Supporting Information

Experimental Section

Materials and Methods. Reactions were carried out under a nitrogen atmosphere using dry glassware which had been flame-dried under a stream of nitrogen. All solvents were reagent grade. Anhydrous ether (J.T.Baker) and THF (Aldrich) were purchased and used directly without further distillation. Reactions were monitored by thin-layer chromatography using precoated silica gel plates (0.25 mm) with a fluorescent indicator (E. Merck). Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution, anisaldehyde, or ninhydrin stain followed by charring with a heat gun. ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform solutions with a Varian 300 spectrometer at ambient temperature. Chemical shifts are reported as δ values relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 283 B spectrometer. Microanalyses were performed by Robertson Labs, Madison, NJ.

Dithiane 5. To a solution of 1,3-dithiane (4.8 g, 39.9 mmol) in THF (80 mL) at -78 ^{o}C was added n-BuLi (17.5 mL of a 2.5 M solution in hexane, 43.7 mmol). The solution was maintained for 30 min at -78 ^{o}C and for 2 h at -23 ^{o}C. Then, the solution was cooled to -78 ^{o}C, and 2-(4-chlorobutoxy)tetrahydro-2*H*-pyran (8.45 g, 43.9 mmol) was added. The reaction mixture was stirred for 2 h at -78 ^{o}C, allowed to warm to room temperature, and maintained overnight. The mixture was quenched with saturated NH_4Cl (100 mL), and the aqueous layer was separated and extracted with ethyl acetate (2 x 50 mL). The combined organic solution was dried over $MgSO_4$ and concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (30:1 hexane-EtOAc) to afford 9.4 g (85%) of mono-alkylated dithiane **5** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51-1.92 (m, 13H), 2.08-2.16 (m, 1H), 2.78-2.93 (m, 4H), 3.38 (m, 1H), 3.49 (m, 1H), 3.74 (m, 1H), 3.85 (m, 1H), 4.05 (t, *J* = 6.9 Hz, 1H), 4.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 98.5, 66.9, 61.9, 47.2, 35.0, 30.5, 30.2, 29.1, 25.8, 25.2, 23.2, 19.4. Anal. Calcd for $C_{13}H_{24}O_2S_2$: C, 56.48; H, 8.75; S, 23.20. Found: C, 56.51; H, 8.66; S, 23.33.

Olefin 7. To a solution of **5** (8.2 g, 29.7 mmol) in THF (120 mL) at -78 ^{o}C was added n-BuLi (13.0 mL of a 2.5 M solution in hexane, 32.5 mmol). The solution was maintained for 30 min at -78 ^{o}C and for 2 h at -23 ^{o}C. Then, the solution was cooled to -78 ^{o}C, and HMPA (11 mL, 63.2 mmol) was added. After 30 min, *cis*-6-iodo-2-hexene (6.9 g, 32.8 mmol) was added, and the mixture was stirred for 2 h at -78 ^{o}C, allowed to warm to room temperature, and maintained overnight. The mixture was quenched with saturated NH_4Cl (200 mL), and the aqueous layer was separated and extracted with ethyl acetate (2 x 100 mL). The combined organic solution was washed with brine (100 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30:1 hexane-EtOAc) to afford 9.3 g (87%) of di-alkylated dithiane **7** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47-1.98 (m, 21H), 2.06 (q, J = 7.2 Hz, 2H), 2.80 (t, J = 6.0 Hz, 4H), 3.40 (dt, J = 9.6, 6.6 Hz, 1H), 3.50 (m, 1H), 3.76 (dt, J = 9.6, 6.6 Hz, 1H), 3.87 (m, 1H), 4.58 (m, 1H), 5.33-5.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.9, 124.3, 98.7, 67.1, 62.1, 53.1, 37.9, 37.5, 30.6, 29.7, 26.6, 25.9, 25.4, 25.3, 23.8, 20.7, 19.5, 12.7. Anal. Calcd for $C_{19}H_{34}O_2S_2$: C, 63.64; H, 9.55; S, 17.88. Found: C, 63.73; H, 9.69; S, 17.67.

