Supporting Information for:

Synthesis of the Highly Functionalized Tricyclic Core of Lactonamycin by Oxidative Dearomatization

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General. All non-aqueous reactions were carried out in oven- or flame-dried glassware under argon, unless otherwise specified. All reagents used were commercially available from Sigma-Aldrich, unless indicated otherwise. Solvents were reagent grade and purified by standard techniques: THF and diethyl ether were distilled from Na-benzophenone; CH_2Cl_2 was distilled from CaH_2; all other solvents were Aldrich "anhydrous" grade solvents, unless indicated otherwise. Reactions were magnetically stirred and monitored by thin layer chromatography on Whatman 250 μm alumina-backed silica gel plates. Flash chromatography was performed with SAI silica gel 60 (particle size 32-63 μm), and Florisil was 200 mesh from Aldrich. Yields reported are for isolated, spectroscopically pure compounds unless otherwise indicated. Melting points are uncorrected. $CDCl_3$ was allowed to stand over K_2CO_3 and 4 Å MS to neutralize and dry it prior to NMR sample preparation. NMR spectra were recorded on Bruker DPX 300, DRX 300, 400 or DMX 500 MHz spectrometers. ^1H and ^{13}C chemical shifts were referenced to residual solvent peaks. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer, and solutions were approximately 5 mg/mL. High resolution mass spectra were acquired in the Columbia University Mass Spectral Core facility on a JEOL HX110 spectrometer.

Dimethoxylactone 13. To a rapidly stirring suspension of 52 g (376 mmol, 10 equiv) of powdered K_2CO_3 in 300 mL of acetone was added 8.0 g (37 mmol, 1 equiv) of bisphenol **12**[1] and 11.5 mL (122 mmol, 2.3 equiv) of dimethyl sulfate. The mixture was then refluxed for 8 h. After cooling to rt, the solid was filtered off and the filtrate was concentrated by rotary evaporation. The residue was then brought up in 300 mL of CH_2Cl_2 and washed with 2 x 200 mL of 0.5 M NaOH, followed by 1 x 200 mL saturated NH_4Cl. The organic phase was then dried with Na_2SO_4, concentrated by rotary evaporation, and the resultant oil was passed through a short pad of silica with CH_2Cl_2. Following concentration of the collected fractions, the crude material was recrystallized from EtOAc to yield 8.23 g (91%) of **13** as a fluffy white powder: m.

p. = 165-167 ˚C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.4 (1H, d, *J* = 8.4 Hz), 8.2 (1H, d, *J* = 8.4 Hz), 7.7 (1H, m), 7.6 (1H, m), 5.55 (2H, s), 4.3 (3H, s), 4.1 (3H, s) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 168.4, 153.3, 144.9, 131.5, 129.4, 129.2, 126.9, 126.8, 124.3, 122.1, 111.8, 67.3, 63.8, 60.4 ppm; IR (CH_2Cl_2) 1762, 1422, 1360 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{12}O_4$ $[M]^+$: 244.0736; found 244.0729.

