Modular Synthesis of Chiral β-Diketiminato-Type Ligands Containing 2-Oxazoline Moiety via Palladium-Catalyzed Amination

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Abstract: A family of new chiral β-diketiminato-type ligands containing oxazoline moiety has been synthesized in moderate to high yields (typically 30–95%) via a Pd-catalyzed amination reaction of chiral oxazolines with primary amines and amides. Notably, (*S*)-*tert*-butylsulfinamide was successfully incorporated into the ligand framework as a coupling partner in amination. Due to the readily available pool of chiral building blocks, this represents a facile and modular approach for synthesizing libraries of novel chiral β-diketiminato-type ligands, with potential applications in asymmetric catalysis.

Key words: chiral auxiliaries, ligands, chirality, nitrogen, amination, palladium

Because the reactivity and selectivity of metal catalysts are largely determined by the auxiliary ligands, ligand design has been a central theme in catalysis, particularly in asymmetric synthesis, which continues to be of great academic and industrial importance.[1] One of the challenges is to derive efficient chiral catalysts for asymmetric induction in different substrates with subtle variations. Since it is not expected that a single catalyst will work for a wide range of substrates, an efficient strategy towards new catalysts would be the design of a search pathway that provides access to a large number of structurally similar ligands with tunable yet diverse substituents.[2] Indeed, many researchers have sought to develop asymmetric catalysts by screening a large pool of chiral ligands.[3] To this end, a modular approach for the ligand library construction is highly desirable.[4]

β-Diketiminato ligands (Figure 1A) have received great attention in coordination chemistry due to the ease of fine tuning of the steric and electronic properties.[5] These ligands are monoanionic upon deprotonation and form strong bonds with metals, usually in a bidentate fashion. Various β-diketiminato metal complexes have been employed in a number of catalytic reactions.[6,7] In a broader sense, the monoanionic, anilinido-imino ligands (Figure 1B) can be included as a variation of the regular β-diketiminato framework.[8] One example is the *ortho*-oxazoline-substituted anilines, in which aniline nitrogens are typically not further functionalized.[9] Due to the presence of an aromatic ring, the resonance in the backbone is attenuated in comparison with the regular ligands and this may offer opportunity for electronic differentiation and stereocontrol upon coordination.[10] Given their extensive applications, it is somewhat surprising that the chiral variants of β-diketiminato ligands are relatively less developed in the literature,[11,12] although these moieties are often incorporated as subcomponents of multidentate or macrocyclic ligands in chiral environments.[13] In principle, stereo-directing groups can be introduced into all the R^1–R^5 substituents. Of particular interest are ligands with chiral substituents at the periphery (R^1 and R^5) that are in close proximity with the open coordination site where catalysis is taking place. Among these, monoanionic, chiral semicorrin[14] and bisoxazoline ligands[15] are some of the successful examples, where chiral substituents are introduced at the periphery (R^1 and R^5) positions. Another approach is to incorporate axial chirality at the backbone, as demonstrated in ligands derived from isoquinoline and 2-aminonaphthalene[16] and in binaphthyl surrogates based on inner N–H–N hydrogen bonding.[17] Variation of backbone with stereogenic heteroatoms can also lead to axial chirality.[18]

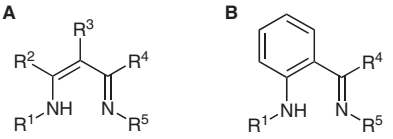

Figure 1 **A**: β-Diketiminato ligands where R^1–R^5 substituents can be stereogenic. **B**: Anilinido-imino variations.

In our effort of constructing a chiral ligand framework, we have envisioned a modular approach for the synthesis of a library of chiral β-diketiminato type ligands based on the direct coupling of two independent building blocks. The synthetic target (see Scheme 1) is a type of anilinido-imino ligands, with imine nitrogen from a chiral oxazoline moiety and amine nitrogen from an aniline/amide moiety. For the modular assembly, a choice of readily available chiral building blocks is critical. The 2-oxazoline was chosen as the imine nitrogen subunit because chiral oxazolines have widespread use as ligands and are readily accessible from the chiral pool of amino alcohols.[19] The ability of varying both chiral and stereo-directing centers independently allows the opportunity to explore the synergy between them. Herein we report the synthesis and characterization of a library of new chiral β-diketiminato type ligands via the Pd-catalyzed Buchwald–Hartwig amination reaction (Scheme 1).

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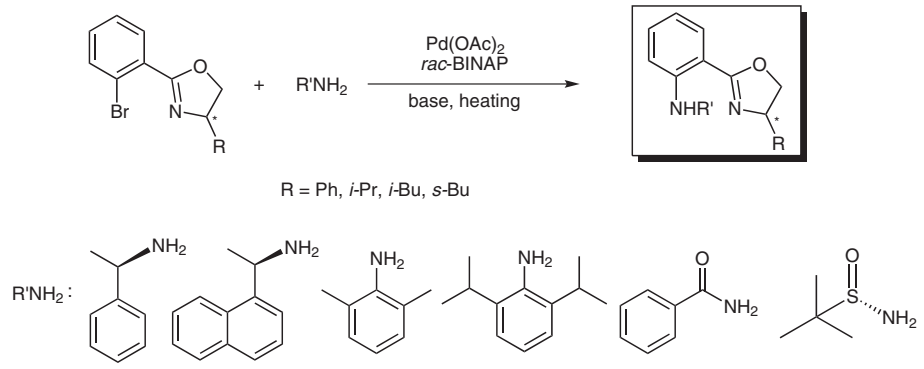
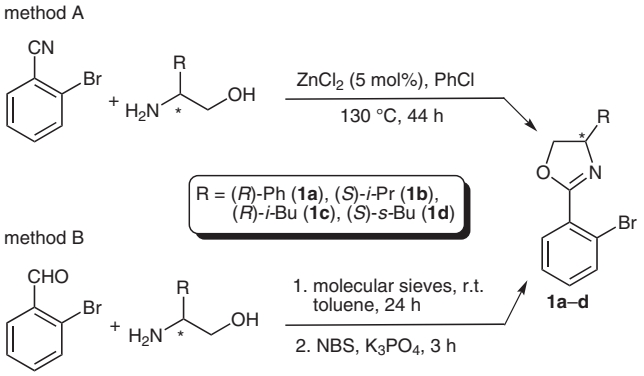


Scheme 1 Synthesis of chiral β-diketiminato type ligands

We started out to synthesize a series of β-diketiminato type ligands containing one or two chiral substituents at the periphery, which are in close proximity with the open coordination site where catalysis would take place. By independently varying two points of diversity, the oxazoline fragment R and the amine component (R′), a library of chiral β-diketiminato type ligands **L1**–**L24** has been generated in a modular fashion (Scheme 1).

Chiral 2-(2′-bromophenyl)oxazolines **1a–d** were prepared from readily available chiral amino alcohols in a single step via two methods (Scheme 2).[20,21] In our hands, the second method seems to give better yields in shorter reaction time and offers another possibility to modify the aryl backbone. The resulting compounds **1a–d** were utilized as the coupling partners for the preparation of chiral β-diketiminato type ligand variants (see below).

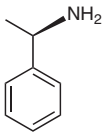
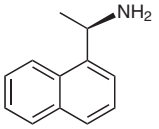
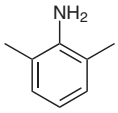
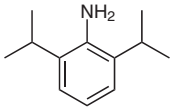
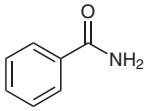
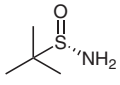


Scheme 2 Synthesis of chiral 2-oxazolines

The desired chiral β-diketiminato-type compounds **L1**–**L24** (Figure 1) were synthesized via a cross coupling strategy, joining the chiral oxazoline and amine/amide moieties in a modular fashion (Scheme 1). The Pd-catalyzed Buchwald–Hartwig amination reaction was chosen because it has been extensively studied and modified with significant improvements for the cross coupling reaction of aryl or alkyl halides with amines or amides.[22,23] It has been previously employed in the library synthesis, including examples involving chiral oxazolines.[24,25] In principle, other cross coupling protocols such as Cu-catalyzed amination could be applied as well.

Thus, heating a mixture of chiral oxazolines **1a–d** and (*R*)-α-methylbenzylamine in the presence of catalytic amount of $Pd(OAc)_2$-BINAP under refluxing toluene afforded compounds **L1–L4** in moderate yields after purification by column chromatography (see Table 1, entries 1–4). Compounds **L1** and **L3** were obtained as yellow solids while **L2** and **L4** are oily.

Table 1 Pd-Catalyzed Amination Reactions of Chiral Oxazolines **1a–d** with Primary Alkyl- or Arylamines and Amides[a]

Entry	R	R′NH_2	Ligand	Time (h)	Yield (%)[b]
1	Ph		**L1**	68	35[c]
2	*i*-Pr		**L2**	37	47
3	*i*-Bu		**L3**	40	56
4	*s*-Bu		**L4**	37	44
5	Ph		**L5**	24	50[c]
6	*i*-Pr		**L6**	24	73
7	*i*-Bu		**L7**	67	30
8	*s*-Bu		**L8**	67	36
9	Ph		**L9**	48	84
10	*i*-Pr		**L10**	48	77
11	*i*-Bu		**L11**	48	74
12	*s*-Bu		**L12**	48	83
13	Ph		**L13**	48	80
14	*i*-Pr		**L14**	48	84
15	*i*-Bu		**L15**	48	75
16	*s*-Bu		**L16**	48	63
17	Ph		**L17**[d]	20	98
18	*i*-Pr		**L18**[d]	20	95
19	*i*-Bu		**L19**[d]	32	98
20	*s*-Bu		**L20**[d]	20	99
21	Ph		**L21**[d]	5 d	84
22	*i*-Pr		**L22**[d]	5 d	60
23	*i*-Bu		**L23**[d]	2 d	70
24	*s*-Bu		**L24**[d]	2 d	<10

[a] Reaction conditions: oxazoline **1a–d** (1.0 equiv), amine (1.2 equiv), *t*-BuONa (1.4 equiv), $Pd(OAc)_2$ (5 mol%), *rac*-BINAP (5 mol%), toluene, 120 °C.

