Supporting Information

Asymmetric Total Synthesis of Mycothiazole

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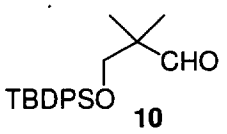
Experimental Section

General: Melting points were determined on a YANAGIMOTO micro melting point apparatus (hot plate) and uncorrected. Infrared (IR) spectra were measured on salt plate with a SHIMADZU FTIR-8100 spectrometer. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter with sodium lamp (λ=589 nm, D line) and were recorded as follows: $[\alpha]_D^T$ (Cg/100ml, solvent). ^1H and ^{13}C NMR spectra were recorded on a JEOL EX-270 spectrometer at 270 MHz and 67.8 MHz, respectively, and were obtained at the indicated field as solution in deuteriochloroform ($CDCl_3$) unless othewise indicated. Chemical shifts were reported in parts per million (ppm, δ) from tetramethylsilane or $CHCl_3$ as internal standard. Spectra splitting patterns are designated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Mass spectra were obtained on a JEOL JMS-SX 102A (EI). Analytical thin layer chromatography (TLC) was performed on a Merck Art. 5715, Kieselgel 60 F_{254}/0.25 mm thickness plates. Visualization was accomplished with UV light, phosphomolybdic acid, or ninhydrin solution followed by heating. Column chromatography was peformed with silica gel BW-820 MH or BW-200 (Fuji Davision Co.). Flash column chromatography was performed with silica gel 60 particle size 40-63μm (Cica-MERCK).

Solvents for extraction and chromatography were reagent grade and distilled from the indicated drying agents: Tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone ketyl. Diethyl ether (Et_2O) was distilled from lithium alminum hydride. Dichloromethane (CH_2Cl_2), toluene, acetone, and acetonitrile (CH_3CN) were dried by distillation from calcium hydride. Hexamethyphosphoramide (HMPA), *N*-methylpyrrolidone (NMP), dimethysulfoxide (DMSO), and methanol (MeOH) were distilled from calcium hydride and stored over 4Å molecular sieves. *N*-ethylpiperidine was distilled from calcium hydride and stored over sodium hydroxide. Triethylamine (Et_3N) was dried over sodium hydroxide. All other commercially available reagents were used as received.



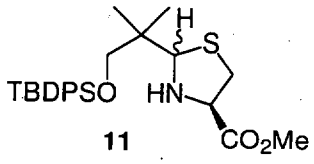
10

3-*tert*-Butyldiphenylsilyloxy-2,2-dimethylpropanal (10). To a stirred solution of methyl hydroxypivalate (**9**) (20 g, 0.151mol) in DMF (300 ml) was added TBDPSCl (41.2 ml, 0.155 mol) and imidazole (24.7 g, 0.363 mol) at 0 °C. After stirring for 14 h at room temperature, 1M aqueous $KHSO_4$ (300 ml) was added, and the mixture was extracted with EtOAc (500 ml). The organic layer was washed with 1M $KHSO_4$ (2 x 100 ml), H_2O (100 ml), and saturated brine (100 ml), dried over $MgSO_4$. Filtration and concentration *in vacuo* gave crude TBDPS ether of **9** (67 g, quant.) as a colorless oil, which was used in the next reaction without further purification. An analytical sample was obtained by column chromatography (silica gel BW-820 MH, hexane:ether = 8:1): IR ν_{max}^{neat} cm^{-1} 1736, 1473, 1429, 1238, 1192, 1153, 1113, 702; ^{1}H-NMR ($CDCl_3$) δ 1.03 (9H, s, **Bu^t**), 1.19 (6H, s, **CH$_3$** x 2), 3.64 (2H, s, TBDPSOC**H$_2$**), 3.67 (3H, s, CO_2C**H$_3$**), 7.41 (m, 6H, Ph), 7.65 (m, 4H, Ph); Anal. calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16. Found: C, 71.41; H, 8.19.

To a stirred solution of the above crude TBDPS ether of **9** (19.2 g, 51.8 mmol) in ether (100 ml) was added dropwise DIBAL (0.94 M in hexane, 138 ml, 129.6 mmol) at -78 °C under argon. After stirring for 30 min at -78 °C, the mixture was treated with 1M aqueous $KHSO_4$ (100 ml) and warmed to room temperature. After stirring for 1 h, the mixture was extracted with EtOAc (3 x 100 ml). The combined extracts were washed with 1M aqueous $KHSO_4$ (3 x 50 ml), H_2O (50 ml), and saturated brine (50 ml), and dried over Na_2SO_4. Filtration and concentration *in vacuo* gave crude alcohol as a colorless oil (18.5 g), which was used in the next reaction without further purification. An analytical sample was obtained by column chromatography (silica gel BW-820 MH, hexane:ether = 5:1): IR ν_{max}^{neat} cm^{-1} 3431, 1473, 1427, 1113, 825, 702; ^{1}H-NMR ($CDCl_3$) δ 0.89 (6H, s, **CH$_3$** x 2), 1.07 (9H, s, **Bu^t**), 2.38 (1H, t, J = 5.9 Hz, disappeared with D_2O, **OH**), 3.48, (2H, s, TBDPSOC**H$_2$**), 3.51 (2H, d, J = 5.6 Hz, **CH$_2$**OH), 7.42 (6H, m, Ph), 7.66 (4H, m, Ph); Anal. calcd for $C_{21}H_{30}O_2Si$: C, 73.63; H, 8.83. Found: C, 73.34; H, 8.64.

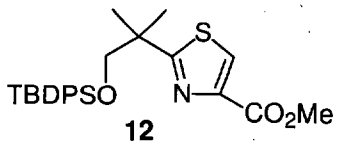
To a stirred solution of the above crude alcohol (18.5 g) and Et_3N (21.7 ml, 155 mmol) in CH_2Cl_2 (150 ml) at 0 °C was added a solution of Py·SO_3 (24.7 g, 155 mmol) in DMSO (150 ml). The resulting solution was stirred at room temperature for 20 min and then quenched with saturated aqueous $NaHCO_3$ (150 ml). After CH_2Cl_2 was removed in vacuo, the residue was extracted with ether (3 x 100 ml). The combined extracts were washed with 1M aqueous $KHSO_4$ (2 x 50 ml) and saturated brine (50 ml),

and dried over $MgSO_4$. Filtration and concentration in vacuo gave crude aldehyde **10** (13.5 g) as a pale yellow oil. This material was used in the next reaction without further purification. An analytical sample, a colorless oil, was obtained by column chromatography (silica gel BW-820 MH, hexane:ether = 5:1): IR ν_{max}^{neat} cm^{-1} 1730, 1474, 1429, 1113, 908, 735; ^{1}H-NMR ($CDCl_3$) δ 1.03 (9H, s, **Bu^t**), 1.06 (6H, s, **CH$_3$** x 2), 3.64 (2H, s, TBDPSOC**H$_2$**), 7.41 (6H, m, Ph), 7.62 (4H, m, Ph), 9.60 (1H, s, **CH**O); ^{13}C-NMR ($CDCl_3$) δ 18.58 (CH_3 x 2), 19.28 (4°), 26.74 (CH_3 x 3), 48.36 (4°), 68.86 (CH_2), 127.71(CH, Ph), 129.76 (CH, Ph), 133.08 (4°, Ph), 135.62 (CH, Ph), 205.71(4°, C=O); HRMS (EI) calcd for $C_{17}H_{19}O_2Si$ (M^+-Bu^t): 283.1154. Found: 283.1152.



