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Synthesis and Catalytic Properties of 4-Aryl-2,3-dihydro-4*H*-pyrimido[2,3-*b*]benzothiazoles for Asymmetric Acyl or Carboxyl Group Transfer Reactions

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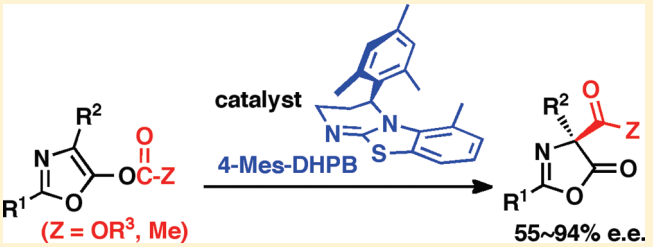
Supporting Information

ABSTRACT: 4-Aryl-2,3-dihydro-4*H*-pyrimido[2,3-*b*]benzothiazoles (4-Ar-DHPBs) were synthesized and their catalytic activity and selectivity in kinetic resolution of a secondary alcohol as well as in the Steglich rearrangement and related reactions were evaluated. 4-Aryl-DHPBs showed low enantioselectivity in the acylative kinetic resolution of 1-phenylethanol. Conversely, they catalyzed the Steglich rearrangement with moderate to excellent enantioselectivity, demonstrating the possibility for remote stereocontrol by introduction of a substituent at the 4-position of DHPB.



INTRODUCTION

Recently, chiral bicyclic isothioureas have attracted much interest as a new class of organic catalysts promoting kinetic resolution of secondary alcohols, α-chiral acids, and 2-oxazolidinones, desymmetrization of diols, dynamic kinetic resolution of azlactones, and enantioselective reactions such as the intramolecular acyl and carboxyl group transfer of oxazolyl acetates and carbonates, aldol addition−lactonization of keto acids, and Michael addition−lactonization reactions.[1−15]

Birman and co-workers first introduced the commercially available 6-phenyl-2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole (tetramisole, **1**) and its benzo derivative 2-phenyl-2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole (benzotetramisole (BTM), **2**) as efficient acyl transfer catalysts for the kinetic resolution of secondary alcohols[1] and 2-oxazolidinones[2] and desymmetrization reactions[3] (Figure 1). Birman et al. also showed that BTM promoted efficient dynamic kinetic resolution of α-substituted azlactones by their enantioselective alcoholysis.[4] The kinetic resolution of secondary alcohols and α-aryl acids catalyzed by BTM and its derivatives have also been synthetically utilized by other groups.[5] After independent studies by Birman[6] and the authors[7] showing that achiral 3,4-dihydro-2*H*-pyrimido[2,1-*b*]-benzothiazole (DHPB, **3**) was a more nucleophilic and efficient catalyst for *O*-acylation than its five-membered derivative **4** or 2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole (**5**), Birman developed homobenzotetramisole (HBTM, **6a**) which was utilized for the kinetic resolution of arylcycloalkanols[8] and α-aryl-, α-aryloxy-, and α-arylthioalkanoic acids.[9]

Dietz and Gröger reported that **1** and **2** catalyzed an enantioselective rearrangement of O-acylated azlactones.[10] Smith and co-workers discovered that **3** can efficiently catalyze the intermolecular carboxyl group transfer of oxazolyl carbonates (Steglich rearrangement),[11] and they successfully applied **6a** and substituted DHPB derivatives such as **6b,c** to the asymmetric Steglich rearrangement.[12]

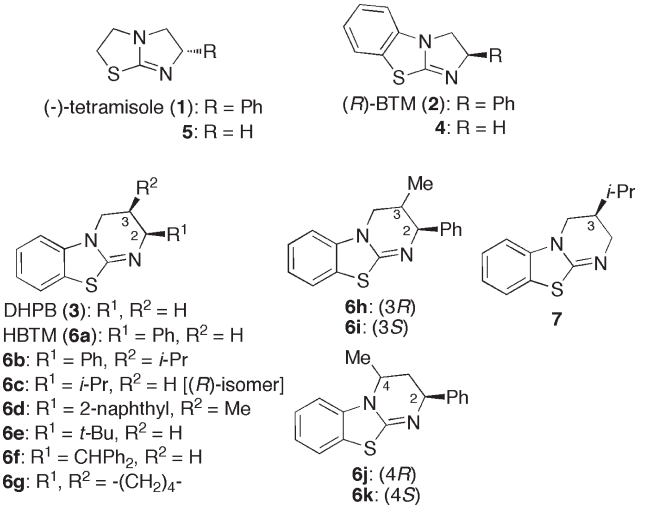


Figure 1. Chiral bicyclic isothioureas.

Furthermore, most recently, Romo et al. used **6a** and its derivative **6d** for an efficient catalytic asymmetric intramolecular aldol addition−lactonization of keto acids,[13] while Smith and co-workers reported efficient asymmetric intra- and intermolecular Michael addition−lactonization reactions catalyzed by **1** or the HBTM derivative **6b**.[14]

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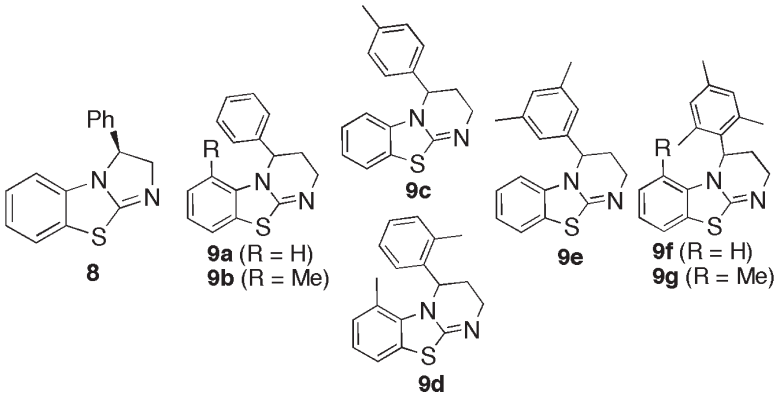
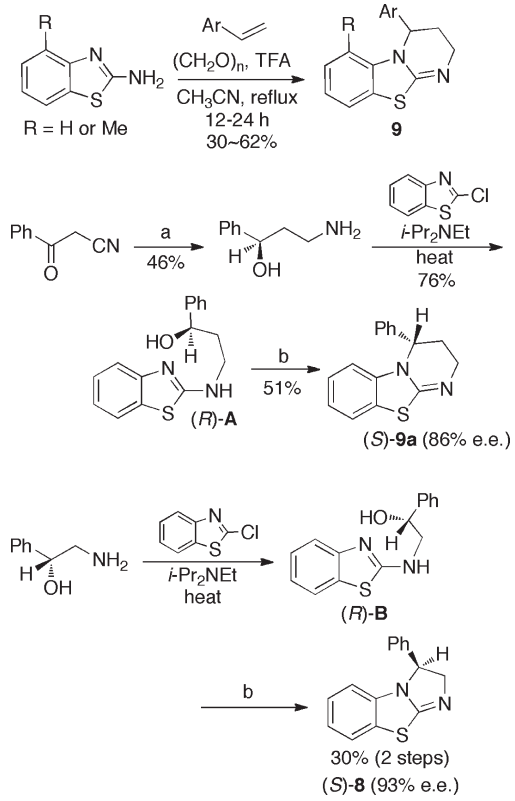


Figure 2. New chiral bicyclic isothioureas **8** and **9**.