Hydrolysis of dithiane in 7. To a mixture of N-chlorosuccinimide (9.7 g, 72.6 mmol) and silver nitrate (13.9 g, 81.8 mmol) in acetonirile (360 mL) and H_2O (90 mL) at room temperature was added dithiane **7** (6.5 g, 18.2 mmol) in CH_3CN (90 mL). After 15 min, the mixture was quenched by succesive addition of saturated $Na_2S_2O_4$ (90 mL), saturated Na_2CO_3 (90 mL), and saturated NaCl (90 mL). The aqueous layer was separated and extracted with methylene chloride (3 x 200 mL), and the combined organic solution was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (20:1 hexane-EtOAc) to afford 4.4 g (90%) of ketone as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52-1.83 (m, 15H), 2.04 (q, J = 7.2 Hz, 2H), 2.38-2.46 (m, 4H), 3.38 (dt, J = 9.9, 6.0 Hz, 1H), 3.50 (m, 1H), 3.74 (dt, J = 9.6, 6.3 Hz, 1H), 3.86 (m, 1H), 4.57 (m, 1H), 5.32-5.51(m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 129.5, 124.6, 98.7, 67.1, 62.2, 42.4, 41.9, 30.6, 29.2, 26.1, 25.4, 23.4, 20.6, 19.5, 12.7. Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found: C, 71.69; H, 10.53.

Oxime 8. To a mixture of ketone prepared above (2.95 g, 11.0 mmol) and hydroxylamine hydrochloride (0.92 g, 13.2 mmol) in CH_3CN (50 mL) and H_2O (5 mL) at room temperature was added sodium acetate (1.35 g, 16.4 mmol). After being stirred for 3 h, the reaction mixture was diluted with methylene chloride (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (2:1 hexane-EtOAc) to afford 3.1 g (99%) of oxime **8** as a ~1:1 mixture of E and Z isomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55-1.82 (m, 15H), 2.07 (m, 2H), 2.20 (m, 2H), 2.36 (m, 2H), 3.40 (m, 1H), 3.50 (m, 1H), 3.75 (m, 1H), 3.85 (m, 1H), 4.59 (m, 1H), 5.42 (m, 2H), 8.72 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 129.7, 129.6, 124.5, 124.4, 98.7, 98.6, 67.0, 66.9, 62.2, 62.1, 33.8, 33.5, 30.7, 30.6, 29.8, 29.3, 27.3, 27.2, 26.9, 26.3, 26.0, 25.4, 22.9, 22.3, 19.5, 19.4, 12.7. Anal. Calcd for $C_{16}H_{29}NO_3$: C, 67.81; H, 10.31; N, 4.94. Found: C, 67.68; H, 10.26; N, 4.92.

Benzyl ester 10. A solution of oxime **8** (6.58 g, 23.3 mmol) and benzyl acrylate (3.82 g, 23.6 mmol) in xylene (100 mL) was maintained for 24 h at 140 ^{o}C. The solution was cooled to room temperature and purified by flash chromatography on silica gel (10:1 hexane-EtOAc) to afford 9.5 g (92%) of benzyl ester **10** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, J = 6.6 Hz, 3H), 1.26-1.90 (m, 18H), 2.43 (q, J = 6.9 Hz, 1H), 2.67 (t, J = 6.9 Hz, 2H), 2.93 (t, J = 6.9 Hz, 2H), 3.37 (m, 1H), 3.49 (m, 1H), 3.73 (m, 1H), 3.86 (m, 1H), 3.94 (quintet, J = 6.6 Hz, 1H), 4.56 (m, 1H), 5.11 (d, J = 12.3 Hz, 1H), 5.13 (d, J = 12.3 Hz, 1H), 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 136.0, 128.4, 128.0, 127.9, 98.8, 77.7, 74.3, 67.5, 67.4, 65.9, 62.2, 54.9, 54.8, 46.4, 37.5, 37.4, 34.2, 32.1, 30.7, 30.3, 30.2, 26.8, 26.4, 25.4, 21.3, 21.2, 19.6, 13.4. Anal. Calcd for $C_{26}H_{39}NO_5$: C, 70.08; H, 8.82; N, 3.14. Found: C, 70.06; H, 8.96; N, 3.01.

