Development and Application of a New General Method for the Asymmetric Synthesis of *syn*- and *anti*-1,3-Amino Alcohols.

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Experimental Section

General Methods. Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. MgBr₂ and ZnBr₂ were purchased from Aldrich. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from Na/benzophenone ketyl. Diisopropylamine (*i*-Pr₂NH) was distilled from CaH₂. Toluene was distilled from Na. All aldehydes and ketones were distilled before use, except for isobutyraldehyde, which was obtained in a Sure/SealTM bottle from Aldrich. The concentration of commercially available solutions of *n*-butyllithium in pentane was determined by titration with 2,6-di-*tert*-butyl-4-methylphenol and 1,10-phenanthroline. All reactions were carried out under a N₂ atmosphere in flame- or oven-dried glassware. Unless otherwise noted, extracts were dried over Na₂SO₄. Chromatography was carried out with Merck 60 230-400 mesh silica gel according to the procedure described by Still.¹ Reactions and chromatography fractions were analyzed with thin layer chromatography on Merck 60 F₂₅₄ 0.25 micron silica plates. IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory and only partial data are listed. ¹H and ¹³C NMR spectra were obtained in CDCl₃ at room temperature. Chemical shifts in NMR spectra are expressed in ppm relative to CDCl₃. Coupling constants are reported in Hz. For **2n-q**, only the chemical shifts of the major isomer were listed. Unless otherwise noted, HPLC analysis was performed with a 25 cm x 5 μm ID Microsorb Si normal phase column with UV detection at 280 nm and at 254 nm. Elemental analyses and mass spectra were obtained from the Microanalytical Laboratory at the University of California, Berkeley. *tert*-Butanesulfinyl imines **1** were prepared as previously described.² Ketone **7** was prepared by the method of Grigg and co-workers.³

General Procedure A for the Addition of Metalloenamine Derived from *tert*-Butanesulfinyl Imine (*R*)-1 to Aldehydes. To a 0.240 M solution of *i*-Pr₂NH (1.20 equiv) in THF was added butyllithium in pentane (1.10 equiv) at 0 °C and the mixture was stirred for 30 min. The solution was then cooled to -78 °C and *tert*-butanesulfinyl imine (*R*)-1 (1.00 equiv) was added. After the reaction solution was stirred for 45 min at

$-78\text{ }^{\circ}\text{C}$, the additive (2.00 equiv) was added. The reaction mixture was stirred for 45 min, and the aldehyde (1.10-1.30 equiv) was added to the solution. Then, the mixture was stirred for 1-3 h at $-78\text{ }^{\circ}\text{C}$. To the reaction mixture was added 2*N* AcOH/THF (5 equiv), which was cooled to $-78\text{ }^{\circ}\text{C}$ before the addition. Brine and/or saturated aqueous NaHCO_3 solution was then added to the mixture with stirring. The organic layer was collected and the brine layer was extracted with EtOAc (2x). The combined organic portions were quickly dried, filtered, and concentrated. The addition products were purified by silica gel chromatography.

β -Hydroxy-*N*-Sulfinyl Imine 2a. General procedure A was followed with 223 mg (1.00 mmol) of (*R*)-**1a**, 368 mg (2.00 mmol) of MgBr_2 , and 112 mg (1.30 mmol) of trimethylacetaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 98:2 dr (98:2 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, $t_R = 6.1$ min; minor diastereomer, $t_R = 9.0$ min). Column chromatography (70:30 hexanes/EtOAc) afforded 198 mg (64%) of **2a**: IR 1568, 1590, 1602, 3311 cm^{-1} ; ^1H NMR (400 MHz) δ 1.00 (s, 9H), 1.38 (s, 9H), 3.27 (d, 1H, $J = 9.4$), 3.31-3.47 (m, 2H), 4.60 (apparent br d, 1H), 7.40-7.52 (m, 3H), 7.84 (d, 2H, $J = 7.0$); ^{13}C NMR (100 MHz) δ 22.9, 25.7, 35.5, 36.1, 59.0, 75.7, 127.5, 128.6, 131.7, 137.4, 177.6. Anal. Calcd. for $\text{C}_{17}\text{H}_{27}\text{NO}_2\text{S}$: C, 65.98; H, 8.79; N, 4.53. Found: C, 66.33; H, 8.92; N, 4.42.

β -Hydroxy-*N*-Sulfinyl Imine 2b. General procedure A was followed with 1.12 g (5.01 mmol) of (*R*)-**1a**, 1.84 g (10.0 mmol) of MgBr_2 , and 469 mg (6.50 mmol) of isobutyraldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 98:2 dr (98:2 hexanes/ethanol, 1.0 mL/min: major diastereomer, $t_R = 11.6$ min; minor diastereomer, $t_R = 21.1$ min). Column chromatography (80:20 hexanes/EtOAc) afforded 1.30 g (88%) of **2b**: IR 1567, 1590, 1601 cm^{-1} ; ^1H NMR (400 MHz) δ 1.00 (d, 3H, $J = 6.7$), 1.01 (d, 3H, $J = 6.7$), 1.37 (s, 9H), 1.74-1.82 (m, 1H), 3.21 (dd, 1H, $J = 12.4, 2.7$), 3.42 (dd, 1H, $J = 12.4, 11.2$), 3.51 (br s, 1H), 4.54 (apparent br d, 1H), 7.43 (t, 2H, $J = 7.3$), 7.49 (t, 1H, $J = 7.3$), 7.84 (d, 2H, $J = 7.3$); ^{13}C NMR (100 MHz) δ 17.8, 18.9, 23.1, 35.7, 38.2, 59.2, 73.0, 127.7, 128.9, 132.0, 137.6, 177.4. Anal. Calcd. for $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{S}$: C, 65.05; H, 8.53; N, 4.74. Found: C, 65.18; H, 8.55; N, 4.56.

β -Hydroxy-*N*-Sulfinyl Imine 2c. General procedure A was followed with 223 mg (1.00 mmol) of (*R*)-**1a**, 368 mg (2.00 mmol) of MgBr_2 , and 112 mg (1.30 mmol) of isovaleraldehyde. After the addition of the aldehyde, the reaction mixture was stirred for

3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 14.9 min; minor diastereomer, t_R = 30.7 min). Column chromatography (80:20 hexanes/EtOAc) afforded 232 mg (75%) of **2c**: IR 1567, 1590, 3319 cm^{-1} ; ^1H NMR (400 MHz) δ 0.90 (d, 3H, J = 6.6), 0.94 (d, 3H, J = 6.7), 1.29-1.41 (m, 1H), 1.36 (s, 9H), 1.52-1.60 (m, 1H), 1.84-1.94 (m, 1H), 3.22 (dd, 1H, J = 12.8, 3.5), 3.36 (dd, 1H, J = 12.8, 10.6), 3.82 (br s, 1H), 4.31 (apparent br d, 1H), 7.44 (t, 2H, J = 7.4), 7.50 (t, 1H, J = 7.4), 7.85 (d, 2H, J = 7.4); ^{13}C NMR (125 MHz) δ 22.1, 22.8, 23.4, 24.7, 41.7, 48.7, 58.8, 66.4, 127.5, 128.6, 131.8, 137.5, 176.7. Anal. Calcd. for $\text{C}_{17}\text{H}_{27}\text{NO}_2\text{S}$: C, 65.98; H, 8.79; N, 4.53. Found: C, 66.09; H, 9.02; N, 4.36.

β -Hydroxy-*N*-Sulfinyl Imine 2d. General procedure A was followed with 223 mg (1.00 mmol) of (*R*)-**1a**, 368 mg (2.00 mmol) of MgBr_2 , and 75.0 mg (1.30 mmol) of propionaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 10.1 min; minor diastereomer, t_R = 16.2 min). Column chromatography (70:30 hexanes/EtOAc) afforded 236 mg (84%) of **2d**: IR 1562, 1588, 3319 cm^{-1} ; ^1H NMR (400 MHz) δ 1.02 (t, 3H, J = 7.4), 1.37 (s, 9H), 1.61-1.66 (m, 2H), 3.25 (dd, 1H, J = 12.8, 3.3), 3.39 (dd, 1H, J = 12.8, 10.8), 3.69 (br s, 1H), 4.43 (apparent br d, 1H), 7.43 (t, 2H, J = 7.4), 7.50 (t, 1H, J = 7.4), 7.85 (d, 2H, J = 7.4); ^{13}C NMR (100 MHz) δ 9.9, 22.9, 32.1, 40.7, 58.9, 69.5, 127.5, 128.6, 131.7, 137.4, 176.7. Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{S}$: C, 64.02; H, 8.24; N, 4.98. Found: C, 63.76; H, 7.98; N, 4.99.

β -Hydroxy-*N*-Sulfinyl Imine 2e. General procedure A was followed with 446 mg (2.00 mmol) of (*R*)-**1a**, 901 mg (4.00 mmol) of ZnBr_2 , and 276 mg (1.30 mmol) of benzaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 92:8 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 8.0 min; minor diastereomer, t_R = 9.8 min). Column chromatography (70:30 hexanes/EtOAc) afforded 519 mg (79%) of **2e**: IR 1572, 1592, 1604, 3286 cm^{-1} ; ^1H NMR (400 MHz) δ 1.43 (s, 9H), 3.46 (dd, 1H, J = 13.1, 3.4), 3.70 (dd, 1H, J = 13.1, 11.3), 4.79-4.91 (m, 1H), 5.61 (apparent br d, 1H), 7.27-7.57 (m, 8H), 7.96 (d, 2H, J = 7.3); ^{13}C NMR (100 MHz) δ 22.9, 43.5, 59.2, 70.6, 125.5, 127.5, 127.7, 128.6, 128.9, 132.1, 137.1, 145.1, 176.0. Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_2\text{S}$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.40; H, 7.20; N, 4.37.

β -Hydroxy-*N*-Sulfinyl Imine 2f. General procedure A was followed with 203 mg (1.00 mmol) of (*R*)-**1b**, 368 mg (2.00 mmol) of MgBr_2 , and 95 mg (1.10 mmol) of

pivaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 99:1 dr (98:2 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 4.9 min; minor diastereomer, t_R = 7.7 min). Column chromatography (90:10 hexanes/EtOAc) afforded 266 mg (92%) of **2f**: IR 1607, 3307 cm^{-1} ; ^1H NMR (500 MHz) δ 0.91 (s, 9H), 1.20 (s, 9H), 1.25 (s, 9H), 2.78 (dd, 1H, J = 12.0, 3.3), 2.90 (dd, 1H, J = 12.0, 11.6), 3.47 (ddd, 1H, J = 11.6, 10.0, 3.3), 4.94 (d, 1H, J = 10.0); ^{13}C NMR (125 MHz) δ 22.7, 25.7, 28.8, 35.7, 36.2, 43.7, 58.3, 75.0, 190.1. Anal. Calcd. for $\text{C}_{15}\text{H}_{31}\text{NO}_2\text{S}$: C, 62.24; H, 10.79; N, 4.84. Found: C, 62.58; H, 11.03; N, 4.64.

β -Hydroxy-*N*-Sulfinyl Imine 2g. General procedure A was followed with 203 mg (1.00 mmol) of (*R*)-**1b**, 368 mg (2.00 mmol) of MgBr_2 , and 79 mg (1.10 mmol) of isobutyraldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 99:1 dr (98:2 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 6.1 min; minor diastereomer, t_R = 7.6 min). Column chromatography (90:10 hexanes/EtOAc) afforded 221 mg (80%) of **2g**: IR 1607, 3308 cm^{-1} ; ^1H NMR (500 MHz) δ 0.91 (d, 3H, J = 6.7), 0.95 (d, 3H, J = 6.7), 1.19 (s, 9H), 1.25 (s, 9H), 1.65 (dt, 1H, J = 5.8, 6.7, 6.7), 2.77 (dd, 1H, J = 12.3, 3.9), 2.89 (dd, 1H, J = 12.3, 11.1), 3.52 (dddd, 1H, J = 11.1, 10.1, 5.8, 3.3), 4.78 (d, 1H, J = 10.1); ^{13}C NMR (125 MHz) δ 17.9, 18.7, 22.7, 28.5, 35.9, 38.6, 43.5, 58.2, 72.4, 189.9. Anal. Calcd. for $\text{C}_{14}\text{H}_{29}\text{NO}_2\text{S}$: C, 61.05; H, 10.61; N, 5.09. Found: C, 61.23; H, 10.69; N, 4.91.

