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Supporting Information

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Short, Enantioselective Total Syntheses of (−)-8-Demethoxyrunanine and (−)-Cepharatines A, C, and D**

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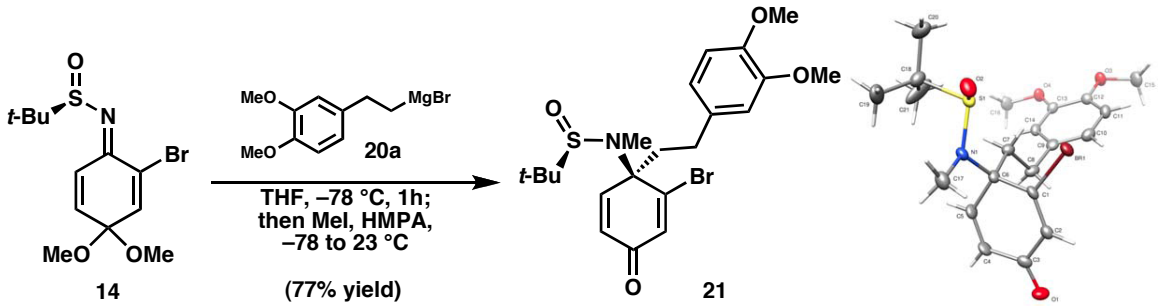
I. Materials and Methods. Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly dried solvents. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), diethyl ether (Et_2O), acetonitrile (MeCN), toluene and benzene were dried by passing through activated alumina columns. Dimethylformamide (DMF) was dried over activated molecular sieves, MeOH was distilled over magnesium oxide, dichloroethane (DCE) and triethylamine (Et_3N) were distilled over calcium hydride. All other commercially obtained reagents were used as received unless specifically indicated. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash column chromatography was performed either as described by Still et al. (Still, W. C., Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.) using silica gel (particle size 0.032-0.063) purchased from Silicycle or using pre-packaged RediSep®Rf columns on a CombiFlash Rf system (Teledyne ISCO Inc.). Microwave experiments were performed using a Biotage Initiator® microwave reactor. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (at 500 MHz and 126 MHz respectively), and are reported relative to internal chloroform (^{1}H, δ = 7.26, ^{13}C, δ = 77.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). Analytical SFC was performed with a Mettler SFC supercritical CO2 analytical chromatography system with Chiralcel AD-H, OJ-H columns (4.6 mm x 25 cm). Melting points were determined using a Büchi B-545 capillary melting point apparatus and the values reported are uncorrected. HRMS were acquired using either an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MM) ionization mode, or obtained from the Caltech Mass Spectral Facility.

II. Experimental Procedures

Preparation of Dienone 21



To a solution of bromo-quinonesulfinylimine **14**[1] (2.96 g, 8.80 mmol, 1.0 equiv) in THF (17 mL) at –78 °C (dry ice/acetone) was added a solution of 3,4-dimethoxyphenethylmagnesium bromide[2] (0.67M solution in THF, 14.3 mL, 9.6 mmol) dropwise by syringe. The solution was then stirred at –78 °C for one hour, then methyl iodide (1.6 mL, 26.1 mmol, 3.0 equiv) and hexamethylphosphoramide (4.5 mL, 26.1 mmol, 3.0 equiv) were sequentially added dropwise by syringe, and the solution stirred at –78 °C for ten minutes. The solution was then warmed to 23 °C and stirred for 2 hours, then quenched by the addition of aqueous acetic acid (10% v/v, 31 mL). After 3.5 hours, the mixture was diluted with H_2O (100 mL) and extracted with EtOAc (3 x 150 mL) and washed with H_2O (3 x 100 mL). The organic layers were then combined, washed with saturated aqueous $NaHCO_3$ (150 mL), then brine (150 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a clear brown oil. The diastereoselectivity was determined by LC/MS: 96:4 dr (5→95% MeCN/H_2O, t = 0–10 min, 1 mL/min. Major diastereomer: t_R = 4.2 min, minor diastereomer: t_R = 4.8 min). Flash chromatography (30% to 80% EtOAc in Hexanes) afforded dienone **21** as a white crystalline solid (3.18 g, 6.76 mmol, 77% yield). A small portion of the solid was recrystallized by vapor fusion of pentane into a solution of **21** in toluene to afford large crystals suitable for single crystal X-ray diffraction.

Major Diastereomer (R_s,*R*)-21 – Melting Point: 136–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 1.7 Hz, 1H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 6.1 Hz, 2.0 Hz, 2H), 6.62 (d, *J* = 2.0 Hz, 1H), 6.44 (dd, *J* = 9.8 Hz, 1.7 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.81 (td, 12.3 Hz, 4.9 Hz, 1H), 2.47 (s, 3H), 2.39 – 2.24 (m, 2H), 1.84 (td, *J* = 12.5 Hz, 5.2 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.0, 150.7, 150.1, 148.9, 147.7, 136.4, 132.4, 129.6, 120.1, 111.7, 111.3, 68.7, 59.2, 55.9, 55.8, 38.2, 29.9, 26.7, 24.2; IR (NaCl/thin film): 3042, 2934, 2864, 2833, 1669, 1592, 1516, 1464, 1419, 1377, 1360, 1258, 1238, 1156, 1140, 1077, 1028, 951, 885, 819, 788; HRMS (ES+) calc'd for $C_{21}H_{29}BrNO_4S$ $[M+H]^+$ 470.0995, found 470.1003; $[\alpha]^{25}_D$: + 22.7 (*c*, 0.85, CH_2Cl_2).

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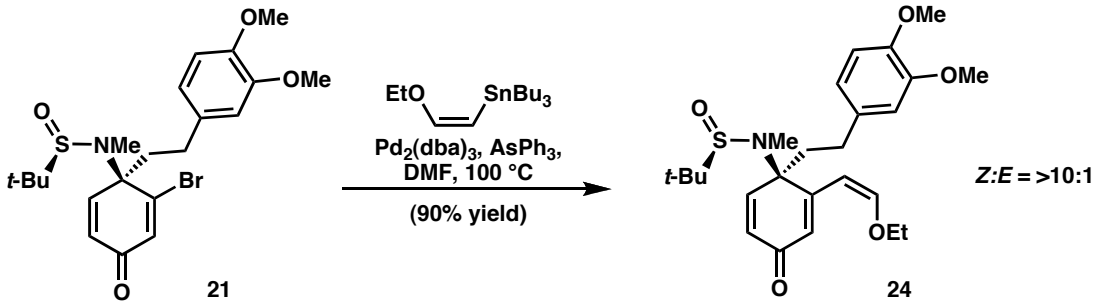
[1] Sulfinimine **14** was prepared from 2-bromo-4-methoxyphenol in two steps as previously described. See K. V. Chuang, R. Navarro, S. E. Reisman. *Chem. Sci*. **2011**, *2*, 1086.

[2] 3,4-Dimethoxyphenethylmagnesium bromide was readily prepared from commercially available 3,4-dimethoxyphenethyl bromide and magnesium turnings (1.1 equiv), activated with catalytic diisobutylaluminum hydride, in refluxing THF.

Minor Diastereomer (R_s,*S*) – 21 – ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 10.0 Hz, 1H), 6.90 (d, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.66 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.53 – 2.45 (m, 1H), 2.39 (s, 3H), 2.38 – 2.31 (m, 1H), 2.27 – 2.17 (m, 2H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) 183.0, 149.9, 149.7, 149.0, 147.7, 136.3, 132.5, 130.9, 120.1, 111.7, 111.4, 68.8, 59.9, 55.9, 55.9, 38.9, 29.8, 27.3, 24.3; IR (NaCl/thin film): 3042, 2956, 2933, 2866, 1834, 1670, 1640, 1597, 1516, 1464, 1454, 1418, 1382, 1360, 1258, 1238, 1157, 1140, 1075, 1029, 952, 924, 887, 816, 779, 733; HRMS (ES+) calc'd for $C_{21}H_{29}BrNO_4S$ $[M+H]^+$ 470.0995, found 470.1002; $[\alpha]_D^{25}$: + 70.6 (*c* 0.96, CH_2Cl_2).

Preparation of Trienone 24

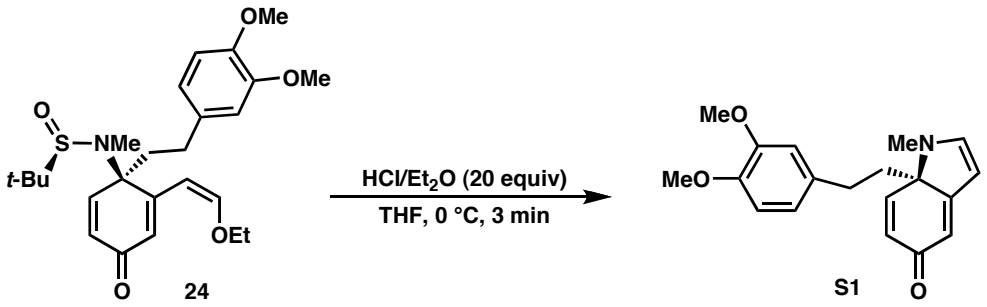


To a solution of dienone **24** (2.30 g, 4.89 mmol) in DMF (49 mL) was added tris(dibenzylideneacetone)dipalladium (224 mg, 0.245 mmol, 0.5 equiv), triphenylarsine (299 mg, 0.979 mmol, 0.20 equiv) and *cis*-2-ethoxyvinyltributylstannane (1.8 mL, 5.4 mmol, 1.1 equiv). The solution was then thoroughly degassed with nitrogen for 30 minutes and the solution heated at 100 °C for 1 hour. Upon cooling to room temperature, the solution was passed through a short plug of Celite, diluted with EtOAc (300 mL), and washed with H_2O (3 x 150 mL). The aqueous layers were then combined and back-extracted with EtOAc (3 x 100 mL), and the organic layers combined and dried over $MgSO_4$, filtered, and concentrated in vacuo to afford a light brown oil. Flash chromatography (50% to 100% EtOAc in Hexanes) afforded **24** (>10:1 mixture of *Z:E*-isomers by ^{1}H NMR) as a tan solid (2.02 g, 4.37 mmol, 91% yield).

The individual olefin isomers could be chromatographically separated for characterization purposes: (*Z*)-**24**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 1.8 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 6.53 (d, *J* = 10.0 Hz, 1H), 6.35 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.15 (d, *J* = 7.0 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 3.81 (s, 3H), 2.53 – 2. 42 (m, 1H), 2.42 (s, 3H), 2.32 – 2.26 (m, 2H), 1.88 – 1.80 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.6, 154.7, 153.5, 149.4, 148.7, 147.4, 133.3, 130.4, 128.7, 119.9, 111.7, 111.2, 98.7, 70.8, 66.5, 58.8, 55.8, 55.7, 38.3, 29.9, 27.0, 24.4, 15.3; IR (NaCl/thin film): 2958, 2934, 2835, 1660, 1623, 1575, 1516, 1464, 1455, 1303, 1261, 1238, 1180, 1156, 1238, 1180, 1156, 1141, 1099, 1055, 1030, 959, 935, 896, 804, 765, 735; HRMS (EI+) calc'd for $C_{25}H_{36}NO_3S$ $[M+H]^+$ 462.2309, found 462.2320; $[\alpha]_D$ ^{25}: – 80 (*c* 1.07, CH_2Cl_2). (*E*)–**24**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 12.7 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.61 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.56 (d, *J* = 2.2 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 6.39 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.82 (d, *J* = 12.5 Hz, 1H), 3.98 (app q, *J* = 7.0 Hz, 1H), 3.85 (app s, 6H), 2.52 – 2.43 (m, 1H), 2.46 (s, 3H), 2.35 – 2.19 (m, 2H), 1.89 (td, *J* = 12.3, 5.0 Hz, 1H), 1.35

(t, J = 7.1 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.7, 157.4, 153.7, 149.8, 148.9, 147.6, 133.1, 130.6, 122.3, 120.0, 111.8, 111.3, 100.3, 67.0, 66.0, 59.0, 55.9, 55.8, 38.5, 29.9, 27.3, 24.5, 14.5; IR (NaCl/thin film): 2956, 2924, 2853, 1659, 1620, 1579, 1516, 1464, 1418, 1388, 1361, 1331, 1260, 1238, 1213, 1142, 1068, 1029, 956, 889, 800, 764; HRMS (EI+) calc'd for $C_{25}H_{36}NO_3S$ $[M+H]^+$ 462.2309, found 462.2330. $[\alpha]_D^{25}$: – 80 (*c* 1.07, CH_2Cl_2).

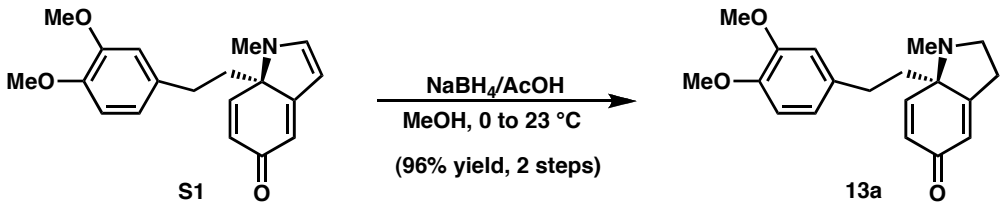
Preparation of Enamine S1



To a solution of trienone **24** (318.3 mg, 0.668 mmol) in THF (13 mL) at 0°C in an ice/water bath was added a solution of hydrogen chloride (2.0 M solution in Et_2O, 7.0 mL, 14 mmol) dropwise by syringe over one minute. The reaction was allowed to stir for 3 minutes at 0 °C and then quenched by the addition of aqueous potassium hydroxide (10% w/v, 10 mL) and stirred for an additional 10 minutes. The mixture was then diluted with H_2O (10 mL), and extracted with EtOAc (5 x 20 mL). The organic layers were then combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to isolate a bright red foam that was used immediately in the next step without further purification.

A sample was purified by flash chromatography (1% to 5% MeOH in CH_2Cl_2) for characterization purposes: ^{1}H NMR (500 MHz, $CDCl_3$): 6.98 (dd, J = 9.9 Hz, 0.6 Hz, 1H), 6.89 (d, J = 3.2 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 6.60 (dd, J = 8.2 Hz, 2.1 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.16 (dd, J = 9.8 Hz, 1.7 Hz, 1H), 5.88 (d, J = 1.5 Hz, 1H), 5.47 (dd, J = 3.3, 0.6 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.04 (s, 3H), 2.41–2.30 (m, 2H), 2.08–1.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): 184.7, 174.5, 153.4, 148.8, 147.4, 140.1, 132.9, 131.1, 120.1, 111.7, 111.3, 109.8, 99.6, 72.6, 55.8, 55.8, 45.8, 31.5, 29.1. IR (NaCl/thin film): 2934, 2834, 1631, 1592, 1568, 1515, 1465, 1313, 1260, 1237, 1156, 1108, 1089, 1050, 1028, 977, 884, 830, 766; HRMS (ES+) calc'd for $[M+H]^+$ 312.1594, found 312.1585. $[\alpha]_D^{25}$: – 1650 (*c* 0.41, CH_2Cl_2).

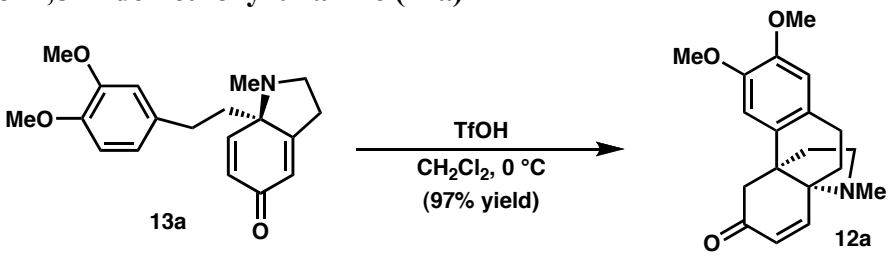
Preparation of Amine 13a



To a solution of crude enamine **S1** (220 mg) in MeOH (14 mL) at 0 °C was added a solution of $NaBH_4$ (50 mg, 1.32 mmol) in AcOH (5 mL), dropwise by syringe. The solution was

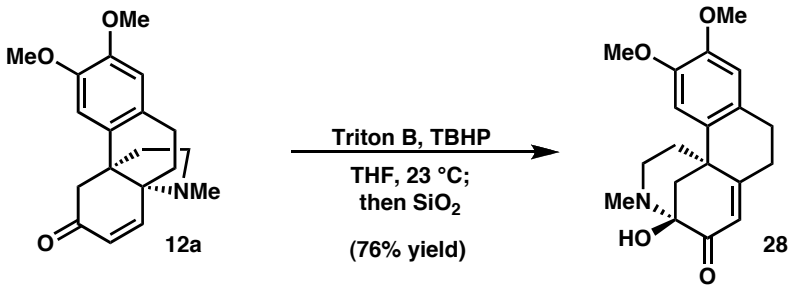
stirred at 0 °C for 10 minutes before warming to 20 °C and stirring continued for 1 hour. The reaction was cooled to 0 °C in an ice/water bath and quenched by the slow addition of potassium hydroxide (30% w/v, 20 mL). The solution was then diluted with H_2O (10 mL) and extracted with EtOAc (5 x 20 mL). The organic layers were then combined, dried over Na_2SO_4, filtered, concentrated in vacuo to afford an orange oil. Purification by flash chromatography (2% to 4% MeOH in CH_2Cl_2) afforded amine **13a** as a yellow oil (200 mg, 0.638 mmol, 96% yield over two steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 10.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.61 (dd, *J* = 8.2 Hz, 2.1 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 6.32 (dd, *J* = 10.0, 1.6 Hz, 1H), 6.18 (dt, *J* = 2.3, 1.5 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.16 (ddd, *J* = 10.5, 8.6, 4.2 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.81 – 2.67 (m, 2H), 2.40 (s, 3H), 2.39 – 2.31 (m, 1H), 2.27 – 2.17 (m, 1H), 1.90–1.79 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.6, 166.9, 148.8, 147.4, 145.9, 133.6, 130.2, 123.3, 119.8, 111.6, 111.3, 66.5, 55.9, 55.8, 51.6, 36.5, 32.0, 29.6, 27.8; IR (NaCl/thin film): 2934, 2834, 2789, 1667, 1642, 1606, 1590, 1515, 1464, 1452, 1418, 1259, 1464, 1452, 1259, 1234, 1176, 1152, 1028, 890, 809, 764; HRMS (EI+) calc'd for $C_{19}H_{24}NO_3$ $[M+H]^+$ 314.1751, found 314.1748. $[\alpha]_D^{25}$: – 40.6 (*c* 0.89, CH_2Cl_2).

