Filling the gaps in the challenging asymmetric hydroboration of 1,1-disubstituted alkenes using simple Ir-phosphite-based PHOX catalysts

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Dedication ((optional))

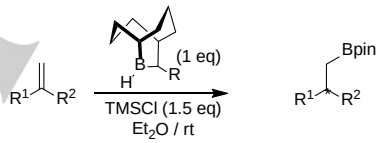
Abstract: We have identified a readily accessible Ir-phosphite/oxazoline PHOX-based catalytic system (**L1a**) that can hydroborate a range of 1,1-disubstituted aryl olefins with high enantioselectivity (up to 94%), excellent yields and perfect regioselectivity. The new phosphite-oxazoline PHOX-based ligands can efficiently hydroborate a broader range of olefins than previous phosphine-oxazoline PHOX ligands. Particularly, we were able to successfully hydroborate a wide range of α-*tert*-butylstyrenes, with aryl substituents that have different electronic and steric properties, thus complementing the results of Cu-NHC catalysts, the only other system reported to date that has attempted these reactions.

Introduction

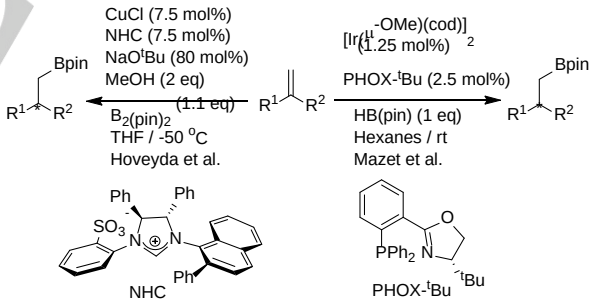
Many of today's pharmaceutical, fragrance and agrochemical compounds, and the chemicals used in functional materials are required as pure enantiomers.[1] As a result, the industrial production of enantiopure chiral compounds is gaining importance and synthetic procedures are constantly evolving towards high selectivity and productivity, atom economy, operational simplicity, cost efficiency, environmental friendliness, and low energy consumption. In comparison to other synthetic approaches, asymmetric catalysis is a smart strategy. A small amount of catalyst can produce large quantities of the desired chiral compound with only a few reaction steps and synthetic operations, thus bringing down the overall production cost, and decreasing the amount of byproducts.

Chiral organoboron compounds have received a great deal of attention lately.[2] They are valuable organic intermediates because the C-B bond can be readily transformed to chiral C-N, C-O and C-C bonds.[2c,3] The synthesis of these compounds by transition-metal catalyzed asymmetric hydroboration is attracting considerable interest. However, whereas the asymmetric hydroboration of monosubstituted olefins (i.e. styrenes) and internal 1,2-disubstituted olefins (i.e. norbornadiene) has been successfully studied, the hydroboration of 1,1-disusbtituted olefins is still a challenge.[2,4] This is because the chiral transition metal catalyst has difficulty in controlling not only the specific boration at the desired terminal β-position rather than at the more substituted α-position (most catalysts favor the Markovnikov regioselectivity),[5] but also the face selectivity coordination (due to the presence of the two relatively similar substituents at the geminal position). To date high regio- and enantioselectivities have been reported in only three publications but the substrate scope is limited (Scheme 1).[6] In 2008 Soderquist and coworkers reported the hydroboration of 1,1-disubstituted alkenes using stoichiometric quantities of chiral boranes with ee's between 28-92% (Scheme 1 (a)).[6a] The highest enantioselectivity was observed only with 2,3,3-trimethylbut-1-ene.

(a) Stoichometric hydroborations, Soderquist et. al



(b) Metal-catalyzed hydroborations, Hoveyda et al. and Mazet et al.



Scheme 1. State of the art in the asymmetric hydroboration of challenging 1,1-disubstituted olefins

Subsequently, two important breakthroughs in the asymmetric hydroboration of 1,1-disubstituted olefins were reported (Scheme 1(b)). They both included metal-catalyzed hydroboration processes instead of expensive and sacrificial stoichiometric chiral auxiliaries. One of them, reported by Hoveyda and coworkers, showed the asymmetric hydroboration of 1,1-disubstituted aryl-alkyl olefins with chiral Cu-based bidentate N-heterocyclic carbene catalysts.[6b] A range of α-methylstyrenes, and some aryl olefins with alkyl substituents other than the typical methyl unit and exocyclic alkenes, were hydroborated with high regioselectivities and enantioselectivities in the range 61-92% ee. Despite this important advance, high catalyst loading (7.5%), long reaction times (48h), low

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temperature (ranging from -15 ºC to -50 ºC) and the presence of an almost equimolar amount of base were required (Scheme 1(b)). Mazet and coworkers also reported the hydroboration of a range of 1,1-disubstituted aryl-alkyl olefins with excellent yields and regioselectivities (with exclusive attack at the desired β-position) but with the Ir-catalyst modified with the readily accessible phosphine-oxazoline PHOX-^{t}Bu ligand (Scheme 1(b)).[6c] Enantioselectivity (up to 92%), however, was only high in the hydroboration of α-methylstyrene **S1**. The introduction of substituents at the aryl ring or the increase of the steric requirements at the alkyl substituent of the substrate decreased the enantioselectivity considerably. Although fewer substrates were successfully hydroborated than for the Cu-carbene based catalysts, the Ir-PHOX catalysts allow this transformation to take place under milder reaction conditions and with lower catalyst loading (Scheme 1(b)) which is more advantageous as a sustainable industrial process. Because of the limited substrate scope of the three advances mentioned, new developments in this field are still needed.

