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Adaptative Biaryl Phosphite–Oxazole and Phosphite–Thiazole Ligands for Asymmetric Ir-Catalyzed Hydrogenation of Alkenes

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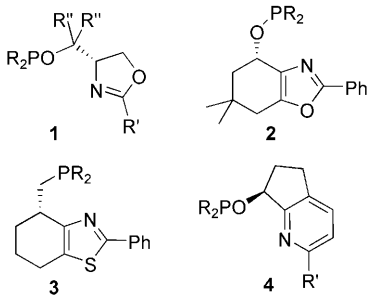
Abstract: A library of readily available phosphite–oxazole/thiazole ligands (**L1a–g–L7a–g**) was applied in the Ir-catalyzed asymmetric hydrogenation of several largely unfunctionalized *E*- and *Z*-trisubstituted and 1,1-disubstituted terminal alkenes. The ability of the catalysts to transfer chiral information to the product could be tuned by choosing suitable ligand components (bridge length, the substituents in the heterocyclic ring and the alkyl backbone chain, the configuration of the ligand backbone, and the substituents/configurations in the biaryl phosphite moiety), so that enantioselectivities could be maximized for each substrate as required. Enantioselectivities were therefore excellent (enantiomeric excess (*ee*) values up to >99%) for a wide range of *E*- and *Z*-trisubstituted and 1,1-disubstituted terminal alkenes. The biaryl phosphite moiety was a very advantageous ligand component in terms of substrate versatility.

Keywords: alkenes · asymmetric catalysis · hydrogenation · iridium · P,N ligands

Introduction

The preparation of enantiomerically enriched compounds currently plays a key role in such important areas as pharmaceuticals, agrochemicals, fine chemicals, and natural product chemistry.[1] As a consequence of its high efficiency, atom economy, and operational simplicity, asymmetric hydrogenation of properly selected prochiral starting materials is one of the most powerful synthetic tools for preparing these compounds.[1] Whereas the rhodium and ruthenium-catalyzed asymmetric hydrogenations of chelating olefins have a long history, the asymmetric hydrogenations of unfunctionalized olefins are less developed because these substrates lack an adjacent polar group to direct the reaction.[1] In recent years, iridium complexes with chiral P,N ligands have become established as efficient catalysts for the hydrogenation of unfunctionalized olefins, and their scope is complementary to those of Rh– and Ru–diphosphine complexes.[1,2] The first chiral ligands developed for this process were the phosphine–oxazolines, which are chiral mimics of Crabtree's catalyst. These ligands were successfully used for the asymmetric hydrogenation of a limited range of alkenes.[3] Since then, the composition of the ligands has been extended by the discovery of new mixed P,N ligands that have considerably broadened the scope of Ir-catalyzed hydrogenation.[4] Of them all, the most successful ligands contain a phosphine or phosphinite moiety as a P-donor group and either an oxazoline,[4b,g] oxazole,[4d] thiazole,[4i] or pyridine[4c] as an N-donor group (**1**–**4**). However, the iridium-catalyzed asymmetric hydrogenation of unfunctionalized olefins is still highly substrate-dependent and the development of efficient chiral ligands that tolerate a broader range of substrates remains a challenge.



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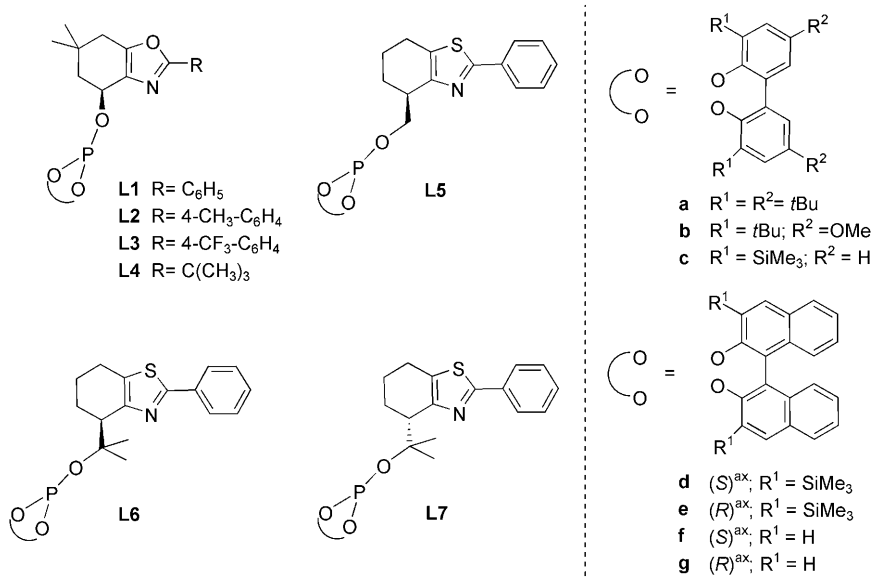
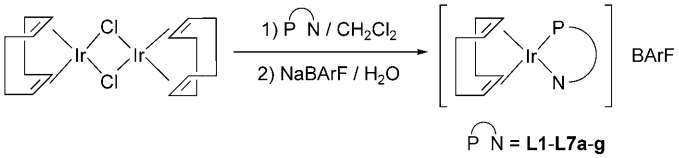
In this context, we have recently discovered that the presence of biaryl phosphite moieties in ligand design is highly advantageous.[5] Ir/phosphite–oxazoline catalytic systems provided greater substrate versatility than previous Ir/phosphinite–oxazoline systems, and high activities and enantioselectivities for several largely unfunctionalized *E*- and *Z*-trisubstituted and 1,1-disubstituted olefins.[5a,c] Despite this success, little attention has been paid to this new class of highly efficient phosphite-containing ligands for this process[5a,c] and their potential as new ligands still needs to be systematically studied. To fully investigate this potential, we therefore decided to go one step further and study whether the biaryl phosphite moiety maintains its effectiveness in combination with N-donor groups other than oxazolines. For this purpose, we took two of the most successful ligand families used in this process (**2** and **3**) and replaced their phosphinite or phosphine moieties with biaryl phosphite groups to give ligands **L1a–g**–**L7a–g**.[6] Ligands **2** and **3** proved to be highly efficient in the hydrogenation of unfunctionalized aryl–alkyl *E*-trisubstituted olefins (including those containing weakly coordinating groups),[4d,i] but they provided low-to-moderate enantioselectivities for the *Z* analogues[7] and enol phosphinates.[8] Moreover, although ligand **2** provided high enantioselectivities for the terminal substrate 2-(4-methoxyphenyl)-1-butene, only moderate enantioselectivities were achieved for other terminal 2-arylbut-1-enes.[9] Therefore, with this new biaryl phosphite–oxazole and phosphite–thiazole design we expect to increase substrate versatility in the hydrogenation of largely unfunctionalized olefins. Interestingly, these ligands combine a priori the advantages of the oxazole/thiazole moieties with those of the phosphite moiety. So they are more stable than their oxazoline counterparts,[10] less sensitive to air and other oxidizing agents than phosphines and phosphinites, and easy to synthesize from readily available alcohols.[11] As well as containing biaryl phosphite moieties in their design, these ligands have a flexible ligand scaffold that enables several parameters to be tuned. Thus, the effect of ligand structure on catalytic performance can be explored. We systematically varied the bridge length (ligands **L1** and **L5**), the substituent in the heterocyclic ring (ligands **L1**–**L4**) and the alkyl backbone chain (ligands **L5** and **L6**), the configuration of the alkyl backbone chain (ligands **L6** vs. **L7**), and the substituents and configurations in the biaryl phosphite moiety (**a–g**) in these ligands and examined their effects on asymmetric hydrogenation. By selecting the best ligand elements, we achieved high enantioselectivities and activities in the reduction of a wide range of *E*- and *Z*-trisubstituted and 1,1-disubstituted olefins.



Results and Discussion

Synthesis of the Ir-catalyst precursors: The catalyst precursors were made by refluxing a dichloromethane solution of the appropriate ligand (**L1a–g**–**L7a–g**) in the presence of 0.5 equivalents of $[\{IrCl(cod)\}_2]$ (cod = 1,5-cyclooctadiene) for 2 h and then exchanging the counterion with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBArF; 1 equiv), in the presence of water (Scheme 1). All complexes were isolated as air-stable orange solids and were used without further purification.

The complexes were characterized by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The spectral assignments (see the Experimental Section) were based on information from ^1H–^1H and ^{13}C–^1H correlation measurements and were as expected for these C_1 iridium complexes. The VT-NMR spectra indicate that only one isomer is present in solution. One singlet in the $^{31}P\{^1H\}$ NMR spectra was obtained in all cases.

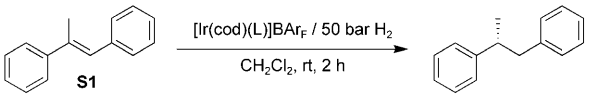


Scheme 1. Synthesis of catalyst precursors [Ir(cod)(P-N)]BArF (P-N = **L1a–g**–**L7a–g**).

