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Osmium-Catalyzed Vicinal Oxyamination of Alkenes by *N*-(4-Toluenesulfonyloxy)carbamates

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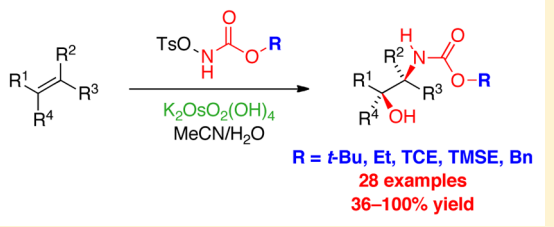
Supporting Information

ABSTRACT: *N*-(4-Toluenesulfonyloxy)carbamates based on a range of common amine protecting groups serve as preformed nitrogen sources in the intermolecular osmium-catalyzed oxyamination reaction of a variety of mono-, di-, and trisubstituted alkenes. The reactions occur with low catalyst loadings and good yields and afford high regioselectivity for unsymmetrically substituted alkenes.



INTRODUCTION

The vicinal amino alcohol is a commonly occurring functional array in natural products and other synthetic targets such as therapeutic agents and chiral auxiliaries. The prevalence of this motif has inspired the development of numerous synthetic approaches to this structural unit and its derivatives.[1] Among the most powerful and general methods of synthesis is the direct oxyamination of alkenes,[2] which is typified by catalytic asymmetric aminohydroxylation (AA) reaction developed by Sharpless and co-workers.[3,4] Despite the success of this process, the reaction suffers from problems with regioselectivity, and the preferred in situ generation of the *N*-chlorocarbamate nitrogen source can lead to chlorination of substrates.[5,6] The catalytic tethered aminohydroxylation (TA) developed by Donohoe et al.[7] addressed both of these concerns, albeit in nonasymmetric form. Tethering the reactive carbamate to an adjacent functionality leads to a secure regiochemical outcome. More recently, the introduction of *N*-(sulfonyloxy)carbamates[6] or *N*-(acyloxy)carbamates[8] as preformed nitrogen sources has improved the efficiency of this process and allowed extension of this method to the synthesis of cyclic amides.[9] Related preformed nitrogen sources have recently been employed in the intermolecular oxyamination reaction of *N*-(acyloxy)-carbamates[10,11] and amides.[12] The recently reported reaction of *N*-(4-chlorobenzoyloxy)carbamates is notable in proceeding under nonbasic conditions and with good enantioselectivity controlled by cinchona alkaloid-derived chiral ligands for mono- and disubstituted alkenes.[10,11] These findings prompted us to report the results of our investigations on the application of nontethered *N*-(sulfonyloxy)carbamates as preformed nitrogen sources in the osmium-catalyzed oxyamination reaction. We find that a range of these preformed nitrogen sources react readily in the vicinal oxyamination reaction. The reactions occur with low catalyst loadings and afford good regioselectivity for unsymmetrically substituted alkenes. The reactions of allylic alcohol derivatives proceed with moderate substrate-derived diastereoselectivity. Furthermore, competition reactions reveal significant variation in the relative rate of addition to alkenes with different substitution patterns. However, preliminary investigations highlight that these nitrogen sources cannot be substituted for the *N*-chlorocarbamates in the Sharpless AA reaction.

RESULTS AND DISCUSSION

The synthesis of preformed nitrogen sources **1**–**6** with different *N*-acyloxy and *N*-sulfonyloxy leaving groups was conducted from *tert*-butyl hydroxycarbamate **7** (Table 1).[13−16] Single-crystal X-ray analysis confirmed the identity of compound **1**. The ability of these nitrogen sources to serve as oxidant in the oxyamination reaction was investigated by reaction with *trans*-stilbene **8** and potassium osmate and hydroquinidine 1,4-phthalazinediyl diether, $(DHQD)_2PHAL$, in aqueous propanol. The nitrogen sources afforded the oxyamination product **9a** in varying yields. However, despite the presence of chiral ligand $(DHQD)_2PHAL$ commonly used in the Sharpless asymmetric dihydroxylation (AD) and asymmetric aminohydroxylation (AA) reactions, the product was afforded in racemic form as judged by HPLC analysis. This absence of asymmetric induction is a feature shared with nitrogen sources in the intramolecular TA reaction, which has been proposed to operate in the secondary catalytic cycle that impedes ligand binding.[7] Alternately, the absence of asymmetric induction could also be explained by the low pH of these reactions. The oxyamination reactions reported here occur at moderately low pH due to the liberation of 1 equiv of sulfonic or carboxylic acid. In contrast, the Sharpless AA and AD and closely related reactions are conducted under high pH, which has been reported to be essential for high enantioselectivity.[17−19]

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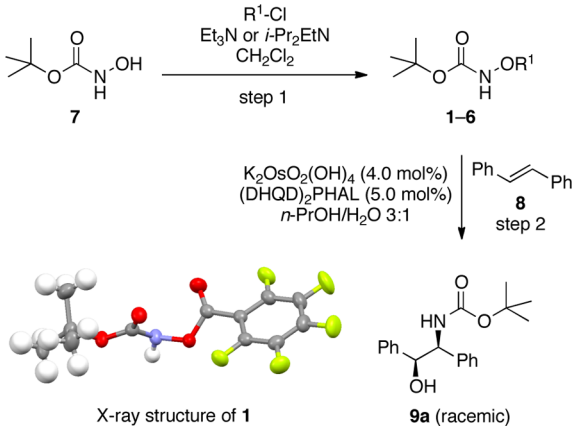
Table 1. Synthesis and Reaction of Preformed Nitrogen Sources 1−6



entry	R^1 [a]	yields (%) step 1[b]	yields (%) step 2[c]
1	C_6F_5CO, **1**	67	71
2	$ClCH_2CO$, **2**	86	29
3	Ms, **3**	93	75
4	Ts, **4**	71	59
5	$MesSO_2$, **5**	58	78
6	*p*-$NO_2C_6H_4SO_2$, **6**	46	62

[a]Ms = methanesulfonyl; Ts = tosyl; Mes = mesityl. [b]Conditions: *tert*-butyl hydroxycarbamate **7**, R^1Cl, Et_3N or *i*-Pr_2NEt, CH_2Cl_2, 0 °C to rt. [c]Conditions: *trans*-stilbene **8** (1.0 equiv), nitrogen source **1−6** (2.0 equiv), $K_2OsO_2(OH)_4$ (4.0 mol %), $(DHQD)_2PHAL$ (5 mol %), *n*-PrOH/H_2O (3:1), 0 °C to rt.

To further explore the potential of this oxyamination reaction, the *N*-(tosyloxy)carbamate **4** was selected for further examination due to its ready availability and chemical stability. This choice was also inspired by the reported application of *N*-(sulfonyloxy)carbamates in a range of oxidation chemistry including the TA reaction, C−H insertion reactions,[20−24] sulfinamide[25] and aziridine formation.[26−39] The related *N*-(methanesulfonyloxy)carbamate reagent **3** proved moderately unstable to long-term 6-month storage in our hands.[13]

The preparation of *N*-(tosyloxy)carbamates **4a−e**, corresponding to commonly used carbamate protecting groups, including the *tert*-butyl- (**a**), ethyl- (**b**), 2,2,2-trichloroethyl- (TCE, **c**), 2-(trimethylsilyl)ethyl- (TMSE, **d**), and benzyl- (**e**) carbamate derivatives, was conducted (Scheme 1).[15,24,40,41] Single-crystal X-ray analysis confirmed the identity of compound **4e**.

The optimization of a number of oxyamination reaction variables was conducted with benzyl *N*-(tosyloxy)carbamate **4e**, *trans*-stilbene **8**, and potassium osmate(VI) dihydrate (Table 2). The reactions proceeded in homogeneous *tert*-butanol, propanol, and acetonitrile/water mixtures, with the highest yield of product **9e** afforded in 3:1 acetonitrile/water. An attempt to use a biphasic dichloromethane/water solvent mixture gave no conversion after 96 h.

Changes to nitrogen source stoichiometry and osmium catalyst loading were also investigated (Table 2). Using 1 equiv of nitrogen source **4e** and 1.0 mol % potassium osmate dihydrate afforded the oxyamination product in 88% yield after 14 h. Lower (0.10 mol %) osmium catalyst loadings resulted in slower conversion to product and lower yield. The low catalyst loadings indicated a similar high level of efficiency to reported

Scheme 1. Preparation of *N*-(Tosyloxy)carbamates 4a−e

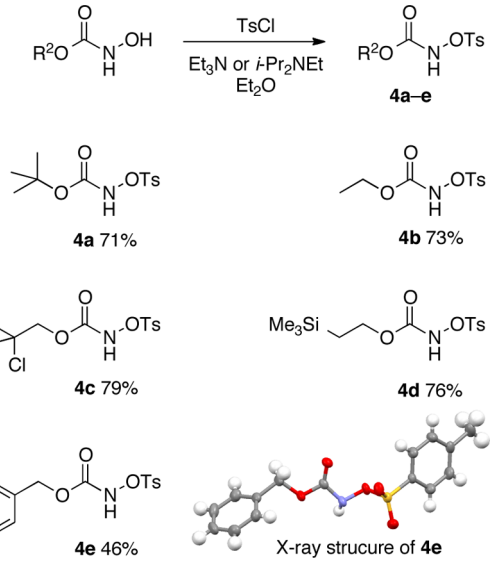
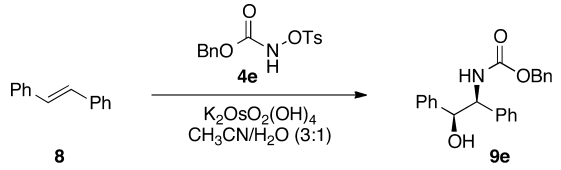


Table 2. Optimizing the Oxyamination Reaction[a]



entry	nitrogen source (equiv)	catalyst loading (mol %)	yield (%)	time (h)
1	2.0	4.0	81	4
2	1.0	4.0	71	5
3	1.0	2.0	71	9
4	1.0	1.0	88	14
5	1.0	0.10	55	96

[a]Conditions: *trans*-stilbene **8** (1.0 equiv), benzyl *N*-(tosyloxy)-carbamate **4e** (see table), $K_2OsO_2(OH)_4$ (see table), MeCN/H_2O (3:1), 0 °C to rt.

N-sulfonyloxy and *N*-acyloxy preformed nitrogen sources employed in the TA reaction.[6,8,9]

To investigate the substrate scope of the oxyamination protocol, the reaction of a range of different alkenes **8** and **10−24** were explored (Table 3). The substrates included alkenes of different electron demand and also different substitution patterns. In the cases noted, aqueous *tert*-butanol was employed to improve the solubility of nitrogen source or substrate.

