Coupling of Bulky, Electron-Deficient Partners in Aryl Amination in the Preparation of Tridentate Bis(oxazoline) Ligands for Asymmetric Catalysis

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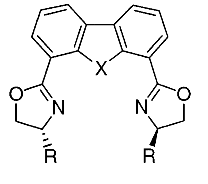
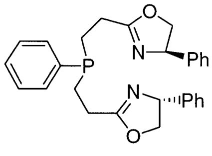
A new class of tridentate bis(oxazoline) ligands **7**, in which an *N*-phenylaniline unit links the two oxazoline rings, has been prepared. The key step in their synthesis is a Hartwig−Buchwald type Pd-catalyzed aryl amination between the two bulky *o*-substituted coupling partners, 2-(2′-bromophenyl)oxazolines **8** and 2-(*o*-aminophenyl)oxazolines **9**. By varying the substituent on the coupling partners, a range of 10 ligands has been prepared in good yield. During the synthesis of 2-(*o*-aminophenyl)oxazolines **9a**−**d**, a number of products of unexpected side reactions were isolated in two of the three steps. Alternatively, the required 2-(*o*-aminophenyl)oxazolines **9** were obtained by a DAST-promoted cyclodehydration of hydroxyamides **12a**−**d** without formation of any byproducts.

Introduction

The design and synthesis of new chiral ligands and their application in asymmetric catalysis continue to be a research focus both in academic and industrial laboratories. Bidentate and tetradentate ligands containing the oxazoline unit have been successful in a range of asymmetric transformations.[1] Chiral tridentate ligands, believed to form a deeper chiral concave pocket around the metal center, have been less extensively used in asymmetric catalysis than their bidentate or tetradentate analogues. Tridentate bis(oxazolinyl)-type ligands have recently been designed by introducing a donor atom into the link between two chiral oxazoline rings. For example, chiral Lewis acid catalysts incorporating the DBFOX/Ph ligand **1**, which has a coordinating oxygen atom, have been used with some success in asymmetric conjugate additions,[2] 1,3-dipolar cycloadditions,[3] and Diels−Alder reactions.[4] Schulz has reported a dibenzothiophene-bis(oxazoline) ligand **2**, which has given up to 77% ee in palladium-catalyzed allylic substitution.[5] Zhang has introduced a phosphorus donor atom into the link between two oxazoline rings, and the resulting ligand **3** gave good conversions and enantioselectivites for the transfer hydrogenation of both aryl alkyl and dialkyl ketones.[6]



1 X = O, R = Ph
2 X = S, R = *i*-Pr



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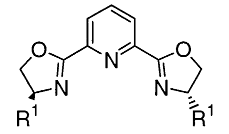
Of particular interest are bis(oxazoline) ligands with a coordinating nitrogen atom. Nishiyama's tridentate "pybox" ligand **4**, in which a pyridine ring links two chiral oxazoline moieties, has been successfully used in various asymmetric reactions, including Diels−Alder reactions,[7] Ru-catalyzed cyclopropanation of olefins,[8] Rh-catalyzed



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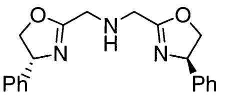

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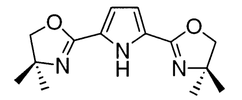

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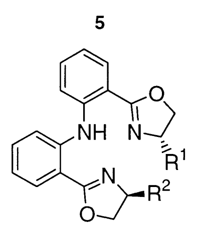

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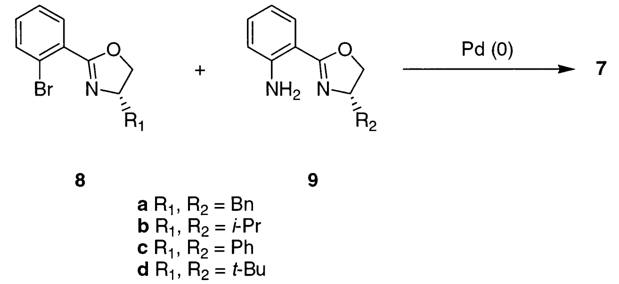
SCHEME 1

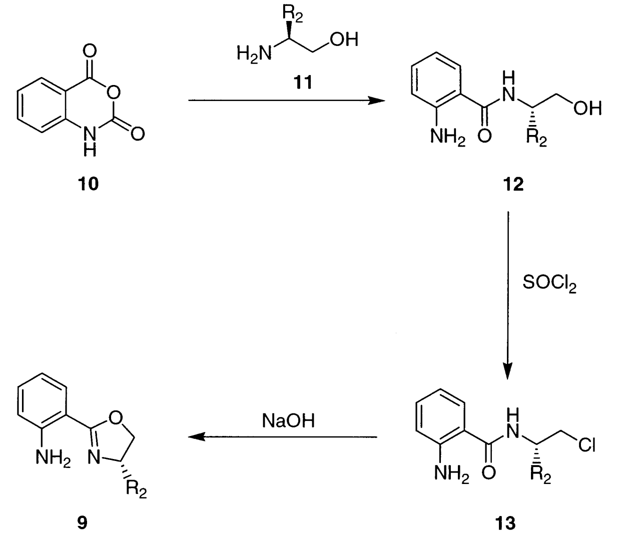


hydrosilylation of ketones,[9] and scandium triflate-catalyzed addition and annulation reactions of allenylsilanes with ethyl glyoxylate.[10] Zhang's bis(oxazolinylmethyl)amine ["(*R*)-Ph-ambox"] **5**, a ligand with a secondary amine link, has given excellent enantioselectivities and conversions in the asymmetric Ru-catalyzed transfer hydrogenation of aromatic ketones.[11] The presence of an NH moiety in this ligand is thought to allow for the formation of a metal–ligand bifunctional catalyst, which can increase the substrate affinity to the metal catalytic site by the formation of a six-membered cyclic transition state by hydrogen bonding to the ketone substrate. Gade has shown that the monoanionic form of the achiral ligand **6** forms a highly active dinuclear Pd catalyst for Suzuki cross-coupling reactions of phenylboronic acid with activated and nonactivated aryl bromides.[12] In this paper, we report the convergent synthesis of a new class of tridentate bis(oxazoline) ligands **7** for asymmetric synthesis, in which an *N*-phenylaniline unit links the two chiral oxazoline rings.[13]

Results and Discussion

Ligand Synthesis. We envisaged that the ligand class **7** could be prepared by a four-step convergent synthesis, in which the key synthetic step would be the formation of an arylamine bond between the two oxazoline components—the 2-(2′-bromophenyl)oxazolines **8** and the 2-(*o*-aminophenyl)oxazolines **9** (Scheme 1). An advantage of this approach is that it would allow for the facile synthesis of both C_2-symmetric and unsymmetrical ligands.

SCHEME 2



Compounds **8a**–**d** were prepared in one step by the zinc-catalyzed condensation of 2-bromobenzonitrile with the appropriate enantiopure amino alcohols according to the procedure of Pfaltz.[14] 2-(*o*-Aminophenyl)oxazolines **9a**–**d** have previously been prepared in three steps from isatoic anhydride,[15] in one-step utilizing a clay-catalyst,[16] and via condensation of 2-aminobenzonitrile with chiral amino alcohols in the presence of a catalytic amount of zinc chloride.[17] The preparation of 2-(*o*-aminophenyl)-oxazolines **9a**–**d**, in the current study, was first attempted following Pfaltz's route (Scheme 2). A number of unexpected and previously unreported byproducts were isolated and identified using this route and these are discussed in detail here.

Synthesis of Hydroxyamides 12a–**d.** Condensation of isatoic anhydride **10** with the amino alcohols **11a**–**d** yielded the required hydroxyamides **12a**–**d** in moderate yields (40–59%, Table 1). In each of the four reactions, two byproducts were isolated by column chromatography and characterized by MS, IR, and NMR as the amino esters **14a**–**d** and the amide ester compounds **15a**–**d**. The hydroxy amides **12a**–**d** were obtained as a result of the nucleophilic attack of the amino group of **11a**–**d** at the ester carbonyl carbon of **10**. Ring opening of **10** by the hydroxy group of the amino alcohols accounted for the formation of amino esters **14a**–**d**. Subsequent attack of **10** by either or both of the free hydroxy or amino groups of **12a**–**d** and **14a**–**d**, respectively, afforded compounds **15a**–**d**.

