

# Supporting Information

## Formal Total Synthesis of *N*-Methylmaysenine

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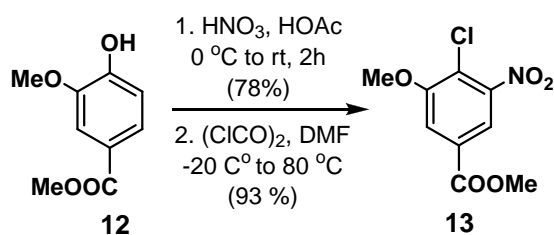
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## 1: General Information

The boiling point of petroleum ether is between 60-90 °C. Silica gel (200-300 mesh) for purification was purchased from Qing Dao Hai Yang Chemical Industry Co. of China. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded at 500 MHz and 125 MHz with Brüker Advance 500 spectrometer or at 400 MHz and 100 MHz with Bruker ARX400 spectrometer or at 300 MHz and 75 MHz with Brüker Advance 300 spectrometer or at 300 MHz and 75 MHz with Varian Mercury 300 spectrometer. High resolution mass spectrometric data were obtained using Bruker Apex IV FTMS. All non-aqueous reactions were carried out in flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Diethyl ether (Et<sub>2</sub>O) and tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under argon. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from CaH<sub>2</sub>. All other commercial reagents were used as received.

### Synthesis of methyl 4- chloro-3-methoxy-5-nitrobenzoate (13)

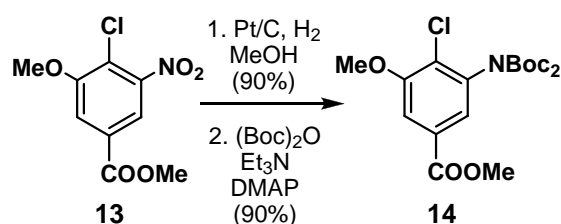


To a solution of methyl vanillate **12** (18.2 g, 100 mmol) in AcOH (100 mL) was slowly added con. H<sub>2</sub>SO<sub>4</sub> (6.5 mL, 100 mmol) in AcOH (37 mL) at 0 °C, and the mixture was warmed to room temperature. After stirring at 25 °C for 2h, a yellowish precipitate was formed, and the solid was filtered off to give phenol **13a** (17.7 g) in 78 % yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.95 (s, 3H), 4.01 (s, 3H), 7.76 (d, *J* = 1.8 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 55.6, 56.9, 117.4, 118.4, 121.4, 133.5, 149.6, 150.1, 165.0; HRMS (ESI): calcd for C<sub>9</sub>H<sub>9</sub>NNaO<sub>6</sub> [M + Na<sup>+</sup>] 250.03221; found 250.03176.

To a solution of phenol **13a** (15.9 g, 70 mmol) in dry DMF (150 mL) was slowly added (COCl)<sub>2</sub> (18.0 mL, 210 mmol) at -20 °C, and the formed mixture was then warmed up to 80 °C. After stirring at the same temperature for 3 h, the mixture was first cooled to room temperature and then poured to an ice water (250 mL) with vigorously stirring. After staying at room temperature for 6 h, the formed crude product was filtered off, and then dissolved in dichloromethane. The organic layer was washed sequentially with saturated aqueous NaHCO<sub>3</sub> (3 x 50 mL) and brine (50 mL), and

then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate/dichloromethane = 8:1:1) to give **17** (16.058 g) in 93 % as white solid;  $R_f$  = 0.40 (hexane/ethyl acetate/dichloromethane = 8:1:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.97 (s, 3H), 4.02 (s, 3H), 7.75 (d,  $J$  = 1.7 Hz, 1H), 8.01 (d,  $J$  = 1.7 Hz, 1H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  52.9, 57.2, 114.9, 117.4, 120.7, 129.9, 149.5, 156.5, 164.4; HRMS (ESI): calcd for  $\text{C}_9\text{H}_8\text{ClNNaO}_5$  [ $\text{M} + \text{Na}^+$ ] 267.99832 found 267.99797.

#### Synthesis of methyl 3-(bis(tert-butoxycarbonyl)amino)-4-chloro-5-methoxybenzoate (**14**)

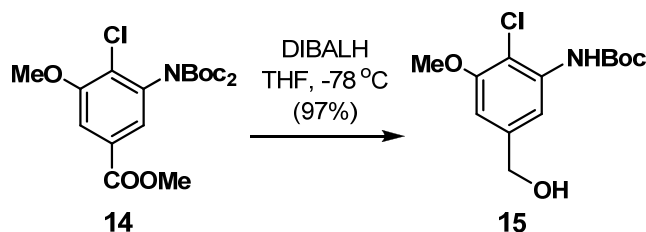


To a solution of nitrobenzene **13** (15.500 g, 63.1 mmol) in ethanol (700 mL) was added 5 % Pt/C (1.55 g), and the mixture was subjected to degas with nitrogen for 3 times and then stirred under balloon pressure of hydrogen at 25 °C until no starting material disappeared. After filtration, the filtrate was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate/dichloromethane = 8:1:1) to give amine **14a** (12.3 g) in 90 % yield as white solid,  $R_f$  = 0.28 (silica gel/hexane/ethyl acetate/dichloromethane = 8:1:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.88 (s, 3H), 3.91 (s, 3H), 4.22 (s, 2H), 6.99 (d,  $J$  = 1.8 Hz, 1H), 7.11 (d,  $J$  = 1.8 Hz, 1H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  52.1, 56.2, 102.0, 109.5, 112.1, 129.1, 144.1, 155.6, 166.6; HRMS (ESI): calcd for  $\text{C}_9\text{H}_{11}\text{ClNO}_3$  [ $\text{M} + \text{H}^+$ ] 216.04220; found 216.04183.

To a solution of amine **14a** (10.8 g, 50 mmol) in dry THF (250 mL) was sequentially added  $\text{Et}_3\text{N}$  (34.85 mL, 250 mmol), DMAP (3.05 g, 25 mmol), and  $\text{Boc}_2\text{O}$  (32.7 g, 150 mmol) at 25 °C, and the reaction was monitored by TLC until the starting material disappeared. The reaction mixture was quenched by addition of a saturated aqueous  $\text{NH}_4\text{Cl}$  (100 mL), and the mixture was extracted with ethyl acetate (3 x 100 mL). The organic extract was washed with aqueous  $\text{NaHCO}_3$  (2 x 20 mL), brine (20 mL), and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate/ dichloromethane = 40:1:1) to give **14** (18.7 g) in 90 % as white solid,  $R_f$  = 0.34 (silica gel/hexane/ ethyl acetate/dichloromethane = 8:1:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.32 (s, 18H),

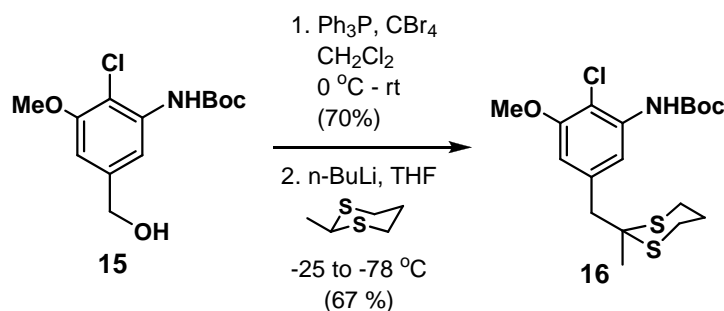
3.84 (s, 3H), 3.88 (s, 3H), 7.48 (d,  $J = 1.7$  Hz, 1H), 7.50 (d,  $J = 1.7$  Hz, 1H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  27.5, 52.1, 56.4, 82.8, 111.4, 122.8, 126.6, 128.8, 138.3, 150.1, 155.3, 165.4; HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{26}\text{ClNNaO}_7$  [ $\text{M} + \text{Na}^+$ ] 438.12900; found 438.13011.

#### Synthesis of *tert*-butyl 2-chloro-5-(hydroxymethyl)-3-methoxyphenylcarbamate (**15**)



To a solution of methyl ester **14** (1.5 g, 3.6 mmol) in dry THF (18 mL) was slowly added  $\text{LiAlH}_4$  (0.55 g, 14.4 mmol) at  $0^\circ\text{C}$ , and the mixture was first warmed up to  $25^\circ\text{C}$ , and then stirred at the same temperature for 2 h. The reaction was quenched carefully with ice water at  $0^\circ\text{C}$ , and the formed mixture was stirred at room temperature for an additional hour. After filtration, the residue was washed with ethyl acetate, and the filtrate was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel hexane/ethyl acetate = 10:1 to give **15** as colorless oil (1.0 g, 97 %);  $R_f = 0.27$  (hexane/ethyl acetate = 4:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.48 (s, 9H), 3.35 (s, 1H), 3.82 (s, 3H), 4.56 (s, 2H), 6.63 (s, 1H), 7.07 (s, 1H), 7.67 (s, 1H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  28.1, 56.0, 64.6, 81.0, 104.1, 1108.9, 109.8, 135.7, 140.9, 152.4, 154.9; HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{18}\text{ClNNaO}_4$  [ $\text{M} + \text{Na}^+$ ] 310.08166; found 310.08132.

#### Synthesis of *tert*-butyl 2-chloro-3-methoxy-5-((2-methyl-1,3-dithian-2-yl)methyl)-phenyl carbamate (**16**)

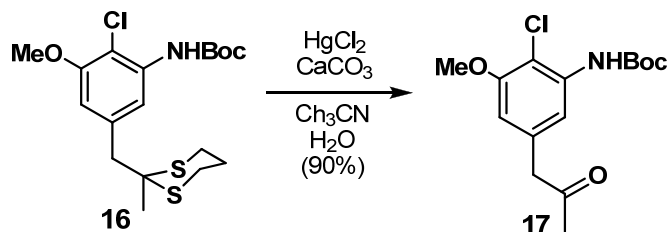


To a solution of benzalcohol **15** (2.9 g, 10 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) was slowly added a solution of  $\text{PPh}_3$  (2.622 g, 10 mmol) and  $\text{CBr}_4$  (3.316 g, 10 mmol) in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$ , and the mixture was stirred at room temperature for 4 h. The reaction was quenched by addition of a saturated aqueous  $\text{NH}_4\text{Cl}$  (15 mL), and the formed mixture was extracted with ethyl acetate (3 x 25

ml). The combined organic phase was washed sequentially with a saturated aqueous  $\text{NaHCO}_3$  (2 x 10 mL) and brine (10 mL), and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 80:1) to give the bromide (2.45 g) in 70% yield as a colorless oil;  $R_f$  = 0.63 (hexane/ethyl acetate = 32:1).

