Supporting Information

Total Synthesis of (–)-Aurantioclavine

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1. General methods and materials. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without purification. 1,4-Dioxane, tetrahydrofuran, diethyl ether, methylene chloride, and toluene were obtained from a Seca Solvent Systems by GlassContour (solvent dried over alumina under an N₂ atmosphere). Methanol and triethylamine were distilled under N₂ over CaH₂ immediately prior to use. Anhydrous *N,N*-dimethylformamide (water <50 ppm) was purchased from Acros. All liquids and reagents were thoroughly degassed using three freeze-pump-thaw cycles prior to introduction to the inert atmosphere box. (*S*)- and (*R*)-*tert*-butanesulfinamide were provided by AllyChem Co. Ltd (Dalian, China). 2,2-Dimethylethenyl MIDA boronate (**9**) was synthesized according to literature procedure and ¹H-NMR data was used to confirm its identity.¹ All reactions were carried out in flame-dried glassware under an inert N₂ atmosphere. Flash column chromatography was carried out either with Merck 60 230-240 mesh silica gel, or using a Biotage SP Flash Purification System (Biotage No. SP1-B1A) with Flash+ 3 cartridges (Biotage No. FPK0-1107-16046). Diastereoselectivity determinations were performed using an Agilent 1100 series LC equipped with a silica normal phase column (Microsorb Si 100 A packing) with a multiwavelength detector. ¹H and ¹³C-NMR spectra were obtained on a Bruker AVB-400, DRX-500, AV-500, or AV-600 at room temperature. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. ¹H NMR resonances are referenced to either the residual solvent peak (CDCl₃, 7.26 ppm; acetone-*d*₆, 2.05 ppm) or TMS (0.00 ppm) and ¹³C NMR resonances are referenced to the residual solvent peak (CDCl₃, 77.23 ppm; acetone-*d*₆, 29.84 ppm). IR spectra were recorded on a Nicolet Avatar 350 FTIR spectrometer equipped with an attenuated total reflectance accessory and only partial data are listed. Melting points were determined on a Laboratory Devices Mel-Temp 3.0 and are reported uncorrected. Elemental analyses and mass spectrometry analyses were performed by the University of California at Berkeley Microanalysis and Mass Spectrometry Facilities.

2. Preparation of 2-15 and (-)-Aurantioclavine ((-)-1)

Lactone 4. In an inert atmosphere box, a 100-mL Fisher-Porter-Bottle (a high pressure reaction vessel) was charged with Pd(OAc)₂ (2.3 mg, 0.010 mmol), cataCXium A (10.8 mg, 0.0300 mmol), and toluene (3 mL). TMEDA (0.225 mL, 1.50 mmol) and 4-bromotryptophol² (480 mg, 2.00 mmol) were then added. The reaction vessel was removed from the inert atmosphere box, and the reaction mixture was purged with synthesis gas by pressurizing with 5 bar H₂/CO (2:1) and evacuating three times. After 21 h at a pressure of 5 bar (refilled as necessary) and 100 °C, the reaction mixture was cooled to room temperature and diluted with saturated aqueous NaHCO₃. The aqueous layer was then washed with EtOAc (3 x 50 mL). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography (40-60% EtOAc/hexanes) afforded 335 mg (90%) of **4** as a pale yellow solid. ¹H NMR (500 MHz, acetone-*d*₆): δ 3.20 (t, 2H, *J* = 5.0), 4.61 (t, 2H, *J* = 5.0), 7.26 (t, 1H, *J* = 8.0), 7.38 (s, 1H), 7.70 (d, 1H, *J* = 8.0), 7.85 (d, 1H, *J* = 7.2), 10.50 (br s, 1H). ¹³C NMR (125 MHz, acetone-*d*₆): δ 28.4, 70.3, 114.8, 117.5, 121.6, 122.2, 124.7, 126.1, 126.8, 138.0, 170.6. HRMS-ESI (*m/z*): [MH]⁺ calcd for C₁₁H₁₀NO₂, 188.0706; found, 188.0711.

