Iridium Complexes with Phosphine−Phosphite Ligands. Structural Aspects and Application in the Catalytic Asymmetric Hydrogenation of N-Aryl Imines

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A family of modularly designed phosphine−phosphites (P−OP), possessing a C−C−O backbone, has been synthesized and evaluated in the iridium-catalyzed asymmetric hydrogenation of N-aryl imines. The enantioselectivity of this reaction is highly dependent on the nature of the ligand, and catalysts bridged by an oxyethylene fragment have produced significantly higher enantiomeric excesses (Δee > 20%) than their *o*-oxyphenylene counterparts. Structural studies by X-ray crystallography and NMR spectroscopy of complexes with the formulation [Ir(COD)(P−OP)]BF_4 and Ir(Cl)(CO)(P−OP), complemented by DFT calculations of model compounds of the chlorocarbonyls, have shown important differences between complexes bridged by an aliphatic or an aromatic bridge, regarding the iridacycle conformation and the location of phosphine substituents. Catalyst optimization has afforded enantioselectivities from 72 to 85% ee in the hydrogenation of several N-aryl imines.

Introduction

The catalytic enantioselective hydrogenation of C═N bonds is a process of exceptional interest, due to the wide-ranging application of chiral amines. Intense efforts have been made during the past few decades in the study of this reaction,[1] but it has been exceedingly difficult to reconcile elevated enantioselectivities, high rates, and broad scope in the reduction of imines,[2] below the exceptional efficiency achieved in the hydrogenation of numerous types of olefins and ketones. In addition, interconversion between *E* and *Z* imine isomers[3] and product racemization[4] are plausible drawbacks affecting the reduction of acyclic substrates. Chiral catalysts based on diverse metals have produced notable advances in the field. *ansa*-Titanocenes have shown excellent levels of enantioselectivity in the hydrogenation of several types of imines,[3,5] particularly cyclic ones. Also, outstanding enantiomeric excesses have been obtained with iridium catalysts derived from C_2-symmetric diphosphines in the reduction of quinolines[6] and N-aryl imines,[7] although high catalyst loadings are needed in these cases. On the other hand, high rates but somewhat lower enantioselectivities have been achieved with iridium complexes bearing phosphine−oxazolines[8] or unsymmetrical diphosphines[9] in the hydrogenation of N-aryl imines. Ruthenium complexes have also been used in the reduction of C═N bonds, and those derived from chiral diamines have shown a high efficiency in transfer hydrogenation processes,[10] while those complexes containing both a diphosphine and a diamine have recently exhibited promising results in the hydrogenation of *N*-(1-phenylethylidene)aniline.[11] Also worth mentioning is a strategy based on substrate chelation, which has efficiently been used in the highly enantioselective hydrogenation of *N*-acylhydrazones catalyzed by rhodium DuPHOS species.[12]

In recent years there has been a notable increase in the study of bifunctional chiral ligands in asymmetric catalysis and they have become extremely useful tools in catalyst design, complementary to the ubiquitous C_2-symmetric ligands.[13] Bifunctional ligands have found one of their most remarkable applications in the Ir-catalyzed hydrogenation of imines, exemplified by some of the results cited above. Among bifunctional ligands, phosphine−phosphites are a particularly interesting class of compounds, due to their unique electronic properties. They possess two strongly coordinating phosphorus functionalities, one of them being a good π-aceptor group.[14] After the pioneering work

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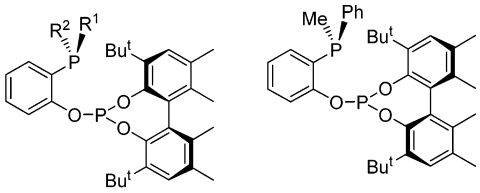
of Takaya and Nozaki,[15] reporting excellent results in the asymmetric hydroformylation of olefins with BINAPHOS ligands, the scope of phosphine−phosphites has greatly been increased. Thus, they have been applied to CO/olefin copolymerization,[16] allylic substitution,[17] hydroboration,[18] conjugate addition,[19] and hydrogenation reactions.[20] In particular, we have been interested in the application of phosphine−phosphites of general structure **4** in the last reaction. Thus, satisfactory results



$R^1 = R^2 = Ph$ (**4a**), Pr^i (**4b**), Me (**4c**)
$R^1 = Ph$, $R^2 = Me$ (**4d**)

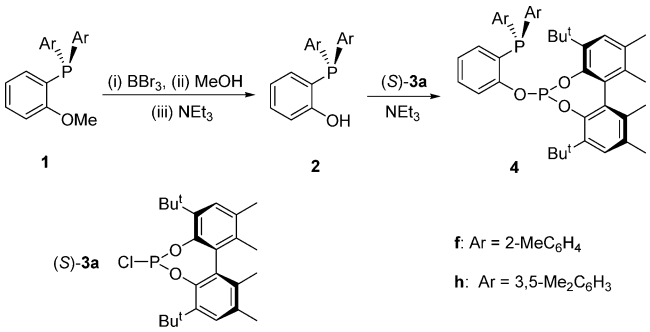
4e

have been obtained in the reduction of several types of olefins,[14,21] facilitated by the easily tunable structure of these ligands. In a preliminary communication,[22] we have recently described the first application of phosphine−phosphites to the asymmetric hydrogenation of imines. In that study, a significant influence of the backbone nature on the enantioselectivity of the reaction was detected, raising an uncommon case where better asymmetric induction was observed with a more flexible ligand.[23] Herein we report full results about the application of a family of phosphine−phosphites in this reaction, covering the synthesis and screening of ligands, along with studies of Ir complexes focused on the influence of the backbone on the structure of the chiral ligand.

Results and Discussion

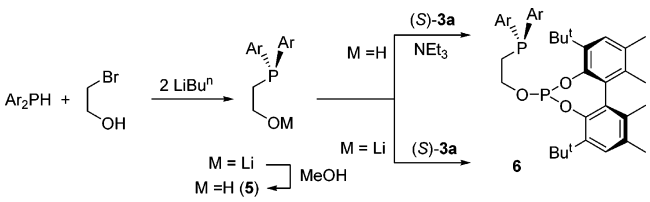
Ligand Synthesis. After obtaining moderate enantioselectivities in the catalytic hydrogenation of *N*-(1-phenylethylidene)-aniline in a preliminary scan using compounds **4a**−**e** (see below), we sought a wider ligand screening. Thus, to complete

Scheme 1



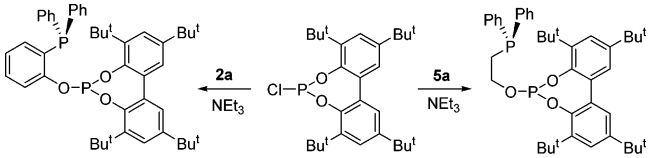
f: Ar = 2-MeC_6H_4
h: Ar = 3,5-$Me_2C_6H_3$

Scheme 2



a: Ar = Ph
f: Ar = 2-MeC_6H_4
g: Ar = 4-MeC_6H_4
h: Ar = 3,5-$Me_2C_6H_3$

Scheme 3



series **4** we first envisioned the synthesis of derivatives bearing PAr_2 groups other than PPh_2. In addition, being aware of the importance of ligand dynamic properties in asymmetric catalysis,[24a] we also tracked the preparation of compounds **6**, which bear an oxyethylene bridge. This backbone should provide a more flexible scaffold for phosphorus functionalities and a direct comparison with the *o*-oxyphenylene backbone of ligands **4**, since both types of structures have a C−C−O link.

For the synthesis of the desired ligands, a set of appropriate hydroxy phosphines were initially prepared. Accordingly, phenols **2f**,**h** were obtained by demethylation of the corresponding *o*-anisyl phosphines **1** (Scheme 1). Alternatively, alcohols **5a**−**h** were produced from the reaction between secondary phosphines Ar_2PH and 2-bromoethanol (Scheme 2).

Subsequent formation of phosphine−phosphites can easily be achieved by condensation of **1** or **2** with the appropriate phosphorochloridite **3** in the presence of NEt_3. Following this methodology, we prepared derivatives **4f**,**h** and **6a**,**f**. Alternatively, compounds **6g**,**h** were obtained by following a more convenient one-pot procedure via the lithium alkoxide. In addition, ligands **4i** and **6i**, which possess a conformationally flexible biaryl fragment, were synthesized from **2a** (Ar = Ph) and **5a**, respectively (Scheme 3).

In addition, the two ethane-bridged ligands **6j**,**k**, possessing a P-stereogenic phosphine group, were also synthesized. For

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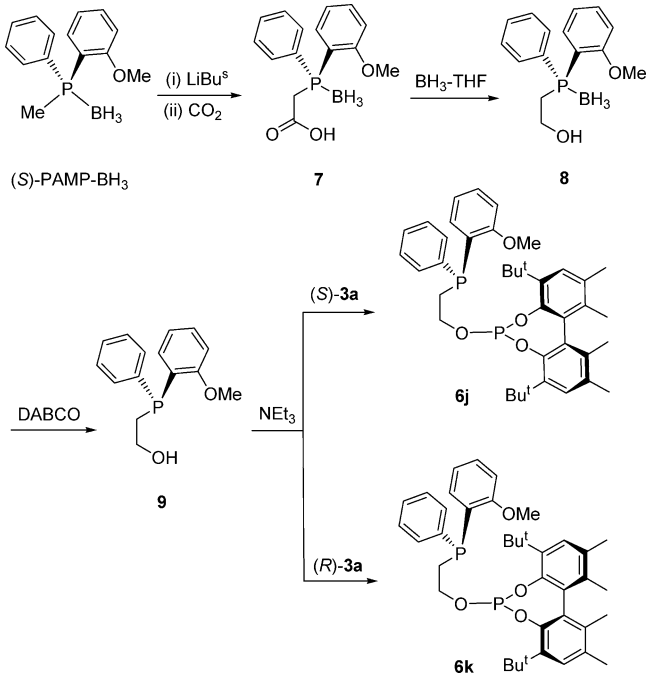
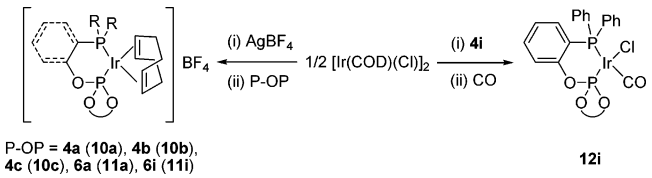
Scheme 4



Scheme 5



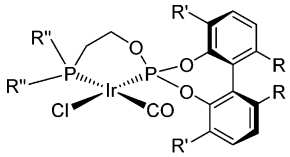
the latter, phosphine−borane **8** was prepared from readily accessible (*S*)-PAMP-borane (Scheme 4).[25] Subsequent deboronation with 1,4-diazabicyclo[2,2,2]octane (DABCO),[26] followed by condensation with each enantiomer of phosphorochloridite **3a**, led to the diastereomeric compounds **6j**,**k**.

Structural Studies of Ir Complexes. To gain insight about the backbone influence in imine hydrogenation, we have examined in detail the structural differences between coordinated **4** and **6**. A series of complexes with the formulation [Ir(COD)(P−OP)]BF_4 (**10**, **11**) were prepared by chloride abstraction from $[Ir(Cl)(COD)]_2$, followed by addition of an stoichiometric amount of the chelating ligand (Scheme 5). Alternatively, the chloro carbonyl complex Ir(Cl)(CO)(**4i**) (**12i**) was synthesized by bubbling carbon monoxide through a mixture of $[Ir(Cl)(COD)]_2$ and **4i** at a Ir/ligand ratio of 1.

The structures of compounds **11i** and **12i** have been studied by single-crystal X-ray diffraction. Figures 1 and 2 show ORTEP diagrams of these complexes, along with selected bond distances and angles. Both compounds display a square-planar coordination geometry, with angles between mutually cis ligands in the range between 89 and 93°. Despite the different natures of the backbones, the bite angle values are very similar: 91° (**11i**) and 89° (**12i**). As observed before in related complexes,[14,16] the Ir−P(phosphite) distance is appreciably shorter than the Ir−P(phosphine) distance (0.09 and 0.17 Å for **11i** and **12i**, respectively). Otherwise, the greater π-acceptor character of the phosphite is not evident in the Ir−C bond values of **11i**. Thus, Ir bonds to olefin atoms C(43) and C(44) are only slightly longer (ca. 0.04 Å) than those of C(47) and C(48). With regard to this study, the most interesting difference between the two complexes lies in the structure of the iridacycle. Thus, **11i** displays a boat conformation facilitated by coplanarity of the fragment P(2)−C(30)−C(29)−O(3) imposed by the benzene ring. In a different manner, rotation allowed around the C(29)−C(30) bond makes possible a twist-boat conformation for the iridacycle of **12i**. As a consequence, the orientation of phenyl substituents, of great importance in asymmetric catalysis,[27] also differs between **11i** and **12i**. For the latter, the aryl group defined by C(35) occupies a pseudoaxial position (φ_1(C(35)−P(2)−Ir(1)−P(1)) = −86°), while that denoted by C(41) is pseudoequatorial (φ_2(C(41)−P(2)−Ir(1)−P(1)) = 150°). Otherwise, Ph groups in **11i** are distributed more symmetrically around the coordination plane, as denoted by the corresponding torsion angles (φ_1(C(37)−P(2)−Ir(1)−P(1)) = −112° and φ_2(C(31)−P(2)−Ir(1)−P(1)) = 128°).

