Chiral Proline-Based P,O and P,N Ligands for Iridium-Catalyzed Asymmetric Hydrogenation

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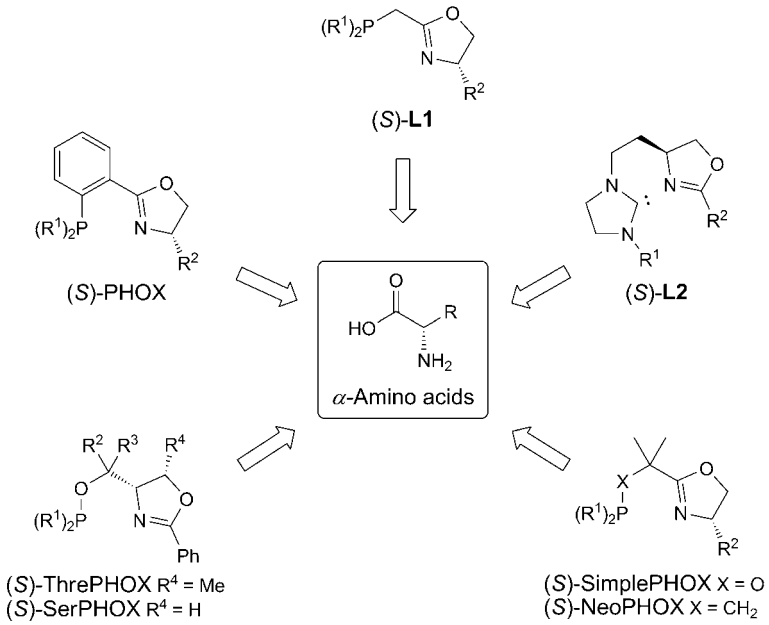
Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

Two new classes of proline-based P,O and P,N ligands were prepared and applied in the iridium-catalyzed asymmetric hydrogenation of alkenes. Both types of ligands induced high enantioselectivities in the hydrogenation of trisubstituted C=C bonds. Iridium complexes derived from P,O ligands bearing sterically demanding amide or urea groups at the pyrrolidine N-atom proved to be especially efficient catalysts for the conjugate reduction of α,β-unsaturated esters and ketones, whereas analogous P,N ligands led to better results with dialkyl-phenyl-substituted alkenes and an allylic alcohol as substrates.

Introduction. – Homogeneous chiral iridium catalysts have considerably enhanced the scope of the asymmetric hydrogenation of alkenes, because, unlike Rh- or Ru-diphosphine complexes, they do not require the presence of a coordinating substituent near the C=C bond. Inspired by the seminal work of *Crabtree et al.* [1] that had uncovered the unusually high reactivity of cationic Ir(monophosphine)(pyridine) catalysts in the hydrogenation of tri- and even tetraalkyl-substituted C=C bonds, initial studies focused on Ir complexes with chiral P,N ligands. The first highly enantioselective Ir-catalyzed hydrogenations were achieved with phosphino-oxazoline (PHOX) ligands, which had originally been developed for enantioselective allylic substitutions [2]. Subsequently, we and other groups developed various other oxazoline-based P,N ligands that were derived from enantiomerically pure α-amino acids (*Scheme 1*) [3]. In addition, *Burgess* and co-workers showed that the chiral C,N ligand **L2** (R^1 = adamantyl, R^2 = 2,5-^{i}Pr$_2$–Ph) containing an N-heterocyclic carbene and an oxazoline as coordinating units also forms efficient enantioselective Ir catalysts [4].

Although high enantioselectivities can be obtained for a wide range of alkenes using oxazoline-based ligands of this type, none of the chiral Ir complexes developed so far is a universally applicable catalyst. Depending on the structure of the alkene, different catalysts perform best. For instance, SimplePHOX and NeoPHOX complexes provide high enantioselectivities in the hydrogenation of various trisubstituted alkenes [5][6]. In contrast, the structurally related phosphino-oxazolines **L1** give poor results with substrates of this type, but form very reactive, highly enantioselective catalysts for the hydrogenation of tetrasubstituted C=C bonds [7]. For a long time, no suitable catalysts were available for the asymmetric hydrogenation of purely alkyl-substituted C=C bonds, until a new class of pyridine-derived P,N ligands led to a breakthrough for this substrate class [8]. P,N Ligands based on other aromatic backbones such as furan or thiophene were also developed and successfully applied to new substrate classes.

Scheme 1. *Chiral Ligands Derived from α-Amino Acids*

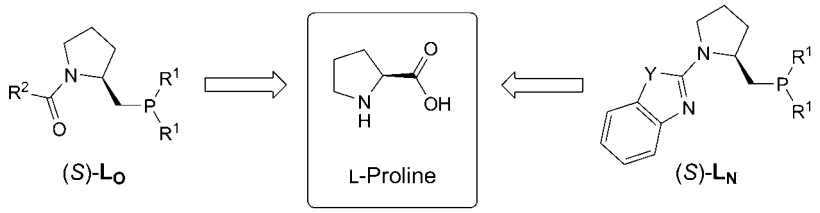


Nevertheless, there are still challenging substrates left that give unsatisfactory results with the available catalysts. Therefore, the search for new efficient ligands to close such methodical gaps continues.

Ideally, a new ligand should be readily accessible from enantiomerically pure precursors through a synthetic route that allows variation of the individual structural elements. Good examples of such ligands are ThrePHOX and SerPHOX which are derived from serine or threonine, respectively, and can be structurally modified at the R^1, R^2, R^3, and R^4 substituents [9][10]. In this way, the catalyst structure can be sterically and electronically tuned for a specific application. Here, we discuss two new classes of modular proline-derived ligands for Ir-catalyzed hydrogenation that fulfill these criteria in an ideal way.

Proline-derived monophosphines $\mathbf{L_O}$ (*Scheme 2*) were originally developed by *Tomioka* and co-workers for enantioselective conjugate additions of organocuprates

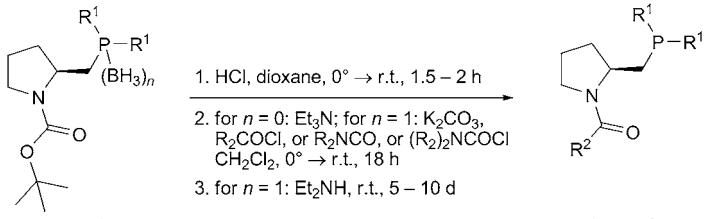
Scheme 2. *Proline-Based P,O and P,N Ligands*



[11]. Later on, they were also successfully applied in the Rh-catalyzed 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds. In a broad automated screening of various metal–ligand combinations in collaboration with *Solvias AG* in Basel, we found that *Tomioka*'s ligand $\mathbf{L_O}$ (R^1 = Ph, R^2 = ^{t}Bu) induced up to 68% ee in the Ir-catalyzed hydrogenation of (*E*)-1,2-diphenylprop-1-ene. We were surprised that this ligand performed so well in view of the hemilabile nature of the Ir–O bond [11f]. Encouraged by this initial result, we optimized the ligand structure for Ir-catalyzed asymmetric hydrogenation by systematic modification of the substituents at the P- and N-atom [12]. Furthermore, we also investigated analogous proline-based P,N ligands $\mathbf{L_N}$ (*Scheme 2*), which would be a useful addition to the known P,N ligands, because the structure of the corresponding Ir complexes differs substantially from the structures of Ir catalysts developed so far.

Ligand Synthesis. – Proline-based P,O ligands were readily prepared from commercially available *N*-Boc-L-proline. The desired carbamate precursors (*S*)-**1**–(*S*)-**4** were obtained in moderate-to-excellent yields (54–97%) according to reported procedures [12][1]). After removal of the Boc protecting group and reaction of the resulting pyrrolidinium salt with various acid chlorides, isocyanates, or carbamoyl chlorides, a series of amides and ureas was obtained. Dialkyl-substituted phosphines (*S*)-**3** and (*S*)-**4** were used as their borane adducts in order to avoid oxidation of the P-atom. In these cases, an additional deprotection step was required to obtain the free ligands (*Scheme 3*). Various derivatives (*S*)-$\mathbf{L_O}$, bearing different R^2 substitutents, were prepared in good yields in this manner (56–96%; *Scheme 3*) [12].

Scheme 3. *Synthesis of Proline-Based P,O Ligands*



	R^1	*n*
(*S*)-**1**	Ph	0
(*S*)-**2**	*o*Tol	0
(*S*)-**3**	^{t}Bu	1
(*S*)-**4**	Cy	1

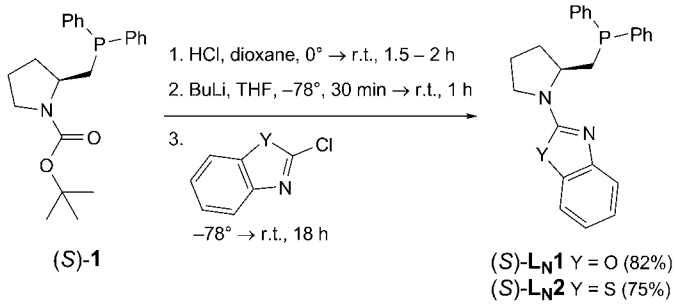
	R^1	R^2	Yield [%]
(*S*)-$\mathbf{L_O}$**1**	Ph	Ph_3C	96
(*S*)-$\mathbf{L_O}$**2**	^{t}Bu	Ph_3C	91
(*S*)-$\mathbf{L_O}$**3**	*o*Tol	^{t}BuNH	56
(*S*)-$\mathbf{L_O}$**4**	Ph	Ph_3CNH	92
(*S*)-$\mathbf{L_O}$**5**	^{t}Bu	Ph_3CNH	88
(*S*)-$\mathbf{L_O}$**6**	Cy	Ph_3CNH	87
(*S*)-$\mathbf{L_O}$**7**	Ph	$^i Pr_2N$	75
(*S*)-$\mathbf{L_O}$**8**	*o*Tol	$^i Pr_2N$	93
(*S*)-$\mathbf{L_O}$**9**	*o*Tol	Cy_2N	81
(*S*)-$\mathbf{L_O}$**10**	^{t}Bu	Cy_2N	69
(*S*)-$\mathbf{L_O}$**11**	Cy	Cy_2N	61

[1]) For the synthesis of *N*-[(*tert*-butoxy)carbonyl]-L-prolinol and (*S*)-*tert*-butyl 2-[(tosyloxy)methyl]-pyrrolidine-1-carboxylate, see [13].

All these ligands could be readily converted to the corresponding [Ir(cod)(**L**)]BAr_F salts (cod = cycloocta-1,5-diene; BAr_F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). From two complexes, crystals suitable for X-ray analysis could be obtained [12a]. The crystal-structure data and NMR analyses clearly confirmed that the ligands were coordinated to the Ir-center in a bidentate fashion through the P- and the C=O O-atom. Although P,O complexes could be isolated in analytically pure form, they proved to be less stable than P,N complexes and could not be stored for longer times. In contrast to P,N complexes, they did not survive purification by chromatography on silica gel. Therefore, they were usually prepared *in situ* when they were applied as catayst for hydrogenation.

In a similar way, proline-based P,N ligands (*S*)-$\mathbf{L_N1}$ and (*S*)-$\mathbf{L_N2}$ were synthesized (*Scheme 4*). After removal of the Boc protecting group, the resulting ammonium salt was deprotonated and then reacted with 2-chlorobenzoxazole or 2-chlorobenzothiazole, respectively. Both ligands were obtained in good yields. They were then converted to the corresponding Ir complexes using standard complexation methods for P,N ligands [14].

Scheme 4. *Synthesis of Proline-Based P,N Ligands* (S)-$\mathbf{L_N1}$ *and* (S)-$\mathbf{L_N2}$



The synthetic route depicted above did not afford the desired dialkylphosphine derivatives (*S*)-$\mathbf{L_N5}$ to (*S*)-$\mathbf{L_N8}$; no conversion of the deprotonated amine was observed. Therefore, a second synthetic route was investigated (*Scheme 5*). Starting from ^{t}BuMe$_2$Si (TBDMS)-protected (*S*)-prolinol **5**, the intermediates (*S*)-**6** and (*S*)-**7** were obtained after deprotonation of the pyrrolidine N-atom, followed by reaction with 2-chlorobenzoxazole or 2-chlorobenzothiazole, respectively, and subsequent removal of the TBDMS protecting group[2]). The alcohols (*S*)-**8** and (*S*)-**9**, were then converted to the bromides (*S*)-**8** and (*S*)-**9**, respectively, through an *Appel* reaction. Subsequent nucleophilic substitution with phosphides generated *in situ* from **10**, **11**, and **12** led to the desired P,N ligands (*S*)-$\mathbf{L_N3}$ to (*S*)-$\mathbf{L_N8}$ in good yields (59–89%). The di(*tert*-butyl) and dicyclohexylphosphine derivatives (*S*)-$\mathbf{L_N5}$–(*S*)-$\mathbf{L_N8}$ were obtained after an additional synthetic step required for the deprotection of the phosphine moiety.

Proline-based ligands (*S*)-$\mathbf{L_N3}$–(*S*)-$\mathbf{L_N8}$ were finally converted to the corresponding Ir complexes by reaction with [Ir(cod)$_2$]BAr_F according to the procedure for proline-based P,O ligand/Ir complexes [12a].

