Chiral Bis(*N*-sulfonylamino)phosphine- and TADDOL-Phosphite-Oxazoline Ligands: Synthesis and Application in Asymmetric Catalysis

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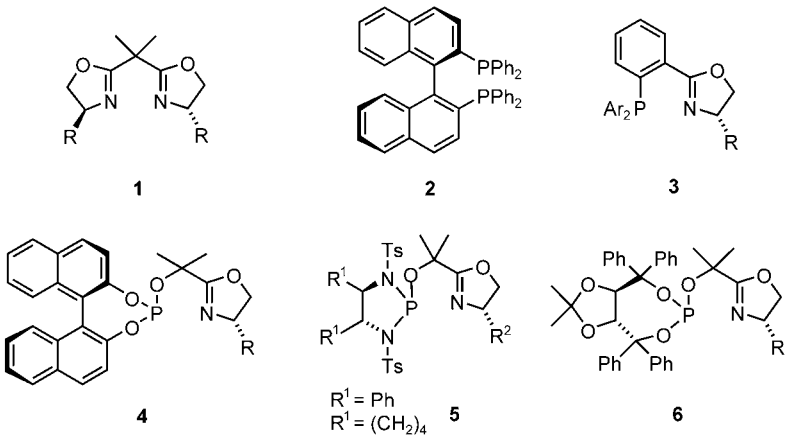
Abstract: A series of N,P-ligands has been prepared, containing a chiral oxazoline ring and as a second chiral unit a bis(*N*-sulfonylamino)phosphine group embedded in a diazaphospholidine ring or a cyclic phosphite group derived from TADDOL. These modular ligands are readily synthesized from chiral amino alcohols and chiral 1,2-diamines or TADDOLs. Palladium and iridium complexes derived from these ligands were found to be efficient catalysts for enantioselective allylic alkylation and olefin hydrogenation, respectively.

Keywords: asymmetric allylic substitution; asymmetric catalysis; asymmetric hydrogenation; N,P ligands; oxazolines

Introduction

For a long time, C_2-symmetrical bidentate ligands such as the bisoxazolines **1** or BINAP **2** have been dominating in asymmetric catalysis.[1] However, for a number of applications, sterically and electronically unsymmetrical ligands proved to be superior. In particular, the phosphinooxazolines **3** (PHOX ligands) were found to be excellent ligands for a wide range of metal-catalyzed reactions.[2] Variation of the PHOX structure led us to phosphite-oxazolines such as **4**, which contain a binaphthyl system as a second chiral unit. These ligands were successfully employed in Pd-catalyzed allylic substitutions[3] and Cu-catalyzed conjugate additions of organozinc reagents to enones.[4] Recently we reported the bis(*N*-sulfonylamino)phosphine- and TADDOL-phosphite-oxazolines **5** and **6** as a further extension of this structural motif (Scheme 1).[5]

These ligands are constructed in a modular fashion, allowing independent structural variation at different positions of the molecule. Ligands **5** can be modified at the substituents of the diazaphospholidine ring (**A**), the sulfonamide groups (**B**) and at the oxazoline ring (**C**) (Scheme 2). The TADDOL-derived ligand **6** can be structurally varied at the cyclic phosphite unit by replacing the phenyl groups with other substituents (**A**; R^1 =



Scheme 1.

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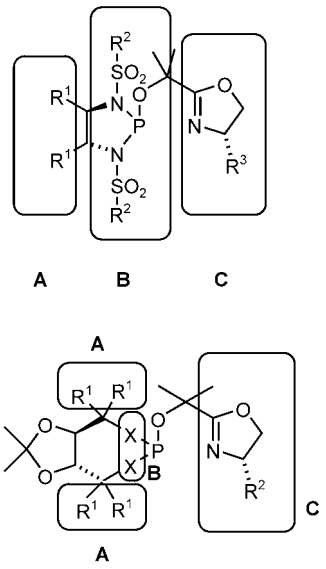
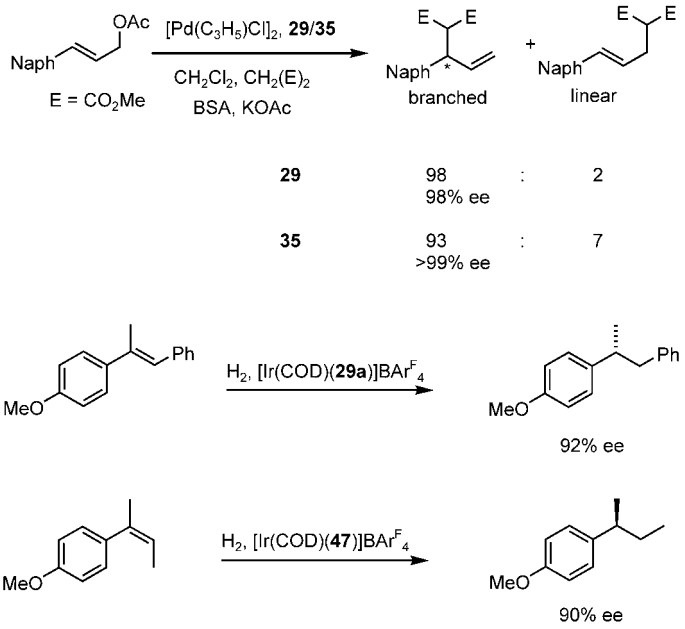


Scheme 2.



Scheme 3.

alkyl, aryl) or introducing heteroatoms other than oxygen (**B**; X=N or S), and at the oxazoline ring (**C**). In this way the steric and electronic properties of the ligands can be optimized for a specific application.

Both ligand classes revealed a considerable potential for asymmetric catalysis. Palladium complexes of ligands **29** and **35** (structures: see Schemes 9 and 13) catalyzed the allylic alkylation of (1′-naphthyl)prop-2-enyl acetate with very high regio- and enantioselectivity. Iridium complexes derived from ligands **29a** and **47** proved to be highly enantioselective catalysts for the hydrogenation of unfunctionalized olefins.

Based on these encouraging results we decided to optimize the ligand syntheses in order to prepare a selection of different derivatives for further studies. Here, we report the synthesis of various representatives of these two ligand classes, the preparation of palladium and iridium complexes and their use in palladium-catalyzed allylic alkylations and iridium-catalyzed hydrogenations.

Results and Discussion

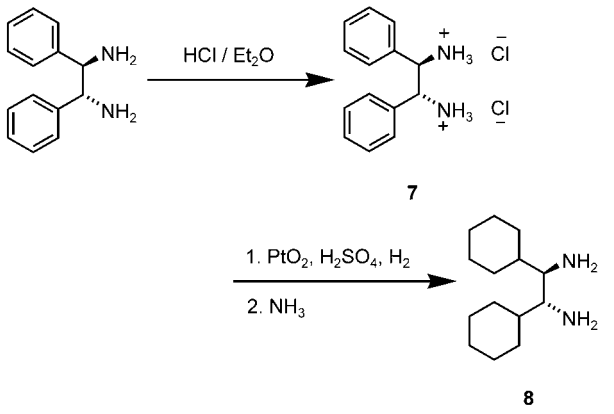
Synthesis of Bis(*N*-sulfonylamino)phosphine-Oxazolines 5

Although the substituents at the two stereogenic centers in the diazaphospholidine ring are too remote from the coordination sphere of the metal center to have a direct influence on a catalytic reaction, they determine the conformation of the ring and the geometry of the *N*-sulfonylamino groups. In this way, they can change the chiral environment of the coordination sphere and, therefore, affect the activity and selectivity of a metal catalyst.

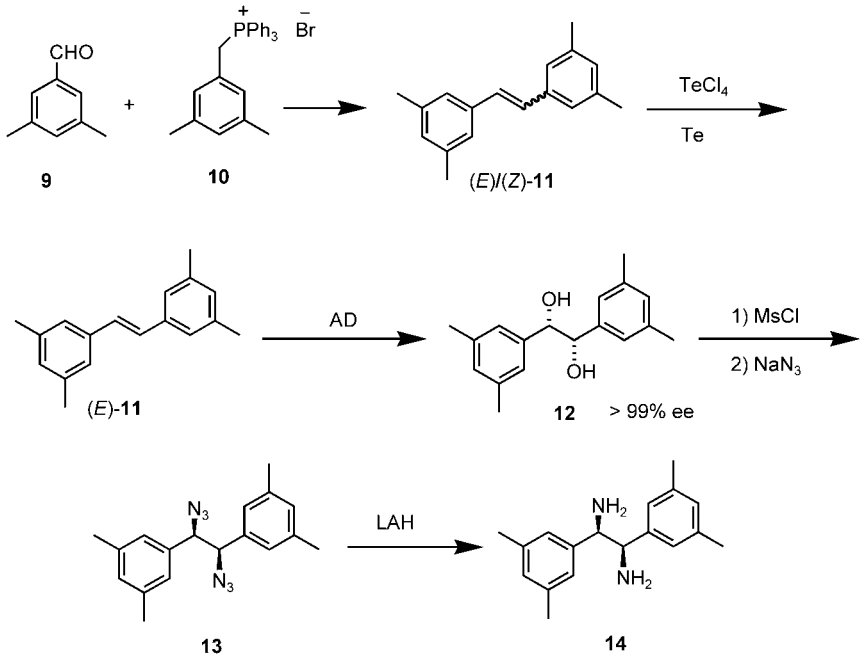
Initial studies with ligands derived from commercially available, enantiomerically pure 1,2-diphenylethylene-1,2-diamine and 1,2-diaminocyclohexane showed that the sterically more demanding 1,2-diphenylethylene backbone often resulted in higher enantioselectivity and reactivity in Ir-catalyzed hydrogenations. Therefore, we prepared a series of other chiral ethylene-1,2-diamines.

(*R*,*R*)-**8** and (*S*,*S*)-1,2-dicyclohexylethylenediamine (**8a**) were synthesized by hydrogenation of 1,2-diphenylethylenediamine hydrochloride (**7**) over platinum(IV) oxide (Scheme 4).

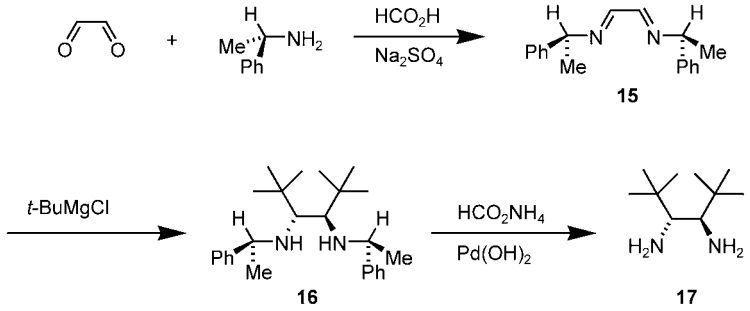
The synthesis of (*R*,*R*)-1,2-bis(3,5-dimethylphenyl)-ethylenediamine (**14**) starts with a Wittig reaction of al-



Scheme 4. Synthesis of (*R*,*R*)- and (*S*,*S*)-1,2-dicyclohexylethylenediamine.



Scheme 5. Synthesis of (*R*,*R*)-1,2-bis(3,5-dimethylphenyl)ethylenediamine.



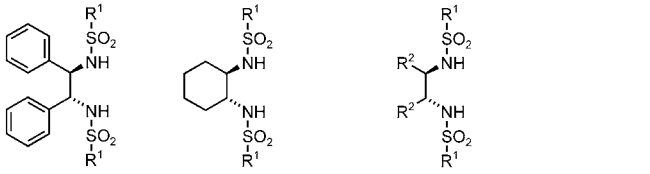
Scheme 6. Synthesis of (*R*,*R*)-1,2-diamino-1,2-di-*tert*-butylethane.

dehyde **9** and Wittig salt **10**, which were both prepared from 3,5-dimethylbenzyl alcohol (Scheme 5). The *E*/*Z*-mixture of **11** was converted to the (*E*)-isomer by treatment with tellurium/tellurium tetrachloride. Asymmetric Sharpless dihydroxylation gave **12** with an enantiomeric excess of > 99%. Diol **12** was mesylated and, because of its low stability, directly converted to the diazide **13**. The desired diamine **14** was then obtained by reduction of **13** with $LiAlH_4$. In contrast to other reports,[6] it was possible to isolate and characterize the diamine **14** without any difficulties.

