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A Phosphite-Pyridine/Iridium Complex Library as Highly Selective Catalysts for the Hydrogenation of Minimally Functionalized Olefins

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Abstract: A modular library of readily available phosphite-pyridine ligands has been successfully applied for the first time in the iridium-catalyzed asymmetric hydrogenation of a broad range of minimally functionalized olefins. The modular ligand design has been shown to be crucial in finding highly selective catalytic systems for each substrate. Excellent enantioselectivities (*ee*s up to 99%) have therefore been obtained in a wide range of *E*- and *Z*-trisubstituted alkenes, including more demanding triaryl-substituted olefins and dihydronaphthalenes. This good performance extends to the very challenging class of terminal disubstituted olefins, and to olefins containing neighbouring polar groups (*ee*s up to 99%). Both enantiomers of the reduction product can be obtained in excellent enantioselectivities by simply changing the configuration of the carbon next to the phosphite moiety. The hydrogenations were also performed using propylene carbonate as solvent, which allowed the iridium catalyst to be reused and maintained the excellent enantioselectivities.

Keywords: asymmetric catalysis; heterodonor P,N ligands; hydrogenation; iridium; olefins

Introduction

The major progress in the field of asymmetric catalysis has been driven by the growing demand for enantiomerically pure pharmaceuticals, agrochemicals, flavours and other fine chemicals. Asymmetric hydrogenation utilizing molecular hydrogen to reduce prochiral olefins has become one of the most sustainable and reliable catalytic methods for the preparation of optically active compounds, mainly because of its high efficiency, atom economy, and operational simplicity.[1] Over many years the scope of this reaction has gradually been extended in terms of reactant structure and catalyst efficiency. Today, an impressive range of chiral phosphorus ligands (mainly diphosphines) has been developed and successfully applied in Rh- and Ru-catalyzed hydrogenation. However, the range of olefins that can be hydrogenated with high enantiomeric excess is limited to substrates with a coordinating group next to the C=C bond, because substrate chelation to the metal plays a pivotal role in stereodiscrimination.[1] With minimally functionalized olefins, these catalysts generally show low reactivity and unsatisfactory enantioselectivity.[1,2] In this context, Pfaltz introduced a new class of hydrogenation catalysts, iridium complexes with chiral P,N ligands, which mimic the Crabtree catalyst[3] and overcome these limitations.[2,4,5] The first successful P,N ligands[6] contained a phosphine or phosphinite moiety as a P-donor group and either an oxazoline,[6b,g,j] oxazole,[6d] thiazole[6i] or pyridine[6c,h,t] as an N-donor group. Among these, the phosphorus/oxazoline ligands have played a dominant role. In recent years, research has focused on the design of ligands containing more robust N-donor groups than oxazolines. In this respect, the use of pyridine-containing ligands as an alternative to oxazolines is of interest because of the robustness and the easy incorporation of the pyridine group. Soon after the successful application of phosphinite-oxazoline ligands,[6b] Pfaltz and co-workers developed the first generation of phosphinite-pyridine ligands (Figure 1),[6h,7] which was successfully used in a limited range of alkenes. The performance was subsequently further improved by introducing a more rigid chiral bicyclic ligand backbone (2nd generation, Figure 1).[6c,8] Although the number of substrates that can be successfully reduced was increased with this 2nd generation, there is still a problem of substrate

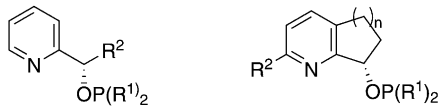


Figure 1. Phosphinite-pyridine ligand libraries developed by Pfaltz and co-workers.

range limitation, since high enantioselectivities are mainly limited to trisubstituted substrates.[9]

Some years ago, we discovered that the presence of biaryl phosphite moieties in ligand design is highly advantageous.[10] Ir/phosphite-oxazoline catalytic systems provide greater substrate versatility than previous Ir systems based on phosphine/phosphinite-oxazoline ligands. However, the use of ligands that combine the phosphite moiety with other nitrogen donor groups rather than oxazoline has been limited.[10d] In this context, Ruffo's group, together with our group, developed a family of pyranoside phosphite-pyridine ligands for this process.[11] Nonetheless, the enantioselectivities and substrate versatility were only moderate. At this point it was unclear whether these unsatisfactory results were due to the large chelate ring size (nine-membered) formed by the pyranoside ligands or to the unsuccessful combination of phosphite and pyridine moieties in the ligand. To address this point and in order to systematically study the possibilities of phosphite-pyridine ligands in this process, we decided to take the 1st generation of Pfaltz's phosphinite-pyridine ligands and replace the phosphinite moiety with a biaryl phosphite group to provide ligands **L1**–**L12a**–**g** (Figure 2).[12]

These ligands *a priori* combine the advantages of both types of successful ligands for this process (phosphite and pyridine). They are therefore less sensitive to air and other oxidizing agents than phosphines and phosphinites, easy to synthesize from readily available alcohols, and more stable than their oxazoline counterparts.[13] The modular construction of these ligands allows sufficient flexibility to fine-tune the steric and electronic properties of both the ligand backbone and the biaryl moiety in order to explore how they affect catalytic performance (activity and selectivity). We thereby studied the effect of systematically varying the substituents in the ligand backbone (R^1 and R^2, ligands **L1**–**L8**), the configuration of the ligand backbone (ligands **L1**–**L7** *vs* **L9**–**L12**), and the substituents and configurations in the biaryl phosphite moiety (**a**–**g**). As a result, the optimal combination for maximum activity and enantioselectivity for a wide range of *E*- and *Z*-trisubstituted and 1,1-disubstituted olefins was obtained.

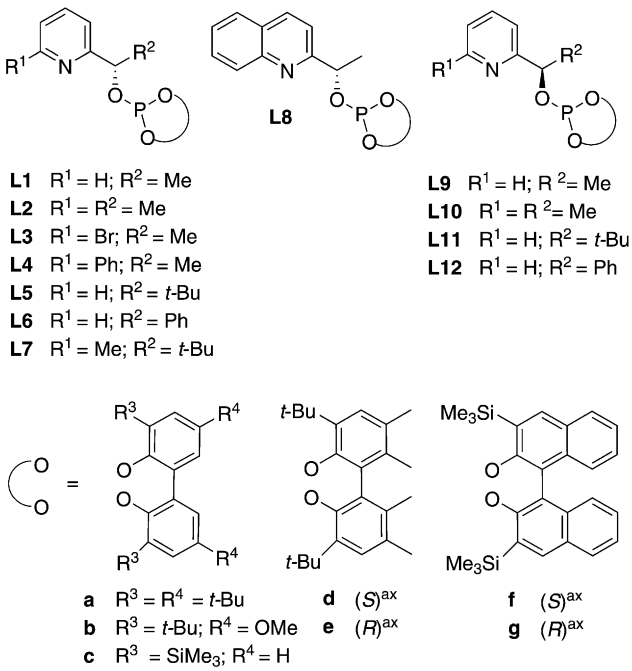


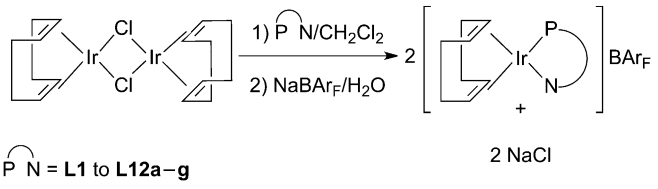
Figure 2. Phosphite-pyridine ligand library **L1**–**L12a**–**g**.

Results and Discussion

Synthesis of the Ir Catalyst Precursors

The catalyst precursors were made by refluxing a dichloromethane solution of the appropriate ligand (**L1**–**L12a**–**g**) in the presence of 0.5 equiv. of $[Ir(\mu\text{-}Cl)cod]_2$ for 1 h. The Cl^-/BAr_F^- counterion exchange was then achieved by a reaction with sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr_F$) (1 equiv.) in the presence of water (Scheme 1). All complexes were isolated as air-stable orange solids in pure form, and they were then used without further purification.

The complexes were characterized by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The spectral assignments were based on information from ^1H-^1H and ^{13}C-^1H correlation measurements, and were as anticipated for these C_1 iridium complexes. The VT-NMR (+40 °C to −70 °C) spectra indicate that only one isomer is present in solution. One singlet in the ^{31}P-{^1H} NMR spectra was obtained in all cases.[14]



Scheme 1. Synthesis of the $[Ir(cod)(\widehat{PN})]BAr_F$ catalyst precursors ($\widehat{PN}$ = **L1**–**L12a**–**g**).

Asymmetric Hydrogenation of Trisubstituted Olefins

Asymmetric Hydrogenation of Minimally Functionalized Trisubstituted Olefins

In a first set of experiments, we used the Ir-catalyzed hydrogenation of substrates *E*-2-(4-methoxyphenyl)-2-butene **S1** and *Z*-2-(4-methoxyphenyl)-2-butene **S2** to study the potential of ligands **L1**–**L12a**–**g**. Substrate **S1** was chosen as a model for the hydrogenation of *E*-isomers because it has been reduced with a wide range of ligands, which enable the efficiency of the various ligand systems to be compared directly.[2] In order to assess the potential of the ligand library **L1**–**L12a**–**g** for the more demanding *Z*-isomers, which are usually hydrogenated less enantioselectively than the corresponding *E*-isomers, we chose substrate **S2** as a model. Excellent activities and enantioselectivities (up to 98% for **S1** and up to 91% for **S2**) were obtained. The results, which are summarized in Table 1, indicate that enantioselectivity is mainly affected by the substituents at the ligand backbone (R^1 and R^2) and by the substituents/configuration at the biaryl phosphite moiety. However, the effect of these ligand parameters on enantioselectivity depends on the substrate type (*E*- or *Z*-isomers). While for the *E*-substrate **S1** the enantioselectivity was best with ligand **L2e** [98% *ee* (*S*)], enantioselectivities for the more demanding *Z*-substrate **S2** were therefore best with ligand **L6c** [91% *ee* (*R*)]. Interestingly, for both types of substrates, the sense of enantioselectivity is controlled by the configuration of the stereogenic carbon next to the phosphite moiety. Ligands **L1**–**L8** therefore provide the opposite enantiomer to ligands **L9**–**L12** (i.e., Table 1; entry 10 *vs.* 25, for substrate **S1**; and entry 17 *vs.* 27 for substrate **S2**).

The effect of the substituents of the ligand backbone (R^1 and R^2) was studied using ligands **L1**–**L8**. While for substrate **S1** the enantioselectivity is highly affected by the substituents at both R^1 and R^2 positions of the ligand backbone, for substrate **S2** the enantioselectivity is mainly affected by the substituent at R^2, and is relatively insensitive to the substituents at R^1. For substrate **S1**, although high enantioselectivities can be obtained by introducing either a methyl substituent at R^1 (ligands **L2**) or a *tert*-butyl substituent at R^2 (ligands **L5**), ligands **L2** provided somewhat higher enantioselectivities than **L5** (i.e., Table 1, entries 10 and 15). However, the introduction of both substituents simultaneously at R^1 and R^2 positions (ligands **L7**) led to lower enantioselectivities (Table 1, entry 20 *vs.* 8 and 13). For substrate **S2**, the introduction of a phenyl substituent at R^2 position has a positive effect on enantioselectivities (Table 1, entry 16 *vs.* 1).

