Studies Toward the Total Synthesis of Wiedemannic Acid

Louis Barriault* and Effie L. O. Sauer

Department of Chemistry, University of Ottawa, Ottawa, K1N 6N5

Experimental Procedures and Copies of ^1H and ^{13}C NMR for **1** and **13-31**

General. All reactions were performed under nitrogen or argon atmosphere with flame-dried glassware. All solvents were distilled prior to use; diethyl ether and THF over sodium and benzophenone. Toluene and dichloromethane (DCM) were dried over calcium hydride. Column chromatography was performed with 60 silica gel (230-400 mesh, Merck). ^1H and ^{13}C NMR were recorded on Bruker instruments at 500 and 125 MHz, respectively, except where noted. IR spectra were recorded with a Bomen instrument. Melting points are uncorrected. The high-resolution mass spectra were recorded at The University of Ottawa Mass Spectrum Center.

4-Allyl-3-hydroxymethyl-4,6-dimethyl-1-methylene-octahydro-naphthalen-4a-ol (13): To a solution of 20 mg (0.053 mmol) **10** in 0.4 mL THF at room temperature was added TBAF (0.1 mL of a 1.0 M solution in THF, 1.000 mmol). After stirring for 2 hours the reaction was concentrated and purified by silica gel flash chromatography (40% EtOAc/hexanes) to give 13 mg of white crystals (91%). ^1H NMR (CDCl_3 , 500MHz): 6.19-6.10 (m, 1H), 5.01 (dddd, $J = 17.2, 0.7, 0.7, 0.7$ Hz, 1H), 4.97 (dddd, $J = 10.2, 1.1, 1.1, 1.1$ Hz, 1H), 4.91 (d, $J = 1.5$ Hz, 1H), 4.65 (s, 1H), 3.92-3.89 (m, 1H), 3.39-3.35 (m, 1H), 2.57-2.50 (m, 1H), 2.45 (dd, $J_{\text{AB}} = 15.6$ Hz, $J_{\text{AX}} = 7.6$ Hz, 1H), 2.20 (dd, $J_{\text{AB}} = 15.6$ Hz, $J_{\text{AX}} = 7.3$ Hz, 1H), 2.18-2.15 (m, 1H), 2.07-2.01 (m, 2H), 1.81 (ddd, $J = 13.2, 3.3, 2.3$ Hz, 1H), 1.77-1.69 (m, 2H), 1.60-1.52 (m, 2H), 1.50 (d, $J = 1.1$ Hz, 1H), 1.15 (dd, $J = 4.8, 4.8$ Hz, 1H), 1.09 (dd, $J = 13.0, 13.0$ Hz, 1H), 0.91 (s, 3H), 0.88 (d, $J = 6.5$ Hz, 3H), 0.86-0.83 (m, 1H); ^{13}C NMR (CDCl_3 , 500 MHz): 148.97, 138.34, 115.77, 108.85, 78.57, 64.21, 44.12, 43.72, 43.52, 40.06, 39.66, 35.87, 34.03, 27.53, 24.61, 22.52, 18.33; IR (neat): 3363 (br, m), 3076 (w), 2950 (m), 2357 (m), 2339 (m), 1632 (w), 1356 (s), 1050 (w), 1002 (w), 888 (w); HRMS (EI) m/z : calculated 264.2089 for $[\text{M}]^+$, found 264.2099; mp = 75.8-77.6 °C.

1-Allyl-8a-hydroxy-1,7-dimethyl-4-methylene-decahydro-naphthalene-2-carbaldehyde (14): To a stirring solution of **13** (130 mg, 0.4927 mmol) in 5 mL DCM was added 250 mg of molecular sieves, 86 mg NMO (0.734 mmol) and 9 mg TPAP (0.026 mmol). The mixture was stirred for 45 minutes and then filtered through a pad of silica washing first with DCM, then a 10:1 EtOAc/MeOH solution and then again with DCM. The filtrate was concentrated and purified by silica gel flash chromatography (5% $\rightarrow$ 10% EtOAc/hexanes) to give 122 mg of a white solid (95%). ^1H NMR (CDCl_3 , 300MHz): 9.85 (d, $J = 2.1$ Hz, 1H), 6.16-6.02 (m, 1H), 5.03 (d, $J = 17.1$ Hz, 1H), 5.02 (d, $J = 10.1$ Hz, 1H), 4.89 (d, $J = 1.5$ Hz, 1H), 4.67 (d, $J = 1.4$ Hz, 1H), 2.93 (ddd, $J = 12.9, 4.1, 2.1$ Hz, 1H), 2.56 (dd, $J = 15.2, 7.9$ Hz, 1H), 2.42-2.14 (m, 4H), 1.82-1.42 (m, 6H), 1.10-1.02 (m, 1H), 1.06 (s, 3H), 0.92-0.77 (m, 1H), 0.87 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 300 MHz): 205.15, 147.13, 136.99, 117.55, 110.09, 78.27, 53.32, 44.84, 43.41, 40.46, 38.99, 33.73, 32.19, 27.47, 24.42, 22.40, 18.41; IR (neat): 3556 (m), 3075 (w), 2948 (m), 2926 (s), 2867 (m), 2846 (m), 2739 (w), 1715 (s), 1644 (m), 1445 (m), 1347 (m), 998 (m), 945 (m), 913 (s); HRMS (EI) m/z : calculated 262.1933 for $[\text{M}]^+$, found 262.1937; mp = 52.8-54.3 °C.

4-Allyl-3-(1-hydroxy-allyl)-4,6-dimethyl-1-methylene-octahydro-naphthalen-4a-ol (15): Method A: A solution of **14** (122 mg, 0.465 mmol) in 4 mL THF was cooled to -78 °C. Vinylmagnesium bromide (1.2 mL of a 0.9 M solution, 1.080 mmol) was added dropwise and the reaction stirred for 45 minutes. A saturated solution of aqueous NH_4Cl was added and the reaction warmed to room temperature. The aqueous phase was extracted three times with EtOAc and the combined organic layers dried with MgSO_4 , filtered and concentrated. Purification by silica gel flash chromatography (2% $\rightarrow$ 4% EtOAc/hexanes) yielded 90 mg of a colourless oil as an inseparable mixture of **15** and

acetal **16**. **Method B** (for the purpose of obtaining **15** in pure form): To a solution of **20** (7 mg, 0.019 mmol) in 1.0 mL THF was added TBAF (0.04 mL of a 1.0 M solution in THF, 0.040 mmol). After stirring for 24 hours the reaction was concentrated and the crude oil purified by silica gel flash chromatography (10% EtOAc/hexanes) to yield 5 mg of a colourless oil (89%). ^1H NMR (CDCl_3 , 500MHz): 6.14-6.05 (m, 1H), 5.90 (ddd, $J = 17.2$, 10.6, 4.5 Hz, 1H), 5.20 (ddd, $J = 17.1$, 1.6, 1.4 Hz, 1H), 5.12 (ddd, $J = 10.5$, 1.6, 1.3 Hz, 1H), 5.00 (dddd, $J = 17.2$, 1.6, 1.5, 1.5 Hz, 1H), 4.98-4.94 (m, 1H), 4.84 (d, $J = 1.6$ Hz, 1H), 4.62 (d, $J = 1.4$ Hz, 1H), 4.55 (s, br. 1H), 2.52 (dd, $J = 15.7$, 7.6 Hz, 1H), 2.33 (dd, $J = 15.7$, 7.2 Hz, 1H), 2.27 (dd, $J = 14.0$, 13.2 Hz, 1H), 2.20-2.17 (m, 1H), 2.12 (dd, $J = 13.3$, 3.6 Hz, 1H), 2.04 (dd, $J = 14.0$, 2.8 Hz, 1H), 1.82-1.78 (m, 1H), 1.73-1.68 (m, 2H), 1.59-1.48 (m, 4H), 1.17-1.14 (m, 1H), 1.15 (s, 3H), 0.88 (d, $J = 6.4$ Hz, 3H), 0.88-0.81 (m, 1H); ^{13}C NMR (CDCl_3 , 500 MHz): 149.67, 141.62, 138.13, 115.88, 113.22, 108.29, 78.93, 70.47, 44.98, 43.95, 43.90, 40.23, 39.75, 33.85, 30.03, 27.45, 24.51, 22.42, 19.49; IR (neat): 3427 (m, br), 3075 (w), 2948 (s), 2925 (s), 2867 (m), 1727 (w), 1637 (w), 1455 (m), 1380 (w), 1204 (w), 1111 (m), 1087 (m), 993 (m), 917 (s); HRMS (EI) m/z : calculated 272.2140 for $[\text{M}-\text{H}_2\text{O}]^+$, found 272.2134.

