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

Jérôme Bayardon,[†] Hugo Laureano,[†] Vincent Diemer,[‡] Mathieu Dutartre,[†] Utpal Das,[†] Yoann Rousselin,[†] Jean-Christophe Henry,[§] Françoise Colobert,[‡] Frédéric R. Leroux,*[,‡] and Sylvain Jugé*[,†]

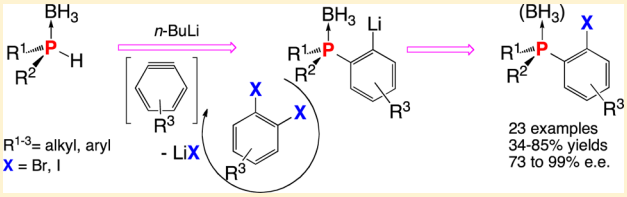
[†]Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB-StereochIM-UMR CNRS 6302), 9 avenue A. Savary BP47870, 21078 Dijon Cedex, France

[‡]Laboratoire de Chimie Moléculaire (UMR CNRS 7509), Université de Strasbourg, ECPM, 25 rue Becquerel, 67087 Strasbourg, France

[§]Synthelor SAS, 13 rue du bois de la champelle, 54500 Vandoeuvre les Nancy, France

Supporting Information

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 the 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 ee 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 obtain the free *o*-halogeno-arylphosphines in high yields.



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 in the phosphines comes from their easy structural design by electrophilic or nucleophilic reactions on the phosphorus atom or at the α or β position of an aliphatic substituent.[2,7,8] Despite this abundant chemistry, the synthesis of P-chirogenic phosphines such as **1** bearing a heteroatom or a functional group at the *ortho* position remains a challenge, and very few stereoselective methods lead to these compounds.

Mostly, the chiral *o*-functionalized phosphines are derived 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] and an 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 reagents for chemoselective coupling of biomolecular fragments by Staudinger ligation[16] and as directing groups 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 a 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 on the coupling reaction of secondary phosphine derivatives **2** with an activated aromatic precursor **3** by direct substitution,[11a,h,14b−e,20] the 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 the *ortho* position[14b,c] (Scheme 1c) or by *o*-lithiation and then trapping **7** by an electrophilic reagent (Scheme 1d).[22]

In the past few decades, the interest in 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 methods (a) and (b) reported in Scheme 1 involve either a racemization of the P center or a lack of reactivity of

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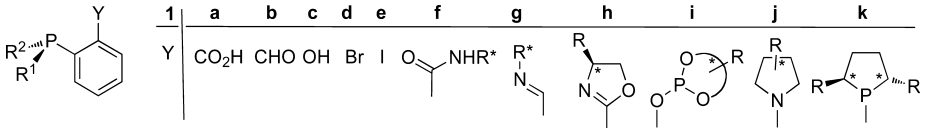


Figure 1. Different types of *o*-substituted or *o*-functionalized chiral phosphines.

Scheme 1. Methods for the Synthesis of *o*-Functionalized Phosphines

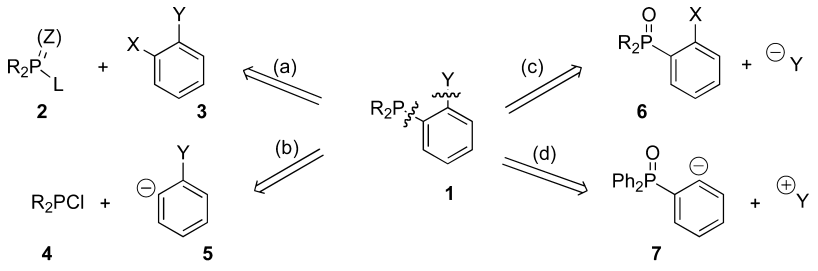
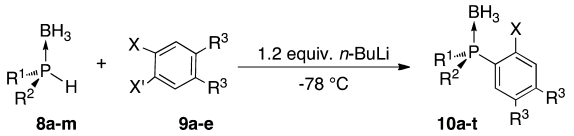


Table 1. Synthesis of *o*-Halogenophenyl Phosphine Boranes 10 from Secondary Phosphine Boranes 8



	$R^1R^2P(BH_3)H$			ArXX′			$R^1R^2P(BH_3)$-*o*-XAr		
entry		R^1	R^2		X,X′	R^3	yield (%)[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[f]

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

the electrophilic P-building blocks.[26] To date, only the enantioselective *o*-lithiation/functionalization of prochiral organophosphorus compounds in the presence of sparteine has been described, but in the phosphinamide series.[27] On the other 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]

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Consequently, the development of stereoselective synthesis of *o*-functionalized P-chirogenic phosphines **1** must be mainly based on 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 that have attracted increasing interest in the recent past as a result of 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 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.