The effect of the phosphite moieties was studied using ligands **L1a**–**g** (Table 1, entries 1–7). Once again, the effect of this moiety on enantioselectivity depends on the substrate type. Regarding the substituents in the tropoisomeric biphenyl phosphite moiety, for substrate **S1**, the presence of *tert*-butyl substituents at *para* positions of the biphenyl phosphite moiety provides higher enantioselectivities than when a methoxy group or hydrogen is present (i.e., **a** > **b** ≈ **c**; Table 1, entry 1 *vs.* 2 and 3). However, the effect for substrate **S2** is opposite. The highest enantioselectivity is therefore obtained using a non-*para*-substituted biphenyl phosphite moiety (Table 1, entry 3 *vs.* 2 and 1). Regarding the configuration of the biaryl phosphite, while for substrate **S1** the enantioselectivity is higher using the enantiopure *R*-biaryl phosphite moiety, for substrate **S2** the presence of the

Table 1. Ir-catalyzed hydrogenation of **S1** and **S2** using ligands **L1**–**L12a**–**g**.[a]

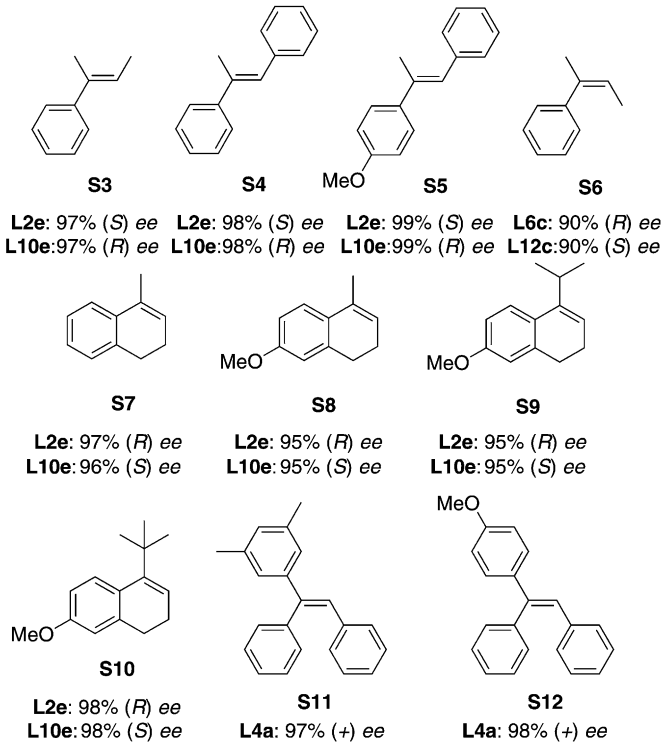
Entry	Ligand	4-MeO-C_6H_4 **S1** *ee* [%][b]	4-MeO-C_6H_4 **S2** *ee* [%][b]
1	**L1a**	61 (*S*)	75 (*R*)
2	**L1b**	48 (*S*)	84 (*R*)
3	**L1c**	50 (*S*)	88 (*R*)
4	**L1d**	27 (*S*)	73 (*R*)
5	**L1e**	64 (*S*)	25 (*R*)
6	**Lif**	38 (*S*)	74 (*R*)
7	**L1g**	58 (*S*)	30 (*R*)
8	**L2a**	90 (*S*)	72 (*R*)
9	**L2d**	87 (*S*)	59 (*R*)
10	**L2e**	98 (*S*)	45 (*R*)
11	**L3a**	58 (*S*)	72 (*R*)
12	**L4a**	63 (*S*)	68 (*R*)
13	**L5a**	89 (*S*)	72 (*R*)
14	**L5d**	45 (*S*)	52 (*R*)
15	**L5e**	90 (*S*)	58 (*R*)
16	**L6a**	80 (*S*)	84 (*R*)
17	**L6c**	74 (*S*)	91 (*R*)
18	**L6d**	55 (*S*)	85 (*R*)
19	**L6e**	90 (*S*)	48 (*R*)
20	**L7a**	62 (*S*)	11 (*R*)
21	**L8a**	70 (*S*)	75 (*R*)
22	**L9a**	60 (*R*)	77 (*S*)
23	**L9d**	36 (*R*)	64 (*S*)
24	**L9e**	66 (*R*)	6 (*S*)
25	**L10e**	97 (*R*)	38 (*S*)
26	**L11e**	88 (*R*)	38 (*S*)
27	**L12e**	72 (*R*)	90 (*S*)
28[c]	**L12e**	98 (*S*)	44 (*R*)
29[c]	**L6c**	74 (*S*)	91 (*R*)

[a] Reactions carried out at room temperature by using 0.5 mmol of substrate and 1 mol% of Ir catalyst precursor at 50 bar of H_2 using dichloromethane (2 mL) as solvent. Full conversions were achieved in all cases.
[b] Enantiomeric excesses determined by GC.
[c] Reaction carried out with 0.25 mol% of Ir catalyst precursor for 3 h.

S-biaryl phosphite moiety provides higher enantioselectivities (Table 1, entries 4–7).

In summary, by the correct choice of the substituents at R^1 and R^2 of the ligand backbone, the configuration of the stereogenic carbon next to the phosphite moiety and the substituents/configuration at the biaryl phosphite moiety, we were able to obtain both enantiomers of the reduction product in high enantioselectivities for both *E*- and *Z*-trisubstituted model substrates (for substrate **S1**, *ee*s up to 98% were obtained using ligands **L2e** and **L10e**; and for substrate **S2**, *ee*s up to 91% were obtained using ligands **L6c** and **L12c**). In addition, the excellent enantioselectivities and activities were maintained at a low catalyst loading (0.25 mol%; Table 1, entries 28 and 29).

We then studied the asymmetric hydrogenation of other *E*- and *Z*-trisubstituted olefins (**S3**–**S12**) by using the phosphite-pyridine ligand library **L1**–**L12a**–**g**. The most noteworthy results are shown in Scheme 2 (see the Supporting Information for a complete set of results). The enantioselectivities are among the best observed for these substrates.[2,6] We first studied the hydrogenation of substrates **S3**–**S6**, related to **S1** and **S2** that differ in the substituents in both the aryl ring and the substituents *trans* to the aryl group. The results followed the same trends as those observed for substrates **S1** and **S2**. For *E*-substrates **S3**–**S5**, the enantioselectivities were therefore best with ligands **L2e** and **L10e**, while ligands **L6c** and **L12c** afforded the highest *ee*s for *Z*-substrate **S6**. We also found that enantioselectivity (*ee* values up to 99%) is relatively insensitive to the electronic nature of the substrate phenyl ring (i.e., substrates **S1**, **S2** and **S4** *vs.* **S3**, **S6** and **S5**, respectively). It should be noted that if the ligands are appropriately tuned, high enantioselectivities can also be obtained for a wide range of the more demanding dihydronaphthalenes (**S7**–**S10**) and triaryl-substituted substrates (**S11** and **S12**). For dihydronaphthalene substrates (**S7**–**S10**), high enantioselectivities (95–98% *ee*) were obtained with Ir-**L2e** and Ir-**L10e** catalysts. Although the corresponding chiral tetraline motif can be found in numerous natural products [i.e., natural antitumor agent (*R*)-(+)-7-demethyl-2-methoxycalamenene],[15] very few catalytic systems are able to hydrogenate this substrate class at high levels of enantioselectivities.[8b,15] Another important class of substrates that have also been scarcely studied is the triaryl-substituted group.[10e,16] This substrate class provides an easy entry point to diarylmethine chiral centers, which are present in several important drugs and natural products.[17] We were again pleased to find that this substrate class could also be reduced in high enantioselectivity but in this case using the Ir-**L4a** catalytic system (Scheme 2, *ee*s ranging from 97% to 98%).

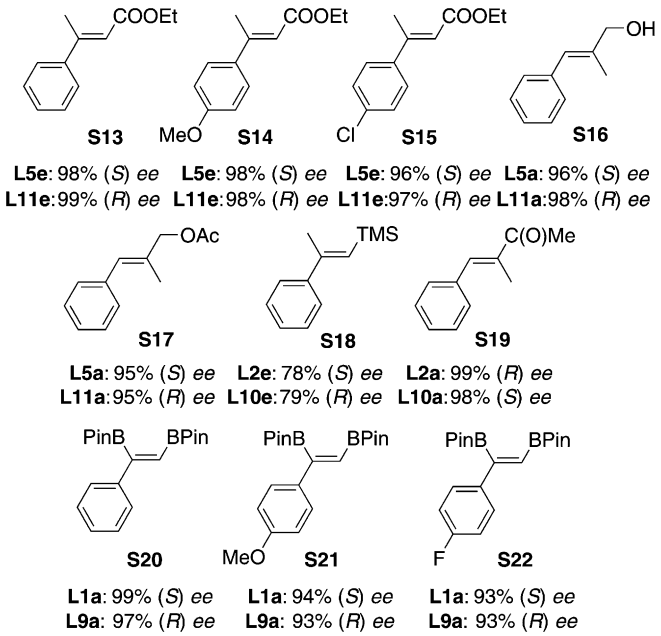


Scheme 2. Selected hydrogenation results of *E*- and *Z*-trisubstituted olefins using [Ir(cod)(**L1**–**L12a**–**g**)]BAr_F catalyst precursors. *Reaction conditions:* 1 mol% catalyst precursor, CH_2Cl_2 as solvent, 50 bar H_2, room temperature, 2 h. Full conversions were achieved in all cases.

Asymmetric Hydrogenation of Trisubstituted Olefins Containing a Neighbouring Polar Group

The reduction of substrates bearing a neighbouring polar group is of great importance because they are important intermediates for the synthesis of high-value chemicals and they enable further functionalization. We therefore decided to study the potential of our phosphite-pyridine ligand library **L1–L12a–g** for the reduction of a wide range of trisubstituted alkenes containing several types of polar groups in greater depth. The results are summarized in Scheme 3 (for a full set of results, see Table SI.2 in Supporting Information). Once again, excellent enantioselectivities in both enantiomers of the reduction products (*ee* values up to 99%) for a range of substrates were obtained under mild reaction conditions by suitable tuning of the ligand parameters.

The reduction of several α,β-unsaturated esters (**S13**–**S15**) followed different trends to those observed for the previous *E*-trisubstituted substrates. Enantioselectivities were therefore best using ligands **L5a**, **L5e**, **L11a** and **L11e** (*ee*s ranging from 96% to 99%). It should be noted that *ee*s are highly independent on the electronic nature of the substrate phenyl ring. We also found that the hydrogenation of allylic alcohol



Scheme 3. Selected hydrogenation results of trisubstituted olefins bearing a neighbouring polar group using [Ir(cod)(**L1**–**L12a**–**g**)]BAr_F catalyst precursors. *Reaction conditions:* 1 mol% catalyst precursor, CH_2Cl_2 as solvent, 50 bar H_2, room temperature, 2 h. Full conversions were achieved in all cases.

S16 and allylic acetate **S17** followed the same trend. High enantioselectivities were therefore also obtained with catalyst systems containing the ligands **L5a**, **L5e**, **L11a** and **L11e** (*ee*s up to 98%). As observed for the *E*-trisubstituted substrate **S1**, the highest enantioselectivities in the hydrogenation of vinylsilane **S18** were obtained using ligands **L2e** and **L10e** (*ee*s up to 78%). Ligand tuning was also essential to achieve the highest levels of enantioselectivity in the reduction of α,β-unsaturated ketone **S19** and several vinylboronates **S20**–**S22**. For substrate **S19**, enantioselectivities are therefore best when using Ir-**L2a** and Ir-**L10a** catalysts (*ee*s up to 99%), while for substrates **S20**–**S22**, Ir-**L1a** and Ir-**L9a** catalytic systems provided the highest enantioselectivities (*ee*s up to 99%). The hydrogenation of vinylboronates provides easy access to chiral borane compounds, which are useful building blocks in organic synthesis because the C–B bond can be readily converted to C–O, C–N and C–C bonds with retention of the chirality. For vinylboronates, our results show that *ee*s are again highly independent of the electronic properties of the phenyl substrate ring.