To a solution of 2-methyl-1,3-dithiane (2.819 g, 21 mmol) in dry THF (63 mL) was slowly added *n*-BuLi (6.16 mL, 2.5 M in hexane, 15.4 mmol) at  $-25\text{ }^\circ\text{C}$  under nitrogen atmosphere, and the formed mixture was stirred at the same temperature for 2 h. To this solution was added a pre-cooled solution ( $-78\text{ }^\circ\text{C}$ ) of the bromide (2.453 g, 7 mmol) made above in THF (21 mL), and the formed mixture was then warmed up to  $-25\text{ }^\circ\text{C}$ , and the reaction mixture was stirred at the same temperature for 1 h. After reaction, the mixture was quenched with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution (10 mL), and the mixture was extracted with ethyl acetate (3 x 20 mL), and the combined reaction mixture was washed with a saturated aqueous  $\text{NaHCO}_3$  solution (2 x 10 mL) and brine (10 mL), and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **16** (1.9 g) in 67% as a colorless oil;  $R_f$  = 0.35 (hexane/ethyl acetate = 16:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.51 (s, 9H), 1.61 (s, 3H), 1.96-2.01 (m, 2H), 2.86-2.95 (m, 4H), 3.20 (s, 2H), 3.87 (s, 3H), 6.60 (d,  $J$  = 1.7, 1H), 7.03 (s, 1H), 7.73 (s, 1H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  25.1, 26.7, 27.6, 28.3, 47.9, 49.1, 56.2, 80.8, 108.7, 109.1, 114.4, 135.6, 135.7, 152.2, 154.3; HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{26}\text{ClNNaO}_3\text{S}_2$  [ $\text{M} + \text{Na}^+$ ] 426.09348; found 426.09211.

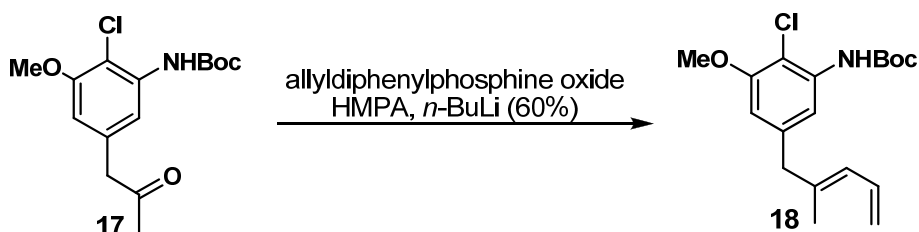
#### Synthesis of *tert*-butyl 2-chloro-3-methoxy-5-(2-oxopropyl)-phenylcarbamate (**17**)



To a solution of **16** (1.57 g, 5 mmol) in  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  (24 mL,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  = 20 : 4) was added  $\text{CaCO}_3$  (7.5 g, 75 mmol) and  $\text{HgCl}_2$  (6.788 g, 25 mmol) at  $20\text{ }^\circ\text{C}$ , and the reaction was monitored by TLC until the starting material disappeared. The reaction was quenched with 10 %  $\text{Na}_2\text{S}$  solution (39 mL), and the mixture was filtrated. The filtrate was extracted with ethyl acetate (3

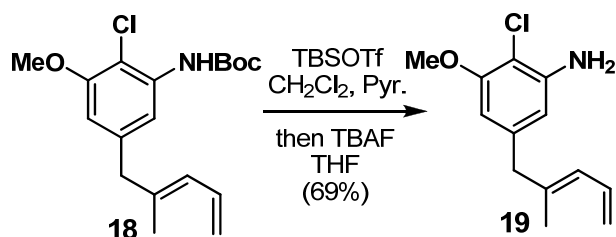
x 20 mL), and the combined organic layers was washed with brine (10 mL), and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **17** (1.41 g) in 90 % as a colorless oil; *R<sub>f</sub>* = 0.32 (hexane/ethyl acetate = 8:1). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.53 (s, 9H), 2.19 (s, 3H), 3.68 (s, 2H), 3.88 (s, 3H), 6.46 (s, 1H), 7.11 (s, 1H), 7.75 (s, 1H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 28.2, 29.3, 51.0, 56.2, 81.0, 106.7, 108.89, 112.7, 133.9, 136.3, 152.2, 155.0, 205.7; HRMS (ESI): calcd for C<sub>15</sub>H<sub>20</sub>ClNNaO<sub>4</sub> [M + Na<sup>+</sup>] 336.09731; found 336.09665.

#### Synthesis of (E)-*tert*-butyl 2-chloro-3-methoxy-5-(2-methylpenta-2,4-dienyl)phenylcarbamate (**18**)



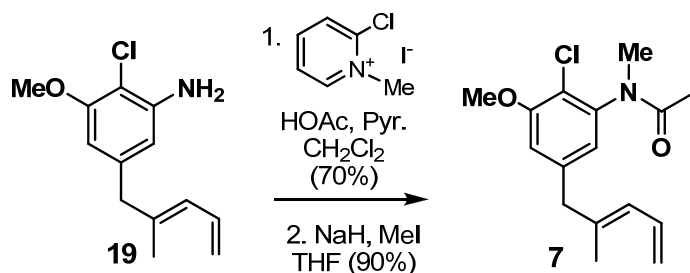
To a solution of allyldiphenylphosphine oxide (1.2 g, 5 mmol) in dry THF (15 mL) was added HMPA (0.87 mL, 5 mmol) and *n*-BuLi (2 mL, 2.5 M in hexane, 5 mmol) at -20 °C, and the reaction mixture was stirred at the same temperature for 30 min. To this solution was added a solution of ketone **21** (0.38 g, 1.21 mmol) in THF (4 mL) at -20 °C, and the formed mixture was warmed up to room temperature, and stirred for an additional 30 min. The reaction mixture was quenched by addition of a saturated aqueous NH<sub>4</sub>Cl (10 mL), and the mixture was extracted with ethyl acetate (3 x 20 mL), and the combined organic layers was washed with a saturated aqueous NaHCO<sub>3</sub> (2 x 50 mL) and brine (5 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 30:1) to give **18** (0.172 g) in 60 % yield as a colorless oil; *R<sub>f</sub>* = 0.75 (hexane/ethyl acetate = 8:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.53 (s, 9H), 1.71 (s, 3H), 3.33 (s, 2H), 3.87 (s, 3H), 5.04 (d, *J* = 10.2 Hz, 1H), 5.15 (dd, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 16.9 Hz, 1H), 5.93 (d, *J* = 10.8 Hz, 1H), 6.43 (d, *J* = 1.6 Hz, 1H), 6.55-6.62 (m, 1H), 7.05 (s, 1H), 7.67 (s, 1H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 16.5, 28.3, 46.5, 56.2, 81.0, 106.3, 112.5, 115.8, 127.3, 133.1, 135.9, 137.8, 139.6, 152.3, 154.8; HRMS (ESI): calcd for C<sub>18</sub>H<sub>24</sub>ClNNaO<sub>3</sub> [M + Na<sup>+</sup>] 360.13369; found 360.13343.

#### Synthesis of (E)-2-chloro-3-methoxy-5-(2-methylpenta-2,4-dienyl)aniline (**19**)



To a solution of diene **18** (44 mg, 0.13 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (1 mL) was added pyridine (0.021 mL, 0.26 mmol) and TMSOTf (0.045 mL, 0.26 mmol) at 0 °C, and the mixture was slowly warmed up to room temperature, and stirred at the same temperature for 4 h. To this solution was added a solution of TBAF (0.164 g, 0.52 mmol) in THF (1.5 mL) at 25 °C, and the formed mixture was stirred at the same temperature for an additional hour. The reaction mixture was quenched by addition of an aqueous solution of  $\text{NH}_4\text{Cl}$  (10 mL), and the mixture was extracted with ethyl acetate (3 x 15 mL), and the combined organic layers were washed with a saturated aqueous solution of  $\text{NaHCO}_3$  (2 x 5 mL) and brine (5 mL), and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **19** (22 mg) in 69 % yield as a colorless oil,  $R_f$  = 0.50 (hexane/ethyl acetate = 8:1).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.70 (s, 3H), 3.23 (s, 2H), 3.85 (s, 3H), 3.96 (s, 2H), 5.06 (d,  $J$  = 10.2 Hz, 1H), 5.15 (dd,  $J_1$  = 1.5 Hz,  $J_2$  = 16.8 Hz, 1H), 5.93 (d,  $J$  = 10.8 Hz, 1H), 6.17 (d,  $J$  = 1.5 Hz, 1H), 6.25 (d,  $J$  = 1.8 Hz, 1H), 6.53-6.66 (m, 1H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  16.4, 46.2, 56.1, 102.5, 109.0, 115.7, 127.3, 127.7, 133.1, 137.9, 139.2, 143.8, 155.5; HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{17}\text{ClNO}$  [ $\text{M} + \text{H}^+$ ] 238.09932; found 238.09914.