Asymmetric hydrogenation of trisubstituted olefins

Asymmetric hydrogenation of unfunctionalized trisubstituted olefins: In a first set of experiments, we used the Ir-catalyzed hydrogenation of *trans*-α-methylstilbene (**S1**) to study the potential of ligands **L1a–g–L7a–g. S1** was chosen as the substrate because it has been hydrogenated by a wide range of catalysts, which enabled the efficiency of the various ligand systems to be compared directly. The results are summarized in Table 1. We found that enantioselectivities were highly affected by the bridge length, the substituents in the heterocyclic ring, and the substituents and configurations in the biaryl phosphite moiety (**a–g**), but not by the substituents in the alkyl backbone chain.

Table 1. Selected results for the Ir-catalyzed hydrogenation of **S1** by using the ligand library **L1a–g–L7a–g**.[a]



Entry	Ligand	Conv. [%][b]	*ee* [%][c]
1	**L1a**	100	90 (*S*)
2	**L1b**	100	90 (*S*)
3	**L1c**	100	85 (*S*)
4	**L1d**	100	84 (*S*)
5	**L1e**	100	37 (*S*)
6	**L1f**	8	50 (*S*)
7	**L1g**	8	12 (*S*)
8	**L2a**	100	89 (*S*)
9	**L3a**	100	82 (*S*)
10	**L4a**	42	83 (*S*)
11	**L5a**	100	98 (*S*)
12	**L5b**	100	97 (*S*)
13	**L5c**	100	95 (*S*)
14	**L5d**	100	85 (*S*)
15	**L5e**	100	90 (*S*)
16	**L6a**	100	98 (*S*)
17	**L7a**	100	98 (*R*)

[a] Reactions carried out by using 1 mmol of **S1** and 0.2 mol% of Ir-catalyst precursor at 50 bar of H_2. [b] Conversion measured by ^{1}H NMR spectroscopy after 2 h. [c] Enantiomeric excesses determined by chiral GC analysis.

The influence of the bridge length indicates that ligands **L5–L7**, which form a seven-membered chelate ring, provided higher enantioselectivity than ligands **L1–L4**, which form a six-membered chelate ring (Table 1, entries 1 and 8–10 vs. 11 and 16–17).

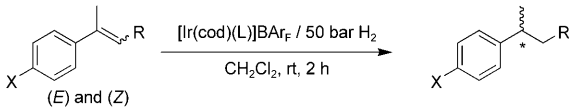
In the heterocyclic ring, electron-withdrawing substituents had a negative effect on enantioselectivity (Table 1, entries 9 vs. 1 and 8), and bulky substituents at this position decreased activity (entries 10 vs. 1).

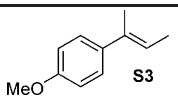
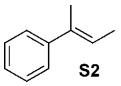
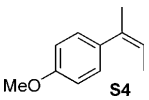
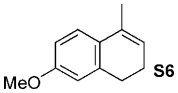
Bulky *ortho* substituents in the biaryl phosphite moiety were highly advantageous for both activity and enantioselectivity (Table 1, entries 1–5 vs 6 and 7). However, substituents in the *para* positions also play a small but crucial role. Therefore, if enantioselectivities have to be high the *para* position needs to be substituted (entries 1 and 2 vs. 3). For phosphite–oxazole ligands **L1**, we also found a cooperative effect between the configuration of the biaryl moiety and the configuration of the ligand backbone on enantioselectivity. This led to a matched combination for ligand **L1d**, which contains an *S*-binaphthyl moiety (entries 4 and 5). This effect was less pronounced for phosphite–thiazole ligands **L5** (entries 14 and 15). In addition, a comparison of the absolute stereochemistry obtained by using ligand **L1c** with those obtained upon using the related binaphthyl ligands **L1d** and **L1e** (entries 3–5) shows that the atropoisomeric biphenyl moiety in ligands **L1a–c** adopts an *S* configuration upon forming a complex with iridium.[12]

In summary, activities and enantioselectivities (enantiomeric excess (*ee*) values up to 98%) were high with ligands **L5a–L7a** (Table 1, entries 11, 16, and 17), which contain the optimal combination of ligand parameters (bridge length, the substituents in the heterocyclic ring, and the substituents and configurations in the biaryl phosphite moiety). In addition, both enantiomers of the hydrogenated product can be accessed in high enantioselectivity simply by changing the configuration of the ligand backbone (entries 16 and 17). These findings clearly show the efficiency of highly modular scaffolds in ligand design.

We then studied the asymmetric hydrogenation of other *E*- and *Z*-trisubstituted olefins (**S2–S6**) by using the phosphite–oxazole/thiazole ligand library **L1a–g–L7a–g**. The most noteworthy results are shown in Table 2. The enantioselectivities are among the best observed for these substrates. In general, the hydrogenation of *E*-trisubstituted olefins (**S2–S3**) followed the same trends as the hydrogenation

Table 2. Selected results for the Ir-catalyzed hydrogenation of largely unfunctionalized *E*- and *Z*-trisubstituted olefins by using the ligand library **L1a–g–L7a–g**.[a]



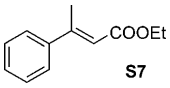
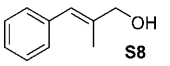
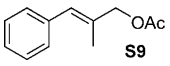
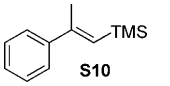
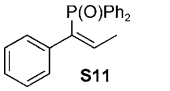
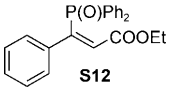
Entry	Substrate	Ligand	Conv. [%][b]	*ee* [%][c]
1		**L5a**	100	99 (*S*)
2		**L6a**	100	99 (*S*)
3		**L7a**	100	98 (*R*)
4		**L5a**	100	99 (*S*)
5		**L6a**	100	99 (*S*)
6		**L7a**	100	99 (*R*)
7		**L5e**	100	90 (*R*)
8		**L5a**	100	78 (*R*)
9		**L6a**	100	93 (*R*)
10		**L7a**	100	93 (*S*)
11		**L5a**	100	99 (*R*)

[a] Reactions carried out by using 1 mmol of substrate and 0.2 mol% of Ir-catalyst precursor at 50 bar of H_2. [b] Conversion measured by ^{1}H NMR spectroscopy or GC analysis after 2 h. [c] Enantiomeric excesses determined by chiral GC analysis.

of **S1**. Again, the catalyst precursors containing ligands **L5a–L7a** provided the best enantioselectivities (*ee* values up to 99%; Table 2, entries 1–6). It should be noted that if ligands are appropriately tuned, high enantioselectivities (*ee* values up to 99%) could also be obtained for the more demanding *Z*-trisubstituted olefins (**S4–S6**), which are usually hydrogenated less enantioselectively than the corresponding *E* isomers (Table 2, entries 7–11). Interestingly, when these excellent results are compared with the moderate enantioselectivity obtained for *Z*-trisubsituted olefins with the related ligands **2** and **3**,[7] we can conclude that the introduction of a biaryl phosphite moiety has been highly advantageous.

Asymmetric hydrogenation of trisubstituted olefins containing a neighboring polar group: We then applied the phosphite–oxazole/thiazole ligand library **L1a–g–L7a–g** in the asymmetric hydrogenation of several trisubstituted olefins containing a neighboring polar group. These substrates are interesting because they allow for further functionalization. The results are summarized in Table 3. Again, enantioselectivities in both enantiomers of the hydrogenation product were excellent (*ee* values up to 99%) under mild reaction conditions. Hydrogenation of α,β-unsaturated ester **S7**, allylic alcohol **S8**, allylic acetate **S9**, and vinylsilane **S10** followed the same trends as those observed for the previous *E*-trisubstituted substrates **S1–S3**. Therefore, enantioselectivities were best with ligands **L5a–L7a** (Table 3, entries 2–4 and 6–14). However, for trisubsituted enol phosphinates **S11–S12**, the enantioselectivity was best with ligand **L1a** (entries 15 and 17). Once again, these results clearly show the efficiency of using modular scaffolds in ligand design and are among the best that have been reported for this type of substrates.[2] They also show that the introduction of a biaryl phosphite moiety in the ligand design is highly advantageous because it overcomes a substrate limitation of the related ligands **2** and **3** by hydrogenating enol phosphinates.[8]

Table 3. Selected results for the Ir-catalyzed hydrogenation of trisubstituted weakly coordinating functionalized olefins by using the ligand library **L1a–g–L7a–g**.[a]

Entry	Substrate	Ligand	Conv. [%][b]	*ee* [%][c]
1	 **S7**	**L1a**	65	99 (*S*)
2		**L5a**	100	99 (*S*)
3		**L6a**	100	98 (*S*)
4		**L7a**	100	98 (*R*)
5	 **S8**	**L1a**	100	84 (*S*)
6		**L5a**	100	96 (*S*)
7		**L6a**	100	96 (*S*)
8		**L7a**	100	96 (*R*)
9	 **S9**	**L5a**	100	95 (*S*)
10		**L6a**	100	94 (*S*)
11		**L7a**	100	94 (*R*)
12	 **S10**	**L5a**	100	98 (*S*)
13		**L6a**	100	97 (*S*)
14		**L7a**	100	97 (*R*)
15[d]	 **S11**	**L1a**	100	91 (*S*)
16[d]		**L5a**	100	20 (*R*)
17[e]	 **S12**	**L1a**	45	92 (*S*)

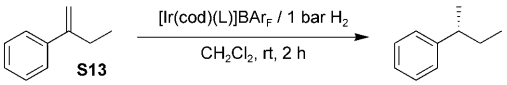
[a] Reactions carried out by using 1 mmol of substrate, dichloromethane as solvent, and 0.2 mol% of Ir-catalyst precursor at 50 bar of H_2 and at room temperature. [b] Conversion measured by ^1H NMR spectroscopy or GC analysis after 2 h. [c] Enantiomeric excesses determined by chiral GC analysis or HPLC. [d] $t=12$ h. [e] 100 bar of H_2, $t=12$ h.