Monomethoxylactone 14. To a solution of 3.5 g (14.3 mmol, 1 equiv) of **13** in 130 mL of CH_2Cl_2 was added quickly 17.5 mL of a 1 M solution of B-iodo-9-BBN in hexanes (17.5 mmol, 1.2 equiv). The resultant purple solution was refluxed for 18 h. After the reaction was allowed to cool to rt, it was dumped into a separatory funnel containing 300 mL of H_2O and an additional 200 mL of CH_2Cl_2. After vigorously shaking the funnel, the layers were separated, and the aqueous layer was extracted with an additional 100 mL of CH_2Cl_2. The aqueous layer was then discarded. The organic layers were combined, and any white precipitate was filtered off. The filtrate was then washed with 3 x 300 mL of 5% K_2CO_3 containing 1% Na_2SO_3. The aqueous washings were combined and extracted with 2 x 150 mL CH_2Cl_2. These organic washings were combined and back-extracted with 200 mL of 5% K_2CO_3 containing 1% Na_2SO_3, which was subsequently extracted with 100 mL of CH_2Cl_2. The aqueous phases were then combined, carefully acidified with 60 g of citric acid monohydrate, and extracted with 4 x 200 mL CH_2Cl_2. The organic extracts were combined, washed once with 150 mL of H_2O, and dried over Na_2SO_4. Following concentration by rotary evaporation, the residue was run through a short pad of silica with CH_2Cl_2. Concentration of the collected fractions provided 2.59 g (79%) of **14** as a white solid[2] contaminated with a *very* small amount of 9-BBN. This material was carried on without further purification, but an analytical sample could be obtained by recrystallization from hexanes/CH_2Cl_2 to yield a white powder: m. p. = 154-156 ˚C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.5 (1H, s), 8.4 (1H, d, *J* = 8.4 Hz), 8.2 (1H, d, *J* = 8.4 Hz), 7.7 (1H, m), 7.6 (1H, m), 5.6 (2H, s), 4.0 (3H, s) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 172.9, 150.6, 142.2, 131.8, 129.4, 126.3, 124.8, 123.5, 122.4, 122.2, 104.1, 69.3, 59.7 ppm; IR (CH_2Cl_2) 3430, 1734, 1651, 1603 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{10}O_4$ $[M]^+$: 230.0579; found 230.0564.

Benzyloxymethoxylactone 15. To a rapidly stirring suspension of 8.5 g (61.5 mmol, 5 equiv) of powdered K_2CO_3 in 260 mL of acetone was added 3.0 g (13 mmol, 1 equiv) of **14** and 2.32 mL (19.5 mmol, 1.5 equiv) of benzyl bromide. The mixture was then refluxed for 12 h. After cooling to rt, the solid was filtered off and the filtrate was concentrated by rotary evaporation. Recrystallization from EtOAc provided 3.32 g of **15** as a fluffy white solid. Flash column chromatography of the mother liquor with 4:1 petroleum ether:EtOAc provided an additional 766 mg of **15** for a combined yield of 98%: m. p. = 148-150 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35

(1H, d, J = 8.5 Hz), 8.2 (1H, d, J = 8.5 Hz), 7.7-7.5 (4H, m), 7.4 (3H, m), 5.6 (2H, s), 5.5 (2H, s), 4.1 (3H, s) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 168.6, 152.1, 145.0, 136.9, 131.5, 129.7, 129.2, 128.8, 128.5, 128.4, 126.9, 126.7, 124.7, 122.0, 112.1, 78.3, 67.3, 60.4 ppm; IR (CH_2Cl_2) 1762, 1425, 1351 cm^{-1}; HRMS (FAB) calcd for $C_{20}H_{16}O_4$ $[M]^+$: 320.1049; found 320.1028.