It should be pointed out that these results surpass the *ee*s achieved using related 1st generation phosphinite-pyridine analogues.[18] This is therefore one of the few catalytic systems that can hydrogenate a wide range of trisubstituted olefins in high activities and enantioselectivities.[2,6]

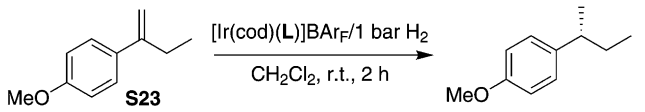
Asymmetric Hydrogenation of 1,1-Disubstituted Terminal Olefins

We next studied the the asymmetric hydrogenation of more demanding terminal olefins. The lower enantioselectivity obtained with 1,1-disubstituted terminal olefins compared with trisubstituted olefins is attributed to two main factors.[2d,e] The first is that the two substituents in the substrate can easily exchange positions in the chiral environment formed by the catalysts, thus reversing the face selectivity. The second reason is that the terminal double bond can isomerize to form the more stable internal alkene, which usually leads to the predominant formation of the opposite enantiomer of the hydrogenated product. Few known catalytic systems provide high enantioselectivities for these substrates, and those that do are usually limited in substrate scope.[2e,19,20] Unlike the hydrogenation of trisubstituted olefins, the enantioselectivity in the reduction of terminal alkenes is highly pressure-dependent. Hydrogenation at an atmospheric pressure of H_2 therefore generally gave significantly higher *ee* values than at higher pressures.[19]

Asymmetric Hydrogenation of Minimally Functionalized 1,1-Disubstituted Terminal Olefins

In an initial set of experiments, we used the Ir-catalyzed asymmetric hydrogenation of 2-(4-methoxyphe-

Table 2. Selected results for the Ir-catalyzed hydrogenation of **S23** using the ligands **L1**–**L12a**–**g**.[a]



Entry	Ligand	*ee* [%][b]	Entry	Ligand	*ee* [%][b]
1	**L1a**	48 (*R*)	14	**L5d**	77 (*R*)
2	**L1b**	49 (*R*)	15	**L5e**	30 (*S*)
3	**L1c**	50 (*R*)	16	**L6a**	63 (*R*)
4	**L1d**	40 (*S*)	17	**L6d**	62 (*R*)
5	**L1e**	58 (*R*)	18	**L6e**	42 (*S*)
6	**L1f**	36 (*S*)	19	**L7a**	33 (*S*)
7	**L1g**	58 (*R*)	20	**L8a**	60 (*R*)
8	**L2a**	72 (*R*)	21	**L9a**	49 (*S*)
9	**L2d**	8 (*S*)	22	**L9d**	56 (*R*)
10	**L2e**	96 (*R*)	23	**L9e**	43 (*S*)
11	**L3a**	42 (*R*)	24	**L10e**	95 (*S*)
12	**L4a**	19 (*R*)	25[c]	**L2e**	96 (*R*)
13	**L5a**	64 (*R*)	26[c]	**L10e**	95 (*S*)

[a] Reactions carried out using 0.5 mmol of **S21** and 1 mol% of Ir catalyst precursor at 1 bar of H_2. Full conversions after 2 h were achieved in all cases.
[b] Enantiomeric excesses determined by chiral GC.
[c] Reaction carried out at 0.25 mol% of Ir catalyst precursor for 3 h.

nyl)but-1-ene **S23**. The results obtained using the ligand library **L1**–**L12a**–**g** under optimized conditions are shown in Table 2. We were again able to fine-tune the ligand parameters to produce high activities and enantioselectivities (*ee*s up to 96%) in the hydrogenation of this substrate using ligands **L2e** and **L10e** at low catalyst loadings (0.25 mol%) and hydrogen pressures (1 bar). Once again, it was possible to obtain both enantiomers of the hydrogenated product by simply changing the configuration of the stereogenic carbon next to the phosphite moiety (see Table 2, entry 10 *vs.* 24). Enantioselectivity is also affected by the substituents at the ligand backbone (R^1 and R^2) and by the substituents/configuration in the biaryl phosphite moiety. Regarding the effect of the substituents at the ligand backbone, we found that enantioselectivities are best with ligands that contain a methyl substituent at R^1 and a hydrogen substituent at R^2 positions (ligands **L2** and **L10**).

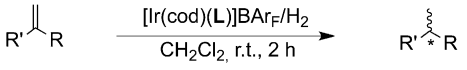
As far as the effect of the substituents/configuration of the phosphite moiety is concerned, enantioselectivity is mainly affected by the configuration of the biaryl phosphite moiety, and is relatively insensitive to the substituents at both *ortho* and *para* positions of the biaryl phosphite group. The best enantioselectivities are therefore obtained using ligands containing an enantiopure *R*-biaryl phosphite moiety (see Table 2, entry 10 *vs.* 9).

We then studied the asymmetric hydrogenation of other 1,1-disubstituted aryl-alkyl substrates (**S24**–**S31**), 1,1-disubstituted pyridyl-alkyl olefins (**S32** and **S33**) and 1,1-diaryl terminal alkenes (**S34**–**S36**) using the phosphite-pyridine ligand library **L1**–**L12a**–**g**. The most noteworthy results are shown in Table 3 (for a complete set of results, see Table SI.3 in Supporting Information). The results follow the same trends as the hydrogenation of **S23** for all substrates. The catalyst precursors containing the phosphite-pyridine ligands **L2e** and **L10e** therefore provided the best enantioselectivities in both enantiomers of the reduction product. These results are again among the best reported for these substrates.[2e]

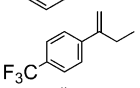
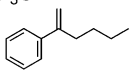
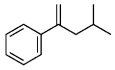
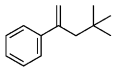
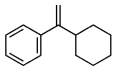
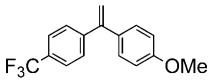
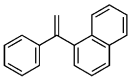
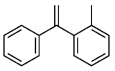
Our results with several 1,1-disubstituted aryl-alkyl substrates (**S24**–**S31**) indicated that enantioselectivity is not affected by the electronic nature of the substrate aryl ring (Table 2, entry 10; and Table 3, entries 1 and 3), but it is slightly affected by the nature of the alkyl chain (*ee*s ranging from 92% to 97%; Table 3, entries 1, 5–16). Enantioselectivities therefore decrease from 97–96% to 92% by increasing the steric bulk of the alkyl substituent. This can be attributed to the restrictions imposed by the Ir catalysts themselves rather than to the presence of an isomerization process under hydrogenation conditions. This is supported by the fact that the hydrogenation of substrate **S31** bearing a *tert*-butyl group, for which isomerization cannot occur, provides the same enantioselectivity as those obtained using substrates **S29** and **S30**, which are more prone to isomerization and also contain bulky alkyl substituents (Table 3, entry 15 *vs.* 11 and 13).

Due to the interest of heterocycles for industry and because the heterocyclic part can be modified post-hydrogenation, we decided to test the scope of our ligand library by performing the hydrogenation of

Table 3. Selected results for the Ir-catalyzed hydrogenation of minimally functionalized 1,1-disubstituted terminal olefins using ligands **L1**–**L12a**–**g**.[a]



R' = aryl, 2-pyridine
R = alkyl, aryl

Entry	Substrate		Ligand	*ee* [%][b]
1		**S24**	**L2e**	97 (*R*)
2			**L10e**	97 (*S*)
3		**S25**	**L2e**	96 (*R*)
4			**L10e**	96 (*S*)
5		**S26**	**L2e**	96 (*R*)
6			**L10e**	96 (*S*)
7		**S27**	**L2e**	96 (*R*)
8			**L10e**	95 (*S*)
9		**S28**	**L2e**	97 (*R*)
10			**L10e**	96 (*S*)
11		**S29**	**L2e**	92 (*R*)
12			**L10e**	91 (*S*)
13		**S30**	**L2e**	92 (*R*)
14			**L10e**	92 (*S*)
15		**S31**	**L2e**	92 (*R*)
16			**L10e**	92 (*S*)
17		**S32**	**L2e**	92 (−)
18			**L10e**	93 (+)
19		**S33**	**L2e**	94 (−)
20			**L10e**	94 (+)
21[c]		**S34**	**L2e**	18 (−)
22[c]		**S35**	**L2e**	80 (−)
23[c]			**L10e**	79 (+)
24[c]		**S36**	**L2e**	82 (−)

[a] Reactions carried out using 0.5 mmol of substrate and 0.25 mol% of Ir catalyst precursor at 1 bar of H_2. Full conversions were achieved in all cases.
[b] Enantiomeric excesses determined by chiral GC (except for entries 22–24 that were measured by HPLC).
[c] Reaction carried out under 50 bar of H_2.

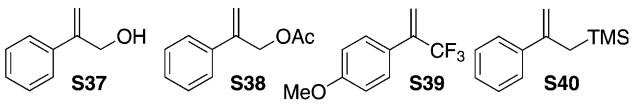
pyridyl-alkyl substrates **S32** and **S33**. We were pleased to see that we also obtained high activities and enantioselectivities under mild reaction conditions (Table 3, entries 17–20).

Finally, we studied the hydrogenation of several diaryl terminal alkenes (**S34**–**S36**; Table 3, entries 21–24). Enantiopure diarylalkanes are important intermediates for the preparation of drugs and research materials.[21] They have traditionally been prepared using rather laborious approaches.[21,22] It has recently been shown that they can be prepared more efficiently using enantioselective hydrogenation.[10c] Substrates differing sterically (**S35** and **S36**) were also hydrogenated with high enantioselectivities (*ee*s up to 82%; Table 3, entries 22–24) using the Ir-**L2e** catalytic system. However, as anticipated, the control of enantioselectivity in substrate **S34**, for which the aryl groups only differ electronically, was less effective (Table 3, entry 21).

Asymmetric Hydrogenation of 1,1-Disubstituted Terminal Olefins Containing a Neighbouring Polar Group

We next examined the asymmetric hydrogenation of 1,1-disubstituted terminal olefins containing a polar neighbouring group (**S37**–**S40**). The results are summarized in Scheme 4 (for a complete set of results, see Table SI.3 in Supporting Information). In all cases, both enantiomers of the hydrogenated product can be obtained in high enantioselectivities by simply changing the configuration of the carbon next to the phosphite moiety.

We initially tested the ligand library in the hydrogenation of the allylic alcohol **S37** and allylic acetate **S38**. Derivatives of the hydrogenation of these products are important intermediates for the synthesis of high-value cosmetics, natural products and drugs.[23] Enantioselectivities followed a different trend to that observed with the previous 1,1,-disubstituted terminal olefins **S23**–**S36**, and the best enantioselectivities (up to 84%) were obtained using ligands **L5e** and **L11e**.



L5e:84% (*S*) *ee* **L5e**:79% (*S*) *ee* **L1c**:99% (+) *ee* **L2e**:95% (*R*) *ee*
L11e:84% (*R*) *ee* **L11e**:79% (*R*) *ee* **L9c**:99% (–) *ee* **L10e**:95% (*S*) *ee*

Scheme 4. Selected hydrogenation results of 1,1-disubstituted terminal olefins containing a neighbouring polar group using [Ir(cod)(**L1**–**L12a**–**g**)]BAr_F catalyst precursors. *Reaction conditions:* 0.5 mol% catalyst precursor, CH_2Cl_2 as solvent, 50 bar H_2, room temperature, 2 h. Full conversions were achieved in all cases.

We then turned our attention to the asymmetric reduction of the trifluoromethyl olefin **S39** and allylic silane **S40**. The hydrogenation of these compounds gave rise to important organic intermediates and a number of innovative new organofluorine[24] and organosilicon[25] drugs are now being developed. For substrate **S39**, an unprecedented high enantioselectivity (*ee* up to 99%) has been obtained with Ir-**L1c** and Ir-**L9c** catalytic systems. However, for substrate **S40**, we also obtained high enantioselectivities but with ligands **L2e** and **L10e**. Once again, these results clearly show the efficiency of using highly modular scaffolds in the ligand design.

Recycling Experiments using Propylene Carbonate as Solvent

Encouraged by the excellent results obtained, we decided to go one step further and study the hydrogenation using propylene carbonate (PC) as an environmentally friendly alternative solvent. PC has recently emerged as a sustainable alternative to standard organic solvents because of its high boiling point, low toxicity and environmentally friendly synthesis.[26] Moreover, Börner's group has demonstrated that PC allows Ir catalysts to be repeatedly recycled by a simple two-phase extraction with an apolar solvent,[27] which for a practical industrial application is of great importance because of the high price of iridium.

Our results indicated that the new Ir-phosphite-pyridine catalytic systems can be used in combination with PC (Table 4). However, higher pressures are required to match the performance achieved using dichlororomethane as solvent (i.e., 50 bar of H_2 are required in the reduction of terminal substrates). Thus, we were able to recycle Ir-**L2e** catalyst up to 3 times in the hydrogenation of terminal olefins **S23** and **S31** without significant losses in enantioselectivities, although reaction time increased after each run.[28]

Table 4. Recycling experiments with the catalyst precursor [Ir(cod)(**L2e**)]BAr_F and **S23** and **S31** as substrates in PC.[a]

Cycle	Substrate	Conv. [%] (h)[b]	*ee* [%][c]
1	**S23**	100 (4)	95 (*R*)
2	**S23**	98 (6)	94 (*R*)
3	**S23**	57 (10)	94 (*R*)
1	**S31**	100 (4)	91 (*R*)
2	**S31**	92 (6)	91 (*R*)
3	**S31**	58 (10)	90 (*R*)

[a] Reactions carried out using 0.5 mmol of substrate and 1 mol% of Ir catalyst precursor using 50 bar of H_2.
[b] Conversion measured by GC.
[c] Enantiomeric excesses determined by chiral GC.

