Supporting Information

Asymmetric Total Syntheses of (-)-Fennebricin A, (-)-Renieramycin J, (-)-Renieramycin G, (-)-Renieramycin M, and (-)- Jorunnamycin A via C-H Activation

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General Information

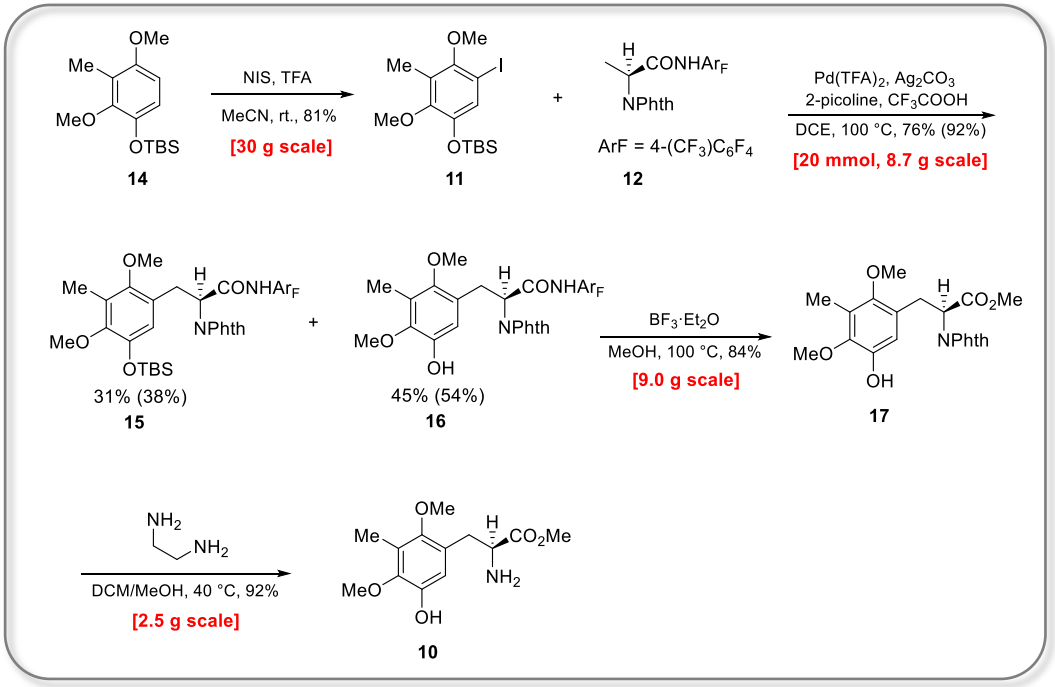
Unless otherwise stated, all oxygen or moisture sensitive reactions were conducted in flame-dried glassware under an atmosphere of nitrogen. All solvents were purified and dried according to standard methods prior to use. The compound **12**[1], compound **14**[2] and compound **20**[3] were prepared according to the reported procedure. Reagents were purchased from commercial sources and were used without further purification.

Chromatographic purification of products was accomplished using forced-flow chromatography on 200-300 mesh silica gel. The TLC glass plates were performed on 0.20 mm or 1.0 mm (preparative) silica gel GF254 plates. Visualization was performed using ultraviolet light (254 nm), iodine vapor or potassium permanganate ($KMnO_4$) in water.

^1H and ^{13}C NMR spectra were acquired on Bruker Avance III-400 or 600 spectrometer (Bruker Corp., Germany), and TMS was used as internal standard. Chemical shifts were given in parts per million (ppm) with reference to residual solvent signals [^1H NMR: $CDCl_3$ (7.26), CD_3OD (3.31), CD_2Cl_2 (5.32); ^{13}C NMR: $CDCl_3$ (77.0), CD_3OD (49.0), CD_2Cl_2 (53.8)]. Peak multiplicities were recorded as follows: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br s = broad singlet. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. In the ^{13}C NMR analysis, peaks that correspond to those of the polyfluoroarylamide auxiliary appeared as nearly invisible, complex sets of multiplets; they are omitted in the following spectroscopic analysis[1]. Infrared (IR) spectra were recorded on a Bruker Tensor-27 Fourier-Transform Infrared spectrometer (Bruker Corp., Germany) with KBr pellets or a Nicolet iS10 Infrared spectrometer (Nicolet Corp., USA). High resolution mass spectral (HRMS) data were obtained at the mass spectrometry service operated at a Agilent 1290 UPLC/6540 Q-TOF (Agilent Corp., USA) for electrospray ionization (ESI) and were reported as (m/z). X-ray analysis was obtained at the X-ray single crystal diffractometer (Bruker Corp., Germany). Optical rotations were measured on a Autopol VI Polarimeter (Rudolph Research Analytical Corp., USA). Melting points were measured on a WRX-5Amelting point apparatus.

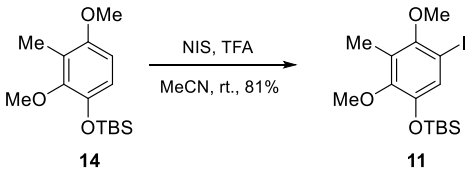
1. Experimental Procedures

(1) Synthesis of amine 10



Scheme S1. Synthesis of amine **10**

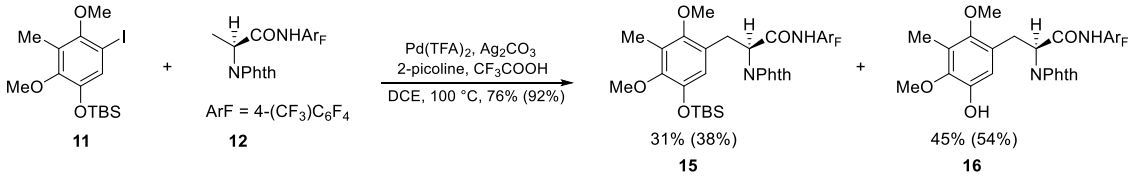
Synthesis of Compound 11



Compound 11. To a solution of compound **14** (30.0 g, 106.4 mmol, 1.0 equiv) in MeCN (210 mL) was added N-iodosuccinimide (31.1 g, 138.3 mmol, 1.3 equiv) and trifluoroacetic acid (1.2 mL, 16.0 mmol, 0.15 equiv) sequentially at room temperature. After stirring 6 h, the reaction was quenched with saturated *aq*. $NaHCO_3$ (200 mL) and saturated *aq*. $Na_2S_2O_3$ (200 mL), extracted with ethyl acetate (3 × 200 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 80:1) to give compound **11** (35.2 g, 81% yield) as a colorless oil.

Compound **11**. $\mathbf{R_f}$ = 0.33 (n-hexane/ethyl acetate 50:1); **IR (ATR)** λ_{max} 2991, 2955, 2931, 2895, 2858, 1579, 1471, 1418, 1396, 1309, 1254, 1233, 1208, 1173, 1095, 1050, 1010, 885, 862, 849, 784 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.24 (s, 3H), 1.00 (s, 9H), 0.18 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7 (s), 150.5 (s), 146.0 (s), 127.4 (d), 126.2 (s), 83.9 (s), 60.4 (q), 59.8 (q), 25.6 (q), 18.2 (s), 10.6 (q), -4.7 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{25}IO_3SiNa$ 431.0510; Found 431.0512.

Synthesis of compound 15 and 16



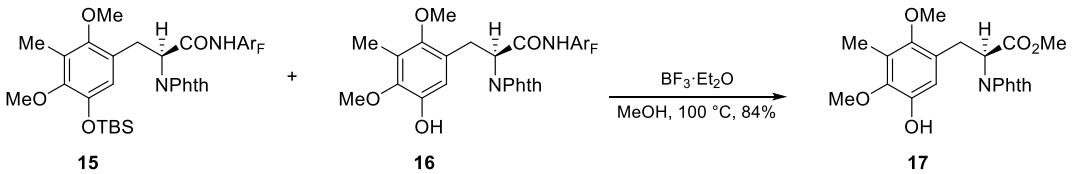
Compound 15 and 16. According to the procedure reported by Yu's group[1]. Compound **12** (8.7 g, 20.0 mmol, 1.0 equiv), $Pd(TFA)_2$ (664.9 mg, 2.0 mmol, 10 mol%), and Ag_2CO_3 (8.3 g, 30.0 mmol, 1.5 equiv) were weighed out open to the air and placed in 150 mL a sealable pressure flask with a magnetic stir bar. The aryl iodide 11 (12.2 g, 30.0 mmol, 1.5 equiv), 2-picoline (395.0 μL, 4.0 mmol, 20 mol%) and DCE (40 mL) were added, followed by CF_3COOH (297.1 μL, 4.0 mmol, 20 mol%). The reaction vessel was sealed and the mixture was first stirred at room temperature for 10 min and then placed in a preheated oil bath at 100 °C. After vigorous stirring for 96 h, the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel with ethyl acetate, concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 to 4:1 to 2:1) to give compound **15** [4.41 g, 31% yield, (38% yield based on recovered **12**)] as a colorless oil, compound **16** [5.37 g, 45% yield, (54% yield based on recovered **12**)] as a colorless oil.

Compound 15. $\mathbf{R_f}$ = 0.42 (n-hexane/ethyl acetate 4:1); $\mathbf{[\alpha]}^{26.5}_{D}$ −57.7° (*c* 0.3, $CHCl_3$); **IR (ATR)** λ_{max} 3269, 2995, 2932, 2859, 1780, 1723, 1657, 1616, 1588, 1510, 1481, 1422, 1382, 1341, 1281, 1237, 1187, 1148, 1064, 1009, 994, 875, 837, 811, 784, 757, 716 cm^{-1}; **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.83 (ddd, J = 4.5, 3.1, 1.6 Hz, 2H), 7.73 (ddd, J = 4.5, 3.1, 1.6 Hz, 2H), 6.50 (s, 1H), 5.28 (dd, J = 8.4, 6.4 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.58 (dd, J = 14.2, 6.4 Hz, 1H), 3.30 (dd, J = 14.2, 8.4 Hz, 1H), 2.08 (s, 3H), 0.94 (s, 9H), 0.05 (d, J = 8.8 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.8 (s), 166.7 (s), 150.8 (s), 149.7 (s), 145.5 (s), 134.4 (d), 131.6 (s), 125.9 (s), 124.1 (s), 123.6 (d), 119.6 (d), 61.0 (q), 59.8 (q), 55.6 (d), 30.5 (t), 25.6 (q), 18.1 (s), 9.6 (q), -4.78 (q), -4.82 (q); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -53.0 (t, J = 22.1 Hz, 3F), -140.8 (m, 2F), -142.3 (m, 2F); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{33}H_{33}F_7N_2O_6SiNa$ 737.1888; Found 737.1911.

Compound 16. $\mathbf{R_f}$ = 0.61 (n-hexane/ethyl acetate 1:1); **[α]**$^{27.1}_{D}$ −51.8° (c 0.3, $CHCl_3$); **IR (ATR)** λ_{max} 3291, 2995, 2944, 2834, 1779, 1716, 1657, 1615, 1509, 1479, 1420, 1382, 1340, 1281, 1235, 1187, 1147, 1111, 1086, 1048, 1000, 953, 889, 875, 840, 818, 756, 716 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.78 (dd, J = 5.6, 3.2 Hz, 2H), 7.70 (dd, J = 5.6, 3.2 Hz, 2H), 6.64 (s, 1H), 5.54 (s, 1H), 5.24 (t, J = 7.4 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.59 (dd, J = 14.2, 7.4 Hz, 1H), 3.28 (dd, J = 14.2, 7.4 Hz, 1H), 2.08 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.8 (s), 166.7 (s), 149.8 (s), 145.7 (s), 145.3 (s), 134.3 (d), 131.5 (s), 125.2 (s), 124.7 (s), 123.5 (d), 114.1 (d), 61.0 (q), 60.7 (q), 55.4 (d), 30.3 (t), 9.6 (q); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.1 (t, J = 22.1 Hz, 3F), -140.9 (m, 2F), -142.3 (m, 2F); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{27}H_{19}F_7N_2O_6Na$ 623.1024; Found 623.1041.

Synthesis of Compound 17

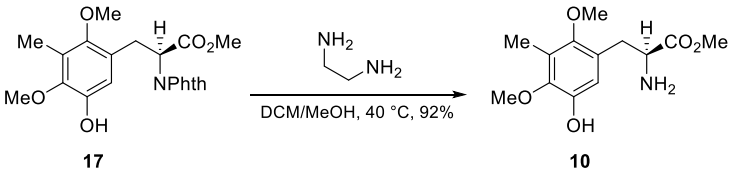


Compound 17. A 350 mL sealable pressure flask was charged with MeOH (100 mL), compound **15** (4.50 g, 6.30 mmol, 1.0 equiv), and compound **16** (4.50 g, 7.50 mmol, 1.0 equiv). $BF_3{\cdot}Et_2O$ (17.42 mL, 138.0 mmol, 10.0 equiv) was added dropwise via syringe at room temperature, and the reaction vessel was sealed. The mixture was placed in a preheated oil bath at 100 °C and stirred for 16 h. Upon complete consumption of the starting material,

the reaction was cooled to room temperature. Et_3N (19.10 mL, 138.0 mmol, 10.0 equiv) was carefully added via syringe, and stirring for 10 min. The solvent was concentrated *in vacuo*, and the crude residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give compound **17** (4.63 g, 84% yield) as a colorless oil, and recovered 2,3,5,6-tetrafluoro-4-aminobenzotrifluoride (2.37 g, 74% yield).

Compound 17. $\mathbf{R_f}$ = 0.64 (n-hexane/ethyl acetate 1:1); $\mathbf{[\alpha]^{27.2}_D}$ −150.0° (*c* 0.3, $CHCl_3$); **IR (ATR)** λ_{max} 3443, 2999, 2953, 2834, 1775, 1744, 1717, 1596, 1485, 1470, 1456, 1437, 1418, 1390, 1339, 1280, 1253, 1198, 1176, 1109, 1088, 1048, 1008, 917, 885, 871, 836, 785, 755, 721 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.51 (s, 1H), 5.38 (s, 1H), 5.20 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.51 (dd, *J* = 14.2, 4.4 Hz, 1H), 3.38 (dd, *J* = 14.2, 11.2 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6 (s), 167.4 (s), 150.7 (s), 144.9 (s), 144.8 (s), 133.9 (d), 131.8 (s), 125.9 (s), 124.3 (s), 123.3 (d), 114.0 (d), 60.63 (q), 60.60 (q), 52.8 (q), 52.3 (d), 29.8 (t), 9.7 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{21}H_{21}NO_7Na$ 422.1210; Found 422.1217.

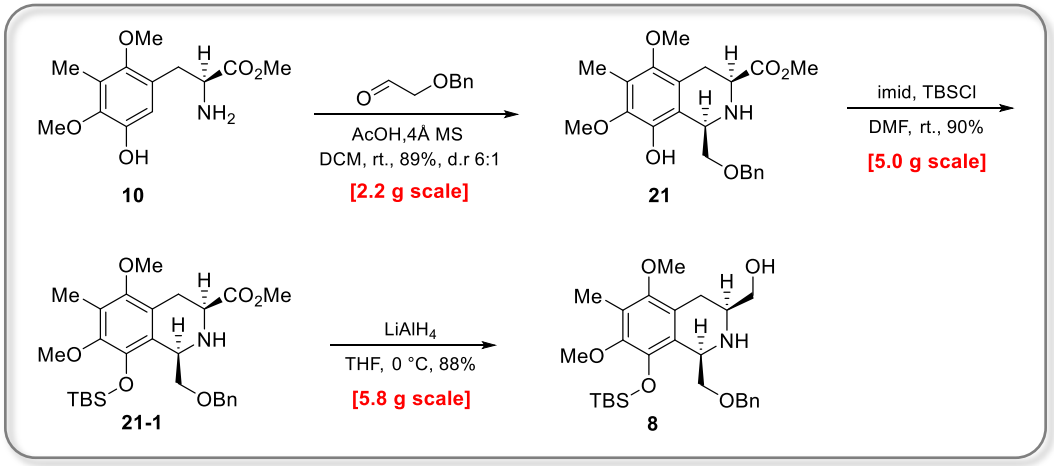
Synthesis of Compound 10



Compound 10. To a solution of compound **17** (2.50 g, 6.27 mmol, 1.0 equiv) in DCM/MeOH (30 mL/30 mL) was added ethylenediamine (3.34 mL, 50.12 mmol, 8.0 equiv) at room temperature. The mixture was placed in a preheated oil bath at 40 °C and stirred for 12 h. Upon complete consumption of the starting material, the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel with ethyl acetate, concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 1:1 to chloroform/methanol 10:1) to give compound **10** (1.55 g, 5.76 mmol, 92% yield) as a pale yellow solid.

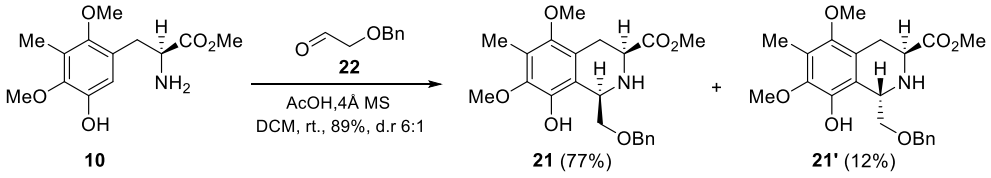
Compound 10. R_f = 0.41 (chloroform/methanol 10:1); $[\alpha]^{24.8}_D$ +6.6° (*c* 0.2, MeOH); **IR (ATR)** λ_{max} 3339, 3285, 2997, 2952, 2933, 2844, 2676, 2637, 2590, 1742, 1594, 1509, 1457, 1436, 1415, 1390, 1378, 1369, 1351, 1329, 1308, 1273, 1239, 1202, 1180, 1137, 1104, 1051, 1044, 1007, 986, 963, 869, 858, 821, 796, 759, 729, 693 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.56 (s, 1H), 3.76 (dd, *J* = 8.6, 5.0 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.64 (s, 3H), 3.02 (dd, *J* = 13.6, 5.0 Hz, 1H), 2.74 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4 (s), 150.4 (s), 145.4 (s), 145.0 (s), 125.9 (s), 124.6 (s), 114.6 (d), 60.5 (q), 60.3 (q), 54.8 (d), 52.0 (q), 35.4 (t), 9.8 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}NO_5$ 270.1336; Found 270.1335; **m.p.** 82 – 84 °C.

(2) Synthesis of amine 8



Scheme S2. Synthesis of amine **8**

Synthesis of Compound 21

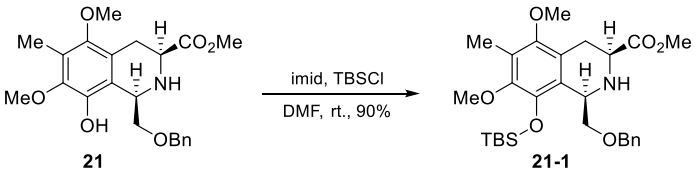


Compound 10. To a solution of compound **10** (2.20 g, 8.18 mmol, 1.0 equiv) in DCM (80 mL) was added 4Å molecular sieves (2.20 g) and acetic acid (514.1 µL, 9.00 mmol, 1.1 equiv)

sequentially at room temperature. The resulting solution was degassed by three freeze-pump-thaw cycles with argon. A solution of benzyloxyacetaldehyde **22** (1.35 g, 9.00 mmol, 1.1 equiv) in DCM (40 mL) was added slowly via springe pump to the degassed solution over 12 h. After stirring 24 h at room temperature (including the addition period), the reaction mixture was flitered though a short pad of celite, and quenched with saturated *aq*. $NaHCO_3$ (100 mL), extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/acetone 20:1) to give compound **21** (2.51 g, 77% yield, major isomer, less polar) as a colorless oil and compound **21'** (0.41 g, 12% yield, minor isomer, more polar) as a colorless oil.

Compound 21. $\mathbf{R_f}$ = 0.45 (n-hexane/ethyl acetate 1:1); $[\alpha]^{24.8}_D$ −85.0° (*c* 0.2, MeOH); **IR (ATR)** λ_{max} 3306, 2991, 2950, 2939, 2860, 1740, 1609, 1511, 1496, 1456, 1436, 1413, 1361, 1334, 1313, 1279, 1245, 1212, 1196, 1179, 1111, 1060, 1029, 1004, 861, 738, 700 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 5H), 6.32 (s, 1H), 4.55 (dd, *J* = 12.0, 19.2 Hz, 2H), 4.51 (m, 1H), 4.09 (dd, *J* = 9.2, 4.2 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.74 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.67 (s, 3H), 3.52 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.23 (dd, *J* = 15.8, 3.2 Hz, 1H), 2.61 (dd, *J* = 15.8, 11.1 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (s), 149.2 (s), 144.1 (s), 142.8 (s), 138.0 (s), 128.3 (d), 127.6 (d), 127.6 (d), 124.8 (s), 122.2 (s), 120.1 (s), 73.4 (t), 73.2 (t), 60.6 (q), 60.4 (q), 54.8 (d), 53.5 (d), 52.1 (q), 27.7 (t), 9.5 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{28}NO_6$ 402.1911; Found 402.1923.

Synthesis of Compound 21-1

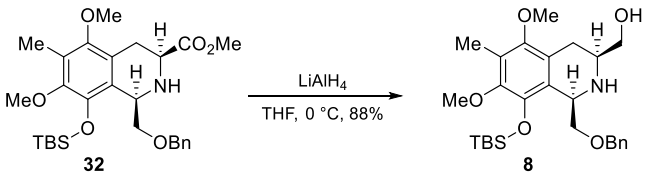


Compound 21-1. To a solution of compound **21** (5.00 g, 12.47 mmol, 1.0 equiv) in DMF (40 mL) was added imidazole (5.09 g, 74.81 mmol, 6.0 equiv) and *tert*-butyldimethylsilyl chloride (5.64 g, 37.41 mmol, 3.0 equiv) sequentially at room temperature. After stirring 12 h,

the reaction was quenched with saturated *aq*. $NaHCO_3$ (80 mL), and extracted with ethyl acetate (3 × 80 mL). The combined organic extracts were washed with water (5 × 40 mL) and brine (40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/acetone 10:1) to give compound **21-1** (5.78 g, 90% yield) as a colorless oil.

Compound 21-1. $\mathbf{R_f}$ = 0.43 (n-hexane/ethyl acetate 4:1); $[\alpha]^{24.7}_D$ −76.5° (*c* 0.2, MeOH); **IR (ATR)** λ_{max} 3063, 3030, 2952, 2932, 2896, 2884, 2857, 1742, 1496, 1454, 1436, 1410, 1391, 1346, 1282, 1253, 1197, 1176, 1113, 1103, 1070, 1030, 1005, 971, 939, 880, 834, 782, 737, 699, 673 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 5H), 4.51 (t, *J* = 5.0 Hz, 1H), 4.48 (dd, *J* = 19.1, 11.7 Hz, 2H), 4.13 (dd, *J* = 7.9, 2.9 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.62 (s, 3H), 3.60 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.50 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.20 (dd, *J* = 15.8, 3.2 Hz, 1H), 2.63 (dd, J = 15.8, 11.1 Hz, 1H), 2.19 (s, 3H), 0.95 (s, 9H), 0.23 (s, 3H), 0.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6 (s), 150.4 (s), 148.1 (s), 142.3 (s), 138.4 (s), 128.2 (d), 127.6 (d), 127.4 (d), 125.0 (s), 124.9 (s), 123.1 (s), 73.3 (t), 73.0 (t), 60.2 (q), 59.9 (q), 54.9 (d), 54.0 (d), 52.1 (q), 28.0 (t), 26.1 (q), 18.5 (s), 9.4 (q), -3.8 (q), -4.5 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{42}NO_6Si$ 516.2776; Found 516.2793.

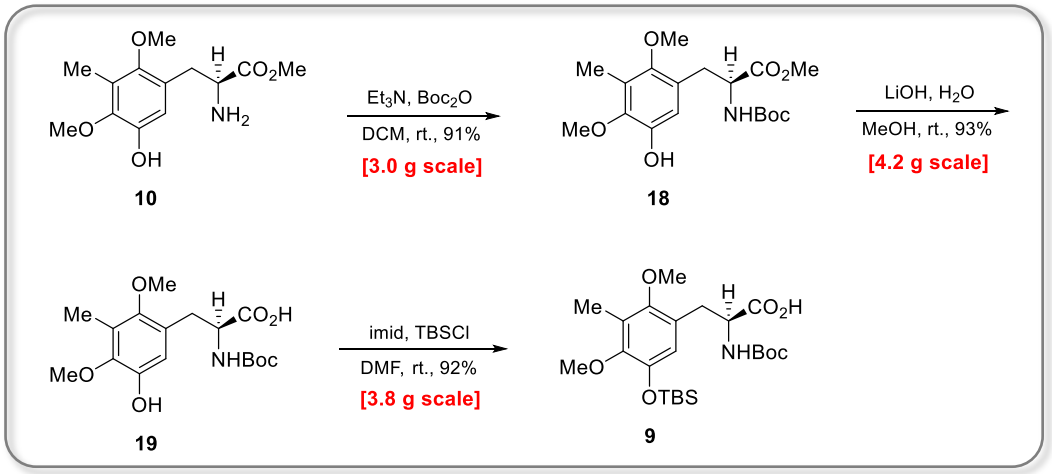
Synthesis of Compound 8



Compound 8. To a solution of compound **32** (5.78 g, 11.22 mmol, 1.0 equiv) in THF (100 mL) was added lithium aluminum hydride (853.0 mg, 22.45 mmol, 2.0 equiv) carefully at 0 °C. After stirring 30 min at the same temperature, the reaction was quenched by the cautious addition of ice-water (20 mL), and extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/methanol 15:1) to give compound **8** (4.81 g, 88% yield) as a pale yellow solid.

Compound 8. R_f = 0.26 (ethyl acetate); $[\alpha]^{27.0}_D$ −74.0° (*c* 0.3, MeOH); **IR (ATR)** λ_{max} 2951, 2931, 2884, 2857, 1496, 1454, 1410, 1391, 1361, 1346, 1312, 1278, 1251, 1194, 1112, 1064, 1027, 1005, 938, 885, 835, 816, 781, 752, 698, 674 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 4.47 (dd, *J* = 25.7, 12.0 Hz, 2H), 4.47 (m, 1H), 4.04 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.76 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.67 (s, 3H), 3.62 (s, 3H), 3.61 (m, 1H), 3.54 (dd, *J* = 10.8, 6.7 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.33 (dd, *J* = 15.5, 10.8 Hz, 1H), 2.19 (s, 3H), 0.96 (s, 9H), 0.23 (s, 3H), 0.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4 (s), 147.9 (s), 142.2 (s), 138.4 (s), 128.2 (d), 127.7 (d), 127.5 (d), 125.7 (s), 125.7 (s), 122.9 (s), 73.3 (t), 66.1 (t), 60.2 (q), 59.9 (q), 53.8 (d), 53.6 (d), 26.7 (t), 26.1 (q), 18.6 (s), 9.4 (q), -3.8 (q), -4.4 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{42}NO_5Si$ 488.2827; Found 488.2830; **m.p.** 105 – 107 °C.

(3) Synthesis of acid 9



Scheme S3. Synthesis of acid **9**

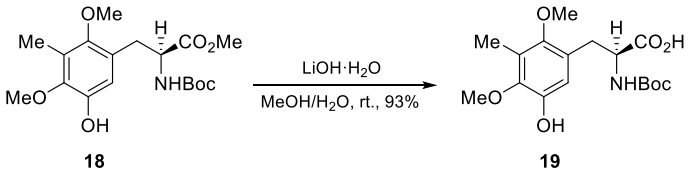
Synthesis of Compound 18

Compound 18. To a solution of compound **10** (3.00 g, 11.15 mmol, 1.0 equiv) in DCM (60

mL) was added triethylamine (4.63 mL, 33.46 mmol, 3.0 equiv) and di-*tert*-butyl dicarbonate (2.92 g, 13.38 mmol, 1.2 equiv) sequentially at room temperature. After stirring 6 h, the reaction was quenched with saturated *aq*. NH_4Cl (100 mL), and extracted with ethyl acetate (3 × 80 mL). The combined organic extracts were brine (40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 2:1) to give compound **18** (3.74 g, 91% yield) as a colorless oil.

Compound 18. $\mathbf{R_f}$ = 0.64 (n-hexane/ethyl acetate 1:1); $[\alpha]^{24.6}_D$ −20.7° (*c* 0.2, MeOH); **IR (ATR)** λ_{max} 3369, 2978, 2952, 2939, 2833, 1741, 1710, 1595, 1504, 1486, 1455, 1438, 1419, 1392, 1367, 1248, 1234, 1197, 1168, 1112, 1051, 1010, 850, 837, 779, 764, 737, 706 cm^{-1}; **^{1}H NMR** (400 MHz, CD_3OD) δ 6.51 (s, 1H), 4.33 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.03 (dd, *J* = 13.7, 5.6 Hz, 1H), 2.80 (dd, *J* = 13.7, 8.7 Hz, 1H), 2.19 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (100 MHz, CD_3OD) δ 174.4 (s), 157.7 (s), 151.3 (s), 147.3 (s), 146.9 (s), 126.4 (s), 125.9 (s), 116.3 (d), 80.6 (s), 61.2 (q), 60.5 (q), 56.0 (d), 52.6 (q), 33.4 (t), 28.6 (q), 9.9 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{18}H_{27}NO_7Na$ 392.1680; Found 392.1691.

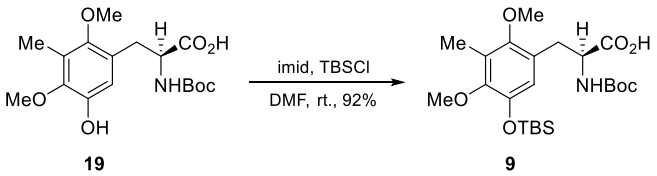
Synthesis of Compound 19



18 **19**

Compound 19. Compound **18** (4.20 g, 11.38 mmol, 1.0 equiv) was dissolved in MeOH (40 mL), then a solution of lithium hydroxide monohydrate (1.91 g, 45.53 mmol, 4.0 equiv) in H_2O (20 mL) was added the reaction mixture at room temperature. After stirring 10 h, methanol was removed under reduced pressure. The resulting mixture was diluted with water (40 mL), acidified to pH 4 with 1N HCl, extracted with ethyl acetate (5 × 40 mL). The combined organic extracts were brine (40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue (3.76 g, 93% yield) was used directly in the next step without purification.

Synthesis of Compound 9

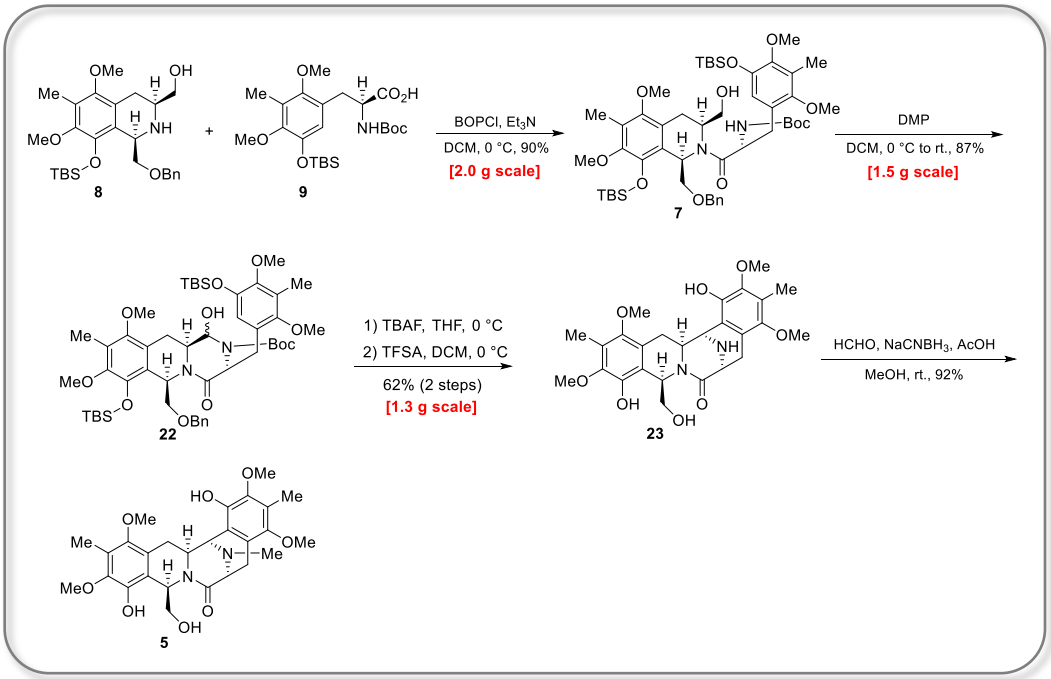


19 **9**

Compound 9. To a solution of compound **19** (3.76 g, 10.59 mmol, 1.0 equiv) in DMF (35 mL) was added imidazole (4.33 g, 63.55 mmol, 6.0 equiv) and *tert*-butyldimethylsilyl chloride (4.79 g, 31.77 mmol, 3.0 equiv) sequentially at room temperature. After stirring 12 h, the reaction was quenched with saturated *aq*. $NaHCO_3$ (60 mL), and extracted with ethyl acetate (3 × 60 mL). The combined organic extracts were washed with water (5 × 30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/methanol 50:1 to 10:1) to give compound **9** (4.57 g, 92% yield) as a colorless oil.