In most asymmetric transformations involving olefins as prochiral reagents (i.e. epoxidation, hydrogenation, etc.), 1,1-disubstituted olefins are systematically challenging substrates,[7] mainly due to face selectivity issues (as in the hydroboration reaction). We recently showed that the highest reported enantioselectivities in the Ir-catalyzed hydrogenation of a very large range of simple 1,1-disubstituted olefins can be achieved by introducing a biaryl phosphite moiety into the ligand.[7c-d,8] Inspired by the work of Prof. Mazet[6c] and the similarities of the elementary steps involved in the hydroboration and hydrogenation, we studied here whether the introduction of a biaryl phosphite moiety into the ligand is also beneficial for the Ir-catalyzed hydroboration. To this end, we took the previously successful PHOX ligand family and replaced the phosphine group with biaryl-phosphite moieties (ligands **L1**-**L4a**-**c**, Figure 1). In this paper we present the application of these phosphite-oxazoline ligands **L1**-**L4a**-**c** in the asymmetric Ir-catalyzed hydroboration of 1,1-disubstituted olefins. These ligands incorporate the advantages of biaryl phosphites such as higher resistance to oxidation than phosphines, facile synthesis from readily available chiral alcohols and a straightforward modular construction.[9] We investigated the catalytic performance by systematically varying the electronic and steric properties of the oxazoline substituents (**L1**-**L4**) and different substituents/configurations in the biaryl phosphite group (**a**-**c**).

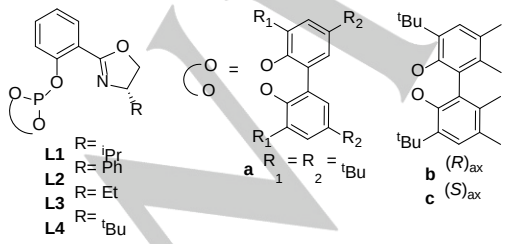
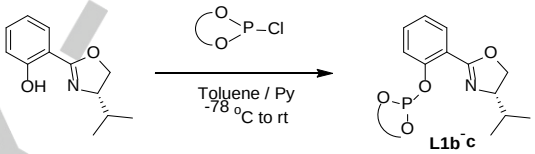


Figure 1. Phosphite-oxazoline PHOX-based ligands **L1**-**L4a**-**c**

Results and Discussion

Ligand synthesis

The new phosphite-oxazoline PHOX-based ligands **L1b** and **L1c** can be straightforwardly synthesized by following the procedure previously described for ligands **L1**-**L4a**[10] (Scheme 2). They were efficiently prepared in only one step by coupling the oxazoline-alcohol (*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenol with one equivalent of the *in-situ* formed phosphorochloridite (**b**-**c**) under basic conditions (Scheme 2). All ligands were isolated in good yields as white solids after purification on neutral alumina. Advantageously they were stable in air and very stable to hydrolysis, so further manipulation/storage was carried out in air. The HRMS-ESI spectra were in agreement with the assigned structure. **L1b** and **L1c** were also characterized by $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The spectral assignments, made using ^1H–^1H and ^{13}C–^1H correlation measurements, were as expected for these C_1-symmetric ligands.



Scheme 2. Synthetic route for the synthesis of new phosphite-oxazoline PHOX-based ligands **L1b** and **L1c**

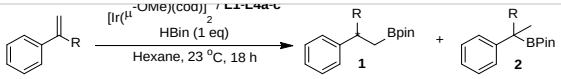
Initial screening experiments of phosphite-oxazoline PHOX-based ligands

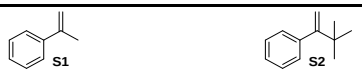
As previously mentioned, the effectiveness of the catalyst in transferring the chiral information to the hydroborated product mainly depends on its ability to sterically differentiate between the two geminal substituents of the olefin. In order to assess the potential of the phosphite-oxazoline PHOX-based ligands **L1**-**L4a**-**c** in the hydroboration of substrates with different steric requirements, we initially evaluated them in the asymmetric Ir-catalyzed hydroboration of model substrate **S1**[2,6] and the hydroboration of more demanding **S2** (Table 1).

For purposes of comparison, we first tested **L1**-**L4a**-**c** using the same optimal reaction conditions found in the previous study of Mazet and coworkers with related Ir-PHOX catalytic systems.[6c] Reactions were therefore performed at room temperature, using 2.5 mol% of in-situ generated catalyst ([Ir(μ-OMe)(cod)]$_2$/L) and hexane as solvent.[6c] The results are collected in Table 1. All of the ligands favoured the attack at the β-position, and the desired primary (pinacolato)boron adduct **1** was achieved with perfect regiocontrol (**1/2** ratio >99). Although enantioselectivities were moderate for α-methylstyrene **S1**, an unprecedentedly high enantioselectivity was achieved for the more challenging α-*tert*-butylstyrene **S2** (ee's up to 88%). It should be pointed out that the hydroboration of **S2** using the related phosphine-oxazoline PHOX-^{t}Bu ligand provided no

conversion under the same reaction conditions (Table 1, entry 7). These important results indicate that both PHOX-based ligand families are complementary so we can successfully hydroborate both substrate types by correctly combining substrate and ligand type (phosphine-N or phosphite-N).

Table 1. Asymmetric hydroboration of α-methylstyrene **S1** and α-*tert*-butylstyrene **S2**.[a]





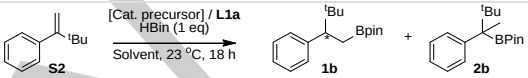
Entry	L*	% Conv (**1a**:**2a**)[b]	%ee[c]	% Conv (**1b**:**2b**)[b]	%ee[c]
1	**L1a**	100 (>99:1)	44 (*S*)	100 (>99:1)	88 (*S*)
2	**L1b**	50 (>99:1)	7 (*S*)	46 (>99:1)	43 (*S*)
3	**L1c**	60 (>99:1)	41 (*S*)	59 (>99:1)	79 (*S*)
4	**L2a**	100 (>99:1)	42 (*S*)	100 (>99:1)	86 (*S*)
5	**L3a**	100 (>99:1)	17 (*S*)	100 (>99:1)	43 (*S*)
6	**L4a**	96 (>99:1)	43 (*S*)	84 (>99:1)	88 (*S*)
7	**PHOX-^{t}Bu**	100 (>99:1)	92 (*S*)[6c]	0	-

[a] All reactions carried out in duplicate using 1 mmol of substrate, 1.25 mol% of [Ir(μ-OMe)(cod)]$_2$, 2.5 mol% of ligand, hexane (2 mL). [b] % Conversion measured by ^{1}H NMR. In all cases regioselectivities >99% were. [c] Determined by HPLC after conversion to the corresponding alcohols.

