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Asymmetric Hydrogenation of Imines and Olefins Using Phosphine-Oxazoline Iridium Complexes as Catalysts

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Abstract: Herein we describe the synthesis of a new class of chiral phosphine-oxazolines and their application as ligands in iridium-catalyzed hydrogenations. Mechanistic aspects of olefin hydrogenation with this class of iridium catalysts are discussed and a selectivity model to help rationalize the results obtained is also presented.

Keywords: catalysis · hydrogenation · imine · iridium · olefin

Introduction

Chiral amines and alkanes are useful synthetic intermediates for the preparation of many biologically active compounds, and the development of an efficient method for their synthesis is one of the most challenging tasks for organic chemists. One procedure of paramount importance in this field is the enantioslective reduction of C=N and C=C double bonds.[1] Implementation of these technologies in industrial processes has led to the large-scale production of optically active compounds,[2] such as the synthesis of the herbicide (1′*S*)-metolachlor.[3]

The first investigations into Ru[4a] and Rh[4b] homogeneous catalysis for the preparation of optically active amines was published in 1975, however, the enatioselectivities were low (15–22%). In recent years a variety of chiral metal catalysts have been successfully applied to this reaction. The chiral titanocene catalysts developed by Buchwald et al.,[5a,b] and their Zr analogues,[5c] were found to be particularly effective in the hydrogenation of cyclic imines. While Ru[6,7] and Rh[8] complexes have been successfully employed in imine hydrogenations[6,8a–e,g] and in asymmetric transfer hydrogenations,[7,8f] they have also been found to be effective in the reduction of cyclic and acyclic imines, sulfonimines,[6a,7c] and the direct reductive amination of ketones.[8c,g] Iridium complexes have been proven to be exceptionally efficient in the catalytic hydrogenation of imines.[9] One of the most remarkable results was achieved by Zhang et al.[9g] in which acyclic imines were reduced with *ee*'s (*ee* = enantiomeric excess) up to >99% by using the *f*-binaphane ligand and Ir as the catalyst.

In 1977 Crabtree[10] reported an achiral iridium complex that displayed high catalytic activity as a homogeneous hydrogenation catalyst. Since this report a number of research groups have evaluated chiral analogues of Crabtree's catalyst in asymmetric reductions.[11,12] In 1997 Pfaltz et al.[13a] reported that chiral nonracemic phosphine-oxazoline based iridium complexes were highly efficient in the hydrogenation of imines. Catalysts of this type have since been evaluated by Pfaltz and other groups[13] for the preparation of various enantioenriched amines.

However, most of these procedures often require high catalyst loadings, elevated pressures, and long reaction times to obtain the desired amines in high yields and with high *ee*'s. Although several useful methods have been described for the hydrogenation of cyclic imines,[5c,7b,9h,14] the enantioselective hydrogenation of acyclic imines is more difficult to achieve.[1] The process is also sometimes further complicated by the interconversion between *E* and *Z* isomers of an acyclic imine in solution.[5a,b]

Asymmetric hydrogenation of unfunctionalized, polysubstituted alkenes has been less developed than the hydrogenation of olefins containing heteroatoms. In the most successful reports, a polar group adjacent to the C=C double bond is required for high selectivity, due to its ability to coordinate to the metal centre. There are only a few literature examples for which Rh and Ru[15] catalysts have successfully hydrogenated tri- and tetrasubstituted alkenes lacking this coordinating functionality. Impressive results in the reduction of unfunctionalized olefins have been achieved by Buchwald and others using titanocene, zirconocene, and cy-

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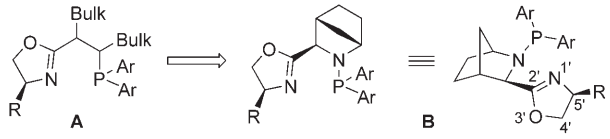
clopentadienyl lanthanide complexes, but turnover frequencies (TOF) and turnover numbers (TON) are low.[16]

Since Pfaltz et al. published the chiral analogue of Crabtree's catalyst for imine hydrogenation,[13a] a number of chiral P,N-containing ligands[17–19] have also been successfully applied to the Ir-catalyzed asymmetric hydrogenation of unfunctionalized olefins. In recent years, many reports describing the use of phosphine-ozaxoline iridium complexes,[18] carbene-oxazoline iridium complexes[19a,c] and phosphine-imidazoline iridium complexes[19b,d,e] have been published, all of which were able to produce yields and enantioselectivities greater than 99%. The mechanism of the asymmetric hydrogenation of olefins has also been investigated by kinetic and computational studies.[20]

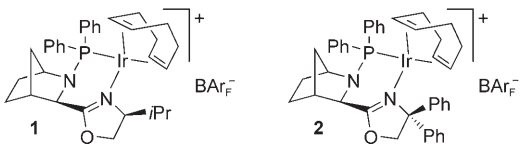
Most of the ligands successfully applied to catalytic hydrogenation, so far, have been built up around a conformationally restricted backbone (structure **A**, Scheme 1). This observation prompted us to investigate the possible use of phosphine-oxazolines of the general structure **B** as ligands for the iridium-catalyzed hydrogenation reactions.



Scheme 1. General structures of proposed phosphine-oxazoline ligands.

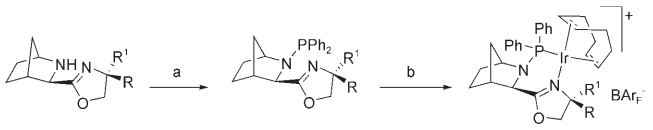
Recently we published the preparation of a new class of 2-aza-norbornane-oxazoline ligands and applied them to the iridium-catalyzed transfer hydrogenation of acetophenone.[21,22] Functionalization of the 2-aza-norbornane-oxazoline with phosphine leads to the novel class of phosphine-oxazoline ligands of general structure **B**.

Preliminary results using these new chiral phosphine-oxazolines in iridium-catalyzed hydrogenations have been very promising.[23] Complex **1** was found to be effective in the reduction of acyclic *N*-aryl imines, whereas complex **2** was potent in the reduction of olefins. Herein we describe the synthesis of a range of new chiral phosphine-oxazolines of this type and their efficient application as ligands in iridium-catalyzed hydrogenations. We will also introduce a discussion on some mechanistic aspects of olefin hydrogenation with this class of iridium catalysts.



Results and Discussion

Synthesis of phosphine-oxazoline ligands: The synthesis of complexes **5a–c** is shown in Scheme 2. Compounds **4a–c** were obtained from the previously described compounds **3a–c** and their subsequent reaction with diphenylphosphine chloride in the presence of diisopropylethyl amine. Iridium complexes **5a–c** were then prepared by refluxing the corresponding phosphine-oxazolines (**4a–c**) and $[Ir(cod)Cl]_2$ in CH_2Cl_2 (cod = 1,5-cyclooctadiene), followed by anion exchange with $NaBAr_F$ in a CH_2Cl_2/H_2O mixture. The crude complexes were purified by column chromatography on silica gel to afford the desired complexes **5a–c** as microcrystalline orange-red solids.



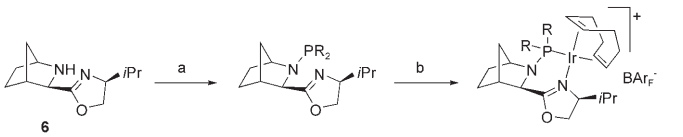
3a: R=*t*Bu, R^1=H
3b: R=Ph, R^1=H
3c: R=H, R^1=Ph

4a: R=*t*Bu, R^1=H (68%)
4b: R=Ph, R^1=H (75%)
4c: R=H, R^1=Ph (70%)

5a: R=*t*Bu, R^1=H (55%)
5b: R=Ph, R^1=H (62%)
5c: R=H, R^1=Ph (60%)

Scheme 2. Synthesis of Ir complexes **5a**, **5b**, and **5c** bearing various substituents at the 5′ position. Reagents and conditions: a) PPh_2Cl, DIPEA, toluene, 4°C, overnight; b) 1) $[Ir(cod)Cl]_2$, CH_2Cl_2, reflux, 2 h; 2) $NaBAr_F$, H_2O. DIPEA = diisopropylethylamine.

To investigate the effect of different phosphine substituents on the enantioselectivity of both imine and olefin reductions Ir complexes **7a–e** were also synthesized (Scheme 3). Based on the results of hydrogenation experiments (Table 1) aminooxazoline **6** was chosen as a starting material and it was reacted with number of dialkyl- and diarylphosphine chlorides. These reactions were strongly dependent on the size of the alkyl or aryl group attached to phosphorus, as the bulky di-*tert*-butyl-, di(2-trifluoromethylphenyl)-, di(2,6-dimethylphenyl)-, and di(1-naphtyl)phosphine chlorides failed to react with compound **6**. As the stability of this type of phosphine-oxazolines is unknown, we decided to directly react the crude ligands with $[Ir(cod)Cl]_2$. Complexes **7a–e** were prepared in a good yields by the same procedure as **5a–c**. All complexes were stable orange-red microcrystalline solids.

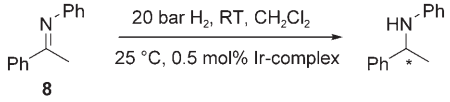


7a: R=cyclohexyl (47%)
7b: R=2-methylphenyl (52%)
7c: R=3,5-dimethylphenyl (32%)
7d: R=2-methoxyphenyl (61%)
7e: R=4-methoxyphenyl (30%)

Scheme 3. Synthesis of Ir complexes **7a–e** with different phosphine substituents. Reagents and conditions: a) PR_2Cl, DIPEA, toluene, 4°C, overnight; b) 1) $[Ir(cod)Cl]_2$, CH_2Cl_2, reflux, 2 h; 2) $NaBAr_F$, H_2O.

Evaluation of the phosphine-oxazoline ligands in the Ir-catalyzed asymmetric hydrogenation of imines: Initially, the influence of the size and configuration of the substituent at

Table 1. Asymmetric hydrogenation of *N*-(1-phenylethylidene)aniline catalyzed by Ir complexes **1**, **2**, and **5**.



