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Iridium Phosphite−Oxazoline Catalysts for the Highly Enantioselective Hydrogenation of Terminal Alkenes

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Abstract: A modular library of readily available phosphite−oxazoline ligands (**L1**−**L16a**−**f**) has been successfully applied for the first time in the Ir-catalyzed asymmetric hydrogenation of a broad range of highly unfunctionalized 1,1,-disubstituted terminal alkenes. Enantioselectivities up to >99% and full conversions were obtained in several 1,1-disubstituted alkenes, including substrate classes that have never been asymmetrically hydrogenated before (i.e., 1,1-heteroaryl-alkyl, 1,1-diaryl, trifluoromethyl, etc.). The results indicated that these catalytic systems have high tolerance to the steric and electronic requirements of the substrate and also to the presence of a neighboring polar group. The asymmetric hydrogenations were also performed using propylene carbonate as solvent, which allowed the Ir catalyst to be reused and maintained the excellent enantioselectivities.

1. Introduction

The challenging conversion of largely unfunctionalized 1,1-disubstituted terminal alkenes into chiral hydrocarbons remains a frontier in the realm of asymmetric catalysis. Asymmetric hydrogenation is potentially a synthetic tool for preparing these compounds (Scheme 1).

Asymmetric hydrogenation is of interest because of its atom economy and operational simplicity.[1] Even so, few studies have been made of the asymmetric hydrogenation of 1,1-disubstituted terminal alkenes. This is mainly due to two reasons. The first one is that the two substituents R^1 and R^2 easily can exchange positions in the chiral environment formed by the catalysts, thus reversing the face selectivity (Scheme 2(a)). The second reason is that the terminal double bond can isomerize to form the more stable internal alkene, which usually leads to the predominant formation of the other enantiomer of the hydrogenated product (Scheme 2(b)). Few catalytic systems, then, provide high enantioselectivities and those that do are limited in substrate scope.[2]

One of these systems uses samarium complexes and provides enantioselectivities up to 96% ee in the asymmetric hydrogenation of 2-phenylbut-1-ene (**S1**) but at −78 °C (or 64% ee at 25 °C).[3] Another system uses $RuCl_2$[(*R*,*R*)-Me-Duphos](dmf)$_n$ in the asymmetric hydrogenation of a limited range of 2-phenylbut-1-enes under basic conditions and provides ee's up to 89%.[4] Recently, M-chiral (iminophosphoranyl)ferrocene catalyst precursors (M = Rh and Ir) have been successfully used in the hydrogenation of 6-methoxy-1-methylene-1,2,3,4-tetrahydronaphthalene (ee's up to 94%; using M = Rh) and 2-(4-methoxyphenyl)-1-butene **S2** (ee's up to 97% using M = Rh).[5] In recent years, iridium complexes with chiral P,N ligands have become established as efficient catalysts for the hydrogenation of unfunctionalized olefins, with complementary scope to Rh− and Ru−diphosphine complexes.[2,6] In this context the groups of Pfaltz and Andersson found that some 2-phenylbut-1-enes can be hydrogenated with high enantioselectivity (88−97% ee) using Ir complexes modified with phosphinite−oxazoline ligands.[7,8] Furthermore, Pfaltz also found that in hydrogenation of terminal alkenes, the selectivity is highly pressure dependent. Hydrogenation at atmospheric pressure of H_2 gave significantly higher ee's than at higher pressures.[7] In 2008, we reported the

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(1) See for instance: (a) *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: Weinheim, 2000. (b) *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002. (c) *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*, Blaser, H. U., Schmidt, E., Eds.; Wiley-VCH: Weinheim, 2004.
(2) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272.
(3) (a) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761. (b) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.
(4) Forman, G. S.; Ohkuma, T.; Hems, W. P.; Noyori, R. *Tetrahedron Lett.* **2000**, *41*, 9471.
(5) Co, T. T.; Kim, T. J. *Chem. Commun.* **2006**, 3537.
(6) For recent reviews, see also: (a) Källström, K.; Munslow, I.; Andersson, P. G. *Chem.−Eur. J.* **2006**, *12*, 3194. (b) Roseblade, S. J.; Pfaltz, A. *Acc. Chem. Res.* **2007**, *40*, 1402. (c) Church, T. L.; Andersson, P. G. *Coord. Chem. Rev.* **2008**, *252*, 513.
(7) (a) Blankenstein, J.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4445. (b) McIntyre, S.; Hörmann, E.; Menges, F.; Smidt, S. P.; Pfaltz, A. *Adv. Synth. Catal.* **2005**, *347*, 282.
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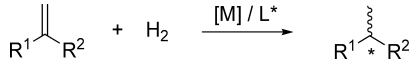
 10.1021/ja904152r CCC: $40.75

Scheme 1. Asymmetric Hydrogenation of Largely Unfunctionalized 1,1-Disubstituted Terminal Alkenes



application of a new type of ligand for the Ir-catalyzed asymmetric hydrogenation of unfunctionalized alkenes: phosphite−oxazoline.[9] We also found that the introduction of a biaryl phosphite moiety into the ligand design is highly adventitious in terms of catalytic activity and substrate versatility.[10] These Ir/phosphite−oxazoline catalytic systems, then, were able to hydrogenate 2-phenylbut-1-enes with higher enantioselectivities (ee's up to 99%) than previous Ir/phosphinite−oxazoline systems. Despite these successes, Ir-catalyzed hydrogenation has not been extended to other 1,1-disubstituted terminal alkenes and the potential of Ir/P,N catalytic systems in this process still needs to be systematically studied. To fully investigate this potential, in this contribution we extend our previous study of 2008 to other amino alcohol-based phosphite−oxazoline ligands (Figure 1) and to other types of 1,1-disubsituted terminal alkenes.

We synthesized and screened a library of 96 potential phosphite−oxazoline ligands (Figure 1),[11] which have the advantages of phosphite ligands: they are obtainable from readily available alcohols and are highly resistant to oxidation.[12] Another advantage of this ligand library design is its highly modular construction which enables a systematic study of the ligand parameters on catalytic performance. With this library (Figure 1), we investigated the effect of systematically varying the substituents in the oxazoline (R) moiety and in the alkyl backbone chain (H, **L1**−**L4**; Me, **L5**−**L11** and Ph, **L15**−**L16**). We also studied the configuration of the alkyl backbone chain (ligands **L5** and **L12**), the presence of a second stereogenic center in the heterocycle ring and its configuration (ligands **L13** and **L14**) and the substituents and configurations in the biaryl phosphite moiety (**a**−**f**). By carefully selecting these elements, we achieved high enantioselectivities and activities in a wide range of 1,1-disubstituted terminal alkenes.

2. Results and Discussions

2.1. Synthesis of the Ir Catalyst Precursors. The catalyst precursors were made by refluxing a dichloromethane solution of the appropriate ligand (**L1**−**L16a**−**f**) in the presence of 0.5 equiv of $[Ir(cod)Cl]_2$ for 2 h followed by counterion exchange with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBArF) (1 equiv), in the presence of water (Scheme 3). All complexes were isolated as air-stable orange solids and were used without further purification.

The complexes were characterized by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The spectral assignments (see Experimental Section) were based on information from ^{1}H−^{1}H and ^{13}C−^{1}H 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−{^{1}H} NMR spectra was obtained in all cases. We were able to obtain [Ir(cod)(**L6a**)]BArF crystals that were suitable for X-ray analysis (Figure 2).[13] The crystal structure confirmed the expected boat conformation of the chelate ring. It also showed that the biphenyl phosphite moiety adopts an R-configuration when coordinated to the iridium center.[14]

2.2. Asymmetric Hydrogenation of 1,1-Aryl-Alkyl Terminal Olefins. 2.2.1. Asymmetric Hydrogenation of 1,1-Phenyl-Alkyl Terminal Olefins. In the first set of experiments, we used the Ir-catalyzed hydrogenation of 2-phenylbut-1-ene **S1** to scope the potential of ligands **L1**−**L16a**−**f**. The results are summarized in Table 1. The reaction proceeded smoothly at room temperature under 1 bar of H_2 at low catalyst loading (0.2 mol %). The results indicate that enantioselectivity is affected by the substituents at the oxazoline and in the alkyl backbone chain, the presence of a second sterogenic center in the oxazoline ring and the substituents/configuration in the biaryl phosphite moiety.

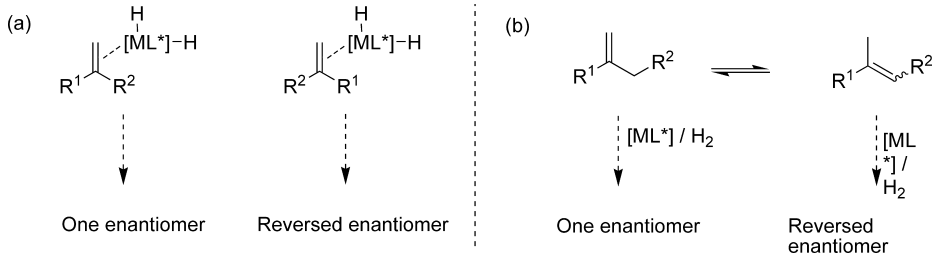
The effect of the substituents and the configuration at the alkyl backbone chain was studied with ligands **L1a**, **L5a**, **L12a**, and **L15a** (Table 1, entries 1, 5, 17 and 20). Our results showed that introducing bulky substituents into the alkyl backbone chain has a positive effect on enantioselectivity (i.e., Ph > Me > H) and that the sense of enantioselectivity is governed by the absolute configuration of the alkyl backbone chain (Table 1, entry 5 vs 17). Both enantiomers of the hydrogenation product can therefore be accessed with high enantioselectivity by changing the absolute configuration of the alkyl backbone chain.