Acid 17. Diisopropylamine (1.20 mL, 8.6 mmol, 1.1 equiv) was dissolved in 50 mL THF. After cooling the solution to 0 ˚C, 3.44 mL of 2.5 M nBuLi in hexanes (8.6 mmol, 1.1 equiv) was added dropwise. The solution was stirred for 0.5 h, cooled to -78 ˚C, and 1.16 mL (8.6 mmol, 1.1 equiv) of t-butyl acetate in 10 mL THF was added dropwise. After stirring for 0.75 h at -78 ˚C, 2.5 g (7.8 mmol, 1 equiv) of **15** dissolved in 45 mL of THF was slowly cannulated into the solution, and the resultant mixture was allowed to stir for 0.5 h before being warmed to 0 ˚C. After 1 h, the reaction was dumped into a separatory funnel containing 100 mL of saturated aqueous NH_4Cl. With the aid of 100 mL of EtOAc, the layers were separated, and the aqueous layer was then washed with an additional 100 mL portion of EtOAc. The organic layers were combined, washed with 50 mL of H_2O, and dried over Na_2SO_4. After concentration by rotary evaporation, the resultant oil was passed through a short pad of silica with 3:1 petroleum ether:EtOAc to provide 3.3 g of crude **16** as a white taffy. This was then dissolved in 50 mL of CH_2Cl_2 and cooled to 0 ˚C. To the chilled solution was added 4 mL of triethylsilane, followed by dropwise addition of 8 mL of trifluoroacetic acid. After warming to rt and stirring for 2 h, the volatiles were removed by rotary evaporation, followed by high vacuum. The white powder thus obtained was recrystallized from 400 mL of CH_2Cl_2 to yield 1.98 g (70%) of **17** as a fluffy white solid: m. p. = 199 ˚C (dec). ^{1}H NMR (d_6-acetone, 400 MHz) δ 10.8 (1H, s), 8.2 (2H, m), 7.6 (4H, m), 7.5-7.3 (3H, m), 5.8 (1H, m), 5.45 (1H, dd, J = 12.6, 1.4 Hz), 5.3 (1H, d, J = 12.6 Hz), 5.2 (1H, d, J = 11.1 Hz), 5.1 (1H, d, J = 11.1 Hz), 4.0 (3H, s), 3.2 (1H, dd, J = 15.7, 2.7 Hz), 2.65 (1H, dd, J = 15.7, 9.2 Hz) ppm; ^{13}C NMR (d_6-acetone, 101 MHz) δ 171.9, 146.4, 144.5, 138.2, 132.2, 130.0, 129.6, 129.4, 129.2, 129.1, 126.8, 126.6, 126.3, 123.1, 122.8, 79.8, 76.5, 70.8, 60.3, 40.1 ppm; IR (KBr) 2930, 1697, 1434, 1347 cm^{-1}; HRMS (FAB) calcd for $C_{22}H_{20}O_5$ $[M]^+$: 364.1311; found 364.1325.

Phenolic acid 18. To a suspension of 1.65 g (4.5 mmol, 1 equiv) of **17** in 125 mL EtOH was added ~ 200 mg of 10% Pd/C, followed by 4.3 mL (45 mmol, 10 equiv) of 1,4-cyclohexadiene. The resulting heterogeneous solution was stirred vigorously for 3 h, and then filtered through celite with the aid of 100 mL of MeOH. After removing the solvents by rotary evaporation (bath temperature < 40 ˚C), 1.21 g (97%) of **18** as a beige solid remained. This material was > 95% pure by NMR, and was used in the next reaction without any further purification; however, an analytically pure white powder was obtained by recrystallization from EtOAc: m. p. = 198 ˚C

(dec). ^{1}H NMR (d_6-acetone, 400 MHz) δ 11.0 (1H, bs), 9.0 (1H, bs), 8.2 (1H, m), 8.1 (1H, m), 7.5 (2H, m), 5.8 (1H, m), 5.35 (1H, dd, *J* = 12.6, 1.4 Hz), 5.2 (1H, d, *J* = 12.6 Hz), 3.9 (3H, s), 3.15 (1H, dd, *J* = 16.5, 5.4 Hz), 2.8 (1H, dd, *J* = 16.5, 7.0 Hz) ppm; ^{13}C NMR (d_6-acetone, 101 MHz) δ 174.3, 143.2, 142.6, 129.5, 127.6, 127.4, 126.5, 125.7, 124.1, 122.8, 122.5, 79.0, 70.4, 60.7, 40.2 ppm; IR (KBr) 3364, 3040, 1705, 1382, 1274, 1167 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{14}O_5$ $[M]^+$: 274.0841; found 274.0853.

