Supporting Information for:

The Total Synthesis of (–)-Lemonomycin

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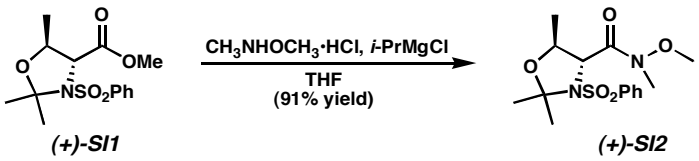
Material and Methods. Unless otherwise stated, reactions were performed at ambient temperature (typically 20 °C) in flame-dried glassware under a nitrogen or argon atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Acrolein was distilled under nitrogen immediately prior to use. All other commercially obtained reagents were used as received. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV, anisaldehyde, permanganate, or CAM staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Preparatory reversed-phase HPLC was performed on a Waters HPLC with a Waters Delta-Pak 25 x 100 mm, 15 μm C_{18} column equipped with a guard, utilizing a flow rate of 10 mL/min and a ramp of 1% B/min (A eluent = 95:5:0.05 water:acetonitrile:trifluoroacetic acid, B eluent = 5:95:0.01 water:acetonitrile:trifluoroacetic acid) with visualization at 270 nm. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a chiralcel AD column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 254 nm. Optical rotations were measured with a Jasco P-1010 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Mercury 300 (at 300 MHz and 75 MHz respectively), Varian Mercury 500 (at 500 MHz and 125 MHz respectively), or on a Varian Mercury 600 (600 MHz for proton only) spectrometer and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). UV spectra were measured on a Beckman-Coulter DU 7400 spectrophotometer. High resolution mass spectra were obtained from the Caltech Mass Spectral Facility. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number (see individual structures for deposition number).

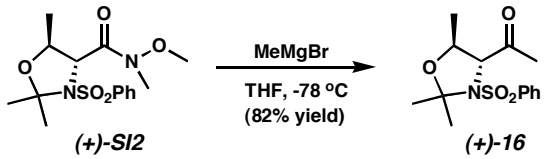
Additional References.

Natural product isolates containing the aminopyranose of lemonomycin (footnote 4); the saccharosacrins (a-b) and the glycothiohexides (c-e):

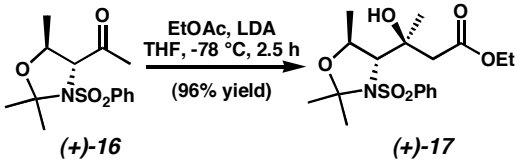
(a) Hegde, V. R.; Patel, M. G.; Das, P. R.; Pramanik, B.; Puar, M. S. *J.Antibiot.* **1997**, *50*, 126-134. (b) Horan, A. C.; Shearer, M. C.; Hegde, V.; Beyazova, M. L.; Brodsky, B. C.; King, A,; Berrie, R,; Cardaci, K, Nimeck, M.. *J.Antibiot.* **1997**, *50*, 119-125. (c) Sasaki, T.; Otani, T.; Matsumoto, H.; Unemi, N.; Hamada, M.; Takeuchi, T.; Hori, M. *J.Antibiot.* **1998**, *51*, 715-721. (d) Northcote, P. T.; Siegel, M.; Borders, D. B.; Lee, M. D. *J.Antibiot.* **1994**, *47*, 901-908. (e) Constatntine, K. L.; Mueller, L.; Huang, S.; Abid, S.; Lam, K. S.; Li, W.; Leet, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 7284-7285.



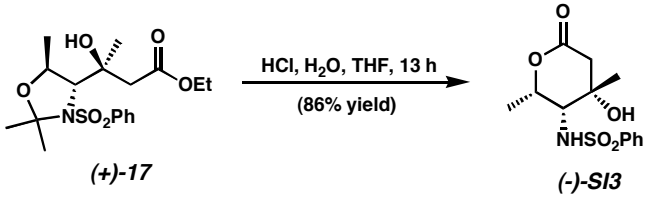
Amide (+)-SI2. A suspension of *N,O*-dimethylhydroxylamine hydrochloride (1.54 g, 15.8 mmol) in tetrahydrofuran (100 mL) was cooled to -78 °C and *i*-propylmagnesium chloride (16.0 mL, 32.0 mmol) was added. After stirring for 5 min, a solution of ester **(+)-SI1**[1] (2.26 g, 7.21 mmol) in tetrahydrofuran (20 mL) was added. The mixture was stirred at -78 °C for 30 min then at -40 °C 12 h. The reaction was quenched with saturated aqueous ammonium chloride (100 mL), extracted with ethyl acetate (4 x 100 mL), washed with brine, and dried over sodium sulfate. Solvent was evaporated and the residue was purified by flash chromatography (4:1 hexanes:ethyl acetate eluent) to provide amide **(+)-SI2** (2.24 g, 91% yield) as a white solid: R_F 0.27 (50:50 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) □ 8.05-8.01 (comp m, 2H), 7.63-7.51 (m, 3H), 4.66 (d, *J* = 7.0 Hz, 1H), 4.26 (m, 1H), 3.80 (s, 3H), 3.23 (s, 3H), 1.54 (s, 3H), 1.49 (s, 3H), 1.35 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 132.8, 128.8, 128.0, 97.3, 74.8, 64.2, 61.4, 27.4, 18.8; IR (NaCl/film) 2982, 1677, 1447, 1344 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{15}H_{22}N_2O_5S+H]^+$: 343.1328, found 343.1312; $[\square]_D^{25}$ +71.9° (c = 1.00, $CHCl_3$).



Ketone (+)-16. Amide **(+)-SI2** (1.64 g, 4.79 mmol) was dissolved in tetrahydrofuran (20 mL) and cooled to - 78 °C. To the solution was added methylmagnesium bromide (1.8 mL, 5.4 mmol). After 45 min, additional methylmagnesium bromide(1.8 mL, 5.4 mmol) was added. The solution was allowed to warm to rt. The reaction was quenched with saturated aqueous ammonium chloride (50 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organics were dried over sodium sulfate and evaporated. The residue was purified by flash chromatography (4:1 to 1:1 hexanes:ethyl acetate eluent) to yield ketone **(+)-16** (1.30 g, 82% yield) as a white solid : R_F 0.38 (70:30 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.86 (m, 2H), 7.64-7.51 (comp m, 3H), 4.22 (m, 1H), 3.70 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 1.69 (s, 3H), 1.49 (s, 3H), 1.26 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 205.5, 139.7, 133.1, 129.2, 127.8, 98.2, 74.6, 72.8, 28.8, 25.8, 25.0, 17.9; IR (NaCl/film) 2987, 1716, 1344, 1157 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{14}H_{19}NO_4S+H]^+$: 298.1113, found 298.1101; $[\square]_D^{26}$ +148.0° (c = 1.00, $CHCl_3$).



Aldol adduct (+)-17. A solution of diisopropylamine (11.3 mL, 80.9 mmol) in tetrahydrofuran (77 mL) was cooled to 0 °C and *n*-butyllithium (30 mL, 76 mmol) was added. After 20 min, the solution was cooled to -78 °C, and a solution of ethyl acetate (7.5 mL, 77 mmol) in tetrahydrofuran (154 mL) was added dropwise over 5 min. After 1 h, a solution of ketone **(+)-16** (4.83 g, 16.2 mmol) in tetrahydrofuran (81 mL) at -78 °C was added via cannula. The reaction was quenched after 2.5 h with saturated aqueous ammonium chloride (100 mL). The mixture was allowed to warm to rt, and partitioned between water (100 mL) and ethyl acetate (50 mL). The aqueous phase was extracted with ethyl acetate (50 mL), and the combined organics were dried over magnesium sulfate. Solvent was evaporated and the residue was purified by flash chromatography (10:10:80 to 15:15:70 ethyl acetate:dichloromethane:hexanes eluent) to provide aldol adduct **(+)-17** (6.01 g, 96% yield) as a colorless oil: R_F 0.61 (50:25:25 hexanes:dichloromethane eluent); ^{1}H NMR (300 MHz, C_6D_6) □ 7.92-7.89 (comp m, 2H), 6.93-6.90 (m, 3H), 4.52 (dq, *J* = 6.6, 2.0 Hz, 1H), 4.12 (d, *J* = 2.4 Hz, 1H), 4.08-3.90 (comp m, 2H), 3.30 (d, *J* = 17.0 Hz, 1H), 2.47 (d, *J* = 17.0 Hz, 1H), 1.62 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 0.96 (t, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 173.9, 140.6, 133.2, 129.1, 128.6, 99.8, 74.9, 72.8, 72.0, 61.0, 42.9, 31.2, 28.8, 24.4, 22.5, 14.4; IR (NaCl/film) 3480, 2986, 1710, 1447, 1346, 1204 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{18}H_{27}NO_6S+H]^+$: 386.1637, found 386.1637; $[□]_D^{26}$ +64.0° (c = 2.00, acetone).



Lactone (-)-SI3. A solution of aldol adduct **(+)-17** (0.467g, 1.21 mmol) in tetrahydrofuran (12 mL) was acidified with aqueous hydrochloric acid (0.242 mL, 0.242 mmol). After 13 h, the reaction was quenched with saturated aqueous sodium bicarbonate (50 mL), extracted with ethyl acetate (2 x 30 mL), and dried over sodium sulfate. Solvent was evaporated and the residue was purified by flash chromatography (25:25:50 to 30:30:40 acetone:dichloromethane:hexanes eluent) to afford lactone **(-)-SI3** (0.312 g, 86% yield) as white solids. Crystals of sufficient quality for X-ray analysis of lactone **(+)-SI3** (prepared in an analogous method) were grown from dichloromethane by slow evaporation (uncorrected mp. 164-165 °C): R_F 0.20 (50:25:25 hexanes:dichloromethane:acetone eluent); ^{1}H NMR (300 MHz, acetone-d_6) □ 8.01-7.90 (comp m, 2H), 7.68-7.56 (comp m, 3H), 4.61 (dq, *J* = 6.6 , 4.5 Hz, 1H), 3.66 (d, *J* = 4.0 Hz, 1H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 171.8, 140.7, 133.2, 129.4, 127.3, 76.0, 69.9, 59.3, 43.2, 27.5, 16.6; IR (NaCl/film) 3496, 3289, 2996, 1738, 1448, 1337 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{13}H_{17}NO_5S+H]^+$: 300.0906, found 300.0909; $[□]_D^{26}$ -74.2° (c = 1.00, $CHCl_3$).

Crystal Structure of (+)-SI3.

