The synthesis of new oxazoline-containing bifunctional catalysts and their application in the addition of diethylzinc to aldehydes†

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The straightforward preparation of new modular oxazoline-containing bifunctional catalysts is reported employing a microwave-assisted Buchwald–Hartwig aryl amination as the key step. Covalent attachment of 2-(*o*-aminophenyl)oxazolines and pyridine derivatives generated in good-to-high yields a series of ligands in two or three steps in which each part was altered independently to tune the activity and the selectivity of the corresponding catalysts. These catalysts prepared *in situ* were subsequently applied in the asymmetric addition of diethylzinc to various aldehydes, producing the corresponding alcohols with enantioselectivities of up to 68%. A transition state model, based on relevant X-ray crystal structures, has also been proposed to explain the observed stereoselectivities.

Introduction

Chiral oxazoline-containing ligands have attracted considerable attention in asymmetric catalysis due to their ready accessibility, modular nature and applicability in a wide range of metal-catalysed transformations.[1] The majority of these ligands are easily synthesised in a few high-yielding steps from commercially available chiral amino alcohols. The wide variety of enantiomerically pure amino alcohols allows for the preparation of highly modular asymmetric building blocks in the design of powerful and selective catalysts. Thus, we have recently reported the straightforward synthesis of tridendate bis(oxazoline)-based ligands **1–2** and proline-oxazoline ligands **3** from the readily available 2-(*o*-aminophenyl)oxazoline scaffold **4** (Scheme 1).[2] The ligands **1–3** were applied to the enantioselective Nozaki–Hiyama–Kishi (NHK) allylation, crotylation and methallylation of a series of aromatic and aliphatic aldehydes, providing the products in both high yields and high enantioselectivities.[2b,2c,3]

In connection with this work, we became interested in the design and synthesis of new oxazoline-containing ligands derived from **4** for applications in asymmetric bifunctional catalysis. Over the past decade, this concept based on the synergistic activation of electrophiles and nucleophiles has found numerous applications in asymmetric catalysis.[4,5] In particular, complexes containing both a Lewis-acidic centre and a Lewis-basic moiety have recently emerged as highly active and selective catalysts. Thus far, many kinds of chiral bifunctional catalysts have been developed; however, very few examples of oxazoline-containing bifunctional catalysts have been reported for this purpose.[6] So, we envisioned that a novel range of oxazoline-containing ligands could be readily made by covalent attachment of the chiral oxazoline framework **4** to pyridine derivatives using a palladium-catalysed

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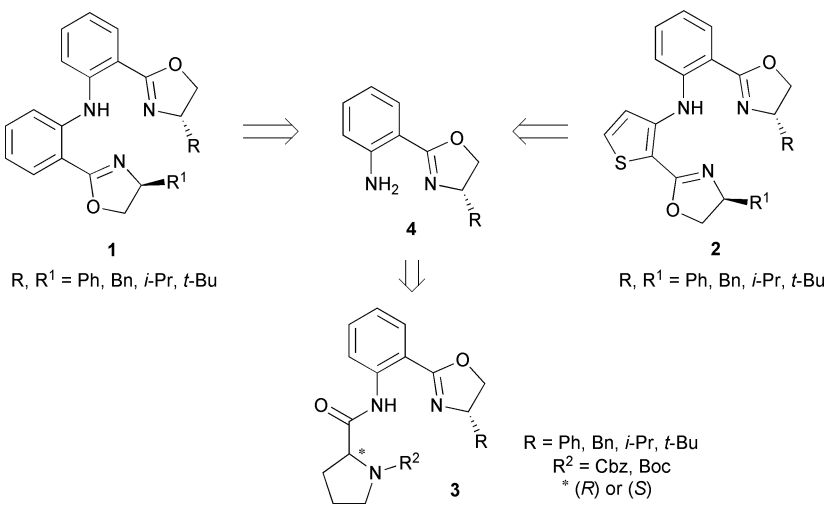
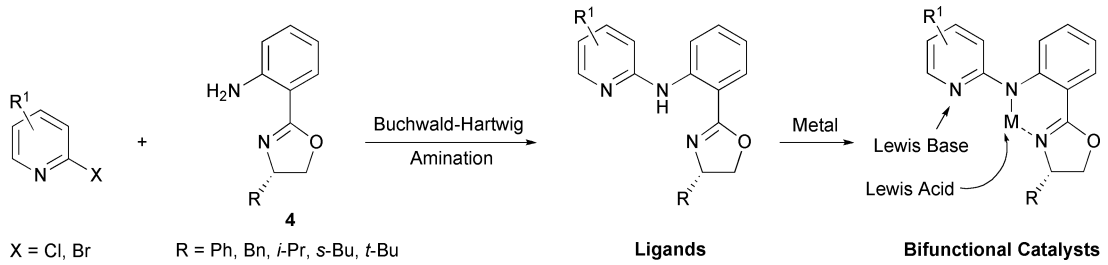


Scheme 1 The 2-(*o*-aminophenyl)oxazoline scaffold in previous ligand design.



Scheme 2 Strategy for designing new bifunctional metal–ligand catalysts.

Buchwald–Hartwig amination (Scheme 2). Coordination of those ligands to metals would produce metal–ligand complexes that could have Lewis acid (metal)–Lewis base (pyridine) bifunctional activity. Moreover, the vast variety of commercially available chiral amino alcohol and pyridine derivatives should allow access to highly modular bifunctional catalysts where each activation site can be independently tuned by using the appropriate coupling partners.

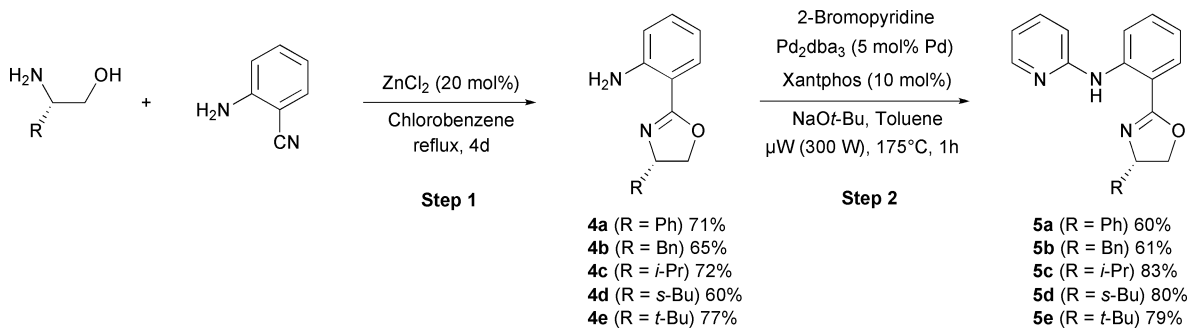
Herein we report the preparation of new modular bifunctional catalysts and their application to an asymmetric benchmark reaction, the addition of diethylzinc to aldehydes. A transition state model, based on relevant X-ray crystal structures, is proposed to explain the observed stereoselectivities.

Results and discussion

Our initial investigation concentrated on the study of the effect of the Lewis-acidic centre in the bifunctional activity of the catalyst. For this purpose, we embarked upon the synthesis of various ligands **5a–e** composed of an oxazoline ring linked by an *N*-phenylaniline unit to an unsubstituted pyridine (Scheme 3). The synthesis started with the preparation of 2-(*o*-aminophenyl)oxazolines **4a–e** from the commercially available 2-aminobenzonitrile by reaction with the appropriate chiral amino alcohol in the presence of $ZnCl_2$ (step 1).[2b,2c,7] This is a shorter and higher-yielding synthesis of **4a–e** than our previous approach based on the ring-opening of isatoic anhydride followed by DAST-promoted cyclisation.[2a]

With the compounds **4a–e** in hand, we envisaged the preparation of ligands **5** through a C–N bond formation using a Buchwald–Hartwig aryl amination (step 2).[8] Conventionally, this reaction requires high temperatures and long reaction times. Nevertheless, the use of microwave heating in palladium-catalysed aryl amination has provided shorter reaction times and higher yields in many cases over the last decade.[9] Therefore, the Buchwald–Hartwig reaction was carried out under microwave irradiation in toluene using NaO*t*-Bu as the base, Pd_2dba_3 (5 mol% Pd) as the palladium source and Xantphos (10 mol%) as the ligand (step 2). The bis(phosphine)-based Xantphos or BINAP ligands are efficient ligands for amination reactions of halogenopyridines due to their ability to prevent the formation of pyridine–palladium complexes.[10] After 1 h of reaction at 175 °C under microwave heating, the ligands **5a–e** were obtained in good yields (60–83%) from amines **4a–e** and 2-bromopyridine as coupling partners. It has to be noted that this cross-coupling requires a one-hour reaction time in order to ensure maximum conversions and to avoid complex purifications of ligands **5a–e** from the corresponding amines **4a–e**. At this stage, we were pleased to get crystals suitable for X-ray analysis after slow evaporation at room temperature of a saturated solution of **5e** in a mixture of pentane/EtOAc (9/1). From the crystallographic structure based on the distance of H1 and N1, we can assume hydrogen bonding takes place between these two atoms (Fig. 1). This also implies that the geometry of this ligand will allow the possible chelation of a metal between the two nitrogens, N1 and N2, to form a six-membered ring.

Since the pioneering work of Oguni in 1984,[11] there has been extensive research into the diethylzinc addition to benzaldehyde, and it is now regarded as one of the benchmark reactions for understanding the catalytic potential of new ligands.[12] However, the ligand-specific nature of catalytic reactions ensures that the search for new catalytic systems still attracts considerable attention in asymmetric synthetic chemistry.[13] In order to probe the bifunctional activity of catalysts derived from ligands **5a–e**, the addition of Et_2Zn to benzaldehyde was chosen as a model reaction. The active bifunctional catalyst was formed *in situ* by mixing the ligands **5a–e** with 2.2 equivalents of Et_2Zn for 30 min at room temperature. Then, benzaldehyde was added dropwise at –20 °C to the solution of bifunctional catalyst in toluene and the



Scheme 3 Preparation of pyridine-derived oxazoline ligands **5**.

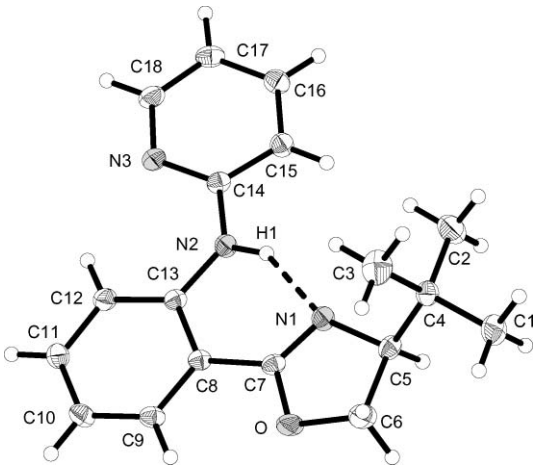
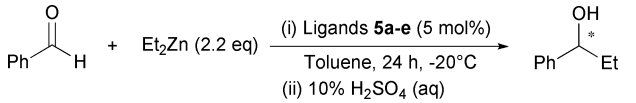


Fig. 1 Crystal structure of ligand **5e**, thermal ellipsoids are drawn on the 15% probability level.

