Azabeyerane and Azatrachylobane: Potent Mechanism-based Inhibitors of Recombinant Kaurene Synthase from *Arabidopsis thaliana*

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SUPPORTING INFORMATION

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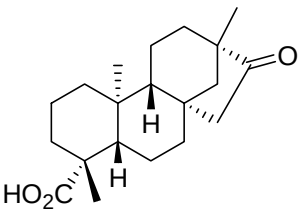
General Aspects and Instrumentation

^{1}H and ^{13}C spectra were recorded in $CDCl_3$ (Chemical shift references ^{1}H, 7.26; ^{13}C, 77.0) with Varian U400 or U500 spectrometers at the University of Illinois. Chemical shifts are in ppm and coupling constants are in Hertz. The abbreviation 'app' is used to describe the apparent multiplicity of the peak and may or may not be a valid first order analysis. Mass spectra were recorded on 70V-SE instruments. Infrared (IR) spectra were obtained using a Spectrum BX spectrophotometer referenced to

polystyrene standard. Data are presented as the frequency of absorption (cm^{-1}). Optical rotations were measured with a JASCO DIP-370 digital polarimeter at 25 ºC.

All reactions were performed in flame-dried glassware under nitrogen. THF and Et_2O were dried and distilled from Na/benzophenone. Benzene and CH_2Cl_2 were dried and distilled from CaH_2. Hexane and ethyl acetate were freshly distilled from CaH_2. TLC analyses were performed on a silica gel 60 F254 precoated-plates (250 μm layer). All retention factors (R_f) are on silica gel TLC plates unless otherwise noted. TLC visualizations were performed with 5% phosphomolybdic acid (0.2 M in 2.5% concd H_2SO_4/EtOH (v/v)), I_2 vapor, or UV light. Commercial reagents were used without further purification unless specifically noted. Column chromatography was performed according to the procedure of Still et al[1] using 100-700 times excess 32-64 μm grade silica gel. Products separated by chromatography are specified in elution order. In some cases the yields of products containing residual amounts of solvent were corrected for the solvent peak integration in ^{1}H NMR spectra and specified individually in the data sections. The purity of reaction products was estimated to be ≥ 90-95% by TLC and NMR analyses unless specified otherwise.

Gas chromatography (GC) was conducted using a Shimadzu Model 14A-GC on a Rtx-5 30-m fused silica capillary column (split ratio~ 100:1). The following program was used: initial temp of 60 ^{o}C for 10 min, ramp 8 ^{o}C/min to 270 ^{o}C, and hold for 10 min. The standard operating conditions were 300 °C injector temp and 310 °C detector temp. A Hewlett-Packard 3395 integrator was used to integrate the FID detector signal.

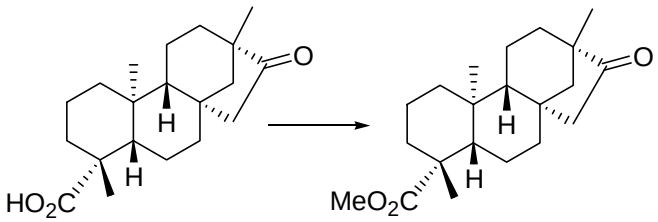


15a

***ent*-16-Oxobeyeran-19-oic Acid (15a, Isosteviol) Method A. From *Stevia rebaudiana*.** Isosteviol was obtained from dried leaves and stems of *Stevia rebaudiana* Bertoni[2] according to a literature procedure[3]

used previously at the University of Illinois[4] with some modification. Dried and ground leaves and stems (500 g) were stirred and heated at 60 °C with five 150-mL portions of 95% ethanol. The extracts were decanted, combined, and concentrated by rotary evaporation. The residual syrupy liquid was leached with ether (2 x 50 mL) and dissolved in 40 mL of 48% HBr, and the solution was allowed to stand at room temp for 20 h. This treatment liberates the aglycone as a solid black precipitate and also effects pinacol rearrangement of steviol to isosteviol.[5] The black precipitate was filtered and further purified by pre-adsorption on 70 g of 0.05-0.2 mm silica gel and elution with 2-3 L of 5:1 hexane-ethyl acetate. The yield of crude isosteviol (**15a**) was 12.5 g (2.4%): mp 228-230 °C (lit.[6] mp 230-231 °C). The ^{1}H and ^{13}C NMR data agree with the literature values for (±)-isosteviol.[7]

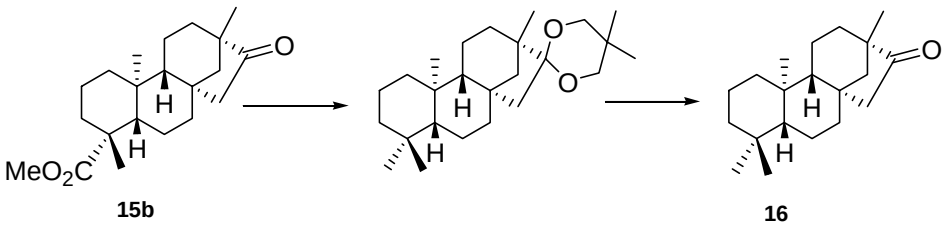
Method B. From Stevia extract sweetener. A mixture of Stevia extract (1.986 g) from the SweetLeaf Company and 48% HBr (10 mL) was stirred vigorously for 36 h. The black mixture was extracted with CH_2Cl_2 (30 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL), and the combined organic extracts were washed with water (1 x 50 mL) and dried ($MgSO_4$). Rotatory evaporation and recrystallization of the dark brown solid from hexane/acetone gave 0.474 mg (24%). The ^{1}H NMR spectra of the resulting isosteviol corresponded well with those of the product from Method A.



15a **15b**

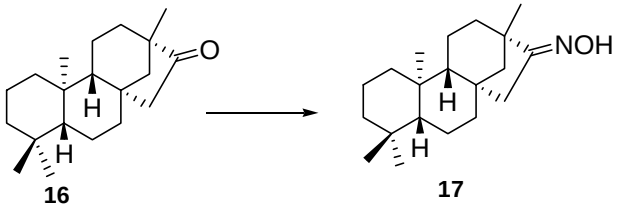
Methyl *ent*-16-Oxobeyeran-19-oate (15b, Isosteviol methyl ester). A solution of 2.18 g (10 mmol) of isosteviol **(1)** in 20 mL of methanol was stirred as ethereal diazomethane (generated from *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide)[8] was added until a deep yellow color persisted. After nitrogen evolution ceased, the solution was heated on a steam bath briefly to expel excess diazomethane and was evaporated. Recrystallization from acetone provided 3.15 g (95%) of white crystalline isosteviol methyl

ester **15b**: mp 201-202 °C (lit.[4a] mp 202-203 °C). The ^{1}H and ^{13}C NMR data agree with the data in the literature.[4b, 9]



15b **16**

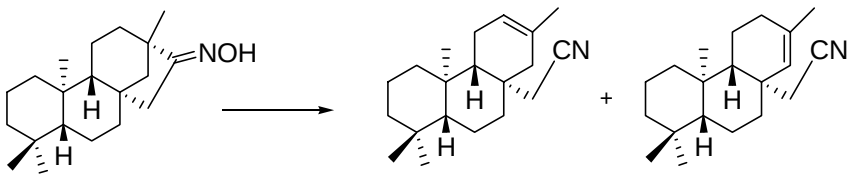
***ent*-Beyeran-16-one (16).** The conversion of the C-19 ester group to a methyl group was carried out according to the literature procedures used previously at the UIUC.[4b, 10] Purification of beyeran-16-one by flash chromatography on silica gel (5% EtOAc/hexane) and recrystallization from hexane gave an analytical sample: mp 103-104 °C (lit.[6] 103.5-104.5 °C; lit[11] 103-104 °C); TLC R_f 0.35 (1:9 EtOAc:hexane); FTIR ($CHCl_3$) ν_{max} 3020, 1730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3H, C10 CH_3), 0.81-0.84 (m, 1H), 0.85 (s, 3H, C4 CH_3), 0.87 (s, 3H, C4 CH_3), 0.89-0.93 (m, 1H), 0.96 (s, 3H, -C13 CH_3), 1.09-1.43 (m, 8H),1.49-1.69 (m,8H), 1.75 (d, 1H, J = 18.4 Hz, $H15_{endo}$), 2.68 (dd, 1H, J = 18.6, 3.6 Hz, $H15_{exo}$); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 14.9,18.3, 19.8, 20.0, 20.1,21.8, 33.1, 33.6, 37.3, 37.6, 39.4, 39.4, 41.3, 41.8, 48.7, 48.8, 54.5, 55.4, 56.3, 223.0. The ^{1}H NMR data agree with the lower field data in the literature.[4b, 7]



16 **17**

***ent*-16-Beyeran-16-one Oxime (17)** A procedure described for **15b**[4a] was followed. A 1.50-g (4.94 mmol) portion of *ent*-beyeran-16-one **(16)** was allowed to react with 3.43 g (49.4 mmol) of $NH_2OH{\cdot}HCl$ in 35 mL of pyridine for 20 h at room temp. The pyridine was evaporated, and the crude product was then extracted from a dilute HCl suspension with ether (3 x 50 mL). The combined ether extracts were washed with water (2 x 20 mL), dried ($MgSO_4$), and evaporated. The solid residue was crystallized from

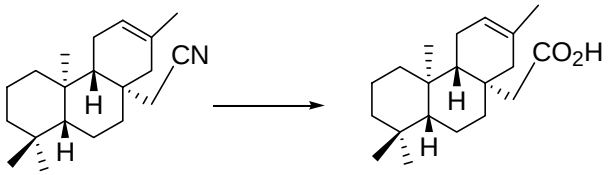
ether and light petroleum ether to afford 1.45 g (92%)of oxime **17** as a white crystals: mp 194-196 ^{o}C; $[\alpha]_D^{25}$ -10.1^{o} (*c* = 1.98, $CHCl_3$); TLC R_f 0.34 (1:4 EtOAc:hexane); FTIR ($CHCl_3$) ν_{max} 3334, 2919, 1681, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.85 (m, 1H), 0.81 (s, 3H, CH_3 at C-10), 0.86 (s, 3H, CH_3 at C-4), 0.92 (s, 3H, CH_3 at C-4), 1.06-1.16 (m, 1H), 1.10 (s, 3H, CH_3 at C-13), 1.18-1.68 (m, 8H), 1.94 (d, 1H, *J* = 18.4 Hz, H at C-15), 3.02 (dd, 1H, *J* = 19.2, 3.2 Hz, H at C-15); ^{13}C NMR (125.64 MHz, $CDCl_3$) δ 14.9, 18.3, 19.9, 20.0, 21.8, 22.1, 33.1, 33.6, 37.0, 37.6, 39.4, 39.5, 40.5, 40.7, 41.9, 43.7, 55.6, 56.3, 56.6, 170.7.



17 **18a** **18b**

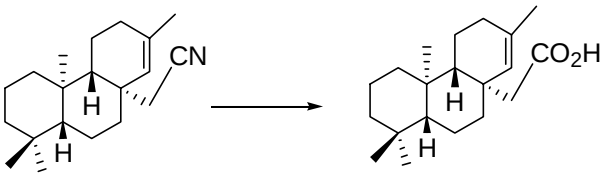
***ent*-8β-Cyanomethyl-13-methyl-12-podocarpene and *ent*-8β-Cyanomethyl-13-methyl-13-podocarpene (18a and 18b)**.[12] A literature procedure[13] was followed with modifications. A solution of p-TsCl (5.1 mmol, 0.98 g) and oxime **17** (1.4 g, 4.65 mmol) in 25 mL of DMF was stirred at room temp for 5 h. Water (60 mL) was added, and the product was extracted with hexane (3 x 100 mL). The combined hexane extracts were washed with satd $NaHCO_3$ (1 x 30 mL), water (1 x 40 mL), and brine, and dried ($MgSO_4$). Evaporation of the solvent afforded 1.35 g of a 2.64:1 mixture of nitriles **18a** and **18b** (GC analysis). A series of three successive column chromatographies using silica gel and 1% ether and hexane as eluent provided **18a** (0.82 g , 62%) and **18b (**0.42g, 32%) as crystalline solids. Data for **18a**: mp 122-125 ^{o}C; $[\alpha]_D^{25}$ -18^{o} (*c* = 2.05, $CHCl_3$); TLC R_f 0.40 (1:9 EtOAc:hexane); FTIR ($CHCl_3$) ν_{max} 3020, 2928, 2245, 1451 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76-0.90 (m, 1H), 0.81 (s, 3H, CH_3 at C-10), 0.82 (s, 3H, CH_3 at C-4), 0.86 (s, 3H, CH_3 at C-4), 1.05-1.44 (m, 6H), 1.46-1.61 (m, 3H), 1.64 (s, 3H, CH_3 at C-13), 1.65-1.85 (m, 3H), 1.96-2.13(m, 3H), 2.40 and 2.51 (app ABdd, 2H, J_{app} = 16, 2 Hz, CH_2CN), 5.34 (bs, 1H, $W_{1/2}$ = 9.5 Hz, H at C-12); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 15.4, 18.2, 18.2, 20.2, 21.5, 22.0, 23.3, 33.1, 33.2, 35.1, 36.8, 38.8, 39.4, 41.6, 45.8, 52.3, 56.5, 119.1, 119.8, 131.1.

Data for **18b**: mp 118-120 °C; TLC R_f 0.40 (1:9 EtOAc:hexane); $[\alpha]_D^{25}$ +56.7° (*c* = 2.13, $CHCl_3$); FTIR ($CHCl_3$) ν_{max} 3019, 2930, 2246, 1451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (s, 3H, CH_3 at C-10), 0.80 (s, 3H, CH_3 at C-4), 0.80-0.83 (m, 1H), 0.84 (s, 3H, CH_3 at C-4), 0.85-0.91 (m, 1H), 1.06-1.75 (m, 10H), 1.63 (s, 3H, CH_3 at C-13), 1.92-2.08 (m, 4H), 2.41 and 2,67 (app ABdd, 2H, J_{app} = 16, 1.6 Hz, CH_2CN), 5.33 (app q, 1H, $J \sim 1$ Hz, H at C-14); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 16.4, 17.4, 18.3, 18.4, 21.2, 23.1, 24.7, 31.6, 33.2, 33.3, 36.8, 36.9, 38.0, 39.4, 41.9, 55.1, 56.8, 119.3, 130.4, 134.2.



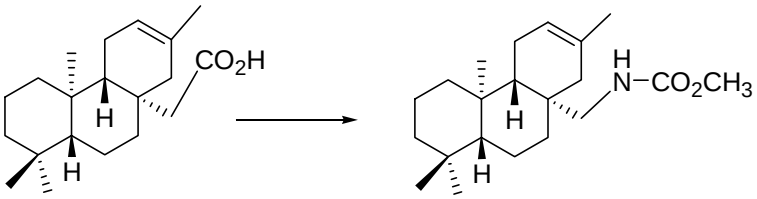
18a **19a**

***ent*-13-Methyl-12-podocarpene-8β-acetic Acid (19a)**.[12] A literature procedure[14] was followed with modifications. A solution of **18a** (500 mg, 1.75 mmol) and 85% KOH (2.5 g, 35.7 mmol) in diethylene glycol (7.5 mL) and water (0.8 mL) in a metal bomb with a glass liner (volume capacity 50 mL) was heated at 195 °C under 450 psi pressure for 18 h. The mixture was cooled to room temp, diluted with water (50 mL), and extracted with ether (35 mL). After acidification of the aq. layer with cold conc HCl, the acidic product was extracted with ether (3 x 60 mL). The combined organic extracts were washed with water (2 x 10 mL), dried ($MgSO_4$), and concentrated. Crystallization of the solid residue from ether-light petroleum afforded 490 mg (90%) of the acid **19a** as white crystals: mp 125-128 °C; TLC R_f 0.4 (1:4 EtOAc:hexane); $[\alpha]_D^{25}$ -28.6° (*c* = 2.13, $CHCl_3$); FTIR($CHCl_3$) ν_{max} 2928, 1700, 1446 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75-0.84 (m, 1H), 0.82 (s, 3H, CH_3), 0.86 (s, 6H, 2xCH_3), 0.87-0.92(m, 1H), 1.06-1.27 (m, 4H), 1.34-1.47 (m,3H), 1.53-1.59 (m, 2H), 1.60 (s, 3H, -CH_3), 1.68-1.88 (m, 2H), 1.96-2.05(m, 2H), 2.21 (dt, 1 H, J = 13.6, 3.2 Hz), 2.35 and 2.46 (app ABdd, 2H, J_{app} = 12.8, 1.2 Hz, CH_2COOH), 5.36 (br s, 1H, =CH); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 15.5,18.4, 18.4, 21.6, 22.3, 23.3, 33.2, 33.4, 35.1, 36.1, 37.1, 38.8, 39.5, 41.8, 45.2, 54.2, 56.0, 119.6, 131.7, 180.1.



18b **19b**

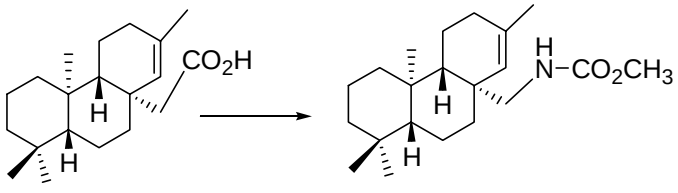
***ent*-13-Methyl-13-podocarpene-8β-acetic Acid (19b)**.[12] Hydrolysis of **18b** (50 mg, 0.17 mmol) as described above for **18a** in a solution of 85% KOH (250 mg), diethylene glycol (0.75 mL), and water (0.08 mL) in a metal bomb with a glass liner (volume capacity 10 mL) and extractive workup furnished **19b** as a white solid: yield, 53 mg (92%); TLC R_f = 0.40 (1:4 ethyl acetate:hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.77-0.93 (m, 2H), 0.80 (s, 3H, CH_3), 0.81 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 1.09-1.19 (m, 4H), 1.33-1.46 (m, 5H), 1.57- 1.73 (m, 4H), 1.61 (s, 3H, CH_3), 1.89-2.08 (m, 3H), 2.25 (dt, 1H, J = 13.2, 3.2 Hz), 2.36 and 2.63 (app ABdd, 2H, J_{app} = 13.2, 1.6 Hz, -CH_2COOH), 5.24 (app q, 1H, J = 1.6 Hz, =CH).



19a **20a**

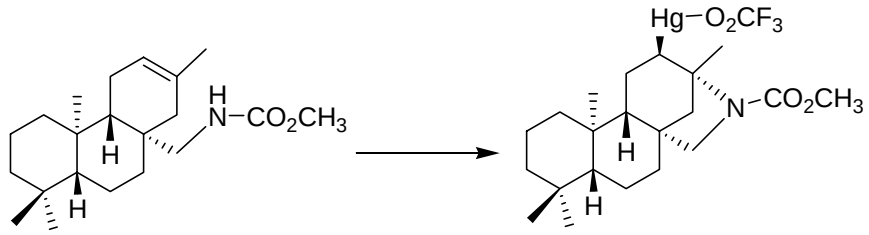
***ent*-*N*-Methoxycarbonyl-8β-aminomethyl-13-methyl-12-podocarpene (20a)**.[12] A literature procedure[15] was followed with modifications. A solution of unsaturated acid **19a** (305 mg, 1.0 mmol), triethylamine (140.5 μL, 1.0 mmol), and diphenyl phosphorylazide (215.5 μL, 1.0 mmol) in benzene (5 mL) was stirred and heated at reflux for 2 h. Methanol (0.40 mL, 10 mmol) and triethylamine (140.5 μL, 1.0 mmol) were added, and the solution was stirred for 15 h at reflux temp to convert the isocyanate to the carbamate. The solution was diluted with 25 mL of ether, washed with 10% aq citric acid (2 x 8 mL) and 10% aq. $NaHCO_3$ (2 x 8 mL), dried ($MgSO_4$), and concentrated. Purification of the crude product (340 mg) by chromatography on silica gel (9:1 hexane:diethylether) provided **20a** (267 mg, 80%) as a sticky oil that was an 11:1 mixture of N-CO_2Me rotamers: TLC R_f 0.23 (1:9 EtOAc:hexane); FTIR($CHCl_3$) ν_{max} 2925, 1722, 1522, 1449 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.76-1.00 (m, 4H), 0.82, 0.84, 0.90 (3s, 3 x

3H, CH_3), 1.11 (td, 1H, J = 12.2, 4.4 Hz), 1.23-1.59 (m, 8 H), 1.60 (s, 3H, CH_3 at C-13), 1.76-2.03 (m, 5H), 3.03 (app dd, 1H, J_{app} = 13.6, 4.4 Hz, CH_2N), 3.48 (app dd, J_{app} = 13.6, 7.6 Hz, 1H CH_2N), 3.64 (s, 2.75 H, CO_2CH_3), 3.68 (s, 0.25 H, CO_2CH_3), 4.42 (br, ~ 0.1H NHCO$_2$Me), 4.50 (br t, ~0.9 H, J=6 Hz, NHCO$_2$,Me), 5.38(m, 1H, H at C-12); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 16.0, 18.50, 18.53, 21.6, 22.3, 23.5, 33.2, 33.4, 37.0, 37.1, 37.4, 39.6, 40.3, 41.9, 43.5, 52.0, 53.5, 57.1, 120.8, 131.0, 157.6.



19b **20b**

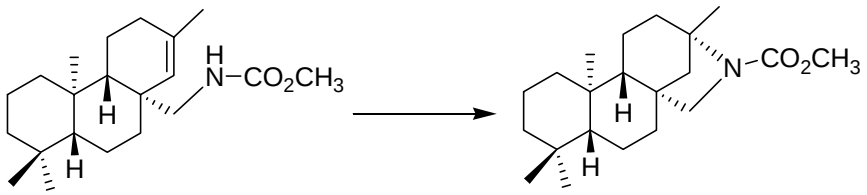
***ent*-*N*-Methoxycarbonyl-8β-aminomethyl-13-methyl-13-podocarpene (20b).** The pure Δ^{13} isomer **19b** (30mg, 0.098 mmol) was converted to carbamate **20b (**26 mg, 82%) following the procedure described above for **20a**. Tentative data from a spectrum of the crude carbamate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83, 0.84, 0.87 (s, 3H, CH_3), 1.10-1.18 (m, 3H), 1.34-1.83 (m, 11H), 1.62 (s, 3H, CH_3), 1.99-2.08 (m, 3H), 2.97-3.04 (m, 1H), 3.66 (s, 3H, CO_2CH_3), 3.71-3.77 (m, 1H), 4.56-4.62 (m, 1H), 5.08 (bs, 1H, =CH).



20a **22**

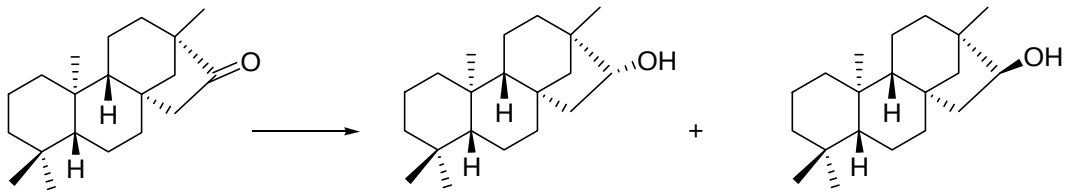
Isolation of Organomercurial Intermediate 22. The reaction of mercuric trifluoroacetate (22 mg, 0.15 mmol) and carbamate **20a** (20 mg, 0.059 mmol) in 2 mL of THF was carried out as described in the Experimental Section for 16 h at room temp. The reaction was judged to be complete by TLC (R_f = 0.22, 1:4 EtOAc : petroleum ether). The reaction mixture diluted with ether (20 mL), and the ethereal solution was washed with water (1 x 10 mL), satd $NaHCO_3$ (1 x 10 mL), and brine (1 x 20 mL), and dried ($MgSO_4$). Evaporation afforded the organomercurial intermediate (**22**) (38 mg, 99%) as a polar white

solid that was a 2:1 mixture of N-CO_2Me rotamers: TLC R_f 0.22 (1:4 EtOAc:hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77-0.89 (m, 3H), 0.80, 0.86, 0.94 (3s, 9H, $3CH_3$), 1.10-1.28 (m, 4H), 1.36-1.68 (m, 6H), 1.51 (s, 1H, CH_3), 1.60 (s, 2H, CH_3), 1.84 (dd, 0.7H, J = 9, 2 Hz), 1.88-2.00 (m, 1.4 H), 2.10 (d, ~0.65H, J = 3 Hz), 2.14 (d, 0.35H, J = 3 Hz), 2.95 (d, ~0.65H, J = 8.8 Hz, H15 endo), 3.02 (d, ~0.35H, J = 8.8Hz, H15 endo), 3.37 (br, 0.35H, $W_{1/2}$ = 7-8 Hz, CHHg), 3.56 (br, 0.65H, $W_{1/2}$ = 7-8 Hz, CHHg), 3.65 (s, 2H, CO_2CH_3), 3.69 (s, 1H, CO_2CH_3), 3.91 (dd, 0.65H, J = 8.8, 1.2 Hz, H15exo), 4.00 (d, 0.35H, J ≅ 8 1H, H15 exo).



20b **23**

Methyl *ent*-16-Azabeyerane-16-carboxylate (23.) from the Δ^{13} Carbamate 20b. The pure Δ^{13} isomer **20b** (10 mg, 0.03 mmol) was converted to cyclic carbamate **23** (9 mg, 95%) following the procedure described in the Experimental Section. The time for complete cyclization (ca. 16 h) estimated by TLC analyses during the reaction was about the same as the Δ^{12} isomer. The spectral data for the product were identical to those given in the Experimental Section.