Hydrolysis of THP group in 10. To a solution of THP ether **10** (4.15 g, 9.32 mmol) in methyl alcohol (200 mL) at room temperature as added *p*-toluenesulfonic acid monohydrate (1.95 g, 10.3 mmol). After 2 h, triethylamine (2.9 mL, 20.8 mmol) was added, the solution was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (2:1 hexane-EtOAc) to afford 3.1 g (93%) of alcohol as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, J = 6.0 Hz, 3H), 1.23-1.72 (m, 11H),

1.84 (m, 1H), 2.12 (br s, 1H), 2.43 (q, *J* = 6.9 Hz, 1H), 2.56-2.77 (m, 2H), 2.88-2.98 (m, 2H), 3.61 (t, *J* = 5.1 Hz, 2H), 3.93 (quintet, *J* = 6.6 Hz, 1H), 5.11 (d, *J* = 12.6 Hz, 1H), 5.12 (d, *J* = 12.6 Hz, 1H), 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 136.0, 128.4, 128.0, 127.9, 77.7, 74.4, 66.0, 62.2, 54.8, 46.3, 37.1, 33.9, 33.0, 32.2, 26.8, 26.4, 20.3, 13.3. Anal. Calcd for $C_{21}H_{31}NO_4$: C, 69.78; H, 8.64; N, 3.87. Found: C, 69.30; H, 8.71; N, 3.68.

Aldehyde 11. To a solution of oxalyl chloride (1.53 mL, 17.5 mmol) in methylene chloride (45 mL) at -55 ^{o}C was added dimethyl sulfoxide (2.5 mL, 35.2 mmol). After 3 min, a solution of alcohol prepared above (5.71 g, 15.8 mmol) in methylene chloride (18 mL) was added, the solution was maintained for 15 min at -55 ^{o}C, and then triethylamine (11 mL, 78.9 mmol) was added. After 5 min, the resultant mixture was allowed to warm to room temperature and quenched with water (150 mL). The aqueous layer was separated and extracted with methylene chloride (2 x 100 mL). The combined extracts were washed with brine (150 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (3:1 hexane-EtOAc) to afford 5.5 g (97%) of aldehyde **11** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.6 Hz, 3H), 1.18-1.90 (m, 10H), 2.38 (t, *J* = 6.9 Hz, 2H), 2.45 (q, *J* = 6.9 Hz, 1H), 2.59-2.76 (m, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 3.93 (quintet, *J* = 6.6 Hz, 1H), 5.11 (d, *J* = 12.3 Hz, 1H), 5.13 (d, *J* = 12.3 Hz, 1H), 7.35 (m, 5H), 9.72 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 172.5, 136.1, 128.4, 128.0, 127.9, 77.4, 74.4, 65.9, 54.6, 46.2, 44.2, 36.8, 34.0, 32.8, 26.8, 26.3, 17.1, 13.3. Anal. Calcd for $C_{21}H_{29}NO_4$: C, 70.16; H, 8.13; N, 3.89. Found: C, 70.03; H, 8.12; N, 3.81.

Enonate 12. To a solution of methyl (triphenylphosphoranylidene)acetate (3.25 g, 9.72 mmol) in methylene chloride (65 mL) at room temperature was a solution of aldehyde **11** (3.25 g, 9.05 mmol) in methylene chloride (45 mL). After being stirred for 18 h, the solution was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (5:1 hexane-EtOAc) to afford 3.5 g (93%) of enonate **12** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.0 Hz, 3H), 1.18-1.88 (m, 10H), 2.16 (m, 2H), 2.40 (q, *J* = 6.9 Hz, 1H), 2.67 (m, 2H), 2.92 (t, *J* = 6.9 Hz, 2H), 3.71

(s, 3H), 3.92 (quintet, J = 6.6 Hz, 1H), 5.11 (d, J = 12.3 Hz, 1H), 5.13 (d, J = 12.3 Hz, 1H), 5.82 (d, J = 15.6 Hz, 1H), 6.95 (dt, J = 15.6, 6.9 Hz, 1H), 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 167.0, 149.3, 136.1, 128.4, 127.9, 120.9, 77.5, 74.4, 65.9, 54.8, 51.3, 46.3, 37.1, 34.0, 32.6, 32.1, 26.8, 26.4, 23.0, 13.3. Anal. Calcd for $C_{24}H_{33}NO_5$: C, 69.37; H, 8.01; N, 3.37. Found: C, 69.29; H, 8.17; N, 3.19.