Table 1 Asymmetric addition of diethylzinc to benzaldehyde using ligands **5a–e**[a]



Entry	Ligand	Yield (%)[b]	*ee* (%) (conf.)[c]
1	**5a**	81	11 (*R*)
2	**5b**	88	6 (*R*)
3	**5c**	78	28 (*R*)
4	**5d**	79	27 (*R*)
5	**5e**	89	58 (*R*)

[a] See experimental section. [b] After column chromatography. [c] The *ee* was determined by HPLC using a Daicel Chiracel OD column. The absolute configuration of the alcohol was assigned by comparison of the sign of the specific rotation to the literature value (see experimental section).

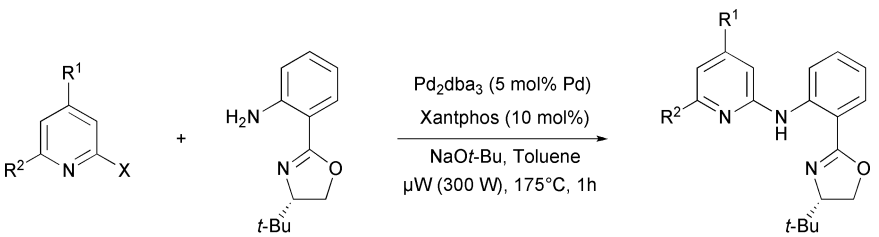
mixture was stirred for 24 hours. The results obtained are depicted in Table 1.

Regardless of the ligands used for this reaction, 1-phenylpropan-1-ol was obtained in good yields (78–89%) after 24 hours of reaction. Whereas the use of **5a** and **5b** resulted in low enantiomeric excess (11 and 6% respectively, entries 1 and 2), a significant increase of the enantioselectivity was observed for the ligands **5c** and **5d** (28 and 27% respectively, entries 4 and 5). The more hindered ligand **5e** (R = *t*-Bu, entry 5) gave the best result by producing the corresponding alcohol in 58% *ee* with a high yield of 89%. Consequently, there is no influence of the oxazoline ring substitution in terms of reactivity, however the R group does influence the enantioselectivity by increasing the enantiomeric excess when R is a bulky substituent.

Having studied the Lewis-acidic moiety, our interest then focused on the influence of the pyridine substitution in order to gain more insight about the effect of the Lewis-basic moiety in the bifunctional activity of these catalysts. Two parameters have been investigated: the influence of steric effects (*ortho*-pyridine substitution) and the influence of electronic effects (*ortho*- and *para*-pyridine substitutions). On the basis of the good results obtained with the zinc complex of **5e** (R = *t*-Bu), we synthesized a set of new pyridine-derived ligands starting from **4e** and 2-halogenopyridines (Table 2).

Using the optimized conditions described above for the palladium-catalysed aryl amination under microwave heating, the pyridine-substituted ligands **6–11** were synthesized in moderate-to-excellent yields (59–92%) whatever the nature of substitution (R^1 and R^2) and the leaving group (X = Cl or Br) of the pyridine ring. It is worthwhile noting the reaction conducted on **4e** with 2,6-dibromopyridine as starting material afforded the desired ligand **11** in 59% yield along with bis(oxazoline)-disubstituted pyridine **12** (**11**/**12**, 70/30 on the basis of ^{1}H NMR spectroscopy recorded on the crude material, entry 6). The formation of this compound prompted us to investigate the synthesis of bis(oxazoline)-containing ligands **12–15** for application to asymmetric addition of diethylzinc to aldehydes. Complexation of these ligands with

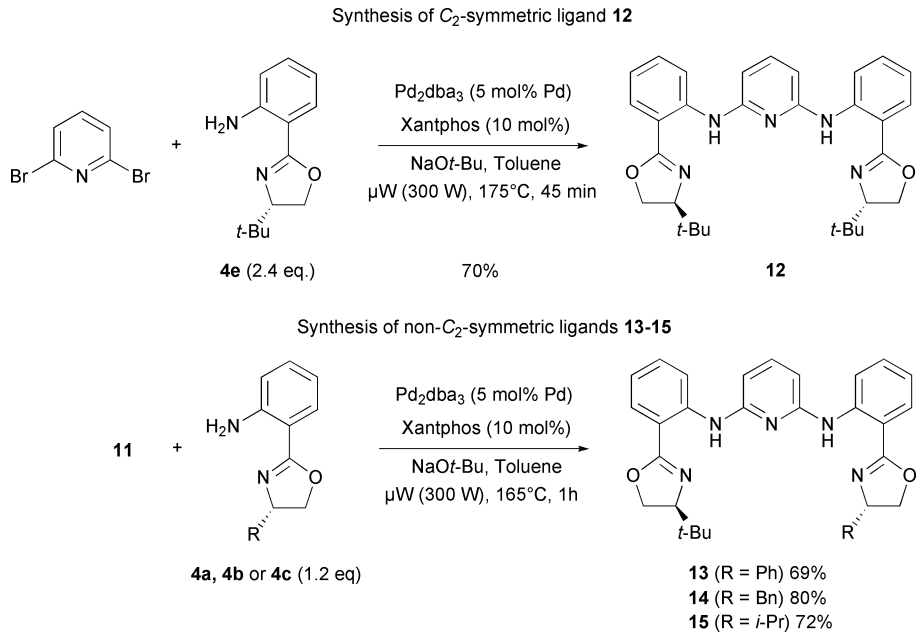
Table 2 Preparation of pyridine-derived oxazoline-containing ligands **6–11**[a]



4e **6-11**

Entry	Ligand	X	R^1	R^2	Yield (%)[b]
1	**6**	Cl	NO_2	H	62
2	**7**	Br	NMe_2	H	66
3	**8**	Br	H	Me	92
4	**9**	Br	H	CF_3	71
5	**10**	Br	H	MeO	71
6[c]	**11**	Br	H	Br	59

[a] See experimental section. [b] After column chromatography. [c] In this case, the reaction time was decreased (30 min) as well as the temperature (160 °C) in order to minimize the amount of disubstituted pyridine **12** (ratio **11**/**12**, 70/30 determined in the crude by ^{1}H NMR spectroscopy).



Scheme 4 Preparation of ligands **12–15**.

metals would produce a bifunctional catalyst possessing two chiral Lewis-acidic centres and one pyridine moiety acting as a Lewis base. These ligands have been synthesized under similar conditions by two different procedures depending on the symmetry of the bis(oxazoline)-containing ligands desired (Scheme 4).

The reaction between the amine **4e** and 2,6-dibromopyridine produced the C_2-symmetric ligand **12** in 70% yield without any trace of compound **11**. The non-C_2-symmetric ligands **13–15** were synthesized in good yields (69–80%) from the corresponding amines **4a–c** and the mono-oxazoline containing ligand **11** by microwave-assisted cross-coupling. This set of new ligands **6–15** was then applied to the asymmetric addition of diethylzinc to benzaldehyde using the conditions described in Table 1. The results obtained in this study are summarized in Table 3.

The use of ligands **6** and **7** bearing a *para*-substituent on the pyridine ring afforded 1-phenylpropan-1-ol in 60–78% yields with good enantioselectivities (entries 1 and 2). By comparison with the result obtained using **5e** (table 1, entry 5) *para*-substituent effects have negligible impact on the selectivity of the catalysts. Concerning the ligands bearing an *ortho*-substituent on the pyridine ring, a substantial loss of catalytic activity and enantioselectivity was observed regardless of the stereoelectronic nature of the substituents (entries 3–6). With bis(oxazolines)-containing ligands **12–15**, active catalysts were formed which produced the desired alcohol in 56–81% yield (entries 7–10). Nevertheless, low enantiomeric excesses were obtained with a reversal of the configuration of 1-phenylpropan-1-ol (in this case, the formation of the (*S*)-enantiomer was favored). Hence, the presence of an *ortho*-substituent on the pyridine ring leads to much less selective bifunctional catalysts while the *para*-substituent did not influence the enantioselective outcome of the reaction. So, the bifunctional catalyst derived from **5e** turned out to be the best ligand in this series in terms of selectivity and activity for this reaction. To evaluate the scope of **5e** in the asymmetric addition of diethylzinc, a diverse range of aldehydes was then tested (Table 4).

Table 3 Asymmetric addition of diethylzinc to benzaldehyde using ligands **6–15**[a]

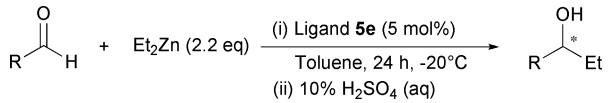
Entry	Ligand	Yield (%)[b]	*ee* (%) (conf.)[c]
1	**6**	60	57 (*R*)
2	**7**	78	53 (*R*)
3	**8**	29	12 (*R*)
4	**9**	11	Racemic
5	**10**	24	32 (*R*)
6	**11**	22	14 (*R*)
7	**12**	66	7 (*S*)
8	**13**	65	8 (*S*)
9	**14**	56	15 (*S*)
10	**15**	81	9 (*S*)

[a] See experimental section. [b] After column chromatography. [c] The *ee* was determined by HPLC using a Daicel Chiracel OD column. The absolute configuration of the alcohol was assigned by comparison of the sign of the specific rotation to the literature value (see experimental section).

Similar levels of conversion and enantiomeric excess to those found with benzaldehyde as substrate were obtained for aromatic aldehydes except in the case of pentafluorobenzaldehyde, which gave both lower yield and enantioselectivity (entries 1–5). On the other hand, the reaction with α,β-unsaturated aldehydes gave exclusively the 1,2-addition compounds in good yields (81–94%) but with low enantiomeric excesses (entries 6 and 7). Unlike α,β-unsaturated aldehydes, 3-phenylpropanal provided the corresponding alcohol in good yield with enantioselectivity comparable to the results obtained with benzaldehyde (entry 8). Surprisingly, the addition of diethylzinc to heptanal gave higher enantiomeric excess (*ee* = 54%) compared to the addition to the hindered cyclohexylcarboxaldehyde (*ee* = 32%, entries 9 and 10). So far, only Soai and co-workers have reported such a phenomenon in the addition of diethylzinc to these aldehydes.[14]

Finally, we wished to probe the mechanism by which the addition of diethylzinc to aldehydes occurred using these

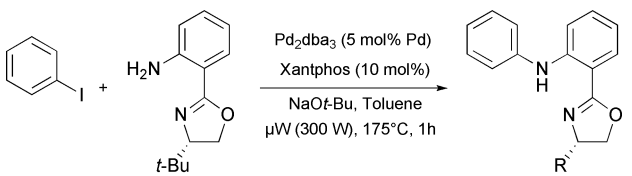
Table 4 Asymmetric addition of diethylzinc to various aldehydes using **5e** as ligand[a]



Entry	R	Yield (%)[b]	*ee* (%) (conf.)[c]
1	*p*-ClC_6H_4	54	55 (*R*)
2	*p*-$MeOC_6H_4$	87	57 (*R*)
3	C_6F_5	34	26 (*R*)
4	2-Naphthyl	90	57 (*R*)
5	1-Naphthyl	76	68 (*R*)
6	PhC≡C	81	13 (*R*)
7	(*E*)-PhCH=CH	94	6 (*R*)
8	$PhCH_2CH_2$	71	55 (*R*)
9	Cyclohexyl	70	32 (*R*)
10	Hexyl	65	54 (*R*)

[a] See experimental section. [b] After column chromatography. [c] The *ee* was determined by HPLC using a Daicel Chiracel OD column or a Daicel Chiracel IA column (see experimental section). The absolute configuration of the alcohol was assigned by comparison of the sign of the specific rotation to the literature value (see experimental section).

oxazoline-containing bifunctional catalysts. In view of the results obtained, we were interested to know whether the nitrogen of the pyridine displayed an influence on the bifunctional activity of the catalyst. For this purpose, we synthesized ligand **16** (an analogue of **5e**), where the pyridine ring was replaced by a phenyl ring (Scheme 5).