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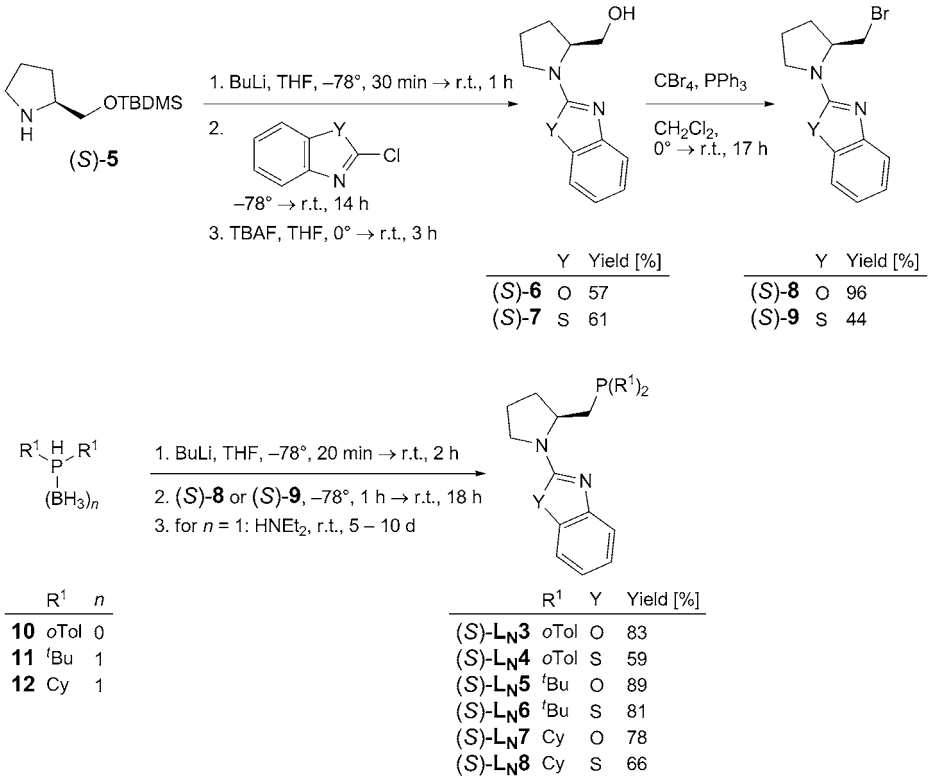
[2]) For the synthesis of (*S*)-2-({[(*tert*-butyl)dimethylsilyl]oxy}methyl)pyrrolidine ((*S*)-**5**), see [15].

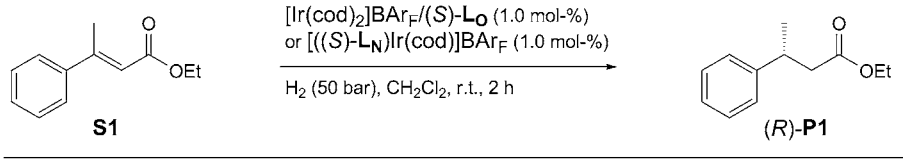
Scheme 5. *Synthesis of Proline-Based P,N Ligands* (*S*)-$\mathbf{L_N3}$ – (*S*)-$\mathbf{L_N8}$

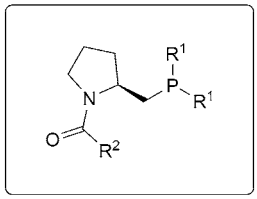


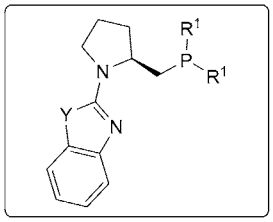
Iridium-Catalyzed Asymmetric Hydrogenation. – To evaluate the potential of these new proline-based ligands in the Ir-catalyzed asymmetric hydrogenation, we investigated their efficiency in the reduction of several trisubstituted functionalized and unfunctionalized alkenes. In general, conversion of the starting material was complete within 2 h, using 1 mol-% of catalyst and 50 bar H_2 pressure for both ligand classes. As mentioned above, the P,O-ligand complexes were generated *in situ* with $[Ir(cod)_2]BAr_F$ prior to the hydrogenation reaction, whereas the more stable P,N ligand complexes were isolated and purified prior to their use.

In the hydrogenation of ethyl (*E*)-3-phenylbut-2-enoate (**S1**), proline-based P,O ligand complexes afforded excellent enantioselectivities of up to 99% ee. The best results are compiled in *Scheme 6*. Dialkylphosphines (*S*)-$\mathbf{L_O5}$ and (*S*)-$\mathbf{L_O6}$ generally gave higher enantioselectivities for this transformation than the corresponding diaryl-substituted phosphine derivatives. Also, ligands with more sterically demanding C=O moieties, such as the trityl-substituted derivatives (*S*)-$\mathbf{L_O2}$, (*S*)-$\mathbf{L_O4}$, and (*S*)-$\mathbf{L_O6}$ provided higher ee values than less hindered amide and urea derivatives. The analogous P,N ligands induced lower enantioselectivities, with the exception of (*S*)-$\mathbf{L_N5}$ and (*S*)-$\mathbf{L_N6}$ that led to the saturated ester (*R*)-**P1** with 98 and 96% ee, respectively. In general,

Scheme 6. *Ir-Catalyzed Asymmetric Hydrogenation of Ethyl (*E*)-3-Phenylbut-2-enoate*







(*S*)-**L**$_O$**2** > 99% conv., 98% ee
(*S*)-**L**$_O$**4** > 99% conv., 92% ee
(*S*)-**L**$_O$**5** > 99% conv., 93% ee
(*S*)-**L**$_O$**6** > 99% conv., 98% ee
(*S*)-**L**$_O$**10** > 99% conv., 99% ee
(*S*)-**L**$_O$**11** > 99% conv., 97% ee

(*S*)-**L**$_N$**3** > 99% conv., 92% ee
(*S*)-**L**$_N$**4** > 99% conv., 85% ee
(*S*)-**L**$_N$**5** > 99% conv., 98% ee
(*S*)-**L**$_N$**6** > 99% conv., 96% ee
(*S*)-**L**$_N$**7** > 99% conv., 95% ee
(*S*)-**L**$_N$**8** > 99% conv., 90% ee

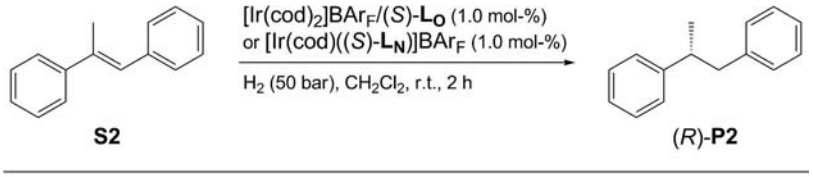
benzoxazoles (*S*)-**L**$_N$**3**, (*S*)-**L**$_N$**5**, and (*S*)-**L**$_N$**7** gave slightly higher enantioselectivities than benzothiazoles (*S*)-**L**$_N$**4**, (*S*)-**L**$_N$**6**, and (*S*)-**L**$_N$**8**.

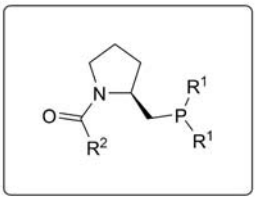
Excellent enantioselectivities were obtained as well in the Ir-catalyzed asymmetric hydrogenation of the unfunctionalized diaryl alkene **S2**. P,O Ligand complexes (*S*)-**L**$_O$**4**, (*S*)-**L**$_O$**6**, and (*S*)-**L**$_O$**10** afforded the product (*R*)-**P2** with 99% ee and full conversion (*Scheme 7*). Also for this substrate, dialkylphosphine-based catalysts gave in general better enantioselectivities than the diarylphosphine analogs. Nevertheless, the sterically demanding ligand (*S*)-**L**$_O$**4** bearing a Ph_2P moiety also induced 99% ee. Overall, the P,N ligand complexes proved to be less selective catalysts. However, three catalysts, (*S*)-**L**$_N$**3**, (*S*)-**L**$_N$**5**, and (*S*)-**L**$_N$**7**, rivaled the P,O ligand complexes with enantioselectivities of 97 and 99% ee. In this reaction too, benzoxazole ligands were superior to the corresponding benzothiazole derivatives. Furthermore, di(*ortho*-tolyl)phosphines gave higher enantioselectivities than diphenylphosphines, in contrast to the P,O-ligand complexes that displayed the opposite trend.

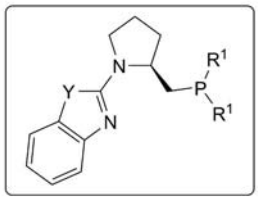
We subsequently compared the performance of P,O and P,N ligands in the Ir-catalyzed asymmetric hydrogenation of the α,β-unsaturated ketone **S5** and three other trisubstituted alkenes including an allylic alcohol (*Scheme 8*).

Proline-based P,O ligands provided only moderate ee values of up to 83% in the hydrogenation of allylic alcohol **S3**. In this case, diarylphosphines generally induced higher enantioselectivities than dialkylphosphines. The best results are compiled in *Scheme 8*, with the highest ee achieved by the di(*ortho*-tolyl)-substituted phosphine (*S*)-**L**$_O$**9**. For this substrate, the corresponding P,N ligands proved to be superior with enantioselectivities of up to 89% ee with (*S*)-**L**$_N$**4**).

Scheme 7. *Iridium-Catalyzed Asymmetric Hydrogenation of* (E)*-1,2-Diphenylprop-1-ene*



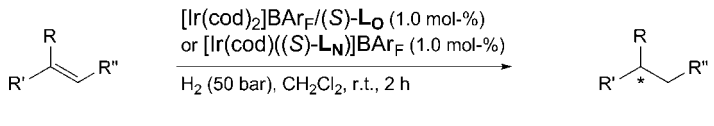


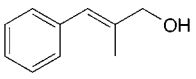


(*S*)-**L$_O$2** >99% conv., 98% ee
(*S*)-**L$_O$4** >99% conv., 99% ee
(*S*)-**L$_O$5** >99% conv., 98% ee
(*S*)-**L$_O$6** >99% conv., 99% ee
(*S*)-**L$_O$10** >99% conv., 99% ee
(*S*)-**L$_O$11** >99% conv., 97% ee

(*S*)-**L$_N$1** >99% conv., 81% ee
(*S*)-**L$_N$3** >99% conv., 97% ee
(*S*)-**L$_N$4** >99% conv., 88% ee
(*S*)-**L$_N$5** >99% conv., 99% ee
(*S*)-**L$_N$6** >99% conv., 95% ee
(*S*)-**L$_N$7** >99% conv., 97% ee

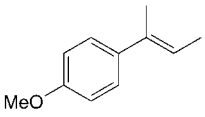
Scheme 8. *Iridium-Catalyzed Asymmetric Hydrogenation of Other Trisubstituted Alkenes*





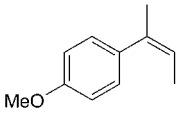
S3

(*S*)-**L$_O$7** >99% conv., 80% ee (*S*)
(*S*)-**L$_O$8** >99% conv., 80% ee (*S*)
(*S*)-**L$_O$9** >99% conv., 83% ee (*S*)
(*S*)-**L$_N$2** >99% conv., 87% ee (*S*)
(*S*)-**L$_N$4** >99% conv., 89% ee (*S*)



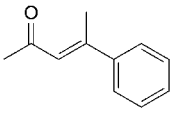
(*E*)-**S4**

(*S*)-**L$_O$1** >99% conv., 53% ee (*R*)
(*S*)-**L$_N$1** >99% conv., 72% ee (*R*)
(*S*)-**L$_N$2** >99% conv., 56% ee (*R*)
(*S*)-**L$_N$3** >99% conv., 86% ee (*R*)
(*S*)-**L$_N$4** 98% conv., 64% ee (*R*)



(*Z*)-**S4**

(*S*)-**L$_O$3** >99% conv., 55% ee (*S*)
(*S*)-**L$_N$2** >99% conv., 76% ee (*S*)
(*S*)-**L$_N$3** >99% conv., 67% ee (*S*)
(*S*)-**L$_N$4** >99% conv., 55% ee (*S*)
(*S*)-**L$_N$8** >99% conv., 55% ee (*S*)



S5

(*S*)-**L$_O$2** 98% yield, 96% ee (*R*)
(*S*)-**L$_N$4** 92% yield, 79% ee (*R*)
(*S*)-**L$_N$5** 63% yield, 90% ee (*R*)
(*S*)-**L$_N$7** 61% yield, 88% ee (*R*)
(*S*)-**L$_N$8** 98% yield, 86% ee (*R*)

In the hydrogenation of the alkenes (*E*)-**S4** and (*Z*)-**S4** as well, P,N ligand complexes outperformed the P,O ligand complexes. While the best P,O ligands afforded up to 55% ee and 53% ee in the reduction of the (*Z*)- and the (*E*)-isomer, respectively, the best P,N ligands induced up to 76% ee and 86% ee. However, these values are distinctly lower than the highest enantioselectivities reported for the hydrogenation of these substrates with other classes of Ir catalysts [8b][9][16].

Proline-based P,N ligands gave lower enantioselectivities than P,O ligands in the reduction of the C=C bond of substrate **S5**. The di(*tert*-butyl)-substituted phosphine (*S*)-$\mathbf{L_N}$**5** provided the best result with 90% ee. Conversion of substrate **S5** was always complete using proline-based P,N ligands (*S*)-$\mathbf{L_N}$**4**–**5** and (*S*)-$\mathbf{L_N}$**7**–**8**. However, it was often accompanied by overreduction to the saturated alcohol in variable amounts. For the P,O ligand complexes, this problem, which had been observed before [17], could be solved by using isolated complexes rather than *in situ* generated catalysts. However, for the analogous P,N complexes overreduction could not be suppressed.

The enantioselectivities induced by the proline-based P,O and P,N ligands are consistent with *Andersson*'s transition-state model for the enantioselective step [3b][18]. According to computational studies, the substrate is coordinated *trans* to the P-atom with the olefin axis arranged orthogonally to coordination plane, as shown in the *Figure*. In the preferred coordination mode, which leads to the major enantiomer, the H-atom points toward the most sterically crowded region of the coordination sphere, minimizing the steric interaction between the substrate and the ligand. In the Ir-PHOX catalyst the interaction with the substituent at the stereogenic center is the enantioselectivity-determining factor. Based on crystal-structure data [12a], we assume that the proline-based P,O ligands adopt a conformation, which results in a sterically similar situation near the substrate (structure **A** in the *Fig.*). An analogous chiral environment is also expected for the related proline-based P,N ligands (structure **B**). In accordance with these qualitative models, the three catalyst types shown in the *Figure* furnish the same product enantiomer in the hydrogenations discussed above.