Attempts to synthesize the 2,4,6-trimethylbenzyl derivative by the same route failed because the two *ortho*-methyl groups shield the double bond so strongly that in the dihydroxylation reaction, hydrolysis of the osmium glycolate is not possible.

Diimine **15** is an important intermediate in the synthesis of various 1,2-dialkyldiamines like (*R*,*R*)-1,2-diamino-1,2-di-*tert*-butylethane (**17**). It was synthesized according to the procedure of Alexakis starting from glyoxal and (*S*)-1-phenylethylamine (Scheme 6).[7] Similar attempts to synthesize **14** or its 2,4,6-trimethylbenzyl derivate by reaction of diimine **15** with the analogous Grignard reagents gave, independent of the reaction conditions, only mixtures of diastereomers as minor products.

Sulfonation of the chiral diamines was achieved under mild conditions. In the presence of *N*,*N*-diisopropylethylamine as base the chiral diamines were coupled at room temperature in good yields with a series of sulfonyl chlorides, such as tosyl chloride, naphthalene-1- and -2-sulfonyl chloride, trifluoromethane- and mesitylenesulfonyl chloride. The only exception was the tosylation of **17** which required harsher conditions with refluxing in pyridine for 24 h. The enantiomers of **18**, **23**, **26** and **28** were also prepared from the corresponding

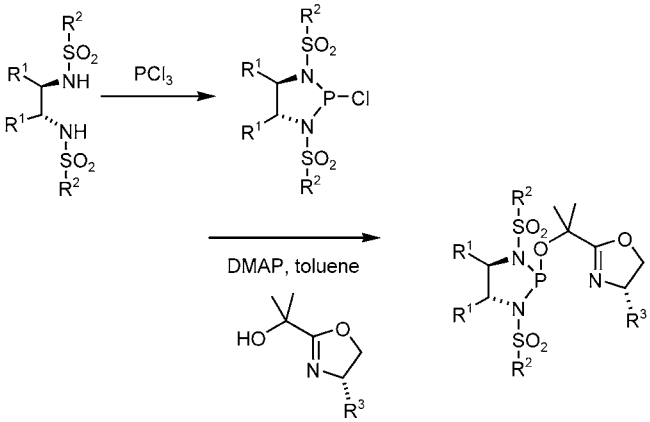


18 R^1 = 4-tolyl
19 R^1 = CF_3
20 R^1 = mesyl
21 R^1 = 1-naphthyl
22 R^1 = 2-naphthyl

23 R^1 = 4-tolyl
24 R^1 = 1-naphthyl
25 R^1 = 2-naphthyl

26 R^1 = 4-tolyl, R^2 = cy
27 R^1 = 4-tolyl, R^2 = 3,5-dimethylbenzyl
28 R^1 = 4-tolyl, R^2 = *t*-butyl

Scheme 7.

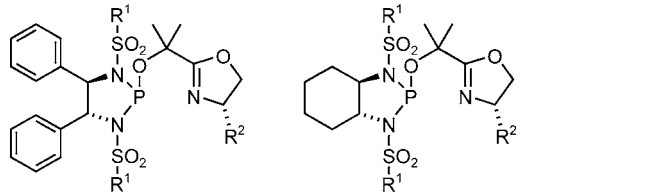


Scheme 8. Synthesis of bis(*N*-sulfonylamino)phosphine-oxazoline ligands.

(*S*,*S*)-diamines to explore possible match-mismatch effects of the two chiral units in the *N*,*P*-ligands.

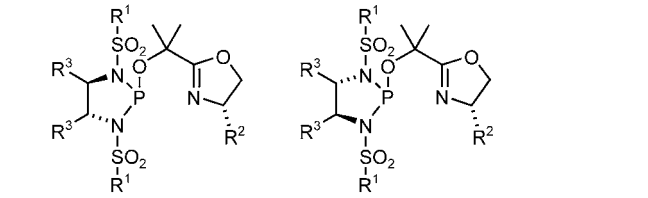
The chiral sulfonyldiamines **18**–**28** were treated with phosphorus trichloride in toluene at −78 °C to give the corresponding *P*-chlorodiazaphospholidines as pale yellow solids in good yields. The products are moisture- and air-sensitive compounds, but they could be clearly identified by mass spectroscopy. They were directly converted to the desired ligands **29**–**39** by reaction with the oxazoline alcohol, triethylamine and DMAP without isolation (Scheme 8). The use of DMAP proved to be advantageous, as it decreased the reaction time from 5 days to 12 hours and also reduced the number of by-products.

Because all attempts to purify the products by column chromatography failed, the crude products were usually purified by crystallization from chloroform/hexanes at 0 °C to give white to pale yellow solids. However, in some cases the by-products dropped out of solution as a yellow oil while the main product remained in solution. In these cases the solution was separated from the oil using a syringe and evaporated to give the pure ligands. Traces of DMAP, which remained as contaminants after crystallization, were removed by sublimation at 90 °C under high vacuum to give the ligands in yields between 50 to 80%. All attempts to convert **28** or its enantiomer



29 R^1 = 4-tolyl, R^2 = *t*-butyl
30 R^1 = 4-tolyl, R^2 = Ph
31 R^1 = CF_3, R^2 = *t*-butyl
32 R^1 = mesityl, R^2 = *t*-butyl
33 R^1 = 1-naphthyl, R^2 = *t*-butyl
34 R^1 = 2-naphthyl, R^2 = *t*-butyl

35 R^1 = 4-tolyl, R^2 = *t*-butyl
36 R^1 = 1-naphthyl, R^2 = *t*-butyl
37 R^1 = 2-naphthyl, R^2 = *t*-butyl



38 R^1 = 4-tolyl, R^2 = *t*-butyl, R^3 = cy
39 R^1 = 4-tolyl, R^2 = *t*-butyl, R^3 = 3,5-xyl

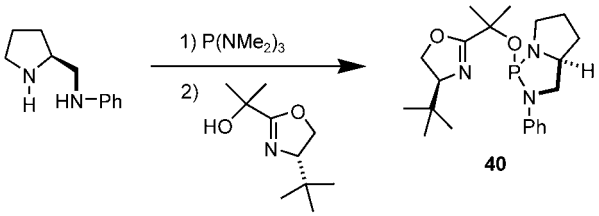
29a R^1 = 4-tolyl, R^2 = *t*-butyl, R^3 = Ph
35a R^1 = 4-tolyl, R^2 = *t*-butyl, R^3 = $(CH_2)_4$
38a R^1 = 4-tolyl, R^2 = *t*-butyl, R^3 = cy

Scheme 9. Bis(*N*-sulfonylamino)phosphine-oxazoline ligands.

(*ent*)-**28** to the corresponding ligands failed, despite extensive screening of various solvents at different temperatures. Steric hindrance could be a possible explanation, consistent with the low reactivity observed in the preparation of **28** and (*ent*)-**28** from the corresponding diamines.

As solids the ligands were found to be quite stable under air. Even in solution under air they showed only traces of oxidation products in the ^{31}P NMR spectra after 24 hours (P ~ 120 ppm, P=O ~ 20 ppm). The only exception was ligand **31** with two trifluoromethylsulfonyl groups, which was oxidized in solution within minutes. In general, the ligands could be stored under argon for months at 0 °C without decomposition.

We were also interested in analogous ligands derived from unsymmetrical diamines, because they contain a stereogenic phosphorus atom. For this purpose commercially available (*S*)-anilinomethylpyrrolidine was chosen, which has been previously used in the synthesis of ligands with stereogenic phosphorus atoms.[8] Thus (*S*)-2-(*N*-phenylaminomethyl)pyrrolidine was reacted with hexamethylphosphorous triamide and the resulting intermediate subsequently refluxed with the oxazoline alcohol for 7 days to afford ligand **40** in 39% overall yield (Scheme 10). In the beginning of the reaction both possible diastereomers could be observed by ^{31}P NMR. Over the course of several days the equilibrium was shifted towards the thermodynamically more stable diastereomer **40**, which was isolated in pure form by column chromatography.



Scheme 10. Synthesis of ligand **40** with a stereogenic phosphorus atom.

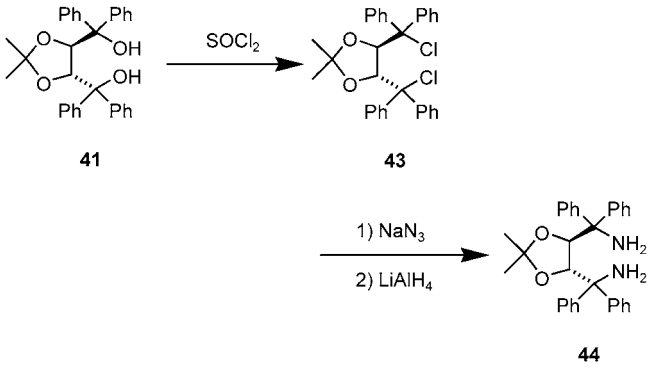
Synthesis of TADDOL-Phosphite-Oxazolines 6

α,α,α′,α′-Tetraaryl-1,2-dioxolane-4,5-dimethanol (TADDOL) derivatives have found numerous applications in stoichiometric and catalytic enantioselective reactions.[9] Because they are readily prepared and their structure can be easily varied, they are an attractive alternative to BINOL. In view of the various successful applications of BINOL-derived phosphite-oxazolines of type **4**, it seemed obvious that analogous TADDOL derivatives **6** could be a useful extension of this ligand family. Independent from our studies, Heldmann and Seebach recently prepared such ligands and reported that corresponding rhodium complexes are efficient catalysts for the enantioselective hydrosilylation of ketones.[9b]

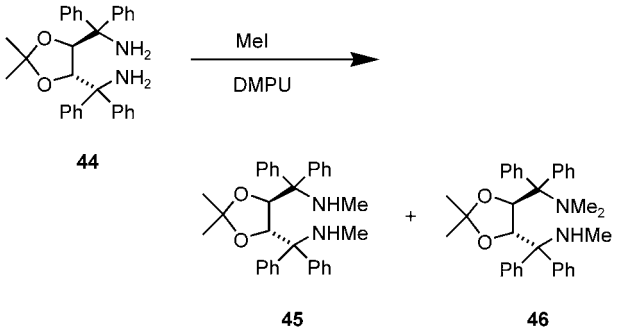
TADDOL **41** and the tetra(2-naphthyl) derivative **42** were prepared by the known procedure *via* the dioxolane-dicarboxylates and subsequent Grignard reaction.[10] By replacing the hydroxy groups with amino groups, which could bear further electron-withdrawing or -donating groups, the steric and electronic properties of the ligand could be additionally changed. (4*R*,5*R*)-2,2-Dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethylamine (TADDAMIN) **44** was prepared from (*R*,*R*)-TADDOL **41** according to the procedure of Seebach et al. (Scheme 11).[11]

All approaches to tosylate TADDAMIN **44** failed. Only monotosylated TADDAMIN was detected as minor product in about 20% yield. Introduction of other electron-withdrawing groups by reacting TADDAMIN with trifluoroacetic anhydride was successful but the resulting product could not be converted to the corresponding N,P-ligand. TADDAMIN **44** reacted with methyl iodide in DMPU to afford the dimethylated TADDAMIN **45** in 38% yield after separation of the trimethylated side product **46** by column chromatography (Scheme 12).[11]

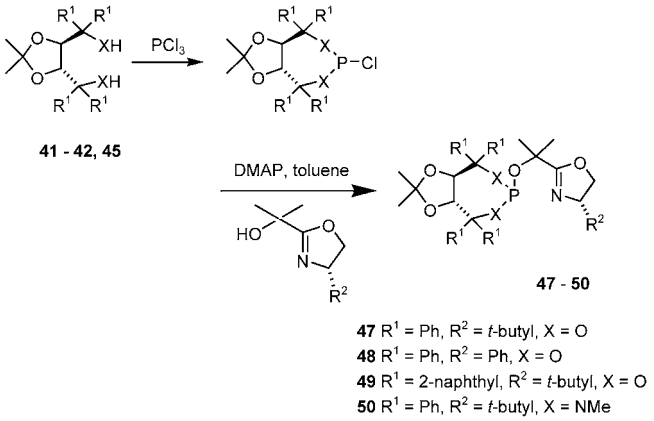
All attempts to prepare sulfur analogues of TADDOL gave unsatisfactory results. Reaction of dichloride **43** with thiourea afforded the desired dithiol but also 50% of the disulfide. Separation of the two compounds was not possible whereas the reduction of the disulfide led to a mixture of products. Direct conversion of the diol **41** to the dithiol with Lawesson's reagent gave only the monothiol in very low yield.



