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The application of pyranoside phosphite-pyridine ligands to enantioselective Ir-catalyzed hydrogenations of highly unfunctionalized olefins

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ABSTRACT

Eight (biaryl)phosphite/pyridine ligands **1**–**2a**–**d** have been prepared by the modular functionalization of positions C-2 and C-3 of two D-glucopyranoside backbones. The chiral ligands were examined in the iridium-catalyzed asymmetric hydrogenation of poorly functionalized alkenes, as a function of the relative position of the coordinating groups and the geometric properties of the biaryl phosphite moieties. Enantiomeric excesses of up to 90% were achieved in the hydrogenation of *E*-2-(4-methoxyphenyl)-2-butene by using **1a** and **1c**, which seemingly combine the beneficial effect of the phosphite at the 2-position with the matching (R_{ax})-configuration of their encumbered biaryl substituents. The results of the hydrogenation of more challenging substrates, such as *Z*-trisubstituted alkenes, alkenes with a neighboring polar group or demanding 1,1-di-substituted alkenes, generally confirmed this trend, and in some significant cases, the chiral hydrogenated products were isolated with ees of 65–79%.

1. Introduction

The increasing demand for enantiomerically pure pharmaceuticals, agrochemicals, flavors, and other fine chemicals has advanced the field of asymmetric catalytic technologies. Asymmetric hydrogenation utilizing molecular hydrogen to reduce prochiral olefins has become one of the most reliable catalytic methods for the preparation of optically active compounds.[1] Over many years the scope of this reaction has gradually been extended in terms of the reactant structure and catalyst efficiency. Nowadays, an impressive number of chiral phosphine ligands have been developed and successfully applied to Rh- and Ru-catalyzed hydrogenations.[1] However, the range of olefins that can be hydrogenated with high enantiomeric excess is limited, because rhodium and ruthenium catalysts require the presence of a coordinating group next to the C=C bond.[1] With minimally functionalized olefins these catalysts generally show low reactivity and unsatisfactory enantioselectivity.[1] In this context, Pfaltz has introduced a new class of hydrogenation catalysts, iridium complexes with chiral N,P ligands, which overcome these limitations.[2–4] The first set of successful P,N ligands[5] contained a phosphine or phosphinite moiety as the P-donor group and either an oxazoline,[5b,g,j] oxazole,[5d] thiazole,[5i] or pyridine[5c] as the *N*-donor group. However, these iridium-phosphine/phosphinite, N catalysts were still highly substrate-dependent and the development of efficient chiral ligands that tolerate a broader range of substrates remained a challenge. Some years ago we discovered that the presence of biarylphosphite moieties in these P,N-ligands provides greater substrate versatility than previous Ir-phosphine/phosphinite, N catalyst systems.[6]

In our efforts to expand upon the range of ligands and improve performance, we herein report the first application of phosphite-pyridine ligands in the Ir-catalyzed asymmetric hydrogenation of minimally functionalized olefins (Fig. 1). These ligands combine a priori the advantages of both types of successful ligands for this process (phosphite and pyridine). Ligands **1**–**2a**–**d** also have the advantage of carbohydrates and phosphite ligands, such as their availability at a low price from readily available alcohols, facile modular constructions, and high resistance to oxidation.[7] Therefore, with these ligands we fully investigated the effects of systematically varying the position of the phosphite group at either C-2 (ligands **1**) or C-3 (ligands **2**) of the pyranoside backbone, as well as the effects of different substituents and configurations in the biaryl phosphite moiety **a**–**d** with the aim of maximizing the catalyst performance.

2. Results and discussions

2.1. Synthesis of phosphite-pyridine ligands

The new ligands **1**–**2a**–**d** were synthesized efficiently in one step from the corresponding pyridyl-alcohols **4** and **7**, which were easily prepared on a large scale from methyl-α-D-glucopyranoside

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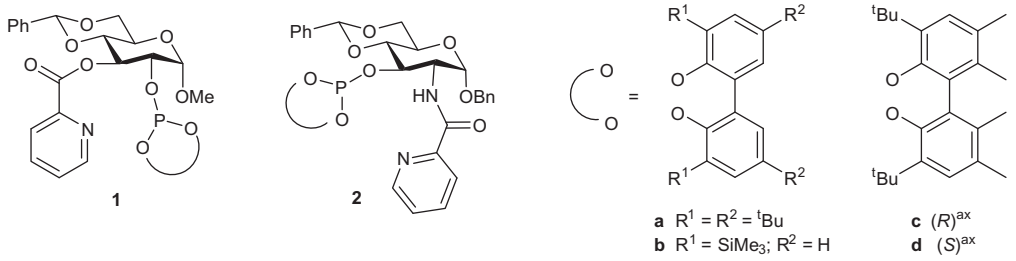
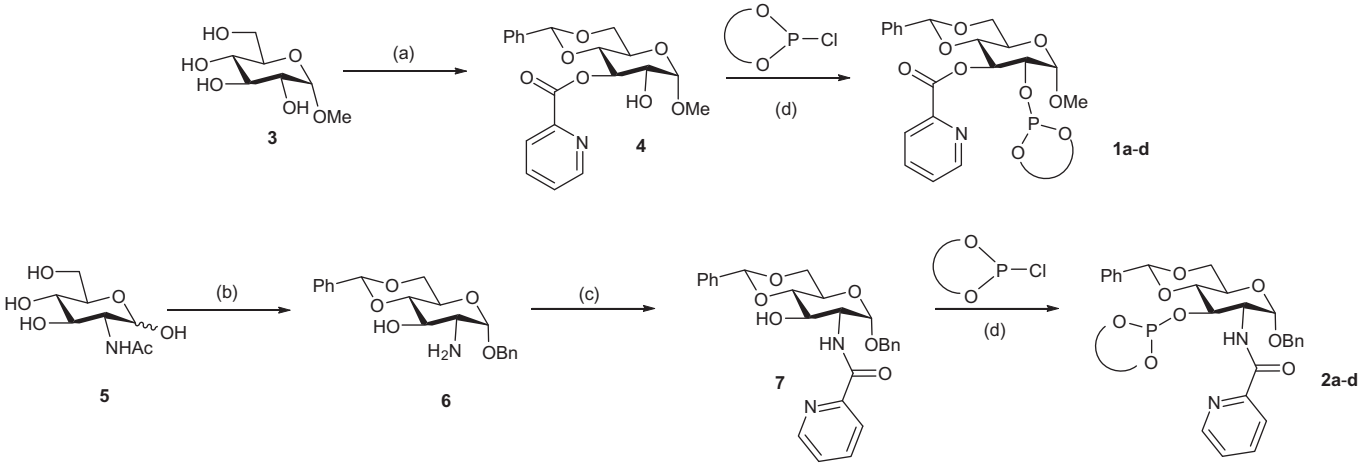


Figure 1. Carbohydrate-based phosphite-pyridine ligands **1**–**2a**–**d**.