The diolefinic derivatives **10** and **11** have also been investigated by NMR techniques. These complexes display in the $^{31}P\{^1H\}$ experiment one doublet around 100 ppm, due to the phosphite group, and another doublet for the phosphine in the interval between 10 and −20 ppm, depending on the nature of the phosphine substituents. Values of $^3J_{PP}$ range around 40 Hz, independent of the backbone nature. For instance, compounds **10a** and **11a** have an identical value (42 Hz) for this coupling constant. On the other hand, the set of olefinic carbons shows in the $^{13}C\{^1H\}$ experiment a similar pattern for complexes **10a**−**c** and **11a**. Then, two doublets are observed in the region between 105 and 100 ppm ($^3J_{PC} \approx 15$ Hz), while another doublet appears at δ ca. 95 ppm ($^3J_{PC} = 8$ Hz) and the fourth doublet resonates around 80 ppm ($^3J_{PC} = 11$ Hz). The two higher field signals have been assigned by analysis of the 2D $^1H-^{13}C$ HETCOR and ^1H NOESY spectra to the olefinic fragment located trans to the phosphine, indicating a higher π-backbonding on that C=C bond.[28] Interestingly, compound **11a** exhibits exchange cross-peaks in the phase-sensitive 2D ^1H-NOESY experiment due to the interconversion of olefinic protons H^a and H^b with H^d and H^c, respectively (Figure 3). This behavior can be explained by a formal rotation of the diolefinic moiety allowed by dissociation of one of the Ir−olefin bonds,[29] presumably the weaker trans to the phosphite. In addition, NOE contacts are in good accord with a structure in solution of **11a** (Figure 4), similar to the X-ray structure of compound **11i**. Finally, the presence of a carbonyl ligand in **12i** is evidenced in the $^{13}C\{^1H\}$ NMR spectrum by a doublet of doublets centered at ca. 180 ppm ($^2J_{CP} = 118$, 15 Hz) and in the IR spectrum by an intense band at 2027 cm^{-1}.

To obtain further insight about the coordination mode of the phosphine−phosphite ligands, DFT calculations at the B3LYP level of theory have been performed with some Ir(Cl)(CO)(P−OP) model complexes (**I**−**V**). First, we have investigated the



relative stability of the simplest model **I** with respect to its isomer featuring phosphite and carbonyl π-acceptor groups in mutually trans positions. The geometries of both complexes have

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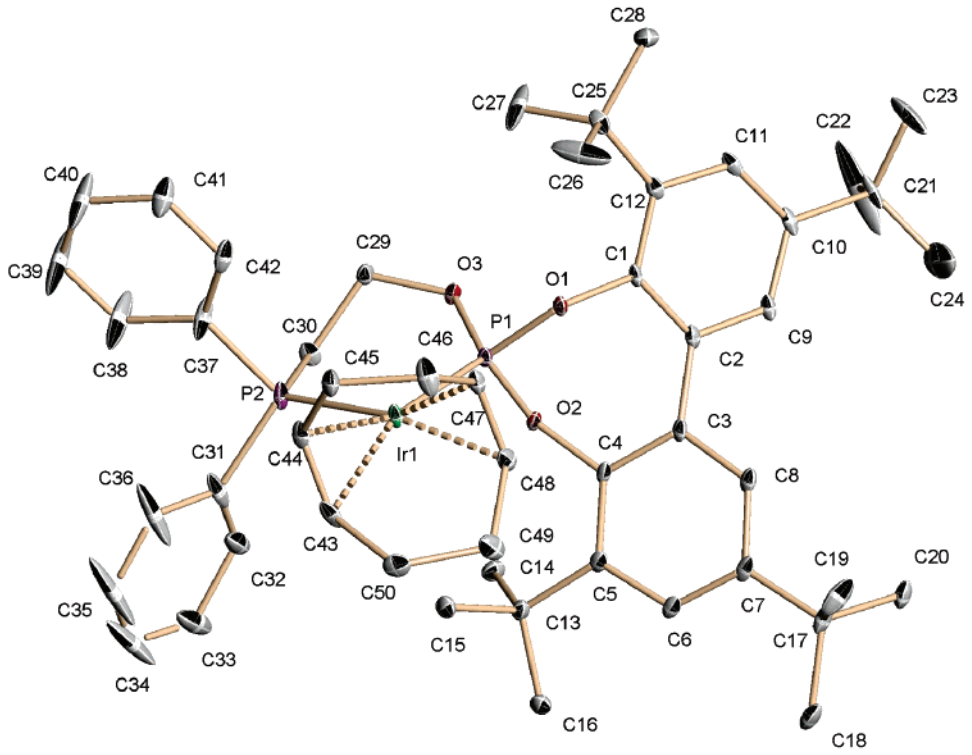

Figure 1. ORTEP view of the cation of **11i**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−P(1) = 2.2275(10), Ir−P(2) = 2.3179(10), Ir−C(43) = 2.272(4), Ir−C(44) = 2.273(4), Ir−C(47) = 2.218(4), Ir−C(48) = 2.237(4), C(43)−C(44) = 1.381(7), C(47)−C(48) = 1.392(7); P(2)−Ir−P(1) = 90.93(4), O(3)−C(29)−C(30)−P(2) = 78.0(4).

been fully optimized. It is worth noting that compound **I** is significantly more stable (9.5 kcal/mol) than its isomer, fully indicative of the electronic dissimilarity between the two phosphorus functionalities. For the structure of model **I**, the computed bond distances and angles match closely the values found for **12i** by X-ray diffraction. For instance, the calculated Ir−P(2) and Ir−P(1) bond distances are 2.381 and 2.197 Å (Figure 5), respectively, which compare well with values of 2.336 and 2.162 Å found in **12i**. Then, we tried to investigate the possible intervention of iridacycle conformations different from those observed in **11i**, as the next target for this analysis. Initially, the simplest model **I** was used, and minimization energy from a set of different starting point conformations led to the two structures **I-A** and **I-B**. The first structure closely resembles the iridacycle structure found in **11i**, while the second conformer adopts a pseudochair conformation for the metallacycle. Compound **I-A** was found to be 0.5 kcal/mol more stable than **I-B**. This small energy difference inspired us to design a series of model complexes where the complexity and steric effects of the substituents were gradually increased (**II**−**V**), to determine if they have any effect on the relative stabilities of the two conformations.[30] In all cases, conformer type **A** was found to be slightly more stable than **B**, as energy differences were lower than 0.7 kcal/mol. These results indicate that even bulky Bu^t substituents in the phosphite have little effect on the relative stabilities of the two conformers, probably because the endo (relative to the backbone) Bu^t substituent is not close enough to interact with the central CH_2, which should move easily as inferred from optimized structures **V-A** and **V-B**. This is an important difference from the benzene-bridged ligands **4**, as the latter produce conformationally rigid complexes caused by an steric impediment between the aromatic backbone and its closer Bu^t group.[21a] In addition, conformer **V-A** closely reproduces the distribution of Ph groups observed in the solid structure of **11i**, as denoted by the torsion angle values φ_1(C(1)−P(2)−Ir(1)−P(1)) = −116° and φ_2(C(2)−P(2)−Ir(1)−P(1)) = 121°, while in conformer **V-B** these phosphine substituents are located around pseudoequatorial ($\varphi_1 = -133°$) and pseudoaxial ($\varphi_2 = 104°$) positions, respectively.

Enantioselective Hydrogenation of N-Aryl Imines. The utility of ligands **4** and **6** has been investigated in the iridium-catalyzed enantioselective hydrogenation of N-aryl imines. A perusal of the literature indicates that two types of catalyst precursors have been used for this reaction: cationic derivatives bearing a chiral chelating ligand as well as a diolefin coligand such as COD and those prepared in situ from $[Ir(COD)(Cl)]_2$ and an stoichiometric amount of chiral ligand.[7−9] Investigation of both types of catalysts with phosphine−phosphites **4** and **6** indicated that the latter precatalysts behaved significantly better than the cationic ones. Catalyst precursors **10a** and **11a** completed reactions under our standard conditions with 4 and 17% ee, respectively (Tables 1 and 2), while the neutral counterparts prepared from **4a** and **6a** gave 36 and 81% ee, respectively.

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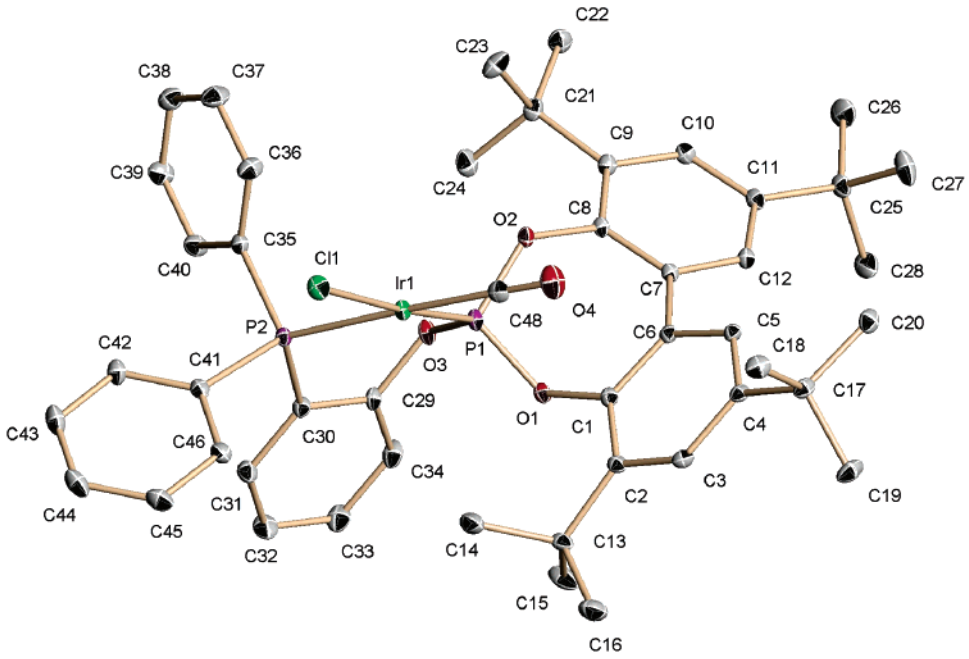

Figure 2. ORTEP view of complex **12i**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−P(1) = 2.1620(5), Ir−P(2) = 2.3356(5); P(2)−Ir−P(1) = 92.57(6), C48−Ir−Cl = 89.17(6), P(2)−Ir−Cl = 89.369(17), O(3)−C(29)−C(30)−P(2) = 7.0(2).

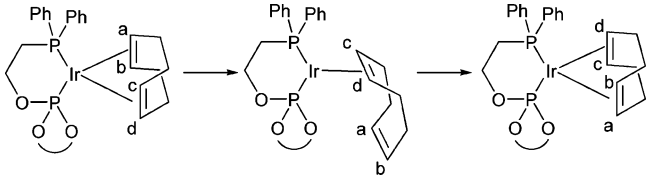

Figure 3. Mechanism proposed for the fluxional behavior of **11a**.

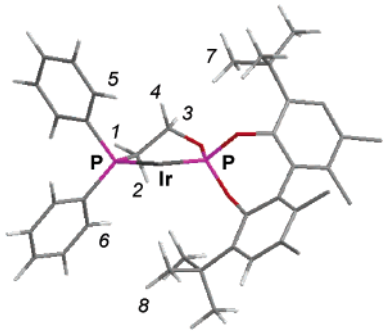

Figure 4. Selected NOE observed in the Ir-**6a** fragment of compound **11a**: H(*1*)↔H(*5*), H(*1*)↔H(*6*), H(*2*)↔H(*6*), H(*2*)↔H(*8*), H(*4*)↔H(*5*), H(*4*)↔H(*7*), H(*6*)↔H(*8*).

