Extending the substrate scope of bicyclic P-oxazoline/thiazole ligands for Ir-catalyzed hydrogenation of unfunctionalized olefins by introducing a biaryl phosphoroamidite group

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Abstract

This study identifies various Ir-bicyclic phosphoroamidite-oxazoline/thiazole catalytic systems that can hydrogenate a wide range of minimally functionalized olefins (including *E*- and *Z*-tri- and disubstituted substrates, vinylsilanes, enol phosphinates, tri- and disubstituted alkenylboronic esters and α,β-unsaturated enones) in high enantioselectivities (ee's up to 99%) and conversions. The design of the new phosphoroamidite-oxazoline/thiazole ligands derives from a previous successful generation of bicyclic *N*-phosphine-oxazoline/thiazole ligands, by replacing an *N*-phosphine group with a π-acceptor biaryl phosphoroamidite moiety. A small but structurally important family of Ir-phosphoroamidite-oxazoline/thiazole precatalysts has therefore been synthesized by changing the nature of the N-donor group (either oxazoline or thiazole) and the configuration at the biaryl phosphoroamidite moiety. The substitution of the *N*-phosphine by a phosphoroamidite group in the bicyclic *N*-phosphine-oxazoline/thiazole ligands extended the range of olefins that can be successfully hydrogenated.

Introduction

Chirality is a fundamental property for a wide variety of technologically and biologically interesting products. Enormous efforts are being made to discover enantioselective routes for creating stereogenic centers.[1] Of these routes, asymmetric hydrogenation is one of the most efficient, sustainable and straightforward. It has high selectivity, perfect atom economy and operational simplicity.[1,2] For this process, the use of Rh/Ru-PP based-catalysts is well known, but it normally requires substrates with a good coordination group close to the C-C double bond to achieve high selectivity.[1-3] To solve this limitation, the asymmetric reduction of olefins with chiral Ir-PN catalysts has emerged as an effective and easy method for producing complex chiral compounds from simple olefins.[4] In 1998 Pfaltz et al. reported the first successful application of an [Ir(PN)(cod)]BAr_F chiral catalyst library (PN= phosphine-oxazoline ligands (PHOX); cod = 1,5-cyclooctadiene) to a limited range of minimally functionalized olefins.[5] Then, Pfaltz and other groups focused their research on Ir-catalysts based on a wide range of new ligands (mainly P,N compounds), which significantly broadened the substrate scope. Most of the ligands were based on replacing the phosphine moiety in previous PHOX ligands with a phosphinite or a carbene group,[6] and the oxazoline moiety with other nitrogen groups such as pyridine,[7] thiazole,[8] oxazole[9] and imidazole[10].[11] The latest breakthrough in the design of ligands for Ir-catalyzed hydrogenation was the substitution of the phosphinite/phosphine group by a π-acceptor biaryl phosphite moiety. In this context, it was recently shown that the presence of biaryl-phosphite groups in ligand design increases activity and substrate versatility.[12] Several mixed phosphite-nitrogen compounds have therefore emerged as extremely effective ligands, providing better substrate versatility than earlier Ir-phosphinite/phosphine-N systems and higher activities and enantioselectivities for many largely unfunctionalized *E*/*Z*-trisubstituted and 1,1-disubstituted olefins. Although Ir-PN catalysts are powerful tools for reducing minimally functionalized olefins and they complement Rh/Ru catalysts, their activity and selectivity for some significant

substrates still need to be improved if they are to be used to synthesize more complex molecules. Therefore, novel, easy to handle, readily accessible, and highly efficient chiral ligands that enhance the application range still need to be found. Here, we report the successful application of a small but structurally valuable library of phosphoroamidite-oxazoline/thiazole ligands **L1**-**L4** (Figure 1) in the Ir-catalyzed hydrogenation of a large number of minimally functionalized alkenes, with the addition of concrete examples with neighboring polar groups.

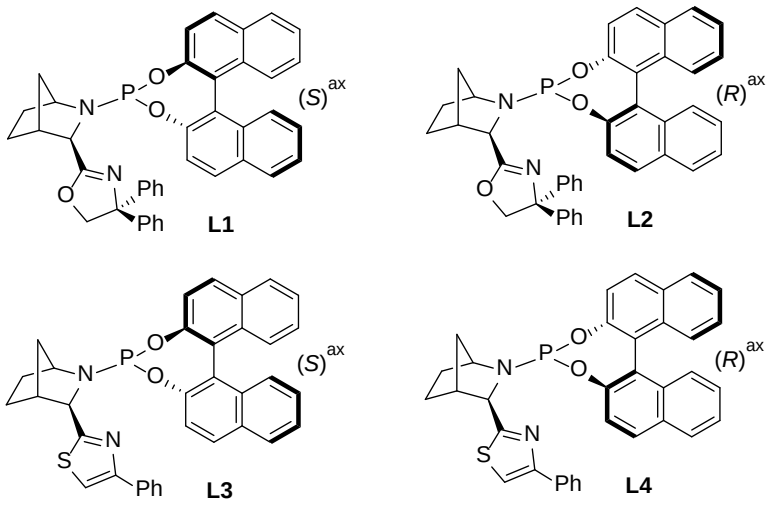


Figure 1. Phosphoroamidite-oxazoline/thiazole ligands **L1**-**L4**

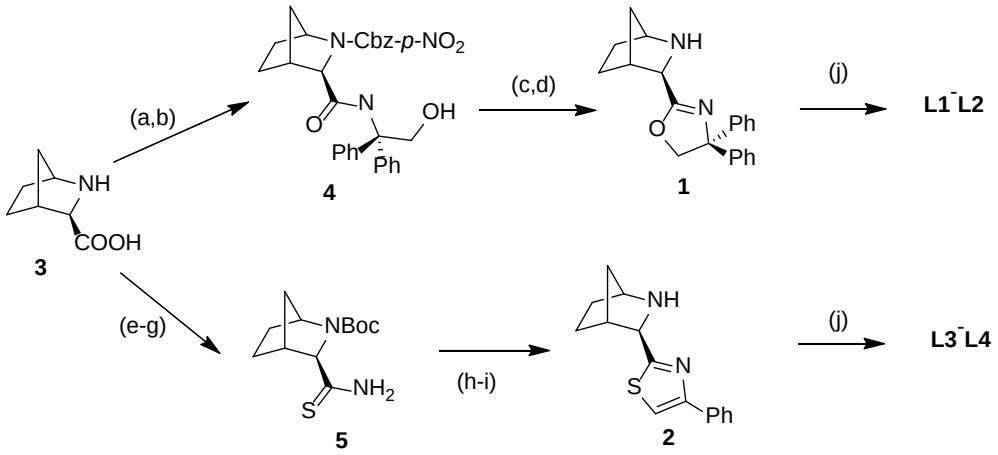
The new ligands are based on a first successful generation of bicyclic *N*-phosphine-oxazoline/thiazole ligands[6h,8g] in which the *N*-phosphine group is replaced by a π-acceptor biaryl phosphoroamidite moiety. The previous generation of bicyclic *N*-phosphine-oxazoline/thiazole ligands was one of the best performing ligand families developed for Ir-catalyzed hydrogenation and proved to be highly efficient in the hydrogenation of many minimally functionalized aryl-alkyl *E*-trisubstituted olefins.[6h,8g,13] Despite this, their enantioselectivity for such important substrates as *Z*-analogues, 1,1-disubstituted olefins and some compounds containing weakly coordinating groups still needs to be improved. With the simple biaryl phosphoroamidite-oxazoline/thiazole design introduced here (Figure 1), we expect to increase substrate versatility in the hydrogenation of largely unfunctionalized olefins.

