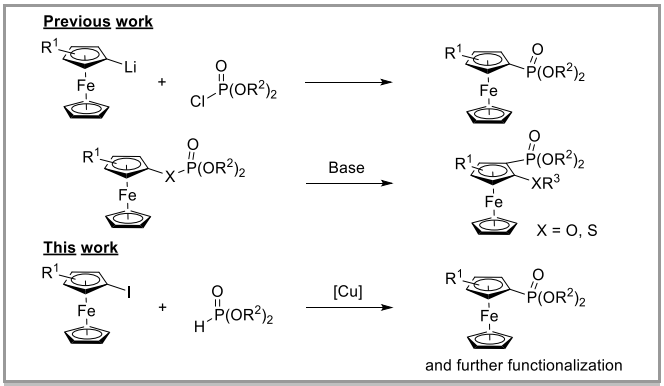
Key words Ferrocene, Phosphonate, Copper, Cross-coupling, Deprotolithiation

Since the serendipitous discovery of ferrocene by Pauson and Miller,[1] its derivatives have found applications in all areas of chemistry.[2] Among all of the ferrocene compounds, ferrocenephosphonates represent an important class of molecules. Indeed, they are suitable substrates for preparing various metal complexes,[3] and they can easily be subjected to functional group transformations leading to many other valuable compounds. For instance, their hydrolysis furnishes the corresponding ferrocenephosphonic acids,[3a,4] used as precursors of metal complexes[5] or as redox-active polymerization catalysts.[6] On the other hand, their reduction represents a practical access to primary phosphines,[7] and therefore to original phosphorus-based functional groups[8] and ligands for catalytic transformations.[7a,9]

The main approach toward ferrocenephosphonates relies on the reaction of a lithiated ferrocene, prepared either by deprotolithiation using *t*BuLi,[10] *t*BuLi-*t*BuOK mixtures[11] and the *n*BuLi·TMEDA chelate[12] or by halogen/lithium exchange,[13] with the required chlorophosphate (Scheme 1, top). By using these methodologies, a few monosubstituted,[3a,3c,4,14] 1,1'-,[3b,3c,5,7a,9a,14c] 1,2-[3c,7b,7d] and 1,3-disubstituted[15] ferrocenephosphonates have been prepared. Extensions to azaferrocene[16] as well as ruthenocene and biferrocene frameworks[8b] have also been documented. A complementary approach to the 2-thiohydroxy- and 2-hydroxyferrocenephosphonate derivatives relies on the anionic phospho-Fries rearrangement[17] initially reported by Bonini[18] and well-studied by Lang (Scheme 1, middle).[9b,9c,19]

Recently, Budnikova reported an original approach toward ferrocenephosphonates based on the electrochemical reduction of ferrocene[20] while Wang described the silver-mediated C-H activation of some ferrocenecarboxamides.[21]

A classical approach to arylphosphonates relies on the metal-catalyzed C-P bond formation from aromatic halides. Initially reported by Hirao using palladium complexes,[22] the reaction was extended to the use of more sustainable nickel and copper catalysts.[23] Given the usefulness of halogenoferrocenes in cross-coupling reactions,[24] it is surprising that the Hirao coupling has never been reported in the ferrocene series. In fact, a nickel-catalyzed version of this coupling from 1,1'-dibromoferrocene was mentioned once by Chan and Luh in a scheme, but it was not further described.[25] Considering our recent interest in copper-promoted reactions of iodoferrocenes,[26] our attention has recently focused on extending the Hirao coupling to the ferrocene series (Scheme 1, bottom).

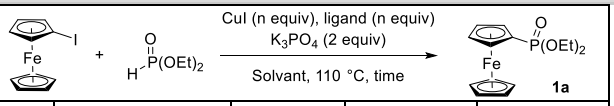


Scheme 1 Approaches toward ferrocenephosphonates.

In the benzene series, the synthesis of phosphonates from aryl iodides has been described by using various catalytic systems often composed of copper(I) iodide and a ligand (diamines,[27]

pyrolidine,[28] or also carboxamides[29]), and sometimes copper salts without additional ligand.[30] We decided to start our study with reaction conditions inspired from the work of Buchwald.[27a] Thus, we reacted iodoferrocene with diethylphosphite in the presence of copper(I) iodide, *N*,*N*'-dimethylethylenediamine (DMEDA) and cesium carbonate in toluene. Pleasingly, *O*,*O*-diethylferrocenephosphonate (**1a**) was isolated in an encouraging 38% yield (Table 1, entry 1). Instead of cesium carbonate, the use of tripotassium phosphate as the base resulted in a better yield (entry 2), which was further slightly improved when dioxane was used as the solvent (entry 3). We then briefly varied the reaction conditions by using another copper source (entry 4) and other ligands (entries 5-7), but without improving the results. Increasing the amount of catalyst had no effect (entry 8) while significant drop in yield was observed by reducing the catalytic loading to 10 mol% (entry 9). Better results were recorded by using 25 mol% of copper iodide and DMEDA, and increasing the reaction time to 24 h resulted in the isolation of compound **1a** in 61% yield (entry 10). A better compromise between catalytic loading (50 mol%) and reaction time (14 h) was finally reached (entry 11). Pleasingly, these optimized reaction conditions also allowed the coupling of bromoferrocene in 51% yield. It is worth noting that carrying out these reactions under inert conditions is mandatory; indeed, working in air reduced the yield of ferrocene **1a** from 73 to 20%.

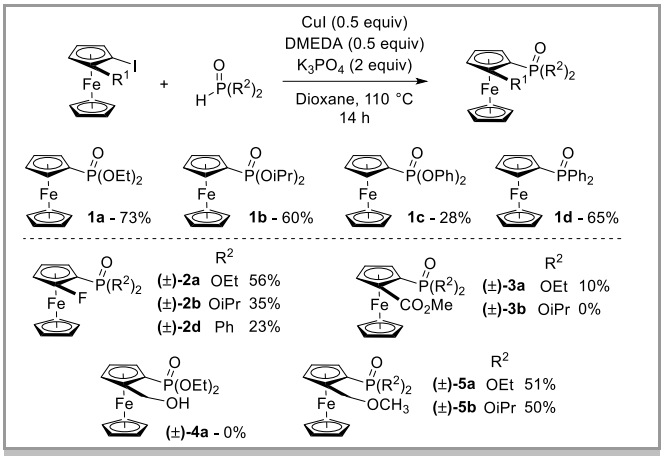
Table 1 Optimization of the Cu-promoted Hirao coupling from iodoferrocene.



Entry	Ligand (n equiv)	Solvent	Time (h)	Yield (%)
1[a]	DMEDA (1)	Toluene	14	38
2	DMEDA (1)	Toluene	14	57
3	DMEDA (1)	Dioxane	14	63
4[b]	DMEDA (1)	Dioxane	14	45
5	Proline (1)	Dioxane	14	15
6	Phenanthroline (1)	Dioxane	14	21
7	/	DMSO	14	39
8	DMEDA (1.5)	Dioxane	14	66
9	DMEDA (0.1)	Dioxane	14	26
10	DMEDA (0.25)	Dioxane	14 - 24 - 48	39 - 61 - 63
11	DMEDA (0.5)	Dioxane	14	73 (51)[c]

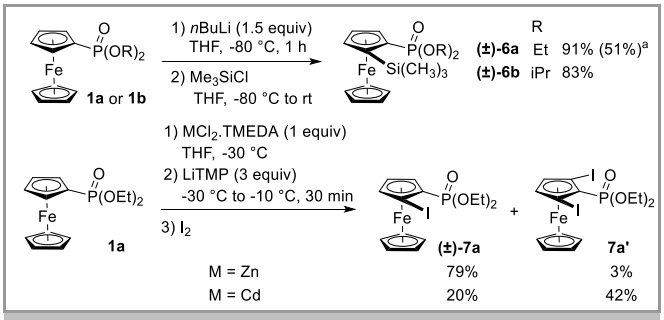
[a] Cs_2CO_3 was used instead of K_3PO_4. [b] Cu_2O was used instead of CuI.
[c] Bromoferrocene was used instead of iodoferrocene.

Once the reaction conditions were optimized, we evaluated the scope of this cross-coupling by first looking at the nature of the phosphorus partner (Scheme 2). The use of diisopropylphosphite gave a slightly reduced yield (compound **1b**, 60% yield) while diphenylphosphite afforded *O*,*O*-diphenylferrocenephosphonate (**1c**) in a low 28% yield. However, it is difficult to rationalize this last result as this reagent has never been tested in a copper-catalyzed Hirao coupling. We were then interested to see if the reaction could be extended to phosphine oxides and therefore reacted iodoferrocene with diphenylphosphine oxide. As observed by others,[28a] the reaction was slightly less efficient, leading to the ferrocene derivative **1d** in 65% yield. A few 2-susbtituted iodoferrocenes were finally involved in the coupling. As already observed during the copper-promoted synthesis of acetamidoferrocenes,[26b] the introduction of a fluorine atom next to the iodine resulted in reduced yields for compounds **(±)-2a,b** and **d** while the presence of an ester group almost prevented the reaction as only the *O*,*O*-diethylphosphonate derivative **(±)-3a** was isolated in 10% yield. A hydroxymethyl group also stopped the coupling, probably due to a reaction between the alcohol and a catalytically active species. Indeed, when the methyl ether derivative was tested, the ferrocenes **(±)-5a** and **(±)-5b** were obtained with yields of 51 and 50%, respectively. Pleasingly, it was possible to scale up the synthesis of **1b** to 5 mmol with good results (83% yield).



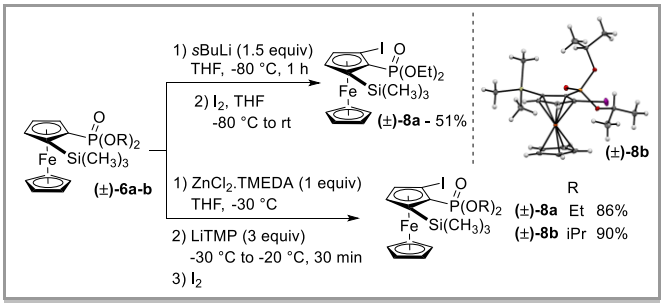
Scheme 2 Scope of the Cu-promoted Hirao coupling from iodoferrocenes.

In the literature, there are only a few examples of ferrocenephosphonate functionalization taking advantage of the *ortho*-directing properties of the phosphonate group. Indeed, Jurkshat reported a set of substituted *O*,*O*-diisopropylferrocenephosphonate derivatives, obtained by deprotolithiation using *t*BuLi or the *n*BuLi·TMEDA chelate (TMEDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine)[3c,15,31] while Korb recently used similar reaction conditions to functionalize *O*,*O*-diethylferrocenephosphonate.[7d] In our hands, we have found that the less expensive *n*BuLi can be used in tetrahydrofuran (THF) in the same way to perform these deprotolithiation-electrophilic trapping sequences, affording the silylated derivatives **(±)-6a-b** in yields of 91 and 83%, respectively (Scheme 3). Although ferrocenephosphonates are compatible with the use of lithium amides,[9b,9c,19a] their deprotolithiation in the presence of an external *in situ* trap[32] has never been reported. Therefore, we treated a mixture of compound **1a** and $ZnCl_2$·TMEDA in THF at -30 °C with LiTMP (TMP = 2,2,6,6-tetramethylpiperidino) before iodolysis, and isolated the desired 2-iodinated derivative **(±)-7a** in 79% yield, together with 3% of *O*,*O*-diethyl-2,5-diiodoferrocenephosphonate (**7a'**). Pleasingly, it was possible to increase the reaction scale up to 5 mmol with close results (yields of 62 and 4% for the compounds **(±)-7a** and **7a'**, respectively). In order to favor the one-step formation of **7a'**, we replaced $ZnCl_2$·TMEDA by $CdCl_2$·TMEDA as the *in situ* trap,[33] and obtained **(±)-7a** and **7a'** with yields of 20 and 42%, respectively.



Scheme 3 Synthesis of 2-substituted ferrocenephosphonates. [a] 1.2 equiv of *n*BuLi used.

In order to reach hetero-1,2,3-trisubstituted ferrocenes, the remaining position next to the phosphonate directing group of compounds **(±)-6a-b** was functionalized by a sequence of deprotolithiation-electrophilic trapping sequence using iodine (Scheme 4). However, when *n*BuLi was employed in the first step, the expected product **(±)-8a** was only isolated in 22% yield. While the use of the *n*BuLi·TMEDA chelate did not change the reaction outcome (23% yield), the more reactive *s*BuLi afforded up to 51% of compound **(±)-8a**. As the rest of the material was the unreacted substrate, we also carried out the deprotolithiation in the presence of $ZnCl_2$·TMEDA as an *in situ* trap to improve the conversion and were able to isolate **(±)-8a** in 86% yield. By using similar reaction conditions, *O*,*O*-diisopropylferrocenephosphonate (**(±)-8b**) was obtained in 90% yield.

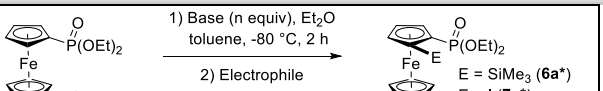


Scheme 4 Synthesis of the 1,2,3-trisubstitued ferrocenes **(±)-8a-b**.

We next briefly evaluated the behavior of *O*,*O*-diethyl-2-iodo-5-(trimethylsiylyl)ferrocenephosphonate (**(±)-8a**) in the 'halogen dance' reaction, a stability-driven isomerisation promoted by lithium amides,[34] recently studied in the ferrocene series.[33b,35] However, when **(±)-8a** was subjected to standard reaction conditions (LiTMP (1.1 equiv) in THF at -50 °C), we did not observe the formation of the expected isomerized 3-iodinated derivative and **(±)-8a** was recovered. Carrying out the reaction at -20 °C led to a mixture of unidentified products which raised the question of the stability of compound **(±)-8a**. Consequently, we did not pursue our investigations.