(*R*)-*N*-tert-Butanesulfinyl aldimine 3. The preparation of 4-formyltryptophol was adapted from Beller's general procedure for hydroformylation.³ In an inert atmosphere box, a 100-mL Fisher-Porter-Bottle (high pressure reaction vessel) was charged with 4-

bromotryptophol² (480 mg, 2.00 mmol), *N,N',N',N'*-tetramethylethylenediamine (0.225 mL, 1.50 mmol), and toluene (2 mL). TMSCl (0.266 mL, 2.10 mmol) was added dropwise, and the reaction mixture was stirred for several minutes. In the mean time, cataCXium A (10.8 mg, 0.0300 mmol) was dissolved in toluene (1 mL) and added to a vial containing Pd(OAc)₂ (2.3 mg, 0.001 mmol). *N,N',N',N'*-Tetramethylethylenediamine (0.225 mL, 1.50 mmol) was added to the resulting catalyst and ligand mixture which was subsequently added to the Fisher-Porter-Bottle. The reaction vessel was removed from the inert atmosphere box, and purged with synthesis gas by pressurizing with 5 bar H₂/CO (2:1) and evacuating three times. After 18 h at a pressure of 5 bar (refilled as necessary) and 100 °C, the reaction mixture was cooled to room temperature. THF (3 mL) and 3 M HCl (3 mL) were added to the reaction mixture. After stirring for 30 min, the reaction mixture was diluted with water (5 mL) and extracted with CH₂Cl₂ (3 x 15 mL). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford aldehyde **5** as a bright yellow oil. Aldehyde **5**, which is unstable, was taken on without purification. ¹H NMR (400 MHz, CDCl₃): δ 3.34 (t, 2H, *J* = 6.4), 3.90 (t, 2H, *J* = 6.4), 7.27 (d, 1H, *J* = 2.4), 7.32 (t, 1H, *J* = 7.6), 7.63 (d, 1H, *J* = 8.0), 7.70 (d, 1H, *J* = 7.2), 8.49 (br s, 1H), 10.31 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 31.7, 63.9, 114.2, 118.2, 121.4, 125.2, 127.1, 128.2, 130.3, 138.2, 193.6. MS (ESI): *m/z* 190 [MH]⁺.

A 0.5 M solution of the crude 4-formyltryptophol and Ti(OEt)₄ (0.84 mL, 4.0 mmol) was prepared in THF (4 mL) under a N₂ atmosphere. Then, (*R*)-*tert*-butanesulfinamide (267 mg, 2.20 mmol) was added. The reaction solution was stirred overnight at room temperature. While rapidly stirring, the reaction was quenched by adding an equal volume of brine (4 mL). The mixture was diluted with EtOAc (10 mL) and stirred vigorously for 20 min. The resulting mixture was filtered through a pad of Celite, which was washed thoroughly with EtOAc (200 mL). The filtrate was transferred to a separatory funnel and washed with brine. The brine was then washed with a small amount of EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Column chromatography (Biotage Flash+ cartridge, 40-100% EtOAc/hexanes) afforded 310 mg (53%, 2 steps) of **3** as a bright yellow solid. mp 129.5-130.5 °C. [α]_D²³ -278.0° (*c* 1.0, CHCl₃). IR 3252, 2899, 1572,

1351, 1269, 1039 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 1.28 (s, 9H), 3.18 (t, 2H, $J = 7.0$), 3.31 (br t, 1H, $J = 6.2$), 3.83 (app q, 2H, $J = 6.4$), 7.13 (d, 1H, $J = 2.5$), 7.21 (t, 1H, $J = 8.0$), 7.49 (d, 1H, $J = 8.0$), 7.87 (d, 1H, $J = 7.5$), 9.13 (br s, 1H), 9.30 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 22.7, 32.0, 58.1, 62.6, 112.3, 116.0, 120.2, 121.8, 126.3, 126.7, 126.8, 138.1, 162.1. HRMS-ESI (m/z): $[\text{MH}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$, 293.1318; found, 293.1325.

Potassium 2,2-dimethylethenyltrifluoroborate (10). To a 5.8 M solution of trimethylborate (0.75 mL, 6.6 mmol) in THF (1.1 mL) cooled to -78°C , was added 2-methyl-1-propenylmagnesium bromide (11 mL, 0.5 M in THF, 5.5 mmol) over 30 min using an addition funnel. The reaction mixture was stirred at -78°C for 15 min and then warmed to room temperature with stirring for 1 h. After cooling the reaction mixture to 0°C , a 30% aqueous HCl solution (8.2 mL) was added, and the mixture was stirred for 1 h at 0°C and then 30 min at room temperature. The reaction mixture was extracted with Et_2O (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and filtered, and concentrated under reduced pressure to ~ 5 mL. To avoid decomposition of the boronic acid, it is important to avoid concentrating to dryness. MeOH (1.5 mL) was added and the solution was concentrated under reduced pressure to ~ 2 mL. The solution of boronic acid was cooled to 0°C , and a 4.5 M solution of KHF_2 (1.51 g, 19.3 mmol) in water was added dropwise. The reaction mixture was stirred for 1 h at 0°C . After removing the water by lyophilization, the dried solids were triturated with hot acetone (100 mL), and filtered to remove inorganic salts. The resulting filtrate was concentrated and redissolved with heating in a minimal amount of acetone (35 mL). Addition of Et_2O (10 mL) and filtration of the precipitate, afforded 564 mg (63%) of **10** as a white solid. Spectral data corresponded to previously reported data.⁴