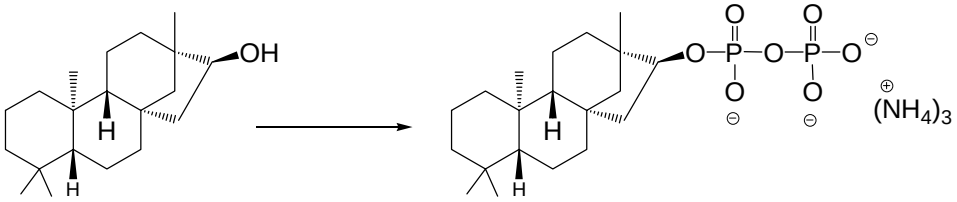


16 **25a** **25b**

***ent*-Beyeran-16β- and 16α-ols (25a and 25b).** A literature procedure for isosteviol methyl ester (**15b**) was followed.[4a] A solution of beyerene-16-one (**16**, 600 mg, 2.09 mmol), isopropyl alcohol (20 mL), acetone (2.5 mL), and 6.27 g (30.5 mmol) of aluminum isopropoxide was stirred and heated at reflux temperature as acetone was distilled (through a Vigreaux distillation apparatus) over a 24-h period.[16] Isopropyl alcohol was added to keep the volume of solvent approximately constant. The mixture was

then heated at reflux temp for an additional 16 h. The solvent was evaporated, 1.5 N HCl (10 mL) was added, and the product was extracted with hexane (3 x 30 mL). The combined ethereal extracts were washed with water (2 x 15 mL) and brine (1 x 15 mL) and dried ($MgSO_4$). Evaporation of the solvent afforded 600 mg of a mixture of **25a** and **25b** according to GC analysis. A series of three successive column chromatographies on silica gel with 4% ether and hexane as eluent provided 180 mg (30%) of **25a** and 220 mg (36%) of **25b** after crystallizations from hexane. Data for **25a**: mp 118-120 °C (lit.[17] for (±)-**25a**, oil); $[\alpha]_D^{25}$ -27° (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77-0.81 (m, 1H), 0.79 (s, 3H, -CH_3), 0.84 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.89 (s, 3H, -CH_3), 0.97-1.77 (m, 18H), 1.85 (app. ddd, 1 H, *J* = 14.3, 4.8, 2.8 Hz), 3.84 (dd, 1H, *J* = 4.8 Hz, CHOH); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 14.8, 18.3, 20.1, 20.1, 21.9, 24.9, 33.1, 33.6, 33.7, 37.6, 39.5, 41.5, 41.9, 42.0, 42.0, 43.1, 55.5, 56.2, 80.7.

Data for **25b**: mp 98-101 °C (lit[11] 98-101 °C, lit[18] 102-103 °C); $[\alpha]_D^{25}$ +5.6° (*c*= 2.0, $CHCl_3$) ; TLC R_f 0.34 (1:9 EtOAc:hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78-0.82 (m, 2H), 0.80 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.87-0.92 (m, 2H), 0.93 (s, 3H, CH_3), 0.98-1.27 (m, 6H), 1.31-1.63(m, 13H), 2.59 (ddd, 1H, *J* = 14.3, 7.6, 2.4 Hz, C*H*CHOH), 3.70-3.74(m, 1H); ^{13}C NMR (100.57 MHz, $CDCl_3$) δ 14.9, 18.4, 19.7, 20.1, 21.2, 21.9, 33.1, 37.5, 38.2, 39.6, 41.0, 41.9, 42.7, 43.7,45.9, 53.6, 55.5, 56.3, 79.3. The ^{1}H NMR data agree with the lower field data in the literature.[11,18]



***ent*-Beyeran-16α-yl Diphosphate, Ammonium Salt (11)**[12] The Cramer-Danilov pyrophosphorylation developed by Assink[19] was followed with modification. A solution of *ent*-beyeran-16 *exo*-ol (**25b**, 80 mg, 0.27 mmol) in CCl_3CN (0.82 mL, 8.1 mmol) was magnetically stirred at room temp as $Bu_4NH_2PO_4$ (0.45 g, 1.35 mmol) in CH_3CN (2 mL) was added. After 20 min 2% ammonia-methanol (5 mL) was added, and 10 min later, the solvent was removed under reduced pressure. A suspension of the remaining yellow oil

in 2 % ammonia-methanol (20 mL) was centrifuged to precipitate most of the inorganic salts. The supernatant was concentrated to yield a cloudy yellow oil that was loaded onto a Dowex® 1x8-400 gravity column (1.5 cm x 17 cm, formate form, Dowex® 1X8-400 chloride form resin was washed in a Buchner funnel successively with 400 mL of 5% NaOH, 200 mL of 1 M formic acid, 200 mL of deionized water, and 200 mL of 0.05 M NH_4HCO_2 in MeOH to exchange chloride with formate anion). The gradient column was eluted with 1.0 L of 0.05 M – 0.5 M NH_4HCO_2 in MeOH. The 30 fractions (~15 mL) collected were analyzed by silica TLC (6:3:1 *i*-PrOH: conc NH_4OH : H_2O as developing solvent, anisaldehyde stain). Fractions 1-5 contained monophosphate (TLC R_f ~ 0.55). Fractions 13-20 containing diphosphate **11** (TLC R_f ~ 0.3) were concentrated separately, the resulting white solids were dissolved in water (5 mL), and the solutions were lyophilized (~0.0025 mm Hg) overnight. The purity of each fraction was assessed by ^{1}H and ^{31}P NMR analyses in D_2O: formate (δ_H ~ 8.2 ppm) and methyl monophosphate (δ_H ~7.8 ppm, s). Fractions free of the methyl monophosphate impurity were combined and concentrated. Dissolution of the residue in water (3 mL) and lyophilization gave diphosphate **11** as a white solid: yield 34 mg (24%); ^{1}H NMR (400 MHz, D_2O) δ 0.64 (s, 3H, CH_3), 0.68 (s, 3H, CH_3), 0.75 (s, 3H, CH_3), 0.77 (s, 3H, CH_3), 0.92-1.22 (m, 8H), 1.3-1.5 (m, 12H), 2.50-2.58 (m, 1H, CHCHOH), 4.04-4.12 (m, 1H, CHOPP); ^{31}P NMR (162 MHz, D_2O) δ -10.11 (d, 1P, J = 20.7 Hz), -9.67 (d, 1P, J = 20.7 Hz).

References

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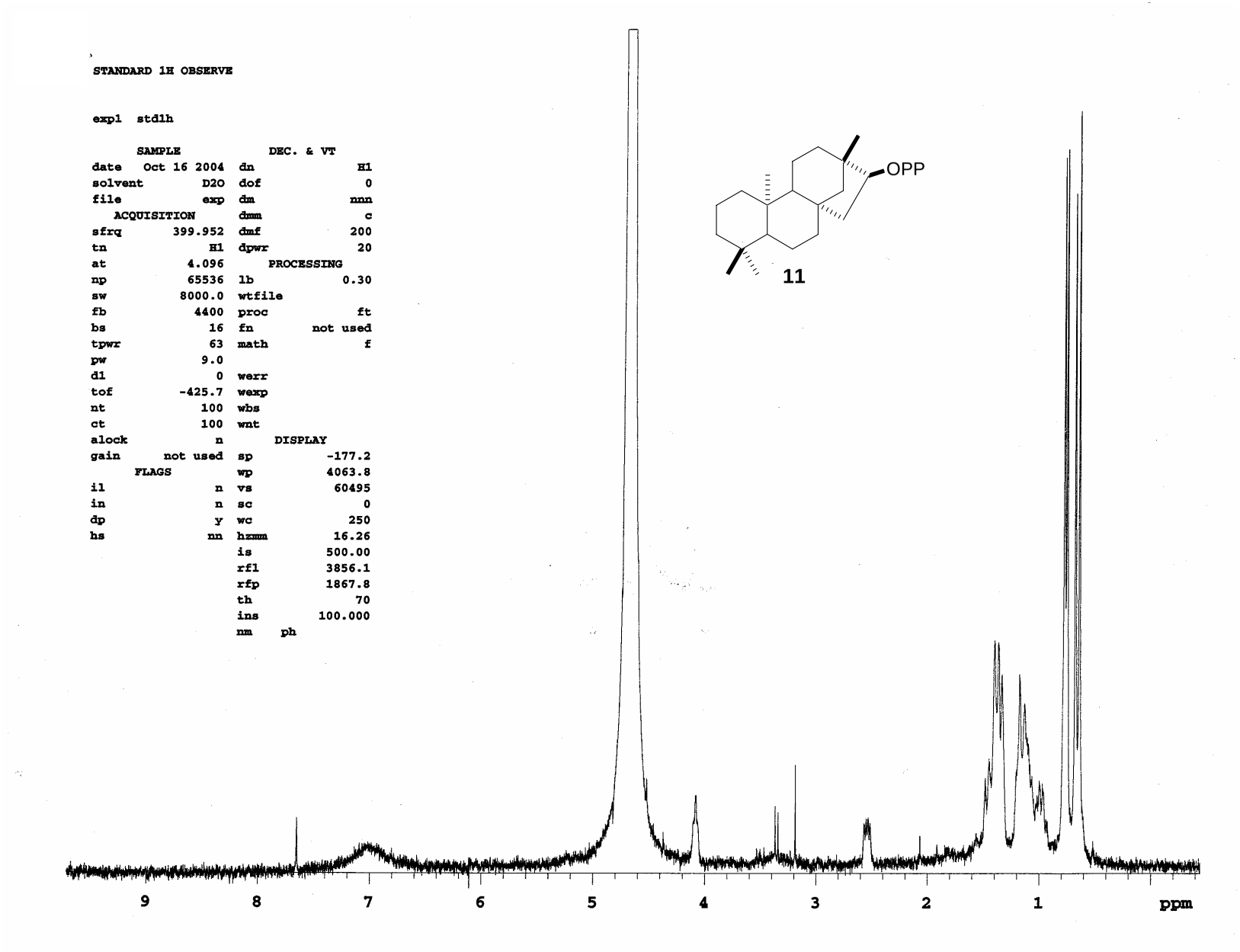
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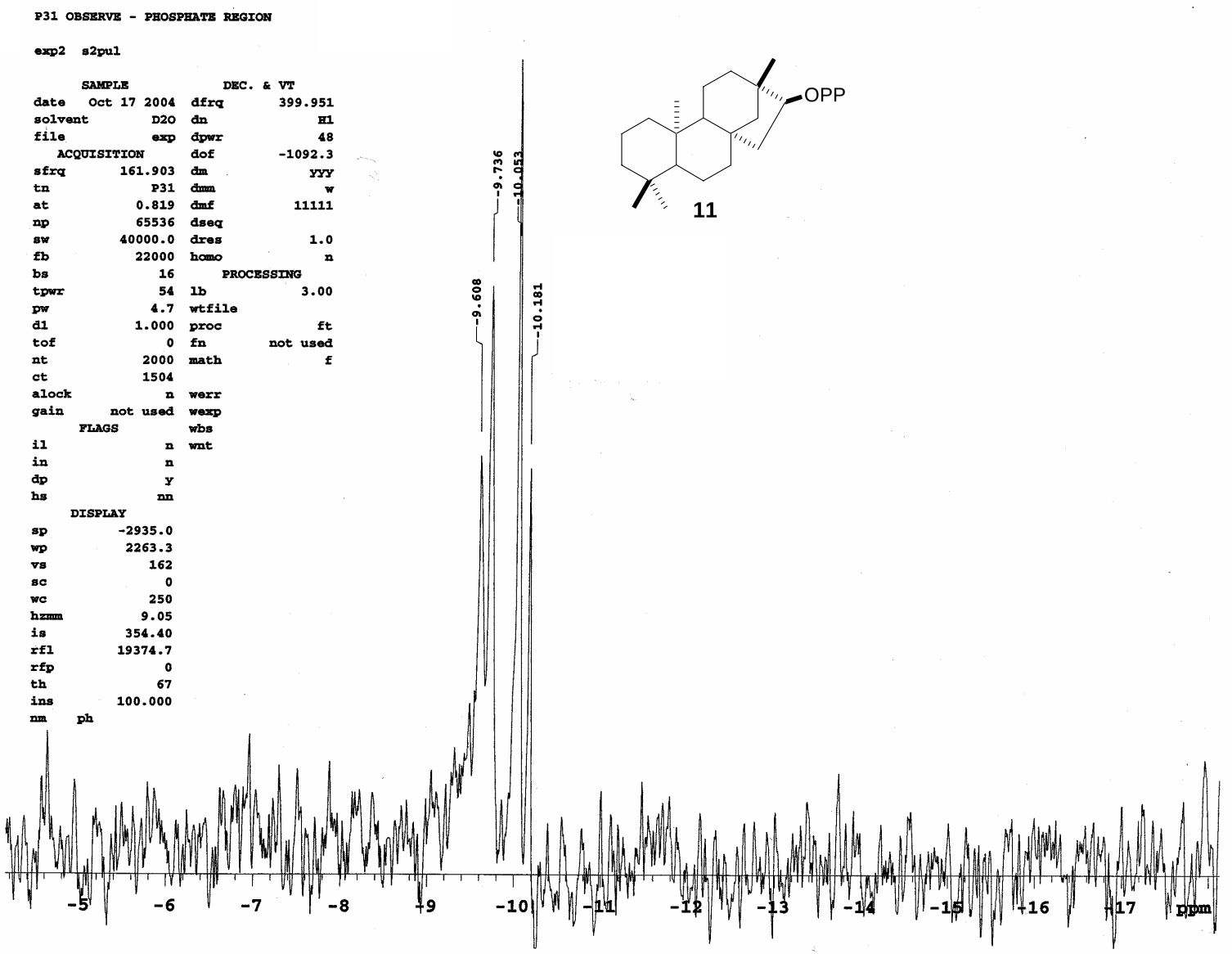
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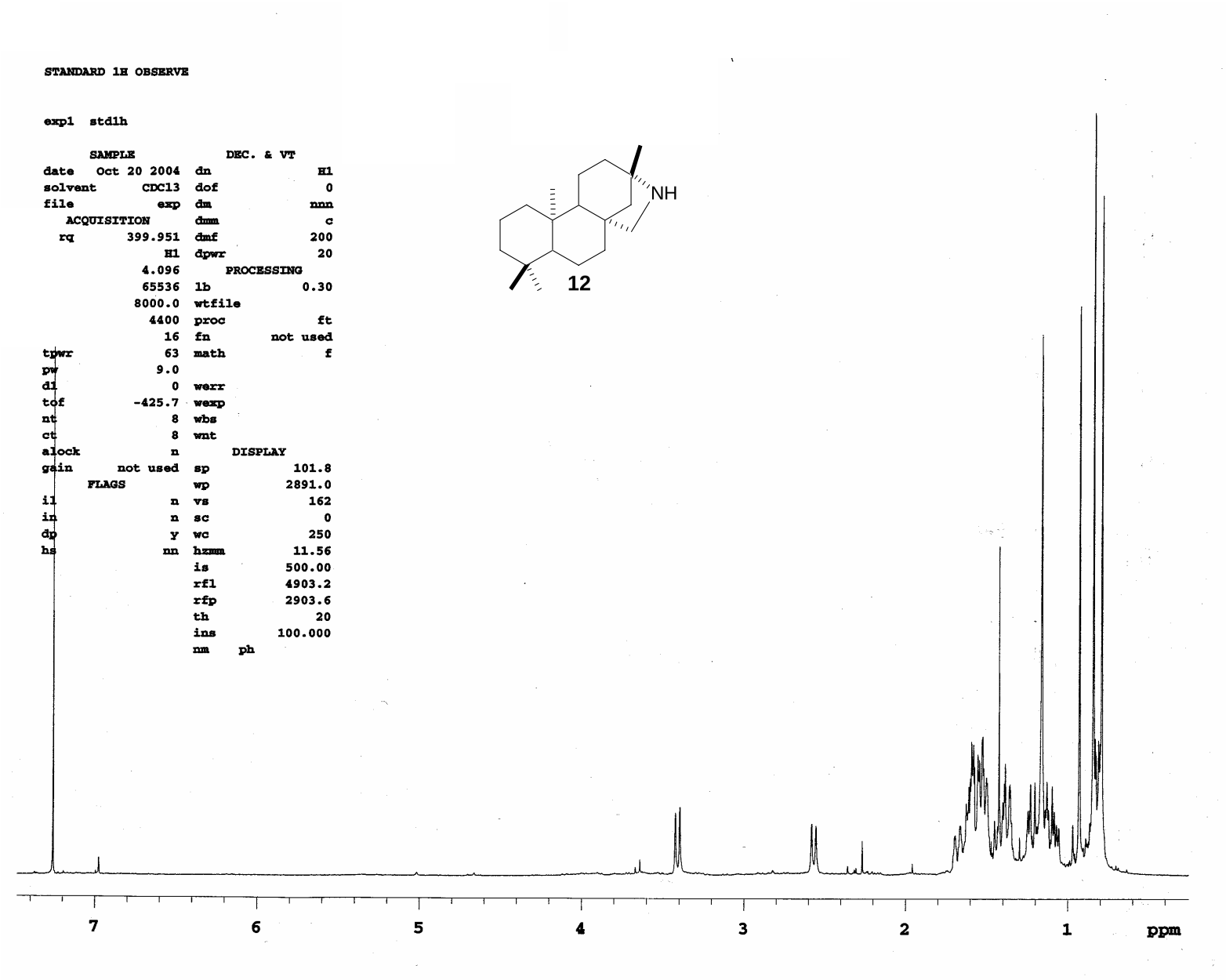
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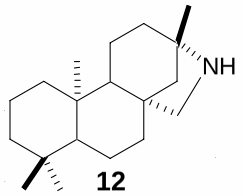

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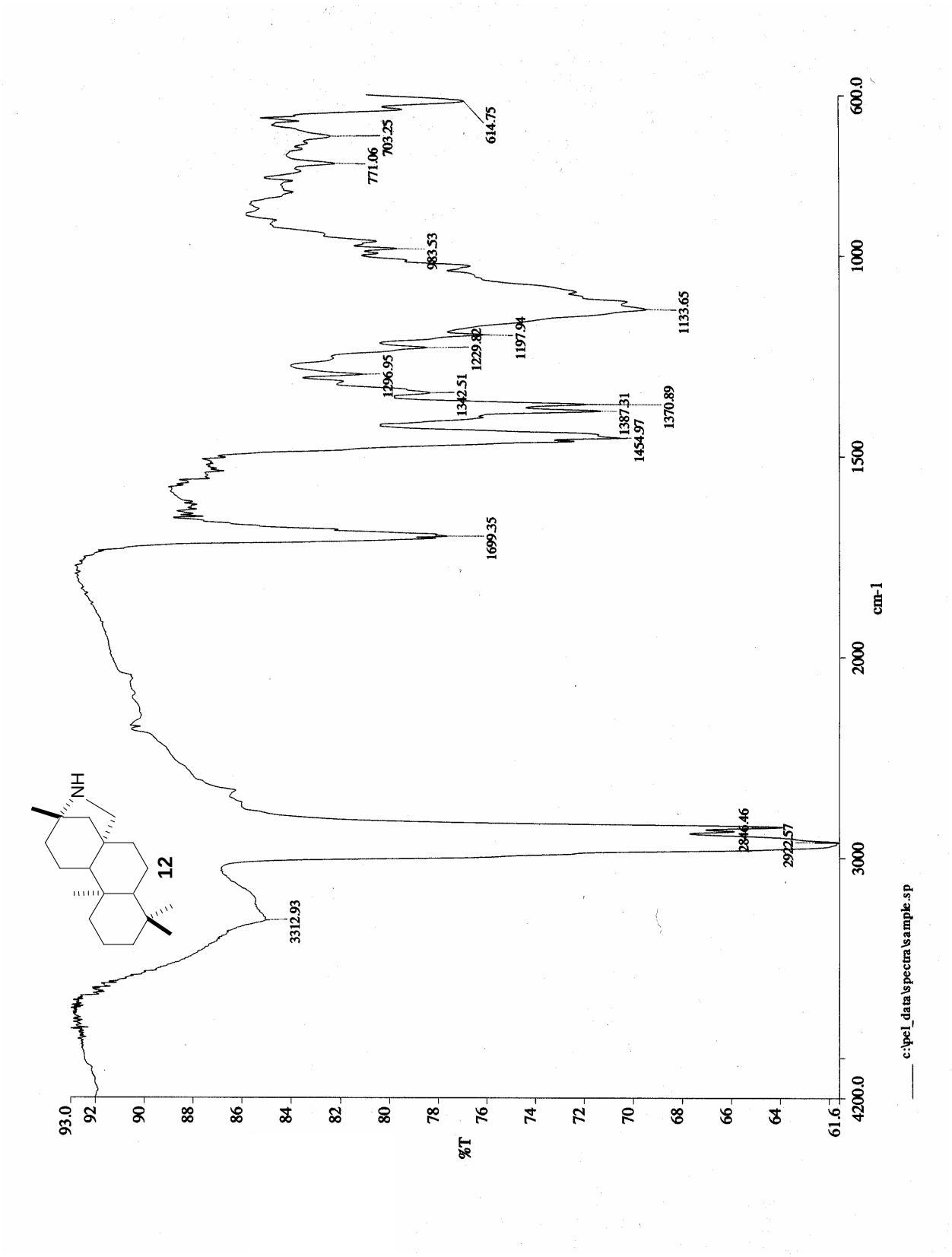
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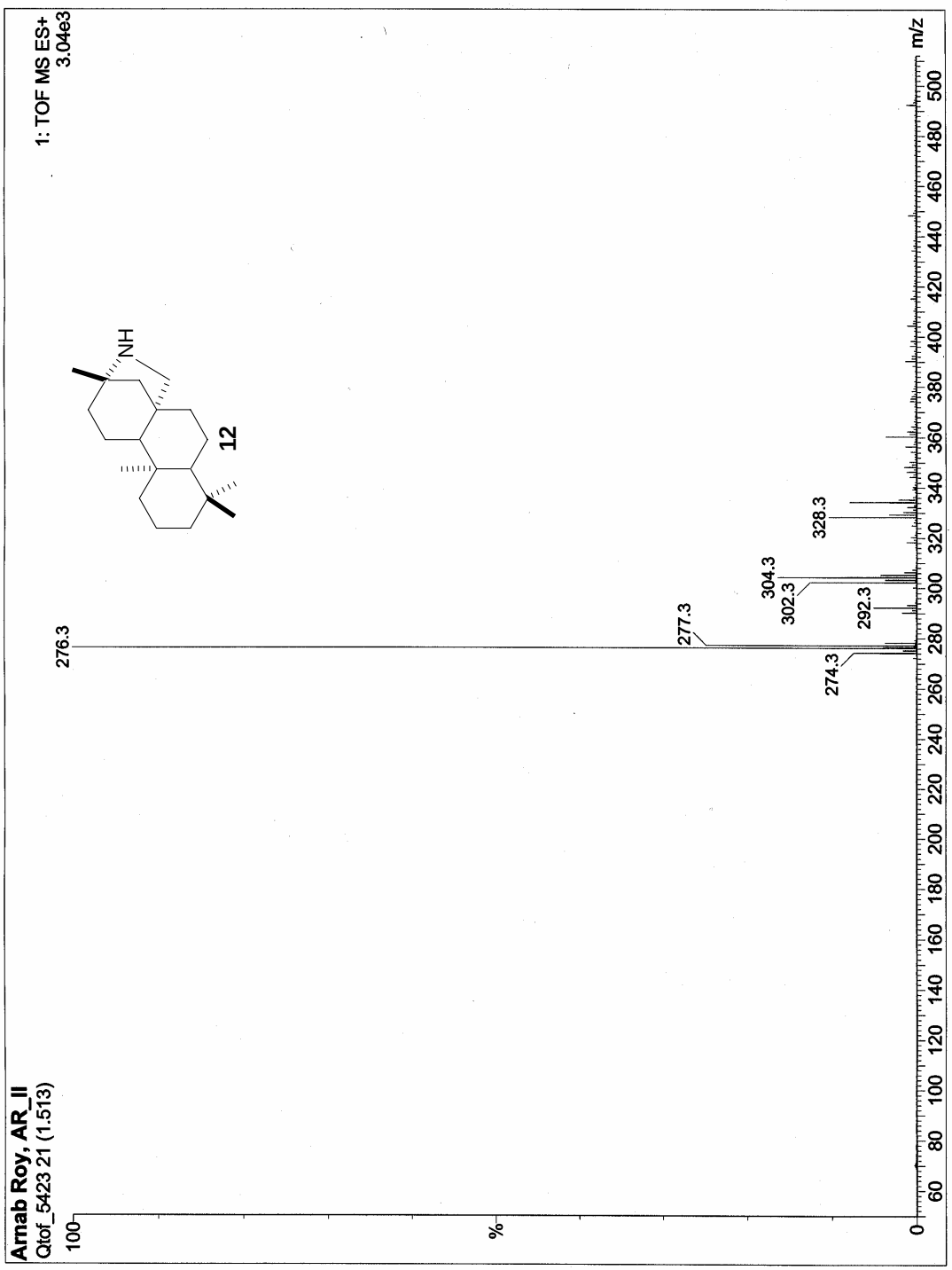
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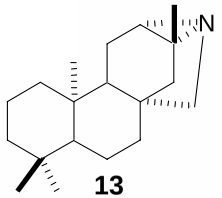

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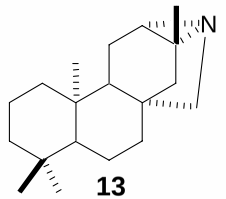