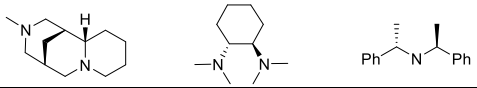
The asymmetric deprotometalation of a ferrocene substituted by a phosphorus group was independently attempted by Simpkins, Bonini and Lang. The former used (*R*)-PEALi (PEA = bis(α-phenylethyl)amino) to deprotometalate *P*,*P*-diphenylferrocenephosphoxide in the presence of chlorotrimethylsilane as an *in situ* trap toward the corresponding 2-silylated derivative, isolated in 95% and 54% ee.[36] During studies on the anionic phospho-Fries rearrangement, Bonini used the *s*BuLi·(-)-sparteine chelate,[18] while Lang employed (*R*)-PEALi in the deprotolithiation step.[9c] However, both faced low enantioselectivities of the resulting phosphonates (<5 and 9%, respectively). As similar reactions were never attempted from ferrocenephosphonates, we subjected compound **1a** to the action of various chiral bases before trapping the lithiated intermediate with a suitable electrophile (Table 2). As both *n*BuLi·(-)-sparteine and *n*BuLi·(+)-sparteine surrogate chelates were used successfully for the enantioselective deprotometalation of ferrocenecarboxamides,[37] they were initially evaluated. However, when compound **1a** was subjected to the action of *n*BuLi·(+)-sparteine surrogate in a diethyl ether-toluene mixture, the expected 2-silylated ferrocene **6a*** was obtained in low yield and enantioselectivity after trapping with chlorotrimethylsilane (entry 1). The use of the *n*BuLi·(*R*,*R*)-TMCDA chelate (TMCDA = *N*,*N*,*N*',*N*'-tetramethylcyclohexane-1,2-diamine), successfully used in the synthesis of non-racemic (aminomethyl)ferrocenes,[38] has not afforded better results in our hands (entry 2). When the more reactive *s*BuLi was evaluated, a better yield of product **6a*** was recorded in the presence of (+)-sparteine surrogate, but without effect on the enantiomeric ratio (entries 3 and 4). We have previously demonstrated that the use of a chiral zinc amide as an *in situ* trap in combination with a chiral lithium amide in THF makes it possible to obtain an enantioenriched product with moderate to good enantioselectivities.[35e, 39] However, when adding of (*S*)-PEALi to a mixture of substrate **1a** and [{(*S*)-PEA}$_2$Zn] (*in situ* prepared from $ZnCl_2$·TMEDA and (*S*)-PEALi in a 1:2 ratio) at -80 °C before warming to -20 °C and iodolysis, we only obtained the desired product **7a*** in 4% yield (entry 5). As we recycled 89% of the starting material, the reaction was carried out at a higher temperature, however still with little improvement in yield and enantioselectivity (entry 6). Taken together, these results show the challenge that asymmetric deprotolithiation of ferrocenephosphonates still represents.

Table 2 Attempts of enantioselective deprotolithiation of compound **1a**.



Entry	Base	E	Yield (%)	er
1	*n*BuLi·(+)-sparteine surrogate (1.5)	$SiMe_3$	24	63:37
2	*n*BuLi·(*R*,*R*)-TMCDA (1.5)	$SiMe_3$	30	36:64
3	*s*BuLi·(+)-sparteine surrogate (1.5)	$SiMe_3$	53	60:40
4	*s*BuLi·(*R*,*R*)-TMCDA (1.5)	$SiMe_3$	33	36:64
5[a,b]	(*S*)-PEALi (1) with [{(*S*)-PEA}$_2$Zn] (2)	I	4	46:54
6[a,c]	(*S*)-PEALi (1) with [{(*S*)-PEA}$_2$Zn] (2)	I	17	53:57

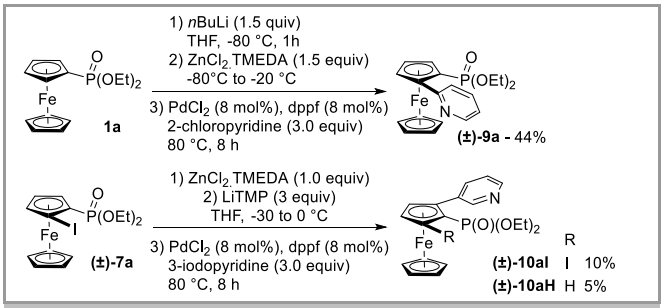
(+)-Sparteine surrogate (*R*,*R*)-TMCDA (*S*)-PEA



[a] The reaction was performed in THF instead of Et_2O-toluene. [b] The first step was performed from -80 to -20 °C over 8 h. [c] The first step was performed from -30 to -10 °C over 1 h.

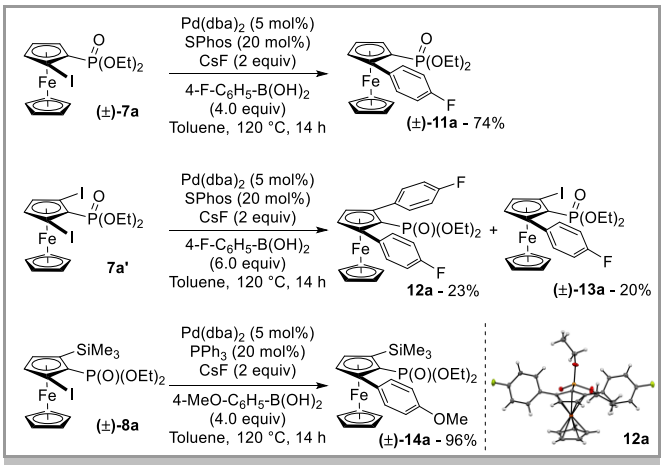
As 2-aryl-substituted ferrocenephosphonates have never been reported, we were eager to see if such compounds could be reached by cross-coupling reactions. Therefore, the compound **1a** was first deprotolithiated by *n*BuLi before adding $ZnCl_2$·TMEDA to perform the transmetalation from a lithium to a zinc species. A Negishi cross-coupling reaction[40] was then attempted with 2-chloropyridine in the presence of palladium(II) chloride and 1,1'-bis(diphenylphosphine)ferrocene (dppf),

leading to the product **(±)-9a** in 44% yield (Scheme 5). We recently demonstrated that a 3-iodoferrocenezinc derivative can selectively react with another halogenated partner in a Negishi cross-coupling.[35d] Therefore, we were eager to see if similar orthogonal reactivity could be achieved from the compound **(±)-7a**. To avoid iodine/lithium exchange, the deprotometalation was carried out with an excess of LiTMP in the presence of $ZnCl_2$·TMEDA before coupling with 3-iodopyridine. However, degradation was mainly observed and we only managed to obtain an inseparable mixture of the compounds **(±)-10aI** and **(±)-10aH** in 10 and 5% yield, respectively. The latter might result either from a competitive iodine/lithium exchange[35a-c,41] from **(±)-7a** during the deprotolithiation step followed by coupling, or from a direct coupling between **(±)-7a** and 3-iodopyridine.[42]



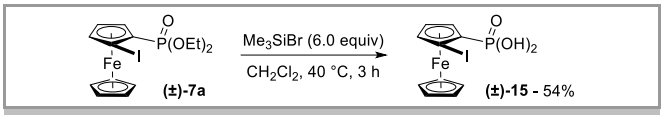
Scheme 5 Negishi cross-couplings in the ferrocenephosphonate series.

Then, we engaged some of our new iodoferrocene derivatives in a Suzuki-Miyaura cross-coupling reaction[43] in the presence of $Pd(dba)_2$ (dba = dibenzylideneacetone), a suitable ligand, and cesium carbonate (Scheme 6). The reaction between compound **(±)-7a** and the electron-deficient 4-fluorophenylboronic acid required the use of 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) as a ligand,[44] and afforded the desired product **(±)-11a** in 74% yield. A double arylation reaction was next attempted under similar conditions from the 1,2,3-trisubstituted ferrocene **7a'**. It gave the expected product **12a** (23% yield) as well as the mono-arylated derivative **(±)-13a** (20% yield) and some starting material (19% recovery). The coupling of the ferrocene **(±)-8a** with 4-methoxyphenylboronic acid was finally performed in the presence of triphenylphosphine as ligand to deliver the product **(±)-14a** in 96% yield. From the same substrate **(±)-8a**, both C-O and C-N bound formations were attempted under reported reaction conditions,[26a,37d] but without any success (not shown).



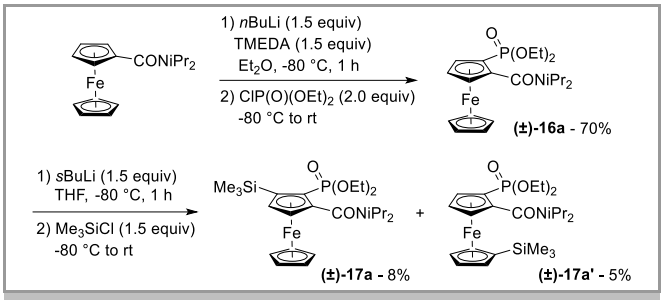
Scheme 6 Suzuki-Miyaura cross-couplings in the ferrocenephosphonate series.

As mentioned earlier, ferrocenephosphonates can be hydrolysed to the corresponding phosphonic acids. However, to our knowledge, only ferrocenephosphonic acid and 1'-substituted ferrocenephosphonic acids have been reported in the literature so far. As the presence of a substituent next to the phosphonate would help to tune its steric and acidic properties,[45] we subjected the ferrocene **(±)-7a** to the action of an excess of bromotrimethylsilane. After 3 h at 40 °C, the expected 2-iodoferrocenephosphonic acid (**(±)-15**) was easily isolated in 54% yield (Scheme 7).



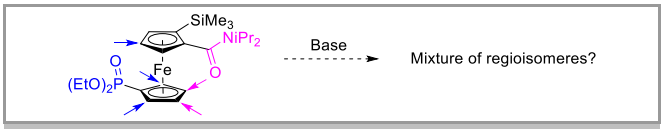
Scheme 7 Synthesis of 2-iodoferrocenephosphonic acid (**(±)-15**).

In his seminal work on the enantioselective functionalization of *N*,*N*-diisopropylferrocenecarboxamide, Snieckus showed that the introduction of a trimethylsilyl group next to this bulky carboxamide was able to reroute a subsequent deprotolithiation toward the unsubstituted cyclopentadienyl (Cp) ring.[37a] A similar behavior has also been reported from 2-trimethylsilylferroeneoxazolidines,[46] and this remote deprotolithiation has recently been applied to the synthesis of 1'-iodoferrocene derivatives.[47] Therefore, we were eager to see if a phosphonate, when positioned next to a carboxamide, would play its role of *ortho*-directing group or if remote functionalization of the unsubstituted Cp ring was reachable. Thus, *N*,*N*-diisopropylferrocenecarboxamide was engaged in a deprotolithiation-electrophilic trapping sequence toward the 1,2-disubstituted ferrocene **(±)-16a**, isolated in 70% yield (Scheme 8). When this substrate was reacted with *s*BuLi before addition of chlorotrimethylsilane as an electrophile, the isomeric products **(±)-17a** and **(±)-17a'** were isolated in low yields. As we found that the substrate **16** was prone to degradation, it was therefore difficult to draw a clear conclusion concerning the directing group ability of a phosphonate when adjacent to a carboxamide.

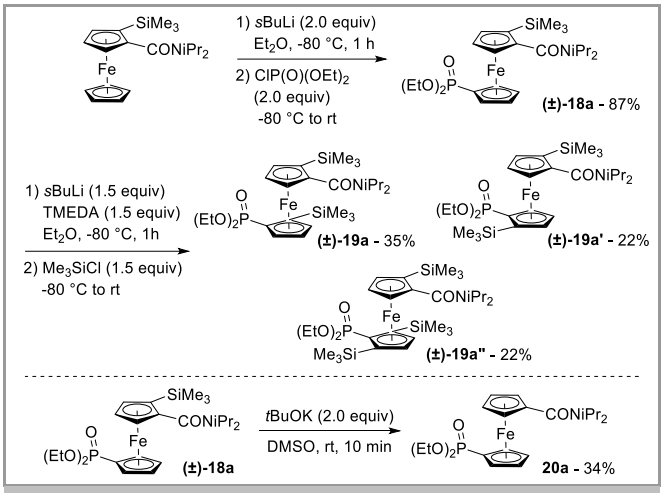


Scheme 8 Regioselectivity study of the deprotolithiation of the substrate **(±)-16a**.

We finally got interested in the functionalization of a substrate bearing a carboxamide and a trimethylsilyl group at adjacent positions of the same Cp ring and a phosphonate on the other. Indeed, the two directing groups are expected to be far from each other to minimize steric repulsion, and with their respective C=O and P=O bonds pointing in opposite directions, each toward the other Cp ring. In this situation, the phosphonate might favor the deprotolithiation of its adjacent positions, but also of at least one of the remaining positions of the disubstituted Cp ring (Scheme 9). In addition, the carboxamide could direct deprotolithiation of a position remote from the phosphonate on the monosubstituted Cp ring. Therefore, (±)-*N*,*N*-diisopropyl-2-trimethylsilylferrocenecarboxamide was engaged in a deprotolithiation-electrophilic trapping sequence to deliver the required substrate **(±)-18a** in 87% yield (Scheme 10, top). When it was reacted with the *n*BuLi·TMEDA chelate at -80 °C in THF, before addition of chlorotrimethylsilane as an electrophile, the isomers **(±)-19a** and **(±)-19a'** were isolated with respective yields of 23 and 11% (not shown). Their structures were studied in solution by two-dimensional NMR spectroscopy which proposed, for the isomer **(±)-19a'**, the same structure as revealed by X-ray diffraction analysis (Figure 1). When *s*BuLi was used instead of *n*BuLi under similar reaction conditions, the same products were obtained in a similar ratio together with the trisilylated product **(±)-19a"**, isolated in 22% yield. Taken together, these results tend to indicate that, on this substrate, the phosphonate acts mainly as a regular *ortho*-directing group. We finally prepared the 1,1'-disubstituted ferrocene **20a** from the ferrocene **(±)-18a** by removing the trimethylsilyl group using *t*BuOK in DMSO (Scheme 10; bottom).[48] However, although complete conversion was achieved within 10 min at rt, the product **20a** was only isolated in 34% yield due to decomposition.



Scheme 9 Potential regioselectivity issues during the phosphonate- (blue arrows) and carboxamide- (purple arrows) directed deprotolithiation of the substrate **(±)-18a**.



Scheme 10 Synthesis and functionalization of the trisubstituted ferrocene **(±)-18a**.