β -Hydroxy-*N*-Sulfinyl Imine 2h. General procedure A was followed with 203 mg (1.00 mmol) of (*R*)-**1b**, 368 mg (2.00 mmol) of MgBr_2 , and 64 mg (1.10 mmol) of propionaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 98:2 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 6.7 min; minor diastereomer, t_R = 9.1 min). Column chromatography (90:10 hexanes/EtOAc) afforded 220 mg (84%) of **2h**: IR 1604, 3361 cm^{-1} ; ^1H NMR (500 MHz) δ 0.91 (t, 3H, J = 7.4), 1.15 (s, 9H), 1.21 (s, 9H), 1.46 (dq, 2H, J = 6.2, 7.4), 2.75 (dd, 1H, J = 12.4, 4.7), 2.80 (dd, 1H, J = 12.4, 10.1), 3.65 (m, 1H), 4.64 (d, 1H, J = 10.2); ^{13}C NMR (125 MHz) δ 10.0, 22.6, 28.2, 32.4, 41.0, 43.3, 58.0, 69.0, 189.4. Anal. Calcd. for $\text{C}_{13}\text{H}_{27}\text{NO}_2\text{S}$: C, 59.73; H, 10.41; N, 5.36. Found: C, 59.92; H, 10.79; N, 5.29.

β -Hydroxy-*N*-Sulfinyl Imine 2i. General procedure A was followed with 203 mg (1.00 mmol) of (*R*)-**1b**, 368 mg (2.00 mmol) of MgBr_2 , and 117 mg (1.10 mmol) of benzaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 1

h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 90:10 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 5.3 min; minor diastereomer, t_R = 6.4 min). Column chromatography (8:1 hexanes/EtOAc) afforded 235 mg (76%) of **2i**: IR 1602, 3345 cm^{-1} ; ^1H NMR (500 MHz) δ 1.29 (s, 9H), 1.32 (s, 9H), 3.00 (dd, 1H, J = 12.8, 3.9), 3.18 (dd, 1H, J = 12.8, 11.3), 4.91 (m, 1H), 5.94 (d, 1H, J = 9.8), 7.21-7.43 (m, 5H); ^{13}C NMR (125 MHz) δ 22.7, 28.4, 43.5, 43.6, 58.4, 70.0, 125.2, 127.1, 128.4, 145.4, 188.4. Anal. Calcd. for $\text{C}_{17}\text{H}_{27}\text{NO}_2\text{S}$: C, 65.98; H, 8.79; N, 4.53. Found: C, 65.93; H, 9.12; N, 4.33.

β -Hydroxy-*N*-Sulfinyl Imine 2j. General procedure A was followed with 189 mg (1.00 mmol) of (*R*)-**1b**, 368 mg (2.00 mmol) of MgBr_2 , and 95 mg (1.10 mmol) of pivaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 99:1 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 4.9 min; minor diastereomer, t_R = 6.4 min). Column chromatography (8:1 hexanes/EtOAc) afforded 234 mg (85%) of **2e**: IR 1612, 1709, 3344 cm^{-1} ; ^1H NMR (500 MHz) δ 0.93 (s, 9H), 1.14 (d, 6H, J = 6.8), 1.26 (s, 9H), 2.54 (dd, 1H, J = 11.8, 3.0), 2.69 (sep, 1H, J = 6.8), 3.08 (dd, 1H, J = 11.8, 11.3), 3.39 (ddd, 1H, J = 11.3, 8.9, 3.0), 4.63 (d, 1H, J = 8.9); ^{13}C NMR (125 MHz) δ 20.3, 21.1, 22.5, 25.7, 35.8, 38.5, 38.5, 58.1, 75.0, 190.1. Anal. Calcd. for $\text{C}_{14}\text{H}_{29}\text{NO}_2\text{S}$: C, 61.05; H, 10.61; N, 5.09. Found: C, 61.13; H, 10.77; N, 5.04.

β -Hydroxy-*N*-Sulfinyl Imine 2k. General procedure A was followed with 189 mg (1.00 mmol) of (*R*)-**1c**, 368 mg (2.00 mmol) of MgBr_2 , and 79 mg (1.10 mmol) of isobutyraldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 97:3 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 6.4 min; minor diastereomer, t_R = 9.4 min). Column chromatography (6:1 hexanes/EtOAc) afforded 212 mg (81%) of **2k**: IR 1622, 3343 cm^{-1} ; ^1H NMR (500 MHz) δ 0.94 (d, 3H, J = 6.8), 0.96 (d, 3H, J = 6.8), 1.15 (d, 3H, J = 6.8), 1.15 (d, 3H, J = 6.8), 1.27 (s, 9H), 1.69 (dt, 1H, J = 5.3, 6.8, 6.8), 2.52 (dd, 1H, J = 11.8, 3.3), 2.69 (tt, 1H, J = 6.8, 6.8), 3.09 (dd, 1H, J = 11.8, 11.2), 3.52 (dddd, 1H, J = 11.2, 9.0, 5.3, 3.3), 4.54 (d, 1H, J = 9.0); ^{13}C NMR (125 MHz) δ 17.5, 18.7, 20.2, 20.9, 22.5, 35.4, 38.8, 41.0, 58.1, 72.1, 189.7. Anal. Calcd. for $\text{C}_{13}\text{H}_{27}\text{NO}_2\text{S}$: C, 59.73; H, 10.41; N, 5.36. Found: C, 59.61; H, 10.66; N, 5.56.

β -Hydroxy-*N*-Sulfinyl Imine 2l. General procedure A was followed with 189 mg (1.00 mmol) of (*R*)-**1c**, 368 mg (2.00 mmol) of MgBr_2 , and 64 mg (1.10 mmol) of propionaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for

3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 91:9 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 9.5 min; minor diastereomer, t_R = 15.1 min). Column chromatography (6:1 hexanes/EtOAc) afforded 181 mg (73%) of **2l**: IR 1622, 1707, 3356 cm^{-1} ; ^1H NMR (500 MHz) δ 0.84 (t, 3H, J = 7.4), 1.01 (d, 6H, J = 6.7), 1.13 (s, 9H), 1.38-1.44 (m, 2H), 2.48 (dd, 1H, J = 12.0, 3.4), 2.56 (sep, 1H, J = 6.7), 2.90 (dd, 1H, J = 12.0, 10.7), 3.57 (br s, 1H), 4.36 (d, 1H, J = 6.4); ^{13}C NMR (125 MHz) δ 9.6, 19.8, 20.5, 22.2, 38.7, 43.1, 57.6, 68.5, 72.1, 189.1; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{12}\text{H}_{26}\text{NO}_2\text{S}$) m/z 248.1684. Found 248.1687.

β -Hydroxy-*N*-Sulfinyl Imine 2m. General procedure A was followed with 189 mg (1.00 mmol) of (*R*)-**1c**, 368 mg (2.00 mmol) of MgBr_2 , and 117 mg (1.10 mmol) of benzaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 1 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 77:23 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 7.1 min; minor diastereomer, t_R = 8.1 min). Column chromatography (6:1 hexanes/EtOAc) afforded 220 mg (75%) of **2m**: IR 1621, 1708, 3322 cm^{-1} ; ^1H NMR (500 MHz) δ 1.19 (d, 3H, J = 6.9), 1.21 (d, 3H, J = 6.6), 1.32 (s, 9H), 2.79-2.88 (m, 2H), 3.34 (dd, 1H, J = 12.0, 11.5), 4.86 (dd, 1H, J = 12.0, 3.2), 5.58 (br s, 1H), 7.23-7.44 (m, 5H); ^{13}C NMR (125 MHz) δ 20.2, 20.9, 22.5, 39.0, 46.3, 58.2, 69.8, 125.4, 127.3, 128.4, 145.1, 188.3. Anal. Calcd. for $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{S}$: C, 65.05; H, 8.53; N, 4.74. Found: C, 65.02; H, 8.54; N, 4.67.

β -Hydroxy-*N*-Sulfinyl Imine 2n. General procedure A was followed with 175 mg (1.00 mmol) of (*R*)-**1d**, 368 mg (2.00 mmol) of MgBr_2 , and 95 mg (1.10 mmol) of pivaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 98:2 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 6.1 min; minor diastereomer, t_R = 10.1 min). Column chromatography (6:1 hexanes/EtOAc) afforded 182 mg (70%) of **2n**: IR 1579, 1708, 3349, 3240 cm^{-1} ; ^1H NMR (500 MHz) δ 0.93 (s, 9H), 1.11 (t, 3H, J = 7.2), 1.27 (s, 9H), 2.36 (dq, 1H, J = 17.7, 7.2), 2.44 (dd, 1H, J = 11.9, 3.1), 2.66 (dq, 1H, J = 17.7, 7.2), 3.14 (dd, 1H, J = 11.9, 11.4), 3.40 (ddd, 1H, J = 11.4, 8.8, 3.1), 4.60 (d, 1H, J = 8.8); ^{13}C NMR (125 MHz) δ 9.9, 22.5, 25.7, 34.0, 35.8, 39.7, 57.9, 75.4, 186.3. Anal. Calcd. for $\text{C}_{13}\text{H}_{27}\text{NO}_2\text{S}$: C, 59.73; H, 10.41; N, 5.36. Found: C, 59.43; H, 10.54; N, 5.51.

β -Hydroxy-*N*-Sulfinyl Imine 2o. General procedure A was followed with 175 mg (1.00 mmol) of (*R*)-**1d**, 368 mg (2.00 mmol) of MgBr_2 , and 79 mg (1.10 mmol) of isobutyraldehyde. After the addition of the aldehyde, the reaction mixture was stirred for

3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 92:8 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 8.8 min; minor diastereomer, t_R = 15.2 min). Column chromatography (4:1 hexanes/EtOAc) afforded 160 mg (65%) of **2o**: IR 1623, 1710, 3357 cm^{-1} ; ^1H NMR (500 MHz) δ 0.94 (d, 3H, J = 6.8), 0.95 (d, 3H, J = 6.8), 1.06 (t, 3H, J = 7.3), 1.27 (s, 9H), 1.69 (dt, 1H, J = 5.4, 6.8, 6.8), 2.36 (dq, 1H, J = 17.7, 7.2), 2.41 (dd, 1H, J = 11.9, 3.2), 2.64 (dq, 1H, J = 17.7, 7.2), 3.14 (dd, 1H, J = 11.9, 11.0), 3.52 (dddd, 1H, J = 11.0, 9.0, 5.4, 3.2), 4.50 (d, 1H, J = 9.0); ^{13}C NMR (125 MHz) δ 9.9, 17.5, 18.6, 22.5, 34.1, 35.3, 42.1, 57.9, 72.4, 185.9. Anal. Calcd. for $\text{C}_{12}\text{H}_{25}\text{NO}_2\text{S}$: C, 58.26; H, 10.19; N, 5.66. Found: C, 58.25; H, 10.46; N, 5.87.

