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Planar Chirality from the Chiral Pool: Diastereoselective Anionic Phospho-Fries Rearrangements at Ferrocene

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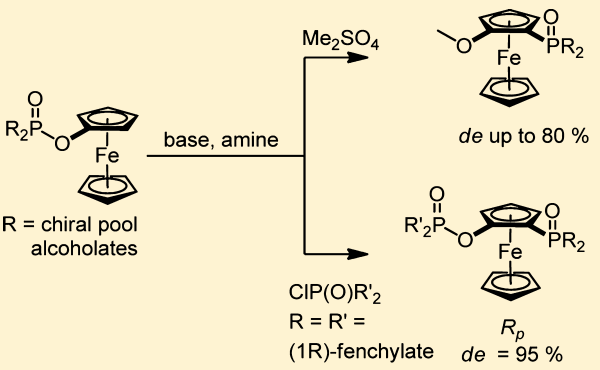
Supporting Information

ABSTRACT: Exclusively, the anionic phospho-Fries rearrangement has successfully been adopted on chiral ferrocenyl phosphates, resulting in diastereomeric enriched 1,2-*P*,*O*-phosphonates (up to 95% de), which can further be converted to an enantiomerically pure phosphane. A simple synthetic protocol for the preparation of all starting materials based on several chiral-pool alcohols, chiral (di)chlorophosphates, and the respective ferrocenyl phosphates is reported. Optimized reaction conditions for the anionic phospho-Fries rearrangement allow conversions at ambient temperature and the use of variable lithium amid bases and diamines in hexane, ensure virtually quantitative yields, and avoid side reactions. The (bi)cyclic alkyl substituents result in air- and moisture-stable compounds and furthermore allow the conversion of 1,1′-substituted derivatives to 1,1′,2,2′-functionalized ferrocenes, which is reported for the first time. Simultaneous rearrangements at diferrocenyl phosphates to phosphinates and even 2-hydroxy-1,3-bis(phosphonato) ferrocenes and their workup under ambient conditions can be performed. Single-crystal diffraction analysis allowed the determination of the absolute configuration of the planar chirality of two diastereomerically pure ferrocenes being the R_p isomers. Furthermore, strong T-shaped $\pi-\pi$ interaction patterns between aromatic C_5H_3 and C_5H_4 cycles for three compounds are observed.



INTRODUCTION

Planar-chiral 1,2-substituted ferrocenes are of growing interest: for example, as supporting ligands for catalytic C,C cross-coupling reactions.[1] The synthetic methodology is frequently based on ortho-directed metalation and subsequent addition of electrophiles.[2] However, only a small percentage of these species contain heteroatoms, especially oxygen, directly bonded at the 1,2-positions at the ferrocene backbone, due to the absence of suitable electrophiles.[1a] This heteroelement, in addition to phosphorus, was shown to act as a hemilabile donating group enhancing the catalytic activity of such molecules as supporting ligands in C,C cross-coupling reactions.[1a]

Recently, it was shown by our group that especially 1,2-*P*,*O*-substituted ferrocenes are available via the anionic phospho-Fries rearrangement, by preferably starting with ferrocenyl phosphates.[1a] The respective rearranged racemic ferrocenyl phosphonate was formed in 94% yield and, thus, with a high regioselectivity. A further conversion to a 1,2-*P*,*O* phosphane, which was used as a supporting ligand in the synthesis of hindered biaryls, resulted in high yields of the appropriate biaryls under mild reaction conditions and with low catalyst loadings.[1a] Enantiomerically pure 1,2-*P*,*O* phosphanes are therefore also promising structural motifs for the adoption of the chiral information from the planar ferrocene backbone to the axial chiral biaryl.

However, the stereoselective formation of the desired phosphane or phosphonate has not yet been achieved. A possible stereoselective formation of the phosphonate could be reached by a stereoselective proceeding of the Fries rearrangement at ferrocene using cheap chiral auxiliaries and should be preferred to a chiral resolution of the formed products, which, however, is of minor importance, due to the high costs of the chiral derivatizing agents, such as Mosher's acid and chiral amines.[3]

It is a fact that the Fries rearrangement does not proceed stereoselectively for phenyl-based compounds,[4a,b] due to the lack of planar chirality formed within the products. However, molecules bearing asymmetric substituents[4c−f] can exhibit an ee of 99% for concerted processes or innocent groups.

Regioselective examples are known on the basis of steric effects of further (bulky) substituents, electronic effects in the aromatic cycle,[5] or just one ortho position available for lithiation, which also results in a high ee or de using chiral substituents.[2c,6]

Three examples for Fries (type) 1,3-X → C rearrangements (X = O, S) have been reported in the literature so far, yielding planar chiral compounds with a detectable ee/de (Scheme 1). Diastereoselective reactions with the use of diaminocyclohexyl-

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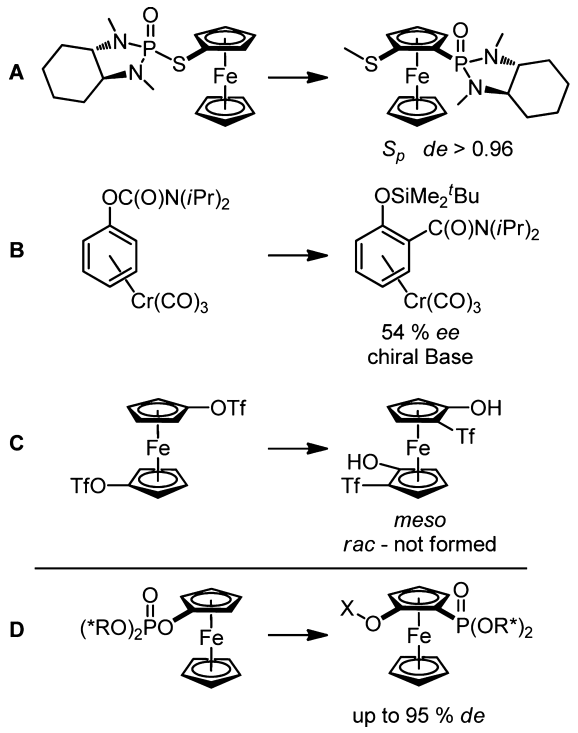
Scheme 1. Synthesis of Planar-Chiral 1,2-Substituted Aromatics via Anionic Fries Type (A) or Fries Rearrangements (B, C; Tf = SO_2CF_3) Described in the Literature[7−9] and Unknown Diastereoselective Anionic Phospho-Fries Rearrangement for the Synthesis of 1,2-*P,O*-Ferrocenes (D)



substituted phosphates (Scheme 1,A) results in an almost diastereomerically pure 1,2-*P,S* ferrocene.[7] Establishing planar chirality by using electron-withdrawing tricarbonyl chromium units allows enantioselective rearrangements with a chiral base, resulting in an acceptable ee of 54% (Scheme 1,B).[8] Interestingly, during the reaction of 1,1′-ferrocenediyl bis(triflates) (Scheme 1,C), only the meso and not the racemic compound is formed; therefore, the rearrangement at the second cyclopentadienyl proceeds stereoselectively, induced by the first cyclopentadienyl.[9]

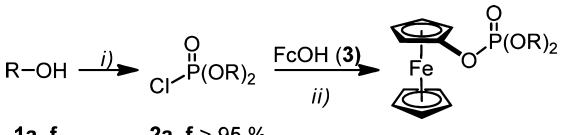
A stereoselective anionic phospho-Fries rearrangement has, to the best of our knowledge, not been reported so far. We herein report for the first time on a stereoselective Fries rearrangement to establish planar chirality at 1,2-*P,O* ferrocenes using chiral pool alcohols. These species are easily available in enantiomerically pure form, and they also can easily be introduced to chiral ferrocenyl phosphates (Scheme 1,D), which are promising educts for high-yielding anionic phospho-Fries rearrangements as key compounds for planar chiral 1,2-*P,O* phosphanes.

RESULTS AND DISCUSSION

The anionic phospho-Fries rearrangement enables an simple access to 1,2-*P,O*-substituted compounds.[1a] Especially phenyl- and naphthyl-based phosphonates, i.e. BINOL derivatives, are known for their use as ligands in asymmetric catalysis.[10] The general reaction conditions therefore include deprotonation ortho to the phosphato moiety with a sterically demanding base to avoid nucleophilic attack and stirring at low temperature for a short time, followed by warming to room temperature. In contrast, when the reaction conditions are adapted for ferrocene, higher temperatures for the lithiation process (−30 °C) are required.[1a] However, attempts to run the reaction enantioselectively by using Simpkins' base did not result in enantiomerically enriched products.[1a,9,11] Therefore, a diastereoselective procedure is needed, which will be reported herein.

The known procedures for the synthesis of (chiral) chlorophosphates are based on the reaction of the respective alcohols in the presence of a base, such as triethylamine or pyridine, and subsequent filtration and distillation of the product mixture.[12] Thus, the applied purification process results in a lower yield of the (di)chlorophosphates and high amounts of ammonium salts.[12] We herein report on a straightforward, high-yielding synthetic protocol including lithiation of cyclohexyl (**1a**, Cy), (1*R*)-menthyl (**1b**, (1*R*)-Mt), (1*S*)-menthyl (**1c**, (1*S*)-Mt), (1*S*)-borneyl (**1d**, Bo), (1*R*)-α-fenchyl (**1e**, Fn) and (1*S*)-isopinocampheyl alcohols (**1f**, Ip) in diethyl ether as the solvent at 0 °C and subsequent addition of $POCl_3$ (Scheme 2). After removal of any lithium salt by simple filtration over

Scheme 2. Synthesis of Dialkylchlorophosphates 2a−f and Further Reaction with FcOLi (3-Li) To Give Dialkylferrocenyl Phosphates 4a−f[a]



1a−f **2a−f** > 95 %

R = Cy, **4a**, 70 %,
R = (1*R*)-Mt, **4b**, 91 %,
R = (1*S*)-Mt, **4c**, 83 %,
R = Bo, **4d**, 46 %,
R = Fn, **4e**, 83 %,
R = Ip, **4f**, 83 %

[a]Legend: (*i*) (1) diethyl ether, BuLi (1 equiv), (2) $POCl_3$ (0.5 equiv), yields based on **1**; (*ii*) (1) diethyl ether, **3**, BuLi, −30 °C, (2) **2a−f**, yields based on **3**.

Celite, the respective chlorophosphates **2a−f** were obtained in quantitative yields without the need for further purification (Experimental Section). Conversion of **2a−f** to the ferrocenyl phosphates **4a−f** is realized by the lithiation of ferrocenol (**3**) using butyllithium (=BuLi) and treatment of **3**-Li with the chlorophosphates **2a−f** (Scheme 2). After the appropriate workup, ferrocenes **4a−f** could be isolated in good to excellent yields (Scheme 2, Experimental Section).

However, the anionic phospho-Fries rearrangement of **4a−f** does not proceed under the reaction conditions which we have reported recently for short-chain diethyl phosphate.[1a] Low yields obtained in the temperature range from −30 to 0 °C and the beginning of ether cleavage at higher temperatures prompted us to use nonpolar instead of polar solvents. The required activity of the lithium base can be enabled by addition of a diamine such as TMEDA (=tetramethylethylenediamine) or chiral (−)-sparteine (=(−)-Spart) (Table SI1, Supporting Information).

Using the optimized reaction conditions (hexane, diamine, base, ambient temperature, 18 h), the desired rearrangement products could be obtained in good to quantitative yields (Table 1). It should be noted that the sterically more demanding aliphatic substituents, in comparison to ethyl groups,[1a] stabilize all phosphates as well as all further products toward hydrolysis and, hence, these compounds can be handled

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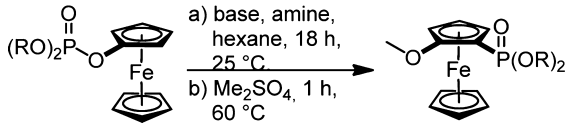
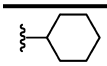
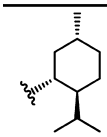
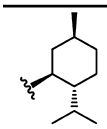
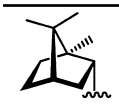
Table 1. Anionic Phospho-Fries Rearrangement of Ferrocenyl Phosphates 4a–f to *O,O*-Dialkyl (2-Methoxyferrocenyl)phosphonates 5a–f



R	Base	Amine	Yield 5[a)]	de[b)]
 **5a**: Cy	LDA	TMEDA	70 %	–
 **5b**: (1*R*)-Mt	LDA	TMEDA	99 %	0.29
	LDA	(−)-Spart	99 %	0.40
	LTMP	(−)-Spart	99 %	0.00
 **5c**: (1*S*)-Mt	LDA	TMEDA	90 %	0.24
	LDA	(−)-Spart	99 %	0.38
	LTMP	TMEDA	87 %	0.37
	LTMP	(−)-Spart	89 %	0.00
 **5d**: Bo	LDA	TMEDA	80 %	0.38
	LDA	(−)-Spart	99 %	0.32
 **5e**: Fn	LDA	TMEDA	29 %	0.72
	LDA	(−)-Spart	79 %	0.58
	LTMP	TMEDA	65 %	0.80
				0.90[c)]
 **5f**: Ip	LDA	TMEDA	57 %	0.40
	LDA	(−)-Spart	72 %	0.30
	LTMP	TMEDA	58 %	0.27
	LTMP	(−)-Spart	80 %	0.13

[a]Isolated yields based on the respective phosphate **4**. [b]The de values were determined by integration of fitted $^{31}P\{^{1}H\}$ NMR spectra. [c]After single recrystallization.

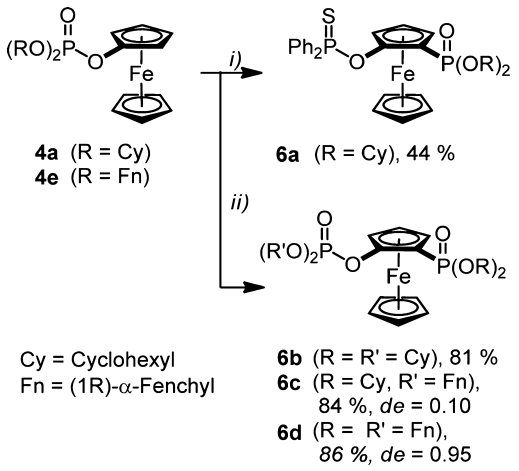
in air and moisture for several weeks without a notable rate of decomposition.

The kinetically controlled lithiation of ferrocenyl phosphates **4a–f** resulted in a diastereomeric excess during the anionic phospho-Fries rearrangement that depends on the demand of the aliphatic substituents (Table 1). The fenchyl derivative **4e** therefore exhibits the highest de (80%) in phosphonate **5e**, due to the three methyl groups located closer to the oxygen-bonded carbon in comparison with the other chiral pool alcohols. The de of the rearrangement products **5a–f** can easily be obtained by the integration of fitted signals in the $^{31}P\{^{1}H\}$ NMR spectra (Table 1) and is further influenced by the required diamine and the base. Instead of LDA (=lithium diisopropylamide) the use of the sterically more demanding base LTMP (=lithium tetramethyl piperidide) resulted in an increased de for **5e** (LDA, de = 0.72; LTMP, de = 0.80). Recrystallization of **5e** further improved the de (0.90), which confirms the fenchyl substituent to be the most appropriate for establishing diastereomerically enriched products. However, when the diamine from the achiral TMEDA is changed to the chiral (−)-sparteine, no further positive influence on the de of **5e** was observed. Interestingly, when (−)-sparteine is used for the rearrangement of the (1*R*)- and (1*S*)-menthyl phosphates **4b,c**, a double stereodifferentiation is not detectable, due to an enhanced de for both of the phosphonates **5b,c** (Table 1, Experimental Section). However, a mismatch situation occurs for **5d–f**, in which (−)-sparteine is not beneficial for the stereoselectivity.

After the anionic phospho-Fries rearrangement, the resulting hydroxy functionality is not limited to react with dimethyl sulfate, as already shown recently.[1a]

However, with the sterically more demanding alkyl groups a limitation in reactivity might occur and, thus, chlorodiphenylphosphane for the synthesis of **6a** and chlorophosphates **6b–d** have been investigated, showing good (**6b–d**) to acceptable (**6a**) yields (Scheme 3).

Scheme 3. Oxygen Functionalization after the Anionic Phospho-Fries Rearrangement of 4a,e[a]



[a]Legend: (*i*) **4a**, LDA, hexane, TMEDA, $ClPPh_2/S_8$, 25 °C, 18 h → 60 °C, 1 h; (*ii*) for **4a**, LDA, hexane, TMEDA, **2a** (**6b**) or **2e** (**6c**), 25 °C, 18 h → 60 °C, 1 h, and for **4e**, LTMP, hexane, TMEDA, **2e**, 25 °C, 18 h → 60 °C, 1 h.

A further enhancement of the de of the formed 1,2-*P,O*-ferrocene is possible by adding a chiral chlorophosphate, which was investigated during the reaction of the fenchyl derivative **4e** by adding the respective fenchyl chlorophosphate **2e** (Scheme 3). The resulting 2-phosphato ferrocenyl phosphonate **6d** could be obtained with a de of 95%,[13] due to a kinetically controlled phosphate formation.[14] Reaction of nonchiral **4a** with chiral **2e** also resulted in the diastereomerically enriched phosphate **6c** (de = 0.10), revealing the chirality of the chlorophosphates to be the main reason for the kinetic phosphate formation. Single crystals of recrystallized **5e** and **6d** exhibited the R_P diastereomer in both cases (Figure 2), which we therefore assume is the mainly formed diastereomer during the rearrangement.

The 2-phosphato phosphonates **6b,d** can undergo a further anionic phospho-Fries rearrangement (Scheme 4). Using LDA as the base, bis(phosphonates) **7a,b** are formed in acceptable (**7a**) to quantitative (**7b**) yields. Interestingly, the −OH functionality in **7b** cannot be converted into the respective methyl ether, even using an excess of methyl sulfate at 60 °C.

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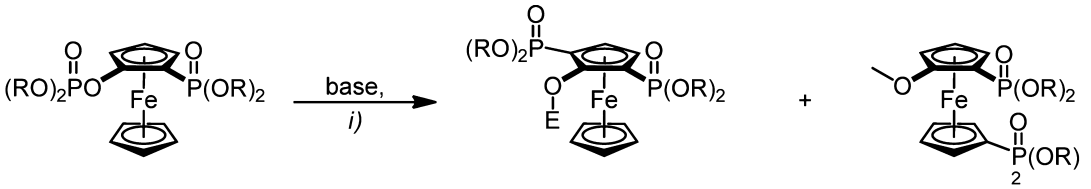
Scheme 4. Consecutive Anionic Phospho-Fries Rearrangement of 6b,d to Bis(phosphonates) 7a−c[c]

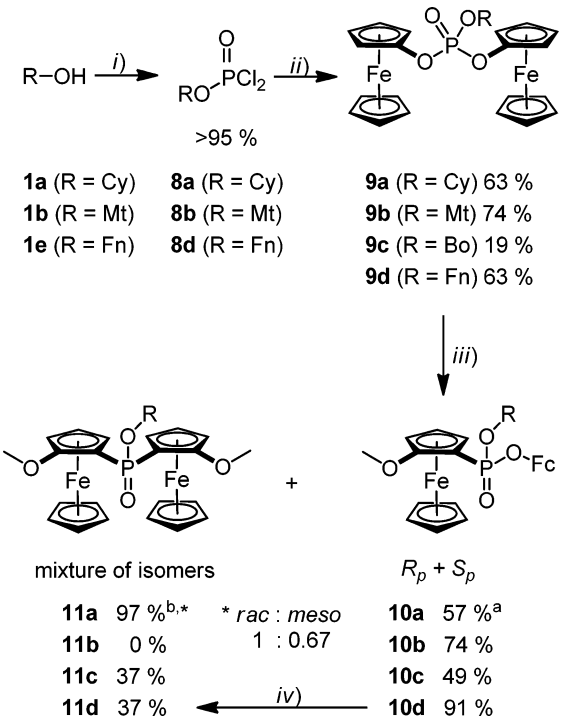


[a]base = LDA. [b]base = LTMP. [c]Legend: (*i*): TMEDA, hexane, 18 h, 25 °C, Me_2SO_4, 60 °C, 1 h. Yields are based on **6b,d**, respectively.

Bis(phosphonato) hydroxyferrocene **7b** is stable toward air and moisture and is most probably stabilized by intramolecular hydrogen bridge bond formation to the phosphonato oxygen atoms.[15] When the base is changed from LDA to LTMP, the increased steric demand resulted in a significantly lower yield of **7b**. Additionally, the formation of **7c** is observed with the phosphonato substituents located at the 1,1′-positions and a resulting de at 0.95, based on the de of the starting material **6d**.[16] The lithiation exclusively occurs ortho to the phosphate and not to the phosphonate substituent, due to the absence of any ortho-methylated product, which indicates a less attractive stabilization of the phosphonato in comparison to the phosphato substituent.