12-Allyl-3,12-dimethyl-7-methylene-11-oxa-

tricyclo[7.2.1.01,6]dodecan-10-ol (16): Originally obtained as part of an inseparable mixture with **15**. For purposes of characterization, **16** was recovered as unreacted material from the RCM reaction of **15** to **17**.

Mixture of isomers (~ 2:1 ratio): ^1H NMR (CDCl_3 , 300MHz): 5.94-5.69 (m, 1H), 5.37 and 5.11-5.05 (s, br and m, 1H), 5.11-5.05 (m, 2H), 4.93 (s, 1H), 4.82 (s, 1H), 2.87-2.78 (m, 1H), 2.58-2.45 (m, 2H), 2.34-1.52 (m, 9H), 1.49-1.32 (m, 1H), 1.07 and 1.01 (s and s, 3H), 0.94-0.77 (m, 1H), 0.88 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 300 MHz): 149.37, 147.01, 136.46, 134.75, 118.74, 118.37, 112.57, 112.06, 101.19, 100.04, 89.71, 86.17, 47.94, 45.98, 45.54, 43.42, 43.01, 42.62, 39.90, 39.54, 38.28, 37.84, 35.32, 34.23, 34.21, 31.57, 28.95, 28.81, 26.90 (2C), 23.10, 23.04, 17.64, 17.09; IR (neat): 3400 (s, br), 3075 (w), 2993 (w), 2948 (s), 2925 (s), 2867 (s), 2843 (m), 1636 (m), 1447 (m), 1381 (m), 1204 (w), 1157 (w), 1139 (w), 1112 (m), 1088 (m), 922 (s); HRMS (EI) m/z : calculated 262.1933 for $[\text{M}]^+$, found 262.1954.

4a,6-Dimethyl-9-methylene-4,4a,5,6,7,8,8a,9,10,10a-decahydro-1H-

phenanthrene-1,4b-diol (17): A solution of **15** (17 mg, 0.0585 mmol), as an inseparable mixture with acetal **16**, in 7 mL DCM was degassed under argon for 20 minutes. Grubb's first generation catalyst (4 mg, 0.05 mmol)

was added and the solution went from pink to dark brown over time. After 45 minutes no further reaction was observed and the solution was concentrated and purified by silica gel flash chromatography (10% → 20% EtOAc/hexanes) to give 10 mg (65%) of a **17** as a white solid (as well as 9 mg of unreacted acetal **16**). ^1H NMR (CDCl_3 , 300MHz): 5.74-5.70 (m, 1H), 5.59 (d, $J = 10.1$ Hz, 1H), 4.97 (d, $J = 1.3$ Hz, 1H), 4.70 (s, 1H), 3.82 (d, $J = 7.7$ Hz, 1H), 2.66 (dd, $J = 13.3$, 4.1 Hz, 1H), 2.48 (d, $J = 18.9$ Hz, 1H), 2.28 (d, $J = 10.0$ Hz, 1H), 1.99 (dd, $J = 14.8$, 13.1 Hz, 1H), 1.73-1.68 (m, 3H), 1.65-1.59 (m, 3H), 1.56-1.49 (m, 3H), 1.39 (s, 1H), 1.08 (dd, $J = 12.9$, 12.5 Hz, 1H), 0.99 (s, 3H), 0.87 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 500 MHz): 148.69, 128.69, 128.17, 110.06, 76.43, 71.47,

45.75, 43.15, 41.91, 38.15, 35.00, 34.01, 32.46, 27.39, 24.71, 22.42, 15.06; IR (neat): 3349 (s), 2944 (s), 2921 (s), 2867 (m), 1646 (w), 1536 (w), 1518 (m), 1443 (m), 1393 (m), 1143 (w), 1097 (w), 1041 (s), 984 (s), 942 (m), 888 (m); HRMS (EI) m/z: calculated 244.1827 for $[M-H_2O]^+$, found 244.1834; mp = 138.2-140.1 °C.

1-Allyl-1,7-dimethyl-4-methylene-8a-trimethylsilanyloxy-decahydro-naphthalene-2-carbaldehyde (19): A solution of **13** (147 mg, 0.559 mmol) in 5 mL THF was cooled to -78 °C. Freshly distilled TMS-Cl (0.28 mL, 2.206 mmol) was then added dropwise followed by KHMDS (407

mg, 2.040 mmol) in one portion. After stirring for 1.5 hours the reaction was quenched with $NaHCO_3$. The reaction mixture was extracted three times with EtOAc and the combined organic layers dried with $MgSO_4$, filtered and concentrated. The crude bis-silated material was dissolved in 5 mL of MeOH and cooled to 0 °C. Anhydrous potassium carbonate was added (75 mg, 0.543 mmol) and the reaction stirred for 30 minutes. The reaction was then diluted with water, extracted three times with DCM and the combined organic layers dried with $MgSO_4$, filtered and concentrated. The crude oil was then dissolved in 5 mL of DCM and put under an atmosphere of nitrogen. Molecular sieves (4 Å) were added (250 mg) followed by NMO (87 mg, 0.747 mmol) and TPAP (5 mg, 0.014 mmol). After stirring for 20 minutes, the reaction was filtered over a pad of silica and washed with a 5% solution of MeOH in EtOAc followed by DCM. The filtrate was concentrated and purification by silica gel flash chromatography (5% EtOAc/hexanes) yielded 165 mg of the aldehyde **19** as a white solid (88% over three steps). 1H NMR ($CDCl_3$, 500MHz): 9.83 (d, J = 3.4 Hz, 1H), 5.82-5.74 (m, 1H), 5.08 (d, J = 1.0 Hz, 1H), 5.06-5.05 (m, 1H), 4.74 (d, J = 1.6 Hz, 1H), 4.53 (d, J = 1.6 Hz, 1H), 2.77 (ddd, J = 13.1, 3.7, 3.7 Hz, 1H), 2.43 (dd, J_{AB} = 14.4, 6.7 Hz, 1H), 2.34 (dd, J = 13.8, 13.8 Hz, 1H), 2.28 (dd, J_{AB} = 14.4, 8.3 Hz, 1H), 2.11-2.06 (m, 2H), 1.77-1.71 (m, 2H), 1.67-1.58 (m, 2H), 1.54-1.46 (m, 1H), 1.15 (s, 3H), 1.07 (dd, J = 13.4, 12.4 Hz, 1H), 0.92-0.83 (m, 1H), 0.88 (d, J = 6.6 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR ($CDCl_3$, 500 MHz): 205.68, 147.13, 136.18, 118.74, 107.89, 84.26, 56.21, 45.43, 43.96, 40.33, 38.90, 33.88, 33.01, 28.21, 24.69, 22.33, 16.48, 2.90 (3C); IR (neat): 2950 (s), 2925 (s), 1715 (s), 1443 (m), 1249 (s), 1176 (w), 1127 (m), 1090 (m), 894 (s); HRMS (EI) m/z: calculated 334.2328 for $[M]^+$, found 334.2327; mp = 59.1-60.6 °C.