Scheme 5 Preparation of ligand **16**.

Under microwave heating, the cross-coupling reaction of iodobenzene and **4e** produced the desired ligand **16** in 92% yield. This ligand was then applied to the asymmetric addition of diethylzinc to benzaldehyde using the conditions depicted in Table 1. Under these conditions using 5 mol% of **16** as catalyst, 1-phenylpropan-1-ol was obtained in only 15% yield with very low enantioselectivity (*ee* = 5% (*R*)) compared to the results obtained with **5e** (yield = 89%, *ee* = 58% (*R*), Table 1, entry 5). The lack of asymmetric induction and catalytic activity attained by **16** suggest that the Lewis acid alone in the Lewis base–Lewis acid bifunctional catalyst derived from **5e** is not sufficient to promote the reaction with high levels of enantioselection.

Having established the crucial role of the Lewis-basic moiety in the reactivity and the selectivity of these ligands, we then examined the structure of the zinc–ligand complex. For this purpose, we embarked upon the preparation of the $ZnCl_2$.**5e** complex which should reflect the structure of the bifunctional catalyst EtZn(II)·**5e** formed *in situ* during the addition of Et_2Zn to aldehydes. Complexation of **5e** with $ZnCl_2$ in acetonitrile at room temperature under an atmosphere of nitrogen gave rise to a yellow solution of the desired zinc complex. After removal of the solvent and washing with diethyl ether, the $ZnCl_2$.**5e** complex was isolated in excellent yield (99%) as a yellow solid. Moreover, crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of a saturated solution of this complex in dichloromethane layered by hexane.

This crystallographic structure, Fig. 2, pointed out a chelation of the zinc by the nitrogen of the oxazoline core N1 and N2 as expected (*vide supra*). Furthermore, it is interesting to note that the chelation of the $ZnCl_2$ to N2 induces a shift of the proton to the pyridyl nitrogen (N3) which behaves as a proton acceptor.[15]

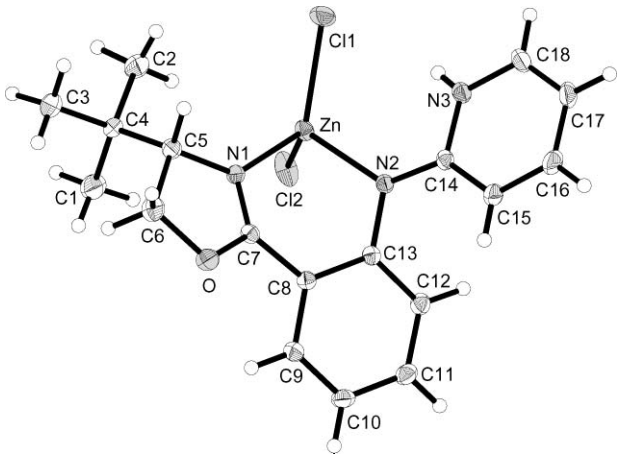


Fig. 2 Crystal structure of $ZnCl_2$·**5e** complex. Thermal ellipsoids are drawn on the 15% probability level.

Based on the above results and X-ray crystal structures, a plausible transition state in catalytic addition of diethylzinc to aldehydes is shown in Fig. 3.

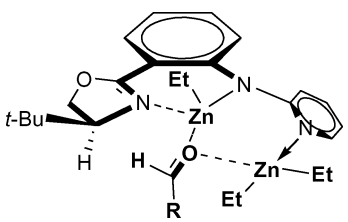


Fig. 3 Proposed transition state for diethylzinc addition to aldehydes.

The diethylzinc reagent would act as a Brønsted base by deprotonating the ligand **5e** to afford the *N*,*N*-chelated EtZn(II) center as a Lewis acid.[16] The aldehyde would approach the chiral Lewis-acidic center *via* the opposite face of the bulky *t*-Bu group and would chelate to this Lewis acid through an *anti* geometry in order to minimize the steric interactions between the *t*-Bu and the R group of the aldehyde. The pyridyl nitrogen would act as a Lewis base by coordinating the diethylzinc reagent leading to a six-membered chelation with the aldehyde. Therefore, the *Re*-face attack should be favored through this transition state to furnish the corresponding (*R*)-configured alcohol. It can be noted that the loss of reactivity using *ortho*-substituted pyridines as ligand (Table 3, entries 3–6) may be explained by a deleterious interaction between the *ortho*-substituent and the diethylzinc. This interaction would lessen the ability of the nitrogen to chelate diethylzinc in order to promote the addition reaction onto the aldehyde.

Conclusion

In summary, we have designed and synthesized a series of novel modular bifunctional oxazoline-containing ligands employing a microwave-assisted Buchwald–Hartwig aryl amination as the key-step. The bifunctional Zn(II) catalyst, which are easily prepared *in situ* from the corresponding ligands, have been applied to the asymmetric addition of diethylzinc to various aldehydes with enantioselectivities up to 68%. From these results and X-ray crystal structures, the bifunctional activity of these catalysts has been proven and a transition state has been suggested to explain the stereoselectivities observed. In the future, the modular construction of these ligands should allow access to a wide variety of new bifunctional catalysts by changing the oxazoline moiety, the metal-containing backbone or the heterocycles (in this case, only pyridine derivatives have been studied). Further applications of these ligands to asymmetric transformations are ongoing in these laboratories and the results of this work will be reported in due course.

Experimental

^{1}H NMR (300, 400 and 500 MHz) and ^{13}C (75, 100 and 125 MHz) spectra were recorded with Varian Oxford 300, 400 or 500 MHz spectrometers using tetramethylsilane as an internal standard. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. Elemental analysis was performed in the School of Chemistry and Chemical Biology, University College of Dublin. Crystal data was collected with a Bruker SMART APEX CCD area detector diffractometer in the School of Chemistry and Chemical Biology, University College of Dublin. Mass spectra were obtained using a Micromass Quattro micro instrument using electrospray ionization. Infrared spectra were recorded with a Perkin-Elmer Infrared FT spectrometer. Optical rotation values were measured at room temperature with a Perkin-Elmer 343 polarimeter. Melting points were determined in open capillary tubes with a Gallenkamp melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel 60 F_{254} or on plastic sheets precoated with aluminium oxide 60 F_{254}, neutral (Merck). Column chromatography separations were performed using Merck Kieselgel 60 (0.040–0.060 mm) or using aluminium oxide 90, standardized. All amination reactions were conducted in a CEM Discover S-Class microwave reactor. HPLC analyses were performed with LC 2010A machine equipped with a UV/Vis detector employing a chiral OD column from Daicel Chemical Industries or with LC Agilent 1200 series machine equipped with a UV/Vis detector employing a chiral IA column from Daicel Chemical Industries. Solvents were dried immediately before use by distillation from standard drying agents. Anhydrous chlorobenzene was purchased from Sigma-Aldrich and used without further purification.

1) General procedure for the synthesis of 2-(*o*-aminophenyl)-oxazolines 4a–4e

Anthranilonitrile (1.29 g, 11 mmol), the required amino alcohol (11.0 mmol) and anhydrous chlorobenzene were added to a Schlenk tube under an atmosphere of nitrogen. The solution was stirred at 60 °C for 15 min, at which point a 1M solution of $ZnCl_2$ in Et_2O (2.2 mL, 2.2 mmol) was added slowly. The mixture was stirred under reflux for 4 days. The solvent was then removed under reduced pressure and the product was purified by flash column chromatography on silica gel.

2-[(4*S*)-4-phenyl-4,5-dihydro-1,3-oxazol-2-yl]aniline 4a. Amine **4a** was obtained as a white solid (1.86 g, 71%) from L-phenylglycinol (1.51 g, 11 mmol) after purification by flash chromatography (pentane/EtOAc, 3/1). All the physical and spectroscopic data were in complete agreement with the reported ones.[2a]

2-[(4*S*)-4-benzyl-4,5-dihydro-1,3-oxazol-2-yl]aniline 4b. Amine **4b** was obtained as a white solid (1.80 g, 65%) from L-phenylalaninol (1.66 g, 11 mmol) after purification by flash chromatography (pentane/EtOAc, 3/1). All the physical and spectroscopic data were in complete agreement with the reported ones.[2a]

2-[(4*S*)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl]aniline 4c. Amine **4c** was obtained as white solid (1.62 g, 72%) from L-valinol (1.13 g, 11 mmol) after purification by flash chromatography (pentane/EtOAc, 3/1). All the physical and spectroscopic data were in complete agreement with the reported ones.[2a]

2-{(4*S*)-4-[(1*S*)-1-methylpropyl]-4,5-dihydro-1,3-yoxazol-2-yl}-aniline 4d. Amine **4d** was obtained as a colourless oil (1.44 g, 60%) from L-isoleucinol (1.29 g, 11 mmol) after purification by flash chromatography (pentane/EtOAc, 95/5). TLC: R_f= 0.32 (pentane/EtOAc, 9/1); $[\alpha]_D^{20}$ +5.1 (*c* 0.33 in $CHCl_3$); found: C, 71.45; H, 8.3; N, 12.6. $C_{13}H_{18}N_2O$ requires C, 71.5; H, 8.3; N, 12.8%; υ_{max}(neat)/cm^{-1} 3460, 3286, 2962, 2875, 1637, 1595, 1491, 1452, 1364, 1259, 1048 and 749; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (3H, d, *J* 6.7, C*H*$_3$CHEt), 0.96 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.27–1.38 (1H, m, CH$_3$C*H*$_2$), 1.59–1.72 (2H, m, CH$_3$C*H*$_2$ and CH$_3$C*H*Et), 4.02 (1H, t, *J* 7.8, C*H*$_2$O), 4.18–4.27 (1H, m, C*H*N), 4.31 (1H, dd, *J* 9.6 and 7.8, C*H*$_2$O), 6.20 (2H, br s, N*H*$_2$), 6.65 (1H, app t, *J* 8.0, Ph-C(4)*H*), 6.70 (1H, app d, *J* 7.6, Ph-C(6)*H*), 7.20 (1H, ddd, *J* 8.0, 7.6 and 1.5, Ph-C(5)*H*), 7.68 (1H, dd, *J* 7.9 and 1.5, Ph-C(3)*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 11.4 (*C*H$_3$CH$_2$), 14.7 (*C*H$_3$CHEt), 26.1 (CH$_3$*C*H$_2$), 39.5 (CH$_3$*C*HEt), 68.7 (*C*H$_2$O), 71.3 (*C*HN), 109.0 (Ph-*C*2), 115.6 (Ph-*C*(6)H), 116.0 (Ph-*C*(4)H), 129.6 (Ph-*C*(3)H), 131.9 (Ph-*C*(5)H), 148.6 (Ph-*C*1), 163.6 (N=*C*O); *m*/*z* (ESI) 219.2 (MH$^+$).

