Supporting information

Total synthesis of (–)-Chamobtusin A

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General Methods. Reported melting points are uncorrected. Unless otherwise stated, ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or CD_3OD on a 400 MHz instrument. Proton chemical shifts are given in δ (ppm) relative to internal CHCl_3 (7.26 ppm) or CD_3OH (4.78 ppm). Carbon chemical shifts are given relative to CDCl_3 (77.05 ppm) or CD_3OD (49.3 ppm). Analytical TLC was carried out with precoated silica gel 60 F_{254} plates (Merck). Flash column chromatography was performed on Silica gel 60N (spherical, neutral, 40–50 mm, Kanto Chemical Co., Inc.).

Experimental Procedures.

4 $\{[\alpha]_{\text{D}}^{25} -42.7$ (c 0.47 CHCl_3) lit.⁴ $[\alpha]_{\text{D}}^{17} -39.1$ (c 0.44, CHCl_3) $\}$ was prepared according to the method of Katerinopoulos and co-workers⁵ from (+)-Wieland–Miescher ketone.⁶ (+)-Wieland–Miescher ketone (>99% ee by HPLC) was prepared according to the literature procedure using L-proline as a chiral catalyst $\{[\alpha]_{\text{D}}^{25} +98.2$ (c 1.0, toluene) $\}$.

(2*R*,4*aS*,8*aS*)- and (2*S*,4*aS*,8*aS*)-2-Hydroxy-5,5,8*a*-trimethyloctahydro-naphthalen-1(2*H*)-one (5). LHMDs (1.0 M in hexane, 20.6 mL, 20.6 mmol) was added to a solution of **4** (2.01 g, 10.3 mmol) in THF (100 mL) at 0 °C under argon. After stirring for 5 min, TMSCl (3.37 mL, 25.8 mmol) was added dropwise to the

mixture at the same temperature, and the mixture was stirred for 5 min. The reaction was quenched with a saturated aqueous solution of NaHCO₃ (100 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 100 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure to afford orange oil, which was used in the next step without further purification. Solid 65% *m*-CPBA (contains ca. 30% water, 3.02 g, 11.4 mmol) was added to a solution of the above residue in CH₂Cl₂ (100 mL) at 0 °C. After stirring for 20 min, the reaction was quenched with successive addition of saturated aqueous Na₂S₂O₃ (50 mL) and saturated aqueous NaHCO₃ (50 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 100 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure to afford a yellow oil, which was used in the next step without further purification. Tetrabutylammonium fluoride (1.0 M in THF, 7.21 mL, 7.21 mmol) was added to a solution of the above residue in THF (35 mL) at room temperature. After stirring 10 min, the reaction was quenched with saturated aqueous NaHCO₃ (30 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 50 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (8;1) to give **5** (2.02 g, 93% from **4**) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.91-0.94 (6H, m), 1.10-1.17 (3H, s), 1.28-2.05 (10H, m), 2.22-2.27 (0.36H, m), 2.44-2.51 (0.64H, m), 3.44 (0.34H, m), 3.63 (0.62H, m), 4.35-4.43 (1H, m). HRMS (ESI) calcd for C₁₃H₂₂O₂Na [M+Na]⁺ 233.1517, found 233.1519.

(1*R*,4*aS*,8*aS*)-1-Hydroxy-5,5,8*a*-trimethyl-1-vinyloctahydronaphthalen-2(1*H*)-one (7**).** Dess–Martin periodinane (1.9 g, 4.50 mmol) was added to a solution of **5** (473 mg, 2.25 mmol) in dry CH₂Cl₂ (23 mL) at 0 °C, and stirring was continued for 2 h at room temperature. The reaction was quenched with successive addition of saturated

aqueous Na₂S₂O₃ (10 mL) and saturated aqueous NaHCO₃ (10 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 30 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure to afford a yellow solid, which was used in the next step without further purification. LHMDS (1.0 M in hexane, 5.63 mL, 5.63 mmol) was added to a solution of the above residue in THF (23 mL) at 0 °C under argon. After stirring for 10 min at 0 °C, TBSCl (1.04 g, 6.75 mmol) was added to the mixture, and the mixture was stirred for 5 min. The reaction was quenched with saturated aqueous NaHCO₃ (30 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 30 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was roughly purified by silica gel flash column chromatography with hexane/EtOAc (4:1) to afford a yellow oil, which was used in the next step without further purification. Vinylmagnesium bromide (1.0 M in THF, 6.75 mL, 6.75 mmol) was added to a solution of the above residue in THF (23 mL) at 0 °C under argon. After stirring for 20 min at 0 °C, the reaction was quenched with saturated aqueous NH₄Cl (30 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 30 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure to afford a dark yellow oil, which was used in the next step without further purification. Tetrabutylammonium fluoride (1.0 M in THF, 2.25 mL, 2.25 mmol) was added to a solution of the above residue at room temperature. After stirring 5 min at room temperature, the reaction was quenched with saturated aqueous NaHCO₃ (30 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 30 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (20:1) to give **7** (408 mg, 77% from **5**) as white crystals. [α]_D²⁵ -20.6 (*c* 1.01, CHCl₃); mp 87-88 °C; IR (KBr) 3469, 1713cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (3H, s), 0.89 (3H, s), 0.99 (3H, s), 1.19-1.23 (1H, m), 1.41-1.55 (5H, m), 1.66-1.77 (1H, m), 1.80-1.84 (1H, m), 2.02-2.09 (1H, m), 2.48-2.58 (2H, m), 3.91 (1H, br s), 5.30 (1H, dd, *J* = 10.6, 1.8 Hz), 5.54 (1H, dd, *J* = 16.6, 1.8 Hz), 6.36 (1H, dd, *J* = 16.6, 10.6 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.5 (CH₂), 18.4 (CH₃), 21.9 (CH₂), 23.4 (CH₃), 32.5 (CH₃), 33.7 (C), 33.8 (CH₂), 37.1 (CH), 41.9 (CH), 46.3 (C), 46.8 (CH), 85.3 (C), 118.3 (CH), 135.4 (CH₂), 211.5 (C); HRMS (ESI) calcd for C₁₅H₂₄O₂Na [M+Na]⁺ 259.1674, found 259.1678. Anal. Calcd

for C₁₅H₂₄O₂: C, 76.23; H, 10.24. Found: C, 76.01; H, 10.08.