Preparation of 7,8-Didemethoxyrunanine (12a)



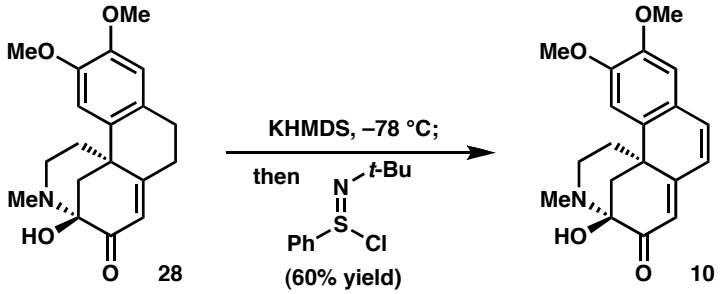
To a solution of amine **13a** (370 mg, 1.18 mmol, 1.0 equiv) in CH_2Cl_2 (24 mL) at 0 °C was added trifluoromethanesulfonic acid (0.522 mL, 5.90 mmol, 5.0 equiv) dropwise by syringe. The solution was stirred for 5 minutes, then quenched with a saturated solution of aqueous $NaHCO_3$ (50 mL). The mixture was then washed with additional saturated aqueous $NaHCO_3$ (3 x 50 mL), then the aqueous layers combined and back extracted with CH_2Cl_2 (1 x 100 mL). The organic layers were then combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a tan foam. Flash chromatography (1% to 2% MeOH in CH_2Cl_2) afforded propellane **12a** as a white foam (360 mg, 1.15 mmol, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (d, *J* = 10.4 Hz, 1H), 6.69 (s, 1H), 6.53 (s, 1H), 6.14 (dd, *J* = 10.4 Hz, 1.0 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.98 – 2.84 (m, 2H), 2.91 (dd, *J* = 16.5 Hz, 1.1 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.56 (d, *J* = 16.5 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.45 (s, 3H), 2.32 – 2.22 (m, 1H), 2.07 – 1.97 (m, 2H), 1.82 – 1.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 150.3, 147.9, 147.1, 135.7, 129.9, 126.3, 111.1, 110.5, 63.1, 56.1, 55.8, 51.6, 49.5, 48.3, 36.2, 33.3, 25.1, 24.6; IR (NaCl/thin film): 2929, 2851, 2832, 2790, 2252, 1681, 1610, 1515, 1464, 1452, 1356, 1255, 1207, 1140, 1068, 1035, 1010, 916, 886, 856, 730; HRMS (EI+) calc'd for $C_{19}H_{24}NO_3$ $[M+H]^+$ 314.1751, found 314.1748. $[\alpha]_D^{25}$: – 243 (*c* 0.44, CH_2Cl_2).

Preparation of Hemiaminal 28



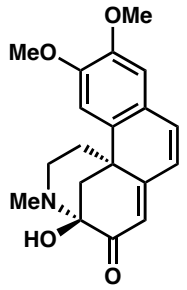
To a solution of enone **12a** (93.8 mg, 0.299 mmol, 1.0 equiv) in THF (3.0 mL) at 23 °C was added *tert*-butylhydroperoxide (214 μL of a 70% aq. solution, 1.50 mmol, 5.0 equiv) and Triton B (110 μL of a 40% solution in methanol, 0.239 mmol, 0.8 equiv) dropwise by syringe, and the solution stirred for 17 hours at room temperature (23 °C). The reaction was then quenched by the addition of a solution of saturated aqueous $Na_2S_2O_3$ (7 mL) and stirred for an additional 30 minutes. H_2O (15 mL) was then added, the solution extracted with CH_2Cl_2 (3 x 20 mL), and the organic layers combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a clear oil. The oil was then redissolved in CH_2Cl_2 (2 mL), then loaded onto dry silica gel and allowed to sit for 2 hours. Flash chromatography (60 to 100% EtOAc in hexanes) afforded hemiaminal **28** as a white foam (75.0 mg, 0.228 mmol, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.57 (s, 1H), 6.21 (s, 1H), 4.27 (br s, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.02 (ddd, *J* = 12.2, 5.3, 1.6 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.67 – 2.57 (m, 2H), 2.46 (td, *J* =12.5, 3.7 Hz, 1H), 2.45 (d, *J* = 12.5 Hz, 1H), 2.28 (td, *J* =13.3, 5.3 Hz, 1H), 2.24 (s, 3H), 2.12 (dd, *J* = 12.5, 2.9 Hz, 1H), 1.70 – 1.64 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 168.0, 148.2, 147.6, 132.2, 127.2, 124.8, 111.0, 108.5, 83.1, 55.9, 55.8, 49.2, 46.8, 43.5, 36.3, 35.9, 31.2, 29.8; IR (NaCl/thin film): 3468, 2933, 2848, 1666, 1619, 1517, 1465, 1354, 1259, 1228, 1187, 1124, 1089, 1006, 914, 870, 789, 729; HRMS (EI+) calc'd for $C_{19}H_{24}NO_4$ $[M+H]^+$ 330.1700, found 330.1713; $[\alpha]_D^{25}$: – 204 (*c* 0.65, CH_2Cl_2).

Preparation of Cepharatine D (10)



To a solution of hemiaminal **28** (30 mg, 91 μmol, 1.0 equiv) in THF (1.8) mL at –78 °C was added a solution of KHMDS in THF (0.21 mL of a 0.9 M solution in THF, 0.191 mmol, 2.1 equiv). The yellow solution was stirred at –78 °C for 10 minutes, then warmed to 0 °C and stirred for 20 minutes. The solution was again cooled to –78 °C, and a solution of *N*-*tert*-butylbenzenesulfinimidoyl chloride (27.6 mg, 0.128 mmol, 1.4 equiv) in THF (0.25 mL) added dropwise. After 50 minutes, the solution was quenched with saturated aqueous ammonium chloride (20 mL), warmed to room temperature, and extracted with EtOAc (3 x 20 mL). The

organic layers were then combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Flash chromatography (1 to 2 % MeOH in CH_2Cl_2) afforded (–)-cepharatine D (**10**) as a bright yellow foam (18.0 mg, 55.0 μmol, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.74 (d, *J* = 9.5 Hz, 1H), 6.72 (s, 1H), 6.32 (d, *J* = 9.3 Hz, 1H), 6.15 (s, 1H), 4.42 (br s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.87 (ddd, *J* = 12.6, 5.1, 1.6 Hz, 1H), 2.75 (d, *J* = 12.2 Hz, 1H), 2.62 (td, *J* = 12.7, 3.7 Hz, 1H), 2.31 (dd, 12.2, 2.9 Hz, 1H), 2.24 (s, 3H), 1.98 (td, *J* = 13.1, 5.1 Hz, 1H), 1.58 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 161.4, 150.3, 147.9, 135.9, 135.5, 124.2, 123.5, 123.2, 111.6, 107.6, 83.0, 56.1, 56.0, 46.8, 56.0, 46.8, 45.0, 43.7, 38.1, 36.0; ^{1}H NMR (500 MHz, methanol-d_4) δ 7.07 (s, 1H), 6.90 (s, 1H), 6.84 (d, *J* = 9.3 Hz, 1H), 6.37 (d, *J* = 9.3 Hz, 1H), 6.10 (s, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 2.82 (dd, *J* = 12.7, 4.9 Hz, 1H), 2.68 (d, *J* = 12.2 Hz, 1H), 2.56 (td, *J* = 12.8, 3.5 Hz, 1H), 2.23 (d, *J* = 12.2, 2.8 Hz, 1H), 2.21 (s, 3H), 1.92 (td, *J* = 13.2, 5.1 Hz, 1H), 1.58 – 1.50 (m, 1H); ^{13}C NMR (126 MHz, methanol-d_4) δ 194.7, 162.7, 151.8, 149.6, 137.1, 136.9, 126.0, 125.4, 124.1, 113.5, 109.5, 84.7, 56.7, 56.6, 47.9, 46.4, 44.9, 39.0, 36.7; IR (NaCl/thin film): 3455, 2925, 2843, 1732, 1650, 1608, 1554, 1516, 1463, 1376, 1340, 1275, 1235, 1190, 1135, 1081, 877, 784; HRMS (EI+) calc'd for $C_{19}H_{21}NO_4$ $[M+H]^+$ 328.1543, found 330.1552; $[\alpha]_D^{25} = -227$ (*c* 0.51, MeOH).



(–)-*Cepharatine D*

Comparison of Spectroscopic Data for Natural[3] and Synthetic (–)-Cepharatine D

^{1}H NMR Data (both spectra are referenced to 3.30 ppm)

Reported[3]	Synthetic
7.06 (s, 1H)	7.07 (s, 1H)
6.89 (s, 1H)	6.90 (s, 1H)
6.84 (d, *J* = 9.2 Hz, 1H)	6.84 (d, *J* = 9.3 Hz, 1H)
6.36 (d, *J* = 9.2 Hz, 1H)	6.37 (d, *J* = 9.3 Hz, 1H)
6.10 (s, 1H)	6.10 (s, 1H)
3.92 (s, 3H)	3.91 (s, 3H)
3.83 (s, 3H)	3.84 (s, 3H)
2.90 (m, 1H)	2.82 (dd, *J* = 12.7, 4.9 Hz, 1H)
2.67 (d, *J* = 12.0 Hz, 1H)	2.68 (d, *J* = 12.2 Hz, 1H)
2.66 (m, 1H)	2.56 (td, *J* = 12.8, 3.5 Hz, 1H)
2.19 (m, 1H)	2.23 (d, *J* = 12.2, 2.8 Hz, 1H)

[3] ^{1}H NMR data (Table 1) for cepharatine D was found to be inconsistent with the authentic spectral data provided in the paper's supporting information. Values listed in the comparison table are those provided in the supporting information. See: L. He, Y.-H. Zhang, H.-Y. Guan, J.-X. Zhang, Q.-Y. Sun, X.-J. Hao, *J. Nat. Prod.* **2011**, *74*, 181.

2.18 (s, 3H)	2.21 (s, 3H)
2.02 (m, 1H)	1.92 (td, J = 13.2, 5.1 Hz, 1H)
1.59 (m, 1H)	1.58 – 1.50 (m, 1H)

^{13}C NMR Comparsion Data (both spectra are referenced to 49.0 ppm)

Reported	**Synthetic**
194.7	194.7
162.7	162.7
151.7	151.8
149.5	149.6
137.0	137.1
136.9	136.9
126.0	126.0
125.3	125.4
124.1	124.1
113.4	113.5
109.3	109.5
84.7	84.7
56.6	56.7
56.5	56.6
47.8	47.9
46.4	46.4
44.8	44.9
39.0	39.0
36.7	36.7

Optical Rotation[*]

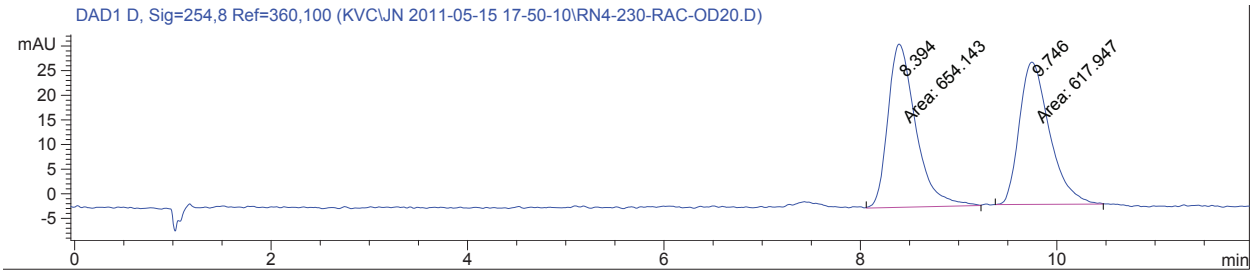
Natural	**Synthetic**
$[\alpha]_D^{17}$: –321 (*c* 1.01, MeOH)	$[\alpha]_D^{17}$: –227 (*c* 0.51, MeOH)[*]

[*] It was noted that synthetic (–)-cepharatine D produced a significantly lower specific rotation than reported by the isolation paper. To eliminate the possibility of racemization during the reaction sequence, racemic cepharatine D was synthesized using racemic *tert-butylsulfinamide* in place of *(R)-tert*-butylsulfnamide by an identical sequence, and the enantiomeric excess of (–)-cepharatine D was determined to be > 99% ee by chiral SFC (see Chiral SFC Traces).

Chiral SFC Traces

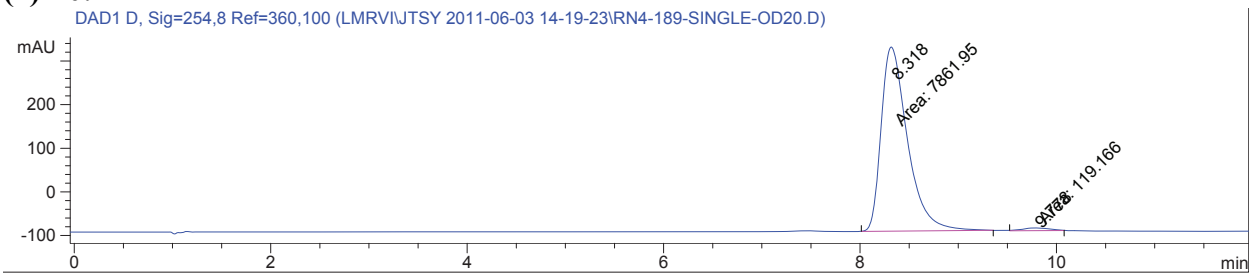
Method Information: OD-H column, 20% IPA, 12.0 minutes.

***rac*-10[4]:**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.394	MM	0.3287	654.14319	33.16994	51.4227
2	9.746	MM	0.3563	617.94702	28.90520	48.5773
Totals :				1272.09021	62.07514	

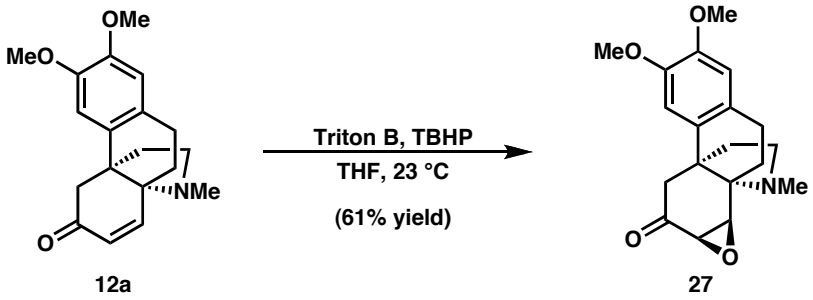
(–)-10:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.318	MM	0.3103	7861.95264	422.33008	98.5069
2	9.778	MM	0.3079	119.16633	6.45073	1.4931
Totals :				7981.11897	428.78081	

[4] ***rac*-10** was prepared using an identical synthetic sequence from racemic *tert*-butylsulfinamide in place of *(R)-tert*-butylsulfinamide.

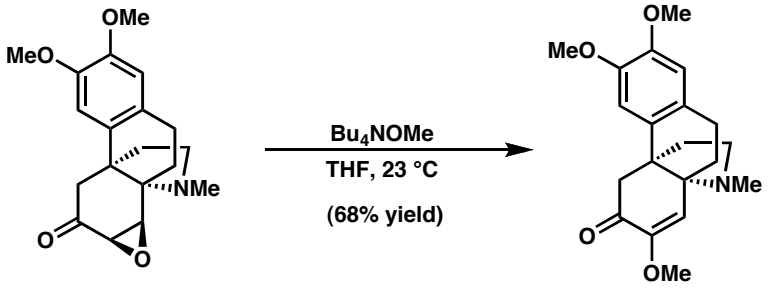
Preparation of Epoxyketone 27



12a 27

To a solution of enone **12a** (62.6 mg, 0.200 mmol, 1.0 equiv) in THF (2.0 mL) at 23 °C was added *tert*-butylhydroperoxide (143 μL of a 70% aq. solution, 1.0 mmol, 3.0 equiv.) and Triton B (73 μL of a 40% solution in methanol, 0.16 μmmol, 0.8 equiv) dropwise by syringe, and the solution stirred for 17 hours at room temperature (23 °C). The reaction was then quenched by the addition of a solution of saturated aqueous $Na_2S_2O_3$ (6 mL) and stirred for an additional 30 minutes. H_2O (15 mL) was then added, the solution extracted with CH_2Cl_2 (3 x 20 mL), and the organic layers combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a clear oil. Flash chromatography (30 to 50% EtOAc in hexanes) on Florisil (100 to 200 mesh) afforded epoxyketone **27** as a white foam (40.0 mg, 0.075 mmol, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.52 (s, 1H), 3.84 (s, 2H), 3.82 (s, 2H), 3.49 (d, J = 3.9 Hz, 1H), 3.32 (dd, J = 3.8, 1.0 Hz, 1H), 2.95 (d, J = 14.0 Hz, 1H), 2.77 (m, 3H), 2.63 (dt, J = 16.0, 3.9 Hz, 1H), 2.56 (s, 3H), 2.50 (dd, J = 14.0, 1.0 Hz, 1H), 2.21 – 2.16 (m, 2H), 2.10 (ddd, J = 13.2, 8.0, 5.3 Hz, 1H), 2.01 – 1.94 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.1, 147.8, 147.2, 134.5, 127.4, 110.7, 110.1, 60.5, 60.4, 56.0, 56.0, 55.7, 52.5, 51.4, 45.8, 37.2, 33.3, 24.9, 24.33; IR (NaCl/thin film): 2934, 2833, 2792, 1716, 1610, 1516, 1464, 1454, 1358, 1330, 1256, 1202, 1142, 1070, 1005, 973, 873, 853, 801, 733; HRMS (EI+) calc'd for $C_{19}H_{23}NO_4$ $[M+H]^+$ 330.1700, found 330.1710; $[\alpha]_D^{25}$: + 30 (*c* 0.70, CH_2Cl_2).