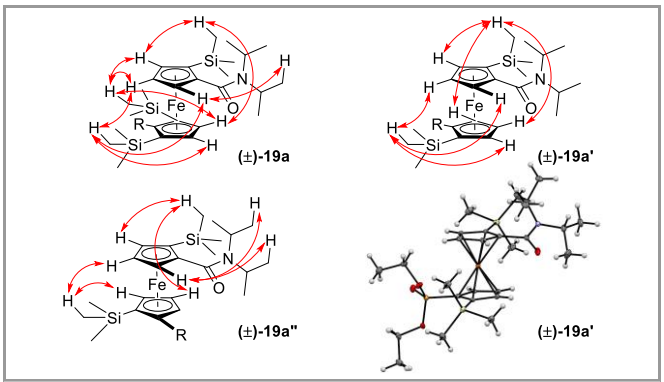


Figure 1 Putative preferred conformations of the ferrocenes **(±)-19a,a',a"** in solution and solid-state structure of the ferrocene **(±)-19a'**. R = P(O)(OEt)$_2$.

In conclusion, we have reported the first copper-promoted Hirao coupling in the ferrocene series. Considering the better availability and reduced toxicity of dialkylphosphites when compared with chlorophosphates, this approach toward *O,O*-dialkylferrocenephosphonates appears complementary to the synthetic routes already reported in the literature. While the enantioselective deprotolithiation of ferrocenephosphonates currently remains an unmet challenge, various polysubstituted derivatives have been prepared as racemates by merging deprotolithiation-electrophilic trapping sequences and cross-coupling reactions. Together with the already reported studies on ferrocenephosphonates, this work lays the foundation for a deeper understanding of their reactivities and properties for potential applications.

General Considerations. Coupling reactions and deprotolithiation experiments were performed under argon using anhydrous solvents and Schlenk technics. THF and Et_2O were distilled under argon over Na/benzophenone. Toluene, dioxane and dichloromethane were distilled over CaH_2 under argon prior to use. Dimethylsulfoxide was distilled over CaH_2 under reduce pressure prior to use. 2,2,6,6-Tetramethylpiperidine was distilled over CaH_2 under reduced pressure and stored over KOH pellets. TMEDA was distilled over CaH_2 under argon and stored over KOH pellets. Unless otherwise stated, the reagents were used without prior purification. Butyllithium reagents were titrated before use.[49] Room temperature (rt) refers to 25 °C. Column chromatography separations were achieved on silica gel (40-63 µm). All TLC analyses were performed on aluminum-backed plates precoated with silica gel (Merck, Silica Gel 60

F254). They were visualized by exposure to UV light. PE refers to petroleum ether. Melting points were measured on a Kofler bench. IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra were recorded on a Bruker AV III HD spectrometer fitted with a BBFO probe at 500 MHz, 126 MHz, 202 MHz and 282 MHz, respectively. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[50] Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. The numbering used in this experimental section is defined in the Supporting Information.

Iodoferrocene,[51] (±)-1-fluoro-2-iodoferrocene,[35b] (±)-2-iodo-*O*-methylferrocenecarboxylate,[33b] (±)-1-iodo-2-(methoxymethyl)ferrocene,[26b] (±)-*N*,*N*-diisopropyl-2-(trimethylsilyl)ferrocenecarboxamide,[47] $ZnCl_2$·TMEDA[52] and $CdCl_2$·TMEDA[53] were prepared as reported previously.

Procedures

General Procedure for the Cu-Catalyzed C-P Bond Formation:

The iodoferrocene (1.0 mmol, unless otherwise specified in the product description), CuI (95 mg, 0.50 mmol) and K_3PO_4 (0.42 g, 2.0 mmol) were introduced in a degassed (argon) Schlenk tube then subjected to three vacuum/argon cycles. Dioxane (2 mL), the phosphorus reagent (1.1 mmol) and *N*,*N*′-dimethylethylenediamine (DMEDA; 50 µL, 0.50 mmol) were next introduced under argon, and the mixture was heated at 110 °C for 14 h in a pre-heated oil bath. It was then allowed to cool to rt before addition of water (10 mL). Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and evaporation of the solvent under reduced pressure led to the crude, which was purified by chromatography over silica gel (the eluent is given in the product description).

***O*,*O*-Diethylferrocenephosphonate (1a)**

[CAS Reg. No. 399043-67-5]

By following the general procedure, using iodoferrocene (0.31 g) and diethylphosphite (0.14 mL), product **1a** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as an orange oil; yield 0.23 g (73%).

Product **1a** can also be synthesized from ferrocene as follows. A solution of *t*BuLi in pentane (1.6 M, 17.3 mL, 27.6 mmol) was added dropwise to a solution of ferrocene (6.17 g, 33.2 mmol) in THF (50 mL) at 0 °C. After addition, the reaction was stirred at 0 °C for 15 min before being warmed to rt and stirred for 15 min. The reaction mixture was cooled to -80 °C and was cannulated onto a solution of chlorodiethylphosphate (4.0 mL, 27.6 mmol) in THF (30 mL) at -80 °C. The reaction mixture was then warmed to rt and water was added. The reaction mixture was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude product. Purification by column chromatography (silica gel; eluent: EtOAc/PE 50:50 to 10:90) gave product **1a** as an orange oil; yield 4.06 g (45%).

R_f (EtOAc/PE 30:70) = 0.25.

IR (film): 3463, 3098, 2981, 1643, 1479, 1443, 1425, 1390, 1370, 1235, 1186, 1107, 1020, 955, 818, 792, 747 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.51 (q, *J* = 2.0 Hz, 2H, H2 and H5), 4.40-4.38 (m, 2H, H3 and H4), 4.30 (s, 5H, Cp), 4.18-4.07 (m, 4H, C*H*$_2$Me), 1.34 (t, *J* = 7.1 Hz, 6H, Me).

^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ (ppm) = 71.7 (d, *J* = 15.6 Hz, 2CH, C2 and C5), 71.3 (d, *J* = 13.9 Hz, 2CH, C3 and C4), 70.0 (5CH, Cp), 67.1 (d, *J* = 215.3 Hz, C, C1, *C*-P(O)(OEt)$_2$), 61.8 (d, *J* = 6.0 Hz, 2CH_2, *C*H$_2$Me), 16.6 (d, *J* = 6.5 Hz, 2CH_3, Me).

^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.8.

The NMR data are similar to those previously obtained.[3a]

***O*,*O*-Diisopropylferrocenephosphonate (1b)**

[CAS Reg. No. 1820955-15-4]

By following the general procedure, but on a 3.0 mmol scale, using iodoferrocene (0.94 g) and diisopropylphosphite (0.55 mL), product **1b** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as an orange oil; yield 0.87 g (83%; 60% at a 1 mmol scale); R_f (EtOAc/PE 30:70) = 0.44.

IR (film): 3464, 3098, 2978, 2935, 1643, 1455, 1425, 1386, 1373, 1234, 1188, 1141, 1106, 1031, 974, 895, 879, 821, 770, 743 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.71 (hept, *J* = 6.4 Hz, 1H, *C*HMe$_2$), 4.69 (hept, 1H, *J* = 6.4 Hz, *C*HMe$_2$), 4.47 (s, 2H, H2 and H5), 4.36 (s, 2H, H3 and H4), 4.28 (s, 5H, Cp), 1.31 (d, *J* = 6.2 Hz, 6H, CH*Me*$_2$), 1.32 (d, *J* = 6.3 Hz, 6H, CH*Me*$_2$).

^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ (ppm) = 71.6 (d, *J* = 15.4 Hz, 2CH, C2 and C5), 71.1 (d, *J* = 14.0 Hz, 2CH, C3 and C4), 70.1 (d, *J* = 6.1 Hz, 2CH, *C*HMe$_2$), 70.0 (5CH, Cp), 68.8 (d, *J* = 216.2 Hz, C, C1, *C*-P(O)(Oi-Pr)$_2$), 24.2 (d, *J* = 4.4 Hz, 4CH_3, CH*Me*$_2$).

^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ (ppm) = 23.3.

***O*,*O*-Diphenylferrocenephosphonate (1c)**

[CAS Reg. No. 399043-62-0]

By following the general procedure, using iodoferrocene (0.31 g) and diphenylphosphite (0.21 mL), product **1c** was isolated by column chromatography (EtOAc/PE 5:95 to 100:0) as a yellow solid; yield 0.12 g (28%); R_f (EtOAc/PE 5:95) = 0.13; mp 89 °C.

IR (film): 3096, 2968, 1589, 1486, 1456, 1423, 1372, 1260, 1214, 1187, 1162, 1107, 1072, 1028, 1005, 926, 891, 816, 772, 763, 729 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.32 (t, *J* = 7.8 Hz, 4H, H3′ and H5′), 7.23 (d, *J* = 8.0 Hz, 4H, H2′ and H6′), 7.15 (t, *J* = 7.4 Hz, 2H, H4′), 4.62 (s, 2H, H2 and H5), 4.46 (s, 2H, H3 and H4), 4.26 (s, 5H, Cp).

^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ (ppm) = 150.9 (d, *J* = 8.0 Hz, 2C, C1′), 129.7 (4CH, C3′ and C5′), 125.0 (2CH, C4′), 120.8 (d, *J* = 4.5 Hz, 4CH, C2′ and C6′), 72.1 (d, *J* = 16.6 Hz, 2CH, C2 and C5), 71.9 (d, *J* = 15.2 Hz, 2CH, C3 and C4), 70.2 (5CH, Cp), 65.5 (d, *J* = 221.6 Hz, C, C1, *C*-P(O)(OPh)$_2$).

^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ (ppm) = 19.8.

The NMR data are similar to those previously obtained.[4]

***P*,*P*-Diphenylferrocenephosphoxide (1d)**

[CAS Reg. No. 54060-24-1]

By following the general procedure, using iodoferrocene (0.31 g) and diphenylphosphine oxide (0.22 g), product **1d** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as an orange solid; yield 0.25 g (65%); R_f (EtOAc/PE 30:70) = 0.27; mp 171 °C (lit.[54] 163-165 °C).

IR (film): 1482, 1435, 1306, 1201, 1165, 1119, 1106, 1065, 1026, 999, 821, 752, 719 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.70-7.66 (m, 4H, H2′ and H6′), 7.51 (tq, *J* = 6.6 and 1.5 Hz, 2H, H4′), 7.46-7.42 (m, 4H, H3′ and H5′), 4.47 (q, *J* = 1.8 Hz, 2H, H3 and H4), 4.37 (q, *J* = 1.9 Hz, 2H, H2 and H5), 4.21 (s, 5H, Cp).

^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ (ppm) = 134.6 (d, *J* = 106.2 Hz, 2C, C1′), 131.6 (d, *J* = 9.8 Hz, 4CH, C2′ and C6′), 131.6 (d, *J* = 2.9 Hz, 2CH, C4′), 128.3 (d, *J* = 12.0 Hz, 4CH, C3′ and C5′), 73.1 (d, *J* = 117.2 Hz, C, C1, *C*-POPh$_2$), 72.4 (d, *J* = 12.9 Hz, 2CH, C2 and C5), 71.7 (d, *J* = 10.6 Hz, 2CH, C3 and C4), 69.8 (5CH, Cp).

^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ (ppm) = 28.7.

The NMR data are similar to those previously obtained.[55]

(±)-*O*,*O*-Diethyl-2-fluoroferrocenephosphonate ((±)-2a)

By following the general procedure, using 1-fluoro-2-iodoferrocene (0.33 g) and diethylphosphite (0.14 mL), product **(±)-2a** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as a brown oil; yield 0.19 g (56%); R_f (EtOAc/PE 30:70) = 0.11.

IR (film): 3417, 2984, 1708, 1526, 1479, 1448, 1427, 1392, 1345, 1293, 1232, 1173, 1093, 1017, 964, 795, 750, 660 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.50 (br s, 1H, H3), 4.39 (s, 5H, Cp), 4.27-4.20 (m, 2H, CH_2), 4.18 (br s, 1H, H5), 4.12 (p, *J* = 7.3 Hz, 2H, CH_2), 4.02 (br s, 1H, H4), 1.39 (t, *J* = 7.1 Hz, 3H, Me), 1.32 (t, *J* = 7.1 Hz, 3H, Me).

^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ (ppm) = 135.8 (dd, *J* = 275.1 and 8.5 Hz, C, C2, C-F), 71.3 (5CH, Cp), 65.9 (dd, *J* = 12.4 and 2.3 Hz, CH, C5), 63.6 (dd,

J = 13.6 and 3.6 Hz, CH, C4), 62.3 (d, *J* = 6.5 Hz, CH_2), 62.2 (d, *J* = 6.0 Hz, CH_2), 59.0 (dd, *J* = 15.1 and 9.8 Hz, CH, C3), 56.2 (dd, *J* = 216.5 and 13.8 Hz, C, C1, *C*-P(O)($OEt)_2$), 16.6 (d, *J* = 6.7 Hz, CH_3), 16.5 (d, *J* = 6.5 Hz, CH_3).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): δ (ppm) = -184.5 (d, *J* = 10.4 Hz).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 21.3 (d, *J* = 9.1 Hz).

(±)-2-Fluoro-*O,O*-diisopropylferrocenephosphonate ((±)-2b)

By following the general procedure, using 1-fluoro-2-iodoferrocene (0.33 g) and diisopropylphosphite (0.18 mL), product **(±)-2b** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as an orange oil; yield 0.13 g (35%); R_f (EtOAc/PE 30:70) = 0.41.

IR (film): 3370, 2980, 2936, 1712, 1522, 1449, 1427, 1386, 1375, 1231, 1174, 1142, 1105, 1092, 979, 897, 885, 825, 771, 743, 661 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.81 (dhept, *J* = 8.0 and 6.2 Hz, 1H, C*H*Me_2), 4.71 (dhept, *J* = 8.3 and 6.2 Hz, 1H, C*H*Me_2), 4.49-4.44 (m, 1H, H3), 4.38 (s, 5H, Cp), 4.15 (s, 1H, H5), 4.00-3.97 (m, 1H, H4), 1.38 (d, *J* = 6.2 Hz, 3H, Me), 1.37 (d, *J* = 6.2 Hz, 3H, Me), 1.33 (d, *J* = 6.2 Hz, 3H, Me), 1.27 (d, *J* = 6.2 Hz, 3H, Me).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 135.7 (dd, *J* = 274.9 and 8.3 Hz, C, C2, C-F), 71.2 (5CH, Cp), 70.85 (d, *J* = 6.5 Hz, CH, *C*HMe_2), 70.65 (d, *J* = 5.8 Hz, CH, *C*HMe_2), 65.9 (dd, *J* = 12.6 and 2.1 Hz, CH, C5), 63.3 (dd, *J* = 13.4 and 3.7 Hz, CH, C4), 58.9 (dd, *J* = 15.1 and 9.8 Hz, CH, C3), 57.7 (dd, *J* = 217.8 and 13.6 Hz, C, C1, *C*-P(O)(Oi-$Pr)_2$), 24.3 (d, *J* = 4.9 Hz, CH_3), 24.3 (d, *J* = 4.3 Hz, CH_3), 24.2 (d, *J* = 4.6 Hz, CH_3), 24.0 (d, *J* = 4.9 Hz, CH_3).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): δ (ppm) = -184.65 (d, *J* = 11.3 Hz).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 18.65 (d, *J* = 11.2 Hz).