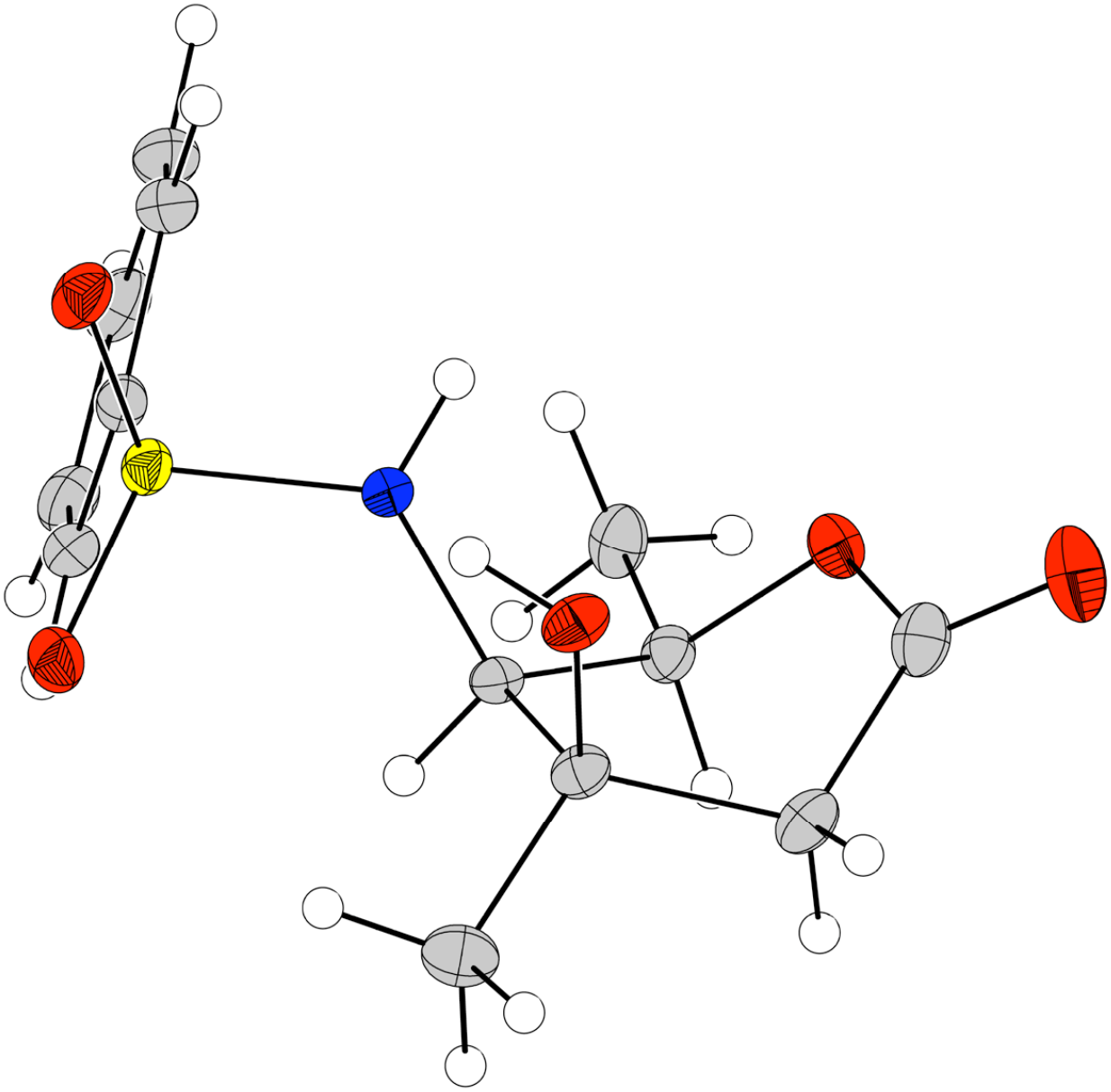


Table 1. Crystal data and structure refinement for (+)-SI3 (CCDC 217756).

Empirical formula	$C_{13}H_{17}NO_5S$
Formula weight	299.34
Crystal Habit	Prism
Crystal size	0.35 x 0.31 x 0.26 mm^3
Crystal color	Colorless
Data Collection	
Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKa
Data Collection Temperature	100(2) K
q range for 21790 reflections used in lattice determination	2.77 to 28.06°
Unit cell dimensions	a = 8.0871(4) Å b = 8.2042(4) Å c = 20.6350(10) Å
Volume	1369.09(12) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	P212121
Density (calculated)	1.452 Mg/m^3
F(000)	632
Data collection program	Bruker SMART v5.054
q range for data collection	1.97 to 28.28°
Completeness to q = 28.28°	96.1 %
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-26 \leq l \leq 26$
Data collection scan type	ω scans at 7 φ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	27404
Independent reflections	3217 [R_{int}= 0.0507]
Absorption coefficient	0.255 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.9366 and 0.9159

Table 1 (cont.)

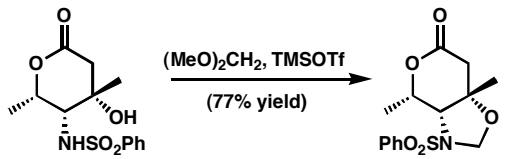
Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3217 / 0 / 249
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	2.819
Final R indices [I>2σ(I), 3121 reflections]	R1 = 0.0288, *w*R2 = 0.0590
R indices (all data)	R1 = 0.0298, *w*R2 = 0.0591
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	0.02(5)
Largest diff. peak and hole	0.449 and -0.350 e.Å^{-3}

Special Refinement Details

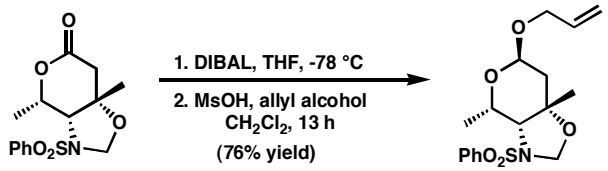
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.



(-)-SI3 *(-)-SI4*

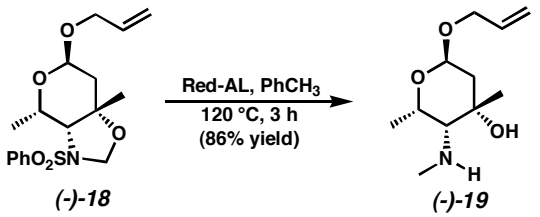
Oxazolidine (-)-SI4. To a suspension of lactone **(-)-SI3** (2.92 g, 9.75 mmol) in dimethoxymethane (49 mL) at 0 °C was added trimethylsilyltriflate (5.3 mL, 29 mmol) dropwise over 3 min. After 20 min, the reaction was quenched with saturated aqueous sodium bicarbonate (100 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (75 mL). The combined organics were dried over magnesium sulfate and solvent was evaporated. The residue was purified by flash chromatography (15:15:70 to 30:30:40 acetone:dichloromethane:hexanes eluent) to provide oxazolidine **(-)-SI4** (2.34 g, 77% yield) as a white solid: R_F 0.46 (50:25:25 hexanes:dichloromethane:acetone eluent); ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.95-7.90 (comp m, 2H), 7.75-7.58 (comp m, 3H), 5.23 (d, *J* = 7.2 Hz, 1H), 4.69 (d, *J* = 7.2 Hz, 1H), 4.49 (dq, *J* =6.3 , 2.7 Hz, 1H), 3.80 (d, *J* = 2.7 Hz, 1H), 2.74 (d, *J* = 16.0 Hz, 1H), 2.54 (d, *J* = 16.0 Hz, 1H), 1.61 (d, *J* = 6.3 Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.3, 137.8, 134.1, 129.8, 128.3, 82.0, 81.7, 75.0, 65.2, 40.9, 25.6, 17.3; IR (NaCl/film) 3430, 2902, 1765, 1446 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{14}H_{17}NO_5S+H]^+$: 312.0906, found 312.0909; $[□]_D^{25}$ -151.0° (c = 1.00, $CHCl_3$).



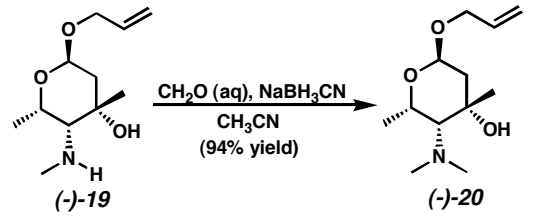
(-)-SI4 *(-)-18*

Bicycle (-)-18. A solution of oxazolidine **(-)-SI4** (1.94 g, 6.23 mmol) in tetrahydrofuran (62 mL) was cooled to -78 °C, and diisobutylaluminum hydride (2.2 mL, 12 mmol) was added dropwise over 1 min. After 30 min, the reaction was quenched with aqueous Rochelle's salt (100 mL, 1 M). Organics were extracted with ethyl acetate (2 x 50 mL), dried over magnesium sulfate, and concentrated. The residue was further dried by azeotropic removal of water with benzene. The crude residue was dissolved in dichloromethane (62 mL) followed by the addition of allyl alcohol (6.35 mL, 93.4 mmol) and methanesulfonic acid (0.81 mL, 1.2 mmol). After 18 h, the reaction was quenched with saturated aqueous sodium bicarbonate (100 mL). Organics were extracted with dichloromethane (50 mL), dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography (10:90 to 15:85 ethyl acetate:hexanes eluent) to afford bicycle **(-)-18** (1.67 g, 76% yield) as a colorless oil: R_F 0.17 (85:15 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.91-7.87 (comp m, 2H), 7.65-7.51 (comp m, 3H), 5.87 (m, 1H), 5.25 (appt. ddd, *J* = 17.1, 3.3, 1.8 Hz, 1H), 5.29-5.12 (comp m, 2H), 4.84 (dd, *J* = 8.1, 6.0 Hz, 1H), 4.81 (d, *J* = 5.7 Hz, 1H), 4.20 (ddt, *J* = 13.2, 5.7, 1.8 Hz, 1H), 4.04 (dq, *J* = 6.6, 2.7 Hz, 1H), 3.96 (ddt, *J* = 11.7, 5.1, 1.2 Hz, 1H), 3.53 (d, *J* = 2.4 Hz, 1H), 2.17 (dd, *J* = 15.6, 6.3 Hz, 1H), 1.64 (dd, *J* = 15.3, 8.4 Hz, 1H), 1.34 (d, *J* = 6.6

Hz, 3H), 0.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 134.8, 133.6, 129.5, 128.1, 117.1, 95.9, 81.4, 81.0, 68.4, 65.7, 65.6, 37.8, 26.3, 17.4; IR (NaCl/film) 2981, 1447, 1353, 1166 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{17}H_{23}NO_5S+H]^+$: 354.1375, found 354.1373; $[\alpha]_D^{26}$ -140.5° (c = 1.00, $CHCl_3$).

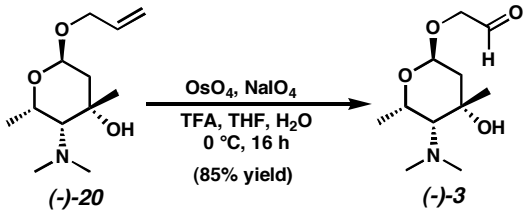


Glycoside (-)-19. To a solution of bicycle **(-)-18** (0.554 g, 1.57 mmol) in toluene (16 mL) was added Red-Al (3.53 mL, 11.7 mmol, 65+% $^{w}/_{w}$ in toluene). The mixture was refluxed for 2.75 h, cooled to 0 °C, and Celite was added (1.0 g) followed by saturated aqueous sodium sulfate (1.0 mL). The solution was allowed to warm to rt. The mixture was filtered, and solids were washed with ethyl acetate (50 mL) and brine (15 mL). The phases were separated and the aqueous phase was extracted with ethyl acetate (2 x 25 mL). The combined organics were dried over sodium sulfate and concentrated under vacuum. Purification of the crude residue by flash chromatography (90:10:0.1:0.5 to 90:10:2:0.5 chloroform:ethyl acetate:methanol:triethylamine eluent) provided glycoside **(-)-19** (0.290 g, 86% yield) as a colorless oil: R_F 0.09 (95:5 dichloromethane:methanol eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (m, 1H), 5.24 (appt. ddd, *J* = 17.7, 3.3, 1.5 Hz, 1H), 5.15 (appt. ddd, *J* = 10.5, 3.3, 1.8 Hz, 1H), 4.79 (d, *J* = 4.2 Hz, 1H), 4.16 (dq, *J* = 5.7, 0.9 Hz, 1H), 4.10 (ddt, *J* = 13.2, 4.8, 1.8 Hz, 1H), 3.89 (ddt, *J* = 13.2, 6.0, 1.5 Hz, 1H), 2.59 (s, 3H), 2.02 (s, 1H), 1.72 (appt. d, *J* = 14.1 Hz, 1H), 1.59 (dd, *J* = 13.8, 4.5 Hz, 1H), 1.41 (s, 3H), 1.26 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.7, 116.6, 90.0, 68.2, 68.0, 67.7, 64.9, 40.0, 38.7, 26.1, 18.5; IR (NaCl/flim) 3345, 2932, 1118 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{11}H_{20}NO_3+H]^+$: 216.1600, found 216.1603; $[\alpha]_D^{26}$ -185.3° (c = 1.00, $CHCl_3$).