(*R_S*, *R*)-*N*-*tert*-Butanesulfinamide 2. In an inert atmosphere box, hydroxy(1,5-cyclooctadiene)rhodium(I) dimer (7.8 mg, 0.017 mmol) was dissolved in DMF (1.05 mL) and added to a pressure tube containing 1,2-bis(diphenylphosphino)benzene (15.2 mg, 0.034 mmol). The resulting mixture of catalyst and ligand was added to a 20-mL pressure tube containing a stirbar and trifluoroborate **10** (166 mg, 1.02 mmol). To the mixture of catalyst, ligand, and trifluoroborate was added aldimine **3** (200 mg, 0.680 mmol) dissolved in DMF (1.05 mL), followed by water (3.3 mL), and triethylamine (0.189 mL, 1.36 mmol). The pressure tube was capped, heated to 60 °C, and stirred for 1 h. Additional trifluoroborate **10** (166 mg, 1.02 mmol) was added twice with stirring at 60 °C for 1 h in between the additions. After the last addition, the reaction mixture was heated to 60 °C and stirred for another 1.5 h. The reaction mixture was cooled to room temperature, diluted with water (10 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford the crude product (97:3 dr). Column chromatography (Biotage Flash+ cartridge, 70-100% EtOAc/hexanes) afforded 193 mg (81%, >99:1 dr) of **2** as an off-white solid. An authentic mixture of *N*-sulfinyl amine diastereomers for diastereoselectivity determination was prepared by the addition of 2-methyl-1-propenylmagnesium bromide to (*R_S*)-sulfinyl imine **3** (69%, 33:67 dr) according to the general literature procedure for Grignard reagent additions to *N*-*tert*-butanesulfinyl imines.⁵ HPLC (silica column, hexanes:EtOH 98:2, 1.0 mL/min, λ = 222 nm): t_{major} = 17.8 min, t_{minor} = 21.7 min.) mp 124.7-126.0 °C. IR 3232, 2919, 1439, 1364, 1287, 1048, 753 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 1.19 (s, 9H), 1.78 (s, 6H), 3.15-3.20 (m, 1H), 3.26-3.32 (m, 1H), 3.67-3.71 (m, 1H), 3.73 (s, 1H), 3.89-3.93 (m, 1H), 4.03 (br s, 1H), 5.58 (d, 1H, *J* = 8.5), 5.98 (d, 1H, *J* = 8.5), 6.94 (d, 1H, *J* = 1.5), 7.14 (t, 1H, *J* = 7.5), 7.22 (d, 1H, *J* = 7.5), 7.25 (d, 1H, *J* = 7.5), 8.82 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 19.1, 22.8, 26.2, 31.5, 51.1, 55.6, 64.4, 111.4, 112.5, 119.2, 122.0, 124.4, 124.6, 125.5, 134.7, 136.4, 137.6. HRMS-ESI (*m/z*): [MNa]⁺ calcd for C₁₉H₂₈N₂O₂SNa, 371.1764; found, 371.1774.

(*R,S,R*)-Spiro[cyclopropane-1,3'-indolenine] (6). To a 0.1 M solution of sulfinamide **2** (100 mg, 0.290 mmol) in THF (2.9 mL) was added triphenylphosphine (90 mg, 0.34 mmol). The reaction mixture was cooled to 0 °C, and diethylazodicarboxylate (0.054 mL, 0.34 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred for 16 h, and then concentrated under reduced pressure.

