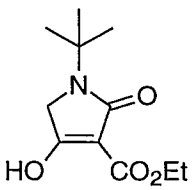
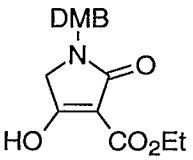
General method for the preparation of tetramic acids 25b-e. To a stirred solution of **23** (47.4 mmol, 1.0 equiv) in CH_2Cl_2 (95 mL) at 0 °C was added a solution of ethyl hydrogen malonate (6.26 g, 47.4 mmol, 1.0 equiv) in CH_2Cl_2 (38 mL), followed by a solution of 1,3-dicyclohexylcarbodiimide (9.9 g, 48.0 mmol, 1.01 equiv) and DMAP (290 mg, 2.37 mmol, 0.05 equiv) in CH_2Cl_2 (20 mL). The mixture was stirred at 0 °C for 15 min and allowed to warm to ambient temperature while stirring for an additional 2 h. After this time the solid urea by-product was removed by filtration. The filtrate was washed with H_2O (80 mL), dried over $MgSO_4$, filtered, and evaporated to a yellow semi-solid. To this was added acetone (30 mL) and the insoluble precipitate again removed via filtration. The filtrate was concentrated *in vacuo* to a yellow oil and used in the next step without further purification.

To a solution of NaOEt/EtOH prepared from sodium metal (1.09 g, 47.4 mmol) and absolute EtOH (31 mL) was added a solution of the crude diester in benzene (200 mL) over 5 min. The resulting mixture was brought to reflux for 6.5 h. The reaction mixture was allowed to cool to room temperature and then diluted with H_2O (100 mL). The layers were separated and the benzene layer further extracted with H_2O (2 x 80 mL). The aqueous layers were combined and residual EtOH was removed *in vacuo*, followed by careful acidification to pH 1 with conc. HCl at 0 °C. The resultant white precipitate was filtered and dried with a slow stream of N_2 gas to give lactams **25b-e** as white powders.

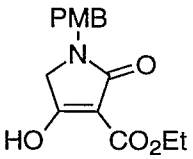


25b. The above procedure was followed using **23b** (7.54 g) to afford **24b** (7.53 g, 70% yield): mp 155-157 °C (dec., EtOH/CH_2Cl_2); IR (thin film/NaCl) 2973.8 (br m), 2933.0 (m), 2526.6 (br m), 1707.4 (s), 1590.3 (s), 1429.7 (s), 1388.7 (m), 1222.3 (m), 1179.3 (w), 1052.1 (m) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6, 315 K) δ 4.12 (q, J = 7.1 Hz, 2H), 3.98 (s, 2H), 1.33 (s, 9H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6, 305 K) δ 177.8, 167.6, 162.5, 98.3, 58.9, 52.9, 47.9, 27.5, 14.2; high resolution mass spectrum (EI) m/z

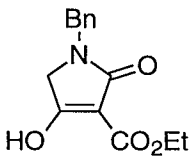
227.1155 [calcd for $C_{11}H_{17}NO_4$ (M^+) 227.1158]; Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16; found: C, 58.08; H, 7.50; N, 6.23.



25c. The above procedure was followed using **24c** (12.00 g) to afford **25c** (12.6 g, 83% yield): mp 154-156 °C (EtOH/CH_2Cl_2); IR (thin film/NaCl) 2937.5 (br m), 2839.5 (w), 2612.4 (br w), 1704.0 (s), 1611.8 (s), 1514.9 (s), 1418.9 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.89 (d, J = 8.2 Hz, 1H), 6.79 (d, J = 1.6 Hz, 1H), 6.70 (dd, J = 1.5, 8.1 Hz, 1H), 4.37 (s, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.80 (s, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 178.8, 167.3, 162.0, 148.8, 148.0, 130.0, 119.8, 111.9, 111.5, 97.8, 59.0, 55.5, 55.4, 49.0, 44.1, 14.3; high resolution mass spectrum (EI) m/z 321.1209 [calcd for $C_{16}H_{19}NO_6$ (M^+) 321.1212]; Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.46; found: C, 59.93; H, 5.92; N, 4.36.



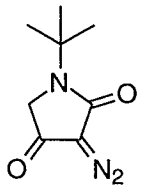
25d. The above procedure was followed using **24d** (10.6 g) to afford **25d** (11.1 g, 80% yield): mp 198-200 °C (dec., EtOH/CH_2Cl_2); IR (thin film/NaCl) 2982.1 (m), 2925.0 (m), 2841.1 (w), 2593.8 (br w), 1703.9 (s), 1609.7 (s), 1512.0 (m), 1447.1 (s), 1247.0 (s), 1038.6 (m) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 7.12 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 4.37 (s, 2H), 4.13 (q, J = 6.8 Hz, 2H), 3.79 (s, 2H), 3.72 (s, 3H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 178.7, 167.3, 162.0, 158.4, 129.6, 128.9, 114.0, 97.8, 59.0, 55.0, 48.9, 43.7, 14.3; high resolution mass spectrum (EI) m/z 291.1107 [calcd for $C_{15}H_{17}NO_5$ (M^+) 291.1107]; Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81; found: C, 61.70; H, 5.86; N, 4.73.