Scheme 1. Synthesis of 8 and 9



Reagents: (a) (*S*)-5,5-diphenyl-2-methyl-3,4-propano-1,3,2-oxazaborolidine (30 mol %), $BH_3 \cdot SMe_2$; (b) MsCl, Et_3N, CH_2Cl_2.

In the design of a new catalyst based on the skeletons of 2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole (**4**) and **3**, it is important to consider the relationships between both features and position of a newly introduced substituent(s) and the catalytic activity and stereoselectivity of the resultant chiral reagent. All chiral bicyclic isothioureas that have been used in the aforementioned asymmetric reactions, except for the 3-isopropyl derivative **7**, have an asymmetric center that has been introduced at the position α to the nucleophilic nitrogen (2-position of **3** and **4**). This substitution (R^1) apparently enables an efficient asymmetric face discrimination of the catalysts. Consistently, the results for the 3-isopropyl derivative **7** show low stereoselectivity ($s = 1.3$) in the kinetic resolution of 1-(naphthalen-1-yl)ethanol with propionic anhydride,[15] supporting the expectation that the absence of a substituent at the 2-position leads to poor stereoselectivity. In addition, the effects of introduction of an additional substituent within the HBTM skeleton have been investigated. In the kinetic resolution of secondary alcohols, Birman showed that the introduction of a methyl group at the 3- or 4-position significantly affected both catalytic activity and stereoselectivity.[9] Smith screened HBTM derivatives **6b**−**g** as catalysts for the kinetic resolution of secondary alcohols and showed that the 2-phenyl-3-isopropyl derivative **6b** was optimal.[15] In the Steglich rearrangement reaction of 2-aryl-4-benzyloxazol-5-yl phenyl carbonate, it has been reported that isothiourea **6c**, having a sterically demanding substituent at the 2-position, gave the highest enatioselectivity at room temperature but proved to be less catalytically active than **6a**,**b**.[12]

Although introduction of an asymmetric center at the position α to the nucleophilic nitrogen (2-position of **3** or **4**) is likely essential to attain efficient enantioselectivity, it may negatively affect the intrinsic reactivity (nucleophilicity) of DHPB, owing to steric obstructions.

Therefore, instead of introducing a substituent at the 2-position of **3** and **4**, we designed 3-phenyl-2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole (**8**) and the 4-substituted DHPB derivatives **9** (Figure 2) and investigated their catalytic properties. These compounds were expected to have a high reactivity similar to that of unsubstituted **3** and **4** because of the absence of steric repulsion around the reactive nitrogen atom. However, we anticipated that effective remote control of stereoselectivity would be a challenge.

RESULTS AND DISCUSSION

As illustrated in Scheme 1, racemic 4-aryl-substituted DHPB derivatives **9** were readily prepared in synthetically useful yields by a one-step reaction of commercially available benzo[*d*]thiazol-2-amines with paraformaldehyde and styrene derivatives in the presence of trifluoroacetic acid.[16] The 4-aryl DHBP derivatives **9** thus obtained were subjected to optical resolution by high-performance liquid chromatography (HPLC) using a chiral stationary column (Dicel: Chiralcel OD-H, hexane/*i*-PrOH), and the resulting optically active catalysts **9** were utilized for the reactions described herein. In addition, an optically active 4-Ph-DHPB derivative, (*S*)-**9a**, was synthesized by the procedure illustrated in Scheme 1. Thus, optically active 3-amino-1-phenylpropan-1-ol, the absolute configuration of which was confirmed by comparing its optical rotation to that reported,[17] was synthesized by the CBS asymmetric reduction[18] of cyanoacetophenone.

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The optically active 2-aminobenzothiazole (*R*)-**A** was obtained from the amino alcohol by heating with 2-chlorobenzothiazole. The resulting (*R*)-**A** was converted to (*S*)-**9a** (86% enantiomeric excess (ee) determined by chiral HPLC) through an intramolecular S_N2 reaction by treatment with MsCl and Et_3N.[9] The synthesis confirmed the absolute stereochemistry of **9a**, which was resolved by chiral HPLC. Considering the close resemblance of the structures of compound **9** analogues, absolute configurations of each fraction from chiral HPLCs of **9** (other than **9a**) were assigned analogously. Similarly, the five-membered analogue (*S*)-**8** (93% ee) was obtained from commercially available (*R*)-2-amino-1-phenylethanol and 2-chlorobenzo[*d*]thiazole via 2-aminobenzothiazole (*R*)-**B**, chiral HPLC separation of which afforded enantiomerically pure (*S*)-**8**.

With optically active **8** and **9a**−**g** in hand, we pursued an investigation of their catalytic activity and selectivity in the kinetic resolution of 1-phenylethanol (Scheme 2, eq 1) and the rearrangement of oxazolyl carbonate **10a** (Steglich rearrangement reaction, eq 2) as benchmark reactions, and the results are summarized in Table 1.

In the kinetic resolution of 1-phenyethanol, all compounds **8** and **9** tested catalyzed acylation in an enantioselective fashion but resulted in low selectivity (*S* range 3−6). The results supported our expectation that the stereocontrol from a remote position would be difficult. It is interesting, however, that the relative bulkiness of a substituent did not necessarily correlate with selectivity.