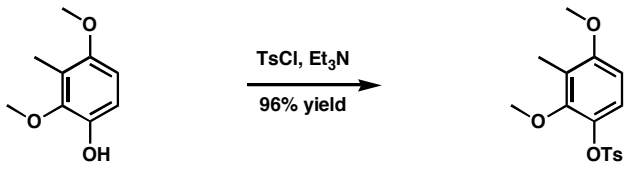


N, N-Dimethyl glycoside (-)-20. To glycoside **(-)-19** (0.430 g, 2.00 mmol) in acetonitrile (20 mL) was added sodium cyanoborohydride (0.377 g, 6.00 mmol). After stirring for 5 min, aqueous formaldehyde (0.75 mL, 10 mmol, 37% $^{w}/_{w}$ in water) was added. The mixture was stirred vigorously for 2 h, and the reaction was quenched with glacial acetic acid (0.86 mL). After concentrating the mixture under vacuum it was diluted with sodium hydroxide (15 mL, 1 M) and brine (40 mL) then extracted with ethyl acetate (3 x 100 mL). The organic layer was dried over sodium sulfate and concentrated. The residue was purified by flash chromatography

(90:10:0.1:0.5 to 90:10:1.5:0.5 chloroform:ethyl acetate:methanol:triethylamine eluent) to yield dimethyl glycoside **(-)-20** (0.429 g, 94% yield) as a colorless oil: R_F 0.45 (90:10 chloroform:methanol eluent); ^{1}H NMR (300 MHz, $CDCl_3$) □ 5.89 (m, 1H), 5.35-5.10 (comp m, 2H), 5.14 (appt. dd, *J* = 10.5, 1.8 Hz, 1H), 4.93 (t, *J* = 2.7 Hz, 1H), 4.25 (dq, *J* = 7.2, 2.7 Hz, 1H), 4.09 (ddt, *J* = 13.2, 5.1, 0.9 Hz, 1H), 3.91 (ddt, *J* = 13.2, 5.7, 1.5 Hz, 1H), 2.68 (s, 3H), 2.21 (d, *J* = 2.7 Hz, 1H), 1.88 (d, *J* = 2.7 Hz, 2H), 1.43 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 134.5, 116.3, 97.0, 69.4, 67.9, 66.2, 62.2, 45.0, 41.0, 29.5, 19.0; IR (NaCl/film) 3288, 2937, 1395, 1119 cm^{-1}; HRMS (FAB) *m/z* calc'd for $[C_{12}H_{22}NO_3 + H]^+$: 230.1756, found 230.1754; $[□]_D^{24}$ -158.5° (c = 1.00, acetone).

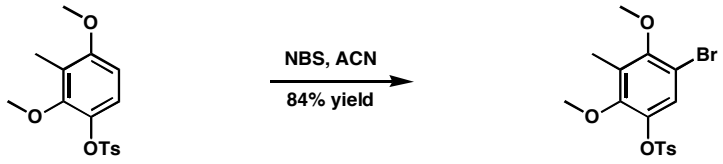


Glycosylated acetaldehyde (-)-3. A solution of glycoside **(-)-20** (0.060 g, 0.26 mmol) in tetrahydrofuran (4.8 mL) and water (0.48 mL) was cooled to 0 °C and trifluoroacetic acid (0.10 mL, 1.3 mmol), osium tetroxide (3.3 mg, 0.013 mmol), and sodium periodate (0.14 g, 0.65 mmol) were added. The mixture was stirred at 0 °C for 16 h, and the reaction was quenched with potassium hydroxide (0.13 mL, 10 M). After diluting with ethanol (5 mL), the mixture was filtered through a pad of silica gel, concentrated, and purified by preparative thin layer chromatography (15:85 methanol:chloroform eluent) to afford aldehyde **(-)-3** as its trifluoroacetate salt (50.1 mg, 55% yield) and aldehyde **(-)-3** (18.4 mg, 30% yield): R_F 0.25 (10:90 methanol:chloroform eluent); ^{1}H NMR (300 MHz, CD_3OD) □ 4.90 (d, *J* = 4.5 Hz, 1H), 4.62 (appt. dt *J* = 8.4, 5.7 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 3.47 (m, 1H), 3.38 (m, 1H), 2.68 (s, 6H), 2.30 (s, 1H), 1.88 (dd, *J* = 13.8, 4.5 Hz, 1H), 1.78 (d, *J* = 14.4 Hz, 1H), 1.39 (s, 3H), 1.35 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD) □ 97.8, 96.7, 69.7, 69.6, 69.2, 67.2, 65.5, 43.9, 40.4, 28.7, 18.0; IR (NaCl/film) 3290, 2937, 2836, 1682, 1127 cm^{-1}; $[□]_D^{25}$ -122.5° (c = 0.45, CH_2Cl_2).



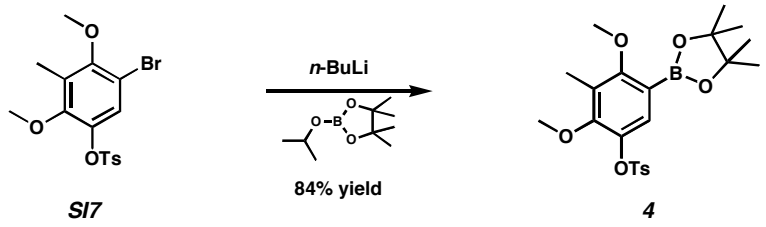
Tosyl Arene SI6. To a solution of **SI5**[2] (10.15 g, 60.4 mmol) in dichloromethane (60 mL) were added triethylamine (8.4 mL, 60.4 mmol) and *p*-toluenesulfonyl chloride (11.5 g, 60.4 mmol). The reaction was maintained at 20 °C for 3.5 h, after which acetonitrile (80 mL) and saturated aqueous sodium bicarbonate (50 mL) were added. After an addition hour the volatiles were removed in vacuo, and the residue was diluted with water (350 mL) and extracted into

dichloromethane (2 x 250 mL). The combined organics were dried over magnesium sulfate, concentrated, and purified by flash chromatography on silica gel (10:90 to 20:80 ethyl acetate:hexanes eluent) to provide **SI6** (18.64 g, 96% yield) as a white solid: R_F 0.67 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 9.3 Hz, 1H), 6.49 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 2.43 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 151.2, 145.1, 136.4, 133.2, 129.6, 128.4, 121.4, 120.4, 105.2, 60.9, 55.8, 21.9, 9.3; IR (NaCl/film) 2941, 1597, 1483, 1371, 1177, 1111 cm^{-1}; HRMS (FAB) calc'd for $[C_{16}H_{18}O_5S+H]^+$: *m/z* 323.0953, found 323.0965.



SI6 ***SI7***

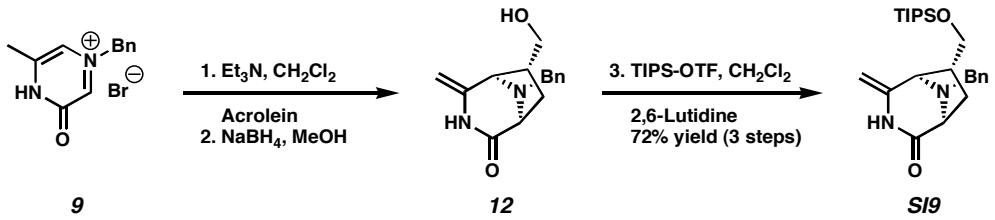
Aryl Bromide SI7. To a solution of **SI6** (1.0 g, 3.1 mmol) in acetonitrile (10 mL) was added *N*-bromosuccinimide (580 mg, 3.2 mmol). After 10.5 h the reaction was diluted with ethyl acetate (150 mL), washed with saturated aqueous sodium bicarbonate (100 mL), dried over sodium sulfate, concentrated, and filtered through a pad of silica gel (30:70 ethyl acetate:hexanes eluent) to provide **SI7** (1.04 g, 84% yield) as a white solid. R_F 0.67 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.15 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.47 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 151.1, 145.6, 139.1, 132.9, 129.8, 128.5, 128.2, 124.7, 110.9, 61.1, 60.6, 22.0, 10.7; IR (NaCl/film) 2940, 1469, 1377, 1177, 554 cm^{-1}; HRMS (FAB) calc'd for $[C_{16}H_{17}BrO_5S+H]^+$: *m/z* 401.0058, found 401.0045.



SI7 ***4***

Arylboronic ester 4. To a chilled (-78 °C) solution of **SI7** (2.5 g, 6.23 mmol) in anhydrous diethyl ether (62 mL) was added *n*-butyllithium (4.3 mL, 2.5M solution in hexanes, 10.9 mmol) dropwise over 5 min. After 20 min a solution of 2-isopropoxy-4,4,5,5-tetramethyldioxaborolane (2.5 mL, 12.5 mmol) in anhydrous diethyl ether (41 mL) was added via cannula over 5 min. The reaction was then warmed to -40 °C over 20 min and quenched with saturated aqueous ammonium chloride (50 mL). After warming to 20 °C, the mixture was diluted with water (100 mL) and extracted with diethyl ether (2 x 100 mL). The combined organics were dried over magnesium sulfate, concentrated, and purified by flash chromotography on silica gel (10:90 to 20:80 ethyl acetate:hexanes eluent) to provide **4** (2.35 g, 84% yield) as a colorless oil: R_F 0.65 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J*

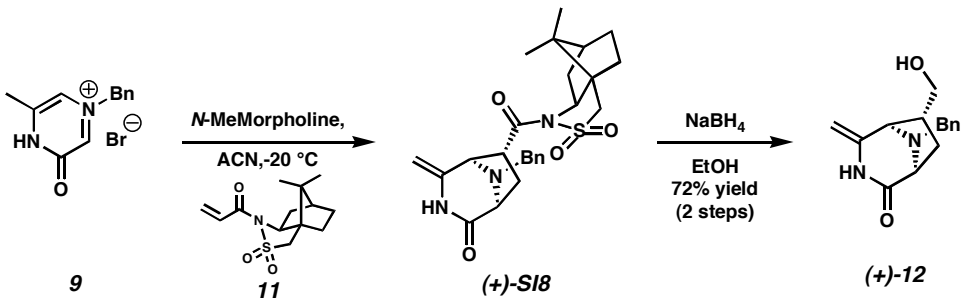
= 8.4 Hz, 2H), 7.22 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.46 (s, 3H), 2.13 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 154.0, 145.0, 138.2, 133.0, 129.5, 128.3, 128.1, 126.2, 83.6, 62.1, 60.7, 24.8, 21.7, 9.5; IR (NaCl/film) 2979, 2935, 1597, 1358, 1178, 1143 cm^{-1}; HRMS (FAB) calc'd for $[C_{22}H_{29}BO_7S+H]^+$: *m/z* 449.1805, found 449.1819.



9 ***12*** ***SI9***

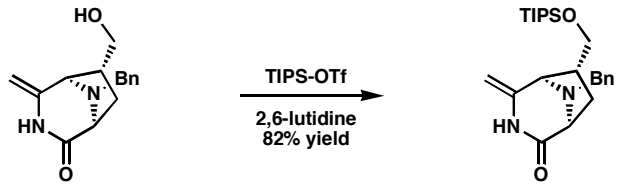
Silyl ether SI9 by racemic dipolar cycloaddition. To a suspension of **9**[3] (10.0 g, 35.6 mmol) in dichloromethane (119 mL) was added triethylamine (14.9 mL, 107 mmol), affording a clear solution, which was cooled to -20 °C over 15 min. Acrolein (7.15 mL, 107 mmol) was then added dropwise over 5 min. The reaction was maintained at -20 °C for 74 h, then warmed to 0 °C and diluted with methanol (71 mL). Sodium borohydride (5.4 g, 142 mmol) was added in portions over 15 min. After an additional 15 min, the reaction was warmed to room temperature, quenched with saturated aqueous ammonium chloride (200 mL) and water (300 mL), and extracted into dichloromethane (200 mL, 250 mL). The combined organics were dried over sodium sulfate, concentrated, and dried aziotropically from benzene (50 mL) to provide racemic **12**, which was used without further purification.

To a solution of crude **12** in dichloromethane (71 mL) were added 2,6-lutidine (4.57 mL, 39.2 mmol) and triisopropylsilyltrifluoromethanesulfonate (10.5 mL, 39.2 mmol). After 75 min the reaction was quenched with water (500 mL) and extracted into dichloromethane (100 mL, 150 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (15:85 ethyl acetate:hexanes eluent) to provide racemic **SI9** (10.65 g, 72% yield) as a white solid: R_F 0.41 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.21 (comp m, 6H), 4.21 (s, 1H), 4.08 (s, 1H), 3.77 (d, *J* = 12.9 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 1H), 3.65 (s, 1H), 3.63-3.54 (comp m, 2H), 3.51 (d, *J* = 6.9 Hz, 1H), 2.34 (app ddd, *J* = 14.3, 9.3, 5.3 Hz, 1H), 2.09 (dd, *J* = 13.4, 9.5 Hz, 1H), 1.69 (ddd, *J* = 13.2, 7.2, 5.2 Hz, 1H), 1.02 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 142.7, 138.4, 128.8, 128.3, 127.2, 90.6, 65.9, 63.2, 61.2, 52.5, 47.1, 32.3, 18.3, 12.2; IR (NaCl/film) 3195, 2943, 2866, 1687, 1650, 1105 cm^{-1}; HRMS (FAB) calc'd for $[C_{24}H_{38}N_2O_2Si+H]^+$: *m/z* 415.2781, found 415.2786.