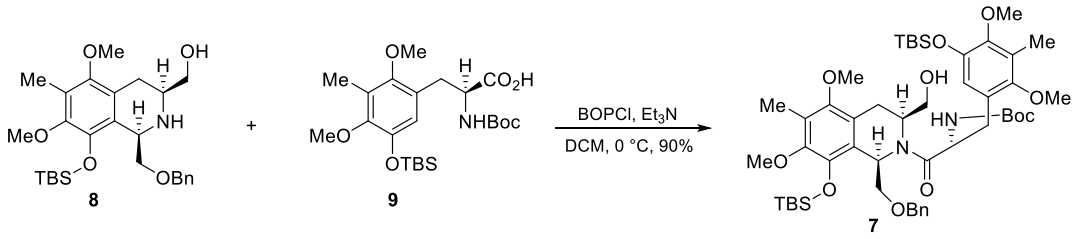
Compound 9. $\mathbf{R_f}$ = 0.58 (chloroform/methanol 10:1); $\mathbf{[\alpha]^{26.6}_D}$ −28.9° (*c* 0.3, $CHCl_3$); **IR (ATR)** λ_{max} 3342, 2956, 2932, 2898, 2859, 1716, 1588, 1484, 1454, 1419, 1392, 1366, 1351, 1251, 1239, 1221, 1167, 1119, 1064, 1014, 869, 839, 816, 783, 757, 688, 665 cm^{-1}; **^{1}H NMR** (400 MHz, CD_3OD) δ 6.64 (s, 1H), 4.24 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.14 (dd, *J* = 14.1, 4.4 Hz, 1H), 2.76 (dd, *J* = 14.1, 9.9 Hz, 1H), 2.18 (s, 3H), 1.37 (s, 9H), 1.02 (s, 9H), 0.17 (s, 6H); **^{13}C NMR** (150 MHz, CD_3OD) δ 178.2 (s), 157.8 (s), 152.9 (s), 150.2 (s), 146.0 (s), 127.3 (s), 126.3 (s), 121.3 (d), 80.3 (s), 61.2 (q), 60.3 (q), 56.9 (d), 33.2 (t), 28.8 (q), 26.3 (q), 19.1 (s), 10.0 (q), -4.3 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{23}H_{39}NO_7SiNa$ 492.2388; Found 492.2400.

(4) Synthesis of pentacyclic intermediate 5



Scheme S4. Synthesis of pentacyclic intermediate **5**

Synthesis of Compound 7

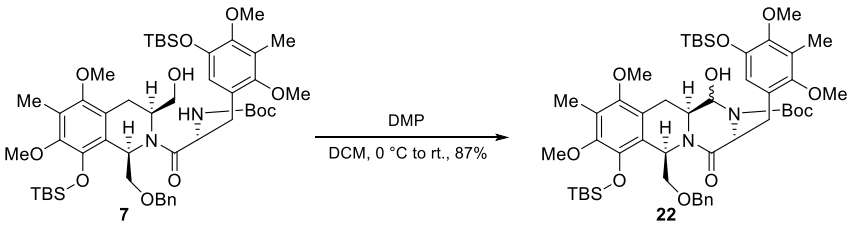


Compound 7. Compound **8** (2.00 g, 4.11 mmol, 1.0 equiv) and triethylamine (1.42 mL, 10.27 mmol, 2.5 equiv) was dissolved in DCM (80 mL), and a solution of compound **9** (2.12 g, 4.52 mmol, 1.1 equiv) in DCM (10 mL) and BOPCl (1.15 g, 4.52 mmol, 1.1 equiv) was added the reaction mixture sequentially at 0 °C. After stirring 12 h at the same temperature, the reaction was quenched with saturated *aq*. NH_4Cl (100 mL), and extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give compound **9** (3.47 g, 90% yield) as a colorless oil.

Compound 7. $\mathbf{R_f}$ = 0.76 (n-hexane/ethyl acetate 1:1); $\mathbf{[\alpha]}^{26.3}_{D}$ +2.9° (*c* 0.3, $CHCl_3$); **IR (KBr)** λ_{max} 3436, 2955, 2932, 2896, 2858, 1714, 1642, 1483, 1472, 1464, 1455, 1415, 1391, 1365,

1349, 1252, 1240, 1218, 1171, 1117, 1064, 1011, 873, 838, 783, 737, 698, 676 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (multiple and broadened resonances due to carbamate rotamers) 7.35 – 7.19 (m, 5H), 6.47 (s, 1H), 6.20 (q, *J* = 5.2 Hz, 1H), 5.41 (d, *J* = 8.7 Hz, 1H), 5.09 (m, 1H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.58 – 4.36 (m, 2H), 3.89 – 3.76 (m, 2H), 3.73 – 3.56 (m, 12H), 3.45 (s, 1H), 2.93 – 2.70 (m, 3H), 2.60 (m, 1H), 2.18 (s, 6H), 1.99 (*br* s, 1H), 1.32 (s, 9H), 1.01 (s, 9H), 0.97 (s, 9H), 0.29 – 0.08 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (multiple and broadened resonances due to carbamate rotamers) 173.2 (s), 155.3 (s), 151.5 (s), 150.3 (s), 149.1 (s), 148.1 (s), 144.6 (s), 141.5 (s), 138.0 (s), 128.2 (d), 127.5 (d), 127.4 (d), 125.2 (s), 124.6 (s), 123.84 (s), 123.76 (s), 121.6 (s), 120.4 (d), 79.3 (s), 73.1 (t), 71.0 (t), 65.6 (t), 60.5 (q), 60.1 (q), 60.0 (q), 59.7 (q), 52.4 (d), 51.6 (d), 47.8 (d), 35.0 (t), 28.2 (q), 26.2 (q), 25.7 (q), 23.1 (t), 18.6 (s), 18.1 (s), 9.8 (q), 9.5 (q), -3.7 (q), -4.4 (q), -4.6 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{50}H_{78}N_2O_{11}Si_2Na$ 961.5036; Found 961.5055.

Synthesis of Compound 22

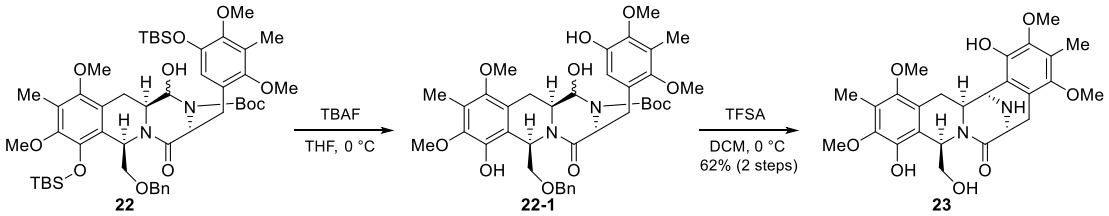


Compound 22. To a solution of compound **7** (1.50 g, 1.60 mmol, 1.0 equiv) in DCM (32 mL) was added Dess-Martin periodinane (1.02 g, 2.40 mmol, 1.5 equiv) at 0 °C, and the reaction was allowed to warm to room temperature. After stirring 30 min, white precipitate was formed. The reaction mixture was filtered through a short pad of silica gel with ethyl acetate, concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 5:1) to give compound **22** (1.30 g, 87% yield) as a colorless oil.

Compound 22. $\mathbf{R_f}$ = 0.31 (n-hexane/ethyl acetate 4:1); $[\alpha]^{27.8}_D$ −85.5° (*c* 0.4, $CHCl_3$); **IR (ATR)** λ_{max} 3413, 2953, 2931, 2896, 2858, 1699, 1650, 1587, 1470, 1462, 1414, 1392, 1363, 1351, 1332, 1291, 1251, 1217, 1164, 1118, 1102, 1065, 1007, 965, 939, 890, 866, 836, 782, 734, 697 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (multiple and broadened resonances due to

carbamate rotamers) 7.31 – 7.09 (m, 5H), 6.74 (d, *J* = 30.3 Hz, 1H), 6.03 – 5.66 (m, 2H), 4.90 – 4.71 (m, 1H), 4.63 – 4.34 (m, 3H), 3.94 – 3.82 (m, 1H), 3.77 – 3.55 (m, 12H), 3.46 – 3.20 (m, 3H), 3.14 – 2.97 (m, 2H), 2.27 – 2.13 (m, 6H), 1.27 – 1.09 (m, 9H), 1.02 (d, *J* = 12.8 Hz, 18H), 0.27 – 0.08 (m, 12H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ (multiple and broadened resonances due to carbamate rotamers) 167.4 (s), 152.9 (s), 151.3 (s), 149.5 (s), 148.8 (s), 148.3 (s), 145.2 (s), 142.0 (s), 138.8 (s), 128.0 (d), 127.1 (d), 127.1 (d), 125.4 (s), 124.9 (s), 124.8 (s), 124.5 (s), 124.0 (s), 121.5 (d), 80.6 (s), 74.6 (d), 73.1 (t), 72.0 (t), 61.0 (q), 60.7 (q), 59.9 (q), 59.6 (q), 57.5 (d), 56.9 (d), 49.8 (d), 36.3 (t), 27.7 (q), 26.1 (q), 25.7 (s), 25.6 (q), 25.4 (t), 18.6 (s), 9.9 (q), 9.6 (q), -3.9 (q), -4.6 (q), -4.6 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{50}H_{76}N_2O_{11}Si_2Na$ 959.4880; Found 959.4883.

Synthesis of Compound 23

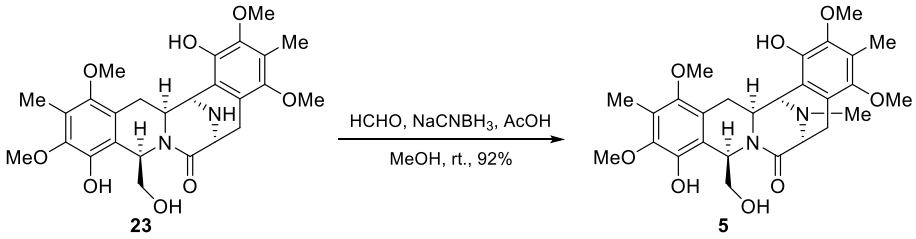


Compound 23. To a solution of compound **22** (1.30 g, 1.39 mmol, 1.0 equiv) in THF (28 mL) was added tetrabutylammonium fluoride (1.0 M in THF, 4.17 mL, 4.17 mmol, 3.0 equiv) at 0 °C. After stirring 2 h at the same temperature, the reaction was quenched with saturated *aq*. NH_4Cl (30 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was used directly in the next step without further purification. A flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with trifluoromethanesulfonic acid (9.83 mL, 111.1 mmol, 80.0 equiv), and a solution of crude compound **22-1** in dry DCM (1 mL) was added to the reaction mixture sequentially at 0 °C. After stirring 2 h at the same temperature, the mixture was poured into ice-water (20 mL), quenched by the cautious addition of saturated *aq*. $NaHCO_3$ (50 mL), and extracted with ethyl acetate (5 × 50 mL). The combined organic extracts were washed with

brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/methanol 20:1) to give compound **23** (430.6 mg, 62% yield, over two steps) as a white solid.

Compound 23. $\mathbf{R_f}$ = 0.25 (chloroform/methanol 10:1); $\mathbf{[\alpha]}^{25.3}_{D}$ −61.4° (*c* 0.3, $CHCl_3$); **IR (KBr)** λ_{max} 3266, 2995, 2938, 2881, 2832, 1626, 1464, 1452, 1410, 1367, 1305, 1275, 1251, 1230, 1192, 1110, 1063, 1033, 1007, 995, 892, 869, 838, 799, 643 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.83 (dd, *J* = 6.8, 4.3 Hz, 1H), 5.78 (s, 1H), 4.60 (d, *J* = 3.4 Hz, 1H), 4.07 (d, *J* = 6.4 Hz, 1H), 3.88 (dt, *J* = 12.7, 2.9 Hz, 1H), 3.763 (s, 3H), 3.758 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.51 (dd, *J* = 15.5, 2.6 Hz, 1H), 3.45 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.32 (dd, *J* = 10.8, 6.7 Hz, 1H), 3.20 (dd, *J* = 17.7, 1.4 Hz, 1H), 3.03 (dd, *J* = 17.6, 6.7 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H), 2.14 (dd, *J* = 15.4, 12.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8 (s), 150.0 (s), 148.3 (s), 144.3 (s), 143.6 (s), 142.12 (s), 142.08 (s), 124.8 (s), 123.5 (s), 123.4 (s), 123.1 (s), 118.4 (s), 117.9 (s), 68.2 (t), 62.2 (d), 61.0 (q), 60.9 (q), 60.8 (q), 60.3 (q), 53.5 (d), 52.1 (d), 49.0 (d), 30.1 (t), 25.8 (t), 9.64 (q), 9.61 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{33}N_2O_8$ 501.2231; Found 501.2234; **m.p.** 271 – 273 °C.

Synthesis of Compound 5

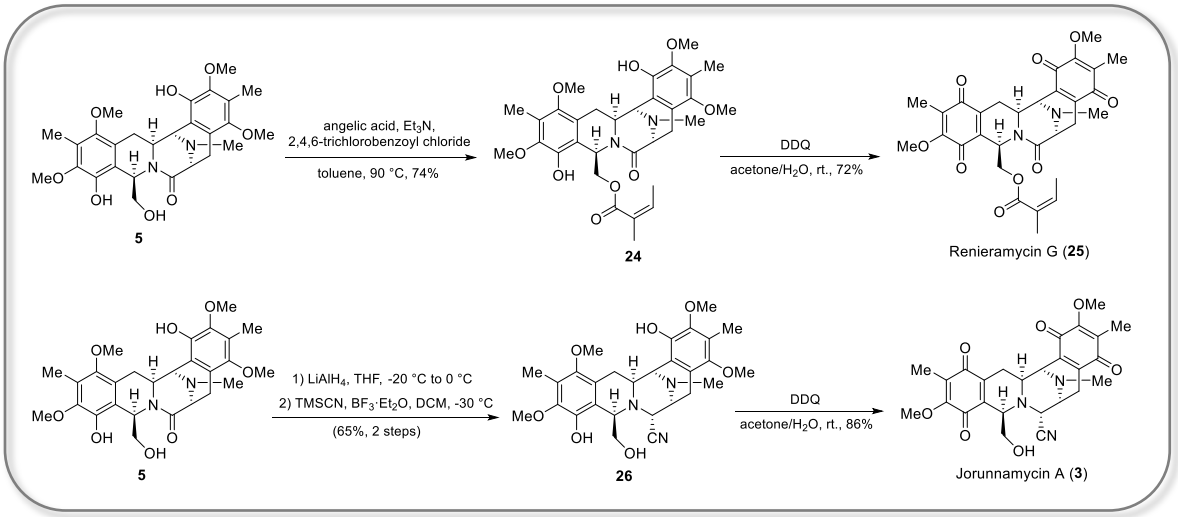


Compound 5. To a solution of compound **23** (420.0 mg, 0.84 mmol, 1.0 equiv) in MeOH (42 mL) was added 37% aqueous formaldehyde (7.0 mL, substrate concentration ~0.12 M), sodium cyanoborohydride (527.9 mg, 8.40 mmol, 10.0 equiv), and acetic acid (10.5 mL, substrate concentration ~0.08 M) sequentially at room temperature. After stirring 4 h, the solvent was removed under reduced pressure. The resulting mixture was diluted with ethyl acetate (20 mL), quenched by the cautious addition of saturated *aq*. $NaHCO_3$ (40 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were brine (20 mL),

dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/methanol 20:1) to give compound **5** (397.2 mg, 92% yield) as a colorless oil.

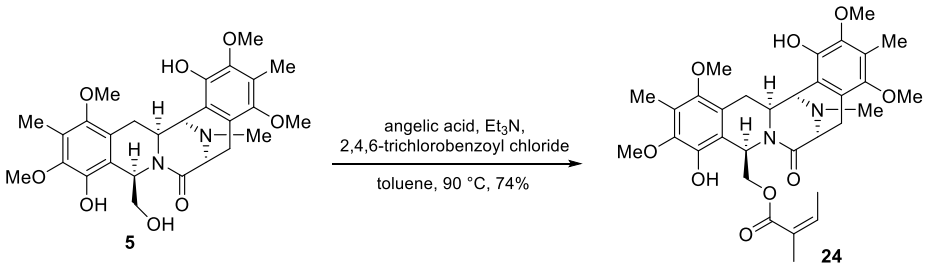
Compound 5. $\mathbf{R_f}$ = 0.47 (chloroform/methanol 10:1); $\mathbf{[\alpha]}^{25.0}_{D}$ −119.7° (*c* 0.3, $CHCl_3$); **IR (KBr)** λ_{max} 2994, 2939, 2876, 2834, 1464, 1414, 1363, 1343, 1318, 1304, 1273, 1226, 1193, 1144, 1110, 1061, 1005, 980, 932, 874, 836, 809, 726 cm^{-1}; **^{1}H NMR** (400 MHz, CD_3OD) δ 5.67 (dd, *J* = 5.5, 4.5 Hz, 1H), 4.41 (dd, *J* = 3.7, 1.3 Hz, 1H), 3.87 (td, J = 12.9, 3.7 Hz, 1H), 3.70 (s, 3H), 3.70 (s, 3H), 3.68 (t, *J* = 1.2 Hz, 1H), 3.66 (s, 3H), 3.66 (s, 3H), 3.53 (dd, *J* = 15.5, 2.5 Hz, 1H), 3.45 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.33 (dd, *J* = 10.3, 4.7 Hz, 1H), 3.16 (dd, *J* = 18.0, 6.9 Hz, 1H), 2.91 (dd, *J* = 18.0, 1.2 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H), 2.20 (dd, *J* = 20.2, 12.9 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 173.4 (s), 150.1 (s), 149.3 (s), 146.3 (s), 145.9 (s), 145.7 (s), 144.5 (s), 126.8 (s), 124.9 (s), 124.4 (s), 122.9 (s), 120.4 (s), 117.6 (s), 65.6 (t), 61.4 (q), 60.8 (q), 60.8 (q), 60.6 (d), 60.5 (q), 59.8 (d), 56.2 (d), 52.8 (d), 40.1 (q), 27.0 (t), 25.2 (t), 9.7 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{35}N_2O_8$ 515.2388; Found 515.2371.

(5) Synthesis of Renieramycin G (25) and Jorunnamycin A (3)



Scheme S5. Synthesis of Renieramycin G (**25**) and Jorunnamycin A (**3**)

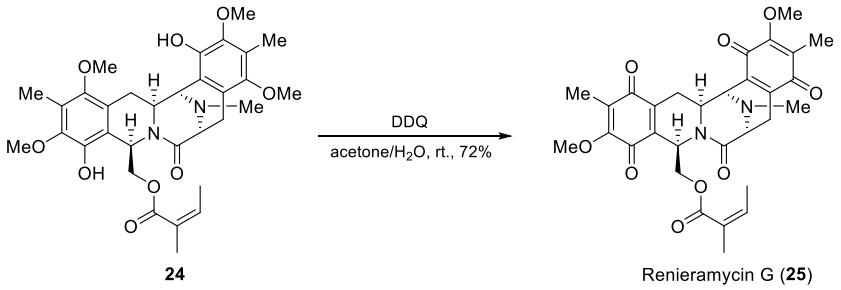
Synthesis of Compound 24



Compound 24. To a solution of angelic acid (21.9 mg, 0.219 mmol, 2.5 equiv) in dry toluene (2.0 mL) was added 2,4,6-trichlorobenzoyl chloride (34.2 μL in 1.0 mL of dry toluene, 0.219 mmol, 2.5 equiv) and triethylamine (30.3 μL in 1.0 mL of dry toluene, 0.219 mmol, 2.5 equiv) slowly in sequence at 0 °C under argon, and the reaction was allowed to warm to room temperature. After stirring 2 h, a solution of compound **5** (45 mg, 0.088 mmol, 1.0 equiv) in dry toluene (4.8 mL) was added to the mixture at room temperature. The reaction mixture was placed in a preheated oil bath at 90 °C and stirred for 48 h, then cooled to room temperature, concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/methanol 20:1) to give compound **24** (38.6 mg, 74% yield) as a colorless oil.

Compound 24. $\mathbf{R_f}$ = 0.51 (chloroform/methanol 10:1); $\mathbf{[\alpha]}^{25.2}_{D}$ −132.5° (*c* 0.3, $CHCl_3$); **IR (KBr)** λ_{max} 2938, 2872, 2857, 1716, 1463, 1414, 1363, 1302, 1274, 1247, 1232, 1193, 1146, 1110, 1084, 1057, 1006, 981, 940, 914, 874, 836, 792, 729 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.85 (*br* s, 2H), 5.77 (m, 1H), 4.39 (dd, *J* = 11.2, 3.8 Hz, 1H), 4.31 (dd, *J* = 12.6, 3.5 Hz, 2H), 3.93 (dt, *J* = 12.3, 3.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.72 (m, 1H), 3.61 (s, 3H), 3.60 (s, 3H), 3.41 (dd, *J* = 15.3, 2.4 Hz, 1H), 3.12 (dd, *J* = 18.2, 7.1 Hz, 1H), 2.92 (d, *J* = 18.2 Hz, 1H), 2.44 (s, 3H), 2.19 (s, 6H), 1.62 (dt, *J* = 7.2, 1.6 Hz, 3H), 1.32 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.2 (s), 166.8 (s), 149.6 (s), 148.0 (s), 143.9 (s), 143.4 (s), 143.0 (s), 142.1 (s), 137.8 (d), 127.3 (s), 126.0 (s), 123.0 (s), 122.9 (s), 122.6 (s), 117.7 (s), 116.4 (s), 64.1 (t), 60.74 (q), 60.65 (q), 60.63 (q), 60.2 (q), 59.5 (d), 57.6 (d), 55.0 (d), 49.1 (d), 40.2 (q), 25.8 (t), 24.3 (t), 20.0 (q), 15.3 (q), 9.54 (q), 9.49 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{32}H_{40}N_2O_9Na$ 619.2626; Found 619.2628.

Synthesis of Renieramycin G (25)

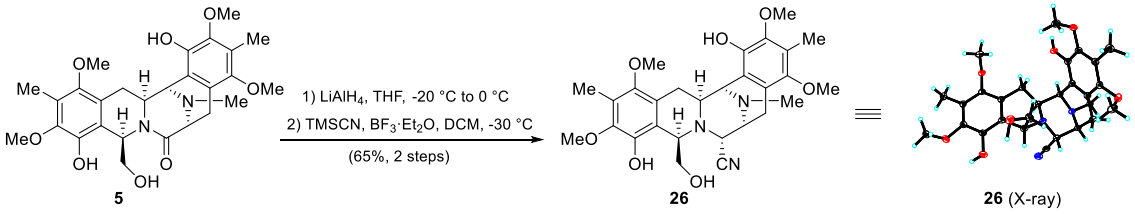


24 Renieramycin G (**25**)

Renieramycin G (25). To a solution of compound **24** (30 mg, 0.050 mmol, 1.0 equiv) in acetone/H_2O (10 mL, v/v, 9:1) was added DDQ (45.7 mg, 0.201 mmol, 4.0 equiv) in one portion at room temperature. After stirring 2 h, the reaction was quenched with saturated *aq*. $NaHCO_3$ (20 mL), and extracted with ethyl acetate (5 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (chloroform/methanol 50:1) to give compound **25** (20.4 mg, 72% yield) as a yellow amorphous powder.

Renieramycin G (25). $\mathbf{R_f}$ = 0.71 (ethyl acetate); $\mathbf{[\alpha]}^{24.7}_{D}$ −164.8° (*c* 0.1, CH_2Cl_2), Lit[4b]: $[\alpha]^{25.0}_{D}$ −162.0° (*c* 0.05, CH_2Cl_2); **IR (KBr)** λ_{max} 2947, 2924, 2855, 1717, 1656, 1616, 1450, 1424, 1373, 1351, 1309, 1262, 1230, 1151, 1121, 1084, 1047, 967, 897, 847, 729 cm^{-1}; **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 5.89 (m, 1H), 5.38 (*br* s, 1H), 4.66 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.31 (dd, *J* = 11.7, 2.4 Hz, 1H), 4.11 (d, *J* = 3.9 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.84 (dt, *J* = 12.1, 2.7 Hz, 1H), 3.67 (d, *J* = 6.9 Hz, 1H), 3.00 (dd, *J* = 16.4, 2.7 Hz, 1H), 2.86 (dd, *J* = 20.7, 7.1 Hz, 1H), 2.63 (d, *J* = 20.7 Hz, 1H), 2.35 (s, 3H), 1.92 (s, 6H), 1.67 (dq, *J* = 7.3, 1.7 Hz, 3H), 1.51 (t, *J* = 1.7 Hz, 3H), 1.47 (ddd, J = 16.4, 12.1, 1.7 Hz, 1H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 186.6 (s), 185.5 (s), 182.8 (s), 180.7 (s), 170.6 (s), 167.2 (s), 156.4 (s), 155.8 (s), 142.4 (s), 142.0 (s), 139.8 (d), 136.4 (s), 135.2 (s), 129.6 (s), 128.8 (s), 127.0 (s), 63.1 (t), 61.31 (q), 61.26 (q), 59.4 (d), 56.5 (d), 53.4 (d), 50.4 (d), 40.0 (q), 25.9 (t), 23.8 (t), 20.5 (q), 15.6 (q), 8.8 (q), 8.7 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}N_2O_9Na$ 587.2000; Found 587.2008. The physical, spectroscopic, and spectrometric data of compound **25** are consistent with those of natural[4a] and synthetic[2b,4b-d] (-)-Renieramycin G.

Synthesis of Compound 26

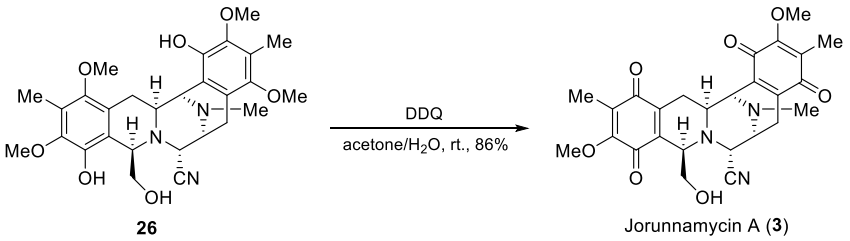


Compound 26. To a solution of compound **5** (150 mg, 0.292 mmol, 1.0 equiv) in dry THF (3 mL) was added lithium aluminum hydride (44.4 mg, 1.167 mmol, 4.0 equiv) at -20 °C under argon. The reaction mixture was stirred at -20 °C for 30 min, and allowed to warm to 0 °C. After stirring 1h at 0 °C, the reaction was quenched by the cautious addition of ice-water (20 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was used directly in the next step without further purification. To a solution of crude product in dry DCM (15 mL) was added trimethylsilyl cyanide (116.7 μL, 0.875 mmol, 3.0 equiv) and boron trifluoride etherate (25.8 μL, 0.204 mmol, 0.7 equiv) sequentially at -30 °C under argon. After stirring 3 h at the same temperature, the reaction was quenched by addition of 10% *aq*. $NaHCO_3$ (30 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 1:1) to give compound **26** (99.6 mg, 65% yield, over two steps) as a pale yellow solid. A sample of compound **26** for X-ray analysis was recrystallized from n-hexane/dichloromethane (10:1) via slow evaporation to afford colorless needles. Crystallographic data for **26** has been deposited with the Cambridge Crystallographic Data Center, Deposition number 1972948.

Compound 26. $\mathbf{R_f}$ = 0.50 (chloroform/methanol 10:1); $\mathbf{[\alpha]}^{26.3}_{D}$ −68.2° (*c* 0.4, $CHCl_3$); **IR (KBr)** λ_{max} 2937, 2870, 2833, 2228, 1631, 1618, 1464, 1414, 1319, 1276, 1252, 1221, 1193, 1150, 1109, 1062, 1005, 981, 872, 830, 804, 754 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.64 (s, 2H), 4.21 (dd, *J* = 2.9, 1.0 Hz, 1H), 4.12 (t, *J* = 3.5 Hz, 1H), 4.08 (d, *J* = 2.6 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.65 (m, 1H), 3.60 (s, 3H), 3.48 – 3.39 (m, 2H), 3.33 (dt, *J* =

11.7, 2.8 Hz, 1H), 3.21 (dd, *J* = 15.8, 2.8 Hz, 1H), 3.10 (dd, *J* = 18.6, 7.9 Hz, 1H), 2.49 (d, *J* = 18.5 Hz, 1H), 2.34 (s, 3H), 2.22 (s, 3H), 2.18 (s, 3H), 1.90 (dd, *J* = 15.8, 12.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6 (s), 148.2 (s), 143.5 (s), 143.4 (s), 143.3 (s), 141.4 (s), 124.8 (s), 123.4 (s), 122.5 (s), 122.2 (s), 118.5 (s), 117.9 (s), 116.8 (s), 63.9 (t), 60.83 (q), 60.80 (q), 60.5 (q), 60.3 (d), 60.0 (q), 58.0 (d), 56.6 (d), 56.5 (d), 55.1 (d), 41.8 (q), 25.7 (t), 21.5 (t), 9.6 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{36}N_3O_7$ 526.2548; Found 526.2557; **m.p.** 200 – 201 °C; crystal data for compound **26** see page S36.

Synthesis of Jorunnamycin A (3)

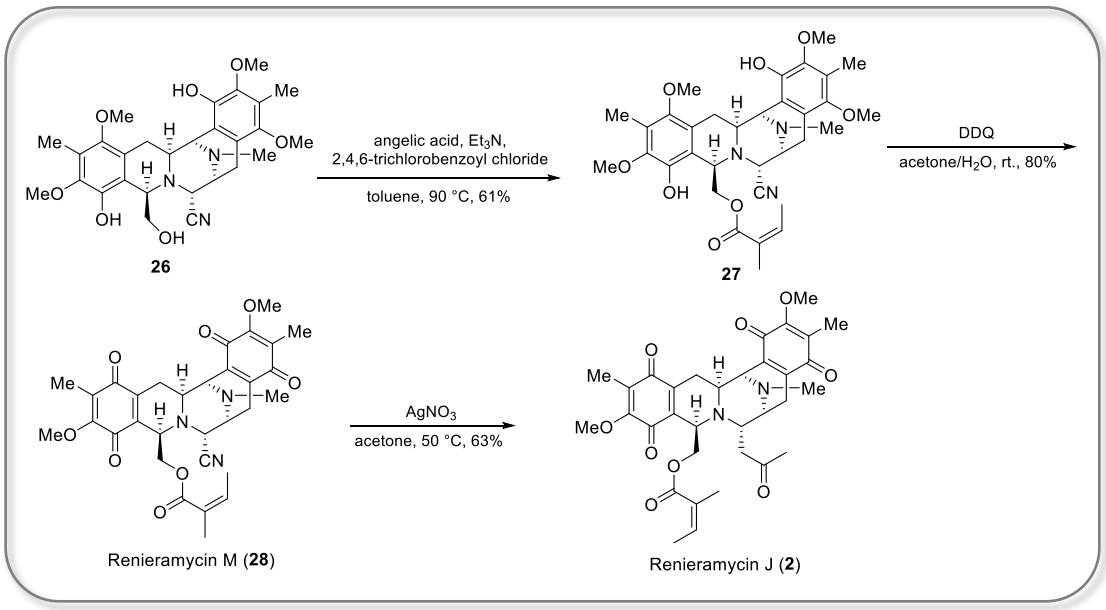


Renieramycin G (25). To a solution of compound **26** (35 mg, 0.067 mmol, 1.0 equiv) in acetone/H_2O (13 mL, v/v, 9:1) was added DDQ (60.5 mg, 0.267 mmol, 4.0 equiv) in one portion at room temperature. After stirring 2 h, the reaction was quenched with saturated *aq*. $NaHCO_3$ (20 mL), and extracted with ethyl acetate (5 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 1:1) to give compound **3** (28.3 mg, 86% yield) as a yellow amorphous powder.