1-(1-Allyl-1,7-dimethyl-4-methylene-8a-trimethylsilanyloxy-decahydro-naphthalen-2-yl)-prop-2-en-1-ol (20): A solution of **19** (127 mg, 0.3796 mmol) in 3 mL THF was cooled to -78 °C. Vinylmagnesium bromide (0.87 mL of a 0.87 M solution, 0.7569 mmol) was then added dropwise and the reaction stirred for 45 minutes. A saturated solution of

aqueous NH_4Cl was added and the reaction warmed to room temperature. The aqueous phase was extracted three times with EtOAc and the combined organic layers dried with $MgSO_4$, filtered and concentrated. No purification was required and 133 mg of a white solid (97%) was obtained. 1H NMR ($CDCl_3$, 500MHz): 6.04-5.99 (m, 1H), 5.88-5.83 (m, 1H), 5.17 (d, J = 17.2 Hz, 1H), 5.10 (d, J = 10.6 Hz, 1H), 5.03 (d, J = 20.8 Hz, 1H), 4.99 (d, J = 11.2 Hz, 1H), 4.66 (s, 2H), 4.45 (s, 1H), 2.49 (dd, J = 15.1, 5.5 Hz, 1H), 2.21 (dd, J = 12.7, 12.7 Hz, 1H), 2.11-2.02 (m, 3H), 1.91 (d, J = 13.4 Hz, 1H), 1.75-1.69 (m, 2H),

1.59-1.48 (m, 3H), 1.24-1.06 (m, 2H), 1.14 (s, 3H), 0.87-0.85 (m, 1H), 0.87 (d, $J = 3.5$ Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (CDCl_3 , 500 MHz): 149.85, 142.38, 138.27, 115.70, 112.91, 106.11, 85.33, 71.42, 47.75, 46.17, 45.03, 39.99, 39.66, 34.08, 30.40, 28.21, 24.84, 22.41, 17.33, 2.96 (3C); IR (neat): 3435 (br, w), 3081 (w), 2950 (s), 2926 (s), 2868 (m), 1646 (w), 1455 (w), 1248 (s), 1119 (s), 1092 (m), 1063 (m), 913 (m), 883 (m), 836 (s), 750 (w); HRMS (EI) m/z : calculated 362.2641 for $[\text{M}]^+$, found 362.2643; mp = 61.4-63.8 °C.

4a,6-Dimethyl-9-methylene-4b-trimethylsilanyloxy-

4a,4b,5,6,7,8,8a,9,10,10a-decahydro-4H-phenanthren-1-one (22):

A solution of **20** (611.7 mg, 1.687 mmol) in 150 mL DCM was degassed under argon for 20 minutes. Grubb's first generation catalyst was added (52 mg, 0.063 mmol) and the resulting pink solution was stirred for 30 minutes and then concentrated. The crude allylic alcohol **21** was redissolved in 15 mL DCM and 840 mg of 4 Å molecular sieves, 400 mg NMO (3.414 mmol) and 15 mg TPAP (0.043 mmol) were added in succession. The resulting dark brown solution was stirred for 45 minutes and then filtered over a pad of silica, washed twice with a 5% solution of MeOH in EtOAc followed by several DCM washes. The filtrate was concentrated and purified by silica gel flash chromatography (100% hexanes $\rightarrow$ 8% EtOAc/hexanes) to yield 511 mg of enone **22** as a colourless oil (91% over 2 steps). ^1H NMR (CDCl_3 , 300 MHz): 6.82-6.76 (m, 1H), 5.93 (dd, $J = 10.0, 2.9$ Hz, 1H), 4.76 (s, 1H), 4.49 (s, 1H), 2.80 (dd, $J = 12.3, 4.0$ Hz, 1H), 2.64-2.53 (m, 2H), 2.17-2.03 (m, 3H), 1.78-1.58 (m, 4H), 1.47 (dddd, $J = 12.5, 3.4, 3.4, 3.4$ Hz, 1H), 1.09 (dd, $J = 13.6$ Hz, 1H), 1.03 (s, 3H), 0.93-0.80 (m, 1H), 0.86 (d, $J = 6.4$ Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (CDCl_3 , 300 MHz): 202.17, 147.72, 146.65, 128.11, 107.75, 83.23, 50.26, 46.59, 43.30, 38.20, 34.30, 33.87, 30.95, 27.93, 24.51, 22.19, 16.34, 2.87 (3C); IR (neat): 2950 (s), 2931 (s), 2866 (m), 1729 (w), 1681 (s), 1647 (w), 1456 (w), 1387 (m), 1250 (m), 1194 (m), 1135 (m), 1058 (m), 836 (s), 751 (w); HRMS (EI) m/z : calculated 332.2172 for $[\text{M}]^+$, found 332.2158.

1,4a,6-Trimethyl-9-methylene-4b-trimethylsilanyloxy-

1,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-phenanthren-1-ol (23):

A solution of **22** (114 mg, 0.3428 mmol) in 3 mL THF was cooled to -78 °C and MeLi (0.69 mL of a 1.3 M solution in ether, 0.8970 mmol) added dropwise. After 20 minutes the reaction was quenched with water and warmed to room temperature. The aqueous phase was extracted three times with EtOAc and the combined organic layers dried with MgSO_4 , filtered and concentrated. Purification by silica gel flash chromatography (10% EtOAc/hexanes) gave 117 mg of a white solid (98%). ^1H NMR (CDCl_3 , 500 MHz): 5.70-5.67 (m, 1H), 5.60-5.57 (m, 1H), 4.73 (s, 1H), 4.48 (s, 1H), 2.39-2.28 (m, 2H), 2.12-2.08 (m, 2H), 1.96 (dd, $J = 12.8, 4.0$ Hz, 1H), 1.80 (dd, $J = 17.3, 5.9$ Hz, 1H), 1.72-1.68 (m, 1H), 1.63-1.44 (m, 4H), 1.21 (s, 3H), 1.18 (dd, $J = 9.3, 9.3$ Hz, 1H), 1.14-1.11 (m, 1H), 1.13 (s, 3H), 0.91-0.83 (m, 1H), 0.86 (d, $J = 6.4$ Hz, 3H), 0.05 (s, 9H); ^{13}C NMR (CDCl_3 , 500 MHz): 150.01, 132.92, 126.03, 106.36, 83.80, 69.53, 44.72, 43.67, 40.80, 38.43, 34.07, 32.82, 31.95, 29.82, 28.07, 24.90, 22.29, 16.81, 2.77 (3C); IR (neat): 3450 (br, m), 3083 (w), 3019 (m), 2949 (s), 2871 (m), 2847 (m), 1646 (m), 1455 (m), 1368 (m), 1249 (s), 1183 (m), 1149 (m), 1061 (s), 1020 (m), 913 (m), 838

(s), 751 (m); HRMS (EI) m/z : calculated 348.2485 for $[M]^+$, found 348.2465; mp = 92.1-93.2 °C.

1,4a,6-Trimethyl-9-methylene-4b-trimethylsilanyloxy-

4a,4b,5,6,7,8,8a,9,10,10a-decahydro-4H-phenanthren-3-one (24): To a solution of **23** (115 mg, 0.330 mmol) in 3 mL DCM was added 200 mg PCC (0.928 mmol) in one portion. The reaction changed colour from a light to a very dark orange and was complete by TLC after 2 hours. An

equal volume of ether was then added and the resulting precipitate filtered off over celite, rinsing thoroughly with additional ether. The filtrate was concentrated and purified by silica gel flash chromatography (10% EtOAc/hexanes). The resulting white solid had a mass of 104 mg (91%). ^1H NMR (CDCl_3 , 500MHz): 5.84 (s, 1H), 4.81 (s, 1H), 4.56 (s, 1H), 2.95 (d, $J = 13.3$ Hz, 1H), 2.51 (dd, $J = 13.2, 3.4$ Hz, 1H), 2.43 (d, $J_{AB} = 15.5$ Hz, 1H), 2.32 (d, $J_{AB} = 15.7$ Hz, 1H), 2.16 (d, $J = 10.9$ Hz, 1H), 2.10 (dd, $J = 13.3, 13.3$ Hz, 1H), 1.91 (s, 3H), 1.76-1.74 (m, 1H), 1.65-1.61 (m, 3H), 1.54-1.46 (m, 1H), 1.07-1.02 (m, 1H), 1.05 (s, 3H), 0.93-0.85 (m, 1H), 0.88 (d, $J = 6.3$ Hz, 3H), 0.10 (s, 9H); ^{13}C NMR (CDCl_3 , 500 MHz): 199.64, 163.84, 148.17, 125.76, 108.19, 82.86, 47.19, 46.46, 43.78, 43.54, 38.44, 34.12, 34.02, 27.94, 24.52, 22.39, 22.18, 15.99, 2.89 (3C); IR (neat): 2952 (m), 2925 (m), 2865 (w), 1673 (w), 1454 (m), 1473 (m), 1251 (m), 1146 (m), 1105 (m), 1056 (m), 889 (w), 837 (s); HRMS (EI) m/z : calculated 346.2328 for $[M]^+$, found 346.2332; mp = 132.2-134.8 °C.

