# Supporting Information:

## "Formal Synthesis of (+)-3-Deoxy-D-*glycero*-D-*galacto*-2-nonulosonic Acid (KDN) via Desymmetrization by Ring-Closing Metathesis"

Steven D. Burke* and Eric A. Voight

*Department of Chemistry, University of Wisconsin-Madison,*

*1101 University Avenue, Madison, WI 53706-1396*

*To whom all correspondence should be sent. Phone: (608) 262-4941. Fax: (608) 265-4534. E-mail: burke@chem.wisc.edu.

## General Procedures

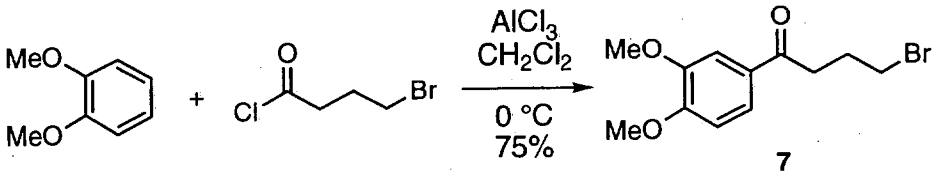
Optical rotations were measured on a Perkin-Elmer 241 digital polarimeter. Concentrations (c) are reported in g/100 mL. Infrared spectra (IR) were obtained on a Matteson Polaris FT-IR equipped with a DTGS detector. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker AC-300 (300 MHz). Proton NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sex), septet (sept), ab quartet (ABq), multiplet (m), apparent (app), and broad (br). Spectra were interpreted assuming first-order behavior, and coupling constants were rounded to the nearest 0.5 hertz (Hz). All expansions were calibrated to 10 Hz/cm. Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on a Bruker AC-300 (75 MHz). Carbon resonances were assigned using Distortionless Enhancement by Polarization Transfer (DEPT) spectra obtained with a phase angle of 90°: (C) not observed, (CH) positive, ($CH_2$) suppressed, ($CH_3$) suppressed or not observed; and with a phase angle of 135°: (C) not observed; (CH) positive; ($CH_2$) negative; ($CH_3$) positive. High resolution mass spectra (HRMS) using electron impact (EI, 70 eV) were recorded on a Kratos MS-80RFA mass spectrometer (DS-55/DS-90 peak matching option). High resolution fast atom bombardment

(FAB) mass spectra were obtained on VG Analytical ZAB-2F (Ion Tech FAB gun, 8 kV, Xe carrier gas).

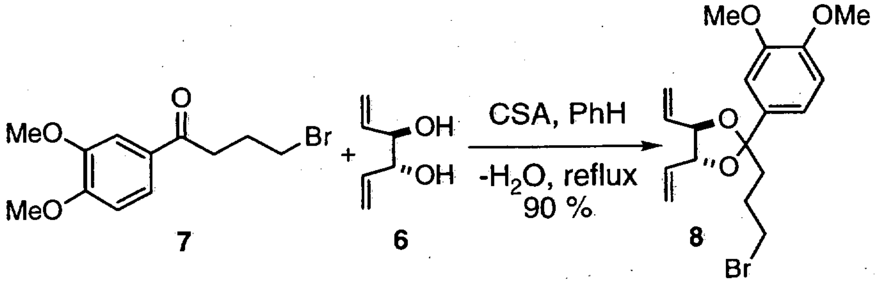
All moisture-sensitive reactions were performed in flame-dried and/or oven dried glassware under a positive pressure of nitrogen unless otherwise noted. "Concentrated" refers to the removal of volatile solvents via distillation using a Buchi rotary evaporator at water aspirator pressure, followed by residual solvent removal at high vacuum when necessary. "Dried" refers to pouring onto, or passing through, anhydrous sodium or magnesium sulfate followed by filtration.

Analytical thin layer chromatography (TLC) was carried out on E. Merck (Darmstadt) TLC plates precoated with silia gel 60 $F_{254}$ (0.25 mm layer thickness). Visualization was accomplished using UV light and/or a *p*-anisaldehyde (PAA) charring solution. Flash column chromatography (FCC) was performed on EM Science silica gel 60 (230-400 mesh). Solvent mixtures for TLC and FCC are reported in either $v_1$:$v_2$ ratios or $V_1/V_{total}$ x 100%. For columns using MeOH-containing eluents, the column was slurry packed in MeOH, washed with 2 column volumes (c.v.) of the same, then 2 c.v. of the first eluent.

Immediately prior to use, toluene ($PhCH_3$) was distilled from sodium naphthalide; benzene (PhH) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl; methanol (MeOH) was distilled from magnesium methoxide; and dichloromethane ($CH_2Cl_2$), hexanes, and triethylamine ($Et_3N$) were distilled from calcium hydride. *Para*-toluenesulfonyl chloride (TsCl) was dissolved in ether ($Et_2O$), washed with 10% sodium hydroxide (NaOH) until clear, dried ($MgSO_4$), and recrystallized ($Et_2O$). Aluminum trichloride ($AlCl_3$) potassium *tert*-butoxide (KO*t*Bu), 18-crown-6 (18-c-6), Grubbs' catalyst, and cesium acetate (CsOAc) were stored, weighed, and sealed from atmospheric moisture in a dry box prior to use. All other reagents were used as supplied, assuming reagent purity designated by supplier.



**Preparation of Compound 7.**[1] Veratrole (9.93 mL, 77.1 mmol) was dissolved in $CH_2Cl_2$ (100 mL), cooled to 0 °C, and $AlCl_3$ (18.6 g, 140 mmol) was added in portions over 10 min with vigorous stirring. After 5 min, 4-bromobutyryl chloride (13.68 g, 70.1 mmol) in $CH_2Cl_2$ (75 mL) was added dropwise via addition funnel. The resulting light yellow solution was stirred at 0 °C for 3 h, poured into concentrated hydrochloric acid (50 mL) and ice (50 g), and the reaction flask rinsed with $CH_2Cl_2$ (4 x 10 mL). The organic layer was separated, the aqueous layer washed with $CH_2Cl_2$ (2 x 150 mL), and the combined organics dried ($MgSO_4$) and concentrated to 50 mL. The resulting light yellow solution was poured into a 250 mL erlenmeyer, rinsing with $Et_2O$ (5 x 10 mL). The solution was swirled to mix solvents thoroughly, and recrystallization gave pure **7** (15.04 g, 75%) as white needles which were used without prolonged storage or exposure to light for extended periods of time. $^1H$ NMR ($CDCl_3$) δ 7.63 (dd, J = 8.5, 2 Hz, 1H), 7.54 (d, J = 2 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 3.56 (t, J = 6.5 Hz, 2H), 3.15 (t, J = 6.5 Hz, 2H), 2.31 (quint, J = 6.5 Hz, 2H).



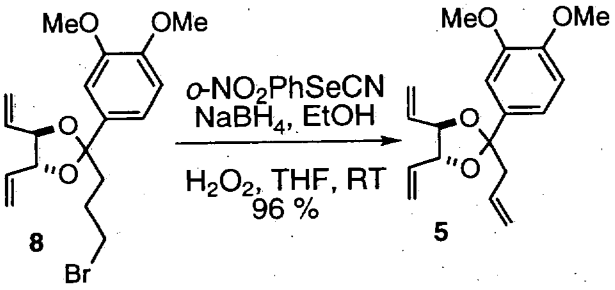
**Preparation of Compound 8.** Ketone **7** (15.04 g, 52.4 mmol) was dissolved in PhH (50 mL), (*R,R*)-1,5-hexadiene-3,4-diol (2.99 g, 26.2 mmol),[2] and camphorsulfonic acid (608 mg, 2.62 mmol) were added, and a Dean-Stark trap was attached. After refluxing 12 h with

---

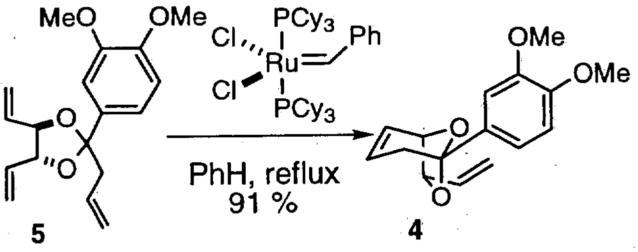
(1) A modification of the procedure found in: Koβmehl, G.; Fohberg. H.-C. *Chem. Ber.* **1986**, *119*, 50-64. Full spectral information for **8** is provided therein.