β -Hydroxy-*N*-Sulfinyl Imine 2p. General procedure A was followed with 525 mg (1.00 mmol) of (*R*)-**1d**, 1.10 g (2.00 mmol) of MgBr_2 , and 192 mg (1.10 mmol) of propionaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 3 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 80:20 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 16.0 min; minor diastereomer, t_R = 26.8 min). Column chromatography (5:1 hexanes/EtOAc) afforded 386 mg (55%) of **2p**: IR 1623, 1708, 3346 cm^{-1} ; ^1H NMR (500 MHz) δ 0.96 (t, 3H, J = 7.4), 1.09 (t, 3H, J = 7.2), 1.25 (s, 9H), 1.49-1.55 (m, 2H), 2.35 (dq, 1H, J = 17.7, 7.2), 2.46 (dd, 1H, J = 12.1, 3.5), 2.62 (dq, 1H, J = 17.7, 7.2), 3.08 (dd, 1H, J = 12.1, 10.8), 3.64-3.70 (m, 1H), 4.40 (d, 1H, J = 9.2); ^{13}C NMR (125 MHz) δ 9.5, 9.6, 22.1, 31.8, 34.1, 44.3, 57.4, 68.8, 185.5; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{11}\text{H}_{24}\text{NO}_2\text{S}$) m/z 234.1528. Found 234.1529.

β -Hydroxy-*N*-Sulfinyl Imine 2q. General procedure A was followed with 175 mg (1.00 mmol) of (*R*)-**1d**, 368 mg (2.00 mmol) of MgBr_2 , and 117 mg (1.10 mmol) of benzaldehyde. After the addition of the aldehyde, the reaction mixture was stirred for 1 h before the addition of 2*N* AcOH/THF. Diastereoselectivity was determined by HPLC analysis; 60:40 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 10.8 min; minor diastereomer, t_R = 12.3 min). Column chromatography (5:1 hexanes/EtOAc) afforded 141 mg (50%) of **2q**: IR 1709, 3250, 3357 cm^{-1} ; ^1H NMR (500 MHz) δ 1.17 (t, 3H, J = 7.2), 1.31 (s, 9H), 2.46 (dq, 1H, J = 17.7, 7.1), 2.69 (dd, 1H, J = 12.4, 3.7), 2.78 (dq, 1H, J = 17.7, 7.1), 3.39 (dd, 1H, J = 12.4, 11.3), 4.86 (ddd, 1H, J = 11.3, 8.9, 3.7), 5.52 (d, 1H, J = 8.9), 7.23-7.42 (m, 5H); ^{13}C NMR (125 MHz) δ 9.81, 22.5, 34.2, 47.5, 58.0, 70.0, 125.4, 127.3, 128.5, 145.0, 184.6. Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{S}$: C, 64.02; H, 8.24; N, 4.98. Found: C, 63.67; H, 8.39; N, 4.66.

General Procedure B for the Hydrolysis of β -Hydroxy Sulfinyl Imines 2.

To a 0.02 M solution of β -hydroxy sulfinyl imine **2** (1.0 equiv) in MeOH was added 1.0

N aqueous AcOH (20 equiv) and the mixture was stirred for 20 h at 40 °C. After the hydrolysis was determined to be complete by TLC, the solvent was reduced to half volume under reduced pressure. Brine was added to the mixture, which was then extracted with 2:8 CH₂Cl₂/hexanes (3x). The combined organic portions were dried, filtered, and concentrated. The β -hydroxy ketones were purified by silica gel chromatography.

(S)-3-Hydroxy-4-methyl-1-phenyl-1-pentanone (3c). The general procedure B was followed with 133 mg (0.450 mmol) of **2c**. The enantiomeric excess was determined by HPLC analysis (Chiralpak AS, 98:2 hexanes/EtOH, 1.0 mL/min, 210 nm: major enantiomer, *t_R* = 6.8 min; minor enantiomer, *t_R* = 8.3 min). Column chromatography (70:30 hexanes/EtOAc) delivered 85.0 mg (98%, 98% ee) of **3c**: [α]_D²³ –67.7 (c 1.43, CHCl₃) [lit. value.⁵ [α]_D²³ –35.7 (c 0.9, CHCl₃, 47% ee)]. IR 1676, 3467 cm^{–1}; ¹H NMR (500 MHz) δ 0.99 (d, 3H, *J* = 6.8), 1.01 (d, 3H, *J* = 6.8), 1.77–1.83 (m, 1H), 3.03 (dd, 1H, *J* = 9.6, 17.4), 3.17 (dd, 1H, *J* = 1.3, 17.4), 3.21 (br s, 1H), 3.99 (m, 1H), 7.47 (t, 2H, *J* = 7.4), 7.58 (t, 1H, *J* = 7.4), 7.96 (d, 2H, *J* = 7.4); ¹³C NMR (125 MHz) δ 17.9, 18.5, 33.1, 42.0, 72.3, 128.0, 128.7, 133.4, 136.9, 201.3. IR, ¹H NMR and ¹³C NMR spectroscopic data and optical rotation are in good agreement with those reported in literature.^{4,5} HRMS (FAB) calcd for [MH]⁺ (C₁₂H₁₇O₂) *m/z* 193.1229. Found 193.1235.

(S)-3-Hydroxy-1,3-diphenyl-1-propanone (3e). General procedure B was followed with 100 mg (0.300 mmol) of **2e**. The enantiomeric excess was determined by HPLC analysis (Chiralpak AS, 94:6 hexanes/EtOH, 1.0 mL/min, 210 nm: major enantiomer, *t_R* = 10.2 min; minor enantiomer, *t_R* = 11.9 min). Column chromatography (70:30 hexanes/EtOAc) delivered 69.0 mg (>99%, 97% ee) of **3e**: [α]_D²³ –94.0 (c 1.29, CHCl₃) [lit. value.⁶ [α]_D²⁴ –37.2 (c 1.28, CHCl₃, 49% ee)]. IR 1667, 3465 cm^{–1}; ¹H NMR (400 MHz) δ 3.38 (d, 2H, *J* = 6.1), 3.61 (br s, 1H), 5.36 (t, 1H, *J* = 6.1), 7.29–7.62 (m, 8H), 7.96 (dd, 2H, *J* = 8.4, 1.3); ¹³C NMR (100 MHz) δ 47.3, 70.0, 125.6, 127.7, 128.0, 128.2, 128.6, 133.7, 136.5, 142.8, 200.2. IR, ¹H NMR and ¹³C NMR spectroscopic data and optical rotation are in good agreement with those reported in literature.^{4,5,6} Anal. Calcd. for C₁₅H₁₄O₂: C, 79.62; H, 6.24. Found: C, 79.28; H, 6.57.

General Procedure C for the Reduction of β -Hydroxy Sulfinyl Imines **2 with Catecholborane.** To a 0.200 M solution of β -hydroxy sulfinyl imine **2** (1.0 equiv) in THF was added catecholborane (5.0 equiv), and the mixture was stirred for 20 h at –10 °C. To this mixture was added MeOH and a saturated solution of sodium potassium tartrate. The resulting mixture was stirred for 1 h, washed with brine, and the brine layer was extracted with EtOAc (2x). The combined organic portions were

dried, filtered, and concentrated. *syn*-1,3-Amino alcohols were isolated by column chromatography.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5a.** General procedure C was followed with 93.0 mg (0.30 mmol) of **2a** and 180 mg (1.50 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R (major) = 13.0 min, t_R (minor) = 6.2 min). Column chromatography (50:50 hexanes/EtOAc) afforded 83.0 mg (89%) of ***syn*-5a**: IR 3194, 3290 cm^{-1} ; ^1H NMR (500 MHz) δ 0.84 (s, 9H), 1.18 (s, 9H), 1.93 (ddd, 1H, J = 14.1, 8.7, 1.7), 2.10 (ddd, 1H, J = 14.1, 10.6, 6.9), 3.09 (dd, 1H, J = 10.6, 1.7), 4.10 (apparent br d, 1H), 4.59 (m, 1H), 7.27-7.38 (m, 5H); ^{13}C NMR (100 MHz) δ 22.6, 25.5, 35.0, 37.9, 55.8, 58.2, 78.0, 127.5, 127.8, 128.7, 142.0. Anal. Calcd. for $\text{C}_{17}\text{H}_{29}\text{NO}_2\text{S}$: C, 65.55; H, 9.38; N, 4.50. Found: C, 65.46; H, 9.57; N, 4.26.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5b.** General procedure C was followed with 89.0 mg (0.300 mmol) of **2b** and 180 mg (1.50 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R (major) = 15.8 min, t_R (minor) = 8.4 min). Column chromatography (50:50 hexanes/EtOAc) afforded 78.0 mg (88%) of ***syn*-5b**: IR 3175, 3244 cm^{-1} ; ^1H NMR (400 MHz) δ 0.85 (d, 6H, J = 6.8), 1.18 (s, 9H), 1.56-1.64 (m, 1H), 1.84 (ddd, 1H, J = 2.0, 7.8, 14.0), 2.01 (ddd, 1H, J = 6.8, 10.3, 14.0), 2.67 (br s, 1H), 3.23 (ddd, 1H, J = 2.0, 5.1, 10.3), 4.08 (br s, 1H), 4.61 (br t, 1H), 7.25-7.38 (m, 5H); ^{13}C NMR (125 MHz) δ 17.3, 18.5, 22.6, 34.3, 40.6, 55.8, 57.8, 74.6, 127.4, 127.8, 128.6, 142.2. Anal. Calcd. for $\text{C}_{16}\text{H}_{27}\text{O}_2\text{S}$: C, 64.60; H, 9.15; N, 4.71. Found: C, 64.51; H, 9.04; N, 4.38.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5c.** General procedure C was followed with 93.0 mg (0.300 mmol) of **2c** and 180 mg (1.50 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: t_R (major) = 52.6 min, t_R (minor) = 20.0 min). Column chromatography (50:50 hexanes/EtOAc) afforded 78.0 mg (84%) of ***syn*-5c**: IR 3273, 3380 cm^{-1} ; ^1H NMR (400 MHz) δ 0.83 (d, 3H, J = 6.7), 0.83 (d, 3H, J = 6.7), 1.19 (s, 9H), 1.21-1.27 (m, 1H), 1.41 (ddd, 1H, J = 14.1, 8.5, 5.8), 1.71 (m, 1H), 1.85 (ddd, 1H, J = 14.2, 7.2, 2.6), 2.15 (ddd, 1H, J = 14.2, 9.8, 7.2), 3.59 (dddd, 1H, J = 9.8, 8.5, 4.7, 2.6), 4.03 (br s, 1H), 4.62 (dd, 1H, J = 7.2, 7.2), 7.27-7.38 (m, 5H); ^{13}C NMR (100 MHz) δ 22.2, 22.6, 23.1, 24.4, 44.3, 47.7, 55.9, 57.7, 68.4, 127.3, 127.9, 128.7, 142.1. Anal. Calcd. for $\text{C}_{17}\text{H}_{29}\text{NO}_2\text{S}$: C, 65.55; H, 9.38; N, 4.50. Found: C, 65.17; H, 9.45; N, 4.43.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5d.** General procedure C was followed with 84.0 mg (0.300 mmol) of **2d** and 180 mg (1.50 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 95:5 dr (94:6 hexanes/*i*-PrOH,

1.0 mL/min: t_R (major) = 19.6 min, t_R (minor) = 11.2 min). Column chromatography (70:30 hexanes/EtOAc) afforded 79.0 mg (94%) of **syn-5d**: IR 3298, 3391 cm^{-1} ; ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 7.4), 1.19 (s, 9H), 1.46 (dq, 2H, J = 7.4, 6.2), 1.85 (ddd, 1H, J = 14.1, 7.8, 2.4), 2.18 (ddd, 1H, J = 14.1, 10.1, 6.6), 3.42 (ddt, 1H, J = 10.1, 6.2, 2.4), 4.60 (dd, 1H, J = 7.8, 6.6), 7.28-7.37 (m, 5H); ^{13}C NMR (100 MHz) δ 9.7, 22.6, 31.1, 43.2, 55.9, 57.3, 71.4, 127.4, 128.0, 128.8, 142.0. Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{S}$: C, 63.56; H, 8.89; N, 4.94. Found: C, 63.59; H, 8.87; N, 4.67.