#### Synthesis of (E)-N-(2-chloro-3-methoxy-5-(2-methylpenta-2,4-dienyl)phenyl)-N-methylacetamide (**7**)



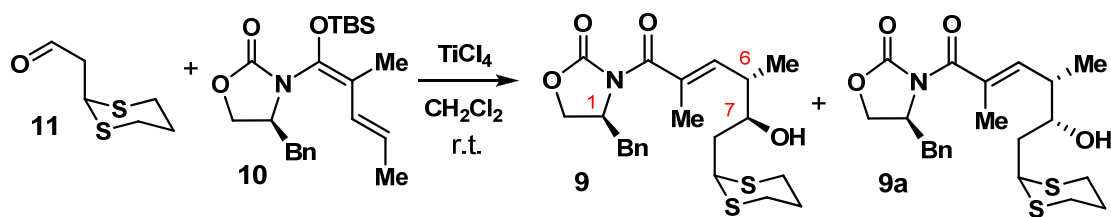
To a solution of amine **19** (161 mg, 0.68 mmol) in  $\text{CH}_2\text{Cl}_2$  was sequentially added  $\text{Et}_3\text{N}$  (0.47 mL, 3.39 mmol),  $\text{AcCl}$  (0.461 mL, 3.39 mmol) and Mukaiyama reagent (518 mg, 2 mmol) at room temperature, and the mixture was stirred under refluxing conditions for 30 min. The reaction was worked up by addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (5 mL), and the mixture was



extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 5 mL) and brine (5 mL), and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 8:1) to give **7a** (132 mg) in 70 % yield as a colorless oil; *R<sub>f</sub>* = 0.31 (hexane/ethyl acetate = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.70 (s, 3H), 2.22 (s, 3H), 3.34 (s, 2H), 3.87 (s, 3H), 5.04 (d, *J* = 10.2 Hz, 1H), 5.15 (dd, *J<sub>1</sub>* = 1.5 Hz, *J<sub>2</sub>* = 16.8 Hz, 1H), 5.93 (d, *J* = 10.8 Hz, 1H), 6.50 (s, 1H), 6.52-6.61 (m, 1H), 7.65 (s, 1H), 7.87 (s, 1H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 16.4, 25.0, 46.4, 56.3, 107.7, 108.8, 114.3, 115.9, 127.5, 133.1, 135.4, 137.6, 139.8, 154.8, 168.3; HRMS (ESI): calcd for C<sub>15</sub>H<sub>18</sub>CINNaO<sub>2</sub> [M + Na<sup>+</sup>] 302.09183; found 302.09167.

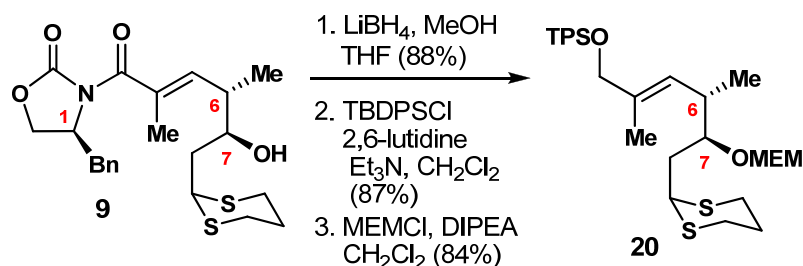
To a solution of acetamide **7a** (92 mg, 0.33 mmol) in THF (1 mL) was added NaH (20 mg, 0.5 mmol) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To this solution was MeI (0.03 mL, 0.5 mmol) at 0 °C, and the formed mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (5 mL), and the mixture was extracted with ethyl acetate (3 x 10 mL), and the combined organic layers were washed with saturated aqueous solution of NaHCO<sub>3</sub> (2 x 5 mL) and brine (5 mL), and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **7** (87 mg) in 90 % yield as a white solid; *R<sub>f</sub>* = 0.17 (hexane/ethyl acetate = 8:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.70 (s, 3H), 1.81 (s, 3H), 3.17 (d, *J* = 3.6 Hz, 3H), 3.35 (s, 2H), 3.92 (s, 3H), 5.09 (d, *J* = 10.2 Hz, 1H), 5.18 (dd, *J<sub>1</sub>* = 1.2 Hz, *J<sub>2</sub>* = 16.8 Hz, 1H), 5.92 (d, *J* = 10.8 Hz, 1H), 6.54-6.62 (m, 1H), 6.74 (dd, *J<sub>1</sub>* = 1.7 Hz, *J<sub>2</sub>* = 17.6 Hz, 2H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 16.2, 21.5, 35.2, 45.6, 56.2, 112.1, 116.2, 119.0, 121.3, 127.8, 132.6, 136.5, 140.3, 142.4, 156.0, 170.1; HRMS (ESI): calcd for C<sub>16</sub>H<sub>20</sub>CINNaO<sub>2</sub> [M + Na<sup>+</sup>] 316.10748; found 316.10695.

**Synthesis of (S)-3-((4S,5S,E)-6-(1,3-dithian-2-yl)-5-hydroxy-2,4-dimethylhex-2-enoyl)-4-benzyloxazolidin-2-one (9) and (S)-3-((4S,5R,E)-6-(1,3-dithian-2-yl)-5-hydroxy-2,4-dimethylhex-2-enoyl)-4-benzyloxazolidin-2-one (9a)**

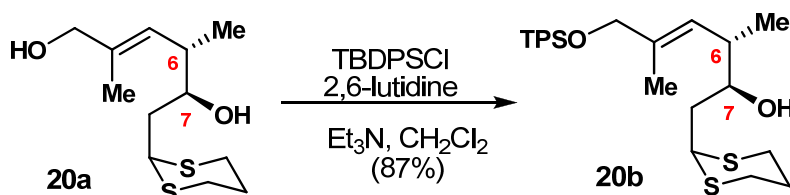


To a solution of aldehyde **11** (10. g, 62 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (185 mL) was slowly added  $\text{TiCl}_4$  (31 mL, 1 M in  $\text{CH}_2\text{Cl}_2$ , 31 mmol) at  $-78^\circ\text{C}$ , and the mixture was stirred at the same temperature for 30 min. To this solution was added a solution of **10** (12.02 g, 31 mmol) in  $\text{CH}_2\text{Cl}_2$  (63 mL) at  $-78^\circ\text{C}$ , and the reaction mixture was warmed up to room temperature and stirred for 2 h. The reaction mixture was quenched by addition of a saturate aqueous solution of sodium-potassium tartrate (400 mL), and the mixture was extracted with ethyl acetate (3 x 200 mL). The combined organic layers were sequentially washed with a saturated aqueous solution of  $\text{NaHCO}_3$  (2 x 50 mL) and brine (50 mL), and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 7:1) to give both *anti* product **9a** (2.37 g) in 17.6 % yield [ $R_f$  = 0.33 (hexane/ethyl acetate = 1:1)] and *syn* product **8** (8.3 g) in 61.3 % yield as a yellow oil [ $R_f$  = 0.31 (hexane/ethyl acetate = 1:1)]. Spectra data for **8a**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.01 (d,  $J$  = 6.6 Hz, 3H), 1.86 (m, 2H), 1.99 (m, 4H), 2.12 (m, 1H), 2.55 (m, 1H), 2.87 (m, 5H), 3.27 (d,  $J$  = 2.9 Hz, 1H), 3.30 (d,  $J$  = 3.4 Hz, 1H), 3.65 (t,  $J$  = 8.8 Hz, 1H), 4.17 (dd,  $J_1$  = 6.5 Hz,  $J_2$  = 9.0 Hz, 1H), 4.30 (t,  $J$  = 8.8 Hz, 1H), 4.38 (dd,  $J$  = 3.5, 10.7 Hz, 1H), 4.78 (dd,  $J$  = 3.2, 6.3 Hz, 1H), 5.76 (dd,  $J$  = 1.3, 10.4 Hz, 1H), 7.18 (d,  $J$  = 7.0, 2H), 7.30 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.9, 16.0, 26.1, 29.9, 30.5, 37.5, 40.0, 40.2, 44.0, 55.0, 66.3, 71.7, 127.4, 128.9, 129.4, 131.4, 134.8, 141.4, 154.0, 171.4; HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{29}\text{NNaO}_4\text{S}_2$  [ $\text{M} + \text{Na}^+$ ] 458.14302; found 458.14249; Spectrum data of **8**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.06 (d,  $J$  = 6.4 Hz, 3H), 1.76-1.82 (m, 1H), 1.87-1.96 (m, 5H), 2.10-2.13 (m, 1H), 2.71-2.76 (m, 1H), 2.79-2.94 (m, 5H), 3.29 (dd,  $J_1$  = 3.1 Hz,  $J_2$  = 13.5, 1H), 3.96 (s, 1H), 4.16-4.19 (m, 1H), 4.25-4.30 (m, 2H), 4.74-4.80 (m, 1H), 5.79 (d,  $J$  = 10.0 Hz, 1H), 7.19 (d,  $J$  = 7.3, 2H), 7.28-7.35 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.8, 14.5, 26.0, 29.6, 30.1, 37.6, 38.6, 39.2, 44.0, 55.0, 66.3, 71.6, 127.4, 128.9, 129.3, 131.1, 134.9, 140.4, 153.5, 171.4; HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{29}\text{NNaO}_4\text{S}_2$  [ $\text{M} + \text{Na}^+$ ] 458.14302; found 458.14152.

**Synthesis (8S,9S,E)-8-((1,3-dithian-2-yl)methyl)-9,11,15,15-tetramethyl-14,14-diphenyl-2,5,7,13-tetraoxa-14-silahexadec-10-ene (20)**

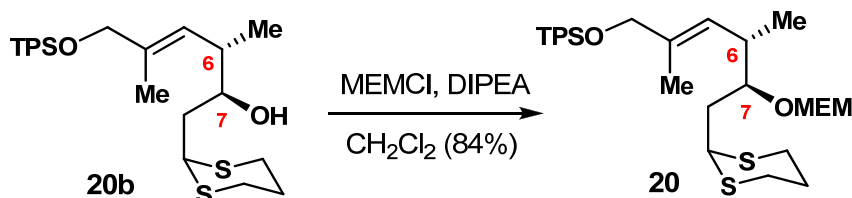


To a solution of alcohol **9** (4.06 g, 10.6 mmol) in dry mixed solvent THF (40 mL) and methanol (1.69 mL, 53 mmol) was added a solution of  $\text{LiBH}_4$  (1.16 g, 53 mmol) in THF (50 mL) at 0 °C, and the mixture was then warmed up to room temperature, and stirred for 5 h. To this solution was slowly added a mixed solution (30 mL, ethyl acetate/water/brine = 1:1:1) to quench the reaction. The mixture was extracted with ethyl acetate (3 x 50 mL), and the combined organic layers were washed with brine (2 x 15 mL), and finally dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 5:1) to give diol **20a** (2.45 g) in 88 % yield;  $R_f$  = 0.25 (hexane/ethyl acetate = 1:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.00 (d,  $J$  = 14.3 Hz, 3H), 1.67 (d,  $J$  = 0.8 Hz, 3H), 1.84-1.92 (m, 3H), 2.09-2.14 (m, 1H), 2.47-2.51 (m, 1H), 2.82-2.86 (m, 4H), 3.72-3.75 (m, 1H), 4.00 (s, 2H), 4.24 (dd,  $J_1$  = 4.5 Hz,  $J_2$  = 9.9 Hz, 1H), 5.24 (dd,  $J_1$  = 0.9 Hz,  $J_2$  = 9.8 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 16.2, 25.9, 30.0, 30.4, 38.3, 40.0, 44.5, 68.5, 72.4, 127.5, 135.9; HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{22}\text{NaO}_2\text{S}_2$  [ $\text{M} + \text{Na}^+$ ] 285.09534; found 285.09491.