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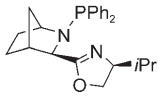
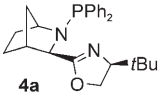
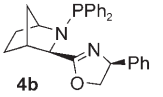
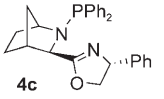
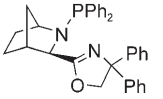
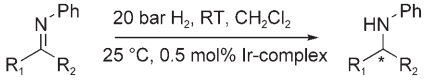
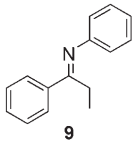
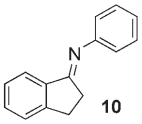
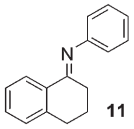
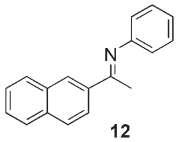
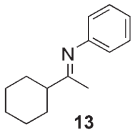
Entry	Ligand	Complex	*t* [h]	Conver. [%][a]	*ee* [%][b]
1		**1**	2	98	90 (*R*)
2	 **4a**	**5a**	12	88	73 (*R*)
3	 **4b**	**5b**	12	66	57 (*R*)
4	 **4c**	**5c**	12	67	52 (*R*)
5		**2**	12	0	n.d.[c]

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC analysis, absolute configuration assigned by comparison of retention times with literature values. [c] n.d. = not determined.[13a]

Table 2. Asymmetric hydrogenation of various imines catalyzed by Ir complex **1**.



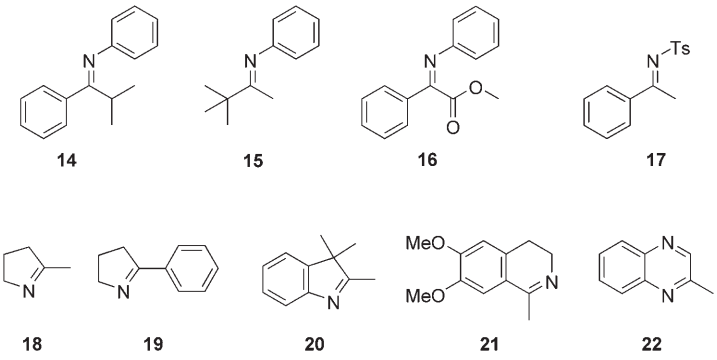
Entry	Imine	*t* [h]	Conver. [%][a]	*ee* [%][b]
1	 **9**	6	99	78 (+)
2	 **10**	12	95	58 (+)
3	 **11**	12	50	53 (+)
4	 **12**	1	99	91 (+)
5	 **13**	12	70	30 (+)

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC analysis, the sign of optical rotation is noted.

the 5′-position was studied. Complexes **5a–c** were tested in the reduction of *N*-(1-phenylethylidene)aniline (**8**),[13a] the reactivity and selectivity of these complexes was directly compared to previously published results for complexes **1** and **2** (Table 1). By using 0.5 mol% of complex **5a** under a H_2 pressure of 20 bar at room temperature (standard conditions), the corresponding (*R*)-*N*-phenyl-*N*-(1-phenylethyl)-amine was produced with 88% conversion and 73% *ee* (entry 2). To our surprise, the diastereomeric complexes **5b** and **5c** produced almost identical results and the (*R*)-amine was obtained with 66 and 67% conversion and an optical purity of 57 and 52%, respectively (entry 3 and 4). To conclude, under standard conditions the Ir complex **1** was the most efficient ligand in the series, with a high *ee* (90%) and full conversion after 2 h.

In our previous publication,[23] we reported the reduction of acyclic aromatic *N*-aryl imines by using complex **1**, with conversions up to 99% and *ee*'s up to 89%. To investigate the scope of the reaction, a group of more complex imines was tested with **1** (Table 2). It can be clearly seen that even a small change in the structure of the starting material has a dramatic effect on *ee* and the percentage conversion. When **9**[24] was hydrogenated in presence of **1** under standard conditions, full conversion was achieved in 6 h (entry 1). Despite of the fact that the structure of **9** only differs from **8** by an additional CH_3 group, the *ee* of the product was markedly lower (78%). Imine **10**, derived from 1-indanone,[25] (entry 2) was hydrogenated with 95% conversion in 12 h and moderate optical purity (58%). When the conformationally more flexible imine **11**, derived from 1-tetralone,[26] (entry 3) was hydrogenated, only 50% conversion was obtained after 12 h and the optical purity of the resulting amine was only 53%. One can imagine that such cyclic structures may cause conformational strain upon coordination to iridium in the transition state. Aromatic imine **12**[24] (entry 4) was hydrogenated with full conversion, after 1 hour with high *ee* (91%). However, when the aromatic group was exchanged for a bulky and flexible aliphatic group, such as cyclohexyl, as in **13**[24] (entry 5), reduction could only be achieved with relatively poor *ee* (30%).

When the acyclic imines **14–17** were subjected to hydrogenation under standard conditions with Ir complex **1**, no reac-



14 **15** **16** **17**

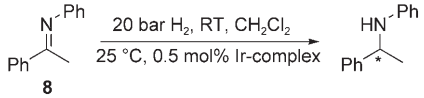
18 **19** **20** **21** **22**

tion was observed. For imines **14** and **15** this could be explained by their steric bulk. Compared to **8**, imines **16** and **17** have relatively electron-deficient C=N double bonds, which might result in a diminished ability to coordinate to iridium. It was also found that none of the cyclic imines **18**–**22** were able to undergo hydrogenation reactions under our conditions.

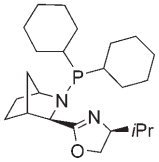
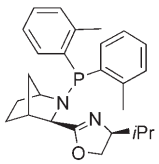
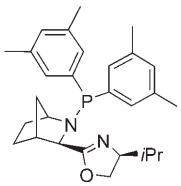
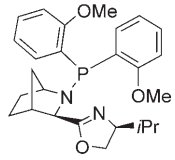
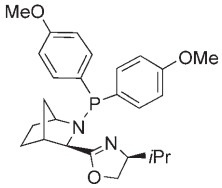
The influence of the phosphine substituents in the ligand on the outcome of the reaction was also investigated (ligands **7a**–**e**, Scheme 3). The results of this study are summarized in the Table 3. Aminooxazoline **6** was chosen as the starting material as the ligand prepared from this compound and diphenylphosphine chloride had been proven to be the most efficient in the previous experiments (Table 1). When **8** was hydrogenated with complex **7a** as the catalyst, full conversion was observed in 4 h with an *ee* of the resulting (*R*)-*N*-phenyl-*N*-(1-phenylethyl)amine of 86% (Table 3, entry 1). Complexes **7b** and **7c** gave very similar results (entries 2 and 3), full conversion and 92% *ee* in 4 and 3 h, respectively. Complex **7d** was found to be the least efficient in the series, producing the amine with only 61% conversion after 20 h (entry 4), and complex **7e** was moderately more efficient than **7d** (entry 5).

In summary, the introduction of substituents on to the aromatic rings attached to phosphorus had a very moderate effect on the resulting *ee*. To our satisfaction, catalysts **7b** and **7c** gave (*R*)-*N*-phenyl-*N*-(1-phenylethyl)amine with 92% *ee*, which is still the best result of our study and one of the best published so far.

Table 3. Asymmetric hydrogenation of *N*-(1-phenylethylidene)aniline catalyzed by Ir complexes **7**.



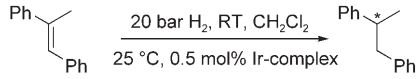
8

Entry	Ligand	Complex	*t* [h]	Conver. [%][a]	*ee* [%][b]
1		**7a**	4	99	86 (*R*)
2		**7b**	4	99	92 (*R*)
3		**7c**	3	99	92 (*R*)
4		**7d**	20	61	90 (*R*)
5		**7e**	6	99	90 (*R*)

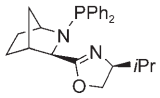
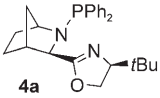
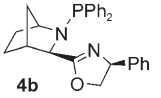
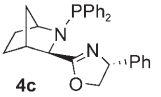
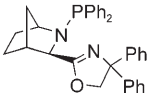
[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC analysis, absolute configuration assigned by a comparison of retention times with literature values.[13a]

Evaluation of phosphine-oxazoline ligands in Ir-catalyzed asymmetric hydrogenations of olefins: The Ir complexes **1**, **5a**, **5b**, and **5c** were evaluated in the hydrogenation of *trans*-α-methylstilbene (**23**). To see the importance of the 5′-substituent of the ligand, the enantioselectivities and conversions obtained in these studies were compared to those obtained with complex **2**.[23] Hydrogenation, catalyzed by Ir complex **1** produced (*R*)-1,2-diphenylpropane with full conversion and 82% *ee* in <0.5 h (Table 4, entry 1). The use of catalyst **5a** gave the product with an enantiomeric purity of 92% in <0.5 hour (entry 2). Ir complexes **5b** and **5c** catalyzed the reduction of **23** with *ee*'s of 73 and 74%, respectively (entries 3 and 4), similar to their reduction of **8**. Iridium complex **2** gave (*R*)-1,2-diphenylpropane with 96% *ee*

Table 4. Asymmetric hydrogenation of *trans*-α-methylstilbene catalyzed by Ir complexes **1**, **2**, and **5**.



23

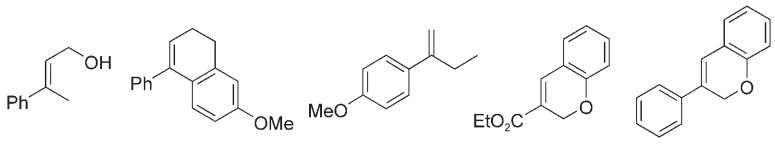
Entry	Ligand	Complex	*t* [h]	Conver. [%][a]	*ee* [%][b]
1		**1**	<0.5	99	82 (*R*)
2	 **4a**	**5a**	<0.5	99	92 (*R*)
3	 **4b**	**5b**	0.5	99	73 (*R*)
4	 **4c**	**5c**	0.5	99	74 (*R*)
5		**2**	12	81	96 (*R*)

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC analysis, absolute configuration assigned by a comparison of retention times with literature values.[18a]

and 81% conversion in 12 h (entry 5). The most sterically hindered Ir complex **2** was the most selective in the series. This shows a direct correlation between the observed *ee* and the steric bulk at the 5′-position of the ligand. Indeed, substantially improved *ee*'s were obtained with more sterically hindered complexes **5a** and **2** (92 and 96% *ee*).