(2) Prepared as described previously: Burke, S. D.; Sametz, G. M. *Org. Lett.* **1999**, *1*, 71-74.

azeotropic removal of water, the reaction mixture was poured into saturated aqueous sodium bicarbonate (50 mL), and the organic layer separated. The aqueous phase was extracted with $CH_2Cl_2$ (4 x 50 mL), the combined organics dried ($MgSO_4$), concentrated, and FCC (15% $Et_2O$/Hexanes) gave pure **8** (9.06 g, 90%) as a clear oil. $^1H$ NMR ($CDCl_3$) δ 7.07 (dd, J = 8.5, 2 Hz, 1H), 7.03 (d, J = 2 Hz, 1H), 6.84 (d, J = 8.5 Hz, 1H), 5.87 (ddd, J = 17.5, 10, 7 Hz, 1H), 5.67 (ddd, J = 17.5, 10, 7.5 Hz, 1H), 5.34 (J = 17.5, 1.5, 1 Hz, 1H), 5.31 (ddd, J = 17.5, 1.5, 1 Hz, 1H), 5.29 (ddd, J = 10, 1.5, 1 Hz, 1H), 5.20 (ddd, J = 10, 1.5, 1 Hz, 1H), 4.14 (ddt, J = 8, 7.5, 1 Hz, 1H), 3.96 (ddt, J = 8, 7, 1 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.3-3.5 (m, 2H), 1.8-2.1 (m, 4H); $^{13}C$ NMR ($CDCl_3$) δ 148.6 (C x 2), 136.1 (C), 134.4 (CH), 133.0 (CH), 119.4 ($CH_2$), 119.1 ($CH_2$), 117.7 (CH), 110.5 (CH), 110.3 (C), 108.8 (CH), 83.9 (CH), 81.8 (CH), 55.9 ($CH_3$), 55.8 ($CH_3$), 40.0 ($CH_2$), 33.8 ($CH_2$), 27.2 ($CH_2$); IR (thin film) 3082, 2999, 2956, 2935, 2834, 1516, 1464, 1409, 1264, 1020 cm$^{-1}$; $[\alpha]^{24}_D$ −20° (c = 1.4, $CHCl_3$); HRMS (FAB) calcd. for $C_{18}H_{23}O_4BrNa$ (M+Na$^+$) 405.0677, found 405.0681.

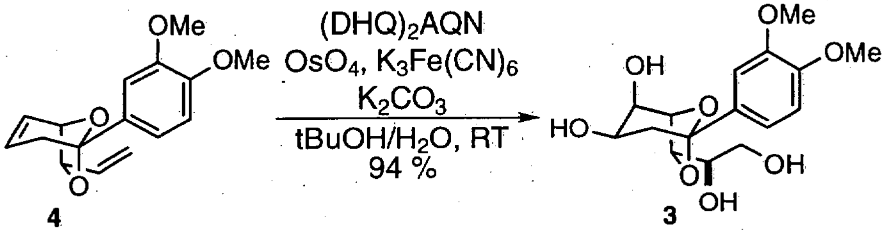


**Preparation of Compound 5.** To a solution of *ortho*-nitrophenylselenocyanate (127 mg, 0.550 mmol) in ethanol (4 mL) was added sodium borohydride (23 mg, 0.60 mmol) slowly at 0 °C. After stirring 15 min, ketal **8** (192 mg, 0.500 mmol) was added in ethanol (2 mL) over 20 min. After stirring overnight at RT, additional *ortho*-nitrophenylselenocyanate (5 mg, 0.02 mmol) and sodium borohydride (2 mg, 0.05 mmol) were added, and the reaction stirred an additional 3 h. The reaction was poured into water (10 mL), extracted with $CH_2Cl_2$ (3 x 10 mL), dried ($MgSO_4$), concentrated, and dissolved in THF (6 mL). The solution was cooled to 0 °C and hydrogen peroxide (30% in water, 0.07 mL, 0.6 mmol) was added slowly over 15 min. After stirring at RT overnight, the reaction was diluted with $CH_2Cl_2$ (20 mL), the organic layer washed with water (20 mL), and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 20 mL), dried ($MgSO_4$), and concentrated. Purification by FCC (20-50% $CH_2Cl_2$/Hexanes, gradient elution) gave pure **5** (145 mg, 96%) as a slightly yellow oil. $^1H$ NMR ($CDCl_3$) δ 7.08 (dd, J = 8, 2 Hz, 1H), 7.04 (d, J = 2 Hz, 1H), 6.84 (d, J = 8 Hz, 1H), 5.88 (ddd, J = 17.5, 10.5, 7 Hz, 1H), 5.83 (ddt, J = 18, 9.5, 7 Hz, 1H), 5.68 (ddd, J = 18, 10, 7.5 Hz, 1H), 5.34 (ddd, J = 17.5, 1.5, 1 Hz, 1H), 5.31 (ddd, J = 17, 2, 1 Hz, 1H), 5.29 (ddd, J = 10, 1.5, 1 Hz, 1H), 5.20 (ddd, J = 10.5, 2, 1 Hz, 1H), 5.0-5.13 (m, 2H), 4.17 (ddt, J = 8, 7.5, 1 Hz, 1H), 3.96 (ddt, J = 8, 7, 1 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.68 (ABqdt, J = 14, 7, 1.5 Hz, 2H); $^{13}C$ ($CDCl_3$) δ 148.5 (C), 148.4 (C), 136.3 (C), 134.4 (CH), 133.2 (CH), 132.4 (CH), 119.4 ($CH_2$), 119.1 ($CH_2$), 118.4 ($CH_2$), 117.9 (CH), 110.4 (CH), 110.1 (C), 109.0 (CH), 84.0 (CH), 81.9 (CH), 55.9 ($CH_3$), 55.8 ($CH_3$), 46.1 ($CH_2$); IR (thin film) 3079, 2997, 2931, 2849, 1506, 1264, 1030 $cm^{-1}$; $[\alpha]^{24}_D$ −22° (c = 0.58, $CHCl_3$); HRMS (EI) calcd. for $C_{15}H_{17}O_4$ (M-allyl$^+$) 261.1127, found 261.1136.

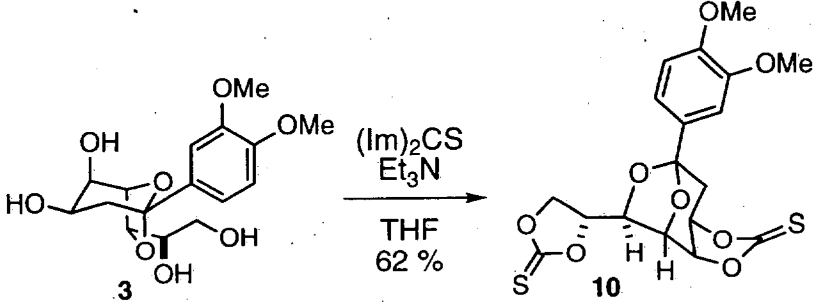


**Preparation of Compound 4.** Triene **5** (400 mg, 1.32 mmol) was dissolved in PhH (130 mL) and the clear solution stirred and brought to reflux. Grubbs' catalyst (23 mg, 0.027 mmol) was added via syringe pump in PhH (15 mL) over 1.5 h, and the reaction was cooled to RT. Air was blown into the reaction flask for 2 d, and the resulting dark brown solution was poured through a pad of silica gel. The pad was washed with $CH_2Cl_2$ (500 mL), combined organics concentrated, and FCC (25% $Et_2O$/Hexanes) gave pure **4** (330 mg, 91%) as an oil with light brown discoloration that did not appear as an impurity in any spectra. $^1H$ NMR ($CDCl_3$) δ 7.14-7.2 (m, 2H), 6.8-6.9 (m, 1H), 6.17 (ddt, J = 10, 4.5, 2 Hz, 1H), 5.86

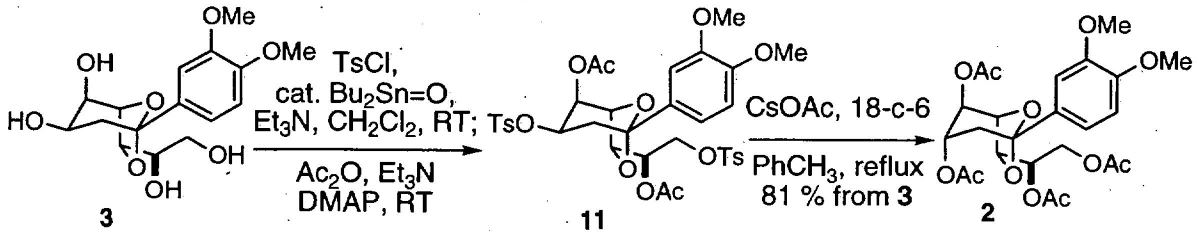
(ddd, J = 17, 10, 7 Hz, 1H), 5.85 (ddd, J = 10, 4, 2.5 Hz, 1H), 5.19 (ddd, J = 17, 2, 1.5 Hz, 1H), 5.09 (ddd, J = 10, 2, 1), 4.66 (ddd, J = 7, 1.5, 1 Hz, 1H), 4.56 (d, J = 4.5 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.73 (ddd, J = 18, 2.5, 2 Hz, 1H), 2.47 (ddd, J = 18, 4, 2 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 148.9 (C), 148.6 (C), 137.5 (CH), 133.6 (C), 128.1 (CH), 125.8 (CH), 117.4 (CH), 116.6 ($CH_2$), 110.6 (CH), 108.4 (CH), 107.5 (C), 86.2 (CH), 77.1 (CH), 55.84 ($CH_3$), 55.81 ($CH_3$), 39.4 ($CH_2$); IR (thin film) 3039, 2998, 2934, 2836, 1519, 1269, 1028 $cm^{-1}$; $[\alpha]^{24}_D$ +97° (c = 2.6, $CHCl_3$); HRMS (FAB) calcd. for $C_{16}H_{18}O_4Na$ ($M+Na^+$) 297.1103, found 297.1089.