In addition to a single anionic phospho-Fries rearrangement at one aryl or ferrocenyl substituent, simultaneous rearrangements are possible by replacing the alkyl with further aryl or ferrocenyl substituents, which has been reported for up to "triple-Fries" rearrangements.[17] For ferrocenyls, the simultaneous formation of two planar chiral ferrocene backbones should be possible. With the chiral pool alcohols **1a,b,d,e** as starting materials, the dichlorophosphates **8a,b,d** were synthesized in a more simple "one-pot" approach, in comparison to literature methodologies[12a] (Scheme 5), including deprotonation of the alcohols **1a,b,d,e** and dropwise addition of the formed alcoholates to an excess (>3 equiv) of $POCl_3$. After removal of all volatiles dichlorophosphates **8a,b,d** were obtained as pure colorless oils in quantitative yields, avoiding the need for further purification. The alkyl diferrocenyl phosphates **9a−d** are accessible by reacting **8a−d** with deprotonated FcOLi (**3**-Li) (Scheme 5), whereas borneyl derivative **9c** was obtained as a side product during the synthesis of **4d**. However, the subsequent anionic phospho-Fries rearrangement primarily yields the monorearranged phosphonates **10a−d**, as a mixture of the two possible isomers with regard to the planar chirality. For **10b−d** four diastereomers were formed, due to the asymmetrically substituted phosphorus, whereas **10a** can be obtained as a mixture of two diastereomers (de = 0.45) (Table SI2, Supporting Information), which indicates that the positions at the prochiral ferrocenes in the achiral phosphate are kinetically not equal. Thus, a stereoselective anionic phospho-Fries rearrangement is possible without a further chiral input. The second rearrangement to phosphinates **11a−d** is only observed in low yields. Nevertheless, when the amount of base (>8 equiv) is increased for the nonchiral cyclohexyl-substituted **9a**, a quantitative conversion to the *meso* and the *racemic* isomers is possible. After their separation, the racemic product is obtained as the main diastereomer (de = 0.20).

Scheme 5. Synthesis and Anionic Phospho-Fries Rearrangement of Alkyldiferrocenyl Phosphates 9a−d[c]



[a]Using 2 equiv of LDA. [b]Using >8 equiv of LDA. [c]Legend: (*i*) BuLi, diethyl ether, >3 equiv of $POCl_3$, 25 °C, 18 h; (*ii*) BuLi, diethyl ether, **3**, **8a,b,d** (for **9a,b,d**)/**2d** (for **9c**), 25 °C, 18 h, yields are based on **3**; (*iii*) hexane, TMEDA, LDA (**9a−c**)/LTMP (**9d**), 18 h, Me_2SO_4, 60 °C, 1 h, yields for **10a−d** and **11a−c** are based on **9a−d**; (*iv*) hexane, TMEDA, LDA, **10d**, 18 h, Me_2SO_4, 60 °C, 1 h, yield based on **10d**.

Attempts to achieve **11d** by a similar approach failed, resulting in an almost quantitative formation of **10d**. However, lithiation of **10d** resulted in the formation of the desired phosphinate **11d**. With regard to the stereoselectivity of the rearrangement, the decreased number of chiral substituents produced an unspecific mixture of isomers for **10b−d** and **11b−d** (Table SI2, Supporting Information). For **10d** the influence of the amount of the base was examined (Table SI2), showing only a slight change in the integrals of the signals; however, when the base was changed from LTMP to LDA a significant change of the integral of each signal in the $^{31}P\{^1H\}$ NMR was observed, but with none of the diastereomers formed primarily. Borneyl derivative **11c**, however, only resulted in the formation of two diastereomers instead of four, indicating a high stereoselectivity for one rearrangement. The disfavored

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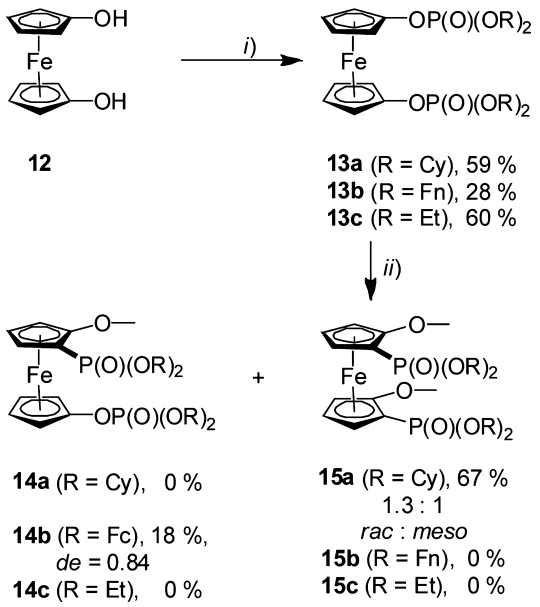
formation of phosphinates **11a–d** as well as the decreased diastereoselectivity can both be explained by the fact that anionic Fries rearrangements, in general, are favored for electron-poor compounds,[1a,5e,11a] such as phosphates, which prevent the nucleophilic attack at the phosphorus atom due to the higher acidity of the ferrocenyl protons.

The rearrangement products **10a–d** are more electron rich in comparison to phosphates **9a–d**, due to the ferrocenyl substituent. Furthermore, the lithium ion is well stabilized by the hydroxy oxygen and the P=O moiety,[15a] and a further lithiation is less desirable.

Recently, a 1,1′-substituted ferrocene bearing sterically nondemanding ethyl groups, **13c**, could not be converted to the respective rearrangement compounds **14c** and **15c**, due to its instability.[1a] When the sterically more demanding (bi)cyclic alcohols **1a,e** were used, the stability of phosphates **13a,b** as well as of the corresponding phosphonates **14b** and **15a**, respectively, is increased. However, the increased steric demand requires stirring in hexane (**13a**, 4 h, 60 °C bath temperature) or tetrahydrofuran (**13b**, 12 h, 80 °C bath temperature) to complete the reaction of both hydroxyl moieties with the chlorophosphates (Scheme 6). However, the conversion of

Scheme 6. Synthesis of 1,1′-Ferrocenediyl Phosphates 13a–c and Anionic Phospho-Fries Rearrangement to Phosphonates 14a–c and 15a–c[a]

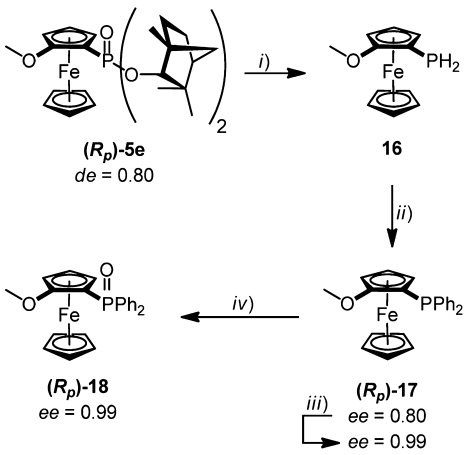


[a]Legend: (*i*) BuLi, for **13a**, hexane, **2a**, 12 h, 60 °C, 4 h, for **13b**, tetrahydrofuran, **2e**, 12 h, 80 °C, 12 h, for **13c**, NEt_3, $ClP(O)(OEt)_2$, CH_2Cl_2, −20 °C;[1a] (*ii*) LDA (R = Cy)/LTMP (R = Fn), TMEDA, hexane, 25 °C, 18 h, Me_2SO_4, 50 °C, 1 h, for **13c**, LDA, tetrahydrofuran, −30 °C, Me_2SO_4.

cyclohexyl-substituted **13a** proceeds to the expected double-rearranged product **15a** as a mixture of both diastereomers with a de of 13%. Obviously, the lithiation of the C_5H_4 cycle is influenced by the configuration established at the first cyclopentadienyl ring. Using the reaction protocol for diastereomerically enriched fenchyl derivatives, a slight increase of the de (0.84) of **14b** in comparison to that for singly substituted **5e** (de = 0.80) could be detected (Scheme 6). Nevertheless, the rearrangement product containing phosphonates at both cyclopentadienyls (**15b**) could not be obtained for the fenchyl substituent during this reaction. This is attributed to the steric demand of the chiral fenchyl substituents or an unfavorable stabilization of the lithiated species, which prevents the rearrangement to **15b**.

Furthermore, the highly diastereomerically enriched phosphonate **5e** could be converted to **16**, revealing that the recently reported reaction conditions for the reduction of ferrocenyl phosphonates can be adopted on sterically more demanding derivatives (Scheme 7).[1a,18]

Scheme 7. Conversion of Phosphonate 5e to Enantiomerically Pure (R_p)-17[a]



[a]Legend: (*i*) (1) $Li[AlH_4]$ (>3 equiv), Me_3SiCl (>3 equiv), tetrahydrofuran, 25 °C, (2) **5e**, 50 °C, 12 h; (*ii*) PhI (2 equiv), K_3PO_4 (2 equiv), $[Pd(dppf)Cl_2]$ (4 mol %), toluene, 110 °C, 12 h, 65%, yield based on **5e**; (*iii*) crystallization from hexane; (*iv*) atmospheric conditions, 2 weeks, 95/5 (v/v) hexane/^{t}BuOMe.

When **16** was used under palladium-catalyzed Stelzer P,C cross-coupling reaction conditions,[1a,19] the respective diphenylphosphino ferrocene **17** could be obtained in 65% yield (ee = 0.80). Single recrystallization from hexane increased the ee to >0.99, evidenced by chiral HPLC (Figure SI7, Supporting Information). Furthermore, single crystals of the corresponding enantiopure phosphine oxide **18** could be obtained from a sample solution of **17** after standing for 2 weeks under atmospheric conditions (Scheme 7), revealing the expected planar chiral *R* isomer (Figure 4).

All compounds were analyzed using ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy, resulting in complex spectra, due to the signals of several formed diastereomers, especially for **5a–f**, **10a–d**, and **11a–d**. In general, the $^{31}P\{^1H\}$ NMR shift is a meaningful indication of a successful conversion of chlorophosphates **2** and **8** (2.3 (**2a**) to 5.9 (**2e**); 5.7 (**8a**) to 8.4 ppm (**8d**)) to phosphates **4** and **9** (−4.3 (**4e**) to −6.8 (**4a**); −9.8 (**9c,d**) to −10.9 ppm (**9a**)) and **13** (−6.9 (**a**) to −4.3 ppm (**b**)). Furthermore, the phosphato substituents in ferrocenes **6a–d** (−3.5 (**6d**) to −7.4 ppm (**6b**)) and **14b** (−4.5 ppm) exhibit similar values (Experimental Section). The distinction between phosphonates **10a–d** (19.8 (**10b**) to 21.5 ppm (**10d**)) and phosphinates **11a–d** (34.2 (**11a**) to 38.0 ppm (**11d**)) is also rather simple by comparing with the chemical shifts of phosphonates **5a–f** and **7a–c** (20.6 (**5b**) to 23.2 ppm (**5d**); 19.8(**7a**) to 25.8 ppm (**7b**)) and **15a** (20.8 ppm), due to the formation of up to four diastereomers.

A further indicator of a successful anionic phospho-Fries rearrangement is the $^1J_{C,P}$ coupling constant of the ferrocenyl

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C−P bond, which displays a significant decrease from 217(2) Hz for phosphonates to 160(3) Hz for the more electron rich phosphinates **11a−d**. The verification of the 1,1′-substitution pattern in the unexpectedly formed bis(phosphonate) **7c** in comparison to bis(phosphonate) **7b** (Scheme 4) is indicated by the absence of the C_5H_5 signal in the ^1H and in the $^{13}C\{^1H\}$ NMR spectra and the appearance of the $^{31}P\{^1H\}$ resonances as singlets at 21.3 and 23.8 ppm, in comparison with **7b**, where doublets for both signals (21.3 and 25.8 ppm; $^3J_{P,P}$ = 3.7 Hz) are characteristic. Additional 2D $^{31}P/^1H$ experiments allow the assignment of three (21.3 ppm) and four (23.8 ppm) ^1H signals to the respective phosphorus resonance (Figure SI1, Supporting Information). Since **11a** can be separated into both of its diastereomers, the classification as a *meso* (pseudochiral phosphorus atom) and a *racemic* compound (prochiral P atom and ferrocenyl substituents) can be realized by the fact that the racemic stereoisomers exhibits double signal sets for all atoms in the $^{13}C\{^1H\}$ (Supporting Information) and ^1H NMR spectra.

The molecular structures of **4a,b,e**, **5e**, **6d**, **9b**, **10a,c,d**, and **18** in the solid state have been determined by single-crystal X-ray diffraction analysis (Figures 1−4). Suitable crystals were obtained by crystallization from hexane solutions at ambient temperature. The ORTEP diagrams with selected bond lengths, bond angles, and torsion angles are shown in Figures 1−4. Compounds with cyclohexyl substituents (**4a**, **10a**) crystallize in the noncentrosymmetric space group $P2_1/c$, whereas the chiral substituents lead to the chiral Sohncke space groups[20,21] $P1$ (**4e**), $P2_12_12_1$ (**4b**, **5e**, **18**), $P2_1$ (**9b**, **10c,d**), and $C2$ (**6d**) with one (**4a,b**, **5e**, **9b**, **10a**, **18**) or two molecules (**4e**, **6d**, **10c,d**) in the asymmetric unit. Thus, the absolute configuration for **5e**, **6d**, and **18** could be determined as the R_p diastereomer (Figures 2 and 4), whereas for **10c,d** a mixture of the R_pS^P and the S_pR^P diastereomers emerges (Figure 3). The two molecules of **4e** in the asymmetric unit differ from each other in the conformation of the P═O bond directed to either the right or left side with regard to the plane view of the ferrocene (Figure 1).

The conformation of the ferrocenyls is rather eclipsed (angles in deg: **4a**, 4.5(3); **4f**, 6.7(6); **5f**, 5.66(17); **6d**, 8.6(3); **9b**, 1.1(7); **10a**, 8.3(2); **10d**, 3.7(7), 8.5(7), 9.0(8); **18**, 9.7(3)) or slightly deviates (angles in deg: **4b**, 11.7(3); **6d**, 11.5(2); **9b**, 23.7(7); **10a**, 10.5(2); **10d**, 14.4(9)). For all singly substituted (di)ferrocenyl phosphates **4a,b,e** and **9b** the phosphato moiety is located above the binding cyclopentadienyl substituent (C−C−O−P in deg: **4a**, 18.0(6); **4b**, 30.6(4); **4e**, 72.6(8); **9b**, 19.6(15), 89.8(9)), in contrast to the case for phosphonato ferrocenyls, where instead the P═O bond is directed toward the metallocenyl backbone (C−C−P═O in deg: **5e**, 174.86(15); **6d**, 158.5(3); **10a**, 168.3(2); **10c**, 175.9(4); **10d**, 175.3(11)).

The methyl and further O-bonded substituents in the doubly substituted ferrocenes **5e**, **6d**, **10a,c,d**, and **18** are consequently directed away from the remaining free electron pairs in the vacant space between these two substituents. Interestingly, in cyclohexyl phosphonate **10a** an unfavorable axial conformation is observed, in contrast to phosphate **4a**, with the oxygen atom located in the equatorial position.

Compounds **5e**, **9b**, and **10a,c,d** exhibit T-shaped $\pi-\pi$ interactions between the aromatic cyclopentadienyl planes. Obviously, strong intramolecular π contacts are present in **10a,c,d** (4.556(3)−4.675(7) Å; Figure SI2, Supporting Information) between the unsubstituted C_5H_5 cycle and the

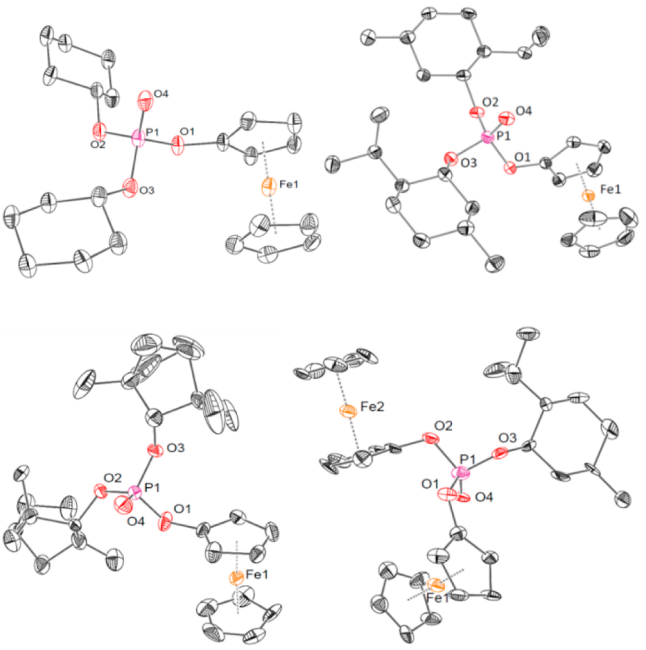

Figure 1. ORTEP diagram (50% probability level) of the molecular structures of **4a** (top left), **4b** (top right), **4e** (bottom left), and **9b** (bottom right) with the atom-numbering scheme. All hydrogen atoms and further molecules in the asymmetric unit (**4e**) have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): for **4a**, O1−P1 1.594(3), O2−P1 1.574(3), O3−P1 1.568(3), O4−P1 1.461(3), D1−Fe1 1.6511(6), D2−Fe1 1.6561(6), O1−P1−O2 100.25(14), O1−P1−O3 102.84(14), O2−P1−O3 10400(15), D−Fe1−D 179.34(4), C5−C1−O1−P1 18.0(6); for **4b**, O1−P1 1.5799(18), O2−P1 1.5646(17), O3−P1 1.5671(19), O4−P1 1.4544(18), average D−Fe1 1.645, O1−P1−O2 101.50(9), O1−P1−O3 101.23(10), O2−P1−O3 104.95(9), D−Fe1−D 178.60(3), C5−C1−O1−P1 30.6(4); for **4f**, O1−P1 1.596(5), O2−P1 1.563(5), O3−P1 1.574(5), O4−P1 1.444(5), average D−Fe 1.65, O1−P1−O2 100.1(3), O1−P1−O3 101.8(3), O2−P1−O3 102.2(3), average D−Fe−D 178, C2−C1−O1−P1 72.6(8), C35−C31−O5−P2 65.5(9); **9b**, O1−P1 1.605(10), O2−P1 1.581(11), O3−P1 1.542(10), O4−P1 1.437(9), average D−Fe 1.65, O1−P1−O2 99.2(5), O1−P1−O3 103.6(6), O2−P1−O3 103.4(6), average D−Fe−D 178, C2−C1−O1−P1 19.6(15), 12−C11−O2−P1 89.8(9). D1 denotes the centroids of the C_5H_4 and D2 of C_5H_5 ligands.

top of the C_5H_3 plane. Furthermore, a dimer between two molecules is formed on the basis of weaker $\pi-\pi$ interactions between the two C_5H_5 substituents (4.794(4)−4.901(2) Å; Figure SI3, Supporting Information). The distance between the similarly arranged ferrocenyls in phosphate **9b**, in contrast, exceeds the range of T-shaped $\pi-\pi$ interactions (>5.0 Å); a one-dimensional helical pattern is formed by the C_5H_5 cycles (4.571(7) Å) of both ferrocenyls (Figure SI4, Supporting Information). A one-dimensional zigzag T-shaped $\pi-\pi$ interaction can be found between the C_5H_5 cyclopentadienyls in phosphonate **5e** (4.7827(12) Å) in the solid state (Figure SI5, Supporting Information).

In phosphane oxide **18** T-shaped intermolecular $\pi-\pi$ interactions can be observed between the C_5H_5 and phenyl rings (Figure SI6, Supporting Information), whereas intramolecular interactions are not present.

The P═O bond is significantly enlarged in **18** (P═O 1.491(2) Å) in comparison to those in the phosphates and phosphonates **4a,b,f**, **5e**, **6d**, **9b** and **10a,c,d** (**9b**, 1.437(9) Å, to **10c**, 1.469(4) Å), due to the more electron rich phenyl rings,

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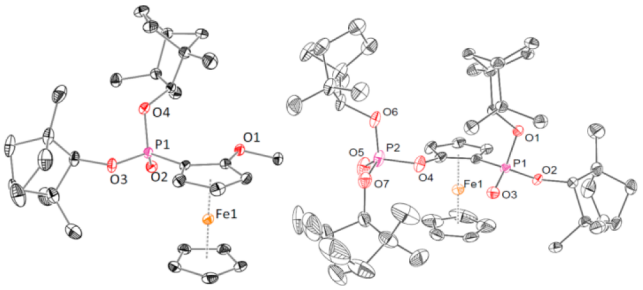

Figure 2. ORTEP diagram (50% probability level) of the molecular structures of **5e** (left) and **6d** (right) with the atom-numbering scheme. All hydrogen atoms, solvent molecules (**6d**, CH_2Cl_2), and a second, similar molecule of **6d** in the asymmetric unit have been omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): for **5e**, P1−O2 1.4639(13), P1−O3 1.5770(12), P1−O4 1.5915(13), average D−Fe 1.647, C1−P1−O2 117.06(8), C1−P1−O3 99.70(8), C1−P1−O4 106.96(8), O3−P1−O4 101.40(7), O3−P1−O2 117.12(17), O4−P1−O2 112.68(7), C1−C2−O1−C12 165.52(16), D−Fe1−D 178.97(3), C2−C1−P1−O3 174.86(15), C2−C1−P1−O4 79.96(17); for **6d**, C1−P1 1.772(4), O1−P1 1.589(2), O2−P1 1.575(2), O3−P1 1.464(2), P2−O4 1.592(2), P2−O5 1.453(3), P2−O6 1.567(3), P2−O7 1.558(3), Fe−D1 1.6405(4), Fe−D2 1.6458(5), O1−P1−O2 101.43(11), O1−P1−C1 105.46(13), O2−P1−C1 100.07(13), O6−P2−O7 103.58(14), O6−P2−O4 101.33(13), O4−P2−O7 101.98(13), C2−C1−P1−O3 30.9(3), C2−C1−P1−O2 158.5(3), C2−C1−P1−O1 96.5(3), C1−C2−O4−P2 173.5(2). D1 denotes the centroids of the C_5H_4 and D2 of C_5H_5 ligands.

