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Stereoselective Synthesis of *o*-Bromo (or Iodo)aryl P-Chirogenic Phosphines Based on Aryne Chemistry

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ABSTRACT

The efficient synthesis of chiral or achiral tertiary phosphines bearing an *o*-bromo (or iodo)aryl substituent, is described. The key step of this synthesis is based on the reaction of a secondary phosphine borane with the 1,2-dibromo- (or diiodo)arene, owing to the formation *in situ* of an aryne species in presence of *n*-butyllithium. When P-chirogenic secondary phosphine boranes were used, the

corresponding *o*-halogeno-arylphosphine boranes were obtained without racemization, in moderate to good yields and with e.e. up to 99%. The stereochemistry of the reaction with complete retention of the configuration at the P-atom, has been established by X-ray structures of P-chirogenic *o*-halogenophenyl phosphine borane complexes. The decomplexation of the borane was easily achieved without racemization using DABCO®, to afford in high yields the free *o*-halogeno-arylphosphines.

KEYWORDS

P-chirogenic phosphines; secondary phosphine boranes: *o*-halogeno arylphosphines; aryne chemistry; stereoselective synthesis.

Introduction

Chiral tertiary phosphines are the most popular organophosphorus compounds finding numerous applications as ligands in asymmetric catalyzed reactions by transition metal complexes,[1,2] or for coordinating polymers,[3] as precursors of quaternary phosphonium salts[4] or Wittig reagents,[5] and also as organocatalysts.[6] The interest for the phosphines comes from their easy structural designing by electrophilic or nucleophilic reactions on the phosphorus atom, or in α or β position of an aliphatic substituent.[2,7,8] Despite of this abundant chemistry, the synthesis of P-chirogenic phosphines such as **1**, bearing a heteroatom or a functional group in *ortho* position, remains a challenge and very few stereoselective methods lead to these compounds.

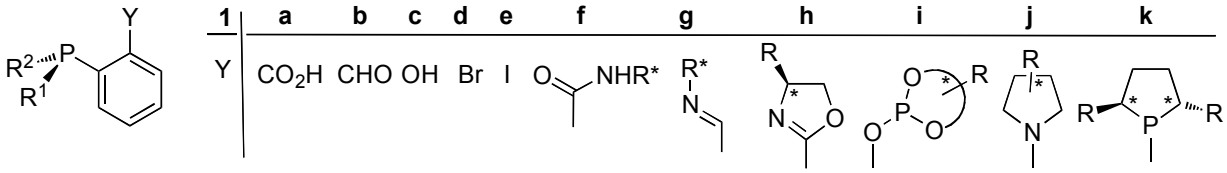


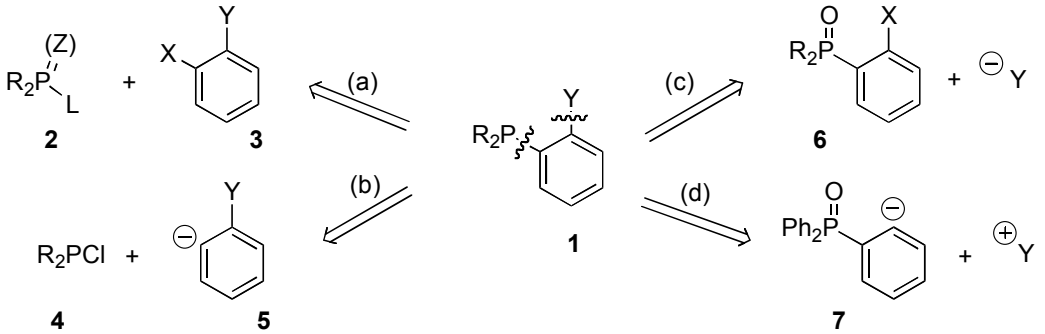
Figure 1. Different types of *o*-substituted or *o*-functionalized chiral phosphines

Mostly, the chiral *o*-functionalized phosphines derive from the diphenylphosphinoaryl precursor **1a-d** with R^1= R^2= Ph, and bear the chirality on the carbon backbone. Such phosphines have hybrid structures

with chelating arms such as **1f-k**: amide,[9] imine,[10] oxazoline[11] or heterocycle,[12] phosphinite,[13] amino[14] or phospholano[15] group (Figure 1). The hybrid chiral ligands **1f-k** have widely demonstrated their efficiency in numerous asymmetric reactions catalyzed by transition-metal complexes.[1,2,9-15] In addition, *o*-functionalized phosphines **1** can be used as reagent for chemoselective coupling of biomolecular fragments by Staudinger ligation,[16] and as directing group in stereoselective hydroformylation of acyclic substrates.[17] Moreover, the *o*-halogeno phosphines **1d**,**e**, or their oxide derivatives, can also be used for the preparation of challenging ligands such as ambiphilic phosphine-boranes,[18] or bearing a bisaryl as substituent or bridge.[19,20]

Usually, the *o*-functionalized phosphines **1** are obtained using two strategies involving P-C or C-Y bond formation (Scheme 1). In the first case, the synthesis is based either on the coupling reaction of secondary phosphine derivatives **2** with an activated aromatic precursor **3**, by direct substitution,[11a,h,14b-e,20] or catalysis with a transition metal complex[11h,12b,15f,19b,21] (Scheme 1a), or the reaction of a chlorophosphine **4** with an organometallic aryl reagent **5**[11a,d,12a,14a] (Scheme 1b). In the second case, the *o*-functionalization of a phosphine can also be achieved from the corresponding oxide precursor, either by direct substitution of **6** bearing a leaving group X in *ortho* position[14b,c] (Scheme 1c), or by *o*-lithiation and then trapping of **7** by electrophilic reagent (Scheme 1d).[22]

Scheme 1. Methods for the synthesis of *o*-functionalized phosphines



X = F, Br, OTf, OMe ; Z = lone pair, O; L = H, TMS, (*n*-Bu)$_3$Sn
Y = Br, I, CHO, oxazoline, imino, heterocyclic, amino, phosphino...

In the last decades, the interest of phosphines bearing chirality on the phosphorus atom (P-chirogenic), greatly expanded thanks to the development of new stereoselective synthetic methods, using the chemistry of their borane complexes.[2,8,23,24] However, the stereoselective synthesis of *o*-

functionalized P-chirogenic phosphines is scarcely reported,[25] because the methods (a) and (b) reported on Scheme 1, involve either a racemization of the P-center or a lack of reactivity of the electrophilic P-building blocks.[26] To date, only the enantioselective *o*-lithiation/ functionalization of prochiral organophosphorus compounds in presence of sparteine has been described, but in the phosphinamide series.[27] On another hand, the P-chirogenic *o*-hydroxy derivatives **1c** (Y= OH) can be stereoselectively prepared by the ephedrine-borane complex methodology, either *via* a Fries rearrangement[28] of an aryl phosphinite, or using an *o*-lithiated phenate reagent.[29]

Consequently, the development of stereoselective synthesis of *o*-functionalized P-chirogenic phosphines **1** must be mainly based on the strategies (b) and (c) (Scheme 1), and consequently the access to the *o*-halogenophenyl phosphines **1d**,**e**, as chiral synthons (Figure 1).

We recently described an efficient stereoselective synthesis of P-chirogenic quaternary phosphonium triflates, by quaternization of phosphines using aryne chemistry.[4d] Arynes (1,2-dehydrobenzenes) are highly reactive intermediates which have attracted increasing interest in recent past, due to their wide synthetic applications.[30] They undergo numerous reactions such as aryl coupling, Diels-Alder, 1,3-dipolar cycloaddition, transition metal catalyzed reactions,[30,31] and addition with a variety of S-, N-, O-, S-, Se- and P-nucleophiles.[4d,32,33]

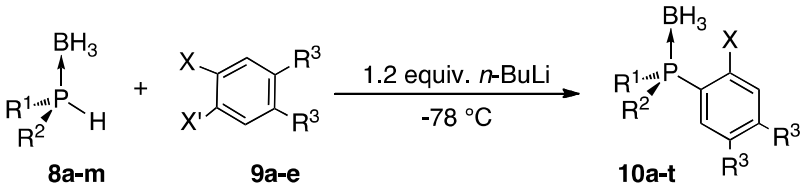
As the reaction of secondary phosphines with an aryne led easily to the quaternary phosphonium salt,[4d] we report herein the use of their borane complexes for the efficient synthesis of *o*-bromo- or *o*-iodoarylphosphines, using the aryne chemistry.[34] In addition, the stereoselective synthesis of P-chirogenic *o*-bromo- or *o*-iodoarylphosphines is described without racemization, using chiral secondary phosphine borane.

Results and discussion

In our laboratory, we have recently developed the stereoselective synthesis of P-chirogenic secondary phosphine boranes **8**, using the ephedrine methodology.[24b] After deprotonation with *n*-butyllithium, resulting phosphides react with different primary alkylhalides at -78°C, to afford stereoselectively the corresponding tertiary P-chirogenic phosphine boranes, with e.e. up to 99%.[24b] In continuation of this

work, we have extended this reaction to the preparation of P-chirogenic arylphosphines bearing functional groups in *ortho* position, using the arynes as electrophilic reagents. Firstly, we investigated the reaction of secondary chiral and achiral phosphine boranes **8** with 1,2-dihalogenoarene **9**, as aryne precursor.[35] The results are summarized in Table 1.