**Preparation of Compound 3.** Diene **4** (1.94 g, 7.07 mmol) was dissolved in *tert*-butanol (35 mL) and $(DHQ)_2AQN$ (320 mg, 0.354 mmol) was added. While stirring vigorously, water (35 mL), potassium carbonate (5.86 g, 42.4 mmol), and potassium ferricyanide (14.0 g, 42.4 mmol) were added, and the resulting yellow-orange biphasic mixture cooled to 0 °C. Osmium tetroxide (2.5 wt.% solution in *tert*-butanol, 0.93 mL, 0.071 mmol) was then added and the reaction stirred vigorously at 0 °C for 31 h. Anhydrous sodium sulfite (21 g) was then added, reaction warmed to RT and stirred 30 min, water (50 mL) and ethyl acetate (150 mL) were added, and the aqueous layer was extracted with ethyl acetate (7 x 150 mL). The combined organics were dried ($MgSO_4$), concentrated, and FCC (10-15% MeOH/EtOAc, gradient elution) gave **3** contaminated with coeluting $(DHQ)_2AQN$ ligand. Recrystallization from ethyl acetate gave, after 3 crops of crystals, pure **3** (2.28 g, 94%) as white pellets. $^1$H NMR ($CD_3OD$) δ 7.06 (d, J = 2 Hz, 1H), 7.01 (dd, J = 8.5, 2 Hz, 1H), 6.83 (d, J = 8.5 Hz, 1H), 4.61 (dd, J = 2.5, 0.5 Hz, 1H), 3.98 (ddd, J = 11, 6.5, 4 Hz, 1H), 3.77 (dd, J = 9, 0.5 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.70 (dd, J = 4, 2.5 Hz, 1H), 3.65 (dd, J = 11.5, 3 Hz, 1H), 3.49 (dd, J = 11.5, 5.5 Hz, 1H), 3.29 (ddd, J = 9, 5.5, 3 Hz, 1H), 2.11 (dd, J = 13, 6.5 Hz, 1H), 1.94 (dd, J = 13, 11 Hz, 1H); $^{13}$C NMR ($CD_3OD$) δ 150.6 (C), 150.0 (C), 134.5 (C), 119.1 (CH), 112.4 (CH), 110.6 (CH), 109.2 (C), 81.2 (CH), 77.9 (CH), 73.3 (CH), 69.8 (CH), 66.0 (CH), 64.2 ($CH_2$), 56.5 ($CH_3$ x 2), 42.4 ($CH_2$); IR (thin film) 3362, 3002, 2934, 2836, 1519, 1263, 1025 $cm^{-1}$; $[\alpha]^{24}_D$ +43° (c = 0.85, MeOH); mp 138-139 °C; HRMS (FAB) calcd. for $C_{16}H_{22}O_8Na$ (M+$Na^+$) 365.1212, found 365.1229.

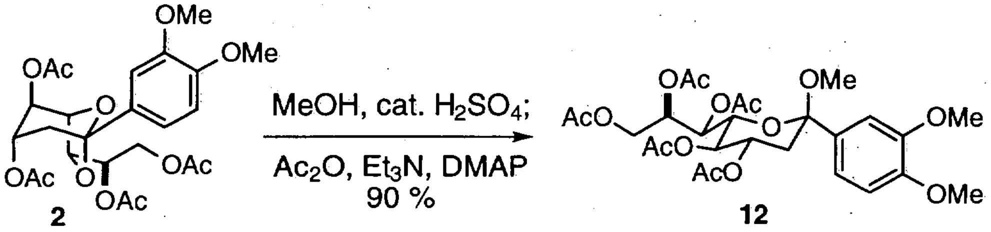


**Preparation of Compound 10.** To a suspension of tetraol **3** (60.5 mg, 0.177 mmol) in THF (2 ml) was added thiocarbonyl diimidazole (175 mg, 0.884 mmol) and $Et_3N$ (0.25 mL, 1.8 mmol). After stirring at RT for 20 h, the reaction mixture was concentrated and FCC ($Et_2O$) gave **2** which was recrystallized from acetone/MeOH to provide pure **2** (46.7 mg, 62%) as clear plates suitable for X-ray crystallographic analysis. $^1$NMR (Acetone-$d_6$) δ 7.14 (d, J = 2 Hz, 1H), 7.07 (dd, J = 8.5, 2 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 5.60 (td, J = 8, 4.5 Hz, 1H), 5.36 (ddd, J = 8.5, 5.5, 3.5 Hz, 1H), 5.33 (dd, J = 8, 1.5 Hz, 1H), 5.18 (br s, 1H), 4.77 (dd, J = 3.5, 1.5 Hz, 1H), 4.76 (dd, J = 9, 8,5 Hz, 1H), 4.55 (dd, J = 9, 5.5 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.73 (ddd, J = 15, 8, 1 Hz, 1H), 2.33 (dd, J = 15, 4.5 Hz, 1H); $^{13}$C NMR (Acetone-$d_6$) δ 192.6 (C), 191.8 (C), 150.7 (C), 149.8 (C), 131.7 (C), 118.5 (CH), 112.1 (CH), 103.4 (CH), 108.6 (C), 82.3 (CH), 79.1 (CH), 76.5 (CH), 75.9 (CH), 75.8 (CH), 70.4 ($CH_2$), 56.0 ($CH_3$), 55.9 ($CH_3$), 39.7 ($CH_2$); X-ray data: see supporting information pages 12-21.



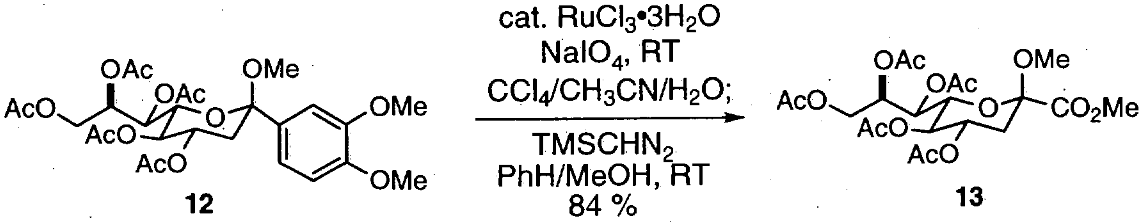
**Preparation of Compound 2.** To a suspension of tetraol **3** (963 mg, 2.81 mmol) in $CH_2Cl_2$ (56 mL), $Et_3N$ (0.822 mL, 2.81 mmol), dibutyltin oxide (35 mg, 0.14 mmol), and TsCl (1.12 g, 5.90 mmol) were added. The reaction stirred 16 h at RT, at which time a clear, homogeneous solution was observed. $Et_3N$ (3.92 mL, 28.1 mmol), acetic anhydride (1.33 mL, 14.1 mmol), and 4-dimethylamino pyridine (34 mg, 0.28 mmol) were then added. After stirring 30 min at RT, the reaction mixture was washed with water (25 mL), the aqueous layer extracted with $CH_2Cl_2$ (3 x 20 mL), and the combined organics dried ($Na_2SO_4$), concentrated and FCC (0.5 % $Et_3N/Et_2O$) gave pure **11**. $PhCH_3$ (10 mL) was added to the combined pure fractions of **11**, the clear solution concentrated to remove all $Et_2O$ and $Et_3N$, and activated 4Å molecular sieves (1 g) were added. After stirring 10 min at RT while flushing with a stream of nitrogen, CsOAc (5.39 g, 28.1 mmol) and 18-c-6 (1.49 g, 5.62 mmol) were added. The reaction was refluxed 18 h, cooled to RT, and water (100 mL) and $CH_2Cl_2$ (100 mL) were added. The organic layer was separated, aqueous layer extracted with $CH_2Cl_2$ (3 x 100 mL), and combined organics were dried ($Na_2SO_4$) and concentrated. Purification by FCC (0-10% $Et_2O/CH_2Cl_2$, gradient elution) gave monotosylate triacetate and pure **2** (608 mg). The recovered monotosylate triacetate was resubjected to the identical reaction conditions with CsOAc (2.70 g, 14.1 mmol) and 18-c-6 (0.745 g, 2.81 mmol), giving pure **2** (434 mg). A second recycling using CsOAc (1.35 g, 7.05 mmol) and 18-c-6 (0.373 g, 1.41 mmol) provided more pure **2** (121 mg, total = 1.16 g, 81%) as white flakes. $^1H$ NMR ($CDCl_3$) $\delta$ 7.08 (dd, J = 8, 2 Hz, 1H), 7.04 (d, J = 2 Hz, 1H), 6.86 (d, J = 8 Hz, 1H), 5.04 (ddd, J = 6, 2.5, 1.5 Hz, 1H), 4.98 (ddd, J = 8, 5.5, 3 Hz, 1H), 4.80 (d, J = 1.5 Hz, 1H), 4.58 (d, J = 1 Hz, 1H), 4.55 (dd, J = 8, 1 Hz, 1H), 4.46 (dd, J = 12.5, 3 Hz, 1H), 4.14 (dd, J = 12.5, 5.5 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 2.39 (dd, J = 15, 6 Hz, 1H), 2.18 (s, 3H), 2.17

(dd, J = 15, 2.5 Hz, 1H), 2.16 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 170.5 (C), 170.0 (C), 169.8 (C), 169.6 (C), 149.4 (C), 148.7 (C), 131.7 (C), 117.6 (CH), 110.7 (CH), 108.2 (CH), 107.6 (C), 77.2 (CH), 74.1 (CH), 71.1 (CH), 69.4 (CH), 68.2 (CH), 62.3 ($CH_2$), 56.0 ($CH_3$), 55.9 ($CH_3$), 37.4 ($CH_2$), 21.2 ($CH_3$), 21.0 ($CH_3$), 20.9 ($CH_3$), 20.7 ($CH_3$); IR (thin film) 2968, 2943, 2838, 1743, 1740, 1734, 1223 cm$^{-1}$; $[\alpha]^{24}_{D}$ +51° (c = 1.1, $CDCl_3$); mp 45-46 °C; HRMS (FAB) calcd. for $C_{24}H_{30}O_{12}Na$ (M+Na$^+$) 533.1635, found 533.1622.