2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]aniline 4e. Amine **4e** was obtained as a white solid (1.85 g, 77%) from L-*tert*-leucinol (1.29 g, 11 mmol) after purification by flash chromatography (pentane/EtOAc, 3/1). All the physical and spectroscopic data were in complete agreement with the reported ones.[2a]

2) General procedure for the microwave-assisted palladium-catalysed aryl amination

An oven-dried microwave vial was charged with Pd_2dba_3 (15.7 mg, 0017 mmol, 5 mol% Pd), Xantphos (39.7 mg, 0.069 mmol, 10 mol%), 2-(*o*-aminophenyl)oxazoline (0.69 mmol) and NaO*t*-Bu (99.0 mg, 1.03 mmol) (2-halogenopyridine derivatives that were solids at room temperature were added as solids following the addition of NaO*t*-Bu). Then, the vial was capped and it

was evacuated and backfilled with nitrogen. This procedure was repeated three times. Toluene (2.7 mL) and the 2-halogenopyridine derivative (or iodobenzene) were added through the septum. Next, the punctured cap was replaced with a new cap and the mixture was heated at 175 °C in a CEM Discover microwave apparatus. The initial power supplied was 300W. Once the temperature was reached (IR measurement), the power dropped and fluctuated to maintain the temperature at the desired value. The total heating time of the reaction was 1h. The reaction vials were cooled to room temperature using propelled air flow and the mixture was filtered over silica and rinsed well with 75 mL of solvent (pentane/EtOAc, 1/1). The filtrate was subsequently evaporated under reduced pressure and the residue purified by column chromatography.

***N*-{2-[(4*S*)-4-phenyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}pyridin-2-amine 5a.** Ligand **5a** was obtained as a white solid (131 mg, 60%) from amine **4a** (164 mg, 0.69 mmol) and 2-bromopyridine (198 µL, 327 mg, 2.07 mmol) after purification by flash chromatography. Two purifications using column chromatography were required to yield pure compound **5a**. The first one was carried out on silica gel (pentane/EtOAc, 90/10) and the second one on alumina (pentane/EtOAc, 96/4). Mp: 88–89 °C; TLC: $R_f = 0.28$ (pentane/CH_2Cl_2, 55/45); $[\alpha]_D^{20}$ +236.2 (*c* 1.0 in $CHCl_3$); found: C, 76.1; H, 5.6; N, 13.0. $C_{20}H_{17}N_3O$ requires C, 76.2; H, 5.4; N, 13.3%; υ_{max}(KBr)/cm^{-1} 3275, 3189, 2899, 1627, 1593, 1534, 1479, 1449, 1345, 1151, 1065 and 751; δ_H (300 MHz; $CDCl_3$; Me_4Si) 4.09 (1H, t, *J* 8.3, C*H*N), 4.67 (1H, dd, *J* 10.0 and 8.3, CH_2O), 5.46 (1H, dd, *J* 10.0 and 8.3, CH_2O), 6.67–6.73 (2H, m, Pyr-C(5)*H* + Pyr-C(3)*H*), 6.86 (1H, app t, *J* 7.8, Ph-C(4)*H*), 7.20–7.34 (5H, m, *Ph*-CHN), 7.35–7.45 (2H, m, Pyr-C(4)*H* + Ph-C(5)*H*), 7.83 (1H, dd, *J* 7.9 and 1.6, Ph-C(3)*H*), 8.17–8.23 (1H, m, Pyr-C(6)*H*), 8.68 (1H, d, *J* 8.5, Ph-C(6)*H*), 11.54 (1H, br s, N*H*); δ_C (75 MHz; $CDCl_3$; Me_4Si) 70.0 (*C*HN), 73.2 (*C*H_2O), 110.0 (Ph-*C*2), 112.8 (Pyr-*C*(3)H or Pyr-*C*(5)H), 115.3 (Pyr-*C*(5)H or Pyr-*C*(3)H), 117.6 (Ph-*C*(6)H), 119.1 (Ph-*C*(4)H), 126.1 (2C, *Ph*-CHN), 127.6 (1C, *Ph*-CHN), 128.8 (2C, *Ph*-CHN), 129.7 (Ph-*C*(3)H), 132.5 (Ph-*C*(5)H), 137.3 (Pyr-C(4)H), 142.3 (C^{IV}, *Ph*-CHN), 142.9 (Ph-*C*1), 147.4 (Pyr-*C*(6)H), 155.2 (Pyr-*C*2), 165.2 (N=*C*O); *m*/*z* (ESI) 316.2 (MH^+).

***N*-{2-[(4*S*)-4-benzyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}pyridin-2-amine 5b.** Ligand **5b** was obtained as a viscous oil (139 mg, 61%) from amine **4b** (174 mg, 0.69 mmol) and 2-bromopyridine (198 µL, 327 mg, 2.07 mmol) after purification by flash chromatography. Two purifications using column chromatography were required to yield pure compound **5b**. The first one was carried out on silica gel (pentane/EtOAc, 90/10) and the second one on alumina (pentane/EtOAc, 96/4). TLC: R_f= 0.30 (pentane/CH_2Cl_2, 55/45); $[\alpha]_D^{20}$ +23.7 (*c* 0.5 in $CHCl_3$); found: C, 76.1; H, 5.9; N, 12.5. $C_{21}H_{19}N_3O$ requires C, 76.5; H, 5.9; N, 12.8%; υ_{max}(neat)/cm^{-1} 3288, 3086, 3026, 1630, 1594, 1536, 1480, 1450, 1347, 1152, 1061 and 751; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.78 (1H, dd, *J* 13.6 and 6.6, PhCH_2), 2.89 (1H, dd, *J* 13.6 and 7.9, PhCH_2), 3.93 (1H, app t, *J* 8.0, CH_2O), 4.25 (1H, app t, *J* 8.5, CH_2O), 4.54 (1H, app qd, *J* 8.0 and 6.6, C*H*N), 6.41 (1H, app d, *J* 8.4, Pyr-C(3)*H*), 6.64 (1H, app dd, *J* 7.1 and 5.1, Pyr-C(5)*H*), 6.78 (1H, app t, *J* 7.5, Ph-C(4)*H*), 7.10–7.26 (5H, m, *Ph*-CH_2), 7.28–7.40 (2H, m, Pyr-C(4)*H* + Ph-C(5)*H*), 7.72 (1H, dd, *J* 7.9 and 1.3, Ph-C(3)*H*), 8.17 (1H, app d, *J* 4.9, Pyr-C(6)*H*), 8.72 (1H, d, *J* 8.4, Ph-C(6)*H*), 11.50 (1H, br s, N*H*); δ_C (75 MHz; $CDCl_3$; Me_4Si) 42.2 (Ph*C*H_2), 67.9 (*C*HN), 70.5 (*C*H_2O), 111.2 (Ph-*C*2), 112.8 (Pyr-*C*(3)H), 115.3 (Pyr-*C*(5)H), 117.3 (Ph-*C*(6)H), 118.7 (Ph-*C*(4)H), 126.3 (2C, *Ph*-CH_2), 128.4 (1C, *Ph*-CH_2), 129.2 (2C, *Ph*-CH_2), 129.3 (Ph-*C*(3)H), 132.3 (Ph-*C*(5)H), 136.9 (Pyr-*C*(4)H), 138.3 (C^{IV}, *Ph*-CH_2), 142.8 (Ph-*C*1), 147.4 (Pyr-*C*(6)H), 155.3 (Pyr-*C*2), 164.1 (N=*C*O); *m*/*z* (ESI) 330.2 (MH^+).

***N*-{2-[(4*S*)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}pyridin-2-amine 5c.** Ligand **5c** was obtained as a white solid (161 mg, 83%) from amine **4c** (141 mg, 0.69 mmol) and 2-bromopyridine (198 µL, 327 mg, 2.07 mmol) after purification by flash chromatography on silica gel (pentane/EtOAc, 90/10). Mp: 74–77 °C; TLC: R_f= 0.30 (pentane/EtOAc, 95/5); $[\alpha]_D^{20}$ +10.5 (*c* 0.56 in $CHCl_3$); found: C, 72.7; H, 6.85; N, 14.4. $C_{17}H_{19}N_3O$ requires C, 72.6; H, 6.8; N, 14.9%; υ_{max}(KBr)/cm^{-1} 3436, 3023, 2956, 1633, 1562, 1540, 1418, 1349, 1148, 1047 and 748; δ_H (500 MHz; $CDCl_3$; Me_4Si) 1.01 (3H, d, *J* 6.7, (CH_3)$_2$CH), 1.09 (3H, d, *J* 6.7, (CH_3)$_2$CH), 1.83 (1H, octuplet, *J* 6.7, (CH$_3$)$_2$C*H*), 4.05 (1H, app t, *J* 8.1, CH_2O), 4.16 (1H, ddd, *J* 9.4, 8.1 and 6.7, C*H*N), 4.39 (1H, dd, *J* 9.4 and 8.3, CH_2O), 6.77 (1H, dd, *J* 7.8 and 4.9, Pyr-C(5)*H*), 6.83 (1H, d, *J* 8.3, Pyr-C(3)*H*), 6.89 (1H, app t, *J* 7.5, Ph-C(4)*H*), 7.44 (1H, app td, *J* 8.2 and 1.5, Ph-C(5)*H*), 7.52 (1H, app td, *J* 8.0 and 1.9, Pyr-C(4)*H*), 7.84 (1H, dd, *J* 7.9 and 1.5, Ph-C(3)*H*), 8.29 (1H, dd, *J* 4.9 and 1.4, Pyr-C(6)*H*), 8.83 (1H, d, *J* 8.6, Ph-C(6)*H*), 11.77 (1H, br s, N*H*); δ_C (125 MHz; $CDCl_3$; Me_4Si) 18.9 (2C, (*C*H$_3$)$_2$CH), 33.4 ((CH$_3$)$_2$*C*H), 69.2 (*C*H_2O), 72.9 (*C*HN), 111.5 (Ph-*C*2), 112.6 (Pyr-*C*(3)H), 115.3 (Pyr-*C*(5)H), 117.4 (Ph-*C*(6)H), 118.6 (Ph-*C*(4)H), 129.4 (Ph-*C*(3)H), 132.2 (Ph-*C*(5)H), 137.1 (Pyr-*C*(4)H), 142.9 (Ph-*C*1), 147.6 (Pyr-*C*(6)H), 155.5 (Pyr-*C*2), 163.8 (N=*C*O); *m*/*z* (ESI) 282.2 (MH^+).