Cyclization of Hydroxy Amides 12a–**d.** Hydroxy amides **12a**–**d** were converted in good yields (87–99%) to the corresponding chloro amides **13a**–**d** by reaction with thionyl chloride. Base-induced cyclization of these chloro amides **13a**–**d** afforded the required oxazolines **9a**–**d** in 52–72% yield (Table 2). However, further byproducts, which were dependent on the nature of the

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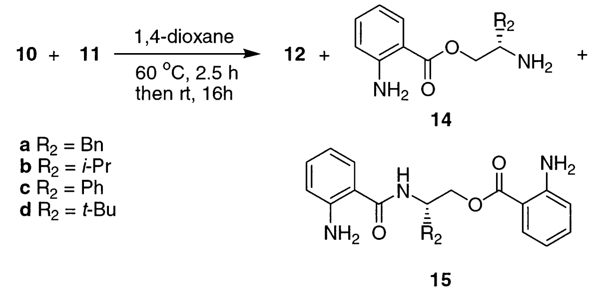
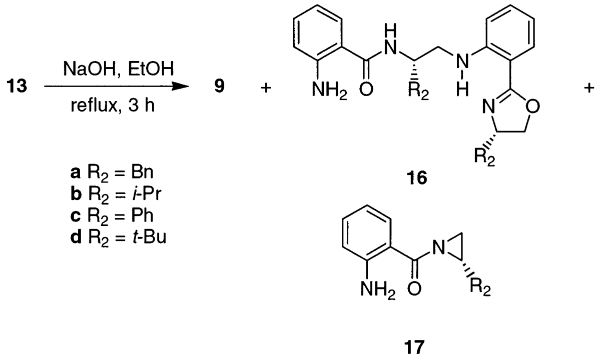
TABLE 1. Ring Opening of Isatoic Anhydride 10 with Amino Alcohols 11a−d



11	R$_2$	**12** (%)	**14** (%)	**15** (%)
a	Bn	52	16	19
b	*i*-Pr	59	3	9
c	Ph	47	24	14
d	*t*-Bu	40	19	6

TABLE 2. Cyclization of Chloro Amides 13a−d

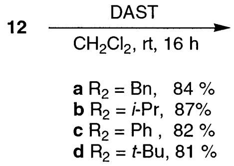


13	R$_2$	**9** (%)	**16** (%)	**17** (%)
a	Bn	60	7	
b	*i*-Pr	67	10	
c	Ph	72	6	
d	*t*-Bu	52		23

chloroamide substituent R$_2$, were observed in each of the four reactions. When R$_2$ is benzyl, isopropyl, or phenyl, the aniline nitrogen of the product oxazolines **9a−c** undergoes a nucleophilic substitution with the starting chloro amides to give the byproducts **16a−c**. When R$_2$ is *tert*-butyl, its steric bulk prevents a similar condensation and, instead, the *N*-acylaziridine **17d** was formed by the elimination of chloride by the deprotonated amide nitrogen. *N*-Acylazridine compounds have been previously reported as common byproducts in the conversion of hydroxy amides to oxazolines.[18]

Alternative Synthesis of Oxazolines 9a−d. Cyclodehydration of β-hydroxyamides to oxazolines has been achieved using a variety of reagents including PPh$_3$/DEAD,[19] BF$_3$·OEt$_2$,[20] sulfonyl chlorides,[21] the Burgess reagent,[22] and the Vilsmeier reagent.[23] Diethylaminosulfur trifluoride (DAST)[24] has been used for the dehydrative cyclization of highly functionalized β-hydroxyamides to 2-oxazolines at both room temperature[25] and at −78 °C with short reaction times.[26] In light of the byproducts observed in our initial attempts to prepare oxazolines **9a−d**, we wished to investigate whether the use of DAST proved to be a more effective synthetic approach. Gratifyingly, reaction of the hydroxy amides **12a−d** with an equimolar amount of DAST in CH$_2$Cl$_2$ at room temperature in the absence of base resulted in a smooth cyclization to the oxazolines **9a−d** in a single step with good yields and no evidence of the previously observed byproducts **16a−c** and **17d** (Scheme 3).

SCHEME 3



Pd-Catalyzed Aryl Amination. The formation of an aryl−amine bond by the Pd-catalyzed reaction of an aryl bromide with an aryl/alkylamine has been extensively studied by the groups of Hartwig and Buchwald.[27] A variety of Pd precursors, ligands, bases, and solvents has been used in an attempt to increase yields, to decrease reaction times, and to reduce β-hydride elimination and diarylation products. To date, both electron-rich and electron-poor aryl halides and triflates and both primary and secondary aryl/alkylamines have been successfully employed.

Palladium complexes incorporating the bulky monodentate ligand tri-*o*-tolylphosphine **18** were the first catalysts to give reasonable yields for the tin-free reaction between aryl halides and amines.[28] These catalysts gave high yields for the reaction of secondary amines with aryl bromides, while primary amines could only be efficiently coupled with electron poor aryl halides.[29] The second-generation catalysts based upon the chelating bis(phosphine) ligands, BINAP [2,2′-bis(diphenylphosphine)-1,1′-binaphthyl, **19**] and DPPF [1,1′-bis(diphenylphosphino)-ferrocene, **20**] are the most commonly used catalysts for Pd-catalyzed aryl amination.[30,31] These catalyze the reac-

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SCHEME 4

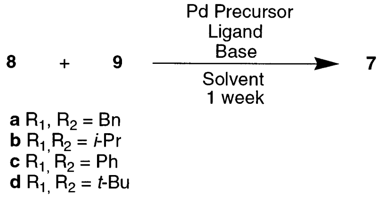
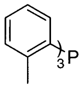


TABLE 3. Optimization of the Aryl Amination Step



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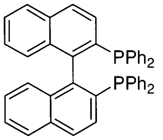

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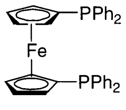

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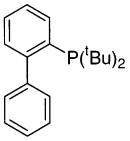

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entry	Pd precursor	ligand	base	solvent	yield (%)
1	Pd_2dba_3	**18**	NaO^tBu	toluene	3
2	Pd_2dba_3	**19**	NaO^tBu	toluene	12
3	Pd_2dba_3	**20**	NaO^tBu	toluene	72
4	Pd_2dba_3	**21**	NaO^tBu	toluene	33
5	Pd_2dba_3	**19**	NaO^tBu	dme	5
6	Pd_2dba_3	**20**	NaO^tBu	dme	6
7	$Pd(OAc)_2$	**20**	NaO^tBu	toluene	47
8	$Pd(OAc)_2$	**21**	NaO^tBu	toluene	49
9	Pd_2dba_3	**20**	Cs_2CO_3	toluene	27
10	Pd_2dba_3	**21**	Cs_2CO_3	toluene	44
11[b]	Pd_2dba_3	**20**	NaO^tBu	toluene	18
12[c]	Pd_2dba_3	**20**	NaO^tBu	toluene	66

[a] Reaction conditions: 1.0 equiv of aryl bromide, 1.2 equiv of arylamine, 1.2 equiv of base, 5 mol % Pd precursor, 10 mol % ligand, solvent (2 mL/mmol solvent), 90 °C, 1 week. [b] 1 mol % Pd precursor used. [c] Reaction conducted at reflux temperature.

tion of electron-rich, electron-poor, and electron-neutral aryl halides and triflates with primary alkylamines, anilines, cyclic secondary amines, and less successfully with acyclic secondary amines. Catalysts derived from Pd_2dba_3 and (*o*-biphenyl)P(*t*-Bu)$_2$ **21** give excellent results in the amination of anilines with electron-rich or -neutral aryl bromides and are also effective for the reaction of primary and secondary anilines at room temperature with aryl bromides and aryl chlorides.[27]

The key step in our projected synthesis of the ligands **7** was a Pd-catalyzed aryl amination between aryl bromide **8** and the aniline **9** (Scheme 4). This would represent an extension to the aryl amination methodology, as both partners are o-substituted with bulky substituents, and the arylamine component is electron-deficient.

Our aryl amination was optimized using a variety of Pd precursors, ligands, bases, and solvents employing the isopropyl-substituted substrates **8b** and **9b** (Table 3).

Following the standard literature procedure employing sodium *tert*-butoxide as the base and toluene as the solvent, the four ligands **18**−**21** were tested in our amination using Pd_2dba_3 as the palladium source. Of the ligands tested under the above conditions, DPPF (entry 3) was the most effective, giving 72% yield after 1 week at 90 °C. This result is somewhat surprising, as it has been thought that the BINAP/Pd system was the most active and general catalyst for the coupling of aryl bromides with primary amines.[27] However, this system gave a disappointing yield of only 12% of the bis(oxazoline) product **7b** (entry 2).The biphenyl ligand **21** gave the optimum yield (33%) of those monodentate ligands examined (entry 4). Changing the solvent from toluene to 1,2-dimethoxyethane had a dramatic effect on the activity of the Pd/DPPF system, with the yield dropping from 72% to 6% (entry 3 vs entry 6). Using Pd(OAc)$_2$ instead of Pd_2dba_3 as the Pd precursor increased the efficiency of the Pd/**21** system (entry 8 vs entry 4) system but decreased the efficacy of the Pd/DPPF system (entry 7 vs entry 3).

