Pergamon

Tetrahedron Vol. 51, No. 41, pp. 11087-11110, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00696-6

New Trialkylsilyl Enol Ether Chemistry: α–*N*-Tosylamination of Triisopropylsilyl Enol Ethers

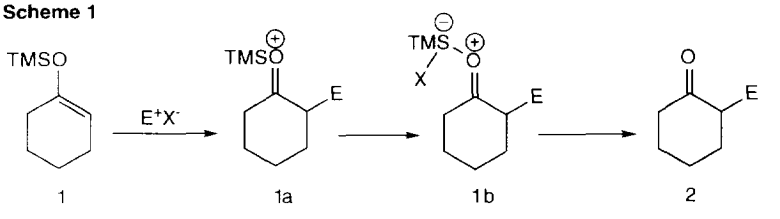
Philip Magnus*, Jérôme Lacour, Iain Coldham, Benjamin Mugrage and William B. Bauta

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712.

Abstract: Triisopropylsilyl enol ethers react with $(TsN)_2Se$ to give α-*N*-tosylamino derivatives in modest to good yields. In the absence of 1,3-diaxial interactions the *N*-tosylamino group prefers an axial conformation. The axial *N*-tosylamino derivatives can be readily transformed into the azabicyclo[3.3.1]nonane skeleton, the core structure of a number of alkaloids.

The traditional chemistry of trialkylsilyl enol ethers has almost exclusively involved the prototype trimethylsilyl (TMS) enol ethers.[1] Typically, TMS enol ethers react with a wide range of electrophiles (E) to give α-functionalized carbonyl derivatives, **Scheme 1**. The TMS enol ether **1** forms the oxonium ion intermediate **1a**, which undergoes nucleophilic attack at the silicon atom by X^- to give the "ate" intermediate **1b**, which then leads to the α-functionalized derivative **2**.

Scheme 1

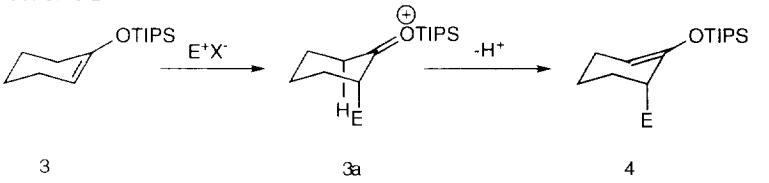


This type of chemistry has been widely used in organic synthesis, and is most notable in instances avoiding anion exchange (equilibration), and consequently maintains the regiospecificity of the original TMS enol ether. The process shown in **Scheme 1** is subject to defined elements of stereoelectronic control. The electrophile adds to **1** from an axial trajectory (maximum overlap) to give **1a** where E is in an axial conformation. Conformational relaxation in the final product leads to the thermodynamically more stable equatorial conformer **2**. Expressed in a different way, the desilylation process precludes further regiospecific silyl enol ether chemistry and allows rapid conformational equilibration.

We became intrigued by the idea of preventing the desilylation step (**1b**) by surrounding the Si atom with bulky substituents. In this way one might observe truly kinetic silyl enol ether electrophilic chemistry. Triisopropylsilyl (TIPS) enol ethers provide the steric bulk, and both the kinetic and thermodynamic enol ethers

are, in most cases, readily available. **Scheme 2** outlines this notion with the stereoelectronic and conformational details.[2] The electrophile adds to **3** from an axial trajectory to give **3a** where E is in an axial configuration. The intermediate onium ion **3a** should be prevented from desilylation by the bulky triisopropyl groups, and as a consequence is expected to undergo axial proton loss to give **4**. We anticipated that **4** would prefer the depicted axial conformation because of steric reasons ($A^{1,3}$-strain) and possibly the stabilizing electronic interaction between the σ^*(E-C) and the π-system. While we have examined a variety of electrophiles, the vast majority of effort has been concentrated on the introduction of a nitrogen atom α- to the enol ether functionality.[3] Our particular interest in nitrogen functionalization stems from past indole alkaloid research, and more topically our recent research on the esperamicin-calicheamicin antitumor agents.[4]

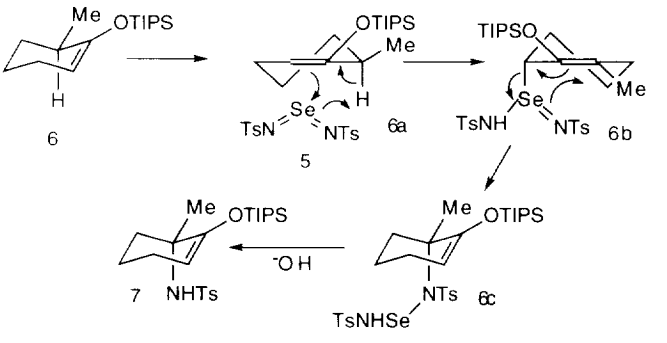
Scheme 2



3 3a 4

Initially, we decided to examine the Sharpless aminating reagent **5**, which is usually thought to be TsN=Se=NTs, although recent work suggests otherwise.[5,6] Nevertheless, from the mechanistic point of view it is conveniently simple to use the selenodiimide formulation for **5** since it readily allows prediction of the regiochemistry of *N*-tosylamination. For example, one would predict that treatment of **6** with **5** should give **7**. This arises from an initial "ene" reaction **6a** to give the intermediate **6b**, followed by [2.3]-sigmatropic rearrangement to give **6c**, which upon hydrolysis or reduction of the N-Se bond provides **7**, **Scheme 3**. In the event, treatment of **6** with **5** (generated *in situ* from selenium metal and chloroamine-T) gave after hydrolysis **7** (39%). We have treated a number of TIPS enol ethers with **5**, and in general the yields of the α-*N*-tosylamine

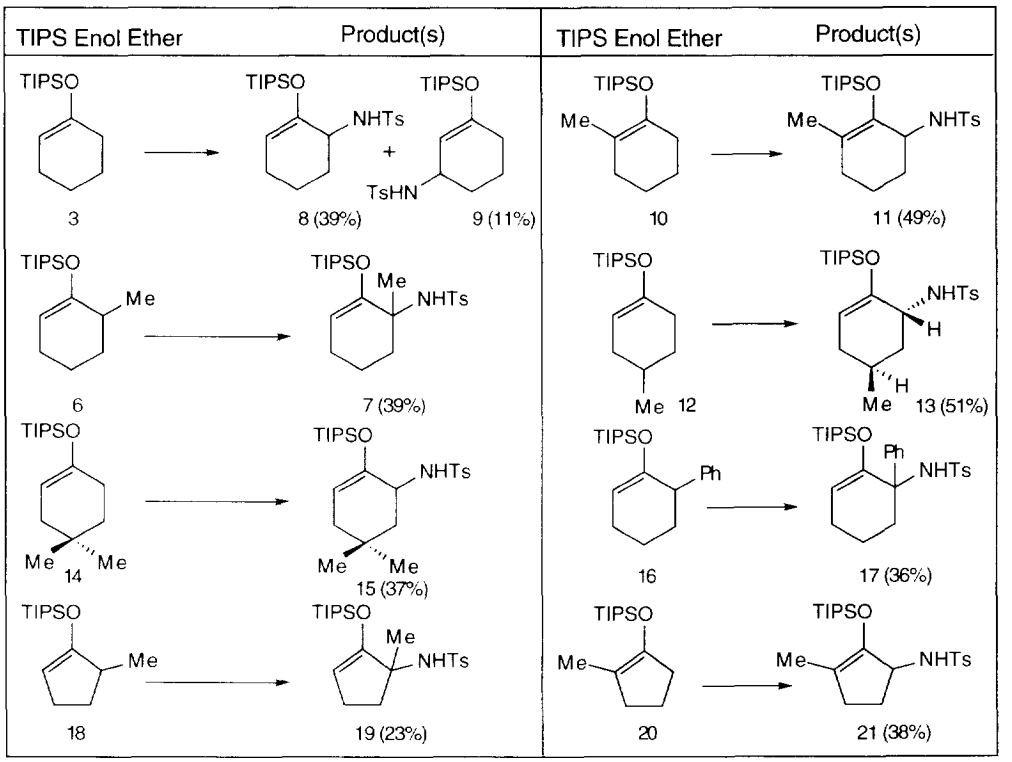
Scheme 3



range from 23 to 51%. **TABLE 1** shows eight examples of the α-amination reaction. In the cyclohexenyl systems the -NHTs group occupies an axial conformation, except in the 4,4-dimethyl case (**15**) where there is a 1,3-diaxial interaction between the -NHTs group and the *gem*-methyl which causes the -NHTs group to become

equatorial. If the corresponding *tert*-butyldimethylsilyl or trimethylsilyl enol ethers are used, the yield of the α-amination products are negligible. The trialkyl silyl groups are too labile and extensive dehydrogenation takes place to give a large number of products many of which contain selenium.

TABLE 1



Yields for isolated and purified products.

The α-aminated adducts **7**, **8**, **11**, **13**, and **15** gave suitable crystals for single crystal X-ray crystallographic analysis.[7] In **7**, **8**, **11**, and **13**, the -NHTs group is in an axial conformation. **Figure 1** shows a Chem 3D representation of **11** (H's on the -TIPS and *p*-tolyl removed) which clearly illustrates that the cyclohexenyl ring is in a sofa conformation with the -NHTs group axially oriented. **Figure 2** shows a Chem 3D representation of **15** (H's on the -TIPS, and *p*-tolyl group removed) and illustrates that the 4,4-dimethyl adduct **15** prefers the -NHTs substituent to occupy an equatorial conformation. For the compounds **7**, **8**, **11**, and **13**, which lack any 1,3-NHTs/methyl diaxial interactions, the axial conformer is the thermodynamically more stable conformer. When the π–σ* stabilization is allowed to compete against 1,3-NHTs/methyl diaxial interactions, substrate **15** prefers the -NHTs group in an equatorial conformation. It is highly probable that the observed pseudo-axial orientation for the α-amino TIPS enol ethers ensues from both effects ($A^{(1,3)}$ and π–σ*) acting in unison.[8]

Figure 1, Chem 3D of **11** from X-ray coordinates.

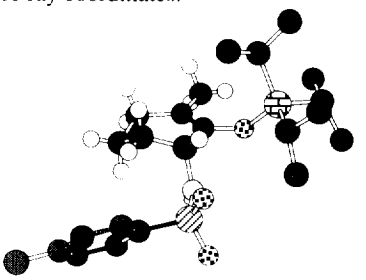
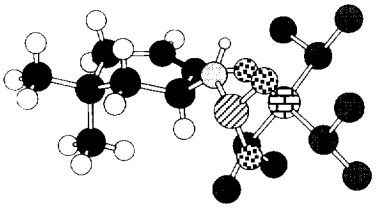
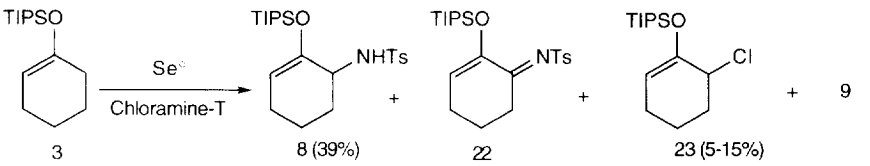


Figure 2, Chem 3D of **15** from X-ray coordinates.



Only in the simplest case, namely **3**, did we observe the regioisomeric β-NHTs adduct **9** (11%). The major by-product isolated from the α-amination reaction with **3** is the α-chloro compound **23** (5-15%), **Scheme 4**. Treatment of **3** with chloramine-T and a catalytic amount of tellurium metal (10%) forms exclusively **23** (65%). The α-amino silyl enol ether **8** was not detected by thin layer chromatography (TLC) or by ^{1}H NMR spectroscopy.