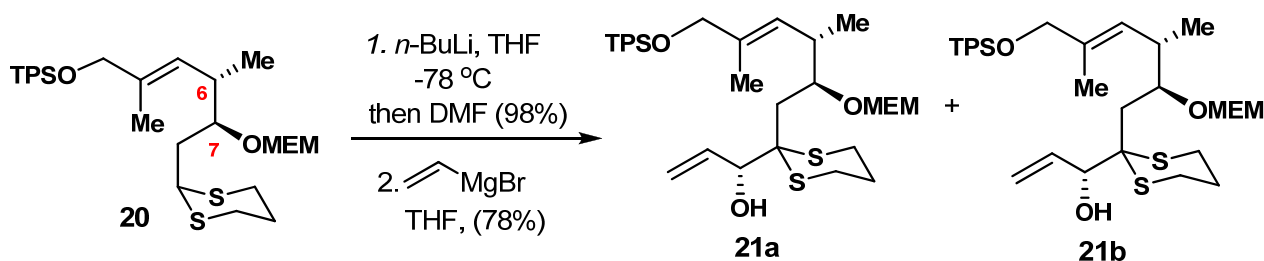
To a solution of diol **20a** (3.4 g, 13 mmol) in  $\text{CH}_2\text{Cl}_2$  was added DMAP (0.317 g, 2.6 mmol),  $\text{Et}_3\text{N}$  (0.27 mL, 19.5 mmol) and TBDPSCI (4.0 mL, 15.6 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. The reaction was worked up by addition of water (5 mL), and the mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were sequentially washed with a saturated aqueous solution  $\text{NaHCO}_3$  (2 x 10 mL) and brine (10 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **20b** (5.66 g) in 87 % yield as a yellowish oil;  $R_f$  = 0.48 (hexane/ethyl acetate = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02 (d,  $J$  = 6.7 Hz, 3H), 1.08 (s, 9H), 1.64 (d,  $J$  = 0.7 Hz, 3H), 1.74-1.80 (m, 2H), 1.92-1.99 (m, 2H),

2.11-2.14 (m, 1H), 2.51-2.53 (m, 1H), 2.84-2.87 (m, 3H), 2.95 (d,  $J = 2.6$  Hz, 1H), 3.71-3.75 (m, 1H), 4.08 (s, 2H), 4.26-4.29 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 9.9$  Hz, 1H), 5.28 (dd,  $J_1 = 1.3$  Hz,  $J_2 = 10.0$  Hz, 1H), 7.39-7.44 (m, 6H), 7.68-7.70 (m, 4H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  13.9, 16.6, 19.3, 26.0, 26.8, 29.9, 30.3, 38.3, 39.9, 44.5, 68.7, 72.6, 125.8, 127.6, 129.6, 133.7, 133.8, 135.5, 135.5; HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{40}\text{NaO}_2\text{S}_2\text{Si}$  [ $\text{M} + \text{Na}^+$ ] 523.21312; found 523.21270.



To a solution of alcohol **S10** (6.00 g, 12.2 mmol) in dichloromethane was added DIPEA (13.0 mL, 73.2 mmol) and MEMCl (4.18 mL, 36.6 mmol) at 0 °C. After stirred for 3 h at room temperature, water was added. The mixture was extracted with saturated aqueous  $\text{NaHCO}_3$  (2 x 100 mL), brine (100 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **20** (6.00 g) in 84 % yield as a yellowish oil;  $R_f = 0.40$  (hexane/ethyl acetate = 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.00 (d,  $J = 6.9$  Hz, 3H), 1.07 (s, 9H), 1.65 (s, 3H), 1.83-1.91 (m, 3H), 2.08-2.11 (m, 1H), 2.79-2.89 (m, 5H), 3.39 (s, 3H), 3.56-3.58 (m, 2H), 3.74-3.79 (m, 3H), 4.05 (s, 2H), 4.13-4.16 (dd,  $J_1 = 4.8$  Hz,  $J_2 = 9.7$  Hz, 1H), 4.80 (dd,  $J_1 = 7.0$  Hz,  $J_2 = 12.6$  Hz, 2H), 5.33 (d,  $J = 8.7$  Hz, 1H), 7.37-7.42 (m, 6H), 7.67-7.69 (m, 4H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  13.8, 16.7, 19.2, 25.9, 26.8, 29.7, 30.2, 36.1, 38.3, 43.8, 58.9, 67.5, 68.7, 71.7, 79.4, 95.7, 125.9, 127.5, 129.5, 133.7, 133.7, 134.6, 135.4; HRMS (ESI): calcd for  $\text{C}_{32}\text{H}_{48}\text{NaO}_4\text{S}_2\text{Si}$  [ $\text{M} + \text{Na}^+$ ] 611.26555; found 611.26411.

#### Synthesis of (8S,9S,E)-8-((2-(1-methoxyallyl)-1,3-dithian-2-yl)methyl)-9,11,15,15-tetramethyl-14,14-diphenyl-2,5,7,13-tetraoxa-14-silahexadec-10-ene (**21a** and **21b**)

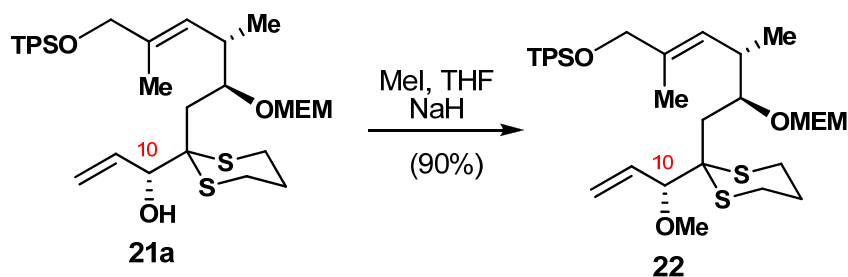


To a solution of dithioketal **20** (5.4 g, 9.17 mmol) in dry THF (60 mL) was slowly added

*n*-BuLi (21 mL, 2.2 M in hexane, 45.85 mmol) at -78 °C, and the mixture was stirred at -20 °C for 2h. After cooling back to -78 °C, DMF (7.2 mL, 91.7 mmol) was slowly added to the above solution, and the formed mixture was warmed up to 0 °C, which was stirred at the same temperature for 2 h. The reaction mixture was quenched with a saturated aqueous solution of NH<sub>4</sub>Cl (25 mL), and the formed mixture was extracted with ethyl acetate (3 x 50 mL), and the combined organic layers was sequentially washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 200 mL) and brine (20 mL), and finally dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 5:1) to give its corresponding aldehyde (6.00 g) in 84 % yield as a yellowish oil; *R*<sub>f</sub> = 0.54 (hexane/ethyl acetate = 2:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.99 (d, *J* = 1.9 Hz, 3H), 1.07 (s, 9H), 1.62 (s, 3H), 1.78-1.86 (m, 2H), 2.07-2.12 (m 2H), 2.53 (dd, *J*<sub>1</sub> = 3.4 Hz, *J*<sub>2</sub> = 10.4 Hz, 1H), 2.60 (dd, *J*<sub>1</sub> = 3.2 Hz, *J*<sub>2</sub> = 11.2 Hz, 1H), 2.68-2.74 (m, 1H), 2.88-2.92 (m, 1H), 3.38 (s, 3H), 3.41-3.47 (m, 1H), 3.50-3.55 (m, 2H), 3.60-3.64 (m, 1H), 3.75-3.80 (m, 2H), 4.05 (s, 2H), 4.70 (dd, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 38.9 Hz, 2H), 5.25 (dd, *J*<sub>1</sub> = 1.2 Hz, *J*<sub>2</sub> = 9.2 Hz, 1H), 7.38-7.43 (m, 6H), 7.68-7.71 (m, 4H), 8.86 (s, 1H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 13.9, 14.4, 19.4, 24.7, 26.6, 26.7, 26.9, 35.1, 38.3, 56.0, 59.0, 67.7, 68.9, 71.8, 96.1, 125.4, 127.7, 129.6, 133.9, 134.0, 136.2, 187.6; HRMS (ESI): calcd for C<sub>33</sub>H<sub>48</sub>NaO<sub>5</sub>S<sub>2</sub>Si [M + Na<sup>+</sup>] 639.26046; found 639.25884.