3 and *N*-acetyl-D-glucosamine **5**, respectively, using standard procedures (Scheme 1).[8] The reaction of **4** and **7** with 1 equiv of the acterized by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The spectroscopic assignments were based on data from



Scheme 1. Synthesis of phosphite-pyridine ligands **1**–**2a**–**d**. Reagents (a) Ref[8a]; (b) Ref[8b]; (c) DMAP, picolinic acid, DCC; (d) $ClP(OR)_2$; $(OR)_2$ = **a**–**d**/Py/toluene (yields: 18–59%).

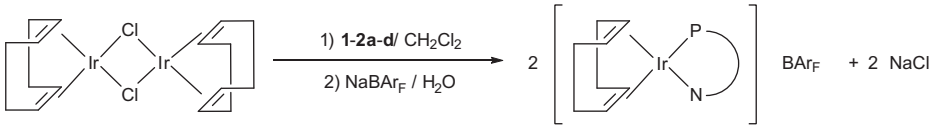
corresponding phosphorochloridite in dry toluene under argon and in the presence of pyridine, provided the desired ligands **1**–**2a**–**d**. All of the ligands were stable during purification on neutral alumina under an argon atmosphere and could be isolated in moderate yields as white solids. Rapid ring inversions (tropoisomerization) in the biphenyl-phosphorus moieties **a**–**b** occurred on the NMR timescale since the expected diastereoisomers were not detected by low-temperature ^{31}P NMR.[9]

2.2. Synthesis of the Ir-catalyst precursors

The catalyst precursors were made by refluxing a dichloromethane solution of the appropriate ligand in the presence of 0.5 equiv of $[Ir(\mu\text{-}Cl)cod]_2$ for 1 h and then exchanging the counterion with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr_F$) (1 equiv), in the presence of water (Scheme 2).

^{1}H–^{1}H and ^{13}C–^{1}H correlation measurements and were as expected for these C_1 iridium complexes. The elemental analysis of C, H, and N matched the stoichiometry $[Ir(cod)(P\text{–}N)]_n(BAr_F)_n$.

For all complexes, variable temperature NMR measurements (from +40 °C to −80 °C) indicated that only one isomer was present in solution. In this context, the ^{31}P NMR spectra showed one sharp signal. The ^{1}H and ^{13}C NMR showed four signals for the olefinic protons and four signals for the olefinic carbon atoms of the coordinated cyclooctadiene, as expected for C1-symmetrical complexes. Two of the four signals, those located *trans* to the phosphorus atom, appeared shifted to a lower field. The ^{13}C NMR spectra also showed the expected four signals of the methylenic carbons of the cyclooctadiene, except for complexes containing ligands **1c** and **2c** in which only three signals were observed. This is probably due to an overlap of the signals. The signals from the phosphite-pyridine ligands in these complexes pro-



Scheme 2. Synthesis of catalyst precursors $[Ir(cod)(\mathbf{1}\text{–}\mathbf{2a}\text{–}\mathbf{d})]BAr_F$ (yields: 93–98%).

All complexes were isolated as air-stable orange solids and were used without further purification. The complexes were char-

duced the expected ^{1}H and ^{13}C NMR pattern for the gluco-pyranoside nucleus.

2.3. Asymmetric hydrogenation

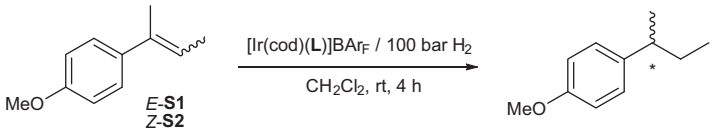
In a first set of experiments, we used the Ir-catalyzed hydrogenation of *E*-2-(4-methoxyphenyl)-2-butene **S1** to study the potential of phosphite-pyridine ligands **1**–**2a**–**d**. Substrate **S1** was chosen as a model for the hydrogenation of trisubstituted olefins because it has already been reduced with a wide range of ligands, which enable the efficiency of the various ligand systems to be compared directly.[2] The results, which are summarized in Table 1, indicate that the enantioselectivities are highly affected by the position of the phosphite moiety at either C-2 (ligands **1**) or C-3 (ligands **2**) of the pyranoside backbone as well as the substituents/configuration of the biaryl phosphite moiety.

With ligands **1** and **2**, we studied how the position of the phosphite moiety affected the product outcome. The results indicate an important effect on both the activity and enantioselectivity. Therefore, ligands **1** with the phosphite group attached at C-2 generally provided higher activities and enantioselectivities than when ligands **2** were used (Table 1, entries 1–4 vs 5–7).

We next investigated the effect of the substituents/configuration at the biaryl phosphite moiety. We found that for ligands **1**, in which the phosphite moiety is attached to C-2, the presence of bulky *tert*-butyl groups at the *para*-positions of the biphenyl phosphite moiety is crucial for high enantioselectivity (Table 1, entry 1 vs 2). We also observed a cooperative effect between the position of the phosphite moiety (at either C-3 or C-2) and the configuration of the biaryl phosphite group (Table 1, entries 3, 4, 6, and 7). This effect was seen for ligand **1c**, which contains an (*R*)-biaryl phosphite moiety attached to C-2 (Table 1, entry 3). Moreover, by comparing the results of tropoisomeric ligands **a**–**b** with those of enantiopure ones **c**–**d**, we can conclude that if enantioselectivity has to be high, tropoisomerization has to be avoided upon coordination in the active species. For instance, ligands **1** efficiently control the tropoisomerization of the biaryl phosphite moiety when bulky *tert*-butyl substituents at both the *ortho*- and *para*-positions of the biaryl phosphite moiety are present. The biphenyl moiety adopts an (*R*)-configuration in the active species (Table 1, entries 1 vs 3 and 4). In a similar way, the low enantioselectivity obtained when using ligand **1b** (Table 1, entry 2) can be explained by the lack of appropriate substituents at the *para*-position of the biphenyl moiety to prevent the tropoisomerization of the biphenyl unit.

The best enantioselectivities (ee's of up to 88%; Table 1, entry 1) were obtained when using ligand **1a**, which has the appropriate combination of ligand parameters. The enantioselectivity can also be improved by controlling not only the structural, but also the reaction parameters. In this case, the enantioselectivity was further improved (ee's up to 90%) with Ir-**1a** catalyst precursor by lowering the reaction temperature to 5 °C (Table 1, entry 9). We also performed the reaction at a low catalyst loading (0.5 mol %) using the Ir-**1a** catalyst precursor (entry 8) and the high enantioselectivity and activity were maintained.