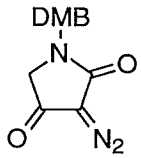
25e. The above procedure was followed using **24e** (9.15 g) to afford **25e** (8.79 g, 71% yield): mp 152-154 °C (dec., EtOH/CH_2Cl_2); IR (thin film/NaCl) 2980.0 (m), 2929.8 (m), 1707.3 (s), 1447.1 (s), 1255.0 (m), 1139.4 (m), 1045.4 (m), 933.6 (w), 797.0 (m), 703.0 (m) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 7.18-7.33 (comp m, 5H), 4.45 (s, 2H), 4.12 (q, J = 7.0 Hz, 2H), 3.81 (s, 2H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 179.4, 167.7,

162.1, 137.8, 128.6, 127.1, 97.4, 58.9, 49.4, 44.3; high resolution mass spectrum (EI) *m/z* 261.0997 [calcd for $C_{14}H_{15}NO_4$ (M^+) 261.1101]; Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36; found: C, 64.18; H, 5.75; N, 5.44.

Diazo lactams 17b-e. A solution of ester **25** (33.5 mmol, 1.0 equiv) and H_2O (1mL) was heated to reflux in CH_3CN (1.5 L) for 2 h. The volume of CH_3CN was reduced to approximately 35% the original volume (ca. 560 mL) *in vacuo*. The solution was cooled to 0 °C and treated sequentially with MsN_3 (8.12 g, 67.0 mmol, 2.0 equiv) in CH_3CN (168 mL) via addition funnel followed by Et_3N (9.34 mL, 67.0 mmol, 2.0 equiv) in CH_3CN (96 mL). After 15 min the ice bath was removed and the dark orange solution was allowed to warm to 25 °C, stirred for an additional 2 h, and concentrated *in vacuo*. The dark orange residue was dissolved in a minimum of EtOAc and filtered through a pad of silica gel (EtOAc eluent). The filtrate was washed once with 1N NaOH solution, dried over $MgSO_4$, filtered and concentrated to give **17b-e** as yellow solids, which were recrystallized from acetone/hexanes.

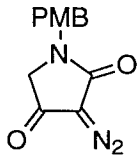


17b. The above procedure was followed using **25b** (7.60 g) to afford **17b** (4.85 g, 80% yield): mp 83-85 °C (dec.); IR (CCl_4) 2980.8 (s), 2123.4 (s), 1718.8 (m), 1689.4 (s), 1441.6 (m), 1390.5 (s), 1347.9 (m), 1262.6 (w), 1224.3 (s), 1177.3 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.7, 161.7, 66.7, 55.7, 53.3, 28.0; high resolution mass spectrum (CI) *m/z* 182.0929 [calcd for $C_8H_{12}N_3O_2$ (M+H) 182.0930]; Anal. Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.19; found: C, 53.06; H, 6.15; N, 23.17.

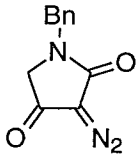


17c. The above procedure was followed using **25c** (10.75 g) to afford **17c** (8.29 g, 90% yield): mp 145-147 °C (EtOAc); IR (CCl_4) 2960.7 (br w), 2925.8 (br w), 2126.1 (s), 1695.2 (s), 1515.1 (m), 1451.2 (w), 1401.1 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.83 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 6.79 (s, 1H), 4.53 (s, 2H), 3.88 (s, 6H), 3.71 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.7, 161.7, 149.5, 149.0, 127.7, 120.8, 111.3, 111.2, 66.0, 56.0, 55.9, 53.9, 46.5;

high resolution mass spectrum (CI) *m/z* 276.0981 [calcd for $C_{13}H_{14}N_3O_4$ (M+H) 276.0984]; Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27; found: C, 56.81; H, 4.81; N, 15.36.



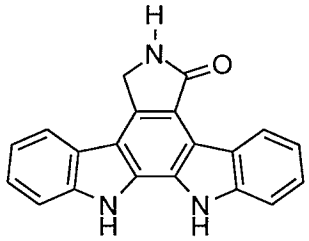
17d. The above procedure was followed using **25d** (9.75 g) to afford **17d** (7.22 g, 88% yield): mp 91-93 °C (EtOAc); IR (CCl_4) 2926.3 (br w), 2841.5 (w), 2129.8 (s), 1693.9 (s), 1613.3 (w), 1511.7 (m), 1458.8 (m), 1401.9 (s), 1361.2 (m), 1243.4 (m), 1223.0 (m), 1174.1 (m), 1040.0 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.51 (s, 2H), 3.77 (s, 3H), 3.66 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.7, 161.6, 159.4, 129.6, 127.2, 114.3, 65.9, 55.2, 53.8, 46.0; high resolution mass spectrum (CI) *m/z* 246.0885 [calcd for $C_{12}H_{12}N_3O_3$ (M+H) 246.0879].