In contrast, the Steglich rearrangement reaction catalyzed by 4-Ar-DHPB **9** gave comparatively better results. Phenyl-substituted derivatives **9a**,**b** catalyzed the formation of **11a** in moderate yields along with a protonated byproduct. Introduction of a methyl group on the benzo moiety (at the 6-position of DHPB) improved the ee from 68% to 79%, presumably because of a more convex orientation of the phenyl moiety induced by steric repulsion between the methyl and phenyl groups. Interestingly, introduction of an alkylated aryl group minimized formation of the protonated byproduct to furnish **11a** in excellent yield, although the reason is unclear at this time. Although **9c**,**e** with para or meta substitution(s) on the phenyl group also gave moderate enantioselectivity, introduction of a methyl group at the ortho position(s) was more effective, and compound **9g** having a methyl substituent on the benzo moiety and a 2,4,6-trimethylphenyl (mesityl) motif as the Ar group exhibited the maximum ee (up to 94% at −40 °C in CH_2Cl_2). In contrast to DHPB derivatives, the reaction with the five-membered analogue **8** did not proceed at all, even at room temperature. Therefore, the high efficiency of the DHPB structure as a catalophore was further demonstrated.[6,7,11a] The absolute stereochemistry of product **11a**, acquired by the (*S*)-**9a**-catalyzed reaction, was confirmed to be *S* by comparison of its HPLC chromatogram with that reported.[12] These results suggested the possibility that remote stereocontrol by 4-Ar-DHPB **9** can be achieved efficiently in certain reactions such as the Steglich rearrangement.

The Steglich rearrangement reaction,[19] which involves intramolecular transposition of a carboxyl group from enol oxygen to carbonyl α in azlactones, is a versatile method for the synthesis of α-quaternary α-amino acids, and its asymmetric reaction has been enabled by the development of chiral acyl transfer catalysts, including metallocene-derived planar chiral 4-aminopyridines,[20,21] 3-substituted 4-(dimethylamino)pyridines,[22] phosphabicyclic compounds,[23] bicyclic imidazole,[24] bicyclic isothioureas,[12] and ammonium betaine type catalysts.[25] The method has also been successfully applied to the related rearrangements of O-acylated benzofuranones, oxindoles, and 5-arylfuran enol carbonates.[26]

On the basis of its exemplary performance in the Steglich rearrangement reaction, **9g** (4-Mes-DHPB) was selected from the synthesized 4-Ar-DHBPs **9** and used to investigate the effects of catalyst loading, concentration, and temperature for the reaction of **10a** (Table 2). Lower temperature reasonably provided better stereoinduction (runs 1−3). In the range of 2−10 mol % catalyst load the selectivities were similar (runs 3−5) but a

Scheme 2

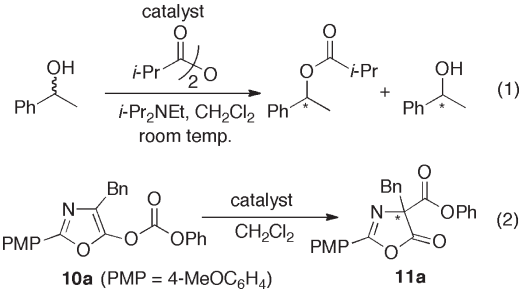

Table 1. Kinetic Resolution of 1-Phenylethanol and Steglich Rearrangement of 10a Catalyzed by 8 or 9

kinetic resolution[a]			Steglich rearrangement[b]		
cat. (1 mol %)	C_{HPLC}[c]	*S*[d]	cat. (amt, mol %)	conditions	ee, % (yield, %) of **11a**
8	0.42	3.6	**8** (5)	25 °C, 12 h	no reaction
9a	0.50	3.3	**9a** (4)	−40 °C, 12 h	68 (56)[e]
9b	not tested		**9b** (4)	−40 °C, 16 h	79 (75)[e]
9c	not tested		**9c** (4)	−20 °C, 5 h	36 (98)
			9c (4)	25 °C, 1 h	45 (96)
9d	0.62	5.9	**9d** (10)	25 °C, 1 h	76 (99)
9e	0.65	4.4	**9e** (4)	−40 °C, 16 h	68 (99)
9f	not tested		**9f** (5)	−40 °C, 16 h	80 (99)
9g	0.70	3.0	**9g** (5)	−40 °C, 12 h	94 (99)
			9g (5)	25 °C, 1 h	83 (93)

[a] Conditions: 1-phenylethanol (1.0 mmol), anhydride (0.75 mmol), *i*-Pr_2NEt (0.75 mmol), CH_2Cl_2 (4 mL), and catalyst (1 mol %) at room temperature. [b] Conditions: **10a** (0.1 mmol), catalyst (4−10 mol %), solvent (1 mL). [c] Conversion: $C_{HPLC} = ee_A/(ee_A + ee_B)$. [d] Selectivity: $S = \ln((1 - C_{HPLC})(1 - ee_A))/\ln((1 - C_{HPLC})(1 + ee_A))$. [e] In addition to **11a**, the product of protonation of the enolate intermediate was obtained.

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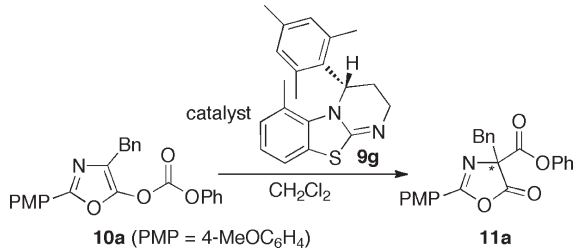
Table 2. 9g-Catalyzed Rearrangement Reaction of 10a under Various Conditions[a]



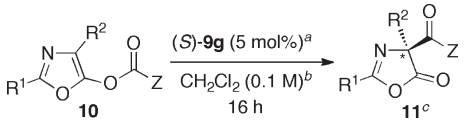
run	loading of **9g**, mol %	solvent [concn, M][b]	temp, °C	time, h	yield of **11a**, %	ee of **11a**, %[c]
1	5	CH_2Cl_2	−40	16	99	94
2	5	CH_2Cl_2	0	12	97	83
3	5	CH_2Cl_2	25	1	93	83
4	2	CH_2Cl_2	25	2	94	82
5	10	CH_2Cl_2	25	1	91	82
6	5	CH_2Cl_2 [0.05]	25	2	70	84
7	5	CH_2Cl_2 [0.15]	25	0.5	99	78
8	5	CH_2Cl_2 [0.20]	25	0.25	95	75
9	5	toluene	−40	16	85[e]	83
10	5	Et_2O	−40	16	<10	not determined
11	5	Et_2O	0	12	91	86
12	5	$ClCH_2CH_2Cl$	−20	16	95	82

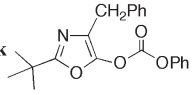
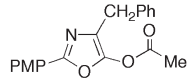
[a] Conditions: **10a** (0.1 mmol), catalyst **9g** (4−10 mol %, >99% ee), solvent (unless otherwise indicated, 1 mL). [b] Concentration (mmol of **10a**/mL of solvent). Unless otherwise indicated, 0.10 M. [c] Determined by chiral HPLC.

concentration of less than 0.1 M of the substrate was preferred for improving the ee (runs 3 and 6−8). With regard to the solvent, the results for the reactions run at 0 °C suggest that diethyl ether gives slightly better results than CH_2Cl_2 (run 11), but the reaction in ether at low temperature proceeded very slowly (run 10), because of the low solubility of the reaction intermediate(s). Therefore, among the solvents tested, CH_2Cl_2 was the best overall in terms of selectivity and solubility.