[b] Isolated yields.

[c] Exists as a ~9:1 mixture of two stereoisomers.

[d] Reaction conditions: oxazoline **1a–d** (1.0 equiv), benzamide or sulfonamide (4.0 equiv), Cs_2CO_3 (2 equiv), $Pd(OAc)_2$ (10 mol%), *rac*-BINAP (20 mol%), toluene, heating.

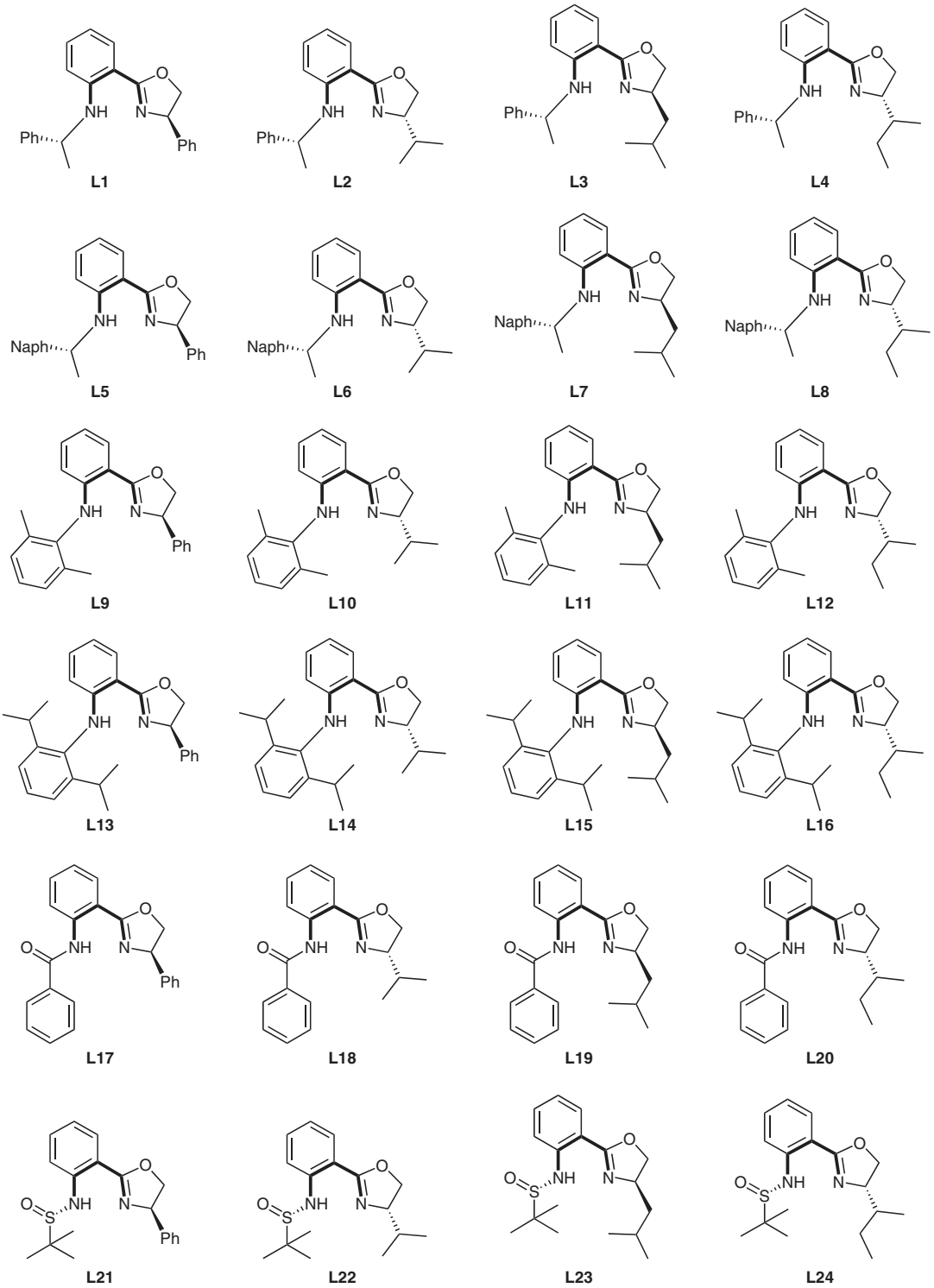


Figure 2 Structure of ligands **L1**–**L24**

In order to vary the amine terminal, the phenyl substituent R′ in **L1**–**L4** was replaced with naphthalene, a sterically bulkier substituent. Thus, ligands **L5**–**L8** were similarly synthesized from Pd-catalyzed amination of chiral oxazolines **1a**–**d** with (*R*)-1-(1-naphthyl)ethylamine in moderate yields as oily compounds (Table 1, entries 5–8). It is noted that the synthesis of **L1**, **L7**, and **L8** required longer reaction times and the isolated yields were generally rather low. Attempts were made to improve the coupling reactions without much success; yields of 30–73% were typically obtained for the series of alkylamines, in part, due to formation of several unidentified by-products and subsequent difficulty in isolation. Use of state of the art phosphine ligands instead of BINAP, or other coupling protocols such as Cu-catalyzed amination may improve the yields, and efforts along these lines are ongoing.

We were interested in the effect of one stereogenic center in conjunction with a bulky substituent on catalytic selectivity. In this context, *ortho*-substituted anilines were used as the coupling partner. 2,6-Dimethylaniline and 2,6-diisopropylaniline were separately treated with chiral oxazolines **1a–d** under similar conditions as above to afford ligands **L9–L16**. Yields of this series were generally higher (63–84%; see Table 1), presumably due to the enhanced nucleophilicity upon deprotonation of arylamines compared to alkylamines utilized in ligands **L1–L8**.

A primary amide as a coupling partner was also employed to synthesize ligands **L17–L20**. Initial attempts under same conditions afforded minimal amount of the desired products, possibly because of the side reactions at high temperatures.[8d] In subsequent experiments, the reaction temperature was reduced to 100 °C, the Pd and BINAP loadings were increased to 10 mol% and 20 mol%, respectively, and 4 equivalents of the amide (see Table 1) were employed. Under these conditions, compounds **L17–L20** were obtained in very high yields (>95%) and in shorter reaction times (see Table 1). This approach can be used to expand the library of chiral β-diketiminato type ligands to incorporate chiral amide substituents when they are potentially beneficial, and a pool of chiral amides is available as well.

Under similar conditions, a chiral sulfinamide, (*S*)-*tert*-butylsulfinamide,[26] can be coupled to the oxazoline moiety, resulting in compounds **L21–L24**. The reactions require longer reaction times, and the yields are generally good (60–84%), except the one with *sec*-butyl substituent (**L24**), despite the structural similarity and multiple attempts. To the best of our knowledge, sulfinamides have not previously been studied as coupling partners in the Buchwald–Hartwig amination reaction.

The structures of the synthesized compounds **L1–L24** are shown in Figure 2, and they have been characterized by ^{1}H and ^{13}C NMR spectroscopy. Characteristic is the NH signal in the downfield region of 9–10 ppm for **L1–L16**, 13.2–13.4 ppm for **L17–L20**, and 11–12 ppm for **L21–L24**. The observation is consistent with the presence of an intramolecular hydrogen bonding interaction between the NH group and the imino nitrogen, which is typical for this type of compounds. Also noteworthy is that the ^{1}H NMR ($CDCl_3$) spectra of **L1** and **L5** showed two distinct N-H peaks at δ = 9.08 and 8.82 (minor) for **L1**; and at δ = 9.21 and 8.88 (minor) for **L5**, respectively. Guiry and co-workers have also observed the presence of two distinct NH peaks in a similar ligand framework.[27] At elevated temperature (30 °C), these peaks coalesced to a single resonance, which is attributed to the presence of rotamers resulting from hindered rotation. When ligand **L1** was subjected to the VT-NMR experiment in the range of 0–55 °C, however, no obvious shift or coalescence was observed, suggesting the presence of a mixture of diastereomers resulting from minor racemization. Preliminary investigations suggested that the racemization occurred at the oxazoline side, not the amine side; and this process is rather specific to oxazolines with aryl substituents at the 4-position.[21] It should be noted that, in the isolated samples, only one set of signals was detected for the remaining ligands. Furthermore, the formulation of these compounds was confirmed with mass spectrometry (GC-MS and HRMS) and optical rotations, which are in agreement with the intended structures.