To a solution of vinylmagnesium bromide (64 mL, 0.7 M in Et<sub>2</sub>O, 45 mmol) was slowly added a solution of the aldehyde made above (5.56 g, 9 mmol) in ethyl ether (25mL) at -78 °C, and the mixture was then warmed up to 0 °C, and stirred at the same temperature for 30 min. The reaction was worked up by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (25 mL), and the mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic layer was sequentially washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 20 mL) and brine (20 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give allylic alcohol as a pair of diastereoisomers (**21a** and **21b**) (4.54 g) in 78 % yield. Spectra data for **21a**, *R*<sub>f</sub> = 0.21 (hexane/ethyl acetate = 15:1): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.01 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 9H), 1.69 (s, 3H), 1.80-1.88 (m, 2H), 1.98-2.06 (m, 2H), 2.62-2.64 (m, 2H), 2.89-2.95 (m, 3H), 3.09 (d, *J* = 1.8 Hz, 1H), 3.39 (s, 3H), 3.56-3.58 (m, 2H), 3.68-3.72 (m, 1H), 3.82-3.86 (m, 1H), 3.95-3.98 (m, 1H), 4.06 (s, 2H), 4.55-4.56 (m, 1H), 4.88 (dd, *J*<sub>1</sub> = 7.1 Hz, *J*<sub>2</sub> = 73.9 Hz, 2H), 5.28-5.34 (m, 2H), 5.44-5.48(m,

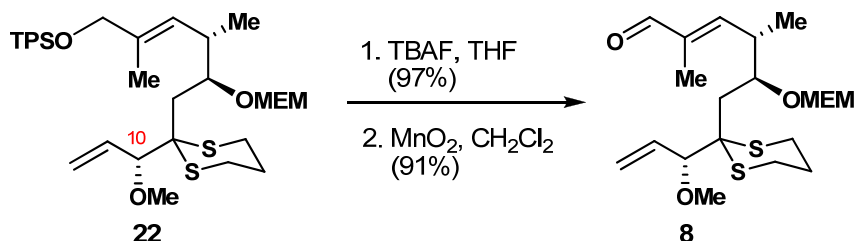
1H), 6.13-6.20 (m, 1H), 7.36-7.42 (m, 6H), 7.68-7.69 (m, 4H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 14.7, 19.3, 24.5, 25.7, 25.8, 26.8, 26.9, 36.4, 36.9, 57.7, 58.9, 67.5, 68.9, 71.8, 73.0, 79.2, 95.9, 117.8, 126.0, 127.6, 129.5, 133.9, 134.5, 135.5, 135.5, 135.6, 135.6; HRMS (ESI): calcd for  $\text{C}_{35}\text{H}_{52}\text{NaO}_5\text{S}_2\text{Si}$  [ $\text{M} + \text{Na}^+$ ] 667.29176; found 667.29029; Spectrum data of compound **21b**,  $R_f$  = 0.17 (hexane/ethyl acetate = 15:1).:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.03 (d,  $J$  = 6.9 Hz, 3H), 1.07 (s, 9H), 1.67 (s, 3H), 1.85-1.90 (m, 2H), 2.10-2.14 (m, 2H), 2.67-2.74 (m, 3H), 2.82-2.85 (m, 1H), 3.00-3.01 (m, 1H), 3.39 (s, 3H), 3.56-3.58 (m, 2H), 3.68 (d,  $J$  = 4.2 Hz, 1H), 3.71-3.75 (m, 1H), 3.80-3.83 (m, 1H), 3.95-3.97 (m, 1H), 4.06 (s, 2H), 4.41-4.43 (m, 1H), 4.89 (dd,  $J_1$  = 7.1 Hz,  $J_2$  = 20.0 Hz, 2H), 5.27-5.30 (m, 1H), 5.36-5.38 (m, 1H), 5.43-5.47 (m, 1H), 6.15-6.22 (m, 1H), 7.36-7.42 (m, 6H), 7.67-7.68 (m, 4H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 14.4, 19.3, 24.8, 25.3, 25.9, 26.8, 26.8, 35.4, 35.6, 57.2, 58.9, 67.9, 68.5, 71.8, 73.9, 79.1, 95.5, 99.9, 125.4, 127.6, 129.5, 133.8, 133.8, 135.1, 135.5, 135.5, 135.9; HRMS (ESI): calcd for  $\text{C}_{35}\text{H}_{52}\text{NaO}_5\text{S}_2\text{Si}$  [ $\text{M} + \text{Na}^+$ ] 667.29176; found 667.29097.



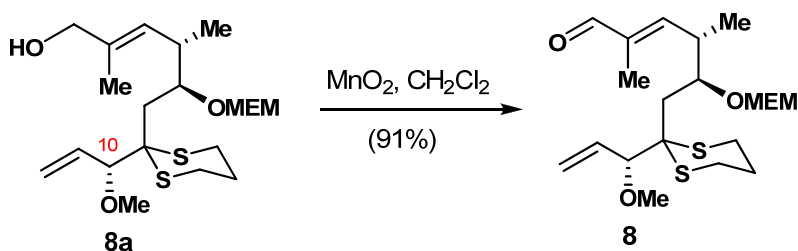
To a solution of **21a** (1.0 g, 1.56 mmol) in THF (8 mL) was slowly added NaH (186 mg, 60 %, 4.65 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h. To this solution was added MeI (0.58 mL, 9.36 mmol) at 0 °C, and the formed mixture was then warmed up to room temperature, and stirred at the same temperature for 8 h. The reaction was quenched by addition of a saturated solution of  $\text{NH}_4\text{Cl}$  (10 mL), and the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed (2 x 5 mL), and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 5:1) to give **22** (0.92 g, 90 %) as a yellowish oil;  $R_f$  = 0.56 (hexane/ethyl acetate = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.01 (d,  $J$  = 6.9 Hz, 3H), 1.07 (s, 9H), 1.69 (s, 3H), 1.86-1.99 (m, 3H), 2.07-2.11 (m, 1H), 2.71-2.78 (m, 2H), 2.90-2.99 (m, 3H), 3.27 (s, 3H), 3.39 (s, 3H), 3.56-3.58 (m, 2H), 3.66-3.70 (m, 1H), 3.83-3.87 (m, 2H), 3.91-3.93 (m, 1H), 4.06 (s, 2H), 4.90 (dd,  $J_1$  = 6.9 Hz,  $J_2$  = 89.0 Hz, 2H), 5.28-5.36 (m, 3H), 5.90-5.97 (m, 1H), 7.36-7.43 (m,

6H), 7.67-7.69 (m, 4H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  13.9, 14.1, 15.0, 19.3, 24.8, 26.6, 26.7, 26.8, 26.9, 36.7, 38.0, 55.4, 57.1, 58.9, 67.4, 69.1, 71.8, 79.6, 89.5, 96.1, 119.9, 126.3, 127.5, 129.5, 133.9, 133.9, 134.1, 135.4, 135.5, 135.6; HRMS (ESI): calcd for  $\text{C}_{36}\text{H}_{54}\text{NaO}_5\text{S}_2\text{Si}$  [ $\text{M} + \text{Na}^+$ ] 681.30741; found 681.30551.

**Synthesis of (4S,5S,E)-6-(2-(1-methoxyallyl)-1,3-dithian-2-yl)-5-((2-methoxyethoxy)methoxy)-2,4-dimethylhex-2-enal (**8**)**



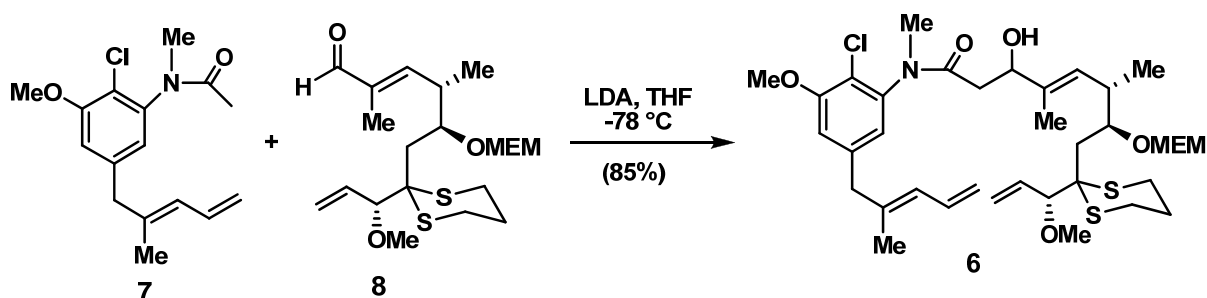
To a solution of **22** (920 mg, 1.40 mmol) in THF (7 mL) was added a solution of TBAF (7 mL, 1M in THF, 7.0 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. The reaction was worked up by addition of water (15 mL), and the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (2 x 5 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 5:1) to give alcohol **8a** (570 mg) in 97 % yield as a oil;  $R_f$  = 0.21 (silica gel, hexane: ethyl acetate = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.01 (d,  $J$  = 6.9 Hz, 3H), 1.48 (s, 1H), 1.75 (d,  $J$  = 1.0 Hz, 3H), 1.88-1.92 (m, 2H), 1.98-2.05 (m, 2H), 2.68-2.76 (m, 2H), 2.88-2.91 (m, 1H), 2.98-3.07 (m, 2H), 3.31 (s, 3H), 3.40 (s, 3H), 3.57-3.59 (m, 2H), 3.65-3.69 (m, 1H), 3.84-3.92 (m, 3H), 4.00-4.01 (m, 2H), 4.78 (d,  $J$  = 6.9 Hz, 1H), 4.97 (d,  $J$  = 6.9 Hz, 1H), 5.29-5.32 (m, 2H), 5.37-5.40 (m, 1H), 5.91-5.98 (m, 1H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  14.2, 15.0, 24.8, 26.8, 26.8, 37.0, 38.4, 55.1, 57.2, 59.0, 67.5, 69.0, 71.9, 79.4, 89.6, 96.2, 119.9, 128.0, 134.2, 136.3; HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{36}\text{NaO}_5\text{S}_2$  [ $\text{M} + \text{Na}^+$ ] 443.18964 found 443.18910.



To a solution of alcohol **8a** (42 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added activated  $\text{MnO}_2$

(210 mg, 500 % base on the weight of SM) at 0 °C, and the mixture was stirred at 0 °C for 2 h. The reaction was worked up by dilution with and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), followed by filtration. The filtrate was concentrated under vacuum to give **8** (38 mg) in 91 % yield; *R<sub>f</sub>* = 0.36 (silica gel, hexane: ethyl acetate = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.12 (d, *J* = 7.3 Hz, 3H), 1.80 (d, *J* = 1.2 Hz, 3H), 1.85-2.03 (m, 4H), 2.66-2.72 (m, 2H), 2.98-3.06 (m, 2H), 3.17-3.20 (m, 1H), 3.27 (s, 3H), 3.37 (s, 3H), 3.55-3.57 (m, 2H), 3.64-3.68 (m, 1H), 3.79-3.86 (m, 2H), 4.00-4.02 (m, 1H), 4.77 (d, *J* = 7.1 Hz, 1H), 4.98 (d, *J* = 7.1 Hz, 1H), 5.27 (dd, *J<sub>1</sub>* = 0.65 Hz, *J<sub>2</sub>* = 17.3 Hz, 1H), 5.35 (dd, *J<sub>1</sub>* = 1.3 Hz, *J<sub>2</sub>* = 10.4 Hz, 1H), 5.86-5.93 (m, 1H), 6.42-6.44 (dd, *J<sub>1</sub>* = 1.3 Hz, *J<sub>2</sub>* = 9.7 Hz, 1H), 9.40 (s, 1H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 9.5, 15.0, 24.5, 26.7, 26.8, 39.0, 39.3, 54.3, 57.2, 58.9, 67.6, 71.8, 78.5, 89.5, 96.2, 120.0, 133.9, 139.8, 155.5, 195.4; HRMS (ESI): calcd for C<sub>20</sub>H<sub>34</sub>NaO<sub>5</sub>S<sub>2</sub> [*M* + Na<sup>+</sup>] 441.17399; found 441.17338.

