were collected on a Rigaku AFC5S single-crystal, automated four-circle diffractometer using Mo Kα radiation. The cell was determined to be C-centered monoclinic following data reduction of the primitive triclinic unit cell, obtained from a least-squares fit of 22 random reflections. Crystal symmetry was confirmed by the Laue symmetry check. Intensity statistics and systematic absences indicated crystalline in the acentric spacegroup *Cc* (no 9), which was confirmed by successful refinement of the structure. The structure was solved with SHELXS86[63] followed by successive least-squares full-matrix difference refinements (TEXSAN v. 2.0)[64] to convergence with $R = 0.063$ and $R_w = 0.068$. The fluorine and oxygen atoms were refined anisotropically to convergence; carbon atoms were refined with isotropic thermal parameters. The hydrogen atoms were included in calculated positions but were not refined. Equivalent reflections were averaged, and the data were corrected for Lp effects and anomalous dispersion. Corrections for decay and absorption were not applied.

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Acknowledgment. We wish to thank Ian Henderson and Terry D. Marriot for obtaining high-resolution mass spectral data for this paper, and Dr. K. Whitmire for overall care of the X-ray diffraction facility at Rice. Financial support for this work was obtained from The Robert Welch Foundation and The National Science Foundation (CHE-8906969). X-ray and NMR data were recorded on machines purchased, in part, by The National Science Foundation.

Supplementary Material Available: An ORTEP diagram and tables of crystallographic data collection, atomic coordinates, and anisotropic thermal parameters are available (4 pages). Ordering information is given on any current masthead page.

Manipulation of Substrate-Controlled Diastereoselectivities in Hydroborations in Acyclic Allylamine Derivatives

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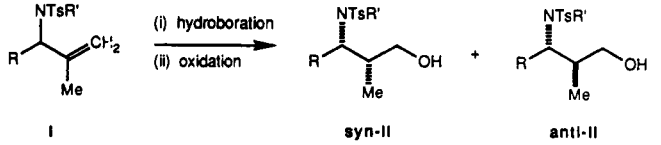
Racemic, and optically active, 2-methyl-3-(*N*-tosylamino)alkenes I were prepared and subjected to both catalyzed and uncatalyzed hydroborations. Data obtained for the catalyzed hydroborations of these allylamine derivatives are consistent with the theory of secondary orbital interactions in transition metal mediated processes presented in the preceding paper. Surprisingly, diastereoselectivities for conventional (uncatalyzed) hydroborations of the same substrates can be extremely sensitive to the borane used; anti products result when borane–tetrahydrofuran complex is reacted with substrates I (R′ = Bn), while with 9-BBN (9-borabicyclo[3.3.1]nonane) these reactions are syn selective. Some of these results are contrary to expectations based upon experimental and theoretical data in the current literature for hydroboration of allylic alcohols. Methodology described in this paper facilitates syntheses of amine alcohols II with extremely high syn and anti selectivities.

The previous paper illustrates that catalyzed and uncatalyzed hydroborations of chiral allylic alcohol derivatives tend to be syn and anti selective, respectively, and gives a model describing secondary orbital effects to account for this difference. As a test of this rationale we decided to explore catalyzed and uncatalyzed hydroborations of allylic *amines* I. Consequently, this paper describes routes to racemic and optically active alkenes I and hydroborations of these. The objectives of this study were (i) to explore "stereocomplementary" behavior which could be exploited in organic syntheses and (ii) to use arguments based on reactive conformations to develop highly diastereoselective syntheses of products II via logical manipulation of the N-protecting groups of substrates I.



I syn-II anti-II

Hydroborations of α-chiral allylic amines have considerable potential in asymmetric syntheses but, to the best of our knowledge, they have been almost[1] totally neglected. Lack of activity in this area is unfortunate because it encompasses preparations of chiral amino alcohols, valuable starting materials for syntheses of new amino acid analogues, β-lactams, and other substances of pharmaceutical interest.[2-8]

Syntheses of Allylamine Derivatives 2–15. This study focuses upon *N*-tosyl-protected allylamine derivatives, principally because absolute stereochemistry at enolizable centers can be preserved when proximal TsN*H* protons are removed preferentially.[9-11] However, there are other reasons for using this particular N-protecting group. Firstly, nitrogen nucleophilicity of tosylamides is poor, hence this functionality has low affinity for com-

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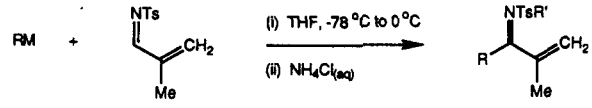
Table I. Preparation of Racemic Allylic Amines 2–5

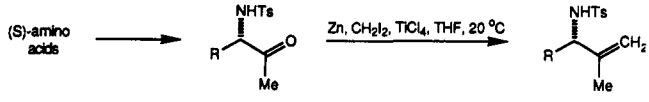


(1) (2) - (5)

entry	R	M	compd	% yield[a]
1	^{n}Bu	Li	2	37
2	^{t}BuO$_2$CCH$_2$	Li	3	59[b]
3	MeC(=CH$_2$)	MgBr	4	72
4	C$_6$F$_5$	MgBr	5	69

[a] Isolated yield after chromatography unless otherwise indicated. [b] Yield after isolation via crystallization.

Table II. Preparation of Optically Active Allylamine Derivatives 6–10



(6) - (10)

entry	R	compd	% yield[a]
1	PhCH2	6	59
2	^{i}PrCH$_2$	7	58
3	^{i}Pr	8	61
4	BnOCH$_2$	9	56[b]
5	Ph	10	35

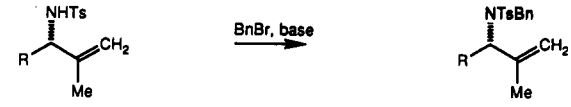
[a] Isolated yields after chromatography. [b] In this case the methylenation was performed on the nonbenzylated compound (R = HOCH$_2$) and the benzyl group was added in a second step. The yield shown here is for the methylenation process.

plexation to boranes; this is important because formation of *N*-borane adducts can be detrimental in hydroboration/oxidation procedures.[12-17] Sulfonyl functionalities also tend to impart crystallinity, hence substrates and products containing it are easily manipulated. Finally, cleavage of tosyl groups from nitrogen has been explored for other amino acid derivatives; removal can be effected via chemical reduction, electrolysis, or treatment with acid.[18,19] For these reasons *N*-tosyl-protected compounds are generally useful in organic synthesis.

N-Tosyl-2-methylpropenimine (1) is conveniently prepared via titanium tetrachloride mediated condensation of 4-methylbenzenesulfonamide with 2-methylpropenal, a modification of a literature procedure originally used for preparation of *C*-arylaldimines.[20] 1,2-Addition of organolithium and organomagnesium reagents to imine 1 provides direct access to a variety of racemic allylamine derivatives, as shown in Table I.

Optically active substrates for the hydroboration study were prepared via Zn/TiCl$_4$-mediated methylenations[21-25] of nonracemic ketones derived from amino acids[9,10,26] (Table II); in all cases but one the products were optically pure to within the limits of ^{1}H NMR detection {Eu(hfc)$_3$ chiral shift experiments}. The alkene derived from phenylglycine is exceptional due to the ability of the aromatic α-substituent to promote racemization; this derivative had an enantiomeric excess of only 48% after the methylenation step.

Table III. Preparation of *N*-(Benzyltosyl)allylamine Derivatives 11–15

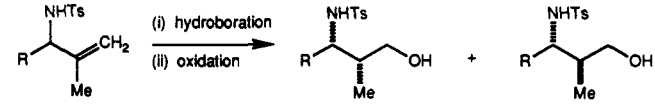


(11) - (15)

entry	R	product	method	isolated yield, %
1	MeC(=CH$_2$)	11	NaH[a]	46
2	PhCH$_2$	12	NaH[b]	53
3	Bu	13	K$_2$CO$_3$/Me$_2$CO[c]	96
4	^{i}PrCH$_2$	14	K$_2$CO$_3$/Me$_2$CO[c]	85
5	^{t}BuO$_2$CCH$_2$	15	K$_2$CO$_3$/Me$_2$CO[c]	86

[a] NaH, BnBr, DMF, 60 °C, 16 h. [b] NaH, BnBr, THF, catalytic NBu$_4$NI, 65 °C, 7 h. [c] K$_2$CO$_3$, BnBr, Me$_2$CO, catalytic NBu$_4$NI, 25 °C, 24 h.

Table IV. Catalyzed and Uncatalyzed Hydroborations of *N*-Tosylallylamine Derivatives 6–10, 2, and 3



(16) - (22)

entry	R	substrate	product	method	syn:anti[a]
1	PhCH$_2$	6	16	catalyzed	7.0:1.0
2	PhCH$_2$	6	16	uncatalyzed	1.0:1.0
3	^{i}PrCH$_2$	7	17	catalyzed	4.0:1.0
4	^{i}PrCH$_2$	7	17	uncatalyzed	2.0:1.0
5	^{i}Pr	8	18	catalyzed	6.7:1.0
6	^{i}Pr	8	18	uncatalyzed	1.0:7.4
7	BnOCH$_2$	9	19	catalyzed	4.0:1.0
8	BnOCH$_2$	9	19	uncatalyzed	1.0:1.0
9	Ph	10	20	catalyzed	1.0:1.0
10	Ph	10	20	uncatalyzed	1.0:1.0
11	^{n}Bu	2	21	catalyzed	5.3:1.0
12	^{t}BuO$_2$CCH$_2$	3	22	catalyzed	3.7:1.0

[a] Ratios determined via ^{1}H NMR at 300 MHz.

Some of the N-tosylated allylamine derivatives whose syntheses are described above were N-benzylated (Table III) to increase steric demands around the nitrogen and to remove the acidic NH group. Attempts to do this by treatment with sodium hydride and then benzyl bromide in DMF or THF did not work well (entries 1 and 2), but benzyl bromide/potassium carbonate/catalytic tetra-*n*-butylammonium iodide in acetone proved to be more convenient and gave better yields (entries 3–5).

Hydroborations of Allylamine Derivatives. In preliminary studies[27,28] allylamine derivatives 6–10 were

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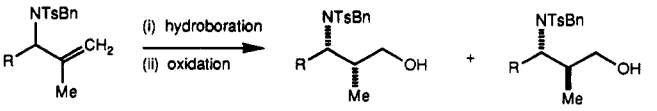
hydroborated with 9-BBN and with catecholborane in the presence of 2 mol % $[RhCl(COD)]_2 \cdot 4PPh_3$ (COD = cyclooctadiene); in both cases the organoborane intermediates were oxidized with alkaline peroxide (Table IV). Alcohols formed in the conventional hydroborations (with 9-BBN) were contaminated with oxidation products from 9-BBN so further purification was obligatory. In contrast, catechol, the major byproduct from the catalyzed processes, is easily removed via base extraction. Consequently, crude ^1H NMR spectra of the rhodium-mediated processes after oxidation and aqueous workup tend to be relatively clean; the only perceptible impurity in these reactions, traces of triphenylphosphine oxide, can be removed via passage through a short silica column. Indeed, all but one of the catalyzed reactions each gave pure samples of the major diastereomers (syn, see below) after a single recrystallization of the crude reaction mixtures. The 1:1 diastereomeric mixture formed via catalyzed hydroboration of the phenylglycine derivative (**10**) (entry 5) could not be purified in this way; however, this is the least interesting example because the starting material is not accessible in optically pure form and hydroboration of this alkene is not stereoselective. Racemic substrates **2** and **3** were also hydroborated under the catalyzed conditions, and in both cases syn products were formed predominantly. Sodium acetate was used as a base when oxidizing the borane derived from β-amino ester **3** because more basic conditions seem to decompose the product **22**.

Single-crystal X-ray diffraction studies were used to identify diastereoisomers of alcohol **16**,[29] and a chemical correlation was used to establish relative configurations of the butyl-substituted compounds (**21**) (vide infra, Scheme II). Other stereochemical assignments in Table IV are based upon chemical shift data since proton and carbon-13 NMR spectra of amino alcohol products **16-22** fall into two categories. One set of compounds, including *syn*-**16** and *syn*-**21**, have NMR resonances for certain functional groups which are at significantly higher field than the other group of compounds, which includes *anti*-**16** and *anti*-**21**. The resonances in question are (with ranges of chemical shift differences in parentheses) (i) the N*H*Ts resonance ($\Delta\delta$ = 0.11–0.60 ppm at 300 MHz); the C*H*$_3$ resonance of the 2-methyl substituent ($\Delta\delta$ = 0.08–0.23 ppm at 300 MHz); and (iii) the *C*H$_3$ resonance of the 2-methyl substituent ($\Delta\delta$ = 2.9–5.9 ppm at 300 MHz).