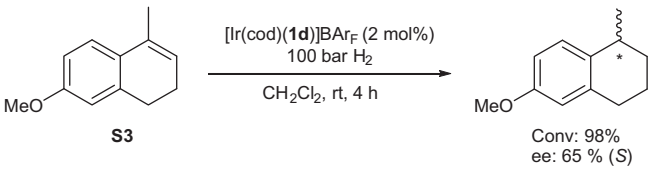
Table 1
Results for the Ir-catalyzed hydrogenation of **S1** using ligands **1**–**2a**–**d**[a]



Entry	Ligand	Substrate	Conv[b] (%)	ee[b] (%)	Entry	Ligand	Substrate	Conv[b] (%)	ee[b] (%)
1	**1a**	**S1**	100	88 (*S*)	9[d]	**1a**	**S1**	89	90 (*S*)
2	**1b**	**S1**	100	15 (*S*)	10	**1a**	**S2**	100	0
3	**1c**	**S1**	100	79 (*S*)	11	**1b**	**S2**	100	0
4	**1d**	**S1**	100	11 (*R*)	12	**1c**	**S2**	84	23 (*S*)
5	**2a**	**S1**	82	2 (*R*)	13	**1d**	**S2**	69[e]	38 (*R*)
6	**2c**	**S1**	75	15 (*R*)	14	**2a**	**S2**	28	2 (*S*)
7	**2d**	**S1**	62	3 (*S*)	15	**2c**	**S2**	85[f]	0
8[c]	**1a**	**S1**	100	88 (*S*)	16	**2d**	**S2**	43[g]	0

[a] Reactions carried out using 0.5 mmol of substrate and 2 mol % of Ir-catalyst precursor.
[b] Conversion and enantiomeric excesses determined by chiral GC.
[c] Reaction carried out at 0.5 mol % of Ir-catalyst precursor.
[d] Reaction carried out at 5 °C.
[e] 9% of **S1** observed.
[f] 15% of **S1** observed.
[g] 23% of **S1** observed.

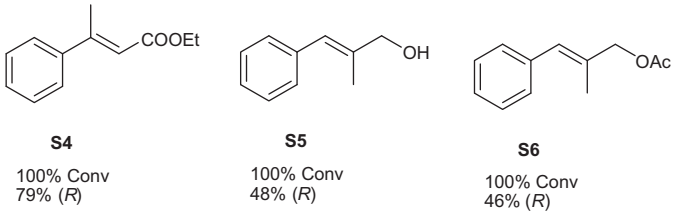
In order to assess the potential of ligands **1**–**2a**–**d** for the more demanding *Z*-isomers, which are usually hydrogenated with less enantioselectivity than the corresponding *E*-isomers, we chose *Z*-2-(4-methoxyphenyl)-2-butene **S2** as the model substrate. However, low enantioselectivities were obtained (Table 1, entries 10–16). A plausible explanation for this could be the competition between direct hydrogenation versus *Z*/*E*-isomerization of the substrate. The hydrogenation of the *E*-isomer produces the opposite configuration of the hydrogenated product to that when the *Z*-isomer is hydrogenated,[2] which results in low enantioselectivity. This is supported by the presence of high amounts of **S1** in the reaction mixture (i.e. 23% of **S1** was observed when using the Ir-**2d** catalytic system after 4 h). In this respect we next decided to evaluate these ligands in the hydrogenation of 7-methoxy-4-methyl-1,2-dihydronaphthalene **S3** (Scheme 3), which has a *Z*-configuration and for



Scheme 3. Asymmetric hydrogenation of **S3.**

which *Z*/*E*-isomerization is not possible. Enantioselectivities of up to 65% were obtained when using the Ir-**1d** catalyst precursor.

We next studied the asymmetric hydrogenation of trisubstituted olefins **S4**–**S6** containing a neighboring polar group. These substrates are interesting because they allow for further functionalization and are therefore important synthons for the synthesis of more complex chiral molecules. The results are summarized in Scheme 4. The reduction of these substrates follows the same trend as those observed for the previous *E*-trisubstituted substrate **S1**. Again, the highest enantioselectivities were obtained when using the Ir-**1a** catalyst precursor. High enantioselectivities were obtained in the hydrogenation of α,β-unsaturated ester **S4** (ee's of up to 79%). Conversely, the reduction of allylic alcohol **S5** and allylic acetate **S6** gave lower enantioselectivities (ee's of up to 48%).



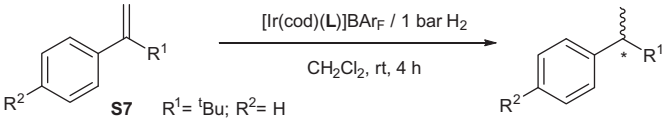
Scheme 4. Selected hydrogenation results of other trisubstituted olefins using the [Ir(cod)(**1a**)]BAr_F catalyst precursor. Reaction conditions: 2 mol % catalyst precursor, CH_2Cl_2 as solvent, 100 bar H_2, 4 h.

Next, we screened ligands **1**–**2a**–**d** in the asymmetric hydrogenation of more demanding terminal olefins. Enantioselectivity was more difficult to control in these substrates than in trisubstituted olefins. There are two main reasons for this:[2d,e] (a) the two substituents in the substrate can easily exchange positions in the chiral environment formed by the catalysts, thus reversing the facial selectivity; and (b) the terminal double bond can isomerize to form the more stable internal alkene, which usually leads to predominant formation of the opposite enantiomer of the hydrogenated product.

Initially we used the Ir-catalyzed hydrogenation of 3,3-dimethyl-2-phenyl-1-butene **S7**. The results using ligands **1**–**2a**–**d** are shown in Table 2. Enantioselectivities were again affected by the position of the phosphite moiety at either the C-2 or C-3 position of the pyranoside backbone as well as the substituents/configuration of the biaryl phosphite moiety. However, the effect of these ligand parameters was different from the effect observed in the reduction of trisubstituted olefins. Thus, the presence of an enantiopure biaryl phosphite moiety has a very positive effect on the enantioselectivity (ee's increased from 38% for Ir-**1a** to 65% for Ir-**1c**; Table 2, entries 1 vs 3). The cooperative effect between the position of the phosphite and the configuration of the biaryl group is also present, but in this case, both enantiomers of the hydrogenated product can be obtained in good enantioselectivities [ligand **1c** affords 65% (*S*) and ligand **2d** affords 72% (*R*)]. The best enantioselectivities were therefore obtained using the catalyst precursor Ir-**2d** (ee's up to 72%, Table 2, entry 7).