Column chromatography (EtOAc + 1% NEt₃) using NEt₃-treated silica gel afforded 96.8 mg (99%) of **6** as a white foam. IR 3174, 2923, 1735, 1542, 1254, 1048, 959, 744 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 1.20 (s, 9H), 1.75 (s, 3H), 1.83 (s, 3H), 1.93-1.99 (m, 2H), 2.02-2.06 (m, 1H), 2.50-2.56 (m, 1H), 3.33 (s, 1H), 4.97 (d, 1H, *J* = 9.0), 5.35 (d, 1H, *J* = 9.0), 7.36-7.40 (m, 2H), 7.66-7.68 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 13.3, 14.3, 19.1, 22.8, 26.1, 37.8, 50.0, 55.5, 121.2, 124.2, 125.2, 127.6, 135.4, 136.6, 137.0, 157.3, 175.6. HRMS-ESI (*m/z*): [MH]⁺ calcd for C₁₉H₂₇N₂OS, 331.1839; found, 331.1845.

(*R*)-*N*-*tert*-Butanesulfinyl aldimine **11.** This procedure was adapted from that reported by Higuchi for the tosylation of a tryptophol derivative.⁶ A 0.07 M solution of aldimine **3** (436 mg, 1.49 mmol) and NEt₃ (2.10 mL, 14.9 mmol) in CH₂Cl₂ (21 mL) was cooled to -20 °C. 4-(Dimethylamino)pyridine (182 mg, 1.49 mmol) and *p*-toluenesulfonyl chloride (2.84 g, 14.9 mmol) were added. The reaction mixture was stirred at -20 °C for 43 h. The resulting solution was washed with water (15 mL). The aqueous layer was then back extracted with CH₂Cl₂ (20 mL). The combined organic layers were dried over Na₂SO₄,

filtered, and concentrated under reduced pressure. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 700 mg (78%) of **11** as an off-white foam. $[\alpha]_D^{23} -107.2^\circ$ (c 1.0, CHCl_3). IR 2924, 1590, 1358, 1174, 1082 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 1.23 (s, 9H), 2.33 (s, 3H), 2.36 (s, 3H), 3.18-3.23 (m, 1H), 3.27-3.32 (m, 1H), 4.24-4.28 (m, 1H), 4.30-4.34 (m, 1H), 7.12 (d, 2H, $J = 8.0$), 7.26 (d, 2H, $J = 8.0$), 7.36 (t, 1H, $J = 8.5$), 7.53 (d, 2H, $J = 8.0$), 7.55 (s, 1H), 7.78 (d, 2H, $J = 8.0$), 7.86 (d, 1H, $J = 8.5$), 8.14 (d, 1H, $J = 8.5$), 8.89 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 21.76, 21.79, 22.7, 28.0, 58.1, 68.5, 117.3, 117.5, 124.3, 124.6, 127.1, 127.5, 127.79, 127.82, 129.2, 129.9, 130.0, 132.4, 134.9, 136.4, 144.9, 145.6, 160.1. HRMS-ESI (m/z): $[\text{MH}]^+$ calcd for $\text{C}_{29}\text{H}_{33}\text{N}_2\text{O}_6\text{S}_3$, 601.1495; found, 601.1524.

(*R,S,R*)-*N*-tert-Butanesulfinamide 12. In an inert atmosphere box, hydroxy(1,5-cyclooctadiene)rhodium(I) dimer (1.4 mg, 0.0031 mmol) was dissolved in dioxane (0.2 mL), and the resulting solution was added to a pressure tube containing 1,2-bis(diphenylphosphino)benzene (2.8 mg, 0.0063 mmol). The resulting mixture of catalyst and ligand was added to a 20-mL pressure tube containing a stirbar and MIDA boronate **9** (53 mg, 0.25 mmol). To the mixture of catalyst, ligand, and MIDA boronate was added sulfinyl imine **11** (75.1 mg, 0.125 mmol) dissolved in dioxane (0.2 mL), followed by water (0.6 mL), and K_3PO_4 (53.1 mg, 0.250 mmol). The pressure tube was capped, removed from the inert atmosphere box, heated to 60 $^\circ\text{C}$, and stirred for 20 h. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL). The organic layer was washed with brine (10 mL) and the aqueous layer was back-extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure to afford the crude product (97:3 dr). Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 64.1 mg (78%, >99:1 dr) of **12** as a pale yellow foam. An authentic mixture of