Initially, ligands derived from a benzene backbone were examined. All catalysts completed the reactions under the conditions specified. From these results it can be seen that ligand **4a** (Table 1, entry 2) produced higher enantioselectivities than isopropyl (**4b**) or methyl (**4c**) derivatives (entries 3 and 4), while other PAr_2 groups did not afford a sufficient enhancement on enantioselectivity (entries 7 and 8). Otherwise, catalyst optimization using an aliphatic backbone caused an important improvement. Thus, the catalyst derived from **6a** yielded amine **14a** with 81% ee (entry 2, Table 2; Scheme 6), 45% higher than **4a**. This difference is more general, and ligands **6f**,**h** (entries 3 and 5) produced enantioselectivities 23 and 40% higher than their counterparts **4f**,**h**, respectively.

To complete this screening, a set of ligands with P-stereogenic phosphine groups were also examined in the hydrogenation of **13a**. The catalyst derived from **4d** produced (*R*)-**14a** with 46% ee (entry 5), while diastereomeric **4e** led to the same amine enantiomer with a significantly lower enantioselectivity (12% ee, entry 6, Table 1). Therefore, in the latter examples the product configuration is determined by phosphine chirality. Otherwise, for the couple formed by **6j**,**k**, the dominant chiral induction proceeds from the phosphite. Thus, the former produced (*R*)-**14a** with 84% ee, while **6k** gave (*S*)-**14a** with a lower optical purity (56% ee, entry 7, Table 2).

Finally, with the intent of giving some generalization to the best catalyst of the series, we also investigated the hydrogenation of other *N*-aryl imines (Table 3). Notably, **6j** gave a good level of enantiomeric excess,[7−9] between 72 and 85% ee, for these reactions.

To get valuable information for ligand design, it is of interest to make some correlations between the structures of the Ir complexes and the results observed in the hydrogenations, without the intention of making a mechanistic proposal. It can first be concluded that both phosphite and phosphine groups have an important influence on the reaction, and their cooperation is necessary for the achievement of a high enantioselectivity. With the aid of a quadrant diagram,[31] it is easy to visualize the steric features of the metal−ligand fragment. Thus, it can be observed how a phosphite group with *S* configuration offers the higher steric hindrance at Q2 (Figure 6), and an (*R*)-phosphite in Q1, while for the phosphine group, the main encumbrance should be expected from a pseudoaxial aryl ring.[32] Accordingly, examination of results collected in Tables 1 and 2 shows that ligands blocking two diagonally arranged quadrants afford low to moderate enantioselectivities. A clear example is provided by the ligand **4e** (Figure 6a), the least enantioselective along the series. In addition, ligand **6k** increases the size of the diagonally opposed substituent to the quadrant blocked by the phosphite (Figure 6b), in comparison to **6a**, and this cause a

(31) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.
(32) (a) Nagel, U.; Rieger, B. *Organometallics* **1989**, *8*, 1534. (b) Gridnev, I. D.; Higashi, N.; Asakura, K.; Imamoto, T. *J. Am. Chem. Soc.* **2000**, *122*, 7183.

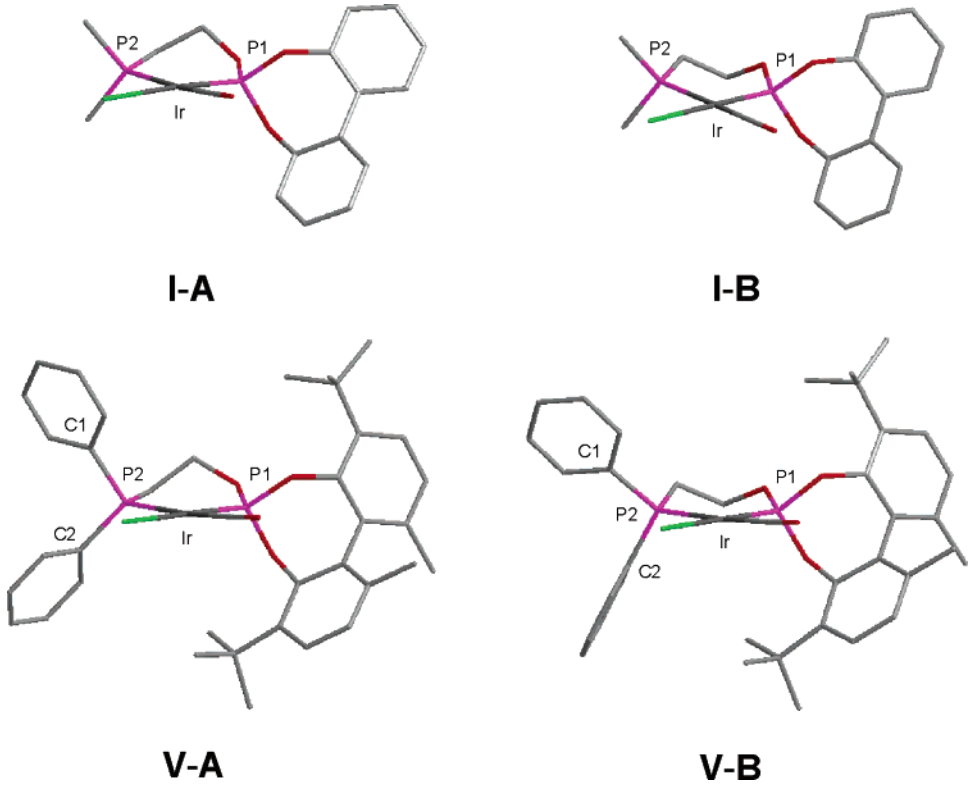

Figure 5. Optimized structures for model complexes **I** and **V**.

Table 1. Hydrogenation of 13a Using Ligands 4[a]

entry	precatalyst	P−OP	% ee (confign)
1	[Ir(COD)(P−OP)]BF_4	**4a**	4 (*R*)
2	$^1/_2$ [Ir(COD)Cl] + P−OP	**4a**	36 (*R*)
3		**4b**	25 (*R*)
4		**4c**	20 (*R*)
5		**4d**	46 (*R*)
6		**4e**	12 (*R*)
7		**4f**	47 (*R*)
8		**4h**	42 (*R*)

[a] All hydrogenations were completed under the conditions specified. Reactions were carried out at room temperature with an initial hydrogen pressure of 30 bar, in methylene chloride with S/C = 100. The reaction time was 24 h. The conversion was determined by ^{1}H NMR and enantiomeric excess (ee) by chiral HPLC. The configuration was determined by comparison of the optical rotation with the literature value.[11]

Table 2. Hydrogenation of 13a with Precatalysts Derived from Ligands 6[a]

entry	precatalyst	P−OP	% ee (confign)
1	[Ir(COD)(P−OP)]BF_4	**6a**	16 (*R*)
2	$^1/_2$ [Ir(COD)Cl] + P−OP	**6a**	81 (*R*)
3		**6f**	70 (*R*)
4		**6g**	76 (*R*)
5		**6h**	82 (*R*)
6		**6j**	84 (*R*)
7		**6k**	56 (*S*)

[a] All hydrogenations were completed under the conditions specified. Reactions were carried out at room temperature with an initial hydrogen pressure of 30 bar, in methylene chloride with S/C = 100. The reaction time was 24 h. The conversion was determined by ^{1}H NMR and enantiomeric excess (ee) by chiral HPLC. The configuration was determined by comparison of the optical rotation with the literature value.[11]

severe decrease in enantioselectivity. A second interesting observation comes from the occupation of the phosphine quadrant adjacent to that blocked by the phosphite. Thus, an increase in ee has been observed on moving from ligand **4e** to **4a** (Figure 6c) or from **4c** to **4d** (Figure 6d). Catalyst enhancement produced by ligand **6a** can then be explained by these

Scheme 6

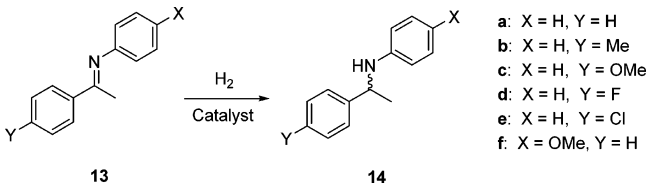

Table 3. Hydrogenation of Imines 13 with the Precatalyst $^1/_2$ [Ir(Cl)(COD)]$_2$ + 6j[a]

entry	product	% ee	entry	product	% ee
1	**14b**	72 (−)	4	**14e**	82 (−)
2	**14c**	85 (+)	5	**14f**	81 (+)
3	**14d**	79 (−)			

[a] All hydrogenations were completed under the conditions specified. Reactions were carried out at room temperature with an initial hydrogen pressure of 30 bar, in methylene chloride with S/C = 100. The reaction time was 24 h. The conversion was determined by ^{1}H NMR and enantiomeric excess (ee) by chiral HPLC. The configurations were not determined.

two effects. Thus, in conformer A (Figure 6e) a release of steric hindrance is produced at Q4, with respect to Ir-**4a**, caused by the displacement of the upper Ph toward a more pseudoequatorial position. In addition, there is a growth of steric impediment at Q3, as the lower phenyl moves to a more pseudoaxial location. These displacements further continue to reach conformer B, which shows the most effective blocking of the adjacent quadrants Q2 and Q3 (Figure 6f).

Conclusions

A family of structurally diverse chiral phosphine−phosphites has been prepared and evaluated in the iridium-catalyzed hydrogenation of *N*-aryl imines. Ligand screening has clearly identified the nature of the backbone as a critical variable in this reaction, and ethane-bridged ligands have significantly

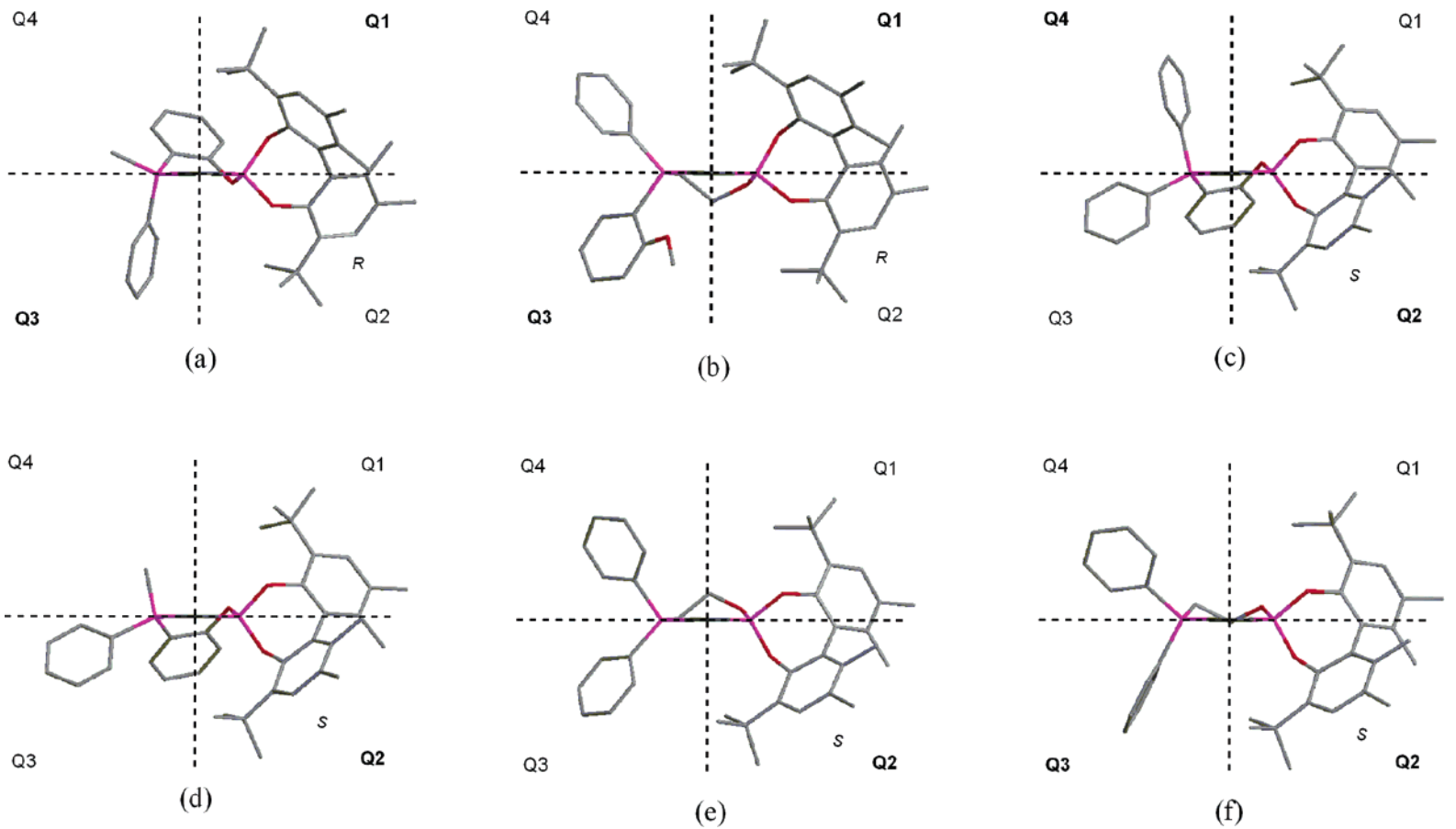

Figure 6. Quadrant diagrams for the fragments: (a) Ir-**4e**; (b) Ir-**6k**; (c) Ir-**4a**; (d) Ir-**4d**; (e) Ir-**6a** (conformer A); (f) Ir-**6a** (conformer B).

