identical in all respects with the THBC prepared from 6-methoxytryptamine and dimethyl 2-ketoglutarate.

Methyl 8,10-dimethoxy-2,3,5,6,11,11b-hexahydro-3-oxo-1*H*-indolizino[8,7-*b*]indole-11b-carboxylate (14f): mp 220–221 °C; ^{1}H NMR ($CDCl_3$) δ 2.18–2.80 (m, 6 H), 3.20 (m, 1 H), 3.77 (s, 3 H), 3.82 (s, 3 H), 3.91 (s, 3 H), 4.51 (m, 1 H), 6.36 (s, 1 H), 6.49 (s, 1 H), 8.27 (s, 1 H); IR (KBr) 3325, 3178, 2952, 1743, 1694, 1658 cm^{-1}; mass spectrumm, CI (CH_4) *m/e* 345 (MH^+, 100). Anal. Calcd for $C_{18}H_{20}N_2O_5$: C, 62.79; H, 5.86; N, 8.14. Found: C, 61.83; H, 5.86; N, 7.73.

1,1-Dicarbethoxy-5,6-benzo-1,2,3,4-tetrahydro-β-carboline (14i): mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 1.40 (t, J = 6.0 Hz, 6 H), 3.20–3.40 (m, 4 H), 4.40 (q, J = 6.0 Hz, 4 H), 7.30–7.60 (m, 4 H), 7.90 (d, J = 8.0 Hz, 1 H), 8.20 (d, J = 8.0 Hz, 1 H), 9.00 (s, 1 H); IR (KBr) 3410, 3044, 2967, 2925, 1743 cm^{-1}; mass spectrum, CI (CH_4) *m/e* 367 (MH^+, 100). Anal. Calcd for $C_{15}H_{15}N_2Cl\cdot0.25H_2O$ (hydrochloride salt): C, 68.57; H, 5.90; N, 10.67. Found: C, 68.65; H, 5.97; N, 10.55.

1,1-Dicarbethoxy-6-(benzyloxy)-1,2,3,4-tetrahydro-β-carboline (14h): ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 6.0 Hz, 6 H), 2.70 (t, J = 5.0 Hz, 2 H), 3.20 (t, J = 5.0 Hz, 2 H), 4.25 (q, J = 6.0 Hz, 4 H), 5.00 (s, 2 H), 6.90–7.60 (m, 8 H), 8.50 (br s, 1 H); IR (neat) 3445, 3550, 3070, 3035, 2980, 1735 cm^{-1}; mass spectrum, CI (CH_4) *m/e* 423 (MH^+, 100). Anal. Calcd for $C_{24}H_{26}H_2O_5$: C, 68.25; H, 6.16. Found: C, 67.98; H, 6.57.

Acknowledgment. This work on the Pictet–Spengler reaction was supported by a grant from NIH (NS 22287). The technical assistance of Mr. Frank Laib, Mr. Keith Krumnow, and Dr. Noel Wittaker is gratefully acknowledged. We wish to thank Mrs. Anju Gupta for careful preparation of this manuscript.

Registry No. **5a** amine, 62-53-3; **5b** amine, 2735-04-8; **5c** amine, 104-94-9; **5d** amine, 6373-46-2; (±)-**6**, 119695-04-4; **7a**, 57073-81-1; **7b**, 94850-49-4; **7c**, 104742-98-5; **7d**, 101783-07-7; **8a**, 17952-82-8; **8b**, 94850-36-9; **8c**, 17952-87-3; **8d**, 51086-22-7; **8e**, 6722-13-0; **9a**, 5956-86-5; **9b**, 94850-43-8; **9c**, 52648-13-2; **9d**, 54987-14-3; **9e**, 109336-82-5; **9f**, 20731-72-0; (±)-**14a**·HCl, 129968-01-0; (±)-14b·HCl, 129968-03-2; **14c**, 129968-04-3; (±)-**14d**, 115757-58-9; (±)-**14e**, 79888-13-4; (±)-**14f**, 129968-07-6; (±)-**14g**, 129968-05-4; **14h**, 129968-09-8; **14i**, 129968-08-7; **14i**·HCl, 129968-10-1; (±)-**14j**, 129968-06-5; **15**, 609-09-6; **16**, 328-50-7; **17**, 13192-04-6; **18**, 91720-57-9; **19**, 129968-02-1; **20**, 26579-67-9; **21**, 26579-69-1; PhCHO, 100-52-7; $PhCOCO_2H$, 611-73-4; $C_6H_{11}CHO$, 2043-61-0; 4-bromo-3-nitroanisole, 5344-78-5; 3-amino-4-bromoanisole hydrochloride, 129968-11-2.

Supplementary Material Available: Proton and carbon NMR spectra for intermediates **7b**, **9e,f**, **14b,c**, and **19** (17 pages). Ordering information is given on any current masthead page.

The Addition of γ-(Trimethylsilyl)allylboronates to Imines

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The addition of γ-(trimethylsilyl)allylboronates to imines is described and compared with the addition of simple allylboronates to imines. The addition of γ-(trimethylsilyl)allylboronates to imines is found to be more efficient than the addition of simple allylboronates to imines. The stereoselectivity is dependant upon the nature of the imine; imines derived from aromatic aldehydes give anti products and imines derived from aliphatic aldehydes give syn products. Proof of stereochemistry was established by conversion of the anti and syn derivatives to their respective *Z*- and *E*-dienes by a methylation/E-2 elimination process. With α-alkoxy aldehydes the reaction proceeds with excellent selectivity giving the product of Felkin–Ahn addition.

Although a large body of information now exists on the addition of allylboronates to aldehydes and ketones,[2-4] little work on the related additions of allylboronates or allylboranes to the isoelectronic imines[5] and their derivatives[6-8] has been reported in the literature. In our initial work in this area, we explored the additions of ethylene glycol and pinacol allylboronates **1** and **2** to sulfenimines **3** (eq 1) and found that the reactivity of sulfenimines is greatly reduced in comparison with aldehydes and ketones.[8] That the steric bulk of the boronate ester had a profound effect on the reactivity was evident when a 10-fold increase in rate was observed in the reaction of the ethylene glycol boronate **2** over the pinacol boronate **1**. The *Z*–*E* isomerization and the relative rates of reaction for each isomer must also

(1) Address correspondence to this author at the Upjohn Co., 1500-91-2, Kalamazoo, MI 49001.

(2) For reviews, see: (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (c) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243. (d) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357.

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(5) (a) Yamamoto, Y.; Kamatsu, T.; Maruyama, K. *J. Org. Chem.* **1985**, *50*, 3115. (b) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 814. (c) Yamamoto, Y.; Ito, W.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1004. (d) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Am. Chem. Soc.* **1984**, *106*, 5031. (e) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1131. (f) Yamamoto, Y.; Komatsu, T.; Maruyama, K.; Nishi, S.; Ito, W. *J. Am. Chem. Soc.* **1986**, *108*, 7778.

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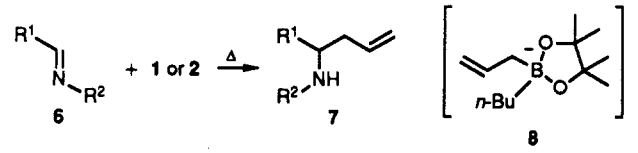
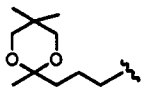
0022-3263/91/1956-0365$02.50/0

Table I. Reactions of Imines with Boronates



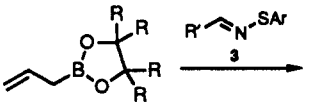
imine	R^1	R^2	boronate	% yield of 7
6a	Ph	*i*-Bu	1	37
			8	86
6b	Ph	Bn	1	23
			8	41
6c	Bu	Bn	2	75
			8	10

Table II. Reaction of γ-(Trimethylsilyl)allylboronate with Aldimines

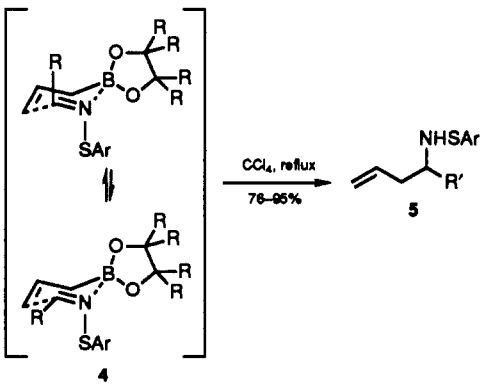
entry	aldimines R	yields,[a] %	syn:anti ratio[b] 12:13
a	$CH_3CH_2CH_2CH_2$	86	4.7:1
b		83	4.6:1
c	$CH(CH_3)_2$	87	10.7:1
d	cyclohexyl	70	6.5:1
e	phenyl	94	1:50[c]
f	furanyl	98	1:20
g	thiophenyl	99	1:21

[a] Yields refer to isolated chromatographically pure material. [b] Product ratios were determined by ^1H NMR. [c] A ratio of 1:50 indicates that the syn isomer was not detected.

be considered. Furthermore, the reduced dipole of an imine as compared with a carbonyl further reduces the imine's reactivity.[9]

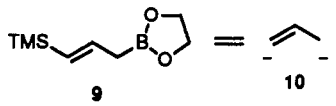


1: R = CH_3
2: R = H

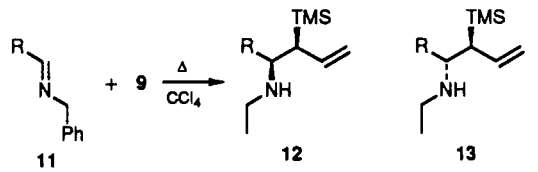


These factors then readily explain our initial results where after refluxing a solution of 1 and 6 in toluene for 7 days only a 37% and 23% yield of adducts **7a** and **7b** were obtained (eq 2) (see Table I). In an effort to increase the reactivity of boronate 1, the ate complex 8[10] was prepared and reacted with the imines. That the reactivity of the boronate was increased was clear from our first case where a nonenolizable imine was used, but it appears that the basicity was also increased since in a readily enolizable imine **6c**[11] only a 10% yield was obtained. However, we did find that by switching from the pinacol derivative 1 to the ethylene glycol derivative 2 that the addition proceeded smoothly in 5 h in refluxing CCl_4 to afford a 75% yield of the adduct **7c**.