In trial experiments two substrates (**2** and **3**) were reacted with BH_3·THF. A gas (presumably hydrogen) was evolved, and the reactions gave near 1:1 mixtures of diastereomers. It seemed likely that hydroborations of the other NHTs compounds with borane also would give poor selectivity, hence no further experiments in this series were attempted. However, we reasoned that N-benzylation of these substrates would exclude reactions of boranes with the acidic N*H*Ts group, and expose stereochemical effects of this enhanced steric requirement on their hydroboration reactions. Consequently, we focused our efforts on the *N*-benzyltosyl-protected compounds, as described below.

Table V depicts hydroborations of *N*-(benzyltosyl)-amines **12–15** under catalyzed conditions, with 9-BBN, and with BH_3·THF complex. These particular substrates (**12–15**) were selected because they have substitution patterns similar to those used in our previous comparative studies.[27,30] All the hydroborations of these alkenes are highly diastereoselective. *The catalyzed processes and the*

Table V. Hydroborations of *N*-(Benzyltoxyl) Substrate 12–15



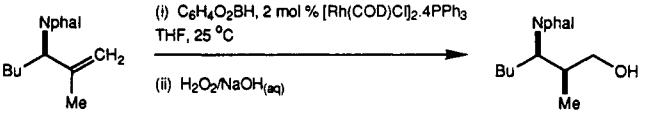
(12) - (15) syn (23) - (26) anti

entry	substrate	product	R	method[a]	syn:anti[b]
1	12	23	$PhCH_2$	$C_6H_4O_2BH$/ cat. [Rh][c]	18:1.0
2	12	23	$PhCH_2$	9-BBN[d]	13:1.0
3	12	23	$PhCH_2$	BH_3[e]	1.0:17
4	13	24	Bu	$C_6H_4O_2BH$/ cat. [Rh]	10:1.0
5	13	24	Bu	9-BBN	7.0:1.0[f]
6	13	24	Bu	BH_3	1.0:21
7	14	25	$^iPrCH_2$	$C_6H_4O_2BH$/ cat. [Rh]	6.0:1.0
8	14	25	$^iPrCH_2$	9-BBN	25:1.0
9	14	25	$^iPrCH_2$	BH_3	1.0:20
10	15	26	$^tBuO_2CCH_2$	9-BBN[g]	5.3:1.0
11	15	26	$^tBuO_2CCH_2$	BH_3[g]	1.0:52

[a] Oxidation with $NaOH/H_2O_2$ unless otherwise indicated. [b] Ratios determined by HPLC. [c] Catalyzed hydroborations were performed using THF solutions of 2 mol % of $[Rh(COD)Cl]_2 \cdot 4PPh_3$, 3 equiv of catecholborane at 25 °C for 48 h. [d] 9-BBN hydroborations were performed using THF solutions of 3 equiv of 9-BBN at −78 °C to 25 °C then at 25 °C for 24 h. [e] BH_3 hydroborations were performed using THF solutions of 3 equiv of BH_3·THF at −78 °C to 25 °C then at 0 °C for 24 h. [f] Ratio determined by ^1H NMR at 300 MHz. [g] Oxidation with $NaOAc/H_2O_2$; use of more basic conditions tends to decompose the product.

9-BBN hydroborations proceed in a syn sense (entries 1, 2, 4, 5, 7, 8, and 10), but a dramatic reversal to anti selectivity is observed for hydroborations of these substrates with borane-tetrahydrofuran complex (entries 3, 6, 9, and 11).

Syn diastereoselectivity in the catalyzed hydroborations depicted in Table V is consistent with observations for catalyzed hydroborations of *phthaloyl-protected* allylamine derivatives. Proton NMR analyses of crude reaction mixtures formed in the latter reactions indicate the desired products are formed with complete syn selectivity, as illustrated below. These hydroborations are complicated



(27) (28)

syn:anti > 95:5

by reduction of the phthaloyl group; nevertheless, they compare favorably with conventional hydroborations of the same alkenes, transformations which give intractable mixtures due to extensive reduction of that N-protecting functionality.[31]

The amino alcohol assigned as *syn*-**23** (Table V) was shown to be identical with a sample formed via N-benzylation of *syn*-**16**, one of the compounds that was analyzed via single-crystal X-ray diffraction;[29] consequently, that particular stereochemical assignment is confirmed unambiguously. Mitsunobu inversion[32] of the known[33] anti alcohol **29** was used to establish the stereochemistry of *syn*-**28** also (Scheme I). Relative stereo-

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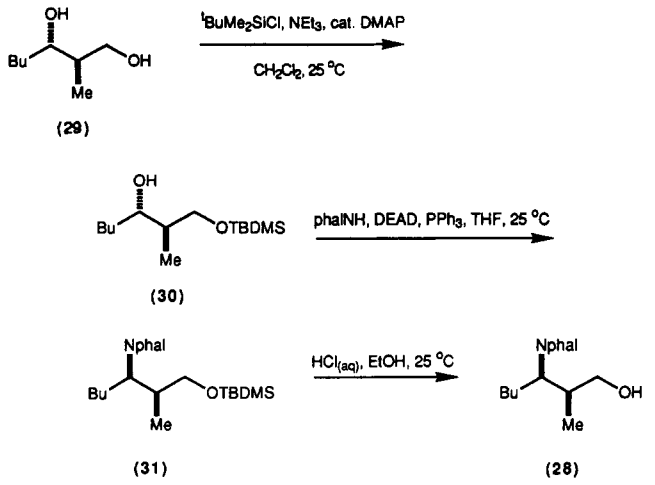
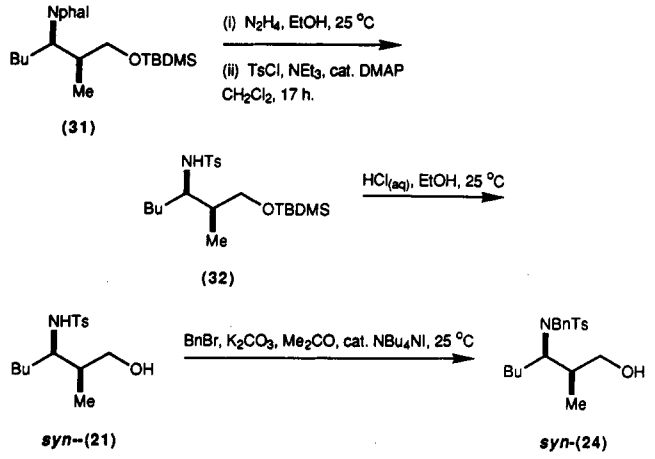
Scheme I. Conformation of the Syn Stereochemistry of Compound 28



Scheme II. Conformation of the Stereochemistry of *syn*-21 and *syn*-24



chemistries of the butyl-substituted compounds *syn*-**21** and *syn*-**24** were elucidated by removing protecting groups from the *N*-phthaloyl derivative **31** and then adding *N*-tosyl and *N*-benzyl functionalities in that order (Scheme II). Finally, chemical shift arguments were used for stereochemical assignments of compounds **25** and **26**, similar to the approach described above for the NHTs derivatives **16–22**. For instance, the CH_3 NMR signal for the 2-methyl substituent of the syn compounds appear at higher field than the corresponding peaks for the anti alcohols for all the products **23–26**; furthermore, diastereotopic protons of the *N*-benzyl substituent in the anti series give widely separated ^1H NMR AB patterns, whereas the corresponding signals for the syn compounds are less separated and more perturbed. Parenthetically, we also note the syn compounds have higher retention times on silica HPLC columns eluted with ethyl acetate/hexane mixtures.

Curiously, attempted hydroboration of diene **11** under the catalytic conditions with 1 equiv of catecholborane gave, after oxidative workup, a mixture of the starting material, the product of hydrogenation of one of the two double bonds, and a small amount of a monohydroboration product (relative stereochemistry not assigned). The first two components accounted for 46% of the material recovered (approximate ratio 2:1), while the alcohol was formed in 14% yield. Formation of hydrogenation products in catalyzed *hydroborations* is an enigma within the field, and, in this work, generation of so much hydrogenation product only for this particular allylamine substrate

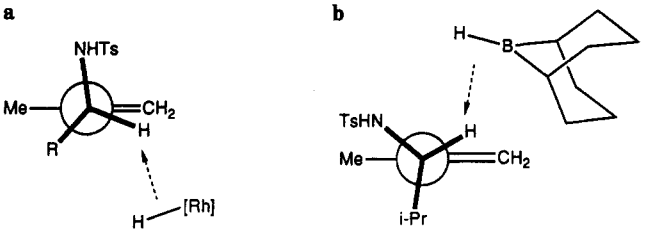


Figure 1. Reactive conformations in catalyzed and 9-BBN hydroborations of *N*-tosyl protected allylic amine derivatives. (a) Preferential orientation in catalyzed hydroborations of N-tosyl protected allylic amine derivatives. (b) Preferential orientation in 9-BBN hydroboration of *N*-tosyl protected allylic amine substrate **8**.

is a surprising observation; it shows nonreacting double bonds can alter the course of catalyzed hydroboration reactions.

Discussion

Catalyzed hydroborations of alkenes **6–10** (Table IV, entries 1, 3, 5, 7, 9, 11, and 12) conform to the model presented in the previous paper wherein the predominant product arises from approach of a rhodium complex anti to the group which is largest and has the best σ-electron-withdrawing capability, i.e. the NHTs entity (Figure 1a). Uncatalyzed hydroborations of the same substrates with 9-BBN exhibit poor selectivity, except when R = ^{i}Pr (entry 6) the reaction is appreciably anti selective. The latter observations reflect two opposing factors: (i) electronic influences favoring a reactive conformation in which the R functionality orients anti to the approaching borane and (ii) steric demands which guide the NHTs group to this same position.[34,35] For the substrate with the largest alkyl substituent, **8** (R = ^{i}Pr, entry 6), the steric differences between the isopropyl and NHTs groups are outweighed by electronic factors and anti selectivity results, presumably via the reactive conformation shown in Figure 1b. Steric demands of ^{i}Pr and Ph groups are similar but the latter is less σ-donating, hence no anti selectivity is observed when R = Ph (entry 10). The other alkyl groups are smaller so in entries 2, 4, and 8 the opposing steric and electronic effects balance, and very little selectivity is observed.

Enhanced bulk around the nitrogen for the *N*-benzyl substrates **12–15** (Table V) accentuates steric effects in hydroborations of these alkenes. Electronic parameters reinforce these steric factors in the catalyzed processes and appreciable syn selectivities result (Table V, entries 1, 4, and 7; Figure 2a). Hindrance in 9-BBN hydroborations excludes NBnTs from the same face of the alkene as the borane, even from the outside position hence these transformations are also syn selective; the reactive conformation shown in Figure 2b accounts for the observed stereoselectivities. Borane, however, is smaller so it can tolerate the NBnTs group in the outside position; consequently, we propose *anti selectivity* in these reactions results via the reactive conformation shown in Figure 2c.

