Supporting Information

Palladium(0)-Catalyzed Synthesis of Medium-Sized Heterocycles by Using Bromoallenes as an Allyl Dication Equivalent

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The known compounds **1**,¹ **S1**,² **S4**,³ **13b–d**,¹ **S9**,⁴ **S12**,¹ **33**,¹ **39**,⁵ **41**,⁶ **43**,⁷ **47**,⁸ **S13**,⁹ **S15**,¹⁰ and **63**⁷ were synthesized according to the literature.

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(2S,3S)-3-Isopropyl-2-(1-methoxyvinyl)-N-(2,4,6-trimethylphenylsulfonyl)aziridine (3). To a stirred mixture of NaOMe (5.2 mg, 0.096 mmol) and Pd(PPh₃)₄ (4.6 mg, 0.004 mmol) in MeOH (1 mL) under nitrogen was added dropwise a solution of the bromoallene **1** (29.8 mg, 0.08 mmol) in MeOH (1 mL) at room temperature, and the mixture was stirred for 6 h at this temperature. Concentration under reduced pressure gave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (8:1) to give **3** (20.9 mg, 81% yield; 92% de) as a crystalline mass. This mass was recrystallized from *n*-hexane–Et₂O to give a pure **3** as colorless

crystals: mp 107–109 °C; $[\alpha]^{26}_D$ –41.2 (*c* 1.00, CHCl₃); IR (KBr) cm^{–1}: 1668 (C=C), 1319 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.78 (d, *J* = 6.9 Hz, 3H, CMe), 0.87 (d, *J* = 6.9 Hz, 3H, CMe), 1.42–1.54 (m, 1H, CHMe₂), 2.31 (s, 3H, PhMe), 2.55 (dd, *J* = 9.6, 7.2, Hz, 1H, 3-H), 2.72 (s, 6H, 2 × PhMe), 3.35 (d, *J* = 7.2 Hz, 1H, 2-H), 3.54 (s, 3H, OMe), 4.03 (d, *J* = 2.4 Hz, 1H, C=CHH), 4.09 (d, *J* = 2.4 Hz, 1H, C=CHH), 6.96 (s, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 19.0, 20.6, 21.0, 23.0 (2C), 26.0, 42.9, 50.8, 55.2, 83.6, 131.7 (2C), 132.4, 140.1 (2C), 142.9, 156.4; MS (FAB) *m/z* (%) 324 (MH⁺, 98), 140 (100); HRMS (FAB) calcd for C₁₇H₂₆NO₃S (MH⁺): 324.1633; found: 324.1655.

(2R)-2-[N-(4-Methylphenylsulfonyl)amino]but-3-yn-1-ol (S2). To a stirred solution of **S1** (2.25 g, 10 mmol) in MeOH (5 mL) at 0 °C was added trifluoroacetic acid (17 mL), and the mixture was stirred for 1.5 h at 50 °C. The mixture was concentrated under reduced pressure, and the residue was dissolved in CH₂Cl₂ (13 mL). The solution was made neutral with Et₃N at 0 °C. Further Et₃N (2.8 mL, 20 mmol) and TsCl (1.9 g, 10 mmol) were added to the stirred mixture at 0 °C. The mixture was stirred for 2.5 h at this temperature, followed by quenching with saturated NaHCO₃. The whole was extracted with EtOAc. The extract was washed successively with water, 4% HCl, water, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (3:5) to give **S2** (1.73 g, 72%) as colorless needles: mp 115 °C (*n*-hexane–EtOAc); $[\alpha]^{29}_D$ –83.4 (*c* 1.02, CHCl₃); IR (KBr) cm^{–1}: 3493 (OH), 3236 (NHSO₂), 2106 (C≡C), 1329 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.15 (d, *J* = 2.4 Hz, 1H, C≡CH), 2.43 (s, 3H, PhMe), 2.59 (dd, *J* = 6.6, 6.6 Hz, 1H, OH), 3.67–3.79 (m, 2H, 1-CH₂), 4.14–4.21 (m, 1H, 2-H), 5.35 (d, *J* = 8.4 Hz, 1H, NH), 7.30–7.33 (m, 2H, Ph), 7.78–7.81 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.7, 47.6, 65.4, 73.9, 79.1, 127.3 (2C), 129.5 (2C), 136.8, 143.7. Anal. Calcd for C₁₁H₁₃NO₃S: C, 55.21; H, 5.48; N, 5.85. Found: C, 55.18; H, 5.42; N, 5.84.

(2R)-2-Ethynyl-N-(4-methylphenylsulfonyl)aziridine (S3). To a stirred mixture of the amino alcohol **S2** (2.15 g, 9.0 mmol) and PPh₃ (2.83 g, 10.8 mmol) in THF (10 mL) was added dropwise diethyl azodicarboxylate (1.7 mL, 10.8 mmol) at 0 °C, and the mixture was stirred for 30 min. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **S3** (1.73 g, 87% yield) as colorless needles: mp 74–76 °C (*n*-hexane–Et₂O); $[\alpha]^{29}_D$ –101 (*c* 0.99, CHCl₃); IR (KBr) cm^{–1}: 3290 (NSO₂), 2129 (C≡C), 1329 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.17 (d, *J* = 1.8 Hz, 1H, C≡CH), 2.43 (d, *J* = 4.5 Hz, 1H, 3-CHH), 2.46 (s, 3H, PhMe), 2.76 (d, *J* = 7.2 Hz, 1H, 3-CHH), 3.22 (ddd, *J* = 7.2, 4.5, 1.8 Hz, 1H, 2-H), 7.32–7.38 (m, 2H, Ph), 7.83–7.86 (m, 2H, Ph); ¹³C-NMR

(67.8 MHz, CDCl₃) δ : 21.8, 27.7, 34.2, 71.0, 78.2, 127.9 (2C), 129.8 (2C), 134.3, 145.0; Anal. Calcd for C₁₁H₁₁NO₂S: C, 59.71; H, 5.01; N, 6.33. Found: C, 59.48; H, 5.04; N, 6.29.

(aS)-1-Bromo-4-[N-(4-methylphenylsulfonyl)amino]buta-1,2-diene (13a). To a stirred solution of the aziridine **S3** (1.33 g, 6 mmol) in CH₂Cl₂ (6 mL) was added dropwise methanesulfonic acid (0.8 mL, 12 mmol) at 0 °C, and the mixture was stirred for 15 min at this temperature. The mixture was made alkaline with saturated NaHCO₃ at 0 °C. The whole was extracted with ether, and the extract was washed with water and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude sulfonate. A mixture of CuBr·DMS (2.46 g, 12 mmol) and LiBr (1.04 g, 12 mmol) was dissolved in THF (8 mL) at room temperature under nitrogen, and the mixture was stirred for 2 min. A solution of the above crude sulfonate in THF (5 mL) was added to this reagent at room temperature. The mixture was stirred for 3 h and quenched with saturated NH₄Cl and 28% NH₄OH. The whole was extracted with ether. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **13a** (700 mg, 39% yield) as colorless crystals: mp 105 °C (*n*-hexane–EtOAc); [α]_D²⁷ +123 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3251 (NHSO₂), 1961 (C=C=C), 1336 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.44 (s, 3H, PhMe), 3.71–3.77 (m, 2H, 4-CH₂), 4.77 (dd, *J* = 6.3, 5.7 Hz, 1H, NH), 5.30 (ddd, *J* = 5.7, 5.7, 5.7 Hz, 1H, 3-H), 6.00 (ddd, *J* = 5.7, 2.4, 2.4 Hz, 1H, 1-H), 7.31–7.34 (m, 2H, Ph), 7.75–7.78 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 21.5, 40.8, 75.0, 96.9, 127.2 (2C), 129.8 (2C), 136.7, 143.8, 201.7. Anal. Calcd for C₁₁H₁₂BrNO₂S: C, 43.72; H, 4.00; N, 4.64. Found: C, 43.83; H, 4.02; N, 4.58.

(aS)-1-Bromo-4-[N,N-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]buta-1,2-diene (15a). To a stirred mixture of the bromoallene **13a** (170 mg, 0.56 mmol) and PPh₃ (441 mg, 1.68 mmol) in THF (2 mL) under nitrogen were added a solution of TBSOCH₂CH₂OH (296 mg, 1.68 mmol) in THF (1 mL) and diethyl azodicarboxylate (40% solution in toluene; 731 mg, 1.68 mmol) at 0 °C, and the mixture was stirred for 30 min at room temperature. Concentration under reduced pressure gave an oily residue, which was purified by short column chromatography over silica gel with *n*-hexane–EtOAc (8:1) to give an oil. This oil was dissolved in a 1% HCl solution in ethanol (2 mL), which was prepared from conc. HCl and EtOH, and the mixture was stirred for 5 h at room temperature. Water was added to the mixture, and the whole was extracted with EtOAc. The extract was washed with brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **15a** (150 mg, 77% yield) as a colorless oil: [α]_D²⁸ +101 (*c* 1.11, CHCl₃); IR (KBr) cm⁻¹: 3539 (OH), 1961 (C=C=C), 1342 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ :

2.26-2.29 (m, 1H, OH), 2.44 (s, 3H, *PhMe*), 3.25-3.40 (m, 2H, CH₂), 3.76-3.81 (m, 2H, CH₂), 4.04 (dd, *J* = 6.6, 2.1 Hz, 2H, CH₂), 5.23 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H, 3-H), 5.92 (ddd, *J* = 6.6, 2.1, 2.1 Hz, 1H, 1-H), 7.31-7.34 (m, 2H, Ph), 7.71-7.74 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.6, 47.2, 50.0, 61.0, 74.0, 95.8, 127.2 (2C), 129.8 (2C), 136.2, 143.7, 202.7; MS (FAB) *m/z* (%) 348 (MH⁺, ⁸¹Br, 98), 346 (MH⁺, ⁷⁹Br, 100); HRMS (FAB) calcd for C₁₃H₁₇BrNO₃S (MH⁺, ⁷⁹Br): 346.0112; found: 346.0110.

(4*S*,a*S*)-1-Bromo-4-[*N,N*-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]-5-methylhexa-1,2-diene (15c). By a procedure identical with that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **13c** (344 mg, 1.0 mmol) was converted into **15c** (308 mg, 79% yield) as a colorless oil: [α]_D²⁶ +77.7 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3523 (OH), 1957 (C=C=C), 1336 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 0.95 (d, *J* = 6.0 Hz, 3H, CMe), 1.01 (d, *J* = 6.5 Hz, 3H, CMe), 1.79-1.89 (m, 1H, 5-H), 2.44 (s, 3H, *PhMe*), 2.61 (dd, *J* = 5.5, 5.5 Hz, 1H, OH), 3.22 (ddd, *J* = 15.5, 5.5, 5.5 Hz, 1H, CHH), 3.28 (ddd, *J* = 15.5, 6.5, 5.5 Hz, 1H, CHH), 3.78-3.87 (m, 2H, CH₂), 4.06 (dd, *J* = 8.5, 8.5 Hz, 1H, 4-H), 5.05 (dd, *J* = 8.5, 6.0 Hz, 1H, 3-H), 5.87 (d, *J* = 6.0 Hz, 1H, 1-H), 7.30-7.32 (m, 2H, Ph), 7.70-7.72 (m, 2H, Ph); ¹³C-NMR (125 MHz, CDCl₃) δ : 20.0, 20.3, 21.5, 30.9, 46.9, 62.1, 63.9, 73.8, 97.0, 127.5 (2C), 129.7 (2C), 136.7, 143.7, 202.8; MS (FAB) *m/z* (%) 390 (MH⁺, ⁸¹Br, 8.2), 388 (MH⁺, ⁷⁹Br, 9.2), 216 (100); HRMS (FAB) calcd for C₁₆H₂₃BrNO₃S (MH⁺, ⁷⁹Br): 388.0582; found: 388.0571.

(4*S*,a*S*)-1-Bromo-4-[*N,N*-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]-5-phenylpenta-1,2-diene (15d). By a procedure identical with that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **13d** (305 mg, 0.78 mmol) was converted into **15d** (317 mg, 96% yield) as a colorless oil: [α]_D²⁴ +41.1 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3498 (OH), 1957 (C=C=C), 1338 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.38 (dd, *J* = 5.7, 5.7 Hz, 1H, OH), 2.42 (s, 3H, *PhMe*), 2.89 (dd, *J* = 14.1, 6.6, 1H, PhCHH), 2.98 (dd, *J* = 14.1, 8.1 Hz, 1H, PhCHH), 3.27-3.42 (m, 2H, CH₂), 3.77-3.87 (m, 2H, CH₂), 4.84-4.91 (m, 1H, 4-H), 5.20 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 6.02 (dd, *J* = 5.7, 2.1 Hz, 1H, 1-H), 7.13-7.30 (m, 7H, Ph), 7.61-7.64 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 21.5, 38.6, 46.7, 57.4, 62.3, 75.6, 98.9, 126.7, 127.3 (2C), 128.6 (2C), 129.0 (2C), 129.8 (2C), 136.4, 136.9, 143.8, 202.8; MS (FAB) *m/z* (%) 460 (MNa⁺, ⁸¹Br, 100), 458 (MNa⁺, ⁷⁹Br, 96); HRMS (FAB) calcd for C₂₀H₂₃BrNO₃S (MH⁺, ⁷⁹Br): 436.0582; found: 436.0581.

(2*S*,3*S*)-2-[*N*-(4-Methylphenylsulfonyl)amino]-5-trimethylsilylpent-4-yn-1,3-diol (S5). By a procedure similar to that described for the preparation of the bromoallene **S2** from **S1**, the bromoallene **S4** (5.57 g, 17 mmol) was converted into **S5** (3.8 g, 77% yield) as colorless needles: mp 108 °C (*n*-hexane–EtOAc); $[\alpha]^{28}_{\text{D}} -9.7$ (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3510 (OH), 3263 (NHSO₂), 2177 (C≡C), 1325 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.15 (s, 9H, SiMe₃), 2.40-2.47 (m, 1H, OH), 2.43 (s, 3H, PhMe), 2.88 (d, *J* = 4.2 Hz, 1H, OH), 3.33-3.40 (m, 1H, 2-H), 3.70 (ddd, *J* = 11.7, 6.6, 5.4 Hz, 1H, 1-CHH), 3.84 (ddd, *J* = 11.7, 4.8, 3.9 Hz, 1H, 1-CHH), 4.51 (dd, *J* = 4.8, 4.2 Hz, 1H, 3-H), 5.35 (d, *J* = 7.5 Hz, 1H, NH), 7.30-7.33 (m, 2H, Ph), 7.78-7.81 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : -0.2 (3C), 21.6, 58.1, 62.2, 63.7, 92.6, 102.4, 127.1 (2C), 129.7 (2C), 137.0, 143.7. Anal. Calcd for C₁₅H₂₃NO₄SSi: C, 52.76; H, 6.79; N, 4.10. Found: C, 52.81; H, 6.81; N, 4.07.

(3*S*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(4-methylphenylsulfonyl)amino]-1-trimethylsilylpent-1-yn-3-ol (S6). To a stirred solution of the amino alcohol **S5** (3.41 g, 10 mmol) in a mixed solvent of CHCl₃ (15 mL) and DMF (15 mL) were added imidazole (2.04 mL, 30 mmol) and *tert*-butyldimethylsilyl chloride (1.8 g, 12 mmol) at 0 °C, and the mixture was stirred for 3.5 h at this temperature. Saturated NaHCO₃ (15 mL) was added to the mixture, and the whole was extracted with Et₂O. The extract was washed successively with water, 4% HCl, water, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **S6** (3.7 g, 81%) as colorless crystals: mp 67 °C (*n*-hexane); $[\alpha]^{28}_{\text{D}} -10.3$ (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3506 (OH), 3290 (NHSO₂), 2177 (C≡C), 1335 (NHSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 0.02 (s, 6H, SiMe₂), 0.14 (s, 9H, SiMe₃), 0.85 (s, 9H, CMe₃), 2.42 (s, 3H, PhMe), 3.17 (d, *J* = 5.5 Hz, 1H, OH), 3.37-3.42 (m, 1H, 4-H), 3.57 (dd, *J* = 10.5, 5.5 Hz, 1H, 5-CHH), 3.81 (dd, *J* = 10.5, 4.0 Hz, 1H, 5-CHH), 4.39 (dd, *J* = 5.5, 5.5 Hz, 1H, 3-H), 5.02 (d, *J* = 8.5 Hz, 1H, NH), 7.30-7.31 (m, 2H, Ph), 7.77-7.78 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : -5.71, -5.68, -0.31 (3C), 18.2, 21.5, 25.7 (3C), 57.7, 62.8, 64.0, 92.0, 102.3, 127.1 (2C), 129.8 (2C), 137.4, 143.7. Anal. Calcd for C₂₁H₃₇NO₄SSi₂: C, 55.34; H, 8.18; N, 3.07. Found: C, 55.34; H, 7.96; N, 3.13.

