Supporting Information

A Highly *cis*-Selective Synthesis of 2-Ethynylaziridines by Intramolecular Amination of Chiral Bromoallenes: Improvement of Stereoselectivity Based on the Computational Investigation

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The known compounds **S1**,¹ **S2**,¹ **S6**,¹ **S8**,³ **S10**,⁴ **6b**,¹ **6f**,¹ **8b**,¹ **8f**,¹ **10g**,² and **11g**² were synthesized according to the literatures.

- 1 Ohno, H.; Toda, A.; Takemoto, Y.; Fujii, N.; Ibuka, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2949–2962.
- 2 Ohno, H.; Hamaguchi, H.; Tanaka, T. *J. Org. Chem.* **2001**, 66, 1867–1875.
- 3 Serrat, X.; Caborrocas, G.; Rafel, S.; Ventura, M.; Linden, A.; Villalgordo, J. M. *Tetrahedron: Asymmetry* **1999**, 10, 3417–3430.
- 4 Supporting Information of the following literature: Ohno, H.; Miyamura, K.; Tanaka, T.; Oishi, S.; Toda, A.; Takemoto, Y.; Fujii, N.; Ibuka, T. *J. Org. Chem.* **2002**, 67, 1359–1367.

(3*S*,4*S*)-5-Methyl-4-[*N*-(4-methylphenylsulfonyl)amino]hex-1-yn-3-ol (6d). Trifluoroacetic acid (3 mL) was added to the amino alcohol **S1** (653 mg, 2.87 mmol) under stirring at 0 °C, and the mixture was stirred for 30 minutes at room temperature. The mixture was concentrated under reduced pressure to oil, which was made alkaline with 28% NH₄OH at 0 °C and the whole was extracted with CH₂Cl₂. The extract was dried over MgSO₄, and filtration and solvent evaporation gave an oily residue. To stirred mixture of this oil and Et₃N (0.99 mL, 7.18 mmol) in CHCl₃ (8 mL) was added TsCl (656 mg, 3.44 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature, followed by quenching with saturated NaHCO₃. The mixture was made acidic with 1 N HCl, and the whole was extracted with a mixed solvent of Et₂O–EtOAc (1:1). The extract was washed successively with water, saturated NaHCO₃, and brine, and dried over MgSO₄. Filtration and solvent evaporation followed by flash chromatography over silica gel with *n*-hexane–EtOAc (1:2) gave **6d** (493 mg, 61% yield) as colorless crystals: mp 113 °C (*n*-hexane–Et₂O); [α]_D²⁵ –22.1

(*c* 1.24, CHCl₃); IR (KBr) cm⁻¹: 3498 (OH), 3275 (NHSO₂), 2118 (C≡C), 1323 (NHSO₂); ¹H NMR (270 MHz, CDCl₃) δ: 0.72 (d, *J* = 6.8 Hz, 3H, CMe), 0.84 (d, *J* = 6.8 Hz, 3H, CMe), 2.04-2.16 (m, 1H, 5-H), 2.36 (d, *J* = 2.2 Hz, 1H, C≡CH), 2.42 (s, 3H, PhMe), 2.89 (d, *J* = 5.7 Hz, 1H, OH), 3.23-3.31 (m, 1H, 4-H), 4.35-4.40 (m, 1H, 3-H), 5.15 (d, *J* = 9.5 Hz, 1H, NH), 7.29 (d, *J* = 8.1 Hz, 2H, Ph), 7.79 (d, *J* = 8.1 Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ: 17.2, 20.1, 21.6, 29.4, 63.3, 63.5, 74.7, 82.2, 127.2 (2C), 129.4 (2C), 137.9, 143.3. *Anal.* Calcd for C₁₄H₁₉NO₃S: C, 59.76; H, 6.81; N, 4.98. Found: C, 59.63; H, 6.69; N, 4.97.

(3*S*,4*S*)-4-[*N*-(*tert*-Butoxycarbonyl)amino]-1-trimethylsilyl-5-phenylhex-1-yn-3-ol (S3) and Its (3*R*,4*S*)-Isomer (S4). To a stirred solution of oxalyl chloride (7.48 mL, 78 mmol) in CH₂Cl₂ (60 mL) at -78 °C under nitrogen was added dropwise a solution of DMSO (17.0 mL, 240 mmol) in CH₂Cl₂ (20 mL). After 30 minutes, a solution of the alcohol **S2** (15.1 g, 60 mmol) in CH₂Cl₂ (50 mL) was added to the above reagent at -78 °C, and the mixture was stirred for 1 h at this temperature. Diisopropylethylamine (52.3 mL, 300 mmol) was added to the above solution at -78 °C and the mixture was stirred for 30 minutes with warming to 0 °C. The mixture was made acidic with 1 N 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 gave a crude aldehyde as a crystalline mass. To a stirred solution of trimethylsilylacetylene (21.2 mL, 150 mmol) in dry THF (50 mL) under nitrogen was added *n*-BuLi (1.6 M solution in *n*-hexane; 93.8 mL, 150 mmol) at 0 °C, and the mixture was stirred for 20 minutes at this temperature. The crude aldehyde in dry THF (60 mL) was added to the above stirred reagent at -78 °C, and the mixture was stirred for 1 h at this temperature, followed by quenching with saturated NH₄Cl (10 mL). The mixture was made acidic with 1 N 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 repeated flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) gave, in order of elution, **S3** (7.97 g, 38% yield) and **S4** (3.63 g, 17% yield). Compound **S3**: colorless crystals; mp 104 °C (*n*-hexane–Et₂O); [α]_D²⁵ -64.6 (*c* 1.11, CHCl₃); IR (KBr) cm⁻¹: 3438 (OH), 2175 (C≡C), 1678 (NHCO₂), 1497 (NHCO₂); ¹H NMR (300 MHz, CDCl₃) δ: 0.17 (s, 9H, SiMe₃), 1.40 (s, 9H, CMe₃), 2.88 (dd, *J* = 13.2, 7.5 Hz, 1H, 5-CHH), 3.00-3.06 (m, 1H, OH), 3.03 (dd, *J* = 13.2, 6.6 Hz, 1H, 5-CHH), 3.90-4.00 (m, 1H, 4-H), 4.34 (dd, *J* = 5.1, 5.1 Hz, 1H, 3-H), 4.84 (d, *J* = 8.4 Hz, 1H, NH), 7.19-7.32 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ: -0.22 (3C), 28.3 (3C), 36.9, 56.3, 64.2, 79.7, 91.0, 104.2, 126.5, 128.5 (2C), 129.3 (2C), 137.7, 156.0; MS (EI) *m/z* (%) 348 (*M* + 1, 0.2), 164 (100). *Anal.* Calcd for C₁₉H₂₉NO₃Si: C, 65.67; H, 8.41; N, 4.03. Found: C, 65.87; H, 8.25; N, 4.11.

Compound **S4**: colorless solid; mp 97 °C; $[\alpha]^{25}_{\text{D}} -5.40$ (c 1.19, CHCl_3); IR (KBr) cm^{-1} : 3379 (OH), 2179 ($\text{C}\equiv\text{C}$), 1693 (NHCO_2), 1525 (NHCO_2); ^1H NMR (300 MHz, CDCl_3) δ : 0.22 (s, 9H, SiMe_3), 1.40 (s, 9H, CMe_3), 2.80-2.95 (m, 2H, 5- CH_2), 3.20 (d, J = 5.4 Hz, 1H, OH), 4.00-4.10 (m, 1H, 4-H), 4.37-4.42 (m, 1H, 3-H), 4.76 (d, J = 7.8 Hz, 1H, NH), 7.21-7.32 (m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : -0.15 (3C), 28.2 (3C), 37.4, 56.5, 65.3, 80.0, 91.9, 103.1, 126.6, 128.5 (2C), 129.1 (2C), 137.4, 156.4; MS (EI) m/z (%) 348 ($M + 1$, 0.2), 120 (100). *Anal.* Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_3\text{Si}$: C, 65.67; H, 8.41; N, 4.03. Found: C, 65.61; H, 8.19; N, 4.09.