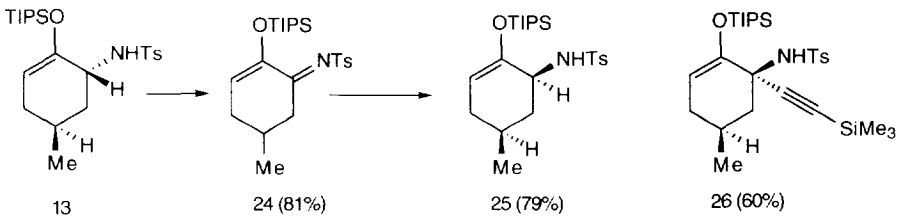
Scheme 4



The α-*N*-tosylamine yields depend on the molar ratio between the Sharpless reagent **5** and the silyl enol ether. The optimal conditions that were used by Sharpless (**5** 0.63 eq to 0.83 eq with respect to the alkene do not, in our case, bring the reaction to completion. 1.05 Equivalents of **5** are necessary to complete the reaction. If an excess of the selenodiimide **5** is used, the α-imino silyl enol ether **22** is formed by over-oxidation of **8**. The α-imino silyl enol ether **22** can be prepared independently by oxidation of **8** with selenium dioxide in aqueous dioxane in 57% yield, **Scheme 4**.

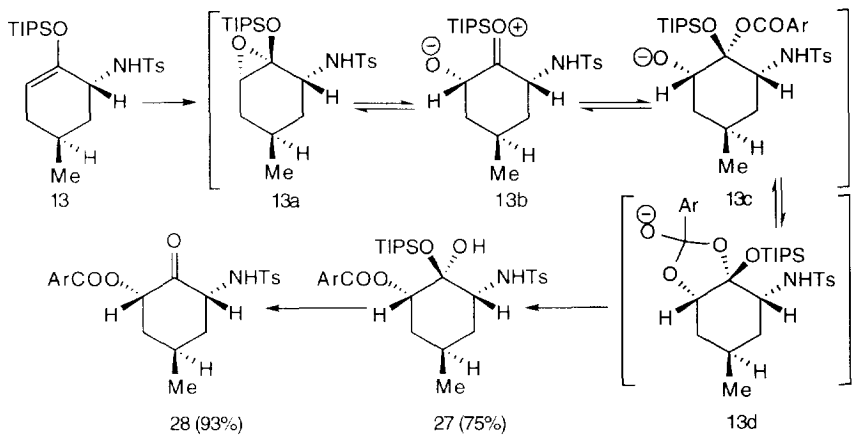
The α-*N*-tosylamination reaction with **12** forms only one stereoisomer **13**. The -NHTs functional group is in the axial position (X-ray). Oxidation of **13** with SeO_2/dioxane gave the imine **24** (81%) which upon reduction with $NaBH_4$ or $LiAlH_4$ gave exclusively the equatorial adduct **25** (79%), **Scheme 5**. This corresponds to the delivery of hydride from an axial trajectory.[9] Similarly addition of lithium trimethylsilylacetylide gave only axial addition, resulting in **26** (60%). The equatorial conformation of the -NHTs group in both **25** and **26** was confirmed by X-ray crystallography. All of the crystal structures show the cyclohexenyl ring in a sofa conformation.

Scheme 5



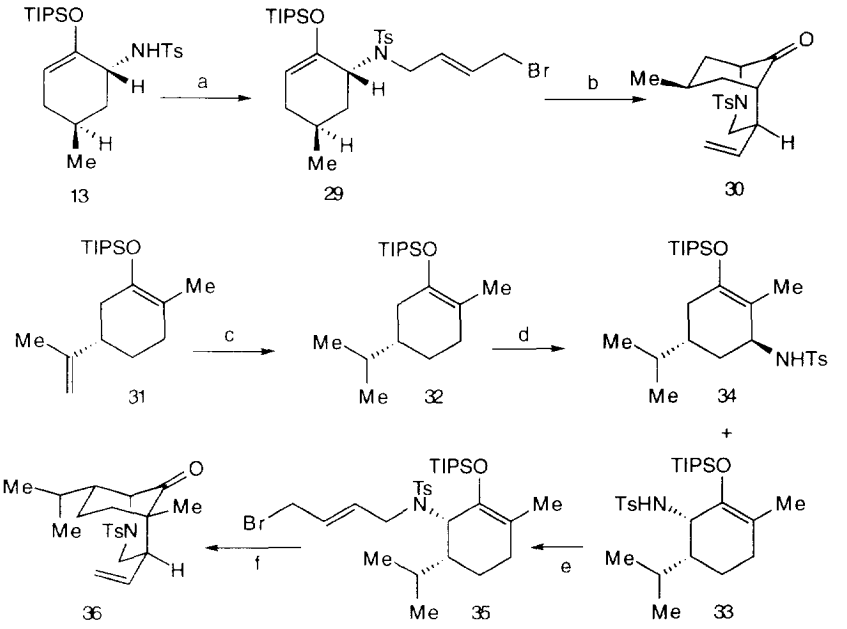
To illustrate some of the synthetic potential of the aminated adduct **13** we have carried out the following transformations. Exposure of **13** to *m*-$ClC_6H_4CO_3H/CH_2Cl_2/20°C$ followed by $NaHCO_3/H_2O$ gave the α-OCOAr-α'-NHTs ketone **28** (70%), **Scheme 6**.[10] None of the *trans*-diastereomer could be detected. When **13** was treated with *m*-$ClC_6H_4CO_3H/20°C/NaHCO_3$ the hemiacetal **27** was isolated as a moderately stable compound. Aqueous $NaHCO_3$ converted **27** into **28**. The epoxide **13a** could be observed both by tlc and ^1H NMR; presumably the zwitterion **13b** is trapped by the *m*-chlorobenzoate anion in a reversible manner and only **13c** can undergo benzoyl-transfer to the ortho-ester intermediate **13d** which collapses to the hemiacetal **27**. ^1H NMR data shows that the α'-TsNH and α-OCOAr groups are axial in **27** and relax to an equatorial conformation in **28**.

Scheme 6 (Ar = *m*-C_6H_4Cl)



Since the -NHTs group is in an axial conformation in **13** it is ideally situated for intramolecular reactions to construct azabicyclic structures. *N*-Alkylation of **13** with *E*-1,4-dibromo-2-butene/NaH/THF readily gave **29** (98%). After investigating a number of Lewis acids it was found that treatment of **29** with 1.1 equivalents of silver (I) trifluoromethanesulfonate gave a single bicyclic product **30** albeit in low yield (20%).

Scheme 7

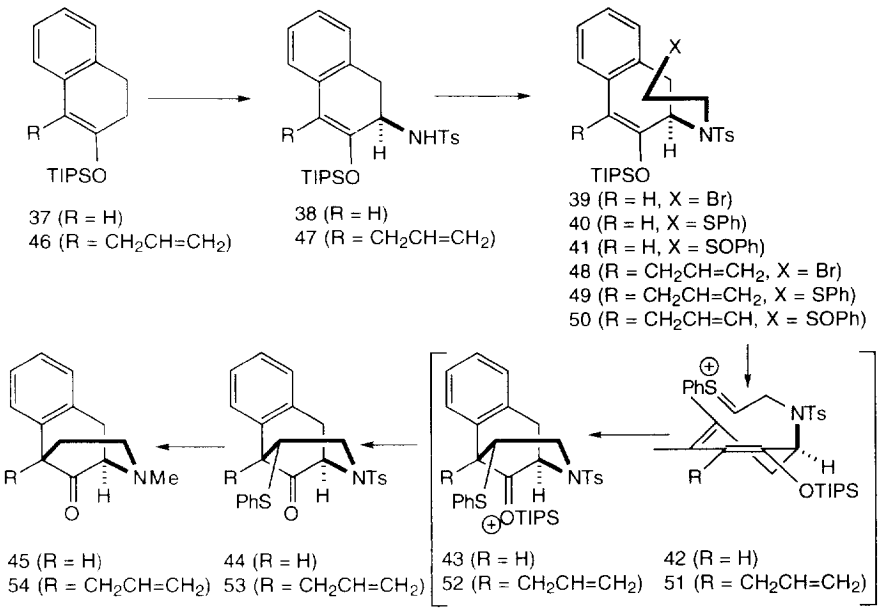


Conditions:- a) NaH/*E*-1,4-dibromo-2-butene/THF reflux (98%). b) AgOTf/CH_2Cl_2/-60 to 0°C (20%). c) H_2/Rh/Alumina (100%). d) Se (powder)/chloramine-T/CH_2Cl_2 (27%of **33**). e) NaH/*E*-1,4-dibromo-2-butene/DMF/25°C (88%). f) AgOTf/CH_3NO_2/25°C (51%).

Hydrogenation of dihydrocarvone TIPS enol ether **31** over rhodium on alumina gave **32** (100%). Unfortunately, the α-*N*-tosylamination reaction, which had always been regioselective (except with **3**) gave a complex mixture of products. ^{1}H NMR analysis of the crude reaction mixture revealed the formation of a (2:1) mixture of amino silyl enol ethers, probably the α **33** and β **34** isomers. The two products α **33** and β **34** were not separable by chromatography, however **33** (27%) was isolated by recrystallization from hexane. The large amount of the β isomer **34** is probably due to the steric hindrance introduced by the isopropyl group which shields the approach of the reagent to the α-face of the TIPS enol ether. Alkylation of the tosylamide anion of **33** with *E*-1,4-dibromobutene/DMF gave **35** (88%). When **35** was treated with silver (I) trifluoromethanesulfonate in nitromethane a single bicyclic derivative **36** was obtained in 51% yield. The structure and stereochemistry of **36** was verified by single crystal X-ray analysis.

The morphine alkaloids have generated enormous synthetic interest for many years.[11] The axial -NHTs functionality offers a very simple strategy for the synthsis of the benzomorphine pharmacophore directly from the TIPS enol ether of β-tetralone.[12]

Scheme 8



β-Tetralone was converted into the triisopropylsilyl enol ether **37** (94%) by treatment with KHMDS/TIPSCl/THF/0 °C. Exposure of **37** to $(TsN)_2Se$ at 25°C for 40h gave the axially aminated adduct **38** (71%). Remarkably, this reaction did not result in any aromatization products, which suggests that there is little or no charge build-up in the "ene"/[2.3]sigmatropic rearrangement process. The -NHTs group was assigned an axial (pseudo) configuration on the basis of the methine couplings (ABX, J_{AX} 6.0 Hz, J_{BX} 6.0 Hz). Treatment of **38** with NaH/$BrCH_2CH_2Br$/THF/80°C gave the *N*-alkylated compound **39** (84%), which was directly converted into the sulfide **40** (NaSPh/THF/80°C)(94%). When the derived sulfoxides **41** (*m*-CPBA/CH_2CH_2/-78°C)(97%) were treated with trifluoroacetic acid anhydride/2,6-di-*t*-butyl-4-methylpyridine/CH_2Cl_2/0°C, followed by addition of chlorobenzene and rapid heating to 130°C, the benzomorphanone **44** was isolated in 50% yield, **Scheme 8**.[13] The overall structure of **44** and the stereochemistry of the -SPh substituent was determined by single crystal X-ray crystallography. The sulfonium ion **42** is ideally aligned with respect to the π-system of the triisopropylsilyl enol ether to give the oxonium ion **43**. For the case **44** (R=H), only the axial-SPh (synclinal attack) diastereomer was formed. This stereochemical outcome appears to be a consequence of aligning the =SPh ion away from the benzo-portion of **44** (R=H). Removal of the -SPh and -Ts groups and concommitant *N*-methylation of **44** to give **45** (60%) was accomplished by treatment of **44** with Na/NH_3/THF, followed by methyl iodide.

Starting with the 1-allyl derivative of β-tetralone, its triisopropylsilyl enol ether derivative **46** (97%) was converted into **47** (59%), **48** (87%), **49** (87%) and **50** (99%) as described for **37**. When **50** was exposed to the Pummerer reaction conditions (TFAA/2,6-di-*t*-butyl-4-methylpyridine/ CH_2Cl_2 at 0°C then PhCl at 130°C) the benzomorphanone adduct **53** was isolated as a mixture of epimers(1.7:1, 79% yield) at the C-SPh bond. Treatment of **53** with Na/NH_3/THF, followed by methyliodide gave **54** (57%).

