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Indene Derived Phosphorus-Thioether Ligands for the Ir-Catalyzed Asymmetric Hydrogenation of Olefins with Diverse Substitution Patterns and Different Functional Groups

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Abstract: A family of phosphite/phosphinite-thioether ligands have been tested in the Ir-catalyzed asymmetric hydrogenation of a range of olefins (50 substrates in total). The presented ligands are synthesized in three steps from cheap indene and they are air-stable solids. Their modular architecture has been crucial to maximize the catalytic performance for each type of substrate. Improving most Ir-catalysts reported so far, this ligand family presents a broader substrate scope, covering different substitution patterns with different functional groups, ranging from unfunctionalized olefins, through olefins with poorly coordinative groups, to olefins with coordinative functional groups. α,β-Unsaturated acyclic and cyclic esters, ketones and amides were hydrogenated in enantioselectivities ranging from 83 to 99% ee. Enantioselectivities ranging from 91 to 98% ee were also achieved for challenging substrates such as unfunctionalized 1,1′-disubstituted olefins, functionalized tri- and 1,1′-disubstituted vinyl phosphonates, and β-cyclic enamides. The catalytic performance of the Ir-ligand assemblies was maintained when the environmentally benign 1,2-propylene carbonate was used as solvent.

Keywords: phosphorus-thioether ligands; asymmetric hydrogenation; iridium; α-β unsaturated compounds; β-cyclic enamides

Introduction

One major goal in the fine chemicals industry is to develop synthetic methodologies that produce chiral target compounds with high enantioselectivities and with a minimum environmental impact. Chemical transformations with high atom economy are therefore highly desirable. In this respect, the asymmetric hydrogenation (AH) of olefins has become a key process in asymmetric catalysis.[1] The structural diversity of prochiral olefins that can be used make this reaction even more interesting since it allows the preparation of very diverse chiral compounds with a range of functionalities. However, the versatility and broad applicability of chiral catalysts in this process remains an issue. Rh- and Ru-complexes have been established

as the optimal catalysts for the reduction of olefins bearing coordinating functional groups.[2] They are used, for example, in the synthesis of optically active α-amino acids and many pharmaceutically relevant compounds. Their efficiency relies in the chelating ability of the substrate which is key in transferring the chiral information from the catalyst to the product.[2] However, these catalysts behave in a less efficient manner and with poor enantiocontrol in the hydrogenation of substrates lacking coordinating groups adjacent to the double bond. Pioneered by Pfaltz et al.,[3] Ir-complexes of the type [Ir(cod)(P,N)*]BAr_F (BAr_F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were developed for the AH of unfunctionalized olefins.[4] Compared with functionalized olefins, the reduction of unfunctionalized substrates is less mature and has less synthetic utility. Essentially, most Ir-catalysts are still specific for a type of olefins with limited substitution patterns. For example, the most successful cases have been reported for *E*-trisubstituted alkenes and to a lesser extent for Z-trisubstituted and 1,1′-disubstituted.[4] The most used P,N-ligands have been phosphine/phosphinite-oxazoline ligands. Several modifications of their chiral backbone and coordinating groups have led to the discovery of other good performing ligands such as P-oxazole/imidazole/thiazole, P-pyridine and carbene-oxazoline/pyridine ligands.[4] Among them, our research group found that the introduction of a biaryl phosphite moiety improved the scope of successful substrates.[5,6] More recently, we also showed that phosphinite/phosphite-thioether ligands exhibit excellent performance in this transformation, providing enantioselectivities comparable to the best ones reported with Ir–P,N catalysts.[7] From a common simple backbone, the right combination of ligand parameters provided P,S-ligands that were appropriate in the AH of unfunctionalized trisubstituted olefins and the more challenging unfunctionalized 1,1′-disubstituted olefins.

Along the path from absolutely non-functionalized olefins to analogues bearing coordinating functional groups, there is a broad range of interesting alkene substrates with intermediate coordinating properties. α,β-Unsaturated esters, amides and ketones, among others, are examples of olefins containing functional groups that in most of the cases do not form stable chelate rings with the metal. Consequently, enantioselectivity is more difficult to control in these substrates.[4e,f] Remarkably, their hydrogenated products showcase interesting properties. For instance, many carboxylic acid derivatives with a stereogenic center at the α- or β-position exhibit biological activity (Figure 1).[1f,8] However, most of the methods used to prepare such compounds produce large amounts of chemical waste.[9] Enzyme-mediated reactions of racemic starting materials have also been used, although most of the reported methods are limited in substrate scope, usually require long reaction times and produce the enantiopure materials in low yields.[10] In contrast, the AH of α,β-unsaturated esters is a highly atom economic approach that allows the synthesis of a broad range of chiral carboxylic derivatives. The use of esters instead of the free acids is a better alternative, since they are easier to handle and can be later converted to the desired target molecule. The reduction of α,β-unsaturated ketones and amides also gives access to highly valuable building blocks,[1f,11] and their AH opens a direct, atom efficient path for preparing optically pure ketones and amides, whose synthesis up to now has mainly relied on non-catalytic methods with a limited substrate scope. For the AH of these three types of poorly coordinating substrates, Ir-catalysts have proved to be superior to Rh- and Ru-catalysts.[4e] However, the efficiency of those Ir-catalysts is still highly dependent on the substitution pattern and the geometry of the substrates.[12,13,14] The discovery of a family of catalysts with a wide substrate scope remains a central task in AH of this type of olefins.

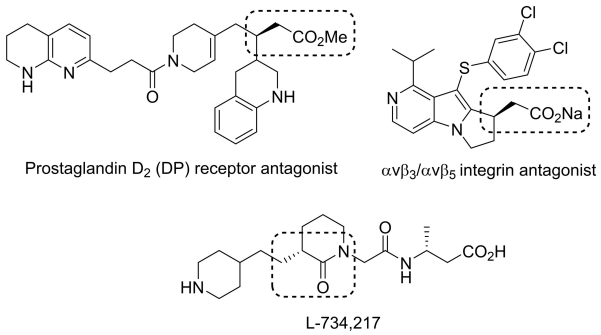


Figure 1. Examples of chiral carboxylic acid derivatives with biological activity.

To sum up, research is still needed to increase the synthetic utility of the AH of olefins, by searching for catalysts able to efficiently perform the reduction of prochiral olefins with functional groups with varying coordinating abilities. For this purpose, further development in the area of chiral ligands is a key task. Moreover, to be industrially interesting these ligands should be synthesized in few steps, from readily available materials and be easy to handle (preferably solid and air stable). As said above, P,thioether-ligands have proved to be excellent for the AH of olefins. The thioether moiety imparts higher stability with respect to commonly used phosphines and oxazolines, and involves the introduction of an additional chiral center close to the metal with a different steric environment around the sulfur than the trivalent phosphorus.[15,7f]

To continue the improvement of Ir-catalysts with air-stable and readily available ligands, we would like to disclose here the study of a simple but modular P,S-

ligand family (Figure 2, ligands **L1-L8a-f**) for the AH of olefins. These ligands are easily synthesized in only three steps from unexpensive indene.[16] The substrates studied cover different substitution patterns with different functional groups, ranging from unfunctionalized olefins, through olefins with poorly coordinative groups to olefins with a coordinative functional group that can also anchor the substrate to the metal. As a result, a broad range of α,β-unsaturated esters, ketones and amides have been hydrogenated with enantioselectivities up to 99% ee. In addition, the modularity of these P,S-ligands allowed us to identify highly enantioselective catalytic systems (up to 98% ee) for other challenging substrates: unfunctionalized 1,1′-disubstituted olefins, functionalized tri- and 1,1′-disubstituted vinyl phosphonates and β-cyclic enamides.

Results and Discussion

Synthesis of the Ir-Catalyst Precursors

The catalyst precursors were prepared in a two-step, one pot procedure. First, 0.5 equivalent of $[Ir(\mu\text{-}Cl)(cod)]_2$ reacts with one equivalent of the appropriate P,S-ligand (**L1-L8a-f**). Then, Cl^-/BAr_F^- counterion exchange was performed by reaction with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr_F$; 1 equiv) in the presence of water (Scheme 1). The Ir-catalyst precursors were isolated in pure form as air-stable red-orange solids in high yields (typically above 90%) after a simple extraction workup. Advantageously, no further purification was required.

The HRMS-ESI spectra of these materials were in agreement with the assigned structures showing the heaviest ions at m/z values corresponding to the loss of the BAr_F anion from the molecular species. The complexes were also characterized by ^{31}P, ^1H and ^{13}C NMR spectroscopy. The spectral assignments were made using ^1H–^1H and ^{13}C–^1H correlation measurements, which were in agreement with what expected for these C_1-symmetric iridium complexes. Variable-temperature (VT) NMR spectra in CD_2Cl_2 (+35 to −85 °C) indicated that only one isomer was present, except for ligands **L3** that showed two isomers in solution, and for ligands **L1d–e**, **L5d** and **L6b** that depicted broad NMR signals, which may be indicative of rapid exchange between the two possible diastereomers formed upon coordination of the thioether moiety to the metal atom (note that the coordinated S atom is a stereogenic center), to the interconversion of the different conformers of the six-membered chelate ring, or to both phenomena taking simultaneously place. To provide some light on the origin of these isomers, DFT calculations for [Ir(cod)**L3e**]BAr_F were performed (Figure 3). The population of isomers obtained by DFT calculation agree to that found by NMR spectroscopy. These DFT calculation also indicates that both isomers arise from the different coordination of the thioether group and different conformers of the chelate-ring. Thus, the major diastereoisomer shows an *R*-configuration of the S atom with a chair conformation of the chelate ring (Figure 3). On the other hand, the minor isomer adopts an *S*-configuration of the S atom with a boat conformation of the chelate ring (Figure 3). Unfortunately due to signal overlap in the ^1H-NMR spectrum, these studies could not be validated by NOE experiments.