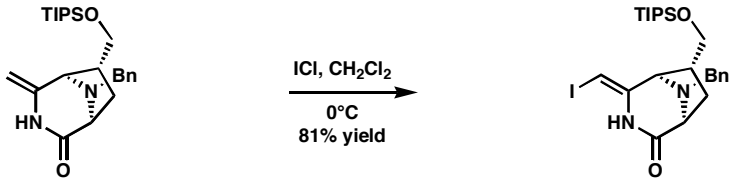
Diazabicycles (+)-SI8 and (+)-12. To a chilled (-20 °C) suspension of **9** (421.5 mg, 1.5 mmol) in acetonitrile (15 mL) were added **11**[4] (485 mg, 1.8 mmol) and *N*-methylmorpholine (495 μL, 4.5 mmol), which afforded a clear solution. The reaction was maintained at -20 °C for 72 h, after which ethanol (15 mL) and sodium borohydride (570 mg, 15 mmol) were added. The reaction was warmed to 20 °C for 4.5 h, after which additional sodium borohydride (570 mg, 15 mmol) was added. After an addition 1.5 h the reaction was quenched with saturated aqueous ammonium chloride (125 mL) and extracted with ethyl acetate (100 mL, 50 mL). The organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (40:60 to 85:15 ethyl acetate:hexanes eluent) to provide **(+)-12** (278 mg, 72% yield, 94.7% ee) as a colorless oil: R_F 0.11 (70:30 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 7.38-7.25 (comp m, 5H), 4.32 (d, *J* = 1.2 Hz, 1H), 4.15 (br s, 1H), 3.81 (d, *J* = 13.2 Hz, 1H), 3.73 (m, 1H), 3.72 (d, *J* = 12.9 Hz, 1H), 3.60 (d, *J* = 6.0 Hz, 1H), 3.57 (m, 1H), 3.56 (s, 1H), 2.81 (br s, 1H), 2.37 (m, 1H), 2.21 (dd, *J* = 12.9, 9.0 Hz, 1H), 2.09 (ddd, *J* = 13.2, 7.3, 5.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 141.7, 137.7, 129.0, 128.7, 127.8, 91.2, 66.2, 63.2, 63.0, 52.6, 45.5, 32.9; IR (NaCl/film) 3354, 3210, 2936, 1676, 1317 cm^{-1}; HRMS (FAB) calc'd for $[C_{15}H_{18}N_2O_2+H]^+$: *m/z* 259.1447, found 259.1457; $[\alpha]_D^{23}$ +44.2° (c = 0.5, $CHCl_3$). HPLC analysis (Chiracel AD column, 10:90 2-propanol:hexanes, 1 mL/min, λ = 254 nm) showed the product to be of 94.7% ee (t_{fast} = 17.95 min, major; t_{slow} = 22.28 min, minor).

An analytical sample of the intermediate cycloadduct **(+)-SI8** was prepared by flash chromatography on silica gel (20:20:60 acetone:dichloromethane:hexanes eluent): R_F 0.33 (25:25:50 acetone:dichloromethane:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (br s, 1H), 7.32-7.22 (comp m, 5H), 4.37 (d, *J* = 1.2 Hz, 1H), 4.32 (d, *J* = 0.6 Hz, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 3.89 (dd, *J* = 8.1, 4.8 Hz, 1H), 3.75 (br d, *J* = 7.2 Hz, 1H), 3.68 (br s, 1H), 3.59 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.57 (d, *J* = 13.2 Hz, 1H), 3.41 (s, 2H), 3.06 (ddd, *J* = 13.2, 7.8, 3.9 Hz, 1H), 2.15 (dd, *J* = 13.5, 9.0 Hz, 1H), 2.06 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.96-1.79 (comp m, 4H), 1.46-1.30 (comp m, 2H), 0.92 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 170.9, 139.2, 138.1, 128.8, 128.5, 127.5, 93.8, 65.8, 63.4, 63.3, 53.3, 52.1, 49.1, 48.5, 47.9, 44.8, 38.5, 33.0, 31.3, 26.6, 20.7, 20.0; IR (NaCl/film) 3313, 3199, 2958, 1695, 1653, 1330, 1211, 1133 cm^{-1}; HRMS (FAB) calc'd for $[C_{25}H_{31}N_3O_4S+H]^+$: *m/z* 470.2114, found 470.2127; $[\alpha]_D^{25}$ +137.3° (c = 0.5, acetone).



(+)-12 *(+)-SI9*

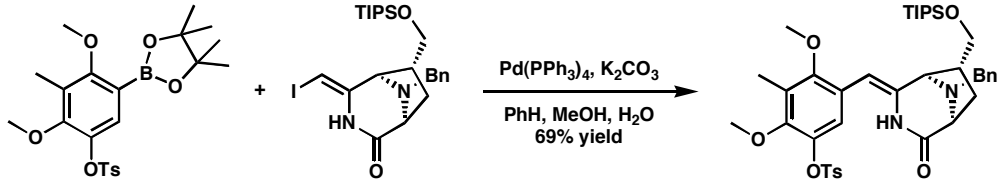
Silyl ether (+)-SI9. To a solution of **12** (1.9 g, 7.36 mmol) in dichloromethane (25 mL) were added 2,6-lutidine (1.03 mL, 8.83 mmol) and triisopropylsilyl-trifluoromethanesulfonate (2.37 mL, 8.83 mmol). After 15 min the reaction was quenched with water (150 mL) and extracted with dichloromethane (50 mL, 30 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (15:85 to 30:70 ethyl acetate:hexanes eluent) to provide **(+)-SI9** (2.50 g, 82% yield) as a colorless oil: R_F 0.41 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.35-7.21 (comp m, 6H), 4.21 (s, 1H), 4.08 (s, 1H), 3.77 (d, *J* = 12.9 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 1H), 3.65 (s, 1H), 3.63-3.54 (comp m, 2H), 3.51 (d, *J* = 6.9 Hz, 1H), 2.34 (app ddd, *J* = 14.3, 9.3, 5.3 Hz, 1H), 2.09 (dd, *J* = 13.4, 9.5 Hz, 1H), 1.69 (ddd, *J* = 13.2, 7.2, 5.2 Hz, 1H), 1.02 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 172.4, 142.7, 138.4, 128.8, 128.3, 127.2, 90.6, 65.9, 63.2, 61.2, 52.5, 47.1, 32.3, 18.3, 12.2; IR (NaCl/film) 3195, 2943, 2866, 1687, 1650, 1105 cm^{-1}; HRMS (FAB) calc'd for $[C_{24}H_{38}N_2O_2Si+H]^+$: *m/z* 415.2781, found 415.2786; $[\alpha]_D^{23}$ +25.7° (c = 1.5, acetone).



(+)-SI9 *(+)-5*

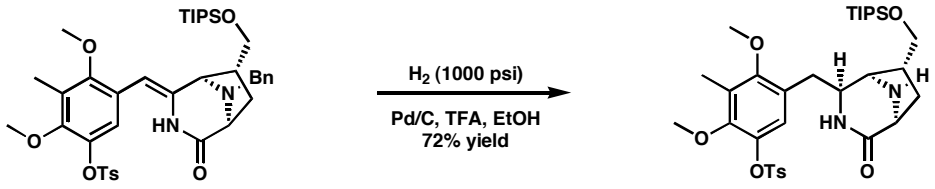
Iodoeneamide (+)-5. (Note: reaction run in a foil-wrapped flask to exclude light.) To a cooled (0 °C) solution of (+)-**SI9** (10.65 g, 25.7 mmol) in dichloromethane (128 mL) was added a cooled (0 °C) solution of iodine monochloride (6.26 g, 38.6 mmol) in dichloromethane (38.6 mL) via cannula over 5 min. After 30 min, additional iodine monochloride (1.25 g, 7.7 mmol) in dichloromethane (7.7 mL) was added. After an additional 15 min, the reaction was quenched with saturated aqueous sodium bisulfite (100 mL) followed by saturated aqueous sodium bicarbonate (100 mL). After stirring vigorously for 15 min (caution, gas evolution) the reaction was diluted with water (150 mL) and the phases were separated. The aqueous phase was extracted with dichloromethane (150 mL), and the combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (10:90 ethyl acetate:hexanes eluent) to provide (+)-**5** (11.32 g, 82% yield) as a colorless oil: R_F 0.65 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.37 (br s, 1H), 7.33-7.24 (comp m, 5H), 4.98 (s, 1H), 3.85 (s, 1H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 13.2 Hz, 1H), 3.64-3.54 (comp m, 2H), 3.52 (d, *J* = 7.2 Hz, 1H), 2.33 (m, 1H), 2.09 (dd, *J* = 13.2, 9.3 Hz, 1H), 1.69 (ddd, *J* = 13.2, 7.2, 5.5 Hz, 1H), 1.02 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 171.1, 144.1, 137.7, 128.7, 128.5, 127.5, 65.7, 63.5, 62.8, 52.6, 46.6, 32.1, 18.3, 12.2; IR (NaCl/film) 2941, 2864,

1703, 1632, 1280, 1104, 683 cm^{-1}; HRMS (FAB) calc'd for $[C_{24}H_{37}IN_2O_2Si+H]^+$: *m/z* 541.1748, found 541.1755; $[\alpha]_D^{25}$ +47.3° (c = 1.0, acetone).



4 *(+)-5* *(+)-13*

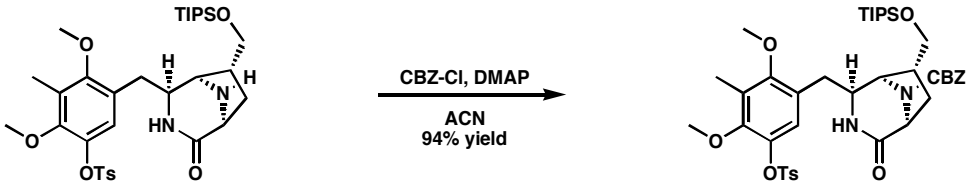
Aryl eneamide (+)-13. To a benzene (138 mL) solution of aryl boronic ester **4** (3.1 g, 6.9 mmol) and iodoeneamide **(+)-5** (3.75 g, 6.9 mmol) were added methanol (27.6 mL), 2.0 M aqueous potassium carbonate (13.8 mL, 27.6 mmol) and tetrakis(triphenylphosphine)palladium (399 mg, 345 μmol, 5 mol%). The reaction was deoxygenated by twice freezing under vacuum, flushing with argon, and melting. The reaction was then sealed under argon and heated to 70 °C for 3.5 h. The mixture was then cooled to 23 °C, diluted with water (50 mL) and saturated aqueous sodium chloride (50 mL), and extracted with ethyl acetate (100 mL) followed by dichloromethane (100 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (15:85 to 20:80 ethyl acetate:hexanes eluent) to provide **(+)-13** (3.47 g, 69% yield) as a yellow oil: R_F 0.37 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.35-7.19 (comp m, 7H), 6.75 (s, 1H), 5.17 (s, 1H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.72-3.58 (comp m, 4H), 3.67 (s, 3H), 3.64 (s, 3H), 3.52 (d, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 2.35 (m, 1H), 2.14 (s, 3H), 2.09 (dd, *J* = 12.6, 9.0 Hz, 1H), 1.69 (ddd, *J* = 12.6, 7.2, 6.0 Hz, 1H), 1.01 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 153.9, 150.6, 145.5, 139.2, 138.3, 137.4, 135.1, 133.4, 129.9, 128.9, 128.6, 127.6, 127.5, 123.8, 122.2, 100.2, 66.0, 63.8, 62.8, 61.2, 60.3, 52.8, 47.4, 32.6, 22.1, 18.4, 12.3, 10.2; IR (NaCl/film) 2942, 2865, 1694, 1661, 1378, 1178, 1110, 993, 551 cm^{-1}; HRMS (FAB) calc'd for $[C_{40}H_{54}N_2O_7SSi+H]^+$: *m/z* 735.3499, found 735.3508; $[\alpha]_D^{25}$ +40.1° (c = 0.5, acetone).