Conclusions

We have reported the first successful application of phosphite-pyridine ligands in the Ir-catalyzed asymmetric hydrogenation of minimally functionalized olefins. These ligands combine the advantages of both types of successful ligands for this process (phosphite and pyridine). They are therefore more robust than their oxazoline and phosphine/phosphinite counterparts, and the incorporation of the desired diversity is easier to achieve in both the pyridine and the phosphite moieties. The modular ligand design has been shown to be crucial in finding highly selective catalytic systems for each substrate. By carefully selecting the ligand components, we obtained excellent enantioselectivities (*ee*s up to 99%) in a wide range of *E*- and *Z*-trisubstituted alkenes, including more demanding triaryl-substituted olefins, and dihydronaphthalenes. The good performance extends to the very challenging class of terminal disubstituted olefins (*ee*s up to 99%). These catalysts are also very tolerant to the presence of a neighbouring polar group. A range of allylic alcohols, acetates, α,β-unsaturated esters and ketones, allylic silanes, vinylboronates and trifluoromethyl olefins were thus hydrogenated with high enantioselectivities. Note that both enantiomers of the reduction product can be obtained in excellent enantioselectivities by simply changing the configuration of the carbon next to the phosphite moiety. The new Ir-phosphite-pyridine catalyst library not only performs well in traditional organic solvents but also in propylene carbonate, an alternative environmentally friendly solvent, which allowed the catalyst to be reused while maintaining the excellent enantioselectivities. We also demonstrated that the introduction of a biaryl phosphite moiety into the ligand design is highly advantageous in terms of substrate versatility. The efficiency of this ligand design is therefore also corroborated by the fact that these Ir-phosphite-pyridine catalysts provided higher enantioselectivity and broader substrate versatility than their phosphinite-pyridine analogues.[18] In addition the results of our phosphite-pyridine catalyst library compare very well with the ones achieved using the second generation of phosphinite-pyridine ligands (Figure 1),[29] which can be considered as the state of the art for this transformation, with the added advantatge that our Ir-phosphite-pyridine systems are able to expand the scope to a broad range of disubstituted substrates. These results open up a new class of Ir catalysts for the highly enantioselective hydrogenation of minimally functionalized olefins, including those with a neighbouring polar group, which is of great practical interest.

Experimental Section

General Considerations

All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. Phosphorochloridites were easily prepared in one step from the corresponding biaryls. Enantiopure phosphite-pyridine ligands **L1–L12a–g** were prepared as previously described.[12] ^{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 that of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H and ^{13}C assignments were made on the basis of ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC experiments.

Typical Procedure for the Preparation of [Ir(cod)(L)]BAr_F (L = L1–L12a–g)

The corresponding ligand (0.074 mmol) was dissolved in CH_2Cl_2 (2 mL) and $[Ir(\mu\text{-}Cl)(cod)]_2$ (25 mg, 0.037 mmol) was added. The reaction was refluxed at 50 °C for 1 hour. After 5 min at room temperature, $NaBAr_F$ (77.1 mg, 0.082 mmol) and water (2 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 with $MgSO_4$ and the solvent was evaporated to give the product as an orange solid.

[Ir(cod)(L1a)]BAr_F: Yield: 118 mg (93%). ^{31}P NMR ($CDCl_3$): $\delta = 06.0$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.29$ (s, 9H, CH_3, *t*-Bu), 1.33 (s, 18H, CH_3, *t*-Bu), 1.51 (s, 9H, CH_3, *t*-Bu), 1.87 (b, 2H, CH_2, cod), 2.13 (b, 3H, CH_3), 2.18 (b, 4H, CH_2, cod), 2.36 (b, 2H, CH_2, cod), 3.94 (b, 1H, CH=, cod), 4.29 (b, 1H, CH=, cod), 4.71 (b, 1H, CH=, cod), 5.35 (b, 1H, CH=, cod), 6.12 (m, 1H, CHO), 7.1–8.6 (m, 20H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 25.3$ (b, CH_2, cod), 29.0 (b, CH_2, cod), 30.9 (CH_3), 31.1 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.9 (CH_3, *t*-Bu), 33.0 (b, CH_2, cod), 34.8 (C, *t*-Bu), 35.4 (C, *t*-Bu), 35.5 (C, *t*-Bu), 36.3 (b, CH_2, cod), 65.8 (b, CH=, cod), 69.9 (b, CH=, cod), 77.2 (CHO), 100.7 (d, CH=, cod, $J_{C,P} = 20.9$ Hz), 104.5 (d, CH=, cod, $J_{C,P} = 12.5$ Hz), 117.7 (b, CH=, BAr_F), 119–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 139–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^{1}J = 49$ Hz); anal. calcd. (%) for $C_{75}H_{72}BF_{24}IrNO_3P$: C 52.21, H 4.21, N 0.81; found: C 52.16, H 4.17, N 0.78.

[Ir(cod)(L1b)]BAr_F: Yield: 117 mg (95%). ^{31}P NMR ($CDCl_3$): $\delta = 109.0$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.21$ (s, 9H, CH_3, *t*-Bu), 1.41 (s, 9H, CH_3, *t*-Bu), 1.76 (b, 2H, CH_2, cod), 2.02 (b, 3H, CH_3), 2.05 (b, 4H, CH_2, cod), 2.29 (b, 2H, CH_2, cod), 3.73 (s, 6H, CH_3, CH_3O), 4.13 (b, 1H, CH=, cod), 4.30 (b, 1H, CH=, cod), 4.59 (b, 1H, CH=, cod), 5.22 (b, 1H, CH=, cod), 6.03 (m, 1H, CHO), 6.5–8.5 (m, 20H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 25.5$ (b, CH_2, cod), 29.1 (b, CH_2, cod), 31.0 (CH_3, *t*-Bu), 31.2 (CH_3), 31.8 (CH_3, *t*-Bu), 33.5 (b, CH_2, cod), 35.6 (C, *t*-Bu), 35.7 (C, *t*-Bu), 36.7 (b, CH_2, cod), 55.8 (CH_3, CH_3O), 55.9 (CH_3, CH_3O), 66.3 (b, CH=, cod), 70.2 (b, CH=, cod), 77.4 (CHO), 100.4 (d, CH=, cod, $J_{C,P} = 21.7$ Hz), 104.7 (d, CH=, cod, $J_{C,P} = 11.7$ Hz), 113–116 (aromatic carbons), 117.7 (b, CH=, BAr_F), 120–133 (aromatic carbons), 135.0 (b, CH=, BAr_F), 139–159 (aromatic carbons),

161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{69}H_{60}BF_{24}IrNO_5P$: C 49.53, H 3.61, N 0.84; found: C 49.46, H 3.57, N 0.79.

[Ir(cod)(L1c)]BAr_F: Yield: 112 mg (92%). ^{31}P NMR ($CDCl_3$); $\delta = 109.1$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 0.20$ (s, 9H, CH_3, $SiMe_3$), 0.48 (s, 9H, CH_3, $SiMe_3$), 1.78 (b, 2H, CH_2, cod), 1.89 (b, 3H, CH_3), 2.19 (b, 4H, CH_2, cod), 2.40 (b, 2H, CH_2, cod), 4.16 (b, 1H, CH=, cod), 4.20 (b, 1H, CH=, cod), 4.73 (b, 1H, CH=, cod), 5.38 (b, 1H, CH=, cod), 6.19 (m, 1H, CHO), 7.2–8.7 (m, 22H, CH=); ^{13}C NMR ($CDCl_3$): $\delta =$ 0.8 (CH_3, $SiMe_3$), 1.5 (CH_3, $SiMe_3$), 26.2 (b, CH_2, cod), 29.6 (b, CH_2, cod), 31.9 (CH_3), 34.4 (b, CH_2, cod), 37.5 (b, CH_2, cod), 67.9 (b, CH=, cod), 71.6 (b, CH=, cod), 78.2 (CHO), 101.2 (d, CH=, cod, $J_{C,P} = 21$ Hz), 106.0 (d, CH=, cod, $J_{C,P} =$ 11.6 Hz), 117.7 (b, CH=, BAr_F), 120–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 137–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{65}H_{56}BF_{24}IrNO_3PSi_2$: C 47.45, H 3.43, N 0.85; found: C 47.38, H 3.38, N 0.81.

[Ir(cod)(L1d)]BAr_F: Yield: 118 mg (96%). ^{31}P NMR ($CDCl_3$): $\delta = 103.0$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (s, 9H, CH_3, *t*-Bu), 1.50 (s, 9H, CH_3, *t*-Bu), 1.77 (b, 6H, CH_3-Ar), 1.78 (b, 3H, CH_3), 2.15 (b, 2H, CH_2, cod), 2.26 (b, 6H, CH_3-Ar), 2.28 (b, 4H, CH_2, cod), 2.37 (b, 2H, CH_2, cod), 3.82 (b, 1H, CH=, cod), 4.43 (b, 1H, CH=, cod), 4.60 (b, 1H, CH=, cod), 5.23 (b, 1H, CH=, cod), 6.09 (m, 1H, CHO), 7.2–8.6 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 16.6$ (CH_3-Ar), 16.7 (CH_3-Ar), 17.4 (CH_3-Ar), 17.5 (CH_3-Ar), 20.4 (CH_3), 25.0 (b, CH_2, cod), 28.6 (b, CH_2, cod), 31.2 (CH_3, *t*-Bu), 32.4 (CH_3, *t*-Bu), 33.6 (b, CH_2, cod), 34.8 (C, *t*-Bu), 34.9 (C, *t*-Bu), 36.7 (b, CH_2, cod), 65.8 (b, CH=, cod), 70.7 (b, CH=, cod), 77.2 (CHO), 99.6 (d, CH=, cod, $J = 24.4$ Hz), 104.0 (d, CH=, cod, $J = 12.3$ Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{71}H_{64}BF_{24}IrNO_3P$: C 51.09, H 3.86, N 0.84; found: C 51.04, H 3.84, N 0.81.

[Ir(cod)(L1e)]BAr_F: Yield: 120 mg (97%). ^{31}P NMR ($CDCl_3$): $\delta = 102.3$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (s, 9H, CH_3, *t*-Bu), 1.50 (s, 9H, CH_3, *t*-Bu), 1.72 (b, 6H, CH_3-Ar), 1.79 (b, 3H, CH_3), 2.13 (b, 2H, CH_2, cod), 2.24 (s, 3H, CH_3-Ar), 2.25 (s, 3H CH_3-Ar), 2.27 (b, 4H, CH_2, cod), 2.43 (b, 2H, CH_2, cod), 3.49 (b, 1H, CH=, cod), 4.12 (b, 1H, CH=, cod), 4.77 (b, 1H, CH=, cod), 5.33 (b, 1H, CH=, cod), 5.46 (m, 1H, CHO), 7.2–8.6 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 16.5$ (CH_3-Ar), 16.6 (CH_3-Ar), 20.3 (CH_3-Ar), 20.4 (CH_3-Ar), 24.8 (b, CH_2, cod), 25.2 (CH_3), 28.5 (b, CH_2, cod), 31.9 (CH_3, *t*-Bu), 32.3 (CH_3, *t*-Bu), 32.9 (b, CH_2, cod), 34.9 (C, *t*-Bu), 35.0 (C, *t*-Bu), 36.8 (b, CH_2, cod), 63.7 (b, CH=, cod), 67.6 (b, CH=, cod), 80.8 (CHO), 102.5 (b, CH=, cod), 102.7 (b, CH=, cod), 117.7 (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, $^1J = 49$ Hz); anal. calcd. (%) for $C_{71}H_{64}BF_{24}IrNO_3P$: C 51.09, H 3.86, N 0.84; found: C 51.02, H 3.83, N 0.82.