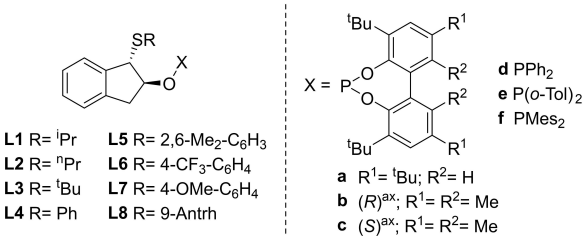
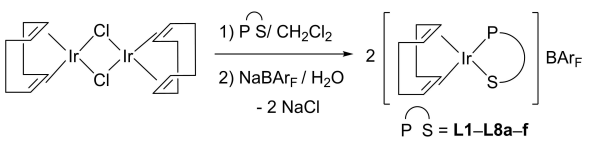


Figure 2. A readily available phosphite/phosphinite-thioether ligand library **L1**–**L8a**–**f**.



Scheme 1. Synthesis of [Ir(cod)(P–S)]BAr_F (P–S = **L1**–**L8a**–**f**).

Catalytic Experiments

In a first set of experiments the efficiency of phosphite/phosphinite-thioether ligands **L1-L8a-f** was evaluated in the AH of olefins with relevant poorly coordinative groups. We initially chose two ester substrates with different structural diversity, the α,β-unsaturated acyclic ester **S1** ((*E*)-3-phenylbut-2-enoate) and the α,β-unsaturated lactone with an exocyclic

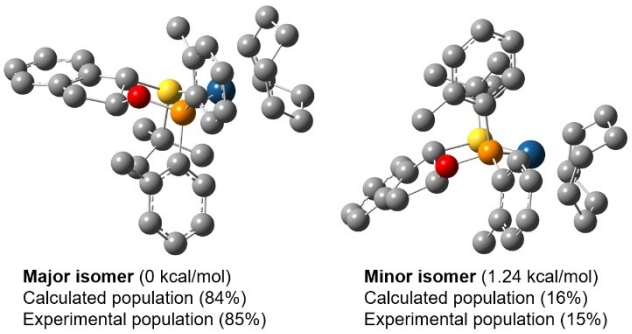
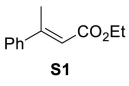
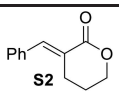


Figure 3. DFT-calculated structures for [Ir(cod)**L3e**]BAr_F complex. Hydrogen atoms have been omitted for simplicity.

double bond **S2** ((*E*)-3-benzylidenetetrahydro-2H-pyran-2-one). Although less studied,[12e,i,13f] the hydrogenation of substrates like **S2** is important because it gives access to cyclic carbonyl compounds with an α-chiral center.[1f,8a] To compare our results with the state of the art, we used the same optimal reaction conditions found in previous studies with other Ir–P,S catalytic systems.[7b] The results (Table 1) indicated that although the configuration of the phosphite moiety affects enantioselectivity (being better with an *S*-configuration for **S1** and the *R*-configuration for **S2**), the best enantioselectivities were achieved with the *o*-tolyl phosphinite moiety (**e**) for both substrates. In addition, a bulky thioether moiety is needed to maximize enantioselectivity, although each substrate requires a different thioether substituent. Thus, while for the α,β-unsaturated acyclic ester **S1** the highest enantioselectivity was achieved with Ir–**L8e** containing an anthracyl thioether group (entry 19, ee up to 94%), precatalyst Ir–**L3e**, containing a *tert*-butyl thioether group, was the best for cyclic substrate **S2** (**L3e**, entry 8, 94% ee). Enantioselectivities were maintained when the reaction was performed at low catalyst loading (0.5 mol%, entries 20 and 21) or when dichloromethane was replaced by the environmentally friendly solvent 1,2-propylene carbonate[17] (PC; entries 22 and 23).

Encouraged by these initial results, we investigated Ir–**L8e** and Ir–**L3e** in the reduction of a broad range of acyclic and cyclic α,β-unsaturated esters (**S3**–**S13**) with different substitution patterns and geometries (Figure 4). Advantageously, for acyclic α,β-unsaturated esters (**S3**–**S7**) the enantioselectivities were quite independent of the steric nature of the alkyl substituent in the substrate (**S1** and **S5**–**S7**, ee′s up to 98%) and the electronic properties of the phenyl ring (**S1** and **S3**–**S4**, ee′s up to 95%). The Ir–**L8e** catalytic system also provided high enantioselectivities independently of the geometry of the olefin substrate. Thus, high enantioselectivities were also attained in the reduction of the more challenging Z-analogue ((*E*)-**S7** vs (*Z*)-**S7**). Interestingly, the hydrogenation of acyclic ester **S8** containing substituents at both α and β positions also provided 98% of enantioselectivity. The scope was then extended to other cyclic α,β-unsaturated esters (lactones, **S9**–**S13**). Remarkably, with Ir–**L3e** all α,β-

Table 1. Ir-catalyzed asymmetric hydrogenation of **S1** and **S2** using **L1**–**L8a**–**f**.[a]

		 **S1**	 **S2**
Entry	Ligand	% ee[b]	% ee[b]
1	**L1a**	20 (*S*)	17 (*S*)
2	**L1b**	7 (*S*)	28 (*S*)
3	**L1c**	25 (*S*)	2 (*R*)
4	**L1d**	30 (*S*)	32 (*S*)
5	**L1e**	11 (*S*)	38 (*S*)
6	**L2b**	11 (*S*)	21 (*S*)
7	**L3b**	13 (*S*)	25 (*S*)
8	**L3e**	86 (*S*)	94 (*S*)
9	**L4b**	21 (*S*)	28 (*S*)
10	**L5b**	22 (*S*)	29 (*S*)
11	**L5c**	43 (*S*)	3 (*S*)
12	**L5d**	77 (S)	40 (*S*)
13	**L5e**	84 (*S*)	50 (*S*)
14	**L6b**	19 (*S*)	22 (*S*)
15	**L7b**	20 (*S*)	21 (*S*)
16	**L8b**	26 (*S*)	19 (*S*)
17	**L8c**	49 (*S*)	6 (*R*)[c]
18	**L8d**	90 (*S*)	48 (*S*)
19	**L8e**	94 (*S*)	62 (S)
20[d]	**L3e**	85 (*S*)	94 (*S*)[e]
21[d]	**L8e**	94 (*S*)	62 (*S*)[f]
22[g]	**L3e**	86 (*S*)	94 (*S*)
23[g]	**L8e**	93 (*S*)	61 (*S*)

[a] Reaction conditions: substrate (0.5 mmol), Ir-catalyst precursor (2 mol%), H_2 (100 bar), CH_2Cl_2 (2 mL), rt for 4 h (substrate **S1**) or 20 h (substrate **S2**). Full conversions were achieved in all cases unless otherwise stated.
[b] Enantiomeric excesses determined by HPLC analysis.
[c] 27% conversion.
[d] Reactions carried out using 0.5 mol% of catalyst precursors.
[e] Reaction carried out during 32 h.
[f] 98% conversion after 32 h.
[g] Reactions carried out using PC (1,2-propylene carbonate) as solvent.

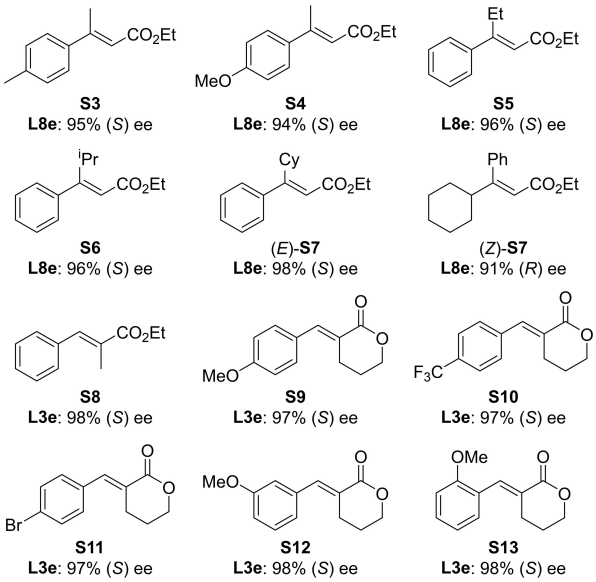


Figure 4. Substrate scope of the asymmetric hydrogenation of trisubstituted acyclic and cyclic α,β-unsaturated esters **S3**–**S13** with [Ir(cod)(**L1**–**L8a**–**f**)]BAr_F catalyst precursors. Reaction conditions: catalyst precursor (2 mol%), CH_2Cl_2, rt, H_2 (100 bar), 4 h for **S3**–**S8** or 20 h for **S9**–**S13**. Full conversions were achieved in all cases.

unsaturated lactones with an exocyclic double bond were reduced with comparable high enantioselectivities (ee′s up to 98%) regardless of the substitution pattern on the aryl moiety.

