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Synthesis of Ferrocene-based Phosphine Ligands via Cu-catalyzed Reductive Coupling of Ferrocenyl Ketone-derived Tosylhydrazones and *H*-phosphorus Oxides

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ABSTRACT

Ferrocene-based phosphine oxides with various substituents at phosphorous atoms were synthesized by Cu-catalyzed reductive coupling of ferrocenyl ketone-derived tosylhydrazones and *H*-phosphorus oxides. Followed by the reduction of ferrocene-based phosphine oxides, 1-substituted ferrocene-based phosphine ligand **7** and 1,1'-disubstituted ferrocene-based phosphine ligand **9** were obtained. Josiphos type ligand **8** were produced after ortho-lithiation of **7** and trapping with chlorodiphenyl phosphine or chlorodicyclohexylphosphine.

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1. Introduction

Since its discovery in 1951, ferrocene has been among the most important structural motifs in ligand architectures due to its high thermal stability, conformational rigidity and planar chirality.¹ Ferrocene-based phosphine ligands are of fundamental importance in transition metal-catalyzed organic reactions.² Achiral ferrocene phosphine such as 1,1'-bis (diphenylphosphino) ferrocene (DPPF),³ has been successfully applied in transition-metal catalyzed coupling reactions.⁴ Moreover, chiral ferrocene-based phosphine ligands have become indispensable and powerful tools for chemists in dealing with asymmetric transformations.^{2,5} Some of them, such as Josiphos⁶ N,N-dimethyl-1-[2and (diphenylphosphino)ferrocenyl]ethylamine (PPFA)⁷, have found their industrial application in the production of pharmaceuticals and agrochemicals. Selected examples of chiral and achiral ferrocene phosphine ligands are shown in Figure 1. These chiral ferrocene phosphine ligands are all prepared from N,N-dimethyl-1-ferrocenylethylamine (Ugi's amine)⁸ as a chiral precursor. Despite their wide application, synthesis of ferrocene phosphine ligands often requires sensitive reagents, tedious synthetic routes and resolution steps.9 Therefore, inexpensive and readily available starting materials, as well as short synthetic steps are most desirable in designing new ferrocene-based phosphine ligands.





Recently, *N*-tosylhydrazones which are readily prepared from carbonyl compounds have been used as a source of the safe generation of diazo compounds and carbenes.¹⁰ They have emerged as a new type of cross-coupling partner in C-C(X) bond formation including their reactions with aryl halides,¹¹ arylsulfonates,¹² alkynes,¹³ *H*-phosphonates,¹⁴ azoles,¹⁵ arylboronic acids,¹⁶ benzylic halides.^{17,18}

Inspired by our previous work, ¹⁹ in this paper we have synthesized 1-substituted and 1,1'-disubstituted ferrocene-based phosphine oxides from readily available ferrocenyl ketone/aldehyde derived tosylhydrazones and secondary phosphine oxides without using sensitive reagents. Moreover, the

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ferrocene-based phosphine oxides can be readily converted to the M corresponding ferrocene-based phosphine through reduction treatment^{20,21} and as useful ligands for transition metal complexes.

2. Results and discussion

Initially, tosylhydrazone 1a and diphenylphosphine oxide 2a were chosen as the model substrates to screen the best reaction conditions (Table 1). To our delight, CuCl was found to promote the reaction between 1a and 2a in dioxane with K_2CO_3 as base at reflux temperature for 12 h to produce diphenyl (1ferrocenylethyl) phosphine oxide 3a in 61% yield (Table 1, entry 1). 1 H, 31 P and 13 C NMR spectra of **3a** was consistent with literature reported.²² After screening several kind of Cu catalysts, CuI was found to be the most efficient compared to others (Table 1, entries 1-5). Various bases, such as K₂CO₃, Cs₂CO₃, Na₂CO₃, KOH, LiO'Bu and KO'Bu were tested. K₂CO₃ gave the highest yield of 3a (Table 1, entries 5-10). Changing the solvent under identical condition resulted in the decreased formation of 3a (Table 1, entries 11–15). When the amount of diphenylphosphine oxide was increased, 3a's yield dramatically decreased (Table 1, entry 16). This outcome was also observed when the reaction was carried out at lower reaction temperature of 90 °C (Table 1, entry 17). In the control experiment, no product 3a was detected under metal-free condition (Table 1, entry 18). Thus, the optimized condition was obtained as the following: 10 mol % of CuI, 3 equivalent of K₂CO₃, in dioxane and reflux under argon (Table 1, entry 5).

> O II Ph

catalyst, base

Table 1

Optimization of reaction conditions^a

NNHTs

Fe	2	+ H—P< — Ph	solvent	Fe	FII
1a		2a		3a	
entry	1a:2a	catalyst (mol%)	base (equiv.)	solvent	yield ^b (%)
1	1:1.2	CuCl(10%)	K ₂ CO ₃ (3)	dioxane	61
2	1:1.2	CuCl ₂ (10%)	K ₂ CO ₃ (3)	dioxane	56
3	1:1.2	CuBr(10%)	K ₂ CO ₃ (3)	dioxane	35
4	1:1.2	SIMesCuCl(10%) ^c	K ₂ CO ₃ (3)	dioxane	0
5	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	dioxane	83
6	1:1.2	CuI(10%)	Cs ₂ CO ₃ (3)	dioxane	44
7	1:1.2	CuI(10%)	Na ₂ CO ₃ (3)	dioxane	7
8	1:1.2	CuI(10%)	KOH(3)	dioxane	24
9	1:1.2	CuI(10%)	LiOtBu(3)	dioxane	20
10	1:1.2	CuI(10%)	KOtBu(3)	dioxane	0
11	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	DME	30
12	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	DMF	15
13	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	DCE	35
14	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	THF	28
15	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	toluene	31
16	1:2	CuI(10%)	K ₂ CO ₃ (3)	dioxane	19
17^d	1:1.2	CuI(10%)	K ₂ CO ₃ (3)	dioxane	56
18	1:1.2	_	K ₂ CO ₃ (3)	dioxane	0

^{*a*}Reactions were carried out with 0.25 mmol of **1a** and 0.30 mmol of **2a** in the presence of catalyst and base under argon atmosphere at reflux temperature for 12 h. ^{*b*}Yield of isolated product. ^{*c*}SIMes = 1,3-bis(2,4,6-

90°C. Table 2

Reaction of various ferrocenyl ketone-derived N-tosylhydrazones with H-phosphorus oxides and H-phosphonates a,b

trimethylphenyl)-2-imidazolidinylidene. ^dThe reaction temperature was



^{*a*} Reactions were carried out with 0.25 mmol of **1a-g** and 0.30 mmol of **2a-h** in the presence of 10 mol% of CuI and 3.0 equivalent of K_2CO_3 at reflux

With this optimized reaction condition in hand, the scope of the reaction was studied using a set of tosylhydrazones 1 and Hphosphorus oxides or H-phosphonates 2 (Table 2). Various ferrocenyl ketones or aldehyde derived tosylhydrazones were investigated. Steric hindrance of ferrocenyl ketones dramatically decreased production yields (3a-e). Electron-withdrawing group (-F) on phenyl ring of H-phosphorus oxide decreased the reaction efficiency to some extent (3u), while electron-donating groups (- CH_3 , -OCH₃) on phenyl ring of *H*-phosphorus oxides increased production yields, generating product 3t and 3v in 94%, 81% yields. Bis(3,5-dimethylphenyl)phosphine oxide reacted with ferrocenyl ketones derived tosylhydrazones to give products 3ggood 3k in moderate while to yields, bis(2.6dimethylphenyl)phosphine oxide led to low yield (3w) due to steric hindrance. Moreover, ethyl phenylphosphinate or diethyl phosphonate could also be used as substrates generating corresponding products (31-3s) in 49-84% yields. Finally, the molecular structure of 3u (Figure 2) and 3w (Figure 3) were unambiguously confirmed through X-ray crystallography.



Fig. 2. Molecular structure of **3u** with thermal ellipsoids drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1-O1 = 1.484(3), P1 - C18 = 1.797(4), P1-C11 = 1.833(4), P1 - C12 = 1.810(4), C9 -C11 = 1.494(6); C9 - C11-P1 = 109.0(3), C12-P1-C11 = 104.9(2), O1-P1-C11 = 113.98(18), C18-P1-C12 = 105.55(17), C18-P1-C11 = 109.39(18).



Fig. 3. Molecular structure of **3w** with thermal ellipsoids drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1-O1 = 1.4924(13), P1 - C19 = 1.8560(17), P1- C10 = 1.8523(17), P1 - C11 =1.8394(17), C9 -C10 = 1.517(2); C9 - C10-P1 = 107.16(12), C11-P1-C10 = 105.87(8), O1-P1-C10 = 107.61(8), C11-P1-C19 = 114.46(8).

Table 3

Reaction of various 1,1'-ferrocenyl di-ketone-derived *N*-tosylhydrazones **4a-e** with *H*-phosphorus oxides and ethyl phenylphosphinate^{*a*}



^{*a*} Reactions were carried out with 0.15 mmol of **4a-e** and 0.36 mmol of **2a-f** in the presence of 20 mol% of CuI and 6.0 equivalent of K_2CO_3 at reflux temperature under argon atmosphere for 18 h.

Single crystals suitable for X-ray diffraction measurement were obtained by slow diffusion of hexane into a concentrated dichloromethane solution of compounds. Crystals of compound 3u were twinned and contain two independent molecules of enantiomers. The ORTEP representation of the structure shows that the planes of the cyclopentadienyl rings are almost parallel to each other (tilt angles are $2.2^{\circ}(S)$ and $4.4^{\circ}(R)$ for the two independent molecules of 3u, 4.9° for 3w,). Carbon atom linked to the Cp ring is almost coplanar with the substituted Cp ring. Bulkier diphenylphosphinyl moiety is located farther away from the Cp ring. This phenyl ring is almost orthogonal to another phenyl ring, the dihedral angles between them are $74.2^{\circ}(S)$, $69.9^{\circ}(R)$ for **3u** and 83.5° for **3w**. The phosphorus oxygen distance is 1.484(3) (S) and 1.492(3) (R) for the two independent molecules of 3u and 1.492(3) in 3w, typical for a P-O double bond. The bond length of C-P in **3w** (1.839(17)-1.856(17) Å) is longer than that of the corresponding C-P bond (1.797(4)-1.833(4) Å) (*S*) and (1.794(4)-1.826(4) Å) (*R*) in **3u**, which Pis well MA explained by the increased steric hindrance of *ortho* methyl substituted phenyl groups around P1 in **3w**. The shortest distance between the corresponding atoms H18 and O1 is 242.2 pm in **3w**, which is smaller than the sum of the van der Waals radii of these elements (272 pm).²³ The bond angles around phosphorus are 107.9(2)-114.0(18)° (*S*) and 106.1(17)-114.2(16)° (*R*) for **3u** and 105.9(8)-114.5(8)° for **3w**, similar to the ones (104.8(13)-113.2(13)°) reported for [1-(1-naphthalenyl)ethyl] diphenyl-phosphine oxide.²⁴

Inspired by these results, we delightfully found that product 5a was generated in 65% yield through the reaction of 1,1'ferrocenyl di-ketone-derived *N*-tosylhydrazone 4a with diphenylphosphine oxide by extending reaction time. Interestingly, byproduct 6 were produced at the same time and 6a was isolated in 31% yield (Table 3). The reaction displayed the similar steric and electron effect with the reductive coupling of ferrocenyl ketone derived tosylhydrazones 1 with *H*-phosphorus oxides and ethyl phenylphosphinate 2 (Table 3).

Furthermore, 1-substituted ferrocenyl phosphines ligand 7 and 1,1'-bis-substituted ferrocenyl phosphines ligand 9 were produced in good yield by reduction of (P=O) bond. Josiphos type ligand 8 were synthesized in moderate yield through *ortho*-lithiation of Cp ring of 7 followed by reaction with Ph₂PCl or Cy₂PCl (Scheme 1).



Scheme 1. Synthesis of 1-substituted, 1,2- disubstituted and 1,1'-disubstituted ferrocenyl phosphine ligands.