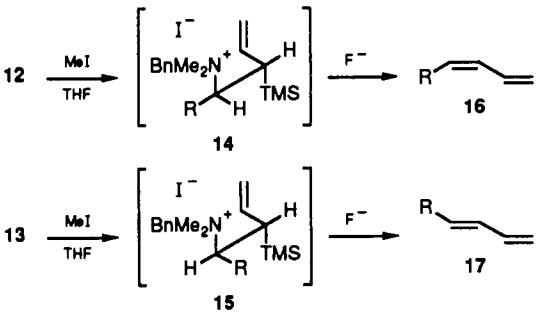
At this point we felt we had a reasonable understanding of the factors that determined successful additions and thus turned our attention to the potentially more useful γ-(trimethylsilyl)allylboronate 9,[7a,b,12] which should serve as a synthon for the dianion 10 by taking advantage of the



reactions of allylsilanes[13] as well as the allylboronate. Thus, when boronate 9 (1.2 equiv) was treated with a variety of benzyl imines 11 in refluxing anhydrous carbon tetrachloride, the reaction smoothly provides the corresponding homoallylamines 12 and 13 in excellent yield.



That the diastereoselectivity is critically dependent on the nature of the R substituent of the imine is clear from an examination of the results presented in Table II. When R is a primary or a secondary alkyl group (entries a–d), the syn product 12 predominates. In contrast, aromatic imines produce anti products 13 exclusively (entries e–g). These stereochemical assignments were secured by the stereospecific conversion of the syn and anti diastereomers to the dienes 16 and 17, respectively. Thus, after chromatographic separation, the pure *syn*-homoallylamine 12 was treated with excess methyl iodide in refluxing THF for 2 h, converting it to the quaternary ammonium iodide 14. The 1,2-elimination of the β-silyl ammonium salt 14



was achieved by adding tetra-*n*-butylammonium fluoride (2.0 equiv, 1.0 M solution in THF) to the reaction mixture and refluxing for 10 h, providing the *cis*-1,3-diene **16**. Application of the same procedure to the *anti*-homoallylamine **13** afforded the *trans*-1,3-diene **17**. The ster-

(9) (a) Trost, B. M.; Bonk, P. *J. Am. Chem. Soc.* **1985**, *107*, 1778. (b) Keck, G. E.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 146.

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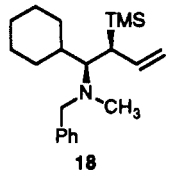
eochemistry in each case is determined by a stereospecific anti elimination of the silane and the ammonium substituents.[14] In the case of the *syn*-cyclohexyl derivative **12d** only small quantities of the *cis*-1,3-diene were formed even after refluxing for 48 h with the major product being the tertiary amine **18**. In this case quaternization is impaired because of steric congestion about the amine. The ketal **12b** gave only the ketone **19** as a result of HI cleavage of the ketal.



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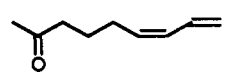
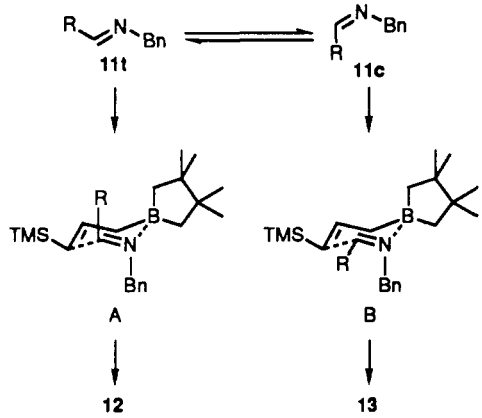


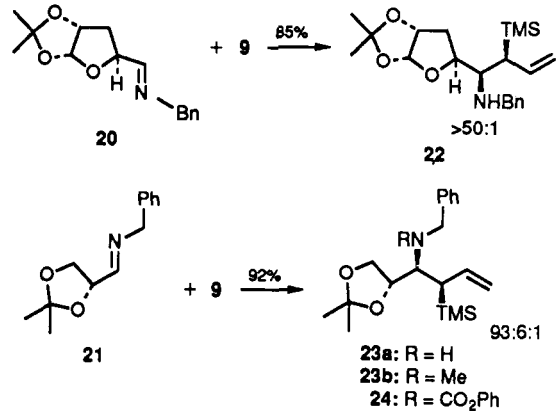
19

The stereochemical dichotomy between the alkyl and aryl groups may be attributed to a partitioning of the reaction between the transition state structures A and B where the barrier for E/Z isomerization is lower than the barrier for proceeding through transition-state structure A with its two axially oriented substituents thus directing the reaction through the thermodynamically more favorable structure B with its single axial substituent. As R



increases in size the syn/anti ratio increases because of an increased diaxial-like interaction between R and the axial B–O bond in C (see entries a, c, and d in Table II). Boat transition-state structures are not expected to be significant contributors based on the computational results of Houk. He finds that in the reaction of an allylboronate with formaldehyde the boat transition state is 8 kcal higher in energy than the chair form. He also determined that an equatorial methyl group is favored by 5.5 kcal over an axial one, thus showing that the axial substituent will not force the reaction to proceed through a boat transition state especially since the calculated preference for an equatorial group was indicated to be high.[15]

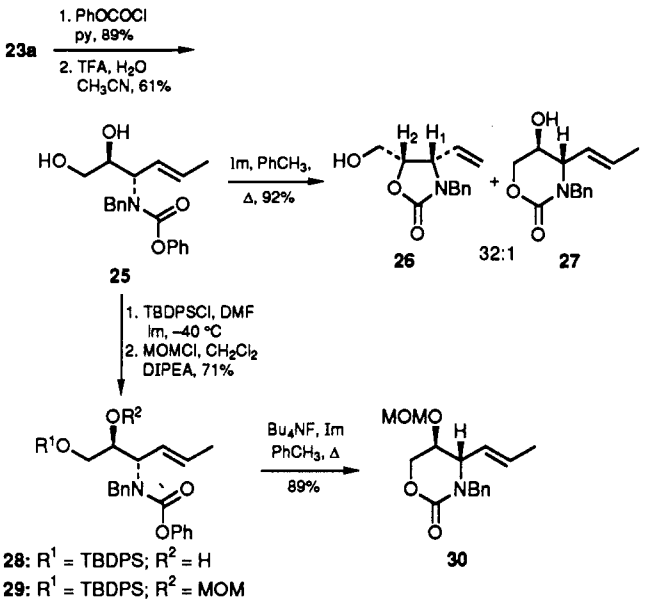
The 1,2-asymmetric induction has also been examined in the addition of allylboronate **9** to imines having a chiral center at the α-position. The reaction of α,β-dialkoxy imines **20** and **21** with boronate **9** produced in each case nearly single stereoisomeric adducts **22** (>50:1) and **23a** (93:6:1) containing three contiguous stereogenic centers. That the centers at C-3 and C-4 are in a syn relationship is inferred from our earlier results. The quaternization–elimination procedure used to establish the silane–amine relationship fails in this case because steric factors prevent quaterization as with the cyclohexyl derivative. The only product that could be isolated from the reaction with amine **21** was the *N*-methyl derivative **23b**. Further support for the 3,4-syn stereochemistry comes from energy minimizations using simulated annealing on the syn and anti isomers. The H–H dihedral angle for the syn isomer is calculated to be 63° with a calculated coupling constant of 2 Hz. The observed coupling was found to be 0°, which is in good agreement with the calculation. The calculated coupling constant for the anti isomer is 13 Hz and the calculated dihedral angle is 180°. Thus based on these considerations and our other results it is clear that the stereochemistry of **23** is 3,4-syn. The relative stereo-



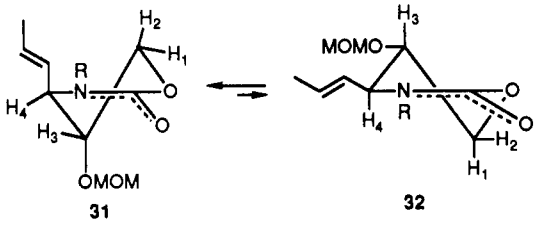
chemistry at C-4 and C-5 was proven by converting **23** to cyclic carbamates **30**. Protection of the amine group of **23** with phenyl chloroformate in pyridine provided the carbamate **24** in 89% yield. When exposed to trifluoroacetic acid/H_2O/CH_3CN (2:1:5) for 36 h at room temperature, **24** is converted to diol **25** in 61% yield. The cyclization of diol **25** is performed in the presence of a catalytic amount of imidazole in refluxing toluene to give the five-membered 1,3-oxazolidin-2-one **26** and the six-membered 1,3-oxazin-2-one **27** in 92% yield and a 32:1 ratio. We felt that the stereochemistry of 1,3-oxazolidin-2-one **26** remained uncertain as a result of the $J_{1,2}$ coupling constant of 9.2 Hz, which falls in the range of both cis and trans vicinal coupling constants for five-membered ring compounds which are 0–11 Hz and 4.5–10 Hz, respectively.[16,17] Although the structure of the six-membered 1,3-oxazin-2-one **27** was established to be trans by ^1H NMR analysis, it was possible that this was derived from the previously undetected anti isomer present in the original condensation mixture. To unambiguously establish the stereochemistry of **23** the diol **25** was selectively silylated in 80% yield with *tert*-butyldiphenylchlorosilane at the primary hydroxyl to afford **28**, which was converted to the MOM derivative **29** in 71% yield. Fluoride-induced release of the silyl group with subsequent cyclization afforded in 89% yield the six-membered ring 1,3-oxazin-2-one **30**, whose stereochemistry was established as follows. In general, the N-substituted 1,3-oxazine-2-ones are known to exist in the half-chair conformations because of the partial double bond character of the N–CO bond.[18] That the OMOM group of urethane **30** was in a pseudoaxial orientation was

(14) Bac, N. V.; Langlois, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7666.
(15) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 1236.