Jorunnamycin A (3). $\mathbf{R_f}$ = 0.20 (n-hexane/ethyl acetate 1:1); **[α]**$^{24.7}_{D}$ −124.2° (*c* 0.3, $CHCl_3$), Lit[4b]: $[\alpha]^{25.0}_{D}$ −122.0° (*c* 0.15, $CHCl_3$); **IR (KBr)** λ_{max} 3441, 2944, 2853, 2228, 1656, 1618, 1558, 1449, 1374, 1311, 1237, 1190, 1153, 1078, 963, 890, 771, 730 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.12 (d, *J* = 2.7 Hz, 1H), 4.07 (d, *J* = 2.2 Hz, 1H), 4.02 (s, 3H), 3.98 (s, 3H), 3.89 (q, *J* = 3.4 Hz, 1H), 3.71 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.48 (m, 1H), 3.41 (d, *J* = 7.5 Hz, 1H), 3.17 (dt, *J* = 11.5, 3.3 Hz, 1H), 2.92 (dd, *J* = 17.5, 2.7 Hz, 1H), 2.82 (dd, *J* = 21.0, 7.5 Hz, 1H), 2.30 (s, 3H), 2.25 (d, *J* = 21.0 Hz, 1H), 1.94 (s, 3H), 1.93 (s, 3H), 1.40 (ddd, *J* = 17.5,

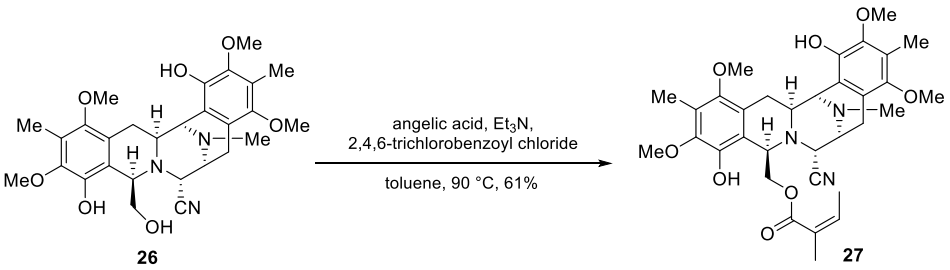
11.5, 2.7 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.3 (s), 185.5 (s), 182.3 (s), 181.4 (s), 155.5 (s), 155.3 (s), 141.6 (s), 141.4 (s), 136.0 (s), 135.6 (s), 128.9 (s), 128.6 (s), 116.9 (s), 64.0 (t), 61.10 (q), 61.08 (q), 59.0 (d), 57.9 (d), 54.4 (d), 54.3 (d), 54.2 (d), 41.6 (q), 25.3 (t), 21.4 (t), 8.8 (q), 8.7 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}N_3O_7$ 494.1922; Found 494.1919. The physical, spectroscopic, and spectrometric data of compound **3** are consistent with those of natural[5] and synthetic[2b, 4b] Jorunnamycin A.

(6) Synthesis of Renieramacin M (28) and Renieramacin J (2)



Scheme S6. Synthesis of Renieramacin M (**28**) and Renieramacin J (**2**)

Synthesis of Compound 27

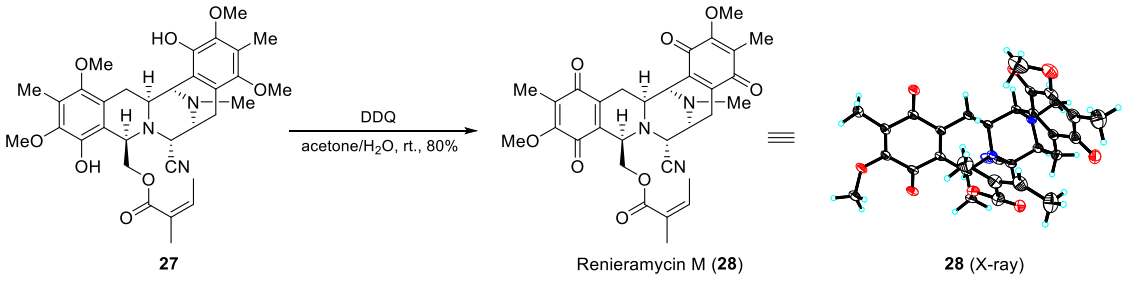


Compound 27. To a solution of angelic acid (28.6 mg, 0.286 mmol, 2.5 equiv) in dry toluene (3.0 mL) was added 2,4,6-trichlorobenzoyl chloride (44.6 µL in 1.5 mL of dry toluene, 0.286 mmol, 2.5 equiv) and triethylamine (39.5 µL in 1.5 mL of dry toluene, 0.286 mmol, 2.5 equiv)

slowly in sequence at 0 °C under argon, and the reaction was allowed to warm to room temperature. After stirring 2 h, a solution of compound **26** (60.0 mg, 0.114 mmol, 1.0 equiv) in dry toluene (5.4 mL) was added to the mixture at room temperature. The reaction mixture was placed in a preheated oil bath at 90 °C and stirred for 48 h, then cooled to room temperature, concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 1:1) to give compound **27** (42.3 mg, 61% yield) as a colorless oil.

Compound 27. $\mathbf{R_f}$ = 0.67 (n-hexane/ethyl acetate 2:3); $\mathbf{[\alpha]}^{25.0}_{D}$ −76.3° (*c* 0.2, $CHCl_3$); **IR (KBr)** λ_{max} 3429, 2937, 2831, 2227, 1712, 1646, 1617, 1463, 1414, 1388, 1353, 1319, 1275, 1253, 1232, 1192, 1154, 1109, 1062, 1004, 981, 915, 870, 850, 830, 754 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.95 (dddd, *J* = 8.7, 7.2, 5.8, 1.5 Hz, 1H), 5.60 (s, 1H), 5.52 (s, 1H), 4.32 (dd, *J* = 5.8, 2.8 Hz, 1H), 4.22 – 4.12 (m, 3H), 3.95 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.59 (s, 3H), 3.58 (s, 3H), 3.38 (dt, *J* = 7.9, 2.0 Hz, 1H), 3.25 (m, 1H), 3.22 (m, 1H), 3.04 (dd, *J* = 18.3, 8.1 Hz, 1H), 2.44 (d, *J* = 18.3 Hz, 1H), 2.28 (s, 3H), 2.19 (s, 6H), 1.97 (dd, *J* = 15.1, 11.4 Hz 1H), 1.82 (dd, *J* = 7.2, 1.5 Hz, 3H), 1.56 (p, *J* = 1.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.4 (s), 148.4 (s), 148.3 (s), 143.4 (s), 143.1 (s), 142.9 (s), 141.6 (s), 139.0 (d), 127.1 (s), 125.5 (s), 124.2 (s), 122.3 (s), 121.9 (s), 118.3 (s), 117.3 (s), 116.9 (s), 66.9 (t), 61.1 (d), 60.9 (q), 60.7 (q), 60.5 (q), 59.8 (q), 57.0 (d), 56.6 (d), 56.1 (d), 55.2 (d), 41.7 (q), 25.8 (t), 21.2 (t), 20.4 (q), 15.6 (q), 9.6 (q), 9.4 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{33}H_{42}N_3O_8$ 608.2966; Found 608.2972.

Synthesis of Renieramycin M (28)

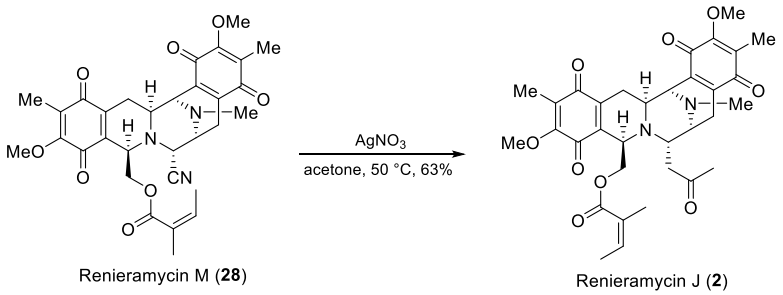


27 Renieramycin M (**28**) **28** (X-ray)

Renieramycin M (28). To a solution of compound **27** (40.0 mg, 0.066 mmol, 1.0 equiv) in acetone/H_2O (13 mL, v/v, 9:1) was added DDQ (59.8 mg, 0.264 mmol, 4.0 equiv) in one portion at room temperature. After stirring 2 h, the reaction was quenched with saturated *aq*. $NaHCO_3$ (20 mL), and extracted with ethyl acetate (5 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give compound **28** (30.3 mg, 80% yield) as a yellow solid. A sample of compound **28** for X-ray analysis was recrystallized from n-hexane/ethyl acetate/methanol (10:1:1) via slow evaporation to afford pale yellow needles. Crystallographic data for **28** has been deposited with the Cambridge Crystallographic Data Center, Deposition number 1972949.

Renieramycin M (28). $\mathbf{R_f}$ = 0.75 (n-hexane/ethyl acetate 1:1); $\mathbf{[\alpha]}^{25.1}_{D}$ −56.3° (*c* 0.2, $CHCl_3$), Lit[6]: $\mathbf{[\alpha]}^{20.0}_{D}$ −49.5° (*c* 1.0, $CHCl_3$); **IR (KBr)** λ_{max} 2943, 2927, 2852, 2235, 1709, 1697, 1651, 1616, 1447, 1376, 1307, 1235, 1189, 1151, 1081, 1045, 967, 959, 895, 769, 727 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.96 (q, *J* = 7.3 Hz, 1H), 4.54 (dd, *J* = 11.7, 3.0 Hz, 1H), 4.09 (dd, *J* = 11.7, 2.4 Hz, 1H) 4.07 (d, J = 2.2 Hz, 1H), 4.02 (s, 3H), 4.00 (m,1H), 3.99 (m, 1H), 3.98 (s, 3H), 3.39 (d, *J* = 7.5 Hz, 1H), 3.11 (dt, *J* = 11.4, 3.0 Hz, 1H), 2.89 (dd, *J* = 17.5, 3.0 Hz, 1H), 2.75 (dd, *J* = 21.0, 7.5 Hz, 1H), 2.30 (d, *J* = 21.0 Hz, 1H), 2.28 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.81 (dd, *J* = 7.3, 1.5 Hz, 3H), 1.57 (s, 3H), 1.36 (ddd, *J* = 17.5, 11.4, 3.0 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 185.9 (s), 185.5 (s), 182.5 (s), 181.0 (s), 166.5 (s), 155.8 (s), 155.2 (s), 142.0 (s), 141.3 (s), 140.6 (d), 135.7 (s), 135.0 (s), 128.6 (s), 128.4 (s), 126.2 (s), 116.9 (s), 61.9 (t), 61.1 (q), 61.0 (q), 58.5 (d), 56.2 (d), 54.5 (d), 54.2 (d), 54.1 (d), 41.5 (q), 25.4 (t), 21.1 (t), 20.4 (q), 15.7 (q), 8.7 (q), 8.6 (q); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{31}H_{33}N_3O_8Na$ 598.2160; Found 598.2155; **m.p.** 195 – 197 °C; crystal data for compound **28** see page S39. The physical, spectroscopic, and spectrometric data of compound **28** are consistent with those of natural[6] and synthetic[2b] Renieramycin M.

Synthesis of Renieramycin J (2)

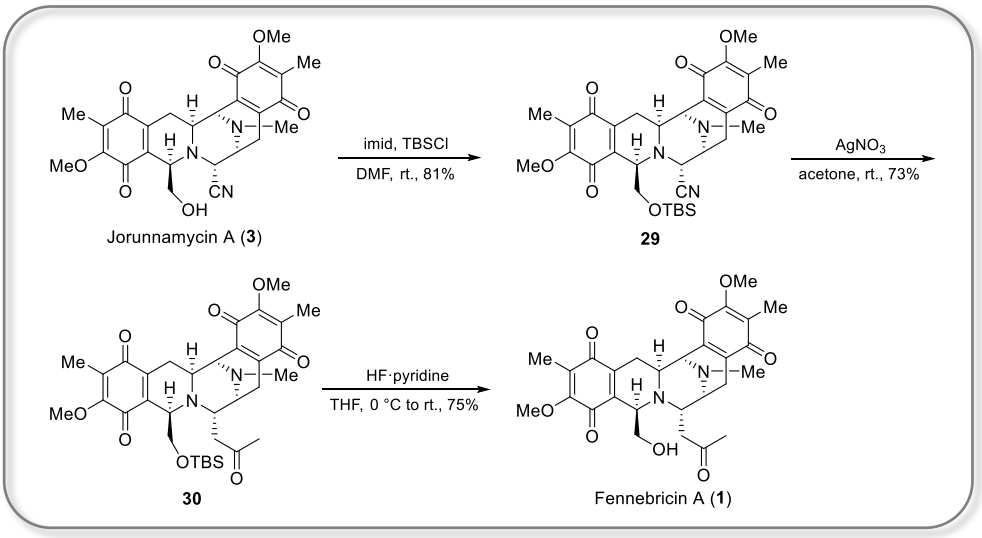


Renieramycin M (**28**) Renieramycin J (**2**)

Renieramycin J (2). To a solution of compound **28** (20.0 mg, 0.035 mmol, 1.0 equiv) in dry acetone (3.5 mL) was added $AgNO_3$ (118.3 mg, 0.696 mmol, 20.0 equiv) in one portion at room temperature. The reaction mixture was placed in a preheated oil bath at 50 °C and stirred for 1 h. Upon complete consumption of the starting material, the reaction mixture was cooled to room temperature and concentrated. The resulting residue was diluted with water (10 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 1:1) to give compound **2** (13.3 mg, 63% yield) as a yellow amorphous powder.

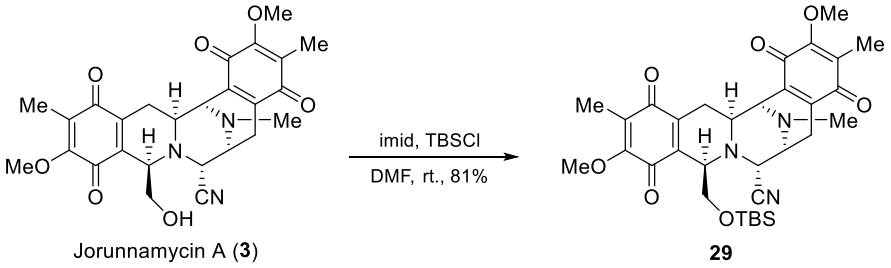
Renieramycin J (2). $\mathbf{R_f}$ = 0.59 (n-hexane/ethyl acetate 1:1); $\mathbf{[\alpha]}^{24.3}_{D}$ −10.9° (*c* 0.1, $CHCl_3$); **IR (KBr)** λ_{max} 2927, 2854, 1712, 1654, 1616, 1528, 1454, 1384, 1374, 1360, 1307, 1233, 1150, 1082, 1045, 1005, 973, 847, 772, 729 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.93 (qq, *J* = 7.2, 1.6 Hz, 1H), 4.17 (dd, *J* = 11.1, 3.2 Hz, 1H), 4.10 (dd, *J* = 11.1, 3.3 Hz, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.87 (*br* s, 1H), 3.81 (*br* s, 1H), 3.44 (m, 1H), 3.41 (m, 1H), 2.95 – 2.88 (m, 2H), 2.83 (dd, *J* = 16.8, 2.8 Hz, 1H), 2.74 (dd, *J* = 21.0, 7.2 Hz, 1H), 2.36 (d, *J* = 16.5 Hz, 1H), 2.26 (d, *J* = 21.0 Hz, 1H), 2.19 (s, 3H), 2.16 (s, 3H), 1.91 (s, 6H), 1.79 (dq, *J* = 7.2, 1.6 Hz, 3H), 1.59 (s, 3H), 1.25 (ddd, *J* = 16.8, 11.1, 2.0 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.3 (s), 186.6 (s), 185.6 (s), 182.9 (s), 181.2 (s), 167.1 (s), 156.0 (s), 155.1 (s), 143.4 (s), 141.5 (s), 139.6 (d), 137.2 (s), 135.0 (s), 128.7 (s), 128.1 (s), 126.7 (s), 64.5 (t), 60.88 (q), 60.87 (q), 58.8 (d), 55.01 (d), 54.99 (d), 53.5 (d), 52.3 (d), 41.7 (q), 38.5 (t), 30.9 (q), 25.4 (t), 23.1 (t), 20.4 (q), 15.5 (q), 8.7 (q), 8.6 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{33}H_{39}N_2O_9$ 607.2650; Found 607.2654. The physical, spectroscopic, and spectrometric data of compound **2** are consistent with those of natural[6] Renieramycin J.

(7) Synthesis of Fennebricin (1)



Scheme S7. Synthesis of Fennebricin (**1**)

Synthesis of Compound 29

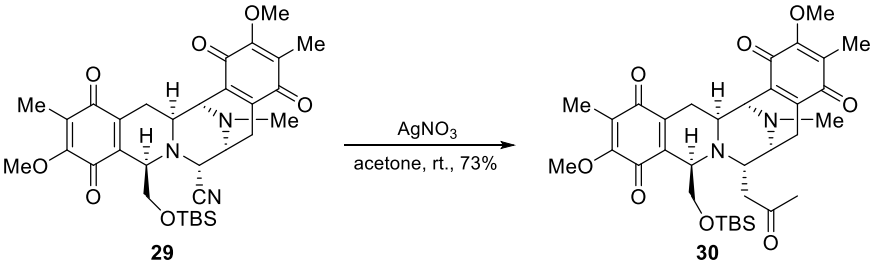


Compound 29. To a solution of compound **3** (50.0 mg, 0.101 mmol, 1.0 equiv) in DMF (1.0 mL) was added imidazole (41.4 mg, 0.609 mmol, 6.0 equiv) and *tert*-butyldimethylsilyl chloride (45.9 mg, 0.304 mmol, 3.0 equiv) sequentially at room temperature. After stirring 2 h, the reaction was quenched with saturated *aq*. $NaHCO_3$ (5 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with water (5 × 5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ ethyl acetate 10:1 to 2:1) to give compound **29** (49.9 mg, 81% yield) as a yellow oil.

Compound 29. $\mathbf{R_f}$ = 0.56 (n-hexane/ethyl acetate 2:1); $\mathbf{[\alpha]}^{25.3}_{D}$ −69.7° (*c* 0.1, $CHCl_3$); **IR (KBr)** λ_{max} 2952, 2931, 2856, 2228, 1656, 1618, 1463, 1449, 1375, 1311, 1253, 1235, 1190,

1151, 1111, 1093, 1081, 960, 839, 778 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.17 (d, J = 2.7 Hz, 1H), 4.02 (*br* s, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.84 (dt, J = 4.9, 2.3 Hz, 1H), 3.63 (dd, J = 9.8, 2.1 Hz, 1H), 3.44 (dd, J = 9.8, 5.3 Hz, 1H), 3.35 (dt, J = 7.5, 1.8 Hz, 1H), 3.09 (dt, J = 11.5, 2.9 Hz, 1H), 2.88 (dd, J = 16.9, 2.7 Hz, 1H), 2.77 (dd, J = 20.7, 7.5 Hz, 1H), 2.28 (s, 3H), 2.27 (m, 1H), 1.934 (s, 3H), 1.926 (s, 3H), 1.40 (ddd, J = 16.9, 11.5, 2.7 Hz, 1H), 0.73 (s, 9H), -0.11 (d, J = 12.2 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.5 (s), 185.6 (s), 182.5 (s), 181.2 (s), 155.5 (s), 155.3 (s), 141.90 (s), 141.87 (s), 136.2 (s), 135.4 (s), 128.8 (s), 128.6 (s), 117.4 (s), 66.1 (t), 61.04 (q), 60.97 (q), 59.9 (d), 58.2 (d), 54.6 (d), 54.5 (d), 54.4 (d), 41.6 (q), 25.7 (q), 25.4 (t), 21.4 (t), 17.9 (s), 8.7 (q), 8.6 (q), -5.66 (q), -5.71 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{42}N_3O_7Si$ 608.2787; Found 608.2787.

Synthesis of Compound 30



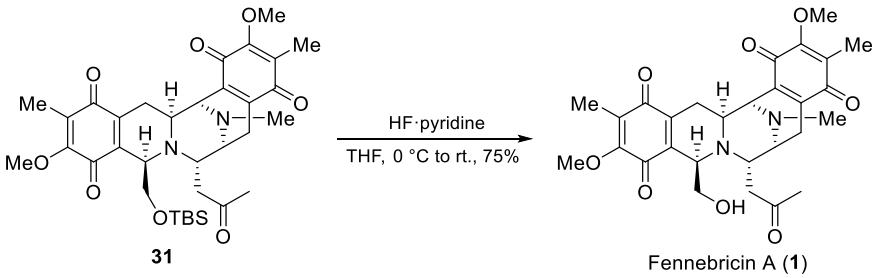
29 **30**

Compound 30. To a solution of compound **30** (32.0 mg, 0.053 mmol, 1.0 equiv) in dry acetone (5.0 mL) was added $AgNO_3$ (89.6 mg, 0.527 mmol, 10.0 equiv) in one portion at room temperature. After stirring 5 h, the reaction mixture was concentrated. The resulting residue was diluted with water (10 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give compound **30** (24.6 mg, 73% yield) as a yellow oil.

Compound 30. **R_f** = 0.34 (n-hexane/ethyl acetate 2:1); **[α]**$^{25.0}_D$ −6.7° (*c* 0.1, $CHCl_3$); **IR (KBr)** λ_{max} 2951, 2931, 2856, 1712, 1654, 1616, 1463, 1447, 1409, 1374, 1360, 1306, 1252, 1235, 1189, 1148, 1109, 1092, 1049, 1006, 974, 937, 838, 777, 695, 652 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.93 (s, 3H), 3.87 (d, J = 3.7 Hz, 1H), 3.59 (*br* s, 1H), 3.54 (dd, J = 9.7,

2.7 Hz, 1H), 3.45 (d, *J* = 9.7 Hz, 1H), 3.42 (dd, *J* = 15.2, 9.4 Hz, 1H), 3.32 (d, *J* = 9.4 Hz, 1H), 2.90 (td, *J* = 8.4, 2.4 Hz, 2H), 2.79 (dd, *J* = 14.0, 2.2 Hz, 1H), 2.74 (dd, *J* = 20.9, 7.2 Hz, 1H), 2.33 (d, *J* = 15.8 Hz, 1H), 2.25 (d, *J* = 20.9 Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), 1.36 (ddd, *J* = 16.4, 11.5, 2.2 Hz, 1H), 0.66 (s, 9H), -0.19 (s, 3H), -0.21 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.6 (s), 187.0 (s), 185.8 (s), 183.0 (s), 181.6 (s), 155.5 (s), 155.3 (s), 143.2 (s), 142.8 (s), 138.0 (s), 135.2 (s), 128.7 (s), 128.6 (s), 65.4 (t), 60.9 (q), 60.8 (q), 59.4 (d), 55.9 (d), 55.1 (d), 55.0 (d), 52.4 (d), 41.7 (q), 38.4 (t), 31.0 (q), 25.7 (t), 25.6 (q), 23.3 (t), 17.9 (s), 8.7 (q), 8.6 (q), -5.7 (q), -5.8 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{34}H_{47}N_2O_8Si$ 639.3096; Found 639.3114.

Synthesis of Fennebricin A (1)

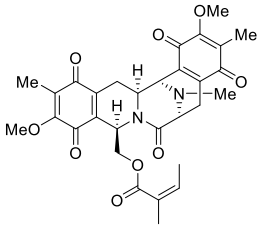


Fennebricin A (1). To a solution of compound **30** (22.0 mg, 0.034 mmol, 1.0 equiv) in dry THF (2.4 mL) was added pyridine hydrofluoride (0.3 mL, HF 65% in pyridine) at 0 °C, and the reaction was allowed to warm to room temperature slowly. After stirring 2 h, the reaction was quenched with saturated *aq*. KF (5 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (petroleum ether/ ethyl acetate 1:1) to give compound **1** (13.6 mg, 75% yield) as a yellow amorphous powder.

Fennebricin A (1). $\mathbf{R_f}$ = 0.27 (n-hexane/ethyl acetate 1:1); $\mathbf{[\alpha]}^{25.4}_{D}$ −96.2° (*c* 0.2, $CHCl_3$), Lit[7]: $[\alpha]^{25.0}_{D}$ −96.2° (*c* 0.04, $CHCl_3$); **IR (KBr)** λ_{max} 3435, 2973, 2934, 2897, 1709, 1654, 1618, 1448, 1374, 1307, 1236, 1189, 1149, 1082, 1049, 968, 880, 772 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 3.97 (m, overlapped, 1H), 3.95 (s, 3H), 3.67 (dd, *J* = 11.2, 3.8

Hz, 1H), 3.63 (m, 1H), 3.48 (dd, *J* = 17.8, 9.0 Hz, 1H), 3.38 (d, *J* = 8.9 Hz, 1H), 3.34 (m, overlapped, 1H), 3.00 (dt, *J* = 11.5, 3.2 Hz, 1H), 2.94 (d, *J* = 7.3 Hz, 1H), 2.84 (dd, *J* = 17.4, 2.3 Hz, 1H), 2.81 (dd, *J* = 21.0, 7.3 Hz, 1H), 2.41 (d, *J* = 17.8 Hz, 1H), 2.22 (d, *J* = 21.0 Hz, 1H), 2.19 (s, 3H), 2.18 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.32 (ddd, *J* = 17.4, 11.5, 2.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.9 (s), 186.3 (s), 185.6 (s), 182.6 (s), 181.8 (s), 155.5 (s), 155.4 (s), 143.0 (s), 141.8 (s), 137.5 (s), 135.7 (s), 128.9 (s), 128.8 (s), 62.7 (t), 60.99 (q), 60.96 (q), 58.2 (d), 55.00 (d), 54.99 (d), 54.9 (d), 51.7 (d), 41.8 (q), 39.0 (t), 30.9 (q), 25.5 (t), 23.3 (t), 8.8 (q), 8.7 (q); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{33}N_2O_8$ 525.2231; Found 525.2231. The physical, spectroscopic, and spectrometric data of compound **1** are consistent with those of natural[7] Fennebricin A.

2. NMR data comparison of synthetic and natural products

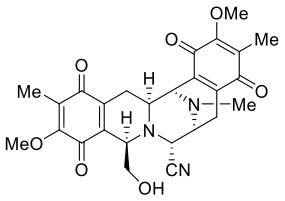


Renieramycin G (**25**)

Table S1. NMR data comparison of synthetic and natural Renieramycin G[4a] (**25**)[a]

^{1}H NMR		^{13}C NMR	
Natural[b]	**This work[c]**	**Natural[d]**	**This work[e]**
5.90, m, 1H	5.89, m, 1H	186.6	186.8
5.40, brs, 1H	5.38, brs, 1H	185.6	185.7
4.67, dd, 11.7, 2.8, 1H	4.66, dd, 11.7, 2.8, 1H	182.9	183.0
4.32, dd, 11.7, 2.6, 1H	4.31, dd, 11.7, 2.4, 1H	180.8	180.9
4.12, brd, 4.0, 1H	4.11, d, 3.9, 1H	170.7	170.8
4.01, s, 3H	4.00, s, 3H	167.3	167.4
3.98, s, 3H	3.97, s, 3H	156.6	156.6
3.85, dt, 12.2, 3.0, 1H	3.84, dt, 12.1, 2.7, 1H	156.0	156.0
3.67, d, 7.1, 1H	3.67, d, 6.9, 1H	142.6	142.6
3.01, dd, 16.5, 3.0, 1H	3.00, dd, 16.4, 2.7, 1H	142.2	142.2
2.87, dd, 20.6, 6.1, 1H	2.86, dd, 20.7, 7.1, 1H	139.5	140.0
2.64, d, 20.6, 1H	2.63, d, 20.7, 1H	136.6	136.6
2.36, s, 3H	2.35, s, 3H	135.5	135.4
1.93, s, 6H	1.92, s, 6H	129.6	129.8
1.68, dq, 7.3, 1.6, 3H	1.67, dq, 7.3, 1.7, 3H	128.8	129.0
1.52, t, 1.6, 3H	1.51, t, 1.7, 3H	127.3	127.2
1.49, ddd, 16.5, 12.2, 1.6, 1H	1.47, ddd, 16.4, 12.1, 1.7, 1H	63.3	63.3
		61.3	61.5
		61.2	61.5
		59.6	59.6
		56.6	56.7
		53.2	53.6
		50.5	50.6
		40.1	40.2
		26.1	26.1
		24.0	24.0
		20.5	20.7
		15.6	15.8
		8.8	9.0
		8.8	8.9

[a] All data were recorded in CD_2Cl_2 and to the solvent signal (5.32 ppm for ^{1}H, 53.8 ppm for^{13}C); [b] Measured at 500 MHz, δ [ppm, mult, J (Hz)]; [c] Measured at 125 MHz, δ (ppm); [d] Measured at 400 MHz, δ [ppm, mult, J (Hz)]; [e] Measured at 150 MHz, δ (ppm).

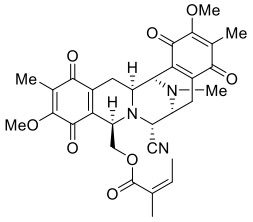


Jorunnamycin A (**3**)

Table S2. NMR data comparison of synthetic and natural Jorunnamycin A[5a] (**3**)[a]

^{1}H NMR		**^{13}C NMR**	
Natural[b]	**This work[c]**	**Natural[d]**	**This work[e]**
4.15, d, 2.4, 1H	4.12, d, 2.7, 1H	186.3	186.3
4.07, d, 2.6, 1H	4.07, d, 2.2, 1H	185.5	185.5
4.03, s, 3H	4.02, s, 3H	182.3	182.3
3.98, s, 3H	3.98, s, 3H	181.4	181.4
3.89, ddd, 3.7, 3.1, 2.4, 1H	3.89, q, 3.4, 1H	155.7	155.5
3.71, dd, 11.3, 3.1, 1H	3.71, dd, 11.5, 3.3, 1H	155.4	155.3
3.48, dd, 11.3, 3.7, 1H	3.48, m, 1H	141.7	141.6
3.41, dd, 7.6, 2.4, 1H	3.41, d, 7.5, 1H	141.4	141.4
3.17, ddd, 11.6, 2.6, 2.4, 1H	3.17, dt, 11.5, 3.3, 1H	136.1	136.0
2.92, dd, 17.4, 2.4, 1H	2.92, dd, 17.5, 2.7, 1H	135.6	135.6
2.82, dd, 21.1, 7.6, 1H	2.82, dd, 21.0, 7.5, 1H	128.8	128.9
2.30, s, 3H	2.30, s, 3H	128.6	128.6
2.27, d, 21.1, 1H	2.25, d, 21.0, 1H	116.9	116.9
1.93, s, 3H	1.94, s, 3H	64.2	64.0
1.93, s, 3H	1.93, s, 3H	61.1	61.10
1.42, ddd, 17.4, 11.6, 2.4, 1H	1.40, ddd, 17.5, 11.5, 2.7, 1H	61.0	61.08
		59.1	59.0
		58.0	57.9
		54.5	54.4
		54.3	54.3
		54.2	54.2
		41.5	41.6
		25.4	25.3
		21.5	21.4
		8.7	8.8
		8.7	8.7

[a] All data were recorded in $CDCl_3$ and to the solvent signal (7.26 ppm for ^{1}H, 77.0 ppm for^{13}C); [b] Measured at 500 MHz, δ [ppm, mult, J (Hz)]; [c] Measured at 125 MHz, δ (ppm); [d] Measured at 400 MHz, δ [ppm, mult, J (Hz)]; [e] Measured at 150 MHz, δ (ppm).

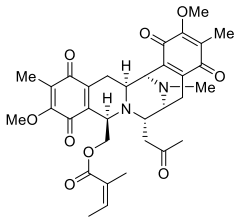


Renieramycin M (**28**)

Table S3. NMR data comparison of synthetic and natural Renieramycin M[6] (**28**)[a]

^{1}H NMR		^{13}C NMR	
Natural[b]	**This work**[c]	**Natural**[d]	**This work**[e]
5.96, qq, 7.3, 1.5, 1H	5.96, q, 7.3, 1H	185.9	185.9
4.53, dd, 11.6, 3.1, 1H	4.54, dd, 11.7, 3.0, 1H	185.4	185.5
4.10, dd, 11.6, 2.5, 1H	4.09, dd, 11.7, 2.4, 1H	182.5	182.5
4.07, d, 2.5, 1H	4.07, d, 2.2, 1H	180.9	181.0
4.02, s, 3H	4.02, s, 3H	166.5	166.5
4.01, d, 3.1, 1H	4.00, m, 1H (overlapped)	155.8	155.8
3.99, m, 1H (overlapped)	3.99, m, 1H (overlapped)	155.2	155.2
3.99, s, 3H	3.98, s, 3H	142.0	142.0
3.40, ddd, 7.6, 2.5, 1.8, 1H	3.39, d, 7.5, 1H	141.3	141.3
3.11, ddd, 11.3, 3.1, 2.8, 1H	3.11, dt, 11.4, 3.0, 1H	140.5	140.6
2.89, dd, 17.4, 2.8, 1H	2.89, dd, 17.5, 3.0, 1H	135.7	135.7
2.76, dd, 20.6, 7.6, 1H	2.75, dd, 21.0, 7.5, 1H	135.0	135.0
2.30, d, 20.6, 1H	2.30, d, 21.0, 1H	128.6	128.6
2.28, s, 3H	2.28, s, 3H	128.6	128.4
1.94, s, 3H	1.93, s, 3H	126.3	126.2
1.90, s, 3H	1.90, s, 3H	116.9	116.9
1.82, dq, 7.3, 1.5, 3H	1.81, dd, 7.3, 1.5, 3H	62.0	61.9
1.58, s, 3H	1.57, s, 3H	61.0	61.1
1.36, 17.4, 11.3, 2.7, 1H	1.36, 17.5, 11.4, 3.0, 1H	60.9	61.0
		58.5	58.5
		56.3	56.2
		54.6	54.5
		54.2	54.2
		54.1	54.1
		41.5	41.5
		25.4	25.4
		21.3	21.1
		20.4	20.4
		15.7	15.7
		8.7	8.7
		8.6	8.6

[a] All data were recorded in $CDCl_3$ and to the solvent signal (7.26 ppm for ^{1}H, 77.0 ppm for^{13}C); [b] Measured at 500 MHz, δ [ppm, mult, J (Hz)]; [c] Measured at 125 MHz, δ (ppm); [d] Measured at 400 MHz, δ [ppm, mult, J (Hz)]; [e] Measured at 150 MHz, δ (ppm).