Scheme 11. Synthesis of TADDAMIN.



Scheme 12. Synthesis of methylated TADDAMIN.



Scheme 13. TADDOL-phosphite-oxazoline ligands.

The TADDOL-phosphite-oxazoline ligands were prepared in the same manner as the bis(*N*-sulfonylamino)phosphine-oxazoline ligands. Reaction of the TADDOL derivatives **41**, **42** and **45** with phosphorus trichloride at −78 °C in toluene and subsequent reaction with oxazoline alcohol, triethylamine and DMAP gave ligands **47**–**50** in 50–80% yield (Scheme 13). The TADDOL-phosphite ligands were purified by column chromatography or recrystallization. Ligand **47a** derived from (*S*,*S*)-TADDOL was prepared in order to study *match*/*mismatch* effects of the two chiral units.

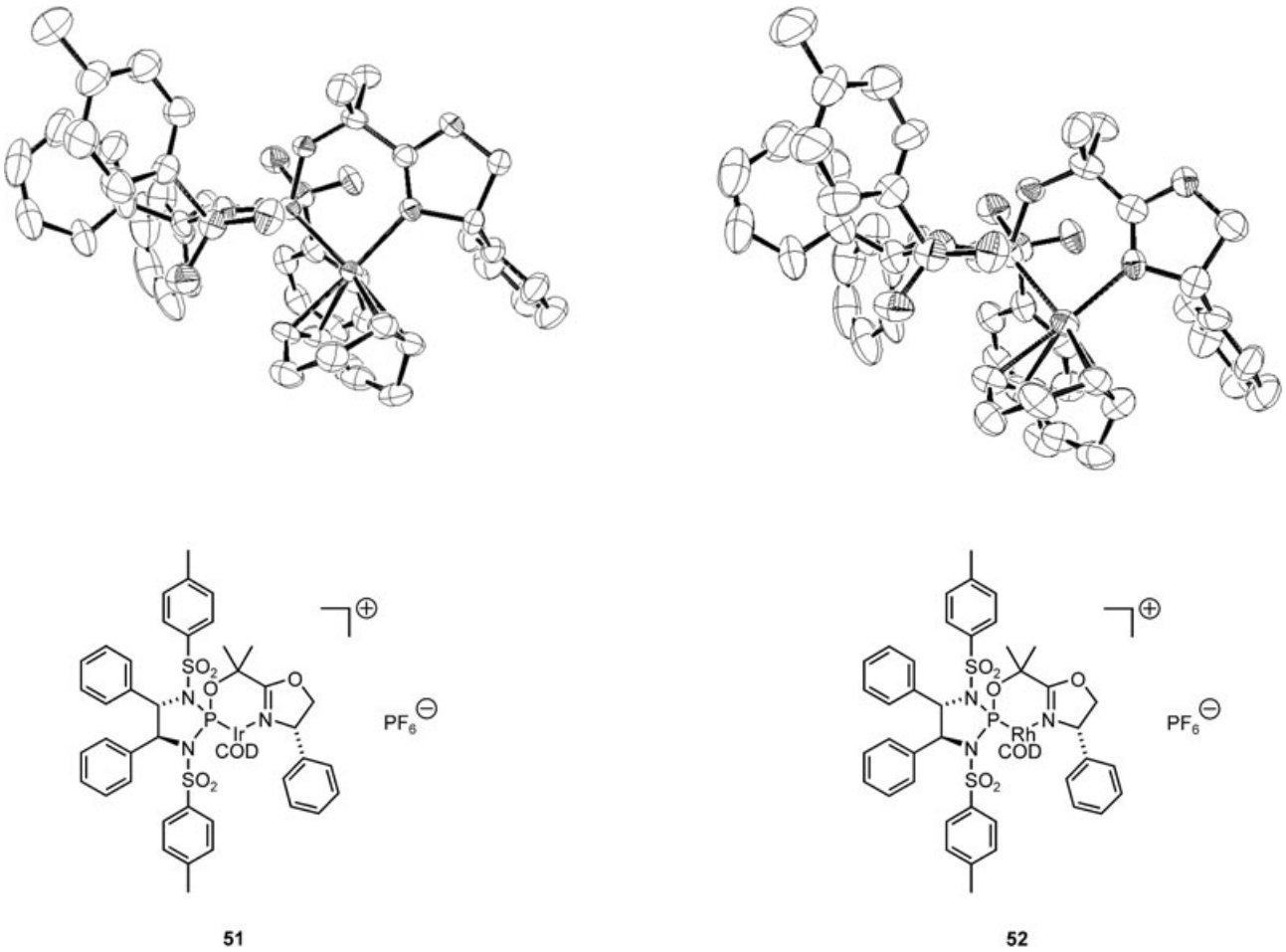


Figure 1. X-ray structures of Ir- and Rh-complexes of ligand **30a**.

X-Ray Structures

Structural information about the bis(*N*-sulfonylamino)-phosphine-oxazoline ligands geometry could be obtained from crystal structures of an Ir and an Rh complex derived from ligand **30a**.[12] Addition of the ligand to a solution of $[M(COD)Cl]_2$ (X = Ir, Rh) followed by anion exchange from Cl^- to PF_6^- afforded the complexes **51** and **52** in good yields. Slow recrystallization from ethyl acetate/cyclohexane at $-18\,^{\circ}C$ yielded orange needles suitable for X-ray analyses.

The two complexes adopt a similar geometry with the diazaphospholidine ring in a nearly planar conformation. The tosyl and phenyl groups of the diazaphospholidine ring shield the coordination sphere next to the phosphorus atom, similar to the *P*-phenyl groups of the PHOX ligand **3** or the BINOL moiety of ligand **4**. One of the sulfonyl oxygen atoms and one tolyl group are located relatively close to the coordination sphere and, therefore, are expected to interact more strongly with a metal-bound reactant than the BINOL group in ligands **4**. This could explain the higher selectivity often observed for ligands **5** compared to **4**.

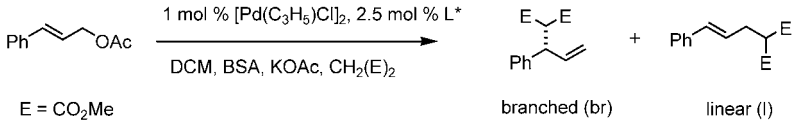
Applications in Asymmetric Catalysis

With this diverse set of bis(*N*-sulfonylamino)phosphine-oxazoline and TADDOL-derived ligands in hand, we evaluated their scope in the Pd-catalyzed allylic alkylation and Ir-catalyzed hydrogenation of olefins.

Pd-Catalyzed Allylic Alkylation

Allylic alkylation is one of the most efficient methods for C–C bond formation. Mild reaction conditions and high tolerance of functional groups are advantages which make this reaction a powerful tool for organic synthesis. PHOX ligands **3** were found to be excellent ligands for this reaction.[2,13] The best results were obtained with symmetrically substituted allyl systems whereas for 1- and 3-monosubstituted substrates only moderate enantioselectivities and low branched/linear ratios could be achieved. This led to the design of chiral phosphite-oxazoline ligands of type **4**, which gave improved regio- and enantioselectivities for 1- and 3-monoarylallyl acetates.[3] Because the new ligands of type **5**

Table 1. Enantioselective Pd-catalyzed allylic alkylation of (*E*)-3-phenyl-2-propen-1-yl acetate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]	br/l
1	**29**	100	94 (*S*)	84:16
2	**29a**	100	93 (*S*)	53:47
3	**30**	100	89 (*S*)	38:62
4	**32**	100	94 (*S*)	33:67
5	**33**	100	94 (*S*)	67:33
6	**34**	100	94 (*S*)	84:16
7	**35**	100	95 (*S*)	60:40
8	**35a**	100	88 (*S*)	30:70
9	**36**	100	90 (*S*)	65:35
10	**37**	100	96 (*S*)	62:38
11	**38**	100	91 (*S*)	82:18
12	**39**	100	96 (*S*)	77:23
13	**47**	100	87 (*S*)	26:74
14	**47a**	100	70 (*S*)	18:82
15	**50**	100	97 (*S*)	21:79

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

and **6** have similar steric and electronic properties as BINOL-derived ligands **4**, we decided to examine their potential for enantio- and regiocontrol in allylic alkylation.

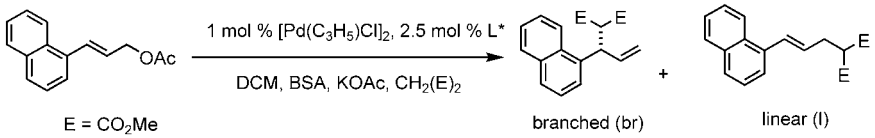
Using (*E*)-3-phenyl-2-propen-1-yl acetate as substrate (Table 1), the new bis(*N*-sulfonylamino)phosphine-oxazoline ligands **29–39** gave similar or better results in terms of enantio- and regioselectivity in comparison to PHOX ligands **3** and phosphite-oxazolines **4**. In general, ligands derived from (*R*,*R*)-diamines and (*S*)-oxazolines were superior to the corresponding diastereomers derived from (*S*,*S*)-diamines for all substrates reported (Entries 1, 2, 7, 8). Ligand **29** proved to be the most effective for regio- and enantiocontrol. Variations of the substituent in the oxazoline ring or of the tosyl group resulted in lower regio- and enantioselectivities (Entries 3–6). Ligands **35** and **37**, containing cyclohexanediamine as the chiral backbone afforded even better enantioselectivities than ligand **29** but lower regioselectivities (Entries 7 and 10). Additional methyl substituents at the chiral diphenyldiamine backbone had the same effect (Entry 12). The TADDOL-derived ligand **50** showed the highest ee value of 97%, but as observed for all other TADDOL-derived ligands, the regioselectivity was significantly lower (Entry 15). In all cases, (*R*,*R*)-TADDOL-derived ligands with (*S*)-oxazoline units showed better results than the corresponding (*S*,*S*) diastereoisomers (Entries 13 and 14).

With (*E*)-3-(1′-naphthyl)-2-propen-1-yl acetate as substrate, ligand **29** again gave significantly higher enantio- and regioselectivity than PHOX ligands **3** or BINOL-derived ligands **4** (Table 2, Entry 1). Replacement of the tosyl groups with (2′-naphthyl)sulfonyl groups in ligand **34** resulted in an exceptionally high regioselectivity (>99.5:0.5) with similar enantiocontrol (Entry 4). Ligand **35** with a chiral cyclohexanediamine backbone afforded a very high ee of 99.4% which is the best value reported so far for a Pd catalyst but with a slightly lower regioselectivity (Entry 5). TADDOL-derived ligands such as **47** gave moderate to good enantiomeric excesses but low regioselectivities (Entry 9).