Enol ether 19. To a suspension of 735 mg (2.68 mmol, 1 equiv) of **18** in 30 mL of CH_2Cl_2 was added 1.21 g (2.73 mmol, 1.02 equiv) of $Pb(OAc)_4$ in 10 mL of CH_2Cl_2. The heterogeneous mixture was stirred vigorously for 2.5 h, after which time it was filtered through a plug of celite with the aid of 100 mL of CH_2Cl_2. The filtrate was added to a separatory funnel containing 100 mL of CH_2Cl_2 and 100 mL of saturated aqueous $NaHCO_3$. The funnel was shaken, the layers separated, and the aqueous solution was extracted again with 100 mL of CH_2Cl_2. The organic layers were combined, washed with 100 mL of H_2O, and then dried over Na_2SO_4. Following concentration by rotary evaporation, the crude material was run through a short plug of florisil with 1:1 petroleum ether:EtOAc to provide 542 mg (74%) of **19** as a bright yellow solid: m. p. = 142 ˚C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.9 (1H, d, *J* = 7.7 Hz), 7.7 (2H, m), 7.5 (1H, m), 5.1 (1H, d, *J* = 12.8 Hz), 4.95 (1H, d, *J* = 12.8 Hz), 4.8 (1H, d, *J* = 4.8 Hz), 4.0 (3H, s), 3.2 (1H, dd, *J* = 17.9, 4.8 Hz), 2.8 (1H, d, *J* = 17.9 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 192.3, 174.8, 150.0, 135.6 (2 overlapping signals), 129.6, 128.4, 127.5, 124.2, 110.7, 88.4, 79.4, 69.0, 59.2, 37.8 ppm; IR (CH_2Cl_2) 1790, 1696, 1664, 1597 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{12}O_5$ $[M + H]^+$: 273.0755; found 273.0770.

α-Hydroxyketone 20b. To 37 mg (0.14 mmol, 1 equiv) of **19** dissolved in 3 mL of CH_2Cl_2 at 0 ˚C was added 2.3 mL of a 0.065 M solution of DMDO in acetone (0.16 mmol, 1.2 equiv). After stirring for 2 h, the volatiles were removed by rotary evaporation, and the crude material was purified by flash column chromatography with 3:1 petroleum ether:EtOAc to provide 30 mg (80%) of **20b** as a white solid: m. p. = 187 ˚C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.2 (2H, m), 7.9 (2H, m), 5.4 (1H, d, *J* = 4.8 Hz), 4.55 (1H, d, *J* = 10.9 Hz), 4.25 (1H, d, *J* = 10.9 Hz), 3.0 (1H, dd, *J* = 18.5, 4.8 Hz), 2.95 (1H, s), 2.9 (1H, d, *J* = 18.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 189.4, 187.6, 172.7, 135.1, 134.8, 134.7, 134.6, 128.2, 127.8, 93.9, 83.5, 76.2, 72.5, 36.3 ppm; IR (CH_2Cl_2) 3542, 1811, 1716, 1594 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{10}O_6$ $[M]^+$: 274.0477; found 274.0481.

Allylic alcohol 21. A solution of 730 mg (2.7 mmol, 1 equiv) of **19** in 35 mL of CH_2Cl_2 was diluted with 35 mL of MeOH and then cooled to -35 ˚C. A 1 M solution of LiHMDS in THF