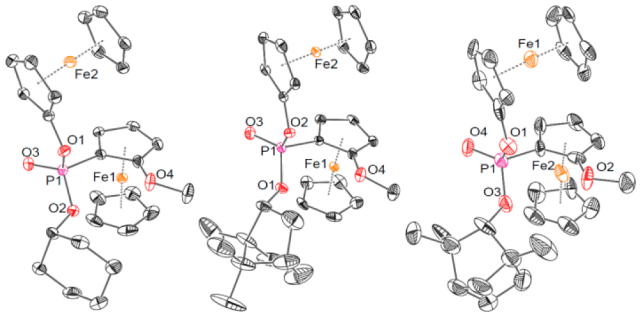

Figure 3. ORTEP diagram (50% probability level) of the molecular structures of **10a** (left), S_P,R^P-**10c** (middle), and S_P,R^P-**10d** (right) with the atom-numbering scheme. All hydrogen atoms, solvent molecules (**10c**, diethyl ether), and R_P,S^P-**10c** and R_P,S^P-**10d**, which are also present in the asymmetric unit have been omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): for **10a**, P1−O1 1.612(2), P1−O2 1.565(2), P1−O3 1.461(2), P1−C11 1.756(3), D−Fe1 1.6414(4)/1.6432(4), D−Fe2 1.6521(4)/1.6571(4), O1−P1−C11 106.79(12), O2−P1−O2 99.42(11), C2−C1−O1−P1 12.4(4); for **10c**, P1−C1 1.753(6), P1−O2 1.611(3), P1−O3 1.571(3), P1−O4 1.469(4), C1−P1−O2 106.5(2), C1−P1−O1 103.5(2), O1−P1−O2 100.18(18), D−Fe1−D 175.43(64), D−Fe2−D 179.63(36), average D−Fe 1.651, C16−C12−O2−P1 11.7(8); **10d**, P1−O1 1.593(10), P1−O3 1.587(10), P1−O4 1.453(11), P1−C11 1.768(8), O1−P1−C11 105.5(6), O3−P1−C11 104.1(6), O1−P1−O3 99.6(5), C2−C1−O1−P1 179.7(9). D denotes the centroids of the C_5H_4 and C_5H_5 ligands.

and does not exceed the C_5H_3 plane (C2−C1−P1═O2 6.3(4)°). Interestingly, the P═O moiety is rotated away from the −OMe group, in contrast to the recently reported solid-state structure of *rac*-**17**, whose free electron pair at the phosphorus atom is directed toward the vacant space between the 1,2-substituents.

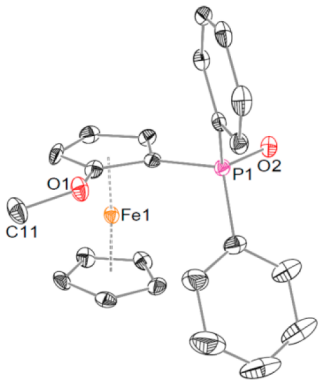

Figure 4. ORTEP diagram (50% probability level) of the molecular structure of (R_p)-**18** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg) for (R_p)-**18**: P1−O2 1.491(2), P1−C1 1.787(3), P1−C_{Ph} 1.787(3) and 1.808(3), D−Fe1 1.6485(6) and 1.6516(6), D−Fe−D 176.44(4), C2−C1−P1−O2 6.3(4), C1−C2−O1−C11 165.8(4) D denotes the centroids of the C_5H_4 and C_5H_5 ligands.

The anionic phospho-Fries rearrangement was successfully applied for the first time for the synthesis of novel planar-chiral 1,2-*P*,*O* ferrocenes **5a−f**, **6a−d**, **7a−c**, **10a−d**, **11a,c,d**, **14a**, and **15b**, resulting in diastereomerically enriched products (de up to 95%). Using easily available and enantiopure chiral pool alcohols, i.e. (1*R*)- and (1*S*)-menthol, (1*S*)-borneol, (1*R*)-*α*-fenchol, and (1*S*)-isopinocampheol, chiral (di)-chlorophosphates **2a−f** and novel (di)ferrocenyl phosphates **4a−f** and **9a−d** could be obtained by a straightforward synthetic protocol. Treatment of the phosphates under optimized reaction conditions (hexane, diamine, base, ambient temperature) avoid the ether cleavage and yield the ferrocenyl phosphonates in yields of up to 90% with 80% de for the fenchyl derivative. This is due to the location of the three methyl substituents close to the phosphate moiety and, thus, the highest impact of the chirality on the lithiation process.

Further improvement by a subsequent stereoselective phosphate formation increases the de to 95%, which is, to the best of our knowledge, the only protocol for the synthesis of diastereomerically pure planar chiral 1,2-*P*,*O*-ferrocenes reported in the literature. This gives access to planar chiral 1,2-*P*,*O* ferrocenyl phosphanes and the investigations of their behavior on the enantiomeric excess of atropselective biaryl synthesis, which is currently under investigation. The absolute configuration of the planar chirality could be determined by single-crystal X-ray diffraction analysis for two examples and proved to be the R_p diastereomer. Attempts to convert diferrocenyl phosphates to double-rearrangement products primarily yielded the single transformed compounds, even with a de of 45% for nonchiral cyclohexyl substituents, which has not been expected so far.

Single-crystal diffraction analyses exhibit intermolecular T-shaped *π*−*π* interactions between C_5H_5 substituents for several compounds and strong intramolecular interactions for ferrocenyl phosphonates (**10a,c,d**). Furthermore, the bulky alkyl (bi)cycles allow the consecutive rearrangement to 2-hydroxy-1,3-bis(phosphonates), as well as rearrangements of 1,1′-ferrocenediyl phosphates to compounds stable toward air and moisture, which failed for the respective diethyl derivatives recently.

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The sterically demanding fenchyl phosphonate **5e** could furthermore be converted into the respective enantiomerically pure phosphane, whose racemic mixture has already been investigated as an excellent supporting ligand for the synthesis of hindered biaryls. These results give access to atropselective reactions that are under current investigation.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran and hexane were purified by distillation from sodium/benzophenone ketyl; diethyl ether was purified by distillation from sodium; dichloromethane, *N*,*N*-dimethylformamide, *N*,*N*-diisopropylamine, and acetonitrile were purified by distillation from calcium hydride. For column chromatography either silica with a particle size of 40−60 μm (230−400 mesh (ASTM), Fa. Macherey-Nagel) or alumina with a particle size of 90 μm was used. The assignment and labeling of the H and C atoms in the NMR of the (bi)cyclic aliphatic substituents follows the IUPAC recommendations.[19]

Reagents. Butyllithium (BuLi) (2.5 M solution in hexane), ferrocene, lithium tetramethylpiperidide (LTMP), (−)-sparteine, and the alcohols **1a**−**f** were purchased from commercial suppliers and used without further purification. $POCl_3$ and TMEDA were distilled prior to use.

Instruments. NMR spectra (500.3 MHz for ^1H, 125.8 MHz for $^{13}C\{^1H\}$ and 202.5 MHz for $^{31}P\{^1H\}$ spectra) are reported with chemical shifts in δ (ppm) downfield from tetramethylsilane with the solvent as the reference signal (chloroform-*d*: ^1H at 7.26 ppm and $^{13}C\{^1H\}$ at 77.00 ppm) or by external standards ($^{31}P\{^1H\}$ relative to 85% H_3PO_4 0.0 ppm and $P(OMe)_3$ 139.0 ppm).

The HPLC measurements were performed with an UV detector operating at 245 nm equipped with a Chiralcel OD-H column (4.6 × 250 mm) using a 95/5 (v/v) hexane/^{t}BuOMe mixture (0.5 mL/min) as the solvent. Retention times *t* are reported in minutes. The area of the integrals is reported relative to 100%.

Single-Crystal X-ray Diffraction Analysis. Data were collected at 110 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å; **4a**,**b**,**e**, **5e**, **6d**, **9b**, **10a**,**d**, and **18**) or Cu Kα radiation (λ = 1.54184 Å; **10c**). The molecular structures were solved by direct methods using SHELXS-97[22] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[23,24] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions. Graphics of the molecular structures have been created by using ORTEP.[25]

Synthesis of Dialkyl Chlorophosphates 2a−e: General Procedure. The respective alcohols **2a**−**f** (2 equiv) were dissolved in 10 mL of tetrahydrofuran; an equal volume of diethyl ether was added, and the mixture was cooled to −30 °C. The dropwise addition of BuLi (2 equiv) resulted in the formation of a colorless precipitate. After the mixture was stirred for an additional 10 min at −30 °C, $POCl_3$ (1 equiv) was slowly added and the solution was warmed to ambient temperature and stirred overnight. All volatiles were removed under reduced pressure. The resulting residue was suspended in diethyl ether and filtered through a plug of Celite (minimum 5 cm) with diethyl ether to remove the lithium salt. After removal of all volatiles the respective chlorophosphates **2a**−**f** were obtained as colorless oils and used without further purification.

*Dicyclohexyl Chlorophosphate (**2a**).* Cyclohexanol **1a** (6.75 mL, 64.1 mmol), BuLi (26 mL, 65 mmol), and $POCl_3$ (3 mL, 32 mmol) were reacted as described in the general procedure above. The analytical data are in agreement with the data given in ref 26.

Yield: 8.90 g (31.7 mmol, 99% based on **1a**). ^1H NMR ($CDCl_3$, δ): 1.25−1.42 (m, 6 H), 1.48−1.56 (m, 2 H), 1.59−1.66 (m, 4 H), 1.70−1.81 (m, 4 H), 1.92−2.03 (m, 4 H), 4.54−4.61 (m, 2 H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.3 (CH_2), 25.0 (CH_2), 32.7 (d, $^3J_{C,P}$ = 4.7 Hz, CH_2), 33.0 (d, $^3J_{C,P}$ = 4.7 Hz, CH_2), 80.1 (d, $^2J_{C,P}$ = 7.4 Hz, C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 2.3.

*Bis((1R)-menthyl) Chlorophosphate (**2b**).* (1*R*)-Menthol (**1b**; 10.00 g, 64.0 mmol), BuLi (25.6 mL, 64.0 mmol), and $POCl_3$ (3 mL, 32.0 mmol) were reacted as described in the general procedure above.

Yield: 12.46 g (31.7 mmol, 99% based on **1b**). ^1H NMR ($CDCl_3$, δ): 0.80−0.85 (m, 6 H, CH_3), 0.86−0.89 (m, 2H), 0.90−0.96 (m, 12H, CH_3), 0.99−1.08 (m, 2H), 1.18−1.27 (m, 2H), 1.37−1.52 (m, 4H), 1.64−1.73 (m, 4H), 2.10−2.16 (m, 2H, $CH(CH_3)_2$), 2.29−2.36 (m, 2H, H6), 4.31−4.43 (m, 2H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.77 (CH_3), 15.82 (CH_3), 20.89 (CH_3), 20.93 (CH_3), 21.84 (CH_3), 21.92 (CH_3), 22.91(CH_2), 25.56 ($CH(CH_3)_2$), 25.59 ($CH(CH_3)_2$), 31.60, 31.62, 33.89 (CH_2), 42.2 (d, $^3J_{C,P}$ = 61.2 Hz, C6), 48.35, 48.38, 48.42, 48.44, 82.1 (d, $^2J_{C,P}$ = 8.3 Hz, C1), 82.3 (d, $^2J_{C,P}$ = 8.4 Hz, C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 3.3. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{20}H_{38}ClO_3P$ + Na 415.2139, found 415.2137 $[M + Na]^+$ (19%); $(C_{20}H_{38}ClO_3P)_2$ + Na 807.4386, found 807.4484 $[M + Na]^+$ (100%).

*Bis((1S)-menthyl)) Chlorophosphate (**2c**).* (1*S*)-Menthol (**1c**; 5.00 g, 32.0 mmol), BuLi (12.8 mL, 32.0 mmol), and $POCl_3$ (1.5 mL, 16.0 mmol) were reacted as described in the general procedure above.

Yield: 6.21 g (15.8 mmol, 99% based on **1c**). ^1H NMR ($CDCl_3$, δ): 0.80−0.85 (m, 6H, CH_3), 0.86−0.89(m, 2H), 0.90−0.96 (m, 12H, CH_3), 0.99−1.08 (m, 2H), 1.18−1.27 (m, 2H), 1.37−1.52 (m, 4H), 1.64−1.73 (m, 4H), 2.10−2.16 (m, 2H, $CH(CH_3)_2$), 2.29−2.36 (m, 2H, H6), 4.31−4.43 (m, 2H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.77 (CH_3), 15.82 (CH_3), 20.89 (CH_3), 20.93 (CH_3), 21.84 (CH_3), 21.92 (CH_3), 22.91(CH_2), 25.56 ($CH(CH_3)_2$), 25.59 ($CH(CH_3)_2$), 31.60, 31.62, 33,89 (CH_2), 42.2 (d, $^3J_{C,P}$ = 61.2 Hz, C6), 48.35, 48.38, 48.42, 48.44, 82.1 (d, $^2J_{C,P}$ = 8.3 Hz, C1), 82.3 (d, $^2J_{C,P}$ = 8.4 Hz, C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 3.3. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{20}H_{38}ClO_3P$ + Na 415.2139, found 415.2123 $[M + Na]^+$ (17%); $(C_{20}H_{38}ClO_3P)_2$ + Na 807.4386, found 807.4431 $[M + Na]^+$ (100%).

*Bis((1S)-borneyl) Chlorophosphate (**2d**).* (1*S*)-Borneol (**1d**; 5.82 g, 37.7 mmol), BuLi (15.1 mL, 37.7 mmol), and $POCl_3$ (1.8 mL, 18.9 mmol) were reacted as described in the general procedure above.

Yield: 7.25 g (16.7 mmol, 99% based on **1d**). ^1H NMR ($CDCl_3$, δ): 0.887 (s, 6H, CH_3), 0.892 (s, 6H, CH_3), 0.924 (s, 3H, CH_3), 0.925 (s, 3H, CH_3), 1.28−1.37 (m, 6H), 1.70−1.80 (m, 4H, CH_2, H4), 1.89−1.96 (m, 2H, CH_2), 2.32−2.42 (m, 2H, CH_2), 4.68−4.75 (m, 2H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.1 (CH_3), 13.3 (CH_3), 18.75 (CH_3), 18.78 (CH_3), 19.9 (CH_3), 26.42 (CH_2), 26.47 (CH_2), 27.87 (CH_2), 27.90 (CH_2), 36.5 (d, $^3J_{C,P}$ = 1.3 Hz, CH_2), 36.8 (d, $^3J_{C,P}$ = 1.5 Hz, CH_2), 44.8, 47.68 (C1/C7), 47.72 (C1/C7), 49.78−49.88 (m, C1/C7), 86.86−86.98 (m, C2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.4. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{20}H_{34}ClO_3P$ 411.1826, found 411.1850 $[M]^+$.

*Bis((1R)-α-fenchyl)) Chlorophosphate (**2e**).* (1*R*)-α-Fenchol (**1e**; 6.01 g, 39.0 mmol), BuLi (15.6 mL, 39.0 mmol), and $POCl_3$ (1.8 mL, 19.5 mmol) were reacted as described in the general procedure above.

Yield: 7.51 g (19.3 mmol, 99% based on **1e**). ^1H NMR ($CDCl_3$, δ): 0.973 (s, 3H, CH_3), 0.977 (s, 3H, CH_3), 1.05−1.11 (m, 8H), 1.16 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.19−1.24 (m, 2H), 1.41−1.51 (m, 2H), 1.52−1.57 (m, 2H), 1.68−1.75 (m, 6H), 4.09 (dd, $^3J_{H,P}$ = 11.2 Hz, $J_{H,H}$ = 1.8, 1H, H2), 4.14 (dd, $^3J_{H,P}$ = 11.5 Hz, $J_{H,H}$ = 1.8, 1H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.4 (CH_3), 20.95 (CH_3), 20.98 (CH_3), 25.7−25.8 (m, C5/C6), 29.6 (CH_3), 29.9 (CH_3), 39.5−39.6 (m, C3), 40.8 (C7), 40.9 (C7), 47.9 (C4), 48.0 (C4), 49.3 (d, $^3J_{C,P}$ = 6.6 Hz, C1), 49.5 (d, $^3J_{C,P}$ = 4.9 Hz, C1), 93.0−93.1 (m, C2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.9. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{20}H_{34}ClO_3P$ + Na 411.1826, found 411.1850 $[M + Na]^+$ (23%); $(C_{20}H_{34}ClO_3P)_2$ + Na 799.3760, found 799.3864 $[M_2 + Na]^+$ (100%).

*Bis((1S)-isopinocampheyl) Chlorophosphate (**2f**).* (1*S*)-Isopinocampheol (**1f**; 5.94 g, 38.5 mmol), BuLi (15.4 mL, 38.5 mmol), and $POCl_3$ (1.8 mL, 19.3 mmol) were reacted as described in the general procedure above.

Yield: 7.43 g (19.1 mmol, 99% based on **1f**). ^1H NMR ($CDCl_3$, δ): 0.93 (s, 3H, H9/H10), 0.94 (s, 3H, H9/H10), 1.11−1.13 (m, 2H, CH_2), 1.19 (s, 3H, H8), 1.20 (s, 3H, H8), 1.24 (s, 6H, H9/H10), 1.82−1.87 (m, 2H, H1), 1.94−2.00 (m, 2H, H5), 2.04−2.11 (m, 2H, H4), 2.24−2.32 (m, 2H, H2), 2.36−2.44 (m, 2H, CH_2), 2.58−2.69 (m, 2H, H4), 4.84−4.93 (m, 2H, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.0 (C2), 20.2 (C2), 24.0 (C9/C10), 27.3 (C9/C10), 27.4 (C9/C10), 33.7 (C7), 33.8 (C7), 36.3 (d, $^3J_{C,P}$ = 2.9 Hz, C4), 36.7 (d, $^3J_{C,P}$

dx.doi.org/10.1021/om500953c | *Organometallics* XXXX, XXX, XXX−XXX

= 2.8 Hz, C4), 38.21 (C6), 38.25 (C6), 41.38 (C5), 41.43 (C5), 44.95 (d, $^3J_{C,P}$ = 6.7 Hz, C2), 45.14 (d, $^3J_{C,P}$ = 6.5 Hz, C2), 47.6 (C1), 81.58 (C3), 81.63 (C3), 81.64 (C3), 81.7 (C3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 3.6. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{34}ClO_3P$ + Na 411.1826, found 411.1821 $[M + Na]^+$ (8%); $(C_{20}H_{34}ClO_3P)_2$ + Na 799.3760, found 799.3807 $[M_2 + Na]^+$ (100%).

Synthesis of Dialkylferrocenyl Phosphates 4a–f, Alkyl Diferrocenyl Phosphates 9a–d, and 1,1′-Ferrocenediyl Tetraalkyl Bis(phosphates) 13a,b: General Procedure. Ferrocenol (**3**; 1 equiv) was dissolved in 10 mL of diethyl ether and cooled to −30 °C. Dropwise addition of BuLi (1 equiv) resulted in the formation of an orange solid. The respective dialkyl chlorophosphate **2a–f** (1 equiv) was added in a single portion, and the mixture was warmed to room temperature and stirred overnight. All volatiles were removed under reduced pressure. The residue was purified using column chromatography on silica with different eluents for each compound (see below). All volatiles were removed under reduced pressure.

*Dicyclohexyl Ferrocenyl Phosphate (**4a**).* Ferrocenol (**3**; 1.00 g, 4.95 mmol), BuLi (2.2 mL, 5.5 mmol), and dicyclohexyl chlorophosphate (**2a**; 1.54 g, 5.5 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 7 cm column size) using a 97/3 (v/v) dichloromethane/ethyl acetate mixture. Compound **4a** was obtained as an orange solid.

Yield: 1.49 g (3.46 mmol, 70% based on **3**). ^1H NMR ($CDCl_3$, δ): 1.23–1.38 (m, 6H, CH_2), 1.48–1.59 (m, 6H, CH_2), 1.70–1.80 (m, 4H, CH_2), 1.90–2.00 (m, 4H, CH_2), 3.84–3.89 (m, 2H, C_5H_4), 4.25 (s, 5H, C_5H_5), 4.38–4.44 (m, 4H, C_5H_4, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.5 (CH_2), 25.1 (CH_2), 33.19 (CH_2), 33.23 (CH_2), 33.25 (CH_2), 33.29 (CH_2), 59.8 (d, $^3J_{C,P}$ = 3.8 Hz, C_5H_4), 62.6 (C_5H_4), 69.4 (C_5H_5), 77.8 (d, $^2J_{C,P}$ = 6.4 Hz, C1), 117.7 (d, $^2J_{C,P}$ = 5.0 Hz, C–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −6.8. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{31}FeO_4P$ 446.1304, found 446.1302 $[M]^+$.