As expected, the enantio- and regioselectivites with 2-alkenyl acetates, (*E*)-2-buten-1-yl acetate and (*E*)-2-hexen-1-yl acetate, were lower. However, both new ligand classes gave better results than PHOX ligands **3** and BINOL-derived ligands **4** (Tables 3 and 4). Ligand **29** again proved to be most effective for enantio- and regiocontrol (Entry 1, Tables 3 and 4). TADDOL-derived ligand **50** afforded a high ee of 62% for (*E*)-2-hexen-1-yl acetate but with low regioselectivity (Entry 6, Table 4). Recently, a further variant of N,P-ligands, containing a ferrocene backbone, was reported that resulted in high regio- and enantioselectivity for the 1,3-dimethylallyl acetate (97:3, 94% ee).[14]

All synthesized ligands were also tested in the Pd-catalyzed allylic alkylation of three symmetrically substituted allyl substrates. With (*E*)-1,3-diphenyl-2-propenyl acetate as substrate, only moderate enantioselectivities could be achieved (Table 5). Interestingly, substitution

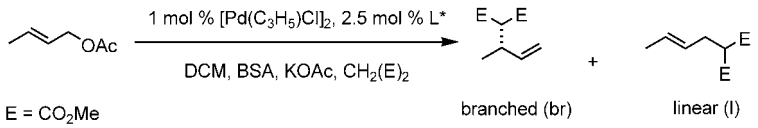
Table 2. Enantioselective Pd-catalyzed allylic alkylation of (*E*)-3-(1′-naphthyl)-2-propen-1-yl acetate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]	br/l
1	**29**	100	98 (*S*)	98:2
2	**30**	100	85 (*S*)	93:7
3	**33**	100	93 (*S*)	93:7
4	**34**	100	97 (*S*)	>99.5:0.5
5	**35**	100	99.4 (*S*)	93:7
6	**37**	100	98 (*S*)	93:7
7	**38**	100	89 (*S*)	99.5:0.5
8	**39**	100	97 (*S*)	93:7
9	**47**	100	94 (*S*)	66:34

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

Table 3. Enantioselective Pd-catalyzed allylic alkylation of (*E*)-2-buten-1-yl acetate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]	br/l
1	**29**	100	60 (*S*)	55:45
2	**30**	100	4 (*S*)	64:36
3	**34**	100	41 (*S*)	45:55
4	**35**	100	50 (*S*)	26:74
5	**36**	100	40 (*S*)	23:77
6	**38**	100	48 (*S*)	56:44
7	**39**	100	48 (*S*)	44:56
8	**40**	100	41 (*R*)	33:67
9	**50**	100	39 (*S*)	33:67

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

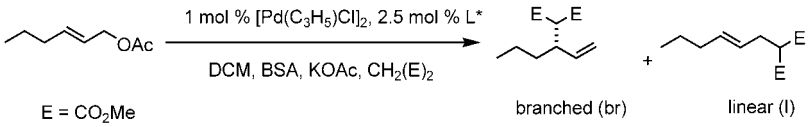
of the *tert*-butyl group of the oxazoline ring with a phenyl group in ligand **30** improved the ee from 60% to 88% (Entries 1 and 2) whereas the same exchange resulted in lower enantioselectivity for the unsymmetrical substrate (*E*)-3-phenyl-2-propen-1-yl acetate (Entries 1 and 2, Table 1). Ligand **40** containing a stereogenic phosphorus atom afforded an ee of 84% (Entry 6).

Using (*E*)-4-hepten-3-yl acetate as substrate, bis(*N*-sulfonylamino)phosphine-oxazoline ligands **29** and **35** gave unsatisfactory enantioselectivities (Entries 1–2, Table 6). However, the ee induced by the TADDOL-derived ligand **47** was in the same range as with PHOX and BINOL-derived ligands (**47**: 61%; **3**: 79%; **4**: 50%) (Entry 3)

With 2-cyclohexen-1-yl acetate, ligand **38** with cyclohexanediamine as chiral backbone afforded a respectable enantiomeric excess of 85% (Entry 5, Table 7). Ligand **40** containing a stereogenic phosphorus atom gave a somewhat lower ee of 75% (Entry 6). In general, most new ligands proved to be superior to analogous phosphite or PHOX ligands for this substrate.

In summary, both new ligand classes, bis(*N*-sulfonylamino)phosphine-oxazoline and TADDOL-derived ligands, induced high enantioselectivities and regiocon-

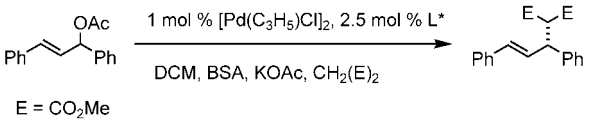
Table 4. Enantioselective Pd-catalyzed allylic alkylation of (*E*)-2-hexen-1-yl acetate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]	br/l
1	**29**	100	51	21:79
2	**34**	100	54	17:83
3	**35**	100	26	9:91
4	**38**	100	44	33:67
5	**39**	100	52	16:84
6	**50**	79	62	8:92

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

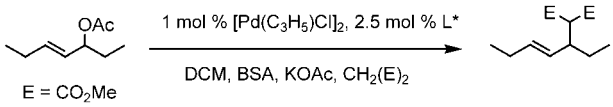
Table 5. Enantioselective Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenyl-2-propen-1-yl acetate.[a]



Entry	Ligand	Conversion [%]	ee [%][c]
1	**29**	100	60 (*S*)
2	**30**	100	88 (*S*)
3	**35**	100	52 (*S*)
4	**37**	100	60 (*S*)
5	**38**	100	65 (*S*)
6	**40**	100	84 (*S*)
7	**48**	100	56 (*S*)

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

Table 6. Enantioselective Pd-catalyzed allylic alkylation of (*E*)-4-hepten-3-yl acetate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29**	53	20
2	**35**	100	9
3	**47**	100	61

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

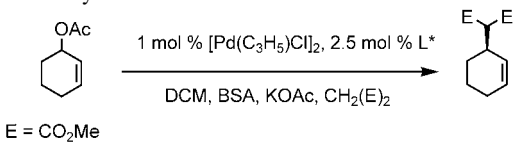
trol in the Pd-catalyzed allylic alkylation, in most cases surpassing the selectivities obtained with phosphine- or phosphite-oxazolines. In particular, bis(*N*-sulfonylamino)phosphine-oxazoline ligands proved to be very efficient in the allylic alkylation of 3-arylallyl acetates. Recent studies showed that these ligands are also suitable for kinetic resolution of racemic 1,3-disubstituted allyl esters.[15]

Ir-Catalyzed Hydrogenation of Olefins

Iridium phosphinooxazoline complexes have emerged as a promising new class of catalysts for the enantioselective hydrogenation of imines and olefins. Remarkably high enantioselectivities were obtained in the hydrogenation of trisubstituted 1-alkyl-1,2-diarylalkenes, a substrate class of unfunctionalized alkenes for which very few catalytic systems have been reported before. In order to extend the application range of these catalysts to other substrate classes, we started a systematic investigation of Ir complexes containing other N,P-ligands, including the new ligand classes **5** and **6**.

Iridium(COD) complexes with bis(*N*-sulfonylamino)phosphine-oxazoline and TADDOL-derived ligands were readily prepared according to our standard protocol by refluxing a solution of $[Ir(COD)Cl]_2$ and the corresponding N,P-ligand in dichloromethane.[16] For the exchange of the chloride ion with BAr_F {tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, the complexes were treated with $NaBAr_F$ in a two-phase dichloromethane-water system. The resulting orange/red BAr_F salts were purified by column chromatography

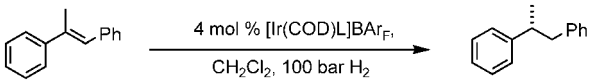
Table 7. Enantioselective Pd-catalyzed allylic alkylation of 2-cyclohexen-1-yl acetate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29**	100	71 (*R*)
2	**33**	74	65 (*R*)
3	**34**	100	71 (*R*)
4	**35**	100	1 (*R*)
5	**38**	100	85 (*R*)
6	**40**	100	75 (*R*)
7	**47**	100	46 (*S*)

[a] All reactions were carried out with 1 mol % of $[Pd(C_3H_5)Cl]_2$ and 2.5 mol % of ligand in CH_2Cl_2 at room temperature for 20 h.
[b] Determined by GC. The yields of the pure products were 85–95% (100% conversion).
[c] Determined by GC or HPLC using chiral columns.

Table 8. Enantioselective Ir-catalyzed hydrogenation of (*E*)-1,2-diphenylpropene.[a]



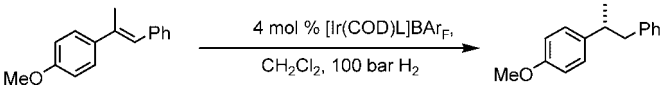
Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29**	16	86 (*R*)
2	**29a**	49	87 (*R*)
3	**35**	15	94 (*R*)
4	**35a**	11	72 (*R*)
5	**37**	73	91 (*R*)
6	**38**	71	68 (*R*)
7	**38a**	59	92 (*R*)
8	**47**	100	75 (*R*)
9	**47a**	100	48 (*R*)
10	**50**	69	84 (*R*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

on silica gel. All complexes were stable against oxygen and moisture. Hydrogenations were carried out in dichloromethane at room temperature for 2 h at 100 bar hydrogen pressure using 4 mol % catalyst. Lower catalyst loading or hydrogen pressure resulted in reduced conversions and enantioselectivities.

Using (*E*)-1,2-diphenylpropene as substrate, both new ligand classes induce moderate to high enantioselectivities but mostly with low conversions. Longer reaction times did not result in higher conversions suggesting that the catalyst is deactivated during the reaction. In

Table 9. Enantioselective Ir-catalyzed hydrogenation of (*E*)-2-(4-methoxyphenyl)-phenylpropene.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29a**	57	92 (*R*)
2	**36**	26	74 (*R*)
3	**38a**	60	92 (*R*)
4	**48**	100	85 (*R*)
5	**49**	100	85 (*R*)
6	**50**	78	84 (*R*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

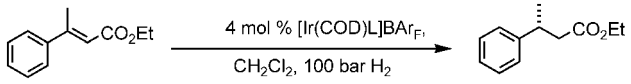
general, this particular trisubstituted alkene is an unproblematic substrate, reacting with high enantioselectivity with many different Ir catalysts.[17] Interestingly, ligands **29a** and **38a** containing 1,2-diphenyl- and 1,2-dicyclohexyldiamine backbones were more efficient for this substrate than the corresponding diastereomers **29** and **38**, in contrast to allylic alkylation where ligands **29** and **38** gave better results (Table 8, Entries 1 and 2, 6 and7). However, replacement of ligand **35** containing a cyclohexanediamine backbone and TADDOL-derived ligand **47** by the corresponding diastereomers **35a** and **47a** resulted in lower ees and conversions (Entries 3 and 4, 8 and 9). Substitution of the *p*-tolyl substituents of ligand **35** with sterically more demanding 2-naphthyl groups (ligand **37**) resulted in higher conversion with similar enantioselectivity (Entries 3 and 5). The TADDAMIN-derived ligand **50** afforded a higher ee than the TADDOL-derived ligand **47** (Entries 8 and 10).

As shown in Table 9, the *p*-methoxy derivative gave very similar results as the unsubstituted methylstilbene. Both ligands systems show comparable or lower enantioselectivities than PHOX ligands although with lower conversions.

Ethyl β-methylcinnamate could be reduced to the corresponding saturated ester with up to 92% ee, while Ir-PHOX complexes gave lower enantioselectivities of up to 82% ee (Table 10). The TADDOL-derived ligands, in general, gave higher conversions than bis(*N*-sulfonylamino)phosphine-oxazoline ligands (Entries 6–8). The highest ee was achieved using ligand **40** containing a stereogenic phosphorus atom (Entry 5). Substitution of the tolyl substituents of ligand **35** with 1-naphthyl substituents resulted again in higher conversions, but this time with a significant decrease in enantiocontrol (Entries 2 and 3).