(2.95 mL, 2.95 mmol, 1.1 equiv) was then added dropwise, and the resultant solution was stirred for 1.5 h at -35 ˚C. The reaction was quenched by dumping into 100 mL of ice cold aqueous NH_4Cl, and then extracted with 2 x 150 mL CH_2Cl_2. The organic extracts were combined, washed with 100 mL of H_2O, and then dried over Na_2SO_4. After concentration by rotary evaporation, the crude material was loaded onto a flash chromatography column and eluted first with 3:1 petroleum ether:EtOAc to provide 294 mg (40%) of recovered **19**. Elution with 1:1 petroleum ether:EtOAc then provided 413 mg (51%) of **21** as a pale yellow solid: m. p. = 142 ˚C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.9 (1H, d, *J* = 7.4 Hz), 7.6 (2H, m), 7.4 (1H, m), 5.15 (1H, d, *J* = 13.5 Hz), 4.75 (1H, d, *J* = 13.5 Hz), 4.3 (1H, dd, *J* = 8.5, 3.7 Hz), 3.9 (3H, s), 3.75 (3H, s), 3.15 (1H, dd, *J* = 15.8, 3.7 Hz) 3.05 (1H, s), 2.9 (1H, dd, *J* = 15.8, 8.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 195.9, 172.1, 147.6, 135.3, 134.7, 129.2, 129.0, 127.5, 123.7, 117.5, 78.7, 76.8, 66.9, 58.8, 52.1, 35.0 ppm; IR (CH_2Cl_2) 3538, 1737, 1703, 1663, 1597 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{16}O_6$ $[M]^+$: 304.0947; found 304.0953.

α-Hydroxyketone 20a. A stock solution of TFPAA was prepared by dissolving 1 mL of trifluoroacetic anhydride in 5 mL of CH_2Cl_2 at 0 ˚C, and then adding 178 μL of 30% H_2O_2. The mixture was stirred for 5 min at 0 ˚C and then used immediately in the following procedure (the molarity is approximately 0.3 M). To a vigorously stirred suspension of 1.75 g (16.5 mmol, 25 equiv) of Na_2CO_3 in 40 mL of CH_2Cl_2 at 0 ˚C was added 4.4 mL of stock TFPAA (1.32 mmol, 2 equiv). After 2 min, a solution of 200 mg (0.66 mmol, 1 equiv) of **21** in 10 mL of CH_2Cl_2 precooled to 0 ˚C was quickly cannulated into the reaction flask, and stirring was continued for 10 min. The reaction was quenched with saturated aqueous Na_2SO_3, and then dumped into a separatory funnel with 100 mL of CH_2Cl_2 and 100 mL of saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted again with 50 mL of CH_2Cl_2, the organic layers were combined, washed with 50 mL of H_2O, and dried over Na_2SO_4. This entire procedure was then repeated with an additional 200 mg of **21**, and the resulting organic phases were combined and concentrated by rotary evaporation to provide 361 mg of crude diol as a yellow foam. This material was then dissolved in 15 mL of benzene, ~ 25 mg of p-toluenesulfonic acid was added, and the solution was refluxed for 0.75 h. After cooling to rt, the mixture was dumped into a separatory funnel containing 75 mL of EtOAc and 50 mL of saturated aqueous $NaHCO_3$, shaken, separated, and the aqueous layer was extracted with an additional 50 mL of EtOAc. The organic phases were combined, washed with 2 x 50 mL of H_2O, dried over Na_2SO_4, and concentrated by rotary evaporation. The resultant pale yellow solid was then recrystallized from CH_2Cl_2/pentane to yield 184 mg (51%) of **20a** as a fluffy white solid: m. p. = 173 ˚C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.2 (2H, m), 7.9 (2H, m), 4.85 (1H, dd, *J* = 7.0, 2.4 Hz), 4.45 (1H, d, *J* = 9.8 Hz), 4.05 (1H, d, *J* = 9.7 Hz), 3.4 (1H, s), 3.0 (1H, dd, *J* = 18.7, 7.0 Hz), 2.9 (1H, dd, *J* = 18.7, 2.4 Hz)

ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 191.7, 189.3, 173.4, 136.2, 135.8, 133.2, 132.2, 128.3, 128.1, 91.9, 83.7, 80.9, 75.2, 35.9 ppm; IR (CH_2Cl_2) 3530, 1807, 1702, 1594 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{10}O_6$ $[M]^+$: 274.0477; found 274.0466.