We studied the effect of the oxazoline substituent using ligands **L5**−**L11a** (Table 1, entries 5, 11−16). Our results showed that enantioselectivity is dependent on both the electronic and steric properties of the substituents in the oxazoline moiety. Therefore, either bulky or electron-withdrawing substituents in this position decreased enantioselectivities. Enantioselectivities were best with ligand **L5a**, which contains a phenyl-oxazoline group (Table 1, entry 5).

To study how a second stereogenic center in the oxazoline and its configuration affect the catalytic performance, we also tested ligands **L13a** and **L14a** (Table 1, entries 18 and 19). The results show a cooperative effect between the configuration of this second stereocenter and the configuration of the alkyl backbone chain on enantioselectivity that results in a matched combination for ligand **L13a**, which contains an *R*-configuration at the second stereocenter and an *S*-configuration at the alkyl backbone chain (Table 1, entry 18 vs 19).

Finally, the effects of the biaryl phosphite moiety were studied using ligands **L5a-f** (Table 1, entries 5−10). The results indicated that enantioselectivity is mainly affected by the configuration of the biaryl phosphite moiety (Table 1, entries 9 and 10), while the substituents at both ortho and para positions of

Scheme 2



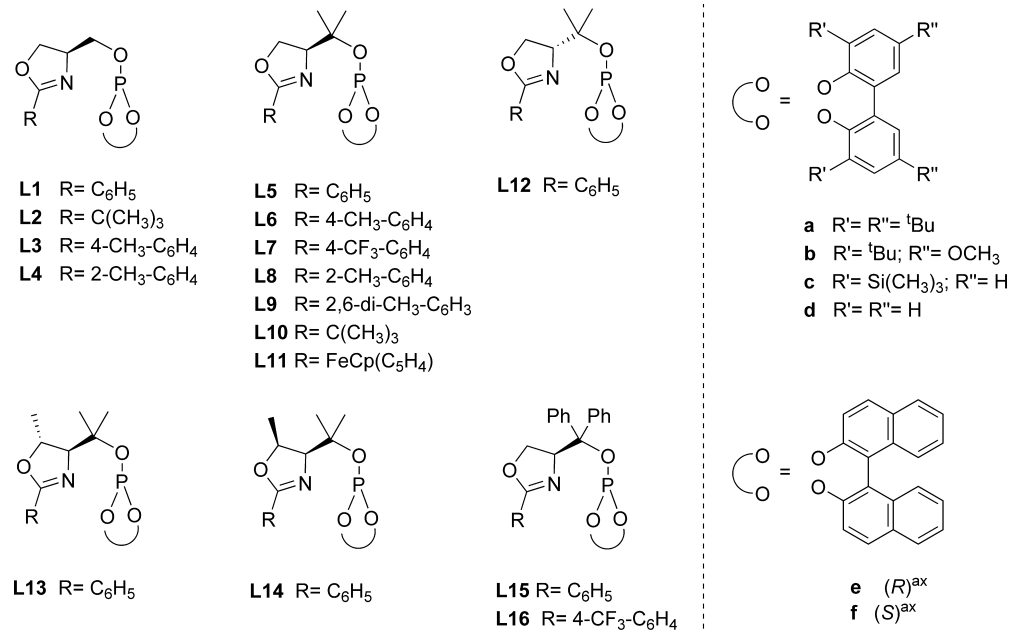
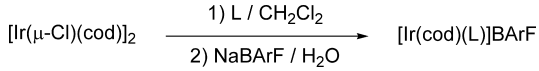


Figure 1. Phosphite−oxazoline ligand library **L1**−**L16a**−**f**.

Scheme 3. Synthesis of Iridium Catalyst Precursors [Ir(cod)(L)]BArF (L = **L1**−**L16a**−**f**)



the biphenyl phosphite moiety has little effect on enantioselectivity (Table 1, entries 5−8). The best enantioselectivities were therefore obtained when an enantiopure *S*-binaphthyl phosphite moiety was present in the ligand (Table 1, entry 10). Moreover, comparing the results of using atropoisomerically flexible biphenyl phosphite based ligands (**a**−**d**) with enantiopure binaphthyl phosphite ligands (**e** and **f**), we can conclude that the biphenyl phosphite moiety in ligands **L5a**−**d** and **L6a** adopts an *R*-configuration upon complexation to the iridium.[14] This is in agreement with the configuration of the biphenyl phosphite moiety observed in the X-ray structure of the [Ir(cod)(**L6a**)]-BArF (vide supra).

In summary, phenyl substituents need to be present in the oxazoline and in the alkyl backbone chain, and there must also be an enantiopure (*S*)-binaphthyl phosphite moiety if enantioselectivities are to be excellent. The best result (100% conversion; 99% ee) was therefore obtained with ligand **L15f** (Table 1, entry 22), which contains the optimal combination of the ligand parameters. Using ligand **L15f**, then, we were able to obtain the highest level of enantioselectivity (99% ee; Table 1, entry 22), which was an improvement on the enantioselectivity previously communicated using ligand **L5f**.[10] Moreover, both enantiomers of the hydrogenation product can be accessed in high enantioselectivity simply by changing the absolute configuration of the alkyl backbone chain. These results clearly show the efficiency of using highly modular scaffolds in the ligand design.

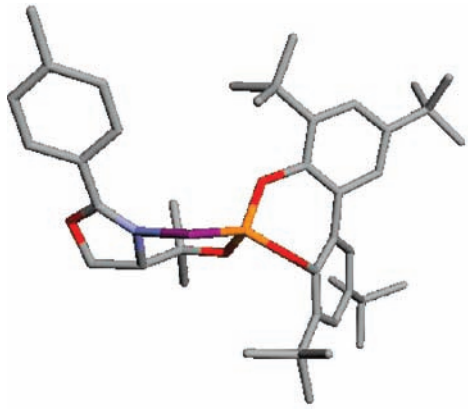
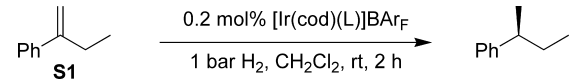


Figure 2. Structure of the [Ir(cod)(**L6a**)]BArF in the crystal (H atoms, BArF ion and cod ligand have been omitted for clarity).

Table 1. Selected Results for the Ir-Catalyzed Hydrogenation of **S1** Using the Ligand Library **L1**−**L16a**−**f**[a]

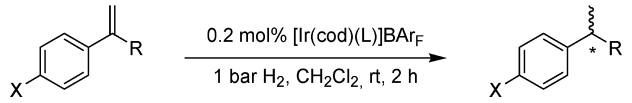


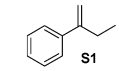
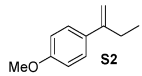
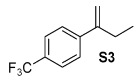
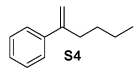
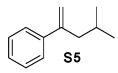
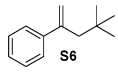
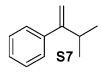
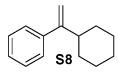
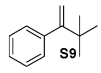
entry	ligand	% conv[b]	% ee[c]	entry	ligand	% conv[b]	% ee[c]
1	**L1a**	100	67 (*S*)	13	**L8a**	100	53 (*S*)
2	**L2a**	100	14 (*S*)	14	**L9a**	100	35 (*S*)
3	**L3a**	100	65 (*S*)	15	**L10a**	100	46 (*S*)
4	**L4a**	100	24 (*S*)	16	**L11a**	100	50 (*S*)
5	**L5a**	100	88 (*S*)	17	**L12a**	100	87 (*R*)
6	**L5b**	100	85 (*S*)	18	**L13a**	100	85 (*S*)
7	**L5c**	100	87 (*S*)	19	**L14a**	100	62 (*S*)
8	**L5d**	100	89 (*S*)	20	**L15a**	100	92 (*S*)
9	**L5e**	100	88 (*S*)	21	**L15c**	100	91 (*S*)
10	**L5f**	100	95 (*S*)	22	**L15f**	100	99 (*S*)
11	**L6a**	100	85 (*S*)	23	**L16a**	100	78 (*S*)
12	**L7a**	100	60 (*S*)				

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

We then studied the asymmetric hydrogenation of other 1,1-disubstituted aryl-alkyl substrates (**S2**-**S10**) using the phosphite−oxazoline ligand library **L1**−**L16a**-**f**. The most noteworthy results are shown in Table 2. In general, they follow the same trends as for the hydrogenation of **S1**. Again, the catalyst precursor containing the phosphite−oxazoline ligand **L15f** provided the best enantioselectivities (ee's up to >99%).

Table 2. Selected Results for the Ir-Catalyzed Hydrogenation of Aryl-Alkyl Terminal Olefins Using the Ligand Library **L1**−**L16a**−**f**[a]



Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1		**L15f**	100	99 (*S*)
2		**L5f**	100	97 (*S*)
3		**L15f**	100	>99 (*S*)
4		**L15f**	100	96 (*S*)
5		**L15f**	100	94 (*S*)
6		**L5f**	100	93 (*S*)
7		**L15f**	100	93 (*S*)
8		**L15f**	100	90 (*S*)
9		**L5f**	100	88 (*S*)
10		**L15f**	100	97 (*S*)
11		**L15f**	100	97 (*S*)
12		**L15f**	100	>99 (*S*)
13		**L15f**	100	25 (*R*)
14[d]		**L15f**	99[e]	87 (*R*)

[a] Reactions carried out 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 or GC. [c] Enantiomeric excesses determined by chiral GC. [d] Reaction carried out at 100 bar of H_2 and 1 mol % of catalyst precursor using PC as solvent at 40 °C for 10 h. [e] 8% of non-hydrogenated isomerized trisubstituted olefin observed by ^{1}HNMR.

Our results using several para-substituted 2-phenylbut-2-enes (**S1**−**S3**) indicated that enantioselectivity is relatively insensitive to the electronic effects in the aryl ring (Table 2, entries 1−4). However, the enantioselectivity (up to >99%) was highest with electron-rich alkene **S2** (Table 2, entry 3), and lowest (up to 96%) with the electron-deficient alkene **S3** (Table 2, entry 4). A similar trend was obtained using the previously published Ir/phosphinite−oxazoline (ee's up to 94% for **S2**)[7] and Ru/Me-Duphos (ee's up to 86% for **S1**)[4] catalysts.