(16) Gaudemer, A. *Stereochemistry, Fundamentals and Methods*; Hagan, H. B., Ed.; Georg Theime: Stuttgart, 1977; Vol. 1, p 44.
(17) Even though the literature (Cardillo, G.; Orena, M.; Sandri, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1489. Meyers, A. I.; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2250) indicates that *cis*- and *trans*-1,3-oxazolidin-2-ones have coupling constants of 9–11 Hz and 5–6 Hz, respectively, we felt that since the other isomer was not available for comparison it was best to prepare the six-membered ring derivative.
(18) (a) Pojarlieff, I.; Lyajpova, M.; Kurtev, B. *J. Chem. Res. (S)* **1980**, 231; *J. Chem. Res. (M)* **1980**, 3119. (b) Kurtev, B.; Lyapova, M.; Mishev, S.; Nakova, O.; Orakovats, A.; Pojarlieff, I. *Bulg. Akad. Nauk., Izv. Khim. Inst.* **1982**, *15*, 375.



clearly established by the H_1–H_3 and H_2–H_3 coupling constants of 2.4 and 1.7 Hz, respectively. An equatorial arrangement would force a trans diaxial relationship with a resulting much larger J value. Although the 2.2-Hz coupling constant of H_3 and H_4 is not particularly diagnostic, the H_2–H_4 coupling of 2.4 Hz resulting from the unique W relationship of these protons serves to establish the anti mode of addition in the reaction (compare conformers **31** and **32**). Conformers derived from a syn ad-



$J_{1,3}$ = 2.4 Hz
$J_{2,3}$ = 1.7 Hz
$J_{3,4}$ = 2.2 Hz
$J_{1,4}$ = 2.4 Hz

duct would not be consistent with this data. The preference for the pseudo trans diaxial conformer **31** over the all equatorial conformer **32** is due to $A^{1,2}$ strain between the benzyl and vinyl substituents.[19] These stereochemical assignments are in accord with our previous findings[7a] and those of Hoffmann[6c] on the addition of allylboronates to the related oxime derivatives and also the results of Yamamoto on the addition of allylboranes to imines.[5b]

In conclusion, we have shown that sterically unencumbered allylboronates readily add to imines, that γ-(trimethylsilyl)allylboronates readily add to imines with a high degree of diastereoselectivity, and that the additions to 1,2-alkoxy imines are also highly selective, favoring the product derived from a Felkin-controlled addition to the imine. The high selectivity, the excellent yields achieved in these reactions, and the introduction of the reactive allylsilane functionality portends favorably for the further exploitation of this chemistry in the synthesis of complex molecular frameworks.

Experimental Section

^{1}H NMR spectra were obtained on a Bruker 360-MHz or a 300-MHz NMR spectrometer and are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). ^{13}C NMR spectra were measured at 90.56 MHz or at 75.30 MHz. Infrared spectra were recorded on either a Beckman Acculab I or a Nicolet 5-DX FT-IR spectrometer using sodium chloride plates or potassium bromide pellets. Data are reported in wavenumbers (cm^{-1}). Mass spectra were obtained on a Finnigan 4021 GC/MS system. A solid probe was used for nonvolatile samples. The ionization mode was electron impact (EI) or chemical ionization (CI) as indicated. Molecular masses are given in atomic mass units (amu), followed by percent intensity relative to the most abundant ion. Elemental analysis was carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, or Galbraith Microanalytical Laboratory, Inc., Knoxville, TN. Melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. All boiling points are uncorrected. Kugelrohr distillations were done on a Büchi apparatus, and the temperatures reported are the oven temperatures at distillation. Column chromatography was carried out using Merck 70–230-mesh silica gel. Flash chromatography utilized Merck 230–400-mesh silica gel from EM reagents. The reactions were monitored by thin-layer chromatography (TLC) using Merck 0.25 mm plates with fluorescent background. For visualization, vanillin/methanol/H_2SO_4, 1:90:10, or phosphomolybdic acid/ethanol, 5:95, solutions, followed by heat, were used, or the spots were visualized under ultraviolet light. The following solvents were dried and purified by distillation under an argon atmosphere, just prior to use, and transferred using syringes. Diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl. Toluene, benzene, pyridine, and dimethyl sulfoxide were distilled from calcium hydride. Methylene chloride was distilled from P_2O_5 and methanol from $Mg(OMe)_2$. Dimethylformamide was left overnight over $MgSO_4$ before distilling.

2-Allyl-4,4,5,5-tetramethyl-1,3-dioxa-2-borolane (1). A 3-L four-necked round-bottomed Morton flask was fitted with a 1-L dropping funnel, a 500-mL dropping funnel, a thermometer, a mechanical stirrer, and an inlet for argon. The flask was charged with 100 mL of anhydrous diethyl ether, and a solution of freshly distilled trimethyl borate (51.96 g, 0.50 mol) in 200 mL of anhydrous diethyl ether was prepared in the 500-mL dropping funnel. Allylmagnesium bromide (500 mL of a 1.0 M solution in ether, 0.50 mol) was pressure-transferred with argon to the 1-L dropping funnel via cannula. The ether was cooled to −78 °C, and the reactants were added simultaneously dropwise over 2 h, keeping the temperature of the mixture below −60 °C. After the addition of the reagents was completed, the mixture was stirred at −78 °C for 3 h and then warmed slowly to 0 °C. After addition of phenothiazine (1.00 g), the mixture was hydrolyzed by the addition of 400 mL of cold (0 °C) saturated ammonium chloride solution. The two-phase mixture was stirred at room temperature for 30 min, the ethereal layer was separated, and the aqueous layer was extracted with two 300-mL portions of ether. The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure until 300 mL of ether remained (Anhydrous, concentrated allylboronic acid is unstable). A solution of the crude allylboronic acid was treated with anhydrous pinacol (65.0 g, 0.55 mol). The resulting solution was stirred overnight at room temperature, and then pentane (500 mL) was added in order to separate water and excess pinacol. The organic layer was separated and dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation of crude product (78–80 °C at 15 mmHg) afforded 50.41 g (60%) of pure pinacol allylboronate (1) (lit.[20] bp 50–53 °C at 5 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 5.94–5.79 (m, 1 H), 5.04–4.90 (m, 2 H), 1.73 (br d, J = 7.4 Hz, 2 H), 1.25 (s, 12 H) ppm. IR (neat): 3078, 2979, 2933, 1637, 1457, 1420, 1371, 1350, 1326, 1145 cm^{-1}.

2-Allyl-1,3-dioxa-2-borolane (2). Allyboronic acid was prepared from 0.4 mol of allylmagnesium bromide and 0.4 mol (41.56 g) of trimethylborate using the above procedure. A solution of the crude acid in 300 mL of dry benzene was treated with ethylene glycol (27.31 g, 440 mol) and heated to reflux until removal of water was complete (Dean–Stark trap). The reaction mixture was allowed to cool and concentrated under reduced pressure. Distillation of crude product (75–78 °C at 30 mmHg) afforded 30.0 g (67%) of ethylene glycol allylboronate **2**, which was contaminated

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with a small amount of an impurity. This reagent was stored in the freezer under argon. Hydrolysis readily occurs upon exposure to moist air or wet solvents. ^{1}H NMR (360 MHz, $CDCl_3$): 5.96–5.81 (m, 1 H), 5.05–4.93 (m, 2 H), 4.21 (s, 4 H), 1.80 (br d, J = 7.3 Hz, 2 H) ppm. IR (neat): 3078, 2976, 2909, 1638, 1483, 1416, 1374, 1326, 1101 cm^{-1}.

Preparation of Imines 11. All imines were prepared according to the reported procedure,[11b,21] and used immediately for subsequent reactions. General procedure: In a 50-mL round-bottomed flask equipped with a dropping funnel and a magnetic stirrer was placed freshly distilled benzylamine (10.72 g, 100 mmol). After the amine was cooled to 0 °C, freshly distilled isobutyraldehyde (7.21 g, 100 mmol) was added dropwise with rapid stirring over a 1-h period. A few minutes later, a reaction occurred with evolution of heat and separation of water. The reaction mixture was stirred at 0 °C for an additional 1 h and allowed to warm up to room temperature. Anhydrous diethyl ether (20 mL) was added, and then the organic layer was separated. Barium oxide (5.0 g) was added, and the reaction mixture was then placed in the refrigerator and left overnight at 5 °C. Barium oxide was filtered off and rinsed with anhydrous ether (20 mL). The solvent was evaporated (25 °C at 25 mmHg) under reduced pressure, and distillation of crude product (110–112 °C at 18 mmHg) afforded 13.06 g (81%) of *N*-isobutylidenebenzylamine **11c** (lit.[6c] 105 °C at 15 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 7.65 (dt, J = 5.0, 1.3 Hz, 1 H), 7.34–7.23 (m, 5 H), 4.55 (s, 2 H), 2.50 (m, 1 H), 1.11 (d, J = 6.9 Hz, 6 H) ppm. IR (neat): 3060, 3030, 2960–2820, 1670, 1450, 1370 cm^{-1}.