We then tested whether high enantioselectivities could also be achieved with olefins containing relevant, poorly coordinative groups other than the alkoxycarbonyl. For that purpose, we selected representative sets of substrates and found that enantioselectivities were also high for a range of α,β-unsaturated ketones (**S14**–**S21**), lactams (**S22**–**S27**) and the α,β-unsaturated amide **S28**. The results of these AH reactions are shown in Figure 5. We again found that the ligand components must be selected for each particular substrate type in order to obtain the highest enantioselectivity. Up to 87% enantiomeric excess could be obtained for a range of α,β-unsaturated ketones (substrates **S14**–**S18**) independently of the nature of the alkyl substituent and the electronic nature of the phenyl ring, with the Ir–**L3e** catalytic system. In addition, higher enantioselectivities of up to 92% ee were achieved with more challenging β,β′-disubstituted enones **S19** and **S20**, even in the reduction of substrate **S19** containing two β,β′-substituents with different size.[18] Like the lactone **S2**, cyclic α,β-unsaturated ketone **S21** and lactams **S22**–**S27** are challenging substrates whose hydrogenation has been usually overlooked[12e,i,13f,19] despite these frameworks are part of several natural products and have numerous synthetic utilities.[1f,8a] For the challenging cyclic ketone **S21** enantioselectivity was as high as 88%. Rh/Ru-catalysts have usually failed in affording high enantioselectivities for lactams. A possible reason is the exocyclic nature of the double bond, which cannot rotate towards the carbonyl oxygen, and this hampers the chelation of such substrates to the metal. Gratifyingly, high asymmetric induction (up to 99% ee) was also achieved in the reduction of several valuable lactams **S22**–**S27** but, unlike ketones, using the Ir–**L8e** catalytic system. Other challenging substrates are α,β-unsaturated amides,[12j,13c,14a] which can give access to important subunits in natural products. Ir–**L8e** catalyst was also able to reduce substrate **S28** yielding the corresponding amide with an α-stereogenic center with 84% ee.

Interestingly, we also found that the Ir–P,S catalysts are able to hydrogenate trisubstituted and 1,1′-disubstituted olefins lacking any extra functional group in ee's as high as 98% (substrates **S29**–**S38**, Figure 6). While the best enantioselectivity in the reduction of the unfunctionalized trisubstituted olefin **S29** is again achieved with phosphinite-based ligands (ligand **L8e**), for 1,1′-disubstituted olefins a phosphite moiety with a *R*-configuration is needed to maximize enantioselectivity (ligand **L5c**). 1,1′-Disubstituted substrates are less hindered than the trisubstituted olefins, so they are more easily hydrogenated but, in turn, face-selectivity

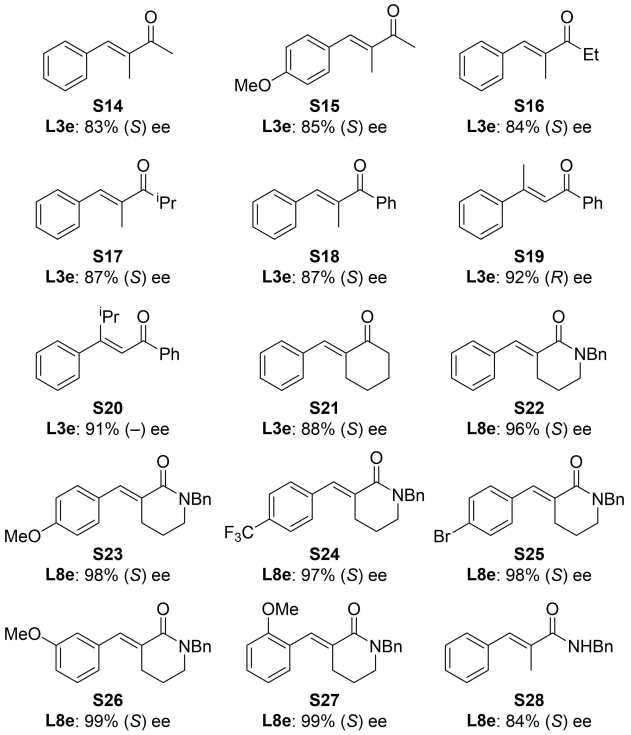


Figure 5. Substrate scope of the asymmetric hydrogenation of trisubstituted acyclic and cyclic α,β-unsaturated enones **S14**–**S21**, lactams **S22**–**S27** and amide **S28** with [Ir(cod)(**L1**–**L8a**–**f**)]BAr_F catalyst precursors. Reaction conditions: catalyst precursor (2 mol%), CH_2Cl_2, rt, H_2 (100 bar), 4 h for **S14**–**S21** or 20 h for **S22**–**S28**. Full conversions were attained in all cases.

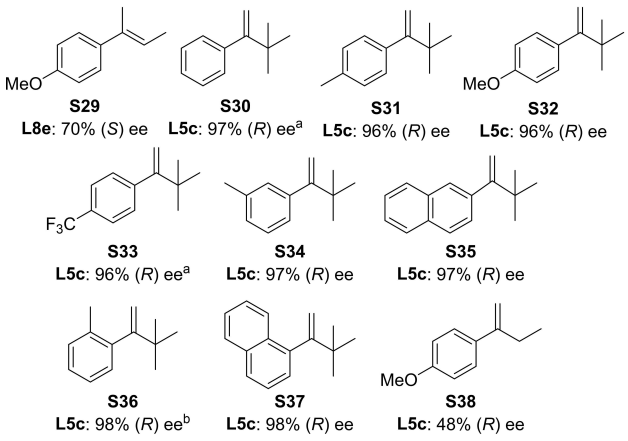
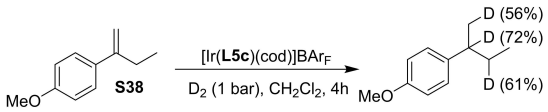


Figure 6. Selected results for the hydrogenation of trisubstituted and 1,1′-disubstituted olefins **S29**–**S38** with [Ir(cod)(**L1**–**L8a**–**f**)]BAr_F catalyst precursors. Reaction conditions: catalyst precursor (2 mol%), CH_2Cl_2, H_2 (100 bar **S29** and 1 bar for **S30**–**S38**), rt, 4 h. Full conversions were achieved in all cases. [a] The reaction using 1,2-propylene carbonate as solvent yielded the hydrogenation product in 96% ee. [b] The reaction using 1,2-propylene carbonate as solvent yielded the hydrogenation product in 98% ee.

is more difficult to control. Probably for this reason, the effective AH of a large range of 1,1′-disubstituted olefins has only been achieved quite recently, and with a few catalytic systems.[4e,20] It is to note that excellent enantioselectivities, comparable to the best ones reported previously, have been achieved with the present set of P-thiother ligands for a broad range of terminal olefins (**S30–S37**), independently of the electronic and steric properties of the substituents in the aryl moiety of the substrate (ee′s up to 98%). Like in other cases reported in the literature, the hydrogenation of the α-alkylstyrene derivative **S38** proceeded with a lower enantioselectivity than that of the analogue **S29**.[20] This result is in agreement with a competing isomerization pathway that was corroborated by studying the incorporation of deuterium in **S38** (Scheme 2).[21] It was found that deuterium was not only inserted in the double bond but also at the allylic position. Again, the results were maintained by using 1,2-propylene carbonate as solvent.

To further establish the potential of the P,S-ligands **L1–L8a–f** we studied the AH of substrates bearing strongly coordinating groups. We first considered the reduction of challenging tri- and di-substituted enol phosphinates (**S39–S43**, Figure 7). The hydrogenation of both types of substrates opens up an interesting route for obtaining chiral organophosphinates, which can be easily transformed into high-value compounds such as alcohols (an alternative route to the hydrogenation of ketones) and phosphines.[22] The Ir–**L8e** catalytic system can hydrogenate trisubstituted enol phosphinates (**S39–S41**) in high enantioselectivities (ee′s up to 94%). Remarkably, high enantioselectivities (ee′s up to 97%) can also be achieved in the reduction of 1,1′-disubstituted enol phosphinates **S42** and **S43** but, unlike trisubstituted enol phosphinates, using the Ir–**L1f** catalytic system. Among these results it should be noted that the efficient reduction of purely alkyl-substituted enol phosphinates (tri- and disubstituted substrates **S40** and **S42**, respectively) is a plausible alternative to the AH of prochiral alkyl-alkyl ketones to chiral alcohols by Rh/Ru-catalysts, which remains a challenging reaction due to the difficulty in differentiating enantiofaces involving two alkyl groups.[23]



Scheme 2. Deuterium labeling study of substrate **S38** with [Ir(cod)(**L5c**)]BAr_F catalyst precursor. The percentages of incorporation of deuterium in different positions are shown in brackets.

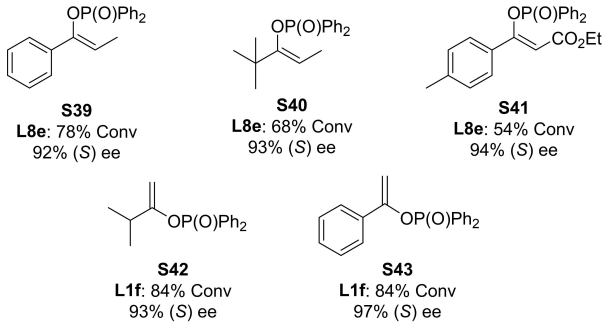
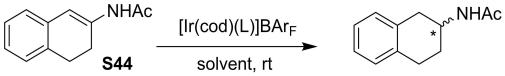


Figure 7. Asymmetric hydrogenation of tri- and 1,1′-disubstituted enol phosphinates **S39–S43** with [Ir(cod)(**L1–L8a–f**)]BAr_F catalyst precursors. Reaction conditions: catalyst precursor (2 mol%), CH_2Cl_2, H_2 (100 bar for **S39–S41** and 50 bar for **S42–S43**), rt, 4 h.