Several α-alkylstyrenes bearing increasingly sterically demanding alkyl substituents (**S4**−**S9**) were equally reactive and were hydrogenated with similar results using the Ir−**L15f** catalytic system (full conversion, 90−99% ee; Table 2, entries 5−12). This represents the first catalysts able to hydrogenate **S4**−**S9** with high enantioselectivities.

Under standard conditions, our catalyst systems were unable to hydrogenate 1-methylene-1,2,3,4-tetrahydronaphthalene **S10** with high enantioselectivities (Table 2, entry 13). This has been attributed to the fact that this olefin easily isomerizes to the trisubstituted internal olefin under reaction conditions. The hydrogenation of the trisubstituted olefin produces the opposite configuration of the hydrogenated product than when **S10** is hydrogenated, which results in low enantioselectivities.[15] Recently, Börner and co-workers discovered that the use of propylene carbonate (PC) as solvent reduces the isomerization considerably so **S10** can be hydrogenated in high enantioselectivities (up to 85% ee).[15] Using this strategy we also managed to hydrogenate **S10** in high enantioselectivities (ee's up to 87%, Table 2, entry 14).

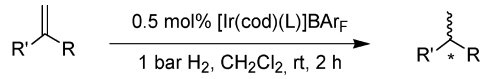
In conclusion, our Ir/phosphite−oxazoline catalytic system is highly tolerant to the steric and electronic properties of the α-alkylstyrene derivatives so enantioselectivities can be high in the asymmetric hydrogenation of this type of aryl-alkyl 1,1-disubsituted alkenes.

2.2.2. Asymmetric Hydrogenation of 1,1-Heteroaromatic-Alkyl Terminal Olefins. We then applied this ligand library in the asymmetric hydrogenation of 1,1-heteroaromatic alkenes. This is interesting because heterocycles are used in industry and because the heterocyclic part can be modified posthydrogenation. Despite this, no previous studied have been made. The results are summarized in Table 3. Again enantioselectivities were excellent under mild reaction conditions (ee's up to >99%). Even though it has been reported that the catalytic activity using Ir complexes with P,N ligands can be diminished in the presence of coordinating groups (or solvents),[2,16] the heteroaromatic alkenes **S11**-**S14** were hydrogenated in 100% conversion using 1 bar of H_2. Hydrogenation of alkenes with thiophene **S12** and pyridyl **S13**-**S14** substituents followed the same trends as those observed for the previous substrates **S1**-**S9**. Therefore, enantioselectivities were best when ligand **L15f** was used (Table 3, entries 2−4). However, for furan-substituted substrate **S11** the enantioselectivity was best with ligand **L5a** (Table 3, entry 1). Once again, these results clearly show the efficiency of using highly modular scaffolds in the ligand design.

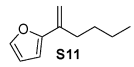
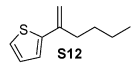
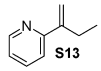
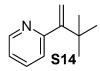
2.3. Asymmetric Hydrogenation of 1,1-Diaryl Terminal Olefins. To further study the potential of this ligand library, we also screened **L1**−**L16a**−**f** in the Ir-catalyzed hydrogenation of 1,1-diaryl terminal olefins (**S15**−**S17**). Enantiopure diaryla-

(9) Diéguez, M.; Mazuela, J.; Pàmies, O.; Verendel, J. J.; Andersson, P. G. *J. Am. Chem. Soc.* **2008**, *130*, 7208.
(10) Diéguez, M.; Mazuela, J.; Pàmies, O.; Verendel, J. J.; Andersson, P. G. *Chem. Commun.* **2008**, 3888.
(11) Part of this ligand library has also been successfully applied in the Pd-catalyzed allylic substitution reaction. See: Diéguez, M.; Pàmies, O. *Chem.*−*Eur. J.* **2008**, *14*, 3653.
(12) (a) Diéguez, M., Pàmies, O.; Ruiz, A.; Claver, C. In *Methodologies in Asymmetric Catalysis*; Malhotra, S. V., Ed.; American Chemical Society: Washington, DC, 2004. (b) Diéguez, M. ; Pàmies, O.; Claver, C. In *Trivalent Phosphorus Compounds in Asymmetric Catalysis, Synthesis and Applications*; Börner, A. Ed.; Wiley: Weinheim, 2008; p 506.
(13) Crystals of [Ir(cod)(**L6a**)]BArF could be obtained by slow evaporation of a solution of the compound in ethanol.
(14) The rapid ring inversions (atropoisomerization) in the biaryl phosphite moiety is usually stopped upon coordination to the metal center. See for example: (a) Buisman, G. J. H.; van der Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929. (b) Diéguez, M.; Pàmies, O.; Ruiz, A.; Claver, C.; Castillón, S. *Chem.*−*Eur. J.* **2001**, *7*, 3086. (c) Pàmies, O.; Diéguez, M.; Net, G.; Ruiz, A.; Claver, C. *J. Org. Chem.* **2001**, *66*, 8364. (d) Diéguez, M.; Pàmies, O.; Ruiz, A.; Claver, C. *New J. Chem.* **2002**, *26*, 827. (e) Pàmies, O.; Diéguez, M. *Chem.*−*Eur. J.* **2008**, *14*, 944.
(15) Similar behavior has been observed using related Ir-phosphinite−oxazoline ligands. See: Bayardon, J.; Holz, J.; Schäffner, B.; Andrushko, V.; Verevkin, S.; Preetz, A.; Börner, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5971.
(16) Pfaltz and coworkers have successfully hydrogenated trisubstituted aryl alkenes with one aromatic heterocyclic substituent. See: Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hormann, E.; McIntyre, S.; Menges, F.; Schonleber, M.; Smidt, S. P.; Wustenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, *345*, 33.

Table 3. Selected Results for the Ir-Catalyzed Hydrogenation of Heteroaryl-Alkyl Terminal Olefins Using the Ligand Library **L1**−**L16a**−**f**[a]



R' = 2-furan, 2-thiophene, 2-pyridine
R = alkyl

Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1	 S11	**L5a**	100	99 (-)
2	 S12	**L15f**	100	96 (-)
3	 S13	**L15f**	100	99 (+)
4	 S14	**L15f**	100	>99 (+)

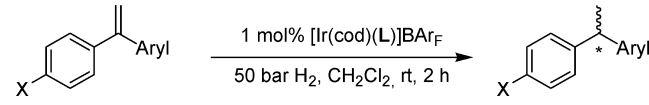
[a] Reactions carried out using 1 mmol of substrate and 0.5 mol % of Ir catalyst precursor at 1 bar of H_2. [b] Conversion measured by ^{1}H NMR. [c] Enantiomeric excesses determined by chiral HPLC.

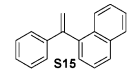
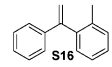
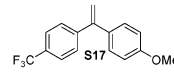
lkanes are important intermediates for the preparation of drugs and research materials.[17] To date optically active diarylalkanes can be prepared through some rather laborious approaches.[17,18] The asymmetric hydrogenation can provide a more efficient approach to prepare these compound. However, to our knowledge there is no enantioselective hydrogenation of this kind of substrates.

In a first set of experiments we examined the Ir-catalyzed asymmetric hydrogenation of diaryl alkenes **S15** and **S16**. In contrast to the previous aryl-alkyl substrates **S1**−**S14**, enantioselectivities are slightly better at higher pressures (i.e., using Ir/**L5a**; 26% ee at 1 bar and 30% ee at 50 bar). The enantioselectivity is also mainly affected by the substituents at the oxazoline and at the biaryl phosphite moieties, while the substituents in the alkyl backbone chain have little effect. Although high enantioselectivities (ee's up to 90%) can be obtained by replacing the bulky tetra *tert*-butyl substituted biphenyl phosphite moieties by less sterically demanding *S*-binaphthyl phosphite moieties (Table 4, entries 2, 4, 5, and 8 vs 3, 7, and 9), the enantiocontrol is highest (>99% ee) with bulky substituents on the oxazoline ring (ligand **L9a**, Table 4, entries 6 and 10).

We also tested the Ir/phosphite−oxazoline catalytic systems in the asymmetric hydrogenation of **S17**. We anticipated that for this substrate enantiodiscrimination would be more difficult to control because it would be mainly due to the electronic differentiation of both phenyl substituents.[19] While the effect of the pressure dependence on enantioselectivity is similar to that observed for **S15** and **S16**, the effect of the ligand parameters on enantioselectivity is different. Therefore, the presence of bulky oxazoline substituents and/or the replacement

Table 4. Selected Results for the Ir-Catalyzed Hydrogenation of 1,1-Diaryl Terminal Alkenes **S15**−**S17** Using the Ligand Library **L1**−**L16a**−**f**[a]



Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1	 S15	**L1a**	100	26 (+)
2		**L5a**	100	30 (+)
3		**L5f**	100	90 (+)
4		**L6a**	100	31 (+)
5		**L7a**	100	30 (+)
6		**L9a**	100	>99 (+)
7		**L15f**	100	90 (+)
8	 S16	**L5a**	100	23 (+)
9		**L5f**	100	64 (+)
10		**L9a**	99	99 (+)
11	 S17	**L1a**	100	43 (+)
12		**L5a**	100	61 (+)
13		**L5f**	100	38 (+)
14		**L6a**	100	60 (+)
15		**L7a**	100	65 (+)
16		**L9a**	100	39 (+)
17		**L15a**	100	63 (+)

[a] Reactions carried out using 1 mmol of substrate and 1 mol % of Ir catalyst precursor at 50 bar of H_2. [b] Conversion measured by ^{1}H NMR. [c] Enantiomeric excesses determined by chiral HPLC.

of a bulky tetra *tert*-butyl-phenyl phosphite moiety by an *S*-binaphthyl moiety has a negative effect on enantioselectivity (Table 4, entry 11 vs entries 13 and 16). Enantioselectivity is highest (ee's up to 65%) using ligand **L7a** (Table 4, entry 15).