Interestingly, in addition to having the a priori advantages of the π-acceptor properties of the phosphoroamidite moiety, ligands **L1**-**L4** are also more robust to air and other oxidizing agents than phosphines and phosphinites and are easily synthesized from readily available alcohols. Although phosphoroamidite-based ligands have been successfully used in other enantioselective reactions,[14] their potential as a source of highly effective chiral ligands in Ir-catalyzed hydrogenation is still unexplored.[15]

Results and discussion

Synthesis of ligands

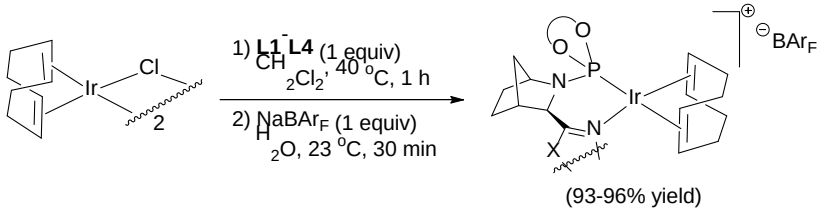
Scheme 1 shows the sequence of ligand synthesis. Ligands **L1**-**L4** were synthesized very efficiently from the appropriate, easily accessible amino-oxazoline **1** and amino-thiazole **2** compounds.[8g,16] Compounds **1** and **2** were prepared in 4 and 5 steps, respectively, following previously reported procedures from (1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]-heptane-3-carboxylic acid (**3**),[17] readily available in a multigram scale from a stereoselective aza-Diels Alder reaction. The last step of the synthesis is the same for all ligands (scheme 1, step j). Treating compounds **1** and **2** with 1 eq of the appropriate phosphorochloridite formed in situ[18] in the presence of triethylamine provided direct access to the desired phosphoroamidite-oxazoline/thiazole ligands **L1**-**L4**. All ligands were stable during purification on neutral silica under an atmosphere of argon and they were isolated as white solids. They were stable in air and very stable to hydrolysis, so further manipulation/storage was carried out in air. The elemental analyses and the HRMS-ESI spectra were in agreement with the assigned structure. The ligands were also characterized by $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The spectral assignments, made using ^{1}H–^{1}H and ^{13}C–^{1}H correlation measurements, were as expected for these C_1-symmetric ligands.



Scheme 1. Synthetic route for the synthesis of new phosphoroamidite-oxazoline/thiazole ligands **L1**-**L4**. (a) *p*-NO_2-CbzCl, NaOH, dioxane/H_2O, rt (86% yield). (b) EDC, HOBt, 2-amino-2,2-diphenylethanol, CH_2Cl_2, rt (83% yield). (c) MsCl, NEt_3, CH_2Cl_2, 0 ^oC (79% yield). (d) Pd/C, H_2, EtOH, rt (61% yield). (e) Boc_2O, THF/H_2O, rt (72% yield). (f) NH_4HCO_3, Py, dioxane (90% yield). (g) Lawesson's reagent, THF, rt (87% yield). (h) Phenacyl bromide, $CaCO_3$, MeOH, reflux (80% yield). (i) HCl, THF, rt (97% yield). (j) $ClP(OR)_2$, NEt_3, toluene, 80 °C (36-64% yield).

Synthesis of Ir-catalyst precursors

The Ir-catalyst precursors were prepared in a two-step, one-pot procedure (Scheme 2). First, $[Ir(\mu\text{-}Cl)(cod)]_2$ reacts with one equivalent of the appropriate ligand. Then, Cl^-/BAr_F^- counterion exchange was achieved by reaction with $NaBAr_F$ in the presence of water. The iridium catalyst precursors were isolated in pure form as air-stable orange solids in excellent yields (92-96%) after simple extraction workup. No further purification was needed. The elemental analyses were in agreement with the assigned structures. The HRMS-ESI spectra of [Ir(cod)(**L1**-**L4**)]BAr_F displayed the heaviest ions at m/z which correspond to the loss of the BAr_F anion from the molecular species. The ^1H, ^{13}C, and ^{31}P NMR spectra show the expected pattern for these C_1-complexes. The VT-NMR in CD_2Cl_2 (+35 to -85 °C) spectra show that only one isomer is present in solution. In all cases, one singlet in the ^{31}P-{^1H} NMR spectra was observed.

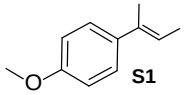
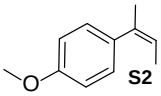


Scheme 2. Synthetic route for the synthesis of catalyst precursors [Ir(cod)(**L1**-**L4**)]BAr_F

Asymmetric Ir-catalyzed hydrogenation of trisubstituted substrates

The asymmetric hydrogenation of minimally functionalized trisubstituted olefins is highly dependent on the olefin geometry.[4] In this respect, Z-trisubstituted olefins are commonly hydrogenated less enantioselectively than the related *E*-isomers. In order to evaluate the efficiency of ligands **L1**-**L4** in the hydrogenation of olefins with different geometry, we initially tested them in the asymmetric reduction of the model substrate **S1** and the hydrogenation of *Z*-substrate **S2** (Table 1). In general, the enantioselectivities were found to be highly dependent on the configuration of the biaryl phosphoroamidite group. Ligands containing an *S*-binaphthyl phosphoroamidite group yielded the highest enantioselectivities for both substrates (entries 1 *vs* 2). However, while for substrate **S1** the nature of the N-donor group had little effect on enantioselectivity, for the more demanding substrate **S2** the presence of the thiazole group had a positive effect on enantioselectivity. Of the four ligands, phosphoroamidite-thiazole ligand **L3** provided excellent activities and enantioselectivities for both substrate types (ee's up to 97%; entry 3), thus overcoming one of the limitations encountered with the parent *N*-phosphine-oxazoline/thiazole ligands in the reduction of *Z*-olefin **S2** (ee's up to 83%[19]). We also studied these reactions at a low catalyst loading (0.25 mol%) using ligand **L3**, which had provided the best results, and the excellent enantioselectivities were maintained (Table 1, entry 5).

Table 1. Ir-catalyzed hydrogenation of **S1** and **S2** using ligands **L1**-**L4**[a]

		 S1		 S2	
Entry	Ligand	% Conv[b]	% ee[c]	% Conv[b]	% ee[c]
1	**L1**	100	92 (*R*)	100	82 (*S*)
2	**L2**	100	37 (*R*)	100	3 (*S*)
3	**L3**	100	95 (*R*)	100	97 (*S*)
4	**L4**	100	95 (*R*)	100	56 (*S*)
5[d]	**L3**	100	95 (*R*)	100	97 (*S*)

[a] Reactions carried out at room temperature using 0.5 mmol of substrate and 2 mol% of Ir-catalyst precursor at 50 bar of H_2 with dichloromethane (2 mL) as solvent. [b] Conversion measured by ^{1}H-NMR after 2 h. [c] Enantiomeric excess determined by GC. [d] Reaction carried out at 0.25 mol% of Ir-catalyst precursor for 3 h.

To further establish the extent of the new ligands **L1**-**L4** we selected a representative family of substrates, some of which contained poorly coordinative groups. The most noteworthy results are shown in Figure 2 (for a complete series of results, see Table SI-1 in Supporting Information). We again found that the ligand components must be selected particularly for each substrate in order to obtain the highest enantioselectivity. With the aim to compare these results with the first generation of ligands and the state of art for each substrate, we have collected all the results in Table SI-3 in the Supporting Information.