(±)-2-Fluoro-*P,P*-diphenylferrocenephosphoxide ((±)-2d)

By following the general procedure, using 1-fluoro-2-iodoferrocene (0.33 g) and diphenylphosphine oxide (0.22 g), product **(±)-2d** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as an orange oil; yield 94 mg (23%); R_f (EtOAc/PE 30:70) = 0.30.

IR (film): 3424, 3055, 1657, 1591, 1483, 1437, 1415, 1378, 1339, 1239, 1192, 1163, 1117, 1106, 1071, 1026, 999, 927, 825, 749, 722, 693, 656 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.85 (d, *J* = 8.1 Hz, 1H, H2' or H6'), 7.83 (d, *J* = 7.2 Hz, 1H, H2' or H6'), 7.67 (dd, *J* = 8.3 and 1.4 Hz, 1H, H2' or H6'), 7.65 (dd, *J* = 8.3 and 1.3 Hz, 1H, H2' or H6'), 7.57-7.53 (m, 1H, H4'), 7.52-7.47 (m, 3H, H4', H3' or/and H5'), 7.45-7.41 (m, 2H, H3' or/and H5'), 4.58 (hept, *J* = 1.5 Hz, 1H, H3), 4.27 (s, 5H, Cp), 4.09 (hept, *J* = 1.45 Hz, 1H, H4), 4.06 (hept, *J* = 1.3 Hz, 1H, H5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 136.0 (dd, *J* = 274.3 and 7.0 Hz, C, C2, C-F), 134.3 (d, *J* = 63.4 Hz, C1'), 133.4 (d, *J* = 65.0 Hz, C1'), 131.9 (d, *J* = 2.6 Hz, CH, C4'), 131.9 (d, *J* = 2.6 Hz, CH, C4'), 131.8 (d, *J* = 2.2 Hz, CH, C2' and C6'), 131.5 (d, *J* = 10.1 Hz, 2CH, C2' and C6'), 128.4 (d, *J* = 9.5 Hz, 2CH, C3' and C5'), 128.4 (d, *J* = 9.8 Hz, 2CH, C3' and C5'), 71.1 (5CH, Cp), 67.1 (dd, *J* = 9.7 and 2.4 Hz, CH, C5), 63.6 (dd, *J* = 10.0 and 3.5 Hz, CH, C4), 61.9 (dd, *J* = 114.8 and 13.6 Hz, C, C1, *C*-P(O)($OPh)_2$), 59.5 (dd, *J* = 15.7 and 6.6 Hz, CH, C3).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 470 MHz): δ (ppm) = -183.2 (d, *J* = 10.0 Hz).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 26.5 (dd, *J* = 10.0 and 2.0 Hz).

(±)-*O,O*-Diethyl-2-(methoxycarbonyl)ferrocenephosphonate ((±)-3a)

By following the general procedure, using 2-iodo-*O*-methylferrocenecarboxylate (0.33 g) and diethylphosphite (0.37 g), product **(±)-3a** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as a yellow solid; yield 38 mg (10%); R_f (EtOAc/PE 30:70) = 0.11.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 5.03 (q, *J* = 2.3 Hz, 1H, H3), 4.79 (q, *J* = 2.2 Hz, 1H, H5), 4.55 (q, *J* = 2.6 Hz, 1H, H4), 4.36 (s, 5H, Cp), 4.22 (p, *J* = 7.4 Hz, 4H, CH_2Me), 3.83 (s, 3H, OMe), 1.36 (t, *J* = 7.1 Hz, 6H, CH_2*Me*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 170.5 (C, C=O), 78.3 (d, *J* = 13.0 Hz, CH, C5), 75.6 (d, *J* = 11.8 Hz, CH, C3), 73.8 (d, *J* = 13.4 Hz, C, C2, C-CO_2Me), 72.4 (d, *J* = 13.3 Hz, CH, C4), 71.8 (5CH, Cp), 69.0 (d, *J* = 216.3 Hz, C, C1, *C*-P(O)($OEt)_2$), 62.4 (d, *J* = 6.5 Hz, CH_2), 62.3 (d, *J* = 5.9 Hz, CH_2), 52.0 (CH_3, OMe), 16.7 (d, *J* = 5.7 Hz, CH_3, CH_2*Me*), 16.6 (d, *J* = 6.2 Hz, CH_3, CH_2*Me*).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 22.8.

(±)-*O,O*-Diethyl-2-(methoxymethyl)ferrocenephosphonate ((±)-5a)

By following the general procedure, using 1-iodo-2-(methoxymethyl)ferrocene (0.36 g) and diethylphosphite (0.37 g), product **(±)-5a** was isolated by column chromatography (EtOAc/PE 30:70 to 100:0) as an orange oil; yield 0.19 g (51%); R_f (EtOAc/PE 30:70) = 0.22.

IR (film): 3465, 2980, 2908, 2818, 1642, 1444, 1409, 1391, 1370, 1230, 1190, 1170, 1085, 1020, 955, 901, 815, 792, 745 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.59 (d, *J* = 11.1 Hz, 1H, CH_2OMe), 4.48 (s, 1H, H4 or H5), 4.47 (s, 1H, H4 or H5), 4.36 (q, *J* = 2.7 Hz, 1H, H3), 4.28 (d, *J* = 11.1 Hz, 1H, CH_2OMe), 4.26 (s, 5H, Cp), 4.15 (p, *J* = 7.1 Hz, 2H, CH_2Me), 4.09 (p, *J* = 7.3 Hz, 2H, CH_2Me), 3.35 (s, 3H, OMe), 1.35 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.30 (t, *J* = 7.1 Hz, 3H, CH_2*Me*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 86.8 (d, *J* = 16.6 Hz, C, C2, *C*-CH_2OMe), 73.5 (d, *J* = 14.6 Hz, CH, C4 or C5), 73.3 (d, *J* = 14.3 Hz, CH, C4 or C5), 70.6 (d, *J* = 13.5 Hz, CH, C3), 70.5 (5CH, Cp), 69.3 (CH_2, *C*H_2OMe), 66.5 (d, *J* = 211.5 Hz, C, C1, *C*-P(O)($OEt)_2$), 61.8 (d, *J* = 5.9 Hz, CH_2, *C*H_2Me), 61.7 (d, *J* = 5.9 Hz, CH_2, *C*H_2Me), 58.2 (CH_3, OMe), 16.6 (d, *J* = 6.4 Hz, CH_3, CH_2*Me*), 16.5 (d, *J* = 6.7 Hz, CH_3, CH_2*Me*).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.2.

(±)-*O,O*-Diisopropyl-2-(methoxymethyl)ferrocenephosphonate ((±)-5b)

By following the general procedure, using 1-iodo-2-(methoxymethyl)ferrocene (0.36 g) and diisopropylphosphite (0.18 mL), product **(±)-5b** was isolated by column chromatography (EtOAc/PE 10:90 to 30:70) as a brown oil; yield 0.20 g (50%); R_f (EtOAc/PE 10:90) = 0.10.

IR (film): 3464, 2978, 2932, 1642, 1456, 1408, 1385, 1373, 1230, 1172, 1141, 1105, 975, 896, 884, 816, 772, 695 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.75 (hept, *J* = 6.6 Hz, 1H, C*H*Me_2), 4.68 (hept, *J* = 6.9 Hz, 1H, C*H*Me_2), 4.61 (d, *J* = 11.0 Hz, 1H, CH_2), 4.46 (br s, 2H, H4 and H5), 4.33 (d, *J* = 2.6 Hz, 1H, H3), 4.28 (d, *J* = 11.1 Hz, 1H, CH_2), 4.25 (s, 5H, Cp), 3.35 (s, 3H, OMe), 1.34 (d, *J* = 6.3 Hz, 3H, CH*Me*$_2$), 1.32 (d, *J* = 6.3 Hz, 3H, CH*Me*$_2$), 1.30 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 1.27 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 86.6 (d, *J* = 16.5 Hz, C, C2, *C*-CH_2OMe), 73.4 (d, *J* = 14.5 Hz, CH, C4 or C5), 73.1 (d, *J* = 14.1 Hz, CH, C4 or C5), 70.5 (5CH, Cp), 70.4 (d, *J* = 13.9 Hz, CH, C3), 70.3 (d, *J* = 6.6 Hz, CH, *C*HMe_2), 70.1 (d, *J* = 6.1 Hz, CH, *C*HMe_2), 69.4 (CH_2), 67.9 (d, *J* = 212.1 Hz, C, C1, *C*-P(O)(Oi-$Pr)_2$), 58.2 (CH_3, OMe), 24.3 (d, *J* = 4.2 Hz, CH_3, CH*Me*$_2$), 24.2 (d, *J* = 3.8 Hz, CH_3, CH*Me*$_2$), 24.2 (d, *J* = 2.7 Hz, CH_3, CH*Me*$_2$), 24.1 (d, *J* = 4.2 Hz, CH_3, CH*Me*$_2$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 22.7.

(±)-*O,O*-Diethyl-2-(trimethylsilyl)ferrocenephosphonate ((±)-6a)

To *O,O*-diethylferrocenephosphonate (**1a**; 0.32 g, 1.0 mmol) in THF (2 mL) at -80 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (1.1 mL, 1.5 mmol). The mixture was stirred for 1 h at this temperature before addition of chlorotrimethylsilane (0.19 mL, 1.5 mmol) and warming to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude. Purification by column chromatography (silica gel; eluent: EtOAc/PE 20:80 to 50:50) gave product **(±)-6a** as an orange oil; yield 0.36 g (91%; 51% by using 1.2 equiv of base); R_f (EtOAc/PE 20:80) = 0.11.

IR (film): 3455, 3097, 2980, 2902, 1653, 1444, 1391, 1279, 1241, 1184, 1164, 1143, 1108, 1097, 1023, 957, 860, 836, 818, 753, 692 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.73 (s, 1H, H5), 4.50 (q, *J* = 2.5 Hz, 1H, H4), 4.34 (s, 1H, H3), 4.28 (s, 5H, Cp), 4.18-4.00 (m, 4H, CH_2), 1.34 (t, *J* = 6.8 Hz, 3H, CH_2*Me*), 1.32 (t, *J* = 6.6 Hz, 3H, CH_2*Me*), 0.32 (s, 9H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 78.7 (d, *J* = 17.2 Hz, CH, C3), 77.2 (d, *J* = 17.2 Hz, CH, C5), 75.6 (d, *J* = 22.7 Hz, C, C2, *C*-$SiMe_3$), 72.6 (d, *J* = 13.0 Hz, CH, C4), 71.4 (d, *J* = 214.6 Hz, C, C1, *C*-P(O)($OEt)_2$), 70.0 (5CH, Cp), 61.6 (d, *J* = 6.7 Hz, CH_2), 61.6 (d, *J* = 6.2 Hz, CH_2), 16.6 (d, *J* = 6.1 Hz, CH_3, CH_2*Me*), 16.5 (d, *J* = 6.2 Hz, CH_3, CH_2*Me*), 0.7 ($3CH_3$, $SiMe_3$).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 27.8.

(±)-*O,O*-Diisopropyl-2-(trimethylsilyl)ferrocenephosphonate ((±)-6b)

To *O,O*-diisopropylferrocenephosphonate (**1b**; 0.37 g, 1.0 mmol) in THF (2 mL) at -80 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (1.1 mL, 1.5 mmol). The mixture was stirred for 1 h at this temperature before addition of chlorotrimethylsilane (0.19 mL, 1.5 mmol) and warming to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude. Purification by column chromatography (silica gel; eluent: EtOAc/PE 30:70 to 50:50) gave product **(±)-6b** as a brown oil; yield 0.36 g (87%); R_f (EtOAc/PE 30:70) = 0.60.

IR (film): 2977, 1718, 1453, 1384, 1373, 1277, 1240, 1180, 1141, 1107, 1072, 1044, 1000, 972, 894, 882, 859, 836, 817, 769, 753 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.77 (dhept, *J* = 7.8 and 6.2 Hz, 1H, C*H*Me_2), 4.70-4.69 (m, 1H, H5), 4.62 (dhept, *J* = 8.5 and 6.2 Hz, 1H, C*H*Me_2), 4.48 (q, *J* = 2.3 Hz, 1H, H4), 4.32-4.33 (m, 1H, H3), 4.27 (s, 5H, Cp), 1.38 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 1.32 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 1.30 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 1.26 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 0.34 (s, 9H, $SiMe_3$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 78.6 (d, *J* = 17.2 Hz, CH, C3), 77.0 (d, *J* = 13.4 Hz, CH, C5), 75.4 (d, *J* = 22.5 Hz, C, C2, *C*-$SiMe_3$), 73.2 (d, *J* = 215.6 Hz, C, C1, *C*-P(O)(Oi-Pr)$_2$), 72.4 (d, *J* = 13.3 Hz, CH, C4), 70.1 (d, *J* = 6.0 Hz, CH, *C*HMe_2), 70.0 (5CH, Cp), 69.9 (d, *J* = 6.4 Hz, CH, *C*HMe_2), 24.5 (d, *J* = 4.0 Hz, CH_3, CH*Me*$_2$), 24.3 (d, *J* = 4.8 Hz, CH_3, CH*Me*$_2$), 24.2 (d, *J* = 4.9 Hz, CH_3, CH*Me*$_2$), 24.0 (d, *J* = 3.9 Hz, CH_3, CH*Me*$_2$), 0.9 ($3CH_3$, $SiMe_3$).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.4.