Table 1. Synthesis of *o*-halogenophenylphosphine boranes **10** from secondary phosphine boranes **8**



8a-m **9a-e** **10a-t**

entry	$R^1R^2P(BH_3)H$			ArXX'			$R^1R^2P(BH_3)o$-XAr		
		R^1	R^2		X,X'	R^3		Yields (%) [a]	ee (%)[b]
1	**8a**	Ph	Ph	**9a**	Br	H	**10a**	75	-
2	**8b**	*c*-Hex	*c*-Hex	**9a**	Br	H	**10b**	63	-
3	**8c**	Me	Me	**9a**	Br	H	**10c**	42	-
4	**8d**	*i*-Pr	*i*-Pr	**9a**	Br	H	**10d**	55	-
5	(±)-**8e**	Ph	*p*-An	**9a**	Br	H	**(±)-10e**	60	-
6	(±)-**8f**	Ph	*t*-Bu	**9a**	Br	H	**(±)-10f**	34	-
7	**8g**	*o*-Tol	*o*-Tol	**9a**	Br	H	**10g**	40[c]	-
8	**8h**	*t*-Bu	*t*-Bu	**9a**	Br	H	**10h**	0	-
9	**8a**	Ph	Ph	**9b**	Br	Me	**10i**	56	-
10	**8b**	*c*-Hex	*c*-Hex	**9b**	Br	Me	**10j**	53	-
11	**8a**	Ph	Ph	**9c**	I	H	**10k**	50	-
12	**8b**	*c*-Hex	*c*-Hex	**9c**	I	H	**10l**	56	-
13	**8a**	Ph	Ph	**9d**	Cl	H	**10m**	0	-
14	**8a**	Ph	Ph	**9e**	I,Br	H	**10a**,**10k**[h]	72	-
15	(*S*)-**8i**[d]	*o*-An	Ph	**9a**	Br	H	**(*R*)-10n**	53	95
16	(*R*)-**8i**[e]	Ph	*o*-An	**9a**	Br	H	**(*S*)-10n**	53	95
17	(*S*)-**8i**[d]	*o*-An	Ph	**9c**	I	H	**(*R*)-10o**	42[c]	95[f]
18	(*S*)-**8j**[d]	Fc	Ph	**9a**	Br	H	**(*S*)-10p**	47	99[g]
19	(*R*)-**8j**[e]	Ph	Fc	**9a**	Br	H	**(*R*)-10p**	50	99[g]
20	(*S*)-**8j**[d]	Fc	Ph	**9c**	I	H	**(*S*)-10q**	55	99[g]
21	(*R*)-**8k**[d]	*i*-Pr	Ph	**9a**	Br	H	(*S*)-**10r**	48	95
22	(*S*)-**8k**[e]	Ph	*i*-Pr	**9a**	Br	H	(*R*)-**10r**	48	95
23	(*R*)-**8l**[d]	*c*-Hex	Ph	**9a**	Br	H	(*S*)-**10s**	47	95

24	(*S*)-**8l**[e]	Ph	*c*-Hex	**9a**	Br	H	(*R*)-**10s**	63	95
25	(*R*)-**8m**[e]	Ph	*o*-Tol	**9a**	Br	H	(*S*)-**10t**	66[c]	73

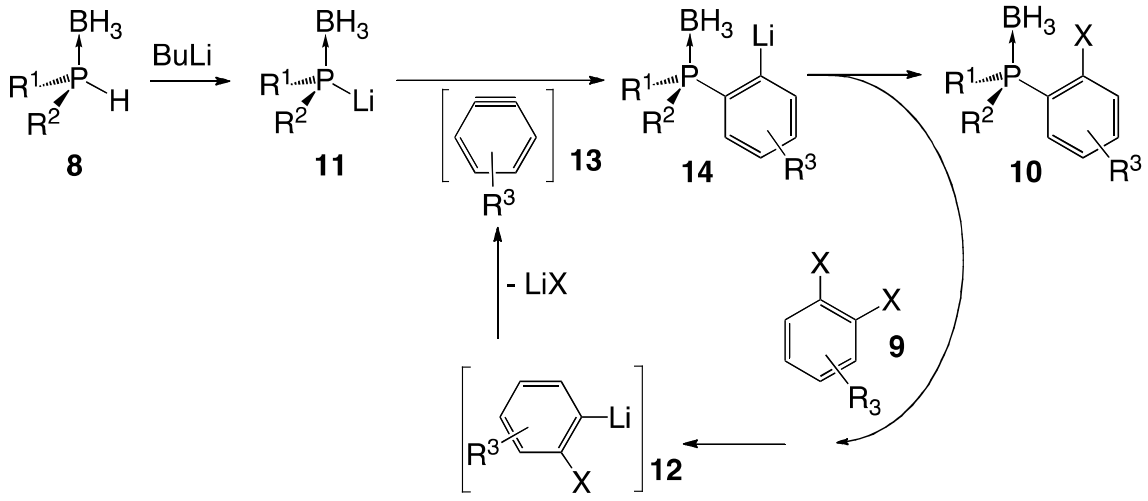
[a] Isolated yields. [b] Determined by HPLC on chiral column. [c] Isolated after decomplexation. [d] Prepared from (-)-ephedrine. [e] prepared from (+)-ephedrine. [f] ee values determined by ^{1}H and/or ^{31}P NMR of the corresponding phosphine oxide with (*R*)-3,5-dinitro-*N*-(1-phenyl-ethyl)-benzamide as chiral reagent. [g] After recrystallization. [h] **10a**, **10k** ratio 1 : 9 determined by ^{31}P NMR.

The reaction of the secondary alkyl- or arylphosphine boranes **8a-f** with *n*-BuLi (1.2 equiv.) and dibromobenzene **9a** (1.4 equiv.), affords the corresponding *o*-bromophenylphosphine boranes **10a-f** in satisfying to good yield, ranging from 34 to 75% (entries 1-6).[35] When the di(*o*-tolyl)phosphine borane **8g** reacts with **9a**, a mixture of *o*-bromophenylphosphine borane **10g** and the corresponding free phosphine is obtained (entry 7). The steric hindrance of the phosphine boranes **8g** and **10g**, due to the tolyl and bromophenyl substituents, explains the moderate yield and the partial decomplexation of the borane, as already observed with a tolylphosphine borane.[36] This is again demonstrated by the use of the di(*tert*-butyl)phosphine borane **8h**, which does not afford the product **10h**, in these conditions (entry 8). On the other hand, in these conditions the reaction of the diphenylphosphine borane **8a** (or dicyclohexylphosphine borane **8b**) with the 4,5-dibromo-*o*-xylene **9b**, leads under these conditions to the phosphine boranes **10i (**or **10j**) in 56% and 53% yield, respectively (entries 9,10). In addition, the secondary phosphine boranes **8a** (or **8b**) react with 1,2 diiodobenzene **9c**, to afford the corresponding *o*-iodophenylphosphine boranes **10k** (or **10l**), in 50 and 56% yield, respectively (entries 11,12).

The synthesis of the *o*-halogenophenylphosphine boranes **10** was explained by a mechanism involving an aryne intermediate (Scheme 2). Thus, the reaction begins by the deprotonation of the secondary phosphine borane **8** giving the corresponding phosphide **11**, while the excess of *n*-BuLi (0.2 equiv.) promotes the halogen-metal exchange with the 1,2-dihalogenoarene **9**, generating the anion **12** and then the aryne **13** by LiX elimination (Scheme 2). The reaction of the phosphide borane **11** with the aryne **13** leads then to the *o*-lithiated phosphine borane **14**, which gives a new halogen-metal exchange with the 1,2-dihalogenobenzene **9** to afford on one hand, the corresponding *o*-halophenylphosphine borane **10**, and on the other hand the aryne **13** from the anion **12**, continuing thus the reaction. This mechanism was supported by the absence of reaction without an excess of base, or by using the 1,2-dichlorobenzene **9d**, because no halogen-metal exchange occurs under these conditions (entry 13). A

further evidence of the aryne mechanism is given by the use of 1-bromo-2-iodobenzene **9e**, which leads to a mixture of *o*-bromo and *o*-iodophenylphosphine borane **10a** and **10k** in 1 : 9 ratio, proving thus a better halogen-metal exchange of the anion **14** with the iodo than with the bromo substituent of the reagent **9e** (entry 14).

Scheme 2. Proposed mechanism for the formation of *o*-bromophosphine boranes **10**



Interestingly under these conditions, the P-chirogenic phosphine boranes **8i-m** reacted with the 1,2-dihalogenobenzene **9a (**or **9c**) to afford the corresponding *o*-halogenophenyl phosphine boranes **10n-t** in 42-66% yields, and with enantiomeric excesses up to 99 % (entries 15-25). The analysis by HPLC on chiral column of the starting secondary phosphine boranes **8** and their *o*-halogenophenyl derivatives **10**, proves that the reaction proceeds without racemisation. As typical example, the (*S*)-ferrocenylphenylphosphine borane **8j** (94% e.e.) reacts with the 1,2-dibromobenzene **9a** to afford the (*S*)-*o*-bromophenylferrocenylphosphine borane **10p** in 47% yield and an enantiomeric purity superior to 99% after recrystallization (entry 18). Crystals of **10p** were grown from methylene chloride/hexane as solvent and its ORTEP drawing is shown in Figure 2. The crystal contains discrete molecules of **10p** with normal non-bonded interactions. The distorted tetrahedral geometry of the P atom is typical of phosphine borane adducts. The Cp rings are parallel within 0.93(22)° and the (*S*)-configuration of the P atoms is supported by refinement of the Flack x parameter. Consequently, the (*S*)-absolute configurations of the starting secondary phosphine borane **8j** and the product **10p**, proves a reaction mechanism with retention of configuration at the P-center.

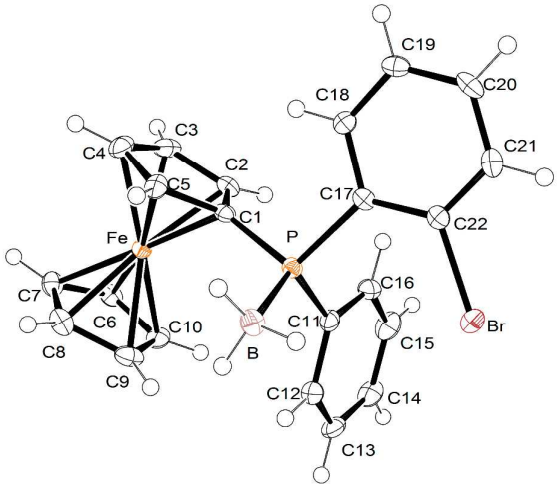


Figure 2. ORTEP[37] view of (*S*)-**10p** showing thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å], angles [°] and dihedral angles [°]: P–B 1.930(3), C1–P 1.784(3), C11–P 1.811 (3), C17–P 1.831(3); C1–P–C11 104.44(13), C1–P–C17 103.29(13), C11–P–C17 107.12(13), C1–P–B 112.53(15); C2–C1–P–B -161.56(25), C12–C11–P–B (19.58(30), C22–C17–P–B 70.80(28).

As well, in the case of the reaction of the ferrocenylphenylphosphine borane (*S*)-**8j** having 94% e.e. with the 1,2-diodobenzene **9c**, the *o*-iodophenylphosphine borane **10q** is obtained in 55% yield and with an enantiomeric excess of 99%, after recrystallization (entry 20). The structure of **10q** has also been determined by single crystal X-ray diffraction, and is similar to the bromo derivatives **10p** (Figure 3). The crystal contains discrete molecules of compound **10q** with normal non-bonded interactions. The distorted tetrahedral geometry of the P-atom is typical of phosphine borane adducts. The Cp rings are parallel within 0.76(31)° and the (*S*)-configuration of the P-atom is supported by refinement of the Flack x parameter.