1,4a,6-Trimethyl-9-methylene-4b-trimethylsilanyloxy-1-vinyl-

dodecahydro-phenanthren-3-one (25): To a suspension of CuI (104 mg, 0.546 mmol) in 2 mL THF at -78 °C was added 1.25 mL of a 0.87 M solution (1.088 mmol) of vinylmagnesium bromide dropwise. The resulting pale yellow mixture was immersed in a -10 °C bath

(acetone/ice) for ten minutes. The now olive green suspension was recooled to -78 °C for 10 minutes, and enone **24** (60 mg, 0.1731 mmol) was cannulated into the reaction mixture using 1 mL THF. After 1 hour at -78 °C the reaction, now rust brown in colour, was quenched with a saturated solution of aqueous NH_4Cl and warmed to room temperature. The aqueous phase was extracted three times with EtOAc and the combined organic layers dried with MgSO_4 , filtered and concentrated. Purification by silica gel flash chromatography (5% EtOAc/hexanes) yielded 52.2 mg of a white solid (80%). ^1H NMR (C_6D_6 , 500MHz): 5.68 (dd, $J = 17.3, 10.7$ Hz, 1H), 4.93 (d, $J = 10.7$ Hz, 1H), 4.87 (d, $J = 17.5$ Hz, 1H), 4.85-4.84 (m, 1H), 4.64-4.63 (m, 1H), 2.43-2.37 (m, 2H), 2.31-2.25 (m, 3H), 2.17 (dd, $J = 12.7, 2.2$ Hz, 1H), 1.94 (dd, $J = 13.9, 12.9$ Hz, 1H), 1.83 (d, $J = 10.7$ Hz, 1H), 1.65-1.50 (m, 4H), 1.34-1.32 (m, 1H), 0.98 (s, 3H), 0.94 (s, 3H), 0.92-0.87 (m, 1H), 0.81 (d, $J = 6.5$ Hz, 1H), 0.75-0.67 (m, 1H), 0.14 (s, 9H); ^{13}C NMR (C_6D_6 , 500 MHz): 209.01, 149.29, 149.23, 111.69, 107.22, 84.55, 54.46, 48.56, 48.44, 44.78, 44.46, 43.87, 38.10, 34.13, 33.43, 28.48, 25.25, 22.24, 18.50, 18.05, 2.97 (3C); IR (neat): 3081 (w), 2947 (m), 2928 (m), 2871 (w), 2851 (w), 1709 (s), 1642 (w), 1448 (w), 1279 (m), 1261 (m), 1247 (s), 1123 (m), 1059 (m), 912 (w), 834 (s); HRMS (EI) m/z : calculated 374.2641 for $[M]^+$, found 374.263, mp = 112.2-113.0 °C.

Imidazole-1-carbothioic acid O-(1,4a,6-trimethyl-9-methylene-4b-trimethylsilanyloxy-1-vinyl-tetradecahydro-phenanthren-3-yl) ester (27): A solution of **25** (21.1 mg, 0.056 mmol) in 2 mL of THF was cooled to -78 °C. DIBAL-H (0.07 mL of a 1.0 M solution in toluene, 0.105 mmol) was added dropwise and the reaction allowed to warm to 0 °C. The reaction was quenched with a few drops of acetone followed by a

1:1 solution of 1 M NaOH (aq.) and 1 M sodium tartrate (aq.) and stirred vigorously for 1 hour. After extracting the aqueous phase three times with EtOAc, drying over MgSO₄, filtering and concentrating, the crude product was dissolved in 3 mL DCM.

Thiocarbonyldiimidazole (34 mg of 90% pure, 0.172 mmol) followed by DMAP (7 mg, 0.057 mmol) were added. The reaction was stirred at ambient temperature for 36 hours and then concentrated. Purification by silica gel flash chromatography (10% EtOAc/hexanes) yielded 23 mg of a clear, colourless oil (84% for two steps). ¹H NMR (CDCl₃, 500MHz): 8.35 (s, 1H), 7.64 (s, 1H), 7.03 (s, 1H), 5.96-5.93 (m, 1H), 5.59 (dd, J = 17.5, 10.8 Hz, 1H), 5.01 (d, J = 10.8 Hz, 1H), 4.96 (d, J = 17.4 Hz, 1H), 4.65 (s, 1H), 4.45 (s, 1H), 2.15-2.02 (m, 3H), 1.99-1.94 (m, 2H), 1.89 (dd, J = 14.7, 14.5 Hz, 1H), 1.73-1.70 (m, 1H), 1.65 (dd, J = 15.6, 3.5 Hz, 1H), 1.62-1.54 (m, 3H), 1.49-1.41 (m, 1H), 1.32 (s, 3H), 1.26-1.24 (m, 1H), 1.19 (s, 3H), 1.11 (dd, J = 12.6, 13.1 Hz, 1H), 0.90-0.83 (m, 1H), 0.85 (d, J = 6.4 Hz, 3H), 0.13 (s, 9H); ¹³C NMR (CDCl₃, 500 MHz): 183.48, 150.16, 149.57, 136.91, 130.88, 118.02, 111.83, 106.61, 84.73, 81.34, 43.36, 43.07, 41.86, 40.96, 38.51, 38.09, 34.70, 34.02, 32.93, 28.16, 24.79, 22.25, 19.58, 19.30, 3.05 (3C); IR (neat): 3085 (w), 2952 (s), 2926 (s), 2869 (m), 1728 (w), 1645 (m), 1573 (w), 1531 (w), 1458 (m), 1386 (s), 1327 (s), 1281 (s), 1247 (s), 1232 (s), 1188 (s), 1113 (s), 1092 (s), 1061 (m), 971 (s), 836 (s); HRMS (EI) m/z: calculated 330.2378 for [M-OTMS-Im]⁺, found 330.2017.

Trimethyl-(3,4b,8-trimethyl-10-methylene-8-vinyl-dodecahydro-phenanthren-4a-yloxy)-silane (28): To a solution of **27** (20 mg, 0.041 mmol) in 2 mL degassed benzene was added 29 mg (0.083 mmol)

Ph₃SnH as a solution in 1 mL degassed benzene, followed by 1.5 mg of AIBN (0.009 mmol). The reaction mixture was brought to reflux and allowed to react for 1 hour 15 minutes. After cooling the room temperature and reaction was concentrated and purified by silica gel flash chromatography (100% hexanes) to give 11 mg of a clear colourless oil (74%). ¹H NMR (CDCl₃, 500MHz): 5.58 (dd, J = 17.5, 10.8 Hz, 1H), 4.90 (d, J = 10.8 Hz, 1H), 4.86 (d, J = 17.8 Hz, 1H), 4.59 (s, 1H), 4.39 (s, 1H), 2.06-1.92 (m, 3H), 1.79 (dd, J = 12.8, 3.4 Hz, 1H), 1.70-1.67 (m, 1H), 1.63-1.50 (5H), 1.48-1.41 (m, 2H), 1.35 (dd, J = 13.0, 3.8 Hz, 1H), 1.31-1.20 (m, 2H), 1.10-1.05 (m, 1H), 1.08 (s, 3H), 0.98 (s, 3H), 0.88-0.80 (m, 1H), 0.85 (d, J = 6.4 Hz, 3H), 0.12 (s, 9H); ¹³C NMR (CDCl₃, 500 MHz): 151.95, 150.80, 110.36, 105.73, 84.62, 44.23, 43.66, 42.43, 39.87, 39.68, 37.90, 34.24, 33.38, 31.90, 28.22, 24.93, 22.36, 18.50, 17.61, 17.22, 2.99 (3C); IR (neat): 3085 (w), 2949 (s), 2869 (m), 1645 (m), 1455 (m), 1246 (s), 1181 (m), 1124 (s), 1090 (s), 1059 (s), 907 (m), 881 (m), 831 (s), 748 (m); HRMS (EI) m/z: calculated 360.2848 for [M]⁺, found 360.2825.