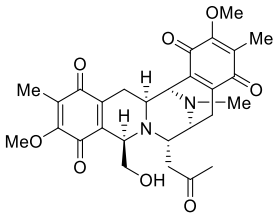


Renieramycin J (**2**)

Table S4. NMR data comparison of synthetic and natural Renieramycin J[6] (**2**)[a]

^{1}H NMR		^{13}C NMR	
Natural[b]	**This work[c]**	**Natural[d]**	**This work[e]**
5.93, qq, 7.3, 1.6, 1H	5.93, qq, 7.2, 1.6, 1H	208.1	208.3
4.16, dd, 11.0, 2.7, 1H	4.17, dd, 11.1, 3.2, 1H	186.7	186.6
4.09, dd, 11.0, 3.4, 1H	4.10, dd, 11.1, 3.3, 1H	185.6	185.6
4.00, s, 3H	4.00, s, 3H	182.9	182.9
3.96, s, 3H	3.96, s, 3H	181.2	181.2
3.86, brs, 1H	3.87, brs, 1H	167.0	167.1
3.81, brs, 1H	3.81, brs, 1H	156.0	156.0
3.44, m, 1H	3.44, m, 1H	155.1	155.1
3.41, m, 1H	3.41, m, 1H	143.4	143.4
2.90 – 2.93, m, 2H	2.88 – 2.95, m, 2H	141.6	141.5
2.82, brd, 16.8, 1H	2.83, dd, 16.8, 2.8, 1H	139.4	139.6
2.74, dd, 20.8, 7.3, 1H	2.74, dd, 21.0, 7.2, 1H	137.2	137.2
2.35, d, 16.5, 1H	2.36, d, 16.5, 1H	135.0	135.0
2.26, d, 20.8, 1H	2.26, d, 21.0, 1H	128.7	128.7
2.19, s, 3H	2.19, s, 3H	128.0	128.1
2.16, s, 3H	2.16, s, 3H	126.8	126.7
1.90, s, 6H	1.91, s, 6H	64.6	64.5
1.79, dq, 7.3, 1.6, 3H	1.79, dq, 7.2, 1.6, 3H	60.8	60.88
1.59, dq, 1.6, 3H	1.59, s, 3H	60.8	60.87
1.25, ddd, 16.8, 11.2, 2.0, 1H	1.25, ddd, 16.8, 11.1, 2.0, 1H	58.9	58.8
		55.1	55.01
		55.1	54.99
		53.5	53.5
		52.3	52.3
		41.7	41.7
		38.6	38.5
		30.9	30.9
		25.5	25.4
		23.1	23.1
		20.3	20.4
		15.5	15.5
		8.6	8.7
		8.6	8.6

[a] All data were recorded in $CDCl_3$ and to the solvent signal (7.26 ppm for ^{1}H, 77.0 ppm for^{13}C); [b] Measured at 500 MHz, δ [ppm, mult, J (Hz)]; [c] Measured at 125 MHz, δ (ppm); [d] Measured at 400 MHz, δ [ppm, mult, J (Hz)]; [e] Measured at 150 MHz, δ (ppm).



Fennebricin A (**1**)

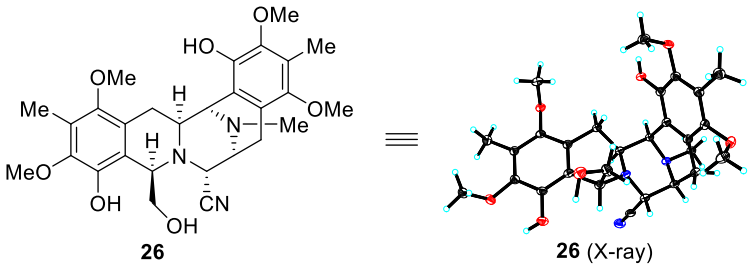
Table S5. NMR data comparison of synthetic and natural Fennebricin[7] (**1**)[a]

^{1}H NMR		^{13}C NMR	
Natural[b]	**This work**[c]	**Natural**[d]	**This work**[e]
3.98, s, 3H	3.98, s, 3H	208.0	207.9
3.97, 1H (overlapped)	3.97, m, 1H (overlapped)	185.6	186.3
3.96, s, 3H	3.95, s, 3H	185.5	185.6
3.67, dd, 11.0, 3.5, 1H	3.67, dd, 11.2, 3.8, 1H	183.1	182.6
3.61, m, 1H	3.63, m, 1H	180.8	181.8
3.48, d, 16.5, 1H	3.48, dd, 17.8, 9.0, 1H	155.0	155.5
3.40, m, 1H	3.38, d, 8.9, 1H	155.0	155.4
3.35, dd, 11.0, 3.7, 1H	3.34, m, 1H (overlapped)	143.6	143.0
3.05, brd, 11.8, 1H	3.00, dt, 11.5, 3.2, 1H	142.5	141.8
2.92, m, 1H	2.94, d, 7.3, 1H	135.8	137.5
2.83, dd, 16.7, 2.2, 1H	2.84, dd, 17.4, 2.3, 1H	135.0	135.7
2.85, dd, 20.1, 7.3, 1H	2.81, dd, 21.0, 7.3, 1H	128.5	128.9
2.42, d, 16.5, 1H	2.41, d, 17.8, 1H	126.8	128.8
2.20, d, 20.1, 1H	2.22, d, 21.0, 1H	63.7	62.7
2.19, s, 3H	2.19, s, 3H	61.5	60.99
2.18, s, 3H	2.18, s, 3H	61.5	60.96
1.95, s, 3H	1.93, s, 3H	58.5	58.2
1.92, s, 3H	1.92, s, 3H	55.3	55.00
1.25, dd, 16.7, 11.8, 1H	1.32, ddd, 17.4, 11.5, 2.4, 1H	54.5	54.99
		54.5	54.9
		51.5	51.7
		41.5	41.8
		38.5	39.0
		30.8	30.9
		23.7	25.5
		23.4	23.3
		8.5	8.8
		8.5	8.7

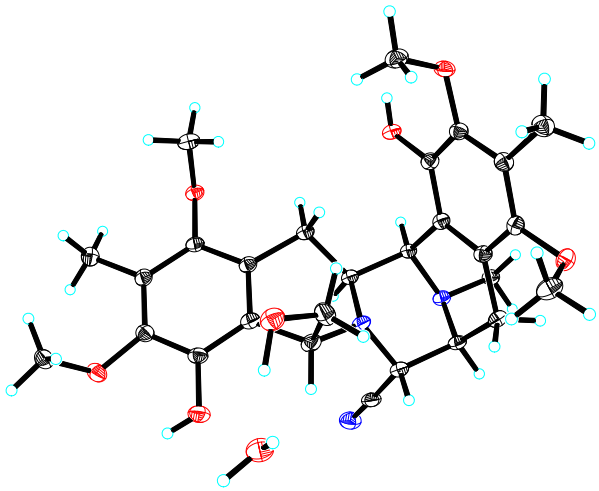
[a] All data were recorded in $CDCl_3$ and to the solvent signal (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C); [b] Measured at 400 MHz, δ [ppm, mult, J (Hz)]; [c] Measured at 100 MHz, δ (ppm); [d] Measured at 400 MHz, δ [ppm, mult, J (Hz)]; [e] Measured at 150 MHz, δ (ppm).

3. X-ray crystallographic data

(1) X-ray crystallographic data of compound 26

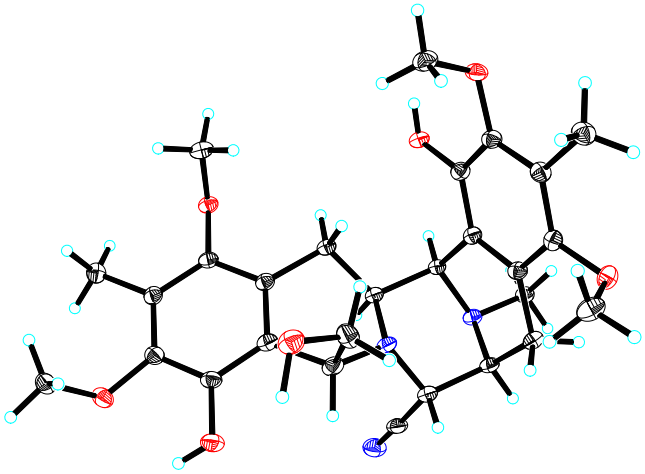


Crystal data for **26**: $C_{28}H_{35}N_3O_7 \bullet H_2O$, M = 543.60, a = 12.5972(5) Å, b = 9.4343(3) Å, c = 12.6471(5) Å, α = 90 °, β = 118.542(2) °, γ = 90 °, V = 1320.38(9) Å^3, T = 100.(2) K, space group $P1211$, Z = 2, μ(Cu Kα) = 0.832 mm^{-1}, 21394 reflections measured, 5185 independent reflections (R_{int} = 0.0733). The final R_1 values were 0.0498 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1237 ($I > 2\sigma(I)$). The final R_1 values were 0.0573 (all data). The final $wR(F^2)$ values were 0.1325 (all data). The goodness of fit on F^2 was 1.032. Flack parameter = 0.20(12).



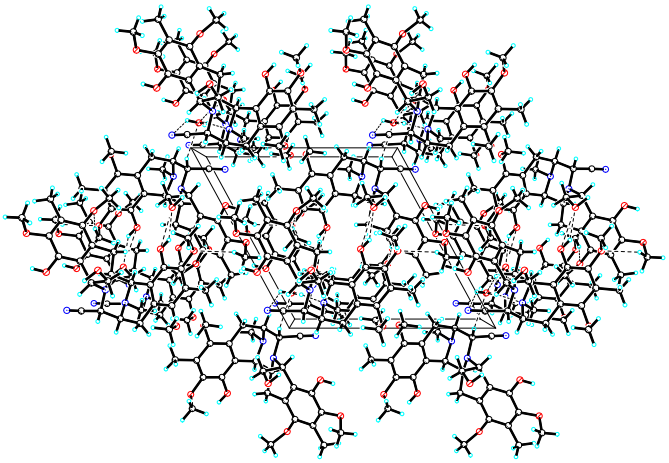
View of the molecules in an asymmetric unit.

Displacement ellipsoids are drawn at the 30% probability level.



View of a molecule of **26** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **26**.

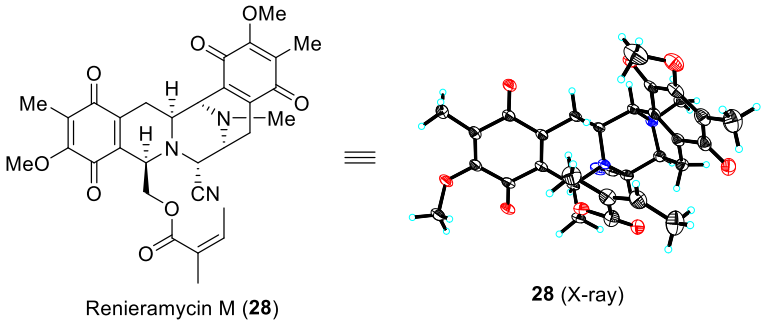
Hydrogen-bonds are shown as dashed lines.

Table S5. **Crystal data and structure refinement for 26.**

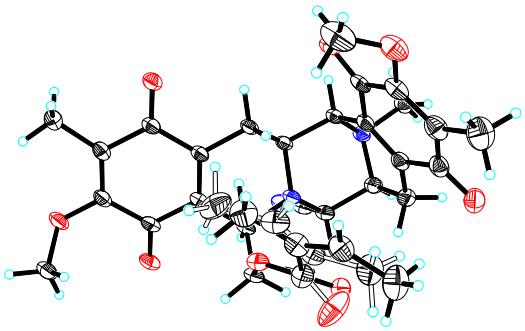
Identification code	global	
Empirical formula	C28 H37 N3 O8	
Formula weight	543.60	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.5972(5) Å	= 90 °.

	b = 9.4343(3) Å = 118.542(2)°.
	c = 12.6471(5) Å = 90°.
Volume	1320.38(9) $Å^3$
Z	2
Density (calculated)	1.367 Mg/m^3
Absorption coefficient	0.832 mm^{-1}
F(000)	580
Crystal size	0.220 x 0.070 x 0.010 mm^3
Theta range for data collection	3.98 to 72.51 °.
Index ranges	-15<=h<=15, -11<=k<=11, -15<=l<=13
Reflections collected	21394
Independent reflections	5185 [R(int) = 0.0733]
Completeness to theta = 72.51 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.78
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5185 / 1 / 364
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1237
R indices (all data)	R1 = 0.0573, wR2 = 0.1325
Absolute structure parameter	0.20(12)
Largest diff. peak and hole	0.579 and -0.326 $e.Å^{-3}$

(2) X-ray crystallographic data of compound 28

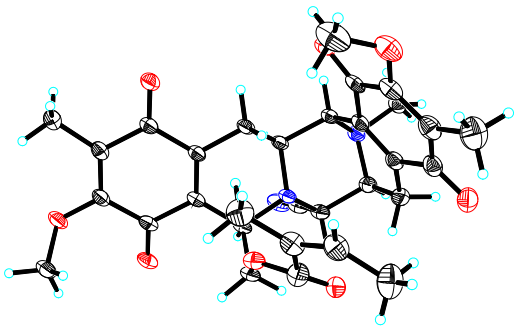


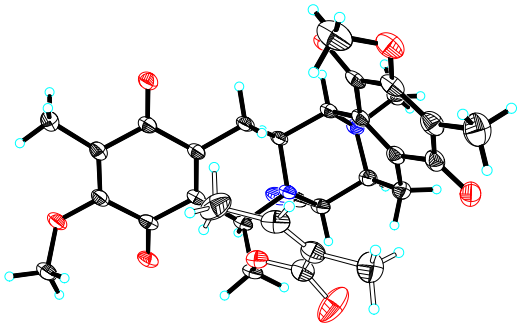
Crystal data for **28**: $C_{31}H_{33}N_3O_8$, M = 575.60, a = 8.6975(2) Å, b = 15.6191(4) Å, c = 21.5360(5) Å, α = 90 °, β = 90 °, γ = 90 °, V = 2925.60(12) Å^3, T = 100.(2) K, space group $P212121$, Z = 4, μ(Cu Kα) = 0.787 mm^{-1}, 30751 reflections measured, 5770 independent reflections (R_{int} = 0.0395). The final R_1 values were 0.0348 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0942 ($I > 2\sigma(I)$). The final R_1 values were 0.0360 (all data). The final $wR(F^2)$ values were 0.0952 (all data). The goodness of fit on F^2 was 1.031. Flack parameter = 0.02(6).



View of the molecules in an asymmetric unit.

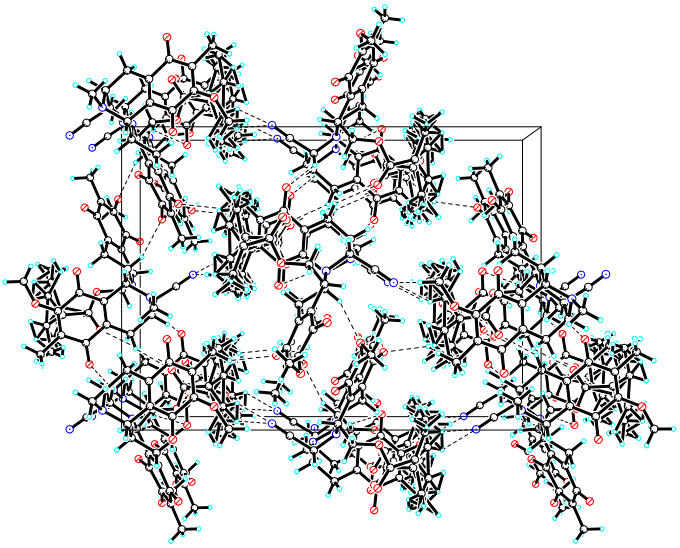
Displacement ellipsoids are drawn at the 30% probability level.





View of a molecule of **28** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **28**.

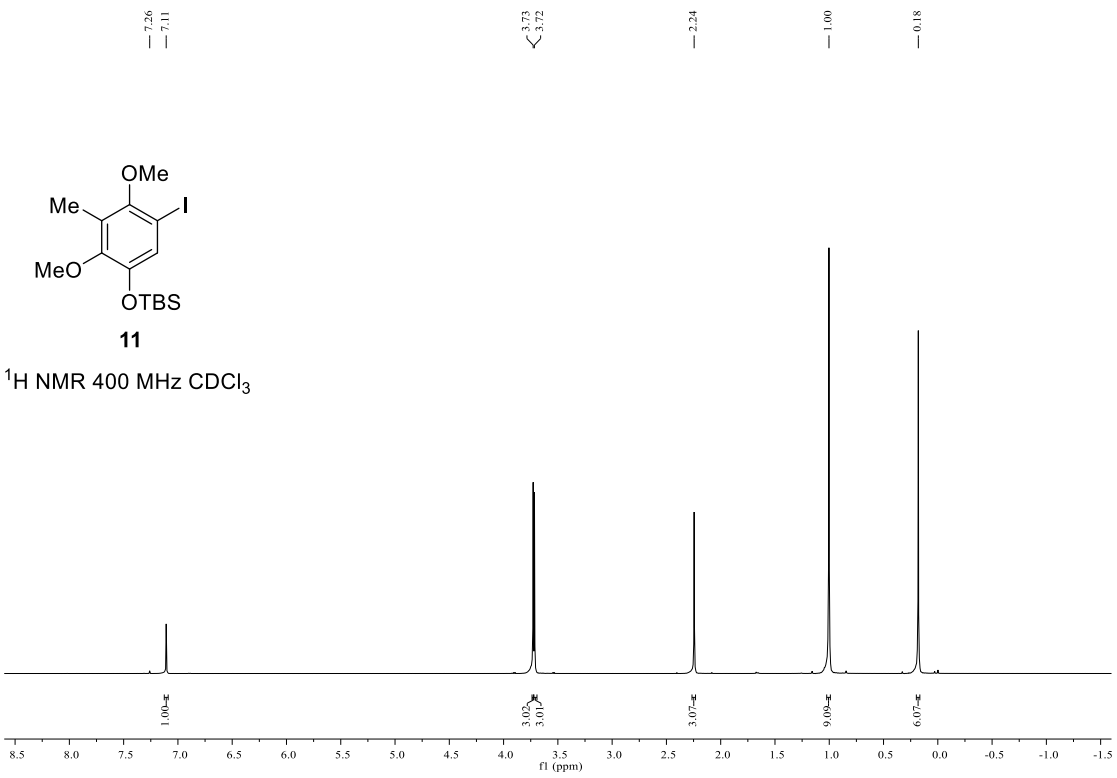
Hydrogen-bonds are shown as dashed lines.

Table S6. **Crystal data and structure refinement for 28.**

Identification code	global	
Empirical formula	C31 H33 N3 O8	
Formula weight	575.60	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.6975(2) Å	= 90°.
	b = 15.6191(4) Å	= 90°.
	c = 21.5360(5) Å	= 90°.

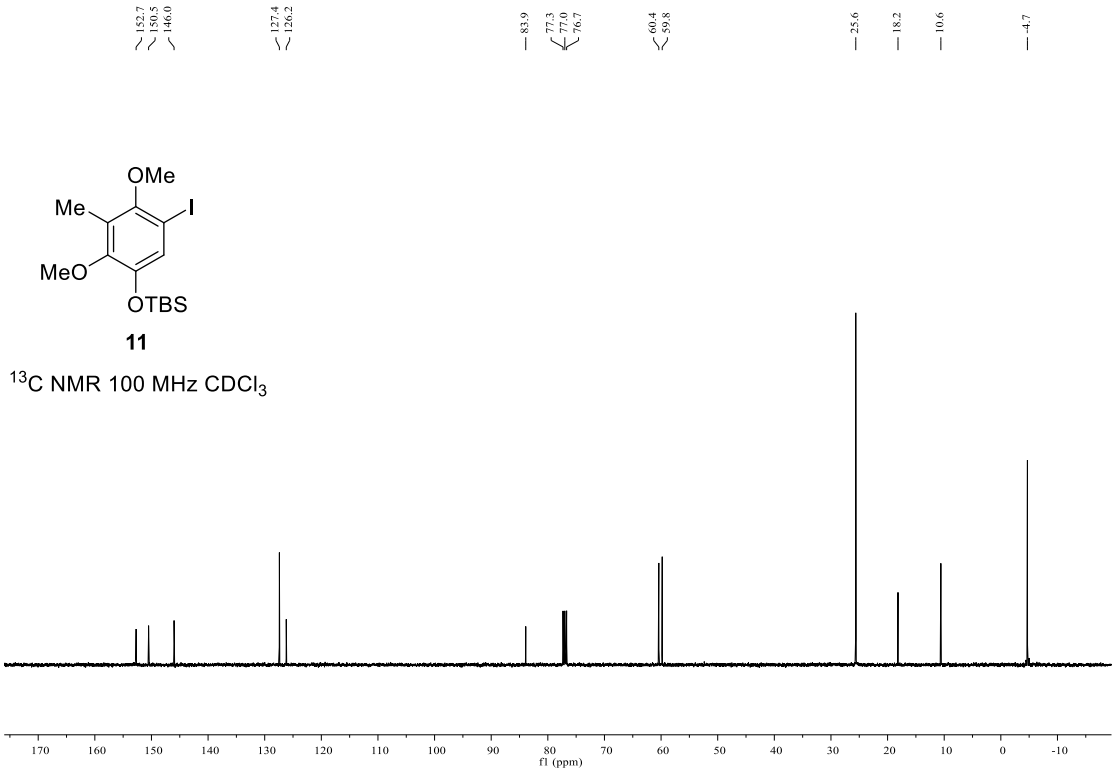
Volume	2925.60(12) $Å^3$
Z	4
Density (calculated)	1.307 Mg/m^3
Absorption coefficient	0.787 mm^{-1}
F(000)	1216
Crystal size	0.700 x 0.340 x 0.250 mm^3
Theta range for data collection	3.50 to 72.30 °.
Index ranges	-10<=h<=10, -14<=k<=19, -26<=l<=26
Reflections collected	30751
Independent reflections	5770 [R(int) = 0.0395]
Completeness to theta = 72.30 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.83 and 0.72
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5770 / 186 / 443
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0942
R indices (all data)	R1 = 0.0360, wR2 = 0.0952
Absolute structure parameter	0.02(6)
Largest diff. peak and hole	0.235 and -0.157 $e.Å^{-3}$