α-Iodolactones 23a,b. Lactone **20a** (180 mg, 0.66 mmol, 1 equiv) was dissolved in 12 mL of THF and 208 μL (1.64 mmol, 2.5 equiv) of TMSCl was added. The solution was then cooled to -78 ˚C and 1.35 mL of a 1M solution of LiHMDS in THF (1.35 mmol, 2.1 equiv) was added dropwise, and the mixture was stirred for 0.5 h. To the colorless reaction was then added 163 mg (0.72 mmol, 1.1 equiv) of N-iodosuccinimide in 2 mL of THF, and the resultant mixture was stirred in the dark for 0.5 h. The solution was then dumped into a separatory funnel containing 75 mL of saturated aqueous NH_4Cl and 100 mL of CH_2Cl_2. After separation, the aqueous layer was extracted with an additional 75 mL of CH_2Cl_2, the organic layers were combined, washed with 50 mL of H_2O, and dried over Na_2SO_4. Following concentration by rotary evaporation, the crude product was purified by flash column chromatography with 9:1 followed by 3:1 petroleum ether:EtOAc to provide 267 mg (86%) of **23** as a 2:1 unseparable mixture of diastereomers as a sticky white taffy. ^1H NMR ($CDCl_3$, 400 MHz) **23a**: δ 8.3 (2H, m), 7.9 (2H, m), 4.85 (1H, s), 4.75 (1H, d, *J* = 8.5 Hz), 4.6 (1H, s), 3.9 (1H, d, *J* = 8.5 Hz), 0.1 (9H, s) ppm; **23b**: δ 8.3 (2H, m), 7.9 (2H, m), 4.95 (1H, d, *J* = 6.0 Hz), 4.8 (1H, d, *J* = 8.5 Hz), 4.45 (1H, d, *J* = 6.0 Hz), 3.85 (1H, d, *J* = 8.5 Hz), 0.1 (9H, s) ppm; IR (CH_2Cl_2) 1798, 1706, 1594, 1188 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{17}IO_6Si$ $[M + H]^+$: 472.9909; found 472.9904.

α-Ketolactone 24. To 250 mg (0.53 mmol, 1 equiv) of **23a,b** in 35 mL of CH_2Cl_2 was added 20 mL of a 0.07 M solution of DMDO in acetone (1.4 mmol, 2.6 mmol) and the resultant solution was stirred for 12 h in the dark. An additional 10 mL of DMDO was added and stirring was continued for 6h. The volatiles were then removed by rotary evaporation, the crude residue was loaded on the top of a flash chromatography column, and eluted with 3:1 and then 1:1 petroleum ether:EtOAc to first obtain 42 mg (17%) of **23a,b** and then 135 mg (71%) of **24** as a white taffy. This material was pure, but difficult to analyze by NMR due to its ability to exist as the hydrate, the ketone, or the enol ether. IR (CH_2Cl_2) 3521, 1811, 1705, 1595, 1195 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{16}O_7Si$ $[M + H]^+$: 361.0735; found 361.0756. HRMS (FAB) calcd for $C_{17}H_{18}O_8Si$ $[M + H]^+$: 379.0841; found 379.0861.

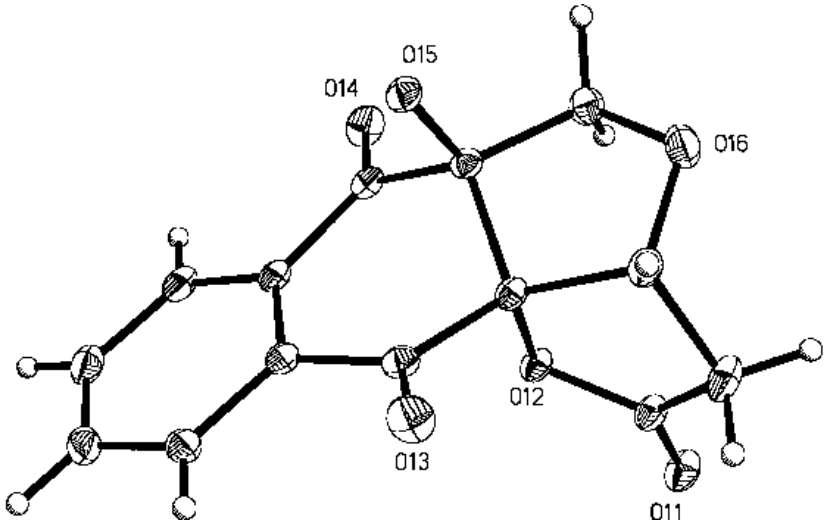
Vinyl triflate 25. A solution of 135 mg (0.36 mmol, 1 equiv) of the hydrated ketolactone **24** was dissolved in 10 mL of benzene and refluxed under Dean-Stark conditions for 5 h. Following removal of the benzene while maintaining anhydrous conditions, the residue was brought up in 10 mL of CH_2Cl_2 and cooled to -78 ˚C. Following the addition of 187 μL (1.07 mmol, 3 equiv)