***N*-Benzylidenebenzylamine (6b).** Yield: 90%. Bp: 125–127 °C (0.1 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 8.40 (s, 1 H), 7.79 (m, 2 H), 7.43–7.25 (m, 8 H), 4.83 (d, J = 0.4 Hz, 2 H) ppm. IR (neat): 3100, 3087, 3015, 2880, 2840, 1655, 1645, 1605, 1585, 1500, 1460 cm^{-1}.[6c]

***N*-Pentylidenebenzylamine (11a).** Yield: 72%. Bp: 130–133 °C (18 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 7.78 (tt, J = 4.9, 1.3 Hz, 1 H), 7.35–7.21 (m, 5 H), 4.56 (s, 2 H), 2.31 (dd, J = 7.3, 4.9 Hz, 2 H), 1.55 (m, 2 H), 1.37 (qt, J = 7.3, 7.3 Hz, 2 H), 0.93 (t, J = 7.3 Hz, 3 H) ppm. IR (neat): 3070, 3038, 2960–2840, 1668, 1495, 1450 cm^{-1}.

***N*-[4-(2,5,5-Trimethyl-1,3-dioxan-2-yl)butylidene]benzylamine (11b).** Yield: 64%. Bp: 142–152 °C (0.1 mmHg) (Kugelrhor). ^{1}H NMR (360 MHz, $CDCl_3$): 7.79 (t, J = 4.8 Hz, 1 H), 7.35–7.23 (m, 5 H), 4.57 (s, 2 H), 3.48 (AB q, J = 11.4 Hz, Δ = 30.7 Hz, 4 H), 2.34 (q, J = 5.0 Hz, 2 H), 1.74 (m, 4 H), 1.37 (s, 3 H), 1.00 (s, 3 H), 0.90 (s, 3 H) ppm. IR (neat): 3060, 3030, 2960, 2860, 1670, 1380 cm^{-1}.[6c]

***N*-(Cyclohexylmethylidene)benzylamine (11d).** Yield: 71%. Bp: 113–115 °C (0.1 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 7.64 (dt, J = 5.0, 1.3 Hz, 1 H), 7.34–7.20 (m, 5 H), 4.55 (s, 2 H), 2.24 (m, 1 H), 1.87–1.65 (m, 5 H), 1.34–1.21 (m, 5 H) ppm. IR (neat): 3060, 3030, 2920, 2850, 1665, 1605, 1495, 1445, 1345 cm^{-1}.[9b]

***N*-Furfurylidenebenzylamine (11f).** Yield: 85%. Bp: 115–117 °C (0.1 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 8.12 (s, 1 H), 7.51 (d, J = 1.2 Hz, 1 H), 7.35–7.24 (m, 5 H), 6.77 (d, J = 3.4 Hz, 1 H), 6.48 (dd, J = 3.4, 1.7 Hz, 1 H), 4.79 (s, 2 H) ppm. IR (neat): 3110, 3090, 3060, 3030, 2880, 2830, 1640, 1610, 1585, 1485, 1360, 1160 cm^{-1}.[9b]

***N*-(Thiopheneylmethylidene)benzylamine (11g).** Yield: 88%. Bp: 119–120 °C (0.1 mmHg). ^{1}H NMR (360 MHz, $CDCl_3$): 8.45 (s, 1 H), 7.40 (d, J = 5.0 Hz, 1 H), 7.36–7.24 (m, 6 H), 7.07 (dd, J = 5.0, 3.6 Hz, 1 H), 4.78 (s, 2 H) ppm. IR (neat): 3060, 3020, 2860, 2830, 1625, 1490, 1430, 1345, 1220 cm^{-1}.[22]

***N*-Benzylideneisobutylamine (6a).** Yield: 63%. Bp: 131–134 °C (15 mmHg) [lit.[23] bp 140 °C (16 mmHg)]. ^{1}H NMR (60 MHz, $CDCl_3$): 8.2 (t, J = 1 Hz, 1 H), 7.9 (m, 2 H), 7.6–7.4 (m, 3 H), 3.5 (dd, J = 6, 1 Hz, 2 H), 2.1 (m, 1 H), 1.0 (d, J = 6 Hz, 6 H) ppm.

***N*-(3-Deoxy-1,2-*O*-isopropylidene-1,4-D-*xylo*-furanylidene)benzylamine (20).** Yield: 76%. Bp: 125–135 °C (0.1 mmHg) (Kugelrhor). ^{1}H NMR (360 MHz, $CDCl_3$): 7.75 (d, J = 6.0 Hz, 1 H), 7.35–7.23 (m, 5 H), 5.89 (d, J = 3.6 Hz, 1 H), 4.78 (m, 2 H), 4.63 (s, 2 H), 2.32 (dd, J = 13.5, 4.6 Hz, 1 H), 1.83 (ddd, J = 13.5, 11.0, 4.6 Hz, 1 H), 1.51 (s, 3 H), 1.33 (s, 3 H) ppm. IR (neat): 3050, 3020, 2970, 2920, 2840, 1665, 1490, 1430, 1370, 1210, 1160, 1090–1010 cm^{-1}.

***N*-(2,3-*O*-Isopropylidene-D-glycerylidene)benzylamine (21).** Yield: 92%. Bp: 86–96 °C (0.1 mmHg) (Kugelrhor). ^{1}H NMR (300 MHz, $CDCl_3$): 7.77 (dt, J = 5.0, 1.4 Hz, 1 H), 7.37–7.23 (m, 5 H), 4.63 (m, 3 H), 4.22 (dd, J = 8.5, 6.7 Hz, 1 H), 3.97 (dd, J = 8.5, 6.2 Hz, 1 H), 1.46 (s, 3 H), 1.41 (s, 3 H) ppm. IR (neat): 3087, 3063, 3029, 2986, 2935, 2878, 1672, 1603, 1459, 1380, 1371, 1252, 1214, 1154 cm^{-1}.[24]

General Procedures for the Reaction of Imines with Allylboronates. *N*-(1-Phenyl-3-butenyl)isobutylamine (6a): Method A (the reaction of imine with allylboronate **1**). A solution of *N*-benzylideneisobutylamine (774 mg, 4.80 mmol) in dry toluene (3 mL) was prepared under argon in a 25-mL round-bottomed flask fitted with a reflux condenser and a magnetic stirrer. Allylboronate **1** (1.00 g, 5.90 mmol) was added via syringe, and the resulting solution was refluxed for 7 days. After cooling to room temperature, the mixture was poured into aqueous 2.0 N HCl (5 mL) and stirred for 20 min. The aqueous layer was separated, made alkaline with 3.0 N NaOH solution, and extracted three times with 10-mL portions of diethyl ether. The ethereal extracts were washed with brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Bulb-to-bulb distillation of the crude product [43–50 °C (0.1 mmHg)] provided 361 mg (37%) of homoallylamine **7a** as a pale yellow liquid. The analytical sample was obtained by flash chromatography (silica, eluting with 95:5:1 hexane/ethyl acetate/Et_3N). ^{1}H NMR (360 MHz, $CDCl_3$): 7.32–7.21 (m, 5 H), 5.79–5.67 (m, 1 H), 5.12–5.02 (m, 2 H), 3.61 (dd, J = 7.8, 5.9 Hz, 1 H), 2.39 (m, 2 H), 2.25 (m, 2 H), 1.68 (m, 1 H), 1.42 (br s, NH), 0.86 (d, J = 5.2 Hz, 3 H), 0.84 (d, J = 5.2 Hz, 3 H) ppm. IR (neat): 3340 (br, w), 3079, 3063, 3025, 2954–2800, 1638, 1601, 1466, 1453 cm^{-1}. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.80; H, 10.44; N, 6.85.

Method B (the reaction of an imine with a tetravalent boronate complex **8**). In a 25-mL round-bottomed flask equipped with a magnetic stirrer and a rubber septum was placed a solution of pinacol allylboronate (1.68 g, 10.0 mmol) in dry THF (10 mL). *n*-Butyllithium (10.0 mmol, 4.0 mL of a 2.5 M solution in hexane) was added dropwise with stirring at 0 °C. The solution was allowed to warm up to room temperature and after 40 min was cooled again to 0 °C. *N*-Benzylideneisobutylamine (806 mg, 5.0 mmol) was added dropwise via syringe. The reaction mixture was stirred for 36 h at room temperature and then worked up as described in the above procedure. This procedure afforded 874 mg (86%) of **7a**.

***N*-(1-Phenyl-3-butenyl)benzylamine (7b).** Method A: A mixture of *N*-benzylidenebenzylamine (980 mg, 5.0 mmol) and pinacol allylboronate **1** (924 mg, 5.5 mmol) in 5 mL of toluene was refluxed under argon for 4 days and then worked up according to the above procedure to give 273 mg (23%) of **7b** as a pale yellow liquid. The analytical sample was obtained by flash chromatography (silica, eluting with 40:1:1 methylene chloride/ethyl acetate/Et_3N). ^{1}H NMR (360 MHz, $CDCl_3$): 7.38–7.19 (m, 10 H), 5.76–5.64 (m, 1 H), 5.10–5.01 (m, 2 H), 3.69 (dd, J = 7.7, 6.0 Hz, 1 H), 3.58 (AB q, J = 13.3 Hz, $\Delta\nu$ = 55.6 Hz, 2 H), 2.42 (m, 2 H), 1.75 (br s, NH) ppm. IR (neat): 3327, 3083, 3064, 3028, 3003, 2977–2800, 1641, 1601, 1583, 1453 cm^{-1}. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.14; H, 7.99; N, 5.85. Method B: The reaction of *N*-benzylidenebenzylamine (980 mg, 5.0 mmol) with tetravalent allylboronate complex (10.0 mmol, prepared by the above procedure) gave 474 mg (40%) of **7b**.