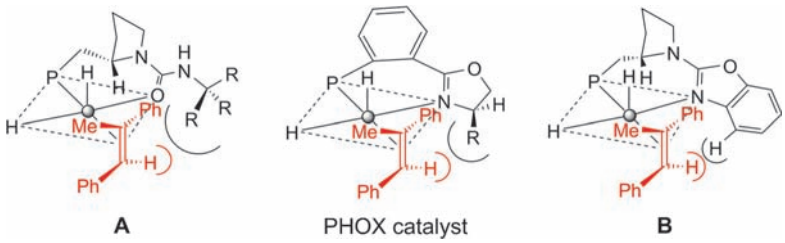


Figure. *Qualitative models to rationalize the enantioselectivity*

Conclusions. – We have developed efficient practical syntheses of two new classes of chiral P,O and P,N ligands for Ir-catalyzed asymmetric hydrogenation starting from commercially available proline derivatives. Both types of ligands form seven-membered chelate rings. The structures of the N- or O-donor, and the phosphine moiety can be easily modified, allowing the electronic and steric properties to be tuned

for a specific application. Both proline-derived P,O and P,N ligands gave high enantioselectivities in the hydrogenation of trisubstituted olefins. Iridium complexes derived from P,O ligands bearing sterically demanding amide or urea groups at the pyrrolidine N-atom proved to be especially efficient catalysts for the conjugate reduction of α,β-unsaturated esters and ketones, where they afforded similar or even better enantioselectivities than the state-of-the-art catalysts. Some of the proline-based P,N ligands also performed very well, indicating a promising potential of this ligand class. In view of these results, it would seem worthwhile to explore further applications of proline-derived ligands of this type.

We thank the *Swiss National Science Foundation* for financial support of this work.

Experimental Part

General. Commercially available reagents were purchased from *Acros*, *Aldrich*, or *Fluka*, and used as received. Et_2NH was distilled from CaH_2. The solvents were collected from a purification column system (*PureSolv*, *Innovative Technology Inc.*), or purchased from *Aldrich* or *Fluka* in sure/sealed™ bottles over molecular sieves. All prep. reactions with air- or moisture-sensitive compounds were carried out in flame-dried glassware under inert atmosphere using *Schlenk* techniques. Column chromatography (CC): *Fluka* silica gel *60* (*Buchs*, particle size 40–63 nm), distilled eluents. TLC: *Macherey-Nagel* (*Polygram SIL/UV254*, 0.2 mm silica with fluorescence indicator); UV light (254 nm) or basic permanganate soln. for visualization. HPLC: *Shimadzu* systems, *SLC-10A* system controller, *CTO-10AC* column oven, *LC10-AD* pump system, *DGU-14A* degasser, and *SPD-M10A* diode-array or UV/VIS detector, chiral columns *Chiracel OD-H* or *OJ* (4.6 × 250 mm). GC: *Carlo Erba HRGC Mega2 Series 800* (*HRGS Mega2*) instruments, *Restek Rtx-1701* (30 m × 0.25 mm × 0.25 μmol) for achiral phases, *Chiraldex* γ-cyclodextrin *TFA G-TA* (30 m × 0.25 mm × 0.12 μm) column for enantiomer separation. M.p.: *Büchi 535* apparatus; not corrected. Optical rotations ($[\alpha]_D^{20}$): *Perkin Elmer Polarimeter 341*, Na lamp, 1-dm cuvette, *c* in g/100 ml. IR Spectra: *Shimadzu FTIR-8400S* spectrometer, $\tilde{\nu}$ in cm^{-1}; *s* (strong), *m* (medium), *w* (weak). NMR Spectra: *Bruker Avance 400* (400 MHz) or *Bruker Avance 500* (500 MHz) spectrometer, δ in ppm, *J* in Hz. MS: *VG70-250* spectrometer (EI) or *MAR 312* spectrometer (FAB), or *Finnigan MAT LCQ* (ESI-MS); *m*/*z* in rel. %. HR-MS: *Thermo Fisher Scientific LTQ Orbitrap XL* (ESI-MS) spectrometer. Elemental analyses: *Leco CHN-900* (C, H, and N). For the syntheses and anal. data of P,O ligands (*S*)-$\mathbf{L_O}$, see [12a].

*2-{(2*S*)-2-[(Diphenylphosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzoxazole* ((*S*)-$\mathbf{L_N1}$). HCl (4.0M in 1,4-dioxane; 2.00 ml) was added dropwise at 0° to a soln. of (*S*)-**1** (300 mg, 812 μmol, 1.0 equiv.) in 1,4-dioxane (1 ml). The mixture was stirred at r.t. for 1.5–2 h and then reduced to dryness. The crude product was treated three times with benzene (2 × 2 ml), and the solvent was evaporated each time. Drying under high vacuum afforded a colorless foam that was dissolved in THF (8 ml). A 1.6M soln. of BuLi (800 μl, 1.28 mmol, 1.6 equiv.) in hexanes was slowly added at −78° in a acetone/dry ice bath, and the resulting soln. was stirred for 30 min at −78° and for 1 h at r.t., accompanied by a color change to yellow. After cooling the soln. again to −78°, 2-chlorobenzoxazole (187 mg, 1.22 mmol, 1.5 equiv.) was added, and the mixture was allowed to warm to r.t. overnight. At 0° in an ice bath, aq. sat. $NaHCO_3$ (5 ml) was added dropwise. AcOEt (10 ml) was added, and the layers were separated. The aq. layer was extracted with AcOEt (2 × 10 ml). The combined org. layers were washed with brine (20 ml) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the crude product was purified by CC (SiO_2; cyclohexane/AcOEt 4:1) to give (*S*)-$\mathbf{L_N1}$ (257 mg, 665 μmol, 82%). Colorless solid. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.26. M.p. 87–89°. $[\alpha]_D^{20} = -85.2$ ($c = 0.520$, $CHCl_3$). IR (neat): 3054*w*, 2951*w*, 2875*w*, 1636*s*, 1576*s*, 1458*m*, 1383*m*, 1355*m*, 1243*m*, 1149*w*, 1002*w*, 912*m*, 794*w*, 736*s*, 695*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.68–7.59 (*m*, 2 arom. H); 7.45–7.33 (*m*, H–C(7), 5 arom. H); 7.26–7.20 (*m*, 3 arom. H); 7.20–7.10 (*m*, H–C(4), H–C(5)); 6.99 (*t*, *J* = 7.7, H–C(6)); 4.31–4.16 (*m*, H–C(2′)); 3.72–3.56 (*m*, CH_2(5′)); 2.86 (*dt*, *J* = 14, 3.0, 1 H of CH_2P); 2.33 (*t*, *J* = 12, 1 H of CH_2P); 2.23–2.05 (*m*,

CH_2(3′), 1 H of CH_2(4′)); 2.05–1.91 (*m*, 1 H of CH_2(4′)). ^{13}C-NMR (101 MHz, $CDCl_3$): 160.5 (*s*, C(2)); 148.9 (*s*, C(7a)); 143.4 (br. *s*, C(3a)); 138.6 (*d*, ^1J(C,P) = 12, C(1) of Ph); 137.7 (*d*, ^1J(C,P) = 12, C(1) of Ph′); 133.1 (*d*, ^2J(C,P) = 19, C(2), C(6) of Ph); 132.7 (*d*, ^2J(C,P) = 19, C(2), C(6) of Ph′); 129.0 (*s*, C(4) of Ph); 128.7 (*d*, ^3J(C,P) = 7.0, C(3), C(5) of Ph); 128.6 (*s*, C(4) of Ph′); 128.5 (*d*, ^3J(C,P) = 7.0, C(3), C(5) of Ph′); 123.9 (*s*, C(5)); 120.2 (*s*, C(6)); 116.2 (*s*, C(4)); 108.6 (*s*, C(7)); 57.5 (*d*, ^2J(C,P) = 21, C(2′)); 48.4 (*s*, C(5′)); 33.7 (*d*, ^1J(C,P) = 15, CH_2P); 31.7 (*d*, ^3J(C,P) = 7.6, C(3′)); 24.1 (br. *s*, C(4′)). ^{31}P-NMR (162 MHz, $CDCl_3$): −22.8 (*s*). EI-MS (70 eV): 386 (4, M^+), 310 (20), 309 (100), 187 (27).

*2-{(2*S*)-2-[(Diphenylphosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzothiazole* ((*S*)-**L$_N$2**). Compound (*S*)-**L$_N$2** (75%) was prepared as described for (*S*)-**L$_N$1**, using 2-chlorobenzothiazole instead of 2-chlorobenzoxazole. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.23. M.p.: 101–105°. $[\alpha]_D^{20} = -61.6$ (*c* = 0.530, $CHCl_3$). IR (neat): 3066*w*, 2964*w*, 2918*w*, 2867*w*, 1595*m*, 1564*m*, 1533*s*, 1481*m*, 1452*m*, 1441*s*, 1431*m*, 1363*m*, 1313*m*, 1269*m*, 1254*w*, 1186*w*, 1124*m*, 1066*m*, 1018*m*, 914*m*, 852*m*, 734*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.70 (*m*, 2 arom. *o*-H); 7.57 (*d*, *J* = 8.0, H–C(4)); 7.54 (*d*, *J* = 7.8, H–C(7)); 7.45–7.34 (*m*, 5 arom. H); 7.31–7.25 (*m*, H–C(5)); 7.26–7.22 (*m*, 3 arom. H); 7.05–7.02 (*m*, H–C(6)); 4.02–4.08 (*m*, H–C(2′)); 3.62–3.44 (*m*, CH_2(5′)); 2.99 (br. *d*, ^2J(H,P) = 14, 1 H of CH_2P); 2.24–2.09 (*m*, 1 H of CH_2P, CH_2(3′), 1 H of CH_2(4′)); 2.05–1.99 (*m*, 1 H of CH_2(4′)). ^{13}C-NMR (126 MHz, $CDCl_3$): 164.6 (*s*, C(2)); 153.1 (*s*, C(3a)); 138.6 (*d*, ^1J(C,P) = 12, C(1) of Ph); 137.4 (*d*, ^1J(C,P) = 12, C(1) of Ph′); 133.4 (*d*, ^2J(C,P) = 19, C(2), C(6) of Ph); 132.7 (*d*, ^2J(C,P) = 19, C(2), C(6) of Ph′); 130.7 (*s*, C(7a)); 128.9–128.5 (*m*, arom. CH); 125.8 (*s*, C(5)); 120.8 (*d*, C(6)); 120.7 (C(7)); 118.8 (*s*, C(4)); 59.3 (*d*, ^2J(C,P) = 21, C(2′)); 50.2 (*s*, C(5′)); 32.3 (*d*, ^1J(C,P) = 15, *C*H_2P); 31.4 (*d*, ^3J(C,P) = 7.5, C(3′)); 23.9 (*s*, C(4′)). ^{31}P-NMR (202 MHz, $CDCl_3$): −21.6 (*s*). ESI-MS: 403 (100, $[M+H]^+$). Partial oxidation was observed during recording.

*[(2*S*)-1-(1,3-Benzoxazol-2-yl)pyrrolidin-2-yl]methanol* ((*S*)-**6**). *(2*S*)-2-({[(*tert*-Butyl)(dimethyl)silyl]oxy}methyl)pyrrolidine* [15] ((*S*)-**5**; 1.00 g, 4.64 mmol, 1.0 equiv.) was dissolved in THF (15 ml), and a 1.6M soln. of BuLi (3.30 ml, 5.28 mmol, 1.1 equiv.) in hexanes was slowly added at −78° in an acetone/dry ice bath. The resulting soln. was then stirred for 30 min at −78° and for 1 h at r.t. After cooling the soln. again to −78°, 2-chlorobenzoxazole (700 µl, 6.13 mmol, 1.3 equiv.) was added, and the mixture was allowed to warm to r.t. over 14 h. At 0° in an ice bath, aq. sat. $NaHCO_3$ (10 ml) was added dropwise. AcOEt (30 ml) was added, and the layers were separated. The aq. layer was extracted with AcOEt (2 × 30 ml). The combined org. layers were washed with brine (40 ml) and dried ($MgSO_4$). The solvents were evaporated under reduced pressure and the crude product, 2-[(2*S*)-2-({[(*tert*-butyl)(dimethyl)silyl]oxy}methyl)pyrrolidin-1-yl)-1,3-benzoxazole, was dried *in vacuo*. The residue was then dissolved in THF (10 ml) and ^{t}Bu$_4$NF (TBAF) · 3 H_2O (2.93 g, 9.29 mmol, 2.0 equiv.) was added portionwise, at 0° in an ice bath. The resulting mixture was allowed to stir at r.t. for 3 h. AcOEt (30 ml) and H_2O (50 ml) were added. The resulting layers were separated, and the aq. layer was extracted with AcOEt (3 × 50 ml). The org. extracts were combined, washed with brine (70 ml), and dried ($MgSO_4$). The solvents were removed under reduced pressure, and the residue was filtered through a plug of SiO_2 (5 × 5 cm), eluting with AcOEt. After evaporation of the solvent, the product was purified by CC (SiO_2 (5 × 15 cm); cyclohexane/AcOEt 1:1 → 3:7) to give (*S*)-**6** (576 mg, 2.64 mmol, 57%). Yellowish semisolid. R_f (SiO_2; cyclohexane/AcOEt 7:3) 0.11. $[\alpha]_D^{20} = -70.6$ (*c* = 0.720, $CHCl_3$). IR (neat): 3270*w*, 2929*w*, 2873*m*, 1631*s*, 1573*s*, 1458*s*, 1386*m*, 1354*m*, 1242*s*, 1168*w*, 1151*w*, 1052*m*, 1003*m*, 962*w*, 912*m*, 793*w*, 753*m*, 737*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.31 (*d*, *J* = 7.8, H–C(7)); 7.24 (*d*, *J* = 8.0, H–C(4)); 7.15 (*t*, *J* = 7.8, H–C(6)); 7.00 (*t*, *J* = 7.8, H–C(5)); 5.99–5.76 (br. *s*, OH); 4.19–4.08 (*m*, H–C(2′)); 3.86–3.71 (*m*, CH_2O, 1 H of CH_2(5′)); 3.70–3.59 (*m*, 1 H of CH_2(5′)); 2.24–2.14 (*m*, 1 H of Pyr); 2.09–1.99 (*m*, 1 H of Pyr); 1.99–1.89 (*m*, 1 H of Pyr); 1.82–1.68 (*m*, 1 H of Pyr). ^{13}C-NMR (101 MHz, $CDCl_3$): 162.0 (*s*, C(2)); 148.9 (*s*, C(7a)); 142.4 (*s*, C(3a)); 124.2 (*s*, C(5)); 120.7 (*s*, C(6)); 116.1 (*s*, C(4)); 108.9 (*s*, C(7)); 66.6 (*s*, C(2′)); 63.1 (*s*, CH_2O); 48.8 (*s*, C(5′)); 29.6 (*s*, C(4′)), 24.4 (*s*, C(3′)). EI-MS (70 eV): 218 (20, M^+), 188 (20), 187 (100).