(1*R*,4*aS*,8*aS*)-1-Hydroxy-1-(2-hydroxyethyl)-5,5,8*a*-trimethyloctahydro-naphthalen-2(1*H*)-one (8). Cyclohexene (165 μ L, 1.63 mmol) was added to a solution of BH₃·THF (0.93 M in THF, 0.83 mL, 0.776 mmol) at 0 °C under argon. After stirring for 1 h at the same temperature, a solution of **7** (91.7 mg, 0.388 mmol) in THF (2.5 mL) was added to the mixture at 0 °C. After stirring for 2 h at 0 °C, 3N NaOH (0.65 mL) and 30% H₂O₂ (220 μ L) was added to the mixture, which was stirred at room temperature for 30 min. The reaction was quenched with saturated aqueous NH₄Cl (5 mL) at 0 °C, and the resulting mixture was extracted with AcOEt (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (2;1) to give **8** (63.3 mg, 65%) as white crystals. $[\alpha]_D^{25}$ -29.3 (*c* 1.00, CHCl₃); mp 115-118 °C; IR (KBr) 3409, 1710cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (3H, s), 0.89 (3H, s), 0.99 (3H, s), 1.19-1.23 (1H, m), 1.41-1.55 (5H, m), 1.66-1.77 (1H, m), 1.80-1.84 (1H, m), 2.02-2.09 (1H, m), 2.48-2.58 (2H, m), 3.91 (1H, br s), 5.30 (1H, dd, *J* = 10.6, 1.8 Hz), 5.54 (1H, dd, *J* = 16.6, 1.8 Hz), 6.36 (1H, dd, *J* = 16.6, 10.6 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.5 (CH₂), 18.4 (CH₃), 21.9 (CH₂), 23.4 (CH₃), 32.5 (CH₃), 33.7 (C), 33.8 (CH₂), 37.1 (CH), 41.9 (CH), 46.3 (C), 46.8 (CH), 85.3 (C), 118.3 (CH), 135.4 (CH₂), 211.5 (C); HRMS (ESI) calcd for C₁₅H₂₆O₃Na [M+Na]⁺ 277.1780, found 277.1777. Anal. Calcd for C₁₅H₂₆O₃: C, 70.83; H, 10.30; N, 0.00. Found: C, 70.69; H, 10.32; N, 0.01.

2-(2-((1*R*,4*aS*,8*aS*)-1-Hydroxy-5,5,8*a*-trimethyl-2-oxodecahydronaphthalen-1-yl)ethoxy)-1*H*-isoindole-1,3(2*H*)-dione (9). *N*-Hydroxyphthalimide (609 mg, 3.66 mmol) and triphenyl phosphine (653 mg, 2.44 mmol) were added to a solution of **8** (310 mg, 1.2 mmol) in THF (12 mL) at room temperature under argon. To the mixture was added diethyl azodicarboxylate (40% in toluene, 1.11 mL, 2.44 mmol) at 0 °C. After stirring for 1h at room temperature, the reaction was quenched with saturated aqueous NaHCO₃ (20 mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 30 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (4;1) to give **9** (487 mg, 100%) as white crystals. $[\alpha]_D^{25} -18.4$ (*c* 1.00, CHCl₃); mp 157-158 °C; IR (KBr) 3465, 1732cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (3H, s), 0.88 (3H, s), 0.99 (3H, s), 1.19-1.30 (1H, m), 1.45-1.58 (5H, m), 1.67 (1H, td, *J* = 13.0, 5.08 Hz), 1.79 (1H, dd, *J* = 13.0, 3.16 Hz), 2.02-2.08 (1H, m), 2.32-2.38 (1H, m), 2.52-2.64 (2H, m), 2.78 (1H, td, *J* = 13.7, 7.62 Hz), 3.98 (1H, s), 4.04-4.10 (1H, m), 4.16-4.21 (1H, m), 7.72-7.74 (2H, m), 7.80-7.83 (2H, m); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.2 (CH₃), 18.5 (CH₂), 22.1 (CH₃), 23.8 (CH₂), 32.1 (CH₂), 32.2 (CH₂), 33.8 (C), 33.9 (CH₃), 37.1 (CH₂), 42.0 (CH₂), 46.4 (C), 46.9 (CH), 74.8 (CH₂), 82.3 (C), 123.5 (CH x 2), 129.0 (C x 2), 134.5 (CH x 2), 163.3 (C x 2), 213.9 (C); HRMS (ESI) calcd for C₂₃H₂₉NO₅Na [M+Na]⁺ 422.1943, found 422.1947. Anal. Calcd for C₂₃H₂₉NO₅: C, 69.15; H, 7.32; N, 3.51. Found: C, 69.02; H, 7.35; N, 3.66.