Conclusions

Research presented in this paper highlights hydroborations which are fundamentally different to those in Still's pioneering study[33] and which are beyond the realms

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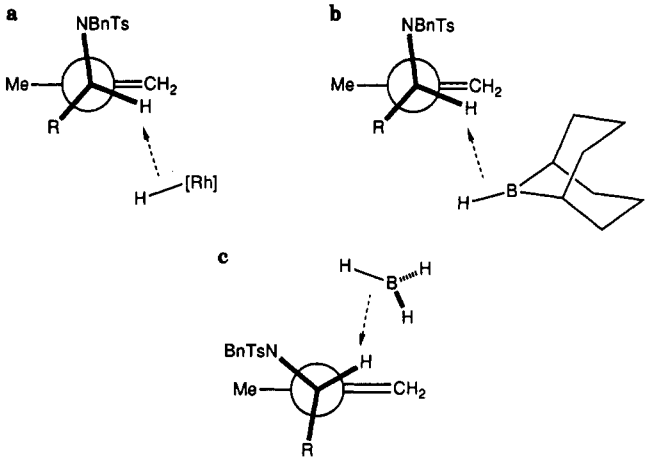

Figure 2. Reactive conformations in catalyzed, 9-BBN, and borane hydroborations of substrates **12–15** (Table V). (a) Preferential orientation in catalyzed hydroborations governed by steric and electronic effects. (b) Preferential orientation in 9-BBN hydroborations governed predominantly by steric effects. (c) Preferential orientation in BH_3 hydroborations governed predominantly by electronic effects.

of Houk's calculations[34,35] for hydroborations of chiral allylic compounds. Excellent syn selectivity in hydroborations of chiral allylamine derivatives can be obtained using catalyzed hydroborations or, for the *N*-benzyltosyl substrates, by using a sterically encumbered borane. Equally good anti selectivity can be obtained by hydroborating these substrates with borane–tetrahydrofuran complex. We know of no other hydroboration processes where such vastly different stereoselectivities can be obtained by fine tuning the reaction conditions. McGarvey and co-workers have observed complementarity between thexylborane and borane in hydroborations of chiral enol ethers,[36] but most of the selectivities observed are moderate. Furthermore, the trends in McGarvey's study are the reverse of those demonstrated here (i.e. the larger borane gives higher anti selectivity), underlining how subtle stereoelectronic perturbations can have a profound effect on stereoselection.

Amino acids have been used extensively as chirons in nonracemic synthesis.[2] The usual approach in such work is sequential reduction of the carboxyl termini of amino acids to aldehydes or ketones, and stereoselective manipulation of this functionality directed by the substrate chirality.[37-39] Transformations of amino acids into allylic amines are less common, however, presumably due to problems associated with racemization. Wittig reactions of amino aldehydes,[40] for example, give products of variable optical purity.[41] It is possible to convert methionine into an optically pure allylamine derivative,[42] but this strategy is specific to that particular amino acid and hence lacks generality. One must normally resort to circuitous routes to prepare optically active allylamine derivatives,[43] approaches which can be inefficient and experimentally inconvenient. These restrictions are unfortunate because reactions of allylic amines can proceed with high diastereofacial selectivity and afford valuable precursors to biologically active compounds.[43-49] Other approaches to amino alcohols, like additions of organometallics or metal hydrides to alcohol–imine derivatives, tend to be limited by poor diastereofacial selectivity and/or lack of generality.[50-56]

The asymmetric and racemic preparations of allylamine derivatives described here, coupled with these methods for stereocontrolled elaboration of these substrates via hydroboration reactions, expose new possibilities for organic syntheses of chiral molecules containing nitrogen.

Experimental Section

General Procedures. Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 Series FTIR or a Beckman 4200 Series spectrophotometer and values are quoted in cm^{-1}. Low-resolution (EI) and high-resolution (EI) mass spectra were determined on a Finnigan 3300 mass spectrometer and a CAC 21/110 C high-resolution mass spectrometer, respectively. HPLC was performed on a Rainin HPLC pump and a 4.6 mm × 25 cm 60-Å pore size silica column (Rainin Si 83-101-C) with an ISCO V4 UV–visible detector interfaced with an Apple Macintosh plus. Optical rotations were determined on a JASCO digital polarimeter. High-field NMR spectra were recorded on a Bruker AF300 (^1H at 300 MHz, ^{13}C at 75.4 MHz) or a Bruker AC250 (^1H at 250 MHz, ^{13}C at 62.5 MHz) instrument in $CDCl_3$. ^1H chemical shifts are reported in δ ppm relative to $CHCl_3$ (7.25 ppm) or TMS (0.0 ppm) as an internal reference, and ^{13}C chemical shifts are reported in δ ppm relative to $CDCl_3$ (77.0 ppm) as an internal reference. In cases where abbreviated DEPT sequence experiments were carried out during ^{13}C NMR experiments, the carbon multiplicities are listed as (C) quaternary, (CH_2) methylene, and (CH/CH_3) methine/methyl. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Thin-layer chromatography was performed on silica gel 60 F_{254} plates from Whatman. Flash chromatography was performed on SP silica gel 60 (230–400-mesh ASTM). Tetrahydrofuran (THF) was distilled immediately before use from sodium benzophenone ketyl. Borane–THF complex and 9-BBN solutions were purchased from Aldrich Chemical Co. and used as received. Catecholborane was purchased from Aldrich and distilled under reduced pressure before use. Organic solutions were dried over magnesium sulfate.

***N*-Tosyl-2-methylpropenimine (1).** A solution of methacrolein (6.4 g, 7.53 mL, 90 mmol), 4-methylbenzenesulfonamide (15.4 g, 90 mmol), and triethylamine (28.3 g, 39 mL, 280 mmol) in 200 mL of dichloromethane was cooled to 0 °C with stirring under nitrogen, a solution of titanium tetrachloride (9.5 g, 5.5 mL, 50 mmol) in 25 mL dichloromethane was added, and the mixture was stirred at 0 °C for 90 min. The mixture was then filtered through Celite, and the solvents were evaporated to give a solid crystalline mass. The solids were broken up and refluxed with stirring for 10 min with 100 mL of ether. The ether solution was decanted off the residual solid, filtered through Celite, and then evaporated to give 5.63 g of the crude imine. A second extraction of the residue in the same way gave 4.9 g. Combined yield 10.5 g, 47 mmol, 52% crude product,[57] which was used without further

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purification. This product is slightly sensitive to atmospheric moisture and should be stored under nitrogen: 90-MHz ^{1}H NMR 1.90 (s, 3 H), 2.42 (s, 3 H), 5.96 (s, 1 H), 6.08 (s, 1 H), 7.30 (m, 2 H), 7.80 (m, 2 H), 8.56 (s, 1 H).

2-Methyl-3-(*N*-tosylamino)-1-heptene (2). A solution of 4.9 g (22 mmol) of imine 1 in 30 mL of THF was cooled to −78 °C under nitrogen; 10.4 mL of a 2.0 M solution of *n*-butyllithium was added with stirring. The solution was warmed to 0 °C and stirred at that temperature for 20 min, and then a dilute aqueous solution of ammonium chloride was added. The mixture was diluted with 200 mL of ether, washed with water, 1 × 50 mL, and then dried. Evaporation of the solvents gave crude material which was purified by flash chromatography, eluting with 10% ethyl acetate in hexane to give 2.3 g (8.2 mmol), 40%, of 2-methyl-3-(*N*-tosylamino)-1-heptene: TLC *Rf* 0.43 (20% ethyl acetate in hexane); mp 89–90 °C; 250-MHz ^{1}H NMR 0.76 (m, 3 H), 1.11 (m, 4 H), 1.40 (m, 2 H), 1.44 (s, 3 H), 2.36 (s, 3 H), 3.65 (m, 1 H), 4.61 (s, 1 H), 4.68 (s, 1 H), 5.48 (d, J = 7.7 Hz), 7.23 (m, 2 H), 7.72 (m, 2 H); ^{13}C NMR 13.9, 17.2, 21.5, 22.2, 27.8, 33.4, 59.7, 113.2, 127.2, 129.3, 138.0, 142.9, 143.4; IR ($CHBr_3$) 3262 (st br), 3060 (m), 3039 (m), 2930 (st), 2868 (t), 1652 (w), 1597 (m), 1496 (w), 1448 (st), 1326 (st br), 1162 (st br); MS *m/e* (%) 281 (M^+, <1), 224 (95), 155 (100), 91 (60); HRMS calcd for $C_{15}H_{23}NO_2S$ 281.144935, found 281.14547.

***tert*-Butyl 4-Methyl-3-(*N*-tosylamino)-4-pentenoate (3).** A solution of 2.73 g (3.8 mL, 27 mmol) of diisopropylamine in 30 mL of THF was cooled to 0 °C, 11.9 mL of a 2.1 M solution of *n*-butyllithium (25 mmol) in hexane was added, and the mixture was stirred at 0 °C for 20 min. This solution of LDA was cooled to −78 °C, 3.22 g (3.73 mL, 27 mmol) of *tert*-butyl acetate was added, and the resulting mixture was stirred at −78 °C for 35 min. At −78 °C a solution of 5.63 g (25 mmol) of imine 1 in 30 mL of THF was added, and the mixture was stirred for 3 min. The mixture was warmed to 0 °C, 30 mL of aqueous ammonium chloride was added, and then the mixture was diluted with 200 mL of ether. The organic layer was washed twice with saturated aqueous ammonium chloride and then dried. Evaporation of the solvents gave crude material which crystallized on standing. Recrystallization from ether/hexane gave 5.08 g (15 mmol), 59%, of *tert*-butyl 4-methyl-3-(*N*-tosylamino)-4-pentenoate: TLC R_f 0.09 (5% ethyl acetate in hexane); mp 91–92 °C; 250-MHz ^{1}H NMR 1.40 (s 9 H), 1.59 (s, 3 H), 2.41 (s, 3 H), 2.43 (m, 2 H), 4.03 (m, 1 H), 4.78 (s, 1 H), 4.84 (s, 1 H), 5.61 (d, J = 7.8 Hz, 1 H), 7.75 (m, 2 H); ^{13}C NMR 18.8 (CH/CH_3), 21.5 (CH/CH_3), 28.0 (CH/CH_3), 39.2 (CH_2), 55.8 (CH/CH_3), 81.6 (CH/CH_3), 113.4 (CH_2), 127.2 (CH/CH_3), 129.5 (CH/CH_3), 137.7 (C), 142.5 (C), 143.3 (C), 170.2 (C); IR ($CHBr_3$) 3227 (st br), 3025 (m), 2991 (st), 2937 (st), 1710 (st br), 1647 (w), 1599 (w), 1495 (w), 1456 (st br), 1329 (st br), 1166 (st br). Anal. Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42; N, 4.13. Found: C, 60.32; H, 7.52; N, 4.08.

2,4-Dimethyl-3-(*N*-tosylamino)-1,4-pentadiene (4). Magnesium, 0.19 g (7.92 mmol), was placed in a two-neck round-bottom flask equipped with a septum and a reflux condenser. A crystal of iodine was added, and the apparatus was flushed with nitrogen; 2 mL of THF was added, and then 2-bromopropene, 0.87 g (7.2 mmol), was added slowly with further THF to maintain a steady exothermic reaction. The total volume of THF added was 15 mL. After the addition of 2-bromopropene was complete, the mixture was stirred at 25 °C for 15 min and then cooled to 0 °C. A solution of the tosyl imine 1, 1.6 g (7.2 mmol), in 10 mL of THF was added with stirring at 0 °C, and the mixture was stirred at 0 °C for 10 min. Saturated aqueous ammonium chloride (10 mL) was added, and the mixture was diluted with 100 mL of ether. The organic layer was dried, and evaporation of the solvent gave the crude product as a crystalline solid. Flash chromatography eluting with 15 and then 20% ethyl acetate/hexane gave 1.37 g (5.1 mmol), 72%, of the product: TLC R_f 0.41 (in 20 % ethyl acetate in hexane); mp 75–76 °C; 300-MHz ^{1}H NMR 1.52 (s, 6 H), 2.40 (s, 3 H), 4.15 (d, J = 8.0 Hz, 1 H), 4.83 (d, J = 9.7 Hz, 4 H), 5.33 (d, J = 8.0 Hz, 1 H), 7.24 (m, 2 H), 7.73 (m, 2 H); 75.42-MHz ^{13}C NMR 18.7 (CH/CH_3), 21.3 (CH/CH_3), 63.8 (CH/CH_3), 113.2 (CH_2), 127.0 (CH/CH_3), 129.1 (CH/CH_3), 137.9 (C), 141.5 (C), 142.9 (C); IR ($CHBr_3$) 3270 (st), 2970 (m), 2930 (m), 2910 (m), 2850 (m), 1585 (w), 1420 (m), 1375 (m), 1305 (st), 1065 (st); MS *m/e* (%) 265 (M^+, <1), 224 (40), 155 (60), 110 (35), 91 (100); HRMS calcd for $C_{14}H_{19}NO_2S$ 265.113635, found 265.11308. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.61; H, 7.36; N, 5.20.