We first considered the reduction of substrates **S3**-**S4**, which differ from **S1** in the substituent in the aryl ring and the substituents *trans* to the aryl group. For both substrates Ir-**L3** provided also excellent enantioselectivities (up to 98%). For the more demanding dihydronaphthalenes **S5**-**S7** enantioselectivities were as high as 70% but, unlike *Z*-**S2**, using the Ir/**L1** catalytic system. Remarkably, the Ir/**L3** catalyst also provided high enantioselectivities in the reduction of triarylsubstituted substrates **S8** and **S9** (ee's up to 91%), surpassing the enantioselectivities obtained using the first generation of ligands. This latter substrate class has received few attention[8f,11c,12e] although it provides an easy entry point to diarylmethine chiral centers, which are

present in several important drugs.[20] We then looked into the hydrogenation of a broad range of key trisubstituted olefins with neighboring polar groups. Hydrogenation of these olefins is of particular interest because they can be further functionalized and become important intermediates for more complex chiral molecules. Interestingly, the reduction of allylic alcohol **S10** and vinylsilane **S11** with Ir/**L3** proceeded with higher enantioselectivities than those achieved when the first generation of bicyclic *N*-phosphine-oxazoline/thiazole ligands was used.[8g,13a] The Ir/**L1** catalytic system can also hydrogenate the sterically demanding enol phosphinates **S12**-**S16** with comparable high enantioselectivities to those achieved with the first generation of ligands, which constitute the state of art for this substrate class.[13b] The effective hydrogenation of this type of substrate opens up an appealing route for obtaining chiral organophosphinates, which can be easily transformed into high-value compounds such as alcohols and phosphines. The excellent results obtained up to this point encouraged us to test the hydrogenation of α,β-unsaturated enones **S17**-**S20** for which the related *N*-phosphine-oxazoline/thiazole counterparts provided low enantiocontrol.[21] The hydrogenation of this type of substrate is an elegant path for obtaining ketones with a stereogenic center in the α position of the carbonyl moiety. Nonetheless, they have been less studied and less successfully hydrogenated than other trisubstituted olefins.[6i,w] We found that a range of enones could be hydrogenated with comparable excellent enantioselectivities to the best ones reported. Interestingly, all four of the tested ligands provided similar high enantioselectivities (i.e. between 96-98% ee for substrate **S17;** see Supporting information) regardless of the configuration of the biaryl phosphoroamidite group and the nature of the N-donor group. This indicates that the bicyclic phosphoroamidite-N ligand's backbone is particularly well suited to the specific electronic and steric requirements of α,β-unsaturated enones. We also found that the hydrogenation of **S17**-**S20** yields products with opposite configuration than those achieved with the other *E*-trisubstituted olefins studied. This behavior has been observed previously and it is attributed to the strong polarization of the double bond.[4h,8i]

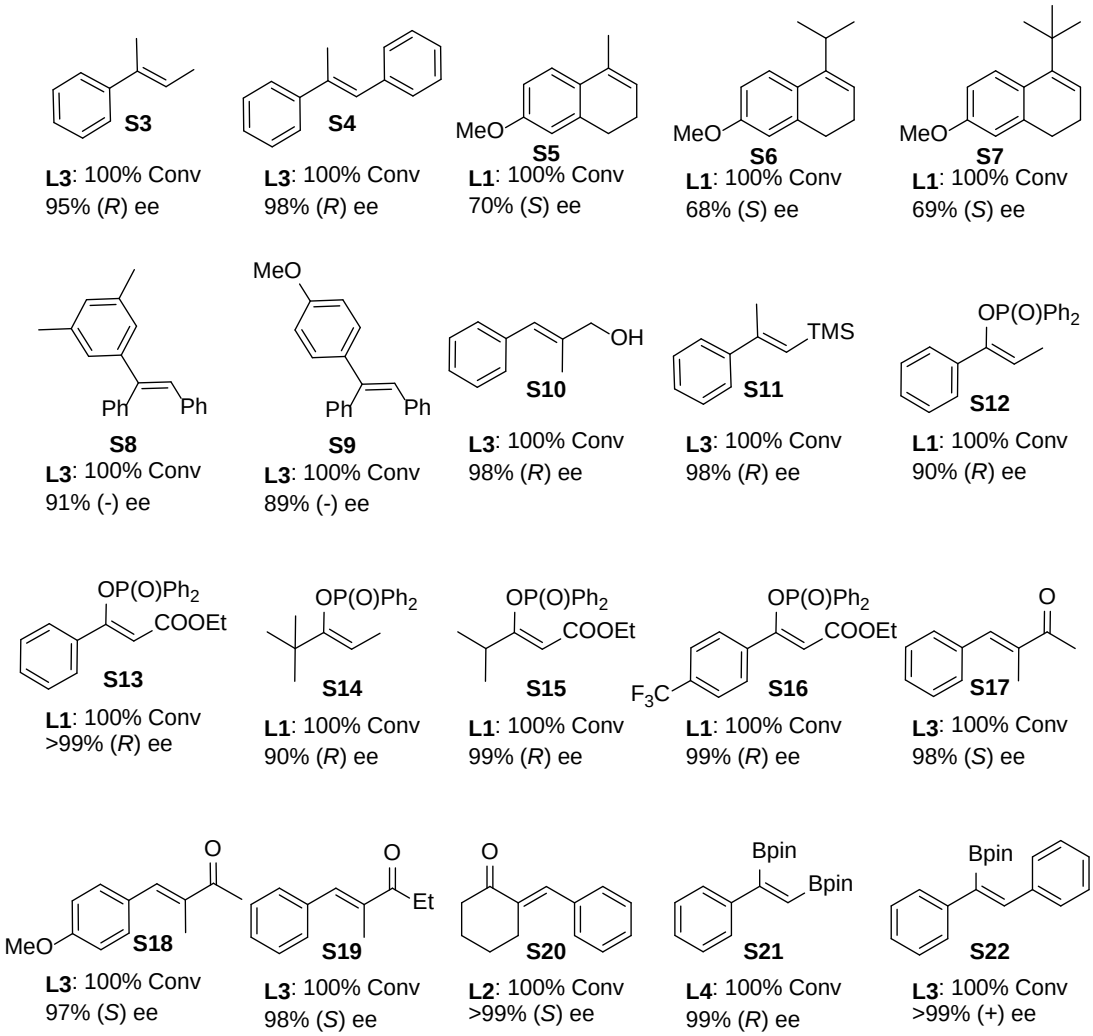


Figure 2. Selected results for the hydrogentaion of trisubstituted olefins **S3**-**S22** using [Ir(cod)(**L1**-**L4**)]BAr_F catalyst precursors. Reaction conditions: 2 mol % catalyst precursor, CH_2Cl_2 as solvent, 50 bar H_2, 4 h.

We finally turned our attention to the asymmetric reduction of alkenylboronic esters. Among the existing methods for preparing chiral organoboron compounds, this is one of the most sustainable and most straightforward. The synthesis of chiral organoboron compounds has recently received considerable attention because they are valuable organic intermediates since the C-B bond can be readily transformed into chiral C-N, C-O and C-C bonds. In this field, the reduction of alkenylboronic esters has been less investigated and only a few catalytic systems have been used effectively.[11d,13c,22] Our results show that by correctly choosing the N-donor group (thiazole rather than

oxazoline) and the configuration of the biaryl group (*R* for **S21** and *S* for **S22**) of the ligand enantioselectivities can be excellent for the reduction of two types of alkenylboronic esters containing one of or two (pinacolato)boron groups. The enantioselectivities achieved are among the best reported in the literature, surpassing the ones obtained with the first generation of ligands.[11d,13c,22]

In summary, the simple substitution of the *N*-phosphine by a phosphoroamidite group in the bicyclic *N*-phosphine-oxazoline/thiazole ligands extended the range of hydrogenated trisubstituted olefins and let to enantioselectivities that for most of the substrates were among the best reported so far (see Table SI-3).[23]

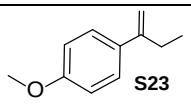
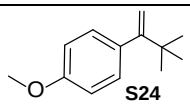
Asymmetric Ir-catalyzed hydrogenation of 1,1-disubstituted substrates

Unlike trisubstituted olefins, 1,1-disubstituted olefins have not been successfully hydrogenated until very recently.[4e,h] This is because the catalyst has the added difficulty of controlling not only the face selectivity coordination (only two substituents compared with the three of trisubstituted olefins), but also the isomerization of the olefins to form the more stable *E*-trisubstituted substrates, which are hydrogenated to form the opposite enantiomer.[4e,h] In order to estimate how effective ligands **L1**-**L4** are at reducing this type of substrate, we first studied the hydrogenation of substrates **S23** and **S24**, which have different steric requirements at the alkyl chain (Table 2). In addition, while substrate **S23** is prone to isomerization, **S24** cannot isomerize. In all cases full conversions were achieved using 1 bar of H_2.[24]

We found that the effect of the ligand parameters on enantioselectivity is different for the two substrates. While for **S23** the effect is like the one observed for **S1** and **S2** (the enantioselectivity was highest with phosphoroamidite-thiazole ligand **L3**), the enantioselectivity for **S24** was best with the phosphoroamidite-oxazoline ligand **L1**. We also found that enantioselectivities are highly dependent on the nature of the alkyl chain of the substrate (Table 2). While enantioselectivities up to 93% can be achieved with **S24**, only moderate enantiocontrol was obtained in the reduction of **S23** (up to 65% ee). This suggests that competition between isomerization and direct hydrogenation may be

responsible for the moderate enantioselectivities achieved using **S23**. However, face selectivity issues cannot be excluded.