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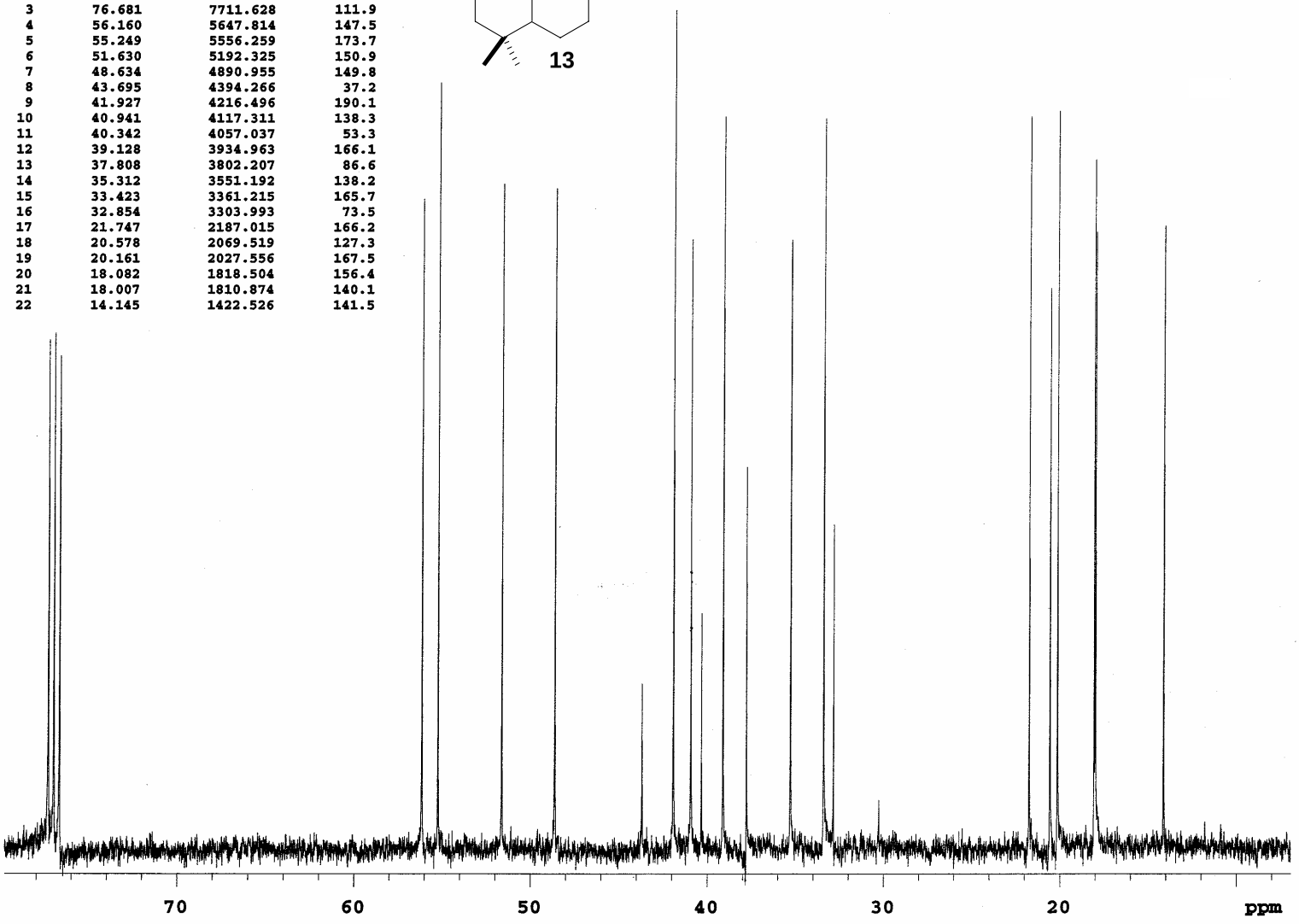

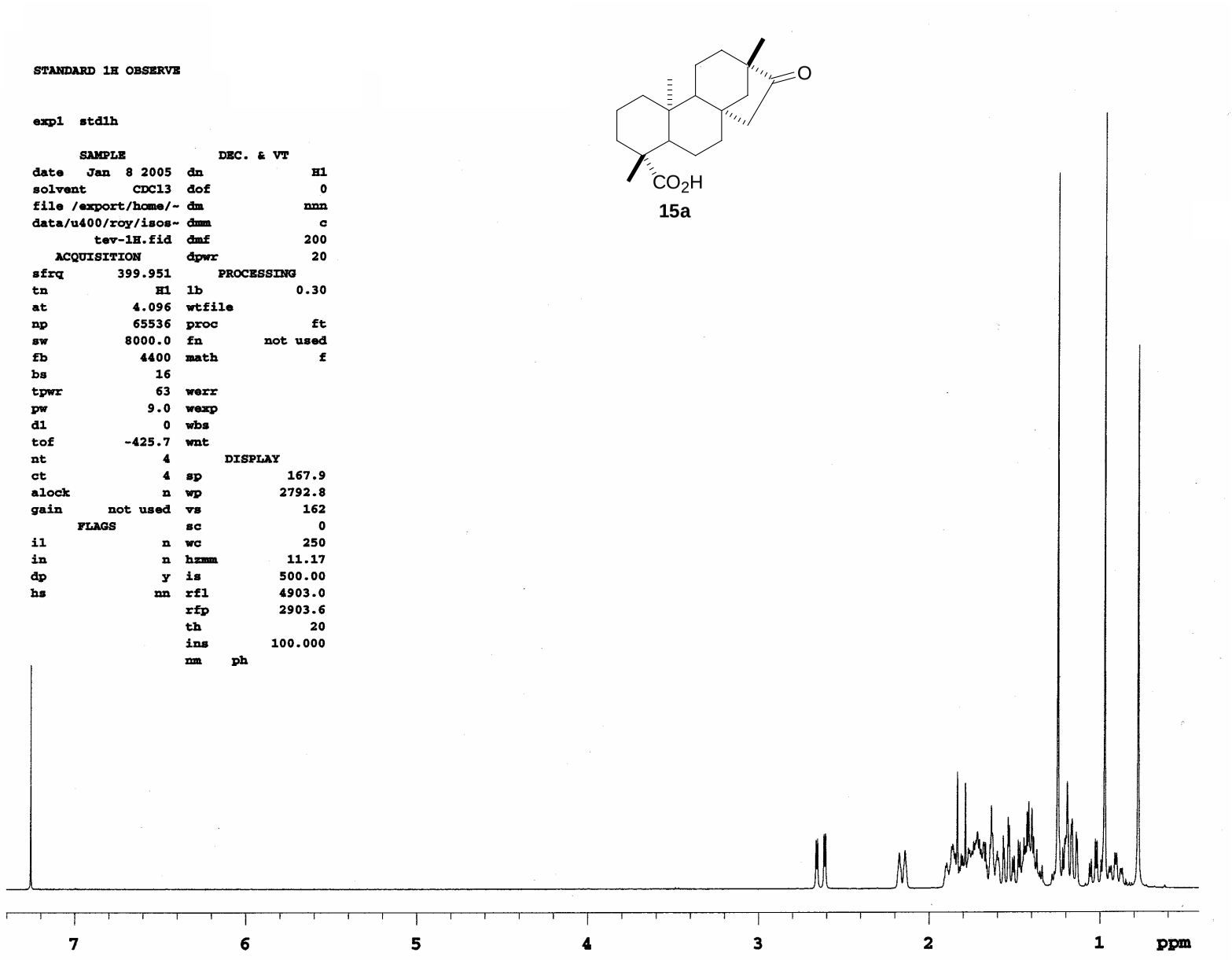
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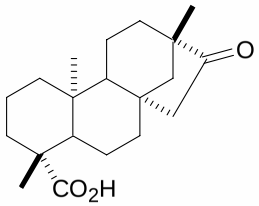

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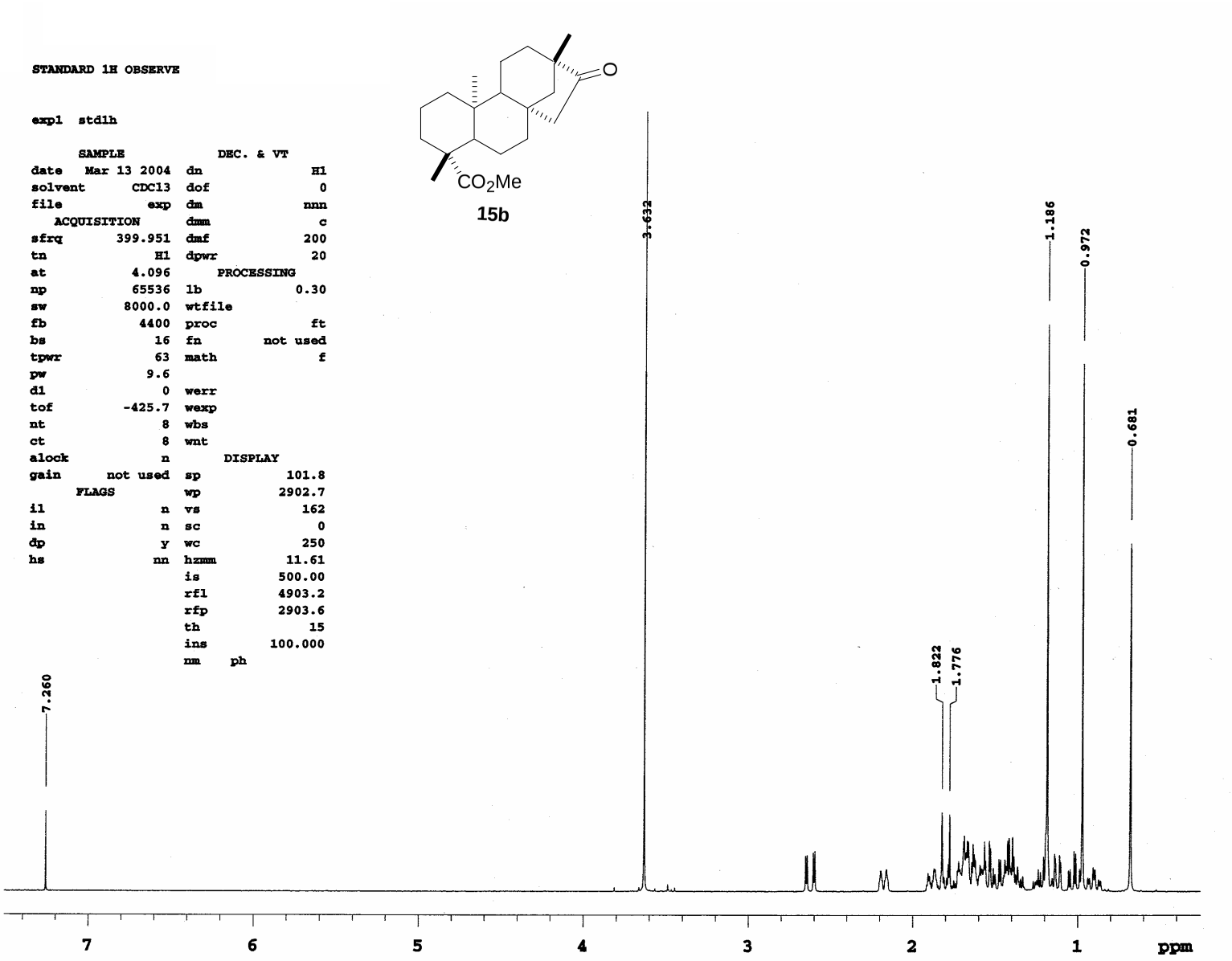
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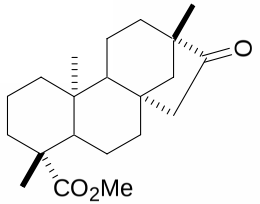
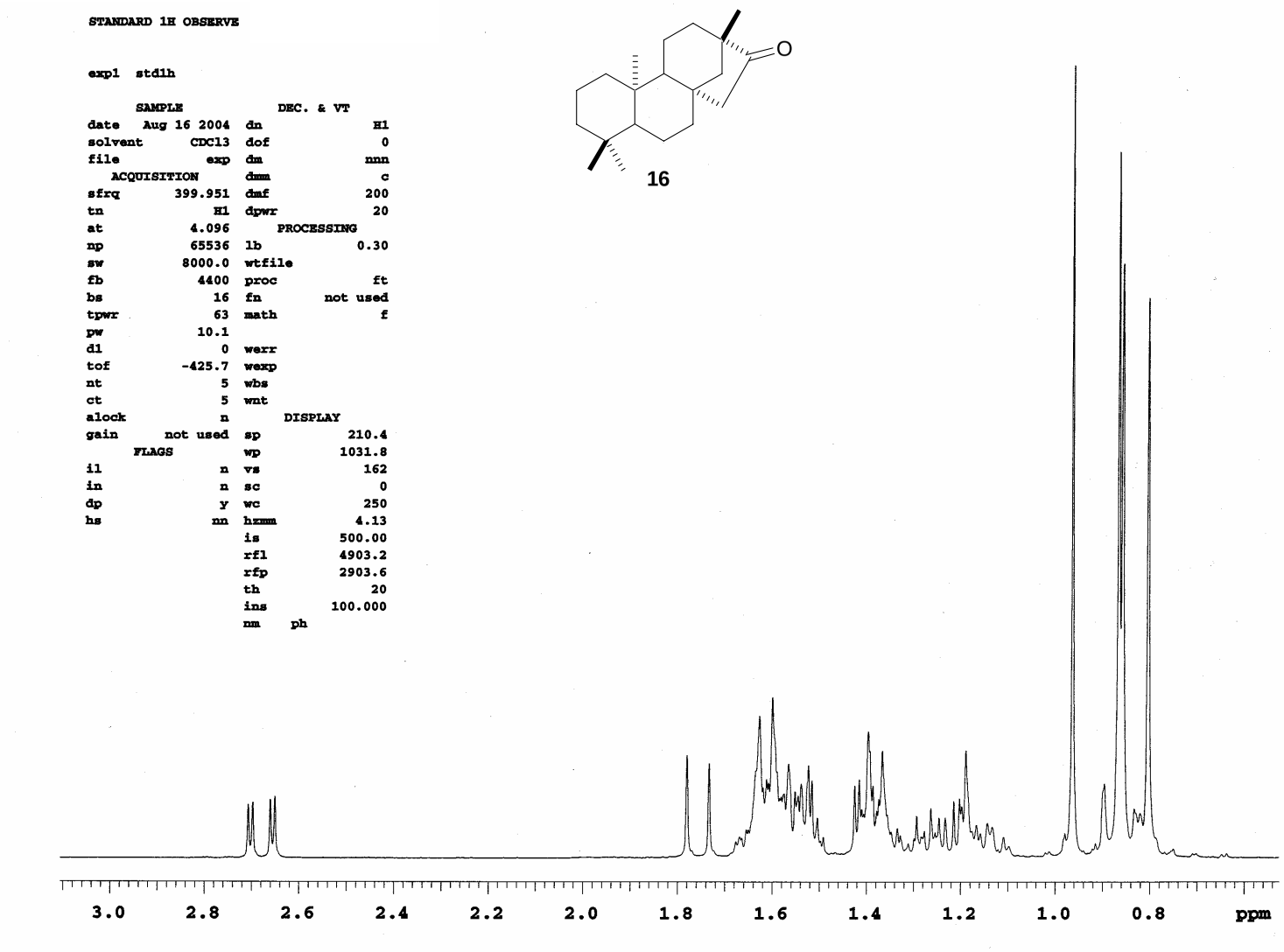
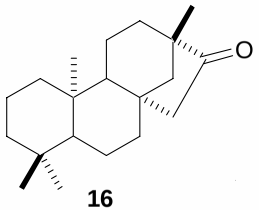
13	41.428	5205.352	22.4
14	39.757	4995.451	24.6
15	39.398	4950.340	13.3
16	37.889	4760.693	26.9
17	37.259	4681.520	25.6
18	28.811	3620.046	25.1
19	21.652	2720.602	19.7
20	20.268	2546.605	23.9
21	19.813	2489.526	20.1
22	18.890	2373.529	22.1
23	13.117	1648.081	23.0



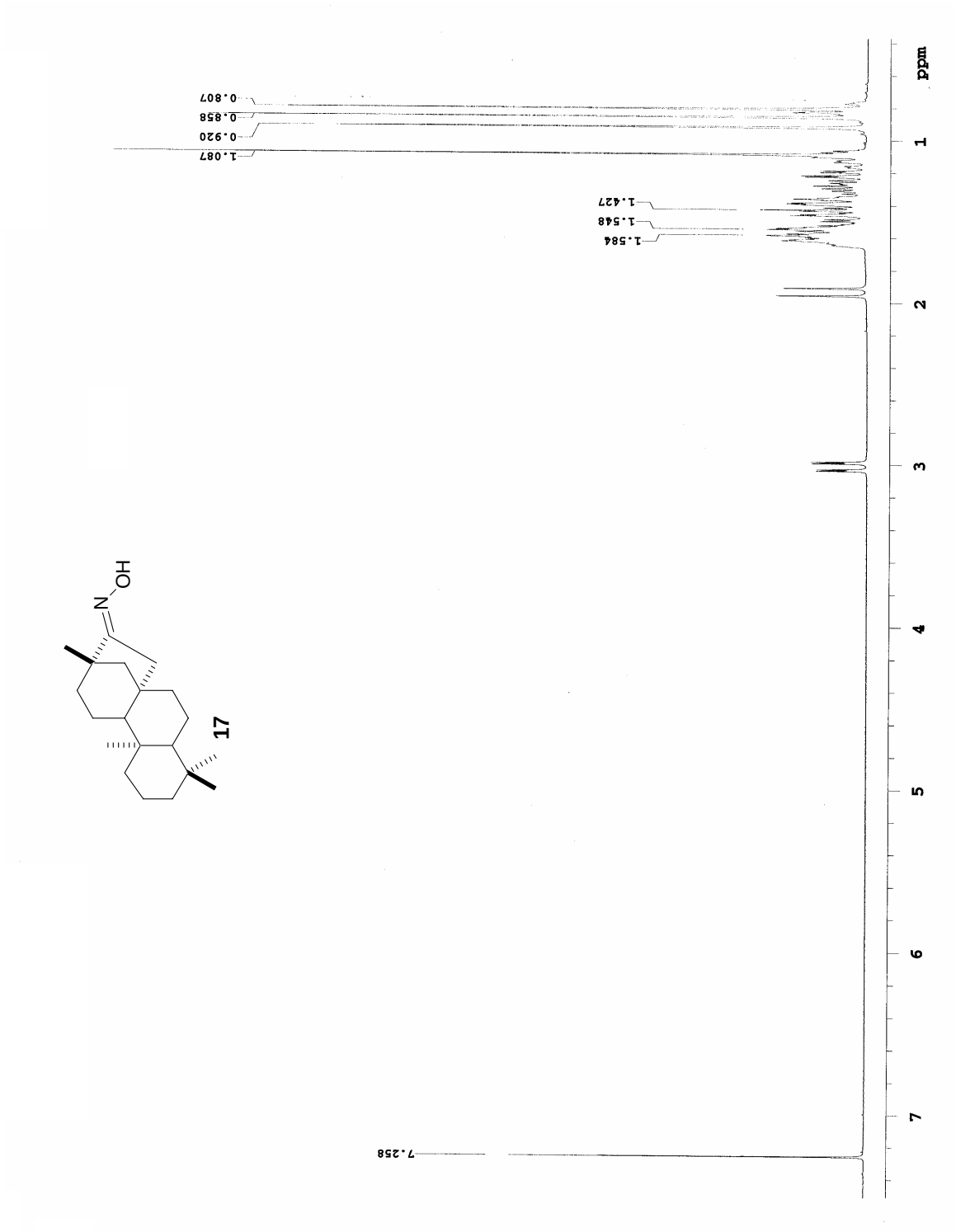
15b


STANDARD 1H OBSERVE
expl std1h
SAMPLE
date Aug 16 2004
solvent CDCl3
file exp
ACQUISITION
sfrq 399.951
tn H1
at 4.096
np 65536
sw 8000.0
fb 4400
bs 16
tpwr 63
pw 10.1
d1 0
tof -425.7
nt 5
ct 5
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 20
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
DISPLAY
sp 210.4
wp 1031.8
vs 162
sc 0
wc 250
hzmm 4.13
is 500.00
rfl 4903.2
rfp 2903.6
th 20
ins 100.000
nm ph
O
16
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm

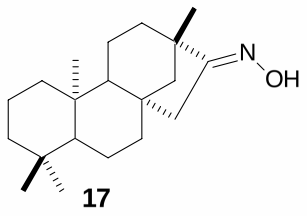
INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	223.027	22429.179	26.0
2	77.319	7775.717	88.4
3	77.000	7743.673	90.0
4	76.681	7711.628	87.5
5	56.289	5660.784	85.7
6	55.378	5569.229	91.2
7	54.551	5486.066	87.0
8	48.801	4907.740	88.6
9	48.732	4900.873	61.6
10	41.859	4209.629	83.2
11	41.290	4152.407	94.8
12	39.416	3963.955	52.1
13	39.401	3962.429	90.6
14	37.603	3781.607	40.8
15	37.368	3757.955	86.0
16	33.612	3380.289	96.5
17	33.142	3332.985	57.9
18	21.823	2194.645	89.3
19	20.063	2017.637	97.4
20	19.987	2010.008	84.6
21	19.888	2000.089	75.8
22	18.325	1842.919	89.3
23	14.926	1501.111	82.9



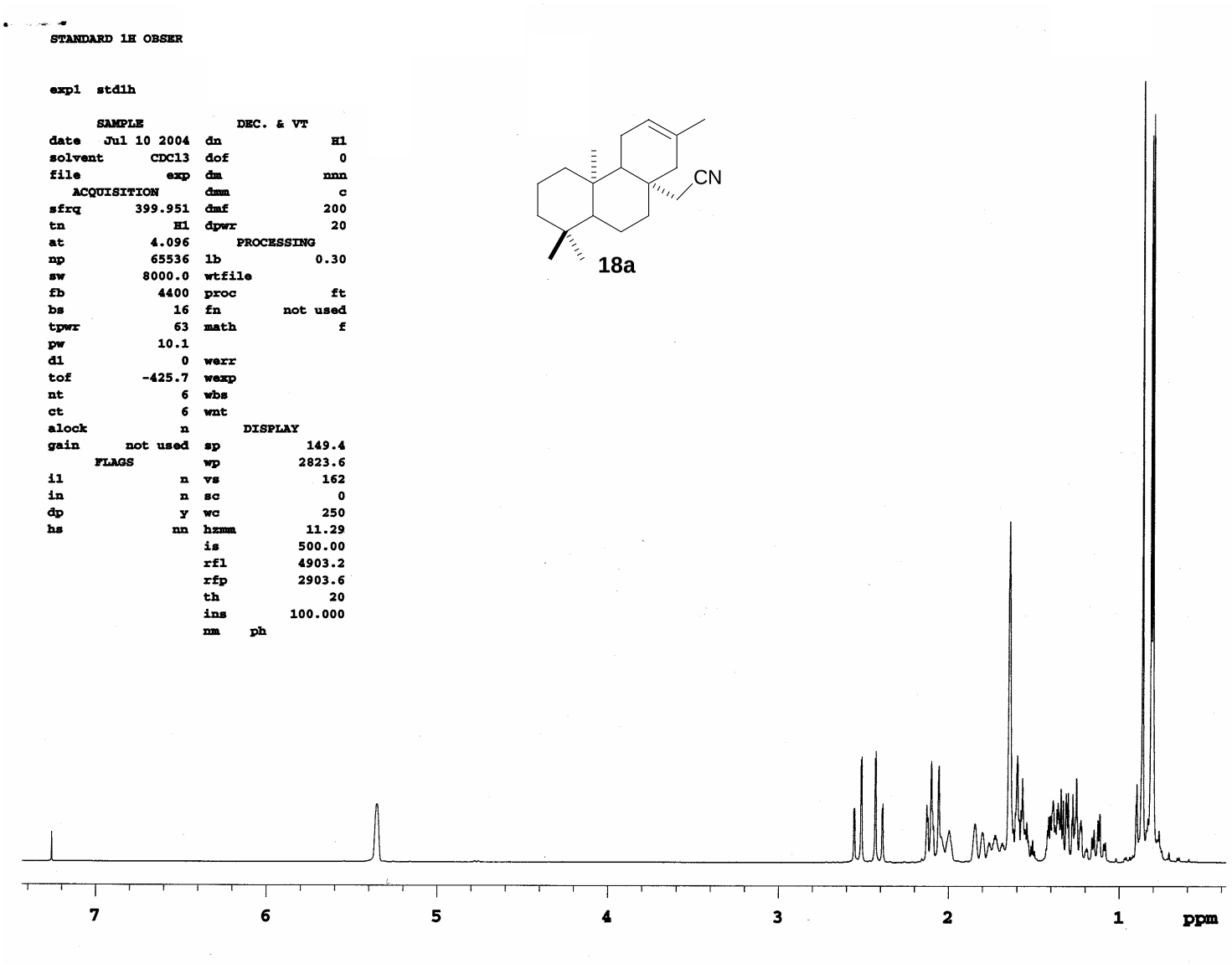
16


17
N
OH
7.258
1.584
1.548
1.427
1.087
0.920
0.858
0.807
ppm
1
2
3
4
5
6
7

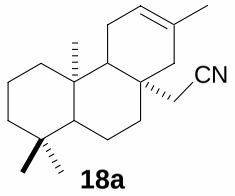
INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	170.675	21445.065	6.9
2	77.256	9707.177	41.5
3	77.000	9674.955	41.2
4	76.751	9643.654	38.7
5	56.580	7109.191	19.4
6	56.360	7081.572	21.5
7	55.605	6986.749	20.2
8	43.772	5499.950	16.0
9	41.911	5266.112	18.1
10	40.666	5109.607	17.3
11	40.563	5096.719	14.9
12	39.508	4964.149	19.7
13	39.457	4957.705	16.0
14	37.647	4730.312	11.8
15	37.039	4653.901	17.5
16	33.639	4226.734	17.7
17	33.141	4164.132	15.0
18	22.158	2784.124	17.8
19	21.821	2741.776	17.7
20	20.055	2519.907	17.5
21	19.997	2512.542	17.4
22	18.355	2306.323	14.5
23	14.912	1873.633	15.4