In conclusion, a library of twenty four new chiral β-diketiminato type ligands containing oxazoline moiety has been synthesized via the Pd-catalyzed Buchwald–Hartwig amination reaction of chiral oxazolines and primary amines and amides. By independently varying two components (R and R′), this modular synthetic approach opens a pathway to obtain different combinations of chirality (e.g., *RR*, *RS*, *SS*, and *SR*), allowing exploration of the synergistic interactions between two chiral or stereo-directing centers in catalysis. It also offers the opportunity to introduce additional coordinating groups to stabilize the ligation. The ligand framework presented here should be widely applicable in a range of metal-based catalytic reactions. These compounds themselves are also potential chiral proton sources,[17] with the NH proton located in a chiral microenvironment. Considering the availability of large numbers of various chiral amines and amides, this methodology will allow the synthesis of a large family of new chiral β-diketiminato-type ligands for high throughput screening in asymmetric catalysis as well as in other applications. Our ongoing efforts involve optimizing and expanding the chiral β-diketiminato type ligands and searching for applications in asymmetric catalyses.

All air- or moisture-sensitive reactions were carried out under a dry N_2 atmosphere, employing standard Schlenk line and dry box techniques. Solvents were dried over Na/benzophenone and distilled under N_2. Deuterated solvents were purchased from Cambridge Isotope Laboratory and used as received. 2-(2′-Bromophenyl)oxazolines **1a–d** were prepared and purified according to a modified literature procedure. 2-Bromobenzonitrile, 2-bromobenzaldehyde, (*S*)-*tert*-butylsulfinamide, (*R*)-2-phenylglycinol, (*R*)-α-methylbenzylamine, (*R*)-(+)-1-(1-naphthyl)ethylamine, (*R*)-leucinol, *N*-bromosuccinimide, Cs_2CO_3, and K_3PO_4 were purchased from Aldrich while L-Valinol and L-isoleucinol were purchased from Fluka and used as received.

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 NMR spectrometer and referenced to the residual peaks in $CDCl_3$ or C_6D_6 at 298 K. Melting points were obtained on a Mel-Temp apparatus and were uncorrected. Optical rotations were recorded on a Rudolph Autopol III polarimeter with sodium D line (589 nm) at r.t. GC/MS analyses were performed on an HP 5890 GC/HP 5971/B MSD system with electron impact ionization (70 eV). High-resolution mass spectrometry (HRMS) was performed using high-resolution time of flight G1969A instrumentation (Agilent, Santa Clara, CA, USA).

Amination of Chiral Oxazolines with Primary Amines; General Procedure

An oven dried Schlenk flask was charged with $Pd(OAc)_2$ (5 mol%), *rac*-BINAP (5 mol%), chiral aryl bromide **1a–d** (1.2 mmol, 1.0 equiv), the appropriate primary amine (1.4 mmol, 1.2 equiv), *t*-BuONa (1.7 mmol, 1.4 equiv), and anhyd degassed toluene (15 mL), and the mixture was refluxed under N_2 flow at 120 °C until an appropriate amount of the ligand was formed as judged by TLC

(hexane–EtOAc, 9:1) and ^{1}H NMR spectroscopy. The crude product was then purified by column chromatography on silica gel eluting with a mixture of hexanes and EtOAc.

(4*R*)-4,5-Dihydro-2-{2′-[(*R*)-α-methylbenzylamino]phenyl}-4-phenyloxazole (L1)

Yield: 35%; mp 56–59 °C; $[\alpha]_D$ –367.5 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.54 [3 H, d, *J* = 5.0 Hz, PhCH(CH_3)N], 4.13 [1 H, t, *J* = 5.0 Hz, NCH(R)CH_2O], 4.59 [1 H, q, *J* = 5.0 Hz, PhC*H*(Me)N], 4.72 [1 H, t, *J* = 5.0 Hz, NCH(R)CH_2O], 5.54 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 6.45 (1 H, d, *J* = 10.0 Hz, ArH), 6.57 (1 H, t, *J* = 10.0 Hz, ArH), 7.13 (1 H, t, *J* = 10.0 Hz, ArH), 7.18 (1 H, d, *J* = 10.0 Hz, ArH), 7.29 (1 H, t, *J* = 10.0 Hz, ArH), 7.35 (2 H, m, ArH), 7.78 (2 H, d, *J* = 5.0 Hz, ArH), 9.08 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 24.1 [PhCH(*C*H_3)N], 59.4 [Ph*C*H(Me)N], 69.0 [NCH(R)*C*H_2O], 71.8 [N*C*H(R)CH_2O], 107.3 (CH_{arom}), 110.9 (CH_{arom}), 113.5 (CH_{arom}), 124.8 (CH_{arom}), 125.4 (CH_{arom}), 125.7 (CH_{arom}), 126.4 (CH_{arom}), 127.5 (CH_{arom}), 127.6 (CH_{arom}), 128.9 (CH_{arom}), 131.5 (CH_{arom}), 141.9 (CH_{arom}), 144.4 (CH_{arom}), 147.4 (CH_{arom}), 164.7 (CH_{arom}).

GC/MS: *m*/*z* = 342 $[M]^+$, 327, 207, 194, 129.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{23}N_2O$ $[M + H]^+$: 343.18048; found: 343.18155.

(4*S*)-4,5-Dihydro-2-{2′-[(*R*)-α-methylbenzylamino)phenyl}-4-isopropyloxazole (L2)

Yield: 47%; $[\alpha]_D$ –250.0 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.91 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 0.98 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 1.51 [3 H, d, *J* = 5.0 Hz, PhCH(CH_3)N], 1.71 [1 H, m, $(CH_3)_2$C*H*], 3.92 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 4.05 [1 H, t, *J* = 5.0 Hz, NCH(R)CH_2O], 4.26 [1 H, t, *J* = 5.0 Hz, NCH(R)CH_2O], 4.56 [1 H, q, *J* = 5.0 Hz, PhC*H*(Me)N], 6.38 (1 H, d, *J* = 10.0 Hz, ArH), 6.46 (1 H, t, *J* = 10.0 Hz, ArH), 7.02 (1 H, t, *J* = 10.0 Hz, ArH), 7.13 (1 H, d, *J* = 10.0 Hz, ArH), 7.22 (1 H, m, ArH), 7.28 (3 H, m, ArH), 7.63 (1 H, d, *J* = 5.0 Hz, ArH), 9.09 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 19.0 [(*C*H_3)$_2$CH], 19.3 [(*C*H_3)$_2$CH], 25.2 [PhCH(*C*H_3)N], 33.7 [$(CH_3)_2$*C*H], 52.9 [Ph*C*H(Me)N], 69.1 [NCH(R)*C*H_2O], 73.1 [N*C*H(R)CH_2O], 108.8 (CH_{arom}), 111.9 (CH_{arom}), 114.5 (CH_{arom}), 126.0 (CH_{arom}), 126.9 (CH_{arom}), 128.8 (CH_{arom}), 129.9 (CH_{arom}), 132.3 (CH_{arom}), 145.7 (CH_{arom}), 148.4 (CH_{arom}), 164.1 (CH_{arom}).

GC/MS: *m*/*z* = 308 $[M]^+$, 293, 222, 207, 194, 152, 129.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{25}N_2O$ $[M + H]^+$: 309.19614; found: 309.19786.

Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.08. Found: C, 77.69; H, 7.99; N, 9.07.

(4*R*)-4,5-Dihydro-2-{2′-[(*R*)-α-methylbenzylamino)phenyl}-4-isobutyloxazole (L3)

Yield: 56%; mp 65–68 °C; $[\alpha]_D$ –262.0 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.89 [6 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 1.35 (1 H, m, *i*-PrCH_2), 1.49 [3 H, d, *J* = 5.0 Hz, PhCH(CH_3)N], 1.56 (1 H, m, *i*-PrCH_2), 1.84 [1 H, m, $(CH_3)_2$C*H*], 3.77 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 4.33 [2 H, m, NCH(R)CH_2O], 4.50 [1 H, q, *J* = 5.0 Hz, PhC*H*(Me)N], 6.33 (1 H, d, *J* = 10.0 Hz, ArH), 6.46 (1 H, t, *J* = 10.0 Hz, ArH), 7.02 (1 H, t, *J* = 10.0 Hz, ArH), 7.13 (1 H, m, ArH), 7.21 (1 H, m, ArH), 7.23 (3 H, m, ArH), 7.64 (1 H, d, *J* = 5.0 Hz, ArH), 9.02 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 22.6 [(*C*H_3)$_2$CH] , 23.4 [(*C*H_3)$_2$CH], 25.3 [$(CH_3)_2$*C*H], 26.1 [PhCH(*C*H_3)N], 46.0 [*i*-Pr*C*H_2], 53.2 [Ph*C*H(Me)N], 65.4 [NCH(R)*C*H_2O], 71.5 [N*C*H(R)CH_2O], 108.9 (CH_{arom}), 111.9 (CH_{arom}), 114.6 (CH_{arom}), 125.8 (CH_{arom}), 126.0 (CH_{arom}), 126.9 (CH_{arom}), 128.8 (CH_{arom}), 129.1 (CH_{arom}), 129.8 (CH_{arom}), 132.3 (CH_{arom}), 145.7 (CH_{arom}), 148.4 (CH_{arom}), 164.0 (CH_{arom}).

GC/MS: *m*/*z* = 322 $[M]^+$, 307, 207, 194, 129.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{27}N_2O$ $[M + H]^+$: 323.21179; found: 323.21277.