All nitrogen sources were effective in the reaction to afford oxyamination products **9**, **25−34**, **36**, **38**, and **39**, with unsymmetrical alkenes also affording the minor oxyamination products **40−44**. The *tert*-butyl- (**4a**), 2,2,2-trichloroethyl- (TCE; **4c**), and benzyl- (**4e**) substituted nitrogen sources generally affording higher yields than the ethyl (**4b**) or 2-(trimethylsilyl)ethyl (TMSE; **4d**) variants. Alkene substitution patterns were observed to influence the transformation in two ways. The reactions with mono- and disubstituted alkenes were complete within 48 h, but in some instances the reactions of trisubstituted alkenes required longer reaction times (entries 10 and 13). Furthermore, despite a number of attempts the nitrogen sources could not be successfully employed for the oxyamination of tetrasubstituted alkenes (entry 14). The lower reactivity associated with higher levels of alkene substitution has

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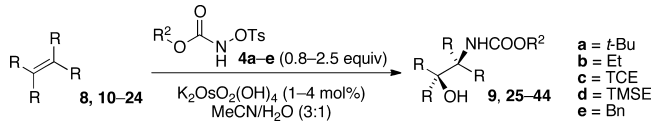
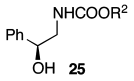
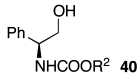
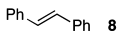
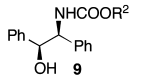
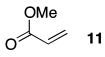
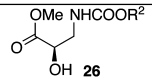
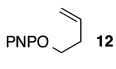
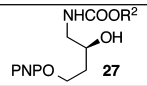
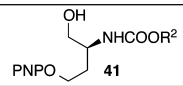
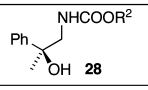
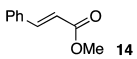
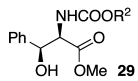
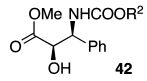
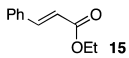
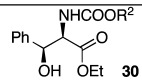
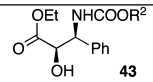
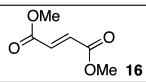
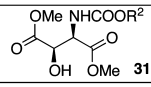
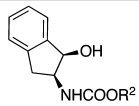
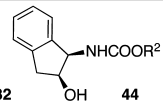
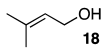
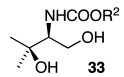
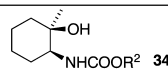
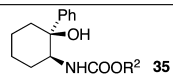
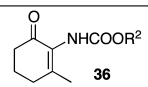
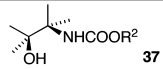
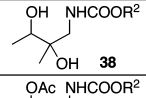
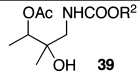
Table 3. Oxyamination of Alkenes 8 and 10–24[a]



entry	alkene	products	R^2	yield (%)
1	 10	 25  40	*t*-Bu[b]	83
			Et	76 (24:1)[c]
			TCE[d]	100 (10.1:1)[c]
			TMSE	39
			Bn	85 (16:1)[c]
2	 8	 9	*t*-Bu[b]	86
			Et[b]	42
			TCE[b,e]	80
			TMSE[b]	50
			Bn	61
3	 11	 26	Bn	65
4	 12	 27  41	TMSE	81 (7.1:1)[c]
5	 13	 28	*t*-Bu[b]	68
			TCE[e]	91
6	 14	 29  42	*t*-Bu[b]	65 (1.7:1)[c]
			Et	82 (1.6:1)[c]
			TCE	82 (1.3:1)[c]
			TMSE	49 (1.6:1)[c]
7	 15	 30  43	Bn	82 (1.3:1)[c]
8	 16	 31	Bn	86
9	 17	 32  44	TCE	43 (1:1)[c]
			TMSE	71 (2.1:1)[c]
10	 18	 33	*t*-Bu[b]	54
			TCE	NR[f]
			Bn	64
11	 19	 34	Et	74
12	 20	 35	Et	NR[f]
13	 21	 36	Et	36
14	 22	 37	*t*-Bu	NR[f]
15	 23	 38	Bn	45[g]
16	 24	 39	Bn	68[h]

[a]Conditions: alkene (1.0 equiv), nitrogen source **4a–e** (0.8–2.5 equiv), $K_2OsO_2(OH)_4$ (1–4 mol %), $MeCN/H_2O$ (3:1), 0 °C to rt. TCE = 2,2,2-trichloroethyl; TMSE = 2-(trimethylsilyl)ethyl; PNP = *p*-nitrophenyl. [b]*t*-BuOH/H_2O (3:1). [c]Ratio of major regioisomer to minor regioisomer. [d]X-ray analysis proved the identity of both the major **25c** and minor **40c** regioisomers. [e]X-ray analysis proved the identity of the products **9c** and **28c**. [f]No reaction. [g]Affords a 2.4:1 mixture of anti:syn diastereomers. [h]Affords a 2.6:1 mixture of anti:syn diastereomers.

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also been recently highlighted for *N*-(4-chlorobenzoyloxy)-carbamates in the intermolecular oxyamination reaction.[11] In the case of the intramolecular TA variants involving preformed nitrogen sources, the proximity effects largely override this lower reactivity.[6,8,9]

The regioselectivity of the oxyamination reaction was strongly influenced by alkene substitution. Unsymmetrical mono- (entries 1, 3, and 4), 1,1-di- (entries 5, 15, and 16) and trisubstituted (entries 10, 11, and 13) alkenes gave high regioselectivity that favored addition of the nitrogen to the less substituted alkene carbon. In unsymmetrically substituted cis-1,2- (entry 9) and trans-1,2-disubstituted (entries 6 and 7) alkenes, low regioselectivity was observed. These trends in regioselectivity are in common with other intermolecular osmium-catalyzed oxyamination protocols based on *N*-(acyloxy)carbamates[10,11] and are also observed to exert considerable influence on the Sharpless AA reaction.[4] No significant trend in reactivity was evident upon the introduction of electron-withdrawing carbonyl groups (entries 3, 6−8, and 13). In the case of 3-methylcyclohexenone **21**, the adjacent ketone facilitated the dehydration of the expected oxyamination product to give enone **36**, a reaction presumably promoted by the mildly acidic reaction conditions (entry 13). The oxyamination of chiral allylic alcohol derivatives **23** and **24** afforded moderate diastereoselectivity favoring the anti-substituted product, consistent with Kishi's empirical rule for the osmium-catalyzed dihydroxylation reaction (entries 15 and 16).[42,43]

To provide further insight into the reaction, a series of competition experiments were performed by reacting 1 equiv of nitrogen source with 1 equiv each of two different alkenes (Table 4). Under these conditions, the relative yield of product

Table 4. Competition Experiments[a]

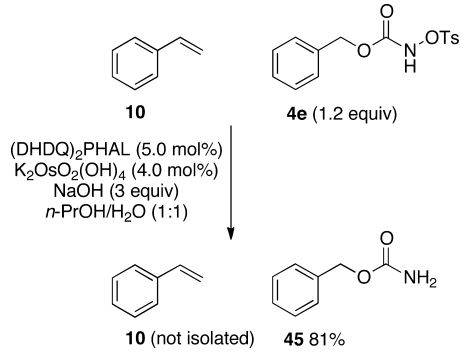
entry	alkene substrates A	alkene substrates B	product yields (%) A	product yields (%) B	time (h)
1	Ph, Ph **8**	Ph **10**	43	36[b]	24
2	**17**	Ph **10**	39[c]	29[b]	24
3	OH **18**	Ph **10**	0	65[c]	16
4	OH **23**	OAc **24**	34[d]	16[d]	96

[a]Conditions: alkene A (1.0 equiv), alkene B (1.0 equiv), BnOCONHOTs **4e** (1.0 equiv), $K_2OsO_2(OH)_4$ (4.0 mol %), MeCN/H_2O (3:1), rt. [b]One regioisomer was afforded. [c]Two regioisomers were afforded. [d]Two diastereomers were afforded.

derived from each alkene correlates to the relative rate of addition of the catalytically active imidoosmium species to the alkenes. Competition between monosubstituted alkene styrene **10** and the 1,2-disubstituted alkenes *trans*-stilbene **8** and indene **17** indicated a similar rate of addition to the two alkene classes (entries 1 and 2). In contrast, competition between styrene **10** and the trisubstituted alkene 3-methylbut-2-en-1-ol **18** afforded only the product from the monosubstituted alkene (entry 3). This result suggested that either the allylic alcohol functionality or, consistent with the trends observed above (Table 3), the higher level of alkene substitution dramatically slowed addition of the osmium catalyst to this substrate. In a final experiment, the competition reaction of 3-methylbut-3-en-2-ol **23** and its acetate derivative **24** was performed. Oxyamination of this substrate pair slightly favored addition to the allylic alcohol **23** over the acetate ester **24**, suggesting that the presence of an unprotected allylic alcohol did not in itself slow the rate of osmium catalyst addition (Table 4, cf. entries 1−3 with entry 4). However, this reaction was also relatively slow and proceeded in moderate yield. In this respect the competition reaction correlated with the reactivity of other allylic alcohol substrates that also gave slow conversion and moderate yields (Table 3, entries 10 and 15) but not the higher reactivity of protected allylic or homoallylic alcohols (Table 3, entries 4 and 16). Together these results suggest that allylic alcohols may serve to retard catalyst turnover through slower hydrolysis or reoxidation steps. Slow catalytic turnover was recently reported for the racemic oxyamination of functionalized substrates including allylic and homoallylic alcohols using *N*-(4-chlorobenzoyloxy)carbamate-derived nitrogen sources, the effects of which could be ameliorated by the use of increased catalyst loading or heating of the reaction mixture.[11] These competition reactions also highlight the potential for the selective partial oxyamination of appropriately substituted polyene substrates.

Finally, we investigated the potential of *N*-(tosyloxy)-carbamates to serve as nitrogen source in the Sharpless asymmetric aminohydroxylation (AA). The use of preformed nitrogen sources eliminates the presence of potentially problematic chlorinating agents in the reaction.[5,6] Conducting the reaction under conditions typical for the Sharpless AA protocol, but using benzyl *N*-(tosyloxy)carbamate **4e** in place of benzyl carbamate and *tert*-butyl hypochlorite, gave benzyl carbamate **45** as the major product in 81% yield (Scheme 2).

Scheme 2. Attempted Asymmetric Aminohydroxylation Reaction



No amino alcohol product was isolated from the reaction. Styrene **10** was observed at the conclusion of the reaction by thin-layer chromatography (TLC) but was not isolated. The formation of carbamate byproducts has previously been observed for *N*-(acyloxy)carbamates in both the intra- and intermolecular variants of the oxyamination reaction.[8,11] The result stands in marked contrast to the successful intermolecular asymmetric aminohydroxylation of mono- and disub-

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stituted[10] but not trisubstituted alkenes[11] mediated by the recently reported *N*-(4-chlorobenzoyloxy)carbamate reagents and hints at a subtle interplay of addition, hydrolysis, and reoxidation steps within the catalytic cycle to afford products with high enantioselectivity.[4,7]

CONCLUSION

In conclusion, we have developed a range of preformed *N*-(sulfonyloxy)carbamate nitrogen sources that are suitable for the intramolecular vicinal oxyamination reaction of a wide variety of mono-, di-, and trisubstituted alkenes. These reactions proceed with low catalyst loadings comparable with leading osmium-catalyzed oxyamination protocols[6,8−11] and afford good regioselectivity for unsymmetrically substituted alkenes. Competition reactions reveal similar rates of catalyst addition to mono- and disubstituted alkenes but much slower addition to more highly substituted substrates, highlighting the potential selective partial oxyamination of appropriately substituted polyene substrates. The reactions of allylic alcohol derivatives proceed with moderate substrate-derived diastereoselectivity. However, preliminary investigations highlight that these nitrogen sources cannot be substituted for the *N*-chlorocarbamates in the enantioselective Sharpless AA reaction procedure. This study provides a range of new preformed nitrogen sources for the intramolecular osmium-catalyzed oxyamination reaction but also serves to highlight the ongoing challenge associated with developing new and general nitrogen sources for the asymmetric aminohydroxylation reaction.[10,11]

EXPERIMENTAL SECTION

General Procedure 1 for Synthesis of *tert*-Butyl Carbamate-Based Preformed Nitrogen Sources. To a solution of *tert*-butyl *N*-hydroxycarbamate **7**[44] in dichloromethane cooled to 0 °C was added carboxylic acid chloride or sulfonyl chloride. To this mixture was added triethylamine, and the mixture was stirred at room temperature until the reaction was complete. The mixture was quenched with water and separated. The aqueous layer was extracted with dichloromethane, and the combined dichloromethane layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure to afford crude product. Purification was conducted by flash chromatography with the specified solvents.

tert-Butyl N-(Pentafluorobenzoyloxy)carbamate ***1***. General procedure 1 was followed with *tert*-butyl *N*-hydroxycarbamate **7** (665.7 mg, 5.0 mmol), pentafluorobenzoyl chloride (1.15 g, 5.0 mmol), and triethylamine (505.9 mg, 5.0 mmol). Purification by flash chromatography with 15% ethyl acetate/*n*-hexane afforded the title compound as a white solid (1.10 g, 67%), mp 70−73 °C. R_f 0.53 (40% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3276 (N−H), 2985, 2938 (C−H), 1783, 1741 (C═O). ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (1H, s), 1.51 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 155.3, 146.1 (d, J = 267 Hz), 144.3 (d, J = 261 Hz), 138.1 (d, J = 257 Hz), 105.4, 84.3, 28.0. LRMS (ESI+) m/z 350 ($[M + Na]^+$, 8%). HRMS (ESI+) $[M + Na]^+$ calcd for $C_{12}H_{10}F_5NO_4Na$ 350.0428, found 350.0427.