In summary, the one step direct introduction of -NHTs functionality α- to a TIPS enol ether group while retaining the TIPS enol ether is a useful transformation. While, in some cases, the yields are not as good as one would like, the directness can offset that deficiency.[14]

Experimental

Unless noted otherwise, all starting materials were obtained from commercial suppliers and were used without further purification. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen prior to use. *N,N*-Dimethylformamide (DMF), hexane and benzene were distilled from calcium hydride. Methanol (MeOH) was distilled from magnesium methoxide and stored over 3Å molecular sieves under argon. Triethylamine was distilled from calcium hydride and stored under argon. All reactions involving organometallic reagents or other moisture sensitive reactants were executed under an atmosphere of dry nitrogen or argon using oven dried and/or flame dried glassware.

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a General Electric QE-300 (300 MHz) spectrometer as solutions in deuterochloroform ($CDCl_3$), unless otherwise indicated. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.24 ppm) as internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants are given in hertz (Hz). ^{13}C-NMR spectra were recorded on General Electric QE-300 (75 MHz) instrument as solutions in $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in parts per million (ppm, δ) downfield from TMS and are referenced to the center line of $CDCl_3$ (77.0 ppm) as internal standard; (e) or (o) indicate even or odd numbers of hydrogens carried by the carbon. IR spectra were recorded either neat on sodium chloride plates or as solutions in solvent as indicated using a Perkin-Elmer 1600 FT-IR spectrometer, and are reported in wave numbers (cm^{-1}). Low resolution chemical ionization (CI) mass spectra were obtained on a TSQ 70 instrument, and the exact mass determinations were obtained on a VG analytical ZAB2-E instrument.

Routine monitoring of reactions were performed using MERCK Alufolien Kieselgel 60 F_{254} silica gel, aluminum-backed TLC plates. Flash chromatography was performed using silica gel MERCK Kieselgel 60H F_{254} and Florisil 100-200 Mesh with the solvent indicated.

6-Methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 6. General procedure for the synthesis of TIPS enol ethers from ketones under kinetic conditions. Under an argon atmosphere, potassium hexamethyldisilazide (10 mL, 0.5 M, 5 mmol) was added dropwise, over ten minutes, to a solution, cooled to -78°C, of 2-methylcyclohexanone **5** (0.55 mL, 4.55 mmol) in tetrahydrofuran (15 mL). After stirring for 15 minutes at -78°C, triisopropylsilyl trifluoromethanesulfonate (1.34 mL, 5. 00 mmol) was added. The reaction mixture was stirred for 30 minutes at -78°C and then slowly warmed to room temperature. Saturated aqueous solution of ammonium chloride (30 mL) was added and the phases were separated. The organic phase was washed with aqueous solutions of ammonium chloride (2 x 20 mL) and sodium chloride (20 mL), dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product of the reaction was analyzed by ^{1}H NMR spectroscopy to determine a (>10:1) ratio between the tri- and tetrasubstituted isomers. The product was purified by flash chromatography over silica gel (eluent hexanes, Rf 0.56) to give a

colorless oil **6** (806 mg, 66%). bp 60°C/1.75 mmHg. IR (film) 2942, 2892, 2866, 1660, 1463 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 4.77 (1H, t, J = 3.7 Hz), 2.24-2.14 (1H, m), 2.00-1.94 (2H, m), 1.84-1.72 (1H, m), 1.64-1.52 (1H, m), 1.50-1.32 (2H, m), 1.20-1.08 (21H, m), 1.03-1.00 (3H, d, J = 7.0 Hz). ^{13}C NMR (75 MHz, APT, C_6D_6) δ 154.8 (e), 101.8 (o), 34.2 (o), 24.8 (e), 22.1 (e), 20.6 (e), 19.2 (o), 18.4 (o), 13.2 (o). CIMS (MH^+) m/e 269, base 269 (100), 268 (88), 226 (18), 225 (96), 197 (5), 157 (2). HRMS (M^+) m/e calcd for $C_{16}H_{32}OSi$ 268.222. Found 268.222.

2-Methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 10. General procedure for the synthesis of TIPS enol ethers from ketones under thermodynamic conditions. In an oven-dried 200 mL flask, triethylamine (4.15 mL, 28.8 mmol, 2 eq) was added, at 0°C, to a solution of 2-methylcyclohexanone (1.67 g, 14.9 mmol, 1.0 eq) in dichloromethane (50 mL). The solution was placed under an argon atmosphere and was stirred for 2 minutes. Triisopropylsilyl trifluoromethanesulfonate (4.1 mL, 15.2 mmol, 1.02 eq) was added dropwise. After 30 minutes, an aqueous solution of sodium chloride (40 mL) was poured into the reaction mixture and the phases were separated. The organic phase was washed with aqueous solutions of ammonium chloride (30 mL) and sodium chloride (30 mL), dried (magnesium sulfate), filtered, and the solvent was removed under reduced pressure. The crude reaction mixture was analyzed by ^1H NMR spectroscopy to determine a (4:1) ratio between the tetra- and trisubstituted isomers. The product was purified by flash chromatography over silica gel (eluent hexanes, Rf 0.44) to give a colorless oil **10** (2.64 g, 67%). bp 124°C /1.5 mmHg. IR (film) 2927, 1686, 1464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.15-2.05 (2H, m), 1.97-1.90 (2H, m), 1.66-1.58 (2H, m), 1.61 (3H, s), 1.57-1.50 (2H, m), 1.18-1.03 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 143.3 (e), 110.8 (e), 30.4 (2, e), 23.9 (e), 23.0 (e), 18.1 (o), 16.5 (o), 13.2 (o). CIMS (MH^+) m/e 269, base 269 (100), 268 (68), 225 (85), 197 (4), 157 (4). HRMS (M^+) m/e calcd for $C_{16}H_{32}OSi$ 268.222. Found 268.223.

1-Triisopropylsilyl(oxy)-cyclohex-1-ene 3. Synthesized in an analogous manner to **10** from cyclohexanone (4.25 g, 43.3 mmol). The product was purified by flash chromatography over silica gel (eluent hexanes) to give a colorless oil **3** (10.66 g, 97%). bp 115°C /2 mmHg. IR (film) 2934, 2868, 1669, 1465, 1367, 1267, 1189 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.89 (1H, t, J = 3.7 Hz), 2.05-1.97 (4H, m), 1.70-1.61 (2H, m), 1.54-1.48 (2H, m), 1.25-1.00 (21H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 103.5, 29.9, 23.9, 23.3, 22.4, 18.0, 12.7. EIMS m/e 254 (18), base 211 (100), 183 (30). HRMS (M^+) m/e calcd for $C_{15}H_{30}OSi$ 254.207. Found 254.207.

4-Methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 12. Synthesized in an analogous manner to **10** from 4-methylcyclohexanone (2.45 mL, 20.0 mmol). The product was purified by flash chromatography over silica gel (eluent hexanes) to give a colorless oil **12** (5.36 g, 99%). bp 105-110°C/0.1 mmHg. IR (film) 2960, 1666, 1466, 1374, 1194 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.88-4.80 (1H, m), 2.20-1.94 (2H, m), 1.77-1.56 (2H, m), 1.39-1.00 (24H, m), 0.94 (3H, d, J = 6.1 Hz). HRMS (M^+) m/e calcd for $C_{16}H_{32}OSi$ 268.222. Found 268.224.

4,4-Dimethyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 14. Synthesized in an analogous manner to **10** from 4,4-dimethylcyclohexanone (1.33 g, 10.52 mmol). The product was purified by flash chromatography over silica gel (eluent hexanes) to give a colorless oil **14** (1.62 g, 53%). IR (film) 2946, 2867, 1670, 1465 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.77 (1H, t, J = 4.0 Hz), 2.05 (2H, m), 1.80 (2H, m), 1.40

(2H, t, J = 6.50 Hz), 1.20-1.05 (21H, m), 0.92 (6H, s). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 149.5 (e), 102.1 (o), 37.9 (e), 36.1 (e), 28.6 (e), 28.1 (o), 27.5 (e), 18.0 (o), 12.7 (o). CIMS (MH^+) m/e 283, base 283 (100), 282 (17), 240 (4), 239 (21), 175 (6), 127 (7). HRMS (M^+) m/e calcd for $C_{17}H_{34}OSi$ 282.238. Found 282.237.

6-Phenyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 16. Synthesized in an analogous manner to **10** starting from 2-phenylcyclohexanone (870 mg, 5.0 mmol) and using the general procedure for the synthesis of TIPS enol ethers from enolates formed under thermodynamic control. The crude product of the reaction was analyzed by ^1H NMR spectroscopy to determine a (8:1) ratio between the tri- and tetrasubstituted isomers. The product was purified by flash chromatography over silica gel (eluent hexanes) to give a colorless oil **16** (1.32 g, 80%). IR (film) 3057, 2943, 2866, 1661, 1603, 1495, 1464, 1455 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.09 (5H, m), 5.07-5.03 (1H, m), 3.39 (1H, t, J = 5.6 Hz), 2.15-1.95 (3H, m), 1.74-1.42 (3H, m), 1.15-0.95 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 151.0 (e), 144.6 (e), 128.4 (o), 127.8 (o), 125.7 (o), 104.4 (o), 46.5 (o), 33.4 (e), 24.3 (e), 19.9 (e), 17.9 (o), 12.7 (o). HRMS Calcd for $C_{21}H_{34}OSi$ M^+ 330.238. Found m/e 330.238.

5-Methyl-1-triisopropylsilyl(oxy)-cyclopent-1-ene 18. Synthesized in an analogous manner to **6** from 2-methylcyclopentanone (490 μL, 4.55 mmol). The crude product of the reaction was analyzed by ^1H NMR spectroscopy to determine a (2.7:1) ratio between the tri- and tetrasubstituted isomers. The product was purified by flash chromatography over silica gel (eluent hexanes, Rf 0.51) to give a colorless oil **18** (294 mg, 25%). ^1H NMR (300 MHz, $CDCl_3$) δ 4.05 (1H, m), 2.5 (1H, m), 2.20-2.12 (2H, m), 2.12-1.98 (1H, m), 1.43-1.32 (1H, m), 1.20-1.10 (3H, m), 1.10-1.03 (21H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 99.7, 39.6, 30.6, 26.8, 18.8, 18.0, 12.5. CIMS (MH^+) m/e 255, base 255 (100), 254 (84), 253 (84), 212(7), 211 (9), 183 (2), 157 (3). HRMS (M^+) m/e calcd for $C_{15}H_{30}OSi$ 254.207. Found 254.205.

2-Methyl-1-triisopropylsilyl(oxy)-cyclopent-1-ene 20. Synthesized in an analogous manner to **10** from 2-methyl-cyclopentanone (550 mg, 5.6 mmol). The crude product of the reaction was analyzed by ^1H NMR spectroscopy to determine a (4:1) ratio between the tetra- and trisubstituted isomers. The product was purified by flash chromatography over silica gel (eluent hexanes) to give a colorless oil **20** (859 mg, 59%): IR (film) 2942 (w), 2866 (w), 1690 (w), 1465 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.37-2.29 (2H, m), 2.21-2.13 (2H, m), 1.83-1.73 (2H, t, J = 6.5 Hz), 1.58 (3H, s), 1.22-1.03 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 146.7 (e), 112.1 (e), 34.0 (e), 33.5 (e), 19.9 (e), 17.9 (o), 12.9 (o), 11.9 (o). CIMS (MH^+) m/e 255 (22), base 253 (100), 254 (21), 227 (32), 225 (21). HRMS (M^+) m/e calcd for $C_{15}H_{30}OSi$ 254.207. Found 254.207.

6-(4-Methylphenylsulfonyl)amino-1-triisopropylsilyl(oxy)-cyclohex-1-ene 8 (General procedure for the synthesis of α-*N*-tosylamino TIPS enol ethers). In a 100 mL flask, a suspension of selenium powder (200 mg, 2.53 mmol, 1.0 eq) and anhydrous chloramine-T (1.29 g, 5.19 mmol, 2.2 eq) in dichloromethane (20 mL) was stirred under argon at 25°C for 48 hours until it became a white suspension. An equivalent result was obtained if the mixture is heated at reflux for three hours. To this suspension, cooled at 0°C, was added the silyl enol ether **3** (709 mg, 2.79 mmol, 1.1 eq) as a solution in dichloromethane (3 mL).