4. Copies of ^{1}H and ^{13}C NMR spectra



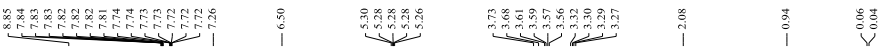
11

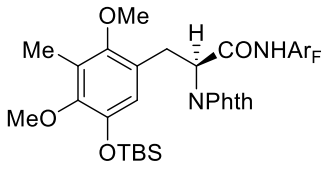
^{1}H NMR 400 MHz $CDCl_3$



11

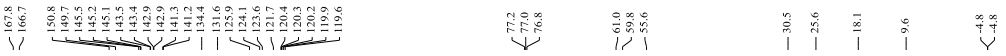
^{13}C NMR 100 MHz $CDCl_3$

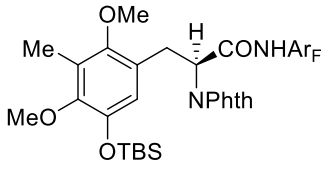




15

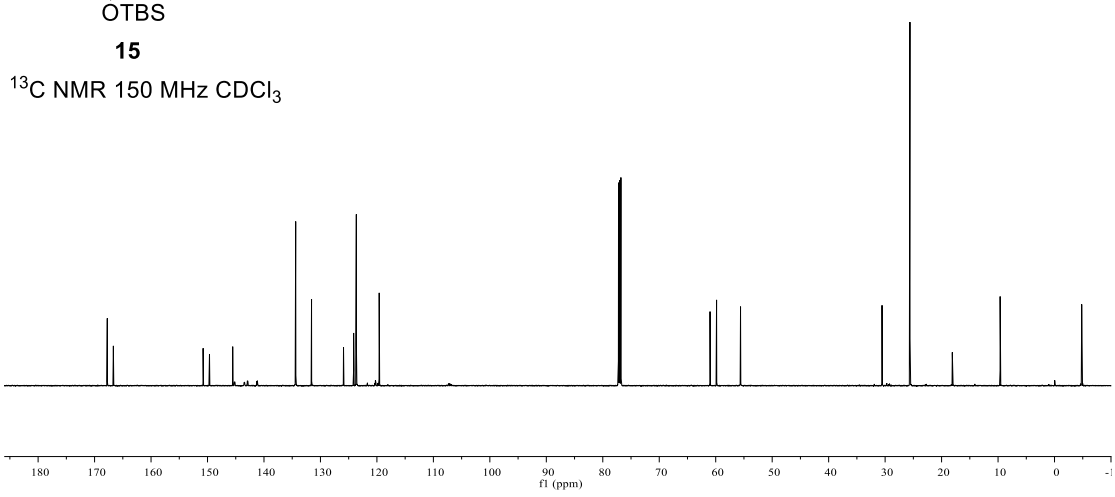
^{1}H NMR 400 MHz $CDCl_3$

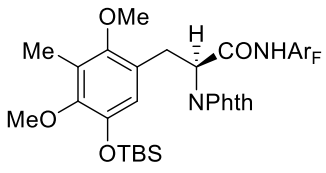




15

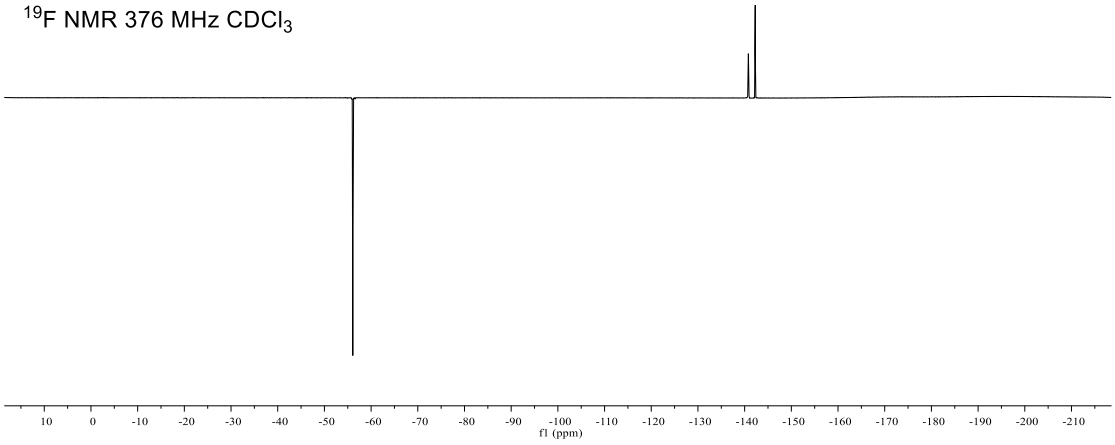
^{13}C NMR 150 MHz $CDCl_3$

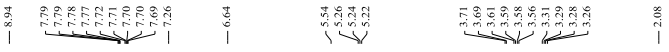


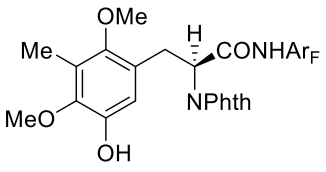


15

^{19}F NMR 376 MHz $CDCl_3$

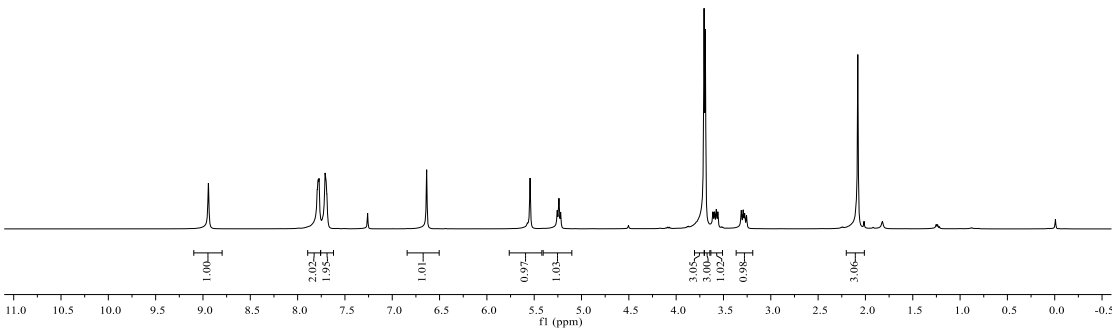


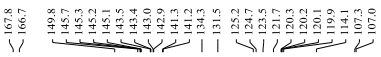


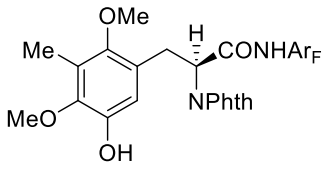


16

^{1}H NMR 400 MHz $CDCl_3$

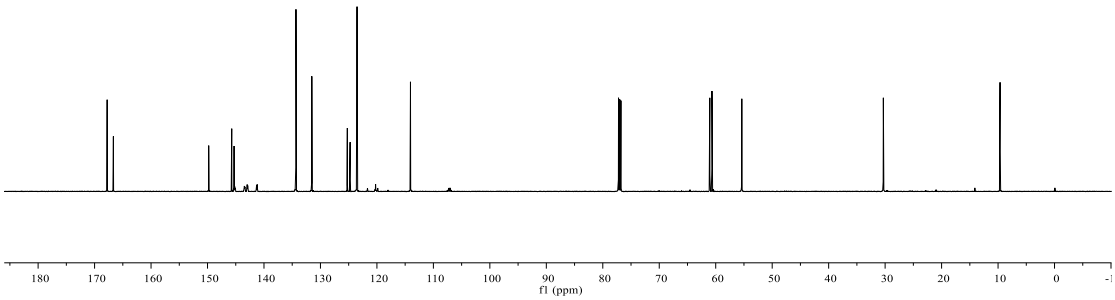


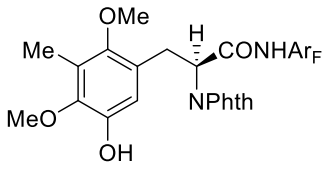




16

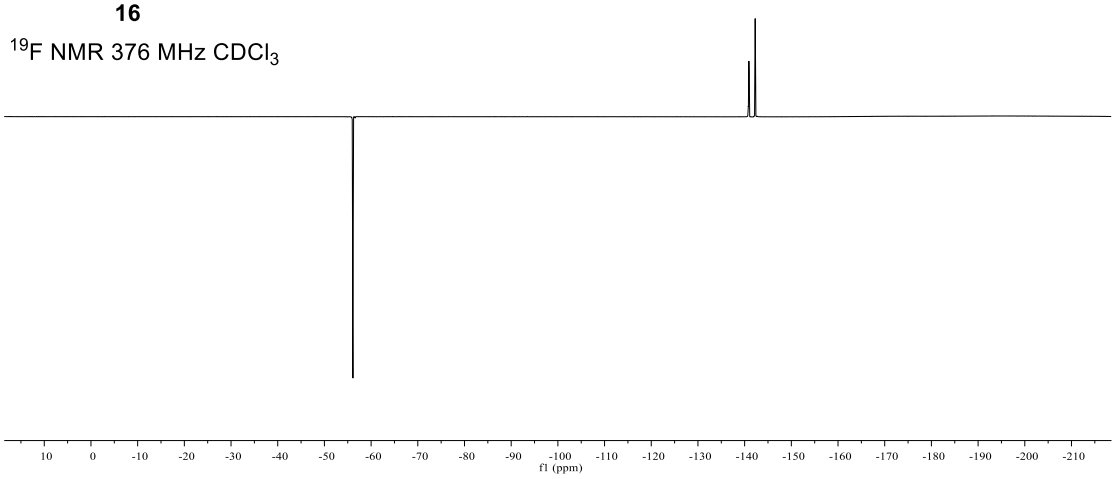
^{13}C NMR 150 MHz $CDCl_3$

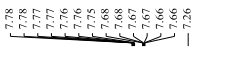


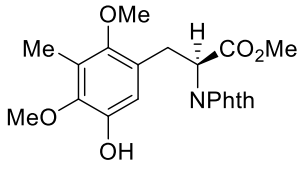


16

^{19}F NMR 376 MHz $CDCl_3$

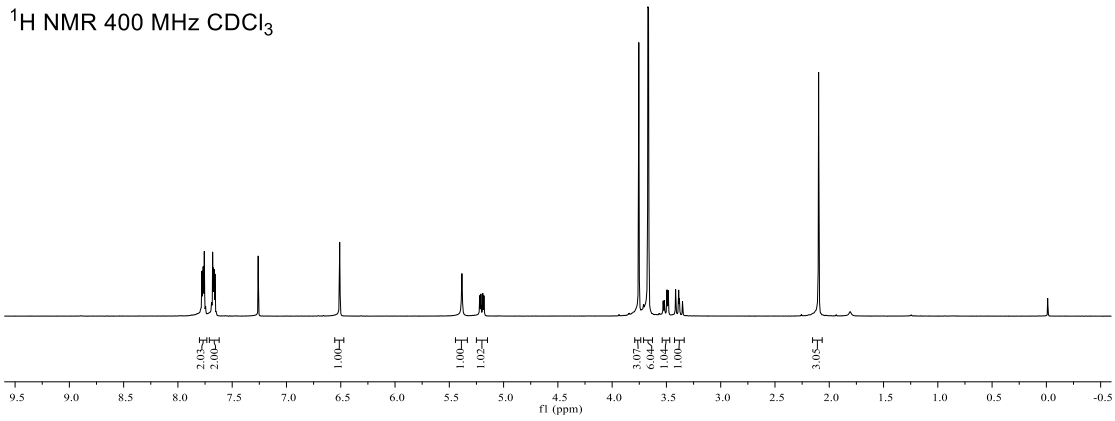


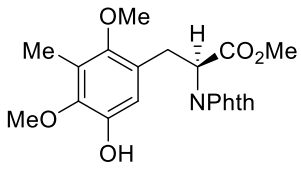




17

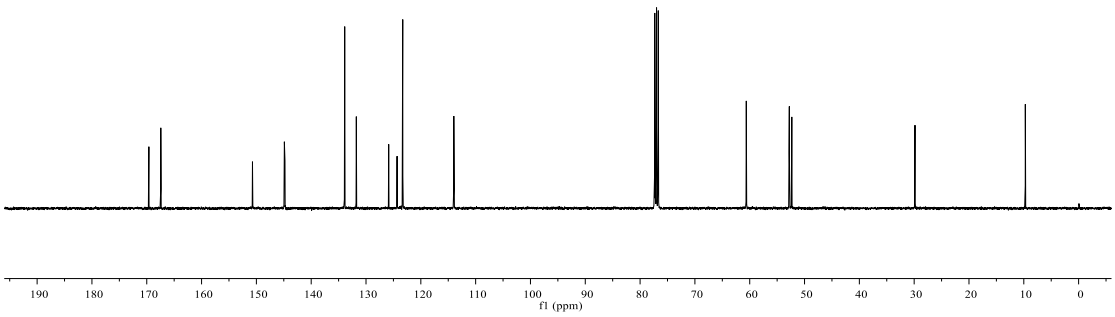
^{1}H NMR 400 MHz $CDCl_3$

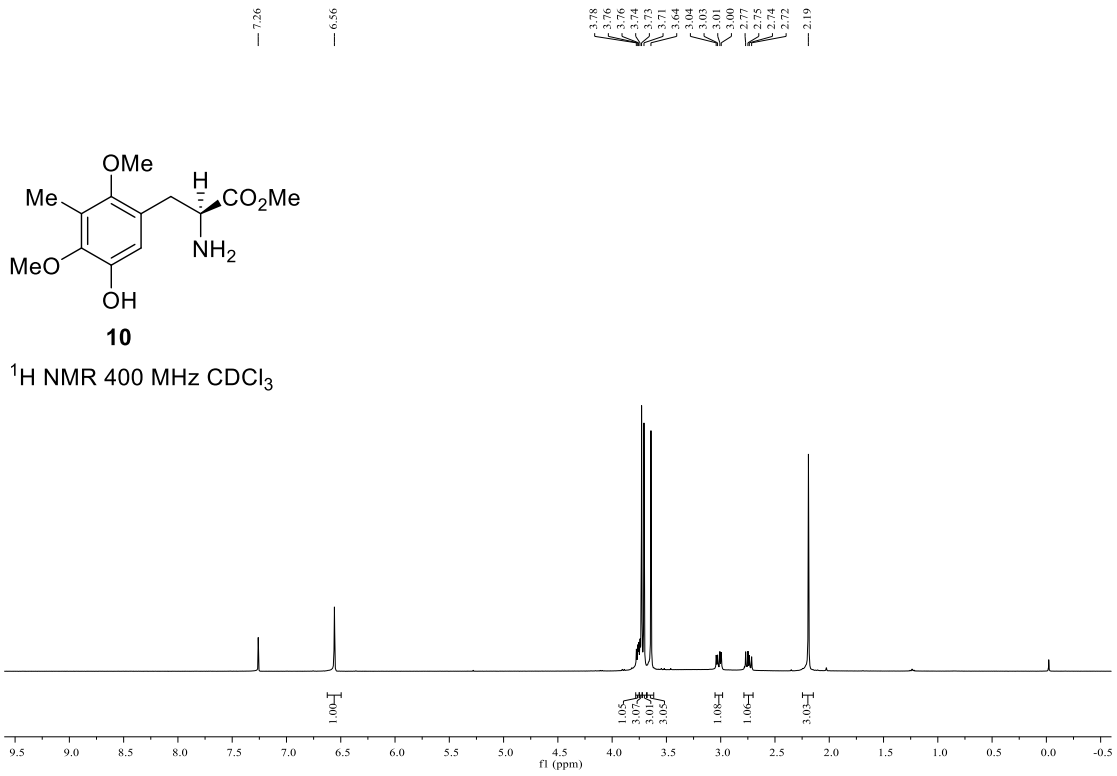




17

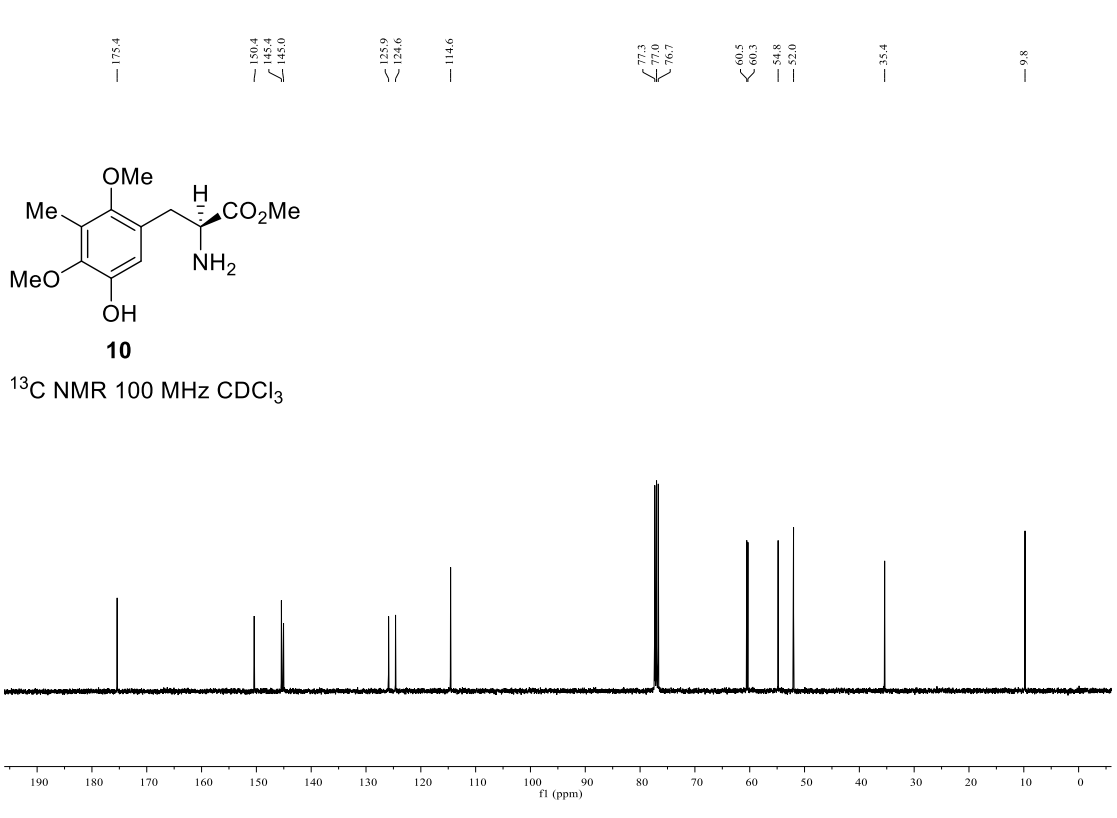
^{13}C NMR 100 MHz $CDCl_3$





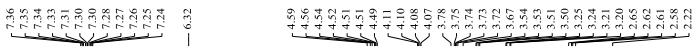
10

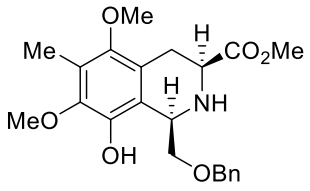
^{1}H NMR 400 MHz $CDCl_3$



10

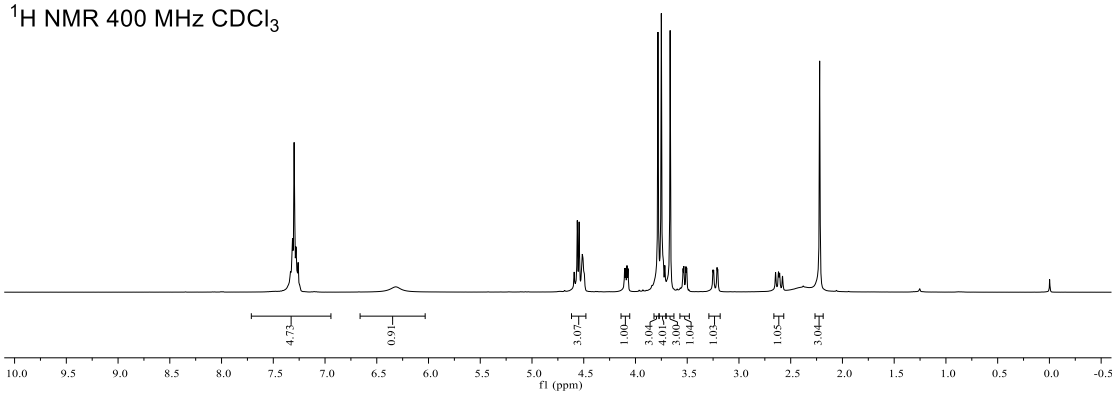
^{13}C NMR 100 MHz $CDCl_3$

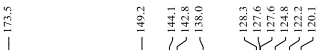


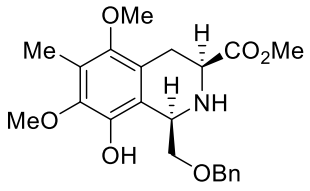


21

^{1}H NMR 400 MHz $CDCl_3$

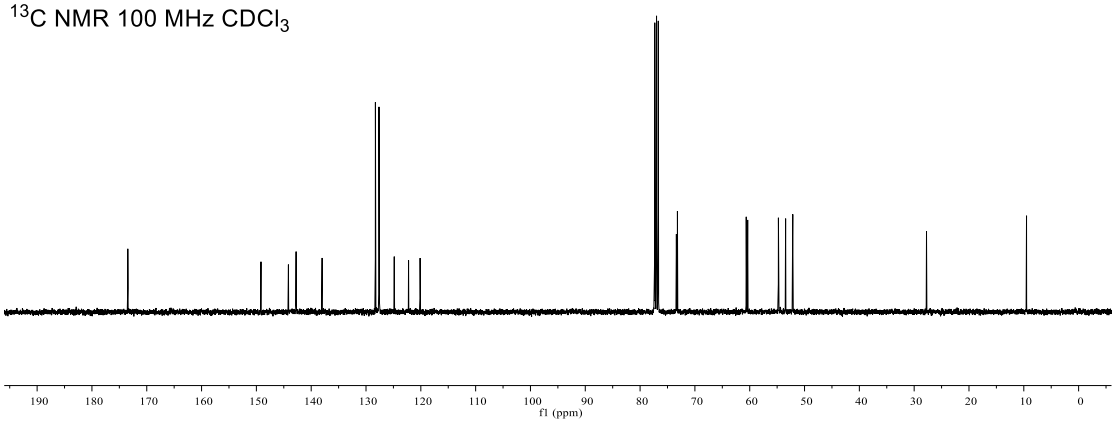






21

^{13}C NMR 100 MHz $CDCl_3$



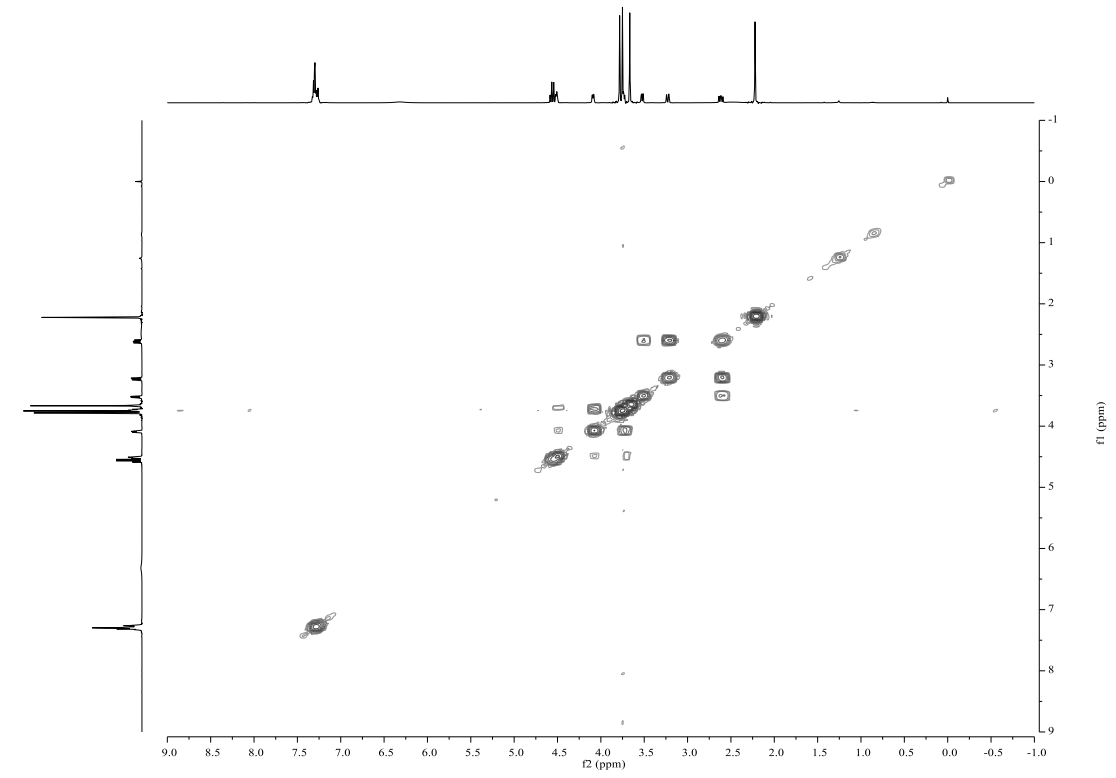


Figure S1. ^{1}H-^{1}H COSY spectrum of compound **21** recorded in $CDCl_3$.

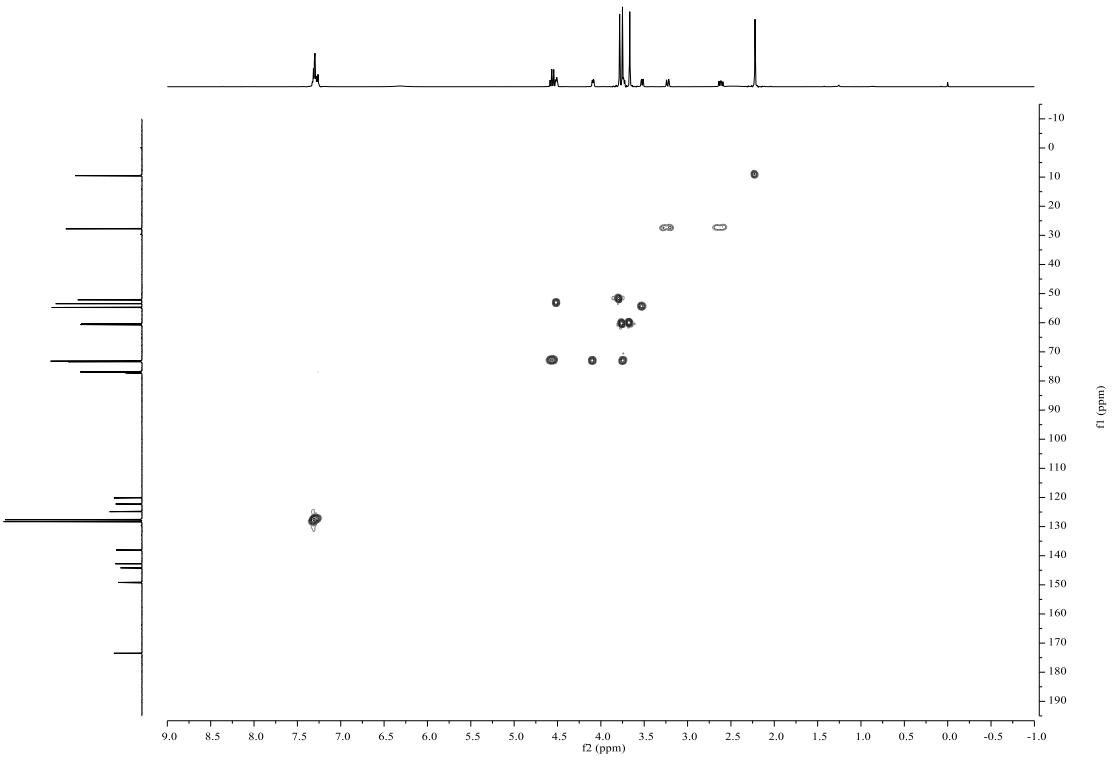


Figure S2. HSQC spectrum of compound **21** recorded in $CDCl_3$.

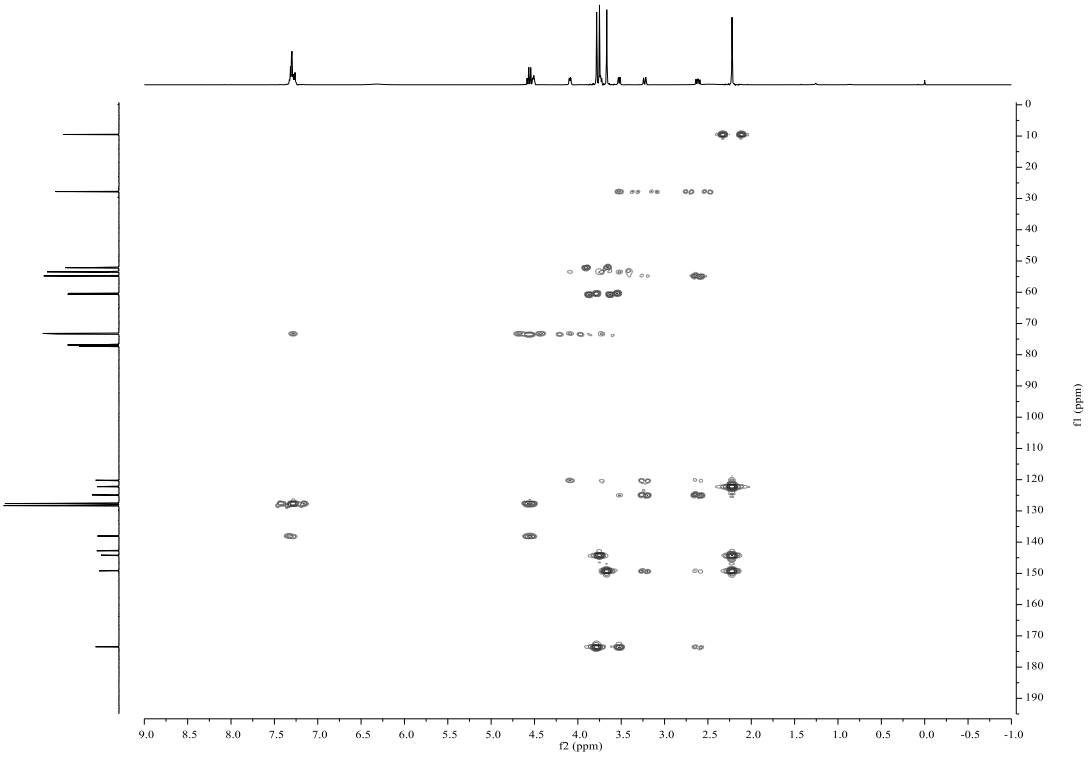


Figure S3. HMBC spectrum of compound **21** recorded in $CDCl_3$.

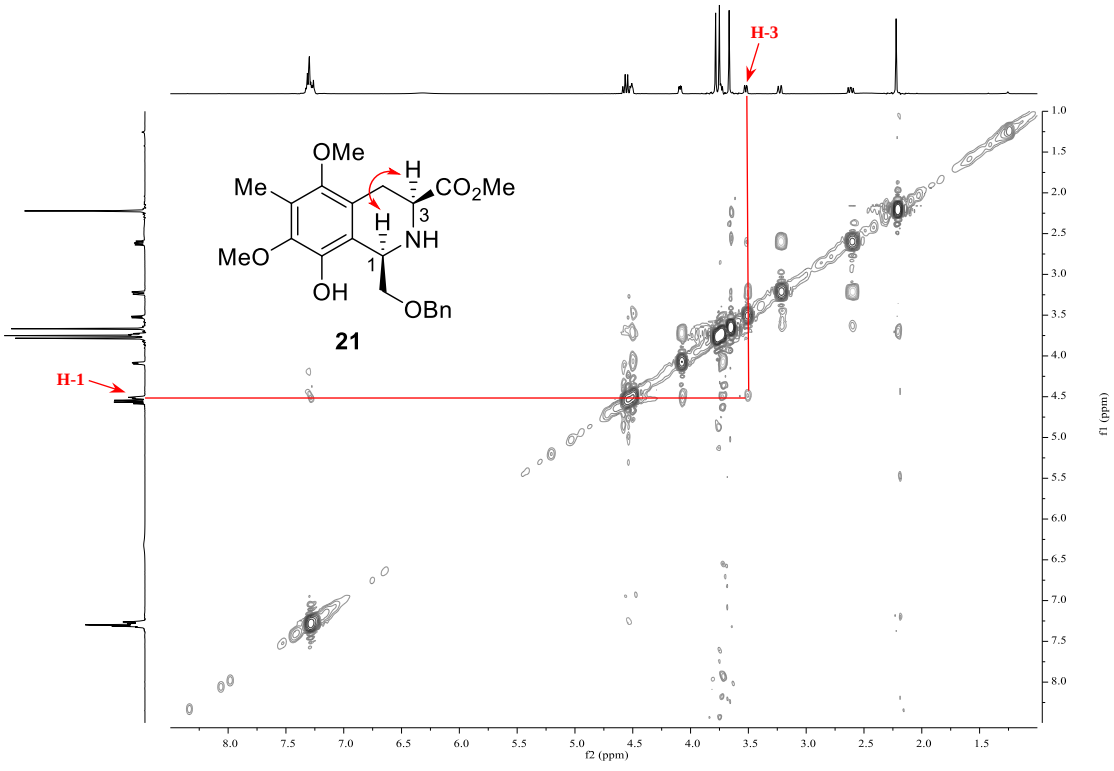
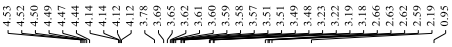
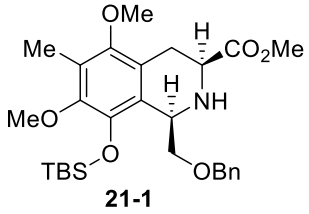


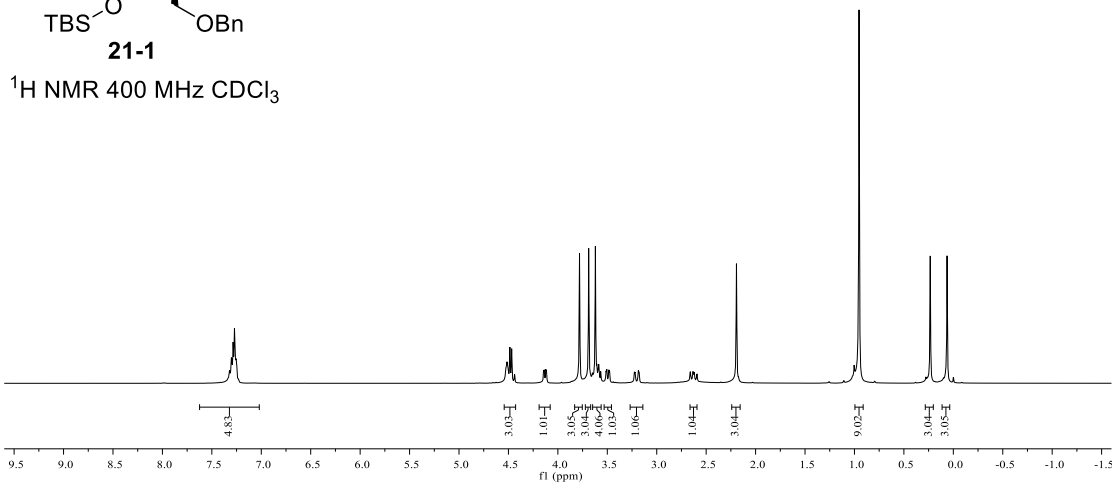
Figure S4. ROESY spectrum of compound **21** recorded in $CDCl_3$.