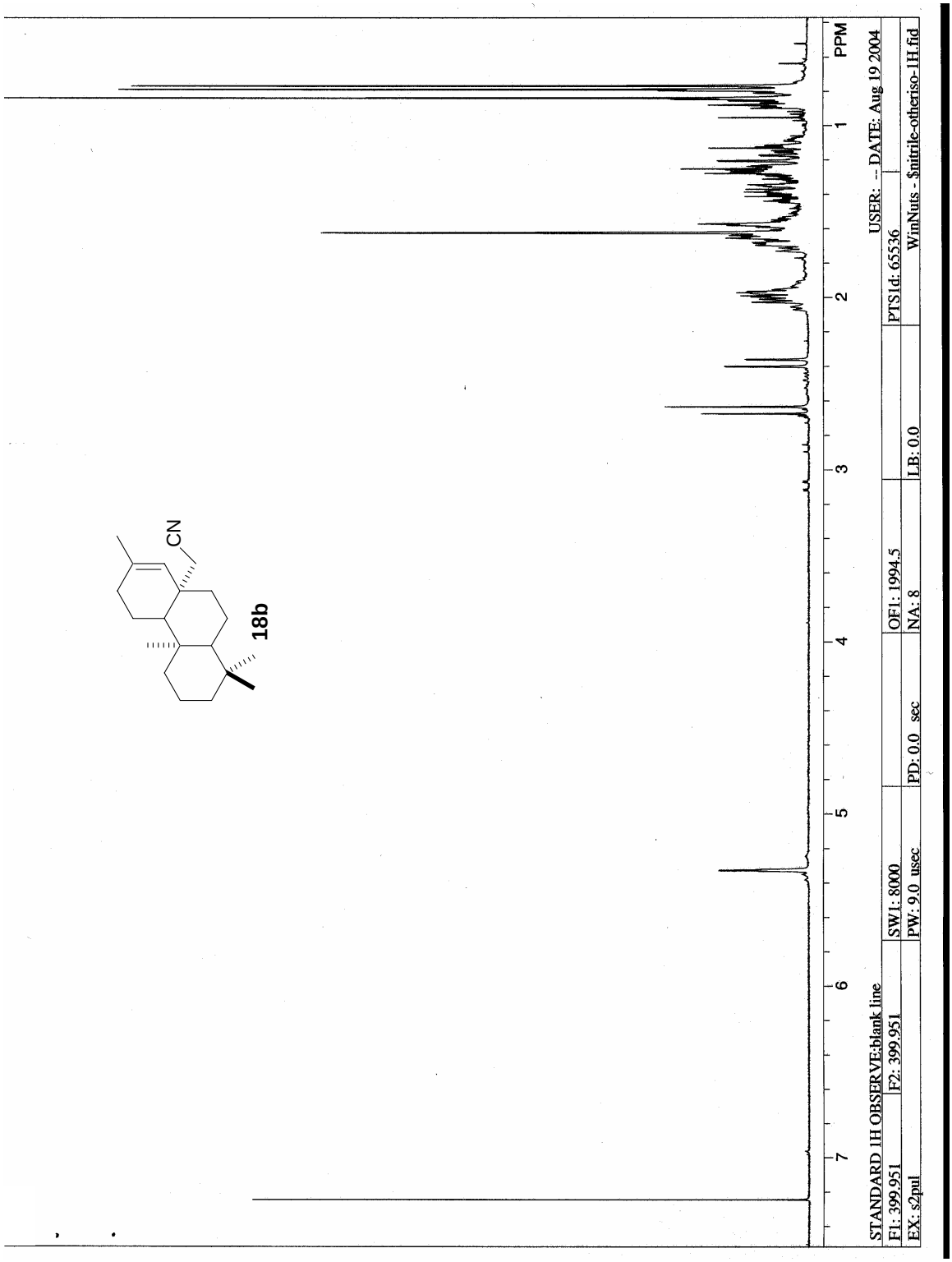
17

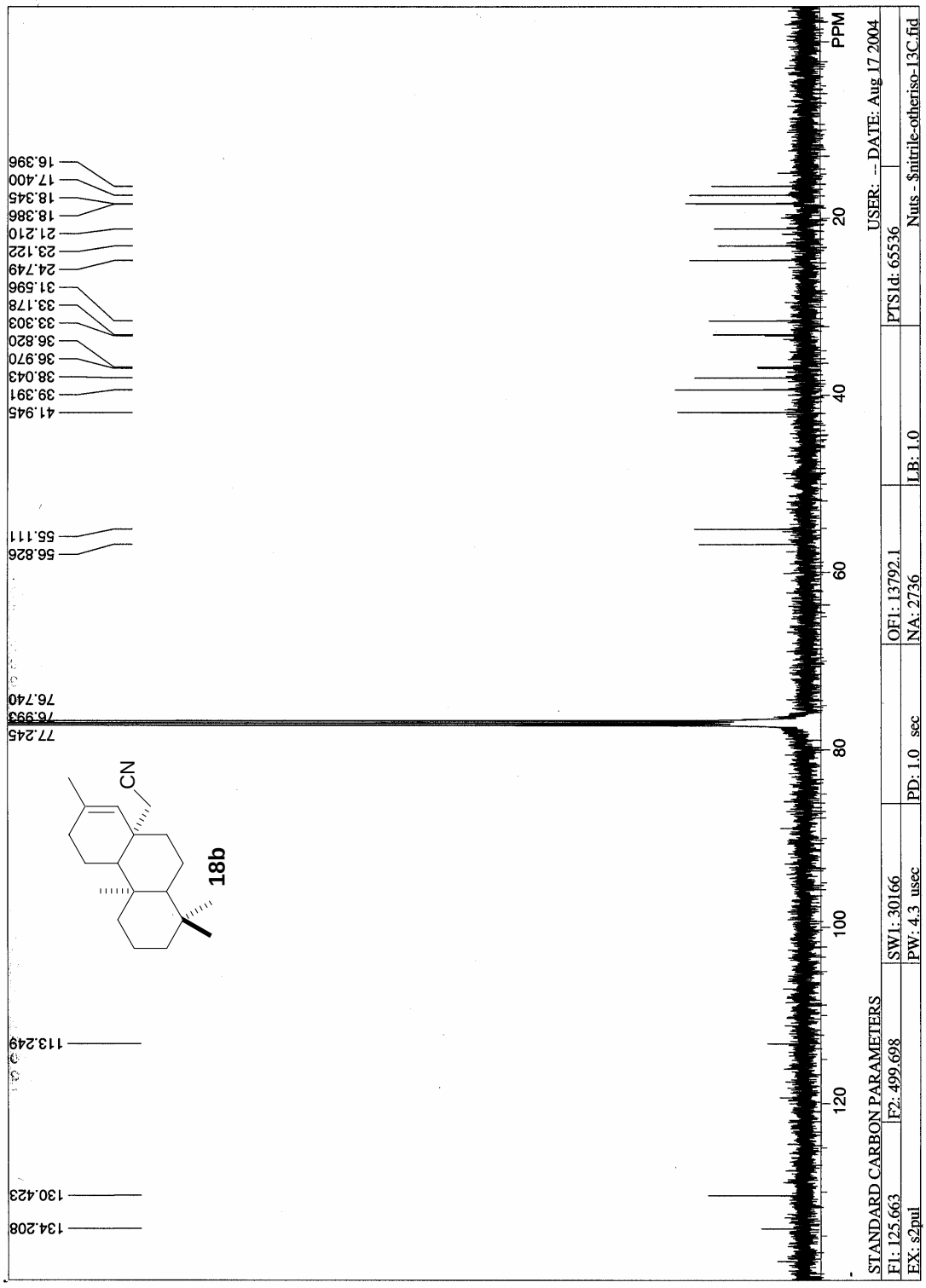

STANDARD 1H OBSER
exp1 std1h
SAMPLE
date Jul 10 2004
solvent CDCl3
file exp
ACQUISITION
sfrq 399.951
tn H1
at 4.096
np 65536
sw 8000.0
fb 4400
bs 16
tpwr 63
pw 10.1
d1 0
tof -425.7
nt 6
ct 6
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 20
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
DISPLAY
sp 149.4
wp 2823.6
vs 162
sc 0
wc 250
hzmm 11.29
is 500.00
rfl 4903.2
rfp 2903.6
th 20
ins 100.000
nm ph
CN
18a
7
6
5
4
3
2
1
ppm

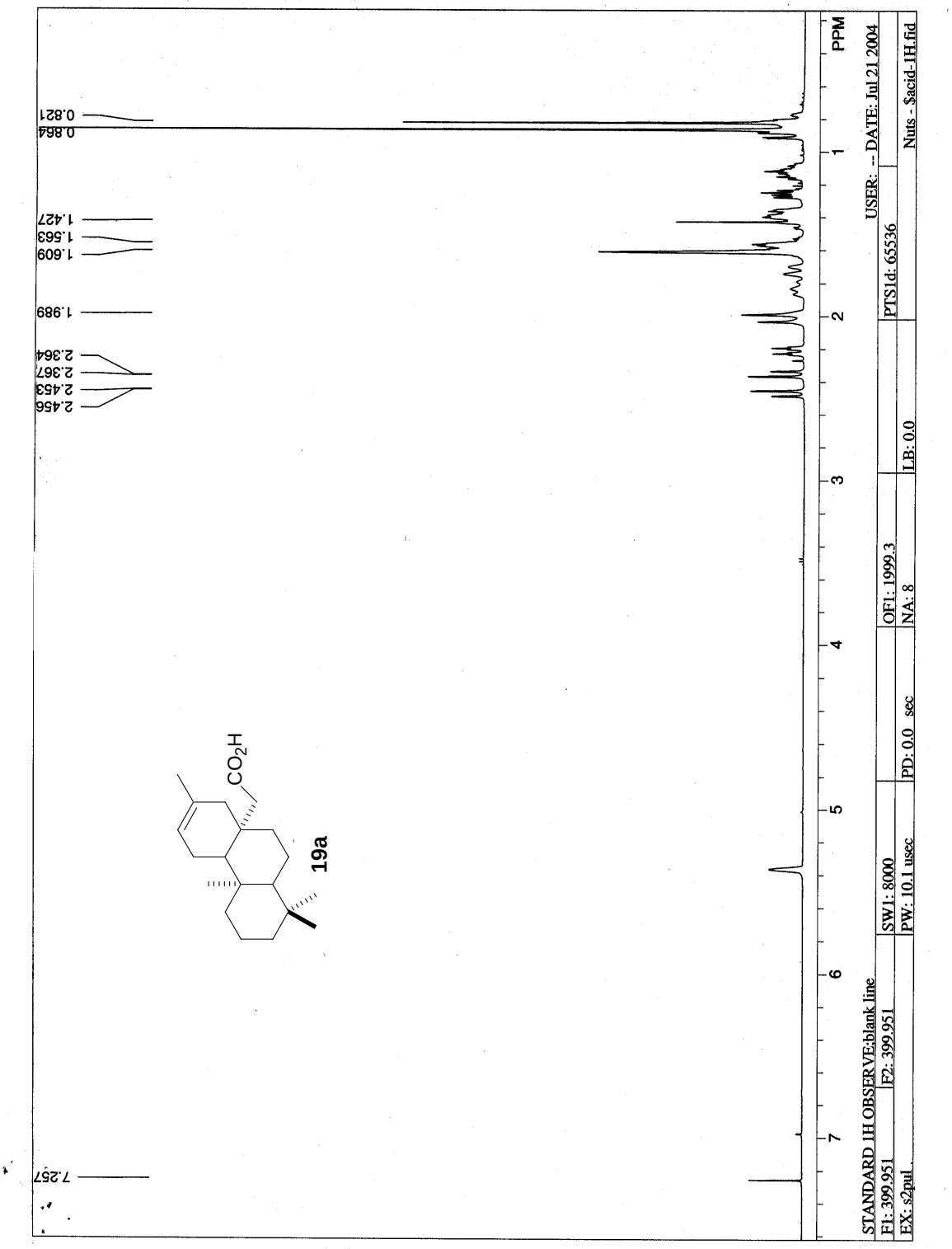
INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	131.092	13183.597	124.8
2	119.781	12046.020	334.5
3	119.136	11981.168	92.6
4	77.319	7775.717	97.4
5	77.000	7743.673	100.0
6	76.681	7711.628	100.9
7	56.554	5687.488	295.5
8	52.313	5260.992	297.8
9	45.865	4612.474	298.1
10	41.624	4185.978	294.6
11	39.370	3959.378	280.9
12	38.862	3908.259	290.7
13	36.867	3707.600	147.3
14	35.168	3536.696	117.4
15	33.263	3345.193	296.8
16	33.104	3329.171	186.8
17	23.310	2344.186	229.3
18	22.012	2213.719	243.1
19	21.534	2165.652	268.7
20	20.267	2038.238	289.1
21	18.249	1835.289	333.2
22	18.227	1833.001	310.0
23	15.374	1546.127	226.4



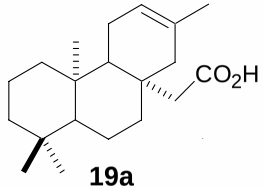
18a


CN
18b
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVE:blank line
F1: 399.951
F2: 399.951
EX: s2pul
SW1: 8000
PW: 9.0 usec
PD: 0.0 sec
OF1: 1994.5
NA: 8
LB: 0.0
PTS1d: 65536
WinNuts - $nitrile-otheriso-1H.fid
USER: -- DATE: Aug 19 2004

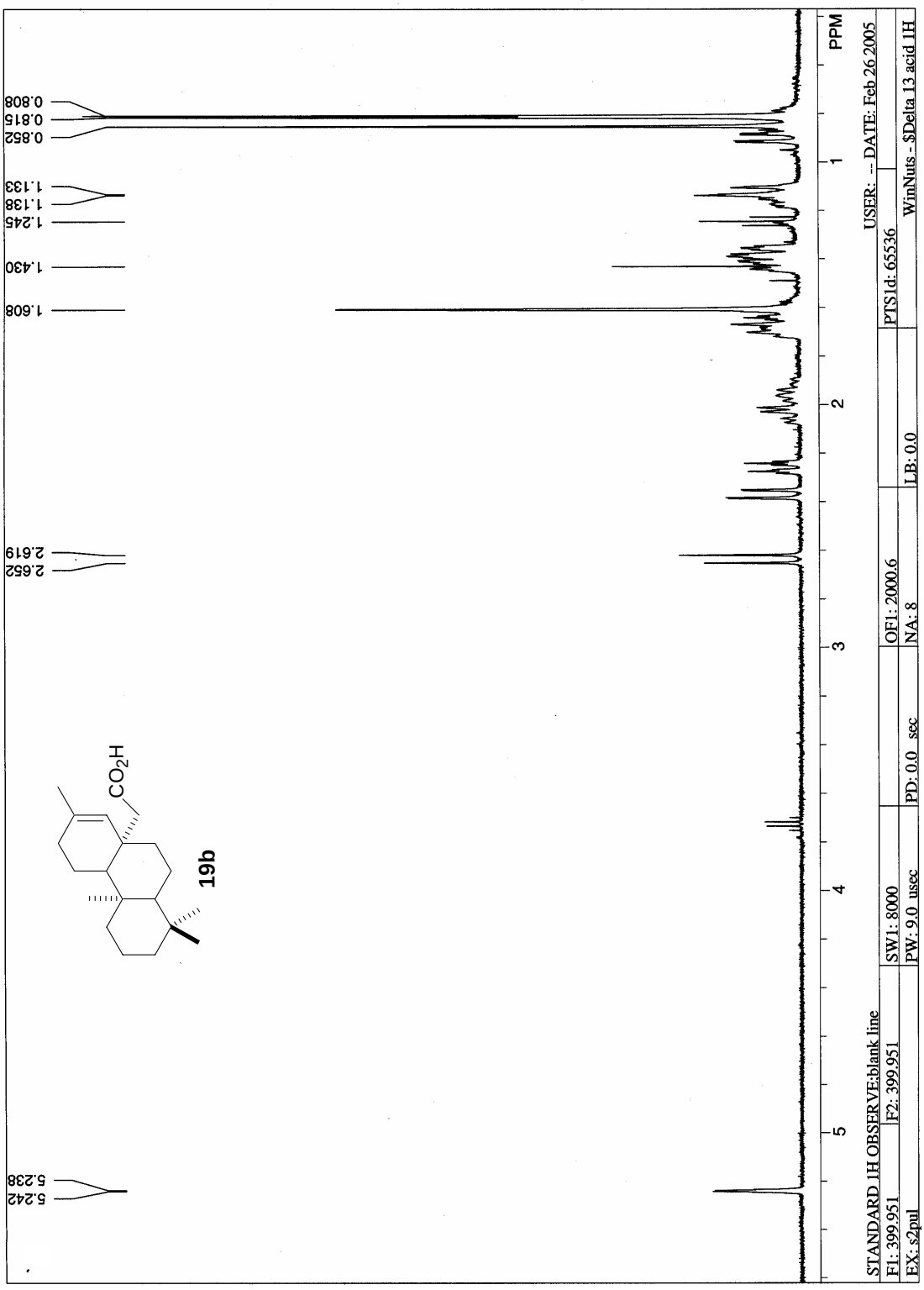

16.396
17.400
18.345
18.386
21.210
23.122
24.749
31.596
33.178
33.303
36.820
36.970
38.043
39.391
41.945
55.111
56.826
76.740
76.993
77.245
113.249
130.423
134.208
CN
18b
PPM
STANDARD CARBON PARAMETERS
F1: 125.663
F2: 499.698
SW1: 30166
PW: 4.3 usec
PD: 1.0 sec
OF1: 13792.1
NA: 2736
LB: 1.0
PTS1d: 65536
USER: -- DATE: Aug 17 2004
EX: s2pul
Nuts - $nitrile-otheriso-13C.fid

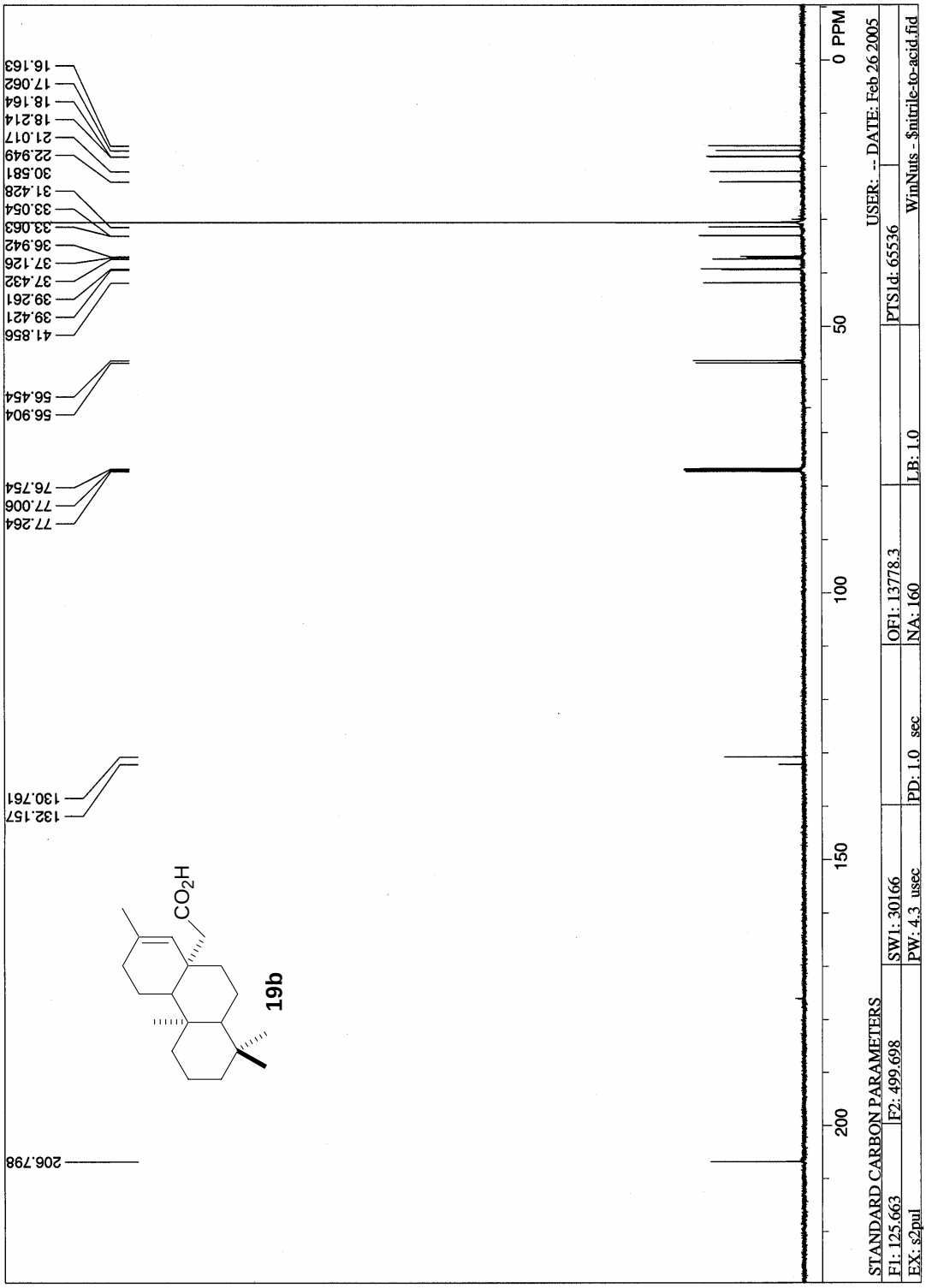

0.821
0.864
1.427
1.563
1.609
1.989
2.364
2.367
2.453
2.456
7.257
PPM
1
2
3
4
5
6
7
CO_2H
19a
STANDARD 1H OBSERVE:blank line
F1: 399.951
F2: 399.951
EX: s2pul
SW1: 8000
PW: 10.1 usec
PD: 0.0 sec
OF1: 1999.3
NA: 8
PTS1d: 65536
LB: 0.0
USER: -- DATE: Jul 21 2004
Nuts - $acid-1H.fid

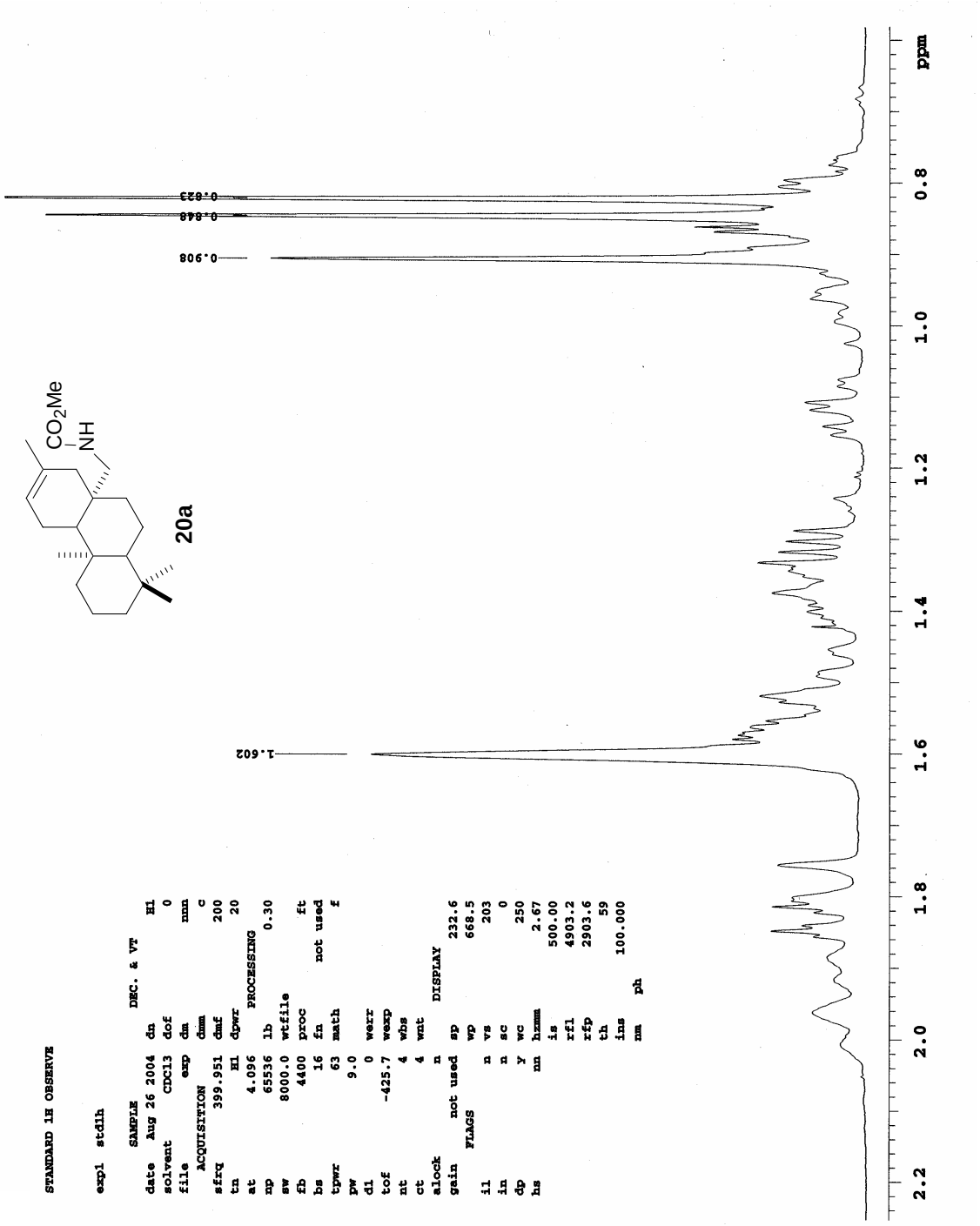
INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	180.132	18115.388	170.0
2	131.745	13249.212	120.6
3	119.622	12029.997	228.2
4	77.311	7774.954	72.0
5	77.000	7743.673	72.1
6	76.681	7711.628	75.4
7	56.987	5730.977	208.7
8	54.157	5446.392	235.3
9	45.250	4550.674	149.4
10	41.806	4204.289	181.3
11	39.545	3976.926	197.6
12	38.824	3904.444	158.7
13	37.110	3732.015	169.3
14	36.055	3625.963	128.5
15	35.152	3535.170	199.0
16	33.392	3358.163	209.8
17	33.172	3336.037	169.0
18	23.363	2349.526	184.0
19	22.270	2239.659	157.1
20	21.633	2175.571	207.9
21	18.394	1849.786	297.8
22	15.480	1556.808	197.9