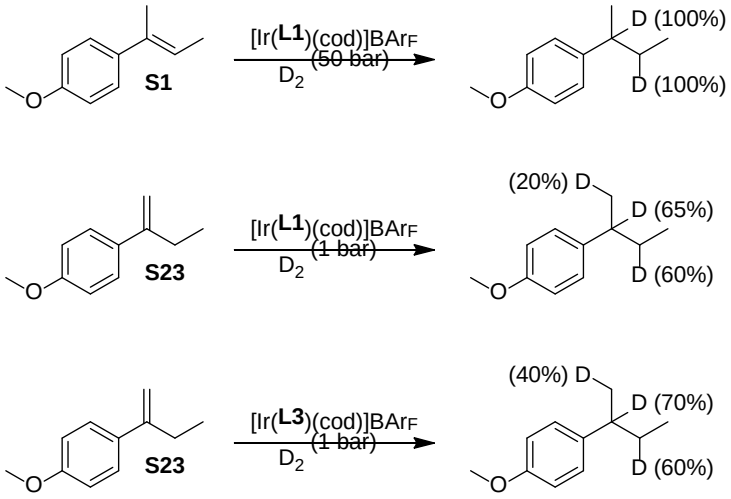
Table 2. Ir-catalyzed hydrogenation of **S23** and **S24** using ligands **L1**-**L4**[a]

		 S23		 S24	
Entry	Ligand	% Conv[b]	% ee[c]	% Conv[b]	% ee[c]
1	**L1**	100	13 (*R*)	100	93 (*S*)
2	**L2**	100	3 (*S*)	100	69 (*S*)
3	**L3**	100	65 (*S*)	100	76 (*S*)
4	**L4**	100	40 (*S*)	100	68 (*S*)
5[d]	**L1**	100	12 (*R*)	100	93 (*S*)

[a] Reactions carried out at room temperature using 0.5 mmol of substrate and 2 mol% of Ir-catalyst precursor at 1 bar of H_2 with dichloromethane (2 mL) as solvent. [b] Conversion measured by ^{1}H-NMR after 2 h. [c] Enantiomeric excess determined by GC. [d] Reaction carried out at 0.25 mol% of Ir-catalyst precursor for 3 h.

To address this point, we performed deuterium labeling experiments (Scheme 3). For this purpose we did the reduction of **S1** and **S23** with deuterium. In contrast to **S1**, the reduction of **S23** with deuterium led to the incorporation of deuterium not only at the expected positions (direct addition to the double bond) but also at the allylic position, which is indicative of the presence of a competing isomerization process. It has been suggested that this isomerization process can proceeds either via the formation of Ir-π-allyl intermediates or via protonation of the double bond at the terminal position, which gives a stabilized carbocation.[6d,25] Accordingly, the mass spectra data of the resulting deuterated products, in the deuterium addition to **S23**, indicated the presence of reduced species with more than two deuteriums incorporated into the product.

We also studied these reactions at a low catalyst loading (0.25 mol%) and the catalytic performance was maintained (Table 2, entry 5).



Scheme 3. Deuterium labeling experiments of substrates **S1** and **S23**. The percentage of incorporation of deuterium atoms is shown in brackets.

In line with the observed isomerization, similar moderate enantioselectivities were achieved in the hydrogenation of substrates **S25**-**S28** regardless of the steric demands of the alkyl substituents (Figure 3).

We then focused on evaluating how the electronic and steric properties of the aryl group of the substrate affected the catalytic performance. For this purpose a wide range of α-*tert*-butylstyrene type substrates (**S29**-**S35)** were tested (Figure 3). Advantageously, we found that enantioselectivity (ee's up to 98%) is relatively insensitive to changes in the electronic and steric properties of the aryl group. However, the highest enantioselectivity of the series was achieved in the hydrogenation of substrates containing either electron withdrawing groups at the *para* position (**S29**) or substituents at the *ortho* position (**S34**-**S35**) of the aryl group.

Finally, we also investigated the hydrogenation of relevant 1,1-disubstituted olefins containing neighboring polar groups (Figure 3, substrates **S36**-**S41**). We were again able to fine tune the ligand to obtain high-to-excellent enantioselectivities (ee's up to 98%). The results are among the best in the literature for each substrate, even in the reduction of such highly appealing substrates as enol phosphinates **S38**-**S39**[26] and pinacolatoboron-containing substrates **S40**[27] and **S41**[28] for which only very few catalytic systems have provided high enantioselectivities. It should be noted that

although **S41** is prone to isomerization it has been hydrogenated with high enantioselecitivity.

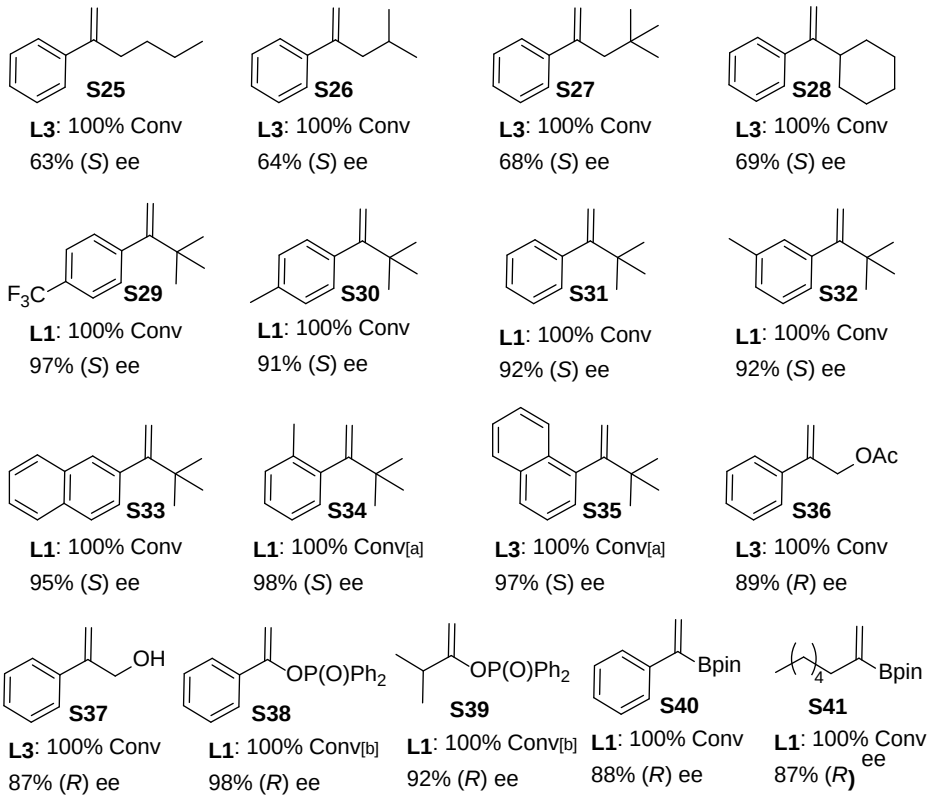


Figure 3. Selected results for the hydrogenation of 1,1-disubstituted olefins **S25-S41** using [Ir(cod)(**L1**-**L4**)]BAr_F catalyst precursors. Reaction conditions: 2 mol % catalyst precursor, CH_2Cl_2 as solvent, 1 bar H_2, 4 h. [a] Reactions carried out for 8 h. [b] Reaction carried out at 50 bar H_2 for 12 h

In summary, although isomerization were not completely suppressed by introducing a biaryl phosphoroamidite group, the face coordination mode of the substrate was successfully controlled, thus facilitating the reduction of a broad range of 1,1-disubstituted substrates with high enantioselectivities, comparable for most of the substrates (except for olefins prone to isomerization) to the best reported so far. Once again the introduction of this group was also advantageous in comparison with related bicyclic ***N***-phosphine-oxazoline/thiazole counterparts that have been efficiently applied in the hydrogenation of very few 1,1-disubstituted substrates[8g,13b,c,26a]. See Table SI-4

in the Supporting Information to compare these results with the first generation of ligands and the state of art for each substrate.