The most selective catalyst **2** was then tested in the enantioselective hydrogenation of various unfunctionalized olefins (Table 5). As the hydrogenation of substrate **23**[18a] did not produce full conversion within 12 h at 20 bar of H_2, the pressure was increased to 80 bar, and in all cases the reaction time was set to 12 h to ensure complete reaction. The optical purity of (*R*)-1,2-diphenylpropane obtained at this higher pressure was 98%, somewhat higher than the 96% obtained at 20 bar (entry 1). Hydrogenation of (*E*)-2-(4-methoxyphenyl)-2-butene (**24**)[18h] gave the product with 99% conversion and excellent *ee* (99%, entry 2). Reduction of acrylic ester **25**[18h] yielded the product with a lower *ee* (69%, entry 3). When complex **1** was employed in the hydrogenation of the same compound, the reaction was complete in <0.5 h (20 bar) and was more selective (88% *ee*, entry 4). In the reduction of acrylic ester **26**[27] with complex **2**, the *ee* of the product was determined as 90% (entry 5). 6-Methoxy-1-methyl-3,4-dihydronaphtalene (**27**)[18h] was hydrogenated with 95% *ee* and full conversion whilst, surprisingly, analogue **28**,[16d] which lacks the methoxy group was reduced with very low conversion and *ee* by using both complexes **1** and **2** (entries 7 and 8). The isomer of compound **28**, 2-methyl-3,4-dihydronaphtalene (**29**),[28] was successfully reduced with full conversion and high *ee* (94%, entry 9). These results and a possible explanation for the observed change in absolute configuration will be discussed later.

During this study, we have found that compounds **31**, **33**, and **34** were unreactive in the hydrogenation reaction with complexes **1** and **2**. The highly reactive terminal alkene **32** did not undergo hydrogenation either. The allylic alcohol **30**



30 **31** **32** **33** **34**

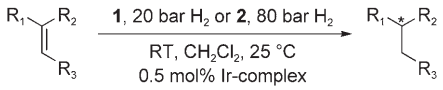
apparently destroyed the catalyst upon addition. This conclusion was based on the observation of a change in color in the reaction mixture and the formation of a dark precipitate.

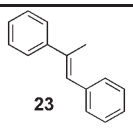
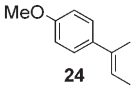
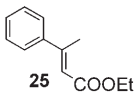
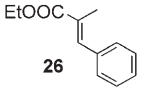
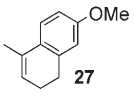
Ir complexes **7a**–**7e**, which contain various phosphorus substituents, were also evaluated in the hydrogenation reaction of **23** (Table 6). Complex **7a** gave the best result in this series, producing a 99% conversion and 92% *ee*. Complexes **7b**, **7c**, and **7e** also yielded (*R*)-1,2-diphenylpropane with full conversion and 78–84% *ee*. The use of catalyst **7d** gave a product with very low optical purity (10%) and 84% conversion after 20 h.

Rationalization of the results of the asymmetric hydrogenation of olefins catalyzed by Ir complex 2: The proposed mechanism[20b] can be used to explain the results of the asymmetric hydrogenation of unfunctionalized olefins by complex **2** (Table 5). To comprehend the catalyst–substrate interactions in the selectivity-determining step, the selectivity-determining transition state was optimized for **23**, which was hydrogenated in the presence of catalyst **2**. This calculated structure (Figure 1b) was found to be very similar to previously reported data.[20b]

The selectivity model (Figure 1c) can be used to rationalize the hydrogenation results shown in Table 5. The enantiofacial selectivity depends on discrimination between the larger and smaller geminal substituents. As seen from computational studies, the chiral pocket of catalyst **2** in the transition state has four unequally filled quadrants. The quadrants A and C are unoccupied and therefore can accommodate large substituents on the alkene double bond. Quadrant D is completely filled by one of the phenyl substituents

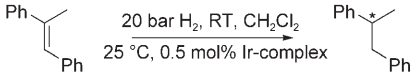
Table 5. Asymmetric hydrogenation of various olefins catalyzed by Ir complexes **1** and **2**.



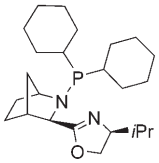
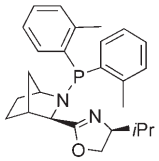
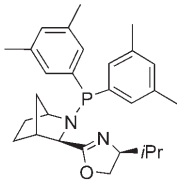
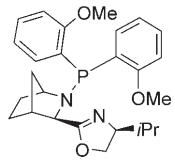
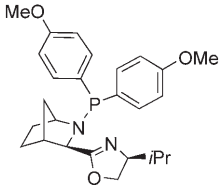
Entry	Olefin	Catalyst	*t* [h]	Conver. [%][a]	*ee* [%][b]
1	 **23**	**2**	12	99	98 (*R*)
2	 **24**	**2**	12	99	99 (*R*)
3	 **25**	**2**	12	99	69 (*R*)
4		**1**	<0.5	99	88 (*R*)
5	 **26**	**2**	12	99	90 (*R*)
6	 **27**	**2**	12	99	95 (*S*)
7	 **28**	**2**	12	30	21 (*S*)
8		**2**	12	36	38 (*S*)
9	 **29**	**2**	12	99	94 (*R*)

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC or chiral GCMS, absolute configuration assigned by comparison of retention times with literature values.[16d,18a,h,27,28]

Table 6. Asymmetric hydrogenation of *trans*-α-methylstilbene catalyzed by Ir complexes **7**.



23

Entry	Ligand	Complex	*t* [h]	Conver. [%][a]	*ee* [%][b]
1		**7a**	0.5	99	92 (*R*)
2		**7b**	0.5	99	78 (*R*)
3		**7c**	0.5	99	82 (*R*)
4		**7d**	20	84	10 (*R*)
5		**7e**	6	99	84 (*R*)

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC, absolute configuration assigned by comparison of retention times with literature values.[18a]

from the oxazoline ligand and so the nonsubstituted position of the alkene will preferentially be oriented towards this quadrant. The semi-hindered quadrant B can tolerate a small alkyl substituent on the olefin. The observed stereoselectivity in the hydrogenation of substrates containing a *trans* orientation of large substituents can be satisfactorily rationalized by using this selectivity model (Table 5). This can be visualized by simply overlaying the olefin structures from Table 5 onto the selectivity model (Figure 1c). According to this model, hydrogen is added to the substrate from underneath the surface of the picture, resulting in the formation of *R* products for compounds **23**–**26** and **29** and *S* products for compounds **27** and **28**. This is exactly the result obtained in our experiments. Compounds **27** and **28** were expected to be poor substrates as they do not fulfill the steric requirements for this selectivity model. Indeed, substrate **28** was reduced with a very low rate of reaction and the resulting product was obtained with low *ee*, a similar result was obtained for both catalysts **1** and **2**. However, the exception to the rule, olefin **27** produced high conversion and selectivity, 99 and 95%, respectively. This model while not quantitative or perfect vide supra, allows for the successful prediction of the absolute configuration of the presented substrates and can be used as an indication of reactivity.

Experimental Section

Commercially available solvents and reagents were used without further purification, apart form the following: chlorodiphenylphosphine was distilled under reduced pressure; dichloromethane was distilled over calcium hydride; whilst toluene, tetrahydrofuran, pentane, and diethyl ether were distilled over sodium. Analytical TLC was performed by using commercially available aluminium-backed plates coated with Kieselgel 60 0.20 mm (UV_{254}), and were visualized under ultra-violet light (at 254 nm) or through staining with ethanolic phosphomolybdic acid followed by heating. Flash column chromatography was carried out by using Kieselgel 60 H silica gel (particle size: 0.063–0.100 mm). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 399.95/100.57 MHz. The chemical shifts are reported with the residual signal of $CDCl_3$ as the internal reference. ^{31}P NMR spectra were recorded at 121.47 MHz by using an internal standard reference. HPLC was performed by using chiral columns, such as Chiralcel OD-H and OJ, and was monitored at 254 nm (UV detector). HRMS was performed by Instrumentstationen Kemicentrum at Lund University (Sweden). Optical rotations were recorded on a thermostated polarimeter by using a 1.0 dm cell.

General procedure for the preparation of ligands 4a, 4b, and 4c: Aminooxazolines **3a**, **3b**, or **3c** (1.0 equiv) were coevaporated with dry toluene (3×20 mL) and redissolved in dry toluene (10 mL mmoL) under a nitrogen atmosphere. Diisopropylethylamine (3.0 equiv) was added to the solution and the mixture was stirred for 15 min at room temperature. Freshly distilled Ph_2PCl (1.5 equiv) was added dropwise and the reaction mixture was kept at 4°C (fridge) overnight.

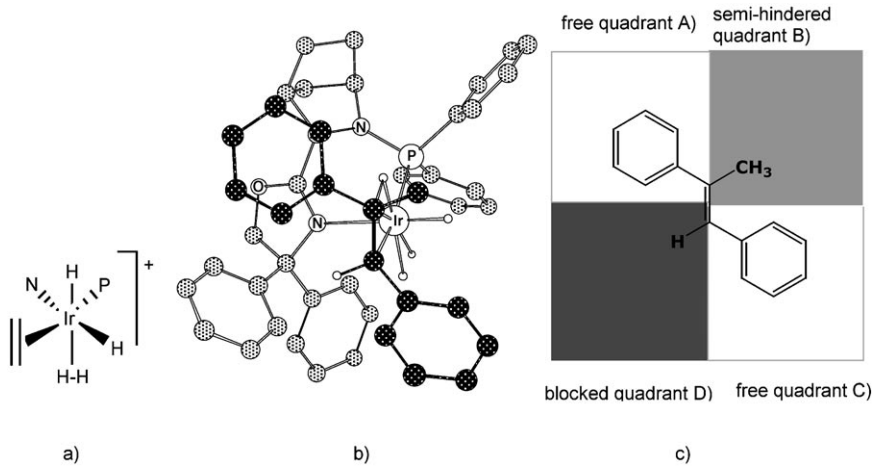


Figure 1. a) Simplified structure of the Ir complex with the coordinated olefin; b) selectivity-determining transition state for the hydrogenation of olefin **23** with Ir complex **2**; c) selectivity model for asymmetric olefin hydrogenation with Ir complex **2**.