N-Sulfinyl-1,3-Amino Alcohol syn-5e. General procedure C was followed with 99.0 mg (0.300 mmol) of **2e** and 180 mg (1.50 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R (major) = 18.8 min, t_R (minor) = 10.2 min). Column chromatography (50:50 hexanes/EtOAc) afforded 83.0 mg (84%) of **syn-5e**: IR 3178, 3242 cm^{-1} ; ^1H NMR (400 MHz) δ 1.20 (s, 9H), 2.04 (ddd, 1H, J = 14.2, 7.2, 3.2), 2.54 (ddd, 1H, J = 14.2, 10.1, 6.6), 4.17 (d, 1H, J = 4.1), 4.52 (dd, 1H, J = 10.1, 3.2), 4.69 (m, 1H), 7.22-7.40 (m, 10H); ^{13}C NMR (100 MHz) δ 22.6, 45.9, 56.0, 57.4, 72.1, 125.6, 127.4, 127.5, 128.0, 128.5, 128.7, 141.8, 144.6. Anal. Calcd. for $\text{C}_{19}\text{H}_{25}\text{NO}_2\text{S}$: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.51; H, 7.88; N, 4.15.

N-Sulfinyl-1,3-Amino Alcohol syn-5f. General procedure B was followed with 58 mg (0.200 mmol) of **2f** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 95:5 dr (98:2 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 13.4 min; minor diastereomer, t_R = 8.7 min). Column chromatography (7:3 hexanes/EtOAc) afforded 46 mg (79%) of **syn-5f**: IR 3260, 3294 cm^{-1} ; ^1H NMR (500 MHz) δ 0.90 (s, 9H), 0.96 (s, 9H), 1.24 (s, 9H), 1.85 (ddd, 1H, J = 15.3, 10.0, 8.8 Hz), 1.91 (ddd, 1H, J = 15.3, 3.0, 2.6 Hz), 3.01 (ddd, 1H, J = 8.8, 6.4, 2.6 Hz), 3.22 (dd, 1H, J = 10.0, 3.0 Hz), 4.02 (d, 1H, J = 6.4 Hz); ^{13}C NMR (125 MHz) δ 22.8, 25.7, 27.3, 31.2, 35.5, 36.0, 56.5, 65.4, 81.7. Anal. Calcd. for $\text{C}_{15}\text{H}_{33}\text{NO}_2\text{S}$: C, 61.81; H, 11.41; N, 4.81. Found: C, 61.95; H, 11.54; N, 4.42.

N-Sulfinyl-1,3-Amino Alcohol syn-5g. General procedure B was followed with 55 mg (0.200 mmol) of **2g** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 29.4 min; minor diastereomer, t_R = 12.0 min). Column chromatography (5:5 hexanes/EtOAc) afforded 50 mg (91%) of **syn-5g**: IR 3211, 3384 cm^{-1} ; ^1H NMR (500 MHz) δ 0.90 (d, 3H, J = 6.8 Hz), 0.93 (d, 3H, J = 6.8 Hz), 0.96 (s, 9H), 1.23 (s, 9H), 1.68 (dt, 1H, J = 4.5, 6.8, 6.8 Hz), 1.80 (ddd, 1H, J = 15.0, 4.6, 2.6 Hz), 1.86 (ddd, 1H, J = 15.0, 9.2, 9.0 Hz), 3.00 (ddd, 1H, J = 9.2, 6.5, 2.6 Hz), 3.33 (d, 1H, J = 7.2 Hz), 3.43 (br s, 1H), 3.88 (d, 1H, J = 6.5 Hz); ^{13}C NMR (125

MHz) δ 16.6, 18.9, 22.8, 27.2, 34.0, 34.5, 35.6, 56.5, 64.6, 77.3. Anal. Calcd. for $C_{14}H_{31}NO_2S$: C, 60.60; H, 11.26; N, 5.05. Found: C, 60.48; H, 11.49; N, 4.82.

N-Sulfinyl-1,3-Amino Alcohol *syn-5h*. General procedure B was followed with 52 mg (0.200 mmol) of **2h** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 95:5 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 48.2 min; minor diastereomer, t_R = 19.3 min). Column chromatography (4:6 hexanes/EtOAc) afforded 42 mg (50%) of ***syn-5h***: IR 3208, 3359 cm^{-1} ; 1H NMR (500 MHz) δ 0.95 (dd, 1H, J = 7.5, 7.5 Hz), 0.95 (s, 9H), 1.23 (s, 9H), 1.44 (ddq, 1H, J = 15.0, 6.5, 7.5 Hz), 1.56 (ddq, 1H, J = 15.0, 4.4, 7.5 Hz), 1.78 (ddd, 1H, J = 14.8, 5.7, 2.8 Hz), 1.83 (ddd, 1H, J = 14.8, 9.4, 7.9 Hz), 2.99 (ddd, 1H, J = 9.4, 6.5, 2.8 Hz), 3.05 (d, 1H, J = 7.1 Hz), 3.60 (m, 1H), 3.76 (d, 1H, J = 6.5 Hz); ^{13}C NMR (125 MHz) δ 9.7, 22.8, 27.1, 30.7, 35.4, 37.7, 56.4, 64.1, 73.4. Anal. Calcd. for $C_{13}H_{29}NO_2S$: C, 59.27; H, 11.10; N, 5.32. Found: C, 59.04; H, 11.17; N, 5.06.

N-Sulfinyl-1,3-Amino Alcohol *syn-5i*. General procedure B was followed with 62 mg (0.200 mmol) of **2i** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 98:2 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 45.3 min; minor diastereomer, t_R = 9.5 min). Column chromatography (5:5 hexanes/EtOAc) afforded 43 mg (69%) of ***syn-5i***: IR 3154, 3227 cm^{-1} ; 1H NMR (500 MHz) δ 0.88 (s, 9H), 1.29 (s, 9H), 2.05 (ddd, 1H, J = 14.7, 6.7, 1.9 Hz), 2.13 (ddd, 1H, J = 14.7, 9.4, 7.8 Hz), 2.92 (ddd, 1H, J = 9.4, 6.8, 1.9 Hz), 3.80 (d, 1H, J = 6.8 Hz), 4.76 (dd, 1H, J = 7.8, 6.7 Hz), 7.24-7.39 (m, 5H); ^{13}C NMR (125 MHz) δ 22.9, 26.9, 35.3, 40.4, 56.6, 63.4, 74.7, 126.1, 127.6, 128.5, 144.5; HRMS (FAB) calcd for $[MH]^+$ ($C_{17}H_{30}NO_2S$) m/z 312.1997. Found 312.1998.

N-Sulfinyl-1,3-Amino Alcohol *syn-5j*. General procedure B was followed with 55 mg (0.200 mmol) of **2j** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 95:5 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 20.2 min; minor diastereomer, t_R = 8.6 min). Column chromatography (5:5 hexanes/EtOAc) afforded 51 mg (93%) of ***syn-5j***: IR 3277, 3411 cm^{-1} ; 1H NMR (500 MHz) δ 0.87 (s, 9H), 0.92 (d, 3H, J = 6.8 Hz), 0.95 (d, 3H, J = 6.8 Hz), 1.21 (s, 9H), 1.53-1.60 (m, 1H), 1.75-1.79 (m, 1H), 2.07 (dt, 1H, J = 6.1, 6.8, 6.8 Hz), 3.09-3.14 (m, 1H), 3.27 (apparent br d, 1H, J = 9.0 Hz), 3.94 (d, 1H, J = 6.3 Hz); ^{13}C NMR (125 MHz) δ 18.7, 19.1, 22.6, 25.6, 32.0, 32.9, 35.3, 56.1, 62.9, 80.3. Anal. Calcd. for $C_{14}H_{31}NO_2S$: C, 60.60; H, 11.26; N, 5.05. Found: C, 60.72; H, 11.41; N, 4.80.

N-Sulfinyl-1,3-Amino Alcohol *syn-5k*. General procedure B was followed

with 52 mg (0.200 mmol) of **2k** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 96:4 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 38.8 min; minor diastereomer, t_R = 12.9 min). Column chromatography (5:5 hexanes/EtOAc) afforded 43 mg (82%) of **syn-5k**: IR 3209, 3315 cm^{-1} ; ^1H NMR (500 MHz) δ 0.88 (d, 3H, J = 6.8 Hz), 0.91 (d, 3H, J = 6.8 Hz), 0.93 (d, 3H, J = 6.9 Hz), 0.94 (d, 3H, J = 6.9 Hz), 1.21 (s, 9H), 1.58-1.69 (m, 3H), 2.08 (dt, 1H, J = 5.9, 6.8, 6.8 Hz), 3.12-3.16 (m, 1H), 3.46-3.50 (m, 1H), 3.86 (br s, 1H); ^{13}C NMR (125 MHz) δ 16.7, 18.3, 18.7, 19.1, 22.6, 32.1, 34.0, 35.3, 56.1, 62.3, 76.5. Anal. Calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_2\text{S}$: C, 59.27; H, 11.10; N, 5.32. Found: C, 58.97; H, 11.22; N, 4.93.

N-Sulfinyl-1,3-Amino Alcohol syn-5l. General procedure B was followed with 49 mg (0.200 mmol) of **2l** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 95:5 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 49.3 min; minor diastereomer, t_R = 16.4 min). Column chromatography (3:7 hexanes/EtOAc) afforded 40 mg (82%) of **syn-5l**: IR 3178, 3317 cm^{-1} ; ^1H NMR (500 MHz) δ 0.91-0.94 (m, 9H), 1.21 (s, 9H), 1.38-1.66 (m, 4H), 2.02-2.11 (m, 1H), 3.02 (br s, 1H), 3.13-3.18 (m, 1H), 3.58-3.64 (m, 1H), 3.75 (d, 1H, J = 7.0 Hz); ^{13}C NMR (125 MHz) δ 9.6, 17.8, 19.1, 22.6, 30.8, 32.2, 38.0, 56.1, 62.0, 72.9. Anal. Calcd. for $\text{C}_{12}\text{H}_{27}\text{NO}_2\text{S}$: C, 57.79; H, 10.91; N, 5.62. Found: C, 57.91; H, 11.03; N, 5.26.

N-Sulfinyl-1,3-Amino Alcohol syn-5m. General procedure B was followed with 89 mg (0.300 mmol) of **2m** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 90:10 dr (94:6 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 23.8 min; minor diastereomer, t_R = 6.6 min). Column chromatography (5:5 hexanes/EtOAc) afforded 73 mg (81%) of **syn-5m**: IR 3206, 3276 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (d, 3H, J = 6.8 Hz), 0.92 (d, 3H, J = 6.8 Hz), 1.25 (s, 9H), 1.86-2.10 (m, 3H), 3.11-3.15 (m, 1H), 3.55 (br s, 1H), 3.75 (d, 1H, J = 7.4 Hz), 4.76-4.80 (m, 1H), 7.25-7.38 (m, 5H); ^{13}C NMR (125 MHz) δ 17.7, 19.0, 22.7, 32.5, 40.8, 56.2, 61.3, 74.1, 125.9, 127.6, 128.5, 144.6. Anal. Calcd. for $\text{C}_{16}\text{H}_{27}\text{NO}_2\text{S}$: C, 64.60; H, 9.15; N, 4.71. Found: C, 64.22; H, 9.20; N, 4.60.