Finally, we investigated the asymmetric hydrogenation of other 1,1-disubstituted aryl-alkyl substrates with ligands containing the enantiopure biphenyl moieties **1**–**2c**–**d**. The results indicated that enantioselectivity is highly affected by the nature of the alkyl chain (ee's ranging from 16% to 72%, Table 2, entry 7 vs 12) and less affected by the electronic nature of the aryl ring (Table 2, entry 9 vs 12). One plausible explanation for this could be the competition between the direct hydrogenation versus isomerization for the different substrates. This is supported by the high amounts of isomerized internal olefin observed in all cases for substrates **S8**–**S11**.

Table 2
Results for the Ir-catalyzed hydrogenation of **S7–S11** using phosphite-pyridine ligands **1**–**2a**–**d**[a]



S7 R^1= ^{t}Bu; R^2= H
S8 R^1= Et; R^2= 4-OMe
S9 R^1= Et; R^2= 4-CF_3
S10 R^1= ^{i}Bu; R^2= H
S11 R^1= Bu; R^2= H

Entry	Ligand	Substrate	Conv[b] (%)	ee[b] (%)
1	**1a**	**S7**	100	38 (*S*)
2	**1b**	**S7**	100	31 (*S*)
3	**1c**	**S7**	100	65 (*S*)
4	**1d**	**S7**	100	15 (*R*)
5	**2a**	**S7**	100	33 (*S*)
6	**2c**	**S7**	100	38 (*S*)
7	**2d**	**S7**	100	72 (*R*)
8	**1c**	**S8**	99[c]	16 (*R*)
9	**1d**	**S8**	98[d]	20 (*S*)
10	**2c**	**S8**	78[e]	3 (*R*)
11	**2d**	**S8**	96[f]	3 (*R*)
12	**1d**	**S9**	100[g]	16 (*S*)
13	**1d**	**S10**	99[h]	20 (*S*)
14	**1d**	**S11**	100[i]	23 (*S*)

[a] Reactions carried out using 0.5 mmol of substrate and 2 mol % of Ir-catalyst precursor.
[b] Conversion and enantiomeric excesses determined by chiral GC.
[c] 60% of **S1** observed.
[d] 60% of **S1** observed.
[e] 64% of **S1** observed.
[f] 67% of **S1** observed.
[g] 59% of internal olefin observed.
[h] 41% of internal olefin observed.
[i] 48% of internal olefin observed.

3. Conclusions

This work substantiates a versatile strategy aimed at preparing chiral ligands through immediate functionalization of common carbohydrates. Eight ligands **1–2a–d** were prepared, whose ready availability along with an intrinsic modular nature allowed us to refine the structures by switching the coordinating functions between C-2 and C-3, and by introducing biaryl(phosphite) moieties with different geometric properties. The application of these ligands in the enantioselective Ir-catalyzed hydrogenation of minimally functionalized alkenes disclosed a well-balanced combination in **1a** and **1c**, which seemingly couple the beneficial effect of the phosphite in position 2 with the matching (R_{ax})-configuration of their encumbered biaryl substituents. In this case, the hydrogenation of *E*-2-(4-methoxyphenyl)-2-butene yielded the chiral product in 90% ee, and analogous beneficial synergy was generally recognized in the hydrogenation of more challenging substrates. Use of these ligands will be assessed also in other asymmetric reactions of relevant synthetic interest.

4. Experimental

4.1. General

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were purified and dried by standard procedures. Compounds **4** and **6** were prepared as previously described.[8] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to those of $SiMe_4$ (^{1}H and ^{13}C) as the internal standard

or H_3PO_4 (^{31}P) as the external standard. ^1H and ^{13}C assignments were made on the basis of ^1H–^1H gCOSY and ^1H–^{13}C gHSQC experiments. All catalytic experiments were performed three times.

4.2. Synthesis of the intermediate 7

Intermediate **6** (0.715 g, 2.00 mmol) was dissolved in dry DCM, then DMAP (0.024 g, 0.20 mmol), picolinic acid (0.234 g, 1.90 mmol), and DCC (0.516 g, 2.50 mmol) were added. The system was stirred at rt overnight, then the mixture was filtered. The product was purified by chromatography (EtOAc/PE = 3/2) and precipitation (DCM/PE). Yield: 0.647 g (70%). ^1H NMR ($CDCl_3$), δ: 8.60 (dd, 1H, CH=, $^3J_{H-H}$ = 4.7 Hz, $^3J_{H-H}$ = 0.8 Hz), 8.49 (d, 1H, NH, $^3J_{NH-2}$ = 10.0 Hz), 8.17 (d, 1H, CH=, $^3J_{H-H}$ = 7.8 Hz), 7.84 (td, 1H, CH=, $^3J_{H-H}$ = 7.7 Hz, $^3J_{H-H}$ = 1.6 Hz), 7.55–7.20 (m, 10H, CH=), 5.58 (s, 1H, H-7), 4.99 (d, 1H, H-1, $^3J_{1-2}$ = 3.9 Hz), 4.78 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.1 Hz), 4.57 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.1 Hz), 4.42 (td, 1H, H-2, $^3J_{2-1}$ = 3.9 Hz, $^3J_{2-3}$ = $^3J_{2-NH}$ = 10.0 Hz), 4.27 (dd, 1H, H-6, $^2J_{6-6'}$ = 10.2 Hz, $^3J_{6-5}$ = 4.9 Hz), 3.79 (t, 1H, H-3, $^3J_{3-4}$ = $^3J_{3-2}$ = 10.0 Hz), 3.96 (td, 1H, H-5, $^3J_{5-6}$ = 4.9 Hz, $^3J_{5-4}$ = $^3J_{6-6'}$ = 10.2 Hz), 3.79 (t, 1H, H-6', $^2J_{6'-6}$ = $^3J_{6'-5}$ = 10.2 Hz), 3.68 (m, 1H, H-4); ^{13}C NMR ($CDCl_3$), δ: 165.1 (C=O), 149.1–122.6 (17 C, aromatics), 102.0 (C-7), 97.3 (C-1), 82.1 (C-4), 70.5 (C-3), 69.9 (CH_2Ph), 68.9 (C-6), 62.7 (C-5), 54.2 (C-2).

4.3. Typical procedure for the preparation of [Ir(cod)(L)]BAr_F

The corresponding phosphorochloridite (1.1 mmol) produced in situ [10] was dissolved in toluene (5 mL), after which pyridine (0.3 mL, 3.9 mmol) was added. The corresponding pyridine-hydroxyl compound (1 mmol) was azeotropically dried with toluene (3 × 2 mL) and then dissolved in toluene (5 mL) to which pyridine (0.3 mL, 3.9 mmol) was added. The alcohol solution was transferred slowly to a solution of phosphorochloridite. The reaction mixture was stirred at 80 °C for 90 min, after which the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography in alumina (toluene/NEt_3 = 100/1) to produce the corresponding ligand as a white solid.