*Crystal data for **4a**:* $C_{22}H_{31}FeO_4P$, M_r = 446.29, orthorhombic, $P2_1/c$, λ = 0.71073 Å, a = 12.4882(12) Å, b = 18.1115(14) Å, c = 9.7751(9) Å, β = 111.679(11)°, V = 2054.5(3) Å^3, Z = 4, ρ_{calcd} = 1.443 Mg m^{-3}, μ = 0.838 mm^{-1}, T = 110.00(10) K, θ range 3.176–25.999°, 9663 reflections collected, 4006 independent reflections (R_{int} = 0.0719), R1 = 0.0822, wR2 = 0.2037 ($I > 2\sigma(I)$).

*Ferrocenyl Bis((1R)-menthyl) Phosphate (**4b**).* Ferrocenol (**3**; 1.03 g, 5.09 mmol), BuLi (2.1 mL, 5.25 mmol), and bis((1*R*)-menthyl) chlorophosphate (**2b**; 2.00 g, 5.09 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 10 cm column size) using dichloromethane as the eluent (R_f = 0.37). Compound **4b** was obtained as an orange solid.

Yield: 3.00 g (4.64 mmol, 91% based on **3**). Anal. Calcd for $C_{30}H_{47}FeO_4P$ (558.51): C, 64.51; H, 8.48. Found: C, 64.67; H, 8.69. Mp: 79–80 °C. ^1H NMR ($CDCl_3$, δ): 0.77 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.82 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.83–0.87 (m, 2H), 0.89 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.91 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.918 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, CH_3), 0.928 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, CH_3), 0.95–1.05 (m, 2H), 1.11–1.18 (m, 2H), 1.29–1.39 (m, 2H), 1.40–1.50 (m, 2H), 1.62–1.70 (m, 4H), 2.11 (dsept, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, $CH(CH_3)_2$), 2.17 (dsept, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, $CH(CH_3)_2$), 2.21–2.30 (m, 2H), 3.86 (s, 2H, C_5H_4), 4.14–4.28 (m, 7H, C_5H_5, H1), 4.39 (s, 1H, C_5H_4), 4.44 (s, 1H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.8 (CH_3), 20.93 (CH_3), 20.94 (CH_3), 21.93 (CH_3), 21.99 (CH_3), 22.76 (CH_2), 22.85 (CH_2), 25.35 (CH), 25.42 (CH), 31.5 (d, $^4J_{C,P}$ = 2.78 Hz, C5), 34.0 (CH_2), 42.5 (CH_2), 42.7 (CH_2), 48.44 (C2), 48.46 (C2), 48.50 (C2), 48.52 (C2), 60.0 (d, $^3J_{C,P}$ = 3.5 Hz, C_5H_4), 60.1 (d, $^3J_{C,P}$ = 3.2 Hz, C_5H_4), 62.62 (C_5H_4), 62.64 (C_5H_4), 69.5 (C_5H_5), 79.8 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 118.6[27] (d, $^2J_{C,P}$ = 4.3 Hz, C–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −6.3. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.2400, found 568.2453 $[M]^+$.

*Crystal data for **4b**:* $C_{30}H_{47}FeO_4P$, M_r = 558.50, orthorhombic, $P2_12_12_1$, λ = 0.71073 Å, a = 7.3970(2) Å, b = 18.0245(4) Å, c = 21.8203(6) Å, V = 2909.24(13) Å^3, Z = 4, ρ_{calcd} = 1.275 Mg m^{-3}, μ = 0.606 mm^{-1}, T = 110.00(10) K, θ range 2.91–26.00°, 18502 reflections collected, 5616 independent reflections (R_{int} = 0.0590), R1 = 0.0382, wR2 = 0.0879 ($I > 2\sigma(I)$), absolute structure parameter[28] −0.018(14).

*Ferrocenyl Bis((1S)-menthyl) Phosphate (**4c**).* Ferrocenol (**3**; 608 mg, 3.01 mmol), BuLi (1.3 mL, 3.25 mmol), and bis((1*S*)-menthyl) chlorophosphate (**2c**; 1.18 g, 3.01 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 10 cm column size) on silica using dichloromethane (R_f = 0.37). Compound **4c** was obtained as an orange oil.

Yield: 1.40 g (2.51 mmol, 83% based on **3**). ^1H NMR ($CDCl_3$, δ): 0.77 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.82 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.83–0.87 (m, 2H), 0.89 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.91 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 0.918 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, CH_3), 0.928 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, CH_3), 0.95–1.05 (m, 2H), 1.11–1.18 (m, 2H), 1.229–1.39 (m, 2H), 1.40–1.50 (m, 2H), 1.62–1.70 (m, 4H), 2.11 (dsept, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, $CH(CH_3)_2$), 2.17 (dsept, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, $CH(CH_3)_2$), 2.21–2.30 (m, 2H), 3.85 (pt, $^{3+4}J_{H,H}$ = 2.0 Hz, 2H, C_5H_4), 4.16–4.25 (m, 7H, C_5H_5, H1), 4.37 (dd, $J_{H,H}$ = 3.4 Hz,, $J_{H,H}$ = 1.5 Hz, 1H, C_5H_4), 4.44 (dd, $J_{H,H}$ = 3.4 Hz, $J_{H,H}$ = 1.5 Hz, 1H, C_5H_4). $^{13}C\{^1H\}$NMR ($CDCl_3$, δ): 15.8 ($CH(CH_3)_2$), 20.93 ($CH(CH_3)_2$), 20.95 ($CH(CH_3)_2$), 21.93 ($CH(CH_3)$), 21.99 ($CH(CH_3)$), 22.76 (CH_2), 22.85 (CH_2), 25.35 ($CH(CH_3)_2$), 25.43 ($CH(CH_3)_2$), 31.5 (d, $^4J_{C,P}$ = 2.8 Hz, C5), 34.0 (CH_2), 42.5 (CH_2), 42.7 (CH_2), 48.45 (C2), 48.47 (C2), 48.51 (C2), 48.53 (C2), 60.0 (d, $^3J_{C,P}$ = 3.9 Hz, C_5H_4), 60.1 (d, $^3J_{C,P}$ = 3.3 Hz, C_5H_4), 62.52 (C_5H_4), 62.55 (C_5H_4), 69.4 (C_5H_5), 79.78 (d, $^2J_{C,P}$ = 6.8 Hz, C1), 79.79 (d, $^2J_{C,P}$ = 6.8 Hz, C1), 117.8 (d, $^2J_{C,P}$ = 4.3 Hz, C_{C5H4}–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −6.3.

*Bis((1S)-borneyl) Ferrocenyl Phosphate (**4d**).* Ferrocenol (**3**; 1.00 g, 4.95 mmol), BuLi (2.0 mL, 5.00 mmol), and bis((1*S*)-borneyl) chlorophosphate (**2d**; 1.92 mg, 4.95 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 15 cm) using a 95/5 (v/v) toluene/diethyl ether mixture (R_f = 0.33). Compound **4d** was obtained as an orange solid.

Yield: 1.26 g (2.27 mmol, 46% based on **3**). Anal. Calcd for $C_{30}H_{43}FeO_4P$ (554.48): C, 64.98; H, 7.82. Found: C, 64.88; H, 7.83. Mp: 210–212 °C. ^1H NMR ($CDCl_3$, δ): 0.86–0.90 (m, 18H, CH_3), 1.22–1.30 (m, 6H), 1.66–1.69 (m, 2H), 1.70–1.77 (m, 2H), 1.91–1.97 (m, 2H), 2.25–2.34 (m, 2H), 3.86 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 4.24 (s, 5H, C_5H_5), 4.39 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 4.58–4.62 (m, 2H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.28 (CH_3), 13.34 (CH_3), 18.8 (CH_3), 19.9 (CH_3), 26.4 (CH_2), 26.5 (CH_2), 27.9 (CH_2), 28.0 (CH_2), 36.8 (d, $^3J_{C,P}$ = 1.7 Hz, C3), 37.1 (d, $^3J_{C,P}$ = 1.8 Hz, C3), 44.8, 47.65 (C7), 47.66 (C7), 49.66 (d, $^3J_{C,P}$ = 1.3 Hz, C1), 49.71 (d, $^3J_{C,P}$ = 1.3 Hz, C1), 60.06 (d, $^3J_{C,P}$ = 0.6 Hz, C_5H_4), 60.08 (d, $^3J_{C,P}$ = 1.0 Hz, C_5H_4), 62.6 (C_5H_4), 69.4 (C_5H_5), 84.66 (d, $^2J_{C,P}$ = 2.2 Hz, C2), 84.71 (d, $^2J_{C,P}$ = 2.3 Hz, C2), 117.7 (d, $^2J_{C,P}$ = 4.6 Hz, C_{C5H4}–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −4.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{43}FeO_4P$ 554.2243, found 554.2242 $[M]^+$.

*Bis((1R)-α-fenchyl) Ferrocenyl Phosphate (**4e**).* Ferrocenol (**3**; 814 mg, 4.03 mmol), BuLi (1.65 mL, 4.13 mmol), and bis((1*R*)-α-fenchyl) chlorophosphate (**2e**; 1.57 g, 4.04 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 7 cm) using dichloromethane as the eluent (R_f = 0.38). Compound **4e** was obtained as an orange oil.

Yield: 1.85 g (3.33 mmol, 83% based on **3**). Anal. Calcd for $C_{30}H_{43}FeO_4P$ (554.48): C, 64.98; H, 7.82. Found: C, 64.67; H, 7.86. Mp: 64–68 °C. ^1H NMR ($CDCl_3$, δ): 0.91 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.03–1.09 (m, 11H), 1.14–1.20 (m, 5H), 1.40–1.47 (m, 2H), 1.49–1.53 (m, 2H), 1.68–1.75 (m, 6H), 3.85 (pt, $^{3+4}J_{H,H}$ = 2.0 Hz, 2H, C_5H_4), 3.97–4.01 (m, 2H, C_5H_4), 4.24 (s, 5H, C_5H_5), 4.41–4.45 (m, 2H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.36 (CH_3), 19.36 (CH_3), 20.8 (CH_3), 21.1 (CH_3), 25.67 (C5/C6), 25.74 (C5/C6), 25.95 (C5/C6), 25.98 (C5/C6), 29.9 (CH_3), 39.5 (d, $^3J_{C,P}$ = 2.5 Hz, C3), 39.7 (d, $^3J_{C,P}$ = 2.5 Hz, C3), 40.94 (CH_2), 40.97 (CH_2), 47.93 (C4), 47.95 (C4), 49.29 (C1), 49.33 (C1), 60.1–60.2 (m, C_5H_4), 62.6 (C_5H_4), 69.4 (C_5H_5), 91.0–91.2 (m, C2), 118.3 (HMBC, C_{C5H4}–O). $^{31}P\{^1H\}$

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NMR ($CDCl_3$, δ): −4.3. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{43}FeO_4P$ 554.2243, found 554.2265 $[M]^+$.

Crystal data for ***4e****:* $C_{60}H_{86}Fe_2O_8P_2$, M_r = 1108.92, triclinic, $P1$, λ = 0.71073 Å, a = 11.6913(4) Å, b = 11.8705(4) Å, c = 12.0874(4) Å, α = 62.396(3)°, β = 77.005(3)°, γ = 69.734(3)°, V = 1390.35(9) Å^3, Z = 1, ρ_{calcd} = 1.324 Mg m^{-3}, μ = 0.633 mm^{-1}, T = 110.0(10) K, θ range 3.106−24.997°, 10832 reflections collected, 7207 independent reflections (R_{int} = 0.0156), R1 = 0.0425, wR2 = 0.1058 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.012(8).

*Ferrocenyl Bis((1S)-isopinocampheyl) Phosphate (****4f****).* Ferrocenol (**3**; 830 mg, 4.11 mmol), BuLi (1.65 mL, 4.13 mmol), and bis((1*S*)-isopinocampheyl) chlorophosphate (**2f**; 1.60 g, 4.11 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 7 cm) using a 8/2 (v/v) hexane/diethyl ether mixture as the eluent (R_f = 0.32). Compound **4f** was obtained as an orange oil.

Yield: 1.90 g (3.43 mmol, 83% based on **3**). ^{1}H NMR ($CDCl_3$, δ): 0.92 (s, 3H, H9/H10), 0.93 (s, 3H, H9/H10), 1.107 (d, $J_{H,H}$ = 9.9 Hz, 1H, H7), 1.112 (d, $J_{H,H}$ = 9.9 Hz, 1H, H7), 1.16 (d, $J_{H,H}$ = 7.4 Hz, 3H, H8), 1.19 (d, $J_{H,H}$ = 7.4 Hz, 3H, H8), 1.22 (s, 6H, H9/H10), 1.80−1.84 (m, 2H, H1), 1.93−1.98 (m, 2H, H5), 1.99−2.04 (m, 2H, H4), 2.19−2.28 (m, 2H, H2), 2.36−2.40 (m, 2H, H7), 2.53−2.62 (m, 2H, H4), 3.86 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 4.25 (s, 5H, C_5H_5), 4.42 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 4.73−4.79 (m, 2H, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.24 (C8), 20.26 (C8), 23.89 (C9/C10), 23.91 (C9/C10), 27.40 (C9/C10), 27.41 (C9/C10), 33.76 (C7), 33.79 (C7), 36.7 (d, $^3J_{C,P}$ = 3.0 Hz, C4), 36.8 (d, $^3J_{C,P}$ = 3.3 Hz, C4), 38.20 (C6), 38.22 (C6), 41.46 (C5), 45.19 (C2), 45.24 (C2), 45.27 (C2), 45.32 (C2), 47.7 (C1), 59.89 (C_5H_4), 59.91 (C_5H_4), 62.6 (C_5H_4), 69.5 (C_5H_5), 79.32 (C3), 79.34 (C3), 79.38 (C3), 79.40 (C3), 117.8−117.9 (m, $C_{C_5H_4}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −6.0. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{43}FeO_4P$ 554.2243, found 554.2246 $[M]^+$.

*Cyclohexyl Diferrocenyl Phosphate (****9a****).* Ferrocenol (**3**; 900 mg, 4.45 mmol), BuLi (1.8 mL, 4.5 mmol), and **8a** (485 mg, 2.23 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 15 cm) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **9a** was obtained as an orange solid.

Yield: 771 mg (1.41 mmol, 63% based on **3**). Anal. Calcd for $C_{26}H_{29}Fe_2O_4P$ (548.17): C, 56.97; H, 5.33. Found: C, 57.34; H, 5.43. Mp: 90−93 °C. ^{1}H NMR ($CDCl_3$, δ): 1.31−1.40 (m, 2H, CH_2), 1.49−1.63 (m, 4H, CH_2), 1.71−1.81 (m, 2H, CH_2), 1.92−2.01 (m, 2H, CH_2), 3.87−3.92 (m, 4H, C_5H_4), 4.26 (s, 10H, C_5H_5), 4.37−4.43 (m, 4H, C_5H_4), 4.46−4.53 (m, 1H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.5 (CH_2), 25.0 (CH_2), 33.2 (d, $^3J_{C,P}$ = 2.9 Hz, C2/C6), 59.73−59.76 (m, C_5H_4), 62.73−62.74 (m, C_5H_4), 69.6 (C_5H_5), 79.0 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 117.7 (d, $^2J_{C,P}$ = 5.3 Hz, $C_{C_5H_4}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −10.9. HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{29}Fe_2O_4P$ 548.0497, found 548.0490 $[M]^+$.

*Diferrocenyl (1R)-Menthyl Phosphate (****9b****).* Ferrocenol (**3**; 1.10 g, 5.44 mmol), BuLi (2.2 mL, 5.5 mmol), and **8b** (745 mg, 2.73 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 15 cm) using a 5/95 (v/v) hexane/dichloromethane mixture as the eluent. Compound **9b** was obtained as an orange solid.

Yield: 1.222 g (2.02 mmol, 74% based on **3**). Anal. Calcd for $C_{30}H_{37}Fe_2O_4P$ (604.28): C, 59.63; H, 6.17. Found: C, 59.88; H, 6.31. Mp: 90−92 °C. ^{1}H NMR ($CDCl_3$, δ): 0.80 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3), 0.88−0.94 (m, 11H), 0.978−1.06 (m, 1H), 1.19, (m, 2H), 1.35−1.50 (m, 2H), 1.63−1.70 (m, 2H), 2.07−2.15 (m, 1H), 2.21−2.28 (m, 1H), 3.86−3.92 (m, 4H, C_5H_4), 4.20−4.35 (m, 11H, C_5H_5, H1), 4.37−4.44 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.7 (CH_3), 20.9 (CH_3), 21.9 (CH_3), 22.8 (d, $^3J_{C,P}$ = 27.0 Hz, CH_2), 25.4 (CH), 31.6 (CH), 33.9 (CH_2), 42.5 (CH_2), 48.4 (d, $^3J_{C,P}$ = 7.3 Hz, CH), 59.8−59.9 (m, C_5H_4), 62.71 (C_5H_4), 62.74 (C_5H_4), 69.53 (C_5H_5), 69.56 (C_5H_5), 81.0 (d, $^2J_{C,P}$ = 7.4 Hz, C1), 117.7 (d, $^2J_{C,P}$ = 5.9 Hz, $C_{C_5H_4}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −10.7. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{37}Fe_2O_4P$ 604.1124, found 604.1167 $[M]^+$.

Crystal data for ***9b****:* $C_{30}H_{37}Fe_2O_4P$, M_r = 604.26, monoclinic, $P2_1$, λ = 0.71073 Å, a = 14.1041(13) Å, b = 5.8359(5) Å, c = 16.704(2) Å, β = 92.648(9)°, V = 1371.4(2) Å^3, Z = 2, ρ_{calcd} = 1.461 Mg m^{-3}, μ = 1.149 mm^{-1}, T = 110.2(6) K, θ range 2.892−24.997°, 5764 reflections collected, 4257 independent reflections (R_{int} = 0.0229), R1 = 0.0908, wR2 = 0.1454 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.02(6).

*(1S)-Borneyl Diferrocenyl Phosphate (****9c****).* The title compound was obtained as a byproduct during the synthesis of **4d** by reacting ferrocenol (**3**; 1.00 g, 4.95 mmol), BuLi (2.0 mL, 5.00 mmol), and bis((1*S*)-borneyl) chlorophosphate (**2d**; 1.92 mg, 4.95 mmol) as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 15 cm) using a 95/5 (v/v) toluene/diethyl ether mixture (R_f = 0.43) as the eluent. Compound **9c** was obtained as an orange solid.

Yield: 260 mg (0.43 mmol, 17% based on **3**). Anal. Calcd for $C_{30}H_{47}FeO_4P$ (602.26): C, 59.83; H, 5.86. Found: C, 60.44; H, 6.00. ^{1}H NMR ($CDCl_3$, δ): 0.86 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.22−1.31 (m, 3H, CH_2), 1.67 (t, $J_{H,H}$ = 4.5 Hz, H4), 1.70−1.78 (m, 1H, CH_2), 1.89−1.95 (m, 1H, H6), 2.26−2.33 (m, 1H, H3), 3.89−3.90 (m, 4H, C_5H_4), 4.261 (s, 5H, C_5H_5), 4.264 (s, 5H, C_5H_5), 4.40−4.43 (m, 4H, C_5H_4), 4.64−4.68 (m, 1H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.2 (CH_3), 18.8 (CH_3), 19.9 (CH_3), 26.4 (C5/C6), 27.9 (C5/C6), 36.7 (C3), 44.7 (C4), 47.8 (C7), 49.8 (d, $^3J_{C,P}$ = 6.2 Hz, C1), 59.79 (C_5H_4), 59.83 (C_5H_4), 59.86 (C_5H_4), 59.89 (C_5H_4), 62.76 (C_5H_4), 62.79 (C_5H_4), 69.6 (C_5H_5), 85.9 (d, $^2J_{C,P}$ = 6.8 Hz, C2), 117.64 ($C_{C_5H_4}$−O), 117.66 ($C_{C_5H_4}$−O), 117.68 ($C_{C_5H_4}$−O), 117.71 ($C_{C_5H_4}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −9.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.0963 $[M]^+$.

*(1R)-α-Fenchyl Diferrocenyl Phosphate (****9d****).* Ferrocenol (**3**; 1.00 g, 4.95 mmol), BuLi (2.0 mL, 5.0 mmol), and **8d** (680 mg, 2.50 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 15 cm) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **9d** was obtained as an orange solid.