The temperature was slowly allowed to increase to 25°C and after 3 hours the reaction mixture was quenched with a saturated solution of sodium bicarbonate (40 mL). After 1.5 hr of stirring, the mixture was filtered through a celite pad. The organic phase was separated, washed with aqueous solutions of ammonium chloride (2 x 20 mL), sodium chloride (20 mL), and dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. Hexane (20 mL) was added to the crude reaction mixture. The mixture was filtered, separating the insoluble *p*-toluenesulfonamide. The solvent was removed under reduced pressure to give an oil. The crude mixture was purified by flash chromatography over silica gel (eluent hexanes 85, ethyl acetate 15) to give two compounds. The less polar fraction (Rf 0.51) is a colorless solid **8** (418 mg, 39%). M.p 84-86°C (hexane). IR (film) 3277, 2942, 2922, 2866, 1663, 1597, 1463 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (2H, d, J = 8.14 Hz), 7.26 (2H, d, J = 8.14 Hz), 5.03 (1H, d, J = 4.17 Hz), 4.93 (1H, t, J = 3.5 Hz), 3.63 (1H, t, J = 4 Hz), 2.39 (3H, s), 2.06-1.83 (3H, m), 1.84-1.72 (1H, m), 1.70-1.52 (1H, m), 1.52-1.40 (1H, m), 1.08-0.80 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 146.9 (e), 142.8 (e), 137.4 (e), 129.3 (o), 126.9 (o), 106. (o), 52.5 (o), 30.0 (e), 23.3 (2, e), 21.2 (o), 17.7 (o), 12.4 (o). CIMS (MH^+) m/e 424 (15), base 380 (100), 422 (4), 381 (22), 285 (7), 284 (44), 269 (6), 253 (47). HRMS (M^+) m/e calcd for $C_{22}H_{37}NO_3SiS$ 423.226. Found 423.226. Anal calcd for $C_{22}H_{37}NO_3SiS$ C, 62.37.; H, 8.80, N, 3.31. Found C, 62.38.; H, 8.88.; N, 3.42%.

The more polar fraction (Rf 0.43) is a colorless oil **9** (119 mg, 11%). IR (film) 3272, 2944, 2892, 2966, 1659, 1463 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 8.2 Hz), 7.30 (2H, d, J = 8.2 Hz), 4.70 (1H, d, J = 8.7 Hz), 4.40 (1H, d, J = 4.0 Hz), 3.96-3.92 (1H, m), 2.42 (3H, s), 2.00-1.92 (2H, m), 1.75-1.45 (4H, m), 1.05-0.95 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 155.1 (e), 143.0 (e), 138.6 (e), 129.6 (o), 126.8 (o), 103.3 (o), 49.5 (o), 29.9 (e), 29.3 (e), 21.4 (o), 19.1 (e), 12.8 (o), 12.4 (o). CIMS (MH^+) m/e 424 (50), base 253 (100), other 380 (4). HRMS (M^+) m/e calcd for $C_{22}H_{37}NO_3SSi$ 423.226. Found 423.225.

6-(4-Methylphenylsulfonyl)amino-6-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 7. Synthesized in an analogous manner to **8** from **6** (610 mg, 2.27 mmol, 1.1 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 9, ethyl acetate 1) to give a colorless solid **7** (353 mg, 39%). M.p 75-79°C (hexane). IR (film) 3377, 3287, 2943, 2922, 2893, 1660, 1600, 1464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (2H, d, J = 8.22 Hz), 7.19 (2H, d, J = 8.22 Hz), 4.95 (1H, s), 4.67 (1H, t, J = 4.0 Hz), 2.34 (3H, s), 2.10-2.03 (1H, m), 1.92-1.84 (2H, m), 1.74-1.65 (1H, m), 1.55-1.45 (1H, m), 1.45-1.35 (1H, m), 1.30 (3H, s), 1.20-1.00 (21H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 142.5, 140.7, 129.3, 126.9, 102.5, 58.8, 35.3, 25.3, 23.8, 21.4, 18.7, 17.6, 12.7. CIMS (MH^+) m/e 438 (9), base 267 (100), 439 (2), 437 (2), 436 (4), 394 (21), 284 (9), 268 (24). HRMS (M^+) m/e calcd for $C_{23}H_{39}NO_3SiS$ 437.242. Found 437.237. Anal calcd for $C_{23}H_{39}NO_3SiS$, C, 63.11.; H, 8.98.; N, 3.20. Found C, 63.54.; H, 8.89.; N, 3.31%.

6-(4-Methylphenylsulfonyl)amino-2-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 11. Synthesized in an analogous manner to **8** from **10** (748 mg, 2.79 mmol, 1.1 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 9, ethyl acetate 1) to give a colorless solid **11** (542 mg, 49%). M.p 150-152°C (hexane). IR (film) 3280, 2942, 2922, 2865, 1676 (w), 1463 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (2H, d, J = 8.3 Hz), 7.28 (2H, d, J = 8.3 Hz), 4.68 (1H, d, J = 3.83 Hz), 3.88 (1H, s), 2.41 (3H, s), 1.95-1.85 (2H, m), 1.85-1.75 (2H, m), 1.59 (3H, s), 1.56-1.42 (2H, m), 1.10-1.00 (21H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 141.0, 139.0, 129.4, 126.8, 117.0, 53.6, 30.1, 28.9, 21.4, 18.0, 17.1,

13.4. CIMS (MH^+) m/e 438 (16), base 267 (100), 437 (1), 436 (4), 394 (20), 268 (22). HRMS (M^+) m/e calcd for $C_{23}H_{39}NO_3SiS$ 437.242. Found 437.237. Anal calcd for $C_{23}H_{39}NO_3SiS$ C, 63.11.; H, 8.98.; N, 3.20. Found C, 62.98.; H, 8.98.; N, 3.13%.

***trans*-6-(4-Methylphenylsulfonyl)amino-4-methyl-1-triisopropyl-silyl(oxy)-cyclohex-1-ene 13**. Synthesized in an analogous manner to **8** from **12** (211 mg, 0.785 mmol, 1.02 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 9, ethyl acetate 1) to give a colorless solid **13** (171 mg, 51%). M.p 135-136°C (ether). IR ($CHCl_3$) 3282, 2946, 2867, 1665, 1600, 1330, 1201 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.77 (2H, d, J = 8.3 Hz), 7.28 (2H, d, J = 8.3 Hz), 4.91 (1H, dd, J = 5.0, 2.1 Hz), 4.57 (1H, d, J = 4.2 Hz), 3.67-3.59 (1H, m), 2.41 (3H, s), 2.13-1.97 (2H, m), 1.89-1.50 (2H, m), 1.32 (1H, ddd, J = 11.3, 11.1, 4.2 Hz), 1.05-0.93 (21H, m), 0.90 (3H, d, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.2, 143.0, 137.6, 129.4, 127.1, 106.5, 53.0, 37.7, 32.0, 23.1, 21.4, 20.8, 17.8, 12.5. Anal calcd for $C_{23}H_{39}NO_3SiS$, C, 63.11.; H, 8.98.; N, 3.20. Found C, 63.10.; H, 9.17.; N, 3.17%.

6-(4-Methylphenylsulfonyl)amino-4,4-dimethyl-1-triisopropyl-silyl(oxy)-cyclohex-1-ene 15. Synthesized in an analogous manner to **8** from **14** (1.0 g, 3.54 mmol, 1.02 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 23, ethyl acetate 2) to give a colorless solid **15** (580 mg, 37%). M.p 87-90°C (hexane). IR ($CHCl_3$) 3338, 1668, 1599, 1464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (2H, d, J = 8.2 Hz), 6.76 (2H, d, J = 8.2 Hz), 4.98 (1H, d, J = 3.6 Hz), 4.64 (1H, t, J = 2.1 Hz), 3.77 (1H, br), 1.77-1.73 (1H, m), 1.72 (3H, s), 1.60-1.52 (1H, m), 1.36-1.29 (2H, m), 0.88-0.74 (21H, m), 0.60 (3H, s), 0.58 (3H, s). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 146.4 (e), 142.9 (e), 138.7 (e), 129.6 (o), 127.6 (o), 104.2 (o), 52.0 (o), 44.0 (e), 37.8 (e), 30.6 (o), 29.7 (e), 26.0 (o), 21.1 (o), 18.2 (o), 13.0 (o). CIMS. (MH^+) m/e 452 (41), base 281 (100), 451 (2), 408 (26), 298 (2), 297 (7), 296 (16), , 253 (12), 172 (3). HRMS (MH^+) m/e calcd for $C_{24}H_{42}NO_3SiS$ 452.265. Found 452.265.

6-(4-Methylphenylsulfonyl)amino-6-phenyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 17. Synthesized in an analogous manner to **8** from **16** (456 mg, 1.379 mmol, 1.1 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 9, ethyl acetate 1) to give a colorless solid **17** (162 mg, 26%). M.p 99-100°C (hexanes). IR (film) 3392, 3364, 3058, 3028, 2943, 2922, 2893, 1668, 1599, 1495, 1464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (2H, d, J = 8.2 Hz), 7.46 (2H, d, J = 8.2 Hz), 7.22-7.10 (5H, m), 5.35 (1H, s), 4.97 (1H, dd, J = 3.95, 3.7 Hz), 2.34 (3H, s), 2.27 (1H, dd, J = 12.6, 3.0 Hz), 1.98-1.85 (3H, m), 1.3-1.0 (5H, m), 1.00-0.90 (18H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 148.5 (e), 144.1 (e), 142.6 (e), 140.7 (e), 129.3 (o), 127.7 (o), 127.3 (o), 127.1 (o), 126.8 (o), 104.4 (o), 65.0 (e), 33.8 (e), 23.6 (e), 21.4 (o), 18.4 (e), 18.1 (o), 12.7 (o). CIMS (MH^+) m/e 500 (10), base 329 (100), 501 (3), 499 (2), 456 (23), 330 (31), 285 (2), 284 (5), 253 (3). HRMS (M^+) m/e calcd for $C_{28}H_{41}NO_3SiS$ 499.258. Found 499.251. Anal calcd for $C_{28}H_{41}NO_3SiS$, C, 67.29.; H, 8.27.; N, 2.80. Found C, 67.15.; H, 8.38.; N, 2.67%.

5-(4-Methylphenylsulfonyl)amino-5-methyl-1-triisopropylsilyl(oxy)-cyclopent-1-ene 19. Synthesized in an analogous manner to **8** from **18** (220 mg, 0.864 mmol, 1.1 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 9, ethyl acetate 1) to give a colorless oil **19** (75 mg, 23%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (2H, d, J = 8.2 Hz), 7.26 (2H, d, J = 8.2 Hz), 4.8 (1H, s), 4.55 (1H, t, J = 2.3 Hz), 2.4 (3H, s), 2.35-2.25 (1H, m), 2.15-2.05 (2H, m), 1.95-1.85 (1H, m), 1.29 (3H,

s), 1.20-1.15 (3H, m), 1.15-1.05 (18H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 142.6, 140.5, 129.3, 126.7, 100.5, 66.2, 35.7, 25.1, 24.5, 21.4, 17.9, 12.3. SMIE (MH^+ -43) m/e 380, base 284 (100), 285 (20), 252 (8), 209 (32). HRMS (MH^+) m/e calcd for $C_{22}H_{38}NO_3SiS$ 424.234. Found 424.231.

5-(4-Methylphenylsulfonyl)amino-2-methyl-1-triisopropylsilyl(oxy)-cyclopent-1-ene 21. Synthesized in an analogous manner to **8** from **20** (468 mg, 1.84 mmol, 1.1 eq). The product was purified by flash chromatography over silica gel (eluent hexanes 9, ethyl acetate 1) to give a colorless solid **21** (270 mg, 38%). M.p 107-108°C (hexane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.4 (2H, d, J = 8.2 Hz), 7.28 (2H, d, J = 8.2 Hz), 4.53 (1H, d, J = 6.1 Hz), 4.1 (1H, br), 2.42 (3H, s), 2.28-2.15 (1H, m), 2.10-1.95 (2H, m), 1.68-1.59 (1H, m), 1.57 (3H, s), 1.05-0.85 (21H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 143.1, 138.1, 129.5, 127.1, 117.7, 60.0, 30.9, 28.5, 21.4, 17.8, 12.9, 12.6. CIMS (MH^+) m/e 424 (6), base 253 (100), 423 (2), 380 (16), 284 (9), 200 (8). HRMS (MH^+) m/e calcd for $C_{22}H_{38}NO_3SiS$ 424.234. Found 424.231. Anal calcd for $C_{22}H_{37}NO_3SiS$, C, 62.38.; H, 8.81.; N, 3.31. Found C, 62.09.; H, 8.79.; N, 3.30%.

