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Ligand Design

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: ■■Please give academic titles for all authors■■ ■■Phosphine changed to phosphane throughout in accordance with IUPAC, ok?■■This study identifies a series of 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* values up to 99%) and conversions. The design of the new phosphoroamidite–oxazoline/thiazole ligands derives from a previous successful generation of bicyclic *N*-phosphane–oxazoline/thiazole ligands, by replacing the *N*-phosphane group with a π-acceptor biaryl phosphoroamidite moiety. A small but structurally important family of Ir-phosphoroamidite–oxazoline/thiazole precatalysts has thus 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*-phosphane by a phosphoroamidite group in the bicyclic *N*-phosphane–oxazoline/thiazole ligands extended the range of olefins that can be successfully hydrogenated.

Introduction

Chirality is a fundamental property of a wide variety of technologically and biologically interesting products. Enormous efforts are being made to discover enantioselective routes that can be used to create stereogenic centers.[1] Of these routes, asymmetric hydrogenation is one of the most efficient, sustainable, and straightforward. This approach can be used to achieve high selectivity, has perfect atom economy, and is operationally simple.[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 address this limitation, the asymmetric reduction of olefins with chiral Ir-PN catalysts has emerged as an effective and straightforward 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 = phosphane–oxazoline ligands (PHOX); cod = 1,5-cyclooctadiene) to a limited range of minimally functionalized olefins.[5] Pfaltz and other groups then focused on Ir catalysts based on a wide range of new ligands (mainly P,N compounds), which significantly broadened the substrate scope. Most of the ligand designs were based on replacing the phosphane 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/phosphane group by a π-acceptor biaryl phosphite moiety. In this context, it was recently shown that the presence of biaryl-phosphite groups in the ligand increases activity and substrate versatility.[12] Several mixed phosphite-nitrogen compounds have thus emerged as extremely effective ligands that provide better substrate versatility than earlier Ir-phosphinite/phosphane-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 hydro-

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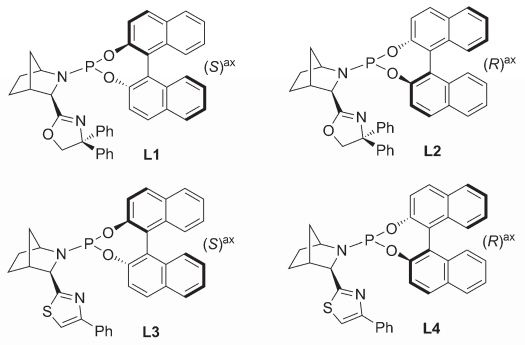


Figure 1. Phosphoroamidite–oxazoline/thiazole ligands **L1**–**L4**.

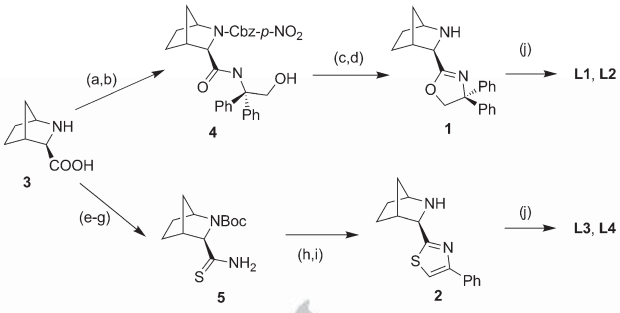
genation of a large number of minimally functionalized alkenes, with the addition of concrete examples with neighboring polar groups.

