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CONJUGATE ADDITION OF AMINES TO (Rs)-10-ISOBORNYL VINYL SULFOXIDES†

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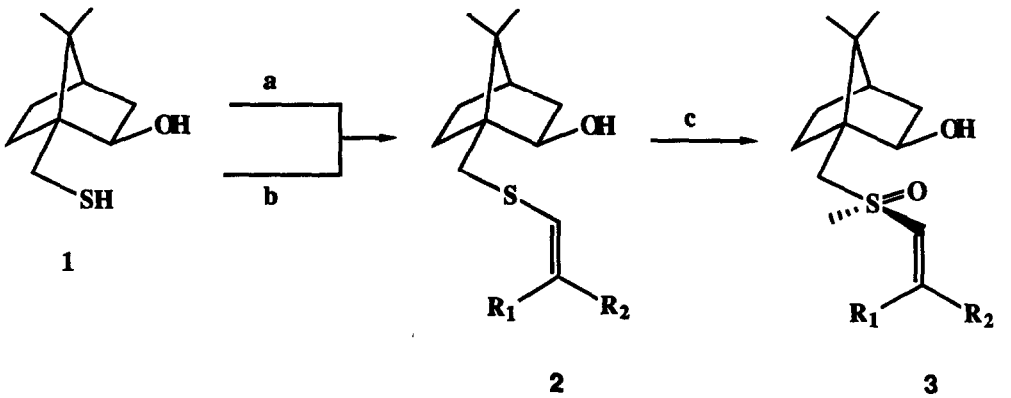
Abstract: Chiral (**E**) and (**Z**) (**Rs**)10-Isobornyl vinyl sulfoxides have been prepared; the (**Z**) isomers undergo highly diastereoselective conjugate addition with benzylamine whereas the (**E**) isomers show poor product diastereoselection.

Chiral β-amino sulfoxides are useful compounds for asymmetric synthesis.[1-9] These compounds can be conveniently prepared by either conjugate addition of amines to chiral vinyl sulfoxides[1,3-7] or addition of the α-carbanion of a chiral sulfoxide to an imine.[2,8,9] The former method generally suffers from modest diastereoselection while the generality of the latter process has not been demonstrated.[8,9] De Lucchi[10] has recently described the use of chiral (**Rs**)-10-isobornyl vinyl sulfoxides as useful dienophiles for asymmetric Diels-Alder reactions.[11] These substrates have three major advantages over the traditional chiral p-tolyl vinyl sulfoxides:[12] (i) they are readily prepared in optically pure form without resort to classical resolution techniques since the isoborneol moiety enables the diastereoselective oxidation of sulfur; (ii) either (**E**) or (**Z**) vinyl sulfoxides can be selectively prepared; (iii) their Diels-Alder reactions are generally highly diastereoselective because of their conformational rigidity due to intramolecular hydrogen bonding.

This paper describes the stereoselective synthesis of the (**E**) and (**Z**) chiral vinyl sulfoxides **3a**, **3b**, **7a**, and **7b** and their conjugate addition reactions with benzylamine. The chiral (**E**) and (**Z**) β-styryl sulfoxides **2a** and **2b** were prepared in a stereoselective manner from the reaction of 10-mercaptoisoborneol **1**[10,13] with (**E**) β-bromostyrene[15] and phenylacetylene[16] respectively according to Scheme I. Stereoselective oxidation (d.e. *ca* 90:10) of **2a** and **2b** with *m*-chloroperbenzoic acid (m-CPBA) in dichloromethane[10] gave **3a** and **3b** respectively,which could be obtained diastereomerically pure after simple column chromatography. The stereochemistry at sulfur in **3a,b** was assumed to be (**R**) from previous work.[10] The known vinyl sulfides **4A** and **4B**[10] were converted to the vinyl sulfoxides **7a** and **7b** respectively (Scheme II), by first lithium aluminium hydride reduction of the ester moiety of