(6a*S*,10a*S*,10b*R*)-7,7,10a-Trimethyl-10b-hydroxy-2,5,6,6a,7,8,9,10,10a,10b-decahydro-1*H*-naphtho[2,1-*c*][1,2]oxazine. Hydrazine monohydrate (100 μ L, 2.06 mmol) was added to a solution of **9** (329 mg, 0.824 mmol) in CHCl_3 (8.2 mL) at room temperature. After stirring for 20 min at the same temperature, the mixture was filtered, and the filtrate was concentrated under reduced pressure to afford a yellow oil, which was used in the next step without further purification. Acetic acid (47.0 μ L, 0.824 mmol) was added to a solution of the above residue in EtOH (8.2 mL) at the room temperature. The mixture was heated at reflux for 12 h. After cooling, the reaction was quenched with saturated aqueous NaHCO_3 (10 mL) at 0 $^\circ\text{C}$, and the resulting mixture was extracted with Et_2O (3 $\times$ 20 mL). The combined extracts were washed with brine, then dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (2;1) to give the title compound (175 mg, 84%) as white crystals. $[\alpha]_D^{25} -102.7$ (c 1.00, CHCl_3); mp 173-175 $^\circ\text{C}$; IR (KBr) 3291cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.86 (3H, s), 0.90-0.95 (1H, m), 0.95 (3H, s), 1.05-1.09 (1H, m), 1.25 (3H, s), 1.42-1.52 (5H, m), 1.68-2.00 (5H, m), 2.37-2.43 (1H, m), 2.57-2.64 (1H, m), 4.15-4.27 (2H, m); ^{13}C NMR (100.6 MHz, CDCl_3) δ 17.5 (CH_3), 18.5 (CH_2), 21.1 (CH_2), 22.9 (CH_3), 25.4 (CH_2), 29.1 (CH_2), 33.2 (CH_3), 33.7 (C), 34.6 (CH_2), 42.2 (C), 42.4 (CH_2), 43.6 (CH), 63.8 (CH_2), 67.1 (C), 159.9 (C); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 252.1964, found 252.1966. Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_2$: C, 71.67; H, 10.02; N, 5.57. Found: C, 71.57; H, 9.91; N, 5.67.

(6a*S*,10a*S*,10b*R*)-7,7,10a-Trimethyl-10b-trimethylsilyloxy-2,5,6,6a,7,8,9,10,10a,10b-decahydro-1*H*-naphtho[2,1-*c*][1,2]oxazine (3). 2,6-lutidine (76.5 μL , 0.422 μmol) was added to a solution of the above oxime ether (53.1 mg, 0.211 mmol) in CH_2Cl_2 (2.1 mL) at 0 $^\circ\text{C}$ under argon. After stirring for 10 min, TMSOTf (49.0 μL , 0.422 μmol) was added dropwise to the mixture at the same temperature. After stirring for 5 min, the reaction was quenched with saturated aqueous NaHCO_3 (5 mL) at 0 $^\circ\text{C}$, and the resulting mixture was extracted with Et_2O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/ EtOAc (20;1) to give **3** (67.9 mg, 100%) as a colorless oil. $[\alpha]_D^{25} -143.9$ (c 0.60, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 0.13 (9H, s), 0.84 (3H, s), 0.84-0.89 (1H, m), 0.95 (3H, s), 1.03-1.10 (1H, m), 1.16 (3H, s), 1.40-1.50 (5H, m), 1.66-1.73 (2H, m), 1.80-1.85 (1H, m), 1.88-1.96 (1H, m), 2.33-2.40 (1H, m), 2.57-2.66 (1H, m), 4.11-4.23 (2H, m); ^{13}C NMR (100.6 MHz, CDCl_3) δ 2.26 ($\text{CH}_3 \times 3$), 18.6 (CH_2), 18.9 (CH_3), 21.6 (CH_2), 23.0 (CH_3), 26.3 (CH_2), 29.7 (CH_2), 33.2 (CH_3), 33.7 (C), 34.5 (CH_2), 42.6 (CH_3), 43.1 (CH), 43.5 (C), 63.4 (CH_2), 69.8 (C), 158.2 (C); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{34}\text{NO}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 324.2359 found 324.2356.

mL) at 0 °C, and the resulting mixture was extracted with Et₂O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (2;1) to give **12** (21.1 mg, 85%) as white crystals. $[\alpha]_D^{25} -63.3$ (*c* 0.26, CHCl₃); mp 112-114 °C; IR (KBr) 1545cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.11 (9H, s), 0.81 (6H, s), 0.90 (3H, s), 1.05-1.71 (9H, m), 2.13-2.19 (3H, m), 2.59-2.68 (1H, m), 3.54 (1H, d, *J* = 10.3 Hz), 4.25-4.31 (1H, m), 5.14-5.21 (1H, m), 5.58 (1H, dd, *J* = 10.2, 1.32 Hz), 5.70 (1H, dd, *J* = 16.8, 1.16 Hz), 6.28 (1H, dt, *J* = 16.8, 10.3 Hz), 7.67-7.84 (8H, m), 8.13-8.15 (1H, m), 8.22-8.24 (1H, m); ¹³C NMR (100.6 MHz, CDCl₃) δ 1.87 (CH₃ x 3), 14.1 (CH₃), 18.5 (CH₂), 21.1 (CH₂), 21.9 (CH₃), 27.3 (CH₂), 31.9 (CH₂), 32.1 (CH₂), 33.6 (CH₃), 33.9 (C), 41.7 (CH₂), 47.4 (C), 48.3 (CH), 53.8 (CH), 61.2 (C), 69.4 (CH₂), 81.3 (C), 124.2 (CH₂), 124.4 (CH), 124.8 (CH), 128.8 (CH), 129.7 (C), 130.0 (CH), 131.6 (CH), 132.4 (CH), 132.7 (CH), 133.4 (CH), 134.8 (CH), 135.0 (C), 147.1 (C), 148.5 (C); HRMS (ESI) calcd for C₃₃H₄₅N₃O₁₀NaSiS₂ [M+Na]⁺ 758.2213, found 758.2205. Anal. Calcd for C₃₃H₄₅N₃O₁₀SiS₂: C, 53.86; H, 6.16; N, 5.71. Found: C, 53.95; H, 6.18; N, 5.81.