tert-Butyl N-(2-Chloroacetoxy)carbamate ***2***. General procedure 1 was followed with minor modifications, with *tert*-butyl *N*-hydroxycarbamate **7** (100 mg, 0.751 mmol), chloroacetyl chloride (56.6 mg, 0.50 mmol), and *N*,*N*-diisopropylethylamine (64.7 mg, 0.50 mmol). Purification by flash chromatography with 30% ethyl acetate/*n*-hexane provided the title compound as a yellow oil (90.0 mg, 86%). R_f 0.33 (30% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3271 (N−H), 2982 (C−H), 1795, 1737 (C═O). ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (1H, s), 4.20 (2H, s), 1.47 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 155.2, 84.3, 38.9, 28.2. LRMS (EI+) m/z 212 ($[M + H]^+$, 10%), 210 (8), 194 ($[M - CH_3]^+$, 80). HRMS (EI+) $[M - CH_3]^+$ calcd for $C_6H_9NO_4{}^{35}Cl$ 194.0220, found 194.0222; $[M - CH_3]^+$ calcd for $C_6H_9NO_4{}^{37}Cl$ 196.0191, found 196.0193.

tert-Butyl N-(Methanesulfonyloxy)carbamate ***3***.[13] General procedure 1 was followed with minor modifications, with *tert*-butyl *N*-hydroxycarbamate **7** (1.0 g, 7.51 mmol), methanesulfonyl chloride (946.4 mg, 8.26 mmol), and triethylamine (836.0 mg, 8.26 mmol) to afford the title compound as a white solid (1.47 g, 93%), mp 75−76 °C (lit.[13] 83−85 °C). R_f 0.31 (40% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3292 (N−H), 1741 (C═O). ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (1H, s), 3.17 (3H, s), 1.51 (9H, s). LRMS (EI+) m/z 196 ($[M - CH_3]^+$, 15%). HRMS (EI+) $[M - CH_3]^+$ calcd for $C_5H_{10}NO_5S$ 196.0280, found 196.0276. The ^{13}C NMR data matched the literature.[13]

tert-Butyl N-(Tosyloxy)carbamate ***4a***.[15,45] General procedure 1 was followed with minor modifications, with *tert*-butyl *N*-hydroxycarbamate **7** (1.96 g, 14.7 mmol), toluenesulfonyl chloride (3.09 g, 16.2 mmol) and triethylamine (1.64 g, 16.2 mmol). Purification by flash chromatography with 25% ethyl acetate/*n*-hexane afforded the title compound as a white solid (3.01 g, 71%), mp 91−93 °C (lit.[15] 97 °C). R_f 0.18 (25% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3289 (N−H), 3071, 2982, 2934 (C−H), 1768, 1730, 1709 (C═O), 1597. LRMS (ESI+) m/z 310 ($[M + Na]^+$, 25%). HRMS (ESI+) $[M + Na]^+$ calcd for $C_{12}H_{17}NO_5SNa$ 310.0725, found 310.0719. The ^1H and ^{13}C NMR data matched the literature.[45]

tert-Butyl N-(Mesitylsulfonyloxy)carbamate ***5***.[14] General procedure 1 was followed with minor modifications, with *tert*-butyl *N*-hydroxycarbamate **7** (399.4 mg, 3.00 mmol), mesitylsulfonyl chloride (722.0 mg, 3.06 mmol), and triethylamine (309.6 mg, 3.06 mmol). Purification by flash chromatography with 20% ethyl acetate/*n*-hexane provided the title compound as a white solid (550.8 mg, 58%), mp 110−113 °C (lit.[14] 104−105.5 °C). R_f 0.24 (20% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3292 (N−H), 1768, 1732, 1705 (C═O), 1603. ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (1H, s), 6.98 (2H, s), 2.66 (6H, s), 2.31 (3H, s), 1.30 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 144.7, 142.2, 131.9, 128.7, 84.1, 27.9, 23.4, 21.4.

tert-Butyl N-(p-Nitrophenylsulfonyloxy)carbamate ***6***.[16] General procedure 1 was followed with minor modifications, with *tert*-butyl *N*-hydroxycarbamate **7** (0.798 g, 6.00 mmol), diethyl ether (60 mL), *p*-nitrophenylsulfonyl chloride (1.46 g, 6.60 mmol), and triethylamine (0.618 g, 6.11 mmol). Purification by flash chromatography with 25% ethyl acetate/*n*-hexane provided the title compound as a white-yellow solid (0.881 g, 46%), mp 86−91 °C (lit.[16] 91−92 °C). R_f 0.58 (50% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3306 (N−H), 3109, 1733 (C═O). ^{13}C NMR (75 MHz, acetone-d_6) δ 154.7, 151.8, 139.7, 131.4, 124.5, 83.1, 27.3. LRMS (ESI+) m/z 341 ($[M + Na]^+$, 50%). The ^1H NMR data matched the literature.[16]

Assay of *tert*-Butyl Carbamate-Based Preformed Nitrogen Sources in the Oxyamination Reaction. To a mixture of *trans*-stilbene **8** (1.0 equiv), $(DHQD)_2PHAL$ (5.0 mol %), and potassium osmate dihydrate (4.0 mol %) in *n*-propanol/water (3:1) cooled to 0 °C was added nitrogen source (2.0 equiv). This mixture was stirred at room temperature until the reaction was complete. Water was added, and the mixture was extracted with ethyl acetate (5.0 mL). The aqueous layer was further extracted with ethyl acetate (3 × 10 mL). Combined ethyl acetate layers were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. Purification was performed by flash chromatography (1:9:5 ethyl acetate/dichloromethane/*n*-hexane) to afford *tert*-butyl (1*R**,2*R**)-2-hydroxy-1,2-diphenylethylcarbamate **9a**[46] as a white solid (Table 2). The reaction product was analyzed by HPLC (chiral column OD-H in 7.5% 2-propanol/*n*-hexane; flow rate 1.0 mL·min^{-1}). The enantiomeric excess (ee) was calculated from the relative peak area of the two peaks, retention times 10.0 and 11.4 min. The products were racemic.

General Procedure 2 for Synthesis of *N*-(Tosyloxy)-carbamate Preformed Nitrogen Sources.[40] To a solution of alkyl *N*-hydroxycarbamate in diethyl ether at 0 °C was added toluenesulfonyl chloride. Triethylamine was added dropwise over 30 min and the reaction was stirred at room temperature until complete. The mixture was filtered, and the filtrate was extracted with diethyl ether, washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure to afford crude product. Purification was conducted by flash chromatography with the specified solvents.

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Ethyl N-(Tosyloxy)carbamate ***4b***.[40] General procedure 2 was followed with ethyl *N*-hydroxycarbamate[47] (400.0 mg, 3.81 mmol), toluenesulfonyl chloride (725.6 mg, 3.81 mmol), and triethylamine (385.1 mg, 3.81 mmol). Purification by flash chromatography with 30% ethyl acetate/*n*-hexane afforded the title compound as a colorless solid (715.4 mg, 73%). R_f 0.22 (30% ethyl acetate/*n*-hexane). LRMS (ESI+) *m*/*z* 282 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{10}H_{13}NO_5SNa$ 282.0412, found 282.0412. IR, ^{1}H, and ^{13}C NMR data matched the literature.[40]

2,2,2-Trichloroethyl N-(Tosyloxy)carbamate ***4c***.[24] General procedure 2 was followed with 2,2,2-trichloroethyl *N*-hydroxycarbamate[48] (900.0 mg, 4.32 mmol), toluenesulfonyl chloride (905.5 mg, 4.75 mmol), and triethylamine (436.9 mg, 4.32 mmol). Purification by flash chromatography with 20% ethyl acetate/*n*-hexane afforded the title compound as a white solid (1.37 g, 79%), mp 133−135 °C (lit.[24] 123 °C). R_f 0.25 (20% ethyl acetate/*n*-hexane). LRMS (ESI+) *m*/*z* 386 ([M + Na]$^+$, 100%), 384 ([M + Na]$^+$, 98). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{10}H_{10}{}^{35}Cl_3NO_5SNa$ 383.9243, found 383.9238. IR, ^{1}H, and ^{13}C NMR data matched the literature.[24]

2-(Trimethylsilyl)ethyl N-(Tosyloxy)carbamate ***4d***. General procedure 2 was followed with 2-(trimethylsilyl)ethyl *N*-hydroxycarbamate[49] (761.0 mg, 4.29 mmol), toluenesulfonyl chloride (1.1 equiv, 900.2 mg, 4.72 mmol), and triethylamine (434.4 mg, 4.29 mmol). Purification by flash chromatography with 20% ethyl acetate/*n*-hexane afforded the title compound as a colorless oil (1.08 g, 76%). R_f 0.21 (20% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3287 (N−H), 1741, 1711 (C═O), 1597. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (1H, s), 7.87 (2H, d, *J* = 8.1 Hz), 7.36 (2H, d, *J* = 8.4 Hz), 4.08 (2H, m), 2.46 (3H, s), 0.84 (2H, m), 0.00 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 147.7, 131.9, 131.3, 131.2, 67.4, 23.4, 18.9, 0.0. LRMS (ESI+) *m*/*z* 354 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{21}NO_5SSiNa$ 354.0807, found 354.0804.

Benzyl N-(Tosyloxy)carbamate ***4e***.[41] General procedure 2 was followed with benzyl *N*-hydroxycarbamate[50] (936.3 mg, 5.60 mmol), toluenesulfonyl chloride (1.28 g, 6.72 mmol), and triethylamine (680.0 mg, 6.72 mmol). Purification by flash chromatography provided the title compound as a white solid (814.0 mg, 46%), mp 119−121 °C (lit.[41] 120−123 °C). R_f 0.11 (80% dichloromethane/*n*-hexane). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 146.1, 134.5, 130.0, 129.7, 129.5, 128.7, 128.6, 128.3, 68.6, 21.8. LRMS (ESI+) *m*/*z* 344 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{15}H_{15}NO_5SNa$ 344.0569, found 344.0568. IR and ^{1}H NMR IR data matched the literature.[41]

General Procedure 3 for Assay of *N*-(Tosyloxy)carbamate Preformed Nitrogen Sources in the Oxyamination Reaction. To a mixture of alkene and potassium osmate dihydrate in acetonitrile/water (3:1) or the specified solvent was added the nitrogen source at 0 °C. The mixture was stirred at room temperature until the reaction was complete. The mixture was then extracted with ethyl acetate (3 × 5 mL). The combined ethyl acetate fractions were dried (Na_2SO_4) and concentrated under reduced pressure to afford crude product. Purification was performed by flash chromatography with the indicated solvents.