6-(4-Methylphenylsulfonyl)imino-1-triisopropylsilyl(oxy)-cyclohex-1-ene 22. Selenium dioxide (30.6 mg, 0.275 mmol) was added to a solution of **8** (109 mg, 0.257 mmol) in aqueous dioxan (5 mL) at 25°C. The reaction temperature was brought to 50°C. After 3 hours, 3 spatulas of sodium sulfate were added, and 30 minutes later the mixture was filtered through a celite pad. The solvent was removed under reduced pressure and the product was purified by flash chromatography over silica gel (hexanes/ethyl acetate 17/3) to give a colorless solid **22** (62 mg, 57%). M.p 89°C (hexane). IR (film) 1620, 1583 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (2H, d, J = 8.25 Hz), 7.29 (2H, d, J = 8.25 Hz), 6.15 (1H, t, J = 4.7 Hz), 3.23 (2H, t, J = 6.6 Hz), 2.43 (3H, s), 2.42-2.30 (2H, m), 1.95-1.85 (2H, m), 1.00-0.85 (21H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 147.9, 143.1, 138.7, 130.0, 128.3, 127.0, 32.5, 24.5, 21.9, 21.4, 17.7, 12.5. CIMS (MH^+) m/e 422, base 378 (100), 421, 266, 180, 152. HRMS (MH^+) m/e calcd for $C_{22}H_{36}NO_3SiS$ 422.219. Found 422.216.

6-Chloro-1-triisopropylsilyl(oxy)-cyclohex-1-ene 23. Tellurium powder (25 mg, 0.197 mmol, 0.10 eq) and anhydrous chloramine-T (1.29 g, 5.19 mmol, 2.2 eq) were added to a solution of **3** (500 mg, 1.965 mmol, 1.0 eq) in dichloromethane (30 mL) at 25°C. The mixture was stirred under argon at 25°C for 16 hours. The reaction was quenched with a saturated solution of sodium bicarbonate (30 mL) and filtered through a celite pad. The organic phase was separated, washed with an aqueous solution of ammonium chloride and dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure. Hexane (20 mL) was added to the crude reaction. The mixture was filtered, separating the insoluble *p*-toluenesulfonamide, and the product was purified by flash chromatography over silica gel (hexanes/ethyl acetate 9/1) to give a colorless oil **23** (367 mg, 65%). IR (film) 2944, 2866, 1661, 1463 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.98 (1H, dd, J = 4.75, 3.2 Hz), 4.49 (1H, t, J = 2.7 Hz), 2.20-1.95 (4H, m), 1.92-1.75 (1H m), 1.70-1.55 (1H, m), 1.22-1.06 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 148.7 (e), 106.6 (o), 58.2 (o), 33.0 (e), 23.7 (e), 17.9 (o), 17.0 (e), 12.6 (o). CIMS (M^+) m/e 290 (^{37}Cl, 7), 288 (^{35}Cl, 22), base 253 (100), 290 (4), 288 (11), 287 (6), 254 (25), 247 (16), 245 (43). HRMS (M^+) m/e calcd for $C_{15}H_{29}OSi^{35}Cl$ 288.168. Found 288.167.

6-(4-Methylphenylsulfonyl)imino-4-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 24. Sulfonamide **13** (917 mg, 2.09 mmol) was dissolved in THF (8.0 mL) and SeO_2 (290 mg, 2.61 mmol) was added. The resulting heterogenous mixture was heated to reflux under argon for 4 h, at which time red residues had formed on the sides of the flask. Ether was added and the mixture filtered through a pad of Celite with added ethyl ether. After solvent removal, the residue was chromatographed on silica gel with 5% EtOAc in hexane as eluent to give sulfonimide **24** (739 mg, 81%). IR (film) 2945, 2857, 1621, 1582, 1462 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.82-1.18 (24H, m), 1.92-2.22 (2H, m), 2.37 (1H, d, J = 13 Hz), 2.42 (3H, s), 2.57 (1H, dd, J = 1.2 Hz, J = 17 Hz), 3.61 (1H, d, J = 17 Hz), 6.09 (1H, d, J = 4.6 Hz), 7.28 (2H, d, J = 7.9 Hz), 7.82 (2H, d, J= 7.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.5, 17.7, 20.7, 21.4, 29.5, 32.7, 40.3, 127.1, 127.5, 128.9, 138.7, 143.1, 147.9, 176.0. HRMS Calcd for $C_{23}H_{37}NO_3SSi$ M^+ 435.226. Found m/e 435.226.

***Cis*-6-(4-Methylphenylsulfonyl)amino-4-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 25.** Sulfonimide **24** (106 mg, 0.24 mmol) was dissolved in THF (7.0 mL) and cooled to -50°C under argon. Lithium aluminum hydride powder (14 mg, 0.36 mmol) was added and the mixture stirred at -50°C for 3.5 h. Ethanol (2 mL) was added, followed by CH_2Cl_2, and the mixture transferred to a separatory funnel, where the organic phase was washed with water. The aqueous phase was back-extracted with CH_2Cl_2 and the combined organic phases dried ($MgSO_4$) and filtered. After solvent removal, the residue was chromatographed on a preparatory TLC plate (2 mm) and eluted with 15% EtOAc in hexane. This afforded sulfonamide **25** (84 mg, 79%). M.p. 118-120°C (from Et_2O). IR ($CHCl_3$) 3339, 3023, 2950, 2870, 1668, 1458, 1399, 1353, 1317, 1230, 1226, 1214, 1204, 1162, 1093, 1075, 1012, 883, 859 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (3H, d, J = 6.2 Hz), 0.95-1.10 (21H, m), 1.25-1.41 (1H, m), 1.55-1.74 (2H, m), 1.94-2.05 (1H, m), 2.22-2.30 (1H, m), 2.42 (3H, s), 3.67-3.76 (1H, m), 4.84-4.90 (1H, m), 5.04 (1H, d, J = 2.0 Hz), 7.28 (2H, d, J = 8.0 Hz), 7.76 (2H, d, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.6, 17.9, 21.37, 21.43, 27.54, 32.16, 39.58, 53.32, 105.1, 127.2, 129.5, 137.0, 143.2, 146.2. Anal calcd for $C_{23}H_{39}NO_3SSi$: C, 63.11.; H, 8.98.; N, 3.20. Found. C, 63.28.; H, 8.67.; N, 3.18%.

***Cis*-6-(4-Methylphenylsulfonyl)amino-6-(trimethylsilylethyn)-4-methyl-1-triisopropyl silyl(oxy)-cyclohexene 26.** To a solution of **13** (43.7 mg, 0.1 mmol) in THF (1 mL) at -78°C was added trimethylsilylethynyl lithium (3.0 eq. 1.5 M solution in THF). After 0.5h at -78°C the mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate (3 x 5 mL). The dried (Na_2SO_4) organic phase was evaporated *in vacuo* to give **26** (32 mg, 60%). M.p. 119-120°C (from Hexane). IR ($CHCl_3$) 3354, 2869, 1671, 1464, 1389, 1316, 1251, 1214, 1159, 1093, 1005 and 845 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.00 (9H, s), 1.01-1.30 (24H, m), 1.31-2.07 (4H, m), 2.48-2.54 (4H, m), 4.85 (1H, d, J = 5 Hz), 5.60 (1H, s), 7.32 (2H, d, J = 7.9 Hz), 7.84 (2H, d, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.82, 142.75, 138.81, 129.20, 127.72, 104.70, 103.20, 88.26, 55.96, 44.33, 32.05, 25.86, 21.52, 21.30, 18.14, 18.06, 12.60, -0.49. Anal calcd for $C_{28}H_{47}NO_3SSi_2$: C, 62.99.; H, 8.87.; N, 2.62. Found. C, 63.06.; H, 8.95.; N, 2.50%. HRMS Calcd for $C_{25}H_{40}NO_3Si_2S$ (M^+ - *i*Pr) 490.227. Found m/e 490.227.

2α-(4-Methylphenylsulfonyl)amino-4β-methyl-6α-(3-chlorobenzoyloxy)-cyclohex-1-one 28. To a solution of **13** (43.7 mg, 0.1 mmol) in dichloromethane (1.0 mL) at 25°C was added *m*-

chloroperoxybenzoic acid (17.2 mg, 0.1 mmol), followed by $NaHCO_3$ (10 mg). The mixture was stirred at 25°C for 3h at which point tlc indicated that **13** had been consumed. The above suspension was directly chromatographed over silica gel eluting with ethyl acetate to give **27** (45 mg, 75%). IR (film) 3625-3333, 3029-2868, 1709-1681, 1599, 1575, 1460, 1428 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (3H, d, J = 6.4 Hz), 1.13-0.94 (21H, m), 1.73-1.59 (3H, m), 1.98-1.86 (2H, m), 2.42 (3H, s), 3.33-3.31 (1H, m), 4.17 (1H, s), 5.15 (1H, s), 5.17 (1H, d, J = 7.6 Hz), 7.28 (2H, d, J = 8.2 Hz), 7.46 (1H, t, J = 7.9 Hz), 7.58 (2H, d, J = 8.4 Hz), 7.72 (2H, d, J = 8.2 Hz), 7.96 (1H, d, J = 8.9 Hz), 8.04 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.6, 143.6, 136.2, 134.7, 133.3, 131.4, 130.0, 129.6, 127.7, 127.3, 93.42, 57.63, 35.67, 21.39, 21.05, 20.43, 18.09, 17.58, 12.74.

A solution of **27** (45 mg) in tetrahydrofuran (0.5 mL) was treated with saturated aqueous $NaHCO_3$ solution (0.5 mL). After 1h the mixture was extracted with dichloromethane (4 mL), dried ($MgSO_4$) and evaporated to give **28** (28.9 mg, 95%). M.p. 159-162°C (from heptane). IR (film) 3276, 3026-2846, 1745, 1721 and 1255 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.34 (3H, d, J = 7.3 Hz), 2.81 (1H, ddd, J's = 4.7, 13.1 and 17.7 Hz), 2.10 (1H, ddd, J's = 4.9, 12.9 and 17.8 Hz),2.43 (3H, s), 2.50-2.22 (3H, m), 4.14 (1H,ddd, J's = 5.1, 5.7 and 12.1 Hz), 5.51 (1H, dd, J = 6.7 and 12.9 Hz), 5.63 (1H, d, J = 5.1 Hz), 7.31 (2H, d, J = 8.1 Hz), 7.39 (1H, t, J = 7.8 Hz), 7.55 (1H, d J = 8.1 Hz), 7.81 (2H, d, J = 8.2 Hz), 7.91 (1H, d, J = 7.9 Hz), 8.00 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.0, 164.0, 143.8, 136.5, 134.5, 133.4, 130.8, 129.9, 129.8, 129.7, 127.9, 126.8, 73.31, 56.19, 42.10, 38.67, 25.62, 21.50, 18.02. Anal calcd for $C_{21}H_{22}ClNO_5S$: C, 57.86.; H, 5.09.; N, 3.21. Found. C, 57.86.; H, 5.02.; N, 3.19%.