(3S,4S)-4-[N-(tert-Butoxycarbonyl)amino]-5-phenylpent-1-yn-3-ol (S5). To a stirred solution of **S3** (5.04 g, 14.5 mmol) in MeOH (35 ml) was added dropwise NaOMe (78.3 mg, 1.45 mmol) in MeOH (1.45 mL) at 0 °C, and the mixture was stirred for 3 h at room temperature. The mixture was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (7:3) to give **S5** (3.91 g, 98% yield) as colorless crystals: mp 83 °C (*n*-hexane–EtOAc); $[\alpha]^{27}_{\text{D}} -60.9$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 3442 (OH), 3300 (NHCO_2), 2118 ($\text{C}\equiv\text{C}$), 1682 (NHCO_2); ^1H NMR (300 MHz, CDCl_3) δ : 1.40 (s, 9H, CMe_3), 2.49 (m, 1H, $\text{C}\equiv\text{CH}$), 2.88 (dd, J = 13.2, 7.5 Hz, 1H, PhCHH), 3.06 (dd, J = 13.2, 6.3 Hz, 1H, PhCHH), 3.15 (br s, 1H, OH), 3.97 (m, 1H, 4-H), 4.38 (m, 1H, 3-H), 4.85 (d, J = 7.8 Hz, 1H, NH), 7.20-7.33 (m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 28.2 (3C), 36.5, 56.2, 63.7, 74.3, 79.9, 82.5, 126.6, 128.5 (2C), 129.3 (2C), 137.6, 156.2; MS (FAB) m/z (%) 276 (MH^+ , 35), 220 (100). *Anal.* Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{S}$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.75; H, 7.57; N, 5.04.

(3S,4S)-4-[N-(4-Methylphenylsulfonyl)amino]-5-phenylpent-1-yn-3-ol (6e). By a procedure identical with that described for the preparation of the tosylate **6d** from **S1**, the alcohol **S5** (964 mg, 3.5 mmol) was converted into **6e** (642 mg, 56% yield) as colorless crystals: mp 152–154 °C (*n*-hexane–EtOAc); $[\alpha]^{23}_{\text{D}} -49.9$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 3508 (OH), 3292 (NHSO_2), 2119 ($\text{C}\equiv\text{C}$), 1329 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 2.39 (s, 3H, PhMe), 2.43 (d, J = 2.1 Hz, 1H, $\text{C}\equiv\text{CH}$), 2.65 (d, J = 4.5 Hz, 1H, OH), 2.72 (dd, J = 13.5, 7.8 Hz, 1H, PhCHH), 3.04 (dd, J = 13.8, 6.0 Hz, 1H, PhCHH), 3.50-3.59 (m, 1H, 4-H), 4.42-4.50 (m, 1H, 3-H), 4.99 (d, J = 8.1 Hz, 1H, NH), 6.99-7.03 (m, 2H, Ph), 7.12-7.16 (m, 5H, Ph), 7.52-7.54 (m, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 21.5, 36.6, 59.0, 63.8, 75.2, 81.5, 126.6, 127.0 (2C), 128.6 (2C), 129.3 (2C), 129.5 (2C), 136.4, 136.9, 143.2; MS (FAB) m/z (%) 330 (MH^+ , 19), 136 (100). *Anal.* Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.50; H, 5.81; N, 4.25.

(4S,aS)-1-Bromo-5-methyl-4-[N-(2,4,6-trimethylphenylsulfonyl)amino]hexa-1,2-diene (7b) (Table 1, entry 2). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **6b** (155 mg, 0.5 mmol) was converted into **7b** (90% de) as a crystalline mass. Recrystallization from *n*-hexane gave pure **7b** (141 mg, 76% yield) as colorless

crystals: mp 64 °C; $[\alpha]^{24}_{\text{D}} +153$ (*c* 1.25, CHCl₃); IR (KBr) cm⁻¹: 3280 (NHSO₂), 1959 (C=C=C), 1325 (NHSO₂); ¹H NMR (270 MHz, CDCl₃) δ : 0.86 (d, *J* = 6.8 Hz, 3H, CMe), 0.92 (d, *J* = 7.0 Hz, 3H, CMe), 1.82-1.94 (m, 1H, 5-H), 2.30 (s, 3H, PhMe), 2.63 (s, 6H, 2 × PhMe), 3.63-3.71 (m, 1H, 4-H), 4.73 (d, *J* = 8.4 Hz, 1H, NH), 5.11 (dd, *J* = 7.0, 5.7 Hz, 1H, 3-H), 5.86 (dd, *J* = 5.7, 1.6 Hz, 1H, 1-H), 6.94 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ : 18.2, 18.3, 21.0, 23.2 (2C), 33.0, 57.7, 74.2, 99.4, 131.9 (2C), 134.2, 138.8 (2C), 142.1, 201.2. *Anal.* Calcd for C₁₆H₂₂BrNO₂S: C, 51.61; H, 5.96; N, 3.76. Found: C, 51.48; H, 5.86; N, 3.75.

(4*S*,a*S*)-1-Bromo-5-methyl-4-[*N*-(4-methylphenylsulfonyl)amino]hexa-1,2-diene (7d) (Table 1, entry 4). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **6d** (225 mg, 0.8 mmol) was converted into **7d** (84% de) as a crystalline mass. Recrystallization from *n*-hexane–Et₂O gave pure **7d** (178 mg, 65% yield) as colorless crystals: mp 97 °C (*n*-hexane–Et₂O); $[\alpha]^{23}_{\text{D}} +116$ (*c* 1.02, CHCl₃); IR (KBr) cm⁻¹: 3280 (NHSO₂), 1959 (C=C=C), 1329 (NHSO₂); ¹H NMR (270 MHz, CDCl₃) δ : 0.90 (d, *J* = 6.8 Hz, 3H, CMe), 0.91 (d, *J* = 6.8 Hz, 3H, CMe), 1.82-1.94 (m, 1H, 5-H), 2.42 (s, 3H, PhMe), 3.70-3.78 (m, 1H, 4-H), 4.81 (d, *J* = 8.6 Hz, 1H, NH), 5.18 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 5.94 (dd, *J* = 5.7, 1.6 Hz, 1H, 1-H), 7.29 (d, *J* = 8.1 Hz, 2H, Ph), 7.75 (d, *J* = 8.1 Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ : 18.1, 18.2, 21.6, 33.3, 57.4, 74.7, 99.8, 127.2 (2C), 129.6 (2C), 137.4, 143.3, 201.0. *Anal.* Calcd for C₁₄H₁₈BrNO₂S: C, 48.84; H, 5.27; N, 4.07. Found: C, 48.88; H, 5.21; N, 4.03.

(4*S*,a*S*)-1-Bromo-4-[*N*-(4-methylphenylsulfonyl)amino]-5-phenylpenta-1,2-diene (7e) (Table 1, entry 5). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **6e** (165 mg, 0.50 mmol) was converted into **7e** (160 mg, 81% yield, 86% de). Recrystallization from *n*-hexane–Et₂O gave almost pure **7e** as colorless needles: mp 75 °C; $[\alpha]^{28}_{\text{D}} +85.0$ (*c* 0.50, CHCl₃, 96% de); IR (KBr) cm⁻¹: 3271 (NHSO₂), 1959 (C=C=C), 1331 (NHSO₂); ¹H NMR (300 MHz, CDCl₃) δ : 2.41 (s, 3H, PhMe), 2.89-2.92 (m, 2H, 5-CH₂), 4.10-4.19 (m, 1H, 4-H), 4.54 (d, *J* = 7.5 Hz, 1H, NH), 5.31 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 6.01 (dd, *J* = 5.7, 2.4 Hz, 1H, 1-H), 7.07-7.09 (m, 2H, Ph), 7.22-7.24 (m, 5H, Ph), 7.60-7.63 (m, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ : 21.5, 41.8, 52.6, 75.4, 101.4, 127.0, 127.1 (2C), 128.6 (2C), 129.5 (2C), 129.6 (2C), 135.7, 137.0, 143.4, 200.9; MS (EI) *m/z* (%) 393 (M⁺, ⁸¹Br, 3.2), 391 (M⁺, ⁷⁹Br, 3.7), 91 (100); HRMS (EI) calcd for C₁₈H₁₈BrNO₂S (M⁺): 391.0241, found: 391.0251.