**Synthesis of (6*S*,7*S*,*E*)-*N*-(2-chloro-3-methoxy-5-((*E*)-2-methylpenta-2,4-dienyl)phenyl)-3-hydroxy-8-(2-(1-methoxyallyl)-1,3-dithian-2-yl)-7-((2-methoxyethoxy)methoxy)-*N*,4,6-trimethyl-4-enamide (**6**)**

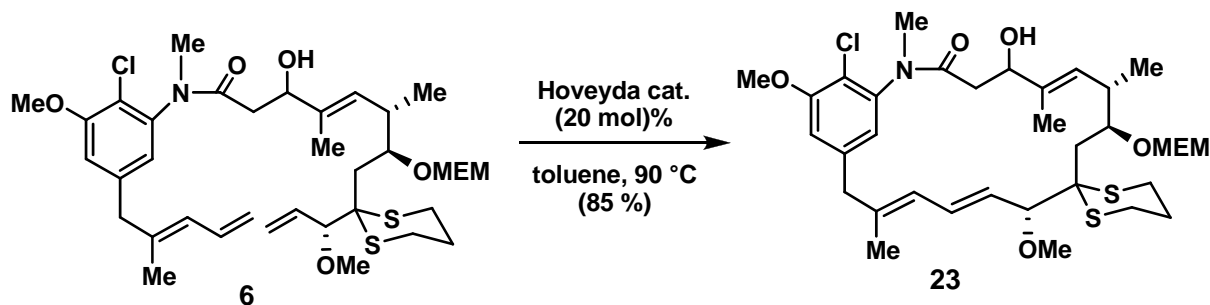


To a solution of *i*-Pr<sub>2</sub>NH (0.021 mL, 0.15 mmol) in THF (0.5 mL) was added *n*-BuLi (0.064 mL, 2.2 M in hexane, 0.14 mmol) at -78 °C, and the mixture was warm up to 0 °C, then stirred at the same temperature for 30 min. To this solution was added a solution of amide **7** (35.3 mg, 0.12 mmol) in THF (0.3 mL) at -78 °C, and the mixture was stirred at the same temperature for 1 h. To this solution was added a solution of aldehyde **7** (42 mg, 0.1 mmol) in THF (0.5 mL) at -78 °C, and the formed mixture was stirred at the same temperature for 3 h. The reaction was quenched by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (1 mL), and the mixture was then warmed up to room temperature, and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were sequentially washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 3 mL) and brine (3 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified



by a flash column chromatography on silica gel (hexane/ethyl acetate = 3:1) to give product **4** (60 mg) in 85 % yield as a oil;  $R_f$  = 0.31 (hexane/ethyl acetate = 3:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.93-0.99 (m, 3H), 1.54 (s, 2H), 1.66-1.70 (m, 5H), 1.77-2.27 (m, 7H), 2.55-2.95 (m, 5H), 3.19 (s, 3H), 3.26-3.28 (m, 3H), 3.35-3.37 (m, 5H), 3.53-3.55 (m, 2H), 3.61-3.67 (m, 1H), 3.79-3.82 (m, 3H), 3.91-3.92 (m, 3H), 4.31-4.42 (m, 1H), 4.72-4.75 (m, 1H), 4.88-4.93 (m, 1H), 5.09-5.11 (m, 1H), 5.17-5.33 (m, 4H), 5.88-5.96 (m, 2H), 6.54-6.61 (m, 1H), 6.69-6.77 (m, 2H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 14.5, 14.5, 16.4, 16.4, 22.6, 24.8, 24.9, 26.7, 26.7, 28.8, 29.7, 35.5, 35.6, 35.6, 36.4, 38.0, 38.9, 45.9, 55.4, 56.4, 56.4, 56.5, 56.9, 57.1, 58.9, 67.4, 71.9, 73.0, 73.2, 73.4, 73.5, 79.3, 79.3, 79.4, 79.5, 89.4, 89.7, 90.1, 95.9, 96.0, 96.1, 112.4, 112.5, 116.6, 119.1, 119.3, 119.8, 119.9, 120.1, 121.3, 121.8, 127.4, 127.6, 127.7, 128.2, 128.2, 132.8, 134.2, 134.2, 134.3, 136.5, 136.6, 136.9, 137.1, 140.6, 140.7, 141.5, 141.6, 156.3, 156.3, 172.6, 172.8; HRMS (ESI): calcd for  $\text{C}_{36}\text{H}_{54}\text{ClNNaO}_7\text{S}_2$   $[\text{M} + \text{Na}^+]$  734.29224; found 734.29301.

**Synthesis of (6S,7S,E)-N-(2-chloro-3-methoxy-5-((E)-2-methylpenta-2,4-dienyl)phenyl)-3-hydroxy-8-(2-(1-methoxyallyl)-1,3-dithian-2-yl)-7-((2-methoxyethoxy)methoxy)-N,4,6-trimethyl-4-enamide (**23**)**

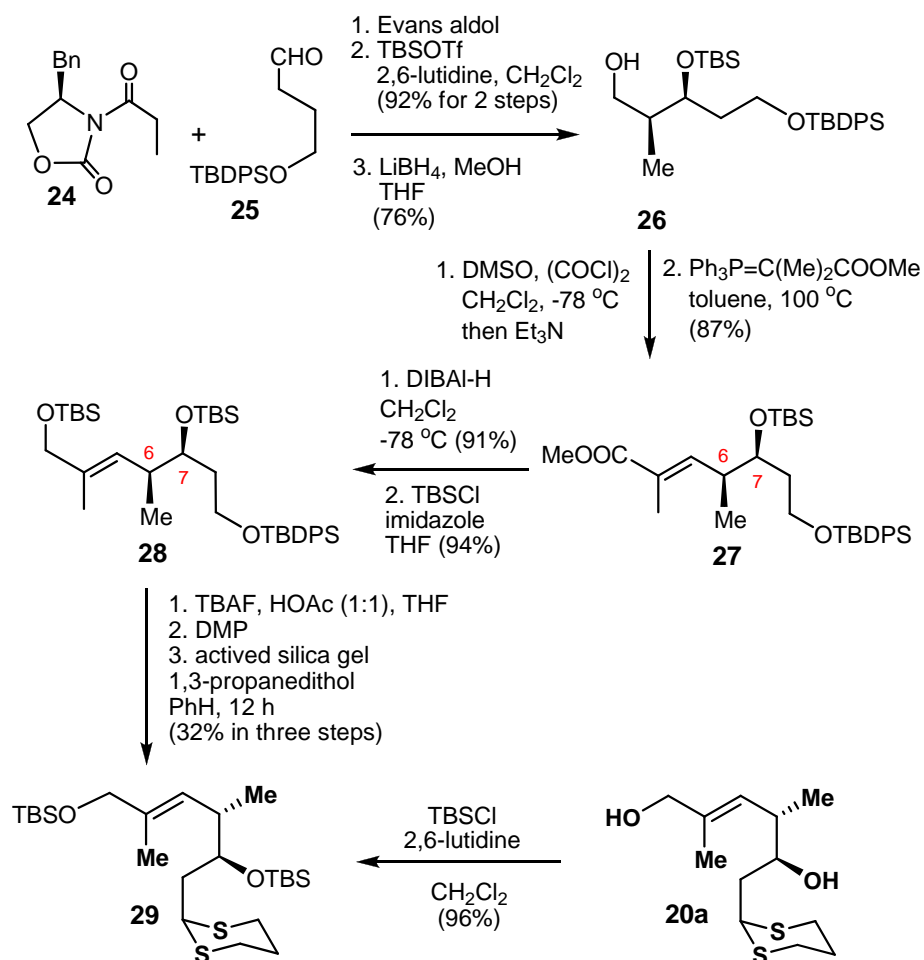


To a solution of **6** (60 mg, 0.084 mmol) in toluene (170 mL) was added Hoveyda catalyst (10.6 mg, 0.017 mmol), and the reaction mixture was stirred at 90 °C for 4 h under nitrogen atmosphere. After cooling to room temperature, the mixture was filtrated, and the filtrate was concentrated under vacuum. The residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 5:1 to 1:1) to give **23** (49 mg) in 85 %;  $R_f$  = 0.26 (hexane/ethyl acetate = 2:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02-1.06 (m, 3H), 1.25-1.28 (m, 3H), 1.43-1.71 (m, 5H), 1.81-1.85 (m, 2H), 1.92 (s, 3H), 2.02-2.06 (m, 1H), 2.28-2.35 (m, 1H), 2.56-2.70 (m, 2H), 2.87-2.88 (m, 1H), 3.19-3.22 (m, 5H), 3.26 (d,  $J$  = 1.6 Hz, 3H), 3.32 (s, 2H), 3.37-3.39 (m, 4H), 3.53-3.57 (m, 3H), 3.67-3.70 (m, 1H), 3.76-3.83 (m, 2H), 3.92-3.97 (m, 4H), 4.03-4.04 (m, 1H), 4.17-4.32 (m, 1H),

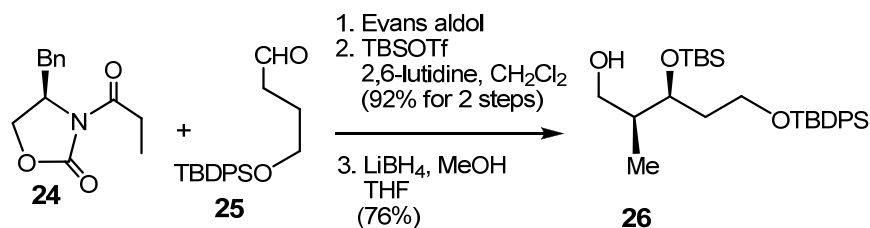


Na<sup>+</sup>] 688.25038; found 688.25027.