**Preparation of Compound 12.** Inverted tetraacetate **2** (223 mg, 0.437 mmol) was dissolved in MeOH (10 mL) and concentrated sulfuric acid (1 drop) was added at 0 °C. After stirring at 0 °C for 3 h, the clear solution was poured into saturated aqueous sodium bicarbonate (15 mL), $CH_2Cl_2$ (30 mL) was added, layers separated, and the aqueous phase extracted with $CH_2Cl_2$ (2 x 30 mL). The combined organics were dried ($MgSO_4$), concentrated, and dissolved in $CH_2Cl_2$ (10 mL). $Et_3N$ (0.488 mL, 3.50 mmol), acetic anhydride (0.165 mL, 1.75 mmol), and 4-dimethylamino pyridine (5.3 mg, 0.044 mmol) were then added at RT, and reaction stirred 2 h. After pouring into water (15 mL) and adding $CH_2Cl_2$ (20 mL), the separated aqueous phase was extracted with $CH_2Cl_2$ (2 x 20 mL). The combined organics were dried ($MgSO_4$), concentrated, and FCC (20-50% $Et_2O$/Hexanes, gradient elution) gave **2** (37 mg, ~90% pure by $^1$H NMR) and pure **12** (229 mg, 90%, 100% based on recovered **2**) as white flakes. $^1$H NMR ($CDCl_3$) δ 7.04 (dd, J = 8, 2 Hz, 1H), 6.94 (d, J = 2 Hz, 1H), 6.87 (d, J = 8 Hz, 1H), 5.48 (dd, J = 6, 2 Hz, 1H), 5.43 (ddd, J = 11.5, 9.5, 5.5 Hz, 1H), 5.38 (td, J = 6, 2.5 Hz, 1H), 4.95 (t, J = 9.5 Hz, 1H), 4.54 (dd, J = 12.5, 2.5 Hz, 1H), 4.22 (dd, J = 12.5, 6 Hz, 1H), 4.19 (dd, J = 9.5, 2 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.95 (s, 3H), 2.54 (dd, J = 13, 5.5 Hz, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.76 (dd, J

= 13, 11.5 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 170.6 (C), 170.3 (C), 170.04 (C), 169.97 (C), 169.9 (C), 149.0 (C), 148.9 (C), 131.9 (C), 118.2 (CH), 110.8 (CH), 108.8 (CH), 101.2 (C), 70.2 (CH), 70.1 (CH), 69.2 (CH), 68.3 (CH), 67.6 (CH), 62.0 ($CH_2$), 55.9 ($CH_3$ x 2), 49.4 ($CH_3$), 42.0 ($CH_2$), 21.0 ($CH_3$), 20.9 ($CH_3$), 20.8 ($CH_3$), 20.7 ($CH_3$), 20.6 ($CH_3$); IR (thin film) 2940, 2836, 1751, 1734, 1237, 1223, 1035 cm$^{-1}$; $[\alpha]^{24}_D$ +13° (c = 0.30, $CHCl_3$); mp 50-51 °C; HRMS (FAB) calcd. for $C_{27}H_{36}O_{14}Na$ (M+Na$^+$) 607.2003, found 607.2033.



**Preparation of Compound 13.** Aryl methyl glycoside **12** (62 mg, 0.106 mmol) was dissolved in $CH_3CN$ (0.6 mL), $CCl_4$ (0.6 mL), and water (0.9 mL). Sodium periodate (272 mg, 1.27 mmol) and ruthenium(III)chloride trihydrate (1.1 mg, 0.0053 mmol) were then added, and the reaction stirred at RT 6 h. Ethyl acetate (50 mL), saturated aqueous ammonium chloride (10 mL) and water (10 mL) were then added, the organic layer separated, and the aqueous layer extracted with ethyl acetate (4 x 20 mL). The combined organics were dried ($MgSO_4$), concentrated, and dissolved in PhH (1.6 mL) and MeOH (0.5 mL). Trimethylsilyl diazomethane (2M in hexanes, 0.11 mL, 0.21 mmol) was added and the reaction stirred at RT for 2 h. Glacial acetic acid (0.5 mL) was then added and the yellow solution was stirred at RT an additional 30 min, concentrated, and FCC (25-50% $Et_2O$/Hexanes, gradient elution) gave pure **13** (45 mg, 84%) which could be recrystallized from $Et_2O$/Hexanes to give analytically pure clear square plates. $^1$H NMR ($CDCl_3$) δ 5.42 (dd, J = 5.5, 2.5 Hz, 1H), 5.32 (ddd, J = 11.5, 10, 5 Hz, 1H), 5.31 (ddd, J = 6.5, 5.5, 2 Hz, 1H), 4.90 (t, J = 10 Hz, 1H), 4.71 (dd, J = 12.5, 2.5 Hz, 1H), 4.15 (dd, J = 12.5, 6.5 Hz, 1H), 4.06 (dd, J = 10, 2 Hz, 1H), 3.82 (s, 3H), 3.26 (s, 3H), 2.52 (dd, J = 13, 5 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.84 (dd, J = 13, 11.5 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 170.6 (C), 170.2 (C), 170.00 (C), 169.92 (C), 169.8 (C), 167.1 (C), 98.7 (C), 70.8 (CH), 69.9 (CH), 69.1 (CH), 67.8 (CH), 67.4 (CH), 62.0 ($CH_2$), 52.7 ($CH_3$), 51.3 ($CH_3$), 36.9 ($CH_2$), 21.0 ($CH_3$), 20.8 ($CH_3$), 20.72 ($CH_3$), 20.67 ($CH_3$), 20.6 ($CH_3$); IR (thin film) 2956, 1748, 1373, 1220, 1050 $cm^{-1}$; $[\alpha]^{24}_D$ –6.8° (c = 0.28, $CHCl_3$); mp 115-116 °C; HRMS (FAB) calcd. for $C_{21}H_{30}O_{14}Na$ ($M+Na^+$) 529.1533, found 529.1555.

## Characterization Data Comparison

| | Experimental | Ogura et al.[1] | Mononen et al.[2] |
|---|---|---|---|
| Melting Point | 115-116 °C | 117-118 °C | "syrup" |
| Optical Rotation | $[\alpha]^{24}_D$ -6.8°<br>(c = 0.28; $CHCl_3$) | $[\alpha]^{24}_D$ -6.3°<br>(c = 0.13; $CHCl_3$) | $[\alpha]^{24}_D$ -6.5°<br>(c = 1; $CHCl_3$) |
| Infrared ($cm^{-1}$) | 1748, 1373,<br>1220, 1050 | 1751, 1373,<br>1244, 1058 | not reported |

## $^1$H NMR Comparison: Chemical Shifts and Coupling Constants

e = experimental
o = Ogura et al.[1]
m = Mononen et al.[2]

-OAc:
e = δ2.12, 2.08, 2.04, 2.02, 2.00
o = δ1.97-2.12
m = δ2.16, 2.12, 2.07, 2.06, 2.03

e = δ4.06, 10, 2
o = δ4.05, 10, 2.2
m = δ4.10, 10, 2.2

e = δ5.32, 11.5, 10, 5
o = δ5.30, 11.4, 10, 5.3
m = δ5.36, 11.7, 10, 5.1

e = δ5.31, 6.5, 5.5
o = δ5.29, 6.8, 2.2
m = δ5.34, 6.6, 5.4

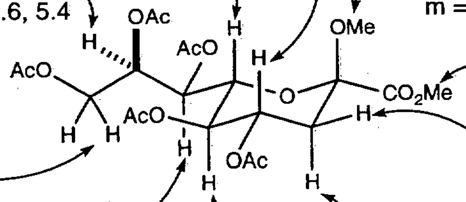
e = δ4.15, 12.5, 6.5
o = δ4.14, 12.5, 6.8
m = δ4.20, 12.6, 6.6

&

e = δ4.71, 12.5, 2.5
o = δ4.70, 12.5, 2.2
m = δ4.76, 12.6, 2.4

e = δ3.26
o = δ3.25
m = δ3.30

e = δ3.82
o = δ3.80
m = δ3.86



e = δ2.52, 13, 5
o = δ2.51, 13, 5.3
m = δ2.56, 12.9, 5.1

e = δ5.42, 5.5, 2.5
o = δ5.40, 5.4, 2.2
m = δ5.46, 5.4, 2.2

e = δ4.90, 10, 10
o = δ4.88, 10, 10
m = δ4.94, 10, 10

e = δ1.84, 13, 11.5
o = δ1.83, 13, 11.4
m = δ1.88, 12.9, 11.7

1) Nakamura, M.; Takayanagi, H.; Furuhata, K.; Ogura, H. *Chem. Pharm. Bull.* **1992**, *40*, 879-885.
2) Mononen, I.; Lengstad, B.; Lönngren, J. *Acta Chem. Scand. B* **1980**, *34*, 775-776.