(3*S*,4*S*)-5-(*tert*-Butyldimethylsiloxy)-4-[*N*-(4-methylphenylsulfonyl)amino]pent-1-yn-3-ol (S7). To a solution of **S6** (3.3 g, 7.24 mmol) in MeOH (15 mL) was added dropwise NaOMe (1.0 M solution in MeOH; 2.9 mL, 2.9 mmol) at 0 °C, and the mixture was stirred for 5 h at room

temperature. Concentration under reduced pressure gave a crystalline mass, which was filtered through a short pad of SiO₂ with *n*-hexane–EtOAc (1:1) and concentrated. The residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **S7** (2.77 g, 100% yield) as colorless crystals: mp 73 °C (*n*-hexane–Et₂O); [α]²⁸_D +16.7 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3506 (OH), 3304 (NHSO₂), 2119 (C≡C), 1331 (NHSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 0.017 (s, 3H, SiMe), 0.022 (s, 3H, SiMe), 0.85 (s, 9H, CMe₃), 2.31 (d, *J* = 2.5 Hz, 1H, 1-H), 2.42 (s, 3H, PhMe), 3.22 (d, *J* = 5.0 Hz, 1H, OH), 3.40-3.45 (m, 1H, 4-H), 3.62 (dd, *J* = 10.5, 6.0 Hz, 1H, 5-CHH), 3.78 (dd, *J* = 10.5, 4.0 Hz, 1H, 5-CHH), 4.45 (ddd, *J* = 5.0, 5.0, 2.5 Hz, 1H, 3-H), 5.10 (d, *J* = 8.5 Hz, 1H, NH), 7.29-7.31 (m, 2H, Ph), 7.77-7.78 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : -5.71, -5.68, 18.1, 21.5, 25.7 (3C), 57.5, 63.0, 63.2, 74.7, 81.0, 127.2 (2C), 129.7 (2C), 137.4, 143.7. Anal. Calcd for C₁₈H₂₉NO₄SSi: C, 56.36; H, 7.62; N, 3.65. Found: C, 56.44; H, 7.46; N, 3.67.

(4*R*,a*S*)-1-Bromo-5-(*tert*-butyldimethylsiloxy)-4-[*N*-(4-methylphenylsulfonyl)amino]penta-1,2-diene (S8). To a stirred mixture of the propargylic alcohol **S7** (2 g, 5.2 mmol) and Et₃N (3.6 mL, 26 mmol) in THF (20 mL) was added MsCl (0.8 mL, 10.4 mmol) at -78 °C, and the mixture was stirred for 0.5 h with warming to 60 °C. The mixture was made acidic with 4% HCl at 60 °C, and the whole was extracted with Et₂O. The extract was washed with water, saturated NaHCO₃, water, and brine, and dried over MgSO₄. Concentration of the filtrate under reduced pressure followed by rapid filtration through a short pad of SiO₂ with Et₂O gave a crude mesylate, which was used without further purification. A mixture of CuBr·DMS (2.14 g, 10.4 mmol) and LiBr (904 mg, 10.4 mmol) were dissolved in THF (10 mL) at room temperature under nitrogen. After stirring for 2 min, a solution of the above crude mesylate in THF (15 mL) was added to this reagent at room temperature. The mixture was stirred for 4 h at this temperature and quenched with saturated NH₄Cl (10 mL) and 28% NH₄OH (10 mL). The whole was extracted with Et₂O. The extract was washed with water, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash column chromatography over silica gel with *n*-hexane–Et₂O–EtOAc (10:1:1) to give **S8** (1.19 g, 51% yield) as a colorless oil: [α]²⁶_D +74.2 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3263 (NHSO₂), 1961 (C=C=C), 1331 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.01 (s, 3H, SiMe), 0.03 (s, 3H, SiMe), 0.85 (s, 9H, CMe₃), 2.42 (s, 3H, PhMe), 3.59 (dd, *J* = 9.9, 5.1 Hz, 1H, 5-CHH), 3.66 (dd, *J* = 9.9, 4.5 Hz, 1H, 5-CHH), 3.88-3.96 (m, 1H, 4-H), 4.98 (d, *J* = 7.5 Hz, 1H, NH), 5.34 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 6.03 (dd, *J* = 5.7, 2.1 Hz, 1H, 1-H), 7.29-7.31 (m, 2H, Ph), 7.73-7.76 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : -5.6, -5.5, 18.2, 21.5, 25.8 (3C), 53.1, 65.2, 75.0, 99.4, 127.2 (2C), 129.7 (2C), 137.2, 143.6, 201.3; MS (FAB) *m/z* (%) 448 (MH⁺, ⁸¹Br, 18), 446 (MH⁺, ⁷⁹Br, 18), 73 (100); HRMS (FAB) calcd for C₁₈H₂₉BrNO₃SSi (MH⁺, ⁷⁹Br): 446.0821; found: 446.0805.

(4*R*,a*S*)-1-Bromo-5-(*tert*-butyldimethylsiloxy)-4-[*N,N*-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]penta-1,2-diene (15e). To a stirred solution of PPh₃ (1.02 g, 3.9 mmol) in THF (2 mL) under nitrogen were added a solution of the bromoallene **S8** (350 mg, 0.78 mmol) in THF (1

mL), a solution of 2-(trimethylsiloxy)ethanol (524 mg, 3.9 mmol) in THF (1.5 mL), and diethyl azodicarboxylate (40% solution in toluene; 1.07 g, 3.9 mmol) at $\tilde{\text{C}}$, and the mixture was stirred for 1 h at room temperature. Concentration under reduced pressure gave an oily residue, which was purified by short column chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give an oil. To a solution of this oil in MeOH (2 mL) was added dropwise NaOMe (1.0 M solution in MeOH; 0.16 mL, 0.16 mmol) at 0 °C, and the mixture was stirred for 40 min at this temperature. The mixture was quenched with 4% HCl, and the whole was extracted with EtOAc. The extract was washed with water, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc–Et₂O (5:1:1) to give **15e** (320 mg, 84%) as colorless oil: $[\alpha]^{28}_{\text{D}} +18.5$ (*c* 1.02, CHCl₃); IR (KBr) cm⁻¹: 3550 (OH), 1957 (C=C=C), 1336 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.07 (s, 3H, SiMe), 0.08 (s, 3H, SiMe), 0.88 (s, 9H, CMe₃), 2.43 (s, 3H, PhMe), 3.17 (ddd, *J* = 15.6, 8.4, 3.9 Hz, 1H, CHH), 3.27–3.31 (m, 1H, OH), 3.44 (ddd, *J* = 15.6, 4.2, 3.3 Hz, 1H, CHH), 3.66–3.81 (m, 3H, 5-CH₂ and CHH), 3.86–3.93 (m, 1H, CHH), 4.58–4.65 (m, 1H, 4-H), 5.12 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 5.99 (dd, *J* = 5.7, 2.4 Hz, 1H, 1-H), 7.29–7.32 (m, 2H, Ph), 7.72–7.75 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : -5.6, -5.4, 18.2, 21.5, 25.7 (3C), 47.2, 57.4, 62.4, 62.9, 74.6, 96.0, 127.4 (2C), 129.8 (2C), 137.0, 143.7, 202.5; MS (FAB) *m/z* (%) 492 (MH⁺, ⁸¹Br, 11), 490 (MH⁺, ⁷⁹Br, 10), 73 (100); HRMS (FAB) calcd for C₂₀H₃₃BrNO₄SSi (MH⁺, ⁷⁹Br): 490.1083; found: 490.1063.

(aS)-1-Bromo-4-[(N,N-(3-hydroxypropyl)(4-methylphenylsulfonyl)amino]buta-1,2-diene (17a). By a procedure similar to that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **13a** (363 mg, 1.2 mmol) was converted into **17a** (412 mg, 95% yield) by the reaction with TBSOCH₂CH₂CH₂OH: colorless oil; $[\alpha]^{26}_{\text{D}} +69.7$ (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3556 (OH), 1961 (C=C=C), 1336 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.69–1.82 (m, 2H, 2'-CH₂), 2.30 (dd, *J* = 6.3, 6.0 Hz, 1H, OH), 2.44 (s, 3H, PhMe), 3.24–3.41 (m, 2H, CH₂), 3.72–3.78 (m, 2H, CH₂), 3.88–4.06 (m, 2H, CH₂), 5.17 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H, 3-H), 5.91 (ddd, *J* = 6.6, 1.8, 1.8 Hz, 1H, 1-H), 7.31–7.34 (m, 2H, Ph), 7.69–7.72 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.6, 30.6, 44.2, 46.1, 58.8, 73.8, 95.7, 127.0 (2C), 129.8 (2C), 136.4, 143.6, 202.7; MS (FAB) *m/z* (%) 362 (MH⁺, ⁸¹Br, 99), 360 (MH⁺, ⁷⁹Br, 100); HRMS (FAB) calcd for C₁₄H₁₉BrNO₃S (MH⁺, ⁷⁹Br): 360.0269; found: 360.0266.

(4*S*,a*S*)-1-Bromo-4-[*N,N*-(3-hydroxypropyl)(4-methylphenylsulfonyl)amino]-5-methylhexa-1,2-diene (17c). By a procedure identical with that described for the preparation of the bromoallene **17a** from **13a**, the bromoallene **13c** (448 mg, 1.3 mmol) was converted into **17c** (360 mg, 69% yield) as a colorless oil: $[\alpha]^{25}_{\text{D}} +89.5$ (*c* 1.03, CHCl_3); IR (KBr) cm^{-1} : 3548 (OH), 1957 ($\text{C}=\text{C}=\text{C}$), 1336 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 0.94 (d, $J = 6.6$ Hz, 3H, CMe), 0.98 (d, $J = 6.6$ Hz, 3H, CMe), 1.82-1.94 (m, 3H, 5-H and 2'- CH_2), 2.05-2.07 (m, 1H, OH), 2.43 (s, 3H, PhMe), 3.20 (ddd, $J = 15.0, 7.8, 6.0$ Hz, 1H, CHH), 3.34 (ddd, $J = 15.0, 7.5, 7.5$ Hz, 1H, CHH), 3.65-3.81 (m, 2H, CH_2), 3.98 (dd, $J = 9.0, 9.0$ Hz, 1H, 4-H), 5.06 (dd, $J = 9.0, 5.7$ Hz, 1H, 3-H), 5.84 (d, $J = 5.7$ Hz, 1H, 1-H), 7.27-7.30 (m, 2H, Ph), 7.68-7.71 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 20.0, 20.5, 21.5, 30.9, 33.4, 41.8, 59.7, 63.9, 73.6, 97.3, 127.4 (2C), 129.6 (2C), 137.4, 143.4, 202.7; MS (FAB) m/z (%) 404 (MH^+ , ^{81}Br , 14), 402 (MH^+ , ^{79}Br , 15), 230 (100); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{25}\text{BrNO}_3\text{S}$ (MH^+ , ^{79}Br): 402.0739; found: 402.0738.

(4*S*,a*S*)-1-Bromo-4-[*N,N*-(3-hydroxypropyl)(4-methylphenylsulfonyl)amino]-5-phenylpenta-1,2-diene (17d). By a procedure identical with that described for the preparation of the bromoallene **17a** from **13a**, the bromoallene **13d** (275 mg, 0.70 mmol) was converted into **17d** (309 mg, 96% yield) as a colorless oil: $[\alpha]^{28}_{\text{D}} +55.2$ (*c* 1.01, CHCl_3); IR (KBr) cm^{-1} : 3510 (OH), 1957 ($\text{C}=\text{C}=\text{C}$), 1336 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 1.85-1.93 (m, 2H, 2'- CH_2), 2.14 (dd, $J = 6.0, 5.7$ Hz, 1H, OH), 2.41 (s, 3H, PhMe), 2.91 (dd, $J = 14.1, 6.3$ Hz, 1H, PhCHH), 3.00 (dd, $J = 14.1, 8.4$ Hz, 1H, PhCHH), 3.31-3.46 (m, 2H, CH_2), 3.68-3.74 (m, 2H, CH_2), 4.77-4.84 (m, 1H, 4-H), 5.20 (dd, $J = 6.0, 5.7$ Hz, 1H, 3-H), 6.00 (dd, $J = 5.7, 2.1$ Hz, 1H, 1-H), 7.11-7.26 (m, 7H, Ph), 7.60-7.63 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 21.5, 33.4, 38.8, 41.4, 57.2, 59.2, 75.6, 99.3, 126.7, 127.1 (2C), 128.5 (2C), 129.0 (2C), 129.8 (2C), 137.1, 137.2, 143.5, 202.7; MS (FAB) m/z (%) 452 (MH^+ , ^{81}Br , 23), 450 (MH^+ , ^{79}Br , 23), 230 (100); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{25}\text{BrNO}_3\text{S}$ (MH^+ , ^{79}Br): 450.0738; found: 450.0763.

(3*R*,5*R*)-6-Methyl-5-[*N*-(4-methylphenylsulfonyl)amino]hept-1-yn-3-ol (S10). To a stirred solution of the amino alcohol **S9** (280 mg, 1.16 mmol) in EtOAc (2 mL) was added 3N HCl (1 mL) at room temperature. After stirring for 1.5 h at 50 °C, the mixture was made basic with 28% NH_4OH . The whole was extracted with CHCl_3 . The extract was washed with water, and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give an oily residue. To a stirred solution of the residue in CHCl_3 (2 mL) were added Et_3N (0.32 mL, 2.32 mmol) and TsCl (221 mg,

1.16 mmol) at 0 °C. The mixture was stirred for 2 h at this temperature, followed by quenching with saturated NaHCO₃. The mixture was made acidic with 4% HCl, and the whole was extracted with Et₂O. The extract was washed successively with water, saturated NaHCO₃, and brine, and dried over MgSO₄. Filtration and solvent evaporation followed by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) gave **S10** (280 mg, 82% yield) as colorless crystals: mp 74 °C (*n*-hexane–Et₂O); [α]²⁷_D –16.4 (*c* 0.76, CHCl₃); IR (KBr) cm^{–1}: 3516 (OH), 3290 (NHSO₂), 2116 (C≡C), 1321 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.66 (d, *J* = 6.6 Hz, 3H, CMe), 0.73 (d, *J* = 6.6 Hz, 3H, CMe), 1.53–1.72 (m, 2H, 4-CHH and 6-H), 1.79–1.88 (m, 1H, 4-CHH), 2.43 (s, 3H, PhMe), 2.44 (d, *J* = 2.4 Hz, 1H, C≡CH), 3.14 (d, *J* = 5.4 Hz, 1H, OH), 3.32–3.41 (m, 1H, 5-H), 4.62–4.69 (m, 1H, 3-H), 4.77 (d, *J* = 9.3 Hz, 1H, NH), 7.30–7.32 (m, 2H, Ph), 7.75–7.78 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 18.0, 18.2, 21.5, 31.9, 39.9, 55.5, 58.5, 72.6, 84.3, 127.1 (2C), 129.7 (2C), 137.6, 143.6. Anal. Calcd for C₁₅H₂₁NO₃S: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.89; H, 7.09; N, 4.72.

(5*R*,a*S*)-1-Bromo-5-[*N*-(4-methylphenylsulfonyl)amino]-6-methylhepta-1,2-diene (S11). By a procedure identical with that described for the preparation of the bromoallene **S8** from **S7**, the propargylic alcohol **S10** (236 mg, 0.8 mmol) was converted into **S11** (249 mg, 87% yield) as colorless crystals: mp 84 °C (*n*-hexane); [α]²⁵_D +51.0 (*c* 1.06, CHCl₃); IR (KBr) cm^{–1}: 3284 (NHSO₂), 1956 (C=C=C), 1325 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.81 (d, *J* = 6.0 Hz, 3H, CMe), 0.83 (d, *J* = 5.7 Hz, 3H, CMe), 1.73–1.84 (m, 1H, 6-H), 2.13–2.31 (m, 2H, 4-CH₂), 2.43 (s, 3H, PhMe), 3.11–3.20 (m, 1H, 5-H), 4.65 (d, *J* = 8.4 Hz, 1H, NH), 5.10 (ddd, *J* = 7.5, 7.5, 5.4 Hz, 1H, 3-H), 5.90 (ddd, *J* = 5.4, 1.8, 1.8 Hz, 1H, 1-H), 7.30–7.32 (m, 2H, Ph), 7.75–7.78 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 17.8, 18.7, 21.5, 30.8, 31.3, 58.6, 72.5, 96.1, 127.1 (2C), 129.6 (2C), 137.8, 143.4, 203.0; MS (FAB) *m/z* (%) 360 (MH⁺, ⁸¹Br, 26), 358 (MH⁺, ⁷⁹Br, 26), 226 (100); HRMS (FAB) calcd for C₁₅H₂₁BrNO₂S (MH⁺, ⁷⁹Br): 358.0476; found: 358.0478.

(5*R*,a*S*)-1-Bromo-4-[*N,N*-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]-5-methylhepta-1,2-diene (17e). By a procedure identical with that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **S11** (227 mg, 0.63 mmol) was converted into **17e** (96 mg, 38% yield) as a colorless oil: [α]²⁶_D +41.4 (*c* 0.98, CHCl₃); IR (KBr) cm^{–1}: 3543 (OH), 1956 (C=C=C), 1335 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.87 (d, *J* = 6.6 Hz, 3H, CMe), 0.96 (d, *J* = 6.6 Hz, 3H, CMe), 1.67–1.77 (m, 1H, 6-H), 2.10–2.21 (m, 1H, 4-CHH), 2.39–2.49 (m, 1H, 4-CHH), 2.43 (s, 3H, PhMe), 2.73 (m, 1H, OH), 3.19 (ddd, *J* = 15.6, 5.1, 5.1 Hz, 1H, CHH), 3.32 (ddd, *J* = 15.6, 6.6, 5.4 Hz, 1H, CHH), 3.58 (ddd, *J* = 9.0, 9.0, 5.7 Hz, 1H, 5-H), 3.80–3.87 (m, 2H, CH₂), 4.99 (ddd, *J* = 8.1, 6.6, 5.7 Hz, 1H, 3-H), 5.90 (ddd, *J* = 5.7, 1.8, 1.8 Hz, 1H, 1-H), 7.29–7.32 (m, 2H, Ph), 7.71–7.74 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 20.2, 20.7, 21.5, 31.1, 32.4, 46.3, 62.5, 64.3, 72.5, 97.8, 127.5 (2C), 129.6 (2C), 136.9, 143.6, 202.4; MS (FAB) *m/z* (%) 404 (MH⁺, ⁸¹Br, 36), 402 (MH⁺, ⁷⁹Br, 37), 136 (100); HRMS (FAB) calcd for C₁₇H₂₅BrNO₃S (MH⁺, ⁷⁹Br): 402.0739; found: 402.0733.

