Supporting Information

Palladium(0)-Catalyzed Stereoselective Cyclization of Allenenes: Divergent Synthesis of Pyrrolidines and 3-Azabicyclo[3.1.0]hexanes from Single Allenenes

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General Methods. All reactions were carried out under a positive pressure of argon, and glassware and syringes were dried in an electric oven at 100 °C prior to use. THF was distilled from sodium benzophenone ketyl under N₂. Other solvents and reagents were used without further purification. Melting points are uncorrected. ¹H NMR spectra (270, 300 or 500 MHz) were recorded in CDCl₃. Chemical shifts are reported in parts per million downfield from internal Me₄Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, m = multiplet). For flash chromatography, silica gel 60 (230–400 mesh, Merck) was employed. Known compounds methyl (4*S*,2*Z*)-2-bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-6-methylhept-2-enoate,¹ (2*S*)-2-[*N*-(*tert*-butoxycarbonyl)amino]-3,3-dimethylbutan-1-ol,¹ **16d**,² and **16e**² were synthesized according to the following literature.

- 1 Ohno, H.; Takemoto, Y.; Fujii, N.; Tanaka, T.; Ibuka, T. *Chem. Pharm. Bull.* **2004**, 52, 111–119.
- 2 Ohno, H.; Miyamura, K.; Tanaka, T.; Oishi, S.; Toda, A.; Takemoto, Y.; Fujii, N.; Ibuka, T. *J. Org. Chem.* **2002**, 67, 1359–1367.

Methyl (4*S*,2*Z*)-2-Bromo-6-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-enoate (13a**).** Trifluoroacetic acid (2 mL) was added to a solution of methyl (4*S*,2*Z*)-2-bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-6-methylhept-2-enoate* (550 mg, 1.57 mmol) in CHCl₃ (2 mL) under stirring at 0 °C, and the mixture was stirred for 1.5 h at this temperature. The mixture was concentrated under reduced pressure to an oily residue, which was dissolved in CHCl₃ (4 mL). The solution was made alkaline with Et₃N at 0 °C, and further Et₃N (0.44 mL, 3.14 mmol) and 2,4,6-trimethylphenylsulfonyl chloride (343 mg, 1.57 mmol) were added to the mixture with stirring at 0 °C. The mixture was stirred for 30 min at this temperature, followed by quenching with 5% NaHCO₃ (1 mL). The mixture was made acidic with 1N HCl, and the whole was extracted with Et₂O. The extract was washed successively with water, saturated NaHCO₃, and brine, and dried over MgSO₄. Concentration of the filtrate under reduced pressure followed by column chromatography over silica gel with *n*-hexane–EtOAc (3:1) gave **13a** (532 mg, 78% yield): colorless crystals; mp 109–111 °C (*n*-hexane–Et₂O); [α]_D²⁶ –7.31 (*c* 1.22, CHCl₃); IR (KBr) cm^{–1}: 3300 (SO₂NH), 1732 (C=O), 1331 (SO₂N), 1159 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.79 (d, *J* = 6.7 Hz, 3H, CMe), 0.90 (d, *J* = 6.7 Hz, 3H, CMe), 1.23–1.29 (m, 1H, 5-CHH), 1.46–1.51 (m, 1H, 5-CHH), 1.63–1.68 (m, 1H, 6-H), 2.28 (s, 3H, Ph-Me), 2.64 (s, 6H, 2 × Ph-Me), 3.75 (s, 3H, OMe), 4.20 (dddd, *J* = 8.5, 7.9, 5.5, 4.9 Hz, 1H, 4-H), 5.09 (d, *J* = 7.9 Hz, 1H, NH), 6.89 (d, *J* = 8.5 Hz, 1H, 3-H), 6.93 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 20.8, 21.1, 23.0 (3C), 24.2, 42.4, 53.1, 53.2, 114.8, 131.9 (2C), 133.7, 139.3 (2C), 142.3, 146.0, 162.1; MS (FAB) *m/z* (%) 434 (MH⁺, ⁸¹Br, 46), 432 (MH⁺, ⁷⁹Br, 46), 136 (100); HRMS (FAB) calcd for C₁₈H₂₇BrNO₄S (MH⁺, ⁷⁹Br) 432.0844; found 432.0844.

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Methyl (4*R*,2*Z*)-2-Bromo-5,5-dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enoate (13c**).** To a stirred solution of oxalyl chloride (1.53 mL, 17.7 mmol) in CH₂Cl₂ (20 mL) at –78 °C under argon was added dropwise a solution of DMSO (4.83 mL, 68 mmol) in CH₂Cl₂ (10

mL). After 30 min, a solution of (2*S*)-2-[*N*-(*tert*-butoxycarbonyl)amino]-3,3-dimethylbutan-1-ol* (2.96 g, 13.6 mmol) in CH₂Cl₂ (15 mL) was added to the above stirred reagent at –78 °C, and the mixture was stirred for 1 h. Diisopropylethylamine (16.7 mL, 95.2 mmol) was added to the above mixture at –78 °C, and the mixture was stirred for 30 min with warming to 0 °C. The mixture was made acidic with 5% HCl, and the whole was extracted with Et₂O. The extract was washed with water, 5% NaHCO₃, and brine, and dried over MgSO₄. Concentration under reduced pressure gave a crude aldehyde, which was dissolved in CHCl₃ (10 mL). A solution of Ph₃P=C(Br)CO₂Me (9.04 g, 21.9 mmol) in CHCl₃ (10 mL) was added to the above stirred solution, and the mixture was stirred for 16 h at room temperature. Concentration under reduced pressure gave a residual oil, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (20:1) to give, in order of elution, the methyl (4*R*,2*E*)-2-bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5,5-dimethylhex-2-enoate (0.72 g, 15% yield) and its (*Z*)-isomer (3.52 g, 74% yield).

(4*R*,2*Z*)-2-Bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5,5-dimethylhex-2-enoate (the major isomer): colorless oil; [α]_D²¹ +52.5 (*c* 1.67, CHCl₃); IR (KBr) cm^{–1}: 3386 (CONH), 1697 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.97 (s, 9H, CMe₃), 1.44 (s, 9H, CMe₃), 3.83 (s, 3H, OMe), 4.46 (dd, *J* = 9.6, 9.0 Hz, 1H, 4-H), 4.65 (d, *J* = 9.0 Hz, 1H, NH), 7.09 (d, *J* = 9.6 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃) δ 26.1 (3C), 28.4 (3C), 35.4, 53.2, 60.2, 79.8, 117.5, 142.9, 155.2, 162.9; MS (FAB) *m/z* (%) 352 (MH⁺, ⁸¹Br, 7), 350 (MH⁺, ⁷⁹Br, 10), 294 (100); HRMS (FAB) calcd for C₁₄H₂₅BrNO₄ (MH⁺, ⁷⁹Br) 350.0967; found 350.0914.

(4*R*,2*E*)-2-Bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5,5-dimethylhex-2-enoate (the minor isomer): colorless oil; [α]_D²⁰ +4.47 (*c* 1.50, CHCl₃); IR (KBr) cm^{–1}: 3267 (CONH), 1720 (C=O), 1695 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.94 (s, 9H, CMe₃), 1.42 (s, 9H, CMe₃), 3.83 (s, 3H, OMe), 4.64–4.68 (m, 1H, NH), 4.79 (dd, *J* = 10.2, 9.6 Hz, 1H, 4-H), 6.39 (d, *J* = 10.2 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃) δ 26.0 (3C), 28.3 (3C), 34.7, 52.8, 58.3, 79.6, 113.0, 143.2, 155.1, 163.0; MS (FAB) *m/z* (%) 352 (MH⁺, ⁸¹Br, 36), 350 (MH⁺, ⁷⁹Br, 38), 294 (100); HRMS (FAB) calcd for C₁₄H₂₅BrNO₄ (MH⁺, ⁷⁹Br) 350.0967; found 350.0957.

By a procedure identical with that described for the synthesis of **13a** (see the Experimental Section), (4*R*,2*Z*)-2-bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5,5-dimethylhex-2-enoate (3.00 g, 8.57 mmol) was converted into **13c** (1.81 g, 49% yield): colorless crystals; mp 107–109 °C (*n*-hexane–Et₂O–CHCl₃); [α]_D²² +28.1 (*c* 2.02, CHCl₃); IR (KBr) cm^{–1}: 3296 (SO₂NH), 1732 (C=O), 1331 (SO₂N), 1155 (SO₂N); ¹H NMR (270 MHz, CDCl₃) δ 0.95 (s, 9H, CMe₃), 2.26 (s, 3H, Ph-Me), 2.64 (s, 6H, 2 × Ph-Me), 3.72 (s, 3H, OMe), 3.97 (dd, *J* = 10.0, 8.9 Hz, 1H, 4-H), 5.03 (d, *J* = 8.9 Hz, 1H, NH), 6.79 (d, *J* = 10.0 Hz, 1H, 3-H), 6.89 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 21.0, 23.1 (2C), 26.2 (3C), 36.0, 53.4, 62.7, 117.5, 131.8 (2C), 134.1, 138.9 (2C), 141.6, 142.0, 161.8; MS (FAB) *m/z* (%) 434 (MH⁺, ⁸¹Br, 47), 432 (MH⁺, ⁷⁹Br, 47), 119 (100); HRMS (FAB) calcd for C₁₈H₂₇BrNO₄S (MH⁺, ⁷⁹Br) 432.0844; found 432.0830.

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(4*S*,2*Z*)-2-Bromo-6-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-en-1-ol (14a). To a stirred solution of the ester **13a** (400 mg, 0.925 mmol) in CH₂Cl₂ (3 mL) under argon was added

dropwise DIBAL-H (0.93 M solution in *n*-hexane; 3.28 mL, 3.05 mmol) at $-78\text{ }^{\circ}\text{C}$, and the mixture was stirred for 3 h at this temperature. The mixture was quenched with saturated NH_4Cl , and the mixture was made acidic with 10% HCl. The whole was extracted with EtOAc, and the extract was washed with water and 5% NaHCO_3 , and dried over MgSO_4 . Concentration of the filtrate under reduced pressure followed by column chromatography over silica gel with *n*-hexane–EtOAc (1:1) gave the alcohol **14a** (333 mg, 89% yield) as colorless crystals: mp $98\text{--}99\text{ }^{\circ}\text{C}$ (*n*-hexane– Et_2O); $[\alpha]^{22}_{\text{D}} +11.6$ (*c* 0.97, CHCl_3); IR (KBr) cm^{-1} : 3477 (OH), 3288 (SO_2NH), 1315 (SO_2N), 1149 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.70 (d, $J = 6.7$ Hz, 3H, CMe), 0.83 (d, $J = 6.7$ Hz, 3H, CMe), 1.24 (ddd, $J = 14.0, 7.9, 6.1$ Hz, 1H, 5-CHH), 1.38 (ddd, $J = 14.0, 8.5, 6.1$ Hz, 1H, 5-CHH), 1.48–1.56 (m, 1H, 6-H), 2.30 (s, 3H, Ph-Me), 2.65 (s, 6H, $2 \times$ Ph-Me), 2.90 (dd, $J = 6.7, 6.1$ Hz, 1H, OH), 4.00 (dd, $J = 14.6, 6.1$ Hz, 1H, 1-CHH), 4.06–4.15 (m, 2H, 1-CHH and 4-H), 5.37 (d, $J = 7.9$ Hz, 1H, NH), 5.84 (d, $J = 8.5$ Hz, 1H, 3-H), 6.69 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 20.8, 21.5, 22.8, 23.0 (2C), 24.2, 43.8, 52.8, 67.5, 126.6, 130.0, 131.8 (2C), 134.1, 139.3 (2C), 142.2. *Anal.* Calcd for $\text{C}_{17}\text{H}_{26}\text{BrNO}_3\text{S}$: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.39; H, 8.13; N, 4.54.

(4*S*,5*S*,2*Z*)-2-Bromo-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-en-1-ol (14b).

By a procedure identical with that described for the synthesis of (4*R*,2*Z*)-2-Bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5,5-dimethylhex-2-enoate (precursor of **13c**), (2*S*,3*S*)-*N*-(2,4,6-trimethylphenylsulfonyl)isoleucinol* (10.0 g, 33.3 mmol) was converted into the enoate **13b** containing its (*E*)-isomer (8.9 g, *ca.* 62% yield). It was extremely difficult to obtain the enoate **13b** in a pure form. By a procedure identical with that described for the synthesis of **14a**, the crude enoate **13b** (1.00 g, *ca.* 2.31 mmol) was converted into the alcohol **14b** (556 mg, 60% yield): colorless crystals; mp $86\text{ }^{\circ}\text{C}$ (*n*-hexane–EtOAc); $[\alpha]^{22}_{\text{D}} +36.8$ (*c* 1.00, CHCl_3); IR (KBr) cm^{-1} : 3444 (OH), 3286 (SO_2NH), 1321 (SO_2N), 1153 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.82 (d, $J = 5.5$ Hz, 3H, CMe), 0.85 (t, $J = 6.7$ Hz, 3H, CMe), 1.03–1.12 (m, 1H, 6-CHH), 1.41–1.49 (m, 1H, 6-CHH), 1.50–1.56 (m, 1H, 5-H), 2.28 (br s, 1H, OH), 2.30 (s, 3H, Ph-Me), 2.65 (s, 6H, $2 \times$ Ph-Me), 3.97 (dd, $J = 14.6, 6.7$ Hz, 1H, 1-CHH), 4.04 (dd, $J = 14.6, 6.7$ Hz, 1H, 1-CHH), 4.07–4.11 (m, 1H, 4-H), 5.04 (br s, 1H, NH), 5.73 (d, $J = 9.2$ Hz, 1H, 3-H), 6.95 (s, 2H, Ph); ^{13}C NMR (67.8 MHz, CDCl_3) δ 11.5, 14.9, 21.0, 23.1 (2C), 25.1, 39.6, 58.3, 67.8, 126.8, 128.2, 131.7 (2C), 134.5, 139.2 (2C), 142.0. *Anal.* Calcd for $\text{C}_{17}\text{H}_{26}\text{BrNO}_3\text{S}$: C, 50.49; H, 6.48; N, 3.46. Found: C, 50.74; H, 6.37; N, 3.50.

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(4*R*,2*Z*)-2-Bromo-5,5-dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-en-1-ol (14c).

By a procedure identical with that described for the synthesis of **14a**, the enoate **13c** (1.70 g, 3.93 mmol) was converted into the alcohol **14c** (1.42 g, 89% yield): colorless crystals; mp $147\text{--}148\text{ }^{\circ}\text{C}$ (*n*-hexane– Et_2O – CHCl_3); $[\alpha]^{25}_{\text{D}} +54.9$ (*c* 1.02, CHCl_3); IR (KBr) cm^{-1} : 3467 (OH), 3286 (SO_2NH), 1325 (SO_2N), 1153 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.86 (s, 9H, CMe_3), 2.16 (dd, $J = 7.3, 6.7$ Hz, 1H, OH), 2.30 (s, 3H, Ph-Me), 2.67 (s, 6H, $2 \times$ Ph-Me), 3.93 (dd, $J = 9.4, 8.5$ Hz, 1H, 4-H), 3.96 (dd, $J = 14.6, 6.7$ Hz, 1H, 1-CHH), 4.03 (dd, $J = 14.6, 7.3$ Hz, 1H, 1-CHH), 5.13 (d,

$J = 8.5$ Hz, 1H, NH), 5.75 (d, $J = 9.4$ Hz, 1H, 3-H), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 20.9, 23.0 (2C), 26.0 (3C), 35.5, 62.8, 67.8, 125.6, 128.8, 131.8 (2C), 134.8, 139.2 (2C), 142.1. *Anal.* Calcd for $\text{C}_{17}\text{H}_{26}\text{BrNO}_3\text{S}$: C, 50.49; H, 6.48; N, 3.46. Found: C, 50.40; H, 6.33; N, 3.46.