# X-ray Data for Compound 10

**Experimental**

A colorless prism-shaped crystal of dimensions 0.43 x 0.38 x 0.20 mm was selected for structural analysis. Intensity data for this compound were collected using a Bruker SMART ccd area detector(1) mounted on a Bruker P4 goniometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). The sample was cooled to 173(2) K. The intensity data, which nominally covered one and a half hemispheres of reciprocal space, were measured as a series of $\phi$ oscillation frames each of 0.4 ° for 20 sec / frame. The detector was operated in 512 x 512 mode and was positioned 5.00 cm from the sample. Coverage of unique data was 99.2 % complete to 25.00 degrees in $\theta$. Cell parameters were determined from a non-linear least squares fit of 3995 peaks in the range $2.58 < \theta < 28.89°$. The first 50 frames were repeated at the end of data collection and yielded 181 peaks showing a variation of -0.44 % during the data collection. A total of 4672 data were measured in the range $2.59 < \theta < 29.20°$. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.8694 and 0.9361. The data were merged to form a set of 3712 independent data with R(int) = 0.0181.

The monoclinic space group P2(1) was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on $F^2$ (3). Hydrogen atom positions were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 255 parameters were refined against 1 restraints and 3712 data to give $wR(F^2) = 0.0903$ and S = 1.034 for weights of $w = 1/[\sigma^2(F^2) + (0.0640\ P)^2]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0328 for the 3499 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.361 and -0.251 e/Å$^3$, respectively. The absolute structure was determined by refinement of the Flack parameter(4). The polar axis restraints were taken from Flack and Schwarzenbach(5).

## Comment

The displacement ellipsoids were drawn at the 50% probability level.

## Acknowledgment

The authors thank the National Science Foundation (grant CHE-9709005) and the University of Wisconsin for funds to purchase the diffractometer and computers.
This structure was determined by Michael Kavana.

## References

(1) (a) Data Collection: SMART Software Reference Manual (1994). Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA. (b) Data Reduction: SAINT Software Reference Manual (1995). Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.

(2) G. M. Sheldrick (1996). SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany.

(3) (a) G. M. Sheldrick (1994). SHELXTL Version 5 Reference Manual. Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA. (b) *International Tables for Crystallography, Vol C,* Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, Kluwer: Boston (1995).

(4) H. D. Flack, *Acta Cryst. A39*, 876-881 (1983).

(5) H. D. Flack and D. Schwarzenbach, *Acta Cryst. A44*, 499-506 (1988).

Table 1. Crystal data and structure refinement for 00115.

| | | |
|---|---|---|
| Identification code | 00115 | |
| Empirical formula | C18 H18 O8 S2 | |
| Formula weight | 426.44 | |
| Crystal system | Monoclinic | |
| Space group | P2(1) | |
| Unit cell dimensions | $a$ = 6.2079(6) Å | $\alpha$= 90° |
| | $b$ = 8.9567(8) Å | $\beta$= 91.385(2)° |
| | $c$ = 16.5736(15) Å | $\gamma$= 90° |
| Volume | 921.26(15) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.537 Mg/m$^3$ | |
| Wavelength | 0.71073 Å | |
| Temperature | 173(2) K | |
| $F$(000) | 444 | |
| Absorption coefficient | 0.335 mm$^{-1}$ | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 0.9361 and 0.8694 | |
| Theta range for data collection | 2.59 to 29.20°. | |
| Reflections collected | 4672 | |
| Independent reflections | 3712 [R(int) = 0.0181] | |
| Data / restraints / parameters | 3712 / 1 / 255 | |
| wR($F^2$ all data) | wR = 0.0903 | |
| R($F$ obsd data) | R = 0.0328 | |
| Goodness-of-fit on $F^2$ | 1.034 | |
| Observed data [I > 2$\sigma$(I)] | 3499 | |
| Absolute structure parameter | 0.07(6) | |
| Largest and mean shift / s.u. | 0.000and 0.000 | |
| Largest diff. peak and hole | 0.361 and -0.251 e/Å$^3$ | |

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for 00115. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 0.7354(2) | 0.48364(18) | 0.26832(7) | 0.0212(3) |
| C(2) | 0.5103(3) | 0.5192(2) | 0.27045(11) | 0.0198(4) |
| C(3) | 0.4863(3) | 0.6886(2) | 0.26721(12) | 0.0211(4) |
| C(4) | 0.5856(3) | 0.7505(2) | 0.18959(12) | 0.0227(4) |
| C(5) | 0.7788(3) | 0.6628(2) | 0.16023(12) | 0.0230(4) |
| C(6) | 0.7826(3) | 0.4993(3) | 0.18452(10) | 0.0217(4) |
| C(7) | 0.5920(4) | 0.4186(3) | 0.14500(11) | 0.0243(4) |
| C(8) | 0.6150(4) | 0.2494(3) | 0.14599(12) | 0.0250(4) |
| C(9) | 0.4251(4) | 0.1660(3) | 0.10617(15) | 0.0332(5) |
| O(10) | 0.5310(3) | 0.05711(19) | 0.05533(9) | 0.0316(4) |
| O(11) | 0.7944(3) | 0.20655(18) | 0.09496(9) | 0.0297(4) |
| O(12) | 0.9591(2) | 0.74108(19) | 0.19990(9) | 0.0267(3) |
| O(13) | 0.6831(2) | 0.89626(17) | 0.20716(8) | 0.0246(3) |
| O(14) | 0.4172(2) | 0.45491(17) | 0.19709(8) | 0.0240(3) |
| C(15) | 0.4143(3) | 0.4507(2) | 0.34438(11) | 0.0198(4) |
| C(16) | 0.5142(3) | 0.4791(2) | 0.41992(11) | 0.0201(4) |
| C(17) | 0.4276(3) | 0.4228(2) | 0.48952(11) | 0.0198(4) |
| C(18) | 0.2377(3) | 0.3391(2) | 0.48609(12) | 0.0207(4) |
| C(19) | 0.1347(3) | 0.3139(2) | 0.41158(13) | 0.0241(4) |
| C(20) | 0.2249(3) | 0.3696(2) | 0.34153(12) | 0.0236(4) |
| O(21) | 0.5354(2) | 0.44639(18) | 0.56260(8) | 0.0241(3) |
| O(22) | 0.1666(2) | 0.28820(18) | 0.55887(9) | 0.0260(3) |
| C(23) | 0.4332(4) | 0.5550(3) | 0.61261(12) | 0.0273(5) |
| C(24) | -0.0349(4) | 0.2113(3) | 0.55845(16) | 0.0346(5) |
| C(25) | 0.8957(4) | 0.8780(3) | 0.21993(12) | 0.0247(4) |
| C(26) | 0.7403(4) | 0.0877(3) | 0.05169(12) | 0.0275(4) |
| S(27) | 1.05442(9) | 1.00717(7) | 0.25657(3) | 0.03144(14) |
| S(28) | 0.91030(11) | -0.01363(8) | 0.00110(4) | 0.03970(16) |

Table 3. Bond lengths [Å] and angles [°] for 00115.

| | | | |
|---|---|---|---|
| O(1)-C(6) | 1.433(2) | O(10)-C(26) | 1.331(3) |
| O(1)-C(2) | 1.435(2) | O(11)-C(26) | 1.322(3) |
| C(2)-O(14) | 1.452(2) | O(12)-C(25) | 1.332(3) |
| C(2)-C(15) | 1.506(3) | O(13)-C(25) | 1.342(3) |
| C(2)-C(3) | 1.525(3) | C(15)-C(20) | 1.382(3) |
| C(3)-C(4) | 1.543(3) | C(15)-C(16) | 1.407(3) |
| C(4)-O(13) | 1.466(3) | C(16)-C(17) | 1.380(3) |
| C(4)-C(5) | 1.523(3) | C(17)-O(21) | 1.386(2) |
| C(5)-O(12) | 1.463(3) | C(17)-C(18) | 1.397(3) |
| C(5)-C(6) | 1.519(3) | C(18)-O(22) | 1.372(2) |
| C(6)-C(7) | 1.521(3) | C(18)-C(19) | 1.395(3) |
| C(7)-O(14) | 1.440(2) | C(19)-C(20) | 1.393(3) |
| C(7)-C(8) | 1.523(3) | O(21)-C(23) | 1.436(3) |
| C(8)-O(11) | 1.466(2) | O(22)-C(24) | 1.428(3) |
| C(8)-C(9) | 1.531(3) | C(25)-S(27) | 1.628(2) |
| C(9)-O(10) | 1.457(3) | C(26)-S(28) | 1.638(2) |