[Ir(cod)(L1f)]BAr_F: Yield: 119 mg (92%). ^{31}P NMR (C_6D_6): $\delta = 112.1$ (s); ^{1}H NMR (C_6D_6): $\delta = 0.17$ (s, 9H, CH_3, $SiMe_3$), 0.48 (s, 9H, CH_3, $SiMe_3$), 1.09 (b, 3H, CH_3), 1.29 (b, 2H, CH_2, cod), 1.67 (b, 2H, CH_2, cod), 1.82 (b, 2H, CH_2, cod), 1.93 (b, 2H, CH_2, cod), 3.64 (b, 1H, CH=, cod), 4.06 (b, 1H, CH=, cod), 4.12 (b, 1H, CH=, cod), 4.80 (b, 1H, CH=, cod), 5.76 (m, 1H, CHO), 6.6–8.5 (m, 26H, CH=); ^{13}C NMR (C_6D_6): $\delta = 0.0$ (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 17.5 (d, CH_3, $J_{C,P} = 10.9$ Hz), 25.0 (b, CH_2, cod), 28.4 (b, CH_2, cod), 34.1 (b, CH_2, cod), 37.1 (b, CH_2, cod), 66.3 (b, CH=, cod), 71.2 (b, CH=, cod), 76.8 (d, CH, $J_{C,P} = 7$ Hz), 100.5 (d, CH=, cod, $J_{C,P} = 22.5$ Hz), 105.6 (d, CH=, cod, $J_{C,P} = 11.6$ Hz), 117.7 (b, CH=, BAr_F), 121–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 137–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{73}H_{60}BF_{24}IrNO_3PSi_2$: C 50.23, H 3.46, N 0.80; found: C 50.20, H 3.44, N 0.76.

[Ir(cod)(L1g)]BAr_F: Yield: 123 mg (95%). ^{31}P NMR (C_6D_6): $\delta = 107.6$ (s); ^{1}H NMR (C_6D_6): $\delta = 0.05$ (s, 9H, CH_3, $SiMe_3$), 0.48 (s, 9H, CH_3, $SiMe_3$), 1.40 (b, 2H, CH_2, cod), 1.71 (b, 3H, CH_2, cod), 1.85 (b, 3H, CH_2, cod), 1.9 (d, 3H, CH_3, $3J_{H,H} = 6.8$ Hz), 2.99 (b, 1H, CH=, cod), 3.70 (b, 1H, CH=, cod), 4.61 (b, 1H, CH=, cod), 4.63 (m, 1H, CHO), 4.80 (b, 1H, CH=, cod), 6.1–8.4 (m, 26H, CH=); ^{13}C NMR (C_6D_6): $\delta = 0.9$ (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 24.9 (b, CH_2, cod), 25.9 (d, CH_3, $J_{C,P} = 3.9$ Hz), 28.3 (b, CH_2, cod), 33.0 (b, CH_2, cod), 37.1 (b, CH_2, cod), 65.1 (b, CH=, cod), 68.6 (b, CH=, cod), 81.0 (s, CHO), 104.6 (s, CH=, cod), 104.8 (d, CH=, cod, $J_{C,P} = 7$ Hz), 117.7 (b, CH=, BAr_F), 121–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 137–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{73}H_{60}BF_{24}IrNO_3PSi_2$: C 50.23, H 3.46, N 0.80; found: C 50.18, H 3.42, N 0.76.

[Ir(cod)(L2a)]BAr_F: Yield: 124 mg (96%). ^{31}P NMR ($CDCl_3$): $\delta = 110.7$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H, CH_3, *t*-Bu), 1.35 (s, 9H, CH_3, *t*-Bu), 1.36 (s, 9H, CH_3, *t*-Bu), 1.58 (s, 9H, CH_3, *t*-Bu), 1.73 (b, 3H, CH_3), 1.98–2.53 (b, 8H, CH_2, cod), 3.16 (b, 3H, CH_3-Py), 3.95 (b, 1H, CH=, cod), 4.59 (b, 1H, CH=, cod), 5.05 (b, 1H, CH=, cod), 5.25 (b, 1H, CH=, cod), 6.24 (m, 1H, CHO), 7.0–8.0 (m, 19H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 17.9$ (b, CH_3), 23.9 (b, CH_2, cod), 27.8 (b, CH_2, cod), 29.1 (CH_3-Py), 30.4 (CH_3, *t*-Bu), 30.9 (C, *t*-Bu), 31.2 (C, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.4 (CH_3, *t*-Bu), 34.7 (b, CH_2, cod), 35.2 (C, *t*-Bu), 35.4 (C, *t*-Bu), 37.5 (b, CH_2, cod), 70.4 (b, CH=, cod), 72.9 (b, CH=, cod), 75.4 (CHO), 88.6 (d, CH=, cod, $J_{C,P} = 26$ Hz), 104.1 (b, CH=, cod), 117.7 (b, CH=, BAr_F), 120–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 139–158 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{76}H_{74}BF_{24}IrNO_3P$: C 52.48, H 4.29, N 0.80 found: C 52.43, H 4.26, N 0.77.

[Ir(cod)(L2d)]BAr_F: Yield: 118 mg (95%). ^{31}P NMR ($CDCl_3$): $\delta = 103.1$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.26$ (s, 9H, CH_3, *t*-Bu), 1.44 (s, 9H, CH_3, *t*-Bu), 1.65 (s, 3H, CH_3-Ar), 1.68 (s, 3H, CH_3-Ar), 1.74 (b, 3H, CH_3), 2.15 (b, 2H, CH_2, cod), 2.19 (s, 3H, CH_3-Ar), 2.24 (s, 3H, CH_3-Ar), 2.28 (b, 4H, CH_2, cod), 2.37 (b, 2H, CH_2, cod), 3.04 (s, 3H, CH_3-Py), 3.80 (b, 1H, CH=, cod), 4.42 (b, 1H, CH=, cod), 4.57 (b, 1H, CH=, cod), 5.21 (b, 1H, CH=, cod), 6.06 (m, 1H, CHO), 7.2–8.6 (m, 17H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 16.5$ (CH_3-Ar), 16.8 (CH_3-Ar), 17.1 (CH_3-Ar), 17.4 (CH_3-Ar), 20.2 (CH_3), 25.1 (b, CH_2, cod), 28.5 (b, CH_2, cod), 29.3 (CH_3-Py), 31.2 (CH_3, *t*-Bu), 31.9 (CH_3, *t*-Bu), 33.6 (b, CH_2, cod), 34.8 (C, *t*-Bu), 34.9 (C, *t*-Bu), 36.2 (b, CH_2, cod), 65.9 (b, CH=, cod), 70.3 (b, CH=, cod), 77.7 (CHO), 99.8 (d, CH=, cod, $J = 24.4$ Hz), 103.6 (d, CH=, cod, $J = 12.0$ Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{72}H_{66}BF_{24}IrNO_3P$: C 51.37, H 3.95, N 0.83; found. C 51.33, H 3.92, N 0.79.

[Ir(cod)(L2e)]BAr$_F$: Yield: 114 mg (93%). ^{31}P NMR ($CDCl_3$): $\delta = 102.9$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.19$ (s, 9H, CH_3, *t*-Bu), 1.44 (s, 9H, CH_3, *t*-Bu), 1.71 (b, 6H, CH_3-Ar), 1.76 (b, 3H, CH_3), 2.13 (b, 2H, CH_2, cod), 2.23 (s, 3H, CH_3-Ar), 2.29 (b, 4H, CH_2, cod), 2.52 (b, 2H, CH_2, cod), 2.85 (s, 3H, CH_3-Ar), 3.07 (s, 3H, CH_3-Py), 3.56 (b, 1H, CH=, cod), 4.09 (b, 1H, CH=, cod), 4.73 (b, 1H, CH=, cod), 5.31 (b, 1H, CH=, cod), 5.39 (m, 1H, CHO), 7.2–8.6 (m, 17H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 16.8$ (CH_3-Ar), 16.9 (CH_3-Ar), 20.5 (CH_3-Ar), 20.8 (CH_3-Ar), 24.8 (b, CH_2, cod), 25.1 (CH_3), 28.8 (b, CH_2, cod), 29.8 (CH_3-Py), 31.7 (CH_3, *t*-Bu), 32.2 (CH_3, *t*-Bu), 32.8 (b, CH_2, cod), 34.6 (C, *t*-Bu), 34.8 (C, *t*-Bu), 36.5 (b, CH_2, cod), 64.9 (b, CH=, cod), 69.3 (b, CH=, cod), 80.1 (CHO), 102.3 (b, CH=, cod), 102.9 (b, CH=, cod), 117.7 (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, $^1J = 49$ Hz); anal. calcd. (%) for $C_{72}H_{66}BF_{24}IrNO_3P$: C 51.37, H 3.95, N 0.83; found. C 51.35, H 3.93, N 0.80.

[Ir(cod)(L3a)]BAr$_F$: Yield: 128 mg (96%). ^{31}P NMR ($CDCl_3$): $\delta = 108.4$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H, CH_3, *t*-Bu), 1.37 (s, 9H, CH_3, *t*-Bu), 1.38 (s, 9H, CH_3, *t*-Bu), 1.58 (s, 9H, CH_3, *t*-Bu), 1.60 (b, 3H, CH_3), 1.79 (b, 2H, CH_2, cod), 2.29 (b, 4H, CH_2, cod), 2.53 (b, 2H, CH_2, cod), 4.31 (b, 1H, CH=, cod), 4.75 (b, 1H, CH=, cod), 5.16 (b, 1H, CH=, cod), 5.30 (b, 1H, CH=, cod), 6.11 (m, 1H, CHO), 7.0–7.7 (m, 19H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 17.8$ (b, CH_3), 23.8 (b, CH_2, cod), 28.0 (b, CH_2, cod), 30.7 (C, *t*-Bu), 31.2 (C, *t*-Bu), 31.5 (CH_3, *t*-Bu), 31.7 (CH_3, *t*-Bu), 34.9 (C, *t*-Bu), 35.0 (C, *t*-Bu), 35.4 (b, CH_2, cod), 37.6 (b, CH_2, cod), 72.3 (b, CH=, cod), 74.9 (b, CH=, cod), 75.0 (CHO), 89.0 (d, CH=, cod, $J_{C,P} = 26.7$ Hz), 102.8 (d, CH=, cod, $J_{C,P} = 8.4$ Hz), 117.7 (b, CH=, BAr_F), 120–132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 139–150 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{75}H_{71}BBrF_{24}IrNO_3P$: C 49.93, H 3.97, N 0.78; found: C 49.88, H 3.94, N 0.75.

[Ir(cod)(L4a)]BAr$_F$: Yield: 125 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta = 98.2$ (s); ^{1}H NMR ($CDCl_3$), $\delta = 1.33$ (s, 9H, CH_3, *t*-Bu), 1.34 (s, 9H, CH_3, *t*-Bu), 1.38 (s, 9H, CH_3, *t*-Bu), 1.54 (b, 3H, CH_3), 1.59 (s, 9H, CH_3, *t*-Bu), 1.89 (b, 2H, CH_2, cod), 2.19 (b, 4H, CH_2, cod), 2.63 (b, 2H, CH_2, cod), 4.62 (b, 1H, CH=, cod), 4.68 (b, 1H, CH=, cod), 4.79 (b, 1H, CH=, cod), 5.29 (b, 1H, CH=, cod), 6.07 (m, 1H, CHO), 7.1–8.2 (m, 24H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 17.2$ (d, CH_3, $J_{C,P} = 10.8$), 23.2 (b, CH_2, cod), 28.4 (b, CH_2, cod), 30.2 (CH_3, *t*-Bu), 30.5 (CH_3, *t*-Bu), 30.9 (C, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.4 (CH_3, *t*-Bu), 34.7 (b, CH_2, cod), 35.0 (C, *t*-Bu), 35.3 (C, *t*-Bu), 35.6 (C, *t*-Bu), 35.7 (b, CH_2, cod), 70.6 (b, CH=, cod), 73.1 (b, CH=, cod), 74.6 (CHO), 83.2 (d, CH=, cod, $J_{C,P} = 29.4$ Hz), 97.6 (d, CH=, cod, $J_{C,P} = 7$ Hz), 117.7 (b, CH=, BAr_F), 120–133 (aromatic carbons), 135.0 (b, CH=, BAr_F), 137–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{81}H_{76}BF_{24}IrNO_3P$: C 54.00, H 4.25, N 0.78; found: C 53.96, H 4.22, N 0.76.