Finally, we focused on the reduction of cyclic β-enamides, which is another challenging type of functionalized olefins. While the enantioselective reduction of α-enamides can be carried out with success,[2] the AH of β-enamides remains a puzzling transformation, albeit the corresponding reduction products are key units in biologically active natural products and drugs such as rotigotine,[24] alnespirone[25] and robalzotan.[26] Most of the currently available catalysts, predominantly based on Rh and Ru, provide unsatisfactory enantioselectivities in reducing cyclic β-enamides.[27] More recently, it has been shown that Ir–P,X (X = N or S) catalysts can reduce cyclic β-enamides with higher enantioselectivities than the Rh/Ru-catalysts.[28] We first studied the reduction of the benchmark *N*-(3,4-dihydronaphthalen-2-yl)acetamide **S44** (Table 2) under previously reported conditions.[28c] Like for disubstituted olefins **S30–S37**, the presence of a phosphite group instead of a phosphinite moiety had a positive effect on the enantioselectivity (e.g. entries 2 and 11 vs 4 and 13). Regarding the effect of the thioether group, the bulkiness of the thioether group and its electronic nature had an important role on the enantioselectivity. The presence of an electron-poor thioether group worsened enantioselectivity (entry 14 (**L6b**) vs 15 (**L7b**)). The bulkiness of the thioether substituents has a different effect depending on the configuration of the phosphite group. While for ligands with less bulky thioether substituents the presence of (*R*)-biaryl phosphite moieties resulted in a matched combination (e.g. **L1b–c**, entry 2 vs 3), for ligands containing bulkier thioether substituents, the best enantioselectivity was achieved with (*S*)-biaryl phosphite moieties (e.g. **L5** and **L8**, entries 10 and 16 vs 11 and 17). As expected, the highest enantioselectivity of the series (91% ee, entry 6) is therefore provided with ligand **L2b**, which contains the optimal bulkiness of the thioether substituent in combination with the optimal configuration of the phosphite moiety. Advantageously, high enantioselectivities were still attained by lowering the hydrogen pressure to 10 bar of H_2 (entry 20). We were also pleased to find out that

Table 2. Ir-catalyzed asymmetric hydrogenation of **S44** using **L1–L8a–f**.[a]



Entry	Ligand	% Conv[b]	% ee[b]
1	**L1a**	20	33 (*S*)
2	**L1b**	35	88 (*S*)
3	**L1c**	18	39 (*R*)
4	**L1d**	70	64 (*S*)
5	**L1e**	100	83 (*S*)
6	**L2b**	85	91 (*S*)
7	**L3b**	70	61 (*S*)
8	**L3e**	80	17 (*R*)
9	**L4b**	50	57 (*S*)
10	**L5b**	100	66 (*S*)
11	**L5c**	100	77 (*R*)
12	**L5d**	41	70 (*R*)
13	**L5e**	62	63 (*R*)
14	**L6b**	34	21 (*S*)
15	**L7b**	57	73 (*S*)
16	**L8b**	100	30 (*S*)
17	**L8c**	100	74 (*R*)
18	**L8d**	100	21 (*R*)
19	**L8e**	100	65 (*R*)
20[c]	**L2b**	98	92 (*S*)
21[c,d]	**L2b**	86	91 (*S*)

[a] Reaction conditions: Substrate (0.5 mmol), Ir-catalyst precursor (1 mol%), H_2 (50 bar), CH_2Cl_2 (2 mL), rt, 18 h.
[b] Conversion measured by ^{1}H-NMR and enantiomeric excesses determined by HPLC.
[c] Reaction carried out using 10 bar of H_2 for 24 h.
[d] Reaction carried out using 1,2-propylene carbonate as solvent.

the enantioselectivity using 1,2-propylene carbonate remained as high as those observed with dichloromethane (entry 21).

We subsequently tested the scope of the Ir/**L2b** catalytic system in the reduction of a range of cyclic β-enamides derived from tetralones (Figure 8; substrates **S45–S49**). The high catalytic performance of this catalyst was maintained independently of the different substitution pattern of the 3,4-dihydronaphthalene core (92–94% ee). In addition, it could also effectively hydrogenate enamide **S50**, derived from 3-chromanone, in high enantioselectivity (95% ee). Among all these results, it is to note the high enantioselectivity achieved in the AH of **S49** and **S50**, whose hydrogenated products are key intermediates for the synthesis of rotigotine and alnespirone. The former is a dopamine agonist used for the treatment of Parkinson's disease,[24] while alnespirone is a selective 5-HT1 A receptor with antidepressant and anxiolytic properties.[25]

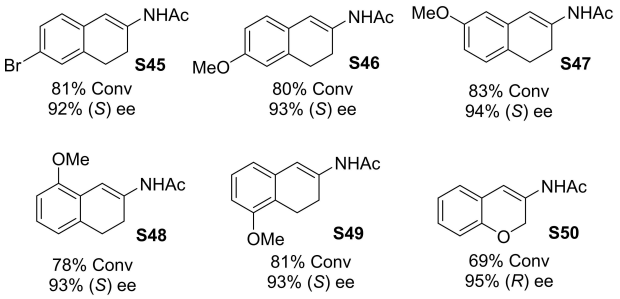


Figure 8. Asymmetric hydrogenation of functionalized olefins **S45–S50** with [Ir(cod)(**L2b**)]BAr$_F$ catalyst precursors. Reaction conditions: Catalyst precursor (2 mol%), CH_2Cl_2, H_2 (50 bar), rt, 18 h.

Conclusion

The asymmetric hydrogenation of diversely substituted olefins bearing variably coordinating functional groups is in no case a problem that can be addressed with a single catalyst. Bearing this consideration in mind, the design of modular, easy-to-assemble ligands that can adapt to manifold substrates becomes a fundamental task towards the development of efficient and widely applicable AH methodologies. In an effort towards this end, we have shown the utility of an indene-based phosphite/phosphinite-thioether ligand library for the Ir-catalyzed asymmetric hydrogenation of a broad range of substrates (50 olefins in total). The high modularity of these ligands helped us to identify highly enantioselective catalysts for AH of substrates covering different substitution patterns with different functional groups and coordination abilities, ranging from unfunctionalized olefins, through olefins with poorly coordinative groups, to olefins with coordinative functional groups. A range of α,β-unsaturated esters, ketones, even the much less studied lactones and lactams, and α,β-unsaturated amides were hydrogenated with enantioselectivities up to 99%. The best enantioselectivities were obtained with ligands containing an *o*-tolyl phosphinite moiety (e) and bulky thioether groups (ligand **L8e** for acyclic α,β-unsaturated esters, lactams and amides and ligand **L3e** for cyclic esters and α,β-unsaturated ketones). Enantioselectivities up to 98% ee were also achieved for other challenging substrates such as unfunctionalized 1,1′-disubstituted olefins, functionalized tri- and 1,1′-disubstituted vinyl phosphonates and β-cyclic enamides. While for the functionalized tri- and 1,1′-disubstituted vinyl phosphonates the best enantioselectivities are still achieved with phosphinite-based ligands **L8e** and **L1f**, respectively, for unfunctionalized 1,1-disubstituted substrates and cyclic β-enamides a phosphite moiety is needed to maximize enantioselectivities (ligands **L5c** and **L2b**, respectively). Usefully, friendly 1,2-propylene carbonate can be used with no loss of

enantioselectivity. These results open up the use of air stable, readily available and modular ligands to advance in the AH of a broad type of substrates with diverse functional groups with different coordination abilities and with different substitution patterns.

Experimental Section

General Considerations

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were purified and dried by standard procedures. Phosphorochloridites are easily prepared in one step from the corresponding biaryls.[29] Phosphite/phosphinite-thioether ligands **L1-L8a-f** were prepared as previously reported.[16] Substrates **S1**,[30] **S2**,[12e] **S3**–**S4**,[30] **S5**–**S7**,[12g] **S8**,[31] **S9**–**S10**,[32] **S11**,[33] **S12**,[32] **S13**,[33] **S14**,[34] **S15**–**S18**,[13b] **S19**,[35] **S20**,[13a] **S21**,[36] **S22**,[37] **S28**,[6g] **S29**,[38] **S30**–**S37**,[6g] **S38**,[39] **S39**–**S43**,[22b] **S44**,[40] **S45**–**S46**,[27j] **S47**,[41] **S48**,[27j] **S49**,[27i] **S50**[27a] were prepared following the reported procedures. ^{1}H, ^{13}C and ^{31}P 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, ^{13}C and ^{31}P assignments were made on the basis of ^{1}H–^{1}H gCOSY, ^{1}H–^{13}C gHSQC and ^{1}H–^{31}P gHMBC experiments.

Computational Details

All calculations were performed using the Gaussian 16 program.[42] Optimizations of [Ir(cod)**L3e**]BAr_F complexes were performed employing the B3LYP–D3[43] density functionaland the 6–31G(d)[44] basis set for all elements except for Ir for which SDD[45] was used. Solvation correction was applied in the course of the optimizations using the PCM model with the default parameters for dichloromethane.[46] The complexes were treated with charge +1 and in the singlet state. No symmetry constraints were applied. The energies were further refined by performing single-point calculations using the above-mentioned parameters, with the exception that the density functional used was PBE–D2[47,48] and the basis set was 6–311+G**[49] for all elements except for iridium. All energies reported are Gibbs free energies at 298.15 K and calculated as $\Delta G_{reported} = \Delta G_{B3LYP/6\text{-}31G(d)} + (\Delta E_{PBE\text{-}D2/6\text{-}311+G(d,p)} - \Delta E_{B3LYP/6\text{-}31G(d)})$.