(4*S*,a*S*)-1-Bromo-4-{*N,N*-[3-(*N*-methanesulfonyl)aminopropyl](4-methylphenylsulfonyl)-amino}penta-1,2-diene (21). To a stirred mixture of PPh₃ (197 mg, 0.75 mmol) and MsNHBoc (146 mg, 0.75 mmol) in THF (2 mL) under nitrogen were added a solution of bromoallene **17b** (187 mg, 0.50 mmol) in THF (2 mL) and diethyl azodicarboxylate (0.12 mL, 0.75 mmol) at 0 °C, and the mixture was stirred for 1 h at this temperature. Concentration under reduced pressure gave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give the corresponding *N*-Boc derivative. To a stirred solution of this bromoallene in EtOAc (4 mL) was added 3N HCl (4 mL) at room temperature. After stirring for 1.5 h at 60 °C, the mixture was made basic with 28% NH₄OH. The whole was extracted with EtOAc. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (5:4) to give **21** (225 mg, 98% yield) as a colorless oil: $[\alpha]^{23}_{\text{D}} -22.4$ (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 3294 (NHSO₂), 1957 (C=C=C), 1325 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.18 (d, *J* = 6.9 Hz, 3H, CMe), 1.84–1.96 (m, 2H, 2'-CH₂), 2.44 (s, 3H, PhMe), 2.99 (s, 3H, SO₂Me), 3.21–3.32 (m, 4H, 1'-CH₂ and 3'-CH₂), 4.64–4.73 (m, 1H, 4-H), 4.99 (dd, *J* = 6.3, 6.3 Hz, 1H, NH), 5.17 (dd, *J* = 5.7, 5.4 Hz, 1H, 3-H), 6.09 (dd, *J* = 5.7, 2.7 Hz, 1H, 1-H), 7.31–7.34 (m, 2H, Ph), 7.68–7.71 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 17.4, 21.5, 31.4, 39.9, 40.2, 40.7, 51.1, 75.5, 101.2, 127.0 (2C), 130.0 (2C), 136.9, 143.9, 202.2; MS (FAB) *m/z* (%) 453 (MH⁺, ⁸¹Br, 24), 451 (MH⁺, ⁷⁹Br, 23), 307 (100); HRMS (FAB) calcd for C₁₆H₂₄BrN₂O₄S₂ (MH⁺, ⁷⁹Br): 451.0361; found: 451.0345.

(4*S*,a*S*)-1-Bromo-4-{*N,N*-[2-(*N*-methanesulfonyl)aminoethyl](4-methylphenylsulfonyl)amino}-5-phenylpenta-1,2-diene (23). By a procedure identical with that described for the preparation of the bromoallene **21** from **17b**, the bromoallene **15d** (225 mg, 0.50 mmol) was converted into **23** (229 mg, 89% yield) as a colorless oil: $[\alpha]^{25}_{\text{D}} +25.6$ (*c* 0.83, CHCl₃); IR (KBr) cm⁻¹: 3282 (NHSO₂), 1957 (C=C=C), 1333 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.42 (s, 3H, PhMe), 2.86 (dd, *J* = 14.1, 6.9 Hz 1H, PhCHH), 2.95 (s, 3H, SO₂Me), 2.98 (dd, *J* = 14.1, 8.1 Hz, 1H, PhCHH), 3.33–3.42 (m, 4H, 1'-CH₂ and 2'-CH₂), 4.82–4.89 (m, 2H, 4-H and NH), 5.17 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 6.03 (dd, *J* = 5.7, 2.4 Hz, 1H, 1-H), 7.13–7.29 (m, 7H, Ph), 7.60–7.63 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 21.5, 38.4, 40.3, 43.5, 44.5, 57.2, 75.7, 98.6, 126.8, 127.3 (2C), 128.6 (2C), 129.0 (2C), 130.0 (2C), 136.1, 136.6, 144.1, 202.8; MS (FAB) *m/z* (%) 515 (MH⁺, ⁸¹Br, 7), 513 (MH⁺, ⁷⁹Br, 6), 136 (100); HRMS (FAB) calcd for C₂₁H₂₆BrN₂O₄S₂ (MH⁺, ⁷⁹Br): 513.0510; found: 513.0517.

7-Methoxymethyl-4-(4-methylphenylsulfonyl)-2H,3H,4H,5H-1,4-oxazepine (24a) and 6-Methoxy-7-methylene-4-(4-methylphenylsulfonyl)-1,4-oxazepane (25a) (Table 1, entry 1). To a stirred mixture of NaOMe (8.1 mg, 0.15 mmol) and Pd(PPh₃)₄ (11.6 mg, 0.01 mmol) in MeOH (0.5 mL) under nitrogen was added dropwise a solution of the bromoallene **15a** (35 mg, 0.10 mmol) in MeOH (1 mL) at room temperature, and the mixture was stirred for 6 h at this temperature. Concentration under reduced pressure gave an oily residue, which was purified by flash column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give, in order to elution, **25a** (8.4 mg, 28% yield) and **24a** (18 mg, 61% yield).

Compound **24a**: colorless oil; IR (KBr) cm⁻¹: 1678 (C=C–O), 1335 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 2.42 (s, 3H, PhMe), 3.26 (s, 3H, OMe), 3.55–3.56 (m, 2H, CH₂), 3.62 (s, 2H, MeOCH₂), 3.86 (d, *J* = 5.5 Hz, 1H, 5-CH₂), 4.08–4.10 (m, 2H, CH₂), 4.92 (t, *J* = 5.5 Hz, 1H, 6-H), 7.28–7.30 (m, 2H, Ph), 7.66–7.68 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.6, 44.1, 50.8, 58.2, 70.1, 72.7, 102.0, 127.3 (2C), 129.5 (2C), 135.4, 143.3, 156.8. MS (FAB) *m/z* (%) 298 (MH⁺, 100); HRMS (FAB) calcd for C₁₄H₂₀NO₄S (MH⁺): 298.1113; found: 298.1089.

Compound **25a**: colorless needles; mp 112 °C (*n*-hexane–Et₂O); IR (KBr) cm⁻¹: 1641 (C=C–O), 1352 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 2.30 (dd, *J* = 11.5, 10.5 Hz, 1H, 5-CHH), 2.41–2.46 (m, 1H, 3-CHH), 2.44 (s, 3H, PhMe), 3.51–3.53 (m, 1H, 3-CHH), 3.54 (s, 3H, OMe), 3.70–3.75 (m, 2H, 2-CHH and 5-CHH), 3.96–3.99 (m, 1H, 2-CHH), 4.01 (dd, *J* = 10.5, 3.0 Hz, 1H, 6-H), 4.06 (d, *J* = 3.0 Hz, 1H, C=CHH), 4.20 (d, *J* = 3.0 Hz, 1H, C=CHH), 7.33–7.34 (m, 2H, Ph), 7.62–7.64 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.6, 45.4, 49.0, 55.0, 66.0, 75.8, 82.7, 127.7 (2C), 129.6 (2C), 132.1, 143.8, 159.7. Anal. Calcd for C₁₄H₁₉NO₄S: C, 56.55; H, 6.44; N, 4.71. Found: C, 56.42; H, 6.32; N, 4.67.

(5S)-5-Isopropyl-7-methoxymethyl-4-(4-methylphenylsulfonyl)-2H,3H,4H,5H-1,4-oxazepine (24c) (Table 1, entry 3). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **15c** (38.8 mg, 0.10 mmol) was converted into **24c** (21 mg, 62% yield) as a colorless oil: [α]_D²⁶ +16.0 (*c* 1.74, CHCl₃); IR (KBr) cm⁻¹: 1672 (C=C–O), 1331 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 0.99 (d, *J* = 6.5 Hz, 3H, CMe), 1.00 (d, *J* = 7.5 Hz, 3H, CMe), 1.93–2.03 (m, 1H, Me₂CH), 2.40 (s, 3H, PhMe), 3.18 (s, 3H, OMe), 3.35–3.39 (m, 1H, CHH), 3.44 (d, *J* = 13.0 Hz, 1H, MeOCHH), 3.48 (d, *J* = 13.0 Hz, 1H, MeOCHH), 3.83–3.87 (m, 1H, CHH), 4.00–4.09 (m, 3H, 2 × CHH and 5-H), 4.85 (d, *J* = 6.5 Hz, 1H, 6-H),

7.23-7.25 (m, 2H, Ph), 7.68-7.70 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 20.0, 20.2, 21.4, 33.1, 45.5, 57.9, 60.7, 69.9, 72.7, 106.2, 127.4 (2C), 129.2 (2C), 137.9, 142.8, 154.9; MS (FAB) m/z (%) 340 (MH^+ , 25), 296 (100); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_4\text{S}$ (MH^+): 340.1583; found: 340.1579.

(5*S*)-5-Benzyl-7-methoxymethyl-4-(4-methylphenylsulfonyl)-2*H*,3*H*,4*H*,5*H*-1,4-oxazepine

(24d) (Table 1, entry 4). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **15d** (51 mg, 0.12 mmol) was converted into **24d** (34 mg, 73% yield) as a colorless oil: $[\alpha]^{26}_{\text{D}} +47.8$ (c 1.07, CHCl_3); IR (KBr) cm^{-1} : 1687 ($\text{C}=\text{C}-\text{O}$), 1329 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 2.38 (s, 3H, PhMe), 2.91-3.03 (m, 2H, PhCH_2), 3.23 (s, 3H, OMe), 3.49-3.57 (m, 1H, CHH), 3.56 (d, J = 12.9 Hz, 1H, MeOCHH), 3.64 (d, J = 12.9, 1H, MeOCHH), 3.91-4.02 (m, 2H, CHH and CHH), 4.16-4.24 (m, 1H, CHH), 4.75-4.84 (m, 1H, 5-H), 4.83 (d, J = 6.3 Hz, 1H, 6-H), 7.12-7.29 (m, 7H, Ph), 7.49-7.51 (m, 2H, Ph); ^{13}C -NMR (67.8 MHz, CDCl_3) δ : 21.5, 40.9, 45.7, 56.0, 57.9, 70.9, 73.0, 107.0, 126.5, 127.1 (2C), 128.3, (2C) 129.0 (2C) 129.3 (2C), 137.2, 137.3, 142.9, 155.0; MS (FAB) m/z (%) 388 (MH^+ , 10), 296 (100); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{S}$ (MH^+): 388.1583; found: 388.1582.

(5*R*)-5-(*tert*-Butyldimethylsilyloxymethyl)-7-methoxymethyl-4-(4-methylphenylsulfonyl)-2*H*,3*H*,4*H*,5*H*-1,4-oxazepine (24e) (Table 1, entry 5).

By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **15e** (61 mg, 0.125 mmol) was converted into **24e** (41 mg, 74% yield) as a colorless oil: $[\alpha]^{28}_{\text{D}} +46.4$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 1678 ($\text{C}=\text{C}-\text{O}$), 1333 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 0.03 (s, 6H, SiMe_2), 0.86 (s, 9H, CMe_3), 2.40 (s, 3H, PhMe), 3.26 (s, 3H, OMe), 3.53 (ddd, J = 15.6, 7.8, 3.0 Hz, 1H, CHH), 3.61 (d, J = 12.9 Hz, 1H, MeOCHH), 3.68 (d, J = 12.9 Hz, 1H, MeOCHH), 3.69 (dd, J = 10.8, 6.3 Hz, 1H, TBSOCHH), 3.76 (dd, J = 10.8, 6.6 Hz, 1H, TBSOCHH), 3.84-3.94 (m, 2H, CHH and CHH), 4.20 (ddd, J = 13.2, 7.2, 3.0 Hz, 1H, CHH), 4.61-4.67 (m, 1H, 5-H), 4.85 (d, J = 7.2 Hz, 1H, 6-H), 7.24-7.26 (m, 2H, Ph), 7.71-7.74 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : -5.50, -5.47, 18.3, 21.5, 25.8 (3C), 46.2, 56.4, 58.0, 64.2, 70.8, 73.2, 103.5, 127.3 (2C), 129.5 (2C), 137.8, 143.0, 155.5; MS (FAB) m/z (%) 464 (MNa^+ , 95), 296 (100); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{35}\text{NNaO}_5\text{SSi}$ (MNa^+): 464.1903; found: 464.1896.

(7Z)-8-Methoxymethyl-5-(4-methylphenylsulfonyl)-3,4,5,6-tetrahydro-2H-1,5-oxazocine (26a) (Table 2, entry 1). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **17a** (36 mg, 0.10 mmol) was converted into **26a** (20.8 mg, 67% yield) as a colorless oil: IR (KBr) cm^{-1} : 1672 (C=C–O), 1333 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 1.89 (tt, J = 5.5, 5.5 Hz, 2H, 3-CH₂), 2.42 (s, 3H, PhMe), 3.29 (s, 3H, OMe), 3.46–3.48 (m, 2H, CH₂), 3.76 (s, 2H, MeOCH₂), 3.93 (d, J = 7.5 Hz, 2H, 6-CH₂), 4.04 (t, J = 5.5 Hz, 2H, CH₂), 5.05 (t, J = 7.5 Hz, 1H, 7-H), 7.29–7.31 (m, 2H, Ph), 7.68–7.70 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.6, 29.8, 42.7, 45.8, 58.3, 70.3, 72.4, 106.1, 127.0 (2C), 129.6 (2C), 136.6, 143.0, 155.6; MS (FAB) m/z (%) 312 (MH⁺, 76), 212 (100); HRMS (FAB) calcd for C₁₅H₂₂NO₄S (MH⁺): 312.1270; found: 312.1264.

(6S,7Z)-8-Methoxymethyl-6-methyl-5-(4-methylphenylsulfonyl)-3,4,5,6-tetrahydro-2H-1,5-oxazocine (26b) (Table 2, entry 2). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **17b** (37.4 mg, 0.10 mmol) was converted into **26b** (27.4 mg, 84% yield) as a colorless oil: $[\alpha]_D^{26} +52.3$ (c 1.00, CHCl₃); IR (KBr) cm^{-1} : 1678 (C=C–O), 1335 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 1.17 (d, J = 7.0 Hz, 3H, CMe), 1.88–2.04 (m, 2H, 3-CH₂), 2.41 (s, 3H, PhMe), 3.33 (s, 3H, OMe), 3.31 (ddd, J = 14.5, 9.0, 3.5 Hz, 1H, CHH), 3.73 (ddd, J = 14.5, 5.0, 5.0 Hz, 1H, CHH), 3.74 (s, 2H, MeOCH₂), 3.98 (ddd, J = 12.5, 6.5, 4.5 Hz, 1H, CHH), 4.09 (ddd, J = 12.5, 8.5, 3.5 Hz, 1H, CHH), 4.58 (qd, J = 7.0, 5.0 Hz, 1H, 6-H), 4.91 (d, J = 5.0 Hz, 1H, 7-H), 7.27–7.28 (m, 2H, Ph), 7.72–7.73 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 19.6, 21.5, 29.1, 42.1, 50.7, 58.2, 70.7, 73.4, 113.6, 127.0 (2C), 129.5 (2C), 138.3, 142.9, 151.9; MS (FAB) m/z (%) 326 (MH⁺, 92), 212 (100); HRMS (FAB) calcd for C₁₆H₂₄NO₄S (MH⁺): 326.1426; found: 326.1423.

(6S,7Z)-6-Isopropyl-8-methoxymethyl-5-(4-methylphenylsulfonyl)-3,4,5,6-tetrahydro-2H-1,5-oxazocine (26c) (Table 2, entry 3). To NaH (6 mg, 0.15 mmol) was added MeOH (0.5 mL) at 0 °C under nitrogen, and the solution was stirred for 20 min at room temperature. To the stirred mixture were added Pd(PPh₃)₄ (17.3 mg, 0.015 mmol) and a solution of the bromoallene **17c** (40.2 mg, 0.10

mmol) in THF (0.5 mL) at room temperature. After stirring for 12 h at this temperature, the mixture was poured into ice–water (1 mL) saturated with NH₄Cl. The whole was extracted with Et₂O, and the extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **26c** (10.5 mg, 30% yield) as a colorless oil: [α]_D²³ –9.1 (*c* 0.65, CHCl₃); IR (KBr) cm^{–1}: 1678 (C=C–O), 1329 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 0.64 (d, *J* = 6.5 Hz, 3H, CMe), 0.89 (d, *J* = 7.0 Hz, 3H, CMe), 1.82–1.89 (m, 1H, 3-CHH), 1.96–2.05 (m, 1H, 3-CHH), 2.33–2.41 (m, 1H, Me₂CH), 2.41 (s, 3H, PhMe), 3.28–3.34 (m, 1H, CHH), 3.30 (s, 3H, OMe), 3.72 (d, *J* = 13.0 Hz, 1H, MeOCHH), 3.76 (ddd, *J* = 16.0, 7.5, 3.0 Hz, 1H, CHH), 3.82 (d, *J* = 13.0 Hz, 1H, MeOCHH), 3.82–3.85 (m, 1H, 6-H), 3.91 (ddd, *J* = 12.0, 8.0, 4.5 Hz, 1H, CHH), 4.01 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H, CHH), 5.34 (d, *J* = 7.5 Hz, 1H, 7-H), 7.25–7.27 (m, 2H, Ph), 7.69–7.71 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 20.2 (2C), 21.5, 29.3, 30.0, 42.7, 58.0, 60.8, 70.5, 72.2, 115.3, 127.1 (2C), 129.3 (2C), 138.6, 142.7, 152.5; MS (FAB) *m/z* (%) 354 (MH⁺, 29), 310 (100); HRMS (FAB) calcd for C₁₈H₂₈NO₄S (MH⁺): 354.1739; found: 354.1730.