Using 5 mol % of **9g** at 0.10 M in CH_2Cl_2, the reactions of other substrates **10b**−**l** were explored (Table 3). The phenyl carbonates **10b**−**f**, with primary and secondary alkyl groups as the R^2 substituent, were rearranged to the corresponding **11** in good ee (over 76%). Although less hindered esters such as ethyl ester **10g** and allyl ester **10h** gave poor ee, the substrates **10i**,**j** with a sterically demanding ester moiety were more selective (~80% ee). With regard to the R^1 substituent, a *tert*-butyl group (**10k**) was comparable to an aryl moiety (*p*-$MeOC_6H_4$, PMP). This is interesting because reactions of the *tert*-butyl-bearing substrates catalyzed by the ferrocene-derived planar chiral 4-aminopyridines developed by Fu gave ee values lower than those of the corresponding PMP-substituted derivatives.[20] Substrate **10l**, featuring an acetate instead of a carbonate, effectively rearranged to the corresponding α-acylated azlactone **11l** with 80% ee, which is currently the highest ee for an acyl group transfer on azlactones.[10] The reaction at lower temperature did not necessarily afford better ee values; this was possibly because of the low solubility of the intermediate(s) at low temperature.

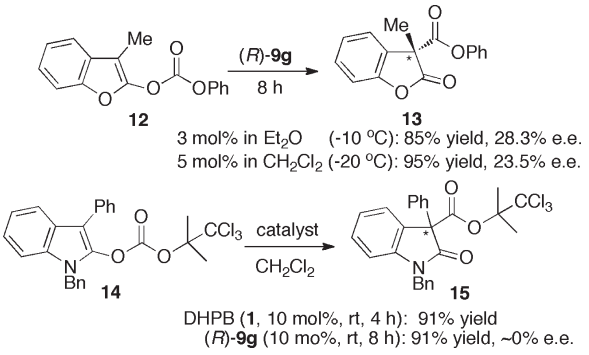
Table 3. Steglich Rearrangement Reactions Catalyzed by 9g



Substrate **10**	R^2	R^3	Temp, °C	Yield, %[d]	Ee, %[e]
10a	$PhCH_2$	Ph	-40	99	94
10b	Me	Ph	-30	91	91
10c	Et	Ph	-40	93	77
10d	*i*-Bu	Ph	-40	98	89
10e	$MeS(CH_2)_2$	Ph	-40	89	82
10f	*i*-Pr	Ph	-30	57	77
10g	$PhCH_2$	Et	0	75 (12 h)	55
10h	*i*-Bu	allyl	-30	90	55
10i	*i*-Bu	CH_2CCl_3	-30	89	77
10j	*i*-Bu	CMe_2CCl_3	-30	89	81
10k			-40	87 (12 h)	93
10l			-40	89 (4 h)	80
		(in $ClCH_2CH_2Cl$)	-10	96 (1 h)	80

[a] >99.9% ee. [b] Concentration of the substrate. [c] The absolute stereochemistry of **11a**−**d**,**f**,**g**,**k** was confirmed as depicted.[12,22a] For **11e**,**h**−**j**, it was assigned analogously. [d] Isolated yield. [e] Determined by chiral HPLC analysis.

Scheme 3. Results of the Related Rearrangement Reactions



DHPB and its derivatives such as **9g** effectively catalyzed the carboxyl group transfer reaction of benzofuran-2-one derivative **12** and indolin-2-one derivative **14** (Scheme 3). However, unfortunately, the reactions with (*R*)-**9g** resulted in poor enantioselectivity.

On the basis of the stereochemical results, it can be postulated that the Steglich rearrangement reactions proceed through an ion-pair intermediate consisting of the N-acylated iminium cation and the enolate of an azlactone, as shown in Figure 3i.[12] Substituents on the Ar and benzo moieties affect the efficiency with which one face of the catalyst plane is blocked and thereby influence the level of stereoselectivity in the product. The added methyl substitutent of **9g** induces a larger torsion angle of C−Ar to the catalyst plane, making the structure more convex compared to **9f** (Figure 3ii) and leading to a higher ee value for the product.

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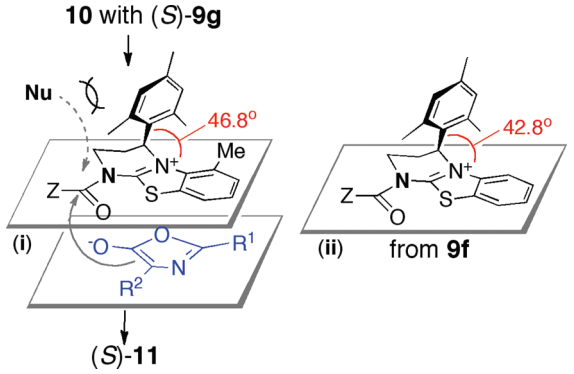

Figure 3. Proposed intermediates with **9**. Angles were calculated by MM2 (Z = OMe).

CONCLUSION

We have synthesized 4-aryl-DHPBs (**9**) and explored their catalytic activity and selectivity in the kinetic resolution of a secondary alcohol as well as in the Steglich rearrangement and related reactions. Although 4-aryl-DHPBs (**9**) showed low enantioselectivity in the acylative kinetic resolution of 1-phenylethanol, they catalyzed the Steglich rearrangement with moderate to excellent enatioselectivity, which demonstrated the possibility for remote stereocontrol by introduction of a substituent at the 4-position of DHPB.

Further investigation of the application of these new catalysts to other reactions by taking advantage of the high reactivity of 1-aryl-DHPB as well as a more efficient preparation of optically pure **9** not requiring HPLC separation is underway.