Compound **1a** Yield: 489 mg (59%). ^{31}P NMR (C_6D_6), δ: 144.7. ^1H NMR (C_6D_6), δ: 1.25 (s, 9H, CH_3, ^{t}Bu), 1.29 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 9H, CH_3, ^{t}Bu), 1.63 (s, 9H, CH_3, ^{t}Bu), 2.89 (s, 3H, CH_3, CH_3–O), 3.41 (m, 1H, H-6), 3.66 (m, 1H, H-4), 3.95 (m, 1H, H-5), 4.04 (dd, 1H, H-6', $^3J_{6'-6}$ = 10.0 Hz, $^3J_{6'-5}$ = 4.8 Hz), 4.13 (d, 1H, H-1, $^3J_{1-2}$ = 3.1 Hz), 5.02 (m, 1H, H-2), 5.05 (s, 1H, H-7), 6.43 (m, 1H, H-3), 6.5–8.4 (m, 13H, CH=). ^{13}C NMR (C_6D_6), δ: 31.0 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.4 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 54.3 (CH_3–O), 62.6 (C-5), 68.7 (C-6), 71.5 (d, C-3, $^3J_{C-P}$ = 4.2 Hz), 72.7 (C-2), 79.7 (C-4), 99.5 (C-1), 101.3 (C-7), 124–164 (aromatic carbons). Anal. calcd (%) for $C_{48}H_{60}NO_9P$: C 69.80, H 7.32, N 1.70; found: C 69.78, H 7.30, N 1.69.

Compound **1b** Yield: 265 mg (36%). ^{31}P NMR (C_6D_6), δ: 146.6. ^1H NMR (C_6D_6), δ: 0.48 (s, 9H, CH_3–Si), 0.50 (s, 9H, CH_3–Si), 2.82 (s, 3H, CH_3–O), 3.37 (m, 1H, H-6), 3.72 (m, 1H, H-4), 3.94 (m, 1H, H-5), 4.03 (dd, 1H, H-6', $^3J_{6'-6}$ = 10.0 Hz, $^3J_{6'-5}$ = 4.8 Hz), 4.24 (d, 1H, H-1, $^3J_{1-2}$ = 3.5 Hz), 4.88 (m, 1H, H-2), 5.05 (s, 1H, H-7), 6.40 (m, 1H, H-3), 6.5–8.4 (m, 13H, CH=). ^{13}C NMR (C_6D_6), δ: −0.1 (CH_3–Si), −0.2 (CH_3–Si), 54.5 (CH_3–O), 62.6 (C-5), 68.6 (C-6), 71.3 (d, C-3, $^3J_{C-P}$ = 4.3 Hz), 72.6 (d, C-2, $^2J_{C-P}$ = 3.7 Hz), 79.7 (C-4), 99.7 (C-1), 101.3 (C-7), 124–165 (aromatic carbons). Anal. calcd (%) for $C_{38}H_{44}NO_9PSi_2$: C 61.19, H 5.95, N 1.88; found: C 61.21, H 5.98, N 1.86.

Compound **1c** Yield: 261 mg (34%). ^{31}P NMR (C_6D_6), δ: 138.6. ^1H NMR (C_6D_6), δ: 1.56 (s, 9H, CH_3, ^{t}Bu), 1.62 (s, 9H, CH_3, ^{t}Bu), 1.65 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.84 (s, 3H, CH_3, CH_3–O), 3.35 (m, 1H, H-6), 3.62 (m, 1H, H-4), 3.91 (m, 1H, CH, H-5), 4.01 (dd, 1H, H-6', $^3J_{6'-6}$ = 10.4 Hz, $^3J_{6'-5}$ = 4.8 Hz), 4.38 (d, 1H, H-1, $^3J_{1-2}$ = 3.2 Hz), 4.89 (m, 1H, H-2), 5.09 (s, 1H, H-7), 6.34 (m, 1H, H-3), 6.5–8.4 (m, 11H, CH=). ^{13}C NMR (C_6D_6), δ: 16.9 (CH_3), 17.0 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 32.0 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 55.1 (CH_3–O), 63.2 (C-5), 69.3 (C-6), 72.2 (C-3), 73.3 (C-2), 80.4 (C-4), 100.4 (C-1), 101.9 (C-7), 125–165 (aromatic carbons). Anal. calcd (%) for $C_{44}H_{52}NO_9P$: C 68.65, H 6.81, N 1.82; found: C 68.68, H 6.82, N 1.80.

Compound **1d** Yield: 315 mg (41%). ^{31}P NMR (C_6D_6), δ: 137.7. ^1H NMR (C_6D_6), δ: 1.54 (s, 3H, CH_3), 1.62 (s, 9H, CH_3, ^{t}Bu), 1.65 (s, 3H, CH_3), 1.67 (s, 9H, CH_3, ^{t}Bu), 2.02 (s, 6H, CH_3), 3.03 (s, 3H, CH_3, CH_3–O), 3.35 (m, 1H, H-6), 3.56 (m, 1H, H-4), 3.89 (m, 1H, CH, H-5), 4.02 (dd, 1H, H-6', $^3J_{6'-6}$ = 10.0 Hz, $^3J_{6'-5}$ = 4.8 Hz), 4.55 (m, 1H, H-2), 4.91 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 5.09 (s, 1H, H-7), 6.34 (m, 1H, H-3), 6.5–8.4 (m, 11H, CH=). ^{13}C NMR (C_6D_6), δ: 16.9 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 31.9 (d, CH_3, ^{t}Bu, J_{C-P} = 8.5 Hz), 32.4 (CH_3, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.7 (C, ^{t}Bu), 55.4 (CH_3–O), 63.2 (C-5), 69.2 (C-6), 71.2 (d, C-3, J_{C-P} = 9.8 Hz), 75.0 (d, C-2, J_{C-P} = 11.2 Hz), 80.3 (C-4), 100.0 (C-1), 101.9 (C-7), 125–165 (aromatic carbons). Anal. calcd (%) for $C_{44}H_{52}NO_9P$: C 68.65, H 6.81, N 1.82; found: C 68.69, H 6.82, N 1.79.