Asymmetric hydrogenation of 1,1-disubstituted terminal olefins

Asymmetric hydrogenation of unfunctionalized 1,1-disubstituted terminal olefins: To further study the potential of the phosphite–oxazole/thiazole ligand library **L1a–g–L7a–g**, we also screened it in the Ir-catalyzed hydrogenation of more demanding substrates: terminal olefins. Enantioselectivity is more difficult to control in these substrates than in trisubstituted olefins. There are two main reasons for this:[2d] 1) the two substituents in the substrate can easily exchange positions in the chiral environment formed by the catalysts, thus reversing the face selectivity and 2) 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.[13,14] Pfaltz found that in the hydrogenation of terminal alkenes, the selectivity is highly pressure dependent. Hydrogenation at an atmospheric pressure of H_2 gave significantly higher *ee* values than at higher pressures.[4b,13a]

In a first set of experiments, we examined the Ir-catalyzed asymmetric hydrogenation of 2-phenylbut-1-ene (**S13**). Table 4shows the results obtained by using the ligand library **L1a–g–L7a–g** in optimized conditions. We were again able to fine-tune ligand parameters to produce high activities and enantioselectivities (*ee* values up to 94%) in the hydrogena-

Table 4. Selected results for the Ir-catalyzed hydrogenation of **S13** by using the ligands **L1a–g–L7a–g**.[a]



Entry	Ligand	Conv. [%][b]	*ee* [%][c]
1	**L1a**	100	53 (*R*)
2	**L2a**	100	50 (*R*)
3	**L3a**	100	43 (*R*)
4	**L4a**	100	5 (*R*)
5	**L5a**	100	94 (*R*)
6	**L5b**	100	94 (*R*)
7	**L5c**	100	90 (*R*)
8	**L5d**	100	89 (*R*)
9	**L5e**	100	3 (*R*)
10	**L6a**	100	90 (*R*)
11	**L7a**	100	90 (*S*)

[a] Reactions carried out by using 1 mmol of **S13** and 0.2 mol% of Ir-catalyst precursor at 1 bar of H_2. [b] Conversion measured by GC analysis after 2 h. [c] Enantiomeric excesses determined by chiral GC analysis.

tion of this substrate. In contrast to the hydrogenation of *E*-trisubstituted olefins (**S1**–**S3** and **S7**–**S10**), among the other ligand parameters, activities and enantioselectivities were also affected by the subsitutents in the alkyl backbone chain. Therefore, ligand **L5** provided better enantioselectivities than ligands **L6** and **L7** that contain methyl substitutents at the alkyl backbone chain (Table 4, entries 5 vs. 10 and 11). Interestingly, the effect of bridge length was more pronounced in this reaction than in the reduction of *E*-trisubstituted olefins. The ligands that formed seven-membered chelate rings (**L5**) provided much higher enantioselectivities than the one that formed a six-membered chelate ring (**L1**). The effect of the substituents in the biaryl phosphite moiety followed the same trend as those observed for *E*-trisubstituted olefins. However, by using ligands **L5d** and **L5e**, we found an important cooperative effect between the configuration of the biaryl moiety and the configuration of the ligand backbone on enantioselectivity. Ligand **L5d**, which contains an *S*-binaphthyl moiety, performed better than **L5e** (Table 4, entries 8 and 9). In addition, a comparison of the results obtained upon using ligand **L5c** with those from the related binaphthyl ligands **L5d** and **L5e** (Table 4, entries 7–9) shows that the atropoisomeric biphenyl moieties in ligands **L5a–c** adopt an *S* configuration upon coordination to iridium.[12]

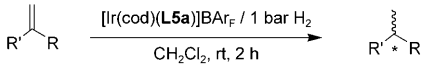
In summary, enantioselectivities were best when phosphite–thiazole ligands **L5a** and **L5b** were used. Once again, it was possible to access both enantiomers of the hydrogenation product. These results, which again clearly show the efficiency of using modular scaffolds in ligand design, are among the best that have been reported for this demanding substrate class.[13,14]

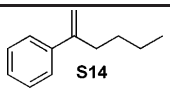
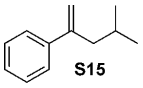
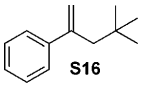
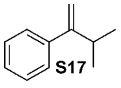
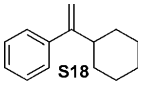
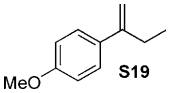
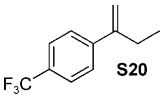
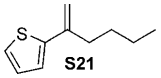
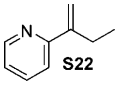
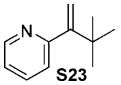
We then studied the asymmetric hydrogenation of other 1,1-disubstituted aryl–alkyl substrates (**S14**–**S20**) and 1,1-disubstituted heteroaryl–alkyl olefins (**S21**–**S23**) by using the phosphite–oxazole/thiazole ligand library **L1a–g**–**L7a–g**. The most noteworthy results are shown in Table 5. They follow the same trends as the hydrogenation of **S13**. Again, the catalyst precursor containing the phosphite–thiazole ligands **L5a** and **L5b** provided the best enantioselectivities (*ee* values up to 99%).

The hydrogenations of 1,1-disubstituted aryl–alkyl substrates bearing increasingly bulky alkyl substituents (**S14**–**S18**) all gave similar high activities and enantioselectivities (full conversion, *ee* values up to 95%; Table 5, entries 1–5). Our results with several *para*-substituted 2-phenylbut-2-enes (**S13**, **S19**–**S20**) indicated that enantioselectivity (*ee* values up to 97%) is relatively insensitive to the electronic nature of the substrate phenyl ring (Table 4, entry 5 and Table 5, entries 6 and 7). This is, therefore, one of only two catalytic systems able to hydrogenate a wide range of α-alkylstyrenes in high enantioselectivities.[5c]

We then decided to apply this ligand library in the asymmetric hydrogenation of 1,1-heteroaromatic alkenes (**S21**–**S23**) because heterocycles are used in industry and because the heterocyclic part can be modified post-hydrogenation. Despite this, only one previous study has been made.[5c]

Table 5. Selected results for the Ir-catalyzed hydrogenation of largely unfunctionalized 1,1-disubstituted terminal olefins by using ligand **L5a**.[a]



Entry	Substrate	Conv. [%][b]	*ee* [%][c]
1	 **S14**	100	95 (*R*)
2	 **S15**	100	94 (*R*)
3	 **S16**	100	85 (*R*)
4	 **S17**	100	95 (*R*)
5	 **S18**	100	94 (*R*)
6	 MeO **S19**	100	97 (*R*)
7	 F$_3$C **S20**	100	94 (*R*)
8	 **S21**	100	90 (+)
9	 **S22**	100	99 (−)
10	 **S23**	100	96 (−)

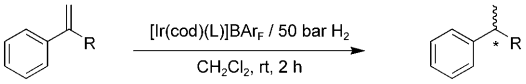
[a] Reactions carried out by using 1 mmol of substrate and 0.2 mol% of Ir-catalyst precursor at 1 bar of H_2. [b] Conversion measured by ^{1}H NMR spectroscopy or GC analysis. [c] Enantiomeric excesses determined by chiral GC analysis.

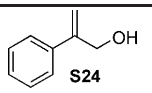
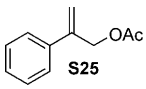
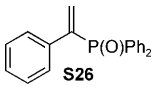
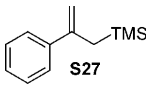
Under standard conditions, our catalyst systems were also able to hydrogenate several 1,1-heteroaromatic alkenes with high activities and enantioselectivities (*ee* values up to 99%; Table 5, entries 8–10).

Asymmetric hydrogenation of 1,1-disubstituted terminal olefins containing a neighboring polar group: Encouraged by the excellent results obtained up to this point, we examined the asymmetric hydrogenation of 1,1-disubstituted terminal olefins containing a polar neighboring group (**S24**–**S27**). The results are summarized in Table 6.