(2R)-tert-Butyl 2-Hydroxy-2-phenylethylcarbamate* ***25a***.[51] General procedure 3 was followed with styrene **10** (40.0 mg, 0.384 mmol), *tert*-butyl *N*-(tosyloxy)carbamate **4a** (132.4 mg, 0.461 mmol), and potassium osmate dihydrate (4.0 mol %, 5.7 mg, 0.015 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 2:2:6 ethyl acetate/dichloromethane/*n*-hexane afforded the title compound as a white solid (75.6 mg, 83%), mp 120−121 °C (lit.[51] 120−121 °C). R_f 0.20 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). LRMS (ESI +) *m*/*z* 260 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + H]$^+$ calcd for $C_{13}H_{20}NO_3$ 238.1443, found 238.1448; [M + Na]$^+$ calcd for $C_{13}H_{19}NO_3Na$ 260.1263, found 260.1266. IR, ^{1}H and ^{13}C NMR data matched the literature.[51]

Ethyl (R)-2-Hydroxy-2-phenylethylcarbamate* ***25b***[52,53] *and Ethyl (R*)-2-Hydroxy-1-phenylethylcarbamate* ***40b***.[52,54] General procedure 3 was followed with styrene **10** (40.0 mg, 0.384 mmol), potassium osmate dihydrate (1.4 mg, 0.004 mmol), and ethyl *N*-(tosyloxy)carbamate **4b** (79.7 mg, 0.307 mmol). Purification by flash chromatography with 2:3:5 ethyl acetate/dichloromethane/*n*-hexane afforded ethyl (*R**)-2-hydroxy-2-phenylethylcarbamate **25b** as a white solid (46.7 mg, 73%), mp 85−86 °C (lit.[52] 85.5−87 °C). R_f 0.23 (40% ethyl acetate/*n*-hexane). LRMS (ESI+) *m*/*z* 232 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{11}H_{15}NO_3Na$ 232.0950, found 232.0952. IR, ^{1}H and ^{13}C NMR data matched the literature.[53] A second fraction afforded ethyl (*R**)-2-hydroxy-1-phenylethylcarbamate **40b** as a colorless solid (2.3 mg, 3%), mp 61−63 °C (lit.[52] 62−63 °C). R_f 0.13 (40% ethyl acetate/*n*-hexane). LRMS (ESI+) *m*/*z* 232 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{11}H_{15}NO_3Na$ 232.0950, found 232.0951. IR, ^{1}H and ^{13}C NMR data matched the literature.[54]

2,2,2-Trichloroethyl (R)-2-Hydroxy-2-phenylethylcarbamate* ***25c*** *and 2,2,2-Trichloroethyl (R*)-2-Hydroxy-1-phenylethylcarbamate* ***40c***. General procedure 3 was followed with styrene **10** (30.0 mg, 0.288 mmol), potassium osmate dihydrate (1.1 mg, 0.003 mmol), and 2,2,2-trichloroethyl *N*-(tosyloxy)carbamate **4c** (125.3 mg, 0.346 mmol). Purification by flash chromatography with 30% ethyl acetate/*n*-hexane afforded 2,2,2-trichloroethyl (*R**)-2-hydroxy-2-phenylethylcarbamate **25c** as a white solid (82.1 mg, 91%), R_f 0.24 (30% ethyl acetate/*n*-hexane). Recrystallization via slow evaporation from chloroform/*n*-hexane provided white crystals, mp 116−118 °C. IR (thin film, cm^{-1}) ν_{max} 3397 (O−H), 3317 (N−H), 3085, 3062, 2960, 2894 (C−H), 1710 (C═O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (5H, m), 5.37 (1H, s), 4.87 (1H, m), 4.72 (2H, s), 3.61 (1H, ddd, *J* = 14.0, 7.6, 4.0 Hz), 3.36 (1H, ddd, *J* = 13.2, 8.0, 4.8 Hz), 2.37 (1H, d, *J* = 3.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.1, 128.7, 128.2, 125.8, 77.2, 74.6, 73.4, 48.4. LRMS (ESI+) *m*/*z* 336 ([M + Na]$^+$, 95%), 334 (100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{11}H_{12}{}^{35}Cl_3NO_3Na$ 333.9780, found 333.9787; [M + Na]$^+$ calcd for $C_{11}H_{12}{}^{35}Cl_2{}^{37}ClNO_3Na$ 335.9751, found 335.9756. A second fraction afforded 2,2,2-trichloroethyl (*R**)-2-hydroxy-1-phenylethylcarbamate **40c** as a white solid (8.0 mg, 9%), R_f 0.11 (30% ethyl acetate/*n*-hexane). Recrystallization via slow evaporation from chloroform/*n*-hexane afforded white crystals, mp 135−137 °C. IR (thin film, cm^{-1}) ν_{max} 3322 (O−H), 3204 (N−H), 3052, 2951, 2927, 2853 (C−H), 1706 (C═O), 1560. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.40 (5H, m), 5.76 (1H, br s), 4.88 (1H, m), 4.73 (2H, s), 3.88−3.98 (2H, m), 1.82 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 138.5, 128.9, 128.1, 126.5, 95.6, 74.7, 66.2, 57.1. LRMS (ESI+) *m*/*z* 336 ([M + Na]$^+$, 99%), 334 (100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{11}H_{12}{}^{35}Cl_3NO_3Na$ 333.9780, found 333.9782; [M + Na]$^+$ calcd for $C_{11}H_{12}{}^{35}Cl_2{}^{37}ClNO_3Na$ 335.9751, found 335.9749.

2-(Trimethylsilyl)ethyl (R)-2-Hydroxy-2-phenylethylcarbamate* ***25d***. General procedure 3 was followed with styrene **10** (35.0 mg, 0.336 mmol), potassium osmate dihydrate (4.9 mg, 0.013 mmol), and 2-(trimethylsilyl)ethyl *N*-(tosyloxy)carbamate **4d** (136.5 mg, 0.412 mmol). Purification by flash chromatography with 2:2:6 ethyl acetate/dichloromethane/*n*-hexane provided the title compound as a colorless solid (37.1 mg, 39%), mp 75−77 °C. R_f 0.23 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3361 (O−H), 3266 (N−H), 3072, 2953, 2929, 2899 (C−H), 1679 (C═O), 1554. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.37 (5H, m), 5.03 (1H, s), 4.84 (1H, m), 4.17 (2H, m), 3.54 (1H, m), 3.30 (1H, ddd, *J* = 14.0, 8.4, 5.6 Hz), 2.88 (1H, s), 0.98 (2H, m), 0.09 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.1, 130.1, 129.4, 127.3, 75.4, 64.9, 50.0, 19.2, 0.0. LRMS (ESI+) *m*/*z* 304 ([M + Na]$^+$, 100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{14}H_{23}NO_3SiNa$ 304.1345, found 304.1345.

Benzyl (R)-2-Hydroxy-2-phenylethylcarbamate* ***25e***[10,52] *and Benzyl (R*)-2-Hydroxy-1-phenylethylcarbamate* ***40e***.[10,52] General procedure 3 was followed with styrene **10** (30.0 mg, 0.288 mmol), potassium osmate dihydrate (1.1 mg, 0.003 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (111.1 mg, 0.346 mmol). Purification by flash chromatography with 2:3:5 ethyl acetate/dichloromethane/*n*-hexane provided (*R**)-benzyl 2-hydroxy-2-phenylethylcarbamate **25e** as a white solid (61.7 mg, 80%), mp 109−111 °C (lit.[52] 114−115 °C). R_f 0.25 (2:3:5 ethyl acetate/dichloromethane/*n*-hexane). LRMS (ESI+) *m*/*z* 294 ([M + Na]$^+$, 100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{17}NO_3Na$ 294.1106, found 294.1108. IR, ^{1}H and ^{13}C NMR data matched the literature.[10] A second fraction afforded (*R**)-benzyl 2-hydroxy-1-phenylethylcarbamate **40e** as a white solid (4.2 mg, 5%),

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mp 81−82 °C (lit.[52] 83−84.5 °C). R_f 0.16 (2:3:5 ethyl acetate/dichloromethane/*n*-hexane). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 139.0, 136.2, 128.9, 128.5, 128.2, 127.9, 126.5, 125.8, 67.0, 66.6, 57.1. LRMS (ESI+) *m*/*z* 294 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{17}NO_3Na$ 294.1106, found 294.1107. IR and ^{1}H NMR data matched the literature.[10]

tert-Butyl (1R,2R*)-2-Hydroxy-1,2-diphenylethylcarbamate* ***9a***.[46] General procedure 3 was followed with *trans*-stilbene **8** (60.0 mg, 0.333 mmol), potassium osmate dihydrate (4.0 mol %, 4.9 mg, 0.013 mmol), and *tert*-butyl *N*-(tosyloxy)carbamate **4a** (191.3 mg, 0.666 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 1:9:5 ethyl acetate/dichloromethane/*n*-hexane afforded the title compound as a white solid (89.9 mg, 86%), mp 130−131 °C (lit.[46] 137−138 °C). R_f 0.15 (1:9:5 of ethyl acetate/dichloromethane/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3415 (O−H, N−H), 3088, 3064, 3031, 3006, 2977, 2929 (C−H), 1691 (C═O), 1604, 1586. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23−7.31 (10H, m), 5.48 (1H, s), 4.89 (2H, s), 2.94 (1H, s), 1.34 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 140.8, 139.9, 128.5, 128.2, 127.7, 127.5, 126.9, 126.3, 79.8, 77.4, 60.7, 28.2. LRMS (ESI+) *m*/*z* 336 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{19}H_{23}NO_3Na$ 336.1576, found 336.1572.

Ethyl (1R,2R*)-2-Hydroxy-1,2-diphenylethylcarbamate* ***9b***.[46] General procedure 3 was followed with *trans*-stilbene **8** (30.0 mg, 0.166 mmol), potassium osmate dihydrate (4.0 mol %, 2.5 mg, 0.007 mmol), and ethyl *N*-(tosyloxy)carbamate **4b** (86.3 mg, 0.333 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 10% dichloromethane/*n*-hexane provided the title compound as a white solid (20.1 mg, 42%), mp 120−122 °C (lit.[46] 122−123.5 °C). R_f 0.23 (20% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3346 (br, O−H, N−H), 3062, 3032, 2978, 2922 (C−H), 1686 (C═O), 1533. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−7.31 (10H, m), 5.64 (1H, d, *J* = 6.9 Hz), 4.91 (2H, s), 4.00 (2H, s), 2.74 (1H, s), 1.56 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 140.7, 139.9, 128.5, 128.3, 127.8, 127.6, 126.9, 126.2, 76.9, 61.1, 61.0, 14.5. LRMS (ESI+) *m*/*z* 308 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{17}H_{19}NO_3Na$ 308.1263, found 308.1258.

2,2,2-Trichloroethyl (1R,2R*)-2-Hydroxy-1,2-diphenylethylcarbamate* ***9c***. General procedure 3 was followed with *trans*-stilbene **8** (50.0 mg, 0.277 mmol), potassium osmate dihydrate (4.0 mol %, 4.1 mg, 0.011 mmol), and 2,2,2-trichloroethyl *N*-(tosyloxy)carbamate **4c** (201.2 mg, 0.555 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 1:3:6 ethyl acetate/dichloromethane/*n*-hexane provided the title compound as a white solid (85.4 mg, 80%), mp 118−121 °C. R_f 0.20 (1:3:6 ethyl acetate/dichloromethane/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3423 (br, O−H, N−H), 3088, 3063, 3031, 3006, 2953, 2925 (C−H), 1720 (C═O), 1603, 1586, 1509. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−7.38 (10H, m), 5.93 (1H, d, *J* = 6.3 Hz), 4.99−5.04 (2H, m), 4.57−4.67 (2H, m), 2.19 (1H, d, *J* = 2.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 140.3, 139.4, 128.7, 128.4, 128.0, 127.8, 126.8, 126.1, 110.0, 95.4, 74.4, 61.0. LRMS (ESI+) *m*/*z* 414 ([M + Na]$^+$, 32%), 412 (94), 410 (100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{17}H_{16}{}^{35}Cl_3NO_3Na$ 410.0093, found 410.0090; [M + Na]$^+$ calcd for $C_{17}H_{16}{}^{35}Cl_2{}^{37}ClNO_3Na$ 412.0064, found 412.0060; [M + Na]$^+$ calcd for $C_{17}H_{16}{}^{35}Cl^{37}Cl_2NO_3Na$ 414.0034, found 414.0040.

2-(Trimethylsilyl)ethyl (1R,2R*)-2-hydroxy-1,2-diphenylethylcarbamate* ***9d***. General procedure 3 was followed with *trans*-stilbene **8** (95.0 mg, 0.527 mmol), potassium osmate dihydrate (7.7 mg, 0.021 mmol), and 2-(trimethylsilyl)ethyl *N*-(tosyloxy)carbamate **4d** (174.7 mg, 0.527 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 1:6:3 ethyl acetate/dichloromethane/*n*-hexane provided the title compound as a white solid (93.3 mg, 50%), mp 134−135 °C. R_f 0.34 (1:7:2 ethyl acetate/dichloromethane/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3339 (br, O−H, N−H), 3063, 3029, 2954, 2897 (C−H), 1689 (C═O), 1602, 1586, 1537. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.30 (10H, m), 5.61 (1H, d, *J* = 7.8 Hz), 4.93 (2H, s), 4.04 (2H, m), 2.72 (1H, s), 0.91 (2H, m), 0.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 142.2, 141.5, 130.0, 129.8, 129.3, 129.1, 128.4, 127.7, 78.5, 64.8, 62.5, 19.1, 0.0. LRMS (ESI+) *m*/*z* 380 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{20}H_{27}NO_3SiNa$ 380.1658, found 380.1659.