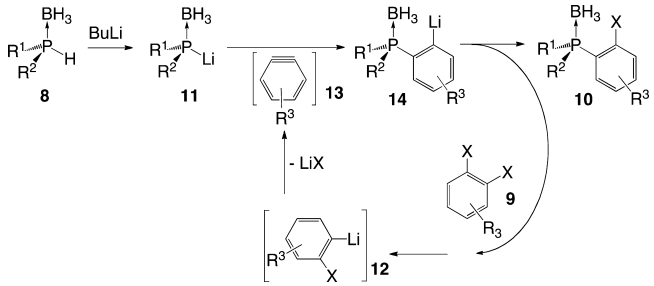
RESULTS AND DISCUSSION

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 stereoselectively produce the corresponding tertiary P-chirogenic phosphine boranes, with ee up to 99%.[24b] In continuation of this work, we have extended this reaction to the preparation of P-chirogenic arylphosphines bearing functional groups at the *ortho* position, using the arynes as electrophilic reagents. First, we investigated the reaction of the secondary chiral and achiral phosphine boranes **8** with 1,2-dihalogenoarene **9**, as the aryne precursor.[35] The results are summarized in Table 1.

The reaction of the secondary alkyl- or arylphosphine boranes **8a–f** with *n*-BuLi (1.2 equiv) and dibromobenzene **9a** (1.4 equiv) produces the corresponding *o*-bromophenylphosphine boranes **10a–f** in satisfactory to good yields, ranging from 34 to 75% (entries 1–6), respectively.[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] Again, this is demonstrated by the use of the di(*tert*-butyl)phosphine borane **8h**, which does not produce the product **10h** under these conditions (entry 8). On the other hand, under these conditions the reaction of the diphenylphosphine borane **8a** (or dicyclohexylphosphine borane **8b**) with the 4,5-dibromo-*o*-xylene **9b** leads to the phosphine boranes **10i** and **10j** in 56 and 53% yields, respectively (entries 9 and 10). In addition, the secondary phosphine boranes **8a** and **8b** react with 1,2 diiodobenzene **9c** to produce the corresponding *o*-iodophenylphosphine boranes **10k** and **10l**, in 50 and 56% yield, respectively (entries 11 and 12).

The synthesis of the *o*-halogenophenyl phosphine 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

Scheme 2. Proposed Mechanism for the Formation of *o*-Bromophosphine Boranes 10



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 produce, on one hand, the corresponding *o*-halophenylphosphine borane **10** and, on the other hand, the aryne **13** from the anion **12**, thus continuing 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). 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 a 1:9 ratio, thus proving that a better halogen–metal exchange of the anion **14** occurred with the iodo than with the bromo substituent of the reagent **9e** (entry 14).

Interestingly under these conditions, the P-chirogenic phosphine boranes **8i–m** reacted with the 1,2-dihalogenobenzene **9a** (or **9c**) to produce the corresponding *o*-halogenophenyl phosphine boranes **10n–t** in 42–66% yields and with enantiomeric excesses up to 99% (entries 15–25). The analysis of the starting secondary phosphine boranes **8** and their *o*-halogenophenyl derivatives **10** on the chiral column by HPLC proves that the reaction proceeds without racemization. As a typical example, the (*S*)-ferrocenylphenylphosphine borane **8j** (94% ee) reacts with the 1,2-dibromobenzene **9a** to produce 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 the solvent, and its ORTEP drawing is shown in Figure 2. The crystal contains discrete molecules of **10p** with normal nonbonded 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** confirm a reaction mechanism with retention of configuration at the P center.