As far as the effect of the ligand parameters on activities and enantioselectivities is concerned, we found that bulky *tert*-butyl groups are needed at the *ortho* and *para* positions of the biaryl phosphite moiety to achieve the highest activities and enantioselectivities (Table 1, entry 1 vs 2 and 3). We also found that ligands with an *S* biaryl phosphite group provided better enantioselectivities than ligands with an *R* biaryl phosphite group (Table 1, entry 2 vs 3). This is an advantage because it means that the inexpensive 3,3',5,5'-tetra-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl phosphite moiety (**a**) can be used. For the oxazoline substituent, the enantioselectivities are highest with bulky isopropyl and *tert*-butyl groups (ligands **L1a** and **L4a**, Table 1, entries 1 and 6), but the activities are best when the sterical demand on the oxazoline substituents is decreased. The tradeoff between activities and enantioselectivities is therefore best with ligand **L1a** (Table 1, entry 1). This result contrasts with the one described by Mazet's group, which required the presence of a *tert*-butyl oxazoline substituent to achieve high enantioselectivity, and it has an economic advantage because **L1a** is derived from L-valinol, which is around eight times cheaper than the L-*tert*-leucinol required for the synthesis of the PHOX-^{t}Bu ligand.

We next optimized the reaction conditions by evaluating a variety of solvents and catalyst precursors using ligand **L1a**, which had provided the best results (Table 2). Although in all cases regioselectivity towards the desired β-adduct **1** remained excellent, activity and enantioselectivity were highly dependent on the solvent and the nature of the catalyst precursor. The combination of hexane and [Ir(μ-Cl)(cod)]$_2$ as catalyst precursor was found to be optimal (Table 2, entry 5). Under these new reaction conditions we were therefore able to increase the enantioselectivity to 92% while maintaining the excellent yield and regioselectivity of the desired β-compound **1**. To the best of our knowledge Ir-**L1a** is the first catalytic system that can hydroborate **S2** with perfect regioselectivity, excellent yield and high enantioselectivity.

Table 2. Asymmetric hydroboration of α-*tert*-butylstyrene **S2**. Effect of the solvent and catalyst precursors[a]



Entry	Solvent	[Cat. precursor]	% Conv (**1b**:**2b**)[b]	%ee[c]
1	Hexane	[Ir(μ-OMe)(cod)]$_2$	100 (>99:1)	88 (*S*)
2	THF	[Ir(μ-OMe)(cod)]$_2$	88 (>99:1)	76 (*S*)
3	CH_2Cl_2	[Ir(μ-OMe)(cod)]$_2$	100 (>99:1)	80 (*S*)
4	Toluene	[Ir(μ-OMe)(cod)]$_2$	96 (>99:1)	83 (*S*)
5	Hexane	[Ir(μ-Cl)(cod)]$_2$	100 (>99:1)[d]	92 (*S*)
6	Hexane	[Ir(cod)**L1a**]BAr$_F$	61 (>99:1)	66 (*S*)

[a] All reactions carried out in duplicate using 1 mmol of substrate, 1.25 mol% of Ir-catalyst precursor, 2.5 mol% of ligand, solvent (2 mL). [b] Determined by ^{1}H NMR. [c] Determined by HPLC after conversion to the corresponding alcohol. [d] 91% of isolated yield.

Asymmetric hydroboration of other 1,1-disubstituted olefins: scope and limitations

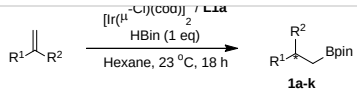
The unprecedented results obtained up to this point with Ir-**L1a** catalyst in the hydroboration of **S2** encouraged us to test Ir-**L1a** in the hydroboration of other 1,1-disubstituted olefins (Table 3).

First, we studied the hydroboration of several phenyl/alkyl olefins bearing alkyl substituents with different steric demands (**S3**-**S5**; Table 3, entries 3-5). Excellent regioselectivities of the desired β-adduct **1** were achieved. Enantioselectivities were moderate regardless of the steric demands of the alkyl substituent (entries 3-5). However, enantioselectivities were not as low as those observed with related Ir-PHOX catalysts when the steric hindrance on alkyl substituents was increased (i.e. ee's decreased from 92% to 31% when the Me was replaced by an Et substituent).[6c]

We next studied several α-*tert*-butylstyrenes that had aryl substituents with different electronic and steric properties (**S6**-**S10**; Table 3, entries 6-10). Advantageously, Ir-**L1a** is very tolerant to variations in the substituents of the aryl ring and can hydroborate a wide range of α-*tert*-butylstyrenes with

comparable high enantioselectivities (up to 94%) and yields and perfect regioselectivity. Accordingly, our results using several *para*-substituted α-*tert*-butylstyrenes (**S6**-**S8**) indicated that enantioselectivity is relatively insensitive to the electronic effects in the aryl ring (ee's in the range 90-94%; entries 2, 6-8). Enantioselectivities were, however, highest in the hydroboration of electron-rich olefins **S6** and **S7** (entries 6-7). Enantioselectivities were also excellent in the hydroboration of *meta*-substituted olefins (**S9**-**S10**; entries 9-10). Again these results contrast with the ones described by Mazet's group with related Ir-PHOX catalysts where the introduction of any type of substituent at the aryl ring of the substrate had a negative effect on enantioselectivity.[6c]

Table 3. Asymmetric hydroboration of 1,1-disubstituted olefins. Scope and limitations[a]



1a-k

Entry	Substrate	R^1	R^2	**1**:**2**	% Yield [b]	%ee[c]
1	**S1**	C_6H_5	Me	>99:1	93	50 (*S*)
2	**S2**	C_6H_5	^{t}Bu	>99:1	91	92 (S)
3	**S3**	C_6H_5	Et	>99:1	90	55 (S)
4	**S4**	C_6H_5	^{i}Bu	>99:1	88	56 (S)
5	**S5**	C_6H_5	^{i}Pr	>99:1	89	58 (S)
6	**S6**	4-Me-C_6H_4	^{t}Bu	>99:1	92	94 (S)
7	**S7**	4-OMe-C_6H_4	^{t}Bu	>99:1	91	93 (S)
8	**S8**	4-CF_3-C_6H_4	^{t}Bu	>99:1	94	90 (S)
9	**S9**	2-Naph	^{t}Bu	>99:1	89	87 (S)
10	**S10**	3-Me-C_6H_4	^{t}Bu	>99:1	90	92 (*S*)
11	**S11**	4-OMe-C_6H_4	CF_3	>99:1	88	18 (*S*)
12[d]	**S11**	4-OMe-C_6H_4	CF_3	-	0	nd

[a] All reactions carried out in duplicate using 1 mmol of substrate, 1.25 mol% of [Ir(μ-Cl)(cod)]$_2$, 2.5 mol% of **L1a**, hexane (2 mL). [b] Determined by ^{1}H NMR. [c] Determined by HPLC or GC after conversion to the corresponding alcohol. [d] Reaction carried out using the Ir-PHOX-^{t}Bu catalyst. The hydrogenated product was isolated in 45% yield and 0% ee.