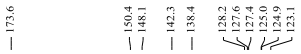


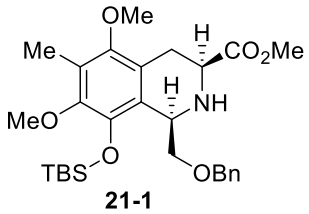


21-1

^{1}H NMR 400 MHz $CDCl_3$

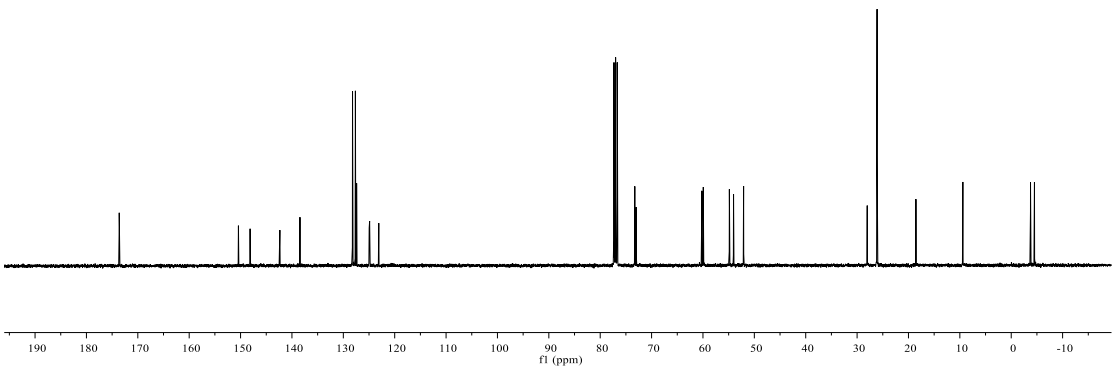


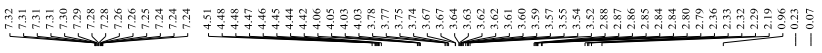


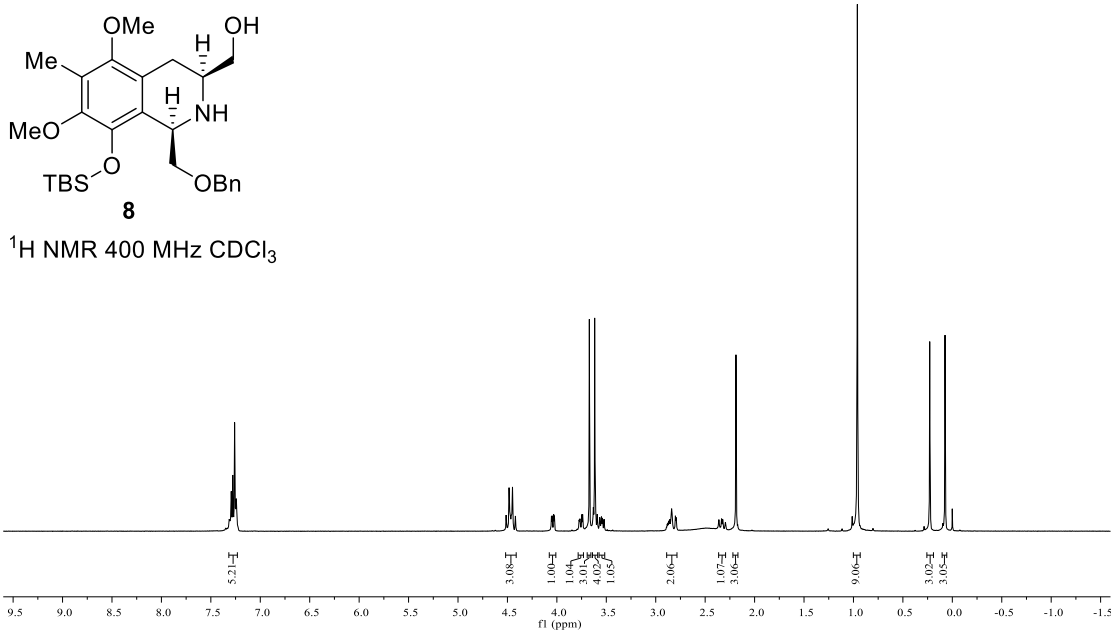


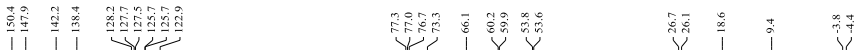
21-1

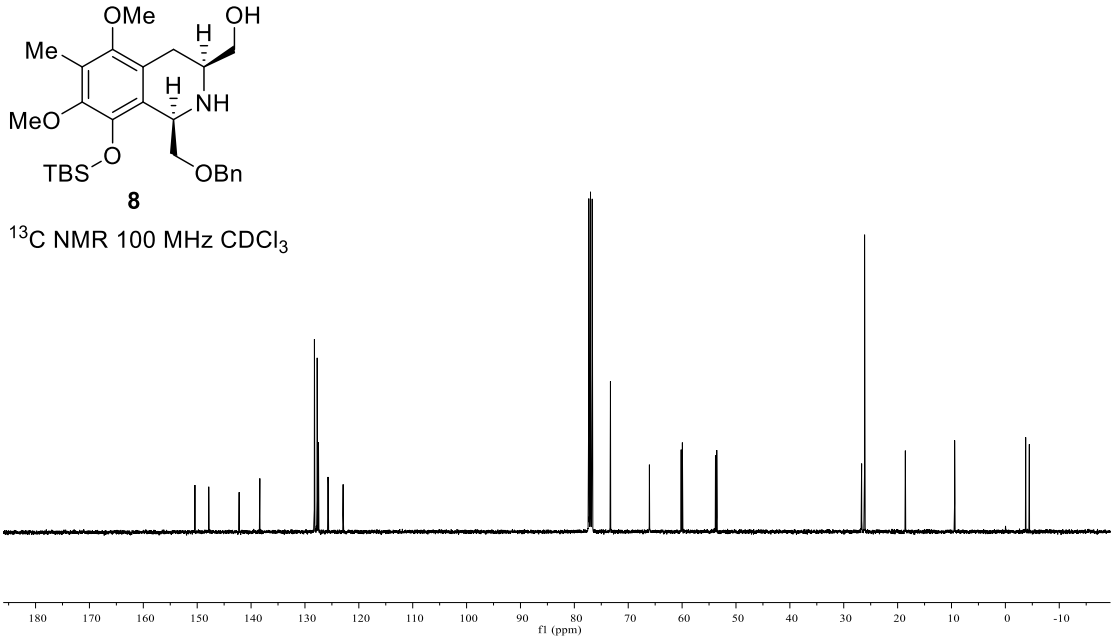
^{13}C NMR 100 MHz $CDCl_3$

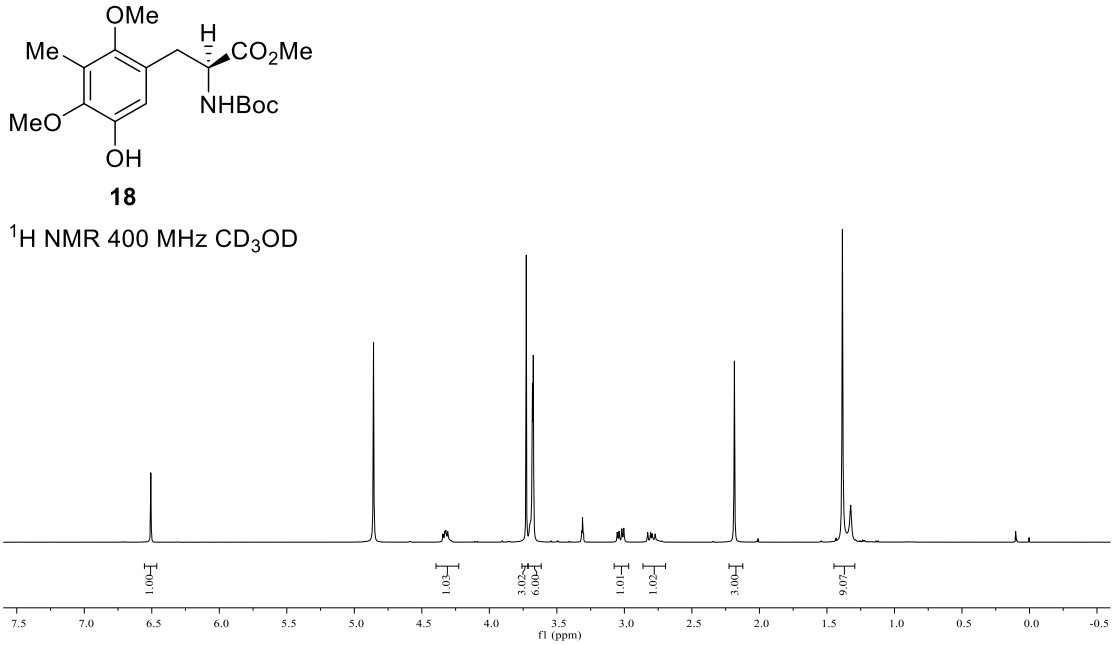


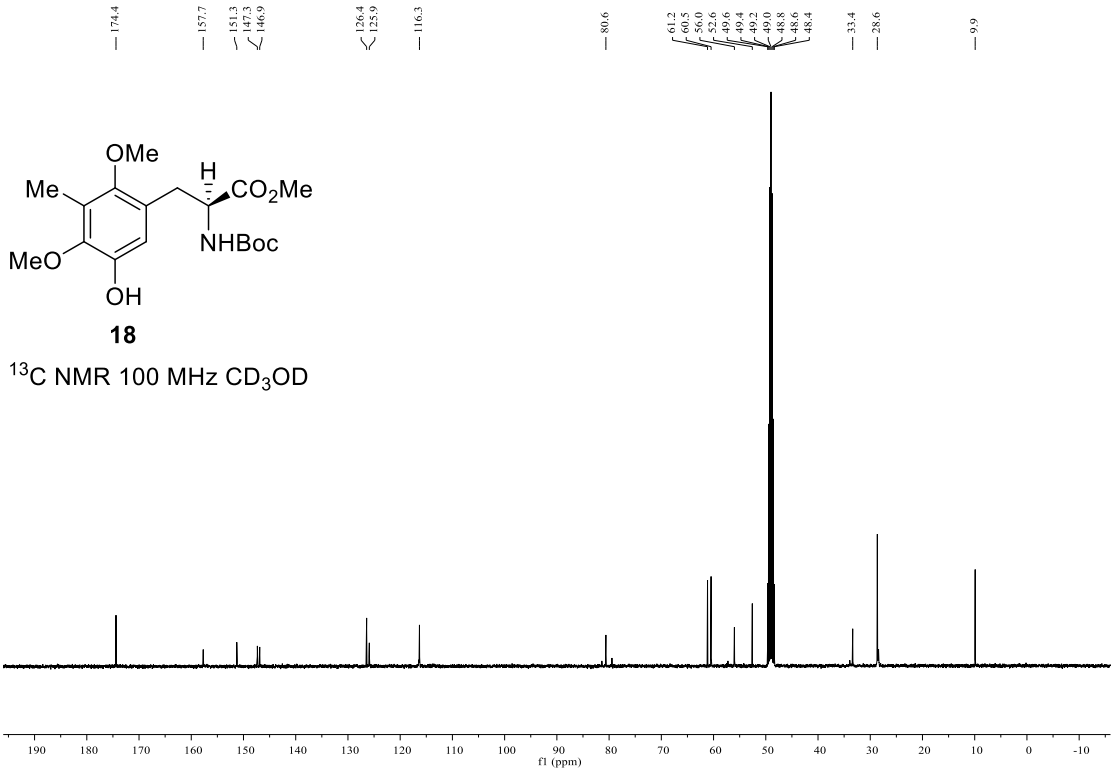


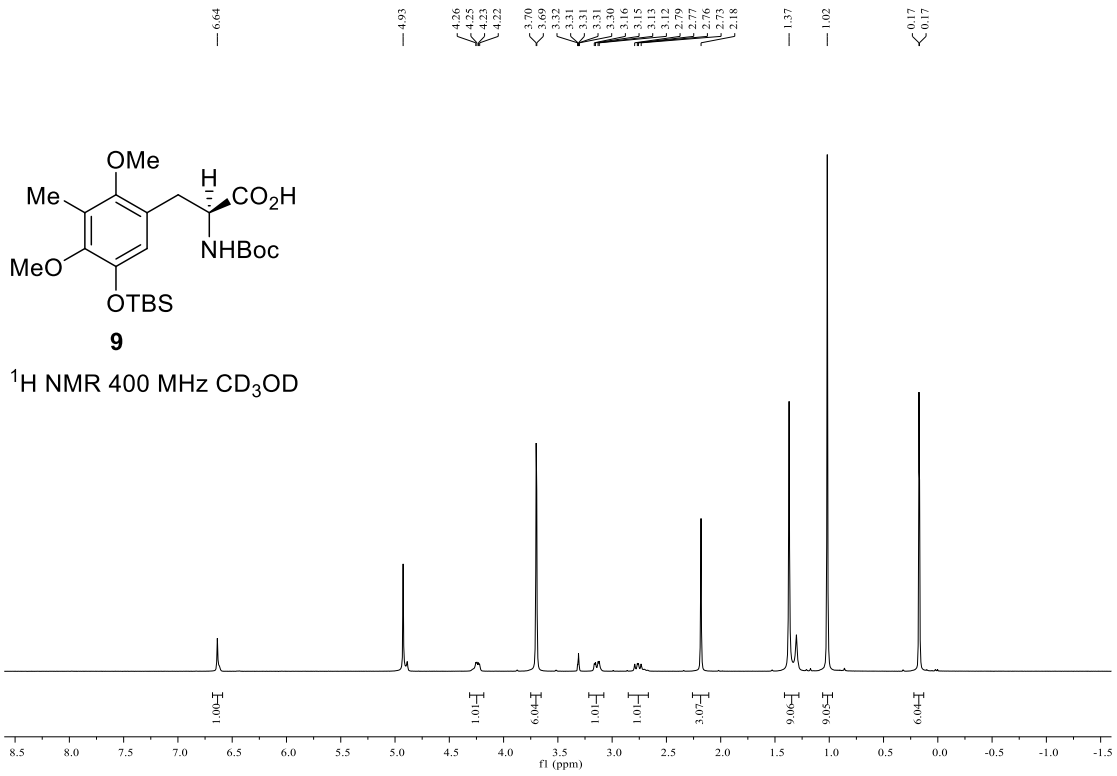

OMe
OH
H
Me
H
NH
MeO
O
TBS
OBn
8
1H NMR 400 MHz CDCl3
5.21
3.08
1.00
1.04
3.01
4.02
1.05
2.06
1.07
3.06
9.06
3.02
3.05
f1 (ppm)




OMe
OH
H
Me
H
NH
MeO
O
TBS
OBn
8
13C NMR 100 MHz CDCl3
f1 (ppm)

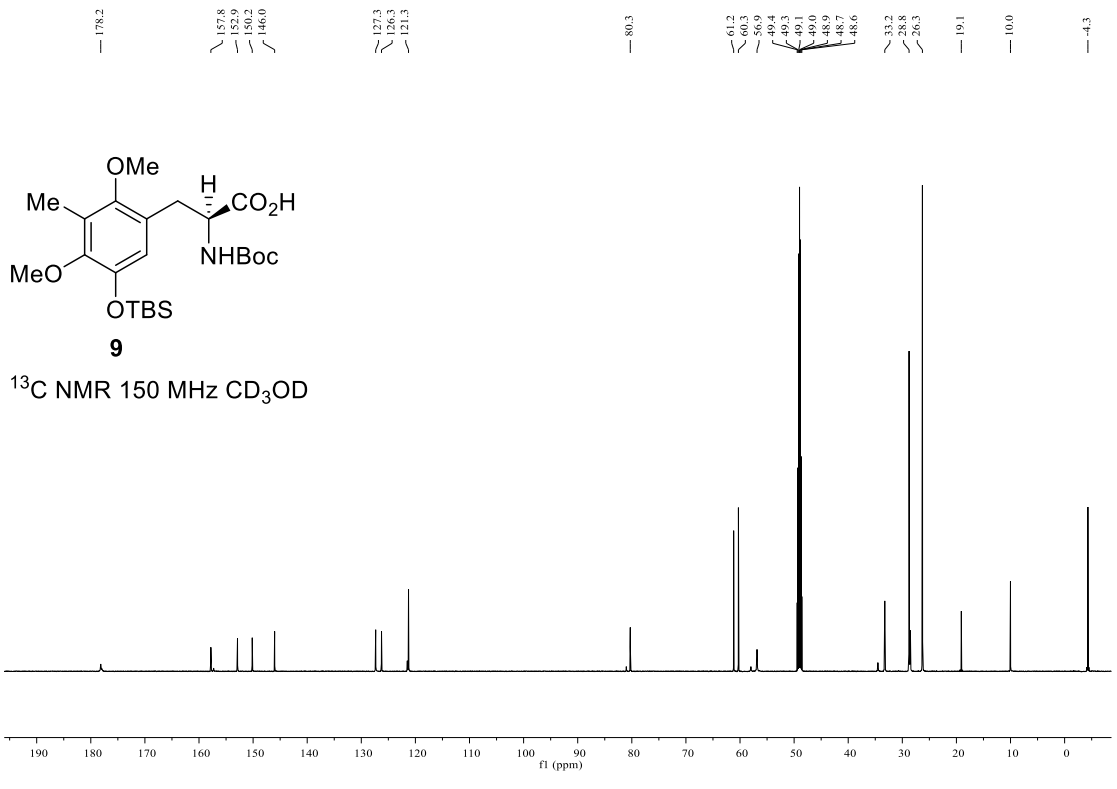

6.51
4.86
4.34
4.33
4.32
4.31
3.73
3.68
3.67
3.32
3.31
3.31
3.31
3.30
3.05
3.04
3.02
3.00
2.83
2.81
2.79
2.77
2.19
1.39
OMe
Me
MeO
OH
H
CO2Me
NHBoc
18
1H NMR 400 MHz CD3OD
1.00
1.03
3.02
6.00
1.01
1.02
3.00
9.07
f1 (ppm)


174.4
157.7
151.3
147.3
146.9
126.4
125.9
116.3
80.6
61.2
60.5
56.0
52.6
49.6
49.4
49.2
49.0
48.8
48.6
48.4
33.4
28.6
9.9
OMe
Me
MeO
OH
H
CO2Me
NHBoc
18
13C NMR 100 MHz CD3OD
f1 (ppm)



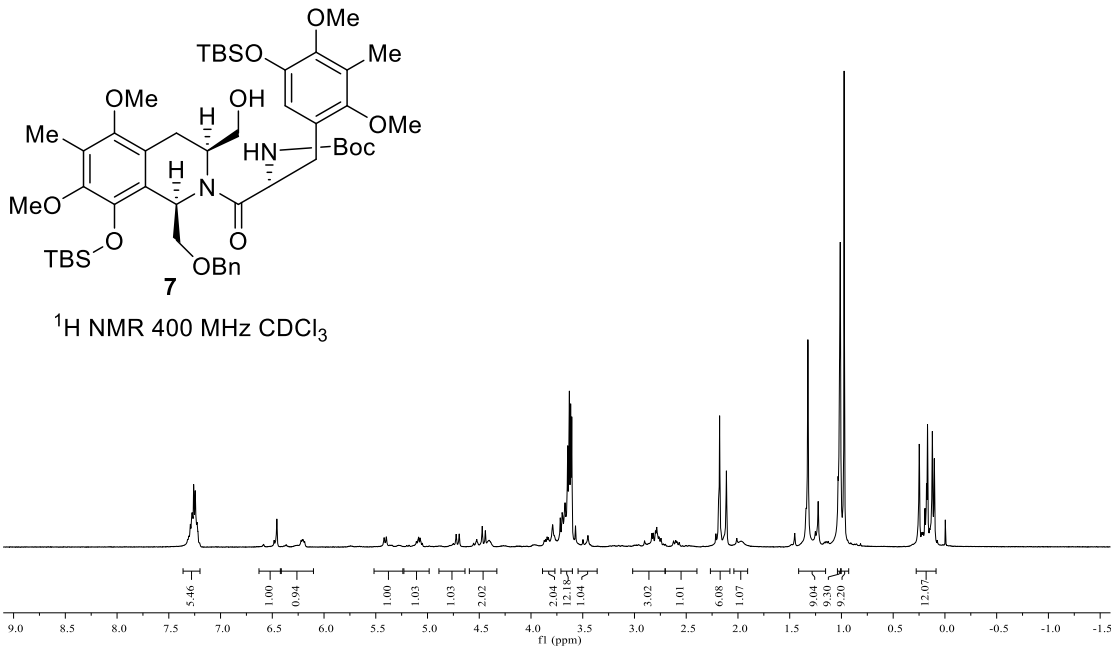
9

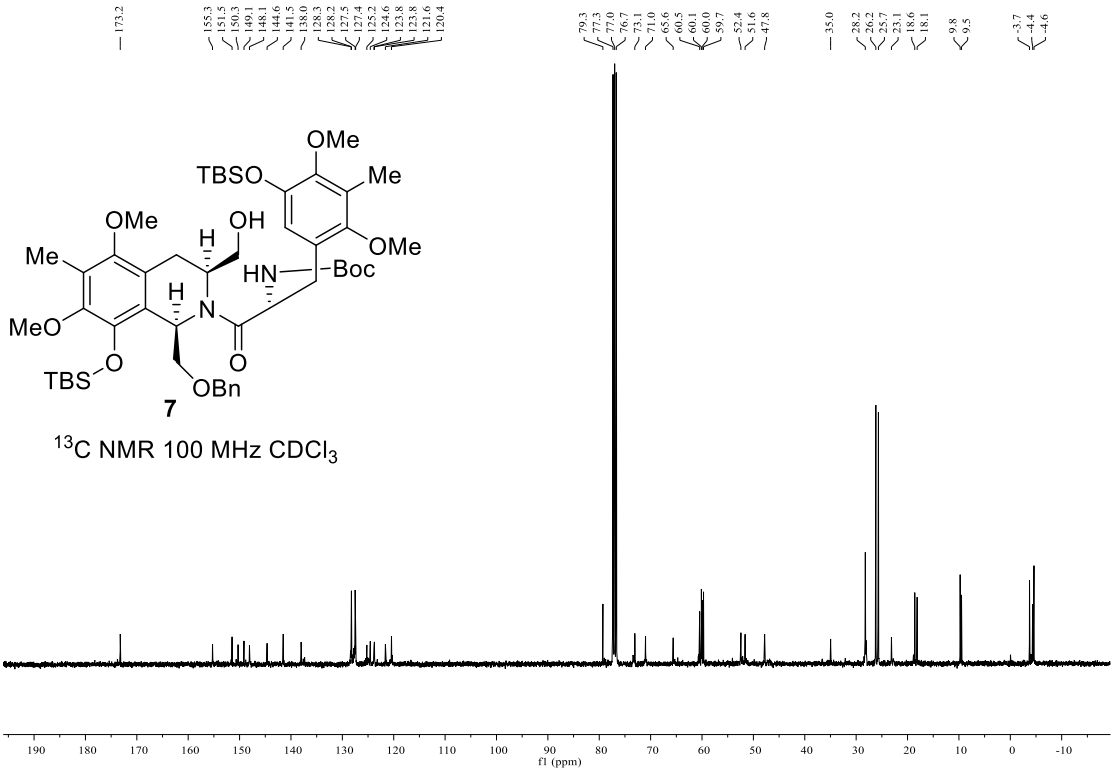
^{1}H NMR 400 MHz CD_3OD

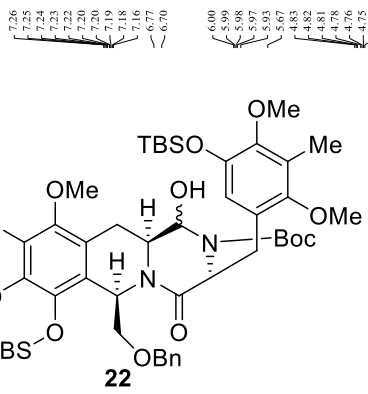


9

^{13}C NMR 150 MHz CD_3OD

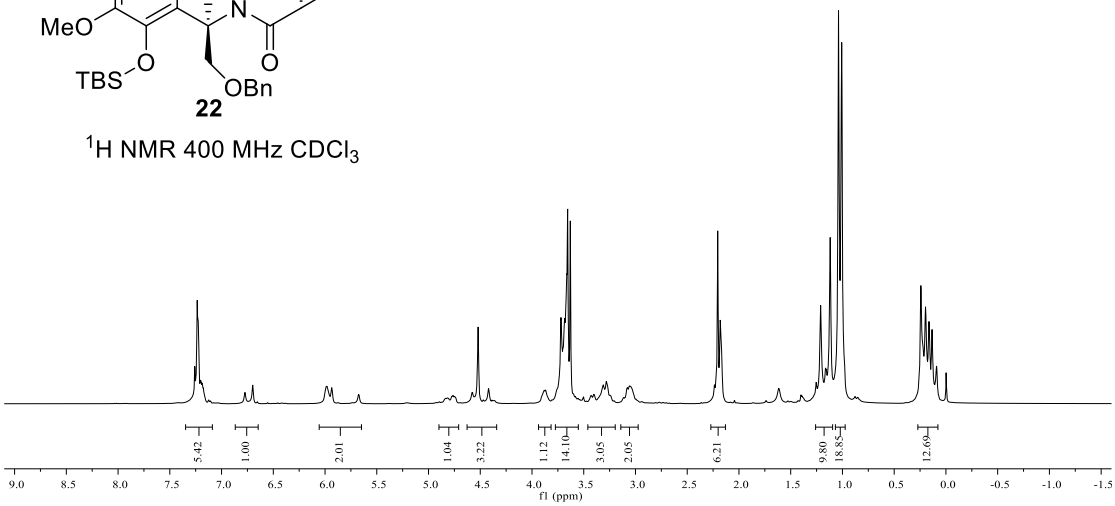

OMe
TBSO
Me
OMe
OH
H
HN
Boc
OMe
Me
H
N
MeO
O
TBS
O
OBn
7
1H NMR 400 MHz CDCl3
f1 (ppm)

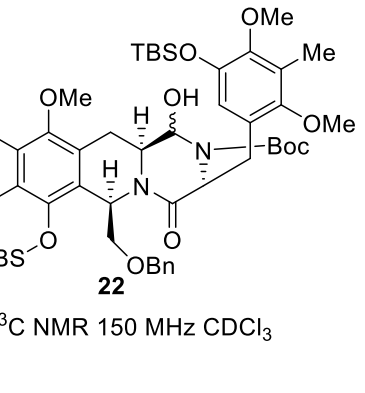

OMe
TBSO
Me
OMe
OH
H
HN
Boc
OMe
Me
H
N
MeO
O
TBS
O
OBn
7
13C NMR 100 MHz CDCl3
f1 (ppm)



22

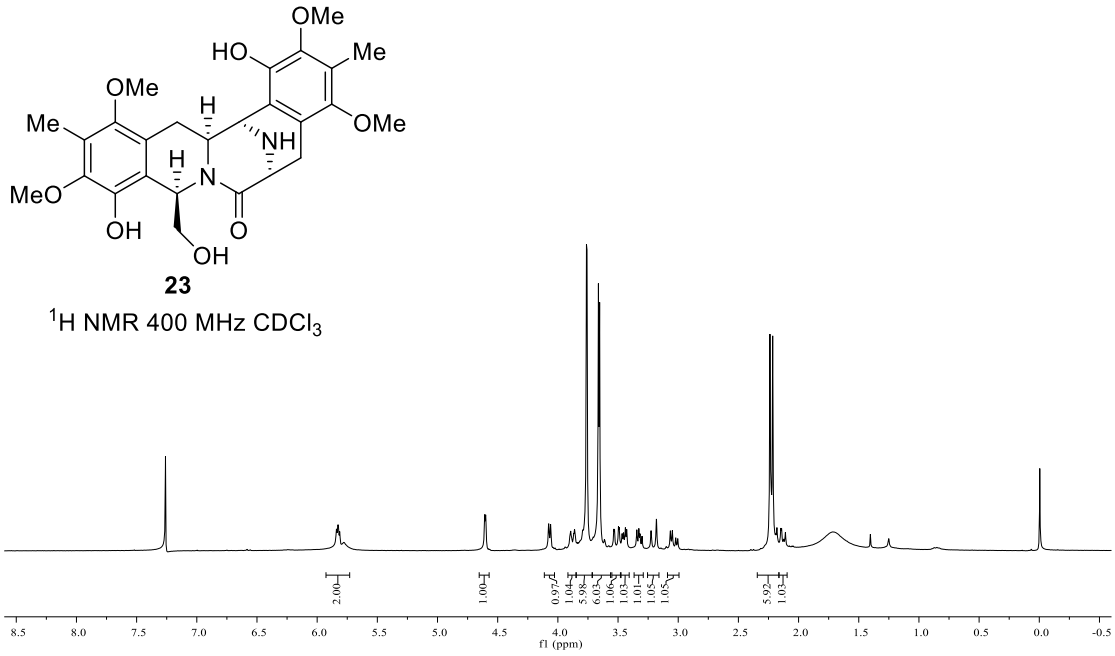
^{1}H NMR 400 MHz $CDCl_3$

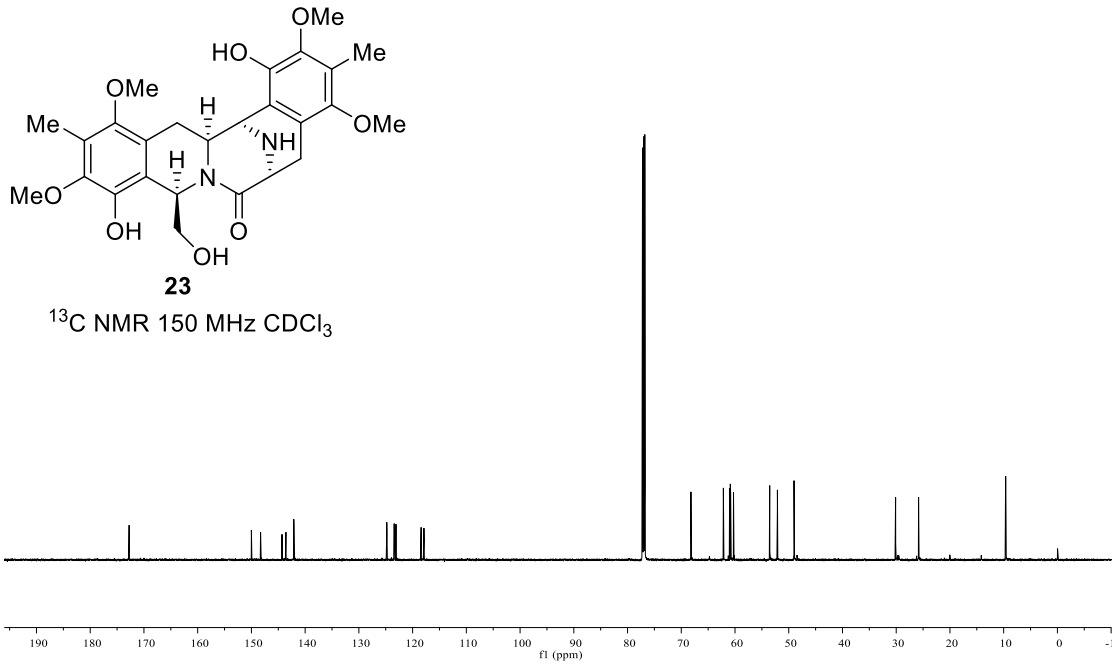


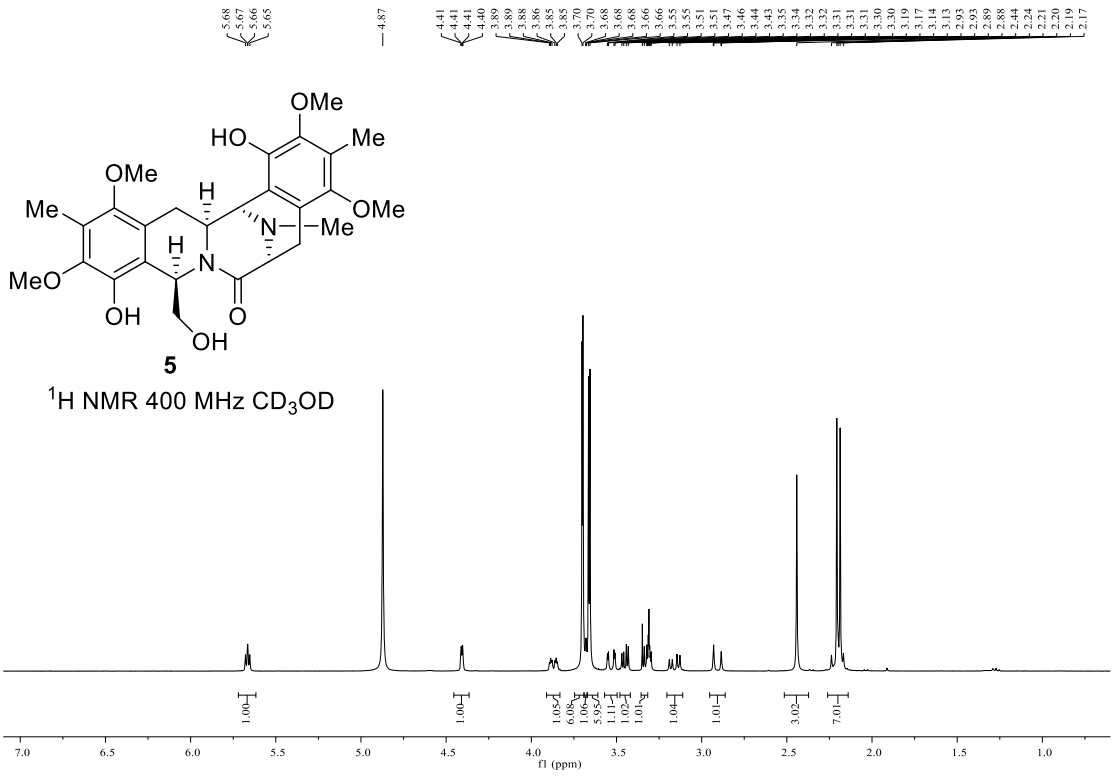


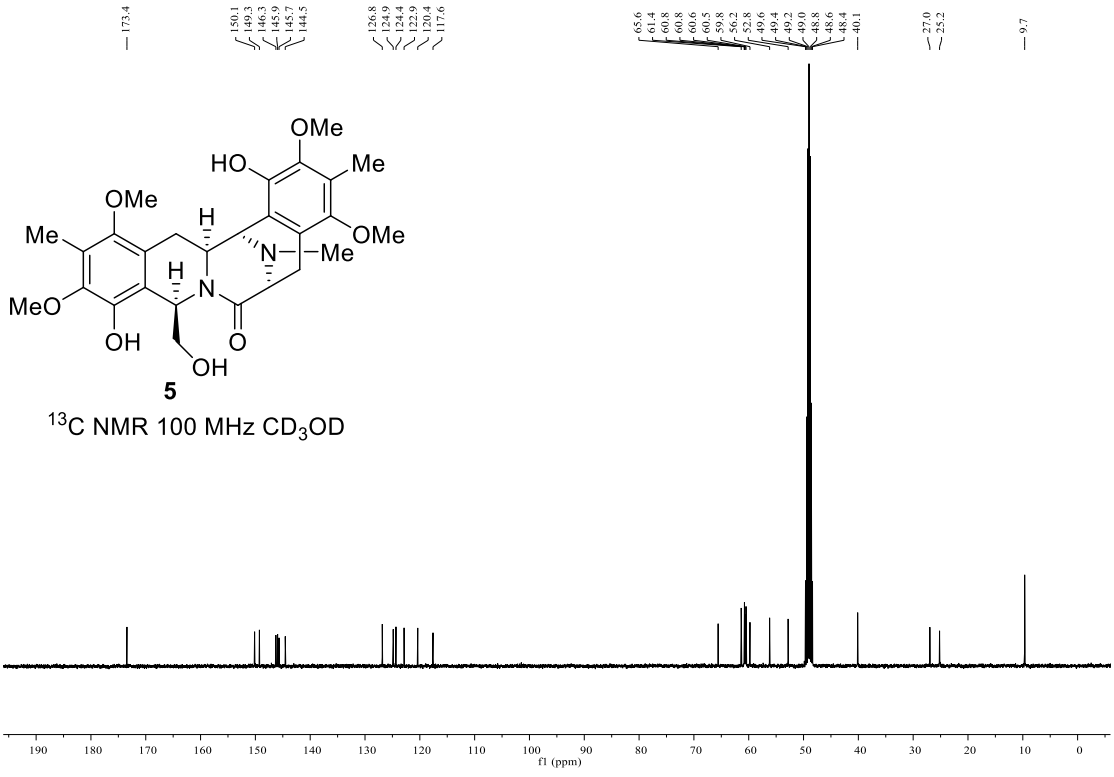
22

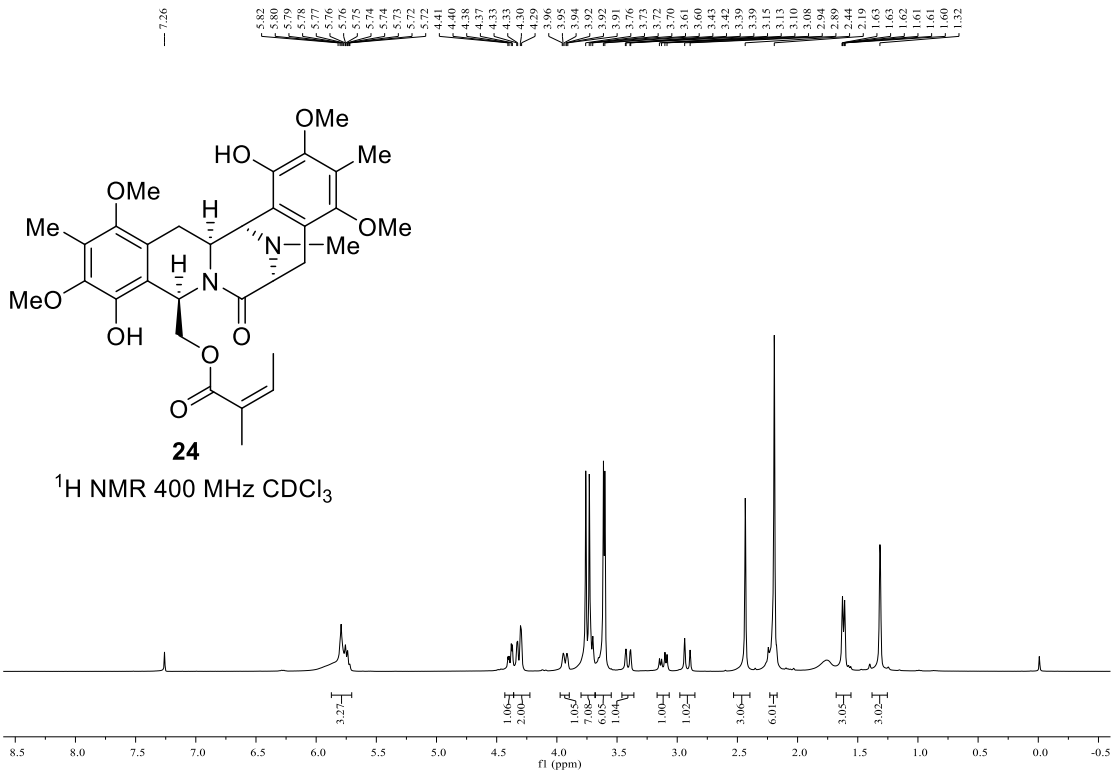
^{13}C NMR 150 MHz $CDCl_3$

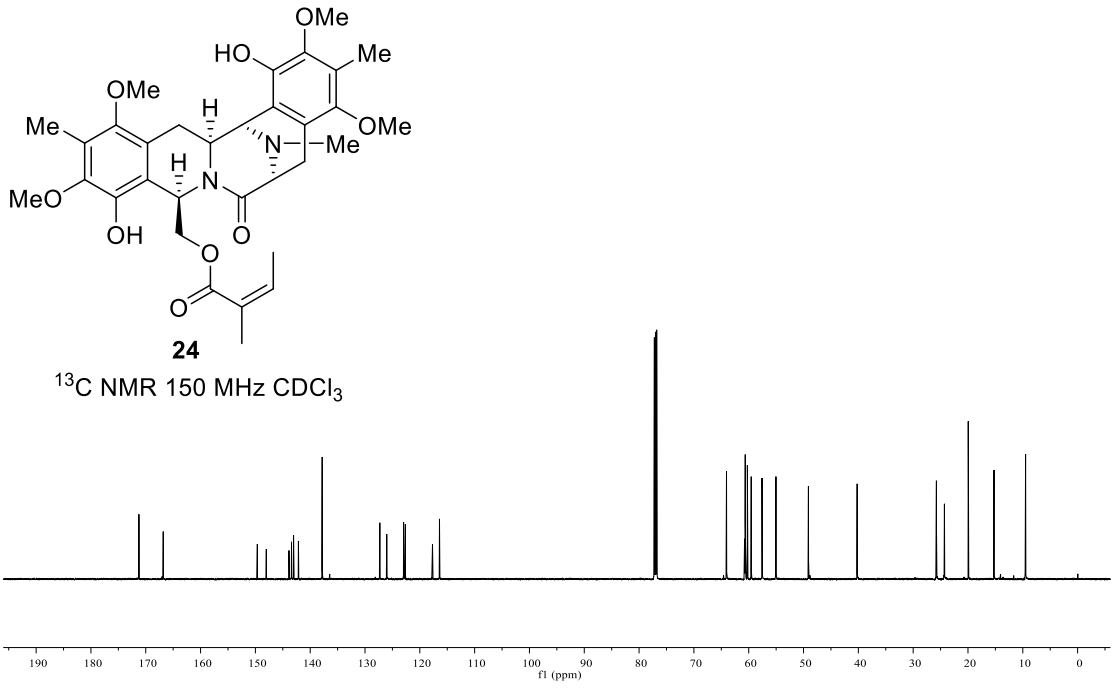

OMe
HO
Me
OMe
Me
H
OMe
NH
H
N
MeO
OH
O
OH
23
1H NMR 400 MHz CDCl3
f1 (ppm)