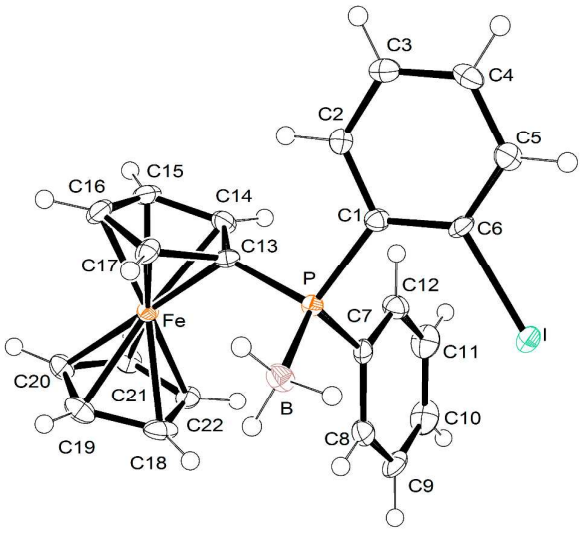
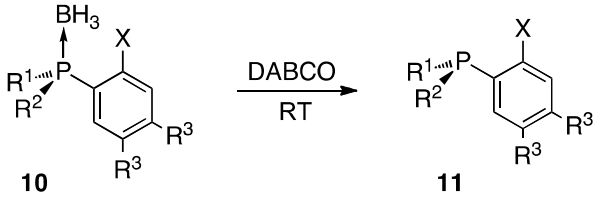


Figure 3. ORTEP[37] view of compound (*S*)-**10q** showing thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å], angles [°] and dihedral angles [°]: P–B 1.931(5), C1–P 1.828(4), C13–P 1.791 (4), C7–P 1.814 (4); C13–P–C1 104.11(18), C7–P–C1 106.89(18), C13–P–C7 105.03(18), C1–P–B 110.9(2); C2–C1–P–B -103.95(35), C8–C7–P–B 14.26(41), C17–C13–P–B 16.76(40).

The decomplexation of the *o*-halogenophenylphosphine borane **10** was achieved using DABCO®, and affords the corresponding free phosphines **11** in good to excellent yields and with enantiomeric excess up to 99%, after recrystallization. The results are reported in the Table 2.

Table 2. Decomplexation in free *o*-halogenoaryl phosphines **11**



10 **11**

		Phosphine boranes **10**				Phosphines **11**		
entry		R^1	R^2	R^3	X		Rdt (%)	ee (%)
1	**10a**	Ph	Ph	H	Br	**11a**	79	-
2	**10g**	*o*-Tol	*o*-Tol	H	Br	**11b**	40[a]	-
3	**10i**	Ph	Ph	Me	Br	**11c**	84	-
4	**10k**	Ph	Ph	H	I	**11d**	83	-
5	(*R*)-**10n**	*o*-An	Ph	H	Br	(*R*)-**11e**	90	99
6	(*R*)-**10o**	*o*-An	Ph	H	I	(*R*)-**11f**	42[b]	95
7	(*S*)-**10p**	Fc	Ph	H	Br	(*S*)-**11g**	75	99

8	**(*S*)-10r**	*i*-Pr	Ph	H	Br	**(*S*)-11h**	82	95
9	(*S*)-**10t**	Ph	*o*-Tol	H	Br	(*S*)-**11i**	66[c]	73

[a] Overall yield starting from secondary phosphine borane **8g**. [b] Overall yield starting from secondary phosphine borane **8i**. [c] Overall yield starting from secondary phosphine borane **8m**.

Interestingly, the free phosphine (*R*)-**11e** has been obtained in 45 % yield and with 99% e.e., by a two steps reaction sequence starting from the secondary phosphine borane (*S*)-**8i**, *i.e.* reaction with the 1,2-bromobenzene **9a** and then decomplexation. The structure of the (*R*)-(2-bromophenyl)-(2-methoxyphenyl)-phenylphosphine **11e** has been determined by single crystal X-ray diffraction (Figure 4). The compound crystallizes in a non-centrosymmetric space group $P2_1$ with an absolute (*R*)-configuration on the phosphorus atom. The structure adopts a propeller-shaped conformation with the phenyl rings twisted away to the base of the PC_3 pyramid by 59.49(10), 44.44(11) and 43.56(11)°. The bromide is located *cis* to the phosphorus lone pair. The P-C bond lengths and the C-P-C bond angles, mean value 1.841(3) Å and 101.4(6)°, are similar to those recorded for triphenylphosphine, mean value 1.831(2) Å and 102.8(5)°.[38] The molecules are linked in the crystal lattice through edge-to-face C-H…π interactions between the phenyl groups.[39]

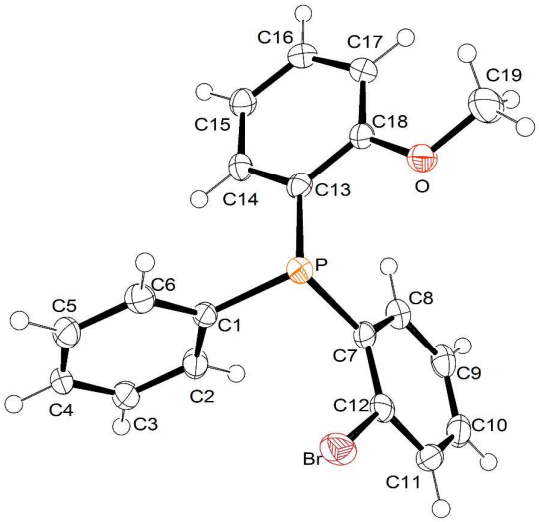
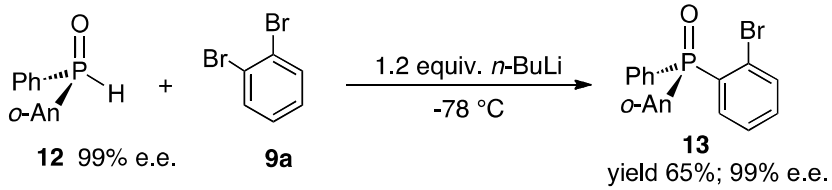


Figure 4. ORTEP[37] view of (*R*)-(2-bromophenyl)-(2-methoxyphenyl)-phenylphosphine **11e** showing thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å], angles [°] and dihedral angles [°]: C1–P 1.838(3); C7–P 1.844(3), C13–P 1.841(3); C1–P–C7 100.78(12), C1–P–C13

102.08(12), C13–P–C7 101.47(12); O–C18–C13–P 6.08(33), Br–C12–C7–P 0.63(32), C6–C1–P–C13 -96.74(22).

Finally, this synthetic strategy was preliminary extended to secondary phosphine oxide. Interestingly in the conditions where the aryne is promoted from the 1,2-dibromobenzene **9a** by reaction with the *n*-butyllithium, the P-chirogenic phosphine oxide **12** leads to the corresponding *o*-bromophenyl phosphine oxide **13** in 65% yield (Scheme 3). The analysis by HPLC on chiral column of the starting secondary phosphine boranes **12** and the *o*-bromophenyl derivative **13**, proves that the reaction proceeds without racemization.

Scheme 3. (*S*)-*o*-Anisyl-o-bromophenylphenylphosphine oxide **13** from the secondary phosphine oxide **12**.



12 99% e.e. **9a** **13** yield 65%; 99% e.e.

Conclusion

In conclusion, we have developed an efficient synthesis of *o*-halogenoaryl tertiary phosphines. This synthesis is based on the reaction between a secondary phosphine borane and an aryne, generated *in situ* from 1,2-dibromo- or 1,2-diiodoarene and *n*-butyllithium, as base. Interestingly, under these conditions, the use of P-chirogenic secondary phosphine boranes led to the corresponding *o*-bromo- or *o*-iodoarylphosphine boranes in good yields and with enantiomeric excesses up to 99%. The stereochemistry of the reaction with retention at the P-atom has been determined by the X-ray structure of the P-chirogenic phosphine boranes. The free *o*-halogenoarylphosphines are obtained in yields up to 90% and without racemization, by decomplexation of their borane complexes using the DABCO® at room temperature. Interestingly, the free *o*-halogenoarylphosphines can be prepared by a two steps reaction sequence starting from the secondary phosphine borane, *i.e.* reaction with the *n*-butyllithium and the1,2-halogenobenzene, and then decomplexation. The interest of these compounds for the

preparation of various chiral and achiral *o*-functionalized phosphines useful in catalysis and organocatalysis, will prompt further exploration in other development soon.

EXPERIMENTAL SECTION

General experimental methods. All reactions were carried out using standard Schlenk techniques under inert atmosphere. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF), toluene, diethyl ether (Et_2O) were distilled from sodium/benzophenone and stored under argon. Methyl alcohol (MeOH) was distilled from sodium. Methylene chloride (CH_2Cl_2) was distilled from CaH_2 under argon prior to use. Hexane and 2-propanol for HPLC were of chromatographic grade and used without purification. *n*-butyllithium, 1,2-dibromobenzene, 1,2-diiodobenzene, 4,5-dibromo-*o*-xylene, borane-dimethylsulfur complex, DABCO® and diphenyl-, di-*o*-tolyl-, di-*c*-hexyl-, di-*i*-propyl, *t*-butylphenylphosphine were purchased from commercial sources and used without purification. The secondary phosphine borane **8** which were prepared by reaction of the corresponding secondary phosphine with borane dimethylsulfure complex in THF, are in agreement with the data of the literature.[40] The dimethylphosphine borane **8b**, which was prepared by reaction of dimethylchlorophosphine with $LiAlH_4$, then complexation with borane dimethylsulfure, corresponds to what is described in literature.[40b] The P-chirogenic secondary phosphine boranes **8i-m**, were prepared using the ephedrine methodology.[24b,41] The *o*-anisylphenylphosphine oxide **12** was prepared according to the literature.[42] Reactions were monitored by thin-layer chromatography (TLC) using 0.25 mm E. Merck precoated silica gel plates. Flash chromatography was performed with the indicated solvents using silica gel 60 (60AAC, 35-70 μm; SDS). ^1H and (^1H decoupled) ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded at 500 or 300 MHz and 125 or 75.5 MHz and 121 or 202 MHz, respectively at ambient temperature using TMS as internal reference for ^1H and ^{13}C NMR, and 85% phosphoric acid as external reference for ^{31}P NMR. Data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad singlet, coupling constant(s) in Hertz, integration. HPLC analyses were performed on a chromatograph equipped with a UV detector at λ = 210 nm and λ = 254 nm. Infra-red spectra were recorded on a FT-IR instrument. Melting points were measured on a Kofler

melting points apparatus and are uncorrected. Optical rotation values were measured on polarimeter at 589 nm (sodium lamp). High Resolution Mass Spectra (HRMS) were recorded on mass spectrometer under electron spray ionization (ESI) conditions, with a micro-Q-TOF or Orbitrap detector.