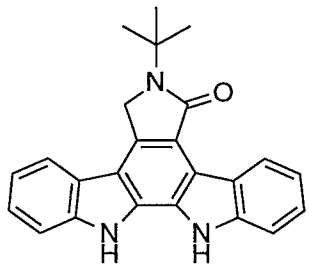
17e. The above procedure was followed using **25e** (8.74 g) to afford **17e** (6.54 g, 86% yield): mp 87-88 °C (EtOAc); IR (CCl_4) 3072.1 (w), 3033.8 (m), 2922.9 (m), 2867.6 (w), 2124.0 (s), 1695.7 (s), 1447.8 (s), 1405.1 (s), 1358.2 (s), 1230.3 (s), 1187.6 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.25 (comp m, 5H), 4.60 (s, 2H), 3.70 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.5, 161.7, 135.1, 128.9, 128.1, 128.1, 65.8, 53.8, 46.5; high resolution mass spectrum (CI) *m/z* 219.0779 [calcd for $C_{11}H_{10}N_3O_2$ (M+H) 216.0773]; Anal. Calcd for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.21; N, 19.53; found: C, 61.47; H, 4.27; N, 19.53.

Indolocarbazoles 4a-e. Method A. A mixture of 2,2'-biindole (**20**) (200 mg, 0.86 mmol, 1.0 equiv), diazo tetramic acid **17a-e** (2.2 mmol, 2.5 equiv), $Rh_2(OAc)_4$ (38 mg, 0.086 mmol, 0.1 equiv) and pinacolone (8.6 mL) in a pressure tube fitted with a rubber septum was degassed with a stream of N_2 for 1 h. The septum was removed and the tube was flushed with N_2, sealed, and placed into a pre-heated sand bath (120 °C). After 6 h the tube was removed from the sand bath, allowed to cool to room temperature, and carefully opened. After removing the solvent *in vacuo*, the residue was dissolved in EtOAc (15 mL), washed with 1N NaOH (15 mL) solution, and dried

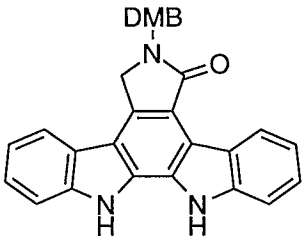
over $MgSO_4$. Filtration and removal of the solvent was followed by flash chromatography (1:1 EtOAc:hexanes eluent) to provide **4a-e** as pale yellow solids.



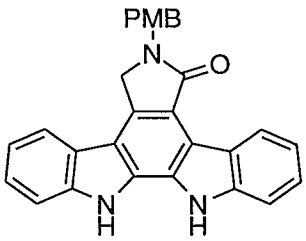
4a. The above procedure was followed using **17a** (275 mg) to afford **4a** (67 mg, 25% yield): mp >330 °C (dec., EtOAc/hexanes); IR (thin film/NaCl) 3343.7 (m), 3306.5 (w), 1645.7 (s), 1454.1 (s), 1389.3 (m), 1348.5 (m), 1329.9 (m), 1316.6 (w), 1277.0 (m), 1260.7 (w), 1050.7 (m) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 11.40 (br s, 1H), 11.20 (br s, 1H), 9.23 (d, J = 7.9 Hz, 1H), 8.35 (br s, 1H), 8.03 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.47 (app.t, J = 7.6 Hz, 1H), 7.42 (app.t, J = 7.4 Hz, 1H), 7.30 (app.t, J = 7.4 Hz, 1H), 7.22 (app.t, J = 7.5 Hz, 1H), 4.95 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.4, 139.2, 139.1, 132.9, 127.8, 125.4, 125.2, 125.0, 125.0, 122.8, 122.6, 121.1, 119.9, 118.9, 118.9, 115.6, 114.1, 111.9, 111.3, 45.3; high resolution mass spectrum (EI) m/z 311.1061 [calcd for $C_{20}H_{13}N_3O$ (M^+) 311.1059].



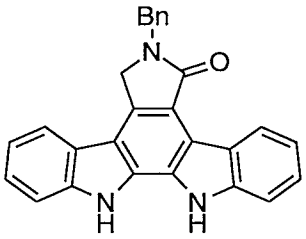
4b. The above procedure was followed using **17b** (400 mg) to afford **4b** (126 mg, 40% yield): mp >300 °C (dec., EtOAc/hexanes); IR (thin film/NaCl) 3485.3 (br m), 3456.0 (br m), 3343.1 (br s), 3249.7 (br m), 2979.7 (m), 1654.4 (w), 1600.5 (s), 1578.2 (s), 1465.8 (w), 1446.5 (m), 1385.0 (s), 1364.0 (m), 1335.9 (w), 1225.3 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 11.45 (br s, 1H), 11.29 (br s, 1H), 9.24 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.47 (app.t, J = 7.5 Hz, 1H), 7.41 (app.t, J = 7.5 Hz, 1H), 7.30 (app.t, J = 7.5 Hz, 1H), 7.21 (app.t, J = 7.5 Hz, 1H), 5.13 (s, 2H), 1.65 (s, 9H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 169.9, 139.2, 139.0, 129.9, 127.6, 125.4, 125.3, 124.9, 122.7, 122.4, 122.0, 121.2, 119.7, 118.8, 115.1, 113.6, 111.8, 111.2, 101.9, 53.6, 48.1, 27.8; high resolution mass spectrum (FAB) m/z 368.1764 [calcd for $C_{24}H_{22}N_3O_1$ (M+H) 368.1763].