(*E*)- and (*Z*)-2-aryl-2-butenes are more difficult to hydrogenate with high enantioselectivity than (*E*)-1-alkyl-1,2-diarylalkenes. With (*E*)-2-aryl-2-butene as substrate,

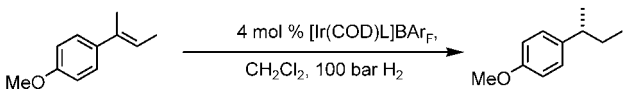
Table 10. Enantioselective Ir-catalyzed hydrogenation of ethyl β-methylcinnamate.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29a**	43	86 (*R*)
2	**35**	32	91 (*R*)
3	**36**	100	65 (*R*)
4	**37**	46	81 (*R*)
5	**40**	80	92 (*R*)
6	**47**	100	75 (*R*)
7	**48**	100	76 (*R*)
8	**49**	100	87 (*R*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

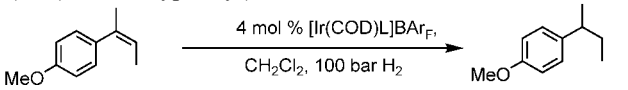
Table 11. Enantioselective Ir-catalyzed hydrogenation of (*E*)-2-(4-methoxyphenyl)-2-butene.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29a**	100	85 (*R*)
2	**35**	65	84 (*R*)
3	**37**	100	71 (*R*)
4	**38a**	100	90 (*R*)
5	**40**	100	91 (*R*)
6	**48**	100	84 (*R*)
7	**49**	100	81 (*R*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

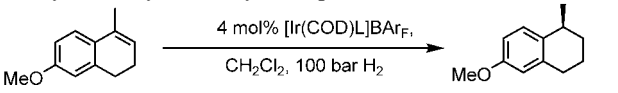
Table 12. Enantioselective Ir-catalyzed hydrogenation of (*Z*)-2-(4-methoxyphenyl)-2-butene.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29a**	100	35 (*R*)
2	**35**	55	42 (*R*)
3	**36**	100	44 (*S*)
4	**38a**	100	44 (*R*)
5	**47**	100	90 (*S*)
6	**49**	100	95 (*S*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

Table 13. Enantioselective Ir-catalyzed hydrogenation of 6-methoxy-1-methyl-3,4-dihydronaphthalene.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29a**	100	55 (*S*)
2	**37**	100	25 (*S*)
3	**38a**	100	86 (*S*)
4	**47**	100	35 (*S*)
5	**48**	70	61 (*S*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

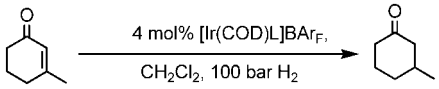
the best results were achieved with bis(*N*-sulfonylamino)phosphine-oxazoline ligands **38a** and **40** with up to 91% ee (Table 11, Entries 4 and 5). TADDOL-derived ligands **48** and **49** gave similar enantioselectivities as PHOX ligands (Entries 6 and 7).

For the corresponding (*Z*)-alkene remarkably high enantioselectivities of up to 95% ee could be obtained using TADDOL-derived ligands **47** and **49** (Table 12, Entries 5 and 6). Replacement of the phenyl groups in the TADDOL backbone with sterically more demanding 2-naphthyl groups increased the enantiomeric excess from 90% to 95%. Ir complexes of bis(*N*-sulfonylamino)phosphine-oxazoline ligands gave only moderate to low enantioselectivities (Entries 1–4). Using PHOX ligands, the (*E*)- and (*Z*)-isomers afford products of opposite absolute configuration. Interestingly, ligands **29a**, **35** and **38a** afforded products of the same configuration (*R*) with both isomers, whereas the other ligands behaved in the same way as PHOX ligands. The reason for this difference remains unclear at this point. A possible explanation could be that partial *cis-trans* isomerization takes place during hydrogenation. Thus, in those reactions (Table 12, Entries 1, 2 and 4) which afford the unexpected (*R*)-enantiomer, the major pathway proceeds *via* hydrogenation of the more stable (*E*)-isomer.

Hydrogenation of 6-methoxy-1-methyl-3,4-dihydronaphthalene with an endocyclic double bond gave only moderate enantioselectivities using PHOX ligands. Ligand **38a** afforded a clearly improved enantiocontrol of 86% ee, whereas all other tested ligands gave lower enantioselectivities (Table 13).

With 3-methyl-2-cyclohexenone as substrate, PHOX ligands gave very low conversions and enantioselectivities (15% conversion, 3% ee). Ligands **36** and **47** afford-

Table 14. Enantioselective Ir-catalyzed hydrogenation of 3-methyl-2-cyclohexenone.[a]



Entry	Ligand	Conversion [%][b]	ee [%][c]
1	**29a**	6	3 (*S*)
2	**36**	100	41 (*R*)
3	**38a**	12	4 (*S*)
4	**47**	97	58 (*R*)
5	**49**	8	54 (*R*)

[a] All reactions were carried out with 4 mol % of catalyst in CH_2Cl_2 at 100 bar at room temperature for 2 h.
[b] Determined by GC.
[c] Determined by GC or HPLC using chiral columns.

ed respectable ee values for this demanding substrate with essentially full conversion (Entries 2 and 4). Comparison of the results for ligands **47** and **49** in which phenyl groups were replaced by 2-naphthyl groups clearly shows the sensitivity of this substrate to small changes in the ligand structure: the conversion decreased from 97% to 8% with similar enantioselectivity (Entries 4 and 5).

In conclusion, iridium complexes derived from Bis(*N*-sulfonylamino)phosphine- and TADDOL-phosphite-oxazolines proved to be efficient catalysts for enantioselective hydrogenation. Several types of olefins, for which Ir-PHOX complexes gave unsatisfactory ee values, could be hydrogenated with good enantioselectivity. However, catalyst activity was lower than with Ir-PHOX complexes, requiring higher catalyst loadings (4 mol %) to achieve full conversion. More recently, we found that replacement of the *N*-sulfonyl groups in ligands **5** by *N*-aryl or *N*-alkyl substituents resulted in higher catalyst activity and often higher enantioselectivity.[17]

Conclusion

With the bis(*N*-sulfonylamino)phosphine- and TADDOL-phosphite-oxazolines we have added two useful ligand classes to the family of chiral oxazoline-based N,P-ligands. The two chiral units in these ligands are derived from readily available chiral precursors. Our results show that ligands of this type can induce high enantioselectivities both in Pd- and Ir-catalyzed reactions. The modular construction and facile synthesis of these ligands should make it possible to optimize their structure for many other metal-catalyzed processes.

Experimental Section

General Remarks

NMR spectra were recorded on a Bruker Advance DRX 500 (^{1}H: 500 MHz, ^{13}C: 125.8 MHz), Bruker AMX 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz), Varian Gemini 300 (^{1}H: 300 MHz, ^{13}C: 85 MHz, ^{31}P: 122 MHz) or on a Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz, ^{31}P: 81 MHz). All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ value in $CDCl_3$). MS was measured on Finnegan MAT 312 (FAB), VG 70-SE (70 eV) (EI) in *m/z* (% of basic peak). IR spectra were obtained with a Perkin Elmer 1600 FTIR-spectrometer. Optical rotation was measured with a Perkin Elmer 341 polarimeter. Melting points were obtained on a Büchi 535 apparatus, values are uncorrected. HPLC was measured on a Shimadzu SCL-10A. Elemental analyses were performed by the Microanalytical Laboratory of the Institut für Organische Chemie, Universität Basel. Column chromatography was conducted on silica gel 60, 0.040–0.063 nm, 230–400 mesh, available from Uetikon Chemie. TLC was performed with Macherey-Nagel Polygram SIL G/UV_{254} plates, detection by UV or common detecting agents [alkaline $KMnO_4$ solution, $Ce(SO_4)_2$/phosphomolybdic acid solution] followed by heating. Solvents were dried and distilled shortly before use. All reagents were purchased from Fluka, Aldrich and Strem and used without further purification. All reactions were carried out under an atmosphere of argon.

For analytical data of compounds **19–27**, ligands **30–39**, **47–50** and iridium complexes **29a–40**, **47–50** see Supporting Information.

(*R*,*R*)-1,2-Dicyclohexylethane-1,2-diamine (8)

(*R*,*R*)-1,2-Diphenylethylenediamine (1.0 g, 4.71 mmol) was dissolved in a mixture of CH_2Cl_2 and Et_2O (60 mL, 1:1). A solution of HCl in ether (4.71 mL, 9.42 mmol, 2 N in Et_2O) was added and the reaction mixture was stirred overnight at room temperature. The precipitate was filtered off and dissolved in 25% sulfuric acid (60 mL) and hydrogenated at 1 atm hydrogen pressure after addition of PtO_2 (0.9 g) for 24 h. The reaction mixture was filtered through a silica gel pad and washed with MeOH and the filtrate was evaporated under reduced pressure. The residue was carefully added to 25% aqueous NH_4OH (300 mL) and MTBE (300 mL) was added. The two phase system was stirred overnight at room temperature and the phases were separated. The organic phase was dried over $MgSO_4$ and concentrated. The product was obtained as a white solid; yield: 896 mg (85%); mp 78 °C; $[\alpha]_D^{20}$: 29.4 (*c* 0.52, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89–1.41 (m, 16H, $6\times CH_2 + 2\times NH_2$), 1.61–1.88 (m, 8H, $4\times CH_2$), 2.43 (d, J = 6.4 Hz, 2H, $2\times CH$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.6, 28.7, 30.4 (CH_2), 40.6 (CH_2CH), 55.6 (NH_2CH); MS (FAB): *m/z* = 225; MS (EI): *m/z* = 141 (11), 113 (13), 112 (100), 95 (26), 56 (16), 55 (13), 41. IR (NaCl): ν = 3381 w, 3050 m, 2925 s, 2852 s, 2360 s, 1578 m, 1449 m, 1388 w, 1362 w, 1303 w, 1265 m, 1196 w, 1166 w, 1082 w, 958 w, 892 w, 819 w, 738 s, 704 w, 668 w cm^{-1}.

3,5-Dimethylbenzaldehyde (9)

3,5-Dimethylbenzyl alcohol (22.72 g, 166.8 mmol) was dissolved in CH_2Cl_2 (1200 mL) and freshly grinded molecular sieves 4 Å (30 g) were added. The suspension was stirred at room temperature for 15 min then cooled to 0 °C and pyridinium dichromate (115.97 g, 308.3 mmol) was added. The reaction mixture was stirred at 0 °C for 1 h and followed by 2 h at room temperature. After filtration through a silica pad and washing with MTBE (2000 mL) the combined organic phases were dried over $MgSO_4$ and evaporated to give the product as a pale yellow liquid; yield: 18.80 g (84%); bp 199 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 6H, 2 × CH_3), 7.42 (s, 1H, H_{Ar}), 7.47 (s, 2H, H_{Ar}), 9.93 (s, 2H, C*H*O); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.9 (*C*H$_3$), 127.4, 136.4 (H*C*$_{Ar}$), 137.7, 138.6 (*C*$_{Ar}$), 192.6 (*C*HO); MS (EI): *m/z* = 134 (M^+, 90), 133 (100), 105 (71), 103 (12), 91 (23), 79 (15), 77 (24), 63 (10), 51 (13), 43 (29), 39 (15).

3,5-Dimethylbenzylphosphonium Bromide (10)

3,5-Dimethylbenzyl bromide (56.42 g, 283.4 mmol) and PPh_3 (74.30 g, 283.2 mmol) were dissolved in toluene (640 mL) and heated at 80 °C for 3 h. After cooling to room temperature the solid was filtered off and washed with a small amount of MTBE to give the product as a white solid; yield: 98.25 g (75%); mp 223 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 6H, 2 × CH_3), 5.24 (s, 1H, CH_{2a}), 5.29 (s, 1H, CH_{2b}), 6.58 (s, 2H, H_{Ar}), 6.84 (s, 1H, H_{Ar}), 7.23–7.80 (m, 15H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.0 (*C*H$_3$), 126.3, 126.4, 129.1, 129.9, 130.1 (H*C*$_{Ar}$), 138.2, 138.3 (*C*$_{Ar}$); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.7; MS (FAB): *m/z* = 461; MS (EI): *m/z* = 380 (24), 379 (22), 263 (15), 262 (72), 261 (10), 195 (10), 185 (10), 184 (19), 183 (100), 165 (13), 152 (16), 119 (59), 115 (13), 108 (23), 107 (22), 91 (16), 77 (17), 51 (25), 39 (12); IR (NaCl): ν = 3045 w, 2989 w, 2878 w, 2849 m, 2729 m, 2483 w, 2360 w, 2257 w, 2006 w, 1811 w, 1597 w, 1588 w, 1482 w, 1438 w, 1407 m, 1378 w, 1333 w, 1266 w, 1249 m, 1190 w, 1176 w, 1157 m, 1109 s, 1028 w, 995 m, 952 w, 860 m, 763 m, 743 m, 726 w, 704 w, 690 m, 626 w, 552 w, 523 w, 500 w cm^{-1}.