Also, in the case of the reaction of the ferrocenylphenylphosphine borane (*S*)-**8j** having 94% ee with the 1,2-diodobenzene **9c**, the *o*-iodophenylphosphine borane **10q** is obtained in 55% yield 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 structures of bromo derivatives **10p** (Figure 3). The crystal

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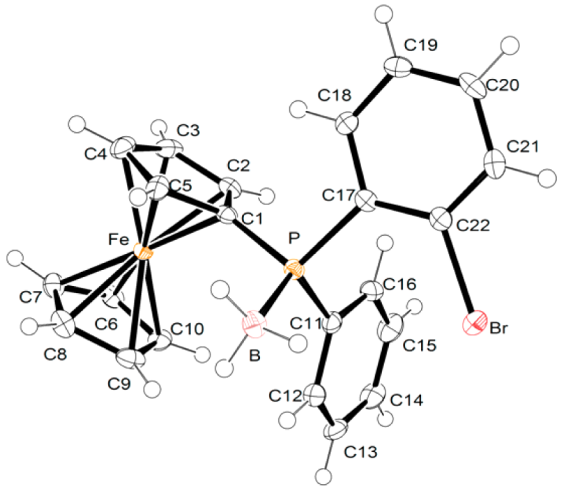

Figure 2. ORTEP[37] view of (*S*)-**10p** showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): P–B 1.930(3), C1–P 1.784(3), C11–P 1.811(3), C17–P 1.831(3); C1–P–C11 104.44(13), C1–P–C17 103.29(13), C11–P–C17 107.12(13), C1–P–B 112.53(15);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

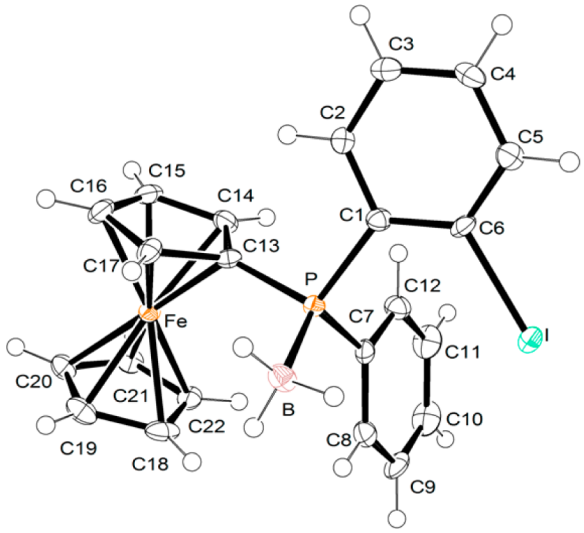

Figure 3. ORTEP[37] view of compound (*S*)-**10q** showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å), angles (deg) and dihedral angles (deg): P–B 1.931(5), C1–P 1.828(4), C13–P 1.791(4), C7–P 1.814(4); C13–P–C1 104.11(18), C7–P–C1 106.89(18), C13–P–C7 105.03(18), C1–P–B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

contains discrete molecules of compound **10q** with normal nonbonded 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.

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

Table 2. Decomplexation in Free *o*-Halogenoaryl Phosphines 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 the secondary phosphine borane **8g**. [b]Overall yield starting from the secondary phosphine borane **8i**. [c]Overall yield starting from the secondary phosphine borane **8m**.

Interestingly, the free phosphine (*R*)-**11e** was obtained in 45% yield and with 99% ee by a two-step 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** was determined by single crystal X-ray diffraction (Figure 4). The compound crystallizes

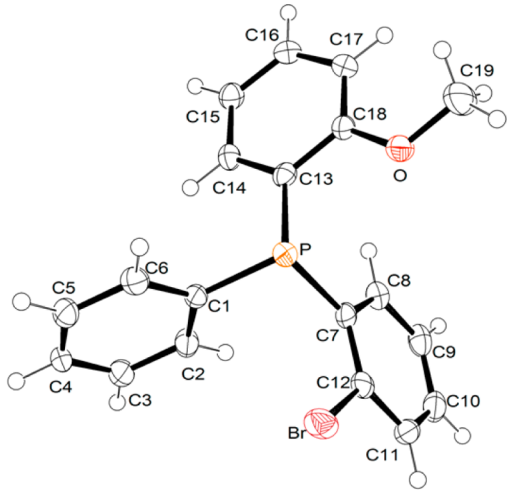

Figure 4. ORTEP[37] view of (*R*)-(2-bromophenyl)-(2-methoxyphenyl)-phenylphosphine **11e** showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å), angles (deg) and dihedral angles (deg): C1–P 1.838(3), C7–P 1.844(3), C13–P 1.841(3); C1–P–C7 100.78(12), C1–P–C13 102.08(12), 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).