2-Methyl-1-(*N*-tosylamino)-1-(pentafluorophenyl)-2-propene (5). Magnesium, 0.1 g (4 mmol), was placed in a two-neck flask equipped with a septum and a reflux condenser. A crystal of iodine was added, and the apparatus was flushed with nitrogen. Ether, 2 mL, was added followed by slow addition of 0.74 g of bromopentafluorobenzene (0.37 mL, 3 mmol) in ether to maintain a steady exothermic reaction. The total volume of ether added was 15 mL. After the addition of bromopentafluorobenzene was complete the mixture was stirred at 25 °C for 15 min and then cooled to 0 °C. A solution of 0.6 g of tosyl imine 1 (2.7 mmol) in 5 mL of THF was added with stirring at 0 °C, and the mixture was stirred at 0 °C for 10 min. Saturated aqueous ammonium chloride, 10 mL, was added, and the mixture was diluted with 100 mL of ether. The organic layer was dried, and evaporation of the solvent gave crude product which was purified by flash chromatography, eluting with 15% ethyl acetate in hexane to give 0.73 g (1.9 mmol), 69%, of the product: mp 135–137 °C; 90-MHz ^{1}H NMR 1.76 (s, 3 H), 2.38 (s, 3 H), 4.80 (s, 1 H), 4.98 (s, 1 H), 5.08–5.48 (m, 2 H), 7.16 (m, 2 H), 7.60 (m, 2 H); MS *m/e* (%) 391 (M^+, <1), 155, (10), 91 (100); HRMS calcd for $C_{17}H_{14}F_5NO_2S$ 391.06651, found 391.06625.

3-Methyl-2-(*N*-tosylamino)-1-phenyl-3-butene (6). Zinc dust, 3.96 g (60.6 mmol 18 equiv), was suspended in 60 mL of THF with vigorous stirring under nitrogen. Diiodomethane, 8.84 g (33 mmol 10 equiv), was added, and the mixture was stirred at 25 °C for 30 min. The stirred suspension was cooled to 0 °C, and titanium tetrachloride, 1.29 g (6.6 mmol, 2 equiv), was added slowly. The mixture was warmed to 25 °C and stirred for 40 min. A solution of 3-(*N*-tosylamino)-4-phenyl-2-butanone, 1.07 g (3.3 mmol, 1 equiv), in 10 mL of THF was added and stirred at 25 °C for 40 min. The dark brown mixture was cooled to 0 °C and diluted with 100 mL ether, and then 100 mL of 2 M HCl was added and the mixture was stirred for 5 min at 0 °C. The aqueous and organic layers were separated, and the aqueous layer was extracted with 2 × 50 mL of ether. The ether extracts and the organic layer were combined and washed with saturated aqueous sodium bicarbonate and then dried. Evaporation of the solvents and flash chromatography of the crude alkene eluting with 15% ethyl acetate in hexane gave 0.48 g, 44%, of the product as a crystalline solid: TLC R_f 0.12 (10% ethyl acetate in hexane); mp 116–118 °C; $[\alpha]_D$ = +0.27°, c = 0.83 ($CHCl_3$); 300-MHz ^{1}H NMR 1.64 (s, 3 H), 2.41 (s, 3 H), 2.76 (m, 2 H), 3.79 (br q, J = 6.8 Hz, 1 H), 4.76 (NH, d, J = 6.4 Hz, 1 H), 4.76 (m, 2 H), 7.0 (m, 2 H), 7.20 (m, 5 H), 7.53 (m, 2 H); 75.42-MHz ^{13}C NMR 17.9 (CH/CH_3), 21.3 (CH/CH_3), 40.1 (CH_2), 60.2 (CH/CH_3), 113.5 (CH_2), 126.5 (CH/CH_3), 126.9 (CH/CH_3), 128.3 (CH/CH_3), 128.9 (CH/CH_3), 129.1 (CH/CH_3), 136.3 (C), 136.8 (C), 142.8 (C), 143.0 (C); MS *m/e* (%), 315 (M^+, <1), 224 (100), 155 (40), 91 (45); HRMS calcd for $C_{18}H_{21}NO_2S$ 315.129285, found 315.12905.

2,5-Dimethyl-3-(*N*-tosylamino)-1-hexene (7). Similar to preparation of **6** using 1.42 g (5 mmol) of 5-methyl-3-(*N*-tosylamino)-2-hexanone. Purification by flash chromatography eluting with 15% ethyl acetate in hexane yielded 0.82 g, 58%, of **7**: TLC R_f 0.20 (10% ethyl acetate in hexane); mp 99–100 °C; $[\alpha]_D$ = +0.27°, c = 1.49 ($CHCl_3$); 300-MHz ^{1}H NMR 0.77–0.82 (overlapping d, 6 H), 1.31 (m, 2 H), 1.48 (s, 3 H), 1.50 (m, 1 H), 2.41 (s, 3 H), 3.79 (br q, J = 7.6 Hz, 1 H), 4.64 (m, 1 H), 4.73 (br s, 1 H), 5.23 (NH, d, J = 7.6 Hz, 1 H), 7.26 (m, 2 H), 7.74 (m, 2 H); ^{13}C NMR 16.7 (CH/CH_3), 21.3 (CH/CH_3), 22.0 (CH/CH_3), 24.1 (CH/CH_3), 42.8 (CH_2), 57.8 (CH/CH_3), 113.0 (CH_2), 127.0 (CH/CH_3), 129.0 (CH/CH_3), 137.7 (C), 142.7 (C), 143.3 (C); IR 3270 (st), 2950 (st), 2920 (st), 2860 (m), 1590 (w), 1420 (m br), 1315 (st); MS *m/e* (%) 281 (M^+, ~1), 224 (60), 155 (100), 91 (95). Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.23; N, 4.98. Found: C, 63.93; H, 8.23; N, 4.97.

2,4-Dimethyl-3-(*N*-tosylamino)-1-pentene (8). Similar to preparation of **6** using 0.81 g (3 mmol) of 4-methyl-3-(*N*-tosylamino)-2-pentanone. Purification by flash chromatography eluting with 15% ethyl acetate in hexane gave 0.49 g, 1.8 mmol, 61%, of the product: TLC R_f 0.14 (10% ethyl acetate in hexane); mp 75–81 °C (racemic sample); $[\alpha]_D$ = +0.36° (c = 0.36 ($CHCl_3$)); 300-MHz ^{1}H NMR 0.79 (d, J = 6.7 Hz, 3 H), 0.89 (d, J = 6.7 Hz,

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3 H), 1.47 (s, 3 H), 1.69 (m, 1 H), 2.41 (s, 3 H), 3.43 (t, J = 8.3 Hz, 1 H), 4.67 (m, 2 H), 4.77 (d, J = 8.5 Hz, 1 H), 7.25 (m, 2 H), 7.71 (m, 2 H); ^{13}C NMR 17.7 (CH/CH_3), 18.2 (CH/CH_3), 19.5 (CH/CH_3), 21.3 (CH/CH_3), 30.0 (CH/CH_3), 65.5 (CH/CH_3), 113.7 (CH_2), 127.0 (CH/CH_3), 129.0 (CH/CH_3), 142.3 (C), 142.7 (C); IR 3270 (st), 2960 (st), 2920 (st), 1590 (w), 1425 (br st), 1315 (st), 1090 (st), 1035 (st); MS m/e (%), 267 (M^+, <1), 224 (15), 155 (30), 91 (100); HRMS calcd for $C_{14}H_{21}NO_2S$ 267.129285, found 267.12865.

1-(Benzyloxy)-3-methyl-2-(*N*-tosylamino)-3-butene (9). Sodium hydride, 0.42 g (9 mmol of a 50% dispersion in mineral oil), was placed in a flask equipped with a reflux condenser and flushed with nitrogen. The hydride was washed with dry hexane three times. THF (5 mL) was added, followed by a solution of 0.42 g (1.75 mmol) of 3-methyl-2-(*N*-tosylamino)-3-buten-1-ol in 5 mL of THF. The mixture was stirred at 25 °C for 5 min, 0.33 g (0.23 mL, 1.9 mmol) of benzyl bromide was added, and the mixture was refluxed for 2 h. On cooling, the mixture was diluted with 100 mL of ether, washed with 2 × 20 mL of water, and then dried. Evaporation of the solvent gave a mixture of O-benzylated and N,O-dibenzylated compounds. Flash chromatography eluting with 15% ethyl acetate in hexane gave 0.243 g (0.7 mmol), 40%, of **9**, 1-(benzyloxy)-3-methyl-2-(*N*-tosylamino)-3-butene, and 0.205 g (0.47 mmol), 27%, of 1-(benzyloxy)-3-methyl-2-(benzyltosylamino)-3-butene. For **9**: TLC R_f 0.09 (10% ethyl acetate in hexane); mp 93–94 °C; $[\alpha]_D$ = +0.70° (c = 1.58); ^{1}H NMR 1.63 (s, 3 H), 2.41 (s, 3 H), 3.35 (m, 1 H), 3.46 (m, 1 H), 3.84 (m, 1 H), 4.38 (s, 2 H), 4.86 (br s, 1 H), 4.90 (br s, 1 H), 5.10 (d, J = 6.0 Hz, 1 H), 7.19–7.36 (m, 7 H), 7.69–7.72 (m, 2 H); ^{13}C NMR 18.7 (CH/CH_3), 21.3 (CH/CH_3), 58.2 (CH/CH_3), 70.5 (CH_2), 72.8 (CH_2), 114.0 (CH_2), 127.0 (CH/CH_3), 127.4 (CH/CH_3), 127.6 (CH/CH_3), 128.2 (CH/CH_3), 129.2 (CH/CH_3), 137.0 (C), 137.1 (C), 141.6 (C), 143.0 (C); MS m/e (%) 224 (60), 155 (65), 91 (100). Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 66.18, H, 6.71; N, 4.03.

2-Methyl-1-(*N*-tosylamino)-1-phenyl-2-propene (10). The procedure for preparation of **6** was followed except using 1.52 g (5 mmol) of 1-(*N*-tosylamino)-1-phenyl-2-propanone. Purification by flash chromatography, eluting with 20% ethyl acetate in hexane, gave 0.85 g (2.8 mmol), 56%, of the product: TLC R_f 0.14 (10% ethyl acetate in hexane); mp 124–128 °C; $[\alpha]_D$ = −0.57° (c = 2.9 ($CHCl_3$)]; 48% ee by ^{1}H NMR using Eu(hfc)$_3$ as chiral shift; 300-MHz ^{1}H NMR 1.54 (s, 3 H), 2.38 (s, 3 H), 4.83 (d, J = 7.8 Hz, 1 H), 4.89 (m, 1 H), 4.96 (m, 1 H), 5.37 (d, J = 7.8 Hz, 1 H), 7.06–7.20 (m, 7 H), 7.64 (m, 2 H); ^{13}C NMR 19.2 (CH/CH_3), 21.3 (CH/CH_3), 62.6 (CH/CH_3), 113.2(CH2) 126.7 (CH/CH_3), 127.0 (CH/CH_3), 127.3 (CH/CH_3), 128.2 (CH/CH_3), 129.1 (CH/CH_3), 137.2 (C), 138.7 (C), 142.9 (C), 143.1 (C); IR 3250 (st), 2960 (st), 2930 (st), 1580 (w), 1420 (br st), 1305 (st), 1085 (st); MS m/e (%) 301 (M^+, ~1), 260 (30), 155 (75), 146 (100), 91 (100); HRMS calcd for $C_{17}H_{19}NO_2S$ 301.113635, found 301.11349.