Yield: 935 mg (1.55 mmol, 63% based on **3**). Anal. Calcd for $C_{30}H_{35}Fe_2O_4P$ (602.26): C, 59.83; H, 5.86. Found: C, 59.90; H, 6.00. Mp: 129−132 °C. ^{1}H NMR ($CDCl_3$, δ): 0.90 (s, 3H, CH_3), 1.04−10.8 (m, 4H, CH_3, CH_2), 1.11 (s, 3H, CH_3), 1.16−1.21 (m, 1H, CH_2), 1.42−1.47 (m, 1H, CH_2), 1.50−1.54 (m, 1H, CH_2), 1.67−1.74 (m, 3H, CH_2, CH), 3.87−3.90 (m, 4H, C_5H_4), 4.04 (dd, $^3J_{C,P}$ = 8.5 Hz, $J_{H,H}$ = 1.8 Hz, 1H, H2), 4.25 (s, 5H, C_5H_5), 4.25 (s, 5H, C_5H_5), 4.38−4.46 (m, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 20.8 (CH_3), 25.7 (C5/C6), 25.9 (C5/C6), 29.9 (CH_3), 39.6 (d, $^3J_{C,P}$ = 2.7 Hz, C3), 40.9 (C7), 47.9 (C4), 49.3 (d, $^3J_{C,P}$ = 5.1 Hz, C1), 59.91 (C_5H_4), 59.93 (C_5H_4), 59.94 (C_5H_4), 59.96 (C_5H_4), 59.98 (C_5H_4), 59.98 (C_5H_4), 62.71 (C_5H_4), 62.72 (C_5H_4), 62.75 (C_5H_4), 69.54 (C_5H_5), 59.54 (C_5H_5), 92.3 (d, $^2J_{C,P}$ = 7.4 Hz, C2), 117.77 (d, $^2J_{C,P}$ = 4.9 Hz, $C_{C_5H_4}$−O), 117.81 (d, $^2J_{C,P}$ = 4.7 Hz, $C_{C_5H_4}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −9.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.1005 $[M]^+$.

*1,1′-Ferrocenediyl Tetracyclohexyl Bis(phosphate) (****13a****).* With 1,1′-diacetoxyferrocene[29] (712 mg, 2.36 mmol) as the starting material, 1,1′-ferrocenediol (**12**) was prepared as described in the standard procedure for the synthesis of ferrocenol[7,9,29,30] (**3**) using KOH/HCl (3 mL, 6 mmol) in 50 mL of ethanol. Ferrocenediol (**12**; 515 mg, 2.36), BuLi (1.9 mL, 4.75 mmol), and dicyclohexyl chlorophosphate (**8a**; 1.40 g, 5.0 mmol) were then reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 10 cm) using an 80/20 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **13a** was obtained as an orange oil.

Yield: 980 mg (1.39 mmol, 59% based on **12**). ^{1}H NMR ($CDCl_3$, δ): 1.23−1.38 (m, 12H, CH_2), 1.47−1.57 (m, 12H, CH_2), 1.70−1.77 (m, 8H, CH_2), 1.89−1.98 (m, 8H, CH_2), 3.96 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 4H, C_5H_4), 4.37−4.43 (m, 4H, H1), 4.44 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.5 (CH_2), 25.1 (CH_2), 33.21 (CH_2), 33.25 (CH_2), 33.27 (CH_2), 33.30 (CH_2), 61.2 (d, $^3J_{C,P}$ = 3.7 Hz, C_5H_4), 64.6 (C_5H_4), 77.9 (d, $^2J_{C,P}$ = 6.4 Hz, C1), 118.1 ($^2J_{C,P}$ = 4.8 Hz, $C_{C_5H_4}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −6.9. HRMS (ESI-TOF,

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m/*z*): calcd for $C_{34}H_{52}FeO_8P_2$ + Na 729.2380, found 729.2333 [M + Na]$^+$.

*1,1′-Ferrocenediyl Tetrakis((1R)-α-fenchyl) Bis(phosphate) (**13b**).* Ferrocenediol (**12**; 254 mg, 1.16 mmol), BuLi (0.95 mL, 2.38 mmol), and dicyclohexyl chlorophosphate (**8d**; 1.00 g, 2.58 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 × 10 cm) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **13b** was obtained as an orange oil.

Yield: 400 mg (0.43 mmol, 37% based on **12**). ^{1}H NMR ($CDCl_3$, δ): 0.90−1.19 (m, 44H), 140−1.46 (m, 4H, CH_2), 1.49−1.51 (m, 4H, CH_2), 1.70−1.71 (m, 12H, CH_2, CH), 3.95−4.00 (m, 8H, C_5H_4, H2), 4.47−4.50 (m, 4H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.37 (CH_3), 19.39 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 25.67 (C5/C6), 25.72 (C5/C6), 25.94 (C5/C6), 25.97 (C5/C6), 29.91 (CH_3), 29.93 (CH_3), 39.5−39.6 (m, C3), 40.93 (C7), 40.96 (C7), 47.92 (C4), 47.94 (C4), 49.28 (C1), 49.32 (C1), 61.3 (d, $^2J_{C,P}$ = 3.4 Hz, C_5H_4), 61.4 (d, $^2J_{C,P}$ = 3.8 Hz, C_5H_4), 64.59 (C_5H_4), 64.65 (C_5H_4), 91.1−91.2 (m, C2), 118.3 (d, $^2J_{C,P}$ = 4.4 Hz, $C_{C_5H_4}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −4.3. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{50}H_{76}FeO_8P_2$ + H 923.4439, found 923.4426 [M + H]$^+$.

Anionic Phospho-Fries Rearrangement: General Procedure. *Procedure A (using Lithium Diisopropylamide (LDA) as the Base).* In a Schlenk tube hexane (3 mL) and diisopropylamine (0.05 mL, 0.36 mmol) were cooled to −30 °C. Afterward, BuLi (0.15 mL, 0.38 mmol) was added dropwise, followed by addition of a diamine (tetramethylethylenediamine: 0.05 mL, 0.33 mmol or (−)-sparteine (0.08 mL, 0.35 mmol)). The mixture was stirred for 10 min at −30 °C, and the corresponding ferrocenyl phosphate **4a**−**f**, **6a**,**d**, **9a**−**c**, or **13a**,**b** was added in a single portion. The obtained reaction mixture was warmed to ambient temperature, and stirring was continued overnight. The reaction mixture was quenched by adding dimethyl sulfate (0.15 mL, 1.58 mmol) and stirred at 50 °C for 1 h to complete methylation. All volatiles were removed under reduced pressure. Purification was realized using column chromatography on silica using different solvent mixtures as eluents (see below).

Procedure B (using Lithium Tetramethylpiperidide (LTMP) as the Base). In a Schlenk tube LTMP (56 mg, 0.38 mmol) was suspended in 3 mL of hexane and cooled to −30 °C. The addition of the diamine and the respective ferrocenyl phosphate as well as the reaction conditions and workup procedures were realized as described in procedure A.

*O,O-Dicyclohexyl 2-Methoxyferrocenyl Phosphonate (**5a**).* Ferrocenyl dicyclohexyl phosphate (**4a**) (100 mg, 0.224 mmol) was reacted as described in procedure A. Compound **5a** was obtained as an orange oil.

Yield: 100 mg (0.217 mmol, 97% based on **4a**). ^{1}H NMR ($CDCl_3$, δ): 1.26−1.38 (m, 6H, CH_2), 1.17−1.62 (m, 6H, CH_2), 1.72−1.80 (m, 4H, CH_2), 1.87−1.98 (m, 4H, CH_2), 3.68 (s, 3H, OCH_3), 3.98−3.99 (m, 1H, C_5H_3), 4.16−4.17 (m, 1H, C_5H_3), 4.21−4.22 (m, 1H, C_5H_3), 4.31 (s, 5H, C_5H_5), 4.47−4.55 (m, 2H, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.57 (CH_2), 23.59 (CH_2), 25.35 (CH_2), 25.36 (CH_2), 33.6 (d, $^2J_{C,P}$ = 4.7 Hz, CH_2), 33.7 (d, $^2J_{C,P}$ = 3.2 Hz, CH_2), 33.8 (d, $^2J_{C,P}$ = 3.8 Hz, CH_2), 33.9 (d, $^2J_{C,P}$ = 3.2 Hz, CH_2), 55.0 (d, $J_{C,P}$ = 11.4 Hz, C_5H_3), 58.0 (OCH_3), 59.1 (d, $^1J_{C,P}$ = 216.6 Hz, C−P), 63.4 (d, $J_{C,P}$ = 14.0 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 69.9 (C_5H_5), 74.76 (d, $^2J_{C,P}$ = 6.5 Hz, C1), 74.82 (d, $^2J_{C,P}$ = 7.2 Hz, C1), 128.4 (d, $^2J_{C,P}$ = 10.4 Hz, $C_{C_5H_3}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 21.2 ($^1J_{P,C}$ = 216.8 Hz). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{23}H_{33}FeO_4P$ + H 461.1539, found 461.1530 [M + H]$^+$.

*O,O-Bis((1R)-menthyl) 2-Methoxyferrocenyl Phosphonate (**5b**).* Ferrocenyl bis((1*R*)-menthyl) phosphate (**4b**; 100 mg, 0.18 mmol) was reacted as described in procedure A. Compound **5b** was obtained as an orange oil as a mixture of two diastereomers.

Yield: 101 mg (0.18 mmol, 99% based on **4b**). ^{1}H NMR ($CDCl_3$, δ): 0.41−1.06 (m, 22H), 1.12−1.50 (m, 6H), 1.57−1.71 (m, 4H), 2.02−2.48 (m, 4H), 3.62−3.68 (m, 3H, OCH_3), 3.92−4.32 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.4−15.8 (m, CH_3), 21.1−21.3 (m, CH_3), 22.01−22.04 (m, CH_3), 22.5−22.7 (m, CH_2), 24.6−25.4 (m, CH), 31.4−31.5 (m, CH), 34.1−34.2 (m, CH_2), 43.2−43.5 (m, CH_2), 48.7−49.1 (m, CH), 54.6−54.8 (m, C_5H_3), 57.4 (OCH_3), 57.5 (d, $^1J_{C,P}$ = 216.9 Hz, C−P), 57.9 (OCH_3), 58.5 (d, $^1J_{C,P}$ = 216.4 Hz, C−P), 63.4 (d, $J_{C,P}$ = 14.5 Hz, C_5H_3), 66.7 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 68.1 (d, $J_{C,P}$ = 14.4 Hz, C_5H_3), 69.93 (C_5H_5), 69.96 (C_5H_5), 76.4 (d, $^2J_{C,P}$ = 6.3 Hz, C1), 76.6 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 76.7 (d, $^2J_{C,P}$ = 6.8 Hz, C1), 76.9 (d, $^2J_{C,P}$ = 7.6 Hz, C1), 127.9 (d, $^2J_{C,P}$ = 9.0 Hz, $C_{C_5H_3}$−O), 129.0 (d, $^2J_{C,P}$ = 10.9 Hz, C_5H_3). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.6, 21.8. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{31}H_{49}FeO_4P$ 572.2713, found 572.2733 [M]$^+$.

*O,O-Bis((1S)-menthyl) 2-Methoxyferrocenyl Phosphonate (**5c**).* Ferrocenyl bis((1*S*)-menthyl) phosphate (**4c**; 100 mg, 0.18 mmol) was reacted as described in procedure A. Compound **5c** was obtained as an orange oil as a mixture of two diastereomers.

Yield: 101 mg (0.18 mmol, 99% based on **4c**). ^{1}H NMR ($CDCl_3$, δ): 0.41−0.57 (m, 3 H, CH_3), 0.78−0.94 (m, 19H, CH_2, CH_3), 0.98−1.49 (m, 6H, CH_2, CH), 1.55−1.68 (m, 4H, CH_2, CH), 2.00−2.49 (m, 4H, CH_2, CH), 3.61−3.67 (3H, OCH_3), 3.96−4.30 (m, 10H, C_5H_5, C_5H_3, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.4−15.8 (CH_3), 20.9−21.3 (CH_3), 21.98 (CH_3), 22.02 (CH_3), 22.6−22.8 (CH_2), 24.6 (CH), 25.1 (CH), 25.4 (CH), 31.4−31.5 (CH), 34.1−34.2 (CH_2), 43.2−43.5 (m, C6), 48.7 (d, $^3J_{C,P}$ = 7.4 Hz, C2), 48.8 (d, $^3J_{C,P}$ = 7.4 Hz, C2), 48.9 (d, $^3J_{C,P}$ = 6.4 Hz, C2), 49.1 (d, $^3J_{C,P}$ = 7.4 Hz, C2), 54.7−54.9 (m, C_5H_3), 57.4 (OCH_3), 57.6 (d, $^1J_{C,P}$ = 216.7 Hz, C−P), 57.9 (OCH_3), 58.6 (d, $^1J_{C,P}$ = 216.6 Hz, C−P), 63.4 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 66.7 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 69.92 (C_5H_5), 69.94 (C_5H_5), 76.4 (d, $^2J_{C,P}$ = 6.3 Hz, C1), 76.6 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 76.7 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 76.9 (d, $^2J_{C,P}$ = 7.6 Hz, C1), 127.9 (d, $^2J_{C,P}$ = 9.1 Hz, $C_{C_5H_3}$−O), 129.0 (d, $^2J_{C,P}$ = 10.9 Hz, $C_{C_5H_3}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.6 ($^1J_{P,C}$ = 216.4 Hz), 21.8 ($^1J_{P,C}$ = 216.9 Hz).

*O,O-Bis((1S)-borneyl) 2-Methoxyferrocenyl Phosphonate (**5d**).* Bis((1*S*)-borneyl) ferrocenyl phosphate (**4d**; 100 mg, 0.18 mmol) was reacted as described in procedure A. Compound **5d** was obtained as an orange oil as a mixture of two diastereomers.

Yield: 102 mg (0.18 mmol, 99% based on **4d**). ^{1}H NMR ($CDCl_3$, δ): 0.79−0.93 (m, 18H, CH_3), 1.20−1.32 (m, 6H, CH_2), 1.60−1.67 (m, 2H, H4), 1.69−1.78 (m, 2H, CH_2), 1.99−2.13 (m, 2H, CH_2), 2.17−2.36 (m, 2H, CH_2), 3.65−3.66 (m, 3H, OCH_3), 3.98−4.00 (m, 1H, C_5H_3), 4.15−4.17 (m, 1H, C_5H_3), 4.20−4.24 (m, 1H, C_5H_3), 4.32 (s, 5H, C_5H_5), 4.59−4.73 (m, 2H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 13.2−13.4 (CH_3), 18.80−18.82 (m, CH_3), 19.90−19.93 (CH_3), 26.5−26.9 (C5/C6), 28.08−28.15 (C5/C6), 37.1−37.8 (m, C3), 44.86−44.93 (C4), 47.4−47.5 (C7), 49.6−49.7 (C1), 54.7−54.9 (m, C_5H_3), 57.7 (OCH_3), 57.9 (OCH_3), 58.3 (d, $^1J_{C,P}$ = 218.1 Hz, C−P), 58.7 (d, $^1J_{C,P}$ = 217.9 Hz, C−P), 63.41 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 63.44 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 66.95 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 67.03 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 69.8 (C_5H_5), 69.9 (C_5H_5), 81.24 (d, $^2J_{C,P}$ = 6.9 Hz, C2), 81.27 (d, $^2J_{C,P}$ = 6.1 Hz, C2), 81.5 (d, $^2J_{C,P}$ = 7.1 Hz, C2), 81.7 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 128.4 (d, $^2J_{C,P}$ = 9.9 Hz, $C_{C_5H_3}$−O), 128.6 (d, $^2J_{C,P}$ = 10.3 Hz, $C_{C_5H_3}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 22.9, 23.2. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{31}H_{45}FeO_4P$ 568.2400, found 568.2414 [M]$^+$

*(R_P)-O,O-Bis((1R)-α-fenchyl) 2-Methoxyferrocenyl Phosphonate (**5e**).* Ferrocenyl bis((1*R*)-α-fenchyl) phosphate (**4e**; 100 mg, 0.18 mmol) was reacted as described in procedure B. Compound **5e** was obtained as an orange solid. The spectroscopic data correspond to the single diastereomer, which was obtained after crystallization (de = 0.80).

Yield: 90 mg (0.16 mmol, 88% based on **4e**). Mp: 186−188 °C. ^{1}H NMR ($CDCl_3$, δ): 0.87 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.96−1.06 (m, 5H), 1.10−1.18 (m, 8H), 1.39−1.52 (m, 4H), 1.64−1.87 (m, 6H), 3.68 (s, 3H, OCH_3), 3.99−4.06 (m, 3H, H2, C_5H_3), 4.14−4.18 (m, 1H, C_5H_3), 4.19−4.23 (m, 1H, C_5H_3), 4.35 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.6 (CH_3), 21.1 (CH_3), 21.4 (CH_3), 25.8−26.2 (m, C5/C6), 29.7 (CH_3), 29.8 (CH_3), 39.1 (d, $^3J_{C,P}$ = 2.2 Hz, C7), 39.7 (d, $^3J_{C,P}$ = 2.2 Hz, C7), 41.07 (CH_2), 41.09 (CH_2), 48.0 (C4), 48.1 (C4), 49.25 (d, $^3J_{C,P}$ = 4.8 Hz, C1), 49.34 (d, $^3J_{C,P}$ = 4.4 Hz, C1), 54.8 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 57.8

dx.doi.org/10.1021/om500953c | *Organometallics* XXXX, XXX, XXX−XXX

(OCH_3), 58.2 (d, $^1J_{C,P}$ = 216.6 Hz, C−P), 63.6 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3), 69.8 (C_5H_5), 87.8 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 88.0 (d, $^2J_{C,P}$ = 6.7 Hz, C2), 128.8 (d, $^2J_{C,P}$ = 10.3 Hz, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 22.4. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.2400, found 568.2433 $[M]^+$.

Crystal data for ***5e****:* $C_{31}H_{45}FeO_4P$, M_r = 568.49, orthorhombic, $P2_12_12_1$, λ = 0.71073 Å, a = 7.7485(2) Å, b = 10.6896(3) Å, c = 34.4462(10) Å, V = 2853.12(14) Å^3, Z = 4, ρ_{calcd} = 1.323 Mg m^{-3}, μ = 0.619 mm^{-1}, T = 110.00(10) K, θ range 2.88−26.00°, 25582 reflections collected, 5602 independent reflections (R_{int} = 0.0363), R1 = 0.0269, wR2 = 0.0580 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.000(10).

*O,O-Bis((1S)-isopinocampheyl) 2-Methoxyferrocenyl Phosphonate (****5f****).* Ferrocenyl bis((1*S*)-isopinocampheyl) phosphate (**4f**; 100 mg, 0.18 mmol) was reacted as described in procedure A. Compound **5f** was obtained as an orange oil as a mixture of two diastereomers.

Yield: 85 mg (0.15 mmol, 80% based on **4f**). ^1H NMR ($CDCl_3$, δ): 0.90−0.93 (m, 6H), 1.05−1.21 (m, 14H), 1.77−1.83 (m, 2H), 1.89−2.08 (m, 4H, 2.15−2.26 (m, 2H), 2.33−2.39 (m, 2H), 2.46−2.60 (m, 2H), 3.67/3.68 (s, 3H, OCH_3), 3.99−4.00 (m, 1H, C_5H_3), 4.16−4.18 (m, 1H, C_5H_3), 4.22−4.27 (m, 1H, C_5H_3), 4.320/4.321 (s, 5H, C_5H_5), 4.70−4.85 (m, 2H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.95 (CH_3), 20.02 (CH_3), 23.78 (CH_3), 23.81 (CH_3), 23.83 (CH_3), 27.43 (CH_3), 27.47 (CH_3), 27.49 (CH_3), 27.50 (CH_3), 33.6 (CH_2), 33.7 (CH_2), 33.8 (CH_2), 37.1 (d, $^3J_{C,P}$ = 3.1 Hz, CH_2), 27.3 (d, $^3J_{C,P}$ = 2.87 Hz, CH_2), 37.4 (d, $^3J_{C,P}$ = 2.5 Hz, CH_2), 37.5 (d, $^3J_{C,P}$ = 2.2 Hz, CH_2), 38.15 (C6), 38.17 (C6), 38.20 (C6), 41.52 (C5), 41.53 (C5), 41.56 (C5), 41.60 (C5), 45.5−45.8 (m, C2), 47.7 (C1), 47.8 (C1), 55.03 (d, $J_{C,P}$ = 11.3 Hz, C_5H_3), 55.09 (d, $J_{C,P}$ = 11.3 Hz, C_5H_3), 57.96 (OCH_3), 57.99 (OCH_3), 58.5 (d, $^1J_{C,P}$ = 215.8 Hz, C−P), 58.7 (d, $^1J_{C,P}$ = 215.7 Hz, C−P), 63.4 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 63.4 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 67.4 (d, $J_{C,P}$ = 12.9 Hz, C_5H_3), 70.0 (C_5H_5), 75.9 (d, $^2J_{C,P}$ = 6.8 Hz, C3), 76.0 (d, $^2J_{C,P}$ = 7.3 Hz, C3), 76.2 (d, $^2J_{C,P}$ = 6.8 Hz, C3), 76.3 (d, $^2J_{C,P}$ = 7.4 Hz, C3), 128.4 (d, $^2J_{C,P}$ = 10.1 Hz, C−O), 128.6 (d, $^2J_{C,P}$ = 10.2 Hz, C−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.24, 21.28. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.24000, found 568.2453 $[M]^+$.