General Procedure for the Preparation of [Ir(cod)(L1-L8a-f)]BAr_F

The corresponding ligand (0.037 mmol) was dissolved in CH_2Cl_2 (2 mL) and [Ir(μ-Cl)(cod)]$_2$ (12.5 mg, 0.0185 mmol) was added. The reaction mixture was refluxed at 50 °C for 1 h. After 5 min at room temperature, $NaBAr_F$ (38.6 mg, 0.041 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 dried with $MgSO_4$, filtered through a plug of celite and the solvent was evaporated to give the product as red-orange solids.

[Ir(cod)(L1a)]BAr_F: Yield: 67 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 114.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.49 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.63 (d, 6H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.91-2.10 (m, 5H, CH_2, cod), 2.22-2.27 (m, 3H, CH_2, cod), 3.02 (dd, 1H, CH_2, $^{2}J_{H\text{-}H}$ = 14.8 Hz, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 3.26 (dd, 1H, CH_2, $^{2}J_{H\text{-}H}$ = 15.2 Hz, $^{3}J_{H\text{-}H}$ = 7.6 Hz), 3.68–3.75 (m, 1H, CH, ^{i}Pr), 4.25 (d, 1H, CH–S, $^{3}J_{H\text{-}H}$ = 18.8 Hz), 4.47 (b, 1H, CH=, cod), 4.76 (b, 1H, CH=, cod), 4.98–5.07 (m, 1H, CH-OP), 5.09 (b, 1H, CH=cod), 5.43 (b, 1H, CH=, cod), 7.16–7.71 (m, 20H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.6 (CH_3, ^{i}Pr), 25.6 (CH_3, ^{i}Pr), 28.4 (b, CH_2, cod), 29.9 (CH_2, cod), 30.9 (b, CH_2, cod), 31.3 (CH_3, ^{t}Bu), 31.5 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 33.6 (b, CH_2, cod), 35.0 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 37.5 (d, CH_2, $^{3}J_{C\text{-}P}$ = 7.6 Hz), 48.3 (b, CH, ^{i}Pr), 55.0 (CH–S), 75.7 (b, CH=, cod), 78.4 (b, CH=, cod), 82.5 (CH-OP), 100.8 (b, CH=, cod), 104.3 (b, CH=, cod), 117.6-149.1 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^{1}J_{C\text{-}B}$ = 49.7 Hz). MS HR-ESI [found 947.4136 $C_{48}H_{67}IrO_3PS$ $(M)^+$ requires 947.4172].

[Ir(cod)(L1b)]BAr_F: Yield: 60 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 108.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$ = 6.4 Hz), 1.41 (s, 9H, CH_3, ^{t}Bu), 1.50 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.78 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.93–2.15 (m, 6H, CH_2, cod), 2.25 (b, 2H, CH_2, cod), 2.27 (s, 6H, CH_3), 2.89 (dd, 1H, CH_2, $^{2}J_{H\text{-}H}$ = 15.2 Hz, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 3.35 (dd, 1H, CH_2, $^{2}J_{H\text{-}H}$ = 15.6 Hz, $^{3}J_{H\text{-}H}$ = 8.4 Hz), 3.61–3.77 (m, 1H, CH, ^{i}Pr), 3.86 (b, 1H, CH=, cod), 4.53 (d, 1H, CH–S, $^{3}J_{H\text{-}H}$ = 11.2 Hz), 4.97 (b, 1H, CH=, cod), 5.06–5.13 (m, 2H, CH–OP, CH=, cod), 5.37 (b, 1H, CH=, cod), 7.20-7.70 (m, 18H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.8 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 24.7 (CH_3, ^{i}Pr), 24.9 (CH_3, ^{i}Pr), 28.9 (CH_2, cod), 30.0 (CH_2, cod), 31.8 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 32.3 (CH_2, cod), 32.5 (d, CH_2, cod, $J_{C\text{-}P}$ = 4.6 Hz), 34.7 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 38.2 (d, CH_2, $^{3}J_{C\text{-}P}$ = 6.8 Hz), 44.7 (CH, ^{i}Pr), 55.1 (CH–S), 71.9 (CH=, cod), 79.2 (CH-OP), 81.5 (CH=, cod), 98.0 (d, CH=, cod, $J_{C\text{-}P}$ = 16.9 Hz), 106.7 (d, CH=, cod, $J_{C\text{-}P}$ = 13.2 Hz), 117.4-145.0 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^{1}J_{C\text{-}B}$ = 49.7 Hz). MS HR-ESI [found 891.3519, $C_{44}H_{59}IrO_3PS$ $(M)^+$ requires 891.3546].

[Ir(cod)(L1c)]BAr_F: Yield: 62 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 111.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.60 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.63 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.77 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.82-1.91 (m, 2H, CH_2, cod), 2.03-2.15 (m, 4H, CH_2, cod), 2.22 (b, 2H, CH_2, cod), 2.28 (s, 6H, CH_3), 3.09 (dd, 1H, CH_2, $^{2}J_{H\text{-}H}$ = 15.2 Hz, $^{3}J_{H\text{-}H}$ = 9.2 Hz), 3.28 (dd, 1H, CH_2, $^{2}J_{H\text{-}H}$ = 15.6 Hz, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 3.63–3.70 (m, 1H, CH, ^{i}Pr), 3.85 (b, 1H, CH=, cod), 4.22 (d, 1H, CH–S, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 4.86 (b, 1H, CH=, cod), 4.92–4.98 (m, 1H, CH-OP), 5.03 (b, 1H, CH=cod), 5.41 (b, 1H, CH=, cod), 7.22–7.72 (m, 18H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 20.3 (CH_3), 24.0 (CH_3, ^{i}Pr), 25.6 (CH_3, ^{i}Pr), 28.1 (CH_2, cod), 29.7 (CH_2, cod), 30.6 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 32.0 (CH_3, ^{t}Bu), 33.3 (d, CH_2, cod, $J_{C\text{-}P}$ = 4.0 Hz), 34.7 (C, ^{t}Bu), 37.4 (d, CH_2, $^{3}J_{C\text{-}P}$ = 8.9 Hz), 48.2 (CH, ^{i}Pr), 54.4 (CH–S), 72.5 (CH=, cod), 79.9 (CH=, cod), 83.0 (d, CH-OP, $^{3}J_{C\text{-}P}$ = 5.5 Hz), 99.3 (d, CH=, cod, $J_{C\text{-}P}$ = 17.2 Hz), 104.6 (d, CH=, cod, $J_{C\text{-}P}$ = 10.8 Hz), 117.4-144.7 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^{1}J_{C\text{-}B}$ = 50.0 Hz). MS HR-ESI [found 891.3518, $C_{44}H_{59}IrO_3PS$ $(M)^+$ requires 891.3546].

[Ir(cod)(L1d)]BAr$_F$: Yield: 54 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 107.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (d, 6H, CH_3, ^{i}Pr, $^3J_{H-H}$ = 6.8 Hz), 1.95 –2.15 (m, 8H, CH_2, cod), 2.72 (b, 1H, CH, ^{i}Pr), 3.34 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 9.5 Hz), 3.52–3.57 (m, 2H, CH_2, CH=cod), 3.83 (b, 1H, CH=, cod), 4.20 (b, 1H, CH–S), 4.96 (b, 1H, CH=, cod), 5.11 (b, 1H, CH-OP), 5.23 (b, 1H, CH=, cod), 7.32–7.74 (m, 26H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.5 (CH_3, ^{i}Pr), 24.8 (CH_3, ^{i}Pr), 29.5 (CH_2, cod), 30.5 (CH_2, cod), 31.9 (CH_2, cod), 32.7 (CH_2, cod), 38.0 (d, CH_2, $^3J_{C-P}$ = 10.6 Hz), 48.5 (b, CH, ^{i}Pr), 57.2 (CH–S), 98.2 (b, CH=, cod), 101.0 (bs, CH=, cod), 117.7-136.9 (aromatic carbons), 161.8 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 693.1915, $C_{32}H_{37}$IrOPS (M)$^+$ requires 693.1926].

[Ir(cod)(L1e)]BAr$_F$: Yield: 54 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 116.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (m, 6H, CH_3, ^{i}Pr and CH_3, *o*-Tol), 1.57 (s, 3H, CH_3, *o*-Tol), 1.63 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$ = 5.2 Hz), 1.78 (b, CH_2, cod), 2.05–2.36 (m, 6H, CH_2, cod), 2.85 (b, 1H, CH=, cod), 2.97 (b, 1H, CH, ^{i}Pr), 3.18–3.24 (m, 1H, CH_2), 3.41–3.44 (m, 1H, CH_2), 3.82 (b, 1H, CH=, cod), 3.92 (b, 1H, CH–S), 3.99 (b, 1H, CH=, cod), 4.62–4.83 (b, 1H, CH=, cod), 5.09 (b, 1H, CH-OP), 5.35 (b, 1H, CH=, cod), 6.52–8.34 (m, 24H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.5 (CH_3, *o*-Tol), 22.2 (CH_3, *o*-Tol), 24.2 (CH_3, ^{i}Pr), 24.4 (CH_3, ^{i}Pr), 27.5 (CH_2, cod), 29.8 (CH_2, cod), 32.2 (CH_2, cod), 34.2 (CH_2, cod), 37.5 (CH_2), 49.8 (b, CH, ^{i}Pr), 57.6 (CH–S), 75.9 (CH=, cod), 77.2 (b, CH-OP), 87.4 (b, CH=, cod), 93.6 (b, CH=, cod), 101.0 (b, CH=, cod), 117.4-143.1 (aromatic carbons), 161.7 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 721.2243, $C_{34}H_{41}$IrOPS (M)$^+$ requires 721.2240].