***N*-(2-{(4*S*)-4-[(1*S*)-1-methylpropyl]-4,5-dihydro-1,3-oxazol-2-yl}phenyl)pyridin-2-amine 5d.** Ligand **5d** was obtained as a white solid (163 mg, 80%) from amine **4d** (151 mg, 0.69 mmol) and 2-bromopyridine (198 µL, 327 mg, 2.07 mmol) after purification by flash chromatography on silica gel (pentane/EtOAc, 95/5). Mp: 43–45 °C; TLC: R_f= 0.37 (pentane/EtOAc, 90/10); $[\alpha]_D^{20}$ +55.2 (*c* 0.5 in $CHCl_3$); found: C, 73.15; H, 7.2; N, 14.15. $C_{18}H_{21}N_3O$ requires C, 73.2; H, 7.2; N, 14.2%; υ_{max}(KBr)/cm^{-1} 3285, 3021, 2962, 2929, 1632, 1594, 1480, 1450, 1347, 1150, 1062 and 751; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.94 (3H, d, *J* 6.7, CH_3CHEt), 0.99 (3H, t, *J* 7.2, CH_3CH$_2$), 1.23–1.39 (1H, m, CH$_3$CH_2), 1.62–1.78 (2H, m, CH$_3$CH_2 and CH$_3$C*H*Et), 4.06 (1H, t, *J* 7.9, CH_2O), 4.23–4.32 (1H, m, C*H*N), 4.37 (1H, dd, *J* 9.6 and 7.9, CH_2O), 6.75–6.80 (1H, m, Pyr-C(5)*H*), 6.82 (1H, d, *J* 8.3, Pyr-C(3)*H*), 6.90 (1H, app t, *J* 7.5, Ph-C(4)*H*), 7.45 (1H, ddd, *J* 8.4, 7.4 and 1.6, Ph-C(5)*H*), 7.53 (1H, ddd, *J* 8.3, 7.5 and 1.9, Pyr-C(4)*H*), 7.84 (1H, app dd, *J* 7.8 and 1.6, Ph-C(3)*H*), 8.28 (1H, m, Pyr-C(6)*H*), 8.77 (1H, d, *J* 8.4, Ph-C(6)*H*), 11.73 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 11.2 (*C*H$_3$CH$_2$), 15.0 (*C*H$_3$CHEt), 25.9 (CH$_3$*C*H$_2$), 39.5 (CH$_3$*C*HEt), 68.8 (*C*H_2O), 71.5 (*C*HN), 111.5 (Ph-*C*2), 112.5 (Pyr-*C*(3)H), 115.3 (Pyr-*C*(5)H), 117.5 (Ph-*C*(6)H), 119.0 (Ph-*C*(4)H), 129.4 (Ph-*C*(3)H), 132.2 (Ph-*C*(5)H), 137.3 (Pyr-*C*(4)H), 142.7 (Ph-*C*1), 147.3 (Pyr-*C*(6)H), 155.3 (Pyr-*C*2), 163.6 (N=*C*O); *m*/*z* (ESI) 296.3 (MH^+).

***N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}pyridin-2-amine 5e.** Ligand **5e** was obtained as a white solid (161 mg, 79%) from amine **4e** (151 mg, 0.69 mmol) and 2-bromopyridine (198 µL, 327 mg, 2.07 mmol) after purification by

flash chromatography on silica gel (pentane/EtOAc, 95/5). Mp: 129–132 °C; TLC: R_f= 0.23 (pentane/EtOAc, 95/5); $[\alpha]_D^{20}$ +30.2 (*c* 1.0 in $CHCl_3$); found: C, 73.4; H, 7.2; N, 13.6. $C_{18}H_{21}N_3O$ requires C, 73.2; H, 7.2; N, 14.2%; υ_{max}(KBr)/cm^{-1} 3436, 3288, 3025, 2966, 1633, 1594, 1482, 1451, 1419, 1149, 1073 and 751; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.95 (9H, s, $(CH_3)_3C$), 4.08–4.17 (2H, m, CH_2O + CHN), 4.23–4.31 (1H, m, CH_2O), 6.74–6.77 (1H, m, Pyr-C(5)*H*), 6.76 (1H, d, *J* 8.0, Pyr-C(3)*H*), 6.88 (1H, app t, *J* 8.0, Ph-C(4)*H*), 7.43 (1H, td, *J* 8.0 and 1.5, Ph-C(5)*H*), 7.50 (1H, app td, *J* 8.0 and 1.6, Pyr-C(4)*H*), 7.83 (1H, dd, *J* 7.9 and 1.5, Ph-C(3)*H*), 8.30 (1H, app dd, *J* 4.8 and 1.6, Pyr-C(6)*H*), 8.84 (1H, d, *J* 8.0, Ph-C(6)*H*), 11.81 (1H, br s, N*H*); δ_C (125 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, $(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 67.1 (CH_2O), 76.2 (*C*HN), 104.4 (Ph-*C*2), 112.6 (Pyr-*C*(3)H), 115.3 (Pyr-*C*(5)H), 117.4 (Ph-*C*(6)H), 118.7 (Ph-*C*(4)H), 129.3 (Ph-*C*(3)H), 132.3 (Ph-*C*(5)H), 137.1 (Pyr-*C*(4)H), 142.9 (Ph-*C*1), 147.6 (Pyr-*C*(6)H), 155.6 (Pyr-*C*2), 163.8 (N=*C*O); *m*/*z* (ESI) 296.2 (MH^+).

***N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-4-nitropyridin-2-amine 6.** Ligand **6** was obtained as a red solid (143 mg, 62%) from amine **4e** (151 mg, 0.69 mmol) and 2-chloro-4-nitropyridine (328 mg, 2.07 mmol) after purification by flash chromatography on silica gel (pentane/EtOAc, 96/4). Mp: 173–175 °C; TLC: R_f= 0.36 (pentane/EtOAc, 96/4); $[\alpha]_D^{20}$ +45.4 (*c* 1.0 in $CHCl_3$); found: C, 63.4; H, 6.1; N, 16.2. $C_{18}H_{20}N_4O_3$ requires C, 63.5; H, 5.9; N, 16.5%; υ_{max}(KBr)/cm^{-1} 3448, 2962, 2868, 1639, 1523, 1483, 1454, 1352, 1057, 971, 753 and 745; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.02 (9H, s, $(CH_3)_3C$), 4.17–4.27 (2H, m, CH_2O + CHN), 4.35 (1H, t, *J* 12.6, CH_2O), 7.00 (1H, td, J 7.8 and 0.6, Ph-C(4)*H*), 7.41 (1H, dd, *J* 5.5 and 1.7, Pyr-C(5)*H*), 7.45–7.52 (2H, m, Pyr-C(3)*H* + Ph-C(5)*H*), 7.88 (1H, dd, *J* 7.8 and 1.4, Ph-C(3)*H*), 8.48 (1H, d, *J* 5.5, Pyr-C(6)*H*), 8.82 (1H, br d, *J* 8.5, Ph-C(6)*H*), 12.43 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, $(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 67.4 (CH_2O), 76.0 (*C*HN), 105.2 (Pyr-*C*(3)H), 106.9 (Pyr-*C*(5)H), 112.3 (Ph-*C*2), 118.1 (Ph-*C*(6)H), 120.4 (Ph-*C*(4)H), 129.5 (Ph-*C*(3)H), 132.3 (Ph-*C*(5)H), 141.7 (Ph-*C*1), 150.1 (Pyr-*C*(6)H), 154.9 (Pyr-*C*4), 156.9 (Pyr-*C*2), 163.9 (N=*C*O); *m*/*z* (ESI) 341.4 (MH^+).

***N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-4-dimethylaminopyridin-2-amine 7.** Ligand **7** was obtained as a brown solid (154 mg, 66%) from amine **4e** (151 mg, 0.69 mmol) and 2-bromo-4-dimethylaminopyridine[17] (416 mg, 2.07 mmol) after purification by flash chromatography on silica gel (pentane/EtOAc, 65/35). Mp: 127–129 °C; TLC: R_f= 0.35 (pentane/EtOAc, 65/35); $[\alpha]_D^{20}$ +22.5 (*c* 1.0 in $CHCl_3$); found: C, 70.7; H, 7.7; N, 16.3. $C_{20}H_{26}N_4O$ requires C, 71.0; H, 7.7; N, 16.3%; υ_{max}(KBr)/cm^{-1} 3434, 3186, 2959, 1615, 1600, 1535, 1503, 1309, 1287, 1162, 1053, 810 and 752; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.99 (9H, s, $(CH_3)_3C$), 2.99 (6H, s, $N(CH_3)_2$), 4.10–4.34 (3H, m, CH_2O + CHN), 6.00 (1H, d, *J* 2.3, Pyr-C(3)*H*), 6.20 (1H, dd, *J* 6.1 and 2.3, Pyr-C(5)*H*), 6.83 (1H, app td, J 7.7 and 0.9, Ph-C(4)*H*), 7.40 (1H, ddd, *J* 8.5, 7.3 and 1.6, Ph-C(5)*H*), 7.80 (1H, dd, *J* 7.7 and 1.6, Ph-C(3)*H*), 8.00 (1H, d, *J* 6.1, Pyr-C(6)*H*), 8.74 (1H, app d, *J* 8.5, Ph-C(6)*H*), 11.59 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, $(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 39.1 (2C, $N(CH_3)_2$), 67.0 (CH_2O), 76.1 (*C*HN), 93.4 (Pyr-*C*(3)H), 101.6 (Pyr-*C*(5)H), 110.9 (Ph-*C*2), 117.4 (Ph-*C*(6)H), 118.0 (Ph-*C*(4)H), 129.2 (Ph-*C*(3)H), 132.1 (Ph-*C*(5)H), 143.6 (Ph-*C*1), 147.6 (Pyr-*C*(6)H), 155.7 (Pyr-*C*4), 156.4 (Pyr-*C*2), 163.8 (N=*C*O); *m*/*z* (ESI) 339.3 (MH^+).

***N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-6-methylpyridin-2-amine 8.** Ligand **8** was obtained as a white solid (196 mg, 92%) from amine **4e** (151 mg, 0.69 mmol) and 2-bromo-6-methylpyridine (236 μL, 357 mg, 2.07 mmol) after purification by flash chromatography on silica gel (pentane/EtOAc, 97/3). Mp: 49–51 °C; TLC: R_f= 0.32 (pentane/EtOAc, 97/3); $[\alpha]_D^{20}$ +22.7 (*c* 1.0 in $CHCl_3$); found: C, 73.7; H, 7.4; N, 13.4. $C_{19}H_{23}N_3O$ requires C, 73.8; H, 7.4; N, 13.6%; υ_{max}(KBr)/cm^{-1} 3284, 3193, 2960, 1631, 1570, 1450, 1342, 1157, 1053, 783 and 752; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.99 (9H, s, $(CH_3)_3C$), 2.51 (3H, s, CH_3-Pyr-C6), 4.10–4.22 (2H, m, CH_2O + CHN), 4.24–4.36 (1H, m, CH_2O), 6.58–6.66 (1H, m, Pyr-C(3)*H*), 6.63 (1H, d, *J* 7.4, Pyr-C(5)*H*), 6.88 (1H, app t, *J* 7.4, Ph-C(4)*H*), 7.38–7.46 (2H, m, Ph-C(5)*H* and Pyr-C(4)*H*), 7.83 (1H, dd, *J* 7.8 and 1.9, Ph-C(3)*H*), 8.92 (1H, br s, Ph-C(6)*H*), 11.75 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, $(CH_3)_3C$), 24.4 (CH_3-Pyr-C6), 33.9 ($(CH_3)_3C$), 67.1 (CH_2O), 76.2 (*C*HN), 109.2 (Pyr-*C*(3)H), 111.2 (Ph-*C*2), 114.3 (Pyr-*C*(5)H), 117.3 (Ph-*C*(6)H or Ph-*C*(4)H), 118.6 (Ph-*C*(4)H or Ph-*C*(6)H),129.3 (Ph-*C*(3)H), 132.1 (Ph-*C*(5)H), 137.5 (Pyr-*C*(4)H), 143.1 (Ph-*C*1), 154.9 (Pyr-*C*6), 156.5 (Pyr-*C*2), 163.7 (N=*C*O); *m*/*z* (ESI) 310.3 (MH^+).