(+)-13 *(-)-14*

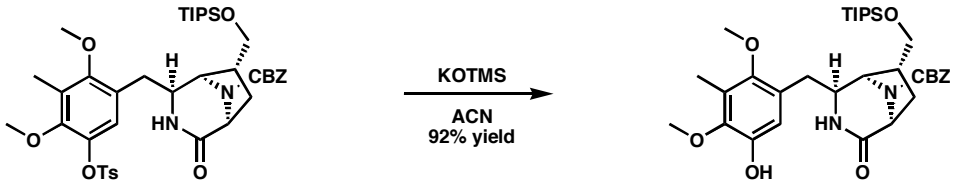
Ketopiperazine (-)-14. To an ethanol (58 mL) solution of **(+)-13** (2.13 g, 2.90 mmol) were added trifluoroacetic acid (4.5 mL, 58 mmol) and palladium on carbon (10% w/w, 4.26 g). The reaction was pressurized to 1000 psi with hydrogen in a stainless steel reaction vessel for 28 h. The reaction was then diluted with water (175 mL), saturated aqueous sodium bicarbonate (175 mL), and saturated aqueous sodium chloride (175 mL), and extracted with ethyl acetate (150 mL, 2 x 100 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography (100 chloroform to 5:95 triethylamine:chloroform eluent) to provide **(-)-14** (1.345 g, 72% yield) and a colorless oil: R_F 0.52 (10:90 methanol:chloroform); ^{1}H NMR

(300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 1H), 5.30 (s, 1H), 3.79-3.68 (comp m, 6H), 3.67 (s, 3H), 3.59 (app q, *J* = 8.5 Hz, 1H), 3.47 (s, 1H), 2.69 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.63-2.49 (comp m, 2H), 2.47 (s, 3H), 2.23-2.04 (comp m, 2H), 2.15 (s, 3H), 1.62 (ddd, *J* = 12.8, 6.6, 6.6 Hz, 1H), 1.07 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 156.1, 150.9, 145.5, 138.9, 133.2, 129.9, 128.5, 127.3, 125.7, 122.2, 66.3, 61.0, 60.8, 60.3, 60.0, 58.8, 38.6, 35.2, 33.0, 22.1, 18.4, 12.2, 10.3; IR (NaCl/film) 2943, 2866, 1678, 1483, 1377, 1178, 1109, 1008 cm^{-1}; HRMS (FAB) calc'd for $[C_{33}H_{50}N_2O_7SSi+H]^+$: *m/z* 647.3186, found 647.3183; $[\alpha]_D^{23}$ -15.9° (c = 1.0, acetone).



(-)-14 ***(-)-SI10***

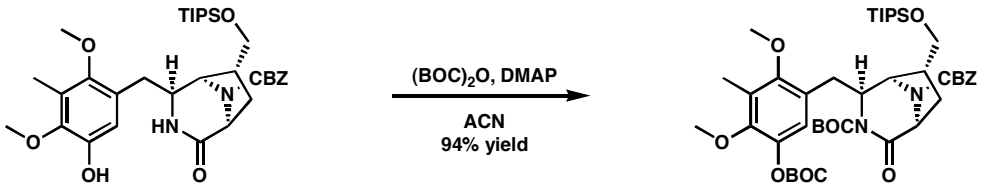
Carbamate (-)-SI10. To a solution of **(-)-14** (700 mg, 1.08 mmol) in acetonitrile (21.6 mL) were added *N,N*-dimethylaminopyridine (463 mg, 3.8 mmol) and benzyl-chloroformate (543 μL, 3.8 mmol). After 40 min, the reaction was quenched into saturated aqueous ammonium chloride (150 mL) and extracted into ethyl acetate (3 x 50 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (25:25:50 ethyl acetate:dichloromethane:hexanes eluent) to provide **(-)-SI10** (794 mg, 94% yield) as a white foam: R_F 0.46 (70:30 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, 50°C) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.35-7.23 (comp m, 7H), 6.74 (s, 1H), 5.36 (s, 1H), 5.17 (d, *J* = 12.3 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 6.6 Hz, 1H), 4.33 (s, 1H), 3.93 (m, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.62 (m, 1H), 3.48 (app t, *J* = 9.5 Hz, 1H), 2.70 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.65-2.54 (comp m, 2H), 2.42 (s, 3H), 2.15 (dd, *J* = 12.6, 8.7 Hz, 1H), 2.13 (s, 3H), 1.65 (ddd, *J* = 12.8, 6.6, 6.0 Hz, 1H), 1.05 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 50 °C) δ 170.9, 156.2, 153.8, 151.2, 145.4, 139.0, 136.3, 133.5, 129.8, 128.6, 128.5, 128.2, 128.0, 127.3, 125.1, 122.1, 67.5, 65.7, 60.9, 60.7, 59.1, 58.8, 56.4, 39.1, 34.0, 32.6, 21.9, 18.3, 12.3, 10.3; IR (NaCl/film) 2943, 2866, 1709, 1685, 1378, 1178, 1109 cm^{-1}; HRMS (FAB) calc'd for $[C_{41}H_{56}N_2O_9SSi+H]^+$: *m/z* 781.3554, found 781.3528; $[\alpha]_D^{25}$ -20.8° (c = 1.0, acetone).



(-)-SI10 ***(-)-2***

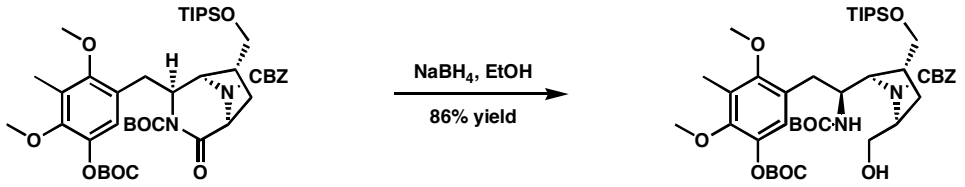
Phenol (-)-2. To a solution of **(-)-SI10** (1 g, 1.28 mmol) in acetonitrile (25 mL) was added potassium trimethylsilanoate (90% grade, 1.82 g, 12.8 mmol). The reaction was maintained at 20 °C for 1.5 h, quenched with saturated aqueous ammonium chloride (25 mL), and stirred vigorously for 10 min. The mixture was diluted with saturated aqueous sodium chloride (150

mL), acidified to pH 5 with concentrated hydrochloric acid, and extracted with ethyl acetate (3 x 100 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (50:50 to 80:20 ethyl acetate:hexanes eluent) to provide **(-)-2** (735 mg, 92% yield) as a white foam: R_F 0.42 (70:30 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, 50 °C) □ 7.37-7.29 (comp m, 5H), 6.59 (s, 1H), 6.03 (s, 1H), 5.66 (s, 1H), 5.19 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 4.52 (d, *J* = 6.6 Hz, 1H), 4.39 (s, 1H), 4.05 (br s, 1H), 3.77 (s, 3H), 3.69-3.61 (comp m, 4H), 3.52 (m, 1H), 2.76 (dd, *J* = 13.8, 3.9 Hz, 1H), 2.71-2.61 (comp m, 2H), 2.23 (s, 3H), 2.20 (dd, *J* = 13.2, 8.7 Hz, 1H), 1.67 (ddd, *J* = 12.8, 6.6, 6.0 Hz, 1H), 1.08 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 50 °C) □ 171.3, 154.0, 150.5, 145.9, 145.5, 136.4, 128.6, 128.2, 128.0, 125.5, 125.2, 114.2, 67.5, 65.8, 60.8, 59.0, 56.6, 39.3, 34.1, 32.7, 18.3, 12.3, 10.2; IR (NaCl/film) 3306, 2943, 2865, 1709, 1679, 1457, 1418, 1307, 1112 cm^{-1}; HRMS (FAB) calc'd for $[C_{34}H_{50}N_2O_7Si+H]^+$: *m/z* 627.3465, found 627.3469; $[\alpha]_D^{24}$ -30.5° (c = 1.0, acetone).



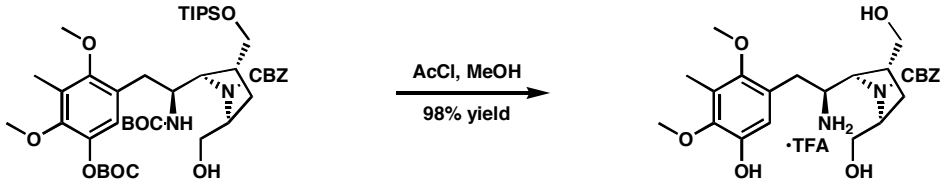
(-)-2 *(-)-SI11*

Activated lactam (-)-SI11. To a solution of **(-)-2** (960 mg, 1.53 mmol) in acetonitrile (15.3 mL) were added *N,N*-dimethylaminopyridine (935 mg, 7.66 mmol) and di-*tert*-butyl dicarbonate (1.67 g, 7.66 mmol). The reaction was maintained at 20 °C for 25 min, diluted with water (150 mL), and extracted with ethyl acetate (2 x 75 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (10:90 to 20:80 ethyl acetate:hexanes) to provide **(-)-SI11** (1.22 g, 96% yield) as an off-white foam: R_F 0.63 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, 50°C) □ 7.40-7.22 (comp m, 5H), 6.86 (s, 1H), 5.16 (d, *J* = 12.8 Hz, 1H), 5.04 (d, *J* = 12.8 Hz, 1H), 4.64 (app d, *J* = 6.6 Hz, 2H), 3.93 (d, *J* = 4.5 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 3.61 (br s, 1H), 3.28 (dd, *J* = 9.3, 7.8 Hz, 1H), 3.10 (dd, *J* = 13.7, 4.4 Hz, 1H), 2.84-2.70 (comp m, 2H), 2.21 (s, 3H), 2.17 (dd, *J* = 13.8, 8.7 Hz, 1H), 2.05 (m, 1H), 1.57 (s, 9H), 1.54 (s, 9H), 0.99 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 50 °C) □ 169.8, 155.2, 153.4, 152.4, 151.8, 150.1, 140.7, 136.3, 128.6, 128.1, 127.9, 126.2, 124.8, 121.2, 84.1, 83.4, 79.4, 67.4, 65.8, 60.7, 60.1, 57.1, 38.5, 32.9, 30.6, 28.6, 28.2, 28.0, 18.2, 12.2, 10.2; IR (NaCl/film) 2943, 2866, 1762, 1717, 1275, 1234, 1154 cm^{-1}; HRMS (FAB) calc'd for $[C_{44}H_{66}N_2O_{11}Si+H]^+$: *m/z* 827.4515, found 827.4498; $[\alpha]_D^{23}$ -26.2° (c = 1.0, $CHCl_3$).



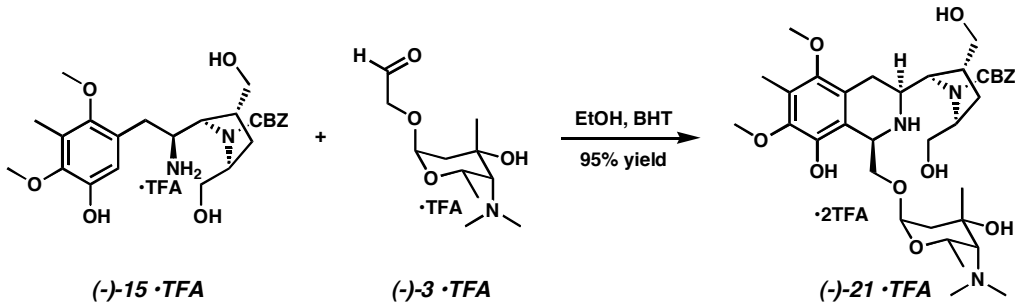
(-)-SI11 ***(-)-SI12***

Protected aminotriol (-)-SI12. To a solution of **(-)-SI11** (1.22 g, 1.47 mmol) in ethanol (14.7 mL) was added sodium borohydride (1.12 g, 29.5 mmol). The reaction was maintained at 20 °C for 1 h 45 min, then quenched slowly (caution, gas evolution) with saturated aqueous ammonium chloride (100 mL), diluted with water (20 mL), and extracted with dichloromethane (50 mL, 2 x 25 mL). The combined organics were dried over sodium sulfate, concentrated, and purified by flash chromatography and silica gel (25:75 to 35:65 ethyl acetate:hexanes eluent) to provide **(-)-SI12** (1.05 g, 86 % yield) as a white foam: R_F 0.27 (30:70 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, 50 °C) □ 7.43-7.29 (comp m, 5H), 6.73 (s, 1H), 5.18 (s, 2H), 4.10 (m, 1H), 3.97-3.85 (comp m, 2H), 3.80 (dd, *J* = 11.6, 2.9 Hz, 1H), 3.75 (s, 3H), 3.63 (dd, *J* = 11.7, 6.6 Hz, 1H), 3.59-3.47 (comp m, 5H), 2.84 (br d, *J* = 11.7 Hz, 1H), 2.46 (br t, *J* = 11.6 Hz, 1H), 2.35 (m, 1H), 2.20 (s, 3H), 2.02-1.86 (comp m, 2H), 1.56 (s, 9H), 1.26 (s, 9H), 1.06 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 50 °C) □ 157.5, 155.9, 155.2, 151.9, 149.6, 140.4, 136.5, 128.6, 128.3, 128.2, 127.2, 125.5, 121.6, 83.2, 79.2, 67.9, 67.2, 65.8, 65.3, 61.3, 60.7, 60.6, 55.0, 42.4, 33.1, 29.3, 28.5, 28.0, 18.3, 12.3, 10.1; IR (NaCl/film) 3353, 2943, 2866, 1761, 1698, 1275, 1233, 1156 cm^{-1}; HRMS (FAB) calc'd for $[C_{44}H_{70}N_2O_{11}Si+H]^+$: *m/z* 831.4828, found 831.4827; $[\alpha]_D^{24}$ -7.6° (c = 1.0, acetone).