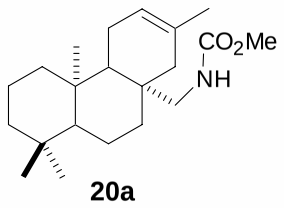
19a


0.808
0.815
0.852
1.133
1.138
1.245
1.430
1.608
2.619
2.652
5.238
5.242
CO2H
19b
PPM
STANDARD 1H OBSERVE:blank line
F1: 399.951
F2: 399.951
EX: s2pul
SW1: 8000
PW: 9.0 usec
PD: 0.0 sec
OF1: 2000.6
NA: 8
LB: 0.0
PTS1d: 65536
USER: -- DATE: Feb 26 2005
WinNuts - $Delta 13 acid 1H

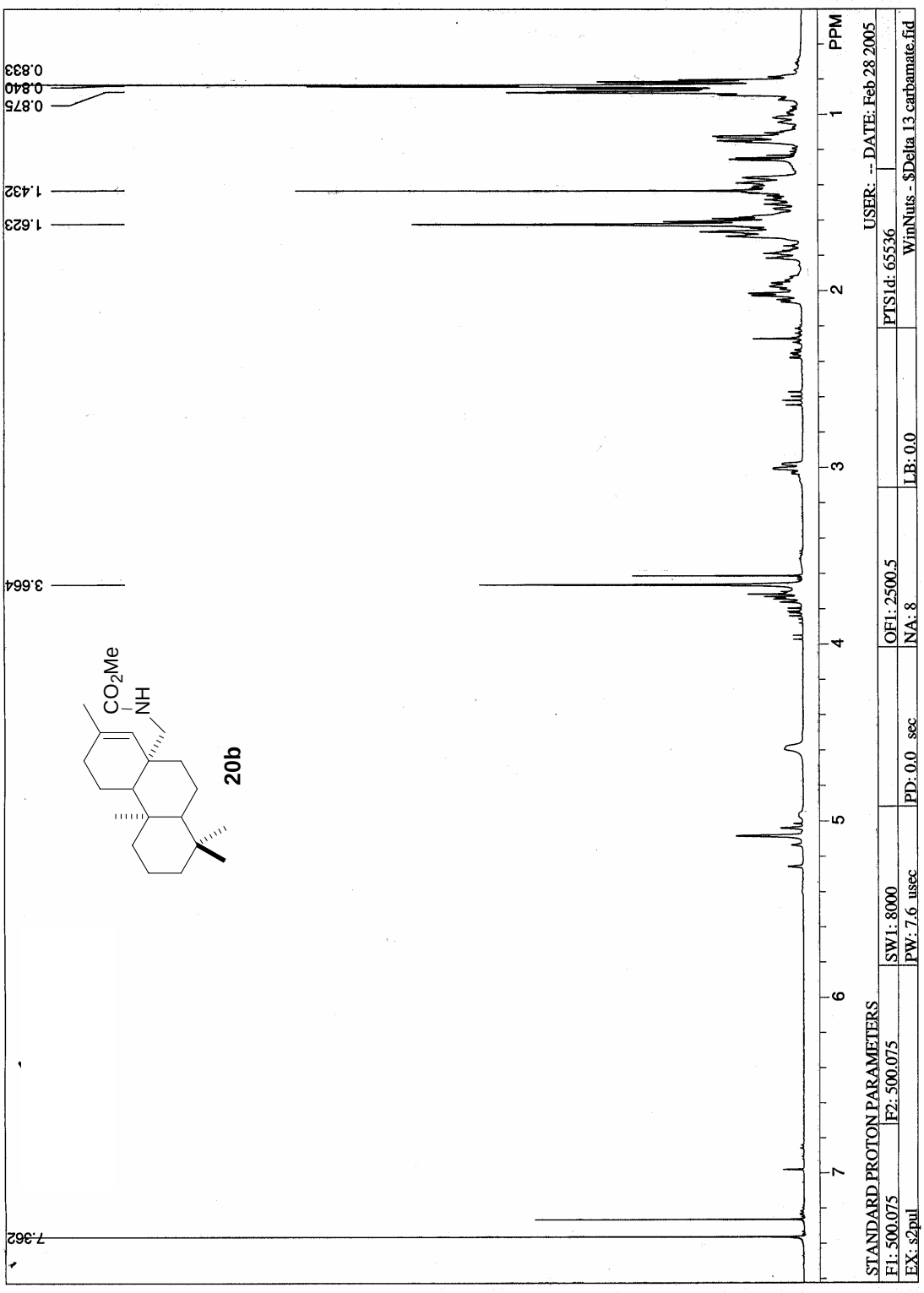

16.163
17.062
18.164
18.214
21.017
22.949
30.581
31.428
33.054
33.063
36.942
37.126
37.432
39.261
39.421
41.856
56.454
56.904
76.754
77.006
77.264
130.761
132.157
206.798
CO2H
19b
200
150
100
50
0 PPM
STANDARD CARBON PARAMETERS
F1: 125.663
F2: 499.698
EX: s2pul
SW1: 30166
PW: 4.3 usec
PD: 1.0 sec
OF1: 13778.3
NA: 160
PTS1d: 65536
LB: 1.0
USER: -- DATE: Feb 26 2005
WinNuts - $nitrile-to-acid.fid

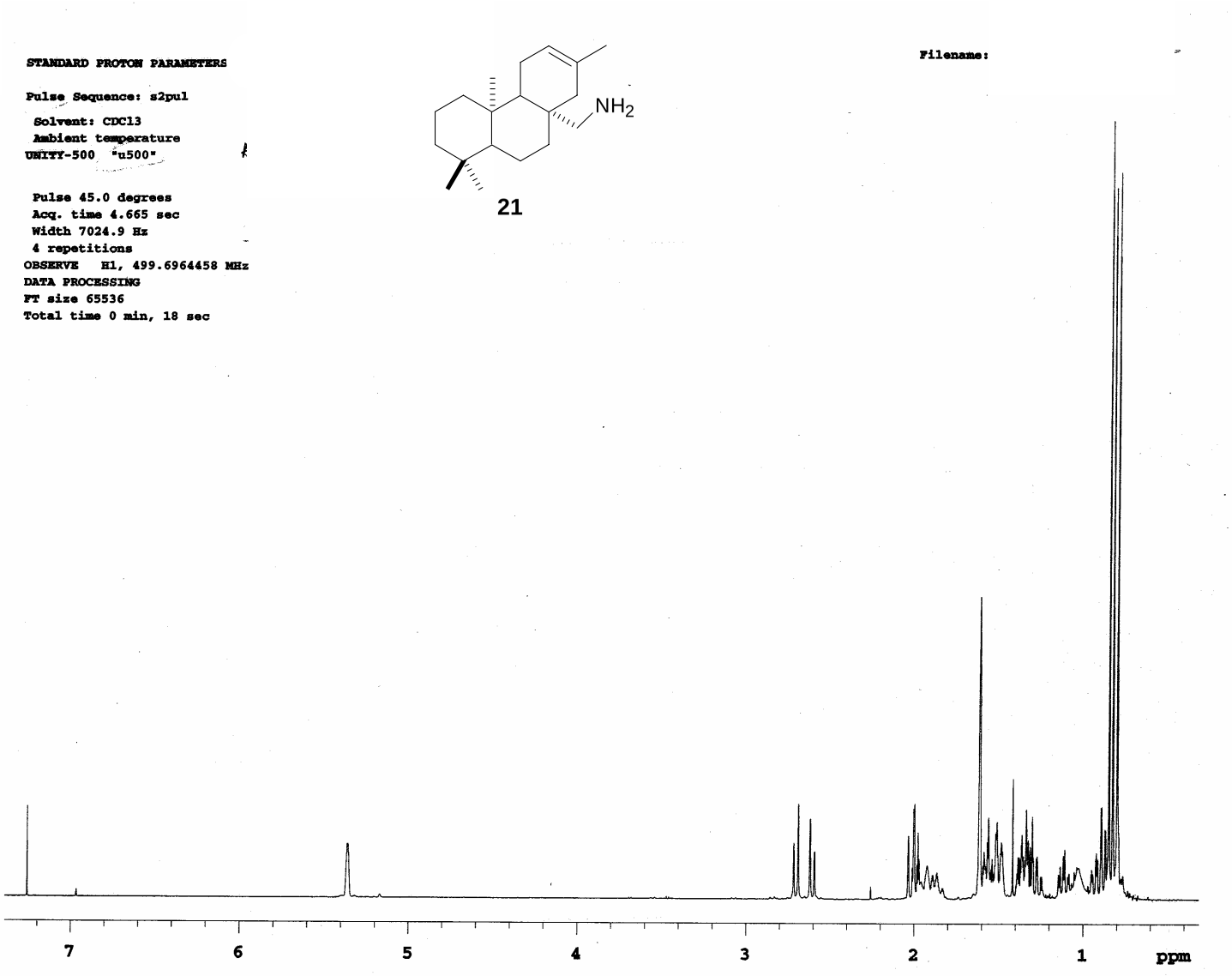

STANDARD 1H OBSERVE
expl stdih
SAMPLE
date Aug 26 2004
solvent CDCl3
file esp
ACQUISITION
sfrq 399.951
tn H1
at 4.096
np 65536
sw 8000.0
fb 4400
bs 16
tpwr 63
pw 9.0
d1 0
tof -425.7
nt 4
ct 4
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 20
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
DISPLAY
sp 232.6
wp 668.5
vs 203
sc 0
wc 250
hzmm 2.67
is 500.00
rf1 4903.2
rfp 2903.6
th 59
ins 100.000
nm ph
CO2Me
NH
20a
1.602
0.908
0.848
0.823
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm

INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	157.577	15847.100	18.3
2	131.039	13178.256	32.7
3	120.813	12149.782	77.0
4	77.319	7775.717	97.1
5	77.000	7743.673	102.0
6	76.681	7711.628	92.5
7	57.138	5746.236	83.3
8	53.451	5375.436	118.5
9	52.040	5233.525	47.3
10	43.528	4377.481	70.8
11	41.897	4213.444	82.7
12	40.326	4055.511	68.5
13	39.636	3986.081	99.9
14	37.383	3759.481	69.4
15	37.140	3735.066	78.7
16	37.049	3725.911	54.4
17	33.385	3357.400	118.0
18	33.233	3342.141	57.9
19	23.507	2364.022	68.9
20	22.316	2244.237	69.8
21	21.618	2174.045	142.4
22	18.530	1863.519	107.9
23	18.500	1860.467	84.6
24	15.951	1604.111	123.2

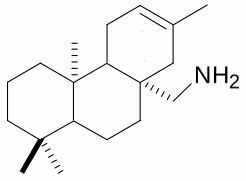


20a

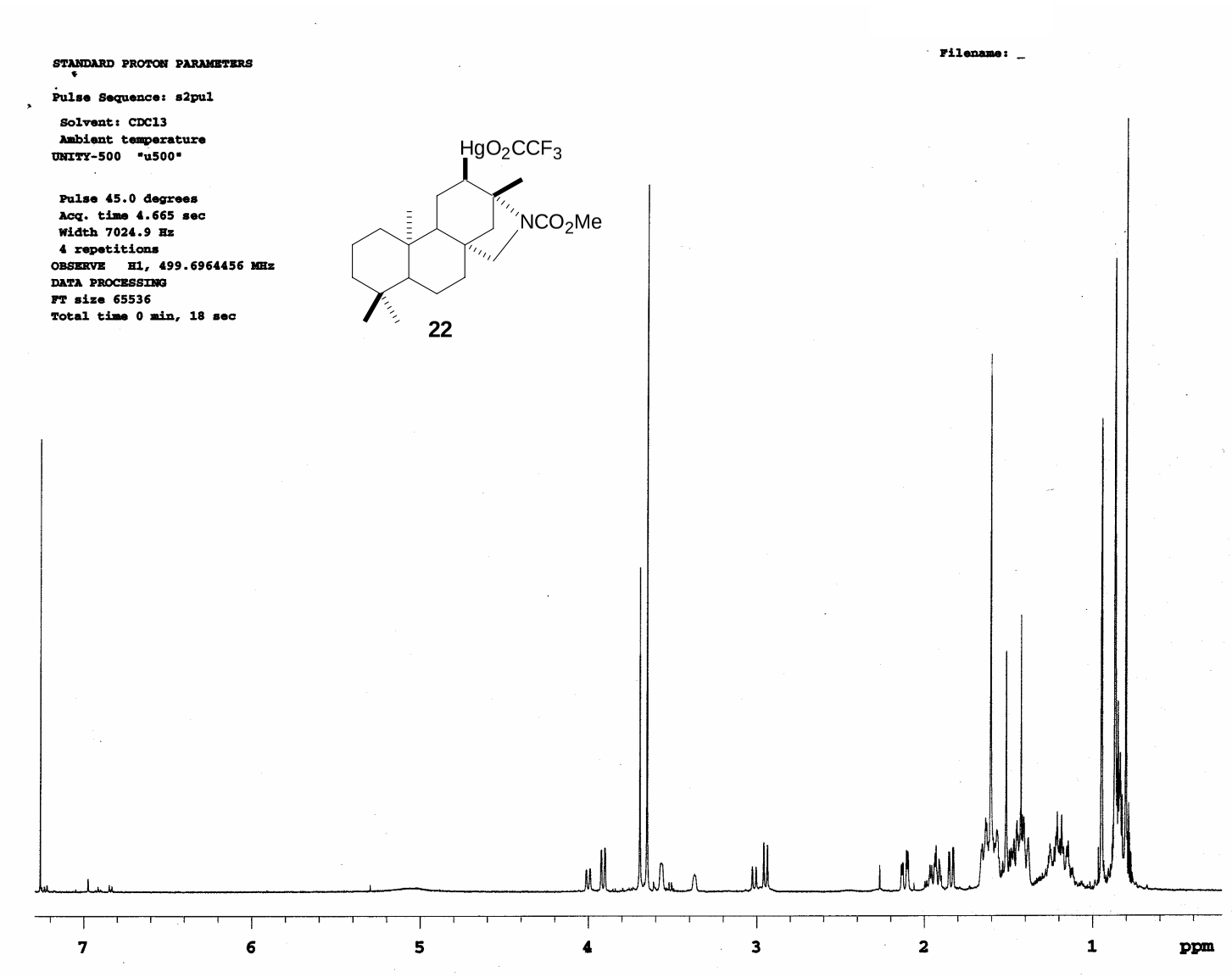

0.833
0.840
0.875
1.432
1.623
3.664
7.362
CO2Me
NH
20b
PPM
STANDARD PROTON PARAMETERS
F1: 500.075
F2: 500.075
SW1: 8000
PW: 7.6 usec
PD: 0.0 sec
OF1: 2500.5
NA: 8
LB: 0.0
PTS1d: 65536
USER: -- DATE: Feb 28 2005
EX: s2pul
WinNuts - $Delta 13 carbamate.fid

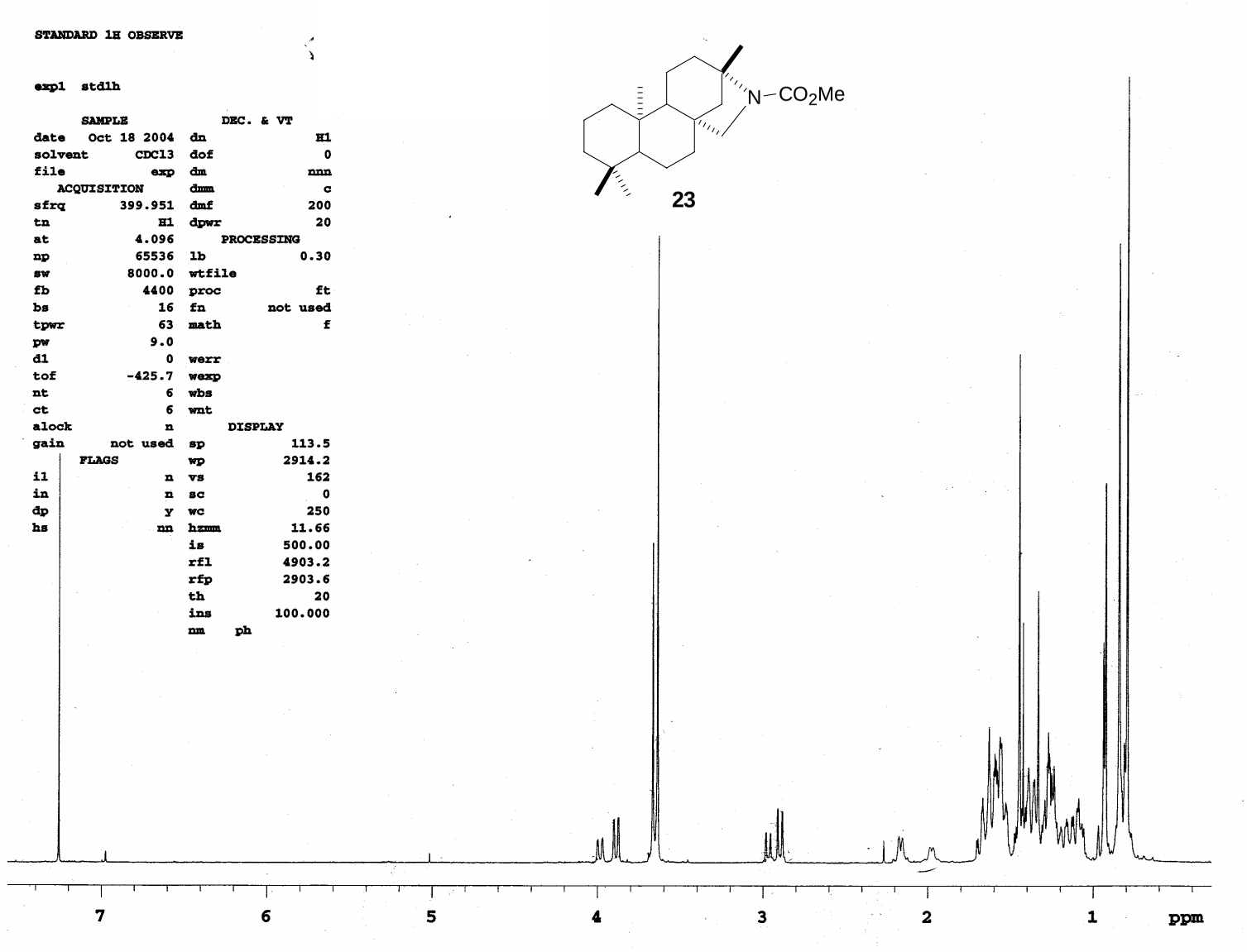

STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "u500"
Pulse 45.0 degrees
Acq. time 4.665 sec
Width 7024.9 Hz
4 repetitions
OBSERVE H1, 499.6964458 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 18 sec
NH2
21
Filename:
7
6
5
4
3
2
1
ppm

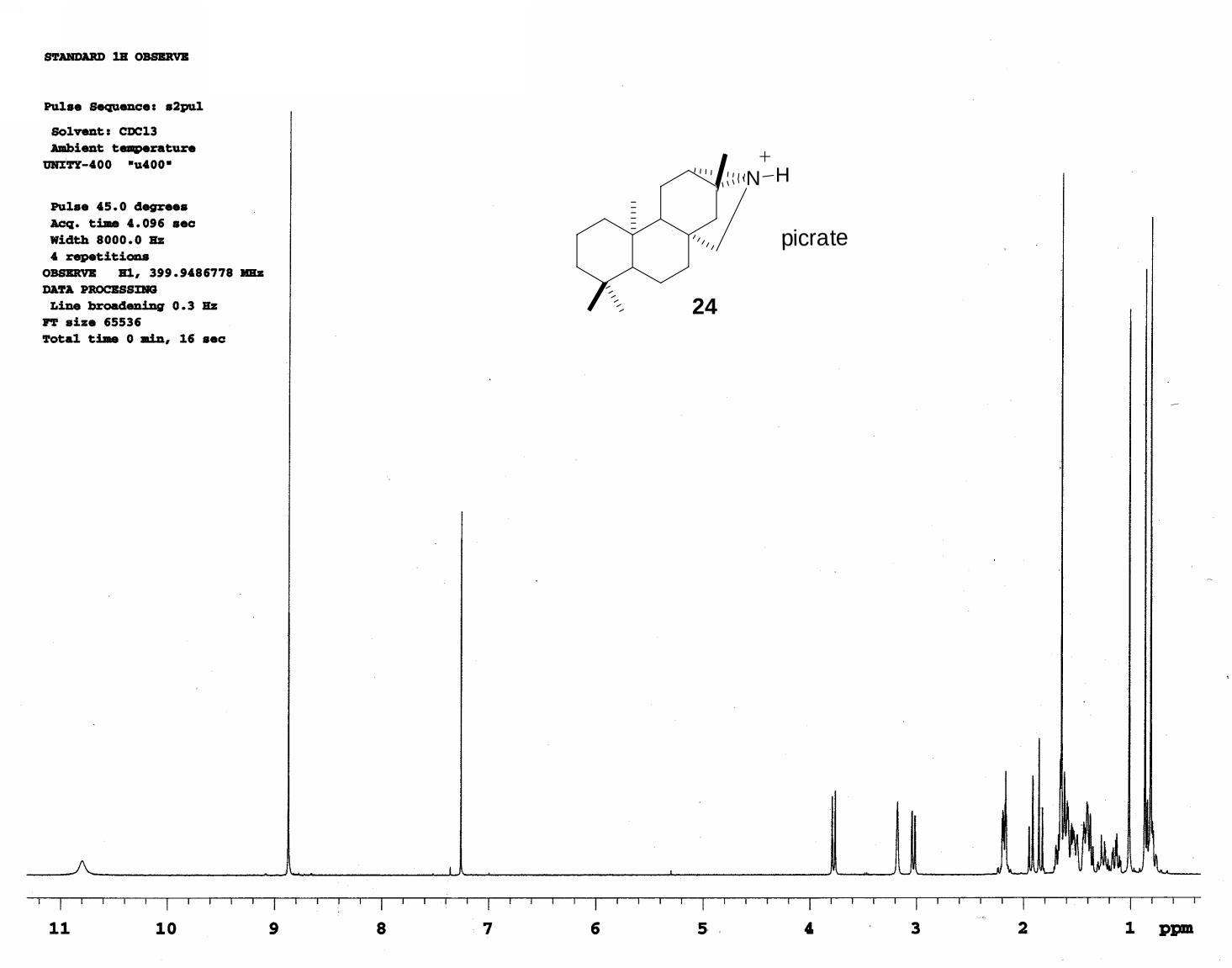
INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	131.168	13191.226	16.6
2	120.926	12161.227	44.1
3	77.319	7775.717	93.3
4	77.000	7743.673	95.1
5	76.681	7711.628	94.0
6	57.214	5753.866	41.5
7	53.838	5414.347	39.7
8	42.572	4281.348	40.1
9	41.920	4215.733	55.3
10	40.304	4053.222	24.3
11	39.735	3996.000	40.9
12	37.079	3728.963	24.1
13	36.563	3677.081	34.4
14	33.423	3361.215	40.4
15	33.233	3342.140	21.3
16	30.297	3046.874	9.0
17	23.560	2369.363	39.1
18	22.414	2254.156	40.4
19	21.656	2177.859	47.3
20	18.568	1867.334	49.6
21	18.416	1852.074	39.4
22	15.966	1605.637	37.7



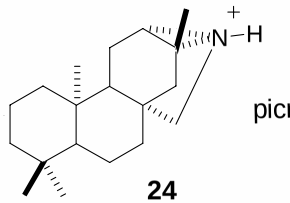
21


STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-500 "u500"
Pulse 45.0 degrees
Acq. time 4.665 sec
Width 7024.9 Hz
4 repetitions
OBSERVE H1, 499.6964456 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 18 sec
Filename: _
HgO2CCF3
NCO2Me
22
7
6
5
4
3
2
1
ppm


STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Oct 18 2004
solvent CDCl3
file exp
ACQUISITION
sfrq 399.951
tn H1
at 4.096
np 65536
sw 8000.0
fb 4400
bs 16
tpwr 63
pw 9.0
d1 0
tof -425.7
nt 6
ct 6
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 20
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
DISPLAY
sp 113.5
wp 2914.2
vs 162
sc 0
wc 250
hzmm 11.66
is 500.00
rfl 4903.2
rfp 2903.6
th 20
ins 100.000
nm ph
N–CO2Me
23
7
6
5
4
3
2
1
ppm


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-400 "u400"
Pulse 45.0 degrees
Acq. time 4.096 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 399.9486778 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 16 sec
N–H
picrate
24
11
10
9
8
7
6
5
4
3
2
1
ppm

INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	161.846	20335.720	1.4
2	141.682	17802.177	1.9
3	128.384	16131.254	1.2
4	126.559	15902.020	12.9
5	77.256	9707.177	17.7
6	77.000	9674.955	17.7
7	76.751	9643.654	17.9
8	55.019	6913.099	7.3
9	53.305	6697.674	4.7
10	50.880	6392.950	5.7
11	49.524	6222.635	7.3
12	45.868	5763.246	6.1
13	44.688	5615.027	6.8
14	41.545	5220.081	6.3
15	39.977	5023.069	4.7
16	38.739	4867.484	6.8
17	37.823	4752.407	4.4
18	34.453	4328.923	6.3
19	33.251	4177.941	6.4
20	32.870	4130.069	4.6
21	21.586	2712.316	6.4
22	19.660	2470.193	6.5
23	17.703	2224.388	5.9
24	17.088	2147.056	7.1
25	17.066	2144.294	6.3
26	14.120	1774.206	6.5



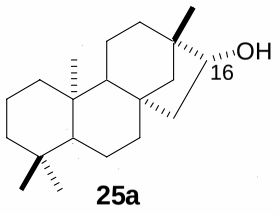
picrate

24

STANDARD 1H OBSERVE

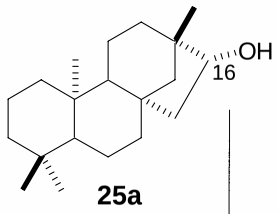
exp1 std1h

SAMPLE		DEC. & VT	
date	Jul 11 2004	dn	H1
solvent	CDCl3	dof	0
file	exp	dm	nnn
ACQUISITION		dmm	c
sfrq	399.951	dmf	200
tn	H1	dpwr	20
at	4.096	PROCESSING	
np	65536	lb	0.30
sw	8000.0	wtfile	
fb	4400	proc	ft
bs	16	fn	not used
tpwr	63	math	f
pw	10.1		
d1	0	werr	
tof	-425.7	wexp	
nt	6	wbs	
ct	6	wnt	
alock	n	DISPLAY	
gain	not used	sp	160.1
FLAGS		wp	2879.5
il	n	vs	162
in	n	sc	0
dp	y	wc	250
hs	nn	hzmm	11.52
		is	500.00
		rfl	4903.0
		rfp	2903.6
		th	20
		ins	100.000
		nm	ph

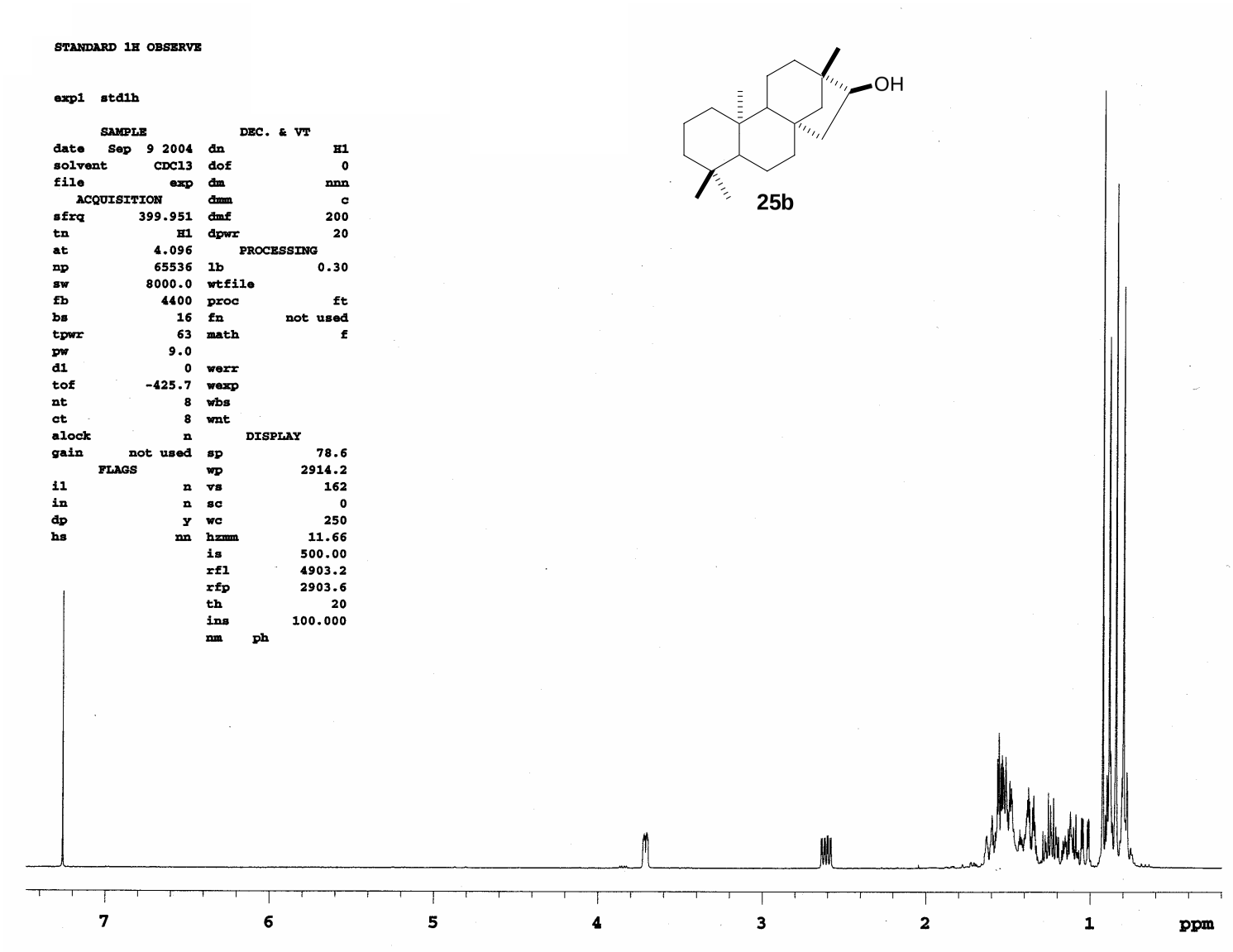


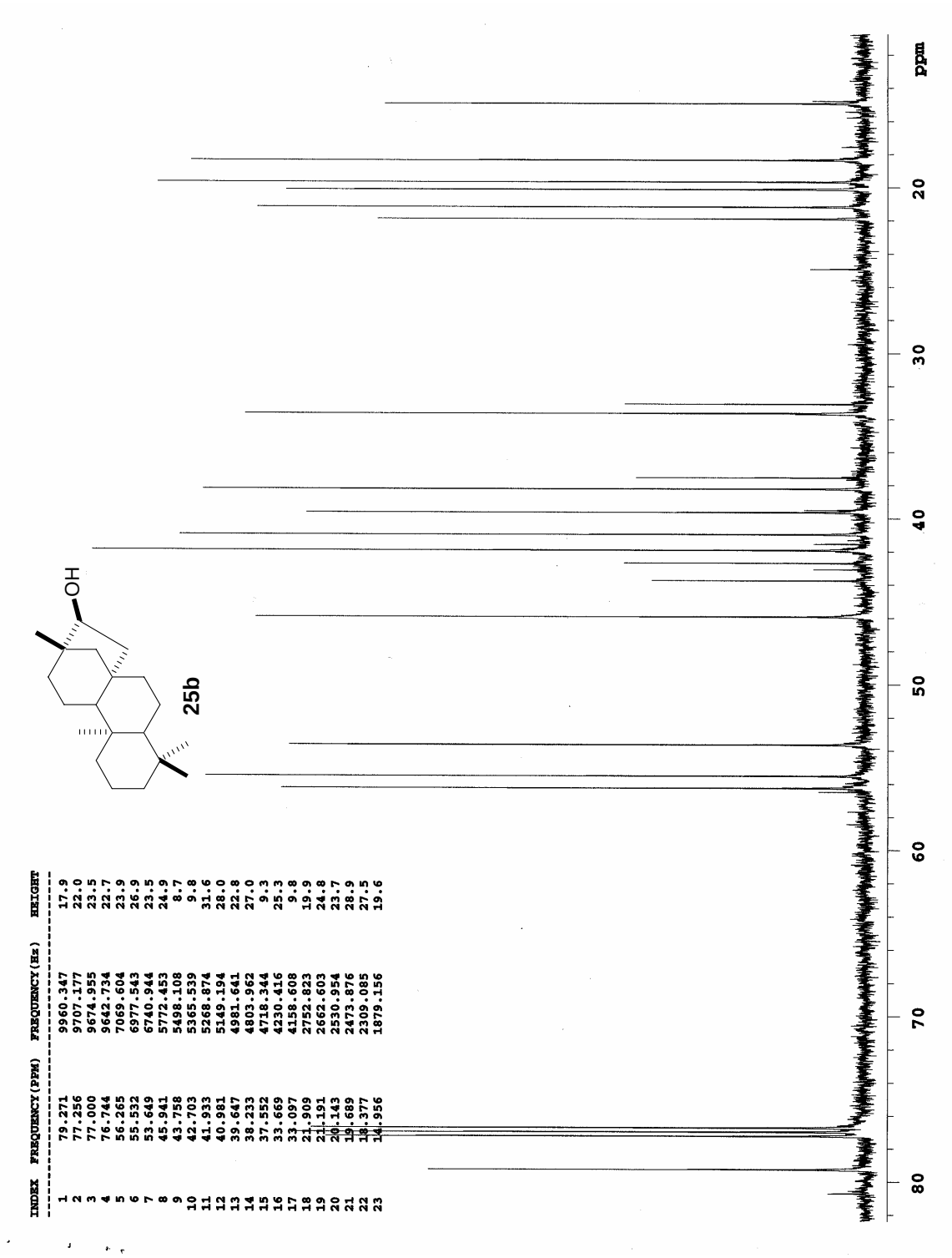
25a

INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	80.702	8115.998	155.1
2	77.319	7775.717	77.0
3	77.000	7743.673	81.5
4	76.681	7711.628	81.8
5	56.493	5681.384	177.9
6	56.243	5656.207	156.5
7	55.538	5585.251	197.5
8	43.073	4331.703	148.5
9	42.018	4225.651	103.1
10	42.003	4224.126	115.0
11	41.958	4219.548	198.1
12	41.555	4179.111	164.8
13	39.507	3973.111	190.0
14	37.663	3787.711	58.4
15	33.726	3391.733	185.7
16	33.643	3383.341	165.8
17	33.081	3326.881	63.7
18	24.926	2506.696	145.3
19	21.944	2206.852	151.9
20	20.116	2022.978	201.4
21	20.101	2021.452	195.6
22	18.325	1842.919	149.4
23	14.805	1488.904	164.0



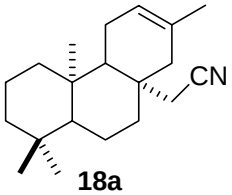
25a


STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Sep 9 2004
solvent CDCl3
file exp
ACQUISITION
sfrq 399.951
tn H1
at 4.096
np 65536
sw 8000.0
fb 4400
bs 16
tpwr 63
pw 9.0
d1 0
tof -425.7
nt 8
ct 8
alock n
gain not used
FLAGS
i1 n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 20
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
DISPLAY
sp 78.6
wp 2914.2
vs 162
sc 0
wc 250
hzmm 11.66
is 500.00
rfl 4903.2
rfp 2903.6
th 20
ins 100.000
nm ph
OH
25b
7
6
5
4
3
2
1
ppm



INDEX	FREQUENCY(PPM)	FREQUENCY(Hz)	HEIGHT
1	79.271	9960.347	17.9
2	77.256	9707.177	22.0
3	77.000	9674.955	23.5
4	76.744	9642.734	22.7
5	56.265	7069.604	23.9
6	55.532	6977.543	26.9
7	53.649	6740.944	23.5
8	45.941	5772.453	24.9
9	43.758	5498.108	8.7
10	42.703	5365.539	9.8
11	41.933	5268.874	31.6
12	40.981	5149.194	28.0
13	39.647	4981.641	22.8
14	38.233	4803.962	27.0
15	37.552	4718.344	9.3
16	33.669	4230.416	25.3
17	33.097	4158.608	9.8
18	21.909	2752.823	19.9
19	21.191	2662.603	24.8
20	20.143	2530.954	23.7
21	19.689	2473.876	28.9
22	18.377	2309.085	27.5
23	14.956	1879.156	19.6

ORTEP diagram and Tables of crystal data, atomic coordinates, bond angles and bond lengths, and anisotropic displacement parameters from the X-ray crystal determination with unsaturated nitrile 18a (ID code g30bam)



18a

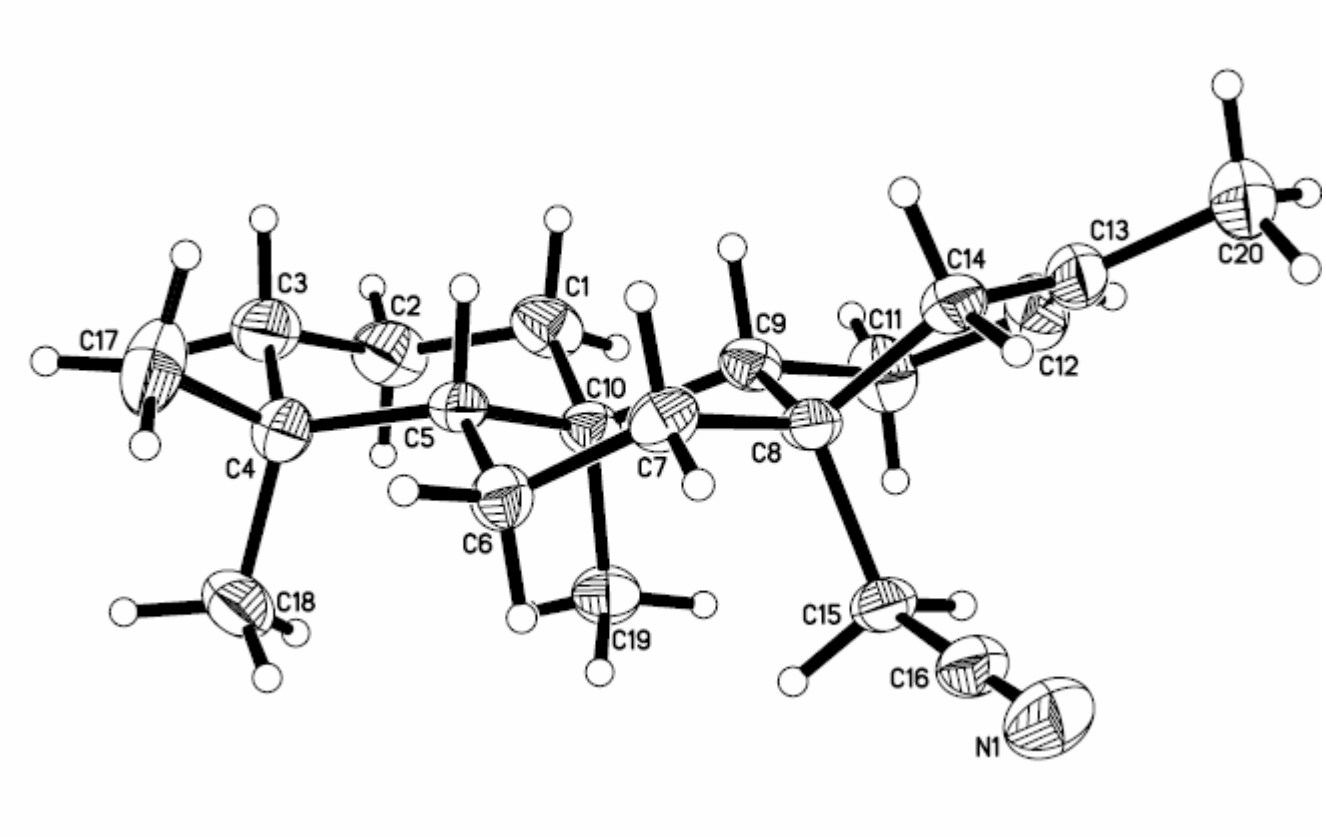


Table 1. Crystal data and structure refinement for unsaturated nitrile **18a**

Identification code	g30bam	
Empirical formula	C20 H31 N	
Formula weight	285.46	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.903(6) Å	α= 90°.
	b = 9.454(7) Å	β= 97.736(12)°.
	c = 11.846(9) Å	γ = 90°.

Volume	877.0(12) $Å^3$
Z	2
Density (calculated)	1.081 Mg/m^3
Absorption coefficient	0.061 mm^{-1}
F(000)	316
Crystal size	0.70 x 0.32 x 0.20 mm^3
Theta range for data collection	1.73 to 25.56°.
Index ranges	-9<=h<=9, -11<=k<=11, -14<=l<=14
Reflections collected	9150
Independent reflections	1735 [R(int) = 0.1151]
Completeness to theta = 25.56°	99.1 %
Absorption correction	Numerical
Max. and min. transmission	0.99213 and 0.96142
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1735 / 1 / 194
Goodness-of-fit on F^2	0.911
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1138
R indices (all data)	R1 = 0.0616, wR2 = 0.1241
Absolute structure parameter	-10(10)
Largest diff. peak and hole	0.211 and -0.149 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for g30bam. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-144(3)	6220(3)	6674(3)	53(1)
C(2)	590(4)	7589(3)	6233(3)	60(1)
C(3)	1980(4)	7283(3)	5495(3)	59(1)
C(4)	3462(3)	6369(3)	6079(2)	50(1)
C(5)	2674(3)	5027(3)	6579(2)	38(1)
C(6)	3986(3)	3945(3)	7114(2)	41(1)
C(7)	3141(3)	2505(3)	7196(2)	39(1)
C(8)	1628(3)	2526(3)	7894(2)	34(1)
C(9)	408(3)	3783(3)	7518(2)	38(1)
C(10)	1242(3)	5267(3)	7347(2)	37(1)
C(11)	-1084(3)	3820(4)	8236(3)	55(1)
C(12)	-1828(3)	2376(4)	8382(3)	57(1)
C(13)	-1122(3)	1177(3)	8120(2)	49(1)
C(14)	585(3)	1157(3)	7671(2)	42(1)
C(15)	2326(3)	2594(3)	9196(2)	41(1)
C(16)	3278(3)	1312(3)	9586(2)	47(1)
C(17)	4557(5)	5921(4)	5151(3)	74(1)
C(18)	4635(4)	7249(4)	6969(3)	63(1)
C(19)	1876(3)	5990(3)	8501(2)	46(1)
C(20)	-1956(5)	-245(4)	8214(3)	68(1)
N(1)	4013(3)	300(3)	9890(2)	68(1)

Table 3. Bond lengths [Å] and angles [°] for g30bam.

C(1)-C(2)	1.538(5)
C(1)-C(10)	1.553(4)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.521(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.542(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(17)	1.547(5)
C(4)-C(18)	1.549(4)
C(4)-C(5)	1.564(4)
C(5)-C(6)	1.532(4)
C(5)-C(10)	1.561(4)
C(5)-H(5A)	1.0000
C(6)-C(7)	1.525(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.543(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(14)	1.538(4)
C(8)-C(9)	1.557(4)
C(8)-C(15)	1.568(3)
C(9)-C(11)	1.544(4)
C(9)-C(10)	1.575(4)
C(9)-H(9A)	1.0000
C(10)-C(19)	1.550(4)
C(11)-C(12)	1.506(5)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.318(5)
C(12)-H(12A)	0.9500
C(13)-C(20)	1.508(4)
C(13)-C(14)	1.515(4)

C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.468(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-N(1)	1.151(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(2)-C(1)-C(10)	113.0(2)
C(2)-C(1)-H(1A)	109.0
C(10)-C(1)-H(1A)	109.0
C(2)-C(1)-H(1B)	109.0
C(10)-C(1)-H(1B)	109.0
H(1A)-C(1)-H(1B)	107.8
C(3)-C(2)-C(1)	111.7(3)
C(3)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2B)	109.3
C(1)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	107.9
C(2)-C(3)-C(4)	114.4(2)
C(2)-C(3)-H(3A)	108.7
C(4)-C(3)-H(3A)	108.7
C(2)-C(3)-H(3B)	108.7
C(4)-C(3)-H(3B)	108.7
H(3A)-C(3)-H(3B)	107.6
C(3)-C(4)-C(17)	107.4(2)
C(3)-C(4)-C(18)	110.7(3)

C(17)-C(4)-C(18)	106.9(3)
C(3)-C(4)-C(5)	107.9(2)
C(17)-C(4)-C(5)	109.6(3)
C(18)-C(4)-C(5)	114.2(2)
C(6)-C(5)-C(10)	111.0(2)
C(6)-C(5)-C(4)	114.6(2)
C(10)-C(5)-C(4)	117.4(2)
C(6)-C(5)-H(5A)	104.0
C(10)-C(5)-H(5A)	104.0
C(4)-C(5)-H(5A)	104.0
C(7)-C(6)-C(5)	110.1(2)
C(7)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6A)	109.6
C(7)-C(6)-H(6B)	109.6
C(5)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
C(6)-C(7)-C(8)	113.6(2)
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7A)	108.8
C(6)-C(7)-H(7B)	108.8
C(8)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(14)-C(8)-C(7)	109.5(2)
C(14)-C(8)-C(9)	107.25(18)
C(7)-C(8)-C(9)	110.5(2)
C(14)-C(8)-C(15)	108.3(2)
C(7)-C(8)-C(15)	109.41(18)
C(9)-C(8)-C(15)	111.8(2)
C(11)-C(9)-C(8)	110.4(2)
C(11)-C(9)-C(10)	114.5(2)
C(8)-C(9)-C(10)	117.62(18)
C(11)-C(9)-H(9A)	104.2
C(8)-C(9)-H(9A)	104.2
C(10)-C(9)-H(9A)	104.2
C(19)-C(10)-C(1)	108.6(2)
C(19)-C(10)-C(5)	113.86(19)
C(1)-C(10)-C(5)	107.6(2)
C(19)-C(10)-C(9)	111.7(2)

C(1)-C(10)-C(9)	107.74(19)
C(5)-C(10)-C(9)	107.1(2)
C(12)-C(11)-C(9)	112.4(3)
C(12)-C(11)-H(11A)	109.1
C(9)-C(11)-H(11A)	109.1
C(12)-C(11)-H(11B)	109.1
C(9)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.9
C(13)-C(12)-C(11)	124.6(2)
C(13)-C(12)-H(12A)	117.7
C(11)-C(12)-H(12A)	117.7
C(12)-C(13)-C(20)	123.1(3)
C(12)-C(13)-C(14)	121.3(3)
C(20)-C(13)-C(14)	115.7(3)
C(13)-C(14)-C(8)	114.2(2)
C(13)-C(14)-H(14A)	108.7
C(8)-C(14)-H(14A)	108.7
C(13)-C(14)-H(14B)	108.7
C(8)-C(14)-H(14B)	108.7
H(14A)-C(14)-H(14B)	107.6
C(16)-C(15)-C(8)	111.9(2)
C(16)-C(15)-H(15A)	109.2
C(8)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15B)	109.2
C(8)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
N(1)-C(16)-C(15)	179.5(3)
C(4)-C(17)-H(17A)	109.5
C(4)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(4)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(4)-C(18)-H(18A)	109.5
C(4)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(4)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5

H(18B)-C(18)-H(18C)	109.5
C(10)-C(19)-H(19A)	109.5
C(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(10)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(13)-C(20)-H(20A)	109.5
C(13)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(13)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for g30bam. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	44(1)	44(2)	65(2)	2(2)	-8(1)	4(1)
C(2)	59(2)	44(2)	71(2)	11(2)	-14(2)	6(2)
C(3)	73(2)	47(2)	52(2)	11(2)	-9(2)	-12(2)
C(4)	56(2)	49(2)	42(2)	9(1)	2(1)	-9(1)
C(5)	43(1)	38(1)	31(1)	-2(1)	-2(1)	-8(1)
C(6)	36(1)	48(2)	39(1)	1(1)	8(1)	0(1)
C(7)	43(1)	42(1)	34(1)	-1(1)	5(1)	7(1)
C(8)	31(1)	42(1)	27(1)	-3(1)	1(1)	-2(1)
C(9)	31(1)	42(2)	39(1)	-1(1)	-3(1)	-1(1)
C(10)	35(1)	37(1)	38(1)	1(1)	-2(1)	1(1)
C(11)	33(1)	57(2)	76(2)	8(2)	10(1)	10(1)
C(12)	33(1)	71(2)	68(2)	17(2)	7(1)	-2(2)
C(13)	42(1)	56(2)	46(2)	14(2)	-4(1)	-7(2)
C(14)	45(1)	43(2)	35(1)	4(1)	-3(1)	-1(1)
C(15)	37(1)	55(2)	28(1)	-1(1)	1(1)	-2(1)
C(16)	39(1)	62(2)	37(1)	6(1)	-3(1)	-3(1)
C(17)	92(2)	73(2)	62(2)	18(2)	32(2)	-6(2)
C(18)	57(2)	57(2)	70(2)	6(2)	-7(2)	-20(2)
C(19)	50(1)	44(2)	43(2)	-9(1)	3(1)	1(1)
C(20)	67(2)	70(2)	65(2)	15(2)	5(2)	-21(2)
N(1)	63(2)	76(2)	60(2)	21(2)	-10(1)	8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for g30bam.

	x	y	z	U(eq)
H(1A)	-729	5680	6019	63
H(1B)	-1007	6469	7174	63
H(2A)	-341	8130	5782	72
H(2B)	1067	8181	6889	72
H(3A)	2450	8193	5264	71
H(3B)	1459	6795	4794	71
H(5A)	2077	4531	5893	45
H(6A)	4927	3865	6644	49
H(6B)	4476	4267	7885	49
H(7A)	4007	1825	7549	47
H(7B)	2730	2164	6417	47
H(9A)	-142	3513	6738	46
H(11A)	-673	4220	8996	66
H(11B)	-1991	4451	7861	66
H(12A)	-2881	2325	8683	68
H(14A)	384	983	6840	50
H(14B)	1268	357	8027	50
H(15A)	3084	3427	9343	49
H(15B)	1358	2716	9638	49
H(17A)	3909	5255	4625	111
H(17B)	5607	5465	5511	111
H(17C)	4848	6758	4729	111
H(18A)	3937	7741	7470	94
H(18B)	5266	7944	6576	94
H(18C)	5442	6618	7424	94
H(19A)	2984	5592	8816	69
H(19B)	1048	5826	9033	69
H(19C)	1996	7009	8383	69
H(20A)	-3024	-124	8539	102
H(20B)	-1186	-863	8709	102
H(20C)	-2202	-671	7456	102

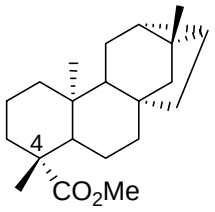
Table 6. Torsion angles [°] for g30bam.