N-sulfinyl amine diastereomers for diastereoselectivity determination was prepared according to the general literature procedure by in situ sulfinyl cleavage with HCl followed by resulfinylation upon addition of NEt₃.⁷ HPLC (silica column, hexanes:EtOH 90:10, 1.0 mL/min, λ = 220 nm): t_{major} = 12.7 min, t_{minor} = 16.5 min.). IR 3264, 2927, 1364, 1174, 1040 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.15 (s, 9H), 1.73 (s, 3H), 1.75 (s, 3H), 2.33 (s, 3H), 2.40 (s, 3H), 3.29 (app t, 2H, J = 6.0), 3.45 (s, 1H), 4.27-4.33 (m, 1H), 4.35-4.40 (m, 1H), 5.36 (d, 1H, J = 8.8), 5.56 (d, 1H, J = 8.8), 7.23 (d, 2H, J = 8.4), 7.24 (d, 2H, J = 8.4), 7.28 (t, 1H, J = 8.0), 7.36 (d, 1H, J = 7.6), 7.39 (s, 1H), 7.65 (d, 2H, J = 7.6), 7.75 (d, 2H, J = 8.4), 7.91 (d, 1H, J = 8.4). ¹³C NMR (100 MHz, CDCl₃): δ 19.2, 21.7, 21.8, 22.8, 26.1, 27.3, 51.7, 55.5, 69.1, 113.2, 117.0, 122.7, 125.0, 125.2, 125.5, 127.1, 127.3, 127.9, 130.0, 130.2, 132.6, 135.1, 135.9, 136.1, 137.2, 145.0, 145.2. HRMS-ESI (m/z): [MH]⁺ calcd for C₃₃H₄₁N₂O₆S₃, 657.2121; found, 657.2153.

(*R*, *R*)-Azepine 7. A 0.01 M solution of sulfinamide **12** (90.6 mg, 0.138 mmol) in THF (14.4 mL) was cooled to 0 °C. NaH (11.5 mg, 0.29 mmol) was added, and the reaction mixture was stirred at 0 °C for 10 min. The reaction mixture was then warmed to room temperature and stirred for 20 h. The reaction was quenched with saturated aqueous NH₄Cl (15 mL), and the resulting mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 57.0 mg (85%, >99:1 dr) of **7** as a white foam. HPLC (silica column, hexanes:EtOH 98:2, 1.0 mL/min, λ = 222 nm): t_{major} = 33.3 min, t_{minor} = 35.7 min.). IR 2920, 1362, 1175, 1143, 1067, 934 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 1.02 (s, 9H), 1.64 (s, 3H), 1.86 (s, 3H), 2.33 (s, 3H), 2.97-3.08 (m, 2H), 3.54-3.56 (m, 1H), 3.92-3.98 (m, 1H), 5.34 (d, 1H, J = 9.0), 5.67 (d, 1H, J = 9.0), 6.88 (d, 1H, J = 7.5), 7.18 (t, 1H, J = 8.0), 7.21 (d, 2H, J = 8.3), 7.38 (s, 1H), 7.74 (d, 2H, J = 8.3), 7.83 (d, 1H, J =

8.3). ^{13}C NMR (125 MHz, CDCl_3): δ 18.6, 21.7, 23.6, 26.5, 29.9, 46.6 (br), 57.2 (br), 58.0, 111.9, 120.6, 121.8, 123.4, 123.6, 124.6, 127.0, 128.4, 130.0, 135.3, 135.4, 136.3, 138.9, 145.0. HRMS-ESI (m/z): $[\text{MH}]^+$ calcd for $\text{C}_{26}\text{H}_{33}\text{N}_2\text{O}_3\text{S}_2$, 485.1927; found, 485.1949.

(*R*,*R*)-Azepine 13. To a 0.15 M solution of azepine **7** (30.0 mg, 0.061 mmol) in MeOH (0.4 mL) was added HCl (0.023 mL, 4 M in dioxane, 0.093 mmol). The reaction mixture was stirred at room temperature for 35 min. The reaction was quenched with saturated aqueous NaHCO_3 (3 mL) and the resulting mixture was diluted with CH_2Cl_2 (5 mL). The organic layer was removed, and the aqueous layer was back-extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure to afford the crude product. Column chromatography (SiO_2 , 50-80% EtOAc/hexanes + 1% NEt_3) using NEt_3 -treated silica gel afforded 22.7 mg (98% yield) of **13** as a pale yellow oil. IR 3349, 2920, 1597, 1364, 1293, 1175, 1142, 1091, 907 cm^{-1} . ^1H NMR (600 MHz, CDCl_3): δ 1.79 (s, 3H), 1.82 (s, 3H), 1.94 (br s, 1H), 2.32 (s, 3H), 2.89-2.99 (m, 2H), 3.00-3.09 (m, 1H), 3.41-3.50 (m, 1H), 4.80 (d, 1H, $J = 9.0$), 5.36 (d, 1H, $J = 9.0$), 6.95 (d, 1H, $J = 7.5$), 7.16-7.21 (m, 3H), 7.36 (s, 1H), 7.73 (d, 2H, $J = 8.0$), 7.88 (d, 1H, $J = 8.2$). ^{13}C NMR (150 MHz, CDCl_3): δ 18.5, 21.7, 26.0, 30.8, 48.0, 62.3, 111.9, 122.1, 122.5, 122.7, 124.2, 127.0, 127.3, 129.1, 129.9, 134.3, 135.5, 136.3, 139.4, 144.8. HRMS-FAB (m/z): $[\text{MH}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$, 381.1637; found, 381.1632.