(4*S*)-4,5-Dihydro-2-{2′-[(*R*)-α-methylbenzylamino]phenyl}-4-*sec*-butyloxazole (L4)

Yield: 44%; $[\alpha]_D$ –223.7 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.79 [1 H, m, $MeCH_2$C*H*(Me)], 0.86 [3 H, d, *J* = 5.0 Hz, $MeCH_2$CH(CH_3)], 0.90 [3 H, t, *J* = 5.0 Hz, C$H_3$$CH_2$CH(Me)], 1.25 [1 H, m, Me*C*H_2CH(Me)], 1.51 [3 H, d, *J* = 5.0 Hz, PhCH(CH_3)N], 1.60 [1 H, m, Me*C*H_2CH(Me)], 3.91 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 4.16 [1 H, m, NCH(R)CH_2O], 4.26 [1 H, m, NCH(R)CH_2O], 4.55 [1 H, q, *J* = 5.0 Hz, PhC*H*(Me)N], 6.40 (1 H, d, *J* = 10.0 Hz, ArH), 6.47 (1 H, t, *J* = 10.0 Hz, ArH), 7.04 (1 H, t, *J* = 10.0 Hz, ArH), 7.14 (1 H, t, *J* = 10.0 Hz, ArH), 7.19 (1 H, m, ArH), 7.25 (3 H, m, ArH), 7.63 (1 H, d, *J* = 5.0 Hz, ArH), 9.07 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 11.4 [MeCH(CH_2*C*H_3)], 15.4 [*C*H_3CH(CH_2Me)], 25.1 [Me*C*H(CH_2Me)], 26.2 [PhCH(*C*H_3)N], 40.1 [MeCH(*C*H_2Me)], 52.9 [Ph*C*H(Me)N], 65.9 [NCH(R)*C*H_2O], 71.8 [N*C*H(R)CH_2O], 108.8 (CH_{arom}), 111.8 (CH_{arom}), 114.5 (CH_{arom}), 126.0 (CH_{arom}), 126.9 (CH_{arom}), 128.8 (CH_{arom}), 129.9 (CH_{arom}), 132.3 (CH_{arom}), 145.7 (CH_{arom}), 148.4 (CH_{arom}), 164.0 (CH_{arom}).

GC/MS: *m*/*z* = 322 $[M]^+$, 307, 265, 207, 194, 129.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{27}N_2O$ $[M + H]^+$: 323.21179; found: 323.21346.

(4*R*)-4,5-Dihydro-2-{2′-[(*R*)-1-(1-naphthyl)ethylamino]phenyl}-4-phenyloxazole (L5)

Yield: 50%; $[\alpha]_D$ –303.7 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.57 [3 H, d, *J* = 5.0 Hz, ArCH(CH_3)N], 4.05 [1 H, t, *J* = 5.0 Hz, NCH(R)CH_2O], 4.62 [1 H, t, *J* = 5.0 Hz, NCH(R)CH_2O], 5.28 [1 H, q, *J* = 5.0 Hz, ArC*H*(Me)N], 5.48 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 6.19 (1 H, d, *J* = 5.0 Hz, ArH), 6.48 (1 H, t, *J* = 5.0 Hz, ArH), 6.94 (1 H, t, *J* = 5.0 Hz, ArH), 7.22 (1 H, d, *J* = 5.0 Hz, ArH), 7.25 (1 H, m, ArH), 7.30 (2H, m, ArH), 7.38–7.48 (5 H, m, ArH), 7.64 (1 H, d, *J* = 5.0 Hz, ArH), 7.71 (1 H, d, *J* = 5.0 Hz, ArH), 7.81 (1 H, d, *J* = 5.0 Hz, ArH), 8.10 (1 H, d, *J* = 5.0 Hz, ArH), 9.16 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 24.3 [ArCH(*C*H_3)N], 49.8 [Ar*C*H(Me)N], 70.5 [NCH(R)*C*H_2O], 73.3 [N*C*H(R)CH_2O], 108.8 (CH_{arom}), 112.4 (CH_{arom}), 115.0 (CH_{arom}), 122.9 (CH_{arom}), 125.8 (CH_{arom}), 126.1 (CH_{arom}), 126.4 (CH_{arom}), 126.8 (CH_{arom}), 127.7 (CH_{arom}), 128.0 (CH_{arom}), 129.2 (CH_{arom}), 129.6 (CH_{arom}), 130.3 (CH_{arom}), 131.0 (CH_{arom}), 133.0 (CH_{arom}), 134.5 (CH_{arom}), 140.7 (CH_{arom}), 143.4 (CH_{arom}), 148.7 (CH_{arom}), 165.9 (CH_{arom}).

GC/MS: *m*/*z* = 391, 281, 207, 193, 167, 149.

HRMS (ESI): *m*/*z* calcd for $C_{27}H_{25}N_2O$ $[M + H]^+$: 393.19614; found: 393.19700.

(4*S*)-4,5-Dihydro-2-{2′-[(*R*)-1-(1-naphthyl)ethylamino]phenyl}-4-isopropyloxazole (L6)

Yield: 73%; $[\alpha]_D$ –359.4 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.06 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 1.12 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 1.82 [3 H, d, *J* = 5.0 Hz, ArCH(CH_3)N], 1.87 [1 H, m, $(CH_3)_2$C*H*], 4.10 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 4.25 [1 H, q, *J* = 5.0 Hz, ArC*H*(Me)N],

4.43 [1 H, t, J = 5.0 Hz, NCH(R)CH_2O], 5.51 [1 H, t, J = 5.0 Hz, NCH(R)CH_2O], 6.40 (1 H, d, J = 10.0 Hz, ArH), 6.60 (1 H, t, J = 10.0 Hz, ArH), 7.08 (1 H, t, J = 10.0 Hz, ArH), 7.44 (1 H, t, J = 10.0 Hz, ArH), 7.65–7.56 (3 H, m, ArH), 7.82–7.78 (2 H, m, ArH), 7.98 (1 H, d, J = 10.0 Hz, ArH), 8.29 (1 H, d, J = 10.0 Hz, ArH), 9.44 (1 H, br, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 19.2 [(CH_3)$_2$CH], 19.6 [(CH_3)$_2$CH], 24.2 [ArCH(CH_3)N], 34.0 [(CH_3)$_2$CH], 49.4 [ArCH(Me)N], 69.4 [NCH(R)CH$_2$O], 73.4 [NCH(R)CH$_2$O], 109.1 (CH_{arom}), 112.2 (CH_{arom}), 114.9 (CH_{arom}), 122.8 (CH_{arom}), 123.0 (CH_{arom}), 125.9 (CH_{arom}), 126.4 (CH_{arom}), 127.8 (CH_{arom}), 129.6 (CH_{arom}), 130.1 (CH_{arom}), 131.2 (CH_{arom}), 132.6 (CH_{arom}), 134.5 (CH_{arom}), 140.9 (CH_{arom}), 148.4 (CH_{arom}), 164.4 (CH_{arom}).

GC/MS: m/z = 358 [M]$^+$, 355, 281, 221, 147.

HRMS (ESI): m/z calcd for $C_{24}H_{27}N_2O$ [M + H]$^+$: 359.21179; found: 359.21334.

(4*R*)-4,5-Dihydro-2-{2′-(*R*)-1-(1-naphthyl)ethylamino]phenyl}-4-isobutyloxazole (L7)

Yield: 30%; [α]$_D$ –318.3 (c = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.07 [6 H, m, (CH_3)$_2$CH], 1.52 (1 H, m, i-PrCH_2), 1.71 (1 H, m, i-PrCH_2), 1.78 [3 H, d, J = 5.0 Hz, ArCH(CH_3)N], 2.01 [1 H, m, (CH_3)$_2$CH], 3.95 [1 H, t, J = 5.0 Hz, NCH(R)CH$_2$O], 4.52 [2 H, m, NCH(R)CH_2O], 5.43 [1 H, q, J = 5.0 Hz, ArCH(Me)N], 6.31 (1 H, d, J = 5.0 Hz, ArH), 6.58 (1 H, t, J = 5.0 Hz, ArH), 7.04 (1 H, t, J = 5.0 Hz, ArH), 7.43 (1 H, t, J = 5.0 Hz, ArH), 7.66–7.55 (3 H, m, ArH), 7.80–7.77 (2 H, m, ArH), 7.97 (1 H, d, J = 10.0 Hz, ArH), 8.27 (1 H, d, J = 10.0 Hz, ArH), 9.32 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 22.9 [(CH_3)$_2$CH], 23.7 [(CH_3)$_2$CH], 24.2 [(CH_3)$_2$$C$H], 26.4 [ArCH($CH_3$)N], 46.3 ($i$-Pr$CH_2$), 49.6 [Ar$C$H(Me)N], 65.6 [NCH(R)$CH_2$O], 71.8 [N$C$H(R)CH$_2$O], 109.2 ($CH_{arom}$), 112.3 ($CH_{arom}$), 114.9 ($CH_{arom}$), 122.8 ($CH_{arom}$), 122.9 ($CH_{arom}$), 125.8 ($CH_{arom}$), 126.4 ($CH_{arom}$), 127.7 ($CH_{arom}$), 129.6 ($CH_{arom}$), 130.1 ($CH_{arom}$), 131.0 ($CH_{arom}$), 132.6 ($CH_{arom}$), 134.5 ($CH_{arom}$), 140.8 ($CH_{arom}$), 148.4 ($CH_{arom}$), 164.3 ($CH_{arom}$).

GC/MS: m/z = 362, 341, 238, 217, 147.

HRMS (ESI): m/z calcd for $C_{25}H_{29}N_2O$ [M + H]$^+$: 373.22744; found: 373.22927.