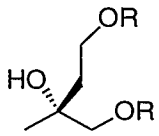
4c. The above procedure was followed using **17c** (605 mg) to afford **4c** (257 mg, 62% yield): mp >202 °C (dec., EtOAc); IR (thin film/NaCl) 3487.5 (br s), 3352.0 (br s), 3232.0 (br s), 3022.3 (m), 1579.1 (s), 1571.2 (s), 1517.7 (s), 1462.9 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 11.50 (br s, 1H), 11.35 (br s, 1H), 9.28 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.45 (app.t, J = 6.9 Hz, 1H), 7.44 (app.t, J = 7.1 Hz, 1H), 7.26 (app.t, J = 7.1 Hz, 1H), 7.25 (app.t, J = 7.1 Hz, 1H), 7.02 (s, 1H), 6.92 (s, 2H), 4.94 (s, 2H), 4.82 (s, 2H), 3.74 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 169.2, 148.9, 148.1, 139.1, 139.0, 130.6, 130.0, 127.7, 125.3, 124.9, 124.9, 124.8, 122.6, 122.3, 120.7, 119.9, 119.7, 118.8, 118.2, 115.4, 113.8, 112.3, 112.1, 111.7, 111.1, 55.5, 49.3, 45.4; high resolution mass spectrum (FAB) m/z 462.1813 [calcd for $C_{29}H_{24}N_3O_3$ (M+H) 462.1818].



4d. The above procedure was followed using **17d** (539 mg) to afford **4d** (204 mg, 55% yield): mp 190-200 °C (dec., acetone); IR (thin film/NaCl) 3429.3 (br s), 3351.3 (br s), 2912.4 (m), 1609.7 (s), 1580.3 (s), 1512.0 (s), 1465.5 (s), 1402.1 (w), 1250.6 (s), 1238.4 (s), 1177.3 (m), 1030.8 (w), 748.9 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 11.53 (br s, 1H), 11.37 (br s, 1H), 9.28 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.47 (app.t, J = 7.0 Hz, 1H), 7.45 (app.t, J = 7.1 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.28 (app.t, J = 7.9 Hz, 1H), 7.26 (app.t, J = 7.8 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 4.94 (s, 2H), 4.83 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 169.2, 158.4, 139.1, 139.0, 130.0, 129.9, 128.9, 127.7, 125.3, 124.9, 124.8, 122.6, 122.2, 120.7, 119.7, 118.8, 118.2, 115.4, 113.9, 113.8, 111.7, 111.1, 54.9, 49.2, 45.0; high resolution mass spectrum (FAB) m/z 432.1699 [calcd for $C_{28}H_{22}N_3O_2$ (M+H) 432.1712].



4e. The above procedure was followed using **17e** (473 mg) to afford **4e** (200 mg, 58% yield).

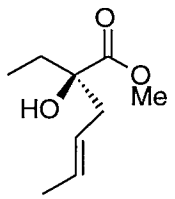


Triol 42. To a cooled (0 °C) solution of (+)-**40** (1.56 g, 8.38 mmol, 1.0 equiv) in CH_2Cl_2 (84 mL) was added DIBAL-H (6.72 mL, 37.69 mmol, 4.5 equiv) in a dropwise fashion over a period of 8 minutes. After stirring for 10 minutes at 0 °C the ice bath was removed, the mixture warmed to 25 °C, and stirred for 30 minutes. The reaction was quenched with EtOAc (10 mL) followed by MeOH (5 mL). A saturated solution of sodium potassium tartrate (80 mL) was added and the mixture was stirred vigorously for 1.5 hours. The phases were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated NaCl solution and dried over $MgSO_4$. After removal of the solvent, a crude oil (845 mg) was obtained and used in the next step without further purification.

To a cooled solution (0 °C) of the above oil (845 mg) in THF (74 mL) was added a solution of H_5IO_6 (1.20 g, 5.26 mmol) in H_2O (1.5 mL). After 20 minutes at 0 °C, the reaction mixture was allowed to warm to 25 °C and stirred for 40 minutes. An excess of $NaBH_4$ (250 mg, 6.6 mmol, 5.0 equiv) was added followed by 1M HCl (3 mL). After the vigorous reaction had ceased, the reaction mixture was extracted with EtOAc and the organic layers dried with $MgSO_4$. Evaporation of the filtrate produced a colorless oil which was filtered through silica gel (5% MeOH/CH_2Cl_2 eluent) to afford an oil (349 mg) which was used in the subsequent reaction without further purification.

A solution of the derived oil (349 mg) in a cooled (-78 °C) mixture of CH_2Cl_2 (15 mL) and MeOH (3 mL) was treated with O_3 until the solution turned a pale blue (5-6 minutes). The mixture was purged with argon before an excess of $NaBH_4$ (250 mg,

6.6 mmol, 5.0 equiv) was added at -78 °C. After warming to ambient temperature the mixture was concentrated *in vacuo*. Flash chromatography (10% MeOH/CH_2Cl_2 eluent) provided triol (*R*)-**46** (245 mg, 25% yield over 3 steps).