Preparation of 8-Demethoxyrunanine (1)

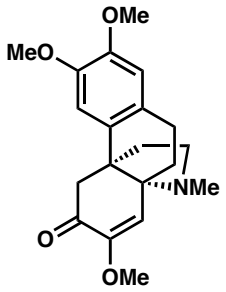


27 1

To epoxyketone **27** (40.8 mg, 0.124 mmol, 1.0 equiv) was added a freshly prepared solution of tetrabutylammonium methoxide[5] (2.5 mL of a 0.5 M solution in THF, 1.2 mmol, 10

[5] Tetrabutylammonium methoxide (Bu_4OMe) was prepared from tetrabutyl ammonium hydroxide as previously described. See V. Di Bussolo, M. Caselli, M. R. Romano, M. Pineschi, and P. Crotti. *J. Org. Chem*. 2004, *69*, 8702 – 8708.

equiv) by syringe and the solution was then heated to 50 °C for 11 hours. The reaction was then cooled, diluted with saturated aqueous sodium chloride (10 mL), and extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were then combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to isolate a brown oil that was purified by flash chromatography (SiO_2 deactivated with 0.5% Et_3N, 40 to 80% EtOAc in Hexanes) to isolate synthetic (–)-8-demethoxyrunanine **1** as a white foam (29.1 mg, 84.8 mmol, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.52 (s, 1H), 5.64 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.65 (s, 3H), 3.04 (d, *J* = 16.6 Hz, 1H), 2.92 (td, *J* = 9.3, 3.7 Hz, 1H), 2.87 (ddd, *J* = 15.9, 12.8, 4.9 Hz), 2.66 (d, *J* =16.4 Hz, 1H), 2.55 (ddd, *J* = 15.9, 5.0, 2.8 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.42 (s, 3H), 2.26 (ddd, *J* = 13.3, 9.6, 6.2 Hz, 1H), 2.09 – 1.99 (m, 2H), 1.80 (ddd, *J* = 13.9, 12.8, 5.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 151.2, 147.9, 147.1, 135.3, 126.4, 114.7, 111.1, 110.6, 63.7, 56.0, 55.8, 55.0, 51.5, 49.6, 48.1, 36.4, 33.5, 26.7, 25.0; IR (NaCl/thin film): 2926, 2848, 2832, 2787, 1693, 1624, 1515, 1463, 1451, 1376, 1356, 1282, 1257, 1217, 1205, 1156, 1136, 1114, 1095, 1066, 1051, 1013, 962, 883, 858, 800, 731, 665 cm^{-1}; HRMS (EI+) calc'd for $C_{20}H_{26}NO_4$ $[M+H]^+$ 344.1856, found 344.1863; $[\alpha]_D^{20}$: – 185 (*c* 0.51, $CHCl_3$).



(–)-8-*Demethoxyrunanine*

Comparison of Spectroscopic Data for Natural[6] and Synthetic 8–Demethoxyrunanine

^{1}H NMR Comparison Data

Reported	Synthetic
6.65 (s, 1H)	6.67 (s, 1H)
6.51 (s, 1H)	6.52 (s, 1H)
5.63 (s, 1H)	5.64 (s, 1H)
3.82 (s, 3H)	3.84 (s, 3H)
3.81 (s, 3H)	3.83 (s, 3H)
3.63 (s, 3H)	3.65 (s, 3H)
3.04 (d, *J* = 16.4 Hz, 1H)	3.04 (d, *J* = 16.6 Hz, 1H)
2.84 (m, 1H)	2.92 (td, *J* = 9.3, 3.7 Hz, 1H)
2.84 (m, 1H)	2.87 (ddd, *J* = 15.9, 12.8, 4.9 Hz)
2.65 (d, *J* = 16.4 Hz, 1H)	2.66 (d, *J* =16.4 Hz, 1H)
2.55 (ddd, *J* = 16.0, 4.8, 2.8 Hz, 1H)	2.55 (ddd, *J* = 15.9, 5.0, 2.8 Hz, 1H)
2.41 (s, 3H)	2.42 (s, 3H)
2.39 (m, 1H)	2.44 – 2.37 (m, 1H)
2.25 (m, 1H)	2.26 (ddd, *J* = 13.3, 9.6, 6.2 Hz, 1H)
2.05 (m, 1H)	2.09 – 1.99 (m, 2H)

[6] X. Wang, H. Jin, Z. Li, G. Qin, *Fitoterapia* **2007**, *78*, 593.

2.01 (ddd, J = 14.0, 4.8, 2.8 Hz, 1H)	–
1.79 (ddd, J = 14.0, 13.2, 4.8 Hz, 1H)	1.80 (ddd, J = 13.9, 12.8, 5.1 Hz, 1H)

^{13}C NMR Comparison Data

Reported	Synthetic
193.2	193.2
151.1	151.2
147.8	147.9
147.0	147.0
135.2	135.3
126.3	126.4
114.6	114.7
111.0	111.1
110.4	110.6
63.7	63.8
56.0	56.1
55.7	55.8
54.9	55.1
51.4	51.5
49.5	49.7
48.0	48.1
36.3	36.4
33.4	33.5
26.6	26.7
24.8	25.0

Optical Rotation

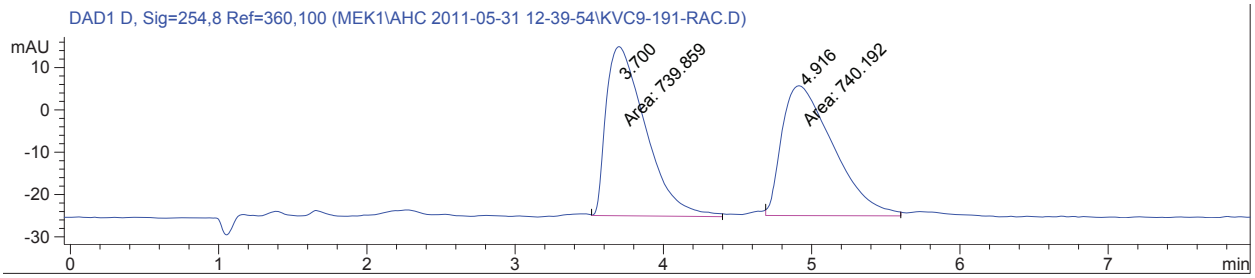
Natural	Synthetic
$[\alpha]_D^{20}$: – 244 (c 0.48, $CHCl_3$)	$[\alpha]_D^{20}$: – 185 (c 0.51, $CHCl_3$)*

* It was noted that synthetic (–)-8-demethoxyrunanine produced a significantly lower specific rotation than reported by the isolation paper. To eliminate the possibility of racemization during the reaction sequence, racemic 8-demethoxyrunanine was synthesized using racemic *tert-butylsulfinamide* in place of *(R)-tert*-butylsulfnamide by an identical sequence, and the enantiomeric excess of 8-demethoxyrunanine was determined to be > 98% ee by chiral SFC (see Chiral SFC Traces).

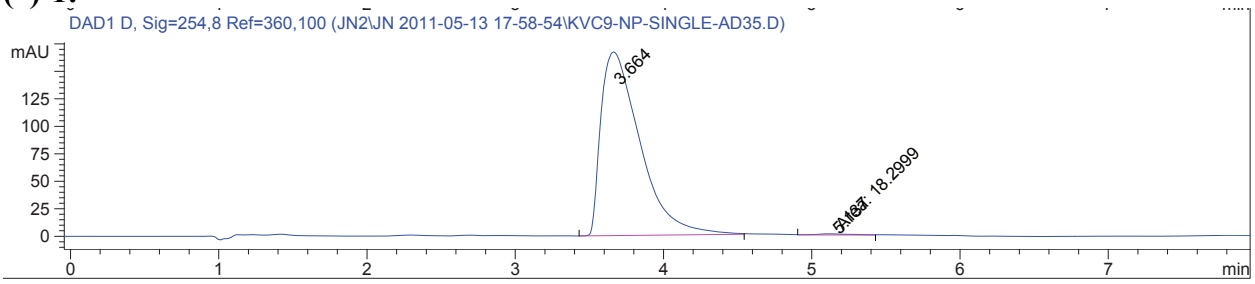
Chiral SFC Traces

Method Information:AD column, 35% IPA, 8.0 minutes.

***rac*-1[7]:**



(–)-1:

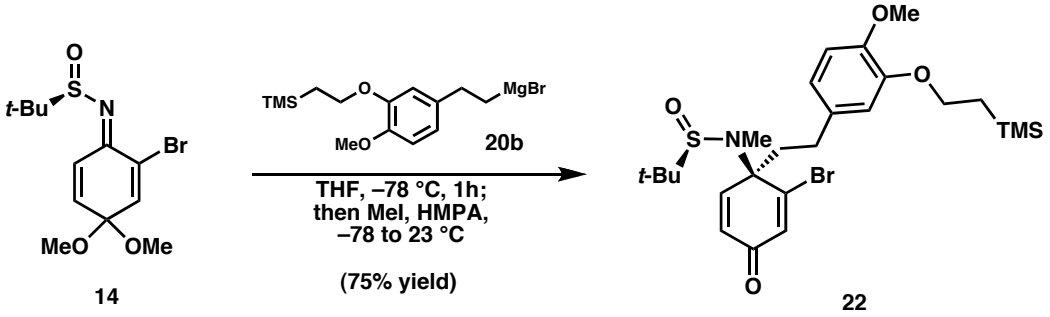


Signal 2: DAD1 D, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.664	BB	0.2798	3058.54810	166.89442	99.4052
2	5.137	MM	0.2913	18.29991	1.04703	0.5948
Totals :				3076.84801	167.94145	

[7] *Rac*-**1** was prepared using an identical synthetic sequence from racemic *tert*-butylsulfinamide in place of *(R)-tert*-butylsulfinamide.

Preparation of Dienone 22



To a solution of bromo-quinonesulfinylimine **14** (2.49 g, 7.42 mmol) in THF (15 mL) at –78 °C (dry ice/acetone) was added a solution of Grignard reagent **20b**[8] (0.51M solution in THF, 16.0 mL, 8.16 mmol) dropwise by syringe. The solution was then stirred at -78 °C for one hour, then methyl iodide (1.4 mL, 22 mmol) and hexamethylphosphoramide (3.9 mL, 22 mmol) sequentially added dropwise by syringe, and the solution stirred at – 78 °C for 10 minutes. The solution was then warmed to 23 °C and stirred for an additional 2.0 hours, then quenched by the addition of aqueous acetic acid (10% v/v, 30 mL). After 3.5 hours, the mixture was diluted with EtOAc (150 mL) and washed with H_2O (3 x 100 mL), and the aqueous layers combined and back extracted with EtOAc (3 x 100 mL). The ethereal layers were then combined, dried over $MgSO_4$, filtered, and concentrated in vacuo to afford a clear brown oil. The diastereoselectivity was determined by LC/MS: 96:4 d.r. (5→95% MeCN/H_2O, t = 0–10 min, 1 mL/min. Major diastereomer: t_R = 6.7 min, minor diastereomer: t_R = 7.2 min). Flash chromatography (20% to 50% EtOAc in Hexanes) afforded a single diastereomer (R_s,*R*) of dienone **22** as a white solid foam (3.09 g, 5.55 mmol, 75% yield).

Major Diastereomer (R_s,*R*) – 22

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.92 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 10.0 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.64 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 6.43 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.81 (s, 3H), 2.80 (td, *J* = 12.3, 5.0 Hz, 1H), 2.46 (s, 3H), 2.38 – 2.22 (m, 2H), 1.84 (td, *J* = 12.4, 5.2 Hz, 1H), 1.21 (s, 9H), 1.21 – 1.16 (m, 2H), 0.07 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.1, 150.7, 150.1, 148.3, 148.2, 136.4, 132.2, 129.6, 120.0, 113.4, 111.7, 68.8, 66.3, 59.2, 55.9, 38.2, 29.8, 26.7, 24.2, 17.8, – 1.4; IR (NaCl/thin film): 3045, 2951, 2900, 2866, 2834, 1670, 1640, 1592, 1515, 1463, 1455, 1442, 1425, 1360, 1292, 1253, 1236, 1156, 1137, 1079, 1055, 1032, 950, 886, 859, 839, 786; HRMS (EI+) calc'd for $C_{25}H_{38}BrNO_4SSi$ $[M+Na]^+$ 578.1366, found 578.1555; $[\alpha]_D^{25}$: + 16.9 (*c* 0.92, CH_2Cl_2).

Minor Diastereomer (R_s,*S*) – 22[9]

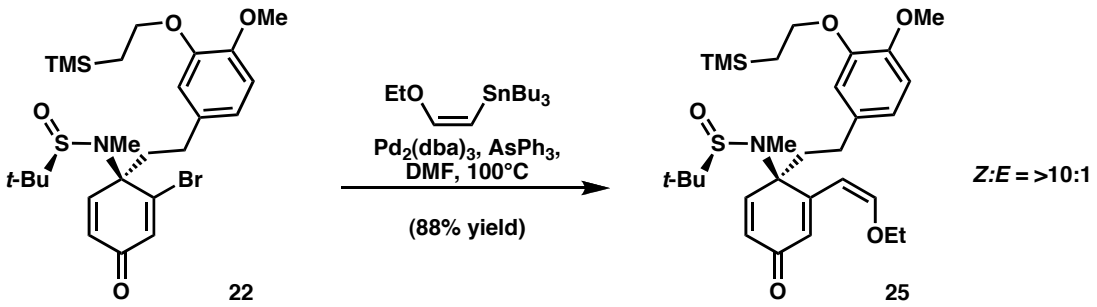
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, *J* = 10.0 Hz, 1H), 6.90 (d, *J* = 1.6 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.64 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.53 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.09 (m, *J* = 9.3, 7.6 Hz, 2H), 3.83 (s, 3H), 2.53 – 2.43 (m, 1H), 2.38 (d, *J* = 8.7 Hz, 3H), 2.37 – 2.27 (m, 2H), 2.26 – 2.15 (m, 3H), 1.28 (s, 9H), 1.25 – 1.15 (m, 2H), 0.08 (s, 9H); ^{13}C

[8] Grignard reagent **20b** was readily prepared from 3-trimethylsilylethoxy-4-methoxyphenethyl bromide and magnesium turnings (1.1 equiv), activated with catalytic diisobutylaluminum hydride, in refluxing THF.

[9] Minor diastereomer **(R_s,*S*) – 22** was inseparable from several impurities. ^{1}H and ^{13}C NMR data were tabulated from samples of ~85% purity and are listed for reference.

NMR (126 MHz, $CDCl_3$): δ 183.0, 149.9, 149.7, 148.3, 148.2, 136.4, 132.3, 130.9, 120.0, 113.4, 111.7, 68.8, 66.4, 59.8, 55.9, 38.9, 29.7, 27.3, 24.3, 17.8, –1.4.

Preparation of Trienone 25



To a solution of dienone **22** (1.28 g, 2.30 mmol, 1.0 equiv) in DMF (19 mL) was added tris(dibenzylideneacetone)dipalladium (105 mg, 0.115 mmol, 0.05 equiv), triphenylarsine (141 mg, 0.460 mmol 0.20 equiv) and *cis*-2-ethoxyvinyltributylstannane (0.84 mL, 2.53 mmol, 1.1 equiv). The solution was then thoroughly degassed with nitrogen for 30 minutes and the solution heated at 100 °C for 1 hour. Upon cooling to room temperature, the solution was passed through a short plug of Celite, diluted with EtOAc (200 mL), and washed with H_2O (3 x 100 mL). The aqueous layers were then combined and back extracted with EtOAc (3 x 75 mL), then the organic layers combined, washed with brine (1 x 250 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a light brown oil. Flash chromatography (50% to 100% EtOAc in hexanes) afforded **25** (>10:1 mixture of *Z:E*-isomers by ^{1}H NMR) as a tan solid (1.11 g, 88% yield).

(Z)-**25**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 7.1 Hz, 1H), 6.59 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.55 (d, *J* = 10.0 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.38 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.17 (d, *J* = 7.3 Hz, 1H), 4.09 – 4.02 (m, 4H), 3.81 (s, 3H), 2.51 (ddd, *J* = 12.7, 10.3, 7.1 Hz, 1H), 2.45 (s, 3H), 2.33 – 2.26 (m, 2H), 1.90 – 1.80 (m, 1H), 1.35 (t, *J* = 7.08 Hz, 3H), 1.24 (s, 9H), 1.21 – 1.16 (m, 2H), 0.07 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.7, 154.8, 153.6, 149.5, 148.2, 148.0, 133.2, 130.5, 128.8, 119.9, 113.5, 111.6, 98.8, 70.7, 66.6, 66.3, 58.9, 55.9, 38.3, 29.9, 27.1, 24.4, 17.8, 15.4, –1.4; IR (NaCl/thin film): 2952, 2899, 2834, 1661, 1623, 1576, 1515, 1453, 1384, 1302, 1258, 1157, 1137, 1099, 1055, 957, 896, 859, 839, 803, 767 cm^{-1}; HRMS (EI+) calc'd for $C_{29}H_{45}NO_5SSi$ $[M+H]^+$ 547.2860, found 548.2850; $[\alpha]_D^{25}$: – 66 (*c* 1.34, CH_2Cl_2).

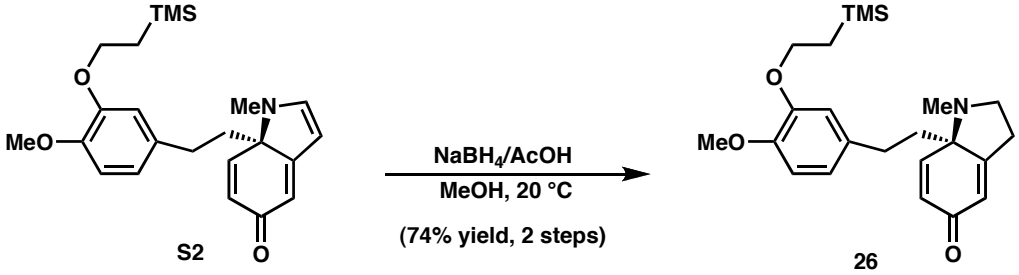
(E)–**25**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, *J* = 12.7 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.59 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 6.45 (dd, *J* = 2.0, 0.5 Hz, 1H), 6.39 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.81 (d, *J* =12.8 Hz, 1H), 4.09 – 4.04 (m, 2H), 3.98 (q, *J* = 4.0 Hz, 2H), 3.82 (s, 3H), 2.48 (td, *J* = 12.5, 4.8 Hz, 1H), 2.46 (s, 3H), 2.35 – 2.17 (m, 2H), 1.89 (td, *J* = 12.3, 4.9 Hz, 1H), 1.35 (t, *J* = 7.0 Hz, 1H), 1.26 (s, 9H), 1.22 – 1.17 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.7, 157.4, 153.7, 149.8, 148.3, 148.1, 133.0, 130.6, 122.3, 120.0, 113.5, 111.7, 100.2, 67.1, 66.4, 66.0, 59.9, 56.0, 38.3, 29.8, 27.4, 24.5, 17.9, 14.5, – 1.4.; IR (NaCl/thin film): 2951, 2926, 1660, 1620, 1580, 1515, 1456, 1442, 1386, 1361,

1329, 1256, 1235, 1213, 1140, 1069, 1033, 948, 859, 838 cm^{-1}. HRMS (EI+) calc'd for $C_{29}H_{45}NO_5SSi$ $[M+H]^+$ 547.2860, found 548.2857; $[\alpha]_D^{25}$: – 71 (*c* 0.20, CH_2Cl_2).