(4*S*)-4,5-Dihydro-2-{2′-[(*R*)-1-(1-naphthyl)ethylamino]phenyl}-4-*sec*-butyloxazole (L8)

Yield: 36%; [α]$_D$ –303.1 (c = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.97 [6 H, m, CH_3CH$_2$CH(CH_3)], 1.03 [1 H, m, MeCH$_2$CH(Me)], 1.59 [2 H, m, MeCH_2CH(Me)], 1.80 [3 H, d, J = 5.0 Hz, ArCH(CH_3)N], 4.09 [1 H, t, J = 5.0 Hz, NCH(R)CH$_2$O], 4.32 [1 H, t, J = 5.0 Hz, NCH(R)CH_2O], 4.43 [1 H, t, J = 5.0 Hz, NCH(R)CH_2O], 5.47 [1 H, q, J = 5.0 Hz, ArCH(Me)N], 6.39 (1 H, d, J = 5.0 Hz, ArH), 6.58 (1 H, t, J = 5.0 Hz, ArH), 7.07 (1 H, t, J = 5.0 Hz, ArH), 7.44 (1 H, t, J = 5.0 Hz, ArH), 7.63–7.55 (3 H, m, ArH), 7.79 (2 H, d, J = 10.0 Hz, ArH), 7.96 (1 H, d, J = 10.0 Hz, ArH), 8.27 (1 H, d, J = 10.0 Hz, ArH), 9.39 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 11.7 [MeCH(CH$_2$$CH_3$)], 14.6 [$CH_3$CH(CH$_2$Me)], 25.7 [Me$C$H(CH$_2$Me)], 35.1 [ArCH($CH_3$)N], 40.3 [MeCH($CH_2$Me)], 49.4 [Ar$C$H(Me)N], 69.2 [NCH(R)$CH_2$O], 72.0 [N$C$H(R)CH$_2$O], 109.1 ($CH_{arom}$), 112.1 ($CH_{arom}$), 114.8 ($CH_{arom}$), 122.8 ($CH_{arom}$), 123.0 ($CH_{arom}$), 125.8 ($CH_{arom}$), 126.4 ($CH_{arom}$), 127.7 ($CH_{arom}$), 129.6 ($CH_{arom}$), 130.1 ($CH_{arom}$), 131.2 ($CH_{arom}$), 132.6 ($CH_{arom}$), 134.5 ($CH_{arom}$), 140.9 ($CH_{arom}$), 148.2 ($CH_{arom}$), 164.3 ($CH_{arom}$).

GC/MS: m/z = 372 [M]$^+$, 357, 272, 257, 243, 155.

HRMS (ESI): m/z calcd for $C_{25}H_{29}N_2O$ [M + H]$^+$: 373.22744; found: 373.22947.

(4*R*)-4,5-Dihydro-2-[2′-(2,6-dimethylanilino)phenyl]-4-phenyloxazole (L9)

Yield: 84%; mp 110–115 °C; [α]$_D$ –7.1 (c = 0.98, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.12 (3 H, s, ArCH_3), 2.16 (3 H, s, ArCH_3), 4.12 [1 H, t, J = 5.0 Hz, NCH(R)CH_2O], 4.70 [1 H, t, J = 5.0 Hz, NCH(R)CH_2O], 5.41 [1 H, t, J = 5.0 Hz, NCH(R)CH$_2$O], 6.25 (1 H, d, J = 10.0 Hz, ArH), 6.60 (1 H, t, J = 10.0 Hz, ArH), 7.03 (3 H, m, ArH), 7.13 (1 H, t, J = 10.0 Hz, ArH), 7.25 (5 H, m, ArH), 7.81 (1 H, d, J = 10.0 Hz, ArH), 9.91 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 20.1 (ArCH$_3$), 32.1 (ArCH$_3$), 70.1 [NCH(R)CH$_2$O], 73.0 [NCH(R)CH$_2$O], 108.1 (CH_{arom}), 112.3 (CH_{arom}), 116.5 (CH_{arom}), 126.2 (CH_{arom}), 126.6 (CH_{arom}), 127.5 (CH_{arom}), 127.7 (CH_{arom}), 128.2 (CH_{arom}), 128.4 (CH_{arom}), 130.0 (CH_{arom}), 133.8 (CH_{arom}), 136.4 (CH_{arom}), 137.1 (CH_{arom}), 138.1 (CH_{arom}), 140.4 (CH_{arom}), 143.0 (CH_{arom}), 147.6 (CH_{arom}), 148.0 (CH_{arom}), 165.2 (CH_{arom}).

GC/MS: m/z = 342 [M]$^+$, 222, 194, 120.

HRMS (ESI): m/z calcd for $C_{23}H_{23}N_2O$ [M + H]$^+$: 343.18048; found: 343.18171.

Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.09; H, 6.60; N, 8.10.

(4*S*)-4,5-Dihydro-2-[2′-(2,6-dimethylanilino)phenyl]-4-isopropyloxazole (L10)

Yield: 77%; [α]$_D$ –7.8 (c = 2.30, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.92 [3 H, d, J = 5.0 Hz, (CH_3)$_2$CH], 0.98 [3 H, d, J = 5.0 Hz, (CH_3)$_2$CH], 1.81 [1 H, m, (CH_3)$_2$CH], 2.19 (6 H, s, ArCH_3), 4.03 [1 H, J = 5.0 Hz, NCH(R)CH_2O], 4.19 [1 H, J = 5.0 Hz, NCH(R)CH_2O], 4.34 [1 H, t, J = 5.0 Hz, NCH(R)CH$_2$O], 6.21 (1 H, d, J = 10.0 Hz, ArH), 6.61 (1 H, t, J = 10.0 Hz, ArH), 7.12 (3 H, m, ArH), 7.27 (1 H, m, ArH) 7.78 (1 H, d, J = 10.0 Hz, ArH), 9.96 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 18.8 [(CH_3)$_2$CH]), 19.0 [(CH_3)$_2$CH]), 19.1 [(CH_3)$_2$$C$H]), 21.4 (Ar$CH_3$), 34.2 (Ar$CH_3$), 70.1 [NCH(R)$CH_2$O], 73.2 [N$C$H(R)CH$_2$O], 109.0 ($CH_{arom}$), 112.1 ($CH_{arom}$), 115.7 ($CH_{arom}$), 126.6 ($CH_{arom}$), 128.8 ($CH_{arom}$), 128.9 ($CH_{arom}$), 130.2 ($CH_{arom}$), 132.5 ($CH_{arom}$), 136.9 ($CH_{arom}$) 137.3 ($CH_{arom}$), 138.6 ($CH_{arom}$), 148.1 ($CH_{arom}$), 164.3 ($CH_{arom}$).

GC/MS: m/z = 308 [M]$^+$, 265, 222, 194.

HRMS (ESI): m/z calcd for $C_{20}H_{26}N_2O$ [M + H]$^+$: 309.19614; found: 309.19726.

(4*R*)-4,5-Dihydro-2-[2′-(2,6-dimethylanilino)phenyl]-4-isobutyloxazole (L11)

Yield: 74%; [α]$_D$ +12.2 (c = 1.50, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.91 [6 H, d, J = 5.0 Hz, (CH_3)$_2$CH], 1.18 [1 H, m, (CH_3)$_2$CH], 1.46 (1 H, m, i-PrCH_2), 1.78 (1 H, m, i-PrCH_2), 2.13 (6 H, s, ArCH_3) 3.84 [1 H, t, J = 5.0 Hz, NCH(R)CH$_2$O], 4.35 [2 H, m, NCH(R)CH_2O], 6.10 (1 H, d, J = 10.0 Hz, ArH), 6.56 (1 H, t, J = 10.0 Hz, ArH), 7.04 (4 H, m, ArH), 7.71 (1 H, d, J = 10.0 Hz, ArH), 9.86 (1 H, s, ArNH).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 14.6 [(CH_3)$_2$CH], 18.8 [(CH_3)$_2$CH], 23.0 [(CH_3)$_2$$C$H], 24.1 ($i$-Pr$CH_2$), 26.1 (Ar$CH_3$), 46.3 (Ar$CH_3$), 65.6 [NCH$_2(R)CH_2$O] 71.8 [N$CH_2$(R)CH$_2$O] 108.9 ($CH_{arom}$), 112.2 ($CH_{arom}$), 115.3 ($CH_{arom}$), 126.2 ($CH_{arom}$), 128.4 ($CH_{arom}$), 129.3 ($CH_{arom}$), 130.1 ($CH_{arom}$), 133.1 ($CH_{arom}$), 136.7 ($CH_{arom}$), 137.4 ($CH_{arom}$), 138.6 ($CH_{arom}$), 148.1 ($CH_{arom}$), 164.2 ($CH_{arom}$).

GC/MS: m/z = 322 [M]$^+$, 194, 222, 180.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{26}N_2O$ [M + H]$^+$ 323.21179; found: 323.21451.

Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69. Found: C, 77.83; H, 8.81; N, 8.65.