outperformed their benzene counterparts. A detailed structural study by NMR and X-ray diffraction performed with complexes with the formulations [Ir(COD)(P−OP)]BF_4 and Ir(Cl)CO(P−OP) has demonstrated important conformational differences between coordinated **4** and **6**. As a complement to the latter, model compounds of the chloro carbonyls have been analyzed by DFT methods. From theoretical data, two participating conformations can be expected, characterized by a dissimilar distribution of phosphine substituents. Comparison of the results obtained with this family of phosphine−phosphites suggest that, in contrast to olefin hydrogenation,[14] a scheme of two sterically blocked adjacent quadrants in the Ir−ligand fragment is preferable for this type of hydrogenation. Ligand optimization has pointed to **6j** as the best ligand of the series, and it has produced 84% ee in the hydrogenation of imine **14a**. Similarly, enantioselectivities between 72 and 85% ee have been obtained with ligand **6j** in the reduction of several N-aryl imines **14**.

Experimental Section

General Comments. All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen using the following desiccants: sodium−benzophenone ketyl for benzene, diethyl ether (Et_2O), and tetrahydrofuran (THF); sodium for petroleum ether and toluene; CaH_2 for dichloromethane (CH_2Cl_2); NaOMe for methanol (MeOH). NMR spectra were obtained on Bruker DPX-300, DRX-400, and DRX-500 spectrometers. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. GC analyses were performed by using a Hewlett-Packard Model HP 6890 chromatograph. HRMS data were obtained using a JEOL JMS-SX 102A mass spectrometer. Elemental analyses were run by the Analytical Service of the Instituto de Investigaciones Químicas. Optical rotations were measured on a Perkin-Elmer Model 341 polarimeter.

(2-Hydroxyphenyl)bis(*o*-tolyl)phosphine (1f). Over a solution of *o*-anisyldi-*o*-tolylphosphine (2.600 g, 8.11 mmol) in CH_2Cl_2 (50 mL), cooled to −78 °C, was added BBr_3 (1.7 mL, 18.6 mmol). The mixture was stirred overnight at room temperature and the solvent evaporated. The residue was treated with a portion of toluene (25 mL), and the volatiles were removed under reduced pressure. The solid obtained was treated with MeOH (20 mL) at 0 °C and stirred for 2 days at room temperature. Solvent evaporation yielded (2-hydroxyphenyl)di-*o*-tolylphosphonium bromide as a white solid (2.020 g, 65%). Without further purification, the phosphonium salt (1.830 g, 4.73 mmol) was suspended in Et_2O (30 mL) and NEt_3 (0.9 mL, 6.1 mmol) was added. The suspension was stirred for 2 h and filtered. Solvent evaporation gave **1f** as a white solid (1.200 g, 83%). Spectroscopic data obtained for this compound agree with the published values.[42]

(2-Hydroxyphenyl)bis(3,5-dimethylphenyl)phosphine (1g). This product was prepared by following the procedure described for **1f**. White solid (0.583 g, 60%). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 12H, 4 Me), 6.98 (m, 9H, 9 H arom), 7.30 (m, 1H, H arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −30.0. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 21.6 (4 Me), 115.8 (CH arom), 121.2 (CH arom), 121.5 (d, J_{CP} = 6 Hz, C_q arom), 131.1 (2 CH arom), 131.2 (2 CH arom), 131.5 (2 CH arom), 131.7 (CH arom), 134.9 (d, J_{CP} = 4 Hz, 2 C_q arom), 135.1 (d, J_{CP} = 5 Hz, CH arom), 138.4 (d, J_{CP} = 7 Hz, 4 C_q arom), 159.4 (d, J_{CP} = 18 Hz, C_q arom). HRMS (CI): *m*/*z* 334.1491, $[M]^+$ (exact mass calculated for $C_{22}H_{23}OP$ 334.1487).

(2-Hydroxyethyl)diphenylphosphine (5a). This compound was prepared by a modification of the literature procedure as follows. A solution of Ph_2PH (1.00 g, 5.37 mmol) and 2-bromoethanol (0.671 g, 5.37 mmol) in THF (20 mL) was treated with $LiBu^n$ (7.1 mL, 1.6 M in hexanes). The mixture was stirred for 2 h and evaporated and the residue extracted in CH_2Cl_2. The resulting solution was treated with an excess of solid NH_4Cl in CH_2Cl_2. The suspension was filtered and the solution evaporated. The remaining residue was extracted with Et_2O (2 × 15 mL), and the volatiles were removed, yielding **5a** as a colorless oil (0.848 g, 70%).

(2-Hydroxyethyl)bis(*o*-tolyl)phosphine (5f). This compound was prepared by following the procedure described for **5a**. Colorless oil (0.503 g, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.66 (brm, 1H, OH), 2.31 (t, 2H, J_{HH} = 6.8 Hz, PCH_2), 2.4 (s, 6H, 2 Me), 3.77 (m, 2H, CH_2O), 7.19 (m, 8H, 8 H arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −46.5. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 21.3 (*Me*−Ar), 21.6 (*Me*−Ar), 31.2 (d, J_{CP} = 13 Hz, PCH_2), 60.5 (d, J_{CP} = 23 Hz, CH_2OH), 126.4 (2 CH arom), 128.9 (2 CH arom), 130.3 (CH arom), 130.4 (CH arom), 132.4 (2 CH arom), 136.4 (d, J_{CP} = 12 Hz, 2 C_q arom), 142.6 (d, J_{CP} = 26 Hz, 2 C_q arom). HRMS (EI): *m*/*z* 258.1181, $[M]^+$ (exact mass calculated for $C_{16}H_{19}OP$ 258.1173).

(2-Hydroxyethyl)bis(*p*-tolyl)phosphine (5g). The preparation of this compound is analogous to that described for **5a**. Colorless oil (0.341 g, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.78 (br m, 2H, PCH_2), 2.28 (s, 6H, 2 Me), 3.72 (br m, 2H, CH_2O), 3.91 (br s, 1H, OH), 7.17 (m, 8H, 8 H arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −27.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 21.5 (2 *Me*−Ar), 32.0 (d, J_{CP} = 11 Hz, PCH_2), 60.2 (d, J_{CP} = 23 Hz, CH_2OH), 129.5 (2 CH arom), 129.6 (2 CH arom), 131.3 (d, J_{CP} = 13 Hz, C_q arom), 132.8 (2 CH arom), 133.0 (2 CH arom), 134.5 (d, J_{CP} = 9 Hz, C_q arom), 138.9 (2 C_q arom). HRMS (EI): *m*/*z* 258.1175, $[M]^+$ (exact mass calculated for $C_{16}H_{19}OP$ 258.1173).

(2-Hydroxyethyl)bis(3,5-xylyl)phosphine (5h). This compound was prepared as described for **5a**. Colorless oil (0.324 g, 85%). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.62 (br s, 1H, OH), 2.28 (s, 12H, 4 *Me*−Ar), 2.35 (t, J_{HH} = 7.2 Hz, 2H, PCH_2), 3.75 (q, J_{HH} = 8.4 Hz, 2H, CH_2O), 6.9 (s, 1H, CH arom), 7.03 (s, 2H, 2 H arom), 7.05 (s, 3H, 3 H arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −25.6. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 21.6 (4 *Me*−Ar), 32.4 (d, J_{CP} = 13 Hz, PCH_2), 60.6 (d, J_{CP} = 23 Hz, CH_2OH), 130.5 (2 CH arom), 130.7 (2 CH arom), 130.8 (2 CH arom), 131.5 (d, J_{CP} = 19 Hz, C_q arom), 137.8 (d, J_{CP} = 11 Hz, C_q arom), 138.2 (2 C_q arom), 138.3 (2 C_q arom). HRMS (EI): *m*/*z* 286.1485, $[M]^+$ (exact mass calculated for $C_{18}H_{23}OP$ 286.1486).

(*S*)-(2-Carboxyethyl)(*o*-anisyl)phenylphosphine−Borane (7). $LiBu^s$ (3.5 mL of a 1.3 M in cyclohexane solution, 4.5 mmol) was added at −78 °C to a solution of (*S*)-phenyl(*o*-anisyl)methylphosphine−borane (1.000 g, 4.10 mmol) in Et_2O (50 mL). The reaction mixture was stirred for 2 h at the same temperature. CO_2 dried through Drierite was bubbled through the solution, and the mixture was stirred overnight at room temperature. The resulting mixture was quenched with an aqueous solution of HCl (1 M; 10 mL), and the organic layer was separated and extracted with two portions of a saturated solution of Na_2CO_3 (2 × 20 mL). The aqueous phase was separated and acidified with concentrated HCl until precipitation of a white solid was complete. The mixture was extracted with AcOEt (3 × 30 mL), and the organic phases were combined, dried with Na_2SO_4, and filtered. Evaporation of the solution provided product **10** as a white solid (1.020 g, 86%). $[\alpha]^{20}_D$ = +2.7° (*c* 1.0, THF). ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (br m, 3H, BH_3), 3.42 (dd, J_{HH} = 18.0, J_{HP} = 14.4 Hz, 1H, PC*H*H), 3.58 (dd, J_{HH} = 17.6, J_{HP} = 17.6 Hz, 1H, PCH*H*), 3.69 (s, 3H, OCH_3), 6.89 (dd, J_{HH} = 11.2, J_{HP} = 4.4 Hz, 1H, H arom), 7.06 (td, $^3J_{HH}$ = 9.6, J_{HH} = 2.4 Hz, 1H, H arom), 7.37 (m, 3H, 3 H arom), 7.53 (t, J_{HH} = 10.0 Hz, 1H, H arom), 7.67 (dd, J_{HP} = 15.2, J_{HH} = 9.6 Hz, 2H, 2 H arom), 7.86 (dd, J_{HP} = 18.8, J_{HH} = 10.4 Hz, 1H, 1 H arom), 9.62 (br s, 1H, COOH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 13.5 (br m). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 32.8 (d, J_{CP} = 31 Hz, PCH_2), 55.6 (OCH_3), 111.4 (d, J_{CP} = 4

Hz, CH arom), 114.7 (d, J_{CP} = 54 Hz, C_q arom), 121.5 (d, J_{CP} = 13 Hz, CH arom), 128.7 (CH arom), 128.8 (CH arom), 128.9 (d, J_{CP} = 59 Hz, C_q arom), 131.3 (CH arom), 131.8 (CH arom), 131.9 (CH arom), 134.7 (CH arom), 136.4 (d, J_{CP} = 16 Hz, CH arom), 161.4 (OC_q), 173.8 (COOH). HRMS (FAB): *m*/*z* 311.0980, $[M + Na]^+$ (exact mass calculated for $C_{15}H_{18}BO_3PNa$ 311.0984).