*[(2*S*)-1-(1,3-Benzothiazol-2-yl)pyrrolidin-2-yl]methanol* ((*S*)-**7**). (2*S*)-2-({[(*tert*-Butyl)(dimethyl)silyl]oxy}methyl)pyrrolidine [15] (750 mg, 3.48 mmol, 1.0 equiv.) was dissolved in THF (5 ml), and a 1.6M soln. of BuLi (2.50 ml, 4.00 mmol, 1.2 equiv.) in hexanes was slowly added at −78° in a acetone/dry ice bath. The resulting soln. was then stirred for 30 min at −78° and for 1 h at r.t. After cooling the soln. again to −78°, 2-chlorobenzothiazole (540 µl, 4.15 mmol, 1.2 equiv.) was added, and the mixture was allowed to warm to r.t. over 14 h. At 0° in an ice bath, aq. sat. $NaHCO_3$ (10 ml) was added dropwise. AcOEt (20 ml) was added, and the layers were separated. The aq. layer was extracted with AcOEt (2 ×

20 ml). The combined org. extracts were washed with brine (30 ml) and dried ($MgSO_4$). The solvents were evaporated under reduced pressure, and the crude product was purified by CC (SiO_2 (4 × 15 cm); cyclohexane/AcOEt 19:1). The isolated hydroxy-protected compound 2-[(2*S*)-({[(*tert*-butyl)(dimethyl)silyl]oxy}methyl)pyrrolidin-1-yl)-1,3-benzothiazole (331 mg, 949 μmol, 1.0 equiv.) was then dissolved in THF (7 ml) and ^{t}Bu$_4$NF · 3 H_2O (599 mg, 1.90 mmol, 2.0 equiv.) was added at 0° in an ice bath. The resulting mixture was stirred at r.t. for 3 h. AcOEt (10 ml) and H_2O (20 ml) were added. The layers were separated, and the aq. layer was extracted with AcOEt (3 × 10 ml). The org. layers were combined, washed with brine (15 ml) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The product was purified by CC (SiO_2 (4 × 10 cm); cyclohexane/AcOEt 1:1) to afford (*S*)-**7** (199 mg, 849 μmol, 57% over two steps). Yellowish semisolid. R_f (SiO_2; cyclohexane/AcOEt 1:1) 0.24. $[\alpha]_D^{20} = -104$ ($c = 0.989$, $CHCl_3$). IR (neat): 3265*m*, 2906*m*, 2869*m*, 1594*m*, 1564*m*, 1528*s*, 1473*w*, 1442*s*, 1359*s*, 1314*m*, 1274*m*, 1253*m*, 1238*m*, 1185*w*, 1153*w*, 1124*w*, 1067*w*, 1047*m*, 1016*m*, 925*w*, 902*w*, 848*w*, 749*s*, 724*s*, 684*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (*d*, *J* = 7.9, H–C(4)); 7.54 (*d*, *J* = 8.1, H–C(7)); 7.31 (*t*, *J* = 7.7, H–C(5)); 7.09 (*t*, *J* = 7.7, H–C(6)); 6.65–6.45 (br. *s*, OH); 4.30–4.20 (*m*, H–C(2′)); 3.86–3.71 (*m*, CH_2O); 3.60–3.51 (*m*, 1 H of CH_2(5′)); 3.50–3.40 (*m*, 1 H of CH_2(5′)); 2.27–2.16 (*m*, 1 H of Pyr); 2.13–2.193 (*m*, 2 H of Pyr); 1.83–1.70 (*m*, 1 H of Pyr). ^{13}C-NMR (101 MHz, $CDCl_3$): 167.2 (*s*, C(2)); 151.7 (*s*, C(3a)); 130.2 (*s*, C(7a)); 130.2 (C(5)); 126.1 (*s*, C(6)); 120.7 (*s*, C(7)); 118.6 (*s*, C(4)); 66.8 (*s*, C(2′)); 64.8 (*s*, CH_2O); 51.8 (*s*, C(5)); 29.8 (*s*, C(4′)), 21.0 (*s*, C(3′)). EI-MS (70 eV): 234 (20, M^+), 204 (21), 203 (100).

*2-[(2*S*)-2-(Bromomethyl)pyrrolidin-1-yl]-1,3-benzoxazole* ((*S*)-**8**). Compound (*S*)-**6** (336 mg, 1.54 mmol, 1.0 equiv.), Br_4C (765 mg, 2.31 mmol, 1.5 equiv.), and Ph_3P (605 mg, 2.31 mmol, 1.5 equiv.) were dissolved in CH_2Cl_2 (10 ml) at 0° in an ice bath. The resulting mixture was allowed to warm to r.t. overnight. The solvent was evaporated, and the crude was purified by CC (SiO_2 (4 × 17 cm); cyclohexane/AcOEt 4:1) to furnish (*S*)-**8** (417 mg, 1.48 mmol, 96%). Colorless solid. M.p. 51–54°. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.25. $[\alpha]_D^{20} = -59.1$ ($c = 0.981$, $CHCl_3$). IR (neat): 2956*w*, 2875*w*, 1630*s*, 1569*s*, 1456*s*, 1435*m*, 1381*m*, 1345*m*, 1328*m*, 1281*m*, 1244*s*, 1224*m*, 1203*m*, 1189*m*, 1137*m*, 1085*w*, 1004*m*, 902*m*, 824*m*, 795*m*, 739*s*, 644*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38 (*d*, *J* = 8.3, H–C(4)); 7.28 (*d*, *J* = 7.9, H–C(7)); 7.17 (*td*, *J* = 7.7, 1.0, H–C(5)); 7.02 (*td*, *J* = 7.8, 1.1, H–C(6)); 4.39–4.31 (*m*, H–C(2′)); 3.79–3.67 (*m*, CH_2(5′), 1 H of CH_2Br); 3.61 (*dd*, *J* = 9.9, 8.3, 1 H of CH_2Br); 2.24–1.95 (*m*, 4 H of Pyr). ^{13}C-NMR (101 MHz, $CDCl_3$): 160.5 (*s*, C(2)); 149.0 (*s*, C(7a)); 143.3 (*s*, C(3a)); 124.1 (*s*, C(5)); 120.8 (*s*, C(6)); 116.5 (*s*, C(4)); 109.9 (*s*, C(7)); 59.6 (*s*, C(2′)); 49.0 (*s*, C(5′)); 34.4 (*s*, *C*H_2Br), 30.2 (*s*, C(4′)), 23.8 (*s*, C(3′)). EI-MS (70 eV): 282 (17), 280 (17, M^+), 201 (20), 188 (13), 187 (100).

*2-[(2*S*)-2-(Bromomethyl)pyrrolidin-1-yl]-1,3-benzothiazole* ((*S*)-**9**). Compound (*S*)-**7** (321 mg, 1.37 mmol, 1.0 equiv.), Br_4C (683 mg, 2.06 mmol, 1.5 equiv.), and Ph_3P (539 mg, 2.05 mmol, 1.5 equiv.) were dissolved in CH_2Cl_2 (8 ml) at 0° in an ice bath. The resulting mixture was allowed to warm to r.t. overnight. The solvent was evaporated, and the crude product purified by CC (SiO_2 (4 × 17 cm); cyclohexane/AcOEt 4:1) to provide (*S*)-**9** (180 mg, 606 μmol, 44%). Colorless solid. M.p. 130–133°. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.47. $[\alpha]_D^{20} = -113$ ($c = 0.123$, $CHCl_3$). IR (neat): 3439*w*, 2959*w*, 2872*w*, 1594*m*, 1558*m*, 1530*s*, 1473*m*, 1442*m*, 1418*m*, 1358*m*, 1325*m*, 1269*m*, 1246*m*, 1120*m*, 1065*w*, 1017*w*, 912*w*, 880*w*, 751*s*, 727*s*, 684*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.53 (*t*, *J* = 7.4, 2 H of BzTh); 7.27–7.16 (*m*, 1 H of BzTh); 7.00 (*t*, *J* = 7.4, 1 H of BzTh); 4.38–4.25 (*m*, H–C(2′)); 5.76 (*d*, *J* = 9.8, 1 H of CH_2Br); 3.62–3.52 (*m*, 1 H of CH_2Br, 1 H of CH_2(5′)); 3.47–3.38 (*m*, 1 H of CH_2(5′)); 2.20–1.98 (*m*, 4 H of Pyr). ^{13}C-NMR (101 MHz, $CDCl_3$): 164.9 (*s*, C(2)); 153.0 (*s*, C(3a)); 130.8 (*s*, C(7a)); 126.1 (*s*, C(5)); 121.3 (*s*, C(6)); 120.8 (*s*, C(7)); 119.2 (*s*, C(4)); 61.3 (*s*, C(2′)); 51.2 (*s*, C(5′)); 34.0 (*s*, *C*H_2Br), 30.1 (*s*, C(3′)); 23.8 (*s*, C(4′)). EI-MS (70 eV): 298 (17), 296 (17, M^+), 217 (30), 216 (18), 204 (13), 203 (100).

*2-[(2*S*)-2-{[Bis(2-methylphenyl)phosphanyl]methyl}pyrrolidin-1-yl]-1,3-benzoxazole* ((*S*)-$\mathbf{L_N3}$). *Bis(2-methylphenyl)phosphine* (**10**; 91.4 mg, 427 μmol, 1.2 equiv.) was dissolved in THF (5 ml), and a 1.6M soln. of BuLi (270 μl, 432 μmol, 1.2 equiv.) in hexanes was slowly added at −78° in an acetone/dry ice bath. The resulting soln. was stirred for 20 min at −78° and then for 2 h at r.t. A soln. of (*S*)-**8** (100 mg, 356 μmol, 1.0 equiv.) in THF (3 ml) was added, after cooling the soln. again to −78°. The mixture was allowed to warm to r.t. overnight. At 0° in an ice bath, aq. sat. $NaHCO_3$ was added dropwise to quench the reaction. AcOEt was then added, and the layers were separated. The aq. layer was extracted with AcOEt (3×). The combined org. layers were washed with brine, dried ($MgSO_4$), and then

reduced to dryness under reduced pressure. CC (SiO_2 (5 × 17 cm); cyclohexane/AcOEt 4:1) afforded (*S*)-**L$_N$3** (122 mg, 294 μmol, 83%). Colorless solid. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.35. $[\alpha]_D^{20} = -87.1$ ($c = 0.421$, $CHCl_3$). IR (neat): 3054*w*, 2969*w*, 2875*w*, 1636*s*, 1576*s*, 1457*s*, 1381*m*, 1355*m*, 1283*w*, 1243*m*, 1148*w*, 1031*w*, 1003*w*, 917*m*, 739*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.78–7.73 (*m*, 1 H of *o*Tol); 7.38–7.28 (*m*, H–C(7), 2 H of *o*Tol/*o*Tol′); 7.22–7.10 (*m*, H–C(4), H–C(5), 4 H of *o*Tol/*o*Tol′); 7.08–6.97 (*m*, H–C(6), 1 H of *o*Tol/*o*Tol′); 4.28–4.16 (*m*, H–C(2′)); 3.77–3.69 (*m*, 1 H of CH_2(5′)); 3.68–3.61 (*m*, 1 H of CH_2(5′)); 2.87–2.80 (*m*, 1 H of CH_2P); 2.49 (*s*, Me of *o*Tol); 2.44 (*s*, Me of *o*Tol′); 2.39–1.96 (*m*, 1 H of CH_2P, 4 H of Pyr). ^{13}C-NMR (101 MHz, $CDCl_3$): 160.6 (*s*, C(2)); 148.9 (*s*, C(7a)); 143.4 (*s*, C(3a)); 142.6 (*d*, ^2J(C,P) = 26, C(2) of *o*Tol); 141.8 (*d*, ^2J(C,P) = 26, C(2) of *o*Tol′); 136.6 (*d*, ^1J(C,P) = 12, C(1) of *o*Tol); 135.6 (*d*, ^1J(C,P) = 13, C(1) of *o*Tol′); 131.8 (*s*, C(6) of *o*Tol); 131.6 (*s*, C(6) of *o*Tol′); 130.2 (*d*, ^3J(C,P) = 4.8, C(3) of *o*Tol); 130.1 (*d*, ^3J(C,P) = 5.0, C(3) of *o*Tol′); 128.8 (*s*, C(4) of *o*Tol); 128.6 (*s*, C(2) of *o*Tol′); 126.3 (*s*, C(5) of *o*Tol); 126.1 (*s*, C(5) of *o*Tol′); 123.9 (*s*, C(5)); 120.2 (*s*, C(6)); 116.2 (*s*, C(4)); 108.6 (*s*, C(7)); 57.4 (*d*, ^2J(C,P) = 23, 1 H, C(2′)); 48.2 (*s*, C(5′)); 32.7 (*d*, ^1J(C,P) = 15, *C*H$_2$P); 31.6 (*d*, ^3J(C,P) = 7.7, C(3′)); 24.0 (*s*, C(4′)); 21.4 (*d*, ^3J(C,P) = 5.9, Me of *o*Tol), 21.2 (*s*, Me of *o*Tol′). ^{31}P-NMR (162 MHz, $CDCl_3$): −43.2 (*s*). EI-MS (70 eV): 414 (5, M^+), 324 (21), 323 (100), 187 (27).