(±)-*O,O*-Diethyl-2-iodoferrocenephosphonate ((±)-7a)

To a stirred, cooled (-15 °C) solution of 2,2,6,6-tetramethylpiperidine (0.76 mL, 4.5 mmol) in THF (5 mL) was added dropwise *n*BuLi (~1.4 M in hexanes, 3.2 mL, 4.5 mmol). After 5 min at this temperature, the formed LiTMP solution cooled to -30 °C and was cannulated onto a solution of $ZnCl_2$·TMEDA (0.38 g, 1.5 mmol) and *O,O*-diethylferrocenephosphonate (**1a**; 0.48 g, 1.5 mmol) in THF (5 mL) at -30 °C. The mixture was warmed to -10 °C and kept at this temperature for 15 min before addition of a solution of I_2 (1.14 g, 4.5 mmol) in THF (5 mL). The mixture was allowed to reach rt and stirred for 1 h before addition of an aqueous saturated solution of $Na_2S_2O_3$. Extraction with EtOAc, drying over $MgSO_4$ and concentration under reduced pressure led to the crude. Purification by chromatography over silica gel (eluent: EtOAc/PE 70:30 to 80:20) gave product **(±)-7a** as an orange oil; yield 0.53 g (79%); R_f (EtOAc/PE 80:20) = 0.32.

IR (film): 3456, 3085, 2978, 2904, 1476, 1442, 1412, 1390, 1363, 1325, 1291, 1240, 1193, 1163, 1107, 1097, 1019, 955, 923, 816, 792, 745 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.64 (dd, *J* = 3.7 and 2.3 Hz, 1H, H3), 4.60 (dd, *J* = 3.6 and 2.3 Hz, 1H, H5), 4.37 (dd, *J* = 4.9 and 2.4 Hz, 1H, H4), 4.31 (s, 5H, Cp), 4.29-4.18 (m, 2H, CH_2), 4.17-4.07 (m, 2H, CH_2), 1.40 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.32 (t, *J* = 7.1 Hz, 3H, CH_2*Me*).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 79.7 (d, *J* = 12.7 Hz, CH, C3), 73.9 (d, *J* = 14.9 Hz, CH, C5), 73.0 (5CH, Cp), 71.9 (d, *J* = 12.6 Hz, CH, C4), 70.4 (d, *J* = 219.7 Hz, C, C1, *C*-P(O)(OEt)$_2$), 62.3 (d, *J* = 6.4 Hz, CH_2), 62.1 (d, *J* = 5.7 Hz, CH_2), 40.8 (d, *J* = 14.5 Hz, C, C2,), 16.6 (d, *J* = 6.8 Hz, CH_3, CH_2*Me*), 16.5 (d, *J* = 6.4 Hz, CH_3, CH_2*Me*).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 22.8.

***O,O*-Diethyl-2,5-diiodoferrocenephosphonate (7a')**

Product **7a'** was also obtained in the previous reaction as a brown oil; yield 18 mg (3%); R_f (EtOAc/PE 80:20) = 0.50.

However, the following protocol afforded product **7a'** more efficiently. To a stirred, cooled (-15 °C) solution of 2,2,6,6-tetramethylpiperidine (1.01 mL, 6.0 mmol) in THF (6.5 mL) was added dropwise *n*BuLi (~1.3 M in hexanes, 4.6 mL, 6.0 mmol). After 5 min at this temperature, the formed LiTMP solution was cooled to -30 °C and was cannulated onto a solution of $CdCl_2$·TMEDA (0.60 g, 2.0 mmol) and *O,O*-diethylferrocenephosphonate (**1a**; 0.64 g, 2.0 mmol) in THF (6.4 mL) at -30 °C. The mixture was warmed to -10 °C and kept at this temperature for 2 h before addition of a solution of I_2 (1.52 g, 6.0 mmol) in THF (10 mL). The mixture was allowed to reach rt and stirred for 1 h before addition of an aqueous saturated solution of $Na_2S_2O_3$. Extraction with EtOAc, drying over $MgSO_4$ and concentration under reduced pressure led to the crude. Purification by chromatography over silica gel (eluent: EtOAc/PE 70:30 to 80:20) gave product **7a'** as a brown oil; yield 0.49 g (42%).

IR (film): 3084, 2977, 2927, 2902, 1475, 1441, 1412, 1390, 1367, 1325, 1247, 1197, 1162, 1107, 1097, 1064, 1046, 1019, 951, 856, 824, 793, 746 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.73 (d, *J* = 1.7 Hz, 2H, H3 and H4), 4.32 (s, 5H, Cp), 4.22 (p, *J* = 7.2 Hz, 4H, CH_2), 1.39 (t, *J* = 7.1 Hz, 6H, Me).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 81.3 (d, *J* = 11.8 Hz, 2CH, C3 and C4), 75.9 (5CH, Cp), 70.5 (d, *J* = 222.1 Hz, C, C1, *C*-P(O)(OEt)$_2$), 62.4 (d, *J* = 6.0 Hz, 2CH_2), 41.5 (d, *J* = 14.5 Hz, 2C, C2 and C5, C-I), 16.6 (d, *J* = 6.5 Hz, CH_3).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 19.5.

(±)-*O,O*-Diethyl-2-iodo-5-(trimethylsilyl)ferrocenephosphonate ((±)-8a)

To a stirred, cooled (-30 °C) solution of 2,2,6,6-tetramethylpiperidine (0.48 mL, 3.0 mmol) in THF (4 mL) was added dropwise *n*BuLi (~1.6 M in hexanes, 3.0 mmol). After 5 min at this temperature, the formed LiTMP solution was cannulated onto a solution of $ZnCl_2$·TMEDA (0.25 g, 1.0 mmol) and *O,O*-diethyl-2-(trimethylsilyl)ferrocenephosphonate (**(±)-6a**; 0.39 g, 1.0 mmol) in THF (4 mL) at -30 °C. After 30 min at this temperature, a solution of I_2 (0.75 g, 3.0 mmol) in THF (4 mL) was added. The mixture was allowed to reach rt and stirred for 1 h before addition of an aqueous saturated solution of $Na_2S_2O_3$ (10 mL). Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and concentration under reduced pressure led to the crude. Purification by chromatography over silica gel (eluent: EtOAc/PE 20:80 to 100:0) gave product **(±)-8a** as a brown oil; yield 0.45 g (86%); R_f (EtOAc/PE 20:80) = 0.37.

IR (film): 2978, 2901, 1643, 1442, 1390, 1370, 1313, 1238, 1196, 1164, 1119, 1108, 1073, 1050, 1024, 962, 871, 838, 819, 751, 688 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.79 (t, *J* = 2.1 Hz, 1H, H3), 4.38 (t, *J* = 2.5 Hz, 1H, H4), 4.29 (s, 5H, Cp), 4.28 (p, *J* = 7.0 Hz, 2H, CH_2), 4.09-4.01 (m, 1H, CH_2), 4.00-3.92 (m, 1H, CH_2), 1.46 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.28 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 0.33 (s, 9H, $SiMe_3$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 82.0 (d, *J* = 12.0 Hz, CH, C3), 79.3 (d, *J* = 15.7 Hz, CH, C4), 79.2 (d, *J* = 23.4 Hz, C, C5, *C*-$SiMe_3$), 73.5 (d, *J* = 219.8 Hz, C, C1, *C*-P(O)(OEt)$_2$), 73.0 (5CH, Cp), 61.9 (d, *J* = 6.4 Hz, CH_2), 61.7 (d, *J* = 5.4 Hz, CH_2), 45.4 (d, *J* = 15.9 Hz, C, C2, *C*-I), 16.7 (d, *J* = 6.8 Hz, CH_3, CH_2*Me*), 16.4 (d, *J* = 6.2 Hz, CH_3, CH_2*Me*), 0.92 ($3CH_3$, $SiMe_3$).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 24.5.

(±)-2-Iodo-*O,O*-diisopropyl-5-(trimethylsilyl)ferrocenephosphonate ((±)-8b)

To a stirred, cooled (-30 °C) solution of 2,2,6,6-tetramethylpiperidine (0.48 mL, 3.0 mmol) in THF (4 mL) was added dropwise *n*BuLi (~1.6 M in hexanes, 3.0 mmol). After 5 min at this temperature, the formed LiTMP solution was cannulated onto a solution of $ZnCl_2$·TMEDA (0.25 g, 1.0 mmol) and *O,O*-diisopropyl-2-(trimethylsilyl)ferrocenephosphonate (**(±)-6b**; 0.45 g, 1.0 mmol) in THF (4 mL) at -30 °C. After 30 min at this temperature, a solution of I_2 (0.75 g, 3.0 mmol) in THF (4 mL) was added. The mixture was allowed to reach rt and stirred for 1 h before addition of an aqueous saturated solution of $Na_2S_2O_3$ (10 mL). Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and concentration under reduced pressure led to the crude. Purification by chromatography over silica gel (eluent: EtOAc/PE 20:80 to 100:0) gave product **(±)-8b** as an orange solid; yield 0.495 g (90%); R_f (EtOAc/PE 20:80) = 0.48; mp 117 °C.

IR (film): 3082, 2975, 1450, 1373, 1318, 1238, 1178, 1140, 1125, 1107, 1078, 1007, 966, 886, 856, 821, 773, 748 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.89 (dhept, *J* = 6.3 and 6.2 Hz, 1H, C*H*Me_2), 4.77 (t, *J* = 2.1 Hz, 1H, H3), 4.50 (dhept, *J* = 8.4 and 6.2 Hz, 1H, C*H*Me_2), 4.35 (t, *J* = 2.6 Hz, 1H, H4), 4.26 (s, 5H, Cp), 1.49 (d, *J* = 6.1 Hz, 6H,

CH*Me*$_2$), 1.30 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 1.09 (d, *J* = 6.2 Hz, 3H, CH*Me*$_2$), 0.35 (s, 9H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 82.0 (d, *J* = 11.8 Hz, CH, C3), 79.4 (d, *J* = 23.9 Hz, C, C5, *C*-$SiMe_3$), 79.0 (d, *J* = 16.2 Hz, CH, C4), 74.8 (d, *J* = 218.8 Hz, C, C1, *C*-P(O)(Oi-Pr)$_2$), 73.1 (5CH, Cp), 70.7 (d, *J* = 6.9 Hz, CH, *C*HMe_2), 70.1 (d, *J* = 5.2 Hz, CH, *C*HMe_2), 45.4 (d, *J* = 15.3 Hz, C, C2, C-I), 24.7 (d, *J* = 4.0 Hz, CH_3, CH*Me*$_2$), 24.3 (d, *J* = 5.4 Hz, CH_3, CH*Me*$_2$), 24.2 (d, *J* = 4.2 Hz, CH_3, CH*Me*$_2$), 23.6 (d, *J* = 4.3 Hz, CH_3, CH*Me*$_2$), 1.0 ($3CH_3$, $SiMe_3$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 21.7.

Deprotonation of *O,O*-diethylferrocenephosphonate (1a) with *n*BuLi·(+)-sparteine surrogate by using chlorotrimethylsilane as electrophile:

*n*BuLi (1.5 M in hexane; 1.1 mL, 1.4 mmol) was added dropwise to a solution of (+)-sparteine surrogate (322 mg, 1.5 mmol) in Et_2O (15 mL) at -80 °C. After 30 min at this temperature, a solution of *O,O*-diethylferrocenephosphonate (**1a**; 0.32 g, 1.0 mmol) in toluene (2.5 mL) was added dropwise and the reaction mixture was stirred at the same temperature for 2 h. Chlorotrimethylsilane (0.25 mL, 2.0 mmol) was added and the reaction mixture was warmed to rt. Aqueous HCl (1 M) was added, and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, eluting with EtOAc/PE (20:80 to 10:90) to give the title product **6a*** as an orange oil in 24% yield (0.09 g). The *ee* (26%) was determined by HPLC analysis on a Chiralpak IA-3 column, hexane-isopropanol 90:10, 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, t (major) = 4.39 min, t (minor) = 5.25 min. Starting material was also recovered in 46% yield (0.15 g).

Deprotonation of *O,O*-diethylferrocenephosphonate (1a) with *n*BuLi·(*R,R*)-TMCDA by using chlorotrimethylsilane as electrophile. *n*BuLi (1.5 M in hexane; 1.1 mL, 1.5 mmol) was added dropwise to a solution of (*R,R*)-TMCDA (0.255 g, 1.5 mmol) in Et_2O (15 mL) at −80 °C. After 30 min at this temperature, a solution of *O,O*-diethylferrocenephosphonate (**1a**; 0.32 g, 1.0 mmol) in toluene (2.5 mL) was added dropwise and the reaction mixture was stirred at the same temperature for 2 h. Chlorotrimethylsilane (0.25 mL, 2.0 mmol) was added and the reaction mixture was warmed to rt. Aqueous HCl (1 M) was added, and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, eluting with EtOAc/PE (20:80 to 10:90) to give the title product **6a*** as an orange oil in 30% yield (0.12 g). The *ee* (28%) was determined by HPLC analysis on a Chiralpak IA-3 column, hexane-isopropanol 90:10, 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, t (major) = 4.39 min, t (minor) = 5.25 min. Starting material was also recovered in 29% yield (0.93 g).

Deprotonation of *O,O*-diethylferrocenephosphonate (1a) with (*S*)-PEALi by using [{(*S*)-PEA}$_2$Zn] as *in situ* trap. *n*BuLi (1.4 M in hexane; 1.4 mL, 2.0 mmol) was added dropwise to a solution of (*S*)-PEAH (0.46 mL, 2.0 mmol) in THF (6 mL) at −15 °C. After 5 min at this temperature, $ZnCl_2$·TMEDA (0.25 g, 1.0 mmol) was added in one portion and the reaction mixture was stirred for 15 min. *O,O*-Diethylferrocenephosphonate (**1a**; 0.32 g, 1.0 mmol) was added in one portion at the same temperature, and the reaction mixture was stirred for another 15 min. The reaction mixture was cooled to -30 °C and a cooled (-30 °C) solution of (*S*)-PEALi (prepared by adding *n*BuLi (0.71 mL, 1.0 mmol) dropwise to a solution of (*S*)-PEAH (0.23 mL, 1.0 mmol) in THF (6 mL) at −15 °C and stirring for 5 min) was then added at -30 °C by cannula. After addition, the reaction mixture was warmed to -10 °C over a period of 1 h, and kept at this temperature for a further 15 min. A solution of I_2 (0.76 g, 3.0 mmol) in THF (5 mL) was added and the reaction mixture was stirred for 1 h at rt. A saturated aqueous solution of $Na_2S_2O_3$ was added to the reaction mixture which was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, eluting with EtOAc/PE (20:80 to 10:90) to give the title product **7a*** as an orange oil in 17% yield (0.08 g). The *ee* (14%) was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 85:15, 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, t (major) = 28.98 min, t (minor) = 26.91 min. Starting material was also recovered in 52% yield (0.17 g).