[Ir(cod)(L2b)]BAr$_F$: Yield: 62 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 107.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, 3H, CH_3, Pr, $^3J_{H-H}$ = 6.8 Hz), 1.42 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.57–1.67 (m, 2H, CH_2, Pr), 1.78 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.94–1.99 (m, 2H, CH_2, cod), 2.04 (m, 2H, CH_2, cod), 2.18 (m, 2H, CH_2, cod), 2.22–2.30 (m, 2H, CH_2, cod), 2.28 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.77–2.81 (m, 2H, CH_2, Pr), 2.95 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 9.2 Hz), 3.34 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 7.6 Hz), 3.44 (b, 1H, CH=, cod), 4.43 (d, 1H, CH–S, $^3J_{H-H}$ = 8.8 Hz), 4.93–5.01 (m, 2H, CH-OP and CH=cod), 5.05–5.09 (m, 1H, CH=, cod), 5.31 (b, 1H, CH=, cod), 7.22–7.70 (m, 18H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2 (CH_3, Pr), 16.5 (CH_3), 16.7 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 21.8 (CH_2, Pr), 29.2 (CH_2, cod), 29.6 (CH_2, cod), 31.9 (CH_3, ^{t}Bu, CH_2, cod), 32.3 (CH_3, ^{t}Bu), 33.1 (CH_2, cod), 35.0 (C, ^{t}Bu), 37.3 (CH_2, Pr), 38.1 (d, CH_2, $^3J_{C-P}$ = 6.8 Hz), 53.8 (CH–S), 70.9 (CH=, cod), 79.3 (CH–OP), 82.1 (CH=, cod), 98.5 (d, CH=, cod, J_{C-P} = 17.5 Hz), 108.8 (d, CH=, cod, J_{C-P} = 14.6 Hz), 117.4–137.0 (aromatic carbons), 161.7 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 50.5 Hz). MS HR-ESI [found 889.3509, $C_{44}H_{59}IrO_3PS$ (M)$^+$ requires 889.3523].

[Ir(cod)(L3b)]BAr$_F$: Yield: 60.2 mg (92%). Major isomer (65%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 107.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9H, CH_3, ^{t}Bu), 1.45 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.77 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.00–2.40 (m, 8H, CH_2, cod), 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.82 (m, 1H, CH_2), 3.41 (m, 1H, CH_2), 3.79 (m, 1H, CH=, cod), 4.78 (m, 1H, CH–S), 4.95 (m, 1H, CH=, cod), 5.24 (m, 1H, CH=, cod), 5.48 (m, 1H, CH=, cod), 5.67 (m, 1H, CH-OP), 7.20–7.80 (m, 18H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.7 (CH_3), 20.3 (b, CH_3), 28.4–33.0 (CH_2, cod), 31.6–34.0 (CH_3, ^{t}Bu), 34.5–35.2 (C, ^{t}Bu), 38.4 (CH_2), 58.9 (CH–S), 68.9 (CH=, cod), 79.4 (CH=, cod), 81.0 (CH-OP), 99.4 (d, CH=, cod, J_{C-P} = 14.3 Hz), 110.5 (d, CH=, cod, J_{C-P} = 18.2 Hz), 117.4–135.9 (aromatic carbons), 161.6 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 49.7 Hz). Minor isomer (35%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 105.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9H, CH_3, ^{t}Bu), 1.48 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 9H, CH_3, ^{t}Bu), 1.77 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.00–2.40 (m, 8H, CH_2, cod), 3.12 (s, 3H, CH_3), 3.27 (s, 3H, CH_3), 3.12 (m, 1H, CH_2), 3.27 (m, 1H, CH_2), 4.12 (m, 1H, CH–S), 4.48 (m, 1H, CH=, cod), 4.56 (m, 1H, CH=, cod), 4.94 (m, 1H, CH-OP), 5.48 (m, 1H, CH=, cod), 6.02 (m, 1H, CH=, cod), 7.20–7.80 (m, 18H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.7 (CH_3), 20.3 (b, CH_3), 28.4–33.0 (CH_2, cod), 31.6–34.0 (CH_3, ^{t}Bu), 34.5–35.2 (C, ^{t}Bu), 36.5 (CH_2), 49.9 (CH–S), 68.9 (CH=, cod), 81.3 (CH–OP), 82.9 (CH=, cod), 93.5 (b, CH=, cod), 95.7 (b, CH=, cod), 117.4-135.9 (aromatic carbons), 161.6 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 905.3711, $C_{45}H_{61}IrO_3PS$ (M)$^+$ requires 905.3703].

[Ir(cod)(L3e)]BAr$_F$: Yield: 52.6 mg (89%). Major isomer (85%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 116.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9H, CH_3, ^{t}Bu), 1.70–2.40 (m, 8H, CH_2, cod), 2.27 (s, 3H, CH_3, *o*-Tol), 2.72 (s, 3H, CH_3, *o*-Tol), 2.92 (b, 1H, CH=, cod), 3.28 (dd, 1H, CH_2, $^2J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 7.6 Hz), 3.42 (dd, 1H, CH_2, $^2J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.93 (b, 1H, CH=, cod), 4.21 (d, 1H, CH–S, $^3J_{H-H}$ = 9.6 Hz), 4.82 (b, 1H, CH=, cod), 5.08 (m, 1H, CH-OP), 5.47 (b, 1H, CH=, cod), 6.42 (m, 1H, CH=), 7.00-7.80 (m, 22H, CH=), 8.24 (dd, 1H, $^3J_{H-H}$ = 17.6 Hz, $^3J_{H-H}$ = 7.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.4 (CH_3, *o*-Tol), 22.5 (CH_3, *o*-Tol), 27.3 (CH_2, cod), 29.7 (CH_2, cod), 30.0 (CH_2, cod), 31.5 (CH_2, cod), 31.9 (CH_3, ^{t}Bu), 34.0 (C, ^{t}Bu), 37.5 (d, CH_2, $^3J_{C-P}$ = 4.2 Hz), 52.5 (CH–S), 74.4 (CH=, cod), 76.6 (CH=, cod), 87.4 (CH-OP), 93.6 (d, CH=, cod, J_{C-P} = 15.2 Hz), 104.0 (d, CH=, cod, J_{C-P} = 16.0 Hz), 117.4–142.9 (aromatic carbons), 161.6 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 48.8 Hz). Minor isomer (15%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 115.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 9H, CH_3, ^{t}Bu), 1.70–2.40 (m, 8H, CH_2, cod), 2.29 (s, 3H, CH_3, *o*-Tol), 2.60 (s, 3H, CH_3, *o*-Tol), 2.92 (b, 1H, CH=, cod), 3.12 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.42 (m, 1H, CH_2), 3.57 (m, 1H, CH=, cod), 4.24 (b, 1H, CH–S), 4.76 (b, 1H, CH=, cod), 5.09 (m, 1H, CH-OP), 5.29 (b, 1H, CH=, cod), 6.60 (m, 1H, CH=), 7.00–7.80 (m, 22H, CH=), 8.65 (dd, 1H, $^3J_{H-H}$ = 17.6 Hz, $^3J_{H-H}$ = 7.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.2 (CH_3, *o*-Tol), 22.7 (CH_3, *o*-Tol), 27.0 (CH_2, cod), 29.3 (CH_2, cod), 29.5 (CH_2, cod), 30.0 (CH_2, cod), 31.5 (CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 37.0 (b, CH_2), 52.9 (CH–S), 70.6 (CH=, cod), 76.0 (CH=, cod), 86.4 (CH-OP), 94.2 (b, CH=, cod), 103.8 (b, CH=, cod), 117.4-142.9 (aromatic carbons), 161.6 (q, C–B, BAr$_F$, $^1J_{C-B}$ = 48.8 Hz). MS HR-ESI [found 735.2398, $C_{35}H_{43}$IrOPS (M)$^+$ requires 735.2396].

[Ir(cod)(L4b)]BAr$_F$: Yield: 61 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 104.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9H, CH_3, ^{t}Bu), 1.59 (s, 9H, CH_3, ^{t}Bu), 1.63-1.91 (m, 4H, CH_2, cod), 1.75 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.12-2.36 (m, 4H, CH_2, cod), 2.29 (s, 6H, CH_3), 2.89 (b,

1H, CH=, cod), 3.00 (dd, 1H, CH_2, $^2J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.37 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 8.0 Hz), 4.19 (m, 1H, CH=, cod), 4.67 (m, 1H, CH=, cod), 4.81–4.91 (m, 1H, CH-OP), 5.17 (b, 1H, CH=, cod), 5.21 (d, 1H, CH–S, $^3J_{H-H}$ = 9.6 Hz), 6.23-7.74 (m, 23H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (CH_3), 16.6 (CH_3), 20.2 (CH_3), 20.5 (CH_3), 26.4 (CH_2, cod), 29.9 (CH_2, cod), 31.1 (CH_2, cod), 31.8 (CH_3, ^{t}Bu), 32.8 (CH_3, ^{t}Bu), 34.7 (CH_2, cod), 35.0 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 37.8 (d, CH_2, $^3J_{C-P}$ = 7.4 Hz), 55.9 (CH–S), 67.9 (CH=, cod), 78.6 (CH=, cod), 79.4 (CH-OP), 101.2 (d, CH=, cod, J_{C-P} = 14.5 Hz), 106.0 (d, CH=, cod, J_{C-P} = 15.3 Hz), 117.4-143.6 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C-B}$ = 50.4 Hz). MS HR-ESI [found 923.3367, $C_{47}H_{57}IrO_3PS$ $(M)^+$ requires 923.3366].