Benzyl (1R,2R*)2-Hydroxy-1,2-diphenylethylcarbamate* ***9e***.[10,55] General procedure 3 was followed with *trans*-stilbene **8** (100.0 mg, 0.555 mmol), potassium osmate dihydrate (4.0 mol %, 8.2 mg, 0.022 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (356.6 mg, 1.11 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 10% ethyl acetate/dichloromethane afforded the title compound as a white solid (116.3 mg, 61%), mp 148−150 °C (lit.[55] 149−151 °C). R_f 0.22 (20% ethyl acetate/dichloromethane). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 140.5, 136.3, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 126.9, 126.2, 67.0, 66.9, 61.0. LRMS (ESI+) *m*/*z* 370 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{22}H_{21}NO_3Na$ 370.1419, found 370.1420. IR and ^{1}H NMR data matched the literature.[10]

Methyl (S)-3-(Benzyloxycarbonylamino)-2-hydroxypropanoate* ***26e***.[56] General procedure 3 was followed with methyl acrylate **11** (31.4 mg, 0.365 mmol), potassium osmate dihydrate (1.3 mg, 0.004 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (135.3 mg, 0.421 mmol). Purification by flash chromatography (3:2:5 ethyl acetate/dichloromethane/*n*-hexane) provided the title compound as a colorless oil (60.2 mg, 65%). R_f 0.11 (3:2:5 ethyl acetate/dichloromethane/*n*-hexane). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 156.7, 136.3, 128.5, 128.2, 128.1, 70.1, 67.0, 52.8, 44.2. LRMS (ESI+) *m*/*z* 276 ([M + Na]$^+$, 100%), 254 ([M + H]$^+$, 20). HRMS (ESI+) [M + H]$^+$ calcd for $C_{12}H_{16}NO_5$ 254.1028, found 254.1029; [M + Na]$^+$ calcd for $C_{12}H_{15}NO_5Na$ 276.0848, found 276.0855. IR and ^{1}H NMR data matched the literature.[56]

2-(Trimethylsilyl)ethyl (S)-2-Hydroxy-4-(4-nitrophenoxy)-butylcarbamate* ***27d***[57] *and 2-(Trimethylsilyl)ethyl (S*)-1-Hydroxy-4-(4-nitrophenoxy)butan-2-ylcarbamate* ***41d***.[57] General procedure 3 was followed with 1-(but-3-enyloxy)-4-nitrobenzene **12**[58] (65.0 mg, 0.336 mmol), potassium osmate dihydrate (4.0 mol %, 4.9 mg, 0.014 mmol), and 2-(trimethylsilyl)ethyl *N*-(tosyloxy)carbamate **4d** (133.8 mg, 0.404 mmol). Purification by flash chromatography with 50% ethyl acetate/*n*-hexane afforded 2-(trimethylsilyl)ethyl (*S**)-2-hydroxy-4-(4-nitrophenoxy)butylcarbamate **27d** as a colorless oil (88.8 mg, 71%), R_f 0.5 (70% ethyl acetate/*n*-hexane). LRMS (ESI+) *m*/*z* 393 ([M + Na]$^+$, 100%), 371 ([M + H]$^+$, 10). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{26}N_2O_6SiNa$ 393.1458, found 393.1452. IR, ^{1}H, and ^{13}C NMR data matched the literature.[57] A second fraction afforded 2-(trimethylsilyl)ethyl (*S**)-1-hydroxy-4-(4-nitrophenoxy)butan-2-ylcarbamate **41d** as a colorless oil (11.9 mg, 10%), R_f 0.36 (70% ethyl acetate/*n*-hexane). LRMS (ESI+) *m*/*z* 393 ([M + Na]$^+$, 100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{26}N_2O_6SiNa$ 393.1458, found 393.1456. IR, ^{1}H, and ^{13}C NMR data matched the literature.[57]

(R)-tert-Butyl 2-Hydroxy-2-phenylpropylcarbamate* ***28a***. General procedure 3 was followed with α-methyl styrene **13** (45.0 mg, 0.381 mmol), potassium osmate dihydrate (4 mol %, 5.6 mg, 0.015 mmol), and *tert*-butyl *N*-(tosyloxy)carbamate **4a** (131.3 mg, 0.457 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 2:2:6 ethyl acetate/dichloromethane/*n*-hexane afforded the title compound as a colorless solid (65.1 mg, 68%), mp 122−124 °C. R_f 0.22 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3354 (N−H, O−H), 2974, 2925 (C−H), 1691 (C═O), 1533. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (2H, m), 7.36 (2H, m), 7.28 (1H, m), 4.76 (1H, s), 3.52 (1H, dd, *J* = 14.4, 7.6 Hz), 3.32 (1H, dd, *J* = 14.4, 5.6 Hz), 3.14 (1H, s), 1.54 (3H, s), 1.41 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 145.7, 128.3, 127.0, 125.0, 79.8, 75.0, 52.0, 28.3, 27.5. LRMS (ESI+) *m*/*z* 274 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{14}H_{21}NO_3Na$ 274.1419, found 274.1419.

(R)-2,2,2-Trichloroethyl 2-Hydroxy-2-phenylpropylcarbamate* ***28c***. General procedure 3 was followed with α-methyl styrene **13** (30.0 mg, 0.254 mmol), potassium osmate dihydrate (0.9 mg, 0.003 mmol), and 2,2,2-trichloroethyl *N*-(tosyloxy)carbamate **4c** (110.5 mg, 0.305 mmol). Purification by flash chromatography with 25% ethyl acetate/*n*-hexane provided the title compound as a colorless solid (75.6 mg, 91%), R_f 0.22 (30% ethyl acetate/*n*-hexane). Recrystallization via slow evaporation from chloroform/*n*-hexane solvent provided

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colorless crystals, mp 132−133 °C. IR (thin film, cm^{-1}) ν_{max} 3422 (O−H), 3331 (N−H), 3062, 3002, 2935, 2851 (C−H), 1716 (C═O). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (2H, m), 7.36 (2H, m), 7.26 (1H, m), 5.22 (1H, s), 4.72−4.65 (2H, m), 3.60 (1H, dd, J = 14.0, 6.8 Hz), 3.45 (1H, dd, J = 14.0, 5.6 Hz), 2.23 (1H, s), 1.53 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 145.0, 128.5, 127.3, 124.9, 77.2, 74.7, 74.5, 52.2, 27.5. LRMS (ESI+) m/z 350 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{12}H_{14}{}^{35}Cl_3NO_3Na$ 347.9937, found 347.9941; [M + Na]$^+$ calcd for $C_{12}H_{14}{}^{35}Cl_2{}^{37}ClNO_3Na$ 349.9907, found 349.9911.

Methyl (2S,3R*)-3-(tert-Butoxycarbonylamino)-2-hydroxy-3-phenylpropanoate* ***42a***[59] *and Methyl (2S*,3R*)-2-(tert-Butoxycarbonylamino)-3-hydroxy-3-phenylpropanoate* ***29a***.[60] General procedure 3 was followed with *trans*-methyl cinnamate **14** (40.0 mg, 0.247 mmol), *tert*-butyl *N*-(tosyloxy)carbamate **4a** (85.1 mg, 0.296 mmol), and potassium osmate dihydrate (3.6 mg, 0.010 mmol) in *tert*-butanol/water (3:1). The product was afforded as a mixture of two regioisomers after purification by flash chromatography with 2:2:6 ethyl acetate/dichloromethane/*n*-hexane. R_f 0.23 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). LRMS (ESI+) m/z 318 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{15}H_{21}NO_5Na$ 318.1317, found 318.1317. Further purification by preparative HPLC afforded methyl (2*S**,3*R**)-3-(*tert*-butoxycarbonylamino)-2-hydroxy-3-phenylpropanoate **42a** as a white solid (17.5 mg, 24%) at t_R 12.76 min (2% 2-propanol/98% *n*-hexane, flow rate 10 mL·min^{-1}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 155.1, 139.1, 128.6, 127.7, 126.7, 79.9, 73.5, 56.0, 53.1, 28.2. IR and ^1H NMR data matched the literature.[59] A second fraction (t_R 21.00 min) afforded methyl (2*S**,3*R**)-2-(*tert*-butoxycarbonylamino)-3-hydroxy-3-phenylpropanoate **29a** as a colorless solid (29.7 mg, 41%). IR, ^1H, and ^{13}C NMR data matched the literature.[60]

Methyl (2S,3R*)-3-(Ethoxycarbonylamino)-2-hydroxy-3-phenylpropanoate* ***42b***[10,55] *and Methyl (2S*,3R*)-2-(Ethoxycarbonylamino)-3-hydroxy-3-phenylpropanoate* ***29b***. General procedure 3 was followed with *trans*-methyl cinnamate **14** (40.0 mg, 0.247 mmol), potassium osmate dihydrate (0.9 mg, 0.003 mmol), and ethyl *N*-(tosyloxy)carbamate **4b** (161.1 mg, 0.622 mmol). Purification by flash chromatography with 40% ethyl acetate/*n*-hexane gave a mixture of regioisomers, R_f 0.22 (40% ethyl acetate/*n*-hexane). Further separation by preparative HPLC (solvent 2% 2-propanol/98% *n*-hexane, flow rate 10 mL·min^{-1}) afforded methyl (2*S**,3*R**)-3-(ethoxycarbonylamino)-2-hydroxy-3-phenylpropanoate **42b** (t_R 22.42 min) as a colorless solid (20.4 mg, 31%). LRMS (ESI+) m/z 290 ([M + Na]$^+$, 100). HRMS (ESI+) [M + H]$^+$ calcd for $C_{13}H_{18}NO_5$ 268.1185, found 268.1182; [M + Na]$^+$ calcd for $C_{13}H_{17}NO_5Na$ 290.1004, found 290.1005. IR, ^1H, and ^{13}C NMR data matched the literature.[10] A second fraction (t_R 30.03 min) afforded methyl (2*S**,3*R**)-2-(ethoxycarbonylamino)-3-hydroxy-3-phenylpropanoate **29b** (33.3 mg, 51%) as a colorless oil. IR (thin film, cm^{-1}) ν_{max} 3401 (O−H, N−H), 3020, 2955, 2931, 2851 (C−H), 1720, 1701 (C═O), 1622, 1516. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.36 (4H, m), 7.30 (1H, m), 5.48 (1H, d, J = 8.4 Hz), 5.25 (1H, m), 4.57 (1H, d, J = 7.6 Hz), 4.00−4.01 (2H, m), 3.76 (3H, s), 2.81 (1H, s), 1.16 (3H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 156.5, 139.6, 128.4, 128.1, 125.9, 73.7, 61.3, 59.7, 52.6, 14.4. LRMS (ESI+) m/z 290 ([M + Na]$^+$, 95). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{17}NO_5Na$ 290.1004, found 290.1004; [M + H]$^+$ calcd for $C_{13}H_{18}NO_5$ 268.1185, found 268.1184.