(±)-*O,O*-Diethyl-2-(2-pyridyl)ferrocenephosphonate ((±)-9a)

To *O,O*-diethylferrocenephosphonate (**1a**; 0.32 g, 1.0 mmol) in THF (2 mL) at -80 °C was added dropwise a 1.5 M hexane solution of *n*BuLi (1.1 mL, 1.5 mmol). The mixture was stirred for 1 h at this temperature before addition of $ZnCl_2$·TMEDA (0.38 g, 1.5 mmol). After warming to -20 °C, $PdCl_2$ (14 mg, 80 µmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf; 44 mg, 80 µmol) and 2-chloropyridine (0.28 mL, 3.0 mmol) were introduced and the mixture was stirred for 8 h at 80 °C in a pre-heated oil bath. Cooling to rt, addition of H_2O, extraction with EtOAc, drying over $MgSO_4$ and removal of the solvent under reduced pressure led to the crude from which the coupled product **(±)-9a** was isolated by purification by column chromatography on silica gel (eluent: EtOAc) as an orange oil; yield 0.17 g (44%); R_f (EtOAc) = 0.26.

IR (film): 3454, 3086, 2980, 2904, 1588, 1565, 1481, 1443, 1419, 1390, 1292, 1239, 1169, 1095, 1021, 955, 816, 785, 743 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 8.52 (dq, *J* = 4.7 and 0.7 Hz, 1H, H6'), 8.12 (d, *J* = 8.0 Hz, 1H, H3'), 7.63 (td, *J* = 7.8 and 1.8 Hz, 1H, H4'), 7.13 (ddd, *J* = 7.4, 4.9 and 0.9 Hz, 1H, H5'), 5.13 (dd, *J* = 4.3 and 2.9 Hz, 1H, H3), 4.73 (dd, *J* = 4.0 and 2.3 Hz, 1H, H5), 4.56 (q, *J* = 2.5 Hz, 1H, H4), 4.26 (s, 5H, Cp), 4.26-4.16 (m, 2H, CH_2), 4.11-3.97 (m, 2H, CH_2), 1.34 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.19 (t, *J* = 7.1 Hz, 3H, CH_2*Me*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 157.3 (C, C2'), 148.8 (CH, C6'), 135.7 (CH, C4'), 123.8 (CH, C3'), 121.4 (CH, C5'), 88.5 (d, *J* = 14.9 Hz, C, C2), 76.0 (d, *J* = 13.7 Hz, CH, C5), 73.8 (d, *J* = 13.3 Hz, CH, C3), 71.6 (5CH, Cp), 71.2 (d, *J* = 13.2 Hz, CH, C4), 66.2 (d, *J* = 211.9 Hz, C, C1, *C*-P(O)(OEt)$_2$), 62.1 (d, *J* = 6.8 Hz, CH_2), 62.1 (d, *J* = 6.2 Hz, CH_2), 16.6 (d, *J* = 6.3 Hz, CH_3, CH_2*Me*), 16.3 (d, *J* = 6.8 Hz, CH_3, CH_2*Me*).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.6.

(±)-*O,O*-Diethyl-2-iodo-5-(2-pyridyl)ferrocenephosphonate ((±)-10aI)

To a stirred, cooled (-15 °C) solution of 2,2,6,6-tetramethylpiperidine (0.51 mL, 3.0 mmol) in THF (3 mL) was added dropwise *n*BuLi (~1.4 M in hexanes, 2.15 mL, 3.0 mmol). After 5 min at this temperature, the formed LiTMP solution was cannulated onto a solution of $ZnCl_2$·TMEDA (0.25 g, 1.0 mmol) and *O,O*-diethyl-2-iodoferrocenephosphonate (**(±)-7a**; 0.48 g, 1.0 mmol) in THF (4 mL) at -30 °C. The mixture was warmed to -10 °C before addition of $PdCl_2$ (14 mg, 80 µmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf; 44 mg, 80 µmol) and 3-iodopyridine (307 mg, 1.5 mmol). The mixture was next stirred for 8 h at 80 °C in a pre-heated oil bath. Cooling to rt, addition of H_2O, extraction with EtAOc, drying over $MgSO_4$ and removal of the solvent under reduced pressure led to the crude from which an inseparable mixture of the coupled product **(±)-10aI** and deiodinated coupled product **(±)-10aH** was obtained in a 67:33 ratio by purification by column chromatography on silica gel, eluting with EtOAc/PE (90:10 to 100:0).

NMR data of coupled product **(±)-10aI**:

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 8.77 (dd, *J* = 2.3 and 0.9 Hz, 1H, H2'), 8.49 (dd, *J* = 4.9 and 1.7 Hz, 1H, H6'), 7.91 (ddd, *J* = 7.9, 2.3 and 1.7 Hz, 1H, H4'), 7.22 (dd, *J* = 8.0 and 4.7 Hz, 1H, H5'), 4.82 (t, *J* = 2.3 Hz, 1H, H3 or H4), 4.59 (t, *J* = 2.5 Hz, 1H, H3 or H4), 4.37 (s, 5H, Cp), 4.26-3.93 (m, 4H, CH_2), 1.29 (td, *J* = 7.1 and 0.4 Hz, 3H, CH_2*Me*), 1.11 (td, *J* = 7.1 and 0.5 Hz, 3H, CH_2*Me*).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 21.1.

NMR data of deiodinated coupled product **(±)-10aH**:

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 8.86 (dd, *J* = 2.4, 0.9 Hz, 1H, H2'), 8.48 (dd, *J* = 4.0 and 1.7 Hz, 1H, H6'), 8.15 (ddd, *J* = 7.9, 2.4 and 1.7 Hz, 1H, H4'), 7.22 (dd, *J* = 7.9 and 4.8 Hz, 1H, H5'), 4.74 (td, *J* = 2.5 and 1.5 Hz, 1H, H3 or H5), 4.68 (ddd, *J* = 3.2, 2.5 and 1.5 Hz, 1H, H3 or H5), 4.53 (q, *J* = 2.6 Hz, 1H, H4), 4.30 (s, 5H, Cp), 4.26-3.93 (m, 4H, CH_2), 1.28 (t, *J* = 7.3 Hz, 3H, CH_2*Me*), 1.16 (td, *J* = 7.1 and 0.5 Hz, 3H, CH_2*Me*).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 24.8.

(±)-*O,O*-Diethyl-2-(4-fluorophenyl)ferrocenephosphonate ((±)-11a)

O,*O*-Diethyl-2-iodoferrocenephosphonate (**(±)-7a**, 0.18 g, 0.40 mmol), CsF (0.12 g, 0.8 mmol), 4-fluorophenylboronic acid (0.23 g, 1.6 mmol), $Pd(dba)_2$ (11.5 mg, 20 µmol) and Sphos (32 mg, 0.08 mmol) were placed in a Schlenk tube subjected to three vacuum/argon cycles before degassed toluene (4 mL) was added. The resulting mixture was heated for 14 h at 110 °C in, a pre-heated oil bath before cooling and addition of H_2O. Extraction with EtOAc, drying over $MgSO_4$ and removal of the solvent under reduced pressure led to the coupled product **(±)-11a** which was isolated by purification by column chromatography on silica gel (eluent: EtOAc/PE 80:20) as an orange oil; yield 0.12 g (74%); R_f (EtOAc/PE 80:20) = 0.43.

IR (film): 3500, 3085, 2981, 2906, 1605, 1519, 1479, 1436, 1390, 1328, 1233, 1161, 1122, 1096, 1050, 1022, 955, 811, 791, 746, 722, 667 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.71-7.69 (m, 2H, H2' and H6'), 6.98 (t, *J* = 8.7 Hz, 2H, H3' and H5'), 4.66 (dd, *J* = 3.8 and 2.2 Hz, 1H, H5), 4.59 (t, *J* = 3.4 Hz, 1H, H3), 4.45 (dd, *J* = 5.0 and 2.5 Hz, 1H, H4), 4.27 (s, 5H, Cp), 4.17-4.05 (m, 2H, CH_2), 4.04-3.92 (m, 2H, CH_2), 1.26 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.15 (t, *J* = 7.1 Hz, 3H, CH_2*Me*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 162.0 (d, *J* = 245.8 Hz, C, C4', C-F), 133.3 (d, *J* = 3.2 Hz, C, C1'), 131.2 (d, *J* = 7.9 Hz, 2CH, C2' and C6'), 114.5 (d, *J* = 21.3 Hz, 2CH, C3' and C5'), 90.3 (d, *J* = 15.0 Hz, C, C2), 74.5 (d, *J* = 14.8 Hz, CH, C5), 73.5 (d, *J* = 13.7 Hz, CH, C3), 71.4 (5CH, Cp), 70.3 (d, *J* = 13.6 Hz, CH, C4), 66.2 (d, *J* = 212.4 Hz, C, C1, *C*-P(O)$(OEt)_2$), 62.0 (d, *J* = 5.8 Hz, CH_2), 61.9 (d, *J* = 6.4 Hz, CH_2), 16.5 (d, *J* = 6.3 Hz, CH_3, CH_2*Me*), 16.3 (d, *J* = 6.8 Hz, CH_3, CH_2*Me*).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 470 MHz): δ (ppm) -115.9.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.4.

***O,O*-Diethyl-2,5-di(4-fluorophenyl)ferrocenephosphonate (12a)**

O,*O*-Diethyl-2,5-diiodoferrocenephosphonate (**7a'**, 0.29 g, 0.50 mmol), CsF (0.30 g, 2.0 mmol), 4-fluorophenylboronic acid (0.42 g, 3.0 mmol), $Pd(dba)_2$ (14.4 mg, 25 µmol) and Sphos (41 mg, 0.10 mmol) were placed in a Schlenk tube subjected to three vacuum/argon cycles before degassed toluene (4 mL) was added. The resulting mixture was heated for 14 h at 110 °C in a pre-heated oil bath before cooling and addition of H_2O. Extraction with EtOAc, drying over $MgSO_4$ and removal of the solvent under reduced pressure led to the coupled product **12a** which was isolated by purification by column chromatography on silica gel (eluent: EtOAc/PE 80:20) as an orange solid; yield 0.06 g (23%); R_f (EtOAc/PE 80:20) = 0.53; mp 136-137 °C.

IR (film): 2988, 2906, 1604, 1514, 1431, 1414, 1388, 1333, 1297, 1270, 1243, 1216, 1157, 1123, 1095, 1061, 1030, 972, 959, 937, 834, 819, 810, 788, 752, 722, 683, 664 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.67 (dd, *J* = 8.6 and 5.5 Hz, 4H, H2' and H6'), 7.02 (t, *J* = 8.7 Hz, 4H, H3' and H5'), 4.61 (d, *J* = 3.0 Hz, 2H, H3 and H4), 4.28 (s, 5H, Cp), 3.86 (p, *J* = 6.8 Hz, 1H, C*H*H), 3.84 (p, *J* = 6.8 Hz, 1H, CH*H*), 3.72 (p, *J* = 7.3 Hz, 1H, C*H*H), 3.70 (p, *J* = 7.4 Hz, 1H, CH*H*), 0.91 (t, *J* = 7.1 Hz, 6H, CH_2*Me*),

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 162.1 (d, *J* = 246.0 Hz, 2C, C4', C-F), 133.6 (d, *J* = 3.2 Hz, C, C1'), 131.9 (d, *J* = 7.9 Hz, 2CH, C2' and C6'), 114.4 (d, *J* = 21.4 Hz, 2CH, C3' and C5'), 93.3 (d, *J* = 14.9 Hz, 2C, C2 and C5), 73.0 (5CH, Cp), 72.9 (2CH, C3 and C4), 65.2 (d, *J* = 212.0 Hz, C, C1, *C*-P(O)$(OEt)_2$), 61.6 (d, *J* = 6.4 Hz, CH_2), 16.0 (d, *J* = 7.3 Hz, CH_3, CH_2*Me*).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 470 MHz): δ (ppm) -115.8.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 24.1.

(±)-*O,O*-Diethyl-2-(4-fluorophenyl)-5-iodoferrocenephosphonate ((±)-13a)

Product **(±)-13a** was also obtained in the previous reaction as an orange oil; yield 61 mg (20%); R_f (EtOAc/PE 80:20) = 0.45.

IR (film): 3081, 2980, 2903, 1604, 1517, 1431, 1412, 1390, 1372, 1328, 1278, 1220, 1158, 1099, 1050, 1022, 956, 880, 827, 811, 794, 747, 722, 667 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.53 (dd, *J* = 8.6 and 5.5 Hz, 2H, H2' and H6'), 6.97 (t, *J* = 8.7 Hz, 2H, H3' and H5'), 4.76 (t, *J* = 2.3 Hz, 1H, H4), 4.53 (t, *J* = 2.4 Hz, 1H, H3), 4.33 (s, 5H, Cp), 4.18 (dp, *J* = 10.2 and 7.1 Hz, 1H, C*H*H), 4.11-3.95 (m, 3H, CH*H* and CH_2), 1.26 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.12 (t, *J* = 7.1 Hz, 3H, CH_2*Me*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 162.2 (d, *J* = 246.5 Hz, C, C4', C-F), 132.5 (d, *J* = 3.3 Hz, C, C1'), 132.0 (d, *J* = 8.0 Hz, 2CH, C2' and C6'), 114.3 (d, *J* = 21.4 Hz, 2CH, C3' and C5'), 92.9 (d, *J* = 14.4 Hz, C, C2), 79.1 (d, *J* = 12.9 Hz, CH, C4), 75.2 (d, *J* = 12.4 Hz, CH, C3), 74.4 (5CH, Cp), 68.0 (d, *J* = 217.3 Hz, C, C1, *C*-P(O)$(OEt)_2$), 62.1 (d, *J* = 5.9 Hz, CH_2), 61.9 (d, *J* = 6.2 Hz, CH_2), 44.1 (d, *J* = 15.1 Hz, C, C5, C-I), 16.5 (d, *J* = 6.3 Hz, CH_3, CH_2*Me*), 16.2 (d, *J* = 6.9 Hz, CH_3, CH_2*Me*).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 470 MHz): δ (ppm) -115.4.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 21.6.