11

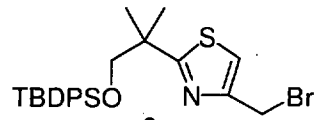
Thiazolidine 11. To a stirred solution of the crude aldehyde **10** (13.5 g, 40 mmol) in toluene (100 ml) was added (S)-H-Cys-OMe·HCl (7.6 g, 44 mmol) and Et_3N (6.4 ml, 46 mmol) successively at 0 °C. After being stirred for 12 h, the mixture was filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 250 g, hexane:ether = 8:1 to 4:1) to give thiazolidine **11** as a colorless oil (16.8 g, 71% from methyl hydroxypivalate, ca. 2:1 diastereomixture by ^{1}H-NMR), which formed a solid foam under high vacuum: IR ν_{max} $CDCl_3$ cm^{-1} 3310, 1746, 1472, 1482, 1361, 1198, 1173, 1152, 1113, 826, 702; HRMS (EI) calcd for $C_{25}H_{35}NO_3SSi$: 457.2107. Found: 457.2109.



12

Thiazole 12. A suspension of CMD (1.3 g, 15 mmol) in benzene (5 ml) was refluxed with stirring for 3 h using Dean-stark apparatus (molecular sieves type 4A). To the resulting suspension was added pyridine (51 μl) followed by a solution of the thiazolidine **11** (115 mg, 0.25 mmol) in benzene (1 ml), and then the mixture was refluxed for 12 h. The resulting mixture was filtered through the pad of celite and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-200, 9 g, hexane:ether = 9:1) to give thiazole **12** (70 mg, 62 %) as a colorless oil: IR ν_{max}^{neat} cm^{-1} 1736, 1724, 1485, 1429, 1244, 1221, 1118, 1105, 910,

735; ^{1}H-NMR ($CDCl_3$) δ 1.00 (9H, s, **Bu^t**), 1.48 (6H, s, **CH$_3$** x 2), 3.76 (2H, s, TBDPSOC**H$_2$**), 3.94 (3H, s, CO_2**CH$_3$**), 7.37 (6H, m, Ph), 7.55 (4H, m, Ph), 8.09 (1H, s, thiazole-5 -H); ^{13}C-NMR ($CDCl_3$) δ 19.23 (4°), 25.32 (CH_3 x 2), 26.79 (CH_3 x 3), 43.33 (4°), 52.22 (CH_3), 72.29 (CH_2), 127.12 (CH, thiazole-5), 127.58 (CH, Ph), 129.60 (CH, Ph), 133.08 (4°, Ph), 135.54 (CH, Ph), 146.02 (4°, C=O), 162.12 (4°, thiazole-4), 178.63 (4°, thiazole-2); Anal. calcd for $C_{25}H_{31}NO_3SSi$·1/12hexane: C, 66.48; H, 7.00; N, 3.04. Found: C, 66.65; H, 7.17; N, 2.99.

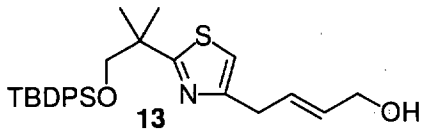


6

Bromide 6. To a stirred solution of the thiazole **12** (1.82 g, 4.01 mmol) in ether (20 ml) was added dropwise DIBAL (0.94 M in hexane, 8.75 ml, 8.22 mmol) at -78 °C under argon. After stirring for 30 min, the reaction was quenched with 1M aqueous $KHSO_4$ and warmed to room temperature. After being stirred for 1 h, the mixture was extracted with ether (50 ml). The extract was washed with 1M aqueous $KHSO_4$ (3 x 10 ml), H_2O (10 ml), and saturated brine (10 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 70 g, hexane:ether = 4:1 to 2:1) to give alcohol (1.54 g, 91 %) as a colorless solid: mp 107-108 °C (hexane-ether); IR ν_{max} $CDCl_3$ cm^{-1} 3370, 1427, 1390, 1361, 1113, 1059, 908, 735; ^{1}H-NMR ($CDCl_3$) δ 1.00 (9H, s, **Bu^t**), 1.44 (6H, s, **CH$_3$** x 2), 2.67 (1H, brs, disappeared with D_2O, **OH**), 3.73 (2H, s, TBDPSOC**H$_2$**), 4.72 (2H, s, **CH$_2$**OH), 7.03 (1H, s, thiazole-5-**H**), 7.33 (6H, m, Ph), 7.56 (4H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 19.28 (4°), 25.36 (CH_3 x 2), 26.74 (CH_3 x 3), 43.07 (4°), 60.92 (CH_2OH), 72.58 (CH_2), 113.55 (CH, thiazole-5), 127.58 (CH, Ph), 129.58 (CH, PH), 133.35 (4°, Ph), 135.60 (CH, Ph), 155.38 (4°, thiazole-4), 178.63 (4°, thiazole-2); Anal. calcd for $C_{24}H_{31}NO_2SSi$: C, 67.72; H, 7.34; N, 3.29. Found: C,67.56; H, 7.20; N, 3.16.