The new ligands are based on a first successful generation of bicyclic *N*-phosphane–oxazoline/thiazole ligands[6h,8g] in which the *N*-phosphane group is replaced by a π-acceptor biaryl phosphoroamidite moiety. The previous generation of bicyclic *N*-phosphane–oxazoline/thiazole ligands was one of the best-performing ligand families developed for Ir-catalyzed hydrogenation, and they proved to be highly efficient in the hydrogenation of many minimally functionalized aryl–alkyl *E*-trisubstituted olefins.[6h,8g,13] Despite this, the enantioselectivity achieved by using these ligands 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 fundamental advantages of the π-acceptor properties of the phosphoroamidite moiety, ligands **L1**–**L4** are also more robust to air and other oxidizing agents than phosphanes and phosphinites and they 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 remains unexplored.[15]

Results and Discussion

Synthesis of ligands

The sequence of ligand synthesis is summarized in Scheme 1. 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 four and five steps, respectively, by following previously reported procedures from (1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]heptane-3-carboxylic acid (**3**),[17] which is readily available on 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 one equivalent of

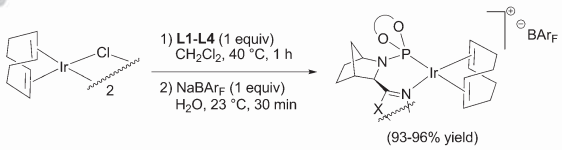


Scheme 1. Synthetic route used for the synthesis of new phosphoroamidite–oxazoline/thiazole ligands **L1**–**L4**: a) *p*-NO_2-CbzCl, NaOH, dioxane/H_2O, RT (86% yield); b) EDC, HOBt, 2-amino-2,2-diphenylethanol, CH_2Cl_2, RT (83% yield); c) MsCl, NEt_3, CH_2Cl_2, 0 °C (79% yield); d) Pd/C, H_2, EtOH, 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).

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 all were isolated as white solids. The ligands were stable in air and very stable to hydrolysis, so further manipulation/storage was carried out in air. Elemental analyses and HRMS-ESI spectra were consistent with the assigned structure. The ligands were also characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy. The spectral assignments, based on ^1H–^1H and ^{13}C–^1H correlation measurements, were as expected for these C_1-symmetric ligands.

Synthesis of Ir catalyst precursors

The Ir catalyst precursors were prepared in a two-step, one-pot procedure (Scheme 2). First, [{Ir(μ-Cl)(cod)}$_2$] reacts with one



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

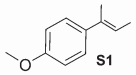
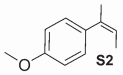
equivalent of the appropriate ligand. Then, Cl^-/BAr_F^- counterion exchange was achieved by reaction with $NaBAr_F$ in the presence of water. The iridium catalyst precursors were isolated in pure form as air-stable orange solids in excellent yields (92–96%) after simple extraction workup. No further purification was required. The elemental analyses were consistent with the assigned structures. The HRMS-ESI spectra of [Ir(cod)(**L1**–**L4**)]BAr_F displayed the *m*/*z* signals for the heaviest ions that correspond to the loss of the BAr_F anion from the molecular

species. The ^{1}H, ^{13}C, and ^{31}P NMR spectra show the expected pattern for these C_1-complexes. Variable-temperature (VT) NMR spectra in CD_2Cl_2 (+35 to −85 °C) showed that only one isomer was present in solution. In all cases, one singlet in the ^{31}P-{^{1}H} NMR spectra was observed.

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 corresponding *E* isomers. To evaluate the efficiency of ligands **L1**–**L4** in the hydrogenation of olefins with different geometry, we initially tested the ligands 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. Reactions conducted with ligands containing an *S*-binaphthyl phosphoroamidite group proceeded with the highest enantioselectivities for both substrates (Table 1, entries 1 vs. 2). However, whereas 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* values up to 97%; Table 1, entry 3), thus overcoming one of the limitations encountered with the parent *N*-phosphane–oxazoline/thiazole ligands in the reduction of *Z*-olefin **S2** (*ee* values 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]

					
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] Reaction conditions: Substrate (0.5 mmol), Ir catalyst precursor (2 mol%), H_2 (50 bar), CH_2Cl_2 (2 mL), RT; [b] conversion measured by ^{1}H NMR spectroscopic analysis after 2 h; [c] enantiomeric excess determined by GC analysis; [d] reaction carried out at 0.25 mol% of Ir catalyst precursor for 3 h.