(*E*)-1,2-Bis(3,5-dimethylphenyl)ethene (11)

n-BuLi (45 mL, 72.0 mmol, 1.6 M in hexanes) was added dropwise at −78 °C to a suspension of **10** (27.85 g, 60.4 mmol) in THF (555 mL) and stirred for 2 h at room temperature. After adding 9 (8.11 g, 60.4 mmol) dissolved in THF (18 mL) the solution was stirred for 3 h at room temperature. The solvent was evaporated. The residue was dissolved in MTBE (250 mL), filtered through silica and washed with MTBE. The solvent was removed and the residue was purified by chromatography (hexanes/EtOAc, 4:1) to give the product as an (*E*)/(*Z*)-mixture. The mixture was dissolved in $CHCl_3$ (300 mL) and $TeCl_4$ (2.15 g) and a small amount of tellurium were added and the reaction mixture was stirred for 5 h at room temperature. After filtration over Celite the organic phase was washed with 5% aqueous Na_2CO_3-solution (100 mL) and dried over Na_2SO_4. After evaporation of the solvent the solid was recrystallized from hexanes and purified by chromatography (hexanes/EtOAc, 4:1) to give the product as a white solid; 6.97 g (49%); mp 207 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 12H, 4 × CH_3), 6.47 (s, 2H, 2 × C*H*), 6.92 (s, 2H, H_{Ar}), 7.03 (s, 4H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3 (*C*H$_3$), 124.3 (*C*H), 128.5, 129.2 (H*C*$_{Ar}$), 137.4, 138.1 (*C*$_{Ar}$); MS (EI): *m/z* = 237 ($[M+H]^+$, 27), 236 (100), 221 (12), 206 (33); IR (KBr): ν = 3050 m, 1600 s, 1580 m, 1450 s, 960 m cm^{-1}.

(*S*,*S*)-1,2-Bis(3,5-dimethylphenyl)ethane-1,2-diol (12)

A mixture of potassium osmate (78 mg, 0.21 mmol), *O*-(4-chlorobenzoyl)hydroquinine (1.31 g, 2.82), $K_3Fe(CN)_6$ (20.87 g, 63.40 mmol) and K_2CO_3 (8.74 g, 63.40 mmol) were dissolved in a mixture of *tert*-butyl alcohol/water (280 mL, 1:1) and stirred for 5 min. Compound **11** (5.0 g, 21.2 mmol) was added and the heterogeneous reaction mixture was stirred for two days at room temperature. Na_2SO_3 (105 g, 833.1 mmol) was added and the reaction mixture was stirred for further 30 min. After separation of the phases the water phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were evaporated and the residue was dissolved in EtOAc (150 mL) and washed with 1 N H_2SO_4 (2 × 100 mL), saturated $NaHCO_3$ (2 × 100 mL) and brine (2 × 100 mL). The organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by chromatography (hexanes/EtOAc, 4:1) to give the product as a white solid; yield: 3.34 g (59%); mp 106 °C [< 99% ee based on chiral HPLC (Chiralcel OD)]; $[\alpha]_D^{20}$: −66.3 (*c* 0.89, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 12H, 4 × CH_3), 2.65 (br s, 2H, 2 × O*H*), 4.68 (s, 2H, 2 × C*H*), 6.84 (s, 4H, H_{Ar}), 6.89 (s, 2H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3 (*C*H$_3$), 78.4 (*C*-OH), 124.4, 129.4 (H*C*$_{Ar}$), 137.7, 140.1 (*C*$_{Ar}$); MS (EI): *m/z* = 137 (12), 136 (100), 135 (36), 121 (27), 107 (41), 105 (11), 91 (26); IR (KBr): ν = 3885 m, 2909 m, 2880 w, 1647 m, 1636 m, 1609 m, 1464 s, 1159 s, 1072 m, 849 w, 727 m, 704 w, 687 m cm^{-1}.

(*R*,*R*)-1,2-Diazido-1,2-bis(3,5-dimethylphenyl)ethane (13)

A mixture of triethylamine (2.47 mL, 17.70 mmol) and methanesulfonyl chloride (1.37 mmol, 17.70 mmol) was added dropwise to a solution of **12** (2.2 g, 8.14 mmol) in CH_2Cl_2 (31 mL) and stirred for 3 h at room temperature. The reaction mixture was quenched with water and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by chromatography (Et_2O) to give the bismesylate as a white solid; yield: 3.44 g (99%).

The bismesylate (3.44 g, 8.06 mmol) was dissolved in DMF (44 mL) and NaN_3 (1.16 g, 17.84 mmol) was added. The reaction mixture was heated at 80 °C overnight. After cooling to room temperature H_2O (40 mL) was added and the water phase was extracted with EtOAc (3 × 150 mL). The combined organic phases were dried over Na_2SO_4 and the solvent evaporated. The residue was purified by chromatography (hexanes/EtOAc, 8:1) to give the product as a pale yellow oil which crystallized upon cooling (4 °C); yield: 1.39 g (54%); mp 38 °C; $[\alpha]_D^{20}$: −141.5 (*c* 0.99, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 12H, 4 × CH_3), 4.57 (s, 2H, 2 × C*H*), 6.74 (s, 4H, H_{Ar}), 6.90 (s, 2H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.2 (*C*H$_3$), 70.4 (*C*H), 125.4, 130.1 (H*C*$_{Ar}$), 135.8, 138.0 (*C*$_{Ar}$); MS

(EI): $m/z = 236$ (24), 133 (34), 132 (100), 131 (18), 116 (25), 106 (11), 105 (79), 103 (14), 91 (12), 79 (17), 77 (21); IR (KBr): $\nu =$ 3320 m, 3018 m, 2920 w, 2855 w, 2479 m, 2120 m, 2074 m, 1609 m, 1470 s, 1380 m, 1305 s, 1291 m, 1252 w, 934 m, 849 m cm^{-1}.

(*R*,*R*)-1,2-Bis(3,5-dimethylphenyl)ethane-1,2-diamine (14)

A solution of **13** (2.19 g, 6.84 mmol) in THF (44 mL) was added dropwise at 0 °C to a suspension of $LiAlH_4$ (524 mg, 13.81 mmol) in THF (44 mL) and stirred for 3 h at room temperature. The reaction was quenched by adding a saturated aqueous KF solution (26.0 mL, 468.1 mmol). The reaction mixture was filtered over Celite and washed with EtOAc. The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by chromatography (EtOAc/MeOH, 4:1) to give the product as a white solid; yield: 730 mg (40%); mp 56 °C; $[\alpha]_D^{20}$: 61.0 (*c* 0.24, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.46$ (br s, 4H, $2 \times NH_2$), 2.30 (s, 12H, $4 \times CH_3$), 4.15 (s, 2H, $2 \times CH$), 6.90 (s, 2H, H_{Ar}), 6.97 (s, 4H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 21.3$ (CH_3), 69.0 (*C*H), 124.6, 128.6 (HC_{Ar}), 137.9, 143.3 (C_{Ar}); MS (EI): $m/z =$ 135 (13), 134 (100), 107 (11), 91 (11). IR (NaCl): $\nu = 3639$ w, 3378 m, 3300 m, 3011 m, 2911 m, 2867 m, 2733 w, 1606 s, 1461 m, 1378 m, 1300 w, 1261 w, 1156 w, 1089 w, 1037 w, 959 w, 848 s, 708 m cm^{-1}.

N,*N*′-Bis((*S*)-1-phenylethyl)ethanediimine (15)

A mixture of glyoxal (4.67 mL, 32.24 mmol, 40% aqueous solution), α-(*S*)-methylbenzylamine (8.0 g, 66.02 mmol), formic acid (0.21 mL, 5.57 mmol) and $MgSO_4$ (16.5 g) was stirred in CH_2Cl_2 (65 mL) for 30 min at 20 °C. (It is important to keep the temperature below 20 °C, as even slightly higher temperatures give by-products and decreased yields.) The reaction mixture was filtered over Celite and evaporated. The residue was dissolved in cyclohexane (70 mL), dried over Na_2SO_4 and the solvent was evaporated to give the product as a pale yellow oil; yield: 7.75 g (90%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.58$ (d, $J = 7.0$ Hz, 6H, $2 \times CH_3$), 4.51 (q, $J = 7.0$ Hz, 2H, $2 \times CH$), 7.10–7.38 (m, 10H, H_{Ar}), 8.05 (s, 2H, N=C*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 24.0$ (CH_3), 69.7 (*C*H), 126.7, 127.2, 128.6 (HC_{Ar}), 143.7 (C_{Ar}), 160.7 (*C*=N).

N,*N*′-Bis((*S*)-1-phenylethyl)-(*R*,*R*) -1,2-di-*tert*-butylethane-1,2-diamine (16)

A solution of *tert*-butylmagnesium chloride (40.5 mL, 81.0 mmol, 2M in Et_2O) in hexanes (400 mL) was heated at 50 °C for 20 min. Then a solution of **15** (7.5 g, 28.37 mmol) in hexanes (120 mL) was added dropwise and the reaction mixture was stirred at 50 °C for 45 min. After cooling to room temperature the reaction was quenched by adding sat. NH_4Cl sol. (120 mL) and MTBE (120 mL). After subsequent stirring at room temperature for further 30 min the phases were separated. The aqueous phase was extracted with MTBE ($2 \times$ 100 mL). The combined organic phases were dried over Na_2CO_3 and filtered over silica. After evaporation of the solvent the product was obtained as a pale yellow oil; yield: 8.29 g (77%); $[\alpha]_D^{20}$: 29.5 (*c*0.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.79$ (s, 18H, $2 \times t$-butyl), 1.23 (d, $J = 6.5$ Hz, 6H, $2 \times CH_3$), 2.36 (s, 2H, $2 \times HC$-*t*-butyl), 3.71 (q, $J = 6.5$ Hz, 2H, $2 \times CH$), 7.15–7.45 (m, 10H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 23.6$, 35.8 (CH_3), 57.0 (H*C*), 62.2 (H*C*-*t*-butyl), 126.4, 126.8, 128.1 (HC_{Ar}), 147.8 (C_{Ar}).

(*R*,*R*)-1,2-Di-*tert*-butylethane-1,2-diamine (17)

To a solution of **16** (4.60 g, 12.09 mmol) in MeOH (150 mL) were added $Pd(OH)_2$ (1.23 g) and ammonium formate (4.60 g, 72.68 mmol). The reaction mixture was heated at 60 °C under vigorous stirring for 2 h. After cooling to room temperature the mixture was filtered over Celite and the solvent evaporated. The residue was dissolved in MTBE (60 mL) and stirred with K_2CO_3 (10 g) for 30 min. After filtration and evaporation of the solvent the product was obtained after distillation of the residue as a colorless liquid; yield: 1.21 g (58%); bp 242 °C; $[\alpha]_D^{20}$: −15.6 (*c* 0.67, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (s, 18H, $6 \times CH_3$), 2.55 (s, 2H, $2 \times CH$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 26.6$ ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 57.2 (*C*H); MS (EI): $m/z = 174$ ($[M+2H]^+$, 10), 173 ($[M+H]^+$, 100), 86 (15).

General Procedure for the Bis-Sulfonylation of Chiral Diamines

The diamine (1 equiv.) was dissolved in CH_2Cl_2 (3.5 mL/mmol), cooled to 0 °C and stirred for 15 min. After adding *N*,*N*-diisopropylethylamine (4.5 equivs.) the reaction mixture was stirred for further 10 min at 0 °C. After cooling the reaction mixture to −40 °C the sulfonyl chloride (2 equivs.) was added. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched by addition of 1 M HCl. The phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by recrystallization or chromatography to give the product.