Methyl (2S,3R*)-2-Hydroxy-3-phenyl-3-[(2,2,2-trichloroethoxy)carbonylamino]propanoate* ***42c***[61] *and Methyl (2S*,3R*)-3-Hydroxy-3-phenyl-2-[(2,2,2-trichloroethoxy)carbonylamino]propanoate* ***29c***. General procedure 3 was followed with *trans*-methyl cinnamate **14** (40.0 mg, 0.247 mmol), potassium osmate dihydrate (0.9 mg, 0.003 mmol), and 2,2,2-trichloroethyl *N*-(tosyloxy)carbamate **4c** (107.3 mg, 0.296 mmol). Purification by flash chromatography with 25% ethyl acetate/*n*-hexane afforded a mixture of both regioisomers, R_f 0.22 (30% ethyl acetate/*n*-hexane). Further separation by preparative HPLC with 4% 2-propano/96% *n*-hexane at a flow rate of 10 mL·min^{-1} provided methyl (2*S**,3*R**)-2-hydroxy-3-phenyl-3-[(2,2,2-trichloroethoxy)carbonylamino]propanoate **42c** (t_R 7.82 min) as a colorless oil (33.1 mg, 36%). IR (thin film, cm^{-1}) ν_{max} 3351 (O−H, N−H), 3066, 3020, 2955, 2855 (C−H), 1735 (C═O), 1522. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 154.0, 138.3, 128.7, 128.1, 126.7, 95.4, 74.6, 73.2, 56.6, 53.2. LRMS (ESI+) m/z 396 ([M + Na]$^+$, 18%), 394 (50), 392 (53). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{35}Cl_3NO_5Na$ 391.9835, found 391.9839; [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{35}Cl_2{}^{37}ClNO_5Na$ 393.9806, found 393.9808; [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{35}Cl^{37}Cl_2NO_5Na$ 395.9776, found 395.9770; [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{37}Cl_3NO_5Na$ 397.9747, found 397.9747. The ^1H NMR data matched the literature.[61] A second fraction (t_R 10.22 min) afforded methyl (2*S**,3*R**)-3-hydroxy-3-phenyl-2-[(2,2,2-trichloroethoxy)carbonylamino]propanoate **29c** as a colorless oil (42.2 mg, 46%). IR (thin film, cm^{-1}) ν_{max} 3431 (O−H, N−H), 3065, 3029, 2955 (C−H), 1733 (C═O), 1606, 1521. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.27 (5H, m), 5.85 (1H, d, J = 9.6 Hz), 5.35 (1H, t, J = 3.2 Hz), 4.66−4.61 (2H, m), 4.55 (1H, d, J = 12.0 Hz), 3.80 (3H, s), 2.67 (1H, d, J = 4.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.5, 139.3, 128.5, 128.3, 125.8, 95.2, 74.6, 73.5, 59.9, 52.8. LRMS (ESI+) m/z 396 ([M + Na]$^+$, 32%), 394 (98), 392 (100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{35}Cl_3NO_5Na$ 391.9835, found 391.9835; [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{35}Cl_2{}^{37}ClNO_5Na$ 393.9806, found 393.9801; [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{35}Cl^{37}Cl_2NO_5Na$ 395.9776, found 395.9781; [M + Na]$^+$ calcd for $C_{13}H_{14}{}^{37}Cl_3NO_5Na$ 397.9747, found 397.9747.

Methyl (2S,3R*)-2-Hydroxy-3-phenyl-3-{[2-(trimethylsilyl)-ethoxy]carbonylamino}propanoate* ***42d*** *and Methyl (2S*,3R*)-3-Hydroxy-3-phenyl-2-{[2-(trimethylsilyl)ethoxy]carbonylamino}-propanoate* ***29d***.[62] General procedure 3 was followed with *trans*-methyl cinnamate **14** (56.0 mg, 0.345 mmol), potassium osmate dihydrate (4.0 mol %, 5.0 mg, 0.014 mmol), and 2-(trimethylsilyl)ethyl *N*-(tosyloxy)carbamate **4d** (147.4 mg, 0.445 mmol). Purification by flash chromatography with 2:2:6 ethyl acetate/dichloromethane/*n*-hexane provided a mixture of both regioisomers, R_f 0.22 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). Further separation by preparative HPLC with 2% 2-propanol/98% *n*-hexane at a flow rate of 10 mL·min^{-1} afforded methyl (2*S**,3*R**)-2-hydroxy-3-phenyl-3-{[2-(trimethylsilyl)ethoxy]carbonylamino}propanoate **42d** (t_R 12.24 min) as a colorless liquid (22.3 mg, 19%). IR (thin film, cm^{-1}) ν_{max} 3370 (br, O−H, N−H), 3067, 3021, 2953 (C−H), 1721, 1697 (C═O), 1603, 1514. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.36 (5H, m), 5.51 (1H, d, J = 9.0 Hz), 5.25 (1H, d, J = 9.3 Hz), 4.49 (1H, m), 4.12 (2H, m), 3.85 (3H, s), 3.15 (1H, s), 0.96 (2H, m), 0.00 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 157.5, 140.5, 130.2, 129.4, 128.2, 74.9, 65.0, 57.8, 54.7, 19.1, 0.0. LRMS (ESI+) m/z 362 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{25}NO_5SiNa$ 362.1400, found 362.1402. A second fraction (t_R 19.87 min) afforded methyl (2*S**,3*R**)-3-hydroxy-3-phenyl-2-{[2-(trimethylsilyl)ethoxy]-carbonylamino}propanoate **29d** as a colorless liquid (34.9 mg, 30%). IR (thin film, cm^{-1}) ν_{max} 3401 (O−H, N−H), 3065, 3029, 2953, 2898 (C−H), 1752, 1724, 1701 (C═O), 1606, 1513. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.38 (5H, m), 5.42 (1H, d, J = 8.4 Hz), 5.26 (1H, m), 4.58 (1H, d, J = 7.2 Hz), 4.06−4.03 (2H, m), 3.76 (3H, s) 2.76 (1H, s), 0.91 (2H, t, J = 7.6 Hz), 0.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 158.1, 141.1, 130.0, 129.7, 127.4, 75.3, 65.2, 61.2, 54.2, 19.1, 0.0. LRMS (ESI+) m/z 362 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{25}NO_5SiNa$ 362.1400, found 362.1400; [M + H]$^+$ calcd for $C_{16}H_{26}NO_5Si$ 340.1580, found 340.1580.

Ethyl (2S,3R*)-3-(Benzyloxycarbonylamino)-2-hydroxy-3-phenylpropanoate* ***43e***[63] *and Ethyl (2S*,3R*)-2-(Benzyloxycarbonylamino)-3-hydroxy-3-phenylpropanoate* ***30e***.[63] General procedure 3 was followed with *trans*-ethyl cinnamate **15** (50.0 mg, 0.284 mmol), potassium osmate dihydrate (1.0 mol %, 1.1 mg, 0.003 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (109.9 mg, 0.341 mmol). Purification by flash chromatography with 2:2:6 ethyl acetate/dichloromethane/*n*-hexane afforded a mixture of two regioisomers, R_f 0.33 (3:2:5 ethyl acetate/dichloromethane/*n*-hexane). Further purification by preparative HPLC with 1% 2-propanol/99% *n*-hexane at a flow rate of 10 mL·min^{-1} provided ethyl (2*S**,3*R**)-3-(benzyloxycarbonylamino)-2-hydroxy-3-phenylpropanoate **43e** (t_R 9.20 min) as a white solid (34.5 mg, 35%), mp 86−88 °C. IR (thin

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film, cm^{-1}) ν_{max} 3367 (O−H, N−H), 3089, 3064, 2981, 2960, 2934, 2851 (C−H), 1730 (C═O), 1604, 1586, 1519. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.40 (10H, m), 5.69 (1H, d, J = 9.2 Hz), 5.29 (1H, d, J = 8.8 Hz), 5.12−5.03 (2H, m), 4.47 (1H, s), 4.29−4.23 (2H, m), 3.19 (1H, d, J = 4.0 Hz), 1.28 (3H, t, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.7, 155.6, 138.9, 136.3, 128.6, 128.5, 128.1, 128.1, 127.8, 126.7, 73.4, 67.0, 62.6, 56.4, 14.0. LRMS (ESI+) m/z 366 ([M + Na]$^+$, 100%), 344 (5). HRMS (ESI+) [M + H]$^+$ calcd for $C_{19}H_{22}NO_5$ 344.1498, found 344.1496; [M + Na]$^+$ calcd for $C_{19}H_{21}NO_5Na$ 366.1317, found 366.1317. A second fraction afforded ethyl (2*S**,3*R**)-2-(benzyloxycarbonylamino)-3-hydroxy-3-phenylpropanoate **30e** (t_R 14.68 min) as a white solid (45.7 mg, 47%), mp 78−80 °C. IR (thin film, cm^{-1}) ν_{max} 3423 (O−H, N−H), 3064, 3032, 2981, 2962, 2937(C−H), 1726 (C═O), 1605, 1518. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27−7.37 (10H, m), 5.59 (1H, d, J = 8.8 Hz), 5.25 (1H, s), 5.01 (2H, s), 4.59 (1H, d, J = 6.8 Hz), 4.24−4.16 (2H, m), 2.73 (1H, d, J = 3.2 Hz), 1.24 (3H, t, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 156.3, 139.6, 136.2, 128.4, 128.2, 128.1 (2C), 127.9, 126.0, 73.8, 67.0, 61.8, 59.9, 14.0. LRMS (ESI+) m/z 366 ([M + Na]$^+$, 100%), 344 (14). HRMS (ESI+) [M + H]$^+$ calcd for $C_{19}H_{22}NO_5$ 344.1498, found 344.1498; [M + Na]$^+$ calcd for $C_{19}H_{21}NO_5Na$ 366.1317, found 366.1317.

Dimethyl (2S,3S*)-2-(Benzyloxycarbonylamino)-3-hydroxysuccinate* ***31e***.[10,55] General procedure 3 was followed with dimethyl fumarate **16** (40.0 mg, 0.278 mmol), potassium osmate dihydrate (1.0 mg, 0.003 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (107.8 mg, 0.335 mmol). Purification by flash chromatography with 40% ethyl acetate/*n*-hexane provided the title compound as a white solid (74.6 mg, 86%), mp 124−126 °C (lit.[55] 129−130 °C). R_f 0.23 (50% ethyl acetate/*n*-hexane). LRMS (ESI+) m/z 334 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{14}H_{17}NO_7Na$ 334.0903, found 334.0903. IR, ^1H, and ^{13}C NMR data matched the literature.[10]

2,2,2-Trichloroethyl (1R,2S*)-2-Hydroxy-2,3-dihydro-1H-inden-1-ylcarbamate* ***44c***[64] *and 2,2,2-Trichloroethyl (1R*,2S*)-1-Hydroxy-2,3-dihydro-1H-inden-2-ylcarbamate* ***32c***. General procedure 3 was followed with indene **17** (30.0 mg, 0.258 mmol), potassium osmate dihydrate (0.9 mg, 0.003 mmol), and 2,2,2-trichloroethyl *N*-(tosyloxy)carbamate **4c** (110.1 mg, 0.304 mmol). Purification by flash chromatography with 20% ethyl acetate/*n*-hexane provided 2,2,2-trichloroethyl (1*R**,2*S**)-2-hydroxy-2,3-dihydro-1*H*-inden-1-ylcarbamate **44c** as a colorless oil (17.5 mg, 21%). R_f 0.20 (30% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3411 (O−H), 3350 (N−H), 3074, 3045, 3028, 2952, 2926, 2853 (C−H), 1717 (C═O), 1599, 1514. LRMS (ESI+) m/z 348 (30%), 346 ([M + Na]$^+$, 40). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{12}H_{12}{}^{35}Cl_3NO_3Na$ 345.9780, found 345.9768; [M + Na]$^+$ calcd for $C_{12}H_{12}{}^{35}Cl_2{}^{37}ClNO_3Na$ 347.9751, found 347.9756. The ^1H and ^{13}C NMR data matched the literature.[64] A second fraction afforded 2,2,2-trichloroethyl (1*R**,2*S**)-1-hydroxy-2,3-dihydro-1*H*-inden-2-ylcarbamate **32c** as a colorless solid (18.3 mg, 22%), mp 112−115 °C. R_f 0.16 (30% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3404 (O−H), 3328 (N−H), 3072, 3026, 2925, 2849 (C−H), 1714 (C═O), 1514. ^1H NMR (300 MHz, $CDCl_3$) δ 7.46−7.38 (4H, m), 5.70 (1H, d, J = 8.1 Hz), 5.18 (1H, dd, J = 8.7, 5.1 Hz), 4.88 (1H, d, J = 11.7 Hz), 4.76 (1H, d, J = 12.3 Hz), 4.67 (1H, m), 3.19 (1H, dd, J = 16.5, 4.8 Hz), 2.96 (1H, d, J = 16.5 Hz), 1.90 (1H, d, J = 4.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 140.0, 139.5, 128.5, 127.4, 125.5, 124.5, 95.5, 74.7, 73.5, 59.3, 39.7. LRMS (ESI+) m/z 348 ([M + Na]$^+$, 24%), 346 ([M + Na]$^+$, 25). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{12}H_{12}{}^{35}Cl_3NO_3Na$ 345.9780, found 345.9773; [M + Na]$^+$ calcd for $C_{12}H_{12}{}^{35}Cl_2{}^{37}ClNO_3Na$ 347.9751, found 347.9743.