Crystal Structure Determination

Diffraction data were collected on a diffractometer equipped with a nitrogen jet stream low-temperature system. The X-ray source was graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) from a sealed tube. The lattice parameters were obtained by least-squares fit to the optimized setting angles of the entire set of collected reflections. No significant temperature drift was observed during the data collections. Data were reduced by using DENZO[43] software without applying absorption corrections; the missing absorption corrections were partially compensated by the data scaling procedure in the data reduction. Excepted for compound **10b** multi-scan absorption corrections were applied.[44] The structure was solved by direct methods using the SIR92[45] program. Refinements were carried out by full-matrix least-squares on F^2 using the SHELXL97[46] program on the complete set of reflections. Absolute configurations of all compounds were determined reliably from anomalous scattering, using the Flack method.[47] For all compound, anisotropic thermal parameters were used for non-hydrogen atoms. All H atoms, on carbon atom, were placed at calculated positions using a riding model with C-H = 0.95 Å (aromatic), 0.98 Å (methyl), 0.99 Å (methylene) or 1.00 Å (methine) with $U_{iso}(H) = 1.2U_{eq}(CH)$, $U_{iso}(H) = 1.5U_{eq}(CH_3)$ or $U_{iso}(H) = 1.2U_{eq}(CH_2)$. All H atoms, on boron atom, were placed at calculated positions using a riding model with B-H = 0.98 Å with $U_{iso}(H) = 1.5U_{eq}(BH_3)$.

Preparation of (4-methoxyphenyl)-phenylphosphine borane (8e).

(4-Methoxyphenyl)-phenylphosphine borane was prepared according to a method adapted from Imamoto.[48]

To a solution of dichlorophenylphosphine (5.37 g, 30.0 mmol) in THF was added under argon, at -78 °C over a period of 3 hours a 0.25 M solution of 4-methoxyphenylmagnesium bromide in THF (120.0 mL, 30.0 mmol) (prepared by dilution of a commercially available 1.0 M solution). Then a 1.0 M solution of $LiAlH_4$ in THF (30.0 mL, 30.0 mmol) was added dropwise at -78 °C and the mixture was

allowed to reach 25 °C. After 2 additional hours stirring at 25 °C, a 1.0 M solution of BH_3·THF in THF (36.0 mL, 36.0 mmol) was added dropwise. Ten minutes later, the mixture was poured into a vigorously stirred mixture of 1 M HCl (300mL), CH_2Cl_2 (300 mL) and ice (300 g). At 25 °C, the mixture was diluted with CH_2Cl_2 (300 mL) and the aqueous layer was separated and extracted with CH_2Cl_2 (2 × 150 mL). All the organic layers were combined, dried over Na_2SO_4 and evaporated under reduced pressure. Purification of the residue by column chromatography (cyclohexane/CH_2Cl_2 6:4) provided (4-methoxyphenyl)-phenylphosphine borane as a colourless solid. Yield 19 % (1.31 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (br q, *J* = 114 Hz, 3H), 3.84 (s, 3 H), 6.29 (dq, *J* = 378, 6.9 Hz, 1H), 6.95-6.99 (m, 2H), 7.40-7.53 (m, 3H), 7.57-7.67 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.4, 114.8 (d, *J* = 11.2 Hz), 116.4 (d, *J* = 61.5 Hz), 127.1 (d, *J* = 57.2 Hz), 129.0 (d, *J* = 10.3 Hz), 131.4 (d, *J* = 2.5 Hz), 132.7 (d, *J* = 9.4 Hz), 134.9 (d, *J* = 10.5 Hz), 162.4 (d, *J* = 2.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ - 0.7 (br.s).

General procedure for the synthesis of *o*-halogenoarylphosphine borane (10). To a solution of secondary phosphine borane **8** (0.83 mmol) in dry THF (2 mL), was added *n*-BuLi (0.83 mmol) dropwise under argon at -78°C. The resulting solution was stirred at this temperature during one hour and 1,2-dihalogenoarene **9** (1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After one hour at -78°C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue, which was purified by column chromatography on silica gel and/or by recrystallization.

(2-Bromophenyl)-diphenylphosphine borane (10a)[49]. Purification: column chromatography (elution with 2:1 petroleum ether/ethyl acetate) and/or recrystallization in methylene chloride/hexane. Colourless solid; Yield 75% (0.22 g); mp 134-136°C; R_f 0.62 (petroleum ether/ethyl acetate 2:1); IR (neat) 3052, 2924, 2854, 2814, 2379, 2340, 1558, 1480, 1436, 1424, 1128, 1106, 1058, 1025, 998, 738, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.31 (m, 3H), 7.36-7.49 (m, 6H), 7.57-7.64 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 127.3 (d, *J* = 9.1 Hz), 128.0 (d, *J* = 5.9 Hz), 128.1 (d, *J* = 58.7 Hz), 128.8

(d, J = 10.4 Hz), 130.1 (d, J = 57.3 Hz), 131.3 (d, J = 2.4 Hz), 132.7 (d, J = 2.1 Hz), 133.3 (d, J = 9.6 Hz), 135.1 (d, J = 5.9 Hz), 136.6 (d, J = 10.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 26.6 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{17}PBBrNa$ $[M+Na]^+$ 377.0240, found 377.0227; Anal calcd for $C_{18}H_{17}PBBr$: C, 60.90; H, 4.83; found: C, 61.06; H, 5.13.

(2-Bromophenyl)-dicyclohexylphosphine borane (10b). The same general procedure as above was used except that after adding *n*-BuLi at -78°C, the resulting solution was stirred 30 minutes at this temperature then 30 minutes at room temperature. Purification: column chromatography (elution with 3:1 petroleum ether/methylene chloride) and/or recrystallization in methylene chloride/methyl alcohol. Colourless solid; Yield 63% (0.19 g); mp 134-136°C; R_f 0.24 (petroleum ether/methylene chloride 3:1); IR(neat) 2930, 2851, 2379, 1446, 1418, 1274, 1061, 890, 854, 758, 736 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16-1.37 (m, 10H), 1.55-1.70 (m, 6H), 1.80-1.85 (m, 2H), 1.93-1.97 (m, 2H), 2.77-2.85 (m, 2H), 7.27-7.40 (m, 2H), 7.60 (dt, J = 1.8, 7.7 Hz), 8.07 (ddd, J = 1.7, 7.6, 12.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.7 (d, J = 1.3 Hz), 26.8 (d, J = 9.5 Hz), 27.0 (d, J = 8.5 Hz), 27.8, 28.8, 32.9 (d, J = 32.3 Hz), 127.1 (d, J = 3.1 Hz), 127.3 (d, J = 10.9 Hz), 128.0 (d, J = 46.3 Hz), 132.4 (d, J = 2.1 Hz), 134.0 (d, J = 4.4 Hz), 140.1 (d, J = 15.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 40.9 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{29}PBrBNa$ $[M+Na]^+$ 389.1179, found 389.1157; Anal calcd for $C_{18}H_{29}PBrB$: C, 58.89; H, 7.96; found: C, 58.68; H, 8.29.

(2-Bromophenyl)-dimethylphosphine borane (10c). The same general procedure as above was used except that after adding *n*-BuLi at -78°C, the resulting solution was stirred 30 minutes at this temperature then 30 minutes at room temperature. Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). Colourless oil; Yield 42% (0.080 g); R_f 0.49 (petroleum ether/ethyl acetate 3:1); IR (neat) 3077, 2375, 2360, 2335, 1580, 1559, 1453, 1413, 1302, 1289, 1273, 1256, 1144, 1109, 1071, 1022, 946, 919, 755 cm^{-1}; ^{1}H NMR (300 MHz, Acetone d^6) δ 1.55 (d, J = 10.4 Hz, 6H), 7.24-7.33 (m, 2H), 7.52-7.59 (m, 1H), 7.70-7.77 (m, 1H); ^{13}C NMR (75.5 MHz, Acetone d^6) δ 12.0 (d, J = 40.1 Hz), 127.5, 128.6 (d, J = 10.9 Hz), 131.8 (d, J = 50.6 Hz), 134.2 (d, J = 2.2 Hz), 135.4 (d, J = 4.7 Hz), 137.0 (d, J = 15.7 Hz); ^{31}P NMR (121 MHz, Acetone d^6) δ 11.1-12.5 (m); HRMS (ESI-Q-TOF)

calcd for $C_8H_{13}PBrBNa$ $[M+Na]^+$ 252.9925, found 252.9923; Anal calcd for$C_8H_{13}PBrB$: C, 41.62; H, 5.68; found: C, 41.29; H, 6.07.

(2-Bromophenyl)-diisopropylphosphine borane (10d). The same general procedure as above was used except that after adding *n*-BuLi at -78°C, the resulting solution was stirred 30 minutes at this temperature then 30 minutes at room temperature. Purification: column chromatography (elution with 3:1 petroleum ether/methylene chloride). Colourless solid; Yield 55% (0.13 g); mp 92-94°C; R_f 0.26 (petroleum ether/methylene chloride 3:1); IR (neat) 2974, 2932, 2871, 2393, 2373, 2349, 1574, 1557, 1453, 1422, 1389, 1370, 1261, 1110, 1071, 1046, 1021, 931 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (dd, *J* = 7.1, 15.9 Hz, 6H), 1.27 (dd, *J* = 7.0, 15.8 Hz, 6H), 2.95-3.09 (m, 2H), 7.22-7.35 (m, 2H), 7.55 (tt, *J* = 1.8, 7.7 Hz, 1H), 8.04 (ddd, *J* = 1.5, 7.5, 12.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.5 (d, *J* = 2.8 Hz), 18.7, 22.8 (d, *J* = 33.1 Hz) 126.7 (d, *J* = 3.1 Hz), 127.3 (d, *J* = 10.9 Hz), 128.7 (d, *J* = 46.6 Hz), 132.6 (d, *J* = 2.2 Hz), 134.2 (d, *J* = 4.4 Hz), 139.8 (d, *J* = 14.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 48.4-49.9 (m); HRMS (ESI-Q-TOF) calcd for $C_{12}H_{21}PBrBNa$ $[M+Na]^+$ 309.0552, found 309.0545; Anal calcd for$C_{12}H_{21}PBrB$: C, 50.22; H, 7.38; found: C, 50.57; H, 7.53.