(*R*,*R*)-Azepine 14. To a 0.05 M solution of azepine **7** (39.7 mg, 0.082 mmol) in anhydrous MeOH (1.6 mL) was added flame-dried Mg⁰ powder (29.9 mg, 1.23 mmol). The mixture was stirred for 2 h and then concentrated under reduced pressure. After diluting with CH₂Cl₂, the reaction mixture was filtered through a pad of Celite and then concentrated under reduced pressure. Column chromatography (SiO₂, 50% EtOAc/hexanes) afforded 26.3 mg (97%) of **14** as a white solid. decomp >210 °C. ¹H NMR (600 MHz, CDCl₃): δ 1.11 (s, 9H), 1.66 (s, 3H), 1.94 (s, 3H), 3.03-3.14 (m, 2H), 3.60-3.64 (m, 1H), 4.07-4.13 (m, 1H), 5.48 (d, 1H, *J* = 9.0), 5.80 (d, 1H, *J* = 9.0), 6.78 (d, 1H, *J* = 7.8), 7.00 (s, 1H), 7.08 (t, 1H, *J* = 7.8), 7.21 (d, 1H, *J* = 7.8), 8.44 (br s, 1H). ¹³C NMR (150 MHz, CDCl₃): δ 18.7, 23.8, 26.6, 30.3, 47.9, 57.2, 57.9, 109.6, 114.2, 117.8, 121.88, 121.94, 124.4, 125.1, 134.3, 137.5, 137.9. HRMS-ESI (*m/z*): [MH]⁺ calcd for C₁₉H₂₇N₂OS, 331.1839; found, 331.1854.

(-)-Aurantioclavine ((-)-1). To a 0.05 M solution of sulfinamide **7** (56.0 mg, 0.115 mmol) in anhydrous MeOH (2.3 mL) was added HCl (0.043 mL, 4 M in dioxane, 0.173 mmol). After stirring the mixture for 30 min, flame-dried Mg⁰ powder (28.1 mg, 1.15 mmol) was added. The reaction was followed by TLC and more Mg⁰ powder (2 x 14.1 mg, 0.58 mmol) was added at hourly intervals until the reaction had gone to completion. The reaction mixture was diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃. The organic layer was removed and the aqueous layer was back-extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography (SiO₂, 50-60% EtOAc/hexanes + 1% NEt₃) using NEt₃-treated silica gel afforded 25.9 mg (99% yield, >99% ee) of (-)-Aurantioclavine as an off-white solid. For enantiopurity determination, authentic (+)-Aurantioclavine was prepared by deprotection of **ent-15** following the same procedure as described above. HPLC (Chiralcel IA, hexanes:EtOH 96:4 + 1% Et₂NH,

1.0 mL/min, λ = 280 nm): t_R = 22.9 min, t_S = 27.5 min). mp 189.2-190.1 °C (lit.⁸ mp 188-189 °C). $[\alpha]_D^{23}$ -28.3° (c 1.0, CHCl₃) [lit.⁸ $[\alpha]_D^{22}$ -34 (c 1.25, CHCl₃)]. IR 3290, 3031, 2919, 1613, 1416, 1338, 1259, 1123, 881, 736 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 1.851 (s, 3H), 1.852 (s, 3H), 2.99-3.06 (m, 2H), 3.11-3.15 (m, 1H), 3.53-3.58 (m, 1H), 4.89 (d, 1H, J = 9.0), 5.46 (d, 1H, J = 9.0), 6.84 (d, 1H, J = 7.8), 7.02 (s, 1H), 7.10 (t, 1H, J = 7.8), 7.22 (d, 1H, J = 8.4), 8.08 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 18.5, 26.0, 31.1, 49.1, 62.8, 109.4, 115.7, 118.0, 121.2, 121.6, 125.5, 127.9, 133.4, 137.3, 138.6. HRMS-ESI (m/z): $[MH]^+$ calcd for C₁₅H₁₉N₂, 227.1543; found, 227.1538. Characterization data matches both isolated natural⁸ and synthetic⁹ material [For a 100 MHz ¹H-NMR spectrum of isolated natural material, see page 231 in reference 8 and for 300 MHz ¹H-NMR and 75 MHz ¹³C-NMR spectra of isolated synthetic material, see S19-S20 in the supporting information of reference 9].