N-Sulfinyl-1,3-Amino Alcohol syn-5n. General procedure B was followed with 52 mg (0.200 mmol) of **2n** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 92:8 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 25.0 min; minor diastereomer, t_R = 13.5 min). Column chromatography (5:5 hexanes/EtOAc) afforded 43 mg (82%) of **syn-5n**: IR 3256, 3392 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (s, 9H), 0.95 (t, 3H, J = 7.3 Hz), 1.22 (s,

9H), 1.59-1.82 (m, 4H), 1.93 (br s, 1H), 3.24-3.33 (m, 2H), 4.10 (d, 1H, $J = 3.8$ Hz); ^{13}C NMR (125 MHz) δ 10.6, 22.6, 25.6, 28.2, 35.3, 36.7, 55.8, 59.1, 80.3. Anal. Calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_2\text{S}$: C, 59.27; H, 11.10; N, 5.32. Found: C, 58.89; H, 11.40; N, 4.94.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5o.** General procedure B was followed with 49 mg (0.200 mmol) of **2o** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 97:3 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 43.4$ min; minor diastereomer, $t_R = 18.2$ min). Column chromatography (5:5 hexanes/EtOAc) afforded 45 mg (91%) of ***syn*-5o**: IR 3216, 3334 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (d, 3H, $J = 6.8$ Hz), 0.89 (d, 3H, $J = 6.9$ Hz), 0.93 (t, 3H, $J = 7.4$ Hz), 1.19 (s, 9H), 1.57-1.65 (m, 3H), 1.70-1.80 (m, 2H), 3.18 (br s, 1H), 3.21-3.27 (m, 1H), 3.47-3.50 (m, 1H), 3.98 (d, 1H, $J = 4.1$ Hz); ^{13}C NMR (125 MHz) δ 10.5, 16.9, 18.6, 22.5, 28.3, 34.4, 39.3, 55.7, 58.6, 76.6. Anal. Calcd. for $\text{C}_{12}\text{H}_{27}\text{NO}_2\text{S}$: C, 57.79; H, 10.91; N, 5.62. Found: C, 57.58; H, 10.84; N, 5.95.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5p.** General procedure B was followed with 70 mg (3.00 mmol) of **2p** and 180 mg (15.0 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 94:6 dr (94:6 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 19.8$ min; minor diastereomer, $t_R = 9.4$ min). Column chromatography (2:8 hexanes/EtOAc) afforded 53 mg (76%) of ***syn*-5p**: IR 3207, 3327 cm^{-1} ; ^1H NMR (500 MHz) δ 0.92 (t, 3H, $J = 7.3$ Hz), 0.94 (t, 3H, $J = 7.3$ Hz), 1.21 (s, 9H), 1.40-1.80 (m, 6H), 2.03 (br s, 1H), 3.24-3.30 (m, 1H), 3.64 (br s, 1H), 3.88 (d, 1H, $J = 5.5$ Hz); ^{13}C NMR (125 MHz) δ 9.6, 10.4, 22.6, 28.6, 31.2, 42.0, 55.8, 58.4, 73.1. Anal. Calcd. for $\text{C}_{11}\text{H}_{25}\text{NO}_2\text{S}$: C, 56.13; H, 10.71; N, 5.95. Found: C, 56.25; H, 10.75; N, 5.65.

***N*-Sulfinyl-1,3-Amino Alcohol *syn*-5q.** General procedure B was followed with 56 mg (0.200 mmol) of **2q** and 120 mg (1.00 mmol) of catecholborane. Diastereoselectivity was determined by HPLC analysis; 76:24 dr (94:6 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 24.3$ min; minor diastereomer, $t_R = 8.3$ min). Column chromatography (7:3 hexanes/EtOAc) afforded 39 mg (69%) of ***syn*-5q**: IR 3187, 3284 cm^{-1} ; ^1H NMR (500 MHz) δ 0.93 (t, 3H, $J = 7.4$ Hz), 1.24 (s, 9H), 1.59-1.67 (m, 1H), 1.72-1.81 (m, 1H), 1.86 (ddd, 1H, $J = 14.7, 3.9, 3.9$ Hz), 2.09 (ddd, 1H, $J = 14.7, 9.6, 9.6$ Hz), 3.27-3.34 (m, 1H), 3.76 (br s, 1H), 3.85 (d, 1H, $J = 5.9$ Hz), 4.80 (dd, 1H, $J = 9.6, 3.9$ Hz), 7.23-7.37 (m, 5H); ^{13}C NMR (125 MHz) δ 10.3, 22.6, 28.7, 44.7, 55.9, 57.9, 74.0, 125.6, 127.4, 128.5, 144.9. Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{S}$: C, 63.56; H, 8.89; N, 4.94. Found: C, 63.55; H, 8.99; N, 4.55.

General Procedure D for the Reduction of β -Hydroxy Sulfinyl Imines **2 with LiBHET_3 .** To a -78 °C solution of β -hydroxy *N*-sulfinyl imine **2** (1.00 equiv) in

THF (0.200 M) was added LiBHEt₃ (2.50 equiv, 1.00 M in THF) and the resulting solution was stirred for 3 h. To this solution was added 1.00 mL of a saturated aqueous solution of NH₄Cl. The resulting mixture was gradually warmed to rt with stirring, washed with brine, and the brine layer was extracted with EtOAc (2x). The combined organic portions were dried, filtered, and concentrated. *anti*-1,3-Amino alcohols were isolated by column chromatography.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5a.** General procedure D was followed with 155 mg (0.500 mmol) of **2a** and 1.25 mL of LiBHEt₃ (1.25 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis, >99:1 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R(major) = 6.1 min, t_R(minor) = 12.9 min); LCMS analysis, >99:1 dr, MH⁺ Calcd: 312.5. Found: 312.1 (C8, 15 cm) 70-90% MeOH / H₂O / 0.10% TFA, t_R(major) = 18.0 min, t_R(minor) = 17.5 min). Column chromatography (70:30 hexanes/EtOAc) afforded 113 mg (73.0%) of ***anti*-5a**: [α]_D²³ = -90.4 (c = 1.0, CHCl₃); IR 3226 cm⁻¹; ¹H NMR (500 MHz) δ 0.85 (s, 9H), 1.24 (s, 9H), 1.39-1.52 (m, 1H), 1.75-1.96 (m, 2H), 3.34-3.37 (m, 1H), 4.16 (d, 1H, *J* = 6.6), 4.73 – 4.78 (m, 1H), 7.23-7.35 (m, 5H); ¹³C NMR (125 MHz) δ 22.7, 25.0, 34.8, 39.6, 55.7, 57.6, 74.9, 126.4, 126.9, 128.3, 143.2. Anal. Calcd. for C₁₇H₂₉NO₂S: C, 65.55; H, 9.38; N, 4.50. Found: C, 65.65; H, 9.31; N, 4.35.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5b.** General procedure D was followed with 148 mg (0.500 mmol) of **2b** and 1.25 mL of LiBHEt₃ (1.25 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis, >99:1 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R(major) = 8.31 min, t_R(minor) = 14.6 min); LCMS analysis, >99:1 dr, MH⁺ Calcd: 297.5. Found: 297.3 (C8, 15 cm) 70-90% MeOH / H₂O / 0.10% TFA, t_R(major) = 17.0 min, t_R(minor) = 16.4 min). Column chromatography (70:30 hexanes/EtOAc) afforded 126 mg (85.0%) of ***anti*-5b**: [α]_D²³ = -92.7 (c = 1.0, CHCl₃); IR 3220 cm⁻¹; ¹H NMR (500 MHz) δ 0.88 (d, 3H, *J* = 6.8), 0.93 (d, 3H, *J* = 6.7), 1.23 (s, 9H), 1.68-1.75 (m, 1H), 1.85-1.90 (m, 1H), 1.98-2.03 (m, 1H), 3.46-3.50 (m, 1H), 4.29 (br s, 1H), 4.74 (br d, 1H), 7.23-7.45 (m, 5H); ¹³C NMR (125 MHz) δ 18.0, 18.8, 22.7, 33.6, 42.2, 55.7, 57.0, 72.9, 126.5, 127.1, 128.4, 143.3. Anal. Calcd for C₁₆H₂₇NO₂S: C, 64.60; H, 9.15; N, 4.71. Found: C, 64.52; H, 9.03; N, 4.64.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5c.** General procedure D was followed with 155 mg (0.500 mmol) of **2c** and 1.25 mL of LiBHEt₃ (1.25 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis, >99:1 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R(major) = 7.65 min, t_R(minor) = 15.8 min); LCMS analysis, >99:1 dr, MH⁺ Calcd: 312.5. Found: 312.1 (C8, 15 cm) 70-90% MeOH / H₂O / 0.10% TFA, t_R(major) = 18.2 min, t_R(minor) = 17.8 min). Column chromatography (70:30

hexanes/EtOAc) afforded 129 mg (83.0%) of **anti-5c**: $[\alpha]_D^{23} = -99.8$ (c = 1.0, CHCl₃); IR 3224 cm⁻¹; ¹H NMR (500 MHz) δ 0.88 (m, 6H), 1.24 (s, 9H), 1.38-1.46 (m, 1H), 1.51-1.61 (m, 2H), 1.73-1.76 (m, 1H), 1.89-1.94 (m, 2H), 3.85-3.88 (m, 1H), 4.07 (t, 1H, $J = 6.7$), 4.73 (dd, 1H, $J = 8.6, 4.4$), 7.23-7.36 (m, 5H); ¹³C NMR (125 MHz) δ 22.2, 22.6, 23.1, 24.5, 45.2, 45.9, 55.5, 56.5, 66.3, 126.6, 127.0, 128.3, 143.1. Anal. Calcd. for C₁₇H₂₉NO₂S: C, 65.55; H, 9.38; N, 4.50. Found: C, 65.35; H, 9.29; N, 4.43.

N-Sulfinyl-1,3-Amino Alcohol anti-5d. General procedure D was followed with 141 mg (0.500 mmol) of **2d** and 1.25 mL of LiBHEt₃ (1.25 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis, >99:1 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R (major) = 12.1 min, t_R (minor) = 19.6 min); LCMS analysis, >99:1 dr, MH⁺ Calcd: 284.4. Found: 284.1 (C₈, 15 cm) 70-90% MeOH / H₂O / 0.10% TFA, t_R (major) = 15.4 min, t_R (minor) = 14.8 min). Column chromatography (70:30 hexanes/EtOAc) afforded 97.8 mg (67.0%) of **anti-5d**: $[\alpha]_D^{23} = -134.0$ (c = 1.0, CHCl₃); IR 3225 cm⁻¹; ¹H NMR (500 MHz) δ 0.93 (t, 3H, $J = 7.4$), 1.22 (s, 9H), 1.50-1.62 (m, 2H), 1.88-1.98 (m, 2H), 3.68-3.69 (m, 1H), 4.54 (br s, 1H), 4.72 (br d, 1H), 7.23-7.45 (m, 5H); ¹³C NMR (125 MHz) δ 10.1, 22.7, 29.8, 44.4, 55.6, 56.6, 69.8, 126.6, 127.1, 128.4, 143.2. Anal. Calcd. for C₁₅H₂₅NO₂S: C, 63.56; H, 8.89; N, 4.94. Found: C, 63.45; H, 8.93; N, 4.76.

N-Sulfinyl-1,3-Amino Alcohol anti-5e. General procedure D was followed with 165 mg (0.500 mmol) of **2e** and 1.25 mL of LiBHEt₃ (1.25 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis, >99:1 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: t_R (major) = 10.6 min, t_R (minor) = 18.8 min); LCMS analysis, >99:1 dr, MH⁺ Calcd: 312.5. Found: 312.1 (C₈, 15 cm) 70-90% MeOH / H₂O / 0.10% TFA, t_R (major) = 17.0 min, t_R (minor) = 16.4 min). Column chromatography (70:30 hexanes/EtOAc) afforded 151 mg (91.0%) of **anti-5e**: $[\alpha]_D^{23} = -121.6$ (c = 1.0, CHCl₃); IR 1615, 3228 cm⁻¹; ¹H NMR (500 MHz) δ 1.22 (s, 9H), 2.15-2.31 (m, 2H), 4.07 (t, 1H, $J = 6.7$), 4.50 (br s, 1H), 4.65-4.67 (m, 1H), 4.86 (dd, 1H, $J = 8.3, 4.1$), 7.20-7.37 (m, 10H); ¹³C NMR (125 MHz) δ 22.6, 46.7, 55.6, 56.7, 71.0, 125.8, 126.7, 127.5, 128.4, 128.4, 128.4, 142.6, 143.7. Anal. Calcd. for C₁₆H₂₇NO₂S: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.72; H, 7.73; N, 4.19.