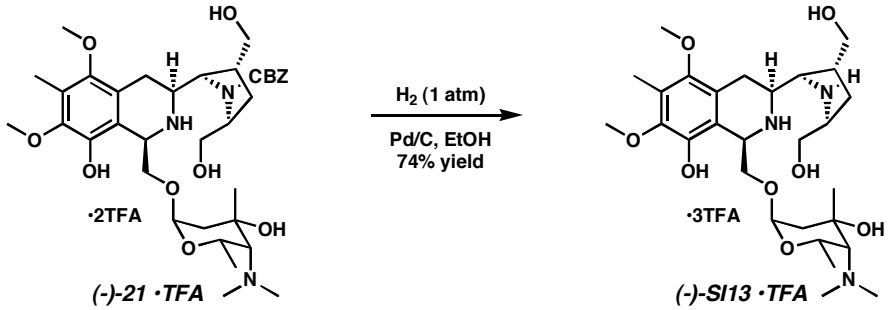
(-)-SI12 ***(-)-15 ·TFA***

Aminotriol (-)-15. To a cooled (0 °C) solution of **(-)-SI12** (250 mg, 300 □mol) in methanol (6 mL) was added acetyl chloride (427 □L, 6 mmol) dropwise over 30 sec. The reaction was warmed to 20 °C for 9 h, concentrated, and purified by preparative HPLC to provide **(-)-15** trifluoroacetate (175 mg, 98% yield) as a colorless, highly viscous oil: R_F 0.11 (10:90 methanol:chloroform); ^{1}H NMR (300 MHz, CD_3OD, 50 °C) □ 7.32 (br s, 5H), 6.63 (s, 1H), 5.12 (br s, 2H), 4.11-4.01 (comp m, 2H), 3.99 (app t, *J* = 3.0 Hz, 1H), 3.90 (app td, *J* = 7.4, 2.4 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.59-3.46 (comp m, 3H), 2.92 (br s, 1H), 2.75 (m, 1H), 2.50 (ddd, *J* = 13.8, 6.3, 3.7 Hz, 1H), 2.19 (s, 3H), 2.17 (dd, *J* = 15.3, 7.8 Hz, 1H), 2.02 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 75 °C) □ 154.7, 149.2, 145.8, 145.4, 136.3, 128.0, 127.4, 127.0, 124.0, 123.3, 115.2, 66.1, 63.0, 62.1, 60.9, 59.9, 59.1, 58.5, 54.6, 30.3, 28.4, 9.2; IR (NaCl/film) 3272, 2946, 2896, 1694, 1674, 1418, 1204, 1134 cm^{-1}; HRMS (FAB) calc'd for $[C_{25}H_{34}N_2O_7+H]^+$: *m/z* 475.2444, found 475.2445; $[\alpha]_D^{24}$ -11.4° (c = 0.48, methanol).



(-)-15 ·TFA *(-)-3 ·TFA* *(-)-21 ·TFA*

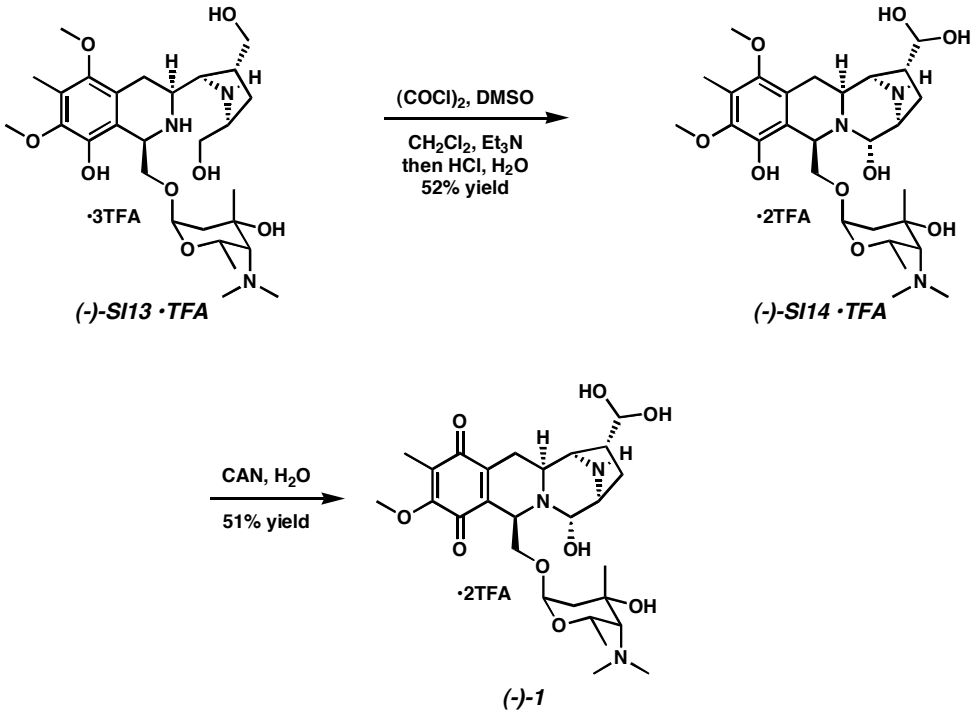
Tetrahydroisoquinoline (-)-21. To neat **(-)-15** trifluoroacetate (50 mg, 85 μmol) were added 2,6-di-*tert*-butyl-4-methyl phenol (9.3 mg, 42.5 μmol) and a solution of **(-)-3** trifluoroacetate (50 mg, 144.7 μmol) in ethanol (1.7 mL). The reaction was sealed under argon in a foil-wrapped vial at 20 °C. After 36 h, additional **(-)-3** (5 mg, 21.6 μmol) was added. After 63 h, the reaction was concentrated and purified by preparative HPLC to provide **(-)-21** bis-trifluoroacetate (74 mg, 95% yield) as a colorless, highly viscous oil: R_F 0.27 (10:90 methanol:chloroform); ^{1}H NMR (300 MHz, CD_3OD, 45 °C) δ 7.43-7.32 (comp m, 5H), 5.29 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.12 (d, *J* = 3.3 Hz, 1H), 4.97 (s, 1H), 4.51 (br d, *J* = 7.8 Hz, 1H), 4.18 (m, 1H), 4.02 (br d, *J* = 8.7 Hz, 1H), 3.83 (app d, *J* = 9.9 Hz, 1H), 3.80-3.57 (comp m, 6H), 3.73 (s, 3H), 3.64 (s, 3H), 3.36 (d, *J* = 6.6 Hz, 1H), 3.04 (s, 6H), 3.01 (s, 1H), 2.62-2.46 (comp m, 2H), 2.21 (s, 3H), 2.13-2.01 (comp m, 3H), 1.93 (ddd, *J* = 21.9, 11.3, 10.8 Hz, 1H), 1.44 (d, *J* = 6.9 Hz, 3H), 1.19 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD, 50 °C) δ 159.5, 150.1, 146.8, 144.4, 137.4, 129.7, 129.4, 128.9, 126.0, 124.0, 115.5, 98.1, 72.1, 69.5, 67.9, 66.8, 64.9, 64.5, 63.9, 63.5, 61.7, 61.3, 61.2, 57.5, 55.4, 44.8, 39.9, 30.8, 30.5, 21.9, 18.6, 10.0; IR (NaCl/film) 3307, 3064, 2945, 1682, 1204, 1180, 1131 cm^{-1}; HRMS (FAB) calc'd for $[C_{36}H_{53}N_3O_{10}+H]^+$: *m/z* 688.3809, found 688.3835; $[\alpha]_D^{26}$ -71.3° (c = 0.5, methanol).



(-)-21 ·TFA *(-)-SI13 ·TFA*

Tetrahydroisoquinoline (-)-SI13. To a solution of **(-)-21** bis-trifluoroacetate (74 mg, 80.7 μmol) in ethanol (8 mL) was added palladium on carbon (10% w/w, 15 mg). The reaction was purged and flushed with hydrogen, then maintained under a balloon of hydrogen for 30 min. The mixture was filtered through celite, concentrated, and purified by preparative HPLC to provide **(-)-SI13** tris-trifluoroacetate (53.5 mg, 74% yield) as a colorless, highly viscous oil: R_F 0.25 (10:90 methanol: chloroform, eluted twice); ^{1}H NMR (300 MHz, D_2O) δ 5.17 (s, 1H), 5.11 (d, *J* = 3.9 Hz, 1H), 4.66 (dd, *J* = 10.8, 3.3 Hz, 1H), 4.01-3.85 (comp m, 4H), 3.82-3.61 (comp m, 5H), 3.77 (s, 3H), 3.71 (s, 3H), 3.34 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.04 (s, 6H), 3.00 (s, 1H), 2.89 (dd, *J* = 16.5, 12.6 Hz, 1H), 2.75 (m, 1H), 2.24 (s, 3H), 2.22-1.93 (comp m, 3H), 1.89 (d, *J* = 15.0 Hz,

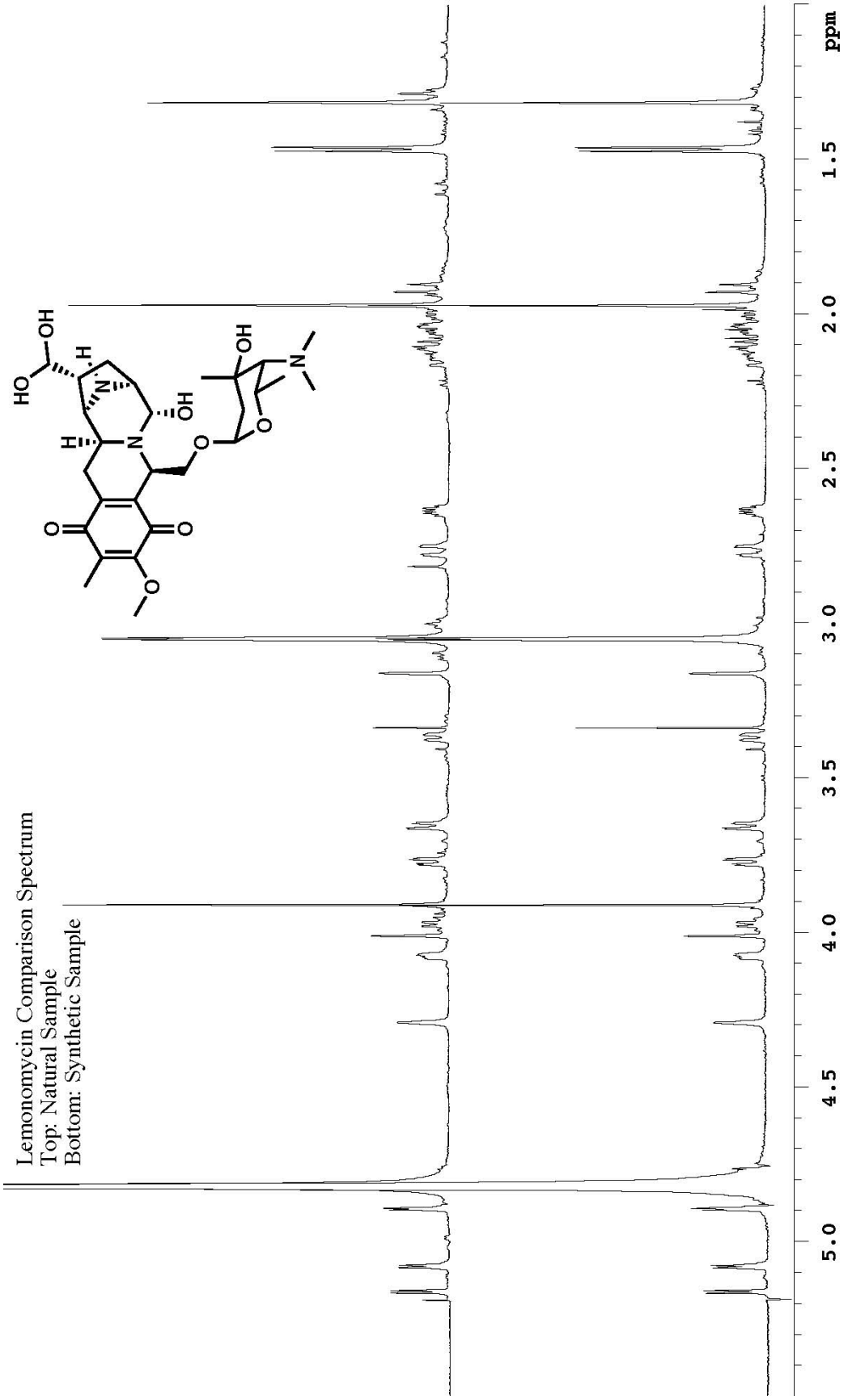
1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, D_2O) □ 148.2, 145.0, 142.9, 125.6, 122.3, 114.1, 96.2, 70.2, 67.2, 64.2, 64.0, 62.5, 62.1, 61.1, 61.0, 60.9, 60.1, 55.6, 54.2, 47.2, 43.5, 41.9, 37.3, 28.5, 27.9, 24.8, 17.5, 9.1; IR (NaCl/film) 3296, 2947, 1682, 1468, 1417, 1204, 1131, 1054, 1004, 800, 723 cm^{-1}; HRMS (FAB) calc'd for $[C_{28}H_{47}N_3O_8+H]^+$: *m/z* 554.3441, found 554.3463; $[\alpha]_D^{24}$ -83.1° (c = 0.25, methanol).