(*S,S*, *R*)-Azepine 15. To a 0.17 M solution of sulfinyl imine **ent-11** (785 mg, 1.31 mmol) in CH₂Cl₂ (7.9 mL) at -48 °C was added dropwise a solution of 2-methyl-1-propenylmagnesium bromide (5.2 mL, 0.5 M in THF, 2.62 mmol). The reaction mixture was stirred at -48 °C for 15 min and then warmed to room temperature with stirring overnight. The reaction was quenched with saturated aqueous NH₄Cl (10 mL) and the resulting mixture was diluted with EtOAc (20 mL). The organic layer was removed and the aqueous layer was back-extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford the crude product (81:19 dr). Column chromatography (Biotage Flash+ cartridge, 12-100% methyl *t*-butyl ether/hexanes) afforded 456 mg (72%, >99:1 dr) of **15** as a white solid. HPLC (silica column, hexanes:EtOH 98:2, 1.0 mL/min, λ = 222 nm): t_{minor} = 35.5 min, t_{major} = 38.6 min.). mp 88.1-90.9 °C. IR 2920, 1362, 1172, 1143, 1073, 938 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 1.05 (s, 9H), 1.70 (s, 3H), 1.92 (s, 3H), 2.34 (s, 3H), 3.05-

3.08 (m, 2H), 3.22-3.28 (m, 1H), 3.64-3.68 (m, 1H), 5.45 (d, 1H, $J = 9.5$), 5.50 (d, 1H, $J = 9.5$), 6.89 (d, 1H, $J = 7.0$), 7.20 (t, 1H, $J = 7.5$), 7.24 (d, 2H, $J = 8.0$), 7.37 (s, 1H), 7.76 (d, 2H, $J = 8.5$), 7.83 (d, 1H, $J = 8.0$). ^{13}C NMR (125 MHz, CDCl_3): δ 19.0, 21.7, 23.2, 26.3, 28.1, 37.1 (br), 57.9, 65.8 (br), 112.0, 121.0, 121.8, 122.8, 123.8, 124.5, 127.1, 128.4, 130.0, 135.46, 135.52, 136.1, 137.8, 145.0. HRMS-ESI (m/z): $[\text{MH}]^+$ calcd for $\text{C}_{26}\text{H}_{33}\text{N}_2\text{O}_3\text{S}_2$, 485.1927; found, 485.1938.

(-)-Aurantoclavine ((-)-1). To a 0.05 M solution of sulfonamide **15** (10.6 mg, 0.022 mmol) in anhydrous MeOH (0.4 mL) was added HCl (0.008 mL, 4 M in dioxane, 0.173 mmol). After stirring the mixture for 30 min, flame-dried Mg^0 powder (8.0 mg, 0.33 mmol) was added. The reaction was followed by TLC and more Mg^0 powder (3 x 4.0 mg, 0.16 mmol) was added at hourly intervals until the reaction had gone to completion. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous NaHCO_3 . The organic layer was removed and the aqueous layer was back-extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Column chromatography (SiO_2 , 50-60% EtOAc/hexanes + 1% NEt_3) using NEt_3 -treated silica gel afforded 4.8 mg (98% yield, >99% ee) of (-)-Aurantoclavine as an off-white solid. HPLC (Chiralcel IA, hexanes:EtOH 96:4 + 1% Et_2NH , 1.0 mL/min, $\lambda = 280$ nm): $t_R = 24.2$ min). ^1H -NMR and ^{13}C -NMR data corresponded to the data reported for the synthesis of (-)-Aurantoclavine by addition of the MIDA boronate (vide supra).