To further establish the versatility of the reaction with 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 the Supporting Information). We again found that the ligand components must be selected to suit each substrate to obtain the highest enantioselectivity. With the aim of comparing these results with the first generation of ligands and the state-of-art catalytic systems for each substrate, we have collected the results in Table SI-3 in the Supporting Information.

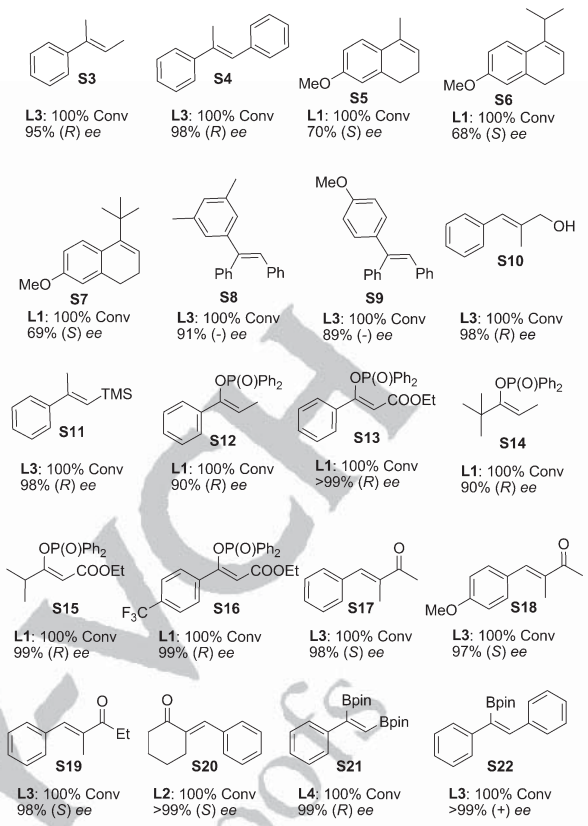


Figure 2. Selected results for the hydrogenation of trisubstituted olefins **S3**–**S22** by using [Ir(cod)(**L1**–**L4**)]BAr_F catalyst precursors. Reaction conditions: Catalyst precursor (2 mol%), CH_2Cl_2, H_2 (50 bar), 4 h.

We first considered the reduction of substrates **S3** and **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** also provided 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 triaryl-substituted substrates **S8** and **S9** (*ee* values up to 91%), surpassing the enantioselectivities obtained by using the first generation of ligands. This latter substrate class has received little 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 impor-

tant 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*-phosphane–oxazoline/thiazole ligands was used.[8g,13a] The Ir/**L1** catalytic system can also hydrogenate the sterically demanding enol phosphinates **S12**–**S16** with high enantioselectivities that were comparable 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 to chiral organophosphinates, which can be easily transformed into high-value compounds such as alcohols and phosphanes. 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*-phosphane–oxazoline/thiazole counterparts provided low enantiocontrol.[21] Although hydrogenation of this type of substrate is an elegant path to ketones with a stereogenic center in the α-position to the carbonyl moiety, such substrates 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 excellent enantioselectivities that were comparable to the best values previously reported. Interestingly, all four of the tested ligands provided similar high enantioselectivities (96–98% *ee* for substrate **S17**; see the Supporting Information) irrespective of the configuration of the biaryl phosphoroamidite group and the nature of the N-donor group. This indicates that the backbone of the bicyclic phosphoroamidite–N ligand is particularly well suited to the specific electronic and steric requirements of α,β-unsaturated enones. We also found that hydrogenation of **S17**–**S20** yields products with opposite configuration to those achieved with the other *E*-trisubstituted olefins studied. This behavior has been observed previously and has been attributed to the strong polarization of the double bond.[4h,8i]