Compound **2a** Yield: 156 mg (18%). ^{31}P NMR (C_6D_6), δ: 147.7. ^1H NMR (C_6D_6), δ: 1.21 (s, 9H, CH_3, ^{t}Bu), 1.23 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 3.53 (m, 1H, H-6), 3.79 (m, 1H, H-4), 4.07 (m, 2H, H-5 and H-6'), 4.15 (d, 1H, CH_2–Ph, $^2J_{H-H}$ = 12.0 Hz), 4.41 (d, 1H, CH_2–Ph, $^2J_{H-H}$ = 12.0 Hz), 4.79 (m, 1H, H-3), 5.13 (m, 1H, H-2), 5.31 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 5.42 (s, 1H, H-7), 6.53 (m, 1H, CH=), 6.9–7.1 (m, 10 H, CH=), 7.22 (d, 1H, CH=, J = 2.4 Hz), 7.54 (dd, 1H, CH=, J = 10.8 Hz, J = 2.8 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ = 7.2 Hz), 7.88 (m, 1H, NH), 8.01 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz), 8.82 (d, 1H, CH=, $^3J_{H-H}$ = 8.4 Hz). ^{13}C NMR (C_6D_6), δ: 31.6 (CH_3, ^{t}Bu), 31.7 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 34.8 (C, ^{t}Bu), 34.9 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 54.9 (C-3), 64.2 (C-4), 69.3 (C-6), 70.4 (CH_2–Ph), 72.8 (d, C-2, J_{C-P} = 16.8 Hz), 81.5 (C-5), 99.3 (C-1), 102.1 (C-7), 122–165 (aromatic carbons). Anal. calcd (%) for $C_{54}H_{65}N_2O_8P$: C 71.98, H 7.27, N 3.11; found: C 72.03, H 7.29, N 3.08.

Compound **2c** Yield: 144 mg (18%). ^{31}P NMR (C_6D_6), δ: 140.1. ^1H NMR (C_6D_6), δ: 1.44 (s, 9H, CH_3, ^{t}Bu), 1.59 (s, 9H, CH_3, ^{t}Bu), 1.61 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 3.44 (m, 1H, H-6), 3.83 (m, 1H, H-4), 4.08 (m, 2H, H-5, and H-6'), 4.17 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.35 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.92 (m, 1H, H-3), 5.08 (m, 1H, H-2), 5.12 (s, 1H, H-7), 5.29 (d, 1H, H-1, $^3J_{1-2}$ = 3.2 Hz), 6.53 (m, 1H, CH=), 6.9–7.2 (m, 11H, CH=), 7.53 (m, 2H, CH=), 8.04 (m, 1H, NH), 8.23 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz), 8.82 (d, 1H, CH=, $^3J_{H-H}$ = 8.4 Hz). ^{13}C NMR (C_6D_6), δ: 16.2 (CH_3), 16.5 (CH_3), 19.9 (CH_3), 20.0 (CH_3), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 34.6 (C, ^{t}Bu), 34.7 (C, ^{t}Bu), 54.7 (C-3), 63.7 (C-4), 68.5 (C-6), 69.5 (CH_2-Ph), 72.6 (d, C-2, J_{C-P} = 19.1 Hz), 80.3 (C-5), 97.3 (C-1), 101.5 (C-7), 121–165 (aromatic carbons). Anal. calcd (%) for $C_{50}H_{57}N_2O_8P$: C 71.07, H 6.80, N 3.32; found: C 71.12, H 6.83, N 3.28.

Compound **2d** Yield: 109 mg (13%). ^{31}P NMR (C_6D_6), δ: 140.8. ^1H NMR (C_6D_6), δ: 1.45 (s, 3H, CH_3), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.66 (s, 3H, CH_3), 1.67 (s, 9H, CH_3, ^{t}Bu), 1.83 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 3.55 (m, 1H, H-6), 3.80 (m, 1H, H-4), 4.03 (m, 1H, H-5), 4.08 (m, 1H, H-6'), 4.13 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.37 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.85 (m, 1H, H-3), 5.07 (m, 1H, H-2), 5.14 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 5.49 (s, 1H, H-7), 6.52 (m, 1H, CH=), 6.9–7.2 (m, 11H, CH=), 7.78 (m, 2H, CH=), 7.94 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz), 8.05 (m, 1H, NH), 8.56 (d, 1H, CH=, $^3J_{H-H}$ = 8.8 Hz). ^{13}C NMR (C_6D_6), δ: 16.2 (CH_3), 16.3 (CH_3), 19.9 (CH_3), 20.0 (CH_3), 31.3 (d, CH_3, ^{t}Bu, J_{C-P} = 5.0 Hz), 31.5 (CH_3, ^{t}Bu), 34.6 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 53.5 (C-3), 63.4 (C-4), 68.5 (C-6), 69.4 (CH_2-Ph), 71.8 (d, C-2, J_{C-P} = 10.9 Hz), 81.2 (C-5), 97.8 (C-1), 101.2 (C-7), 125–165 (aromatic carbons). Anal. calcd (%) for $C_{50}H_{57}N_2O_8P$: C 71.07, H 6.80, N 3.32; found: C 71.13, H 6.83, N 3.29.

4.4. Typical procedure for the preparation of [Ir(cod)(L)]BAr_F

The corresponding ligand (0.037 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and [Ir(μ-Cl)cod]$_2$ (12.5 mg, 0.0185 mmol) was added. The reaction was refluxed at 45 °C for 1 h. After 5 min at room temperature, $NaBAr_F$ (38.6 mg, 0.041 mmol) and water (2.5 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were filtered through a Celite plug, dried over $MgSO_4$ and the solvent was evaporated to give the product as an orange solid.

4.4.1. [Ir(cod)(1a)]BAr_F

Yield: 71 mg (96%). ^{31}P NMR (CD_2Cl_2), δ: 96.0. ^{1}H NMR (CD_2Cl_2), δ: 1.32 (s, 9H, CH_3, ^{t}Bu), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.64 (s, 9H, CH_3, ^{t}Bu), 1.71 (b, 4H, CH_2, cod), 1.98 (b, 2H, CH_2, cod), 2.16 (b, 2H, CH_2, cod), 2.72 (s, 3H, CH_3–O), 3.39 (m, 2H, H-6, and CH= cod), 3.43 (m, 1H, H-4), 3.48 (m, 1H, H-2), 3.62 (m, 1H, CH=, cod), 3.91 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 4.19 (m, 1H, H-5), 4.47 (m, 2H, H-6', and CH= cod), 5.08 (s, 1H, H-7), 5.24 (m, 1H, H-3), 5.71 (m, 1H, CH= cod), 6.9–7.5 (m, 23H, CH=), 7.81 (m, 1H, CH=), 8.72 (m, 1H, CH=). ^{13}C NMR (CD_2Cl_2), δ: 24.8 (b, CH_2, cod), 28.7 (b, CH_2, cod), 31.0 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 32.0 (b, CH_2, cod), 34.3 (C, ^{t}Bu), 34.4 (C, ^{t}Bu), 34.8 (b, CH_2 cod), 35.3 (C, ^{t}Bu), 54.1 (CH_3–O), 62.2 (C-5), 63.7 (CH=, cod), 68.6 (C-6), 68.9 (CH=, cod), 73.2 (b, C-3), 76.9 (b, C-2), 80.3 (C-4), 98.2 (C-1), 101.3 (C-7), 102.4 (b, CH=, cod), 106.5 (b CH=, cod), 117.6 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–158 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.7 (C=O). Anal. calcd (%) for $C_{88}H_{84}BF_{24}IrNO_9P$: C 53.12, H 4.26, N 0.70; found: C 53.09, H 4.24, N 0.67.