Scheme I

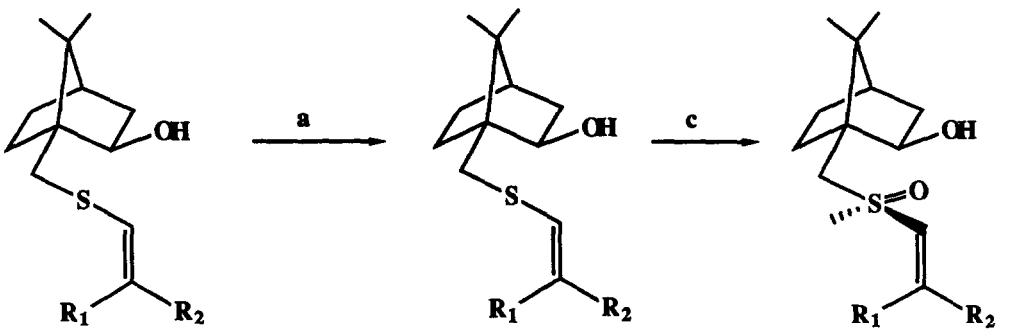


1 2 3

a $R_1 = H, R_2 = Ph$
b $R_1 = Ph, R_2 = H$

Reagents; [a] (E) PhCH=CHBr, NaH, HMPA; [b] PhC≡CH, n-heptane; [c] m-CPBA, CH_2Cl_2.

Scheme II



4A R_1=H, R_2=COOEt
4B R_1=COOEt, R_2=H

b → **5A** R_1=H, R_2=CH_2OH → **6a**

b → **5B** R_1=CH_2OH, R_2=H → **6b**

7a
7b

a $R_1 = H, R_2 = CH_2OSi^tBuMe_2$
b $R_1 = CH_2OSi^tBu, R_2 = H$

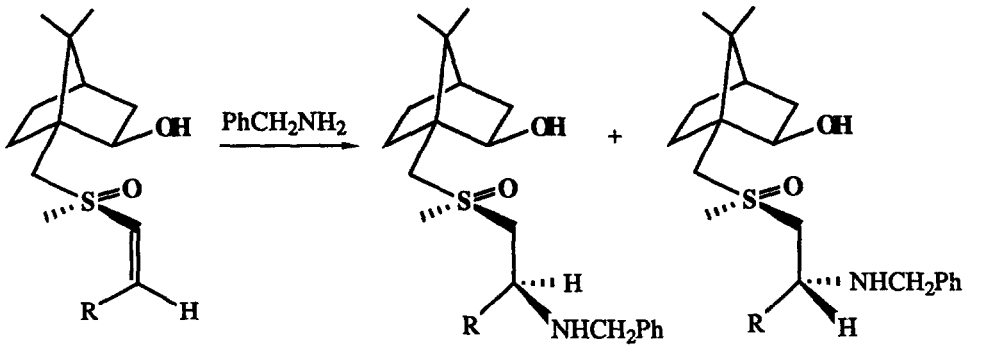
Reagents; [a] $LiAlH_4$, ether; [b] t-$BuMe_2SiCl$, Et_3N, DMAP; [c] m-CPBA, CH_2Cl_2.

4A(4B) to **5A(5B)** and then selective protection of the primary alcohol group of **5A(5B)** with tert-butyldimethylsilylchloride to give **6a(6b)**. Finally, oxidation of **6a(6b)** with m-CPBA and then column chromatography gave diastereomerically pure **7a(7b)**.

The diastereoselectivity of the reactions of vinyl sulfoxides **3a,3b,7a** and **7b** with benzylamine under a variety of conditions is summarized in **Table 1**. The (**Z**) vinyl sulfoxides **3b** and **7b** underwent highly diastereoselective addition of benzylamine giving a mixture of diastereomeric adducts **8** and **9** (diastereoselection, **8:9**, 91-93: 9-7) while their (**E**) counterparts showed very poor product diastereoselection and were less reactive. Not unexpectedly the β-styryl sulfoxides **3a** and **3b** were much less susceptible to conjugate addition than their less conjugated counterparts **7a** and **7b**.[6] For example the reaction of **3b** with benzylamine in ethanol required heating at 105° for 10 days in a sealed tube for complete conversion of the vinyl sulfoxide, whereas the analogous reaction of **7b** required 8 days at 30°. The reaction solvent had only a modest effect on the diastereoselection of these reactions. Similar trends have been observed in the analogous reactions of (**E**) and (**Z**) p-tolyl vinyl sulfoxides,[6] however both (**E**) and (**Z**) isomers give the same diastereomeric adduct with a similar diastereoselection (d.e., 86:14) under kinetically controlled conditions.