(±)-*O,O*-Diethyl-2-(4-methoxyphenyl)-5-(trimethylsilyl)ferrocenephosphonate ((±)-14a)

O,*O*-Diethyl-2-iodo-5-(trimethylsilyl)ferrocenephosphonate (**(±)-8a**, 0.29 g, 0.55 mmol), CsF (0.17 g, 1.1 mmol), 4-methoxyphenylboronic acid (0.33 g, 2.2 mmol), $Pd(dba)_2$ (16 mg, 29 µmol) and PPh_3 (28 mg, 0.11 mmol) were placed in a Schlenk tube subjected to three vacuum/argon cycles before degassed toluene (4 mL) was added. The resulting mixture was heated for 14 h at 110 °C in a pre-heated oil bath before cooling and addition of H_2O. Extraction with EtOAc, drying over Na_2SO_4 and removal of the solvent under reduced pressure led to the coupled product **(±)-14a** which was isolated by purification by column chromatography on silica gel (eluent: EtOAc/PE 10:90) as an orange solid; yield 0.26 g (96%); R_f (EtOAc/PE 10:90) = 0.11; mp 104 °C.

IR (film): 2946, 1611, 1523, 1433, 1331, 1307, 1241, 1216, 1190, 1151, 1100, 1070, 1048, 1030, 980, 966, 946, 902, 839, 753 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.62 (d, *J* = 8.7 Hz, 2H, H2' and H6'), 6.84 (d, *J* = 8.7 Hz, 2H, H3' and H5'), 4.67 (t, *J* = 2.5 Hz, 1H, H3), 4.43 (t, *J* = 2.6 Hz, 1H, H4), 4.27 (s, 5H, Cp), 4.01-3.87 (m, 3H, CH_2), 3.83 (s, 3H, OMe), 3.85-3.75 (m, 1H, CH_2), 1.15 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.10 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 0.38 (s, 9H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 158.7 (C, C4', C-OMe), 131.5 (2CH, C2' and C6'), 129.7 (C, C1'), 112.8 (2CH, C3' and C5'), 96.0 (d, *J* = 17.2 Hz, C, C2), 78.7 (d, *J* = 22.8 Hz, C, C5, *C*-$SiMe_3$), 77.6 (d, *J* = 16.9 Hz, CH, C4), 75.2 (d, *J* = 13.2 Hz, CH, C3), 71.3 (5CH, Cp), 70.7 (d, *J* = 212.4 Hz, C, C1, *C*-P(O)$(OEt)_2$), 61.5 (d, *J* = 6.6 Hz, CH_2), 61.2 (d, *J* = 5.6 Hz, CH_2), 55.4 (CH_3, OMe), 16.3 (d, *J* = 7.1 Hz, CH_3, CH_2*Me*), 16.2 (d, *J* = 6.4 Hz, CH_3, CH_2*Me*), 1.3 ($3CH_3$, $SiMe_3$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 27.7.

(±)-2-Iodoferrocenephosphonic acid ((±)-15)

Bromotrimethylsilane (0.95 mL, 7.20 mmol) was added dropwise to a solution of *O*,*O*-diethyl-2-iodoferrocenephosphonate (**(±)-7a**, 0.54 g, 1.20 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred at 40 °C for 3 h. After cooling, volatiles were removed under vacuum and methanol (5 mL) was added. Volatiles were removed under vacuum and the residue was dissolved in EtOAc. The organic layer was washed with water to remove oxidized by-products and then extracted with NaOH (10%). The combined basic layers were washed with diethyl ether and then acidified with HCl (35%) until pH 1. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over $MgSO_4$, filtrated and concentrated under vacuum. Cyclohexane was added to the crude product and volatiles were removed under vacuum to give the title product **15**; yield 0.25 g (54%); R_f (EtOAc) = 0.07.

IR (film): 2923, 2847, 2274, 1669, 1449, 1410, 1362, 1293, 1198, 1106, 1059, 1000, 953, 898, 823 cm^{-1}.

^1H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) = 5.17 (br s, 2H, OH), 4.60 (d, *J* = 1.2 Hz, 1H, H3), 4.46 (s, *J* = 13.4 Hz, 1H, H5), 4.37 (d, *J* = 2.1 Hz, 1H, H4), 4.26 (s, 5H, Cp).

$^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 126 MHz): δ (ppm) = 78.2 (d, *J* = 11.6 Hz, CH, C3), 75.8 (d, *J* = 209.2 Hz, C, C1, *C*-P(O)$(OH)_2$), 72.8 (d, *J* = 14.3 Hz, CH, C5), 72.1 (5CH, Cp), 70.7 (d, *J* = 11.7 Hz, CH, C4), 41.2 (d, *J* = 13.9 Hz, C, C2, C-I).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 16.1.

(±)-2-(Diisopropylaminocarbonyl)-*O,O*-diethylferrocenephosphonate ((±)-16a)

To a solution of *N,N,N',N'*-tetramethylethylenediamine (TMEDA; 0.22 mL, 1.5 mmol) in Et_2O (3 mL) at -80 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (1.1 mL, 1.5 mmol) and the reaction mixture was stirred at the same temperature for 30 min. To the formed chelate was next added, at -80 °C, *N,N*-diisopropylferrocenecarboxamide (0.31 g, 1.0 mmol) in Et_2O (3 mL). The mixture was then stirred for 1 h at this temperature before addition of diethyl chlorophosphate (0.29 mL, 2.0 mmol) and warming to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude. Purification by column chromatography (silica gel; eluent: EtOAc/PE 80:20 to 100:0) gave product **(±)-16a** as an orange oil; yield 0.31 g (70%); R_f (EtOAc/PE 80:20) = 0.10.

IR (film): 2972, 2932, 1739, 1634, 1444, 1369, 1335, 1296, 1245, 1209, 1166, 1124, 1097, 1052, 1023, 988, 957, 875, 818, 792, 758, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.52 (q, *J* = 2.4 Hz, 1H, H5), 4.46 (s, 5H, Cp), 4.39 (q, *J* = 1.4 Hz, 1H, H3), 4.37 (q, *J* = 2.5 Hz, 1H, H4), 4.35-4.25 (m, 2H, CH_2), 4.11 (p, *J* = 7.2 Hz, 2H, CH_2), 3.57 (t, *J* = 5.9 Hz, 1H, C*H*Me_2), 3.37 (t, *J* = 5.9 Hz, 1H, C*H*Me_2), 1.46 (t, *J* = 7.2 Hz, 6H, CH*Me*$_2$), 1.38 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.30 (t, *J* = 7.1 Hz, 3H, C*H*$_2$Me), 1.06 (d, *J* = 5.1 Hz, 3H, CH*Me*$_2$), 0.93 (d, *J* = 5.3 Hz, 3H, CH*Me*$_2$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 165.8 (C, C=O), 93.0 (d, *J* = 15.5 Hz, C, C2, *C*-CONi-Pr_2), 71.6 (5CH, Cp), 70.9 (d, *J* = 16.2 Hz, CH, C3 or C5), 70.7 (d, *J* = 13.1 Hz, CH, C3 or C5), 69.7 (d, *J* = 13.7 Hz, CH, C4), 67.0 (d, *J* = 218.3 Hz, C, C1, *C*-P(O)$(OEt)_2$), 62.6 (d, *J* = 6.2 Hz, CH_2), 61.7 (d, *J* = 5.9 Hz, CH_2), 50.8 (CH, *C*HMe_2), 45.8 (CH, *C*HMe_2), 20.9 (2CH_3, CH*Me*$_2$), 20.4 (d, *J* = 6.6 Hz, 2CH_3, CH*Me*$_2$), 16.8 (d, *J* = 5.9 Hz, CH_3, CH_2*Me*), 16.6 (d, *J* = 6.5 Hz, CH_3, CH_2*Me*).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 24.85.

(±)-2-(Diisopropylaminocarbonyl)-*O,O*-diethyl-5-(trimethylsilyl)ferrocenephosphonate ((±)-17a)

To 2-(diisopropylaminocarbonyl)-*O,O*-diethylferrocenephosphonate (**(±)-16a**; 0.45 g, 1.0 mmol) in THF (2 mL) at -80 °C was added dropwise a 1.3 M cyclohexane solution of *s*BuLi (1.2 mL, 1.5 mmol). The mixture was stirred for 1 h at this temperature before addition of chlorotrimethylsilane (0.19 mL, 1.5 mmol) and warming to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude. Purification by column chromatography (silica gel; eluent: EtOAc/PE 20:80 to 50:50) gave product **(±)-17a** as an orange oil; yield 41 mg (8%); R_f (EtOAc/PE 20:80) = 0.17.

IR (film): 2965, 2931, 1792, 1715, 1634, 1444, 1369, 1336, 1311, 1239, 1214, 1164, 1138, 1109, 1079, 1051, 1024, 961, 927, 869, 839, 817, 754, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 4.48 (t, *J* = 2.3 Hz, 1H, H3 or H4), 4.46 (s, 5H, Cp), 4.31 (t, *J* = 2.5 Hz, 1H, H3 or H4), 4.44-3.98 (m, 4H, CH_2), 3.50 (hept, *J* = 6.5 Hz, 1H, C*H*Me_2), 3.37 (hept, *J* = 6.8 Hz, 1H, C*H*Me_2), 1.48 (d, *J* = 6.6 Hz, 6H, CH*Me*$_2$), 1.37 (t, *J* = 7.0 Hz, 3H, CH_2*Me*), 1.27 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.04 (d, *J* = 6.6 Hz, 3H, CH*Me*$_2$), 0.93 (d, *J* = 6.6 Hz, 3H, CH*Me*$_2$), 0.36 (s, 9H, $SiMe_3$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ (ppm) = 166.2 (C, C=O), 97.9 (d, *J* = 17.8 Hz, C, C2, *C*-CONi-Pr_2), 77.0 (d, *J* = 17.0 Hz, CH, C3 or C4), 74.9 (d, *J* = 23.2 Hz, C, C5, *C*-$SiMe_3$), 72.1 (d, *J* = 12.5 Hz, CH, C3 or C4), 71.6 (5CH, Cp), 71.5 (d, *J* = 220.2 Hz, C, C1, *C*-P(O)$(OEt)_2$), 62.8 (d, *J* = 6.0 Hz, CH_2), 60.8 (d, *J* = 6.5 Hz, CH_2), 50.7 (s, CH, *C*HMe_2), 45.7 (s, CH, *C*HMe_2), 20.8 (d, *J* = 5.9 Hz, 2CH_3, CH*Me*$_2$), 20.4 (d, *J* = 6.3 Hz, 2CH_3, CH*Me*$_2$), 17.1 (d, *J* = 4.5 Hz, CH_3, CH_2*Me*), 16.4 (d, *J* = 7.1 Hz, CH_3, CH_2*Me*), 1.0 (3CH_3, $SiMe_3$).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz): δ (ppm) = 26.6.

(±)-2-(Diisopropylaminocarbonyl)-*O,O*-diethyl-1'-(trimethylsilyl)ferrocenephosphonate ((±)-17a')

In the previous reaction, product **(±)-17a'** was also isolated as an orange oil; yield 25 mg (5%); R_f (EtOAc/PE 20:80) = 0.10.

IR (film): 2966, 1698, 1635, 1445, 1368, 1336, 1296, 1246, 1209, 1165, 1135, 1097, 1023, 988, 962, 902, 832, 756, 693 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 4.87 (br s, 1H, H3' or H4'), 4.76 (br s, 1H, H3' or H4'), 4.48 (br s, 1H, H2' or H5'), 4.41 (br s, 1H, H2' or H5'), 4.32 (br s, 1H, H3, H4 or H5), 4.29 (br s, 1H, H3, H4 or H5), 4.26 (br s, 1H, H3, H4 or H5), 4.54-4.17 (m, 2H, CH_2), 4.12 (p, *J* = 7.2 Hz, 2H, CH_2), 3.55 (br s, 1H, C*H*Me_2), 3.37 (br s, 1H, C*H*Me_2), 1.46 (br s, 6H, CH*Me*$_2$), 1.39 (t, *J* = 6.9 Hz, 3H, CH_2*Me*), 1.30 (t, *J* = 6.9 Hz, 3H, C*H*$_2$Me), 1.06 (d, *J* = 4.3 Hz, 3H, CH*Me*$_2$), 0.93 (d, *J* = 4.5 Hz, 3H, CH*Me*$_2$), 0.22 (s, 9H, $SiMe_3$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ (ppm) = 165.6 (C, C=O), 92.6 (d, *J* = 15.5 Hz, C, C2, CONi-Pr_2), 76.4 (2 x CH), 75.5 (CH), 75.4 (CH), 74.3 (C, C1', C($SiMe_3$)), 71.1 (d, *J* = 16.1 Hz, CH), 70.7 (d, *J* = 13.1 Hz, CH), 69.8 (d, *J* = 13.5 Hz, CH), 67.6 (d, *J* = 218.0 Hz, C, C1, *C*-P(O)$(OEt)_2$), 62.5 (d, *J* = 6.1 Hz, CH_2), 61.7 (d, *J* = 5.9 Hz, CH_2), 50.7 (CH, *C*HMe_2), 45.8 (CH, *C*HMe_2), 20.8 (CH_3, CH*Me*$_2$), 20.7 (CH_3, CH*Me*$_2$), 20.5 (2CH_3, CH*Me*$_2$),16.8 (d, *J* = 5.8 Hz, CH_3, CH_2*Me*), 16.6 (d, *J* = 6.5 Hz, CH_3, CH_2*Me*), -0.1 (3CH_3, $SiMe_3$).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz): δ (ppm) = 24.7.

(±)-1'-(Diisopropylaminocarbonyl)-*O,O*-diethyl-2'-(trimethylsilyl)ferrocenephosphonate ((±)-18a)

To (±)-*N,N*-diisopropyl-2-(trimethylsilyl)ferrocenecarboxamide (0.39 g, 1.0 mmol) in Et_2O (2 mL) at -80 °C was added dropwise a 1.3 M cyclohexane solution of *s*BuLi (1.5 mL, 2.0 mmol). The mixture was stirred for 1 h at this temperature before addition of diethyl chlorophosphate (0.29 mL, 2.0 mmol) and warming to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude. Purification by column chromatography (silica gel; eluent: EtOAc/PE 20:80 to 50:50) led to product **(±)-18a** as an orange oil; yield 0.45 g (87%); R_f (EtOAc/PE 20:80) = 0.10.