Preparation of Enamine S2

To a solution of trienone 25 (702 mg, 1.28 mmol, 1.0 equiv) in THF (12.8 mL) at 0 °C in an ice/water bath was added a solution of hydrogen chloride (2.0 M solution in Et_2O, 12.8 mL, 25.6 mmol) dropwise by syringe over one minute. The reaction was allowed to stir for 15 minutes at 0 °C and then quenched by the addition of aqueous potassium hydroxide (10% w/v, 13 mL) and stirred for an additional 5 minutes. The mixture was then diluted with H_2O (50 mL), and extracted with EtOAc (3 x 50 mL). The organic layers were then combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to isolate a bright red foam. Column chromatography (2% MeOH in CH_2Cl_2) afforded a red foam of adequate purity for the next step. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (dd, *J* = 9.7, 0.5 Hz, 1H), 6.89 (d, *J* = 3.17 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 8.1, 2.2 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.18 (dd, *J* = 9.9, 1.6 Hz, 1H), 5.91 (d, *J* = 1.5 Hz, 1H), 5.49 (dd, *J* = 3.3, 0.6 Hz, 1H), 4.08 – 4.04 (m, 2H), 3.81 (s, 3H), 3.05 (s, 1H), 2.42 – 2.31 (m, 2H), 2.11 – 1.99 (m, 2H), 1.19 – 1.16 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.8, 174.5, 153.3, 148.3, 148.0, 140.1, 132.8, 131.2, 120.0, 113.6, 111.7, 110.0, 99.7, 72.7, 66.4, 56.0, 45.7, 31.6, 29.1, 17.9, –1.4; IR (NaCl/thin film): 2951, 2916, 1631, 1569, 1514, 1424, 1248, 1157, 1137, 1108, 108, 1050, 1032, 859, 837, 649; HRMS (EI+) calc'd for $C_{23}H_{31}NO_3Si$ $[M+H]^+$ 398.2146, found 398.2149; $[\alpha]_D^{25}$: –1185 (*c* 0.22, CH_2Cl_2).

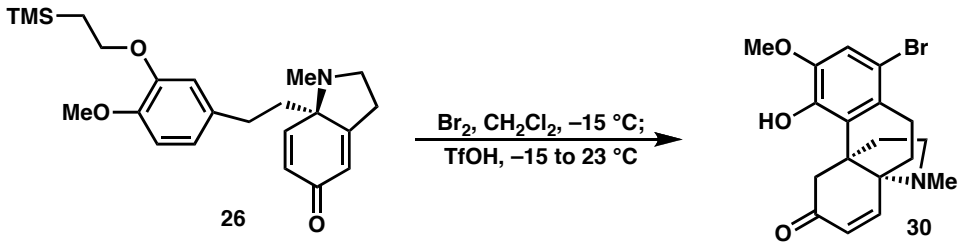
Preparation of Amine 26



To a solution of enamine **S2** in MeOH (26 mL) at 23 °C was added a solution of $NaBH_4$ (97 mg, 2.56 mmol) in AcOH (9.8 mL), dropwise by syringe. The solution was stirred at 20 °C for 1 hour, then a second portion of $NaBH_4$ (97 mg, 2.56 mmol) in AcOH (9.8 mL) was added and stirring continued for one additional hour. The reaction was cooled to 0 °C in an ice/water

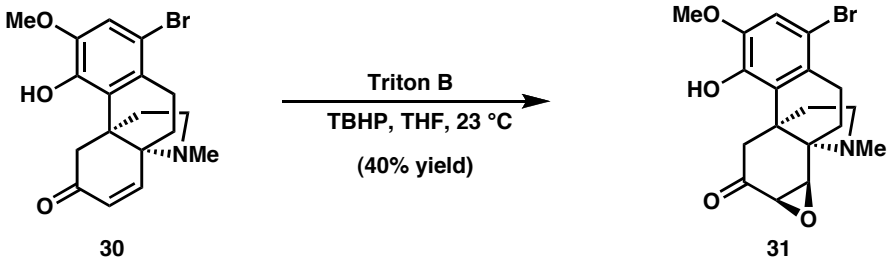
bath and neutralized by the slow addition of aqueous potassium hydroxide (30% w/v, 65 mL). The solution was then diluted with H_2O (50 mL) and extracted with EtOAc (3 x 100 mL) and the organic layers combined, then dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography (2% MeOH in CH_2Cl_2) afforded amine **26** as a yellow oil (379 mg, 0.948 mmol, 77% yield over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98 (d, *J* = 10.0 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.61 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.56 (d, *J* = 1.7 Hz, 1H), 6.34 (dd, *J* = 10.0, 1.5 Hz, 1H), 6.20 (app d, *J* = 1.7 Hz, 1H), 4.10 – 4.05 (m, 2H), 3.82 (s, 3H), 3.18 (ddd, *J* = 10.5, 8.5, 4.2 Hz, 1H), 3.05 (td, *J* = 10.0, 7.0 Hz, 1H), 2.79 – 2.68 (m, 2H), 2.42 (s, 3H), 2.36 (ddd, *J* = 13.9, 10.7, 6.4 Hz, 1H), 2.22 (ddd, *J* = 14.0, 10.9, 6.5 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.22 – 1.17 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.7, 167.0, 148.2, 147.9, 146.0, 133.5, 130.2, 123.3, 119.8, 113.4, 111.6, 66.6, 66.3, 56.0, 51.6, 36.5, 32.0, 29.6, 27.8, 17.9, – 1.4; IR (NaCl/thin film): 2949, 2850, 1669, 1644, 1606, 1589, 1514, 1442, 1424, 1305, 1253, 1234, 1176, 1150, 1137, 1032, 1013, 942, 890, 859, 839, 695; HRMS (EI+) calc'd for $C_{23}H_{33}NO_3Si$ $[M+H]^+$ 400.2302, found 400.2283;

Preparation of Bromopropellane 30



To a solution of amine **26** (414 mg, 1.04 mmol, 1.0 equiv) in CH_2Cl_2 (21 mL) at –15 °C (ice/NaCl) was added bromine (80 μL, 1.55 mmol, 1.5 equiv) dropwise by syringe. The solution was stirred for 20 minutes, then trifluoromethanesulfonic acid (550 μL, 6.22 mmol, 6.0 equiv) was added dropwise by syringe and the solution was warmed to room temperature (23 °C). After 12 minutes, the reaction was quenched by the slow dropwise addition of saturated aqueous sodium bicarbonate (50 mL) and the reaction diluted with CH_2Cl_2 (60 mL) and washed with aqueous sodium bicarbonate (2 x 100 mL). The aqueous layers were then back extracted with CH_2Cl_2 (1 x 100 mL), the organic layers combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a light brown foam. Flash chromatography (20 to 30% EtOAc in hexanes) afforded propellane **30** as an off-white amorphous solid (302 mg, 0.798 mmol, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98 (s, 1H), 6.82 (d, *J* = 10.3 Hz, 1H), 6.15 (dd, *J* = 10.4, 1.1 Hz, 1H), 5.95 (s, 1H), 3.86 (s, 3H), 3.62 (dd, *J* = 16.6, 1.2 Hz, 1H), 2.89 – 2.81 (m, 2H), 2.69 – 2.55 (m, 2H), 2.44 (s, 3H), 2.41 – 2.36 (m, 1H), 2.04 – 1.96 (m, 2H), 1.77 – 1.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.3, 149.7, 145.4, 143.2, 130.8, 130.2, 127.4, 114.0, 112.9, 63.2, 56.4, 51.6, 48.0, 43.8, 33.4, 33.2, 25.8, 24.8; IR (NaCl/thin film): 3338, 2926, 2850, 2790, 1673, 1601, 1470, 1436, 1420, 1388, 1357, 1314, 1314, 1276, 1235, 1125, 1064, 1038, 879, 785. HRMS (EI+) calc'd for $C_{18}H_{20}BrNO_3$ $[M+H]^+$ 378.0699, found 378.0683. $[\alpha]_D$ ^{25}: –226 (*c* 0.42, CH_2Cl_2).

Preparation of Epoxyketone 31

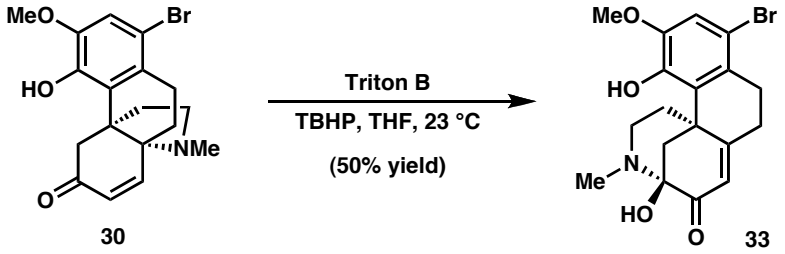


30 31

To a solution of enone **30** (13.3 mg, 0.035 mmol, 1.0 equiv) in THF (0.70 mL) at 28 °C was added *tert*-butylhydroperoxide (100 μL of a 5.5M solution, 0.550 mmol, 16.0 equiv.) and Triton B (0.05 mL of a 40% solution in methanol, 105 μmmol, 3.0 equiv) dropwise by syringe, and the solution stirred for 16 hours at 28 °C. The reaction was then quenched by the addition of a solution of saturated aqueous $Na_2S_2O_3$ (2 mL) and stirred for an additional 30 minutes. H_2O (10 mL) was then added, the solution extracted with CH_2Cl_2 (3 x 15 mL), and the organic layers combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a clear oil. Flash chromatography (1 to 2% MeOH in CH_2Cl_2) on Florisil afforded epoxyketone **31** as a white foam (5.3 mg, 0.014 mmol, 40% yield).^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (s, 1H), 5.93 (s, 1H), 3.84 (s, 3H), 3.51 (d, *J* = 3.91 Hz, 1H), 3.29 (dd, *J* = 3.91, 1.0 Hz, 1H), 3.21 (dd, *J* = 14.2, 1.0 Hz, 1H), 2.95 – 2.81 (m, 2H), 2.74 – 2.64 (m, 1H), 2.67 (d, *J* = 13.9 Hz, 1H), 2.58 (ddd, *J* = 16.6, 11.8, 6.3 Hz, 1H), 2.51 (s, 3H), 2.42 (ddd, *J* = 14.4, 9.3, 6.8 Hz), 2.20 – 2.09 (m, 2H), 2.06 – 1.96 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 207.4, 145.3, 142.8, 130.3, 127.8, 113.9, 113.0, 60.7, 59.2, 56.4, 55.6, 51.8, 51.4, 40.3, 34.0, 33.3, 25.7, 23.2; IR (NaCl/thin film): 3420, 2937, 2791, 1717, 1603, 1470, 1436, 1356, 1313, 1277, 1238, 876 cm^{-1}; HRMS (EI+) calc'd for $C_{18}H_{20}BrNO_4$ $[M+H]^+$ 394.0648, found 394.0632; $[\alpha]^{25}_D$: – 11 (*c* 0.24, CH_2Cl_2).

Longer epoxidation times and additional equivalents of Triton B resulted in higher overall conversion, but resulted in an oxidative rearrangement of the desired epoxide into an unidentified lactone side product: ^{1}H NMR (300 MHz, $CDCl_3$): 6.99 (s, 1H), 4.44 (d, *J* = 1.9 Hz, 1H), 3.83 (s, 3H), 3.04 – 2.83 (m, 5H), 2.83 – 2.64 (m, 3H), 2.36 (s, 3H), 2.20 (ddd, *J* = 18.4, 12.7, 4.0 Hz, 3H), 2.04 – 1.80 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 176.4, 145.2, 142.1, 130.1, 127.1, 115.0, 114.0, 85.0, 80.4, 73.9, 56.3, 55.6, 54.4, 41.9, 34.2, 27.3, 23.7; IR (NaCl/thin film): 3351, 2930, 2849, 2791, 1784, 1605, 1470, 1434, 1292, 1274; HRMS (EI+) calc'd for $C_{18}H_{20}BrNO_5$ $[M+H]^+$ 410.0598, found 410.0599.

Preparation of Hemiaminal 33

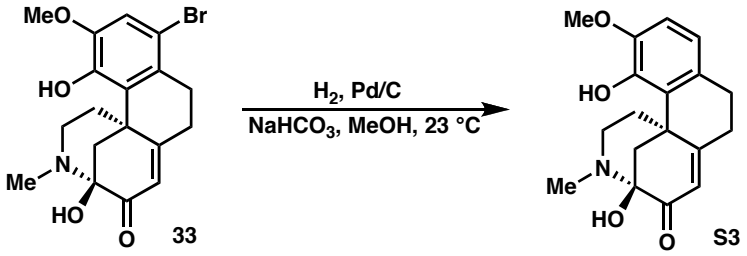


30 33

To a solution of enone **30** (105.5 mg, 0.279 mmol, 1.0 equiv) in THF (5.6 mL) at 23 °C was added *tert*-butylhydroperoxide (1.01 mL of a 5.5M solution in decane, 5.58 mmol, 20.0

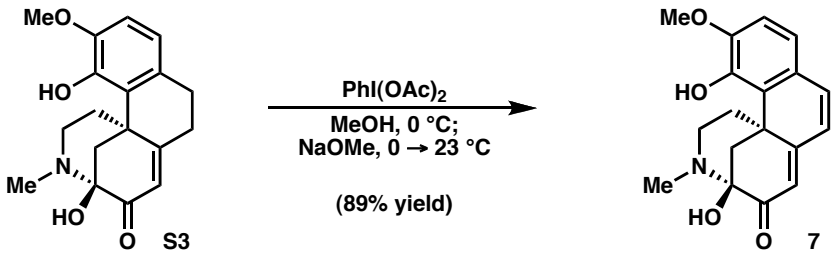
equiv) and Triton B (0.64 mL of a 40% solution in methanol, 1.40 mmol, 5.0 equiv) dropwise by syringe, and the solution stirred for 18.5 hours at room temperature (23 °C). The reaction was then quenched by the addition of saturated aqueous $Na_2S_2O_3$ (10 mL) and saturated ammonium chloride (5 mL), then stirred for an additional 30 minutes. H_2O (15 mL) was then added, the solution extracted with CH_2Cl_2 (3 x 30 mL), and the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a clear oil. The oil was then redissolved in CH_2Cl_2 (2 mL) and concentrated onto dry SiO_2 and allowed to sit for 2 hours. Flash chromatography (1 to 4% MeOH in CH_2Cl_2) afforded hemiaminal **33** as a light yellow foam (55.2 mg, 0.140, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (s, 1H), 6.19 (br s, 1H), 6.16 (d, J = 1.3 Hz, 1H), 4.17 (br s, 1H), 3.88 (s, 3H), 3.42 (d, J = 12.7 Hz, 1H), 3.36 (td, J = 13.2, 5.6 Hz, 1H), 3.28 – 3.21 (m, 1H), 3.01 (ddd, J = 12.2, 5.5, 1.4 Hz, 1H), 2.65 – 2.53 (m, 2H), 2.52 – 2.43 (m, 2H), 2.21 (s, 3H), 1.91 (dd, J = 12.7, 2.7 Hz, 1H), 1.42 (dddd, J = 13.5, 4.1, 2.6, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 194.8, 167.6, 145.9, 144.1, 128.4, 127.2, 123.8, 113.7, 113.6, 83.2, 77.3, 77.0, 76.8, 56.4, 49.1, 44.8, 42.0, 36.1, 31.7, 31.1, 29.1; IR (NaCl/thin film): 3447, 2929, 2841, 1665, 1599, 1471, 1436, 1275, 1234, 1179, 1-83, 1035, 885; HRMS (EI+) calc'd for $C_{18}H_{20}BrNO_4$ $[M+H]^+$ 394.0648, found 330.0649; $[\alpha]_D^{25}$ = – 179 (*c* 0.79, CH_2Cl_2).

Preparation of Dihydrocepharatine A (S3)

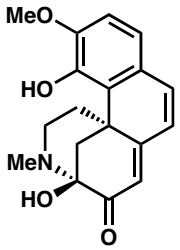


To a solution of bromohemiaminal **33** (32.8 mg, 0.083 mmol, 1.0 equiv) in MeOH (0.83 mL) at 23 °C was added sodium bicarbonate (42 mg, 0.50 mmol, 6.0 equiv) and Pd/C (3.2 mg of 10 wt% palladium on activated carbon). The solution was then placed under an atmosphere of hydrogen and the solution stirred for 1.5 hours at room temperature (23 °C). The reaction was then diluted with EtOAc, filtered through a plug of Celite, and concentrated in vacuo to isolate a a yellow oil. Flash chromatography (1 to 4% MeOH in CH_2Cl_2) afforded hemiaminal **S3** as a white foam (20.8 mg, 0.066 mmol, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.73 (d, J = 8.3 Hz, 1H), 6.61 (app d, J = 8.3 Hz, 1H), 6.19 (br s, 1H), 6.15 (d, J = 1.2 Hz, 1H), 4.18 (br s, 1H), 3.88 (s, 2H), 3.44 (d, J = 12.7 Hz, 1H), 3.34 (td, J = 13.2, 5.6 Hz, 1H), 3.01 (ddd, J = 12.2, 5.5, 1.4 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.61 – 2.42 (m, 3H), 2.22 (s, 3H), 1.99 (dd, J = 12.7, 2.7 Hz, 1H), 1.41 (dddd, J = 13.5, 4.1, 2.7, 1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 168.7, 145.6, 144.5, 129.4, 125.5, 124.0, 119.3, 109.1, 83.3, 77.3, 77.0, 76.8, 56.2, 49.2, 44.5, 42.2, 36.1, 31.7, 31.1, 29.3; IR (NaCl/thin film): 3469, 2934, 2842, 2801, 1664, 1484, 1440, 1277, 1234, 1189, 1079, 965; HRMS (EI+) calc'd for $C_{18}H_{21}NO_4$ $[M+H]^+$ 316.1543, found 316.1541; $[\alpha]_D^{25}$ = – 284 (*c* 0.21, CH_2Cl_2).