(4*S*)-4,5-Dihydro-2-[2′-(2,6-dimethylanilino)phenyl]-4-*sec*-butyloxazole (L12)

Yield: 83%; $[\alpha]_D$ +20.0 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.94 [6 H, m, C*H*$_3$CH$_2$CH(C*H*$_3$)], 1.38 [1 H, m, MeC*H*$_2$CH(Me)] 1.60 [1 H, m, MeC*H*$_2$CH(Me)], 1.84 [1 H, m, MeCH$_2$C*H*(Me)], 2.18 (6 H, s, ArC*H*$_3$), 3.88 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH$_2$O], 4.42 [2 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 6.22 (1 H, d, *J* = 10.0 Hz, ArH), 6.62 (1 H, t, *J* = 10.0 Hz, ArH), 7.09 (3 H, m, ArH), 7.25 (1 H, m, ArH), 7.73 (1 H, d, *J* = 10.0 Hz, ArH), 9.91 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 11.7 [MeCH(CH$_2$*C*H$_3$)], 14.7 [*C*H$_3$MeCH(CH$_2$Me)], 15.1 [Me*C*H(CH$_2$Me)], 18.8 [MeCH(*C*H$_2$Me)], 26.2 (Ar*C*H$_3$), 39.9 (Ar*C*H$_3$), 68.6 [NCH(R)*C*H$_2$O], 71.6 [N*C*H(R)CH$_2$O], 108.9 (CH$_{arom}$), 112.1 (CH$_{arom}$), 115.7 (CH$_{arom}$), 126.5 (CH$_{arom}$), 128.7 (CH$_{arom}$), 130.1 (CH$_{arom}$), 131.9 (CH$_{arom}$), 137.0 (CH$_{arom}$), 137.1 (CH$_{arom}$), 138.5 (CH$_{arom}$), 148.0 (CH$_{arom}$), 164.6 (CH$_{arom}$).

GC/MS: *m*/*z* = 322 [M]$^+$, 222, 194, 208.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{28}N_2O$ [M + H]$^+$: 323.21179; found: 323.21403.

(4*R*)-4,5-Dihydro-2-[2′-(2,6-diisopropylanilino)phenyl]-4-phenyloxazole (L13)

Yield: 80%; mp 80–85 °C; $[\alpha]_D$ +53.3 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.98 (3 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 1.01 [3 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 1.09 [6 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 3.00 [2 H, m, 2 × (CH$_3$)$_2$C*H*], 4.13 (1 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 4.67 [1 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 5.44 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH$_2$O], 6.22 (1H, d, *J* = 10 Hz, ArH), 6.60 (1 H, t, *J* = 10.0 Hz, ArH), 6.77 (1 H, t, *J* = 10.0 Hz, ArH), 7.03 (3 H, d, *J* = 10.0 Hz, ArH), 7.43–7.28 (5 H, m, ArH), 8.06 (1 H, d, *J* = 10.0 Hz, ArH), 9.89 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 22.4 [(*C*H$_3$)$_2$CH], 23.0 [(*C*H$_3$)$_2$CH], 24.4 [*C*H$_3$)$_2$CH], 24.9 [(*C*H$_3$)$_2$CH], 28.1 [(CH$_3$)$_2$*C*H], 28.6 [(CH$_3$)$_2$*C*H], 70.1 [N*C*H(R)CH$_2$O], 73.2 [NCH(R)*C*H$_2$O], 107.7 (CH$_{arom}$), 112.2 (CH$_{arom}$), 115.1 (CH$_{arom}$), 118.7 (CH$_{arom}$), 122.9 (CH$_{arom}$), 124.0 (CH$_{arom}$), 126.6 (CH$_{arom}$), 127.7 (CH$_{arom}$), 128.9 (CH$_{arom}$), 130.0 (CH$_{arom}$), 133.7 (CH$_{arom}$), 136.1 (CH$_{arom}$), 140.5 (CH$_{arom}$), 143.0 (CH$_{arom}$), 148.9 (CH$_{arom}$), 149.7 (CH$_{arom}$), 165.5 (CH$_{arom}$).

GC/MS: *m*/*z* = 398 [M]$^+$, 236, 220, 193.

HRMS (ESI): *m*/*z* calcd for $C_{27}H_{32}N_2O$ [M + H]$^+$ 399.24309; found: 399.24452

(4*S*)-4,5-Dihydro-2-[2′-(2,6-diisopropylanilino)phenyl]-4-isopropyloxazole (L14)

Yield: 84%; $[\alpha]_D$ +6.9 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.88 [3 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 0.94 [3 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 1.03 [3 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 1.16 [6 H, m, (C*H*$_3$)$_2$CH], 1.24 [3 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 1.76 [1 H, m, (CH$_3$)$_2$C*H*], 3.01 [2 H, m, 2 × (CH$_3$)$_2$C*H*], 4.01 [1 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 4.14 [1 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 4.31 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH$_2$O], 6.14 (1 H, d, *J* = 10.0 Hz, ArH), 6.51 (1 H, t, *J* = 10.0 Hz, ArH), 7.04 (1 H, t, *J* = 10.0 Hz, ArH), 7.21 (2 H, m, ArH), 7.26 (1 H, t, *J* = 10.0 Hz, ArH) 7.71 (1 H, d, *J* = 10.0 Hz, ArH), 9.81 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 18.4 [(*C*H$_3$)$_2$CH], 18.5 [(*C*H$_3$)$_2$CH], 23.0 (*C*H$_3$)$_2$CH], 24.7 (*C*H$_3$)$_2$*C*H], 24.8 (*C*H$_3$)$_2$CH], 28.3 (*C*H$_3$)$_2$CH], 28.4 [(CH$_3$)$_2$C*H*], 30.7 [(CH$_3$)$_2$C*H*], 33.2 [(CH$_3$)$_2$C*H*], 68.8 [NCH(R)*C*H$_2$O], 72.7 [N*C*H(R)CH$_2$O], 108.6 (CH$_{arom}$), 112.4 (CH$_{arom}$), 115.2 (CH$_{arom}$), 119.0 (CH$_{arom}$), 122.9 (CH$_{arom}$), 124.1 (CH$_{arom}$), 127.5 (CH$_{arom}$), 129.8 (CH$_{arom}$), 132.6 (CH$_{arom}$), 135.7 (CH$_{arom}$), 140.8 (CH$_{arom}$), 148.2 (CH$_{arom}$), 150.0 (CH$_{arom}$), 164.3 (CH$_{arom}$).

GC/MS: *m*/*z* = 364 [M]$^+$, 236, 162, 114.

HRMS (ESI): *m*/*z* calcd for $C_{24}H_{34}N_2O$ [M + H]$^+$: 365.25874; found: 365.26028.

(4*R*)-4,5-Dihydro-2-[2′-(2,6-diisopropylanilino)phenyl]-4-isobutyloxazole (L15)

Yield: 75%; mp 65–68 °C; $[\alpha]_D$ +2.8 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.90 [6 H, d, *J* = 5.0 Hz, (C*H*$_3$)$_2$CH], 1.11–1.05 [12 H, m, (C*H*$_3$)$_2$CH], 1.34 (1 H, m, *i*-PrC*H*$_2$), 1.57 (1 H, m, *i*-PrC*H*$_2$), 1.82 [1 H, m, (CH$_3$)$_2$C*H*], 3.10 [2 H, m, 2 × (CH$_3$)$_2$C*H*], 3.84 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH$_2$O], 4.35 [2 H, m, NCH(R)C*H*$_2$O], 6.16 (1 H, d, *J* = 10.0 Hz, ArH), 6.55 (1 H, t, *J* = 10.0 Hz, ArH), 7.04 (1 H, t, *J* = 10.0 Hz, ArH), 7.20 (3 H, m, ArH), 7.74 (1 H, d, *J* = 10.0 Hz, ArH), 9.88 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 22.4 [(*C*H$_3$)$_2$CHCH$_2$], 22.6 [(*C*H$_3$)$_2$CHCH$_2$], 23.0 (*i*-Pr*C*H$_2$), 23.2 [(*C*H$_3$)$_2$CH], 24.9 [(*C*H$_3$)$_2$CH], 25.0 [(*C*H$_3$)$_2$CH], 25.7 [(*C*H$_3$)$_2$CH], 28.5 [(CH$_3$)$_2$*C*HCH$_2$], 28.9 [(CH$_3$)$_2$*C*H], 46.3 [(CH$_3$)$_2$*C*H], 65.2 [NCH(R)*C*H$_2$O], 71.8 [N*C*H(R)CH$_2$O], 108.1 (CH$_{arom}$), 112.1 (CH$_{arom}$), 114.8 (CH$_{arom}$), 118.7 (CH$_{arom}$), 122.8 (CH$_{arom}$), 124.1 (CH$_{arom}$), 127.6 (CH$_{arom}$), 129.8 (CH$_{arom}$), 132.2 (CH$_{arom}$), 135.4 (CH$_{arom}$), 147.8 (CH$_{arom}$), 149.2 (CH$_{arom}$), 164.1 (CH$_{arom}$).

GC/MS: *m*/*z* = 378 [M]$^+$ 236, 128, 162.

HRMS (ESI): *m*/*z* calcd for $C_{25}H_{36}N_2O$ [M + H]$^+$: 379.27439; found: 379.27593.