N-Sulfinyl-1,3-Amino Alcohol anti-5f. General procedure C was followed with 58 mg (0.200 mmol) of **2f**, and 0.50 mL of LiBHEt₃ (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; >99:1 dr (98:2 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 8.5$ min; minor diastereomer, $t_R = 12.5$ min). Column chromatography (8:2 hexanes/EtOAc) afforded 48 mg (83%) of **anti-5f**: IR 3340, 3378 cm⁻¹; ¹H NMR (500 MHz) δ 0.88 (s, 9H), 0.89 (s, 9H), 1.27 (s, 9H), 1.29

(ddd, 1H, $J = 14.3, 11.4, 2.6$ Hz), 1.71 (ddd, 1H, $J = 14.3, 11.6, 3.3$ Hz), 2.98 (d, 1H, $J = 7.4$ Hz), 3.20 (ddd, 1H, $J = 11.4, 7.4, 3.3$ Hz), 3.32 (ddd, 1H, $J = 11.6, 6.0, 2.6$ Hz), 3.98 (d, 1H, $J = 6.0$ Hz); ^{13}C NMR (125 MHz) δ 23.0, 26.1, 26.6, 31.4, 34.8, 35.5, 56.3, 61.6, 73.3. Anal. Calcd. for $\text{C}_{15}\text{H}_{33}\text{NO}_2\text{S}$: C, 61.81; H, 11.41; N, 4.81. Found: C, 61.59; H, 11.68; N, 4.69.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5g.** General procedure C was followed with 55 mg (0.200 mmol) of **2g**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; >99:1 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, $t_R = 9.7$ min; minor diastereomer, $t_R = 23.0$ min). Column chromatography (7:3 hexanes/EtOAc) afforded 53 mg (96%) of ***anti*-5g**: IR 3340, 3378 cm^{-1} ; ^1H NMR (500 MHz) δ 0.86 (s, 9H), 0.88 (d, 3H, $J = 6.7$ Hz), 0.95 (d, 3H, $J = 6.7$ Hz), 1.25 (s, 9H), 1.34 (ddd, 1H, $J = 14.4, 10.5, 2.8$ Hz), 1.65-1.71 (m, 1H), 1.73 (ddd, 1H, $J = 14.4, 10.5, 3.1$ Hz), 3.10 (d, 1H, $J = 7.0$ Hz), 3.19 (ddd, 1H, $J = 11.5, 7.1, 3.1$ Hz), 3.34-3.40 (m, 1H), 4.13 (d, 1H, $J = 6.3$ Hz); ^{13}C NMR (125 MHz) δ 18.6, 19.1, 22.9, 26.4, 33.6, 34.4, 35.4, 56.3, 61.2, 71.5. Anal. Calcd. for $\text{C}_{14}\text{H}_{31}\text{NO}_2\text{S}$: C, 60.60; H, 11.26; N, 5.05. Found: C, 60.44; H, 11.20; N, 4.74.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5h.** General procedure C was followed with 52 mg (0.200 mmol) of **2h**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; >99:1 dr (97:3 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, $t_R = 15.1$ min; minor diastereomer, not observed). Column chromatography (6:4 hexanes/EtOAc) afforded 50 mg (96%) of ***anti*-5h**: IR 3272, 3319 cm^{-1} ; ^1H NMR (500 MHz) δ 0.86 (s, 9H), 0.93 (t, 1H, $J = 7.4$ Hz), 1.25 (s, 9H), 1.37 (ddd, 1H, $J = 14.4, 11.4, 2.8$ Hz), 1.43 (ddq, 1H, $J = 13.6, 4.9, 7.4$ Hz), 1.53 (ddq, 1H, $J = 13.6, 7.1, 7.4$ Hz), 1.67 (ddd, 1H, $J = 14.4, 10.2, 3.0$ Hz), 3.14 (d, 1H, $J = 6.9$ Hz), 3.19 (ddd, 1H, $J = 11.4, 6.9, 3.0$ Hz), 3.55-3.63 (m, 1H), 4.21 (br s, 1H); ^{13}C NMR (125 MHz) δ 10.6, 22.9, 26.4, 29.8, 35.3, 37.2, 56.3, 61.0, 68.1. Anal. Calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_2\text{S}$: C, 59.27; H, 11.10; N, 5.32. Found: C, 59.21; H, 11.31; N, 5.13.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5i.** General procedure C was followed with 62 mg (0.200 mmol) of **2i**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; >99:1 dr (98:2 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, $t_R = 9.1$ min; minor diastereomer, $t_R = 44.4$ min). Column chromatography (5:5 hexanes/EtOAc) afforded 59 mg (95%) of ***anti*-5i**: IR 3215, 3335, 3347 cm^{-1} ; ^1H NMR (500 MHz) δ 0.89 (s, 9H), 1.32 (s, 9H), 1.61 (ddd, 1H, $J = 14.4, 11.3, 2.8$ Hz), 2.04 (ddd, 1H, $J = 14.4, 10.8, 2.9$ Hz), 3.24 (d, 1H, $J = 7.5$ Hz), 3.32 (ddd, 1H, $J = 11.3, 7.5, 2.9$ Hz), 4.67 (br s, 1H), 7.22-7.40 (m, 5H); ^{13}C NMR (125 MHz) δ 23.0, 26.4, 35.4, 40.3, 56.4, 61.5, 68.8, 125.6, 126.8, 128.2, 144.7; HRMS

(FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{17}\text{H}_{30}\text{NO}_2\text{S}$) m/z 312.1997. Found 312.2001.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5j.** General procedure C was followed with 55 mg (0.200 mmol) of **2j**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 99:1 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 8.2 min; minor diastereomer, t_R = 18.3 min). Column chromatography (7:3 hexanes/EtOAc) afforded 53 mg (96%) of ***anti*-5j**: IR 3261, 3384 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (s, 9H), 0.88 (d, 6H, J = 6.7 Hz), 1.22 (s, 9H), 1.54 (ddd, 1H, J = 14.5, 8.9, 2.5 Hz), 1.65 (ddd, 1H, J = 14.5, 11.4, 3.4 Hz), 1.71 (dsep, 1H, J = 6.7, 5.6 Hz), 3.24 (dddd, 1H, J = 8.9, 8.4, 5.6, 3.4 Hz), 3.31 (d, 1H, J = 8.4 Hz), 3.35-3.38 (m, 1H), 3.54 (d, 1H, J = 6.4 Hz); ^{13}C NMR (125 MHz) δ 18.2, 19.8, 22.8, 25.8, 33.2, 33.9, 34.9, 56.0, 59.9, 74.3. Anal. Calcd. for $\text{C}_{14}\text{H}_{31}\text{NO}_2\text{S}$: C, 60.60; H, 11.26; N, 5.05. Found: C, 60.36; H, 11.43; N, 4.86.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5k.** General procedure C was followed with 52 mg (0.200 mmol) of **2k**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 99:1 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 11.2 min; minor diastereomer, t_R = 33.8 min). Column chromatography (5:5 hexanes/EtOAc) afforded 49 mg (94%) of ***anti*-5k**: IR 3258, 3366 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (d, 3H, J = 6.8 Hz), 0.87 (d, 6H, J = 6.8 Hz), 0.93 (d, 3H, J = 6.7 Hz), 1.22 (s, 9H), 1.53 (ddd, 1H, J = 14.6, 9.6, 2.6 Hz), 1.62-1.73 (m, 3H), 3.25-3.30 (m, 1H), 3.45 (d, 1H, J = 7.7 Hz), 3.46 (br s, 1H), 3.72 (br s, 1H); ^{13}C NMR (125 MHz) δ 18.0, 18.2, 18.9, 19.4, 22.8, 33.4, 33.9, 36.6, 56.0, 59.2, 72.1; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{13}\text{H}_{30}\text{NO}_2\text{S}$) m/z 264.1997. Found 264.1994.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5l.** General procedure C was followed with 49 mg (0.200 mmol) of **2l**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 98:2 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 15.9 min; minor diastereomer, t_R = 50.1 min). Column chromatography (5:5 hexanes/EtOAc) afforded 46 mg (94%) of ***anti*-5l**: IR 3230, 3425 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (d, 3H, J = 6.7 Hz), 0.88 (d, 3H, J = 6.7 Hz), 0.93 (t, 3H, J = 7.4 Hz), 1.23 (s, 9H), 1.42-1.72 (m, 5H), 3.28-3.34 (m, 1H), 3.45 (d, 1H, J = 7.4 Hz), 3.64-3.69 (m, 1H), 3.84 (br s, 1H); ^{13}C NMR (125 MHz) δ 10.4, 17.8, 19.3, 22.8, 30.2, 33.5, 39.3, 56.0, 58.7, 68.8; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{12}\text{H}_{28}\text{NO}_2\text{S}$) m/z 250.1841. Found 250.1838.

***N*-Sulfinyl-1,3-Amino Alcohol *anti*-5m.** General procedure C was followed with 59 mg (0.200 mmol) of **2m**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 92:8 dr (94:6 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 6.7 min; minor diastereomer, t_R = 25.0 min).

Column chromatography (6:4 hexanes/EtOAc) afforded 50 mg (85%) of **anti-5m**: IR 3215, 3401 cm^{-1} ; ^1H NMR (500 MHz) δ 0.88 (d, 3H, $J = 6.8$ Hz), 0.90 (d, 3H, $J = 6.8$ Hz), 1.26 (s, 9H), 1.72-1.80 (m, 2H), 1.96 (ddd, 1H, $J = 14.7, 10.6, 3.0$ Hz), 3.36-3.41 (m, 1H), 3.55 (d, 1H, $J = 7.9$ Hz), 4.36 (br s, 1H), 4.91 (dd, 1H, $J = 10.3, 1.8$ Hz), 7.21-7.39 (m, 5H); ^{13}C NMR (125 MHz) δ 17.9, 19.2, 22.9, 33.3, 42.2, 56.2, 59.2, 69.7, 125.6, 127.0, 128.3, 144.8; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{16}\text{H}_{28}\text{NO}_2\text{S}$) m/z 298.1841. Found 298.1840.

N-Sulfinyl-1,3-Amino Alcohol anti-5n. General procedure C was followed with 52 mg (0.200 mmol) of **2n**, and 0.50 mL of LiBHET_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 97:3 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 11.5$ min; minor diastereomer, $t_R = 21.7$ min). Column chromatography (7:3 hexanes/EtOAc) afforded 47 mg (90%) of **anti-5n**: IR 3253, 3458 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (s, 9H), 0.93 (t, 3H, $J = 7.4$ Hz), 1.22 (s, 9H), 1.48-1.58 (m, 3H), 1.82 (ddd, 1H, $J = 14.8, 11.4, 3.6$ Hz), 3.30-3.43 (m, 3H), 3.58 (d, 1H, $J = 9.0$ Hz); ^{13}C NMR (125 MHz) δ 11.0, 22.7, 25.7, 29.4, 34.9, 36.0, 55.8, 57.1, 74.8. Anal. Calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_2\text{S}$: C, 59.27; H, 11.10; N, 5.32. Found: C, 59.23; H, 11.46; N, 5.17.

N-Sulfinyl-1,3-Amino Alcohol anti-5o. General procedure C was followed with 49 mg (0.200 mmol) of **2o**, and 0.50 mL of LiBHET_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 95:5 dr (97:3 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 15.7$ min; minor diastereomer, $t_R = 37.6$ min). Column chromatography (6:4 hexanes/EtOAc) afforded 46 mg (94%) of **anti-5o**: IR 3259, 3370 cm^{-1} ; ^1H NMR (500 MHz) δ 0.87 (d, 3H, $J = 6.8$ Hz), 0.91 (d, 3H, $J = 6.7$ Hz), 0.91 (t, 3H, $J = 7.4$ Hz), 1.21 (s, 9H), 1.46-1.56 (m, 3H), 1.63 (dtt, 1H, $J = 5.9, 6.7, 6.8$ Hz), 1.80 (ddd, 1H, $J = 14.7, 10.5, 3.5$ Hz), 3.33-3.39 (m, 1H), 3.45-3.54 (m, 2H), 3.69 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR (125 MHz) δ 10.7, 17.9, 18.7, 22.7, 29.7, 34.1, 38.8, 55.8, 56.5, 72.4; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{12}\text{H}_{28}\text{NO}_2\text{S}$) m/z 250.1841. Found 250.1836.