(6*S*,7*Z*)-6-Benzyl-8-methoxymethyl-5-(4-methylphenylsulfonyl)-3,4,5,6-tetrahydro-2*H*-1,5-oxazocine (26d) (Table 2, entry 4). By a procedure identical with that described for the preparation of the 1,5-oxazocine **26c** from **17c**, the bromoallene **17d** (45 mg, 0.10 mmol) was converted into **26d** (22.8 mg, 57% yield) as a colorless oil: [α]_D²² +10.7 (*c* 1.01, CHCl₃); IR (KBr) cm^{–1}: 1678 (C=C–O) 1333 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.88–2.13 (m, 2H, 3-CH₂), 2.39 (s, 3H, PhMe), 2.93 (dd, *J* = 13.8, 6.0 Hz, 1H, PhCHH), 3.00 (dd, *J* = 13.8, 8.4 Hz, 1H, PhCHH), 3.27 (s, 3H, OMe), 3.40 (ddd, *J* = 15.0, 8.4, 3.3 Hz, 1H, CHH), 3.71 (d, *J* = 12.9 Hz, 1H, MeOCHH), 3.76 (d, *J* = 12.9 Hz, 1H, MeOCHH), 3.72–3.80 (m, 1H, CHH), 3.97–4.13 (m, 2H, CH₂), 4.63 (ddd, *J* = 8.4, 6.0, 6.0 Hz, 1H, 6-H), 5.05 (d, *J* = 6.0 Hz, 1H, 7-H), 7.06–7.25 (m, 7H, Ph), 7.57–7.60 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 21.4, 29.2, 39.8, 42.8, 56.3, 58.1, 70.6, 72.9, 113.0, 126.4, 127.0 (2C), 128.4 (2C), 129.2 (2C), 129.5 (2C), 138.0, 138.1, 142.9, 152.8; MS (FAB) *m/z* (%) 402 (MH⁺, 30), 310 (100); HRMS (FAB) calcd for C₂₂H₂₈NO₄S (MH⁺): 402.1739; found: 402.1774.

(5*R*,7*Z*)-5-Isopropyl-8-Methoxymethyl-4-(4-methylphenylsulfonyl)-3,4,5,6-tetrahydro-2*H*-1,4-oxazepine (26e) (Table 2, entry 5). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **17e** (28.1 mg, 0.07 mmol) was

converted into **26e** (18 mg, 73% yield) as a colorless oil: $[\alpha]^{28}_D -5.46$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 1678 ($\text{C}=\text{C}-\text{O}$), 1335 (NSO_2); ^1H -NMR (500 MHz, CDCl_3) δ : 0.76 (d, $J = 6.5$ Hz, 3H, CMe), 0.95 (d, $J = 7.0$ Hz, 3H, CMe), 1.74-1.82 (m, 1H, Me_2CH), 2.20-2.30 (m, 2H, 6- CH_2), 2.41 (s, 3H, PhMe), 3.25-3.32 (m, 1H, CHH), 3.30 (s, 3H, OMe), 3.56 (d, $J = 13.0$ Hz, 1H, MeOCHH), 3.60 (ddd, $J = 9.5, 9.5, 4.5$ Hz, 1H, 5-H), 3.66 (d, $J = 13.0$ Hz, 1H, MeOCHH), 3.67-3.71 (m, 1H, CHH), 3.85-3.89 (m, 1H, CHH), 4.06 (ddd, $J = 13.5, 12.5, 2.0$ Hz, 1H, CHH), 5.18 (dd, $J = 8.5, 8.5$ Hz, 1H, 7-H), 7.27-7.28 (m, 2H, Ph), 7.69-7.71 (m, 2H, Ph); ^{13}C -NMR (67.8 MHz, CDCl_3) δ : 19.9, 20.5, 21.5, 27.3, 30.4, 43.6, 58.2, 63.9, 70.1, 71.5, 114.1, 127.3 (2C), 129.3 (2C), 138.9, 142.7, 153.3; MS (FAB) m/z (%) 354 (MH^+ , 71), 198 (100); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{28}\text{BrNO}_4\text{S}$ (MH^+): 354.1739; found: 354.1765.

(5S)-7-Methoxymethyl-5-methyl-1,4-bis(4-methylphenylsulfonyl)-2,3,4,5-tetrahydro-1H-1,4-diazepine (27a) (Table 3, entry 1). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **20** (41 mg, 0.08 mmol) was converted into **27a** (18 mg, 48% yield) as a colorless oil: $[\alpha]^{28}_D +17.2$ (c 1.03, CHCl_3); IR (KBr) cm^{-1} : 1664 ($\text{C}=\text{C}-\text{N}$), 1336 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 1.29 (d, $J = 7.2$ Hz, 3H, CMe), 2.40 (s, 3H, PhMe), 2.42 (s, 3H, PhMe), 3.10 (s, 3H, OMe), 3.03-3.22 (m, 1H, CHH), 3.57-3.67 (m, 2H, CHH and CHH), 3.83 (d, $J = 12.9$ Hz, 1H, MeOCHH), 3.87-3.94 (m, 1H, CHH), 4.20 (d, $J = 12.9$ Hz, 1H, MeOCHH), 4.60 (qd, $J = 7.2, 7.2$ Hz, 1H, 5-H), 5.88 (d, $J = 7.2$ Hz, 1H, 6-H), 7.29-7.32 (m, 2H, Ph), 7.65-7.68 (m, 2H, Ph), 7.77-7.80 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 16.8, 21.4, 21.5, 45.0, 50.0, 50.3, 57.4, 73.3, 126.9 (2C), 127.2 (2C), 128.4, 129.67 (2C), 129.72 (2C), 137.3, 137.9, 139.3, 143.3, 143.7; MS (FAB) m/z (%) 465 (MH^+ , 100); HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_5\text{S}_2$ (MH^+): 465.1518; found: 465.1514.

5-Benzyl-1-methanesulfonyl-7-methoxymethyl-4-(4-methylphenylsulfonyl)-2,3,4,5-tetrahydro-1H-1,4-diazepine (27b) (Table 3, entry 2). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **23** (51.3 mg, 0.10 mmol) was converted into **27b** (24.4 mg, 53% yield) as a colorless oil: $[\alpha]^{26}_D -28.2$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 1662 ($\text{C}=\text{C}-\text{N}$), 1338 (NSO_2); ^1H -NMR (500MHz, CDCl_3) δ : 2.39 (s, 3H, PhMe), 2.81 (dd, $J = 13.5, 7.5$ Hz, 1H, PhCHH), 3.10 (s, 3H, SO_2Me), 3.14 (dd, $J = 13.5, 8.5$ Hz, 1H, PhCHH), 3.18-3.27 (m, 1H, CHH), 3.21 (s, 3H, OMe), 3.55 (ddd, $J = 14.5, 9.5, 1.5$ Hz, 1H, CHH), 3.71 (d, $J = 13.5$ Hz, 1H, MeOCHH), 3.80-3.83 (m, 1H, CHH), 3.91-3.94 (m, 1H, CHH), 4.44 (d, $J = 13.5$ Hz, 1H, MeOCHH), 4.77 (ddd, $J = 8.5, 7.5, 7.0$ Hz, 1H, 5-H), 5.64 (d, $J = 7.0$ Hz, 1H, 6-H), 7.11-7.29 (m, 7H, Ph), 7.45-7.47 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 21.5, 36.4, 40.7, 45.3, 50.3,

55.2, 57.5, 73.0, 125.6, 126.6, 127.1 (2C), 128.5 (2C), 129.2 (2C), 129.7 (2C), 137.3 (2C), 140.4, 143.4; MS (FAB) m/z (%) 465 (MH^+ , 31), 373 (100); HRMS (FAB) calcd for $C_{22}H_{29}N_2O_5S_2$ (MH^+): 465.1518; found: 465.1508.

(6S)-8-Methoxymethyl-6-methyl-1-(methanesulfonyl)-5-(4-methylphenylsulfonyl)-1H,2H,3H,4H,5H,6H-1,5-diazocine (27c) (Table 3, entry 3). By a procedure identical with that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **21** (68 mg, 0.15 mmol) was converted into **27c** (38 mg, 63% yield) as colorless crystals: 113 °C (*n*-hexane–Et₂O); $[\alpha]_D^{26} +146$ (*c* 1.00, CHCl₃); IR (KBr) cm^{-1} : 1674 (C=C–N), 1335 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.04 (d, *J* = 7.2 Hz, 3H, CMe), 1.88–1.99 (m, 1H, 3-CHH), 2.10–2.21 (m, 1H, 3-CHH), 2.42 (s, 3H, PhMe), 3.14 (s, 3H, SO₂Me), 3.25–3.38 (m, 2H, 2-CHH and 4-CHH), 3.35 (s, 3H, OMe), 3.62 (ddd, *J* = 14.7, 6.9, 3.6 Hz, 1H, CHH), 3.86 (ddd, *J* = 13.5, 7.8, 4.2 Hz, 1H, CHH), 3.95 (d, *J* = 13.2 Hz, 1H, MeOCHH), 4.11 (d, *J* = 13.2 Hz, 1H, MeOCHH), 4.65–4.74 (m, 1H, 6-H), 5.78 (d, *J* = 4.8 Hz, 1H, 7-H), 7.29–7.31 (m, 2H, Ph), 7.68–7.71 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 17.5, 21.5, 28.1, 40.4, 44.9, 50.0, 52.0, 58.3, 74.4, 127.0 (2C), 129.7 (2C), 133.8, 135.4, 137.6, 143.4. Anal. Calcd for C₁₇H₂₆N₂O₅S₂: C, 50.72; H, 6.51; N, 6.96. Found: C, 50.72; H, 6.39; N, 6.90.

(4S,aR)-1-Bromo-4-[(N,N-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]penta-1,2-diene (28). By a procedure identical with that described for the preparation of the bromoallene **15a** from **13a**, the (4S,aR)-bromoallene **S12** (215 mg, 0.68 mmol) was converted into **28** (214 mg, 87% yield) as a colorless oil; $[\alpha]_D^{23} -217$ (*c* 1.00, CHCl₃); IR (KBr) cm^{-1} : 3545 (OH), 1959 (C=C=C), 1335 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.24 (d, *J* = 6.9 Hz, 3H, CMe), 2.44 (s, 3H, PhMe), 2.54 (dd, *J* = 6.0, 5.7 Hz, 1H, OH), 3.17 (ddd, *J* = 15.3, 5.7, 5.7 Hz, 1H, CHH), 3.28 (ddd, *J* = 15.3, 5.7, 5.7 Hz, 1H, CHH), 3.77–3.83 (m, 2H, CH₂), 4.73–4.83 (m, 1H, 4-H), 5.11 (dd, *J* = 5.7, 4.5 Hz, 1H, 3-H), 5.85 (dd, *J* = 5.7, 2.7 Hz, 1H, 1-H), 7.31–7.34 (m, 2H, Ph), 7.73–7.75 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 18.5, 21.5, 46.1, 51.8, 62.8, 74.9, 101.0, 127.3 (2C), 129.9 (2C), 136.7, 143.8, 202.3; MS (FAB) m/z (%) 362 (MH^+ , ⁸¹Br, 40), 360 (MH^+ , ⁷⁹Br, 40), 136 (100); HRMS (FAB) calcd for C₁₄H₁₉BrNO₃S (MH^+ , ⁷⁹Br): 360.0269; found: 360.0271.

(4S,aR)-1-Bromo-4-[(N,N-(4-methylphenylsulfonyl)[2-[(N-(4-methylphenylsulfonyl)amino]ethyl]amino]penta-1,2-diene (29). By a procedure similar to that described for the preparation of the bromoallene **21** from **17b**, the bromoallene **28** (108 mg, 0.4 mmol) was converted into **29** (126 mg, 82% yield) by the reaction with TsNHBoc: colorless needles; mp 114 °C (*n*-hexane–Et₂O);

$[\alpha]^{25}_D -186$ (c 1.01, CHCl_3); IR (KBr) cm^{-1} : 3284 (NHSO_2), 1959 ($\text{C}=\text{C}=\text{C}$), 1335 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 1.13 (d, J = 6.9 Hz, 3H, CMe), 2.43 (s, 3H, PhMe), 2.44 (s, 3H, PhMe), 3.11-3.23 (m, 4H, 2 $\times$ CH_2), 4.63-4.73 (m, 1H, 4-H), 4.98 (dd, J = 5.7, 4.8 Hz, 1H, 3-H), 5.16 (dd, J = 5.7, 5.1 Hz, 1H, NH), 5.88 (dd, J = 5.7, 2.7 Hz, 1H, 1-H), 7.29-7.34 (m, 4H, Ph), 7.65-7.68 (m, 2H, Ph), 7.74-7.77 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 18.1, 21.51, 21.53, 43.6, 44.0, 51.7, 75.1, 100.6, 127.1 (2C), 127.2 (2C), 129.8 (2C), 130.0 (2C), 136.4, 136.8, 143.6, 144.0, 202.5; MS (FAB) m/z (%) 515 (MH^+ , ^{81}Br , 26), 513 (MH^+ , ^{79}Br , 24), 136 (100); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{26}\text{BrN}_2\text{O}_4\text{S}_2$ (MH^+ , ^{79}Br): 513.0517; found: 513.0521.

(5S)-7-Benzylloxymethyl-5-methyl-4-(4-methylphenylsulfonyl)-2H,3H,4H,5H-1,4-oxazepine (31) and (5S,6R)-6-Benzylloxy-5-methyl-7-methylene-4-(4-methylphenylsulfonyl)-1,4-oxazepane (32). By a procedure similar to that described for the preparation of the 1,5-oxazepine **26c** from **17c**, the bromoallene **15b** (54 mg, 0.15 mmol) was converted into, in order to elution, **32** (3.5 mg, 6% yield) and **31** (47 mg, 81% yield) by the reaction with BnOH.

Compound **31**: colorless crystals; mp 101 °C (n -hexane–EtOAc); $[\alpha]^{29}_D +23.7$ (c 0.92, CHCl_3); IR (KBr) cm^{-1} : 1674 ($\text{C}=\text{C}-\text{O}$), 1329 (NSO_2); ^1H -NMR (500 MHz, CDCl_3) δ : 1.29 (d, J = 6.5 Hz, 3H, CMe), 2.35 (s, 3H, PhMe), 3.48 (ddd, J = 14.5, 6.5, 2.5 Hz, 1H, CHH), 3.64 (d, J = 12.5 Hz, 1H, PhCHH), 3.68 (d, J = 12.5 Hz, 1H, PhCHH), 3.90 (ddd, J = 12.5, 6.5, 3.0 Hz, 1H, CHH), 4.05 (ddd, J = 14.5, 7.5, 3.0 Hz, 1H, CHH), 4.12 (ddd, J = 12.5, 7.5, 2.5 Hz, 1H, CHH), 4.38 (d, J = 12.0 Hz, 1H, BnOCHH), 4.41 (d, J = 12.0 Hz, 1H, BnOCHH), 4.69 (dq, J = 7.5, 6.5 Hz, 1H, 5-H), 4.88 (d, J = 7.5 Hz, 1H, 6-H), 7.22-7.35 (m, 7H, Ph), 7.68-7.70 (m, 2H, Ph); ^{13}C -NMR (67.8 MHz, CDCl_3) δ : 20.4, 21.5, 45.1, 50.3, 70.4, 70.9, 72.1, 108.0, 127.1 (2C), 127.6 (3C), 128.3 (2C), 129.4 (2C), 137.6, 137.7, 143.0, 154.6. Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_4\text{S}$: C, 65.09; H, 6.50; N, 3.61. Found: C, 64.88; H, 6.50; N, 3.55.

Compound **32**: colorless oil; $[\alpha]^{28}_D +26.4$ (c 0.25, CHCl_3); IR (KBr) cm^{-1} : 1633 ($\text{C}=\text{C}-\text{O}$), 1348 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 1.22 (d, J = 6.9 Hz, 3H, CMe), 2.41 (s, 3H, PhMe), 3.24 (ddd, J = 12.3, 3.9, 3.9 Hz, 1H, CHH), 3.42 (ddd, J = 12.3, 8.7, 3.9 Hz, 1H, CHH), 3.67 (ddd, J = 11.4, 3.9, 3.9 Hz, 1H, CHH), 3.90 (d, J = 3.9 Hz, 1H, 6-H), 3.95 (ddd, J = 11.4, 8.7, 3.9 Hz, 1H, CHH), 4.04 (qd, J = 6.9, 3.9 Hz, 1H, 5-H), 4.32 (d, J = 3.0 Hz, 1H, $\text{C}=\text{CHH}$), 4.47 (d, J = 3.0 Hz, 1H, $\text{C}=\text{CHH}$), 4.74 (d, J = 12.6 Hz, 1H, PhCHH), 4.78 (d, J = 12.6 Hz, 1H, PhCHH), 7.25-7.36 (m, 7H, Ph), 7.66-7.68 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 15.4, 21.5, 41.8, 50.6, 62.5, 69.5, 78.7, 86.4, 127.3 (3C), 127.8 (2C), 128.4 (2C), 129.6 (2C), 136.5, 136.6, 143.4, 157.6; MS (FAB) m/z (%) 388 (MH^+ , 40), 91 (100); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{S}$ (MH^+): 388.1538; found: 388.1568.