(4*S*)-4,5-Dihydro-2-[2′-(2,6-diisopropylanilino)phenyl]-4-*sec*-butyloxazole (L16)

Yield: 63%; mp 58–62 °C; $[\alpha]_D$ +18.7 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.82 [3 H, d, *J* = 5.0 Hz, MeCH$_2$CH(C*H*$_3$)], 0.89 [3 H, t, *J* = 5.0 Hz, C*H*$_3$CH$_2$CH(Me)], 1.11–1.04 [12 H, m, 2 × (C*H*$_3$)$_2$CH], 1.22 [2 H, m, MeC*H*$_2$CH(Me)], 1.57 [1 H, m, MeCH$_2$C*H*(Me)], 3.08 [2 H, m, 2 × (C*H*$_3$)$_2$C*H*], 3.95 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH$_2$O], 4.22 [1 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 4.35 [1 H, t, *J* = 5.0 Hz, NCH(R)C*H*$_2$O], 6.12 (1 H, d, *J* = 10.0 Hz, ArH), 6.56 (1 H, t, *J* = 10.0 Hz, ArH), 7.04 (1 H, t, *J* = 10.0 Hz, ArH), 7.21 (2 H, m, ArH), 7.25 (1 H, t, *J* = 10.0 Hz, ArH) 7.69 (1 H, d, *J* = 10.0 Hz, ArH), 9.93 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 11.7 [*C*H$_3$CH(CH$_2$*C*H$_3$)], 14.7 [MeCH(*C*H$_2$Me)], 14.8 [*C*H$_3$CH(CH$_2$CH$_3$)], 22.5 [(*C*H$_3$)$_2$CH], 23.3 [(*C*H$_3$)$_2$CH], 25.2 [(*C*H$_3$)$_2$CH], 26.3 [(*C*H$_3$)$_2$CH], 28.5 [Me*C*H(CH$_2$Me)], 28.5 [(CH$_3$)$_2$*C*H], 39.7 [(CH$_3$)$_2$*C*H], 68.6 [NCH(R)*C*H$_2$O], 71.8 [N*C*H(R)C*H*$_2$O], 108.2 (CH$_{arom}$), 112.0 (CH$_{arom}$), 115.2 (CH$_{arom}$), 118.8 (CH$_{arom}$), 123.0 (CH$_{arom}$), 123.9 (CH$_{arom}$), 127.5 (CH$_{arom}$), 129.7 (CH$_{arom}$), 132.4 (CH$_{arom}$), 135.5 (CH$_{arom}$), 147.8 (CH$_{arom}$), 149.7 (CH$_{arom}$), 164.1 (CH$_{arom}$).

GC/MS: *m*/*z* = 378 [M]$^+$, 236, 128, 162.

HRMS (ESI): *m*/*z* calcd for $C_{25}H_{36}N_2O$ [M + H]$^+$: 379.27439; found: 379.27582.

Amination of Chiral Oxazolines with Amides; General Procedure

An oven-dried Schlenk flask was charged with $Pd(OAc)_2$ (10 mol%), *rac*-BINAP (20 mol%), chiral aryl bromide **1a–d** (0.6

mmol, 1.0 equiv), benzamide or sulfinamide (2.4 mmol, 4.0 equiv), Cs_2CO_3 (1.2 mmol, 2.0 equiv), and anhyd degassed toluene (15 mL). The mixture was heated under N_2 flow until an appropriate amount of the ligand was formed as judged by TLC (hexane–EtOAc, 8:2) and ^{1}H NMR spectroscopy. The crude product was then purified by column chromatography.

(4*R*)-4,5-Dihydro-2-[2′-(benzamido)phenyl]-4-phenyloxazole (L17)

Yield: 98%; mp 118–122 °C; $[\alpha]_D$ –132.2 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 3.81 [1 H, t, *J* = 10.0 Hz, NCH(R)CH_2O], 4.20 [1 H, t, *J* = 10.0 Hz, NCH(R)CH_2O], 5.08 [1 H, t, *J* = 10.0 Hz, NC*H*(R)CH_2O], 6.96 (1 H, t, *J* = 10.0 Hz, ArH), 7.07 (2 H, t, *J* = 10.0 Hz, ArH), 7.11–7.28 (6 H, m, ArH), 7.38 (1 H, t, *J* = 10.0 Hz, ArH), 8.06 (1 H, d, *J* = 5.0 Hz, ArH), 8.24 (2 H, d, *J* = 5.0 Hz, ArH), 9.65 (1 H, d, *J* = 5.0 Hz, ArH), 13.37 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 70.3 [NCH(R)*C*H_2O], 73.3 [N*C*H(R)CH_2O], 113.7 (CH_{arom}), 120.5 (CH_{arom}), 122.6 (CH_{arom}), 127.2 (CH_{arom}), 128.0 (CH_{arom}), 128.2 (CH_{arom}), 128.4 (CH_{arom}), 128.7 (CH_{arom}), 129.2 (CH_{arom}), 129.8 (CH_{arom}), 131.7 (CH_{arom}), 133.5 (CH_{arom}), 136.0 (CH_{arom}), 141.7 (CH_{arom}), 142.0 (CH_{arom}), 165.3 (CH_{arom}), 166.0 (CH_{arom}).

GC/MS: *m*/*z* = 342 $[M]^+$, 341, 325, 251, 207, 147.

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{19}N_2O_2$ $[M + H]^+$: 343.1441; found: 343.14494.

(4*S*)-4,5-Dihydro-2-[2′-(benzamido)phenyl]-4-isopropyloxazole (L18)

Yield: 95%; $[\alpha]_D$ +83.0 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.78 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 0.88 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 1.52 [1 H, m, (CH$_3$)$_2$C*H*], 3.68 [1 H, t, *J* = 10.0 Hz, NC*H*(R)CH_2O], 3.81 [1 H, t, *J* = 10.0 Hz, NCH(R)CH_2O], 4.02 [1 H, t, *J* = 10.0 Hz, NCH(R)CH_2O], 6.94 (1 H, d, *J* = 10.0 Hz, ArH), 7.31 (3 H, m, ArH), 7.39 (1 H, t, *J* = 10.0 Hz, ArH), 7.97 (1 H, d, *J* = 10.0 Hz, ArH), 8.34 (2 H, m, ArH), 9.53 (1 H, d, *J* = 10.0 Hz, ArH), 13.29 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 19.0 [(*C*H$_3$)$_2$CH], 19.2 [(*C*H$_3$)$_2$CH], 33.4 [(CH$_3$)$_2$*C*H], 69.6 [NCH(R)*C*H_2O], 73.2 [N*C*H(R)CH_2O], 113.9 (CH_{arom}), 120.3 (CH_{arom}), 122.5 (CH_{arom}), 127.6 (CH_{arom}), 128.0 (CH_{arom}), 128.2 (CH_{arom}), 128.8 (CH_{arom}), 129.8 (CH_{arom}), 131.9 (CH_{arom}), 133.0 (CH_{arom}), 136.2 (CH_{arom}), 141.4 (CH_{arom}), 164.2 (CH_{arom}), 165.9 (CH_{arom}).

GC/MS: *m*/*z* = 308 $[M]^+$, 250, 207, 178, 146.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{21}N_2O_2$ $[M + H]^+$: 309.15975; found: 309.16149.

(4*R*)-4,5-Dihydro-2-[2′-(benzamido)phenyl]-4-isobutyloxazole (L19)

Yield: 98%; mp 86–89 °C; $[\alpha]_D$ –16.6 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.85 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 0.94 [3 H, d, *J* = 5.0 Hz, (CH_3)$_2$CH], 1.03 (2 H, m, *i*-PrCH_2), 1.40 [(CH$_3$)$_2$C*H*], 3.50 [1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 4.03 [2 H, m, NCH(R)CH_2O], 6.95 (1 H, t, *J* = 10.0 Hz, ArH), 7.32 (3 H, m, ArH), 7.38 (1 H, t, *J* = 10.0 Hz, ArH), 7.99 (1 H, d, *J* = 10.0 Hz, ArH), 8.32 (2 H, m, ArH), 9.55 (1 H, d, *J* = 10.0 Hz, ArH), 13.21 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 20.8 [(*C*H$_3$)$_2$CH], 22.1 [(*C*H$_3$)$_2$CH], 25.4 [(CH$_3$)$_2$*C*H], 45.8 [*i*-Pr*C*H_2], 65.0 [NCH(R)*C*H_2O], 71.9 [N*C*H(R)CH_2O], 114.1 (CH_{arom}), 120.4 (CH_{arom}), 122.0 (CH_{arom}), 122.5 (CH_{arom}), 124.2 (CH_{arom}), 127.7 (CH_{arom}), 128.8 (CH_{arom}), 129.7 (CH_{arom}), 132.3 (CH_{arom}), 133.9 (CH_{arom}), 141.3 (CH_{arom}), 164.0 (CH_{arom}), 165.9 (CH_{arom}).

GC/MS: *m*/*z* = 322 $[M]^+$, 265, 245, 224, 146.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{23}N_2O_2$ $[M + H]^+$: 323.17540; found: 323.17817.