***N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-6-(trifluoromethyl)pyridin-2-amine 9.** Ligand **9** was obtained as a white solid (178 mg, 71%) from amine **4e** (151 mg, 0.69 mmol) and 2-bromo-6-trifluoromethylpyridine (468 mg, 2.07 mmol) after careful purification by flash chromatography on silica gel (pentane/EtOAc, 99/1). Mp: 59–62 °C; TLC: R_f= 0.10 (pentane/EtOAc, 99/1); $[\alpha]_D^{20}$ +24.1 (*c* 1.0 in $CHCl_3$); found: C, 62.9; H, 5.6; N, 11.4. $C_{19}H_{20}F_3N_3O$ requires C, 62.8; H, 5.6; N, 11.6%; υ_{max}(KBr)/cm^{-1} 3434, 3285, 2963, 2906, 1664, 1545, 1469, 1280, 1138, 804 and 753; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.99 (9H, s, $(CH_3)_3C$), 4.18 (1H, dd, *J* 11.6 and 8.0, CHN), 4.19 (1H, dd, *J* 13.3 and 8.0, CH_2O), 4.32 (1H, dd, *J* 13.3 and 11.6, CH_2O), 6.89 (1H, d, *J* 8.4, Pyr-C(3)*H*), 6.96 (1H, td, *J* 8.3 and 1.1, Ph-C(4)*H*), 7.11 (1H, d, *J* 7.3, Pyr-C(5)*H*), 7.49 (1H, td, *J* 8.3 and 1.7, Ph-C(5)*H*), 7.62 (1H, dd, *J* 8.4 and 7.3, Pyr-C(4)*H*), 7.88 (1H, dd, *J* 8.3 and 1.7, Ph-C(3)*H*), 8.98 (1H, dd, *J* 8.3 and 1.1, Ph-C(6)*H*), 12.26 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, $(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 67.2 (CH_2O), 76.1 (*C*HN), 111.1 (q, $J^3_{C\text{-}F}$ 3.1, Pyr-*C*(5)H), 111.7 (Ph-*C*2), 115.3 (Pyr-*C*(3)H), 118.0 (Ph-*C*(6)H), 119.7 (Ph-*C*(4)H), 121.7 (q, $J^1_{C\text{-}F}$ 274, CF_3), 129.3 (Ph-*C*(3)H), 132.5 (Ph-*C*(5)H), 137.8 (Pyr-*C*(4)H), 142.1 (Ph-*C*1), 146.0 (q, $J^2_{C\text{-}F}$ 34, Pyr-*C*6), 155.4 (Pyr-*C*2), 164.0 (N=*C*O); *m*/*z* (ESI) 364.2 (MH^+).

***N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-6-methoxypyridin-2-amine 10.** Ligand **10** was obtained as a white powder (159 mg, 71%) from amine **4e** (151 mg, 0.69 mmol) and 2-bromo-6-methoxypyridine (254 μL, 389 mg, 2.07 mmol) after purification by flash chromatography. Two careful purifications using column chromatography were required to yield pure compound **10**. The first one was carried out on silica gel (pentane/CH_2Cl_2, 85/15) and the second one on silica gel (pentane/EtOAc, 99/1). Mp: 60–63 °C; TLC: R_f= 0.10 (pentane/EtOAc, 99/1); $[\alpha]_D^{20}$ +14.8 (*c* 1.0 in $CHCl_3$); found: C, 70.0; H, 7.05; N, 12.8. $C_{19}H_{23}N_3O_2$ requires C, 70.1; H, 7.1; N, 12.9%; υ_{max}(KBr)/cm^{-1}

3287, 3192, 2962, 2868, 1633, 1590, 1577, 1446, 1281, 1259, 1147, 1051, 786 and 750; δ_H (500 MHz; C_6D_6; 65 °C; Me_4Si) 0.79 (9H, s, (CH_3)$_3$C), 3.74–3.88 (3H, m, CH_2O + CHN), 3.81 (3H, s, CH_3O-Pyr-C6), 6.26 (1H, d, *J* 7.8, Pyr-C(3)*H* or Pyr-C(5)*H*), 6.44 (1H, d, *J* 7.8, Pyr-C(5)*H* or Pyr-C(3)*H*), 6.79 (1H, app td, *J* 7.5 and 1.0, Ph-C(4)*H*), 7.11 (1H, t, *J* 7.8, Pyr-C(4)*H*), 7.29 (1H, ddd, *J* 8.7, 7.2 and 1.6, Ph-C(5)*H*), 8.05 (1H, dd, *J* 7.8 and 1.6, Ph-C(3)*H*), 8.93 (1H, app d, *J* 8.7, Ph-C(6)*H*), 12.06 (1H, br s, N*H*); δ_C (125 MHz; C_6D_6; 65 °C; Me_4Si) 25.5 (3C, (CH_3)$_3$C), 33.4 ((CH_3)$_3$*C*), 52.8 (CH_3O-Pyr-C6), 66.6 (CH_2O), 76.1 (*C*HN), 100.8 (Pyr-*C*(3)H or Pyr-*C*(5)H), 102.9 (Pyr-*C*(5)H or Pyr-*C*(3)H), 111.7 (Ph-*C*2), 117.9 (Ph-*C*(6)H), 118.5 (Ph-*C*(4)H), 129.4 (Ph-*C*(3)H), 131.8 (Ph-*C*(5)H), 139.5 (Pyr-*C*(4)H), 143.5 (Ph-*C*1), 154.1 (Pyr-*C*2), 163.7 (Pyr-*C*6), 164.0 (N=*C*O); *m*/*z* (ESI) 326.4 (MH^+).

6-bromo-*N*-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]-phenyl}pyridin-2-amine 11. Ligand **11** was prepared from amine **4e** (151 mg, 0.69 mmol), 2,6-dibromopyridine (136 mg, 0.58 mmol), NaO*t*-Bu (66.3 mg, 0.69 mmol), Xantphos (33.6 mg, 0.058 mmol), Pd_2dba_3 (13.3 mg, 0.015 mmol, 5 mol% Pd) in 2.3 mL of toluene. The mixture was heated at 160 °C for 30 min in a microwave apparatus with an initial power supplied being 300W. The compound **11** was obtained as a white powder (128 mg, 59%) after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 80/20). Mp: 68–71 °C; TLC: R_f = 0.26 (pentane/CH_2Cl_2, 80/20); $[\alpha]_D^{20}$ +16.0 (*c* 1.0 in $CHCl_3$); found: C, 58.1; H, 5.4; N, 10.9. $C_{18}H_{20}BrN_3O$ requires C, 57.8; H, 5.4; N, 11.2%; υ_{max}(KBr)/cm^{-1} 3274, 3047, 2962, 2904, 1633, 1586, 1523, 1449, 1357, 1281, 1159, 1054, 777 and 752; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.55 (9H, s, (CH_3)$_3$C), 4.12–4.22 (2H, m, CH_2O + CHN), 4.3 (1H, dd, *J* 13.1 and 11.7, CH_2O), 6.66 (1H, d, *J* 8.1, Pyr-C(3)*H*), 6.83–6.98 (2H, m, Pyr-C(5)*H* and Ph-C(4)*H*), 7.34 (1H, app t, *J* 7.8, Pyr-C(4)*H*), 7.48 (1H, app td, *J* 8.5 and 1.3, Ph-C(5)*H*), 7.81 (1H, dd, *J* 7.8 and 1.3, Ph-C(3)*H*), 8.81 (1H, d, *J* 8.5, Ph-C(6)*H*), 12.10 (1H, br s, N*H*); δ_C (75 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, (CH_3)$_3$C), 34.1 ((CH_3)$_3$*C*), 67.2 (CH_2O), 76.1 (*C*HN), 110.6 (Pyr-*C*(3)H), 111.6 (Ph-*C*2), 117.5 (Ph-*C*(6)H), 118.2 (Pyr-*C*(5)H or Ph-*C*(4)H), 119.6 (Ph-*C*(4)H or Pyr-*C*(5)H), 129.3 (Ph-*C*(3)H), 132.4 (Ph-*C*(5)H), 139.0 (Pyr-*C*(4)H), 139.4 (Pyr-*C*6), 142.0 (Ph-*C*1), 155.1 (Pyr-*C*2), 163.8 (N=*C*O); *m*/*z* (ESI) 374.1/376.1 in a ratio 1/1 (MH^+).

***N*²-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-*N*⁶-(2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl)-pyridine-2,6-diamine 12.** Ligand **12** was prepared from amine **4e** (141 mg, 0.69 mmol), 2,6-dibromopyridine (68 mg, 0.29 mmol), NaO*t*-Bu (66.3 mg, 0.69 mmol), Xantphos (16.8 mg, 0.029 mmol), Pd_2dba_3 (6.6 mg, 0.007 mmol, 5 mol% Pd) in 1.1 mL of toluene. The mixture was heated at 175 °C for 45 min in a microwave apparatus with an initial power supplied being 300W. The compound **12** was obtained as a white powder (104 mg, 70%) after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 55/45). Mp: 140–142 °C; TLC: R_f= 0.37 (pentane/CH_2Cl_2, 55/45); $[\alpha]_D^{20}$ –3.7 (*c* 1.0 in $CHCl_3$); found: C, 72.4; H, 7.2; N, 13.4. $C_{31}H_{37}N_5O_2$ requires C, 72.8; H, 7.3; N, 13.7%; υ_{max}(KBr)/cm^{-1} 3428, 3100, 2958, 2919, 1634, 1567, 1434, 1357, 1283, 1255, 1154, 1054 and 749; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.01 (18H, s, (CH_3)$_3$C), 4.14–4.22 (4H, m, CH_2O + CHN), 4.27–4.33 (2H, m, CH_2O), 6.39 (2H, d, *J* 7.9, Pyr-C(5)*H* and Pyr-C(3)*H*), 6.89 (2H, app td, *J* 7.8 and 1.1, Ph-C(4)*H*), 7.39 (2H, ddd, *J* 8.7, 7.5 and 1.7, Ph-C(5)*H*), 7.43 (1H, t, *J* 7.9, Pyr-C(4)*H*), 7.84 (2H, dd, *J* 7.8 and 1.7, Ph-C(3)*H*), 8.72 (2H, app d, *J* 8.7, Ph-C(6)*H*), 11.68 (2H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.9 (6C, (CH_3)$_3$C), 33.9 (2C, (CH_3)$_3$*C*), 67.1 (2C, CH_2O), 76.3 (2C, *C*HN), 103.0 (Pyr-*C*(3)H and Pyr-*C*(5)H), 111.5 (2C, Ph-*C*2), 118.4 (2C, Ph-*C*(6)H), 118.6 (2C, Ph-*C*(4)H), 129.3 (2C, Ph-*C*(3)H), 131.8 (Pyr-*C*(4)H), 138.5 (2C, Ph-*C*(5)H), 142.9 (2C, Ph-*C*1), 153.9 (2C, Pyr-*C*2), 163.7 (2C, N=*C*O); *m*/*z* (ESI) 512.2 (MH^+).