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Crystallographic data of compound **12**

Identification code	p212121
Empirical formula	C ₃₃ H ₄₅ N ₃ O ₁₀ S ₂ Si
Formula weight	735.93
Temperature	90 K
Wavelength	0.71073 Å

Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 8.2031(5) Å $\alpha = 90^\circ$. b = 11.1707(6) Å $\beta = 90^\circ$. c = 39.186(2) Å $\gamma = 90^\circ$.
Volume	3590.8(4) Å ³
Z	4
Density (calculated)	1.361 Mg/m ³
Absorption coefficient	0.241 mm ⁻¹
F(000)	1560
Crystal size	0.22 x 0.13 x 0.07 mm ³
Theta range for data collection	2.08 to 25.02°.
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 13, -38 ≤ l ≤ 46
Reflections collected	17449
Independent reflections	6353 [R(int) = 0.0316]
Completeness to theta = 25.02°	99.9 %
Absorption correction	Analytical
Max. and min. transmission	0.9833 and 0.9488
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6353 / 6 / 448
Goodness-of-fit on F ²	1.018
Final R indices [I > 2sigma(I)]	R1 = 0.0310, wR2 = 0.0669
R indices (all data)	R1 = 0.0351, wR2 = 0.0692
Absolute structure parameter	0.03(5)
Largest diff. peak and hole	0.233 and -0.267 e.Å ⁻³

(3a*S*,5a*S*,9a*S*,9b*R*)-3a-Allyl-6,6,9a-trimethyl-3-((2-nitrobenzenesulfonyl)-9b-(trimethylsilyloxy)perhydro-1*H*-benzo[*e*]indole (2). PPh₃ (0.583 mg, 2.18 μmol) was added to a solution of Pd₂(dba)₃CHCl₃ (0.563 mg, 0.544 μmol) in THF (200 μL) at room temperature under argon and the mixture was stirred for 10 min. Et₃N (8.0 μL, 54.4 μmol) and HCO₂H (2.0 μL, 54.4 μmol) were added to the mixture at room temperature. After stirring for 10 min, a solution of **12** (10.0 mg, 13.6 μmol) in THF (500 μL) was added to the mixture, and the mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by silica gel flash column chromatography with hexane/EtOAc (5;1) to give **2** (6.70 mg, 92%) as a yellow oil: $[\alpha]_D^{25} +17.0$ (*c* 1.25, CHCl₃); IR (neat) 1543 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.09 (9H, s), 0.82 (3H, s), 0.86 (3H, s), 1.10 (3H, s), 1.10-1.63 (11H, m), 1.87 (1H, dd, *J* = 13.5, 6.84), 2.36-2.45 (2H, m), 2.77 (1H, dd, *J* = 17.0, 7.06 Hz), 3.10 (1H, dd, *J* = 17.0, 6.80 Hz), 3.40-3.47 (1H, m), 3.79 (1H, dd, *J* = 9.80, 9.00 Hz), 4.86-4.98 (2H, m), 6.12-6.18 (1H, m); ¹³C NMR (100.6 MHz, CDCl₃) δ 2.75 (CH₃ × 3), 15.1 (CH₃), 18.3 (CH₂), 19.8 (CH₂), 21.7 (CH₃), 30.7 (CH₂), 33.4 (CH₃), 33.9 (C), 34.5 (CH₂), 37.9 (CH₂), 38.9 (CH₂), 41.7 (CH₂), 43.3 (C), 46.0 (CH₂), 49.6 (CH), 77.3 (C), 92.3 (C), 114.0 (CH₂), 123.6 (CH), 130.7 (CH), 131.2 (CH), 133.1 (CH), 134.5 (C), 137.6 (CH), 148.7 (C); HRMS (ESI) calcd for C₂₇H₄₂N₂O₅NaSiS [M+Na]⁺ 557.2481, found 557.2491.

2-((3a*S*,5a*S*,9a*S*,9b*R*)-6,6,9a-Trimethyl-3-[(2-nitrobenzenesulfonyl)-9b-(trimethylsilyloxy)perhydro-1*H*-benzo[*e*]indol-3a-yl]acetaldehyde (13). *N*-Methyl morpholine *N*-oxide (30.0 mg, 0.248 mmol) and osmium(IV) tetroxide (4 wt.% in H₂O, 120 μ L, 18.6 μ mol) was added to a stirred solution of **2** (66.3 mg, 0.124 mmol) in MeCN/H₂O (4:1, 1.2 mL) at room temperature under argon. After stirring for 17 h at room temperature, the reaction was quenched with saturated aqueous Na₂S₂O₃ (2.0 mL) at 0 $^{\circ}$ C, and the resulting mixture was extracted with Et₂O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was roughly purified by silica gel flash column chromatography with hexane/EtOAc (1:1.5) to afford a colorless oil, which was used in the next step without further purification. NaIO₄ (53.0 mg, 0.248 mmol) was added to a stirred solution of the above residue in (THF/H₂O 2:1, 1.2 mL) at room temperature. After stirring for 2h, the reaction was quenched with saturated aqueous Na₂S₂O₃ (2.0 mL) at 0 $^{\circ}$ C, and the resulting mixture was extracted with Et₂O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (2;1) to give **13** (53.2 mg, 80% from **2**) as white crystals: $[\alpha]_D^{25} +68.3$ (*c* 0.56, CHCl₃); mp 220-222 $^{\circ}$ C; IR (KBr) 1708, 1544cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ 0.12 (9H, s), 0.81 (3H, s), 0.85 (3H, s), 1.04 (3H, s), 1.04-1.63 (11H, m), 1.98 (1H, dd, *J* = 13.6, 7.08 Hz), 2.24 (1H, dt, *J* = 13.6, 3.16 Hz), 2.37-2.46 (1H, m), 2.82 (1H, dd, *J* = 17.0, 5.86 Hz), 3.22 (1H, d, *J* = 17.0 Hz), 3.50-3.58 (1H, m), 3.91 (1H, t, *J* = 9.54 Hz), 7.54-7.56 (1H, m), 7.67-7.71 (2H, m), 8.00-8.03 (1H, m), 9.66 (1H, d, *J* = 5.84 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 2.63 (CH₃ x 3), 15.4 (CH₃), 18.2 (CH₂), 19.4 (CH₂), 21.5 (CH₃), 29.9 (CH₂), 33.4 (C), 33.7 (CH₃), 34.8 (CH₂), 38.4 (CH₂), 41.5 (CH₂), 42.7 (C), 46.4 (CH₂), 46.6 (CH₂), 49.7 (CH), 77.3 (C), 92.5 (C), 123.9 (CH), 130.6 (CH), 131.5 (CH), 133.8 (CH), 134.0 (C), 148.7