For further application of this approach to chiral ferrocenyl phosphine ligands, we examined various types of chiral ligands to induce enantioselectivity (Table 4). Tridentate chiral oxazoline pyridine ligand L1, gave 71% yield of racemic 3a (entry 1). No improvement was observed with bidentate oxazoline ligand L2 and spiral bidentate oxazoline ligand L3 (entry 2 and entry 3). Monodentate phosphoramidite ligand like TADDOL-derived phosphoamidite L4 was also examined and showed no enantioselectivity (entry 4). Although, the enantioselectivity increased a little to 45:55 er with a yield of 78% when axial chiral diphosphine (S)-BINAP (L5) was added (entry 5). Other axial chiral diphosphine like synphos (L6) did not afford better result (entry 6). Planar chiral diphosphine Josiphos (L7) and Pstereogenic diphosphine (L8) had low catalytic and enantioselective activity (entry 7 and entry 8). The reason for low enantioselectivity was probably the high reaction temperature, since the diazo compounds were generated in situ from tosylhydrazone in the presence of base and thermal condition.

Table 4

Asymmetric Cu-catalyzed reductive coupling reaction^a



NUSCR	IPT l 1	71	50:50	
2	L2	76	50:50	
3	L3	32	50:50	
4	L4	22	50:50	
5	L5	75	45:55	
6	L6	78	46:54	
7	L7	trace	_	
8	L8	24	50:50	





3. Conclusions

In summary, Cu-catalyzed reductive coupling of ferrocenyl ketone tosylhydrazones and *H*-phosphorus oxides or *H*-phosphonates was shown to be a practical and efficient method for the synthesis of ferrocene-based phosphine ligands in moderate to good yields. 1-substituted, 1,2- and 1,1'-bis-substituted ferrocenyl phosphine ligands could be obtained from this procedure, which is of operational simplicity and functional group tolerance. Research on synthesis of chiral ferrocenyl phosphine oxides through enantioselective Cu-catalyzed reductive coupling reaction is under way.

4. Experimental section

4.1. General Experimental Methods:

All reactions were carried out in oven dried glassware under argon unless otherwise specified. All NMR experiments were carried out on a Bruker AVANCE 500MHz nuclear magnetic resonance spectrometer using CDCl₃ or DMSO-*d*₆ as the solvent with tetramethylsilane as the internal standard (³¹P NMR with 85% H₃PO₄ as the external standard). Chemical shift values (δ) were given in parts per million. HRMS data were obtained on a Bruker QTOF mass mass spectrometer. The melting points were determined on an X-4 binocular microscope melting point apparatus and uncorrected. HPLC analyses were performed on a LC-20A instrument using Chiralpak® AD-H columns (0.46cm Diameter x 25cm Length). THF, DCE, dioxane, toluene, DMF and DME were dried according to literature techniques. 0.30 mmol *H*-phosphorus oxide or *H*-phosphonate, 0.25 mmol *N*-Tosylhydrazone, 0.025mmol of CuI and 0.75 mmol K_2CO_3 were charged into 25 mL oven-dried flasks, and backfilled with Argon three times. 3 mL freshly distilled 1,4-dioxane was then injected into the flask, which were heated up to reflux for 12 h. The solvent was eliminated under vacuum pump and ammonia water and dichloromethane was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over Na₂SO₄. The concentrated residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (1:3) as eluent to get the product.

4.2.1. Diphenyl(1-ferrocenylethyl)phosphine oxide (3a).²² Yellow solid, 85.5 mg (83% yield); mp 155 – 156° C; Rf (petroleum ether/ethyl acetate 1:3) = 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.83 - 7.71 (m, 2H, P(O)Ph₂), 7.58 - 7.39 (m, 6H, P(O)Ph₂), 7.29 -7.38 (m, 2H, P(O)Ph₂), 4.18 – 4.08 (m, 6H, Cp and Cp'), 4.08 – 4.05 (m, 1H, Cp), 3.95 - 3.87 (m, 1H, Cp), 3.54 - 3.45 (m, 1H,*Cp*), 3.45 - 3.32 (m, 1H, CHCH₃), 1.60 (dd, $J_{\text{H-P}} = 15.8$, $J_{\text{H-H}} = 7.2$ Hz, 3H, CHCH₃); ${}^{13}\text{C}{}^{1}\text{H}$ NMR (126 MHz, CDCl₃) δ 131.94 (d, $J_{C-P} = 93.7$ Hz, P(O)Ph₂), 131.82 (d, $J_{C-P} = 8.6$ Hz, P(O)Ph₂), 131.50 (d, $J_{C-P} = 2.6$ Hz, P(O) Ph_2), 131.35 (d, $J_{C-P} = 2.8$ Hz, $P(O)Ph_2$), 131.29 (d, $J_{C-P} = 8.6$ Hz, $P(O)Ph_2$), 130.48 (95.6 Hz, $P(O)Ph_2$), 128.33 (d, $J_{C-P} = 11.2$ Hz, $P(O)Ph_2$), 127.79 (d, $J_{C-P} = 11.4$ Hz, P(O) Ph_2), 85.50 (s, Cp), 69.29 (d, $J_{C-P} = 1.8$ Hz, Cp), 68.39 (s, Cp'), 67.53 (s, Cp), 67.38 (d, $J_{C-P} = 1.3$ Hz, *Cp*), 67.17 (s, *Cp*), 35.61 (d, $J_{C-P} = 66.4$ Hz, *C*HCH₃), 13.84 (d, $J_{C-P} = 1.5$ Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.86.

4.2.2. Diphenyl(1-ferrocenylpropyl)phosphine oxide (3b). Yellow solid, 57.4 mg (54% yield); mp 166 – 167°C; R_f (petroleum ether/ethyl acetate 1:3) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.86 -7.70 (m, 2H, P(O)Ph₂), 7.55 - 7.36(m, 6H, P(O)Ph₂), 7.34 -7.25 (m, 2H, P(O)Ph₂), 4.12 – 4.08 (m, 5H, Cp'), 4.08 – 4.03 (m, 2H, Cp), 3.94 – 3.79 (m, 1H, Cp), 3.56 – 3.38 (m, 1H, Cp), 3.22 - 3.03 (m, 1H, CHCH₂CH₃), 2.29 - 2.04 (m, 2H, CHCH₂CH₃), 1.15 (t, $J_{\text{H-H}} = 7.4$ Hz, 3H, CHCH₂CH₃); ¹³C{¹H} NMR (126) MHz, CDCl₃) δ 132.87 (d, J_{C-P} = 92.9 Hz, P(O)Ph₂), 131.88 (d, $J_{C-P} = 8.4$ Hz, P(O)Ph₂), 131.36 (d, $J_{C-P} = 2.1$ Hz, P(O)Ph₂), 131.28 (d, $J_{C-P} = 8.6$ Hz, P(O)Ph₂), 131.16 (d, $J_{C-P} = 1.8$ Hz, $P(O)Ph_2$, 130.41 (s, $P(O)Ph_2$), 128.19 (d, $J_{C-P} = 11.1$ Hz, $P(O)Ph_2$), 127.67 (d, $J_{C-P} = 11.2$ Hz, $P(O)Ph_2$), 86.32 (s, Cp), 69.43 (s, Cp), 68.46 (s, Cp'), 67.93 (s, Cp), 67.49 (s, Cp), 66.81 (s, Cp), 42.48 (d, $J_{C-P} = 65.2$ Hz, CHCH₂CH₃), 23.42 (s, CHCH₂CH₃), 14.69 (d, $J_{C-P} = 4.7$ Hz, CHCH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.76. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₅H₂₅FeOP 428.0992; Found: 428.0997.

4.2.3. Diphenyl(1-ferrocenylbutyl)phosphine oxide (**3c**). Yellow solid, 78.3 mg (71% yield); mp 161-162°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.71 (m, 2H, P(O)Ph₂), 7.54 – 7.36 (m, 6H, P(O)Ph₂), 7.35 – 7.28 (m, 2H, P(O)Ph₂), 4.10 – 4.07 (m, 5H, *Cp*'), 4.07 – 4.04 (m, 2H, *Cp*), 3.91 – 3.84 (m, 1H, *Cp*), 3.49 – 3.42 (m, 1H, *Cp*), 3.26 – 3.16 (m, 1H, *CHCH*₂CH₂CH₃), 2.21 – 1.92 (m, 2H, CHCH₂CH₂CH₃), 1.70 – 1.46 (m, 2H, CHCH₂CH₂CH₃), 0.92 (t, $J_{H-H} = 7.3$ Hz, 3H, CHCH₂CH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 132.84 (d, $J_{C-P} = 93.2$ Hz, P(O)Ph₂), 131.93 (d, $J_{C-P} = 8.3$ Hz, P(O)Ph₂), 131.19 (d, $J_{C-P} = 2.0$ Hz, P(O)Ph₂), 131.30 (d, $J_{C-P} = 8.6$ Hz, P(O)Ph₂), 131.19 (d, $J_{C-P} = 2.0$ Hz, P(O)Ph₂), 130.76 (d, $J_{C-P} = 95.8$ Hz, P(O)Ph₂), 128.20 (d, $J_{C-P} = 11.2$ Hz, P(O)Ph₂), 127.69 (d, $J_{C-P} = 11.2$ Hz, P(O)Ph₂), 86.54 (s, *Cp*),

69.46 (s, *Cp*), 68.49 (s, *Cp*'), 67.98 (s, *Cp*), 67.50 (s, *Cp*), 66.84 (s, *Cp*), 40.80 (d, $J_{C-P} = 65.4$ Hz, CHCH₂CH₂CH₂CH₃), 32.30 (s, CHCH₂CH₂CH₂CH₃), 22.92 (d, $J_{C-P} = 4.6$ Hz, CHCH₂CH₂CH₂CH₃), 14.46 (s, CHCH₂CH₂CH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.94. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₆H₂₇FeOP 442.1149; Found: 442.1142.

4.2.4. (2-Methyl-1-ferrocenylpropyl)diphenylphosphine oxide (3d). Yellow solid, 78.7 mg (71% yield); mp $211 - 212^{\circ}$ C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, $CDCl_3$) δ 7.80 - 7.67 (m, 2H, P(O)Ph₂), 7.59 - 7.51 (m, 2H, $P(O)Ph_2$, 7.51 – 7.37 (m, 4H, $P(O)Ph_2$), 7.37 – 7.29 (m, 2H, P(O)Ph₂), 4.15 – 4.11 (m, 1H, Cp), 4.11 – 4.08 (m, 1H, Cp), 4.05 -3.91 (m, 6H, Cp' and Cp), 3.65 - 3.54 (m, 1H, Cp), 3.37 (d, J_{H-} P = 15.0 Hz, 1H, CHCH(CH₃)₂), 2.75 - 2.56 (m, 1H, CHC*H*(CH₃)₂), 1.27 (d, $J_{\text{H-P}} = 7.0$ Hz, 3H, CHCH(CH₃)₂), 1.10 (d, $J_{\text{H-P}} = 7.0$ Hz, 3H, CHCH(CH₃)₂); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 134.78 (d, J_{C-P} = 94.1 Hz, P(O)Ph₂), 132.24 (d, J_{C-P} = 93.5 Hz, $P(O)Ph_2$), 132.04 (d, $J_{CP} = 8.2$ Hz, $P(O)Ph_2$), 131.17 – 130.93 (m, P(O)P h_2), 128.24 (d, $J_{C-P} = 11.2$ Hz, P(O)P h_2), 127.77 (d, $J_{C-P} = 11.1$ Hz, P(O)P h_2), 85.09 (s, Cp), 70.12 (s, Cp), 68.75 (d, $J_{C-P} = 4.4$ Hz, Cp), 68.64 (s, Cp'), 67.34 (s, Cp'), 66.98 (s, *Cp*'), 46.22 (d, $J_{C-P} = 66.6$ Hz, *C*HCH(CH₃)₂), 32.13 (s, CHCH(CH₃)₂), 23.00 (s, CHCH(CH₃)₂), 21.45 (d, $J_{C-P} = 9.8$ Hz, CHCH(CH_{3})₂); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 32.30. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for C₂₆H₂₇FeOP 442.1149; Found: 442.1135.