We then looked into the hydroboration of aryl/trifluoromethyl olefins. Due to the unique properties of the fluorine, the efficient hydroboration of these substrates opens up an appealing route for obtaining organic intermediates for the preparation of drugs, agrochemicals, and materials. To the best of our knowledge only Hoveyda and coworkers have attempted the hydroboration of this substrate class with their Cu-NHC catalysts although they obtained undesired difluoroallylboronates.[6b] Here we have tested the new Ir-**L1a** and related Ir-PHOX catalysts in the hydroboration of the model 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **S11** substrate (Table 3, entries 11 and 12). While Ir-PHOX-^{t}Bu was found to be inadequate, because it provided exclusively the hydrogenated product in racemic form, the Ir-**L1a** catalyst gave the desired hydroborated product with perfect regioselectivity and good yield, albeit with low enantiocontrol. This result opens up new possibilities for further research and it demonstrates once again that the behavior is not that observed with the Ir-phosphine-oxazoline PHOX catalysts.

Conclusions

We have identified a readily accessible Ir-phosphite/oxazoline PHOX-based catalytic system (**L1a**) that can hydroborate a range of 1,1-disubstituted aryl olefins with high enantioselectivity (up to 94%), excellent yields and perfect regioselectivity. The new phosphite-oxazoline PHOX-based ligands can efficiently hydroborate a broader range of olefins than previous phosphine-oxazoline PHOX ligands. Particularly, we were able to successfully hydroborate a wide range of α-*tert*-butylstyrenes, with aryl substituents that have different electronic and steric properties, thus complementing the results of Cu-NHC catalysts, the only other system reported to date that has attempted these reactions. In addition, the introduction of a biaryl phosphite moiety allows for the first time the highly regioselective hydroboration of aryl/trifluoromethyl olefins. Another advantage over previous PHOX ligands is that the new ligands are stable to air and therefore easier to handle and can be manipulated and stored in air. This contribution opens up the path for the synthesis of new Ir phosphite-based catalysts for the challenging hydroboration of 1,1-disubstituted olefins. Further studies on the design of new Ir/phosphite-based catalysts to further broaden the scope of this hydroboration reaction are currently underway.

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.[11] Intermediate compound (*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenol,[12] ligands **L1**-**L4a**[10] and substrates **S2**,[13] **S3**,[14] **S4**,[15] **S5**,[13] **S11**[7c] were prepared as previously reported. Substrates **S6**-**S10** were prepared using the Wittig olefination procedure (see Supporting Information for details). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to those of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H, ^{13}C and 31P assignments were made on the basis of ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC.

General procedure for the preparation of phosphite-oxazoline ligands L1-L4a-c

The corresponding phosphorochloridite (1.1 mmol) produced in situ was dissolved in toluene (5 mL) and pyridine (0.36 mL, 4.6 mmol) was added. Hydroxyl-oxazoline intermediate (1 mmol) was azeotropically dried with toluene (3 x 1 mL) and then dissolved in toluene (5 mL), to which pyridine (0.36 mL, 4.6 mmol) had been added. The hydroxyl-

oxazoline solution was transferred slowly at -78ºC to the solution of phosphorochloridite. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The pyridine salts were then removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography (Al_2O_3; toluene/NEt_3 = 100/1) to produce the corresponding ligand.

L1b: Yield: 423 mg (72%); ^{31}P NMR (C_6D_6), δ: 132.6 ppm (s); ^1H NMR (C_6D_6), δ: 0.62 (d, 6H, $^3J_{H-H}$= 6.4 Hz, CH_3, ^{i}Pr), 1.27 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.39 (m, 1H, CH, ^{i}Pr), 1.61 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 3.03 (dd, 1H, $^2J_{H-H}$= 11.6 Hz, $^3J_{H-H}$= 5.2 Hz, CH_2-O), 3.12 (dd, 1H, $^2J_{H-H}$= 11.2 Hz, $^3J_{H-H}$= 5.2 Hz, CH_2-O), 4.22 (m, 1H, CH-N), 6.7-7.5 (m, 6H, CH=), 8.59 (d, 1H, $^3J_{H-H}$= 6.4 Hz, CH=). ^{13}C NMR (C_6D_6), δ: 16.2 (CH_3, ^{i}Pr), 16.4 (CH_3, ^{i}Pr), 17.8 (CH_3), 19.1 (CH_3), 19.9 (CH_3), 20.0 (CH_3), 28.6 (CH, ^{i}Pr), 31.0 (d, CH_3, ^{t}Bu, J_{C-P}=5.3 Hz), 31.3 (CH_3, ^{t}Bu), 34.4 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 45.3 (CH_2-O), 55.4 (CH-N), 118.4-150.9 (aromatic carbons), 163.4 (C=N). MS HR-ESI [found 610.3067, $C_{36}H_{46}NO_4P$ (M-Na)$^+$ requires 610.3062].