(4*R*,a*S*)-1-Bromo-5-(*tert*-butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-penta-1,2-diene (7f) (Table 1, entry 6). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **6f** (247 mg, 0.60 mmol) was converted into **7f** (230 mg, 81% yield, 78% de). Separation of the diastereomixture by flash chromatography over silica gel with *n*-hexane–Et₂O (5:2) gave pure **7f** as a colorless oil: $[\alpha]_D^{26} +81.8$ (*c* 2.04, CHCl₃); IR (KBr) cm⁻¹: 3309 (NH₂SO₂), 1961 (C=C=C), 1332 (NH₂SO₂); ¹H NMR (300 MHz, CDCl₃) δ : 0.04 (s, 6H, SiMe₂), 0.87 (s, 9H, CMe₃), 2.29 (s, 3H, PhMe), 2.63 (s, 6H, 2 $\times$ PhMe), 3.62–3.64 (m, 2H, 5-CH₂), 3.84–3.90 (m, 1H, 4-H), 5.17 (d, *J* = 6.9 Hz, 1H, NH), 5.27 (dd, *J* = 6.9, 6.0 Hz, 1H, 3-H), 5.93 (dd, *J* = 5.7, 1.5 Hz, 1H, 1-H), 6.94 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ : –5.56 (2C), 18.2, 20.9, 23.1 (2C), 25.8 (3C), 53.3, 65.2, 74.3, 98.9, 132.0 (2C), 134.0, 138.9 (2C), 142.3, 201.4; MS (FAB) *m/z* (%) 476 (MH⁺, ⁸¹Br, 26), 474 (MH⁺, ⁷⁹Br, 26), 119 (100), 73 (92); HRMS (FAB) calcd for C₂₀H₃₃BrNO₃SSi (MH⁺, ⁷⁹Br): 474.1134, found: 474.1154.

To investigate the aziridination reaction of bromoallenes bearing a methyl group, the bromoallene **7g** was synthesized from **10g** via the acid-mediated ring-opening reaction and bromination.

(4*S*,a*S*)-1-Bromo-4-[*N*-(4-methylphenylsulfonyl)amino]penta-1,2-diene (7g). To a solution of the aziridine **10g** (47.1 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) was added dropwise methanesulfonic acid (26 μ L, 0.40 mmol) at 0 °C with stirring, and the mixture was stirred for 15 minutes. The mixture was made alkaline with saturated NaHCO₃ at 0 °C and the whole was extracted with Et₂O. The extract was washed with water, and dried over MgSO₄. Concentration under reduced pressure gave a crude mesylate. A mixture of CuBr·DMS (82.2 mg, 0.40 mmol) and LiBr (34.8 mg, 0.40 mmol) were dissolved in THF (2 mL) at room temperature under nitrogen. After stirring for 2 minutes, a solution of the above crude mesylate in THF (1 mL) was added to this reagent at room temperature. The mixture was stirred for 1 h with warming to 50 °C and quenched with saturated NH₄Cl (0.5 mL) and 28% NH₄OH (0.5 mL). The whole was extracted with Et₂O. The extract was washed with water, 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 **7g** (44.6 mg, 71% yield, 90% de). Further purification of the diastereomeric mixture by flash chromatography over silica gel with *n*-hexane–EtOAc (9:1) gave

pure **7g** as a colorless oil: $[\alpha]^{22}_{\text{D}} +23.1$ (c 0.51, CHCl_3); IR (KBr) cm^{-1} : 3273 (NHSO_2), 1959 ($\text{C}=\text{C}=\text{C}$), 1329 (NHSO_2); ^1H NMR (500 MHz, CDCl_3) δ : 1.26 (d, $J = 7.0$ Hz, 3H, CMe), 2.43 (s, 3H, PhMe), 4.02-4.09 (m, 1H, 4-H), 4.78 (d, $J = 8.0$ Hz, 1H, NH), 5.27 (dd, $J = 5.5, 5.5$ Hz, 1H, 3-H), 6.05 (dd, $J = 5.5, 2.5$ Hz, 1H, 1-H), 7.30-7.32 (m, 2H, Ph), 7.76-7.78 (m, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 21.5, 21.6, 47.5, 75.2, 102.8, 127.1 (2C), 129.8 (2C), 137.5, 143.6, 200.7; MS (FAB) m/z (%) 318 (MH^+ , ^{81}Br , 10), 316 (MH^+ , ^{79}Br , 10), 69 (100); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{15}\text{BrNO}_2\text{S}$ (MH^+): 316.0007, found: 315.9994.

(3R,4S)-5-Methyl-4-[N-(4-methylphenylsulfonyl)amino]hex-1-yn-3-ol (8d). By a procedure identical with that described for the preparation of the bromoallene **6d** from **S1**, the alcohol **S6** (682 mg, 3.0 mmol) was converted into **8d** (581 mg, 69% yield) as colorless needles: mp 96 °C (n -hexane– Et_2O); $[\alpha]^{25}_{\text{D}} -49.5$ (c 1.02, CHCl_3); IR (KBr) cm^{-1} : 3491 (OH), 3284 (NHSO_2), 2116 ($\text{C}\equiv\text{C}$), 1325 (NHSO_2); ^1H NMR (270 MHz, CDCl_3) δ : 0.75 (d, $J = 6.8$ Hz, 3H, CMe), 0.85 (d, $J = 6.8$ Hz, 3H, CMe), 1.73-1.86 (m, 1H, 5-H), 2.43 (s, 3H, PhMe), 2.51 (d, $J = 2.2$ Hz, 1H, $\text{C}\equiv\text{CH}$), 3.06 (d, $J = 8.9$ Hz, 1H, OH), 3.16 (ddd, $J = 9.7, 8.1, 3.0$ Hz, 1H, 4-H), 4.46 (ddd, $J = 8.9, 3.0, 2.2$ Hz, 1H, 3-H), 5.00 (d, $J = 9.7$ Hz, 1H, NH), 7.31 (d, $J = 8.1$ Hz, 2H, Ph), 7.79 (d, $J = 8.1$ Hz, 2H, Ph); ^{13}C NMR (67.8 MHz, CDCl_3) δ : 19.1, 20.0, 21.6, 30.6, 64.0 (2C), 75.7, 81.1, 127.2 (2C), 129.6 (2C), 137.2, 143.7. *Anal.* Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{S}$: C, 59.76; H, 6.81; N, 4.98. Found: C, 59.58; H, 6.72; N, 4.93.

(3R,4S)-4-[N-(tert-Butoxycarbonyl)amino]-5-phenylpent-1-yn-3-ol (S7). To a stirred solution of **S4** (2.95 g, 8.5 mmol) in THF (10 ml) was added dropwise TBAF (1.0 M in THF; 8.5 mL, 8.5 mmol) at 0 °C, and the mixture was stirred for 15 minutes at this temperature. The mixture was concentrated under reduced pressure, and 1 N HCl (5 mL) was added to the residue. The whole was extracted with Et_2O , and the extract was washed with brine and dried over MgSO_4 . Concentration under reduced pressure followed by filtration through a short pad of Al_2O_3 gave a crystalline mass, which was recrystallized from n -hexane– EtOAc to give **S7** (2.21 g, 94% yield) as colorless needles: mp 117 °C (n -hexane– EtOAc); $[\alpha]^{24}_{\text{D}} -26.2$ (c 1.44, CHCl_3); IR (KBr) cm^{-1} : 3356 (OH), 3272 (NHCO_2), 2114 ($\text{C}\equiv\text{C}$), 1691 (NHCO_2); ^1H NMR (300 MHz, CDCl_3) δ : 1.40 (s, 9H, CMe_3), 2.55 (d, $J = 1.5$ Hz, 1H, $\text{C}\equiv\text{CH}$), 2.82-2.95 (m, 2H, 5- CH_2), 3.56 (d, $J = 6.6$ Hz, 1H, OH), 4.05-4.15 (m, 1H, 4-H), 4.38-4.42 (m, 1H, 3-H), 4.82 (d, $J = 7.8$ Hz, 1H, NH), 7.20-7.32 (m, 5H, Ph); ^{13}C NMR

(75 MHz, CDCl₃) δ : 28.2 (3C), 37.4, 56.6, 64.8, 74.9, 80.2, 81.5, 126.7, 128.6 (2C), 129.1 (2C), 137.1, 156.5; MS (FAB) m/z (%) 276 (MH⁺, 32), 220 (100), 176 (33); HRMS (FAB) calcd for C₁₆H₂₂NO₃ (MH⁺): 276.1600, found: 276.1603.