(*S*)-(2-Hydroxyethyl)(*o*-anisyl)phenylphosphine−Borane (8). A solution of **10** (0.822 g, 2.85 mmol) in THF (15 mL) was treated with $BH_3{\cdot}SMe_2$ (1.1 mL, 11.4 mmol) at 0 °C. The reaction mixture was stirred for 4 h at room temperature. The mixture was quenched at 0 °C with water (20 mL), and CH_2Cl_2 (20 mL) was added in order to facilitate the separation of the phases. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The organic phases were combined and dried over Na_2SO_4, and the solvent was removed. The residue was chromatographed on silica (AcOEt/hexanes, 1:1) to yield the desired product as a colorless oil (0.600 g, 76%). Spectroscopic data for this compound match with those previously reported in the literature.[33]

(*S*)-(2-Hydroxyethyl)(*o*-anisyl)phenylphosphine (9). A solution of (*S*)-(*o*-anisyl)(2-hydroxyethyl)phenylphosphine−borane (0.590 mg, 2.15 mmol) in toluene (15 mL) was treated with DABCO (0.723 g, 6.44 mmol). The mixture was stirred for 4 days. The solvent was removed, and the residue was filtered through a plug of silica (eluent Et_2O). Evaporation of the solution provided the product as a colorless oil (0.366 g, 65%). $[\alpha]^{20}_D = -12°$ (*c* 1.1, THF). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74 (br s, 1H, OH), 2.37 (m, 2H, PCH_2), 3.77 (s, 3H, OCH_3), 3.79 (m, 2H, CH_2O), 6.89 (m, 2H, 2 H arom), 7.06 (m, 1H, H arom), 7.30 (m, 4H, 4 H arom), 7.47 (m, 2H, 2 H arom). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −35.5. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 30.8 (d, J_{CP} = 10 Hz, PCH_2), 55.9 (OCH_3), 60.6 (d, J_{CP} = 22 Hz, OCH_2), 110.7 (CH arom), 121.3 (CH arom), 125.7 (d, J_{CP} = 17 Hz, C_q arom), 128.7 (CH arom), 128.8 (CH arom), 129.2 (CH arom), 130.7 (CH arom), 132.7 (d, J_{CP} = 4 Hz, CH arom), 133.3 (CH arom), 133.6 (CH arom), 136.6 (br s, C_q arom), 161.3 (d, J_{CP} = 13 Hz, OC_q). HRMS (EI): *m*/*z* 260.0970, $[M]^+$ (exact mass calculated for $C_{15}H_{17}O_2P$ 260.0966).

2-(Bis(*o*-tolyl)phosphino)phenyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (4f). A solution of **1f** (0.950 g, 3.10 mmol) in toluene (40 mL) was added dropwise to (*S*)-3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-bisphenoxyphosphorus chloride ((*S*)-**3a**; 1.297 g, 3.10 mmol) and NEt_3 (0.8 mL, 5.7 mmol) dissolved in toluene (40 mL). The resulting suspension was stirred for 24 h and filtered, and the volatiles were removed, yielding compound **4f** as a foamy white solid (1.500 g, 70%). $[\alpha]^{20}_D$ = +306° (*c* 1.0, THF). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.21 (s, 9H, CMe_3), 1.28 (s, 9H, CMe_3), 1.81 (s, 3H, Me), 1.83 (s, 3H, Me), 2.23 (s, 3H, Me), 2.25 (s, 3H, Me), 2.26 (s, 3H, Me), 2.28 (s, 3H, Me), 6.95 (m, 14H, 14 H arom). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ −39.9 (d, P−C), 130.0 (d, J_{PP} = 44 Hz, P−O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 16.6 (Me), 16.8 (Me), 20.4 (Me), 20.5 (Me), 21.1 (d, J_{CP} = 22 Hz, Me), 21.3 (d, J_{CP} = 22 Hz, Me), 31.2 (d, J_{CP} = 5 Hz, C*Me*$_3$), 31.3 (C*Me*$_3$), 34.8 (*C*Me$_3$), 34.9 (*C*Me$_3$), 121.9 (d, J_{CP} = 9 Hz, CH arom), 124.8 (CH arom), 125.6 (C_q arom), 126.3 (2 CH arom), 128.2 (CH arom), 128.5 (C_q arom), 128.7 (CH arom), 128.8 (CH arom), 128.9 (CH arom), 129.3 (C_q arom), 130.2 (m, 2 CH arom), 130.4 (CH arom), 130.9 (C_q arom), 132.2 (C_q arom), 132.4 (d, J_{CP} = 6 Hz, C_q arom), 133.2 (CH arom), 133.5 (CH arom), 134.6 (C_q arom), 135.0 (CH arom), 135.1 (d, J_{CP} = 5 Hz, C_q arom), 135.4 (C_q arom), 137.8 (C_q arom), 138.8 (C_q arom), 142.6 (d, J_{CP} = 13 Hz, C_q arom), 143.0 (d, J_{CP} = 14 Hz, C_q arom), 144.7 (C_q arom), 145.4 (d, J_{CP} = 7 Hz, C_q arom), 155.0 (m, C_q arom). HRMS (CI): *m*/*z* 688.3243, $[M]^+$ (exact mass calculated for $C_{44}H_{50}O_3P_2$ 688.3235).

2-(Diphenylphosphino)phenyl 3,3′,5,5′-Tetra-*tert*-butylbiphenyl-2,2′-diyl Phosphite (4i). The synthesis of this compound was effected as described for **6a**, using the phosphorochloridite **7**. White solid (0.252 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.35 (s, 36H, 4 CMe_3), 6.35 (m, 1H, H arom), 6.71 (m, 1H, H arom), 6.89 (m, 1H, H arom), 6.99 (m, 1H, H arom), 7.24 (m, 12H, 12 H arom), 7.41 (d, J_{CP} = 2.4 Hz, 2H, 2 H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 162.1 MHz): δ −17.2 (d, P−C), 132.5 (d, P−O, J_{PP} = 31 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 30.9 (2 C*Me*$_3$), 31.5 (2 C*Me*$_3$), 34.7 (2 *C*Me$_3$), 35.3 (2 *C*Me$_3$), 121.5 (CH arom), 124.0 (CH arom), 124.7 (2 CH arom), 126.6 (2 CH arom), 128.3 (2 CH arom), 128.5 (2 CH arom), 128.5 (2 CH arom), 129.6 (CH arom), 132.9 (2 C_q arom), 133.6 (C_q arom), 133.7 (CH arom), 133.8 (2 CH arom), 134.0 (2 CH arom), 136.7 (d, J_{CP} = 12 Hz, 2 C_q arom), 145.8 (OC_q arom), 146.6 (2 OC_q arom). HRMS (EI): *m*/*z* 716.3565, $[M]^+$ (exact mass calculated for $C_{42}H_{54}O_3P_2$ 716.3548).

2-(Bis(3,5-dimethylphenyl)phosphino)phenyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (4h). A solution of (2-hydroxyphenyl)bis(3,5-dimethylphenyl)phosphine (0.325 g, 0.97 mmol) in toluene (20 mL) was added dropwise over (*S*)-3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-bisphenoxyphosphorus chloride ((*S*)-**3a**; 0.39 g, 1.0 mmol) and NEt_3 (0.2 mL, 1.3 mmol) dissolved in toluene (40 mL). The resulting suspension was stirred for 24 h, the mixture was filtered, and the volatiles were removed. The solid obtained was dissolved in Et_2O and passed through a short pad of neutral alumina. The solution was evaporated, yielding **4h** as a foamy white solid (0.370 g, 52%). $[\alpha]^D_{20}$ = +314° (*c* 0.9, THF). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.30 (s, 9H, CMe_3), 1.34 (s, 9H, CMe_3), 1.80 (s, 3H, Me), 1.82 (s, 3H, Me), 2.20 (s, 6H, 2 Me), 2.21 (s, 6H, 2 Me), 2.22 (s, 3H, Me), 2.27 (s, 3H, Me), 6.36 (m, 1H, H arom), 6.74 (m, 1H, H arom), 6.82 (m, 4H, 4 H arom), 6.91 (m, 3H, 3 H arom), 7.05 (m, 1H, H arom), 7.09 (s, 1H, H arom), 7.15 (s, 1H, H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −18.0 (d, P−C), 126.0 (d, J_{PP} = 41 Hz, P−O). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 16.8 (Ar−*Me*), 17.0 (Ar−*Me*), 20.7 (Ar−*Me*), 20.7 (Ar−*Me*), 21.6 (4 Ar−*Me*), 31.4 (d, J_{CP} = 6 Hz, C*Me*$_3$), 31.5 (C*Me*$_3$), 34.9 (*C*Me$_3$), 35.0 (*C*Me$_3$), 121.9 (d, J_{CP} = 6 Hz, CH arom), 124.2 (CH arom), 128.0 (CH arom), 128.4 (CH arom), 129.7 (CH arom), 130.1 (dd, J_{CP} = 23, 5 Hz, C_q arom), 130.3 (CH arom), 130.6 (CH arom), 131.1 (d, J_{CP} = 5 Hz, C_q arom), 131.3 (CH arom), 131.6 (CH arom), 131.8 (C_q arom), 132.0 (CH arom), 132.3 (CH arom), 132.8 (C_q arom), 134.4 (CH arom), 134.6 (C_q arom), 135.3 (C_q arom), 136.8 (s, C_q arom), 136.8 (d, J_{CP} = 25 Hz, C_q arom), 137.6 (C_q arom), 137.7 (C_q arom), 137.7 (C_q arom), 137.8 (C_q arom), 137.8 (C_q arom), 137.8 (C_q arom), 138.6 (d, J_{CP} = 2 Hz, C_q arom), 145.1 (C_q arom), 145.6 (d, J_{CP} = 6 Hz, C_q arom), 154.8 (dd, J_{CP} = 20, 4 Hz, C_q arom). HRMS (EI): *m*/*z* 716.3552, $[M]^+$ (exact mass calculated for $C_{46}H_{54}O_3P_2$ 716.3548).

2-(Diphenylphosphino)ethyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (6a). Over a solution of (*S*)-**3a** (0.350 g, 0.84 mmol) and NEt_3 (0.24 mL, 1.68 mmol) in toluene (30 mL) was added **5a** (0.195 g, 0.84 mmol) in toluene (20 mL). The mixture was stirred for 16 h, filtered, and evaporated. The resulting residue was dissolved in Et_2O (20 mL) and the solution filtered through a short pad of neutral alumina. Solvent evaporation produced **6a** as a white foamy solid (0.338 g, 70%). $[\alpha]^{20}_D$ = +117° (*c* 1.0, THF). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.37 (s, 9H, CMe_3), 1.47 (s, 9H, CMe_3), 1.77 (s, 6H, 2 Ar−*Me*), 2.19 (s, 3H, Ar−*Me*), 2.26 (s, 3H, Ar−*Me*), 2.32 (m, 2H, PCH_2), 3.36 (m, 1H, OC*H*H), 3.92 (m, 1H, OCH*H*), 7.04 (s, 1H, H arom), 7.07 (s, 1H, H arom), 7.30 (m, 10H, 10 H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −24.4 (P−C), 128.9 (P−O). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 16.8 (*Me*−Ar), 16.9 (*Me*−Ar), 20.7 (*Me*−Ar), 20.8 (*Me*−Ar), 30.4 (d, J_{CP} = 12.8 Hz, PCH_2), 31.3 (C*Me*$_3$), 31.6 (d, J_{CP} = 5 Hz, C*Me*$_3$), 34.8 (*C*Me$_3$), 34.9 (*C*Me$_3$), 62.4 (d, J_{CP} = 29 Hz, CH_2O), 127.5 (d, J_{CP} = 6 Hz, C_q arom), 128.6 (d, J_{CP} = 11 Hz, CH arom), 128.7 (d, J_{CP} = 2 Hz, CH arom),

(33) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

128.9 (CH arom), 129.0 (C_q arom), 129.3 (C_q arom), 130.8 (C_q arom), 131.7 (CH arom), 131.9 (d, J_{CP} = 4.7 Hz, C_q arom), 132.6 (CH arom), 132.7 (CH arom), 132.8 (CH arom), 132.9 (CH arom), 133.0 (CH arom), 134.6 (CH arom), 135.2 (CH arom), 136.9 (CH arom), 137.6 (C_q arom), 137.8 (C_q arom), 137.9 (C_q arom), 138.1 (C_q arom), 138.3 (OC_q), 145.7 (2 OC_q). HRMS (EI): *m*/*z* 612.2908, $[M]^+$ (exact mass calculated for $C_{38}H_{46}O_3P_2$ 612.2922).