**Evans' classical approach applied to the confirmation of C-6 and C-7 *syn*-selectivity of the TiCl<sub>4</sub>-mediated vinylogous Mukaiyama aldol reaction.**

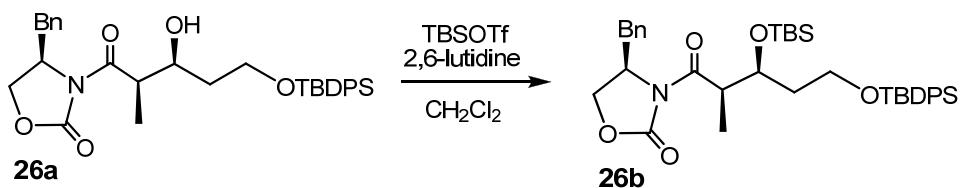


**Synthesis (2S,3S)-3-(tert-butyldimethylsilyloxy)-5-(tert-butyldiphenylsilyloxy)-2-methylpentan-1-ol (**26**)**

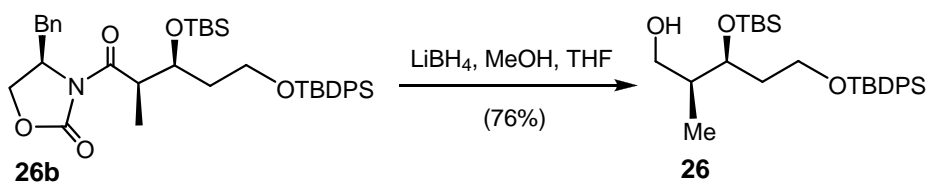


To a solution of **24** (4.7 g, 20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added *n*-Bu<sub>2</sub>BOTf (23.5 mL, 1M in CH<sub>2</sub>Cl<sub>2</sub>, 23.5 mmol) and dry Et<sub>3</sub>N (3.67 mL, 26.3 mmol) at 0 °C, and the mixture was cooled to -78 °C. To this solution was added a solution of aldehyde **25** (6.9 g, 22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (66 mL), and the mixture was first stirred at -78 °C for 3 h, and then at 0 °C for an additional hour. The reaction was quenched by addition of aqueous phosphate buffer solution (pH 7, 22 mL), followed by addition of methanol (66 mL). To this cloudy solution was added by a methanol-30% aqueous

hydrogen peroxide solution (2: 1, 66 mL) by syringe and the addition speed was controlled at such a rate to keep the internal temperature below +10° C. After addition, the reaction mixture was stirred for an additional 1 hr, and the volatile material was removed under vacuum, and the water bath temperature was controlled between 25–30 °C. The resulting slurry was extracted with diethyl ether (3 x 150 ml), and the combined organic extracts were sequentially washed with aqueous solution of sodium bicarbonate (5%, 50 mL) and brine (50 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 6:1) to give colorless oil. *R*<sub>f</sub> = 0.15 (hexane/ethyl acetate = 8:1).

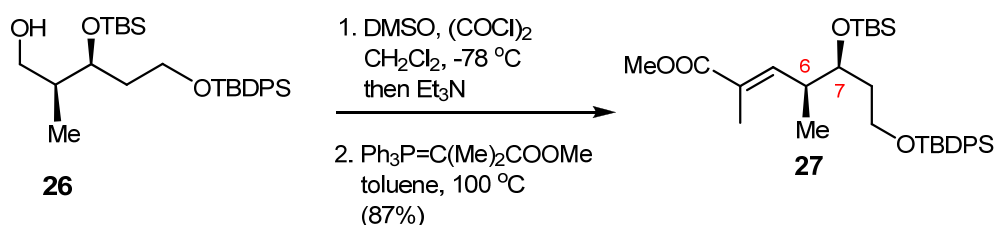


To a solution of **26a** in CH<sub>2</sub>Cl<sub>2</sub> (90 mL) was sequentially added 2,6-lutidine (2.9 mL, 25 mmol) and TBSOTf (4.6 mL, 20 mmol) at 0 °C, and the mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (20 mL), and then extracted with ethyl acetate (3 x 25 mL). The combined organic layers was sequentially washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 20 mL) and brine 20 mL), and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 15:1) to give **26b** (12.2 g) in 92 % yield for two steps); *R*<sub>f</sub> = 0.74 (hexane/ethy acetate = 4:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.03 (s, 3H), 0.04 (s, 3H), 0.89 (s, 9H), 1.10 (s, 9H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.83-1.96 (m, 2H), 2.80 (dd, *J*<sub>1</sub> = 9.7 Hz, *J*<sub>2</sub> = 13.4 Hz, 1H), 3.31 (dd, *J*<sub>1</sub> = 3.0 Hz, *J*<sub>2</sub> = 13.4 Hz, 1H), 3.38 (t, *J* = 6.4 Hz, 2H), 3.92-3.96 (m, 1H), 4.07-4.11 (m, 1H), 4.16-4.20 (m, 1H), 4.58-4.61 (m, 1H), 7.24-7.27 (m, 2H), 7.29-7.32 (m, 1H), 7.35-7.37 (m, 2H), 7.38-7.46 (m, 6H), 7.71-7.73 (m, 4H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ -4.8, -4.4, 12.1, 18.0, 19.1, 25.8, 26.9, 37.6, 38.2, 43.3, 55.7, 60.6, 65.9, 70.5, 127.3, 127.6, 128.9, 129.4, 129.5, 133.9, 135.4, 135.5, 135.6, 152.9, 175.0; HRMS (ESI): calcd for C<sub>38</sub>H<sub>53</sub>NNaO<sub>5</sub>Si<sub>2</sub> [*M* + Na<sup>+</sup>] 682.33545; found 682.33279.



To a solution of **26b** (11.89 g, 18 mmol) in dry THF (90 mL) was sequentially added methanol (3.6 mL, 90 mmol) and a solution of LiBH<sub>4</sub> (1.99 g, 90 mmol) in THF (45 mL) at 0 °C, and the mixture was stirred for at 0 °C for 5 hours. The reaction was quenched by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (25 mL), and the formed mixture was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were sequentially washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 30 mL) and brine (30 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = (10:1) to give **26** (6.7 g) in 76 % yield; R<sub>f</sub> = 0.28 (hexane/ethyl acetate = 4:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.05 (s, 3H), 0.12 (s, 3H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 1.09 (s, 9H), 1.72-1.76 (m, 2H), 1.96-2.00 (m, 1H), 2.63 (d, *J* = 2.8 Hz, 1H), 3.50-3.55 (m, 1H), 3.68 (t, *J* = 8.6 Hz, 1H), 3.72-3.78 (m, 2H), 4.03-4.06 (m, 1H), 7.38-7.46 (m, 6H), 7.67-7.70 (m, 4H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ -4.6, -4.5, 12.0, 17.9, 19.2, 25.8, 26.9, 35.3, 39.8, 60.9, 65.9, 72.4, 127.6, 129.6, 129.6, 133.9, 135.6, 135.6; HRMS (ESI): calcd for C<sub>28</sub>H<sub>46</sub>NaO<sub>3</sub>Si<sub>2</sub> [M + Na<sup>+</sup>] 509.28777; found 509.28633.

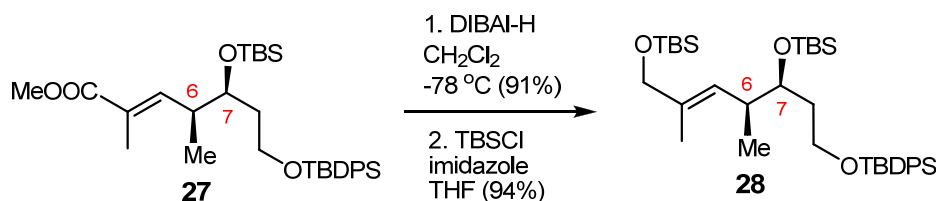
**Synthesis of (4S,5S,E)-methyl 5-(tert-butyldimethylsilyloxy)-7-(tert-butyldiphenylsilyloxy)-2,4-dimethylhept-2-enoate (**27**)**



To a solution of DMSO (2.8 mL, 40 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 mL) was slowly added (COCl)<sub>2</sub> (3.44 mL, 40 mmol) at -78 °C, and the mixture was stirred at the same temperature for 15 min. To this solution was added alcohol **26** (9.7 g, 20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at -78 °C, and the mixture was stirred at the same temperature for 30 min. To this solution was added Et<sub>3</sub>N (11.2 mL, 80 mmol) and the mixture was stirred for 30 min. and then warmed up to 0 °C, and the mixture was stirred at the same temperature for 1 h. The reaction was quenched by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (50 mL), and the mixture was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were sequentially washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2 x 30 mL) and brine (30 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was utilized in the next step without further purification.

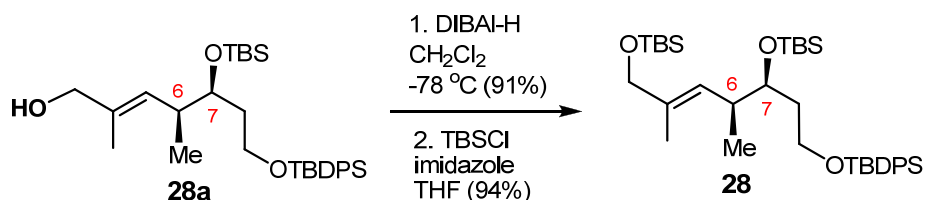
To a solution of the crude product made above in toluene (100 mL) was Wittig reagent (20.9 g, 60 mmol) at 20 °C, and the reaction mixture was warmed up to 100 °C, and stirred at the same temperature for 8 h under nitrogen atmosphere. After cooling to the room temperature, the reaction mixture was mixed with a solution of hexane and ethyl acetate (100 mL, 10:1), and the formed precipitate was filtered off, and the filtrate was concentrated under vacuum. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 60:1) to give **27** (8.649 g) in 87 % yield;  $R_f$  = 0.28 (hexane/ethyl acetate = 60:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.03 (s, 3H), 0.06 (s, 3H), 0.89 (s, 9H), 0.98 (d,  $J$  = 6.8 Hz, 3H), 1.07 (s, 9H), 1.69-1.78 (m, 2H), 1.83 (d,  $J$  = 1.1 Hz, 3H), 2.60-2.64 (m, 1H), 3.66-3.80 (m, 5H), 3.84-3.88 (m, 1H), 6.73 (dd,  $J_1$  = 1.2 Hz,  $J_2$  = 10.1 Hz, 1H), 7.37-7.45 (m, 6H), 7.66-7.69 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.6, -4.4, 12.6, 14.5, 18.1, 19.1, 25.9, 26.9, 37.8, 38.5, 51.6, 60.7, 72.3, 126.6, 127.6, 127.7, 129.6, 129.6, 133.9, 133.9, 134.8, 135.5, 145.6, 168.7; HRMS (ESI): calcd for  $\text{C}_{32}\text{H}_{50}\text{NaO}_4\text{Si}_2$  [ $\text{M} + \text{Na}^+$ ] 577.31398 found 577.31244.