We initially tested the ligand library in the hydrogenation of the allylic alcohol **S24**. Derivatives of the hydrogenation product 2-phenylpropanol are frequently used as components of fragrance mixtures (i.e. commercial odorants Muguesia and Pamplefleur) and also as intermediates for the

Table 6. Selected results for the Ir-catalyzed hydrogenation of 1,1-disubstituted terminal olefins containing a neighboring polar group by using the ligand library **L1a–gL7a–g**.[a]



Entry	Substrate	Ligand	Conv. [%][b]	*ee* [%][c]
1		**L5a**	100	87 (*S*)
2		**L6a**	100	90 (*S*)
3	**S24**	**L7a**	100	90 (*R*)
4		**L5a**	100	83 (*S*)
5		**L6a**	100	87 (*S*)
6	**S25**	**L7a**	100	87 (*R*)
7[d]		**L1a**	100	82 (*R*)
	S26			
8		**L5a**	100	93 (*R*)
	S27			

[a] Reactions carried out by using 1 mmol of substrate and 0.5 mol% of Ir-catalyst precursor at 50 bar of H_2. [b] Conversion measured by ^{1}H NMR spectroscopy measured after 2 h. [c] Enantiomeric excesses determined by chiral GC or HPLC analysis. [d] $t = 12$ h.

synthesis of natural products and drugs (i.e. modulators of dopamine D3 receptors).[15] Iridium complexes containing ligands **L5a–L7a** proved to be the most selective catalysts, giving 90% *ee* at room temperature in both enantiomers of the hydrogenation product (Table 6, entries 1–3). Similarly, the hydrogenation of the allylic acetate **S25** also proceeds with high activity and enantioselectivity with the catalyst systems containing ligands **L5a–L7a** (Table 6, entries 4–6). These results are among the best that have been reported for these substrate types.[5c,13a]

We next screened ligands **L1a–g–L7a–g** in the asymmetric hydrogenation of the enol phosphinate **S26** and the allylic silane **S27**. The hydrogenation of these compounds gave rise to important chiral organic intermediates and a number of innovative new organosilicon[16] drugs are being developed. As previously observed for the trisubstituted enol phosphinates, if *ee* values have to be high for substrate **S26**, phosphite–oxazole ligand types (**L1**) need to be used. Enantioselectivities (*ee* values up to 82%) were best with catalyst precursor Ir–**L1e** (Table 6, entry 7). However, for the hydrogenation of **S27**, the best result (*ee* values up to 93%) was obtained with the Ir–**L5a** catalyst precursor (Table 6, entry 8). This is, therefore, one of the two catalytic systems able to hydrogenate allylic silane **S27** in high enantioselectivities.[5c] It is also noteworthy that phosphite–oxazole ligands **L1** provide better conversions and enantioselectivities than those obtained with related phosphinite–oxazole ligands **2** in the hydrogenation of enol phosphinate **S26**.[8] This shows once again the benefits of incorporating a biaryl phosphite moiety into the ligand design for the hydrogenation of enol phosphinates.

Conclusion

A library of readily available phosphite–oxazole/thiazole ligands (**L1a–g–L7a–g**) was applied in the Ir-catalyzed asymmetric hydrogenation of several largely unfunctionalized *E*- and *Z*-trisubstituted and 1,1-disubstituted terminal alkenes. This ligand library combines the advantages of the oxazole/thiazole moieties with those of the phosphite moiety. They are more stable than their oxazoline counterparts, less sensitive to air and other oxidizing agents than phosphines and phosphinites, and easy to synthesize from readily available alcohols. Moreover, the highly modular nature of the ligand library enables the bridge length, the substituents in the heterocyclic ring and the alkyl backbone chain, the configuration of the ligand backbone, and the substituents/configurations in the biaryl phosphite moiety to be easily and systematically varied. We found that the effectiveness at transferring the chiral information in the product can be tuned by choosing suitable ligand components, so that enantioselectivities can be maximized for each substrate as required. Enantioselectivities were therefore excellent (*ee* values up to >99%) in a wide range of *E*- and *Z*-trisubstituted and 1,1-disubstituted terminal alkenes. It should be noted that these catalytic systems also have a high tolerance to the presence of a neighboring polar group and, therefore, tri- and disubstituted allylic alcohols, acetates, esters, silanes, and enol phosphinates can be hydrogenated in high enantioselectivities (*ee* values up to 99%). We also demonstrated that the introduction of a biaryl phosphite moiety into the ligand design is highly advantageous in terms of substrate versatility. Therefore, these Ir–phosphite–oxazole/thiazole catalytic systems provided higher enantioselectivities for a wider range of *E*- and *Z*-trisubstituted and 1,1-disubstituted substrates than their related phosphinite–oxazole (**2**) and phosphine–thiazole (**3**) counterparts. These results show that these catalytic systems are among the few alternatives that provide high substrate versatility for *E*- and *Z*-trisubstituted and 1,1-disubstituted terminal alkenes.

Experimental Section

General considerations: All reactions were carried out by using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. Phosphite–oxazole/thiazole ligands **L1a–g–L7a–g** were prepared as previously described.[6] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded by using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ (^{1}H and ^{13}C) as an internal standard or H_3PO_4 (^{31}P) as an 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)]BArF: The corresponding ligand (0.074 mmol) was dissolved in CH_2Cl_2 (2 mL) and [{IrCl(cod)}$_2$] (25 mg, 0.037 mmol) was added. The reaction was refluxed at 50°C for 1 h. After 5 min at room temperature, NaBArF (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)]BArF: Yield: 127 mg (93%); ^{31}P NMR ($CDCl_3$): δ = 108.9 ppm; ^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 1.37 (s, 9H; CH_3, *t*Bu), 1.39 (s, 9H; CH_3, *t*Bu), 1.51 (s, 9H; CH_3, *t*Bu), 1.59 (s, 9H; CH_3, *t*Bu), 1.68 (m, 4H; CH_2, cod), 1.81 (dd, 1H, $^2J_{H-H}$ = 18.1, $^3J_{H-H}$ = 8.8 Hz; CH_2), 2.04 (m, 1H; CH_2), 2.35 (m, 4H; CH_2, cod), 2.54 (d, 1H, $^2J_{H-H}$ = 17.4 Hz; CH_2–C=), 2.68 (d, 1H, $^2J_{H-H}$ = 17.1 Hz; CH_2–C=), 4.03 (m, 1H; CH=, cod), 4.39 (brs, 2H; CH=, cod), 5.35 (brs, 1H; CH=, cod), 5.61 (s, 1H; CH–O), 6.90–8.20 ppm (m, 21H; CH=); ^{13}C NMR ($CDCl_3$): δ = 24.6 (CH_2, cod), 27.1 (CH_2, cod), 28.4 (CH_3), 29.2 (CH_3), 31.1 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 32.6 (CH_3, *t*Bu), 34.6 (CH_2, cod), 35.0 (CH_2-C=), 35.1 (brs; C, *t*Bu), 35.6 (brs; C, *t*Bu), 36.0 (CMe_2), 37.5 (brs; CH_2, cod), 42.2 (brs; CH_2), 69.5 (brs; CH–O), 70.1 (CH=, cod), 70.9 (CH, cod), 91.7 (d, J_{C-P} = 23.6 Hz; CH=, cod,), 105.5 (brs; CH=, cod), 113–116 (aromatic carbon atoms), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs, CH=BAr_F), 136–157 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}$ = 49.5 Hz; C-B, BAr_F), 165.9 ppm (C=N); elemental analysis calcd (%) for $C_{83}H_{80}BF_{24}IrNO_4P$: C 54.02, H 4.37, N 0.76; found: C 53.98, H 4.48, N 0.77.

[Ir(cod)(L1b)]BArF: Yield: 126 mg (95%); ^{31}P NMR ($CDCl_3$): δ = 111.6 ppm; ^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 3H; CH_3), 1.08 (s, 3H; CH_3), 1.49 (s, 9H; CH_3, *t*Bu), 1.56 (s, 9H; CH_3, *t*Bu), 1.65 (m, 4H; CH_2, cod), 1.81 (dd, 1H, $^2J_{H-H}$ = 14.1, $^3J_{H-H}$ = 6.6 Hz; CH_2), 2,07 (dd, 1H, $^2J_{H-H}$ = 14.4, $^3J_{H-H}$ = 6.6 Hz; CH_2), 2.22 (m, 2H; CH_2, cod), 2.43 (m, 2H; CH_2, cod), 2.53 (d, 1H, $^2J_{H-H}$ = 17.4 Hz; CH_2–C=), 2.67 (d, 1H, $^2J_{H-H}$ = 17.1 Hz; CH_2–C=), 3.84 (s, 3H; CH_3–O), 3.86 (s, 3H; CH_3–O), 4.02 (m, 1H; CH=, cod), 4.44 (brs, 1H; CH=, cod), 4.59 (brs, 1H; CH=, cod), 5.34 (brs, 1H; CH=, cod), 5.58 (s, 1H; CH–O), 6.60–8.20 ppm (m, 21H; CH=); ^{13}C NMR ($CDCl_3$): δ = 24.5 (CH_2, cod), 27.1 (CH_2, cod), 28.4 (CH_3), 29.1 (CH_3), 31.1 (CH_3, *t*Bu), 32.2 (CH_3, *t*Bu), 34.7 (CH_2, cod), 35.0 (CH_2–C=), 35.6 (brs; C, *t*Bu), 36.0 (CMe_2), 37.6 (CH_2, cod), 42.4 (brs; CH_2), 55.8 (CH_3–O), 69.6 (brs; CH–O), 70.5 (CH=, cod), 70.9 (CH=, cod), 91.2 (d, J_{C-P} = 23.6 Hz; CH=, cod), 105.5 (brs; CH=, cod), 113–116 (aromatic carbon atoms), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–157 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}$ = 49.5 Hz; C-B, BAr_F), 165.7 ppm (C=N); elemental analysis calcd (%) for $C_{77}H_{68}BF_{24}IrNO_3PSSi_2$: C 51.57, H 3.82, N 0.78; found: C 51.62, H 3.85, N 0.75.