The solution was warmed to room temperature and washed with saturated $NaHCO_3$ (150 mL). The water phase was extracted with CH_2Cl_2 (2× 100 mL) and the combined organic extracts were dried over $MgSO_4$. Removal of the solvent in vacuo yielded the crude compounds as yellow oils. Purification by column chromatography on deactivated silica (pentane/Et_3N 1%) yielded the pure ligands **4a**, **4b**, or **4c**.

Ligand 4a: Yield: 180 mg, 0.44 mmol, 68% (white foam); $[\alpha]_D^{22}=+28$ ($c=1.35$ in $CHCl_3$); ^{1}H NMR (C_6D_6): $\delta=7.81$–7.77 (m, 2H; CH arom.), 7.65–7.60 (m, 2H; CH arom.), 7.28–7.23 (m, 2H; CH arom.), 7.15–7.09 (m, 4H, CH arom.), 3.86 (d, J(H,H)=3.9 Hz, 1H; CH next to oxaz.), 3.80–3.60 (m, 4H; CH oxaz., 2×CH_2 oxaz., CHN), 2.50–2.48 (m, 1H; CH_2CHCH in bc), 2.37–2.34 (m, 1H, CHCH_2CH in bc), 1.24–1.15 (m, 1H, CH_2 in bc), 1.02–0.92 (m, 4H, CH_2 in bc); 0.815 ppm (s, 9H, CH_3 in *t*Bu); ^{13}C NMR (C_6D_6): $\delta=168.5$ (d, ^3J(P,C)=1.9 Hz; 1C, quat. C oxaz.), 141.8 (d, ^1J(P,C)=15.0 Hz; 1C, quat. C *ipso* to P in arom.), 141.7 (d, ^1J-(P,C)=10.1 Hz; 1C, quat. C *ipso* to P in arom.), 134.7 (d, J(P,C)= 22.8 Hz, 2C, arom.), 133.1 (d, J(P,C)=17.5 Hz, 2C; Ar), 129.7 (s, 2C; arom.), 129.0 (d, J(P,C)=8.2 Hz, 2C; arom.), 128.7 (s, 2C; arom.), 76.6 (s, 1C; CH oxaz.), 69.2 (s, 1C; CH_2 oxaz.), 64.8 (d, ^2J(P,C)=26.6 Hz; 1C, CH next to oxaz.), 59.8 (d, ^2J(P,C)=3.3 Hz; 1C, CHN), 44.8 (d, ^3J(P,C)= 5.6 Hz; 1C; CH_2CHCH in bc), 37.9 (s, 1C; CHCH_2CH in bc), 34.2 (s, 1C; CH_2CH_2CH in bc), 31.9 (s, 1C; quat. C in *t*Bu), 29.1 (s, 1C; CH_2CH_2CH in bc), 26.6 ppm (s, 3C; CH_3 in *t*Bu); ^{31}P NMR (C_6D_6): $\delta=$ 43.4 ppm; IR (neat): $\tilde{\nu}=3051.9$, 2953.4, 2902.5, 2868.7, 1673.6, 1478.6, 1434.6, 1363.6, 1309.2, 1209.6, 1193.8, 1181.2, 1151.7, 1091.4, 1073.9, 1026.9, 984.8, 955.05 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{25}H_{32}N_2OP$ $[M+H]^+$: 407.2252; found: 407.2257.

Ligand 4b: Yield: 280 mg, 0.66 mmol, 75% (white foam); $[\alpha]_D^{22}=+23$ ($c=0.2$ in $CHCl_3$); ^{1}H NMR (C_6D_6): $\delta=7.80$–7.76 (m, 2H; CH arom.), 7.61–7.57 (m, 2H; CH arom.), 7.17–6.97 (m, 11H; CH arom.), 4.87 (t, J-(H,H)=9.7, 1H; CH oxaz.), 4.05 (dd, J(H,H)=8.2, 9.7 Hz; CH_2 oxaz.), 3.86 (d, J(H,H)=4.2 Hz, 1H; CH next to oxaz.), 3.74 (brs, 1H, CHN), 3.64 (dd, J(H,H)=8.2, 8.9 Hz, 1H; CH_2 oxaz.), 2.48–2.44 (m, 2H, CH_2CHCH in bc, CHCH_2CH in bc), 1.20–0.88 ppm (m, 5H; CH_2 in bc); ^{13}C NMR (C_6D_6): $\delta=169.8$ (s, 1C; quat. C oxaz.), 144.0 (s, 1C; quat C *ipso* to oxaz. in arom.), 141.7 (d, ^1J(P,C)=13.5 Hz, 1C; quat. C *ipso* to P in arom.), 140.7 (d, ^1J(P,C)=10.3 Hz, 1C; quat. C *ipso* to P in arom.), 133.9 (d, J(P,C)=21.0 Hz, 2C, arom.), 133.7 (d, J(P,C)=19.0 Hz, 2C; arom.), 129.5 (s, 2C, oxaz.-arom.), 129.3 (s, 2C; arom.), 129.0 (d, J(P,C)= 6.6 Hz, 2C; arom.), 128.8 (d, J(P,C)=5.8 Hz, 2C; arom.), 127.9 (s, 2C; oxaz.-arom.), 127.7 (s, 1C; oxaz.-arom.), 75.3 (s, 1C; CH oxaz.), 70.6 (s, 1C; CH_2 oxaz.), 64.1 (d, ^2J(P,C)=18.8 Hz, 1C; CH next to oxaz.), 61.1 (d, ^2J(P,C)=4.5 Hz, 1C; CHN), 44.9 (d, ^3J(P,C)=5.2 Hz, 1C; CH_2CHCH in bc), 38.2 (d, ^3J(P,C)=3.3 Hz, 1C; CHCH_2CH in bc), 32.2 (d, 1C, ^3J-(P,C)=2.4 Hz; CH_2CH_2CH in bc), 29.1 ppm (s, 1C; CH_2CH_2CH in bc); ^{31}P NMR (C_6D_6): δ 45.2 ppm; IR (neat): $\tilde{\nu}=2973.1$, 2869.9, 2360.1, 2341.7, 1654.1, 1477.8, 1434.4, 1308.9, 1180.0, 1147.0, 1072.9, 986.1 cm^{-1}; HRMS (FAB$^+$): : calcd for $C_{27}H_{28}N_2OP$: 427.1939 $[M+H]^+$; found: 427.1937.

Ligand 4c: Yield: 230 mg, 0.54 mmol, 70% (white foam); $[\alpha]_D^{22}=+18$ ($c=1.0$ in $CHCl_3$); ^{1}H NMR (C_6D_6): $\delta=7.84$–7.80 (m, 2H; CH arom.), 7.65–7.61 (m, 2H; CH arom.), 7.21–7.00 (m, 11H; CH arom.), 4.91 (t, J-(H,H)=9.1, 1H; CH oxaz.), 4.09 (dd, J(H,H)=8.3, 10.3 Hz; CH_2 oxaz.), 3.90 (d, J(H,H)=4.2 Hz, 1H; CH next to oxaz.), 3.78 (brs, 1H; CHN), 3.68 (dd, J(H,H)=8.3, 9.1 Hz, 1H; CH_2 oxaz.), 2.52–2.49 (m, 2H; CH_2CHCH in bc, CHCH_2CH in bc), 1.24–0.92 ppm (m, 5H; CH_2 in bc); ^{13}C NMR (C_6D_6): $\delta=169.9$ (s, 1C; quat. C oxaz.), 144.0 (s, 1C quat. C *ipso* to oxaz. in arom.), 141.7 (d, ^1J(P,C)=13.8 Hz, 1C; quat. C *ipso* to P in arom.), 140.7 (d, ^1J(P,C)=10.3 Hz, 1C; quat. C *ipso* to P in arom.), 133.9 (d, J(P,C)=21.6 Hz, 2C; arom.), 133.7 (d, J(P,C)=19.2 Hz, 2C; arom.), 129.5 (s, 2C; oxaz.-arom.), 129.3 (s, 2C; arom.), 129.0 (d, J(P,C)= 6.5 Hz, 2C; arom.), 128.9 (d, J(P,C)=5.6 Hz, 2C; arom.), 127.9 (s, 2C; oxaz.-arom.), 127.6 (s, 1C; oxaz.-arom.), 75.3 (s, 1C; CH oxaz.), 70.6 (s, 1C; CH_2 oxaz.), 64.1 (d, ^2J(P,C)=18.8 Hz, 1C; CH next to oxaz.), 61.1 (d, ^2J(P,C)=4.85 Hz, 1C; CHN), 44.9 (d, ^3J(P,C)=4.5 Hz, 1C, CH_2CHCH in bc); 38.2 (d, ^3J(P,C)=3.2 Hz, 1C; CHCH_2CH in bc); 32.2 (d, 1C, ^3J(P,C)=2.2 Hz; CH_2CH_2CH in bc); 29.1 ppm (s, 1C, CH_2CH_2CH in bc); ^{31}P NMR (C_6D_6): $\delta=45.1$ ppm; IR (neat): $\tilde{\nu}=3052.6$, 2970.2, 2869.9, 2360.3, 2342.0, 1655.0, 1478.7, 1434.4, 1309.0, 1180.2, 1149.55, 1091.1, 1072.6, 1044.9, 986.2, 949.9 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{27}H_{28}N_2OP$: 427.1939 $[M+H]^+$; found: 427.1950.

General procedure for the preparation of Ir complexes 5a, 5b, and 5c: $[Ir(cod)Cl]_2$ (1.0 equiv) was added to a solution of ligand **4a**, **4b**, or **4c** (2.0 equiv) in CH_2Cl_2 (5 mL/50 mg of ligand) under a nitrogen atmosphere. The reaction mixture was heated to reflux for 1 h. After cooling to room temperature, water (5 mL) was added and the biphasic solution was stirred vigorously. $NaBAr_F{\cdot}3H_2O$ (1.5 equiv) was added to the emulsion and reaction mixture was stirred for 0.5 h. The phases were separated and the water phase was extracted with CH_2Cl_2 (2×20 mL). The combined organic extracts were concentrated under reduced pressure and the resulting complexes purified by column chromatography on silica gel (pentane/CH_2Cl_2 1:1).