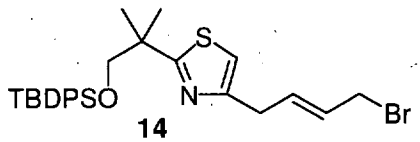
To a stirred solution of this alcohol (300 mg, 0.705 mmol) in CH_2Cl_2 (2.3 ml) at 0 °C under argon was added Et_3N (150 μl, 10.6 mmol) followed by Ms_2O (160 mg, 0.92 mmol). After 20 min at 0 °C, acetone (2.3 ml) was added followed by LiBr (367 mg, 4.23 mmol). After 1 h at room temperature, saturated aqueous NH_4Cl (5 ml) was added, and the mixture was extracted with ether (3 x 10 ml). The combined extracts were washed with saturated aqueous NH_4Cl (5 ml) and saturated brine (5 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 20 g, hexane:ether = 20:1 to 10:1) to give

bromide **6** (344 mg, quant.) as a colorless oil: IR ν_{max} $CDCl_3$ cm^{-1} 1471, 1428, 1251, 1113, 1059, 909, 737, 702; ^{1}H-NMR ($CDCl_3$) δ 0.99 (9H, s, **Bu^t**), 1.45 (6H, s, **CH$_3$** x 2), 3.73 (2H, s, TBDPSOC**H$_2$**), 4.57 (2H, s, C**H$_2$**Br), 7.18 (1H, s, thiazole-5-**H**), 7.37 (6H, m, Ph), 7.58 (4H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 19.25 (4°), 25.29 (CH_3 x 2), 26.70 (CH_3 x 3), 27.53 (CH_2Br), 43.13 (4°), 72.53 (CH_2), 116.86 (CH, thiazole-5), 127.57 (CH, Ph), 129.54 (CH, PH), 133.24 (4°, Ph), 135.56 (CH, Ph), 151.27 (4°, thiazole-4), 178.47 (4°, thiazole-2); Anal. calcd for $C_{24}H_{30}BrNOSSi$: C, 59.00; H, 6.19; N, 2.87. Found: C,59.21; H, 6.37; N, 2.76.



13

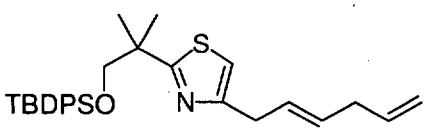
Alcohol 13. To a stirred solution of the bromide **6** (250 mg, 0.512 mmol) and vinylstannane **7**[1] (195.4 mg, 0.563 mmol) in previously degassed NMP (2.5 ml) was added $Pd(CH_3CN)_2Cl_2$ (13.3 mg, 10 mol%) under argon. After stirring for 10 min at room temperature, 28 % aqueous NH_3 (3 ml) was added. After 30 min at room temperature, the mixture was diluted with EtOAc (40 ml), and then washed with H_2O (10 ml), 1M aqueous $KHSO_4$ (10 ml), and saturated brine (10 ml), dried over $NaSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 25 g, hexane:EtOAc = 3:1 to 2:1) to give **13** (225 mg, 94 %) as a colorless oil: IR ν_{max} $CDCl_3$ cm^{-1} 3346, 1471, 1427, 1113, 1061, 824, 737, 702; ^{1}H-NMR ($CDCl_3$) δ 0.99 (9H, s, **Bu^t**), 1.44 (6H, s, **CH$_3$** x 2), 1.67 (1H, brs, disappeared with D_2O, **OH**), 3.54 (2H, d, J = 6.6 Hz, C**H$_2$**), 3.73 (2H, s, TBDPSOC**H$_2$**), 4.12 (2H, t, J = 5.6 Hz, C**H$_2$**OH), 5.76 (1H, m, CH=C**H**CH_2OH), 5.92 (1H, m, C**H**=CHCH_2OH), 6.78 (1H, s, thiazole-5-**H**), 7.37 (6H, m, Ph), 7.56 (4H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 19.27 (4°), 25.34 (CH_3 x 2), 26.70 (CH_3 x 3), 34.41 (CH2), 42.93 (4°), 63.16 (CH_2OH), 72.65 (CH_2), 112.51 (CH, thiazole-5), 127.53 (CH, Ph), 129.11 (CH, vinyl), 129.51 (CH, PH), 131.11 (CH, vinyl), 133.41 (4°, Ph), 135.54 (CH, Ph), 154.45 (4°, thiazole-4), 177.70 (4°, thiazole-2); Anal. calcd for $C_{27}H_{35}NO_2SSi$: C, 69.63; H, 7.57; N, 3.01. Found: C,69.39; H, 7.67; N, 3.07.



14

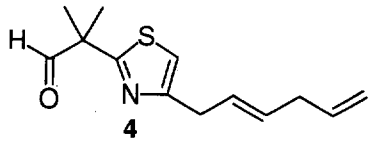
Bromide 14. To a stirred solution of **13** (16.0 mg, 0.0344 mmol) in CH_2Cl_2 (0.6 ml) was added CBr_4 (22.8 mg, 0.0688 mmol) and Ph_3P (27.1 mg, 0.103

mmol) at 0 °C. After stirring for 10 min at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 ml) and then extracted with ether (30 ml). The organic layer was washed with H_2O (5 ml) and saturated brine (5 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 9 g, hexane:ether = 30:1) to give bromide **14** (26.0 mg, 95 %) as a pale yellow oil: IR $\nu_{max}^{CDCl_3}$ cm^{-1} 1472, 1427, 1206, 1113, 1059, 738, 702; ^{1}H-NMR ($CDCl_3$) δ 0.99 (9H, s, **Bu^t**), 1.44 (6H, s, **CH$_3$** x 2), 3.55 (2H, d, *J*=6.6 Hz, **CH$_2$**), 3.73 (2H, s, TBDPSOC**H$_2$**), 3.96 (2H, d, *J* = 7.3 Hz, **CH$_2$**Br), 5.85 (1H, m, CH=C**H**CH$_2$Br), 5.99 (1H, m, C**H**=CHCH$_2$Br), 6.78 (1H, s, thiazole-5-**H**), 7.37 (6H, m, Ph), 7.56 (4H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 19.32 (4°), 25.34 (CH_3 x 2), 26.69 (CH_3 x 3), 32.85 (CH_2), 34.25 (CH_2), 43.02 (4°), 72.69 (CH_2), 112.83 (CH, thiazole-5), 127.56 (CH, Ph), 128.23 (CH, vinyl), 129.56 (CH, Ph), 132.83 (CH, vinyl), 133.46 (4°, Ph), 135.62 (CH, Ph), 153.67 (4°, thiazole-4), 177.86 (4°, thiazole-2); Anal. calcd for $C_{27}H_{34}BrNOSSi$: C, 61.35; H, 6.48; N, 2.65. Found: C, 61.44; H, 6.65; N, 2.59.