***E*-6-*N,N'*-[(4-Methylphenylsulfonyl)-(4-bromo-2-butene)]amino-4-methyl-1-triiso propylsilyl(oxy)-cyclohex-1-ene 29**. At 0°C, in an oven-dried, three-necked, round-bottomed 50 mL flask, equipped with a thermometer, a magnetic stirring bar and an argon inlet, sodium hydride (17 mg, 0.57 mmol, 1.25 eq, 80% suspension in mineral oil) and *E*-1,4-dibromo-2-butene (977 mg, 4.57 mmol, 10 eq) were added to a solution of **13** (200 mg, 0.46 mmol, 1 eq) in THF (20 mL). After 15 minutes, more sodium hydride (51 mg, 1.71 mmol, 3.75 eq, 80% in suspension in mineral oil) was added. The solution was heated at reflux for one hour and then cooled to 25°C. The reaction was quenched with a saturated solution of ammonium chloride and the phases were separated. Ether was added to the organic phase, which was washed with an aqueous solution of sodium chloride (20 mL) and dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The product was purified by flash chromatography over silica gel (eluent hexanes/ethyl acetate 9/1) to give a colorless oil **29** (255 mg, 98%). IR (film) 2946, 2925, 2892, 1662, 1598, 1464 cm^{-1}. ^1H NMR (300 MHz, C_6D_6) δ 7.71 (2H, d, J = 8.1 Hz), 7.25 (2H, d, J = 8.1 Hz), 5.86-5.68 (2H, m), 5.02 (1H, t, J = 3.85 Hz), 4.32-4.25 (1H, m), 4.03-3.84 (3H, m), 3.71 (1H, dd, J = 16.6, 7.2 Hz), 2.40 (3H, s), 2.16 (1H, td, J = 4.8, 16.9 Hz), 2.05 (1H, td, J = 2.9, 13.6 Hz), 1.87-1.80 (1H, m), 1.67-1.50 (2H, m), 1.10-0.95 (24H, m). ^{13}C NMR (75 MHz, APT, C_6D_6) δ 145.5 (e), 142.6 (e), 138.0 (e), 133.9 (o), 129.3 (o), 127.8 (o), 127.2 (o), 108.5 (o), 56.8 (o), 46.3 (e), 39.5 (e), 31.9 (e), 31.7 (e), 23.9 (o), 21.3 (o), 20.6 (o), 18.0 (o), 17.9 (o), 12.8 (o). CIMS (MH^+) m/e 572 (17), base 267 (100), 570 (8), 526 (3), 490 (8), 416 (18), 415 (12), 414 (8), 334 (4), 207 (6), 175 (48). HRMS (M^+) m/e calcd for $C_{27}H_{45}NO_3SiSBr$ 570.206. Found 570.207.

***N*-(4-Methylphenylsulfonyl)-6-Methyl-3-vinyl-1-aza-bicyclo[3.3.1]-nonan-9-one 30.** At -60°C, in an oven-dried, three-necked, 50 mL flask, wrapped with aluminum foil, equipped with a thermometer, a magnetic stirring bar and an argon inlet, silver trifluoromethanesulfonate (I) (100 mg, 0.389 mmol, 1.1 eq) was added to a solution of **29** (202 mg, 0.353 mmol, 1 eq) in dichloromethane. The temperature was slowly allowed to increase. After 30 minutes at 0°C, the mixture was filtered through a celite pad. The solvent was removed under reduced pressure. The product was purified by flash chromatography over silica gel (eluent hexanes/ethyl acetate 4/1) to give a white solid **30** (23 mg, 20%). M.p 165-168°C (hexanes). ^{1}H NMR (300 MHz, C_6D_6) δ 7.6 (2H, d, J = 8.2 Hz), 6.7 (2H, d, J = 8.2 Hz), 5.20-5.05 (1H, m), 4.73 (1H, d, J = 17.0 Hz), 4.68 (1H, d, J = 10.2 Hz), 3.98-3.94 (1H, m), 3.90-3.82 (1H, dd, J = 11.8, 5.45 Hz), 2.80-2.70 (1H, m), 2.58-2.48 (1H, m), 2.39-2.22 (1H, m), 2.18-2.11 (2H, m), 1.82 (3H, s), 1.48-1.40 (1H, m), 1.33-1.24 (1H, m), 1.19-1.09 (1H, td, J = 13.0, 4.0 Hz), 0.60 (3H, d, J = 6.5 Hz). ^{13}C NMR (75 MHz, APT, C_6D_6) δ 209.1 (e), 143.5 (e), 138.0 (o), 134.4 (e), 129.9 (o), 127.8 (o), 115.9 (e), 63.3 (o), 50.2 (o), 48.2 (e), 44.8 (e), 44.5 (o), 42.8 (e), 22.6 (o), 21.1 (o), 20.1 (o). CIMS (MH+) m/e 334, base 334 (100), 335 (7), 180 (7), 178 (6). HRMS (M+) m/e calcd for $C_{18}H_{23}NO_3S$ 333.140. Found 333.140.

(5*S*)-(+)-5-Isopropenyl-2-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 31. Synthesized in an analogous manner to **8** from (+)-dihydrocarvone (15 mL, 91.2 mmol, 1 eq). The crude product of the reaction was analyzed by ^{1}H NMR spectroscopy to determine a (88/12) ratio between the tetra- and trisubstituted isomers. The product is purified by flash chromatography over silica gel (eluent hexanes/ethyl acetate 4/1) to give a colorless oil **31** (24.10 g, 85%). bp 129-130 °C /0.6 mmHg. $[\alpha]^{25}_D$ = +59.2 (c = 1.75, $CHCl_3$). IR (film) 2943, 2866, 1688, 1645, 1464 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72 (2H, m), 2.30-1.91 (5H, m), 1.74 (3H, s), 1.80-1.70 (1H, m), 1.63 (3H, s), 1.45-1.06 (21H, m). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 149.4 (e), 142.7 (e), 110.2 (e), 108.7 (e), 42.6 (o), 35.7 (e), 30.4 (e), 27.9 (e), 20.8 (o), 18.1 (o), 16.2 (o), 13.2 (o). CIMS (MH+) m/e 309, base 309 (100), 308 (43), 265 (14), 173 (23), 157 (11), 153 (20), 151 (31). HRMS (M+) m/e calcd for $C_{19}H_{36}OSi$ 308.254. Found 308.254.

(5*S*)-(+)-5-Isopropyl-2-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 32. To a solution of **31** (24.10 g, 77.5 mmol) in ethyl acetate (80 mL) was added a catalytic amount of rhodium adsorbed on alumina. The suspension was stirred vigorously under an hydrogen atmosphere for 48 hours. The mixture was filtered through a celite pad and the solvent removed under reduced pressure to give a colorless oil **32** (23.91 g, 100%). No further purification is necessary. [a]$^{25}_D$ = +60.2 (c = 1.07, $CHCl_3$). IR (film) 2944, 2867, 1690, 1464 cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10-1.80 (4H, m), 1.76-1.64 (1H, m), 1.61 (3H, s), 1.55-1.40 (1H, sept., J = 6.6 Hz), 1.42-1.25 (2H, m), 1.18-1.05 (21H, m), 0.89 (3H, d, J = 6.6 Hz), 0.88 (3H, d, J = 6.6 Hz). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 143.1 (e), 110.3 (e), 41.8 (o), 34.2 (e), 32.3 (o), 30.6 (e), 26.5 (e), 20.1 (o), 19.7 (o), 18.1 (o), 16.2 (o), 13.2 (o). CIMS (MH+) m/e 311, base 311 (100), 310 (67), 267 (62), 169 (17), 153 (34), 151 (15). HRMS (M+) m/e calcd for $C_{19}H_{38}OSi$ 310.269. Found 310.269.

(+)-(5*R*,6*S*)-5-Isopropyl-6-(4-methylphenylsulfonyl)amino-2-methyl-1-triisopropyl sily(oxy)-cyclohex-1-ene 33. At 0°C, in a 500 mL flask, selenium powder (4.0 g, 50.66 mmol, 1 eq) and anhydrous chloramine-T (24.22 g, 106.4 mmol, 2.1 eq, dried over phosphorous pentoxide) were added to 100 mL of dichloromethane. The mixture was heated at reflux for three hours. The suspension was cooled to 25°C,

diluted with dichloromethane (50 mL), and stirred for 16 hours at 25°C. To this white suspension, at 0°C, was added the silyl enol ether **32** (15.73 g, 50.66 mmol, 1 eq) in dichloromethane (25 mL). The mixture was stirred for 6 hours at 0°C. The reaction mixture was quenched with a saturated solution of sodium bicarbonate (60 mL). After one hour of stirring, the mixture was filtered through a celite pad. The organic phase was separated, washed with aqueous solutions of sodium bicarbonate (100 mL), water (100 mL), sodium chloride (2 x 100 mL) and dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure. Hexane (150 mL) was added to the residue. The crude mixture was filtered, separating the insoluble *p*-toluenesulfonamide. The solvent was removed under reduced pressure to give an oil (24.92 g) which contains a (2:1) mixture of α- and β-amino isomers **33/34** respectively. The α-amino isomer was recrystallized several times from hexane to give 4.0 g of **33**. The crude mixture was purified by flash chromatography over silica gel (hexanes/ethyl acetate 4/1) and recrystallized again to give **33** (2.46 g). The α-amino product **33** is thus obtained as a white solid (6.46 g, 27%). M.p 131°C (hexane). $[\alpha]^{25}_{D}$ = +69.6 (c = 1.96, $CHCl_3$). IR (film) 3281, 2947, 2868, 1683, 1464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (2H, d, J = 8.1 Hz), 7.20 (2H, d, J = 8.1 Hz), 4.47 (1H, d, J = 8.3 Hz), 4.09 (1H, d, J = 8.0 Hz, br), 2.38 (3H, s), 2.00-1.92 (2H, m), 1.78-1.70 (1H, m), 1.53 (3H, s), 1.40-0.95 (24H, m), 0.93 (3H, d, J = 6.4 Hz), 0.77 (3H, d, J = 6.4 Hz). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 144.5 (e), 142.2 (e), 140.0 (e), 129.0 (o), 126.5 (o), 114.2 (e), 55.7 (o), 47.5 (o), 29.8 (e), 27.7 (o), 21.3 (o), 21.3 (o), 20.4 (o), 20.3 (e), 18.0 (o), 17.9 (o), 16.9 (o), 13.4 (o). CIMS (MH+) m/e 480, base 309 (100), 464, 436. HRMS (M+) m/e calcd for $C_{26}H_{45}NO_3SiS$ 479.289. Found 479.289.

***E*-(5*R*,6*S*,)-5-Isopropyl-6-[*N*,*N'*-(4-methylphenylsulfonyl)-(4-bromo-2-butene)] amino-2-methyl-1-triisopropylsilyl(oxy)-cyclohex-1-ene 35**. At 0°C, in a three-necked, round-bottomed 100 mL flask, equipped with a thermometer, a magnetic stirring bar and an argon inlet, sodium hydride (510 mg, 16.8 mmol, 1.25 eq, 80% suspension in mineral oil) and *E*-1,4-dibromo-2-butene (3.17 g, 14.81 mmol, 1.10 eq) were added to a solution of **33** (6.46 g, 13.46 mmol, 1 eq) in anhydrous DMF (70 mL). After 30 minutes of stirring at 25°C, the reaction was quenched with a saturated solution of ammonium chloride and the phases were separated. Ether (100 mL) was added to the organic phase, which was washed with aqueous solutions of sodium chloride (2 x 60 mL). The aqueous phase was extracted several times with ether. The organic phases were combined and dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The product was purified by flash chromatography over silica gel (hexanes/ethyl acetate 4/1) to give a colorless oil **35** (7.23 g, 88%). ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 142.7 (e), 141.0 (e), 138.2 (e), 133.7 (o), 129.1 (o), 128.1 (o), 126.4 (o), 117.7 (e), 56.5 (o), 47.7 (o), 47.0 (e), 32.1 (e), 30.0 (e), 27.7 (o), 22.8 (o), 21.4 (o), 20.0 (o), 19.9 (e), 18.1 (o), 18.0 (o), 17.3 (o), 13.8 (o). CIMS (MH+) m/e 613 (5), base 309 (100), 570 (5), 532 (21), 480 (5), 436 (8), 349 (12), 335 (16), 281 (27), 265 (30), 227 (11), 175 (71). HRMS (M+) m/e calcd for $C_{30}H_{50}NO_3SiSBr$ 613.244. Found 613.246.

(+)-(3*R*,4*S*,7*R*,)-7-Isopropyl-4-methyl-1-(4-methylphenylsulfonyl)-3-vinyl-1-azabicyclo [3.3.1]-nonan-9-one 36. At 25°C, in a round-bottomed 100 mL flask, wrapped with aluminum foil, silver trifluoromethanesulfonate (3.34 g, 12.99 mmol, 1.1 eq) was added to a solution of **35** (7.235 g, 11.81 mmol, 1 eq) in nitromethane (20 mL). After 30 minutes of stirring, the mixture was filtered through a celite pad. Ether and an aqueous solution of sodium chloride were added to the crude reaction mixture.