4.2.5. (2,2-Dimethyl-1-ferrocenylpropyl)diphenylphosphine oxide (3e). orange solid, 30.4 mg (27% yield); mp217 – 218°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.76 (m, 2H, P(O)Ph₂), 7.49 – 7.32 (m, 5H, $P(O)Ph_2$, 7.24 – 7.17 (m, 1H, $P(O)Ph_2$), 7.16 – 7.10 (m, 2H, $P(O)Ph_2$, 4.28 – 4.16 (m, 1H, Cp), 4.05 – 4.00 (m, 5H, Cp'), 3.99 – 3.96 (m, 1H, Cp), 3.82 – 3.73 (m, 1H, Cp), 3.67 – 3.57 (m, 1H, *Cp*), 3.04 (d, $J_{\text{H-P}} = 9.8$ Hz, 1H, CHC(CH₃)₃), 1.33 (s, 9H, CHC(CH₃)₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.30 (d, $J_{\text{C-P}}$ = 88.8 Hz, $P(O)Ph_2$), 134.54 (d, J_{C-P} = 98.0 Hz, $P(O)Ph_2$), 130.98 (d, $J_{C-P} = 8.3$ Hz, P(O)Ph₂), 130.70 (d, $J_{C-P} = 2.7$ Hz, P(O)Ph₂), 130.57 (d, $J_{C-P} = 8.5$ Hz, P(O)Ph₂), 129.96 (d, $J_{C-P} = 2.6$ Hz, $P(O)Ph_2$), 128.30 (d, $J_{C-P} = 11.0$ Hz, $P(O)Ph_2$), 127.19 (d, $J_{C-P} =$ 11.2 Hz, P(O)Ph₂), 86.47 (s, Cp), 72.41 (d, $J_{C-P} = 3.3$ Hz, Cp), 71.06 (d, $J_{C-P} = 5.7$ Hz, Cp), 69.51 (s, Cp'), 67.64 (s, Cp), 65.65 (s, *Cp*), 47.99 (d, $J_{C-P} = 66.8$ Hz, *C*HC(CH₃)₃), 35.96 (d, $J_{C-P} = 1.3$ Hz, CHC(CH₃)₃), 30.65 (d, $J_{C-P} = 6.3$ Hz CHC(*C*H₃)₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 31.64; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₇H₂₉FeOP 456.1305; Found: 456.1302.

4.2.6. (*Ferrocenylmethyl*)*diphenylphosphine oxide* (**3***f*).²⁵ Yellow solid, 76.0 mg (76% yield); mp 198 – 199°C; R_f (petroleum ether/ethanol100:1) = 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.72 – 7.61 (m, 4H, P(O)*Ph*₂), 7.54 – 7.47 (m, 2H, P(O)*Ph*₂), 7.47 – 7.38 (m, 4H, P(O)*Ph*₂), 4.14 – 4.04 (m, 5H, *Cp*'), 4.03 – 3.95 (m, 4H, *Cp*), 3.42 (d, *J*_{H-P} = 12.7 Hz, 2H, CH₂P(O)Ph₂); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 132.29 (d, *J*_{C-P} = 97.8 Hz, P(O)*Ph*₂), 131.67 (d, *J*_{C-P} = 2.7 Hz, P(O)*Ph*₂), 131.18 (d, *J*_{C-P} = 9.2 Hz, P(O)*Ph*₂), 128.34 (d, *J*_{C-P} = 11.6 Hz, P(O)*Ph*₂), 77.67 (d, *J*_{C-P} = 2.6 Hz, *Cp*), 69.75 (d, *J*_{C-P} = 67.4 Hz, CH₂P(O)Ph₂); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 28.71.

4.2.7. Bis(3,5-dimethylphenyl)(1-ferrocenylethyl)phosphine oxide (3g). Yellow solid, 107.4 mg (91% yield); mp 181 – 182°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.30 (m, 2H, P(O)Ph₂), 7.20 – 6.99 (m, 4H, P(O)Ph₂), 4.22 – 4.40 (m, 7H, *Cp*' and *Cp*), 3.93 (m, 1H, *Cp*), 3.52 (m, 1H, *Cp*), 3.39 – 3.22 (m, 1H, CHCH₃), 2.35 (s, 6H, Ph-CH₃), 1.57 (dd, J_{H-P} = 15.2, J_{H-H} = 6.2 Hz,

3H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.90 (d, J_{C-P} = 11.7 Hz, P(O) Ph_2), 137.29 (d, J_{C-P} = 12.0 Hz, P(O) Ph_2), 133.15 (d, J_{C-P} = 1.9 Hz, P(O) Ph_2), 132.95 (d, J_{C-P} = 2.2 Hz, P(O) Ph_2), 131.69 (d, J_{C-P} = 92.8 Hz, P(O) Ph_2), 130.40 (d, J_{C-P} = 95.2 Hz, P(O) Ph_2), 129.37 (d, J_{C-P} = 8.6 Hz, P(O) Ph_2), 128.85 (d, J_{C-P} = 8.5 Hz, P(O) Ph_2), 85.93 (s, *Cp*), 69.79 (s, *Cp*), 69.48 (s, *Cp*), 68.37 (s, *Cp*), 67.50 (s, *Cp*), 67.00 (s, *Cp*), 35.38 (d, J_{C-P} = 65.9 Hz, CHCH₃), 21.26 (s, Ph-CH₃), 21.12 (s, Ph-CH₃), 13.93 (s, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 34.39; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₈H₃₁FeOP 470.1462; Found: 470.1460.

Bis(3,5-dimethylphenyl)(1-ferrocenylpropyl)phosphine 4.2.8. oxide (3h). Yellow solid, 71.5 mg (59% yield); mp 134 – 135°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.42 - 7.32 (m, 2H, P(O)Ph₂), 7.15 - 6.98 (m, 4H, $P(O)Ph_2$, 4.14 – 4.02 (m, 7H, Cp' and Cp), 3.90 (m, 1H, Cp), 3.50 (m, 1H, Cp), 3.16 – 2.99 (m, 1H, CHCH₂CH₃), 2.34 (s, 6H, Ph-CH₃), 2.24 (s, 6H, Ph-CH₃), 2.22 – 2.05 (m, 2H, CHCH₂CH₃), 1.14 (t, $J_{\text{H-H}} = 7.2$ Hz, 3H, CHCH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.71 (d, J_{C-P} = 11.8 Hz, P(O)Ph₂), 137.12 (d, $J_{C-P} = 11.9$ Hz, P(O)Ph₂), 133.03 (d, $J_{C-P} = 2.2$ Hz, P(O)Ph₂), 132.79 (d, $J_{C-P} = 2.4$ Hz, P(O)Ph₂), 132.04 (s, P(O)Ph₂), 130.40 (d, $J_{C-P} = 94.8$ Hz, P(O)*Ph*₂), 129.49 (d, $J_{C-P} = 8.5$ Hz, P(O)*Ph*₂), 128.91 (d, $J_{C-P} = 8.6$ Hz, P(O)Ph₂), 86.55 (s, Cp), 69.60 (s, Cp), 68.40 (s, Cp'), 68.00 (s, Cp), 67.37 (s, Cp), 66.64 (s, Cp), 42.24 (d, $J_{C-P} = 64.9$ Hz, CHCH₂CH₃), 23.35 (s, CHCH₂CH₃), 21.23 (s, Ph-CH₃), 21.08 (s, 6H, Ph-CH₃), 14.77 (d, J_{C-P} = 5.0 Hz, CHCH₂*C*H₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 34.67; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for C₂₉H₃₃FeOP 484.1618; Found: 484.1613.

4.2.9. Bis(3,5-dimethylphenyl)(1-ferrocenylbutyl)phosphine oxide (3*i*). Yellow oil, 97.8 mg (79% yield); mp156 – 157° C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.39 - 7.32 (m, 2H, P(O)Ph₂), 7.13 - 6.99 (m, 4H, P(O)Ph₂), 4.10 – 4.06 (m, 7H, Cp' and Cp), 3.94 – 3.83 (m, 1H, *Cp*), 3.52 – 3.44 (m, 1H, *Cp*), 3.21 – 3.08 (m, 1H, CHCH₂CH₂CH₃), 2.33 (s, 6H, Ph-CH₃), 2.23 (s, 6H, Ph-CH₃), 2.17 - 1.92 (m, 2H, CHCH₂CH₂CH₃), 1.69 - 1.44 (m, 2H, CHCH₂CH₂CH₃), 0.92 (t, $J_{H-H} = 7.3$ Hz, 3H, CHCH₂CH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.70 (d, $J_{C-P} = 11.8$ Hz, $P(O)Ph_2$), 137.13 (d, $J_{C-P} = 11.9$ Hz, $P(O)Ph_2$), 133.02 (d, $J_{C-P} =$ 2.5 Hz, $P(O)Ph_2$), 132.78 (d, $J_{C-P} = 2.5$ Hz, $P(O)Ph_2$), 132.53 (d, $J_{C-P} = 92.4$ Hz, P(O)Ph₂), 130.56 (d, $J_{C-P} = 94.7$ Hz, P(O)Ph₂), 129.52 (d, $J_{C-P} = 8.5$ Hz, P(O)Ph₂), 128.90 (d, $J_{C-P} = 8.6$ Hz, P(O)Ph₂), 86.86 (s, Cp), 69.62 (s, Cp), 68.42 (s, Cp'), 68.04 (s, *Cp*), 67.39 (s, *Cp*), 66.63 (s, *Cp*), 40.53 (d, $J_{C-P} = 64.9$ Hz, CHCH₂CH₂CH₃), 32.23 (s, CHCH₂CH₂CH₃), 22.92 (d, $J_{C-P} = 4.9$ Hz, CHCH₂CH₂CH₃), 21.24 (s, Ph-CH₃), 21.09 (s, Ph-CH₃), 14.43 (s, CHCH₂CH₂CH₃); ${}^{31}P{}^{1}H$ NMR (202 MHz, CDCl₃) δ 34.48; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{35}FeOP$ 498.1775; Found: 498.1770.

4.2.10. Bis (3,5-dimethylphenyl)(2-methyl-1-ferrocenylpropyl) phosphine oxide (**3***j*). Yellow oil, 99.6 mg (80% yield); mp 169-170°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.29 (m, 2H, P(O)Ph₂), 7.23 – 7.13 (m, 2H, P(O)Ph₂), 7.13 – 7.06 (m, 1H, P(O)Ph₂), 7.06 – 6.99 (m, 1H, P(O)Ph₂), 4.14 (m, 1H, *Cp*), 4.11 (m, 1H, *Cp*), 4.01 – 3.97 (m, 1H, *Cp*), 3.97 – 3.92 (m, 5H, *Cp*'), 3.72 (m, 1H, *Cp*), 3.39 – 3.24 (m, 1H, CHCH(CH₃)₂), 2.70 – 2.51 (m, 1H, CHCH(CH₃)₂), 2.33 (s, 6H, Ph-CH₃), 2.26 (s, 6H, Ph-CH₃), 1.21 (d, *J*_{H+H} = 7.0 Hz, 3H, CHCH(CH₃)₂), 1.10 (d, *J*_{H+H} = 7.0 Hz, 3H, CHCH(CH₃)₂); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.77 (d, *J*_{C-P} = 11.8 Hz, P(O)Ph₂), 137.23 (d, *J*_{C-P} = 11.8 Hz, P(O)Ph₂), 132.80 (d, *J*_{C-P} = 2.6 Hz, P(O)Ph₂), 132.67 (d, *J*_{C-P} = 2.7 Hz, P(O)Ph₂), 132.34 (d, *J*_{C-P} =

92.9 Hz, P(O)*Ph*₂), 129.55 (d, $J_{C-P} = 8.3$ Hz, P(O)*Ph*₂), 128.65 (d, $J_{C-P} = 8.6$ Hz, P(O)*Ph*₂), 85.16 (s, *Cp*), 70.43 (d, $J_{C-P} = 1.9$ Hz, *Cp*), 68.77 (d, $J_{C-P} = 5.1$ Hz, *Cp*), 68.59 (s, *Cp*'), 67.12 (s, *Cp*), 66.80 (s, *Cp*), 45.77 (d, $J_{C-P} = 66.6$ Hz, CHCH(CH₃)₂), 31.79 (s, CHCH(CH₃)₂), 22.54 (s, CHCH(CH₃)₂), 21.77 (d, $J_{C-P} = 10.3$ Hz, CHCH(*C*H₃)₂), 21.30 (s, Ph- CH₃), 21.15 (s, Ph-CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.02; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₃₀H₃₅FeOP 498.1775; Found: 498.1759.