(C), 200.0 (CH); HRMS (ESI) calcd for $C_{26}H_{40}N_2O_6NaSiS$ $[M+Na]^+$ 559.2274, found 559.2263. Anal. Calcd for $C_{26}H_{40}N_2O_6SiS$: C, 58.18; H, 7.51; N, 5.22. Found: C, 58.15; H, 7.47; N, 5.33.

(3a*S*,5a*S*,9a*S*,9b*R*)-6,6,9a-Trimethyl-3a-(3-methylbut-2-enyl)-3-((2-nitrobenzenesulfonyl)-9b-(trimethylsilyloxy)perhydro-1*H*-benzo[*e*]indole (14). *n*-BuLi (1.65 M solution in hexane, 0.64 mL, 1.06 mmol) was added dropwise to a stirred suspension of isopropyltriphenylphosphonium iodide (481 mg, 1.09 mmol) in dry THF (7.0 mL) at 0 °C under argon, and stirring was continued for 30 min at the same temperature. A solution of **13** (146 mg, 0.272 mmol) in dry THF (3.0 mL) was added dropwise to the above mixture at 0 °C. After stirring for 10 h at room temperature, the reaction was quenched with saturated aqueous NH_4Cl (15 mL) at 0 °C, and the resulting mixture was extracted with Et_2O (3 x 20 mL). The combined extracts were washed with brine, then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/ $EtOAc$ (5;1) to give **14** (131 mg, 86%) as a yellow oil. $[\alpha]_D^{25} +41.9$ (c 0.65, $CHCl_3$); IR (neat) 1547 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.09 (9H, s), 0.82 (3H, s), 0.86 (3H, s), 1.06 (3H, s), 1.06-1.68 (16H, m), 1.86-1.89 (1H, m), 2.39-2.48 (2H, m), 2.79-2.95 (2H, m), 3.44-3.51 (1H, m), 3.85 (1H, t, $J = 9.56$ Hz), 5.4-5.43 (1H, m), 7.50-7.53 (1H, m), 7.58-7.62 (2H, m), 8.02-8.05 (1H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 2.85 ($CH_3 \times 3$), 15.2 (CH_3), 17.9 (CH_3), 18.3 (CH_2), 19.8 (CH_2), 21.6 (CH_3), 25.9 (CH_3), 30.9 (CH_2), 33.4 (CH_2), 33.5 (C), 33.8 (CH_3), 34.7 (CH_2), 39.1 (CH_2), 41.7 (CH_2), 43.3 (C), 46.2 (CH_2), 49.7 (CH), 77.2 (C), 92.6 (C), 123.4 (CH), 123.5 (CH), 128.1 (C), 130.9 (CH), 131.0 (CH), 132.9 (CH), 134.6 (C), 148.6 (C); HRMS (ESI) calcd for $C_{29}H_{46}N_2O_5NaSiS$ $[M+Na]^+$ 585.2794, found 585.2793.

(3a*S*,5a*S*,9a*S*,9b*R*)-6,6,9a-Trimethyl-3a-(3-methylbut-2-enyl)-3-((2-nitrobenzenesulfonyl)-9b-hydroxyperhydro-1*H*-benzo[*e*]indole. Tetrabutylammonium fluoride (1.0 M solution in THF, 465 μ L, 0.466 mmol) was added to a solution of **14** (131 mg, 0.233 mmol) in THF (2.3 mL) at room temperature. After stirring for 5 min at the same temperature, the reaction was quenched with saturated aqueous NaHCO₃ (3 mL) at 0 $^{\circ}$ C, and the resulting mixture was extracted with Et₂O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (4;1) to give the title compound (113 mg, 99%) as a yellow oil. [α]_D²⁵ +25.8 (*c* 0.6, CHCl₃); IR (neat) 3510, 1543 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.84 (3H, s), 0.87 (3H, s), 1.06 (3H, s), 1.06-1.44 (8H, m), 1.54-1.75 (10H, m), 2.31-2.36 (2H, m), 2.80 (1H, br s), 2.90-2.94 (2H, m), 3.61-3.68 (1H, m), 3.85 (1H, t, *J* = 9.10 Hz), 5.33-5.36 (1H, m), 7.53-7.55 (1H, m), 7.60-7.65 (2H, m), 8.03-8.05 (1H, m); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.8 (CH₃), 18.2 (CH₂), 18.4 (CH₃), 19.9 (CH₂), 21.8 (CH₃), 26.1 (CH₃), 31.8 (CH₂), 33.3 (CH₂), 33.6 (CH₃), 33.8 (CH₂), 33.9 (C), 39.7 (CH₂), 41.8 (CH₂), 42.6 (C), 47.2 (CH₂), 49.5 (CH), 74.9 (C), 88.8 (C), 120.5 (CH), 123.7 (CH), 130.5 (CH), 131.2 (CH), 133.1 (CH), 134.1 (C), 135.0 (C), 148.5 (C); HRMS (ESI) calcd for C₂₆H₃₈N₂O₅NaS [M+Na]⁺ 513.2399, found 513.2397.