Ir complex 5a: Yield: 122 mg, 0.08 mmol, 55% (bright-orange foam); $[\alpha]_D^{22}=+28$ ($c=1.0$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta=7.77$–7.71 (m, total 10H; 8H *ortho* CH Ar, BAr_F, 2H CH arom.), 7.60–7.44 (m, total 10H; 4H *para* CH arom. BAr_F, 6H CH arom.), 7.40–7.34 (m, 2H; CH arom.); 5.00–4.92 (m, 1H; CH cod), 4.71–4.64 (m, 1H; CH cod), 4.62 (dd, J-(H,H)=9.9, 3.4 Hz, 1H; CH_2 oxaz.), 4.43 (d, J(H,H)=6.7 Hz, 1H; CH next to oxaz.), 4.30 (t, J(H,H)=9.9 Hz, 1H; CH oxaz.), 3.84 (brs, 1H; CHN), 3.78 (dd, J(H,H)=9.9 Hz, 3.4 Hz, 1H; CH_2 oxaz.), 3.60–3.49 (m, 2H; CH cod), 3.04 (brs, 1H; CH_2CHCH in bc), 2.74–2.67 (m, 1H; CH cod), 2.42–2.24 (m, 4H; CH_2 cod), 2.01–1.84 (m, 2H; CH_2 cod), 1.62–1.53 (m, 2H; CH_2 cod), 1.47–1.25 (m, 6H; CH_2 bc), 0.83 ppm (s, 9H; CH_3 *t*Bu); ^{13}C NMR ($CDCl_3$): $\delta=173.9$ (s, 1C; quat. C oxaz.), 161.6 (q, ^1J-(B,C)=50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 133.3 (d, J(P,C)=13.25 Hz, 2C; arom.), 132.0 (d, J(P,C)= 24.0 Hz, 2C; arom.), 131.5 (d, J(P,C)=11.0 Hz, 2C; arom.); 130.4 (d, ^1J-(P,C)=16.4 Hz, 1C; quat. C *ipso* to P in arom.), 129.8 (d, ^1J(P,C)= 7.4 Hz, 1C; quat. C *ipso* to P in arom.), 129.1 (d, J(P,C)=11.2 Hz, 2C; arom.); 128.8 (qq, ^2J(F,C)=31.3 Hz, ^3J(B,C)=3.1 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 128.75 (d, J(P,C)=10.1 Hz, 2C; arom.), 124.5 (q, ^1J(F,C)= 272.3 Hz, 8C; CF_3 in BAr_F); 117.35 (sept, ^3J(C,F)=4.1 Hz, 4C; CH *para* to B in BAr_F), 94.9 (d, ^2J(P,C)=12.0 Hz, 1C; cod CH), 90.7 (d, ^2J(P,C)= 14.4 Hz, 1C; cod CH), 72.2 (s, 1C; CH oxaz.), 72.0 (s, 1C; CH_2 oxaz.), 64.5 (d, ^2J(P,C)=10.2 Hz, 1C; cod CH); 63.75 (s, 1C; CH next to oxaz.), 63.1 (s, 1C, CHN), 58.5 (d, ^2J(P,C)=6.6 Hz, 1C; cod CH), 40.0 (d, ^3J-(P,C)=6.4 Hz, 1C; CH_2CHCH in bc), 37.9 (d, ^3J(P,C)=4.0 Hz, 1C; CHCH_2CH in bc), 36.0 (d, ^3J(P,C)=4.4 Hz, 1C; cod CH_2), 33.9 (s, 1C; cod CH_2), 32.7 (s, 1C; cod CH_2), 29.6 (s, 1C; quat. C in *t*Bu), 29.5 (s, 1C; CH_2CH_2CH in bc), 28.2 (s, 1C; cod CH_2), 27.1 (s, 1C; CH_2CH_2CH in bc), 25.2 ppm (s, 3C; CH_3 in *t*Bu); ^{31}P NMR ($CDCl_3$): $\delta=51.8$ ppm; IR (neat): $\tilde{\nu}=2960.3$, 2360.1, 2341.9, 1611.0, 1354.4, 1277.45, 1159.2, 1127.0, 887.0, 839.2, 714.35, 682.45, 670.0 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{33}H_{43}IrN_2OP$: 707.2742 $[M]^+$; found: 707.2740.

Ir complex 5b: Yield: 143 mg, 0.09 mmol, 62% (bright-orange foam); $[\alpha]_D^{22}=+33$ ($c=1.1$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta=7.70$–7.55 (m, total 10H; *ortho* 8H CH arom. BAr_F, 2H CH arom.), 7.48–7.36 (m, total 8H; 4H *para* CH arom. BAr_F, 4H CH arom.), 7.29–7.22 (m, 7H; CH arom.), 6.91–6.89 (m, 2H; CH arom.), 5.14 (dd, J(H,H)=10.3, 5.8 Hz, 1H; CH_2 oxaz.), 5.02–4.97 (m, 1H; CH cod), 4.86–4.80 (m, 1H; CH cod), 4.78 (t, J-(H,H)=10.4 Hz, 1H; CH oxaz.), 4.47–4.42 (m, 2H; CH_2 oxaz., CH next to oxaz.), 3.78 (brs, 1H; CHN), 3.12–3.04 (m, 2H; CH cod, CH_2CHCH in bc); 2.38–1.22 ppm (m, 15H; CH cod (1H), CH_2 cod (8H), CH_2 bc (6H)); ^{13}C NMR ($CDCl_3$): $\delta=174.6$ (s, 1C; quat. C oxaz.), 161.6 (q, ^1J-(B,C)=50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 138.4 (s, 1C; quat. C *ipso* to oxaz. arom.), 134.9 (d, ^2J(P,C)=13.5 Hz, 2 C; CH arom.), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 132.4 (d, J(P,C)=1.7 Hz, 1C; arom.), 131.7 (d, J(P,C)=2.3 Hz, 1C; arom.), 131.3 (d, J(P,C)=10.3 Hz, 2C; arom.), 130.7 (d, 1C; quat. C *ipso* to P in arom.), 130.1 (d, 1C; quat. C *ipso* to P in arom.), 129.7 (s, 2C; oxaz. arom.), 129.6 (s, 1C; oxaz. arom.), 129.0 (d, J(P,C)=10.9 Hz, 2C; arom.), 128.8 (qq, ^2J(F,C)=27.5 Hz, ^3J-(B,C)=2.9 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 128.6 (d, J(P,C)= 9.7 Hz, 2C; arom.), 125.9 (s, 2C; CH oxaz. arom.), 124.5 (q, ^1J(F,C)= 274.6 Hz, 8C; CF_3 in BAr_F), 117.35 (sept, ^3J(C,F)=4.5 Hz, 4C; CH *para* to B in BAr_F), 93.6 (d, ^2J(P,C)=12.8 Hz, 1C; cod CH), 92.5 (d, ^2J(P,C)= 12.6 Hz, 1C; cod CH), 77.9 (s, 1C; CH oxaz.), 67.5 (s, 1C; CH_2 oxaz.),

65.0 (s, 1C; CH next to oxaz.), 64.7 (d, ^2J(P,C) = 11.4 Hz, 1C; cod CH), 62.75 (s, 1C, CHN), 58.5 (d, ^2J(P,C) = 5.7 Hz, 1C; cod CH), 40.1 (d, ^3J(P,C) = 6.8 Hz; CH_2CHCH in bc), 38.4 (d, ^3J(P,C) = 3.9 Hz, 1C; $CHCH_2CH$ in bc), 34.4 (d, ^3J(P,C) = 4.5, 1C; cod CH_2), 31.5 (d, ^3J(P,C) = 1.9, 1C; cod CH_2), 30.4 (s, 1C; CH_2CH_2CH in bc), 28.9 (d, ^3J(P,C) = 2.4, 1C; cod CH_2); 26.7 (s, 1C; CH_2CH_2CH in bc), 26.6 ppm (s, 1C; cod CH_2); ^{31}P NMR ($CDCl_3$): δ 51.2 ppm; IR (neat): $\tilde{\nu}$ = 2927.4, 2359.7, 2341.85, 1610.4, 1355.1, 1277.6, 1126.6, 887.4, 839.4, 759.7, 713.3, 682.4, 670.3 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{35}H_{39}IrN_2OP$: 727.2429 $[M]^+$; found: 727.2425.

Ir complex 5c: Yield: 134 mg, 0.08 mmol, 60 % (bright-orange foam); $[\alpha]_D^{22}$ = +37 (c = 1.2 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 7.77–7.61 (m, total 10H; 8H *ortho* CH arom. BAr_F, 2H CH arom.), 7.55–7.43 (m, total 8H; 4H *para* CH Ar BAr_F, 4H CH arom.), 7.35–7.26 (m, 7H; CH arom.), 6.97–6.94 (m, 2H; CH arom.), 5.21–5.16 (m, 1H; CH_2 oxaz.), 5.06–5.01 (m, 1H; CH cod), 4.93–4.79 (m, 2H; CH cod, C*H* oxaz.), 4.52–4.47 (m, 2H; CH_2 oxaz., CH next to oxaz.), 3.83 (brs, 1H; CHN), 3.17–3.11 (m, 2H; CH cod, CH_2CHCH in bc), 2.41–1.24 ppm (m, 15H: 1H CH cod; 8H CH_2 cod; 6H CH_2 bc), ^{13}C NMR ($CDCl_3$): δ = 174.6 (s, 1C; quat. C oxaz.), 161.6 (q, ^1J(B,C) = 50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 138.4 (s, 1C; quat. C *ipso* to oxaz. arom.), 134.9 (d, ^2J(P,C) = 13.8 Hz, 2C; CH arom.), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 132.4 (d, J(P,C) = 3.1 Hz, 1C; arom.), 131.7 (d, J(P,C) = 2.3 Hz, 1C; arom.), 131.3 (d, J(P,C) = 11.5 Hz, 2C; arom.), 130.7 (d, 1C; quat. C *ipso* to P in arom.), 130.1 (d, 1C; quat. C *ipso* to P in arom.), 129.7 (s, 2C; oxaz. arom.), 129.55 (s, 1C; oxaz. arom.), 129.0 (d, J(P,C) = 12.1 Hz, 2C; arom.), 128.8 (qq, ^2J(F,C) = 27.5 Hz, ^3J(B,C) = 2.9 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 128.6 (d, J(P,C) = 10.8 Hz, 2C; arom.), 125.9 (s, 2C; CH oxaz. arom.), 124.5 (q, ^1J(F,C) = 274.6 Hz, 8C; CF_3 in BAr_F), 117.35 (sept, ^3J(C,F) = 4.5 Hz, 4C; CH *para* to B in BAr_F), 93.7 (d, ^2J(P,C) = 12.5 Hz, 1C; cod CH), 92.5 (d, ^2J(P,C) = 13.0 Hz, 1C; cod CH), 77.9 (s, 1C; CH oxaz.), 67.5 (s, 1C; CH_2 oxaz.), 65.0 (s, 1C; CH next to oxaz.), 64.8 (d, ^2J(P,C) = 10.1 Hz, 1C; cod CH), 62.7 (s, 1C; CHN), 58.5 (d, ^2J(P,C) = 5.8 Hz, 1C; cod CH), 40.1 (d, ^3J(P,C) = 7.3 Hz, CH_2CHCH in bc), 38.4 (d, ^3J(P,C) = 3.4 Hz, 1C; $CHCH_2CH$ in bc), 34.4 (d, ^3J(P,C) = 4.4, 1C; cod CH_2), 31.55 (s, 1C; cod CH_2), 30.4 (s, 1C; CH_2CH_2CH in bc), 28.9 (s, 1C; cod CH_2), 26.7 (s, 1C; CH_2CH_2CH in bc), 26.6 ppm (s, 1C; cod CH_2); ^{31}P NMR ($CDCl_3$): δ = 51.2 ppm; IR (neat): $\tilde{\nu}$ = 2926.4, 2359.4, 2341.8, 1610.3, 1355.1, 1278.3, 1126.6, 887.4, 839.4, 746.7, 713.3, 698.4, 682.4, 670.3 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{35}H_{39}IrN_2OP$ $[M]^+$: 727.2429; found: 727.2430.