The stereochemical outcome of the conjugate addition reaction of **3a** was determined by reductive desulfuration of a 94:6 mixture of **8a** and **9a** over Raney Nickel to give (R)-(+)-N-benzyl-l-phenylethylamine ($[\alpha]_D^{20}$ +47.4° (c 0.12,EtOH); lit.[13] $[\alpha]_D^{20}$ +56.2° (c 1.071, EtOH). While we have been unsuccessful in the reductive desulfurization of **8b**, the relative stereochemistry of this compound was based on a comparison of the ^{1}H NMR specta of **8b** with those of **8a** and **9a**.

Interestingly the (**E**) and (**Z**) isoborneol vinyl sulfoxides described by De Lucchi[10] undergo Diels-Alder reactions with similar diastereoselectivities as the conjugate addition reactions of **3** and **7** with benzylamine, however in the opposite stereochemical sense. We have recently invoked nucleophilic attack of amine on the **s-cis** and **s-trans** conformations of (**R**) (**E**) and (**Z**) vinyl p-tolyl sulfoxides respectively to account for the stereochemical outcome of these reactions. Theoretical calculations on the addition of hydride to methyl vinyl sulfoxide suggest a reactive **s-cis** conformation.[17] If one assumes the sulfinyl group of **3b(7b)** is intramolecularly hydrogen bonded then the **s-trans** conformation **11** appears unlikely due to unfavourable steric interactions between the β-vinyl substituent and the C-10 hydrogens. Additions of amine to the **s-cis** conformation **10** from the least sterically demanding olefinic face gives the observed adduct **8**.



3b R = Ph **8a** R = Ph **9a** R = Ph

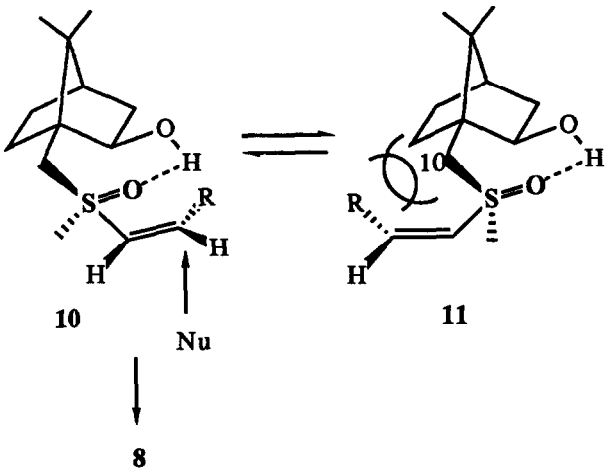
7b R = $CH_2OSi^tBuMe_2$ **8b** R = $CH_2OSi^tBuMe_2$ **9b** R = $CH_2OSi^tBuMe_2$

Table 1 Diastereoselective additions of benzylamine to vinyl sulfoxides **3** and **7**

Sulfoxide	Temp./Time (° C) /(days)	Solvent	Yield (%)[a]	Diastereoselection[c] 8 : 9
3 b	105/10	EtOH	47	91 : 9
3 b	85/7	EtOH	44[b]	92 : 8
3 a	105/12	EtOH	25[b]	43 : 57
7 b	80/2	EtOH	79	88 : 12
7 b	30/8	EtOH	95	93 : 7
7 b	80/7	benzene	95	89 : 11
7 a	80/3	EtOH	98[b]	40 : 60
7 a	80/7	benzene	32[b]	22 : 78
7 a	30/12	EtOH	98[b]	33 : 67

[a] Isolated yield after chromatography. [b] Conversion by ^1H NMR spectroscopic analysis. [c] Determined by ^1H NMR spectroscopic (400 MHz) analysis on crude reaction mixtures.