TABLE 4. Yields for Pd-Catalyzed Aryl Amination of 8a−d with 9a−d

7	R_1	R_2	yield (%)	7	R_1	R_2	yield (%)
a	Bn	Bn	63	**f**	^{t}Bu	Bn	58
b	^{i}Pr	^{i}Pr	72	**g**	^{t}Bu	^{i}Pr	63
c	Ph	Ph	43	**h**	^{i}Pr	Ph	78
d	^{t}Bu	^{t}Bu	73	**i**	^{t}Bu	Ph	73
e	Ph	Bn	68	**j**	Bn	^{i}Pr	61

The weak base cesium carbonate, which has also proven successful in aryl aminations,[27,32] was tested in our system instead of sodium *tert*-butoxide. Using cesium carbonate, a significant decrease in the yield was obtained with the Pd/DPPF system (entry 9 vs entry 3), while a slight increase in yield was observed when the monodentate biphenyl ligand **21** was used (entry 10 vs entry 4). The above reactions were carried out using a relatively high Pd catalyst loading of 5 mol %, and a reduction of the loading to 1 mol % using DPPF as the ligand resulted in a corresponding decrease in yield (entry 11 vs entry 3). Carrying out the reaction at reflux temperature (110 °C) instead of the standard 90 °C did not increase the reaction yields.

It was found therefore that the best conditions for the coupling of the bulky *o*-substituted aryl bromide **8b** and the hindered *o*-substituted aniline **9b** were Pd_2dba_3 (2.5 mol %), DPPF (2 equiv/Pd), NaO^tBu, and toluene at 90 °C for 1 week (entry 3). Using these optimized conditions, four C_2-symmetrical **7a**−**d** and six unsymmetrical ligands **7e**−**j** were prepared in moderate to good yield by varying the substituent on the coupling partners (Table 4).

Conclusions

A new class of tridentate bis(oxazoline) ligands **7** has been prepared in good yield by employing Pd-catalyzed aryl amination between the oxazoline *o*-substituted aryl bromides **8** and the oxazoline *o*-substituted anilines **9** as the key step. This represents the first report of the coupling of two such electron-deficient and bulky partners in an aryl amination. During the synthesis of anilines **9a**−**d**, a number of products of unexpected side reactions were isolated in two of the three steps. The reaction of amino alcohols with isatoic anhydride gave the expected hydroxy amides **12a**−**d** in addition to the amino esters **14a**−**d** and the amide esters **15a**−**d**. The attempted ring closure of chloro amides **13a**−**d** gave the required oxazoline *o*-substituted anilines **9** and byproducts that were dependent on the amino alcohol substituent. The *tert*-butyl-substituted chloro amide **13d** gave the *N*-acylaziridine **17d**, while the less bulky substituted chloro amide

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(32) Wolfe, J. P.; Buchwald, S. L. *Tetrahedron. Lett.* **1997**, *38*, 6359.

analogues **13a**−**c** did not afford any of the corresponding *N*-acylaziridines but instead gave the condensation products **16a**−**c** as the byproduct. The oxazoline *o*-substituted anilines **9** were obtained by a DAST-promoted cyclodehydration of hydroxy amides **12a**−**d** without formation of any byproducts.

This new class of tridentate bis(oxazoline) ligands **7** is currently being tested in the asymmetric transfer hydrogenation of acetophenone. The results obtained to date demonstrate good to excellent conversions (up to 97%) but with low enantioselectivities (18% ee using ligand **7b**). The application of these and related oxazoline-containing ligands to the transfer hydrogenation of ketones will be reported in due course.

Experimental Section

General Remarks. ^1H (300 MHz) and ^{13}C (75 MHz) spectra were recorded at room temperature in $CDCl_3$. Chemical shifts (δ) are given in parts per million relative to $CHCl_3$ (7.26, ^1H) and $CDCl_3$ (77.0, ^{13}C). Coupling constants are given as absolute values expressed in hertz. Low-resolution electron-impact MS spectra were measured at an ionization potential of 70 eV. Isomers were assumed to have the same response factors. Elemental analyses were performed by Ms. Anne Connolly, Department of Chemistry, University College Dublin. Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F 254 (0.25 mm, Macherey-Nagel). Column chromatography separations were performed using Merck Kieselgel 60 (Art. 7734). Solvents were dried immediately before use by distillation from standard drying agents. Isatoic anhydride, 2-bromobenzonitrile, DAST, Pd_2dba_3, $Pd(OAc)_2$, and cesium carbonate were used as received from Aldrich Chemical Co. Tri-*o*-tolylphosphine, DPPF, BINAP, and *o*-biphenyl-di-*tert*-butylphosphine were used as received from Strem Chemical Co. Sodium *tert*-butoxide was stored over anhydrous calcium sulfate in a desiccator prior to use. Amino alcohols were prepared from their corresponding amino acids using a standard reduction procedure.[33] The 2-(2′-bromophenyl)oxazolines **8** were prepared according to literature procedures.[14]

General Procedure for the Synthesis of Hydroxy Amides (12a−d) and Byproducts (14a−d and 15a−d). A mixture of isatoic anhydride **10** (12.6 mmol) and the appropriate amino alcohol **11a**−**d** (13.2 mmol) in anhydrous 1,4-dioxane (13 mL) was stirred under an atmosphere of nitrogen at 60 °C for 2.5 h. The resulting brown solution was stirred at room temperature for a further 16 h. The solvent was removed in vacuo to give a dark brown oil, which was purified by flash column chromatography on silica gel (5 × 40 cm) using CH_2Cl_2/MeOH 100:4 followed by AcOEt as the eluting solvents, affording the three products.

***N*-[(1S)-1-Benzyl-2-hydroxyethyl]-2-aminobenzamide (12a).** Yield: 52%, white solid. Mp: 121−122 °C (lit.[15] mp: 123−124 °C). $[\alpha]_D = -41.7$ (*c* = 1.00 in EtOH) (lit.[15] $[\alpha]_D = -39.8$ (*c* = 1.00 in EtOH)). ^1H NMR ($CDCl_3$): $\delta = 7.21-7.35$ (m, 6H), 7.16 (dt, *J* = 8.2, 1.5 Hz, 1H), 6.65 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.60 (ddd, *J* = 7.9, 7.0, 1.2 Hz, 1H), 6.35 (d, *J* = 7.3 Hz, 1H), 5.35 (s, br, 2H), 4.26−4.36 (m, 1H), 3.74 (dd, *J* = 11.1, 3.8 Hz, 1H), 3.64 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.13 (s, br, 1H), 2.89−3.01 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 170.1$, 148.7, 138.0, 132.7, 129.5, 129.0, 127.6, 127.0, 117.6, 117.1, 116.4, 64.5, 53.2, 37.4. IR (KBr): $\nu = 3430$, 3388, 3295, 1619, 770, 701 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 270 [M$^+$], 179, 136, 120 (100), 92, 91, 65.

(2*S*)-2-Amino-3-phenylpropyl 2-Aminobenzenecarboxylate (14a). Yield: 16%, yellow solid. Mp: 66−68 °C. $[\alpha]_D = +15.8$ (*c* = 1.00 in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.86$ (dd, *J* = 8.5, 1.5 Hz, 1H), 7.20−7.34 (m, 6H), 6.62−6.67 (m, 2H), 5.72 (s, br, 2H), 4.28 (dd, *J* = 10.8, 4.4 Hz, 1H), 4.13 (dd, *J* = 10.8, 6.7 Hz, 1H), 3.38−3.47 (m, 1H), 2.91 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.68 (dd, *J* = 13.5, 8.1 Hz, 1H), 1.66 (s, br, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 168.1$, 150.9, 138.5, 134.5, 131.3, 129.6, 128.9, 126.8, 117.0, 116.5, 110.8, 68.8, 52.0, 41.1. IR (KBr): $\nu = 3426$, 3120, 1690, 1624, 752, 696 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 270 [M$^+$], 179, 161, 120 (100), 91, 65. Anal. Calcd for $C_{16}H_{18}O_2N_2$: C 71.06, H 6.71, N 10.4. Found: C 70.63, H 6.76, N 9.99.

(2*S*)-2-[(2-Aminophenyl)carbonylamino]-3-phenylpropyl 2-Aminobenzenecarboxylate (15a). Yield: 19%, yellow solid. Mp: 144−146 °C. $[\alpha]_D = -29.31$ (*c* = 1.01 in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.86$ (dd, *J* = 8.2, 1.6 Hz, 1H), 7.16−7.36 (m, 8H), 6.60−6.66 (m, 4H), 6.38 (d, *J* = 8.1 Hz, 1H), 5.71 (s, br, 2H), 5.44 (s, br, 2H), 4.67−4.74 (m, 1H), 4.32−4.40 (m, 2H), 3.12 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.00 (dd, *J* = 13.8, 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 169.2$, 168.4, 151.0, 149.0, 137.4, 134.7, 132.6, 131.4, 129.6, 129.0, 127.4, 127.1, 117.5, 117.1, 116.9, 116.6, 116.2, 110.4, 67.3, 50.2, 37.9. IR (KBr): $\nu = 3489$, 3427, 3312, 1687, 1619, 750 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 389 [M$^+$], 253, 161, 137, 120 (100), 92, 65. Anal. Calcd for $C_{23}H_{23}O_3N_3$: C 70.90, H 5.95, N 10.83. Found: C 70.55, H 6.00, N 10.53.

***N*-[(1S)-1-Hydroxymethyl-2-methylpropyl]-2-aminobenzamide (12b).** Yield: 59%, white solid. Mp: 104−105 °C (lit.[15] mp 107−108 °C). $[\alpha]_D = -47.5$ (*c* = 1.00 in EtOH) (lit.[15] $[\alpha]_D = -48.0$ (*c* = 1.01 in EtOH)). ^1H NMR ($CDCl_3$): $\delta = 7.34$ (dd, *J* = 7.9, 1.5 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.0, 1.5 Hz, 1H), 6.68 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.65 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1H), 6.26 (d, *J* = 7.3 Hz, 1H), 5.43 (s br, 2H), 3.86−3.95 (m, 1H), 3.71−3.82 (m, 2H), 2.80 (s, br, 1H), 1.93−2.05 (m, 1H), 1.03 (d, *J* = 4.7 Hz, 3H), 1.01 (d, *J* = 4.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 170.3$, 148.7, 132.6, 127.5, 117.6, 117.1, 116.8, 64.0, 57.3, 29.5, 19.9, 19.2. IR (KBr): $\nu = 3364$, 3319, 3272, 1621, 1561, 724 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 222 [M$^+$], 191, 120 (100), 92, 65, 39.

(2*S*)-2-Amino-3-methylbutyl 2-Aminobenzenecarboxylate (14b). Yield: 3%, yellow oil. ^1H NMR ($CDCl_3$): $\delta = 7.86$ (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 7.26 (ddd, *J* = 8.2, 7.2, 1.6 Hz, 1H), 6.61−6.69 (m, 2H), 5.72 (s, br, 2H), 4.35 (dd, *J* = 11.0, 4.1 Hz, 1H), 4.12 (dd, *J* = 11.0, 7.6 Hz, 1H), 2.94 (m, br, 1H), 1.69−1.82 (m, br, 3H), 1.01 (d, *J* = 3.1 Hz, 3H), 0.99 (d, *J* = 3.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 168.3$, 150.8, 134.4, 131.3, 117.0, 116.5, 111.0, 68.0, 55.8, 19.5, 19.2. IR (neat): $\nu = 3459$, 3372, 1690, 1619, 1244, 1107, 754 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 222 [M$^+$], 179, 120 (100), 92, 72, 65, 55. Anal. Calcd for $C_{12}H_{18}O_2N_2$: C 64.81, H 8.16, N 12.65. Found: C 64.72, H 8.19, N 11.96.

(2*S*)-2-[(2-Aminophenyl)carbonylamino]-3-methylbutyl 2-Aminobenzenecarboxylate (15b). Yield: 9%, white solid. Mp: 122−124 °C. $[\alpha]_D = -90.95$ (*c* = 1.05 in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.82$ (dd, *J* = 8.2, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.26 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.3, 1.5, 1H), 6.60−6.68 (m, 4H), 6.23 (d, *J* = 8.8 Hz, 1H), 5.70 (s, br, 2H), 5.42 (s, br, 2H), 4.48 (dd, *J* = 11.4, 5.9 Hz, 1H), 4.40 (dd, *J* = 11.4, 4.1 Hz, 1H), 4.32−4.35 (m, 1H), 2.01−2.08 (m, 1H), 1.08 (d, *J* = 4.7 Hz, 3H), 1.06 (d, *J* = 4.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 169.2$, 168.2, 150.7, 148.7, 134.4, 132.3, 131.2, 127.1, 117.3, 116.8, 116.7, 116.5, 116.4, 110.4, 64.5, 53.5, 29.9, 19.5, 18.8. IR (KBr): $\nu = 3483$, 3362, 1674, 1634, 1619, 752 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 341 [M$^+$], 205, 161, 137, 120 (100), 92, 65.

***N*-[(1S)-2-Hydroxy-1-phenylethyl]-2-aminobenzamide (12c).** Yield: 47%. white solid. Mp: 146−148 °C. $[\alpha]_D = +70.6$ (*c* = 1.00 in EtOH). ^1H NMR ($CDCl_3$): $\delta = 7.29-7.42$ (m, 6H), 7.22 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 1H), 6.76 (d, *J* = 6.0 Hz, 1H), 6.63−6.69 (m, 2H), 5.50 (br s, 2H), 5.20−5.25 (m, 1H), 3.99 (app t, *J* = 5.0 Hz, 2H), 2.49 (s, br, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 169.8$, 149.5, 139.4, 132.9, 129.2, 128.2, 127.6, 126.9, 117.7, 116.9, 116.0, 67.0, 56.2. IR (KBr): $\nu = 3381$, 3293, 1638, 1584, 781, 705 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) 256 [M$^+$], 225, 120 (100), 106, 92, 65, 39.

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[33] Dickman, D. A. *Org. Synth.* **1990**, *7*, 530.

(2*S*)-2-Amino-2-phenylethyl 2-Aminobenzenecarboxylate (14c). Yield: 24%, white solid. Mp: 76−78 °C. $[\alpha]_D = +19.4$ ($c = 1.01$ in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.84$ (m, 1H), 7.24−7.47 (m. 6H), 6.61−6.67 (m, 2H), 5.69 (s, br, 2H), 4.37−4.48 (m, 2H), 4.27 (dd, $J = 10.0$, 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 167.8$, 150.6, 134.2, 134.2, 131.1, 128.6, 127.7, 126.8, 116.7, 116.3, 110.6, 69.8, 54.8. IR (KBr): $\nu = 3444$, 3290, 1686, 1621, 699, 661 cm^{-1}. MS (70 eV, EI): *m/z* (%) 256 [M^+], 119, 120, 106 (100), 92, 79, 65. Anal. Calcd for $C_{15}H_{16}O_2N_2$: C 70.26, H 6.29, N 10.97. Found: C 69.94, H 6.37, N 10.59.

(2*S*)-2-[(2-Aminophenyl)carbonylamino]-3-phenylethyl 2-Aminobenzenecarboxylate (15c). Yield: 14%, white solid. Mp: 142−144 °C. $[\alpha]_D = -1.5$ ($c = 1.00$ in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.77$ (ddd, $J = 8.1$, 1.8, 0.4 Hz, 1H), 7.22−7.45 (m, 7H), 7.19 (ddd, $J = 8.4$, 7.6, 1.8 Hz, 1H), 6.94 (d, $J = 6.9$ Hz, 1H), 6.60−6.66 (m, 4H), 5.67 (s, br, 2H), 5.50−5.56 (m, 3H), 4.71 (dd, $J = 11.6$, 7.5 Hz, 1H), 4.55 (dd, $J = 11.6$, 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 169.1$, 168.7, 151.0, 149.3, 139.0, 134.8, 132.8, 131.5, 129.2, 128.2, 127.5, 126.9, 117.6, 117.0, 116.8, 116.7, 115.7, 110.3, 66.6, 53.6. IR (KBr): $\nu = 3486$, 3377, 3302, 1691, 1635, 1615, 752 cm^{-1}. MS (70 eV, EI): *m/z* (%) 375 [M+], 239, 225, 120 (100), 92, 65. Anal. Calcd for $C_{22}H_{21}O_3N_3$: C 70.35, H 5.64, N 11.24. Found: C 69.96, H 5.69, N 10.97.

***N*-[(1S)-1-Hydroxymethyl-2,2-dimethylpropyl]-2-aminobenzamide (12d).** Yield: 40%. white solid. Mp: 100−102 °C. $[\alpha]_D = -6.3$ ($c = 1.00$ in EtOH). ^1H NMR ($CDCl_3$): $\delta = 7.35$ (dd, $J = 8.5$, 1.5 Hz, 1H), 7.21 (ddd, $J = 8.2$, 7.0, 1.5 Hz, 1H), 6.64−6.69 (m, 2H), 6.25 (d, $J = 8.2$ Hz, 1H), 5.39 (s, br, 2H), 4.01 (ddd, $J = 9.1$, 7.6, 3.5 Hz, 1H), 3.93 (dd, $J = 11.0$, 3.5 Hz, 1H), 3.65 (dd, $J = 11.0$, 7.6 Hz, 1H), 2.65 (s, br, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$): $\delta = 170.6$, 148.5, 132.5, 127.5, 117.7, 117.2, 116.4, 63.2, 59.7, 34.1, 27.3. IR (KBr): $\nu = 3343$, 1632, 1590, 1368, 755, 685 cm^{-1}. MS (70 eV, EI): *m/z* (%) 236 [M^+], 205, 179, 161, 120 (100), 92, 65.

(2*S*)-2-Amino-3,3-dimethylbutyl 2-Aminobenzenecarboxylate (14d). Yield: 19%, white solid. Mp: 82−84 °C. $[\alpha]_D = +44.55$ ($c = 0.22$ in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.85$ (ddd, $J = 7.9$, 1.5, 0.4 Hz, 1H), 7.26 (ddd, $J = 9.8$, 7.1, 1.5 Hz, 1H), 6.61−6.67 (m, 2H), 5.73 (s, br, 2H), 4.50 (dd, $J = 10.8$, 3.1 Hz, 1H), 4.04 (dd, $J = 10.8$, 8.9 Hz, 1H), 2.88 (dd, $J = 8.9$, 3.1 Hz, 1H), 1.53 (s, br, 2H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$): $\delta = 168.2$, 150.6, 134.1, 131.1, 116.8, 116.3, 110.8, 67.0, 58.9, 33.5, 26.5. IR (KBr): $\nu = 3416$, 3369, 1686, 1628, 1242, 754 cm^{-1}. MS (70 eV, EI): *m/z* (%) 236 [M^+], 179, 120 (100), 92, 86, 69. 65. Anal. Calcd for $C_{13}H_{20}O_2N_2$: C 66.04, H 8.53, N 11.90. Found: C 66.18, H 8.34, N 11.61.

(2*S*)-2-[(2-Aminophenyl)carbonylamino]-3,3-dimethylbutyl 2-Aminobenzenecarboxylate (15d). Yield: 6%, white solid. Mp: 82−84 °C. $[\alpha]_D = -63.1$ ($c = 1.00$ in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.80$ (dd, $J = 7.9$, 1.6 Hz, 1H), 7.31 (dd, $J = 7.8$, 1.3 Hz, 1H), 7.22 (ddd, $J = 8.2$, 7.1, 1.3 Hz, 1H), 7.18 (ddd, $J = 8.2$, 7.2, 1.6 Hz, 1H), 6.56−6.66 (m, 4H), 6.16 (d, $J = 8.9$ Hz, 1H) 5.65 (s, br, 2H), 5.34 (s, br, 2H), 4.37−4.53 (m, 3H), 1.08 (s, 9H). ^{13}C NMR ($CDCl_3$): $\delta = 169.3$, 168.3, 150.5, 148.5, 134.3, 132.2, 131.4, 126.9, 117.2, 116.8, 116.72, 116.70, 116.4, 110.5, 63.8, 55.6, 34.2, 27.0. IR (KBr): $\nu = 3467$, 3360, 1691, 1651, 1618, 745 cm^{-1}. MS (70 eV, EI): *m/z* (%) 355 [M+], 219, 161, 137, 120 (100), 92, 65.

General Procedure for the Cyclization of Chloro Amides 13a−d To Give 9a−d: Method a. Chloroamide (23.6 mmol) was added to a suspension of NaOH pellets (1.01 g, 25.3 mmol) in EtOH (170 mL) and the resulting pale yellow mixture was refluxed for 3 h. After cooling to room temperature, the solvent was removed in vacuo to give a yellow residue. This was dissolved in CH_2Cl_2 (100 mL) and washed with a saturated solution of $NaHCO_3$ (4 × 50 mL). The aqueous layers were separated and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, evaporated to give a yellow/brown residue, and purified by flash column chromatography on silica gel (6 × 35 cm, hexane/AcOEt 3:1) to give two products.

Alternative Procedure for the Synthesis of 2-(*o*-Aminophenyl)oxazolines (9a−d): Method b. DAST (98 μL, 0.74 mmol) was added slowly and dropwise to a solution of the hydroxy amide (0.74 mmol) in dry CH_2Cl_2 (7 mL) under an atmosphere of nitrogen at room temperature. After stirring of the resulting yellow solution at room temperature under a nitrogen atmosphere for 18 h, the reaction mixture was poured on to a saturated solution of $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to give a yellow/brown solid, which was purified by flash column chromatography on silica gel [3 × 30 cm, CH_2Cl_2/pet. ether (40−60 °C) 19:1] to yield product.

2-[(4*S*)-4-(Benzyl)-4,5-dihydro-1,3-oxazol-2-yl]aniline (9a). Yield: 60% (method a), 84% (method b), white solid. Mp: 56−57 °C (lit.[15] mp: 56−57 °C). $[\alpha]_D = +24.7$ ($c = 1.00$ in $CHCl_3$) (lit.[15] $[\alpha]_D = +24.8$ ($c = 1.25$ in $CHCl_3$)). ^1H NMR ($CDCl_3$): $\delta = 7.67$ (dd, $J = 7.9$, 1.5 Hz, 1H),), 7.16−7.68 (m, 6H), 6.61−6.69 (m, 2H), 6.07 (s, br, 2H), 4.54−4.64 (m, 1H), 4.26 (dd, $J = 9.1$, 8.5 Hz, 1H), 4.01 (dd, $J = 8.5$, 7.3 Hz, 1H), 3.12 (dd, $J = 13.8$, 6.2 Hz, 1H), 2.76 (dd, $J = 13.8$, 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 164.4$, 148.9, 138.7, 122.3, 129.9, 129.5, 128.8, 126.7, 116.3, 115.9, 109.3, 70.5, 68.4, 42.6. IR (KBr): $\nu = 3402$, 3256, 1631, 1166, 1056, 968 cm^{-1}. MS (70 eV, EI), *m/z* (%) 252 [M^+], 161 (100), 133, 106, 91, 65, 32.

2-Amino-*N*-((1S)-1-benzyl-2-[2-((4S)-4-benzyl-4,5-dihydrooxazol-2-yl)phenylamino]ethyl)benzamide (16a). Yield: 7%, white solid. Mp: 130−132 °C. $[\alpha]_D = +2.21$ ($c = 0.995$ in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 8.79$ (app t, $J = 5.3$ Hz, 1H), 7.72 (dd, $J = 7.9$, 1.8 Hz, 1H), 7.13−7.33 (m, 13H), 6.75 (d, $J = 8.5$ Hz, 1H), 6.65 (dd, $J = 5.3$, 0.9 Hz, 1H), 6.62 (ddd, $J = 6.2$, 4.1, 0.9 Hz, 1H), 6.57 (ddd, $J = 7.9$, 5.3, 1.2 Hz, 1H), 6.08 (d, $J = 8.05$ Hz, 1H), 5.42 (s, br, 2H), 4.49−4.62 (m, 2H), 4.25 (app t, $J = 8.4$ Hz, 1H), 3.99 (dd, $J = 8.4$, 7.6 Hz, 1H), 3.30−3.47 (m, 2H), 2.98−3.08 (m, 2H), 2.91 (dd, $J = 13.9$, 7.3 Hz, 1H), 2.72 (dd, $J = 13.8$, 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 169.0$, 164.5, 149.2, 148.7, 138.3, 137.6, 132.7, 132.2, 130.0, 129.4, 129.1, 128.6, 128.5, 127.4, 126.7, 126.5, 117.2, 116.6, 116.3, 114.9, 110.7, 108.8, 70.2, 68.0, 50.2, 44.7, 42.2, 38.2. IR (KBr): $\nu = 3303$, 1633, 1587, 1523, 744, 714 cm^{-1}. MS (70 eV, EI): *m/z* (%) 504 [M^+], 265 (100), 131, 120, 117, 105, 91, 77, 65. Anal. Calcd for $C_{32}H_{32}O_2N_4$: C 76.13, H 6.39, N 11.14. Found: C 75.89, H 6.38, N 10.93.

2-[(4*S*)-4-Isopropyl-4,5-dihydro-1,3-oxazol-2-yl]aniline (9b). Yield: 67% (method a), 87% (method b), white solid. Mp: 64−65 °C (lit.[15] mp: 67−69 °C). $[\alpha]_D = +10.2$ ($c = 1.00$ in EtOH) (lit.[15] $[\alpha]_D = +8.7$ ($c = 1.00$ in EtOH)). ^1H NMR ($CDCl_3$): $\delta = 7.67$ (dd, $J = 7.9$, 1.5 Hz, 1H), 7.19 (ddd, $J = 8.2$, 7.3, 1.5 Hz, 1H), 6.69 (dd, $J = 8.2$, 1.2 Hz, 1H), 6.65 (ddd, $J = 7.9$, 7.3, 1.2 Hz, 1H), 6.12 (s, br, 2H), 4.32 (dd, $J = 9.1$, 7.6 Hz, 1H), 4.11 (ddd, $J = 9.1$, 7.6, 6.7 Hz, 1H), 4.00 (app. t, $J = 7.6$ Hz, 1H), 1.79 (m, 1H), 1.03 (d, $J = 6.7$ Hz, 3H), 0.94 (d, $J = 6.7$ Hz, 3H), ^{13}C NMR ($CDCl_3$): $\delta = 163.8$, 148.9, 132.1, 129.8, 116.2, 115.9, 109.5, 73.2, 69.0, 33.5, 19.2, 18.8. IR (KBr): $\nu = 3402$, 3259, 1640, 1607, 1491, 746 cm^{-1}. MS (70 eV, EI): *m/z* (%) 204 [M^+], 161 (100), 133, 118, 106, 92, 65, 39.

2-Amino-*N*-((1S)-1-{[2-((4S)-4-isopropyl-4,5-dihydrooxazol-2-yl-phenylamino]methyl}-2-methylpropyl)benzamide (16b). Yield: 10%, brown solid. Mp: 96−98 °C. $[\alpha]_D = -85.8$ ($c = 0.30$ in $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 8.74$ (s, br, 1H), 7.71 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.28 (ddd, $J = 8.4$, 7.2, 1.8 Hz. 1H), 7.23 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.17 (ddd, $J = 8.1$, 7.3, 1.6 Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.65 (dd, $J = 8.2$, 0.88 Hz, 1H), 6.55−6.63 (m, 2H), 6.11 (d, $J = 9.1$ Hz, 1H), 5.44 (s, br, 2H), 4.19−4.29 (m, 2H), 3.93−4.04 (m, 2H), 3.40−3.54 (m, 2H), 2.04−2.13 (m, 1H), 1.67−1.75 (m, 1H), 1.05 (app t, $J = 7.2$ Hz, 6H), 0.95 (d, $J = 6.7$ Hz, 3H), 0.87 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 169.3$, 164.1, 149.5, 148.9, 132.8, 132.4, 130.2, 127.5, 117.4, 116.83, 116.76, 114.9, 110.6, 109.1, 73.0, 68.7, 54.3, 44.3, 33.3, 30.2, 19.8, 19.2, 18.9, 18.7. IR (KBr): $\nu = 3455$, 3397, 1633, 1530, 1250, 748 cm^{-1}. MS (70 eV, EI): *m/z* (%) 408 [M^+], 257, 217 (100), 131, 120, 92, 65, 41. Anal.

Calcd for $C_{24}H_{32}O_2N_4$: C 70.52, H 7.89, N 13.76. Found: C 70.82, H 7.91, N 13.54.

2-[(4*S*)-4-Phenyl-4,5-dihydro-1,3-oxazol-2-yl]aniline (9c). Yield: 72% (method a), 82% (method b), white solid. Mp: 74−77 °C (lit.[15] mp: 73−74 °C). $[\alpha]_D = +185.1$ ($c = 1.00$ in CHCl$_3$) (lit.[15] $[\alpha]_D = +190.1$ ($c = 1.25$ in CHCl$_3$)). ^{1}H NMR (CDCl$_3$): δ = 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.23−7.38 (m, 5H), 7.22 (ddd, J = 8.2, 7.0, 1.5 Hz, 1H), 6.70 (ddd, J = 8.2, 1.2, 0.6 Hz, 1H), 6.68 (ddd, J = 7.9, 7.0, 1.2 Hz, 1H), 6.12 (s, br, 2H), 5.43 (dd, J = 10.0, 8.2 Hz, 1H), 4.67 (dd, J = 10.0, 8.2 Hz, 1H), 4.11 (app t, J = 8.2 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ = 165.3, 149.1, 143.1, 132.6, 130.1, 129.0, 127.8, 126.9, 116.3, 116.0, 109.0, 73.3, 70.5. IR (KBr): ν = 3416, 3273, 1633, 1597, 1488, 747 cm^{-1}. MS (70 eV, EI): m/z (%) 238 [M$^+$], 207, 120, 118 (100), 91, 65, 39.

2-Amino-*N*-{(1S)-1-phenyl-2-[2-((4S)-4-phenyl-4,5-dihydrooxazol-2-yl)phenylamino]ethyl}benzamide (16c). Yield: 6%, white solid. Mp: 90−92 °C. $[\alpha]_D = +114.08$ ($c = 1.03$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 8.71 (app t, J = 5.0 Hz, 1H), 7.78 (dd, J = 7.9, 1.6 Hz, 1H), 7.15−7.36 (m, 13H), 6.82 (d, J = 8.5 Hz, 1H), 6.67 (ddd, J = 7.9, 7.2, 1.0 Hz, 1H), 6.65 (m, 1H), 6.62 (dd, J = 8.2, 0.9 Hz, 1H), 6.55 (ddd, J = 7.9, 7.2, 1.2 Hz, 1H), 5.44 (dd, J = 13.2, 5.9 Hz, 1H), 5.37 (s, br, 2H), 5.24 (dd, J = 10.0, 8.3 Hz, 1H), 4.60 (dd, J = 10.0, 8.3 Hz, 1H), 4.06 (app t, J = 8.3 Hz, 1H), 3.63−3.81 (m, 2H). ^{13}C NMR (CDCl$_3$): δ = 168.7, 165.1, 149.1, 148.9, 142.6, 140.1, 132.9, 132.3, 130.2, 128.7, 128.7, 127.56, 127.53, 127.4, 126.6, 126.5, 126.5, 117.4, 116.6, 115.2, 110.6, 108.9, 72.9, 70.1, 52.9, 48.1. IR (KBr): ν = 3447, 3309, 1633, 1567, 1156, 748 cm^{-1}. MS (70 eV, EI): m/z (%) 476 [M$^+$].

2-[(4*S*)-4-(*tert*-Butyl)-4,5-dihydro-1,3-oxazol-2-yl]aniline (9d). Yield: 52% (method a), 81% (method b), white solid. Mp: 66−67 °C (lit.[15] mp: 64−65 °C). $[\alpha]_D = +35.0$ ($c = 1.00$ in EtOH) (lit.[15] $[\alpha]_D = +33.0$ (c=1.02 in EtOH). ^{1}H NMR (CDCl$_3$): δ = 7.67 (dd, J = 7.9, 1.8 Hz, 1H), 7.19 (ddd, J = 8.2, 7.3, 1.8 Hz, 1H), 6.70 (dd, J = 8.2, 1.2 Hz, 1H), 6.65 (ddd, J = 7.9, 7.3, 1.2 Hz, 1H), 6.14 (s br, 2H), 4.20−4.28 (m, 1H), 4.06−4.14 (m, 2H), 0.94 (s, 9H). ^{13}C NMR (CDCl$_3$): δ = 163.7, 148.9, 132.1, 129.8, 116.2, 115.9, 109.4, 76.6, 67.2, 34.1, 26.2. IR (KBr): ν = 3425, 3273, 1639, 1608, 1053, 749 cm^{-1}. MS (70 eV, EI): m/z (%) 218 [M$^+$], 161(100), 133, 106, 65, 41, 32.

(2-Aminophenyl)((2*S*)-*tert*-butylaziridin-1-yl)methanone (17d). Yield: 23%, white solid. Mp: 98−99 °C. $[\alpha]_D = +126.03$ ($c = 0.365$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ =8.01 (dd, J = 8.3, 1.6 Hz, 1H), 7.24 (ddd, J = 8.2, 7.2, 1.6 Hz, 1H), 6.63−6.68 (m, 2H), 5.83 (s, br, 2H), 2.48 (dd, J = 6.3, 4.0 Hz, 1H), 2.34 (dd, J = 3.8, 0.7 Hz, 1H), 2.28 (dd, J = 6.3, 0.7 Hz, 1H), 1.00 (s, 9H). ^{13}C NMR (CDCl$_3$): δ = 182.2, 150.6, 133.9, 131.6, 117.1, 116.2, 114.3, 46.5, 30.8, 30.7, 26.8. IR (KBr): ν = 3454, 3338, 1639, 1613, 1586, 771 cm^{-1}. MS (70 eV, EI): m/z (%) 218 [M$^+$], 147, 136, 120 (100), 98, 92, 65. Anal. Calcd for $C_{13}H_{18}ON_2$: C 71.49, H 8.31, N 12.88. Found: C 71.19, H 8.29, N 12.71.

General Procedure for the Synthesis of Bis(oxazoline) Ligands (7a−j). An oven-dried Schlenk tube was charged with 2-(2′-bromophenyl)oxazoline (1.00 mmol), sodium *tert*-butoxide (0.115 g, 1.2 mmol), DPPF (55 mg, 0.10 mmol), Pd$_2$(dba)$_3$ (23 mg, 0.025 mmol), and 2-(*o*-aminophenyl)oxazoline (1.2 mmol). After the addition of dry, degassed toluene (8 mL) via syringe, the Schlenk tube was capped and the reaction mixture (a brown suspension) was heated at 90 °C for 1 week. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a brown oil. This was adsorbed onto silica gel and subjected to flash column chromatography on silica gel (3 × 30 cm) using pet. ether (40−60 °C)/AcOEt 19:1 followed by pet. ether (40−60 °C)/AcOEt 9:1 as the eluents to yield product.

Bis[2-((4*S*)-4-benzyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7a). Yield: 63%, yellow solid. Mp: 35−39 °C. $[\alpha]_D = +88.76$ ($c = 1.05$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 10.89 (s, 1H), 7.81 (dd, J = 7.9, 1.6 Hz, 2H), 7.47 (dd, J = 8.4, 1.0 Hz, 2H), 7.30 (ddd, J = 8.4, 7.2, 1.6 Hz, 2H), 7.17−7.26 (m, 10H), 6.90 (ddd, J = 7.8, 7.2, 1.2 Hz, 2H), 4.44−4.52 (m, 2H), 4.23 (dd, J = 8.4, 9.4 Hz, 2H), 3.99 (dd, J = 8.4, 7.6 Hz, 2H), 3.16 (dd, J = 13.8, 5.6 Hz, 2H), 2.72 (dd, J = 13.8, 8.2 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 163.4, 143.5, 138.4, 131.6, 130.7, 129.6, 128.7, 126.6, 120.0, 118.5, 116.1, 70.9, 68.4, 42.1. IR (KBr): ν = 3434, 3230, 1639, 1578, 746, 699 cm^{-1}. MS (70 eV, EI): m/z (%) 487 [M+], 396, 262, 146, 91 (100), 57, 43. Anal. Calcd for $C_{32}H_{29}O_2N_3$: C 78.80, H 5.99, N 8.65. Found: C 78.70, H 6.09, N 8.54.

Bis[2-((4*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7b). Yield: 72%, pale yellow crystals. Mp: 114−115 °C. $[\alpha]_D = +2.12$ ($c = 0.33$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 10.72 (s, 1H), 7.81 (dd, J = 7.9, 1.5 Hz, 2H), 7.40 (dd, J = 8.5, 1.2 Hz, 2H), 7.26 (ddd, J = 8.5, 7.3, 1.5 Hz, 2H), 6.89 (ddd, J = 7.9, 7.3, 1.2 Hz, 2H), 4.32 (dd, J = 8.8, 7.3 Hz, 2H), 3.98−4.12 (m, 4H), 1.74−1.85 (m, 2H), 1.01 (d, J = 6.7 Hz, 6H), 0.91 (d, J = 6.7 Hz, 6H). ^{13}C NMR (CDCl$_3$): δ = 162.9, 143.5, 131.4, 130.7, 120.0, 118.8, 116.5, 73.3, 69.5, 33.3, 19.3, 18.6. IR (KBr): ν = 3288, 3188, 1638, 979, 742 cm^{-1}. MS (70 eV, EI): m/z (%) 391 (100, [M$^+$]), 348, 262, 233, 219, 205, 69. Anal. Calcd for $C_{24}H_{29}O_2N_3$: C 73.59, H 7.46, N 10.77. Found: C 73.61, H 7.35, N 10.53.

Bis[2-((4*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7c). Yield: 43%, yellow solid. Mp: 54−56 °C. $[\alpha]_D = +210.97$ ($c = 0.155$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 11.07 (s, 1H), 7.87 (dd, J = 7.8, 1.6 Hz, 2H), 7.53 (dd, J = 8.3, 0.9 Hz, 2H), 7.32 (ddd, J = 8.3, 7.3, 1.6 Hz, 2H), 7.12−7.26 (m, 10H), 6.92 (ddd, J = 7.8, 7.3, 0.9 Hz, 2H), 5.17 (dd, J = 10.0, 8.2 Hz, 2H), 4.46 (dd, J = 10.0, 8.2 Hz, 2H), 3.98 (app t, J = 8.2 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 164.4, 143.4, 142.9, 131.8, 130.9, 128.7, 127.5, 126.9, 120.1, 118.4, 116.0, 74.0, 70.3. IR (KBr): ν = 3431, 1636, 1576, 1473, 1270, 759 cm^{-1}. MS (70 eV, EI): m/z (%) 459 [M$^+$], 219 (100), 192 (17), 120, 103, 91, 77. Anal. Calcd for $C_{30}H_{25}O_2N_3$: C 78.38, H 5.48, N 9.18. Found: C 78.38, H 5.58, N 9.07.

Bis[2-((4*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7d). Yield: 73%, white solid. Mp: 116−118 °C. $[\alpha]_D = -6.43$ ($c = 0.14$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 10.79 (s, 1H), 7.82 (dd, J = 7.8, 1.5 Hz, 2H), 7.39 (dd, J = 8.3, 1.0 Hz, 2H), 7.26 (ddd, J = 8.3, 7.1, 1.8 Hz, 2H), 6.88 (ddd, J = 8.3, 6.6, 1.3 Hz, 2H), 4.24 (dd, J = 9.4, 7.6 Hz, 2H), 4.11 (app t, J = 7.6 Hz, 2H), 4.05 (dd, J = 9.4, 7.8 Hz, 2H), 0.91 (s, 18H). ^{13}C NMR (CDCl$_3$): δ = 162.7, 143.7, 131.4, 130.7, 120.0. 118.9, 116.6, 76.7, 67.8, 34.2, 26.2. IR (KBr): ν = 3430, 3174, 1649, 1458, 966, 746 cm^{-1}. MS (70 eV, EI): m/z (%) 419 [M$^+$], 362, 262 (100), 233, 205, 166, 57. Anal. Calcd for $C_{26}H_{33}O_2N_3$: C 74.40, H 7.92, N 10.05. Found: C 74.06, H 7.83, N 9.93.

[2-((4*S*)-Phenyl-4,5-dihydrooxazol-2-yl)phenyl][2-((4S)-4-benzyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7e). Yield: 68%, yellow oil. $[\alpha]_D = +107.03$ ($c = 0.185$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = [11.03 and 10.99 (s, 1H)], [7.92 and 7.94 (dd, J = 8.0, 1.5 Hz, 1H)], [7.76 and 7.78 (dd, J = 8.0, 1.5 Hz, 1H)], 7.44−7.54 (m, 2H), 7.13−7.36 (m, 10H), 6.86−7.06 (m, 4H), [5.39 and 5.42 (app t, J = 8.0 Hz, 1H)], 4.67 (dd, J = 8.2, 10.0 Hz, 1H), [4.25−4.35 and 4.35−4.45 (m, 1H)], [4.13 and 4.11 (app t, J = 8.2 Hz, 1H)], [3.99 and 4.04 (dd, J = 9.2, 8.5 Hz, 1H)], [3.84 and 3.81 (dd, J = 7.4, 4.4 Hz, 1H)], [2.88 and 2.99 (dd, J = 13.6, 4.9 Hz, 1H)], 2.44 (d, J = 13.6, 8.7 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ = 164.3, [163.4, 163.3], 143.7, 143.3, [143.0, 142.9], [138.4, 138.3], [131.7, 131.8], [131.5, 131.6], [130.8, 130.9], 130.7, 129.5, [128.9, 128.8], [128.5, 128.6], [127.73, 127.66], 127.07, [126.48, 126.51], 120.1, [119.98, 120.04], [118.59, 118.63], [118.25, 118.38], 116.3, 115.7, [73.9. 73.8], 70.8, [70.73, 70.67], 68.12, [41.7, 41.6]. IR (neat): ν = 3437, 1637, 1518, 699, 625 cm^{-1}. MS (70 eV, EI): m/z (%) 473 [M$^+$], 262, 233, 103, 91 (100), 77. [The majority of peaks in both the ^{1}H and ^{13}C NMR spectra appeared as two signals in a ratio of 1.5:1.]