Conclusion

We have identified new Ir-bicyclic phosphoroamidite-oxazoline/thiazole catalytic systems that can hydrogenate a wide range of minimally functionalized olefins (including *E*- and *Z*-tri- and disubstituted substrates, vinylsilanes, enol phosphinates, tri- and disubstituted alkenylboronic esters and α,β-unsaturated enones) with enantioselectivities up to 99% and with high conversions. These catalytic systems derive from a previous successful generation of Ir-bicyclic *N*-phosphine-oxazoline/thiazole catalysts, by replacing an *N*-phosphine group of the ligand with a π-acceptor biaryl phosphoroamidite moiety. The simple substitution of the *N*-phosphine by a phosphoroamidite group extended the range of successfully hydrogenated olefins with enantioselectivities comparable for most of the substrates to the best reported so far. In this respect, the new Ir-phosphoroamidite-oxazoline/thiazole catalysts have been able to efficiently hydrogenate not only minimally functionalized model olefins (i.e. **S1**, **S2**, **S4** and **S10**), but also a wide range of demanding olefins (**S5**-**S9** and **S11**-**S41**) that have recently received a great deal of attention because the resulting hydrogenated compounds can be easily stereoselectively transformed into high-value organic compounds. Therefore, the effective hydrogenation of these substrates with the Ir-bicyclic phosphoroamidite-oxazoline/thiazole catalysts reported in the present study opens up an appealing route that is more efficient, straightforward, sustainable and selective than alternative methods.[29] Another important advantage of the new ligands, in front of previous bicyclic *N*-phosphine-oxazoline/thiazole ligands, is that they are solid and stable to air and therefore easier to handle and can be manipulated and stored in air.

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 were easily prepared in one step from the corresponding binaphthols.[18] Intermediate amine-oxazoline/thiazole compounds **1**[16]-**2**[8g] were prepared as previously reported. Neutral silica (pH= 7, 0.040-0.063 mm) was purchased from Merck. ^{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 and ^{13}C assignments were made on the basis of ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC.

General procedure for the preparation of phosphoroamidite-oxazoline/thiazole ligands L1-L4

The corresponding phosphorochloridite (0.5 mmol) produced *in situ* was dissolved in toluene (2 mL), and triethylamine (0.3 mL, 2.15 mmol) was added. The amino-oxazoline/thiazole compound (0.5 mmol) was azeotropically dried with toluene (3 x 3 mL) and then dissolved in toluene (2 mL) to which triethylamine (0.3 mL, 2.15 mmol) was added. The phosphorochloridite solution was then transferred slowly to the amino-oxazoline/thiazole solution. The reaction mixture was stirred at 80 ºC for 2 h, after which the triethylamine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography on neutral silica (dichloromethane as eluent) to produce the corresponding ligand as a white solid.

L1: Yield: 118 mg (37%). $[\alpha]_D^{23}$ = +102.41 (c = 0.1 in CH_2Cl_2).^{31}P NMR (161.9 MHz, C_6D_6, 25 ºC): δ= 153 ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ= 0.70 (d, ^{2}J(H,H)= 10.0 Hz, 1H; CH_2,), 0.75 (m, 1H; CH_2), 1.0 (m, 2H; CH_2), 1.65 (m, 1H; CH_2), 1.9 (b, 1H; CH_2), 2.40 (b, 1H; CH), 3.35 (b, 1H; CH), 3.80 (b, 1H; CH), 4.47 (d, ^{2}J(H,H)= 8.4 Hz, 1H; CH_2), 4.56 (d, ^{2}J(H,H)= 8.4 Hz, 1H; CH_2), 6.80-8.81 ppm (m,

12H; CH=); ^{13}C NMR (100.6 MHz, C_6D_6, 25 ºC): δ= 27.6 (CH_2), 34.4 (CH_2), 36.8 (CH_2), 42.1 (CH), 53.5 (C), 58.2 (CH), 61.4 (d, ^2J(C,P)= 20.4 Hz; CH,), 80.6 (CH_2), 122.3-167.4 ppm (aromatic carbons); TOF-MS (ESI+): m/z= 633.2307, calcd. for $C_{41}H_{33}N_2O_3P$ $[M+H]^+$: 633.2307; elemental analysis calcd (%) for $C_{41}H_{33}N_2O_3P$: C 77.83, H 5.26, N 4.43; found: C 77.81, H 5.24, N 4.39.

L2: Yield: 114 mg (36%). $[\alpha]_D^{23}$ = -112.24 (c = 0.1 in CH_2Cl_2); ^{31}P NMR (161.9 MHz, C_6D_6, 25 ºC): δ= 146.2 ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ= 0.56 (d, ^2J(H,H)= 10.0 Hz, 1H; CH_2,), 0.85 (m, 1H; CH_2), 1.10 (m, 2H; CH_2), 1.72 (m, 1H; CH_2), 1.82 (b, 1H; CH_2) 2.46 (b, 1H; CH), 3.63 (b, 1H; CH), 3.97 (s, 1H; CH), 4.47 (d, ^2J(H,H)= 8.8 Hz, 1H; CH_2), 4.56 (d, ^2J(H,H)= 8.8 Hz, 1H; CH_2), 6.86-7.67 ppm (m, 12H, CH=); ^{13}C NMR (100.6 MHz, C_6D_6, 25 ºC): δ= 28.7 (CH_2), 33.6 (CH_2), 43.6 (CH), 46.1 (CH_2), 54.1 (C), 57.6 (CH), 62.5 (d, ^2J(C,P)= 19.2 Hz; CH), 81.4 (CH_2), 123.1-168.5 ppm (aromatic carbons); TOF-MS (ESI+): m/z= 633.2304, calcd. for $C_{41}H_{33}N_2O_3P$ $[M+H]^+$: 633.2307; elemental analysis calcd (%) for $C_{41}H_{33}N_2O_3P$: C 77.83, H 5.26, N 4.43; found: C 77.80, H 5.24, N 4.37..

L3: Yield: 182 mg (64%). $[\alpha]_D^{23}$ = +188.18 (c = 0.11 in CH_2Cl_2); ^{31}P NMR (161.9 MHz, C_6D_6, 25 ºC): δ= 155.5 ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ= 0.65 (d, ^2J(H,H)= 10.0 Hz, 1H; CH_2,), 0.80 (m, 1H; CH_2), 1.10 (m, 1H; CH_2), 1.22 (m, 1H; CH_2), 1.80 (b, 2H; CH_2) 2.45 (b, 1H; CH), 3.40 (b, 1H; CH), 4.63 (d, ^3J(H,P)= 4.0 Hz 1H; CH,), 6.82-7.98 ppm (m, 13H; CH=); ^{13}C NMR (100.6 MHz, C_6D_6, 25 ºC): δ= 28.3 (CH_2), 32.5 (CH_2), 36.2 (CH_2), 46.4 (CH), 59.1 (CH), 66.3 (d, ^2J(C,P)= 24.2 Hz; CH,), 133.7-176.4 ppm (aromatic carbons); TOF-MS (ESI+): m/z= 571.1599, calcd. for $C_{35}H_{27}N_2O_2PS$ $[M+H]^+$: 571.1609; elemental analysis calcd (%) for $C_{35}H_{27}N_2O_2PS$: C 73.67, H 4.77, N 4.91, S 5.62; found: C 73.69, H 4.76, N 4.87, S 5.57.