4b-Hydroxy-1,4a,6-trimethyl-9-oxo-tetradecahydro-phenanthrene-1-carbaldehyde (29): To a solution of **28** (34 mg, 0.094 mmol) in 2 mL THF was added 0.28 mL of a 1.0 M solution of TBAF (0.280 mmol).

After 5 hours at room temperature the reaction was quenched with a saturated solution of aqueous NH_4Cl and the aqueous phase extracted three times with EtOAc. The combined organic layers were dried with MgSO_4 , filtered and concentrated. Further purification was not required and the crude material was dissolved in 4 mL of 5:1 THF/ H_2O . To this solution was added 0.06 mL of 4% aqueous solution of OsO_4 (0.009 mmol) followed by 44 mg of NMO (0.376 mmol). After 4 hours of stirring at room temperature, 121 mg (0.566 mmol) of NaIO_4 was added and reaction was allowed to proceed for another 10 hours. An aqueous solution of Na_2SO_3 was added and the biphasic mixture stirred vigorously for 30 minutes. The aqueous phase was extracted three times with diethyl ether and the combined organic phases dried over MgSO_4 , filtered and concentrated. Purification by silica gel flash chromatography (30% EtOAc/hexanes) yielded 23 mg of a white solid (83% for two steps). ^1H NMR (CDCl_3 , 500MHz): 9.19 (s, 1H), 2.72 (dd, J = 14.1, 3.4 Hz, 1H), 2.39 (dd, J = 12.0, 4.1 Hz, 1H), 2.31 (dd, J = 14.2, 14.2 Hz, 1H), 1.85-1.79 (m, 2H), 1.76-1.64 (m, 3H), 1.62-1.54 (m, 6H), 1.50-1.42 (m, 1H), 1.30-1.21 (m, 2H), 1.23 (s, 3H), 1.11 (s, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.79 (dddd, J = 12.8, 12.8, 12.8, 3.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 500 MHz): 209.56, 205.02, 80.17, 51.77, 49.43, 40.86, 40.62, 38.73, 38.48, 32.91, 31.93, 30.37, 27.74, 22.36, 21.13, 17.03, 16.49, 13.64; IR (neat): 3514 (br, w), 2946 (s), 2868 (w), 1712 (s), 1456 (m), 1374 (m), 1315 (w), 1247 (w), 1156 (w), 1066 (w), 1023 (w), 946 (w), 880 (w), 736 (w); HRMS (EI) m/z : calculated 292.2038 for $[\text{M}]^+$, found 292.2054; mp = 117.3-119.6 °C.

4b-Hydroxy-1,4a,6-trimethyl-9-oxo-tetradecahydro-phenanthrene-1-carboxylic acid (30): To a solution of **29** (12.5 mg, 0.041 mmol) in 1.0 mL of a 3:1 tBuOH: H_2O solution was added 49 mg (0.408 mmol)

NaH_2PO_4 followed by 0.36 mL (4.075 mmol) cyclopentene. The reaction was cooled to 0 °C and 22 mg (0.243 mmol) NaClO_2 in 0.5 mL of 3:1 tBuOH: H_2O added. After 15 minutes the reaction was quenched with a saturated aqueous solution of Na_2SO_3 and brine. The aqueous phase was extracted three times with EtOAc and the combined organic phases dried over MgSO_4 , filtered and concentrated. Purification by silica gel flash chromatography (30% EtOAc/hexanes and 1% AcOH) yielded 9.2 mg (78%) of a white solid. ^1H NMR (CDCl_3 , 300MHz): 2.92 (dd, J = 13.8, 3.0 Hz, 1H), 2.34 (dd, J = 11.9, 3.8 Hz, 1H), 2.33 (dd, J = 14.4, 13.4 Hz, 1H), 2.09 (dd, J = 14.4, 3.2 Hz, 1H), 1.82-1.75 (m, 2H), 1.68-1.47 (m, 9H), 1.25-1.17 (m, 1H), 1.21 (s, 3H), 1.18 (s, 3H), 0.88 (d, J = 6.1 Hz, 3H), 0.82-0.69 (m, 1H), 2 exchangeable protons do not appear; ^1H NMR (CD_3OD , 500MHz): 3.01 (dd, J = 14.0, 3.4 Hz, 1H), 2.48 (dd, J = 13.9, 14.0 Hz, 1H), 2.47 (dd, J = 10.9, 4.6 Hz, 1H), 1.97 (dd, J = 14.5, 3.3 Hz, 1H), 1.84-1.75 (m, 1H), 1.74-1.58 (m, 9H), 1.52-1.49 (m, 1H), 1.31-1.26 (m, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.89-0.79 (m, 1H), 2 exchangeable protons do not appear; ^{13}C NMR (CDCl_3 , 300 MHz): 211.86, 182.69, 80.58, 52.09, 47.10, 41.54, 41.14, 40.80, 38.98, 36.55, 33.35, 30.72, 27.98, 22.78, 21.47, 18.18, 16.88, 16.44; ^{13}C NMR (CD_3OD , 500MHz): 212.72, 180.28, 79.71, 51.43, 46.48, 41.19, 40.41, 40.31, 37.95,

36.22, 32.91, 30.15, 27.02, 21.35, 20.81, 17.49, 15.51, 15.26; IR (neat): 3526 (m, br), 2952 (s), 2873 (m), 1698 (s), 1454 (m), 1390 (m), 1367 (m), 1268 (m), 1242 (s), 1151 (s), 1128 (m), 736 (m); HRMS (EI) m/z: calculated 308.1988 for $[M]^+$, found 308.1974; mp = 178.6-180.9 °C.

4b-Hydroxy-1,4a,6,8a-tetramethyl-9-oxo-tetradecahydro-phenanthrene-1-carboxylic acid methyl ester (31): To a solution of **30** (4.5 mg, 0.015 mmol) in 0.5 mL ether cooled to 0 °C was added a solution of diazomethane in ether dropwise until a faint yellow colour persisted. A small amount of silica gel (0.2 mL) was added and the reaction mixture was concentrated. Purification by silica gel flash chromatography (20% EtOAc/hexanes) yielded 4.4 mg of a white solid (94%). ^1H NMR (CDCl_3 , 300MHz): 3.63 (s, 3H), 2.93 (dd, $J = 14.0, 3.5$ Hz, 1H), 2.37-2.28 (m, 2H), 1.93 (dd, $J = 14.3, 3.5$ Hz, 1H), 1.85-1.69 (m, 3H), 1.67-1.40 (m, 9H), 1.27-1.19 (m, 1H), 1.23 (s, 3H), 1.19 (s, 3H), 0.90 (d, $J = 6.2$ Hz, 3H), 0.86-0.70 (m, 1H); ^{13}C NMR (CDCl_3 , 500 MHz): 210.20, 178.07, 80.02, 52.19, 51.65, 47.17, 41.27, 40.98, 40.60, 38.73, 36.25, 33.01, 30.45, 27.75, 22.39, 21.20, 17.88, 16.53, 16.38; IR (neat): 3522 (m, br), 2948 (s), 2867 (m), 1710 (s), 1456 (m), 1391 (w), 1372 (w), 1255 (m), 1241 (m), 1197 (w), 1152 (m), 1092 (w); HRMS (EI) m/z: calculated 322.2144 for $[M]^+$, found 322.2135; mp = 186.3-191.6 °C.

ppm

S10

Current Data Parameters
NAME effie_134
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20030212
Time 13.05
PULPROG zgdc
SOLVENT CDCl3
AQ 1.0485960
FIDRES 0.476837
DQ 16.0
RG 32768
NUCLEUS 13C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SNH 31250.00
TD 65536
NS 1361
DS 0