General procedure for the preparation of Ir complexes 7a, 7b, 7c, 7d, and 7e: The aminooxazoline **6** (1.0 equiv) was coevaporated with dry toluene (3 × 20 mL) and redissolved in dry toluene (10 mL mmoL) under a nitrogen atmosphere. Diisopropylethylamine (3.0 equiv) was added to the solution and the mixture was stirred for 15 min at room temperature. Freshly prepared Ar_2PCl (1.5 equiv) was then added and the reaction mixture was kept at 4 °C (fridge) overnight. After this time, the solution was warmed to room temperature and washed with saturated $NaHCO_3$ (150 mL). The water phase was extracted twice with CH_2Cl_2 (2 × 100 mL) and the combined organic extracts were dried over $MgSO_4$. Removal of the solvent in vacuo yielded the crude compounds as yellow oils. $[Ir(cod)Cl]_2$ (1.0 equiv) was added to a solution of crude ligand (2.0 equiv) in CH_2Cl_2 (5 mL/50 mg of ligand) under a nitrogen atmosphere. The reaction mixture was heated to reflux for 1 h. After cooling to room temperature, water (5 mL) was added and the biphasic solution stirred vigorously. $NaBAr_F \cdot 3H_2O$ (1.5 equiv) was added to the emulsion and reaction mixture was stirred for 0.5 h. The phases were separated and the water phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were concentrated under reduced pressure and the resultant complexes **7a–e** purified by column chromatography on silica gel (pentane/CH_2Cl_2 1:1).

Ir complex 7a: Yield: 354 mg, 0.25 mmol, 47 % (bright-orange foam); $[\alpha]_D^{22}$ = +32 (c = 1.0 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.70 (brs, 8H; *ortho* CH arom. BAr_F), 7.53 (brs, 4H; *para* CH arom. BAr_F), 4.71–4.64 (m, 1H; CH cod), 4.61–4.57 (m, 1H; CH cod), 4.51 (dd, J(H,H) = 9.8, 4.1 Hz, 1H; CH_2 oxaz.), 4.25 (t, J(H,H) = 9.8 Hz, 1H; C*H* oxaz.), 3.91–3.86 (m, 2H; CH_2 oxaz., CH next to oxaz.), 3.67–3.61 (m, 2H; CHN, CH cod), 3.37–3.30 (m, 1H; CH cod), 3.01 (brs, 1H; CH_2CHCH in bc), 2.56–1.21 (m, 37H: 8H CH_2 cod; 6H CH_2 bc; 1H CH *iso*propyl; 2H CH cyclohexyl; 20H CH_2 cyclohexyl), 0.94 (d, J(H,H) = 7.1 Hz, 3H, CH_3 *i*Pr), 0.74 ppm (d, J(H,H) = 7.1 Hz, 3H; CH_3 *i*Pr); ^{13}C NMR ($CDCl_3$): δ = 174.0 (s, 1C; quat. C oxaz.), 161.6 (q, ^1J(B,C) = 50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 128.8 (qq, ^2J(F,C) = 32.1 Hz, ^3J(B,C) = 3.0 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 124.5 (q, ^1J(F,C) = 272.0 Hz, 8C; CF_3 in BAr_F), 117.4 (sept, ^3J(C,F) = 3.8 Hz, 4C; CH *para* to B in BAr_F), 91.8 (d, ^2J(P,C) = 12.8 Hz, 1C; cod CH), 90.8 (d, ^2J(P,C) = 11.0 Hz, 1C; cod CH), 70.2 (s, 1C; CH oxaz.), 68.1 (s, 1C; CH_2 oxaz.), 64.9 (d, ^2J(P,C) = 6.9 Hz, 1C; cod CH), 63.4 (s, 1C; CH next to oxaz.), 60.5 (s, 1C, CHN), 57.5 (d, ^2J(P,C) = 5.6 Hz; cod CH), 40.0 (d, ^3J(P,C) = 6.3 Hz, CH_2CHCH in bc), 38.1 (s, 1C; $CHCH_2CH$ in bc), 37.0 (d, ^1J(P,C) = 38.0 Hz, 1C; quat. C next to P in cyclohex.), 35.4 (d, ^1J(P,C) = 28.7 Hz, 1C; quat. C next to P in cyclohex.), 33.8 (s, 1C; cod CH_2), 32.4 (s, 1C; CH *i*Pr), 31.7 (s, 1C; cod CH_2), 30.8 (s, 1C, CH_2CH_2CH in bc), 29.9–29.7 (mult. sign.; CH_2 in cyclohex and CH_2 cod), 28.4 (s, 1C; cod CH_2), 27.4 (s, 1C; CH_2CH_2CH in bc), 26.9–25.9 (mult. sign.; CH_2 in cyclohex.), 19.3 (s, 1C; CH_3 *i*Pr), 14.2 ppm (s, 1C; CH_3 *i*Pr); ^{31}P NMR ($CDCl_3$): δ = 63.3 ppm; IR (neat): $\tilde{\nu}$ = 2937.5, 2858.2, 2360.2, 2341.9, 1610.85, 1354.8, 1277.9, 1126.1, 887.4, 839.4, 761.35, 713.6, 682.4, 670.1 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{32}H_{53}IrN_2OP$: 705.3525 $[M]^+$; found: 705.3547.

Ir complex 7b: Yield: 395 mg, 0.25 mmol, 52 % (bright-orange foam); $[\alpha]_D^{22}$ = +32 (c = 1.0 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 8.75–8.68 (m, 1H; CH arom.), 7.73 (brs, 8H; *ortho* CH arom. BAr_F), 7.55 (brs, total 5H; 4H *para* CH arom. BAr_F, 1H CH arom.), 7.44–7.33 (m, 4H; CH arom.), 7.17–7.11 (m, 1H; CH arom.), 6.99–6.92 (m, 1H; CH arom.), 4.98–4.91 (m, 1H; CH cod), 4.66–4.61 (m, 1H; CH cod), 4.55 (dd, J(H,H) = 9.8, 4.6 Hz, 1H; CH_2 oxaz.), 4.32–4.26 (m, 2H; C*H* oxaz. and CH next to oxaz.), 4.06–4.01 (m, 1H; CH_2 oxaz.), 3.74 (brs, 1H; CHN), 3.19–3.13 (m, 1H; CH cod), 3.02–2.98 (m, 1H; CH_2CHCH in bc), 2.67 (brs, 3H; CH_3–Ar), 2.36–2.20 (m, total 8H; 3H CH_3–Ar, 4 CH_2 cod, 1H CH cod), 2.07–1.96 (m, 2H; CH_2 cod) 1.81–1.27 (m, total 8H; 2H CH_2 cod, 5H CH_2 bc, 1H CH *i*Pr), 1.10–1.05 (m, 1H, $CHCH_2CH$ in bc), 0.94 (d, J(H,H) = 7.3 Hz, 3H; CH_3 *i*Pr), 0.51 ppm (d, J(H,H) = 7.3 Hz, 3H; CH_3 *i*Pr); ^{13}C NMR ($CDCl_3$): δ = 173.5 (s, 1C; quat. C oxaz.), 161.6 (q, ^1J(B,C) = 50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 141.5–139.3 (m, 2C; quat. C *ipso* to P in arom.), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 132.9 (d, J(P,C) = 6.9 Hz, 2C; arom.), 132.5 (s, 1C; C–CH_3), 131.9 (s, J(P,C) = 8.2 Hz, 2C; arom.), 131.5 (s, 1C; C–CH_3), 128.8 (qq, ^2J(F,C) = 31.5 Hz, ^3J(B,C) = 2.8 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 126.2 (d, J(P,C) = 16.9 Hz, 2C; arom.), 125.3 (d, J(P,C) = 9.8 Hz, 2C; arom.), 124.5 (q, ^1J(F,C) = 274.2 Hz, 8C; CF_3 in BAr_F), 117.4 (sept, ^3J(C,F) = 3.8 Hz, 4C; CH *para* to B in BAr_F), 92.9 (m, 1C; cod CH), 90.5 (m, 1C; cod CH), 69.8 (s, 1C; CH oxaz.), 68.1 (s, 1C; CH_2 oxaz.), 65.4 (s, 1C; CH next to oxaz.), 64.4 (s, 1C; cod CH), 63.2 (d, ^2J(P,C) = 10.8 Hz, 1C; CHN), 59.75 (s, 1C; cod CH), 39.8 (d, ^3J(P,C) = 6.8 Hz; CH_2CHCH in bc), 38.2 (m, 1C; $CHCH_2CH$ in bc), 35.6 (d, ^3J(P,C) = 3.4, 1C; cod CH_2), 32.5 (s, 2C; cod CH_2), 31.6 (s, 1C; CH_2CH_2CH in bc), 30.8 (s, 1C, CH *i*Pr), 27. 9 (s, 1C; cod CH_2), 26.2 (s, 1C; CH_2CH_2CH in bc), 26.0 (s, 1C; CH_3–Ar), 25.8 (s, 1C, CH_3–Ar), 23.5 (d, ^3J(P,C) = 7.8, 1C; cod CH_2), 18.25 (s, 1C, CH_3 *i*Pr), 14.0 ppm (s, 1C; CH_3 *i*Pr); ^{31}P NMR ($CDCl_3$): δ = 51.2 ppm; IR (neat): $\tilde{\nu}$ = 2969.9, 2890.6, 2360.0, 2341.8, 1619.4, 1354.9, 1277.5, 1126.8, 1079.0, 887.4, 839.6, 757.65, 714.0, 682.3, 670.4 cm^{-1}; HRMS (FAB$^+$): calcd for $C_{34}H_{45}IrN_2OP$: 721.2899 $[M]^+$; found: 721.2920.