R-(-)-**44**

Ester (-)-44. To a solution of (-)-**41b** (382 mg, 2.05 mmol, 1.0 equiv) in ethylvinylether (1.4 mL) at 0 °C was added 2,2,2-trifluoroacetic acid (8.7 μL). The mixture was warmed to reflux for 24 hours. During that time ethylvinylether (1.4 mL) was added twice to replace evaporated solvent. The reaction mixture was cooled to 25 °C and quenched by adding Et_3N (45 μL). The mixture was partitioned between Et_2O (4 mL) and H_2O (0.4 mL). The organic layer was separated and washed with H_2O (0.5 mL), saturated NaCl solution (0.5 mL), dried over $MgSO_4$, and concentrated to afford an oil (538 mg) which was used in the next step without further purification.

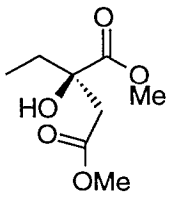
To a cooled solution (0 °C) of the derived oil (538 mg) in MeOH (10 mL) was added $NaBH_4$ (58 mg, 6.1 mmol). The reaction mixture was stirred for 2 hours at 0 °C, quenched by addition of H_2O (136 μL) and then partitioned between H_2O (3 mL) and Et_2O (30 mL). The organic layer was dried over $MgSO_4$ and concentrated to provide an oil (490 mg) which was used without further purification.

To a cooled solution (-78 °C) of the derived oil (490 mg) in THF (17.8 mL) was added $KN(SiMe_3)_2$ (9.4 mL, 0.4 M in toluene, 3.8 mmol). The mixture was stirred for 5 minutes and treated with CS_2 (1.2 mL, 20.0 mmol) followed by iodomethane (1.2 mL, 20.0 mmol). After 10 minutes at -78 °C the reaction was warmed to 0 °C, quenched with saturated NH_4Cl solution (15 mL), and diluted with CH_2Cl_2 (120 mL). The organic layer was washed with H_2O (30 mL), saturated NaCl solution (30 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford an oil (659 mg) that was used without further purification.

A solution of *n*-Bu_3SnH (1.53 mL, 5.69 mmol) and AIBN (62 mg, 0.39 mmol) in benzene (22.3 mL) was heated to reflux and treated dropwise with a solution of the crude oil obtained above (659 mg) in benzene (3.7 mL) over 10 min. The reflux was

continued for an additional hour, then allowed to cool to room temperature. The solvent was evaporated and the residue filtered through silica gel (0→5% EtOAc/hexanes gradient eluent) to provide an oil (469 mg).

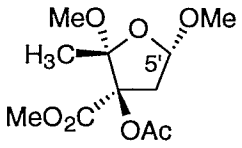
A solution of the derived oil (469 mg) in THF (20 mL) was treated with 1N HCl (2 mL). The mixture was stirred at 25 °C for 15 minutes, the solvent was evaporated, and the residue partitioned between CH_2Cl_2 (133 mL) and H_2O (67 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 67 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to provide a yellow oil which was purified by flash chromatography (5% EtOAc/hexanes eluent) to provide (-)-**44** as a pale yellow oil (153 mg, 44% yield over 5 steps): $[\alpha]^{20}_D$ -8.53 (*c* 1.06, $CHCl_3$); IR (thin film/NaCl) 3530.1 (w), 3028.8 (w), 2962.2 (m), 2955.8 (m), 2936.6 (m), 2922.8 (m), 2880.7 (w), 2855.8 (w), 1733.9 (s), 1459.2 (m), 1378.4 (w), 1339.5 (w), 1293.4 (w), 1243.1 (s), 1211.6 (s), 1152.5 (s), 1068.7 (m), 1019.8 (m), 970.7 (m), 871.4 (w), 805.1 (w), 749.2 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.83 (m, 1H), 5.37 (m, 1H), 3.76 (s, 3H), 3.12 (s, 1H), 2.40 (dd, *J* = 7.3, 13.8 Hz, 1H), 2.31 (dd, *J* = 7.1, 13.8 Hz, 1H), 1.78 (m, 1H), 1.67 (m, 1H), 1.65 (d, *J* = 6.3 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 129.6, 124.7, 78.0, 52.4, 42.4, 31.6, 18.0, 7.8; high resolution mass spectrum (CI) *m/z* 173.1177 [calcd for $C_9H_{17}O_3$ (M+H) 173.1178].



R-(-)-**45**

Diester (-)-45. A cooled solution (-78 °C) of (-)-**44** (153 mg) in CH_2Cl_2 (4.3 mL) and 2.5 N NaOH (1.2 mL) in MeOH, was treated with O_3 until the solution turned pale blue. Diethylether (14 mL) and H_2O (14 mL) were added and the reaction mixture was allowed to warm to 25 °C followed by extraction with Et_2O (3 x 60 mL). After evaporation of the solvent the crude product was filtered through a pad of silica gel (20% EtOAc/hexanes) to afford (-)-**45** as a colorless oil (74 mg, 44% yield, $[\alpha]^{20}_D$ -13.88 (*c* 1.03, $CHCl_3$)

X-RAY CRYSTALLOGRAPHY REPORT FOR FURANOSE (±)-**30a**



A. Crystal Data

Empirical Formula ..... $C_{11}H_{18}O_7$

Formula Weight 262.26

Crystal Color/Habit ..... colorless plate

Crystal Dimensions (mm) ..... 0.10 X 0.18 X 0.22

Crystal System ..... monoclinic

No. Reflections Used for Unit

Cell Determination (2_ range) ..... 25(15.4 - 20.7°)