**Synthesis of (8S,9S,E)-9-(tert-butyldimethylsilyloxy)-2,2,3,3,6,8,14,14-octamethyl-13,13-diphenyl-4,12-dioxa-3,13-disilapentadec-6-ene (28)**



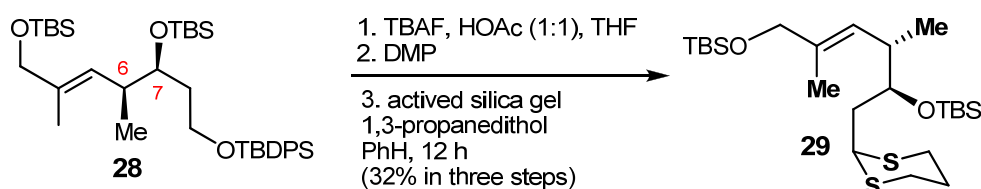
To a solution of methyl ester **27** (7.2 g, 13.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (65 mL) was added DIBAL-H (32.5 mL, 1M in diethyl ether, 32.5 mmol) at  $-78^\circ\text{C}$ , and the mixture was stirred at the same temperature for 2 h. After warming up to room temperature, the reaction was quenched by careful addition of a solution of a saturated aqueous sodium-potassium tartrate (150 mL) with vigorous stirring, and the mixture was stirred until the organic phase was transparent. After separation of the organic layer, the water phase was extracted with ethyl acetate (3 x 50 mL), and the combined organic layers were washed with brine (2 x 25 mL), and finally dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **28a** (6.24 g) in 91 % in yield;  $R_f$  = 0.29 (hexane/ethyl acetate = 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.06 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 0.95 (d,  $J$  = 6.8 Hz, 3H), 1.10 (s, 9H), 1.51 (s, 1H), 1.66 (d,  $J$  = 0.9 Hz, 3H), 1.71-1.84 (m, 2H), 2.50-2.54 (m,

1H), 3.75-3.80 (m, 3H), 4.00 (s, 2H), 5.35 (d,  $J = 8.7$  Hz, 1H), 7.39-7.47 (m, 6H), 7.70-7.72 (m, 4H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  -4.4, -4.4, 13.8, 15.8, 18.1, 19.1, 25.9, 26.9, 37.5, 37.7, 60.9, 69.0, 73.1, 127.6, 129.5, 129.7, 134.0, 134.0, 135.5; HRMS (ESI): calcd for  $\text{C}_{31}\text{H}_{50}\text{NaO}_3\text{Si}_2$  [ $\text{M} + \text{Na}^+$ ] 549.31907; found 549.31796.



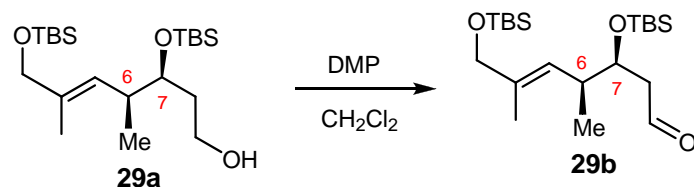
To a solution of alcohol **28a** (5.3 g, 10 mmol) and imidazole (1.36 g, 20 mmol) in THF (50 mL) was added TBSCl (2.23 g, 15 mmol) at 0 °C, and the reaction mixture was stirred at the same temperature for 2 h. The reaction was quenched by addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (25 mL), and the mixture was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with brine (2 x 15 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 100:1) to give **28** (6.03 g) in 94 % yield;  $R_f = 0.37$  (silica gel, hexane/ethyl acetate = 100:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.01 (s, 3H), 0.05 (s, 3H), 0.09 (s, 6H), 0.87 (s, 9H), 0.92 (d,  $J = 6.8$  Hz, 3H), 0.94 (s, 9H), 1.07 (s, 9H), 1.59 (s, 3H), 1.68-1.82 (m, 2H), 2.45-2.52 (m, 1H), 3.70-3.78 (m, 3H), 4.01 (s, 2H), 5.31 (d,  $J = 9.4$  Hz, 1H), 7.38-7.45 (m, 6H), 7.67-7.70 (m, 4H);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.2, -5.2, -4.4, 13.7, 15.8, 18.1, 18.4, 19.2, 26.0, 26.0, 26.9, 37.4, 37.7, 61.0, 68.8, 73.3, 127.6, 128.2, 129.5, 133.7, 134.1, 135.6; HRMS (ESI): calcd for  $\text{C}_{37}\text{H}_{64}\text{NaO}_3\text{Si}_3$  [ $\text{M} + \text{Na}^+$ ] 663.40555; found 663.40463.

### Synthesis of (8*S*,9*S*,*E*)-9-((1,3-dithian-2-yl)methyl)-2,2,3,3,6,8,11,11,12,12-decamethyl-4,10-dioxo-3,11-disilatridec-6-ene (**29**)



To a solution of **28** (2.2 g, 3.43 mmol) in THF (31 mL) was added a solution of TBAF/HOAc (1:1) in THF (1M, 3.43 mL), and the formed mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of a saturated aqueous solution of  $\text{NaHCO}_3$  (10 mL), and the mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic extracts were washed

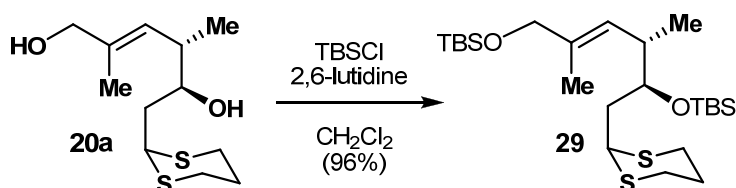
with brine (2 x 10 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 12:1) to give the primary alcohol **29a** (830 mg) in 60 %; *R<sub>f</sub>* = 0.30 (hexane/ethyl acetate = 8:1).



To a solution of **29a** (2.42 g, 6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added Dess-Martin reagent (4.32 g, 10.2 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was worked up by addition of diethyl ether (100 mL), and the formed precipitate was filtered off. The filtration was concentrated under vacuum, and the residue **29b** was utilized in the next step without purification.

To a solution of **29b** made above in benzene (50 mL) was added 1,3-propanedithiol (0.66 mL, 6 mmol) and SiO<sub>2</sub>-SOCl<sub>2</sub> (1.2 g) at room temperature, and the mixture was stirred at the same temperature for 12 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NaHCO<sub>3</sub> (15 mL), and the mixture was sequentially washed with a saturated aqueous solution of NH<sub>4</sub>Cl (2 x 25 mL) and brine (20 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 80:1) to give **29** (1.6 g, 54 %; *R<sub>f</sub>* = 0.70 (hexane/ethyl acetate = 30:1). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.01-0.08 (m, 12H), 0.86-0.90 (m, 21H), 1.58 (d, *J* = 1.5 Hz, 3H), 1.75-1.90 (m, 3H), 2.04-2.11 (m, 1H), 2.44-2.51 (m, 1H), 2.74-2.90 (m, 4H), 3.77-3.83 (m, 1H), 3.96 (s, 2H), 4.04 (dd, *J<sub>1</sub>* = 6.3 Hz, *J<sub>2</sub>* = 8.7 Hz, 1H), 5.26 (dd, *J<sub>1</sub>* = 1.5 Hz, *J<sub>2</sub>* = 8.4 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -5.3, -5.2, -4.3, -4.2, 1.0, 13.8, 15.8, 18.2, 18.4, 25.9, 26.0, 26.0, 30.1, 30.6, 37.7, 40.6, 44.2, 68.6, 72.5, 127.3, 134.2; HRMS (ESI): calcd for C<sub>24</sub>H<sub>50</sub>NaO<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> [*M* + Na<sup>+</sup>] 513.26830; found 513.26746.

#### Synthesis of (8*S*,9*S*,*E*)-9-((1,3-dithian-2-yl)methyl)-2,2,3,3,6,8,11,11,12,12-decamethyl-4,10-dioxo-3,11-disilatridec-6-ene (**29**) from **20a**





To a solution of diol **20a** (2.45 g, 9.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (45 mL) was added 2,6-lutidine (6.16 mL, 53 mmol) and TBSOTf (12.2 mL, 53 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. The reaction was worked up by addition of a saturated aqueous solution of NH<sub>4</sub>Cl (15 mL), and the mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were sequentially washed with a saturated aqueous NaHCO<sub>3</sub> (2 x 15 mL) and brine (15 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 200:1) to give **28** (4.39 g) in 96 % yield; *R<sub>f</sub>* = 0.30 (hexane/ethyl acetate = 200:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.07 (m, 12H), 0.89 (s, 18H), 0.90 (d, *J* = 8.1 Hz, 3H), 1.60 (s, 3H), 1.84 (m, 3H), 2.10 (d, *J* = 14 Hz, 1H), 2.50 (m, 1H), 2.81 (m, 4H), 3.82 (m, 1H), 3.84 (s, 2H), 4.06 (dd, *J* = 5.9, 8.7 Hz, 1H), 5.28 (d, *J* = 9.5 Hz, 1H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ -5.2, -5.2, -4.2, -4.2, 13.8, 15.8, 18.2, 18.4, 26.0, 26.0, 30.1, 30.6, 37.7, 40.7, 44.2, 68.7, 72.7, 127.4, 134.3; HRMS (ESI): calcd for C<sub>24</sub>H<sub>50</sub>NaO<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> [M + Na<sup>+</sup>] 513.26830; found 513.26746.