EXPERIMENTAL SECTION

General Considerations. NMR spectra were recorded in $CDCl_3$ at 600 MHz for ^1H and 150 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00) or residual $CHCl_3$ (δ 7.26 for ^1H NMR) and $CDCl_3$ (δ 77.0 for ^{13}C NMR). IR spectra were recorded on an FT/IR instrument. High-resolution mass spectra (HR-MS) were measured on an instrument equipped with ESI ionization. All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. A temperature of 0 °C and reflux conditions were obtained using an ice/water bath and using an oil bath equipped with a contact thermometer, respectively. Lower temperatures were obtained using a MeOH bath with a cooler. Room temperature refers to 20−25 °C. Enantiomeric excesses of catalysts **8** and **9** and products **11**, **13** and **15** were determined by HPLC using a Chiralcel OD-H column (*i*-PrOH/hexanes eluent) with a UV detector (254 nm). Similarly, optical resolution of a racemic mixture of **9** was performed on HPLC using a Chiralcel IA column (hexanes/EtOH/Et_2NH eluent) or OD-H column (*i*-PrOH/hexanes eluent) with a UV detector (254 nm). Azlactone substrates **10**[20a] and benzofuran and indol derivatives **12**[27] and **14**[22a] were prepared by the reported procedure.

(*R*)-3-Amino-1-phenylpropan-1-ol. In a 50 mL three-neck flask, to a solution of (*S*)-1-methyl-3,3-diphenylhexahydropyrrolo[1,2-*c*]-[1,3,2]oxazaborole (30 mol %, 83.1 mg) in THF (10 mL) was added 1.6 mL of $BH_3 \cdot Me_2S$ (2 M in THF), and the mixture was heated to 40 °C for $^1/_2$ h. Then a THF solution of 3-oxo-3-phenylpropanenitrile (1.0 mmol, 145 mg in 8 mL of THF) was added slowly over a period of 2.5 h, keeping the temperature at 60 °C. After the addition was complete, the mixture was treated with methanol (10 mL), the solvent was evaporated, and the crude residue was purified by silica gel column chromatography (eluent NH_4OH−MeOH−EtOAc, 1:10:90) to give 130 mg of (*R*)-3-amino-1-phenylpropan-1-ol as a colorless oil, the absolute configuration of which was confirmed by comparison of its sign of optical rotation with that reported.[17] ^1H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, 2H, *J* = 7.8 Hz), 7.33 (t, 2H, *J* = 7.8 Hz), 7.25−7.22 (m, 1H), 4.91−4.90 (m, 1H), 3.03−3.02 (m, 1H), 2.95 (*br s*, 2H), 2.92−2.89 (m, 1H), 1.85−1.82 (m, 1H), 1.75−1.71 (m, 1H).

4-Phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine ((*S*)-9a). A mixture of (*R*)-3-amino-1-phenylpropan-1-ol (0.5 mmol, 75.6 mg), 2-chlorobenzothiazole (0.5 mmol, 84 mg), and diisopropylethylamine (0.75 mmol) was heated to 110 °C for 24 h. After it was cooled, the mixture was diluted with 0.5 mL of dichloromethane and purified by silica gel column chromatography using MeOH−$CHCl_3$ (1:99) as eluent to yield 142 mg (0.375 mmol) of (*R*)-3-(benzo[*d*]thiazol-2-ylamino)-1-phenylpropan-1-ol ((*R*)-**A**). ^1H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, 1H, *J* = 7.8 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.38 (d, 2H, *J* = 7.2 Hz), 7.34 (t, 2H, *J* = 6.6 Hz), 7.29−7.26 (m, 3H), 7.08 (t, 1H, *J* = 6.6 Hz), 5.66 (s, 1H), 4.86−4.83 (m, 1H), 4.36 (s, 1H), 3.95−3.90 (m, 1H), 3.54−3.50 (m, 1H), 2.06−1.97 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 151.8, 144.1, 130.1, 128.5, 127.4, 126.0, 125.6, 121.8, 120.7, 118.9, 71.6, 42.3, 39.6. To a THF (3 mL) solution of (*R*)-**A** (0.35 mmol, 100 mg) under an argon atmosphere at 0 °C were added triethylamine (1.05 mmol, 0.147 mL) and then methanesulfonyl chloride (0.52 mmol, 0.04 mL). The mixture was stirred for 1 h at the same temperature and then at room temperature for 1 h. After the excess mesyl chloride was quenched with 0.2 mL of MeOH, 1 mL of triethylamine was added and the mixture was refluxed for another 24 h. After it was cooled to room temperature, the reaction mixture was diluted with dichloromethane (5 mL) and washed with water (2 × 5 mL) and brine (5 mL). The organic layer was dried over unhydrous magnesium sulfate, filtered, evaporated, and purified by column chromatography on silica gel (MeOH−$CHCl_3$, 1:90) to yield 100 mg (54%) of (*S*)-**9a**. The enantiomeric excess of the obtained (*S*)-**9a** was determined by HPLC analysis with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 10.96 min (major isomer), t_R = 16.99 min (minor isomer), ee = 86.4%. ^1H NMR (600 MHz, $CDCl_3$): δ 7.35 (t, 2H, *J* = 6.6 Hz), 7.30−7.22 (m, 4H), 7.01 (t, 1H, *J* = 7.8 Hz), 6.94 (t, 1H, *J* = 7.8 Hz), 6.47 (d, 1H, *J* = 7.2 Hz), 5.23 (br d, 1H, *J* = 4.2 Hz), 3.32 (d, 1H, *J* = 14.4 Hz), 3.28 (t, 1H, *J* = 12.6 Hz), 2.30−2.26 (m, 1H), 2.01 (d, 1H, *J* = 12.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 140.5, 140.2, 128.9, 127.7, 125.8, 125.7, 122.3, 121.8, 121.7, 108.2, 55.6, 41.2, 27.6. IR (thin film): 2928, 2372, 2320, 1625, 742, 700 cm^{-1}. HRMS for $C_{16}H_{14}N_2S + H^+$: calcd 267.0950, found 267.0946 [M + H^+].

(*S*)-3-Phenyl-2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole ((*S*)-8). According to a procedure similar to that for the preparation of (*S*)-**9a**, (*S*)-**8** (93% ee) was synthesized from (*R*)-2-amino-2-phenylethanol and 2-chlorobenzothiazole. Optically pure (*S*)-**8** was obtained by purification using HPLC with a Chiralcel OD-H column (Daicel). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.31 (m, 5H), 7.28 (d, 1H, *J* = 1.5 Hz), 6.97 (dt, 1H, *J* = 1.0, 7.5 Hz), 6.90 (dt, 1H, *J* = 1.0, 7.5 Hz), 6.28 (d, 1H, *J* = 7.5 Hz), 5.22 (dd, 1H, *J* = 8.0, 10 Hz), 4.76 (dd, 1H, *J* = 10, 14 Hz), 4.14 (dd, 1H, *J* = 8.0, 14 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 139.4, 136.5, 129.1, 128.3, 127.1, 126.4, 126.3, 123.0, 121.3, 108.8, 70.9, 62.2. IR (thin film): 3033, 2865, 1607, 1586, 1469, 746 cm^{-1}. HRMS for $C_{15}H_{12}N_2S + H^+$: calcd 253.0799, found 253.0785 [M + H^+].