Ethylene Glycol (*E*)-1-(Trimethylsilyl)-1-propene-3-boronate (9). A 2-L three-necked round-bottomed flask equipped with an argon inlet, a dropping funnel and a thermometer was charged with *sec*-butyllithium (40.0 mmol, 308 mL of 1.30 M in

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cyclohexane) in dry tetrahydrofuran (250 mL). The solution was cooled to −78 °C, and allyltrimethylsilane (46.80 g, 41.0 mmol) was added dropwise with vigorous stirring. The yellow color of the allylic anion appeared immediately. Stirring at −78 °C was continued for 30 min after the addition was completed. The resulting solution was allowed to warm slowly to −20 °C and after 2 h was cooled again to −78 °C. After the trimethylborate (41.56 g, 40.0 mmol) was added in three portions keeping the temperature below −55 °C, the reaction mixture was stirred for 1 h at −78 °C, warmed to 0 °C, and hydrolyzed by the addition of 500 mL of cold (0 °C) saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 400 mL). The combined extracts were washed with brine and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure until 100 mL of ether remained (anhydrous, concentrated allylboronic acid is unstable). To a solution of crude allylboronic acid was added ethylene glycol (24.83 g, 40.0 mmol) and dry toluene (200 mL). After the remaining volatile solvent (ether and tetrahydrofuran) was removed at 5 °C under reduced pressure, the resulting solution was heated to reflux and water was removed using a Dean–Stark trap. After 4 h, evolution of water had ceased. The mixture was cooled, concentrated, and distilled [94–95 °C (15 mmHg)], providing 25.78 g (35%) of the allylboronate, which is readily hydrolyzed upon exposure to moist air.[7] ^{1}H NMR (300 MHz, $CDCl_3$): 6.08 (dt, J = 18.3, 7.1 Hz, 1 H), 5.62 (dt, J = 18.3, 1.5 Hz, 1 H), 4.20 (s, 4 H), 1.89 (br d, J = 7.1 Hz), 0.04 (s, 9 H) ppm. ^{13}C NMR (75.30 MHz, $CDCl_3$): 142.02, 130.98, 65.63, 20.3 (br m), −1.06 ppm. IR (neat) 2956, 2910, 1613, 1482, 1400, 1372, 1247, 1017, 989, 878 cm^{-1}.

***N*-Benzyl-2-(trimethylsilyl)-3-butenylamines (12 and 13).** General procedure: A 50-mL two necked round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was charged with a solution of imine **11** (3.0 mmol) in dry carbon tetrachloride (3 mL). (Trimethylsilyl)allylboronate **9** (3.6 mmol) was added via syringe, and the resulting solution was refluxed under argon until the reaction was complete (reaction progress was monitored by ^{1}H NMR (60 MHz) or alumina TLC whenever possible). The reaction mixture was cooled to room temperature and diluted by the addition of anhydrous diethyl ether (30 mL). Triethanolamine (3.0 mmol, 3.0 M in acetone) was added to facilitate workup. The reaction mixture was stirred for an additional 3 h and poured into 20 mL of 2.0 N aqueous NaOH solution. The organic layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined extracts were washed with brine and dried over sodium sulfate, and the solvent was removed under reduced pressure to afford the crude product. The ratio of diastereomers was determined by 300-MHz ^{1}H NMR integration or GC–MS analysis of the crude product. The resulting crude product was purified by chromatography on silica gel with ethyl acetate/hexane/1% Et_3N. The diastereomers were separated, whenever possible, by chromatography.

***N*-Benzyl-1-butyl-2-(trimethylsilyl)-3-butenylamine (12a and 13a).** Yield: 86%. Bp: 108–118 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}H NMR analysis of the crude product indicated a 4.7:1 ratio of diastereomers which were separated by chromatography on silica, eluting with 95:5:1 hexane/ethyl acetate/Et_3N. For the syn isomer **12a** (major product). ^{1}H NMR (360 MHz, $CDCl_3$): 7.34–7.22 (m, 5 H), 5.71 (dt, J = 16.9, 10.6 Hz, 1 H), 4.98 (dd, J = 10.6, 2.3 Hz, 1 H), 4.90 (dd, J = 16.9, 12.3 Hz, 1 H), 3.70 (AB q, J = 12.9 Hz, $\Delta\nu$ = 62.8 Hz, 2 H), 2.68 (m, 1 H), 2.03 (dd, J = 10.6, 5.0 Hz, 1 H), 1.50–1.21 (m, 6 H and NH), 0.89 (t, J = 7.1 Hz, 3 H), 0.01 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 141.16, 136.55, 128.25, 128.15, 126.64, 114.77, 57.21, 51.18, 39.58, 32.68, 28.31, 22.86, 14.15, −1.70 ppm. For the anti isomer **13a** (minor product): ^{1}H NMR (360 MHz, $CDCl_3$): 7.32–7.21 (m, 5 H), 5.69 (dt, J = 16.9 and 10.1 Hz, 1 H), 4.95 (dd, J = 10.1, 1.3 Hz, 1 H), 4.86 (dd, J = 16.9, 1.3 Hz, 1 H), 3.72 (AB q, J = 12.6 Hz, $\Delta\nu$ = 85.5 Hz), 2.70 (dt, J = 7.8, 4.8 Hz, 1 H), 1.82 (dd, J = 10.9, 5.0 Hz, 1 H), 1.64–1.56 (m, 1 H), 1.46–1.19 (m, 5 H and NH), 0.90 (t, J = 7.0 Hz, 3 H), 0.00 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 141.16, 136.74, 128.25, 128.15, 126.64, 114.41, 57.57, 51.79, 40.04, 32.96, 28.38, 22.93, 14.15, −1.70 ppm. IR (neat, as a mixture): 3320 (w), 3060, 3020, 1620, 1610 (sh) cm^{-1}. MS (CI, 40 eV, as a mixture): m/z (relative intensity), 290 ([M + H]$^+$, 88.0), 218 (0.1), 200 (1.0), 180 (29.5), 176 (16.0), 156 (0.4), 125 (2.9), 108 (7.3), 90 (100.0). Anal. Calcd for $C_{18}H_{31}NSi$: C, 74.67; H, 10.79; N, 4.84. Found (as a mixture): C, 74.77; H, 10.87; N, 4.77.

***N*-Benzyl-1-(2,5,5-trimethyl-1,3-dioxan-2-yl)-2-(trimethylsilyl)-3-butenylamine (12b and 13b).** Yield: 83%. Bp: 147–157 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}H NMR analysis of the crude product indicated a 4.6:1 ratio of diastereomers, which were separated by chromatography on silica gel, eluting with 85:15:1 hexane/ethyl acetate/Et_3N. For the syn isomer **12b** (major product). ^{1}H NMR (360 MHz, $CDCl_3$): 7.45–7.19 (m, 5 H), 5.70 (dt, J = 16.9, 10.1 Hz, 1 H), 4.99 (dd, J = 10.1, 2.3 Hz, 1 H), 4.91 (dd, J = 16.9, 2.3 Hz, 1 H), 3.71 (AB q, J = 12.9 Hz, $\Delta\nu$ = 63.4 Hz, 2 H), 3.48 (AB q, J = 11.7 Hz, $\Delta\nu$ = 35.0 Hz, 4 H), 2.71 (m, 1 H), 2.04 (dd, J = 11.0, 4.9 Hz, 1 H), 1.70–1.37 (m, 6 H), 1.36 (s, 3 H), 1.19 (br, NH), 1.00 (s, 3 H), 0.91 (s, 3 H), 0.01 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 141.09, 136.44, 128.24, 128.12, 126.61, 114.86, 99.02, 70.32, 57.07, 51.13, 39.49, 37.83, 33.22, 29.93, 22.81, 22.58, 20.51, 19.84, −1.69 ppm.

For the anti isomer **13b** (minor isomer). ^{1}H NMR (360 MHz, $CDCl_3$): 7.43–7.19 (m, 5 H), 5.70 (dt, J = 16.9, 10.2 Hz, 1 H), 4.95 (dd, J = 10.2, 2.3 Hz, 1 H), 4.87 (dd, J = 16.9, 2.3 Hz, 1 H), 3.73 (AB q, J = 12.6 Hz, $\Delta\nu$ = 84.4 Hz, 2 H), 3.48 (AB q, J = 17.5 Hz, $\Delta\nu$ = 30.7 Hz, 4 H), 2.72 (dt, J = 7.5, 4.6 Hz, 1 H), 1.83 (dd, J = 10.9, 4.8 Hz, 1 H), 1.70–1.28 (m, 9 H), 1.05 (br, NH), 0.99 (s, 3 H), 0.91 (s, 3 H), 0.00 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 141.09, 136.57, 128.24, 128.18, 126.70, 114.48, 99.02, 70.34, 57.58, 51.86, 39.99, 37.75, 33.62, 29.96, 22.79, 22.59, 20.60, 20.06, −1.75 ppm. IR (neat, as a mixture): 3200 (w), 3060, 3030, 1625, 1610 (sh) cm^{-1}. MS (EI, 70 eV, as a mixture): m/z (relative intensity), 404 ([M + 1]$^+$, 1.8), 388 (2.6), 314 (0.2), 290 (99.0), 281 (3.5), 232 (32.8), 204 (21.3), 188 (3.8), 178 (4.4), 164 (13.7), 157 (18.7), 146 (100.0), 141 (13.7), 129 (24.3), 91 (71.3). Anal. Calcd for $C_{24}H_{41}NO_2Si$: C, 71.41; H, 10.24; N, 3.47. Found (as a mixture): C, 71.45; H, 10.17; N, 3.58.