4.2.11. (2,2-Dimethyl-1-ferrocenylpropyl)bis(3,5-dimethylphenyl) phosphine oxide (3k). Yellow oil, 75.8 mg (59% yield); mp 213 -214°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.46 - 7.36 (m, 2H, P(O)Ph₂), 7.07 - 7.00 (m, 1H, $P(O)Ph_2$), 6.98 – 6.89 (m, 2H, $P(O)Ph_2$), 6.84 – 6.77 (m, 1H, P(O)Ph₂), 4.24 – 4.15 (m, 1H, Cp), 4.07 – 4.00 (m, 5H, Cp'), 4.00 - 3.95 (m, 1H, Cp), 3.82 - 3.74 (m, 1H, Cp), 3.66 - 3.57 (m, 1H, Cp), 2.98 (d, $J_{\text{H-P}} = 10.0$ Hz, 1H, CHC(CH₃)₃), 2.32 (s, 6H, Ph-CH₃), 2.16 (s, 6H, Ph-CH₃), 1.33 (s, 9H, CHC(CH₃)₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.73 (d, $J_{C-P} = 11.6$ Hz, P(O) Ph_2), 136.95 (d, $J_{C-P} = 88.4$ Hz, P(O)Ph₂), 136.43 (d, $J_{C-P} = 11.7$ Hz, $P(O)Ph_2$), 134.00 (d, $J_{C-P} = 97.0$ Hz, $P(O)Ph_2$), 132.37 (s, $P(O)Ph_2$), 131.53 (s, $P(O)Ph_2$), 128.68 (d, $J_{C-P} = 8.2$ Hz, $P(O)Ph_2$), 128.16 (d, $J_{C-P} = 8.4$ Hz, P(O)P h_2), 86.64 (s, Cp), 72.41 (d, $J_{C-P} =$ 2.5 Hz, Cp), 71.08 (d, J = 5.4 Hz, Cp), 69.38 (s, Cp'), 67.31 (s, *Cp*), 65.34 (s, *Cp*), 48.00 (d, $J_{C-P} = 66.1$ Hz, *C*HC(CH₃)₃), 35.85 (s, CHC(CH₃)₃), 30.70 (d, $J_{C-P} = 6.0$ Hz, CHC(CH₃)₃), 21.30 (s, Ph-CH₃), 21.15 (s, Ph-CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 32.44; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{31}H_{37}FeOP$ 512.1931; Found: 512.1919.

4.2.12. Ethyl phenyl(1-ferrocenylethyl)phosphinate (31). brown oil, 79.9 mg (84% yield); R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.67 – 7.17 (m, 5H, Ph), 4.27 - 3.98 (m, 9H, Cp' and Cp), 3.98 - 3.71 (m, 2H, OCH₂CH₃), 3.17 - 2.76 (m, 1H, CHCH₃), 1.65 - 1.37 (m, 3H, CHCH₃), 1.32 -1.21 (m, 3H, OCH₂CH₃); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 132.61 (d, $J_{C-P} = 9.0$ Hz, Ph), 132.27 (d, $J_{C-P} = 9.1$ Hz, Ph), 131.79 (d, $J_{C-P} = 2.5$ Hz, Ph), 129.24 (d, $J_{C-P} = 121.0$ Hz, Ph), 127.87 (d, $J_{C-P} = 12.0$ Hz, Ph), 127.74 (d, $J_{C-P} = 12.2$ Hz, Ph), 85.54 (s, Cp), 85.42 (s, Cp), 69.69 (s, Cp), 69.35 (s, Cp), 68.30 (m, *Cp*'), 67.45 (s, *Cp*), 67.29 (d, $J_{C-P} = 1.5$ Hz, *Cp*), 67.06 (s, *Cp*), 66.64 (s, *Cp*), 66.51 (s, *Cp*), 60.64 (d, $J_{C-P} = 6.8$ Hz, OCH₂CH₃), 35.40 (m, CHCH₃), 35.27 (d, J_{C-P} = 95.3 Hz), 16.33 (d, $J_{C-P} = 6.2$ Hz, OCH₂CH₃), 13.61 (s, CHCH₃), 13.05 (s, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 43.47, 42.98; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{23}FeO_2P$ 382.0785; Found: 382.0781.

4.2.13. Ethyl phenyl(1-ferrocenylpropyl)phosphinate (3m). brown oil, 44.4 mg (45% yield); Rf (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.62 – 7.28 (m, 5H, Ph), 4.61 – 3.40 (overlapped signals, m, 11H, Cp', Cp, OCH₂CH₃), 2.85 - 2.60 (m, 1H, CHCH₂CH₃), 2.30 - 1.81 (m, 2H, CHCH₂CH₃), 1.47 – 1.05 (overlapped signals, m, 6H, CHCH₂CH₃, OCH₂CH₃); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 132.75 (d, $J_{C-P} = 9.1$ Hz, Ph), 132.38 (d, $J_{C-P} = 9.1$ Hz, Ph), 131.77 (s, Ph), 130.55 (s, Ph), 129.59 (s, Ph), 128.57 (s, Ph), 127.90 (d, $J_{C-P} = 12.0$ Hz, Ph), 127.75 (d, $J_{C-P} = 12.0$ Hz, Ph), 86.39 (s, *Cp*), 86.23 (s, *Cp*), 70.00 (d, $J_{C-P} = 1.5$ Hz, *Cp*), 69.65 (d, $J_{C-P} = 1.7$ Hz, Cp), 69.26 (s, Cp), 68.45 (d, $J_{C-P} = 1.4$ Hz, Cp'), 67.44 (s, *Cp*), 67.31 (d, $J_{C-P} = 2.1$ Hz, *Cp*), 67.25 (s, *Cp*), 67.08 (s, *Cp*), 67.02 (s, *Cp*), 60.65 (d, $J_{C-P} = 6.9$ Hz, OCH₂CH₃), 60.53 (d, $J_{C-P} = 6.9$ Hz, OCH₂CH₃), 42.67 (d, $J_{C-P} = 93.3$ Hz, CHCH₂CH₃), 42.25 (d, $J_{C-P} = 93.3$ Hz, CHCH₂CH₃), 23.39 (s, CHCH₂CH₃), 22.83 (s, CHCH₂CH₃), 16.40 (d, $J_{C-P} = 6.3$ Hz, OCH₂CH₃), 14.33 (d, $J_{C-P} = 3.3$ Hz, CHCH₂CH₃), 14.25 (d, $J_{C-P} = 4.2$ Hz, CHCH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 43.75, 43.26;

HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{21}H_{25}FeO_2P$ 396.0942; M/CHC(CH₃)₃), 30.35 (s, CHC(CFound: 396.0924. ³¹P{¹H} NMR (202 MHz, CDC

4.2.14. Ethyl phenyl(1-ferrocenylbutyl)phosphinate (3n). brown oil, 74.4 mg (73% yield); R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.55 – 7.23 (m, 5H, *Ph*), 4.18 - 3.68 (m, 11H, overlapped signals, m, 11H, Cp', Cp, OCH₂CH₃), 2.95 - 2.64 (m, 1H, CHCH₂CH₂CH₃), 2.05 - 1.87 (m, 2H, CHCH₂CH₂CH₃), 1.81 - 1.20 (m, 2H, CHCH₂CH₂CH₃), 1.33 -1.21 (m, 3H, OCH₂CH₃), 1.09 - 0.88 (m, 3H, CHCH₂CH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 132.68 (d, $J_{C-P} = 9.0$ Hz, *Ph*), 132.31 (d, $J_{C-P} = 9.1$ Hz, Ph), 131.71 (d, $J_{C-P} = 2.4$ Hz, Ph), 130.00 (d, $J_{C-P} = 120.1$ Hz, Ph), 128.99 (d, $J_{C-P} = 120.1$ Hz, Ph), 127.85 (d, $J_{C-P} = 12.0$ Hz, Ph), 127.70 (d, $J_{C-P} = 12.0$ Hz, Ph), 86.46 (s, *Cp*), 86.35 (s, *Cp*), 69.95 (d, $J_{C-P} = 1.9$ Hz, *Cp*), 69.62 (d, $J_{C-P} = 1.6$ Hz, Cp), 69.24 (s, Cp), 68.41 (s, Cp'), 67.43 (d, $J_{C-P} =$ 1.7 Hz, *Cp*), 67.39 (s, *Cp*), 67.27 (d, $J_{C-P} = 2.1$ Hz, *Cp*), 67.21 (s, Cp), 67.02 (s, Cp), 66.96 (s, Cp), 60.61 (d, $J_{C-P} = 7.0$ Hz, OCH_2CH_3), 60.48 (d, $J_{C-P} = 7.0$ Hz, OCH_2CH_3), 40.64 (d, $J_{C-P} =$ 93.2 Hz, CHCH₂CH₂CH₃), 40.17 (d, $J_{C-P} = 93.9$ Hz, CHCH₂CH₂CH₃), 32.22 (s, CHCH₂CH₂CH₃), 31.61 (s, $CHCH_2CH_2CH_3$), 22.39 (d, $J_{C-P} = 4.1$ Hz, $CHCH_2CH_2CH_3$), 16.35 (d, $J_{C-P} = 6.2$ Hz, OCH₂CH₃), 14.40 (d, $J_{C-P} = 11.0$ Hz, CHCH₂CH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 43.75, 43.23; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₂H₂₇FeO₂P 410.1098; Found: 410.1085.

4.2.15. Ethyl (2-methyl-1-ferrocenylpropyl)(phenyl)phosphinate (30). brown oil, 50.0 mg (49% yield); R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.72 – 7.62 (m, 1H, Ph), 7.55 – 7.38 (m, 3H, Ph), 7.34 – 7.27 (m, 1H, Ph), 4.33 – 3.92 (m, 10H, Cp' and Cp overlapped with OCH_2CH_3), 3.87 – 3.57 (m, 1H, OCH₂CH₃), 3.07 - 2.80 (m, 1H, CHCH(CH₃)₂), 2.77 - 2.18 (m, 1H, CHCH(CH₃)₂), 1.37 - 0.86 (m, 9H, CHCH(CH_3)₂ and OCH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 132.92 (d, J_{C-P} = 9.3 Hz, Ph), 132.31 (d, J_{C-P} = 9.2 Hz, Ph), 131.74 (d, $J_{C-P} = 2.6$ Hz, Ph), 131.59 (d, $J_{C-P} = 2.6$ Hz, Ph), 130.98 (d, $J_{C-P} = 90.1$ Hz, Ph), 128.18 (d, $J_{C-P} = 12.0$ Hz, Ph), 127.76 (d, $J_{C-P} = 11.9$ Hz, Ph), 86.02 (s, Cp), 84.10 (s, Cp), 70.76 (s, *Cp*), 70.32 (s, *Cp*), 68.87 (s, *Cp*'), 68.61 (s, *Cp*'), 67.88 (d, *J*_{C-P} = 3.9 Hz, Cp), 67.47 (s, Cp), 67.10 (s, Cp), 67.07 (s, Cp), 66.94 (s, *Cp*), 60.39 (d, $J_{C-P} = 6.7$ Hz, OCH₂CH₃), 59.99 (d, $J_{C-P} = 6.8$ Hz, OCH₂CH₃), 46.68 (d, $J_{C-P} = 94.3$ Hz, CHCH(CH₃)₂), 46.11 (d, $J_{C-P} = 96.7 \text{ Hz}, CHCH(CH_3)_2), 31.57 (s, CHCH(CH_3)_2), 30.60 (s, CHCH(CH_3)_2), 30.60$ CHCH(CH₃)₂), 23.60 (s, CHCH(CH₃)₂), 21.82 (d, $J_{C-P} = 12.2$ Hz, CHCH(CH_{3})₂), 20.97 (overlapped signals, m, CHCH(CH_{3})₂), 16.35 (d, $J_{C-P} = 6.7$ Hz, OCH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 43.78, 41.60; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₂H₂₇FeO₂P 410.1098; Found: 410.1097.