3. References

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4. NMR spectra

Lactone **4** ^1H -NMR (500 MHz, acetone- d_6):

Lactone **4** ^{13}C -NMR (125 MHz, acetone- d_6):

Aldimine **3** ^1H -NMR (500 MHz, CDCl_3):

Aldimine **3** ^{13}C -NMR (125 MHz, CDCl_3):

Trifluoroborate **10** ^1H -NMR (400 MHz, acetone- d_6):

Trifluoroborate **10** ^{19}F -NMR (376 MHz, acetone- d_6):

Sulfinamide **2** ^1H -NMR (500 MHz, CDCl_3):

Sulfinamide **2** ^{13}C -NMR (125 MHz, CDCl_3):

Indolenine **6** ^1H -NMR (600 MHz, CDCl_3):

Indolenine **6** ^{13}C -NMR (150 MHz, CDCl_3):

Aldimine **11** ^1H -NMR (500 MHz, CDCl_3):

Aldimine **11** ^{13}C -NMR (125 MHz, CDCl_3):

Sulfinamide **12** ^1H -NMR (400 MHz, CDCl_3):

Sulfinamide **12** ^{13}C -NMR (100 MHz, CDCl_3):

Azepine **7** ^1H -NMR (500 MHz, CDCl_3):

Azepine **7** ^{13}C -NMR (125 MHz, CDCl_3):

Azepine **13** ^1H -NMR (600 MHz, CDCl_3):

Azepine **13** ^{13}C -NMR (150 MHz, CDCl_3):

Azepine **14** ^1H -NMR (600 MHz, CDCl_3):

Azepine **14** ^{13}C -NMR (150 MHz, CDCl_3):

(-)-Aurantioclavine ((-)-**1**) ^1H -NMR (using MIDA boronate; 600 MHz, CDCl_3):

(-)-Aurantioclavine ((-)-**1**) ^{13}C -NMR (using MIDA boronate; 100 MHz, CDCl_3):

Azepine **15** ^1H -NMR (500 MHz, CDCl_3):

Azepine **15** ^{13}C -NMR (125 MHz, CDCl_3):

(-)-Aurantioclavine ((-)-**1**) ^1H -NMR (using Grignard reagent; 600 MHz, CDCl_3):

(-)-Aurantioclavine ((-)-**1**) ^{13}C -NMR (using Grignard reagent; 150 MHz, CDCl_3):

5. HPLC traces

Crude sulfinamide **2** HPLC trace (Grignard reagent addition):

Crude sulfinamide **2** HPLC trace (MIDA boronate addition):

Crude sulfinamide **2** HPLC trace (trifluoroborate addition):

Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.798	MM	0.3960	3.02141e4	1271.71143	97.2117
2	21.677	MM	0.4711	866.63190	30.65735	2.7883

Totals : 3.10807e4 1302.36877

Pure sulfinamide **2** HPLC trace (trifluoroborate addition):

Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.612	BB	0.3476	2.64609e4	1170.97949	100.0000

Totals : 2.64609e4 1170.97949

Crude sulfinamide **12** HPLC trace (trifluoroborate addition):

Signal 1: MWD1 B, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.290	BB	0.3277	6407.19775	294.58557	98.1025
2	17.623	BP	0.5330	123.93127	3.58809	1.8975

Totals : 6531.12902 298.17366

Crude sulfinamide **12** HPLC trace (MIDA boronate addition):

Signal 1: MWD1 B, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.730	MM	0.3481	1.35397e4	648.33002	97.4295
2	16.514	MM	0.5723	357.21783	10.40351	2.5705

Totals : 1.38969e4 658.73353

Pure sulfonamide **12** HPLC trace (MIDA boronate addition):

Signal 1: MWD1 B, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.002	MM	0.3627	2.38397e4	1095.46936	99.4668
2	17.341	BB	0.4697	127.78332	3.88544	0.5332

Totals : 2.39675e4 1099.35480

Pure azepine **7** HPLC trace:

Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.384	BB	0.6374	2396.14429	57.36041	100.0000

Totals : 2396.14429 57.36041

Crude azepine **15** HPLC trace:

Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.521	MM	0.6858	438.30548	10.65206	18.8315
2	38.595	MM	0.7277	1889.21008	43.26659	81.1685

Totals : 2327.51556 53.91865

Pure azepine **15** HPLC trace:

Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.117	MM	0.6583	3725.90308	94.33401	100.0000

Totals : 3725.90308 94.33401

Authentic ($\pm$)-Aurantioclavine (($\pm$)-**1**) HPLC trace:

Pure (-)-Aurantioclavine ((-)-**1**) HPLC trace (MIDA boronate addition):

Pure (–)-Aurantioclavine ((–)-**1**) HPLC trace (Grignard reagent addition):

Signal 1: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.241	BB	0.5554	4036.94702	109.17168	100.0000

Totals : 4036.94702 109.17168