[Ir(cod)(L1c)]BArF: Yield: 120 mg (92%); ^{31}P NMR ($CDCl_3$): δ = 107.6 ppm; ^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 9H; CH_3–Si), 0.50 (s, 9H; CH_3–Si), 1.06 (s, 3H; CH_3), 1.07 (s, 3H; CH_3), 1.61 (m, 4H; CH_2, cod), 1.81 (dd, 1H, $^2J_{H-H}$ = 14.1, $^3J_{H-H}$ = 5.7 Hz; CH_2), 2,07 (m, 2H; CH_2 + CH_2, cod), 2.16 (m, 1H; CH_2, cod), 2.43 (m, 2H; CH_2, cod), 2.53 (d, 1H, $^2J_{H-H}$ = 17.4 Hz; CH_2–C=), 2.67 (d, 1H, $^2J_{H-H}$ = 17.5 Hz; CH_2–C=), 4.07 (m, 1H; CH=, cod), 4.27 (brs, 1H; CH=, cod), 4.41 (brs, 1H; CH=, cod), 5.50 (brs, 1H; CH=, cod), 5.64 (s, 1H; CH–O), 7.20–8.10 ppm (m, 23H; CH=); ^{13}C NMR ($CDCl_3$): δ = 0.34 (CH_3–Si), 0.86 (CH_3–Si), 24.6 (CH_2, cod), 27.4 (CH_2, cod), 28.4 (CH_3), 28.8 (CH_3), 34.3 (CH_2, cod), 35.2 (CH_2–C=), 36.0 (CMe_2), 37.7 (d, J_{C-P} = 6.8 Hz; CH_2, cod), 42.4 (d, J_{C-P} = 9.1 Hz; CH_2), 65.6 (d, J_{C-P} = 3.7 Hz; CH–O), 70.3 (CH=, cod), 70.5 (CH=, cod), 93.4 (d, J_{C-P} = 22.5 Hz; CH=, cod), 107.1 (d, J_{C-P} = 10.8 Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–153 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}$ = 49.2 Hz; C-B, BAr_F), 165.9 ppm (C=N); elemental analysis calcd (%) for $C_{73}H_{64}BF_{24}IrNO_3PSSi_2$: C 49.66, H 3.65, N 0.79; found: C 49.68, H 3.69, N 0.78.

[Ir(cod)(L1d)]BArF: Yield: 130 mg (94%); ^{31}P NMR ($CDCl_3$): δ = 107.7 ppm; ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 9H; CH_3–Si), 0.54 (s, 9H; CH_3–Si), 1.04 (s, 3H; CH_3), 1.18 (s, 3H; CH_3), 1.49 (m, 2H; CH_2, cod), 1.53 (m, 2H; CH_2, cod), 1.78 (dd, 1H, $^2J_{H-H}$ = 14.2, $^3J_{H-H}$ = 5.6 Hz; CH_2), 2.09 (brs, 2H; CH_2 + CH_2 cod), 2.14 (m, 1H; CH_2, cod), 2.25 (m, 2H; CH_2, cod), 2.56 (d, 1H, $^2J_{H-H}$ = 17.2 Hz; CH_2–C=), 2.63 (d, 1H, $^2J_{H-H}$ = 17.2 Hz; CH_2–C=), 3.81 (m, 1H; CH=, cod), 4.20 (brs, 2H; CH=, cod), 5.41 (brs, 1H; CH=, cod), 5.49 (s, 1H; CH–O), 7.20–8.10 ppm (m, 27H; CH=); ^{13}C NMR ($CDCl_3$): δ = 0.3 (CH_3–Si), 1.2 (CH_3–Si), 25.4 (CH_2, cod), 29.7 (CH_2, cod), 30.0 (CH_3), 31.2 (CH_3), 32.3 (CH_2, cod), 33.6 (CH_2–C=), 35.4 (CMe_2), 36.2 (d, J_{C-P} = 7.2 Hz; CH_2, cod), 42.8 (d, J_{C-P} = 8.4 Hz; CH_2), 61.3 (d, J_{C-P} = 4.2 Hz; CH–O), 70.0 (CH=, cod), 70.4 (CH=, cod), 97.8 (d, J_{C-P} = 20.4 Hz; CH=, cod), 106.8 (d, J_{C-P} = 9.6 Hz; CH=, cod), 117.8 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–153 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}$ = 49.2 Hz; C-B, BAr_F), 168.1 ppm (C=N); elemental analysis calcd (%) for $C_{81}H_{68}BF_{24}IrNO_4PSi_2$: C 52.15, H 3.67, N 0.75; found: C 52.17, H 3.69, N 0.74.

[Ir(cod)(L1e)]BArF: Yield: 134 mg (97%); ^{31}P NMR ($CDCl_3$): δ = 108.0 ppm; ^{1}H NMR ($CDCl_3$): δ = 0.23 (s, 9H, CH_3–Si), 0.60 (s, 9H; CH_3–Si), 1.09 (s, 3H; CH_3), 1.20 (s, 3H; CH_3), 1.58 (m, 4H; CH_2, cod), 1.73 (dd, 1H, $^2J_{H-H}$ = 14.1, $^3J_{H-H}$ = 5.7 Hz; CH_2), 2.07 (m, 2H; CH_2 + CH_2, cod), 2.16 (m, 1H; CH_2, cod), 2.27 (m, 2H; CH_2, cod), 2.58 (d, 1H, $^2J_{H-H}$ = 17.3 Hz; CH_2–C=), 2.67 (d, 1H, $^2J_{H-H}$ = 17.5 Hz; CH_2–C=), 3.81 (m, 1H; CH=, cod), 4.22 (brs, 2H; CH=, cod), 5.36 (brs, 1H; CH=, cod), 5.51 (s, 1H; CH–O), 7.20–8.10 ppm (m, 27H; CH=); ^{13}C NMR ($CDCl_3$): δ = 0.5 (CH_3–Si), 0.9 (CH_3–Si), 25.6 (CH_2, cod), 29.9 (CH_2, cod), 30.1 (CH_3), 30.8 (CH_3), 32.2 (CH_2, cod), 33.4 (CH_2–C=), 35.2 (CMe_2), 36.1 (d, J_{C-P} = 6.8 Hz; CH_2, cod), 42.9 (d, J_{C-P} = 9.1 Hz; CH_2), 61.4 (d, J_{C-P} = 3.7 Hz; CH–O), 69.5 (CH=, cod), 70.1 (CH=, cod), 97.1 (d, J_{C-P} = 22.5 Hz; CH=, cod), 107.3 (d, J_{C-P} = 10.8 Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–153 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}$ = 49.2 Hz; C-B, BAr_F), 167.9 ppm (C=N); elemental analysis calcd (%) for $C_{81}H_{68}BF_{24}IrNO_4PSi_2$: C 52.15, H 3.67, N 0.75; found: C 52.13, H 3.70, N 0.73.