2-(Trimethylsilyl)ethyl (1R,2S*)-1-Hydroxy-2,3-dihydro-1H-inden-2-ylcarbamate* ***32d*** *and 2-(Trimethylsilyl)ethyl (1R*,2S*)-2-Hydroxy-2,3-dihydro-1H-inden-1-ylcarbamate* ***44d***.[64] General procedure 3 was followed with indene **17** (39.2 mg, 0.338 mmol), potassium osmate dihydrate (4.0 mol %, 4.9 mg, 0.014 mmol), and 2-(trimethylsilyl)ethyl *N*-(tosyloxy)carbamate **4d** (148.0 mg, 0.447 mmol). Purification by flash chromatography with 30% ethyl acetate/*n*-hexane afforded a mixture of both regioisomers, R_f 0.38 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). Further separation by preparative HPLC with 1% 2-propanol/99% *n*-hexane at a flow rate of 8 mL·min^{-1} provided 2-(trimethylsilyl)ethyl (1*R**,2*S**)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl carbamate **32d** (t_R 33.81 min) as an oil (47.8 mg, 48%). IR (thin film, cm^{-1}) ν_{max} 3413 (O−H, N−H), 3071, 3046, 2952, 2897, (C−H), 1718, 1691 (C═O), 1512. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, d, J = 6.8 Hz), 7.20−7.28 (3H, m), 5.25 (1H, s), 5.00 (1H, m), 4.38 (1H, m), 4.14 (2H, t, J = 8.4 Hz), 3.20 (1H, dd, J = 16.0, 7.6 Hz), 2.84 (1H, dd, J = 16.0, 7.6 Hz), 1.91 (1H, s), 0.96 (2H, t, J = 8.4 Hz), 0.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 143.5, 142.5, 130.8, 128.8, 126.7, 126.6, 76.2, 64.7, 56.3, 38.3, 19.2, 0.0. LRMS (ESI+) m/z 316 ([M + Na]$^+$, 100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{15}H_{23}NO_3SiNa$ 316.1345, found 316.1344. A second fraction (t_R 41.53 min) afforded 2-(trimethylsilyl)-ethyl (1*R**,2*S**)-2-hydroxy-2,3-dihydro-1*H*-inden-1-ylcarbamate **44d** as an oil (22.5 mg, 23%). IR (thin film, cm^{-1}) ν_{max} 3408 (O−H), 3323 (N−H), 3047, 2952, 2897 (C−H), 1720, 1694 (C═O), 1609, 1518. LRMS (ESI+) m/z 316 ([M + Na]$^+$, 100). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{15}H_{23}NO_3SiNa$ 316.1345, found 316.1344. IR, ^1H, and ^{13}C NMR data matched the literature.[64]

(S)-tert-Butyl 1,3-Dihydroxy-3-methylbutan-2-ylcarbamate* ***33a***.[65] General procedure 3 was followed with 3-methyl-2-buten-1-ol **18** (34.7 mg, 0.406 mmol), *tert*-butyl *N*-(tosyloxy)carbamate **4a** (140.1 mg, 0.488 mmol), and potassium osmate dihydrate (5.9 mg, 0.016 mmol) in *tert*-butanol/water (3:1). Purification by flash chromatography with 5:2:3 ethyl acetate/dichloromethane/*n*-hexane afforded the title compound as a yellow oil (47.8 mg, 54%). R_f 0.33 (60% ethyl acetate/dichloromethane/*n*-hexane). LRMS (ESI+) m/z 242 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{10}H_{21}NO_4Na$ 242.1368; found 242.1366. IR, ^1H, and ^{13}C NMR data matched the literature.[65]

Benzyl (R)-(1,3-Dihydroxy-3-methylbutan-2-ylcarbamate* ***33e***.[66] General procedure 3 was followed with 3-methyl-2-buten-1-ol **18** (64.3 mg, 0.747 mmol), potassium osmate dihydrate (9.2 mg, 0.025 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (200 mg, 0.622 mmol) in acetonitrile/water (3:1). Purification by flash chromatography with 3:2:5 ethyl acetate/dichloromethane/*n*-hexane provided the title compound as a yellow oil (101.0 mg, 64%). R_f 0.13 (3:2:5 ethyl acetate/dichloromethane/*n*-hexane). LRMS (ESI+) m/z 276 ([M + Na]$^+$, 100%), 236 (20). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{19}NO_4Na$ 276.1212, found 276.1212. IR, ^1H, and ^{13}C NMR data matched the literature.[66]

Ethyl (1S,2R*)-2-Hydroxy-2-methylcyclohexylcarbamate* ***34b***.[46] General procedure 3 was followed with 1-methylcyclohex-1-ene **19** (48.5 mg, 0.504 mmol), potassium osmate dihydrate (4.0 mol %, 7.43 mg, 0.020 mmol), and ethyl *N*-(tosyloxy)carbamate **4b** (161.6 mg, 0.620 mmol). Purification by flash chromatography provided the title compound as a brown oil (75.1 mg, 74%). R_f 0.22 (2:2:6 ethyl acetate/dichloromethane/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3436 (O−H), 3395 (N−H), 2931, 2855 (C−H), 1696 (C═O), 1515. ^1H NMR (400 MHz, $CDCl_3$) δ 5.01 (1H, d, J = 8.0 Hz), 4.10 (2H, q, J = 6.8 Hz), 3.40 (1H, m), 1.67−1.76 (4H, m), 1.53 (1H, s), 1.41−1.51 (4H, m), 1.22−1.25 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 71.4, 60.7, 56.0, 39.0, 29.1, 27.7, 24.8, 21.0, 14.6. LRMS (ESI+) m/z 224 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{10}H_{19}NO_3Na$ 224.1263, found 224.1258.

Ethyl 2-Methyl-6-oxocyclohex-1-enylcarbamate ***36b***.[67] General procedure 3 was followed with 3-methylcyclohex-2-enone **21** (58.2 mg, 0.528 mmol), potassium osmate dihydrate (7.79 mg, 0.021 mmol), and ethyl *N*-(tosyloxy)carbamate **4b** (165.9 mg, 0.640 mmol). Purification by flash chromatography provided the title compound as a brown viscous oil (37.4 mg, 36%). R_f 0.42 (60% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3317 (N−H), 2925, 2852 (C−H), 1727 (C═O), 1672, 1639. ^1H NMR (400 MHz, $CDCl_3$) δ 6.42 (1H, s), 4.13 (2H, q, J = 6.9 Hz), 2.49−2.44 (4H, m), 1.97 (2H, m), 1.94 (3H, s), 1.26 (3H, t, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 154.3, 151.7, 129.6, 61.4, 36.8, 32.2, 29.7, 21.3, 14.5. LRMS (ESI+) m/z 220 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{10}H_{15}NO_3Na$ 220.0950, found 220.0950. A second fraction afforded recovered starting material **21** (23.2 mg, 40%).

Benzyl (2S,3R*)-2,3-Dihydroxy-2-methylbutylcarbamate* ***(2S*,3R*)-38e*** *and Benzyl (2R*,3R*)-2,3-Dihydroxy-2-methylbutyl-*

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carbamate (2R,3R*)-38e.* General procedure 3 was followed with 3-methylbut-3-en-2-ol **23** (48.5 mg, 0.56 mmol), potassium osmate dihydrate (8.30 mg, 0.02 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (217 mg, 0.68 mmol). Purification by flash chromatography with 40% ethyl acetate/*n*-hexane afforded a mixture of two diastereomers as a colorless oil (64.6 mg, 45%), R_f 0.27 (70% ethyl acetate/*n*-hexane). Integration of the NH signal of the 400 MHz ^{1}H NMR spectrum showed a 2.4:1 ratio of benzyl (2*S**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*S**,3*R**)-38e** and benzyl (2*R**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*R**,3*R**)-38e**.

To a solution of (2*R**,3*S**)-4-(benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl acetate **(2*S**,3*R**)-39e** (20.0 mg, 0.068 mmol) in methanol (0.5 mL) and dichloromethane (3.0 mL) was added a freshly prepared solution of ammonia in methanol (2.0 mL, 10%). This mixture was stirred at room temperature until the reaction was complete (9 h), quenched with aqueous hydrochloric acid (3.0 mL, 1.0 M), and extracted with dichloromethane (3 × 10 mL). The combined dichloromethane extracts were washed with brine (5 mL), dried over sodium sulfate, and concentrated under reduced pressure to afford benzyl (2*S**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*S**,3*R**)-38e** as a yellow oil (17.0 mg, 99%). R_f 0.35 (80% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3401 (O−H, N−H), 3066, 3033, 2925, 2854 (C−H), 1700 (C═O), 1525. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.38 (5H, m), 5.28 (1H, s), 5.12 (2H, s), 3.68 (1H, q, J = 6.8 Hz), 3.50 (1H, dd, J = 14.8, 6.0 Hz), 3.12 (1H, dd, J = 14.4, 6.4 Hz), 2.29 (1H, m), 2.05 (1H, m), 1.19 (3H, d, J = 6.8 Hz), 1.13 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.07, 136.17, 128.55, 128.25, 128.13, 74.68, 71.34, 67.19, 47.09, 20.67, 16.66. LRMS (ESI+) m/z 276 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{19}NO_4Na$ 276.1212, found 276.1213.

To a solution of (2*R**,3*R**)-4-(benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl acetate **(2*R**,3*R**)-39e** (20 mg, 0.07 mmol) in dichloromethane (3.0 mL) and methanol (0.5 mL) was added a freshly prepared solution of ammonia in methanol (2.0 mL, 10%). This reaction mixture was stirred at room temperature, quenched with aqueous hydrochloric acid (3.0 mL, 1.0 M), and extracted with dichloromethane (3 × 5 mL). The combined dichloromethane extracts were washed with brine (5 mL) and dried over sodium sulfate. Purification by flash chromatography with 50% ethyl acetate/*n*-hexane afforded benzyl (2*R**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*R**,3*R**)-38e** as a colorless liquid (10.1 mg, 59%). R_f 0.33 (80% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3368 (O−H, N−H), 3066, 3033, 2976, 2923, 2853 (C−H), 1700 (C═O), 1649 (C═C), 1538. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.37 (5H, m), 5.12 (3H, br s), 3.67 (1H, q, J = 4.5 Hz), 3.40 (1H, dd, J = 14.1, 7.2 Hz), 3.09 (1H, dd, J = 14.1, 5.7 Hz), 2.97 (1H, s), 2.62 (1H, s), 1.17 (3H, d, J = 6.6 Hz), 1.09 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.79, 136.12, 128.59, 128.32, 128.16, 74.36, 69.90, 67.23, 48.63, 20.19, 16.61. LRMS (ESI+) m/z 276 ([M + Na]$^+$, 25%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{13}H_{19}NO_4Na$ 276.1212, found 276.1214.

(2R,3S*)-4-(Benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl Acetate (2R*,3S*)-39e and (2R*,3R*)-4-(Benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl Acetate (2R*,3R*)-39e.* General procedure 3 was followed with 3-methylbut-3-en-2-yl acetate **24** (27.1 mg, 0.21 mmol), potassium osmate dihydrate (3.10 mg, 0.0084 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (81.6 mg, 0.25 mmol). Purification by flash chromatography with gradient elution by 60−100% diethyl ether/*n*-hexane afforded (2*R**,3*S**)-4-(benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl acetate **(2*R**,3*S**)-39e** as a colorless oil (30.4 mg, 49%). R_f 0.14 (80% diethyl ether/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3415 (N−H, O−H), 3090, 3066, 3034, 2985, 2943 (C−H), 1724 (C═O), 1532. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.36 (5H, m), 5.31 (1H, br s), 5.07−5.15 (2H, m), 4.90 (1H, q, J = 6.4 Hz), 3.34 (1H, dd, J = 14.0, 7.2 Hz), 3.15 (1H, dd, J = 14.4, 5.6 Hz), 2.50 (1H, s), 2.06 (3H, s), 1.25 (3H, d, J = 6.0 Hz), 1.16 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 157.8, 136.3, 128.5, 128.2, 128.1, 73.8, 73.3, 67.1, 47.4, 21.2, 20.6, 14.3. LRMS (ESI+) m/z 318 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + H]$^+$ calcd for $C_{15}H_{22}NO_5$ 296.1498, found 296.1499; [M + Na]$^+$ calcd for $C_{15}H_{21}NO_5Na$ 318.1317, found 318.1318. A second fraction afforded (2*R**,3*R**)-4-(benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl acetate **(2*R**,3*R**)-39e** as a colorless oil (12.1 mg, 19%). R_f 0.09 (80% diethyl ether/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3584 (O−H), 3419 (N−H), 3090, 3066, 3033, 2984, 2942 (C−H), 1722 (C═O), 1529. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.38 (5H, m), 5.16 (1H, s), 5.08−5.14 (2H, m), 4.89 (1H, q, J = 6.4 Hz), 3.34 (1H, dd, J = 13.6, 6.0 Hz), 3.17 (1H, dd, J = 14.0, 6.0 Hz), 2.09 (3H, s) 1.44 (1H, s), 1.25 (3H, d, J = 6.4 Hz), 1.16 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 157.0, 136.3, 128.5, 128.2, 128.1, 74.3, 74.1, 67.0, 47.8, 30.3, 20.4, 14.8. LRMS (ESI+) m/z 318 ([M + Na]$^+$, 100). HRMS (ESI+) [M + H]$^+$ calcd for $C_{15}H_{22}NO_5$ 296.1498; found 296.1498; [M + Na]$^+$ calcd for $C_{15}H_{21}NO_5Na$ 318.1317, found 318.1317. The anti- and syn-diastereomeric structures were confirmed by NOESY_1D analysis of their acetonide derivatives.