L1c: Yield: 376 mg (64%); ^{31}P NMR (C_6D_6), δ: 133.9 ppm (s); ^1H NMR (C_6D_6), δ: 0.55 (d, 3H, $^3J_{H-H}$= 6.4 Hz, CH_3, ^{i}Pr), 0.63 (d, 3H, $^3J_{H-H}$= 6.8 Hz, CH_3, ^{i}Pr), 1.35 (s, 9H, CH_3, ^{t}Bu), 1.39 (s, 9H; CH_3, ^{t}Bu), 1.42 (m, 1H, CH, ^{i}Pr), 1.65 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.35 (m, 2H, CH_2-O), 4.28 (m, 1H, CH-N), 6.7-7.7 (m, 6H, CH=), 8.60 (d, 1H, $^3J_{H-H}$= 8.0 Hz, $^4J_{H-H}$= 2.0 Hz, CH=). ^{13}C NMR (C_6D_6), δ: 16.2 (CH_3, ^{i}Pr), 16.6 (CH_3, ^{i}Pr), 18.1 (CH_3), 19.1 (CH_3), 20.0 (CH_3), 21.4 (CH_3), 28.6 (CH, ^{i}Pr), 31.2 (d, CH_3, ^{t}Bu, J_{C-P}= 4.6 Hz), 31.4 (CH_3, ^{t}Bu), 34.4 (C, ^{t}Bu), 34.7 (C, ^{t}Bu), 45.6 (CH_2-O), 55.5 (CH-N), 119.3-150.4 (aromatic carbons), 163.4 (C=N). MS HR-ESI [found 610.3068, $C_{36}H_{46}NO_4P$ (M-Na)$^+$ requires 610.3062].

General procedure for the asymmetric hydroboration of 1,1-disubstituted substrates

The corresponding ligand ($2.5.10^{-2}$ mmol) and $[Ir(\mu\text{-Cl})(cod)]_2$ (8.4 mg; $2.5.10^{-5}$ mmol) were dissolved in hexane (2 mL) and stirred for 10 minutes at room temperature. Then, the slightly turbid solution was cooled to 0°C and the desired 1,1-disubstituted olefin (1.0 mmol) was slowly added. After 5 minutes, pinacolborane (150 µL, 1.0 mmol) was added dropwise. The ice bath was then removed and the reaction was stirred at room temperature. After 18 hours, the volatiles were evaporated and the crude mixture was purified by column chromatography (SiO_2; Et_2O/cyclohexane (9:1)) to give the hydroborated product as colorless oil.

Enantiomeric excesses were determined after oxidation of the pinacolborane derivatives to the corresponding alcohols. Pinacolborane derivative (0.25 mmol) were dissolved in Et_2O (2 mL) and cooled to 0°C. NaOH (3N, 2.0 mL) and H_2O_2 (30%, 1.5 mL) were then added. The resulting solution was stirred at room temperature for 2 h. Then, the solution was extracted twice with Et_2O (2 mL) and dried over $MgSO_4$. The crude was purified by column chromatography (SiO_2; Et_2O/cyclohexane (4:1)) to yield the desired chiral primary alcohol.

4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (1a). ^1H NMR ($CDCl_3$), δ: 1.08 (s, 12H, CH_3, Bpin), 1.09 (m, 2H, CH_2), 1.20 (d, $^3J_{H-H}$= 8 Hz, 3H, CH_3), 2.95 (m, 1H, CH), 7.0-7.2 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 24.6 (CH_3, Bpin), 24.7 (CH_3, Bpin), 24.9 (CH_3), 35.8 (CH), 82.9 (C, Bpin), 125.7 (CH=), 126.6 (CH=), 128.1 (CH=), 149.2 (C). HRMS calcd. for $C_{15}H_{23}BO_2$ (M+): 246.1791; found: 246.1794. Enantiomeric excesses determined after oxidation to phenylpropan-1-ol. ^1H NMR ($CDCl_3$), δ: 1.23 (d, $^3J_{H-H}$= 8 Hz, 3H, CH_3), 2.95 (m, 1H, CH), 3.71 (m, 2H, CH_2), 7.2-7.4 (m, 5H, CH=).^{13}C NMR ($CDCl_3$), δ: 17.5 (CH_3), 42.4 (CH), 68.7 (CH_2), 126.7 (CH=), 127.4 (CH=), 128.6 (CH=), 143.6 (C). HRMS calcd. for $C_9H_{12}O$ (M+): 136.0888; found: 136.0885. Ee determined by HPLC using Chiracel IA column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R 38.9 min (*R*); t_R 41.7 min (*S*).

2-(3,3-Dimethyl-2-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1b). ^1H NMR ($CDCl_3$), δ: 0.83 (s, 9H, CH_3, ^{t}Bu), 0.91 (s, 6H, CH_3, Bpin), 0.96 (s, 6H, CH_3, Bpin), 1.18 (m, 2H, CH_2), 2.67 (m, 1H, CH), 7.05-7.20 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 24.2 (CH_3, Bpin), 24.5 (CH_3, Bpin), 27.7 (CH_3, ^{t}Bu), 34.0 (C, ^{t}Bu), 51.6 (CH), 82.7 (C, Bpin), 125.6 (CH=), 127.1 (CH=), 129.7 (CH=), 144.3 (C). HRMS calcd. for $C_{18}H_{29}BO2$ (M+): 288.2261; found: 288.2259. Enantiomeric excesses determined after oxidation to 3,3-dimethyl-2-phenylbutan-1-ol. ^1H NMR ($CDCl_3$), δ: 0.87 (s, 9H, CH_3, ^{t}Bu), 2.65 (m, 1H, CH), 4.01 (m, 2H, CH_2), 7.05-7.35 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 28.4 (CH_3, ^{t}Bu), 33.1 (C, ^{t}Bu), 58.9 (CH), 62.6 (CH_2), 125.6 (CH=), 126.8 (CH=), 127.1 (CH=), 128.2 (CH=), 140.2 (C). HRMS calcd. for $C_{12}H_{18}O$ (M+): 178.1358; found: 178.1357. Ee determined by HPLC using Chiracel IA column (hexane/2-propanol=98/2, 0.5 mL/min, 220 nm). t_R 23.0 min (*S*); t_R 25.2 min (*R*).

4,4,5,5-Tetramethyl-2-(2-phenylbutyl)-1,3,2-dioxaborolane (1c). ^1H NMR ($CDCl_3$), δ: 0.73 (t, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3), 1.08 (s, 12H, CH_3, Bpin), 1.12 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 2.65 (m, 1H, CH), 7.0-7.2 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 12.2 (CH_3), 24.6 (CH_3, Bpin), 24.7 (CH_3, Bpin), 35.8 (CH), 43.3 (CH_2), 82.9 (C, Bpin), 125.7 (CH=), 127.4 (CH=), 128.0 (CH=), 147.2 (C). HRMS calcd. for $C_{16}H_{25}BO2$ (M+): 260.1948; found: 260.1947. Enantiomeric excesses determined after oxidation to 2-phenylbutan-1-ol. ^1H NMR ($CDCl_3$), δ: 0.85 (t, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3), 1.5-1.8 (m, 2H, CH_2), 2.65 (m, 1H; CH), 3.75 (m, 2H, CH_2), 7.20-7.35 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 12.5 (CH_3), 25.7 (CH_2), 50.5 (CH), 67.3 (CH_2), 126.7 (CH=), 128.1 (CH=), 128.6 (CH=), 142.2 (C). HRMS calcd. for $C_{10}H_{14}O$ (M+): 150.1045; found: 150.1043. Ee determined by GC using CP-Chirasil-Dex CB column (90 kPa H_2, 110 °C isotherm). t_R 8.8 min (*S*); t_R 9.2 min (*R*).