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; they are valuable organic intermediates because 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, excellent enantioselectivities can be achieved for the reduction of two types of alkenylboronic esters containing either one or two (pinacolato)boron groups. The enantioselectivities achieved are among the best reported, and they surpass those obtained with the first generation of ligands.[11d,13c,22]

In summary, the simple substitution of the *N*-phosphane by a phosphoroamidite group in the bicyclic *N*-phosphane–oxazoline/thiazole ligands extended the range of hydrogenated trisubstituted olefins and led to enantioselectivities that, for most of the substrates, were among the best reported so far (see Table SI-3 in the Supporting Information).[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] To estimate how effective systems with 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, whereas substrate **S23** is prone to isomerization, **S24** cannot isomerize. In all cases, full conversions were achieved by using 1 bar of H_2.[24]

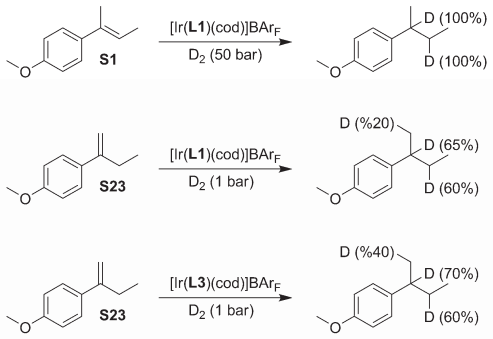
Table 2. Ir-catalyzed hydrogenation of **S23** and **S24** using ligands **L1**–**L4**.[a]

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] Reaction conditions: substrate (0.5 mmol), Ir catalyst precursor (2 mol%), H_2 (1 bar), CH_2Cl_2 (2 mL), RT; [b] conversion measured by ^{1}H NMR spectroscopic analysis after 2 h; [c] enantiomeric excess determined by GC analysis; [d] reaction carried out with 0.25 mol% of Ir catalyst precursor for 3 h.

We found that the effect of the ligand parameters on enantioselectivity is different for the two substrates. Whereas for **S23** the effect is like that 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). Whereas 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 by using **S23**. However, face selectivity issues cannot be excluded.

To address this point, we performed deuterium labeling experiments (Scheme 3). For this purpose we performed the reduction of **S1** and **S23** with deuterium. In contrast to **S1**, the reduction of **S23** with deuterium led to the incorporation of



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

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 proceed either through the formation of Ir-π-allyl intermediates or through 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 deuterium atoms incorporated into the product.

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

In line with the observed isomerization, similar moderate enantioselectivities were achieved in the hydrogenation of substrates **S25**–**S28** irrespective 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* values 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** and **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* values up to 98%). The results are among the best reported for each substrate, even in the reduction of such highly appealing substrates as enol phosphinates **S38** and **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 enantioselectivity.

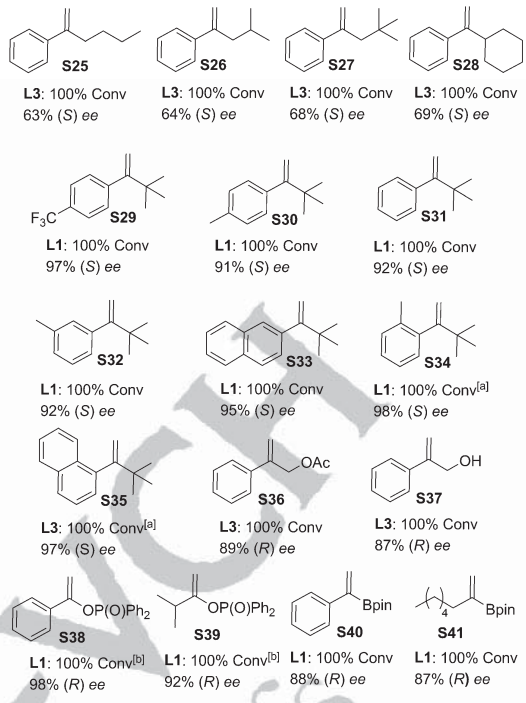


Figure 3. Selected results for the hydrogenation of 1,1-disubstituted olefins **S25**–**S41** by using [Ir(cod)(**L1**–**L4**)]BAr$_F$ catalyst precursors. Reaction conditions: Catalyst precursor (2 mol%), CH_2Cl_2, H_2 (1 bar), 4 h. [a] Reactions carried out for 8 h; [b] reaction carried out at 50 bar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