In conclusion (Z)-(Rs) 10-isobornyl vinyl sulfoxides undergo highly diastereoselective conjugate addition reactions with benzylamine and the stereochemical outcome of these reactions is readily rationalized assuming nucleophilic addition to a s-cis ground state conformation. Their isomeric (E) analogues however, show poor product diastereoseletion even when compared to their p-tolyl vinyl sulfoxide counterparts.



Experimental

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Jeol FX 90Q Fourier Transform NMR Spectrometer and on a Jeol JNM/GX400 Fourier Transform NMR Spectrometer. Each signal is described in terms of its chemical shift in p.p.m. from T.M.S. (internal standard). Multiplicity and coupling constants are then given. Abbreviations used to denote NMR spectral signals are: s, singlet; d, doublet; t, triplet; q, quartet; hept, heptet; br, broad; v, variable in position. All spectra were run in $CDCl_3$. Infrared spectra were recorded on a Perkin Elmer Infrared Spectrophotometer - Model 783 as thin films unless otherwise noted. Major absorptions are listed in wavenumbers (cm^{-1}). Mass Spectra were recorded on a Vacuum Generator V.G. 12-12 mass spectrometer in the chemical ionization mode with isobutane. High resolution mass spectra were recorded on a JEOL JMS-DX300 mass spectrometer at the Victorian College of Pharmacy. Elemental analyses were performed at the Australian National University Analytical Services Unit.

(E) - (1S, 2R, 4R) 7,7-dimethyl-1-[(2'-phenylethenyl) thio]methyl-bicyclo[2.2.1]heptan-2-ol. 2a

To a stirred suspension of 'oil free' sodium hydride (from 452 mg (9.41 mmol) of 50% NaH in oil) in dry hexamethylphosphoroustriamide (HMPA, 10 mL) at 0°C was added dropwise a solution of 10-mercaptoisoborneol **1** (1.73 g, 9.3 mmol) in HMPA (5 mL). After the evolution of hydrogen gas subsided β-bromostyrene (1.146 g, 6.26 mmol) was added and the mixture was stirred at room temperature for 1h. The reaction mixture was poured into water and extracted with ether (3X). The combined extracts were washed with water (5X), dried and evaporated giving an oil (2.06 g) of sufficient purity to be converted to the sulfoxide **3a**. A small quantity of **2a** could be obtained analytically pure by column chromatography on silica gel. ^{1}H NMR: 7.27 (m, 5H), 6.81 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 15.6 Hz, 1H), 3.91 (t, 1H), 3.14 (d, J = 11.7 Hz, 1H), 2.80 (d, J = 11.7 Hz, 1H), 2.2-1.2 (m, 7H), 1.11 (s, 3H), 0.897 (s, 3H); ^{13}C NMR: 137.06, 128.63, 127.22, 126.88, 125.76, 125.51, 76.85, 52.28, 47.89, 45.36, 39.70, 32.53, 31.17, 27.17, 20.69; MS: 288 (M^+), 271 (M-OH), 136, 135.

(Z) - (1S, 2R, 4R) 7,7-dimethyl-1-[(2'-phenylethenyl) thio]methyl-bicyclo[2.2.1] heptan-2-ol. 2b.

To a solution of phenylacetylene (1.86 g, 18 mmol) in n-heptane (1 mL) at 0° was added a solution of 10-mercaptoisoborneol (0.61 g, 3.3 mmol) in a n-heptane (5 mL). The reaction mixture was stirred at room temperature for 5 days. The solution was then concentrated by evaporation and the mixture was purified by column chromatography (EtOAc/hexane, 1:9). Pure **2b** (389 mg, 41%) was obtained as a colourless oil. ^{1}H NMR analysis of the crude reaction mixture showed *ca* 15% of the (E) isomer **2a**. ^{1}H NMR: d 7.6-7.2 (m, 5H), 6.46 (d, J = 11 Hz, 1H), 6.29 (d, J = 1 Hz, 1H), 3.95 (t, 1H), 3.16 (d, J = 11.8 Hz, 1H), 2.83 (d, J = 11.8 Hz, 1H), 1.9-1.2 (m, 7H), 1.09 (s, 3H), 0.88 (s, 3H).