(2,2-dimethyl-1-ferrocenylpropyl) 4.2.16. Ethyl (phenvl) phosphinate (3p). brown oil, 59.8 mg (56% yield); R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.79 -7.64 (m, 1H, Ph), 7.52 - 7.32 (m, 3H, Ph), 7.30 - 7.21 (m, 1H, *Ph*), 4.19 - 3.84 (m, 9H, *Cp*' and *Cp* overlapped with OCH₂CH₃), 3.84 - 3.53 (m, 1H, OCH₂CH₃), 2.90 - 2.63 (m, 1H, CHC(CH₃)₃), 1.40 - 0.98 (m, 12H, CHC(CH₃)₃ and OCH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 134.39 (d, J_{C-P} = 118.9 Hz, *Ph*), 132.25 (d, $J_{C-P} = 121.5$ Hz, Ph), 132.11 (s, Ph), 132.04 (s, Ph), 131.96 (s, *Ph*), 131.34 (d, $J_{C-P} = 2.6$ Hz, *Ph*), 131.04 (d, $J_{C-P} = 2.6$ Hz, *Ph*), 128.05 (d, $J_{C-P} = 12.1$ Hz, Ph), 127.50 (d, $J_{C-P} = 12.0$ Hz, Ph), 85.14 (d, $J_{C-P} = 4.2$ Hz, Cp), 84.88 (d, $J_{C-P} = 1.9$ Hz, Cp), 71.76 (d, $J_{C-P} = 2.7$ Hz, Cp), 71.42 (d, $J_{C-P} = 2.7$ Hz, Cp), 70.74 (d, $J_{C-P} =$ 7.5 Hz, *Cp*), 70.03 (d, $J_{C-P} = 9.3$ Hz, *Cp*), 69.30 (s, *Cp*'), 69.25 (s, Cp'), 67.26 (s, Cp), 66.68 (s, Cp), 66.37 (s, Cp), 66.26 (s, Cp), 60.17 (d, $J_{C-P} = 6.7$ Hz, OCH_2CH_3), 59.96 (d, J = 7.1 Hz, OCH₂CH₃), 49.83 (d, J_{C-P} = 122.4 Hz, CHC(CH₃)₃), 49.06 (d, J_{C-P} = 122.5 Hz, CHC(CH₃)₃), 35.24 (s, CHC(CH₃)₃), 35.11 (s,

CHC(CH₃)₃), 30.35 (s, CHC(CH₃)₃), 16.29 (m, OCH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 43.21, 42.89; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₃H₂₉FeO₂P 424.1255; Found: 424.1256.

4.2.17. Ethyl (ferrocenyl(phenyl)methyl) (phenyl)phosphinate (3q). Yellow solid, 69.9 mg (63% yield); mp 188-189°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.04 (m, 10H, Ph), 4.33 – 3.71 (m, 11H, Cp' and Cp overlapped with OCH₂CH₃), 1.23 and 1.10 (two triplet, $J_{H-H} =$ 7.0 Hz, 3H, OCH₂CH₃); ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CDCl₃) δ 137.02 (d, $J_{C-P} = 5.5$ Hz, Ph), 136.71 (d, $J_{C-P} = 2.6$ Hz, Ph), 132.30 (d, $J_{C-P} = 9.2$ Hz, Ph), 131.99 (d, $J_{C-P} = 9.2$ Hz, Ph), 131.83 (d, $J_{C-P} = 2.6$ Hz, Ph), 131.65 (d, $J_{C-P} = 2.6$ Hz, Ph), 130.77 (d, $J_{C-P} = 4.7$ Hz, Ph), 130.03 (s, Ph), 129.98 (s, Ph), 129.92 (s, *Ph*), 129.78 (d, $J_{C-P} = 4.9$ Hz, *Ph*), 128.02 (d, $J_{C-P} = 1.1$ Hz, Ph), 127.88 (s, Ph), 127.82 (s, Ph), 127.78 (s, Ph), 127.72 (s, *Ph*), 127.03 (d, $J_{C-P} = 2.0$ Hz, *Ph*), 126.90 (d, $J_{C-P} = 2.3$ Hz, *Ph*), 84.36 (d, $J_{C-P} = 3.7$ Hz, Cp), 84.15 (s, Cp), 70.18 (d, $J_{C-P} = 2.4$ Hz, *Cp*), 69.99 (d, $J_{C-P} = 2.3$ Hz, *Cp*), 69.52 (s, *Cp*), 68.44 (s, *Cp*'), 68.37 (s, Cp'), 68.25 (s, Cp), 68.21 (s, Cp), 68.03 (s, Cp), 67.08 (s, Cp), 61.15 (s, OCH₂CH₃), 61.09 (s, OCH₂CH₃), 61.03 (s, OCH_2CH_3), 50.04 (d, $J_{C-P} = 13.9$ Hz, CHPh), 49.31 (d, $J_{C-P} = 14.1$ Hz, CHPh), 16.39 (d, $J_{C-P} = 6.3$ Hz, OCH₂CH₃), 16.27 (d, $J_{C-P} = 6.0$ Hz, OCH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 38.50, 38.22; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₅H₂₅FeO₂P 444.0942; Found: 444.0947.

4.2.18. Diethyl (1-ferrocenylethyl)phosphonate (**3***r*). brown oil, 59.9 mg (69% yield); R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 4.38 – 4.26 (m, 1H, *Cp*), 4.26 – 4.04 (m, 8H, *Cp*', *Cp*), 4.01 – 3.84 (m, 4H, OCH₂CH₃), 2.99 – 2.81 (m, 1H, CHCH₃), 1.58 (dd, *J*_{H-P} = 17.8, *J*_{H-H} = 7.0 Hz, 3H, CHCH₃), 1.22 (m, 6H, OCH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 85.67 (d, *J*_{C-P} = 1.3 Hz, *Cp*), 69.32 (d, *J*_{C-P} = 2.2 Hz, *Cp*), 68.48 (s, *Cp*'), 67.61 (s, *Cp*), 67.38 (s, *Cp*), 66.46 (d, *J*_{C-P} = 2.1 Hz, *Cp*), 61.98 (d, *J*_{C-P} = 5.7 Hz, OCHCH₃), 14.23 (d, *J*_{C-P} = 4.5 Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 28.36; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₁₆H₂₃FeO₃P 350.0734; Found: 350.0738.

4.2.19. Diethyl (1-ferrocenylpropyl)phosphonate (**3**s). brown oil, 44.1 mg (49% yield); R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 4.32 – 4.23 (m, 1H, *Cp*), 4.22 – 4.05 (m, 8H, *Cp*, *Cp*'), 4.01 – 3.75 (m, 4H, OCH₂CH₃), 2.72 – 2.56 (m, 1H, *CHC*H₂CH₃), 2.26 – 1.95 (m, 2H, *CHCH*₂CH₃), 1.31 – 1.15 (overlapped signals, m, 9H, *CHCH*₂CH₃, *OCH*₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 86.22 (d, *J*_{C-P} = 1.7 Hz, *Cp*), 69.35 (d, *J*_{C-P} = 2.3 Hz, *Cp*), 68.47 (s, *Cp*'), 67.36 (s, *Cp*), 67.12 (s, *Cp*), 67.09 (s, *Cp*), 61.92 (d, *J*_{C-P} = 7.1 Hz, OCH₂CH₃), 61.52 (d, *J*_{C-P} = 7.2 Hz, OCH₂CH₃), 39.35 (d, *J*_{C-P} = 134.3 Hz, *CHCH*₂CH₃), 23.73 (d, *J*_{C-P} = 3.4 Hz, *CHCH*₂CH₃), 16.29 (d, *J*_{C-P} = 6.0 Hz, OCH₂CH₃), 13.80 (d, *J*_{C-P} = 3.8 Hz, *CHCH*₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 28.97; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₁₇H₂₅FeO₃P 364.0891; Found: 364.0883.

4.2.20. (1- Ferrocenylethyl)di-p-tolylphosphine oxide (**3t**). Yellow solid, 103.6 mg (94% yield); mp 56 – 57°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.68 – 7.58 (m, 2H, *Ph*), 7.43 – 7.33 (m, 2H, *Ph*), 7.26 – 7.21 (m, 2H, *Ph*), 7.16 – 7.08 (m, 2H, *Ph*), 4.15 – 4.03 (m, 7H, *Cp*', *Cp*), 3.95 – 3.88 (m, 1H, *Cp*), 3.57 – 3.48 (m, 1H, *Cp*), 3.41 – 3.30 (m, 1H, CHCH₃), 2.37 (s, 3H, Ph-CH₃), 2.32 (s, 3H, Ph-CH₃), 1.58 (dd, *J*_{H-P} = 15.8, *J*_{H-H} = 7.3 Hz, 3H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 141.69 (d, *J*_{C-P} = 2.7 Hz, *Ph*), 141.54 (d, *J*_{C-P} = 2.7 Hz, *Ph*), 131.81 (d, *J*_{C-P} = 8.9 Hz, *Ph*), 128.83 (d, *J*_{C-P} = 96.4 Hz, *Ph*), 128.46 (d, $J_{C-P} = 11.7$ Hz, *Ph*), 127.17 (d, $J_{C-P} = M$ 97.9 Hz, *Ph*), 85.68 (s, *Cp*), 69.32 (s, *Cp*), 68.30 (s, *Cp*^{*}), 67.35 (s, *Cp*), 67.10 (s, *Cp*), 35.63 (d, $J_{C-P} = 66.7$ Hz, CHCH₃), 21.39 (d, $J_{C-P} = 3.9$ Hz, Ph-CH₃), 13.79 (s, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 34.25; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₆H₂₇FeOP 442.1149; Found: 442.1130.

4.2.21. Bis(4-fluorophenyl)(1- ferrocenylethyl)phosphine oxide (3u). Yellow solid, 70.1mg (62% yield); mp 203 – 204°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.69 (m, 2H, Ph), 7.52 – 7.40 (m, 2H, Ph), 7.19 - 7.15 (m, 2H, Ph), 7.10 - 6.97 (m, 2H, Ph), 4.16 - 4.05 (m, 7H, *Cp*', *Cp*), 3.42 – 3.35 (m, 1H, *Cp*), 3.55 – 3.44 (m, 1H, *Cp*), 3.42 -3.25 (m, 1H, CHCH₃), 1.59 (dd, $J_{\text{H-P}} = 16.1$, $J_{\text{H-H}} = 7.2$ Hz, 3H, CHCH₃); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 164.87 (d, J_{C-P} = 253.3 Hz, Ph), 134.50 (s, Ph), 134.43 (s, Ph), 134.36 (s, Ph), 134.29 (s, Ph), 133.85 (s, Ph), 133.77 (s, Ph), 133.70 (s, Ph), 128.13 (d, $J_{C-P} = 3.3$ Hz, Ph), 127.36 (d, $J_{C-P} = 3.3$ Hz, Ph), 126.40 (d, $J_{C-P} = 3.5$ Hz, Ph), 125.62 (d, $J_{C-P} = 2.1$ Hz, Ph), 116.08 (dd, $J_{C-P} = 21.5$, 13.4 Hz, Ph), 115.86 (dd, $J_{C-P} = 21.2$, 12.3 Hz, Ph), 115.30 (dd, $J_{C-P} = 21.2$, 12.5 Hz, Ph), 85.25 (s, Cp), 69.31 (d, $J_{C-P} = 1.5$ Hz, Cp), 68.53 (s, Cp'), 67.74 (s, Cp), 67.42 (s, *Cp*), 67.37 (s, *Cp*), 36.01 (d, *J*_{C-P} = 67.5 Hz, *C*HCH₃), 13.84 (d, $J_{C-P} = 1.2$ Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 32.95; ^{19}F NMR (470 MHz, CDCl₃) δ -106.85, -107.15; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for C₂₄H₂₁F₂FeOP 450.0648; Found: 450.0669.