*O,O-Dicyclohexyl 2-(Diphenylthiophosphinato)ferrocenyl Phosphonate (****6a****).* Dicyclohexyl ferrocenyl phosphate (**4a**; 100 mg, 0.22 mmol), diisopropylamine (0.07 mL, 0.50 mmol), BuLi (0.2 mL, 0.50 mmol), TMEDA (0.07 mL, 0.46 mmol), $ClPPh_2$ (0.17 mL, 0.93 mmol), and sulfur (60 mg, 1.9 mmol) were reacted as described in the general procedure. The obtained reaction mixture was filtered through a pad of Celite using hexane to remove the excess of sulfur. Compound **6a** was purified by column chromatography (silica, 2 × 8 cm column size) using a 90/10 (v/v) dichloromethane/ethyl acetate mixture as the eluent and obtained as an orange oil.

Yield: 65 mg (0.098 mmol, 44% based on **4a**). ^1H NMR ($CDCl_3$, δ): 1.19−1.31 (m, 6H, CH_2), 1.41−1.54 (m, 6H, CH_2), 1.63−1.78 (m, 4H, CH_2), 1.82−1.88 (m, 1H, CH_2), 1.88−2.02 (m, 3H, CH_2), 3.96 (ddd, $J_{H,H} = J_{H,H} = J_{H,P}$ = 2.8 Hz, 1H, C_5H_3), 4.19−4.23 (m, 6H, C_5H_5, C_5H_3), 4.45−4.54 (m, 2H, H1), 4.60−4.62 (m, 1H, C_5H_3), 7.39−7.43 (m, 2H, Ph), 7.45−7.49 (m, 1H, Ph), 7.50−7.56 (m, 3H, Ph), 7.96−8.00 (m, 2H, Ph), 8.12−8.17 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.55 (CH_2), 23.64 (CH_2), 23.70 (CH_2), 23.72 (CH_2), 25.21 (CH_2), 25.24 (CH_2), 33.7 (d, $J_{C,P}$ = 4.5 Hz, CH_2), 33.9−34.0 (m, CH_2), 59.8 (dd, $^1J_{C,P}$ = 217.1 Hz, $^3J_{C,P}$ = 5.4 Hz, $C_{C_5H_3}P$), 62.8 (dd, $J_{C,P}$ = 10.3 Hz, $J_{C,P}$ = 5.5 Hz, C_5H_3), 64.6 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 66.9 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 71.3 (C_5H_5), 75.1 (d, $^2J_{C,P}$ = 6.3 Hz, C1), 75.2 (d, $^2J_{C,P}$ = 6.5 Hz, C1), 118.8 (dd, $^2J_{C,P}$ = 9.2 Hz, $^2J_{C,P}$ = 6.8 Hz, $C_{C_5H_3}$−O), 128.4 (d, $J_{C,P}$ = 5.5 Hz, Ph), 128.5 (d, $J_{C,P}$ = 5.5 Hz, Ph), 131.5 (d, $J_{C,P}$ = 11.8 Hz, Ph), 131.8 (d, $J_{C,P}$ = 11.9 Hz, Ph), 131.9 (d, $J_{C,P}$ = 3.0 Hz, Ph), 132.1 (d, $J_{C,P}$ = 3.0 Hz, Ph), 134.0 (d, $^1J_{C,P}$ = 111.1 Hz, C_{Ph}−P), 134.4 (d, $^1J_{C,P}$ = 111.4 Hz, C_{Ph}−P.) $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.4 (PO_3), 80.3 (P═S). HRMS (ESI-TOF, m/z): calcd for $C_{34}H_{40}FeO_4P_2S$ + H 663.1545, found 663.1477 $[M + H]^+$.

*Dicyclohexyl 2-(O,O-Dicyclohexylphosphonato)ferrocenyl Phosphate (****6b****).* Dicyclohexyl ferrocenyl phosphate (**4a**; 100 mg, 0.22 mmol), diisopropylamine (0.07 mL, 0.50 mmol), BuLi (0.2 mL, 0.50 mmol), TMEDA (0.07 mL, 0.46 mmol), and **2a** (375 mg, 1.7 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 8 cm) using an 80/20 (v/v) dichloromethane/ethyl acetate mixture (R_f = 0.43) as the eluent. Compound **6b** was obtained as and orange oil.

Yield: 150 mg (0.188 mmol, 81% based on **4a**). ^1H NMR ($CDCl_3$, δ): 1.28−1.41 (m, 12H, CH_2), 1.45−1.65 (m, 12H, CH_2), 1.67−1.81 (m, 8H, CH_2), 1.83−1.89 (m, 1H, CH_2), 1.89−2.06 (m, 7H, CH_2), 4.02−4.05 (m, 1H, C_5H_3), 4.22−4.25 (m, 1H, C_5H_3), 4.36 (s, 5H, C_5H_5), 4.40−4.47 (m, 1H, H1), 4.48−4.54 (m, 1H, H1), 4.78−4.82 (m, 1H, C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.45 (CH_2), 23.49 (CH_2), 23.60 (CH_2), 23.62 (CH_2), 23.7 (CH_2), 25.11 (CH_2), 25.14 (CH_2), 25.30 (CH_2), 25.34 (CH_2), 33.2 (d, $^3J_{C,P}$ = 4.7 Hz, CH_2), 33.27 (d, $^3J_{C,P}$ = 4.5 Hz, CH_2), 33.31 (d, $^3J_{C,P}$ = 4.2 Hz, CH_2), 33.5 (d, $^3J_{C,P}$ = 4.4 Hz, CH_2), 33.8 (d, $^3J_{C,P}$ = 3.7 Hz, CH_2), 33.9 (d, $^3J_{C,P}$ = 3.9 Hz, CH_2), 59.7 (dd, $^1J_{C,P}$ = 217.0 Hz, $^3J_{C,P}$ = 8.6 Hz, C−P), 62.0 (d, $J_{C,P}$ = 11.3, C_5H_3), 64.5 (d, $J_{C,P}$ = 13.8, C_5H_3), 67.4 (d, $J_{C,P}$ = 13.1, C_5H_3), 71.2 (C_5H_5), 74.9 (d, $^2J_{C,P}$ = 5.9 Hz, C1), 75.1 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 77.91 (d, $^2J_{C,P}$ = 6.4 Hz, C1), 77.94 (d, $^2J_{C,P}$ = 6.3 Hz, C1), 118.5 (dd, $^2J_{C,P}$ = 8.9 Hz, $^2J_{C,P}$ = 5.0 Hz, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −7.4 (PO_4), 19.8 (PO_3). HRMS (ESI-TOF, m/z): calcd for $C_{34}H_{52}FeO_7P_2$ + Na 713.2340, found 713.2373 $[M + Na]^+$.

*2-(O,O-Dicyclohexylphosphonato)ferrocenyl Bis((1R)-α-fenchyl) Phosphate (****6c****).* Dicyclohexyl ferrocenyl phosphate (**4a**; 100 mg, 0.22 mmol), diisopropylamine (0.07 mL, 0.50 mmol), BuLi (0.2 mL, 0.50 mmol), TMEDA (0.07 mL, 0.46 mmol), and **2e** (370 mg, 0.95 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 12 cm) using an 80/20 (v/v) dichloromethane/ethyl acetate mixture (R_f = 0.45) as the eluent. Compound **6c** was obtained as an orange oil in a mixture of diastereomers (de = 0.10).

Yield: 150 mg (0.188 mmol, 81% based on **4a**). ^1H NMR ($CDCl_3$, δ): 0.84−1.58 (m, 40H, C_6H_{11}, C_6H_{17}), 1.67−1.77 (m, 8H, C_6H_{11}, C_6H_{17}), 1.92−2.03 (m, 4H, C_6H_{11}), 3.98−4.13 (m, 3H, C_5H_3, $C_{10}H_{17}$), 4.18−4.23 (m, 1H, C_5H_3), 4.36 (s, 5H, C_5H_5), 4.44−4.57 (m, 1H, C_6H_{11}), 4.89−4.98 (m, 1H, C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.4−19.5 (m, CH_3), 20.7−21.1 (m, CH_3), 23.76−23.84 (m, Cy_{CH2}), 25.7−26.0 (m, C5/C6), 29.8−30.0 (m, CH_3), 33.8−34.0 (m, Cy_{CH2}), 39.5−39.7 (m, C3), 40.9−41.0 (m, C7), 47.9−48.0 (C4), 49.2−49.4 (m, C1), 59.7 (d, $^1J_{C,P}$ = 218.7 Hz, $^3J_{C,P}$ = 8.4 Hz, C−P), 62.5 (d, $J_{C,P}$ = 10.6 Hz, C_5H_3), 62.7 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 64.30 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 64.36 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3), 67.5 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 67.6 (d, $J_{C,P}$ = 12.4 Hz, C_5H_3), 71.21 (C_5H_5), 71.23 (C_5H_5), 74.9 (d, $^2J_{C,P}$ = 6.4 Hz, Cy_{C1}), 75.05 (d, $^2J_{C,P}$ = 5.8 Hz, Cy_{C1}), 75.18 (d, $^2J_{C,P}$ = 6.7 Hz, Cy_{C1}), 91.3−91.5 (m, Fn_{C1}), 119.0−119.2 (m, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −4.4 (PO_4), −3.7 (PO_4), 19.88 (PO_3), 19.93 (PO_3). HRMS (ESI-TOF, m/z): calcd for $C_{42}H_{64}FeO_7P_2$ + H 799.3550, found 799.3496 $[M + H]^+$.

*Bis((1R)-fenchyl) (2-(O,O-Bis((1R)-α-fenchyl)phosphonato)-ferrocenyl) Phosphate (****6d****).* Ferrocenyl bis((1*R*)-α-fenchyl) phosphate (**4e**; 300 mg, 0.54 mmol), LTMP (210 mg, 1.41 mmol), TMEDA (0.15 mL, 1.0 mmol), and **2e** (420 mg, 1.08 mmol) were reacted as described in the general procedure. Compound **6e** was purified using column chromatography (silica, 2 × 12 cm column size) using a 96/4 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **6d** was obtained as an orange oil in a mixture of two diastereomers (de = 0.95).[31]

Yield: 422 mg (0.465 mmol, 86% based on **4e**). ^1H NMR ($CDCl_3$, δ): 0.73 (s, 3H, CH_3), 0.88−1.27 (m, 41H, $C_{10}H_{17}$), 1.34−1.58 (m, 8H, $C_{10}H_{17}$), 1.61−1.81 (m, 11H, $C_{10}H_{17}$), 1.86−1.90 (m, 1H, $C_{10}H_{17}$), 3.89 (dd, $^3J_{H,P}$ = 10.2 Hz, $J_{H,H}$ = 1.5 Hz, 1H, H2), 4.04−4.10 (m, 3H, H2, C_5H_3), 4.14 (dd, $^3J_{H,P}$ = 8.7 Hz, $J_{H,H}$ = 1.5 Hz, 1H, H2), 4.23 (dd, $^3J_{H,P}$ = 9.5 Hz, $J_{H,H}$ = 1.4 Hz, 1H, H2), 4.41 (s, 5H, C_5H_5), 4.97−4.98 (m, 1H, C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.66 (CH_3), 19.67 (CH_3), 19.9 (CH_3), 20.9 (CH_3), 21.1 (CH_3), 21.5 (CH_3), 22.0 (CH_3), 25.77 (C5/C6), 25.81 (C5/C6), 25.89 (C5/C6), (C5/C6), 26.00 (C5/C6), 26.03 (C5/C6), 26.13 (C5/C6), 26.14 (C5/C6), 29.7 (CH_3), 29.86 (CH_3), 29.89 (CH_3), 30.1 (CH_3), 39.3 (d, $^3J_{C,P}$ = 1.4 Hz, C3), 39.55 (d, $^3J_{C,P}$ = 2.5 Hz, C3), 39.64 (d, $^3J_{C,P}$ =

dx.doi.org/10.1021/om500953c | *Organometallics* XXXX, XXX, XXX−XXX

2.6 Hz, C3), 39.8 (d, $^3J_{C,P}$ = 1.2 Hz, C3), 40.8 (C7), 41.0 (C7), 41.2 (C7), 47.96 (C4), 47.98 (C4), 48.05 (C4), 48.2 (C4), 49.1 (d, $^3J_{C,P}$ = 5.6 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 5.1 Hz, C1), 49.5 (d, $^3J_{C,P}$ = 5.2 Hz, C1), 59.1 (dd, $^1J_{C,P}$ = 217.1 Hz, $^3J_{C,P}$ = 10.0 Hz, C−P), 62.0 (d, $J_{C,P}$ = 10.8, C_5H_3), 64.7 (d, $J_{C,P}$ = 12.8, C_5H_3), 66.8 (d, $J_{C,P}$ = 10.3, C_5H_3), 71.2 (C_5H_5), 87.6 (d, $^2J_{C,P}$ = 5.5 Hz, $C2_{PO_3}$), 88.3 (d, $^2J_{C,P}$ = 7.8 Hz, $C2_{PO_3}$), 91.1 (d, $^2J_{C,P}$ = 6.5 Hz, $C2_{PO4}$), 91.7 (d, $^2J_{C,P}$ = 6.6 Hz, $C2_{PO_4}$), 120.69 ($C_{C_5H_3}$−O), 120.73 ($C_{C_5H_3}$−O), 120.78 ($C_{C_5H_3}$−O), 120.81 ($C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −3.5 (d, $^4J_{P,P}$ = 0.9 Hz, PO_4), 19.6 (d, $^4J_{P,P}$ = 1.9 Hz, PO_3; dd $^1J_{P,C}$ = 216.9 Hz, 1.9 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{50}H_{76}FeO_7P_2$ + H 907.4489, found 907.4409 $[M + H]^+$.

Crystal data for ***6d****:* $C_{50.25}H_{76.5}Cl_{0.5}FeO_7P_2$, M_r = 928.12, monoclinic, *C*2, λ = 0.71073 Å, a = 43.1922(8) Å, b = 8.5461(2) Å, c = 26.5582(5) Å, β = 90.458(2)°, V = 9803.0(3) Å^3, Z = 8, ρ_{calcd} = 1.258 Mg m^{-3}, μ = 0.449 mm^{-1}, T = 110.00(10) K, θ range 2.875−25.50°, 41406 reflections collected, 16504 independent reflections (R_{int} = 0.0229), R1 = 0.0333, *wR2* = 0.0807 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.005(4).

*1,3-Bis(O,O-dicyclohexylphosphonato)-2-methoxyferrocene (****7a****).* Dicyclohexyl 2-(*O*,*O*-dicyclohexylphosphonato)ferrocenyl phosphate (**6a**; 68 mg, 0.10 mmol), diisopropylamine (0.03 mL, 0.20 mmol), BuLi (0.08 mL, 0.20 mmol), TMEDA (0.03 mL, 0.20 mmol), and Me_2SO_4 (0.1 mL, 0.8 mmol) were reacted as described in the general procedure. Compound **7a** was purified using column chromatography (silica, 2 × 10 cm column size) using a 95/5 (v/v) ethyl acetate/methanol mixture as the eluent. Compound **7a** was obtained as an orange oil.

Yield: 28 mg (0.04 mmol, 41% based on **6a**). ^1H NMR ($CDCl_3$, δ): 1.24−1.34 (m, 12H, CH_2), 1.42−1.56 (m, 12H, CH_2), 1.64−1.80 (m, 8H, CH_2), 1.81−2.02 (m, 8H, CH_2), 3.91 (m, 3H, OCH_3), 4.35−4.22 (m, 2H, C_5H_2), 4.43−4.57 (m, 9H, C_5H_5, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.55 (CH_2), 23.57 (CH_2), 25.23 (CH_2), 33.50 (CH_2), 33.52 (CH_2), 33.53 (CH_2), 33.65 (CH_2), 33.77 (CH_2), 33.78 (CH_2), 33.79 (CH_2), 33.86 (CH_2), 63.7 (CH_3), 64.1 (dd, $^1J_{C,P}$ = 212.1 Hz, $^3J_{C,P}$ = 10.6 Hz, C−P), 69.3 (pt, $^{2+3}J_{C,P}$ = 13.6 Hz, C_5H_2), 72.1 (C_5H_5), 75.14 (C1), 75.19 (C1), 75.21 (C1), 75.27 (C1), 128.1 (t, $^2J_{C,P}$ = 10.9 Hz, $C_{C_5H_2}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 19.8. HRMS (ESI-TOF, m/z): calcd for $C_{35}H_{54}FeO_7P_2$ + Na 727.2587, found 727.2589 $[M + Na]^+$.

*1,3-Bis(O,O-bis((1R)-α-fenchyl)phosphonato)-2-hydroxyferrocene (****7b****).* Bis((1*R*)-α-fenchyl) 2-(*O*,*O*-bis((1*R*)-α-fenchylphosphonato)-ferrocenyl phosphate (**6d**; 100 mg, 0.11 mmol), diisopropylamine (0.05 mL, 0.36 mmol), BuLi (0.15 mL, 0.38 mmol), TMEDA (0.06 mL, 0.4 mmol), and Me_2SO_4 (0.2 mL, 2.1 mmol) were reacted as described in the general procedure. Compound **7b** was purified using column chromatography (silica, 2 × 10 cm column size) using a 70/30 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **7b** was obtained as an orange oil.

Yield: 99 mg (0.109 mmol, 99% based on **6d**). ^1H NMR ($CDCl_3$, δ): 0.79 (s, 3H, CH_3), 0.94−1.28 (m, 41H), 1.30−1.35 (m, 1H, CH_2), 1.39−1.56 (m, 6H, CH_2), 1.59−1.61 (m, 1H, CH_2), 1.65−1.89 (m, 11H), 1.91−1.98 (m, 1H, CH_2), 3.50 (dd, $^3J_{H,P}$ = 9.5 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, H2), 3.87 (dd, $^3J_{H,P}$ = 9.7 Hz, $J_{H,H}$ = 1.5 Hz, 1H, H2), 4.12 (dd, J = 5.0 Hz, J = 2.6 Hz, 1H, C_5H_2), 4.21 (dd, $^3J_{H,P}$ = 10.2 Hz, $J_{H,H}$ = 1.3 Hz, 1H, H2), 4.30 (dd, $^3J_{H,P}$ = 9.0 Hz, $J_{H,H}$ = 1.4 Hz, 1H, H2), 4.42 (dd, J = 4.8 Hz, J = 2.7 Hz, 1H, C_5H_2), 4.48 (s, 5H, C_5H_5), 7.60 (s, 1H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.4 (CH_3), 19.7 (CH_3), 19.8 (CH_3), 21.5 (CH_3), 21.6 (2 C, CH_3), 21.7 (CH_3), 25.81 (CH_2−CH_2), 25.87 (C5/C6), 25.95 (C5/C6), 25.97 (C5/C6), 26.02 (C5/C6), 29.4 (CH_3), 29.7 (CH_3), 29.9 (CH_3), 30.1 (CH_3), 39.24 (C3), 39.26 (C3), 39.4 (d, $^3J_{C,P}$ = 1.9 Hz, C3), 39.8 (d, $^3J_{C,P}$ = 1.9 Hz, C3), 40.4 (C7), 40.9 (C7), 41.0 (C7), 41.1 (C7), 47.83 (C4), 47.85 (C4), 48.09 (C4), 48.12 (C4), 49.1 (d, $^3J_{C,P}$ = 6.9 Hz, C1), 49.2 (d, $^3J_{C,P}$ = 4.9 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 5.7 Hz, C1), 49.5 (d, $^3J_{C,P}$ = 4.7 Hz, C1), 53.8 (dd, $^1J_{C,P}$ = 211.0 Hz, $^3J_{C,P}$ = 11.1 Hz, C−P), 57.5 (dd, $^1J_{C,P}$ = 214.8 Hz, $^3J_{C,P}$ = 12.3 Hz, C−P), 65.0 (dd, $J_{C,P}$ = 13.2 Hz, $J_{C,P}$ = 12.6 Hz, C_5H_2), 68.9 (pt, $^{2+3}J_{C,P}$ = 13.7 Hz, C_5H_2), 72.0 (C_5H_5), 88.6 (d, $^2J_{C,P}$ = 6.5 Hz, C2), 88.8 (d, $^2J_{C,P}$ = 5.4 Hz, C2), 89.0 (d, $^2J_{C,P}$ = 7.3 Hz, C2), 90.9 (d, $^2J_{C,P}$ = 8.9 Hz, C2), 130.0 (dd, $^2J_{C,P}$ = 13.8 Hz, $^2J_{C,P}$ = 10.5 Hz, C−OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.3 (d, $^3J_{P,P}$ = 3.7 Hz), 25.8 (d, $^3J_{P,P}$ = 3.7 Hz).

*1,1′-Bis(O,O-bis((1R)-α-fenchyl)phosphonato)-2-methoxyferrocene (****7c****).* Bis((1*R*)-α-fenchyl) 2-(*O*,*O*-bis((1*R*)-α-fenchyl)-phosphonato)ferrocenyl phosphate (**6d**; 45 mg, 0.05 mmol), LTMP (24 mg, 0.16 mmol), TMEDA (0,03 mL, 0.20 mmol), and Me_2SO_4 (0.1 mL, 1.05 mmol) were reacted as described in the general procedure. Purification was realized using column chromatography (silica, 2 × 12 cm column size) using a 85/15 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **7c** was obtained as an orange oil.