(3*R*,4*S*)-4-[*N*-(4-Methylphenylsulfonyl)amino]-5-phenylpent-1-yn-3-ol (8e). By a procedure identical with that described for the preparation of the tosylate **6d** from **S1**, the alcohol **S7** (964 mg, 3.5 mmol) was converted into **8e** (906 mg, 79% yield) as a colorless oil: $[\alpha]^{24}_{\text{D}} -34.8$ (*c* 1.82, CHCl₃); IR (KBr) cm⁻¹: 3452 (OH), 2118 (C $\equiv$ C), 1325 (NH₂SO₂); ¹H NMR (300 MHz, CDCl₃) δ : 2.38 (s, 3H, PhMe), 2.60 (d, *J* = 2.4 Hz, 1H, C $\equiv$ CH), 2.65 (d, *J* = 13.8, 8.4 Hz, 1H, 5-CHH), 2.89 (dd, *J* = 13.8, 6.6 Hz, 1H, 5-CHH), 3.39 (d, *J* = 7.8 Hz, 1H, OH), 3.59 (dddd, *J* = 8.4, 8.4, 6.6, 2.7 Hz, 1H, 4-H), 4.47 (ddd, *J* = 7.8, 2.7, 2.4 Hz, 1H, 3-H), 5.43 (d, *J* = 8.4 Hz, 1H, NH), 6.93-6.97 (m, 2H, Ph), 7.08-7.15 (m, 5H, Ph), 7.53 (d, *J* = 8.4 Hz, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ : 21.5, 36.9, 59.8, 64.1, 75.9, 81.0, 126.6, 126.9 (2C), 128.5 (2C), 129.0 (2C), 129.6 (2C), 136.4, 136.5, 143.3; MS (FAB) m/z (%) 330 (MH⁺, 95), 274 (82), 91 (100); HRMS (FAB) calcd for C₁₈H₂₀NO₃S (MH⁺): 330.1164, found: 330.1153.

(4*S*,*aR*)-1-Bromo-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hexa-1,2-diene (9b) (Table 1, entry 8). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **8b** (309 mg, 2.0 mmol) was converted into **9b** (241 mg, 65% yield, 99% de) as colorless prisms: mp 71 °C; $[\alpha]^{24}_{\text{D}} -251$ (*c* 1.25, CHCl₃); IR (KBr) cm⁻¹: 3278 (NH₂SO₂), 1959 (C=C=C), 1325 (NH₂SO₂); ¹H NMR (270 MHz, CDCl₃) δ : 0.88 (d, *J* = 6.8 Hz, 3H, CMe), 0.90 (d, *J* = 6.8 Hz, 3H, CMe), 1.81-1.93 (m, 1H, 5-H), 2.30 (s, 3H, PhMe), 2.64 (s, 6H, 2 $\times$ PhMe), 3.78-3.86 (m, 1H, 4-H), 4.66 (d, *J* = 8.9 Hz, 1H, NH), 5.24 (dd, *J* = 5.7, 5.7 Hz, 1H, 3-H), 5.80 (dd, *J* = 5.7, 2.4 Hz, 1H, 1-H), 6.94 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ : 17.9, 18.3, 21.0, 23.4 (2C), 33.2, 56.7, 75.5, 100.4, 131.8 (2C), 134.6, 138.7 (2C), 142.0, 200.8. Anal. Calcd for C₁₆H₂₂BrNO₂S: C, 51.61; H, 5.96; N, 3.76. Found: C, 51.50; H, 5.84; N, 3.71.

(4*S*,*aR*)-1-Bromo-5-methyl-4-[*N*-(4-methylphenylsulfonyl)amino]hexa-1,2-diene (9d) (Table 1, entry 10). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **8d** (225 mg, 0.8 mmol) was converted into **9d** (225 mg, 82% yield, 99% de) as colorless needles: mp 86 °C (*n*-hexane); $[\alpha]^{22}_{\text{D}} -282$ (*c* 1.02, CHCl₃); IR (KBr) cm⁻¹: 3277 (NH₂SO₂), 1959 (C=C=C), 1329 (NH₂SO₂); ¹H NMR (300 MHz, CDCl₃) δ : 0.90 (d, *J* = 7.2 Hz, 3H,

CMe), 0.94 (d, $J = 6.9$ Hz, 3H, CMe), 1.81-1.92 (m, 1H, 5-H), 2.43 (s, 3H, PhMe), 3.83-3.90 (m, 1H, 4-H), 4.68 (d, $J = 9.3$ Hz, 1H, NH), 5.18 (dd, $J = 5.7, 5.7$ Hz, 1H, 3-H), 5.73 (dd, $J = 5.7, 2.2$ Hz, 1H, 1-H), 7.29 (d, $J = 8.1$ Hz, 2H, Ph), 7.74 (d, $J = 8.1$ Hz, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 17.6, 18.4, 21.5, 33.3, 56.8, 75.5, 100.4, 127.2 (2C), 129.6 (2C), 137.9, 143.4, 200.9. *Anal.* Calcd for $\text{C}_{14}\text{H}_{18}\text{BrNO}_2\text{S}$: C, 48.84; H, 5.27; N, 4.07. Found: C, 48.75; H, 5.21; N, 4.00.

(4*S*,a*R*)-1-Bromo-4-[*N*-(4-methylphenylsulfonyl)amino]-5-phenylpenta-1,2-diene (9e) (Table 1, entry 11). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **8e** (191 mg, 0.58 mmol) was converted into **9e** (136 mg, 60% yield, 82% de) as a colorless oil: $[\alpha]_D^{22} -130$ (c 1.00, CHCl_3 , 82% de); IR (KBr) cm^{-1} : 3261 (NHSO_2), 1959 ($\text{C}=\text{C}=\text{C}$), 1329 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 2.41 (s, 3H, PhMe), 2.85-2.88 (m, 2H, 5- CH_2), 4.13-4.23 (m, 1H, 4-H), 4.71 (d, $J = 8.4$ Hz, 1H, NH), 5.32 (dd, $J = 5.7, 5.4$ Hz, 1H, 3-H), 5.84 (dd, $J = 5.7, 2.4$ Hz, 1H, 1-H), 7.05-7.08 (m, 2H, Ph), 7.21-7.26 (m, 5H, Ph), 7.60-7.63 (m, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 21.5, 41.8, 52.6, 75.5, 101.5, 127.0, 127.1 (2C), 128.6 (2C), 129.5 (2C), 129.6 (2C), 135.7, 137.2, 143.4, 200.9; MS (FAB) m/z (%) 394 (MH^+ , ^{81}Br , 16), 392 (MH^+ , ^{79}Br , 18), 91 (100); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{19}\text{BrNO}_2\text{S}$ (MH^+): 392.0320, found: 392.0335.

(4*R*,a*R*)-1-Bromo-5-(*tert*-butyldimethylsiloxy)-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-penta-1,2-diene (9f) (Table 1, entry 12). By a procedure identical with that described for the preparation of the bromoallene **7a** from **6a**, the alcohol **8f** (247 mg, 0.60 mmol) was converted into **9f** (264 mg, 93% yield, 50% de). Separation of the diastereomixture by flash chromatography over silica gel with *n*-hexane– Et_2O (5:2) gave pure **9f** as a colorless oil: $[\alpha]_D^{26} -133$ (c 1.51, CHCl_3); IR (KBr) cm^{-1} : 3288 (NHSO_2), 1961 ($\text{C}=\text{C}=\text{C}$), 1333 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 0.03 (s, 6H, SiMe_2), 0.87 (s, 9H, CMe_3), 2.30 (s, 3H, PhMe), 2.64 (s, 6H, $2 \times \text{PhMe}$), 3.55-3.64 (m, 2H, 5- CH_2), 3.91-3.98 (m, 1H, 4-H), 5.15 (d, $J = 7.5$ Hz, 1H, NH), 5.30 (dd, $J = 5.7, 5.4$ Hz, 1H, 3-H), 5.84 (dd, $J = 5.4, 2.1$ Hz, 1H, 1-H), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : -5.57, -5.54, 18.2, 20.9, 23.1 (2C), 25.8 (3C), 52.9, 65.1, 74.9, 99.6, 132.0 (2C), 134.3, 138.9 (2C), 142.2, 201.4; MS (FAB) m/z (%) 476 (MH^+ , ^{81}Br , 36), 474 (MH^+ , ^{79}Br , 36), 119 (84), 73 (100); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{33}\text{BrNO}_3\text{SSi}$ (MH^+ , ^{79}Br): 474.1134, found: 474.1127.

To investigate the aziridination reaction of bromoallenes bearing a methyl group, the bromoallene **9g** was synthesized from **11g** via the acid-mediated ring-opening reaction and bromination.