4.4.2. [Ir(cod)(1b)]BAr_F

Yield: 69 mg (98%). ^{31}P NMR (CD_2Cl_2), δ: 96.5. ^{1}H NMR (CD_2Cl_2), δ: 0.01 (s, 9H, CH_3–Si), 0.35 (s, 9H, CH_3–Si), 1.68 (b, 4H, CH_2, cod), 1.95 (b, 2H, CH_2, cod), 2.29 (b, 2H, CH_2, cod), 2.65 (s, 3H, CH_3–O), 3.45 (m, 4H, H-6, H-4, H-2, and CH= cod)), 3.59 (m, 1H, CH=, cod), 3.94 (d, 1H, H-1, $^3J_{1-2}$ = 3.2 Hz), 4.21 (m, 1H, H-5), 4.44 (m, 2H, H-6', and CH= cod), 5.06 (s, 1H, H-7), 5.19 (m, 1H, H-3), 5.66 (m, 1H, CH= cod), 6.8–7.5 (m, 25H, CH=), 7.82 (m, 1H, CH=), 8.71 (m, 1H, CH=). ^{13}C NMR (CD_2Cl_2), δ: −0.7 (CH_3–Si), 0.6 (CH_3–Si), 24.9 (b, CH_2, cod), 29.4 (b, CH_2, cod), 32.1 (b, CH_2, cod), 37.5 (b, CH_2, cod), 54.3 (CH_3–O), 62.0 (C-5), 63.2 (CH=, cod), 68.5 (C-6), 69.9 (CH=, cod), 75.0 (b, C-3), 77.8 (b, C-2), 80.8 (C-4), 97.3 (C-1), 101.8 (C-7), 107.2 (b, CH=, cod), 109.7 (b CH=, cod), 117.6 (b, CH=, BAr_F), 120.5–132.8 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–156 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.4 (C=O). Anal. calcd (%) for $C_{78}H_{68}BF_{24}IrNO_9PSi_2$: C 49.06, H 3.59, N 0.73; found: C 49.02, H 3.58, N 0.72.

4.4.3. [Ir(cod)(1c)]BAr_F

Yield: 66 mg (93%). ^{31}P NMR (CD_2Cl_2), δ: 92.5. ^{1}H NMR (CD_2Cl_2), δ: 1.56 (s, 9H, CH_3, ^{t}Bu), 1.62 (s, 9H, CH_3, ^{t}Bu), 1.68 (s, 3H, CH_3), 1.78 (b, 7H, CH_3, and CH_2, cod), 1.99 (b, 2H, CH_2, cod), 2.03 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.14 (b, 2H, CH_2, cod), 2.76 (s, 3H, CH_3–O), 3.34 (m, 1H, H-6), 3.41 (m, H, CH=, cod), 3.52 (m, 1H, H-4), 3.56 (m, 2H, H-2, and CH=, cod), 4.02 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 4.32 (m, 1H, H-5), 4.46 (m, 2H, H-6', and CH= cod), 5.02 (s, 1H, H-7), 5.23 (m, 1H, H-3), 5.86 (m, 1H, CH= cod), 6.9–7.5 (m, 21H, CH=), 7.82 (m, 1H, CH=), 8.72 (m, 1H, CH=). ^{13}C NMR (CD_2Cl_2), δ: 16.9 (CH_3), 17.0 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 23.9 (b, CH_2, cod), 26.4 (b, CH_2, cod), 29.9 (b, CH_2, cod), 32.3 (CH_3, ^{t}Bu), 32.5 (CH_3, ^{t}Bu), 32.8 (b, CH_2, cod), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 54.8 (CH_3–O), 62.3 (C-5), 63.9 (CH=, cod), 68.3 (C-6), 69.2 (CH=, cod), 72.3 (C-3), 77.8 (b, C-2), 80.1 (C-4), 99.9 (C-1), 101.4 (C-7), 101.9 (b, CH=, cod), 103.9 (b CH=, cod), 117.6 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–158 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.7 (C=O). Anal. calcd (%) for $C_{84}H_{76}BF_{24}IrNO_9P$: C 52.18, H 3.96, N 0.72; found: C 52.17, H 3.92, N 0.71.

4.4.4. [Ir(cod)(1d)]BAr_F

Yield: 68 mg (96%). ^{31}P NMR (CD_2Cl_2), δ: 93.6. ^{1}H NMR (CD_2Cl_2), δ: 1.53 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 3H, CH_3), 1.65 (s, 9H, CH_3, ^{t}Bu),), 1.69 (s, 3H, CH_3), 1.86 (b, 4H, CH_2, cod), 1.95 (b, 2H, CH_2, cod), 1.99 (s, 6H, CH_3), 2.08 (b, 2H, CH_2, cod), 2.79 (s, 3H, CH_3–O), 3.34 (m, H, CH=, cod), 3.38 (m, 1H, H-6), 3.48 (m, 1H, H-4), 3.53 (m, 2H, H-2, and CH=, cod), 4.09 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 4.46 (m, 2H, H-5, and CH= cod), 4.49 (m, 1H, H-6'), 5.02 (s, 1H, H-7), 5.19 (m, 1H, H-3), 5.68 (m, 1H, CH= cod), 6.9–7.5 (m, 21H, CH=), 7.82 (m, 1H, CH=), 8.70 (m, 1H, CH=). ^{13}C NMR (CD_2Cl_2), δ: 16.9 (CH_3), 17.0 (CH_3), 20.7 (CH_3), 22.9 (b, CH_2, cod), 24.6 (b, CH_2, cod), 28.8 (b, CH_2, cod), 30.7 (b, CH_2, cod), 32.1 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 54.7 (CH_3–O), 62.5 (C-5), 64.2 (CH=, cod), 68.6 (C-6), 69.3 (CH=, cod), 72.9 (C-3), 77.1 (b, C-2), 80.0 (C-4), 99.6 (C-1), 101.3 (C-7), 102.4 (b, CH=, cod), 103.5 (b CH=, cod), 117.6 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–158 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.7 (C=O). Anal. calcd (%) for $C_{84}H_{76}BF_{24}IrNO_9P$: C 52.18, H 3.96, N 0.72; found: C 52.16, H 3.94, N 0.70.