Yield: 12 mg (0.013 mmol, 26% based on **6d**). ^1H NMR ($CDCl_3$, δ): 0.65 (s, 3H, CH_3), 0.87−1.26 (m, 37H, $C_{10}H_{17}$), 1.38−1.57 (m, 8H, $C_{10}H_{17}$), 1.59−1.87 (m, 12H, $C_{10}H_{17}$), 3.74−3.76 (m, 4H, OCH_3, H2), 4.00−4.05 (m, 2H, H2), 4.18 (dd, $J_{H,P}$ = 9.73 Hz, $J_{H,H}$ = 1.5 Hz, H2), 4.27−4.30 (m, 2H, C_5H_3), 4.43−4.45 (m, 1H, C_5H_4), 4.46−4.47 (m, 1H, C_5H_3), 4.66−4.68 (m, 1H, C_5H_4), 4.70−4.72 (m, 1H, C_5H_4), 4.73−4.75 (m, 1H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.15 (CH_3), 19.23 (CH_3), 19.6 (CH_3), 19.7 (CH_3), 21.1 (CH_3), 21.45 (CH_3), 21.48 (CH_3), 21.7 (CH_3), 25.77 (C5/C6), 25.84 (C5/C6), 25.95 (C5/C6), 26.0 (C5/C6), 26.1 (C5/C6), 26.2 (C5/C6), 29.65 (CH_3), 29.67 (CH_3), 29.69 (CH_3), 29.74 (CH_3), 29.80 (CH_3), 39.10 (C3), 39.11 (C3), 39.15 (C3), 39.16 (C3), 39.70 (C3), 39.71 (C3), 39.72 (C3), 39.73 (C3), 40.8 (C7), 41.0 (C7), 41.1 (C7), 47.94 (C4), 47.98 (C4), 48.03 (C4), 48.08 (C4), 49.1 (d, $^3J_{C,P}$ = 5.4 Hz, C1), 49.2 (d, $^3J_{C,P}$ = 5.1 Hz, C1), 49.3 (d, $^3J_{C,P}$ = 4.7 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 5.2 Hz, C1), 56.9 (d, $J_{C,P}$ = 11.4 Hz, C_5H_3), 58.0 (OCH_3), 58.7 (d, $^1J_{C,P}$ = 215.1 Hz, $C_{C_5H_3}P$), 66.0 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 11.9 Hz, C_5H_3), 68.4 (d, $^1J_{C,P}$ = 216.8 Hz, C_{C5H4}−P), 71.8 (d, $J_{C,P}$ = 13.1 Hz, C_5H_4), 73.7 (d, $J_{C,P}$ = 13.4 Hz, C_5H_4), 74.6 (d, $J_{C,P}$ = 16.4 Hz, C_5H_4), 75.0 (d, $J_{C,P}$ = 14.0 Hz, C_5H_4), 88.0 (d, $^2J_{C,P}$ = 6.3 Hz, C2), 88.1 (d, $^2J_{C,P}$ = 6.5 Hz, C2), 88.3 (d, $^2J_{C,P}$ = 5.9 Hz, C2), 88.5 (d, $^2J_{C,P}$ = 7.8 Hz, C2), 129.8 (d, $^2J_{C,P}$ = 10.4 Hz, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.3 (C_5H_3), 23.8 (C_5H_4).

*1′-(Bis((1R)-α-fenchyl)phosphato)-2-methoxyferrocenyl O,O-Bis-((1R)-α-fenchyl) Phosphonate (****14b****).* 1,1′-Ferrocenediyl tetrakis-((1*R*)-α-fenchyl) bis(phosphate) (**13b**; 120 mg, 0.13 mmol), LTMP (115 mg, 0.78 mmol), TMEDA (0.12 mL, 0.78 mmol), and Me_2SO_4 (0.22 mL, 2.3 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 12 cm column size) using a 90/10 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **14b** was obtained as an orange oil as a mixture of both diastereomers (de = 0.84).

Yield: 22 mg (0.024 mmol, 18% based on **13b**). ^1H NMR ($CDCl_3$, δ): 0.85−1.28 (m, 44H), 1.44−1.52 (m, 8H, CH_2), 1.66−1.75 (m, 12H, CH_2, CH), 3.74 (s, OCH_3), 3.95−4.04 (m, 4H, H2), 4.13−4.14 (m, 2H, C_5H_X), 4.21−4.23 (m, 2H, C_5H_X), 4.28−4.29 (m, 1H, C_5H_X), 4.49−4.50 (m, 1H, C_5H_X), 4.58−4.59 (m, 1H, C_5H_X). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.18 (CH_3), 19.37 (CH_3), 19.41 (CH_3), 19.61 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 21.4, 25.6−26.2 (m, C5/C6), 29.7−29.8 (m, CH_3), 39.1 (d, $^3J_{C,P}$ = 2.2 Hz, C3), 39.5 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 39.6 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 39.7 (d, $^3J_{C,P}$ = 2.2 Hz, C3), 40.9−41.1 (m, C7), 47.9−48.1 (m, C4), 49.2−49.3 (m, C1), 57.5 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 57.9 (OCH_3), 58.4 (d, $^1J_{C,P}$ = 218.4 Hz, C−P), 60.7 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 62.0 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 64.8 (C_5H_4), 66.0 (d, $J_{C,P}$ = 13.8 Hz, C_5H_3), 66.3 (C_5H_4), 67.8 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3) 87.8 (d, $^2J_{C,P}$ = 6.1 Hz, C2), 88.1 (d, $^2J_{C,P}$ = 8.7 Hz, C2), 91.3 (d, $^2J_{C,P}$ = 7.0 Hz, C2), 118.5 (d, $^2J_{C,P}$ = 4.4 Hz, CO_{PO_4}), 129.5 (d, $^2J_{C,P}$ = 10.1 Hz, CO_{PO_3}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −4.5 (PO_4), 22.0 (PO_3, major), 22.2 (PO_3, minor).

*O,O,O,O-Tetracyclohexyl 2,2′-Dimethoxy-1,1′-ferrocenediyl Bis-(phosphonate) (****15a****).* 1,1′-Ferrocenediyl tetracyclohexyl bis-(phosphate) (**13a**; 100 mg, 0.14 mmol), diisopropylamine (0.08 mL, 0.57 mmol), BuLi (0.23 mL, 0.58 mmol), TMEDA (0.09 mL, 0.60 mmol), and Me_2SO_4 (0.3 mL, 3.2 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm) using a 95/5 (v/v) ethyl

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acetate/methanol mixture as the eluent. Compound **15a** was obtained as an orange oil as a mixture of diastereomers (de = 0.20).

Yield: 70 mg (0.095 mmol, 67% based on **13a**). ^{1}H NMR ($CDCl_3$, δ): 1.18−1.39 (m, 12H, CH_2), 1.43−1.60 (m, 12H, CH_2), 1.63−1.80 (m, 8H, CH_2), 1.87−1.98 (m, 8H, CH_2), 3.71 (s, 3.6H*, OCH_3), 3.83 (s, 2.4H*, OCH_3), 4.12−4.17 (m, 1.6H*, C_5H_3), 4.21−4.22 (m, 1H, C_5H_3), 4.36−4.43 (m, 4H, Cy_{C1}, C_5H_3), 4.45−4.57 (m, 3.4H*, Cy_{C1}, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.5−23.7 (CH_2), 25.1−25.3 (CH_2), 33.5−33.9 (m, CH_2), 57.5 (d, $J_{C,P}$ = 11.1 Hz, C_5H_3), 58.0 (OCH_3), 58.2 (OCH_3), 58.4 (d, $^1J_{C,P}$ =215.6 Hz, C−P), 58.5 (d, $^1J_{C,P}$ =215.1 Hz, C−P), 59.4 (d, $J_{C,P}$ =11.1 Hz, C_5H_3), 64.8 (d, $J_{C,P}$ = 13.8 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ =14.0 Hz, C_5H_3), 68.9 (d, $J_{C,P}$ =13.1 Hz, C_5H_3), 74.68−74.73 (m, C1), 75.0 (d, $^2J_{C,P}$ = 6.2 Hz, C1), 75.22 (d, $^2J_{C,P}$ = 6.0 Hz, C1), 75.23 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 129.0 (d, $^2J_{C,P}$ = 9.8 Hz, $C_{C_5H_3}$−O), 129.5 (d, $^2J_{C,P}$ = 10.6 Hz, $C_{C_5H_3}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.75 (major), 20.81 (minor).

*O-Cyclohexyl O-Ferrocenyl (2-Methoxyferrocenyl)phosphonate (**10a**).* Cyclohexyl diferrocenyl phosphate (**9a**; 100 mg, 0.18 mmol), diisopropylamine (0.1 mL, 0.72 mmol), BuLi (0.30 mL, 0.75 mmol), TMEDA (0.11 mL, 0.73 mmol), and Me_2SO_4 (0.3 mL, 3.2 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using an 85/15 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **10a** was obtained as an orange solid as a mixture of diastereomers (de = 0.45).

Yield: 58 mg (0.10 mmol, 57% based on **9a**). Mp: 111−114 °C. Anal. Calcd for $C_{27}H_{31}Fe_2O_4P$ (562.20): C, 57.68; H, 5.56. Found: C, 57.87; H, 5.66. ^{1}H NMR ($CDCl_3$, δ): 1.33−1.43 (m, 3H, CH_2), 1.47−1.54 (m, 1H, CH_2), 1.58−1.68 (m, 2H, CH_2), 1.72−1.82 (m, 2H, CH_2), 1.88−2.02 (m, 2H, CH_2), 3.71/3.73 (s, 3H, OCH_3), 3.81−3.85 (m, 2H, $C_5H_{3/4}$), 4.04−4.07 (m, 1H, $C_5H_{3/4}$), 4.16/4.19 (s, 5H, C_5H_5), 4.21−4.24 (m, 1H, $C_5H_{3/4}$), 4.29−4.31 (m, 1H, $C_5H_{3/4}$), 4.32 (s, 5H, C_5H_5), 4.38−4.40 (m, 1H, $C_5H_{3/4}$), 4.42−4.47 (m, 1H, $C_5H_{3/4}$), 4.55−4.66 (m, 1H, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.50 (CH_2), 23.54 (CH_2), 25.24 (CH_2), 25.29 (CH_2), 33.6−33.8 (m, CH_2), 55.26 (d, $J_{C,P}$ = 11.6 Hz, $C_5H_{3/4}$), 55.31 (d, $J_{C,P}$ = 11.6 Hz, $C_5H_{3/4}$), 57.0 (d, $^1J_{C,P}$ = 218.0 Hz, C−P), 58.2 (OCH_3), 60.0 (d, $J_{C,P}$ = 3.6 Hz, $C_5H_{3/4}$), 60.1 (d, $J_{C,P}$ = 3.9 Hz, $C_5H_{3/4}$), 60.26 (d, $J_{C,P}$ = 3.3 Hz, $C_5H_{3/4}$), 60.33 (d, $J_{C,P}$ = 3.6 Hz, $C_5H_{3/4}$), 62.4−62.5 (m, $C_5H_{3/4}$), 63.9 (d, $J_{C,P}$ = 13.7 Hz, $C_5H_{3/4}$), 64.0 (d, $J_{C,P}$ = 14.6 Hz, $C_5H_{3/4}$), 67.2 (d, $J_{C,P}$ = 12.8 Hz, $C_5H_{3/4}$), 67.4 (d, $J_{C,P}$ = 14.1 Hz, $C_5H_{3/4}$), 69.27 (C_5H_5), 69.33 (C_5H_5), 70.08 (C_5H_5), 70.13 (C_5H_5), 75.7 (d, $^2J_{C,P}$ = 6.2 Hz, C1), 76.1 (d, $^2J_{C,P}$ = 7.1 Hz, C1), 117.5 (d, $^2J_{C,P}$ = 4.8 Hz, $C_{C_5H_4}$−O), 128.6 (d, $^2J_{C,P}$ = 10.3 Hz, $C_{C_5H_3}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.06 (minor), 20.09 (major). HRMS (ESI-TOF, m/z): calcd for $C_{27}H_{31}Fe_2O_4P$ 562.0654, found 562.0654 [M]+.

*Crystal data for **10a**:* $C_{27}H_{31}Fe_2O_4P$, M_r = 562.19, monoclinic, $P2_1/c$, λ = 0.71073 Å, a = 13.9652(7) Å, b = 8.1909(5) Å, c = 21.2807(12) Å, β = 97.814(5)°, V = 2411.6(2) Å^3, Z = 4, ρ_{calcd} = 1.548 Mg m^{-3}, μ = 1.302 mm^{-1}, T = 109.95(10) K, θ range 2.945−24.998°, 11049 reflections collected, 4244 independent reflections (R_{int} = 0.0399), R1 = 0.0404, wR2 = 0.0913 ($I > 2\sigma(I)$).

*O-Ferrocenyl O-(1R)-Menthyl (2-Methoxyferrocenyl)-phosphonate (**10b**).* Diferrocenyl (1*R*)-menthyl phosphate (**9b**; 200 mg, 0.33 mmol), diisopropylamine (0.09 mL, 0.65 mmol), BuLi (0.27 mL, 0.68 mmol), TMEDA (0.10 mL, 0.66 mmol), and Me_2SO_4 (0.2 mL, 2.1 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **10b** was obtained as an orange oil as a mixture of isomers.

Yield: 155 mg (0.25 mmol, 74% based on **9b**). ^{1}H NMR ($CDCl_3$, δ): 0.74−0.96 (m, 10H, CH_3, CH_2), 1.00−1.09 (m, 1H, CH_2), 1.15−1.25 (m, 1H, CH_2), 1.32−1.39 (m, 1H, CH), 1.44−1.52 (m, 1H, CH), 1.62−1.71 (m, 2H, CH_2, CH), 2.11−2.49 (m, 2H, CH_2), 3.67−3.72 (m, 3H, OCH_3), 3.78−3.87 (m, 2H, $C_5H_{3/4}$), 4.01−4.07 (m, 1H, $C_5H_{3/4}$), 4.11−4.58 (m, 15H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.6−15.7 (m, CH_3), 21.1−21.2 (m, CH_3), 22.0−22.1 (m, CH_3), 22.6−22.8 (m, CH_2), 31.5−31.6 (m, CH_3), 34.07−34.13 (m, CH_2), 43.1−43.4 (m, CH_2), 48.6−49.0 (m, C1), 55.0−55.3 (m, C_5H_3), 56.17−56.21 (m, C−P), 56.8 (d, $^1J_{C,P}$ = 218.3 Hz, C−P), 57.90−57.94 (OCH_3), 58.1 (C−P), 59.8−60.5 (m, C_5H_4), 62.3−62.5 (m, C_5H_4), 63.7−64.0 (m, C_5H_3), 66.7−67.8 (m, C_5H_3), 69.2−69.3 (m, C_5H_5), 70.0−70.2 (m, C_5H_5), 77.6−78.3 (m, C1), 117.6−117.7 (m, $C_{C_5H_4}$−O), 128.3−128.9 (m, $C_{C_5H_3}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ):[32] 19.8, 20.1, 20.4, 21.0. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{41}Fe_2O_4P$ 632.1437, found 632.1400 [M]$^+$.

*Crystal data for **10b**:* $C_{30}H_{37}Fe_2O_4P$, M_r = 604.26, monoclinic, $P2_1$, λ = 0.71073 Å, a = 14.1041(13) Å, b = 5.8359(5) Å, c = 16.704(2) Å, β = 92.648(9)°, V = 1371.4(2) Å^3, Z = 2, ρ_{calcd} = 1.461 Mg m^{-3}, μ = 1.149 mm^{-1}, T = 110.2(6) K, θ range 2.892−24.997°, 5764 reflections collected, 4257 independent reflections (R_{int} = 0.0229), R1 = 0.0908, wR2 = 0.1454 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.02(6).

*O-(1S)-Borneyl O-Ferrocenyl (2-Methoxyferrocenyl)phosphonate (**10c**).* (1*S*)-Borneyl diferrocenyl phosphate (**9c**; 100 mg, 0.18 mmol), diisopropylamine (0.05 mL, 0.36 mmol), BuLi (0.15 mL, 0.38 mmol), TMEDA (0.05 mL, 0.33 mmol), and Me_2SO_4 (0.13 mL, 1.37 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using an 80/20 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **10c** was obtained as an orange oil as a mixture of isomers (Table SI2, Supporting Information).

Yield: 55 mg (0.089 mmol, 49% based on **9c**). ^{1}H NMR ($CDCl_3$, δ): 0.82 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.19−1.33 (m, 3H, CH_2), 1.60−1.64 (m, 1H, H4), 1.66−1.74 (m, 1H, CH_2), 1.91−2.10 (m, 1H, CH_2), 2.12−2.35 (m, 1H, H3), 3.63−3.66 (m, 3H, OCH_3), 3.71−3.78 (m, 2H, $C_5H_{3/4}$), 3.97−4.02 (m, 1H, $C_5H_{3/4}$), 4.06−4.12 (m, 5H, C_5H_5), 4.15−4.17 (m, 1H, $C_5H_{3/4}$), 4.22−4.40 (m, 8H, $C_5H_{3/4}$, C_5H_5), 4.64−4.75 (m, 1H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ):[33] 13.2 (CH_3), 13.3 (CH_3), 18.9 (CH_3), 20.0 (CH_3), 26.5 (C5/C6), 26.6 (C5/C6), 28.10 (C5/C6), 28.12 (C5/C6), 37.2 (d, $^3J_{C,P}$ = 1.3 Hz, C3), 37.6 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 44.91 (C4), 44.95 (C4), 47.5 (C7), 47.6 (C7), 49.7 (d, $^3J_{C,P}$ = 6.5 Hz, C1), 49.8 (d, $^3J_{C,P}$ = 5.5 Hz, C1), 55.20 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 55.25 (d, $J_{C,P}$ = 11.5 Hz, C_5H_3), 56.6 (d, $^1J_{C,P}$ = 218.4 Hz, C−P), 56.8 (d, $^1J_{C,P}$ = 218.8 Hz, C−P), 58.0 (OCH_3), 58.1 (OCH_3), 59.9 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 60.0 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 60.2 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 62.36 (C_5H_4), 62.39 (C_5H_4), 62.41 (C_5H_4), 63.99 (d, $J_{C,P}$ = 14.7 Hz, C_5H_3), 64.04 (d, $J_{C,P}$ = 14.6 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 67.5 (d, $J_{C,P}$ = 14.6 Hz, C_5H_3), 69.2 (C_5H_5), 69.3 (C_5H_5), 70.07 (C_5H_5), 70.09 (C_5H_5), 82.70 (d, $^2J_{C,P}$ = 7.5 Hz, C2), 82.73 (d, $^2J_{C,P}$ = 7.5 Hz, C2), 117.5 (m, $C_{C_5H_4}$−O), 128.5 (d, $^2J_{C,P}$ = 9.8 Hz, C_{C5H3}−OCH_3), 128.7 (d, $^2J_{C,P}$ = 10.0 Hz, C−OCH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.54, 20.61, 21.06, 21.11. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.0963 [M]$^+$.

*O-(1R)-α-Fenchyl O-Ferrocenyl (2-Methoxyferrocenyl)-phosphonate (**10d**).* (1*R*)-α-Fenchyl diferrocenyl phosphate (**9d**; 134 mg, 0.22 mmol), LTMP (130 mg, 0.88 mmol), TMEDA (0.13 mL, 0.86 mmol), and Me_2SO_4 (0.3 mL, 3.2 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using a 90/10 (v/v) dichloromethane/ethyl acetate mixture as the eluent. Compound **10d** was obtained as an orange oil as a mixture of isomers (Table SI2, Supporting Information).