2.4. 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 (**S18**−**S21**). The results are summarized in Table 5.

We initially tested the ligand library in the hydrogenation of the allylic alcohol **S18**. 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 synthesis of natural products and drugs (i.e., modulators of dopamine D3 receptors).[20] Complex Ir−**L15f** proved to be the most selective

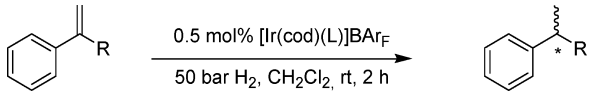
(17) (a) Fessard, T. C.; Andrews, S. P.; Motoyohsi, H.; Carreira, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 9331. (b) Prat, L.; Dupas, G.; Duflos, J.; Quéguiner, G.; Bourguignon, J.; Levacher, V. *Tetrahedron Lett.* **2001**, *42*, 4515. (c) Wilkinson, J. A.; Rossington, S. B.; Ducki, S.; Leonard, J.; Hussain, N. *Tetrahedron* **2006**, *62*, 1833.

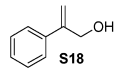
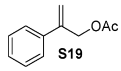
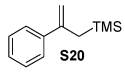
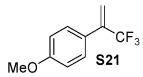
(18) (a) Okamoto, K.; Nishibayashi, Y.; Uemura, S.; Toshimitsu, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 3588. (b) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793.

(19) In this context, Noyori and coworkers have found moderate enantioselectivities in the Ru-catalyzed asymmetric transfer hydrogenation of differently para-substituted benzophenone derivatives. See: Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521.

(20) See for instance: (a) Abate, A.; Brenna, E.; Fuganti, C.; Gatti, G. G.; Givenzana, T.; Malpezzi, L.; Serra, S. *J. Org. Chem.* **2005**, *70*, 1281. (b) Drescher, K.; Haupt, A.; Unger, L.; Rutner, S. C.; Braje, W.; Grandel, R.; Henry, C.; Backfisch, G.; Beyerbach, A.; Bisch, W. WO Patent 2006/040182 A1, 2006.

Table 5. Selected Results for the Ir-Catalyzed Hydrogenation of 1,1-Disubstituted Terminal Olefins Containing a Neighboring Polar Group Using the Ligand Library **L1**−**L16a**−**f**[a]



Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1	 **S18**	**L15f**	100	95 (*R*)
2	 **S19**	**L15f**	100	91 (*R*)
3	 **S20**	**L15f**	100	96 (*S*)
4	 **S21**	**L15f**	100	75 (-)

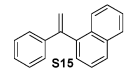
[a] Reactions carried out using 1 mmol of substrate and 0.5 mol % of Ir catalyst precursor at 50 bar of H_2. [b] Conversion measured by ^{1}H NMR. [c] Enantiomeric excesses determined by chiral GC.

catalyst, giving 95% ee at room temperature (Table 5, entry 1). This result competes favorably with the results obtained using related phosphinite−oxazoline ligands.[7b] In addition, the enantioselectivities and activities obtained are higher than those reported in the asymmetric Zr-catalyzed methylalumination of α-olefins[21] and the lipase-mediated kinetic resolution of racemic 2-phenyl propanol.[20a] Similarly, the hydrogenation of the allylic acetate **S19** also proceeds with high activity and enantioselectivity with the catalyst system Ir−**L15f** (Table 5, entry 2).

We next screened ligands **L1**−**L16a**−**f** in the asymmetric hydrogenation of the allylic silane **S20** and the trifluoromethyl olefin **S21**. The hydrogenation of these compounds gave rise to important organic intermediates and a number of innovative new organosilicon[22] and organofluorine[23] drugs are being developed. The enantioselectivities (96% ee for **S20** and 75% ee for **S21**) were best with ligand **L15f** (Table 5, entries 3 and 4). To the best of our knowledge this is the first successful asymmetric hydrogenation of allylic silanes and terminal trifluoromethyl olefins.

2.5. Recycling Experiments. Encouraged by the excellent results obtained, we decided to go one step further and to study the recycling of our catalyst systems. For a practical application, catalyst recycling is an extremely important topic because of the very high price of iridium. Recently, propylene carbonate (PC) has emerged as an environmentally friendly alternative to standard organic solvents that allow catalyst to be repeatedly recycled by a simple two-phase extraction with an apolar solvent.[15] For this purpose, substrates **S9**, **S14**, and **S15** were hydrogenated in PC with the catalyst precursor [Ir(cod)(**L15f**)]BArF (substrates **S9** and **S14**) and [Ir(cod)(**L9a**)]BArF (substrate **S15**), and the products were removed by extraction with hexane (Table 6). Catalysts can be used up to five times with no significant losses in enantioselectivity, although the reaction time increased. This is probably due to the iridium catalyst partially passing into the hexane phase[15] and/or the formation of inactive triiridium hydride clusters.[24]

Table 6. Recycling Experiments with the Catalyst [Ir(cod)(**L**)]BArF and **S9**, **S14**, and **S15** as Substrates in PC[a]

Cycle	Substrate	Ligand	% Conv (h)[b]	% ee[c]
1	 **S9**	**L15f**	98 (4)	99 (S)
2			98 (4)	99 (S)
3			94 (6)	98 (S)
4			95 (10)	97 (S)
5			82 (12)	97 (S)
1[d]	 **S14**	**L15f**	98 (12)	99 (+)
2[d]			94 (12)	99 (+)
3[d]			84 (18)	97 (+)
1[d]	 **S15**	**L9a**	100 (12)	99 (+)
2[d]			95 (15)	99 (+)
3[d]			93 (24)	99 (+)

[a] Reactions carried out using 1 mmol of substrate and 1 mol % of Ir catalyst precursor at 50 bar of H_2. [b] Conversion measured by ^{1}H NMR. [c] Enantiomeric excesses determined by chiral GC. [d] Reaction carried out at 100 bar and 40 °C.

3. Conclusions

A library of readily available phosphite−oxazoline ligands (**L1**−**L16a**−**f**) has been applied in the Ir-catalyzed asymmetric hydrogenation of several 1,1,-disubstituted terminal largely unfunctionalized alkenes. We found that their effectiveness at transferring the chiral information in the product can be tuned by correctly choosing the ligand components. Enantioselectivities were therefore excellent (ee's up to >99%) in a wide range of 1,1-disubstituted terminal alkenes. These Ir/phosphite−oxazoline catalytic systems, then, compete favorably in terms of enantioselectivity and, more important, in terms of substrate versatility with a few other ligand series that also have provided high ee's for a limited range of 1,1-aryl-alkyl disubstituted alkenes. Of particular note are the unprecedented excellent enantioselectivities (ee's up to >99%) obtained with 1,1-heteroaryl-alkyl and 1,1-diaryl substrates, for which no asymmetric hydrogenation was reported. It should be noted that these catalytic systems also have high tolerance to the presence of a neighboring polar group and therefore 1,1-disubstituted allylic alcohols, acetates, and silanes can be hydrogenated in high enantioselectivities (ee's up to 96%). The asymmetric hydrogenations were also performed using propylene carbonate as solvent, which allowed the Ir catalyst to be reused and maintained the excellent enantioselectivities. These results open up a new class of Ir catalysts for the highly enantioselective

(21) Wipf, P.; Ribe, S. *Org. Lett.* **2000**, *2*, 1713.
(22) See for instance: (a) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev* **1997**, *97*, 2063. (b) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599. (c) Bains, W.; Tacke, R. *Curr. Opin. Drug Discovery Dev.* **2003**, *6*, 526.
(23) See for instance: Schlosser, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1496. (b) Smart, B. E. *J. Fluorine Chem.* **2001**, *109*, 3. (c) *Asymmetric Fluoroorganic Chemistry: Synthesis, Application and Future Directions*; Ramachandran, P. V., Ed.; American Chemical Society: Washington, DC, 2000. (d) A special issue has been devoted to "Fluorine in the Life Sciences", *ChemBioChem* **2004**, *5*, 559.
(24) (a) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331. (b) Smidt, S. P.; Pfaltz, A.; Martinez-Viviente, E.; Pregosin, P. S.; Albinati, A. *Organometallics* **2003**, *22*, 1000.

Ir-catalyzed hydrogenation of largely unfunctionalized 1,1-disubstituted terminal alkenes, which is of great practical interest.

4. Experimental Section

4.1. General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. Phosphite−oxazoline ligands **L1**−**L7a**−**f** and **L11**−**L16a** were prepared as previously described.[11] [Ir(cod)(L)]BArF (L= **L3a**, **L5a**−**c**, **L5e**−**f**, **L6a**, **L7a**, **L13a**, and **L16a**) were prepared previously.[10] Substrates **S1**,[25] **S2**−**S3**,[7b] **S4**,[26] **S5**,[27] **S6**,[28] **S7**,[29] **S8**,[30] **S9**,[29] **S10**,[31] **S15**,[32] **S16**,[33] **S17**,[34] **S18**,[35] and **S20**[36] were prepared as previously described. ^{1}H, ^{13}C−{^{1}H}, and ^{31}P−{^{1}H} NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H and ^{13}C assignments were made on the basis of ^{1}H−^{1}H gCOSY and ^{1}H−^{13}C gHSQC experiments.