Omega Scan Peak Width

at Half-height 0.21

Lattice Parameters:

a ..... 7.752 (5)Å

b ..... 21.447 (4)Å

c ..... 8.243 (3)Å

ß ..... 104.88 (4)°

V ..... 1325 (1)$Å^3$

Space Group ..... $P2_1/a$ (#14)

Z value 4

Dcalc ..... 1.315 g/cm^3

F000 560

μ(MoKα) 1.03 cm-1

B. Intensity Measurements

Diffractometer ..... Rigaku AFC5S

Radiation ..... MoKα (λ= 0.71069 Å)

Temperature ..... 23 °C

Attenuators ..... Zr foil (factors: 2.3, 5.3, 11.7)

Take-off Angle ..... 6.0°

Detector Aperture ..... 6.0 mm hor./6.0 mm vert.

Crystal to Detector Distance ..... 285 mm

Scan Type ω-2θ

Scan Rate ..... 6.0°/min in ω (2 rescans)

Scan Width ..... (1.57 + 0.30 tanθ)°

2θmax ..... 50.0°

No. of Reflections Measured:

Total : 2599

Unique: ..... 2417 (Rint = .046)

Corrections ..... Lorentz-polarization

Decay (-7.60% decline)

C. Structure Solution and Refinement

Structure Solution ..... Direct Methods

Refinement ..... Full-matrix least-squares

Function Minimized ..... $\Sigma w (|Fo| - |Fc|)^2$

Least-squares Weights ..... $4Fo^2/s^2(Fo^2)$

p-factor 0.03

Anomalous Dispersion ..... All non-hydrogen atoms

No. Observations (I>3.00s(I)) 884

No. Variables 163

Reflection/Parameter Ratio 5.42

Residuals: R; Rw 0.042; 0.046

Goodness of Fit Indicator 1.38

Max Shift/Error in Final Cycle 0.00

Maximum Peak in Final Diff. Map .....0.16 e-/Å^3

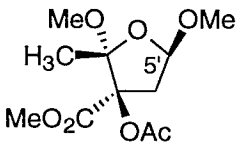
Minimum Peak in Final Diff. Map .....-0.16 e-/Å^3

Positional parameters and B(eq) for furanos (±)-**30a**

atom	x	y	z	B(eq)
O1	0.1039(4)	0.0971(1)	0.1315(4)	3.7(1)
O2	0.3557(4)	0.0683(1)	0.0421(4)	4.1(2)
O3	0.3498(4)	0.1393(2)	0.4305(4)	3.6(1)
O4	0.5196(5)	0.2250(2)	0.4962(4)	5.5(2)
O5	0.6482(4)	0.1639(2)	0.1791(4)	5.1(2)
O6	0.6719(4)	0.1021(2)	0.4028(4)	4.2(2)
O7	0.0336(4)	0.1724(2)	-0.0825(4)	4.9(2)
C1	0.2843(6)	0.0780(2)	0.1818(6)	3.5(2)
C2	0.3819(6)	0.1380(2)	0.2645(5)	3.0(2)
C3	0.2792(6)	0.1884(2)	0.1527(6)	4.0(2)
C4	0.0924(6)	0.1625(2)	0.0902(6)	3.6(2)
C5	0.2976(7)	0.0211(2)	0.2917(6)	4.8(3)
C6	0.2607(8)	0.0251(3)	-0.0811(7)	6.2(3)
C7	0.4271(7)	0.1864(3)	0.5341(6)	4.2(3)
C8	0.3765(7)	0.1817(3)	0.6978(7)	5.9(3)
C9	0.5822(6)	0.1373(2)	0.2758(6)	3.6(2)
C10	0.8639(6)	0.1001(3)	0.4247(7)	5.6(3)
C11	-0.1523(8)	0.1593(3)	-0.1459(7)	6.0(3)
H1	0.2780	0.2258	0.2144	4.7
H2	0.3300	0.1965	0.0615	4.7
H3	0.0145	0.1827	0.1455	4.4

H4	0.2582	0.0312	0.3885	5.8
H5	0.2248	-0.0112	0.2309	5.8
H6	0.4181	0.0074	0.3248	5.8
H7	0.1411	0.0389	-0.1229	7.4
H8	0.3167	0.0227	-0.1708	7.4
H9	0.2614	-0.0149	-0.0313	7.4
H10	0.4296	0.2150	0.7692	7.0
H11	0.2504	0.1840	0.6776	7.0
H12	0.4174	0.1431	0.7502	7.0
H13	0.9167	0.0739	0.5169	6.7
H14	0.8891	0.0842	0.3257	6.7
H15	0.9115	0.1410	0.4459	6.7
H16	-0.2195	0.1867	-0.0954	7.2
H17	-0.1857	0.1651	-0.2642	7.2
H18	-0.1753	0.1174	-0.1204	7.2