2-(Bis(*o*-tolyl)phosphino)ethyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (6f). This compound was prepared by following the procedure described for **6a**. White foamy solid (0.454 g, 55%). $[\alpha]^{20}_D$ = +105° (*c* 1.0, THF). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.42 (s, 9H, CMe_3), 1.54 (s, 9H, CMe_3), 1.84 (s, 3H, OAr−*Me*), 1.86 (s, 3H, OAr−*Me*), 2.34 (m, 14H, 2 OAr−*Me*, 2 PAr−*Me*, PCH_2), 3.4 (m, 1H, OC*H*H), 3.9 (m,1H, OC*H*H), 7.17 (m, 10H, 10 H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −44.9 (P−C), 128.2 (P−O). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 16.6 (OAr−*Me*), 16.8 (OAr−*Me*), 20.6 (2 OAr−*Me*), 21.0 (d, J_{CP} = 17 Hz, PAr−*Me*), 21.4 (d, J_{CP} = 17 Hz, PAr−*Me*), 29.0 (d, J_{CP} = 14 Hz, PCH_2), 31.0 (2 C*Me*$_3$), 31.4 (*C*Me$_3$), 31.5 (*C*Me$_3$), 62.3 (d, J_{CP} = 29 Hz, OCH_2), 125.6 (d, J_{CP} = 18 Hz, CH arom), 127.8 (CH arom), 128.2 (CH arom), 128.4 (d, J_{CP} = 19 Hz, CH arom), 129.1 (C_q arom), 130.1 (CH arom), 130.3 (C_q arom), 130.8 (CH arom), 131.4 (CH arom), 131.7 (2 C_q arom), 132.4 (2 C_q arom), 134.4 (CH arom), 135.0 (CH arom), 135.6 (d, J_{CP} = 12 Hz, C_q arom), 135.8 (d, J_{CP} = 12 Hz, C_q arom), 136.9 (CH arom), 138.3 (C_q arom), 141.8 (C_q arom), 142.1 (d, J_{CP} = 25 Hz, C_q arom), 142.4 (C_q arom), 145.6 (OC_q arom), 145.7 (OC_q arom). HRMS (EI): *m*/*z* 640.3244, $[M]^+$ (exact mass calculated for $C_{40}H_{50}O_3P_2$ 640.3235).

2-(Bis(*p*-tolyl)phosphino)ethyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (6g). A solution of (*p*-tolyl)$_2$PH (0.200 g, 0.93 mmol) and 2-bromoethanol (0.117 g, 0.93 mmol) in THF (20 mL) was treated with LiPh (1.0 mL, 1.9 M solution in cyclohexanes−Et_2O). The reaction mixture was stirred for 2 h, and then a solution of (*S*)-**3a** (0.444 g, 0.93 mmol) in THF (20 mL) was added. The suspension was stirred for 16 h and filtered, and the volatiles were evaporated. The remaining residue was dissolved in Et_2O and filtered through a short pad of neutral alumina. Solvent evaporation yielded **6g** as a white solid (0.302 g, 50%). $[\alpha]^{20}_D$ = +108° (*c* 1.0, THF). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.32 (s, 9H, CMe_3), 1.43 (s, 9H, CMe_3), 1.74 (s, 6H, 2 PAr−*Me*), 2.16 (s, 3H, OAr−*Me*), 2.40 (m, 2H, PCH_2), 2.23 (s, 3H, OAr−*Me*), 2.29 (s, 3H, OAr−*Me*), 2.31 (s, 3H, OAr−*Me*), 3.32 (m, 1H, OC*H*H), 3.87 (m, 1H, OC*H*H), 7.29 (m, 10H, 10 H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −26.5 (P−C), 127.3 (P−O). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 16.5 (Ar−*Me*), 16.6 (Ar−*Me*), 20.3 (Ar−*Me*), 20.4 (Ar−*Me*), 21.3 (2 PAr−*Me*), 30.2 (d, J_{CP} = 11 Hz, PCH_2), 31.0 (C*Me*$_3$), 31.3 (d, J_{CP} = 9 Hz, C*Me*$_3$), 34.5 (*C*Me$_3$), 34.6 (*C*Me$_3$), 62.3 (d, J_{CP} = 30 Hz, OCH_2), 126.6 (C_q arom), 126.8 (C_q arom), 127.2 (C_q arom), 127.7 (CH arom), 128.0 (CH arom), 128.7 (2 C_q arom), 129.2 (CH arom), 129.3 (d, J_{CP} = 3 Hz, CH arom), 129.3 (CH arom), 129.4 (2 C_q arom), 130.5 (CH arom), 131.4 (C_q arom), 132.3 (CH arom), 132.4 (d, J_{CP} = 3 Hz, CH arom), 132.6 (CH arom), 134.3 (2 C_q arom), 134.9 (C_q arom), 136.6 (C_q arom), 138.0 (OC_q arom), 138.5 (d, J_{CP} = 5 Hz, OC_q arom), 145.4 (OC_q arom). HRMS (EI): *m*/*z* 640.3257, $[M]^+$ (exact mass calculated for $C_{40}H_{50}O_3P_2$ 640.3235).

2-(Bis(3,5-xylyl)phosphino)ethyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (6h). This compound was synthesized as described for **6g**. White foamy solid (0.332 g, 60%). $[\alpha]^{20}_D$ = +108° (*c* 1.0, THF). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.33 (s, 9H, CMe_3), 1.44 (s, 9H, CMe_3), 1.75 (s, 6H, 2 PAr−*Me*), 2.17 (m, 2H, PCH_2), 2.16 (s, 3H, OAr−*Me*), 2.21 (s, 6H, 2 PAr−*Me*), 2.22 (s, 3H, OAr−*Me*), 2.24 (s, 3H, OAr−*Me*), 2.29 (s, 3H, OAr−*Me*), 3.4 (m, 1H, O−C*H*H), 3.9 (m, 1H, O−CH*H*), 6.92 (m, 5H, 5 H arom), 7.00 (s, 1H, H arom), 7.12 (s, 1H, H arom), 7.22 (s, 1H, H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −25.5 (P−C), 129.2 (P−O). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 16.7 (OAr−*Me*), 16.8 (OAr−*Me*), 20.6 (OAr−*Me*), 20,7 (OAr−*Me*), 21.6 (4 Ar−*Me*), 30.6 (d, J_{CP} = 13.5 Hz, PCH_2), 31.3 (C*Me*$_3$), 31.6 (d, J_{CP} = 5 Hz, C*Me*$_3$), 34.8 (*C*Me$_3$), 34.9 (*C*Me$_3$), 62.6 (d, J_{CP} = 31 Hz, OCH_2), 127.4 (d, J_{CP} = 6 Hz, C_q arom), 127.9 (CH arom), 128.2 (CH arom), 129.3 (C_q arom), 130.2 (CH arom), 130.4 (CH arom), 130.5 (CH arom), 130.7 (CH arom), 130.8 (CH arom), 131.2 (C_q arom), 131.8 (d, J_{CP} = 14 Hz, C_q arom), 132.5 (C_q arom), 134.6 (C_q arom), 135.2 (C_q arom), 136.9 (C_q arom), 137.4 (C_q arom), 137.5 (C_q arom), 137.7 (C_q arom), 137.8 (C_q arom), 138.0 (d, J_{CP} = 7 Hz, CH arom), 138.2 (C_q arom), 145.4 (d, J_{CP} = 4 Hz, OC_q arom), 145.6 (d, J_{CP} = 5 Hz, OC_q arom), 154.5(d, J_{CP} = 3 Hz, OC_q arom). HRMS (EI): *m*/*z* 668.3557, $[M]^+$ (exact mass calculated for $C_{42}H_{54}O_3P_2$ 668.3548).

2-(Diphenylphosphino)ethyl 3,3′,5,5′-Tetra-*tert*-butylbiphenyl-2,2′-diyl Phosphite (6i). The synthesis of this ligand was effected as described for **8a**, starting from phosphine **5a**. White solid (0.344 g, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (s, 18 H, 2 CMe_3), 1.42 (s, 18 H, 2 CMe_3), 2.35 (t, J_{HP} = 8.3 Hz, 2H, PCH_2), 3.81 (m, 2H, OCH_2), 7.09 (d, J_{CP} = 2.3 Hz, 2H, 2 H arom), 7.25 (m, 10H, 10 H arom), 7.37 (d, J_{CP} = 2.1 Hz, 2H, 2 H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −24.6 (P−C), 133.5 (P−O). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 30.3 (d, J_{CP} = 16 Hz, PCH_2), 31.3 (d, J_{CP} = 3 Hz, 2 C*Me*$_3$), 31.8 (2 C*Me*$_3$), 34.9 (2 *C*Me$_3$), 35.7 (2 *C*Me$_3$), 62.6 (d, J_{CP} = 46 Hz, CH_2O), 124.4 (2 CH arom), 126.8 (2 CH arom), 128.6 (2 CH arom), 128.7 (2 CH arom), 128.9, (2 CH arom), 132.6 (2 CH arom), 132.7 (C_q arom), 132.8 (C_q arom), 132.9 (2 CH arom), 137.6 (C_q arom), 137.8 (C_q arom), 139.9 (2 C_q arom), 146.6 (4 C_q arom). HRMS (EI): *m*/*z* 668.3503, $[M]^+$ (exact mass calculated for $C_{42}H_{54}O_3P_2$ 668.3548).

2-((*S*)-(*o*-Anisyl)phenylphosphino)ethyl (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (6j). White foamy solid (0.155 g, 63%). $[\alpha]^{20}_D$ = +376° (*c* 1.0, THF). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (s, 9H, CMe_3), 1.46 (s, 9H, CMe_3), 1.71 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.35 (m, 2H, PCH_2), 3.49 (m, 1H, OC*H*H), 3.72 (s, 3H, OCH_3), 3.83 (m, 1H, OC*H*H), 6.84 (m, 2H, 2 H arom), 6.93 (m, 1H, H arom), 7.03 (s, 1H, H arom), 7.15 (s, 1H, H arom), 7.31 (m, 6H, 6 H arom). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −34.2 (P−C), 127.5 (P−O). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 16.8 (Me), 16.9 (Me), 20.7 (Me), 20.8 (Me), 28.5 (d, J_{CP} = 14 Hz, PCH_2), 31.3 (C*Me*$_3$), 31.6 (d, J_{CP} = 5 Hz, C*Me*$_3$), 34.9 (*C*Me$_3$), 34.9 (*C*Me$_3$), 55.7 (OMe), 62.9 (d, J_{CP} = 31 Hz, OCH_2), 110.4 (CH arom), 121.2 (CH arom), 125.9 (d, J_{CP} = 14 Hz, C_q arom), 127.9 (CH arom), 128.4 (CH arom), 128.5 (CH arom), 128.6 (CH arom), 128.9 (CH arom), 130.4 (CH arom), 130.8 (C_q arom, 131.7 (C_q arom), 131.9 (d, J_{CP} = 5 Hz, C_q arom), 132.5 (C_q arom), 132.6 (CH arom), 132.9 (CH arom), 133.2 (CH arom), 134.6 (C_q arom), 135.2 (C_q arom), 136.6 (d, J_{CP} = 11 Hz, C_q arom), 136.9 (C_q arom), 138.3 (C_q arom), 145.6 (m, 2 OC_q arom), 161.1 (d, J_{CP} = 13 Hz, OC_q arom). HRMS (EI): *m*/*z* 642.3029, $[M]^+$ (exact mass calculated for $C_{39}H_{48}O_4P_2$ 642.3028).

2-((*S*)-(*o*-Anisyl)phenylphosphino)ethyl (*R*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diyl Phosphite (6k). White foamy solid (0.154 g, 63%). $[\alpha]^{20}_D$ = −358° (*c* 1.0, THF). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 9H, CMe_3), 1.45 (s, 9H, CMe_3), 1.76 (s, 3H, Me), 1.77 (s, 3H, Me), 2.15 (s, 3H, Me), 2.25 (s, 3H, Me), 2.35 (m, 2H, PCH_2), 3.32 (m, 1H, OC*H*H), 3.70 (s, 3H, OMe), 3.95 (m, 1H, OC*H*H), 6.83 (m, 2H, 2 H arom), 6.94 (m, 1H, H arom), 6.97 (s, 1H, H arom), 7.15 (s, 1H, H arom), 7.31 (m, 6H, 6 H arom). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −34.7 (P−C), 126.9 (P−O). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 16.8 (Me), 17.0 (Me), 20.7 (2 Me), 28.5 (d, J_{CP} = 12 Hz, PCH_2), 31.3 (C*Me*$_3$), 31.6 (d, J_{CP} = 5 Hz, C*Me*$_3$), 34.8 (*C*Me$_3$), 34.9 (*C*Me$_3$), 55.7 (OMe), 62.9 (d, J_{CP} = 31 Hz, OCH_2), 110.4 (CH arom), 121.2 (CH arom), 125.7 (d, J_{CP} = 14 Hz, C_q arom), 128.0 (CH arom), 128.4 (CH arom), 128.6 (CH arom), 128.7 (CH arom), 128.9 (CH arom), 130.4

(CH arom), 130.7 (C_q arom), 131.7 (C_q arom), 132.0 (d, J_{CP} = 5 Hz, C_q arom), 132.1 (d, J_{CP} = 3 Hz, CH arom), 132.6 (C_q arom), 133.1 (CH arom), 133.4 (CH arom), 134.6 (C_q arom), 135.2 (C_q arom), 136.8 (C_q arom), 136.9 (d, J_{CP} = 13 Hz, C_q arom), 138.3 (C_q arom), 145.8 (m, 2 OC_q arom), 161.1 (d, J_{CP} = 14 Hz, OC_q arom). HRMS (EI): *m*/*z* 642.3057, $[M]^+$ (exact mass calculated for $C_{39}H_{48}O_4P_2$ 642.3028).