2,4-Dimethyl-3-(benzyltosylamino)-1,4-pentadiene (11). Sodium hydride, 0.3 g (6 mmol), of a 50% dispersion in mineral oil was placed in a round-bottomed flask under nitrogen, washed three times with hexane, and then suspended in 5 mL of DMF. A solution of 0.53 g of **4** (2 mmol) in 5 mL of DMF was added, and the mixture was stirred at 25 °C for 5 min. Then 0.171 g of benzyl bromide (0.26 mL, 1.0 mmol) was added, and the mixture was stirred at 25 °C for 2 h. The solution was diluted with 200 mL of ether, washed with 2 × 50 mL of water, and dried. Evaporation of the solvent gave the crude benzylated material, which was purified by flash chromatography, eluting with 5% ethyl acetate in hexane, to give 0.33 g, 46%, of the product as a clear viscous oil which crystallizes on standing: TLC R_f 0.20 (5% ethyl acetate in hexane); mp 114–117 °C; ^{1}H NMR 1.57 (s, 1 H), 2.38 (s, 3 H), 4.50 (s, 2 H), 4.75 (s, 1 H), 4.77 (s, 2 H), 4.93 (s, 2 H), 7.21 (m, 5 H), 7.35 (m, 2 H), 7.57 (m, 2 H); ^{13}C NMR 21.3 (CH/CH_3), 21.9 (CH/CH_3), 48.8 (CH_2), 67.8 (CH/CH_3), 115.6 (CH_2), 126.8 (CH), 127.2 (CH), 127.7 (CH), 128.7 (CH), 128.9 (CH), 137.6 (C), 137.8 (C), 140.7 (C), 142.7 (C); IR ($CHBr_3$) 3090 (m), 3031 (m), 2967 (m), 2919 (m), 1648 (w), 1598 (m), 1495 (st), 1454 (st), 1331 (st br), 1160 (st br); MS m/e (%) 355 (M^+, ~1), 314 (20), 200 (10), 158 (15), 91 (100); HRMS calcd for $C_{21}H_{25}NO_2S$ 355.160589, found 355.16112.

2-Methyl-3-(benzyltosylamino)-4-phenyl-1-butene (12). Sodium hydride, 0.1 g (2 mmol), of a 50% dispersion of sodium hydride in mineral oil was placed in a round-bottomed flask and washed with 2 mL of hexane and then 2 mL of THF. A reflux condenser was fitted, capped with a septum and an outlet to a bubbler. Compound **6**, 0.25 g (0.8 mmol), was added as a solution in 2 mL of THF, and the mixture was stirred at 25 °C for 15 min. Benzyl bromide, 0.171 g (120 μL, 1.0 mmol), was added, and the mixture was refluxed for 7 h. On cooling the mixture was diluted with 70 mL of ethyl acetate, washed with 2 × 20 mL of water, and then dried. Evaporation of the solvent gave the crude benzylated material, which was purified by flash chromatography, eluting with 10% ethyl acetate in hexane, to give 0.172 g, 0.42 mmol, 53%, of the product as a clear viscous oil: TLC R_f 0.26 (10% ethyl acetate in hexane); ^{1}H NMR 1.48 (s, 3 H), 2.42 (s, 3 H), 2.87 (d, J = 7.3 Hz, 2 H), 4.19 (d, J = 15.5 Hz, 1 H), 4.61 (d, J = 15.5 Hz, 1 H), 4.68 (t, J = 7.4 Hz, 1 H), 5.02 (s, 1 H), 5.08 (s, 1 H), 7.10 (m, 2 H), 7.26 (m, 10 H), 7.60 (m, 2 H); ^{13}C NMR 21.3 (CH/CH_3), 22.1 (CH/CH_3), 38.0 (CH_2), 47.8 (CH_2), 63.1 (CH/CH_3), 116.3 (CH_2), 125.9 (CH), 127.1 (CH), 127.2 (CH), 128.0 (CH), 128.1 (CH), 128.7 (CH), 128.9 (CH), 129.3 (CH), 137.7 (C), 137.9 (C), 138.6 (C), 140.3 (C), 142.9 (C); IR (neat liquid film) 3040 (st), 2940 (st), 1650 (m), 1600 (st), 1490 (st), 1450 (st br), 1330 (st br); MS m/e (%) 405 (M^+, ~1), 315 (45), 274 (5), 250 (5), 196 (10), 155 (90), 91 (100); HRMS calcd for $C_{25}H_{27}NO_2S$ 405.176235, found 405.17570.

2-Methyl-3-(benzyltosylamino)-1-heptene (13). To a solution of 0.83 g (2.9 mmol) of **2** in 10 mL of acetone was added 1.24 g (9 mmol) of anhydrous potassium carbonate and catalytic tetra-*n*-butylammonium iodide. The mixture was stirred under nitrogen at 25 °C while 0.42 mL (0.605 g, 3.5 mmol) of benzyl bromide was added then for a further 24 h. The solution was diluted with 150 mL of ether, washed with 3 × 50 mL of water, and then dried. Evaporation of the solvent gave the crude product which was purified by flash chromatography, eluting with 2% ethyl acetate in hexane to give 1.04 g, 2.8 mmol, 96%, of **13** as a clear viscous oil: TLC R_f 0.3 (5% ethyl acetate in hexane); ^{1}H NMR 0.77 (m, 3 H), 1.10–1.32 (m, 6 H), 1.45 (s, 3 H), 2.41 (s, 3 H), 4.10 (d, J = 15.7 Hz, 1 H), 4.21 (t, J = 7.7 Hz, 1 H), 4.44 (d, J = 15.7 Hz, 1 H), 7.72–7.32 (m, 7 H), 7.65 (m, 2 H); ^{13}C NMR 13.7 (CH/CH_3), 21.3 (CH/CH_3), 22.0 (CH/CH_3), 22.2 (CH_2), 28.8 (CH_2), 30.7 (CH_2), 47.4 (CH_2), 62.1 (CH/CH_3), 114.7 (CH_2), 127.0 (CH), 127.0 (CH), 127.80 (CH), 128.4 (CH), 129.1 (CH), 137.9 (C), 141.6 (C), 142.7 (C); IR (neat liquid film) 3020 (m), 2950 (st), 2860 (m), 1640 (w), 1595 (m), 1485 (m), 1450 (st), 1530 (st), 1150 (s); MS m/e (%), 371 (M^+, <1), 314 (10), 244 (5), 228 (10), 91 (100); HRMS calcd for $C_{22}H_{29}NO_2S$ 371.191885, found 371.19106.

2,5-Dimethyl-3-(benzyltosylamino)-1-hexene (14). Anhydrous potassium carbonate, 0.414 g (1.5 mmol, 3 equiv), was added to a vigorously stirred solution of 0.154 g (0.55 mmol) of compound **7** and catalytic (20 mg) tetra-*n*-butylammonium iodide in 5 mL of acetone. To this was added 0.103 g (72 μL, 0.605 mmol, 1.1 equiv) of benzyl bromide. The mixture was stirred at 25 °C for 24 h, diluted with 100 mL ether, and washed with 3 × 20 mL of water. The ether solution was dried and the solvents were evaporated. The crude product was purified by flash chromatography, eluting with 2% ethyl acetate in hexane, to give 0.173 g, 85%, of the benzylated product as a clear viscous oil: TLC R_f 0.11 (2.5% ethyl acetate in hexane); ^{1}H NMR 0.69 (d, J = 6.4 Hz, 3 H), 0.82 (d, J = 6.4 Hz, 3 H), 1.10 (m, 1 H), 1.47 (s, 3 H), 1.46 (m, 2 H), 2.41 (s, 3 H), 4.10 (d, J = 15.6 Hz, 1 H), 4.31 (t, J = 6.7 Hz, 1 H), 4.45 (d, J = 15.6 Hz, 1 H), 4.79 (s, 1 H), 4.96 (s, 1 H), 7.24 (m, 7 H), 7.65 (m, 2 H); ^{13}C NMR 21.3 (CH/CH_3), 21.8 (CH/CH_3), 22.0 (CH/CH_3), 22.7 (CH/CH_3), 24.5 (CH/CH_3), 39.9 (CH_2), 47.4 (CH_2), 60.0 (CH/CH_3), 114.8 (CH_2), 126.9 (CH), 127.1 (CH), 127.9 (CH), 128.2 (CH), 129.1 (CH), 138.0 (C), 138.1 (C), 141.7 (C), 142.7 (C); IR (neat liquid film) 3080 (m), 3040 (m), 2960 (st), 2880 (st), 1650 (w), 1605 (m), 1500 (m), 1460 (st), 1340 (st), 1150 (s); MS m/e (%) 371 (M^+, <1), 330 (20), 314 (65), 260 (15), 260 (10), 155 (50), 91 (100); HRMS calcd for $C_{22}H_{29}NO_2S$ 371.191885, found 371.19106.

***tert*-Butyl 4-Methyl-3-(benzyltosylamino)-4-pentenoate (15).** The preparation this compound is identical with that of **14** except using 0.34 g (1.0 mmol) of **3**. The crude product was purified by flash chromatography, eluting with 5% ethyl acetate in hexane to give 0.37 g, 86%, of the benzylated product as a clear viscous oil: TLC R_f 0.09 (5% ethyl acetate in hexane); ^{1}H NMR 1.34 (s, 9 H), 2.38 (m, 5 H), 4.01 (d, J = 15.6 Hz, 1 H), 4.51 (d,

J = 15.6 Hz, 1 H), 4.62 (t, J = 7.6 Hz, 1 H), 4.77 (s, 1 H), 4.96 (s, 1 H), 7.26 (m, 7 H), 7.70 (m, 2 H); ^{13}C NMR 21.5 (CH/CH_3), 21.8 (CH/CH_3), 27.9 (CH/CH_3), 38.5 (CH_2), 48.0 (CH_2), 58.4 (CH/CH_3), 80.7 (C), 114.7 (CH_2), 127.3 (CH), 127.5 (CH), 128.3 (CH), 128.6 (CH), 129.6 (CH), 137.9 (C), 141.4 (C), 143.3 (C), 169.8 (C); IR (neat liquid film) 3060 (st), 3030 (st), 2960 (st br), 1720 (st br), 1650 (w), 1600 (st), 1490 (st), 1500 (st br), 1310 (st br); MS m/e (%) 356 (10), 332 (10), 274 (30), 260 (30), 228 (65), 155 (100), 91 (100).

***syn*-2-Methyl-3-(*N*-tosylamino)-4-phenyl-1-butanol (*syn*-16).** Chloro(1,5-cyclooctadiene)rhodium(I) dimer, 4.9 mg (0.01 mmol, 0.02 equiv), and triphenylphosphine, 11.0 mg (0.041 mmol, 0.081 equiv), were placed in a Schlenk tube. This was evacuated and flushed with argon five times, 1 mL of THF was added, and the mixture was stirred at 25 °C for 15 min. The catalyst solution was cooled to 0 °C, and a solution of 0.157 g of **6** (0.5 mmol, 1 equiv) in 2 mL of THF was added to it. With stirring at 0 °C, 0.200 g (1.5 mmol, 3 equiv) of catecholborane was added, and then the mixture was warmed to 25 °C and allowed to stand for 48 h. The mixture was cooled to 0 °C, and 1 mL of EtOH, 1 mL of 3 M NaOH, and 0.5 mL of 30% H_2O_2 were added in that order. The mixture was stirred at 25 °C for 4 h, diluted with 20 mL of 1 M NaOH, and extracted with 4 × 30 mL of ether. The combined extracts were washed with 1 × 10 mL of 1 M NaOH and 1 × 10 mL of saturated aqueous ammonium chloride and dried. Evaporation of the solvent gave 0.162 g, 97%, of compound **16** as a 7:1 syn:anti mixture. Recrystallization from chloroform–hexane gave 0.072 g, 43%, of *syn*-**16**: TLC R_f 0.19 (30% ethyl acetate in hexane); mp 134–135 °C; $[\alpha]_D$ = −1.02° (c = 1.38) (>95% ee by 300-MHz ^{1}H NMR of Eu(hfc)$_3$ shift experiment); ^{1}H NMR 0.82 (d, J = 7.0 Hz, 3 H), 1.80 (m, 1 H), 2.41 (s, 1 H), 2.44 (dd, J = 13.6, 6.9 Hz, 1 H), 2.61 (dd, J = 13.6, 8.46 Hz, 1 H), 3.44 (m, 1 H), 3.63 (m, 1 H), 3.78 (m, 1 H), 5.10 (d, J = 9.3 Hz, 1 H), 6.90–7.12 (m, 5 H), 7.20 (m, 2 H), 7.64 (m, 2 H); ^{13}C NMR 9.4 (CH/CH_3), 21.3 (CH/CH_3), 36.9 (CH_2), 38.6 (CH_2), 55.0 (CH/CH_3), 64.1 (CH_2), 126.1 (CH), 126.6 (CH), 128.3 (CH), 128.6 (CH), 129.5 (CH), 137.10 (C), 137.14 (C), 143.1 (C); IR ($CHBr_3$) 3430 (st), 3180 (st), 2930 (st), 2900 (st), 1585 (w), 1400 (m br), 1310 (st), 1080 (st), 1015 (st); MS m/e (%) 333 (M^+, <1), 274 (15), 242 (60), 212 (45), 155 (40), 91 (100). Anal. Calcd for $C_{18}H_{23}NO_3S$: C, 64.83; H, 6.95; N, 4.20. Found: C, 64.73; H, 6.95; N, 4.20.