(4*S*)-4,5-Dihydro-2-[2′-(benzamido)phenyl]-4-*sec*-butyloxazole (L20)

Yield: 99%; $[\alpha]_D$ +99.0 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.73 [3 H, d, *J* = 5.0 Hz, MeCH$_2$CH(CH_3)], 0.83 [3 H, t, *J* = 5.0 Hz, CH_3MeCH$_2$CH(Me)], 1.11 [1 H, m, MeCH$_2$C*H*(Me)], 1.38 [1 H, m, MeCH_2CH(Me)], 1.50 [1 H, m, MeCH_2CH(Me)], 3.70 (1 H, t, *J* = 5.0 Hz, NC*H*(R)CH_2O], 3.93 (1 H, m, NCH(R)CH_2O], 4.02 (1 H, m, NCH(R)CH_2O], 6.95 (1 H, t, *J* = 10.0 Hz, ArH), 7.33 (3 H, m, ArH), 7.40 (1 H, t, *J* = 10.0 Hz, ArH), 7.98 (1 H, d, *J* = 5.0 Hz, ArH), 8.29 (2 H, m, ArH), 9.49 (1 H, d, *J* = 10.0 Hz, ArH), 13.19 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 11.9 [MeCH(CH$_2$*C*H$_3$)], 15.3 [*C*H$_3$CH(CH$_2$Me)], 26.0 [Me*C*H(CH$_2$Me)], 39.8 [MeCH(*C*H$_2$Me)], 63.4 [NCH(R)*C*H_2O], 71.9 [N*C*H(R)CH_2O], 114.0 (CH_{arom}), 120.3 (CH_{arom}), 122.5 (CH_{arom}), 127.5 (CH_{arom}), 128.2 (CH_{arom}), 129.1 (CH_{arom}), 131.9 (CH_{arom}), 132.3 (CH_{arom}), 132.4 (CH_{arom}), 132.9 (CH_{arom}), 136.2 (CH_{arom}), 141.3 (CH_{arom}), 164.0 (CH_{arom}), 166.0 (CH_{arom}).

GC/MS: *m*/*z* = 322 $[M]^+$, 265, 245, 146.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{23}N_2O_2$ $[M + H]^+$: 323.17540; found: 323.17860.

(4*R*)-4,5-Dihydro-2-{2′-[(*S*)-*tert*-butylsulfinamido]phenyl}-4-phenyloxazole (L21)

Yield: 84%; mp 120–122 °C; $[\alpha]_D$ –113.2 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 1.27 (9 H, s, *t*-C_4H_9), 3.81 [1 H, t, *J* = 10.0 Hz, ArC(N)CHCH_2O], 4.21 [1 H, t, *J* = 10.0 Hz, ArC(N)CHCH_2O], 5.13 [1 H, t, *J* = 10.0 Hz, ArC(N)C*H*CH_2O], 6.86 (1 H, t, *J* = 10.0 Hz, ArH), 7.15–7.28 (6 H, br, ArH), 7.68 (1 H, d, *J* = 10.0 Hz, ArH), 8.02 (1 H, d, *J* = 10.0 Hz, ArH), 11.43 (1 H, s, ArN*H*).

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 22.8 [(*C*H$_3$)$_3$C], 56.8 [*C*Me$_3$], 70.1 [PhCH(N)*C*H_2O], 73.4 (Ph*C*H(N)CH_2O], 112.5 (CH_{arom}), 115.4 (CH_{arom}), 120.3 (CH_{arom}), 127.1 (CH_{arom}), 128.0 (CH_{arom}), 128.3 (CH_{arom}), 128.5 (CH_{arom}), 129.1 (CH_{arom}), 130.4 (CH_{arom}), 133.3 (CH_{arom}), 142.7 (CH_{arom}), 146.1 (CH_{arom}), 165.2 (CH_{arom}).

GC/MS (EI): *m*/*z* = 238, 207, 180, 131,118.

GC/MS (CI): *m*/*z* = 342 (M^+).

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{22}N_2O_2S$ $[M + H]^+$: 343.14747; found: 343.15012.

Anal. Calcd for $C_{19}H_{22}N_2O_2S$: C, 66.64; H, 6.48; N, 8.18. Found: C, 66.67; H, 6.52; N, 8.09.

(4*S*)-4,5-Dihydro-2-{2′-[(*S*)-*tert*-butylsulfinamido]phenyl}-4-isopropyloxazole (L22)

Yield: 60%; $[\alpha]_D$ +66.5 (*c* = 0.75, $CHCl_3$).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.82 [3 H, d, *J* = 10.0 Hz, (CH_3)$_2$CH], 0.97 [3 H, d, *J* = 10.0 Hz, [(CH_3)$_2$CH], 1.37 [9 H, s, *t*-C_4H_9], 1.52 [1 H, m, *J* = 5.0 Hz, [(CH$_3$)$_2$C*H*], 3.68 [1 H, t, *J* = 10.0 Hz, ArC(N)C*H*CH_2O], 3.82 [1 H, t, *J* = 10.0 Hz, ArC(N)CHCH_2O], 4.02 [1 H, t, *J* = 10.0 Hz, ArC(N)CHCH_2O], 6.83 (1 H, t, *J* = 10.0 Hz, ArH), 7.19 (1 H, t, *J* = 10.0 Hz, ArH), 7.59 (1 H, d, *J* = 10.0 Hz, ArH), 8.02 (1 H, d, *J* = 10.0 Hz, ArH), 11.29 (1 H, s, ArN*H*).

$^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 18.8 [$(CH_3)_2CH$], 19.0 [$(CH_3)_2CH$], 22.9 [$(CH_3)_3C$], 33.4 [$(CH_3)_2CH$], 56.4 (CMe_3), 69.4 [ArC(N)CHCH_2O], 73.2 [ArC(N)$CHCH_2O$], 113.1 (CH_{arom}), 116.0 (CH_{arom}), 120.3 (CH_{arom}), 130.2 (CH_{arom}), 132.9 (CH_{arom}), 146.2 (CH_{arom}), 164.2 (CH_{arom}).

GC/MS: *m*/*z* = 204, 161, 133, 119, 106.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{25}N_2O_2S$ $[M + H]^+$: 309.16422; found: 309.16874.

(4*R*)-4,5-Dihydro-2-{2′-[(*S*)-*tert*-butylsulfonamido]phenyl}-4-isobutyloxazole (L23)

Yield: 70%; $[\alpha]_D$ +85.4 (*c* = 0.57, $CHCl_3$).

^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.94 [6 H, m, $(CH_3)_2CH$], 1.25 [9 H, s, *t*-C_4H_9], 1.63 [2 H, m, (i-PrCH_2], 1.83 [1 H, m, $(CH_3)_2CH$], 3.87 [1 H, t, *J* = 6.32 Hz, ArC(N)C*H*CH_2O], 4.11 [1 H, t, *J* = 7.55 Hz, ArC(N)CHCH_2O], 4.40 [1 H, t, *J* = 6.95 Hz, ArC(N)CHCH_2O], 6.90 (1 H, t, *J* = 8.48 Hz, ArH), 7.35 (1 H, t, *J* = 7.95 Hz, ArH), 7.41 (1 H, d, *J* = 8.03 Hz, ArH), 7.71 (1 H, d, *J* = 8.48 Hz, ArH), 11.04 (1 H, s, ArN*H*).

$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ = 22.3 [$(CH_3)_2CH$], 22.8 [$(CH_3)_3C$], 23.1 [$(CH_3)_2CH$], 45.7 [*i*-PrCH_2], 56.7 (CMe_3), 64.8 [ArC(N)*C*HCH_2O], 71.7 [Ar*C*(N)CH*C*H_2O], 112.6 (CH_{arom}), 115.1 (CH_{arom}), 120.1 (CH_{arom}), 129.1 (CH_{arom}), 132.6 (CH_{arom}), 144.9 (CH_{arom}), 163.6 (CH_{arom}).

GC/MS: *m*/*z* = 264, 216, 161, 145, 120.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{27}N_2O_2S$ $[M + H]^+$: 323.17987; found: 323.18379.

(4*S*)-4,5-Dihydro-2-{2′-[(*S*)-*tert*-butylsulfonamido]phenyl}-4-*sec*-butyloxazole (L24)

Yield: <10%; $[\alpha]_D$ +64.1 (*c* = 0.85, $CHCl_3$).

^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.75 [3 H, m, $MeCH_2CH(CH_3)$], 0.89 [1 H, m, $MeCH_2CH(Me)$], 0.91 [3 H, m, $CH_3CH_2CH(Me)$], 0.94 [1 H, m, $MeCH_2CH(Me)$], 1.28 [1 H, m, $MeCH_2CH(Me)$], 1.38 [9 H, s, *t*-C_4H_9], 4.13 [1 H, t, *J* = 8.48 Hz, ArC(N)C*H*CH_2O], 4.26 [1 H, t, *J* = 8.08 Hz, ArC(N)CHCH_2O], 4.36 [1 H, t, *J* = 8.90 Hz, ArC(N)CHCH_2O], 6.93 (1 H, t, *J* = 7.64 Hz, ArH), 7.37 (1 H, t, *J* = 8.33 Hz, ArH), 7.46 (1 H, d, *J* = 8.52 Hz, ArH), 7.77 (1 H, d, *J* = 7.22 Hz, ArH), 11.06 (1 H, s, ArN*H*).

$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ = 11.3 [$MeCH(CH_2CH_3)$], 15.0 [$CH_3CH(CH_2Me)$], 23.0 [$(CH_3)_3C$], 25.9 [$MeCH(CH_2Me)$], 39.5 [$MeCH(CH_2Me)$], 56.9 (CMe_3), 69.0 [ArC(N)*C*HCH_2O], 71.6 [Ar*C*(N)CHCH_2O], 112.6 (CH_{arom}), 115.2 (CH_{arom}), 123.8 (CH_{arom}), 132.3 (CH_{arom}), 132.8 (CH_{arom}), 145.0 (CH_{arom}), 163.7 (CH_{arom}).

GC/MS: *m*/*z* = 218, 178, 161, 133.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{27}N_2O_2S$ $[M + H]^+$: 323.17987; found: 323.18127.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. Included are detailed experimental procedures, and characterization of **1a**–**d**.

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