4.4.5. [Ir(cod)(2a)]BAr_F

Yield: 71 mg (93%). ^{31}P NMR (CD_2Cl_2), δ: 92.4. ^{1}H NMR (CD_2Cl_2), δ: 1.23 (s, 9H, CH_3, 1.29 (s, 9H, CH_3, ^{t}Bu), 1.46 (s, 9H, CH_3, ^{t}Bu), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.87 (b, 2H, CH_2, cod), 2.21 (b, 2H, CH_2, cod), 2.29 (b, 4H, CH_2, cod), 3.09 (m, H, CH=, cod), 3.24 (m, 3H, H-5, H4, and H-6), 3.77 (m, 1H, H-2), 3.89 (m, 1H, CH= cod), 4.24 (m, 2H, H-6', and CH= cod), 4.61 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.76 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.91 (m, H-3), 4.98 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 5.09 (s, 1H, H-7), 5.34 (m, 1H, CH= cod), 6.19 (m, 1H, NH), 6.87 (m, 1H, CH=), 7.0–7.9 (m, 25H, CH=), 8.81 (m, 2H, CH=). ^{13}C NMR (CD_2Cl_2), δ: 16.5 (CH_3), 16.7 (CH_3), 20.2 (CH_3), 20.9 (CH_3), 25.2 (b, CH_2, cod), 28.7 (b, CH_2, cod), 29.9 (b, CH_2, cod), 30.9 (CH_3, ^{t}Bu), 31.2 (b, CH_2, cod), 32.1 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 59.0 (C-3), 63.8 (C-4), 68.6 (b, CH=, cod), 68.8 (C-6), 71.2 (CH_2-Ph), 75.1 (b, CH=, cod), 77.6 (C-2), 79.9 (C-5), 98.6 (C-1), 102.8 (b, CH=, cod), 103.1 (C-7), 106.2 (b, CH=, cod), 117.6 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–158 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.6 (C=O). Anal. calcd (%) for $C_{94}H_{89}BF_{24}IrN_2O_8P$: C 54.68, H 4.34, N 1.36; found: C 54.61, H 4.32, N 1.33.

4.4.6. [Ir(cod)(2c)]BAr_F

Yield: 73 mg (94%). ^{31}P NMR (CD_2Cl_2), δ: 91.6. ^{1}H NMR (CD_2Cl_2), δ: 1.20 (s, 9H, CH_3, ^{t}Bu), 1.26 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.69 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.92 (b, 2H, CH_2, cod), 2.23 (b, 2H, CH_2, cod), 2.35 (b, 4H, CH_2, cod), 2.83 (m, H, CH=, cod), 2.92 (m, 1H, H-4), 3.11 (m, 1H, H-6), 3.48 (m, 1H, H-5), 3.69 (m, 1H, H-2), 3.95 (m, 1H, CH= cod), 4.05 (m, 1H, H-6'), 4.32 (m, 1H, CH= cod), 4.60 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.73 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.89 (m, H-3), 5.01 (d, 1H, H-1, $^3J_{1-2}$ = 3.2 Hz), 5.05 (s, 1H, H-7), 5.28 (m, 1H, CH= cod), 6.22 (m, 1H, NH), 6.28 (s, 1H, CH=CH=), 7.0–7.9 (m, 25H, CH=), 8.81 (m, 2H, CH=). ^{13}C NMR (CD_2Cl_2), δ: 16.8 (CH_3), 20.5 (CH_3), 21.4 (CH_3), 25.5 (b, CH_2, cod), 29.1 (b, CH_2, cod), 29.9 (b, CH_2, cod), 30.5 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 35.0 (C, ^{t}Bu), 59.1 (C-3), 63.3 (C-4), 68.4 (C-6), 68.9 (b, CH=, cod), 71.1 (CH_2-Ph), 75.3 (b,

CH=, cod), 77.4 (C-2), 79.8 (C-5), 97.3 (C-1), 102.2 (b, CH=, cod), 103.4 (C-7), 107.0 (b, CH=, cod), 117.6 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–158 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.2 (C=O). Anal. calcd (%) for $C_{90}H_{81}BF_{24}IrN_2O_8P$: C 53.82, H 4.06, N 1.39; found: C 53.79, H 4.05, N 1.35.

4.4.7. [Ir(cod)(2d)]BAr_F

Yield: 75 mg (97%). ^{31}P NMR (CD_2Cl_2), δ: 90.9. ^{1}H NMR (CD_2Cl_2), δ: 1.23 (s, 9H, CH_3, ^{t}Bu), 1.32 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.53 (s, 9H, CH_3, ^{t}Bu), 1.71 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.92 (b, 2H, CH_2, cod), 2.26 (b, 2H, CH_2, cod), 2.33 (b, 4H, CH_2, cod), 3.01 (m, 1H, CH=, cod), 3.24 (m, 1H, H-4), 3.29 (m, 1H, H-6), 3.47 (m, 1H, H-5), 3.69 (m, 1H, H-2), 3.97 (m, 2H, CH= cod and H-6'), 4.39 (m, 1H, CH= cod), 4.61 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.70 (d, 1H, CH_2-Ph, $^2J_{H-H}$ = 12.4 Hz), 4.92 (m, H-3), 5.03 (d, 1H, H-1, $^3J_{1-2}$ = 3.2 Hz), 5.07 (s, 1H, H-7), 5.57 (m, 1H, CH= cod), 6.02 (m, 1H, NH), 6.7–7.7 (m, 26H, CH=), 8.81 (m, 2H, CH=). ^{13}C NMR (CD_2Cl_2), δ: 16.8 (CH_3), 16.9 (CH_3), 20.4 (CH_3), 20.9 (CH_3), 25.1 (b, CH_2, cod), 26.3 (b, CH_2, cod), 28.9 (b, CH_2, cod), 29.3 (b, CH_2, cod), 32.2 (CH_3, ^{t}Bu), 32.5 (CH_3, ^{t}Bu), 34.4 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 59.0 (C-3), 63.5 (C-4), 68.4 (C-6), 69.7(b, CH=, cod), 71.0 (CH_2-Ph), 75.9 (b, CH=, cod), 77.1 (C-2), 79.6 (C-5), 98.3 (C-1), 102.9 (C-7), 103.4 (b, CH=, cod), 106.8 (b, CH=, cod), 117.6 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–158 (aromatic carbons), 161.9 (q, C-B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 166.2 (C=O). Anal. calcd (%) for $C_{90}H_{81}BF_{24}IrN_2O_8P$: C 53.82, H 4.06, N 1.39; found: C 53.77, H 4.03, N 1.36.

4.5. Typical procedure for the hydrogenation of olefins

The alkene (0.5 mmol) and Ir complex (2 mol%) were dissolved in CH_2Cl_2 (2 mL) in a high-pressure autoclave, which was purged four times with hydrogen. Next, it was pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et_2O (1.5 ml) and filtered through a short Celite plug. The enantiomeric excess was determined by chiral GC or chiral HPLC and conversions were determined by ^{1}H NMR. The enantiomeric excesses of the hydrogenated products were determined using the previously described conditions.[5]

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