SI14 and Lemonomycin (-)-1. To a -78 °C solution of dimethyl sulfoxide (7.9 □L, 111.6 □mol) in dichloromethane (744 □L) was added oxalyl chloride (4.9 □L, 55.8 □mol). After 30 min, this solution was added via cannula to a -78 °C solution of **(-)-SI13** (10.0 mg, 11.16 □mol) in 4:1 dichloromethane:dimethyl sulfoxide (560 □L). The reaction was maintained at -78 °C for 1h, after which triethylamine (23.3 □L, 167.4 □mol) was added. After an additional 15 min, the reaction was warmed to 0 °C over 10 min. The reaction was extracted into 1M aqueous hydrochloric acid (2 x 1 ml) and warmed to 20 °C for 41 h. The mixture was then purified by preparative HPLC to provide **SI14** bis-trifluoroacetate (4.6 mg, 52% yield) as a colorless film, which was used immediately in the next reaction.

To a cooled (0 °C) solution of **SI14** (4.6 mg, 5.78 □mol) in water (1.16 mL) was added cerium(IV) ammonium nitrate (7.9 mg, 14.5 □mol). After 10 min, the reaction mixture was purified by preparative HPLC to provide lemonomycin (**(-)-1**, 2.3 mg, 51% yield) as a yellow film: ^{1}H NMR (600 MHz, D_2O) □ 5.16 (d, *J* = 4.8 Hz, 1H), 5.08 (d, *J* = 4.8 Hz, 1H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.29 (s, 1H), 4.08 (dd, *J* = 6.6, 2.4 Hz, 1H), 4.01 (s, 1H), 3.98 (br q, *J* = 7.2 Hz, 1H), 3.91 (s, 3H), 3.77 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.66 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.37 (br d, *J* = 9.6 Hz, 1H), 3.16 (s, 1H), 3.054 (s, 3H), 3.048 (s, 3H), 2.77 (dd, *J* = 17.4, 2.4 Hz, 1H), 2.64 (ddd, *J* = 9.6, 4.8, 4.8 Hz, 1H), 2.17-1.98 (comp m, 4H), 1.97 (s, 3H), 1.92 (d, *J* = 14.4 Hz, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, D_2O) □ 190.3, 184.6, 158.2, 144.6, 140.6, 133.4, 99.8, 92.9, 81.3, 72.6, 71.3, 69.7, 64.9, 64.1, 63.3, 62.8, 54.4, 52.4, 49.7, 44.4, 43.4,

40.6, 31.3, 28.5, 26.5, 19.9, 11.0; IR (NaCl/film) 3249, 3094, 2943, 1673, 1611, 1443, 1387, 1329, 1207, 1137, 802, 724 cm^{-1}; UV-Vis (methanol) λ_{max} 272, 363 nm; HRMS (FAB) calc'd for $[C_{27}H_{41}N_3O_9\text{-}OH]^+$: *m/z* 534.2815, found 534.2839; $[\alpha]_D^{23}$ -124.2° (c = 0.1, H_2O).


Lemonomycin Comparison Spectrum
Top: Natural Sample
Bottom: Synthetic Sample
ppm
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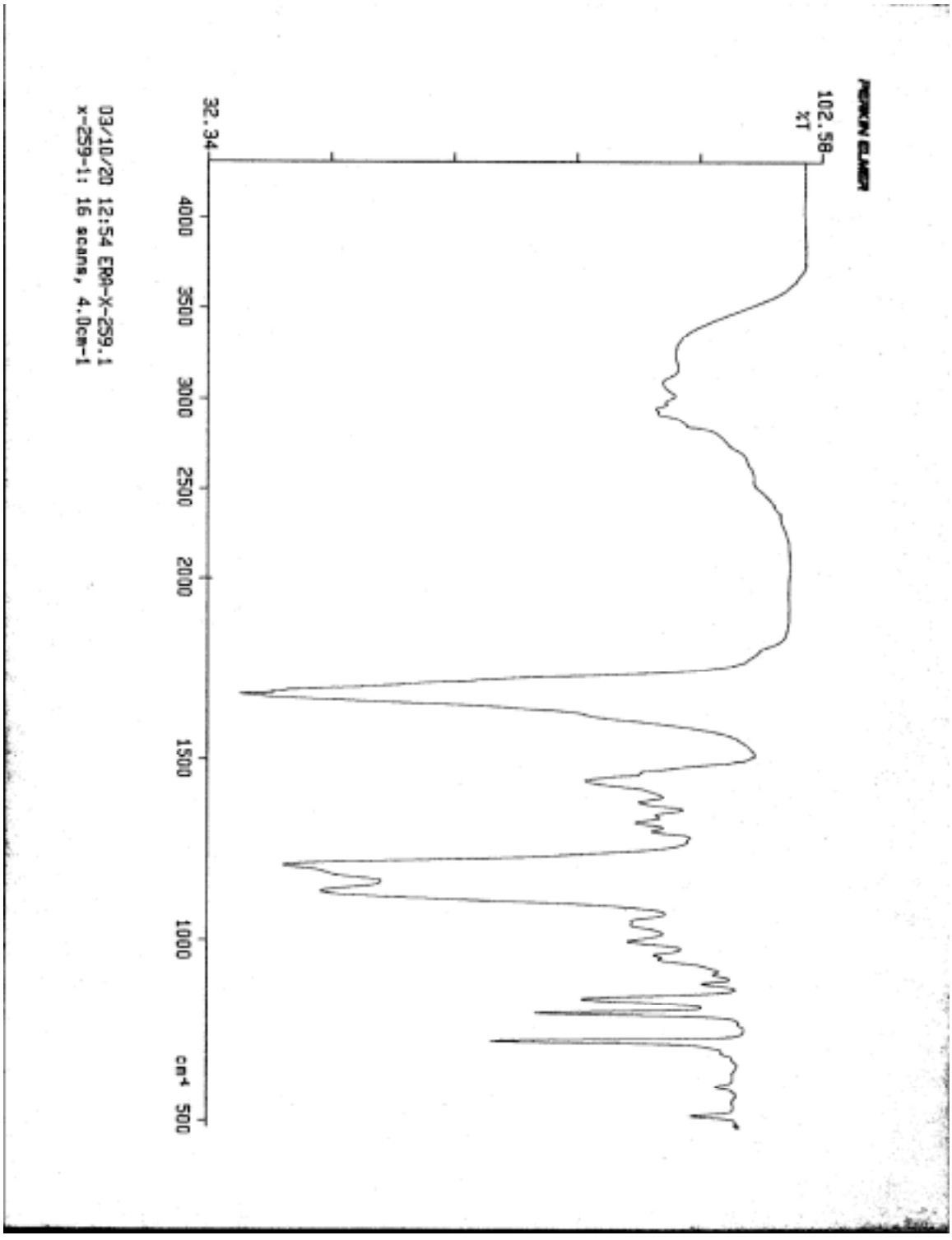
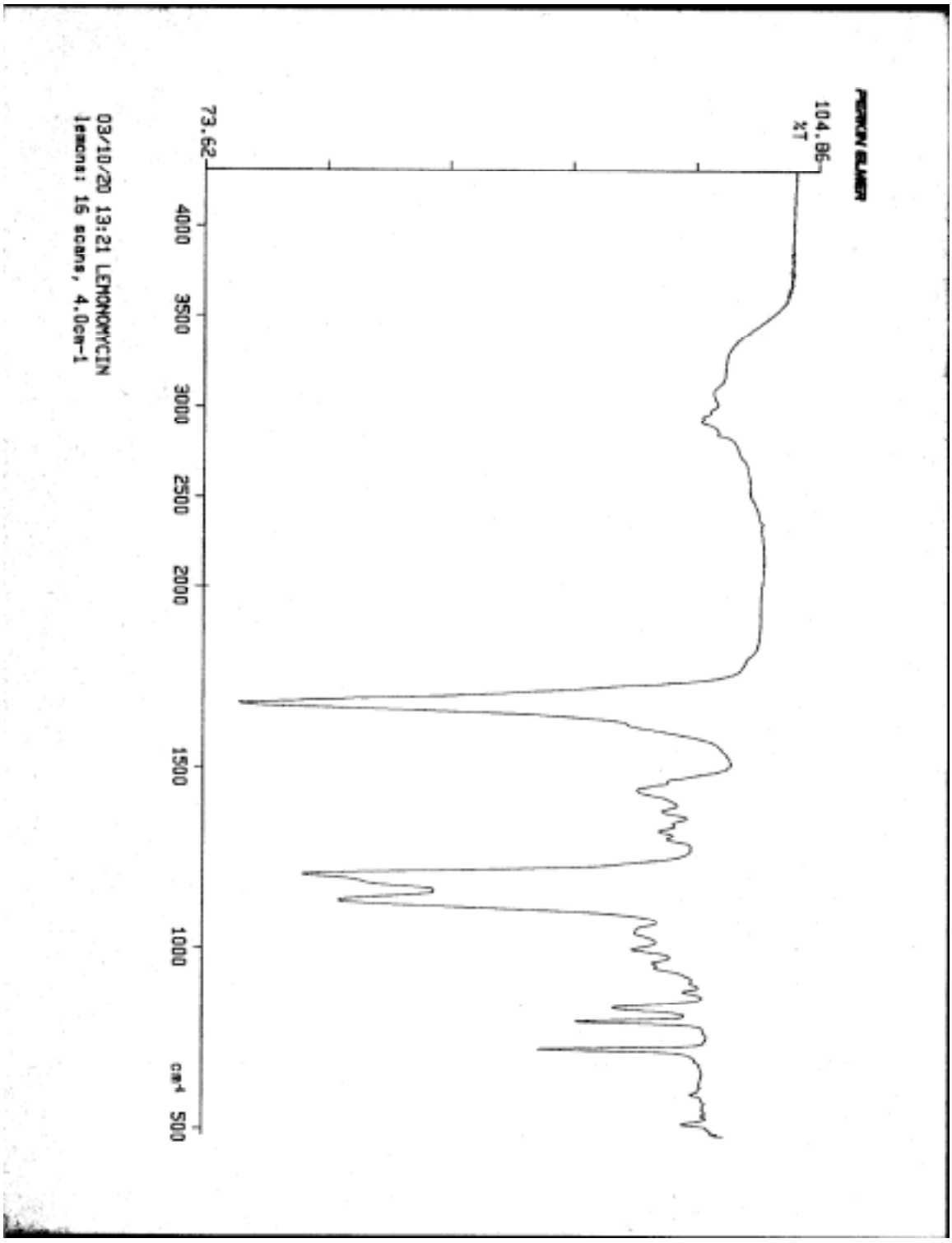
4.5
4.0
3.5
3.0
2.5
2.0
1.5
HO
OH
H
N
OH
H
N
O
O
O
O
OH
N
O
O