(±)-(2-Bromophenyl)-(4-methoxyphenyl)-phenylphosphine borane (10e). Purification by column chromatography with a mixture cyclohexane/CH_2Cl_2 6:4, as eluent. Analytical pure sample can be obtained by crystallization from EtOAc at -20°C. Colourless solid; Yield 60 % (0.19 g); mp 133-136°C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.60-2.10 (m, 3H), 3.85 (s, 3H), 6.96-7.00 (m, 2H), 7.21-7.37 (m, 3H), 7.41-7.55 (m, 3H), 7.57-7.69 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 114.5 (d, *J* = 11.2 Hz), 118.5 (d, *J* = 63.2 Hz), 127.3 (d, *J* = 8.9 Hz), 127.9 (d, *J* = 6.0 Hz), 128.8 (d, *J* = 58.9 Hz), 128.8 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 57.2 Hz), 131.1 (d, *J* = 2.3 Hz), 132.6 (d, *J* = 2.0 Hz), 133.1 (d, *J* = 9.6 Hz), 135.1 (d, *J* = 4.4 Hz), 135.2 (d, *J* = 10.7 Hz), 136.4 (d, *J* = 9.8 Hz), 162.1 (d, *J* = 2.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.3 (br.s). Anal. calcd for $C_{19}H_{19}BBrOP$: C, 59.27; H, 4.97, found: C, 59.17; H, 4.91.

(±)-2-Bromophenyl)-*tert*-butyl-phenylphosphine borane (10f). Purification by column chromatography with a mixture cyclohexane/CH_2Cl_2 8 : 2 as eluent, followed by crystallization from acetonitrile. Colourless solid; Yield 34% (0.095 g); mp 134-136°C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.40-

1.70 (m, 3H), 1.44 (d, J = 14.1 Hz, 9H), 7.31 (br t, J = 7.6 Hz, 1H), 7.37-7.50 (m, 4H), 7.58-7.67 (m, 3H), 8.10 (ddd, J = 10.5, 7.8, 1.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 27.5 (d, J = 2.2 Hz), 32.1 (d, J = 29.5 Hz), 126.7 (d, J = 9.2 Hz), 128.1 (d, J = 1.0 Hz), 128.4 (d, J = 9.7 Hz), 128.9 (d, J = 53.1 Hz), 129.6 (d, J = 43.8 Hz), 130.4 (d, J = 2.2 Hz), 132.2 (d, J = 1.8 Hz), 132.9 (d, J = 8.1 Hz), 135.9 (d, J = 5.1 Hz), 137.0 (d, J = 10.7 Hz); ^{31}P (121 MHz, $CDCl_3$) δ 42.1 (br.s). Anal. calcd for $C_{16}H_{21}BBrP$: C, 57.36; H, 6.32, found: C, 57.54; H, 6.54.

(2-Bromo-4,5-dimethylphenyl)-diphenylphosphine borane (10i). To a solution of diphenylphosphine borane **8a** (0.17 g, 0.83 mmol) in dry THF (2 mL) was added dropwise under argon at -78°C *n*-BuLi (0.83 mmol). The resulting solution was stirred at this temperature during one hour and 4,5-dibromo-*o*-xylene **9b** (0.31 g, 1.16 mmol) was then added followed by *n*-BuLi (0.17 mmol). After stirring to room temperature during one hour, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue which was purified by column chromatography on silica gel using petroleum ether/methylene chloride 3:1 as eluent. Analytical pure sample can be obtained by recrystallization in methylene chloride/hexane. Colourless solid; Yield 56% (0.18 g); mp 152-154°C; R_f 0.45 (petroleum ether/ethyl acetate 3:1); IR (neat) 3050, 2986, 2946, 2917, 2417, 2388, 2357, 1588, 1481, 1471, 1436, 1343, 1136, 1125, 1102, 1062, 1028, 999, 923, 877, 749, 734, 701, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 3H, CH_3), 2.29 (s, 3H), 7.21 (d, J = 12.3 Hz), 7.43-7.56 (m, 7H), 7.65-7.72 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.4, 19.5, 124.7 (d, J = 4.4 Hz), 131.1 (d, J = 2.5 Hz), 133.2 (d, J = 9.6 Hz), 135.9 (d, J = 6.1 Hz), 136.3 (d, J = 9.9 Hz), 137.8 (d, J = 11.8 Hz), 142.6 (d, J = 2.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.5 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{20}H_{21}PBBrNa$ $[M+Na]^+$ 405.0553, found 405.0563; Anal calcd for $C_{20}H_{21}PBBr$: C, 62.71; H, 5.53; found: C, 62.86; H, 5.58.

(2-Bromo-4,5-dimethyl-phenyl)-dicyclohexylphosphine borane (10j). The same procedure as for **10i** was applied starting from dicyclohexylphosphine borane **8b** and 1,2-dibromo-*o*-xylene **9b**. Purification by column chromatography (elution with cyclohexane/CH_2Cl_2 8:2) followed by crystallization in acetonitrile. Colourless solid; Yield 53% (0.17 g); mp 164-166°C; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 0.00-1.30 (m, 3H), 1.10-1.76 (m, 16H), 1.76-1.87 (m, 2H), 1.87-1.99 (m, 2H), 2.23 (s, 3 H), 2.24 (s, 3H), 2.69-2.87 (m, 2H), 7.37 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 12.7 Hz, 1H); ^{13}C (75.5 MHz, $CDCl_3$) δ 19.1, 19.3, 25.8, 26.8-27.0 (m), 27.8, 28.7, 33.0 (d, *J* = 32.6 Hz), 123.8 (d, *J* = 2.8 Hz), 124.3 (d, *J* = 48.5 Hz), 135.0 (d, *J* = 4.9 Hz), 136.1 (d, *J* = 10.9 Hz), 140.7 (d, *J* = 15.0 Hz), 141.9 (d, *J* = 1.9 Hz); ^{31}P NMR (121, $CDCl_3$ MHz) δ 38.7 (br.s). Anal. calcd for $C_{20}H_{33}BBrP$: C, 60.79; H, 8.42, found: C, 60.41; H, 8.06.

(2-Iodophenyl)-diphenylphosphine borane (10k). The same general procedure as above was used, but using the diiodobenzene **9c**. Purification: column chromatography (elution with 1:1 petroleum ether/methylene chloride) and/or recrystallization in ethyl acetate. Colourless solid; Yield 50% (0.17 g); mp 182-184°C; R_f 0.45 (petroleum ether/methylene chloride 1:1); IR (neat) 3051, 2401, 2342, 2245, 1570, 1555, 1480, 1436, 1420, 1311, 1255, 1188, 1165, 1126, 1101, 1054, 1028, 999, 972, 737, 688 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13-7.19 (m, 1H), 7.20-7.27 (m, 1H), 7.33-7.40 (m, 1H), 7.46-7.60 (m, 6H), 7.68-7.75 (m, 4H), 8.03 (ddd, *J* = 1.1, 3.2, 7.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 101.2 (d, *J* = 8.4 Hz), 127.9 (d, *J* = 9.0 Hz), 128.1 (d, *J* = 58.8 Hz), 128.9 (d, *J* = 10.2 Hz), 131.3 (d, *J* = 2.4 Hz), 132.3 (d, *J* = 2.2 Hz), 133.3 (d, *J* = 58.6 Hz), 133.6 (d, *J* = 9.5 Hz), 136.5 (d, *J* = 10.5 Hz), 142.7 (d, *J* = 7.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.5 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{17}IBPNa$ $[M+Na]^+$ 425.0101, found 425.0096; Anal calcd for $C_{18}H_{17}IBP$: C, 53.78; H, 4.26; found: C, 53.97; H, 4.36.

(2-Iodophenyl)-dicyclohexylphosphine borane (10l). The same general procedure as above was used, but using the diiodobenzene **9c**, except that after adding *n*-BuLi at -78°C, the resulting solution was stirred 30 minutes at this temperature then 30 minutes at room temperature. Purification: column chromatography (elution with 2:1 petroleum ether/methylene chloride). Colourless solid; Yield 56% (0.19 g); mp 144-146°C; R_f 0.33 (petroleum ether/methylene chloride 2:1); IR (neat) 2919, 2851, 2397, 2352, 1573, 1556, 1447, 1414, 1345, 1064, 1040, 1004, 918, 887, 852, 818, 762, 734, 714, 639 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.00-1.17 (m, 10H), 1.44-1.56 (m, 6H), 1.63-1.67 (m, 2H), 1.76-1.80 (m, 2H), 2.73-2.85 (m, 2H), 6.92 (tt, *J* = 1.5, 7.5 Hz, 1H), 7.22 (tt, *J* = 1.3, 7.5 Hz, 1H), 7.77 (dt, *J* = 1.5, 7.9 Hz, 1H), 7.86 (ddd, *J* = 0.9, 7.7, 12.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.7 (d, *J* = 1.2 Hz), 26.9

(d, *J* = 3.5 Hz), 27.1 (d, *J* = 2.7 Hz), 27.8, 28.7 (d, *J* = 1.2 Hz), 32.5 (d, *J* = 31.8 Hz), 99.8 (d, *J* = 2.3 Hz), 127.9 (d, *J* = 11.2 Hz), 131.2 (d, *J* = 47.2 Hz), 132.2 (d, *J* = 2.2 Hz), 140.8 (d, *J* = 16.0 Hz), 141.7 (d, *J* = 5.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 41.6 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{29}PIBNa$ $[M+Na]^+$ 437.1030, found 437.1012; Anal calcd for $C_{18}H_{29}PIB$: C, 52.21; H, 7.06; found: C, 52.19; H, 6.98.