*2-[(2*S*)-2-{[Bis(2-methylphenyl)phosphanyl]methyl}pyrrolidin-1-yl]-1,3-benzothiazole* ((*S*)-**L$_N$4**). Compound (*S*)-**L$_N$4** (59%) was prepared as described for (*S*)-**L$_N$3** from (*S*)-**9** and **10**. M.p. 114–118°. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.47. $[\alpha]_D^{20} = -80.7$ ($c = 0.851$, $CHCl_3$). IR (neat): 3055*w*, 2966*w*, 2930*w*, 2874*w*, 1593*m*, 1560*m*, 1531*s*, 1444*s*, 1359*m*, 1318*m*, 1272*m*, 1254*m*, 1184*w*, 1141*w*, 1065*w*, 1016*m*, 925*m*, 909*m*, 847*m*, 754*s*, 748*s*, 725*m*, 680*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.99–7.91 (*m*, H–C(6) of *o*Tol); 7.62 (*d*, *J* = 8.1, H–C(7)); 7.57 (*d*, *J* = 7.8, H–C(4)); 7.40 (*t*, *J* = 7.2, H–C(5) of *o*Tol); 7.36–7.29 (*m*, H–C(4) of *o*Tol, H–C(6)); 7.24–7.20 (*m*, H–C(3) of *o*Tol); 7.20–7.14 (*m*, H–C(3), H–C(4), H–C(6) of *o*Tol′ each); 7.10–7.07 (*m*, H–C(5) of *o*Tol′); 7.07–7.03 (*m*, H–C(5)); 4.23–4.09 (*m*, H–C(2′)); 3.67–3.60 (*m*, 1 H of CH_2(5′)); 3.56–3.47 (*m*, 1 H of CH_2(5′)); 3.04–2.95 (*m*, 1 H of CH_2P); 2.49 (*s*, Me of *o*Tol); 2.46 (*s*, Me of *o*Tol′); 2.31–2.24 (*m*, 1 H of CH_2(3′)); 2.22–2.13 (*m*, 1 H of CH_2(3′), 1 H of CH_2(4′)); 2.10–2.01 (*m*, 1 H of CH_2(4′)); 1.99–1.91 (*m*, 1 H of CH_2P). ^{13}C-NMR (101 MHz, $CDCl_3$): 164.7 (*s*, C(2)); 153.3 (*s*, C(7a)); 142.2 (*d*, ^2J(C,P) = 26, C(2) of *o*Tol); 141.7 (*d*, ^2J(C,P) = 26, C(2) of *o*Tol′); 137.0 (*d*, ^1J(C,P) = 12, C(1) of *o*Tol); 135.6 (*d*, ^1J(C,P) = 13, C(1) of *o*Tol′); 132.5 (*s*, C(6) of *o*Tol); 131.6 (*s*, C(6) of *o*Tol′); 131.0 (*s*, C(3a)); 130.2–130.1 (*m*, C(3) of *o*Tol, C(3) of *o*Tol′); 128.8 (*s*, C(4) of *o*Tol); 128.6 (*s*, C(4) of *o*Tol′); 126.4 (*s*, C(5) of *o*Tol); 126.2 (*s*, C(5) of *o*Tol′); 125.9 (*s*, C(6)); 120.8 (*s*, C(5)); 120.7 (*s*, C(4)); 118.9 (*s*, C(7)); 59.4 (*d*, ^2J(C,P) = 23, C(2′)); 50.1 (*s*, C(5′)); 31.4 (*d*, ^3J(C,P) = 7.9, C(3′)); 31.2 (*d*, ^1J(C,P) = 15, *C*H$_2$P), 24.0 (*s*, C(4′)), 21.4 (*d*, ^3J(C,P) = 12, Me of *o*Tol); 21.3 (*d*, ^3J(C,P) = 12, Me of *o*Tol′). ^{31}P-NMR (162 MHz, $CDCl_3$): −42.5 (*s*). EI-MS (70 eV): 430 (6, M^+), 340 (22), 339 (100), 267 (13), 217 (13), 215 (11), 203 (61).

*2-((2*S*)-2-{[Di(*tert*-butyl)phosphanyl]methyl}pyrrolidin-1-yl)-1,3-benzoxazole Borane* ((*S*)-**L$_N$5**·**BH$_3$**). Compound (*S*)-**L$_N$5**·**BH$_3$** (89%) was prepared as described for (*S*)-**L$_N$3** from (*S*)-**8** and *di*(*tert*-*butyl)phosphine borane adduct* (**11**). M.p. 52–56°. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.36. $[\alpha]_D^{20} = -68.4$ ($c = 0.252$, $CHCl_3$). IR (neat): 2953*m*, 2874*m*, 1637*s*, 1578*s*, 1458*m*, 1382*m*, 1373*m*, 1284*w*, 1244*m*, 1147*w*, 1072*m*, 1023*w*, 919*w*, 813*m*, 740*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33 (*d*, *J* = 7.7, H–C(7)); 7.20 (*d*, *J* = 7.8, H–C(4)); 7.17–7.10 (*m*, H–C(5)); 7.03–6.94 (*m*, H–C(6)); 4.44–4.32 (*m*, H–C(2′)); 3.77–3.67 (*m*, 1 H of CH_2(5′)); 3.67–3.56 (*m*, 1 H of CH_2(5′)); 2.64 (*t*, *J* = 14, 1 H of CH_2P); 2.37–2.26 (*m*, 1 H of CH_2(3′)); 2.26–2.24 (*m*, 1 H of CH_2(3′)); 2.06–1.94 (*m*, CH_2(4′)); 1.63–1.51 (*m*, 1 H of CH_2P); 1.45 (*d*, ^3J(H,P) = 13, *t*Bu); 1.25 (*d*, ^3J(H,P) = 13, *t*Bu); 0.93–0.08 (br. *m*, BH_3). ^{13}C-NMR (101 MHz, $CDCl_3$): 160.5 (*s*, C(2)); 148.9 (*s*, C(7a)); 143.6 (*s*, C(3a)); 124.0 (*s*, C(5)); 120.4 (*s*, C(6)); 116.3 (*s*, C(4)); 108.5 (*s*, C(7)); 57.3 (*d*, ^2J(C,P) = 6.2, C(2′)); 48.1 (*s*, C(5′)); 33.4 (*d*, ^1J(C,P) = 29, Me_3C); 32.8 (*s*, C(3′)); 32.1 (*d*, ^1J(C,P) = 27, Me_3C); 28.2 (br. *s*, Me of *t*Bu); 27.9 (br. *s*, Me of *t*Bu′); 23.6 (*s*, C(4′)), 21.9 (*d*, ^1J(C,P) = 23, *C*H$_2$P). ^{31}P-NMR (162 MHz, $CDCl_3$): 39.8 (br. *d*, ^1J(P,B) = 68). EI-MS (70 eV): 360 (14), 359 (22, [*M* − H]$^+$), 343 (32), 303 (33), 290 (17), 289 (100), 247 (27), 245 (17), 233 (26), 232 (15), 213 (14), 201 (22), 187 (21), 178 (10), 57 (28). Anal calc. for $C_{20}H_{34}BN_2OP$ (360.2502): C 66.67, H 9.51, N 7.78; found: C 66.39, H 9.52, N 7.30.

*2-((2*S*)-2-{[Di(*tert*-butyl)phosphanyl]methyl}pyrrolidin-1-yl)-1,3-benzoxazole* ((*S*)-**L$_N$5**). Compound (*S*)-**L$_N$5**·**BH$_3$** (34.6 mg, 100 μmol) was dissolved in $HNEt_2$ (3.0 ml) under Ar and stirred at r.t. for 5–10 d. The conversion was monitored by ^{31}P-NMR analysis. After completion of the reaction, all

volatiles were removed under high vacuum at 60°, and (*S*)-**L$_N$5** was isolated as a colorless semisolid in quant. yield. ^{31}P-NMR (162 MHz, CD_2Cl_2): 21.2 (*s*).

*2-{(2*S*)-2-[(Di-(*tert*-butyl)phosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzothiazole Borane* ((*S*)-**L$_N$6**·**BH$_3$**). Compound (*S*)-**L$_N$6**·**BH$_3$** (81%) was prepared as described for (*S*)-**L$_N$3** from (*S*)-**9** and **11**. M.p. 171–176°. R_f (SiO_2; cyclohexane/AcOEt 4:1) 0.54. $[\alpha]_D^{20} = -120$ ($c = 0.210$, $CHCl_3$). IR (neat): 2948*m*, 2906*m*, 2871*m*, 1597*m*, 1538*s*, 1444*s*, 1393*w*, 1354*m*, 1316*w*, 1274*m*, 1184*m*, 1147*m*, 1123*m*, 1070*s*, 1019*m*, 921*m*, 815*m*, 753*s*, 678*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61 (*d*, $J = 7.7$, H–C(7)); 7.48 (*d*, $J = 7.8$, H–C(4)); 7.31–7.22 (*m*, H–C(6)); 7.05 (*t*, $J = 7.4$, H–C(5)); 4.52–4.39 (*m*, H–C(2′)); 3.60–3.47 (*m*, 1 H of CH_2(5′)); 3.46–3.33 (*m*, 1 H of CH_2(5′)); 3.06–2.91 (*m*, 1 H of CH_2P); 2.41–2.19 (*m*, 2 H of Pyr); 2.13–1.97 (*m*, 2 H of Pyr); 1.62–1.37 (*m*, 1 H of CH_2P); 1.52 (*d*, ^3J(H,P) = 13, ^{t}Bu); 1.25 (*d*, ^3J(H,P) = 12, ^{t}Bu); 0.93–0.12 (br. *q*, BH_3). ^{13}C-NMR (101 MHz, $CDCl_3$): 164.5 (*s*, C(2)); 153.4 (*s*, C(3a)); 131.0 (*s*, C(7a)); 126.0 (*s*, C(6)); 120.9 (*s*, C(5)); 120.9 (*s*, C(7)); 118.8 (*s*, C(4)); 59.3 (*d*, ^2J(C,P) = 5.7, C(2′)); 50.5 (*s*, C(5′)); 33.7 (*d*, ^1J(C,P) = 27, Me_3C); 32.7 (*s*, C(3′)); 32.2 (*d*, ^1J(C,P) = 27, Me_3C); 28.4 (br. *s*, Me of ^{t}Bu); 28.0 (br. *s*, Me of ^{t}Bu′); 23.9 (*s*, C(4′)); 20.7 (*d*, ^1J(C,P) = 23, CH_2P). ^{31}P-NMR (162 MHz, $CDCl_3$): 39.7 (br. *d*). EI-MS (70 eV): 376 (24), 375 (63, $[M-H]^+$), 374 (14), 343 (12), 320 (12), 319 (60), 318 (14), 306 (18), 305 (100), 263 (21), 261 (13), 249 (30), 248 (15), 231 (15), 229 (17), 217 (20), 215 (13), 203 (33), 57 (24).

*2-((2*S*)-2-{[Di(*tert*-butyl)phosphanyl]methyl}pyrrolidin-1-yl)-1,3-benzothiazole* ((*S*)-**L$_N$6**). Product (*S*)-**L$_N$6** was prepared as described for (*S*)-**L$_N$5** from (*S*)-**L$_N$6**·**BH$_3$**. ^{31}P-NMR (162 MHz, $CDCl_3$): 20.8 (*s*).

*2-{(2*S*)-2-[(Dicyclohexylphosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzoxazole Borane* ((*S*)-**L$_N$7**·**BH$_3$**). Compound (*S*)-**L$_N$7**·**BH$_3$** (78%) was prepared as described for (*S*)-**L$_N$3** from (*S*)-**8** and *dicyclohexylphosphine borane adduct* (**12**). M.p. 159–162°. R_f (SiO_2; cyclohexane/AcOEt 9:1) 0.16. $[\alpha]_D^{20} = -60.7$ ($c = 0.560$, $CHCl_3$). IR (neat): 3288*m*, 2926*m*, 2849*m*, 1635*s*, 1627*s*, 1593*m*, 1523*s*, 1516*s*, 1493*m*, 1381*m*, 1355*m*, 1346*m*, 1331*w*, 1240*m*, 1217*w*, 1192*w*, 1174*m*, 1068*w*, 951*w*, 916*w*, 882*w*, 737*s*, 692*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33 (*d*, $J = 7.7$, H–C(7)); 7.21 (*d*, $J = 7.9$, H–C(4)); 7.15 (*td*, $J = 7.7$, 1.0, H–C(5)); 7.00 (*td*, $J = 7.7$, 1.1, H–C(6)); 4.37–4.25 (*m*, H–C(2′)); 3.75–3.69 (*m*, 1 H of CH_2(5′)); 3.63–3.56 (*m*, 1 H of CH_2(5′)); 2.41 (*t*, $J = 15$, 1 H of CH_2P); 2.32–1.17 (*m*, 1 H of CH_2P, CH_2(3′), CH_2(4′), CH_2(5′), 20 H of Cy and Cy′); 0.82–0.05 (br. *q*, BH_3). ^{13}C-NMR (101 MHz, $CDCl_3$): 160.4 (*s*, C(2)); 149.0 (*s*, C(7a)); 143.5 (*s*, C(3a)); 124.1 (*s*, C(5)); 120.4 (*s*, C(6)); 116.3 (*s*, C(4)); 108.6 (*s*, C(7)); 56.4 (*d*, ^2J(C,P) = 6.3, C(2′)); 48.1 (*s*, C(5′)); 33.1 (*d*, ^1J(C,P) = 33, C(1) of Cy); 32.8 (*s*, C(3′)); 31.9 (*d*, ^1J(C,P) = 34, C(1) of Cy′); 27.3–26.0 (*m*, Cy/Cy′), 23.9 (*d*, ^1J(C,P) = 26, CH_2P), 23.7 (*s*, C(4′)). ^{31}P-NMR (162 MHz, $CDCl_3$): 21.0 (br. *d*). EI-MS (70 eV): 412 (17, M^+), 411 (29, $[M-H]^+$), 396 (13), 395 (50), 394 (12), 329 (11), 316 (20), 315 (100), 313 (25), 292 (10), 247 (11), 233 (13), 215 (17), 213 (17), 201 (12), 187 (13).