(E) - (1S, 2R, 4R) 7,7-dimethyl-1-[(3'-hydroxy-1'-propenyl) thio]methyl-bicyclo[2.2.1] heptan-2-ol. 5A.

To a stirred suspension of lithium aluminium hydride (2.11 g, 55.6 mmol) in 80 mL of dry ether was added a solution of **4A** (3.00 g, 11.1 mmol) in 60 mL of dry ether at -78°C under nitrogen in small portions. The mixture was warmed to room temperature and stirred for 2-3h, or until TLC showed no starting material. Excess hydride was quenched cautiously with ethyl acetate. The resulting mixture was filtered through a pad of celite, dried and evaporated to yield 2.12 g (79%) of **5A** as an oil. Rf 0.20 (30% EtAc/hexane); ^{1}H NMR: 0.85 (s, 3H), 1.06 (s, 3H), 1.05-1.90 (m, 7H), 2.67 (d, J = 11.4 Hz, 1H), 3.01 (d, J = 11.4 Hz, 1H), 3.86 (m, 1H), 4.13 (d d, J = 5.9, 0.9 Hz, 2H), 5.73 (d t, J = 15.2, 5.9 Hz, 1H), 6.34 (d t, J = 15.2, 0.8 Hz, 1H); ^{13}C NMR: 19.96, 20.59, 26.07, 31.02, 31.85, 39.51, 45.21, 47.75, 51.94, 63.49, 76.71, 126.0, 127.7; MS: 242 (M^+, 54%), 227 (M-CH_3, 29%), 225 (M+H^+ - H_2O, 100%), 135 (44%).

(Z) - (1S, 2R, 4R) 7,7-dimethyl-1-[(3'-hydroxy-1'-propenyl) thio]methyl-bicyclo[2.2.1] heptan-2-ol. 5B.

Prepared as described above for the preparation of **5A**, yield (72-90%) as a colourless oil. Rf 0.23 (30% EtOAc/hexane); ^{1}H NMR: 6.21 (d t, J = 10.8, 1.1 Hz, 1H), 5.76 (d t J = 9.6, 6.2 Hz, 1H), 4.27 (d d, J = 6.3, 1.2 Hz, 2H), 3.89 (m, 1H), 3.07 (d, J = 12.8 Hz, 1H), 2.67 (d, J = 12.8 Hz, 1H), 0.90-1.90 (m, 7H), 1.05 (s, 1H), 0.84 (s, 1H); ^{13}C NMR: 19.95, 20.59, 26.98, 31.02, 34.34, 39.75, 45.41, 47.65, 52.62, 59.69, 76.71, 127.46, 128.73; MS: 242 (M^+, 46%), 227 (M-CH_3, 100%), 225 ($M+H^+ - H_2O$, 54%), 135 (44%).

(E) - (1S, 2R, 4R), 7,7-dimethyl-1-[(3'-tert-butyldimethylsiloxy-1'-propenyl) thio]methyl-bicyclo[2.2.1] heptan-2-ol. 6a.

To a stirred solution of tert-butyldimethylsilylchloride (9.72 mmol, 1.47 g), triethylamine (9.72 mmol, 1.34 mL) and 4-dimethylaminopyridine (3.53 mmol, 0.043 g) in 15 mL of dry CH_2Cl_2 was added a solution of the alcohol **5A** (2.12 g, 8.83 mmol) in 10 mL of dry CH_2Cl_2. The mixture was stirred for 2h at room temperature until TLC showed no starting material. The solution was then washed twice with water (10 mL), dried and evaporated to yield an oil (1.94 g, 62%). Rf 0.82 (30% EtOAc/hexane); ^{1}H NMR: 0.06 (s, 6H), 0.85 (s, 3H), 0.89 (s, 9H), 1.05 (s, 3H), 1.05-1.90 (m, 7H), 2.66 (d, J = 11.4 Hz, 1H), 2.98 (d, J = 11.4 Hz, 1H), 3.89 (m, 1H), 4.16 (d d, J = 5.8, 1.4 Hz, 2H), 5.65 (d t J = 15.2, 5.1 Hz, 1H), 6.25 (d t, J = 15.2, 0.8 Hz, 1H); MS: 341 (M - CH_3, 19%), 225 (M - OtBuMe$_2$Si, 31%), 209 (225 - H_2O, 40%), 135 (100%).