General Procedure A: Synthesis of Racemic 4-Ar-DHPBs and Their Optical Resolution by HPLC. To a solution of 1.0 mmol of 2-aminobenzothiazole and paraformaldehyde (1.0 mmol) in 1 mL of dry acetonitrile under an argon atmosphere were added the styrene derivative (1.0 mmol) and trifluoroacetic acid (1.0 mmol). The mixture was refluxed for 12−24 h. The reaction progress was monitored by TLC analysis. After completion of the reaction, the solvent was evaporated

and the residue was dissolved in dichloromethane. The mixture was washed with 5% aqueous sodium bicarbonate and brine, filtered, concentrated under reduced pressure, and chromatographed on silica gel using chloroform as eluent. Enantiomers of the resulting 4-aryl-DHPB **9** were separated by HPLC with a Chiralcel OD-H column.

*6-Methyl-4-phenyl-3,4-dihydro-2H-benzo[4,5]thiazolo[3,2-a]pyrimidine (**9b**).* Following general procedure A, 4-methyl-2-aminobenzothiazole (1.0 mmol, 164 mg), paraformaldehyde (1.0 mmol, 30 mg), styrene (1.0 mmol, 104 mg), and trifluoroacetic acid (1.0 mmol, 114 mg) in 1 mL of acetonitrile gave 6-methyl-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine (**9b**) in 60.5% yield (169.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (t, 2H, J = 8.0 Hz), 7.29−7.26 (m, 1H), 7.15 (t, 3H, J = 7 Hz), 6.85 (t, 1H, J = 7.5 Hz), 6.77 (d, 1H, J = 7.5 Hz), 5.87 (br s, 1H), 3.47−3.43 (m, 1H), 3.11−3.05 (m, 1H), 2.25−2.30 (m, 4H), 2.05 (d, 1H, J = 13.0 Hz). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 157.6, 140.2, 137.5, 137.4, 129.5, 125.6, 122.3, 121.6, 108.2, 55.4, 41.2, 27.6, 20.9. IR (thin film): 2928, 2852, 2372, 2320, 1622, 1165, 755 cm^{-1}. HRMS for $C_{17}H_{16}N_2S$ + H^+: calcd 281.1112, found 281.1117 [M + 1]. Enantiomers were separated by HPLC with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 11.45 min, t_R = 13.38 min.

*4-(p-tolyl)-3,4-dihydro-2H-benzo[4,5]thiazolo[3,2-a]pyrimidine (**9c**).* Following general procedure A, 2-aminobenzothiazole (1.0 mmol, 150 mg), paraformaldehyde (1.0 mmol, 30 mg), 4-methylstyrene (1 mmol, 118.0 mg), and trifluoroacetic acid (1.0 mmol, 114 mg) in 1 mL of acetonitrile gave 4-(*p*-tolyl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine (**9c**) in 55.5% yield (155.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, 1H, J = 6.6 Hz), 7.15 (d, 2H, J = 8.4 Hz), 7.10 (d, 2H, J = 8.4 Hz), 7.00 (t, 1H, J = 7.2 Hz), 6.93 (t, 1H, J = 7.8 Hz), 6.47 (d, 1H, J = 7.8 Hz), 5.17 (d, 1H, J = 5.4 Hz), 3.52−3.49 (m, 1H), 3.31−3.26 (m, 1H), 2.32 (s, 3H), 2.32−2.22 (m, 1H), 1.99−1.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 140.2, 137.6, 137.4, 129.5, 125.6, 122.3, 121.6, 121.6, 108.2, 55.42, 41.3, 27.6, 20.9. IR (thin film): 2924, 1625, 1587, 1471, 1192, 742 cm^{-1}. HRMS for $C_{17}H_{16}N_2S$ + H^+: calcd 281.1112, found 281.1117 [M + 1]. Enantiomers were separated by HPLC with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 11.10 min, t_R = 15.66 min.

*6-Methyl-4-(o-tolyl)-3,4-dihydro-2H-benzo[4,5]thiazolo[3,2-a]pyrimidine (**9d**).* Following general procedure A, 4-methyl-2-aminobenzothiazole (1.0 mmol, 164 mg), paraformaldehyde (1.0 mmol, 30 mg), 2-methylstyrene (1.0 mmol, 118 mg), and trifluoroacetic acid (1.0 mmol, 114 mg) in 1 mL of acetonitrile gave 6-methyl-4-(*o*-tolyl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine (**9d**) in 62.0% yield (182.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23−7.12 (m, 4H), 7.03 (d, 1H, J = 7.8 Hz), 6.83 (t, 1H, J = 7.8 Hz), 6.75 (d, 1H, J = 7.8 Hz), 5.92 (d, 1H, J = 6 Hz), 3.47−3.44 (m, 1H), 3.16−3.10 (m, 1H), 2.21 (s, 3H), 2.20−2.18 (m, 1H), 1.98−1.65 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.4, 140.0, 138.5, 132.3, 131.3, 130.3, 127.6, 126.6, 126.2, 121.7, 119.9, 119.3, 55.1, 40.9, 25.1, 19.4, 18.6. IR (thin film): 2921, 2854, 2320, 1621, 724 cm^{-1}. HRMS for $C_{18}H_{18}N_2S$ + H^+: calcd 295.1269, found 295.0318 [M + 1]. Enantiomers were separated by HPLC with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 9.46 min, t_R = 13.13 min.

*4-(3,5-Dimethylphenyl)-3,4-dihydro-2H-benzo[4,5]thiazolo[3,2-a]pyrimidine (**9e**).* Following general procedure A, 2-aminobenzothiazole (1.0 mmol, 150 mg), paraformaldehyde (1.0 mmol, 30 mg), 3,5-dimethylstyrene (1.0 mmol, 132 mg), and trifluoroacetic acid (1.0 mmol, 114 mg) in 1 mL of acetonitrile gave 4-(3,5-dimethylphenyl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine (**9e**) in 43.5% yield (127.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, 1H, J = 7.2 Hz), 7.02 (t, 1H, J = 6.6 Hz), 6.95 (d, 1H, J = 6.6 Hz), 6.91 (s, 1H), 6.81 (s, 1H), 6.50 (d, 1H, J = 8.4 Hz), 5.14 (br d, 1H, J = 5.4 Hz), 3.52−3.49 (m, 1H), 3.35−3.29 (m, 1H), 2.28 (s, 6H), 2.24−2.20 (m, 1H), 1.98−1.96 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.7, 140.7, 140.3, 138.4, 129.4, 125.7, 123.5, 122.3, 121.7, 121.6, 108.3, 55.6, 41.3, 27.5, 21.3. IR (thin film): 2922, 1623, 1471, 1185, 743 cm^{-1}. HRMS for $C_{18}H_{18}N_2S$ + H^+: calcd 295.1269, found 295.0149 [M + 1]. Enantiomers were separated by HPLC with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 10.97 min, t_R = 13.67 min.