4.2. General Procedure for the Preparation of the Phosphite−Oxazoline Ligands. The corresponding phosphorochloridite (3.0 mmol) produced *in situ* was dissolved in toluene (12.5 mL), and pyridine (1.14 mL, 14 mmol) was added. The corresponding hydroxyl-oxazoline compound (2.8 mmol) was azeotropically dried with toluene (3 × 2 mL) and then dissolved in toluene (12.5 mL) to which pyridine (1.14 mL, 14 mmol) was added. The oxazoline solution was transferred slowly at 0 °C to the solution of phosphorochloridite. The reaction mixture was stirred overnight at 80 °C, and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography in alumina to produce the corresponding ligand as a white solid.

L8a. Yield: 1.4 g (76%). ^{31}P NMR ($CDCl_3$) δ = 148.4 (s). ^{1}H NMR ($CDCl_3$) δ = 1.26 (s, 9H, CH_3, *t*Bu), 1.28 (s, 9H, CH_3, *t*Bu), 1.35 (s, 3H, CH_3), 1.58 (s, 9H, CH_3, *t*Bu), 1.59 (s, 9H, CH_3, *t*Bu), 1.85 (s, 3H, CH_3), 2.65 (s, 3H, CH_3−Ph), 3.87 (m, 1H, CH_2), 4.22 (m, 1H, CH_2), 4.50 (m, 1H, CH), 7.1−8.0 (m, 8H, CH═). ^{13}C NMR ($CDCl_3$) δ = 22.9 (CH_3−Ph), 23.8 (d, CH_3, J_{C-P} = 6.8 Hz), 28.7 (d, CH_3, J_{C-P} = 11 Hz), 31.8 (CH_3, *t*Bu), 31.9 (CH_3, *t*Bu), 34.9 (C, *t*Bu), 35.9 (C, *t*Bu), 68.3 (CH_2), 76.9 (CH), 82.3 (d, CMe_2, J_{C-P} = 4.5 Hz), 124.5 (CH═), 126.0 (CH═), 127.5 (CH═), 127.7 (C), 128.9 (CH═), 129.6 (CH═), 130.8 (CH═), 131.1 (CH═), 131.9 (CH═), 134.3 (C), 138.2 (C), 140.0 (C), 140.9 (C), 146.8 (C), 165.6 (C═N). Anal. Calcd (%) for $C_{41}H_{56}NO_4P$: C 74.85, H 8.58, N 2.13; found: C 74.99, H 8.67, N 2.22.

L9a. Yield: 1.3 g (69%). ^{31}P NMR ($CDCl_3$) δ = 148.9 (s). ^{1}H NMR ($CDCl_3$) δ = 1.23 (s, 9H, CH_3, *t*Bu), 1.24 (s, 9H, CH_3, *t*Bu), 1.46 (s, 3H, CH_3), 1.55 (s, 9H, CH_3, *t*Bu), 1.56 (s, 9H, CH_3, *t*Bu), 1.83 (s, 3H, CH_3), 2.22 (s, 6H, CH_3−Ph), 3.97 (m, 1H, CH_2), 4.19 (m, 1H, CH_2), 4.53 (m, 1H, CH), 6.8−7.5 (m, 7H, CH═). ^{13}C NMR ($CDCl_3$) δ = 20.6 (CH_3−Ph), 24.7 (d, CH_3, J_{C-P} = 6.2 Hz), 28.7 (d, CH_3, J_{C-P} = 12.4 Hz), 31.7 (CH_3, *t*Bu), 31.8 (CH_3, *t*Bu), 31.9 (CH_3, *t*Bu), 35.5 (C, *t*Bu), 35.9 (C, *t*Bu), 36.0 (C, *t*Bu), 68.8 (CH_2), 77.0 (CH), 82.2 (d, CMe_2, J_{C-P} = 4.6 Hz), 124.5 (CH═), 124.6 (CH═), 127.5 (CH═), 127.6 (CH═), 128.0 (C), 129.8 (CH═), 130.3 (CH═), 134.3 (b, CH═), 140.9 (C), 141.0 (C), 146.9 (C), 165.7 (C═N). Anal. Calcd (%) for $C_{42}H_{58}NO_4P$: C 75.08, H 8.70, N 2.08; found: C 75.13, H 8.73, N 2.13.

L10a. Yield: 1.3 g (74%). ^{31}P NMR ($CDCl_3$) δ = 148.9 (s). ^{1}H NMR ($CDCl_3$) δ = 1.14 (s, 9H, CH_3, *t*Bu), 1.22 (s, 9H, CH_3, *t*Bu), 1.23 (s, 9H, CH_3, *t*Bu), 1.30 (s, 3H, CH_3), 1.53 (s, 9H, CH_3, *t*Bu), 1.56 (s, 9H, CH_3, *t*Bu), 1.76 (s, 3H, CH_3), 3.78 (m, 1H, CH_2), 4.12 (m, 1H, CH_2), 4.26 (m, 1H, CH), 7.3−7.6 (m, 4H, CH═). ^{13}C NMR ($CDCl_3$) δ = 23.7 (d, CH_3, J_{C-P} = 6.0 Hz), 28.3 (CH_3, *t*Bu), 28.5 (d, CH_3, J_{C-P} = 12.1 Hz), 31.7 (CH_3, *t*Bu), 31.8 (CH_3, *t*Bu), 31.9 (CH_3, *t*Bu), 33.7 (C, *t*Bu), 34.9 (C, *t*Bu), 36.0 (C, *t*Bu), 69.2 (CH_2), 75.7 (CH), 82.3 (d, CMe_2, J_{C-P} = 4.5 Hz), 124.5 (CH═), 124.6 (CH═), 127.5 (CH═), 127.6 (CH═), 128.0 (C), 129.6 (CH═), 134.3 (b, CH═), 140.8 (C), 140.9 (C), 146.9 (C), 147.1 (C), 175.2 (C═N). Anal. Calcd (%) for $C_{38}H_{58}NO_4P$: C 73.16, H 9.37, N 2.25; found: C 73.22, H 9.41, N 2.29.

L15f. Yield: 1.1 g (64%). ^{31}P NMR ($CDCl_3$) δ = 151.8 (s). ^{1}H NMR ($CDCl_3$) δ = 3.91 (m, 1H, CH_2), 4.48 (m, 1H, CH_2), 5.36 (m, 1H, CH), 6.7−8.3 (m, 27H, CH═). ^{13}C NMR ($CDCl_3$) δ = 69.7 (CH_2), 73.6 (CH), 86.4 (d, CPh_2, J_{C-P} = 6.5 Hz), 122−149 (aromatic carbons), 172.9 (C═N). Anal. Calcd (%) for $C_{42}H_{30}NO_4P$: C 78.37, H 4.70, N 2.18; found: C 78.42, H 4.69, N 2.20.

4.3. 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 $[Ir(COD)Cl]_2$ (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: 125 mg (95%). ^{31}P NMR ($CDCl_3$) δ = 103.6 (s). ^{1}H NMR ($CDCl_3$) δ = 1.36 (s, 9H, CH_3, *t*Bu), 1.38 (s, 9H, CH_3, *t*Bu), 1.57 (b, 18H, CH_3, *t*Bu), 1.71 (b, 4H, CH_2, cod), 2.33 (m, 3H, CH_2, cod), 2.54 (b, 1H, CH_2, cod), 3.74 (m, 1H, CH═, cod), 4.12 (m, 2H, CH_2−OP), 4.21 (m, 2H, CH_2), 4.24 (b, 1H, CH═, cod), 4.66 (m, 1H, CH), 4.84 (b, 1H, CH═, cod), 5.45 (b, 1H, CH═ cod), 7.1 − 8.5 (m, 21H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 24.8 (b, CH_2, cod), 28.8 (b, CH_2, cod), 31.3 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.6 (b, CH_3, *t*Bu), 33.7 (b, CH_2, cod), 34.9 (C, *t*Bu), 35.1 (C, *t*Bu), 35.5 (C, *t*Bu), 36.0 (C, *t*Bu), 37.3 (b, CH_2, cod), 67.1 (CH═, cod), 68.7 (CH), 69.8 (b, CH_2−O and CH_2−OP), 70.2 (CH═, cod), 94.6 (d, CH═, cod, J_{C-P} = 22.2 Hz), 106.1 (d, CH═, cod, J_{C-P} = 12.2 Hz), 117.7 (b, CH═, BAr_F), 119−134 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−149 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.6 Hz), 171.5 (C═N). Anal. Calc (%) for $C_{78}H_{74}BF_{24}IrNO_4P$: C 52.65, H 4.19, N 0.79; found: C 52.62, H 4.22, N 0.83.

[Ir(cod)(L2a)]BArF. Yield: 118 mg (91%). ^{31}P NMR ($CDCl_3$) δ = 106.1 (s). ^{1}H NMR ($CDCl_3$) δ = 1.35 (s, 9H, CH_3, *t*Bu), 1.37 (s, 9H, CH_3, *t*Bu), 1.53 (s, 9H, CH_3, *t*Bu), 1.55 (b, 18H, CH_3, *t*Bu), 1.65 (b, 2H, CH_2, cod), 1.76 (b, 2H, CH_2, cod), 2.07 (m, 1H, CH_2, cod), 2.22 (m, 1H, CH_2, cod), 2.38 (m, 1H, CH_2, cod), 2.51 (m, 1H, CH_2, cod), 3.87 (m, 1H, CH═, cod), 4.08 (m, 3H, CH_2−OP and CH_2−O), 4.32 (b, 1H, CH), 4.48 (b, 1H, CH═, cod), 4.73 (b, 2H, CH═, cod and CH_2−O), 5.47 (b, 1H, CH═, cod), 7.1 − 8.5 (m, 16H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 24.4 (b, CH_2, cod), 28.4 (b, CH_2, cod), 29.2 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 34.5 (C, *t*Bu), 34.8 (b, CH_2, cod), 34.9 (C, *t*Bu), 35.0 (C, *t*Bu), 35.4 (C, *t*Bu), 36.0 (C, *t*Bu), 37.4 (b, CH_2, cod), 67.7 (b, CH═, cod), 69.2 (CH), 69.9 (CH_2−O), 70.0 (CH_2−OP), 70.6 (CH═, cod), 90.5 (d, CH═, cod, J_{C-P} = 26.2 Hz), 103.2 (d, CH═, cod, J_{C-P} = 10.5 Hz), 117.7 (b, CH═, BAr_F), 119−134 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−149 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 182.8 (C═N). Anal. Calc (%) for $C_{76}H_{78}BF_{24}IrNO_4P$: C 51.88, H 4.47, N 0.80; found: C 51.93, H 4.52, N 0.77.