4,4,5,5-Tetramethyl-2-(4-methyl-2-phenylpentyl)-1,3,2-dioxaborolane (1d). ^1H NMR ($CDCl_3$), δ: 0.81 (d, $^3J_{H-H}$= 6.0 Hz, 3H, CH_3, ^{i}Bu), 0.85 (d, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3, ^{i}Bu), 1.02 (s, 12H, CH_3, Bpin), 1.2-1.6 (m, 5H), 2.95 (m, 1H, CH), 7.1-7.3 (m, 5H, CH=) ^{13}C NMR ($CDCl_3$), δ: 22.0 (CH_3, ^{i}Bu), 23.4 (CH_3, ^{i}Bu), 24.6 (CH_3, Bpin), 24.7 (CH_3, Bpin), 29.6 (CH_2, ^{i}Bu), 39.2 (CH, ^{i}Bu), 49.0 (CH), 82.8 (C, Bpin), 125.6 (CH=), 127.4 (CH=), 128.0 (CH=), 147.6 (C). HRMS calcd. for $C_{18}H_{29}BO_2$ (M+): 288.2261; found: 288.2262. Enantiomeric excesses determined after oxidation to 4-methyl-2-phenylpentan-1-ol. ^1H NMR ($CDCl_3$), δ: 0.79 (m, 6H, CH_3, ^{i}Bu), 1.2-1.6 (m, 5H), 2.85 (m, 1H, CH), 3.62 (m, 2H, CH_2), 7.1-7.3 (m, 5H, CH=).^{13}C NMR ($CDCl_3$), δ: 21.8 (CH_3, ^{i}Bu), 23.5 (CH_3, ^{i}Bu), 25.3 (CH_2, ^{i}Bu), 41.1 (CH, ^{i}Bu), 46.4 (CH), 68.0 (CH_2), 126.7 (CH=), 128.1 (CH=), 128.6 (CH=), 142.4 (C). HRMS calcd. for $C_{12}H_{18}O$ (M+): 178.1358; found: 178.1356. Ee determined by HPLC using Chiracel IA column (hexane/2-propanol=98/2, 0.5 mL/min, 220 nm). t_R 22.5 min (*S*); t_R 24.3 min (*R*).

4,4,5,5-Tetramethyl-2-(3-methyl-2-phenylbutyl)-1,3,2-dioxaborolane (1e). ^1H NMR ($CDCl_3$), δ: 0.65 (d, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3, ^{i}Pr), 0.87 (d, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3, ^{i}Pr), 1.02 (s, 12H, CH_3, Bpin), 1.04 (s, 12H, CH_3, Bpin), 1.0-1.2 (m, 2H, CH_2), 1.68 (m, 1H, CH, ^{i}Pr), 2.55 (m, 1H, CH), 7.0-7.2 (m, 5H, CH=).^{13}C NMR ($CDCl_3$), δ: 20.4 (CH_3, ^{i}Pr), 20.6 (CH_3, ^{i}Pr), 24.4 (CH_3, Bpin), 24.6 (CH_3, Bpin), 35.3 (CH, ^{i}Pr), 48.3 (CH), 82.7 (C, Bpin), 125.6 (CH=), 127.7 (CH=), 128.3 (CH=), 146.1 (C). HRMS calcd. for $C_{17}H_{27}BO_2$ (M+): 274.2104; found: 274.2102. Enantiomeric excesses determined after oxidation to 3-methyl-2-phenylbutan-1-ol. ^1H NMR ($CDCl_3$), δ: 0.75 (d, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3, ^{i}Pr), 1.02 (d, $^3J_{H-H}$= 8.0 Hz, 3H, CH_3, ^{i}Pr), 1.93 (m, 1H, CH, ^{i}Pr), 2.55 (m, 1H, CH), 3.8-4.0 (m, 2H, CH_2), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 21.0 (CH_3, ^{i}Pr), 21.1 (CH_3, ^{i}Pr), 30.1 (CH, ^{i}Pr), 55.8 (CH), 65.2 (CH_2), 126.7 (CH=), 128.5 (CH=), 128.7 (CH=), 141.6 (C). HRMS calcd. for $C_{11}H_{16}O$ (M+): 164.1201; found: 164.1202. Ee determined by HPLC using Chiracel IA column (hexane/2-propanol=98/2, 0.5 mL/min, 210 nm). t_R 25.2 min (*S*); t_R 26.5 min (*R*).

2-(3,3-Dimethyl-2-(p-tolyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1f). ^{1}H NMR ($CDCl_3$), δ: 0.85 (s, 9H, CH_3, ^{t}Bu), 0.94 (s, 6H, CH_3, Bpin), 0.97 (s, 6H, CH_3, Bpin), 1.21 (m, 2H, CH_2), 2.27 (s, 3H, CH_3), 2.67 (m, 1H, CH), 6.9-7.1 (m, 4H, CH=). ^{13}C NMR ($CDCl_3$), δ: 20.9 (CH_3), 24.2 (CH_3, Bpin), 24.5 (CH_3, Bpin), 27.7 (CH_3, ^{t}Bu), 34.0 (C, ^{t}Bu), 51.2 (CH), 82.7 (C, Bpin), 127.7 (CH=), 129.5 (CH=), 134.9 (C), 141.2 (C). HRMS calcd. for $C_{19}H_{31}BO_2$ (M+): 302.2417; found: 302.2415. Enantiomeric excesses determined after oxidation to 3,3-dimethyl-2-(p-tolyl)butan-1-ol. ^{1}H NMR ($CDCl_3$), δ: 0.88 (s, 9H, CH_3, ^{t}Bu), 2.33 (s, 3H, CH_3), 2.64 (m, 1H, CH), 4.0 (m, 2H, CH_2), 7.1-7.2 (m, 4H, CH=).^{13}C NMR ($CDCl_3$), δ: 21.0 (CH_3), 28.4 (CH_3, ^{t}Bu), 33.0 (C, ^{t}Bu), 58.9 (CH), 62.5 (CH_2), 128.9 (CH=), 129.6 (CH=), 136.3 (C), 136.7 (C) HRMS calcd. for $C_{13}H_{20}O$ (M+): 192.1514; found: 192.1511. Ee determined by GC using Chiradex B-DM column (77 kPa H_2, 110 °C isotherm). t_R 26.5 min (*S*); t_R 27.5 min (*R*).