(*R*)-(2-Bromophenyl)-(2-methoxyphenyl)-phenylphosphine borane (10n). Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). Colourless solid; Yield 53% (0.17 g); mp 152-154°C; Enantiomeric excess: 95% by HPLC analysis (chiralpak AD, 0.2 mL.min^{-1}, hexane/2-propanol 99:1, t_R (*R*) = 29.4 min, t_R (*S*) = 32.2 min); R_f 0.18 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ -1.3 (c 1.6, $CHCl_3$); IR (neat) 3054, 2940, 2838, 2384, 1589, 1575, 1559, 1478, 1454, 1431, 1277, 1265, 1252, 1164, 1134, 1103, 1059, 1021, 854, 802, 733 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 3H), 6.94 (dd, *J* = 3.8, 8.3 Hz, 1H), 7.08 (tdd, *J* = 0.8, 2.1, 7.5 Hz, 1H), 7.28-7.33 (m, 3H), 7.44-7.54 (m, 4H), 7.60-7.64 (m, 1H), 7.80-7.87 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.4, 111.5 (d, *J* = 4.6 Hz), 116.5 (d, *J* = 57.8 Hz), 121.5 (d, *J* = 12.2 Hz), 126.7 (d, *J* = 6.4 Hz), 127.0 (d, *J* = 9.2 Hz), 128.3 (d, *J* = 59.9 Hz), 128.4 (d, *J* = 10.5 Hz), 131.0 (d, *J* = 61.4 Hz), 131.1, (d, *J* = 2.4 Hz), 131.7 (d, *J* = 2.1 Hz), 133.8 (d, *J* = 1.9 Hz), 133.9 (d, *J* = 9.8 Hz), 134.5, (d, *J* = 6.0 Hz), 135.0 (d, *J* = 9.8 Hz), 135.6 (d, *J* = 9.8 Hz), 161.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.7 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{19}H_{19}BBrOPNa$ $[M+Na]^+$ 407.0346, found 407.0333; Anal calcd for $C_{19}H_{19}BBrOP$: C, 59.27; H, 4.97; found: C, 58.89; H, 5.25.

(*S*)-Ferrocenyl-(2-bromophenyl)-phenylphosphine borane (10p). Purification: recrystallization in methylene chloride/hexane. Orange solid; Yield 47% (0.18 g); mp 208-210°C; Enantiomeric excess: 99% by HPLC analysis (chiralcel OD-H, 0.5 mL.min^{-1}, hexane/2-propanol 98:2, t_R (*R*) = 19.6 min, t_R (*S*) = 23.2 min); R_f 0.39 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ +162.9 (c 0.5, $CHCl_3$); IR (neat) 3092, 3074, 3054, 2408, 2382, 2350, 1571, 1555, 1483, 1450, 1437, 1417, 1387, 1334, 1308, 1271, 1249, 1169, 1130, 1105, 1060, 1053, 1022, 998, 844, 765, 753, 739, 721 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09 (sl, 5H), 4.14-4.16 (m, 1H), 4.51-4.53 (m, 1H), 4.61-4.62 (m, 1H), 4.84-4.87 (m, 1H), 7.22-7.31 (m, 3H), 7.48-7.59 (m, 4H), 7.73-7.80 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 69.2 (d, *J* = 70.1 Hz),

69.9, 72.0, 72.1 (d, *J* = 5.0 Hz), 72.2 (d, *J* = 6.7 Hz), 74.7 (d, *J* = 14.5 Hz), 126.9 (d, *J* = 8.6 Hz), 127.0 (d, *J* = 7.2 Hz), 128.5 (d, J = 10.5 Hz), 129.7 (d, *J* = 61.4 Hz), 131.1 (d, *J* = 2.4 Hz), 132.1 (d, *J* = 2.0 Hz), 132.6 (d, *J* = 9.8 Hz), 132.9 (d, *J* = 58.1 Hz), 134.7 (d, *J* = 5.7 Hz), 135.6 (d, *J* = 8.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.3 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{22}H_{21}PBrBFeNa$ $[M+Na]^+$ 484.9905, found 484.9912; Anal calcd for $C_{22}H_{21}PBrBFe$: C, 57.08; H, 4.57; found: C, 56.78; H, 4.61.

(*S*)-Ferrocenyl-(2-iodophenyl)-phenylphosphine borane (10q). Purification: Recrystallization in methylene chloride/hexane. Orange solid; Yield 55% (0.23 g); mp 218-220°C; Enantiomeric excess: 99% by HPLC analysis (chiralcel OD-H, 0.5 mL.min^{-1}, hexane/2-propanol 98:2, t_R (*R*) = 19.2 min, t_R (*S*) = 25.2 min); R_f 0.54 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ +207.1 (c 0.6, $CHCl_3$); IR (neat) 3124, 3086, 3052, 2407, 2380, 2350, 1553, 1483, 1426, 1387, 1368, 1335, 1100, 1059, 1027, 1010, 821, 739, 716, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07-4.08 (m, 1H), 4.09 (sl, 5H), 4.51-4.52 (m, 1H), 4.62-4.63 (m, 1H), 7.07 (tt, *J* = 1.6, 7.5 Hz), 7.14 (ddd, *J* = 1.7, 7.8, 11.0 Hz, 1H), 7.28-7.33 (m, 2H), 7.50-7.63 (m, 3H), 7.77-7.83 (m, 2H), 7.91 (ddd, *J* = 1.0, 3.1, 7.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 69.8 (d, *J* = 70.0 Hz), 70.0, 71.7 (d, *J* = 3.7 Hz), 72.1 (d, *J* = 8.4 Hz), 72.3 (d, *J* = 6.5 Hz), 74.9 (d, *J* = 14.9 Hz), 100.2 (d, *J* = 9.8 Hz), 127.6 (d, *J* = 8.3 Hz), 128.6 (d, *J* = 10.5 Hz), 129.2 (d, *J* = 60.8 Hz), 131.3 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 2.1 Hz), 133.4 (d, *J* = 9.5 Hz), 135.4 (d, *J* = 9.0 Hz), 136.0 (d, *J* = 58.3 Hz), 142.2 (d, *J* = 7.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 27.5 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{22}H_{21}PIBFeNa$ $[M+Na]^+$ 532.9764, found 532.9747; Anal calcd for $C_{22}H_{21}PIBFe$: C, 51.82; H, 4.15; found: C, 52.03; H, 4.12.

(*S*)-(2-Bromophenyl)-phenylisopropylphosphine borane (10r). Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). Colourless oil; Yield 48% (0.13 g); Enantiomeric excess: 95% by HPLC analysis (lux 5u cellulose 2, 0.2 mL.min^{-1}, hexane/2-propanol 98:2, t_R (*S*) = 35.2 min, t_R (*R*) = 37.7 min); R_f 0.52 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ -45.0 (c 0.3, $CHCl_3$); IR (neat) 2971, 2932, 2872, 2381, 1576, 1453, 1436, 1417, 1271, 1254, 1108, 1065, 1039, 1024, 739, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (dd, *J* = 7.1, 17.1 Hz, 3H), 1.32 (dd, *J* = 7.0, 16.4 Hz, 3H), 3.31-3.45 (m, 1H), 7.23-7.40 (m, 5H), 7.48 (ddd, *J* = 1.3, 2.5, 7.9 Hz, 1H), 7.55-7.61 (m, 2H), 8.08 (ddd, *J* = 1.6, 7.7, 12.5 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.3 (d, *J* = 2.3 Hz), 18.0 (d,

J = 2.1 Hz), 21.3 (d, *J* = 35.7 Hz), 127.4 (d, *J* = 10.8 Hz), 127.7, 128.3 (d, *J* = 55.2 Hz), 128.4, 128.5, 129.6 (d, *J* = 50.6 Hz), 130.6 (d, *J* = 2.3 Hz), 132.4, 132.6, 132.8 (d, *J* = 2.2 Hz), 134.6 (d, *J* = 4.8 Hz), 138.1 (d, *J* = 14.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.0-35.6 (m); HRMS (ESI-Q-TOF) calcd for $C_{15}H_{19}PBBrNa$ $[M+Na]^+$ 343.0396, found 343.0407; Anal calcd for $C_{15}H_{19}PBBr$: C, 56.12; H, 5.97; found: C, 56.50; H, 6.16.

(*S*)-(2-Bromophenyl)-cyclohexylphenylphosphine borane (10s). Purification: column chromatography with a mixture 4:1 petroleum ether/ethyl acetate, as eluent. Colourless oil; Yield 47% (0.14 g); Enantiomeric excess: 95% by HPLC analysis (chiralcel OD-H, 0.2 mL.min^{-1}, hexane/2-propanol 98:2, t_R (*S*) = 26.1 min, t_R (*R*) = 28.1 min); R_f 0.46 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D$ -21.6 (c 0.2, $CHCl_3$); IR (neat) 2936, 2853, 2385, 2348, 1577, 1559, 1489, 1453, 1439, 1421, 1133, 1110, 1057, 1021, 1003, 762, 737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29-1.50 (m, 5H), 1.74-1.83 (m, 3H), 1.90-1.92 (m, 1H), 2.03-2.05 (m, 1H), 3.18-3.24 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.41-7.48 (m, 4H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.65-7.68 (m, 2H), 8.17-8.20 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.8 (d, *J* = 1.5 Hz), 26.7, 26.8, 27.0 (d, *J* = 12.6 Hz), 28.1, 31.3 (d, *J* = 34.7 Hz), 127.4 (d, *J* = 11.0 Hz), 128.0 (d, *J* = 12.6 Hz), 128.4 (d, *J* = 67.3 Hz), 128.5 (d, *J* = 9.9 Hz), 129.1 (d, *J* = 51.1 Hz), 130.6 (d, *J* = 2.4 Hz), 132.4 (d, *J* = 8.7 Hz), 132.8 (d, *J* = 2.2 Hz), 134.5 (d, *J* = 4.7 Hz), 138.3 (d, *J* = 15.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.3-31.6 (m); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{23}PBBrNa$ $[M+Na]^+$ 383.0709, found 383.0723; Anal calcd for $C_{18}H_{23}PBBr$: C, 59.88; H, 6.42; found: C, 60.10; H, 6.16.

Borane decomplexation in free *o*-halogenoarylphosphine (11). General procedure. A solution of *o*-halogenoaryl phosphine borane **10** (0.5 mmol) and DABCO® (1.5 mmol) in 3 mL of dry toluene was stirred under argon at room temperature overnight. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel and/or recrystallization.