Preparation of Cepharatine A (7)



To a solution of hemiaminal **S3** (14.1 mg, 44.8 μmol, 1.0 equiv) in MeOH (0.89 mL) at 0 °C was added a solution of iodobenzene diacetate (15.1 mg, 47 μmol, 1.05 equiv) dropwise by syringe. The solution was stirred for 20 minutes, a solution of sodium methoxide (0.5 M in MeOH, 0.224 mmol, 5.0 equiv) was added dropwise to afford a bright orange solution. After 5 minutes, the reaction was warmed to room temperature and stirred for 20 minutes, then quenched with saturated aqueous ammonium chloride (5 mL), then diluted with H_2O and extracted with EtOAc (3 x 5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo to afford a yellow-orange oil. Flash chromatography on silica gel (deactivated with 0.5% Et_3N, 1 to 3% MeOH in CH_2Cl_2 eluent) afforded cepharatine A (12.5 mg, 40.0 μmol, 89% yield) as a yellow-orange foam. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (d, J = 8.3 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 6.70 (d, J = 9.3 Hz, 1H), 6.29 (d, J = 9.3 Hz, 1H), 6.28 (br s, 1H), 6.12 (s, 1H), 4.29 (br s, 1H), 3.93 (s, 3H), 3.91 (d, J = 13.0 Hz, 1H), 2.91 – 2.84 (m,1H), 2.74 – 2.58 (m, 2H), 2.24 (s, 3H), 2.22 (dd, J = 13.0 Hz, 1H), 1.38 (ddd, J = 6.1, 4.7, 2.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 194.1, 161.4, 148.1, 144.4, 136.0, 125.6, 125.5, 124.1, 123.4, 121.3, 108.7, 83.2, 56.2, 46.6, 44.4, 43.5, 36.2, 31.2; IR (NaCl/thin film): 3447, 2929, 2839, 1648, 1609, 1563, 1483, 1440, 1273, 1239, 1192, 1272, 1075, 969 cm^{-1}; HRMS (EI+) calc'd for $C_{18}H_{19}NO_4$ $[M+H]^+$ 314.1387, found 314.1393; $[\alpha]^{15}_D$ = –537 (*c* 0.38, $CHCl_3$).



(–)-*Cepharatine A*

Comparison of Spectroscopic Data for Natural[3] and Synthetic (–)-Cepharatine A

^{1}H NMR Data (both spectra are referenced to 7.27 ppm)

Reported[3]	**Synthetic**
6.79 (d, J = 8.4 Hz, 1H)	δ 6.79 (d, J = 8.2 Hz, 1H),
6.77 (d, J = 8.4 Hz, 1H)	6.77 (d, J = 8.2 Hz, 1H)
6.71 (d, J = 9.6 Hz, 1H)	6.71 (d, J = 9.3 Hz, 1H)
6.29 (d, J = 9.6 Hz, 1H)	6.30 (d, J = 9.4 Hz, 1H)
-	6.29 (br s, 1H)
6.13 (s, 1H)	6.13 (s, 1H)
4.32 (br s, 1H)	4.30 (br s, 1H)

3.94 (s, 3H)	3.94 (s, 3H)
3.95 (d, J = 12.8 Hz, 1H)	3.92 (d, J = 13.0 Hz, 1H)
2.90 (m, 1H)	2.92 – 2.85 (m, 1H)
2.74 (m, 1H)	2.75 – 2.59 (m, 2H)
2.66 (m, 1H)	-
2.25	2.25 (s, 3H)
2.19 (m, 1H)	2.23 (dd, J = 13.0, 2.7 Hz, 1H),
1.40 (m, 1H)	1.38 (ddd, J = 6.1, 4.7, 2.2 Hz, 1H)

^{13}C NMR Comparsion Data (both spectra are referenced to 77.0 ppm)

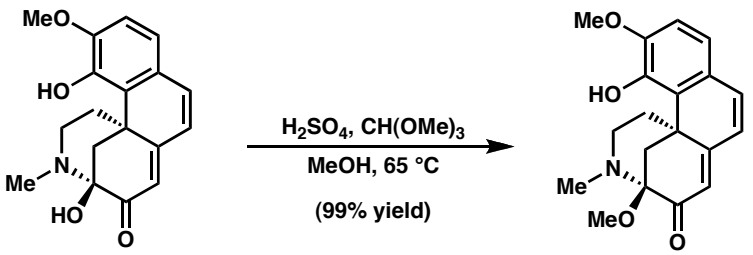
Reported	**Synthetic**
194.0	194.1
161.6	161.4
148.1	148.1
144.4	144.4
136.1	136.0
125.5	125.6
125.4	125.5
124.0	124.1
123.3	123.4
121.2	121.3
108.7	108.7
83.2	83.2
56.1	56.2
46.6	46.6
44.3	44.4
43.4	43.5
36.2	36.2
31.1	31.2

Optical Rotation

Natural	**Synthetic**
$[\alpha]^{15}_{D}$: –716 (c 0.98, $CHCl_3$)	$[\alpha]^{15}_{D}$ = –537 (c 0.38, $CHCl_3$)*

Preparation of Cepharatine C (XX)

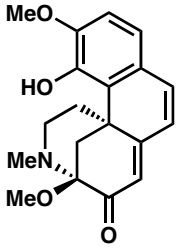
* It was noted that synthetic (–)-cepharatine A produced a lower specific rotation than that reported. It is inferred, based on the total syntheses of 8-demethoxyrunanine and cepharatine D, that the lower observed rotation does not necessarily imply any loss of enantiomeric excess (see above).



7 **8**

To a solution of cepharatine A (7.5 mg, 23.0 μmol mmol, 1.0 equiv) in MeOH (0.46 mL) was added trimethyl orthoformate (0.05 mL) and sulfuric acid (0.050 mL of a 1M solution in methanol). The solution was then stirred for 1 hour at 65 °C, cooled to room temperature, then slowly quenched with saturated aqueous sodium bicarbonate (3 mL) and extracted with EtOAc (4 x 3 mL). The organic layers were then combined, dried over Na_2SO_4, and concentrated in vacuo to isolate a yellow oil. Flash chromatography (0.5 to 4% MeOH in CH_2Cl_2) afforded cepharatine C (**8**) as a yellow-orange foam (7.4 mg, 22.6 μmol, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 9.3 Hz, 1H), 6.26 (t, *J* = 4.7 Hz, 1H), 6.26 (s, 1H), 6.07 (s, 1H), 3.94 (d, *J* = 12.5 Hz, 1H), 3.94 (s, 3H), 3.38 (s, 3H), 2.90 – 2.81 (m, 1H), 2.64 – 2.53 (m, 1H), 2.20 (s, 1H), 2.15 (dd, *J* = 12.4, 2.6 Hz, 1H), 1.44 – 1.34 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.7, 158,0, 147.8, 144.2, 135.0, 126.7, 125.9, 125.5, 123.6, 121.1, 108.7, 87.4, 56.2, 48.6, 46.6, 43.7, 38.8, 36.6, 31.3; ^{1}H NMR (300 MHz, methanol-d4): δ 6.88 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 9.4 Hz, 1H), 6.30 (d, *J* = 9.5 Hz, 1H), 6.02 (s, 1H), 4.14 (d, *J* = 12.5 Hz, 1H), 3.89 (s, 3H), 3.31 (s, 3H), 2.83 (ddd, *J* = 11.7, 4.8, 1.6 Hz, 1H), 2.66 (td, *J* = 12.8, 4.8 Hz, 1H), 2.51 (ddd, *J* = 12.9, 11.6, 3.4 Hz, 1H), 2.10 (s, 3H), 2.02 (dd, *J* = 12.5, 1.3 Hz, 1H), 1.34 – 1.27 (m, 1H); ^{13}C NMR (126 MHz, methanol-*d4*): δ 193.4, 162.6, 150.8, 146.4, 137.9, 126.8, 126.7, 126.5, 123.7, 122.6, 110.5, 88.9, 56.6, 47.7, 45.4, 40.2, 36.9, 32.0; IR (NaCl/thin film): 3338, 2923, 2849, 1658, 1612, 1566, 1483, 1440, 1296, 1274, 1083, 1022, 878 cm^{-1}; HRMS (EI+) calc'd for $C_{19}H_{21}NO_4$ $[M+H]^+$ 328.1543, found 330.1546; $[\alpha]^{16}_D$ = – 550 (*c* 0.38, MeOH).



(–)-*Cepharatine C*

Comparison of Spectroscopic Data for Natural[3] and Synthetic (–)-Cepharatine C

^{1}H NMR Data (both spectra are referenced to 3.30 ppm)

Reported[3]	Synthetic
6.88 (d, *J* = 8.4 Hz, 1H)	6.88 (d, *J* = 8.4 Hz, 1H)
6.80 (d, *J* = 9.2 Hz, 1H)	6.79 (d, *J* = 8.2 Hz, 1H)
6.77 (d, *J* = 8.4 Hz, 1H)	6.76 (d, *J* = 9.4 Hz, 1H)
6.30 (d, *J* = 9.2 Hz, 1H)	6.30 (d, *J* = 9.5 Hz, 1H)

6.03 (s, 1H)	6.02 (s, 1H)
4.14 (d, J = 12.4 Hz, 1H)	4.14 (d, J = 12.5 Hz, 1H)
3.90 (s, 3H)	3.89 (s, 3H)
3.31 (s, 3H)	3.31 (s, 3H)
2.85 (m, 1H)	2.83 (ddd, J = 11.7, 4.8, 1.6 Hz, 1H)
2.69 (m, 1H)	2.66 (td, J = 12.8, 4.8 Hz, 1H)
2.55 (m, 1H)	2.51 (ddd, J = 12.9, 11.6, 3.4 Hz, 1H)
2.10 (s, 3H)	2.10 (s, 3H)
2.02 (m, 1H)	2.02 (dd, J = 12.5, 1.3 Hz, 1H)
1.29 (m, 1H)	1.34 – 1.27 (m, 1H)

^{13}C NMR Comparsion Data (both spectra are referenced to 49.0 ppm)

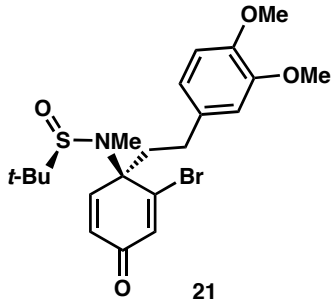
Reported	**Synthetic**
δ 193.6	δ 193.5
162.7	162.6
150.8	150.8
146.5	146.5
137.9	137.9
126.8	126.8
126.7	126.7
126.4	126.5
123.7	123.7
122.6	122.6
110.4	110.5
88.8	88.9
56.6	56.6
49.0	_[10]
47.7	47.7
45.4	45.4
40.1	40.2
36.9	36.9
32.0	32.0

Optical Rotation

Natural	**Synthetic**
$[\alpha]^{20}_{D}$: –332 (*c* 1.01, MeOH)	$[\alpha]^{15}_{D}$ = –550 (*c* 0.56, MeOH)

[10] The corresponding resonance is obscured by the residual solvent peak. Acquisition in $CDCl_3$ shows the analogous signal at δ 48.6 ppm.

III. Crystallographic Information Data for



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By Michael W. Day (e-mail: mikeday@caltech.edu)

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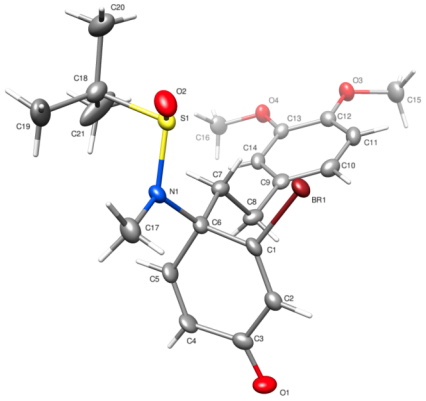
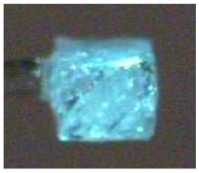


KVC01

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC) and has been placed on hold pending further instructions from me. The deposition number is 818651. Ideally the CCDC would like the publication to contain a footnote of the type: "Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 818651."

Table 1. Crystal data and structure refinement for KVC01 (CCDC 818651).

Empirical formula	$C_{21}H_{28}BrNO_4S$
Formula weight	470.41
Crystallization Solvent	Chloroform/pentane
Crystal Habit	Block
Crystal size	0.23 x 0.20 x 0.19 mm^3
Crystal color	Colorless



Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9986 reflections used in lattice determination	2.71 to 33.39°	
Unit cell dimensions	a = 8.1363(3) Å b = 15.9105(7) Å c = 17.0536(7) Å	α= 90° β= 90° γ = 90°
Volume	2207.63(16) $Å^3$	
Z	4	
Crystal system	Orthorhombic	
Space group	$P\ 2_12_12_1$	
Density (calculated)	1.415 Mg/m^3	
F(000)	976	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	2.39 to 34.32°	
Completeness to θ = 34.32°	99.8 %	
Index ranges	$-12 \le h \le 12, -24 \le k \le 25, -27 \le l \le 26$	
Data collection scan type	ω scans; 7 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	42377	
Independent reflections	9182 [R_{int}= 0.0360]	
Absorption coefficient	1.982 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.7045 and 0.6585	

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	9182 / 0 / 365
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.480
Final R indices [I>2σ(I), 7639 reflections]	R1 = 0.0305, *w*R2 = 0.0353
R indices (all data)	R1 = 0.0403, *w*R2 = 0.0356
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.005
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	-0.006(3)
Largest diff. peak and hole	2.073 and -0.783 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