***N*-Benzyl-1-isopropyl-2-(trimethylsilyl)-3-butenylamine (12c and 13c).** Yield: 87%. Bp: 103–113 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}NMR analysis for the crude product indicated the 10.7:1 ratio of diastereomers, which were inseparable by chromatography. For the syn isomer **12c** (major product). ^{1}H NMR (360 MHz, C_6D_6): 7.35–7.11 (m, 5 H), 5.65 (dt, J = 17.1, 10.1 Hz, 1 H), 4.90 (dd, J = 10.1, 2.2 Hz, 1 H), 4.81 (dd, J = 17.1, 2.2 Hz, 1 H), 3.72 (s, 2 H), 2.60 (dd, J = 8.0, 2.5 Hz, 1 H), 1.94–1.83 (m, 2 H), 0.99 (d, J = 6.9 Hz, 3 H), 0.88 (d, J = 6.9 Hz, 3 H), 0.74 (br, NH), 0.10 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 414.24, 138.62, 128.21, 128.15, 126.68, 113.62, 63.27, 53.41, 40.71, 31.68, 21.58, 17.35, 1.16 ppm. The anti isomer could not be characterized due to overlap with the syn isomer. IR (neat): 3340 (w), 3070, 3020, 1625, 1605 (w) cm^{-1}. MS (CI, 40 eV): m/z (relative intensity), 276 ([M + H]$^+$, 100.0), 232 (1.9), 208 (0.3), 180 (22.9), 162 (9.5), 141 (0.5), 125 (1.9), 108 (3.3), 90 (39.5). Anal. Calcd for $C_{17}H_{19}NSi$: C, 74.11; H, 10.61; N, 5.08. Found: C, 74.24; H, 10.40; N, 5.25.

***N*-Benzyl-1-cyclohexyl-2-(trimethylsilyl)-3-butenylamine (12d and 13d).** Yield: 70%. Bp: 118–127 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}H NMR analysis of the crude product indicated a 6.5:1 ratio of diastereomers, which were inseparable by chromatography. For the syn isomer **12d** (major product): ^{1}H NMR (360 MHz, $CDCl_3$): 7.35–7.20 (m, 5 H), 5.73 (dt, J = 16.9, 10.0 Hz, 1 H), 4.91 (dd, J = 10.0, 2.1 Hz, 1 H), 4.83 (dd, J = 16.9, 2.1 Hz, 1 H), 3.79 (AB q, J = 12.5 Hz, $\Delta\nu$ = 18.5 Hz, 2 H), 2.56 (dd, J = 6.8, 2.3 Hz, 1 H), 1.98 (dd, J = 10.9, 7.0 Hz, 1 H), 1.76–1.09 (m, 1 H), 0.20 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 141.14, 138.58, 128.13, 126.65, 113.80, 63.10, 53.24, 42.65, 40.39, 32.05, 28.16, 27.12, 26.78, 26.68, −1.12 ppm. The anti isomer could not be characterized because of overlap with the syn isomer. IR (neat): 3330 (w), 3060, 3020, 1620, 1605 (sh) cm^{-1}. MS (EI, 70 eV): m/z (relative intensity), 316 ([M + 1]$^+$, 1.9) 232 (44.5), 209 (2.0), 202 (100.0), 178 (2.3), 164 (13.6), 91 (43.9). Anal. Calcd for $C_{20}H_{33}NSi$: C, 76.12; H, 10.54; N, 4.44. Found: C, 76.10; H, 10.49; N, 4.56.

***N*-Benzyl-1-phenyl-2-(trimethylsilyl)-3-butenylamine (13e).** Yield: 94%. Bp: 133–142 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}H NMR analysis of the crude product indicated a 50:1 ratio of diastereomers. For the anti isomer **13e** (major product): ^{1}H NMR (360 MHz, $CDCl_3$): 7.34–7.18 (m, 10 H), 5.69 (dt, J = 17.1, 10.2 Hz, 1 H), 5.03 (dd, J = 10.2, 1.9 Hz, 1 H), 4.93 (dd, J

= 17.1, 1.9 Hz, 1 H), 3.68 (d, J = 9.5 Hz, 1 H), 3.47 (AB q, J = 13.3 Hz, $\Delta\nu$ = 61.4 Hz, 2 H), 2.07 (br, NH), 1.98 (t, J = 9.5 Hz, 1 H), −0.32 (s, 9 H). ^{13}C NMR (360 MHz, $CDCl_3$): 143.58, 140.77, 137.71, 128.38, 128.20, 128.14, 127.23, 126.65, 115.23, 62.37, 51.28, 44.32, −2.24 ppm. IR (neat): 3330 (w), 3080, 3060, 3030, 1630 (m), 1610 (w) cm^{-1}. MS (CI, 40 eV): m/z (relative intensity), 310 ([M + H]$^+$, 19.6), 276 (1.1), 203 (7.8), 196 (6.3), 180 (44.9), 131 (1.8), 107 (4.9), 90 (100.0). Anal. Calcd for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79; N, 4.53. Found: C, 77.73; H, 8.72; N, 5.02.

N-Benzyl-1-furanyl-2-(trimethylsilyl)-3-butenylamine (13f). Yield: 98%. Bp: 119–129 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}H NMR analysis of the crude product indicated a 20:1 ratio of diastereomers. For the anti isomer **13f**. ^{1}H NMR (360 MHz, $CDCl_3$): 7.40 (d, J = 1.8 Hz, 1 H), 7.31–7.20 (m, 5 H), 6.31 (dd, J = 3.1, 1.8 Hz, 1 H), 6.17 (d, J = 3.1 Hz, 1 H), 5.64 (dt, J = 17.0, 10.2 Hz, 1 H), 5.02 (dd, J = 10.2, 1.7 Hz, 1 H), 4.94 (dd, J = 17.0, 1.7 Hz, 1 H), 3.57 (AB q, J = 13.4 Hz, $\Delta\nu$ = 84.5 Hz, 2 H), 2.19 (t, J = 10.2 Hz, 1 H), 1.93 (br, NH), −0.23 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 155.62, 141.28, 140.35, 137.43, 128.18, 128.14, 126.69, 114.91, 109.94, 107.52, 55.33, 51.23, 41.40, −2.75 ppm. IR (neat): 3330 (w), 3110 (sh), 3070, 3030, 1620, 1600 (sh) cm^{-1}. MS (CI, 40 eV): m/z (relative intensity), 300 ([M + H]$^+$, 1.8), 227 (0.1), 209 (0.8), 193 (12.7), 180 (22.6), 170 (0.3), 156 (0.6), 136 (0.8), 121 (2.7), 108 (6.4), 90 (100.0). Anal. Calcd for $C_{18}H_{25}NOSi$: C, 72.19; H, 8.41; N, 4.68. Found: C, 72.08; H, 8.39; N, 4.57.

N-Benzyl-1-thiopheneyl-2-(trimethylsilyl)-3-butenylamine (13g). Yield: 99%. Bp: 122–132 °C (0.1 mmHg) (Kugelrhor). 360-MHz ^{1}H NMR analysis of the crude product indicated a 21:1 ratio of diastereomers. For the anti isomer **13g**. ^{1}H NMR (360 MHz, $CDCl_3$): 7.32–7.22 (m, 6 H), 6.93 (d, J = 3.3 Hz, 2 H), 5.67 (dt, J = 17.0, 10.3 Hz, 1 H), 5.04 (dd, J = 10.3, 1.8 Hz, 1 H), 4.95 (dd, J = 17.0, 1.8 Hz, 1 H), 4.02 (d, J = 9.6 Hz, 1 H), 3.57 (AB q, J = 13.2 Hz, $\Delta\nu$ = 90.7 Hz, 2 H), 2.14 (br, NH), 2.01 (t, J = 10.0 Hz, 1 H), −0.24 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 149.18, 140.43, 137.35, 128.22, 126.73, 125.79, 125.04, 124.48, 115.50, 57.74, 51.15, 45.41, −2.51 ppm. IR (neat): 3330 (w), 3100 (sh), 3070, 3030, 1625, 1605 (sh) cm^{-1}. MS (CI, 40 eV): m/z (relative intensity), 316 ([M + H]$^+$, 6.4), 226 (0.1), 209 (19.4), 196 (0.1), 180 (35.8), 152 (0.1), 137 (2.8), 107 (7.2), 90 (100.0). Anal. Calcd for $C_{18}H_{25}NSSi$: C, 68.52; H, 7.99; N, 4.44. Found: C, 68.62; H, 8.08; N, 4.42.

N-Benzyl-1-(3-deoxy-1,2-*O*-isopropylidene-1,4-furanosyl-α-D-*xylo*-pentyl)-2-(trimethylsilyl)-3-butenylamine (22). Yield: 85%. Bp: 130–140 °C (0.1 mmHg) (Kugelrhor). GC–MS analysis of the crude product indicated a >50:1 ratio of diastereomers. ^{1}H NMR (360 MHz, $CDCl_3$): 7.31–7.21 (m, 5 H), 5.75 (d, J = 4.2 Hz, 1 H), 5.71 (dt, J = 16.9, 10.0 Hz, 1 H), 4.98 (dd, J = 10.0, 2.0 Hz, 1 H), 4.89 (dd, J = 16.9, 2.0 Hz, 1 H), 4.70 (t, J = 4.2 Hz, 1 H), 4.28 (dt, J = 13.3, 5.5 Hz, 1 H), 3.81 (AB q, J = 12.9 Hz, $\Delta\nu$ = 26.7 Hz, 2 H), 3.02 (t, J = 5.5 Hz, 1 H), 2.07 (dd, J = 13.3, 4.4 Hz, 1 H), 1.87 (dd, J = 11.0, 6.0 Hz, 1 H), 1.79 (m, 1 H), 1.49 (s, 3 H), 1.31 (s, 3 H), 1.28 (br, NH), 0.03 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 141.00, 136.40, 128.20, 126.75, 115.08, 110.84, 80.67, 80.11, 59.13, 52.33, 38.85, 35.21, 26.88, 26.36, −1.50 ppm. IR (neat): 3320 (w), 3060, 3020, 1620, 1605 (sh) cm^{-1}. MS (EI, 70 eV): m/z (relative intensity), 376 ([M + 1]$^+$, 0.3), 360 (1.0), 270 (3.7), 262 (53.0), 244 (2.4), 232 (92.9), 204 (25.9), 141 (19.8), 135 (2.9), 121 (2.1), 91 (100.0). Anal. Calcd for $C_{21}H_{33}NO_3Si$: C, 67.16; H, 8.86; N, 3.73. Found: C, 66.92; H, 8.76; N, 3.82.