(1*R*,2*R*)-1,2-*N*,*N*′-Bis(*p*-toluenesulfonylamino)-1,2-diphenylethane (18): White solid (recrystallized from CH_2Cl_2/hexanes); yield: 79%; mp 89 °C; $[\alpha]_D^{20}$: 43.9 (*c* 1.74, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.32$ (s, 6H, $2 \times CH_3$), 4.48 (d, $J = 6.9$ Hz, 2H, $2 \times CH$), 5.64 (br s, 2H, $2 \times NH$), 6.67 (d, $J = 8.4$ Hz, 4H, H_{Ar}), 6.94–7.07 (m, 10H, H_{Ar}), 7.47 (d, $J =$ 8.4 Hz, 4H, H_{Ar}); ^{13}C NMR (101.6 MHz, $CDCl_3$): $\delta = 21.4$ (CH_3), 62.2 (*C*H), 127.2, 127.6, 127.8, 128.1, 129.3 (HC_{Ar}), 136.4, 136.9, 143.2 (C_{Ar}); MS (EI): $m/z = 261$ (16), 260 (100), 155 (31), 106 (35), 91 (49); IR (KBr): $\nu = 3338$ m, 3312 m, 3066 w, 3032 w, 2947 w, 2926 w, 1598 w, 1496 w, 1457 m, 1402 w, 1329 s, 1306 m, 1158 s, 1120 w, 1090 m, 1064 m, 927 m, 813 m, 768 w, 700 m, 670 m, 572 m, 549 m, 524 w cm^{-1}.

General Procedure for the Bis-Sulfonylation to Afford 28 and *ent*-28

The diamine (1 equiv.) was dissolved in pyridine (28 mL/mmol) and heated to 130 °C. A solution of the sulfonyl chloride (2.2

equivs.) in pyridine was added dropwise and the reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature water and 1 N HCl were added and the reaction mixture was stirred for 30 min. CH_2Cl_2 was added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with 1 N HCl and water and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography to give the desired product.

(1*R*,2*R*)-1,2-*N*,*N*′-Bis(*p*-toluenesulfonylamino)-1,2-di-*tert*-butylethane (28): White solid (chromatography, hexanes/EtOAc, 8:1); yield: 48%; mp 71 °C; $[\alpha]_D^{20}$: 39.2 (*c* 0.358, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 [s, 18H, 2 × C(CH_3)$_3$], 2.43 (s, 6H, 2 × CH_3), 3.62 (d, *J* = 9.6 Hz, 2H, 2 × *CH*), 4.44 (d, *J* = 6.1 Hz, 2H, 2 × N*H*), 7.29 (d, *J* = 8.3 Hz, 4H, H_{Ar}), 7.70 (d, *J* = 8.3 Hz, 4H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.5, 27.2 (*C*H_3), 36.0 (*C*(CH$_3$)$_3$), 60.2 (*C*H), 126.4, 129.6 (HC_{Ar}), 139.2, 143.4 (C_{Ar}); MS (FAB): *m/z* = 481; MS (EI): *m/z* = 481 ([M]$^+$, 1), 241 (16), 240 (100), 211 (13), 155 (51), 139 (12), 92 (13), 91 (92), 86 (17), 65 (15), 57 (37), 41 (19); IR (NaCl): ν = 3568 w, 3309 w, 3064 w, 2961 m, 2875 w, 2360 w, 1918 w, 1598 m, 1496 w, 1480 w, 1419 m, 1370 w, 1322 s, 1235 w, 1200 w, 1156 s, 1120 w, 1081 m, 1018 m, 930 m, 886 w, 814 m, 737 w, 708 w, 687 w, 670 m, 554 w cm^{-1}.

(1*S*,2*S*)-1,2-*N*,*N*′-Bis(*p*-toluenesulfonylamino)-1,2-di-*tert*-butylethane (*ent*-28): White solid (chromatography, hexanes/EtOAc, 8:1); yield: 51%; mp 72 °C; $[\alpha]_D^{20}$: −37.1 (*c* 0.262, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 [s, 18H, 2 × C(CH_3)$_3$], 2.43 (s, 6H, 2 × CH_3), 3.62 (d, *J* = 9.6 Hz, 2H, 2 × *CH*), 4.42 (d, *J* = 6.1 Hz, 2H, 2 × N*H*), 7.29 (d, *J* = 8.6 Hz, 4H, H_{Ar}), 7.71 (d, *J* = 8.6 Hz, 4H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.5, 27.1 (*C*H_3), 36.1 [*C*(CH$_3$)$_3$], 60.2 (*C*H), 126.4, 129.7 (HC_{Ar}), 139.3, 143.4 (C_{Ar}); MS (FAB): *m/z* = 481; MS (EI): *m/z* = 241 (16), 240 (100), 211 (13), 155 (32), 91 (50), 86 (17), 57 (24); IR (NaCl): ν = 3568 w, 3319 w, 3065 w, 2960 m, 2875 w, 2360 w, 1918 w, 1598 m, 1480 w, 1418 m, 1369 w, 1322 s, 1236 w, 1200 w, 1155 s, 1120 w, 1078 m, 1017 m, 972 w, 930 m, 890 w, 814 m, 736 w, 708 w, 688 w, 666 m, 542 w cm^{-1}.

(4*R*,5*R*)-4,5-Bis(chlorodiphenylmethyl)-2,2-dimethyl-1,3-dioxolane (43)

To a refluxing solution of (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolan-4,5-dimethanol (6.0 g, 12.86 mmol) and thionyl chloride (2.9 mL, 39.76 mmol) in CH_2Cl_2 (80 mL) was added dropwise a solution of triethylamine (9.03 mL, 64.79 mmol) in CH_2Cl_2 (80 mL). The reaction mixture was heated under reflux for additional 30 min. After cooling to 10 °C the reaction mixture was poured into a cold solution of saturated $NaHCO_3$ (220 mL) and stirred vigorously for 4 h. The organic phase was separated, dried over $MgSO_4$ and evaporated. The residue was heated under reflux in methanol (39 mL) and the product was filtered off as a pale brown solid; yield: 5.29 g (81%); mp 161–164 °C; $[\alpha]_D^{20}$: −11.7 (*c* 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, 6H, 2 × CH_3), 3.45 (s, 2H, 2 × *CH*), 7.14–7.48 (m, 20H, H_{Ar}); ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 28.7 (*C*H_3), 77.8 (*C*-Cl), 84.3 (*C*H), 113.7 [*C*(CH$_3$)$_2$], 127.7, 128.2, 128.2, 128.3, 128.4, 128.4, 129.0, 129.1, 129.1, 129.2 (HC_{Ar}), 143.4, 144.8 (C_{Ar}); MS (EI): *m/z* = 318 (18), 238 (18), 237 (100), 198 (12), 197 (80), 195 (16), 183 (11), 180 (13), 179 (88), 178 (23), 167 (48), 165 (18), 105 (88), 77 (11), 73 (64), 43 (13); IR (KBr): ν = 3590 m, 3090 m, 3060 m, 3010 w, 2940 m, 1950 w, 1900 m, 1810 m, 1600 w, 1490 s, 1450 s, 1380 m, 1370 s, 1320 m, 1300 m, 1180 m, 1080 m, 1066 m, 1040 s, 1020 s, 1000 w, 930 m, 900 w, 870 w, 860 m, 840 m, 650 w, 630 w cm^{-1}.

(4*R*,5*R*)-Bis(aminodiphenylmethyl)-2,2-dimethyl-1,3-dioxolane (44)

To a solution of **43** (5.30 g, 10.49 mmol) in DMF (55 mL) was added dropwise a solution of sodium azide (2.73 g, 41.99 mmol) in water (10 mL) and the reaction mixture was heated at 80 °C for 5 h. After cooling to room temperature Et_2O (160 mL) and water (100 mL) were added and the phases were separated. The aqueous phase was extracted with Et_2O. The combined organic phases were washed with water (2 × 100 mL), concentrated (to 100 mL) and dried over $MgSO_4$. The solution was added dropwise to a suspension of $LiAlH_4$ (3.20 g, 84.32 mmol) in Et_2O (100 mL) and stirred for 2 h at room temperature. The reaction was quenched by adding a saturated aqueous Na_2SO_4 solution (30 mL). The suspension was filtered and washed with Et_2O (300 mL). The solvent was evaporated, the residue was heated under reflux in hexanes (23 mL) for 60 min and the solid was filtered off. The crude product was purified by chromatography (Et_2O) to give the product as a pale yellow solid; yield: 1.33 g (27%); mp 195 °C; $[\alpha]_D^{20}$: 41.5 (*c* 0.51, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 6H, 2 × CH_3), 2.32 (br s, 4H, 2 × NH_2), 4.26 (s, 2H, 2 × *CH*), 7.13–7.56 (m, 20H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.5 (*C*H_3), 62.3 (*C*-NH$_2$), 82.1 (*C*H), 107.3 [*C*(CH$_3$)$_2$], 126.9, 127.5, 127.8, 127.8, 128.1, 128.4, 129.9 (HC_{Ar}), 144.9, 150.5 (C_{Ar}); MS (EI): *m/z* = 466 ([M]$^+$, 20), 465 (54), 431 (18), 237 (40), 195 (13), 183 (22), 182 (100), 180 (18), 179 (50), 178 (19), 167 (34), 105 (21), 104 (13), 56 (12), 43 (11); IR (NaCl): ν = 3360 m, 3150 w, 3090 m, 3060 m, 3010 m, 2990 m, 2940 m, 1950 w, 1890 m, 1820 w, 1600 w, 1500 s, 1450 s, 1380 m, 1370 s, 1350 m, 1170 m, 1070 m, 1030 s, 1000 w, 950 m, 920 w, 890 w, 860 m, 660 m cm^{-1}.

(4*R*,5*R*)-Bis[(*N*-methylamino)diphenylmethyl]-2,2-dimethyl-1,3-dioxolane (45)

To a suspension of **44** (5.0 g, 10.72 mmol) and $NaHCO_3$ (10.75 g, 128.1 mmol) in DMPU (55 mL) was added iodomethane (1.40 mL, 22.49 mmol). After stirring for 24 h the reaction mixture was poured into Et_2O (200 mL), washed with water (5 × 100 mL), dried over K_2CO_3 and the solvent was evaporated. The residue was purified by chromatography (hexanes/EtOAc, 4:1–1:1) to obtain the product as a white solid; yield: 2.02 g (38%); mp 199 °C; $[\alpha]_D^{20}$: 50.3 (*c* 0.62, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, 6H, 2 × CH_3), 2.01 (s, 6H, 2 × N-CH_3), 3.38 (br s, 2H, 2 × N*H*), 4.14 (s, 2H, 2 × *CH*), 7.05–7.41 (m, 16H, H_{Ar}), 7.55–7.65 (m, 4 H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.5, 30.9 (*C*H_3), 67.9 (*C*-NH), 80.4 (*C*H), 107.2 [*C*(CH$_3$)$_2$], 126.6, 127.2, 127.4, 127.9, 129.9, 130.8 (HC_{Ar}), 141.9, 144.5 (C_{Ar}); MS (EI): *m/z* = 494 ([M]$^+$, 28), 493 (72), 431 (24), 237 (28), 208 (10), 197 (17), 196 (100), 182 (11), 179 (49), 178 (15), 167 (22), 118 (10), 105 (12); IR (NaCl): ν = 3230 w, 3090 m, 3060 w, 3010 w, 2990 m, 2940 s, 2800 m, 1600 m, 1490 s, 1450 w, 1380 m, 1370 m, 1340 w, 1170 m, 1100 w, 1080 w, 1020 m, 1000 s, 880 m, 830 w, 640 m cm^{-1}.