in noncentrosymmetric 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,

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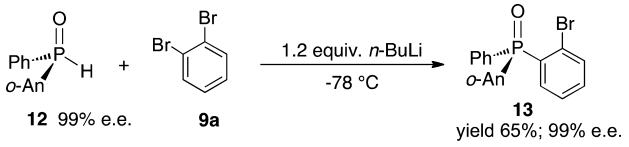
mean values of 1.841(3) Å and 101.4(6)°, respectively, are similar to those recorded for triphenylphosphine, mean values of 1.831(2) Å and 102.8(5)°.[38] The molecules are linked in the crystal lattice through edge-to-face C−H···π interactions between the phenyl groups.[39]

Finally, this synthetic strategy was preliminarily extended to secondary phosphine oxide. Interestingly, under 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 of the starting

Scheme 3. (*S*)-*o*-Anisyl-*o*-bromophenylphenylphosphine Oxide 13 from the Secondary Phosphine Oxide 12



secondary phosphine boranes **12** and the *o*-bromophenyl derivative **13** on a chiral column by HPLC proves that the reaction proceeds without racemization.

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 a 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% without racemization by decomplexation of their borane complexes using DABCO at room temperature. Interestingly, the free *o*-halogenoarylphosphines can be prepared by a two-step reaction sequence starting from the secondary phosphine borane, i.e., reaction with the *n*-butyllithium and the 1,2-halogenobenzene, and then decomplexation. The interest in these compounds for the preparation of various chiral and achiral *o*-functionalized phosphines useful in catalysis and organocatalysis will prompt further exploration in other developmental areas soon.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out using standard Schlenk techniques under an inert atmosphere. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF), toluene, and 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. For HPLC, hexane and 2-propanol 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-, and *t*-butylphenylphosphine were purchased from commercial sources and used without purification. The secondary phosphine borane **8**, which was prepared by reaction of the corresponding secondary phosphine with the borane−dimethylsulfur complex in THF, is in agreement with the data from 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 the 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). ^{1}H (and ^{1}H decoupled), ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded at 500 or 300 MHz, 125 or 75.5 MHz, and 121 or 202 MHz, respectively, at ambient temperature using TMS as an internal reference for ^{1}H and ^{13}C NMR and 85% phosphoric acid as an 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; and integration. HPLC analyses were performed on a chromatograph equipped with a UV detector at λ = 210 and 254 nm. Infrared spectra were recorded on a FT-IR instrument. Melting points were measured on a Kofler melting point apparatus and are uncorrected. Optical rotation values were measured on a polarimeter at 589 nm (sodium lamp). High resolution mass spectra (HRMS) were recorded on a 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 Kα radiation (λ = 0.71073 Å) from a sealed tube. The lattice parameters were obtained by a 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] without applying absorption corrections; the missing absorption corrections were partially compensated by the data-scaling procedure in the data reduction. Except for compound **10b**, multiscan absorption corrections were applied.[44] The structure was solved by direct methods using SIR92[45] . Refinements were carried out by full-matrix least-squares on F^2 using SHELXL97[46] on the complete set of reflections. Absolute configurations of all compounds were determined reliably from anomalous scattering, using the Flack method.[47] For all compounds, anisotropic thermal parameters were used for non-hydrogen atoms. All H atoms on the 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 the 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]

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, was added to a solution of dichlorophenylphosphine (5.37 g, 30.0 mmol) in THF under argon, at −78 °C over a period of 3 h. 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 being stirred for an additional 2 hours 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 (300 mL), 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 colorless 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, 3H), 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

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(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 for 1 h, and 1,2-dihalogenoarene **9** (1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After 1 h at −78 °C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and filtered, and the solvent evaporated giving a residue, which was purified by column chromatography on silica gel or by recrystallization.