4.2.22. Bis(4-methoxyphenyl)(1- ferrocenylethyl)phosphine oxide (3v). Yellow solid, 95.9mg (81% yield); mp 44 – 45°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.74 – 7.54 (m, 2H, Ph), 7.46 – 7.32 (m, 2H, Ph), 7.07 - 6.89 (m, 2H, Ph), 6.89 - 6.75 (m, 2H, Ph), 4.19 - 3.99 (m, 7H, *Cp*, *Cp*'), 3.99 – 3.89 (m, 1H, *Cp*), 3.83 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃), 3.59 - 3.48 (m, 1H, Cp), 3.41 - 3.27 (m, 1H, CHCH₃), 1.58 – 1.56 (m, 3H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 161.99 (d, $J_{C-P} = 2.0$ Hz, *Ph*), 161.93 (d, $J_{C-P} = 2.1$ Hz, *Ph*), 133.72 (d, $J_{C-P} = 9.6$ Hz, *Ph*), 133.06 (d, $J_{C-P} = 9.9$ Hz, *Ph*), 123.40 (d, $J_{C-P} = 100.2$ Hz, Ph), 121.42 (d, $J_{C-P} = 102.0$ Hz, Ph), 113.79 (d, $J_{C-P} = 12.1$ Hz, Ph), 113.29 (d, $J_{C-P} = 12.2$ Hz, Ph), 85.82 (s, Cp), 69.37 (s, Cp), 68.36 (s, Cp'), 67.34 (s, Cp), 67.20 (s, *Cp*), 55.12 (d, $J_{C-P} = 8.5$ Hz OCH₃), 36.00 (d, $J_{C-P} = 67.6$ Hz, CHCH₃), 13.78 (s, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 34.24; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₂₆H₂₇FeO₃P 474.1047; Found: 474.1042.

4.2.23. Bis(2,6-dimethylphenyl)(1- ferrocenylethyl)phosphine oxide (3w). Yellow solid, 22.8mg (19% yield); mp 188 – 189°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.14 (m, 1H, Ph), 7.09 – 6.94 (m, 3H, Ph), 6.81 -6.71 (m, 2H, Ph), 4.40 - 4.31 (m, 1H, Cp), 4.16 - 4.07 (m, 5H, Cp'), 4.05 – 3.97 (m, 1H, Cp), 3.75 – 3.67 (m, 1H, Cp), 3.66 – 3.54 (m, 1H, CHCH₃), 3.43 – 3.35 (m, 1H, Cp), 2.52 (s, 6H, Ph- CH_3), 2.19 (s, 6H, Ph- CH_3), 1.89 (dd, $J_{H-P} = 14.8$, $J_{H-H} = 6.8$ Hz, 3H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 135.05 (d, J_{C-P} = 81.4 Hz, *Ph*), 131.56 (d, J_{C-P} = 89.5 Hz, *Ph*), 130.36 (s, *Ph*), 130.28 (s, *Ph*), 130.12 (d, $J_{C-P} = 2.6$ Hz, *Ph*), 129.45 (d, $J_{C-P} =$ 10.6 Hz, *Ph*), 87.04 (s, *Cp*), 69.17 (d, $J_{C-P} = 2.1$ Hz, *Cp*), 68.34 (s, Cp'), 68.10 (d, $J_{C-P} = 1.5$ Hz, Cp), 67.30 (s, Cp), 66.71 (s, Cp), 38.08 (d, J_{C-P} = 59.8 Hz, CHCH₃), 22.86 (d, J = 3.3 Hz, Ph-CH₃), 22.52 (d, J = 3.9 Hz, Ph-CH₃), 15.57 (d, $J_{C-P} = 2.1$ Hz, CHCH₃); $^{31}P\{^{1}H\}$ NMR (202 MHz, CDCl₃) δ 43.22; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{31}$ FeOP 470.1462; Found: 470.1460.

4.3. General Procedure for Cu-catalyzed Reaction of 1,1'-Ferrocenyl Diketone-derived N-tosylhydrazones with Hphosphorus Oxides and Ethyl Phenylphosphinate: A 0.36 mmol *H*-phosphorus oxide or ethyl phenylphosphinate, 0.15 mmol 1,1'-ferrocenyl diketone-derived *N*-tosylhydrazone, 0.03 mmol of CuI and 0.90 mmol K₂CO₃ were charged into 25 mL oven □dried flask, and backfilled with argon three times. 5 mL freshly □ distilled 1,4 □ dioxane was then injected into the flask, then heated to reflux for 18 h. The crude reaction mixture was allowed to reach room temperature, the solvent was eliminated under vacuum. Ammonia water and dichloromethane was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over Na₂SO₄. The concentrated residue was purified by column chromatography over silica gel using petroleum ether/ dichloromethane/ NEt₃(1:2:0.1) as eluent to get the product **5**.

1,1'-Bis((1-diphenylphosphinyl)ethyl)-ferrocene 4.3.1. (5a). Yellow solid, 62.7 mg (65% yield); mp 178 - 179°C; R_f (petroleum ether/dichloromethane / triethylamine1:3:0.1) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.86 – 7.67 (m, 4H, Ph), 7.67 -7.40 (m, 12H, Ph), 7.40 - 7.29 (m, 4H, Ph), 4.15 - 4.07 (m, 1H, Cp), 4.07 - 3.97 (m, 3H, Cp), 3.94 - 3.84 (m, 2H, Cp), 3.51 -3.39 (m, 2H, Cp), 3.39 - 3.19 (m, 2H, CHCH₃), 1.67 - 1.42 (m, 6H, CHCH₃); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 131.84 (d, J_{C-P} = 15.9 Hz, Ph), 131.49 (d, J_{C-P} = 8.6 Hz, Ph), 131.39 (d, J_{C-P} = 2.5 Hz, Ph), 131.23 (s, Ph), 131.16 (s, Ph), 131.06 (s, Ph), 131.00 (s, Ph), 130.94 (s, Ph), 130.50 (d, $J_{C-P} = 4.4$ Hz, Ph), 129.74 (d, $J_{C-P} = 4.4$ Hz, Ph), 127.63 (d, $J_{C-P} = 11.4$ Hz, Ph), 85.52 (s, *Cp*), 85.39 (s, *Cp*), 69.81 (d, *J*_{C-P} = 1.5 Hz, *Cp*), 69.55 (d, $J_{C-P} = 1.5$ Hz, Cp), 68.25 (s, Cp), 68.06 (s, Cp), 68.02 (s, Cp), 67.69 (s, Cp), 67.64 (s, Cp), 67.31 (s, Cp), 66.70 (s, Cp), 35.26 (d, $J_{C-P} = 66.2 \text{ Hz}, CHCH_3$, 35.08 (d, $J_{C-P} = 66.3 \text{ Hz}, CHCH_3$), 13.73 (d, $J_{C-P} = 1.4$ Hz, CHCH₃), 13.67 (d, $J_{C-P} = 1.3$ Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.45, 33.37; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{38}H_{36}FeO_2P_2$ 642.1540; Found: 642.1535.

1-((1-Diphenylphosphinyl)ethyl)-1'-(1-((4-methylphenyl) 4.3.2. sulfonyl)ethyl)-ferrocene (6a). Yellow solid, 27.7 mg (31% yield); mp 65 – 66°C; R_f (petroleum ether/ dichloromethane/ triethylamine 1:3:0.1) = 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.80 - 7.68 (m, 2H, Ph), 7.57 - 7.50 (m, 1H, Ph), 7.50 - 7.40 (m, 5H, Ph), 7.38 - 7.29 (m, 4H, Ph), 7.20 - 7.15 (m, 2H, Ph), 4.16 -3.78 (m, 8H, Cp), 3.44 - 3.39 (m, 1H, CH(CH₃)S(O)₂Ph-CH₃), 3.36 - 3.24 (m, 1H, CH(CH₃)P(O)Ph₂), 2.43 - 3.32 (s, 3H, Ph-CH₃), 1.67 - 1.58 (m, 3H, CH(CH₃)S(O)₂Ph-CH₃), 1.58 - 1.47 (m, 3H, CH(CH₃)P(O)Ph₂); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 143.95 (s, Ph), 132.67 - 132.31 (m, Ph), 131.68 - 130.99 (m, Ph), 130.96 - 130.26 (m, Ph), 129.22 - 128.87 (m, Ph), 128.88 -128.45 (m, Ph), 128.27 - 127.85 (m, Ph), 127.67 - 127.30 (m, *Ph*), 85.98 (d, $J_{C-P} = 7.5$ Hz, *Cp*), 80.96 (d, $J_{C-P} = 14.9$ Hz, *Cp*), 71.00 (s, *Cp*), 70.75 (s, *Cp*), 69.89 (s, *Cp*), 69.57 (s, *Cp*), 69.24 (s, *Cp*), 69.01 – 68.63 (m, *Cp*), 68.34 – 67.27 (m, *Cp*), 66.92 (s, *Cp*), 66.65 (s, Cp), 61.65 (d, $J_{C-P} = 10.6$ Hz, $CH(CH_3)S(O)_2Ph-CH_3)$, (m, $CH(CH_3)P(O)Ph_2)$, 34.29 21.15 35.25 _ (s. CH(CH₃)S(O)₂Ph-CH₃), 13.64 (s, CH(CH₃)S(O)₂Ph-CH₃), 13.59 (d, $J_{C-P} = 1.3$ Hz, CH(CH₃)P(O)Ph₂); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.30, 33.22; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₃₃H₃₃FeO₃PS 596.1237; Found: 596.1241.

4.3.3. 1,1'-Bis((1-diphenylphosphinyl)propyl)-ferrocene (**5b**). Yellow solid, 53.9 mg (54% yield); mp 191 – 192°C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.80 – 7.67 (m, 4H, *Ph*), 7.56 – 7.36 (m, 12H, *Ph*), 7.35 – 7.27 (m, 4H, *Ph*), 4.06 – 3.92 (m, 4H, *Cp*), 3.88 – 3.75 (m, 2H, *Cp*), 3.40 – 3.29 (m, 2H, *Cp*), 3.16 – 2.98 (m, 2H, *CH*CH₂CH₃), 2.23 – 1.94 (m, 4H, CHCH₂CH₃), 1.15 – 1.02 (m, 6H, CHCH₂CH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 133.18 (d, *J*_{C-P} = 6.6 Hz, *Ph*), 132.44 (d, *J*_{C-P} = 6.9 Hz, *Ph*), 131.99 (d, *J*_{C-P} = 2.4 *Ph*), 131.40 – 131.23 (m, *Ph*), 130.96 (d, $J_{CP} = 4.9$ Hz, *Ph*), 130.20 (d, $J_{CP} = 5.0$ Hz, *Ph*), 128.35 (d, $J_{CP} = 3.2$ Hz, *Ph*), 128.26 (d, $J_{CP} = 3.2$ Hz, *Ph*), 127.81 (s, *Ph*), 127.72 (s, *Ph*), 86.78 (s, *Cp*), 86.56 (s, *Cp*), 70.24 (s, *Cp*), 70.14 (s, *Cp*), 68.73 (s, *Cp*), 68.58 (s, *Cp*), 68.37 (s, *Cp*), 68.08 (s, *Cp*), 67.74 (s, *Cp*), 42.59 (d, $J_{CP} = 65.0$ Hz, CHCH₂CH₃), 42.35 (d, $J_{CP} = 65.0$ Hz, CHCH₂CH₃), 23.51 (d, $J_{CP} = 19.2$ Hz, CHCH₂CH₃), 14.80 (d, J_{C} $_{P} = 4.7$ Hz, CHCH₂CH₃), 14.75 (d, $J_{C-P} = 4.7$ Hz, CHCH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.85, 33.79; HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₄₀H₄₀FeNaO₂P₂ 693.1751; Found: 693.1739.