(3a*S*,5a*S*,9a*S*)-6,6,9a-Trimethyl-3a-(3-methylbut-2-enyl)-3-((2-nitrobenzenesulfonyl)-3,3a,4,5,5a,6,7,8,9,9a-decahydro-2*H*-benzo[*e*]indole (15**).** (Methoxycarbonylsulfamoyl)triethylammonium hydroxide (164 mg, 0.69 mmol) was added to a solution of the above alcohol (113 mg, 0.23 mmol) in THF (2.3 mL) at room temperature. The mixture was heated at reflux for 15 min. After cooling, the mixture was poured into H₂O and extracted with Et₂O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/EtOAc (5;1) to give **15** (101 mg, 93%) as a yellow oil. $[\alpha]_D^{25} +6.33$ (*c* 0.46, CHCl₃); IR (neat) 1545 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.836 (3H, s), 0.842 (3H, s), 0.87-0.91 (1H, m), 1.06 (3H, s), 1.14-1.19 (1H, m), 1.39-1.55 (5H, m), 1.58 (3H, s), 1.60 (3H, s), 1.63-1.77 (4H, m), 2.57-2.67 (2H, m), 2.94 (1H, dd, *J* = 16.6, 7.16 Hz), 4.05 (1H, dd, *J* = 13.6, 2.40 Hz), 4.16 (1H, dd, *J* = 13.7, 2.70 Hz), 4.90-4.93 (1H, m), 5.34-5.35 (1H, m), 7.51-7.54 (1H, m), 7.60-7.63 (2H, m), 7.88-7.91 (1H, m); ¹³C NMR (100.6 MHz, CDCl₃) δ 18.50 (CH₂), 18.53 (CH₃), 19.2 (CH₃), 20.1 (CH₂), 21.5 (CH₃), 33.3 (C), 33.6 (CH₃), 37.3 (CH₂), 38.3 (CH₂), 38.5 (C), 41.2 (CH₂), 42.0 (CH₂), 55.0 (CH), 55.2 (CH₂), 77.1 (C), 113.3 (CH), 119.1 (CH), 123.7 (CH), 129.8 (CH), 131.2 (CH), 132.9 (CH), 134.3 (C), 134.8 (C), 148.7 (C), 153.3 (C); HRMS (ESI) calcd for C₂₆H₃₇N₂O₄S [M+H]⁺ 473.2474, found 473.2474.

3-Methyl-1-((3*aS*,5*aS*,9*aS*)-6,6,9*a*-trimethyl-3-((2-nitrobenzenesulfonyl)-3,3*a*,4,5,5*a*,6,7,8,9,9*a*-decahydro-2*H*-benzo[*e*]indol-3*a*-yl)butane-2,3-diol.

N-Methylmorpholine *N*-oxide (11.9 mg, 98.6 μmol) and osmium(IV) tetroxide (4 wt.% in H_2O , 47.0 μL , 7.40 μmol) was added to a stirred solution of **15** (23.3 mg, 49.3 μmol) in MeCN/Acetone/ H_2O (4:4:1, 1.5 mL) at room temperature under argon. After stirring for 24 h at room temperature, the reaction was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2.0 mL) at 0 $^\circ\text{C}$, and the resulting mixture was extracted with Et_2O (3 x 10 mL). The combined extracts were washed with brine, then dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was roughly purified by silica gel flash column chromatography with hexane/EtOAc (1:1) to give the title compound (23.1 mg, 92%) as a colorless oil. IR (neat) 3543, 1545 cm^{-1} ; ^1H NMR (major diastereomer, 400 MHz, CDCl_3) δ 0.83 (3H, s), 0.85 (3H, s), 1.18 (3H, s), 1.25 (3H, s), 1.26 (3H, s), 1.40-1.75 (8H, m), 1.90-2.57 (5H, m), 3.95-3.98 (1H, m), 4.22-4.33 (2H, m), 5.39 (1H, br s), 7.57-7.61 (1H, m), 7.66-7.70 (2H, m), 7.92-7.94 (1H, m); ^{13}C NMR (major diastereomer, 100.6 MHz, CDCl_3) δ 18.5 (CH_2), 19.6 (CH_2), 21.1 (CH_3), 21.6 (CH_3), 23.9 (CH_3), 26.5 (CH_3), 33.5 (C), 33.6 (CH_3), 38.6 (C), 39.1 (CH_2), 40.9 (CH_2), 41.8 (CH_2), 42.3 (CH_2), 55.0 (CH_2), 55.4 (CH), 73.2 (C), 75.9 (C), 76.1 (CH), 113.9 (CH), 124.0 (CH), 129.7 (CH), 131.6 (CH), 133.3 (CH), 134.7 (C), 148.8 (C), 156.4 (C); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_6\text{NaS}$ $[\text{M}+\text{Na}]^+$ 529.2348, found 529.2332.

3-Hydroxy-3-methyl-1-((3a*S*,5a*S*,9a*S*)-6,6,9a-trimethyl-3-((2-nitrobenzenesulfonyl)-3,3a,4,5,5a,6,7,8,9,9a-decahydro-2*H*-benzo[*e*]indol-3a-yl)butan-2-one (16).