(4*S*,2*Z*)-2-Bromo-6-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-enyl Methylsulfonate (15a). To a stirred mixture of the alcohol **14a** (3.20 g, 7.91 mmol) and Et_3N (5.48 mL, 39.6 mmol) in THF (20 mL) was added MsCl (2.14 mL, 27.7 mmol) at -78°C . The stirring was continued for 4 h with warming to 0°C , followed by quenching with saturated NaHCO_3 (3 mL). The whole was extracted with EtOAc , and the extract was washed with 5% HCl , water, saturated NaHCO_3 , and brine, and dried over MgSO_4 . Concentration of the filtrate under reduced pressure followed by column chromatography over silica gel with n -hexane– EtOAc (1:1) gave the mesylate **15a** (3.80 g, 99% yield) as colorless crystals: mp $84\text{--}85^\circ\text{C}$ (n -hexane– Et_2O); $[\alpha]^{21}_{\text{D}} +6.74$ (c 1.81, CHCl_3); IR (KBr) cm^{-1} : 3332 (SO_2NH), 1333 (SO_2N), 1151 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.75 (d, $J = 6.7$ Hz, 3H, CMe), 0.86 (d, $J = 6.7$ Hz, 3H, CMe), 1.20–1.27 (m, 1H, 5-CHH), 1.41–1.47 (m, 1H, 5-CHH), 1.55–1.63 (m, 1H, 6-H), 2.30 (s, 3H, Ph-Me), 2.64 (s, 6H, $2 \times$ Ph-Me), 3.05 (s, 3H, SO_2Me), 4.10 (ddd, $J = 8.5, 7.9, 5.5$ Hz, 1H, 4-H), 4.59 (s, 2H, 1- CH_2), 5.13 (d, $J = 7.9$ Hz, 1H, NH), 5.94 (d, $J = 8.5$ Hz, 1H, 3-H), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 20.8, 21.2, 22.9, 23.0 (2C), 24.1, 38.4, 43.2, 52.6, 73.0, 117.9, 131.9 (2C), 133.9, 136.7, 139.2 (2C), 142.4. *Anal.* Calcd for $\text{C}_{18}\text{H}_{28}\text{BrNO}_5\text{S}_2$: C, 44.81; H, 5.85; N, 2.90. Found: C, 44.91; H, 5.74; N, 2.86.

(4*S*,5*S*,2*Z*)-2-Bromo-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hept-2-enyl Methylsulfonate (15b). By a procedure identical with that described for the synthesis of **15a**, the alcohol **14b** (3.40 g, 8.41 mmol) was converted into the mesylate **15b** (3.85 g, 95% yield): colorless crystals; mp $101\text{--}103^\circ\text{C}$ (n -hexane– EtOAc); $[\alpha]^{26}_{\text{D}} +29.3$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 3319 (SO_2NH), 1333 (SO_2N), 1155 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.85–0.88 (m, 6H, $2 \times$ CMe), 1.08–1.14 (m, 1H, 6-CHH), 1.23–1.26 (m, 1H, 6-CHH), 1.44–1.49 (m, 1H, 5-H), 2.30 (s, 3H, Ph-Me), 2.63 (s, 6H, $2 \times$ Ph-Me), 3.03 (s, 3H, SO_2Me), 4.00–4.07 (m, 1H, 4-H), 4.55 (s, 2H, 1- CH_2), 4.63 (d, $J = 7.9$ Hz, 1H, NH), 5.86 (d, $J = 9.1$ Hz, 1H, 3-H), 6.94 (s, 2H, Ph); ^{13}C NMR (67.8 MHz, CDCl_3) δ 11.5, 14.9, 21.0, 23.1 (2C), 25.1, 38.5, 39.6, 58.2, 72.9, 119.6, 131.9 (2C), 133.6, 134.1, 139.0 (2C), 142.2. *Anal.* Calcd for $\text{C}_{18}\text{H}_{28}\text{BrNO}_5\text{S}_2$: C, 44.81; H, 5.85; N, 2.90. Found: C, 44.62; H, 5.71; N, 2.87.

(4*R*,2*Z*)-2-Bromo-5,5-dimethyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]hex-2-enyl Methylsulfonate (15c). By a procedure identical with that described for the synthesis of **15a**, the alcohol **14c** (1.32 g, 3.26 mmol) was converted into the mesylate **15c** (1.49 mg, 95% yield): colorless crystals; mp $153\text{--}154^\circ\text{C}$ (n -hexane– Et_2O – CHCl_3); $[\alpha]^{25}_{\text{D}} +43.7$ (c 1.10, CHCl_3); IR (KBr) cm^{-1} : 3327 (SO_2NH), 1356 (SO_2N), 1155 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.91 (s, 9H, CMe_3), 2.30 (s, 3H, Ph-Me), 2.64 (s, 6H, $2 \times$ Ph-Me), 3.04 (s, 3H, SO_2Me), 3.88 (dd, $J = 10.2, 8.5$ Hz, 1H, 4-H), 4.47–4.53 (m, 1H, 1- CH_2), 4.67 (d, $J = 8.5$ Hz, 1H, NH), 5.80 (d, $J = 10.2$ Hz, 1H, 3-H), 6.94 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 20.9, 23.1 (2C), 26.0 (3C), 35.7, 38.5, 62.3, 72.8, 120.6,

132.0 (3C), 134.4, 139.0 (2C), 142.2. *Anal.* Calcd for C₁₈H₂₈BrNO₅S₂: C, 44.81; H, 5.85; N, 2.90. Found: C, 44.55; H, 5.61; N, 2.86.

(4S)-6-Methyl-4-[N-(2,4,6-trimethylphenylsulfonyl)amino]hepta-1,2-diene (16a). To a stirred solution of the mesylate **15a** (3.80 g, 7.88 mmol) and Pd(PPh₃)₄ (181 mg, 2 mol%, 0.157 mmol) in dry THF (30 mL) under argon was added Et₂Zn (0.99 M in *n*-hexane; 16.0 mL, 15.8 mmol) at room temperature. The mixture was stirred for 4 h at this temperature followed by quenching with saturated NH₄Cl (5 mL). The whole was extracted with Et₂O and the extract was washed with water, and dried over MgSO₄. Usual workup followed by column chromatography over silica gel with *n*-hexane–EtOAc (5:1) gave the allene **16a** (1.96 g, 81% yield) as colorless crystals: mp 50–51 °C (*n*-hexane–Et₂O–CHCl₃); [α]_D²⁵ –27.6 (*c* 1.81, CHCl₃); IR (KBr) cm^{–1}: 3300 (SO₂NH), 1956 (C=C=C), 1323 (SO₂N), 1155 (SO₂N); ¹H NMR (270 MHz, CDCl₃) δ 0.79 (d, *J* = 6.8 Hz, 3H, CMe), 0.84 (d, *J* = 6.8 Hz, 3H, CMe), 1.29–1.46 (m, 2H, 5-CH₂), 1.59–1.71 (m, 1H, 6-H), 2.30 (s, 3H, Ph-Me), 2.64 (s, 6H, 2 × Ph-Me), 3.73–3.84 (m, 1H, 4-H), 4.58–4.66 (m, 3H, 1-CH₂ and NH), 4.92 (ddd, *J* = 6.8, 6.8, 6.8 Hz, 1H, 3-H), 6.94 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 21.0, 22.1, 22.4, 23.2 (2C), 24.5, 45.2, 50.7, 77.6, 92.0, 131.7 (2C), 134.7, 138.7 (2C), 141.8, 206.7. *Anal.* Calcd for C₁₇H₂₅NO₂S: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.42; H, 8.10; N, 4.53.

(4S,5S)-5-Methyl-4-[N-(2,4,6-trimethylphenylsulfonyl)amino]hepta-1,2-diene (16b). By a procedure identical with that described for the synthesis of **16a**, the mesylate **15b** (3.60 g, 7.46 mmol) was converted into the amino allene **16b** (2.19 g, 95% yield): colorless crystals; mp 57–58 °C (*n*-hexane); [α]_D²² +18.1 (*c* 1.01, CHCl₃); IR (KBr) cm^{–1}: 3302 (SO₂NH), 1957 (C=C=C), 1323 (SO₂N), 1157 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.79–0.87 (m, 6H, 2 × CMe), 1.06–1.15 (m, 1H, 6-CHH), 1.37–1.43 (m, 1H, 6-CHH), 1.56–1.62 (m, 1H, 5-H), 2.30 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 × Ph-Me), 3.71–3.75 (m, 1H, 4-H), 4.57 (d, *J* = 7.9 Hz, 1H, NH), 4.63–4.65 (m, 2H, 1-CH₂), 4.91 (ddd, *J* = 6.7, 6.1, 6.1 Hz, 1H, 3-H), 6.93 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 11.6, 14.6, 21.0, 23.2 (2C), 25.6, 40.0, 56.1, 77.7, 89.1, 131.7 (2C), 134.6, 138.8 (2C), 141.8, 207.0. *Anal.* Calcd for C₁₇H₂₅NO₂S: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.39; H, 8.11; N, 4.50.

(4R)-5,5-Dimethyl-4-[N-(2,4,6-trimethylphenylsulfonyl)amino]hexa-1,2-diene (16c). By a procedure identical with that described for the synthesis of **16a**, the mesylate **15c** (1.39 g, 2.88 mmol) was converted into the amino allene **16c** (713 mg, 80% yield): colorless crystals; mp 118–120 °C (*n*-hexane–Et₂O); [α]_D²⁵ +33.9 (*c* 2.07, CHCl₃); IR (KBr) cm^{–1}: 3311 (SO₂NH), 1956 (C=C=C), 1325 (SO₂N), 1161 (SO₂N); ¹H NMR (270 MHz, CDCl₃) δ 0.88 (s, 9H, CMe₃), 2.29 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 × Ph-Me), 3.46 (dddd, *J* = 9.7, 7.6, 2.2, 1.9 Hz, 1H, 4-H), 4.46 (ddd, *J* = 10.8, 6.8, 1.9 Hz, 1H, 1-CHH), 4.54 (ddd, *J* = 10.8, 6.8, 2.2 Hz, 1H, 1-CHH), 4.62 (d, *J* = 9.7 Hz, 1H, NH), 4.95 (ddd, *J* = 7.6, 6.8, 6.8 Hz, 1H, 3-H), 6.93 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 21.0, 23.4 (2C), 26.1 (3C), 35.6, 61.4, 77.1, 88.7, 131.7 (2C), 134.8, 138.6 (2C), 141.7, 207.3. *Anal.* Calcd for C₁₇H₂₅NO₂S: C, 66.41; H, 8.26; N, 4.56. Found: C, 66.39; H, 8.13; N, 4.54.

***N*-Allyl-*N*-[(1*S*)-1-isobutylbuta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (17a).** To a stirred suspension of NaH (60% suspension; 97.6 mg, 2.44 mmol) in DMF (3 mL) was a solution of **16a** (500 mg, 1.63 mmol) in DMF (2 mL) at room temperature, and the mixture was stirred for 10 min. Allyl bromide (0.211 mL, 2.44 mmol) was added to the mixture at 0 °C, and the mixture was stirred for 2.5 h at this temperature, followed by quenching with saturated NH₄Cl (1 mL). The whole was extracted with Et₂O and the extract was washed with water and brine, and dried over MgSO₄. Usual workup followed by column chromatography over silica gel with *n*-hexane–EtOAc (5:1) gave the allenene **17a** (552 mg, 98% yield) as a colorless oil: [α]_D²⁶ –84.4 (*c* 1.40, CHCl₃); IR (KBr) cm^{–1}: 1954 (C=C=C), 1321 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.72 (d, *J* = 6.1 Hz, 3H, CMe), 0.76 (d, *J* = 6.1 Hz, 3H, CMe), 1.35–1.42 (m, 1H, Me₂CH), 1.50–1.57 (m, 2H, Me₂CHCH₂), 2.29 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 × Ph-Me), 3.76 (dd, *J* = 16.5, 6.7 Hz, 1H, 1'-CHH), 3.88 (dd, *J* = 16.5, 6.1 Hz, 1H, 1'-CHH), 4.18–4.23 (m, 1H, 1-H), 4.75 (dd, *J* = 6.1, 2.4 Hz, 2H, 4-CH₂), 4.99 (dd, *J* = 10.4, 1.2 Hz, 1H, 3'-CHH), 5.09 (dd, *J* = 17.1, 1.2 Hz, 1H, 3'-CHH), 5.23 (ddd, *J* = 6.7, 6.1, 6.1 Hz, 1H, 2-H), 5.74–5.82 (m, 1H, 2'-H), 6.93 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 20.9, 21.8, 22.5, 23.0 (2C), 24.6, 41.6, 45.8, 53.6, 76.9, 90.3, 116.7, 131.9 (2C), 133.2, 136.1, 140.3 (2C), 142.4, 208.9; MS (FAB) *m/z* (%) 348 (MH⁺, 35), 308 (100); HRMS (FAB) calcd for C₂₀H₃₀NO₂S (MH⁺) 348.1997; found 348.1995.

***N*-Allyl-*N*-[(1*S*)-1-[(1*S*)-1-methylpropyl]buta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (17b).** By a procedure identical with that described for the synthesis of **17a**, the amino allene **16b** (50 mg, 0.163 mmol) was converted into the allenene **17b** (50.5 mg, 89% yield): colorless crystals; mp 51 °C (*n*-hexane–EtOAc); [α]_D²³ –31.2 (*c* 0.99, CHCl₃); IR (KBr) cm^{–1}: 1956 (C=C=C), 1325 (SO₂N), 1157 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.79 (t, *J* = 7.3 Hz, 3H, CMe), 0.84 (d, *J* = 6.7 Hz, 3H, CMe), 0.86–0.92 (m, 1H, MeCHH), 1.59–1.66 (m, 1H, MeCHH), 1.67–1.72 (m, 1H, EtCH), 2.29 (s, 3H, Ph-Me), 2.61 (s, 6H, 2 × Ph-Me), 3.77–3.90 (m, 3H, 1-H and 1'-CH₂), 4.61–4.68 (m, 2H, 4-CH₂), 4.99 (d, *J* = 11.0 Hz, 1H, 3'-CHH), 5.08 (d, *J* = 17.1 Hz, 1H, 3'-CHH), 5.15 (ddd, *J* = 8.5, 6.7, 6.7 Hz, 1H, 2-H), 5.79 (dddd, *J* = 17.1, 11.0, 6.7, 6.1 Hz, 1H, 2'-H), 6.92 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 11.2, 16.6, 21.0, 23.4 (2C), 25.6, 36.9, 46.7, 62.2, 75.8, 88.5, 116.6, 131.8 (2C), 133.7, 135.9 (2C), 140.0, 142.1, 208.9. *Anal.* Calcd for C₂₀H₂₉NO₂S: C, 69.12; H, 8.41; N, 4.03. Found: C, 69.00; H, 8.32; N, 4.01.

***N*-Allyl-*N*-[(1*R*)-1-*tert*-butylbuta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (17c).** By a procedure identical with that described for the synthesis of **17a**, the amino allene **16c** (250 mg, 0.813 mmol) was converted into the allenene **17c** (254 mg, 90% yield): colorless crystals; mp 82–84 °C (*n*-hexane–Et₂O–CHCl₃); [α]_D²² +30.3 (*c* 0.68, CHCl₃); IR (KBr) cm^{–1}: 1956 (C=C=C), 1311 (SO₂N), 1151 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.96 (s, 9H, CMe₃), 2.29 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 × Ph-Me), 3.86 (dd, *J* = 17.1, 6.7 Hz, 1H, 1'-CHH), 3.97 (dd, *J* = 17.1, 6.1 Hz, 1H, 1'-CHH), 4.08 (d, *J* = 8.5 Hz, 1H, 1-H), 4.62 (d, *J* = 6.7 Hz, 2H, 4-CH₂), 4.95 (dd, *J* = 10.4, 1.2 Hz, 1H, 3'-CHH), 5.04 (dd, *J* = 17.1, 1.2 Hz, 1H, 3'-CHH), 5.27 (ddd, *J* = 8.5, 6.7, 6.7 Hz, 1H, 2-H), 5.77–5.84 (m, 1H, 2'-H), 6.91 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 20.9, 23.5 (2C), 27.8 (3C),

37.0, 47.5, 65.9, 75.3, 86.2, 116.2, 131.9 (2C), 133.7, 136.2, 140.3 (2C), 142.2, 209.2; MS (FAB) m/z (%) 348 (MH^+ , 17), 290 (100); HRMS (FAB) calcd for $C_{20}H_{30}NO_2S$ (MH^+) 348.1997; found 348.1978.

N*-Allyl-*N*-[(1*S*)-1-isopropylbuta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (17d).** By a procedure identical with that described for the synthesis of **17a**, the amino allene **16d (300 mg, 1.02 mmol) was converted into the allenene **17d** (367 mg, 99% yield): colorless oil; $[\alpha]^{25}_D -43.3$ (c 0.79, $CHCl_3$); IR (KBr) cm^{-1} : 1956 (C=C=C), 1325 (SO_2N), 1157 (SO_2N); 1H NMR (270 MHz, $CDCl_3$) δ 0.87 (d, J = 6.4 Hz, 3H, CMe), 0.89 (d, J = 6.4 Hz, 3H, CMe), 1.84-1.97 (m, 1H, Me_2CH), 2.29 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 $\times$ Ph-Me), 3.74-3.86 (m, 3H, 1-H and 1'- CH_2), 4.68 (dd, J = 6.8, 1.6 Hz, 2H, 4- CH_2), 4.98 (ddd, J = 10.2, 2.6, 1.5 Hz, 1H, 3'- CHH), 5.09 (ddd, J = 17.1, 2.6, 1.5 Hz, 1H, 3'- CHH), 5.20 (dt, J = 8.2, 6.8 Hz, 1H, 2-H), 5.81 (ddt, J = 17.1, 10.2, 6.4 Hz, 1H, 2'-H), 6.92 (m, 2H, Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.1, 20.8, 21.0, 23.4 (2C), 46.4, 63.3, 75.9, 88.8, 116.6, 131.8 (2C), 133.5, 135.8 (2C), 140.0 (2C), 142.1, 208.9; MS (FAB) m/z (%) 334 (MH^+ , 29), 294 (100); HRMS (FAB) calcd for $C_{19}H_{28}NO_2S$ (MH^+) 334.1841; found 334.1848.

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N*-Allyl-*N*-[(1*S*)-1-benzylbuta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (17e).** By a procedure identical with that described for the synthesis of **17a**, the amino allene **16e (493 mg, 1.45 mmol) was converted into the allenene **17e** (565 mg, 99% yield): colorless crystals; mp 82–83 °C (*n*-hexane–EtOAc); $[\alpha]^{26}_D +104$ (c 1.10, $CHCl_3$); IR (KBr) cm^{-1} : 1954 (C=C=C), 1321 (SO_2N), 1159 (SO_2N); 1H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 3H, Ph-Me), 2.49 (s, 6H, 2 $\times$ Ph-Me), 2.91 (dd, J = 14.7, 7.2 Hz, 1H, Ph- CHH), 2.99 (dd, J = 14.7, 8.7 Hz, 1H, Ph- CHH), 3.86-4.02 (m, 2H, 1'- CH_2), 4.39-4.48 (m, 1H, 1-H), 4.72-4.82 (m, 2H, 4- CH_2), 5.06 (dd, J = 9.0, 1.2 Hz, 1H, 3'- CHH), 5.18 (dd, J = 17.4, 1.2 Hz, 1H, 3'- CHH), 5.30 (ddd, J = 6.3, 6.3, 6.3 Hz, 1H, 2-H), 5.79-5.93 (m, 1H, 2'-H), 6.86 (s, 2H, Ph), 6.96-6.99 (m, 2H, Ph), 7.14-7.16 (m, 3H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 22.8 (2C), 39.0, 46.1, 57.0, 77.6, 89.9, 117.0, 126.2, 128.2 (2C), 129.1 (2C), 131.9 (2C), 132.7, 136.0, 138.1, 140.3 (2C), 142.3, 209.2; MS (FAB) m/z (%) 382 (MH^+ , 34), 290 (100); HRMS (FAB) calcd for $C_{23}H_{28}NO_2S$ (MH^+) 382.1841; found 382.1835.

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Scheme S1^a

^aReagents: (a) (COCl)₂, DMSO, then (*i*-Pr)₂NEt; (b) Ph₃P=C(Br)CO₂Me; (c) DIBAL-H; (d) MsCl, Et₃N; (e) Et₂Zn, cat. Pd(PPh₃)₄; (f) NaH, allyl bromide.

Methyl (4*S*,2*Z*)-2-Bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5-methylhex-2-enoate (S1) and Its (4*S*,2*E*)-Isomer (S2). By a procedure identical with that described for the synthesis of (4*R*,2*Z*)-2-Bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5,5-dimethylhex-2-enoate (precursor of **13c**), *N*-Boc valinol **18** (10.0 g, 49.2 mmol) was converted into the enoate **S1** (8.24 g, 50% yield) and **S2** (4.22 g, 26% yield).

Compound **S1**: colorless solid; [α]_D²⁰ +10.2 (*c* 1.12, CHCl₃); IR (KBr) cm⁻¹: 3340 (CONH), 1718 (C=O), 1700 (C=O); ¹H NMR (300 MHz, CDCl₃, 333 K) δ 0.945 (d, *J* = 6.0 Hz, 3H, CMe), 0.952 (d, *J* = 6.9 Hz, 3H, CMe), 1.43 (s, 9H, CMe₃), 1.81-1.92 (m, 1H, 5-H), 3.83 (s, 3H, OMe), 4.60-4.72 (br s, 2H, NH and 4-H), 6.45 (d, *J* = 9.3 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃, 328 K) δ 18.2, 18.9, 20.4 (3C), 32.7, 52.9, 56.3, 79.8, 112.4, 146.6, 155.3, 163.1; MS (FAB) *m/z* (%) 338 (MH⁺, ⁸¹Br, 37), 336 (MH⁺, ⁷⁹Br, 37), 137 (100); HRMS (FAB) calcd for C₁₃H₂₃BrNO₄ (MH⁺, ⁷⁹Br) 336.0810; found 336.0824.

Compound **S2**: colorless oil; [α]_D¹⁷ +11.6 (*c* 0.96, CHCl₃); IR (KBr) cm⁻¹: 3353 (CONH), 1720 (C=O), 1700 (C=O); ¹H NMR (300 MHz, CDCl₃, 333 K) δ 0.946 (d, *J* = 6.6 Hz, 3H, CMe), 0.954 (d, *J* = 6.3 Hz, 3H, CMe), 1.43 (s, 9H, CMe₃), 1.81-1.92 (m, 1H, 5-H), 3.83 (s, 3H, OMe), 4.53-4.72 (br s, 2H, NH and 4-H), 6.46 (d, *J* = 8.7 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃, 328 K) δ 18.2, 18.9, 28.4 (3C), 32.6, 52.9, 56.3, 79.7, 112.2, 146.4, 155.0, 162.9; MS (FAB) *m/z* (%) 338 (MH⁺, ⁸¹Br, 87), 336 (MH⁺, ⁷⁹Br, 91), 280 (100); HRMS (FAB) calcd for C₁₃H₂₃BrNO₄ (MH⁺, ⁷⁹Br) 336.0810; found 336.0805.

(4*S*,2*Z*)-2-Bromo-4-[*N*-(*tert*-butoxycarbonyl)amino]-5-methylhex-2-en-1-ol (S3). By a procedure identical with that described for the synthesis of **14a**, the enoate **S1** (7.57 g, 22.5 mmol) was converted into the alcohol **S3** (5.89 g, 85% yield): colorless crystals; mp 77 °C (*n*-hexane–Et₂O); [α]_D²² +78.4 (*c* 0.99, CHCl₃); IR (KBr) cm⁻¹: 3400 (OH), 1687 (C=O); ¹H NMR (300 MHz, CDCl₃, 333 K) δ 0.94 (d, *J* = 6.6 Hz, 3H, CMe), 0.95 (d, *J* = 6.9 Hz, 3H, CMe), 1.44 (s, 9H, CMe₃), 1.80-1.94 (m, 1H, 5-H), 2.37-2.47 (br s, 1H, OH), 4.24-4.32 (br s, 3H, 1-CH₂ and 4-H), 4.49-4.59 (br s, 1H, NH), 5.96 (d, *J* = 8.7 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃, 328 K) δ 18.2, 18.6,

24.4 (3C), 32.6, 57.2, 68.1, 79.6, 128.2, 128.8, 155.5. *Anal.* Calcd for C₁₂H₂₂BrNO₃: C, 46.76; H, 7.19; N, 4.54. Found: C, 46.88; H, 7.08; N, 4.54.

(4S,2Z)-2-Bromo-4-[N-(tert-butoxycarbonyl)amino]-5-methylhex-2-enyl Methylsulfonate (S4).

By a procedure identical with that described for the synthesis of **15a**, the alcohol **S3** (3.60 g, 11.7 mmol) was converted into the mesylate **S4** (4.16 g, 92% yield): colorless oil; $[\alpha]^{22}_{\text{D}} +54.3$ (*c* 1.19, CHCl₃); IR (KBr) cm⁻¹: 3371 (CONH), 1697 (C=O); ¹H NMR (300 MHz, CDCl₃, 328 K) δ 0.95 (d, *J* = 6.6 Hz, 3H, CMe), 0.96 (d, *J* = 6.6 Hz, 3H, CMe), 1.44 (s, 9H, CMe₃), 1.81-1.94 (m, 1H, 5-H), 3.06 (s, 3H, SO₂Me), 4.23-4.33 (m, 1H, 4-H), 4.49-4.58 (br s, 1H, NH), 4.84-4.85 (m, 2H, 1-CH₂), 6.10 (d, *J* = 8.7 Hz, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃, 328K) δ 18.2, 18.7, 28.4 (3C), 32.3, 38.8, 57.3, 73.7, 79.8, 119.7, 135.9, 155.3. *Anal.* Calcd for C₁₃H₂₄BrNO₅S: C, 40.42; H, 6.10; N, 3.63. Found: C, 40.51; H, 6.10; N, 3.62.

(4S)-4-[N-(tert-Butoxycarbonyl)amino]-5-methylhexa-1,2-diene (S5).

By a procedure identical with that described for the synthesis of **16a**, the mesylate **S4** (854 mg, 2.24 mmol) was converted into the amino allene **S5** (520 mg, 90% yield): colorless oil; $[\alpha]^{18}_{\text{D}} -2.54$ (*c* 1.07, CHCl₃); IR (KBr) cm⁻¹: 3357 (CONH), 1959 (C=C=C), 1689 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.91 (d, *J* = 6.9 Hz, 3H, CMe), 0.92 (d, *J* = 6.6 Hz, 3H, CMe), 1.45 (m, 9H, CMe₃), 1.81-1.87 (br, 1H, 5-H), 4.05 (br s, 1H, 4-H), 4.57 (br s, 1H, NH), 4.84-4.85 (m, 2H, 1-CH₂), 5.14 (br s, 1H, 3-H); ¹³C NMR (75 MHz, CDCl₃) δ 13.0, 18.4, 28.3 (3C), 32.6, 53.7, 77.8, 79.1, 91.2, 155.5, 207.2; MS (FAB) *m/z* (%) 212 (MH⁺, 15), 156 (100); HRMS (FAB) calcd for C₁₂H₂₂NO₂ (MH⁺) 212.1651; found 212.1675.

N-Allyl-N-[(1S)-1-isopropyl-2,3-butadienyl]-tert-butylcarbamate (19).

By a procedure identical with that described for the synthesis of **17a**, the amino allene **S5** (100 mg, 0.473 mmol) was converted into the allenene **19** (103 mg, 87% yield): colorless oil; $[\alpha]^{26}_{\text{D}} -23.9$ (*c* 1.10, CHCl₃); IR (KBr) cm⁻¹: 1956 (C=C=C), 1691 (C=O); ¹H NMR (300 MHz, CDCl₃, 328K) δ 0.89 (d, *J* = 6.6 Hz, 3H, CMe), 0.94 (d, *J* = 6.6 Hz, 3H, CMe), 1.45 (s, 9H, CMe₃), 1.91-2.08 (m, 1H, Me₂CH), 3.68 (dd, *J* = 15.6, 5.4 Hz, 1H, 1'-CHH), 3.77 (dd, *J* = 15.6, 6.0 Hz, 1H, 1'-CHH), 3.86-3.98 (br, 1H, 1-H), 4.71-4.74 (m, 2H, 4-CH₂), 5.05 (d, *J* = 10.2 Hz, 1H, 3'-CHH), 5.10 (d, *J* = 17.1 Hz, 1H, 3'-CHH), 5.20 (dt, *J* = 6.9, 6.6 Hz, 1H, 2-H), 5.78-5.91 (m, 1H, 2'-H); ¹³C NMR (67.8 MHz, CDCl₃, 328 K) δ 19.7, 20.6, 28.6 (3C), 30.8, 48.1, 62.8, 75.6, 79.5, 89.9, 115.7, 135.8, 155.4, 209.1; MS (FAB) *m/z* (%) 252 (MH⁺, 22), 196 (100); HRMS (FAB) calcd for C₁₅H₂₆NO₂ (MH⁺) 252.1964; found 252.1979.

N-Allyl-N-(2-hydroxy-1,1-dimethylethyl)-4-methylphenylsulfonamide (21).

To a stirred mixture of 2-amino-2-methyl-1-propanol **20** (4.0 g, 44.9 mmol) and Et₃N (15.6 mL, 112 mmol) in DMF (100 mL) was added TsCl (9.41 g, 49.4 mmol) at 0 °C, and the mixture was stirred for 4 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 EtOAc. The extract was washed successively with water,

saturated NaHCO₃, and brine, and dried over MgSO₄. Filtration and solvent evaporation afforded a crystalline mass, which was recrystallized from *n*-hexane–CHCl₃–Et₂O (1:2:1) to give the corresponding tosylate (9.03 g, 83% yield) as colorless crystals. To a stirred solution of the tosylate (4.0 g, 16.4 mmol) in DMF (100 mL) were successively added imidazole (520 mg, 41.0 mmol) and *tert*-butyldimethylsilyl chloride (2.97 g, 19.9 mmol) at 0 °C, and the mixture was stirred for 3 h at this temperature. Water was added to the mixture, and the whole was extracted with EtOAc. The extract was washed with 1 N HCl, water, saturated NaHCO₃, and brine, and dried over MgSO₄. Filtration and solvent evaporation followed by column chromatography over silica gel with *n*-hexane–EtOAc (6:1) gave the corresponding silyl ether (5.43 g, 92% yield). By a procedure identical with that described for the synthesis of **17a**, this silyl ether (4.9 g, 13.7 mmol) was converted into the allylated silyl ether (3.69 g, 68% yield). Finally, this allylated silyl ether (3.47 g, 8.73 mmol) was treated with TBAF (1.0 M in THF, 13.1 mL, 13.1 mmol) in THF (50 mL) at room temperature for 2 h. Saturated NH₄Cl was added to the mixture, and the whole was extracted with EtOAc. The extract was washed with water and brine, and dried over MgSO₄. Filtration and solvent evaporation followed by column chromatography over silica gel with *n*-hexane–EtOAc (3:1) gave the corresponding silyl ether (2.70 g, 99% yield) as a colorless oil: IR (KBr) cm⁻¹: 3529 (OH), 1319 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 1.20 (s, 6H, 2 × CMe), 2.40 (s, 3H, Ph-Me), 2.50–2.67 (br s, 1H, OH), 3.65 (s, 2H, OCH₂), 4.00 (dd, *J* = 6.1, 1.8 Hz, 2H, 1'-CH₂), 5.14 (dd, *J* = 10.4, 1.2 Hz, 1H, 3'-CHH), 5.22 (dd, *J* = 17.1, 1.2 Hz, 1H, 3'-CHH), 5.91–5.98 (m, 1H, 2'-H), 7.26 (d, *J* = 8.5 Hz, 2H, Ph), 7.71 (d, *J* = 8.5 Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 21.5, 24.9 (2C), 49.2, 63.7, 69.6, 116.6, 126.9 (2C), 129.5 (2C), 137.0, 140.0, 143.0. *Anal.* Calcd for C₁₄H₂₁NO₃S: C, 59.34; H, 7.47; N, 4.94. Found: C, 59.34; H, 7.41; N, 5.00.

***N*-Allyl-*N*-(2-hydroxy-1,1-dimethylbut-3-ynyl)-4-methylphenylsulfonamide (22).** To a stirred solution of oxalyl chloride (1.38 mL, 14.3 mmol) in CH₂Cl₂ (15 mL) at –78 °C under argon was added dropwise a solution of DMSO (3.38 mL, 47.7 mmol) in CH₂Cl₂ (5 mL). After 1 h, a solution of the alcohol **21** (2.70 g, 9.53 mmol) in CH₂Cl₂ (15 mL) was added to the above stirred reagent at –78 °C, and the mixture was stirred for 1 h. Diisopropylethylamine (11.5 mL, 66.7 mmol) was added to the above mixture at –78 °C, and the mixture was stirred for 1 h with warming to 0 °C. The mixture was made acidic with 5% HCl, and the whole was extracted with EtOAc. The extract was washed with water, 5% NaHCO₃, and brine, and dried over MgSO₄. Concentration under reduced pressure gave a crude aldehyde. To a stirred solution of trimethylsilylacetylene (1.73 mL, 12.3 mmol) in dry THF (50 mL) under nitrogen was added *n*-BuLi (1.56 M in hexane; 7.86 mL, 12.3 mmol) at 0 °C, and the mixture was stirred for 1 h at this temperature. The crude aldehyde (2.3 g, 8.17 mmol) in dry THF (10 mL) was added to the above stirred reagent at –78 °C, and the mixture was stirred for 3 h at this temperature, followed by quenching with saturated NH₄Cl (10 mL). The whole was extracted with Et₂O, and the extract was washed successively with water and brine, and dried over MgSO₄. Filtration and solvent evaporation afforded a residual oil, which was dissolved in MeOH (20 mL). To this solution was added NaOMe (42.6 mg, 0.79 mmol) in MeOH (1 mL) at 0 °C, and the mixture was stirred for 17 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 (10:3) to give **22** (1.35 g, 48% yield in 3 steps) as a colorless oil: IR (KBr) cm^{-1} : 3500 (OH), 2115 ($\text{C}\equiv\text{C}$), 1321 (NSO_2), 1153 (NSO_2); ^1H NMR (500 MHz, CDCl_3) δ 1.45 (s, 3H, CMe), 1.50 (s, 3H, CMe), 2.42 (s, 3H, CMe), 2.46 (d, $J = 2.4$ Hz, 1H, 4-H), 3.03 (d, $J = 4.2$ Hz, 1H, OH), 4.07 (d, $J = 6.1$ Hz, 2H, 1'- CH_2), 5.06 (dd, $J = 4.2, 2.4$ Hz, 1H, 2-H), 5.11 (d, $J = 10.4$ Hz, 1H, 3'- CHH), 5.16 (d, $J = 17.1$ Hz, 1H, 3'- CHH), 5.85-5.93 (m, 1H, 2'-H), 7.28 (d, $J = 7.9$ Hz, 2H, Ph), 7.77 (d, $J = 7.9$ Hz, 2H, Ph); ^{13}C NMR (67.8 MHz, CDCl_3) δ 21.6, 23.0, 24.6, 49.4, 66.1, 68.1, 74.4, 82.5, 116.9, 127.3 (2C), 129.3 (2C), 136.6, 139.2, 143.1; MS (FAB) m/z (%) 330 (MNa^+ , 70), 91 (100); HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{21}\text{NNaO}_3\text{S}$ (MNa^+) 330.1140; found 330.1119.

***N*-Allyl-4-methyl-*N*-(1,1-dimethylbuta-2,3-dienyl)phenylsulfonamide (23).** By a procedure identical with that described for the synthesis of **15a**, the alcohol **22** (200 mg, 0.651 mmol) was converted into the corresponding mesylate (215 mg, 86% yield). A solution of LiAlH_4 (1.0 M in THF; 5.58 mL, 5.58 mmol) under argon was added to AlCl_3 (74.4 mg, 0.56 mmol), and the mixture was heated under reflux for 3 h. After cooling, the above mesylate (430 mg, 1.12 mmol) in THF (8 mL) was added to the reagent at room temperature, and mixture was stirred for 1 h. The mixture was quenched by saturated NH_4Cl , and the mixture was made acidic with 5% HCl. The whole was extracted with EtOAc, and the extract was washed successively with water, NaHCO_3 and brine, and dried over MgSO_4 . Filtration and solvent evaporation afforded a residual oil, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (8:3) to give **23** (260 mg, 80% yield) as a colorless oil: IR (KBr) cm^{-1} : 1955 ($\text{C}=\text{C}=\text{C}$), 1326 (NSO_2), 1157 (NSO_2); ^1H NMR (500 MHz, CDCl_3) δ 1.40 (s, 6H, CMe), 2.39 (s, 3H, CMe), 4.01 (d, $J = 5.5$ Hz, 2H, 1'- CH_2), 4.77 (d, $J = 6.7$ Hz, 2H, 4- CH_2), 5.13 (dd, $J = 10.4, 1.2$ Hz, 1H, 3'- CHH), 5.21 (dd, $J = 17.1, 1.2$ Hz, 1H, 3'- CHH), 5.29 (t, $J = 6.7$ Hz, 1H, 2-H), 5.91-6.00 (m, 1H, 2'-H), 7.23 (d, $J = 7.9$ Hz, 2H, Ph), 7.69 (d, $J = 7.9$ Hz, 2H, Ph); ^{13}C NMR (67.8 MHz, CDCl_3) δ 21.5, 28.2 (2C), 49.3, 60.7, 78.0, 98.4, 116.6, 127.0 (2C), 129.2 (2C), 137.0, 140.7, 142.5, 206.5; MS (FAB) m/z (%) 292 (MH^+ , 65), 212 (100); HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_2\text{S}$ (MH^+) 292.1371; found 292.1365.

Dibenzyl 2-(1-Isopropyl-3-trimethylsilylprop-2-ynyl)malonate (25). To a stirred solution of trimethylsilylacetylene (2.82 mL, 20.0 mmol) in THF (20 mL) was added EtMgBr (3.0 M solution in Et_2O ; 6.00 mL, 20.0 mmol) at room temperature, and the mixture was stirred for 2 h at this temperature. CuCl (13.2 mg, 0.133 mmol) and a solution of dibenzyl (isopropylidene)malonate **24** (4.50 g, 13.3 mmol) in THF (20 mL) were added to the mixture at 0 °C, and stirring was continued for 1 h at room temperature. The mixture was quenched by 3N HCl, and the whole was extracted with Et_2O . The extract was washed successively with NaHCO_3 , water and brine, and dried over MgSO_4 . Filtration and solvent evaporation afforded a residual oil, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give **25** (5.39 g, 93% yield) as a colorless oil: IR (KBr) cm^{-1} : 2173 ($\text{C}\equiv\text{C}$), 1758 ($\text{C}=\text{O}$), 1739 ($\text{C}=\text{O}$); ^1H NMR (300 MHz, CDCl_3) δ 0.11 (s, 9H, SiMe_3), 0.91 (d, $J = 6.6$ Hz, 3H, CMe), 1.00 (d, $J = 6.6$ Hz, 3H, CMe), 1.62-1.75 (m,

1H, Me₂CH), 3.22 (ddd, $J = 11.1, 3.6, 0.6$ Hz, 1H, 1'-H), 3.64 (d, $J = 11.1$ Hz, 1H, 2-H), 5.10-5.20 (m, 4H, 2 × Ph-CH₂), 7.25-7.37 (m, 10H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 0.00 (3C), 16.7, 21.6, 28.6, 39.5, 55.1, 67.19, 67.24, 89.1, 103.3, 128.1 (4C), 128.2, 128.3, 128.4 (2C), 128.5 (2C), 135.1, 135.3, 167.1, 167.3. *Anal.* Calcd for C₂₆H₃₂O₄Si: C, 71.52; H, 7.39. Found: C, 71.65; H, 7.44.

Dibenzyl 2-(1-Isopropylprop-2-ynyl)malonate (26). To a stirred solution of **25** (5.57 g, 12.8 mmol) in THF (35 mL) was added TBAF (1.0 M in THF; 15.4 mL, 15.4 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. Saturated NH₄Cl was added to the mixture, and the whole was extracted with Et₂O. The extract was washed successively with water and brine, and dried over MgSO₄. Filtration and solvent evaporation afforded a residual oil, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (15:1) to give **26** (4.56 g, 98% yield): colorless oil; IR (KBr) cm⁻¹: 3290 (C≡C), 1759 (C=O), 1736 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.93 (d, $J = 6.6$ Hz, 3H, CMe), 1.00 (d, $J = 6.9$ Hz, 3H, CMe), 1.66-1.77 (m, 1H, Me₂CH), 2.05 (d, $J = 1.5$ Hz, 1H, 3'-H), 3.19 (ddd, $J = 10.5, 3.6, 1.5$ Hz, 1H, 1'-H), 3.65 (d, $J = 10.5$ Hz, 1H, 2-H), 5.14 (s, 2H, Ph-CH₂), 5.17 (s, 2H, Ph-CH₂), 7.25-7.34 (m, 10H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 16.8, 21.4, 28.5, 38.3, 54.8, 67.32, 67.34, 72.6, 80.9, 128.2 (2C), 128.3 (3C), 128.41, 128.44 (2C), 128.5 (2C), 135.0, 135.2, 167.1, 167.3. *Anal.* Calcd for C₂₃H₂₄O₄: C, 75.80; H, 6.64. Found: C, 75.88; H, 6.76.

Dibenzyl 2-(1-Isopropyl-buta-2,3-dienyl)malonate (27). To a mixture of (HCHO)_n (410 mg, 13.7 mmol) and CuBr (394 mg, 2.75 mmol) under nitrogen were added a solution of the alkyne **26** (2.00 g, 5.49 mmol) in dioxane (8.2 mL) and *i*-Pr₂NH (1.54 mL, 11.0 mmol) at room temperature, and the mixture was stirred under reflux for 2 h. After cooling, the mixture was filtered with Et₂O and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **27** (478 mg, 23% yield) as a colorless oil; IR (KBr) cm⁻¹: 1955 (C=C=C), 1755 (C=O), 1736 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.81 (d, $J = 6.6$ Hz, 3H, CMe), 0.91 (d, $J = 6.9$ Hz, 3H, CMe), 1.67-1.78 (m, 1H, Me₂CH), 2.76-2.85 (m, 1H, 1'-H), 3.66 (d, $J = 9.9$ Hz, 1H, 2-H), 4.55 (dd, $J = 6.6, 1.8$ Hz, 2H, C=CH₂), 5.05-5.19 (m, 5H, 2 × Ph-CH₂ and 2'-H), 7.25-7.37 (m, 10H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 17.1, 21.2, 29.5, 44.9, 54.9, 67.0, 67.1, 75.4, 87.1, 128.18, 128.26, 128.31 (4C), 128.5 (4C), 135.2, 135.3, 168.0, 168.3, 208.9. *Anal.* Calcd for C₂₄H₂₆O₄: C, 76.17; H, 6.92. Found: C, 76.15; H, 6.98.

Dibenzyl 2-Allyl-2-(1-isopropylbuta-2,3-dienyl)malonate (28). By a procedure identical with that described for the synthesis of **17a**, the allene **27** (100 mg, 2.74 mmol) was converted into the allenene **28** (105 mg, 92% yield): colorless oil; IR (KBr) cm⁻¹: 1956 (C=C=C), 1728 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.68 (d, $J = 6.7$ Hz, 3H, CMe), 0.94 (d, $J = 6.7$ Hz, 3H, CMe), 2.09-2.13 (m, 1H, Me₂CH), 2.65 (dd, $J = 14.0, 7.9$ Hz, 1H, 1''-CHH), 2.75 (dd, $J = 11.0, 1.8$ Hz, 1H, 1'-H), 2.81 (dd, $J = 14.0, 7.3$ Hz, 1H, 1''-CHH), 4.58-4.66 (m, 2H, 4'-CH₂), 4.96-5.17 (m, 7H, 2 × Ph-CH₂, 2'-H, and 3''-CH₂), 5.65-5.69 (m, 1H, 2''-H), 7.25-7.34 (m, 10H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 18.0, 23.6, 28.8, 39.6, 49.2, 61.1, 67.04, 67.09, 73.7, 85.9, 119.0, 128.19 (2C), 128.24

(2C), 128.42 (2C), 128.46 (2C), 128.5 (2C), 132.5, 135.2, 135.3, 170.2, 170.6, 209.8; MS (FAB) m/z (%) 419 (MH^+ , 40), 91 (100); HRMS (FAB) calcd for $C_{27}H_{31}O_4$ (MH^+) 419.2222; found 419.2227.

2-(1-Isopropylbuta-2,3-dienyl)-2-(prop-2-enyl)propane-1,3-diol (29). To a stirred solution of $LiAlH_4$ (1.0 M in THF; 0.357 mL, 0.357 mmol) was added the malonate **28** (50.0 mg, 0.119 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. Saturated NH_4Cl was added to the mixture, and the whole was extracted with EtOAc. The extract was washed successively with water and brine, and dried over $MgSO_4$. Filtration and solvent evaporation gave a residual oil, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **29** (24.5 mg, 97% yield) as a colorless oil: IR (KBr) cm^{-1} : 3338 (OH), 1955 ($C=C=C$); 1H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, $J = 7.2$ Hz, 3H, CMe), 0.93 (d, $J = 7.2$ Hz, 3H, CMe), 2.01–2.12 (m, 1H, Me_2CH), 2.18–2.37 (m, 5H, 2 $\times$ OH, 1'-H, and 1''-CH₂), 3.68 (dd, $J = 11.0, 4.0$ Hz, 2H, 2 $\times$ OCHH), 3.81 (d, $J = 11.0$ Hz, 2H, 2 $\times$ OCHH), 4.66 (d, $J = 6.6$ Hz, 2H, 4'-CH₂), 5.06–5.14 (m, 3H, 2'-H and 3''-CH₂), 5.79–5.93 (m, 1H, 2''-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 24.3, 26.7, 35.6, 45.2, 47.7, 67.7, 67.8, 73.1, 86.2, 118.0, 134.5, 209.2; MS (FAB) m/z (%) 211 (MH^+ , 100); HRMS (FAB) calcd for $C_{13}H_{23}O_2$ (MH^+) 211.1698; found 211.1711.

5-Allyl-5-(1-isopropylbuta-2,3-dienyl)-2,2-dimethyl-1,3-dioxane (30). To a stirred mixture of $TsOH \cdot H_2O$ (3.90 mg, 0.020 mmol), 2,2-dimethoxypropane (49 μ L, 0.40 mmol), and MS 4A (10 mg) in CH_2Cl_2 (1 mL) was added the diol **29** (42.0 mg, 0.20 mmol) at room temperature, and the mixture was stirred for 1 h. The mixture was dried over $MgSO_4$, and the filtrate was concentrated under reduced pressure. The resulting residual oil was purified by column chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **30** (33.8 mg, 68% yield) as a colorless oil: IR (KBr) cm^{-1} : 1955 ($C=C=C$); 1H NMR (300 MHz, $CDCl_3$) δ 0.88 (d, $J = 6.6$ Hz, 3H, CMe), 0.91 (d, $J = 6.6$ Hz, 3H, CMe), 1.39 (s, 3H, CMe), 1.40 (s, 3H, CMe), 2.01–2.13 (m, 2H, Me_2CH and 1'-H), 2.33 (dd, $J = 14.1, 7.5$ Hz, 1H, 1''-CHH), 2.56 (dd, $J = 14.1, 7.5$ Hz, 1H, 1''-CHH), 3.52 (dd, $J = 11.7, 1.8$ Hz, 1H, OCHH), 3.58 (dd, $J = 11.7, 1.8$ Hz, 1H, OCHH), 3.84 (s, 1H, OCHH), 3.87 (s, 1H, OCHH), 4.65 (d, $J = 6.6$ Hz, 2H, 4'-CH₂), 5.01 (dt, $J = 10.8, 6.6$ Hz, 1H, 2'-H), 5.10–5.19 (m, 2H, 3''-CH₂), 5.77–5.91 (m, 1H, 2''-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) 19.1, 21.3, 24.2, 26.7, 26.8, 36.2, 39.8, 48.5, 65.3, 65.5, 73.2, 85.4, 97.9, 118.1, 134.1, 209.4; MS (FAB) m/z (%) 251 (MH^+ , 19), 136 (100); HRMS (FAB) calcd for $C_{16}H_{27}O_2$ (MH^+) 251.2011; found 251.2005.

General Procedure for Palladium(0)-Catalyzed Pyrrolidine Formation. Synthesis of (2*S*,3*S*)-2-Isopropyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-(1-phenylvinyl)pyrrolidine (31a) (Table 1, entry 2). To a stirred mixture of the allenene **17d** (30.0 mg, 0.090 mmol), $Pd(PPh_3)_4$ (10.4 mg, 0.009 mmol; 10 mol%), and K_2CO_3 (24.9 mg, 0.180 mmol) in 1,4-dioxane (3 mL) under argon was added PhI (0.020 mL, 0.180 mmol), and the mixture was stirred under reflux for 4.5 h. After cooling, water (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 $MgSO_4$. Concentration of the filtrate

followed by flash chromatography over silica gel with *n*-hexane–EtOAc (20:1) gave the pyrrolidine **31a** (22.1 mg, 60% yield): colorless crystals; mp 115–117 °C (*n*-hexane–Et₂O); [α]_D²³ –2.44 (*c* 0.87, CHCl₃); IR (KBr) cm^{–1}: 1321 (SO₂N), 1153 (SO₂N); ¹H NMR (300 MHz, CDCl₃) δ 0.63 (d, *J* = 6.9 Hz, 3H, CMe), 0.79 (d, *J* = 6.9 Hz, 3H, CMe), 1.85–1.95 (m, 1H, Me₂CH), 2.29 (s, 3H, Ph–Me), 2.57 (s, 6H, 2 × Ph–Me), 3.67 (m, 1H, 3-H), 3.75 (dd, *J* = 4.2, 2.4 Hz, 1H, 2-H), 3.92 (ddd, *J* = 14.1, 1.5, 1.5 Hz, 1H, 5-CHH), 4.19–4.26 (m, 1H, 5-CHH), 5.06 (m, 1H, C=CHH), 5.11 (s, 1H, PhC=CHH), 5.14 (d, *J* = 1.5 Hz, 1H, C=CHH), 5.22 (s, 1H, PhC=CHH), 6.91 (s, 2H, Ph), 7.25–7.33 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 16.6, 19.6, 20.9, 23.1 (2C), 32.8, 50.5, 52.3, 69.7, 109.5, 115.0, 127.4 (2C), 127.5, 128.2 (2C), 131.8 (2C), 133.3, 140.1 (2C), 141.3, 142.3, 147.3, 149.4; MS (FAB) *m/z* (%) 410 (MH⁺, 100); HRMS (FAB) calcd for C₂₅H₃₂NO₂S (MH⁺) 410.2154; found 410.2176.

(2S,3S)-2-Isopropyl-3-[1-(4-methoxyphenyl)vinyl]-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)pyrrolidine (31b) (Table 1, entry 6). By a procedure similar to that described for the synthesis of **31a** with PhI, the allenene **17d** (100 mg, 0.300 mmol) was converted into **31b** (79.2 mg, 60% yield) by use of 4-iodoanisole (140 mg, 0.600 mmol) as an aryl halide: colorless crystals; mp 157–158 °C; [α]_D²⁵ –17.5 (*c* 0.91, CHCl₃); IR (KBr) cm^{–1}: 1323 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.66 (d, *J* = 6.7 Hz, 3H, CMe), 0.80 (d, *J* = 6.7 Hz, 3H, CMe), 1.88–1.95 (m, 1H, Me₂CH), 2.29 (s, 3H, Ph–Me), 2.57 (s, 6H, 2 × Ph–Me), 3.64 (m, 1H, 3-H), 3.76 (dd, *J* = 4.3, 2.4 Hz, 1H, 2-H), 3.82 (s, 3H, OMe), 3.92 (d, *J* = 14.0 Hz, 1H, 5-CHH), 4.21 (dd, *J* = 14.0, 1.2 Hz, 1H, 5-CHH), 5.03 (s, 1H, C=CHH), 5.05 (s, 1H, PhC=CHH), 5.13 (s, 1H, C=CHH), 5.16 (s, 1H, PhC=CHH), 6.84 (d, *J* = 8.5 Hz, 2H, Ph), 6.91 (s, 2H, Ph), 7.23 (d, *J* = 8.5 Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 16.8, 19.7, 21.0, 23.2 (2C), 32.9, 50.7, 52.3, 55.3, 69.8, 109.3, 113.4 (2C), 113.9, 128.4 (2C), 131.7 (2C), 133.3, 133.6, 139.9 (2C), 142.1, 147.2, 148.7, 158.9; MS (FAB) *m/z* (%) 440 (MH⁺, 95), 396 (100); HRMS (FAB) calcd for C₂₆H₃₄NO₃S (MH⁺) 440.2259; found 440.2256.

(2S,3S)-2-Isopropyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-[1-(4-methylphenyl)vinyl]pyrrolidine (31c) (Table 1, entry 7). By a procedure similar to that described for the synthesis of **31a** with PhI, the allenene **17d** (80 mg, 0.240 mmol) was converted into **31c** (56.4 mg, 56% yield) by use of 4-iodotoluene (105 mg, 0.480 mmol) as an aryl halide: colorless crystals; mp 142–144 °C (*n*-hexane–CHCl₃–Et₂O); [α]_D²³ –7.56 (*c* 0.23, CHCl₃); IR (KBr) cm^{–1}: 1323 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.66 (d, *J* = 6.7 Hz, 3H, CMe), 0.80 (d, *J* = 6.7 Hz, 3H, CMe), 1.90–1.96 (m, 1H, Me₂CH), 2.29 (s, 3H, Ph–Me), 2.35 (s, 3H, Ph–Me), 2.57 (s, 6H, 2 × Ph–Me), 3.66 (m, 1H, 3-H), 3.77 (dd, *J* = 3.7, 1.8 Hz, 1H, 2-H), 3.92 (d, *J* = 14.0 Hz, 1H, 5-CHH), 4.19 (dd, *J* = 14.0, 1.8 Hz, 1H, 5-CHH), 5.05 (s, 1H, C=CHH), 5.05 (s, 1H, PhC=CHH), 5.13 (d, *J* = 1.8 Hz, 1H, C=CHH), 5.19 (s, 1H, PhC=CHH), 6.91 (s, 2H, Ph), 7.11 (d, *J* = 7.9 Hz, 2H, Ph), 7.19 (d, *J* = 7.9 Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 16.8, 19.7, 21.0, 21.2, 23.2 (2C), 32.9, 50.5, 52.3, 69.9, 109.3, 114.3, 127.2 (2C), 128.7 (2C), 131.7 (2C), 133.3, 137.1, 138.3, 140.0 (2C),

142.1, 147.2, 149.2; MS (FAB) m/z (%) 424 (MH^+ , 100); HRMS (FAB) calcd for $C_{26}H_{34}NO_2S$ (MH^+) 424.2310; found 424.2312.

(2S,3S)-2-Isopropyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-[1-(4-nitrophenyl)vinyl]-pyrrolidine (31d) (Table 1, entry 8). By a procedure similar to that described for the synthesis of **31a** with PhI, the allenene **17d** (100 mg, 0.300 mmol) was converted into **31d** (49.1 mg, 36% yield) by use of 1-iodo-4-nitrobenzene (149 mg, 0.600 mmol) as an aryl halide: yellow crystals; mp 167–169 °C; $[\alpha]^{24}_D$ –62.1 (c 0.23, $CHCl_3$); IR (KBr) cm^{-1} : 1321 (SO_2N), 1155 (SO_2N); 1H NMR (500 MHz, $CDCl_3$) δ 0.60 (d, J = 6.7 Hz, 3H, CMe), 0.77 (d, J = 6.7 Hz, 3H, CMe), 1.79–1.82 (m, 1H, Me_2CH), 2.29 (s, 3H, Ph-Me), 2.54 (s, 6H, 2 $\times$ Ph-Me), 3.62 (dd, J = 4.2, 1.2 Hz, 1H, 2-H), 3.68 (m, 1H, 3-H), 3.91 (d, J = 14.0 Hz, 1H, 5-CHH), 4.36 (dd, J = 14.0, 1.2 Hz, 1H, 5-CHH), 5.10 (s, 1H, C=CHH), 5.22 (s, 1H, C=CHH), 5.34 (s, 1H, PhC=CHH), 5.37 (s, 1H, PhC=CHH), 6.91 (s, 2H, Ph), 7.49 (d, J = 8.5 Hz, 2H, Ph), 8.18 (d, J = 8.5 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 19.6, 20.9, 23.0 (2C), 32.6, 50.6, 52.3, 69.3, 110.2, 118.1, 123.5 (2C), 128.4 (2C), 131.9 (2C), 133.3, 139.9 (2C), 142.5, 146.7, 147.1, 147.4, 148.1; MS (FAB) m/z (%) 455 (MH^+ , 100); HRMS (FAB) calcd for $C_{25}H_{31}N_2O_4S$ (MH^+) 455.2005; found 455.2010.

(2S,3S)-2-Isopropyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-(1-naphthylvinyl)pyrrolidine (31e) (Table 1, entry 9). By a procedure similar to that described for the synthesis of **31a** with PhI, the allenene **17d** (100 mg, 0.300 mmol) was converted into **31e** (34.9 mg, 25% yield) by use of 1-iodonaphthalene (87.6 μ L, 0.600 mmol) as an aryl halide: colorless crystals; mp 198–199 °C; $[\alpha]^{24}_D$ –22.8 (c 0.115, $CHCl_3$); IR (KBr) cm^{-1} : 1319 (SO_2N), 1157 (SO_2N); 1H NMR (500 MHz, $CDCl_3$) δ 0.14 (br s, 3H, CMe), 0.61 (d, J = 6.7 Hz, 3H, CMe), 1.69–1.76 (m, 1H, $CHMe_2$), 2.30 (s, 3H, Ph-Me), 2.64 (s, 6H, 2 $\times$ Ph-Me), 3.57 (s, 1H, 3-H), 3.91 (d, J = 14.0 Hz, 1H, 5-CHH), 3.93 (s, 1H, 2-H), 4.37 (d, J = 14.0 Hz, 1H, 5-CHH), 5.09 (m, 1H, C=CHH), 5.19 (s, 1H, C=CHH), 5.24 (s, 1H, PhC=CHH), 5.49 (s, 1H, PhC=CHH), 6.94 (s, 2H, Ph), 7.28 (d, J = 6.7 Hz, 1H, Ar), 7.39–7.43 (m, 1H, Ar), 7.46–7.51 (m, 2H, Ar), 7.77 (d, J = 8.5 Hz, 1H, Ar), 7.83–7.85 (m, 1H, Ar), 7.98 (d, J = 7.9 Hz, 1H, Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 15.9, 19.0, 21.0, 23.1 (2C), 32.4, 51.8, 52.8, 69.0, 110.0, 116.3, 125.0, 125.3, 125.6, 126.0, 126.6, 127.6, 128.3, 131.0, 131.8 (2C), 133.4, 133.5, 139.6, 140.0 (2C), 142.3, 146.7, 148.5; MS (FAB) m/z (%) 482 (MNa^+ , 60), 471 (100); HRMS (FAB) calcd for $C_{29}H_{33}NNaO_2S$ (MNa^+) 482.2130; found 482.2137.

(2S,3S)-2-Isopropyl-4-methyl-1-(2,4,6-trimethylphenylsulfonyl)-3-(1-phenylvinyl)-2,3-dihydro-1H-pyrrole (32) (Table 1, entry 4). By a procedure similar to that described for the synthesis of **31a** with PhI in dioxane, the allenene **17d** (50 mg, 0.150 mmol) was converted into **31a** (17.3 mg, 28% yield) and **32** (2.0 mg, 3% yield) along with other unidentified products by use of DMSO (3 mL) as the solvent.

Compound **32**: colorless oil; $[\alpha]^{19}_D$ +30.7 (c 0.28, $CHCl_3$); IR (KBr) cm^{-1} : 1344 (SO_2N), 1162 (SO_2N); 1H NMR (300 MHz, $CDCl_3$) δ 0.52 (d, J = 6.9 Hz, 3H, CMe), 0.74 (d, J = 6.6 Hz, 3H, CMe), 1.67 (s, 3H, CMe), 1.85–1.95 (m, 1H, Me_2CH), 2.32 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 $\times$ Ph-Me),

3.33 (d, $J = 3.6$ Hz, 1H, 4-H), 3.71 (dd, $J = 3.9, 3.6$ Hz, 1H, 5-H), 4.75 (s, 1H, C=CHH), 5.05 (s, 1H, C=CHH), 6.23 (s, 1H, 2-H), 6.94 (s, 2H, Ph), 7.13-7.33 (m, 5H, Ph); MS (FAB) m/z (%) 432 (MNa⁺, 100); HRMS (FAB) calcd for C₂₅H₃₁NNaO₂S (MNa⁺) 432.1973; found 432.1983.

(2S,3S)-2-Isobutyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-(1-phenylvinyl)pyrrolidine (33a) (Table 2, entry 1). By a procedure identical with that described for the synthesis of **31a**, the allenene **17a** (100 mg, 0.288 mmol) was converted into **33a** (55.6 mg, 46% yield): colorless oil; $[\alpha]_D^{28} -22.0$ (c 0.99, CHCl₃); IR (KBr) cm⁻¹: 1321 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.38 (d, $J = 6.1$ Hz, 3H, CMe), 0.75 (d, $J = 6.1$ Hz, 3H, CMe), 1.18-1.26 (m, 1H, Me₂CH), 1.35-1.58 (m, 2H, Me₂CHCH₂), 2.29 (s, 3H, Ph-Me), 2.54 (s, 6H, 2 × Ph-Me), 3.57 (s, 1H, 3-H), 3.63-3.66 (m, 1H, 2-H), 3.93 (d, $J = 14.0$ Hz, 1H, 5-CHH), 4.17 (d, $J = 14.0$ Hz, 1H, 5-CHH), 5.10 (s, 1H, PhC=CHH), 5.15 (s, 1H, C=CHH), 5.23 (s, 1H, PhC=CHH), 5.26 (s, 1H, C=CHH), 6.90 (s, 2H, Ph), 7.24-7.33 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 20.7, 20.9, 23.0 (2C), 23.9, 25.1, 43.6, 50.1, 55.0, 62.5, 111.4, 114.8, 127.2 (2C), 127.5, 128.2 (2C), 131.7 (2C), 133.4, 140.2 (2C), 141.3, 142.2, 145.7, 148.4; LRMS (FAB) m/z (%) 424 (MH⁺, 100); HRMS (FAB) calcd for C₂₆H₃₄NO₂S (MH⁺) 424.2310; found 424.2304.

(2S,3S)-2-Isobutyl-3-[1-(4-methoxyphenyl)vinyl]-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)pyrrolidine (33b) (Table 2, entry 2). By a procedure similar to that described for the synthesis of **31a** with PhI, the allenene **17a** (50 mg, 0.144 mmol) was converted into **33b** (30.2 mg, 50% yield) by use of 4-iodoanisole (70.0 mg, 0.288 mmol) as an aryl halide: colorless oil; $[\alpha]_D^{24} -18.9$ (c 0.98, CHCl₃); IR (KBr) cm⁻¹: 1319 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.44 (d, $J = 6.1$ Hz, 3H, CMe), 0.77 (d, $J = 6.7$ Hz, 3H, CMe), 1.23-1.24 (m, 1H, Me₂CHCHH), 1.36-1.43 (m, 2H, Me₂CHCHH and Me₂CH), 2.23 (s, 3H, Ph-Me), 2.54 (s, 6H, 2 × Ph-Me), 3.54 (s, 1H, 3-H), 3.68 (dd, $J = 11.0, 2.4$ Hz, 1H, 2-H), 3.82 (s, 3H, OMe), 3.92 (d, $J = 14.0$ Hz, 1H, 5-CHH), 4.14 (d, $J = 14.0$ Hz, 1H, 5-CHH), 5.02 (s, 1H, C=CH), 5.14 (s, 1H, C=CH), 5.17 (s, 1H, C=CH), 5.24 (s, 1H, C=CH), 6.83 (d, $J = 8.5$ Hz, 2H, Ph), 6.90 (s, 2H, Ph), 7.20 (d, $J = 8.5$ Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 20.9, 21.0, 23.1 (2C), 24.0, 25.2, 43.8, 50.1, 55.1, 55.3, 62.6, 111.1, 113.5 (2C), 113.8, 128.1 (2C), 131.6 (2C), 133.2, 133.6, 140.1 (2C), 142.1, 145.6, 147.7, 158.9; MS (FAB) m/z (%) 454 (MH⁺, 100); HRMS (FAB) calcd for C₂₇H₃₆NO₃S (MH⁺) 454.2416; found 454.2417.

(2S,3S)-4-Methylene-1-(2,4,6-trimethylphenylsulfonyl)-2-[(1S)-1-methylpropyl]-3-(1-phenylvinyl)pyrrolidine (34a) (Table 2, entry 3). By a procedure identical with that described for the synthesis of **31a**, the allenene **17b** (50 mg, 0.144 mmol) was converted into **34a** (39.0 mg, 64% yield): colorless crystals; mp 115–117 °C (*n*-hexane–Et₂O); $[\alpha]_D^{21} -7.36$ (c 1.00, CHCl₃); IR (KBr) cm⁻¹: 1317 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.45 (t, $J = 7.3$ Hz, 3H, CMe), 0.76 (d, $J = 6.7$ Hz, 3H, CMe), 0.88-0.96 (m, 2H, MeCH₂), 1.42-1.49 (m, 1H, EtCH), 2.23 (s, 3H, Ph-Me), 2.58 (s, 6H, 2 × Ph-Me), 3.63 (s, 1H, 3-H), 3.83 (dd, $J = 3.1, 3.1$ Hz, 1H, 2-H), 3.94 (d, $J = 14.0$ Hz, 1H, 5-CHH), 4.29 (d, $J = 14.0$ Hz, 1H, 5-CHH), 5.04 (s, 1H, C=CH), 5.19 (s, 2H, 2

× C=CH), 5.22 (s, 1H, C=CH), 6.91 (s, 2H, Ph), 7.21-7.33 (m, 5H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 11.9, 14.1, 21.0, 23.1 (2C), 26.8, 39.8, 50.6, 52.4, 67.8, 109.2, 115.0, 127.4 (3C), 128.1 (2C), 131.7 (2C), 133.2, 140.1 (2C), 141.4, 142.2, 147.3, 149.5; MS (FAB) *m/z* (%) 424 (MH⁺, 100); HRMS (FAB) calcd for C₂₆H₃₄NO₂S (MH⁺) 424.2310; found 424.2312.

(2S,3S)-3-[1-(4-Methoxyphenyl)vinyl]-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-2-[(1S)-1-methylpropyl]pyrrolidine (34b) (Table 2, entry 4). By a procedure similar to that described for the synthesis of **31a** with PhI, the allenene **17b** (50.5 mg, 0.145 mmol) was converted into **34b** (33.7 mg, 55% yield) by use of 4-iodoanisole (70.5 mg, 0.290 mmol) as an aryl halide: colorless crystals; mp 93–96 °C (*n*-hexane–Et₂O); [α]_D²² –19.5 (*c* 0.96, CHCl₃); IR (KBr) cm^{–1}: 1317 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.52 (t, *J* = 7.3 Hz, 3H, CMe), 0.77 (d, *J* = 6.7 Hz, 3H, CMe), 0.88-1.03 (m, 2H, MeCH₂), 1.46-1.51 (m, 1H, EtCH), 2.29 (s, 3H, Ph-Me), 2.58 (s, 6H, 2 × Ph-Me), 3.60 (s, 1H, 3-H), 3.82 (s, 3H, OMe), 3.85-3.86 (m, 1H, 2-H), 3.94 (d, *J* = 14.0 Hz, 1H, 5-CHH), 4.27 (d, *J* = 14.0 Hz, 1H, 5-CHH), 5.02 (s, 1H, C=CH), 5.07 (s, 1H, C=CH), 5.11 (s, 1H, C=CH), 5.16 (s, 1H, C=CH), 6.84 (d, *J* = 8.5 Hz, 2H, Ph), 6.91 (s, 2H, Ph), 7.23 (d, *J* = 8.5 Hz, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 11.8, 14.0, 20.9, 23.0 (2C), 26.8, 39.8, 50.6, 52.4, 55.3, 68.0, 109.1, 113.5 (2C), 114.2, 128.6 (2C), 131.8 (2C), 133.3, 133.9, 140.2 (2C), 142.3, 147.5, 149.0, 159.0; MS (FAB) *m/z* (%) 454 (MH⁺, 95), 396 (100); HRMS (FAB) calcd for C₂₇H₃₆NO₃S (MH⁺) 454.2416; found 454.2443.

(2R,3S)-2-tert-Butyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-(1-phenylvinyl)pyrrolidine (35) (Table 2, entry 5). By a procedure identical with that described for the synthesis of **31a**, the allenene **17c** (80 mg, 0.230 mmol) was converted into **35** (59.1 mg, 61% yield): colorless crystals; mp 112–113 °C (*n*-hexane–Et₂O–CHCl₃); [α]_D²³ –59.2 (*c* 1.60, CHCl₃); IR (KBr) cm^{–1}: 1329 (SO₂N), 1153 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 0.63 (s, 9H, CMe₃), 2.27 (s, 3H, Ph-Me), 2.60 (s, 6H, 2 × Ph-Me), 3.65 (d, *J* = 1.8 Hz, 1H, 2-H), 3.78 (m, 1H, 3-H), 3.95 (d, *J* = 15.3 Hz, 1H, 5-CHH), 4.62 (dd, *J* = 15.3, 1.8 Hz, 1H, 5-CHH), 5.10 (d, *J* = 1.2 Hz, 1H, C=CHH), 5.11 (s, 1H, PhC=CHH), 5.17 (d, *J* = 1.2 Hz, 1H, C=CHH), 5.24 (s, 1H, PhC=CHH), 6.90 (s, 2H, Ph), 7.26–7.43 (m, 5H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 21.0, 23.5 (2C), 27.3 (3C), 36.6, 52.3, 54.2, 75.2, 108.6, 115.6, 127.2, 127.5 (2C), 127.9 (2C), 131.7 (2C), 134.4, 139.6 (2C), 141.9 (2C), 149.0, 149.2; MS (FAB) *m/z* (%) 424 (MH⁺, 73), 366 (100); HRMS (FAB) calcd for C₂₆H₃₄NO₂S (MH⁺) 424.2310; found 424.2312.

(2S,3S)-2-Benzyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-(1-phenylvinyl)pyrrolidine (36) (Table 2, entry 6). By a procedure identical with that described for the synthesis of **31a**, the allenene **17e** (150 mg, 0.393 mmol) was converted into **36** (104 mg, 58% yield): colorless oil; [α]_D²⁸ –7.05 (*c* 2.59, CHCl₃); IR (KBr) cm^{–1}: 1321 (SO₂N), 1155 (SO₂N); ¹H NMR (500 MHz, CDCl₃) δ 2.29 (s, 3H, Ph-Me), 2.54 (s, 6H, 2 × Ph-Me), 2.56-2.61 (m, 1H, Ph-CHH), 3.03 (dd, *J* = 12.8, 3.7 Hz, 1H, Ph-CHH), 3.65 (s, 1H, 3-H), 3.81 (dd, *J* = 11.6, 3.7 Hz, 1H, 2-H), 4.02 (d, *J* = 14.0 Hz, 1H, 5-CHH), 4.07 (d, *J* = 14.0 Hz, 1H, 5-CHH), 5.00 (s, 1H, PhC=CHH), 5.20 (s, 1H,

PhC=CHH), 5.21 (s, 1H, C=CHH), 5.32 (s, 1H, C=CHH), 6.59-7.26 (m, 10H, Ph), 6.91 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 20.9, 23.0 (2C), 40.5, 49.9, 52.2, 65.4, 112.2, 114.5, 126.5 (3C), 127.1, 128.0 (2C), 128.6 (2C), 129.6 (2C), 131.8 (2C), 133.0, 137.8, 139.7, 140.3 (2C), 142.4, 144.9, 147.6; MS (FAB) m/z (%) 458 (MH^+ , 85), 366 (100); HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{32}\text{NO}_2\text{S}$ (MH^+) 458.2154; found 458.2163.

(2R,3S)-1-(tert-Butoxycarbonyl)-2-isopropyl-4-methylene-3-(1-phenylvinyl)pyrrolidine (37) (Table 2, entry 7). By a procedure identical with that described for the synthesis of **31a**, the allenene **19** (47.8 mg, 0.19 mmol) was converted into **37** (23.5 mg, 41% yield): colorless oil; $[\alpha]_D^{23} +14.0$ (c 1.38, CHCl_3); IR (KBr) cm^{-1} : 1695 (C=O); ^1H NMR (300 MHz, CDCl_3 , 328 K) δ 0.84 (d, J = 6.6 Hz, 3H, CMe), 0.85 (d, J = 6.6 Hz, 3H, CMe), 1.40 (s, 9H, CMe_3), 1.74-1.93 (m, 1H, Me_2CH), 3.55 (br s, 1H, 3-H), 3.55-3.79 (br s, 1H, 2-H), 3.82 (d, J = 15.9 Hz, 1H, 5-CHH), 4.16-4.34 (br s, 1H, 5-CHH), 5.00 (s, 1H, C=CHH), 5.05 (s, 1H, C=CHH), 5.08 (s, 1H, PhC=CHH), 5.13 (s, 1H, PhC=CHH), 7.24-7.39 (m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 328 K) δ 19.2 (2C), 28.5 (3C), 32.4, 50.6, 53.1, 68.1, 79.1, 108.9, 113.4, 127.3 (2C), 127.4, 128.1 (2C), 141.6, 148.1, 150.9, 154.8; MS (FAB) m/z (%) 328 (MH^+ , 10), 272 (100); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{30}\text{NO}_2$ (MH^+) 328.2277; found 328.2269.

2,2-Dimethyl-4-methylene-1-(4-methylphenylsulfonyl)-3-(1-phenylvinyl)pyrrolidine (38) (Table 2, entry 8). By a procedure identical with that described for the synthesis of **31a**, the allenene **23** (50.0 mg, 0.172 mmol) was converted into **38** (37.0 mg, 59% yield): colorless oil; IR (KBr) cm^{-1} : 1338 (NSO_2), 1155 (NSO_2); ^1H NMR (500 MHz, CDCl_3) δ 1.24 (s, 3H, CMe), 1.28 (s, 3H, CMe), 2.41 (s, 3H, Ph-Me), 3.65 (s, 1H, 3-H), 4.12 (dd, J = 14.0, 2.4 Hz, 1H, 5-CHH), 4.19 (dd, J = 14.0, 1.2 Hz, 1H, 5-CHH), 5.12 (s, 1H, C=CHH), 5.13 (m, 2H, C=CHH and PhC=CHH), 5.48 (s, 1H, PhC=CHH), 7.14-7.29 (m, 7H, Ph), 7.70-7.72 (m, 2H, Ph); ^{13}C NMR (67.8 MHz, CDCl_3) δ 21.6, 22.7, 27.7, 52.2, 61.2, 68.3, 108.4, 118.6, 126.4 (2C), 127.0 (2C), 127.3, 128.3 (2C), 129.3 (2C), 138.4, 142.8, 143.5, 144.9, 145.6; MS (FAB) m/z (%) 368 (MH^+ , 83), 69 (100); HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_2\text{S}$ (MH^+) 368.1684; found 368.1690.

N-Allyl-N-[(1S,aR)-1-isobutylpenta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (39). By a procedure identical with that described for the synthesis of **17a**, (5S,aR)-6-methyl-5-[N-(2,4,6-trimethylphenylsulfonyl)amino]hepta-2,3-diene* (13 mg, 0.0423 mmol) was converted into the allenene **39** (12 mg, 82% yield): colorless oil; $[\alpha]_D^{28} -104$ (c 0.859, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.84 (d, J = 6.8 Hz, 3H, CMe), 0.89 (d, J = 6.8 Hz, 3H, CMe), 1.64 (dd, J = 7.0, 3.8 Hz, 3H, CMe), 1.82-1.95 (m, 1H, Me_2CH), 2.29 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 $\times$ Ph-Me), 3.75-3.91 (m, 3H, 1-H and 1'- CH_2), 4.96 (dd, J = 10.3, 1.4 Hz, 1H, 3'-CHH), 5.07 (dd, J = 17.0, 1.4 Hz, 1H, 3'-CHH), 5.03-5.19 (m, 2H, NH and 2-H), 5.81 (dddd, J = 17.0, 10.3, 6.5, 6.5 Hz, 1H, 2'-H), 6.92 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 13.7, 20.3, 21.0, 21.1, 23.6, 30.5, 46.5, 63.8, 87.3, 89.4, 95.2, 116.8, 132.1 (2C), 134.0, 136.3, 140.3 (2C), 142.4, 206.2; MS (FAB) m/z (%) 348 (MH^+ , 24), 119 (100); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{30}\text{NO}_2\text{S}$ (MH^+) 348.1997; found 348.2000.

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(2*S*,3*S*)-2-Isopropyl-4-methylene-1-(2,4,6-trimethylphenylsulfonyl)-3-[(1*Z*)-1-phenylpropenyl]-pyrrolidine (40) (Table 2, entry 9). By a procedure identical with that described for the synthesis of **31a**, the allenene **39** (50.0 mg, 0.172 mmol) was converted into **40** (37.0 mg, 59% yield): colorless oil; $[\alpha]_D^{20} +7.21$ (*c* 0.95, CHCl₃); IR (KBr) cm⁻¹: 1321 (NSO₂), 1155 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.43 (d, *J* = 6.7 Hz, 3H, CMe), 0.71 (d, *J* = 6.7 Hz, 3H, CMe), 1.49 (dd, *J* = 3.9, 0.6 Hz, 3H, CMe), 1.81–1.85 (m, 1H, Me₂CH), 2.30 (s, 3H, Ph-Me), 2.59 (s, 6H, 2 × Ph-Me), 3.42 (s, 1H, 3-H), 3.68 (dd, *J* = 2.1, 0.9 Hz, 1H, 2-H), 3.92 (d, *J* = 8.4 Hz, 1H, 5-CHH), 4.19 (dd, *J* = 8.4, 1.2 Hz, 1H, 5-CHH), 5.06 (s, 1H, C=CHH), 5.16 (s, 1H, C=CHH), 5.49 (q, *J* = 5.5 Hz, 1H, C=CH), 6.92 (s, 2H, Ph), 7.06–7.07 (m, 2H, Ph), 7.26–7.30 (m, 3H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 14.7, 16.3, 19.2, 20.9, 23.0 (2C), 32.4, 52.7, 52.8, 69.0, 109.7, 122.5, 126.7, 128.1 (2C), 129.3 (2C), 131.8 (2C), 133.6, 139.8, 140.1 (2C), 141.5, 142.2, 147.2; MS (FAB) *m/z* (%) 424 (MH⁺, 100); HRMS (FAB) calcd for C₂₆H₃₄NO₂S (MH⁺) 424.2310; found 424.2308.

Dibenzyl (2*R,3*S**)-2-Isopropyl-4-methylene-3-(1-phenylvinyl)cyclopentane-1,1-dicarboxylate (41)**. By a procedure identical with that described for the synthesis of **31a**, the allenene **28** (80 mg, 0.191 mmol) was converted into **41** (37.4 mg, 40% yield): colorless oil; IR (KBr) cm⁻¹: 1728 (C=O), 1497 (C=CH), 1456 (C=CH); ¹H NMR (300 MHz, CDCl₃) δ 0.69 (d, *J* = 6.9 Hz, 3H, CMe), 0.77 (d, *J* = 6.9 Hz, 3H, CMe), 2.00–2.07 (m, 1H, Me₂CH), 2.82 (ddd, *J* = 16.8, 4.6, 2.7 Hz, 1H, 5-CHH), 2.85 (dd, *J* = 11.4, 3.9 Hz, 1H, 2-H), 3.26 (d, *J* = 16.8 Hz, 1H, 5-CHH), 3.61 (dd, *J* = 11.4, 2.4 Hz, 1H, 3-H), 4.96–5.16 (m, 7H, 2 × Ph-CH₂, 3 × C=CH), 5.35 (d, *J* = 1.5 Hz, 1H, C=CH), 7.20–7.36 (m, 15H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 18.3, 23.6, 28.3, 42.3, 51.7, 54.5, 61.4, 67.0, 67.2, 77.2 (2C), 107.6, 116.5, 127.25, 127.32 (2C), 128.0 (2C), 128.15 (2C), 128.18, 128.23, 128.5 (4C), 135.2, 135.5, 141.2, 150.6, 151.4, 171.0, 171.5; MS (FAB) *m/z* (%) 495 (MH⁺, 18), 91 (100); HRMS (FAB) calcd for C₃₃H₃₅O₄ (MH⁺) 495.2535; found 495.2546.

[(2*R,3*S**)-1-Hydroxymethyl-2-isopropyl-4-methylene-3-(1-phenylvinyl)cyclopentyl]-*O,O*-(isopropylidene)methanol (42)**. By a procedure identical with that described for the synthesis of **31a**, the allenene **30** (33 mg, 0.132 mmol) was converted into **41** (11.7 mg, 27% yield): colorless oil; IR (KBr) cm⁻¹: 1382 (C=C), 1369 (C=C); ¹H NMR (300 MHz, CDCl₃) δ 0.81 (d, *J* = 6.6 Hz, 3H, CMe), 0.88 (d, *J* = 6.6 Hz, 3H, CMe), 1.40 (s, 3H, CMe), 1.43 (s, 3H, CMe), 1.62 (dd, *J* = 9.9, 6.6 Hz, 1H, 2-H), 1.84–1.90 (m, 1H, Me₂CH), 2.46 (dd, *J* = 16.5, 2.1 Hz, 1H, 5-CHH), 2.96 (d, *J* = 16.5 Hz, 1H, 5-CHH), 3.33 (dd, *J* = 11.4, 2.4 Hz, 1H, 3-H), 3.51 (dd, *J* = 11.4, 2.1 Hz, 2H, OCH₂), 3.90 (d, *J* = 11.4 Hz, 1H, OCHH), 3.98 (dd, *J* = 11.4, 1.2 Hz, 1H, OCHH), 5.00 (d, *J* = 1.2 Hz, 1H, C=CH), 5.07–5.08 (m, 1H, C=CH), 5.17 (m, 1H, C=CH), 5.26 (d, *J* = 1.5 Hz, 1H, C=CH), 7.24–7.36 (m, 5H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 19.6, 19.9, 24.1, 27.3, 28.3, 42.8, 43.6, 52.0, 53.2, 64.2, 69.1, 97.9, 108.3, 115.8, 127.2, 127.6 (2C), 128.0 (2C), 141.6, 151.9, 152.3; MS (FAB) *m/z*

(%) 349 (MNa⁺, 46), 105 (100); HRMS (FAB) calcd for C₂₂H₃₁O₂ (MH⁺) 327.2324; found 327.2302.

***N*-[*(1S)*-1-Isobutylbuta-2,3-dienyl]-2,4,6-trimethyl-*N*-(2-methylprop-2-enyl)phenylsulfonamide (**49a**). By a procedure similar to that described for the synthesis of **17a** with allyl bromide, the amino allene **16a** (70 mg, 0.23 mmol) was converted into **49a** (87.6 mg, 99% yield) by use of methallyl bromide: colorless oil; [α]_D²² −62.1 (*c* 0.97, CHCl₃); IR (KBr) cm^{−1}: 1953 (C=C=C), 1324 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.75 (d, *J* = 6.7 Hz, 3H, CMe), 0.78 (d, *J* = 6.7 Hz, 3H, CMe), 1.35–1.40 (m, 1H, Me₂CHCHH), 1.48–1.56 (m, 1H, Me₂CH), 1.60–1.68 (m, 1H, Me₂CHCHH), 1.63 (s, 3H, CMe), 2.29 (s, 3H, Ph-Me), 2.61 (s, 6H, 2 × Ph-Me), 3.81 (d, *J* = 15.9 Hz, 1H, 1'-CHH), 3.85 (d, *J* = 15.9 Hz, 1H, 1'-CHH), 4.15–4.18 (m, 1H, 1-H), 4.70 (dd, *J* = 6.7, 1.8 Hz, 2H, 4-CH₂), 4.78 (s, 1H, 3'-CHH), 4.91 (s, 1H, 3'-CHH), 5.15 (dd, *J* = 13.4, 6.7 Hz, 1H, 2-H), 6.93 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 20.0, 20.9, 21.5, 23.0, 23.1 (2C), 25.0, 41.3, 50.4, 54.6, 76.4, 89.5, 113.5, 131.8 (2C), 133.6, 139.9 (2C), 142.1, 142.7, 208.7; MS (FAB) *m/z* (%) 362 (MH⁺, 63), 322 (100); HRMS (FAB) calcd for C₂₁H₃₂NO₂S (MH⁺) 362.2154; found 362.2124.**

2,4,6-Trimethyl-*N*-(2-methylprop-2-enyl)-*N*-{*(1S)*-1-[(*1S*)-1-methylpropyl]-2,3-butadienyl}-phenylsulfonamide (49b**). By a procedure similar to that described for the synthesis of **17a** with allyl bromide, the amino allene **16b** (70 mg, 0.23 mmol) was converted into **49b** (82 mg, 99% yield) by use of methallyl bromide instead of allyl bromide: colorless oil; [α]_D²³ −2.80 (*c* 0.99, CHCl₃); IR (KBr) cm^{−1}: 1956 (C=C=C), 1327 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.80 (t, *J* = 6.7 Hz, 3H, CMe), 0.84 (d, *J* = 6.7 Hz, 3H, CMe), 0.84–0.91 (m, 1H, EtCH), 1.62 (s, 3H, CMe), 1.65–1.67 (m, 2H, MeCH₂), 2.29 (s, 3H, Ph-Me), 2.61 (s, 6H, 2 × Ph-Me), 3.81 (d, *J* = 15.9 Hz, 1H, 1'-CHH), 3.83 (dd, *J* = 15.9, 9.2 Hz, 1H, 1-H), 3.89 (d, *J* = 15.9 Hz, 1H, 1'-CHH), 4.58 (dd, *J* = 11.0, 6.7 Hz, 1H, 4-CHH), 4.63 (dd, *J* = 11.0, 6.7 Hz, 1H, 4-CHH), 4.79 (s, 1H, 3'-CHH), 4.90 (s, 1H, 3'-CHH), 5.12 (ddd, *J* = 9.2, 6.7, 6.7 Hz, 1H, 2-H), 6.92 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 11.3, 16.7, 20.2, 20.9, 23.4 (2C), 25.9, 36.7, 50.9, 63.0, 75.2, 88.1, 114.0, 131.9 (2C), 134.0, 139.8 (2C), 141.9, 142.8, 208.8; MS (FAB) *m/z* (%) 362 (MH⁺, 48), 304 (100); HRMS (FAB) calcd for C₂₁H₃₂NO₂S (MH⁺) 362.2154; found 362.2156.**

***N*-[*(1S)*-1-Isopropylbuta-2,3-dienyl]-2,4,6-trimethyl-*N*-(2-methylprop-2-enyl)phenylsulfonamide (**49c**). By a procedure similar to that described for the synthesis of **17a** with allyl bromide, the amino allene **16d** (200 mg, 0.682 mmol) was converted into **49c** (201 mg, 85% yield) by use of methallyl bromide instead of allyl bromide: colorless crystals; mp 65–66 °C (*n*-hexane–Et₂O); [α]_D²⁴ −2.64 (*c* 0.655, CHCl₃); IR (KBr) cm^{−1}: 1957 (C=C=C), 1327 (NSO₂), 1155 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.87 (d, *J* = 6.7 Hz, 3H, CMe), 0.88 (d, *J* = 6.7 Hz, 3H, CMe), 1.61 (s, 3H, CMe), 1.93–2.01 (m, 1H, Me₂CH), 2.29 (s, 3H, Ph-Me), 2.61 (s, 6H, 2 × Ph-Me), 3.74–3.80 (m, 2H, 1-H and 1'-CHH), 3.97 (d, *J* = 15.9 Hz, 1H, 1'-CHH), 4.65 (d, *J* = 6.7 Hz, 2H, 4-CH₂), 4.77 (s, 1H, C=CHH), 4.89 (s, 1H, C=CHH), 5.16 (dt, *J* = 9.2, 6.7 Hz, 1H, 2-H), 6.92 (s, 2H, Ph); ¹³C NMR**

(75 MHz, CDCl₃) δ 20.1 (2C), 20.8, 20.9, 23.4 (2C), 30.2, 50.7, 64.2, 75.4, 88.8, 114.2, 131.9 (2C), 134.2, 139.9 (2C), 142.0, 143.0, 209.2; MS (FAB) m/z (%) 348 (MH⁺, 50), 119 (100); HRMS (FAB) calcd for C₂₀H₃₀NO₂S (MH⁺) 348.1997; found 348.1994.

General Procedure for Palladium(0)-Catalyzed Cyclopropanation of Allenes. Synthesis of (1*S*,2*S*,5*R*)-2-Isopropyl-3-(2,4,6-trimethylphenylsulfonyl)-1-(1-methylene-3-butenyl)-3-azabicyclo[3.1.0]hexane (50d) (Table 3, entry 4). A mixture of **17d** (50 mg, 0.150 mmol), Pd₂(dba)₃·CHCl₃ (15.5 mg, 0.0015 mmol; 10 mol%), and allyl methyl carbonate (0.102 mL, 0.90 mmol) was refluxed for 5 h. The mixture was diluted with Et₂O, and the organic layer was washed with water 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–EtOAc (20:1) followed by recrystallization from *n*-hexane–Et₂O to give **50d** (36.1 mg, 64% yield) as colorless crystals: [α]_D²⁵ +20.7 (*c* 1.69, CHCl₃); IR (KBr) cm⁻¹: 1327 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.51 (d, *J* = 6.7 Hz, 3H, CMe), 0.94 (d, *J* = 6.7 Hz, 3H, CMe), 0.97-0.99 (m, 1H, 6-CHH), 1.03-1.06 (m, 1H, 6-CHH), 1.09-1.12 (m, 1H, 5-H), 2.00-2.06 (m, 1H, Me₂CH), 2.28 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 × Ph-Me), 2.98 (dd, *J* = 15.9, 7.9 Hz, 1H, 2'-CHH), 3.03 (dd, *J* = 15.9, 6.7 Hz, 1H, 2'-CHH), 3.49 (d, *J* = 9.8 Hz, 1H, 4-CHH), 3.65 (dd, *J* = 9.8, 4.3 Hz, 1H, 4-CHH), 4.05 (d, *J* = 2.4 Hz, 1H, 2-H), 4.85 (d, *J* = 1.2 Hz, 1H, C=CHH), 4.93 (s, 1H, C=CHH), 5.07 (d, *J* = 9.8 Hz, 1H, 4'-CHH), 5.13 (dd, *J* = 17.1, 1.7 Hz, 1H, 4'-CHH), 5.73-5.82 (m, 1H, 3'-H), 6.91 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ 11.9, 16.3, 19.6, 20.1, 20.9, 22.7 (2C), 30.2, 35.0, 39.3, 50.4, 65.8, 113.5, 116.7, 131.8 (2C), 135.2, 136.1, 139.4 (2C), 142.2, 148.4; MS (FAB) m/z (%) 374 (MH⁺, 50), 119 (100); HRMS (FAB) calcd for C₂₂H₃₂NO₂S (MH⁺) 374.2154; found 374.2154.

(1*S*,2*S*,5*R*)-2-Isobutyl-1-(1-methylenebut-3-enyl)-3-(2,4,6-trimethylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (50a) (Table 3, entry 1). By a procedure identical with that described for the synthesis of **50d**, the allenene **17a** (52.0 mg, 0.15 mmol) was converted into **50a** (20.6 mg, 35% yield): colorless oil; [α]_D²⁷ +22.1 (*c* 1.15, CHCl₃); IR (KBr) cm⁻¹: 1323 (NSO₂), 1151 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.69 (d, *J* = 6.7 Hz, 3H, CMe), 0.68-0.70 (m, 1H, 6-CHH), 0.80 (d, *J* = 6.7 Hz, 3H, CMe), 0.97 (dd, *J* = 8.5, 5.5 Hz, 1H, 6-CHH), 1.21-1.30 (m, 2H, Me₂CHCH₂), 1.38 (ddd, *J* = 13.4, 9.8, 3.7 Hz, 1H, 5-H), 1.66-1.73 (m, 1H, Me₂CH), 2.29 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 × Ph-Me), 2.96 (dd, *J* = 15.9, 7.9 Hz, 1H, 2'-CHH), 3.02 (d, *J* = 15.9, 6.1 Hz, 1H, 2'-CHH), 3.23 (d, *J* = 9.8 Hz, 1H, 4-CHH), 3.67 (dd, *J* = 9.8, 4.3 Hz, 1H, 4-CHH), 4.12 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 4.86 (d, *J* = 1.2 Hz, 1H, C=CHH), 4.91 (s, 1H, C=CHH), 5.08 (d, *J* = 9.8 Hz, 1H, 4'-CHH), 5.13 (dd, *J* = 17.1, 1.2 Hz, 1H, 4'-CHH), 5.74-5.82 (m, 1H, 3'-H), 6.92 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 11.6, 21.0, 22.0, 22.9 (2C), 23.5, 24.3, 24.9, 39.3, 40.1, 41.8, 50.8, 59.8, 113.5, 116.8, 131.7 (2C), 134.4, 135.9, 139.6 (2C), 142.3, 147.1; MS (FAB) m/z (%) 388 (MH⁺, 100); HRMS (FAB) calcd for C₂₃H₃₄NO₂S (MH⁺) 388.2310; found 388.2308.

(1S,2S,5R)-1-(1-Methylenebut-3-enyl)-2-[(1S)-1-methylpropyl]-3-(2,4,6-trimethylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (50b) (Table 3, entry 2). By a procedure identical with that described for the synthesis of **50d**, the allenene **17b** (50.0 mg, 0.14 mmol) was converted into **50b** (31.8 mg, 57% yield): colorless oil; $[\alpha]^{26}_D +33.4$ (*c* 0.89, CHCl₃); IR (KBr) cm⁻¹: 1321 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.43 (d, *J* = 6.7 Hz, 3H, CMe), 0.43 (d, *J* = 7.3 Hz, 3H, CMe), 0.99-1.03 (m, 2H, 6-CH₂), 1.10-1.13 (m, 1H, 5-H), 1.20-1.26 (m, 1H, MeCHH), 1.37-1.44 (m, 1H, MeCHH), 1.66-1.70 (m, 1H, EtCH), 2.29 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 × Ph-Me), 2.97 (dd, *J* = 15.9, 7.9 Hz, 1H, 2'-CHH), 3.03 (d, *J* = 15.9, 6.1 Hz, 1H, 2'-CHH), 3.45 (d, *J* = 9.8 Hz, 1H, 4-CHH), 3.67 (dd, *J* = 9.8, 4.3 Hz, 1H, 4-CHH), 4.06 (d, *J* = 2.4 Hz, 1H, 2-H), 4.85 (d, *J* = 1.2 Hz, 1H, C=CHH), 4.91 (s, 1H, C=CHH), 5.07 (d, *J* = 10.4 Hz, 1H, 4'-CHH), 5.12 (dd, *J* = 17.1, 1.2 Hz, 1H, 4'-CHH), 5.73-5.81 (m, 1H, 3'-H), 6.91 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 12.2, 13.0, 13.5, 19.3, 21.0, 22.7 (2C), 27.1, 35.2, 37.4, 39.3, 50.3, 63.3, 113.9, 116.6, 131.7 (2C), 135.3, 136.0, 139.2 (2C), 142.1, 148.1; MS (FAB) *m/z* (%) 388 (MH⁺, 63), 330 (100); HRMS (FAB) calcd for C₂₃H₃₄NO₂S (MH⁺) 388.2310; found 388.2294.

(1S,2S,5R)-2-tert-Butyl-1-(1-methylenebut-3-enyl)-3-(2,4,6-trimethylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (50c) (Table 3, entry 3). By a procedure identical with that described for the synthesis of **50d**, the allenene **17c** (50.0 mg, 0.14 mmol) was converted into **50c** (8.5 mg, 16% yield) along with the isomerized product *N*-allyl-*N*-(1-tert-butylbut-2-ynyl)-2,4,6-trimethylphenylsulfonamide (19.4 mg, 40% yield).

Compound **50c**: colorless oil; $[\alpha]^{22}_D +20.6$ (*c* 0.80, CHCl₃); IR (KBr) cm⁻¹: 1315 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.94 (s, 9H, CMe₃), 1.25-1.27 (m, 1H, 6-CHH), 1.36 (dd, *J* = 4.3, 4.3 Hz, 1H, 6-CHH), 1.61-1.66 (m, 1H, 5-H), 2.29 (s, 3H, Ph-Me), 2.66 (s, 6H, 2 × Ph-Me), 2.90 (dd, *J* = 12.8, 3.1 Hz, 1H, 4-CHH), 2.98 (d, *J* = 15.9, 6.7 Hz, 1H, 2'-CHH), 3.10 (dd, *J* = 15.9 Hz, 1H, 2'-CHH), 4.01 (dd, *J* = 12.8, 7.3 Hz, 1H, 4-CHH), 4.42 (s, 1H, 2-H), 4.88 (s, 1H, C=CHH), 4.98 (s, 1H, C=CHH), 5.06 (d, *J* = 10.4 Hz, 1H, 4'-CHH), 5.16 (d, *J* = 17.1 Hz, 1H, 4'-CHH), 5.81-5.89 (m, 1H, 3'-H), 6.93 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 19.7, 21.0, 23.2 (2C), 27.5, 29.5 (3C), 37.4, 38.1, 43.6, 54.8, 70.8, 113.4, 116.2, 131.8 (2C), 134.2, 137.0 (2C), 140.0, 142.2, 149.4; MS (FAB) *m/z* (%) 388 (MH⁺, 34), 330 (100); HRMS (FAB) calcd for C₂₃H₃₄NO₂S (MH⁺) 388.2310; found 388.2302.

N-Allyl-*N*-(1-tert-butylbut-2-ynyl)-2,4,6-trimethylphenylsulfonamide: colorless oil; $[\alpha]^{22}_D -35.8$ (*c* 0.69, CHCl₃); IR (KBr) cm⁻¹: 1327 (NSO₂), 1159 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 1.02 (s, 9H, CMe₃), 1.83 (d, *J* = 2.4 Hz, 3H, CMe), 2.29 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 × Ph-Me), 3.76-3.81 (m, 1H, 1'-CHH), 3.89 (dd, *J* = 17.1, 6.7 Hz, 1H, 1'-CHH), 4.46 (q, *J* = 2.4 Hz, 1H, 1-H), 4.89 (dd, *J* = 10.4, 1.2 Hz, 1H, 3'-CHH), 4.96 (dd, *J* = 17.1, 1.2 Hz, 1H, 3'-CHH), 5.82-5.89 (m, 1H, 2'-H), 6.91 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 21.0, 23.3 (2C), 27.4 (3C), 37.4, 48.2, 60.9, 75.2, 77.2, 82.8, 115.7, 131.8 (2C), 133.2, 135.8 (2C), 140.5, 142.1; MS (FAB) *m/z* (%) 348 (MH⁺, 32), 290 (100); HRMS (FAB) calcd for C₂₀H₃₀NO₂S (MH⁺) 348.1997; found 348.1995.

(1S,2S,5R)-2-Benzyl-1-(1-methylenebut-3-enyl)-3-(2,4,6-trimethylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (50e) (Table 3, entry 5). By a procedure identical with that described for the synthesis of **50d**, the allenene **17e** (150 mg, 0.408 mmol) was converted into **50e** (27.5 mg, 18% yield): colorless crystals; mp 142–143 °C (*n*-hexane–CHCl₃); [α]²⁶_D +14.7 (*c* 1.00, CHCl₃); IR (KBr) cm⁻¹: 1319 (NSO₂), 1147 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.77 (dd, *J* = 4.9, 4.9 Hz, 1H, 6-CHH), 1.03 (dd, *J* = 7.9, 4.9 Hz, 1H, 6-CHH), 1.22–1.26 (m, 1H, 5-H), 2.28 (s, 3H, Ph-Me), 2.47–2.56 (m, 2H, 2'-CH₂), 2.36 (dd, *J* = 13.4, 10.4 Hz, 1H, Ph-CHH), 2.68 (s, 6H, 2 × Ph-Me), 3.14 (dd, *J* = 13.4, 3.7 Hz, 1H, Ph-CHH), 3.30 (d, *J* = 9.2 Hz, 1H, 4-CHH), 3.68 (dd, *J* = 9.2, 4.9 Hz, 1H, 4-CHH), 4.38 (s, 1H, C=CHH), 4.38–4.40 (m, 1H, 2-H), 4.43 (s, 1H, C=CHH), 4.93 (d, *J* = 17.1 Hz, 1H, 4'-CHH), 4.94 (d, *J* = 9.8 Hz, 1H, 4'-CHH), 5.43–5.52 (m, 1H, 3'-H), 6.94 (s, 2H, Ph), 7.12–7.16 (m, 5H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 10.8, 20.9, 22.9 (2C), 23.7, 38.4, 38.7, 50.6, 62.3, 77.0, 112.6, 116.5, 126.2, 127.8 (2C), 130.0 (2C), 132.0 (2C), 134.5, 136.0, 137.9, 140.0 (2C), 142.6, 145.3; MS (FAB) *m/z* (%) 422 (MH⁺, 85), 330 (100); HRMS (FAB) calcd for C₂₆H₃₂NO₂S (MH⁺) 422.2154; found 422.2139.

2,2-Dimethyl-1-(1-methylenebut-3-enyl)-3-(4-methylphenylsulfonyl)-3-azabicyclo[3.1.0]-hexane (51) (Table 3, entry 6). By a procedure identical with that described for the synthesis of **50d**, the allenene **23** (50.0 mg, 0.17 mmol) was converted into **51** (13.9 mg, 24% yield; 34% yield based on the consumed starting material): colorless oil; IR (KBr) cm⁻¹: 1335 (NSO₂), 1155 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.48 (dd, *J* = 7.9, 4.9 Hz, 1H, 6-CHH), 0.54 (dd, *J* = 4.3, 4.3 Hz, 1H, 6-CHH), 1.32 (s, 3H, CMe), 1.54 (s, 3H, CMe), 1.55–1.58, (m, 1H, 5-H), 2.41 (s, 3H, Ph-Me), 2.81 (d, *J* = 7.3 Hz, 2H, 2'-CH₂), 3.42 (d, *J* = 9.8 Hz, 1H, 4-CHH), 3.58 (dd, *J* = 9.8, 3.7 Hz, 1H, 4-CHH), 5.00–5.05 (m, 4H, 4 × C=CH), 5.72–5.80 (m, 1H, 3'-H), 7.26 (d, *J* = 7.9 Hz, 2H, Ph), 7.68 (d, *J* = 7.9 Hz, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 14.0, 19.7, 21.6, 23.7, 24.9, 40.3, 42.8, 49.8, 67.3, 116.4, 117.3, 126.9 (2C), 129.2 (2C), 135.9, 138.9, 142.6, 145.2; MS (FAB) *m/z* (%) 332 (MH⁺, 100), 316 (77); HRMS (FAB) calcd for C₁₉H₂₆NO₂S (MH⁺) 332.1684; found 332.1704.

(1S,2S,5R)-2-Isobutyl-5-methyl-1-(1-methylenebut-3-enyl)-3-(2,4,6-trimethylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (52a) (Table 3, entry 7). By a procedure identical with that described for the synthesis of **50d**, the allenene **49a** (50.0 mg, 0.14 mmol) was converted into **52a** (20.2 mg, 36% yield): colorless oil; [α]²⁵_D +36.2 (*c* 0.985, CHCl₃); IR (KBr) cm⁻¹: 1321 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ 0.67 (d, *J* = 4.9 Hz, 1H, 6-CHH), 0.84 (d, *J* = 6.7 Hz, 3H, CMe), 0.80–0.81 (m, 1H, 6-CHH), 0.82 (d, *J* = 6.1 Hz, 3H, CMe), 1.02 (s, 3H, CMe), 1.23–1.28 (m, 1H, Me₂CHCHH), 1.38–1.44 (m, 1H, Me₂CHCHH), 1.64–1.71 (m, 1H, Me₂CH), 2.29 (s, 3H, Ph-Me), 2.62 (s, 6H, 2 × Ph-Me), 2.77 (dd, *J* = 16.5, 7.3 Hz, 1H, 2'-CHH), 3.01 (dd, *J* = 16.5, 7.3 Hz, 1H, 2'-CHH), 3.25 (d, *J* = 9.2 Hz, 1H, 4-CHH), 3.42 (d, *J* = 9.2 Hz, 1H, 4-CHH), 4.16 (dd, *J* = 9.8, 2.4 Hz, 1H, 2-H), 4.89 (s, 1H, C=CHH), 4.96 (d, *J* = 1.2 Hz, 1H, C=CHH), 5.100 (d, *J* = 12.2 Hz, 1H, 4'-CHH), 5.102 (d, *J* = 15.3 Hz, 1H, 4'-CHH), 5.75–5.83 (m, 1H, 3'-H), 6.93 (s, 2H, Ph); ¹³C NMR (67.8 MHz, CDCl₃) δ 15.8, 16.9, 21.0, 22.1, 22.9, 24.3, 24.8, 27.6, 29.8, 39.3, 41.8, 44.7,

56.2, 60.8, 114.6, 116.9, 131.7 (2C), 134.4, 135.3, 139.6 (2C), 142.3, 145.4; MS (FAB) m/z (%) 402 (MH^+ , 100); HRMS (FAB) calcd for $C_{24}H_{36}NO_2S$ (MH^+) 402.2467; found 402.2466.

(1S,2S,5R)-5-Methyl-1-(1-methylenebut-3-enyl)-3-(2,4,6-trimethylphenylsulfonyl)-2-[(1S)-1-methylpropyl]-3-azabicyclo[3.1.0]hexane (52b) (Table 3, entry 8). By a procedure identical with that described for the synthesis of **50d**, the allenene **49b** (40.0 mg, 0.11 mmol) was converted into **52b** (17.2 mg, 39% yield): colorless oil; $[\alpha]^{25}_D +21.2$ (c 0.86, $CHCl_3$); IR (KBr) cm^{-1} : 1321 (NSO_2), 1153 (NSO_2); 1H NMR (500 MHz, $CDCl_3$) δ 0.43 (d, $J = 3.5$ Hz, 3H, CMe), 0.72 (d, $J = 5.1$ Hz, 1H, 6-CHH), 0.79 (t, $J = 7.2$ Hz, 3H, MeCH₂), 1.03 (s, 3H, CMe), 1.12 (d, $J = 5.1$ Hz, 1H, 6-CHH), 1.24-1.28 (m, 1H, MeCHH), 1.36-1.46 (m, 1H, MeCHH), 1.66-1.73 (m, 1H, EtCH), 2.29 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 $\times$ Ph-Me), 2.71 (dd, $J = 16.5, 7.2$ Hz, 1H, 2'-CHH), 3.01 (dd, $J = 16.5, 6.9$ Hz, 1H, 2'-CHH), 3.44 (d, $J = 9.6$ Hz, 1H, 4-CHH), 3.48 (d, $J = 9.6$ Hz, 1H, 4-CHH), 4.09 (d, $J = 2.4$ Hz, 1H, 2-H), 4.90-4.91 (m, 1H, C=CHH), 4.95 (ddd, $J = 1.5$ Hz, 1H, C=CHH), 5.04-5.11 (m, 1H, 4'-CHH), 5.07-5.11 (m, 1H, 4'-CHH), 5.74-5.83 (m, 1H, 3'-H), 6.91 (s, 2H, Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.0, 13.5, 15.3, 17.8, 21.0, 22.7 (2C), 23.2, 27.0, 37.6, 39.2, 39.8, 55.6, 66.4, 114.9, 116.8, 131.7 (2C), 135.4 (2C), 139.2 (2C), 142.0, 146.4; MS (FAB) m/z (%) 402 (MH^+ , 78), 344 (100); HRMS (FAB) calcd for $C_{24}H_{36}NO_2S$ (MH^+) 402.2469; found 402.2466.

(1R,2S,5R)-2-Isopropyl-5-methyl-1-(1-methylenebut-3-enyl)-3-(2,4,6-trimethylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (52c) (Table 3, entry 9). By a procedure identical with that described for the synthesis of **50d**, the allenene **49c** (50 mg 0.144 mmol) was converted into **52c** (33 mg, 59% yield): colorless crystals: mp 63–65 °C (n -hexane/Et₂O = 1:1); $[\alpha]^{25}_D +35.8$ (c 1.13, $CHCl_3$); IR (KBr) cm^{-1} : 1325 (NSO_2), 1153 (NSO_2); 1H NMR (500 MHz, $CDCl_3$) δ 0.50 (d, $J = 6.7$ Hz, 3H, CMe), 0.74 (d, $J = 5.3$ Hz, 1H, 6-CHH), 0.94 (d, $J = 7.3$ Hz, 3H, CMe), 1.01 (s, 3H, CMe), 1.09 (d, $J = 5.3$ Hz, 1H, 6-CHH), 2.01-2.07 (m, 1H, Me₂CH), 2.28 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 $\times$ Ph-Me), 2.74 (dd, $J = 16.5, 6.7$ Hz, 1H, 2'-CHH), 3.02 (dd, $J = 16.5, 7.3$ Hz, 1H, 2'-CHH), 3.42 (s, 2H, 4-CH₂), 4.07 (d, $J = 2.4$ Hz, 1H, 2-H), 4.92 (s, 1H, C=CHH), 4.95 (d, $J = 1.2$ Hz, 1H, C=CHH), 5.06-5.08 (m, 1H, 4'-CHH), 5.10 (s, 1H, 4'-CHH), 5.75-5.80 (m, 1H, 3'-H), 6.91 (s, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 16.3, 17.3, 20.0, 20.9, 22.6 (2C), 23.3, 30.4, 39.2, 39.6, 55.8, 66.8, 114.6, 116.9, 131.8 (2C), 135.3, 135.5, 139.4 (2C), 142.2, 146.7; MS (FAB) m/z (%) 388 (MH^+ , 50), 344 (100); HRMS (FAB) calcd for $C_{23}H_{34}NO_2S$ (MH^+) 388.2310; found 388.2316.

Determination of the Stereochemistry. Stereochemistries of the cyclized products were easily confirmed by the NOE analyses shown below.

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 FREQU 6013.2 Hz
 SCANS 16
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 PD 1.551 sec
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 BF 0.12 Hz
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 FREQU 5402.4 Hz
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 POINT 32768
 FREQU 5402.4 Hz
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 PD 0.935 sec
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 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

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 SPINNING 13 Hz
 TEMP 30.4 C

DFILE E:\KM-176.als
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 OBFIN 5800.0 Hz
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 FREQU 5402.4 Hz
 SCANS 16
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 PD 0.935 sec
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 CTEMP 20.5 c
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 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

1H Line

Date : Wed Apr 24 18:22:14 2002
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 SAMPD 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEAT 58.7 usec
 INTVL 100.0 usec
 TIMES 32 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREUL 0.01000 msec
 INJMT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 2.63 usec
 OBNUC 1H
 OBFRQ 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 17
 SCANS 32 times
 SLVNT CDCL3
 SPINNING 12 Hz
 TEMP 22.9 C

DFILE E:\KM-70.als
COMNT KM-70
DATIM Tue, Jan 28 10:45:38 2003
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5402.4 Hz
SCANS 32
ACQTM 6.065 sec
PD 0.935 sec
PW1 5.6 us
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14

DFILE D:\02.05.07.1H.als
COMNT
DATIM Tue May 07 18:54:50 2002
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6020.4 Hz
SCANS 32
ACQTM 5.443 sec
PD 1.554 sec
PW1 5.3 us
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

DFILE F:\04.Z-COOMe\04.Z..COOMe.1
 COMNT Z-COOMe
 DATIM Sat Jan 10 15:51:21 2004
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 32768
 FREQU 20408.10 Hz
 SCANS 16
 ACQTM 1.6056 sec
 PD 1.3940 sec
 PW1 4.30 usec
 IRNUC 1H
 CTEMP 59.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

DFILE F:\E-COOMe\04.E..COOMe.1H.h
 COMNT E-COOMe
 DATIM Sat Jan 10 16:29:28 2004
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 32768
 FREQU 20408.10 Hz
 SCANS 8
 ACQTM 1.6056 sec
 PD 1.3940 sec
 PW1 4.30 usec
 IRNUC 1H
 CTEMP 59.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

DFILE D:\04.Boc.-OH.1H.als
 COMNT Boc.-OH
 DATIM Fri Jan 09 13:48:58 2004
 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 59.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

DFILE D:\03.10.15.Boc.-OMs.1H.als
 COMNT Boc.OMs
 DATIM Wed Oct 15 15:15:12 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6013.2 Hz
 SCANS 32
 ACQTM 5.449 sec
 PD 1.551 sec
 PW1 5.5 us
 IRNUC 1H
 CTEMP 54.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

DFILE C:\WINNMR95\COMMON_DEFAULT.ALS
 COMNT
 DATIM Fri Jul 19 14:50:51 2002
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6038.6 Hz
 SCANS 32
 ACQTM 5.426 sec
 PD 1.200 sec
 PW1 5.8 us
 IRNUC 1H
 CTEMP 20.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 22

DFILE C:\WINNMR95\COMMON_DEFAULT.ALS
 COMNT
 DATIM Tue Sep 09 19:44:58 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 54.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE C:\WINNMR95\COMMON\DEFAULT.ALS
 COMNT Thu Nov 20 11:12:45 2003
 DATIM 1H
 OBNUC NON
 EXMOD
 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 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE F:\KM-71-2.ALS
 COMNT Mon Oct 29 10:49:33 2001
 DATIM 1H
 OBNUC NON
 EXMOD
 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 21.7 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

DFILE D:\KM-75-1.als
 COMNT Wed Nov 07 22:13:29 2001
 DATIM 1H
 OBNUC NON
 EXMOD
 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 23.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 23

Date : Wed May 8 10:22:53 2002
 FileName LoadingID.rmdata
 Comment 1H Line
 SliceHistory
 EXMODE non
 POINT 16384 points
 SAMPO 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEADT 58.7 usec
 INVL 100.0 usec
 TIMES 16 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREOL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 2.63 usec
 OBNUC 1H
 OBFRQ 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 19
 SCANS 16 times
 SLVNT CDCL3
 SPINNING 18 Hz
 TEMP 24.2 C

1H Line

Date : Wed Nov 5 19:34:31 2003
 FileName : LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non
 POINT : 16384 points
 SAMPO : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEATH : 57.2 usec
 INVT : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3516 sec
 ACQIM : 1638.3999 msec
 PREDL : 0.01000 msec
 INMT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 5.50 usec
 DBNUC : 1H
 DBFQ : 500.00 MHz
 OBSE : 162167.63 Hz
 RGAIN : 17
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNING : 14 Hz
 TEMP : 24.3 C

1H Line

Date : Wed Jan 22 17:21:57 2003
 FileName : LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non
 POINT : 16384 points
 SAMPO : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEATH : 58.7 usec
 INVT : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3516 sec
 ACQIM : 1638.3999 msec
 PREDL : 0.01000 msec
 INMT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 2.63 usec
 DBNUC : 1H
 DBFQ : 500.00 MHz
 OBSE : 162167.63 Hz
 RGAIN : 19
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNING : 14 Hz
 TEMP : 26.3 C

DFILE C:\WINNMR95\COMMON\DEFAULT.ALS
 COMNT Thu Nov 27 20:25:56 2003
 DATIM 1H
 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 24.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 22

1H Line

Date : Fri Jun 20 18:59:01 2003
 FileName : seizo5.mdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non
 POINT 16384 points
 SAMPO 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEADT 58.7 usec
 INTVL 100.0 usec
 TIMES 32 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PRECL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.51 Hz
 PW1 2.63 usec
 OBNUC 1H
 OBFRQ 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 21
 SCANS 32 times
 SLVNT CDCL3
 SPINNING 13 Hz
 TEMP 18.3 C

1H Line

Date : Wed Mar 6 15 26 38 2002

FileName : seizoi.nmdata
 Comment : 1H line
 SliceHistory :
 EMOUL : non

POINT : 16384 points
 SAMPD : 16384 points
 FREQU : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 58.7 usec
 INTVL : 100.0 usec
 TIMES : 32 times
 DUMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PRELO : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PWT : 2.63 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSE1 : 162167.63 Hz
 RGAIN : 21

SCANS : 32 times
 SLVNT : CDCL3
 SPINNING : 13 Hz
 TEMP : 26.4 C

1.08
 2.29
 1.03
 2.04
 2.04
 1.00
 1.97
 1.00
 1.00
 6.84
 3.37
 1.01
 1.01
 2.08
 2.74
 1.03
 3.00

8
 6
 4
 2
 0 ppm

52c
 (500 MHz, CDCl₃)