C(10)-C(1)-C(2)-C(3)	56.4(3)
C(1)-C(2)-C(3)-C(4)	-55.6(3)
C(2)-C(3)-C(4)-C(17)	169.1(3)
C(2)-C(3)-C(4)-C(18)	-74.6(3)
C(2)-C(3)-C(4)-C(5)	51.0(3)
C(3)-C(4)-C(5)-C(6)	175.6(2)
C(17)-C(4)-C(5)-C(6)	59.0(3)
C(18)-C(4)-C(5)-C(6)	-60.9(3)
C(3)-C(4)-C(5)-C(10)	-51.4(3)
C(17)-C(4)-C(5)-C(10)	-168.0(2)
C(18)-C(4)-C(5)-C(10)	72.1(3)
C(10)-C(5)-C(6)-C(7)	63.6(3)
C(4)-C(5)-C(6)-C(7)	-160.5(2)
C(5)-C(6)-C(7)-C(8)	-58.1(3)
C(6)-C(7)-C(8)-C(14)	165.4(2)
C(6)-C(7)-C(8)-C(9)	47.4(3)
C(6)-C(7)-C(8)-C(15)	-76.1(3)
C(14)-C(8)-C(9)-C(11)	61.9(2)
C(7)-C(8)-C(9)-C(11)	-178.8(2)
C(15)-C(8)-C(9)-C(11)	-56.6(3)
C(14)-C(8)-C(9)-C(10)	-164.1(2)
C(7)-C(8)-C(9)-C(10)	-44.8(3)
C(15)-C(8)-C(9)-C(10)	77.3(3)
C(2)-C(1)-C(10)-C(19)	70.8(3)
C(2)-C(1)-C(10)-C(5)	-52.9(3)
C(2)-C(1)-C(10)-C(9)	-168.1(2)
C(6)-C(5)-C(10)-C(19)	66.8(3)
C(4)-C(5)-C(10)-C(19)	-67.8(3)
C(6)-C(5)-C(10)-C(1)	-172.8(2)
C(4)-C(5)-C(10)-C(1)	52.6(3)
C(6)-C(5)-C(10)-C(9)	-57.2(2)
C(4)-C(5)-C(10)-C(9)	168.2(2)
C(11)-C(9)-C(10)-C(19)	56.3(3)
C(8)-C(9)-C(10)-C(19)	-75.8(3)
C(11)-C(9)-C(10)-C(1)	-62.9(3)
C(8)-C(9)-C(10)-C(1)	165.0(2)

C(11)-C(9)-C(10)-C(5)	-178.3(2)
C(8)-C(9)-C(10)-C(5)	49.5(3)
C(8)-C(9)-C(11)-C(12)	-44.1(3)
C(10)-C(9)-C(11)-C(12)	-179.6(2)
C(9)-C(11)-C(12)-C(13)	11.8(4)
C(11)-C(12)-C(13)-C(20)	-176.3(3)
C(11)-C(12)-C(13)-C(14)	2.0(5)
C(12)-C(13)-C(14)-C(8)	17.7(4)
C(20)-C(13)-C(14)-C(8)	-163.8(2)
C(7)-C(8)-C(14)-C(13)	-168.4(2)
C(9)-C(8)-C(14)-C(13)	-48.5(3)
C(15)-C(8)-C(14)-C(13)	72.4(3)
C(14)-C(8)-C(15)-C(16)	54.0(3)
C(7)-C(8)-C(15)-C(16)	-65.2(3)
C(9)-C(8)-C(15)-C(16)	172.0(2)

Symmetry transformations used to generate equivalent atoms:

ORTEP diagram and Tables of crystal data, atomic coordinates, bond angles and bond lengths, and anisotropic displacement parameters from the X-ray crystal structure determination of methyl *ent*-trachyloban-19-oate (3 with axial carbomethoxy group at C4, ID code g24fasm)



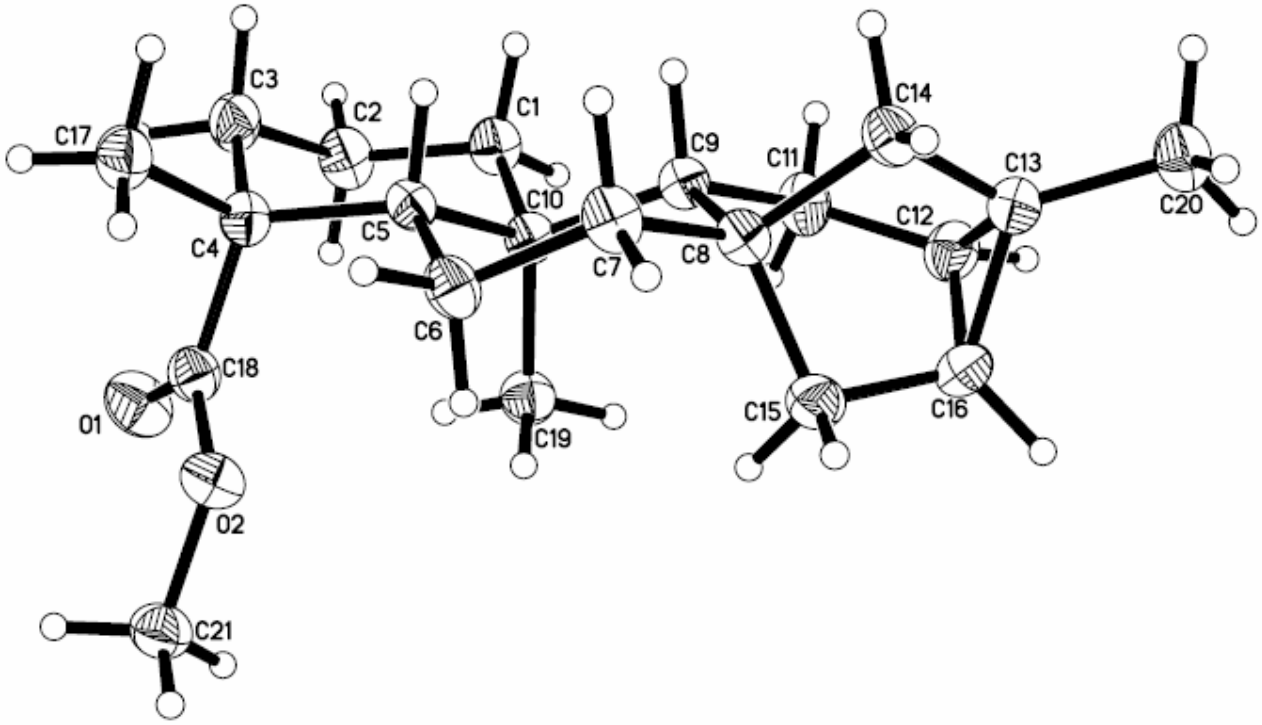


Table 1. Crystal data and structure refinement for g24fasm.

Identification code	g24fasm	
Empirical formula	C21 H32 O2	
Formula weight	316.47	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.430(2) Å	α= 90°.
	b = 8.883(2) Å	β= 90°.
	c = 26.604(7) Å	γ = 90°.

Volume	1755.8(8) $Å^3$
Z	4
Density (calculated)	1.197 Mg/m^3
Absorption coefficient	0.074 mm^{-1}
F(000)	696
Crystal size	0.42 x 0.31 x 0.22 mm^3
Theta range for data collection	2.42 to 25.37°.
Index ranges	-8<=h<=8, -10<=k<=10, -30<=l<=32
Reflections collected	11593
Independent reflections	1875 [R(int) = 0.0415]
Completeness to theta = 25.37°	99.8 %
Absorption correction	Integration
Max. and min. transmission	0.9876 and 0.9629
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1875 / 0 / 213
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1307
R indices (all data)	R1 = 0.0590, wR2 = 0.1401
Absolute structure parameter	-10(10)
Extinction coefficient	0.010(4)
Largest diff. peak and hole	0.299 and -0.210 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for g24fasm. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1420(4)	1307(3)	1711(1)	38(1)
O(1)	2481(3)	-1995(2)	1896(1)	53(1)
O(2)	4424(3)	-418(2)	1531(1)	41(1)
C(2)	-1043(4)	-44(3)	2047(1)	45(1)
C(3)	576(4)	256(4)	2385(1)	43(1)
C(4)	2290(4)	670(3)	2095(1)	35(1)
C(5)	1855(4)	2046(3)	1750(1)	31(1)
C(6)	3440(4)	2763(3)	1467(1)	37(1)
C(7)	2904(4)	4337(3)	1289(1)	38(1)
C(8)	1251(4)	4350(3)	947(1)	32(1)
C(9)	-285(4)	3410(3)	1182(1)	32(1)
C(10)	213(4)	1827(3)	1396(1)	32(1)
C(11)	-1948(4)	3412(4)	826(1)	41(1)
C(12)	-1743(4)	4458(3)	381(1)	42(1)
C(13)	-651(4)	5880(3)	411(1)	38(1)
C(14)	525(4)	5963(3)	875(1)	37(1)
C(15)	1617(4)	3879(3)	397(1)	41(1)
C(16)	47(5)	4544(4)	113(1)	43(1)
C(17)	3753(4)	1109(4)	2482(1)	45(1)
C(18)	3003(4)	-729(3)	1833(1)	36(1)
C(19)	592(4)	627(3)	989(1)	39(1)
C(20)	-1316(5)	7303(4)	171(1)	45(1)
C(21)	5234(4)	-1683(3)	1282(1)	45(1)

Table 3. Bond lengths [Å] and angles [°] for g24fasm.

C(1)-C(2)	1.522(4)
C(1)-C(10)	1.546(4)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
O(1)-C(18)	1.202(3)
O(2)-C(18)	1.353(3)
O(2)-C(21)	1.437(3)
C(2)-C(3)	1.524(4)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.533(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(18)	1.521(4)
C(4)-C(17)	1.548(4)
C(4)-C(5)	1.562(4)
C(5)-C(6)	1.537(4)
C(5)-C(10)	1.554(3)
C(5)-H(5A)	1.0000
C(6)-C(7)	1.529(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.528(4)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(14)	1.543(4)
C(8)-C(9)	1.545(4)
C(8)-C(15)	1.548(4)
C(9)-C(11)	1.557(4)
C(9)-C(10)	1.561(4)
C(9)-H(9A)	1.0000
C(10)-C(19)	1.545(4)
C(11)-C(12)	1.513(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.503(4)

C(12)-C(16)	1.511(4)
C(12)-H(12A)	1.0000
C(13)-C(20)	1.501(4)
C(13)-C(14)	1.513(4)
C(13)-C(16)	1.520(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.510(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	1.0000
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(2)-C(1)-C(10)	114.2(2)
C(2)-C(1)-H(1A)	108.7
C(10)-C(1)-H(1A)	108.7
C(2)-C(1)-H(1B)	108.7
C(10)-C(1)-H(1B)	108.7
H(1A)-C(1)-H(1B)	107.6
C(18)-O(2)-C(21)	116.1(2)
C(1)-C(2)-C(3)	110.7(3)
C(1)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	108.1
C(2)-C(3)-C(4)	113.6(2)
C(2)-C(3)-H(3A)	108.8

C(4)-C(3)-H(3A)	108.8
C(2)-C(3)-H(3B)	108.8
C(4)-C(3)-H(3B)	108.8
H(3A)-C(3)-H(3B)	107.7
C(18)-C(4)-C(3)	108.9(2)
C(18)-C(4)-C(17)	105.5(2)
C(3)-C(4)-C(17)	108.0(2)
C(18)-C(4)-C(5)	116.2(2)
C(3)-C(4)-C(5)	108.1(2)
C(17)-C(4)-C(5)	109.9(2)
C(6)-C(5)-C(10)	110.86(19)
C(6)-C(5)-C(4)	117.0(2)
C(10)-C(5)-C(4)	114.9(2)
C(6)-C(5)-H(5A)	104.1
C(10)-C(5)-H(5A)	104.1
C(4)-C(5)-H(5A)	104.1
C(7)-C(6)-C(5)	109.4(2)
C(7)-C(6)-H(6A)	109.8
C(5)-C(6)-H(6A)	109.8
C(7)-C(6)-H(6B)	109.8
C(5)-C(6)-H(6B)	109.8
H(6A)-C(6)-H(6B)	108.3
C(8)-C(7)-C(6)	113.6(2)
C(8)-C(7)-H(7A)	108.8
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7B)	108.8
C(6)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(7)-C(8)-C(14)	111.2(2)
C(7)-C(8)-C(9)	110.5(2)
C(14)-C(8)-C(9)	107.1(2)
C(7)-C(8)-C(15)	114.9(2)
C(14)-C(8)-C(15)	101.2(2)
C(9)-C(8)-C(15)	111.4(2)
C(8)-C(9)-C(11)	109.9(2)
C(8)-C(9)-C(10)	117.3(2)
C(11)-C(9)-C(10)	114.3(2)
C(8)-C(9)-H(9A)	104.7

C(11)-C(9)-H(9A)	104.7
C(10)-C(9)-H(9A)	104.7
C(19)-C(10)-C(1)	108.5(2)
C(19)-C(10)-C(5)	111.6(2)
C(1)-C(10)-C(5)	108.85(19)
C(19)-C(10)-C(9)	114.2(2)
C(1)-C(10)-C(9)	106.3(2)
C(5)-C(10)-C(9)	107.1(2)
C(12)-C(11)-C(9)	113.4(2)
C(12)-C(11)-H(11A)	108.9
C(9)-C(11)-H(11A)	108.9
C(12)-C(11)-H(11B)	108.9
C(9)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
C(13)-C(12)-C(16)	60.5(2)
C(13)-C(12)-C(11)	121.9(2)
C(16)-C(12)-C(11)	119.3(3)
C(13)-C(12)-H(12A)	114.8
C(16)-C(12)-H(12A)	114.8
C(11)-C(12)-H(12A)	114.8
C(20)-C(13)-C(12)	120.4(3)
C(20)-C(13)-C(14)	119.8(3)
C(12)-C(13)-C(14)	113.4(2)
C(20)-C(13)-C(16)	123.2(2)
C(12)-C(13)-C(16)	60.0(2)
C(14)-C(13)-C(16)	105.5(2)
C(13)-C(14)-C(8)	105.0(2)
C(13)-C(14)-H(14A)	110.8
C(8)-C(14)-H(14A)	110.8
C(13)-C(14)-H(14B)	110.8
C(8)-C(14)-H(14B)	110.8
H(14A)-C(14)-H(14B)	108.8
C(16)-C(15)-C(8)	103.5(2)
C(16)-C(15)-H(15A)	111.1
C(8)-C(15)-H(15A)	111.1
C(16)-C(15)-H(15B)	111.1
C(8)-C(15)-H(15B)	111.1
H(15A)-C(15)-H(15B)	109.0

C(15)-C(16)-C(12)	115.0(2)
C(15)-C(16)-C(13)	107.9(2)
C(12)-C(16)-C(13)	59.5(2)
C(15)-C(16)-H(16A)	119.8
C(12)-C(16)-H(16A)	119.8
C(13)-C(16)-H(16A)	119.8
C(4)-C(17)-H(17A)	109.5
C(4)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(4)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(1)-C(18)-O(2)	121.7(3)
O(1)-C(18)-C(4)	126.1(3)
O(2)-C(18)-C(4)	112.1(2)
C(10)-C(19)-H(19A)	109.5
C(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(10)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(13)-C(20)-H(20A)	109.5
C(13)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(13)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(2)-C(21)-H(21A)	109.5
O(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for g24fasm. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(2)	39(2)	43(1)	7(1)	2(1)	-4(1)
O(1)	56(1)	33(1)	71(1)	4(1)	8(1)	-3(1)
O(2)	38(1)	36(1)	49(1)	-3(1)	5(1)	1(1)
C(2)	35(2)	47(2)	54(2)	16(2)	9(1)	-2(1)
C(3)	42(2)	47(2)	39(1)	12(1)	6(1)	5(2)
C(4)	34(2)	35(1)	35(1)	2(1)	-3(1)	1(1)
C(5)	28(1)	29(1)	35(1)	-1(1)	-2(1)	2(1)
C(6)	29(1)	36(1)	47(2)	4(1)	-2(1)	1(1)
C(7)	32(1)	34(1)	49(2)	4(1)	-3(1)	-5(1)
C(8)	28(1)	30(1)	39(1)	2(1)	2(1)	-1(1)
C(9)	30(1)	31(1)	34(1)	0(1)	-2(1)	-2(1)
C(10)	30(1)	31(1)	34(1)	1(1)	1(1)	-3(1)
C(11)	32(2)	42(2)	47(2)	5(1)	-8(1)	-3(1)
C(12)	44(2)	45(2)	37(1)	1(1)	-7(1)	-2(1)
C(13)	41(2)	38(2)	35(1)	3(1)	1(1)	3(1)
C(14)	36(2)	33(1)	43(2)	2(1)	0(1)	-1(1)
C(15)	50(2)	33(1)	41(1)	2(1)	10(1)	4(1)
C(16)	56(2)	44(2)	29(1)	1(1)	5(1)	4(2)
C(17)	47(2)	46(2)	43(2)	-1(1)	-9(2)	6(2)
C(18)	33(1)	35(2)	39(1)	2(1)	0(1)	0(1)
C(19)	43(2)	32(1)	41(1)	-4(1)	-3(1)	-2(1)
C(20)	41(2)	44(2)	52(2)	9(1)	-1(2)	4(2)
C(21)	46(2)	43(2)	45(2)	-8(1)	0(1)	7(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for g24fasm.

	x	y	z	U(eq)
H(1A)	-1824	2156	1924	46
H(1B)	-2419	1050	1480	46
H(2A)	-806	-940	1836	54
H(2B)	-2112	-255	2258	54
H(3A)	816	-654	2589	51
H(3B)	278	1086	2618	51
H(5A)	1456	2847	1990	37
H(6A)	4499	2831	1692	45
H(6B)	3769	2132	1175	45
H(7A)	2658	4974	1587	46
H(7B)	3930	4789	1106	46
H(9A)	-678	4003	1482	38
H(11A)	-2151	2376	701	49
H(11B)	-3024	3715	1020	49
H(12A)	-2820	4518	156	51
H(14A)	-186	6283	1171	45
H(14B)	1526	6683	825	45
H(15A)	2772	4298	275	50
H(15B)	1644	2770	362	50
H(16A)	83	4594	-263	52
H(17A)	3945	271	2716	68
H(17B)	3360	1999	2670	68
H(17C)	4880	1334	2306	68
H(19A)	533	-378	1140	58
H(19B)	1794	790	847	58
H(19C)	-310	707	721	58
H(20A)	-1916	7061	-147	68
H(20B)	-296	7975	106	68
H(20C)	-2171	7802	396	68
H(21A)	6306	-1349	1099	67
H(21B)	4370	-2122	1046	67
H(21C)	5579	-2440	1532	67

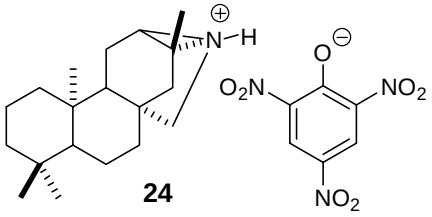
Table 6. Torsion angles [°] for g24fasm.

C(10)-C(1)-C(2)-C(3)	54.4(3)
C(1)-C(2)-C(3)-C(4)	-56.4(4)
C(2)-C(3)-C(4)-C(18)	-72.0(3)
C(2)-C(3)-C(4)-C(17)	173.9(2)
C(2)-C(3)-C(4)-C(5)	55.1(3)
C(18)-C(4)-C(5)-C(6)	-63.8(3)
C(3)-C(4)-C(5)-C(6)	173.5(2)
C(17)-C(4)-C(5)-C(6)	55.8(3)
C(18)-C(4)-C(5)-C(10)	68.9(3)
C(3)-C(4)-C(5)-C(10)	-53.9(3)
C(17)-C(4)-C(5)-C(10)	-171.5(2)
C(10)-C(5)-C(6)-C(7)	63.3(3)
C(4)-C(5)-C(6)-C(7)	-162.3(2)
C(5)-C(6)-C(7)-C(8)	-58.3(3)
C(6)-C(7)-C(8)-C(14)	167.5(2)
C(6)-C(7)-C(8)-C(9)	48.7(3)
C(6)-C(7)-C(8)-C(15)	-78.4(3)
C(7)-C(8)-C(9)-C(11)	-179.1(2)
C(14)-C(8)-C(9)-C(11)	59.6(3)
C(15)-C(8)-C(9)-C(11)	-50.2(3)
C(7)-C(8)-C(9)-C(10)	-46.4(3)
C(14)-C(8)-C(9)-C(10)	-167.7(2)
C(15)-C(8)-C(9)-C(10)	82.5(3)
C(2)-C(1)-C(10)-C(19)	70.0(3)
C(2)-C(1)-C(10)-C(5)	-51.7(3)
C(2)-C(1)-C(10)-C(9)	-166.8(2)
C(6)-C(5)-C(10)-C(19)	67.9(3)
C(4)-C(5)-C(10)-C(19)	-67.6(3)
C(6)-C(5)-C(10)-C(1)	-172.4(2)
C(4)-C(5)-C(10)-C(1)	52.1(3)
C(6)-C(5)-C(10)-C(9)	-57.8(3)
C(4)-C(5)-C(10)-C(9)	166.7(2)
C(8)-C(9)-C(10)-C(19)	-73.4(3)
C(11)-C(9)-C(10)-C(19)	57.4(3)
C(8)-C(9)-C(10)-C(1)	167.0(2)
C(11)-C(9)-C(10)-C(1)	-62.2(3)

C(8)-C(9)-C(10)-C(5)	50.8(3)
C(11)-C(9)-C(10)-C(5)	-178.5(2)
C(8)-C(9)-C(11)-C(12)	-6.9(3)
C(10)-C(9)-C(11)-C(12)	-141.1(2)
C(9)-C(11)-C(12)-C(13)	-30.8(4)
C(9)-C(11)-C(12)-C(16)	40.8(4)
C(16)-C(12)-C(13)-C(20)	113.1(3)
C(11)-C(12)-C(13)-C(20)	-138.8(3)
C(16)-C(12)-C(13)-C(14)	-95.0(3)
C(11)-C(12)-C(13)-C(14)	13.1(4)
C(11)-C(12)-C(13)-C(16)	108.1(3)
C(20)-C(13)-C(14)-C(8)	-168.7(3)
C(12)-C(13)-C(14)-C(8)	39.2(3)
C(16)-C(13)-C(14)-C(8)	-24.3(3)
C(7)-C(8)-C(14)-C(13)	161.7(2)
C(9)-C(8)-C(14)-C(13)	-77.5(3)
C(15)-C(8)-C(14)-C(13)	39.3(3)
C(7)-C(8)-C(15)-C(16)	-158.9(2)
C(14)-C(8)-C(15)-C(16)	-39.0(3)
C(9)-C(8)-C(15)-C(16)	74.5(3)
C(8)-C(15)-C(16)-C(12)	-38.8(3)
C(8)-C(15)-C(16)-C(13)	25.2(3)
C(13)-C(12)-C(16)-C(15)	96.8(3)
C(11)-C(12)-C(16)-C(15)	-15.4(4)
C(11)-C(12)-C(16)-C(13)	-112.2(3)
C(20)-C(13)-C(16)-C(15)	142.2(3)
C(12)-C(13)-C(16)-C(15)	-109.0(3)
C(14)-C(13)-C(16)-C(15)	-0.7(3)
C(20)-C(13)-C(16)-C(12)	-108.8(3)
C(14)-C(13)-C(16)-C(12)	108.4(3)
C(21)-O(2)-C(18)-O(1)	1.6(4)
C(21)-O(2)-C(18)-C(4)	177.7(2)
C(3)-C(4)-C(18)-O(1)	-9.8(4)
C(17)-C(4)-C(18)-O(1)	105.9(3)
C(5)-C(4)-C(18)-O(1)	-132.2(3)
C(3)-C(4)-C(18)-O(2)	174.3(2)
C(17)-C(4)-C(18)-O(2)	-70.0(3)
C(5)-C(4)-C(18)-O(2)	51.9(3)

Symmetry transformations used to generate equivalent atoms:

ORTEP figure and Tables of crystal data, atomic coordinates, bond angles and bond lengths, and anisotropic displacement parameters from the X-ray crystal structure determination of azatrachylobane picrate salt (24, ID code No. g61eam)



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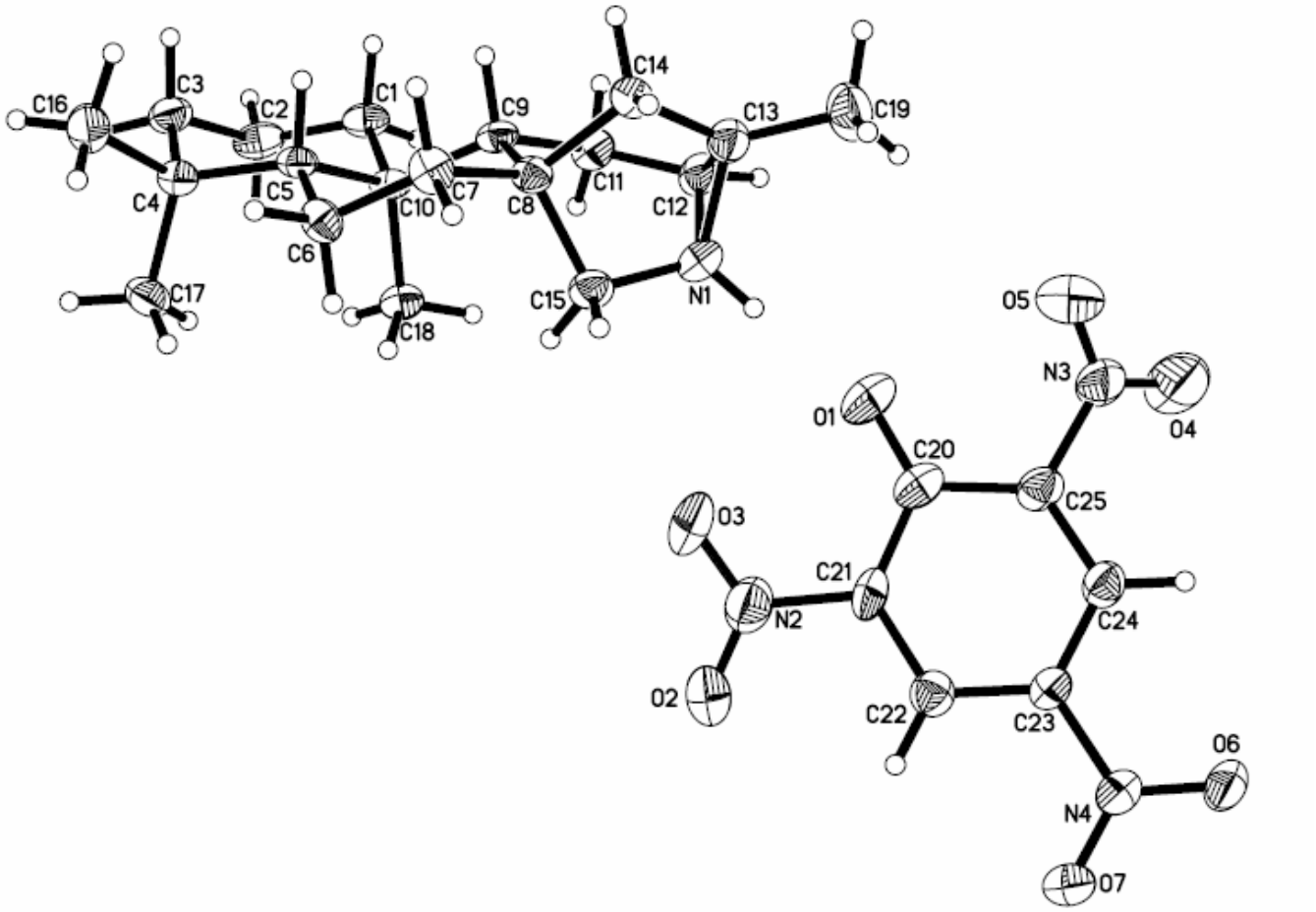

Table 1. Crystal data and structure refinement for g61eam.