of Hünig's base, 120 μL (0.71 mmol, 2 equiv) of trifluoromethanesulfonic anhydride was added dropwise and the reaction was stirred for 1 h. While still at -78 ˚C, 20 mL of CH_2Cl_2 was added, along with 20 mL of H_2O. This mixture was separated, the aqueous layer was extracted with an additional 25 mL portion of CH_2Cl_2, the organic layers were combined, and then dried over Na_2SO_4. Following concentration by rotary evaporation, purification by flash column chromatography with 3:1 petroleum ether:EtOAc provided 106 mg (60%) of **25** as a sticky white taffy. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.3-8.2 (2H, m), 8.0 (2H, m), 5.0 (1H, d, *J* = 10.5 Hz), 4.95 (1H, d, *J* = 10.5 Hz), 0.2 (9H, s) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 189.3, 184.5, 165.4, 165.1, 136.9, 136.2, 132.3, 131.9, 129.1, 128.3, 118.4 (q, *J* = 3.2 Hz), 110.4, 90.5, 87.6, 83.3, 1.4 ppm; IR (CH_2Cl_2) 1820, 1810, 1728, 1711, 1593, 1438, 1240, 1136 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{15}F_3O_9SSi$ $[M + H]^+$: 493.0228; found 493.0232.

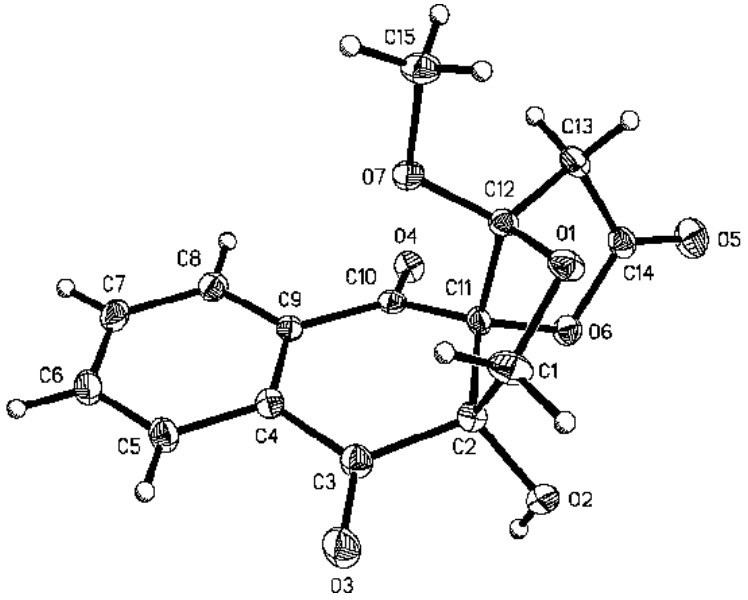
Methoxytriflate 26. To 50 mg (0.10 mmol, 1 equiv) of **25** in 2 mL of CH_2Cl_2 was added 2 mL of MeOH, followed by ~ 10 mg of camphorsulfonic acid. The mixture was allowed to stir at rt for 24 h, after which the solvent was removed under vacuum and the residue purified by flash column chromatography with 9:1 followed by 3:1 petroleum ether:EtOAc to provide 40 mg (88%) of **26** as a white powder: m. p. = 158-160 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.2 (2H, m), 7.9 (2H, m), 5.65 (1H, s), 5.05 (1H, d, *J* = 9.8 Hz), 4.2 (1H, d, *J* = 9.8 Hz), 3.35 (3H, s), 3.3 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 188.8, 186.6, 164.2, 136.2, 135.3, 134.2, 133.3, 128.7, 127.5, 118.2 (q, *J* = 4.2 Hz), 107.6, 89.4, 82.8, 79.7, 74.6, 52.4 ppm; IR (CH_2Cl_2) 3527, 1833, 1705, 1596, 1429, 1222, 1139 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{11}F_3O_{10}S$ $[M + H]^+$: 453.0095; found 453.0121.