The phases were separated and the aqueous phase was extracted several times with ether. The organic phases were combined and dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give an oil. The product was purified by flash chromatography over silica gel (hexanes/ethyl acetate 4/1) to give a white solid **36** (2.261 g, 51%). M.p 107°C (hexane). $[\alpha]^{25}_D$ = + 38 (c = 2.68, dichloromethane). IR ($CHCl_3$) 3019, 2960, 2932, 2872, 1721, 1598, 1493 cm^{-1}. ^1H NMR (300 MHz, C_6D_6) δ 7.73 (2H, d, J = 8.2 Hz), 6.76 (2H, d, J = 8.2 Hz), 5.35-8.18 (1H, m), 4.86 (1H, dd, J = 10.3, 1.3 Hz), 4.73 (1H, d, J = 2.6 Hz), 4.66 (1H, d, J = 17 Hz), 3.73 (1H, dd, J = 15.7, 7.25 Hz), 3.48 (1H, dd, J = 15.7, 12.5 Hz), 1.88-1.67 (2H, m), 1.82 (3H, s), 1.66 (1H, dd, J = 13.9, 4.95 Hz), 1.42-1.20 (3H, m), 1.13 (3H, d, J = 6.5 Hz), 1.25-0.95 (1H, m), 0.78 (3H, d, J = 6.8 Hz), 0.68 (3H, s). ^{13}C NMR (75 MHz, APT, C_6D_6) δ 210.6 (e), 143.3 (e), 137.8 (e), 133.3 (o), 129.8 (o), 127.9 (o), 119.1 (e), 62.1 (o), 52.0 (o), 50.6 (o), 47.2 (e), 47.0 (e), 35.3 (e), 29.5 (o), 25.5 (e), 21.0 (o), 21.0 (o), 20.9 (o), 20.6 (o). CIMS (MH^+) m/e 376, base 376 (100), 361 (23), 360 (97), 347 (100), 336 (26), 292 (32), 263 (72), 262 (100), 249 (21), 222 (71). HRMS (M^+) m/e calcd for $C_{21}H_{29}NO_3S$ 375.187. Found 375.187. Anal calcd for $C_{21}H_{29}NO_3S$ C, 67.17.; H, 7.78.; N, 3.73. Found C, 67.09.; H, 7.74.; N, 3.37%.

2-Triisopropylsilyl(oxy)-3,4-dihydronaphthalene 37. B.p. 152°C at 0.5mm. IR (film) 1640, 1580 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 6.81-6.75 (2H, m), 6.70 (1H, d, J = 6.3 Hz), 6.60 (1H, d, J = 6.3 Hz), 5.56 (1H, s), 3.09 (2H, t, J = 7.2 Hz), 2.66 (2H, t, J = 7.2 Hz), 1.70-1.56 (3H, m), 1.56-1.46 (18H,m). HRMS (M^+) calcd for $C_{19}H_{30}OSi$ 302.206. Found 302.206.

2-Triisopropylsilyl(oxy)-3-(4-methylphenylsulfonyl)amino-3,4-dihydro naphthalene 38. Selenium powder (398 mg, 5.02 mmol) and anhydrous chloramine-T (2.40 g, 10.55 mmol) were stirred in CH_2Cl_2 (25 mL) at room temperature under argon for 2 days. The silyl enol ether **37** (1.65 g, 5.49 mmol) in dry CH_2Cl_2 (5 mL) was added at 0°C. After 40 h, NaOH (50 mL, 0.1M) was added and the mixture was stirred for 30 min, filtered through celite and washed with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (100 g) eluting with hexane/ethyl acetate (5:1) to give the sulphonamide **38** (1.83 g, 71%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 93-94°C. IR ($CHCl_3$) 3685, 3615, 1520 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.71 (2H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.2 Hz), 7.13-7.07 (2H, m), 7.00 (1H, d, J = 7.4 Hz), 6.88 (1H, d, J = 7.4 Hz), 5.66 (1H, s), 4.78 (1H, d, J = 6.7 Hz), 3.90 (1H, q, J = 6.0 Hz), 3.09 (1H, dd, J = 16.0, 5.7 Hz), 2.96 (1H, dd, J = 16.0, 5.7 Hz), 2.38 (3H, s), 1.19-0.97 (21H, m). ^{13}C NMR (75MHz, $CDCl_3$) δ 151.73, 143.26, 137.66, 133.71, 129.57, 128.90, 128.33, 127.10, 127.02, 125.55, 124.94, 106.36, 52.55, 36.66, 21.45, 17.86, 12.50. HRMS (EI) calcd for $C_{26}H_{37}NO_3SSi$ 471.2263. Found 471.2278. Anal calcd for $C_{26}H_{37}NO_3SSi$, C, 66.20.; H, 7.91.; N, 2.97. Found C, 66.16.; H, 7.92.; N, 3.01%.

2-Triisopropylsilyl(oxy)-3-[*N,N'*-(4-methylphenylsulfonyl)-(2-bromoethyl)] amino-3,4-dihydro naphthalene 39. The sulphonamide **38** (1.90 g, 4.03 mmol) in dry THF (15 mL) was added to sodium hydride (369 mg, 12.3 mmol) suspended in THF (20 mL) under argon at room temperature. After 1 h, 1,2-dibromoethane (7.0 mL, 80.7 mmol) was added, and the mixture was heated under reflux for 20 h. Saturated aqueous sodium bicarbonate (120 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 80

mL). The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (200 g) eluting with hexane/ethyl acetate (10:1) to give the bromide **39** (1.96 g, 84%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 102-103°C. IR ($CHCl_3$) 1635, 1600, 1570 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.71 (2H, d, J = 8.2 Hz), 7.25 (2H, d, J = 8.2 Hz), 7.21-6.92 (4H, m), 5.93 (1H, s), 4.47 (1H, dd, J = 7.4, 2.4 Hz), 3.27-3.15 (4H, m), 3.02 (1H, dd, J = 17.1, 2.3 Hz), 2.74-2.68 (1H, m), 2.39 (3H, s), 1.15-0.93 (21H, m). HRMS (EI) calcd for $C_{28}H_{40}BrNO_3SSi$ 577.168. Found 577.167.

2-Triisopropylsilyl(oxy)-3-[*N*,*N'*-(4-methylphenylsulfonyl)-(2-phenylthioethyl)] amino-3,4-dihydro naphthalene 40. Thiophenol (1.6 mL 15.6 mmol) was added to sodium hydride (280 mg, 9.34 mmol) suspended in THF (20 mL) under argon at room temperature. After 30 min. the bromide **39** (1.80 g, 3.11 mmol) in THF (30 mL) was added, and the mixture was heated under reflux for 1 h. Saturated aqueous sodium bicarbonate (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (170 g) eluting with hexane/ethyl acetate (10:1) to give the sulphide **40** (1.83 g, 97%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 95-96°C. IR ($CHCl_3$) 1635, 1595, 1570 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.65 (2H, d, J = 8.3 Hz), 7.21-7.00 (10H, m), 6.83 (1H, d, J = 7.3 Hz), 5.82 (1H, s), 4.52 (1H, dd, J = 7.7, 2.2 Hz), 3.20 (1H, dd, J = 17.3, 7.7 Hz), 3.08-2.89 (4H, m), 2.48-2.35 (1H, m), 2.36 (3H, s), 1.17-0.96 (21H, m). HRMS (EI) calcd for $C_{34}H_{45}NO_3S_2Si$ 607.261. Found 607.257.

***N*-(4-methylphenylsulfonyl)-5,6-benzo-3β-phenylthio-1-aza-bicyclo[3.3.1]-nonan-9-one 44**. *m*-Chloroperoxybenzoic acid (525 mg, 2.58 mmol) in CH_2Cl_2 (12 mL) was added to the sulphide **40** (1.50 g, 2.47 mmol) in CH_2Cl_2 (75 mL) under argon at -78°C. After 20 min. saturated aqueous sodium sulfite (200 mL) and saturated aqueous sodium bicarbonate (100 mL) were added, and the mixture was extracted with CH_2Cl_2 (3 x 100 mL). The combined extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography on silica gel (150 g) eluting with hexane/ethyl acetate (4:1) to give the sulphoxides **41** (1.47 g, 95%). Trifluoroacetic anhydride (54 µl, 0.38 mmol) was added to the sulphoxides (119 mg, 0.19 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (47µl, 0.21 mmol) in CH_2Cl_2 (3.5 ml) under argon at 0°C. After 10 min. the mixture was allowed to warm to room temperature. After 20 min. chlorobenzene (3.5 mL) was added and the mixture was heated to 130°C. After 45 min. the solvent was evaporated under reduced pressure and the residue was purified by column chromatography over silica gel (17 g) eluting with hexane/ethyl acetate (5:1) to give the benzomorphanone **44** (43 mg, 50%) as needles after recrystallization from CH_2Cl_2/hexane. M.p. 140-141°C. IR ($CHCl_3$) 1740, 1595, 1580 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.73 (2H, d, J = 8.2 Hz), 7.33-7.04 (10H, m), 6.79 (1H, d, J = 7.1 Hz), 4.51 (1H, d, J = 6.1 Hz), 3.59-3.39 (6H, m), 2.40 (3H, s). ^{13}C NMR (75MHz, $CDCl_3$) δ 202.50, 143.99, 136.27, 135.88, 134.07, 133.30, 132.56, 129.73, 129.32, 128.54, 128.25, 128.15, 128.04, 127.72, 127.46, 59.39, 53.70, 53.48, 41.52, 37.87, 21.61. HRMS (EI) calcd for $C_{25}H_{23}NO_3S_2$ 449.112. Found 449.113. Anal calcd for $C_{25}H_{23}NO_3S_2$, C, 66.79.; H, 5.16.; N, 3.12. Found C, 66.77.; H, 5.23.; N, 3.11%.

***N*-Methyl-5,6-benzo-1-aza-bicyclo[3.3.1]-nonan-9-one 45**. Sodium metal (250 mg) was added to the sulphonamide **44** (147 mg) in THF (3 mL) and liquid ammonia (5 mL) at -78°C under argon. After

30 min. methyl iodide (0.5 mL) was added to quench the reaction. The ammonia was allowed to evaporate, and saturated aqueous sodium bicarbonate (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (3 g) eluting with hexane/ethyl acetate/10% ammonium hydroxide in ethanol (2:2:1) to give the benzomorphanone **45** (39 mg, 60%) as an oil. IR (film) 1730 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.18-7.07 (3H, m), 6.96-6.90 (1H, m), 3.52 (1H, d, J = 18.3 Hz), 3.48 (1H, bs), 3.25 (1H, d, J = 6.3 Hz), 3.09 (1H, dd, J = 18.3, 6.3 Hz), 2.80-2.71 (1H, m), 2.53-2.33 (2H, m), 2.42 (3H, s), 1.84-1.78 (1H, m). ^{13}C NMR (75MHz, $CDCl_3$) δ 210.76, 137.72, 135.20, 128.30, 127.08, 127.02, 126.90, 66.46, 50.20, 44.28, 41.91, 35.63, 31.74. HRMS (EI) calcd for $C_{13}H_{15}NO$ 201.115. Found 201.114.

1-Allyl-2-triisopropylsilyl(oxy)-3,4-dihydronaphthalene 46. Potassium hexamethyldisilazide (20 mL, 27.4 mmol) was added to 1-allyl-β-tetralone (4.64 g, 24.95 mmol) in THF (120 mL) under argon at 0°C. After 30 min triisopropylsilyl chloride (6.1 mL, 28.7 mmol) was added. After 1 h, the mixture was poured onto brine (150 mL) and was extracted with ether (3 x 100 mL). The combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (140 g) eluting with hexane to give the silyl enol ether **46** (8.3 g, 97%) as an oil. IR (film) 1635, 1600, 1570 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.26-6.92 (4H, m), 5.90-5.77 (1H, m), 5.03 (1H, dd, J = 17.2, 1.8 Hz), 3.28 (2H, d, J = 5.6 Hz), 2.82 (2H, t, J = 7.9 Hz), 2.40 (2H, t, J = 7.9 Hz), 1.28-0.96 (21H, m). ^{13}C NMR (75MHz, $CDCl_3$) δ 150.38, 136.71, 132.76, 126.70, 126.29, 124.14, 122.43, 114.74, 112.47, 29.43, 29.37, 29.23, 18.06, 13.36. HRMS (CI) calcd for $C_{22}H_{34}OSi$ 342.238. Found 342.238.