(4*S*,*aR*)-1-Bromo-4-[*N*-(4-methylphenylsulfonyl)amino]penta-1,2-diene (9g). By a procedure identical with that described for the synthesis of **7g** from **10g**, the aziridine **11g** (47.1 mg, 0.20 mmol) was converted into **9g** (43.6 mg, 69% yield, 92% de) as a colorless oil: $[\alpha]^{24}_{\text{D}} -226$ (*c* 0.95, CHCl_3 , 94% de); IR (KBr) cm^{-1} : 3273 (NHSO_2), 1959 ($\text{C}=\text{C}=\text{C}$), 1329 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 1.24 (d, $J = 6.6$ Hz, 3H, CMe), 2.43 (s, 3H, PhMe), 4.03-4.17 (m, 1H, 4-H), 4.84 (d, $J = 8.4$ Hz, 1H, NH), 5.28 (dd, $J = 5.7, 5.4$ Hz, 1H, 3-H), 5.92 (dd, $J = 5.4, 2.1$ Hz, 1H, 1-H), 7.30-7.33 (m, 2H, Ph), 7.76-7.78 (m, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 21.4, 21.5, 47.5, 75.1, 102.9, 127.1 (2C), 129.7 (2C), 137.6, 143.6, 200.8; MS (FAB) m/z (%) 318 (MH^+ , ^{81}Br , 13), 316 (MH^+ , ^{79}Br , 15), 69 (100); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{15}\text{BrNO}_2\text{S}$ (MH^+): 316.0007, found: 316.0022.

To investigate the aziridination reaction of bromoallenes lacking a 4-substituent, the bromoallene (*S*)-**13** was synthesized from (*R*)-**14** via the acid-mediated ring-opening reaction and bromination.

(2*R*)-2-[(*N*-2,4,6-Trimethylphenylsulfonyl)amino]but-3-yn-1-ol (S9). To a stirred solution of **S8** (300 mg, 1.33 mmol) in MeOH (0.91 mL) at 0 °C was added trifluoroacetic acid (0.86 mL), and the mixture was stirred for 1.5 h at room temperature. The mixture was concentrated reduced pressure, and the residue was dissolved with CHCl_3 (3 mL). The solution was made neutral with Et_3N at 0 °C. Further Et_3N (0.37 mL, 2.66 mmol) and MtsCl (291 mg, 1.33 mmol) were added to the stirred mixture at 0 °C. The mixture was stirred for 1.5 h at this temperature, followed by quenching with saturated NaHCO_3 . The mixture was made acidic with 4% HCl, and the whole was extracted with ether. The extract was washed successively with water, saturated NaHCO_3 , water, and brine, and dried over MgSO_4 . 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 (1:1) to give **S9** (149 mg, 42%) as colorless crystals: mp 124–126 °C (*n*-hexane/EtOAc = 4:1); $[\alpha]^{25}_{\text{D}} -65.1$ (*c* 1.01, CHCl_3); IR (KBr) cm^{-1} : 3500 (OH), 3288 (NHSO_2), 2119 ($\text{C}\equiv\text{C}$), 1328 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 2.12 (d, $J = 2.1$ Hz, 1H, $\text{C}\equiv\text{CH}$), 2.30 (s, 3H, PhMe), 2.65 (s, 6H, 2 × PhMe), 2.86-2.98 (m, 1H, OH), 3.71-3.75 (m, 2H, 1- CH_2), 4.04-4.12 (m, 1H, 2-H), 5.55 (d, $J = 8.4$ Hz, 1H,

NH), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 20.9, 22.9 (2C), 47.0, 65.1, 73.4, 78.8, 131.9 (2C), 133.6, 139.2 (2C), 142.5; MS (EI) m/z (%) 267 (M^+ , 0.6), 119 (100). *Anal.* Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}$: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.26; H, 6.33; N, 5.24.

Synthesis of the Authentic (2*R*)-2-Ethynyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine [(*R*)-14].

To a stirred mixture of the amino alcohol **S9** (600 mg, 2.24 mmol) and PPh_3 (706 mg, 2.69 mmol) in THF (3 mL) was added dropwise diethyl azodicarboxylate (0.424 mL, 2.69 mmol) at 0 °C with stirring, and the mixture was stirred for 30 minutes. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give (*R*)-**14** (498 mg, 89% yield) as colorless crystals: mp 67–68 °C (*n*-hexane); $[\alpha]_D^{26}$ –95.7 (*c* 1.00, CHCl_3); IR (KBr) cm^{-1} : 3288 (NHSO_2), 2129 ($\text{C}\equiv\text{C}$), 1325 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 2.15 (d, J = 1.8 Hz, 1H, $\text{C}\equiv\text{CH}$), 2.32 (s, 3H, *PhMe*), 2.39 (d, J = 4.2 Hz, 1H, 3-*CHH*), 2.70 (s, 6H, 2 $\times$ *PhMe*), 2.78 (d, J = 7.2 Hz, 1H, 3-*CHH*), 3.22 (ddd, J = 7.2, 4.2, 1.8 Hz, 1H, 2-H), 6.98 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 21.0, 23.0 (2C), 26.8, 33.8, 70.6, 78.7, 131.87 (2C), 131.95, 140.2 (2C), 143.5; MS (FAB) m/z (%) 250 (MH^+ , 100); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_2\text{S}$ (MH^+): 250.0902, found: 250.0922.

(a*S*)-1-Bromo-4-[*N*-(2,4,6-methylphenylsulfonyl)amino]buta-1,2-diene [(*S*)-13]. To a solution of the aziridine (*R*)-**14** (388 mg, 1.55 mmol) in CH_2Cl_2 (7.8 mL) was added dropwise methanesulfonic acid (0.227 mL, 3.11 mmol) at 0 °C with stirring, and the mixture was stirred for 20 minutes at this temperature. The mixture was made alkaline with saturated NaHCO_3 at 0 °C. The whole was extracted with ether, and the extract was washed with water and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give a crude sulfonate. A mixture of $\text{CuBr}\cdot\text{DMS}$ (639 mg, 3.11 mol) and LiBr (271 mg, 3.11 mmol) was dissolved in THF (5 mL) at room temperature under nitrogen, and the mixture was stirred for 2 minutes. A solution of the above crude sulfonate in THF (3 mL) was added to this reagent at room temperature. The mixture was stirred overnight and quenched with saturated NH_4Cl and 28% NH_4OH . The whole was extracted with ether. The extract was washed with water and dried over MgSO_4 . 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 (*S*)-**13** (149 mg, 74% yield) as colorless crystals: mp 74–75 °C (*n*-hexane/EtOAc = 10:1); $[\alpha]_D^{25}$ +119 (*c* 1.08, CHCl_3); IR (KBr) cm^{-1} : 3304 (NHSO_2), 1961 ($\text{C}\equiv\text{C}$), 1325 (NHSO_2); ^1H NMR (300 MHz, CDCl_3) δ : 2.31 (s, 3H, *PhMe*), 2.64 (s, 6H, 2 $\times$ *PhMe*), 3.61–3.79 (m, 2H, 4- CH_2), 4.91 (t, J = 6.0 Hz, 1H, NH), 5.29 (ddd, J = 6.0, 5.7, 5.7 Hz, 1H, 3-H), 5.97 (ddd, J = 5.7, 2.7, 2.7 Hz, 1H, 1-H), 6.97 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 20.9, 22.9 (2C), 40.3, 74.7, 97.0, 132.0 (2C), 133.4, 139.1 (2C), 142.4, 201.6; MS (FAB) m/z (%) 332 (MH^+ , ^{81}Br , 43), 330 (MH^+ , ^{79}Br , 45), 119 (100); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{17}\text{BrNO}_2\text{S}$ (MH^+ , ^{79}Br): 330.0163, found: 330.0160.