(4*S*,a*S*)-1-Bromo-4-[*N,N*-(2-hydroxybenzyl)(4-methylphenylsulfonyl)amino]penta-1,2-diene (40). By a procedure similar to that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **13b** (126.5 mg, 0.40 mmol) was converted into **40** (155 mg, 92% yield; >96% de) by the reaction with 2-(*tert*-butyldimethylsiloxy)benzyl alcohol **39**: colorless oil; $[\alpha]_D^{23}$ -36.7 (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 3440 (OH), 1957 ($\text{C}=\text{C}=\text{C}$), 1331 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 1.11 (d, J = 6.9 Hz, 3H, CMe), 2.45 (s, 3H, PhMe), 4.32 (d, J = 15.6 Hz, 1H, PhCHH), 4.50 (d, J = 15.6 Hz, 1H, PhCHH), 4.73-4.83 (m, 1H, 4-H), 5.06 (dd, J = 5.4, 5.4 Hz, 1H, 3-H), 6.00 (dd, J = 5.4, 3.0 Hz, 1H, 1-H), 6.81-6.91 (m, 2H, Ph), 7.16-7.25 (m, 3H, Ph and OH), 7.33-7.35 (m, 2H, Ph), 7.73-7.76 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 18.0, 21.6, 44.8, 51.8, 74.9, 101.2, 117.1, 120.2, 121.8, 127.2 (2C), 130.1 (3C), 131.2, 136.4, 144.2, 155.6, 202.3; MS (FAB) m/z (%) 424 (MH^+ , ^{81}Br , 29), 422 (MH^+ , ^{79}Br , 30), 107 (100); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{21}\text{BrNO}_3\text{S}$ (MH^+ , ^{79}Br): 422.0426; found: 422.0422.

***N*-[2-(*tert*-Butyldimethylsilyloxymethyl)phenyl]-4-methylphenylsulfonamide (42).** By a procedure identical with that described for the preparation of **S6** from **S5**, the alcohol **41** (1.39 g, 5 mmol) was converted into **42** (1.90 g, 97% yield) as colorless needles: mp 125–127 °C (*n*-hexane–EtOAc); IR (KBr) cm^{-1} : 3207 (NHSO_2), 1331 (NHSO_2); ^1H -NMR (500 MHz, CDCl_3) δ : 0.07 (s, 6H, SiMe_2), 0.91 (s, 9H, CMe_3), 2.37 (s, 3H, PhMe), 4.34 (s, 2H, PhCH_2), 6.96-7.04 (m, 2H, Ph), 7.19-7.25 (m, 3H, Ph), 7.52-7.54 (m, 1H, Ph), 7.64-7.65 (m, 2H, Ph), 8.33 (s, 1H, NH); ^{13}C -NMR (67.8 MHz, CDCl_3) δ : -5.3 (2C), 18.2, 21.6, 25.8 (3C), 65.0, 122.2, 124.4, 126.8 (2C), 127.8, 128.7, 129.4 (2C), 130.4, 136.8, 137.2, 143.4. Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_3\text{SSi}$: C, 61.34; H, 7.46; N, 3.58. Found: C, 61.35; H, 7.38; N, 3.59.

1-Bromo-4-[*N,N*-(2-hydroxymethylphenyl)(4-methylphenylsulfonyl)amino]buta-1,2-diene (44). By a procedure similar to that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **43** (149 mg, 1.0 mmol) was converted into **44** (386 mg, 95% yield) by the reaction with **42**: colorless crystals; mp 110 °C (*n*-hexane–Et₂O); IR (KBr) cm^{-1} : 3537 (OH), 1961 ($\text{C}=\text{C}=\text{C}$), 1348 (NSO_2); ^1H -NMR (500 MHz, CDCl_3) δ : 2.46 (s, 3H, PhMe), 2.98 (br s, 1H, OH), 3.92-3.98 (m, 1H, 4- CHH), 4.54-4.57 (m, 2H, 4- CHH and PhCHH), 4.97-4.99 (m, 1H, PhCHH), 5.27-5.33 (m, 1H, 3-H), 5.79-5.88 (m, 1H, 1-H), 6.47-6.48 (m, 1H, Ph), 7.18-7.18 (m, 1H, Ph), 7.31-7.32 (m, 2H, Ph), 7.36-7.38 (m, 1H, Ph), 7.54-7.55 (m, 2H, Ph), 7.61-7.63 (m, 1H, Ph); ^{13}C -NMR (75 MHz, CDCl_3 , 333K) δ : 21.5, 50.5, 61.3, 73.4, 95.1, 127.9, 128.2 (2C), 128.4, 129.3,

129.7 (2C), 131.0, 135.2, 137.1, 142.5, 144.2, 203.7. Anal. Calcd for C₁₈H₁₈NO₃S: C, 52.95; H, 4.44; N, 3.43. Found: C, 52.91; H, 4.48; N, 3.38.

(4*S*,2*Z*)-2-Methoxymethyl-4-methyl-5-(4-methylphenylsulfonyl)-5,6-dihydro-4*H*-benzo[*b*]-1,5-oxazocine (45) (Table 4, entry 3). By a procedure similar to that described for the preparation of the 1,5-oxazepine **26c** from **17c**, the bromoallene **40** (63.3 mg, 0.15 mmol) was converted into **45** (32 mg, 57% yield) as a colorless oil; $[\alpha]_D^{25}$ -236 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 1693 (C=C-O), 1335 (NSO₂); ¹H-NMR (500 MHz, CDCl₃) δ : 1.42 (d, *J* = 6.5 Hz, 3H, CMe), 2.30 (s, 3H, PhMe), 3.24 (s, 3H, OMe), 3.65 (d, *J* = 13.0 Hz, 1H, MeOCHH), 3.74 (d, *J* = 13.0 Hz, 1H, MeOCHH), 4.55 (d, *J* = 16.5 Hz, 1H, 6-CHH), 4.64 (d, *J* = 16.5 Hz, 1H, 6-CHH), 4.75-4.79 (m, 1H, 4-H), 5.18 (d, *J* = 3.0 Hz, 1H, 3-H), 6.62 (d, *J* = 7.5 Hz, 1H, Ph), 6.95-6.96 (m, 2H, Ph), 7.02-7.17 (m, 3H, Ph), 7.24-7.26 (m, 2H, Ph); ¹³C-NMR (125 MHz, CDCl₃) δ : 21.3, 22.7, 45.4, 50.5, 58.3, 70.7, 117.7, 122.1, 124.4, 127.1 (2C), 128.6 (2C), 128.8, 129.0, 130.3, 137.5, 142.2, 150.3, 153.9; MS (FAB) *m/z* (%) 374 (MH⁺, 100); HRMS (FAB) calcd for C₂₀H₂₄NO₄S (MH⁺): 374.1426; found: 374.1427.

(3*Z*)-4-Methoxymethyl-1-(4-methylphenylsulfonyl)-1,6-dihydro-2*H*-benzo[*c*]-1,5-oxazocine (46) (Table 4, entry 4). By a procedure identical with that described for the preparation of the 1,5-oxazepine **26c** from **17c**, the bromoallene **44** (81.7 mg, 0.2 mmol) was converted into **46** (58.6 mg, 82% yield) as a colorless oil: IR (KBr) cm⁻¹: 1678 (C=C-O), 1350 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.42 (s, 3H, PhMe), 2.92 (s, 3H, OMe), 3.49 (s, 2H, MeOCH₂), 4.22 (s, 2H, 6-CH₂), 4.26 (d, *J* = 8.4 Hz, 2H, 2-CH₂), 4.85 (t, *J* = 8.4 Hz, 1H, 3-H), 7.15-7.18 (m, 1H, Ph), 7.23-7.32 (m, 3H, Ph), 7.36-7.44 (m, 3H, Ph), 7.51-7.54 (m, 1H, Ph); ¹³C-NMR (125 MHz, CDCl₃) δ : 21.5, 47.1, 57.5, 70.6, 72.9, 99.4, 127.3 (2C), 128.1, 129.5 (2C), 129.8, 131.1, 131.5, 131.9, 134.1, 139.4, 143.7, 150.3, 156.4; MS (FAB) *m/z* (%) 360 (MH⁺, 57), 136 (100); HRMS (FAB) calcd for C₁₉H₂₂NO₄S (MH⁺): 360.1270; found: 360.1248.

1-Bromo-4-[2-(2-hydroxyethyl)phenyl]buta-1,2-diene (49). To a stirred mixture of the

propargylic alcohol **48** (4.0 g, 13.1 mmol) and Et₃N (3.29 mL, 23.6 mmol) in CH₂Cl₂ (40 mL) was added MsCl (1.42 mL, 18.3 mmol) at 0 °C under nitrogen, and the mixture was stirred for 30 min at this temperature. The mixture was made acidic with 4% HCl, and the whole was extracted with Et₂O. The extract was washed with water, saturated NaHCO₃, water, and brine, and dried over MgSO₄. Usual workup followed by rapid filtration through a short pad of SiO₂ with Et₂O gave a crude mesylate, which was used without further purification. A mixture of CuBr·DMS (5.39 g, 26.2 mmol) and LiBr (2.28 g, 26.2 mmol) were dissolved in THF (20 mL) at room temperature under nitrogen. After stirring for 2 min, a solution of the above crude mesylate in THF (15 mL) was added to this reagent at room temperature. The mixture was stirred for 1.5 h at this temperature and quenched with saturated NH₄Cl (10 mL) and 28% NH₄OH (10 mL). The whole was extracted with Et₂O. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (8:1) to give the bromoallene bearing a protected hydroxy group as an oil. This oil was dissolved in a 1% HCl solution in ethanol (30 mL), which was prepared from conc. HCl and EtOH, and the mixture was stirred for 20 min at room temperature. Water was added to the mixture, and the whole was extracted with EtOAc. The extract was washed with brine and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **49** (2.1 g, 63% yield) as a colorless oil: IR (KBr) cm⁻¹: 3311 (OH), 1956 (C=C=C); ¹H-NMR (300 MHz, CDCl₃) δ: 1.58 (br s, 1H, OH), 2.93 (t, *J* = 6.9 Hz, 2H, PhCH₂), 3.54 (dd, *J* = 7.2, 2.4 Hz, 2H, 4-CH₂), 3.85 (t, *J* = 6.9 Hz, 2H, OCH₂), 5.52 (td, *J* = 7.2, 5.4 Hz, 1H, 3-H), 5.93 (dt, *J* = 5.4, 2.4 Hz, 1H, 1-H), 7.19–7.26 (m, 4H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ: 32.3, 35.8, 63.2, 72.9, 100.0, 126.9, 127.1, 129.9, 130.1, 136.5, 136.9, 202.4; MS (FAB) *m/z* (%) 277 (MNa⁺, ⁸¹Br, 11), 275 (MNa⁺, ⁷⁹Br, 12), 154 (100); HRMS (FAB) calcd for C₁₂H₁₃BrNaO (MNa⁺, ⁷⁹Br): 275.0047; found: 275.0055.

1-Bromo-4-(2-{2-[*N*-(methanesulfonyl)amino]ethyl}phenyl)buta-1,2-diene (50). By a procedure identical with that described for the preparation of the bromoallene **21** from **17b**, the bromoallene **49** (506 mg, 2.0 mmol) was converted into **50** (640 mg, 97% yield) as a colorless oil: IR (KBr) cm⁻¹: 3298 (NH), 1956 (C=C=C), 1317 (NH₂SO₂); ¹H-NMR (300 MHz, CDCl₃) δ: 2.88 (s, 3H, SO₂Me), 2.92–2.97 (m, 2H, PhCH₂), 3.38 (td, *J* = 6.6, 6.0 Hz, 2H, NCH₂), 3.53 (dd, *J* = 6.9, 2.4 Hz, 2H, 4-CH₂), 4.36 (t, *J* = 6.0 Hz, 1H, NH), 5.53 (td, *J* = 6.9, 5.7 Hz, 1H, 3-H), 5.94 (dt, *J* = 5.7, 2.4 Hz, 1H, 1-H), 7.18–7.25 (m, 4H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ: 32.2, 33.4, 40.4, 43.8, 73.2, 100.0, 127.3, 127.4, 129.9, 130.2, 136.0, 136.7, 202.4; MS (FAB) *m/z* (%) 332 (MH⁺, ⁸¹Br, 40), 330 (MH⁺, ⁷⁹Br, 40), 136 (100); HRMS (FAB) calcd for C₁₃H₁₇BrNO₂S (MH⁺, ⁷⁹Br): 330.0163; found: 330.0165.

7-(*tert*-Butyldimethylsilyloxy)-5,5-dimethylhept-1-yn-3-ol (S14). To a stirred solution of oxalyl chloride (2.93 mL, 33.6 mmol) in CH₂Cl₂ (40 mL) at –78 °C under nitrogen was added dropwise a solution of DMSO (7.96 mL, 112 mmol) in CH₂Cl₂ (10 mL). After 45 min, a solution of the alcohol **S13** (5.52 g, 22.4 mmol) in CH₂Cl₂ (10 mL) was added to the above reagent at –78 °C, and the mixture was stirred for 30 min at this temperature. Diisopropylethylamine (27.0 mL, 157 mmol) was added to the above solution at –78 °C and the mixture was stirred for 30 min with warming to 0 °C. The mixture was made acidic with 4% HCl, and the whole was extracted with Et₂O. The extract was washed successively with water, saturated NaHCO₃, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude aldehyde as an oil. To a stirred solution of trimethylsilylacetylene (3.80 mL, 26.9 mmol) in dry THF (10 mL) under nitrogen was added *n*-BuLi (1.56 M solution in *n*-hexane; 17.2 mL, 26.9 mmol) at 0 °C, and the mixture was stirred for 20 min at this temperature. A solution of the crude aldehyde in dry THF (15 mL) was added to the above stirred reagent at –78 °C, and the mixture was stirred for 1 h with warming to –60 °C, followed by quenching with saturated NH₄Cl. The mixture was made acidic with 4% HCl, and the whole was extracted with Et₂O. The extract was washed successively with water, saturated NaHCO₃, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give the TMS derivative as an oil. To a stirred solution of this oil in MeOH (20 mL) was added dropwise NaOMe (605 mg, 11.2 mmol) in MeOH (11.2 mL) at 0 °C, and the mixture was stirred for 2 h at room temperature. The mixture was concentrated under reduced pressure, and the residue was filtered through a short pad of SiO₂ with *n*-hexane–EtOAc (5:1). The residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **S14** (4.56 g, 75% yield) as a colorless oil: IR (KBr) cm^{–1}: 3313 (OH), 2114 (C≡C); ¹H-NMR (300 MHz, CDCl₃) δ: 0.08 (s, 3H, SiMe), 0.09 (s, 3H, SiMe), 0.91 (s, 9H, CMe₃), 0.95 (s, 3H, CMe), 0.99 (s, 3H, CMe), 1.37 (dt, *J* = 14.4, 5.1 Hz, 1H, 6-CHH), 1.60 (dd, *J* = 14.4, 3.9 Hz, 1H, 6-CHH), 1.82–2.02 (m, 2H, 4-CH₂), 2.39 (d, *J* = 1.8 Hz, 1H, 1-H), 3.62 (d, *J* = 6.6 Hz, 1H, OH), 3.67–3.79 (m, 2H, 7-CH₂), 4.43–4.51 (m, 1H, 3-H); ¹³C-NMR (67.8 MHz, CDCl₃) δ: –5.32, –5.23, 18.4, 26.1 (3C), 28.3, 29.0, 32.3, 43.2, 48.5, 59.9, 60.4, 71.5, 86.8; MS (FAB) *m/z* (%) 271 (MH⁺, 63), 73 (100); HRMS (FAB) calcd for C₁₅H₃₁O₂Si (MH⁺): 271.2093; found: 271.2093.