***syn*- and *anti*-2,5-Dimethyl-3-(*N*-tosylamino)-1-hexanol (17).** As for **16** but using 0.141 g (0.5 mmol) of alkene **7** gave 0.150 g (ca. 100%) of a crude 4:1 syn:anti mixture of the alcohols. Purification by flash chromatography eluting with 35% ethyl acetate in hexane and recrystallization of higher R_f fractions from dichloromethane/hexane gives pure syn isomer: TLC R_f 0.24 (30% ethyl acetate in hexane); mp 110–111 °C; $[\alpha]_D$ = −0.12° (c = 1.12 ($CHCl_3$)); ^{1}H NMR 0.63–0.67 (overlapping d, 9 H), 0.89 (m, 1 H), 1.20 (m, 1 H), 1.32 (m, 1 H), 1.80 (m, 1 H), 2.43 (s, 3 H), 2.86 (hydroxyl, 1 H), 3.51 (m, 3 H), 4.73 (d, J = 9.5 Hz, 1 H), 7.31 (m, 2 H), 7.76 (m, 2 H); ^{13}C NMR 9.5 (CH/CH_3), 21.3 (CH/CH_3), 21.8 (CH/CH_3), 22.4 (CH/CH_3), 23.9 (CH/CH_3), 37.1 (CH/CH_3), 41.3 (CH_2), 51.3 (CH/CH_3), 64.1 (CH_2), 126.6 (CH), 129.4 (CH), 137.5 (C), 143.3 (C); IR 3450 (st br), 3180 (st br), 2940 (st br), 1585 (w), 1405 (m br), 1300 (st), 1185 (st), 1005 (st); MS m/e (%) 299 (M^+, ~1), 240 (40), 212 (10), 184 (10), 155 (90), 91 (100); HRMS calcd for $C_{15}H_{25}NO_3S$ 299.155495, found 299.15504.

Recrystallization of lower R_f fractions from dichloromethane-/hexane gives the pure anti isomer: TLC R_f 0.20 (30% ethyl acetate in hexane); mp 84–86 °C; ^{1}H NMR 0.62 (d, J = 6.3 Hz, 3 H), 0.75 (d, J = 6.5 Hz, 3 H), 0.85 (d, J = 7.0 Hz, 3 H), 1.20 (m, 2 H), 1.32 (m, 1 H), 1.70 (m, 1 H), 2.20 (s, 1 H), 2.41 (s, 3 H), 3.35 (m, 1 H), 3.44 (m, 1 H), 3.76 (m, 1 H), 5.12 (d, J = 8.5 Hz, 1 H), 7.26 (m, 2 H), 7.75 (m, 2 H); ^{13}C NMR 13.4 (CH/CH_3), 21.3 (CH/CH_3), 21.6 (CH/CH_3), 22.8 (CH/CH_3), 24.0 (CH/CH_3), 36.6 (CH/CH_3), 41.7 (CH_2), 54.3 (CH/CH_3), 64.2 (CH_2), 126.8 (CH), 129.6 (CH), 136.1 (C), 142.9 (C); MS 299 (M^+, <1), 240 (30), 212 (10), 155 (40), 91 (100); HRMS calcd for $C_{15}H_{25}NO_3S$ 299.155495, found 299.15504.

***syn*-2,4-Dimethyl-3-(*N*-tosylamino)-1-pentanol (*syn*-18).** This material was prepared via a procedure similar to that used for preparation of **16** but using 0.134 g of compound **8** to give 0.141 g, 93%, of a 6.7:1.0 syn:anti mixture. Recrystallization of this from dichloromethane/hexane gave the pure isomer: TLC R_f 0.23 (30% ethyl acetate in hexane); mp 98–99 °C; $[\alpha]_D$ = −0.48° (c = 0.83 ($CHCl_3$)); ^{1}H NMR 0.42 (d, J = 6.7 Hz, 3 H), 0.68 (d, J = 7.0 Hz, 3 H), 0.77 (d, J = 6.7 Hz, 3 H), 1.55 (m, 1 H), 1.94 (m, 1 H), 2.38 (s, 3 H), 3.18 (m, 1 H), 3.36 (m, 2 H), 3.57 (m, 1 H), 5.18 (d, J = 9.5 Hz, 1 H), 7.25 (m, 2 H), 7.72 (m, 2 H); ^{13}C NMR 9.3 (CH/CH_3), 19.9 (CH/CH_3), 19.9 (CH/CH_3), 21.3 (CH/CH_3), 30.4 (CH/CH_3), 36.7 (CH/CH_3), 59.3 (CH/CH_3), 64.1 (CH_2), 126.7 (CH), 129.3 (CH), 138.1 (CH), 143.0 (C); IR ($CHBr_3$) 3450 (st), 3160 (st), 2960 (st), 2920 (st), 2870 (m), 1420 (m br), 1300 (st); MS m/e (%) 285 (M^+, ~1), 242 (25), 226 (55), 212 (60), 155 (95), 91 (100); HRMS calcd for $C_{14}H_{23}NO_3S$ 285.139845, found 285.13964.

***anti*-2,4-Dimethyl-3-(*N*-tosylamino)-1-pentanol (*anti*-18).** A solution of compound **8**, 0.08 g (0.3 mmol), in 2 mL of THF was cooled to −78 °C, and then 9-BBN (2.4 mL of 0.5M solution in THF) was added with stirring. The mixture was allowed to warm slowly (1 h) to 25 °C and then stirred at 25 °C for 72 h. The mixture was cooled to 0 °C, 1 mL of ethanol was added, followed by 0.5 mL of 3 M sodium hydroxide and 0.5 mL of 30% hydrogen peroxide, and then the mixture was stirred at 25 °C for 12 h. The solution was diluted with 50 mL of ether and washed with 1 M sodium hydroxide and saturated aqueous ammonium chloride and dried. Evaporation of the solvent gave crude material which was flashed, eluting with 45% ethyl acetate in hexane, to give 0.033 g, 39%, of a 7.4:1.0 anti:syn mixture: ^{1}H NMR 0.49 (d, J = 6.8 Hz, 3 H), 0.73 (d, J = 6.8 Hz, 3 H), 0.93 (d, J = 7.0 Hz, 3 H), 1.62 (m, 1 H), 1.81 (m, 1 H), 2.40 (s, 3 H), 2.72 (br s, 1 H), 3.11 (dt, J = 8.9, 4.3 Hz, 1 H), 3.48 (m, 1 H), 3.93 (br d, J = 11.4 Hz, 1 H), 5.12 (d, J = 9.3 Hz, 1 H), 7.26 (m, 2 H), 7.75 (m, 2 H); ^{13}C NMR 15.2 (CH/CH_3), 16.0 (CH/CH_3), 20.3 (CH/CH_3), 21.3 (CH/CH_3), 29.1 (CH/CH_3), 37.6 (CH/CH_3), 61.3 (CH/CH_3), 64.3 (CH_2), 126.7 (CH), 129.2 (CH), 136.4 (C), 142.9 (C).

***syn*-4-(Benzyloxy)-2-methyl-3-(*N*-tosylamino)-1-butanol (*syn*-19).** The preparation of this material is similar to that described for compound **16** except that 0.172 g of alkene **9** was used to give 87% crude yield of a 4:1 syn:anti mixture. Recrystallization from dichloromethane/hexane gives pure syn isomer: TLC R_f 0.20 (30% ethyl acetate in hexane); mp 122–123 °C; $[\alpha]_D$ = +0.35° (c = 1.62 ($CHCl_3$)); ^{1}H NMR 0.75 (d, J = 7.0 Hz, 3 H), 1.84 (m, 1 H), 2.33 (s, 3 H), 2.80 (s, 1 H), 3.10 (m, 1 H), 3.25 (m, 1 H), 3.39–3.60 (m, 3 H), 4.21 (m, 2 H), 5.20 (d, J = 9.0 Hz, 1 H), 7.07–7.29 (m, 7 H), 7.65 (m, 2 H); ^{13}C NMR 11.2 (CH/CH_3), 21.3 (CH/CH_3), 38.0 (CH/CH_3), 53.0 (CH/CH_3), 63.9 (CH_2), 69.7 (CH_2), 73.0 (CH_2), 126.8 (CH), 127.4 (CH), 127.6 (CH), 128.2 (CH), 129.4 (CH), 137.1 (C), 137.4 (C), 143.1 (C); IR ($CHBr_3$) 3550 (m), 3350 (m), 2930 (m), 2860 (m), 1585 (w), 1310 (s), 1080 (s); MS m/e (%) 363 (M^+, ~1), 304 (10), 243 (60), 211 (60), 155 (100), 91 (100); HRMS calcd for $C_{19}H_{25}NO_4S$ 363.150405, found 363.14991.

***syn*-2-Methyl-3-(*N*-tosylamino)-3-phenyl-1-propanol (*syn*-20).** The procedure used for the preparation of this material was similar to that for the synthesis of **16** except using 0.150 g of alkene **10** to give 0.143 g, 90%, of a 1:1 mixture of isomers. Recrystallization from dichloromethane–hexane gives the syn isomer: TLC R_f 0.21 (30% ethyl acetate in hexane); mp 154–158 °C; ^{1}H NMR 0.73 (d, J = 7.0 Hz, 3 H), 2.12 (m, 1 H), 2.30 (s, 3 H), 2.39 (br s, 1 H), 3.54 (m, 2 H), 4.61 (dd, J = 9.4, 4.1 Hz, 1 H), 5.97 (d, J = 9.4 Hz, 1 H), 6.99–7.14 (m, 7 H), 7.53 (m, 2 H); ^{13}C NMR 11.3 (CH/CH_3), 21.2 (CH/CH_3), 40.9 (CH/CH_3), 58.8 (CH/CH_3), 64.4 (CH_2), 126.6 (CH), 126.7 (CH), 126.8 (CH), 127.8 (CH), 129.0 (CH), 137.0 (C), 138.3 (C), 142.7 (C); MS m/e (%) 319 (M^+, <1), 260 (60), 155 (100), 104 (20), 91 (100).

***syn*-2-Methyl-3-(*N*-tosylamino)-1-heptanol (*syn*-21).** The procedure used for preparation of this compound was similar to that used for synthesis of **16** except using 0.140 g of alkene **2** which gave the crude product as a 5.3:1.0 syn:anti mixture. This was purified by flash chromatography, eluting with 30% ethyl acetate in hexane to give 0.107 g, 72%, of **21**: TLC R_f 0.13 (20% ethyl acetate in hexane); ^{1}H NMR 0.64 (m, 6 H), 0.86 (m, 2 H), 1.05 (m, 3 H), 1.27 (m, 1 H), 1.80 (m, 2 H), 2.40 (s, 3 H), 3.09 (m, 1 H), 3.43 (m, 2 H), 3.58 (m, 1 H), 5.10 (d, J = 9.3 Hz, 1 H), 7.28 (m, 2 H), 7.75 (m, 2 H); ^{13}C NMR 9.5 (CH/CH_3), 13.5 (CH/CH_3), 21.3 (CH/CH_3), 21.9 (CH_2), 27.9 (CH_2), 31.9 (CH_2), 37.7 (CH/CH_3), 53.4 (CH/CH_3), 64.1 (CH_2), 126.8 (CH), 129.4 (CH), 137.6 (C), 143.2 (C); IR (neat liquid film) 3500 (st br), 3300 (st br), 2930 (st), 2860 (st), 1600 (w), 1450 (m br), 1310 (st), 1160 (st), 1070 (st); MS m/e (%) 299 (M^+, ~1), 240 (100), 212 (15), 155 (80), 91

(55); HRMS calcd for $C_{15}H_{25}NO_3S$ 299.155495, found 299.15504.