X-RAY CRYSTALLOGRAPHY REPORT FOR FURANOSE (±)-**30b**



A. Crystal Data

Empirical Formula ..... $C_{11}H_{18}O_7$

Formula Weight 262.26

Crystal Color/Habit ..... colorless cut block

Crystal Dimensions (mm) ..... 0.38 X 0.40 X 0.45

Crystal System ..... monoclinic

No. Reflections Used for Unit

Cell Determination (2_ range) ..... 8(16.7 - 21.8°)

Omega Scan Peak Width

at Half-height 0.20

Lattice Parameters:

a ..... 8.625 (3)Å

b ..... 22.44 (1)Å

c ..... 8.157 (2)Å

ß ..... 118.87 (2)°

V ..... 1382 (2)$Å^3$

Space Group ..... $P2_1/a$ (#14)

Z value 4

Dcalc ..... 1.260 g/cm^3

F000 560

μ(MoKα) 0.99 cm-1

B. Intensity Measurements

Diffractometer ..... Rigaku AFC5S

Radiation ..... MoKa (λ = 0.71069 Å)

Temperature ..... 23 °C

Attenuators ..... Zr foil (factors: 2.3, 5.3, 11.7)

Take-off Angle ..... 6.0°

Detector Aperture ..... 6.0 mm hor./6.0 mm vert.

Crystal to Detector Distance ..... 285 mm

Scan Type ω-2θ

Scan Rate ..... 8.0°/min in ω (2 rescans)

Scan Width ..... (1.68 + 0.30 tanθ)°

2θmax ..... 49.8°

No. of Reflections Measured:

Total 4006

Unique: ..... 1914 (Rint = .060)

Corrections ..... Lorentz-polarization

Decay (-55.00% decline)

C. Structure Solution and Refinement

Structure Solution ..... Direct Methods

Refinement ..... Full-matrix least-squares

Function Minimized ..... $\sum w (|Fo| - |Fc|)^2$

Least-squares Weights ..... $4Fo^2/\sigma^2(Fo^2)$

p-factor 0.03

Anomalous Dispersion ..... All non-hydrogen atoms

No. Observations (I>3.00s(I)) 1136

No. Variables 163

Reflection/Parameter Ratio 6.97

Residuals: ..... R; Rw 0.055; 0.065

Goodness of Fit Indicator 2.36

Max Shift/Error in Final Cycle 0.00

Maximum Peak in Final Diff. Map .....0.40 e-/Å^3

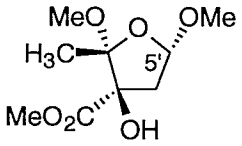
Minimum Peak in Final Diff. Map .....-0.28 e-/Å^3

Positional parameters and B(eq) for (±)-**30b**

atom	x	y	z	B(eq)
O1	0.1799(3)	0.6087(1)	-0.0760(4)	3.9(1)
O2	0.4497(4)	0.5739(1)	0.1627(3)	3.9(1)
O3	0.3938(3)	0.6817(1)	-0.1812(4)	3.8(1)
O4	0.5464(5)	0.6648(2)	-0.3393(5)	5.5(2)
O5	0.7139(4)	0.5665(2)	0.0072(5)	5.6(2)
O6	0.7313(4)	0.6623(2)	0.0910(4)	5.0(1)
O7	0.0270(4)	0.5902(1)	-0.3940(4)	4.7(1)
C1	0.3606(5)	0.6218(2)	0.0424(5)	3.5(2)
C2	0.4416(5)	0.6238(2)	-0.0935(5)	3.1(2)
C3	0.3411(6)	0.5735(2)	-0.2282(5)	3.8(2)
C4	0.1643(5)	0.5702(2)	-0.2242(6)	3.6(2)
C5	0.3740(7)	0.5531(2)	0.2766(6)	5.3(2)
C6	0.3716(6)	0.6785(2)	0.1480(6)	4.8(2)
C7	0.4575(6)	0.6972(2)	-0.3007(6)	4.3(2)
C8	0.4014(8)	0.7593(3)	-0.3736(7)	6.2(3)
C9	0.6452(6)	0.6134(2)	0.0049(6)	4.1(2)
C10	0.9274(7)	0.6539(3)	0.1758(8)	7.4(3)
C11	-0.1452(7)	0.5760(3)	-0.4187(7)	7.3(3)
H1	0.3213	0.5824	-0.3507	4.6
H2	0.4043	0.5371	-0.1871	4.6
H3	0.1422	0.5304	-0.2012	4.3

H4	0.3736	0.5847	0.3539	6.4
H5	0.2560	0.5400	0.1979	6.4
H6	0.4426	0.5210	0.3529	6.4
H7	0.4923	0.6881	0.2289	5.7
H8	0.3165	0.7101	0.0615	5.7
H9	0.3129	0.6728	0.2199	5.7
H10	0.4461	0.7865	-0.2717	7.5
H11	0.4467	0.7692	-0.4556	7.5
H12	0.2758	0.7615	-0.4396	7.5
H13	0.9642	0.6224	0.2646	8.8
H14	0.9561	0.6443	0.0802	8.8
H15	0.9861	0.6896	0.2364	8.8
H16	-0.1584	0.5929	-0.3194	8.8
H17	-0.2333	0.5917	-0.5347	8.8
H18	-0.1578	0.5339	-0.4184	8.8