Benzyl [(4*S,5*R**)-2,2,4,5-Tetramethyl-1,3-dioxolan-4-yl]-methylcarbamate 46.** To a stirred solution of benzyl (2*S**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*S**,3*R**)-38e** (15.0 mg, 0.059 mmol) in 2,2-dimethoxypropane (67.0 mg, 0.64 mmol) and dichloromethane (3.0 mL) were added camphorsulfonic acid (0.6 mg, 0.003 mmol) and *p*-toluenesulfonic acid (0.5 mg, 0.003 mmol). The mixture was stirred until the reaction was complete, quenched with aqueous sodium hydrogen carbonate (3.0 mL, 1.0 M), and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were washed with brine (5 mL), dried over sodium sulfate, and concentrated under reduced pressure. Purification by flash chromatography with 20% ethyl acetate/*n*-hexane afforded the title compound **46** as a colorless oil (14.5 mg, 83%). R_f 0.18 (20% ethyl acetate/*n*-hexane). IR (thin film, cm^{-1}) ν_{max} 3345 (N−H), 3036, 2983, 2933, 2869 (C−H), 1724 (C═O), 1513. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.37 (5H, m), 5.11 (2H, s), 5.06 (1H, d, J = 8.4 Hz), 4.00 (1H, q, J = 6.4 Hz), 3.32 (1H, dd, J = 12.8, 8.8 Hz), 3.10 (1H, m), 1.41 (3H, s), 1.35 (3H, s), 1.24 (3H, d, J = 6.4 Hz), 1.22 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.00, 142.92, 136.72, 128.66, 128.25, 107.47, 81.43, 78.70, 66.95, 45.24, 28.48, 26.71, 21.34, 12.99. LRMS (ESI+) m/z 316 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + H]$^+$ calcd for $C_{16}H_{24}NO_4$ 294.1705, found 294.1700; [M + Na]$^+$ calcd for $C_{16}H_{23}NO_4Na$ 316.1525, found 316.1518.

Benzyl [(4*R,5*R**)-2,2,4,5-Tetramethyl-1,3-dioxolan-4-yl)-methylcarbamate 47.** To a stirred solution of benzyl (2*R**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*R**,3*R**)-38e** (15.0 mg, 0.059 mmol) in 2,2-dimethoxypropane (61.9 mg, 0.59 mmol) and dichloromethane (3.0 mL) were added camphorsulfonic acid (0.600 mg, 0.002 mmol) and *p*-toluenesulfonic acid (0.500 mg, 0.003 mmol). The mixture was stirred until the reaction was complete, quenched with aqueous sodium hydrogen carbonate (3.0 mL, 1.0 M), and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were washed with brine (5 mL), dried over sodium sulfate, and concentrated under reduced pressure. The title compound **47** was afforded without further purification as a colorless oil (14.5 mg, 83%). IR (thin film, cm^{-1}) ν_{max} 3347 (N−H), 2978, 2926, 2862 (C−H), 1717 (C═O), 1537. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.36 (5H, m), 5.06−5.16 (3H, m), 3.95 (1H, q, J = 6.0 Hz), 3.31 (1H, dd, J = 14.0, 6.8 Hz), 3.19 (1H, dd, J = 14.0, 5.2 Hz), 1.32 (3H, s), 1.26 (3H, s), 1.21 (3H, d, J = 6.4 Hz), 1.08 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.65, 136.46, 128.51, 128.14, 128.05, 106.95, 85.50, 82.13, 66.84, 46.14, 28.55, 26.67, 19.61, 14.13. LRMS (ESI+) m/z 316 ([M + Na]$^+$, 88%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{16}H_{23}NO_4Na$ 316.1525, found 316.1523.

General Procedure 4 for Competition Reactions. To a mixture of alkene A (1.0 equiv), alkene B (1.0 equiv), and potassium osmate dihydrate (4.0 mol %) in acetonitrile (1.0 mL) and water (1.0 mL) was added solution benzyl *N*-(tosyloxy)carbamate **4e** (1.0 equiv) in acetonitrile (2.0 mL). This mixture was stirred until the reaction was complete, quenched with aqueous sodium hydrogen sulfite (5.0 mL, 0.05 M), and stirred for 30 min. The mixture was filtered through Celite and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate extracts were washed with brine (10 mL), dried (Na_2SO_4), and concentrated to afford the crude product. Purification by flash chromatography afforded the target compounds.

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*Competition between trans-Stilbene **8** and Styrene **10**.* The reaction was conducted according to general procedure 4 with *trans*-stilbene **8** (70.5 mg, 0.39 mmol), styrene **10** (40.5 mg, 0.39 mmol), potassium osmate dihydrate (5.4 mg, 0.015 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (125 mg, 0.39 mmol). Purification by flash chromatography with 25% ethyl acetate/*n*-hexane afforded benzyl (1*R**,2*R**)-2-hydroxy-1,2-diphenylethylcarbamate **9e** as a white solid (58.2 mg, 43%). A second fraction afforded benzyl (*R**)-2-hydroxy-2-phenylethylcarbamate **25e** as a colorless oil (37.7 mg, 36%).

*Competition between 1H-Indene **17** and Styrene **10**.* The reaction was conducted according to general procedure 4 with 1*H*-indene **17** (49.0 mg, 0.42 mmol), styrene **10** (43.9 mg, 0.42 mmol), potassium osmate dihydrate (5.40 mg, 0.02 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (135.6 mg, 0.42 mmol). Purification by flash chromatography with 20% ethyl acetate/*n*-hexane afforded an inseparable mixture of two regioisomers from 1*H*-indene and one regioisomer from styrene. Further separation by preparative HPLC (SunFire prep silica 5 μm, 2% 2-propanol/98% *n*-hexane, flow rate 0.7 mL·min^{-1}) afforded benzyl (1*R**,2*S**)-1-hydroxy-2,3-dihydro-1*H*-inden-2-ylcarbamate[68] **32e** as an orange oil (26.8 mg, 22%) at t_R 8.57 min. LRMS (ESI+) *m*/*z* 306 ([M + Na]$^+$, 85%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{17}H_{17}NO_3Na$ 306.1106, found 306.1105. IR, ^{1}H, and ^{13}C NMR data matched the literature.[68] A second fraction afforded benzyl (1*R**,2*S**)-2-hydroxy-2,3-dihydro-1*H*-inden-1-ylcarbamate[68] **44e** as an orange oil (20.1 mg, 17%) at t_R 13.44 min. LRMS (ESI+) *m*/*z* 306 ([M + Na]$^+$, 100%). HRMS (ESI+) [M + Na]$^+$ calcd for $C_{17}H_{17}NO_3Na$ 306.1106, found 306.1106. IR, ^{1}H, and ^{13}C NMR data matched the literature.[68] A third fraction afforded benzyl (*R**)-2-hydroxy-2-phenylethylcarbamate **25e** as a colorless oil (33.6 mg, 29%) at t_R 17.90 min.

*Competition between 3-Methylbut-2-en-1-ol **18** and Styrene **10**.* The reaction was conducted according to general procedure 4 with 3-methylbut-2-en-1-ol **18** (39.1 mg, 0.44 mmol), styrene **10** (45.9 mg, 0.44 mmol), potassium osmate dihydrate (5.1 mg, 0.014 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (142 mg, 0.44 mmol). Purification by flash chromatography with gradient elution from 25% to 50% ethyl acetate/*n*-hexane afforded benzyl (*R**)-2-hydroxy-2-phenylethylcarbamate **25e** as a colorless solid (70.3 mg, 59%). A second fraction afforded benzyl (*R**)-2-hydroxy-1-phenylethylcarbamate **40e** as a colorless oil (6.8 mg, 5.7%).

*Competition between 3-Methylbut-3-en-2-yl Acetate **24** and 3-Methylbut-3-en-2-ol **23**.* The reaction was conducted according to general procedure 4 with 3-methylbut-3-en-2-ol **23** (30.0 mg, 0.35 mmol), 3-methylbut-3-en-2-yl acetate **24** (44.6 mg, 0.35 mmol), potassium osmate dihydrate (5.1 mg, 0.014 mmol), and benzyl *N*-(tosyloxy)carbamate **4e** (112 mg, 0.35 mmol). Purification by flash chromatography with 40% ethyl acetate/*n*-hexane afforded a separable mixture of **(2*R**,3*S**)**- and **(2*R**,3*R**)-39e** as a colorless oil (15.9 mg) in the first fraction and **(2*S**,3*R**)**- and **(2*R**,3*R**)-38e** as a colorless oil (29.8 mg) in the second fraction. Separation of the first fraction by preparative HPLC (SunFire silica 5 μm, 4.6 × 150 mm, 5% 2-propanol/*n*-hexane, flow rate 0.6 mL·min^{-1}) afforded 4-(benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl acetate **(2*R**,3*S**)-39e** as a colorless oil (11.2 mg, 11%) at t_R 9.64 min and (2*R**,3*R**)-4-(benzyloxycarbonylamino)-3-hydroxy-3-methylbutan-2-yl acetate **(2*R**,3*R**)-39e** as a colorless oil (4.7 mg, 5%) at t_R 12.98 min. Separation of the second fraction by preparative HPLC (SunFire silica 5 μm, 4.6 × 150 mm, 5% 2-propanol/*n*-hexane, flow rate 0.6 mL·min^{-1}) afforded benzyl (2*S**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*S**,3*R**)-38e** as a colorless oil (24.4 mg, 28%) at t_R 23.60 min and benzyl (2*R**,3*R**)-2,3-dihydroxy-2-methylbutylcarbamate **(2*R**,3*R**)-38e** as a colorless oil (5.4 mg, 6%) at t_R 25.69 min.

Attempted Asymmetric Aminohydroxylation of Styrene 10. The Sharpless AA procedure was adapted with benzyl *N*-(tosyloxy)-carbamate **4e** in place of benzyl carbamate and *tert*-butyl hypochlorite. To a solution of $(DHQD)_2PHAL$ (39.3 mg, 0.050 mmol) in *n*-propanol (4.0 mL) were added freshly prepared sodium hydroxide (120.9 mg, 3.02 mmol) in water (7.5 mL), styrene **10** (105.0 mg, 1.01 mmol), and potassium osmate dihydrate (14.3 mg, 0.039 mmol). Benzyl *N*-(tosyloxy)carbamate **4e** (388.9 mg, 1.21 mmol) in *n*-propanol (3.5 mL) was added, and the mixture was stirred at room temperature (1 h) until TLC indicated the disappearance of the nitrogen source. Aqueous sodium bisulfite (10 mL, 10% w/v) was added and the reaction was stirred for 30 min. The mixture was filtered through Celite, washed with ethyl acetate (5 mL), and extracted with ethyl acetate (3 × 10 mL). The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated to provide the crude product. Purification by flash chromatography with 40% ethyl acetate/*n*-hexane afforded benzyl carbamate **45** as a white solid (148.9 mg, 81%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods; CIFs and seven figures showing anisotropic displacement ellipsoid plots derived from single-crystal X-ray analyses for compounds **1**, **4e**, **9c**, **25c**, **28c**, and **40c** (CCDC nos. 885356−885361, respectively); ^{1}H and ^{13}C NMR spectra; and proof of stereochemistry for compounds **38e** and **39e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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