***tert*-Butyl 5-Hydroxy-4-methyl-3-(*N*-tosylamino)pentanoate (22).** This compound was prepared via a procedure similar to that used to obtain alcohol **16**: ^{1}H NMR 0.73 (d, J = 6.9 Hz, 1 H), 1.34 (s, 9 H), 1.77 (m, 1 H), 2.14 (m, 2 H), 2.34 (s, 3 H), 2.94 (br s, 1 H), 3.41 (m, 2 H), 3.76 (m, 1 H), 5.94 (d, J = 9.2 Hz, 1 H), 7.31 (m, 2 H), 7.77 (m, 2 H); ^{13}C NMR 11.0 (CH/CH_3), 21.4 (CH/CH_3), 27.8 (CH/CH_3), 37.3 (CH_2), 38.8 (CH/CH_3), 51.3 (CH/CH_3), 64.3 (CH_2), 81.2 (C), 126.9 (CH), 129.7 (CH), 137.6 (C), 143.3 (C), 170.7 (C); IR (neat, liquid film) 3480 (st br), 3260 (st br), 2950 (st), 1720 (st br), 1600 (m), 1450 (st), 1310 (st br), 1150 (st br); MS m/e (%) 357 (M^+, <1), 298 (5), 242 (85), 155 (80), 91 (100); HRMS calcd for $C_{17}H_{27}NO_5S$ 357.160965, found 357.16112.

***syn*-2-Methyl-3-(benzyltosylamino)-4-phenyl-1-butanol (*syn*-23). Catalyzed Procedure.** A Schlenk tube was charged with 4.9 mg (0.01 mmol) of chloro(1,5-cyclooctadiene)rhodium(I) dimer and 11.0 mg (0.041 mmol) of triphenylphosphine, evacuated, and flushed with argon five times. THF (0.5 mL) was added, and the resulting bright yellow solution was stirred at 25 °C for 20 min. A solution of 0.172 g (0.42 mmol) of 2-methyl-3-(benzyltosylamino)-4-phenyl-1-butene (**12**) in 2 mL of THF was added, the mixture was cooled in ice, and 0.12 g (1.0 mmol) of catecholborane was added. The mixture was left to stand at 25 °C for 48 h; it was then cooled in ice, and 1 mL of EtOH, 0.5 mL of 3M NaOH, and 0.5 mL of 30% hydrogen peroxide were added in that order. The mixture was stirred vigorously for 10 h at 25 °C and then diluted with 20 mL of 1 M NaOH and extracted with 3 × 50 mL of ether. The combined ether extracts were dried, and evaporation of the solvents gave the crude product which was purified by flash chromatography, eluting with 20% ethyl acetate in hexane to give 0.117 g (0.27 mmol), 65%, of *syn*-2-methyl-3-(benzyltosylamino)-4-phenyl-1-butanol (*syn*-**23**). HPLC analysis of the crude showed it to be 18.2:1.0 syn:anti.

9-BBN Procedure. A solution of 0.19 g (0.47 mmol) of compound **12** in 5 mL of THF was cooled to −78 °C, and then 3 mL of a 0.5 M solution of 9-BBN in THF was added with stirring. The mixture was allowed to warm to 25 °C over 2 h and then stirred at 25 °C for 16 h. The solution was cooled in ice, 1 mL of EtOH, 0.5 mL of 3 M NaOH, and 0.5 mL of 30% hydrogen peroxide were added in that order, and the reaction mixture was stirred at 25 °C for 6 h. The mixture was diluted with 150 mL of ether, washed with 2 × 20 mL of 1 M NaOH, 1 × 20 mL of saturated aqueous ammonium chloride, and then dried. Evaporation of the solvent gave the crude material which was purified by flash chromatography, eluting with 20% ethyl acetate/hexane to give 0.122 g (0.31 mmol), 81%, of the product as a clear viscous oil. HPLC analysis of the crude material showed it to be 12.9:1.0 syn:anti: TLC R_f 0.19 (20% ethyl acetate in hexane); ^{1}H NMR 0.61 (d, J = 7.2 Hz, 3 H), 1.73 (m, 1 H), 2.43 (s, 3 H), 2.87 (m, 2 H), 3.34 (m, 1 H), 3.63 (m, 1 H), 4.28 (m, 2 H), 4.65 (d, J = 16.5 Hz, 1 H), 6.95–7.72 (m, 14 H); ^{13}C NMR 11.7 (CH/CH_3), 21.3 (CH/CH_3), 36.2 (CH_2), 37.2 (CH/CH_3), 49.0 (CH_2), 59.9 (CH/CH_3), 64.0 (CH/CH_3), 126.4 (CH), 126.2 (CH), 127.2 (CH), 127.9 (CH), 128.5 (CH), 128.7 (CH), 129.6 (CH), (CH), 136.7 (C), 37.6 (C), 137.8 (C), 143.5 (C); IR (neat liquid film) 3500 (m br), 3040 (m), 2940 (m), 1600 (m), 1495 (m), 1450 (m), 1330 (st), 1150 (st); MS m/e (%) 423 (M^+, <1), 364 (20), 332 (55), 302 (25), 226 (65), 91 (100); HRMS calcd for $C_{25}H_{29}NO_3S$ 423.186795, found 423.18635.

***anti*-2-Methyl-3-(benzyltosylamino)-4-phenyl-1-butanol (*anti*-23).** A solution of 0.19 g (0.47 mmol) of alkene **12** in 5 mL of THF was cooled to −78 °C, and then 1.5 mL of a 1.0 M solution of borane–THF complex in THF was added with stirring. The mixture was stirred at −78 °C for 5 min and then placed in a refrigerator at −26 °C for 27 h and then in another at 0 °C for 25 h. At 0 °C, 2 mL of ethanol, 1 mL of 3 M NaOH, and 1 mL of 30% hydrogen peroxide were added. The mixture was allowed to warm to 25 °C, stirred for 10 h, then diluted with 150 mL of ether. The ether solution was washed with 2 × 20 mL of 1 M NaOH and 1 × 20 mL of saturated aqueous ammonium chloride and dried. Evaporation of the solvents gave the crude alcohol which was purified by flash chromatography, eluting with 20% ethyl acetate in hexane, to give 0.137 g, 0.32 mmol, 69%, of **23**. HPLC analysis of the crude material showed it to be syn:anti 1.0:16.7: TLC R_f 0.19 (20% ethyl acetate in hexane); ^{1}H NMR 0.84 (d, J = 6.8 Hz, 3 H), 1.52 (m, 1 H), 2.32 (s, 3 H), 2.57 (m, 1 H), 2.86 (m, 2 H), 3.17 (m, 1 H), 3.69 (m, 1 H), 4.17 (m, 1 H), 4.21 (d, J = 15.4 Hz, 1 H), 4.58 (d, J = 15.4 Hz, 1 H), 6.94–7.39 (m, 14 H); ^{13}C NMR 15.33 (CH/CH_3), 21.21 (CH/CH_3), 36.30 (CH_2), 39.20 (CH/CH_3), 48.23 (CH_2), 61.63 (CH/CH_3), 64.21 (CH_2), 125.94 (CH), 126.79 (CH), 127.72 (CH), 128.23 (CH), 128.28 (CH), 128.63 (CH), 128.93 (CH), 129.25 (CH), 136.87 (C), 137.25 (C), 138.61 (C), 142.66 (C); IR 3530 (st br), 3062 (st), 3025 (st), 2963 (st), 1598 (st), 1496 (st), 1455 (st), 1328 (st br); MS m/e (%) 423 (M^+, <1), 364 (70), 332 (70), 226 (10), 91 (100); HRMS calcd for $C_{25}H_{29}NO_3S$ 423.186795, found 423.18635.

***syn*-2-Methyl-3-(benzyltosylamino)-1-heptanol (*syn*-24). Catalyzed Procedure.** As for compound **23** but using 0.185 g (0.5 mmol) of alkene **13**. The crude alcohol was purified by flash chromatography, eluting with 15% ethyl acetate in hexane, to give 0.138 g, 71% combined yield of isomeric alcohols. HPLC analysis of the crude material showed it to be a 10.2:1.0 syn:anti mixture.

9-BBN Procedures. As for compound **23** but using 0.13 g (0.35 mmol) of alkene **13**. The crude material was purified by flash chromatography, eluting with 15% ethyl acetate in hexane, to give 0.109 g (0.28 mmol), 80%, of the product. ^{1}H NMR of the crude material showed it to be a 7.0:1.0 syn:anti mixture: TLC R_f 0.15 (20% ethyl acetate in hexane); mp 82–84 °C; ^{1}H NMR 0.51 (d, J = 7.25 Hz, 3 H), 0.70 (t, J = 7.2 Hz, 3 H), 0.83–1.08 (m, 6 H), 1.50 (m, 1 H), 1.73 (m, 1 H), 2.43 (s, 3 H), 4.05 (d, J = 16.5 Hz, 1 H), 4.54 (d, J = 16.5 Hz, 1 H), 7.22–7.41 (m, 7 H), 7.68 (m, 2 H); ^{13}C NMR 12.0 (CH/CH_3), 13.5 (CH/CH_3), 21.2 (CH/CH_3), 22.3 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 38.4 (CH/CH_3), 48.3 (CH_2), 59.1 (CH/CH_3), 64.3 (CH_2), 127.0 (CH), 127.1 (CH), 128.0 (CH), 128.0 (CH), 129.3 (CH), 136.9 (C), 137.8 (C), 143.2 (C); MS m/e (%) 330 (10), 262 (10), 244 (45), 228 (40), 212 (30), 184 (30), 91 (100). Anal. Calcd for $C_{22}H_{31}NO_3S$: C, 67.83; H, 8.02; N, 3.60. Found: C, 67.73; H, 8.09; N, 3.46.

***anti*-2-Methyl-3-(benzyltosylamino)-1-heptanol (*anti*-24).** As that for *anti*-**23** but using 0.12 g (0.32 mmol) of alkene **13**. The crude alcohol was purified by flash chromatography eluting with 15% ethyl acetate in hexane to give 0.101 g (0.26 mmol), 81%, of *anti*-2-methyl-3-(benzyltosylamino)-1-heptanol. HPLC analysis of the crude material showed it to be a 1.0:20.7 syn:anti mixture: TLC R_f 0.21 (20% ethyl acetate in hexane); ^{1}H NMR 0.50 (m, 2 H), 0.62 (t, J = 7.3 Hz, 3 H), 0.83 (d, J = 6.9 Hz, 3 H), 1.10 (m, 2 H), 1.29 (m, 2 H), 1.50 (m, 1 H), 2.42 (s, 3 H), 2.80 (br s, 1 H), 3.05 (br d, J = 11.6 Hz, 1 H), 3.60 (dt, J = 10.1, 4.1 Hz, 1 H), 3.76 (d, J = 11.9 Hz, 1 H), 3.88 (d, J = 15.3 Hz, 1 H), 4.78 (d, J = 15.3 Hz, 1 H), 7.26–7.45 (m, 7 H), 7.68 (m, 2 H); ^{13}C NMR 13.6 (CH/CH_3), 15.0 (CH/CH_3), 21.2 (CH/CH_3), 22.5 (CH2), 29.1 (CH2), 29.5 (CH2), 38.9 (CH/CH_3), 47.2 (CH2), 60.2 (CH/CH_3), 63.9 (CH2), 127.0 (CH/CH_3), 127.6 (CH/CH_3), 128.2 (CH/CH_3), 128.8 (CH/CH_3), 129.3 (CH/CH_3), 137.3 (C), 137.6 (C), 143.2 (C); IR (neat) 3500 (m br), 3040 (w), 2940 (s), 1600 (m), 1490 (m), 1450 (m), 1320 (s br), 1150 (s); MS m/e (%) 389 (M^+, <1), 330 (70), 262 (10), 234 (10), 226 (15), 166 (45), 91 (100); HRMS calcd for $C_{22}H_{31}NO_3S$ 389.202445, found 389.20328.

***syn*-2,5-Dimethyl-3-(benzyltosylamino)-1-hexanol (*syn*-25). Catalyzed Procedure.** As for compound **23** except using 0.113 g (0.3 mmol) alkene **14**. The crude material was purified by flash chromatography eluting with 20% ethyl acetate/hexane to give 0.094 g (0.24 mmol), 81% yield, of isomeric alcohols. HPLC analysis of the crude material showed it to be a 6.0:1.0 syn:anti mixture.