N-Methylmorpholine *N*-oxide (2.33 mg, 19.3 μ mol) and MS4A (5.0 mg) were added to a stirred solution of the above diol (4.90 mg, 9.67 μ mol) in MeCN (400 μ L) at room temperature under argon. After stirring for 15 min, a solution of TPAP (0.35 mg, 0.97 μ mol) in MeCN (250 μ L) was added dropwise to the above mixture, and the mixture was stirred for 2 h. The solvent was removed under reduced pressure, and the residue was diluted with CHCl₃ and passed through a Celite pad. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with hexane/AcOEt (3:1) to give **16** (3.80 mg, 78%) as a yellow oil. $[\alpha]_D^{25}$ -29.7 (c 0.26, CHCl₃); IR (neat) 3477, 1715, 1546 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.82 (3H, s), 0.83 (3H, s), 0.95 (3H, s), 1.07-1.31 (3H, m), 1.35 (3H, s), 1.36 (3H, s), 1.39-1.74 (8H, m), 2.50 (1H, dt, J = 12.4, 2.93 Hz), 3.45 (1H, d, J = 19.8 Hz), 3.75 (1H, d, J = 19.9 Hz), 4.17 (1H, dd, J = 12.8, 2.68 Hz), 4.37 (1H, dd, J = 12.8, 1.56 Hz), 5.41 (1H, t, J = 2.04 Hz), 7.54-7.56 (1H, m), 7.64-7.67 (2H, m), 7.88-7.90 (1H, m); ¹³C NMR (100.6 MHz, CDCl₃) δ 18.4 (CH₂), 19.1 (CH₃), 20.0 (CH₂), 21.4 (CH₃), 26.9 (CH₃), 27.3 (CH₃), 33.2 (CH₃), 33.6 (C), 37.9 (CH₂), 38.4 (C), 41.9 (CH₂), 42.2 (CH₂), 43.1 (CH₂), 55.3 (C), 55.9 (CH₂), 72.8 (C), 114.5 (CH), 124.0 (CH), 130.0 (CH), 131.4 (CH), 133.4 (CH), 134.2 (C), 148.5 (C), 151.0 (C), 212.1 (C); HRMS (ESI) calcd for C₂₆H₃₆N₂O₆NaS [M+Na]⁺ 527.2192, found 527.2183.

(-)-Chamobtusin A (1). Thiophenol (6.00 μL , 57.8 μmol) and cesium carbonate (18.8 mg, 57.8 μmol) were added to a solution of **16** (14.6 mg, 28.9 μmol) in MeCN (580 μL) at room temperature under argon. After stirring for 14 h at the same temperature, the mixture was directly purified by silica gel flash column chromatography with $\text{CHCl}_3/\text{MeOH}/\text{NH}_4\text{OH}$ (100:9:1) to afford the corresponding amine as a yellow oil, which was used in the next step without further purification. Iodosobenzene (13.4 mg, 61.0 μmol) was added to the above amine in CH_2Cl_2 (500 μL) at room temperature. After stirring for 1 h, the mixture was diluted with CHCl_3 and passed through a Celite pad, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with $\text{CHCl}_3/\text{MeOH}$ (30:1) to give (-)-chamobtusin A (**1**) (7.10 mg, 78 % from **16**) as yellow crystals. $[\alpha]_D^{25}$ -233.2 (c 0.14, MeOH); mp 52-54 $^\circ\text{C}$; IR (neat) 3334, 2930, 1711, 1604, 1518, 1464, 1375, 1236 cm^{-1} ; ^1H NMR (400 MHz, CDOD_3) δ 0.56-0.69 (2H, m), 0.81 (3H, s), 0.90 (3H, s), 1.08 (3H, s), 1.12 (3H, s), 1.13 (3H, s), 1.13-1.25 (1H, m), 1.37-1.74 (8H, m), 2.55 (1H, dt, J = 12.8, 3.02 Hz), 3.31 (1H, d, J = 17.8 Hz), 3.46 (1H, d, J = 17.8 Hz), 6.02 (1H, s), 7.90 (1H, s); ^{13}C NMR (100.6 MHz, CDOD_3) δ 17.6 (CH_3), 19.8 (CH_2), 20.7 (CH_2), 22.4 (CH_3), 27.06 (CH_3), 27.08 (CH_3), 34.5 (CH_3), 35.2 (C), 39.1 (CH_2), 41.8 (C), 42.4 (CH_2), 42.8 (CH_2), 43.5 (CH_2), 59.9 (CH), 78.2 (C), 81.1 (C), 118.4 (CH), 166.0 (CH), 184.8 (C), 213.9 (C); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{32}\text{NO}_2[\text{M}+\text{H}]^+$ 318.2433, found 318.2424.

(-)-1

Crystallographic data of **(-)-chamobtusin A**

Identification code	c2	
Empirical formula	C ₈₀ H ₁₃₄ N ₄ O ₁₃	
Formula weight	1359.91	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 23.3345(19) Å	α = 90°.
	b = 8.6665(7) Å	β = 90.1980(10)°.
	c = 19.1983(16) Å	γ = 90°.
Volume	3882.4(6) Å ³	
Z	2	
Density (calculated)	1.162 Mg/m ³	
Absorption coefficient	0.077 mm ⁻¹	
F(000)	1492.0	
Crystal size	0.35 x 0.20 x 0.11 mm ³	
Theta range for data collection	2.04 to 25.02°.	
Index ranges	-27 ≤ h ≤ 26, -10 ≤ k ≤ 10, -22 ≤ l ≤ 20	
Reflections collected	9363	
Independent reflections	6121 [R(int) = 0.0204]	

Completeness to $\theta = 25.02^\circ$	99.3 %
Absorption correction	Analytical
Max. and min. transmission	0.9912 and 0.9734
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6121 / 55 / 467
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0310$, $wR_2 = 0.0818$
R indices (all data)	$R_1 = 0.0322$, $wR_2 = 0.0828$
Absolute structure parameter	-0.7(6)
Largest diff. peak and hole	0.183 and -0.167 e.Å ⁻³