| | | | |
|---|---|---|---|
| C(6)-O(1)-C(2) | 102.95(14) | O(11)-C(8)-C(9) | 102.22(17) |
| O(1)-C(2)-O(14) | 105.04(14) | C(7)-C(8)-C(9) | 114.17(19) |
| O(1)-C(2)-C(15) | 109.54(15) | O(10)-C(9)-C(8) | 102.82(18) |
| O(14)-C(2)-C(15) | 111.23(16) | C(26)-O(10)-C(9) | 110.07(18) |
| O(1)-C(2)-C(3) | 108.31(17) | C(26)-O(11)-C(8) | 109.71(17) |
| O(14)-C(2)-C(3) | 109.17(16) | C(25)-O(12)-C(5) | 109.01(17) |
| C(15)-C(2)-C(3) | 113.20(16) | C(25)-O(13)-C(4) | 108.82(16) |
| C(2)-C(3)-C(4) | 110.26(16) | C(7)-O(14)-C(2) | 107.53(14) |
| O(13)-C(4)-C(5) | 101.40(16) | C(20)-C(15)-C(16) | 118.80(17) |
| O(13)-C(4)-C(3) | 109.03(16) | C(20)-C(15)-C(2) | 122.65(17) |
| C(5)-C(4)-C(3) | 114.49(17) | C(16)-C(15)-C(2) | 118.40(17) |
| O(12)-C(5)-C(6) | 109.63(17) | C(17)-C(16)-C(15) | 120.38(18) |
| O(12)-C(5)-C(4) | 102.08(16) | C(16)-C(17)-O(21) | 119.04(17) |
| C(6)-C(5)-C(4) | 114.80(17) | C(16)-C(17)-C(18) | 120.50(18) |
| O(1)-C(6)-C(5) | 110.43(16) | O(21)-C(17)-C(18) | 120.43(17) |
| O(1)-C(6)-C(7) | 101.29(15) | O(22)-C(18)-C(19) | 125.02(19) |
| C(5)-C(6)-C(7) | 109.70(17) | O(22)-C(18)-C(17) | 115.58(18) |
| O(14)-C(7)-C(6) | 102.94(15) | C(19)-C(18)-C(17) | 119.41(18) |
| O(14)-C(7)-C(8) | 106.86(17) | C(20)-C(19)-C(18) | 119.65(19) |
| C(6)-C(7)-C(8) | 113.37(18) | C(15)-C(20)-C(19) | 121.23(18) |
| O(11)-C(8)-C(7) | 109.06(17) | C(17)-O(21)-C(23) | 113.40(16) |

| | | | |
|---|---|---|---|
| C(18)-O(22)-C(24) | 117.16(18) | O(11)-C(26)-O(10) | 112.13(19) |
| O(12)-C(25)-O(13) | 111.62(19) | O(11)-C(26)-S(28) | 124.44(18) |
| O(12)-C(25)-S(27) | 124.60(17) | O(10)-C(26)-S(28) | 123.42(17) |
| O(13)-C(25)-S(27) | 123.78(17) | | |

Table 4. Anisotropic displacement parameters ($Å^2$x $10^3$) for 00115. 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) | 22(1) | 24(1) | 18(1) | 0(1) | 1(1) | 5(1) |
| C(2) | 21(1) | 19(1) | 19(1) | -2(1) | -2(1) | 2(1) |
| C(3) | 24(1) | 17(1) | 23(1) | 1(1) | 2(1) | 2(1) |
| C(4) | 26(1) | 19(1) | 24(1) | 1(1) | -2(1) | 0(1) |
| C(5) | 28(1) | 22(1) | 19(1) | -1(1) | 2(1) | 1(1) |
| C(6) | 30(1) | 18(1) | 18(1) | -1(1) | 3(1) | 5(1) |
| C(7) | 33(1) | 23(1) | 17(1) | -1(1) | 2(1) | 3(1) |
| C(8) | 33(1) | 20(1) | 22(1) | -4(1) | 5(1) | 1(1) |
| C(9) | 38(1) | 26(1) | 36(1) | -8(1) | 7(1) | -2(1) |
| O(10) | 34(1) | 29(1) | 32(1) | -10(1) | 5(1) | -4(1) |
| O(11) | 32(1) | 23(1) | 34(1) | -9(1) | 7(1) | -3(1) |
| O(12) | 26(1) | 22(1) | 32(1) | -4(1) | 2(1) | 0(1) |
| O(13) | 26(1) | 19(1) | 29(1) | 1(1) | 0(1) | -1(1) |
| O(14) | 25(1) | 26(1) | 21(1) | -5(1) | -3(1) | 1(1) |
| C(15) | 22(1) | 16(1) | 21(1) | -1(1) | 0(1) | 3(1) |
| C(16) | 21(1) | 17(1) | 23(1) | -1(1) | 0(1) | -2(1) |
| C(17) | 19(1) | 18(1) | 22(1) | -1(1) | -1(1) | 3(1) |
| C(18) | 22(1) | 14(1) | 27(1) | 2(1) | 5(1) | 1(1) |
| C(19) | 21(1) | 19(1) | 32(1) | -2(1) | -1(1) | -1(1) |
| C(20) | 24(1) | 19(1) | 28(1) | -2(1) | -5(1) | -1(1) |
| O(21) | 24(1) | 29(1) | 20(1) | -1(1) | -1(1) | 1(1) |
| O(22) | 26(1) | 23(1) | 29(1) | 5(1) | 6(1) | -2(1) |
| C(23) | 34(1) | 27(1) | 21(1) | -2(1) | 3(1) | -4(1) |
| C(24) | 27(1) | 36(1) | 41(1) | 9(1) | 6(1) | -8(1) |
| C(25) | 28(1) | 23(1) | 23(1) | 3(1) | 2(1) | -1(1) |
| C(26) | 35(1) | 26(1) | 22(1) | -1(1) | 4(1) | -3(1) |
| S(27) | 32(1) | 28(1) | 35(1) | -4(1) | 4(1) | -9(1) |
| S(28) | 46(1) | 37(1) | 37(1) | -13(1) | 15(1) | -2(1) |

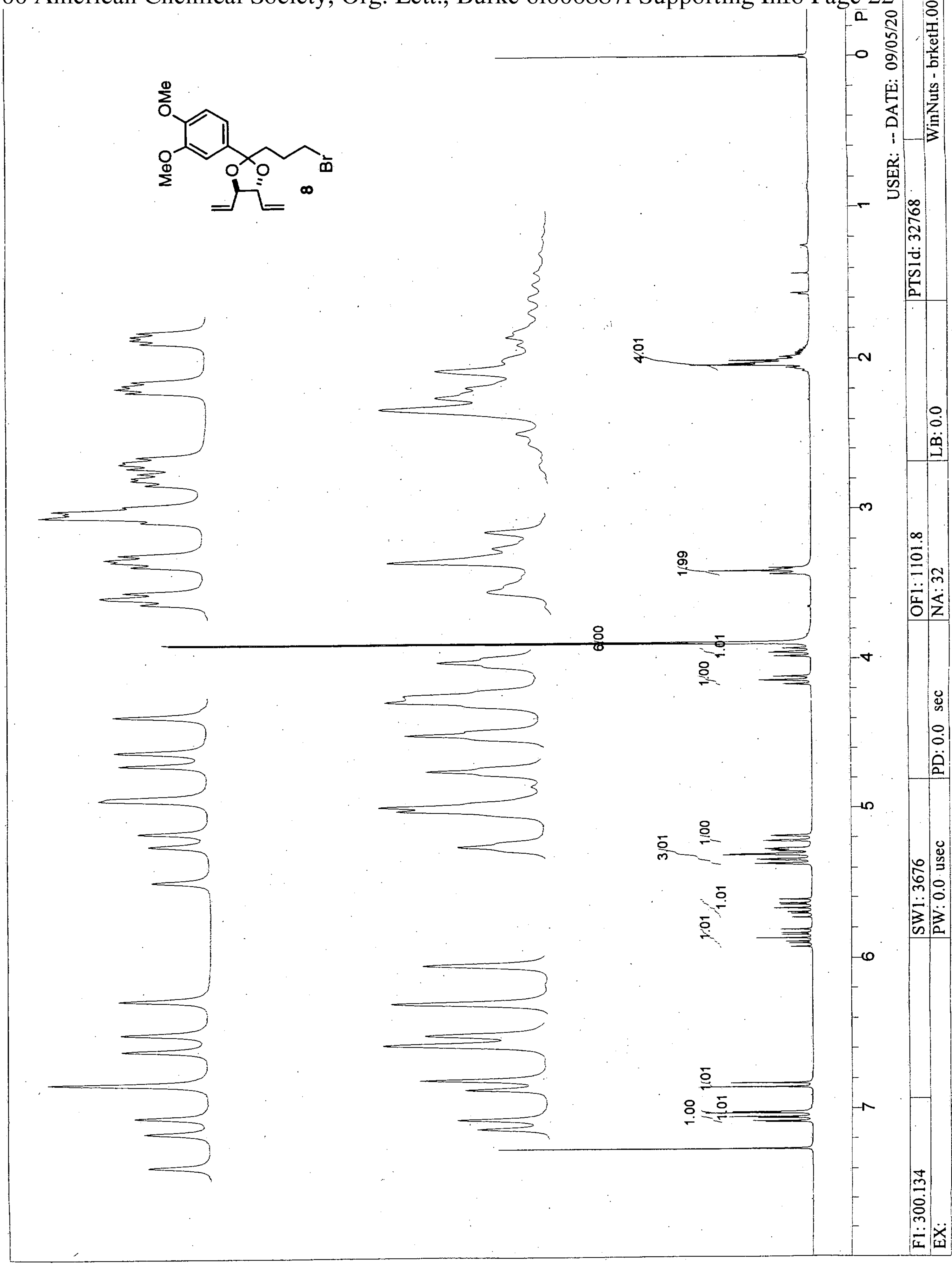
Table 5. Hydrogen coordinates and isotropic displacement parameters for 00115.