(Z) - (1S, 2R, 4R) 7,7-dimethyl-1-[(3'-tert-butyldimethyl siloxy-1'-propenyl) thio]methyl-bicyclo[2.2.1] heptan-2-ol. 6b.

Prepared as described above for the preparation of **6a**, yield 56%, Rf 0.88 (30% EtOAc/hexane); ^{1}H NMR: 0.08 (s, 6H), 0.84 (s, 3H), 0.90 (s, 9H), 1.05 (s, 3H), 1.05-1.90 (m, 7H), 2.67 (d, J = 12.5 Hz, 1H), 3.01 (d, J = 12.5 Hz, 1H), 3.88 (m, 1H), 4.26 (d d, J = 5.8, 1.5 Hz, 2H), 5.66 (d t, J = 9.6, 5.7 Hz, 1H), 6.05 (d t J = 9.5, 1.2 Hz, 1H); ^{13}C NMR: 18.59, 20.25, 20.88, 26.19, 27.32, 31.24, 34.63, 38.85, 45.60, 47.71, 52.47, 60.91, 77.29, 126.54, 129.02; MS: 341 (M - CH_3, 10%), 225 (M - OtBuMe$_2$Si, 52%), 207 (225 - H_2O), 135 (100%).

Preparation of Vinylsulfoxides 3 and 7. A General Procedure:

(E) - (1S, 2R, 4R, 5R) 7,7-dimethyl-1-[(3'-tertbutyldimethysiloxy-1'-propenyl) sulfinyl]methyl-bicyclo[2.2.1] heptan-2-ol. 7a.

To a stirred solution of the vinyl sulfide (1.94 g, 5.48 mmol) in 20 mL of dry CH_2Cl_2 at 0°C was added dropwise a solution of 85% m-CPBA (1.20 g) dissolved in 15 mL of dry CH_2Cl_2. The mixture was stirred overnight. The organic layer was washed with 5% sodium carbonate solution up to neutrality and then with brine. The organic

layer was dried and evaporated to dryness. Diastereomerically pure **7a** 1.70 g (86%) was obtained as an oil after column chromatography (silica gel,30% EtOAc/hexane). Rf = 0.39 (30% EtOAc/hexane), $[\alpha]_D^{20}$ -51.6° (c 0.39 , $CHCl_3$); ^1H NMR: 0.11 (s, 6H), 0.85 (s, 3H), 0.93 (s, 9H),1.09 (s, 3H), 1.15-1.90 (m, 7H), 2.43 (d, 13.1 Hz, 1H), 3.20 (d, 13.1 Hz, 1H), 3.91 (broad, 1H), 4.12, (m, 1H), 4.40 (s, 2H), 6.53 (d t, J = 14.7, 1.7 Hz), 6.59 (d t, J = 14.8, 2.5 Hz); ^{13}C NMR: 138.6, 131.2, 76.9, 62.2, 55.7, 51.4, 48.1, 45.0, 38.4, 30.8, 27.1, 25.8, 20.4, 19.8, 18.3, -5.5; MS: 373 $(M + H)^+$, 355 $(M - H_2O)^+$, 135 $(M - C_{10}H_{15})^+$; HRMS calcd for $C_{19}H_{37}O_3SSi$ 373.2233, found 373.2291.