^1H and ^{13}C NMR spectral data

7

Current Data Parameters
NAME yi-29
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120528
Time 19.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 52.09
DW 60.800 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME yi-29
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120528
Time 19.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 170
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127649 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

8

Current Data Parameters
NAME keto-diol
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20120721
Time 18.28
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SF01 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

8

Current Data Parameters
NAME keto-diol
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120721
Time 18.32
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 169
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127659 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

9

Current Data Parameters
 NAME 956
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120602
 Time 21.18
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 55.5
 DW 60.800 usec
 DE 6.50 usec
 TE 297.4 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PLW1 16.00000000 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

— 213.87

— 163.31

— 134.48

— 128.90

— 123.54

82.25
77.33
77.22
77.01
76.69
74.83

46.93
46.35
42.00
37.10
33.87
33.75
32.19
32.09
23.83
22.10
18.45
14.17

Current Data Parameters
NAME 956
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120602
Time 21.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 497
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127651 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Current Data Parameters
NAME 960
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120604
Time 21.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 62.25
DW 60.800 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

— 159.90

Current Data Parameters
NAME 960
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20120604
Time 21.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 666
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127650 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Current Data Parameters
NAME 914-2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120512
Time_ 22.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 150
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127654 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

11

Current Data Parameters
NAME suzuki
EXPNO 140
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110226
Time 19.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 32
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DM 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCHRK 0.01500000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz

F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 32.00 cm
CY 19.00 cm
F1P 8.000 ppm
F1 3200.24 Hz
F2P -0.500 ppm
F2 -200.01 Hz
PPMCM 0.26562 ppm/cm
HZCM 106.25797 Hz/cm

DPX400 carbon

Current Data Parameters
NAME suzuki
EXPNO 141
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110226
Time 19.09
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3054
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 13004
OW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SF01 100.5986886 MHz

----- CHANNEL 12 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SF02 400.0316001 MHz

F2 - Processing parameters
SI 32768
SF 100.5876190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 30.00 cm
CY 75.00 cm
F1P 140.000 ppm
F1 14082.27 Hz
F2P -10.000 ppm
F2 -1005.88 Hz
PPMCM 5.00000 ppm/cm
HZCM 502.93808 Hz/cm

12

Current Data Parameters
NAME di-Ns
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120713
Time 17.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 62.25
DW 60.800 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME di-Ns
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120713
Time 17.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127644 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

2

Current Data Parameters
 NAME 965-1
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120612
 Time 23.02
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 33.06
 DW 60.800 usec
 DE 6.50 usec
 TE 297.1 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PLW1 16.00000000 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Current Data Parameters
NAME 965-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120612
Time_ 23.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 588
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127652 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

13

Current Data Parameters
 NAME 967
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120611
 Time 22.55
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 55.5
 DW 60.800 use
 DE 6.50 use
 TE 297.4 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 use
 PLW1 16.00000000 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Current Data Parameters
 NAME 968-2
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120611
 Time_ 23.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 948
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 204.44
 DW 20.800 usec
 DE 6.50 usec
 TE 297.6 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PLW1 78.00000000 W
 SFO1 100.6228293 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PLW2 7.09999990 W
 PLW12 0.24961001 W
 PLW13 0.15975000 W
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127652 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

14

Current Data Parameters
NAME 969-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120613
Time 20.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
 NAME 973
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120615
 Time_ 22.31
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 55.5
 DW 60.800 usec
 DE 6.50 usec
 TE 297.3 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PLW1 16.00000000 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Current Data Parameters
 NAME 973
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120615
 Time 22.34
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 304
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 204.44
 DW 20.800 usec
 DE 6.50 usec
 TE 297.5 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PLW1 78.00000000 W
 SFO1 100.6228293 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PLW2 7.09999990 W
 PLW12 0.24961001 W
 PLW13 0.15975000 W
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127652 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

15

Current Data Parameters
 NAME 974
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120616
 Time 20.18
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 55.5
 DW 60.800 use
 DE 6.50 use
 TE 297.4 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 use
 PLW1 16.00000000 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300099 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Current Data Parameters
NAME 974-0
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20120616
Time 22.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 299
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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F2 - Processing parameters
SI                      65536
SF                      400.1300098 MHz
WDW                      EM
SSB                      0
LB                      0.30 Hz
GB                      0
PC                      1.00

```

Current Data Parameters
 NAME 983
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120625
 Time_ 13.18
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 422
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 204.44
 DW 20.800 usec
 DE 6.50 usec
 TE 297.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PLW1 78.00000000 W
 SFO1 100.6228293 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PLW2 7.09999990 W
 PLW12 0.24961001 W
 PLW13 0.15975000 W
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127653 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

16

Current Data Parameters
 NAME 984
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120625
 Time_ 23.39
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 55.5
 DW 60.800 usec
 DE 6.50 usec
 TE 297.3 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PLW1 16.00000000 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

— 212.09

— 151.04
— 148.50

— 134.16
— 133.39
— 131.41
— 130.00
— 123.95

— 114.45

77.37
77.05
76.73
72.77

55.91
55.27
43.05
42.22
41.93
38.43
37.94
33.55
33.16
27.28
26.91
21.41
20.03
19.13

16

Current Data Parameters
NAME 984
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date 20120626
Time 0.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 696
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127648 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

(-)-1

Current Data Parameters
NAME 1005
EXPNO 1
PROCNO 1

F2 - Acquisition Parameter
Date_ 20120712
Time_ 21.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 se
RG 72.93
DW 60.800 us
DE 6.50 us
TE 298.2 K
D1 1.00000000 se
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 us
PLW1 16.00000000 W
SFO1 400.1324710 MH

F2 - Processing parameters
SI 65536
SF 400.1300388 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME 1005
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120712
Time 21.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 501
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6125964 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40