[Ir(cod)(L5a)]BAr$_F$: Yield: 123 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta = 108.8$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.06$ (s, 9H, CH_3, *t*-Bu), 1.18 (s, 9H, CH_3, *t*-Bu), 1.33 (s, 9H, CH_3, *t*-Bu), 1.34 (s, 9H, CH_3, *t*-Bu), 1.40 (s, 9H, CH_3, *t*-Bu), 2.02 (b, 2H, CH_2, cod), 2.21 (b, 4H, CH_2, cod), 2.36 (b, 2H, CH_2, cod), 4.22 (b, 1H, CH=, cod), 4.36 (b, 1H, CH=, cod), 5.16 (b, 1H, CH=, cod), 5.17 (b, 1H, CH=, cod), 5.20 (m, 1H, CHO), 7.1–8.7 (m, 20H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 24.9$ (b, CH_2, cod), 26.9 (CH_3, *t*-Bu), 29.8 (b, CH_2, cod), 30.6 (C, *t*-Bu), 30.9 (CH_3, *t*-Bu), 31.0 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.5 (C, *t*-Bu), 34.7 (b, CH_2, cod), 34.8 (C, *t*-Bu), 35.0 (C, *t*-Bu), 35.4 (C, *t*-Bu), 36.4 (b, CH_2, cod), 63.5 (b, CH=, cod), 65.9 (b, CH=, cod), 89.7 (CHO), 101.1 (d, CH=, cod, $J_{C,P} = 17.6$ Hz), 104.3 (d, CH=, cod, $J_{C,P} = 16.8$ Hz), 117.7 (b, CH=, BAr_F), 120–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138–155 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{78}H_{78}BF_{24}IrNO_3P$: C 53.01, H 4.45, N 0.79; found: C 52.99, H 4.43, N 0.77.

[Ir(cod)(L5d)]BAr$_F$: Yield: 122 mg (96%). ^{31}P NMR ($CDCl_3$): $\delta = 106.4$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.04$ (s, 9H, CH_3, *t*-Bu), 1.21 (s, 9H, CH_3, *t*-Bu), 1.47 (s, 9H, CH_3, *t*-Bu), 1.73 (s, 3H, CH_3-Ar), 1.79 (s, 3H, CH_3-Ar), 2.14 (b, 2H, CH_2, cod), 2.22 (s, 3H, CH_3-Ar), 2.27 (s, 3H, CH_3-Ar), 2.29 (b, 4H, CH_2, cod), 2.33 (b, 2H, CH_2, cod), 3.86 (b, 1H, CH=, cod), 4.41 (b, 1H, CH=, cod), 4.73 (b, 1H, CH=, cod), 5.19 (b, 1H, CH=, cod), 6.01 (m, 1H, CHO), 7.2–8.6 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 16.2$ (CH_3-Ar), 16.5 (CH_3-Ar), 17.2 (CH_3-Ar), 17.5 (CH_3-Ar), 25.0 (b, CH_2, cod), 27.8 (b, CH_2, cod), 30.5 (C, *t*-Bu), 31.1 (CH_3, *t*-Bu), 31.5 (CH_3, *t*-Bu), 32.2 (CH_3, *t*-Bu), 33.4 (b, CH_2, cod), 34.3 (C, *t*-Bu), 34.6 (C, *t*-Bu), 36.1 (b, CH_2, cod), 66.9 (b, CH=, cod), 70.9 (b, CH=, cod), 79.5 (CHO), 99.1 (d, CH=, cod, $J = 24.8$ Hz), 103.4 (d, CH=, cod, $J = 11.6$ Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J = 49$ Hz); anal. calcd. (%) for $C_{74}H_{70}BF_{24}IrNO_3P$: C 51.94, H 4.12, N 0.82; found. C 51.91, H 4.10, N 0.81.

[Ir(cod)(L5e)]BAr$_F$: Yield: 119 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta = 105.2$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.02$ (s, 9H, CH_3, *t*-Bu), 1.25 (s, 9H, CH_3, *t*-Bu), 1.44 (s, 9H, CH_3, *t*-Bu), 1.71 (s, 3H, CH_3-Ar), 1.76 (s, 3H, CH_3-Ar), 2.11 (b, 2H, CH_2, cod), 2.27 (s, 6H, CH_3-Ar), 2.29 (b, 4H, CH_2, cod), 2.37 (b, 2H, CH_2, cod), 3.63 (b, 1H, CH=, cod), 4.26 (b, 1H, CH=, cod), 4.83 (b, 1H, CH=, cod), 5.29 (b, 1H, CH=, cod), 5.51 (m, 1H, CHO), 7.2–8.6 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 16.5$ (CH_3-Ar), 16.6 (CH_3-Ar), 20.1 (CH_3-Ar), 20.4 (CH_3-Ar), 24.9 (b, CH_2, cod), 28.7 (b, CH_2, cod), 30.3 (C, *t*-Bu), 31.1 (CH_3, *t*-Bu), 32.3 (CH_3, *t*-Bu), 32.4 (CH_3, *t*-Bu), 32.6 (b, CH_2, cod), 33.9 (C, *t*-Bu), 34.2 (C, *t*-Bu), 35.9 (b, CH_2, cod), 64.2 (b, CH=, cod), 69.8 (b, CH=, cod), 81.2 (CHO), 102.2 (b, CH=, cod), 104.2 (b, CH=, cod), 117.7 (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, $^1J = 49$ Hz); anal. calcd. (%) for $C_{74}H_{70}BF_{24}IrNO_3P$: C 51.94, H 4.12, N 0.82; found. C 51.90, H 4.11, N 0.80.

[Ir(cod)(L6a)]BAr$_F$: Yield: 123 mg (93%). ^{31}P NMR ($CDCl_3$): $\delta = 103.6$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 1.13$ (s, 9H, CH_3, *t*-Bu), 1.15 (s, 9H, CH_3, *t*-Bu), 1.20 (s, 9H, CH_3, *t*-Bu), 1.23 (s, 9H, CH_3, *t*-Bu), 1.43 (b, 2H, CH_2, cod), 1.62 (b, 2H, CH_2, cod), 1.96 (b, 2H, CH_2, cod), 2.39 (b, 2H, CH_2, cod), 3.70 (b, 1H, CH=, cod), 4.24 (b, 1H, CH=, cod), 4.74 (b, 1H, CH=, cod), 5.30 (b, 1H, CH=, cod), 6.91 (m, 1H, CHO), 7.0–8.5 (m, 25H, CH=); ^{13}C NMR ($CDCl_3$): $\delta = 25.1$ (b, CH_2, cod), 28.6 (b, CH_2, cod), 30.9 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.5 (CH_3, *t*-Bu), 32.1 (CH_3, *t*-Bu), 33.2 (b, CH_2, cod), 34.7 (C, *t*-Bu), 34.8 (C, *t*-Bu), 35.2 (C, *t*-Bu), 35.6 (C, *t*-Bu), 36.7 (b, CH_2, cod), 65.2 (b, CH=, cod), 70.6 (b, CH=, cod), 81.9 (d, CH, $J_{C,P} = 10.1$ Hz), 101.7 (d, CH=, cod, $J_{C,P} = 21$ Hz), 105.0 (d, CH=, cod, $J_{C,P} = 12.4$ Hz), 117.7 (b, CH=, BAr_F), 120–133 (aromatic carbons), 135.0 (b, CH=,

BAr_F), 139–160 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{80}H_{74}BF_{24}IrNO_3P$: C 53.76, H 4.17, N 0.78; found: C 53.73, H 4.15, N 0.76.

[Ir(cod)(L6c)]BAr_F: Yield: 116 mg (92%). ^{31}P NMR ($CDCl_3$): δ = 103.2 (s); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 9H, CH_3, $SiMe_3$), 0.24 (s, 9H, CH_3, $SiMe_3$), 1.75 (b, 2H, CH_2, cod), 1.91 (b, 2H, CH_2, cod), 2.19 (b, 2H, CH_2, cod), 2.53 (b, 2H, CH_2, cod), 4.18 (b, 1H, CH=, cod), 4.44 (b, 1H, CH=, cod), 4.80 (b, 1H, CH=, cod), 5.54 (b, 1H, CH=, cod), 7.03 (m, 1H, CHO), 7.1–8.7 (m, 27H, CH=); ^{13}C NMR ($CDCl_3$): δ = 0.2 (CH_3, $SiMe_3$), 1.3 (CH_3, $SiMe_3$), 25.5 (b, CH_2, cod), 28.9 (b, CH_2, cod), 34.4 (b, CH_2, cod), 37.4 (d, CH_2, cod, $J_{C,P}$ = 6.2 Hz), 67.3 (b, CH=, cod), 72.1 (b, CH=, cod), 82.7 (d, CH, $J_{C,P}$ = 9.3 Hz), 101.4 (d, CH=, cod, $J_{C,P}$ = 21.7 Hz), 106.0 (d, CH=, cod, $J_{C,P}$ = 11.7 Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–160 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{70}H_{58}BF_{24}IrNO_3PSi_2$: C 49.24, H 3.42, N 0.82 found: C 49.21, H 3.40, N 0.79.

[Ir(cod)(L6d)]BAr_F: Yield: 116 mg (92%). ^{31}P NMR ($CDCl_3$): δ = 102.3 (s); ^{1}H NMR ($CDCl_3$): δ = 1.28 (s, 9H, CH_3, *t*-Bu), 1.39 (s, 9H, CH_3, *t*-Bu), 1.68 (s, 3H, CH_3-Ar), 1.73 (s, 3H, CH_3-Ar), 2.12 (b, 2H, CH_2, cod), 2.13 (s, 3H, CH_3-Ar), 2.19 (s, 3H, CH_3-Ar), 2.28 (b, 4H, CH_2, cod), 2.34 (b, 2H, CH_2, cod), 3.92 (b, 1H, CH=, cod), 4.41 (b, 1H, CH=, cod), 4.54 (b, 1H, CH=, cod), 5.33 (b, 1H, CH=, cod), 6.02 (m, 1H, CHO), 7.2–8.6 (m, 23H, CH=); ^{13}C NMR ($CDCl_3$); δ = 16.2 (CH_3-Ar), 16.4 (CH_3-Ar), 17.2 (CH_3-Ar), 17.5 (CH_3-Ar), 20.9 (CH_3), 25.1 (b, CH_2, cod), 27.9 (b, CH_2, cod), 31.9 (CH_3, *t*-Bu), 32.2 (CH_3, *t*-Bu), 34.2 (b, CH_2, cod), 34.9 (C, *t*-Bu), 35.1 (C, *t*-Bu), 36.7 (b, CH_2, cod), 68.2 (b, CH=, cod), 70.2 (b, CH=, cod), 77.2 (CHO), 101.2 (d, CH=, cod, J = 23.8 Hz), 104.1 (d, CH=, cod, J = 16.0 Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{76}H_{66}BF_{24}IrNO_3P$: C 52.72, H 3.84, N 0.81; found. C 52.71, H 3.83, N 0.80.

[Ir(cod)(L6e)]BAr_F: Yield: 119 mg (93%). ^{31}P NMR ($CDCl_3$): δ = 102.1 (s); ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 9H, CH_3, *t*-Bu), 1.44 (s, 9H, CH_3, *t*-Bu), 1.63 (s, 6H, CH_3-Ar), 1.69 (s, 3H, CH_3-Ar), 1.72 (s, 3H, CH_3-Ar), 1.77 (s, 3H, CH_3), 2.11 (b, 2H, CH_2, cod), 2.17 (s, 3H, CH_3-Ar), 2.24 (b, 4H, CH_2, cod), 2.31 (b, 2H, CH_2, cod), 3.98 (b, 1H, CH=, cod), 4.37 (b, 1H, CH=, cod), 4.47 (b, 1H, CH=, cod), 5.26 (b, 1H, CH=, cod), 6.06 (m, 1H, CHO), 7.2–8.6 (m, 23H, CH=); ^{13}C NMR ($CDCl_3$): δ = 16.1 (CH_3-Ar), 16.2 (CH_3-Ar), 17.0 (CH_3-Ar), 17.3 (CH_3-Ar), 20.7 (CH_3), 25.1 (b, CH_2, cod), 27.9 (b, CH_2, cod), 31.9 (CH_3, *t*-Bu), 32.2 (CH_3, *t*-Bu), 34.2 (b, CH_2, cod), 34.8 (C, *t*-Bu), 35.2 (C, *t*-Bu), 36.3 (b, CH_2, cod), 71.1 (b, CH=, cod), 72.6 (b, CH=, cod), 79.2 (CHO), 100.2 (d, CH=, cod, J = 24.8 Hz), 102.6 (d, CH=, cod, J = 12.0 Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{76}H_{66}BF_{24}IrNO_3P$: C 52.72, H 3.84, N 0.81; found. C 52.68, H 3.81, N 0.78.