[Ir(COD)(4a)]BF_4 (10a). A mixture of $[IrCl(COD)]_2$ (0.050 g, 0.075 mmol) and $AgBF_4$ (0.030 g, 0.15 mmol) in DME (2 mL) was stirred for 0.5 h. The suspension was filtered through Celite, and to the solution obtained was added dropwise ligand **4a** (0.100 g, 0.15 mmol) dissolved in DME (10 mL). The color changed from orange to red. The reaction mixture was evaporated, and the resulting solid was washed with Et_2O (2 × 5 mL). The solid obtained was dissolved in CH_2Cl_2 and precipitated by slow addition of Et_2O (30 mL), producing **10a** as a red powder (0.112 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (s, 9H, CMe_3), 1.25 (s, 9H, CMe_3), 1.74 (s, 3H, Ar−*Me*), 1.88 (s, 3H, Ar−*Me*), 2.28 (m, 8H, 4 CH_2 COD), 2.29 (s, 3H, Ar−*Me*), 2.33 (s, 3H, Ar−*Me*), 3.10 (br m, 1H, =CH COD), 4.49 (br m, 1H, =CH COD), 4.90 (br m, 1H, =CH COD), 5.40 (br m, 1H, =CH COD), 7.25 (m, 4H, 4 H arom), 7.24 (s, 1H, H arom), 7.31 (s, 1H, H arom), 7.55 (m, 1H, H arom), 7.52 (m, 6H, 6 H arom), 7.84 (m, 2H, H arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 3.2 (d, P−C), 113.5 (d, P−O, J_{PP} = 42 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 16.6 (Ar−*Me*), 16.7 (Ar−*Me*), 20.4 (Ar−*Me*), 20,6 (Ar−*Me*), 29.4 (CH_2 COD), 30.8 (CH_2 COD), 31.4 (C*Me*$_3$), 31.7 (CH_2 COD), 32.1 (C*Me*$_3$), 32.8 (CH_2 COD), 82.5 (d, J_{CP} = 12 Hz, =CH COD), 95.5 (d, J_{CP} = 8 Hz, =CH COD), 101.0 (d, J_{CP} = 15 Hz, =CH COD), 103.4 (d, J_{CP} = 16 Hz, =CH COD), 123.4 (C_q arom), 123.7 (CH arom), 124.6 (C_q arom), 125.4 (C_q arom), 126.7 (d, J_{CP} = 6 Hz, CH arom), 128.0 (C_q arom), 128.9 (C_q arom), 129.0 (CH arom), 129.7 (CH arom), 129.7 (CH arom), 129.8 (CH arom), 129.9 (CH arom), 132.1 (CH arom), 132.7 (CH arom), 132.9 (2 CH arom), 133.2 (CH arom), 133.3 (CH arom), 134.2 (CH arom), 134.6 (2 C_q arom), 135.0 (2 C_q arom), 135.5 (CH arom), 135.7 (CH arom), 135.9 (2 C_q arom), 137.0 (2 C_q arom), 137.4 (OC_q arom), 137.7 (OC_q arom), 139.1 (OC_q arom). Anal. Calcd for $C_{50}H_{58}BF_4IrO_3P_2 \cdot 0.5CH_2Cl_2$: C, 55.90; H, 5.74. Found: C, 56.19; H, 5.63.

[Ir(COD)(4b)]BF_4 (10b). This complex was prepared as described for **10a**. Red solid (0.130 g, 78%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 0.99 (dd, $^3J_{HP}$ = 14 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, CH*Me*Me), 1.16 (s, 9H, CMe_3), 1.25 (dd, $^3J_{HP}$ = 17.4 Hz, $^3J_{HH}$ = 10.5 Hz, 3H, CH*Me*Me), 1.43 (dd, $^3J_{PH}$ = 18.9 Hz, $^3J_{HH}$ = 9 Hz, 3H, CH*Me*Me), 1.47 (s, 9H, CMe_3), 1.52 (dd, 3H, $^3J_{HP}$ = 19.4 Hz, $^3J_{HH}$ = 7.5 Hz, CH*Me*Me), 1.52 (dd, 1H, $^3J_{HP}$ = 19.4 Hz, $^3J_{HH}$ = 7.5 Hz, C*H*Me$_2$), 1.76 (s, 3H, Ar−*Me*), 1.84 (s, 3H, Ar−*Me*), 2.35 (m, 9H, 4 CH_2 COD, C*H*Me$_2$), 2.29 (s, 3H, Ar−*Me*), 2.31 (s, 3H, Ar−*Me*), 3.42 (br m, 1H, =CH COD), 5.11 (br m, 1H, =CH COD), 5.68 (br m, 1H, =CH COD), 6.01 (br m, 1H, =CH COD), 6.70 (m, 1H, H arom), 7.22 (s, 1H, H arom), 7.33 (s, 1H, H arom), 7.45 (m, 1H, H arom), 7.49 (m, 2H, H arom). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 7.4 (d, P−C), 111.0 (d, P−O, J_{PP} = 37 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 16.5 (Ar−*Me*), 16.7 (Ar−*Me*), 17.3 (CH*Me*Me), 17.6 (d, J_{CP} = 5 Hz, CH*Me*Me), 19.6 (CH*Me*Me), 20.3 (Ar−*Me*), 20.5 (Ar−*Me*), 21.9 (CH*Me*Me), 24.4 (d, J_{CP} = 28 Hz, *C*HMe$_2$), 28.8 (CH_2 COD), 29.3 (CH_2 COD), 29.9 (d, J_{CP} = 29 Hz, *C*HMe$_2$), 31.8 (C*Me*$_3$), 32.5 (C*Me*$_3$), 33.2 (CH_2 COD), 33.4 (CH_2 COD), 35.0 (*C*Me$_3$), 35.2 (*C*Me$_3$), 79.4 (d, J_{CP} = 11 Hz, =CH COD), 90.8 (d, J_{CP} = 8 Hz, =CH COD), 98.1 (d, J_{CP} = 13 Hz, =CH COD), 99.6 (d, J_{CP} = 17 Hz, =CH COD), 113.1 (d, J_{CP} = 7 Hz, C_q arom), 124.0 (CH arom), 126.6 (d, J_{CP} = 3 Hz, CH arom), 129.2 (CH arom), 129.4 (C_q arom), 129.7 (CH arom), 131.9 (CH arom), 133.8 (CH arom), 134.2 (C_q arom), 134.6 (C_q arom), 134.7 (C_q arom), 135.8 (C_q arom), 136.6 (C_q arom), 137.4 (d, J_{CP} = 14 Hz, C_q arom), 138.0 (C_q arom), 143.9 (d, J_{CP} = 7 Hz, OC_q arom), 144.3 (OC_q arom), 144.5 (OC_q arom). Anal. Calcd for $C_{44}H_{62}BF_4IrO_3P_2 \cdot 1.5CH_2Cl_2$: C, 49.35; H, 5.92. Found: C, 49.48; H, 5.72.

[Ir(COD)(4c)]BF_4 (10c). This complex was synthesized as described for **10a**. Red solid (0.108 g, 65%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.12 (s, 9H, CMe_3), 1.48 (s, 9H, CMe_3), 1.76 (s, 3H, Ar−*Me*), 1.86 (s, 3H, Ar−*Me*), 1.89 (d, 3H, J_{HP} = 4.5 Hz, P-Me), 1.97 (d, 3H, J_{HP} = 6.0 Hz, P−*Me*), 2.26 (br m, 9H, 4CH_2 COD and =CH COD), 2.28 (s, 3H, Ar−*Me*), 2.31 (s, 3H, Ar−*Me*), 3.35 (br m, 1H, =CH COD), 5.25 (br m, 1H, =CH COD), 5.39 (br m, 1H, =CH COD), 6.85 (br m, 1H, H arom), 7.21 (s, 1H, H arom), 7.33 (s, 1H, H arom), 7.40 (m, 3H, 3 H arom). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ −23.3 (d, P−C), 114.5 (d, P−O, J_{PP} = 42 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 10.0 (d, J_{CP} = 36 Hz, P−Me), 16.1 (d, J_{CP} = 37 Hz, P−Me), 16.6 (Ar−*Me*), 16.7 (Ar−*Me*), 20.4 (Ar−*Me*), 20.6 (Ar−*Me*), 30.0 (CH_2 COD), 30.8 (CH_2 COD), 31.7 (C*Me*$_3$), 31.8 (C*Me*$_3$), 32.3 (CH_2 COD), 32.4 (CH_2 COD), 34.8 (*C*Me$_3$), 35.2 (*C*Me$_3$), 83.5 (d, J_{CP} = 11 Hz, =CH COD), 94.3 (d, J_{CP} = 7 Hz, =CH COD), 98.8 (d, J_{CP} = 17 Hz, =CH COD), 100.5 (d, J_{CP} = 14 Hz, =CH COD), 123.4 (CH arom), 127.1 (d, J_{CP} = 6 Hz, CH arom), 129.0 (CH arom), 129.6 (2 CH arom), 133.8 (CH arom), 134.2 (C_q arom), 134.6 (C_q arom), 134.7 (C_q arom), 135.8 (C_q arom), 136.7 (C_q arom), 137.5 (d, J_{CP} = 14 Hz, C_q arom), 143.7 (C_q arom), 144.5 (C_q arom), 144.7 (C_q arom), 149.2 (OC_q arom), 150.4 (OC_q arom), 154.3 (d, J_{CP} = 7 Hz, OC_q arom). Anal. Calcd for $C_{40}H_{54}BF_4IrO_3P_2 \cdot 0.5CH_2Cl_2$: C, 50.34; H, 5.74. Found: C, 50.06; H, 5.54.

[Ir(COD)(6a)]BF_4 (11a). This complex was prepared as described for **10a**. Red solid (0.108 g, 65%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.34 (s, 9H, CMe_3), 1.57 (s, 9H, CMe_3), 1.73 (s, 3H, Ar−*Me*), 1.82 (s, 3H, Ar−*Me*), 1.97 (m, 4H, 2 CH_2 COD), 2.23 (m, 10H, Ar−*Me*, 2 CH_2 COD), 3.04 (m, 1H, PC*H*H), 3.19 (m, 1H, PCH*H*), 3.56 (br m, 1H, =CH COD), 4.06 (br m, 1H, *CHHO*), 4.27 (br m, 1H, =CHCOD), 4.71 (br m, 1H, C*H*HO), 4.92 (br m, 1H, =CHCOD), 5.43 (br m, 1H, =CHCOD), 7.15 (br s, 1H, CH arom), 7.20 (br s, 1H, CH arom), 7.35 (m, 2H, 2 CH arom), 7.52 (br m, 3H, 3 CH arom), 7.59 (m, 3H, 3 CH arom), 7.94 (m, 2H, 2 CH arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.4 MHz): δ −5.1 (d, P−C), 98.9 (d, P−O, J_{PP} = 42.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 16.4 (Ar−*Me*), 16.6 (Ar−*Me*), 20.3 (Ar−*Me*), 20.4 (Ar−*Me*), 25.0 (dd, J_{CP} = 9 Hz, CH_2P), 29.3 (CH_2 COD), 30.6 (CH_2 COD), 31.2 (CH_2 COD), 31.6 (C*Me*$_3$), 32.0 (CH_2 COD), 32.4 (C*Me*$_3$), 34.9 (*C*Me$_3$), 35.0 (*C*Me$_3$), 65.1 (OCH_2), 82.6 (d, J_{CP} = 11 Hz, =CH COD), 94.4 (d, J_{CP} = 8 Hz, =CH COD), 98.1 (d, J_{CP} = 14 Hz, =CH COD), 100.5 (d, J_{CP} = 15 Hz, =CH COD), 127.9 (d, J_{CP} = 10 Hz, C_q arom), 128.0 (CH arom), 128.3 (C_q arom), 128.4 (C_q arom), 129.0 (C_q arom), 129.2 (CH arom), 129.5 (CH arom), 129.6 (CH arom), 129.7 (CH arom), 129.8 (CH arom), 131.1 (CH arom), 131.2 (CH arom), 131.9 (CH arom), 133.0 (CH arom), 133.8 (C_q arom), 134.0 (C_q arom), 134.9 (CH arom), 135.0 (CH arom), 135.3 (C_q arom), 136.0 (C_q arom), 136.9 (C_q arom), 137.1 (C_q arom), 143.7 (d, J_{CP} = 13 Hz, OC_q arom), 144.5 (d, J_{CP} = 7 Hz, OC_q arom). Anal. Calcd for $C_{46}H_{58}BF_4IrO_3P_2 \cdot 0.5CH_2Cl_2$: C, 53.58; H, 5.71. Found: C, 53.60; H, 5.37.