N-Sulfinyl-1,3-Amino Alcohol anti-5p. General procedure C was followed with 70 mg (0.300 mmol) of **2p**, and 0.75 mL of LiBHET_3 (0.75 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 93:7 dr (94:6 hexanes/EtOH, 1.0 mL/min: major diastereomer, $t_R = 9.5$ min; minor diastereomer, $t_R = 20.3$ min). Column chromatography (5:5 hexanes/EtOAc) afforded 55 mg (78%) of **anti-5p**: IR 3244, 3390 cm^{-1} ; ^1H NMR (500 MHz) δ 0.92 (t, 3H, $J = 7.4$ Hz), 0.93 (t, 3H, $J = 7.4$ Hz), 1.22 (s, 9H), 1.42-1.56 (m, 5H), 1.76 (ddd, 1H, $J = 14.7, 10.1, 3.5$ Hz), 3.35-3.42 (m, 1H), 3.50 (br s, 1H), 3.66 (d, 1H, $J = 7.8$ Hz), 3.68-3.73 (m, 1H); ^{13}C NMR (125

MHz) δ 10.2, 10.6, 22.7, 29.9, 30.5, 41.8, 55.8, 56.0, 69.1; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{11}\text{H}_{26}\text{NO}_2\text{S}$) m/z 236.1684. Found 236.1678.

N-Sulfinyl-1,3-Amino Alcohol *anti*-5q. General procedure C was followed with 56 mg (0.200 mmol) of **2q**, and 0.50 mL of LiBHEt_3 (0.50 mmol, 1.00 M in THF). Diastereoselectivity was determined by HPLC analysis; 88:12 dr (94:6 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 8.6 min; minor diastereomer, t_R = 25.0 min). Column chromatography (6:4 hexanes/EtOAc) afforded 45 mg (80%) of ***anti*-5q**: IR 3191, 3346 cm^{-1} ; ^1H NMR (500 MHz) δ 0.94 (t, 3H, J = 7.4 Hz), 1.25 (s, 9H), 1.53-1.60 (m, 2H), 1.77 (ddd, 1H, J = 14.8, 8.4, 3.0 Hz), 2.10 (ddd, 1H, J = 14.8, 10.5, 3.4 Hz), 3.40-3.47 (m, 1H), 3.72 (d, 1H, J = 8.1 Hz), 4.04 (br s, 1H), 4.93 (dd, 1H, J = 10.3, 2.2 Hz), 7.22-7.37 (m, 5H); ^{13}C NMR (125 MHz) δ 10.6, 22.7, 29.6, 44.4, 55.9, 56.2, 70.2, 125.6, 127.1, 128.3, 144.8. Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{S}$: C, 63.56; H, 8.89; N, 4.94. Found: C, 63.25; H, 9.19; N, 4.76.

Sulfinyl Imine 7. A mixture of 1.52 g (12.5 mmol) of *tert*-butanesulfinamide, 2.37 g of ketone **6** (15.0 mmol), and 6.0 g of $\text{Ti}(\text{OEt})_4$ (~25.0 mmol) in 25 mL of THF was heated to reflux for 15 h and then was cooled to room temperature. The reaction mixture was poured into 25 mL of brine while rapidly stirring, and the resulting mixture was filtered through a plug of Celite. The filter cake was washed with EtOAc, and the combined filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted once with EtOAc, and the combined organic portions were dried over Na_2SO_4 , filtered and concentrated. Column chromatography (4:6 hexanes/EtOAc) of the crude material afforded 3.21 g (82%) of **7** as a mixture of *E/Z* isomers (8:1 by ^1H NMR in CDCl_3): IR 1621 cm^{-1} ; ^1H NMR (500 MHz) δ 1.25 (s, 9H), 1.66-1.77 (m, 4H), 2.31 (s, 3H), 2.39-2.51 (m, 2H), 3.81-3.98 (m, 4H), 4.85 (t, 1H, J = 4.4 Hz); ^{13}C NMR (125 MHz) δ 19.8, 22.1, 23.0, 33.1, 43.0, 56.2, 64.9, 104.2, 185.0; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{12}\text{H}_{24}\text{NO}_3\text{S}$) m/z 262.1477. Found 262.1473.

β -Hydroxy Sulfinyl Imine 8. To a solution of 485 mg of *i*- Pr_2NH (4.79 mmol) in 20 mL of THF was added 2.0 mL of a 2.20 M solution of butyllithium in pentane (4.40 equiv) at 0 $^\circ\text{C}$ and the mixture was stirred for 30 min. The solution was then cooled to -78 $^\circ\text{C}$ and 1.05 g of *tert*-butanesulfinyl imine **7** (4.02 mmol) was added. After the reaction solution was stirred for 45 min at -78 $^\circ\text{C}$, 1.47 g of MgBr_2 (7.98 equiv) was added. The reaction mixture was stirred for 45 min, and 317 mg of butyraldehyde (4.40 mmol) was added to the solution. Then, the mixture was stirred for 20 h at -78 $^\circ\text{C}$. To the reaction mixture was added 2*N* AcOH/THF (5 equiv), which was cooled to -78 $^\circ\text{C}$ before the addition. Brine and saturated aqueous NaHCO_3

solution was then added to the mixture with stirring. The organic layer was collected and the brine layer was extracted with EtOAc (2x). The combined organic portions were quickly dried, filtered, and concentrated. Diastereoselectivity was determined by HPLC analysis; 82:18 dr (94:6 hexanes/*i*-PrOH, 1.0 mL/min: major diastereomer, t_R = 17.8 min; minor diastereomer, t_R = 24.8 min). Column chromatography (6:4 hexanes/EtOAc) of the crude material afforded 677 mg (51%) of **8** as a mixture of *E/Z* isomers (13:1 by ^1H NMR in CDCl_3): IR 1623, 3348 cm^{-1} ; ^1H NMR (500 MHz) δ 0.91 (t, 3H, J = 6.9 Hz), 1.24 (s, 9H), 1.31-1.51 (m, 4H), 1.62-1.80 (m, 4H), 2.38-2.65 (m, 3H), 3.09 (m, 1H), 3.72-3.79 (m, 1H), 3.82-3.97 (m, 4H), 4.08 (d, 1H, J = 9.3 Hz), 4.84 (t, 1H, J = 4.4 Hz); ^{13}C NMR (125 MHz) δ 14.0, 18.7, 19.7, 22.4, 33.0, 40.6, 41.4, 45.1, 57.7, 64.8, 67.3, 104.3, 184.6; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{16}\text{H}_{32}\text{NO}_4\text{S}$) m/z 334.2052. Found 334.2053.

***N*-Sulfinyl-1,3-amino Alcohol *syn*-9.** To a solution of 50 mg of β -hydroxy sulfinyl imine **8** (0.150 mmol, 1.0 equiv) in 0.75 mL of THF was added 45 mg of catecholborane (0.375 mmol, 2.5 equiv), and the mixture was stirred for 3 h at -48°C . To this mixture was added MeOH and a saturated solution of sodium potassium tartrate. The resulting mixture was stirred for 10 min, washed with brine, and the brine layer was extracted with EtOAc (2x). The combined organic portions were dried, filtered, and concentrated. Diastereoselectivity was determined by HPLC analysis; 93:7 dr (90:10 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 30.4 min; minor diastereomer, t_R = 13.6 min). Column chromatography (19:1 EtOAc/MeOH) of the crude material afforded 36 mg (72%) of ***syn*-9**: IR 3288, 3395 cm^{-1} ; ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 7.0 Hz), 1.18 (s, 9H), 1.25-1.79 (m, 12H), 3.11 (br s, 1H), 3.30-3.36 (m, 1H), 3.65-3.70 (m, 1H), 3.77-3.96 (m, 4H), 3.99 (d, 1H, J = 5.5 Hz), 4.81 (t, 1H, J = 4.7 Hz); ^{13}C NMR (125 MHz) δ 14.0, 18.4, 20.3, 22.5, 33.3, 35.3, 40.6, 42.9, 55.8, 56.5, 64.7, 64.7, 71.2, 104.2; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{16}\text{H}_{34}\text{NO}_4\text{S}$) m/z 336.2209. Found 336.2212.

***N*-Sulfinyl-1,3-amino Alcohol *anti*-9.** To a -78°C solution of 133 mg of β -hydroxy *N*-sulfinyl imine **8** (0.399 mmol, 1.00 equiv) in 2 mL of THF was added 1 mL of a 1.0 M solution of LiBHET_3 (1.00 mmol, 2.51 equiv) and the resulting solution was stirred for 3 h. To this solution was added 1.00 mL of a saturated aqueous solution of NH_4Cl . The resulting mixture was gradually warmed to rt with stirring, washed with brine, and the brine layer was extracted with EtOAc (2x). The combined organic portions were dried, filtered, and concentrated. Diastereoselectivity was determined by HPLC analysis; 91:9 dr (90:10 hexanes/EtOH, 1.0 mL/min: major diastereomer, t_R = 12.5 min; minor diastereomer, t_R = 29.9 min). Column chromatography (3:7

hexane/EtOAc) of the crude material afforded 101 mg (75%) of **anti-9**: IR 3252, 3402 cm^{-1} ; ^1H NMR (500 MHz) δ 0.86 (t, 3H, $J = 7.1$ Hz), 1.17 (s, 9H), 1.25-1.66 (m, 11H), 1.73 (ddd, 1H, $J = 14.7, 10.1, 3.5$), 2.69 (br s, 1H), 3.39-3.45 (m, 1H), 3.60 (d, 1H, $J = 6.0$ Hz), 3.73-3.94 (m, 5H), 4.78 (t, 1H, $J = 4.7$ Hz); ^{13}C NMR (125 MHz) δ 14.0, 18.9, 20.4, 22.6, 33.4, 36.6, 39.8, 42.3, 54.4, 55.7, 64.7, 64.7, 67.5, 104.3; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{16}\text{H}_{34}\text{NO}_4\text{S}$) m/z 336.2209. Found 336.2215.

(-)-8-Epihalosaline (syn-10). A mixture of 70 mg of **syn-9** (0.209 mmol, 1.0 equiv) and 4.7 mg of PtO_2 (0.021 mmol) in 11 mL of TFA/EtOH/ H_2O (5:5:1) was stirred under a hydrogen atmosphere at room temperature for 15 h. An aqueous solution of KOH was added to the resulting mixture until the pH was 14, and then the mixture was extracted with CH_2Cl_2 (5x). The combined organic portions were dried over Na_2SO_4 , filtered and concentrated. Column chromatography (7:1.4:91.6 MeOH/15N NH_4OH aq/ CH_2Cl_2) of the crude material afforded 26 mg (73%) of (-)-8-epihalosaline: $[\alpha]_{\text{D}}^{23} -7.9$ (c 1.5, MeOH) [lit. value.⁷ $[\alpha]_{\text{D}}^{23} -8$ (c 3.7, MeOH)]; ^1H NMR (500 MHz) δ 0.90 (t, 3H, $J = 7.0$ Hz), 1.05-1.64 (m, 11H), 1.78-1.83 (m, 1H), 2.34 (s, 1H), 2.55-2.61 (m, 1H), 2.68-2.73 (m, 1H), 3.01-3.04 (m, 1H), 3.13 (br s, 1H), 3.79-3.84 (m, 1H); ^{13}C NMR (125 MHz) δ 14.1, 18.6, 24.5, 27.2, 34.3, 40.3, 42.4, 45.9, 58.3, 72.8; HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{10}\text{H}_{21}\text{NO}$) m/z 171.1623. Found 171.1622.