General Procedure for the Synthesis of Ligands 29–39 and 47–50

Triethylamine (4.2 equivs.) was dissolved in toluene (1.5 mL/mmol) and cooled to −78 °C. Freshly distilled phosphorus trichloride (1.4 equivs.) and a suspension of sulfonated diamine (1 equiv.) in toluene (18 mL/mmol) were added and the reaction mixture was allowed to slowly warm to room temperature overnight. After filtration under argon and removal of the solvent under high vacuum, the residue was dissolved in toluene (25 mL/mmol) and cooled to −78 °C. A solution of NEt_3 (10 equivs.) and DMAP (1.02 equivs.) in toluene (1 mL/mmol NEt_3) was added very slowly dropwise followed by a solution of the oxazoline alcohol (1 equiv.) in toluene (5 mL/mmol). The reaction mixture was allowed to slowly warm to room temperature overnight. After filtration under argon and evaporation of the solvent, the crude product was recrystallized from chloroform/hexanes at 0 °C. Trace amounts of remaining DMAP were then removed at 90 °C/0.01 mbar to give the desired product.

Ligand 29: White solid; yield: 71%; mp 78 °C; $[\alpha]_D^{20}$: 14.0 (*c* 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 [s, 9H, C(CH_3)$_3$], 1.88 [br s, 6H, C(CH_3)$_2$], 2.24 (s, 3H, C_6H_5-CH_3), 2.34 (s, 3H, C_6H_5-CH_3), 3.90 (dd, *J* = 10.2, 6.7 Hz, 1H, *H*C4′), 4.21 (m, 2H, H_2C5′), 4.61 (d, *J* = 8.3 Hz, 1H, C*H*), 4.84 (d, *J* = 8.2 Hz, 1H, C*H*), 6.84–7.55 (m, 18H, H_{Ar}); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.4, 21.5 (C_6H_5-CH_3), 25.9 [C(CH_3)$_3$], 27.7, 27.8 [2 × d, J_{CP} = 10.7 Hz, C(CH_3)$_2$], 33.8 [*C*(CH_3)$_3$], 62.0 [*C*(CH_3)$_2$], 69.2 (H_2C5'), 72.1 (d, J_{CP} = 6.9 Hz, *C*H), 74.3 (d, J_{CP} = 6.1 Hz, *C*H), 75.7 (H*C*4′), 127.1, 127.4, 127.5, 127.5, 127.5, 127.6, 127.7, 127.7, 127.9, 128.0, 128.1, 128.1, 128.1, 128.6, 128.7, 128.9, 129.5, 129.7 (HC_{Ar}), 136.0, 136.4, 138.6, 138.9, 142.9, 143.6 (C_{Ar}), 167.9 (*C*=N); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 121.3; MS (EI): *m/z* = 734 ($[M+1]^+$, 18), 733 ($[M]^+$, 42), 578 (18), 260 (29), 169 (11), 168 (100), 155 (16), 152 (15), 139 (12), 111 (10), 91 (29); IR (KBr): ν = 3030 w, 2960 m, 2869 w, 1916 m, 1702 m, 1655 m, 1598 m, 1496 w, 1476 w, 1456 w, 1353 s, 1306 w, 1261 m, 1210 w, 1186 m, 1165 s, 1130 m, 1085 m, 1020 w, 975 m, 940 w, 919 m, 875 w, 840 w, 815 m, 760 m, 700 m, 674 s, 586 w, 567 w cm^{-1}; anal. calcd.: C 62.19, H 6.04, N 5.73; found: C 62.08, H 6.09, N 5.66.

Ligand 40

Tris(dimethylamino)phosphine (230 mg, 1.41 mmol) and (*S*)-2-anilinomethylpyrrolidine (250 mg, 1.42 mmol) were dissolved in degassed toluene (3 mL) and heated under reflux for 2 h. (−)-(*S*)-2-[2′-(Hydroxy)prop-2′-yl]-4-*tert*-butyloxazoline (263 mg, 1.42 mmol) was added and the reaction mixture was heated under reflux for 7 days. After cooling to room temperature the solvent was evaporated and the residue was purified by chromatography (hexanes/EtOAc, 2:1) to obtain the product as a colorless viscous oil; yield: 215 mg (39%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 [s, 9H, C(CH_3)$_3$], 1.3–2.04 (m, 4H, 2 × CH_2-7 + -8], 1.47 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 3.09–4.18 (m, 8H, oxazoline + 2 × CH_2-4 + -8 + C*H*), 6.76–7.25 (m, 5H, H_{Ar}); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.7, 26.1 (CH_2), 26.2 [C(CH_3)$_3$], 28.0, 28.8 [C(CH_3)$_2$], 31.7 (CH_2), 33.8 [*C*(CH_3)$_3$], 48.2 (CH), 52.8(CH_2), 62.7 [*C*(CH_3)$_2$], 68.8 (H_2C5'), 75.6 (H*C*4′), 115.8, 116.0, 118.8, 128.8 (HC_{Ar}), 145.8 (C_{Ar}), 169.4 (*C*=N); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 129.6.

General Procedure for the Synthesis of Iridium Complexes of Ligands 29–39 and 47–50

The ligand (1.0 equiv.) was dissolved in CH_2Cl_2 (36 mL/mmol) and $[Ir(COD)Cl]_2$ (0.5 equivs.) was added and heated under reflux for 2 h. After cooling to room temperature $NaBAr_F$ (1.5 equivs.) and water (11 mL/mmol) were added and the reaction mixture was stirred vigorously for 30 min. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed with water and the solvent was evaporated. The residue was purified by chromatography (CH_2Cl_2) to give the product.

Iridium Complex of Ligand 29: Orange solid; yield: 48%; mp 104 °C; $[\alpha]_D^{20}$: 73.8 (*c* 0.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 [s, 9H, C(CH_3)$_3$], 1.48–2.75 [m, 8H, 4 × H_2C(COD)], 2.02 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.28 (s, 6H, 2 × C_6H_5-CH_3), 4.11 (t, *J* = 8.8 Hz, 1H, H_2C4′), 4.23 [br m, 1 H, *H*C(COD)], 4.36 (d, *J* = 9.1 Hz, 2H, H_2C5′), 4.60 (d, *J* = 8.1 Hz, 1H, C*H*), 4.69 [br m, 1H, *H*C(COD)], 4.76 (d, *J* = 8.1 Hz, 1H, C*H*), 4.99 [br m, 1 H, *H*C(COD)], 5.78 [br m, 1 H, *H*C(COD)], 6.51–7.32 (m, 18H, H_{Ar}), 7.53 (br s, 4H, BAr_F), 7.73 (br s, 8 H, BAr_F); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 89.4; MS (FAB): *m/z* = 1034; IR (NaCl): ν = 2964 m, 2307 w, 1732 w, 1610 m, 1598 m, 1458 w, 1399 w, 1354 s, 1278 s, 1162 m, 1126 s, 1025 w, 951 m, 887 w, 839 w, 802 w, 786 w, 741 w, 713 w, 700 w, 682 m, 672 m, 586 w cm^{-1}; anal. calcd.: C 49.37, H 3.61, N 2.21; found: C 49.51, H 3.72, N 2.14.

Iridium Complex 51

Ligand **30a** (579 mg, 0.77 mmol) and $[Ir(COD)Cl]_2$ (258 mg, 0.38 mmol) were dissolved in CH_2Cl_2 (2 mL) and heated at 50 °C for 2 h. After cooling to room temperature NH_4PF_6 (140 mg, 0.86 mmol) was added and the reaction mixture was stirred for 10 min. The solvent was evaporated, the residue dissolved in a small amount of CH_2Cl_2 and washed with some water. The solvent was evaporated. Crystals suitable for X-ray analysis were obtained by slow recrystallization from ethyl acetate/cyclohexane at −18 °C. $[\alpha]_D^{20}$: 33.7 (*c* 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43–3.29 [m, 8H, 4 × H_2 C(COD)], 2.21 (s, 6H, 2 × CH_3), 2.37 (s, 6H, 2 × C_6H_5-CH_3), 3.90 [br m, 1H, *H*C(COD)], 4.24 [br m, 1H, *H*C(COD)], 4.47 (m, 2H, H_2C5′), 4.86 [br m, 1H, *H*C(COD)], 4.93 (s, 1H, C*H*), 4.97 (s, 1H, C*H*), 5.19 (m, 1H, H_2C4′), 5.83 [br m, 1H, *H*C(COD)], 6.62–7.74 (m, 23H, H_{Ar}); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −161.3, −156.0, −151.6, −147.2, −142.8, −138.4, −133.7, 82.7; MS (FAB): *m/z* = 1054; IR (NaCl): ν = 3034 w, 2962 w, 2362 w, 1619 m, 1540 w, 1495 w, 1456 m, 1399 w, 1350 s, 1308 w, 1261 w, 1226 w, 1187 w, 1161 s, 1087 m, 1025 m, 948 s, 916 w, 874 w, 842 s, 784 w, 754 m, 701 m, 671 m, 600 w, 588 w, 557 w cm^{-1}. For the crystal data of iridium complex **51**, see the Supporting Information.

Rhodium Complex 52

Ligand **30a** (579 mg, 0.77 mmol) and $[Rh(COD)Cl]_2$ (189 mg, 0.38 mmol) were dissolved in CH_2Cl_2 (2 mL) and heated at

50 °C for 2 h. After cooling to room temperature NH_4PF_6 (175 mg, 1.07 mmol) was added and the reaction mixture was stirred overnight. Some water was added, the phases separated and the solvent evaporated. Crystals suitable for X-ray analysis were obtained by slow recrystallization from ethyl acetate/cyclohexane at −18 °C. $[\alpha]_D^{20}$: 31.2 (*c* 1.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45–3.21 [m, 8H, 4 × H_2C(COD)], 2.18 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.36 (s, 6H, 2 × C_6H_5-CH_3), 4.23 [br m, 1 H, *H*C(COD)], 4.46 (m, 2H, H_2C5′), 4.55 (m, 1H, H_2 C4′), 4.65 [br m, 1H, *H*C(COD)], 4.81 (s, 1H, C*H*), 4.84 (s, 1H, C*H*), 5.31 [br m, 1 H, *H*C(COD)], 6.14 [br m, 1H, *H*C(COD)], 6.60–7.73 (m, 23H, H_{Ar}); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −159.6, −156.1, −151.6, −147.5, −142.0, −138.1, −133.9, 102.1, 103.7; MS (FAB): *m/z* = 964; IR (NaCl): ν = 3649 w, 3585 w, 3342 w, 3064 w, 2924 w, 2835 w, 2360 w, 1624 s, 1597 m, 1540 m, 1495 m, 1456 m, 1395 w, 1350 s, 1294 w, 1267 w, 1229 w, 1162 s, 1087 m, 1025 m, 948 m, 843 s, 784 w, 766 w, 733 w, 701 m, 672 m, 614 w, 600 w, 588 w, 557 w cm^{-1}; anal. calcd.: C 51.94, H 4.72, N 3.79; found: C 52.07, H 4.83, N 3.85. For the crystal data of rhodium complex 52, see the Supporting Information.

General Procedure for Pd-Catalyzed Allylic Alkylations

A solution of $[Pd(C_3H_5)Cl]_2$ (1 mol %) and chiral ligand (2.5 mol %) in CH_2Cl_2 (1.2 mL/mmol substrate) in a Young tube was degassed four times by freeze-thaw cycles. The reaction mixture was stirred for 2 h at 48 °C. After cooling to room temperature a solution of the substrate (1 equiv.) in CH_2Cl_2 (4 mL/mmol substrate) was added, followed by dimethyl malonate (3 equivs.), BSA (3 equivs.) and catalytic amounts of dry KOAc. Stirring was continued for 20 h at room temperature after four additional freeze-thaw cycles. The reaction mixture was filtered over silica and washed with hexanes/EtOAc (2:1, 200 mL). The solvent was evaporated and the residue was analyzed by GC to determine the conversion and regioselectivity. Enantiomeric excesses were determined after column chromatography over silica.[18]

General Procedure for Ir-Catalyzed Hydrogenations

The alkene (1 equiv.) and Ir complex (4 mol %) were dissolved in CH_2Cl_2 (10 mL/mmol substrate for TADDOL-derived ligands and 2.5 mL/mmol for *N*-sulfonyl-derived ligands) in a high-pressure autoclave without exclusion of oxygen and pressurized to 100 bar for 2 h. The solvent was removed and the residue was suspended in heptanes, filtered through a syringe filter and the filtrate was directly used for GC and chiral HPLC analysis to determine the conversion and ee.[19]

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