[Ir(COD)(6i)]BF_4 (11i). This complex was obtained as described for **10a**. Red solid (0.108 g, 65%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.33 (s, 18H, 2 CMe_3), 1.51 (s, 18H, 2 CMe_3), 2.14 (m, 8H, 4 CH_2 COD), 3.17 (m, 2H, PCH_2), 4.48 (m, 2H, CH_2O), 4.6 (br m, 2H, 2 =CH COD), 4.72 (br m, 2H, 2 =CH COD), 7.14 (br m, 2H, 2 CH arom), 7.47 (br m, 2H, 2 CH arom), 7.59 (m, 6H, 6 CH arom), 7.68 (m, 4H, 4 CH arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.4 MHz): δ −3.53 (d, P−C), 101.0 (d, P−O, J_{PP} = 42.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 125.8 MHz): δ 25.0 (PCH_2), 30.0 (2 CH_2 COD), 31.4 (2 C*Me*$_3$), 31.5 (2 CH_2 COD), 31.7 (2 C*Me*$_3$), 34.8 (2 *C*Me$_3$), 35.6 (2 *C*Me$_3$), 65.2 (CH_2O), 88.8 (br, 2 =CH COD), 99.7 (d, J_{CP} = 15 Hz, 2 =CH COD), 125.3 (2 CH arom), 127.4 (2 CH arom), 127.9 (C_q arom), 128.4 (C_q arom), 129.6 (2 CH arom), 129.7 (2 CH arom), 130.6 (2 C_q arom), 132.6 (2 CH arom), 133.1 (2 CH

arom), 133.2 (2 CH arom), 139.5 (2 C_q arom), 144.7 (C_q arom), 144.8 (C_q arom), 148.4 (2 C_q arom). Anal. Calcd for $C_{50}H_{66}BF_4IrO_3P_2 \cdot CH_2Cl_2$: C, 53.70; H, 6.01. Found: C, 53.58; H, 6.05.

Ir(Cl)(CO)(4a) (12i). A solution of ligand **4a** (0.100 g, 0.14 mmol) in THF (5 mL) was added slowly over a stirred solution of $[Ir(COD)Cl]_2$ (0.047 g, 0.07 mmol) in THF (5 mL). The mixture was stirred for 0.5 h, and then CO was bubbled through the solution for 0.25 h, changing the solution color from orange to yellow. The solvent was evaporated and the resulting solid crystallized from *n*-hexane as pale yellow crystals (0.090 g, 66%). IR: ν(CO) 2027 cm^{-1} (Nujol mull). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.28 (s, 18H, 2 CMe_3), 1.32 (s, 18H, 2 CMe_3), 6.7 (t, $J_{HH} = 8$ Hz, 1H, H arom), 7.14 (m, 3H, 3 H arom), 7.50 (m, 14H, 14 H arom). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 10.6 (d, P−C), 101.6 (d, P−O, $J_{PP} = 49$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 31.7 (2 C*Me*$_3$), 31.9 (2 C*Me*$_3$), 35.0 (2 *C*Me$_3$), 35.8 (2 *C*Me$_3$), 119.8 (d, $J_{CP} = 7$ Hz, C_q arom), 120.6 (d, $J_{CP} = 8$ Hz, C_q arom), 122.9 (2 C_q arom), 125.6 (2 CH arom), 125.7 (C_q arom), 127.0 (2 CH arom), 127.8 (2 C_q arom), 128.8 (2 CH arom), 128.9 (2 CH arom), 131.4 (2 CH arom), 131.6 (CH arom), 133.4 (CH arom), 135.1 (2 CH arom), 135.2 (2 CH arom), 140.3 (d, $J_{CP} = 4$ Hz, CH arom), 144.8 (2 C_q arom), 145.0 (2 OC_q arom), 147.7 (CH arom), 155.2 (C_q arom), 178.0 (dd, $J_{CP} = 119$, 15 Hz, CO). Anal. Calcd for $C_{47}H_{54}ClIrO_4P_2$: C, 58.04; H, 5.60. Found: C, 57.62; H, 5.59.

General Procedure for Catalytic Hydrogenations. These reactions were performed from the appropriate phosphine−phosphite, imine, and $[Ir(COD)Cl]_2$ as exemplified by entry 1 of Table 3. Over a solution of $[Ir(COD)Cl]_2$ (0.0033 g, 4.9 μmol) in CH_2Cl_2 (1 mL) was added dropwise a solution of **6a** (0.0069 g, 10.8 μmol) in CH_2Cl_2 (1 mL). The mixture was stirred for 15 min and then transferred to the pressure reactor, and finally a solution of substrate **13a** (0.192 g, 0.98 mmol) in CH_2Cl_2 (8 mL) was added. The reactor was purged three times with H_2 and then pressurized to 30 atm of H_2. The reaction mixture was stirred for 22 h, the volatiles were evaporated, and the conversion was determined by ^1H NMR on the resulting residue. The latter was redissolved in a *n*-hexane−AcOEt (1:1) mixture and the solution filtered through Celite to remove metal impurities. The enantiomeric excess was determined in the resulting solution by chiral HPLC.

***N*-(1-Phenyl)-1-phenylethylamine (14a).** Chiralcel OJ, 30 °C, *n*-hexane−^{i}PrOH (93:7), flow 1 mL/min, $t_R = 15.5$ min (*R*), $t_R = 17.7$ min (*S*).

***N*-(1-Phenyl)-1-(*p*-tolyl)ethylamine (14b).** Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.53 (d, $J_{HH} = 6.9$ Hz, 3H, CH_3), 4.0 (br s, 1H, NH), 4,5 (q, $J_{HH} = 6.3$ Hz, 1H, CH), 6.54 (d, $J_{HH} = 8.1$ Hz, 2H, 2 H arom), 6.68 (t, $J_{HH} = 7.2$ Hz, 1H, 1 H arom), 7.10−7.18 (m, 4H, 4 H arom), 7.28 (d, $J_{HH} = 7.8$ Hz, 2H, 2 H arom). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 75.5 MHz): δ 21.4 (Ar−*Me*), 25.4 (CH_3), 53.4 (CH), 113.6 (2), 117.4, 126.0 (2), 129.4 (2), 129.6 (2) (9 CH arom), 136.7 (C_q arom), 142.5 (C_q arom), 147.6 (N−C_q). $[\alpha]^{20}_D = -2.6°$ (*c* 1.0, MeOH). Chiracel OJ, 30 °C, *n*-hexane−^{i}PrOH (93:7), flow 1.0 mL/min, $t_R = 11.6$ min (−), $t_R = 13.9$ min (+). HRMS (EI): *m*/*z* 211.1362, $[M]^+$ (exact mass calculated for $C_{15}H_{17}N$ 211.1361).

***N*-(1-Phenyl)-1-(*p*-methoxyphenyl)ethylamine (14c).** Chiralcel AD, 30 °C, *n*-hexane, flow 1.0 mL/min, $t_R = 8.4$ min (−), $t_R = 9.2$ min (+).

***N*-(1-Phenyl)-1-(*p*-fluorophenyl)ethylamine (14d).** Chiralcel OJ, 30 °C, *n*-hexane−^{i}PrOH (99:1), flow 1.0 mL/min, $t_R = 30.2$ min (+), $t_R = 34.0$ min (−).

***N*-(1-Phenyl)-1-(*p*-chlorophenyl)ethylamine (14e).** Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.47 (d, $J_{HH} = 6.6$ Hz, 3H, CH_3), 3.99 (br s, 1H, NH), 4.4 (q, $J_{HH} = 2.1$ Hz, 1H, CH), 6.46 (d, $J_{HH} = 7.8$ Hz, 2H, 2 H arom), 6.6 (t, $J_{HH} = 7.2$ Hz, 1H, 1 H arom), 7.23−7.31 (m, 4H, 4 H arom). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 75.5 MHz): δ 25.4 (CH_3), 53.2 (CH), 113.5 (2CH arom), 117.4 (2CH arom), 129.0 (2CH arom), 129.4 (2CH arom), 132.6 (C_q arom), 144.1 (C_q arom), 147.2 (Cl−C_q arom). $[\alpha]^{20}_D = -6.7°$ (*c* 1.0, MeOH). Chiralcel OJ, 30 °C, *n*-hexane−^{i}PrOH (93:7), flow 1.0 mL/min, $t_R = 14.3$ min (+), $t_R = 16.2$ min (−). HRMS (EI): *m*/*z* 231.0810, $[M]^+$ (exact mass calculated for $C_{15}H_{17}N$ 231.0815).

Table 4. Crystallographic Data and Structure Refinement Details for 11i and 12i

	11i	12i
chem formula	$C_{51}H_{68}BCl_2F_4IrO_3P_2$ $((C_{50}H_{66}O_3P_2Ir)^+(BF_4)^- \cdot CH_2Cl_2)$	$C_{47}H_{54}ClIrO_4P_2$
fw	1140.90	972.49
cryst size, mm	0.35 × 0.32 × 0.27	0.35 × 0.29 × 0.23
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
a, Å	9.3435(4)	12.7635(3)
b, Å	13.4875(7)	13.3844(3)
c, Å	39.710(2)	26.0174(7)
α, deg	90.0	90.0
β, deg	90.0	98.6940(10)
γ, deg	90.0	90.0
V, Å^3	5004.3(4)	4393.53(19)
Z	4	4
D_{calcd}, g cm^{-3}	1.514	1.470
μ, mm^{-1}	2.895	3.214
F(000)	2320	1968
θ range, deg	2.16−30.79	2.22−30.54
no. of measd rflns	48 981	34 557
no. of unique rflns	14 714 ($R_{int} = 0.0259$)	13 414 ($R_{int} = 0.0206$)
min, max transm factors	0.4307, 0.508	0.3992, 0.5252
no. of data/restraints/ params	14714/554/578	13414/0/496
$R(F)$ ($F^2 \geq 2\sigma(F^2)$)[a]	0.0363	0.0227
no. of obsd reflections	13 567	12 034
$R_w(F^2)$ (all data)[b]	0.0904	0.0555
GOF (all data)[c]	1.032	1.058
abs structure param[d]	−0.001(5)	

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 13 567 (for **11i**) or 12 034 (for **12i**) observed reflections. [b] $R_w(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$. [c] GOF $= (\sum[w(F_o^2 - F_c^2)^2]/(n - p))^{1/2}$, where *n* and *p* are the number of data and parameters. [d] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

***N*-(*p*-Methoxyphenyl)-1-phenylethylamine (14f).** Chiralcel AD, 30 °C, *n*-hexane−^{i}PrOH (99:1), flow 1.0 mL/min, $t_R = 8.0$ min (+), $t_R = 8.6$ min (−).

Computational Details. The electronic structures and geometries of the model complexes **I**−**V** were computed within the density functional theory at the B3LYP level.[34,35] Two different basis sets have been used depending on the size of the system. For cases **I** and **II**, all the H, C, O, and P atoms were described using the 6-31G* basis set. For cases **III**−**V** the O and P atoms, and the H and C atoms corresponding to the iridacycle, were described with the 6-31G* basis set while other H and C atoms were described with the 3-21G* basis set. In all cases, the Ir atom is described with the Stuttgart Relativistic Small Core ECP Basis Set.[36] For cases **I**−**III** vibrational frequency calculations were done by diagonalization of the analytically computed Hessian to ensure that the optimized structures were real minima (NImag = 0). All the calculations were performed using the Gaussian98 package.[37] *XYZ* coordinates of all optimized complexes are given in the Supporting Information.

X-ray Structure Determinations. Crystallographic data were collected with a Bruker-Nonius X8Apex-II CCD diffractometer using graphite-monochromated Mo Kα_1 radiation ($\lambda = 0.710\,73$ Å). The data were reduced (SAINT)[38] and corrected for Lorentz−polarization and absorption effects by multiscan methods (SADABS).[39] Structures were solved by direct methods (SIR-2002)[40] and refined against all F^2 data by full-matrix least-squares

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techniques (SHELXTL-6.12).[41] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. A summary of cell parameters and data collection and structure solution and refinement details is given in Table 4.

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Supporting Information Available: Crystallographic details as CIF files and tables giving *XYZ* coordinates of the optimized structures of model complexes **I**−**V**. This material is available free of charge via the Internet at http://pubs.acs.org.

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