15

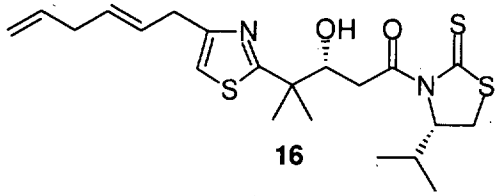
Skipped diene 15. To a stirred solution of the bromide **14** (165 mg, 0.312 mmol) and tri-*n*-butylvinylstannane (148 mg, 0.468 mmol) in previously degassed NMP (3 ml) at room temperature under argon was added and $Pd(CH_3CN)_2Cl_2$ (8.0 mg, 10 mol%). After stirring for 40 min, 1N aqueous NaOH (5 ml) and ether (10 ml) were added[2]. After stirring for 1 h, the mixture was filtered and the filtrate was washed with 1N aqueous NaOH (5 ml), H_2O (5 ml), and saturated brine (5 ml). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel BW-200, 20 g, hexane:ether = 50:1 to 30:1) to give skipped diene **15** (127 mg, 85 %) as a colorless oil: IR $\nu_{max}^{CDCl_3}$ cm^{-1} 1472, 1427, 1206, 1113, 1059, 738, 702; ^{1}H-NMR ($CDCl_3$) δ 0.99 (9H, s, **Bu^t**), 1.44 (6H, s, **CH$_3$** x 2), 2.80 (2H, m, **CH$_2$**), 3.50 (2H, d, *J* = 6.3 Hz, **CH$_2$**), 3.73 (2H, s, TBDPSOC**H$_2$**), 5.04 (2H, m, CH=C**H$_2$**), 5.50~5.90 (3H, m, vinyl-**H** x 3), 6.76 (1H, s, thiazole-5 -**H**), 7.37 (6H, m, Ph), 7.56 (4H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 19.32 (4°), 25.39 (CH_3 x 2), 26.74 (CH_3 x 3), 34.90 (CH_2), 36.62 (CH_2), 42.95 (4°), 72.72 (CH_2), 112.20 (CH, thiazole-5), 115.11 (CH_2, vinyl), 127.57 (CH, Ph), 128.10 (CH, vinyl), 129.52 (CH, Ph), 130.01 (CH, vinyl), 133.50 (4°, Ph), 135.63 (CH, Ph), 136.95 (CH, vinyl), 155.33 (4°, thiazole-4), 177.47 (4°, thiazole-2); Anal. calcd for $C_{29}H_{37}NOSSi$: C, 73.21; H, 7.84; N, 2.94. Found: C, 72.93; H, 7.72; N, 2.84.



4

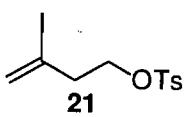
Aldehyde 4. To a stirred solution of **15** (404 mg, 0.849 mmol) in THF (3.0 ml) was added TBAF·x H_2O (555 mg) at room temperature. After stirring for 2 h at 55 °C, H_2O (3.0 ml) was added, and the mixture was extracted with EtOAc (30 ml). The extract was washed with H_2O (5 ml) and saturated brine (5 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820MH, 30 g, hexane:ether = 10:1 to 8:1) to give free alcohol of **15** (203 mg, quant.) as a colorless oil: IR ν_{max} $CDCl_3$ cm^{-1} 3389, 1522, 1464, 1427, 1206, 1113, 1059, 738, 702; ^{1}H-NMR ($CDCl_3$) δ 1.39 (6H, s, C**H**$_3$ x 2), 2.81 (2H, t, *J* = 6.3 Hz, C**H**$_2$), 3.46 (2H, d, *J* = 6.3 Hz, C**H**$_2$), 3.69 (2H, s, HOC**H**$_2$), 4.29 (1H, brs, disappeared with D_2O, O**H**), 5.05 (2H, m, CH=C**H**$_2$), 5.50~5.90 (3H, m, vinyl-**H** x 3), 6.77 (1H, s, thiazole-5-**H**); ^{13}C-NMR ($CDCl_3$) δ 25.39 (CH_3 x 2), 34.90 (CH_2), 36.62 (CH_2), 42.95 (4°), 72.72 (CH_2), 112.20 (CH, thiazole-5), 115.11 (CH_2, vinyl), 127.57 (CH, Ph), 128.10 (CH, vinyl), 129.52 (CH, Ph), 130.01 (CH, vinyl), 133.50 (4°, Ph), 135.63 (CH, Ph), 136.95 (CH, vinyl), 155.33 (4°, thiazole-4), 177.47 (4°, thiazole-2); HRMS (EI) calcd for $C_{13}H_{19}NOS$: 237.1187. Found: 237.1189.

To a stirred solution of this alcohol (356 mg, 1.50 mmol) and Et_3N (627 μl, 4.50 mmol) in CH_2Cl_2 (5.0 ml) at 0 °C was added a solution of Py·SO_3 (717 mg, 4.50 mmol) in DMSO (5.0 ml). The resulting solution was stirred at room temperature for 20 min and quenched with saturated aqueous $NaHCO_3$ (10 ml). After CH_2Cl_2 was removed *in vacuo*, the residue was extracted with ether (3 x 15 ml). The combined organic layer was washed with 1M aqueous $KHSO_4$ (2 x 10 ml) and saturated brine (10 ml) and dried over $MgSO_4$. Filtration, concentration *in vacuo*, and purification by column chromatography (silica gel BW-820 MH, 20 g, hexane:ether = 10:1 to 8:1) gave aldehyde **4** (335 mg, 95 %) as a colorless oil: IR ν_{max} $CDCl_3$ cm^{-1} 1736, 1516, 1462, 1064, 972, 910; ^{1}H-NMR ($CDCl_3$) δ 1.57 (6H, s, C**H**$_3$ x 2), 2.81 (2H, t, *J* = 6.3 Hz, C**H**$_2$), 3.52 (2H, m, C**H**$_2$), 5.00 (2H, m, CH=C**H**$_2$), 5.50~5.90 (3H, m, vinyl-**H** x 3), 6.86 (1H, s, thiazole-5-**H**), 9.69 (1H, s, C**H**O); ^{13}C-NMR ($CDCl_3$) δ 22.86 (CH_3 x 2), 34.74 (CH_2), 36.53 (CH_2), 51.74 (4°), 113.39 (CH, thiazole-5), 115.18 (CH_2, vinyl), 127.58 (CH, vinyl), 130.38 (CH, vinyl), 136.78 (CH, vinyl), 156.73 (4°, thiazole-4), 171.46 (4°, thiazole-2), 200.04 (4°, C=O); HRMS (EI) calcd for $C_{13}H_{17}NOS$: 235.1031. Found: 235.1035.