*4-Mesityl-3,4-dihydro-2H-benzo[4,5]thiazolo[3,2-a]pyrimidine (**9f**).* Following general procedure A, 2-aminobenzothiazole (1.0 mmol, 150 mg), paraformaldehyde (1.0 mmol, 30 mg), 2,4,6-trimethylstyrene (1.0 mmol, 146 mg), and trifluoroacetic acid (1.0 mmol, 114 mg) in 1 mL of acetonitrile gave 4-mesityl-3,4-dihydro-2*H*-benzo[4,5]thiazolo-[3,2-*a*]pyrimidine (**9f**) in 45.0% yield (138.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27−7.25 (m, 1H), 6.93−6.89 (m, 3H), 6.72 (s, 1H), 6.16−6.15 (m, 1H), 5.39 (t, 1H, J = 6.6 Hz), 3.57−3.53 (m, 2H), 2.47 (s, 3H), 2.25−2.17 (m, 4H), 2.05−1.98 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.3, 140.1, 137.0, 135.5, 134.9, 132.8, 132.0, 130.1, 125.6, 123.8, 121.9, 121.6, 109.1, 53.8, 43.7, 26.4, 20.6, 20.5, 19.6. IR (thin film): 2930, 2372, 2320, 1620, 1471, 742 cm^{-1}. HRMS for $C_{19}H_{20}N_2S$ + H^+: calcd 309.1425, found 309.0308 [M + 1]. Enantiomers were separated by HPLC with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 0.5 mL/min): t_R = 17.87 min, t_R = 18.50 min.

*4-Mesityl-6-methyl-3,4-dihydro-2H-benzo[4,5]thiazolo[3,2-a]pyrimidine (**9g**).* Following general procedure A, 4-methyl-2-aminobenzothiazole (1.0 mmol, 150 mg), paraformaldehyde (1.0 mmol, 30 mg), 2,4,6-trimethylstyrene (1.0 mmol, 146 mg), and trifluoroacetic acid (1.0 mmol, 114 mg) in 1 mL of acetonitrile gave 4-mesityl-6-methyl-3,4-dihydro-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine (**9g**) in 62.0% yield (200 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, 1H, J = 7.8 Hz), 6.89 (s, 1H), 6.83 (t, 1H, J = 7.8 Hz), 6.76−6.75 (m, 2H), 5.83 (br s, 1H), 3.55−3.51 (m, 1H), 3.26 (dt, 1H, J = 11.4, 3.0 Hz), 2.83 (s, 3H), 3.24 (s, 3H), 2.15 (m, 4H), 2.10 (s, 3H), 1.98−1.95 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0, 139.5, 137.2, 136.6, 136.1, 134.0, 132.3, 130.6, 130.3, 123.0, 121.8, 120.0, 119.8, 56.1, 42.5, 27.0, 20.5, 20.1, 20.0, 19.0. IR (thin film): 3060, 2960, 2850, 1471, 758 cm^{-1}. HRMS for $C_{20}H_{22}N_2S$ + H^+: calcd 323.1582, found 323.0483 [M + 1]. Enantiomers were separated by HPLC with a Chiralcel OD-H column (10% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 7.69, t_R = 10.38 min.

General Procedure B: Kinetic Resolution of 1-Phenylethanol. To a mixture of 1-phenylethanol (0.030 mL, 0.25 mmol), diisopropylethylamine (24 mg, 0.75 equiv) and catalyst **8** or **9** (2.5 μmol, 1 mol %) in CH_2Cl_2 (1.0 mL) was added isobutyric anhydride (0.031 mL, 0.75 equiv) at room temperature. The resulting mixture was stirred at this temperature. After production of the corresponding ester was checked by TLC, water was added. The mixture was extracted with ether, dried over $MgSO_4$, concentrated, and chromatographed on silica gel to separate the remaining alcohol from the resulting ester. The resulting ester was saponified by using 2 M aqueous KOH and neutralized by addition of 1 M aqueous HCl to yield the corresponding alcohol. The enantiomeric excess of these alcohols thus obtained was independently determined by chiral HPLC analysis (Chiralcel OD-H column). The selectivity value S was calculated using the equation $S = \ln((1 - C_{HPLC})(1 - ee_A))/\ln((1 - C_{HPLC})(1 + ee_A))$.

General Procedure C: Asymmetric Rearrangement of Azlactone Carbonates or Acetates 10, Benzofuran Derivative 12, and Indol Derivative 14. A solution of the substrate carbonate or acetate (0.1 mmol, 0.2 M solution in CH_2Cl_2) under argon was cooled to the required temperature, and the chiral catalyst (0.05 mmol, 0.5 mL, 0.01 M solution in CH_2Cl_2, 5 mol %) was added. After the specified time, aqueous 0.1 M HCl (5 mL) was added and the aqueous phase was extracted with Et_2O (three times), dried ($MgSO_4$), and concentrated in vacuo. The product was then purified by column chromatography. The spectroscopic data (^{1}H and ^{13}C NMR and IR) of the resulting rearrangement products **11a**,[12] **11b**,[12] **11c**,[12] **11d**,[22a] **11e**,[12] **11f**,[12] and **11j**[12] were in good agreement with those reported. The absolute stereochemistry of the products **11a**,[12] **11b**,[12] **11c**,[12] **11f**,[12] **11j**,[12] **13**,[27] and **15**[22a] was determined by comparison of

their chromatograph on a chiral HPLC with those reported (Chiralcel OD-H column). On the basis of the results, the absolute stereochemistry of **11d,e,g−i,k,l** was assigned analogously . Data shown in Table 1 were obtained by using the following: **9a**, >99.9% ee; **9b**, 84.7% ee; **9c**, 90.0% ee; **9d**, >99.9% ee; **9e**, >99.9% ee; **9f**, 98.3% ee; **9g**, >99.9% ee. With use of **9b,c,f**, ee values when optically pure catalyst could be used were calculated by assuming a simple proportion between enantioselectivity and catalyst optical purity.