7-Bromo-3,3-dimethylhepta-5,6-dien-1-ol (51). By a procedure identical with that described for the preparation of the bromoallene **49** from **48**, the propargylic alcohol **S14** (4.39 g, 16 mmol) was converted into **51** (2.52 g, 72% yield) as a colorless oil: IR (KBr) cm^{–1}: 3309 (OH), 1954 (C=C=C); ¹H-NMR (300 MHz, CDCl₃) δ: 0.96 (s, 6H, 2 × CMe), 1.55–1.59 (m, 3H, 2-CH₂ and OH), 2.08 (dd, *J* = 8.4, 1.8 Hz, 2H, 4-CH₂), 3.63–3.80 (m, 2H, 1-CH₂), 5.37 (td, *J* = 8.4, 5.7 Hz, 1H, 5-H), 5.93 (dt, *J* = 5.7, 1.8 Hz, 1H, 7-H); ¹³C-NMR (75 MHz, CDCl₃) δ: 27.1, 27.2, 33.4, 41.4, 43.8, 59.5, 71.5, 97.3, 203.2; MS (FAB) *m/z* (%) 243 (MNa⁺, ⁸¹Br, 13), 241 (MNa⁺, ⁷⁹Br, 13), 154 (100); HRMS (FAB) calcd for C₉H₁₅BrNaO (MNa⁺, ⁷⁹Br): 241.0204; found: 241.0218

S22

1-Bromo-5,5-dimethyl-7-[*N*-(4-methylphenylsulfonyl)amino]hepta-1,2-diene (53). By a procedure similar to that described for the preparation of the bromoallene **17a** from **15a**, the bromoallene **51** (43.8 mg, 0.2 mmol) was converted into **53** (68.2 mg, 92% yield) by the reaction with TsNHBoc: colorless oil; IR (KBr) cm^{-1} : 3263 (NHSO₂), 1954 (C=C=C); ¹H-NMR (300 MHz, CDCl₃) δ : 0.88 (s, 6H, 2 $\times$ CH₃), 1.39-1.45 (m, 2H, 6-CH₂), 1.97 (dd, J = 8.1, 1.5 Hz, 2H, 4-CH₂), 2.44 (s, 3H, PhMe), 2.90-2.97 (m, 2H, 7-CH₂), 4.58 (t, J = 6.0 Hz, 1H, NH), 5.25 (td, J = 8.1, 5.4 Hz, 1H, 3-H), 5.86 (dt, J = 5.4, 1.5 Hz, 1H, 1-H), 7.31-7.34 (m, 2H, Ph), 7.74-7.77 (m, 2H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 21.5, 26.8, 26.9, 33.5, 39.3, 40.6, 40.7, 71.7, 96.7, 127.1 (2C), 129.7 (2C), 136.7, 143.4, 203.2; MS (FAB) m/z (%) 374 (MH⁺, ⁸¹Br, 50), 372 (MH⁺, ⁷⁹Br, 50), 155 (100); HRMS (FAB) calcd for C₁₆H₂₃BrNO₂S (MH⁺, ⁷⁹Br): 372.0633; found: 372.0639.

1-Bromo-7-[*N,N*-(*tert*-butoxycarbonyl)(methanesulfonyl)amino]-5,5-bis(hydroxymethyl)-hepta-1,2-diene (S17). To a stirred mixture of PPh₃ (78.7 mg, 0.3 mmol) and MsNHBoc (58.6 mg, 0.3 mmol) in THF (2 mL) under nitrogen were added a solution of bromoallene **52** (29.1 mg, 0.10 mmol) in THF (2 mL) and diethyl azodicarboxylate (40% solution in toluene; 130 mg; 0.3 mmol) at 0 °C, and the mixture was stirred for 20 min at room temperature. Concentration under reduced pressure gave an oily residue, which was purified by short column chromatography over silica gel with *n*-hexane–EtOAc (5:3) to give the *N*-Boc derivative. To a stirred solution of this bromoallene in MeOH (2 mL) was added TsOH·H₂O (11 mg, 0.06 mmol) at 0 °C, and the mixture was stirred for 30 min at room temperature. Saturated NaHCO₃ (1 mL) was added to the mixture, and the whole was extracted with EtOAc. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:5) to give **S17** (31 mg, 72% yield) as a colorless oil: IR (KBr) cm^{-1} : 3404 (OH), 1954 (C=C=C), 1724 (C=O), 1352 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.56 (s, 9H, CMe₃), 1.74 (t, J = 8.1 Hz, 2H, 6-CH₂), 2.10 (ddd, J = 14.1, 8.4, 1.5 Hz, 1H, 4-CHH), 2.18 (ddd, J = 14.1, 8.4, 1.5 Hz, 1H, 4-CHH), 2.44 (br s, 1H, OH), 2.52 (br s, 1H, OH), 3.28 (s, 3H, SO₂Me), 3.61 (s, 4H, 2 $\times$ OCH₂), 3.71-3.78 (m, 2H, 7-CH₂), 5.42 (ddd, J = 8.4, 8.4, 5.7 Hz, 1H, 3-H), 6.00 (ddd, J = 5.7, 1.5, 1.5 Hz, 1H, 1-H); ¹³C-NMR (75 MHz, CDCl₃) δ : 28.0 (3C), 30.8, 31.0, 42.0, 42.6 (2C), 66.7, 66.8, 72.2, 85.2, 95.5, 151.5, 203.4; MS (FAB) m/z (%) 452 (MNa⁺, ⁸¹Br, 13), 450 (MNa⁺, ⁷⁹Br, 16), 77 (100); HRMS (FAB) calcd for C₁₅H₂₆BrNNaO₆S (MNa⁺, ⁷⁹Br): 450.0562; found: 450.0559.

5,5-Bis(benzyloxymethyl)-1-bromo-7-[*N*-(methanesulfonyl)amino]hepta-1,2-diene (54). To a

stirred solution of diol **S17** (21 mg, 0.049 mmol) and benzyl 2,2,2-trichloroacetimidate (37 μ L, 0.147 mmol) in a mixture of CH₂Cl₂ (0.5 mL) and *n*-hexane (1 mL) under nitrogen was added trifluoromethanesulfonic acid (3 drops) at room temperature, and the mixture was stirred for 1.5 h at this temperature. Saturated NaHCO₃ (1 mL) was added to the mixture, and the whole was extracted with Et₂O. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give the dibenzylated bromoallene bearing an *N*-Boc amino group as an oily residue. To a stirred solution of this bromoallene in EtOAc (1 mL) was added 3N HCl (1 mL) at room temperature. After stirring for 2 h at 65 °C, the mixture was made basic with 28% NH₄OH. The whole was extracted with Et₂O. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **54** (8.4 mg, 34% yield) as a colorless oil: IR (KBr) cm⁻¹: 3298 (NHSO₂), 1954 (C=C=C), 1321 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.68 (t, *J* = 7.2 Hz, 2H, 6-CH₂), 2.26 (dd, *J* = 8.1, 1.8 Hz, 2H, 4-CH₂), 2.77 (s, 3H, SO₂Me), 3.14 (td, *J* = 7.2, 5.7 Hz, 2H, 7-CH₂), 3.32–3.39 (m, 4H, 2 $\times$ CH₂OBn), 4.44–4.53 (m, 4H, 2 $\times$ CH₂Ph), 4.97 (t, *J* = 5.7 Hz, 1H, NH), 5.28 (td, *J* = 8.1, 5.7 Hz, 1H, 3-H), 5.91 (dt, *J* = 5.7, 1.8 Hz, 1H, 1-H), 7.27–7.39 (m, 10H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 32.1, 33.7, 38.8, 40.0, 42.2, 71.9, 72.5 (2C), 73.5 (2C), 96.0, 127.7 (6C), 128.4 (4C), 137.71, 137.74, 203.4; MS (FAB) *m/z* (%) 510 (MH⁺, ⁸¹Br, 7), 508 (MH⁺, ⁷⁹Br, 7), 91 (100); HRMS (FAB) calcd for C₂₄H₃₁BrNO₄S (MH⁺, ⁷⁹Br): 508.1157; found: 508.1147.

7-Benzyloxymethyl-4,4-dimethyl-2H,3H,4H,5H-oxepine (55) (Table 5, entry 1). To NaH (12.0 mg, 0.30 mmol) was added THF (0.5 mL) and BnOH (0.5 mL) at 0 °C under nitrogen, and the solution was stirred for 20 min at room temperature. To the stirred mixture were added Pd(PPh₃)₄ (11.6 mg, 0.01 mmol) and a solution of the bromoallene **51** (43.9 mg, 0.20 mmol) in THF (1 mL) at room temperature. After stirring for 5 h at this temperature, the mixture was poured into ice–water (1 mL) saturated with NH₄Cl. The whole was extracted with Et₂O, and the extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (15:1) to give **55** (35.3 mg, 72% yield) as a colorless oil: IR (KBr) cm⁻¹: 1672 (C=C–O); ¹H-NMR (500 MHz, CDCl₃) δ : 0.99 (s, 6H, 2 $\times$ CMe), 1.69 (t, *J* = 5.0 Hz, 2H, 3-CH₂), 2.03 (d, *J* = 6.0 Hz, 2H, 5-CH₂), 3.88 (s, 2H, BnOCH₂), 3.98 (t, *J* = 5.0 Hz, 2H, 2-CH₂), 4.55 (s, 2H, PhCH₂), 4.92 (t, *J* = 6.0 Hz, 1H, 6-H), 7.27–7.36 (m, 5H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 29.2 (2C), 31.6, 38.9, 45.0, 67.8, 71.2, 72.0, 107.0, 127.4, 127.6 (2C), 128.2 (2C), 138.2, 155.3; MS (FAB) *m/z* (%) 247 (MH⁺, 25), 91 (100); HRMS (FAB) calcd for C₁₆H₂₃O₂ (MH⁺): 247.1698; found: 247.1699.

10-Methoxymethyl-3,3-dimethyl-2,4,9-trioxaspiro[5.6]dodec-10-ene (56) (Table 5, entry 2). To NaH (7.2 mg, 0.18 mmol) was added MeOH (0.6 mL) at room temperature under nitrogen, and the solution was stirred for 10 min at this temperature. To the stirred mixture were added Pd(PPh₃)₄ (6.9 mg, 0.006 mmol) and a solution of the bromoallene **52** (35 mg, 0.12 mmol) in MeOH (0.6 mL) at room temperature. After stirring for 2 h at 50 °C, the mixture was poured into ice–water (1 mL) saturated with NH₄Cl. The whole was extracted with Et₂O, and the extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **56** (21 mg, 72% yield) as a colorless oil: IR (KBr) cm⁻¹: 1672 (C=C–O); ¹H-NMR (300 MHz, CDCl₃) δ: 1.40 (s, 3H, CMe), 1.42 (s, 3H, CMe), 1.75 (t, *J* = 5.7 Hz, 2H, 7-CH₂), 2.28 (d, *J* = 6.0 Hz, 2H, 12-CH₂), 3.33 (s, 3H, OMe), 3.63 (s, 4H, 1-CH₂ and 5-CH₂), 3.75 (s, 2H, MeOCH₂), 4.08 (t, *J* = 5.7 Hz, 2H, 8-CH₂), 4.84 (t, *J* = 6.0 Hz, 1H, 11-H); ¹³C-NMR (67.8 MHz, CDCl₃) δ: 22.6, 25.0, 29.5, 34.8, 36.2, 58.0, 67.5, 68.6 (2C), 73.5, 98.1, 103.0, 155.4; MS (FAB) *m/z* (%) 243 (MH⁺, 100); HRMS (FAB) calcd for C₁₃H₂₃O₄ (MH⁺): 243.1596; found: 243.1577.

4-Methoxymethyl-1,6-dihydro-2H-benzo[d]oxocine (57) and **4-Methylene-1,4-dihydro-2H-benzo[d]oxocine (58)** (Table 5, entry 3). By a procedure identical with that described for the preparation of the 1,4-oxazepine **26c** from **17c**, the bromoallene **49** (50.6 mg, 0.20 mmol) was converted into, in order to elution, **58** (24 mg, 70% yield) and **57** (5.5 mg, 13% yield).

Compound **57**: colorless oil; IR (KBr) cm⁻¹: 1675 (C=C–O); ¹H-NMR (500 MHz, CDCl₃) δ: 3.13 (t, *J* = 5.0 Hz, 2H, 1-CH₂), 3.30 (s, 3H, OMe), 3.40 (d, *J* = 7.5 Hz, 2H, 6-CH₂), 3.73 (s, 2H, MeOCH₂), 4.00 (t, *J* = 5.0 Hz, 2H, 2-CH₂), 5.47 (t, *J* = 7.5 Hz, 1H, 5-H), 7.08–7.15 (m, 4H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ: 31.9, 37.9, 58.2, 71.8, 73.3, 117.4, 126.5, 126.7, 128.7, 130.2, 138.8, 141.1, 152.4; MS (FAB) *m/z* (%) 211 (MLi⁺, 100); HRMS (FAB) calcd for C₁₃H₁₆O₂Na (MNa⁺): 227.1048; found: 227.1054.

Compound **58**: colorless oil; IR (KBr) cm⁻¹: 1712 (C=C–O); ¹H-NMR (300 MHz, CDCl₃) δ: 3.01 (t, *J* = 6.0 Hz, 2H, 1-CH₂), 4.08 (t, *J* = 6.0 Hz, 2H, 2-CH₂), 4.89 (s, 1H, C=CHH), 4.93 (s, 1H, C=CHH), 6.15 (d, *J* = 12.3 Hz, 1H, CH=CH), 6.24 (d, *J* = 12.3 Hz, 1H, CH=CH), 7.14–7.25 (m, 4H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ: 34.3, 76.3, 108.5, 126.4, 127.83, 127.84, 128.1, 129.2, 130.0, 137.3, 137.8, 160.9; MS (FAB) *m/z* (%) 173 (MH⁺, 70), 172 (100); HRMS (FAB) calcd for C₁₂H₁₃O (MH⁺): 173.0966; found: 173.0953.

7-(Methoxymethyl)-4,4-dimethyl-1-(4-methylphenylsulfonyl)-2,3,4,5-tetrahydro-1H-azepine (59). By a procedure identical with that described for the preparation of **56** from **52**, the bromoallene **53** (74.5 mg, 0.2 mmol) was converted into **59** (48.9 mg, 76%) as a colorless oil: IR (KBr) cm^{-1} : 1668 (C=C–N), 1346 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 0.88 (s, 6H, 2 × CMe), 1.56 (t, J = 6.0 Hz, 2H, 3-CH₂), 1.75 (d, J = 7.2 Hz, 2H, 5-CH₂), 2.42 (s, 3H, PhMe), 3.28 (s, 3H, OMe), 3.40–3.44 (m, 2H, 2-CH₂), 4.08 (s, 2H, MeOCH₂), 5.71 (t, J = 7.2 Hz, 1H, 6-H), 7.27–7.30 (m, 2H, Ph), 7.77–7.80 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃, 333 K) δ : 21.3, 28.2 (2C), 29.6, 38.6, 42.7, 45.7, 58.0, 74.2, 126.7, 127.2 (2C), 129.4 (2C), 139.0, 139.8, 143.0; MS (FAB) m/z (%) 324 (MH⁺, 100); HRMS (FAB) calcd for C₁₇H₂₆NO₂S (MH⁺): 324.1633; found: 324.1630

4,4-Bis(benzyloxymethyl)-1-methanesulfonyl-7-(methoxymethyl)-2,3,4,5-tetrahydro-1H-azepine (60) (Table 5, entry 5). By a procedure identical with that described for the preparation of **56** from **52**, the bromoallene **54** (36 mg, 0.07 mmol) was converted into **60** (24.4 mg, 76% yield) as a colorless oil: IR (KBr) cm^{-1} : 1666 (C=C–N), 1336 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.82 (t, J = 5.7 Hz, 2H, 3-CH₂), 2.26 (d, J = 7.2 Hz, 2H, 5-CH₂), 2.98 (s, 3H, SO₂Me), 3.19 (s, 3H, OMe), 3.31–3.40 (m, 6H, 2-CH₂ and 2 × BnOCH₂), 4.03 (s, 2H, MeOCH₂), 4.48 (s, 4H, 2 × PhCH₂), 5.51 (t, J = 7.2 Hz, 1H, 6-H), 7.24–7.35 (m, 10H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 31.0, 34.9, 38.3, 40.5, 45.0, 57.7, 72.5, 73.2 (4C), 124.7 (2C), 127.3 (4C), 127.4, 128.2 (4C), 138.5 (2C), 139.9; MS (FAB) m/z (%) 460 (MH⁺, 7), 91 (100); HRMS (FAB) calcd for C₂₅H₃₄NO₅S (MH⁺): 460.2158; found: 460.2135.

3-Methanesulfonyl-4-methoxymethyl-1H,2H,3H,6H-benzo[d]azocine (61) and 3-Methanesulfonyl-4-methylene-1H,2H,3H,4H-benzo[d]azocine (62) (Table 5, entry 6). By a procedure identical with that described for the preparation of the 1,5-oxazepine **26c** from **17c**, the bromoallene **50** (66 mg, 0.2 mmol) was converted into, in order to elution, **62** (2.5 mg, 5% yield) and **61** (33.5 mg, 60% yield).

Compound **61**: colorless crystals; mp 88 °C (*n*-hexane–Et₂O); IR (KBr) cm^{-1} : 1670 (C=C–N), 1336 (NSO₂); ¹H-NMR (300 MHz, CDCl₃, 333 K) δ : 2.60–4.00 (m, 14H), 5.98 (t, J = 7.2 Hz, 1H, 5-H), 7.10–7.15 (m, 4H, Ph); MS (FAB) m/z (%) 282 (MH⁺, 68), 250 (100); HRMS (FAB) calcd for C₁₄H₂₀NO₃S (MH⁺): 282.1164; found: 282.1147. Anal. Calcd for C₁₄H₁₉NO₃S: C, 59.76; H, 6.81; N, 4.98. Found: C, 59.69; H, 6.77; N, 4.97.

Compound **62**: colorless solid; IR (KBr) cm^{-1} : 1630 (C=C–N), 1331 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.07 (s, 3H, SO₂Me), 2.96 (t, J = 6.0 Hz, 2H, 1-CH₂), 3.76 (t, J = 6.0 Hz, 2H, 2-CH₂), 5.53 (d, J = 0.6 Hz, 1H, C=CHH), 5.68 (s, 1H, C=CHH), 6.30 (d, J = 12.6 Hz, 1H, CH=CH), 6.34 (d, J = 12.6 Hz, 1H, CH=CH), 7.14-7.29 (m, 4H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 32.7, 39.4, 53.4, 126.2, 127.0, 128.3, 128.4, 129.2, 129.7, 130.0, 136.9, 137.3, 142.2; MS (FAB) m/z (%) 250 (MH⁺, 80), 136 (100); HRMS (FAB) calcd for C₁₃H₁₆NO₂S (MH⁺): 250.0902; found: 250.0898.