α-Hydroxyketone 27. To 35 mg (0.077 mmol) of **26** in 8 mL of THF (ACS grade, directly from the bottle) with 15 small drops of HOAc was added 62 mg (0.46 mmol, 6 equiv) of LiI. The reaction was then gently refluxed in the dark for 5 h. After cooling to rt, the mixture was quenched with 10 mL of H_2O and extracted with 2 x 10 mL of CH_2Cl_2. Drying the organic extract with Na_2SO_4, followed by rotary evaporation and flash column chromatography with 3:1 petroleum ether:EtOAc provided 13 mg (55%) of **27** as a white solid: m. p. = 172-174 ˚C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.2 (2H, m), 7.9 (2H, m), 4.7 (1H, d, *J* = 9.8 Hz), 4.15 (1H, d, *J* = 9.8 Hz), 3.3 (1H, bs), 3.2 (3H, s), 3.1 (1H, d, *J* = 17.1 Hz), 3.0 (1H, d, *J* = 17.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 191.1, 188.2, 170.5, 135.4, 135.1, 134.2, 133.7, 128.2, 127.2, 113.2, 83.0, 77.2, 75.2, 52.5, 37.4 ppm; IR (CH_2Cl_2) 3545, 1811, 1703, 1597, 1296, 1138 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{12}O_7$ $[M + H]^+$: 305.0653; found 305.0652.

X-Ray Crystallography of 20b. Crystals suitable for diffraction were grown by dissolving 10 mg of **20b** in 3 mL of THF and allowing the solution to slowly evaporate over a period of three days. Crystal data for **20b**: monoclinic, a = 9.611 (2) Å, b = 19.139 (5) Å, c = 7.2205 (19) Å, α = 90.00˚ β = 99.829 (5)˚, γ = 90.00˚, space group = $P2_1/c$; G.O.F. = 1.002; R = 4.91%.



X-Ray Crystallography of 27. Crystals suitable for diffraction were grown by dissolving approximately 3 mg of **27** in 2 mL of CCl_4 and allowing the solvent to slowly evaporate over a period of two days. Crystal data for **27**: monoclinic, a = 6.9645 (5) Å, b = 21.3792 (15) Å, c = 16.1535 (11) Å, α = 90.00˚ β = 94.5210 (10)˚, γ = 90.00˚, space group = $P2_1/n$; G.O.F. = 1.028; R = 3.98%.



1. Napolitano, E.; Spinelli, G.; Fiaschi, R.; Marsili, A. *Synthesis* **1985**, 38-40.

2. This material has been previously reported; see: Ozaki, Y.; Imaizumi, K.; Okamura, K.; Morozumi, M.; Hosoya, A.; Kim, S.-W. *Chem. Pharm. Bull.* **1996**, *44*, 1785-1789. However, we could not duplicate the published procedure, nor did our independently synthesized material match the physical characteristics reported by these authors (yellow oil vs. white solid).