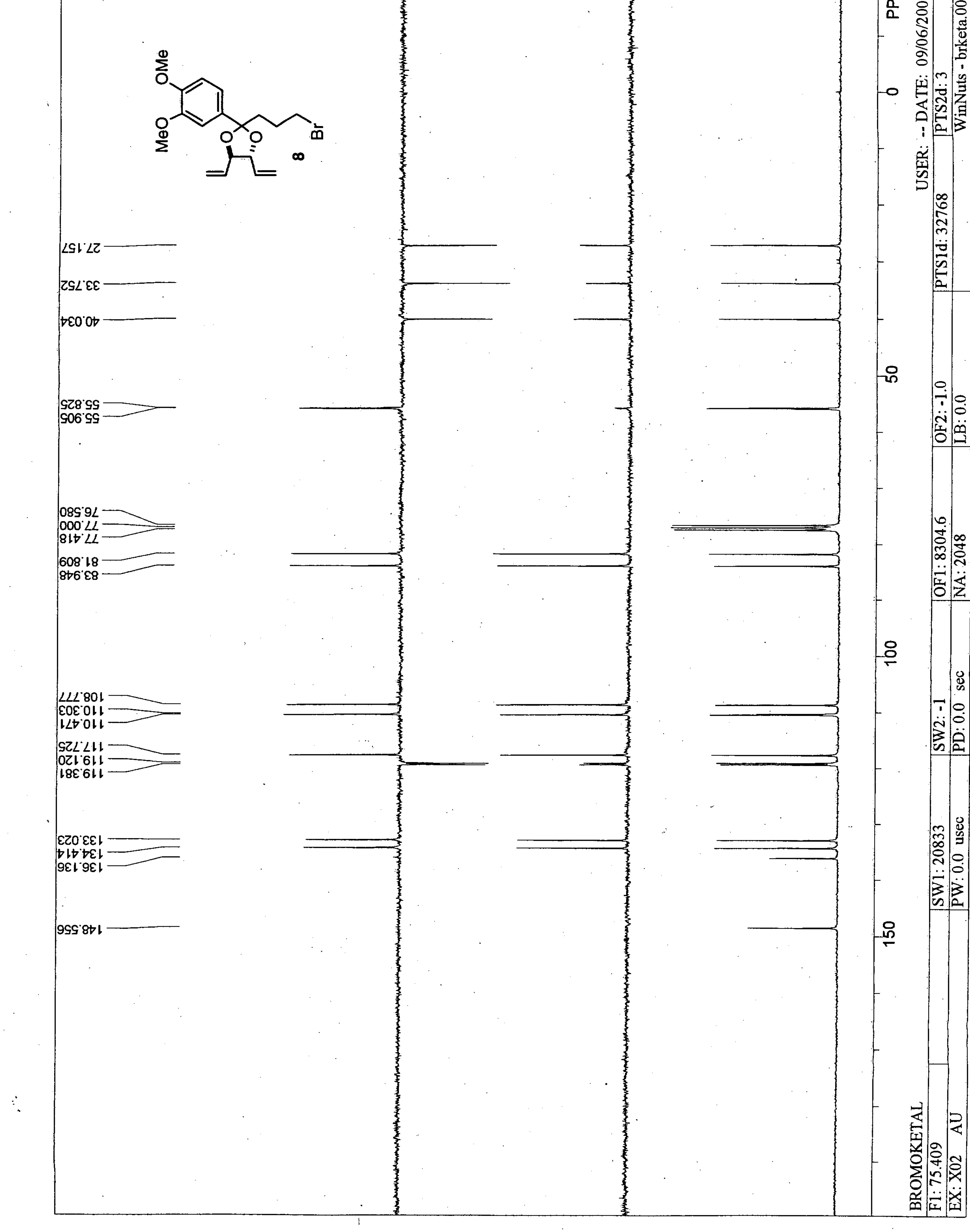
| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3A) | 0.5595 | 0.7337 | 0.3150 | 0.025 |
| H(3B) | 0.3317 | 0.7155 | 0.2684 | 0.025 |
| H(4) | 0.4731 | 0.7595 | 0.1456 | 0.027 |
| H(5) | 0.7887 | 0.6721 | 0.1003 | 0.028 |
| H(6) | 0.9224 | 0.4508 | 0.1713 | 0.026 |
| H(7) | 0.5631 | 0.4562 | 0.0890 | 0.029 |
| H(8) | 0.6407 | 0.2129 | 0.2024 | 0.030 |
| H(9A) | 0.3360 | 0.1163 | 0.1470 | 0.040 |
| H(9B) | 0.3330 | 0.2345 | 0.0735 | 0.040 |
| H(16) | 0.6419 | 0.5374 | 0.4230 | 0.024 |
| H(19) | 0.0038 | 0.2590 | 0.4086 | 0.029 |
| H(20) | 0.1548 | 0.3515 | 0.2909 | 0.028 |
| H(23A) | 0.5172 | 0.5670 | 0.6630 | 0.041 |
| H(23B) | 0.2874 | 0.5213 | 0.6248 | 0.041 |
| H(23C) | 0.4254 | 0.6508 | 0.5842 | 0.041 |
| H(24A) | -0.0616 | 0.1727 | 0.6126 | 0.052 |
| H(24B) | -0.0308 | 0.1281 | 0.5201 | 0.052 |
| H(24C) | -0.1506 | 0.2804 | 0.5423 | 0.052 |

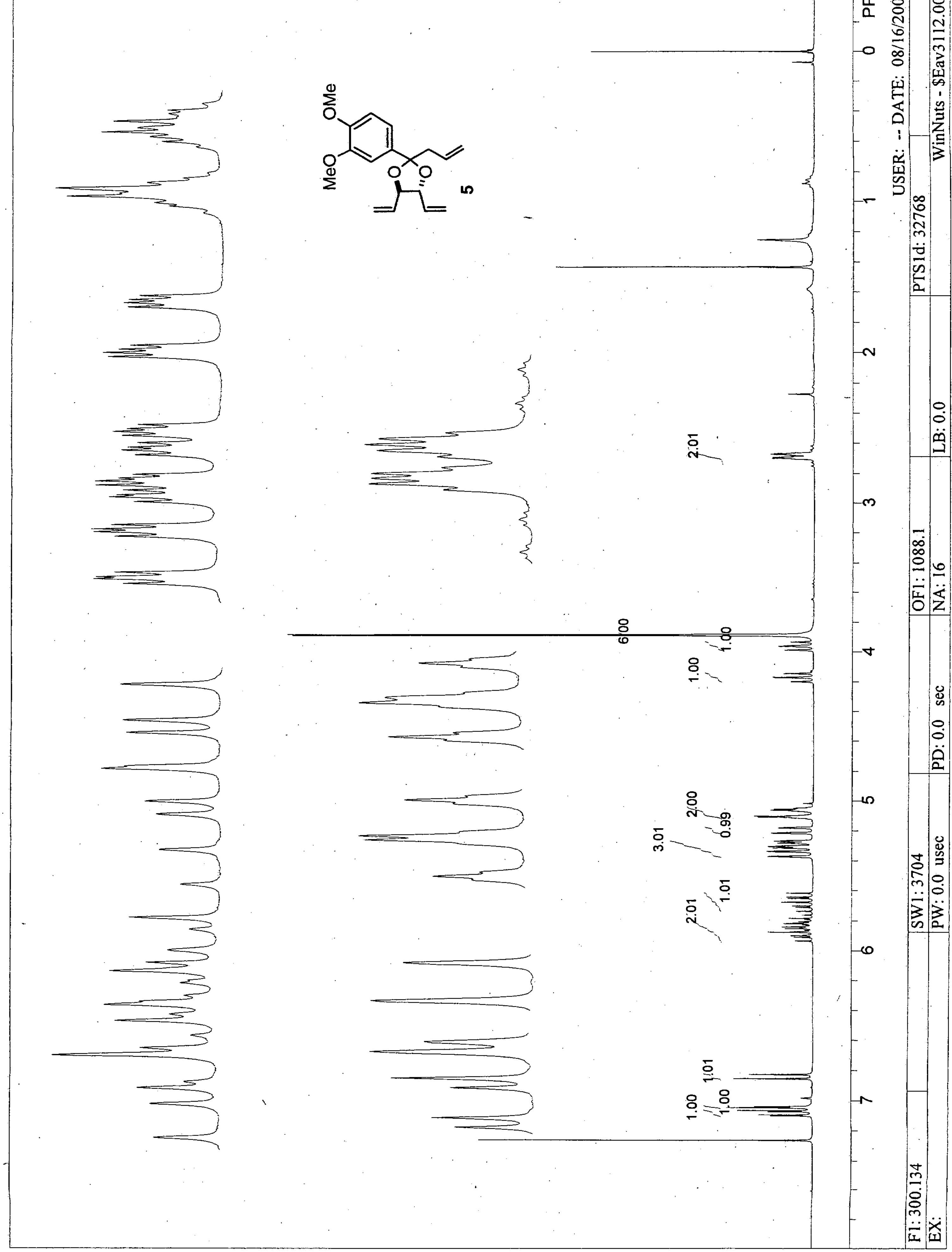
Table 6. Torsion angles [°] for 00115.