Ethyl (4*R*)-4-[*N*-(*tert*-Butoxycarbonyl)-*N*-(2,4,6-trimethylphenylsulfonyl)amino]-5-methylhexanoate (S11). To a stirred solution of the ester **S10** (1.5 g, 5.49 mmol) in CH₂Cl₂ (5 mL) was added dropwise trifluoroacetic acid (5 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. Concentration under reduced pressure gave an oily residue, which was dissolved in CHCl₃ (5 mL). The mixture was made neutral with Et₃N at 0 °C. To this mixture, further Et₃N (1.53 mL, 11.0 mmol) and MtsCl (1.44 mg, 6.59 mmol) were added at 0 °C, and the mixture was stirred for 1.5 h at room temperature. Saturated NaHCO₃ (3 mL) was added to the reaction mixture at 0 °C, and the mixture was stirred for 30 min at this temperature. The mixture was made acidic with 1 N HCl, and the whole was extracted with Et₂O. The extract was washed with water, saturated NaHCO₃, 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 (7:1) to give the *N*-Mts derivative (1.34 g, 69% yield) as a colorless solid. To a stirred mixture of the solid (1.75 g, 4.92 mmol) and DMAP (997 mg, 8.16 mmol) in CH₂Cl₂ (10 mL) were added Et₃N (1.66 mL, 12.0 mmol) and a solution of Boc₂O (2.64 g, 12.1 mmol) in CH₂Cl₂ (12 mL) at room temperature, and the mixture was heated under reflux for 7.5 h. The solution was concentrated under reduced pressure and the residue was dissolved in EtOAc (40 mL), and 1 N HCl (10 mL) was added. The whole was extracted with EtOAc, 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 **S11** (1.75 g, 78% yield; 54% yield for 2 steps) as colorless crystals: mp 71–72 °C (*n*-hexane–Et₂O); [α]_D²⁵ +36.9 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 1728 (C=O), 1342 (NSO₂). ¹H NMR (300 MHz, CDCl₃) δ: 0.99 (d, *J* = 6.9 Hz, 3H, CMe), 1.06 (d, *J* = 6.9 Hz, 3H, CMe), 1.26 (t, *J* = 7.2 Hz, 3H, CH₂Me), 1.32 (s, 9H, CMe₃), 2.13–2.34 (m, 3H, 3-CH₂ and 5-H), 2.30 (s, 3H, PhMe), 2.42–2.51 (m, 2H, 2-CH₂), 2.63 (s, 6H, 2 × PhMe), 3.92 (ddd, *J* = 8.7, 5.4, 5.4 Hz, 1H, 4-H), 4.13 (q, *J* = 7.2 Hz, 2H, OCH₂), 6.94 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ: 14.2, 20.6, 20.88, 20.94, 22.9 (2C), 27.8 (3C), 28.8, 32.6, 33.3, 60.4, 63.7, 83.6, 131.8 (2C), 134.7, 140.0 (2C), 142.7, 151.4, 173.1; MS (FAB) *m/z* (%) 456 (MH⁺, 2.8), 200 (100); HRMS (FAB) calcd for C₂₃H₃₈NO₆S (MH⁺): 456.2420, found: 456.2402. *Anal.* Calcd for C₂₃H₃₇NO₆S: C, 60.64; H, 8.09; N, 2.81. Found: C, 65.50; H, 5.81; N, 4.25.

(4*R*)-4-[*N,N*-(*tert*-Butoxycarbonyl)(2,4,6-trimethylphenylsulfonyl)]-5-methylhexan-1-ol (S12). DIBAL-H (1.04 M solution in toluene; 10.4 mL, 10.9 mmol) was added dropwise to a stirred

solution of the ester **S11** (1.65 g, 3.62 mmol) in CH₂Cl₂ (8 mL) at –78 °C under nitrogen. After stirring for 1.5 h with warming to –30 °C, saturated NH₄Cl was added dropwise with stirring at –78 °C. The mixture was made acidic with 4% HCl at 0 °C and the whole was extracted with EtOAc. The extract was washed with 4% HCl and 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 **S12** (1.37 g, 92% yield) as colorless needles: mp 82 °C (*n*-hexane–Et₂O); [α]²⁵_D +34.4 (*c* 0.95, CHCl₃); IR (KBr) cm^{–1}: 3566 (OH), 1720 (C=O), 1340 (NSO₂); ¹H NMR (300 MHz, CDCl₃) δ : 1.02 (d, *J* = 7.2 Hz, 3H, CMe), 1.05 (d, *J* = 6.6 Hz, 3H, CMe), 1.30 (s, 9H, CMe₃), 1.39 (br s, 1H, OH), 1.68–1.77 (m, 2H, 2-CH₂), 1.91–2.01 (m, 2H, 3-CH₂), 2.25–2.36 (m, 1H, 5-H), 2.30 (s, 3H, PhMe), 2.64 (s, 6H, 2 × PhMe), 3.61–3.67 (m, 2H, 1-CH₂), 3.80 (ddd, *J* = 8.7, 5.1, 4.8 Hz, 1H, 4-H), 6.94 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ : 20.7, 20.9, 21.1, 22.9 (2C), 27.8 (3C), 30.6, 32.2, 32.9, 62.8, 64.4, 83.4, 131.8 (2C), 135.0, 139.9 (2C), 142.6, 151.5; MS (FAB) *m/z* (%) 414 (MH⁺, 16), 158 (100); HRMS (FAB) calcd for C₂₁H₃₆NO₅S (MH⁺): 474.2314, found: 414.2324.

(3*S*,6*R*)-6-[*N,N*-(*tert*-Butoxycarbonyl)(2,4,6-trimethylphenylsulfonyl)amino]-7-methyl-1-trimethylsilyloct-1-yn-3-ol and Its (3*R*,6*R*)-Isomer (S13**).** The alcohol **S12** (460 mg, 1.11 mmol) was dissolved in CH₂Cl₂ (5 mL), and Dess-Martin periodinane (943 mg, 2.22 mmol) was added at room temperature. After 20 min, the mixture was quenched with saturated NaHCO₃ and saturated Na₂S₂O₃ at this temperature 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 (4:1) to give the corresponding aldehyde. To a stirred solution of trimethylsilylacetylene (0.27 mL, 1.89 mmol) in THF (4 mL) under nitrogen was added *n*-BuLi (1.58 M solution in *n*-hexane; 1.19 mL, 1.89 mmol) at 0 °C, and the mixture was stirred for 30 min at this temperature. The aldehyde in THF (4 mL) was added to the above reagent at –78 °C, and the mixture was stirred for 2 h at this temperature, followed by quenching with saturated NH₄Cl (1 mL). The mixture was made acidic with 4% HCl at 0 °C and the whole extracted with Et₂O. The extract was washed with water, saturated NaHCO₃, 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 (5:1) to give an inseparable diastereomixture **S13** [262 mg, 46% yield; (3*S*):(3*R*) = 64:36, ¹H NMR (500 MHz)] as a colorless oil: [α]²⁶_D +16.1 [*c* 0.35, CHCl₃; (3*S*):(3*R*) = 64:36]; IR (KBr) cm^{–1}: 3535 (OH), 2172 (C≡C), 1724 (C=O), 1342 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ : 0.17 (s, 9H, SiMe₃), 1.03 (d, *J* = 6.5 Hz, 3H, CMe), 1.06 (d, *J* = 7.0 Hz, 1.92H, CMe), 1.07 (d, *J* = 6.5 Hz, 1.08H, CMe), 1.31 (s, 9H, CMe₃), 1.83–1.88 (m, 3H, OH and 4-CH₂), 2.02–2.05 (m, 2H, 5-CH₂), 2.27–2.36 (m, 1H, 7-H), 2.30 (s, 3H, PhMe), 2.64 (s, 6H, 2 × PhMe), 3.90 (m, 1H, 6-H), 4.34 (ddd, *J* = 6.0, 6.0, 5.5 Hz, 0.36H, 3-H), 4.38 (ddd, *J* = 6.0, 6.0, 5.0 Hz, 0.64H, 3-H), 6.93 (s, 2H, Ph); ¹³C NMR [(3*S*)-isomer; 75 MHz, CDCl₃] δ : –0.15 (3C), 20.7, 20.9, 21.1, 22.9 (2C), 27.9 (3C), 30.1, 32.9, 36.7, 62.6, 63.9, 83.4, 89.7, 106.2, 131.8 (2C), 134.9, 139.9 (2C), 142.6, 151.4; ¹³C NMR [(3*R*)-isomer; 75 MHz, CDCl₃] δ : –0.15 (3C), 20.7, 20.9, 21.1, 22.9 (2C), 27.9 (3C), 30.3, 32.9, 37.0, 62.7, 64.0, 83.4, 89.7,

106.3, 131.8 (2C), 134.9, 139.9 (2C), 142.6, 151.4; MS (FAB) m/z (%) 510 (MH^+ , 3.8), 193 (100); HRMS (FAB) calcd for $C_{26}H_{44}NO_5SSi$ (MH^+): 510.2709, found: 510.2718.