F1 - Processing parameters
SI 32768
MC2 QF
SF 125.7591504
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters
CX 22.00
F1P 220.000
F1 27667.01
F2P -10.000
F2 -1257.59
PPMCM 10.45455
HZCM 1314.75476

S11

Integral

ppm

Current Data Parameters
NAME effie_134
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20030212
Time 12.57
PULPROG zg
SOLVENT CDCl3
AQ 4.6530805 sec
FIDRES 0.107456 Hz
DM 71.0 usec
RG 1024
NUCLEUS 1H
HL1 0 dB
D1 0.0100000 sec
P1 5.6 usec
DE 88.8 usec
SF01 500.1381707 MHz
SWH 7042.25 Hz
TD 65536
NS 16
DS 0

F1 - Processing parameters
SI 32768
MC2 GF
SF 500.1354311 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0

1D NMR plot parameters
CX 22.00 cm
F1P 9.000 ppm
F1 4501.22 Hz
F2P -1.000 ppm
F2 -500.14 Hz
PPMCM 0.45455 ppm/
HZCM 227.33429 Hz/c

¹³C with proton decoupling

S12

Current Data Parameters
NAME effie_210
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030408
Time 15.54
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 29
DS 0
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 512
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SF01 75.4752653 MHz

===== CHANNEL f2 =====
CPOPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 13.48 dB
PL13 15.63 dB
SF02 300.1314860 MHz

F2 - Processing parameters
SI 65536
SF 75.4677536 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 11.50000 ppm/cm
HZCM 867.87909 Hz/cm

ppm

S13

Current Data Parameters

NAME effie_210
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030408
Time 15.51
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDC13
NS 8
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 45.3
DW 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 300.1319477 MHz

F2 - Processing parameters

SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm

ELS-210

S14

S15

^{13}C with proton decoupling

S16

ppm

F2 - Acquisition Parameters

Date_ 20040623
Time 18.03
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 272
DS 0
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 3649.1
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
d11 1.00000000 sec
d12 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====

NUC1 ^{13}C
P1 5.00 usec
PL1 -6.00 dB
SF01 75.4752653 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 ^1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 13.48 dB
PL13 15.63 dB
SF02 300.1314860 MHz

F2 - Processing parameters

SI 65536
SF 75.4677190 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
CY 9.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 11.50000 ppm/cm
HZCM 867.87878 Hz/cm

¹H NMR

S17

Current Data Parameters
NAME effie_other_isomer
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040623
Time 18.01
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 143.7
DM 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 300.1319477 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 9.000 ppm
F1 2701.17 Hz
F2P -1.000 ppm
F2 -300.13 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm

ppm

S18

Current Data Parameters
 NAME effie_212
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date 20030406
 Time 4.25
 PULPROG zgdc
 SOLVENT CDCl3
 AQ 1.0485960
 FIDRES 0.476837
 DW 16.0
 RG 32768
 NUCLEUS 13C
 D11 0.0300000
 P31 80.0
 S2 18
 HL1 22
 D1 1.0000000
 P1 2.0
 DE 20.0
 SF01 125.7724464
 SWH 31250.00
 TD 65536
 NS 1926
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 GF
 SF 125.7591485
 WDW EM
 SSB 0
 LB 1.00
 GB 0

1D NMR plot parameters
 CX 22.00
 F1P 220.000
 F1 27667.01
 F2P -10.000
 F2 -1257.59
 PPMCM 10.45455
 HZCM 1314.75476

ppm

200

150

100

50

0

ELS-212 in CDCl₃

S19

Current Data Parameters

NAME effie_212
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date 20030406
Time 4.18
PULPROG zg
SOLVENT CDCl3
AQ 4.6530805 sec
FIDRES 0.107456 Hz
DM 71.0 usec
RG 2048
NUCLEUS 1H
HL1 0 dB
D1 0.0100000 sec
P1 5.6 usec
DE 88.8 usec
SF01 500.1381707 MHz
SWH 7042.25 Hz
TD 65536
NS 16
DS 0

F1 - Processing parameters

SI 32768
MC2 OF
SF 500.1354311 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0

1D NMR plot parameters

CX 22.00 cm
F1P 9.000 ppm
F1 4501.22 Hz
F2P -1.000 ppm
F2 -500.14 Hz
PPMCM 0.45455 ppm/
HZCM 227.33429 Hz/c

ppm

S20

Current Data Parameters
NAME effie_277
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20030530
Time 21.44
PULPROG zgdc
SOLVENT CDCl3
AQ 1.0485960
FIDRES 0.476837
DW 16.0
RG 32768
NUCLEUS 13C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SWH 31250.00
TD 65536
NS 146
DS 0

F1 - Processing parameters
SI 32768
MC2 QF
SF 125.7591495
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters
CX 22.00
F1P 60.811
F1 7647.60
F2P 10.859
F2 1365.64
PPMCM 2.27056
HZCM 285.54340

S21

Current Data Parameters
NAME effie_277
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20030530
Time 21.32
PULPROG zg
SOLVENT CDC13
AQ 4.6530805 sec
FIDRES 0.107456 Hz
DQ 71.0 usec
RG 512
NUCLEUS 1H
HL1 0 dB
D1 0.0100000 sec
P1 5.6 usec
DE 88.8 usec
SFO1 500.1381707 MHz
SWH 7042.25 Hz
TD 65536
NS 16
DS 0

F1 - Processing parameters
SI 32768
MC2 GF
SF 500.1354311 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0

1D NMR plot parameters
CX 22.00 cm
F1P 6.010 ppm
F1 3005.59 Hz
F2P 4.303 ppm
F2 2152.13 Hz
PPMCM 0.07757 ppm/
HZCM 38.79332 Hz/c

ELS-278 SOUAmx COCl_2

S23

Current Data Parameters
 NAME effie_278c
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20030532
 Time 3.56
 PULPROG zg
 SOLVENT CDC13
 AQ 4.6530805 sec
 FIDRES 0.107456 Hz
 DW 71.0 usec
 RG 512
 NUCLEUS 1H
 HL1 0 dB
 D1 0.0100000 sec
 P1 5.6 usec
 DE 88.8 usec
 SF01 500.1381707 MHz
 SWH 7042.25 Hz
 TD 65536
 NS 16
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 GF
 SF 500.1354311 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0

1D NMR plot parameters
 CX 22.00 cm
 F1P 6.184 ppm
 F1 3092.72 Hz
 F2P 4.274 ppm
 F2 2137.81 Hz
 PPMCM 0.08679 ppm/
 HZCM 43.40512 Hz/c

Integral

ppm

8

7

6

5

4

3

2

1

0

S24

Current Data Parameters
NAME effie_279
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20030600
Time 1.53
PULPROG zgdc
SOLVENT CDCl3
AQ 1.0485960
FIDRES 0.476837
DQ 16.0
RG 32768
NUCLEUS 13C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SWH 31250.00
TD 65536
NS 423
DS 0

F1 - Processing parameters
SI 32768
MC2 QF
SF 125.7591485
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters
CX 22.00
F1P 48.186
F1 6059.85
F2P 10.310
F2 1296.61
PPMCM 1.72163
HZCM 216.51093

S25

Current Data Parameters
NAME effie_279
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20030600
Time 1.46
PULPROG zg
SOLVENT CDC13
AQ 4.6530805 sec
FIDRES 0.107456 Hz
DM 71.0 usec
RG 2048
NUCLEUS 1H
HL1 0 dB
D1 0.0100000 sec
P1 5.6 usec
DE 88.8 usec
SF01 500.1381707 MHz
SWH 7042.25 Hz
TD 65536
NS 16
DS 0

F1 - Processing parameters
SI 32768
MC2 QF
SF 500.1354311 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0

1D NMR plot parameters
CX 22.00 cm
F1P 5.826 ppm
F1 2913.68 Hz
F2P 3.558 ppm
F2 1779.72 Hz
PPMCM 0.10306 ppm/
HZCM 51.54357 Hz/c