In summary, although isomerization was 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 that were comparable for most of the substrates (except for olefins prone to isomerization) to the best reported so far. Once again, the introduction of the biaryl phosphoroamidite group was also advantageous compared with related bicyclic *N*-phosphane–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 systems 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 were derived from a previous successful generation of Ir-bicyclic *N*-phosphane–oxazoline/thiazole catalysts, by replacing the *N*-phosphane group of the ligand with a π-acceptor biaryl phosphoroamidite moiety. The simple substitution of the *N*-phosphane

by a phosphoroamidite group extended the range of olefins that could be successfully hydrogenated, and furnished enantioselectivities that were 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 over previous bicyclic *N*-phosphane–oxazoline/thiazole ligands, is that they are solid and stable to air. The ligands are therefore easier to handle and can be manipulated and stored in air.

Experimental Section

General considerations

All reactions were carried out by 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] and **2**[8g] were prepared as reported previously. Neutral silica (pH 7, 0.040–0.063 mm) was purchased from Merck. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with 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 based on the results of ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC experiments.

Preparation of phosphoroamidite–oxazoline/thiazole ligands L1–L4: General procedure

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 (3×3 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 °C 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.

Ligand 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 °C): $\delta = 153$ ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 0.70$ (d, ^2J(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,■■Please use standard abbreviations throughout■■ 1H; CH_2), 2.40 (b, 1H; CH), 3.35 (b, 1H; CH), 3.80 (b, 1H; CH), 4.47 (d, ^2J(H,H) = 8.4 Hz, 1H; CH_2), 4.56 (d, ^2J(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 °C): $\delta = 27.6$ (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 (Ar); TOF-MS (ESI+): *m/z* calcd for $C_{41}H_{33}N_2O_3P$: 633.2307 $[M+H]^+$; found: 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.

Ligand 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 °C): $\delta = 146.2$ ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 0.56$ (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 °C): $\delta = 28.7$ (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 (Ar); TOF-MS (ESI+): *m/z* calcd for $C_{41}H_{33}N_2O_3P$: 633.2307 $[M+H]^+$; 633.2304; 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.

Ligand 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 °C): $\delta = 155.5$ ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 0.65$ (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 °C): $\delta = 28.3$ (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 (Ar); TOF-MS (ESI+): *m/z* calcd for $C_{35}H_{27}N_2O_2PS$: 571.1609 $[M+H]^+$; found: 571.1599; 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.