[Ir(cod)(L5b)]BAr_F: Yield: 64 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 104.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 9H, CH_3, ^{t}Bu), 1.60 (s, 9H, CH_3, ^{t}Bu), 1.65-1.84 (m, 4H, CH_2, cod), 1.76 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 2.13-2.38 (m, 4H, CH_2, cod), 2.29 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.72 (m, 1H, CH=, cod), 2.95 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.08 (s, 3H, CH_3), 3.38 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 7.6 Hz), 3.92 (m, 1H, CH=, cod), 4.72 (m, 1H, CH=, cod), 4.89 (m, 1H, CH-OP), 5.12 (d, 1H, CH–S, $^3J_{H-H}$ = 8.8 Hz), 5.18 (b, 1H, CH=, cod), 6.08-7.70 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 22.8 (CH_3), 22.9 (CH_3), 25.7 (CH_2, cod), 30.5 (CH_2, cod), 31.0 (CH_2, cod), 31.8 (CH_3, ^{t}Bu), 32.7 (CH_3, ^{t}Bu), 35.0 (CH_2, cod), 35.2 (C, ^{t}Bu), 37.8 (d, CH_2, $^3J_{C-P}$ = 7.6 Hz), 53.7 (CH–S), 66.2 (CH=, cod), 77.7 (CH=, cod), 80.0 (CH-OP), 102.1 (d, CH=, cod, J_{C-P} = 13.8 Hz), 104.6 (d, CH=, cod, J_{C-P} = 16.1 Hz), 117.4–143.8 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 951.3674, $C_{49}H_{61}IrO_3PS$ $(M)^+$ requires 951.3679].

[Ir(cod)(L5c)]BAr_F: Yield: 63 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 108.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9H, CH_3, ^{t}Bu), 1.59 (s, 9H, CH_3, ^{t}Bu), 1.71–1.89 (m, 4H, CH_2, cod), 1.71 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.97–2.20 (m, 4H, CH_2, cod), 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 2.99–3.08 (m, 2H, CH_2 and CH=cod), 3.31 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 8.4 Hz), 4.26 (m, 1H, CH=, cod), 4.67 (m, 1H, CH=, cod), 4.74 (m, 1H, CH=, cod), 4.80 (d, 1H, CH–S, $^3J_{H-H}$ = 8.8 Hz), 5.31-5.35 (m, 1H, CH-OP), 5.88–7.63 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.7 (CH_3), 16.8 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 23.5 (CH_3), 24.3 (CH_3), 27.6 (CH_2, cod), 29.9 (d, CH_2, cod, J_{C-P} = 10.0 Hz), 31.8 (CH_3, ^{t}Bu), 32.1 (CH_2, cod), 32.9 (CH_3, ^{t}Bu), 34.2 (CH_2, cod), 35.1 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 37.5 (d, CH_2, $^3J_{C-P}$ = 9.2 Hz), 56.4 (CH–S), 67.3 (CH=, cod), 77.4 (CH=, cod), 86.3 (d, CH-OP, $^2J_{C-P}$ = 6.0 Hz), 103.4 (d, CH=, cod, J_{C-P} = 14.8 Hz), 104.7 (d, CH=, cod, J_{C-P} = 13.9 Hz), 117.7-144.7 (aromatic carbons), 161.9 (q, C–B, BAr_F, $^1J_{C-B}$ = 50.1 Hz). MS HR-ESI [found 951.3641, $C_{49}H_{61}IrO_3PS$ $(M)^+$ requires 951.3679].

[Ir(cod)(L5d)]BAr_F: Yield: 55 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 114.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75–1.86 (m, 2H, CH_2, cod), 1.93–2.01 (m, 2H, CH_2, cod), 2.10–2.15 (m, 1H, CH_2, cod), 2.20–2.40 (m, 3H, CH_2, cod), 2.57 (s, 3H, CH_3), 3.02 (s, 3H, CH_3), 3.07 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.19 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.27 (m, 1H, CH=, cod), 3.41 (m, 1H, CH=, cod), 3.88 (m, 1H, CH=, cod), 4.49–4.58 (m, 1H, CH-OP), 5.05 (d, 1H, CH–S, $^3J_{H-H}$ = 8.4 Hz), 5.11 (m, 1H, CH=, cod), 6.09–7.94 (m, 29H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.2 (CH_3), 23.6 (CH_3), 27.3 (CH_2, cod), 30.7 (CH_2, cod), 31.0 (CH_2, cod), 33.6 (CH_2, cod), 38.3 (d, CH_2, $^3J_{C-P}$ = 7.6 Hz), 52.9 (CH–S), 69.3 (CH=, cod), 74.9 (CH=, cod), 82.5 (CH–OP), 97.2 (d, CH=, cod, J_{C-P} = 10.0 Hz), 98.6 (d, CH=, cod, J_{C-P} = 13.0 Hz), 117.4–143.2 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 755.2085, $C_{37}H_{39}IrOPS$ $(M)^+$ requires 755.2083].

[Ir(cod)(L5e)]BAr_F: Yield: 56 mg (96%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 118.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68–1.85 (m, 2H, CH_2, cod), 1.95–2.19 (m, 2H, CH_2, cod), 2.23 (s, 3H, CH_3), 2.25–2.47 (m, 4H, CH_2, cod), 2.53 (s, 3H, CH_3), 2.92 (s, 4H, CH=, cod and CH_3), 3.03 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.15 (s, 3H, CH_3), 3.15–3.20 (m, 2H, CH=cod, CH_2), 3.75 (m, 1H, CH=, cod), 4.32-4.42 (m, 1H, CH-OP), 5.08 (b, 1H, CH=, cod), 5.24 (d, 1H, CH–S, $^3J_{H-H}$ = 8.4 Hz), 5.89–9.06 (m, 27H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (CH_3), 22.3 (d, CH_3, $^3J_{C-P}$ = 6.9 Hz), 23.1 (CH_3), 26.7 (CH_2, cod), 29.9 (CH_2, cod), 31.7 (CH_2, cod), 34.3 (CH_2, cod), 38.3 (d, CH_2, $^3J_{C-P}$ = 7.6 Hz), 52.0 (CH–S), 67.9 (CH=, cod), 77.2 (CH=, cod), 81.4 (CH-OP), 96.5 (d, CH=, cod, J_{C-P} = 9.2 Hz), 96.8 (d, CH=, cod, J_{C-P} = 13.8 Hz), 117.4–143.5 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 783.2401, $C_{39}H_{43}IrOPS$ $(M)^+$ requires 783.2396].

[Ir(cod)(L6b)]BAr_F: Yield: 69 mg (97%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 104.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 9H, CH_3, ^{t}Bu), 1.64–1.71 (m, 4H, CH_2, cod), 1.76 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.08–2.22 (m, 4H, CH_2, cod), 2.29 (s, 6H, CH_3), 2.99-3.05 (m, 2H, CH_2 and CH=, cod), 3.39 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 7.6 Hz), 4.10 (m, 1H, CH=, cod), 4.76 (b, 1H, CH=, cod), 4.84–4.92 (m, 1H, CH-OP), 5.13 (b, 1H, CH=, cod), 5.23 (d, 1H, CH–S, $^3J_{H-H}$ = 9.2 Hz), 6.23–7.89 (m, 22H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (CH_3), 16.6 (CH_3), 20.2 (CH_3), 20.4 (CH_3), 26.6 (CH_2, cod), 29.8 (CH_2, cod), 31.2 (CH_2, cod), 31.8 (CH_3, ^{t}Bu), 32.8 (CH_3, ^{t}Bu), 34.5 (CH_2, cod), 35.0 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 37.7 (CH_2), 56.1 (CH–S), 68.9 (CH=, cod), 79.3 (CH=, cod), 79.7 (CH-OP), 100.9 (d, CH=, cod, J_{C-P} = 13.7 Hz), 105.4 (d, CH=, cod, J_{C-P} = 15.3 Hz), 117.4–143.5 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C-B}$ = 49.7 Hz). MS HR-ESI [found 991.3222, $C_{48}H_{56}F_3IrO_3PS$ $(M)^+$ requires 991.3240].