1-Allyl-2-triisopropylsilyl(oxy)-3-(4-methylphenylsulfonyl)amino-3,4-dihydro naphthalene 47. Selenium powder (1.83 g, 23.11 mmol) and anhydrous chloramine-T (10.78 g, 47.38 mmol) were stirred in CH_2Cl_2 (100 mL) at room temperature under argon for 6 days. The silyl enol ether **46** (8.3 g, 24.27 mmol) in dry CH_2Cl_2 (40 mL) was added. After 2 h, NaOH (250 mL, 0.1M) was added and the mixture was stirred for 90 min. then was filtered through celite and was washed with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (350 g) eluting with hexane/ethyl acetate (10:1) to give the sulphonamide **47** (7.34 g, 59%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 83-84°C. IR ($CHCl_3$) 3305, 3260, 1630, 1600, 1355, 1155 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.60 (2H, d, J = 8.2 Hz), 7.23 (2H, d, J = 8.2 Hz), 7.17-7.10 (2H, m), 6.92 (1H, td, J = 7.1, 1.7 Hz), 6.52 (1H, d, J = 7.4 Hz), 5.82-5.71 (1H, m), 5.03-4.95 (2H, m), 4.42 (1H, d, J = 8.2 Hz), 4.08-4.03 (1H, m), 3.28 (1H, dd, J = 15.8, 5.4 Hz), 3.18 (1H, dd, J = 15.8, 6.1 Hz), 2.79 (1H, dd, J = 16.0, 6.1 Hz), 2.65 (1H, dd, J = 16.0, 3.9 Hz), 2.41 (3H, s), 1.27-1.00 (21H, m). ^{13}C NMR (75MHz, $CDCl_3$) δ 148.19, 143.25, 139.09, 135.56, 134.64, 129.58, 128.79, 128.47, 126.94, 125.29, 123.22, 116.44, 115.64, 53.18, 35.01, 29.54, 21.54, 18.08, 13.44. HRMS (CI) calcd for $C_{29}H_{41}NO_3SSi$ 511.258. Found 511.258. Anal calcd for $C_{29}H_{41}NO_3SSi$, C, 68.06.; H, 8.08.; N, 2.74. Found C, 68.03.; H, 8.01.; N, 2.73%.

1-Allyl-2-triisopropylsilyl(oxy)-3-[*N,N'*-(4-methylphenylsulfonyl)-(2-bromoethyl)] amino-3,4-dihydro naphthalene 48. The sulphonamide **48** (5.90 g, 11.5 mmol) in dry THF (40 mL) was added to sodium hydride (1.38 g, 46.2 mmol) suspended in THF (60 mL) under argon at room temperature.

After 1 h, 1,2-dibromoethane (14.9 mL, 173 mmol) was added and the mixture was heated under reflux for 20 h. Saturated aqueous sodium bicarbonate (300 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 150 mL). The combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (400 g) eluting with hexane/ethyl acetate (15:1) to give the bromide **48** (6.18 g, 87%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 110-111°C. IR (film) 1620, 1600, 1570 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.70 (2H, d, J = 8.2 Hz), 7.29 (2H, d, J = 8.2 Hz), 7.24 (1H, d, J = 7.7 Hz), 7.13 (1H, t, J = 7.6 Hz), 6.96 (1H, td, J = 7.4, 1.0 Hz), 6.67 (1H, d, J = 7.4 Hz), 5.89-5.76 (1H, m), 5.12 (1H, dd, J = 16.9, 1.6 Hz), 5.07 (1H, dd, J = 9.6, 1.6 Hz), 4.63 (1H, d, J = 5.0 Hz), 3.50-3.42 (1H, m), 3.27-3.07 (4H, m), 3.01-2.78 (3H, m), 2.42 (3H, s), 1.34-1.19 (3H, m), 1.13-1.07 (18H, m). ^{13}C NMR (75MHz, $CDCl_3$) δ 145.37, 143.57, 138.05, 135.44, 134.38, 129.80, 127.35, 127.24, 127.09, 126.02, 123.53, 121.03, 116.55, 55.34, 46.81, 34.93, 30.32, 29.65, 21.56, 18.14, 13.65. HRMS (CI) calcd for $C_{31}H_{44}BrNO_3SSi$ 619.197. Found 619.199.

1-Allyl-2-triisopropylsilyl(oxy)-3-[*N,N'*-(4-methylphenylsulfonyl)-(2-phenylthio ethyl)]amino-3,4-dihydro naphthalene 49. Thiophenol (5.0 mL, 48.5 mmol) was added to sodium hydride (890 mg, 29.5 mmol) suspended in THF (80 mL) under argon at room temperature. After 1 h the bromide **48** (6.04 g, 9.7 mmol) in THF (40 mL) was added and the mixture was heated under reflux for 3 h. Saturated aqueous sodium bicarbonate (200 mL) was added and the mixture was extracted with CH_2Cl_2 (4 x 100 mL). The combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (300 g) eluting with hexane/ethyl acetate (15:1) to give the sulphide **49** (5.47 g, 86%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 94-95°C. IR ($CHCl_3$) 1625, 1600, 1580, 1570 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.58 (2H, d, J = 8.2 Hz), 7.21-7.08 (9H, m), 6.93 (1H, td, J = 7.2, 1.2 Hz), 6.66 (1H, d, J = 7.2 Hz), 5.80-5.71 (1H, m), 5.06 (1H, dd, J = 15.7, 1.5 Hz), 5.02 (1H, dd J = 10.3, 1.5 Hz), 4.67 (1H, d, J = 5.4 Hz), 3.28-3.24 (2H, m), 3.08-2.65 (6H, m), 2.38 (3H, s), 1.36-1.08 (21H, m). HRMS (EI) calcd for $C_{37}H_{49}NO_3S_2Si$ 647.292. Found 647.292.

***N*-(4-methylphenylsulfonyl)-4-allyl-5,6-benzo-3β-phenylthio-1-aza-bicyclo[3.3.1]-nonan-9-one 53β**. *m*-Chloroperoxybenzoic acid (1.69 g, 8.35 mmol) in CH_2Cl_2 (50 mL) was added to the sulphide **49** (5.30 g, 8.19 mmol) in CH_2Cl_2 (200 mL) under argon at -78°C. After 20 min. sodium sulfite (250 mL) and saturated aqueous sodium bicarbonate (200 mL) were added and the mixture was extracted with CH_2Cl_2 (3 x 150 mL). The combined extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography on silica gel (300 g) eluting with hexane/ethyl acetate (5:1) to give the sulphoxides **50** (5.40 g, 99%). Trifluoroacetic anhydride (4.5 mL, 32 mmol) was added to the sulphoxides **50** (5.3 g, 8.0 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (3.26 g, 16.0 mmol) in CH_2Cl_2 (100 mL) under argon at 4°C. After 10 min the mixture was allowed to warm to room temperature. After 45 min chlorobenzene (75 mL) was added and the mixture was heated to 130°C. After 40 min the solvent was evaporated under reduced pressure and the residue was purified by column chromatography over silica gel (300 g) eluting with hexane/ethyl acetate (5:1) to give the benzomorphanones **53α** and **53β** (3.1 g, 79%) as a 1.7:1 mixture of diastereomers, both as needles after recrystallization from CH_2Cl_2/hexane. *Less polar (minor) product.* M.p. 148-149°C. IR ($CHCl_3$) 1730, 1600 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.37 (2H, d, J = 8.2 Hz), 7.30-7.09 (8H, m), 7.14 (2H, d, J = 8.2 Hz), 6.89 (1H, s), 5.34-5.24 (1H, m), 5.13 (1H, dd, J = 16.8, 1.5 Hz), 4.89 (1H, d, J = 10.0 Hz), 4.65 (1H, d, J

= 6.6 Hz), 3.82 (1H, dd, J = 15.0, 4.9 Hz), 3.59 (1H, dd, J = 18.4, 6.7 Hz), 3.45-3.29 (2H, m), 2.91-2.78 (3H, m), 2.40 (3H, s).HRMS (EI) calcd for $C_{28}H_{27}NO_3S_2$ 489.143. Found 489.141. Anal calcd for $C_{28}H_{27}NO_3S_2$, C, 68.68.; H, 5.56.; N, 2.86. Found: C, 68.52.; H, 5.63.; N, 2.81%.

More polar (major) product. M.p. 153-154°C. IR ($CHCl_3$) 1735, 1600 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.69 (2H, d, J = 8.3 Hz), 7.22-7.01 (11H, m), 5.49-5.35 (1H, m), 5.03 (1H, d, J = 17.0 Hz), 4.89 (1H, d, J = 10.2 Hz), 4.56 (1H, br s), 3.53-3.27 (6H, m), 2.49 (1H, dd, J = 15.2, 8.2 Hz), 2.39 (3H, s). ^{13}C NMR (75MHz, $CDCl_3$) δ 203.65, 143.81, 138.00, 136.57, 134.67, 134.46, 133.81, 132.58, 129.60, 129.22, 128.48, 127.77, 127.50, 127.42, 118.04, 60.85, 59.92, 55.65, 44.51, 38.36, 35.80, 21.59. HRMS (EI) calcd for $C_{28}H_{27}NO_3S_2$ 489.143. Found 489.144.

***N*-Methyl-4-allyl-5,6-benzo-1-aza-bicyclo[3.3.1]-nonan-9-one 54**. Sodium metal (4 g) was added to the sulphonamides **53**α/β (2.9 g) in THF (50 mL) and liquid ammonia (100 mL) at -78°C under argon. After 3 h, methyl iodide (20 mL) was added to quench the reaction. The ammonia was allowed to evaporate and saturated aqueous sodium bicarbonate (200 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 120 mL) and the combined organic extracts were dried (Na_2SO_4), evaporated, and purified by column chromatography over silica gel (60 g) eluting with hexane/ethyl acetate (2:1) to give the benzomorphanone (818 mg, 57%) as cubes after recrystallization from CH_2Cl_2/hexane. M.p. 76-77°C.IR (film) 1730, 1635 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.19-7.09 (4H, m), 5.78-5.70 (1H, m), 5.08 (1H, dd, J = 17.1, 1.5 Hz), 4.97 (1H, d, J = 10.0 Hz), 3.48 (1H, d, J = 18.2 Hz), 3.32 (1H, d, J = 6.0 Hz), 3.11 (1H, dd, J = 18.2, 5.9 Hz), 2.85 (1H, dd, J = 14.8, 6.0 Hz), 2.65-2.57 (2H, m), 2.51-2.44 (1H, m), 2.42 (3H, s), 2.26 (1H, td, J = 12.8, 4.7 Hz), 1.60 (1H, d, J = 13.0 Hz). ^{13}C NMR (75MHz, $CDCl_3$) δ 210.76, 139.57, 135.66, 135.04, 127.34, 126.89, 126.75, 126.32, 117.51, 66.57, 51.46, 46.22, 42.04, 41.71, 37.35, 32.22, 29.69. HRMS (EI) calcd for $C_{16}H_{19}NO$ 241.147. Found 241.147. Anal calcd for $C_{16}H_{19}NO$, C, 79.63.; H, 7.94.; N, 5.80. Found: C, 79.70.; H, 7.97.; N, 5.86%.

Acknowledgements. The National Science Foundation, the National Institutes of Health (GM 32718) and the Robert A. Welch Foundation are thanked for their support of this research. Rhône Poulenc are thanked for a graduate fellowship to Jérôme Lacour. Drs. B. Mugrage and W. B. Bauta thank the National Institutes of Health for the award of post doctoral fellowships. The Fulbright Commission is thanked for a travel award to Dr. I. Coldham. Dr. Vince Lynch (Austin) and Dr. John C. Huffman (Molecular Structure Center, Indiana University, Bloomington, Indiana 47405) are gratefully thanked for X-ray structural determinations.

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(*Received in USA* 7 *July* 1995; *accepted* 23 *August* 1995)