16

Aldol 16. To a cooled (-45 °C) suspension of stannous triflate (163 mg, 0.39 mmol) in CH_2Cl_2 (1.0 ml) under argon was added *N*-ethylpiperidine (57 µl, 0.416 mmol) and a solution of thiazolidine thione **5** (52.9 mg, 0.260 mmol) in CH_2Cl_2 (1.0 ml). The solution was stirred for 1 h at -45 °C and then 2 h at -15 °C. After the mixture was cooled to -78 °C, a solution of aldehyde **4** (47.0 mg, 0.200 mmol) in CH_2Cl_2 (1.0 ml) was added and the mixture was stirred for 20 min. The reaction was quenched with pH 7 buffer, diluted with EtOAc, and warmed to room temperature. The solid was filtered through the pad of celite, and extracted with EtOAc. The organic layer was washed with H_2O and saturated brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel 60 particle size 40-63µm; Cica-MERCK, 9 + 1 g, hexane:EtOAc = 10:1 to 3:1) gave aldol **16** (65.7 mg, 75 %) as a yellow oil: $[\alpha]_D^{24}$ +233.3 (c 0.77, $CHCl_3$); IR ν_{max} $CDCl_3$ cm^{-1} 3383, 1700, 1468, 1368, 1306, 1261, 1167, 1042, 912, 733; ^{1}H-NMR ($CDCl_3$) δ 0.98 (3H, d, *J* = 7.2 Hz, isopropyl C**H**$_3$), 1.05 (3H, d, *J* = 7.0 Hz, isopropyl C**H**$_3$), 1.43 (3H, s, C**H**$_3$), 1.47 (3H, s, C**H**$_3$), 2.39 (1H, m, isopropyl C**H**), 2.81 (2H, brt, C**H**$_2$), 3.02 (1H, dd, *J* = 1.0, 11.6 Hz, thiazolidine-4-**H**), 3.37 (2H, d, *J* = 5.6 Hz, α-C**H**$_2$), 3.48 (3H, m, C**H**$_2$, thiazolidine-4-**H**), 4.34 (1H, brt, C**H**OH), 4.75 (1H, brs, disappeared with D_2O, O**H**), 4.98~5.17 (3H, m, CH=C**H**$_2$, thiazolidine-3-**H**), 5.52~5.92 (3H, m, vinyl-**H** x 3), 6.78 (1H, s, thiazole-5-**H**); ^{13}C-NMR ($CDCl_3$) δ 17.65 (CH_3), 19.07 (CH_3), 24.51 (CH_3), 26.60 (CH_3), 30.55 (CH_2, thiazolidine-5), 30.78 (CH, isopropyl), 34.65 (CH_2), 36.55 (CH_2), 40.79 (CH_2), 44.17 (4°), 71.81 (CH, thiazolidine-4), 75.04 (CH, β), 112.13 (CH, thiazole-5), 115.11 (CH_2, vinyl), 127.64 (CH, vinyl), 130.30 (CH, vinyl), 136.86 (CH, vinyl), 155.47 (4°, thiazole-4), 172.54 (4°, thiazole-2), 177.84 (4°, C=O), 203.07 (4°, S=O); HRMS (EI) calcd for $C_{21}H_{30}N_2O_2S_3$: 438.1469. Found: 438.1470. Diastereomer ratio was determined by the integration of C**H**OH proton (4.25:4.34 > 1:10) in ^{1}H-NMR of the crude product.

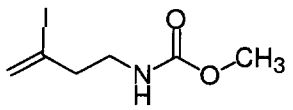


21

Tosylate 21. At room temperature, to CH_3CN (30 ml) was dissolved NaI (6.0 g, 40 mmol) and then added TMSCl (5.08 ml, 40 mmol) followed by H_2O (360 µl,

20 mmol). After 10 min, to the mixture was added a solution of **20** (1.4 g, 20 mmol) in CH_3CN (5.0 ml) and the resulting mixture was allowed to react for 1 h at room temperature. The reaction was quenched with H_2O (60 ml) and extracted with ether (3 x 50 ml). Drying over $MgSO_4$, filtration, and evaporating ether gave crude iodo alcohol (3.8 g) as a reddish brown oil.

This crude iodo alcohol (3.8 g) was dissolved in CH_2Cl_2 (25 ml), and cooled to 0 °C. To the stirred solution was added TsCl (5.72 g, 35 mmol), Et_3N (5.58 ml, 40 mmol), and $Me_3N \cdot HCl$ (190 mg, 2 mmol). After the mixture was stirred for 1 h at 0 °C, the reaction was quenched with H_2O (50 ml) and extracted with ether (3 x 60 ml). The combined extracts were washed with 1M aqueous $KHSO_4$ (50 ml), saturated aqueous $Na_2S_2O_3$ (30 ml), H_2O (40 ml), and saturated brine (50 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 250 g, hexane:ether = 6:1 to 4:1) to give tosylate **21** (3.90 g, 55 % for 2 steps) as a pale brown oil: IR ν_{max} $CDCl_3$ cm^{-1} 1360, 1190, 1176, 978, 909, 816, 774, 664; ^{1}H-NMR ($CDCl_3$) δ 2.45 (3H, s, C**H$_3$**-Ar), 2.72 (2H, dt, *J* = 0.7, 6.3 Hz, C**H$_2$**, allyl), 4.13 (2H, t, *J* = 6.3 Hz, C**H$_2$**OTs), 5.78 (1H, d, *J* = 1.6 Hz, vinyl), 6.11 (1H, dd, *J* = 1.6, 3.0 Hz, vinyl), 7.35 (2H, d, *J* = 7.9 Hz, Ar), 7.80 (2H, dd, *J* = 4.6, 6.6 Hz, Ar); ^{13}C-NMR ($CDCl_3$) δ 21.6 (CH_3), 44.28 (CH_2, allyl), 68.03(CH_2), 103.58 (4°), 127.94 (CH, *p*-tol-*o*), 129.15 (CH_2, vinyl), 129.85(CH, *p*-tol-*m*), 132.72 (4°, *p*-tol), 144.89 (4°, *p*-tol-*p*); HRMS (EI) calcd for $C_{11}H_{13}O_3S$ (M^+-I): 225.0585. Found: 225.0586.

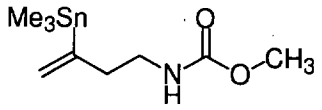


22

Methyl carbamate 22. To a stirred solution of the tosylate **22** (5.42 g, 15.38 mmol) in DMF (40 ml) at 0 °C was added NaN_3 (3.0 g, 46.14 mmol). After being stirred for 2 h at room temperature, the mixture was heated to 50 °C for 3 h. The reaction was quenched with H_2O (80 ml), and extracted with ether (3 x 50 ml). The combined organic layer was washed with 1M aqueous $KHSO_4$ (40 ml), H_2O (40 ml), and saturated brine (50 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give crude azide (3.33 g) as a yellow oil, which was used for the next step without further purification.