IR (film): 3482, 2966, 1627, 1444, 1369, 1331, 1276, 1244, 1204, 1189, 1155, 1097, 1025, 959, 906, 834, 752, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.69-4.67 (m, 1H, H3), 4.62 (br s, 1H, H2), 4.58-4.57 (m, 1H, H4), 4.54 (dd, *J* = 2.0 and 1.2 Hz, 1H, H5'), 4.51 (t, *J* = 2.3 Hz, 1H, H4'), 4.49 (br s, 1H, H5), 4.27 (dd, *J* = 2.2 and 1.1 Hz, 1H, H3'), 4.16-4.03 (m, 4H, CH_2), 3.88 (br s, 1H, C*H*Me_2), 3.38 (br s, 1H, C*H*Me_2), 1.46 (br s, 6H, CH*Me*$_2$), 1.32 (td, *J* = 7.1 and 1.2 Hz, 6H, CH_2*Me*), 1.06 (br s, 3H, CH*Me*$_2$), 1.03 (br s, 3H, CH*Me*$_2$), 0.26 (s, 9H, $SiMe_3$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 168.2 (C, C=O), 94.2 (C, C1', *C*-CONi-Pr_2), 75.4 (CH, C3'), 75.3 (C, C2', *C*-$SiMe_3$), 75.2 (d, *J* = 13.7 Hz, CH, C3), 74.2 (d, *J* = 13.7 Hz, CH, C4), 73.6 (d, *J* = 15.4 Hz, CH, C2), 72.1 (d, *J* = 15.4 Hz, CH, C5), 72.0 (CH, C4'), 71.6 (CH, C5'), 67.3 (d, *J* = 214.3 Hz, C, C1, *C*-P(O)$(OEt)_2$), 61.9 (d, *J* = 6.1 Hz, CH_2), 61.8 (d, *J* = 6.0 Hz, CH_2), 50.4 (CH, *C*HMe_2), 45.9 (CH, *C*HMe_2), 21.1 (br s, 2CH_3, CH*Me*$_2$), 20.8 (2CH_3, CH*Me*$_2$), 16.6 (d, *J* = 4.3 Hz, CH_3, CH_2*Me*), 16.57 (d, *J* = 4.3 Hz, CH_3, CH_2*Me*), 0.6 (3CH_3, $SiMe_3$).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.6.

(*R,R*)- and (*S,S*)-1'-(Diisopropylaminocarbonyl)-*O,O*-diethyl-2,2'-bis(trimethylsilyl)ferrocenephosphonate ((±)-19a)

To a solution of *N,N,N',N'*-tetramethylethylenediamine (TMEDA; 0.22 mL, 1.5 mmol) in Et_2O (3 mL) at -80 °C was added dropwise a 1.3 M cyclohexane solution of *s*BuLi (1.2 mL, 1.5 mmol). To the formed chelate was next added, at -80 °C, 1'-(diisopropylaminocarbonyl)-*O,O*-diethyl-2'-(trimethylsilyl)ferrocenephosphonate (**(±)-18a**; 0.52 g, 1.0 mmol) in Et_2O (3 mL). The mixture was then stirred for 1 h at this temperature before addition of chlorotrimethylsilane (0.25 mL, 2.0 mmol) and warming to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum to give the crude. Purification by column chromatography (silica gel; eluent: EtOAc/PE 30:70) gave product **(±)-19a** as an orange solid; yield 0.21 g (35%); R_f (EtOAc/PE 30:70) = 0.11; mp 95 °C.

IR (film): 2966, 1612, 1445, 1368, 1336, 1278, 1238, 1204, 1156, 1023, 963, 906, 827, 751 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.93 (dd, *J* = 3.3 and 2.1 Hz, 1H, H5), 4.87 (q, *J* = 2.3 Hz, 1H, H4), 4.61 (dd, *J* = 2.1 and 1.1 Hz, 1H, H5'), 4.52 (t, *J* = 2.3 Hz, 1H, H4'), 4.45-4.43 (m, 1H, H3), 4.21 (dd, *J* = 2.2 and 1.1 Hz, 1H, H3'), 4.15 (p, *J* = 7.2 Hz, 2H, CH_2), 4.09-3.95 (m, 2H, CH_2), 3.88 (br s, 1H, C*H*Me_2), 3.39 (br s, 1H, C*H*Me_2), 1.48 (br s, 6H, CH*Me*$_2$), 1.35 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.29 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.08 (s, 3H, CH*Me*$_2$), 1.02 (s, 3H, CH*Me*$_2$), 0.32 (s, 9H, C2-Si*Me*$_3$), 0.26 (s, 9H, C2'-Si*Me*$_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 168.3 (C, C=O), 94.0 (C, C1', *C*-CONi-Pr_2), 80.2 (d, *J* = 16.9 Hz, CH, C5), 80.2 (d, *J* = 17.2 Hz, CH, C3), 77.5 (d, *J* = 13.2 Hz, CH, C4), 75.3 (d, *J* = 22.7 Hz, C, C2, *C*-$SiMe_3$), 75.2 (CH, C3'), 74.9 (C, C2', *C*-$SiMe_3$), 72.2 (CH, C5'), 72.1 (CH, C4'), 71.7 (d, *J* = 213.8 Hz, C, C1, *C*-P(O)$(OEt)_2$), 61.7 (d, *J* = 6.0 Hz, CH_2), 61.6 (d, *J* = 6.3 Hz, CH_2), 50.4 (CH, *C*HMe_2), 45.9 (CH, *C*HMe_2), 21.1 (CH_3, CH*Me*$_2$), 20.8 ($2CH_3$, CH*Me*$_2$), 20.6 (CH_3, CH*Me*$_2$), 16.7 (d, *J* = 6.3 Hz, CH_3, CH_2*Me*), 16.4 (d, *J* = 6.7 Hz, CH_3, CH_2*Me*), 0.7 ($3CH_3$, $SiMe_3$), 0.6 ($3CH_3$, $SiMe_3$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 27.4.

(*R*,*S*)- and (*S*,*R*)-1'-(Diisopropylaminocarbonyl)-*O*,*O*-diethyl-2,2'-bis(trimethylsilyl)ferrocenephosphonate ((±)-19a')

In the previous reaction, product **(±)-19a'** was also isolated as an orange solid; yield 92 mg (22%); R_f (EtOAc/PE 30:70) = 0.20; mp 110 °C.

IR (film): 2956, 1617, 1444, 1370, 1334, 1278, 1235, 1203, 1556, 1128, 1088, 1052, 1025, 964, 940, 905, 829, 749 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.82 (dd, *J* = 4.6 and 2.3 Hz, 1H, H4), 4.76 (d, *J* = 1.2 Hz, 1H, H5), 4.62 (s, 1H, H3), 4.53 (t, *J* = 2.2 Hz, 1H, H4'), 4.49 (s, 1H, H5'), 4.28 (d, *J* = 1.0 Hz, 1H, H3'), 4.17-4.06 (m, 2H, CH_2), 4.08-3.94 (m, 2H, CH_2), 3.87 (br s, 1H, C*H*Me_2), 3.37 (br s, 1H, C*H*Me_2), 1.47 (br s, 6H, CH*Me*$_2$), 1.35 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.29 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.08 (br s, 3H, CH*Me*$_2$), 1.01 (br s, 3H, CH*Me*$_2$), 0.33 (s, 9H, C2-Si*Me*$_3$), 0.27 (s, 9H, C2'-Si*Me*$_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 168.2 (C, C=O), 93.2 (C, C1', *C*-CONi-Pr_2), 83.6 (d, *J* = 16.9 Hz, CH, C3), 77.7 (d, *J* = 16.9 Hz, CH, C5), 76.3 (d, *J* = 22.4 Hz, C, C2, *C*-$SiMe_3$), 76.2 (d, *J* = 12.8 Hz, CH, C4), 76.0 (C, C2', *C*-$SiMe_3$), 75.4 (CH, C3'), 72.5 (CH, C4'), 71.0 (CH, C5'), 70.8 (d, *J* = 214.0 Hz, C, C1, *C*-P(O)$(OEt)_2$), 61.6 (d, *J* = 6.3 Hz, CH_2), 61.5 (d, *J* = 5.9 Hz, CH_2), 50.3 (CH, *C*HMe_2), 45.9 (CH, *C*HMe_2), 21.1 (CH_3, CH*Me*$_2$), 20.8 ($2CH_3$, CH*Me*$_2$), 20.6 (CH_3, CH*Me*$_2$), 16.7 (d, *J* = 6.4 Hz, CH_3, CH_2*Me*), 16.4 (d, *J* = 6.7 Hz, CH_3, CH_2*Me*), 0.7 ($3CH_3$, $SiMe_3$), 0.6 ($3CH_3$, $SiMe_3$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 27.5.

(±)-1'-(Diisopropylaminocarbonyl)-*O*,*O*-diethyl-2,5,2'-tris(trimethylsilyl)ferrocenephosphonate ((±)-19a")

In the previous reaction, product **(±)-19a"** was also isolated as an orange solid; yield 0.14 g (22%); R_f (EtOAc/PE 30:70) = 0.28; mp 158 °C.

IR (film): 2956, 1617, 1445, 1370, 1335, 1279, 1235, 1203, 1156, 1128, 1088, 1052, 1024, 965, 936, 906, 883, 826, 793, 760, 749 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.89 (t, *J* = 2.5 Hz, 1H, H3), 4.72 (t, *J* = 2.5 Hz, 1H, H4), 4.61 (s, 1H, H5'), 4.47 (t, *J* = 2.2 Hz, 1H, H4'), 4.29 (s, 1H, H3'), 4.18-4.01 (m, 4H, CH_2), 3.95 (hept, *J* = 6.6 Hz, 1H, C*H*Me_2), 3.39 (hept, *J* = 6.8 Hz, 1H, C*H*Me_2), 1.51 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.46 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 1.37 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.32 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.12 (d, *J* = 6.6 Hz, 3H, CH*Me*$_2$), 0.97 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 0.35 (s, 9H, $SiMe_3$), 0.35 (s, 9H, $SiMe_3$), 0.27 (s, 9H, C2'-Si*Me*$_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 168.4 (C, C=O), 93.0 (C, C1', *C*-CONi-Pr_2), 86.8 (d, *J* = 16.3 Hz, CH, C3), 82.3 (d, *J* = 16.5 Hz, CH, C4), 82.2 (d, *J* = 24.4 Hz, C, C2 or C5, *C*-$SiMe_3$), 80.2 (d, *J* = 25.4 Hz, C, C2 or C5, *C*-$SiMe_3$), 76.7 (C, C2', *C*-$SiMe_3$), 75.3 (CH, C3'), 74.6 (d, *J* = 217.4 Hz, C, C1, *C*-P(O)$(OEt)_2$), 71.8 (CH, C4'), 70.9 (CH, C5'), 61.3 (d, *J* = 6.5 Hz, CH_2), 61.2 (d, *J* = 6.5 Hz, CH_2), 50.3 (CH, *C*HMe_2), 46.2 (CH, *C*HMe_2), 21.2 (CH_3, CH*Me*$_2$), 21.1 (CH_3, CH*Me*$_2$), 20.8 (CH_3, CH*Me*$_2$), 20.7 (CH_3, CH*Me*$_2$), 16.7 (d, *J* = 6.1 Hz, CH_3, CH_2*Me*), 16.6 (d, *J* = 6.4 Hz, CH_3, CH_2*Me*), 1.5 ($3CH_3$, $SiMe_3$), 1.4 ($3CH_3$, $SiMe_3$), 0.7 ($3CH_3$, C2'-Si*Me*$_3$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 29.4.

1'-(Diisopropylaminocarbonyl)-*O*,*O*-diethylferrocenephosphonate (20a)

*t*BuOK (56 mg, 0.5 mmol) was added to a solution of 1'-(diisopropylaminocarbonyl)-*O*,*O*-diethyl-2'-(trimethylsilyl)ferrocenephosphonate (**(±)-18a**; 0.13 g, 0.25 mmol) in dimethylsulfoxide (0.5 mL) under argon and the mixture was stirred at rt for 10 min. After addition of water (10 mL) and extraction with EtOAc (3 x 10 mL), the organic phase was washed with brine (2 x 10 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel; eluent: EtOAc/PE 50:50) led to product **20a** as a yellow oil; yield 41 mg (34%); R_f (EtOAc/PE 50:50) = 0.11.

IR (film): 3454, 2966, 2929, 1720, 1618, 1462, 1427, 1369, 1319, 1239, 1188, 1163, 1136, 1097, 1024, 959, 805, 764 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.64 (s, 2H, H2' and H5'), 4.55 (s, 2H, H2 and H5), 4.53 (s, 2H, H3 and H4), 4.43 (s, 2H, H3' and H4'), 4.37 (br s, 1H, C*H*Me_2), 4.17-4.06 (m, 4H, CH_2), 3.44 (br s, 1H, C*H*Me_2), 1.61 (br s, 3H, CH*Me*$_2$), 1.48 (s, 3H, CH*Me*$_2$), 1.33 (t, *J* = 7.1 Hz, 6H, CH_2*Me*), 1.25 (s, 3H, CH*Me*$_2$), 1.18 (s, 3H, CH*Me*$_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ (ppm) = 168.5 (C, C=O), 84.2 (C, C1', *C*-CONi-Pr_2), 74.4 (d, *J* = 13.8 Hz, 2CH, C3 and C4), 73.0 (d, *J* = 15.4 Hz, 2CH, C2 and C5), 71.3 (2CH, C2' and C5'), 71.0 (2CH, C3' and C4'), 67.8 (d, *J* = 214.0 Hz, C, C1, *C*-P(O)$(OEt)_2$), 61.9 (d, *J* = 6.1 Hz, $2CH_2$), 50.1 (CH, *C*HMe_2), 46.4 (CH, *C*HMe_2), 29.9 (CH_3, CH*Me*$_2$), 21.3 (CH_3, CH*Me*$_2$), 21.2 (CH_3, CH*Me*$_2$), 21.1 (CH_3, CH*Me*$_2$), 16.6 (d, *J* = 6.3 Hz, $2CH_3$, CH_2*Me*).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ (ppm) = 25.2.

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Conflict of Interest

The authors declare no conflict of interest.

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Biosketches

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