*2-{(2*S*)-2-[(Dicyclohexylphosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzoxazole* ((*S*)-**L$_N$7**). Product (*S*)-**L$_N$7** was prepared as described for (*S*)-**L$_N$5** from (*S*)-**L$_N$7**·**BH$_3$**. ^{31}P-NMR (162 MHz, $CDCl_3$): −11.2 (*s*).

*2-{(2*S*)-2-[(Dicyclohexylphosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzothiazole Borane* ((*S*)-**L$_N$8**·**BH$_3$**). Compound (*S*)-**L$_N$8**·**BH$_3$** (66%) was prepared as described for (*S*)-**L$_N$3** from (*S*)-**9** and **12**. M.p. 120–123°. R_f (SiO_2; cyclohexane/AcOEt 9:1) 0.40. $[\alpha]_D^{20} = -53.8$ ($c = 0.131$, $CHCl_3$). IR (neat): 2922*m*, 2915*m*, 2849*m*, 2369*m*, 1595*m*, 1560*w*, 1536*s*, 1442*s*, 1361*m*, 1318*m*, 1272*m*, 1252*m*, 1180*w*, 1125*m*, 1067*m*, 1016*m*, 1006*m*, 931*m*, 858*m*, 801*m*, 754*s*, 726*s*, 679*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61 (*d*, $J = 7.7$, H–C(7)); 7.50 (*d*, $J = 7.3$, H–C(4)); 7.29 (*t*, $J = 7.8$, H–C(6)); 7.06 (*t*, $J = 7.5$, H–C(5)); 4.46–4.33 (*m*, H–C(2′)); 3.61–3.48 (*m*, 1 H of CH_2(5′)); 3.48–3.34 (*m*, 1 H of CH_2(5′)); 2.72–2.58 (*m*, 1 H of CH_2P); 2.33–1.11 (*m*, 1 H of CH_2P, CH_2(3′), CH_2(4′), CH_2(5′), 20 H of Cy and Cy′); 0.79–0.10 (br. *q*, BH_3). ^{13}C-NMR (101 MHz, $CDCl_3$): 164.5 (*s*, C(2)); 153.4 (*s*, C(3a)); 131.0 (*s*, C(7a)); 126.1 (*s*, C(6)); 121.0 (*s*, C(5)); 120.9 (*s*, C(7)); 118.8 (*s*, C(4)); 58.1 (br. *s*, C(2′)); 50.4 (*s*, C(5′)); 33.2 (*d*, ^1J(C,P) = 32, C(1) of Cy); 32.6 (*s*, C(3′)); 32.0 (*d*, ^1J(C,P) = 33, C(1) of Cy′); 27.4–25.9 (*m*, Cy/Cy′); 23.8 (*s*, C(4′)); 22.8 (*d*, ^1J(C,P) = 27, CH_2P). ^{31}P-NMR (162 MHz, $CDCl_3$): 21.5 (br.). EI-MS (70 eV): 428 (26), 427 (85, $[M-H]^+$), 426 (19), 395 (17), 345 (14), 332 (21), 331 (100), 292 (12), 249 (11), 231 (20), 217 (13), 203 (18).

*2-{(2*S*)-2-[(Dicyclohexylphosphanyl)methyl]pyrrolidin-1-yl}-1,3-benzothiazole* ((*S*)-**L$_N$8**). Product (*S*)-**L$_N$8** was prepared as described for (*S*)-**L$_N$5** from (*S*)-**L$_N$8**·**BH$_3$**. ^{31}P-NMR (162 MHz, $CDCl_3$): −10.9 (*s*).

Synthesis of Ir Complexes: General Procedure 1 (*GP 1*). Ligand (200–300 μmol, 1.0 equiv.) and bis(cycloocta-1,5-diene)diiridium(I) dichloride (0.50 equiv.) were dissolved in CH_2Cl_2 (5 ml). The resulting soln. was heated at reflux for 2 h, before it was allowed to cool to r.t. At r.t., $NaBAr_F$ (1.3 equiv.) was added, and the resulting mixture was allowed to stir for 5 min. H_2O (5 ml) was then added, and the resulting biphasic mixture was vigorously stirred for 30 min. The layers were separated, and the aq. layer was extracted with CH_2Cl_2 (3 × 10 ml). The combined org. extracts were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The product was purified by CC (SiO_2: elution of the side products with cyclohexane/CH_2Cl_2 100:0 → 1:1, and then of the product 1:1 → 0:100 to afford the desired complex.

General Procedure 2 (*GP 2*). Ligand (10.0–20.0 mg, 1.0 equiv.) and $[Ir(cod)_2]BAr_F$ (1.0 equiv.) were mixed in abs. CH_2Cl_2 (1–2 ml) and stirred for 1 h at r.t. The solvent was evaporated, and the residue was purified by CC (SiO_2; elution of the side products with cyclohexane/CH_2Cl_2 100:0 → 1:1, and then of the product 1:1 → 0:100 to furnish the desired complex.

*[(η⁴-Cycloocta-1,5-diene)((*S*)-2-{2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}benzo[*d*]oxazole)iridium(I)] Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-**C$_N$1**). Complex (*S*)-**C$_N$1** (89%) was prepared according to *GP 1* from (*S*)-**L$_N$1** and $[Ir(cod)Cl]_2$. M.p. 131–133°. $[\alpha]_D^{20} = -36.3$ (*c* = 0.860, $CHCl_3$). IR (neat): 2928*w*, 2848*w*, 1643*m*, 1618*m*, 1589*m*, 1467*m*, 1436*w*, 1402*w*, 1353*s*, 1271*s*, 1251*m*, 1113*s*, 999*w*, 885*m*, 838*m*, 742*m*, 711*m*, 680*s*, 667*s*. ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.76 (br. *s*, H–C(4), 8 *o*-H of Ar_F); 7.58 (br. *s*, 4 *p*-H of Ar_F); 7.50–7.44 (*m*, 2 arom. *o*-H); 7.44–7.38 (*m*, H–C(5), 3 arom. H); 7.32–7.27 (*m*, 1 *p*-H of Ph/Ph′); 7.23–7.11 (*m*, H–C(6), H–C(7), 4 arom. H); 5.87–5.77 (*m*, H–C(2′)); 5.13–5.06 (*m*, 1 H of cod); 4.97–4.88 (*m*, 1 H of cod); 3.96–3.88 (*m*, 1 H of cod); 3.74–3.65 (*m*, 1 H of CH_2(5′)); 3.65–3.56 (*m*, 1 H of CH_2(5′)); 3.31 (*ddd*, *J* = 15, 10, 2.2, 1 H of CH_2P); 3.10–2.98 (*m*, 1 H of CH_2P, 1 H of cod); 2.71–2.56 (*m*, 1 H of CH_2(3′), 1 H of cod); 2.44–2.36 (*m*, 1 H of cod); 2.33–2.08 (*m*, CH_2(4′), 1 H of CH_2(3′), 4 H of cod); 1.75–1.65 (*m*, 1 H of cod); 1.65–1.56 (*m*, 1 H of cod). ^{13}C-NMR (101 MHz, CD_2Cl_2): 161.9 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F), 158.9 (*s*, C(2)); 147.6 (*s*, C(7a)); 138.7 (*s*, C(3a)); 134.9 (*s*, *o*-C of Ar_F); 133.6 (*d*, ^2J(C,P) = 13, C(2), C(6) of Ph); 131.9 (*d*, ^4J(C,P) = 2.3, C(4) of Ph); 131.2 (*d*, ^4J(C,P) = 2.5, C(4) of Ph′); 130.9 (*d*, ^3J(C,P) = 9.4, C(3), C(5) of Ph); 130.4 (*d*, ^1J(C,P) = 51, C(1) of Ph); 129.5–128.5 (*m*, CH of Ph′, *m*-C of Ar_F); 127.4 (*d*, ^1J(C,P) = 50, C(1) of Ph′); 125.4 (*s*, C(5)); 124.7 (*q*, ^1J(C,F) = 272, CF_3); 123.7 (*s*, C(6)); 117.7–117.4 (*m*, *p*-C of Ar_F); 117.4 (*s*, C(4)); 110.3 (*s*, C(7)); 97.7 (*d*, ^2J(C,P) = 9.6, CH of cod), 88.1 (*d*, ^2J(C,P) = 15, CH of cod); 66.1 (*s*, CH of cod); 61.1 (*s*, CH of cod); 60.5 (*d*, ^2J(C,P) = 5.8, C(2′)); 49.9 (*s*, C(5′)); 41.1 (*d*, ^1J(C,P) = 29, CH_2P); 36.1 (*d*, ^3J(C,P) = 4.3, CH_2 of cod); 34.8 (*d*, ^3J(C,P) = 13, C(3′)); 33.5 (*s*, CH_2 of cod); 29.2 (*d*, ^3J(C,P) = 1.6, CH_2 of cod); 26.2 (*d*, ^3J(C,P) = 2.6, CH_2 of cod); 23.5 (*s*, C(4′)). ^{31}P-NMR (162 MHz, CD_2Cl_2): 15.6 (*s*). ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.8 (*s*). FAB-MS (NBA): 688 (34), 687 (100, M^+), 686 (27), 685 (67), 577 (23), 575 (23), 573 (10). Anal calc. for $C_{64}H_{47}BF_{24}IrN_2OP$ (1550.03): C 49.59, H 3.06, N 1.81; found: C 49.40, H 3.39, N 1.81.

*[(η⁴-Cycloocta-1,5-diene)((*S*)-2-{2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}benzo[*d*]thiazole)iridium(I)] Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-**C$_N$2**). Complex (*S*)-**C$_N$2** (81%) was prepared according to *GP 1* from (*S*)-**L$_N$2** and $[Ir(cod)Cl]_2$. M.p. 69–71°. $[\alpha]_D^{20} = +17.9$ (*c* = 1.08, $CHCl_3$). IR (neat): 2889*w*, 1610*w*, 1534*m*, 1452*m*, 1352*s*, 1272*s*, 1113*s*, 1024*w*, 999*w*, 937*w*, 885*m*, 838*m*, 744*m*, 711*m*, 686*m*, 669*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.34 (*d*, ^2J = 8.2, H–C(4)); 7.77 (*s*, 8 *m*-H of Ar_F); 7.56 (*s*, 4 *p*-H of Ar_F); 7.55–7.51 (*m*, H–C(5)); 7.49 (*d*, *J* = 7.9, H–C(7)); 7.47–7.37 (*m*, 5 H of Ph/Ph′); 7.32–7.28 (*m*, 1 H of Ph/Ph′); 7.28–7.22 (*m*, H–C(6)); 7.20–7.10 (*m*, 4 H of Ph/Ph′); 6.35–6.22 (*m*, H–C(2′)); 4.85–4.77 (*m*, 1 H of cod); 4.51–4.42 (*m*, 1 H of cod); 4.12–4.06 (*m*, 1 H of cod); 3.52–3.34 (*m*, CH_2(5′), 1 H of CH_2P); 3.02–2.87 (*m*, 1 H of CH_2P, 1 H of cod); 2.78–2.63 (*m*, 1 H of CH_2(3′), 1 H of cod); 2.36–2.10 (*m*, 1 H of CH_2(3′), CH_2(4′), 4 H of cod); 2.10–1.97 (*m*, 1 H of cod); 1.63–1.45 (*m*, 2 H of cod). ^{13}C-NMR (101 MHz, $CDCl_3$): 165.8 (*s*, C(2)); 162.0 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F); 148.6 (*s*, C(3a)); 135.0 (*s*, *o*-C of Ar_F); 133.2 (*d*, ^2J(C,P) = 13, C(2), C(6) of Ph); 132.1 (*s*, C(4) of Ph); 131.5 (*s*, C(4) of Ph′); 130.7 (*d*, ^3J(C,P) = 9.4, C(3), C(5) of Ph); 130.1 (*d*, ^1J(C,P) = 51, C(1) of Ph); 129.5–128.6 (*m*, *o*-C of Ph′, *m*-C of Ph′, *m*-C of Ar_F); 128.0 (*d*, ^1J(C,P) = 50, C(1) of Ph′); 127.1 (*s*, C(5)); 126.8 (*s*, C(7a)); 128.4 (*q*, ^1J(C,F) = 272, CF_3); 124.2 (*s*, C(6)); 122.1 (*s*, C(4)); 121.9 (*s*, C(7)); 117.1 (*s*, *p*-C of Ar_F); 97.3 (*d*, ^2J(C,P) = 9.4, CH of cod); 89.6 (*d*, ^2J(C,P) = 15, CH of cod); 65.3 (*s*, CH of cod); 61.9 (*s*, CH of cod); 61.9 (*d*, ^2J(C,P) = 6.7, C(2′)); 53.5 (*s*, C(5′)); 40.8 (*d*, ^1J(C,P) = 31, CH_2P), 36.7 (*d*, ^3J(C,P) = 3.6, CH_2 of cod); 35.8 (*d*, ^3J(C,P) = 13, C(3′)); 33.6 (*s*, CH_2 of cod); 28.7 (*s*, CH_2 of cod); 25.9 (*s*, CH_2 of cod); 23.8 (*s*, C(4′)).