L4: Yield: 163 mg (57%). $[\alpha]_D^{23}$ = -133.64 (c = 0.11 in CH_2Cl_2); ^{31}P NMR (161.9 MHz, C_6D_6, 25 ºC): δ= 147.5 ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ= 0.76 (d, ^2J(H,H)= 10.0 Hz, 1H; CH_2), 1.10 (m, 1H; CH_2), 1.23 (m, 1H; CH), 1.78 (m, 1H; CH_2), 1.98 (d, ^2J(H,H)= 10.0 Hz, 1H; CH_2), 2.40 (b, 1H; CH), 3.84 (b, 1H; CH), 4.78 (d, ^3J(C,P)= 3.2 Hz, 1H; CH), 6.86-8.07 ppm (m, 13H; CH=). ^{13}C NMR (100.6 MHz, C_6D_6,

25 ºC): δ= 28.2 (CH_2), 33.5 (CH_2), 36.7 (CH_2), 46.7 (CH), 58.7 (CH), 65.4 (d, ^2J(C,P)= 17.4 Hz; CH), 113.3-175.8 ppm (aromatic carbons); TOF-MS (ESI+): m/z= 571.1602, calcd. for $C_{35}H_{27}N_2O_2PS$ $[M+H]^+$: 571.1609; elemental analysis calcd (%) for $C_{35}H_{27}N_2O_2PS$: C 73.67, H 4.77, N 4.91, S 5.62; found: C 73.64, H 4.75, N 4.87, S 5.59.

General procedure for the preparation of [Ir(cod)(L1-L4)]BAr_F

The corresponding ligand (0.074 mmol) was dissolved in CH_2Cl_2 (5 mL) and [Ir(μ-Cl)(cod)]$_2$ (25.0 mg, 0.037 mmol) was added. The reaction mixture was refluxed at 40 ºC for 1 hour. After 5 min at room temperature, $NaBAr_F$ (77.2 mg, 0.080 mmol) and water (5 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered through a plug of celite and the solvent was evaporated to give the product as an orange solid.

[Ir(cod)(L1)]BAr_F: Yield 127 mg (96%). ^{31}P NMR (161.9 MHz, $CDCl_3$, 25 ºC), δ: 112.0 ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 1.26 (s, 7H; CH_2 and CH), 1.56 (m, 4H; CH_2, cod), 1.90 (m, 2H; CH_2, cod), 2.04 (m, 1H; CH_2, cod), 2.27 (m, 1H; CH_2, cod), 2.43 (m, 1H; CH), 3.91 (m, 1H; CH=, cod), 4.35 (m, 1H; CH), 4.49 (b, 1H; CH=, cod), 4.61 (d, ^2J(H,H)= 9.2 Hz, 1H; CH=, cod), 5.21 (d, ^2J(H,H)= 9.2 Hz, 2H; CH_2), 6.68 - 8.02 ppm (m, 32H, CH=); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC) δ: 22.9 (b; CH_2, cod), 27.2 (CH_2), 27.4 (b; CH_2, cod), 29.9 (CH), 30.6 (CH_2), 31.0 (b; CH_2, cod), 34.1 (CH_2), 38.7 (b; CH_2, cod), 57.6 (CH=, cod), 58.5 (CH), 62.0 (CH=, cod), 62.4 (CH), 82.6 (CPh_2), 86.6 (CH_2), 97.7 (CH=, cod), 101.3 (CH=, cod), 119.5-133 (aromatic carbons), 135.0 (b; CH=, BAr_F), 136-149 (aromatic carbons), 162.0 (q, ^1J(C,B)= 49.8 Hz; C-B, BAr_F,), 173.0 ppm (C=N); TOF-MS (ESI+): m/z= 933.2795, calcd. for $C_{81}H_{57}BF_{24}IrN_2O_3P$ $[M\text{-}BArF]^+$: 933.2797; elemental analysis calcd (%) for $C_{81}H_{57}BF_{24}IrN_2O_3P$: C 54.16, H 3.20, N 1.56; found: C 54.13, H 3.16, N 1.53.

[Ir(cod)(L2)]BAr_F: Yield 123 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$, 25 ºC), δ: 102.9 ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 1.21 (s, 7H; CH_2 and CH), 1.59

(m, 4H; CH_2, cod), 1.85 (m, 2H; CH_2, cod), 2.01 (m, 1H; CH_2, cod), 2.35 (m, 1H; CH_2, cod), 3.50 (m, 1H; CH), 3.69 (m, 1H; CH), 4.27 (b, 1H; CH= cod), 4.58 (b, 1H; CH= cod), 4.68 (b, 1H; CH= cod), 4.95 (d, ^2J(H,H)= 9.2 Hz, 1H; CH_2), 5.22 (d, ^2J(H,H)= 9.2 Hz, 1H; CH_2), 5.29 (b, 1H; CH= cod), 7.0 – 8.3 ppm (m. 32H; CH=); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 24.5 (b; CH_2, cod), 25.7 (CH_2), 28.7 (b; CH_2, cod), 29.4 (CH), 31.7 (CH_2), 32.0 (b; CH_2, cod), 38.3 (CH_2), 39.3 (b; CH_2, cod), 57.5 (CH=, cod), 58.5 (CH), 62.3 (CH=, cod), 65.9 (CH), 82.9 (CPh_2), 86.3 (CH_2), 93.8 (CH=, cod), 100.5 (CH=, cod), 117.7 (b; CH=, BArF), 119-131 (aromatic carbons), 135.0 (b; CH=, BAr_F), 136-150 (aromatic carbons), 161.9 (q, ^1J(C,B)= 49.8 Hz; C-B, BAr_F), 173.3 ppm (C=N); TOF-MS (ESI+): m/z= 933.2792, calcd. for $C_{81}H_{57}BF_{24}IrN_2O_3P$ $[M\text{-}BArF]^+$: 933.2797; elemental analysis calcd (%) for $C_{81}H_{57}BF_{24}IrN_2O_3P$: C 54.16, H 3.20, N 1.56; found: C 54.12, H 3.16, N 1.52.

[Ir(cod)(L3)]BAr_F: Yield 119 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$, 25 ºC), δ: 104.3 ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 1.26 (s, 7H; CH_2 and CH), 1.36 (m, 2H; CH_2, cod), 1.63 (m, 2H; CH_2, cod), 1.73 (m, 2H; CH_2, cod), 2.11 (m, 1H; CH_2, cod), 2.25 (m, 1H; CH_2, cod), 2.77 (m, 1H; CH), 2.98 (m, 1H; CH), 3.36 (m, 1H; CH= cod), 4.39 (b, 1H; CH= cod), 4.47 (b, 1H; CH= cod), 4.84 (b, 1H; CH= cod), 5.00 (s, 1H; CH=), 6.7 – 8.2 ppm (m. 27H; CH=); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 25.3 (b; CH_2, cod), 28.3 (CH_2), 29.8 (b; CH_2, cod), 31.3 (CH), 31.7 (CH_2), 32.9 (b; CH_2, cod), 37.7 (CH_2), 40.9 (b; CH_2, cod), 53.7 (CH), 60.0 (CH), 62.3 (CH=, cod), 65.2 (CH=), 65.4 (CH=, cod), 94.5 (d, J(C,P)= 21.3 Hz; CH=, cod), 103.6 (d, J(C,P)= 11.4 Hz; CH=, cod), 116.7 (C), 117.7 (b; CH=, BAr_F), 119-131 (aromatic carbons), 135.0 (b; CH=, BAr_F), 136-148 (aromatic carbons), 161.9 (q, ^1J(C,B)= 49.8 Hz; C-B, BAr_F), 170.8 ppm (C=N); TOF-MS (ESI+): m/z= 871.2087, calcd. for $C_{75}H_{51}BF_{24}IrN_2O_2PS$ $[M\text{-}BArF]^+$: 871.2090; elemental analysis calcd (%) for $C_{75}H_{51}BF_{24}IrN_2O_2PS$: C 51.94, H 2.96, N 1.62, S 1.85; found: C 54.89, H 2.94, N 1.59, S 1.81.