2-(2-(4-Methoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g). ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 9H, CH_3, ^{t}Bu), 0.90 (s, 6H, CH_3, Bpin), 0.97 (s, 6H, CH_3, Bpin), 1.22 (m, 2H, CH_2), 2.65 (m, 1H, CH), 3.76 (s, 3H, OCH_3), 6.75 (d, 2H, $^3J_{H-H}$= 8.0 Hz, CH=), 7.07 (d, 2H, $^3J_{H-H}$= 8.0 Hz, CH=). ^{13}C NMR ($CDCl_3$), δ: 24.2 (CH_3, Bpin), 24.6 (CH_3, Bpin), 27.6 (CH_3, ^{t}Bu), 34.1 (C, ^{t}Bu), 50.7 (CH), 55.2 (OCH_3), 82.7 (C, Bpin), 112.5 (CH=), 130.4 (CH=), 136.6 (C), 157.7 (C). HRMS calcd. for $C_{19}H_{31}BO_3$ (M+): 318.2366; found: 318.2365. Enantiomeric excesses determined after oxidation to 2-(4-methoxyphenyl)-3,3-dimethylbutan-1-ol. ^{1}H NMR ($CDCl_3$), δ: 0.87 (s, 9H, CH_3, ^{t}Bu), 2.63 (m, 1H, CH), 3.82 (s, 3H, CH_3O), 3.97 (m, 2H, CH_2), 6.87 (d, 2H, $^3J_{H-H}$= 8.4 Hz, CH=), 7.14 (d, 2H, $^3J_{H-H}$= 8.4 Hz, CH=). ^{13}C NMR ($CDCl_3$), δ: 28.3 (CH_3, ^{t}Bu), 33.1 (C, ^{t}Bu), 55.2 (OCH_3), 58.1 (CH), 62.5 (CH_2), 113.6 (CH=), 130.6 (CH=), 131.6 (C), 158.4 (C). HRMS calcd. for $C_{13}H_{20}O_2$ (M+): 208.1463; found: 208.1460. Ee determined by GC using CP-Chirasil-Dex CB column (90 kPa H_2, 110 °C for 40 min, 5 °C/min until 150 °C, 20 °C/min until 170 °C). t_R 49.6 min (*S*); t_R 49.9 min (*R*).

2-(3,3-Dimethyl-2-(4-(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1h). ^{1}H NMR ($CDCl_3$), δ: 0.86 (s, 6H, CH_3, Bpin), 0.88 (s, 6H, CH_3, Bpin), 0.95 (s, 9H, CH_3, ^{t}Bu), 1.27 (m, 2H, CH_2) 2.77 (m, 1H, CH), 7.28 (d, 2H, $^3J_{H-H}$= 8.0 Hz, CH=), 7.47 (d, 2H, $^3J_{H-H}$= 8.0 Hz, CH=). ^{13}C NMR ($CDCl_3$), δ: 24.1 (CH_3, Bpin), 24.5 (CH_3, Bpin), 27.6 (CH_3, ^{t}Bu), 29.7 (C, ^{t}Bu), 51.6 (CH), 82.9 (C, Bpin), 124.1 (CH=), 132.2 (CH=), 128.9 (C), 152.3 (C). HRMS calcd. for $C_{19}H_{28}BF_3O_2$ (M+): 356.2134; found: 356.2133. Enantiomeric excesses determined after oxidation to 3,3-dimethyl-2-(4-(trifluoromethyl)phenyl)butan-1-ol. ^{1}H NMR ($CDCl_3$), δ: 0.87 (s, 9H, CH_3, ^{t}Bu), 2.76 (m, 1H, CH), 4.06 (m, 2H, CH_2), 7.34 (d, 2H, $^3J_{H-H}$= 7.6 Hz, CH=), 7.59 (d, 2H, $^3J_{H-H}$= 7.6 Hz, CH=). ^{13}C NMR ($CDCl_3$), δ: 28.3 (CH_3, ^{t}Bu), 32.1 (C, ^{t}Bu), 58.8 (CH), 62.5 (CH_2), 125.0 (CH=), 130.6 (CH=), 145.8 (C), 160.0 (C). HRMS calcd. for $C_{13}H_{17}BF_3O$ (M+): 246.1231; found: 246.1229. Ee determined by HPLC using Chiracel IA column (hexane/2-propanol=98/2, 0.5 mL/min, 220 nm). t_R 32.7 min (*S*); t_R 38.4 min (*R*).

2-(3,3-Dimethyl-2-(naphthalen-2-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1i). ^{1}H NMR ($CDCl_3$), δ: 0.81 (s, 9H, CH_3, ^{t}Bu), 0.87 (s, 6H, CH_3, Bpin), 0.91 (s, 6H, CH_3, Bpin), 1.2-1.4 (m, 2H, CH_2), 2.89 (m, 1H, CH), 7.4-7.8 (m, 7H, CH=). ^{13}C NMR ($CDCl_3$), δ: 24.1 (CH_3, Bpin), 24.5 (CH_3, Bpin), 27.8 (CH_3, ^{t}Bu), 34.4 (C, ^{t}Bu), 51.7 (CH), 82.7 (C, Bpin), 124.4 (CH=), 125.4 (CH=), 126.3 (CH=), 127.3 (CH=), 127.7 (CH=), 132.2 (C), 133.0 (C). HRMS calcd. for $C_{22}H_{31}BO_2$ (M+): 338.2417; found: 338.2415. Enantiomeric excesses determined after oxidation to 3,3-dimethyl-2-(naphthalen-2-yl)butan-1-ol. ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 9H, ^{t}Bu), 2.79 (m, 1H, CH), 4.07 (m, 2H, CH_2), 7.30-7.77 (m, 7H, CH=) ^{13}C NMR ($CDCl_3$), δ: 28.5 (CH_3, ^{t}Bu), 33.7 (C, ^{t}Bu), 59.1 (CH), 62.6 (CH_2), 125.5 (CH=), 126.1 (CH=), 127.5 (CH=), 127.6 (CH=), 127.7 (CH=), 132.5 (C), 133.2 (C), 137.7 (C). HRMS calcd. for $C_{16}H_{20}O$ (M+): 228.1514; found: 228.1513. Ee determined by HPLC using Chiracel IA column (hexane/2-propanol=98/2, 0.5 mL/min, 220 nm). t_R 40.4 min (*S*); t_R 44.5 min (*R*).