(-)-Halosaline (anti-10). A mixture of 70 mg of **anti-9** (0.209 mmol, 1.0 equiv) and 4.7 mg of PtO_2 (0.021 mmol) in 11 mL of TFA/EtOH/ H_2O (5:5:1) was stirred under a hydrogen atmosphere at room temperature for 15 h. An aqueous solution of KOH was added to the resulting mixture until the pH was 14, and then the mixture was extracted with CH_2Cl_2 (5x). The combined organic portions were dried over Na_2SO_4 , filtered and concentrated. Column chromatography (15:2.5:82.5 MeOH/15N NH_4OH aq/ CH_2Cl_2) of the crude material afforded 29 mg (81%) of (-)-halosaline: $[\alpha]_{\text{D}}^{23} -18.2$ (c 0.6, 95% EtOH) [lit. value.⁸ $[\alpha]_{\text{D}}^{20} -19.5$ (c 0.6, 95% EtOH)]; ^1H NMR (500 MHz) δ 0.90 (t, 3H, $J = 7.1$ Hz), 1.26-1.59 (m, 11H), 1.78-1.80 (m, 1H), 2.53-2.58 (m, 1H), 2.85-2.89 (m, 1H), 3.02-3.06 (m, 1H), 3.43 (s, 1H), 3.51 (br s, 1H), 3.85-3.90 (m, 1H); ^{13}C NMR (125 MHz) δ 14.1, 19.0, 24.6, 25.9, 31.3, 40.0, 41.9, 46.8, 54.7, 68.6; HRMS (FAB) calcd for $[\text{MH}]^+$ ($\text{C}_{10}\text{H}_{22}\text{NO}$) m/z 172.1701. Found 172.1705.

Table S1. Crystal Data and Structural Refinement for *anti*-5h

	<i>anti</i> -5h
Empirical Formula	SO ₂ NC ₁₃ H ₂₉
Formula Weight	263.44
Temperature (°C)	-139 (1)
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 X 0.19 X 0.11 mm
Crystal System	orthorhombic
a (Å)	9.389(1)
b (Å)	10.800(1)
c (Å)	16.087(2)
V (Å ³)	1631.3(3)
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)
Z values	4
D _{calc}	1.073 g/cm ³
F ₀₀₀	584.00
μ(MoKα)	1.92 cm ⁻¹
Diffractometer	Bruker SMART CCD
Radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame
Scan Type	ω (0.3 degrees per frame)
2θ _{max}	49.4°
No. Reflections Measured	Total: 7456
	Unique: 1813 (R _{int} = 0.081)
Transmission Factors	T _{max} = 1.00, T _{min} = 0.54
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observation (I>3.00σ(I))	1519
No. Variables	154
Reflection/Parameter Ratio	9.86
Residual: R; R _w ; R _{all} ^a	0.052; 0.055; 0.108
Goodness of Fit Indicator ^b	1.71
Max Shift/Error in Final Cycle	0.01
Maximum peak in Final Diff. Map	0.29 e ⁻ / Å ³
Minimum peak in Final Diff. Map	-0.25 e ⁻ / Å ³

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}$

^b Goodness of Fit = $[(\sum w(|F_o| - |F_c|)^2) / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$

Table S2. Atomic Coordinates and B(eq) Values for *anti*-5h

atom	x	y	z	B(eq)
S(1)	-0.0547(2)	0.1302(1)	0.13812(9)	2.41(3)
O(1)	-0.1017(3)	0.2637(3)	0.1369(2)	2.94(10)
O(2)	-0.1370(4)	0.3302(3)	-0.0288(2)	2.33(10)
N(1)	0.0517(5)	0.0968(4)	0.0589(2)	1.7(1)
C(1)	0.0741(6)	0.1220(5)	0.2237(3)	2.1(1)
C(2)	-0.0169(6)	0.1258(6)	0.3017(3)	3.3(2)
C(3)	0.1723(6)	0.2328(5)	0.2205(3)	2.4(2)
C(4)	0.1550(7)	-0.0008(5)	0.2177(3)	2.9(2)
C(5)	-0.0186(5)	0.0759(5)	-0.0211(3)	1.9(1)
C(6)	0.0250(5)	0.1739(5)	-0.0844(3)	1.8(1)
C(7)	0.0056(6)	0.3066(5)	-0.0573(4)	2.1(1)
C(8)	0.0371(6)	0.3956(5)	-0.1277(4)	2.9(2)
C(9)	0.0327(8)	0.5320(6)	-0.1032(4)	4.7(2)
C(10)	0.0039(6)	-0.0606(5)	-0.0503(4)	2.2(2)
C(11)	-0.0650(7)	-0.1455(5)	0.0121(4)	3.9(2)
C(12)	0.1627(7)	-0.0904(5)	-0.0559(4)	3.1(2)
C(13)	-0.0645(7)	-0.0774(5)	-0.1358(4)	4.0(2)
H(1)	-0.0724	0.1993	0.3018	3.9346
H(2)	-0.0780	0.0557	0.3028	3.9346
H(3)	0.0430	0.1247	0.3493	3.9346
H(4)	0.2347	0.2312	0.2670	2.8925
H(5)	0.2266	0.2303	0.1707	2.8925
H(6)	0.1175	0.3067	0.2218	2.8925
H(7)	0.0889	-0.0674	0.2174	3.5107
H(8)	0.2091	-0.0021	0.1679	3.5107
H(9)	0.2169	-0.0088	0.2641	3.5107
H(10)	-0.1179	0.0860	-0.0119	2.2240
H(11)	0.1230	0.1620	-0.0968	2.1702
H(12)	-0.0300	0.1615	-0.1332	2.1702
H(13)	0.0698	0.3232	-0.0130	2.4780
H(14)	0.1294	0.3777	-0.1486	3.5180
H(15)	-0.0314	0.3825	-0.1703	3.5180
H(16)	0.1043	0.5480	-0.0629	5.6654
H(17)	0.0494	0.5818	-0.1509	5.6654
H(18)	-0.0581	0.5512	-0.0806	5.6654
H(19)	-0.1516	-0.1097	0.0311	4.7173
H(20)	-0.0843	-0.2231	-0.0132	4.7173
H(21)	-0.0026	-0.1571	0.0580	4.7173
H(22)	0.1885	-0.1440	-0.0116	3.6893
H(23)	0.1821	-0.0699	-0.1075	3.6893
H(24)	0.2162	-0.0160	-0.0523	3.6893
H(25)	-0.0748	0.0010	-0.1618	4.7802
H(26)	-0.0055	-0.1289	-0.1691	4.7802
H(27)	-0.1553	-0.1149	-0.1296	4.7802
H(28)	0.1403	0.1398	0.0552	4.0680
H(29)	-0.1607	0.2796	0.0033	4.0680

Table S3. Anisotropic Displacement Parameters for *anti*-5h

atom	U11	U22	U33	U12	U13	U23
S(1)	0.0221(7)	0.0409(10)	0.0287(9)	0.0002(6)	0.0039(8)	-0.0080(9)
O(1)	0.035(2)	0.040(3)	0.036(2)	0.021(2)	-0.003(2)	-0.008(2)
O(2)	0.020(2)	0.024(3)	0.044(3)	0.006(2)	-0.001(2)	0.001(2)
N(1)	0.017(2)	0.031(3)	0.016(3)	0.004(3)	0.007(2)	-0.007(2)
C(1)	0.037(4)	0.024(3)	0.018(3)	-0.002(4)	-0.004(3)	0.003(3)
C(2)	0.047(4)	0.047(4)	0.031(4)	-0.011(4)	0.006(3)	-0.001(3)
C(3)	0.029(4)	0.032(4)	0.031(4)	-0.002(3)	-0.007(3)	0.001(3)
C(4)	0.045(4)	0.028(4)	0.039(4)	0.000(4)	0.009(4)	0.001(3)
C(5)	0.014(3)	0.035(4)	0.022(3)	0.003(3)	0.004(3)	-0.006(3)
C(6)	0.009(3)	0.031(4)	0.028(3)	0.000(3)	-0.007(3)	-0.007(3)
C(7)	0.015(4)	0.033(4)	0.031(4)	-0.002(3)	-0.005(3)	0.001(3)
C(8)	0.027(3)	0.030(4)	0.054(4)	0.002(3)	-0.002(4)	0.007(3)
C(9)	0.050(5)	0.039(4)	0.091(6)	-0.006(4)	-0.007(5)	0.007(4)
C(10)	0.025(4)	0.021(4)	0.036(4)	-0.003(3)	-0.003(3)	-0.012(3)
C(11)	0.054(4)	0.027(4)	0.069(5)	-0.004(4)	0.014(4)	-0.005(4)
C(12)	0.052(4)	0.026(4)	0.038(4)	0.017(3)	0.010(4)	0.000(3)
C(13)	0.066(4)	0.032(4)	0.054(4)	0.003(4)	-0.022(5)	-0.018(4)

Table S4. Bond Lengths(Å) for *anti*-5h

atom	atom	distance	atom	atom	distance
S1	O1	1.508(3)	C5	C6	1.524(7)
S1	N1	1.659(4)	C5	C10	1.561(7)
S1	C1	1.835(5)	C6	C7	1.509(7)
O2	C7	1.438(6)	C7	C8	1.515(7)
N1	C5	1.465(6)	C8	C9	1.525(8)
C1	C2	1.518(7)	C10	C11	1.506(8)
C1	C3	1.512(7)	C10	C12	1.529(8)
C1	C4	1.531(8)	C10	C13	1.528(8)

Table S5. Bond Angles(°) for *anti*-5h

atom	atom	atom	angle	atom	atom	atom	angle
O1	S1	N1	112.0(2)	C6	C5	C10	114.7(4)
O1	S1	C1	104.4(2)	C5	C6	C7	115.7(4)
N1	S1	C1	99.7(2)	C2	C7	C6	111.9(4)
S1	N1	C5	115.9(3)	C2	C7	C8	107.9(5)
S1	C1	C2	104.4(4)	C6	C7	C8	111.3(5)
S1	C1	C3	109.7(4)	C7	C8	C9	114.4(5)
S1	C1	C4	108.8(4)	C5	C10	C11	108.5(4)
C2	C1	C3	110.5(5)	C5	C10	C12	110.4(4)
C2	C1	C4	110.8(5)	C5	C10	C13	109.0(5)
C3	C1	C4	112.4(5)	C11	C10	C12	109.3(5)
N1	C5	C6	111.0(4)	C11	C10	C13	110.3(5)
N1	C5	C10	110.4(4)	C12	C10	C13	109.4(5)

Table S6. Torsion Angles(°) for *anti*-5h

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S1	N1	C5	C6	115.9(4)	N1	C5	C6	C7	-53.4(6)
S1	N1	C5	C10	-115.6(4)	N1	C5	C10	C11	62.6(5)
O1	S1	N1	C5	-79.0(4)	N1	C5	C10	C12	-57.1(6)
O1	S1	C1	C2	75.1(4)	N1	C5	C10	C13	-177.3(5)
O1	S1	C1	C3	-43.3(4)	C1	S1	N1	C5	171.1(4)
O1	S1	C1	C4	-166.6(4)	C5	C6	C7	C8	-173.9(5)
O2	C7	C6	C5	-53.1(6)	C6	C5	C10	C11	-171.0(5)
O2	C7	C8	C9	62.1(6)	C6	C5	C10	C12	69.3(6)
N1	S1	C1	C2	-169.1(4)	C6	C5	C10	C13	-50.9(6)
N1	S1	C1	C3	72.5(4)	C6	C7	C8	C9	-174.8(4)
N1	S1	C1	C4	-50.8(4)	C7	C6	C5	C10	-179.5(4)

Table S7. Non-Bonded Contacts out to 3.60 Å for *anti*-5h

atom	atom	distance	ADC	atom	atom	distance	ADC
O1	C4	3.491(7)	4	O1	O2	2.780(5)	1
O2	N1	3.066(6)	45503				

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