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[Ir(cod)(L4a)]BArF. Yield: 122 mg (92%). ^{31}P NMR ($CDCl_3$) δ = 102.0 (s). ^{1}H NMR ($CDCl_3$) δ = 1.37 (s, 9H, CH_3, *t*Bu), 1.38 (s, 9H, CH_3, *t*Bu), 1.55 (s, 9H, CH_3, *t*Bu), 1,61 (b, 4H, CH_2, cod) 1.72 (s, 9H, CH_3, *t*Bu), 2.17 (m, 3H, CH_2, cod), 2.33 (b, 1H, CH_2, cod), 2.36 (s, 3H, CH_3−Ph), 3.47 (m, 1H, CH═, cod), 4.26 (b, 5H, CH-N, CH_2−O, CH_2−OP and CH═, cod), 4.83 (b, 2H, CH_2−O and CH═, cod), 5.27 (b, 1H, CH═, cod), 7.1 − 8.3 (m, 20H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 25.6 (b, CH_2, cod), 29.3 (b, CH_2, cod), 31.3 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.6 (b, CH_3, *t*Bu), 32.4 (b, CH_2, cod), 34.9 (C, *t*Bu), 35.0 (C, *t*Bu), 35.5 (b, CH_2, cod), 36.0 (C, *t*Bu), 36.1 (CH_3−Ph), 36.2 (C, *t*Bu), 65.1 (CH), 66.0 (CH═, cod), 69.0 (CH_2−O), 72.2 (CH═, cod), 70.7 (CH_2−OP), 99.0 (d, CH═, cod, J_{C-P} = 20.2 Hz), 106.8 (d, CH═, cod, J_{C-P} = 13.7 Hz), 117.7 (b, CH═, BAr_F), 119−134 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−149 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 174.4 (C═N). Anal. Calc (%) for $C_{79}H_{76}BF_{24}IrNO_4P$: C 52.91, H 4.27, N 0.78; found: C 52.33, H 4.20, N 0.75.

[Ir(cod)(L5d)]BArF. Yield: 109 mg (93%). ^{31}P NMR ($CDCl_3$) δ = 102.4 (s). ^{1}H NMR ($CDCl_3$) δ = 1.29 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.67 (m, 3H, CH_2, cod), 2.22 (m, 2H, CH_2, cod), 2.40 (m, 3H, CH_2, cod), 3.58 (m, 1H, CH═, cod), 3.94 (b, 1H, CH═, cod), 4.58 (dd, 1H, CH_2, $^2J_{H-H}$ = 10.2 Hz, $^3J_{H-H}$ = 3 Hz), 4.73 (t, 1H, CH_2, $^2J_{H-H}$ = 9 Hz), 4.90 (dd, 1H, CH, $^3J_{H-H}$ = 8.7 Hz, $^3J_{H-H}$ = 2.4 Hz), 5.00 (b, 1H, CH═, cod), 5.42 (b, 1H, CH═, cod), 7.1 − 7.8 (m, 25H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 20.9 (CH_3), 25.4 (b, CH_2, cod), 27.0 (CH_3), 29.3 (b, CH_2, cod), 32.1 (b, CH_2, cod), 36.9 (b, CH_2, cod), 66.1 (CH═, cod), 68.0 (CH═, cod), 70.6 (CH_2), 73.6 (CH), 86.0 (d, CMe_2, J_{C-P} = 6.5 Hz), 100.4 (d, CH═, cod, J_{C-P} = 18.7 Hz), 108.8 (d, CH═, cod, J_{C-P} = 14.0 Hz), 117.7 (b, CH═, BAr_F), 119−132 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−150 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 172.6 (C═N). Anal. Calc (%) for $C_{64}H_{46}BF_{24}IrNO_4P$: C 48.56, H 2.93, N 0.88; found: C 48.63, H 2.98, N 0.90.

[Ir(cod)(L8a)]BArF. Yield: 129 mg (96%). ^{31}P NMR ($CDCl_3$) δ = 96.2 (s). ^{1}H NMR ($CDCl_3$) δ = 1.08 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, *t*Bu), 1.38 (s, 9H, CH_3, *t*Bu), 1.54 (s, 9H, CH_3, *t*Bu), 1.72 (s, 9H, CH_3, *t*Bu), 1.62 (b, 4H, CH_2, cod), 2.11 (m, 2H, CH_2, cod), 2.24 (b, 2H, CH_2, cod), 2.36 (s, 3H, CH_3−Ph), 3.42 (m, 1H, CH═, cod), 4.19 (b, 1H, CH═, cod), 4.33 (b, 1H, CH═, cod), 4.48 (dd, 1H, CH_2, $^2J_{H-H}$ = 9.3 Hz, $^3J_{H-H}$ = 2.7 Hz), 4.70 (m, 2H, CH and CH_2), 5.19 (b, 1H, CH═, cod), 7.1 − 8.4 (m, 20H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 20.6 (CH_3), 21.6 (b, CH_2, cod), 25.4 (CH_3), 26.9 (b, CH_2, cod), 29.2 (b, CH_2, cod), 31.2 (CH_3−Ph), 31.3 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.6 (b, CH_3, *t*Bu), 34.9 (C, *t*Bu), 35.0 (C, *t*Bu), 35.4 (b, CH_2, cod), 35.8 (C, *t*Bu), 36.0 (C, *t*Bu), 65.0 (CH═, cod), 69.5 (CH═, cod), 70.6 (CH_2), 72.7 (CH), 84.6 (b, C, CMe_2), 98.5 (d, CH═, cod, J_{C-P} = 19.9 Hz), 106.8 (b, CH═, cod), 117.7 (b, CH═, BAr_F), 119−134 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−149 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 175.1 (C═N). Anal. Calc (%) for $C_{81}H_{80}BF_{24}IrNO_4P$: C 53.41, H 4.43, N 0.77; found: C 53.48, H 4.39, N 0.83.

[Ir(cod)(L9a)]BArF. Yield: 124 mg (91%). ^{31}P NMR ($CDCl_3$) δ = 94.1 (s). ^{1}H NMR ($CDCl_3$) δ = 1.12 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.35 (s, 9H, CH_3, *t*Bu), 1.37 (s, 9H, CH_3, *t*Bu), 1.58 (s, 9H, CH_3, *t*Bu), 1.59 (s, 9H, CH_3, *t*Bu), 1.72 (b, 4H, CH_2, cod), 2.02 (m, 2H, CH_2, cod), 2.15 (b, 2H, CH_2, cod), 2.26 (s, 3H, CH_3−Ph), 2.80 (s, 3H, CH_3−Ph), 3.70 (m, 1H, CH═, cod), 4.01 (b, 2H, CH═, cod), 4.42 (dd, 1H, CH_2, $^2J_{H-H}$ = 10.2 Hz, $^3J_{H-H}$ = 5.1 Hz), 4.27 (t, 1H, CH_2, $^2J_{H-H}$ = 10.5 Hz), 4.51 (dd, 1H, CH, $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 5.1 Hz), 5.19 (b, 1H, CH═, cod), 7.1 − 7.9 (m, 19H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 20.5 (CH_3), 22.6 (b, CH_2, cod), 23.3 (CH_3), 27.7 (b, CH_2, cod), 29.7 (b, CH_2, cod), 31.2 (CH_3−Ph), 31.4 (CH_3, *t*Bu), 31.6 (b, CH_3, *t*Bu), 34.9 (C, *t*Bu), 35.0 (b, CH_2, cod), 35.2 (C, *t*Bu), 35.4 (b, C, *t*Bu), 35.8 (CH_3−Ph), 63.9 (CH═, cod), 66.0 (CH═, cod), 69.3 (CH_2), 74.0 (CH), 83.5 (b, C, CMe_2), 103.4 (d, CH═, cod, J_{C-P} = 18.0 Hz), 106.0 (d, CH═, cod, J_{C-P} = 10.5 Hz), 117.7 (b, CH═, BAr_F), 119−134 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−149 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.8 Hz), 176.6 (C═N). Anal. Calc (%) for $C_{82}H_{82}BF_{24}IrNO_4P$: C 53.66, H 4.50, N 0.76; found: C 53.69, H 4.47, N 0.73.

[Ir(cod)(L10a)]BArF. Yield: 119 mg (90%). ^{31}P NMR ($CDCl_3$) δ = 102.5 (s). ^{1}H NMR ($CDCl_3$) δ = 1.16 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.34 (s, 9H, CH_3, *t*Bu), 1.37 (s, 9H, CH_3, *t*Bu), 1.54 (s, 9H, CH_3, *t*Bu), 1.55 (s, 18H, CH_3, *t*Bu and *t*Bu-C═N), 1.71 (m, 4H, CH_2, cod), 2.07 (m, 1H, CH_2, cod), 2.20 (m, 1H, CH_2, cod), 2.37 (m, 1H, CH_2, cod), 2.55 (m, 1H, CH_2, cod), 4.09 (m, 1H, CH═, cod), 4.16 (dd, 1H, CH_2, $^2J_{H-H}$ = 10.5 Hz, $^3J_{H-H}$ = 3 Hz), 4.25 (t, 1H, CH_2, $^2J_{H-H}$ = 10.5), 4.51 (b, 2H, CH and CH═, cod), 4.76 (b, 1H, CH═, cod), 5.36 (b, 1H, CH═, cod), 7.1 − 7.8 (m. 16H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 21.1 (CH_3), 24.5 (b, CH_2, cod), 26.4 (CH_3), 28.3 (b, CH_2, cod), 29.4 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.3 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 34.5 (C, *t*Bu), 34.7 (b, CH_2, cod), 34.9 (C, *t*Bu), 35.3 (C, *t*Bu), 35.8 (C, *t*Bu), 37.6 (b, CH_2, cod), 69.1 (CH═, cod), 69.5 (CH═, cod), 69.6 (CH_2), 74.8 (CH), 83.8 (d, CMe_2, J_{C-P} = 5.7 Hz), 89.6 (d, CH═, cod, J_{C-P} = 26.2 Hz), 103.1 (d, CH═, cod, J_{C-P} = 10.5 Hz), 117.7 (b, CH═, BAr_F), 119−131 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−150 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.8 Hz), 183.9 (C═N). Anal. Calc (%) for $C_{78}H_{82}BF_{24}IrNO_4P$: C 52.41, H 4.62, N 0.78; found: C 52.38, H 4.60, N 0.75.