^{31}P-NMR (162 MHz, CD_2Cl_2): 15.6 (*s*). ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.8 (*s*). FAB-MS (NBA): 705 (11), 704 (37), 703 (100), 702 (27), 701 (60), 595 (12), 594 (16), 593 (30), 592 (10), 591 (18). Anal calc. for $C_{64}H_{47}BF_{24}IrN_2PS$ (1566.25): C 49.08, H 3.02, N 1.79; found: C 49.06, H 2.94, N 2.02.

*{(η⁴-Cycloocta-1,5-diene)[(*S*)-2-(2-{[bis(2-methylphenyl)phosphino]methyl}pyrrolidin-1-yl)benzo-[*d*]oxazole]iridium(I)} Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-**C$_N$3**). Complex (*S*)-**C$_N$3** (55%) was prepared according to *GP 2* from (*S*)-**L$_N$3** and $[Ir(cod)_2]BAr_F$. M.p. 72–77°. $[\alpha]_D^{20} = -37$ ($c = 0.140$, $CHCl_3$). IR (neat): 2965*w*, 2888*w*, 1647*m*, 1620*m*, 1468*m*, 1404*w*, 1355*m*, 1274*s*, 1117*s*, 1003*w*, 887*m*, 840*m*, 745*m*, 713*m*, 680*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 8.32–8.19 (br. *m*, H–C(6) of *o*Tol); 7.81 (*d*, *J* = 7.8, H–C(4)); 7.73 (br. *s*, 8 *o*-H of Ar_F); 7.56 (*s*, 4 *p*-H of Ar_F); 7.48–6.80 (*m*, 10 H of *o*Tol/*o*Tol′ and BzOx); 5.96–5.85 (*m*, H–C(2′)); 4.98–4.89 (*m*, 1 H of cod); 4.68–4.53 (*m*, 1 H of cod); 3.98–3.89 (*m*, 1 H of cod); 3.89–3.74 (*m*, 2 H of cod); 3.61–3.52 (*m*, 1 H of CH_2P); 2.77–2.58 (*m*, 1 H of CH_2P, 1 H of $CH_2(5')$, 1 H of $CH_2(3')$); 2.58–1.98 (*m*, 8 H of cod and Pyr, Me of *o*Tol); 1.93 (*s*, Me of *o*Tol′); 1.67–1.43 (*m*, 1 H of $CH_2(4')$, 2 H of cod). ^{13}C-NMR (101 MHz, CD_2Cl_2): 161.8 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F); 158.0 (*s*, C(2)); 147.7 (*s*, C(7a)); 141.7 (br., C(2) of *o*Tol); 141.2 (br, C(2) of *o*Tol′); 140.3 (br. *d*, C(6) of *o*Tol); 138.8 (*s*, C(3a)); 134.9 (*s*, *o*-C of Ar_F); 132.8–132.3 (*m*, C(4) of *o*Tol, C(3) of *o*Tol, C(3) of *o*Tol′); 131.6 (br. *s*, C(6) of *o*Tol′); 130.0 (br., C(1) of *o*Tol); 129.3–128.4 (*m*, *m*-C of Ar_F); 128.4 (*q*, ^1J(C,F) = 272, CF_3); 127.9–125.0 (*m*, C(1) of *o*Tol′, C(4) of *o*Tol′, C(5) of *o*Tol, C(5) of *o*Tol, C(5)); 123.7 (*s*, C(6)); 117.8–117.4 (*m*, *p*-C of Ar_F, C(4′)); 110.4 (*s*, C(7)); 96.9 (br. *d*, CH of cod); 87.2 (*d*, ^2J(C,P) = 15, CH of cod); 66.7 (*s*, CH of cod); 62.6 (*s*, CH of cod); 59.6 (br. *d*, ^2J(C,P) = 4.0, C(2′)); 50.0 (*s*, CH_2 of cod); 43.9 (*d*, ^1J(C,P) = 26, *C*H_2P); 36.8 (br. *s*, C(5′)); 36.0 (*d*, ^3J(C,P) = 11, C(3′)); 33.9 (*s*, CH_2 of cod); 28.4 (*s*, CH_2 of cod); 25.6 (*s*, C(4′)); 24.0 (br. *s*, Me of *o*Tol); 23.1 (*s*, CH_2 of cod); 21.8 (br. *s*, Me of *o*Tol). ^{31}P-NMR (162 MHz, CD_2Cl_2): 26.1/10.2 (2 br. *s*). These signals indicate the presence of a mixture of rotamers in a ratio of 25:1. ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.8 (*s*). ESI-MS: 715 (100, M^+). Anal calc. for $C_{66}H_{51}BF_{24}IrN_2OP$ (1578.09): C 50.23, H 3.26, N 1.78; found: C 50.69, H 3.94, N 1.93.

*{(η⁴-Cycloocta-1,5-diene)-[(*S*)-2-(2-{[bis(2-methylphenyl)phosphino]methyl}pyrrolidin-1-yl)ben-zo[*d*]thiazole]iridium(I)} Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-**C$_N$4**). Complex (*S*)-**C$_N$4** (97%) was prepared according to *GP 2* from (*S*)-**L$_N$4** and $[Ir(cod)_2]BAr_F$. M.p. 118–121°. $[\alpha]_D^{20} = -1.0$ ($c = 0.271$, $CHCl_3$). IR (neat): 3064*w*, 2964*w*, 2889*w*, 1787*w*, 1545*m*, 1453*m*, 1355*m*, 1275*s*, 1116*s*, 888*m*, 839*m*, 744*m*, 714*m*, 681*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 8.52 (*d*, *J* = 8.3, H–C(4)); 8.18–8.08 (*m*, H–C(6) of *o*Tol); 7.75 (*s*, 8 *o*-H of Ar_F); 7.69–7.60 (*m*, H–C(5), H–C(7)); 7.57 (*s*, 4 *p*-H of Ar_F); 7.44–7.22 (*m*, H–C(6), H–C(6) of *o*Tol′, H–C(5) of *o*Tol, H–C(4) of *o*Tol, H–C(3) of *o*Tol); 7.18–7.10 (*m*, H–C(3) of *o*Tol′); 7.08–6.95 (*m*, H–C(4) of *o*Tol′); 6.94–6.85 (*m*, H–C(5) of *o*Tol′); 6.54–6.41 (*m*, H–C(2′)); 4.82–4.72 (*m*, 1 H of cod); 4.31–4.20 (*m*, 1 H of cod); 4.14–4.05 (*m*, 1 H of cod); 3.77–3.64 (*m*, 1 H of CH_2P); 3.63–3.52 (*m*, 2 H of cod); 2.85–2.65 (*m*, $CH_2(5')$, 1 H of CH_2P); 2.65–2.55 (*m*, 1 H of cod); 2.46–2.15 (*m*, $CH_2(3')$, $CH_2(4')$, Me of *o*Tol, 2 H of cod); 2.15–1.95 (*m*, 3 H of cod); 1.90 (*s*, Me of *o*Tol′); 1.57–1.44 (*m*, 1 H of cod). ^{13}C-NMR (101 MHz, CD_2Cl_2): 165.2 (*s*, C(2)); 161.8 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F); 148.8 (*s*, C(3a)); 141.5 (br. *s*, C(2) of *o*Tol); 140.6 (br. *d*, C(2) of *o*Tol′); 139.4 (*d*, ^2J(C,P) = 30, C(6) of *o*Tol); 134.9 (*s*, *o*-C of Ar_F); 132.7–132.3 (*m*, C(4) of *o*Tol, C(3) of *o*Tol, C(3) of *o*Tol′); 131.5 (br. *s*, C(6) of *o*Tol′); 131.0 (br. *s*, C(4) of *o*Tol); 130.3 (br. *d*, C(1) of *o*Tol); 129.5–128.4 (*m*, *m* -C of Ar_F); 127.2 (*s*, C(7a)); 127.0 (*s*, C(5)); 126.7 (*d*, ^3J(C,P) = 9.6, C(5) of *o*Tol); 125.6 (*d*, ^3J(C,P) = 9.6, C(5) of *o*Tol′); 125.0 (*q*, ^1J(C,F) = 272, CF_3); 125.2 (br. *d*, C(1) of *o*Tol′); 124.0 (*s*, C(6)); 120.6 (*s*, C(7)); 121.8 (*s*, C(4)); 117.7–117.4 (*m*, *p*-C of Ar_F); 96.2 (*d*, ^2J(C,P) = 8.1, CH of cod); 87.9 (*d*, ^2J(C,P) = 16, CH of cod); 66.3 (*s*, CH of cod); 63.1 (*s*, CH of cod); 62.2 (*d*, ^2J(C,P) = 9.0, C(2′)); 53.9 (*s*, CH_2 of cod); 43.7 (*d*, ^1J(C,P) = 29, *C*H_2P), 37.2 (br. *s*, C(5′)); 36.7 (*d*, ^3J(C,P) = 13, C(3′)); 34.0 (*s*, CH_2 of cod); 28.3 (*s*, CH_2 of cod); 25.5 (*s*, CH_2 of cod); 24.3 (*s*, C(4′)); 23.0 (*d*, ^3J(C,P) = 5.6, Me of *o*Tol); 21.6 (br. *s*, Me of *o*Tol′). ^{31}P-NMR (162 MHz, CD_2Cl_2): 22.4/3.32 (br. *s*). These signals indicate the presence of a mixture of rotamers in a ratio of 17:1. ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.8 (*s*). FAB-MS (NBA): 733 (12), 732 (38), 731 (100, M^+), 730 (24), 729 (59), 623 (11), 622 (11), 621 (21), 620 (11), 619 (19), 617 (13).

*{(η⁴-Cycloocta-1,5-diene)-[(*S*)-2-(2-{[di(*tert*-butyl)phosphino]methyl}pyrrolidin-1-yl)benzo[*d*]oxa-zole]iridium(I)} Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-**C$_N$5**). Complex (*S*)-**C$_N$5** (95%) was prepared according to *GP 2* from (*S*)-**L$_N$5** and $[Ir(cod)_2]BAr_F$. M.p. 210–213°. $[\alpha]_D^{20} = +7.1$ ($c = 0.220$, $CHCl_3$). IR (neat): 2968*w*, 2892*w*, 1650*m*, 1622*m*, 1469*m*, 1406*w*, 1354*m*, 1272*s*, 1162*s*, 1121*s*, 1005*w*, 887*m*, 840*m*, 714*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 7.73 (br. *s*, 8 *o*-H of Ar_F); 7.59–7.52 (*m*, 4 *p*-H of Ar_F,

H–C(4)); 7.40–7.33 (*m*, H–C(5), H–C(7)); 7.23 (*td*, *J* = 7.8, 1.1, H–C(6)); 5.32–5.20 (*m*, 2 H of cod); 4.45–4.37 (*m*, 1 H of cod); 4.13–4.05 (*m*, H–C(2′)); 3.97–3.76 (*m*, CH_2(5′), CH of cod); 2.82 (*ddd*, ^2J(H,P) = 16, ^2J = 12, *J* = 1.8, 1 H of CH_2P); 2.70–2.57 (*m*, 2 H of cod); 2.42–2.34 (*m*, 1 H of cod); 2.34–2.22 (*m*, 1 H of CH_2(3′)); 2.20–1.95 (*m*, 1 H of CH_2(3′), CH_2(4′), 2 H of cod); 1.95–1.77 (*m*, 1 H of CH_2P, 1 H of cod); 1.46–1.22 (*m*, Me_3C, 2 H of cod); 1.17 (*d*, ^3J(H,P) = 14, Me_3C). ^{13}C-NMR (101 MHz, CD_2Cl_2): 161.8 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F); 157.5 (*s*, C(2)); 148.0 (*s*, C(7a)); 138.9 (*s*, C(3a)); 134.9 (*s*, *o*-C of Ar_F); 129.5–128.4 (*m*, *m*-C of Ar_F); 125.2 (*s*, C(5)); 124.7 (*q*, ^1J(C,F) = 272, CF_3); 123.8 (*s*, C(6)); 118.8 (*s*, C(4)); 117.5 (br. *s*, *p*-C of Ar_F); 110.4 (*s*, C(7)); 92.0 (*d*, ^2J(C,P) = 8.5, CH of cod); 82.9 (*d*, ^2J(C,P) = 15, CH of cod); 65.7 (*s*, CH of cod); 58.5 (*s*, CH of cod); 57.9 (*d*, ^2J(C,P) = 7.4, C(2′)); 49.7 (*s*, C(5′)); 38.5 (*d*, ^3J(C,P) = 4.2, CH_2 of cod); 38.3 (*d*, ^1J(C,P) = 17, Me_3C); 36.5 (*d*, ^3J(C,P) = 8.1, CH_2 of cod); 36.0 (*d*, ^1J(C,P) = 18, Me_3C); 34.3 (*d*, ^1J(C,P) = 21, *C*H_2P); 33.7 (*s*, C(3′)); 30.7 (*d*, ^2J(C,P) = 4.5, Me of ^{t}Bu); 30.0–29.2 (br. *m*, Me of ^{t}Bu′); 28.8 (*s*, CH_2 of cod); 24.6 (*s*, C(4′)); 24.1 (*s*, CH_2 of cod). ^{31}P-NMR (162 MHz, CD_2Cl_2): 46.8 (*s*). ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.9 (*s*). FAB-MS (NBA): 648 (32), 647 (100, M^+), 646 (21), 645 (61), 537 (12), 423 (12).