Amine 13. To a solution of enonate **12** (1.16 g, 2.79 mmol) in 50% aqueous HOAc (40 mL) was added zinc dust (1.1 g, 16.8 mmol). After being stirred for 20 h at 55 ^{o}C, the mixture was concentrated *in vacuo*, and the residue was basified with saturated $NaHCO_3$. The mixture was extracted with methylene chloride (3 x 100 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resultant residue was purified by flash chromatography on silica gel (1:1 hexane-EtOAc) to afford 1.1 g (94%) of hydroxy amine **13** as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, J = 6.3 Hz, 3H), 1.32-1.74 (m, 10H), 1.85 (m, 1H), 2.21 (m, 2H), 2.53 (t, J = 6.0 Hz, 2H), 2.70 (m, 1H), 2.82 (m, 1H), 3.73 (s, 3H), 3.96 (m, 1H), 5.12 (s, 2H), 5.84 (d, J = 15.6 Hz, 1H), 6.95 (dt, J = 15.6, 6.9 Hz, 1H), 7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 166.8, 148.7, 135.5, 128.4, 128.2, 128.1, 121.2, 66.3, 65.9, 65.3, 51.3, 51.2, 37.9, 37.7, 36.5, 35.1, 32.5, 23.2, 22.2, 21.8, 20.8. Anal. Calcd for $C_{24}H_{35}NO_5$: C, 69.04; H, 8.45; N, 3.35. Found: C, 69.98; H, 8.48; N, 3.30.

Amine 14. A solution of **13** (480 mg, 1.15 mmol) in 1,2-dichlorobenzene (20 mL) was heated to reflux for 24 h. The solution was cooled to room temperature and purified by flash chromatography on silica gel (1:1 hexane-EtOAc) to afford 247 mg (84%) of cyclized amine **14** as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06-1.92 (m, 12H), 1.11 (d, superimposed on m, J = 6.6 Hz, 3H), 2.16 (m, 1H), 2.28 (dd, J = 16.5, 9.0 Hz, 1H), 2.40 (dd, J = 16.5, 3.6 Hz, 1H), 3.08 (m, 1H), 3.66 (s, 3H), 4.24 (qd, J = 6.6, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 65.1, 64.4, 53.7, 51.4, 47.7, 41.3, 33.9, 33.8, 32.0, 22.0, 21.5, 20.3, 19.6. Anal. Calcd for $C_{14}H_{25}NO_3$: C, 65.85; H, 9.87; N, 5.48. Found: C, 65.90; H, 9.66; N, 5.37.

In a same manner, **19** and **20** were prepared from **7** and trans olefin **14**.

19: colorless oil; IR (film) 2943, 1453, 1352, 1275, 1120, 1176, 1034 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42-2.02 (m, 23H), 2.80 (t, *J* = 5.7 Hz, 4H), 3.40 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.50 (m, 1H), 3.76 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.86 (m, 1H), 4.58 (m, 1H), 5.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.7, 125.2, 98.7, 67.0, 62.1, 53.1, 37.8, 37.4, 32.4, 30.6, 29.7, 25.9, 25.4, 25.3, 23.8, 20.7, 19.5, 17.8. Anal. Calcd for $C_{19}H_{34}O_2S_2$: C, 63.64; H, 9.55; S, 17.88. Found: C, 63.82; H, 9.58; S, 17.91.

20: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09-1.20 (m, 2H), 1.15 (d, superimposed on m, *J* = 6.0 Hz, 3H), 1.37-1.73 (m, 10H), 1.99-2.06 (m, 1H), 2.32 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.42 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.06 (m, 1H), 3.59-3.69 (m, 1H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 69.6, 63.4, 57.6, 51.3, 48.4, 41.1, 38.1, 37.7, 31.9, 29.7, 24.4, 22.0, 21.8. Anal. Calcd for $C_{14}H_{25}NO_3$: C, 65.85; H, 9.87; N, 5.48. Found: C, 65.90; H, 9.90; N, 5.34.