[Ir(cod)(L11a)]BArF. Yield:125 mg (88%). ^{31}P NMR ($CDCl_3$) δ = 98.3 (s). ^{1}H NMR ($CDCl_3$) δ = 1.16 (b, 3H, CH_3), 1.28 (b, 3H, CH_3), 1.39 (b, 18H, CH_3, *t*Bu), 1.55 (b, 18H, CH_3, *t*Bu), 1.69 (b, 3H, CH_2, cod), 2.27 (b, 3H, CH_2, cod), 2.46 (b, 2H, CH_2, cod), 4.01 (b, 1H, CH═, cod), 4.30 (b, 9H, CH═, Cp), 4.50 (b, 2H, CH═, cod), 4.70 (b, 2H, CH_2), 4.90 (b, 1H, CH), 5.23 (b, 1H, CH═, cod), 5.42 (b, 1H, CH═, cod), 7.1 − 7.8 (m, 16H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 22.0 (b, CH_2, cod), 28.8 (b, CH_2, cod), 31.5 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 31.9 (CH_3, *t*Bu), 32.1 (CH_3, *t*Bu), 33.7 (b, CH_2, cod), 34.9 (C, *t*Bu), 35.0 (C, *t*Bu), 35.4 (C, *t*Bu), 35.9 (C, *t*Bu), 37.0 (b, CH_2, cod), 67.5 (CH═, cod), 70.4 (CH═, cod), 71.0 (b, CH═, Cp), 71.9 (CH_2), 73.8 (CH), 84.9 (b, CMe_2), 95.0 (CH═, cod), 100.9 (CH═, cod), 117.7 (b, CH═, BAr_F), 119−131 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−150 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.8 Hz), 176.9 (C═N). Anal. Calc (%) for $C_{84}H_{82}BF_{24}FeIrNO_4P$: C 52.67, H 4.32, N 0.73; found: C 52.78, H 4.34, N 0.74.

[Ir(cod)(L12a)]BArF. Yield 123 mg (92%). ^{31}P NMR ($CDCl_3$) δ = 97.8 (s). 1H NMR ($CDCl_3$) δ = 1.06 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.35 (s, 9H, CH_3, *t*Bu), 1.38 (s, 9H, CH_3, *t*Bu), 1.54 (s, 9H, CH_3, *t*Bu), 1.61 (s, 9H, CH_3, *t*Bu), 1.70 (m, 4H, CH_2, cod), 2.32 (m, 3H, CH_2, cod), 2.51 (m, 1H, CH_2, cod), 3.60 (b, 1H, CH═, cod), 4.41 (m, 2H, CH═, cod and CH_2), 4.58 (b, 2H, CH═, cod and CH_2), 4.67 (dd, 1H, CH, $^3J_{H-H}$ = 10. 0 Hz, $^3J_{H-H}$ = 3.2 Hz), 5.32 (b, 1H, CH═, cod), 7.1−8.5 (m, 21H, CH═, aromatics). ^{13}C NMR ($CDCl_3$) δ = 21.3 (CH_3), 24.8 (b, CH_2, cod), 26.5 (m, CH_3), 28.09 (b, CH_2, cod), 31.2 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 33.2 (b, CH_2, cod), 34.8 (C, tBu), 34.9 (C, tBu), 35.2 (C, tBu), 37.3 (b, CH_2, cod), 66.3 (CH═, cod), 69.8 (CH═, cod), 70.0 (CH_2), 71.2 (CH), 84.9 (d, CMe_2, J_{C-P} = 5.2 Hz), 93.5 (d, CH═, cod, J_{C-P} = 21.1 Hz), 106.3 (d, CH═, cod, J_{C-P} = 6.2 Hz), 117.7 (b, CH═, BArF), 119−132 (aromatic carbons), 135.0 (b, CH═, BArF), 135.5−150 (aromatic carbons), 161.9 (q, C−B, BArF, $^1J_{C-B}$ = 48.6 Hz), 173.7 (C═N). Anal. Calc (%) for $C_{80}H_{78}BF_{24}IrNO_4P$: C 53.16, H 4.35, N 0.77; found: C 53.22, H 4.40, N 0.76.

[Ir(cod)(L14a)]BArF. Yield: 124 mg (92%). ^{31}P NMR ($CDCl_3$) δ = 99.1 (s). ^{1}H NMR ($CDCl_3$) δ = 1.12 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.37 (b, 18H, CH_3, *t*Bu), 1.57 (s, 9H, CH_3, *t*Bu), 1.63 (s, 9H, CH_3,*t*Bu), 1.70 (b, 4H, CH_2, cod), 2.15 (s, 3H, CH_3), 2.33 (b, 3H, CH_2, cod), 2.55 (b, 1H, CH_2, cod), 3.65 (b, 1H, CH═, cod), 3.65 (b, 1H, CH═, cod), 4.22 (b, 1H, CH-N), 4.41 (b, 1H, CH═, cod), 4.41 (b, 1H, CH═, cod), 4.61 (b, 1H, CH═, cod), 4.74 (b, 1H, CH−O), 5.25 (b, 1H, CH═, cod), 7.1 − 8.4 (m, 21H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 21.0 (CH_3), 21.8 (CH_3), 24.9 (b, CH_2, cod), 26.2 (b, CH_2, cod), 28.9 (b, CH_2, cod), 31.3 (CH_3,

*t*Bu), 31.4 (CH_3, *t*Bu), 31.6 (b, CH_3, *t*Bu), 33.6 (CH_3), 35.0 (C, *t*Bu), 35.1 (C, *t*Bu), 35.4 (b, C, *t*Bu), 35.8 (C, *t*Bu), 37.2 (b, CH_2, cod), 68.4 (CH═, cod), 70.2 (CH═, cod), 79.1 (CH−O), 80.3 (CH-N), 84.5 (d, C, CMe_2, J_{C-P} = 5.4 Hz), 94.7 (d, CH═, cod, J_{C-P} = 22.2 Hz), 105.7 (d, CH═, cod, J_{C-P} = 12.5 Hz), 117.7 (b, CH═, BAr_F), 119−134 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−149 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.5 Hz), 171.5 (C═N). Anal. Calc (%) for $C_{81}H_{80}BF_{24}IrNO_4P$: C 53.41, H 4.42, N 0.77; found: C 53.49, H 4.40, N 0.78.

[Ir(cod)(L15a)]BArF. Yield: 133 mg (93%). ^{31}P NMR ($CDCl_3$) δ = 92.7 (s). ^{1}H NMR ($CDCl_3$) δ = 1.37 (s, 9H, CH_3, *t*Bu), 1.39 (s, 9H, CH_3, *t*Bu), 1.57 (s, 9H, CH_3, *t*Bu), 1.58 (s, 9H, CH_3, *t*Bu), 1.67 (m, 2H, CH_2, cod), 1.80 (m, 2H, CH_2, cod), 2.30 (m, 1H, CH_2, cod), 2.39 (m, 2H, CH_2, cod), 3.68 (m, 1H, CH═, cod), 4.40 (b, 2H, CH═, cod and CH_2−O), 4.59 (b, 2H, CH═, cod and CH_2−O), 4.69 (dd, 1H, CH, $^2J_{H-H}$ = 12.8 Hz, $^3J_{H-H}$ = 3.2 Hz), 5.35 (b, 1H, CH═ cod), 7.1 − 7.8 (m. 31H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 22.9 (b, CH_2, cod), 28.9 (b, CH_2, cod), 31.4 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 31.7 (CH_3, *t*Bu), 33.4 (b, CH_2, cod), 35.0 (C, *t*Bu), 35.1 (C, *t*Bu), 35.4 (C, *t*Bu), 35.8 (C, *t*Bu), 37.1 (b, CH_2, cod), 68.1 (CH_2), 69.9 (CH), 70.2 (CH═, cod), 73.9 (CH═, cod), 84.8 (b, CPh_2), 95.1 (d, CH═, cod, J_{C-P} = 22 Hz), 106.4 (b, CH═, cod), 117.7 (b, CH═, BAr_F), 119−131 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−150 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.3 Hz), 172.1 (C═N). Anal. Calc (%) for $C_{90}H_{82}BF_{24}IrNO_4P$: C 55.96, H 4.28, N 0.73; found: C 55.93, H 4.26, N 0.70.