Identification code	g61eam
Empirical formula	C25 H34 N4 O7
Formula weight	502.56
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21

Unit cell dimensions	a = 10.701(5) Å	α= 90°.
	b = 7.179(3) Å	β= 104.052(7)°.
	c = 16.525(8) Å	γ = 90°.
Volume	1231.5(10) $Å^3$	
Z	2	
Density (calculated)	1.355 Mg/m^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	536	
Crystal size	0.60 x 0.20 x 0.12 mm^3	
Theta range for data collection	1.96 to 25.30°.	
Index ranges	-12<=h<=12, -8<=k<=8, -19<=l<=19	
Reflections collected	9799	
Independent reflections	2444 [R(int) = 0.0577]	
Completeness to theta = 25.30°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.99021 and 0.95830	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2444 / 1 / 332	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1036	
R indices (all data)	R1 = 0.0687, wR2 = 0.1120	
Absolute structure parameter	10(10)	
Largest diff. peak and hole	0.216 and -0.183 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for g61eam. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6859(3)	6807(4)	9415(2)	64(1)
C(1)	8830(3)	4507(5)	5394(2)	38(1)
N(1)	7871(3)	7207(5)	8115(2)	44(1)
O(2)	3022(3)	6679(6)	8257(2)	86(1)
N(2)	4139(4)	7167(6)	8540(2)	66(1)
C(2)	8310(3)	3887(6)	4490(2)	46(1)
N(3)	7682(3)	7465(8)	11124(2)	69(1)
C(3)	8112(3)	5548(5)	3896(2)	43(1)
O(3)	4837(3)	7637(9)	8094(2)	115(2)
N(4)	3191(3)	7623(5)	11265(2)	47(1)
C(4)	7214(3)	7052(5)	4104(2)	37(1)
O(4)	8024(3)	6573(8)	11759(2)	117(2)
C(5)	7704(3)	7578(5)	5049(2)	32(1)
O(5)	8389(3)	8459(7)	10832(2)	97(1)
O(6)	3584(2)	7794(5)	12028(2)	65(1)
C(6)	6933(3)	9124(5)	5345(2)	37(1)
O(7)	2044(2)	7589(5)	10911(2)	64(1)
C(7)	7709(3)	9934(5)	6169(2)	39(1)
C(8)	8157(3)	8497(5)	6855(2)	33(1)
C(9)	8734(3)	6756(5)	6533(2)	32(1)
C(10)	7950(3)	5946(4)	5681(2)	30(1)
C(11)	9100(4)	5304(5)	7249(2)	41(1)
C(12)	9031(3)	6052(6)	8091(2)	44(1)
C(13)	9204(3)	8035(6)	8304(2)	44(1)
C(14)	9190(3)	9332(5)	7586(2)	40(1)
C(15)	7118(3)	7943(6)	7309(2)	39(1)
C(16)	7297(4)	8778(6)	3565(2)	51(1)
C(17)	5811(3)	6356(6)	3857(2)	47(1)
C(18)	6696(3)	4955(5)	5759(2)	37(1)
C(19)	9793(4)	8664(7)	9190(2)	62(1)
C(20)	5997(4)	7149(6)	9792(2)	47(1)
C(21)	4629(4)	7219(6)	9440(2)	44(1)
C(22)	3714(3)	7336(6)	9908(2)	44(1)

C(23)	4128(3)	7444(6)	10772(2)	39(1)
C(24)	5433(3)	7462(6)	11157(2)	45(1)
C(25)	6313(3)	7375(6)	10687(2)	45(1)

Table 3. Bond lengths [Å] and angles [°] for g61eam.

O(1)-C(20)	1.256(4)
C(1)-C(2)	1.528(5)
C(1)-C(10)	1.547(4)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
N(1)-C(15)	1.477(5)
N(1)-C(12)	1.501(5)
N(1)-C(13)	1.507(5)
N(1)-H(1)	0.87(4)
O(2)-N(2)	1.225(4)
N(2)-O(3)	1.218(5)
N(2)-C(21)	1.452(5)
C(2)-C(3)	1.527(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
N(3)-O(4)	1.207(5)
N(3)-O(5)	1.221(5)
N(3)-C(25)	1.469(5)
C(3)-C(4)	1.538(5)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
N(4)-O(7)	1.225(4)
N(4)-O(6)	1.235(4)
N(4)-C(23)	1.443(4)
C(4)-C(17)	1.540(4)
C(4)-C(16)	1.541(5)
C(4)-C(5)	1.569(5)
C(5)-C(6)	1.532(5)
C(5)-C(10)	1.549(5)
C(5)-H(5A)	1.0000
C(6)-C(7)	1.528(5)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.522(5)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900

C(8)-C(15)	1.536(5)
C(8)-C(9)	1.545(5)
C(8)-C(14)	1.546(5)
C(9)-C(11)	1.553(5)
C(9)-C(10)	1.566(5)
C(9)-H(9A)	1.0000
C(10)-C(18)	1.552(4)
C(11)-C(12)	1.511(5)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.467(6)
C(12)-H(12A)	1.0000
C(13)-C(14)	1.505(5)
C(13)-C(19)	1.516(5)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.439(5)
C(20)-C(25)	1.443(5)
C(21)-C(22)	1.390(5)
C(22)-C(23)	1.390(4)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.387(5)
C(24)-C(25)	1.360(4)
C(24)-H(24A)	0.9500

C(2)-C(1)-C(10)	112.9(3)
C(2)-C(1)-H(1A)	109.0
C(10)-C(1)-H(1A)	109.0
C(2)-C(1)-H(1B)	109.0
C(10)-C(1)-H(1B)	109.0
H(1A)-C(1)-H(1B)	107.8
C(15)-N(1)-C(12)	116.6(3)
C(15)-N(1)-C(13)	109.1(3)
C(12)-N(1)-C(13)	58.4(2)
C(15)-N(1)-H(1)	120(3)
C(12)-N(1)-H(1)	120(3)
C(13)-N(1)-H(1)	117(3)
O(3)-N(2)-O(2)	122.2(4)
O(3)-N(2)-C(21)	119.4(4)
O(2)-N(2)-C(21)	118.4(3)
C(3)-C(2)-C(1)	111.2(3)
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2B)	109.4
C(1)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
O(4)-N(3)-O(5)	124.5(4)
O(4)-N(3)-C(25)	117.4(4)
O(5)-N(3)-C(25)	118.1(4)
C(2)-C(3)-C(4)	113.6(3)
C(2)-C(3)-H(3A)	108.8
C(4)-C(3)-H(3A)	108.8
C(2)-C(3)-H(3B)	108.8
C(4)-C(3)-H(3B)	108.8
H(3A)-C(3)-H(3B)	107.7
O(7)-N(4)-O(6)	122.9(3)
O(7)-N(4)-C(23)	118.7(3)
O(6)-N(4)-C(23)	118.4(3)
C(3)-C(4)-C(17)	109.6(3)
C(3)-C(4)-C(16)	108.0(3)
C(17)-C(4)-C(16)	107.3(3)
C(3)-C(4)-C(5)	108.4(3)

C(17)-C(4)-C(5)	114.2(3)
C(16)-C(4)-C(5)	109.2(3)
C(6)-C(5)-C(10)	110.5(2)
C(6)-C(5)-C(4)	114.6(3)
C(10)-C(5)-C(4)	116.7(3)
C(6)-C(5)-H(5A)	104.5
C(10)-C(5)-H(5A)	104.5
C(4)-C(5)-H(5A)	104.5
C(7)-C(6)-C(5)	110.0(3)
C(7)-C(6)-H(6A)	109.7
C(5)-C(6)-H(6A)	109.7
C(7)-C(6)-H(6B)	109.7
C(5)-C(6)-H(6B)	109.7
H(6A)-C(6)-H(6B)	108.2
C(8)-C(7)-C(6)	114.3(3)
C(8)-C(7)-H(7A)	108.7
C(6)-C(7)-H(7A)	108.7
C(8)-C(7)-H(7B)	108.7
C(6)-C(7)-H(7B)	108.7
H(7A)-C(7)-H(7B)	107.6
C(7)-C(8)-C(15)	113.9(3)
C(7)-C(8)-C(9)	111.8(3)
C(15)-C(8)-C(9)	110.8(3)
C(7)-C(8)-C(14)	110.8(3)
C(15)-C(8)-C(14)	100.6(3)
C(9)-C(8)-C(14)	108.2(3)
C(8)-C(9)-C(11)	109.2(3)
C(8)-C(9)-C(10)	116.0(3)
C(11)-C(9)-C(10)	114.6(3)
C(8)-C(9)-H(9A)	105.3
C(11)-C(9)-H(9A)	105.3
C(10)-C(9)-H(9A)	105.3
C(1)-C(10)-C(5)	108.4(3)
C(1)-C(10)-C(18)	108.8(3)
C(5)-C(10)-C(18)	113.2(3)
C(1)-C(10)-C(9)	106.9(2)
C(5)-C(10)-C(9)	106.9(3)
C(18)-C(10)-C(9)	112.3(3)

C(12)-C(11)-C(9)	113.8(3)
C(12)-C(11)-H(11A)	108.8
C(9)-C(11)-H(11A)	108.8
C(12)-C(11)-H(11B)	108.8
C(9)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
C(13)-C(12)-N(1)	61.0(2)
C(13)-C(12)-C(11)	122.3(3)
N(1)-C(12)-C(11)	116.5(3)
C(13)-C(12)-H(12A)	115.3
N(1)-C(12)-H(12A)	115.3
C(11)-C(12)-H(12A)	115.3
C(12)-C(13)-C(14)	115.8(3)
C(12)-C(13)-N(1)	60.6(3)
C(14)-C(13)-N(1)	104.6(3)
C(12)-C(13)-C(19)	121.3(4)
C(14)-C(13)-C(19)	120.0(4)
N(1)-C(13)-C(19)	117.9(3)
C(13)-C(14)-C(8)	104.2(3)
C(13)-C(14)-H(14A)	110.9
C(8)-C(14)-H(14A)	110.9
C(13)-C(14)-H(14B)	110.9
C(8)-C(14)-H(14B)	110.9
H(14A)-C(14)-H(14B)	108.9
N(1)-C(15)-C(8)	103.4(3)
N(1)-C(15)-H(15A)	111.1
C(8)-C(15)-H(15A)	111.1
N(1)-C(15)-H(15B)	111.1
C(8)-C(15)-H(15B)	111.1
H(15A)-C(15)-H(15B)	109.0
C(4)-C(16)-H(16A)	109.5
C(4)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(4)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(4)-C(17)-H(17A)	109.5
C(4)-C(17)-H(17B)	109.5

H(17A)-C(17)-H(17B)	109.5
C(4)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(10)-C(18)-H(18A)	109.5
C(10)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(10)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(13)-C(19)-H(19A)	109.5
C(13)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(13)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(1)-C(20)-C(21)	127.1(4)
O(1)-C(20)-C(25)	120.8(3)
C(21)-C(20)-C(25)	111.9(3)
C(22)-C(21)-C(20)	124.2(3)
C(22)-C(21)-N(2)	116.3(3)
C(20)-C(21)-N(2)	119.5(3)
C(21)-C(22)-C(23)	118.9(3)
C(21)-C(22)-H(22A)	120.6
C(23)-C(22)-H(22A)	120.6
C(24)-C(23)-C(22)	120.4(3)
C(24)-C(23)-N(4)	120.0(3)
C(22)-C(23)-N(4)	119.6(3)
C(25)-C(24)-C(23)	119.8(3)
C(25)-C(24)-H(24A)	120.1
C(23)-C(24)-H(24A)	120.1
C(24)-C(25)-C(20)	124.6(3)
C(24)-C(25)-N(3)	117.5(3)
C(20)-C(25)-N(3)	117.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for g61eam. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	70(2)	68(2)	66(2)	-5(2)	42(2)	4(2)
C(1)	31(2)	29(2)	57(2)	1(2)	16(2)	2(2)
N(1)	46(2)	46(2)	45(2)	3(2)	23(1)	0(2)
O(2)	75(2)	133(3)	44(2)	-7(2)	6(2)	-12(2)
N(2)	73(2)	76(3)	50(2)	-10(2)	22(2)	-13(2)
C(2)	39(2)	39(2)	68(3)	-6(2)	28(2)	5(2)
N(3)	44(2)	113(4)	54(2)	-1(3)	18(2)	22(2)
C(3)	36(2)	50(2)	46(2)	-3(2)	18(2)	-3(2)
O(3)	100(2)	212(5)	43(2)	1(3)	32(2)	-34(3)
N(4)	47(2)	54(2)	44(2)	-1(2)	19(2)	1(2)
C(4)	31(2)	42(2)	38(2)	-1(2)	8(2)	-5(2)
O(4)	65(2)	209(5)	76(2)	46(3)	19(2)	64(3)
C(5)	23(2)	32(2)	41(2)	4(2)	8(1)	-4(2)
O(5)	51(2)	142(4)	100(3)	-7(3)	23(2)	-9(2)
O(6)	57(2)	106(3)	36(2)	4(2)	17(1)	18(2)
C(6)	37(2)	31(2)	39(2)	3(2)	3(2)	4(2)
O(7)	40(2)	95(2)	61(2)	-13(2)	19(1)	-7(2)
C(7)	43(2)	28(2)	43(2)	1(2)	7(2)	5(2)
C(8)	31(2)	29(2)	38(2)	4(2)	8(1)	-3(2)
C(9)	25(2)	31(2)	43(2)	8(2)	13(2)	4(1)
C(10)	22(2)	25(2)	43(2)	3(2)	11(1)	1(1)
C(11)	43(2)	36(2)	45(2)	9(2)	15(2)	8(2)
C(12)	43(2)	52(3)	38(2)	16(2)	12(2)	8(2)
C(13)	41(2)	52(3)	38(2)	6(2)	11(2)	5(2)
C(14)	35(2)	44(2)	40(2)	1(2)	6(2)	-3(2)
C(15)	34(2)	43(2)	44(2)	-2(2)	14(2)	4(2)
C(16)	52(2)	57(3)	41(2)	4(2)	6(2)	-6(2)
C(17)	33(2)	60(3)	46(2)	-8(2)	3(2)	-4(2)
C(18)	35(2)	30(2)	48(2)	0(2)	15(2)	0(2)
C(19)	61(3)	74(3)	44(2)	3(2)	1(2)	10(2)
C(20)	54(2)	40(2)	55(2)	-1(2)	28(2)	2(2)
C(21)	65(2)	40(2)	29(2)	-7(2)	18(2)	-6(2)
C(22)	46(2)	42(2)	43(2)	-2(2)	12(2)	-2(2)

C(23)	42(2)	40(2)	37(2)	1(2)	16(2)	4(2)
C(24)	47(2)	50(2)	38(2)	3(2)	12(2)	11(2)
C(25)	43(2)	47(2)	48(2)	0(2)	18(2)	11(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for g61eam.

	x	y	z	U(eq)
H(1A)	9696	5059	5455	46
H(1B)	8924	3402	5762	46
H(1)	7510(40)	7090(70)	8530(30)	65
H(2A)	8922	3003	4336	55
H(2B)	7479	3233	4437	55
H(3A)	7749	5097	3321	51
H(3B)	8960	6118	3912	51
H(5A)	8574	8136	5094	38
H(6A)	6733	10120	4918	44
H(6B)	6109	8614	5420	44
H(7A)	8474	10582	6068	46
H(7B)	7175	10875	6366	46
H(9A)	9571	7179	6429	39
H(11A)	8514	4222	7110	49
H(11B)	9987	4858	7283	49
H(12A)	9320	5171	8569	53
H(14A)	10042	9364	7452	48
H(14B)	8953	10611	7716	48
H(15A)	6599	9036	7392	47
H(15B)	6538	6978	6993	47
H(16A)	7221	8391	2986	76
H(16B)	8127	9401	3778	76
H(16C)	6596	9639	3587	76
H(17A)	5508	6342	3248	71
H(17B)	5266	7190	4092	71
H(17C)	5767	5094	4075	71
H(18A)	6005	5875	5708	55
H(18B)	6844	4339	6304	55
H(18C)	6448	4024	5316	55
H(19A)	9616	7734	9582	93
H(19B)	9418	9862	9290	93
H(19C)	10727	8803	9271	93

H(22A)	2821	7342	9642	52
H(24A)	5711	7535	11748	53

Table 6. Torsion angles [°] for g61eam.

C(10)-C(1)-C(2)-C(3)	57.2(4)
C(1)-C(2)-C(3)-C(4)	-56.7(4)
C(2)-C(3)-C(4)-C(17)	-73.6(4)
C(2)-C(3)-C(4)-C(16)	169.9(3)
C(2)-C(3)-C(4)-C(5)	51.6(4)
C(3)-C(4)-C(5)-C(6)	177.8(3)
C(17)-C(4)-C(5)-C(6)	-59.8(4)
C(16)-C(4)-C(5)-C(6)	60.4(4)
C(3)-C(4)-C(5)-C(10)	-50.8(3)
C(17)-C(4)-C(5)-C(10)	71.7(4)
C(16)-C(4)-C(5)-C(10)	-168.2(3)
C(10)-C(5)-C(6)-C(7)	63.0(4)
C(4)-C(5)-C(6)-C(7)	-162.6(3)
C(5)-C(6)-C(7)-C(8)	-55.0(4)
C(6)-C(7)-C(8)-C(15)	-81.0(4)
C(6)-C(7)-C(8)-C(9)	45.6(4)
C(6)-C(7)-C(8)-C(14)	166.5(3)
C(7)-C(8)-C(9)-C(11)	-176.9(3)
C(15)-C(8)-C(9)-C(11)	-48.6(4)
C(14)-C(8)-C(9)-C(11)	60.8(3)
C(7)-C(8)-C(9)-C(10)	-45.5(4)
C(15)-C(8)-C(9)-C(10)	82.7(3)
C(14)-C(8)-C(9)-C(10)	-167.9(3)
C(2)-C(1)-C(10)-C(5)	-53.3(4)
C(2)-C(1)-C(10)-C(18)	70.3(4)
C(2)-C(1)-C(10)-C(9)	-168.2(3)
C(6)-C(5)-C(10)-C(1)	-175.1(3)
C(4)-C(5)-C(10)-C(1)	51.6(3)
C(6)-C(5)-C(10)-C(18)	64.1(3)
C(4)-C(5)-C(10)-C(18)	-69.2(3)
C(6)-C(5)-C(10)-C(9)	-60.2(3)
C(4)-C(5)-C(10)-C(9)	166.5(2)
C(8)-C(9)-C(10)-C(1)	168.3(3)
C(11)-C(9)-C(10)-C(1)	-63.0(3)
C(8)-C(9)-C(10)-C(5)	52.4(3)
C(11)-C(9)-C(10)-C(5)	-178.9(3)

C(8)-C(9)-C(10)-C(18)	-72.4(3)
C(11)-C(9)-C(10)-C(18)	56.3(4)
C(8)-C(9)-C(11)-C(12)	-10.1(4)
C(10)-C(9)-C(11)-C(12)	-142.2(3)
C(15)-N(1)-C(12)-C(13)	97.0(3)
C(15)-N(1)-C(12)-C(11)	-17.0(5)
C(13)-N(1)-C(12)-C(11)	-114.0(4)
C(9)-C(11)-C(12)-C(13)	-26.9(5)
C(9)-C(11)-C(12)-N(1)	44.1(4)
N(1)-C(12)-C(13)-C(14)	-92.9(3)
C(11)-C(12)-C(13)-C(14)	11.8(5)
C(11)-C(12)-C(13)-N(1)	104.7(4)
N(1)-C(12)-C(13)-C(19)	106.7(4)
C(11)-C(12)-C(13)-C(19)	-148.7(3)
C(15)-N(1)-C(13)-C(12)	-110.0(3)
C(15)-N(1)-C(13)-C(14)	1.6(4)
C(12)-N(1)-C(13)-C(14)	111.6(3)
C(15)-N(1)-C(13)-C(19)	137.9(4)
C(12)-N(1)-C(13)-C(19)	-112.1(4)
C(12)-C(13)-C(14)-C(8)	37.3(4)
N(1)-C(13)-C(14)-C(8)	-26.7(4)
C(19)-C(13)-C(14)-C(8)	-161.9(3)
C(7)-C(8)-C(14)-C(13)	161.8(3)
C(15)-C(8)-C(14)-C(13)	41.0(3)
C(9)-C(8)-C(14)-C(13)	-75.3(3)
C(12)-N(1)-C(15)-C(8)	-39.2(4)
C(13)-N(1)-C(15)-C(8)	24.3(4)
C(7)-C(8)-C(15)-N(1)	-158.0(3)
C(9)-C(8)-C(15)-N(1)	74.9(3)
C(14)-C(8)-C(15)-N(1)	-39.4(3)
O(1)-C(20)-C(21)-C(22)	170.2(4)
C(25)-C(20)-C(21)-C(22)	-4.9(6)
O(1)-C(20)-C(21)-N(2)	-9.8(7)
C(25)-C(20)-C(21)-N(2)	175.0(4)
O(3)-N(2)-C(21)-C(22)	157.4(5)
O(2)-N(2)-C(21)-C(22)	-21.3(6)
O(3)-N(2)-C(21)-C(20)	-22.5(7)
O(2)-N(2)-C(21)-C(20)	158.7(4)

C(20)-C(21)-C(22)-C(23)	1.8(6)
N(2)-C(21)-C(22)-C(23)	-178.2(4)
C(21)-C(22)-C(23)-C(24)	0.9(6)
C(21)-C(22)-C(23)-N(4)	178.2(4)
O(7)-N(4)-C(23)-C(24)	-179.5(4)
O(6)-N(4)-C(23)-C(24)	0.2(6)
O(7)-N(4)-C(23)-C(22)	3.3(6)
O(6)-N(4)-C(23)-C(22)	-177.1(4)
C(22)-C(23)-C(24)-C(25)	0.1(6)
N(4)-C(23)-C(24)-C(25)	-177.2(4)
C(23)-C(24)-C(25)-C(20)	-3.9(7)
C(23)-C(24)-C(25)-N(3)	177.9(4)
O(1)-C(20)-C(25)-C(24)	-169.5(4)
C(21)-C(20)-C(25)-C(24)	6.0(6)
O(1)-C(20)-C(25)-N(3)	8.7(6)
C(21)-C(20)-C(25)-N(3)	-175.8(4)
O(4)-N(3)-C(25)-C(24)	42.7(7)
O(5)-N(3)-C(25)-C(24)	-136.0(4)
O(4)-N(3)-C(25)-C(20)	-135.6(5)
O(5)-N(3)-C(25)-C(20)	45.7(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for g61eam [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)	0.87(4)	1.78(4)	2.646(4)	177(4)

Symmetry transformations used to generate equivalent atoms: