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Bromotriphenylphosphonium Salt Promoted Tandem One-Pot Cyclization to Optically Active 2-Aryl-1,3-oxazolines

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Optically active 2-aryl-1,3-oxazolines, such as aromatic carbocycles, heterocycle-binding 4-benzyl (or phenyl)-1,3-oxazolines and their 5-benzyl (or phenyl)-1,3-oxazoline isomers were successfully prepared through a bromotriphenylphosphonium salt promoted aziridine ring formation and ring opening sequential process involving tandem one-pot cyclization of chiral 2-amino-3-phenylpropanol or 2-amino-2-phenylethanol with various aromatic acids in toluene at 90 °C in moderate to excellent yields. The mechanism of this tandem process was also substantiated experimentally.

Introduction

Optically active 2-aryl-1,3-oxazoline derivatives, such as chiral pyridine–oxazoline **1** and thiophene–oxazoline **2**, are frequently employed as chiral ligands in many transition-metal-catalyzed asymmetric syntheses.[1] Moreover, the 1,3-oxazoline moiety also widely serves as a fundamental skeleton in many bioactive molecules, natural products, and organomaterials.[2] Bisheterocycles in which the 1,3-oxazoline unit is bound to another heterocyclic moiety exhibit a broad spectrum of biological activities with demonstrable therapeutic value. For example, tubulin polymerization inhibitor (A-289099) **3**, which contains the 1,3-oxazoline moiety, is an antimitotic agent and exhibits some anticancer properties (Figure 1).[3] Moreover, some 1,3-oxazoline–aryl derivatives are also reported to be used as basic materials for the preparation of organic light-emitting diode devices.[4] Up to now, a number of synthetic methods have been established for the construction of the 1,3-oxazoline ring skeleton.[5] Typical methods include the thermal cyclization of *N*-(2-hydroxyethyl)amide intermediates[6] or cyclizations prompted by the Burgess reagent, PPh_3/DIAD, DIC/$Cu(OTf)_2$, DAST/Deoxo-Fluor, or even conducted in $SOCl_2$.[7] Cyclizations of β-hydroxy carboxylic acid derivatives under certain conditions could also yield the corresponding 1,3-oxazolines.[8] Although these approaches are efficient, most of these cyclization conditions have drawbacks in that they use harmful solvents, complicated reaction systems, or produce low yields.

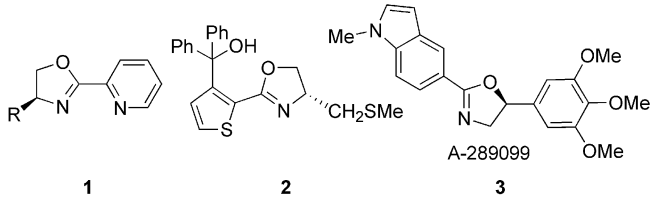

Figure 1. Structures of some chiral ligands and bioactive bisheterocycles containing a 1,3-oxazoline moiety.

On the other hand, chlorotriphenylphosphonium carbontrichloride ($[Ph_3P^+Cl]CCl_3^-$), which is known to be easily generated in situ by the reaction of triphenylphosphane with carbon tetrachloride, serves as chlorination reagent and transforms alcohols and carboxylic acid derivatives into the corresponding chlorides, acyl chlorides, or imidoyl chlorides,[9] Furthermore, $[Ph_3P^+Cl]CCl_3^-$ can also serve as a reagent for the ring-opening reaction of either activated or nonactivated aziridines.[10]

Our recent results revealed that the reaction of amino alcohols with carboxylic acids in the presence of a chlorotriphenylphosphonium salt in CCl_4 represents a direct and efficient approach towards aryl-fused oxazoles and oxazolines.[11] However, the overuse of CCl_4 in these experiments raised great environmental concern. Therefore, the development of a general, reliable, and environmentally friendly method for the synthesis of optically active 2-aryl-1,3-oxazolines is still highly desirable.

In this paper, we wish to report our results on this tandem one-pot approach, which involves bromotriphenylphosphonium salt promoted aziridine ring formation and

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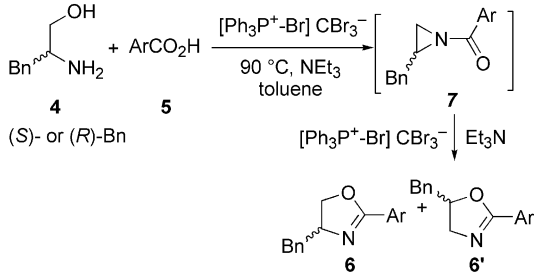
ring opening, to afford optically active 2-aryl-1,3-oxazoline compounds by cyclization of chiral β-amino alcohols with various aromatic heterocyclic acids or carboxylic acids (Scheme 1).



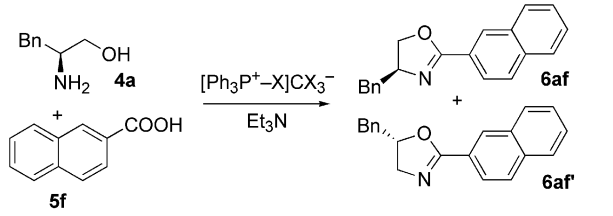
Scheme 1. Synthesis of 2-aryl-1,3-oxazolines by a one-pot process.

Results and Discussion

Our previous study has already shown that intramolecular cyclizations of fluorinated β-hydroxy aryl imidoyl chloride intermediates, which can be generated in situ by $[Ph_3P^+Cl]CCl_3^-$ formed from the reaction of PPh_3 with a large excess amount of CCl_4, could result in the formation of aryl-ring-fused 1,3-diazoles in good yields.[11]

However, when non-fluorinated aryl acids were used to replace the fluorinated carboxylic acids, the formation of the corresponding aryl imidoyl chloride intermediates were not clearly detected, though the reactions still provided good formation of 1,3-oxazolines as final products. Instead, the formation of *N*-aroyl aziridines was distinctly observed, and they were separable as relatively stable intermediates in this tandem one-pot cyclization of aromatic acids with aliphatic β-amino alcohols. This initial result revealed that the cyclizations with fluorinated carboxylic acids or non-fluorinated aromatic acids should proceed through different reaction pathways. Carbon tetrachloride in such cyclization reactions was used as both the reactant and the solvent, and although it was evident that the overuse of CCl_4 represents a serious environmental problem, the reactions provided reasonable results. To reduce the use of CCl_4, a parallel optimization of the reaction condition was made in two ways (Table 1). One was to use toluene or CH_3CN as the solvent to replace CCl_4. The reaction of (*S*)-2-amino-3-phenyl-1-propanol (**4a**) with naphthalene-2-carboxylic acid (**5f**) in the presence of 10 equiv. of CCl_4 provided (*S*)-4-benzyl-2-(2-naphthyl)-1,3-oxazoline (**6af**) in 82% yield in refluxing CH_3CN (Table 1, Entry 2). Furthermore, the reaction time was significantly shortened in CH_3CN. In contrast, the yield of **6af** was reduced to 58% when the volume of CCl_4 was reduced to a theoretical value of 3 equiv. The other optimization examined was the use of CBr_4 as a substitute for CCl_4 as the reactant with the use of toluene or CH_3CN as the solvent. The reaction went to completion within 1 h in the presence of 3 equiv. of CBr_4 in toluene. It is quite interesting that the reaction with the use of CCl_4 as the reactant performed better in polar solvents, such as CH_3CN, whereas the reaction with CBr_4 as the reactant performed better nonpolar solvents, such as toluene. Therefore, 3 equiv. of CBr_4 in toluene at 90 °C was finally chosen as the optimized conditions for the preparation of 2-aryl-1,3-oxazolines (Table 1, Entry 7).

Table 1. Optimization conditions for the synthesis of (*S*)-4-benzyl-2-(2-naphthyl)-1,3-oxazoline.

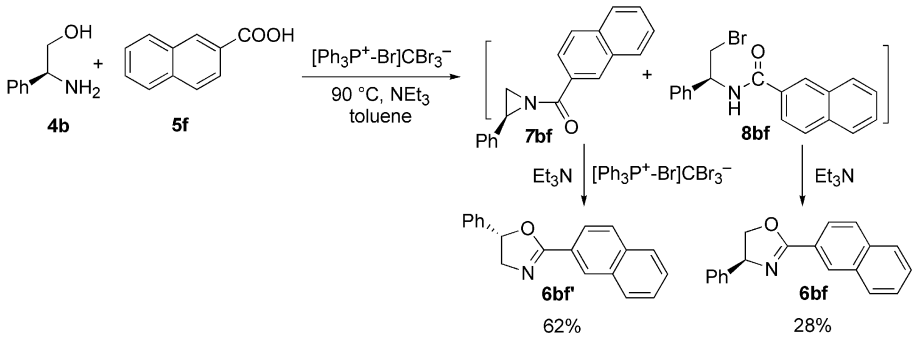


Entry	CX_4	Solvent	Time [h]	Temp. [°C]	Yield [%][a] **6af**	**6af′**[b]
1	CCl_4	CCl_4	16	reflux	73	–
2	CCl_4 (10 equiv.)	CH_3CN	4	reflux	82	trace
3	CCl_4 (3 equiv.)	CH_3CN	3	reflux	58	trace
4	CCl_4 (10 equiv.)	toluene	48	90	31	–
5	CCl_4 (3 equiv.)	toluene	76	90	11	–
6	CBr_4 (3 equiv.)	CH_3CN	1	reflux	30	5
7	*CBr_4 (3 equiv.)*	*toluene*	*1*	*90*	*83*	*13*
8	CBr_4 (2 equiv.)	toluene	10	90	71	10
9	CBr_4 (1 equiv.)	toluene	10	90	45	trace
10	CBr_4 (3 equiv.)	toluene	1	reflux	64	22
11	CBr_4 (3 equiv.)	toluene	72	40	30	trace

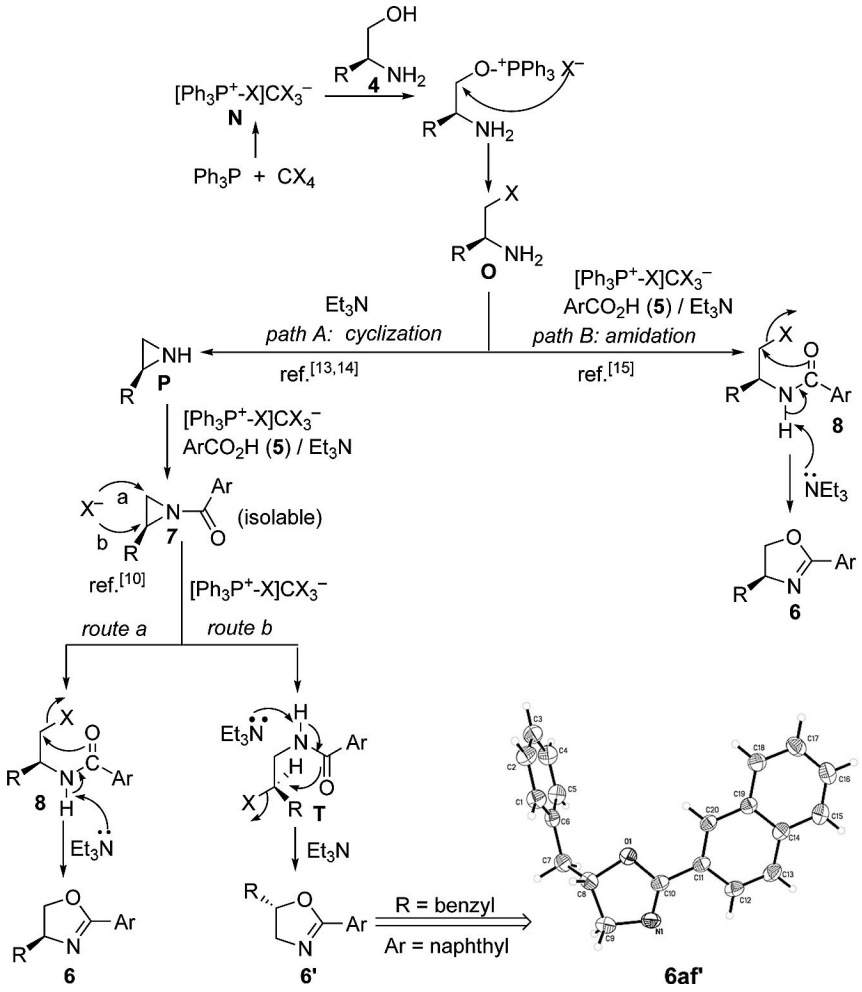
[a] Isolated yield. [b] Benzyl-migrated byproducts (*S*)-5-benzyl-2-(2-naphthyl)-1,3-oxazoline.

It is noteworthy that the benzyl group migrated byproduct **6af′** was also obtained in 5–22% yield under these optimized conditions (Table 1, Entries 6–9); however, only a trace amount of rearranged byproduct **6af′** was detected in the reaction performed with the use of CCl_4 in CH_3CN (Table 1, Entries 2 and 3). Benzyl migrated byproduct **6af′** was easily isolated by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:8) with retention of its configuration (98% *ee*). The structure of **6af′** was also confirmed by X-ray diffraction. The opposite result was obtained in when (*S*)-2-amino-2-phenyl-1-ethanol was used instead of (*S*)-2-amino-3-phenyl-1-propanol under same reaction conditions (3 equiv. of PPh_3/CBr_4 at 90 °C). Phenyl group migrated product **6bf′** was obtained as the major product (62% yield). Compound **6bf** was formed reversely as the minor product (28% yield, Scheme 2).

Further study of the mechanism found that intermediate **7bf**, which was formed and isolated from the reaction of (*S*)-(+)-2-amino-2-phenyl-1-ethanol with naphthalene-2-carboxylic acid, could undergo quick and quantitative conversion into 5-phenyl-1,3-oxazolines **6bf′** with retention of configuration if treated with one equivalent of the bromotriphenylphosphonium salt at 90 °C. However, the formation of benzyl or phenyl group migrated (rearranged) byproduct **6′** was hard to realize in the presence of a chlorotriphenylphosphonium salt. This showed that the reaction that led to the formation of **6** and rearranged **6′** should undergo different reaction pathways (Scheme 3, paths A and B). *N*-Aroyl aziridine **7** should be a key intermediate



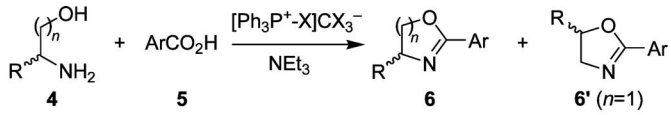
Scheme 2. The reaction of (*S*)-2-amino-3-phenyl-1-ethanol (**4b**) with naphthalene-2-carboxylic acid (**5f**).



Scheme 3. A postulated mechanism for the transformation of β-amino alcohols **4** into 2-aryl-1,3-oxazolines **6** and **6′**.

and dominate the formation of **6** and its corresponding structural isomer **6′** in Path A. On the basis of this consideration, a proposed mechanism for the formation of 4-benzyl-1,3-oxazolines **6** and 5-benzyl-1,3-oxazolines **6′** is assumed in Scheme 3. A reaction initially occurred between chiral β-amino alcohol **4** and salt **N** to form halogenated 1,2-haloamine **O**. Haloamine **O** then underwent chemoselective intramolecular nucleophilic cyclization followed by amidation with the aromatic acid to **7** (path A). The halotriphenylphosphonium salt was then involved as a nucleophile (equivalent of halide anion) in the subsequent ring-opening reaction of **7**. As shown in Scheme 3, if R = benzyl in path A, the halide anion prefers to attack the less sterically hindered position of **7** (route a) and yields ring-opened intermediate **8**, which further leads to cyclized 2-aryl-1,3-oxazoline **6** as the major product. The regioselective aziridine ring-opening reaction also results in the partial formation of **6′** as the minor product if the attacking halide is bro-

Table 2. Synthesis of 2-aryl-1,3-diazolines **6** and **6′** in the presence of halotriphenylphosphonium salts.[a]



4 **5** **6** **6'** (*n*=1)

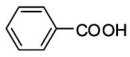
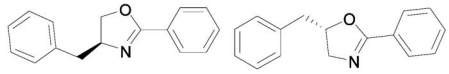
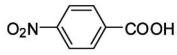
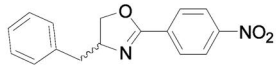
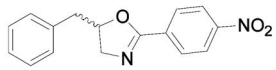
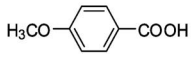
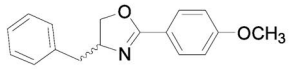
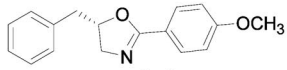
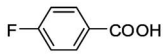
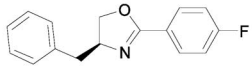
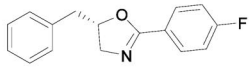
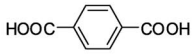
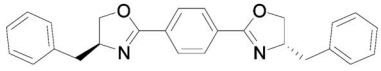
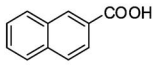
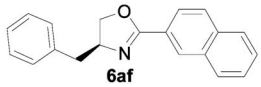
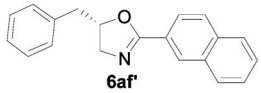
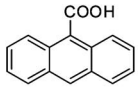
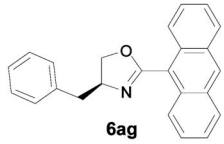
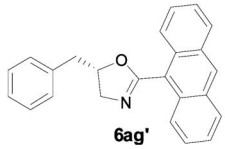
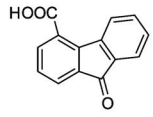
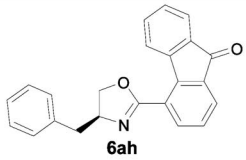
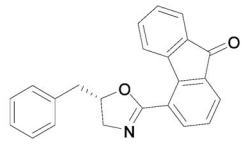
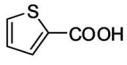
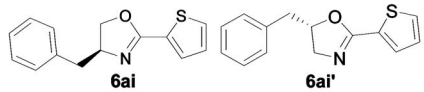
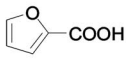
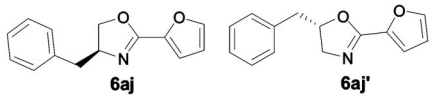
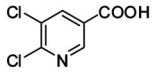
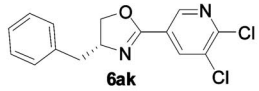
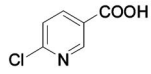
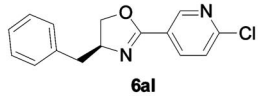
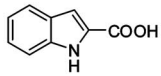
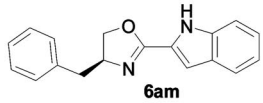
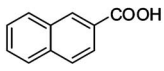
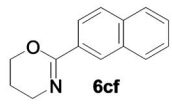
Entry	R	ArCOOH (**5**)	Product **6** or **6'**	X	Time [h]	% Yield[b] of **6**, **6'**
1	Bn (*S*)	 pK_a = 4.19	 **6aa** **6aa'**	Br Cl	2.0 6.0	70, 18 61, trace
2	Bn (*R* or *S*)	 pK_a = 3.42	 **6ab**  **6ab'**	Br Cl	1.5 5.0	71, trace 65, trace
3	Bn (*R* or *S*)	 pK_a = 4.47	 **6ac**  **6ac'**	Br Cl	2 7	66, 16 58, trace
4	Bn (*S*)	 pK_a = 4.14	 **6ad**  **6ad'**	Br Cl	1.5 4	75, 15 72, trace
5	Bn (*S*)	 pK_a = 3.49	 **6ae**	Br Cl	2 5	47[c] 38[c]
6	Bn (*R* or *S*)	 pK_a = 4.17	 **6af**  **6af'**	Br Cl	1 4	83, 14 82, trace
7	Bn (*S*)	 pK_a = 3.68	 **6ag**  **6ag'**	Br	2	75, 11

Table 2. *(Continued)*

Entry	R	ArCOOH (**5**)	Product **6** or **6'**	X	Time [h]	% Yield[b] of **6**, **6'**
8	Bn (*S*)	 $pK_a = 3.51$	 **6ah**  **6ah'**	Br	1.5	62, 10
9	Bn (*S*)	 $pK_a = 3.51$	 **6ai** **6ai'**	Br Cl	2 10	61, 12 36, trace
10	Bn (*S*)	 $pK_a = 3.16$	 **6aj** **6aj'**	Br Cl	1.5 5	76, 13 71, trace
11	Bn(*R*)	 $pK_a = 2.87$	 **6ak**	Br Cl	1.5 7	70[c] 63[c]
12	Bn (*S*)	 $pK_a = 3.24$	 **6al**	Br Cl	1.5 7	71[c] 65[c]
13	Bn (*S*)	 $pK_a = 4.44$	 **6am**	Br Cl	1.5 5.5	60, trace 48, trace
14	H (*n* = 2)	 $pK_a = 4.17$	 **6cf**	Br	1.0	55

[a] The reactions were carried in toluene with bromotriphenylphosphonium carbontrichloride (3 equiv.) at 90 °C when X = Br; or in the refluxing CH_3CN solvent with chlorotriphenylphosphonium carbontrichloride (10 equiv.) when X = Cl. [b] Isolated yield after column chromatography. [c] No benzyl migrated byproducts were observed.

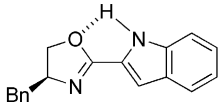
mide. In route b of path A, the configuration of the stereogenic center of **7** is inverted twice (ring opening of **7** and ring closure of **T**). This is the reason why the configuration of the stereogenic center of **6′** is retained. The bromotriphenylphosphonium salt exhibits much more flexibility in this ring-opening and ring-closing process (route b) than the chlorotriphenylphosphonium salt. If R = phenyl, rearranged product **6bf′** is experimentally proved as the sole product from path A. The direct nucleophilic ring-opening reaction of **7** at arylmethyl carbon atom has priority as a result of the stabilization of the corresponding S_N2 reaction transition state through p–π conjugation by the aryl group.[12] Thus, as already mentioned, the ring-opening reaction of intermediate **7bf** only produced **6bf′** quantitatively and no **6bf** can be detected during this transformation. In reality, however, we still isolated **6bf** in 28% yield when we start the reaction from (*S*)-2-amino-2-phenyl-1-ethanol. This result strongly suggests that **6bf** should only be produced from path B. Similar amidation of intermediate **O** with an aromatic acid should also occur simultaneously to form noncyclized amide intermediate **8**, which is followed by ring closure to produce cyclized **6bf**. The selective formation of intermediate **7** in path A or noncyclized intermediate **8** could competitively depend on the acidity of the aro-

matic acid, which dominates its amidation ability. In general, relatively stronger aromatic acids (smaller pK_a value) prefer to undergo amidation of 1,2-haloamine intermediate **O** to form amide intermediate **8** first (path B), but in contrast, weaker aromatic acids (larger pK_a value) have lower amidation ability and therefore prefer to undergo aziridination and to form *N*-aroyl aziridine **7** first (path A).

The difficulty of carbon–halogen bond cleavage should be a crucial point in determining reaction speed. In comparison to the strength of the C–Cl bond in chlorinated intermediate **O**, the C–Br bond is weaker and is obviously much easier to cleave by attack of the nucleophilic amine to form the aziridine (path A). This should be a reason why the reaction is much faster when CBr_4 is used over CCl_4. On the other hand, the weaker nucleophilic chloride anion shows higher regioselectivity in the attack of the less sterically hindered position of **7**. This could possibly be a reason why structural isomer **6′** is only detected when weaker aromatic acids are used. This hypothesis is consistent with the results in this tandem reaction.

This tandem one-pot cyclization process was generally applicable to normal aromatic carbocyclic acids and heterocyclic acids. Reaction of (*S*)- or (*R*)-2-amino-3-phenylpropanol or (*S*)-2-amino-2-phenyl-1-ethanol with different aromatic acids under promotion of bromotriphenylphosphonium salt in toluene at 90 °C provided moderate to excellent overall yields of the desired products in a short reaction times (Table 2). Non-fluorinated aliphatic carboxylic acids failed to yield target products under the same reaction conditions. Structural isomers **6′** were isolable, whereas only a trace amount of **6′** was detected in cases where CCl_4 was used as the reactant in CH_3CN (Table 2). Further application of benzyl or phenyl migrated byproducts **6′** as new types of chiral ligands has potential. In addition, the chemical shift of the N–H group in **6am** appeared at δ = 10.20 ppm in the ^{1}H NMR spectrum, which is unusually downfield shifted. This suggests that a strong hydrogen bond between the hydrogen and oxygen atoms exists. This interaction fixes the nitrogen side of the indole ring and the oxygen side of the 1,3-oxazoline stereoselectively on the same side.

δ = 10.20 ppm (^{1}H NMR)



Conclusions

In conclusion, optically active 2-aryl-1,3-oxazolines, such as aromatic carbocycles, heterocycle-bound 4-benzyl-1,3-oxazolines, and structural isomers of 5-benzyl-1,3-oxazolines were successfully prepared through a sequential process involving aziridine ring formation and ring opening from the tandem one-pot cyclization of chiral 2-amino-3-phenylpropanol with various aryl acids. The reaction can be mildly promoted by a bromotriphenylphosphonium salt in toluene to provide much shorter reaction times and higher yields of products. Other β-amino alcohols, such as 2-amino-2-phenyl-1-ethanol, could also be employed in this tandem one-pot cyclization.

Experimental Section

General Comments: ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded with a Bruker AV-500 spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in ppm downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal chloroform (δ = 77.2 ppm for ^{13}C), and chemical shifts for ^{19}F NMR spectra are reported in ppm downfield from internal fluorotrichloromethane ($CFCl_3$). Infrared spectra (IR) were recorded as KBr pellets. Silica gel (200–400 mesh) was used for flash column chromatography. Elemental analyses were performed with an Elemental Vario EL III instrument. Single-crystal XRD was performed with graphite-monochromatic Mo-K_α radiation (λ = 0.71073 Å) with a Bruker Smart ApexII CCD diffractometer at T = 273(2) K. The structures were solved by direct methods with the SHELXS-97 program and refined by full-matrix least-squares on F^2 with SHELXL-97. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located and included at their calculated position. Optical rotations were recorded on a highly sensitive polarimeter with a 200-mm cell. The enantiomeric purity was determined by chiral HPLC (Sino-Chiral AD 0.46 cm × 25 cm column, *n*-hexane/2-propanol as mobile phase).

CCDC-764713 (for **6af′**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Preparation of 2-Aryl-1,3-oxazolines 6 with the use of Chlorotriphenylphosphonium Salts: A 200-mL, three-necked flask equipped with a condenser was charged with Ph_3P (2.20 g, 8.4 mmol), Et_3N (0.85 g, 8.4 mmol), CCl_4 (4.3 g), substrate **4** (3.3 mmol), and aromatic acid **5** (2.8 mmol) in CH_3CN (15.0 mL) under a nitrogen atmosphere. The solution was stirred for about 10 min at room temperature, and the mixture was then heated at reflux with stirring for 3–10 h. The solvent was evaporated under reduced pressure, and the residue was diluted with petroleum ether (60–90 °C) and filtered. The residual Ph_3PO and Et_3N·HCl solids were washed with petroleum ether (3×). The filtrate was concentrated, and the residue was then purified by column chromatography to afford product **6**.

General Procedure for the Preparation of 2-Aryl-1,3-oxazolines 6 and 6′ with the use of Bromotriphenylphosphonium Salts: A 200-mL, three-necked flask equipped with a condenser was charged with Ph_3P (2.20 g, 8.4 mmol), Et_3N (0.85 g, 8.4 mmol), CBr_4 (16.8 g, 8.4 mmol), substrate **4** (3.3 mmol), and aromatic acid **5** (2.8 mmol) in toluene (15.0 mL) under a nitrogen atmosphere. The solution was stirred for about 10 min at room temperature, and the mixture was then heated at 90 °C with stirring for 1–3 h. The solvent was evaporated under reduced pressure, and the residue was diluted with petroleum ether (60–90 °C) and filtered. The residual Ph_3PO and Et_3N·HCl solids were washed with petroleum ether (3×). The filtrate was concentrated, and the residue was then separated by column chromatography (ethyl acetate/petroleum ether, 1:8) to afford products **6** and **6′**.

(*S*)-4-Benzyl-2-phenyl-1,3-oxazoline (6aa): Clear oil.[14] Yield: 0.46 g, 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (dd, J = 8.0, 1.0 Hz, 2 H, H_{Ar}), 7.48–7.45 (m, 1 H, H_{Ar}), 7.38–7.41 (m, 2 H,

H_{Ar}), 7.30 (d, J = 7.5 Hz, 1 H, H_{Ar}), 7.29 (d, J = 7.0 Hz, 1 H, H_{Ar}), 7.25–7.21 (m, 3 H, H_{Ar}), 4.61–4.54 (m, 1 H, CH), 4.33 (dd, J = 8.5, 8.5 Hz, 1 H, OCH_2), 4.13 (dd, J = 8.0, 8.0 Hz, 1 H. OCH_2), 3.24 (dd, J = 13.5, 5.0 Hz, 1 H, $ArCH_2$), 2.72 (dd, J = 13.5, 8.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.1, 138.1, 131.4, 129.4, 128.6, 128.4, 128.3, 127.8, 126.6, 71.9, 67.9, 41.9 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2962, 1649, 1603, 1495, 1450, 1358, 1084, 780, 697 cm^{-1}.

(*S*)-5-Benzyl-2-phenyl-1,3-oxazoline (6aa′): Clear oil. Yield: 0.12 g, 18%. $[\alpha]^{10}$ = –28.6 (c = 0.826, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.96 (dd, J = 8.0 Hz, 2 H, H_{Ar}), 7.43–7.50 (m, 1 H, H_{Ar}), 7.41–7.42 (m, 2 H, H_{Ar}), 7.33–7.37 (m, 2 H, H_{Ar}), 7.27–7.29 (m, 3 H, H_{Ar}), 4.92–4.98 (m, 1 H, CH), 4.09 (dd, J = 9.5, 14.5 Hz, 1 H, NCH_2), 3.80 (dd, J = 7.0, 14.5 Hz, 1 H, NCH_2), 3.12 (dd, J = 7.5, 14.0 Hz, 1 H, $ArCH_2$), 2.91 (dd, J = 6.0, 14.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.9, 136.9, 131.3, 129.4, 128.7, 128.4, 128.2, 128.0, 126.8, 80.3, 59.6, 41.5 ppm. IR (KBr): $\tilde{\nu}$ = 3028, 2940, 1649, 1603, 1495, 1451, 1258, 1062, 780, 697 cm^{-1}. $C_{16}H_{15}NO$ (237.12): calcd. C 80.98, H 6.37, N 5.90; found C 80.76, H 6.29, N 5.97.

(*R*)-4-Benzyl-2-(4-nitrophenyl)-1,3-oxazoline [(*R*)-6ab]: White solid. Yield: 0.55 g, 71%. M.p. 100.7–101.7 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.26 (d, J = 9.0 Hz, 2 H, H_{Ar}), 8.11 (d, J = 9.0 Hz, 2 H, H_{Ar}), 7.32 (d, J = 8.0 Hz, 1 H, H_{Ar}), 7.30 (d, J = 6.5 Hz, 1 H, H_{Ar}), 7.23–7.26 (m, 3 H, H_{Ar}), 4.68–4.62 (m, 1 H, CH), 4.43 (dd, J = 9.0, 9.0 Hz, 1 H, OCH_2), 4.20 (dd, J = 8.0, 8.0 Hz, 1 H, OCH_2), 3.23 (dd, J = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.79 (dd, J = 14.0, 8.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.3, 149.6, 137.6, 133.7, 129.4, 128.7, 126.8, 123.6, 72.5, 68.3, 41.7 ppm. IR (KBr): $\tilde{\nu}$ = 3026, 2954, 1646, 1521, 1338, 1077, 972, 863, 700 cm^{-1}. $C_{16}H_{14}N_2O_3$ (282.10): calcd. C 68.07, H 5.00, N 9.92; found C 67.91, H 5.21, N 9.97.

(*S*)-4-Benzyl-2-(4-nitrophenyl)-1,3-oxazoline [(*S*)-6ab]: Pale-green solid.[14] Yield: 0.57 g, 73%. M.p. 100.7–101.7 °C. $[\alpha]^{10}$ = +9.2 (c = 0.822, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (d, J = 9.0 Hz, 2 H, H_{Ar}), 8.09 (d, J = 8.5 Hz, 2 H, H_{Ar}), 7.32–7.22 (m, 5 H, H_{Ar}), 4.67–4.61 (m, 1 H, CH), 4.41 (dd, J = 9.0, 9.0 Hz, 1 H, OCH_2), 4.19 (dd, J = 8.0, 8.0 Hz, 1 H, OCH_2), 3.22 (dd, J = 14.0, 5.5 Hz, 1 H, $ArCH_2$), 2.78 (dd, J = 13.5, 8.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.1, 149.5, 137.6, 133.6, 129.3, 129.2, 128.6, 126.7, 123.5, 72.4, 68.2, 41.6 ppm. IR (KBr): $\tilde{\nu}$ = 3026, 2923, 1647, 1521, 1338, 1257, 1078, 758, 701 cm^{-1}.

(*S*)-4-Benzyl-2-(4-methoxyphenyl)-1,3-oxazoline [(*S*)-6ac]: Pale-yellow solid.[14] Yield: 0.49 g, 66%. M.p. 41.2–42.5 °C $[\alpha]^{10}$ = +12.8 (c = 0.641, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.5 Hz, 2 H, H_{Ar}), 7.34 (d, J = 7.5 Hz, 1 H, H_{Ar}), 7.32 (d, J = 7.0 Hz, 1 H, H_{Ar}),7.24–7.29 (m, 1 H, H_{Ar}), 6.94 (d, J = 8.5 Hz, 2 H, H_{Ar}), 4.55–4.61 (m, 1 H, CH), 4.34 (dd, J = 8.0, 8.0 Hz, 1 H, OCH_2), 4.14 (dd, J = 7.5, 7.5 Hz, 1 H, OCH_2), 3.87 (s, 3 H, OCH_3), 3.27 (dd, J = 13.5, 5.0 Hz, 1 H, $ArCH_2$), 2.74 (dd, J = 14.0, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.9, 162.2, 138.2, 130.1, 129.4, 128.6, 126.6, 120.3, 113.8, 71.9, 55.4, 42.0 ppm. IR(KBr): $\tilde{\nu}$ = 3026, 2959, 1647, 1608, 1255, 1029, 840, 756, 701 cm^{-1}.

(*R*)-4-Benzyl-2-(4-methoxyphenyl)-1,3-oxazoline [(*R*)-6ac]: Thick yellow oil. Yield: 0.46 g, 64%. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, J = 9.0 Hz, 2 H, H_{Ar}), 7.30 (dd, J = 7.5, 7.0 Hz, 2 H, H_{Ar}), 7.21–7.26 (m, 1 H, H_{Ar}), 6.91 (d, J = 9.0 Hz, 2 H, H_{Ar}), 4.58–4.52 (m, 1 H, CH), 4.32 (dd, J = 8.5, 8.5 Hz, 1 H, OCH_2), 4.12 (dd, J = 7.0, 8.5 Hz, 1 H, OCH_2), 3.85 (s, 3 H, OCH_3), 3.24 (dd, J = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.72 (dd, J = 13.5, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.8, 162.1, 138.1, 130.0, 129.3, 128.6, 126.5, 120.3, 113.7, 71.8, 67.8, 55.3, 41.9 ppm. IR (KBr): $\tilde{\nu}$ = 3024, 2963, 1642, 1605, 1250, 1032, 845, 757, 705 cm^{-1}. $C_{17}H_{17}NO_2$ (267.13): calcd. C 76.38, H 6.41, N 5.24; found C 76.25, H 6.12, N 5.19.

(*S*)-5-Benzyl-2-(4-methoxyphenyl)-1,3-oxazoline (6ac′): Thick yellow oil. Yield: 0.11 g, 15%. $[\alpha]^{10}$ = –22.5 (c = 1.070, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, J = 9.0 Hz, 2 H, H_{Ar}), 7.31 (d, J = 8.0 Hz, 1 H, H_{Ar}), 7.30 (d, J = 7.0 Hz, 1 H, H_{Ar}), 7.23–7.25 (m, 3 H, H_{Ar}), 6.90 (d, J = 8.5 Hz, 2 H, H_{Ar}), 4.85–4.91 (m, 1 H, CH), 4.03 (dd, J = 14.0, 9.0 Hz, 1 H, NCH_2), 3.80 (s, 3 H, OCH_3), 3.74 (dd, J = 14.5, 7.0 Hz, 1 H, NCH_2), 3.08 (dd, J = 14.0, 7.0 Hz, 1 H, $ArCH_2$), 2.86 (dd, J = 13.5, 6.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.7, 162.0, 137.0, 129.9, 129.4, 128.6, 126.7, 120.4, 113.7, 80.1, 59.5, 55.3, 41.5 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2935, 1647, 1608, 1512, 1256, 1074, 841, 738, 700 cm^{-1}. $C_{17}H_{17}NO_2$ (267.13): calcd. C 76.38, H 6.41, N 5.24; found C 76.52, H 6.23, N 5.12.

(*S*)-4-Benzyl-2-(4-fluorphenyl)-1,3-oxazoline (6ad): Pale-yellow solid. Yield: 0.53 g, 75%. M.p. 46.3–49.5 °C $[\alpha]^{10}$ = +10.1 (c = 0.801, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.0, 2.5 Hz, 1 H, H_{Ar}), 7.93 (dd, J = 5.5, 3.0 Hz, 1 H, H_{Ar}), 7.31 (d, J = 7.5 Hz, 1 H, H_{Ar}), 7.29 (d, J = 7.5 Hz, 1 H, H_{Ar}), 7.21–7.25 (m, 3 H, H_{Ar}), 7.01–7.10 (m, 2 H, H_{Ar}), 4.54–4.60 (m, 1 H, CH), 4.33 (dd, J = 8.5, 8.5 Hz, 1 H, OCH_2), 4.13 (dd, J = 7.5, 8.0 Hz, 1 H, OCH_2), 3.22 (dd, J = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.72 (dd, J = 14.0, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –108.1–108.2 (m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 163.8, 163.2, 138.0, 130.6, 130.6, 129.4, 128.7, 126.6, 115.6, 115.5, 72.1, 68.0, 41.9 ppm. IR (KBr): $\tilde{\nu}$ = 3028, 2965, 1650, 1604, 1509, 1356, 1079, 912, 795, 687 cm^{-1}. $C_{16}H_{14}FNO$ (255.11): calcd. C 75.28, H 5.53, N 5.49; found C 75.44, H 5.38, N 5.32.

(*S*)-5-Benzyl-2-(4-fluorphenyl)-1,3-oxazoline (6ad′): Pale-yellow solid. Yield: 0.11 g, 15%. M.p. 51.3–52.9 °C. $[\alpha]^{10}$ = –6.8 (c = 0.500, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.94 (m, 2 H, H_{Ar}), 7.30–7.33 (m, 2 H, H_{Ar}), 7.23–7.26 (m, 3 H, H_{Ar}) 7.05–7.09 (m, 2 H, H_{Ar}), 4.90–4.95 (m, 1 H, CH), 4.05 (dd, J = 15.0, 9.5 Hz, 1 H, NCH_2), 3.76 (dd, J = 14.5, 7.0 Hz, 1 H, NCH_2), 3.08 (dd, J = 14.0, 7.0 Hz, 1 H, $ArCH_2$), 2.88 (dd, J = 14.0, 6.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7, 163.7, 163.0, 136.8, 130.4, 129.4, 128.7, 126.8, 124.2, 115.6, 115.4, 80.5, 59.6, 41.5 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –108.23–108.17 (m) ppm. IR (KBr): $\tilde{\nu}$ = 3031, 2951, 1649, 1603, 1506, 1407, 1218, 1068, 846, 733, 699 cm^{-1}. $C_{16}H_{14}FNO$ (255.11): calcd. C 75.28, H 5.53, N 5.49; found C 76.07, H 5.38, N 5.60.

(*S*,*S*)-1,4-Bis[2-(4-benzyl-1,3-oxazoline)]benzene (6ae): White solid, Yield: 0.26 g, 47%. M.p. 122.0–123.9 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.99 (s, 4 H, H_{Ar}), 7.32 (d, J = 7.5 Hz, 2 H, H_{Ar}), 7.30 (d, J = 7.5 Hz, 2 H, H_{Ar}), 7.22–7.26 (m, 6 H, H_{Ar}), 4.58–4.64 (m, 2 H, CH), 4.37 (dd, J = 9.0, 9.0 Hz, 2 H, OCH_2), 4.16 (dd, J = 8.0, 8.0 Hz, 2 H, OCH_2), 3.25 (dd, J = 14.0, 5.0 Hz, 2 H, $ArCH_2$), 2.73 (dd, J = 14.0, 8.5 Hz, 2 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6, 138.0, 130.4, 129.4, 128.7, 128.4, 126.7, 72.2, 68.1, 41.9 ppm. IR (KBr): $\tilde{\nu}$ = 3026, 2986, 1644, 1357, 1081, 762, 697 cm^{-1}. $C_{26}H_{24}N_2O_2$ (396.18): calcd. C 78.76, H 6.10, N 7.07; found C 78.57, H 5.94, N 7.12.

(*R*)-4-Benzyl-2-(2-naphthyl)-1,3-oxazoline [(*R*)-6af]: White solid. Yield: 0.64 g, 80%. M.p. 82.3–83.8. $[\alpha]^{25}$ = –14.9 (c = 1.400, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, H_{Ar}), 8.06 (dd, J = 8.5, 1.5 Hz, 1 H, H_{Ar}), 7.92–7.86 (m, 3 H, H_{Ar}), 7.57–7.51 (m, 2 H, H_{Ar}), 7.34–7.25 (m, 5 H, H_{Ar}), 4.68–4.62 (m, 1 H, CH), 4.41 (dd, J = 8.5, 9 Hz, 1 H, OCH_2), 4.21 (dd, J = 7.5, 8 Hz, 1 H, OCH_2), 3.30 (dd, J = 14, 5 Hz, 1 H, $ArCH_2$), 2.79 (dd, J = 13.5,

9 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 164.2, 138.1, 134.9, 132.8, 129.4, 129.0, 128.9, 128.7, 128.2, 127.9, 127.7, 126.7, 126.6, 125.2, 125.0, 72.1, 68.1, 42.0 ppm. IR: $\tilde{\nu}$ = 3055, 2923, 1649, 1365, 1193, 1060, 968, 748, 697 cm^{-1}. $C_{20}H_{17}NO$ (287.13): calcd. C 83.59, H 5.96, N 4.87; found C 83.66, H 6.13, N 4.65.

(*S*)-4-Benzyl-2-(2-naphthyl)-1,3-oxazoline [(*S*)-6af]: White solid. Yield: 0.65 g, 83%. M.p. 83.9–85.5 °C.[14] $[\alpha]^{25}$ = +14.8 (*c* = 1.450, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, H_{Ar}), 8.05 (dd, *J* = 7.0, 1.5 Hz, 1 H, H_{Ar}), 7.90 (d, *J* = 8.0 Hz, 1 H, H_{Ar}), 7.86 (d, *J* = 8.0 Hz, 2 H, H_{Ar}), 7.49–7.56 (m, 2 H, H_{Ar}), 7.22–7.33 (m, 5 H, H_{Ar}), 4.61–4.67 (m, 1 H, CH), 4.40 (dd, *J* = 8.5, 8.5 Hz, 1 H, OCH_2), 4.20 (dd, *J* = 7.5, 8.5 Hz, 1 H, OCH_2), 3.29 (dd, *J* = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.78 (dd, *J* = 14.0, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 164.0, 138.0, 134.7, 132.7, 129.3, 128.9, 128.7, 128.5, 128.1, 127.7, 127.5, 126.5, 125.1, 124.9, 71.9, 67.9, 41.8 ppm. IR (KBr): $\tilde{\nu}$ = 3026, 2981, 1649, 1363, 1259, 1057, 968, 748, 697 cm^{-1}.

(*R*)-5-Benzyl-2-(2-naphthyl)-1,3-oxazoline [(*R*)-6af′]: White solid. Yield: 0.11 g, 13%. M.p. 82.8–83.8 °C. $[\alpha]^{25}$ = +14.4 (*c* = 1.050, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, H_{Ar}), 8.03 (d, *J* = 8.5 Hz, 1 H, H_{Ar}), 7.92 (d, *J* = 8 Hz, 1 H, H_{Ar}), 7.87 (dd, *J* = 8.5, 3 Hz, 2 H, H_{Ar}), 7.57–7.51 (m, 2 H, H_{Ar}), 7.37–7.27 (m, 5 H, H_{Ar}), 5.05–4.99 (m, 1 H, CH), 4.14 (dd, *J* = 14.5, 15 Hz, 1 H, NCH_2), 3.85 (dd, *J* = 14.5, 14.5 Hz, 1 H, NCH_2), 3.18 (dd, *J* = 14, 7 Hz, 1 H, $ArCH_2$), 2.96 (dd, *J* = 14, 6 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 164.1, 136.9, 134.8, 132.8, 129.5, 129.0, 128.8, 128.3, 127.9, 127.6, 126.9, 126.7, 125.3, 124.9, 80.5, 59.8, 41.6 ppm. IR: $\tilde{\nu}$ = 3060, 2924, 1644, 1354, 1271, 1061, 968, 754, 706 cm^{-1}. $C_{20}H_{17}NO$ (287.13): calcd. C 83.59, H 5.96, N 4.87; found C 83.47, H 5.77, N 4.69.

(*S*)-5-Benzyl-2-(2-naphthyl)-1,3-oxazoline [(*S*)-6af′]: White solid. Yield: 0.11 g, 14%. M.p. 82.3–84.1 °C. $[\alpha]^{25}$ = –14.1 (*c* = 1.000, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.48 (s, 1 H, H_{Ar}), 8.08 (d, *J* = 8.5 Hz, 1 H, H_{Ar}), 7.94 (d, *J* = 7.5 Hz, 1 H, H_{Ar}), 7.89 (d, *J* = 8.5 Hz, 1 H, H_{Ar}), 7.87 (d, *J* = 8.5 Hz, 1 H, H_{Ar}), 7.52–7.58 (m, 2 H, H_{Ar}), 7.38 (d, *J* = 7.5 Hz, 1 H, H_{Ar}), 7.36 (d, *J* = 7.0 Hz, 1 H, H_{Ar}), 7.29–7.32 (m, 3 H, H_{Ar}), 4.98–5.04 (m, 1 H, CH), 4.15 (dd, *J* = 15.0, 9.5 Hz, 1 H, NCH_2), 3.87 (dd, *J* = 15.0, 7.5 Hz, 1 H, NCH_2), 3.18 (dd, *J* = 14.0, 7.0 Hz, 1 H, $ArCH_2$), 2.96 (dd, *J* = 14.0, 6.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.0, 136.8, 134.7, 132.7, 129.4, 128.9, 128.7, 128.2, 127.8, 127.5, 126.8, 126.5, 125.2, 124.8, 80.4, 59.7, 41.5 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2924, 1643, 1625, 1353, 1192, 1060, 967, 753, 705 cm^{-1}. $C_{20}H_{17}NO$ (287.13): calcd. C 83.59, H 5.96, N 4.87; found C 83.34, H 5.87, N 4.59.

(*S*)-4-Benzyl-2-(9-anthryl)-1,3-oxazoline (6ag): Pale-green solid. Yield: 0.69 g, 75%. M.p. 93.5–96.1 °C.[17] ^1H NMR (500 MHz, $CDCl_3$): δ = 8.54 (s, 1 H, H_{Ar}), 8.06 (d, *J* = 8.0 Hz, 2 H, H_{Ar}), 8.02 (d, *J* = 7.5 Hz, 2 H, H_{Ar}), 7.48–7.55 (m, 4 H, H_{Ar}), 7.40 (d, *J* = 8.0 Hz, 2 H, H_{Ar}), 7.34–7.35 (m, 3 H, H_{Ar}), 5.03–5.00 (m, 1 H, CH), 4.64 (dd, *J* = 9.0, 9.0 Hz, 1 H, OCH_2), 4.45 (dd, *J* = 8.0, 8.0 Hz, 1 H, OCH_2), 3.41 (dd, *J* = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 3.16 (dd, *J* = 13.0, 7.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 163.5, 137.6, 131.1, 130.1, 129.9, 129.6, 128.8, 128.6, 126.8, 126.8, 125.5, 125.4, 122.8, 71.6, 68.6, 41.7 ppm. IR (KBr): $\tilde{\nu}$ = 3063, 2989, 1657, 1598, 1453, 1194, 984, 735, 679 cm^{-1}.

(*S*)-4-Benzyl-2-(9-anthryl)-1,3-oxazoline (6ag′): Pale-green oil. Yield: 0.10 g, 11%. $[\alpha]^{10}$ = –18.6 (*c* = 0.802, $CHCl_3$)^1H NMR (500 MHz, $CDCl_3$): δ = 8.54 (s, 1 H, H_{Ar}), 8.08 (d, *J* = 8.0 Hz, 2 H, H_{Ar}), 8.02 (d, *J* = 7.5 Hz, 2 H, H_{Ar}), 7.47–7.53 (m, 4 H, H_{Ar}), 7.27–7.32 (m, 5 H, H_{Ar}), 5.21–5.27 (m, 1 H, CH), 4.41 (dd, *J* = 10.0, 14.5 Hz, 1 H, NCH_2), 4.14 (dd, *J* = 8.0, 15.0 Hz, 1 H, NCH_2), 3.41 (dd, *J* = 6.5, 14.0 Hz, 1 H, $ArCH_2$), 3.16 (dd, *J* = 6.5, 14.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 163.4, 131.1, 130.1, 129.7, 129.5, 128.8, 128.5, 126.9, 126.7, 125.5, 125.4, 80.4, 60.1, 41.5 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2924, 1654, 1453, 1300, 1194, 736, 698 cm^{-1}. $C_{24}H_{19}NO$ (337.15): calcd. C 85.43, H 5.68, N 4.15; found C 85.60, H 5.51, N 4.28.

(*S*)-4-(4-Benzyl-4,5-dihydrooxazol-2-yl)-fluoren-9-one (6ah): Green solid. Yield: 0.58 g, 62%. M.p. 111.4–113.6 °C. $[\alpha]^{10}$ = –23.0 (*c* = 0.802, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 7.5 Hz, 1 H, H_{Ar}), 7.85 (dd, *J* = 6.5, 1.0 Hz, 1 H, H_{Ar}), 7.6 (dd, *J* = 7.0, 1.0 Hz, 1 H, H_{Ar}), 7.67 (ddd, *J* = 7.0, 1.0, 0.5 Hz, 1 H, H_{Ar}), 7.40 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1 H, H_{Ar}), 7.31–7.36 (m, 6 H, H_{Ar}), 7.26–7.30 (m, 1 H, H_{Ar}), 4.75–4.81 (m, 1 H, CH), 4.48 (dd, *J* = 8.5, 9.5 Hz, 1 H, OCH_2), 4.24 (dd, *J* = 7.5, 8.5 Hz, 1 H, OCH_2), 3.24 (dd, *J* = 14.0, 5.5 Hz, 1 H, $ArCH_2$), 2.95 (dd, *J* = 14.0, 7.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 162.9, 157.5, 143.5, 142.6, 141.5, 136.8, 129.4, 128.9, 127.2, 50.4, 38.8, 36.8 ppm. IR (KBr): $\tilde{\nu}$ = 3039, 2925, 1657, 1547, 1520, 1194, 984, 875, 735 cm^{-1}. $C_{23}H_{17}NO_2$ (339.13): calcd. C 81.40, H 5.05, N 4.13; found C 81.54, H 4.97, N 4.09.

(*S*)-5-(4-Benzyl-4,5-dihydrooxazol-2-yl)-fluoren-9-one (6ah′): Pale-green solid. Yield: 0.10 g, 10%. M.p. 124.6–126.1 °C. $[\alpha]^{10}$ = –53.4 (*c* = 0.550, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.0 Hz, 1 H, H_{Ar}), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1 H, H_{Ar}), 7.77 (dd, *J* = 7.5, 1.0 Hz, 1 H, H_{Ar}), 7.68 (dd, *J* = 7.0, 1.0 Hz, 1 H, H_{Ar}), 7.42 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1 H, H_{Ar}), 7.35–7.25 (m, 7 H, H_{Ar}), 5.11–5.05 (m, 1 H, CH), 4.25 (dd, *J* = 15.0, 10.0 Hz, 1 H, NCH_2), 3.95 (dd, *J* = 14.5, 7.0 Hz, 1 H, NCH_2), 3.16 (dd, *J* = 14.0, 6.5 Hz, 1 H, $ArCH_2$), 3.04 (dd, *J* = 14.0, 6.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.4, 163.0, 143.8, 143.1, 136.4, 136.2, 135.5, 135.0, 134.4, 129.6, 129.5, 128.8, 128.7, 127.1, 126.3, 126.2, 124.4, 124.1, 80.2, 60.0, 41.4 ppm. IR: $\tilde{\nu}$ = 3063, 2927, 1716, 1646, 1565, 1239, 1114, 740, 697 cm^{-1}. $C_{23}H_{17}NO_2$ (339.13): calcd. C 81.40, H 5.05, N 4.13; found C 81.26, H 4.93, N 4.37.

(*S*)-4-Benzyl-2-(2-thienyl)-1,3-oxazoline (6ai): Yellow oil.[19] Yield: 0.41 g, 61%. $[\alpha]^{10}$ = +23.1 (*c* = 0.806, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 3.5 Hz, 1 H, H_{Ar}), 7.42 (dd, *J* = 5.0, 1.0 Hz, 1 H, H_{Ar}), 7.30 (d, *J* = 8.5 Hz, 1 H, H_{Ar}), 7.28 (d, *J* = 6.5 Hz, 1 H, H_{Ar}), 7.21–7.23 (m, 3 H, H_{Ar}), 7.05 (dd, *J* = 5.0, 3.5 Hz, 1 H, H_{Ar}), 4.58–4.52 (m, 1 H, CH), 4.30 (dd, *J* = 9.0, 9.0 Hz, 1 H, OCH_2), 4.12 (dd, *J* = 8.0 8.0 Hz, 1 H, OCH_2), 3.24 (dd, *J* = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.71 (dd, *J* = 14.0, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.7, 137.8, 130.4, 130.3, 129.9, 129.3, 128.6, 127.6, 126.6, 72.2, 68.0, 41.7 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2924, 1648, 1432, 1256, 1058, 852, 702 cm^{-1}.

(*S*)-5-Benzyl-2-(2-thienyl)-1,3-oxazoline (6ai′): Yellow oil. Yield: 0.08 g, 12%. $[\alpha]^{10}$ = –16.1 (*c* = 0.816, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 3.0 Hz, 1 H, H_{Ar}), 7.45 (d, *J* = 5.0 Hz, 1 H, H_{Ar}), 7.33 (d, *J* = 8.0 Hz, 1 H, H_{Ar}), 7.31 (d, *J* = 7.0 Hz, 1 H, H_{Ar}), 7.25–7.27 (m, 3 H, H_{Ar}), 7.07 (dd, *J* = 5.0, 1.0 Hz, 1 H, H_{Ar}), 4.91–4.97 (m, 1 H, CH), 4.05 (dd, *J* = 14.5, 9.5 Hz, 1 H, NCH_2), 3.77 (dd, *J* = 14.5, 6.5 Hz, 1 H, NCH_2), 3.13 (dd, *J* = 14.0, 7.0 Hz, 1 H, $ArCH_2$), 2.90 (dd, *J* = 14.0, 6.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.8, 136.7, 130.7, 130.3, 129.9, 129.5, 128.7, 127.7, 126.9, 80.9, 59.7, 41.4 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2926, 1646, 1604, 1523, 1432, 1252, 1057, 966, 853, 746, 699 cm^{-1}. $C_{14}H_{13}NOS$ (243.07): calcd. C 69.11, H 5.39, N 5.76; found C 69.35, H 4.97, N 5.98.

(*S*)-4-Benzyl-2-(2-furyl)-1,3-oxazoline [(*S*)-6aj]: Yellow oil. Yield: 0.48 g, 76%. $[\alpha]^{10}$ = +21.9 (*c* = 0.806, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 1.5, 1.0 Hz, 1 H, H_{Ar}), 7.28–7.17 (m, 5 H, H_{Ar}), 6.92 (dd, *J* = 3.5, 1.0 Hz, 1 H, H_{Ar}), 6.43 (dd, *J* = 3.5,

2.0 Hz, 1 H, H_{Ar}), 4.58–4.52 (m, 1 H, CH), 4.26 (dd, *J* = 9.0, 8.5 Hz, 1 H, OCH_2), 4.06 (dd, *J* = 9.0, 8.5 Hz, 1 H, OCH_2), 3.24 (dd, *J* = 13.5, 5.0 Hz, 1 H, $ArCH_2$), 2.70 (dd, *J* = 13.5, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9, 144.9, 142.7, 137.5, 128.9, 128.3, 126.2, 114.1, 111.2, 71.6, 67.5, 41.3 ppm. IR (KBr): ṽ = 3027, 2903, 1670, 1622, 1483, 1169, 1093, 966, 752, 704 cm^{-1}. $C_{14}H_{13}NO_2$ (227.09): calcd. C 73.99, H 5.77, N 6.16; found C 74.08, H 5.81, N 6.35.

(*R*)-4-Benzyl-2-(2-furyl)-1,3-oxazoline [(*R*)-6aj]: Yellow oil. Yield: 0.46 g, 75%. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 1.0 Hz, 1 H, H_{Ar}), 7.31 (d, *J* = 8.5 Hz, 1 H, H_{Ar}), 7.30 (d, *J* = 8.0 Hz, 1 H, H_{Ar}), 7.23–7.24 (m, 3 H, H_{Ar}), 6.95 (d, *J* = 3.5 Hz, 1 H, H_{Ar}), 6.49 (dd, *J* = 3.5, 1.0 Hz, 1 H, H_{Ar}), 4.56–4.62 (m, 1 H, CH), 4.32 (dd, *J* = 8.5, 8.5 Hz, 1 H, OCH_2), 4.12 (dd, *J* = 8.0, 8.0 Hz, 1 H, OCH_2), 3.28 (dd, *J* = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.72 (dd, *J* = 13.5, 9.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2, 145.2, 142.9, 137.7, 129.1, 128.5, 126.5, 114.4, 111.4, 71.9, 67.8, 41.6 ppm. IR (KBr): ṽ = 3027, 2903, 1670, 1622, 1169, 1093, 752, 704 cm^{-1}. $C_{14}H_{13}NO_2$ (227.09): calcd. C 73.99, H 5.77, N 6.16; found C 73.71, H 5.62, N 6.29.

(*S*)-5-Benzyl-2-(2-furyl)-1,3-oxazoline (6aj′): Yellow oil. Yield: 0.08 g, 13%. $[\alpha]^{10}$ = –14.5 (*c* = 1.090, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 1.0 Hz, 1 H, H_{Ar}), 7.23–7.33 (m, 5 H, H_{Ar}), 6.93 (d, *J* = 3.5 Hz, 1 H, H_{Ar}), 6.47 (dd, *J* = 3.5, 2.0 Hz, 1 H, H_{Ar}), 4.89–4.94 (m, 1 H, CH), 4.05 (dd, *J* = 15.0, 9.5 Hz, 1 H, NCH_2), 3.77 (dd, *J* = 14.5, 7.0 Hz, 1 H, NCH_2), 3.11 (dd, *J* = 14.0, 6.5 Hz, 1 H, $ArCH_2$), 2.88 (dd, *J* = 14.0, 7.0 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.3, 145.2, 143.2, 136.5, 129.4, 128.7, 126.9, 114.2, 111.5, 80.6, 59.4, 41.2 ppm. IR (KBr): ṽ = 3028, 2940, 1671, 1649, 1483, 1265, 1091, 753, 702 cm^{-1}. $C_{14}H_{13}NO_2$ (227.09): calcd. C 73.99, H 5.77, N 6.16; found C 73.67, H 5.58, N 6.28.

(*R*)-5-(4-Benzyl-4,5-dihydrooxazol-2-yl)-2,3-dichloropyridine (6ak): Yellow oil. Yield: 0.59 g, 70%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 2.0 Hz, 1 H, H_{Ar}), 8.30 (d, *J* = 2.0 Hz, 1 H, H_{Ar}), 7.30–7.33 (m, 2 H, H_{Ar}),7.23–7.26 (m, 3 H, H_{Ar}), 4.59–4.65 (m, 1 H, CH), 4.40 (dd, *J* = 9.0, 9.0 Hz, 1 H, OCH_2), 4.18 (dd, *J* = 8.0, 8.5 Hz, 1 H, OCH_2), 3.19 (dd, *J* = 14.0, 5.5 Hz, 1 H, $ArCH_2$), 2.77 (dd, *J* = 13.5, 8.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3, 151.7, 146.9, 138.1, 137.4, 130.6, 129.4, 128.8, 126.9, 124.3, 72.5, 68.1, 41.6 ppm. IR (KBr): ṽ = 3027, 2963, 1654, 1608, 1365, 1264, 1043, 701, 697 cm^{-1}. $C_{15}H_{12}Cl_2N_2O$ (306.03): calcd. C 58.65, H 3.94, N 9.12; found C 58.88, H 4.19, N 9.33.

(*S*)-5-(4-Benzyl-4,5-dihydrooxazol-2-yl)-2-chloropyridine (6al): Pale-yellow solid. Yield: 0.53 g, 71%. M.p. 65.0–67.0 °C. $[\alpha]^{10}$ = +7.7 (*c* = 0.812, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.89 (d, *J* = 2.0 Hz, 1 H, H_{Ar}), 8.12 (dd, *J* = 8.5, 2.5 Hz, 1 H, H_{Ar}), 7.30 (dd, *J* = 8.5, 8.0 Hz, 1 H, H_{Ar}), 7.28–7.19 (m, 5 H, H_{Ar}), 4.61–4.55 (m, 1 H, CH), 4.35 (dd, *J* = 8.5, 8.5 Hz, 1 H, OCH_2), 4.13 (dd, *J* = 8.5, 8.0 Hz, 1 H, OCH_2), 3.17 (dd, *J* = 14.0, 5.5 Hz, 1 H, $ArCH_2$), 2.74 (dd, *J* = 14.0, 8.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 160.8, 153.7, 149.3, 138.0, 137.3, 129.0, 128.4, 126.4, 123.8, 122.7, 71.9, 67.7, 41.4 ppm. IR (KBr): ṽ = 3027, 2962, 1647, 1585, 1368, 1278, 1105, 745, 699 cm^{-1}. $C_{15}H_{13}ClN_2O$ (272.07): calcd. C 66.06, H 4.80, N 10.27; found C 66.38, H 4.65, N 9.96.

(*S*)-4-Benzyl-2-(2-indolyl)-1,3-oxazoline (6am): Yellow solid. Yield: 0.46 g, 60%. M.p. 92.1–93.7 °C.[18] $[\alpha]^{10}$ = +23.7 (*c* = 0.803, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 10.20 (s, 1 H, NH), 7.68 (d, *J* = 8.0 Hz, 1 H, H_{Ar}), 7.39 (dd, *J* = 8.5, 1.0 Hz, 1 H, H_{Ar}), 7.26–7.30 (m, 3 H, H_{Ar}), 7.13–7.23 (m, 3 H, H_{Ar}), 7.06 (d, *J* = 1.0 Hz, 1 H, H_{Ar}), 4.66–4.72 (m, 1 H, CH), 4.47 (dd, *J* = 8.0, 8.0 Hz, 1 H, OCH_2), 4.24 (dd, *J* = 7.5, 8.5 Hz, 1 H, OCH_2), 3.15 (dd, *J* = 14.0, 5.5 Hz,1 H, $ArCH_2$), 2.82 (dd, *J* = 14.0, 8.5 Hz, 1 H, $ArCH_2$) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 159.7, 137.6, 129.3, 128.5, 127.8, 126.6, 125.4, 124.4, 122.0, 120.3, 111.7, 106.6, 72.3, 67.5, 41.9 ppm. IR (KBr): ṽ = 3064, 2963, 1651, 1598, 1426, 1242, 1191, 702, 698 cm^{-1}.

(*S*)-4-Phenyl-2-(2-naphthyl)-1,3-oxazoline (6bf): White solid. Yield: 0.20 g, 28%. M.p. 110.6–112.0.[15] $[\alpha]^{25}$ = –55.5 (*c* = 1.016, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.55 (s, 1 H, H_{Ar}), 8.14 (dd, *J* = 8.5, 1.5 Hz, 1 H, H_{Ar}), 7.94–7.88 (m, 3 H, H_{Ar}), 7.59–7.52 (m, 2 H, H_{Ar}), 7.40–7.31 (m, 5 H, H_{Ar}), 5.45 (dd, *J* = 10.0, 10.0 Hz, 1 H, OCH_2), 4.87 (dd, *J* = 10.0, 10.0 Hz, 1 H, OCH_2), 4.35 (t, *J* = 8.0 Hz, 1 H, CH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 165.0, 142.5, 135.0, 132.8, 129.2, 129.1, 128.9, 128.3, 127.9, 127.8, 127.7, 127.0, 126.7, 125.1, 125.0, 75.1, 70.4 ppm. IR: ṽ = 3026, 2912, 1642, 1361, 1194, 1064, 757, 694 cm^{-1}.

(*S*)-5-Phenyl-2-(2-naphthyl)-1,3-oxazoline (6bf′): White solid. Yield: 0.44 g, 62%. M.p. 73.2–76.7 °C.[15] $[\alpha]^{25}$ = +28.4 (*c* = 0.984, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.53 (s, 1 H, H_{Ar}), 8.12 (dd, *J* = 8.5, 1.5 Hz, 1 H, H_{Ar}), 7.93–7.87 (m, 3 H, H_{Ar}), 7.58–7.51 (m, 2 H, H_{Ar}), 7.41–7.34 (m, 5 H, H_{Ar}), 5.73 (dd, *J* = 10.0, 10.0 Hz, 1 H, NCH_2), 4.55 (dd, *J* = 15.0, 10.0 Hz, 1 H, NCH_2), 4.07 (dd, *J* = 15.0, 8.0 Hz, 1 H, CH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 164.3, 141.2, 134.9, 132.8, 129.1, 129.0, 128.9, 128.5, 128.4, 128.0, 127.7, 126.7, 126.0, 125.0, 124.9, 81.3, 63.5 ppm. IR: ṽ = 3033, 2927, 1641, 1354, 1191, 1062, 962, 761, 699 cm^{-1}.

2-(2-Naphthyl)-5,6-dihydro-4*H*-[1,3]oxazine (6cf): Yellow oil.[20] Yield: 0.64 g, 55%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, H_{Ar}), 8.03 (dd, *J* = 8.5, 2.0 Hz, 1 H, H_{Ar}), 7.90 (d, *J* = 7.0 Hz, 1 H, H_{Ar}), 7.89 (d, *J* = 7.0 Hz, 1 H, H_{Ar}), 7.83 (d, *J* = 8.5 Hz, 2 H, H_{Ar}), 7.52–7.46 (m, 2 H, H_{Ar}), 4.40 (t, *J* = 5.5 Hz, 2 H, OCH_2), 3.66 (t, *J* = 6.0 Hz, 2 H, NCH_2), 1.98–2.02 (m, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.7, 134.4, 132.9, 131.4, 129.0, 127.7, 127.7, 127.0, 126.2, 124.2, 65.4, 42.9, 22.0 ppm.

General Procedure for the Preparation of *N*-Aroyl Aziridine 7 with the use of Bromotriphenylphosphonium Salts: A 200-mL, three-necked flask equipped with a condenser was charged with Ph_3P (2.20 g, 8.4 mmol), Et_3N (0.85 g, 8.4 mmol), CBr_4 (16.8 g, 8.4 mmol), substrate **4** (3.3 mmol), and aromatic acid **5** (2.8 mmol) in toluene (15.0 mL) under a nitrogen atmosphere. The solution was stirred for about 10 min at room temperature, and the mixture was then heated at 90 °C with stirring for 0.5 h. The solvent was evaporated under reduced pressure, and the residue was diluted with petroleum ether (60–90 °C) and filtered. The filtrate was concentrated, and the residue was then separated by column chromatography (ethyl acetate/petroleum ether, 1:8) to afford products **7**.

(2*S*)-2-Benzyl-1-(2-naphthoyl)aziridine (7af): Pale-yellow solid.[16] M.p. 43.6–47.5 °C. $[\alpha]^{25}$ = +30.3 (*c* = 0.930, $CHCl_3$);^1H NMR (500 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 9.0, 2.0 Hz, 1 H, H_{Ar}), 7.87–7.92 (m, 3 H, H_{Ar}), 7.60 (dd, *J* = 7.5, 1.0 Hz, 1 H, H_{Ar}), 7.55 (dd, *J* = 7.5, 1.0 Hz, 1 H, H_{Ar}), 7.27–7.35 (m, 5 H, H_{Ar}), 3.24 (dd, *J* = 14.0, 5.0 Hz, 1 H, $ArCH_2$), 2.89–2.93 (m, 1 H), 2.84 (dd, *J* = 14.5, 7.0 Hz, 1 H, $ArCH_2$), 2.62 (d, *J* = 6.0 Hz, 1 H, NCH_2), 2.36 (d, *J* = 3.5 Hz, 1 H, NCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.3, 137.4, 135.5, 132.6, 130.5, 129.5, 128.9, 128.7, 128.3, 128.2, 127.8, 126.9, 126.7, 125.0, 38.9, 38.6, 31.8 ppm. IR (KBr): ṽ = 3056, 2933, 1655, 1571, 1399, 1360, 1128, 782, 739, 697 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 287 (2) $[M]^+$, 196 (27), 155 (100), 127 (47), 91 (9), 77(7). $C_{20}H_{17}NO$ (287.13): calcd. C 83.59, H 5.96, N 4.87; found C 83.68, H 5.83, N 4.65.

(2*S*)-1-(2-Naphthoyl)-2-phenylaziridine (7bf): White solid.[16] M.p. 106.1–107.6 °C. $[\alpha]^{25}$ = +150.6 (*c* = 0.336, $CHCl_3$). ^1H NMR

(500 MHz, $CDCl_3$): δ = 8.53 (s, 1 H, HAr), 8.00 (dd, J = 8.5, 1.5 Hz, 1 H, HAr), 7.85–7.78 (m, 3 H, HAr), 7.57 (td, J = 7.0, 1.5 Hz, 1 H, HAr), 7.49 (td, J = 8.5, 1.0 Hz, 1 H, HAr), 7.44–7.37 (m, 5 H, HAr), 3.53 (dd, J = 6.0, 6.0 Hz, 1 H, CH), 3.04 (d, J = 6.0 Hz, 1 H, NCH_2), 2.52 (d, J = 3.5 Hz, 1 H, NCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.3, 137.3, 135.7, 132.6, 130.9, 130.1, 129.6, 129.0, 128.4, 128.3, 127.9, 126.8, 126.4, 125.1, 40.6, 35.5 ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2993, 1675, 1629, 1391 1303, 1286, 833, 785, 705 cm^{-1}. $C_{19}H_{15}NO$ (273.12): calcd. C 83.49, H 5.53, N 5.12; found C 83.55, H 5.42, N 5.29.

Supporting Information (see footnote on the first page of this article): ^1H, ^{13}C and ^{19}F NMR spectra of all compounds, ORTEP plot of **6af′**and its packing diagram, HPLC traces of (*R*)- and (*S*)-**6af** and **-6af′**.

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