[2-((4*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)phenyl][2-((4S)-4-benzyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7f). Yield: 58%, yellow oil. $[\alpha]_D = +37.4$ ($c = 0.15$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 10.74 (s, 1H), 7.82 (dd, J = 7.6, 1.3 Hz, 1H), 7.79 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.42 (dd, $J = 8.3, 1.0$ Hz, 1H), 7.38 (dd, $J = 8.3, 1.0$ Hz, 1H), 7.15−7.31 (m, 7H), 6.86−6.94 (m, 2H), 4.52−4.62 (m, 1H). 4.25 (app t, $J = 8.3$ Hz, 1H). 4.22 (dd, $J = 9.1, 8.3$ Hz, 1H), 4.08 (app t, $J = 8.2$ Hz, 1H), 4.02 (dd, $J = 8.3, 7.3$ Hz, 1H), 3.98 (dd, $J = 10.0, 8.1$ Hz, 1H), 3.16 (dd, $J = 13.6, 5.4$ Hz, 1H), 2.71 (dd, $J = 13.8, 8.3$ Hz, 1H), 0.92 (s, 9H). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 163.4$, 162.7, 143.9, 143.3, 138.4, 131.5, 131.4, 130.7, 130.6, 129.6, 128.6, 126.6, 120.4, 119.7, 119.6, 118.2, 117.0, 115.9, 76.8, 71.1, 68.3, 67.6, 42.0, 34.1, 26.2. IR (neat): $\nu = 3448$, 3238, 1642, 1580, 746, 706 cm^{-1}. MS (70 eV, EI): m/z (%) 453 [M$^+$], 396, 362, 262 (100), 233, 91, 57.

[2-((4*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)phenyl][2-((4S)-4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7g). Yield: 63%, yellow solid. Mp: 78−80 °C. $[\alpha]_D = -3.26$ (c = 0.215 in CHCl$_3$). ^{1}H NMR (CDCl$_3$): $\delta = 10.74$ (s,1H), 7.82 (app t, $J = 1.6$ Hz, 1H), 7.80 (app t, $J = 1.6$ Hz, 1H), 7.39 (dd, $J = 8.3, 1.0$ Hz, 1H), 7.38 (dd, $J = 8.3, 1.0$ Hz, 1H), 7.23−7.29 (m, 2H), 6.85−6.92 (m, 2H), 4.31 (dd, $J = 8.6, 7.2$ Hz, 1H), 4.24 (dd, $J = 9.1, 7.3$ Hz, 1H), 4.03−4.14 (m, 3H), 3.99 (app t, $J = 7.3$ Hz, 1H), 1.72−1.83 (m, 1H), 1.00 (d, $J = 6.7$ Hz, 3H), 0.92 (s, 9H), 0.90 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (CDCl$_3$): δ = 162.9, 162.8, 143.7, 143.5, 131.38, 131.38, 130.72, 130.67, 120.1, 119.9, 119.0, 118.7, 116.8, 116.4, 76.8, 73.3, 69.6, 67.8, 34.2, 33.3, 26.2, 19.3, 18.7. IR (KBr): ν =1646, 1517, 1455, 908, 825, 747 cm^{-1}. MS (70 eV, EI): m/z (%) 405 [M$^+$], 348, 262 (100), 233, 205, 169, 57. Anal. Calcd. for $C_{25}H_{31}O_2N_3$: C 74.01, H 7.70, N 10.40. Found: C 73.71, H 7.79, N 10.12.

[2-((4*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl)phenyl][2-((4S)-4-phenyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7h). Yield: 78%, yellow solid. Mp: 66−67 °C. $[\alpha]_D = +157.45$ (c = 0.470 in CHCl$_3$). ^{1}H NMR (CDCl$_3$): $\delta = 10.86$ (s, 1H), 7.90 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.78 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.49 (d, J = 8.3, Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.24−7.34 (m, 7H), 6.85−6.95 (m, 2H), 5.42 (dd, $J = 10.0, 8.2$ Hz, 1H), 4.70 (dd, J = 10.0, 8.3 Hz, 1H), 4.16 (app t, $J = 8.3$ Hz, 1H), 4.01−4.09 (m, 1H), 3.79−3.90 (m, 2H), 1.54−1.65 (m, 1H), 0.83 (d, J = 6.7 Hz, 3H), 0.74 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (CDCl$_3$): δ = 164.4, 162.9, 143.6, 143.3, 143.0, 131.7, 131.3, 130.9, 130.7, 128.8, 127.7, 127.1, 120.1, 120.0, 118.9, 118.3, 116.5, 116.1, 74.0, 72.9, 70.7, 69.1, 32.7, 19.2, 18.0. IR (KBr): $\nu = 1644$, 1457, 1272, 1056, 745, 890 cm^{-1}. MS (70 eV, EI): m/z (%) 425 [M$^+$], 262 (100), 233, 219, 103, 91, 77. Anal. Calcd. for $C_{27}H_{27}O_2N_3$: C 76.18, H 6.39, N 9.91. Found: C 76.01, H 6.27, N 9.90.

[2-((4*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl)phenyl][2-((4S)-4-phenyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7i). Yield: 73%, colorless crystals. Mp: 150−152 °C. $[\alpha]_D = +196.0$ (c = 0.125 in CHCl$_3$). ^{1}H NMR (CDCl$_3$): $\delta = 10.77$ (s, 1H), 7.91 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.78 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.47 (dd, $J = 8.5, 0.9$ Hz, 1H), 7.42 (dd, $J = 8.5, 0.9$ Hz, 1H), 7.23−7.35 (m, 7H), 6.94 (ddd, $J = 7.9, 7.3, 1.2$ Hz, 1H), 6.88 (ddd, $J = 7.9, 7.3, 1.2$ Hz, 1H), 5.40 (dd, $J = 10.3, 8.2$ Hz, 1H), 4.70 (dd, $J = 10.3, 8.2$ Hz, 1H), 4.15 (t, $J = 8.2$ Hz, 1H), 4.03 (dd, $J = 10.0, 8.2$ Hz, 1H), 3.91 (app. t, $J = 8.2, 7.9$ Hz, 1H), 3.84 (dd, $J = 10.0, 7.9$ Hz, 1H), 0.81 (s, 9H). ^{13}C NMR (CDCl$_3$): δ = 164.4, 162.9, 143.6, 143.5, 143.0, 131.8, 131.3, 130.9, 130.7, 128.8, 127.6, 127.1, 120.2, 120.0, 119.2, 118.2, 116.5, 116.4, 76.5, 74.1, 70.6, 67.8, 34.0, 26.0. IR (KBr): ν = 3450, 3190, 1644, 1049, 1040, 747 cm^{-1}. MS (70 eV, EI): m/z (%) 439 [M$^+$], 382, 362 (100), 233, 121, 103, 57. Anal. Calcd. for $C_{28}H_{29}O_2N_3$: C 76.48, H 6.65, N 9.60. Found: C 76.29, H 6.66, N 9.54.

[2-((4*S*)-Benzyl-4,5-dihydrooxazol-2-yl)phenyl][2-((4S)-4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl]amine (7j). Yield: 61%, yellow solid. Mp: 66−68 °C. $[\alpha]_D = +54.78$ (c = 0.23 in CHCl$_3$). ^{1}H NMR (CDCl$_3$): $\delta = 10.78$ (s, 1H), 7.82 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.79 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.43 (app t, $J = 7.8$ Hz, 2H), 7.16−7.31 (m, 7H), 6.86−6.92 (m, 2H), 4.53−4.63 (m, 1H), 4.22−4.33 (m, 2H), 3.95−4.05 (m, 3H), 3.18 (dd, $J = 13.6, 5.3$ Hz, 1H), 2.71 (dd, $J = 13.6, 8.3$ Hz, 1H), 1.74−1.83 (m, 1H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl$_3$): δ =163.5, 162.9, 143.7, 143.3, 138.4, 131.5, 131.4, 130.7, 130.6, 129.6, 128.7, 126.6, 120.3, 119.8, 119.2, 118.2, 116.0, 116.7, 73.4, 71.0, 69.3, 68.4, 42.1, 33.2, 19.4, 18.6. IR (KBr): ν = 3437, 1640, 1270, 1052, 746, 704 cm^{-1}. MS (70 eV, EI): m/z (%) 439 [M$^+$], 396, 348, 262 (100), 233, 205, 91.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for **7a**−**j**, **9a**−**d**, **12a**−**d**, **14a**−**d**, **15a**−**d**, **16a**−**c**, and **17d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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