Integral

ppm

¹³C with proton decoupling

S26

Current Data Parameters

NAME effie_289
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030610
Time 16.18
INSTRUM av300
PROBHD 5 mm GNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 57
DS 0
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 8192
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====

NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SF01 75.4752653 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 13.48 dB
PL13 15.63 dB
SF02 300.1314860 MHz

F2 - Processing parameters

SI 65536
SF 75.4677511 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
CY 12.50 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 11.50000 ppm/cm
HZCM 867.87909 Hz/cm

S27

Current Data Parameters
 NAME effie_289
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030610
 Time 16.15
 INSTRUM av300
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 30720
 SOLVENT CDC13
 NS 9
 DS 0
 SWH 5081.301 Hz
 FIDRES 0.165407 Hz
 AQ 3.0228980 sec
 RG 45.3
 DW 98.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 300.1319477 MHz

F2 - Processing parameters
 SI 65536
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 20.00 cm
 F1P 9.000 ppm
 F1 2701.17 Hz
 F2P -1.000 ppm
 F2 -300.13 Hz
 PPMCM 0.50000 ppm/cm
 HZCM 150.06500 Hz/cm

ppm

S28

Current Data Parameters

NAME effie_290
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date 20030612
Time 11.44
PULPROG zgdc
SOLVENT CDC13
AQ 1.0485960
FIDRES 0.476837
DQ 16.0
RG 32768
NUCLEUS ¹³C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SWM 31250.00
TD 65536
NS 169
DS 0

F1 - Processing parameters

SI 32768
MC2 GF
SF 125.7591514
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters

CX 22.00
F1P 220.000
F1 27667.01
F2P -10.000
F2 -1257.59
PPMCM 10.45455
HZCM 1314.75476

S29

Current Data Parameters
 NAME effie_290
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20030612
 Time 11.38
 PULPROG zg
 SOLVENT CDCl3
 AQ 4.6530805 sec
 FIDRES 0.107456 Hz
 DW 71.0 usec
 RG 128
 NUCLEUS 1H
 HL1 0 dB
 D1 0.0100000 sec
 P1 5.6 usec
 DE 88.8 usec
 SF01 500.1381707 MHz
 SNH 7042.25 Hz
 TD 65536
 NS 8
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 GF
 SF 500.1354311 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.000 ppm
 F1 4501.22 Hz
 F2P -1.000 ppm
 F2 -500.14 Hz
 PPMCM 0.45455 ppm/
 HZCM 227.33429 Hz/°

¹³C with proton decoupling

S30

Current Data Parameters
 NAME effie_291
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030611
 Time 17.41
 INSTRUM av300
 PROBHD 5 mm GNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT CDC13
 NS 145
 DS 0
 SWH 17985.611 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110004 sec
 RG 3649.1
 DW 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 d12 0.00002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 5.00 usec
 PL1 -6.00 dB
 SF01 75.4752653 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 70.00 usec
 PL2 -3.00 dB
 PL12 13.48 dB
 PL13 15.63 dB
 SF02 300.1314860 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677503 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 220.000 ppm
 F1 16602.91 Hz
 F2P -10.000 ppm
 F2 -754.68 Hz
 PPMCM 11.50000 ppm/cm
 HZCM 867.87921 Hz/cm

ppm

S31

Current Data Parameters
 NAME effie_257
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20030518
 Time 23.02
 PULPROG zg
 SOLVENT CDC13
 AQ 4.6530805 sec
 FIDRES 0.107456 Hz
 DM 71.0 usec
 RG 2048
 NUCLEUS 1H
 HL1 0 dB
 D1 0.0100000 sec
 P1 5.6 usec
 DE 88.8 usec
 SF01 500.1381707 MHz
 SWH 7042.25 Hz
 TD 65536
 NS 32
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 GF
 SF 500.1354311 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0

1D NMR plot parameters
 CX 22.00 cm
 F1P 9.000 ppm
 F1 4501.22 Hz
 F2P -1.000 ppm
 F2 -500.14 Hz
 PPMCM 0.45455 ppm/
 HZCM 227.33429 Hz/c

ppm

S32

Current Data Parameters
 NAME effie_312
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date 20030626
 Time 14.49
 PULPROG zgdc
 SOLVENT CDCl3
 AQ 1.0485960
 FIDRES 0.476837
 DN 16.0
 RG 32768
 NUCLEUS 13C
 D11 0.0300000
 P31 80.0
 S2 18
 HL1 22
 D1 1.0000000
 P1 2.0
 DE 20.0
 SF01 125.7724464
 SWH 31250.00
 TD 65536
 NS 1536
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 OF
 SF 125.7591187
 WDW EM
 SSB 0
 LB 1.00
 GB 0

1D NMR plot parameters
 CX 22.00
 F1P 59.165
 F1 7440.50
 F2P 14.153
 F2 1779.84
 PPMCM 2.04600
 HZCM 257.30276

S33

Current Data Parameters
 NAME effie_312
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20030626
 Time 14.41
 PULPROG zg
 SOLVENT CDC13
 AQ 4.6530805 sec
 FIDRES 0.107456 Hz
 DN 71.0 usec
 RG 2048
 NUCLEUS 1H
 HL1 0 dB
 D1 0.0100000 sec
 P1 5.6 usec
 DE 88.8 usec
 SF01 500.1381707 MHz
 SWH 7042.25 Hz
 TD 65536
 NS 32
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 OF
 SF 500.1354311 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0

1D NMR plot parameters
 CX 22.00 cm
 F1P 5.850 ppm
 F1 2925.61 Hz
 F2P 4.489 ppm
 F2 2245.24 Hz
 PPMCM 0.06184 ppm/
 HZCM 30.92615 Hz/c

ppm

S34

Current Data Parameters

NAME effie_338_340
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date 20030716
Time 9.18
PULPROG zgdc
SOLVENT CDCl3
AQ 1.0485960
FIDRES 0.476837
DQ 16.0
RG 32768
NUCLEUS 13C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SWH 31250.00
TD 65536
NS 1030
DS 0

F1 - Processing parameters

SI 32768
MC2 QF
SF 125.7591187
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters

CX 22.00
F1P 220.000
F1 27667.01
F2P -10.000
F2 -1257.59
PPMCM 10.45455
HZCM 1314.75452

S35

Current Data Parameters
 NAME effie_338_340
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030717
 Time 14.05
 INSTRUM av300
 PROBHD 5 mm GNP 1H/1
 PULPROG zg30
 TD 30720
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 5081.301 Hz
 FIDRES 0.165407 Hz
 AQ 3.0228980 sec
 RG 228.1
 DW 98.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 300.1319477 MHz

F2 - Processing parameters
 SI 65536
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 7.00 cm
 F1P 9.000 ppm
 F1 2701.17 Hz
 F2P -1.000 ppm
 F2 -300.13 Hz
 PPMCM 0.50000 ppm/cm
 HZCM 150.06500 Hz/cm

Derf.

ppm

S36

Current Data Parameters

NAME effie_447
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date 20031020
Time 3.55
PULPROG zgdc
SOLVENT CDCl3
AQ 1.0485960
FIDRES 0.476837
DQ 16.0
RG 32768
NUCLEUS 13C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SWH 31250.00
TD 65536
NS 3838
DS 0

F1 - Processing parameters

SI 32768
MC2 QF
SF 125.7591504
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters

CX 22.00
F1P 154.678
F1 19452.15
F2P 102.530
F2 12894.07
PPMCM 2.37036
HZCM 298.09476

ppm 200 150 100 50 0

S37

Current Data Parameters
NAME effie_447
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20031020
Time 3.49
PULPROG zg
SOLVENT CDC13
AQ 4.6530805 sec
FIDRES 0.107456 Hz
DW 71.0 usec
RG 4096
NUCLEUS 1H
HL1 0 dB
D1 0.0100000 sec
P1 5.6 usec
DE 88.8 usec
SF01 500.1381707 MHz
SWH 7042.25 Hz
TD 65536
NS 46
DS 0

F1 - Processing parameters
SI 32768
MC2 GF
SF 500.1354311 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0