[Ir(cod)(L1f)]BArF: Yield: 120 mg (94%); ^{31}P NMR ($CDCl_3$): δ = 104.2 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 3H; CH_3), 1.12 (s, 3H; CH_3), 1.52 (m, 4H; CH_2, cod), 1.62 (dd, 1H, $^2J_{H-H}$ = 14, $^3J_{H-H}$ = 5.6 Hz; CH_2), 1.92 (dd, 1H, $^2J_{H-H}$ = 14, $^3J_{H-H}$ = 5.4 Hz; CH_2), 2.09 (m,1H; CH_2 cod), 2.15 (m, 1H; CH_2, cod), 2.25 (m, 2H; CH_2, cod), 2.53 (m, 1H, $^2J_{H-H}$ = 16 Hz; CH_2–C=), 2.61 (d, 1H, $^2J_{H-H}$ = 16 Hz; CH_2–C=), 3.80 (m, 1H; CH=, cod), 4.20 (brs, 2H; CH=, cod), 5.32 (brs, 1H; CH=, cod), 5.59 (m, 1H; CH–O), 6.90–8.30 ppm (m, 29H; CH=); ^{13}C NMR ($CDCl_3$): δ = 24.3 (CH_2, cod), 29.1 (CH_3), 29.9 (CH_2, cod), 30.4 (CH_3), 32.5 (CH_2, cod), 33.1 (CH_2–C=), 35.4 (CMe_2), 36.5 (CH_2), 43.1 (d, J_{C-P} = 9.4 Hz; CH_2), 61.9 (d, J_{C-P} = 3.1 Hz; CH–O), 69.9 (CH=, cod), 70.2 (CH=, cod), 97.3 (d, J_{C-P} = 18.9 Hz; CH=, cod), 107.8 (d, J_{C-P} = 9.9 Hz; CH=, cod), 117.6 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–159 (aromatic carbon atoms), 161.8 (q, $^1J_{C-B}$ = 49.2 Hz; C-B, BAr_F), 167.4 ppm (C=N); elemental analysis calcd (%) for $C_{75}H_{52}BF_{24}IrNO_4P$: C 52.34, H 3.05, N 0.81; found: C 52.36, H 3.07, N 0.79.

[Ir(cod)(L^{1}g)]BArF: Yield: 118 mg (93%); ^{31}P NMR ($CDCl_3$): δ = 103.9 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 0.89 (s, 3H; CH_3), 1.11 (s, 3H; CH_3), 1.53 (m, 4H; CH_2, cod), 1.72 (dd, 1H, $^2J_{H-H}$ = 14.4, $^3J_{H-H}$ = 6.0 Hz; CH_2), 1.88 (dd, $^2J_{H-H}$ = 14.4, $^3J_{H-H}$ = 5.6 Hz, 1H; CH_2), 2.11 (m,1H; CH_2, cod), 2.14 (m, 1H; CH_2, cod), 2.23 (m, 2H; CH_2, cod), 2.48 (m, 1H, $^2J_{H-H}$ = 16 Hz; CH_2–C=), 2.63 (d, 1H, $^2J_{H-H}$ = 16 Hz; CH_2–C=), 3.81 (m, 1H; CH=, cod), 4.22 (brs, 2H; CH=, cod), 5.28 (brs, 1H; CH=, cod), 5.63 (m, 1H; CH–O), 6.90–8.30 ppm (m, 29H; CH=); ^{13}C NMR ($CDCl_3$): δ = 24.1 (CH_2, cod), 28.9 (CH_2, cod), 29.7 (CH_3), 30.6 (CH_3), 32.4 (CH_2, cod), 33.0 (CH_2-C=), 35.6 (CMe_2), 36.8 (CH_2), 43.2 (d, J_{C-P} = 8.4 Hz; CH_2), 61.8 (d, J_{C-P} = 2.8 Hz; CH–O), 68.3 (CH=, cod), 70.1 (CH=, cod), 96.2 (d, J_{C-P} = 16.5 Hz; CH=, cod), 103.6 (d, J_{C-P} = 10.2 Hz; CH=, cod), 117.6 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–159 (aromatic carbon atoms), 161.8 (q, $^1J_{C-B}$ = 49.2 Hz; C-B, BAr_F), 167.7 ppm (C=N); elemental analysis calcd (%) for $C_{75}H_{52}BF_{24}IrNO_4P$: C 52.34, H 3.05, N 0.81; found: C 52.32, H 3.08, N 0.80.

[Ir(cod)(L2a)]BArF: Yield: 132 mg (96%); ^{31}P NMR ($CDCl_3$): δ = 104.7 ppm (s); ^{1}H NMR ($CDCl_3$): δ = 0.86 (s, 3H; CH_3), 0.99 (s, 3H; CH_3), 1.26 (s, 9H; CH_3, *t*Bu), 1.29 (s, 9H; CH_3, *t*Bu), 1.43 (s, 9H; CH_3, *t*Bu), 1.52 (s, 9H; CH_3, *t*Bu), 1.64 (m, 4H; CH_2, cod), 1.73 (dd, 1H, $^2J_{H-H}$ = 14.2, $^3J_{H-H}$ = 6 Hz; CH_2), 2.02 (dd, 1H, $^2J_{H-H}$ = 14.2, $^3J_{H-H}$ = 6.4 Hz; CH_2), 2.13 (m, 2H; CH_2, cod), 2.19 (m, 2H; CH_2, cod), 2.29 (s, 3H; CH_3–Ph), 2.43 (d, 1H, $^2J_{H-H}$ = 19.2 Hz; CH_2–C=), 2.50 (d, 1H, $^2J_{H-H}$ = 19.2 Hz; CH_2–C=), 3.85 (m, 1H; CH=, cod), 4.31 (brs, 2H; CH=, cod), 5.11 (brs, 1H; CH=, cod), 5.45 (m, 1H; CH–O), 7.10–8.20 ppm (m, 20H; CH=); ^{13}C NMR ($CDCl_3$): δ = 21.9 (CH_3–Ph), 23.2 (CH_2, cod), 25.6

(CH_3), 27.3 (CH_2, cod), 27.9 (CH_3), 30.2 (CH_3, *t*Bu), 30.8 (brs; CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.6 (C, *t*Bu), 31.8 (C, *t*Bu), 33.4 (C, *t*Bu), 33.9 (CH_2, cod), 34.5 (CH_2, cod), 34.9 (CMe_2), 36.7 (d, $J_{C-P}=8.0$ Hz; CH_2–C=), 41.2 (d, $J_{C-P}=9.2$ Hz; CH_2), 68.4 (CH–O), 69.8 (CH=, cod), 70.5 (CH=, cod), 89.7 (d, $J_{C-P}=21.2$ Hz; CH=, cod), 103.9 (d, $J_{C-P}=9.2$ Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs, CH=BAr_F), 136–153 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.2$ Hz; C-B, BAr_F), 161.9 ppm (C=N), elemental analysis calcd (%) for $C_{84}H_{82}BF_{24}IrNO_4P$: C 54.26, H 4.44, N 0.75; found: C 54.30, H 4.46, N 0.76.

[Ir(cod)(L3a)]BArF: Yield: 130 mg (92%); ^{31}P NMR ($CDCl_3$): $\delta=$ 108.8 ppm; ^{1}H NMR ($CDCl_3$): $\delta=0.95$ (s, 3H; CH_3), 0.97 (s, 3H; CH_3), 1.28 (s, 9H; CH_3, *t*Bu), 1.29 (s, 9H; CH_3, *t*Bu), 1.41 (s, 9H; CH_3, *t*Bu), 1.49 (s, 9H; CH_3, *t*Bu), 1.59 (m, 4H; CH_2, cod), 1.72 (dd, 1H, $^2J_{H-H}=$ 14.0, $^3J_{H-H}=6$ Hz; CH_2), 1.98 (dd, 1H, $^2J_{H-H}=14.0$, $^3J_{H-H}=6.4$ Hz; CH_2), 2.16 (m, 2H; CH_2, cod), 2.20 (m, 2H; CH_2, cod), 2.40 (d, 1H, $^2J_{H-H}=$ 18.8 Hz; CH_2–C=), 2.54 (d, 1H, $^2J_{H-H}=16.8$ Hz; CH_2–C=), 3.81 (m, 1H; CH=, cod), 4.33 (brs, 2H; CH=, cod), 5.23 (brs, 1H; CH=, cod), 5.51 (m, 1H; CH–O), 7.10–8.20 ppm (m, 20H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=23.3$ (CH_2, cod), 25.8 (CH_3), 27.1 (CH_2, cod), 27.8 (CH_3), 30.0 (CH_3, *t*Bu), 30.3 (brs; CH_3, *t*Bu), 31.1 (CH_3, *t*Bu), 31.9 (brs; C, *t*Bu), 33.4 (C, *t*Bu), 33.7 (brs; C, *t*Bu; CH_2, cod), 34.3 (CH_2, cod), 34.7 (CMe_2), 36.5 (d, $J_{C-P}=$ 7.8 Hz; CH_2–C=), 40.9 (d, $J_{C-P}=8.5$ Hz; CH_2), 68.1 (brs; CH–O), 69.8 (CH=, cod), 70.5 (CH=, cod), 89.4 (d, $J_{C-P}=23.3$ Hz; CH=, cod), 104.2 (d, $J_{C-P}=10.8$ Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–153 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.2$ Hz; C-B, BAr_F), 162.7 ppm (C=N); elemental analysis calcd (%) for $C_{84}H_{79}BF_{27}IrNO_4P$: C 52.73, H 4.16, N 0.73; found: C 52.70, H 4.18, N 0.71.