(Z) **7b:** oil; yield 78%; Rf 0.43 (30% EtOAc/hexane); $[\alpha]_D^{20}$ + 60.3 (c 0.17 , $CHCl_3$); ^1H NMR: 1.10-1.80 (m, 7H), 0.04 (s, 6H), 0.76 (s, 3H), 0.84 (s, 9H), 1.04 (s, 3H), 2.26 (d, 13.1 Hz, 1H), 3.35 (d, 13.1 Hz, 1H), 4.00 (m, 1H), 4.39 (complex m, 2H), 3.97 (broad, 1H), 6.18 (d t J = 10.2, 5.3 Hz, 1H), 6.23 (d, J = 10.2 Hz, 1H); ^{13}C NMR: 140.0, 135.3, 76.9, 60.0, 55.1, 51.5, 48.2, 45.0, 38.4, 30.8, 27.1, 25.9, 20.4, 19.7, 18.3, -5.3; MS: 373 ($M + H)^+$.

(E) **3a:** oil; yield 70%, $[\alpha]_D^{23.5}$ -8.4° (c 1.31, $CHCl_3$); ^1H NMR: 7.4 (m, 5H), 7.28 (d, J = 15.6 Hz, 1H), 6.89 (d, J = 15.6 Hz, 1H), 4.15 (m, 1H), 3.34 (d, J = 13.2 Hz, 1H), 2.53 (d, J = 13.2 Hz, 1H), 1.71-1.1 (m, 7H), 1.11 (s, 3H), 0.85 (s, 3H); ^{13}C NMR: 136.7, 133.6, 130.6, 129.9, 128.9, 127.6, 77.0, 55.1, 51.5, 48.4, 45.2, 38.5, 30.8, 27.4, 20.6, 19.9; MS: 305($M+H^+$,62%); HRMS calcd for $C_{18}H_{25}O_2S$, 305.1575, found 305.1478.

(Z) **3b:** oil; yield 56%; ^1H NMR: 7.39 (m, 5H), 7.07 (d, J = 10.8 Hz, 1H), 6.50 (d, J = 10.8 Hz, 1H), 4.09 (m, 1H), 3.50 (d, 1J = 13.2 Hz, H), 2.50 (d, J = 13.2 Hz, 1H), 1.8 (m, 4H), 1.6 (m, 2H), 1.2 (m, 1H), 1.13 (s, 3H), 0.81 (s, 3H); MS: 305 $(M + H^+$, 85%), 288 $(M - H_2O$, 75%), 271 (87%), 135 (100%).

Addition of Benzylamine to Vinyl Sulfoxides. A General Procedure:

(1S, 2R, 2R, 4R, 5R) 7,7-dimethyl-1-[(2'-benzylamino-2'-phenyl) ethylsulfinyl] methyl-bicyclo[2.2.1] heptan-2-ol. 8a.

A solution of the vinyl sulfoxide **3b** (89 mg, 0.293 mmol) and benzylamine (0.124 mL) in ethanol (1 mL) was heated to 105°C in a sealed tube for 10 days. The solution was then concentrated and purified by preparative TLC ($CHCl_3$) giving 57 mg (47%) of a 94:6 mixture of **8a** and **9a**. A small quantity of diastereomerically pure material could be obtained by further purification by PTLC.

8a: solid; $[\alpha]_D^{20}$ -49.2° (c 0.57, $CHCl_3$); ^1H NMR: 7.4-7.2 (m, 10H), 4.30 (d d, J = 5.2, 8.3 Hz, 1H), 4.08 (d d, J = 4.0, 8.3 Hz, 1H), 3.70 (d, J = 13.0 Hz, 1H), 3.61 (d, 13.0 Hz, 1H), 3.24 (d, J = 13.1 Hz, 1H), 3.02 (two overlapping dd, J = 13.1, 8.3, 5.2 Hz, 2H), 2.35 (d, J = 13.1 Hz, 1H), 1.8 (m, 4H), 1.53 (m, 2H), 1.2 (m, 1H), 1.07 (s, 3H), 0.78 (s,

3H); ^{13}C NMR: 141.25, 139.70, 128.98, 128.42, 128.18, 127.98, 127.12, 126.90, 76.90, 62.04, 56.61, 53.63, 51.40, 51.36, 48.07, 44.99, 38.45, 30.93, 27.13, 20.45, 19.88; MS: 412 (M + H^+), 210, 196, 135 (100%); Anal. Calcd for $C_{25}H_{32}NSO_2$: C, 72.99; H, 8.03. Found: C, 72.90; H, 7.94.