*Ethyl 4-Benzyl-2-(4-methoxyphenyl)-5-oxo-4,5-dihydrooxazole-4-carboxylate (**11g**).* Following general procedure C, **10g** (0.1 mmol) and 0.005 mmol of **9g** in 1 M dichloromethane at 0 °C gave **11g** in 93% yield after 12 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, 2H, J = 6 Hz), 7.20−7.14 (m, 5H), 6.92 (d, 2H, J = 6 Hz), 4.26−4.30 (m, 2H), 3.84 (s, 3H), 3.61 (d, 1H, J = 13.8 Hz), 3.48 (d, 1H, J = 13.8 Hz), 1.29 (t, 3H, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 165.8, 163.4, 162.5, 132.9, 130.3, 130.0, 128.1, 127.4, 117.2, 114.1, 77.4, 63.0, 55.4, 40.1, 13.9. IR (thin film): 2980, 2936, 1822, 1747, 1644, 1607, 1512, 1261, 978, 739, 700 cm^{-1}. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (5% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 8.09 min (minor isomer), t_R = 9.55 min (major isomer). HRMS was measured for the methanolysis product **11g′** (for the structure, see the Supporting Information). HRMS for $C_{21}H_{23}NO_6$ + Na^+: calcd 408.1423, found 408.1414 [M + Na].

*Allyl 4-Isobutyl-2-(4-methoxyphenyl)-5-oxo-4,5-dihydrooxazole-4-carboxylate (**11h**).* Following general procedure C, **10h** (0.1 mmol) and 0.005 mmol of **9g** in 1 M dichloromethane at room temperature gave **11h** in 90% yield after 16 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, 2H, J = 9 Hz), 6.90 (d, 2H, J = 9 Hz), 5.89−5.84 (m, 1H), 5.32−5.29 (m, 1H), 5.24−5.22 (m, 1H), 4.68−4.66 (m, 2H), 3.88 (s, 3H), 2.38 (dd, 1H, J = 6.0, 14.4 Hz), 2.06 (dd, 1H, J = 7.2, 14.4 Hz), 1.74−1.68 (m, 1H), 0.94 (d, 3H, J = 6.6 Hz), 0.89 (d, 3H, J = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.7, 165.7, 163.6, 162.5, 130.7, 130.1, 129.1, 118.9, 117.2, 114.2, 113.8, 76.1, 66.9, 55.5, 42.5, 24.4, 23.7, 22.9. IR (thin film): 2959, 1819, 1750, 1647, 1511, 1424, 1261, 1051, 842, 742 cm^{-1}. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (3% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 5.57 min (minor isomer), t_R′ = 6.58 min (major isomer). HRMS was measured for the methanolysis product **11h′** (for the structure, see the Supporting Information). HRMS for $C_{19}H_{25}NO_6$ + Na^+: calcd 386.1580, found 386.1489 [M + Na].

*2,2,2-Trichloroethyl 4-Isobutyl-2-(4-methoxyphenyl)-5-oxo-4,5-dihydrooxazole-4-carboxylate (**11i**).* Following general procedure C, **10i** (0.1 mmol) and 0.005 mmol of **9g** in 1 M dichloromethane at room temperature gave **11i** in 95% yield after 16 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 9 Hz), 7.01 (d, 2H, J = 9 Hz), 4.79 (s, 2H), 3.89 (s, 3H), 2.43 (dd, 1H, J = 6.0, 14.4 Hz), 2.00 (dd, 1H, J = 7.2, 14.4 Hz), 1.78−1.73 (m, 1H), 0.96 (d, 3H, 7.2 Hz), 0.92 (d, 3H, 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 164.7, 163.7, 163.0, 150.3, 117.3, 114.3, 93.9, 76.1, 74.7, 55.5, 42.2, 24.6, 23.7, 22.9. IR (thin film): 2960, 2358, 1822, 1768, 1649, 1608, 1512, 1307, 1261, 1172, 788 cm^{-1}. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (3% *i*-PrOH in hexanes, flow 1 mL/min): t_R = 13.6 min (minor isomer), t_R′ = 15.79 min (major isomer). HRMS was measured for the methanolysis product **11i′** (for the structure, see the Supporting Information). HRMS for $C_{18}H_{22}Cl_3NO_6$ + Na^+: calcd 476.0410, found 476.0401 [M + Na].

*Phenyl 4-Benzyl-2-(tert-butyl)-5-oxo-4,5-dihydrooxazole-4-carboxylate (**11k**).* Following general procedure C, **10k** (0.1 mmol) and 0.005 mmol of **9g** in 1 M dichloromethane at −40 °C gave **11k** in 93% yield after 16 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (t, 2H, J = 8.4 Hz), 7.28−7.27 (m, 4H), 7.20 (d, 2H, J = 6.6 Hz), 7.13 (d, 2H, J = 7.2 Hz), 3.62 (d, 1H, J = 13.8 Hz), 3.56 (d, 1H, J = 13.8 Hz), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 164.2, 150.2, 132.2, 130.5, 129.5, 128.2, 127.6, 126.5, 121.0, 120.9, 76.7, 39.4, 34.0, 26.2. IR (thin film): 2974, 1824, 1770, 1665, 1592, 1224, 1190, 989, 733, 700, 687 cm^{-1}. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (5% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 4.35 min (minor isomer), t_R′ = 4.66 min (major isomer). HRMS was measured for the methanolysis product **11k′** (for the structure, see the Supporting Information). HRMS for $C_{22}H_{25}NO_5$ + Na^+: calcd 406.1630, found 406.1618 [M + Na].

*4-Acetyl-4-benzyl-2-(4-methoxyphenyl)oxazol-5(4H)-one (**11l**).* Following general procedure C, **10l** (0.1 mmol) and 0.005 mmol of **9g** in 1 M dichloromethane at −40 °C gave **11l** in 89% yield after 4 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, 2H, J = 6 Hz), 7.19−7.18 (m, 2H), 7.11−7.08 (m, 3H), 6.87 (d, 2H, J = 6 Hz), 3.79 (s, 3H), 3.36 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.7, 173.2, 163.5, 162.1, 133.0, 130.2, 129.9, 129.7, 129.5, 128.3, 128.2, 127.4, 127.1, 117.2, 114.2, 82.6, 55.4, 40.9, 27.0. IR (thin film): 3030, 2933, 1817, 1720, 1646, 1607, 1510, 1306, 1261, 1172, 739, 700, 608 cm^{-1}. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (5% *i*-PrOH in hexanes, flow rate 1 mL/min): t_R = 11.61 min (major isomer), t_R′ = 13.48 min (minor isomer). HRMS for $C_{19}H_{17}NO_4$ + H: calcd 324.126, found 324.1238.

■ ASSOCIATED CONTENT

Supporting Information. Text and figures giving experimental procedures and characterization data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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