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

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

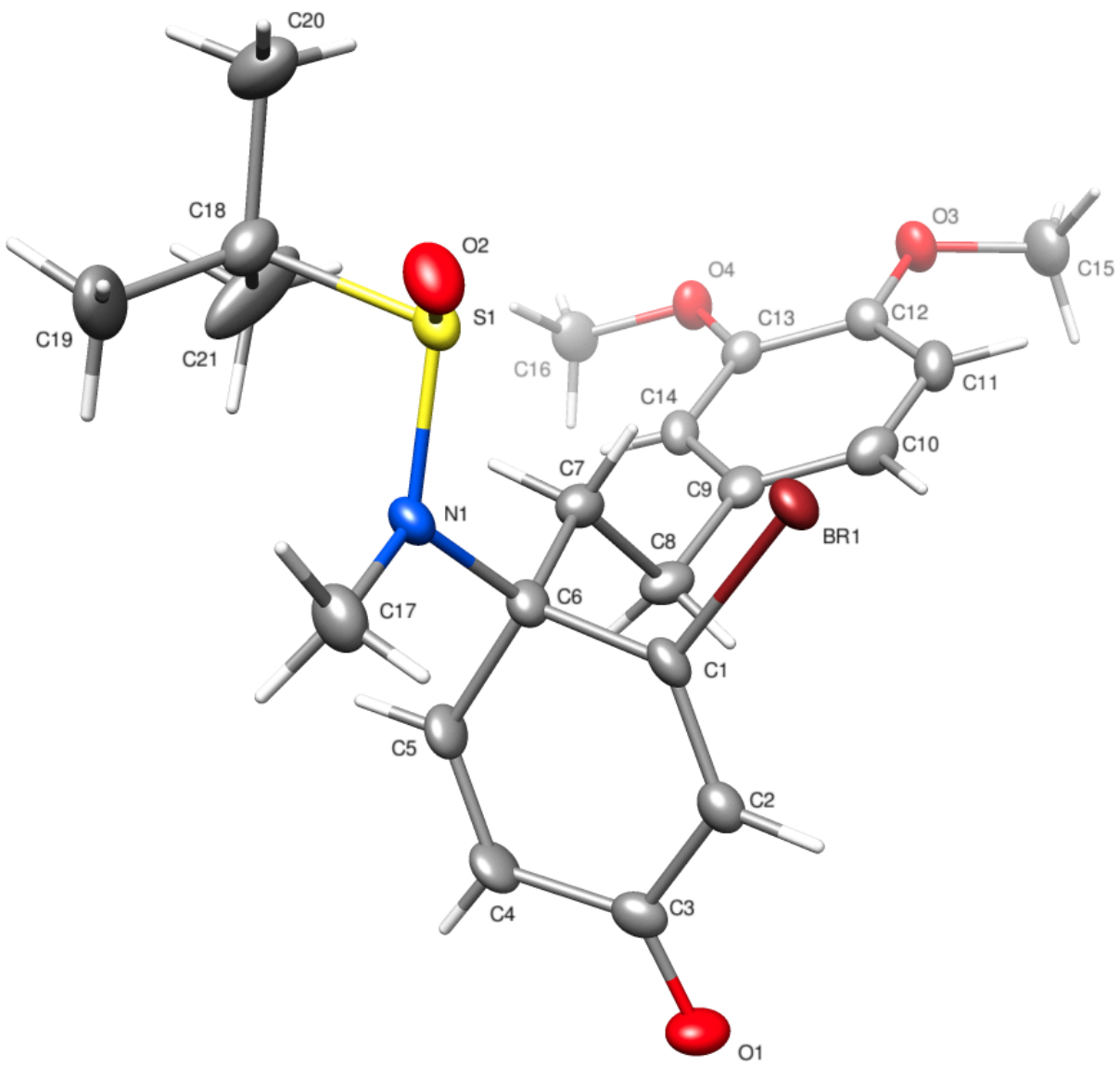

C20
C18
O2
S1
C19
C21
O4
O3
C15
C13
C12
C16
C11
C14
C10
C7
C9
N1
BR1
C8
C17
C6
C1
C5
C2
C4
C3
O1

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for KVC01 (CCDC 818651). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br(1)	4368(1)	11388(1)	-215(1)	21(1)
S(1)	3998(1)	10452(1)	1554(1)	24(1)
O(1)	10613(1)	11690(1)	-578(1)	29(1)
O(2)	2952(1)	11193(1)	1736(1)	31(1)
O(3)	4352(1)	6754(1)	-1925(1)	29(1)
O(4)	6122(1)	6405(1)	-694(1)	27(1)
N(1)	5970(1)	10773(1)	1466(1)	21(1)
C(1)	6597(1)	11226(1)	85(1)	18(1)
C(2)	7774(2)	11624(1)	-304(1)	20(1)
C(3)	9522(2)	11448(1)	-135(1)	21(1)
C(4)	9857(2)	10950(1)	566(1)	25(1)
C(5)	8677(2)	10565(1)	952(1)	23(1)
C(6)	6879(2)	10580(1)	728(1)	19(1)
C(7)	6421(2)	9700(1)	410(1)	21(1)
C(8)	7473(2)	9411(1)	-284(1)	24(1)
C(9)	6653(2)	8715(1)	-732(1)	22(1)
C(10)	5680(2)	8886(1)	-1374(1)	26(1)
C(11)	4886(2)	8252(1)	-1785(1)	26(1)
C(12)	5052(2)	7428(1)	-1548(1)	23(1)
C(13)	6021(2)	7239(1)	-888(1)	21(1)
C(14)	6802(2)	7879(1)	-490(1)	22(1)
C(15)	3860(2)	6904(1)	-2722(1)	38(1)
C(16)	7104(2)	6204(1)	-32(1)	32(1)
C(17)	6370(2)	11599(1)	1812(1)	30(1)
C(18)	4054(2)	9847(1)	2481(1)	33(1)
C(19)	4570(3)	10396(2)	3160(1)	55(1)
C(20)	2286(2)	9569(2)	2594(1)	45(1)
C(21)	5151(3)	9094(2)	2353(2)	72(1)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for KVC01 (CCDC 818651). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	140(1)	282(1)	208(1)	-5(1)	-40(1)	13(1)
S(1)	162(2)	391(2)	169(2)	-54(2)	3(1)	7(2)
O(1)	202(5)	304(6)	358(6)	21(4)	45(5)	-41(5)
O(2)	212(5)	480(8)	245(6)	-90(5)	-10(4)	103(5)
O(3)	314(5)	337(6)	232(5)	-31(4)	-62(5)	0(5)
O(4)	317(5)	260(5)	244(5)	24(5)	-54(4)	17(5)
N(1)	161(6)	291(7)	177(6)	-52(5)	-22(5)	-26(5)
C(1)	144(5)	219(8)	173(7)	-45(6)	-49(5)	13(5)
C(2)	190(6)	211(8)	194(8)	-33(6)	-33(6)	3(5)
C(3)	191(6)	179(6)	261(7)	-65(6)	-1(6)	-21(6)
C(4)	141(7)	338(9)	270(8)	-12(7)	-58(6)	14(6)
C(5)	179(7)	319(9)	193(7)	11(7)	-46(6)	45(6)
C(6)	143(6)	272(8)	166(7)	-6(6)	-5(5)	21(6)
C(7)	177(7)	244(9)	217(8)	10(6)	23(5)	3(6)
C(8)	197(7)	246(9)	282(9)	20(8)	79(7)	17(6)
C(9)	173(6)	282(9)	208(7)	-10(7)	68(5)	36(6)
C(10)	250(7)	241(8)	280(8)	45(6)	68(7)	54(7)
C(11)	237(7)	366(10)	189(8)	19(7)	-5(6)	62(6)
C(12)	205(6)	281(9)	201(7)	-30(6)	19(6)	14(6)
C(13)	220(7)	222(8)	189(7)	-5(6)	44(6)	40(6)
C(14)	182(7)	316(9)	174(7)	11(6)	7(6)	55(6)
C(15)	400(11)	481(12)	250(9)	-52(9)	-68(8)	-23(9)
C(16)	353(9)	249(11)	346(10)	59(7)	-60(7)	24(7)
C(17)	292(9)	386(12)	228(8)	-90(8)	-34(7)	-9(7)
C(18)	281(9)	478(10)	234(8)	35(7)	62(7)	-8(7)
C(19)	523(14)	886(18)	230(9)	147(10)	-120(9)	-257(14)
C(20)	435(11)	607(15)	309(11)	-75(10)	147(9)	-167(11)
C(21)	768(18)	775(19)	615(17)	442(15)	409(14)	334(14)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for KVC01 (CCDC 818651).

	x	y	z	U_{iso}
H(2)	7575(15)	12016(7)	-717(7)	11(3)
H(4)	10891(17)	10871(8)	712(7)	20(4)
H(5)	8878(15)	10213(7)	1383(7)	21(4)
H(7A)	6523(14)	9252(8)	851(7)	15(3)
H(7B)	5340(15)	9725(7)	261(8)	17(3)
H(8A)	7639(16)	9878(8)	-615(7)	19(4)
H(8B)	8477(15)	9260(7)	-87(7)	19(4)
H(10)	5587(18)	9428(7)	-1546(7)	25(4)
H(11)	4253(16)	8356(7)	-2226(7)	13(3)
H(14)	7354(15)	7769(7)	-93(7)	7(3)
H(15A)	2756(18)	7284(8)	-2747(8)	29(4)
H(15B)	3592(16)	6324(9)	-2932(8)	28(4)
H(15C)	4870(20)	7153(9)	-3037(8)	44(5)
H(16A)	8250(17)	6406(8)	-134(8)	35(4)
H(16B)	6996(16)	5643(9)	27(8)	25(4)
H(16C)	6649(15)	6483(8)	472(8)	19(4)
H(17A)	7408(19)	11605(8)	2081(9)	35(4)
H(17B)	5560(20)	11759(9)	2176(9)	56(5)
H(17C)	6400(20)	12014(10)	1427(10)	50(6)
H(19A)	4400(20)	10072(9)	3615(9)	46(5)
H(19B)	3940(30)	10951(12)	3173(11)	85(8)
H(19C)	5730(30)	10510(11)	3114(10)	73(6)
H(20A)	2020(20)	9236(10)	2169(10)	50(5)
H(20B)	1550(20)	10082(11)	2668(10)	60(6)
H(20C)	2350(20)	9202(10)	3050(10)	43(5)
H(21A)	6290(20)	9451(11)	2348(10)	58(6)
H(21B)	4890(20)	8773(11)	1913(11)	67(8)
H(21C)	5110(20)	8738(11)	2781(11)	69(6)

Table 3. Bond lengths [Å] and angles [°] for KVC01 (CCDC 818651).

Br(1)-C(1)	1.9017(12)	C(1)-C(6)-C(7)	108.80(10)
S(1)-O(2)	1.4881(10)	C(8)-C(7)-C(6)	114.05(12)
S(1)-N(1)	1.6903(11)	C(9)-C(8)-C(7)	111.51(11)
S(1)-C(18)	1.8509(15)	C(10)-C(9)-C(14)	118.22(14)
O(1)-C(3)	1.2281(15)	C(10)-C(9)-C(8)	120.94(13)
O(3)-C(12)	1.3741(15)	C(14)-C(9)-C(8)	120.79(13)
O(3)-C(15)	1.4369(17)	C(9)-C(10)-C(11)	121.64(13)
O(4)-C(13)	1.3702(16)	C(12)-C(11)-C(10)	119.88(14)
O(4)-C(16)	1.4191(16)	O(3)-C(12)-C(11)	124.40(13)
N(1)-C(17)	1.4765(18)	O(3)-C(12)-C(13)	116.05(12)
N(1)-C(6)	1.4918(16)	C(11)-C(12)-C(13)	119.54(13)
C(1)-C(2)	1.3254(18)	O(4)-C(13)-C(14)	124.62(12)
C(1)-C(6)	1.5205(17)	O(4)-C(13)-C(12)	115.74(12)
C(2)-C(3)	1.4782(17)	C(14)-C(13)-C(12)	119.64(13)
C(3)-C(4)	1.4596(19)	C(13)-C(14)-C(9)	121.08(13)
C(4)-C(5)	1.3165(19)	C(19)-C(18)-C(21)	113.9(2)
C(5)-C(6)	1.5117(17)	C(19)-C(18)-C(20)	109.55(15)
C(6)-C(7)	1.5475(19)	C(21)-C(18)-C(20)	110.36(17)
C(7)-C(8)	1.531(2)	C(19)-C(18)-S(1)	111.17(12)
C(8)-C(9)	1.502(2)	C(21)-C(18)-S(1)	107.67(12)
C(9)-C(10)	1.3780(19)	C(20)-C(18)-S(1)	103.70(12)
C(9)-C(14)	1.399(2)		
C(10)-C(11)	1.388(2)		
C(11)-C(12)	1.3778(19)		
C(12)-C(13)	1.4066(18)		
C(13)-C(14)	1.379(2)		
C(18)-C(19)	1.509(2)		
C(18)-C(21)	1.510(3)		
C(18)-C(20)	1.518(2)		
O(2)-S(1)-N(1)	108.73(6)		
O(2)-S(1)-C(18)	104.36(6)		
N(1)-S(1)-C(18)	102.14(6)		
C(12)-O(3)-C(15)	115.33(12)		
C(13)-O(4)-C(16)	116.34(11)		
C(17)-N(1)-C(6)	114.27(11)		
C(17)-N(1)-S(1)	116.32(10)		
C(6)-N(1)-S(1)	118.91(8)		
C(2)-C(1)-C(6)	125.04(12)		
C(2)-C(1)-Br(1)	119.32(10)		
C(6)-C(1)-Br(1)	115.46(9)		
C(1)-C(2)-C(3)	120.50(13)		
O(1)-C(3)-C(4)	122.63(12)		
O(1)-C(3)-C(2)	121.08(13)		
C(4)-C(3)-C(2)	116.25(12)		
C(5)-C(4)-C(3)	121.76(13)		
C(4)-C(5)-C(6)	124.86(13)		
N(1)-C(6)-C(5)	105.66(10)		
N(1)-C(6)-C(1)	113.24(10)		
C(5)-C(6)-C(1)	109.88(11)		
N(1)-C(6)-C(7)	111.24(11)		
C(5)-C(6)-C(7)	107.87(11)		

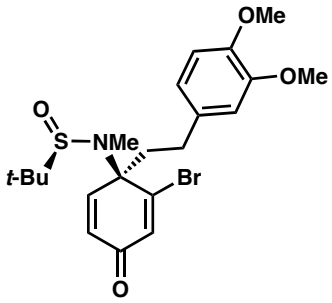
KVC5-205

Sample Name:
KVC5-205
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC5-205
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 21 2010

Temp. 25.0 C / 298.1 K
Sample #33, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420505 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



Major Diastereomer
***(R_S, R)* - 21**

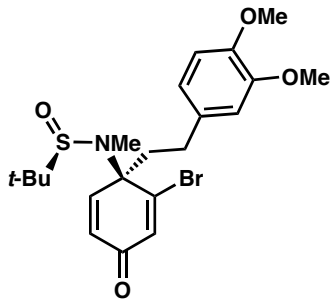
KVC5-205

Sample Name:
KVC5-205
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC5-205
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 21 2010

Temp. 25.0 C / 298.1 K
Sample #33, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6602442 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



Major Diastereomer
***(R_S, R)* - 21**

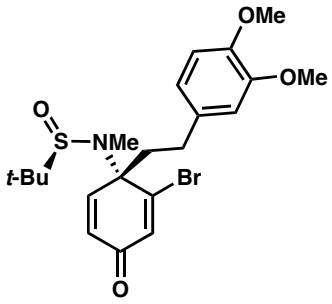
KVC6-061-minor

Sample Name:
KVC6-061-minor
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-061-minor
FidFile: PROTON06

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 31 2010

Temp. 25.0 C / 298.1 K
Sample #39, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420505 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



Minor Diastereomer
(R_S,S) – 21

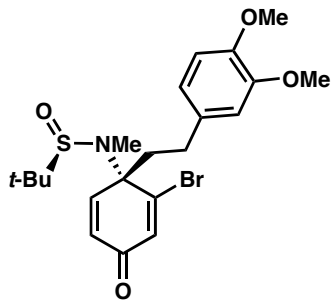
KVC6-061-minor

Sample Name:
KVC6-061-minor
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-061-minor
FidFile: CARBON03

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 31 2010

Temp. 25.0 C / 298.1 K
Sample #39, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1550 repetitions
OBSERVE C13, 125.6602414 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 52 min



Minor Diastereomer
(R_s,S) – 21

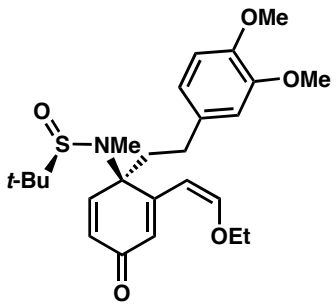
KVC6-067
Z-Isomer

Sample Name:
KVC6-067
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-067
FidFile: PROTON03

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 31 2010

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420502 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



(Z) - 24

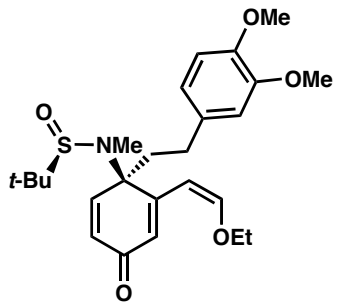
KVC6-067
Z-Isomer

Sample Name:
KVC6-067
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-067
FidFile: CARBON02

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 31 2010

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6602500 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



(Z) - 24

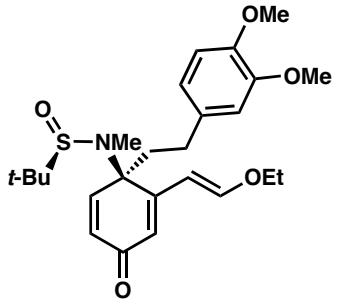
KVC6-067-E

Sample Name:
KVC6-067-E
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-067-E
FidFile: PROTON07

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 13 2011

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



(E) - 24

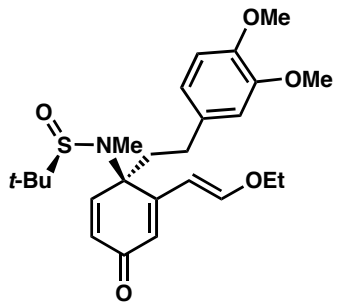
KVC6-067-E

Sample Name:
KVC6-067-E
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-067-E
FidFile: CARBON04

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 13 2011

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
2000 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 8 min



(E) - 24

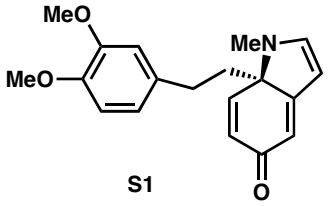
KVC6-037

Sample Name:
KVC6-037
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-037
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 26 2010

Temp. 25.0 C / 298.1 K
Sample #37, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420505 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



S1

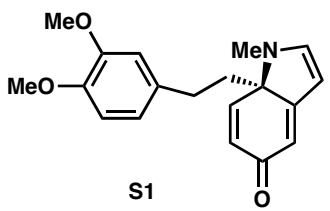
KVC6-037

Sample Name:
KVC6-037
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-037
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 26 2010

Temp. 25.0 C / 298.1 K
Sample #37, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6602471 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



S1

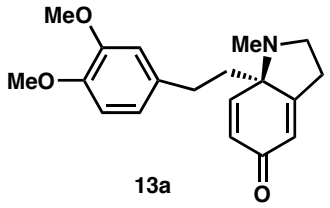
KVC5-239

Sample Name:
KVC5-239
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC5-239
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 16 2010

Temp. 25.0 C / 298.1 K
Sample #35, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420505 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



13a

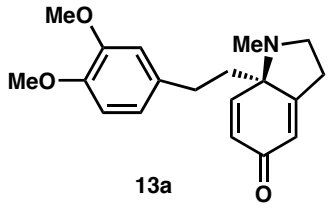
KVC5-239

Sample Name:
KVC5-239
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC5-239
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 16 2010

Temp. 25.0 C / 298.1 K
Sample #35, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6602423 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



13a

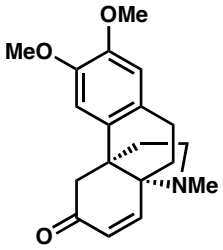
KVC5-243

Sample Name:
KVC5-243
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC5-243
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 16 2010

Temp. 25.0 C / 298.1 K
Sample #36, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420505 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



12a

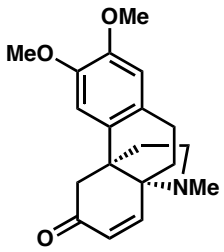
KVC5-243

Sample Name:
KVC5-243
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC5-243
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 16 2010

Temp. 25.0 C / 298.1 K
Sample #36, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6602394 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



12a

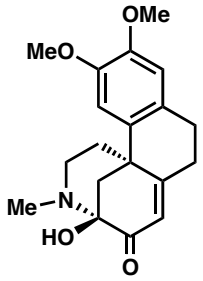
KVC8-027
Hemiaminal

Sample Name:
KVC8-027
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-027
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 28 2011

Temp. 25.0 C / 298.1 K
Sample #42, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290200 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



28

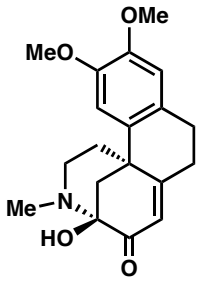
KVC8-027
Hemiaminal

Sample Name:
KVC8-027
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-027
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 28 2011

Temp. 25.0 C / 298.1 K
Sample #42, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6569642 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



28

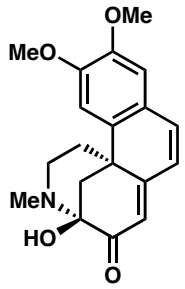
RN4-189
Cepharatine D

Sample Name:
RN4-189
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-189
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 2 2011

Temp. 25.0 C / 298.1 K
Sample #46, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290200 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



Cepharatine D (10)

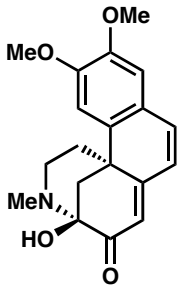
RN4-189
Cepharatine D

Sample Name:
RN4-189
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-189
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 2 2011

Temp. 25.0 C / 298.1 K
Sample #46, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
2000 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 8 min



Cepharatine D (10)