X-RAY CRYSTALLOGRAPHY REPORT FOR C(2')epi-**9a.**



EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula ..... $C_9O_6H_{16}$

Formula Weight 220.22

Crystal Color/Habit ..... colorless cut block

Crystal Dimensions (mm) ..... 0.34 X 0.44 X 0.48

Crystal System ..... triclinic

No. Reflections Used for Unit

Cell Determination (2θ range) ..... 25(17.3 - 33.8°)

Omega Scan Peak Width at Half-height 0.22

Lattice Parameters:

a ..... 7.619 (8)Å

b ..... 9.66 (1)Å

c ..... 7.595 (8)Å

α ..... 91.3 (1)°

ß ..... 98.6 (1)°

γ ..... 99.24 (9)°

V ..... 545 (2)$Å^3$

Space Group ..... P_{-1} (#2)

Z value 2

Dcalc ..... 1.342 g/cm^3

F000 236

μ(MoKα) 1.06 cm-1

B. Intensity Measurements

Diffractometer ..... Rigaku AFC5S

Radiation ..... MoKα (λ = 0.71069 Å)

Temperature ..... 23 °C

Attenuators ..... Zr foil (factors: 2.3, 5.3, 11.7)

Take-off Angle ..... 6.0°

Detector Aperture ..... 6.0 mm hor./6.0 mm vert.

Crystal to Detector Distance ..... 285 mm

Scan Type ω-2θ

Scan Rate ..... 8.0°/min in ω (2 rescans)

Scan Width ..... (1.68 + 0.30 tanθ)°

2θmax ..... 50.0°

No. of Reflections Measured

Total: 2069

Unique: ..... 1912 (Rint = .036)

Corrections ..... Lorentz-polarization

Decay (-15.00% decline)

C. Structure Solution and Refinement

Structure Solution ..... Direct Methods

Refinement ..... Full-matrix least-squares

Function Minimized ..... $\Sigma w (|Fo| - |Fc|)^2$

Least-squares Weights ..... $4Fo^2/\sigma^2(Fo^2)$

p-factor 0.02

Anomalous Dispersion ..... All non-hydrogen atoms

No. Observations (I>3.00s(I)) 1377

No. Variables 200

Reflection/Parameter Ratio 6.89

Residuals: ..... R; Rw 0.038; 0.043

Goodness of Fit Indicator.....2.01

Max Shift/Error in Final Cycle.....0.00

Maximum Peak in Final Diff. Map .....0.18 e-/Å^3

Minimum Peak in Final Diff. Map .....-0.18 e-/Å^3

Positional parameters and B(eq) for C(2')-epi-**9a**.

atom	x	y	z	B(eq)
O1	0.7759(2)	0.7060(1)	0.2591(2)	3.15(6)
O2	0.8680(2)	0.9476(1)	0.2391(2)	3.46(6)
O3	1.2136(2)	0.9218(2)	0.2951(2)	4.19(7)
O4	1.1137(2)	0.5579(2)	0.2443(2)	4.83(8)
O5	1.2615(2)	0.7218(2)	0.0928(2)	4.18(7)
O6	0.7471(2)	0.7810(2)	0.5486(2)	4.21(7)
C1	0.8948(3)	0.8113(2)	0.1882(3)	2.91(8)
C2	1.0833(3)	0.7997(2)	0.2951(3)	3.10(8)
C3	1.0350(3)	0.7611(3)	0.4778(3)	3.9(1)
C4	0.8369(3)	0.7002(3)	0.4472(3)	3.5(1)
C5	0.6925(4)	0.9798(3)	0.1801(5)	4.8(1)
C6	0.8694(4)	0.7869(3)	-0.0111(3)	3.7(1)
C7	1.1541(3)	0.6786(2)	0.2101(3)	3.3(1)
C8	1.3270(5)	0.6127(4)	-0.0001(5)	5.6(1)
C9	0.5627(5)	0.7261(5)	0.5454(5)	6.5(2)
H1	1.114(3)	0.698(2)	0.539(3)	4.1(5)
H2	1.055(3)	0.845(2)	0.555(3)	3.6(5)

H3	0.807(3)	0.599(2)	0.473(3)	4.0(5)
H4	0.679(4)	1.009(3)	0.068(5)	8(1)
H5	0.596(4)	0.909(3)	0.191(4)	7.2(8)
H6	0.676(4)	1.052(4)	0.256(4)	9(1)
H7	0.960(3)	0.853(2)	-0.060(3)	4.2(5)
H8	0.894(3)	0.691(3)	-0.047(3)	4.3(5)
H9	0.745(3)	0.797(2)	-0.060(3)	4.4(5)
H10	1.166(4)	0.984(3)	0.332(4)	6.7(8)
H11	1.219(4)	0.557(3)	-0.071(4)	7.3(8)
H12	1.409(5)	0.660(4)	-0.079(5)	11(1)
H13	1.391(6)	0.564(5)	0.086(6)	13(1)
H14	0.512(5)	0.786(4)	0.618(5)	10(1)
H15	0.497(5)	0.707(4)	0.429(6)	10(1)
H16	0.555(5)	0.633(4)	0.583(5)	12(1)