[Ir(cod)(L4a)]BArF: Yield: 127 mg (94%); ^{31}P NMR ($CDCl_3$): $\delta=$ 115.8 ppm; ^{1}H NMR ($CDCl_3$): $\delta=0.90$ (s, 3H; CH_3), 1.03 (s, 3H; CH_3), 1.25 (s, 9H; CH_3, *t*Bu), 1.29 (s, 9H; CH_3, *t*Bu), 1.37 (s, 9H; CH_3, *t*Bu), 1.47 (s, 9H; CH_3, *t*Bu), 1.49 (m, 1H; CH_2), 1.54 (s, 9H; CH_3, *t*Bu), 1.62 (m, 2H; CH_2, cod), 1.82 (dd, $^2J_{H-H}=14.4$, $^3J_{H-H}=6$ Hz, 1H; CH_2), 1.99 (m, 3H; CH_2, cod+CH_2), 2.20 (m, 4H; CH_2, cod), 2.32 (d, 1H, $^2J_{H-H}=$ 17.2 Hz; CH_2–C=), 2.43 (d, 1H, $^2J_{H-H}=16.8$ Hz; CH_2–C=), 4.32 (brs, 1H; CH=, cod), 4.46 (m, 1H; CH=, cod), 4.76 (brs, 1H; CH=, cod), 5.32 (brs, 1H; CH=, cod), 5.47 (m, 1H; CH–O), 6.90–8.30 ppm (m, 16H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=21.7$ (CH_3), 23.1 (CH_2, cod), 26.4 (CH_2, cod), 27.5 (CH_3), 29.3 (CH_3, *t*Bu), 29.7 (brs; CH_3, *t*Bu), 30.3 (CH_3, *t*Bu), 30.7 (CH_3, *t*Bu), 31.6 (brs; C, *t*Bu), 33.6 (C, *t*Bu), 33.7 (brs; C, *t*Bu), 34.3 (CH_2, cod), 34.8 (CMe_2), 33.9 (s; CH_2–C=), 34.2 (C, *t*Bu), 34.7 (CH_2), 34.9 (C, *t*Bu), 36.5 (CH_2, cod), 40.7 (d, $J_{C-P}=9.3$ Hz; CH_2, cod), 68.4 (brs; CH–O+CH=, cod), 70.4 (CH=, cod), 85.7 (d, $J_{C-P}=27.9$ Hz; CH=, cod), 101.2 (d, $J_{C-P}=8.6$ Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–153 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.2$ Hz; C-B, BAr_F), 174.4 ppm (C=N); elemental analysis calcd (%) for $C_{81}H_{84}BF_{24}IrNO_4P$: C 53.29, H 4.64, N 0.77; found: C 53.26, H 4.65, N 0.78.

[Ir(cod)(L5a)]BArF: Yield: 128 mg (94%); ^{31}P NMR ($CDCl_3$): $\delta=$ 100.2 ppm (s); ^{1}H NMR ($CDCl_3$): $\delta=1.28$ (s, 9H; CH_3, *t*Bu), 1.32 (s, 9H; CH_3, *t*Bu), 1.41 (s, 9H; CH_3, *t*Bu), 1.47 (m, 2H; CH_2, cod), 1.55 (m, 1H; CH_2–CH), 1.60 (s, 9H; CH_3, *t*Bu), 1.76 (m, 1H; CH_2–CH), 1.92 (m, 1H; CH_2), 1.99 (m, 1H; CH_2), 2.09 (m, 4H; CH_2, cod), 2.22 (m, 2H; CH_2, cod), 2.69 (m, 1H; CH_2–C=), 2.99 (dd, 1H, $^2J_{H-H}=17.7$, $^3J_{H-H}=4.8$ Hz; CH_2–C=), 3.41 (m, 1H; CH=, cod), 3.79 (brs, 2H; CH, CH=+cod), 4.51 (m, 1H; CH_2–O), 4.56 (m, 1H; CH_2–O), 4.78 (brs, 1H; CH=, cod), 5.19 (brs, 1H; CH=, cod), 6.50–8.50 ppm (m, 21H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=23.1$ (CH_2–C=), 23.9 (CH_2), 24.7 (CH_2, cod), 29.2 (CH_2, cod), 30.2 (CH_2–CH), 30.4 (CH_3, *t*Bu), 31.1 (CH_3, *t*Bu), 33.9 (CH_2, cod), 35.5 (C, *t*Bu), 36.1 (C, *t*Bu), 37.4 (CH_2, cod), 61.5 (CH=, cod), 70.2 (CH=, cod), 71.3 (brs; CH+CH_2–O), 96.1 (d, $J_{C-P}=22.0$ Hz; CH=, cod), 104.7 (d, $J_{C-P}=11.2$ Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 ppm (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–158 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.5$ Hz; C-B, BAr_F), 168.6 ppm (s, C=N), elemental analysis calcd (%) for $C_{82}H_{78}BF_{24}IrNO_3PS$: C 53.31, H 4.26, N 0.76; found: C 53.28, H 4.28, N 0.75.

[Ir(cod)(L5b)]BArF: Yield: 128 mg (96%); ^{31}P NMR ($CDCl_3$): $\delta=$ 96.4 ppm (s); ^{1}H NMR ($CDCl_3$): $\delta=1.41$ (s, 9H; CH_3, *t*Bu), 1.47 (m, 2H; CH_2, cod), 1.52 (m, 1H; CH_2–CH), 1.63 (s, 9H; CH_3, *t*Bu), 1.81 (m, 1H; CH_2–CH), 1.86 (m, 1H; CH_2), 1.96 (m, 1H; CH_2), 2.08 (m, 4H; CH_2, cod), 2.24 (m, 2H; CH_2, cod), 2.71 (m, 1H; CH_2–C=), 2.96 (dd, 1H, $^2J_{H-H}=17.7$, $^3J_{H-H}=4.8$ Hz; CH_2–C=), 3.46 (m, 1H; CH=, cod), 3.77 (brs, 2H; CH, CH=+cod), 3.82 (s, 3H; CH_3–O), 3.87 (s, 3H; CH_3–O), 4.48 (m, 1H; CH_2–O), 4.59 (m, 1H; CH_2–O), 4.76 (brs, 1H; CH=, cod), 5.19 (brs, 1H; CH=, cod), 6.50–8.50 ppm (m, 21H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=23.4$ (CH_2–C=), 23.5 (CH_2), 24.8 (CH_2, cod), 29.1 (CH_2, cod), 30.0 (CH_2–CH), 30.6 (CH_3, *t*Bu), 31.3 (CH_3, *t*Bu), 33.8 (CH_2, cod), 35.7 (C, *t*Bu), 36.0 (C, *t*Bu), 37.0 (CH_2, cod), 55.9 (CH_3–O), 61.3 (CH=, cod), 69.9 (CH=, cod), 71.6 (brs; CH+CH_2–O), 96.0 (d, $J_{C-P}=23.0$ Hz; CH=, cod), 105.1 (d, $J_{C-P}=12.5$ Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–158 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.5$ Hz; C-B, BAr_F), 169.6 ppm (s; C=N); elemental analysis calcd (%) for $C_{76}H_{66}BF_{24}IrNO_5PS$: C 50.84, H 3.71, N 0.78; found: C 50.89, H 3.79, N 0.75.

[Ir(cod)(L5c)]BArF: Yield: 124 mg (95%); ^{31}P NMR ($CDCl_3$): $\delta=$ 98.6 ppm (s); ^{1}H NMR ($CDCl_3$): $\delta=0.06$ (s, 9H; CH_3-Si), 0.52 (s, 9H; CH_3-Si), 1.30 (m, 2H; CH_2, cod), 1.44 (m, 1H; CH_2–CH), 1.85 (m, 1H; CH_2–CH), 1.89 (m, 1H; CH_2), 2.01 (m, 1H; CH_2), 2.19 (m, 4H; CH_2, cod), 2.39 (m, 2H; CH_2, cod), 2.73 (m, 1H; CH_2–C=), 2.99 (dd, 1H, $^2J_{H-H}=17.4$, $^3J_{H-H}=5.5$; CH_2–C=), 3.47 (m, 1H; CH=, cod), 3.93 (m, 1H; CH), 4.04 (brs, 1H; CH=, cod), 4.42 (brs, 1H; CH=, cod), 4.66 (m, 1H; CH_2–O), 4.76 (m, 1H; CH_2–O), 5.16 (brs, 1H; CH=, cod), 7.20–8.50 ppm (m, 23H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=-0.33$ (CH_3–Si), 0.74 (CH_3–Si), 23.4 (CH_2–C=), 23.5 (CH_2), 24.7 (CH_2, cod), 29.1 (CH_2, cod), 29.9 (CH_2–CH), 33.3 (CH_2, cod), 37.1 (CH_2, cod), 61.7 (CH=, cod), 67.2 (CH=, cod), 70.8 (brs; CH+CH_2–O), 97.2 (d, $J_{C-P}=21.9$ Hz; CH=, cod), 105.3 (d, $J_{C-P}=12.5$ Hz; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–154 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.5$ Hz; C-B, BAr_F), 169.6 ppm (s; C=N); elemental analysis calcd (%) for $C_{72}H_{62}BF_{24}IrNO_3PSSi_2$: C 48.93, H 3.54, N 0.79; found: C 48.95, H 3.56, N 0.78.