(1*R,2*S**,4*S**)-*N*-Benzyl-1-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(trimethylsilyl)-3-butenylamine (23).** Yield: 92%. Bp: 118–128 °C (0.1 mmHg) (Kugelrhor). GC–MS analysis of the crude product indicated a 93:6:1 ratio of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): 7.32–7.20 (m, 5 H), 5.72 (dt, J = 16.8, 10.5 Hz, 1 H), 5.03 (dd, J = 10.5, 2.2 Hz, 1 H), 4.93 (dd, J = 16.8, 2.2 Hz, 1 H), 4.12–3.98 (m, 2 H), 3.78 (AB q, J = 12.8 Hz, $\Delta\nu$ = 41.3 Hz, 2 H), 3.69 (t, J = 7.4 Hz, 1 H), 2.84 (dd, J = 7.4, 4.1 Hz, 1 H), 1.92 (dd, J = 10.5, 4.1 Hz, 1 H), 1.39 (s, 3 H), 1.33 (s, 3 H), 1.24 (br s, NH), 0.25 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 140.88, 136.02, 128.30, 126.91, 115.96, 108.80, 77.18, 68.64, 60.15, 52.13, 39.04, 26.69, 25.43, −1.48 ppm. IR (neat): 3323 (br, w), 3070, 3028, 2985–2809, 1622, 1454, 1379, 1369, 1073, 1039 cm^{-1}. MS (EI, 70 eV): m/z (relative intensity), 334 ([M + 1]$^+$, 0.4), 318 (1.0), 232 (100.0), 220 (43.3), 178 (1.2), 162 (27.3), 144 (24.5), 135 (3.4), 117 (2.0), 113 (2.7), 91 (69.5). Anal. Calcd for $C_{19}H_{31}NO_2Si$: C, 68.42; H, 9.37; N, 4.20; Si, 8.42. Found: C, 68.57; H, 9.44; N, 4.18; Si, 8.35.

(1*R,2*S**,4*S**)-*N*-Benzyl-*N*-methyl-1-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(trimethylsilyl)-3-butenylamine.** To a solution of the homoallylamine **23** (265 mg, 0.80 mmol) and anhydrous potassium carbonate (275 mg, 1.99 mmol) in 5 mL of THF was added methyl iodide (2.26 g, 15.9 mmol). After heating the mixture to reflux for 14 h, it was cooled to room temperature and treated with Bu_4NF (1.6 mL of 1.0 M THF solution, 1.60 mmol). The resulting solution was heated to reflux for 48 h and worked up as described above. Purification by flash chromatography on silica (97:3 ethyl acetate/hexane) afforded 254 mg (92% yield) of the N-methyl derivative **23b**. ^{1}H NMR (360 MHz, $CDCl_3$): 7.30–7.18 (m, 5 H), 6.07 (dt, J = 17, 10.3 Hz, 1 H), 4.97 (dd, J = 17.0, 2.2 Hz, 1 H), 4.93 (dd, J = 10.3, 2.2 Hz, 1 H), 4.36 (dt, J = 9.4, 6.1 Hz, 1 H), 4.21 (dd, J = 8.2, 6.1 Hz, 1 H), 3.75 (dt, J = 8.2, 6.3 Hz, 1 H), 3.56 (AB q, $\Delta\nu$ = 85.5 Hz, J = 8.2 Hz, 2 H), 2.83 (d, J = 9.4 Hz, 1 H), 2.29 (d, J = 10.3 Hz, 1 H), 2.13 (s, 3 H), 1.38 (s, 3 H), 1.35 (s, 3 H), 0.10 (s, 9 H) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$): 139.74, 138.50, 128.49, 128.17, 126.83, 113.61, 108.93, 74.59, 70.23, 65.38, 59.13, 38.67, 33.81, 26.74, 25.59, −1.94 ppm. IR (neat): 3078, 3020, 2980–2763, 1617, 1520, 1378, 1366, 1243, 1064, 1037 cm^{-1}.

(1*E*)-1-Phenyl-1,3-butadiene (17e). In a 10-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was placed a solution of the *anti*-phenylhomoallylamine **13e** (146 mg, 0.47 mmol) in anhydrous THF (3 mL). Methyl iodide (1.34 g, 9.43 mmol) was added with stirring at room temperature, and the mixture was refluxed for 2 h. After the solution was cooled to room temperature, tetrabutylammonium fluoride (0.94 mL of 1.0 M THF solution, 0.94 mmol) was added. The resulting solution was refluxed again for 10 h, quenched with 1 N aqueous hydrochloric acid solution (10 mL), and diluted with ether (20 mL). The organic layer was separated, washed with water (3 × 15 mL), dried over magnesium sulfate, and concentrated under reduced pressure to afford a yellow liquid. Purification by a short column chromatography on silica eluting with 95:5 hexane/ethyl acetate afforded 21 mg (34%) of the (*E*)-diene **17e**.[12] The low yield is probably due to the products volatility. ^{1}H NMR (300 MHz, $CDCl_3$): 7.42–7.19 (m, 5 H), 6.79 (dd, J = 15.9, 10.4 Hz, 1 H, H_4), 6.57 (d, J = 15.9 Hz, 1 H, H_5), 6.51 (ddd, J = 16.8, 10.4, 10.0 Hz, 1 H, H_3), 5.33 (dd, J = 16.8, 0.8 Hz, 1 H, H_2), 5.17 (dd, J = 10.0, 0.8 Hz, 1 H, H_1) ppm. ^{13}C NMR (75.30 MHz, $CDCl_3$): 137.18, 132.86, 129.65, 128.60, 127.63, 126.44, 117.58 ppm. IR (neat): 3083 (w), 3060 (w), 3027, 2925, 1634, 1601 (s), 1494, 1449, 1002, 946, 899, 755, 691 cm^{-1}. MS (EI, 70 eV): m/z (relative intensity), 130 (M$^+$, 87.0), 129 (100.0), 115 (61.4), 102 (10.4), 77 (20.6).

6(*Z*),8-Nonadien-2-one (19). The same procedure as outlined in the above reaction was applied for the *syn*-homoallylamine. To a solution of the homoallylamine **12b** (215 mg, 0.53 mmol) in THF (5 mL) was added methyl iodide (1.51 g, 10.6 mmol). After refluxing for 2 h, the mixture was treated with tetrabutylammonium fluoride (1.06 mL of 1.0 M THF solution, 1.06 mmol). The resulting solution was refluxed for 12 h and worked up as described in the above procedure. Purification by short column chromatography on silica (90:10 hexane/ethyl acetate) afforded 48 mg (65%) of the (*Z*)-dienone **19**.[25] ^{1}H NMR (300 MHz, $CDCl_3$): 6.60 (dddd, J = 17.0, 11.0, 10.2, 1.2 Hz, 1 H, H_3), 6.03 (t, J = 11.0, 1.8 Hz, 1 H, H_4), 5.41 (dt, J = 11.0, 7.5 Hz, 1 H, H_5), 5.20 (dd, J = 17.0, 1.8 Hz, 1 H, H_2), 5.10 (d, J = 10.2 Hz, 1 H, H_1), 2.44 (t, J = 7.3 Hz, 2 H), 2.20 (qd, J = 7.5, 1.2 Hz, 2 H), 2.13 (s, 3 H), 1.68 (m, 2 H) ppm. ^{13}C NMR (75.3 MHz, $CDCl_3$): 208.24, 132.11, 131.47, 130.24, 117.26, 42.81, 29.83, 27.04, 23.66 ppm. IR (neat): 3085 (w), 3006, 2936, 1716 (s), 1436, 1365, 1166, 1001, 904, 797 cm^{-1}. MS (EI, 70 eV): m/z (relative intensity) 138 (M$^+$, 4.3), 95 (2.9), 79 (75.1), 67 (9.8), 43 (100.0).

Phenyl (1*R,2*S**,4*S**)-Benzyl[1-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(trimethylsilyl)-3-butenyl]carbamate (24).** A solution of the homoallylamine **23** (751 mg, 2.25 mmol) in dry pyridine (2 mL) and dry methylene chloride (5 mL) was prepared in a 10-mL round-bottomed flask. Phenyl chloroformate (705

(25) (a) Gras, J.-L.; Bertrand, M. *Tetrahedron Lett.* **1979**, 4549. (b) Wu, T. C.; Maredaz, J.; Gupta, Y. N.; Houk, K. N. *J. Am. Chem. Soc.* **1983**, *105*, 6996.

mg, 4.50 mmol) was added dropwise at room temperature, and the resulting solution was stirred for 5 h. The reaction was quenched with saturated aqueous sodium chloride solution (20 mL) and diluted with diethyl ether (30 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined extracts were washed with water (3 × 50 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting crude product was purified by flash chromatography (silica, eluting with 85:15 hexane/ethyl acetate) to afford 903 mg (89%) of the carbamate **24**, which was contaminated with a small amount of an impurity. This compound displayed broad resonances in ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$): 7.39–7.02 (m, 10 H), 6.07 (br dt, J = 16.9, 10.7 Hz, 1 H), 4.90 (br m, 2 H), 4.68 (br AB q, $\Delta\nu$ = 15.9 Hz, J = 4.6 Hz, 2 H), 4.33 (br m, 2 H), 3.72–3.50 (br m, 2 H), 2.67 (br t, J = 11.5 Hz, 1 H), 1.34 (s, 3 H), 1.26 (s, 3 H) ppm. IR (neat): 3069, 3045, 3032, 2985–2898, 1782, 1716, 1622, 1595, 1245, 1201, 1182, 1162 cm^{-1}.