*(2-Bromophenyl)-diphenylphosphine Borane (**10a**).*[49] Purification was accomplished by column chromatography (elution with 2:1 petroleum ether/ethyl acetate) or recrystallization in methylene chloride/hexane: colorless 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 $C_{18}H_{17}PBBrNa$ $[M + Na]^+$ m/z 377.0240, found m/z 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 for 30 min at this temperature and then for 30 min at room temperature. Purification was accomplished by column chromatography (elution with 3:1 petroleum ether/methylene chloride) or recrystallization in methylene chloride/methyl alcohol: colorless 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 $C_{18}H_{29}PBrBNa$ $[M + Na]^+$ m/z 389.1179, found m/z 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 for 30 min at this temperature and then for 30 min at room temperature. Purification was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate): colorless 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 $C_8H_{13}PBrBNa$ $[M + Na]^+$ m/z 252.9925, found m/z 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 for 30 min at this temperature and then for 30 min at room temperature. Purification was accomplished by column chromatography (elution with 3:1 petroleum ether/methylene chloride): colorless 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}; ^{1}H 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 $C_{12}H_{21}PBrBNa$ $[M + Na]^+$ m/z 309.0552, found m/z 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 was accomplished by column chromatography with a 6:4 mixture of cyclohexane/CH_2Cl_2 as the eluent. The analytically pure sample was obtained by crystallization from EtOAc at −20 °C: colorless solid; yield 60% (0.19 g); mp 133−136 °C; ^{1}H 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 was accomplished by column chromatography with an 8:2 mixture of cyclohexane/CH_2Cl_2 as the eluent, followed by crystallization from acetonitrile: colorless solid; yield 34% (0.095 g); mp 134−136 °C; ^{1}H 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 *n*-BuLi (0.83 mmol) dropwise under argon at −78 °C. The resulting solution was stirred at this temperature for 1 h, and 4,5-dibromo-*o*-xylene **9b** (0.31 g, 1.16 mmol) was then added, followed by *n*-BuLi (0.17 mmol). After being stirred at room temperature for 1 h, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and filtered, and the solvent evaporated giving a residue, which was purified by column chromatography on silica gel using 3:1 petroleum ether/methylene chloride as the eluent. The analytically pure sample was obtained by recrystallization in methylene chloride/hexane: colorless 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 $C_{20}H_{21}PBBrNa$ $[M + Na]^+$ m/z 405.0553, found m/z 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 followed for **10i** was applied starting from dicyclohexylphosphine borane **8b** and 1,2-dibromo-*o*-xylene **9b**.

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Purification was accomplished by column chromatography (elution with cyclohexane/CH_2Cl_2 8:2) followed by crystallization in acetonitrile: colorless 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, 3H), 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 NMR (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 was accomplished by column chromatography (elution with 1:1 petroleum ether/methylene chloride) or recrystallization in ethyl acetate: colorless 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}; ^{1}H 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]$^+$ m/z 425.0101, found m/z 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 for 30 min at this temperature and then for 30 min at room temperature. Purification was accomplished by column chromatography (elution with 2:1 petroleum ether/methylene chloride): colorless 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}; ^{1}H 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]$^+$ m/z 437.1030, found m/z 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 was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate): colorless 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]$^+$ m/z 407.0346, found m/z 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 was accomplished by 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]$^+$ m/z 484.9905, found m/z 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 was accomplished by 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]$^+$ m/z 532.9764, found m/z 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 was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate): colorless 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]$^+$ m/z 343.0396, found m/z 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 was accomplished by column chromatography with a 4:1 mixture of petroleum ether/ethyl acetate as the eluent: colorless 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,

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1559, 1489, 1453, 1439, 1421, 1133, 1110, 1057, 1021, 1003, 762, 737 cm^{-1}; ^1H 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 $C_{18}H_{23}PBBrNa$ $[M + Na]^+$ m/z 383.0709, found m/z 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 or by recrystallization.

*(2-Bromophenyl)-diphenylphosphine (**11a**).*[21a]* Purification was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate): white solid; yield 79% (0.13 g); mp 112−114 °C (lit.[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}; ^1H 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 $C_{18}H_{14}PBrNa$ $[M + Na]^+$ m/z 362.9909, found m/z 362.9910.