[Ir(cod)(L5d)]BArF: Yield: 133 mg (96%); ^{31}P NMR ($CDCl_3$): $\delta=$ 93.8 ppm (s); ^{1}H NMR ($CDCl_3$): $\delta=0.01$ (s, 9H; CH_3–Si), 0.61 (s, 9H; CH_3–Si), 1.15 (m, 2H; CH_2, cod), 1.41 (m, 1H; CH_2–CH), 1.73 (brs, 2H; CH_2, cod), 1.85 (m, 1H; CH_2–CH), 1.96 (m, 1H; CH_2), 2.06 (m, 1H; CH_2), 2.13 (m, 2H; CH_2, cod), 2.33 (m, 2H; CH_2, cod), 2.73 (m, 1H; CH_2–C=), 2.97 (dd, $^2J_{H-H}=18$, $^3J_{H-H}=4.8$ Hz, 1H; CH_2–C=), 3.15 (m, 1H; CH=, cod), 3.71 (brs, 1H; CH=, cod), 4.16 (m, 1H; CH), 4.23 (brs, 1H; CH=, cod), 4.62 (brs, 1H; CH_2–O), 4.73 (m, 1H; CH_2–O), 4.94 (brs, 1H; CH=, cod), 6.70–8.30 ppm (m, 27H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=$ -0.0 (CH_3–Si), 0.4 (CH_3–Si), 23.7 (CH_2–C=), 24.4 (CH_2), 26.1 (CH_2, cod), 28.4 (CH_2, cod), 31.2 (CH_2–CH), 34.3 (CH_2, cod), 36.6 (CH_2, cod), 68.1 (CH=, cod), 70.7 (CH+CH=, cod), 71.9 (CH_2–O), 95.3 (d, $J_{C-P}=$ 22.7 Hz; CH=, cod), 104.2 (brs; CH=, cod), 117.7 ppm (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–154 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.5$ Hz; C-B, BAr_F), 169.3 ppm (s, C=N); elemental analysis calcd (%) for $C_{80}H_{66}BF_{24}IrNO_3PSSi_2$: C 51.45, H 3.56, N 0.75; found: C 51.47, H 3.59, N 0.74.

[Ir(cod)(L5e)]BArF: Yield: 130 mg (94%); ^{31}P NMR ($CDCl_3$): $\delta=$ 103.8 ppm; ^{1}H NMR ($CDCl_3$): $\delta=0.14$ (s, 9H; CH_3–Si), 0.60 (s, 9H; CH_3–Si), 1.17 (m, 2H; CH_2, cod), 1.44 (m, 1H; CH_2–CH), 1.86 (m, 1H; CH_2–CH), 1.90 (m, 1H; CH_2), 1.99 (m, 1H; CH_2), 2.10 (m, 4H; CH_2, cod), 2.32 (m, 2H; CH_2, cod), 2.74 (m, 1H; CH_2–C=), 3.00 (dd, 1H, $^2J_{H-H}=23$, $^3J_{H-H}=5.4$ Hz; CH_2–C=), 3.49 (m, 1H; CH=, cod), 3.85 (m, 1H; CH), 3.97 (brs, 1H; CH=, cod), 4.23 (brs, 1H; CH=, cod), 4.72 (brs, 2H; CH_2–O), 5.17 (brs, 1H; CH=, cod), 6.60–8.30 ppm (m, 27H; CH=); ^{13}C NMR ($CDCl_3$): $\delta=-0.4$ (CH_3–Si), 0.9 (CH_3–Si), 23.4 (brs; CH_2+CH_2-C=), 24.7 (CH_2, cod), 29.2 (CH_2, cod), 31.2 (CH_2–CH), 33.3 (CH_2, cod), 37.1 (CH_2, cod), 61.6 (brs; CH=cod+CH), 67.2 (CH=, cod), 71.1 (CH_2–O), 97.6 (d, $J_{C-P}=21.6$ Hz; CH=, cod), 105.5 (brs; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–154 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B}=49.2$ Hz; C-B, BAr_F), 169.6 ppm (s; C=N); elemental analysis calcd (%) for

$C_{80}H_{66}BF_{24}IrNO_3PSSi_2$: C 51.45, H 3.56, N 0.75; found: C 51.46, H 3.58, N 0.75.

[Ir(cod)(L6a)]BArF: Yield: 129 mg (93%); ^{31}P NMR ($CDCl_3$): $\delta =$ 92.1 ppm (s); ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.34 (s, 9H; CH_3, *t*Bu), 1.35 (s, 9H; CH_3, *t*Bu), 1.37 (s, 9H; CH_3, *t*Bu), 1.46 (m, 2H; CH_2, cod), 1.52 (m, 1H; CH_2–CH), 1.63 (s, 9H; CH_3, *t*Bu), 1.73 (m, 1H; CH_2–CH), 1.77 (m, 1H; CH_2), 1.94 (m, 1H; CH_2), 2.09 (m, 4H; CH_2, cod), 2.27 (m, 2H; CH_2, cod), 2.79 (m, 2H; CH_2–C=), 3.26 (m, 1H; CH=, cod), 3.82 (brs, 1H; CH=, cod), 4.67 (brs, 2H; CH+CH=, cod), 4.89 (brs, 1H; CH=, cod), 6.50–8.50 ppm (m, 21H; CH=); ^{13}C NMR ($CDCl_3$): $\delta = 19.8$ (CH_3), 23.1 (CH_3), 24.6 (CH_2–C=), 25.4 (CH_2), 26.7 (CH_2, cod), 28.9 (CH_2, cod), 29.9 (CH_2–CH), 31.1 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 31.8 (CH_3, *t*Bu), 34.2 (brs; C, *t*Bu; CH_2, cod), 34.9 (C, *t*Bu), 35.7 (C, *t*Bu), 36.1 (C, *t*Bu), 36.8 (CH_2, cod), 53.7 (CH), 60.9 (CH=, cod), 70.1 (CH=, cod), 93.4 (d, $J_{C-P} = 24.2$ Hz; CH=, cod), 94.1 (CMe_2), 103.5 (m; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–158 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B} = 49.5$ Hz; C-B, BAr_F), 170.4 ppm (s, C=N); elemental analysis calcd (%) for $C_{84}H_{80}BF_{24}IrNO_3PS$: C 53.79, H 4.41, N 0.75; found: C 53.78, H 4.43, N 0.74.

[Ir(cod)(L7a)]BArF: Yield: 133 mg (96%); ^{31}P NMR ($CDCl_3$): $\delta =$ 92.5 ppm (s); ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.35 (s, 9H; CH_3, *t*Bu), 1.38 (s, 18H; CH_3, *t*Bu), 1.46 (m, 2H; CH_2, cod), 1.52 (m, 1H; CH_2–CH), 1.63 (s, 9H; CH_3, *t*Bu), 1.73 (m, 1H; CH_2–CH), 1.76 (m, 1H; CH_2), 1.94 (m, 1H; CH_2), 2.09 (m, 4H; CH_2, cod), 2.27 (m, 2H; CH_2, cod), 2.79 (m, 2H; CH_2–C=), 3.26 (m, 1H; CH=, cod), 3.82 (brs, 1H; CH=, cod), 4.67 (brs, 2H; CH+CH=, cod), 4.89 (brs, 1H; CH=, cod), 6.50–8.50 ppm (m, 21H; CH=); ^{13}C NMR ($CDCl_3$): $\delta = 19.9$ (CH_3), 23.1 (CH_3), 24.6 (CH_2–C=), 25.4 (CH_2), 26.7 (CH_2, cod), 28.9 (CH_2, cod), 30.1 (CH_2–CH), 31.1 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 31.7 (CH_3, *t*Bu), 34.2 (brs; C, *t*Bu; CH_2, cod), 34.9 (C, *t*Bu), 35.7 (C, *t*Bu), 36.1 (C, *t*Bu), 36.9 (CH_2, cod), 53.7 (CH), 60.9 (CH=, cod), 70.1 (CH=, cod), 93.4 (d, $J_{C-P} = 24.2$ Hz; CH=, cod), 94.2 (CMe_2), 103.5 (m; CH=, cod), 117.7 (brs; CH=, BAr_F), 119–134 (aromatic carbon atoms), 135.0 (brs; CH=BAr_F), 136–158 (aromatic carbon atoms), 161.9 (q, $^1J_{C-B} = 49.5$ Hz; C-B, BAr_F), 170.6 ppm (s, C=N); elemental analysis calcd (%) for $C_{84}H_{80}BF_{24}IrNO_3PS$: C 53.79, H 4.41, N 0.75; found: C 53.71, H 4.43, N 0.76.

Typical procedure for the hydrogenation of olefins: The alkene (1 mmol) and Ir complex (0.2 mol%) were dissolved in CH_2Cl_2 (2 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 (1.5 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 spectroscopy. The enantiomeric excesses of the hydrogenated products were determined by using the conditions previously described.[4d,5c]

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