[Ir(cod)(L7a)]BAr_F: Yield: 128 mg (97%). ^{31}P NMR ($CDCl_3$); δ = 105.1 (s); ^{1}H NMR ($CDCl_3$): δ = 1.01 (s, 9H, CH_3, *t*-Bu), 1.13 (s, 9H, CH_3, *t*-Bu), 1.28 (s, 9H, CH_3, *t*-Bu), 1.38 (s, 9H, CH_3, *t*-Bu), 1.53 (s, 9H, CH_3, *t*-Bu), 1.80 (b, 2H, CH_2, cod), 2.04 (b, 2H, CH_2, cod), 2.25 (b, 2H, CH_2, cod), 2.43 (b, 2H, CH_2, cod), 3.19 (s, 3H, CH_3, MePy), 3.90 (b, 1H, CH=, cod), 4.38 (b, 1H, CH=, cod), 4.99 (b, 1H, CH=, cod), 5.38 (b, 1H, CH=, cod), 5.73 (d, 1H, CHO, $J_{C,P}$ = 6.4 Hz), 7.0–7.8 (m, 19H, CH=); ^{13}C NMR ($CDCl_3$): δ = 23.9 (b, CH_2, cod), 27.2 (b, CH_2, cod), 28.2 (C, *t*-Bu), 30.0 (CH_3, *t*-Bu), 30.1 (CH_3, MePy), 30.9 (CH_3, *t*-Bu), 31.0 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 34.6 (C, *t*-Bu), 34.8 (b, CH_2, cod), 34.9 (C, *t*-Bu), 35.0 (C, *t*-Bu), 35.4 (C, *t*-Bu), 35.8 (b, CH_2, cod), 37.3 (b, CH_2, cod), 67.4 (b, CH=, cod), 73.8 (b, CH=, cod), 87.6 (s, CHO), 87.9 (d, CH=, cod, $J_{C,P}$ = 26.4 Hz), 103.8 (d, CH=, cod, $J_{C,P}$ = 9.3 Hz), 117.7 (b, CH=, BAr_F), 120–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138–157 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{79}H_{80}BF_{24}IrNO_3P$: C 53.26, H 4.53, N 0.79; found: C 53.23, H 4.51, N 0.76.

[Ir(cod)(L8a)]BAr_F: Yield: 126 mg (96%). ^{31}P NMR ($CDCl_3$): δ = 111.1 (s); ^{1}H NMR ($CDCl_3$): δ = 1.01 (s, 9H, CH_3, *t*-Bu), 1.22 (s, 9H, CH_3, *t*-Bu), 1.29 (s, 9H, CH_3, *t*-Bu), 1.53 (s, 9H, CH_3, *t*-Bu), 1.70 (b, 2H, CH_2, cod), 1.77 (d, 3H, CH_3, $^3J_{H,H}$ = 6.8 Hz), 2.22 (b, 4H, CH_2, cod), 2.58 (b, 2H, CH_2, cod), 4.18 (b, 1H, CH=, cod), 4.57 (b, 1H, CH=, cod), 5.04 (b, 1H, CH=, cod), 5.16 (b, 1H, CH=, cod), 6.29 (m, 1H, CHO), 6.9–9.0 (m, 22H, CH=); ^{13}C NMR ($CDCl_3$): δ = 18.3 (CH_3), 24.0 (b, CH_2, cod), 27.8 (b, CH_2, cod), 30.5 (CH_3, *t*-Bu), 31.0 (CH_3, *t*-Bu), 31.1 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.3 (C, *t*-Bu), 34.7 (b, CH_2, cod), 35.0 (C, *t*-Bu), 35.1 (C, *t*-Bu), 35.3 (C, *t*-Bu), 37.6 (b, CH_2, cod), 70.5 (b, CH=, cod), 72.0 (b, CH=, cod), 77.2 (CHO), 91.0 (d, CH=, cod, $J_{C,P}$ = 24 Hz), 104.5 (d, CH=, cod, $J_{C,P}$ = 9.3 Hz), 117.7 (b, CH=, BAr_F), 119–132 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138–161 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{79}H_{74}BF_{24}IrNO_3P$: C 53.44, H 4.20, N 0.79; found: C 53.41, H 4.17, N 0.76.

[Ir(cod)(L9a)]BAr_F: Yield: 116 mg (92%). ^{31}P NMR ($CDCl_3$): δ = 106.0 (s); ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 9H, CH_3, *t*-Bu), 1.34 (s, 18H, CH_3, *t*-Bu), 1.51 (s, 9H, CH_3, *t*-Bu), 1.87 (b, 2H, CH_2, cod), 2.13 (b, 3H, CH_3), 2.21 (b, 4H, CH_2, cod), 2.36 (b, 2H, CH_2, cod), 3.94 (b, 1H, CH=, cod), 4.29 (b, 1H, CH=, cod), 4.71 (b, 1H, CH=, cod), 5.24 (b, 1H, CH=, cod), 6.12 (m, 1H, CHO), 7.1–8.6 (m, 20H, CH=); ^{13}C NMR ($CDCl_3$): δ = 25.3 (b, CH_2, cod), 29.0 (b, CH_2, cod), 30.7 (C, *t*-Bu), 30.9 (CH_3), 31.1 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.9 (CH_3, *t*-Bu), 33.0 (b, CH_2, cod), 34.8 (C, *t*-Bu), 35.4 (C, *t*-Bu), 35.5 (C, *t*-Bu), 36.3 (b, CH_2, cod), 65.8 (b, CH=, cod), 69.9 (b, CH=, cod), 77.2 (CHO), 100.7 (d, CH=, cod, $J_{C,P}$ = 20.9 Hz), 104.5 (d, CH=, cod, $J_{C,P}$ = 12.5 Hz), 117.7 (b, CH=, BAr_F), 119–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 139–159 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J = 49 Hz); anal. calcd. (%) for $C_{75}H_{72}BF_{24}IrNO_3P$: C 52.21, H 4.21, N 0.81; found: C 52.18, H 4.19, N 0.78.

[Ir(cod)(L9d)]BAr_F: Yield: 118 mg (96%). ^{31}P NMR ($CDCl_3$): δ = 102.9 (s); ^{1}H NMR ($CDCl_3$): δ = 1.19 (s, 9H, CH_3, *t*-Bu), 1.42 (s, 9H, CH_3, *t*-Bu), 1.69 (b, 6H, CH_3, Ar-Me), 1.73 (b, 3H, CH_3), 2.02 (b, 2H, CH_2, cod), 2.18 (b, 6H, CH_3, Ar-Me), 2.29 (b, 4H, CH_2, cod), 2.52 (b, 2H, CH_2, cod), 3.73 (b, 1H, CH=, cod), 4.27 (b, 1H, CH=, cod), 4.52 (b, 1H, CH=, cod), 5.15 (b, 1H, CH=, cod), 6.00 (m, 1H, CHO), 7.1–8.5 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$); δ = 16.6 (CH_3, Ar-Me), 16.7 (CH_3, Ar-Me), 17.3 (CH_3, Ar-Me), 17.4 (CH_3, Ar-Me), 20.3 (CH_3), 25.0 (b, CH_2, cod), 28.5 (b, CH_2, cod), 31.2 (CH_3, *t*-Bu), 32.3 (CH_3, *t*-Bu), 33.5 (b, CH_2, cod), 34.8 (C, *t*-Bu), 34.9 (C, *t*-Bu), 36.7 (b, CH_2, cod), 65.8 (b,

CH=, cod), 70.7 (b, CH=, cod), 77.2 (s, CHO), 99.6 (d, CH=, cod, $J_{C,P}=20.9$ Hz), 104.0 (d, CH=, cod, $J_{C,P}=11.6$ Hz), 117.7 (b, CH=, BAr_F), 120–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–159 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd. (%) for $C_{71}H_{64}BF_{24}IrNO_3P$: C 51.09, H 3.86, N 0.84; found: C 51.06, H 3.84, N 0.81.

[Ir(cod)(L9e)]BAr_F: Yield: 113 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta=102.2$ (s); ^{1}H NMR ($CDCl_3$): $\delta=1.12$ (s, 9H, CH_3, *t*-Bu), 1.43 (s, 9H, CH_3, *t*-Bu), 1.65 (b, 6H, CH_3, Ar-Me), 1.72 (b, 3H, CH_3), 2.05 (b, 2H, CH_2, cod), 2.17 (b, 6H, CH_3, Ar-Me), 2.19 (b, 4H, CH_2, cod), 2.36 (b, 2H, CH_2, cod), 3.42 (b, 1H, CH=, cod), 4.05 (b, 1H, CH=, cod), 4.70 (b, 1H, CH=, cod), 5.33 (b, 1H, CH=, cod), 5.41 (m, 1H, CHO), 7.0–8.5 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$): $\delta=16.7$ (CH_3, Ar-Me), 16.8 (CH_3, Ar-Me), 20.4 (CH_3, Ar-Me), 20.5 (CH_3, Ar-Me), 25.1 (b, CH_2, cod), 25.4 (CH_3), 28.7 (b, CH_2, cod), 32.2 (CH_3, *t*-Bu), 32.5 (CH_3, *t*-Bu), 33.1 (b, CH_2, cod), 35.2 (C, *t*-Bu), 35.3 (C, *t*-Bu), 37.1 (b, CH_2, cod), 64.0 (b, CH=, cod), 67.8 (b, CH=, cod), 81.1 (CHO), 102.7 (b, CH=, cod), 102.9 (b, CH=, cod), 117.7 (b, CH=, BAr_F), 120–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135–159 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd. (%) for $C_{71}H_{64}BF_{24}IrNO_3P$: C 51.09, H 3.86, N 0.84; found: C 51.02, H 3.81, N 0.80.

[Ir(cod)(L10a)]BAr_F: Yield: 124 mg (96%). ^{31}P NMR ($CDCl_3$): $\delta=109.9$ (s); ^{1}H NMR ($CDCl_3$): $\delta=1.32$ (s, 9H, CH_3, *t*-Bu), 1.35 (s, 9H, CH_3, *t*-Bu), 1.39 (s, 9H, CH_3, *t*-Bu), 1.57 (s, 9H, CH_3, *t*-Bu), 1.72 (b, 3H, CH_3), 1.97 (b, 3H, CH_2, cod), 2.18 (b, 1H, CH_2, cod), 2.40 (b, 2H, CH_2, cod), 2.53 (b, 2H, CH_2, cod), 3.19 (b, 3H, CH_3-Py), 3.98 (b, 1H, CH=, cod), 4.61 (b, 1H, CH=, cod), 5.03 (b, 1H, CH=, cod), 5.22 (b, 1H, CH=, cod), 6.21 (m, 1H, CHO), 7.0–8.0 (m, 19H, CH=); ^{13}C NMR ($CDCl_3$): $\delta=17.8$ (b, CH_3), 23.8 (b, CH_2, cod), 27.8 (b, CH_2, cod), 29.1 (CH_3-Py), 30.4 (CH_3, *t*-Bu), 30.9 (C, *t*-Bu), 31.2 (C, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.4 (CH_3, *t*-Bu), 34.6 (b, CH_2, cod), 35.2 (C, *t*-Bu), 35.4 (C, *t*-Bu), 37.7 (b, CH_2, cod), 70.3 (b, CH=, cod), 72.8 (b, CH=, cod), 75.4 (CHO), 89.2 (d, CH=, cod, $J_{C,P}=22.4$ Hz), 104.2 (b, CH=, cod), 117.7 (b, CH=, BAr_F), 120–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 139–158 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd. (%) for $C_{76}H_{74}BF_{24}IrNO_3P$: C 52.48, H 4.29, N 0.81; found. C 52.42, H 4.25, N 0.78.