Yield: 125 mg (0.20 mmol, 91% based on **9d**). ^{1}H NMR ($CDCl_3$, δ): 0.93−1.22 (m, 11H, CH_3, CH_2), 1.44−1.55 (m, 2H, CH_2), 1.69−1.88 (m, 3H, CH_2, CH), 3.38−3.72 (m, 3H, OCH_3), 3.79−3.85 (m, 2H, C_5H_4), 4.04−4.23 (m, 8H, C_5H_5, C_5H_3, H2), 4.25−4.51 (m, 8H, C_5H_5, $C_5H_{3/4}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.18 (CH_3), 19.22 (CH_3), 19.27 (CH_3), 19.31 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 21.2 (CH_3), 21.3 (CH_3), 25.8−26.2 (C5/C6), 29.6−29.8 (CH_3), 39.40 (d, $^3J_{C,P}$ = 3.0 Hz, C3), 39.45−39.47 (m, C3), 39.6 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 41.0−41.1 (C7), 47.85 (C4), 47.90 (C4), 47.99 (C4), 48.02 (C4), 49.16−49.25 (m, C1), 49.32 (d, $^3J_{C,P}$ = 4.7 Hz, C1), 55.0−55.3 (m, C_5H_3), 56.45 (d, $^1J_{C,P}$ = 219.7 Hz, C−P), 56.54 (d, $^1J_{C,P}$ = 219.1 Hz, C−P), 57.0 (d, $^1J_{C,P}$ = 219.6 Hz, C−P), 57.1 (d, $^1J_{C,P}$ = 218.3 Hz, C−P), 57.8−58.0 (OCH_3), 59.8 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4), 59.8 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4), 60.1−60.2 (m, C_5H_4), 60.3−60.4 (m, C_5H_4), 60.6 (d,

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$J_{C,P}$ = 3.1 Hz, C_5H_4), 62.3−62.4 (m, C_5H_4), 63.8−64.1 (m, C_5H_3), 66.8 (d, $J_{C,P}$ = 12.3 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 67.7 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 69.17−62.22 (C_5H_5), 69.97−70.00 (C_5H_5), 88.5 (d, $^2J_{C,P}$ = 7.3 Hz, C2), 88.95 (d, $^2J_{C,P}$ = 7.4 Hz, C2), 89.02 (d, $^2J_{C,P}$ = 7.3 Hz, C2), 89.5 (d, $^2J_{C,P}$ = 7.9 Hz, C2), 117.7 (d, $^2J_{C,P}$ = 4.4 Hz, $C_{C_5H_4}$−O), 117.81 (d, $^2J_{C,P}$ = 4.6 Hz, $C_{C_5H_4}$−O), 117.84 (d, $^2J_{C,P}$ = 4.4 Hz, $C_{C_5H_4}$−O), 128.41 (d, $^2J_{C,P}$ = 9.9 Hz, $C_{C_5H_3}$−O), 128.44 (d, $^2J_{C,P}$ = 10.4 Hz, $C_{C_5H_3}$−O), 128.6 (d, $^2J_{C,P}$ = 10.4 Hz, $C_{C_5H_3}$−O), 129.0 (d, $^2J_{C,P}$ = 11.2 Hz, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.4, 20.7, 20.8, 21.5. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{37}Fe_2O_4P$ 616.1124, found 616.1063 $[M]^+$.

Crystal data for ***10d****:* $C_{31}H_{37}Fe_2O_4P$, M_r = 616.27, monoclinic, $P2_1$, λ = 0.71073 Å, a = 14.7944(13) Å, b = 8.3537(7) Å, c = 22.2802(17) Å, β = 96.930(7)°, V = 2733.4(4) Å^3, Z = 4, ρ_{calcd} = 1.498 Mg m^{-3}, μ = 1.498 mm^{-1}, T = 110.0(3) K, θ range 2.900−24.999°, 22814 reflections collected, 9551 independent reflections (R_{int} = 0.1117), R1 = 0.0679, wR2 = 0.0825 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.01(4).

*rac-O-Cyclohexyl Bis(2-methoxyferrocenyl)phosphinate (rac-**11a**) and meso-O-Cyclohexyl Bis(2-methoxyferrocenyl)phosphinate (meso-**11a**).* The title compounds were obtained as side products during the synthesis of **10a** by reacting cyclohexyl diferrocenyl phosphate (**9a**; 100 mg, 0.18 mmol), diisopropylamine (0.1 mL, 0.72 mmol), BuLi (0.30 mL, 0.75 mmol), TMEDA (0.11 mL, 0.73 mmol), and Me_2SO_4 (0.3 mL, 3.2 mmol) as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using a 97/3 (v/v) ethyl acetate/methanol mixture (***rac*-11a**, R_f = 0.42; ***meso*-11a**, R_f = 0.38); both compounds were obtained as orange oils.

***rac*-11a**: yield 27 mg (0.072 mmol, 39% based on **9a**). ^1H NMR ($CDCl_3$, δ): 1.32−1.46 (m, 3H, CH_2), 1.49−1.62 (m, 2H, CH_2), 1.69−1.89 (m, 4H, CH_2), 2.05−212 (m, 1H, CH_2), 3.67 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.96−3.97 (m, 2H, C_5H_3), 4.01−4.09 (m, 2H, C_5H_3), 4.14−4.17 (m, 2H, C_5H_3), 4.33 (s, 5H, C_5H_5), 4.34 (s, 5H, C_5H_5), 4.72−4.78 (m, 1H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.57 (CH_2), 23.61 (CH_2), 25.6 (CH_2), 33.8 (d, $^3J_{C,P}$ = 4.1 Hz, CH_2), 34.4 (d, $^3J_{C,P}$ = 3.2 Hz, CH_2), 55.0 (d, $J_{C,P}$ = 9.4 Hz, C_5H_3), 58.0 (OCH_3), 58.2 (OCH_3), 63.1 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3), 63.3 (d, $^2J_{C,P}$ = 12.4 Hz, C_5H_3), 63.6 (d, $^1J_{C,P}$ = 161.2 Hz, C−P), 63.8 (d, $^1J_{C,P}$ = 155.3 Hz, C−P), 67.0 (d, $J_{C,P}$ = 15.1 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 10.7 Hz, C_5H_3), 69.8 (C_5H_5), 69.8 (C_5H_5), 73.7 (d, $^2J_{C,P}$ = 5.4 Hz, C1), 128.3 (d, $^2J_{C,P}$ = 7.8 Hz, $C_{C_5H_3}$−O), 128.6 (d, $^2J_{C,P}$ = 10.6 Hz, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 34.2.

***meso*-11a**: yield 40 mg (0.105 mmol, 58% based on **9a**). ^1H NMR ($CDCl_3$, δ): 1.29−1.33 (m, 3H, CH_2), 1.44−1.47 (m, 1H, CH_2), 1.53−1.60 (m, 1H, CH_2), 1.71−1.78 (m, 2H, CH_2), 1.81−1.89 (m, 2H, CH_2), 3.72 (s, 6H, OCH_3), 4.00−4.02 (m, 2H, C_5H_3), 4.18−4.19 (m, 2H, C_5H_3), 4.22−4.26 (m, 12H, C_5H_5, C_5H_3), 4.46−4.53 (m, 1H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.4 (CH_2), 25.5 (CH_2), 33.8 (d, $^3J_{C,P}$ = 3.6 Hz, C2/C6), 54.8 (d, $J_{C,P}$ = 9.0 Hz, C_5H_3), 58.2 (OCH_3), 63.1 (d, $^1J_{C,P}$ = 158.6 Hz, C−P), 63.6 (d, $J_{C,P}$ = 12.7 Hz, C_5H_3), 67.0 (d, $J_{C,P}$ = 14.6 Hz, C_5H_3), 69.9 (C_5H_5), 73.8 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 128.9 (d, $^2J_{C,P}$ = 7.8 Hz, $C_{C_5H_3}$−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 35.6. HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{33}Fe_2O_4P$ + Na 599.0708, found 599.0716 $[M + Na]^+$.

*O-(1S)-Borneyl Bis(2-methoxyferrocenyl)phosphinate (**11c**).* The title compound was obtained as a side product during the synthesis of **10c** by reacting (1*S*)-borneyl diferrocenyl phosphate (**9c**; 100 mg, 0.18 mmol), diisopropylamine (0.05 mL, 0.36 mmol), BuLi (0.15 mL, 0.38 mmol), TMEDA (0.05 mL, 0.33 mmol), and Me_2SO_4 (0.13 mL, 1.37 mmol) as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using a 95/5 (v/v) ethyl acetate/methanol mixture as the eluent. Compound **11c** was obtained as an orange oil as a mixture of diastereomers (Table SI2, Supporting Information).

Yield: 42 mg (0.067 mmol, 37% based on **9c**). ^1H NMR ($CDCl_3$, δ): 0.74 (CH_3), 0.80 (CH_3), 0.84 (CH_3), 1.17−1.30 (m, 3H, CH_2), 1.59−1.60 (m, 1H, H4), 1.68−1.76 (m, 1H, CH_2), 2.07−2.14 (m, 1H, CH_2), 2.16−2.24 (m, 1H, CH_2), 3.71 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.98−4.00 (m, 1H, C_5H_3), 4.00−4.02 (m, 1H, C_5H_3), 4.13−4.14 (m, 1H, C_5H_3), 4.18−4.19 (m, 3H, C_5H_3), 4.27 (s, 5H, C_5H_5), 4.31 (s, 5H, C_5H_5), 4.66−4.71 (m, 1H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.04 (CH_3), 18.7 (CH_3), 19.9 (CH_3), 26.4 (C5/C6), 28.2 (C5/C6), 37.5 (C3), 45.1 (C4), 47.3 (C7), 49.8 (d, $^3J_{C,P}$ = 6.2 Hz, C1), 54.6 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 54.7 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 58.0 (OCH_3), 58.1 (OCH_3), 62.2 (d, $^1J_{C,P}$ = 158.8 Hz, C−P), 62.7 (d, $^1J_{C,P}$ = 158.4 Hz, C−P), 63.5 (C_5H_3), 63.6 (C_5H_3), 67.0 (d, $J_{C,P}$ = 14.1 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 14.5 Hz, C_5H_3), 69.8 (C_5H_5), 69.9 (C_5H_5), 80.4 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 128.8 (d, $^2J_{C,P}$ = 7.6 Hz, $C_{C_5H_3}$−O), 129.3 (d, $^2J_{C,P}$ = 7.3 Hz, $C_{C_5H_3}$O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 36.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.0963 $[M]^+$.

*O-(1R)-α-Fenchyl Bis(2-methoxyferrocenyl)phosphinate (**11d**).* *O*-(1*R*)-α-Fenchyl *O*-ferrocenyl (2-methoxyferrocenyl)phosphonate (**10d**; 168 mg, 0.27 mmol), diisopropylamine (0.08 mL, 0.55 mmol), BuLi (0.22 mL, 0.55 mmol), TMEDA (0.09 mL, 0.55 mmol), and Me_2SO_4 (0.3 mL, 3.16 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 2 × 10 cm column size) using a 98/2 (v/v) ethyl acetate/methanol mixture as the eluent. Compound **11d** was obtained as an orange oil as a mixture of isomers (Table SI2).

Yield: 171 mg (0.265 mmol, 97% based on **10d**). ^1H NMR ($CDCl_3$, δ): 0.69−1.12 (m, 11H, CH_3, CH_2), 1.39−1.46 (m, 2H, CH_2), 1.61−1.67 (m, 1H, H4), 1.71−1.78 (m, 1H, CH_2), 1.85−1.97 (m, 1H, CH_2), 3.55−4.07 (m, 9H, OCH_3, H2, C_5H_3), 4.13−4.43 (m, 14H, C_5H_5, C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.1 (CH_3), 19.32 (CH_3), 19.35 (CH_3), 21.2 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 25.8−26.9 (C5/C6), 29.3 (CH_3), 29.36 (CH_3), 29.40 (CH_3), 29.7 (CH_3), 39.3 (d, $^3J_{C,P}$ = 1.7 Hz, C3), 39.4 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 39.6 (d, $^3J_{C,P}$ = 3.3 Hz, C3), 41.1 (C7), 41.2 (C7), 41.3 (C7), 48.0 (C4), 48.1 (C4), 48.2 (C4), 49.25 (d, $^3J_{C,P}$ = 3.7 Hz, C3), 49.34 (d, $^3J_{C,P}$ = 4.8 Hz, C3), 54.3 (d, $J_{C,P}$ = 9.9 Hz, C_5H_3), 54.6 (d, $J_{C,P}$ = 9.3 Hz, C_5H_3), 54.7 (d, $J_{C,P}$ = 9.0 Hz, C_5H_3), 54.8 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 57.40 (OCH_3), 57.44 (OCH_3), 57.78 (OCH_3), 57.85 (OCH_3), 58.0 (OCH_3), 58.2 (OCH_3), 61.7 (d, $^1J_{C,P}$ = 165.7 Hz, C−P), 62.1 (d, $^1J_{C,P}$ = 159.1 Hz, C−P), 62.4 (d, $^1J_{C,P}$ = 158.6 Hz, C−P), 62.6 (d, $^1J_{C,P}$ = 160.7 Hz, C−P), 63.0 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3), 63.1 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3), 63.5 (d, $J_{C,P}$ = 12.7 Hz, C_5H_3), 63.7 (d, $J_{C,P}$ = 12.9 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 15.0 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 15.0 Hz, C_5H_3), 68.8 (d, $J_{C,P}$ = 9.7 Hz, C_5H_3), 68.8 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 69.6 (C_5H_5), 69.7 (C_5H_5), 69.8 (C_5H_5), 87.5 (d, $^2J_{C,P}$ = 7.2 Hz, C2), 87.8 (d, $^2J_{C,P}$ = 7.2 Hz, C2), 88.0 (d, $^2J_{C,P}$ = 7.0 Hz, C2), 129.0 (d, $^2J_{C,P}$ = 7.5 Hz, $C_{C_5H_3}$−O), 129.1 (d, $^2J_{C,P}$ = 7.1 Hz, $C_{C_5H_3}$O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 35.68, 35.74, 36.7, 38.0. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{39}Fe_2O_4P$ 630.1280, found 630.1222 $[M]^+$.

General Procedure for the Synthesis of Alkyldichlorophosphates 8a−d. The respective alcohols **1a−d** (1 equiv) were dissolved in 10 mL of diethyl ether and cooled to −30 °C. Dropwise addition of BuLi (1 equiv) resulted in the formation of a colorless precipitate. After it was stirred for an additional 10 min at −30 °C, the suspension was added dropwise to a solution containing $POCl_3$ (1 equiv) in 30 mL of diethyl ether at −30 °C. Stirring was continued overnight followed by filtration through a plug of Celite (min 5 cm) with diethyl ether to remove the lithium salt. After removal of all volatiles under reduced pressure, the title compounds **8a−e** were obtained as colorless oils and used without further purification.

*Cyclohexyl Dichlorophosphate (**8a**).* Cyclohexanol (**1a**; 1.8 mL, 17.1 mmol), BuLi (7.4 mL, 18.5 mmol), and $POCl_3$ (4.7 mL, 50 mmol) were reacted as described in the general procedure.

Yield: 3.67 g (16.9 mmol, >95% based on **1a**). ^1H NMR ($CDCl_3$, δ): 1.32−1.45 (m, 3H, CH_2), 1.51−1.56 (m, 1H, CH_2), 1.70−1.84 (m, 4H, CH_2), 1.98−2.06 (m, 2H, CH_2), 4.76−4.83 (m, 1H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.2 (CH_2), 24.7 (CH_2), 33.8 (d, $^3J_{C,P}$ = 4.9 Hz, C2), 84.1 (d, $^2J_{C,P}$ = 9.7 Hz, C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.7.

*(1R)-Menthyl Dichlorophosphate (**8b**).* (1*R*)-Menthol (**1b**; 5.00 g, 32,0 mmol), BuLi (13 mL, 32,5 mmol), and $POCl_3$ (9 mL, 96 mmol) were reacted by using the general procedure.

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Yield: 8.74 g (32.0 mmol, >95%, based on **1b**). ^{1}H NMR ($CDCl_3$, δ): 0.84 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3), 0.88−0.96 (m, 7H), 1.01−1.10 (m, 1H), 1.35 (q, $^3J_{H,H}$ = 11.8 Hz, 1H, H5), 1.43−1.54 (m, 2H), 1.65−1.76 (m, 2H), 2.08 (dsept, $^3J_{H,H}$ = 2.5 Hz, $^3J_{H,H}$ =7.0 Hz, 1H, CH), 2.32−2.37 (m, 1H), 4.63 (dtd, $^3J_{H,P}$ = 10.8 Hz, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 4.64 Hz, 1H, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.8 (CH_3), 20.7 (CH_3), 21.8 (CH_3), 23.0 (d, $^3J_{C,P}$ = 1.7 Hz, CH_2), 25.8 (CH), 31.7 (CH), 33.6 (CH_2), 42.2 (CH_2), 48.2 (d, $^3J_{C,P}$ = 8.2 Hz, CH_2), 86.7 (d, $^2J_{C,P}$ = 10.9 Hz, C1). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 7.1. HRMS (ESI-TOF, m/z): calcd for $C_{10}H_{19}Cl_2O_2P$ + Na 295.0392, found 295.0395 $[M + Na]^+$.

*(1R)-α-Fenchyl Dichlorophosphate (**8d**).* (1*R*)-α-Fenchol (**8d**; 4.23 g, 27.4 mmol), BuLi (12 mL, 30 mmol), and $POCl_3$ (8 mL, 85.5 mmol) were reacted as described in the general procedure.

Yield: 7.36 g (27.1 mmol, > 95%, based on **1d**). ^{1}H NMR ($CDCl_3$, δ): 0.99 (s, 3H, CH_3), 1.12−1.18 (m, 7H), 1.26−1.28 (m, 1H), 1.48−1.54 (m, 1H), 1.56−1.59 (m, 1H), 1.69−1.76 (m, 2H), 1.78−1.79 (m, 1H), 4.33 (dd, $^3J_{H,P}$ = 13.1 Hz, $J_{H,H}$ = 1.8 Hz, 1H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ):19.2 (CH_3), 21.0 (CH_3), 25.65 (C5/C6), 25.73 (C5/C6), 29.6 (CH_3), 39.8 (d, $^3J_{C,P}$ = 2.9 Hz, C3), 40.9 (C7), 47.9 (C4), 49.5 (d, $^3J_{C,P}$ = 5.9 Hz, C1), 97.0 (d, $^2J_{C,P}$ = 11.7 Hz, C2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 8.4. HRMS (ESI-TOF, m/z): calcd for $C_{10}H_{17}Cl_2O_2P$ + Na 293.0235, found 293.0252 $[M + Na]^+$.

Synthesis of (R_p)-(2-Methoxyferrocenyl)diphenylphosphane (17) and (R_p)-(2-Methoxyferrocenyl)diphenylphosphane Oxide (18). Compound **17** was prepared according to the synthesis protocol which was reported recently for the racemic mixture.[1a] Thus, an excess of Li[AlH_4] (0.6 g, 16 mmol) was treated with trimethylsilyl chloride (1.65 mL, 12.9 mmol) at −30 °C in tetrahydrofuran (20 mL). After the suspension was stirred for 5 min, phosphonate **5e** (570 mg, 1.00 mmol) was added in a single portion. The mixture was slowly heated to 50 °C until gas evaporation was no longer detectable. Afterward, the oil bath was replaced by an ice bath. Acidification was realized by dropwise addition of oxygen-free H_2SO_4 (3 mL, ω = 30%). The mixture was extracted three times with oxygen-free diethyl ether (3 × 20 mL) under an argon atmosphere. The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Phosphine **17** was dissolved in 6 mL of toluene, and iodobenzene (0.22 mL, 2.0 mmol), K_3PO_4 (425 mg, 2.0 mmol), and [Pd(dppf)Cl_2] (30 mg, 4 mol %) were added in a single portion. The reaction mixture was degassed and stirred for 18 h at 110 °C. After the mixture was cooled to ambient temperature, water (30 mL) was added in a single portion and the mixture was extracted with diethyl ether (3 × 20 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (column size 2 × 10 cm, silica) using a 7/3 (v/v) hexane/CH_2Cl_2 mixture to give **17** (R_f = 0.14) as an orange solid. HPLC measurements were performed after single recrystallization from hexane. Yield: 260 mg (0.65 mmol, 65% based on **5e**). The spectroscopic data of phosphane **17** are in agreement with those in the literature.[1a] HPLC (t): *rac*-**17**, 26.410 (48.9%), 42.110 (51.1%); (R_p)-**17**, 25.485 (>99.9%); ee = 0.99.

Crystals suitable for single-crystal X-ray analysis of phosphanoxide **18** were obtained by recrystallizing **17** from boiling hexane followed by dissolving **17** (2 mg) in 4 mL of a 95/5 (v/v) hexane/^{t}BuOMe mixture. On exposure to atmospheric conditions for 14 days a few single crystals of **18** could be obtained from this solution.

*Crystal data for **18**:* $C_{23}H_{21}FeO_2P$, M_r = 416.22, orthorhombic, $P2_12_12_1$, λ = 0.71073 Å, a = 8.3581(4) Å, b = 8.5846(4) Å, c = 27.2615(14) Å, V = 1956.04(16) Å^3, Z = 4, ρ_{calcd} = 1.413 Mg m^{-3}, μ = 0.868 mm^{-1}, T = 110.0(10) K, θ range 2.99−25.50°, 5954 reflections collected, 3481 independent reflections (R_{int} = 0.0336), *R1* = 0.0385, *wR2* = 0.0767 ($I > 2\sigma(I)$), absolute structure parameter[28] 0.012(19).

■ ASSOCIATED CONTENT

Supporting Information

Text, Tables SI1 and SI2, Figures SI1−5, and CIF files giving additional experimental and crystallographic data as well as spectroscopic details for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of **4a**,**b**,**e**, **5e**, **6d**, **9b**, **10a**,**c**,**d**, and **18** are also available from the Cambridge Crystallographic Database as file numbers CCDC 1024126 (**4a**), 1024118 (**4b**), 1024119 (**4e**), 1024120 (**5e**), 1024121 (**6d**), 1024123 (**9b**), 1024125 (**10a**), 1024122 (**10c**), 1024124 (**10d**), and 1028721 (**18**).

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Notes

The authors declare no competing financial interest.

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