4.3.4. 1,1'-Bis((1-diphenylphosphinyl)butyl)-ferrocene (5c).Yellow solid, 43.7 mg (42% yield); mp185 – 186° C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.82 - 7.65 (m, 4H, Ph), 7.57 - 7.36 (m, 12H, Ph), 7.36 - 7.22 (m, 4H, Ph), 4.05 - 3.91 (m, 4H, Cp), 3.87 - 3.75 (m, 2H, *Cp*), 3.40 – 3.27 (m, 2H, *Cp*), 3.21 – 3.06 (m, 2H, CHCH₂CH₂CH₃), 2.25 - 1.78 (m, 4H, CHCH₂CH₂CH₃), 1.67 -1.37 (m, 4H, CHCH₂CH₂CH₃), 0.98 – 0.78 (m, 6H, CHCH₂CH₂CH₃); ${}^{13}C{}^{1}H{}^{3}NMR$ (126 MHz, CDCl₃) δ 132.77 (d, $J_{\text{C-P}} = 93.3 \text{ Hz}, Ph$), 131.97 (d, $J_{\text{C-P}} = 4.3 \text{ Hz}, Ph$), 131.90 (d, $J_{\text{C-P}}$ = 4.3 Hz, Ph), 131.52 (s, Ph), 131.39 - 131.19 (m, Ph), 131.06 (d, $J_{C-P} = 14.5$ Hz, Ph), 130.30 (d, $J_{C-P} = 14.1$ Hz, Ph), 128.29 (d, J_{C-P} = 10.2 Hz, Ph), 127.82 (d, J_{C-P} = 2.5 Hz, Ph), 127.73 (d, J_{C-P} = 2.5 Hz, Ph), 87.01 (s, Cp), 86.77 (s, Cp), 70.28 (s, Cp), 70.23 (s, Cp), 68.71 (s, Cp), 68.50 (s, Cp), 68.35 (s, Cp), 68.06 (s, Cp), 67.67 (s, Cp), 40.92 (d, $J_{C-P} = 65.0$ Hz, CHCH₂CH₂CH₃), 40.67 (d, $J_{C-P} = 65.1$ Hz, CHCH₂CH₂CH₃), 32.41 (d, $J_{C-P} = 25.0$ Hz, CHCH₂CH₂CH₃), 22.99 (s, CHCH₂CH₂CH₃), 14.54 (d, $J_{C-P} = 4.7$ Hz, CHCH₂CH₂CH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 33.76, 33.73; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for C₄₂H₄₄FeNaO₂P₂ 721.2064; Found: 721.2051.

1,1'-Bis(1-diphenylphosphinyl-2-methylpropyl)-ferrocene 4.3.5. (5*d*). Yellow solid, 27.8 mg (27% yield); mp 169 – 170° C; R_f (petroleum ether/ethyl acetate 1:2) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.62 (m, 4H, Ph), 7.62 – 7.38 (m, 12H, Ph), 7.38 -7.27 (m, 4H, Ph), 4.04 - 3.21 (m, 10H, Cp overlapped with CHCH₂CH₃), 2.76 – 2.44 (m, 2H, CHCH(CH₃)₂), 1.32 – 1.19 (m, 6H, CHCH(CH₃)₂), 1.17 – 0.98 (m, 6H, CHCH(CH₃)₂); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 135.16 (d, J_{C-P} = 3.5 Hz, *Ph*), 134.41 (d, $J_{C-P} = 3.9$ Hz, Ph), 132.37 - 132.06 (m, Ph), 131.28 (s, Ph), 131.17 (s, Ph), 131.10 (s, Ph), 128.47 - 128.23 (m, Ph), 127.92 -127.62 (m, *Ph*), 86.12 (s, *Cp*), 85.60 (s, *Cp*), 71.10 (d, $J_{C-P} = 1.8$ Hz, *Cp*), 70.97 (d, $J_{C-P} = 1.7$ Hz, *Cp*), 69.33 (d, $J_{C-P} = 3.9$ Hz, *Cp*), 69.26 (d, *J*_{C-P} = 3.6 Hz, *Cp*), 68.64 (s, *Cp*), 68.50 (s, *Cp*), 68.30 (s, *Cp*), 67.92 (s, *Cp*), 46.76 (s, *C*HCH(CH₃)₂), 46.24 (s, CHCH(CH₃)₂), 32.72 (s, CHCH(CH₃)₂), 32.34 (s, CHCH(CH₃)₂), 23.75 (s, CHCH(CH₃)₂), 23.40 (s, CHCH(CH₃)₂), 21.36 – 21.14 (m, CHCH(CH_3)₂); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 32.31, 32.18; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{42}H_{44}FeO_2P_2$ 698.2166; Found: 698.2161.

4.3.6. 1,1'-Bis ((1-(bis (4-fluorophenyl) phosphinyl)) ethyl)ferrocene (5e). Yellow solid, 63.5 mg (59% yield); mp 180 – 181°C; R_f (petroleum ether/ dichloromethane / triethylamine 1:3:0.1) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.62 (m, 4H, *Ph*), 7.50 – 7.36 (m, 4H, *Ph*), 7.22 – 7.09 (m, 4H, *Ph*), 7.08 – 6.69 (m, 4H, *Ph*), 4.12 – 3.96 (m, 4H, *Cp*), 3.95 – 3.88 (m, 2H, *Cp*), 3.48 – 3.39 (m, 2H, *Cp*), 3.34 – 3.19 (m, 2H, CHCH₃), 1.58 – 1.45 (m, 6H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 164.91 (dd, *J*_{C-F} = 253.7, *J*_{C-P} = 3.2 Hz), 134.35 – 134.10 (m, *Ph*), 133.87 – 133.52 (m, *Ph*), 128.04 – 127.52 (m, *Ph*), 127.25 – 126.78 (m, *Ph*), 126.49 – 126.14 (m, *Ph*), 125.66 – 125.35 (m, *Ph*), 116.11 – 115.74 (m, *Ph*), 115.38 (dd, *J*_{C-F} = 21.2, *J*_{C-P} = 1.5 Hz, *Ph*), 85.68 (s, *Cp*), 85.56 (s, *Cp*), 70.04 (d, *J*_{C-P} = 1.7 Hz, *Cp*), 69.81 (d, $J_{CP} = 1.9$ Hz, *Cp*), 68.75 (s, *Cp*), 68.54 (s, *Cp*), 68.51 (s, *Cp*), 68.17 (s, *Cp*), 67.88 (d, $J_{C-P} = 1.2$ Hz, *Cp*), 67.60 (d, $J_{C-P} = 1.3$ Hz, *Cp*), 35.85 (d, $J_{C-P} = 67.2$ Hz, CHCH₃), 35.63 (d, $J_{C-P} = 67.4$ Hz, CHCH₃), 13.98 (d, $J_{C-P} = 1.4$ Hz, CHCH₃), 13.92 (d, $J_{C-P} = 1.5$ Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 32.95, 32.86; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₃₈H₃₂F₄FeO₂P₂ 714.1163; Found: 714.1154.

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4.3.7. 1,1'-Bis((1-(bis(4-methoxy)phosphinyl))ethyl)-ferrocene (5f). Yellow solid, 75.5 mg (66% yield); mp 49 – 50° C; R_f (petroleum ether/ dichloromethane / triethylamine 1:3:0.1) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.56 (m, 4H, Ph), 7.40 – 7.30 (m, 4H, Ph), 6.98 – 6.90 (m, 4H, Ph), 6.87 – 6.79 (m, 4H, Ph), 4.05 – 3.95 (m, 4H, Cp), 3.93 – 3.87 (m, 2H, Cp), 3.84 (s, 6H, OCH₃), 3.80 (s, 6H, OCH₃), 3.50 - 3.40 (m, 2H, Cp), 3.31 -3.19 (m, 2H, CHCH₃), 1.55 – 1.45 (m, 6H, CHCH₃); ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CDCl₃) δ 162.10 (d, J_{C-P} = 2.8 Hz,), 162.04 (s), δ 162.14 - 162.00 (m, Ph), 134.90 - 132.05 (m, Ph), 125.39 -119.12 (m, Ph), 114.61 - 112.52 (m, Ph), 86.16 (s, Cp), 86.01 (s, Cp), 70.27 (s, Cp), 69.95 (s, Cp), 68.41 (s, Cp), 68.32 (s, Cp), 68.10 (s, Cp), 68.00 (s, Cp), 67.95 (s, Cp), 67.55 (s, Cp), 55.24 (s, OCH₃), 55.17 (s, OCH₃), 36.62 - 35.16 (m, CHCH₃), 13.95 (d, $J_{\text{C-P}} = 1.3 \text{ Hz}, \text{CHCH}_3), 13.89 \text{ (d}, J_{\text{C-P}} = 1.3 \text{ Hz}, \text{CHCH}_3); {}^{31}\text{P}\{{}^{1}\text{H}\}$ NMR (202 MHz, CDCl₃) δ 34.34, 34.25; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₄₂H₄₄FeO₆P₂ 762.1963; Found: 762.1955.

4.3.8 1,1'-Bis((1-(bis(4-methylphenyl)phosphinyl))ethyl)ferrocene (5g). Yellow solid, 57.6 mg (55% yield); mp 139 -140°C; R_f (petroleum ether/ dichloromethane / triethylamine 1:3:0.1 = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.53(m, 4H, Ph), 7.38 – 7.30 (m, 4H, Ph), 7.27 – 7.21 (m, 4H, Ph), 7.17 – 7.08 (m, 4H, Ph), 4.08 – 4.03 (m, 1H, Cp), 4.03 – 3.97 (m, 3H, *Cp*), 3.91 – 3.85 (m, 2H, *Cp*), 3.49 – 3.46 (m, 1H, *Cp*), 3.46 – 3.42 (m, 1H, Cp), 3.33 – 3.24 (m, 2H, CHCH₃), 2.40 – 2.36 (m, 6H, Ph-CH₃), 2.35 – 2.31 (m, 6H, Ph-CH₃), 1.56 – 1.47 (m, 6H, CHCH₃); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 141.97 (d, $J_{C-P} =$ 2.6 Hz, Ph), 141.81 (d, $J_{C-P} = 1.4$ Hz, Ph), 131.98 (d, $J_{C-P} = 8.7$ Hz, Ph), 131.55 - 131.24 (m, Ph), 129.33 (s, Ph), 129.24 -129.04 (m, Ph), 128.67 (d, $J_{C-P} = 11.7$ Hz, Ph), 128.56 (s, Ph), 128.42 (s, Ph), 127.58 (s, Ph), 127.52 (s, Ph), 126.81 (s, Ph), 126.74 (s, Ph), 86.10 (s, Cp), 85.96 (s, Cp), 70.30 (s, Cp), 70.00 (s, Cp), 68.43 (s, Cp), 68.39 (s, Cp), 68.20 (s, Cp), 68.01 (s, Cp), 67.66 (s, *Cp*), 35.78 (d, J_{C-P} = 66.5 Hz, *C*HCH₃), 35.62 (d, J_{C-P} = 66.6 Hz, CHCH₃), 21.56 (d, J_{C-P} = 3.9 Hz, Ph-CH₃), 14.03 (d, J_{C-P} = 5.6 Hz, CHCH₃); ${}^{31}P{}^{1}H{}$ NMR (202 MHz, CDCl₃) δ 34.32, 34.23; HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{42}H_{44}FeO_2P_2$ 698.2166; Found: 698.2159.

4.3.9. 1,1'-Bis((1-(ethoxyphenylphosphinyl))ethyl)-ferrocene (**5h**). Yellow oil, 17.2 mg (27% yield); R_f (petroleum ether/ dichloromethane / triethylamine 1:3:0.1) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.29 (m, 10H, *Ph*), 4.07 – 3.57 (m, 12H, overlapped signals, *Cp*, OCH₂CH₃), 3.16 – 2.78 (m, 2H, CHCH₃), 1.48 – 1.42 (m, 6H, CHCH₃), 1.30 – 1.22 (m, 6H, OCH₂CH₃); 1³C{¹H} NMR (126 MHz, CDCl₃) δ 132.69 (d, *J*_{C-P} = 9.3 Hz, *Ph*), 132.37 (d, *J*_{C-P} = 9.1 Hz, *Ph*), 132.00 – 131.81 (m, *Ph*), 129.21 (d, *J*_{C-P} = 120.6 Hz, *Ph*), 128.22 – 127.45 (m, *Ph*), 85.90 – 85.58 (m, *Cp*), 70.66 (s, *Cp*), 70.27 (s, *Cp*), 69.96 (s, *Cp*), 68.71 – 67.72 (m, *Cp*), 67.35 – 66.35 (m, *Cp*), 60.85 – 60.70 (m, *Cp*), 36.14 – 34.58 (m, CHCH₃), 16.41 (d, *J*_{C-P} = 6.3 Hz, OCH₂CH₃), 14.05 – 12.63 (m, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 43.41, 43.37, 43.31, 43.00, 42.96, 42.89, 42.85; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₃₀H₃₆FeO₄P₂ 578.1438; Found: 578.1433.