Ligand 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 °C): $\delta = 147.5$ ppm (s); ^{1}H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 0.76$ (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 °C): $\delta = 28.2$ (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 (Ar); TOF-MS (ESI+): *m/z* calcd for $C_{35}H_{27}N_2O_2PS$: 571.1609 $[M+H]^+$; found: 571.1602; 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 heated to reflux at 40 °C for 1 h. After 5 min at RT, $NaBAr_F$ (77.2 mg, 0.080 mmol) and water (5 mL) were added and the reaction mixture was stirred vigorously for 30 min at RT. 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 °C): $\delta = 112.0$ ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.26$ (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 °C): $\delta = 22.9$ (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 (Ar), 135.0 (b; CH=, BAr_F), 136–149 (Ar), 162.0 (q, $^1J(C,B)=49.8$ Hz; C-B, BAr_F), 173.0 ppm (C=N); TOF-MS (ESI+): *m/z* calcd for $C_{81}H_{57}BF_{24}IrN_2O_3P$: 933.2797 $[M-BArF]^+$; found: 933.2795; 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 °C): $\delta=102.9$ ppm (s); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=1.21$ (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 °C): $\delta=24.5$ (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 (Ar), 135.0 (b; CH=, BAr_F), 136–150 (Ar), 161.9 (q, $^1J(C,B)=49.8$ Hz; C-B, BAr_F), 173.3 ppm (C=N); TOF-MS (ESI+): *m/z* calcd for $C_{81}H_{57}BF_{24}IrN_2O_3P$: 933.2797 $[M-BArF]^+$; found: 933.2792; 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 °C): $\delta=104.3$ ppm (s); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=1.26$ (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 °C): $\delta=25.3$ (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 (Ar), 135.0 (b; CH=, BAr_F), 136–148 (Ar), 161.9 (q, $^1J(C,B)=49.8$ Hz; C-B, BAr_F), 170.8 ppm (C=N); TOF-MS (ESI+): *m/z* calcd for $C_{75}H_{51}BF_{24}IrN_2O_2PS$: 871.2090 $[M-BArF]^+$; found: 871.2087; 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 °C): $\delta=102.5$ ppm (s); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=1.27$ (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 °C): 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 (Ar), 135.0 (b; CH=, BAr_F), 136–150 (Ar), 161.9 (q, $^1J(C,B)=49.8$ Hz; C-B, BAr_F), 172.6 ppm (C=N); TOF-MS (ESI+): *m/z* calcd for $C_{75}H_{51}BF_{24}IrN_2O_2PS$: 871.2090 $[M-BArF]^+$; found: 871.2084; 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 flask, methyltriphenylphosphonium bromide (9.2 mmol) was stirred in anhydrous THF (40 mL). The solution was cooled to 0 °C and *n*BuLi (1.6 M in hexane, 5.4 mL, 8.6 mmol) was added slowly. The reaction was stirred■■ok?■■ at 0 °C for 30 min, then aryl *tert*-butyl ketone[30] (6.2 mmol) in anhydrous THF (6 mL) was added. The mixture was warmed to RT and, after 18 h, sat. NH_4Cl (20 mL) was added and the mixture was extracted with diethyl ether (3×25 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′-disubstituted olefin as a colorless oil.

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

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

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

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

2-(3,3-Dimethylbut-1-en-2-yl)naphthalene (S33): Yield: 808 mg (62%); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=1.29$ (s, 9H), 4.98 (d, $^2J(H,H)=1.6$ Hz, 1H), 5.38 (d, $^2J(H,H)=1.6$ Hz, 1H), 7.41–7.94 ppm (m, 7H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta=29.9$, 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 ppm; TOF-MS (ESI+): *m/z* calcd for $C_{16}H_{18}$: 211.1442 $[M+H]^+$; found: 211.1443.

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

1-(3,3-Dimethylbut-1-en-2-yl)naphthalene (S35): Yield: 730 mg (56%); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=1.20$ (s, 9H), 4.98 (d, $^2J(H,H)=1.6$ Hz, 1H), 5.57 (d, $^2J(H-H)=1.6$ Hz, 1H), 7.26–8.04 ppm (m, 7H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta=30.1$, 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 ppm; TOF-MS (ESI+): *m/z* calcd for $C_{16}H_{18}$: 211.1442 $[M+H]^+$; found 211.1441.

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. The apparatus was pressurized to the desired pressure and, after the required 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 analysis and conversions were determined by ^1H NMR spectroscopic analysis. The enantiomeric excesses of hydrogenated products from **S1** and **S2**,[9] **S3**,[31] **S4** and **S5**,[9] **S6** and **S7**,[32] **S8** and **S9**,[8f] **S10**,[9] **S11**,[13a] **S12**–**S16**,[13b] **S17**,[6i] **S18**–**S20**,[33] **S21**,[13c] **S22**,[22] **S23**,[9] **S25** and **S26**,[31] **S27** and **S28**,[12c] **S31**,[9] **S36**,[9] **S37**,[34] **S38**,[26a] **S39**,[13b] and **S40** and **S41**[22] were determined under the conditions described previously.