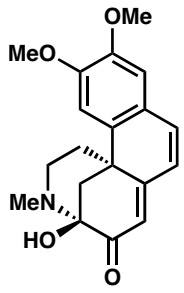
RN4-189

Sample Name:
RN4-189
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-189
FidFile: PROTON05

Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Jun 3 2011

Temp. 25.0 C / 298.1 K
Sample #39, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7309863 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



Cepharatine D (10)

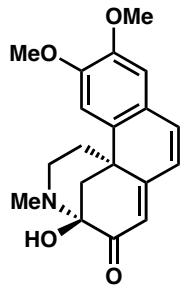
RN4-189
Cepharatine D

Sample Name:
RN4-189
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-189
FidFile: CARBON01

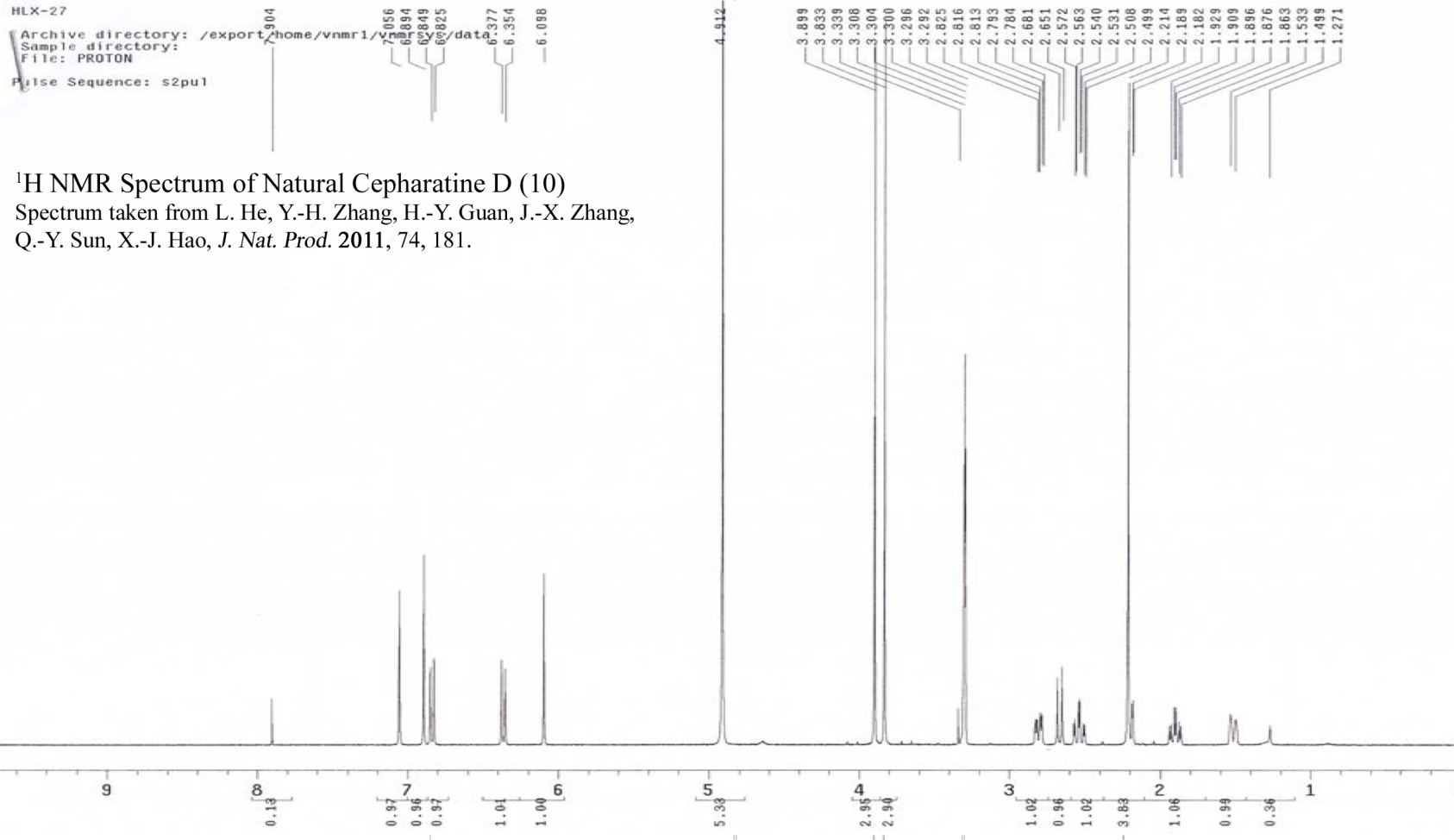
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 2 2011

Temp. 25.0 C / 298.1 K
Sample #46, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
2000 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 8 min



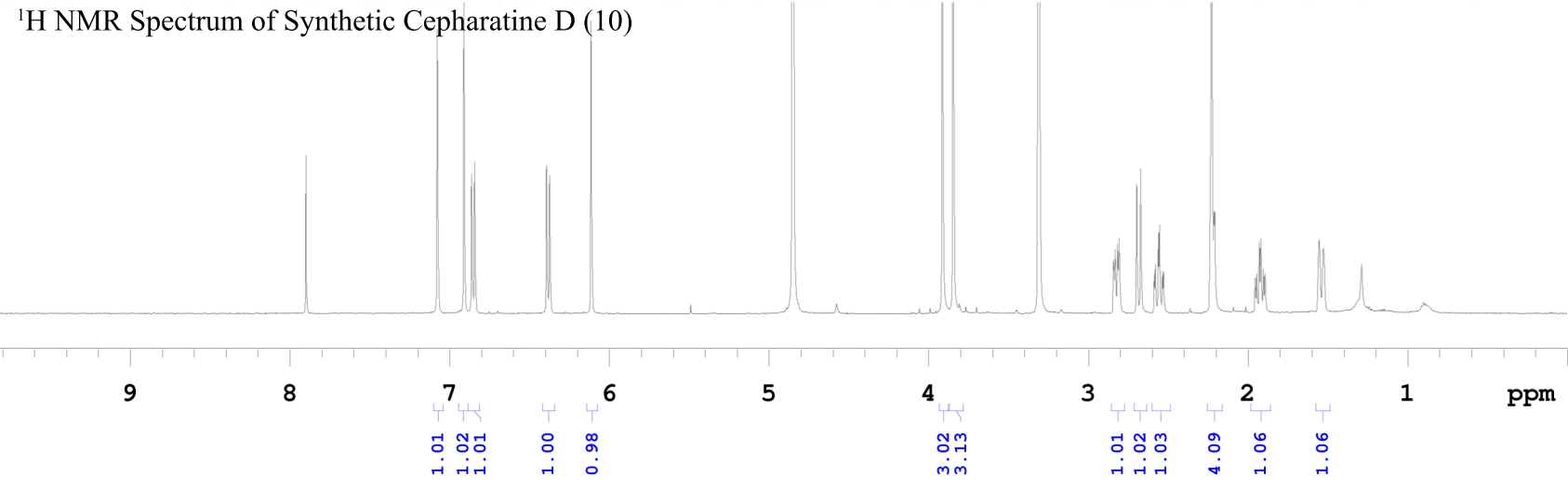
Cepharatine D (10)



^{1}H NMR Spectrum of Natural Cepharatine D (10)

Spectrum taken from L. He, Y.-H. Zhang, H.-Y. Guan, J.-X. Zhang, Q.-Y. Sun, X.-J. Hao, *J. Nat. Prod.* **2011**, 74, 181.

^{1}H NMR Spectrum of Synthetic Cepharatine D (10)



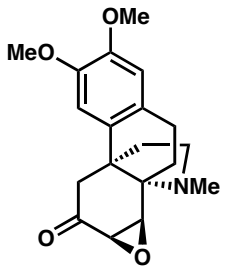
RN4-127

Sample Name:
RN4-127
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-127
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 20 2011

Temp. 25.0 C / 298.1 K
Sample #42, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290200 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



27

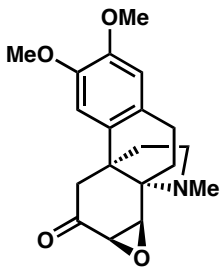
RN4-127

Sample Name:
RN4-127
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-127
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 20 2011

Temp. 25.0 C / 298.1 K
Sample #42, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569642 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



27

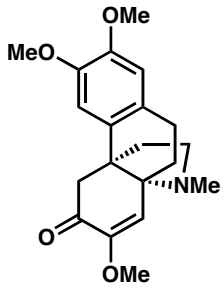
RN4-142

Sample Name:
RN4-142
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-142
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2011

Temp. 25.0 C / 298.1 K
Sample #33, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



1

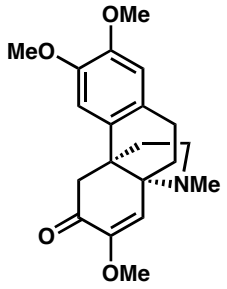
RN4-142

Sample Name:
RN4-142
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
RN4-142
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2011

Temp. 25.0 C / 298.1 K
Sample #33, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569652 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



1

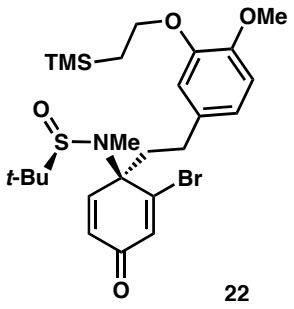
KVC6-089

Sample Name:
KVC6-089
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-089
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 7 2010

Temp. 25.0 C / 298.1 K
Sample #36, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7420505 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



22

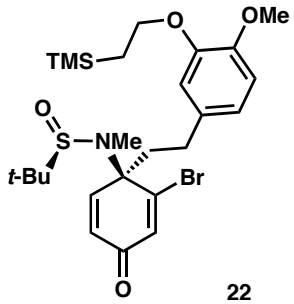
KVC6-089

Sample Name:
KVC6-089
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-089
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 7 2010

Temp. 25.0 C / 298.1 K
Sample #36, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6602471 MHz
DECOUPLE H1, 499.7445450 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



22

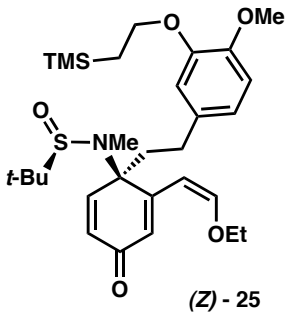
KVC8-033

Sample Name:
KVC8-033
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-033
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 3 2011

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



(Z) - 25

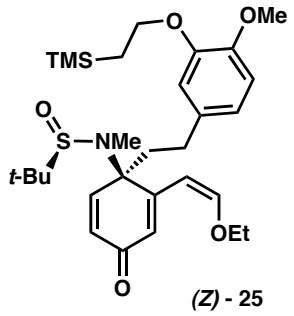
KVC8-033

Sample Name:
KVC8-033
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-033
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 3 2011

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
256 repetitions
OBSERVE C13, 125.6569652 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



(Z) - 25

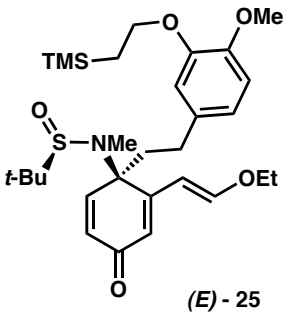
KVC8-089-E

Sample Name:
KVC8-089-E
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-089-E
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 21 2011

Temp. 25.0 C / 298.1 K
Sample #34, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290200 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



(E) - 25

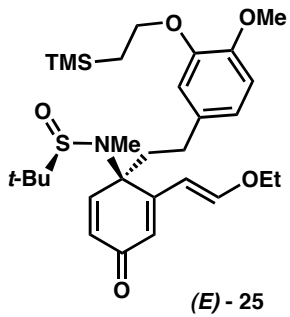
KVC8-089-E

Sample Name:
KVC8-089-E
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-089-E
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 21 2011

Temp. 25.0 C / 298.1 K
Sample #34, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
5000 repetitions
OBSERVE C13, 125.6569614 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 50 min



(E) - 25

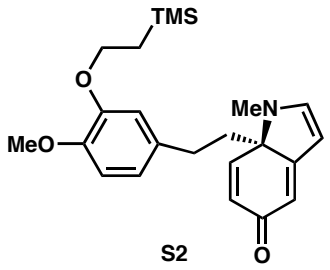
KVC8-041

Sample Name:
KVC8-041
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-041
FidFile: PROTON02

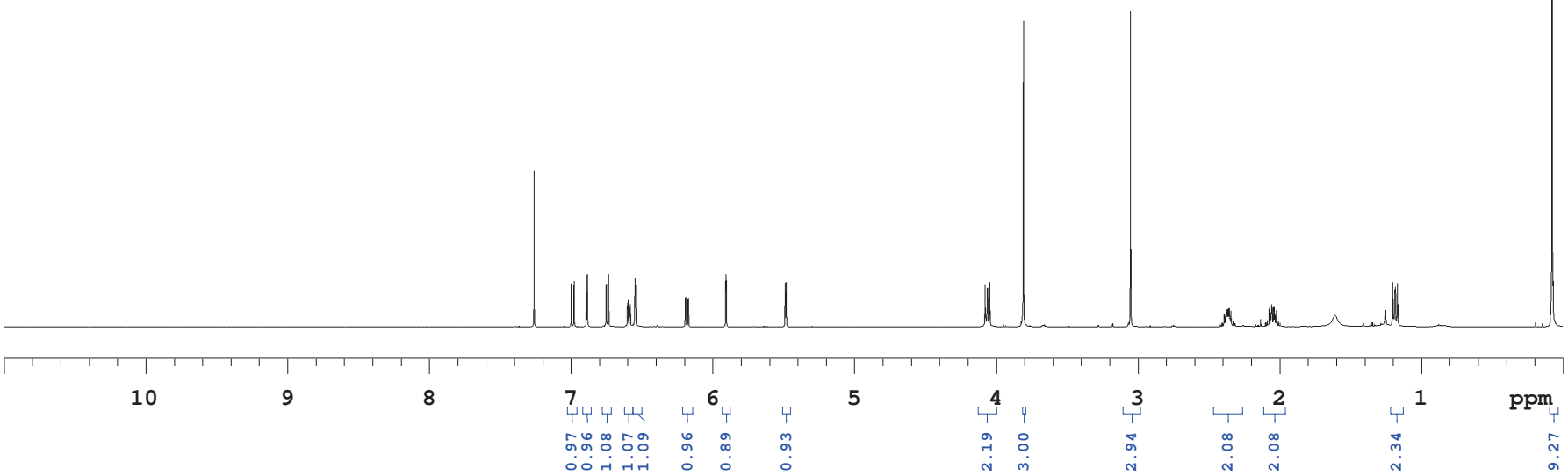
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 4 2011

Temp. 25.0 C / 298.1 K
Sample #44, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



S2



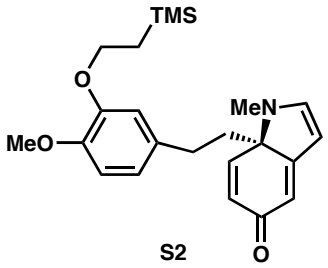
KVC8-041

Sample Name:
KVC8-041
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-041
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 4 2011

Temp. 25.0 C / 298.1 K
Sample #43, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



S2

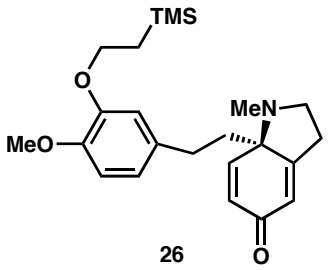
KVC6-101

Sample Name:
KVC6-101
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-101
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 16 2011

Temp. 25.0 C / 298.1 K
Sample #33, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



26

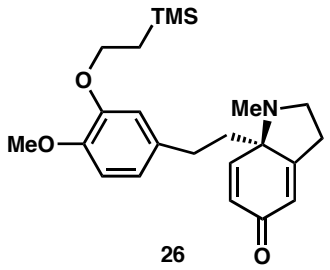
KVC6-101

Sample Name:
KVC6-101
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-101
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 16 2011

Temp. 25.0 C / 298.1 K
Sample #33, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



26

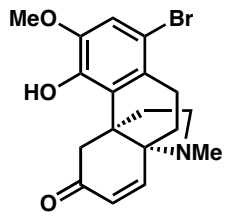
KVC6-153

Sample Name:
KVC6-153
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-153
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 14 2011

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290176 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



30

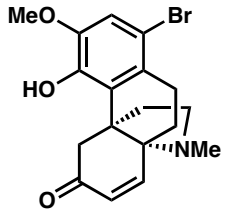
KVC6-153

Sample Name:
KVC6-153
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC6-153
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 14 2011

Temp. 25.0 C / 298.1 K
Sample #41, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



30

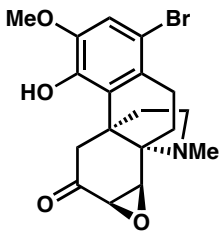
KVC8-259

Sample Name:
KVC8-259
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-259
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 23 2011

Temp. 25.0 C / 298.1 K
Sample #49, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290205 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



31

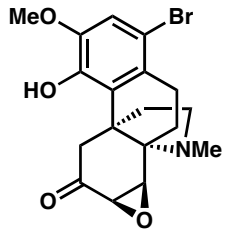
KVC8-259

Sample Name:
KVC8-259
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC8-259
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 23 2011

Temp. 25.0 C / 298.1 K
Sample #49, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



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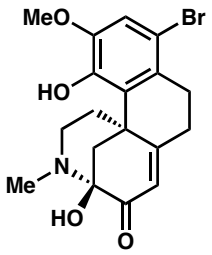
KVC9-277

Sample Name:
KVC9-277
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-277
FidFile: PROTON04

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 20 2011

Temp. 25.0 C / 298.1 K
Sample #48, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



33

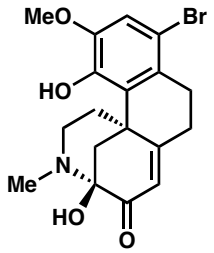
KVC9-277

Sample Name:
KVC9-277
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-277
FidFile: CARBON02

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 18 2011

Temp. 25.0 C / 298.1 K
Sample #43, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6569652 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min



33

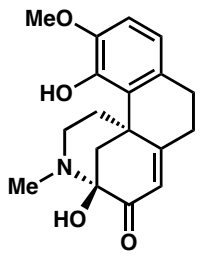
KVC9-297

Sample Name:
KVC9-297
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-297
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 21 2011