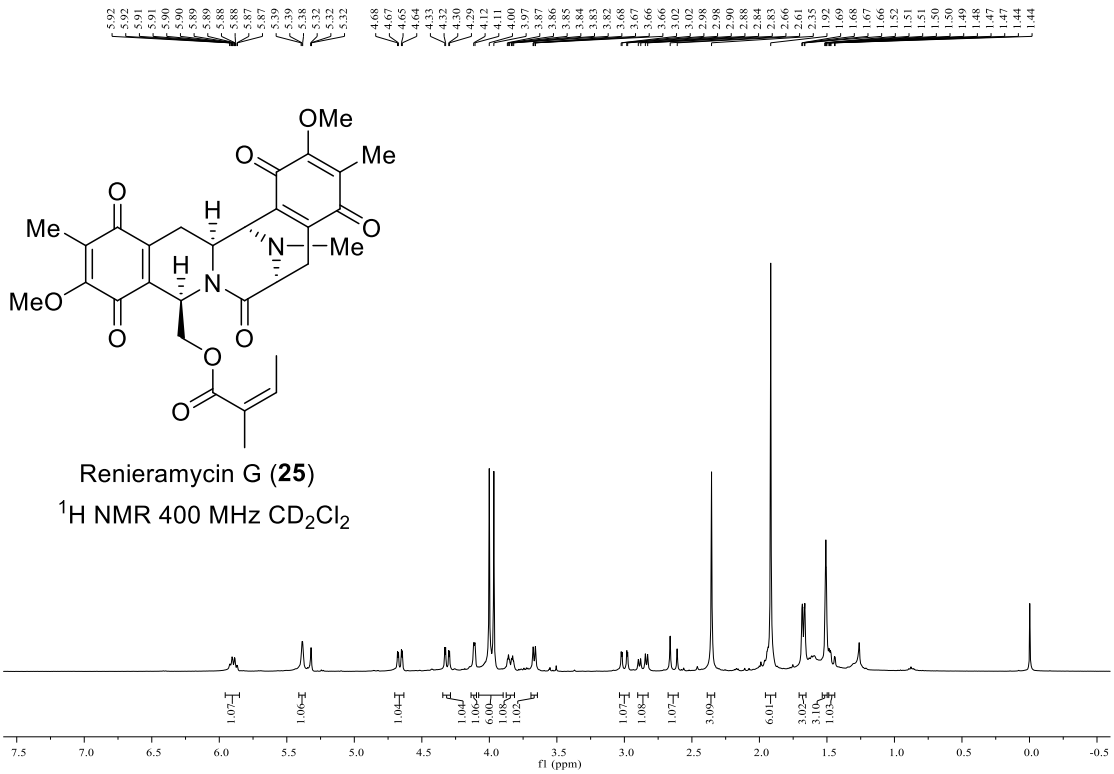

OMe
HO
Me
OMe
Me
H
OMe
NH
H
N
MeO
OH
O
OH
23
13C NMR 150 MHz CDCl3
f1 (ppm)

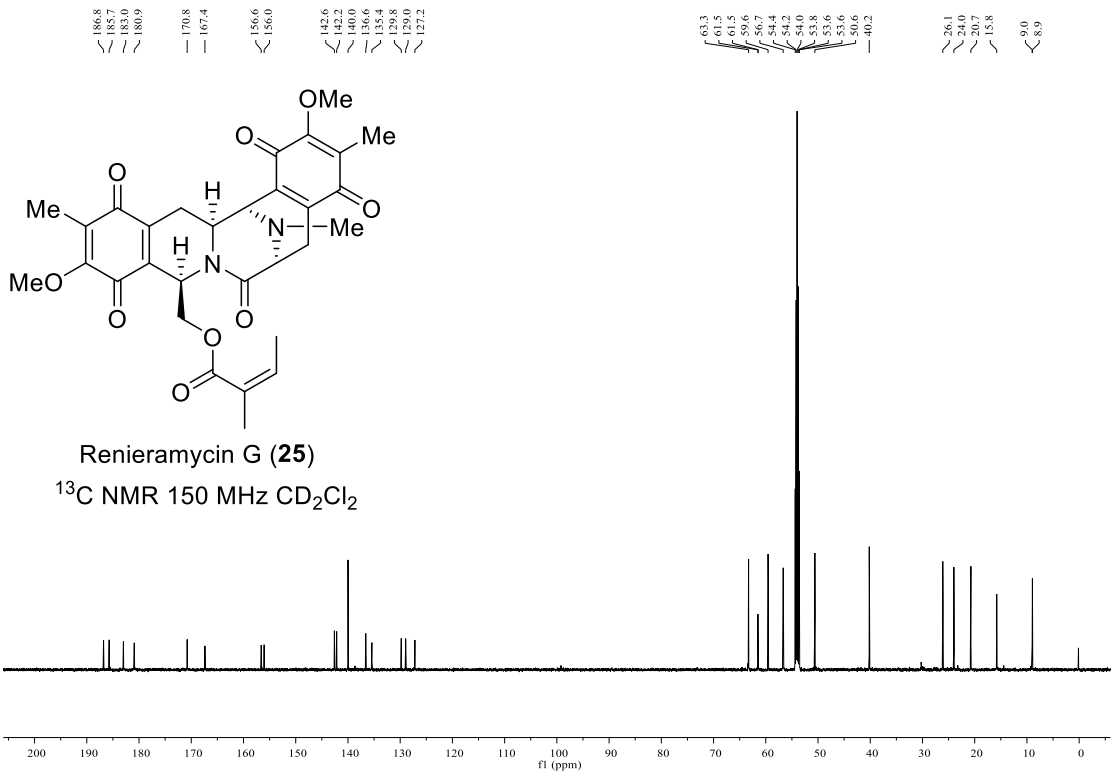

OMe
HO
Me
OMe
Me
H
OMe
N
Me
H
N
MeO
OH
O
OH
5
1H NMR 400 MHz CD3OD
f1 (ppm)

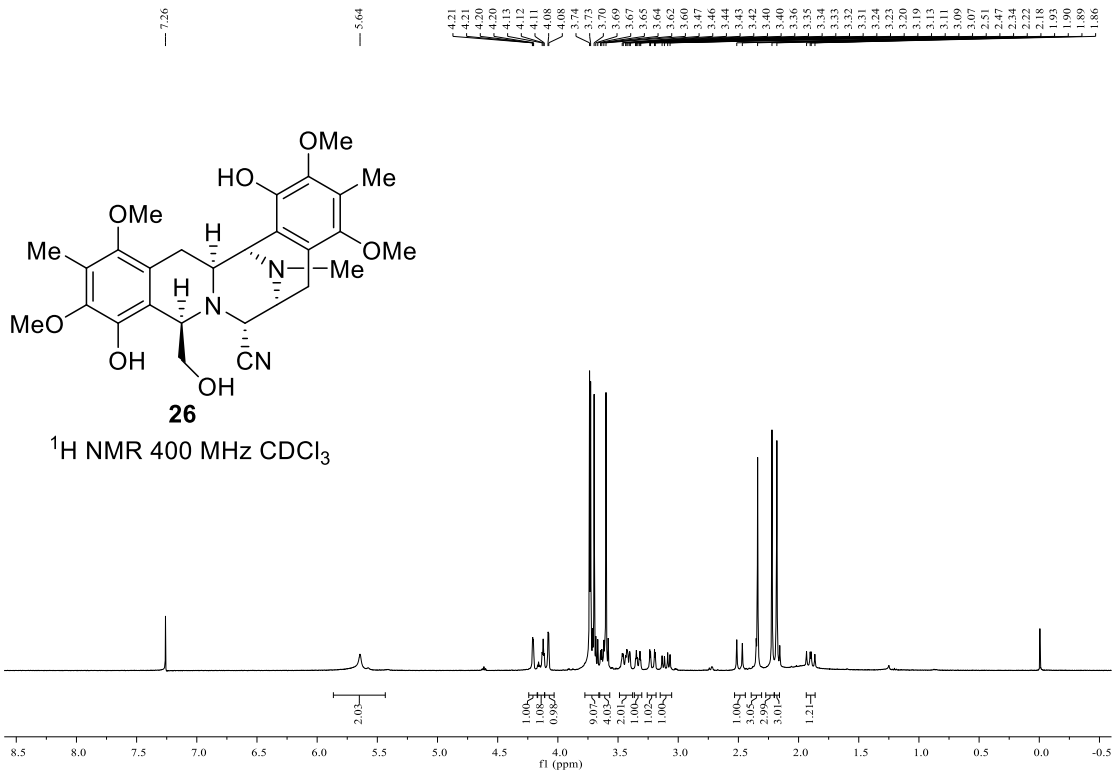

OMe
HO
Me
OMe
Me
H
OMe
N
Me
H
N
MeO
OH
O
OH
5
13C NMR 100 MHz CD3OD
f1 (ppm)

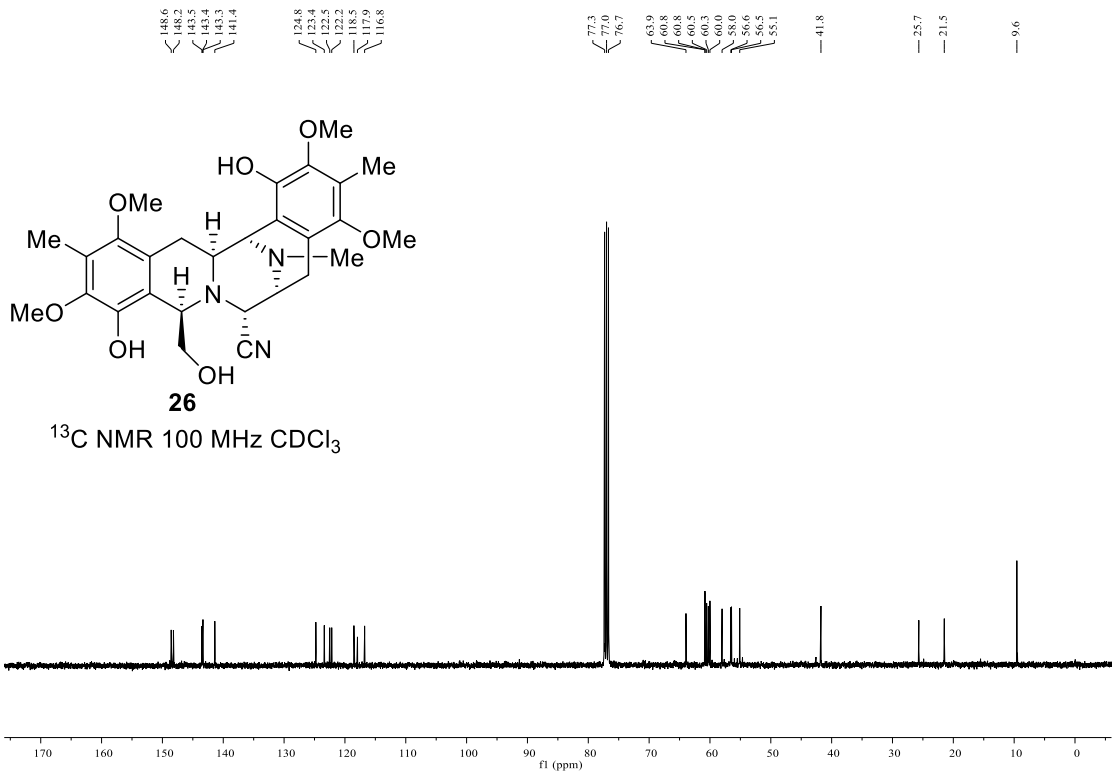

OMe
HO
Me
OMe
Me
OMe
H
N
Me
H
N
MeO
OH
O
O
O
24
1H NMR 400 MHz CDCl3
f1 (ppm)

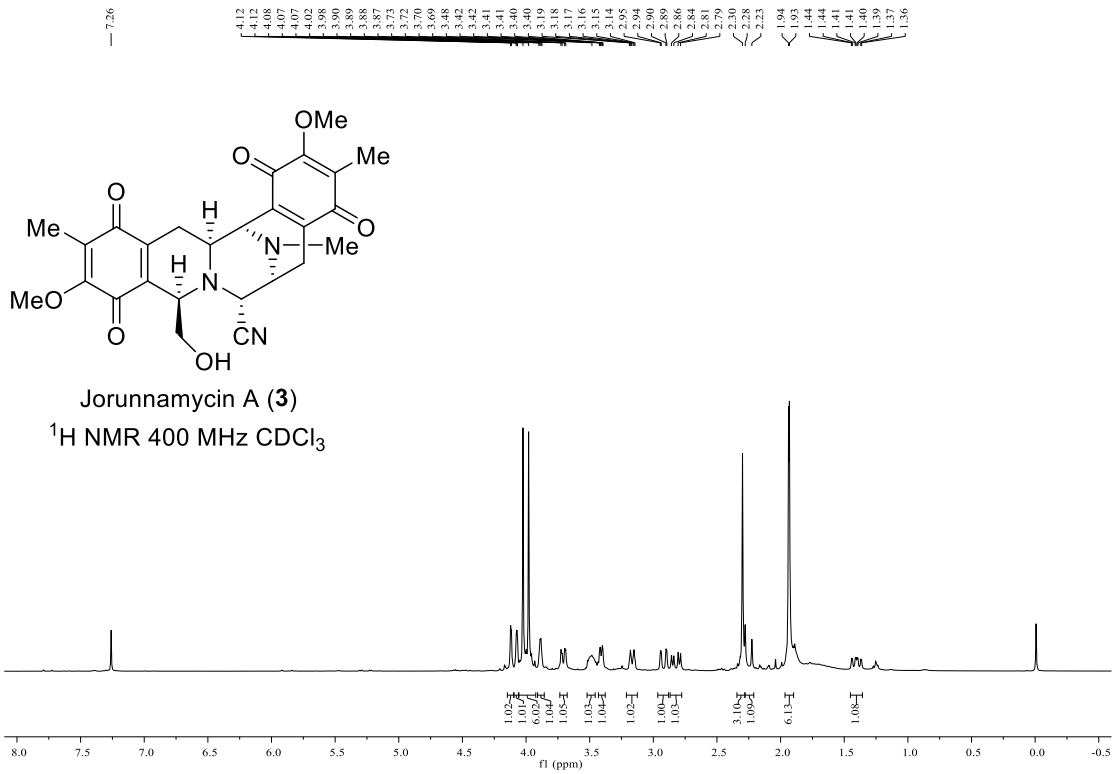

OMe
HO
Me
OMe
Me
OMe
H
N
Me
H
N
MeO
OH
O
O
O
24
13C NMR 150 MHz CDCl3
f1 (ppm)

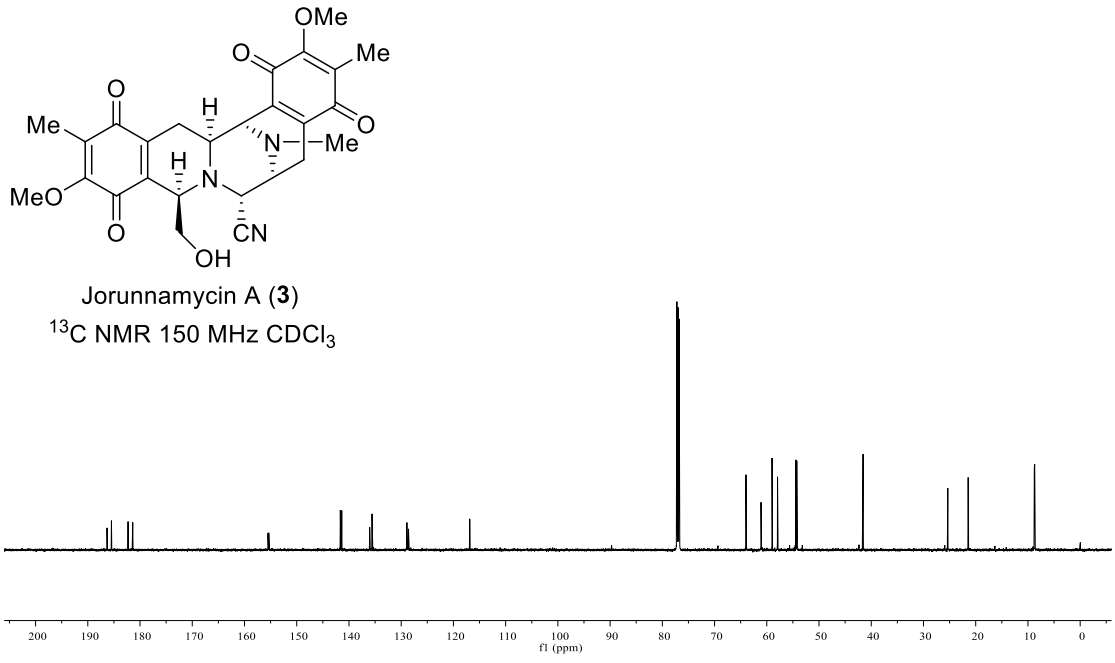

OMe
Me
O
H
N
Me
MeO
Renieramycin G (25)
1H NMR 400 MHz CD2Cl2
f1 (ppm)

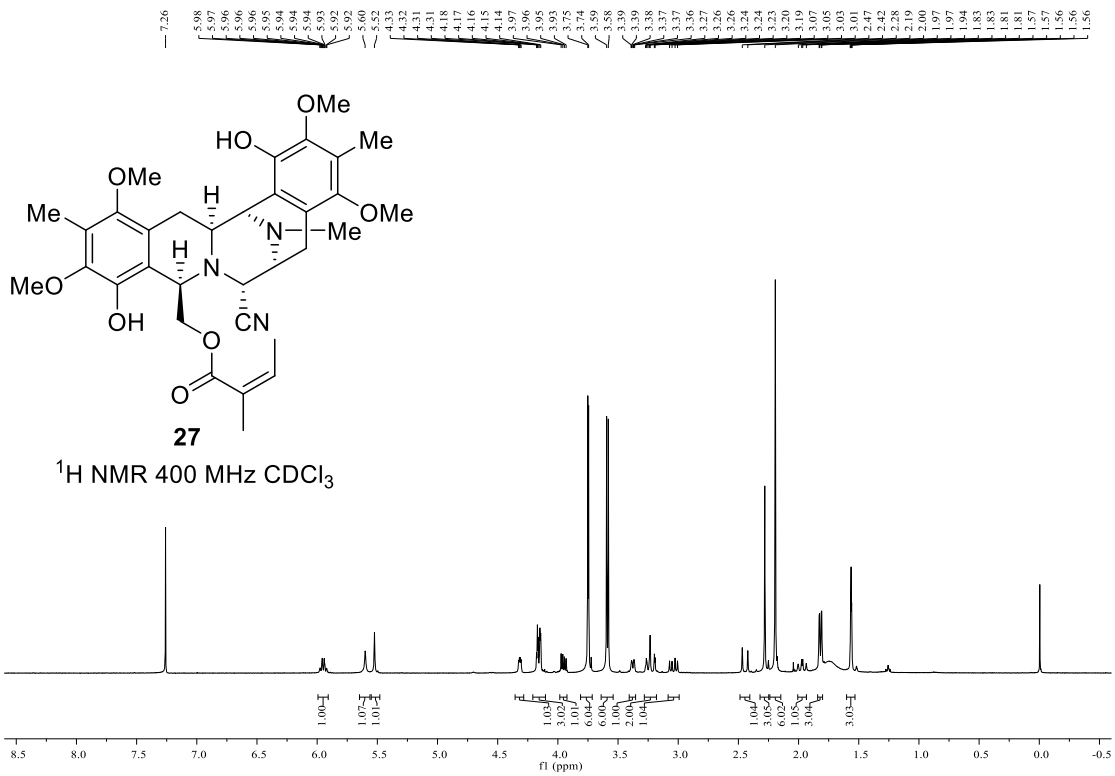

OMe
Me
O
H
N
Me
MeO
Renieramycin G (25)
13C NMR 150 MHz CD2Cl2
f1 (ppm)

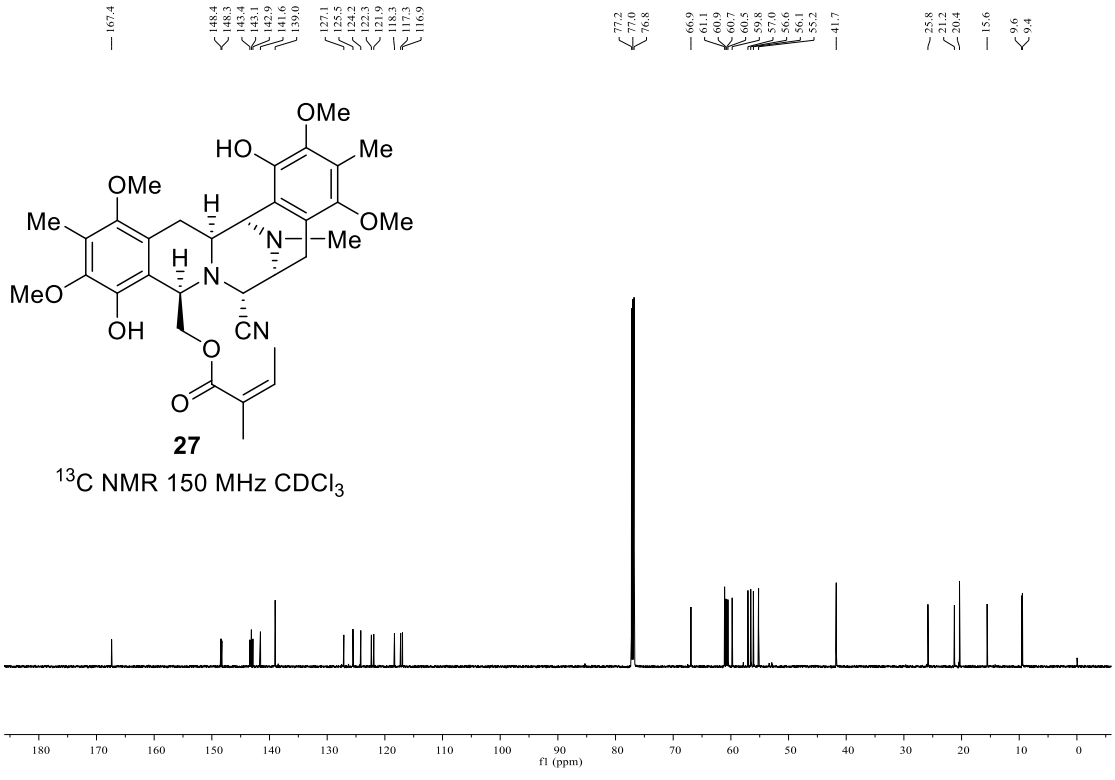

OMe
HO
Me
OMe
Me
H
OMe
N
Me
H
N
MeO
OH
CN
OH
26
1H NMR 400 MHz CDCl3
f1 (ppm)

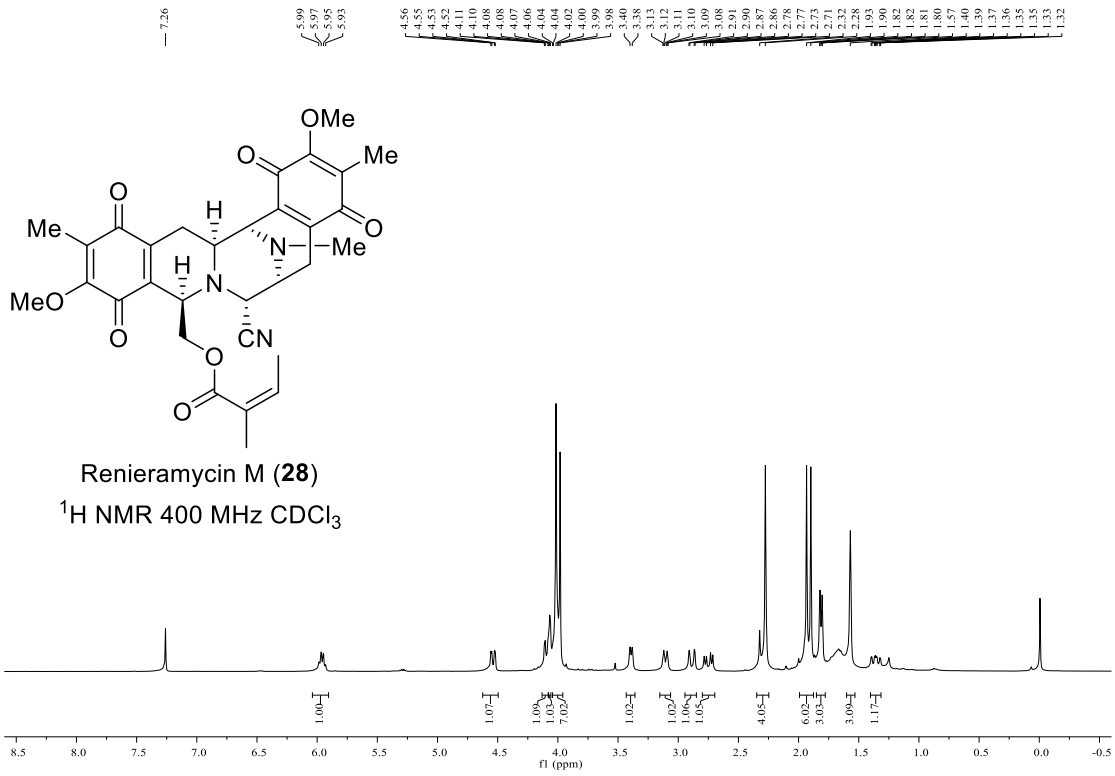

OMe
HO
Me
OMe
Me
H
OMe
N
Me
H
N
MeO
OH
CN
OH
26
13C NMR 100 MHz CDCl3
f1 (ppm)

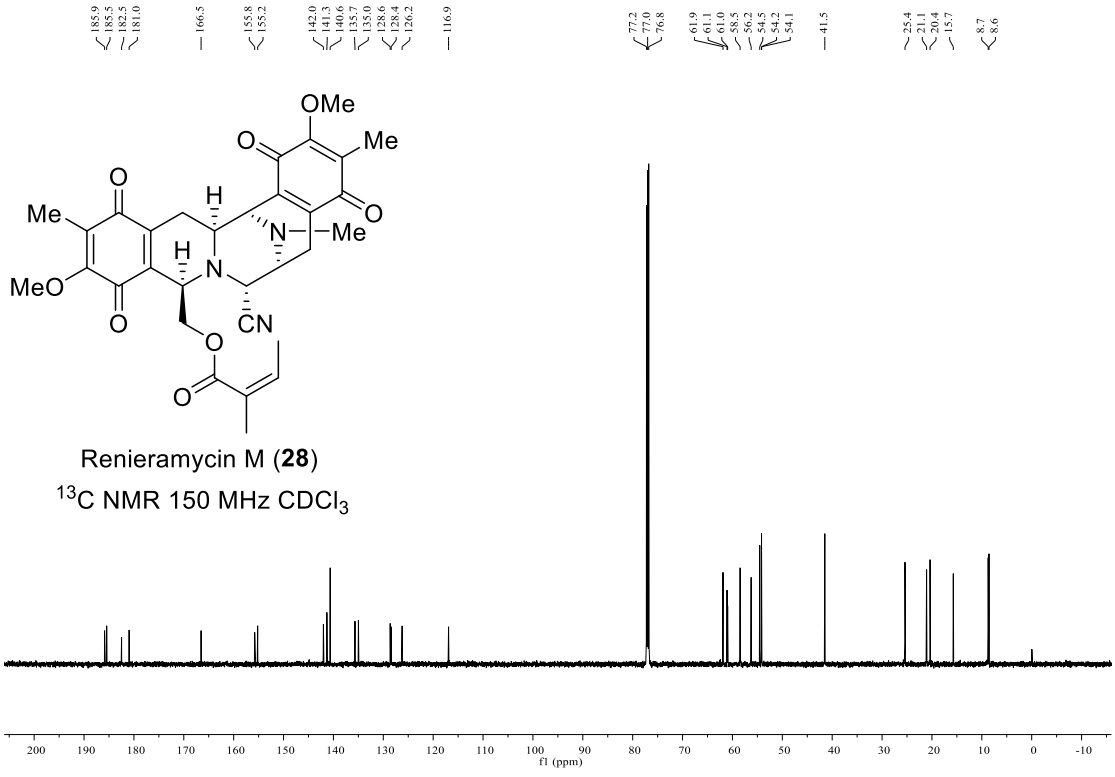

OMe
Me
O
O
Me
H
N
Me
H
N
MeO
O
CN
OH
Jorunnamycin A (3)
1H NMR 400 MHz CDCl3
f1 (ppm)

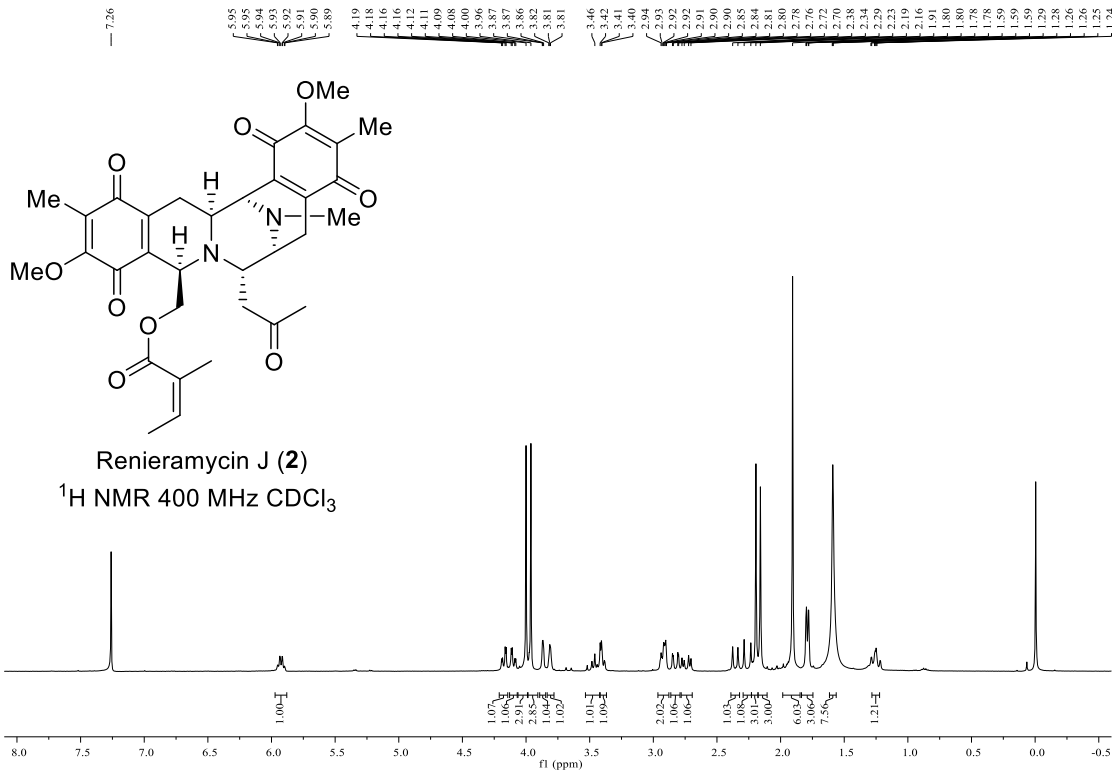

OMe
Me
O
O
Me
H
N
Me
H
N
MeO
O
CN
OH
Jorunnamycin A (3)
13C NMR 150 MHz CDCl3
f1 (ppm)