[Ir(cod)(L4)]BAr_F: Yield 122 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$, 25 ºC), δ: 102.5 ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 1.27 (s, 7H; CH_2 and CH), 1.39 (m, 2H; CH_2, cod), 1.56 (m, 2H; CH_2, cod), 1.89 (m, 2H; CH_2, cod), 2.07 (m, 1H; CH_2,

cod), 2.23 (m, 1H; CH_2, cod), 3.41 (m, 1H; CH= cod), 4.46 (b, 1H; CH= cod), 3.62 (m, 1H; CH), 4.03 (b, 1H; CH= cod), 4.93 (m, 1H; CH), 5.00 (b, 1H; CH= cod), 5.35 (s, 1H; CH=), 7.1 – 8.3 ppm (m. 27H; CH=); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 24.9 (b; CH_2, cod), 27.0 (CH_2), 28.1 (b; CH_2, cod), 29.9 (CH), 31.2 (CH_2), 32.8 (b; CH_2, cod), 37.6 (CH_2), 42.2 (b; CH_2, cod), 58.7 (CH), 65.5 (CH), 65.9 (CH=), 66.0 (CH=, cod), 68.3 (CH=, cod), 97.6 (CH=, cod), 105.7 (CH=, cod), 117.2 (C), 117.7 (b; CH=, BAr_F), 119-131 (aromatic carbons), 135.0 (b; CH=, BAr_F), 136-150 (aromatic carbons), 161.9 (q, ^1J(C,B)= 49.8 Hz; C-B, BAr_F), 172.6 ppm (C=N). TOF-MS (ESI+): m/z= 871.2084, calcd. for $C_{75}H_{51}BF_{24}IrN_2O_2PS$ $[M\text{-}BArF]^+$: 871.2090; elemental analysis calcd (%) for $C_{75}H_{51}BF_{24}IrN_2O_2PS$: C 51.94, H 2.96, N 1.62, S 1.85; found: C 54.90, H 2.94, N 1.60, S 1.83.

General procedure for the preparation of substrates S24, S29, S30, S32-S35.

In a flame dried Schlenk, methyltriphenylphosphonium bromide (9.2 mmol) was stirred in dry THF (40 mL). The mixture solution was cooled to 0 ºC and *n*BuLi solution (1.6 M in hexane, 5.4 mL, 8.6 mmol) was slowly added. The reaction was left at 0 ºC for 30 min and then, aryl *tert*-butyl ketone[30] (6.2 mmol) in dry THF (6 mL) was added. The reaction mixture was warmed to room temperature. After 18 h, NH_4Cl (sat., 20 mL) was added, followed by extraction with diethyl ether (3x25 mL). The organic phases were dried over anhydrous $MgSO_4$. Removal of solvents gave a crude product, which was purified by flash column chromatography on silica gel (100% petroleum ether) to afford the corresponding 1,1'-disubstitued olefin as a colorless oil.

1-(3,3-Dimethylbut-1-en-2-yl)-4-methoxybenzene (S24): Yield 695 mg (59 %). ^{1}H NMR (400 MHz, $CDCl_3$,25 ºC): δ= 1.10 (s, 9H), 3.81 (s, 3H), 4.74 (d, 1H, $^2J_{H\text{-}H}$= 1.6 Hz), 5.14 (d, 1H, $^2J_{H\text{-}H}$= 1.6 Hz), 6.81-7.26 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 29.7, 36.2, 55.1, 111.6, 112.7, 130.0, 135.9, 158.1, 159.4; TOF-MS (ESI+): m/z= 191.1390, calcd. for $C_{13}H_{18}O$ $[M+H]^+$: 191.1391.

1-(3,3-Dimethylbut-1-en-2-yl)-4-(trifluoromethyl)benzene (S29): Yield 862 mg (61 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ= 1.18 (s, 9H), 4.80 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 5.25 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 7.23-7.61 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 29.6, 36.1, 112.3, 124.4, 124.8 (q, $^{1}J_{C-F}$= 6.0 Hz), 129.3, 130.2, 158.7; TOF-MS (ESI+): m/z= 229.1161, calcd. for $C_{13}H_{15}F_3$ $[M+H]^+$: 229.1159.

1-(3,3-Dimethylbut-1-en-2-yl)-4-methylbenzene (S30): Yield 755 mg (70 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ= 1.17 (s, 9H), 2.40 (s, 3H), 4.80 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 5.21 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 7.08-7.15 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 21.1, 29.7, 36.2, 111.5, 128.0, 128.9, 135.7, 140.6, 159.8; TOF-MS (ESI+): m/z= 175.1440, calcd. for $C_{13}H_{18}$ $[M+H]^+$: 175.1442.

1-(3,3-Dimethylbut-1-en-2-yl)-3-methylbenzene (S32): Yield 486 mg (45 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ= 1.11 (s, 9H), 2.35 (s, 3H), 4.75 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 5.15 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 6.93-7.26 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 21.5, 29.7, 36.1, 111.3, 126.1, 126.9, 127.1, 129.7, 136.7, 143.4, 159.9; TOF-MS (ESI+): m/z= 175.1441, calcd. for $C_{13}H_{18}$ $[M+H]^+$: 175.1442.

2-(3,3-Dimethylbut-1-en-2-yl)naphthalene (S33): Yield 808 mg (62 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ= 1.29 (s, 9H), 4.98 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 5.38 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 7.41-7.94 (m, 7H) ; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 29.9, 36.5, 112.1, 125.6, 126.0, 126.7, 127.4, 127.7, 128.0, 128.1, 132.2, 133.0, 141.2, 159.9; TOF-MS (ESI+): m/z= 211.1443, calcd. for $C_{16}H_{18}$ $[M+H]^+$: 211.1442.

1-(3,3-Dimethylbut-1-en-2-yl)-2-methylbenzene (S34): Yield 518 mg (48 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ= 1.17 (s, 9H), 2.30 (s, 3H), 4.81 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 5.34 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 7.09-7.22 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 20.6, 29.9, 36.9, 112.3, 124.4, 126.4, 129.4, 129.9, 135.8, 142.6, 157.8; TOF-MS (ESI+): m/z= 175.1441, calcd. for $C_{13}H_{18}$ $[M+H]^+$: 175.1442.

1-(3,3-Dimethylbut-1-en-2-yl)naphthalene (S35): Yield 730 mg (56 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ= 1.20 (s, 9H), 4.98 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 5.57 (d, 1H, $^{2}J_{H-H}$= 1.6 Hz), 7.26-8.04 (m, 7H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ= 30.1, 37.0,

133.9, 124.6, 125.3, 125.4, 126.2, 126.8, 127.2, 128.0, 132.8, 133.6, 140.7, 156.6; TOF-MS (ESI+): m/z= 211.1441, calcd. for $C_{16}H_{18}$ $[M+H]^+$: 211.1442.

General procedure for the hydrogenation of olefins

The alkene (0.5 mmol) and Ir complex (2 mol%) were dissolved in CH_2Cl_2 (2 mL) in a high-pressure autoclave, which was purged four times with hydrogen. Then, it was pressurized to 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 ^1H NMR. The enantiomeric excesses of hydrogenated products from **S1-S2**,[9] **S3**,[31] **S4-S5**,[9] **S6-S7**[32], **S8-S9**[8f], **S10**,[9] **S11**,[13a] **S12-S16**,[13b] **S17**,[6i] **S18-S20**,[33] **S21**,[13c] **S22**,[22] **S23**,[9] **S25-S26**,[31] **S27-S28**,[12c] **S31**,[9] **S36**,[9] **S37**,[34] **S38**[26a], **S39**[13b] and **S40-S41**[22] were determined using the conditions described previously.