*{(η⁴-Cycloocta-1,5-diene)-[(*S*)-2-(2-{[di(*tert*-butyl)phosphino]methyl}pyrrolidin-1-yl)benzo[*d*]thiazole]-iridium(I)} Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-$\mathbf{C_N6}$). Complex (*S*)-$\mathbf{C_N6}$ (94%) was prepared according to *GP 2* from (*S*)-$\mathbf{L_N6}$ and $[Ir(cod)_2]BAr_F$. M.p. 228–231°. $[\alpha]_D^{20} = +140$ (*c* = 1.30, $CHCl_3$). IR (neat): 2962*w*, 2888*w*, 1611*w*, 1546*m*, 1455*w*, 1353*m*, 1272*s*, 1163*s*, 1122*s*, 1021*w*, 887*m*, 839*w*, 747*w*, 714*m*, 681*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 8.35 (*d*, *J* = 8.2, H–C(4)); 7.73 (br. *s*, 8 *o*-H of Ar_F); 7.65 (*d*, *J* = 7.9, H–C(7)); 7.59–7.51 (*m*, H–C(5), 4 *p*-H of Ar_F); 7.30 (*t*, *J* = 7.7, H–C(6)); 5.76–5.65 (*m*, H–C(2′)); 5.37–5.29 (*m*, 1 H of cod); 4.43–4.34 (*m*, 1 H of cod); 4.07–3.97 (*m*, 1 H of cod); 3.78–3.58 (*m*, CH_2(5′)); 3.37–3.26 (*m*, 1 H of cod); 2.86 (*ddd*, ^2J(H,P) = 16, ^2J = 11, *J* = 1.9, 1 H of CH_2P); 2.75–2.62 (*m*, 2 H of cod); 2.33–2.16 (*m*, 1 H of CH_2(3′), 1 H of CH_2(4′), 1 H of cod); 2.16–1.91 (*m*, 1 H of CH_2P, 1 H of CH_2(3′), 1 H of CH_2(4′), 2 H of cod); 1.82–1.71 (*m*, 1 H of cod); 1.50–1.17 (*m*, ^{t}Bu, 2 H of cod); 1.11 (*d*, ^3J(H,P) = 14, ^{t}Bu′). ^{13}C-NMR (101 MHz, CD_2Cl_2): 164.6 (*s*, C(2)); 161.8 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F); 149.2 (*s*, C(3a)); 134.9 (*s*, *o*-C of Ar_F); 129.5–128.2 (*m*, *m*-C of Ar_F); 127.2 (*s*, C(7a)); 126.8 (*s*, C(5)); 124.7 (*q*, ^1J(C,F) = 272, CF_3); 124.0 (*s*, C(6)); 123.5 (*s*, C(4)); 121.7 (*s*, C(7)); 117.5 (br. *s*, *p*-C of Ar_F); 91.2 (*d*, ^2J(C,P) = 7.6, CH of cod); 83.8 (*d*, ^2J(C,P) = 16, CH of cod); 67.3 (*s*, CH of cod); 59.6 (*d*, ^2J(C,P) = 7.7, C(2′)); 57.5 (*s*, CH of cod); 53.4 (*s*, C(5′)); 38.7 (*d*, ^3J(C,P) = 4.4, CH_2 of cod); 37.6 (*d*, ^1J(C,P) = 16, Me_3C); 37.3 (*d*, ^3J(C,P) = 8.1, CH_2 of cod); 35.7 (*d*, ^1J(C,P) = 18, Me_3C); 34.2 (*s*, C(3′)); 34.0 (*d*, ^1J(C,P) = 21, *C*H_2P), 30.4 (*d*, ^2J(C,P) = 4.6, Me of ^{t}Bu); 28.3 (br. *s*, Me of ^{t}Bu′); 27.0 (*s*, CH_2 of cod); 24.8 (*s*, C(4′)); 24.0 (*d*, ^3J(C,P) = 2.9, CH_2 of cod). ^{31}P-NMR (162 MHz, CD_2Cl_2): 46.7 (*s*). ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.7 (*s*). FAB-MS (NBA): 664 (31), 663 (100, M^+), 662 (21), 661 (59), 555 (11), 553 (15), 497 (12), 441 (11), 439 (14). Anal calc. for $C_{60}H_{55}BF_{24}IrN_2PS$ (1526.12): C 47.22, H 3.63, N 1.84; found: C 46.78, H 3.92, N 1.91.

*[(η⁴-Cyclooctadiene)-((*S*)-2-{2-[(dicyclohexylphosphino)methyl]pyrrolidin-1-yl}benzo[*d*]oxazole)iridium(I)] Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-$\mathbf{C_N7}$). Complex (*S*)-$\mathbf{C_N7}$ (84%) was prepared according to *GP 2* from (*S*)-$\mathbf{L_N7}$ and $[Ir(cod)_2]BAr_F$. M.p.: 142–146°. $[\alpha]_D^{20} = +60.9$ (*c* = 0.330, $CHCl_3$). IR (neat): 2937*w*, 2860*w*, 1648*m*, 1620*w*, 1596*w*, 1467*w*, 1402*w*, 1354*m*, 1273*s*, 1119*s*, 1005*w*, 887*m*, 840*w*, 745*m*, 713*m*, 681*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 7.74 (*s*, 8 *m*-H of Ar_F); 7.61 (*d*, ^2J = 8.0, H–C(4)); 7.57 (*s*, 4 *p*-H of Ar_F); 7.40–7.34 (*m*, H–C(5), H–C(7)); 7.24 (*td*, ^2J = 7.9, *J* = 1.1, H–C(6)); 5.21–5.08 (*m*, H–C(2′)); 4.77–4.70 (*m*, 1 H of cod); 4.70–4.62 (*m*, 1 H of cod); 4.20–4.10 (*m*, 1 H of cod); 3.93–3.77 (*m*, CH_2(5′)); 3.54–3.44 (*m*, 1 H of cod); 2.66–2.54 (*m*, 1 H of CH_2P, 2 H of cod); 2.40–2.24 (*m*, 1 H of CH_2(3′), 1 H of cod); 2.21–1.84 (*m*, 1 H of CH_2P, 10 H of Pyr, cod, Cy/Cy′); 1.84–1.67 (*m*, 5 H of Cy/Cy′); 1.64–1.01 (*m*, 14 H of cod, Cy/Cy′); 0.95–0.82 (*m*, 1 H of cod). ^{13}C-NMR (101 MHz, CD_2Cl_2): 161.8 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar_F); 158.0 (*s*, C(2)); 147.8 (*s*, C(7a)); 138.8 (*s*, C(3a)); 134.9 (*s*, *o*-C of Ar_F); 129.6–128.4 (*m*, *m*-C of Ar_F); 125.4 (*s*, C(5)); 124.6 (*q*, ^1J(C,F) = 272, CF_3); 123.9 (*s*, C(6)); 118.0 (*s*, C(4)); 117.6 (br. *s*, *p*-C of Ar_F); 110.4 (*s*, C(7)); 95.3 (*d*, ^2J(C,P) = 9.5, CH of cod); 86.8 (*d*, ^2J(C,P) = 15, CH of cod); 65.8 (*s*, CH of cod); 58.8 (*s*, CH of cod); 58.8 (*d*, ^2J(C,P) = 6.1, C(2′)); 49.9 (*s*, C(5′)); 37.5 (*d*, ^3J(C,P) = 3.9, CH_2 of cod); 37.0 (*d*, ^1J(C,B) = 26, C(1) of Cy); 35.9 (*d*, ^3J(C,P) = 10, CH_2 of cod); 33.4 (*s*, C(3′)); 33.0 (*d*, ^1J(C,P) = 26, *C*H_2P), 31.6 (*d*, ^1J(C,B) = 26, C(1) of Cy′); 30.1 (*s*, CH_2 of Cy/Cy′); 29.8 (*s*, CH_2 of Cy/Cy′); 29.5 (*s*, CH_2 of Cy/Cy′); 29.0 (*s*, CH_2 of Cy/Cy′); 26.9–26.7 (*m*, CH_2 of cod, CH_2 of Cy/Cy′); 26.1 (*s*, CH_2 of Cy/Cy′); 25.9 (*s*, CH_2 of Cy/Cy′); 24.8 (*d*, ^3J(C,P) = 2.5, CH_2 of cod); 24.3 (*s*, C(4′)).

^{31}P-NMR (162 MHz, CD_2Cl_2): 24.9 (*s*). ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.7 (*s*). FAB-MS (NBA): 700 (34), 699 (100, M^+), 698 (25), 697 (62), 587 (18), 585 (1).

*[(η⁴-1,5-Cyclooctadiene)-((*S*)-2-{2-[(dicyclohexylphosphino)methyl]pyrrolidin-1-yl}benzo[*d*]thiazole)-iridium(I)]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate* ((*S*)-**C$_N$8**). Complex (*S*)-**C$_N$8** (98%) was prepared according to *GP 2* from (*S*)-**L$_N$8** and [Ir(cod)$_2$]BAr$_F$. M.p. 120–124°. $[\alpha]_D^{20} = +123$ (c = 0.450, $CHCl_3$). IR (neat): 2936*m*, 2859*m*, 1611*w*, 1544*m*, 1453*m*, 1354*s*, 1273*s*, 1115*s*, 1003*w*, 887*m*, 839*m*, 747*m*, 713*m*, 680*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 8.29 (*d*, ^2J = 8.1, H–C(4)); 7.74 (br. *s*, 8 *o*-H of Ar$_F$); 7.66 (*d*, ^2J = 7.9, H–C(7)); 7.62–7.50 (*m*, H–C(5), 4 *p*-H of Ar$_F$), 7.31 (*t*, ^2J = 8.1, H–C(6)); 5.63–5.51 (*m*, H–C(2′)); 4.89–4.80 (*m*, 1 H of cod); 4.58–4.50 (*m*, 1 H of cod); 3.71–3.52 (*m*, CH_2(5′), 2 H of cod); 2.74–2.54 (*m*, 1 H of CH_2P, 2 H of cod); 2.38–2.22 (*m*, 1 H of CH_2(3′), 1 H of cod); 2.22–1.82 (*m*, 1 H of CH_2P, 1 H of CH_2(3′), CH_2(4′), 7 H of cod, Cy/Cy′); 1.82–1.55 (*m*, 7 H of Cy/Cy′); 1.55–1.45 (*m*, 1 H of cod, 1 H of Cy/Cy′); 1.45–1.20 (*m*, 8 H of cod, Cy/Cy′); 1.20–1.02 (*m*, 2 H of Cy/Cy′); 0.97–0.81 (*m*, 1 H of cod). ^{13}C-NMR (101 MHz, CD_2Cl_2): 165.2 (*s*, C(2)); 161.8 (*q*, ^1J(C,B) = 50, *ipso*-C of Ar$_F$); 148.8 (*s*, C(3a)); 134.9 (*s*, *m*-C of Ar$_F$); 129.6–128.3 (*m*, *m*-C of Ar$_F$); 127.0 (*s*, C(5)); 127.0 (*s*, C(7a)); 124.7 (*q*, ^1J(C,F) = 272, CF_3); 124.1 (*s*, C(6)); 122.2 (*s*, C(4)); 121.7 (*s*, C(7)); 117.6 (*s*, *p*-C of Ar$_F$); 94.4 (*d*, ^2J(C,P) = 9.2, CH of cod); 92.9 (*d*, ^2J(C,P) = 14, CH of cod); 65.7 (*s*, CH of cod); 60.9 (*d*, ^2J(C,P) = 6.4, C(2′)); 58.1 (*s*, CH of cod); 53.6 (*s*, C(5′)); 37.7 (*d*, ^3J(C,P) = 3.8, CH_2 of cod); 37.2 (*d*, ^1J(C,P) = 25, C(1) of Cy); 36.7 (*d*, ^3J(C,P) = 10, CH_2 of cod); 33.6 (*s*, C(3′)); 32.9 (*d*, ^1J(C,P) = 27, *C*H$_2$P), 32.2 (*d*, ^1J(C,P) = 25, C(1) of Cy′); 29.5–29.2 (*m*, CH_2 of Cy/Cy′); 28.8 (*s*, CH_2 of Cy/Cy′); 27.2–26.6 (*m*, CH_2 of cod, CH_2 of Cy/Cy′); 26.1 (*s*, CH_2 of Cy/Cy′); 25.8 (*s*, CH_2 of Cy/Cy′); 24.8 (br. *d*, ^3J(C,P) = 2.4, CH_2 of cod); 24.6 (*s*, C(4′)). ^{31}P-NMR (162 MHz, CD_2Cl_2): 22.9 (*s*). ^{19}F-NMR (377 MHz, CD_2Cl_2): −62.8 (*s*). FAB-MS (NBA): 716 (36), 715 (100, M^+), 714 (23), 713 (59), 605 (13), 604 (14), 603 (27), 601 (16). Anal calc. for $C_{64}H_{59}BF_{24}IrN_2PS$ (1578.20): C 48.71, H 3.77, N 1.78; found: C 48.78, H 4.06, N 1.91.

Catalytic Hydrogenation at Elevated Pressure: General Procedure for Proline-Based P,N Catalysts. A stock soln. of the precatalyst was prepared in CH_2Cl_2 (5 mM in precatalyst). The substrate (250 μmol) was weighed into a separate vial, and 0.5 ml of the stock soln. (1 mol-% of precatalyst) were added. A stir bar was added, and four vials (1.5 ml) were placed into a 60-ml autoclave (*Premex AG*, CH-Lengnau). The autoclave was purged, pressurized with H_2 gas (*Carbagas*, Switzerland; 99.995%), and placed on a stirring plate. The mixtures were stirred at r.t. for 2 h. After pressure release, the soln. was concentrated in a stream of N_2 and taken up in heptane (3 ml), and filtered through a short plug of SiO_2 (0.5 × 6 cm), eluting with heptane/^{i}PrOH 7:3. The filtrates were analyzed by GC and HPLC [12a][6a].

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