***N*²-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-*N*⁶-(2-[(4*S*)-4-phenyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl)pyridine-2,6-diamine 13.** Ligand **13** was prepared from amine **4a** (159 mg, 0.69 mmol), 6-bromopyridine **11** (217 mg, 0.58 mmol), NaO*t*-Bu (66.3 mg, 0.69 mmol), Xantphos (33.6 mg, 0.058 mmol), Pd_2dba_3 (13.3 mg, 0.015 mmol, 5 mol% Pd) in 2.3 mL of toluene. The mixture was heated at 165 °C for 1h in a microwave apparatus with the initial power supplied being 300W. Compound **13** was obtained as a white powder (213 mg, 69%) after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 70/30). Mp: 138–140 °C; TLC: R_f= 0.35 (pentane/CH_2Cl_2, 70/30); $[\alpha]_D^{20}$ +185.1 (*c* 1.0 in $CHCl_3$); found: C, 73.9; H, 6.5; N, 12.6. $C_{33}H_{33}N_5O_2$ requires C, 74.6; H, 6.3; N, 13.2%; υ_{max}(KBr)/cm^{-1} 3398, 3267, 3030, 2918, 2849, 1629, 1567, 1436, 1268, 1155, 1064, 749 and 697; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.99 (9H, s, (CH_3)$_3$C), 4.12–4.21 (3H, m, *t*Bu-CHCH_2O + *t*Bu-C*H*N + Ph-CHCH_2O), 4.26–4.33 (1H, m, *t*Bu-CHCH_2O), 4.78 (1H, dd, *J* 10.0 and 8.5, Ph-CHCH_2O), 5.54 (1H, dd, *J* 9.0 and 8.5, Ph-C*H*N), 6.30 (1H, d, J 7.8, Pyr-C(5)*H* or Pyr-C(3)*H*), 6.36 (1H, d, *J* 7.8, Pyr-C(3)*H* or Pyr-C(5)*H*), 6.86 (1H, app td, *J* 8.0 and 1.0, Ph-C(4)*H*), 6.91 (1H, app td, *J* 8.0 and 1.0, Ph-C(4)*H*), 7.27–7.45 (8H, m, 2 × Ph-C(5)*H* + Pyr-C(4)*H* + *Ph*-CHN), 7.82 (1H, dd, *J* 7.9 and 1.6, Ph-C(3)*H*), 7.91 (1H, dd, *J* 7.9 and 1.6, Ph-C(3)*H*), 8.68 (1H, app d, *J* 7.8, Ph-C(6)*H*), 8.72 (1H, app d, *J* 7.8, Ph-C(6)*H*), 11.52 (1H, br s, N*H*), 11.85 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 26.0 (3C, (CH_3)$_3$C), 33.9 ((CH_3)$_3$*C*), 67.1 (*t*Bu-CH*C*H$_2$O), 70.0 (Ph-*C*HN), 73.1 (Ph-CH*C*H$_2$O), 76.1 (*t*Bu-*C*HN), 103.2 + 103.3 (Pyr-*C*(3)H + (Pyr-*C*(5)H), 111.3 + 111.5 (2 × Ph-*C*2), 118.3–118.6 (4C, 2 × Ph-*C*(6)H + 2 × (Ph-*C*(4)H)), 126.4 (2C, *Ph*-CHN), 127.5 (1C, *Ph*-CHN), 128.7 (2C, *Ph*-CHN), 129.2 + 129.5 (2 × Ph-*C*(3)H), 131.8 + 132.1 (2 × Ph-*C*(5)H), 138.5 (Pyr-*C*(4)H), 142.3 (C^{IV}, *Ph*CHN), 142.9 + 143.1 (2 × Ph-*C*1), 153.8 (2C, 2 × Pyr-*C*2), 163.7 + 165.2 (2 × N=*C*O); *m*/*z* (ESI) 532.4.2 (MH^+).

***N*²-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-*N*⁶-(2-[(4*S*)-4-benzyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl)pyridine-2,6-diamine 14.** Ligand **14** was prepared from amine **4b** (174 mg, 0.69 mmol), 6-bromopyridine **11** (217 mg, 0.58 mmol), NaO*t*-Bu (66.3 mg, 0.69 mmol), Xantphos (33.6 mg, 0.058 mmol), Pd_2dba_3 (13.3 mg, 0.015 mmol, 5 mol% Pd) in 2.3 mL of toluene. The mixture was heated at 165 °C for 1h in a microwave apparatus with the initial power supplied being 300W. Compound **14** was obtained as a white powder (253 mg, 80%) after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 80/20). Mp: 84–86 °C; TLC: R_f= 0.47 (pentane/CH_2Cl_2, 80/20); $[\alpha]_D^{20}$ –7.2 (*c* 1.0 in $CHCl_3$); found: C, 74.6; H, 6.7; N, 12.6. $C_{34}H_{35}N_5O_2$ requires C, 74.8; H, 6.5; N, 12.8%; υ_{max}(KBr)/cm^{-1} 3189, 3099, 2963, 2902, 1634, 1567, 1436, 1358, 1279, 1256, 1155, 1056 and 750; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.00 (9H, s, (CH_3)$_3$C), 2.88 (1H, dd, *J* 13.6 and 7.6, PhCH_2), 3.04 (1H, dd, *J* 13.6 and 7.6, PhCH_2), 4.01–4.04 (5H, m, *t*Bu-CHCH_2O + *t*Bu-C*H*N + Bn-CHCH_2O),

4.67 (1H, quint, *J* 7.6, Bn-C*H*), 6.15 (1H, d, *J* 7.9, Pyr-C(5)*H* or Pyr-C(3)*H*), 6.38 (1H, d, *J* 7.9, Pyr-C(3)*H* or Pyr-C(5)*H*), 6.87 (2H, app t, *J* 7.5, 2 × Ph-C(4)*H*), 7.20–7.43 (8H, m, 2 × Ph-C(5)*H* + Pyr-C(4)*H* + *Ph*CH_2), 7.83 (2H, d, *J* 7.9, 2 × Ph-C(3)*H*), 8.68 (1H, d, *J* 8.5, Ph-C(6)*H*), 8.73 (1H, d, *J* 8.5, Ph-C(6)*H*), 11.48 (1H, br s, N*H*), 11.65 (1H, br s, N*H*); δ_C (75 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, (CH_3)$_3$C), 33.9 ((CH_3)$_3$*C*), 42.4 (1C, Ph*C*H_2), 67.1 (*t*Bu-CH*C*H_2O), 68.1 (Bn-*C*HN), 70.5 (Bn-CH*C*H_2O), 76.3 (*t*Bu-*C*HN), 103.0 + 103.6 (Pyr-*C*(3)H + (Pyr-*C*(5)H), 111.3 + 111.5 (2 × Ph-*C*2), 118.4–118.6 (4C, 2 × Ph-*C*(6)H) + 2 × Ph-*C*(4)H)), 126.4 (1C, *Ph*CHN), 128.6 (2C, *Ph*CHN), 129.3 (4C, *Ph*CHN + 2 × Ph-*C*(3)H), 131.7 + 131.9 (2 × Ph-*C*(5)H), 138.4 (2C, Pyr-*C*(4)H + C^{IV} *Ph*CH_2), 142.9 (2 × Ph-*C*1), 153.8 + 153.9 (2C, 2 × Pyr-*C*2), 163.7 + 164.2 (2 × N=*C*O); *m*/*z* (ESI) 546.4 (MH^+).

***N*^{2}-{2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-*N*^{6}-(2-[(4*S*)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl)pyridine-2,6-diamine 15.** Ligand **15** was prepared from amine **4c** (141 mg, 0.69 mmol), 6-bromopyridine **11** (217 mg, 0.58 mmol), NaO*t*-Bu (66.3 mg, 0.69 mmol), Xantphos (33.6 mg, 0.058 mmol), Pd_2dba_3 (13.3 mg, 0.015 mmol, 5 mol% Pd) in 2.3 mL of toluene. The mixture was heated at 165 °C for 1h in a microwave apparatus with the initial power supplied being 300W. Compound **15** was obtained as a white powder (208 mg, 72%) after purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 70/30). Mp: 105–108 °C; TLC: R_f= 0.23 (pentane/CH_2Cl_2, 70/30); $[\alpha]_D^{20}$ –9.1 (*c* 1.0 in $CHCl_3$); found: C, 72.1; H, 7.1; N, 13.7. $C_{30}H_{35}N_5O_2$ requires C, 72.4; H, 7.1; N, 13.7%; υ_{max}(KBr)/cm^{-1} 3190, 3100, 2960, 2900, 1643, 1567, 1437, 1357, 1283, 1154, 1061, 784 and 749; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.02 (9H, s, (CH_3)$_3$C), 1.12 (6H, d, *J* 6.7, (CH_3)$_2$CH), 1.83 (1H, octuplet, *J* 6.7, (CH_3)$_2$C*H*), 4.05 (1H, t, *J* 8.1, *i*Pr-CHCH_2O), 4.14–4.23 (3H, m, *t*Bu-CHCH_2O + *i*Pr-C*H*N + *t*Bu-C*H*N), 4.30–4.33 (1H, m, *t*Bu-CHCH_2O), 4.40 (1H, dd, J 9.4 and 8.1, *i*Pr-CHCH_2O), 6.39 (2H, d, *J* 7.9, Pyr-C(5)*H* and Pyr-C(3)*H*), 6.89 (2H, app td, *J* 8.0 and 1.0, 2 × Ph-C(4)*H*), 7.39 (2H, ddd, *J* 8.7, 7.7 and 1.6, 2 × Ph-C(5)*H*), 7.44 (1H, t, *J* 7.9, Pyr-C(4)*H*), 7.85 (2H, dd, *J* 8.0 and 1.6, 2 × Ph-C(3)*H*), 8.70–8.76 (2H, m, 2 × Ph-C(6)*H*), 11.65 (1H, br s, N*H*), 11.68 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 19.0 ((CH_3)$_2$CH), 19.5 ((CH_3)$_2$*C*H), 25.9 (3C, (CH_3)$_3$C), 33.5 ((CH_3)$_2$*C*H), 33.9 ((CH_3)$_3$*C*), 67.1 (*t*Bu-CH*C*H_2O), 69.2 (*i*Pr-CH*C*H_2O), 73.0 (*i*Pr-*C*HCH$_2$O), 76.3 (*t*Bu-*C*HN), 103.0 + 103.1 (Pyr-*C*(3)H + Pyr-*C*(5)H), 111.5 + 111.6 (2 × Ph-*C*2), 118.4–118.6 (4C, 2 × Ph-*C*(6)H) + 2 × (Ph-*C*(4)H)), 129.3 (2C, 2 × Ph-*C*(3)H), 131.8 (2C, 2 × Ph-*C*(5)H), 138.5 (Pyr-*C*(4)H), 142.9 + 143.0 (2 × Ph-*C*1), 154.0 (2C, 2 × Pyr-*C*(2)), 163.7 (2C, 2 × N=*C*O); *m*/*z* (ESI) 498.5 (MH^+).