1-(3,3-Dimethylbutan-2-yl)-4-methoxybenzene (from S24): Enantiomeric excess determined by GC analysis using a Chiraldex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C min^{-1} until 175 °C): t_R = 53.4 (*S*), 53.8 min (*R*); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 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 °C): δ = 16.0, 27.8, 33.7, 49.0, 55.2, 112.8, 129.8, 137.6, 157.6 ppm; TOF-MS (ESI+): *m/z* calcd for $C_{13}H_{20}O$: 193.1548 $[M+H]^+$; found: 193.1547.

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

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

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

2-(3,3-Dimethylbutan-2-yl)naphthalene (from S33): Enantiomeric excess determined by GC analysis using a Chiraldex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C min^{-1} until 175 °C): t_R = 63.5 (*S*), 63.7 min (*R*); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 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 °C): 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 ppm; TOF-MS (ESI+): *m/z* calcd for $C_{16}H_{20}$: 213.1599 $[M+H]^+$; found: 213.1597.

1-(3,3-Dimethylbutan-2-yl)-2-methylbenzene (from S34): Enantiomeric excess determined by GC analysis using a Chiraldex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C min^{-1} until 175 °C): t_R = 39.8 (*S*), 40.5 min (*R*); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 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 °C): δ = 16.7, 20.9, 27.8, 34.8, 42.9, 125.3, 127.6, 130.8, 136.2, 144.2, 166.2 ppm; TOF-MS (ESI+): *m/z* calcd for $C_{13}H_{20}$: 177.1599 $[M+H]^+$; found: 177.1597.

1-(3,3-Dimethylbutan-2-yl)naphthalene (from S35): Enantiomeric excess determined by GC analysis using a Chiraldex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C min^{-1} until 175 °C): t_R = 60.7 (*S*), 61.0 min (*R*); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 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 °C): 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 ppm; TOF-MS (ESI+): *m/z* calcd for $C_{16}H_{20}$: 213.1599 $[M+H]^+$; found: 213.1598.

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Keywords: asymmetric catalysis · hydrogenation · ligand design · iridium · P ligands

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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. a) See Ref. [6a]; b) See Ref. [6g].

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[28] Only one catalytic system has provided high enantioselectivity, see: a) See Ref. [8i] (*ee* values up to 91% at RT and up to 96% at −20 °C). Related *N*-phosphane–oxazoline/thiazole provided low enantioselectivity (*ee* values up to 18%, see Ref. [13c]).

[29] Many of the hydrogenated 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,

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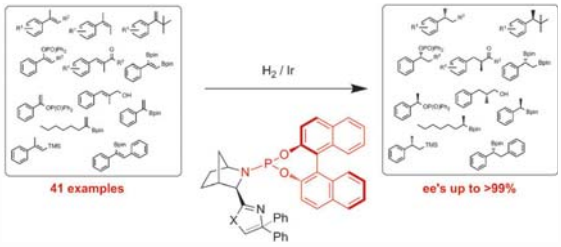

Extending the range: A simple modification of previously developed *N*-phosphane–oxazoline/thiazole ligands extended the range of olefins that can be hydrogenated. High enantioselectivities were achieved, and the results obtained for most of the substrates were comparable to the best enantioselectivities reported so far (see scheme).

Ligand Design

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Extending the Substrate Scope of Bicyclic P-Oxazoline/Thiazole Ligands for Ir-Catalyzed Hydrogenation of Unfunctionalized Olefins by Introducing a Biaryl Phosphoroamidite Group