[Ir(cod)(L15f)]BArF. Yield: 123 mg (92%). ^{31}P NMR ($CDCl_3$) δ = 113.2 (s). ^{1}H NMR ($CDCl_3$) δ = 1.48 (m, 1H, CH_2, cod), 1.70 (m, 2H, CH_2, cod), 1.78 (m, 3H, CH_2, cod), 2.00 (m, 1H, CH_2, cod), 2.10 (m, 1H, CH_2, cod), 3.41 (m, 1H, CH═, cod), 3.94 (m, 1H, CH═, cod), 4.35 (m, 1H, CH_2), 4.47 (b, 2H, CH and CH═, cod), 5.28 (b, 1H, CH═, cod), 6.00 (m, 1H, CH_2), 6.9−8.5 (m. 39H, aromatics). ^{13}C NMR ($CDCl_3$) δ = 22.7 (b, CH_2, cod), 27.0 (b, CH_2, cod), 33.5 (b, CH_2, cod), 38.1 (b, CH_2, cod), 61.2 (CH), 64.6 (CH_2), 70.4 (CH═, cod), 71.8 (CH═, cod), 87.8 (b, CPh_2), 102.1 (d, CH═, cod, J_{C-P} = 17 Hz), 103.0 (b, CH═, cod, J_{C-P} = 17 Hz), 117.7 (b, CH═, BAr_F), 119−131 (aromatic carbons), 135.0 (b, CH═, BAr_F), 136−150 (aromatic carbons), 161.9 (q, C−B, BAr_F, $^1J_{C-B}$ = 49.3 Hz), 173.5 (C═N). Anal. Calc (%) for $C_{90}H_{82}BF_{24}IrNO_4P$: C 54.50, H 3.01, N 0.78; found: C 54.43, H 3.09, N 0.79.

4.4. General Procedure for the Preparation of Terminal Alkenes S11−S14. To a suspension of methyltriphenylphosphonium bromide (5.7 g, 15.9 mmol, 1.5 equiv) in THF (400 mL) at 0 °C under Ar was added *n*-butyllithium (2.5 M, 5.9 mL, 14.8 mmol, 1.4 equiv) dropwise. The resulting orange solution was stirred at 0 °C for 30 min. A solution of the corresponding ketone (10.6 mmol, 1.00 equiv) in THF (10 mL) was added dropwise, and the resulting yellow solution was left overnight at room temperature. The reaction was quenched with water (10 mL), extracted with Et_2O, and dried over $MgSO_4$. The precipitate was removed by filtration through a silica plug. The collected solids were washed with pentane (3 × 10 mL), and the filtrate was concentrated *in vacuo*.

S11. The crude product was purified on silica eluting with pentane. Colorless liquid (1.07 g, 7.10 mmol, 67% Yield).^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, 3H, CH_3, ^3J = 7.2 Hz), 1.38 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 2.36 (t, 2H, CH_2, ^3J = 7.6 Hz), 4.96 (s, 1H, CH_2═), 5.51 (s, 1H, CH_2═), 6.31 (m, 1H, CH═), 6.40 (m, 1H, CH═), 7.36 (m, 1H, CH═). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.8 (CH_3), 22.7 (CH_2), 31.1 (CH_2), 33.1 (CH_2), 106.1 (CH_2═), 109.2 (CH═), 111.2 (CH═), 129.9 (C), 137.9 (CH═), 141.9 (C).

S12. The crude product was purified on silica eluting with pentane. Colorless liquid (1.30 g, 7.80 mmol, 73% Yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, 3H, CH_3, ^3J = 7.7 Hz), 1.41 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 2.48 (t, 2H, CH_2, ^3J = 7.2 Hz), 4.96 (s, 1H, CH_2═), 5.40 (s, 1H, CH_2═), 6.97 (m, 1H, CH═), 7.05 (m, 1H, CH═), 7.18 (m, 1H, CH═) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.1 (CH_3), 22.7 (CH_2), 30.8 (CH_2), 35.4 (CH_2), 110.8 (CH_2═), 123.4 (CH═), 124.2 (CH═), 127.5 (CH═), 142.1 (C), 145.7 (C).

S13. The crude product was purified on silica eluting with pentane/ethyl acetate (99:1). Pale-yellow liquid (0.9 g, 6.8 mmol, 65% Yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.17 (t, 3H, CH_3, ^3J = 7.6 Hz), 2.66 (q, 2H, CH_2, ^3J = 7.4 Hz) 5.29 (s, 1H, CH_2═), 5.77 (s, 1H, CH_2═), 7.17 (m, 1H, CH═), 7.47 (m, 1H, CH═), 7.66 (m, 1H, CH═), 8.61 (m, 1H, CH═) ppm.

S14. The crude product was purified on silica eluting with pentane/ethyl acetate (99:1). Pale-yellow liquid (1 g, 6.2 mmol, 59% Yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.21 (s, 9H, CH_3 *t*Bu), 5.00 (s, 1H, CH_2 ═), 5.31 (s, 1H, CH_2═), 7.17 (m, 2H, Ar), 7.62 (m, 1H, Ar), 8.58 (m, 1H, Ar) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.1 (CH_3), 36.4 (C), 113.5 (CH_2═), 121.6 (CH═), 123.9 (CH═), 136.0 (CH═), 148.4 (CH═), 159.1 (C), 162.5 (C) ppm.

4.5. Preparation of S21. To a suspension of methyltriphenylphosphonium bromide (1.33 g, 3.72 mmol, 1.5 equiv) in Et_2O (20 mL) under Ar was added potassium *tert*-butoxide (0.39 g, 3.47 mmol, 1.4 equiv) dropwise. The resulting orange solution was stirred at 0 °C for 30 min. A solution of 2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone (0.51 g, 2.48 mmol, 1.00 equiv) in Et_2O (10 mL) was added dropwise, and the resulting yellow solution was left for 72 h at room temperature. The reaction was quenched with water (10 mL), extracted with Et_2O, and dried over $MgSO_4$. The crude product was purified on silica eluting with petroleum ether/ethylacetate (99:1) to obtain a colorless liquid (350 mg, 1.74 mmol, 70% yield). The characterization data are in agreement with the previously published data.[37]

4.6. 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. The enantiomeric excesses of hydrogenated products from **S1**,[38] **S2**−**S3**,[7b] **S4**−**S5**,[39] **S7**,[38] **S8**,[39] **S9**,[38] **S10**,[8] **S18**,[40] **S20**[41] were determined using the conditions previously described.

(4-Methylpentan-2-yl)benzene. For characterization details see ref 42. R_t (GC, Chiraldex β-DM, isotherm 75 °C, 100 Kpa H_2) = 17.3 min (*S*), 18.1 min (*R*).

2-(Hexan-2-yl)furan. ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.92 (t, 3H, CH_3, ^3J = 7.7 Hz), 1.32 (m, 7H, 2× CH_2 and CH_3), 1.63 (m, 2H, CH_2), 3.45 (m, 1H, CH), 6.98 (m, 1H, CH═), 7.15 (m, 1H, CH═), 7.28 (m, 1H, CH═). R_t (GC, Chiraldex β-DM, 50 °C for 30 min, 2 °C/min until 175 °C, 100 Kpa H_2) = 36.3 min (+), 37.2 min (−).

2-(Hexan-2-yl)thiophene. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, 3H, CH_3, ^3J = 7.7 Hz), 1.31 (m, 7H, 2x CH_2 and CH_3), 1.62 (m, 2H, CH_2), 3.03 (m, 1H, CH), 6.83 (m, 1H, CH═), 6.94 (m, 1H, CH═), 7.14 (m, 1H, CH═). R_t (GC, Chiraldex β-DM, 50 °C for 30 min, 2 °C/min until 175 °C, 100 Kpa H_2) = 53.7 min (+), 54.2 min (−).

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2-(Butan-2-yl)pyridine. For characterization details see ref 45. R_t (GC, Chiral β-Dex, 50 °C for 60 min, 3 °C/min until 150 °C, 120 Kpa H_2) = 75.1 min (−), 75.4 min (+).

2-(3,3-Dimethylbutan-2-yl)pyridine. For characterization details see ref 44. R_t (GC, Chiral β-Dex, 60 °C for 60 min, 3 °C/min until 150 °C, 120 Kpa H_2) = 63.5 min (−), 65.4 min (+).

1-(1-Phenylethyl)naphthalene. For characterization details see ref 45. R_t (HPLC, Chiracel OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm) = 11.0 min (+), 12.2 min (−).

1-Methyl-2-(1-phenylethyl)benzene. For characterization details see ref 46. R_t (HPLC, Chiracel IB, hexane/2-propanol = 99.8/0.2, 0.5 mL/min, 220 nm) = 8.9 min (+), 9.3 min (−).

1-Methoxy-4-{1-[4-(trifluoromethyl)phenyl]ethyl}benzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.62 (d, 3H, CH_3, ^3J = 7.2 Hz), 3.77 (s, 3H, CH_3−O), 4.28 (q, 1H, CH, ^3J = 7.2 Hz), 6.81 (m, 2H, CH═), 7.15 (m, 2H, CH═), 7.32 (m, 2H, CH═), 7.56 (m, 2H, CH). R_t (GC, Chiraldex β-DM, 50 °C for 30 min, 2 °C/min until 175 °C, 100 Kpa H_2) = 90.1 min (+), 90.4 min (−).

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2-Phenylpropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.34 (d, 3H, CH_3, ^3J = 6.4 Hz), 2.00 (s, 3H, CH_3, OAc), 3.09 (m, 1H, CH), 4.17 (m, 2H, CH_2), 7.21 (m, 3H, CH═), 7.32 (m, 2H, CH═) ppm. For ee determination, the sample was hydrolyzed to the corresponding alcohol by adding 1 mL of methanol and 50 mg of LiOH.

1-Methoxy-4-(1,1,1-trifluoropropan-2-yl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.42 (d, 3H, CH_3, ^3J = 7.2 Hz), 3.41 (q, 1H, CH, ^3J = 7.2 Hz), 3.74 (s, 3H, O−CH_3), 6.81 (m, 2H, CH═), 7.18 (m, 2H, CH═). R_t (GC, Chiraldex β-DM, 50 °C for 30 min, 2 °C/min until 175 °C, 100 Kpa H_2) = 9.2 min (−), 9.6 min (+).

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Supporting Information Available: X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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