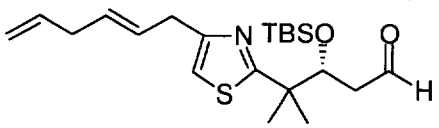
This crude azide (3.33 g) was dissolved in THF (50 ml) and cooled to 0 °C. The solution was treated with Ph_3P (5.9 g, 22.5 mmol) and H_2O (405 µl, 22.5 mmol), and stirred for 12 h at room temperature. To the resulting mixture was added $ClCO_2Me$ (2.32 ml, 30.0 mmol) and Et_3N (4.18 ml, 30 mmol) at 0 °C. After stirring for 4 h at

room temperature, H_2O (80 ml) was added, and the mixture was extracted with ether (3 x 60 ml). The combined extracts were washed with 1M aqueous $KHSO_4$ (40 ml), H_2O (40 ml), and saturated brine (50 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 250 g, hexane:ether = 7:1 to 3:1) to give methylcarbamate **22** (3.05 g, 78 % from **21**) as a pale yellow oil: IR ν_{max} $CDCl_3$ cm^{-1} 3339, 1701, 1536, 1260, 1217, 1130, 1049, 901, 779, 733; ^{1}H-NMR ($CDCl_3$) δ 2.58 (2H, t, J = 6.4 Hz, C**H**$_2$, allyl), 3.35 (2H, m, **CH**$_2$NH), 3.67 (3H, s, **CH**$_3$CO$_2$NH), 4.76 (1H, brs, CH$_3$CO$_2$N**H**), 5.80 (1H, d, J = 1.3 Hz, vinyl), 6.11 (1H, d, J = 1.3 Hz, vinyl); ^{13}C-NMR ($CDCl_3$) δ 39.84 (CH_2, allyl), 45.01(CH_2), 52.11 (CH_3), 107.75 (4°), 128.12 (CH_2, vinyl), 156.84 (4°, C=O); HRMS (EI) calcd for $C_6H_{10}NO_2$ (M^+-I): 128.0712. Found: 128.0723.



3

Trimethylstannane 3. To a stirred solution of **22** (51.0 mg, 0.20 mmol) and $Me_3SnSnMe_3$ (131 mg, 0.40 mmol) in previously degassed NMP (1 ml) at room temperature under argon was added $Pd(CH_3CN)_2Cl_2$ (5.2 mg, 10 mol%). After stirring for 3 h, H_2O (2 ml) was added, and the mixture was extracted with ether (30 ml). The organic layer was washed with 1M aqueous $KHSO_4$ (5 ml), H_2O (5 ml), and saturated brine (5 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 10 g, hexane:ether = 8:1 to 7:1) to give **3** (33.0 mg, 57 %) as a colorless oil: IR ν_{max} $CDCl_3$ cm^{-1} 3346, 1709, 1538, 1258, 1192, 920, 774; ^{1}H-NMR ($CDCl_3$) δ 0.14 (9H, s, **CH**$_3$ x 3), 2.44 (2H, t, J = 6.6 Hz, C**H**$_2$, allyl), 3.21 (2H, m, **CH**$_2$NH), 3.64 (3H, s, **CH**$_3$CO$_2$NH), 4.68 (1H, brs, CH$_3$CO$_2$N**H**), 5.25 (1H, m, vinyl), 5.70 (1H, m, vinyl); ^{13}C-NMR ($CDCl_3$) δ -9.63 (CH$_3$ x 3), 40.13 (CH_2, allyl), 40.49 (CH_2), 51.84 (CH_3), 127.20 (CH_2, vinyl), 152.17 (4°), 156.84 (4°, C=O); HRMS (EI) calcd for $C_8H_{16}NO_2Sn$ (M^+-CH_3): 278.0203. Found: 278.0203.

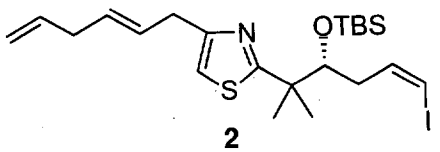


23

Aldehyde 23. To a stirred solution of **16** (71.9 mg, 0.130 mmol) in CH_2Cl_2 (1.3 ml) at 0 °C under argon was added 2,6-lutidine (25.7 µl, 0.221 mmol) and TBSOTf (43.9 µl, 0.191 mmol). After stirring for 30 min, 1M aqueous $KHSO_4$ (3 ml)

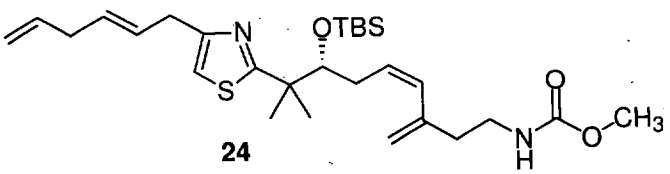
was added, and the mixture was extracted with ether (30 ml). The organic layer was washed with 1M aqueous $KHSO_4$ (2 x 4 ml), H_2O (4 ml), and saturated brine (4 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 10 g, hexane:ether = 8:1) to give TBS ether of aldol **16** (77.7 mg, 96%) as a yellow oil: $[\alpha]_D^{23}$ +240.4 (c 1.3, $CHCl_3$); IR ν_{max} $CDCl_3$ cm^{-1} 1699, 1471, 1368, 1296, 1258, 1169, 1090, 1042, 912, 837, 777, 735; ^{1}H-NMR ($CDCl_3$) δ -0.05 (3H, s, C**H**$_3$), -0.03 (3H, s, C**H**$_3$), 0.80 (9H, s, **Bu**^{t}), 0.94 (3H, d, *J* = 6.9 Hz, isopropyl C**H**$_3$), 1.04 (3H, d, *J* = 6.9 Hz, isopropyl C**H**$_3$), 1.36 (3H, s, C**H**$_3$), 1.44 (3H, s, C**H**$_3$), 2.33 (1H, m, isopropyl C**H**), 2.80 (2H, brt, C**H**$_2$), 2.99 (1H, d, *J* = 11.6 Hz, thiazolidine-4-**H**), 3.35 (2H, d, *J* = 4.9 Hz, α-C**H**$_2$), 3.38~3.50 (3H, m, C**H**$_2$, thiazolidine-4-**H**), 4.74 (1H, brt, C**H**OTBS), 4.98~5.10 (3H, m, CH=C**H**$_2$, thiazolidine-3-**H**), 5.54~5.89 (3H, m, vinyl-**H** x 3), 6.78 (1H, d, *J* = 1.0 Hz, thiazole-5-**H**); ^{13}C-NMR ($CDCl_3$) δ -5.14 (CH_3), -4.56 (CH_3), 17.97 (CH_3), 18.22 (4°, **Bu**^{t}), 19.07 (CH_3), 24.94 (CH_3), 25.29 (CH_3), 25.93 (CH_3 x 3, **Bu**^{t}), 30.66 (CH_2, thiazolidine-5), 30.87 (CH, isopropyl), 34.87 (CH_2), 36.62 (CH_2), 43.34 (α-CH_2), 45.86 (4°), 71.48 (CH, thiazolidine-4), 75.04 (β-CH,), 112.40 (CH, thiazole-5), 115.06 (CH_2, vinyl), 128.10 (CH, vinyl), 129.92 (CH, vinyl), 136.96 (CH, vinyl), 155.24 (4°, thiazole-4), 172.04 (4°, thiazole-2), 177.02 (4°, C=O), 202.57 (4°, S=O); HRMS (EI) calcd for $C_{27}H_{44}N_2O_2S_3Si$: 552.2334. Found: 552.2336.