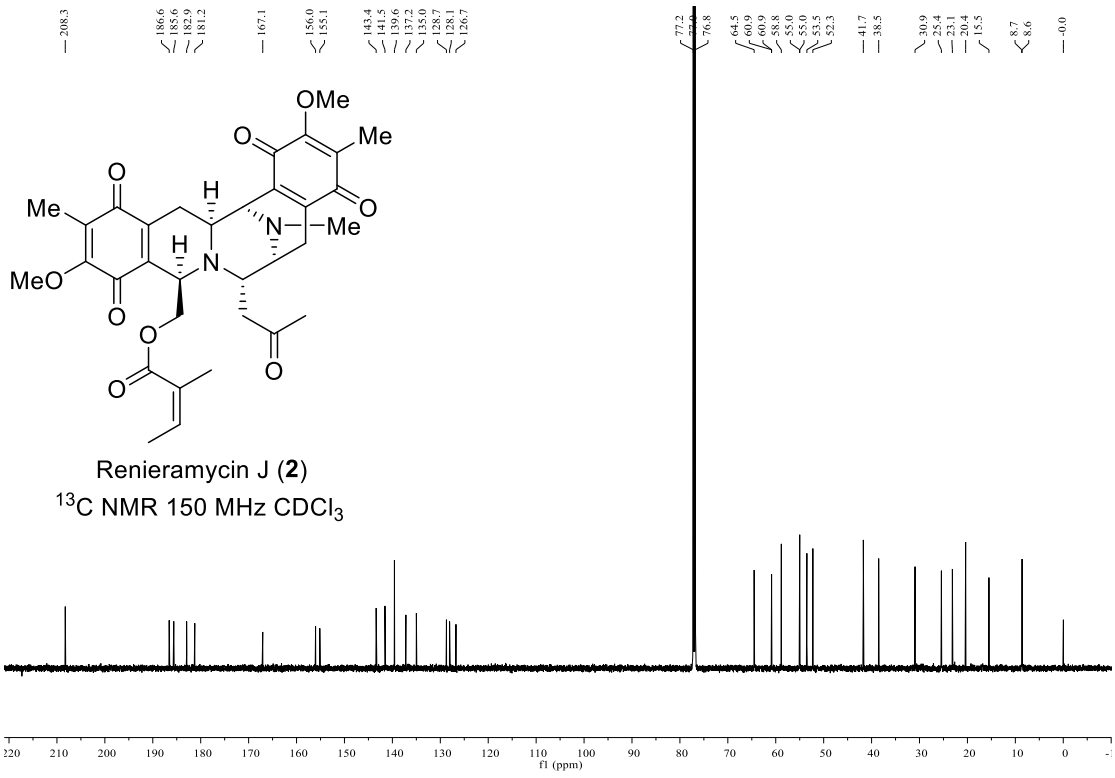

OMe
HO
Me
OMe
Me
H
OMe
N
Me
H
N
MeO
OH
CN
O
O
27
1H NMR 400 MHz CDCl3
f1 (ppm)

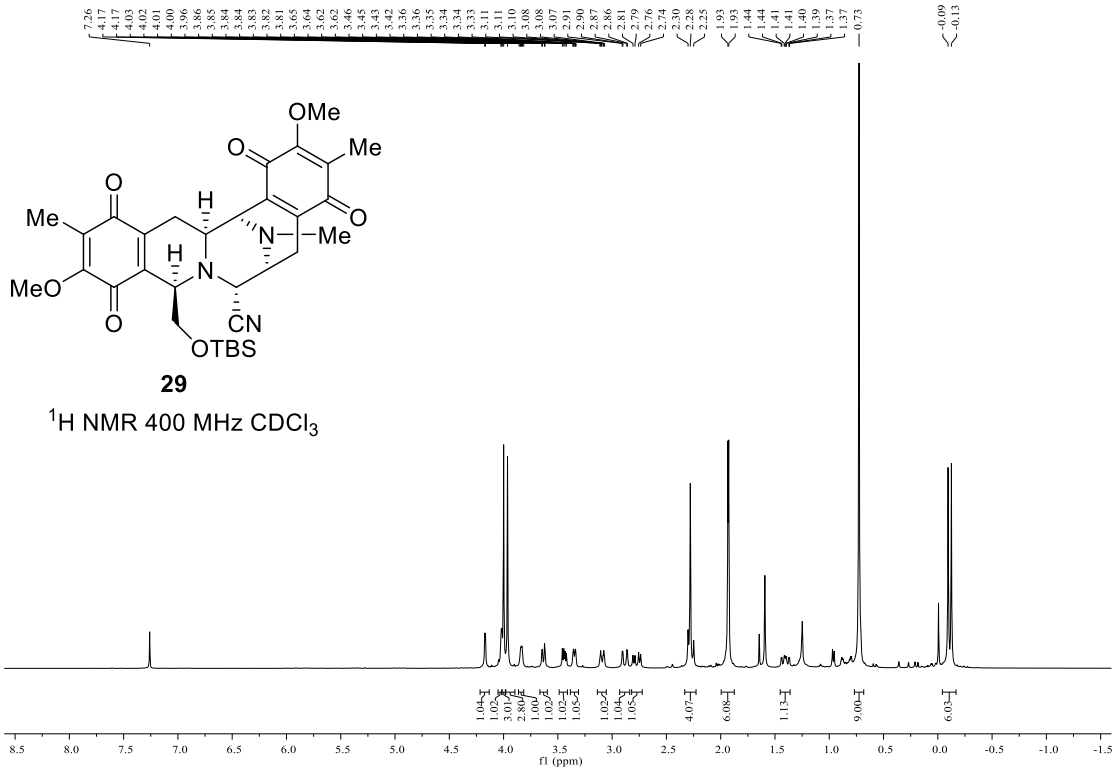

OMe
HO
Me
OMe
Me
H
OMe
N
Me
H
N
MeO
OH
CN
O
O
27
13C NMR 150 MHz CDCl3
f1 (ppm)

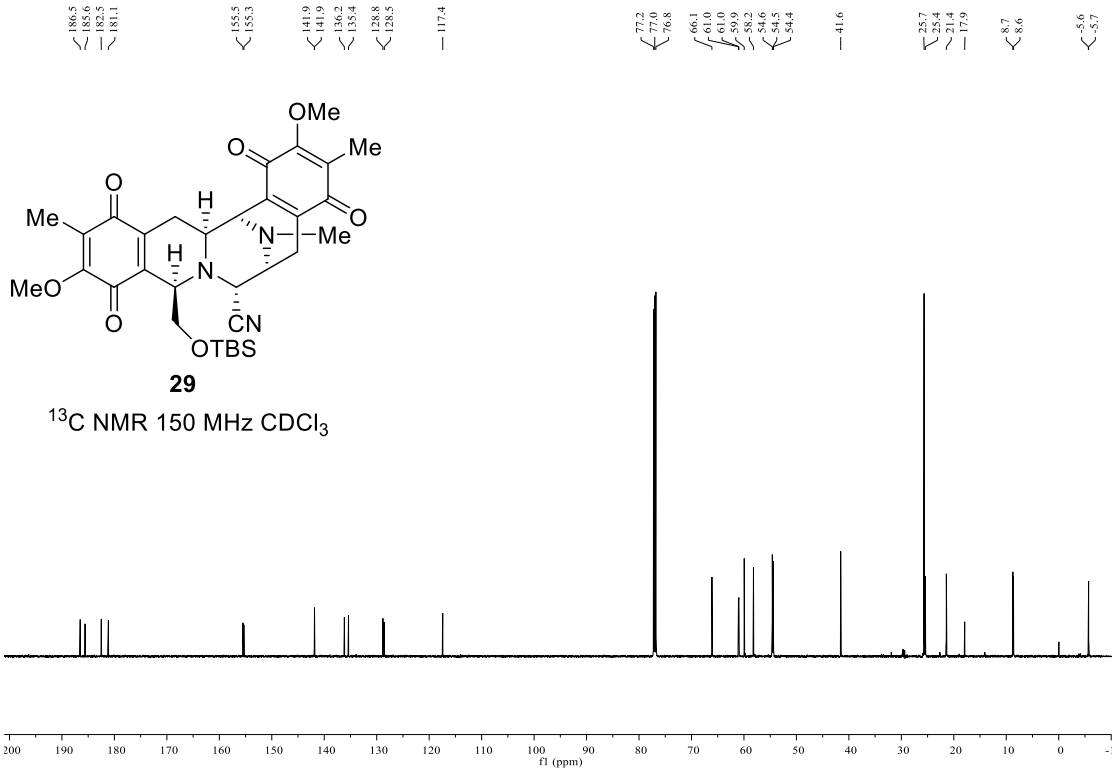

OMe
Me
O
Me
O
H
N
Me
H
N
MeO
O
CN
O
O
Renieramycin M (28)
1H NMR 400 MHz CDCl3
f1 (ppm)

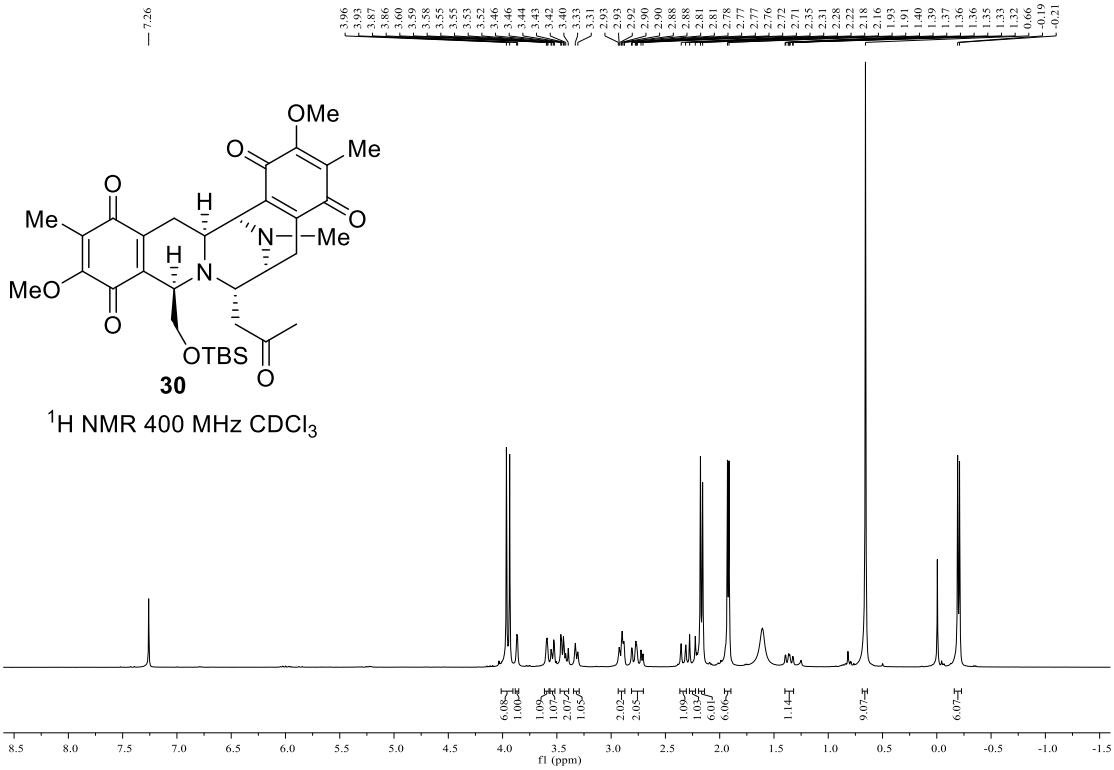

OMe
Me
O
Me
O
H
N
Me
H
N
MeO
O
CN
O
O
Renieramycin M (28)
13C NMR 150 MHz CDCl3
f1 (ppm)

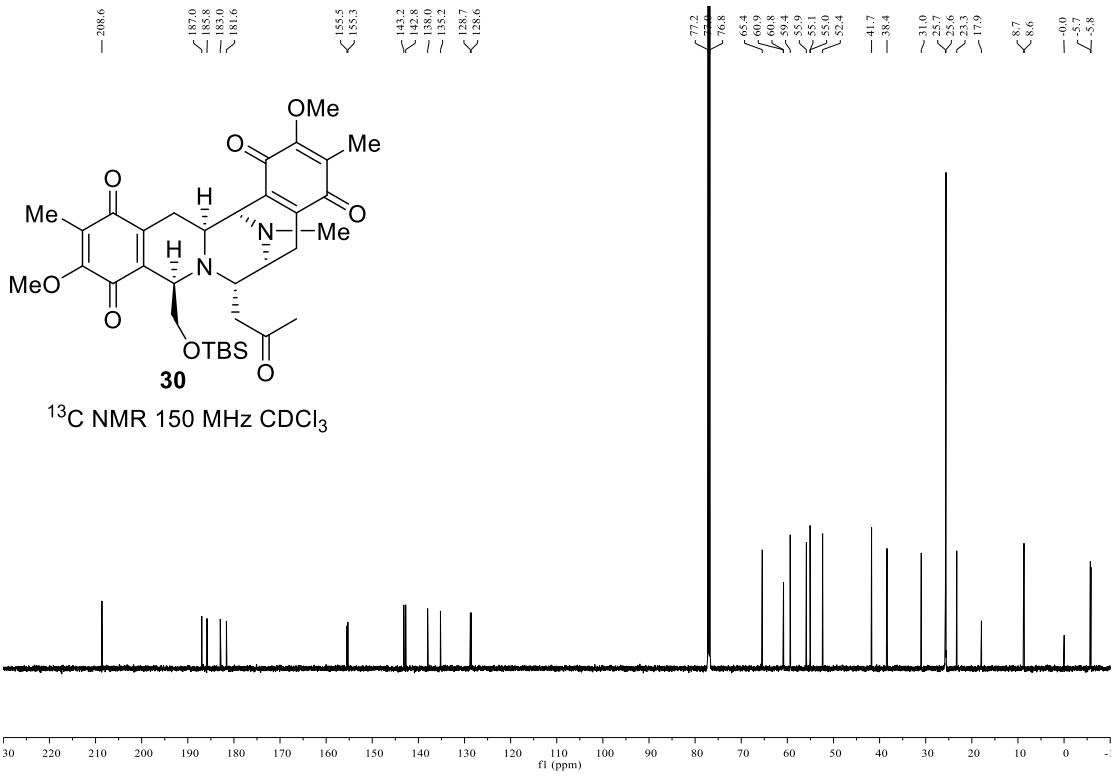

OMe
Me
O
H
N
Me
MeO
Renieramycin J (2)
1H NMR 400 MHz CDCl3
f1 (ppm)

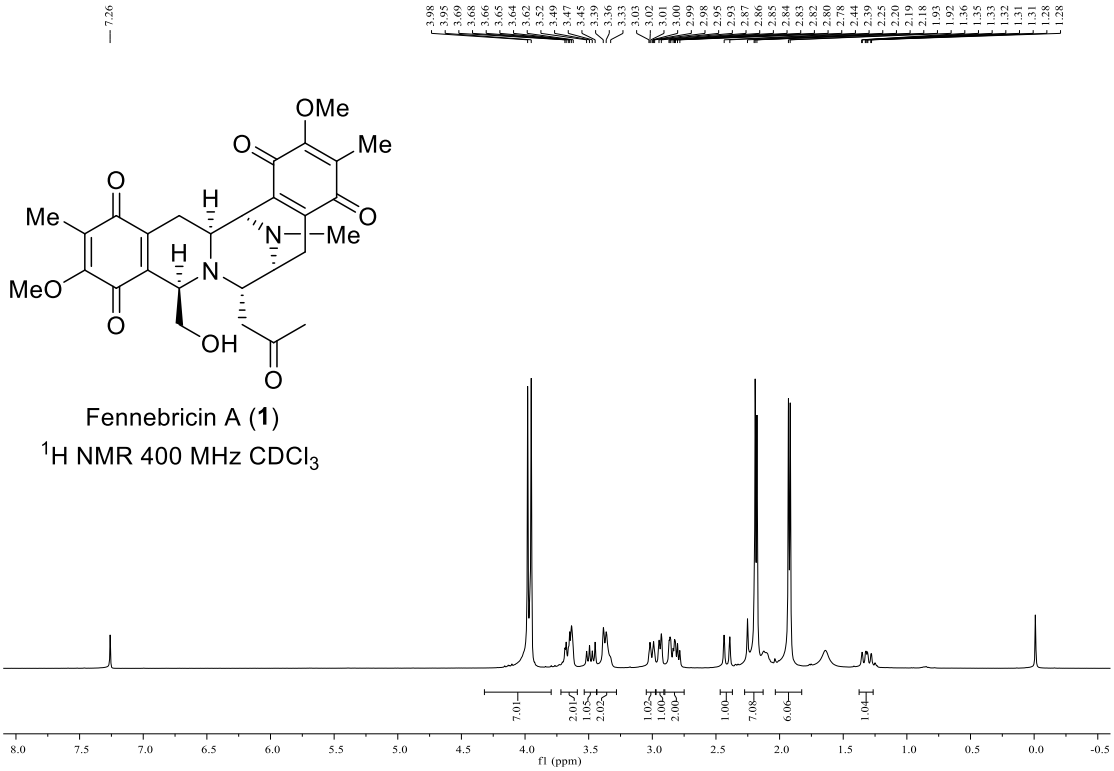

OMe
Me
O
H
N
Me
MeO
Renieramycin J (2)
13C NMR 150 MHz CDCl3
f1 (ppm)

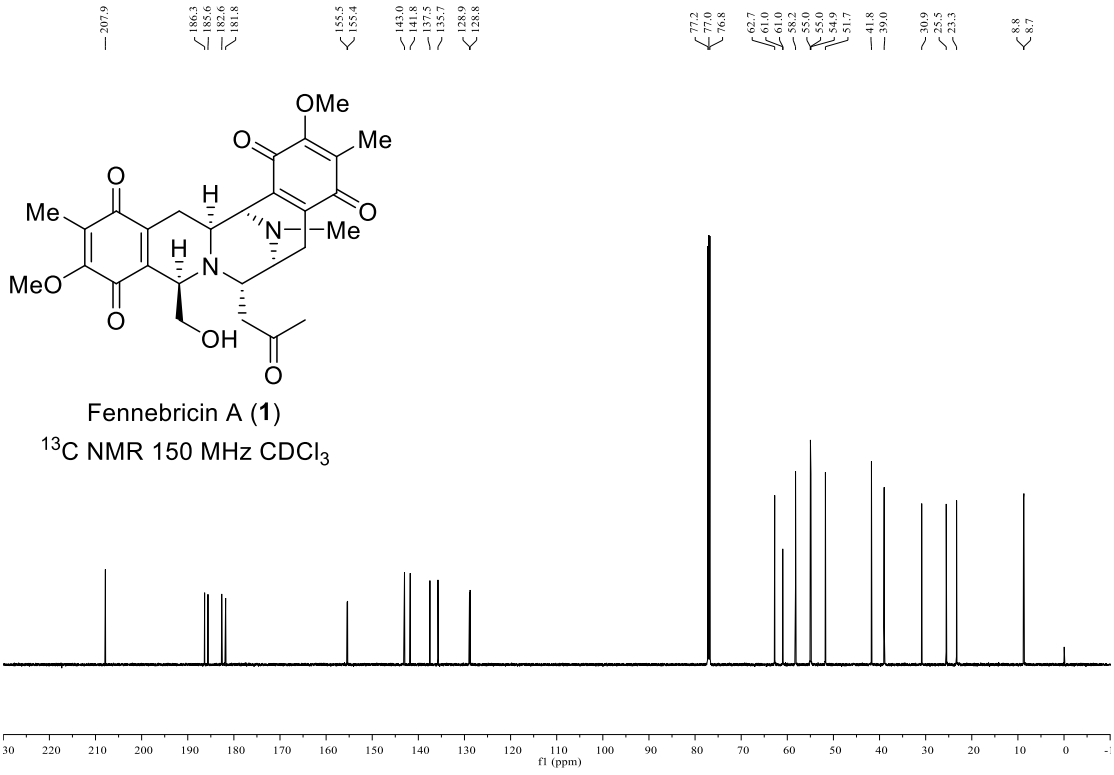

OMe
Me
O
O
Me
O
H
N
Me
H
N
MeO
O
CN
OTBS
29
1H NMR 400 MHz CDCl3
f1 (ppm)


OMe
Me
O
O
Me
O
H
N
Me
H
N
MeO
O
CN
OTBS
29
13C NMR 150 MHz CDCl3
f1 (ppm)


OMe
Me
O
O
H
Me
N
Me
O
H
N
MeO
O
OTBS
O
30
1H NMR 400 MHz CDCl3
f1 (ppm)


OMe
Me
O
O
H
Me
N
Me
O
H
N
MeO
O
OTBS
O
30
13C NMR 150 MHz CDCl3
f1 (ppm)


OMe
Me
O
Me
H
N
Me
H
N
MeO
O
OH
O
Fennebricin A (1)
1H NMR 400 MHz CDCl3
f1 (ppm)


OMe
Me
O
Me
H
N
Me
H
N
MeO
O
OH
O
Fennebricin A (1)
13C NMR 150 MHz CDCl3
f1 (ppm)

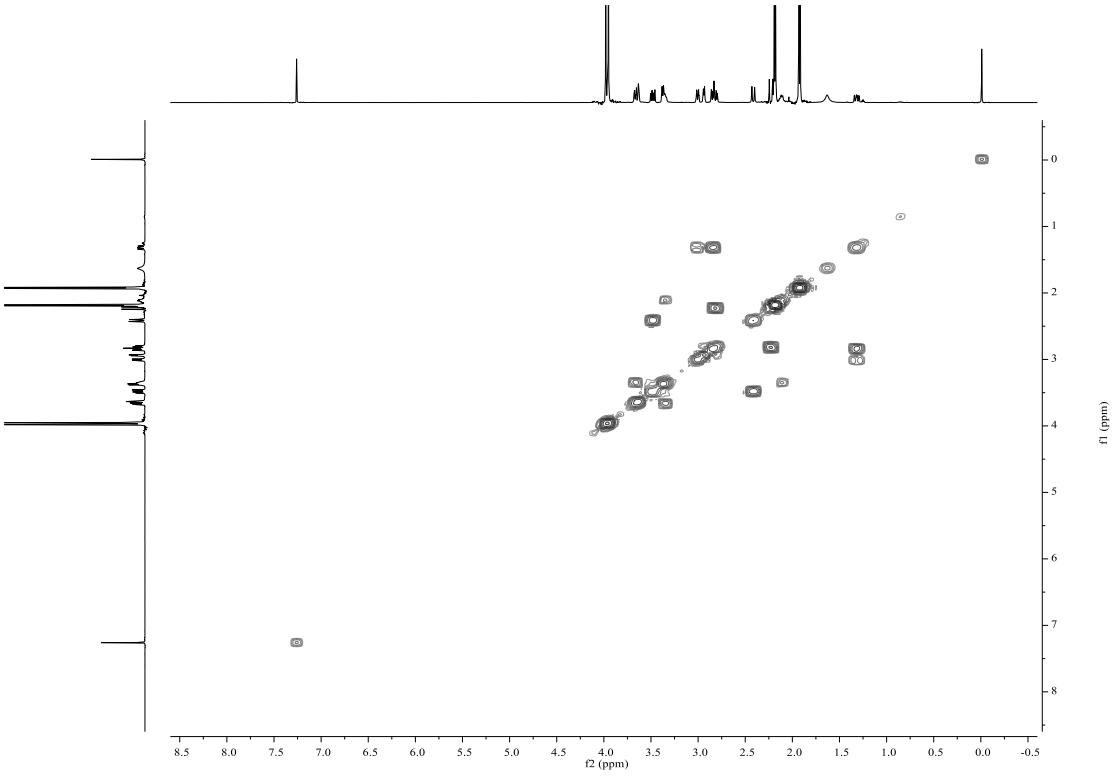


Figure S5. ^{1}H-^{1}H COSY spectrum of Fennebricin A (**1**) recorded in $CDCl_3$.

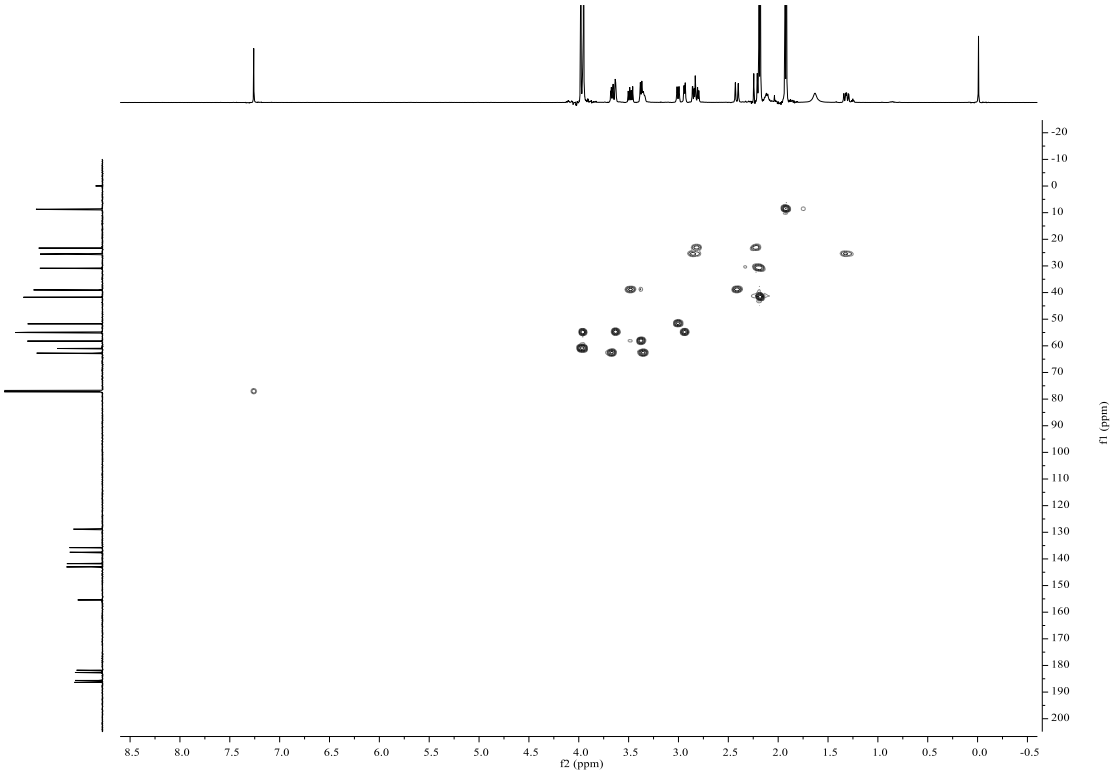


Figure S6. HSQC spectrum of Fennebricin A (**1**) recorded in $CDCl_3$.

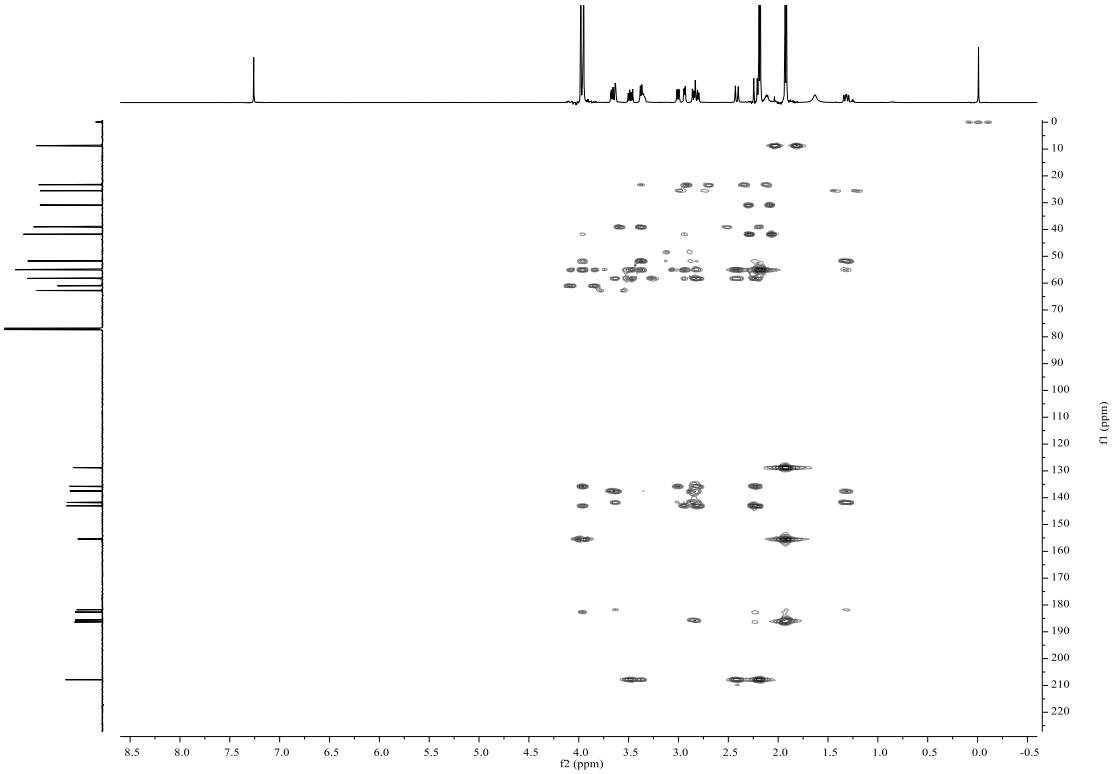


Figure S7. HMBC spectrum of Fennebricin A (**1**) recorded in $CDCl_3$.

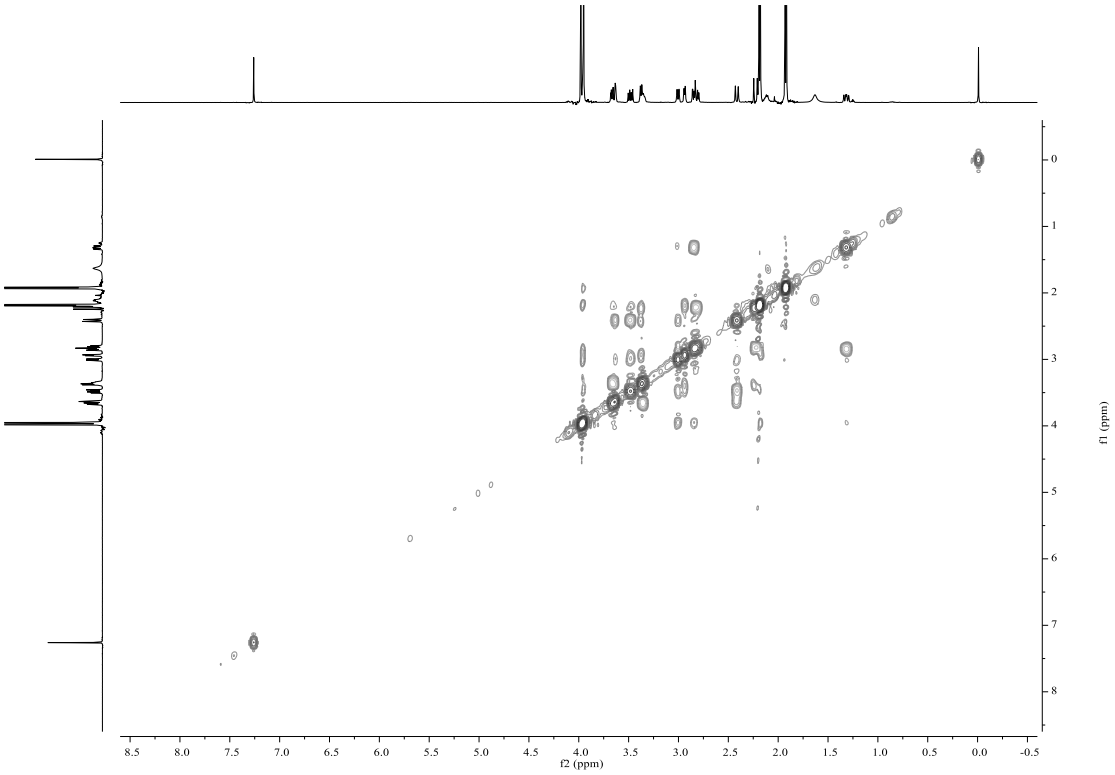


Figure S8. ROESY spectrum of Fennebricin A (**1**) recorded in $CDCl_3$.

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