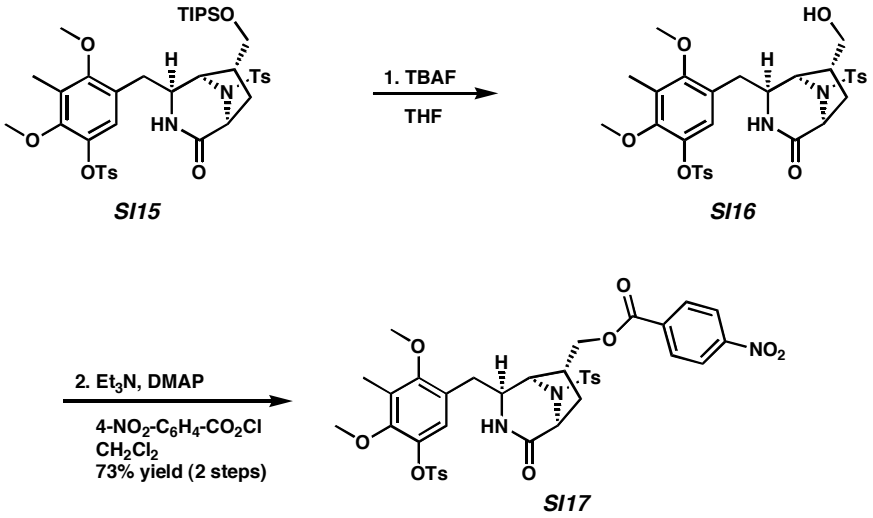
FT-IR of Lemonomycin, Synthetic sample



FT-IR of Lemonomycin, Natural sample



Tosamide SI15. To a solution of **14** (200 mg, 310 μmol) in acetonitrile (6.2 mL) were added triethylamine (130 μL, 930 μmol), *N,N*-dimethylaminopyridine (19 mg, 155 μmol), and *p*-toluenesulfonyl chloride (88.7 mg, 465 μmol). The reaction was maintained at 20 °C for 1.5 h, diluted with ethyl acetate (100 mL), washed with saturated aqueous ammonium chloride (50 mL) and saturated aqueous sodium chloride (50 mL), dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (40:60 to 50:50 ethyl acetate:hexanes) to provide **SI15** (208 mg, 84% yield) as a colorless oil: R_F 0.30 (50:50 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.72 (s, 1H), 5.19 (s, 1H), 4.35 (s, 1H), 4.18 (d, *J* = 6.6 Hz, 1H), 3.89 (m, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 3.61 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.49 (app t, *J* = 9.9 Hz, 1H), 2.72-2.53 (comp m, 3H), 2.48 (s, 3H), 2.40 (s, 3H), 2.17 (dd, *J* = 12.9, 8.7 Hz, 1H), 2.16 (s, 3H), 1.67 (ddd, *J* = 12.9, 6.6, 6.3 Hz, 1H), 1.10 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 156.3, 155.7, 151.3, 145.7, 144.4, 139.1, 137.1, 133.3, 130.1, 130.0, 128.6, 127.6, 125.0, 122.1, 65.0, 61.1, 61.0, 60.8, 60.4, 56.9, 39.8, 34.3, 32.3, 22.0, 21.8, 18.3, 12.1, 10.3; IR (NaCl/film) 3334, 3200, 2943, 2866, 1687, 1483, 1376, 1176, 1182, 1107, 1007, 995, 664, 551 cm^{-1}; HRMS (FAB) calc'd for $[C_{40}H_{56}N_2O_9S_2Si+H]^+$: *m/z* 801.3275, found 801.3296.



Nitrobenzoate SI17. To a solution of **SI15** (175 mg, 219 μmol) in tetrahydrofuran (4.4 mL) was added tetrabutylammonium fluoride (1 M in tetrahydrofuran, 328 μL, 328 μmol). After 10 min, the reaction was diluted with ethyl acetate (50 mL), washed with water (50 mL) followed by saturated aqueous sodium chloride (35 mL), dried over sodium sulfate, concentrated, and filtered through a pad of silica gel (ethyl acetate eluent) to provide **SI16** (140 mg, 99% yield), which was used without further purification.

To a solution of **SI16** (60 mg, 93 μmol) in dichloromethane (1.9 mL) were added *N,N*-dimethylaminopyridine (5.7 mg, 46.5 μmol), triethylamine (25.9 μL, 186 μmol), and 4-nitrobenzoyl chloride (25.9 mg, 139.5 μmol). After 10 min the reaction was diluted with dichloromethane (35 mL), washed with water (35 mL), dried over sodium sulfate, concentrated, and purified by flash chromatography on silica gel (60:40 ethyl acetate:hexanes eluent) to provide **SI17** (54.5 mg, 74% yield) as a white, crystalline solid. Crystals of sufficient quality for X-ray analysis were grown from acetone:water by slow evaporation: m.p. 156.5-158 °C (corrected for benzanilide, mp. 163-163.5 °C[5]); R_F 0.47 (85:15 ethyl acetate:hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 9.3 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 1H), 5.22 (s, 1H), 4.43 (dd, *J* = 11.1, 6.6 Hz, 1H), 4.38-4.28 (comp m, 2H), 4.26 (d, *J* = 6.6 Hz, 1H), 3.93 (ddd, *J* = 8.4, 4.4, 4.1 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.00 (ddd, *J* = 14.3, 7.7, 6.9 Hz, 1H), 2.69 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.59 (dd, *J* = 13.8, 8.7 Hz, 1H), 2.46 (s, 3H), 2.42 (s, 3H), 2.37 (dd, *J* = 13.2, 9.0 Hz, 1H), 2.11 (s, 3H), 2.02 (ddd, *J* = 13.2, 6.6, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 164.6, 156.1, 151.3, 151.0, 145.8, 144.8, 139.1, 136.6, 135.2, 133.2, 131.0, 130.3, 130.0, 128.6, 127.6, 127.5, 124.1, 124.0, 122.2, 67.1, 61.0, 60.94, 60.91, 60.4, 56.7, 36.0, 35.2, 32.2, 22.0, 21.8, 10.3; IR (NaCl/film) 3338, 3207, 2944, 1726, 1688, 1528, 1349, 1275, 1176, 1161, 1105, 1003, 721 cm^{-1}; HRMS (FAB) calc'd for $[C_{38}H_{39}N_3O_{12}S_2+H]^+$: *m/z* 794.2054, found 794.2047.

Crystal structure of SI17.

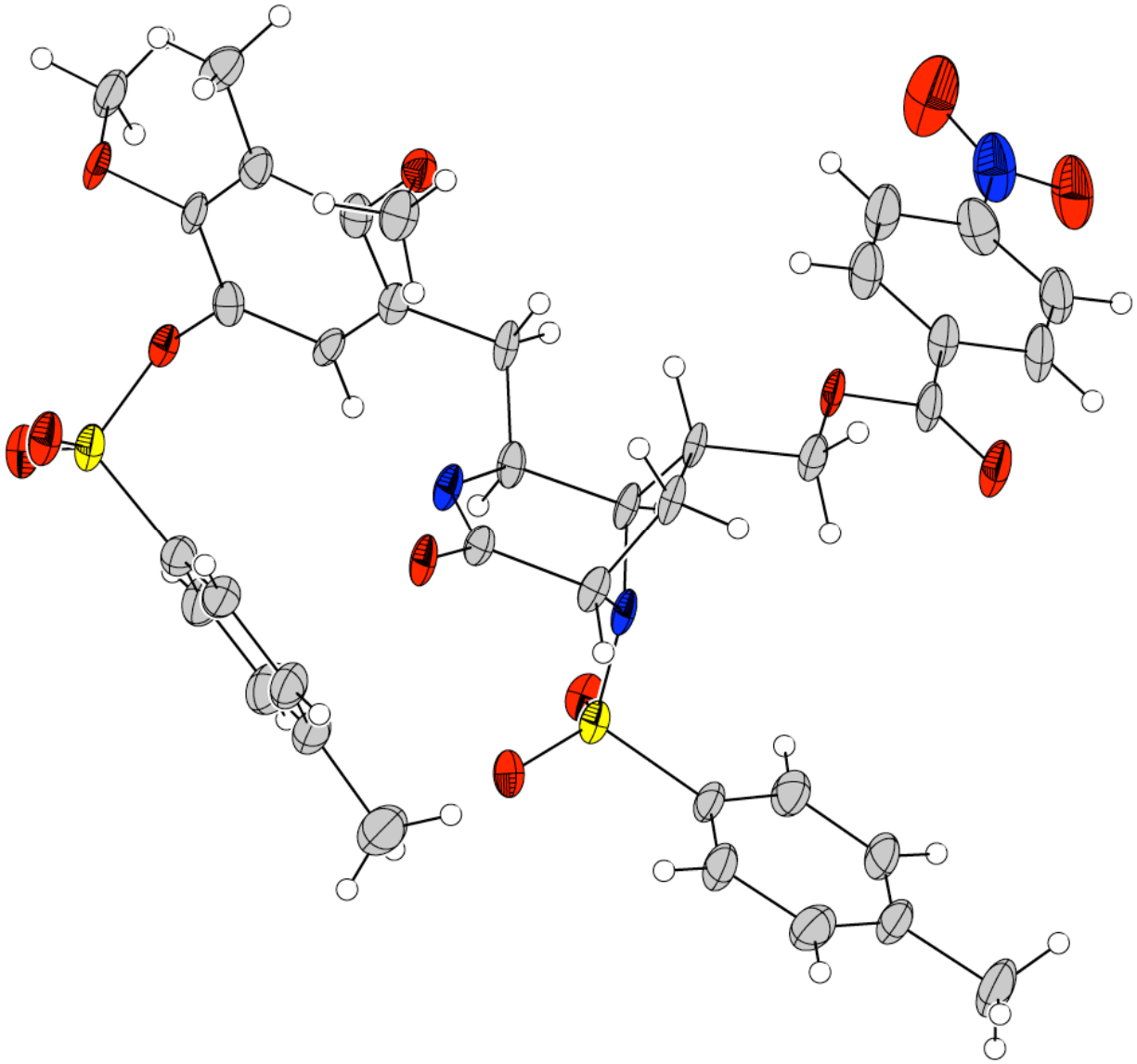


Table 2. Crystal data and structure refinement for SI17 (CCDC 219709).

Empirical formula	$C_{38}H_{38}N_3O_{12}S_2 \cdot C_3H_6O$
Formula weight	850.91
Crystallization Solvent	Acetone
Crystal Habit	Blade
Crystal size	0.59 x 0.21 x 0.07 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 4790 reflections used in lattice determination	2.31 to 27.48°	
Unit cell dimensions	a = 11.907(2) Å b = 13.420(2) Å c = 14.819(3) Å	a= 66.875(2)° b= 69.845(3)° g = 75.856(3)°
Volume	2028.1(6) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.393 Mg/m^3	
F(000)	894	
Data collection program	Bruker SMART v5.054	
q range for data collection	1.56 to 28.18°	
Completeness to q = 28.18°	88.5 %	
Index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-19 \le l \le 18$	
Data collection scan type	□ scans at 3 □ settings	
Data reduction program	Bruker SAINT v6.022	
Reflections collected	17713	
Independent reflections	8831 [R_{int}= 0.1081]	
Absorption coefficient	0.202 mm^{-1}	
Absorption correction	None	
Max. and min. transmission (predicted)	0.9860 and 0.8903	

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8831 / 5 / 517
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.605
Final R indices [I>2s(I), 4683 reflections]	R1 = 0.0784, *w*R2 = 0.1558
R indices (all data)	R1 = 0.1543, *w*R2 = 0.1704
Type of weighting scheme used	Sigma
Weighting scheme used	*w*=1/□2(Fo2)
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	1.430 and -0.784 e.Å^{-3}

Special Refinement Details

Refinement of F2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F2, conventional R-factors (R) are based on F, with F set to zero for negative F2. The threshold expression of F2 > 2□(F2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

References.

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