1D NMR plot parameters
CX 22.00 cm
F1P 9.000 ppm
F1 4501.22 Hz
F2P -1.000 ppm
F2 -500.14 Hz
PPMCM 0.45455 ppm/
HZCM 227.33429 Hz/c

ppm

S38

Current Data Parameters
 NAME effie_450
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date 20031020
 Time 1.23
 PULPROG zgdc
 SOLVENT CDCl3
 AQ 1.0485960
 FIDRES 0.476837
 DW 16.0
 RG 32768
 NUCLEUS 13C
 D11 0.0300000
 P31 80.0
 S2 18
 HL1 22
 D1 1.0000000
 P1 2.0
 DE 20.0
 SF01 125.7724464
 SWH 31250.00
 TD 65536
 NS 244
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 GF
 SF 125.7591495
 WDW EM
 SSB 0
 LB 1.00
 GB 0

1D NMR plot parameters
 CX 22.00
 F1P 155.227
 F1 19521.18
 F2P 81.671
 F2 10270.83
 PPMCM 3.34346
 HZCM 420.47052

S39

Current Data Parameters
 NAME effie_450
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20031020
 Time 1.17
 PULPROG zg
 SOLVENT CDCl3
 AQ 4.6530805 sec
 FIDRES 0.107456 Hz
 DW 71.0 usec
 RG 1024
 NUCLEUS 1H
 HL1 0 dB
 D1 0.0100000 sec
 P1 5.6 usec
 DE 88.8 usec
 SF01 500.1381707 MHz
 SWH 7042.25 Hz
 TD 65536
 NS 16
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 OF
 SF 500.1354311 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0

1D NMR plot parameters
 CX 22.00 cm
 F1P 5.730 ppm
 F1 2865.93 Hz
 F2P 4.155 ppm
 F2 2078.13 Hz
 PPMCM 0.07160 ppm/
 HZCM 35.80922 Hz/c

Integral

ppm

8

7

6

5

4

3

2

1

0

S40

Current Data Parameters
 NAME effie_440Pd
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date 20031012
 Time 1.18
 PULPROG zgdc
 SOLVENT CDCl3
 AQ 1.0485960
 FIDRES 0.476837
 DW 16.0
 RG 32768
 NUCLEUS 13C
 D11 0.0300000
 P31 80.0
 S2 18
 HL1 22
 D1 1.0000000
 P1 2.0
 DE 20.0
 SF01 125.7724464
 SWH 31250.00
 TD 65536
 NS 1386
 DS 0

F1 - Processing parameters
 SI 32768
 MC2 OF
 SF 125.7591495
 WDW EM
 SSB 0
 LB 1.00
 GB 0

1D NMR plot parameters
 CX 22.00
 F1P 56.969
 F1 7164.37
 F2P 7.566
 F2 951.45
 PPMCM 2.24561
 HZCM 282.40555

S41

Current Data Parameters
NAME effie_440Pd
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20031012
Time 0.47
PULPROG zg
SOLVENT CDC13
AQ 4.6530805 sec
FIDRES 0.107456 Hz
DM 71.0 usec
RG 2048
NUCLEUS 1H
HL1 0 dB
D1 0.0100000 sec
P1 5.6 usec
DE 88.8 usec
SF01 500.1381707 MHz
SMH 7042.25 Hz
TD 65536
NS 16
DS 0

F1 - Processing parameters
SI 32768
MC2 GF
SF 500.1354311 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0

1D NMR plot parameters
CX 22.00 cm
F1P 2.938 ppm
F1 1469.37 Hz
F2P 0.549 ppm
F2 274.54 Hz
PPMCM 0.10859 ppm/
HZCM 54.31065 Hz/c

Integral

ppm

CDCl₃

¹³C with proton decoupling

S43

Current Data Parameters
 NAME effie_705acid_cdc13
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040623
 Time 17.50
 INSTRUM av300
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT CDC13
 NS 275
 DS 0
 SWH 17985.611 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110004 sec
 RG 3649.1
 DW 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 d12 0.00002000 sec

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 5.00 usec
 PL1 -6.00 dB
 SF01 75.4752653 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 ¹H
 PCPD2 70.00 usec
 PL2 -3.00 dB
 PL12 13.48 dB
 PL13 15.63 dB
 SF02 300.1314860 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677190 MHz
 MDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 7.00 cm
 F1P 220.000 ppm
 F1 16602.90 Hz
 F2P -10.000 ppm
 F2 -754.68 Hz
 PPMCM 11.50000 ppm/cm
 HZCM 867.87878 Hz/cm

S44

¹H NMR

S46

Current Data Parameters
NAME effie_705acid_cdcl3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040623
Time 17.49
INSTRUM av300
PROBHD 5 mm GNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 8
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 181
DM 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SFO1 300.1319477 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 9.000 ppm
F1 2701.17 Hz
F2P -1.000 ppm
F2 -300.13 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm

¹H NMR

S47

Current Data Parameters
 NAME effie_705acid_cdc13
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040623
 Time 17.49
 INSTRUM av300
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 30720
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 5081.301 Hz
 FIDRES 0.165407 Hz
 AQ 3.0228980 sec
 RG 181
 DM 98.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

----- CHANNEL f1 -----
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 300.1319477 MHz

F2 - Processing parameters
 SI 65536
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 8.00 cm
 F1P 3.317 ppm
 F1 995.61 Hz
 F2P 0.349 ppm
 F2 104.60 Hz
 PPMCM 0.14844 ppm/cm
 HZCM 44.55048 Hz/cm

DDM

S48

Current Data Parameters
NAME effie_517
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 19940304
Time 20.45
PULPROG zgdc
SOLVENT CDCl3
AQ 1.0485960
FIDRES 0.476837
Dw 16.0
RG 32768
NUCLEUS 13C
D11 0.0300000
P31 80.0
S2 18
HL1 22
D1 1.0000000
P1 2.0
DE 20.0
SF01 125.7724464
SWH 31250.00
TD 65536
NS 20480
DS 0

F1 - Processing parameters
SI 32768
MC2 QF
SF 125.7591495
WDW EM
SSB 0
LB 1.00
GB 0

1D NMR plot parameters
CX 22.00
F1P 229.979
F1 28921.93
F2P -18.512
F2 -2328.07
PPMCM 11.29504
HZCM 1420.45447

S49

Current Data Parameters
 NAME effie_517
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040108
 Time 16.32
 INSTRUM av300
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 30720
 SOLVENT CDCl3
 NS 32
 DS 0
 SWH 5081.301 Hz
 FIDRES 0.165407 Hz
 AQ 3.0228980 sec
 RG 574.7
 DW 98.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SFO1 300.1319477 MHz

F2 - Processing parameters
 SI 65536
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 10.00 cm
 F1P 9.000 ppm
 F1 2701.17 Hz
 F2P -1.000 ppm
 F2 -300.13 Hz
 PPMCM 0.50000 ppm/cm
 HZCM 150.06500 Hz/cm

ELS-517 300 MHz CDCl3

This spectrum was taken in MeOH, therefore it has some chemical differences from the 13C NMR spectrum in CDCl₃ in the manuscript

S50

HERTZ
10032.1

9178.

7508.

5508

4148

S51

210 200 190 180 170 160 150 140 130 120 110 100 90
PPM

BB-decoupled spectrum in d-MeOH

* S. W. -10 (MEOH)

NOE (in CDCl_3 , 400 MHz)
Bruker

S53

S54

H-17

CDCl₃

974.44
965.73
945.28

770.69

71.92
71.22
58.68
57.55

¹H NMR (in CDCl₃, 200 MHz)
Bruker

547.28
539.92
530.48
521.75
513.12
511.52
491.69
471.21
461.69
450.35
443.95
433.65
431.90
428.15
419.61
413.67
404.15
403.22
400.00
393.58
373.19
366.17
358.31
350.26
345.99
339.82
334.72
327.05
319.24
315.12
308.51
298.92
294.15
289.42
285.78
279.26
271.96
265.46
251.07
237.82
233.45
229.24
224.46
215.71
206.76
193.00
183.50
180.00
173.99
169.51
159.00

109.44

79.92

71.22

58.68

57.55

S55