9-BBN Procedure. As for compound **23** but using 0.147 g (0.39 mmol) of alkene **14**. The crude material was purified by flash chromatography, eluting with 20% ethyl acetate/hexane, to give 0.122 g (0.28 mmol), 81%, of the product. HPLC analysis of the crude material showed it to be a 25.0:1.0 syn:anti mixture: TLC R_f 0.19 (20% ethyl acetate in hexane); ^{1}H NMR 0.53 (d, J = 7.22 Hz, 3 H), 0.64 (d, J = 6.3 Hz, 3 H), 0.78 (d, J = 6.2 Hz, 3 H), 0.84 (m, 1 H), 1.40 (m, 2 H), 1.74 (m, 1 H), 2.41 (s, 3 H), 2.94 (s, 1 H), 3.35 (m, 1 H), 3.67 (m, 1 H), 4.04 (m, 1 H), 4.21 (d, J = 16.4 Hz, 1 H), 4.46 (d, J = 16.4 Hz, 1 H), 7.22–7.27 (m, 7 H), 7.63 (m, 2 H); ^{13}C NMR 12.1 (CH/CH_3), 21.3 (CH/CH_3), 21.7 (CH/CH_3), 22.8 (CH/CH_3), 24.2 (CH/CH_3), 38.1 (CH/CH_3), 38.4 (CH_2), 48.4 (CH_2), 56.6 (CH/CH_3), 64.3 (CH/CH_3), 127.1 (CH), 127.9 (CH), 128.1 (CH), 129.3 (CH), 137.1 (C), 143.2 (C); IR 3500 (br st), 3040 (w), 2930 (st), 1600 (st), 1500 (st), 1460 (st), 1320 (br st), 1150 (br

s); MS *m/e* (%) 389 (M^+, ≪1), 330 (60), 155 (20), 91 (100); HRMS calcd for $C_{22}H_{31}NO_3S$ 389.202445, found 389.20328.

***anti*-2,5-Dimethyl-3-(benzyltosylamino)-1-hexanol (*anti*-25).** The procedure was the same as that for *anti*-**23** but using 0.257 g (0.69 mmol) of alkene **14**. The crude alcohol was purified by flash chromatography, eluting with 20% ethyl acetate/hexane, to give 0.203 g, 0.52 mmol, 75%, of **25**. HPLC analysis of the crude material showed it to be a 1.0:21 syn:anti mixture: TLC R_f 0.19 (20% ethyl acetate in hexane); ^1H NMR 0.67 (d, J = 6.7 Hz, 3 H), 0.70 (d, J = 7.0 Hz, 3 H), 0.83 (d, J = 6.8 Hz, 3 H), 1.02 (m, 1 H), 1.24 (m, 2 H), 1.41 (m, 1 H), 2.41 (s, 3 H), 2.7 (s, 1 H), 3.18 (m, 1 H), 3.76 (m, 2 H), 4.07 (d, J = 15.3 Hz, 1 H), 4.60 (d, J = 15.3 Hz, 1 H), 7.23–7.36 (m, 7 H), 7.64 (m, 2 H); ^{13}C NMR 15.0 (CH/CH_3), 21.3 (CH/CH_3), 21.5 (CH/CH_3), 23.2 (CH/CH_3), 24.0 (CH/CH_3), 38.7 (CH/CH_3), 38.8 (CH_2), 47.4 (CH_2), 58.1 (CH/CH_3), 64.28 (CH_2), 127.08 (CH), 127.56 (CH), 128.19 (CH), 128.73 (CH), 129.20 (CH), 137.04 (C), 137.7 (C), 143.0 (C); IR (neat liquid film) 3538 (st br), 3064 (m), 3030 (m), 2955 (st br), 1598 (m), 1495 (m), 1455 (m), 1328 (st br); MS *m/e* (%) 389 (M^+, <1), 330 (60), 155 (20), 91 (100); HRMS calcd for $C_{22}H_{31}NO_3S$ found 389.20328.

***syn*-*tert*-Butyl 5-Hydroxy-4-methyl-3-(benzyltosylamino)pentanoate (*syn*-26).** A solution of alkene **15** (1.37 g, 3.2 mmol in 20 mL of THF) was cooled to −78 °C, and then 18 mL of a 0.5 M solution of 9-BBN was added with stirring over 10 min. The mixture was allowed to warm to 25 °C over 2 h then stirred for a further 20 h. With cooling in ice, 3 mL of 95% ethanol, 9 mL of a saturated aqueous sodium acetate, and 3 mL of 30% hydrogen peroxide were added in that order, the mixture was stirred at 0 °C for 30 min and then at 25 °C for a further 12 h. The solution was diluted with 200 mL of ether, washed with 2 × 50 mL of water, 1 × 50 mL of saturated aqueous sodium bicarbonate, and 1 × 50 mL of saturated aqueous ammonium chloride, and then dried. Evaporation of the solvents gave the crude material which was purified by flash chromatography eluting with 20% ethyl acetate in hexane to give 0.890 g (2.0 mmol), 63%, of **26**. HPLC analysis of the crude material showed it to be a 5.3:1.0 syn:anti mixture: TLC R_f 0.14 (20% ethyl acetate in hexane); ^1H NMR 0.67 (d, J = 6.8 Hz, 3 H), 1.40 (s, 9 H), 1.62 (m, 1 H), 2.13 (m, 1 H), 2.36 (m, 1 H), 2.42 (s, 3 H), 2.67 (m, 1 H), 3.39 (m, 2 H), 4.12 (d, J = 15.7 Hz, 1 H), 4.19 (m, 1 H), 4.45 (d, J = 15.7 Hz, 1 H), 7.22–7.40 (m, 7 H), 7.73 (m, 2 H); ^{13}C NMR 13.8 (CH/CH_3), 21.3 (CH/CH_3), 27.6 (CH/CH_3), 38.8 (CH_2), 39.6 (CH/CH_3), 49.1 (CH_2), 56.0 (CH/CH_3), 63.5 (CH_2), 81.6 (C), 127.1 (CH), 127.5 (CH), 128.2 (CH), 128.4 (CH), 129.5 (CH), 137.3 (C), 143.4 (C), 171.6 (C).

***anti*-*tert*-Butyl 5-Hydroxy-4-methyl-3-(benzyltosylamino)pentanoate (*anti*-26).** A solution of alkene **15** (0.657 g 1.5 mmol) in 10 mL of THF was cooled to −78 °C, and then 3 mL of a 1.0 M solution of borane–THF complex was added. The mixture was stirred at −70 °C for 5 min and then stored at −26 °C for 24 h and at 0 °C for 24 h. At 0 °C, 2 mL of ethanol, 4 mL of saturated aqueous sodium acetate, and 1.5 mL of 30% hydrogen peroxide were added in that order; the mixture was stirred at 25 °C for 12 h. The solution was diluted with 200 mL of ether, washed with 2 × 50 mL of water and 1 × 50 mL of saturated aqueous sodium bicarbonate, and then dried. Evaporation of the solvents gave the crude material which was purified by flash chromatography eluting with 20% ethyl acetate in hexane to give 0.207 g (0.46 mmol), 31%, of **26**. HPLC analysis of the crude material showed it to be a 1.0:52 syn:anti mixture: TLC R_f 0.14 (20% ethyl acetate in hexane); ^1H NMR 0.77 (d, J = 6.9 Hz, 3 H), 1.28 (m, 1 H), 1.35 (s, 9 H), 1.94 (m, 1 H), 2.32 (m, 1 H), 2.36 (s, 1 H), 2.50 (s, 1 H), 3.10 (m, 1 H), 3.60 (m, 1 H), 3.84 (d, J = 15.4 Hz, 1 H), 4.32 (m, 1 H), 4.62 (d, J = 15.4 Hz, 1 H), 7.12–7.36 (m, 7 H), 7.71 (m, 2 H); ^{13}C NMR 13.5 (CH/CH_3), 21.2 (CH/CH_3), 27.6 (CH/CH_3), 38.1 (CH_2), 39.4 (CH/CH_3), 48.5 (CH_2), 55.9 (CH/CH_3), 63.5 (CH_2), 80.9 (C), 127.0 (CH), 127.7 (CH), 128.3 (CH), 128.6 (CH), 129.5 (CH), 136.6 (C), 136.9 (C), 143.3 (C), 169.7 (C); IR (neat liquid film) 3539 (st br), 3064 (w), 3030 (m), 2933 (st br), 1728 (st), 1598 (m), 1495 (m), 1456 (m), 1333 (st br), 1155 (st br) cm^{-1}; MS *m/e* (%) 447 (M^+, <1) 389 (65), 332 (65), 297 (65), 236 (60), 91 (100).

Hydroboration of **11** was carried out in the same way as for **12** using 0.256 g (0.73 mmol) of **11** to give after purification by flash chromatography with 20% ethyl acetate in hexane 0.037 g, 14%, of the monohydroborated product 2,4-dimethyl-1-hydroxy-3-(benzyltosylamino)-4-pentene and 0.118 g of the starting material and the reduced product 2,4-dimethyl-3-(benzyltosylamino)-1-pentene as a 2:1 mixture. The latter two compounds were separated by further chromatography, and the reduced material was characterized independently.

2,4-Dimethyl-1-hydroxy-3-(benzyltosylamino)-4-pentene: TLC R_f 0.13 (20% ethyl acetate in hexane); ^1H NMR 0.91 (d, J = 6.7 Hz, 3 H), 1.50 (s, 3 H), 1.72 (br s, 1 H), 1.96 (m, 1 H), 2.38 (s, 3 H), 3.37 (m, 1 H), 3.56 (m, 1 H), 4.19 (m, 2 H), 4.44 (d, J = 15.4 Hz, 1 H), 4.94 (s, 1 H), 5.10 (s, 1 H), 7.22 (m, 7 H), 7.57 (m, 2 H); ^{13}C NMR 14.7 (CH/CH_3), 21.2 (CH/CH_3), 22.7 (CH/CH_3), 35.6 (CH/CH_3), 48.1 (CH_2), 64.1 (CH/CH_3), 65.5 (CH_2), 116.1 (CH_2), 127.2 (CH), 127.3 (CH), 127.9 (CH), 128.8 (CH), 129.0 (CH), 136.8 (C), 138.1 (C), 141.0 (C), 142.7 (C); IR 3480 (br st), 3040 (w), 2930 (st), 1640 (w), 1600 (m), 1490 (m), 1450 (st), 1330 (st br), 1150 (st); MS *m/e* (%) 373 (M^+, <1), 315 (20), 218 (55), 155 (55), 91 (100); HRMS calcd for $C_{21}H_{27}NO_3S$ 373.171145, found 373.17177.

2,4-Dimethyl-3-(benzyltosylamino)-1-pentene: TLC R_f 0.59 (20% ethyl acetate in hexane); ^1H NMR 0.83 (d, J = 6.4 Hz, 3 H), 0.89 (d, J = 6.5 Hz, 3 H), 1.52 (s, 3 H), 1.82 (m, 1 H), 2.38 (s, 3 H), 3.92 (d, J = 11.1 Hz, 1 H), 4.16 (d, J = 15.3 Hz, 1 H), 4.42 (d, J = 15.3 Hz, 1 H), 4.91 (s, 1 H), 5.10 (s, 1 H), 7.22 (m, 7 H), 7.25 (m, 2 H); ^{13}C NMR 20.4 (CH/CH_3), 20.7 (CH/CH_3), 21.2 (CH/CH_3), 22.8 (CH/CH_3), 27.9 (CH/CH_3), 47.6 (CH_2), 69.1 (CH/CH_3), 116.0 (CH_2), 127.1 (CH), 127.2 (CH), 127.8 (CH), 128.9 (CH), 136.9 (C), 138.5 (C), 141.0 (C), 142.5 (C); IR 3087 (m), 3065 (m), 3031 (m), 2964 (st), 2927 (st), 2873 (m), 1647 (m), 1598 (m), 1455 (st), 1338 (st br), 1157 (st) cm^{-1}; MS *m/e* (%) 357 (M^+, ~1), 314 (85), 91 (100); HRMS calcd for $C_{21}H_{27}NO_2S$ 357.176235, found 357.17548.

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