9a: ^1H NMR: 4.22 (dd, J = 6.0, 7.9 Hz, 1H), 4.02 (m, 1H), 3.68 (d, J = 13.2 Hz, 1H), 3.56 (d, J = 13.2, 1H), 3.25 (dd, J = 6.0, 13.0 Hz, 1H), 3.19 (d, J = 12.9 Hz, 1H), 2.87 (dd, J = 6.0, 13.0 Hz, 1H), 2.21 (d, J = 12.9 Hz, 1H), 1.8 (m, 4H), 1.42 (m, 2H), 1.2 (m, 1H), 1.08 (s, 3H), 0.74 (s, 3H); ^{13}C NMR: 141.26, 139.65, 128.83, 128.29, 128.05, 127.07, 126.88, 76.76, 61.20, 58.52, 53.60, 51.21, 51.02, 47.94, 44.92, 38.39, 30.68, 26.98, 20.35, 19.76.

(1S, 2R, 2'R, 4R, 5R) 7,7-dimethyl-1-[(2'-benzylamino-3'-tert-butyldimethylsiloxy) propylsulfinyl] methyl-bicyclo[2.2.1] heptan-2-ol. 8b.

Oil; Rf 0.70 (1:1, EtOAc/hexane); ^1H NMR: 7.4 -7.2 (m, 5H), 4.08 (m, 1H), 3.88 (d, J = 13 Hz, 1H), 3.85 (dd, J = 4.4, 10 Hz), 3.81 (d, 1HJ = 13 Hz, 1H), 3.58 (dd, J = 3.7, 10 Hz, 1H), 3.25 (heptet, 1H), 3.24 (d, J = 13 Hz, 1H), 2.84 (d, J = 6.7 Hz, 2H), 2.44 (d, J = 13 Hz), 1.9-1.2 (m, 7H), 1.12 (s, 3H), 0.89 (s, 9H), 0.83 (s, 3H), 0.07 (s, 6H); ^{13}C NMR: 140.1, 128.5, 128.2, 127.1, 77.49, 63.3, 58.0, 53.9, 53.8, 51.6, 51.5, 48.1, 45.1, 38.5, 31.0, 27.2, 25.9, 20.5, 19.9, 18.3, -5.4; MS: 480 (M + H^+, 86%), 375 (100%); HRMS calcd for $C_{26}H_{46}NO_3SSi$, 480.2968, found 480.2797.

9b: ^1H NMR: 7.4-7.2 (m, 5H), 4.06 (m, 1H), 3.88 (d, J = 13 Hz, 1H), 3.80 (d, J = 13 Hz, 1H), 3.77 (dd, J = 4.6, 10.3 Hz, 1H), 3.72 (dd, J = 4.6, 10.3 Hz, 1H), 3.30 (d, J = 13 Hz, 1H),. 3.18 (heptet, 1H), 2.98 (dd, J = 6.3, 13 Hz, 1H), 2.86 (dd, J = 6.3, 13 Hz, 1H), 2.36 (d, J = 13 Hz, 1H), 1.9-1.2 (m, 7H), 1.12 (s, 3H), 0.89 (s, 9H), 0.80 (s, 3H), 0.07 (s, 6H).

Raney Nickel Reduction of 8a.

To a solution of **8a** (44 mg) in ethanol (2 mL) was added Raney Nickel. Stirring was continued for 3h and the solution was filtered and then evaporated to dryness. The product was purified by acid extraction and then column chromatography (silica gel, EtOAc/hexane, 1:1) to give pure (+)(R)-N-benzyl, N-1-phenylethylamine (6.1 mg). $[a]_D^{20}$ +47.4 (C 0.12, ethanol), lit[13] +56.2 (C 1.07, ethanol); ^1H NMR: (in part) 3.8 (q, J = 6.6 Hz, 1H), 3.65 (d, J = 13.1 Hz, 1H), 3.58 (q, J = 6.6 Hz, 1H), 1.36 (d, J = 6.6 Hz, 3H); MS: 212 (M + H^+).

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† Chiral Sulfur Compounds part 10.

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