Ir complex 7c: Yield: 248 mg, 15 mmol, 32 % (bright-orange foam); $[\alpha]_D^{22}$ = −7 (c = 1.0 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 7.70 (brs, 8H; *ortho* CH arom. BAr_F), 7.55 (brs, 1H; CH arom.), 7.52 (brs, 4H; *para* CH arom. BAr_F), 7.25 (brs, 2H; CH arom.), 7.10 (brs, 1H; CH arom.), 6.86–6.83 (m, 2H; CH arom.), 4.92–4.84 (m, 1H; CH cod), 4.73–4.64 (m, 1H; CH cod); 4.49 (dd, J(H,H) = 9.6, 4.1 Hz, 1H; CH_2 oxaz.), 4.37 (d, J(H,H) = 4.7 Hz; CH next to oxaz.), 4.33–4.27 (m, 1H; C*H* oxaz.), 4.01–3.98 (m, 1H; CH_2 oxaz.), 3.71 (brs, 1H; CHN), 3.30–3.24 (m, 1H; CH cod), 3.01–2.95 (m, 1H; CH_2CHCH in bc), 2.42–1.25 (m, total 27H; 12H CH_3–Ar, 1H CH cod, 8H CH_2 cod, 5H CH_2 bc, 1H CH *i*Pr), 1.13–1.09 (m, 1H, $CHCH_2CH$ in bc), 0.91 (d, J(H,H) = 7.0 Hz, 3H; CH_3 *i*Pr), 0.54 ppm (d, J(H,H) = 7.0 Hz, 3H; CH_3 *i*Pr); ^{13}C NMR ($CDCl_3$): δ = 173.4 (s, 1C; quat. C oxaz.), 161.6 (q, ^1J(B,C) = 50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 138.7 (d, J(P,C) = 12.0 Hz, 1C; arom.), 138.3 (d, J(P,C) =

10.9 Hz, 1C; arom.), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 134.2 (s, 2C; quat. C–CH_3), 133.3 (s, 2C; quat. C–CH_3), 132.7 (d, J(P,C) = 13.8 Hz, 2C; arom.), 130.8 (d, ^1J(P,C) = 32.0 Hz, 1C; quat. C *ipso* to P in arom.), 130.2 (d, ^1J(P,C) = 22.0 Hz, 1C; quat. C *ipso* to P in arom.), 128.7 (d, J-(P,C) = 10.4 Hz, 2C; arom.), 128.8 (qq, ^2J(F,C) = 30.8 Hz, ^3J(B,C) = 3.1 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 124.5 (q, ^1J(F,C) = 274.2 Hz, 8C; CF_3 in BAr_F), 117.35 (sept, ^3J(C,F) = 3.8 Hz, 4C; CH *para* to B in BAr_F), 93.5 (d, ^2J(P,C) = 12.4 Hz, 1C; cod CH), 91.0 (d, ^2J(P,C) = 13.2 Hz, 1C; cod CH), 70.25 (s, 1C; CH oxaz.), 68.2 (s, 1C; CH_2 oxaz.), 65.0 (s, 1C; CH next to oxaz.), 64.6 (d, ^2J(P,C) = 10.0 Hz, 1C; cod CH), 63.0 (s, 1C, CHN), 58.4 (d, ^2J(P,C) = 5.7 Hz; cod CH), 39.9 (d, ^3J(P,C) = 6.9 Hz; CH_2*C*HCH in bc), 37.9 (d, ^3J(P,C) = 2.6 Hz, 1C; CH*C*H_2CH in bc), 35.4 (d, ^3J(P,C) = 3.9 Hz, 1C; cod CH_2), 31.9 (s, 1C; CH *i*Pr), 31.8 (s, 1C; cod CH_2), 30.6 (s, 1C; CH_2*C*H_2CH in bc), 28.65 (s, 1C; cod CH_2), 26.65 (s, 1C, CH_2*C*H_2CH in bc), 26.4 (s, 1C; cod CH_2), 21.3 (s, 2C; CH_3 arom.), 21.2 (s, 2C; CH_3 arom.), 18.3 (s, 1C, CH_3 *i*Pr), 13.6 ppm (s, 1C; CH_3 *i*Pr); ^{31}P NMR ($CDCl_3$): δ = 51.4 ppm; IR (neat): $\tilde{\nu}$ = 2926.8, 2359.4, 2342.15, 1610.9, 1354.8, 1277.5, 1126.1, 887.3, 839.8, 761.8, 713.7, 682.5, 670.2 cm^{-1}; HRMS (FAB^+): calcd for $C_{36}H_{49}IrN_2OP$: 749.3212 $[M]^+$; found: 749.3218.

Ir complex 7d: Yield: 138 mg, 0.085 mmol, 61% (bright-orange foam); $[\alpha]_D^{22}$ = +43.5 (c = 1.0 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 8.76–8.62 (m, 1H; CH arom.), 7.71 (brs, 8H; *ortho* CH arom. BAr_F), 7.63–7.58 (m, 1H; CH arom.), 7.53 (brs, 4H; *para* CH arom. BAr_F), 7.42–7.37 (m, 1H; CH arom.), 7.18–7.15 (m, 1H; CH arom.), 7.07–7.00 (m, 2H; CH arom.), 6.88–6.72 (m, 2H; CH arom.), 4.77–4.68 (m, 1H; CH cod), 4.63–4.53 (m, 1H; CH cod), 4.46 (dd, J(H,H) = 9.8, 4.5 Hz, 1H; CH_2 oxaz.), 4.36 (d, J-(H,H) = 9.9 Hz, 1H; CH next to oxaz.), 4.28 (t, J(H,H) = 9.8 Hz, 1H; C*H* oxaz.), 4.00–3.86 (m, total 5H; 1H CH_2 oxaz., 1H CHN, 3H OCH_3), 3.65 (s, 3H; OCH_3), 3.04–2.92 (m, 1H; CH cod), 2.91–2.85 (m, 1H; CH_2*C*HCH in bc), 2.37–1.97 (m, total 7H; 4H CH_2 cod, 1H CH cod, 2H CH_2 cod), 1.81–1.14 (m, total 9H; 2H CH_2 cod, 6H CH_2 bc, 1H CH *i*Pr), 0.93–0.81 (m, 3H; CH_3 *i*Pr), 0.47–0.39 ppm (m, 3H; CH_3 *i*Pr); ^{13}C NMR ($CDCl_3$): δ = 175.2 (s, 1C; quat. C oxaz.), 161.6 (q, ^1J(B,C) = 50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 160.1 (s, 1C; C–OCH_3), 159.9 (s, 1C; C–OCH_3), 139.9 (m, 2C; arom.), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 132.9 (s, 2C; arom.), 128.8 (qq, ^2J(F,C) = 31.5 Hz, ^3J(B,C) = 2.8 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 124.4 (q, ^1J(F,C) = 274.2 Hz, 8C; CF_3 in BAr_F), 121.2–119.6 (m, 2C; quat. C *ipso* to P in arom.), 117.35 (sept, ^3J-(C,F) = 3.8 Hz, 4C; CH *para* to B in BAr_F), 112.0 (s, 2C, arom.), 110.5 (d, J(P,C) = 5.1 Hz, 2C; arom.), 89.9 (m, 1C; cod CH), 88.65 (m, cod CH), 70.0 (s, 1C; CH oxaz.), 67.5 (s, 1C; CH_2 oxaz.), 65.6 (s, 1C; CH next to oxaz.), 63.05 (s, 1C; cod CH), 62.6 (d, ^2J(P,C) = 10.6 Hz, 1C; CHN), 60.1 (m, 1C; cod CH), 55.6 (s, 1C; OCH_3), 54.6 (s, 1C; OCH_3), 39.1 (m, 1C; CH_2*C*HCH in bc), 38.2 (m, 1C; CH*C*H_2CH in bc), 35.1 (s, 1C; cod CH_2), 32.0 (s, 2C; cod CH_2 and CH *i*Pr), 29.6 (s, 1C; CH_2*C*H_2CH in bc), 29.5 (s, 1C; cod CH_2), 28.4 (s, 1C; cod CH_2), 26.5 (s, 1C; CH_2*C*H_2CH in bc), 18.2 (s, 1C; CH_3 *i*Pr), 13.6 ppm (s, 1C; CH_3 *i*Pr); ^{31}P NMR ($CDCl_3$): δ = 42.0 ppm; IR (neat): $\tilde{\nu}$ = 2961.2, 2359.8, 2342.0, 1466.6, 1354.8, 1277.1, 1126.4, 757.8, 682.4, 670.0 cm^{-1}; HRMS (FAB^+): calcd for $C_{34}H_{45}IrN_2O_3P$: 753.2797 $[M]^+$; found: 753.2784.