Phenyl (2*S,3*S**)-Benzyl[3-(1,2-dihydroxy-4-hexenyl)]-carbamate (25).** To a solution of the carbamate **24** (900 mg, 1.98 mmol) in acetonitrile (5 mL) and water (1 mL) was added trifluoroacetic acid (2 mL). The reaction mixture was stirred for 36 h and poured into ethyl acetate (30 mL). The solution was washed with water (2 × 30 mL) and saturated sodium bicarbonate solution (30 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was flash chromatographed on silica, eluting with 70:30 ethyl acetate/hexane, to yield 413 mg (61%) of the diol **25** as a colorless oil. This compound displayed broad resonances in the NMR. ^{1}H NMR (300 MHz, $CDCl_3$): 7.40–7.07 (m, 10 H), 5.78 (dd, J = 15.3, 7.9 Hz, 1 H), 5.65 (m, 1 H), 4.65 (br AB q, J = 15.7 Hz, $\Delta\nu$ = 58.2 Hz, 2 H), 4.13–3.72 (br m, 2 H), 3.49 (br s, 3 H), 2.29 (br s, 1 H), 1.70 (d, J = 6.0 Hz, 3 H) ppm. IR (neat): 3425 (s, br), 3031, 2939–2880, 1710, 1693, 1690, 1595, 1342, 1211, 1195, 969 cm^{-1}. Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.21; H, 6.88; N, 4.08.

(4*S,5*S**)-3-Benzyl-5-(hydroxymethyl)-4-((*E*)-1′-propenyl)-1,3-oxazolidin-2-one (26) and (4*S**,5*S**)-3-Benzyl-5-(hydroxymethyl)-4-((*E*)-1′-propenyl)perhydro-1,3-oxazin-2-one (27).** A 25-mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was charged with a solution of the diol **25** (176 mg, 0.52 mmol) and imidazole (10 mg, 0.15 mmol) in dry toluene (5 mL). The mixture was refluxed for 26 h and, after cooling, concentrated under reduced pressure. The crude product was flash chromatographed on silica, eluting with 70:30 ethyl acetate/hexane, to afford 114 mg (90%) of the five-membered cyclic carbamate **26**, along with 3.5 mg (2%) of the six-membered carbamate **27**. For compound **26**, R_f 0.37 (70:30 ethyl acetate/hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 7.36–7.22 (m, 5 H), 5.69 (dq, J = 15.2, 6.5 Hz, 1 H), 5.44 (ddq, J = 15.2, 9.2, 1.6 Hz, 1 H), 4.73 (d, J = 15.0 Hz, 1 H, benzylic), 4.53 (m, 1 H), 4.11 (t, J = 9.2 Hz, 1 H), 3.94 (d, J = 15.0 Hz, 1 H, benzylic), 3.75 (m, 2 H), 2.81 (br, OH), 1.76 (dd, J = 6.5, 1.6 Hz, 3 H) ppm. ^{13}C NMR (75.3 MHz, $CDCl_3$): 157.71, 136.16, 134.42, 128.42, 127.82, 124.24, 77.32, 61.48, 59.73, 45.78, 17.69 ppm. IR (neat): 3610–3110 (br), 3064, 3030, 3006, 2937–2857, 1740, 1671, 1636, 1604, 1497, 1087, 1065, 1043 cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.67. Found: C, 68.36; H, 7.01; N, 5.96. For compound **27**, R_f 0.29 (70:30 ethyl acetate/hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 7.36–7.23 (m, 5 H), 5.73 (dqd, J = 15.3, 6.6, 1.1 Hz, 1 H), 5.30 (ddq, J = 15.3, 7.0, 1.7 Hz, 1 H), 5.21 (d, J = 15.2 Hz, 1 H, benzylic), 4.39 (dd, J = 11.7, 2.0 Hz, 1 H), 4.16 (ddd, J = 11.7, 3.0, 2.0 Hz, 1 H), 3.89 (d, J = 15.2 Hz, 1 H, benzylic), 3.82 (q, J = 2.0 Hz, 1 H), 3.73 (m, 1 H), 1.77 (dd, J = 6.6, 1.1 Hz, 3 H) ppm.

Phenyl (2*S,3*S**)-Benzyl[3-[1-[(*tert*-butyldiphenylsilyl)oxy]-2-hydroxy-4-hexenyl]]carbamate (28).** A 25-mL round-bottomed flask equipped with a magnetic stirrer was charged with a solution of the diol **25** (161 mg, 0.42 mmol) and imidazole (86 mg, 1.27 mmol) in dry DMF (3 mL). The solution was cooled to −40 °C and treated with *tert*-butyldiphenylsilyl chloride (129 mg, 0.46 mmol) by dropwise addition via syringe under nitrogen. The reaction mixture was stirred at −40 °C for 1 h and allowed to warm up to 0 °C. The reaction was then quenched with water (2 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with water (3 × 20 mL) and dried over magnesium sulfate. The solvent was evaporated at reduced pressure, and the resulting crude product was purified by flash chromatography over silica, eluting with 85:15 hexane/ethyl acetate to afford 210 mg (80%) of the alcohol **28** as a viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): 7.72–7.06 (m, 20 H), 5.80 (br m, 1 H), 5.44 (br m, 1 H), 4.66 (br AB q, J = 15.6 Hz, $\Delta\nu$ = 45.3 Hz, 2 H), 4.51 (s br, 1 H), 4.13 (br m, 2 H), 3.60 (br m, 1 H), 3.43 (br m, 1 H), 1.63 (d, J = 5.8 Hz, 3 H), 1.0 (s, 9 H) ppm. IR (neat): 3600–3050 (br, s), 3070, 3046, 3030, 3014, 2958–2857, 1698 (s), 1591 cm^{-1}. Anal. Calcd for $C_{36}H_{41}NO_4Si$: C, 74.57; H, 7.13; N, 2.42. Found: C, 74.33; H, 7.09; N, 2.37.

Phenyl (2*S,3*S**)-Benzyl[3-[(*tert*-butyldiphenylsilyl)-oxy]-2-methoxy-4-hexenyl]]carbamate (29).** To a solution of alcohol **27** (200 mg, 0.32 mmol) in dry methylene chloride (2 mL) and diisopropylethylamine (0.5 mL) was added chloromethyl methyl ether (34 mg, 0.42 mmol) under nitrogen. The reaction mixture was stirred for 32 h at room temperature and then poured into 10 mL of water. The solution was extracted with diethyl ether (2 × 15 mL), and the extracts were washed with saturated sodium bicarbonate solution. The ethereal solution was dried over magnesium sulfate, concentrated under reduced pressure, and flash chromatographed, eluting with 85:15 hexane/ethyl acetate, affording 152 mg (71%) of methoxymethyl ether **29** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): 7.73–7.07 (m, 20 H), 5.76–5.56 (br m, 2 H), 4.64–4.43 (br m, 5 H), 4.20 (br m, 1 H), 3.66 (br m, 2 H), 3.26 (s, 3 H), 1.57 (d, J = 5.9 Hz, 3 H), 1.05 (m, 9 H) ppm. IR (neat): 3070, 3045, 3031, 2955–2857, 1717, 1495 cm^{-1}. Anal. Calcd for $C_{38}H_{45}NO_5Si$: C, 73.16; H, 7.27; N, 2.25. Found: C, 73.23; H, 7.24; N, 2.19.

(4*S,5*S**)-3-Benzyl-5-[(methoxymethyl)oxy]-4-((*E*)-1′-propenyl)perhydro-1,3-oxazin-2-one (30).** The silyloxy carbamate **29** (130 mg, 0.21 mmol) and imidazole (7 mg, 0.10 mmol) were dissolved in dry toluene (4 mL) in a 25-mL round-bottomed flask. A solution of tetra-*n*-butylammonium fluoride in tetrahydrofuran (0.42 mL of a 1.0 M tetrahydrofuran solution, 0.42 mmol) was added dropwise at room temperature, and the reaction mixture was refluxed for 3 h. The solvent was then removed under reduced pressure, and the resulting crude product was purified by flash chromatography. Eluting with 70:30 ethyl acetate/hexane afforded the cyclic carbamate **30** as a colorless liquid (55 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.32–7.21 (m, 5 H), 5.72 (dqd, J = 15.3, 6.5, 1.2 Hz, 1 H), 5.31 (ddq, J = 15.3, 6.8, 1.7 Hz, 1 H), 5.24 (d, J = 15.2 Hz, 1 H, benzylic), 4.57 (d, J = 7.2 Hz, 1 H, OCH_2O), 4.48 (d, J = 7.2 Hz, 1 H, OCH_2O), 4.37 (dd, J = 11.8, 1.7 Hz, 1 H), 4.25 (dt, J = 11.8, 2.4 Hz, 1 H), 3.87 (d, J = 15.2 Hz, 1 H, benzylic), 3.78 (m, 1 H, NCH), 3.71 (q, J = 2.2 Hz, 1 H, CHOMOM), 3.22 (s, 3 H), 1.76 (dd, J = 6.8, 1.2 Hz, 3 H) ppm. ^{13}C NMR (75.3 MHz, $CDCl_3$): 153.12, 136.83, 130.91, 128.45, 128.23, 127.43, 127.30, 94.82, 69.86, 65.72, 59.76, 55.61, 50.03, 17.64 ppm. IR (neat): 3064, 3028, 2921–2825, 1695, 1470, 1257, 1216, 1104, 1039 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 66.21; H, 7.19; N, 5.07.

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