2-(3,3-Dimethyl-2-(m-tolyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j). ^{1}H NMR ($CDCl_3$), δ: 0.93 (s, 9H, CH_3, ^{t}Bu), 0.95 (s, 6H, CH_3, Bpin), 0.96 (s, 6H, CH_3, Bpin), 1.23 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.68 (m, 1H, CH), 6.9-7.1 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 21.4 (CH_3), 24.2 (CH_3, Bpin), 24.5 (CH_3, Bpin), 27.7 (CH_3, ^{t}Bu), 34.0 (C, ^{t}Bu), 51.5 (CH), 82.6 (C, Bpin), 126.2 (CH=), 127.0 (CH=), 136.3 (CH=), 138.0 (C), 144.3 (C). HRMS calcd. for $C_{19}H_{31}BO_2$ (M+): 302.2417; found: 302.2414. Enantiomeric excesses determined after oxidation to 3,3-dimethyl-2-(m-tolyl)butan-1-ol. ^{1}H NMR ($CDCl_3$), δ: 0.89 (s, 9H, CH_3, ^{t}Bu), 2.35 (s, 3H, CH_3), 2.65 (m, 1H, CH), 4.01 (m, 2H, CH_2), 7.05-7.2 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 21.6 (CH_3), 28.4 (CH_3, ^{t}Bu), 33.0 (C, ^{t}Bu), 58.9 (CH), 62.6 (CH_2), 126.8 (CH=), 128.05 (CH=), 137.7 (C). HRMS calcd. for $C_{13}H_{20}O$ (M+): 192.1514; found: 192.1512. Ee determined by GC using CP-Chirasil-Dex CB column (90 kPa H_2, 110 °C isotherm). t_R 20.1 min (*S*); t_R 21.9 min (*R*).

4,4,5,5-Tetramethyl-2-(3,3,3-trifluoro-2-(4-methoxyphenyl)propyl)-1,3,2-dioxaborolane (1k). ^{1}H NMR ($CDCl_3$), δ: 1.03 (s, 6H, CH_3, Bpin), 1.09 (s, 6H, CH_3, Bpin), 1.40 (m, 2H, CH_2), 3.54 (m, 1H, CH), 3.79 (s, 3H, CH_3O), 6.84 (d, 2H, $^3J_{H-H}$= 8.4 Hz, CH=), 7.23 (d, 2H, $^3J_{H-H}$= 8.4 Hz, CH=). ^{13}C NMR ($CDCl_3$), δ: 24.3 (CH_3, Bpin), 24.4 (CH_3, Bpin), 44.8 (q, CH, $^3J_{H-F}$= 28.1 Hz), 55.2 (CH_3O), 83.0 (C, Bpin), 113.6 (CH=), 128.5 (d, C, J_{C-F} = 29.7 Hz), 128.7 (C), 130.0 (CH=), 159.2 (C). HRMS calcd. for $C_{16}H_{22}BF_3O_3$ (M+): 330.1614; found: 330.1612. Enantiomeric excesses determined after oxidation to 3,3,3-trifluoro-2-(4-methoxyphenyl)propan-1-ol. ^{1}H NMR ($CDCl_3$), δ: = 3.45 (m, 1H, CH), 3.8 (s, 3H, CH_3O), 3.98 (m, 1H, CH_2), 4.16 (m, 1H, CH_2), 6.92 (d, 2H, $^3J_{H-H}$= 8.4 Hz, CH=), 7.25 (d, 2H, $^3J_{H-H}$= 8.4 Hz, CH=). ^{13}C NMR ($CDCl_3$), δ: 51.5 (q, CH, J_{C-F} = 25.4 Hz), 55.2 (CH_3O), 61.2 (CH_2), 114.3 (CH=), 124.6 (d, C, J_{C-F} = 30.2 Hz), 130.2 (CH=), 159.7 (C). HRMS calcd. for $C_{10}H_{11}F_3O$ (M+): 220.0711; found: 220.0712. Ee determined by GC using CP-Chirasil-Dex CB column (90 kPa H_2, 110 °C isotherm). t_R 28.2 min (*S*); t_R 29.4 min (*R*).

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Keywords: hydroboration • asymmetric catalysis • iridium • phosphite-oxazoline • 1,1-disubstituted olefins

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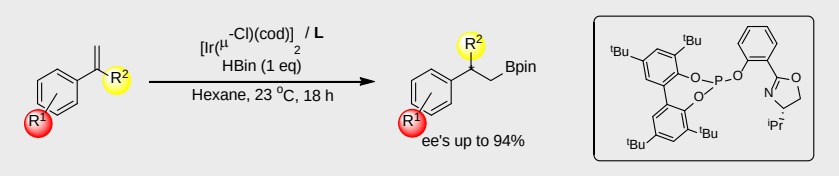

The highly regio- and enantioselective hydroboration of several challenging 1,1-disubstituted olefins has been achieved using Ir-catalysts modified with chiral phosphite-based PHOX ligands. Introducing the biaryl phosphite moiety in the ligand design has been adventitious in terms of substrate versatility. Moreover, the scope of the new phosphite-based catalysts is complementary to that exhibit to the Ir-PHOX-^{t}Bu and Cu-NHC catalysts.

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Filling the gaps in the challenging asymmetric hydroboration of 1,1-disubstituted alkenes using simple Ir-phosphite-based PHOX catalysts