Temp. 25.0 C / 298.1 K
Sample #47, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
FT size 65536
Total time 4 min 0 sec



S3

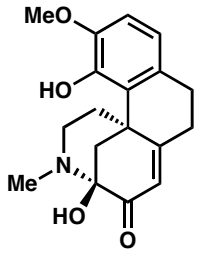
KVC9-297

Sample Name:
KVC9-297
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-297
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 21 2011

Temp. 25.0 C / 298.1 K
Sample #47, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
512 repetitions
OBSERVE C13, 125.6569633 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



S3

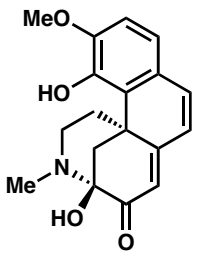
KVC9-301
Cepharatine A

Sample Name:
KVC9-301
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-301
FidFile: PROTON02

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Temp. 25.0 C / 298.1 K
Sample #46, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



Cepharatine A (7)

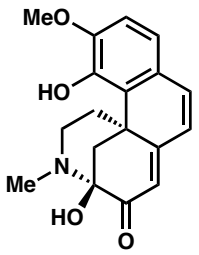
KVC9-301
Cepharatine A

Sample Name:
KVC9-301
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-301
FidFile: CARBON01

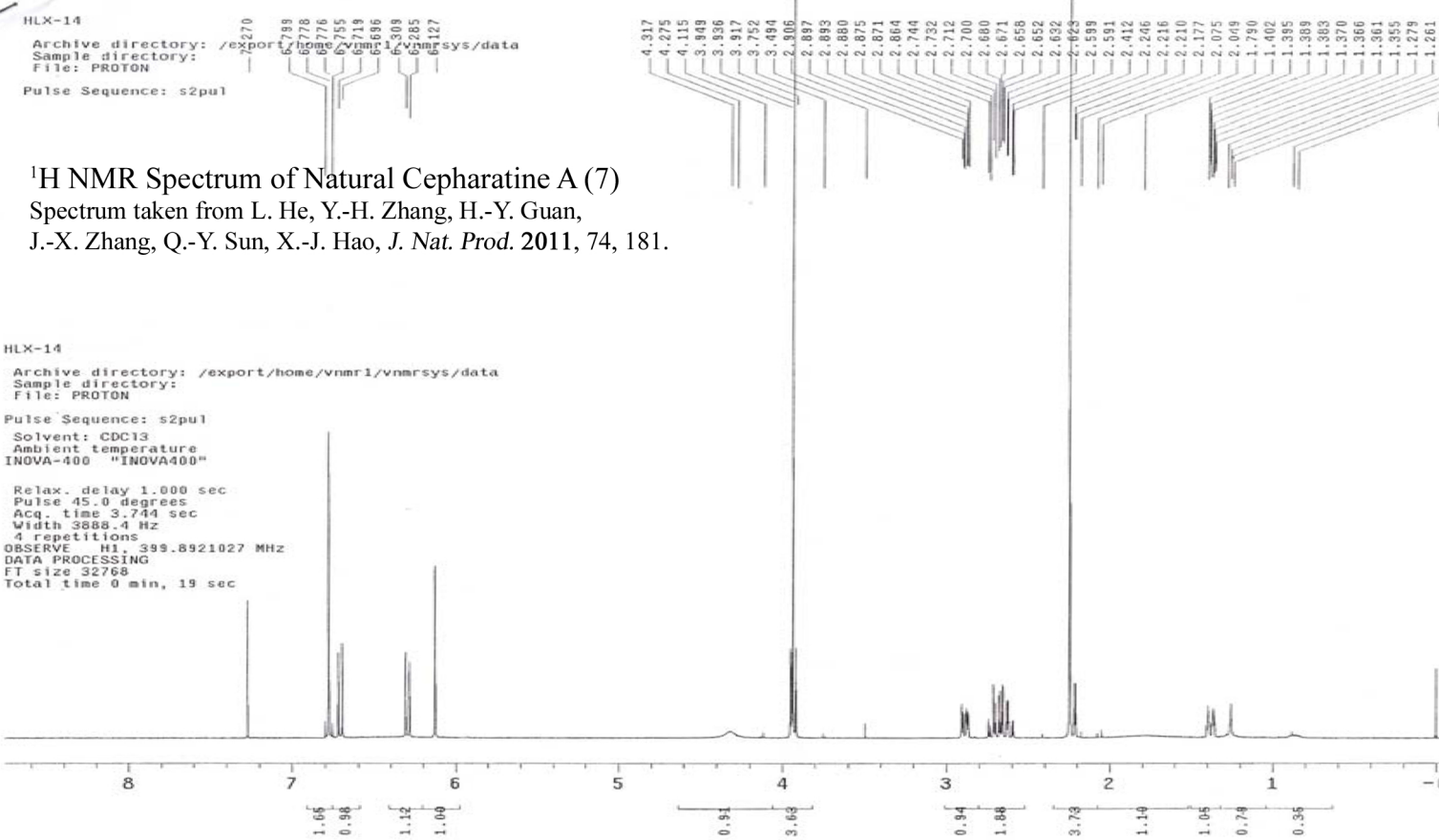
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Temp. 25.0 C / 298.1 K
Sample #46, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6569623 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



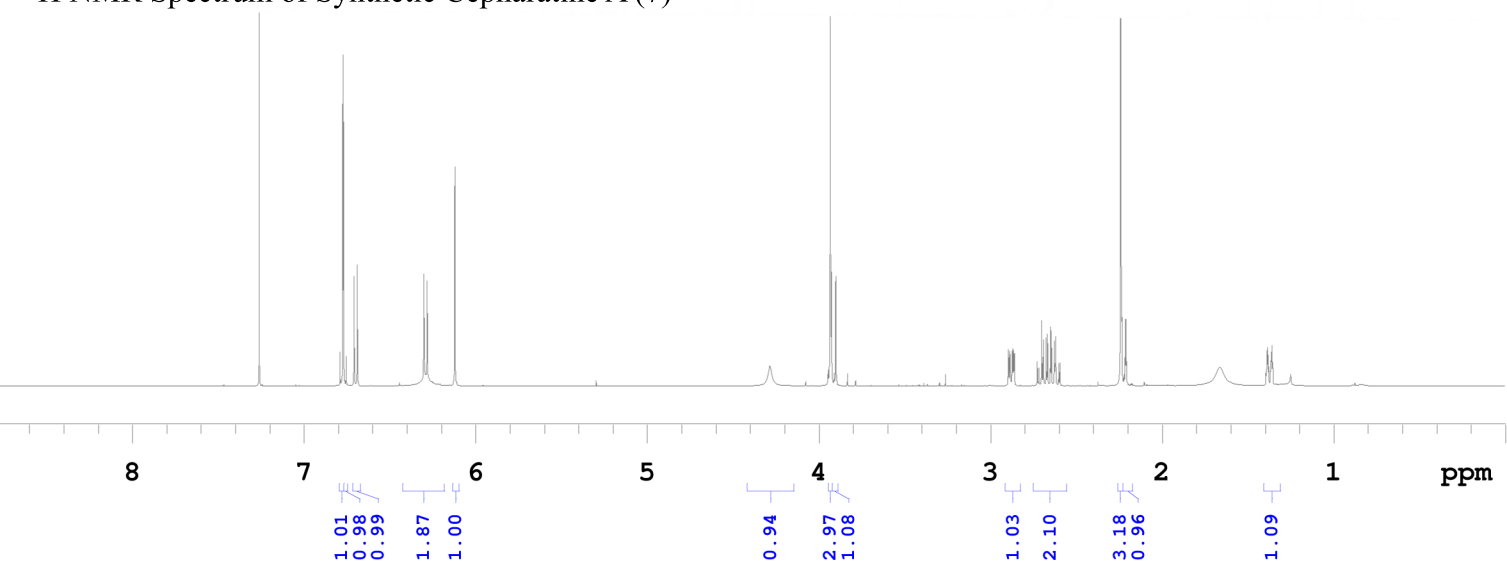
Cepharatine A (7)



^{1}H NMR Spectrum of Natural Cepharatine A (7)

Spectrum taken from L. He, Y.-H. Zhang, H.-Y. Guan, J.-X. Zhang, Q.-Y. Sun, X.-J. Hao, *J. Nat. Prod.* **2011**, 74, 181.

^{1}H NMR Spectrum of Synthetic Cepharatine A (7)



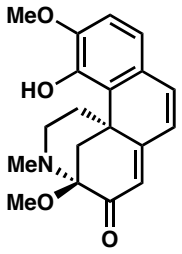
KVC9-303
Cepharatine C, CDCl3

Sample Name:
KVC9-303
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-303
FidFile: PROTON01

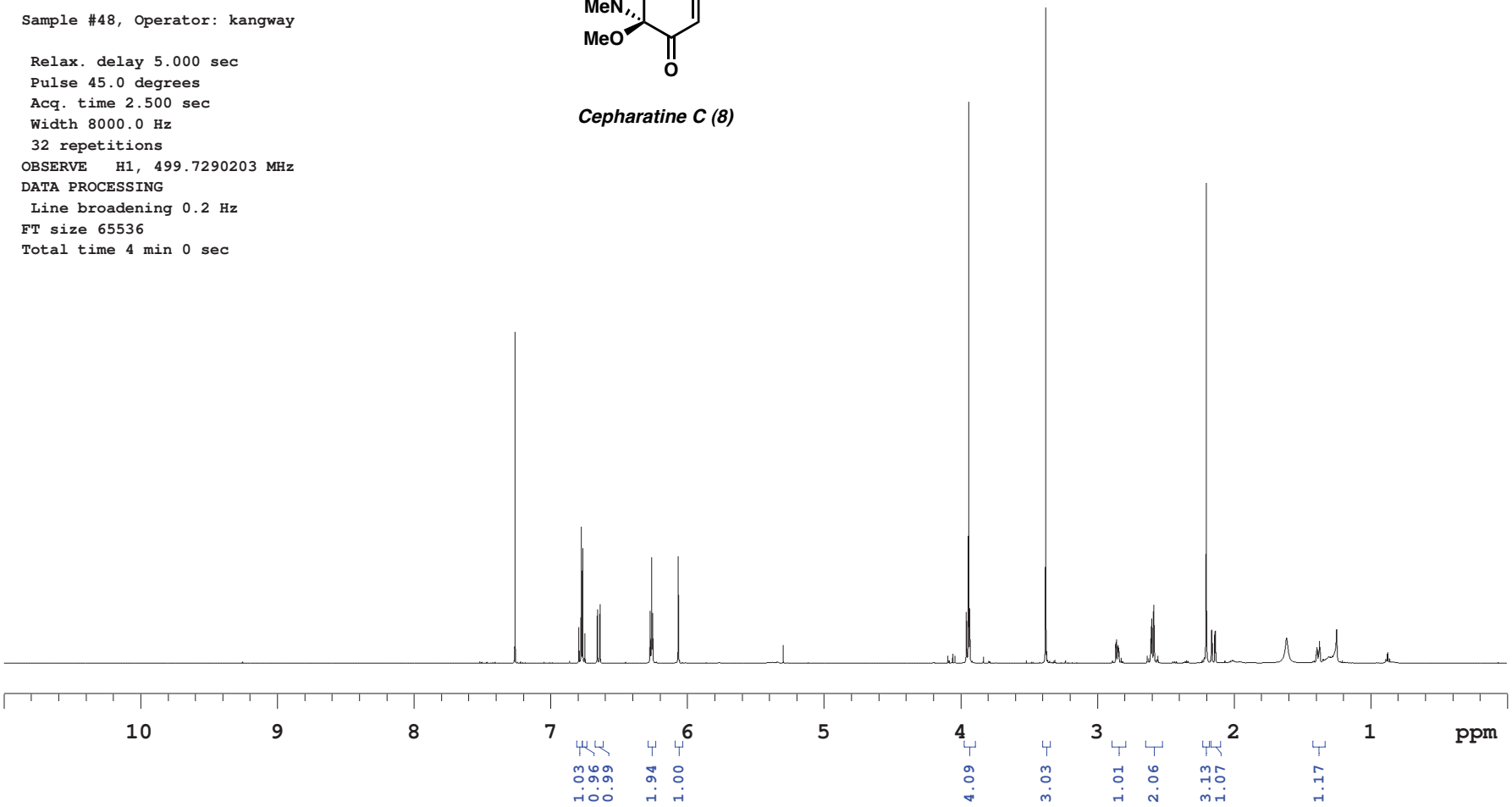
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Sample #48, Operator: kangway

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.500 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7290203 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 0 sec



Cepharatine C (8)



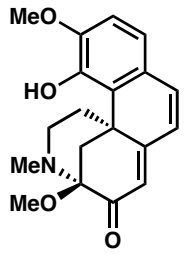
KVC9-303
Cepharatine C, CDCl3

Sample Name:
KVC9-303
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-303
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 22 2011

Sample #48, Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
2000 repetitions
OBSERVE C13, 125.6569633 MHz
DECOUPLE H1, 499.7315163 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 8 min



Cepharatine C (8)

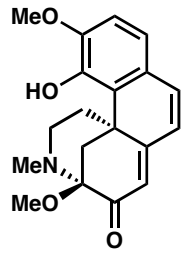
KVC9-303

Sample Name:
KVC9-303
Data Collected on:
hg2.caltech.edu-mercury300
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-303_20110625_03
FidFile: data_s2pul_001

Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Jun 25 2011

Temp. 25.0 C / 298.1 K
Operator: kangway

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.708 sec
Width 4796.2 Hz
64 repetitions
OBSERVE H1, 299.8177476 MHz
DATA PROCESSING
FT size 16384
Total time 6 min 29 sec



Cepharatine C (8)

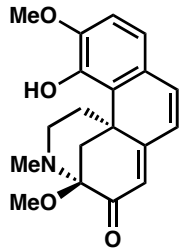
KVC9-303
Cepharatine C, methanol-d4

Sample Name:
KVC9-303
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/kangway/vnmrsys/data
Sample directory:
KVC9-303
FidFile: CARBON02

Pulse Sequence: CARBON (s2pul)
Solvent: cd3od
Data collected on: Jun 25 2011

Sample #20, Operator: kangway

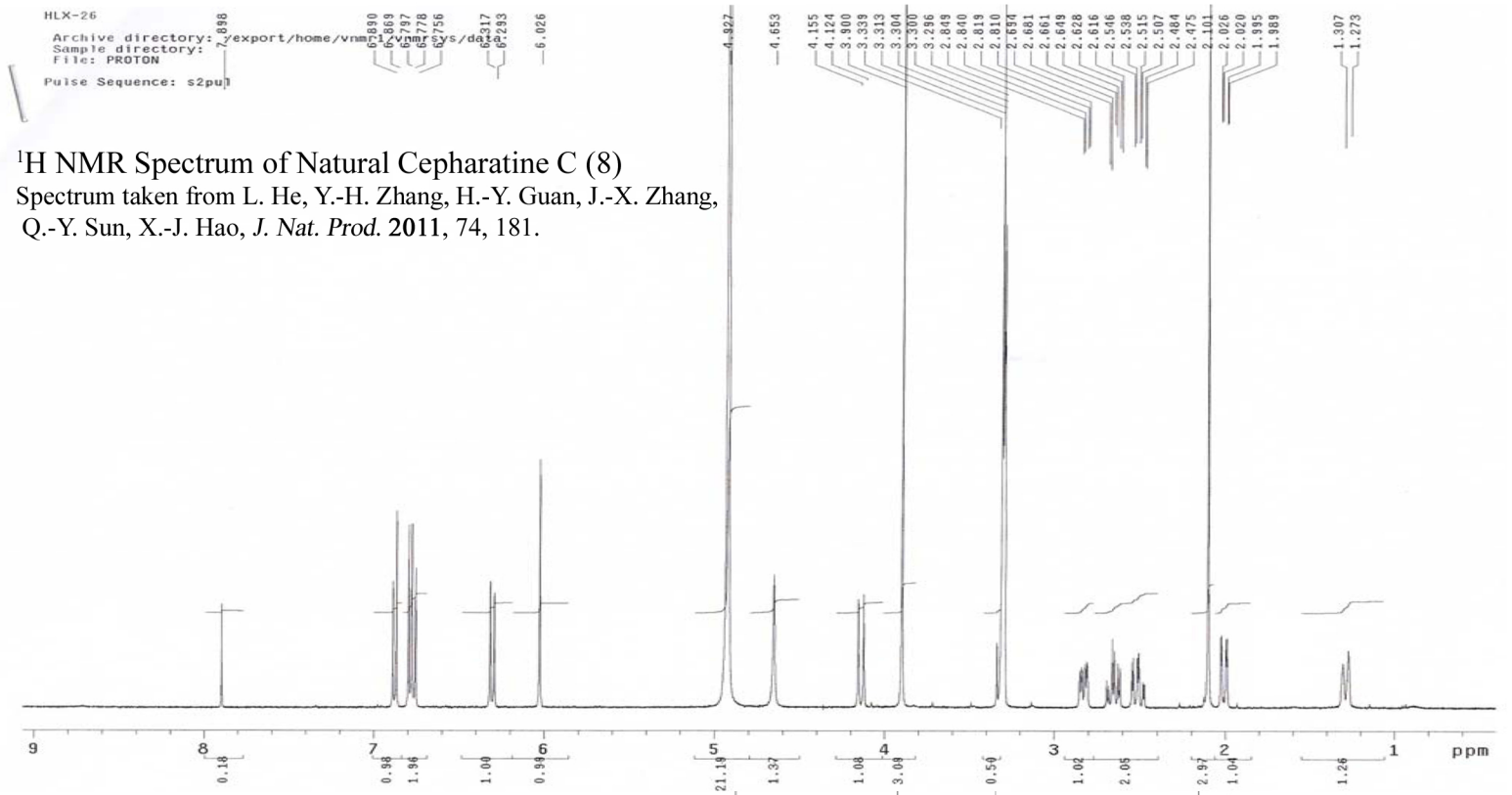
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6572792 MHz
DECOUPLE H1, 499.7334852 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min



Cepharatine C (8)

^{1}H NMR Spectrum of Natural Cepharatine C (8)

Spectrum taken from L. He, Y.-H. Zhang, H.-Y. Guan, J.-X. Zhang, Q.-Y. Sun, X.-J. Hao, *J. Nat. Prod.* **2011**, 74, 181.



^{1}H NMR Spectrum of Synthetic Cepharatine C (8)