Ir complex 7e: Yield: 116 mg, 0.07 mmol, 30% (bright-orange foam); $[\alpha]_D^{22}$ = −15 (c = 1.0 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 7.90–7.84 (m, 2H; CH arom.), 7.71 (brs, 8H; *ortho* CH arom. BAr_F), 7.53 (brs, 4H; *para* CH arom. BAr_F), 7.22–7.16 (m, 2H; CH arom.), 7.07–7.03 (m, 2H; CH arom.), 6.96–6.93 (m, 2H; CH arom.), 4.89–4.85 (m, 1H; CH cod), 4.73–4.66 (m, 1H; CH cod), 4.50 (dd, J(H,H) = 9.8, 4.3 Hz, 1H; CH_2 oxaz.), 4.34–4.29 (m, 2H; C*H* oxaz. and CH next to oxaz.), 4.00–3.96 (m, 1H; CH_2 oxaz.), 3.87 (s, 3H; OCH_3), 3.84 (s, 3H; OCH_3), 3.71 (brs, 1H; CHN), 3.24–3.20 (m, 1H; CH cod), 3.01–2.99 (m, 1H; CH_2*C*HCH in bc), 2.38–2.22 (m, total 5H; 4H CH_2 cod, 1H CH cod), 2.15–1.98 (m, 2H; CH_2 cod), 1.87–1.22 (m, total 8H; 2H CH_2 cod, 5H CH_2 bc, 1H CH *i*Pr), 1.13–1.08 (m, 1H; CHCH_2CH in bc), 0.90 (d, J(H,H) = 6.7 Hz, 3H; CH_3 *i*Pr), 0.52 ppm (d, J(H,H) = 6.7 Hz, 3H; CH_3 *i*Pr); ^{13}C NMR ($CDCl_3$): δ = 173.3 (s, 1C; quat. C oxaz.), 162.8 (s, 1C; C–OCH_3), 162.0 (s, 1C; C–OCH_3), 161.6 (q, ^1J(B,C) = 50.0 Hz, 4C; quat. C *ipso* to B in BAr_F), 136.7 (d, J(P,C) = 15.0 Hz, 2C; arom.), 134.7 (s, 8C; CH *ortho* to B in BAr_F), 133.0 (d, J(P,C) = 11.7 Hz, 2C; arom.), 128.8 (qq, ^2J(F,C) = 31.5 Hz, ^3J-(B,C) = 2.8 Hz, 8C; quat. C *ipso* to CF_3 in BAr_F), 125.1 (q, ^1J(F,C) = 274.2 Hz, 8C; CF_3 in BAr_F), 122.0 (d, ^1J(P,C) = 63.2 Hz, 1C; quat. C *ipso* to P in arom.), 120.7 (d, ^1J(P,C) = 55.4 Hz, 1C; quat. C *ipso* to P in arom.), 117.3 (sept, ^3J(C,F) = 3.8 Hz, 4C; CH *para* to B in BAr_F), 114.4 (d, J(P,C) = 12.5 Hz, 2C; arom.), 114.1 (d, J(P,C) = 11.7 Hz, 2C; arom.), 93.7 (d, ^2J(P,C) = 12.1 Hz, 1C; cod CH), 91.35 (d, ^2J(P,C) = 12.8 Hz, 1C; cod CH), 70.2 (s, 1C; CH oxaz.), 68.2 (s, 1C; CH_2 oxaz.), 64.9 (s, 1C; CH next to oxaz.), 64.5 (d, ^2J(P,C) = 10.2 Hz, 1C; cod CH), 62.8 (s, 1C; CHN), 58.2 (d, ^2J(P,C) = 5.5 Hz; cod CH), 55.3 (s, 1C; OCH_3), 55.2 (s, 1C; OCH_3), 39.8 (d, ^3J(P,C) = 6.8 Hz; CH_2*C*HCH in bc), 37.8 (s, 1C; CH*C*H_2CH in bc), 35.3 (d, ^3J(P,C) = 4.3 Hz, 1C; cod CH_2), 31.93 (s, 1C; CH *i*Pr), 31.87 (s, 1C; cod CH_2), 30.7 (s, 1C; CH_2*C*H_2CH in bc), 28.45 (s, 1C; cod CH_2), 26.6 (s, 1C; CH_2*C*H_2CH in bc), 26.3 (s, 1C; cod CH_2), 18.3 (s, 1C; CH_3 *i*Pr), 13.8 ppm (s, 1C; CH_3 *i*Pr); ^{31}P NMR ($CDCl_3$): δ = 49.5 ppm; IR (neat): $\tilde{\nu}$ = 2967.35, 2359.7, 2341.9, 1597.0, 1500.5, 1354.9, 1277.6, 1126.0, 887.2, 839.0, 713.4, 682.35, 670.0 cm^{-1}; HRMS (FAB^+): calcd for $C_{34}H_{45}IrN_2O_3P$: 753.2797 $[M]^+$; found: 753.2799.

General procedure for the Ir-catalyzed asymmetric hydrogenation of imines (olefins): A vial was charged with imine (olefin, 0.5 mmol) and Ir complex (0.5 mol%). Dry CH_2Cl_2 (2 mL) was added and the vial was placed into a high-pressure hydrogenation apparatus. After purging the system with nitrogen, the pressure of hydrogen gas was adjusted to 20 bar (80 bar for complex **2**) for 12 h. After the pressure had been released, the solvent was removed in vacuo and the conversion was determined by ^{1}H NMR spectroscopy. The reaction time was determined from hydrogen gas consumption graphs. The crude product was dissolved in pentane/diethyl ether 1:1 (v/v) and filtered through a short plug of silica gel, followed by evaporation of the solvents. The *ee's* of the resulting compounds were determined by using the methods and conditions listed below.

Hydrogenation of imine 8: (*R*)-*N*-Phenyl-*N*-(1-phenylethyl)amine.[13a] The pure sample was obtained after purification by column chromatography with toluene as an eluent. The *ee* was determined by chiral HPLC analysis (Chiralcel OD-H, 0.5 mL min^{-1}, *n*-hexane/isopropanol 97:3, v/v). t_R = 17.3 min (*S*) minor, 21.5 min (*R*) major.

Hydrogenation of imine 9: (+)-*N*-Phenyl-*N*-(1-phenylpropyl)amine.[24] The *ee* was determined by chiral HPLC analysis (Chiralcel OD-H, 0.5 mL min^{-1}, *n*-hexane/isopropanol 97:3, v/v). t_R = 12.3 min (−) minor, 14.0 min (+) major.

Hydrogenation of imine 10: (+)-*N*-Phenyl-*N*-(1-indanyl)amine.[25] The *ee* was determined by chiral HPLC analysis (Chiralcel OD-H, 0.5 mL min^{-1}, *n*-hexane/isopropanol 97:3, v/v). t_R = 19.3 min (+) major, 23.3 min (−) minor.

Hydrogenation of imine 11: (+)-*N*-Phenyl-*N*-[1-(1,2,3,4-tetrahydronaphtyl)]amine.[26] The *ee* was determined by chiral HPLC analysis (Chiralcel OD-H, 0.5 mL min^{-1}, *n*-hexane/isopropanol 99:1, v/v); t_R = 24.4 min (+) major, 26.9 min (−) minor.

Hydrogenation of imine 12: (+)-*N*-Phenyl-*N*-[1-(2-naphtyl)ethyl]-amine.[24] The *ee* was determined by chiral HPLC analysis (Chiralcel OD-H, 0.5 mL min^{-1}, *n*-hexane/isopropanol 97:3, v/v). t_R = 27.5 min (−) minor, 32.5 min (+) major.

Hydrogenation of imine 13: (+)-*N*-Phenyl-*N*-(1-cyclohexylethyl)amine.[24] The *ee* was determined by chiral HPLC analysis (Chiralcel OJ, 0.5 mL min^{-1}, *n*-hexane/isopropanol 97:3, v/v). t_R = 16.5 min (+) major, 18.4 min (−) minor.

Hydrogenation of olefin 23: (*R*)-1,2-Diphenylpropane.[18a] The *ee* was determined by chiral HPLC analysis (Chiralcel OJ, 0.5 mL min^{-1}, *n*-hexane/isopropanol 99:1, v/v). t_R = 14.0 min (*R*) major, 19.8 min (*S*) minor.

Hydrogenation of olefin 24: 1-Metoxy-4-(1-(*R*)-methylpropyl)benzene.[18h] The *ee* was determined by chiral GCMS analysis (ChiralDexG-TA (60 °C, 30 min, 5 °C min^{-1}, 175 °C, 100 kPa)). t_R = 37.4 min (*S*) minor, 37.6 min (*R*) major.

Hydrogenation of olefin 25: 3-(*R*)-Phenylbutanoic acid ethyl ester.[18h] The *ee* was determined by chiral GCMS analysis (ChiralDexG-TA (60 °C, 30 min, 5 °C min^{-1}, 175 °C, 100 kPa)). t_R = 44.0 min (*R*) major, 44.1 min (*S*) minor.

Hydrogenation of olefin 26: 2-(*R*)-Methyl-3-phenylpropanoic acid ethyl ester.[27] The *ee* was determined by chiral chiral HPLC analysis (Chiralcel

OB-H, 0.5 mL min^{-1}, *n*-hexane/isopropanol 99.5:0.5, v/v). $t_R = 11.95$ min (*S*) minor, 14.2 min (*R*) major.

Hydrogenation of olefin 27: 7-Methoxy-4-(*S*)-methyl-1,2,3,4-tetrahydronaphtalene.[18h] The *ee* was determined by chiral GCMS analysis (ChiralDexG-TA (60 °C, 30 min, 3 °C min^{-1}, 175 °C, 100 kPa)). $t_R = 46.4$ min (*R*) minor, 46.9 min (*S*) major.

Hydrogenation of olefin 28: 1-(*S*)-methyl-1,2,3,4-tetrahydronaphtalene.[16d] The *ee* was determined by chiral GCMS analysis (ChiralDexG-TA (isotherm 120 °C, 100 kPa)). $t_R = 4.1$ min (*R*) minor, 4.2 min (*S*) major.

Hydrogenation of olefin 29: 2-(*R*)-methyl-1,2,3,4-tetrahydronaphtalene.[28] The *ee* was determined by chiral GCMS analysis (ChiralDexG-TA (60 °C, 30 min, 3 °C min^{-1}, 175 °C, 100 kPa)). $t_R = 34.05$ min (*S*) minor, 34.4 min (*R*) major.

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