[Ir(cod)(L7b)]BAr_F: Yield: 64 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 104.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 9H, CH_3, ^{t}Bu), 1.63-1.94 (m, 4H, CH_2, cod), 1.75 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.07–2.37 (m, 4H, CH_2, cod), 2.29 (s, 6H, CH_3), 2.86 (m, 1H, CH=, cod), 2.98 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.36 (dd, 1H, CH_2, $^2J_{H-H}$ = 15.2 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.84 (s, 3H, CH_3, MeO), 4.30–4.33 (m, 1H, CH=, cod), 4.67 (b, 1H, CH=, cod), 4.79-4.88 (m, 1H, CH-OP), 5.12 (d, 1H, CH–S, $^3J_{H-H}$ = 9.2 Hz), 5.16 (b, 1H, CH=, cod), 6.31–7.71 (m, 22H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (CH_3), 16.6 (CH_3), 20.2 (CH_3), 20.5 (CH_3), 26.3 (CH_2, cod), 30.0 (CH_2,

cod), 31.0 (CH_2, cod), 31.8 (CH_3, ^{t}Bu), 32.8 (CH_3, ^{t}Bu), 34.9 (CH_2, cod), 35.0 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 37.8 (d, CH_2, $^3J_{C\text{-}P}$ = 8.1 Hz), 55.6 (CH_3, MeO), 56.2 (CH–S), 67.7 (CH=, cod), 78.5 (CH=, cod), 79.4 (CH-OP), 101.3 (d, CH=, cod, $J_{C\text{-}P}$ = 14.4 Hz), 106.0 (d, CH=, cod, $J_{C\text{-}P}$ = 16.3 Hz), 116.2–163.4 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C\text{-}B}$ = 50.5 Hz). MS HR-ESI [found 955.3512, $C_{48}H_{56}F_3IrO_3PS$ $(M)^+$ requires 955.3501].

[Ir(cod)(L8b)]BAr_F: Yield: 57.1 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 104.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14–1.17 (m, 2H, CH_2, cod), 1.66 (s, 9H, CH_3, ^{t}Bu), 1.69 (s, 9H, CH_3, ^{t}Bu), 1.73-1.82 (m, 2H, CH_2, cod), 1.79 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.09-2.26 (m, 2H, CH_2, cod), 2.31 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.78 (m, 1H, CH=, cod), 2.93 (dd, 1H, CH^2, $^2J_{H\text{-}H}$ = 15.2 Hz, $^3JH_{\text{-}H}$ = 9.2 Hz), 3.39 (dd, 1H, CH_2, $^2J_{H\text{-}H}$ = 15.6 Hz, $^3J_{H\text{-}H}$ = 8.0 Hz), 3.53 (m, 1H, CH=, cod), 4.83 (b, 1H, CH=, cod), 4.99-5.03 (m, 1H, CH-OP), 5.35 (d, 1H, CH–S, $^3J_{H\text{-}H}$ = 9.2 Hz), 5.37 (b, 1H, CH=, cod), 5.50–9.47 (m, 27H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.7 (CH_3), 20.3 (CH_3), 20.6 (CH_3), 24.9 (CH_2, cod), 30.3 (CH_2, cod), 31.0 (CH_2, cod), 31.9 (CH_3, ^{t}Bu), 32.8 (CH_3, ^{t}Bu), 35.1 (CH_2, cod and C, ^{t}Bu), 35.3 (C, ^{t}Bu), 37.7 (CH2), 54.5 (CH–S), 65.8 (CH=, cod), 78.3 (CH=, cod), 79.9 (CH-OP), 103.1 (CH=, cod, $J_{C\text{-}P}$ = 13.7 Hz), 105.6 (CH=, cod, $J_{C\text{-}P}$ = 16.0 Hz), 117.4–143.9 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C\text{-}B}$ = 49.8 Hz). MS HR-ESI [found 1025.3706, $C_{55}H_{61}IrO_3PS$ $(M)^+$ requires 1025.3703].

[Ir(cod)(L8c)]BAr_F: Yield: 35 mg (24%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 106.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53–1.61 (m, 1H, CH_2, cod), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.75–2.09 (m, 6H, CH_2, cod), 1.80 (s, 3H, CH_3), 1.81 (s, 12H, ^{t}Bu and CH_3), 2.30 (s, 3H, CH_3), 2.32-2.36 (m, 1H, CH_2, cod), 3.01 (m, 1H, CH_2), 3.14 (m, 1H, CH=, cod), 3.26 (m, 1H, CH_2), 4.46 (m, 1H, CH=, cod), 4.87 (m, 1H, CH=, cod), 4.96 (m, 1H, CH=, cod), 5.14 (d, 1H, CH–S, $^3J_{H\text{-}H}$ = 8.3 Hz), 5.39 (d, 1H, CH=, $^3J_{H\text{-}H}$ = 7.8 Hz), 5.55 (m, 1H, CH–OP), 6.39-9.09 (m, 27H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 26.6 (CH_2, cod), 30.0 (CH_2, cod), 31.7 (CH_3, ^{t}Bu), 32.7 (CH_3, ^{t}Bu), 33.0 (CH_2, cod), 34.6 (CH_2, cod), 34.9 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 37.7 (CH_2-O), 53.4 (CH–S), 66.8 (CH=, cod), 78.5 (CH=, cod), 84.1 (CH-OP), 102.2 (b, CH=, cod), 106.6 (b, CH=, cod), 117.4-144.7 (aromatic carbons), 161.1 (q, C–B, BAr_F, $^1J_{C\text{-}B}$ = 51.9 Hz). MS HR-ESI [found 1025.3706, $C_{55}H_{61}IrO_3PS$ $(M)^+$ requires 1025.3703].

[Ir(cod)(L8d)]BAr_F: Yield: 75 mg (60%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 115.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44–1.54 (m, 2H, CH_2, cod), 1.78–1.89 (m, 2H, CH_2, cod), 1.97–2.03 (m, 2H, CH_2, cod), 2.22–2.37 (m, 2H, CH_2, cod), 3.09 (m, 1H, CH_2), 3.25 (m, 1H, CH_2), 3.37 (m, 1H, CH=, cod), 3.54 (m, 2H, CH=, cod), 4.78 (m, 1H, CH=, cod), 5.17 (m, 1H, CH-OP), 5.25 (d, 1H, CH–S, $^3J_{H\text{-}H}$ = 8.7 Hz), 5.49 (d, 1H, CH=, $^3J_{H\text{-}H}$ = 7.8 Hz), 6.58-9.05 (m, 34H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.4 (CH_2, cod), 30.3 (CH_2, cod), 31.3 (CH_2, cod), 32.8 (CH_2, cod), 38.3 (CH_2), 54.2 (CH–S), 70.7 (CH=, cod), 74.1 (CH=, cod), 83.2 (CH-OP), 97.8 (d, CH=, cod, $J_{C\text{-}P}$ = 10.6 Hz), 99.9 (d, CH=, cod, $J_{C\text{-}P}$ = 12.4 Hz), 117.4-137.8 (aromatic carbons), 161.7 (q, C–B, BAr_F, $^1J_{C\text{-}B}$ = 49.9 Hz). MS HR-ESI [found 827.2087, $C_{43}H_{39}IrOPS$ $(M)^+$ requires 827.2083].

[Ir(cod)(L8e)]BAr_F: Yield: 55 mg (43%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 119.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42–1.47 (m, 2H, CH_2, cod), 1.64–1.76 (m, 1H, CH_2, cod), 1.79–2.00 (m, 3H, CH_2, cod), 2.08–2.16 (m, 1H, CH_2, cod), 2.26 (s, 3H, CH_3, *o*-Tol), 2.31–2.39 (m, 2H, CH_2, cod), 2.97 (m, 1H, CH=, cod), 2.99 (m, 1H, CH_2), 3.11 (m, 1H, CH_2), 3.13 (m, 1H, CH=, cod), 3.26 (s, 3H, CH_3, *o*-Tol), 3.43 (m, 1H, CH=, cod), 4.50 (m, 1H, CH-OP), 5.07 (d, 1H, CH=, $^3J_{H\text{-}H}$ = 7.8 Hz), 5.21 (m, 1H, CH=, cod), 5.51 (d, 1H, CH–S, $^3J_{H\text{-}H}$ = 9.0 Hz), 6.49-9.49 (m, 32H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (CH_3, *o*-Tol), 22.2 (CH_3, *o*-Tol), 26.3 (CH_2, cod), 29.9 (CH_2, cod), 31.4 (CH_2, cod), 34.1 (CH_2, cod), 38.3 (CH_2-O), 53.4 (CH–S), 67.8 (CH=, cod), 77.2 (CH=, cod), 81.3 (CH-OP), 97.9 (d, CH=, cod, $J_{C\text{-}P}$ = 9.9 Hz), 98.4 (d, CH=, cod, $J_{C\text{-}P}$ = 12.4 Hz), 117.4–142.9 (aromatic carbons), 161.66 (q, C–B, BAr_F, $^1J_{C\text{-}B}$ = 50.0 Hz). MS HR-ESI [found 855.2399, $C_{45}H_{43}IrOPS$ $(M)^+$ requires 855.2396].

General Procedure for the Hydrogenation of Olefins S1–S43

The alkene (0.5 mmol) and the corresponding catalyst precursor [Ir(cod)(**L**)]BAr_F (2 mol%) were dissolved in the corresponding solvent (2 mL) and placed in a high-pressure autoclave. The autoclave was purged 4 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 plug of celite. The enantiomeric excess was determined by chiral GC or chiral HPLC and conversions were determined by ^{1}H NMR (see Supporting Information for details).

General Procedure for the Hydrogenation of Cyclic β-Enamides S44–S50

The enamide (0.25 mmol) and the corresponding catalyst precursor [Ir(cod)(**L**)]BAr_F (1 mol%) were dissolved in in the corresponding solvent (1 mL) and placed in a high-pressure autoclave, which was purged four times with hydrogen. It was then 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. Conversions were determined by ^{1}H NMR and enantiomeric excesses by HPLC (see Supporting Information for details).

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FULL PAPER

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