To a stirred cooled (-78 °C) solution of the TBS ether of aldol **16** (71.9 mg, 0.130 mmol) in toluene (1.3 ml) under argon was added DIBAL (0.95 M in hexane, 342 μl, 0.325 mmol). After stirring for 1 h, 1M aqueous $KHSO_4$ (2 ml) was added, and the resulting mixture was stirred for 1 h at room temperature. After the reaction mixture was extracted with ether (30 ml), the organic layer was washed with 1M aqueous $KHSO_4$ (3 x 4 ml) and saturated brine (4 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 10 g, hexane:ether = 10:1) to give **23** (43.8 mg, 86%) as a colorless oil: $[\alpha]_D^{23}$ -13.1 (c 2.0, $CHCl_3$); IR ν_{max} $CDCl_3$ cm^{-1} 1728, 1471, 1255, 1049, 1042, 837, 777; ^{1}H-NMR ($CDCl_3$) δ -0.01 (3H, s, C**H**$_3$), 0.03 (3H, s, C**H**$_3$), 0.86 (9H, s, **Bu**^{t}), 1.38 (3H, s, C**H**$_3$), 1.42 (3H, s, C**H**$_3$), 2.39~2.67 (2H, m, α-C**H**$_2$), 2.80 (2H, brt, C**H**$_2$), 3.47 (2H, m, C**H**$_2$), 4.56 (1H, brt, C**H**OTBS), 4.97~5.09 (2H, m, CH=C**H**$_2$), 5.53~5.90 (3H, m, vinyl-**H** x 3), 6.75 (1H, d, *J* = 1.0 Hz, thiazole-5-**H**), 9.56 (1H, t, *J* = 1.8 Hz, CHO); ^{13}C-NMR ($CDCl_3$) δ -4.56 (CH_3), -3.92 (CH_3), 18.39 (4°), 24.48 (CH_3), 26.09 (CH_3), 26.15 (CH_3 x 3, **Bu**^{t}), 35.11 (CH_2), 36.91 (CH_2), 46.06 (α-CH_2), 48.86 (4°), 74.20 (β-CH,), 113.06 (CH, thiazole-5), 115.44 (CH_2, vinyl), 128.25 (CH, vinyl), 130.44 (CH, vinyl), 137.22 (CH, vinyl), 155.80 (4°, thiazole-4), 176.94 (4°, thiazole-2), 201.20 (4°, C=O); HRMS (EI) calcd for $C_{21}H_{35}NO_2SSi$: 393.2158. Found: 393.2115.



2

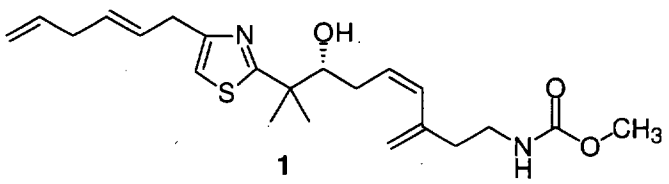
(Z)-Vinyl iodide 2. To a suspension of $Ph_3P^+CH_2I \cdot I^{-3)}$ (237 mg, 0.516 mmol) in THF (1.5 ml) at room temperature under argon was added 1.0 M solution of NaHMDS (516 µl, 0.516 mmol) in THF. After stirring for 5 min, the solution was cooled to -78 °C and HMPA (179 µl, 1.030 mmol) was added. After stirring for 5 min, the solution of aldehyde **23** (40.6 mg, 0.103 mmol) in THF (1.0 ml) was added. After the stirring for 20 min, H_2O (2.0 ml) was added, and the mixture was warmed to room temperature. The resulting mixture was filtered and filtrate was extracted with ether (30 ml). The organic layer was washed with H_2O (5.0 ml) and saturated brine (5.0 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 9 + 1 g, hexane:ether=80:1 to 60:1) to give **2** (43.8 mg, 82%) as a colorless oil: $[\alpha]_D^{23}$ -17.1 (c 0.76, $CHCl_3$); IR ν_{max} $CDCl_3$ cm^{-1} 1471, 1255, 1094, 1048, 970, 912, 837, 776; ^{1}H-NMR ($CDCl_3$) δ -0.01 (3H, s, **CH3**), 0.05 (3H, s, **CH3**), 0.87 (9H, s, **Bu^t**), 1.38 (3H, s, **CH3**), 1.44 (3H, s, **CH3**), 2.80 (2H, brt, *J* = 5.6 Hz, **CH2**), 3.49 (2H, d, *J* = 6.2 Hz, **CH2**), 4.19 (1H, t, *J* = 5.3 Hz, **CH**OTBS), 4.97~5.09 (2H, m, CH=**CH2**), 5.53~5.90 (3H, m, vinyl-**H** x 3), 6.06~6.16 (2H, m, **CH**=**CH**I), 6.73 (1H, s, thiazole-5-**H**); ^{13}C-NMR ($CDCl_3$) δ -4.74 (CH_3), -3.81 (CH_3), 18.17 (4°), 24.49 (CH_3), 25.72 (CH_3), 25.99 (CH_3 x 3, Bu^t), 34.92 (CH_2), 36.64 (CH_2), 39.39 (CH_2), 46.08 (4°), 77.83 (CHOTBS), 82.70 (CHI), 112.31 (CH, thiazole-5), 115.15 (CH_2, vinyl), 128.16 (CH, vinyl), 129.96 (CH, vinyl), 136.96 (CH, vinyl), 138.74 (CH, Z-vinyl), 155.38 (4°, thiazole-4), 177.81 (4°, thiazole-2); HRMS (EI) calcd for $C_{22}H_{36}INOSSi$: 517.1332. Found: 517.1336.