2-(1-Benzyloxyvinyl)tetrahydropyran (64) and 7-(Benzyloxymethyl)-2H,3H,4H,5H-oxepine (65). By a procedure identical with that described for the preparation of the 1,5-oxazepine **26c** from **17c**, the bromoallene **63** (38.2 mg, 0.2 mmol) was converted into, in order to elution, **64** (28.3 mg, 65% yield) and **65** (5.7 mg, 13% yield) by the reaction with BnOH.

Compound **64**: colorless oil; IR (KBr) cm^{-1} : 1662 (C=C–O); ¹H-NMR (300 MHz, CDCl₃) δ : 1.49-1.68 (m, 4H, 2 × CH₂), 1.85-1.89 (m, 2H, CH₂), 3.51 (dd, J = 12.3, 2.4 Hz, 1H, 6-CHH), 3.78-3.81 (m, 1H, 2-H), 4.06-4.11 (m, 1H, 6-CHH), 4.07 (d, J = 2.4 Hz, 1H, C=CHH), 4.28 (d, J = 2.4 Hz, 1H, C=CHH), 4.80 (s, 2H, PhCH₂), 7.27-7.36 (m, 5H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 23.4, 25.8, 30.5, 68.8, 69.2, 78.3, 81.6, 127.3 (2C), 127.6, 128.4 (2C), 137.1, 162.9; MS (FAB) m/z (%) 219 (MH⁺, 18), 91 (100); HRMS (FAB) calcd for C₁₄H₁₉O₂ (MH⁺): 219.1385; found: 219.1393.

Compound **65**: colorless oil; IR (KBr) cm^{-1} : 1685 (C=C–O); ¹H-NMR (300 MHz, CDCl₃) δ : 1.65 (tt, J = 5.7, 5.7 Hz, 2H, CH₂), 1.86 (tt, J = 5.7, 5.7 Hz, 2H, CH₂), 2.16 (td, J = 5.7, 5.7 Hz, 2H, 5-CH₂), 3.86 (s, 2H, CH₂OBn), 3.98 (t, J = 5.7 Hz, 2H, 2-CH₂), 4.55 (s, 2H, PhCH₂), 5.04 (t, J = 5.7 Hz, 1H, 6-H), 7.26-7.36 (m, 5H, Ph); ¹³C-NMR (67.8 MHz, CDCl₃) δ : 25.9, 26.0, 31.8, 71.6, 72.0, 72.4, 108.9, 127.4, 127.6 (2C), 128.2 (2C), 138.2, 155.9; MS (FAB) m/z (%) 219 (MH⁺, 23), 91 (100); HRMS (FAB) calcd for C₁₄H₁₉O₂ (MH⁺): 219.1385; found: 219.1377.

(4S,aS)-1-Bromo-4-{N,N-[4,4-bis(methoxycarbonyl)butyl](4-methylphenylsulfonyl)amino}-5-phenylpenta-1,2-diene (68). To a stirred mixture of PPh₃ (655 mg, 2.5 mmol), the bromoallene **17b** (225 mg, 0.5 mmol) and diisopropylethylamine (0.436 mL, 2.5 mmol) in CH₂Cl₂ (6 mL) under nitrogen was added I₂ (635 mg, 2.5 mmol) at room temperature, and the mixture was stirred for 4.5 h at this temperature. Concentration under reduced pressure gave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give the corresponding iodide. To a stirred suspension of NaH (25.6 mg, 0.63 mmol) in DMF (1.5 mL) under nitrogen was added dimethyl malonate (81.2 mg, 0.71 mmol) at 0 °C, and the mixture was

stirred for 20 min at room temperature. To the stirred mixture was added a solution of the above iodide in DMF (3 mL) at 0 °C, and the mixture was stirred for 2 h at room temperature. The mixture was poured into ice–water (1 mL) saturated with NH₄Cl, and the whole was extracted with Et₂O. The extract was washed with water and brine, and dried over MgSO₄. Concentration under reduced pressure gave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **68** (186 mg, 70% yield) as a colorless oil: [α]¹⁹_D +39.6 (*c* 1.02, CHCl₃); IR (KBr) cm⁻¹: 1957 (C=C=C), 1751 (C=O), 1732 (C=O) 1342 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.64-1.83 (m, 2H, CH₂), 1.86-1.96 (m, 2H, CH₂), 2.40 (s, 3H, *PhMe*), 2.86 (dd, *J* = 14.1, 6.0 Hz, 1H, *PhCHH*), 2.95 (dd, *J* = 14.1, 8.4 Hz, 1H, *PhCHH*), 3.10-3.27 (m, 2H, CH₂), 3.39 [dd, *J* = 7.5, 7.5 Hz, 1H, (MeO₂C)₂CH], 3.75 (s, 6H, 2 $\times$ CO₂Me), 4.75-4.82 (m, 1H, 4-H), 5.20 (dd, *J* = 5.7, 5.7 Hz 1H, 3-H), 6.01 (dd, *J* = 5.7, 2.1 Hz, 1H, 1-H), 7.10-7.24 (m, 7H, Ph), 7.58-7.61 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 21.5, 26.2, 28.6, 38.8, 44.2, 51.1, 52.6 (2C), 57.1, 75.5, 99.2, 126.6, 127.2 (2C), 128.5 (2C), 129.0 (2C), 129.7 (2C), 137.2 (2C), 143.4, 169.5 (2C), 202.7; MS (FAB) *m/z* (%) 566 (MH⁺, ⁸¹Br, 11), 564 (MH⁺, ⁷⁹Br, 12), 91 (100); HRMS (FAB) calcd for C₂₆H₃₁BrNO₆S (MH⁺, ⁷⁹Br): 564.1056; found: 564.1080.

1,3,4,8-tetrahydro-2H-azocine (69). By a procedure identical with that described for the preparation of the 1,5-oxazepine **26c** from **17c**, the bromoallene **68** (56.4 mg, 0.10 mmol) was converted into **69** (16.2 mg, 31%) as a colorless oil: $[\alpha]_D^{26} -18.0$ (*c* 1.58, CHCl₃); IR (KBr) cm⁻¹: 1738 (C=O), 1342 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 1.37-1.49 (m, 1H, 3-CHH), 1.87-1.99 (m, 1H, 3-CHH), 2.35-2.46 (m, 1H, 4-CHH), 2.39 (s, 3H, PhMe), 2.56-2.62 (m, 1H, 4-CHH), 3.03-3.14 (m, 2H, 2-CHH and PhCHH), 3.14 (s, 3H, OMe), 3.25 (dd, *J* = 15.0, 8.7 Hz, 1H, PhCHH), 3.62-3.80 (m, 1H, 2-CHH), 3.69 (s, 6H, 2 $\times$ CO₂Me), 3.76 (d, *J* = 11.7 Hz, 1H, MeOCHH), 4.21 (d, *J* = 11.7 Hz, 1H, MeOCHH), 5.22 (ddd, *J* = 8.7, 8.7, 5.1 Hz, 1H, 8-H), 5.74 (d, *J* = 5.1 Hz, 1H, 7-H), 7.11-7.28 (m, 7H, Ph), 7.51-7.53 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ : 21.4, 28.2, 36.6, 41.1, 44.4, 52.6, 52.9, 58.3, 60.8, 65.8, 68.0, 126.4, 127.0 (2C), 128.5 (4C), 129.5 (2C), 135.1, 137.5, 137.9, 138.6, 142.9, 169.5, 169.8; MS (FAB) *m/z* (%) 516 (MH⁺, 19), 424 (100); HRMS (FAB) calcd for C₂₇H₃₄NO₇S (MH⁺): 516.2056; found: 516.2093.

(2*R*,a*S*)-5-Bromo-2-[*N,N*-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]penta-3,4-dien-1-ol (83). By a procedure similar to that described for the preparation of the bromoallene **15a** from **13a**, the bromoallene **S8** (112 mg, 0.25 mmol) was converted into **83** (80 mg, 85% yield) as colorless crystals: mp 116 °C (*n*-hexane–EtOAc); [α]_D²⁶ –56.0 (*c* 1.00, CHCl₃); IR (KBr) cm^{–1}: 3521 (OH), 3323 (OH), 1957 (C=C=C), 1333 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ : 2.43 (s, 3H, *PhMe*), 2.99 (br s, 1H, OH), 3.16 (ddd, *J* = 15.3, 9.9, 3.9 Hz, 1H, *CHH*), 3.49 (ddd, *J* = 15.3, 3.0, 3.0 Hz, 1H, *CHH*), 3.63–3.79 (m, 4H, 1-CH₂, *CHH* and OH), 4.05–4.13 (m, 1H, *CHH*), 4.57–4.65 (m, 1H, 2-H),

5.01 (dd, $J = 5.7, 5.7$ Hz, 1H, 3-H), 5.98 (dd, $J = 5.7, 2.4$ Hz, 1H, 5-H), 7.31-7.34 (m, 2H, Ph), 7.74-7.77 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 21.6, 45.8, 57.3, 61.8, 62.1, 74.7, 95.5, 127.4 (2C), 129.9 (2C), 136.6, 144.0, 202.6. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{BrNO}_4\text{SSi}$: C, 44.69; H, 4.82; N, 3.72. Found: C, 44.77; H, 4.78; N, 3.69.

(3R)-5-Methoxymethyl-3-[N,N-(2-hydroxyethyl)(4-methylphenylsulfonyl)amino]-2H,3H-furan (86), (1S,6S)-5-Aza-9-methylene-5-(4-methylphenylsulfonyl)-2,8-dioxabicyclo[4.3.0]nonane (87), and (5R)-5-Hydroxymethyl-7-methoxymethyl-4-(4-methylphenylsulfonyl)-2H,3H,4H,5H-1,4-oxazepine (89). By a procedure similar to that described for the preparation of the 1,4-oxazepine **24a** and **25a** from **15a**, the bromoallene **83** (56.4 mg, 0.15 mmol) was converted into, in order of elution, **87** (5 mg, 11% yield), **86** (15 mg, 31% yield), and **89** (22 mg, 45% yield) by treatment with NaOMe (17.8 mg, 0.33 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (17.3 mg, 0.015 mmol) in MeOH (2.25 mL) at room temperature for 5 h.

Compound **86**: colorless oil; $[\alpha]^{24}_{\text{D}} -39.8$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 3533 (OH), 1666 ($\text{C}=\text{C}-\text{O}$), 1335 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 2.45 (s, 3H, PhMe), 2.49 (dd, $J = 6.0, 6.0$ Hz, 1H, OH), 3.05 (ddd, $J = 15.3, 5.4, 5.4$ Hz, 1H, CHH), 3.18 (ddd, $J = 15.3, 6.0, 5.1$ Hz, 1H, CHH), 3.34 (s, 3H, OMe), 3.70-3.81 (m, 2H, CH_2), 3.93 (s, 2H, MeOCH_2), 4.05 (dd, $J = 11.1, 3.0$ Hz, 1H, 2- CHH), 4.27 (dd, $J = 11.1, 9.3$ Hz, 1H, 2- CHH), 4.67 (d, $J = 3.0$ Hz, 1H, 4-H), 5.27 (ddd, $J = 9.3, 3.0, 3.0$ Hz, 1H, 3-H), 7.32-7.34 (m, 2H, Ph), 7.68-7.71 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 21.5, 45.8, 58.9, 61.6, 62.7, 66.9, 74.0, 96.3, 127.1 (2C), 130.0 (2C), 136.4, 143.9, 160.5; MS (FAB) m/z (%) 350 (MNa^+ , 100); HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{21}\text{NNaO}_5\text{S}$ (MNa^+): 350.1038; found: 350.1063.

Compound **87**: colorless oil; $[\alpha]^{27}_{\text{D}} +21.0$ (c 1.21, CHCl_3); IR (KBr) cm^{-1} : 1680 ($\text{C}=\text{C}-\text{O}$), 1352 (NSO_2); ^1H -NMR (500 MHz, CDCl_3) δ : 2.45 (s, 3H, PhMe), 3.16 (ddd, $J = 13.0, 11.5, 3.0$ Hz, 1H, 4- CHH), 3.47 (ddd, $J = 11.5, 11.5, 2.5$ Hz, 1H, 3- CHH), 3.54 (ddd, $J = 13.0, 2.5, 2.5$ Hz, 1H, 4- CHH), 3.91 (ddd, $J = 11.5, 3.0, 2.5$ Hz, 1H, 3- CHH), 3.94-3.96 (m, 2H, 7- CH_2), 4.09 (d, $J = 4.5$ Hz, 1H, 1-H), 4.22 (d, $J = 2.5$ Hz, 1H, $\text{C}=\text{CHH}$), 4.25-4.30 (m, 1H, 6-H), 4.42 (d, $J = 2.5$ Hz, 1H, $\text{C}=\text{CHH}$), 7.33-7.35 (m, 2H, Ph), 7.69-7.71 (m, 2H, Ph); ^{13}C -NMR (75 MHz, CDCl_3) δ : 21.6, 40.5, 53.1, 64.1, 65.7, 73.4, 86.1, 127.2 (2C), 130.1 (2C), 135.8, 144.3, 159.8; MS (FAB) m/z (%) 296 (MH^+ , 100); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_4\text{S}$ (MH^+): 296.0957; found: 296.0972.

Compound **89**: colorless oil; $[\alpha]^{23}_{\text{D}} +3.13$ (c 1.60, CHCl_3); IR (KBr) cm^{-1} : 3427 (OH), 1674 ($\text{C}=\text{C}-\text{O}$), 1327 (NSO_2); ^1H -NMR (300 MHz, CDCl_3) δ : 2.24 (br s, 1H, OH), 2.41 (s, 3H, PhMe), 3.22 (s, 3H, OMe), 3.55-3.76 (m, 3H, CH_2 and CHH), 3.56 (d, $J = 12.9$ Hz, 1H, MeOCHH), 3.64 (d, $J = 12.9$ Hz, 1H, MeOCHH), 3.84 (ddd, $J = 12.3, 6.9, 2.4$ Hz, 1H, CHH), 4.01 (ddd, $J = 15.0, 6.3, 1.8$ Hz, 1H, CHH), 4.13 (ddd, $J = 12.3, 6.6, 1.8$ Hz, 1H, CHH), 4.64 (ddd, $J = 8.1, 6.9, 5.1$ Hz, 1H, 5-H), 4.75 (d, $J = 6.9$ Hz, 1H, 6-H), 7.27-7.29 (m, 2H, Ph), 7.71-7.74 (m, 2H, Ph); ^{13}C -NMR (75

MHz, CDCl₃) δ : 21.5, 46.0, 57.0, 58.1, 62.9, 70.5, 72.9, 101.2, 127.3 (2C), 129.6 (2C), 137.3, 143.5, 156.4; MS (FAB) m/z (%) 328 (MH⁺, 17), 296 (100); HRMS (FAB) calcd for C₁₅H₂₂NO₅S (MH⁺): 328.1219; found: 328.1224.

8-Bromo-4,4-dimethylocta-6,7-dien-1-ol (90). To a stirred solution of oxalyl chloride (0.393 mL, 4.5 mmol) in CH₂Cl₂ (8 mL) at –78 °C under nitrogen was added dropwise a solution of DMSO (1.07 mL, 15.0 mmol) in CH₂Cl₂ (5 mL). After 1 h, a solution of the alcohol **51** (658 mg, 3.0 mmol) in CH₂Cl₂ (5 mL) was added to the above reagent at –78 °C, and the mixture was stirred for 1 h at this temperature. Diisopropylethylamine (3.61 mL, 21.0 mmol) was added to the above solution at –78 °C and the mixture was stirred for 30 min with warming to 0 °C. The mixture was made acidic with 4% HCl, and the whole was extracted with Et₂O. The extract was washed successively with water, saturated NaHCO₃, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give a crude aldehyde as an oil. To a stirred solution of (methoxymethyl)triphenylphosphonium chloride (3.09 g, 9.0 mmol) in THF (15 mL) at 0 °C under argon was added dropwise *n*-BuLi (1.58 M solution in *n*-hexane; 5.69 mL, 9.0 mmol). After 1 h, a solution of the crude aldehyde in dry THF (7 mL) was added to the above stirred reagent at 0 °C, and the mixture was stirred for 3 h at this temperature, followed by quenching with saturated NH₄Cl. The whole was extracted with Et₂O. The extract was washed with brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by short column chromatography over silica gel with *n*-hexane–EtOAc (200:1) to give the corresponding methyl enol ether. To a stirred solution of the methyl enol ether in dioxane/H₂O (9:1, 20 mL) was added *p*-TSA·H₂O (571 mg, 3 mmol) at room temperature, and the mixture was stirred for 5 h at this temperature. To this mixture was added NaBH₄ (114 mg, 3 mmol) at 0 °C, and the mixture was stirred for 5 h at room temperature, followed by quenching with saturated NH₄Cl. The whole was extracted with Et₂O. The extract was washed with brine, and dried over MgSO₄. The mixture was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **90** (128 mg, 18% yield) as a colorless oil: IR (KBr) cm^{–1}: 3325 (OH), 1954 (C=C=C); ¹H-NMR (300 MHz, CDCl₃) δ : 0.93 (s, 6H, 2 × CMe), 1.25–1.59 (m, 5H, 2-CH₂, 3-CH₂, and OH), 2.06 (dd, *J* = 8.1, 1.8 Hz, 2H, 5-CH₂), 3.64 (t, *J* = 6.3 Hz, 2H, 1-CH₂), 5.35 (td, *J* = 8.1, 5.7 Hz, 1H, 6-H), 5.91 (dt, *J* = 5.7, 1.8 Hz, 1H, 8-H); ¹³C-NMR (75 MHz, CDCl₃) δ : 27.0 (2C), 27.5, 33.9, 37.4, 40.9, 63.7, 71.4, 97.5, 202.9; MS (FAB) m/z (%) 241 (MLi⁺, ⁸¹Br, 94), 239 (MLi⁺, ⁷⁹Br, 100); HRMS (FAB) calcd for C₁₀H₁₇BrNaO (MNa⁺, ⁷⁹Br): 255.0360; found: 255.0369.