(2-Bromophenyl)-diphenylphosphine (11a)[21a]**.** Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). White solid; Yield 79% (0.13 g); mp 112-114°C (Litt[21a]: 112-114°C); R_f 0.48 (petroleum ether/ethyl acetate 3:1); IR (neat) 3056, 2925, 2854, 1586, 1572, 1555, 1479, 1448, 1436, 1420, 1312, 1249, 1181, 1161, 1121, 1093, 1073, 1017, 851, 756, 743, 696 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66-6.70 (m, 1H), 7.10-7.13 (m, 2H), 7.18-7.30 (m, 10H), 7.50-7.54 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 127.4, 128.6 (d, *J* = 7.2 Hz), 129.0, 129.5 (d, *J* = 50.3 Hz), 130.2, 133.0 (d, *J* = 2.3 Hz), 134.1 (d, *J* = 20.2 Hz), 135.5, 135.8 (d, *J* = 10.5 Hz), 138.9 (d, *J* = 11.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -5.1 (s); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{14}PBrNa$ $[M+Na]^+$ 362.9909, found 362.9910.

(2-Bromo-4,5-dimethylphenyl)-diphenylphosphine (11c). Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). White solid; Yield 84% (0.155 g); mp 148-150°C; R_f 0.63 (petroleum ether/ethyl acetate 3:1); IR (neat) 3054, 2938, 2918, 1586, 1477, 1457, 1449, 1433, 1383, 1345, 1152, 1117, 1093, 1070, 1022, 996, 911, 880, 747, 740, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.25 (s, 3H), 6.52 (d, J = 3.0 Hz, 1H), 7.28-7.41 (m, 11H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.3, 19.4, 126.9 (d, *J* = 30.8 Hz), 128.5 (d, *J* = 7.1 Hz), 128.9, 133.7, 133.9 (d, *J* = 20.2 Hz), 135.0 (d, *J* = 9.3 Hz), 135.4, 136.0, 136.2 (d, *J* = 10.3 Hz), 139.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ -6.1 (s); HRMS (ESI-Q-TOF) calcd for $C_{20}H_{18}PBrNa$ $[M+Na]^+$ 391.0222, found 391.0240; Anal calcd for $C_{20}H_{18}PBr$: C, 65.06; H, 4.91; found: C, 65.07; H, 5.15.

(2-Iodophenyl)-diphenylphosphine (11d).[21a] Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). White solid; Yield 83% (0.16 g); mp 120-122°C (Litt[21a]: 119-120°C); R_f 0.64 (petroleum ether/ethyl acetate 3:1); IR (neat) 3052, 1568, 1549, 1477, 1434, 1414, 1327, 1265, 1179, 1158, 1118, 1090, 1070, 1027, 971, 947, 740, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (dt, *J* = 2.0, 7.7 Hz, 1H), 6.94 (td, *J* = 1.7, 7.6 Hz, 1H), 7.15-7.21 (m, 5H), 7.24-7.31 (m, 6H), 7.82 (ddd, *J* = 1.1, 3.1, 7.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 107.0 (d, *J* = 39.7 Hz), 128.3, 128.7 (d, *J* = 7.1 Hz), 129.0, 130.1, 134.0 (d, J = 20.0 Hz), 134.2 (d, *J* = 1.0 Hz), 136.3 (d, *J* = 10.9 Hz), 139.8 (d, *J* = 3.8 Hz), 142.3 (d, *J* = 9.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.0 (s); HRMS (ESI-Q-TOF) calcd for $C_{18}H_{14}PINa$ $[M+Na]^+$ 410.9770, found 410.9771.

(*R*)-(2-bromophenyl)-(2-methoxyphenyl)-phenylphosphine (11e). Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). Analytical pure sample can be obtained by recrystallization in methylene chloride/methyl alcohol. Colourless solid; Yield 90% (0.17

g); mp 128-130°C; Enantiomeric excess: 99% by HPLC analysis (chiralpak AD, 0.2 mL.min^{-1}, hexane/2-propanol 99:1, t_R (*R*) = 30.8 min, t_R (*S*) = 35.0 min). R_f 0.41 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ -20.6 (c 0.5, $CHCl_3$); IR (neat) 3063, 2930, 2833, 1581, 1571, 1553, 1458, 1428, 1298, 1271, 1239, 1162, 1128, 1093, 1069, 1041, 1017, 864, 793, 752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 6.78-6.82 (m, 1H), 6.65-6.70 (m, 1H), 6.87-6.96 (m, 2H), 7.18-7.24 (m, 2H), 7.28-7.43 (m, 6H), 7.58-7.63 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.7, 110.3 (d, *J* = 1.5 Hz), 121.2, 124.5 (d, *J* = 12.4 Hz), 127.3, 128.5 (d, *J* = 7.4 Hz), 129.0, 130.0, 130.1 (d, *J* = 32.0 Hz), 130.6, 132.8 (d, *J* = 2.4 Hz), 133.9, 134.1, 134.4, 135.4 (d, *J* = 10.5 Hz), 138.5 (d, *J* = 11.4 Hz), 161.3 (d, *J* = 15.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -15.3 (s); HRMS (ESI-Q-TOF) calcd for $C_{19}H_{16}PBrONa$ $[M+Na]^+$ 393.0014, found 393.0006; Anal calcd for $C_{19}H_{16}PBrO$: C, 61.48; H, 4.34; found: C, 61.37; H, 4.59.

(*S*)-Ferrocenyl-(2-bromophenyl)-phenylphosphine (11g). Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). Orange solid; Yield 75% (0.17 g); Enantiomeric excess: 99% by HPLC analysis after complexation with borane (chiralcel OD-H, 0.5 mL.min^{-1}, hexane/2-propanol 98:2, t_R (*R*) = 19.6 min, t_R (*S*) = 23.2 min). R_f 0.50 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ +207.0 (c 0.6, $CHCl_3$); IR (neat) 3104, 3045, 2926, 2855, 1741, 1552, 1481, 1446, 1436, 1420, 1308, 1270, 1248, 1192, 1163, 1108, 1098, 1016, 1003, 890, 821, 749, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60-3.61 (m, 1H), 3.98 (sl, 5H), 4.21-4.23 (m, 1H), 4.29-4.31 (m, 1H), 4.36-4.39 (m, 1H), 6.84 (dt, *J* = 2.1, 7.4 Hz, 1H), 7.06-7.19 (m, 2H), 7.28-7.32 (m, 3H), 7.34-7.42 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 69.9, 71.7, 72.3, 72.4 (d, *J* = 7.1 Hz), 75.3 (d, *J* = 31.8 Hz), 76.5 (d, *J* = 7.6 Hz), 128.1, 129.0 (d, *J* = 8.0 Hz), 129.4 (d, *J* = 30.3 Hz), 129.9, 130.9, 133.6 (d, *J* = 1.7 Hz), 134.8 (d, *J* = 1.5 Hz), 135.2 (d, *J* = 20.6 Hz), 137.3 (d, *J* = 8.6 Hz), 142.6 (d, *J* = 14.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -16.6 (s); HRMS (ESI-Q-TOF) calcd for $C_{22}H_{18}PFeBr$ $[M]^+$ 447.9675, found 447.9686; Anal calcd for $C_{22}H_{18}PFeBr$: C, 58.84; H, 4.04; found: C, 59.19; H, 4.05.

(*S*)-(2-bromophenyl)-phenylisopropylphosphine (11h). Purification: column chromatography (elution with 3:1 petroleum ether/ethyl acetate). Colourless oil; Yield 82% (0.125 g); Enantiomeric excess: 95% by HPLC analysis after complexation with borane (lux 5u Cellulose-2, 0.2 mL.min^{-1}, hexane/2-propanol 98:2, t_R (*S*) 39.6 min, t_R (*R*) 42.3 min); Rf 0.59 (petroleum ether/ethyl acetate 3:1);

$[\alpha]_D^{20}$ -52.9 (c 0.4; $CHCl_3$); IR (neat) 3054, 2952, 2865, 1556, 1449, 1421, 1384, 1365, 1250, 1228, 1155, 1124, 1096, 1018, 878, 746, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.06 (dd, J = 6.8, 15.5 Hz, 3H), 1.20 (dd, *J* = 6.9, 16.0 Hz, 3H), 2.41-2.47 (m, 1H), 7.19-7.22 (m, 1H), 7.32-7.35 (m, 3H), 7.37 (td, *J* = 1.3, 7.6 Hz, 1H), 7.46-7.50 (m, 3H), 7.59 (ddd, *J* = 1.2, 3.4, 8.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.3 (d, *J* = 19.6 Hz), 19.8 (d, *J* = 19.6 Hz), 25.3 (d, *J* = 9.1 Hz), 127.3, 128.3 (2s), 128.9, 130.0, 131.4 (d, *J* = 30.2 Hz), 132.8, 133.3 (d, *J* = 2.6 Hz), 133.7, 133.8, 136.6 (d, *J* = 13.0 Hz), 138.6 (d, *J* = 14.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -1.4 (s); HRMS (ESI-Q-TOF) calcd for $C_{15}H_{16}PBrNa$ $[M+Na]^+$ 329.0065, found 329.0057.

Synthesis of *o*-halogenoaryl phosphine (11) starting from secondary phosphine borane (8), using a two steps reaction sequence.

(2-bromophenyl)-di(*o*-tolyl)phosphine (11b)[50]. To a solution of secondary phosphine borane **8g** (0.19 g, 0.83 mmol) in dry THF (2 mL) was added dropwise under argon at -78°C *n*-BuLi (0.83 mmol). The resulting solution was stirred at this temperature during one hour and 1,2-dibromobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After one hour at -78°C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under argon atmosphere. DABCO® (0.28 g, 2.49 mmol) was added and the resulting solution was stirred at room temperature overnight. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. White solid; Overall yield 40% (0.12 g); R_f 0.59 (petroleum ether/ethyl acetate 3:1); IR (neat) 3055, 3002, 2973, 1588, 1554, 1466, 1445, 1422, 1377, 1271, 1250, 1201, 1161, 1130, 1099, 1017, 867, 746, 715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.46 (2s, 6H), 6.76-6.78 (m, 3H), 7.12-7.14 (m, 2H), 7.22-7.24 (m, 2H), 7.27-7.29 (m, 2H), 7.32 (td, *J* = 1.3, 7.4 Hz, 2H), 7.64-7.66 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1, 21.3, 126.3, 127.6, 129.0, 130.1, 130.2 (d, *J* = 4.6 Hz), 130.6 (d, *J* = 32.5 Hz), 133.1 (d, *J* = 2.9 Hz), 133.2, 134.0 (d, *J* = 11.4 Hz), 134.7, 137.7 (d, *J* = 10.8 Hz), 142.8 (d, *J* = 27.4 Hz); ^{31}P NMR

(121 MHz, $CDCl_3$) δ -19.7 (s); HRMS (ESI-Q-TOF) calcd for $C_{20}H_{18}PBrNa$ $[M+Na]^+$ 391.0222, found 391.0210; Anal calcd for $C_{20}H_{18}PBr$: C, 65.06; H, 4.91; found: C, 65.14; H, 5.00.