[Ir(cod)(L10e)]BAr_F: Yield: 116 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta=105.2$ (s); ^{1}H NMR ($CDCl_3$): $\delta=1.27$ (s, 9H, CH_3, *t*-Bu), 1.46 (s, 9H, CH_3, *t*-Bu), 1.61 (b, 6H, CH_3, Ar-Me), 1.76 (b, 3H, CH_3), 1.95 (b, 2H, CH_2, cod), 2.07 (b, 2H, CH_2, cod), 2.16 (s, 3H, CH_3, Ar-Me), 2.19 (s, 3H, CH_3, Ar-Me), 2.28 (b, 2H, CH_2, cod), 2.37 (b, 2H, CH_2, cod), 3.04 (s, 3H, CH_3, MePy), 3.77 (b, 1H, CH=, cod), 4.50 (b, 1H, CH=, cod), 4.80 (b, 1H, CH=, cod), 5.10 (b, 1H, CH=, cod), 6.11 (m, 1H, CHO), 7.0–7.7 (m, 17H, CH=); ^{13}C NMR ($CDCl_3$): $\delta=16.5$ (CH_3, Ar-Me), 16.7 (CH_3, Ar-Me), 20.3 (CH_3, Ar-Me), 20.4 (CH_3, Ar-Me), 23.8 (b, CH_2, cod), 27.7 (CH_3, MePy), 29.4 (CH_3), 29.7 (b, CH_2, cod), 30.7 (CH_3, *t*-Bu), 31.9 (CH_3, *t*-Bu), 34.6 (C, *t*-Bu), 34.7 (C, *t*-Bu), 35.5 (b, CH_2, cod), 37.4 (b, CH_2, cod), 71.4 (b, CH=, cod), 72.7 (b, CH=, cod), 75.0 (CHO), 88.2 (d, CH=, cod, $J_{C,P}=27.1$), 103.4 (d, CH=, cod, $J_{C,P}=8.6$ Hz), 117.7 (b, CH=, BAr_F), 120–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135–158 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd. (%) for $C_{72}H_{66}BF_{24}IrNO_3P$: C 51.37, H 3.95, N 0.83; found: C 51.34, H 3.92, N 0.80.

[Ir(cod)(L11a)]BAr_F: Yield: 123 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta=108.4$ (s); ^{1}H NMR ($CDCl_3$): $\delta=1.08$ (s, 9H, CH_3, *t*-Bu), 1.16 (s, 9H, CH_3, *t*-Bu), 1.32 (s, 9H, CH_3, *t*-Bu), 1.37 (s, 9H, CH_3, *t*-Bu), 1.41 (s, 9H, CH_3, *t*-Bu), 2.01 (b, 2H, CH_2, cod), 2.21 (b, 4H, CH_2, cod), 2.36 (b, 2H, CH_2, cod), 4.24 (b, 1H, CH=, cod), 4.34 (b, 1H, CH=, cod), 5.20 (b, 2H, CH=, cod), 5.27 (m, 1H, CHO), 7.1–8.7 (m, 20H, CH=); ^{13}C NMR ($CDCl_3$): $\delta=24.8$ (b, CH_2, cod), 26.8 (CH_3, *t*-Bu), 29.9 (b, CH_2, cod), 30.5 (C, *t*-Bu), 30.7 (CH_3, *t*-Bu), 31.1 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.4 (C, *t*-Bu), 34.6 (b, CH_2, cod), 34.7 (C, *t*-Bu), 35.0 (C, *t*-Bu), 35.4 (C, *t*-Bu), 36.4 (b, CH_2, cod), 63.5 (b, CH=, cod), 66.2 (b, CH=, cod), 89.5 (CHO), 101.0 (d, CH=, cod, $J_{C,P}=16.4$ Hz), 104.1 (d, CH=, cod, $J_{C,P}=18.2$ Hz), 117.7 (b, CH=, BAr_F), 120–131 (aromatic carbons), 135.0 (b, CH=, BAr_F), 138–155 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd. (%) for $C_{78}H_{78}BF_{24}IrNO_3P$: C 53.01, H 4.45, N 0.79; found. C 52.97, H 4.43, N 0.76.

[Ir(cod)(L11e)]BAr_F: Yield: 114 mg (92%). ^{31}P NMR ($CDCl_3$): $\delta=106.5$ (s); ^{1}H NMR ($CDCl_3$): $\delta=1.05$ (s, 9H, CH_3, *t*-Bu), 1.09 (s, 9H, CH_3, *t*-Bu), 1.37 (s, 9H, CH_3, *t*-Bu), 1.55 (s, 3H, CH_3, Ar-Me), 1.74 (s, 3H, CH_3, Ar-Me), 1.95 (b, 2H, CH_2, cod), 2.05 (b, 3H, CH_2, cod), 2.08 (s, 3H, CH_3, Ar-Me), 2.13 (s, 3H, CH_3, Ar-Me), 2.33 (b, 2H, CH_2, cod), 2.58 (b, 1H, CH_2, cod), 4.31 (b, 1H, CH=, cod), 4.32 (b, 1H, CH=, cod), 4.40 (b, 1H, CH=, cod), 5.36 (b, 1H, CH=, cod), 5.38 (m, 1H, CHO), 7.0–8.7 (m, 18H, CH=); ^{13}C NMR ($CDCl_3$); $\delta=16.4$ (CH_3, Ar-Me), 16.5 (CH_3, Ar-Me), 20.2 (CH_3, Ar-Me), 20.4 (CH_3, Ar-Me), 24.7 (b, CH_2, cod), 27.7 (CH_3, *t*-Bu), 28.3 (b, CH_2, cod), 29.7 (C, *t*-Bu), 31.5 (CH_3, *t*-Bu), 31.6 (CH_3, *t*-Bu), 34.4 (b, CH_2, cod), 34.5 (C, *t*-Bu), 35.0 (C, *t*-Bu), 36.9 (b, CH_2, cod), 67.6 (b, CH=, cod), 69.6 (b, CH=, cod), 88.2 (CHO), 97.4 (d, CH=, cod, $J_{C,P}=23.2$ Hz), 102.9 (d, CH=, cod, $J_{C,P}=11.7$ Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135–157 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd- (%) for $C_{74}H_{70}BF_{24}IrNO_3P$: C 51.94, H 4.12, N 0.82; found: C 51.90, H 4.09, N 0.79.

[Ir(cod)(L12c)]BAr_F: Yield: 114 mg (91%). ^{31}P NMR ($CDCl_3$): $\delta=103.2$ (s); ^{1}H NMR ($CDCl_3$): $\delta=0.21$ (s, 9H, CH_3, $SiMe_3$), 0.24 (s, 9H, CH_3, $SiMe_3$), 1.74 (b, 2H, CH_2, cod), 1.90 (b, 2H, CH_2, cod), 2.17 (b, 2H, CH_2, cod), 2.49 (b, 2H, CH_2, cod), 4.17 (b, 1H, CH=, cod), 4.37 (b, 1H, CH=, cod), 4.77 (b, 1H, CH=, cod), 5.52 (b, 1H, CH=, cod), 7.02 (m, 1H, CHO), 7.1–8.7 (m, 27H, CH=); ^{13}C NMR ($CDCl_3$): $\delta=0.2$ (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 25.6 (b, CH_2, cod), 28.9 (b, CH_2, cod), 34.9 (b, CH_2, cod), 36.8 (d, CH_2, cod, $J_{C,P}=6.2$ Hz), 67.6 (b, CH=, cod), 72.3 (b, CH=, cod), 82.3 (d, CH, $J_{C,P}=7.2$ Hz), 101.2 (d, CH=, cod, $J_{C,P}=20.4$ Hz), 105.4 (d, CH=, cod, $J_{C,P}=12.0$ Hz), 117.7 (b, CH=, BAr_F), 120–134 (aromatic carbons), 135.0 (b, CH=, BAr_F), 136–160 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J=49$ Hz); anal. calcd. (%) for $C_{70}H_{58}BF_{24}IrNO_3PSi_2$: C 49.24, H 3.24, N 0.82; found. C 49.21, H 3.22, N 0.80.

[Ir(cod)(L12e)]BAr_F: Yield: 122 mg (94%). ^{31}P NMR ($CDCl_3$): $\delta=101.0$ (s); ^{1}H NMR ($CDCl_3$): $\delta=1.53$ (s, 9H, CH_3, *t*-Bu), 1.60 (s, 9H, CH_3, *t*-Bu), 2.08 (s, 3H, CH_3, Ar-Me), 2.15 (s, 3H, CH_3, Ar-Me), 2.02 (b, 2H, CH_2, cod), 2.39 (b, 4H, CH_2, cod), 2.49 (b, 2H, CH_2, cod), 2.59 (s, 3H, CH_3, Ar-Me), 2.63 (s, 3H, CH_3, Ar-Me), 3.63 (b, 1H, CH=, cod),

4.29 (b, 1H, CH=, cod), 5.32 (b, 1H, CH=, cod), 5.48 (b, 1H, CH=, cod), 6.75 (m, 1H, CHO), 7.5–8.9 (m, 23H, CH=); ^{13}C NMR ($CDCl_3$): δ=16.7 (b, CH_3, Ar-Me), 20.4 (CH_3, Ar-Me), 20.5 (CH_3, Ar-Me), 25.2 (b, CH_2, cod), 28.9 (b, CH_2, cod), 31.3 (b, CH_2, cod), 31.7 (CH_3, *t*-Bu), 32.5 (CH_3, *t*-Bu), 35.0 (C, *t*-Bu), 35.2 (C, *t*-Bu), 36.9 (b, CH_2, cod), 62.8 (b, CH=, cod), 66.5 (b, CH=, cod), 85.8 (CHO), 103.2 (d, CH=, cod, $J_{C,P}$=14 Hz), 105.8 (d, CH=, cod, $J_{C,P}$=18.6 Hz), 117.7 (b, CH=, BAr_F), 120–135 (aromatic carbons), 135.0 (b, CH=, BAr_F), 135–157 (aromatic carbons), 161.9 (q, C–B, BAr_F, ^1J=49 Hz); anal. calcd. (%) for $C_{76}H_{66}BF_{24}IrNO_3P$: C 52.72, H 3.84, N 0.81; found: C 52.69, H 3.82, N 0.78.

Typical Procedure for the Hydrogenation of Olefins

The alkene (0.5 mmol) and the corresponding Ir complex (1 mol%) were dissolved in CH_2Cl_2 (1 mL) in a high-pressure autoclave. The autoclave was purged four times with hydrogen. Then, 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 mL) and filtered through a short plug of celite. The conversions were determined by ^{1}H NMR or GC and enantiomeric excess was determined by chiral GC or chiral HPLC. The enantiomeric excesses of hydrogenated products from **S1**, **S2**,[6d] **S3**,[30a] **S4**,[6d] **S5**,[10e] **S6**[30a] **S7**, **S8**,[6d] **S9**, **S10**,[8b] **S11**, **S12**,[16] **S13**,[6d] **S14**, **S15**,[6r] **S16**, **S17**,[6d] **S18**,[30b] **S19**,[6q] **S20**–**S22**,[6s] **S23**,[19a] **S24**,[6d] **S25**,[19a] **S26**, **S27**,[30c] **S28**,[10c] **S29**,[6d] **S30**,[30c] **S31**–**S35**,[6d] **S36**,[10c] **S37**,[30d] **S38**,[6d] **S39**[10c] and **S40**[30b] were determined using the conditions previously described.

Typical Procedure for Catalyst Recycling

After each catalytic run, the autoclave was depressurized. The colourless propylene carbonate solution was then extracted with dry/deoxygenated hexane under argon atmosphere in order to remove the substrate and the hydrogenated product. Upon extractions, the corresponding amount of substrate was then added for starting a new run.

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[30] a) T. Ohta, H. Ikegami, T. Miyake, H. Takaya, *J. Organomet. Chem.* **1995**, *502*, 169; b) K. Källström, I. J. Munslow, C. Hedberg, P. G. Andersson, *Adv. Synth. Catal.* **2006**, *348*, 2575; c) K. Inagaki, T. Ohta, K. Nozaki, H. Takaya, *J. Organomet. Chem.* **1997**, *531*, 159; d) S. Deerenberg, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **2000**, *19*, 2065.