(Z)-7,8-Dimethoxy-4,4-dimethyloct-6-en-1-ol (91). By a procedure similar to that described for the preparation of **56** from **52**, the bromoallene **90** (36.1 mg, 0.15 mmol) was converted into **91** (15.6

mg, 48%) by treatment with NaH (9 mg, 0.225 mmol) and Pd(PPh₃)₄ (17.3 mg, 0.015 mmol) in MeOH at 50 °C for 40 h: colorless oil; IR (KBr) cm⁻¹: 3425 (OH), 1674 (C=C–O); ¹H-NMR (300 MHz, CDCl₃) δ: 0.88 (s, 6H, 2 × CMe), 1.20–1.26 (m, 2H, CH₂), 1.46–1.60 (m, 2H, CH₂), 1.68 (br s, 1H, OH), 2.01 (d, *J* = 7.5 Hz, 2H, 5-CH₂), 3.33 (s, 3H, OMe), 3.61 (t, *J* = 6.6 Hz, 2H, 1-CH₂), 3.63 (s, 3H, OMe), 3.96 (s, 2H, 8-CH₂), 4.76 (t, *J* = 7.5 Hz, 1H, 6-H); ¹³C-NMR (67.8 MHz, CDCl₃) δ: 27.1 (2C), 27.7, 33.2, 36.4, 37.5, 56.3, 57.2, 63.8, 71.4, 110.1, 151.2; MS (FAB) *m/z* (%) 239 (MNa⁺, 76), 115 (100); HRMS (FAB) calcd for C₁₂H₂₄NaO₃ (MNa⁺): 239.1632; found: 239.1621.

5,5-Dimethyl-7-[N-(4-methylphenylsulfonyl)amino]hepta-1,2-diene (92). To a stirred mixture of InI (283 mg, 1.17 mmol) and Pd(PPh₃)₄ (52 mg, 5 mol%, 0.045 mmol) in THF (9 mL) were added the bromoallene **53** (335 mg, 0.9 mmol) and H₂O (1 mL) at room temperature. The mixture was stirred for 7 h at this temperature and quenched with 4% HCl. The whole was extracted with Et₂O and the extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **92** (200 mg, 76% yield) as a colorless oil; IR (KBr) cm⁻¹: 3290 (NHSO₂), 1954 (C=C=C), 1325 (NHSO₂); ¹H-NMR (300 MHz, CDCl₃) δ: 0.84 (s, 6H, 2 × CMe), 1.36–1.42 (m, 2H, 6-CH₂), 1.84 (dt, *J* = 8.1, 2.4 Hz, 2H, 4-CH₂), 2.44 (s, 3H, PhMe), 2.91–2.98 (m, 2H, 7-CH₂), 4.40 (t, *J* = 6.3 Hz, 1H, NH), 4.57 (dt, *J* = 6.3, 2.4 Hz, 2H, 1-H), 4.90–4.99 (m, 1H, 3-H), 7.31–7.33 (m, 2H, Ph), 7.74–7.77 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ: 21.5, 26.7 (2C), 33.2, 39.4, 40.8, 41.1, 73.7, 85.7, 127.1 (2C), 129.7 (2C), 136.9, 143.4, 209.6; MS (FAB) *m/z* (%) 294 (MH⁺, 100); HRMS (FAB) calcd for C₁₆H₂₄NO₂S (MH⁺): 294.1528; found: 294.1517.

4,4-Dimethyl-1-(4-methylphenylsulfonyl)-2-vinylpiperidine (93). A mixture of PdBr₂ (5.3 mg, 0.02 mmol) and PPh₃ (10.5 mg, 0.04 mmol) were dissolved in MeOH (1 mL) at room temperature under nitrogen and the mixture was stirred for 10 min at this temperature. To the stirred mixture were added a solution of the allene **92** (58.7 mg, 0.2 mmol) in MeOH (1 mL) and a preformed mixture of NaH (12 mg, 0.3 mmol) in MeOH (1 mL) (after stirring for 10 min) at room temperature. The mixture was stirred for 3.5 h at 55 °C and quenched with saturated NH₄Cl. The whole was extracted with Et₂O. The extract was washed with water, and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **93** (30 mg, 51% yield) as a colorless oil: IR (KBr) cm⁻¹: 1346 (NSO₂); ¹H-NMR (300 MHz, CDCl₃) δ: 0.80 (s, 3H, CMe), 0.91 (s, 3H, CMe), 1.22–1.31 (m, 2H, CH₂), 1.35–1.51 (m, 2H, CH₂), 2.43 (s, 3H, PhMe), 3.31–3.35 (m, 2H, 6-CH₂), 4.14–4.19 (m, 1H, 2-H), 5.02–5.10 (m, 2H, CH=CH₂), 5.79–5.90 (m, 1H, CH=CH₂), 7.27–7.30 (m, 2H, Ph), 7.68–7.71 (m, 2H, Ph); ¹³C-NMR (75 MHz, CDCl₃) δ: 21.5, 27.5, 28.9, 30.6, 37.3, 39.9, 43.7, 55.6, 114.2, 127.4 (2C), 129.4 (2C), 136.9, 138.7, 143.0; MS (FAB) *m/z* (%) 294

(MH⁺,100); HRMS (FAB) calcd for C₁₆H₂₄NO₂S (MH⁺): 294.1528; found: 294.1545.

DFILE D:\2001\010823 No280 metoxy azir
 COMNT metoxy aziridine
 DATIM Thu Aug 23 20:41:29 2001
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 21.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE C:\WINNMR95\COMMON_DEFAULT.ALS
 COMNT
 DATIM Tue Jul 16 19:21:08 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 21.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 23

D:\2002.1.24-\NTs, aziridine mud
 COMNT NTs,aziridine
 DATIM Mon Jul 15 15:25:07 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSST 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 FW1 5.8 us
 IRNUC 1H
 CTEMP 21.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 21

D:\2002.1.24-\No534 bromoallene
 COMNT No534 pure bromoallene 1H
 DATIM Wed Aug 07 17:11:01 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSST 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 FW1 5.5 us
 IRNUC 1H
 CTEMP 21.8 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

DFILE D:\2001\No385 main product 1H.a1.
 COMNT No385 main product
 DATIM Mon Dec 17 11:33:32 2001
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSETE 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 22.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 18

Date: Wed May 15 18:57:37 2002
 FileName: se101.mdata
 Comment: 1H Line
 SliceHistory
 EXMODE non
 POINT 16384 points
 SAMPD 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEACT 58.7 usec
 INTVL 100.0 usec
 TIMES 16 times
 DUMY 1 times
 PD 5.3615 sec
 ACQTM 1638.3999 msec
 PRECL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.01 Hz
 PW1 2.63 usec
 OBNUC 1H
 OBFREQ 500.00 MHz
 OBSETE 162167.63 Hz
 RGAIN 20
 SCANS 16 times
 SLVNT CDCL3
 SPINNT 14 Hz
 TEMP 22.1 C

DFILE F:\2002.1.24-\021024 TBSOCH
COMNT TBSOCH2,NHTs,brmoallene
DATIM Thu Oct 24 19:52:59 2002
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 32
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.5 us
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 15

DFILE D:\2002.1.24-\TBSOCH2,NTs,C2H4OH
COMNT Thu Oct 17 19:35:06 2002
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 32
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.5 us
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15

DFILE D:\MO20 date2.als
 COMNT MO20 date2
 DATIM Wed Oct 02 19:24:20 2002
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 22.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

DFILE D:\2002.1.24-020808 iPr, NTS, a
 COMNT iPr, NTS, alkyne
 DATIM Thu Aug 08 17:54:08 2002
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 20.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE D:\2002.1.24\020610 No. 516 1H.a
 COMNT 020610 No. 516
 DATIM Mon Jun 10 22:10:09 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 FW1 5.8 us
 IRNUC 1H
 CTEMP 20.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE D:\2002.1.24\No.516 bromoallene
 COMNT No.516 bromoallene 1H
 DATIM Sat Jun 15 15:24:49 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 26
 ACQTM 5.449 sec
 PD 1.551 sec
 FW1 5.8 us
 IRNUC 1H
 CTEMP 20.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

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DEFILE C:\WINNMR95\COMMON\_DEFAULT.ALS
COMBID TSNC2H4NHTs No454
DATIM Tue Mar 05 11:25:34 2002
OBNUC 1H
EXMOD NON
OBFREQ 300.40 MHz
OBSSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 32
ACQTM 5.449 sec
PD 1.551 sec
PWL 5.8 us
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19

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DFILE D:\2002.1.24-\No457 main 1H.a1s
 COMMENT No457 main 1H-NMR
 DATIM Fri Mar 08 21:10:38 2002
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSEF 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTMP 23.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

Date : Wed Dec 16 10:57:54 2002
 FileName Loading\ID.nmdata
 Comment 1H Line
 SliceHistory
 EXMOD non
 POINT 16384 points
 SAMP 16384 points
 FREQ 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEADT 58.7 usec
 INVT 100.0 usec
 TIMES 16 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3599 msec
 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 2.63 usec
 OBNUC 1H
 OBFREQ 500.00 MHz
 OBSEF 162167.63 Hz
 RGAIN 23
 SCANS 16 times
 SLVNT CDCL3
 SPINNING 14 Hz
 TEMP 26.2 C

DFILE D:\2002.1.24-\No633 NTs,NMs,8cyc
 COMNT
 DATIM Mon Dec 02 16:39:19 2002
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 24.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE D:\2002.1.24-\020419 Me,Ts-upbroi
 COMNT
 DATIM Fri Apr 19 21:13:15 2002
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 17
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 22.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE D:\2002.1.24-\020425 No491TsNC2H
 COMBT No491
 DATIM Thu Apr 25 17:19:20 2002
 OBNUC 1H
 EXMOD NON
 OBFRO 300.40 MHz
 OBSEF 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTMP 24.3 c
 SLVNT CDCl₃
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

Date: Fri Aug 23 19:54:49 2002
 FileName seilzoi.nmdata
 Comment 1H Line
 SliceHistory
 EXMODE non
 POINT 16384 points
 SAMPD 16384 points
 FREQU 10000.0 Hz
 FILT 5000 Hz
 DELAY 40.0 usec
 DEADT 58.7 usec
 INVL 100.0 usec
 TIMES 32 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3859 msec
 PREDL 0.01000 msec
 ININT 1000.0000 msec
 RESOL 0.51 Hz
 PW1 2.53 usec
 OBNUC 1H
 OBFRO 500.00 MHz
 OBSEF 162167.63 Hz
 RGAIN 20
 SCANS 32 times
 SLVNT CDCl₃
 SPINNING 11 Hz
 TEMP 22.9 C

1,1,1,3,3,3-hexafluoro-4-(trifluoromethyl)-2-butene Temp: 60 °C

Chemical Shift (ppm): 7.311, 7.305, 7.283, 7.279, 7.259, 7.241, 7.232, 7.227, 7.208, 7.197, 7.191, 7.169, 6.049, 6.041, 6.030, 6.023, 5.433, 5.415, 5.397, 4.589, 4.567, 4.546, 4.523, 4.503, 4.474, 2.963, 2.941, 2.913, 2.886, 2.891, 2.844, 2.827, 1.417, 1.169, 1.000, 1.062, 2.0767, 2.3122, 5.9915, 11.2335

Integration: 0.000, 0.1169, 1.0000, 1.0620, 2.0767, 2.3122, 11.2335

34
(300 MHz, CDCl₃)

```

Date : Wed Oct 16 10:20:55 2002
Filename: Loading1D.mdata
Comments: 1H Line
Slicer:
History:
EXMODE: non

POINT          16384 points
SAMP0          16384 points
FREQ0          100000 Hz
FILT0          5000 Hz
DELAY          40.0 usec
DEAD0          50.7 usec
INTVL          100.0 usec
TIMES          32 times
DUMMY          1 times
PD             5.3616 sec
ACQ0T          1638.399 msec
IN0T0          0.01000 msec
IN0T1          1000.0000 msec
RES0L          0.61 Hz
PWL0           2.63 usec
DM0C           1H
DBF0RQ         500.00 MHz
DBF0FQ         152167.63 Hz
RGAIN          19
SCANS          32 times

SLVNT          CDCL3
SPINNING      14 Hz
TEMP          22.8 C

```

DFILE D:\2002.1.24-\Bn,NSESC2H4OH,brom
 COMNT Bn,NSESC2H4OH,bromoallene 1H
 DATIM Thu Oct 10 13:49:17 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 24.1 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 RF 0.12 Hz
 RGAIN 14

DFILE D:\2002.1.24-\021016 No615 Bn,NS
 COMNT Bn,NSES,7cycle
 DATIM Wed Oct 16 20:39:53 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 23.7 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 RF 0.12 Hz
 RGAIN 15

DFILE D:\2002.1.24-\Bn,NH,7cycle 1H.al.
 COMNT Bn,NH,7cycle
 DATIM Tue Oct 22 16:21:06 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSST 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 23.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

DFILE D:\2002.1.24-\No642 bromoallene
 COMNT No642 bromoallene 1H
 DATIM Mon Nov 25 18:29:25 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSST 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 17
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 25.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

50
(300 MHz, CDCl₃)

S14
(300 MHz, CDCl₃)

DFILE F:\MO-102-DATA.ALS
 COMNT MO-102
 DATIM Sat Jul 05 10:12:10 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 21.7 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

DFILE D:\2003\802 propargylalcohol 1H..
 COMNT 802 propargylalcohol
 DATIM Fri Jul 18 19:40:10 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 17.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

DFILE D:\2003\808 bromoallene pure 1H.
 COMNT 808 bromoallene
 DATIM Sat Jul 19 10:56:12 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 16.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE D:\NO-105-data2.als
 COMNT NO-105-data
 DATIM Wed Jul 23 21:54:32 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 17.7 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE D:\2003\832 diol 1H.als
 COMNT
 DATIM Wed Jul 30 13:22:34 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 16.8 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE F:\2003\DIEN,NMS,BROMOALLEN
 COMNT diBn,NMS,bromoallene
 DATIM Tue Jul 22 14:55:16 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 18.6 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

DFILE D:\NQ-129-data2.als
 COMNT MO-129-data
 DATIM Thu Jun 26 23:19:38 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 17.8 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 12

DFILE D:\2003\030620 main 7 cycle diBn
 COMNT 030620 main diBn, NMs, 7 cycle
 DATIM Fri Jun 20 20:41:57 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 17.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

DFILE D:\2003\030311 No731 no
COMNT NMR 8cycle main
DATIM Thu Mar 13 14:58:27 2003
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 32
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.5 us
IRNUC 1H
CTEMP 59.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14

DFILE D:\2003\030311 No731 no1 pure 1H
COMNT No731 minor b-elimination
DATIM Wed Mar 12 16:39:13 2003
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.5 us
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22

D:\2003\829 6cycle BnOH.als
 COMNT 829 6cycle BnOH
 DATIM Thu Jul 17 14:09:41 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSPT 130.00 KHz
 OBSIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 FWL 5.5 us
 IRNUC 1H
 CTEMP 17.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

D:\2003\829 7cycle BnOH 1H.als
 COMNT 829 7cycle BnOH
 DATIM Thu Jul 17 14:18:20 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSPT 130.00 KHz
 OBSIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 FWL 5.5 us
 IRNUC 1H
 CTEMP 17.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

DFILE D:\41-25date.als
 COMNT 41-25
 DATIM Thu Nov 07 21:38:08 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 FW1 5.5 us
 IRNUC 1H
 CTEMP 25.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE D:\55-26date.als
 COMNT 55-26
 DATIM Thu Nov 07 23:32:47 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 FW1 5.5 us
 IRNUC 1H
 CTEMP 24.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE D:\2002.1.24-No619 bromoallene
 COMNT No. 619 bromoallene
 DATIM Wed Oct 23 19:22:03 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 25.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE D:\2002.1.24-No605 5cycle 1H.a1.
 COMNT No605 5cycle
 DATIM Wed Nov 13 17:56:49 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 24.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE D:\MO-126\data.als
 COMNT MO-126
 DATIM Fri May 30 21:53:56 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTMP 22.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 17

DFILE D:\NO-121-down-data.als
 COMNT NO-121-down
 DATIM Wed Jul 30 22:38:39 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTMP 17.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 15

DFILE D:\2004\979 allene 1H.als
 COMNT
 DATIM Fri Apr 16 20:29:22 2004
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 32
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 4.3 us
 IRNUC 1H
 CTEMP 20.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 17

DFILE C:\WINNMR95\COMMON_DEFAULT.ALS
 COMNT
 DATIM Tue Apr 20 16:31:54 2004
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 32
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 4.3 us
 IRNUC 1H
 CTEMP 23.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 15