*(2-Bromo-4,5-dimethylphenyl)-diphenylphosphine (**11c**).* Purification was accomplished by 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}; ^1H 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 $C_{20}H_{18}PBrNa$ $[M + Na]^+$ m/z 391.0222, found m/z 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 was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate): white solid; yield 83% (0.16 g); mp 120−122 °C (lit.[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}; ^1H 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 $C_{18}H_{14}PINa$ $[M + Na]^+$ m/z 410.9770, found m/z 410.9771.

*(R)-(2-Bromophenyl)-(2-methoxyphenyl)-phenylphosphine (**11e**).* Purification was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate). An analytically pure sample can be obtained by recrystallization in methylene chloride/methyl alcohol: colorless 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}; ^1H 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 $C_{19}H_{16}PBrONa$ $[M + Na]^+$ m/z 393.0014, found m/z 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 was accomplished by 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}; ^1H 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 $C_{22}H_{18}PFeBr$ $[M]^+$ m/z 447.9675, found m/z 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 was accomplished by column chromatography (elution with 3:1 petroleum ether/ethyl acetate): colorless 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]; R_f 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 $C_{15}H_{16}PBrNa$ $[M + Na]^+$ m/z 329.0065, found m/z 329.0057.

Synthesis of *o*-Halogenoaryl Phosphine (11) Starting from Secondary Phosphine Borane (8), Using a Two-Step 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 *n*-BuLi (0.83 mmol) dropwise under argon at −78 °C. The resulting solution was stirred at this temperature for 1 h, and 1,2-dibromobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After 1 h at −78 °C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and filtered, and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under an 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 3:1 petroleum ether/ethyl acetate as the 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 $C_{20}H_{18}PBrNa$ $[M + Na]^+$ m/z 391.0222, found m/z 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 *n*-BuLi (0.83 mmol) dropwise under argon at −78 °C. The resulting solution was stirred at this temperature for 1 h, and 1,2-dibromobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After 1 h at −78 °C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and filtered, and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under an 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 3:1 petroleum ether/ethyl acetate as the eluent. An analytically 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 *n*-BuLi (0.83 mmol) dropwise under argon at −78 °C. The resulting solution was stirred at this temperature for 1 h, and 1,2-diiodobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After 1 h at −78 °C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and 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 3:1 petroleum ether/ethyl acetate as the eluent: white solid; overall yield 42% (0.145 g); mp 110−112 °C; enantiomeric excess: 95% by ^{1}H NMR or ^{31}P NMR of the corresponding phosphine oxide with (*R*)-3,5-dinitro-*N*-(1-phenyl-ethyl)-benzamide as a 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}; ^{1}H 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 $C_{19}H_{16}PIONa$ $[M + Na]^+$ m/z 440.9876, found m/z 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 *n*-BuLi (0.83 mmol) dropwise under argon at −78 °C. The resulting solution was stirred at this temperature for 1 h, and 1,2-dibromobenzene (0.15 mL, 1.16 mmol) was then added dropwise followed by *n*-BuLi (0.17 mmol). After 1 h at −78 °C, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and filtered, and the solvent evaporated giving a residue which was diluted with dry toluene (5 mL) under an 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 4:1 petroleum ether/ethyl acetate as the 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}; ^{1}H 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 $C_{19}H_{17}PBrNa$ $[M + H]^+$ m/z 355.0246, found m/z 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 *n*-BuLi (0.83 mmol) dropwise under argon at −78 °C. The resulting solution was stirred at this temperature for 1 h, and 1,2-dibromobenzene **9a** (0.28 g, 1.16 mmol) was then added, followed by *n*-BuLi (0.17 mmol). After being stirred at room temperature over 1 h, the reaction mixture was quenched with water (10 mL) and extracted with methylene chloride (3 × 10 mL). The organic phases were dried over $MgSO_4$ and filtered, and the solvent evaporated giving a residue which was purified by column chromatography on silica gel using ethyl acetate as the eluent. An analytically 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 $C_{19}H_{16}PO_2BrNa$ $[M + Na]^+$ m/z 409.0071, found m/z 409.0076.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, and ^{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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AUTHOR INFORMATION

Corresponding Author

*S.J.: e-mail, sylvain.juge@u-bourgogne.fr; tel, +33 (0)3 80 39 61 13. F.R.L. e-mail, frederic.leroux@unistra.fr; tel, 33 (0)3 68 85 26 40.

Notes

The authors declare no competing financial interest.

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