1-(3,3-Dimethylbutan-2-yl)-4-methoxybenzene (from S24). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 53.4 min (*S*); t_R 53.8 min (*R*); ^1H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.78 (s, 9H), 1.16 (d, *J*= 6.8 Hz, 3H), 2.42 (q, *J*= 6.8 Hz, 1H), 3.71 (s, 3H), 6.72 (d, *J*= 7.2 Hz, 2H), 6.94 ppm (d, *J*= 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 16.0, 27.8, 33.7, 49.0, 55.2, 112.8, 129.8, 137.6, 157.6; TOF-MS (ESI+): m/z= 193.1547, calcd. for $C_{13}H_{20}O$ $[M+H]^+$: 193.1548.

1-(3,3-Dimethylbutan-2-yl)-4-(trifluoromethyl)benzene (from S29). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 41.1 min (*S*); t_R 42.0 min (*R*); ^1H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.83 (s, 9H), 1.14 (d, *J*= 6.8 Hz, 3H), 2.44 (q, *J*= 6.8 Hz, 1H), 7.27 (d, *J*= 7.2 Hz, 2H), 7.53 ppm (d, *J*= 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 15.8, 27.7, 32.9, 49.8, 124.3, 129.2, 142.1, 160.4; TOF-MS (ESI+): m/z= 231.1317, calcd. for $C_{13}H_{17}F_3$ $[M+H]^+$: 231.1316.

1-(3,3-Dimethylbutan-2-yl)-4-methylbenzene (from S30). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 39.3 min (*S*); t_R 39.7 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.82 (s, 9H), 1.23 (d, *J*= 6.8 Hz, 3H), 2.33 (s, 3H), 2.43 (q, *J*= 6.8 Hz, 1H), 7.06 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 15.9, 21.0, 27.8, 33.9, 49.5, 128.1, 128.9. 143.2, 163.0; TOF-MS (ESI+): m/z= 177.1598, calcd. for $C_{13}H_{20}$ $[M+H]^+$: 177.1599.

1-(3,3-Dimethylbutan-2-yl)-3-methylbenzene (from S32). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 41.7 min (*S*); t_R 42.5 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.79 (s, 9H), 1.18 (d, *J*= 6.8 Hz, 3H), 2.26 (s, 3H), 2.44 (q, *J*= 6.8 Hz, 1H), 6.92 (m, 3H), 7.06 ppm (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 15.9, 21.6, 27.9, 33.8, 49.8, 126.1, 126.5, 127.3, 129.9, 144.2, 162.3; TOF-MS (ESI+): m/z= 177.1598, calcd. for $C_{13}H_{20}$ $[M+H]^+$: 177.1599.

2-(3,3-Dimethylbutan-2-yl)naphthalene (from S33). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 63.5 min (*S*); t_R 63.7 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.93 (s, 9H), 1.36 (d, *J*= 6.8 Hz, 3H), 2.41 (q, *J*= 6.8 Hz, 1H), 6.8-7.0 (m, 2H), 7.2-7.8 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 15.9, 27.9, 34.0, 50.0, 125.0, 125.6, 126.6, 127.2, 127.5, 127.7, 128.1, 132.1, 133.1, 142.9; TOF-MS (ESI+): m/z= 213.1597, calcd. for $C_{16}H_{20}$ $[M+H]^+$: 213.1599.

1-(3,3-Dimethylbutan-2-yl)-2-methylbenzene (from S34). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 39.8 min (*S*); t_R 40.5 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.83 (s, 9H), 1.23 (d, *J*= 6.8 Hz, 3H), 2.37 (s, 3H), 2.93 (q, *J*= 6.8 Hz, 1H), 6.9-7.2 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 16.7, 20.9, 27.8, 34.8, 42.9, 125.3, 127.6, 130.8, 136.2, 144.2, 166.2; TOF-MS (ESI+): m/z= 177.1597, calcd. for $C_{13}H_{20}$ $[M+H]^+$: 177.1599.

1-(3,3-Dimethylbutan-2-yl)naphthalene (from S35). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 60.7 min (*S*); t_R 61.0 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC), δ: 0.91 (s, 9H), 1.25 (d, *J*= 6.8 Hz, 3H), 2.81 (q, *J*= 6.8 Hz, 1H), 6.8-7.0 (m, 2H), 7.3-8.2 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC), δ: 17.4, 28.6, 35.3, 41.7, 124.7, 125.3, 125.4, 125.5, 125.7, 126.7, 129.3, 133.5, 134.2, 142.6; TOF-MS (ESI+): m/z= 213.1598, calcd. for $C_{16}H_{20}$ $[M+H]^+$: 213.1599.

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Keywords: Asymmetric hydrogenation, iridium, P,N-ligands, phosphoroamidite.

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[24] Unlike the hydrogenation of trisubstituted olefins, the enantioselectivity in the reduction of terminal alkenes is highly pressure-dependent. Hydrogenation at an atmospheric pressure of H_2 therefore generally gave significantly higher ee values than at higher pressures. See: a) ref. 6a. b) ref. 6g.

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[27] Only two catalytic systems have provided high enantioselectivities, see: a) ref. 22 (ee's up to 89%). b) ref. 11d (ee's up to 91%).

[28] Only one catalytic system has provided high enantioselectivity, see: a) ref. 8i (ee's up to 91% at rt and up to 96% at -20°C). Related *N*-phosphine-oxazoline/thiazole provided low enantioselectivity (ee's up to 18%, see ref. 13c).

[29] Many of the hydrogenate products included in this paper can be prepared by other methods, for example 2-phenylpropanol analogues have been prepared by asymmetric Zr-catalyzed methylalumination of terminal olefins and the lipase-mediated kinetic resolution of racemic 2-phenyl propanol, see: a) P. Wipf, S. Ribe, *Org. Lett.* **2000**, *2*, 1713-1716. b) A. Abate, E. Brenna, C. Fuganti, G. G. Gatti, T. Givenzana, L. Malpezzi, S. Serra, *J. Org. Chem.* **2005**, *70*, 1281-1290. Other examples include the conjugate addition using organometallic reagents for the preparation of chiral ketones and the hydroboration of olefins for the preparation of chiral organoboranes, see for instance: c)

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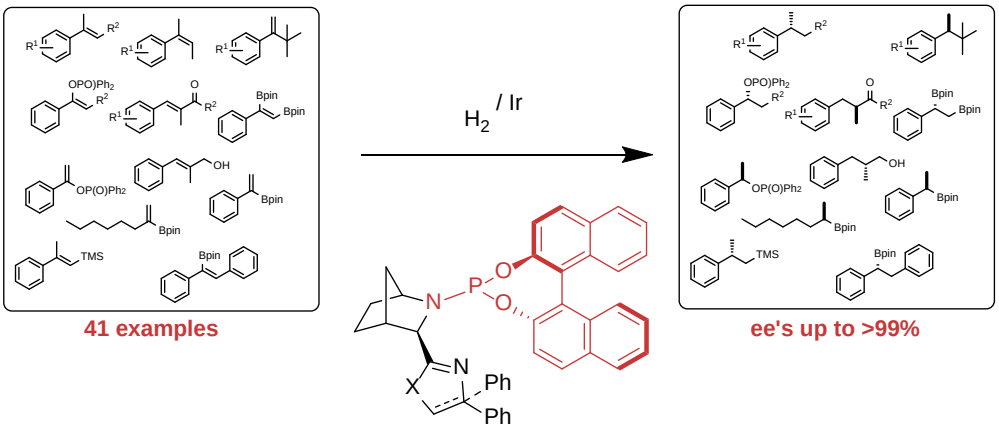

A simple modification on successful previously *N*-phosphine-oxazoline/thiazole ligands extended the range of successfully hydrogenated olefins with high enantioselectivities, comparable for most of the substrates to the best reported so far.