(6*R*,a*S*)-1-Bromo-7-methyl-6-[*N*-(4-methylphenylsulfonyl)amino]octa-1,2-diene (24) and Its (6*R*,a*R*)-isomer (25). To a stirred solution of the diastereomixture of **S13** (470 mg, 0.922 mmol) in MeOH was added NaOMe (19.9 mg, 0.369 mmol) at room temperature, and the mixture was stirred for 3 h at room 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 desilylated derivative. To a stirred solution of this alkyne in CH_2Cl_2 (4 mL) were added Et_3N (0.26 mL, 1.84 mmol) and MsCl (0.107 mL, 1.38 mmol) at 0 °C. After stirring for 1 h, the mixture was quenched with saturated $NaHCO_3$ at 0 °C, and the whole was extracted with Et_2O . The extract was washed with water, 1 N HCl, and brine, and dried over $MgSO_4$. 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 the corresponding sulfonate (470 mg, 99% yield). A mixture of $CuBr \cdot DMS$ (473 mg, 2.31 mmol) and LiBr (200 mg, 2.31 mmol) were dissolved in THF (3 mL) at room temperature under nitrogen. After stirring for 2 min, a solution of the above sulfonate in THF (4 mL) was added to this black reagent at room temperature. The mixture was stirred for 11 h at this temperature and quenched with saturated NH_4Cl (1.5 mL) and 28% NH_4OH (1.5 mL). The whole was extracted with Et_2O . The extract was washed with water, and dried over $MgSO_4$. 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 a diastereomixture of bromoallenes bearing an *N*-Boc group (365 mg, 79% yield for 3 steps). This diastereomixture (260 mg, 0.52 mmol) was dissolved in EtOAc (4 mL), and 3 N HCl (4 mL) was added to the mixture at room temperature. After stirring for 3 h at 65 °C, the mixture was made basic with 28% NH_4OH . The whole was extracted with EtOAc. The extract was washed with water, and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane– Et_2O –EtOAc (28:4:1) to give the (6*R*,a*S*)-bromoallene **24** (77 mg, 37% yield) and (6*R*,a*R*)-bromoallene **25** (128 mg, 61% yield).

Compound 24: colorless crystals; mp 86 °C (*n*-hexane); $[\alpha]_D^{26} +149$ (*c* 0.75, $CHCl_3$); IR (KBr) cm^{-1} : 3296 ($NHSO_2$), 1954 ($C=C=C$), 1317 ($NHSO_2$); 1H NMR (500 MHz, $CDCl_3$) δ : 0.73 (d, J = 7.5 Hz, 3H, CMe), 0.80 (d, J = 6.5 Hz, 3H, CMe), 1.38–1.45 (m, 1H, 5-*CHH*), 1.55–1.61 (m, 1H, 5-*CHH*), 1.66–1.72 (m, 1H, 7-H), 1.97–2.05 (m, 1H, 4-*CHH*), 2.08–2.17 (m, 1H, 4-*CHH*), 2.30 (s, 3H, PhMe), 2.64 (s, 6H, 2 $\times$ PhMe), 3.10–3.16 (m, 1H, 6-H), 4.44 (d, J = 9.0 Hz, 1H, NH), 5.27 (ddd, J = 6.5, 6.5, 5.5 Hz, 1H, 3-H), 5.93 (ddd, J = 5.5, 2.5, 2.5 Hz, 1H, 1-H), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 17.8, 18.1, 20.9, 23.2 (2C), 24.4, 30.3, 31.5, 58.4, 72.9, 100.3, 131.9 (2C), 135.2, 138.5 (2C), 141.9, 201.9; MS (FAB) m/z (%) 402 (MH^+ , ^{81}Br , 46), 400 (MH^+ , ^{79}Br , 46), 119 (100); HRMS (FAB) calcd for $C_{18}H_{27}BrNO_2S$ (MH^+): 400.0946, found: 400.0924.

Compound 25: colorless crystals; mp 101 °C (*n*-hexane); $[\alpha]_D^{25} -115$ (*c* 1.00, $CHCl_3$); IR (KBr) cm^{-1} : 3288 ($NHSO_2$), 1952 ($C=C=C$), 1311 ($NHSO_2$); 1H NMR (300 MHz, $CDCl_3$) δ : 0.72 (d, J = 6.9 Hz, 3H, CMe), 0.80 (d, J = 6.6 Hz, 3H, CMe), 1.37–1.49 (m, 1H, 5-*CHH*), 1.52–1.63 (m, 1H, 5-

CHH), 1.65-1.75 (m, 1H, 7-H), 1.96-2.21 (m, 2H, 4-H), 2.30 (s, 3H, *PhMe*), 2.65 (s, 6H, 2 × *PhMe*), 3.09-3.18 (m, 1H, 6-H), 4.48 (d, $J = 9.0$ Hz, 1H, NH), 5.26 (ddd, $J = 6.0, 6.0, 6.0$ Hz, 1H, 3-H), 5.91 (ddd, $J = 6.0, 2.4, 2.4$ Hz, 1H, 1-H), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 17.5, 18.2, 20.9, 23.2 (2C), 24.4, 30.4, 31.5, 58.0, 72.9, 100.1, 131.9 (2C), 135.1, 138.5 (2C), 141.9, 201.9; MS (FAB) m/z (%) 402 (MH^+ , ^{81}Br , 27), 400 (MH^+ , ^{79}Br , 28), 119 (100); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{27}\text{BrNO}_2\text{S}$ (MH^+): 400.0946, found: 400.0939.

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 CTEMP 20.1 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

¹H NMR spectrum of compound 10a in CDCl₃. The spectrum shows peaks from 0 to 8 ppm. Key features include a triplet at 1.547 ppm (3H), a multiplet at 2.07 ppm (2H), a multiplet at 2.85-2.91 ppm (4H), a multiplet at 4.10-4.16 ppm (4H), a multiplet at 5.34-5.39 ppm (2H), and a multiplet at 7.20-7.29 ppm (4H). Integration values are shown below the baseline: 3.18, 6.29, 2.07, 0.97, 1.01, 0.96, 1.00, 0.03, 2.19, 2.20, and 5.34. Three inset boxes provide expanded views of the 2.85-2.91 ppm, 4.10-4.16 ppm, and 5.34-5.39 ppm regions with peak labels.

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T2		

Time (min)	Temperature (°C)	Pressure (atm)	Flow Rate (L/min)	Sample Concentration (mg/mL)	Retention Time (min)	Peak Area (a.u.)	Peak Width (min)	Peak Height (a.u.)	Peak Shape (Gaussian)	Peak Resolution (Rs)	Peak Identification
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EXPCM NON

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LGAIN

SHEN
LOAN

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0385J
ATCNY

UNITED STATES DEPARTMENT OF AGRICULTURE

30113
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FILED
OPERATOR .

fromHO57

DFILE C:\WINMR95\COMMON\
 COMNT fromHO57
 DATIM Wed May 31 20:22:11
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 32768
 FREQU 5402.4 Hz
 SCANS 16
 ACQTM 6.065 sec
 PD 0.935 sec
 PW1 5.6 us
 IRNUC 1H
 CTEMP 23.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

D:\2000\0006\H060.als
 COMMT H060
 DATIM Fri Jun 09 18:02:52 2000
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 32768
 FREQU 5402.4 Hz
 SCANS 16
 ACQTM 6.065 sec
 PD 0.935 sec
 FW 5.6 us
 IRNUC 1H
 CTMP 23.1 C
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 16

1H Line

Date : Wed Jan 10 20:28:44 2001
 File Name : Loading1D.mdata
 Comment : 1H Line
 Slice History : non
 EXMODE :
 POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 10000.0 Hz
 DELAY : 5000 Hz
 DEADT : 40.0 usec
 INVT : 58.7 usec
 TIMES : 100.0 usec
 DUMMY : 16 times
 PD : 1 times
 ACQTM : 5.3616 sec
 PREDL : 1638.3999 msec
 ININT : 0.01000 msec
 RESOL : 1000.0000 msec
 PM1 : 0.61 Hz
 1H : 2.63 usec
 ORNUC : 500.00 MHz
 OBFRQ : 162167.53 Hz
 OBSET : 24
 RGAIN : 16 times
 SCANS : 16 times
 SLVNT : CDCL3
 SPINNING : 13 Hz
 TEMP : 29.9 C

DFILE COMNT DATIM OBNUC EXMOD OBFRQ OBSET OBFIN POINT FREQU SCANS ACQTM PD PW1 IRNUC CTEMP SLVNT EXREF BF RGAIN

D:\0008\fromHO70\HO42(major).als
HO42{main}
Wed Aug 16 18:03:15 2000

	300.40 MHz
	130.00 KHz
	1150.0 Hz
	32768
	6013.2 Hz
	16
	5.449 sec
	1.551 sec
	5.8 us
1H	19.9 c
CDCL3	
	7.26 ppm
	0.12 Hz
	13

D:\H-28 1H.als
 COMNT
 DATIM Mon Jun 12 16:34:30 2000
 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 5.8 us
 IRNUC 1H
 CTEMP 20.5 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

14-MAY-99 18:31:22

MENUF NON
OBNUC 1H

OFR 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
PW1 4.9 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SP0 32768
TIMES 16
DUMMY 1
FREQU 5405.4 Hz
FLT 2700 Hz
DELAY 74.1 us
ACQTM 3.031 sec
PD 3.969 sec
ADBIT 12
RGAIN 14
BF 0.16 Hz
T1 0.0 %
T2 0.0 %
T3 90.0 %
T4 100.0 %

EXMOD NON
EXPCM NON: Single.coupled: PW1
IRNUC 1H
IFR 270.05 MHz
IRSET 112.00 KHz
IRFIN 5800.0 Hz
IRRPW 48 us
IRATN 511
DFILE Q1H
SF TH5990107
LKSET 64.6 KHz
LKFIN 59.0 Hz
LKLEV 200
LGAIN 20
LKPHS
LKPSIG
CSPED
FLDC
FILDG
FILDG

OPERATOR :
11a
(270 MHz, CDCl₃)

minor

C:\WINNMR95\COMMON_DEFAULT.ALS

DFILE
COMMT H061
DATIM Tue Jun 20 14:33:27 2000
OBNUC 1H
EXMOD NON
OBFREQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQ 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
FW 5.8 us
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12

D:\2001\010420 H.H-179 transazir
 COMET H-179 transaziridine Bn, Ts
 DATIM Fri Apr 20 11:16:31 2001
 DEINUC 1H
 EXMOD NON

DEFILE
 COMET
 DATIM
 DEINUC
 EXMOD
 EXFREQ
 OBSERQ
 OBSERF
 OBSERF
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SILVNT
 EXREF
 BF
 RGAIN

300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 6013.2 Hz
 16
 5.449 sec
 1.551 sec
 5.8 us
 1H
 22.7 C
 CDCL3
 0.00 ppm
 0.12 Hz
 15

DFILE C:\WINNR95\COMMON_DEFAULT.ALS
 COMNT HO40(minor)
 DATIM Wed Aug 16 18:22:33 2000

OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 8
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 20.6 C
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 16

C:\WINNR95\COMMON_DEFAULT.ALS

Thu Aug 24 19:37:20 2000

DFILE
COMNT
DATIM
EXMOD
OBNUC
OBRO
OBSE
OBFIN
POINT
FREOU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

1H
NON
300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
16
5.449 sec
1.551 sec
5.8 us
1H
20.1 C
CDCl3
0.00 ppm
0.12 Hz
17

D:\2001.6.29.allene.2.als

DFILE
COMNT
DATIM Fri Jun 29 12:39:27 2001
OBNUC 1H
EXMOD NON
OBPRO 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 20.7 C
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13

DEFILE D:\2001.6.25.als

COMMIT
 DATIM Mon Jun 25 09:53:42 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
 CTMP 20.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

DFILE D:\2001\010510 TMS allene pure 1.
 COMNT TMS allene pure 1H-NMR
 DATIM Thu May 10 12:11:03 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 20.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

D:\2001\TMS bromoallene from
 COMNT TMS bromoallene 1H
 DATIM Fri Jun 08 15:27:31 2001
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 33
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IIRNUC 1H
 CTEMP 21.4 C
 SIVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

D:\2001.10.17.H.als
 COMNT Wed Oct 17 13:07:09 2001
 DATIM 1H
 OBNUC 1H
 EXMOD NON
 OBRQ 300.40 MHz
 OBSE 130.00 KHz
 OBFN 1150.0 Hz
 POINT 32768
 FREQ 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW 5.8 us
 IRNUC 1H
 CTEMP 21.7 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 19

D:\2001.10.31.H.als
 DEFILE
 COMMT Wed Oct 31 10:43:01 2001
 DATIM 1H
 OBNUC 1H
 EXMOD NON
 OBPRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREOU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.8 us
 IRRUC 1H
 CTEMP 23.5 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE C:\WINNR95\COMMON\DEFAULT.ALS
 COMNT 010222 bromoallene recrystallizat
 DATIM Thu Feb 22 19:51:37 2001

OENUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OFFIN 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 23.5 C
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

D:\2001\010226 No168 allene 1H.a
 010226 H-168 bromoallene 1H
 Tue Feb 27 19:24:22 2001

DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 FW1
 IRNUC
 CTEMP
 SIVNT
 EXREF
 BF
 RGAIN

1H
 CDCL3
 300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 6013.2 Hz
 23
 5.449 sec
 1.551 sec
 5.8 us
 1H
 23.5 C
 0.00 ppm
 0.12 Hz
 18

D:\2002.1.24-1\iPr, N-Mts, bromoa
COMNT iPr, N-Mts bromoallene main 1H
DATIM Thu Feb 14 15:38:30 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
PW1 5.8 us
IRNUC 1H
CTEMP 19.7 C
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15

1H Line

Date : Wed Feb 27 15:14:45 2002
 FileName : se1202.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :
 POINT : 16384 points
 SAMPD : 16384 points
 FREQD : 100000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 57.2 usec
 INVTL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTH : 1638.3999 msec
 PREDL : 0.01000 msec
 INIIT : 1000.0000 msec
 RESOL : 0.61 Hz
 PNL : 5.50 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162167.63 Hz
 RGAIN : 16
 SCANS : 32 times
 SLVNT : CDCl3
 SPINNT : 14 Hz
 TEM : 29.1 C

C:\WINNMR95\COMMON\DEFAULT.ALS

DEFILE
COMMT H073
DATIM Mon Sep 11 10:03:36 2000
OBNUC 1H
EXMOD NON
OBFRO 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 5.8 us
IRNUC 1H
CTEMP 20.8 c
SILNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12

DEFILE C:\WINNMR95\COMMON\DEFAULT.ALS

COMNT HO74minor

DATIM Mon Sep 11 10:19:22 2000

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 5.8 us

IRNUC 1H

CTEMP 20.1 c

SOLNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 13

D:\H-85 main\als.als
 COMPT 001005main H.H.-85
 DATIM Fri Oct 06 13:17:25 2000
 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 5.8 us
 IRNUC 1H
 CTEMP 19.9 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

DFILE C:\WINNMR95\COMMON_DEFAULT.ALS
 COMNT H075
 DATIM Tue Sep 12 14:16:25 2000
 CNUC 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 5.8 us
 IRNUC 1H
 CTMP 20.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 12

D:\2002.1.24-1\1Pr, N-Mts, Boc, CO
 1Pr, N-Mts, Boc, CO2Et 1H
 Thu Feb 14 15:14:58 2002

DFILE
 COMNT
 DATIM
 CENUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 FW1
 IRNUC
 CTMP
 SLVNT
 EXREF
 EF
 RGAIN

1H
 NON
 300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 6013.2 Hz
 16
 5.449 sec
 1.551 sec
 5.8 us
 1H
 21.9 c
 CDCl3
 0.00 ppm
 0.12 Hz
 14

D:\2002.1.24-1Pr, N-Mts, Boc, OH
 COMPT 1Pr, N-Mts, Boc, OH 1H
 DATIM Thu Feb 14 14:51:49 2002
 EXMOD 1H
 EXMOD NON

300.40 MHz
 130.00 KHz
 1150.0 Hz
 32768
 6013.2 Hz
 16
 5.449 sec
 1.551 sec
 5.8 us
 1H
 21.6 C
 CDCL3
 0.00 ppm
 0.12 Hz
 14

1H Line

Date : Fri Feb 8 15:51:32 2002
 File Name : LoadingID.mdata
 Comment : 1H Line
 Slice History : non
 EXMODE : non
 POINT : 16384 points
 SAMPO : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 58.7 usec
 INVTL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3516 sec
 ACQTM : 1638.3999 msec
 PRETL : 0.01000 msec
 INVTM : 1000.0000 msec
 RESOL : 0.61 Hz
 PH1 : 2.53 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162167.53 Hz
 RGAIN : 16
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNING : 12 Hz
 TEMP : 23.3 C