24

TBS ether of mycothiazole 24. A dry round bottom flask was charged LiCl (12.7 mg, 0.30 mmol) and flame dried under high vacuum. Upon cooling, $Pd(Ph_3P)_4$ (11.6 mg, 20 mol%) and CuCl (24.8 mg, 0.25 mmol) were added under argon, followed by the solution of vinyl iodide **2** (25.9 mg, 0.05 mmol) and trimethyl stannane **3** (21.9 mg, 0.075 mmol) in previously degassed DMSO (1.0 ml) was added. After the mixture was stirred for 12 h at room temperature, $Pd(Ph_3P)_4$ (11.6 mg, 20

mol%) was added since TLC indicated that the reaction had not gone to completion. After stirring for 3 h, 1N aqueous NaOH (2 ml) and ether (5 ml) was added, and the resulting mixture was filtered through the pad of celite and extracted with ether (30 ml). The extract was washed with 1N aqueous NaOH (5 ml), H_2O (5 ml), 1M aqueous $KHSO_4$ (5 ml), and saturated brine (5 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-200, 10 g, hexane:EtOAc = 15:1 to 11:1) to give **24** (16.3 mg, 63%) as a pale yellow oil: $[\alpha]_D^{24}$ -0.15 (c 0.91, $CHCl_3$); IR ν_{max} $CDCl_3$ cm^{-1} 3340, 1728, 1520, 1471, 1256, 1096, 1049, 837, 776; ^{1}H-NMR ($CDCl_3$) δ -0.08 (3H, s, **CH$_3$**), 0.04 (3H, s, **CH$_3$**), 0.87 (9H, s, **Bu^t**), 1.34 (3H, s, **CH$_3$**), 1.40 (3H, s, **CH$_3$**), 2.23 (2H, t, *J* = 6.6 Hz, CH_2=CH**CH$_2$**), 2.35 (2H, m, allyl **CH$_2$**), 2.80 (2H, brt, *J* = 6.3 Hz, allyl **CH$_2$**), 3.20 (2H, m, **CH$_2$**NH), 3.47 (2H, d, *J* = 6.3 Hz, **CH$_2$**), 3.65 (3H, s, NHCO$_2$**CH$_3$**), 4.06 (1H, t, *J* = 5.0 Hz, **CH**OTBS), 4.84~5.08 (5H, m, CH=**CH$_2$** x 2, **NH**CO$_2$CH$_3$), 5.49~5.92 (5H, m, vinyl-**H** x 5), 6.73 (1H, d, *J* = 1.0 Hz, thiazole-5-**H**); ^{13}C-NMR ($CDCl_3$) δ -4.65 (CH_3), -3.59 (CH_3), 18.22 (4°), 24.57 (CH_3), 25.90 (CH_3), 26.02 (CH_3 x 3, Bu^t), 33.10 (CH_2), 34.84 (CH_2), 36.62 (CH_2), 37.32 (CH_2), 39.34 (CH_2), 46.22 (4°), 51.95 (CH_3), 79.35 (CHOTBS), 112.29 (CH, thiazole-5), 115.13 (CH_2, vinyl), 115.83 (CH_2, vinyl), 128.07 (CH, vinyl), 129.02 (CH, vinyl), 130.03 (CH, vinyl), 130.78 (CH, vinyl), 136.93 (CH, vinyl), 141.89 (4°, vinyl), 155.27 (4°, thiazole-4), 156.93 (4°, C=O), 178.06 (4°, thiazole-2); HRMS (EI) calcd for $C_{28}H_{46}N_2O_3SSi$: 518.2998. Found: 518.2974.



1

Mycothiazole (1). To a stirred solution of **24** (18.1 mg, 0.035 mmol) in THF (1.0 ml) at 0 °C was added TBAF·x H_2O (60 mg). After stirring for 2 h at room temperature, H_2O (2 ml) was added, and the mixture was extracted with EtOAc (3 x 10 ml). The combined extracts were washed with saturated brine (5 ml), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel BW-820 MH, 10 g, hexane:EtOAc = 6:1 to 2:1) to give **1** (12.7 mg, 90%) as a colorless viscous oil: $[\alpha]_D^{23}$ -26.0 (c 0.64, $CHCl_3$); IR ν_{max} $CDCl_3$ cm^{-1} 3328, 1705, 1522, 1466, 1271, 1055, 972, 908; ^{1}H-NMR ($CDCl_3$) δ 1.39 (3H, s, **CH$_3$**), 1.43 (3H, s, **CH$_3$**), 2.18~2.43 (4H, m, allyl **CH$_2$** x 2), 2.80 (2H, t, *J* = 6.0 Hz, allyl **CH$_2$**), 3.16~3.33 (2H, m, **CH$_2$**NH) 3.46 (2H, d, *J* = 5.6 Hz, **CH$_2$**), 3.63 (3H, s, NHCO$_2$**CH$_3$**), 3.78 (1H, dd, *J* = 3.0, 9.6 Hz, **CH**OH), 4.88~5.09 (5H, m,

decrease 1H with D_2O, CH=C**H**$_2$ x 2, O**H**), 5.43 (1H, brs, N**H**), 5.52~5.91 (5H, m, vinyl-**H** x 5), 6.77 (1H, s, thiazole-5-**H**); ^{13}C-NMR ($CDCl_3$) δ 23.85 (CH_3), 26.67 (CH_3), 30.59 (CH_2), 34.65 (CH_2), 36.57 (CH_2), 37.14 (CH_2), 39.37 (CH_2), 44.55 (4°), 51.83 (CH_3), 78.11 (CHOH), 111.95 (CH, thiazole-5), 115.22 (CH_2, vinyl), 115.85 (CH_2, vinyl), 127.57 (CH, vinyl), 130.44 (CH, vinyl), 130.60 (CH, vinyl), 130.85 (CH, vinyl), 136.80 (CH, vinyl), 142.48 (4°, vinyl), 155.35 (4°,thiazole-4), 157.12 (4°, C=O), 179.37 (4°, thiazole-2); HRMS (EI) calcd for $C_{22}H_{32}N_2O_3S$: 404.2134. Found: 404.2134.

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2) Renaud, P.; Lacote, E.; Quaranta, L. *Tetrahedron Lett.* **1998**, *39*, 2123-2126.
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