(*R*)-(2-bromophenyl)-(2-methoxyphenyl)-phenylphosphine (11e). To a solution of secondary phosphine borane (*S*)-**8i** (0.19 g, 0.83 mmol) in dry THF (2 mL) was added dropwise under argon at -78°C *n*-BuLi (0.83 mmol). The resulting solution was stirred at this temperature during one hour and 1,2-dibromobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After one hour at -78°C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under argon atmosphere. DABCO (0.28 g, 2.49 mmol) was added and the resulting solution was stirred at room temperature overnight. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. Analytical pure sample can be obtained by recrystallization in methylene chloride/methyl alcohol. Colorless solid; Overall yield 45% (0.14 g); Enantiomeric excess: 99% by HPLC analysis (chiralpak AD, 0.2 $mL.min^{-1}$, hexane/2-propanol 99:1, t_R (*R*) = 30.8 min, t_R (*S*) = 35.0 min); R_f 0.41 (petroleum ether/ethyl acetate 3:1). All of the analyses were similar to that already described above.

(*R*)-(2-iodophenyl)-(2-methoxyphenyl)-phenylphosphine (11f). To a solution of secondary phosphine borane (*S*)-**8i** (0.19 g, 0.83 mmol) in dry THF (2 mL) was added dropwise under argon at -78°C *n*-BuLi (0.83 mmol). The resulting solution was stirred at this temperature during one hour and 1,2-diiodobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After one hour at -78°C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under argon atmosphere. DABCO® (0.28 g, 2.49 mmol) was added and the resulting solution was stirred at room temperature overnight. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. White solid; Overall yield 42% (0.145 g); mp 110-112°C; Enantiomeric excess: 95% by ^1H NMR and/or ^{31}P NMR of the

corresponding phosphine oxide with (*R*)-3,5-dinitro-*N*-(1-phenyl-ethyl)-benzamide as chiral reagent; R_f 0.45 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ -24.2 (c 0.4, $CHCl_3$); IR (neat) 3050, 2933, 2835, 1584, 1573, 1554, 1472, 1462, 1431, 1300, 1274, 1241, 1183, 1163, 1130, 1094, 1071, 1043, 1024, 796, 753, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 3H), 6.56 (ddd, *J* = 1.7, 4.4, 7.4 Hz, 1H), 6.72 (dt, *J* = 1.9, 7.7 Hz, 1H), 6.77-6.86 (m, 2H), 6.92 (td, *J* = 1.7, 7.6 Hz, 1H), 7.13-7.32 (m, 7H), 7.81 (ddd, *J* = 1.1, 3.1, 7.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.8, 107.2 (d, *J* = 41.4 Hz), 110.4 (d, *J* = 1.5 Hz), 121.2, 125.0 (d, *J* = 12.7 Hz), 128.1, 128.5, 128.6, 128.9, 130.0, 130.6, 133.9, 134.1, 134.2, 134.5, 135.8 (d, *J* = 10.9 Hz), 139.6 (d, *J* = 3.8 Hz), 141.9 (d, *J* = 9.0 Hz), 161.2 (d, *J* = 15.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 1.8 (s); HRMS (ESI-Q-TOF) calcd for $C_{19}H_{16}PIONa$ $[M+Na]^+$ 440.9876, found 440.9891; Anal calcd for $C_{19}H_{16}PIO$: C, 54.57; H, 3.86; found: C, 54.55; H, 3.90.

(*S*)-(2-bromophenyl)-(2-methylphenyl)-phenylphosphine (11i). To a solution of secondary phosphine borane (*R*)-**8m** (0.18 g, 0.83 mmol) in dry THF (2 mL) was added dropwise under argon at -78°C *n*-BuLi (0.83 mmol). The resulting solution was stirred at this temperature during one hour and 1,2-dibromobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After one hour at -78°C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under argon atmosphere. DABCO® (0.28 g, 2.49 mmol) was added and the resulting solution was stirred at room temperature overnight. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 4:1 as eluent. White solid; Overall yield 66% (0.195 g); mp 90-92°C; Enantiomeric excess: 73% by ^{31}P NMR of the corresponding phosphine oxide with (*R*)-3,5-dinitro-*N*-(1-phenyl-ethyl)-benzamide as chiral reagent; R_f 0.58 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D$ +14.5 (c 0.4, $CHCl_3$); IR (neat) 3054, 1554, 1445, 1436, 1421, 1271, 1250, 1101, 1093, 1018, 744, 716, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (d, *J* = 1.2 Hz, 3H), 6.74-6.79 (m, 2H), 7.12 (td, *J* = 1.2, 7.0 Hz, 1H), 7.19-7.24 (m, 2H), 7.25-7.33 (m, 4H), 7.35-7.42 (m, 3H), 7.61-7.65 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3 (d, *J* = 21.8 Hz),

126.2, 127.5, 128.7 (d, J = 7.3 Hz), 129.1 (d, J = 7.2 Hz), 130.2, 130.2 (d, J = 31.3 Hz), 130.3 (d, J = 4.9 Hz), 133.0, 133.1, 134.2, 134.5, 134.6, 134.7 (d, J = 11.4 Hz), 135.0 (d, J = 10.3 Hz), 138.3 (d, J = 10.8 Hz), 142.5 (d, J = 26.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ -12.2 (s); HRMS (ESI-Q-TOF) calcd for $C_{19}H_{17}PBrNa$ $[M+H]^+$ 355.0246, found 355.0248; Anal calcd for $C_{19}H_{16}PBr$: C, 64.24; H, 4.54; found: C, 64.60; H, 4.66.

Synthesis of (*R*)-(2-Bromophenyl)-(2-methoxyphenyl)-phenylphosphine oxide (13). To a solution of (*R*)-(2-methoxyphenyl)-phenylphosphine oxide **12** (0.19 g, 0.83 mmol) in dry THF (2 mL) was added dropwise under argon at -78°C *n*-BuLi (0.83 mmol). The resulting solution was stirred at this temperature during one hour and 1,2-dibromobenzene **9a** (0.28 g, 1.16 mmol) was then added followed by *n*-BuLi (0.17 mmol). After stirring to room temperature over one hour, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3x10 mL). The organic phases were dried over $MgSO_4$, filtered and the solvent evaporated giving a residue which was purified by column chromatography on silica gel using ethyl acetate as eluent. Analytical pure sample can be obtained by recrystallization in methylene chloride/hexane. White solid; Yield 65% (0.21 g); Enantiomeric excess: 99% by HPLC analysis (chiralpak IB, 1.5 mL.min^{-1}, hexane/2-propanol 90:10, t_R (*R*) = 21.6 min, t_R (*S*) = 25.1 min); R_f 0.28 (ethyl acetate); $[\alpha]_D$ +18.6 (c 0, 8 $CHCl_3$); IR (neat) 3242, 3092, 3062, 2993, 2946, 2847, 1728, 1585, 1476, 1461, 1427, 1276, 1244, 1178, 1132, 1167, 1074, 1010, 883, 865, 800, 772, 737, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.55 (s, 3H), 6.94 (ddd, J = 0.8, 3.8, 8.3 Hz, 1H), 7.11 (tdd, J = 0.8, 2.1, 7.5 Hz, 1H), 7.29-7.36 (m, 2H), 7.40-7.49 (m, 3H), 7.58-7.61 (m, 2H), 7.62-7.66 (m, 1H) 7.76-7.95 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.4, 111.1 (d, J = 7.0 Hz), 120.1 (d, J = 107.2 Hz), 121.3 (d, J = 11.9 Hz), 126.2 (d, J = 4.6 Hz), 126.7 (d, J = 11.6 Hz), 128.1 (d, J = 12.7 Hz), 131.6 (d, J = 2.7 Hz), 132.2 (d, J = 10.6 Hz), 132.3 (d, J = 110.3 Hz), 132.6 (d, J = 2.4 Hz), 133.8 (d, J = 109.0 Hz), 134.3 (d, J = 2.0 Hz), 134,4 (d, J = 7.7 Hz), 135.0 (d, J = 7.3 Hz), 135.2 (d, J = 11.0 Hz), 160.6 (d, J = 3.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.3 (s); HRMS (ESI-Orbitrap) calcd for $C_{19}H_{16}PO_2BrNa$ $[M+Na]^+$ 409.0071, found 409.0076.

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SUPPORTING INFORMATION PARAGRAPH

^{1}H, ^{13}C, ^{31}P of all compounds. Structure and crystallographic data of 2-bromophenyl-dicyclohexylphosphine borane **10b**, 2-bromo-4,5-dimethylphenyl-diphenylphosphine borane **10i**. Crystallographic data of (*S*)-Ferrocenyl-(2-bromophenyl)-phenylphosphine borane **10p**, (*S*)-Ferrocenyl-(2-iodophenyl)-phenylphosphine borane **10q** and (*R*)-(2-bromophenyl)-(2-methoxyphenyl)-phenylphosphine **11e**. This material is available free of charge via the internet at http://pubs.acs.org.

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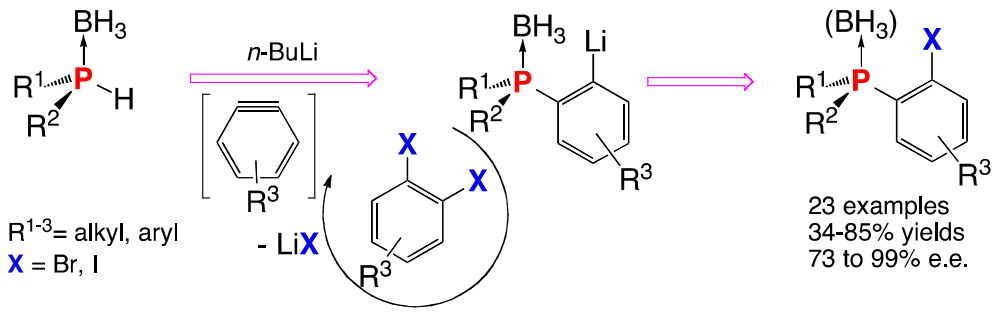
TOC


BH3
R1
P
H
R2
n-BuLi
R3
- LiX
X
X
R3
BH3
Li
R1
P
R2
R3
(BH3)
X
R1
P
R2
R3
R1-3= alkyl, aryl
X = Br, I
23 examples
34-85% yields
73 to 99% e.e.