2-[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazol-2-yl]-*N*-phenylaniline 16. Ligand **16** was obtained as a clear yellow oil (187 mg, 92%) from amine **4e** (151 mg, 0.69 mmol) and iodobenzene (220 μL, 422 mg, 2.07 mmol) after purification by flash chromatography on silica gel (pentane/Et_2O, 98/2). TLC: R_f = 0.48 (pentane/Et_2O, 95/5); $[\alpha]_D^{20}$ +47.3 (*c* 1.0 in $CHCl_3$); found: C, 77.1; H, 7.5; N, 9.1. $C_{19}H_{22}N_2O$ requires C, 77.5; H, 7.5; N, 9.5%; υ_{max}(KBr)/cm^{-1} 3172, 3029, 2960, 1634, 1593, 1457, 1325, 1287, 1135, 1052 969, 747 and 697; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.95 (9H, s, (CH_3)$_3$C), 4.08–4.17 (2H, m, C*H*N + CH_2O), 4.24–4.31 (1H, m, CH_2O), 6.74 (1H, app t, *J* 8.0 and 1.0, Ph-C(4)*H*), 7.02 (1H, t, *J* 7.2, *Ph*-NH), 7.22–7.39 (6H, m, *Ph*-NH + Ph-C(5)*H* + Ph-C(6)*H*), 7.78 (1H, dd, *J* 7.9 and 1.5, Ph-C(3)*H*), 10.67 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.9 (3C, (CH_3)$_3$C), 33.9 ((CH_3)$_3$*C*), 67.0 (*C*H_2O), 76.3 (*C*HN), 110.4 (Ph-*C*2), 113.1 (Ph-*C*(6)H), 116.9 (Ph-*C*(4)H), 121.2 (2C, 2 × *Ph*-NH), 122.5 (*Ph*-NH), 129.2 (2C, 2 × *Ph*-NH), 129.9 (Ph-*C*(3)H), 131.8 (Ph-*C*(5)H), 141.6 (Ph-*C*1), 145.6 (C^{IV}, *Ph*-NH), 163.6 (N=*C*O); *m*/*z* (ESI) 219.2 (MH^+); *m*/*z* (ESI) 295.3 (MH^+).

3) General procedure for addition of diethylzinc to aldehydes

A solution of ligand (0.025 mmol) in toluene (0.5 mL) was cooled to 0 °C. A 1.1M solution of diethylzinc in toluene (1 mL, 1.1 mmol) was added over a period of 5 min. The yellow solution was stirred at room temperature for 30 minutes, cooled at –20 °C and the aldehyde was added (0.5 mmol) dropwise. Then the mixture was stirred at –20 °C for 24 hours. The reaction mixture was quenched with 10% H_2SO_4 aqueous solution (2 mL) and extracted with diethyl ether. The organic layer was washed with 10% H_2SO_4 aqueous solution (3 mL), saturated aqueous $NaHCO_3$ (5 mL) solution and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography.

1-Phenylpropan-1-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 89% (in the case of **5e** as ligand). $[\alpha]_D^{20}$ +19.8 (*c* 1.0 in $CHCl_3$). {Lit.[18] $[\alpha]_D^{20}$ +40.3 (*c* 1.21 in $CHCl_3$) for 96% *ee* (*R*)}. 58% *ee* (*R*, in the case of **5e** as ligand) by HPLC analysis (hexane/2-propanol, 98/2; 0.8 mL/min), t_r = 13.2 min for (*R*) and t_r = 15.9 min for (*S*).

1-(4-Chlorophenyl)propan-1-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 54%. $[\alpha]_D^{20}$ +18.2 (*c* 2.4 in $CHCl_3$). {Lit.[19] $[\alpha]_D^{20}$ +27.3 (*c* 2.4 in $CHCl_3$)}. 55% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 99/1; 1.0 mL/min) using an OD column, t_r = 18.7 min for (*S*) and t_r = 20.1 min for (*R*).

1-(4-Methoxyphenyl)propan-1-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 87%. $[\alpha]_D^{20}$ +14.4 (*c* 1.25 in $CHCl_3$). {Lit.[18] $[\alpha]_D^{20}$ +38.9 (*c* 1.23 in $CHCl_3$) for 96% *ee* (*R*)}. 57% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 95/5; 0.5 mL/min) using an OD column, t_r = 19.1 min for (*R*) and t_r = 21.5 min for (*S*).

1-Pentafluoropropan-1-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 34%. $[\alpha]_D^{20}$ –1.4 (*c* 2.1 in pentane). {Lit.[20] $[\alpha]_D^{20}$ +3.0 (*c* 2.01 in pentane) for 96% *ee* (*S*)}. 26% *ee* (*R*) by HPLC analysis (heptane/EtOH, 99.5/0.5; 0.5 mL/min) using an IA column, t_r = 40.1 min for (*S*) and t_r = 41.6 min for (*R*).

1-(2-Naphthyl)propan-1-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 85/15). Yield : 90%. $[\alpha]_D^{20}$ +21.7 (*c* 1.2 in benzene). {Lit.[21] $[\alpha]_D^{20}$ +29.8 (*c* 4.7 in benzene) for 99% *ee* (*R*)}. 57% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 98/2; 1.0 mL/min) using an OD column, t_r = 26.7 min for (*S*) and t_r = 29.8 min for (*R*).

1-(1-Naphthyl)propan-1-ol. The alcohol was obtained as a white solid after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 76%. $[\alpha]_D^{20}$ +43.8 (*c* 1.2 in $CHCl_3$).

{Lit.[18] $[\alpha]_D^{20}$ +60.3 (*c* 1.11 in $CDCl_3$) for 97% *ee* (*R*)}. 68% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 90/10; 1.0 mL/min) using an OD column, $t_r = 5.3$ min for (*S*) and $t_r = 8.5$ min for (*R*).

1-Phenylpent-1-yn-3-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 81%. $[\alpha]_D^{20}$ +7.5 (*c* 1.25 in Et_2O). {Lit.[22] $[\alpha]_D^{20}$ +21.97 (*c* 1.27 in Et_2O) for 90% *ee* (*R*)}. 13% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 90/10; 1.0 mL/min) using an OD column, $t_r = 5.9$ min for (*R*) and $t_r = 12.0$ min for (*S*).

(*E*)-1-Phenylpent-1-en-3-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 94%. $[\alpha]_D^{20}$ +1.8 (*c* 1.0 in $CHCl_3$). {Lit.[18] $[\alpha]_D^{20}$ +18.4 (*c* 0.61 in $CHCl_3$) for 75% *ee* (*R*)}. 6% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 90/10; 1.0 mL/min) using an OD column, $t_r = 7.4$ min for (*R*) and $t_r = 10.8$ min for (*S*).

1-Phenylpentan-3-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 71%. $[\alpha]_D^{20}$ −12.2 (*c* 2.45 in $CHCl_3$). {Lit.[23] $[\alpha]_D^{20}$ −23.5 (*c* 2.45 in $CHCl_3$) for 97% *ee* (*R*)}. 55% *ee* (*R*) by HPLC analysis (hexane/2-propanol, 95/5; 1.0 mL/min) using an OD column, $t_r = 8.8$ min for (*R*) and $t_r = 12.3$ min for (*S*).

1-Cyclohexypropan-1-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 70%. $[\alpha]_D^{20}$ +1.8 (*c* 1.0 in $CHCl_3$). {Lit.[18] $[\alpha]_D^{20}$ +5.4 (*c* 0.61 in $CHCl_3$) for 93% *ee* (*R*)}. 32% *ee* (*R*) by HPLC analysis of the 3,5-dinitrobenzoate (hexane/2-propanol, 98/2; 1.0 mL/min) using an OD column, $t_r = 8.8$ min for (*S*) and $t_r = 12.3$ min for (*R*).

Nonan-3-ol. The alcohol was obtained as a colourless oil after purification by flash chromatography (pentane/EtOAc, 90/10). Yield : 65%. $[\alpha]_D^{20}$ −4.6 (*c* 1.46 in $CHCl_3$). {Lit.[18] $[\alpha]_D^{20}$ −9.0 (*c* 0.68 in $CHCl_3$) for 72% *ee* (*R*)}. 54% *ee* (*R*) by HPLC analysis of the 3,5-dinitrobenzoate (hexane/2-propanol, 95/5; 1.0 mL/min) using an OD column, $t_r = 8.3$ min for (*S*) and $t_r = 9.2$ min for (*R*).

Preparation of the $ZnCl_2$.complex 5e

To an oven-dried Schlenk tube was added ligand **5e** (50 mg, 0.17 mmol) and dry acetonitrile (2.5 mL) under an atmosphere of nitrogen. A 1M solution of $ZnCl_2$ in Et_2O (170 μL, 0.17 mmol) was added and the solution was stirred at room temperature for 3 hours. The solvents were then removed under vacuum to leave a solid residue. This solid was washed three times with Et_2O and dried under vacuum to leave a yellow solid (72 mg, 99%). Mp: 200–205 °C (decomposition); found: H, 4.5; N, 9.3. $C_{18}H_{21}N_3O$ requires H, 4.9; N, 9.7%; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.07 (9H, s, $(CH_3)_3C$), 4.33 (1H, dd, *J* 10.0 and 6.4, C*H*N), 4.49 (1H, dd, *J* 10.0 and 9.3, CH_2O), 4.56 (1H, dd, *J* 9.3 and 6.4, CH_2O), 6.41 (1H, t, *J* 6.4, Pyr-C(5)*H*), 6.90 (1H, d, *J* 9.4, Pyr-C(3)*H*), 7.17 (1H, t, *J* 7.9, Ph-C(4)*H*), 7.34–7.53 (4H, m, Ph-C(5)*H* + Ph-C(6)*H* + Pyr-C(4)*H* + Pyr-C(6)*H*), 7.74 (1H, d, *J* 7.9, Ph-C(3)*H*), 11.97 (1H, br s, N*H*); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.8 (3C, (CH_3)$_3$C), 34.5 ((CH_3)$_3$*C*), 70.0 (*C*H$_2$O), 74.0 (*C*HN), 109.0 (Pyr-*C*(5)H), 113.4 (Pyr-*C*(3)H), 119.1 (Ph-*C*2), 124.1 (Ph-*C*(4)H), 124.9 (Ph-*C*(6)H), 130.4 (Ph-*C*(3)H), 133.4 (Ph-*C*(5)H), 134.9 (Pyr-*C*(4)H or Pyr-*C*(6)H), 141.2 (Pyr-*C*(6)H or Pyr-*C*(4)H), 146.4 (Ph-*C*1), 156.3 (Pyr-*C*2), 167.9 (N=*C*O).

X-ray structure determination of 5e and $ZnCl_2$.5e

Single-crystal structure of 5e. Crystals suitable for X-ray analysis were grown in pentane/EtOAc (9/1) solution at room temperature. $C_{18}H_{21}N_3O$, $M = 295.38$, orthorhombic, $a = 6.1265(4)$, $b = 13.8082(9)$, $c = 19.2305(13)$ Å, $U = 1626.82(19)$ Å^3, $T = 293$ K, space group $P2_12_12_1$ (no.19), $Z = 4$, 8732 reflections measured, 2067 unique ($R_{int} = 0.0205$) which were used in all calculations. The final $wR(F_2)$ was 0.1009 (all data).

Single-crystal structure of $ZnCl_2$·5e. Crystals suitable for X-ray analysis were grown in a solution of dichloromethane layered by hexane at room temperature. $C_{18}H_{21}N_3OCl_2$ Zn, $M = 431.65$, orthorhombic, $a = 10.4417(6)$, $b = 11.1428(6)$, $c = 17.0180(9)$ Å, $U = 1980.04(19)$ Å^3, $T = 293$ K, space group $P2_12_12_1$ (no.19), $Z = 4$, 13618 reflections measured, 4783 unique ($R_{int} = 0.0194$) which were used in all calculations. The final $wR(F_2)$ was 0.0759 (all data).

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