4.3.10. 1,1'-Bis((1-(bis(3,5-dimethylphenyl)phosphinyl))ethyl)ferrocene (5i). Yellow solid, 30.1 mg (27% yield); mp 225 – 226°C; R_f (petroleum ether/ dichloromethane / triethylamine 1:3:0.1) = 0.6. ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.29 (m, 4H, Ph), 7.16 – 7.10 (m, 2H, Ph), 7.08 – 7.00 (m, 6H, Ph), 4.12 – M 4.07 (m, 1H, *Cp*), 4.07 – 4.01 (m, 3H, *Cp*), 3.94 – 3.87 (m, 2H, *Cp*), 3.50 – 3.41 (m, 2H, *Cp*), 3.35 – 3.21 (m, 2H, *Cp*), 2.35 – 2.31 (m, 12H, Ph-CH₃), 2.26 – 2.21 (m, 12H, Ph-CH₃), 1.57 – 1.47 (m, 6H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 138.17 – 137.78 (m, Ph), 137.37 (d, *J*_{C-P} = 11.9 Hz, Ph), 133.25 (d, *J*_{C-P} = 2.6 Hz, Ph), 133.05 (d, *J*_{C-P} = 2.6 Hz, Ph), 132.21 – 129.62 (m, Ph), 129.44 (d, *J*_{C-P} = 8.6 Hz, Ph), 129.07 – 128.56 (m, Ph), 86.12 (s, *Cp*), 85.99 (s, *Cp*), 70.29 (s, *Cp*), 69.94 (s, *Cp*), 68.39 – 67.40 (m, *Cp*), 36.06 – 34.32 (m, CHCH₃), 21.22 (d, *J*_{C-P} = 17.9 Hz, Ph-CH₃), 13.98 (d, *J*_{C-P} = 6.0 Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 34.46, 34.41; HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₄₆H₅₃FeO₂P₂ 755.2870; Found: 755.2865.

4.4. Synthesis of diphenyl (1-ferrocenylethyl) phosphine 7:

A 0.7mL portion (4.8mmol, 20equiv.) of Et_3N and 0.5mL (4.8mmol, 20equiv.) of $SiHCl_3$ were added to a toluene solution of 100mg (0.24mmol) of **3a**. The suspension was heated to reflux overnight under an inert atmosphere. After the mixture was cooled to room temperature, 5mL of a NaOH solution in degassed water (30%) was added and the mixture was stirred at 60°C for 2h. The two phases were separated under an inert atmosphere, the water phase was extracted twice with dry Et_2O . The organic phase was dried with MgSO₄ and filtered, and the solvent was evaporated under vacuum. The obtained orange oil was purified by aluminium oxide column chromatography (petroleum ether) to afford desired product **7**.

4.4.1. Diphenyl(1-ferrocenylethyl)phosphine (7).²⁶ Yellow solid, 0.99g (96% yield); mp 79 – 80°C; R_f (petroleum ether) = 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.48 (m, 2H, *Ph*), 7.38 – 7.30 (m, 3H, *Ph*), 7.27 – 7.13 (m, 5H, *Ph*), 4.15 – 4.05 (m, 5H, *Cp*'), 4.04 – 4.00 (m, 1H, *Cp*), 4.00 – 4.35 (m, 1H, *Cp*), 3.90 – 3.85 (m, 1H, *Cp*), 3.51 – 3.37 (m, 1H, *Cp*), 3.34 – 3.17 (m, 1H, *CH*CH₃), 1.47 (dd, *J*_{H-P} = 14.7, *J*_{H-H} = 7.1 Hz 3H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.09 (d, *J*_{C-P} = 14.7 Hz, *Ph*), 136.96 (d, *J*_{C-P} = 16.1 Hz, *Ph*), 134.03 (d, *J*_{C-P} = 19.2 Hz, *Ph*), 133.91 (d, *J*_{C-P} = 15.5 Hz, *Ph*), 128.45 (d, *J*_{C-P} = 10.2 Hz, *Ph*), 128.61 (d, *J*_{C-P} = 15.5 Hz, *Ph*), 128.45 (d, *J*_{C-P} = 7.1 Hz, *Ph*), 91.27 (d, *J*_{C-P} = 14.8 Hz, *Cp*), 68.75 (d, *J*_{C-P} = 2.7 Hz, *Cp*), 68.26 (s, *Cp*'), 67.01 (s, *Cp*), 66.65 (s, *Cp*), 66.30 (d, *J*_{C-P} = 19.0 Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 5.61.

4.5. Synthesis of 1-(diphenylphosphino)-2-(1-(diphenylphosphino) ethyl)-ferrocene 8:

A 1.3 M *t*-BuLi in pentane solution (2.3mL, 3.0mmol, 1.2equiv.) was added at -78 °C over 30 min through a syringe pump to a solution of 7 (1g, 2.5mmol, 1equiv.) in THF (20mL). After stirring the solution at room temperature for 1h, the solution was cooled again to -78°C and chlorodiphenylphosphine was added dropwise with a syringe. The reaction was warmed to room temperature overnight. The mixture was then quenched by the addition of saturated NaHCO₃ solution (10mL). The organic layer was separated and dried over MgSO₄ and the solvent was removed under reduced pressure, after which the filtrate was concentrated. The residue was purified by aluminium oxide chromatography (petroleum ether/ethyl acetate 20:1) to afford **8**.

4.5.1. 1-(Diphenylphosphino)-2-(1-(diphenylphosphino)ethyl)ferrocene (8a). Yellow solid, 291.2mg (20% yield); mp 39 – 46°C; R_f (petroleum ether/ ethyl acetate 20:1) = 0.4. ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.27 (m, 20H, *Ph*), 4.36 – 4.30 (m, 2H, *Cp*), 4.07 – 4.03 (m, 2H, *Cp*), 3.92 – 3.89 (m, 1H, *Cp*), 3.89 – 3.85 (m, 1H, *Cp*), 3.80 – 3.77 (m, 1H, *Cp*), 3.41 – 3.37 (m, 1H, *Cp*), 3.09 – 3.01 (m, 1H, *CH*CH₃), 1.51 – 1.40 (m, 3H, CHCH₃); ^{A3}C{¹H} NMR (126 MHz, CDCl₃) δ 139.43 (d, $J_{C-P} = 9.7$ Hz, *Ph*), 137.35 – 136.70 (m, *Ph*), 134.49 – 133.30 (m, *Ph*), 128.99 – 127.70 (m, *Ph*), 92.21 (d, $J_{C-P} = 14.9$ Hz, *Cp*), 75.78 (d, $J_{C-P} = 6.0$ Hz, *Cp*), 73.83 – 72.79 (m, *Cp*), 71.58 – 71.08 (m, *Cp*), 70.47 (s, *Cp*), 69.72 (s, *Cp*), 68.47 (s, *Cp*), 68.20 (s, *Cp*), 67.18 (s, *Cp*), 32.12 (d, $J_{C-P} = 11.3$ Hz, CHCH₃), 17.88 (d, $J_{C-P} = 19.0$ Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 6.55, 5.94, -15.93, -16.37.

4.5.2. *1*-(*Dicyclohexylphosphino*)-2-(*1*-(*diphenylphosphino*) ethyl) -*ferrocene* (**8***b*). Yellow solid, 208.1mg (14% yield); mp 132 – 136°C; R_f (petroleum ether/ ethyl acetate 100:1) = 0.4. ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.20 (m, 10H, *Ph*), 4.19 – 4.16 (m, 1H, *Cp*), 4.16 – 4.12 (m, 6H, *Cp*), 3.85 – 3.79 (m, 1H, *Cp*), 3.64 – 3.54 (m, 1H, *CHCH*₃), 2.28 – 1.10 (m, 25H, CHCH₃ and *Cy*); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 138.72 (d, *J*_{C-P} = 19.0 Hz, *Ph*), 135.97 (d, *J*_{C-P} = 21.3 Hz, *Ph*), 132.01 (d, *J*_{C-P} = 15.2 Hz, *Ph*), 129.24 (s, *Ph*), 128.24 (d, *J*_{C-P} = 4.4 Hz, *Ph*), 127.92 (d, *J*_{C-P} = 7.6 Hz, *Ph*), 127.44 (s, *Ph*), 77.91 (d, *J*_{C-P} = 1.9 Hz, *Cp*), 71.05 (s, *Cp*), 70.09 (d, *J*_{C-P} = 1.9 Hz, *Cp*), 69.43 (s, *Cp*), 68.58 (dd, *J*_{C-P} = 8.8, 3.4 Hz, *Cp*), 67.82 (s, *Cp*), 34.8 – 19.5 (m, *Cy*, CHCH₃, CHCH₃); ³¹P{¹H}</sup> NMR (202 MHz, CDCl₃) δ 4.66, 4.63, -13.39.

4.6. Synthesis of 1,1'-bis((1-diphenylphosphino)ethyl)-ferrocene 9:

A 0.9mL portion (6.2mmol, 40equiv.) of Et_3N and 0.6mL (6.2mmol, 40equiv.) of $SiHCl_3$ were added to a toluene solution of 100mg (0.155mmol) of **3a**. The suspension was heated to reflux overnight under an inert atmosphere. After the mixture was cooled to room temperature, 5mL of a NaOH solution in degassed water (30%) was added and the mixture was stirred at 60°C for 2h. The two phases were separated under an inert atmosphere, and the water phase was extracted twice with dry Et_2O . The organic phase was dried with MgSO₄ and filtered, and the solvent was evaporated under vacuum. The obtained orange oil was purified by aluminium oxide column chromatography (petroleum ether) to afford desired product **9**.

4.6.1. 1,1'-Bis((1-diphenylphosphino)ethyl)-ferrocene (**9**). Yellow solid, 78.8mg(83% yield); mp 41 – 42°C; R_f (petroleum ether/ ethyl acetate 10:1) = 0.4. ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.43 (m, 4H, *Ph*), 7.40 – 7.29 (m, 6H, *Ph*), 7.28 – 7.14 (m, 10H, *Ph*), 4.01 – 3.81 (m, 6H, *Ph*), 3.43 – 3.35 (m, 2H, *Ph*), 3.30 – 3.12 (m, 2H, CHCH₃), 1.41 (dd, *J*_{H-P} = 14.7, *J*_{H-H} = 7.0 Hz, 6H, CHCH₃); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 137.32 – 136.74 (m, *Ph*), 134.23 – 133.83 (m, *Ph*), 133.71 – 133.22 (m, *Ph*), 128.72 – 128.49 (m, *Ph*), 128.25 (d, *J*_{C-P} = 6.6 Hz, *Ph*), 127.83 – 127.64 (m, *Ph*), 91.93 – 90.08 (m, *Cp*), 69.37 (d, *J*_{C-P} = 2.8 Hz, *Cp*), 69.13 (d, *J*_{C-P} = 2.9 Hz, *Cp*), 67.69 (d, *J*_{C-P} = 17.7 Hz, *Cp*), 67.38 (d, *J*_{C-P} = 33.5 Hz, *Cp*), 66.68 (d, *J*_{C-P} = 3.4 Hz, *Cp*), 66.32 (d, *J*_{C-P} = 3.4 Hz, *Cp*), 32.72 – 31.68 (m, CHCH₃), 17.86 (d, *J*_{C-P} = 18.9 Hz, CHCH₃); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 5.73, 5.68; HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₃₈H₃₆FeP₂ 610.1642; Found: 610.1627.

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Supplementary data

Supplementary data (The crystal structure of compound **3u** and **3w** has been deposited at the Cambridge Crystallographic Data Centre (<u>http://www.ccdc.cam.ac.uk/</u>) with deposition number

CCDC 1509037 and 1509038) associated with this article can be MAN Xia, YR Hu, F. D.; Liu, Z. X.; Qu, P. Y.; Ge, R.; Ma, C.; found in the online version, at http://xx. Zhang, Y.; Wang, J. B. *Org. Lett.* 2013, *15*, 1784-1787.

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