| | |
|---|---|
| C(6)-O(1)-C(2)-O(14) | 37.8(2) |
| C(6)-O(1)-C(2)-C(15) | 157.32(16) |
| C(6)-O(1)-C(2)-C(3) | -78.79(18) |
| O(1)-C(2)-C(3)-C(4) | 59.0(2) |
| O(14)-C(2)-C(3)-C(4) | -54.8(2) |
| C(15)-C(2)-C(3)-C(4) | -179.32(16) |
| C(2)-C(3)-C(4)-O(13) | -145.03(17) |
| C(2)-C(3)-C(4)-C(5) | -32.3(2) |
| O(13)-C(4)-C(5)-O(12) | 25.46(18) |
| C(3)-C(4)-C(5)-O(12) | -91.76(19) |
| O(13)-C(4)-C(5)-C(6) | 143.98(16) |
| C(3)-C(4)-C(5)-C(6) | 26.8(2) |
| C(2)-O(1)-C(6)-C(5) | 71.19(19) |
| C(2)-O(1)-C(6)-C(7) | -45.0(2) |
| O(12)-C(5)-C(6)-O(1) | 67.8(2) |
| C(4)-C(5)-C(6)-O(1) | -46.4(2) |
| O(12)-C(5)-C(6)-C(7) | 178.58(14) |
| C(4)-C(5)-C(6)-C(7) | 64.4(2) |
| O(1)-C(6)-C(7)-O(14) | 35.58(19) |
| C(5)-C(6)-C(7)-O(14) | -81.13(17) |
| O(1)-C(6)-C(7)-C(8) | -79.48(19) |
| C(5)-C(6)-C(7)-C(8) | 163.80(16) |
| O(14)-C(7)-C(8)-O(11) | -178.87(15) |
| C(6)-C(7)-C(8)-O(11) | -66.2(2) |
| O(14)-C(7)-C(8)-C(9) | 67.5(2) |
| C(6)-C(7)-C(8)-C(9) | -179.77(17) |
| O(11)-C(8)-C(9)-O(10) | 16.0(2) |
| C(7)-C(8)-C(9)-O(10) | 133.59(18) |
| C(8)-C(9)-O(10)-C(26) | -10.8(2) |
| C(7)-C(8)-O(11)-C(26) | -138.15(19) |
| C(9)-C(8)-O(11)-C(26) | -17.0(2) |
| C(6)-C(5)-O(12)-C(25) | -143.39(16) |
| C(4)-C(5)-O(12)-C(25) | -21.3(2) |
| C(5)-C(4)-O(13)-C(25) | -22.74(19) |
| C(3)-C(4)-O(13)-C(25) | 98.39(19) |
| C(6)-C(7)-O(14)-C(2) | -12.9(2) |
| C(8)-C(7)-O(14)-C(2) | 106.75(18) |
| O(1)-C(2)-O(14)-C(7) | -14.5(2) |
| C(15)-C(2)-O(14)-C(7) | -132.92(17) |
| C(3)-C(2)-O(14)-C(7) | 101.46(18) |
| O(1)-C(2)-C(15)-C(20) | -132.0(2) |
| O(14)-C(2)-C(15)-C(20) | -16.3(3) |
| C(3)-C(2)-C(15)-C(20) | 107.0(2) |
| O(1)-C(2)-C(15)-C(16) | 52.4(2) |
| O(14)-C(2)-C(15)-C(16) | 168.10(17) |
| C(3)-C(2)-C(15)-C(16) | -68.6(2) |
| C(20)-C(15)-C(16)-C(17) | 2.0(3) |
| C(2)-C(15)-C(16)-C(17) | 177.79(18) |
| C(15)-C(16)-C(17)-O(21) | 176.80(18) |
| C(15)-C(16)-C(17)-C(18) | -1.1(3) |
| C(16)-C(17)-C(18)-O(22) | 179.77(18) |
| O(21)-C(17)-C(18)-O(22) | 1.9(3) |
| C(16)-C(17)-C(18)-C(19) | -0.6(3) |
| O(21)-C(17)-C(18)-C(19) | -178.51(18) |
| O(22)-C(18)-C(19)-C(20) | -179.00(19) |
| C(17)-C(18)-C(19)-C(20) | 1.4(3) |
| C(16)-C(15)-C(20)-C(19) | -1.2(3) |
| C(2)-C(15)-C(20)-C(19) | -176.79(19) |
| C(18)-C(19)-C(20)-C(15) | -0.5(3) |
| C(16)-C(17)-O(21)-C(23) | 106.6(2) |
| C(18)-C(17)-O(21)-C(23) | -75.5(2) |
| C(19)-C(18)-O(22)-C(24) | -3.9(3) |
| C(17)-C(18)-O(22)-C(24) | 175.7(2) |
| C(5)-O(12)-C(25)-O(13) | 7.6(2) |
| C(5)-O(12)-C(25)-S(27) | -173.18(15) |
| C(4)-O(13)-C(25)-O(12) | 10.5(2) |

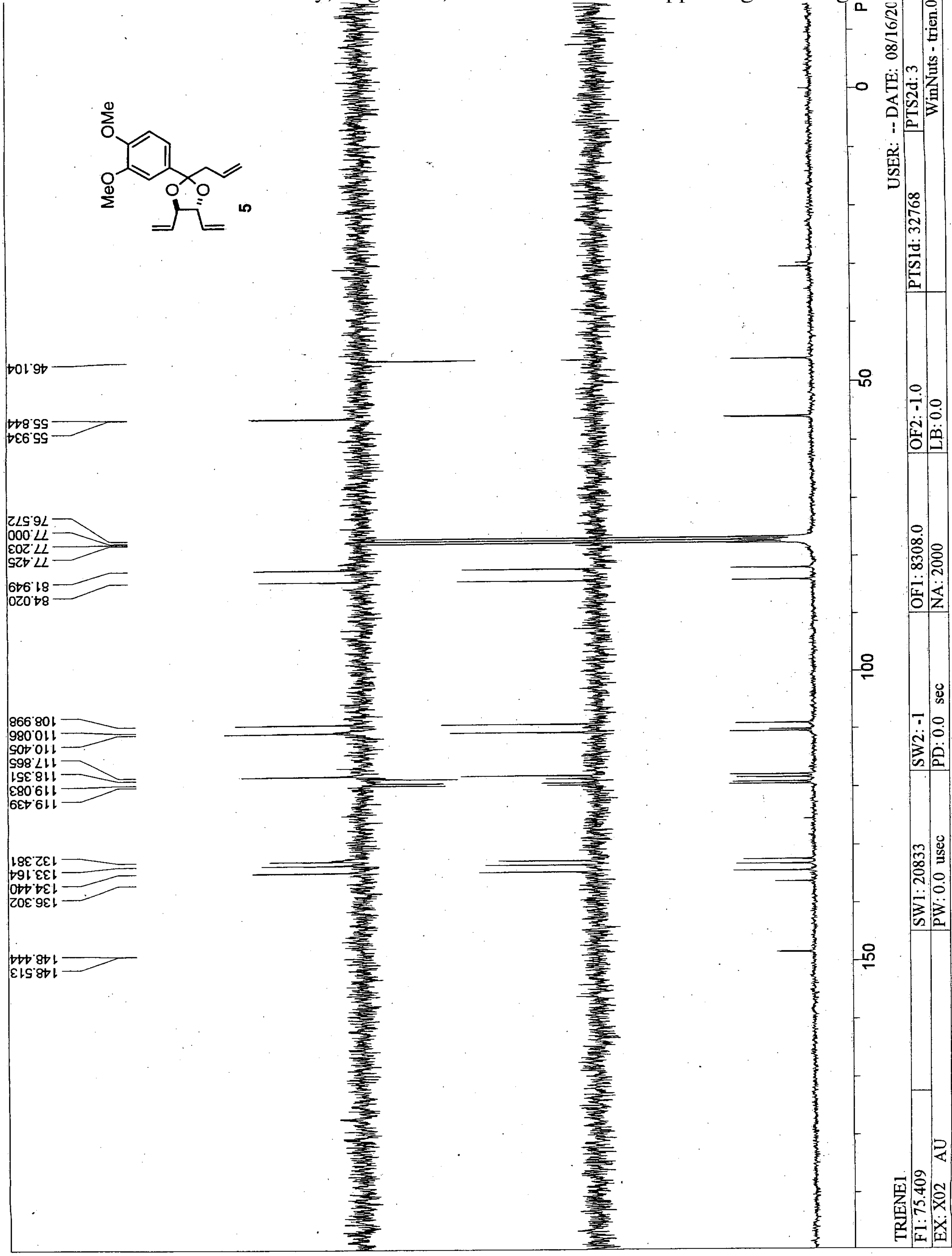
| | |
|---|---|
| C(4)-O(13)-C(25)-S(27) | -168.75(15) |
| C(8)-O(11)-C(26)-O(10) | 11.2(2) |
| C(8)-O(11)-C(26)-S(28) | -167.32(16) |
| C(9)-O(10)-C(26)-O(11) | 0.3(3) |
| C(9)-O(10)-C(26)-S(28) | 178.85(17 |

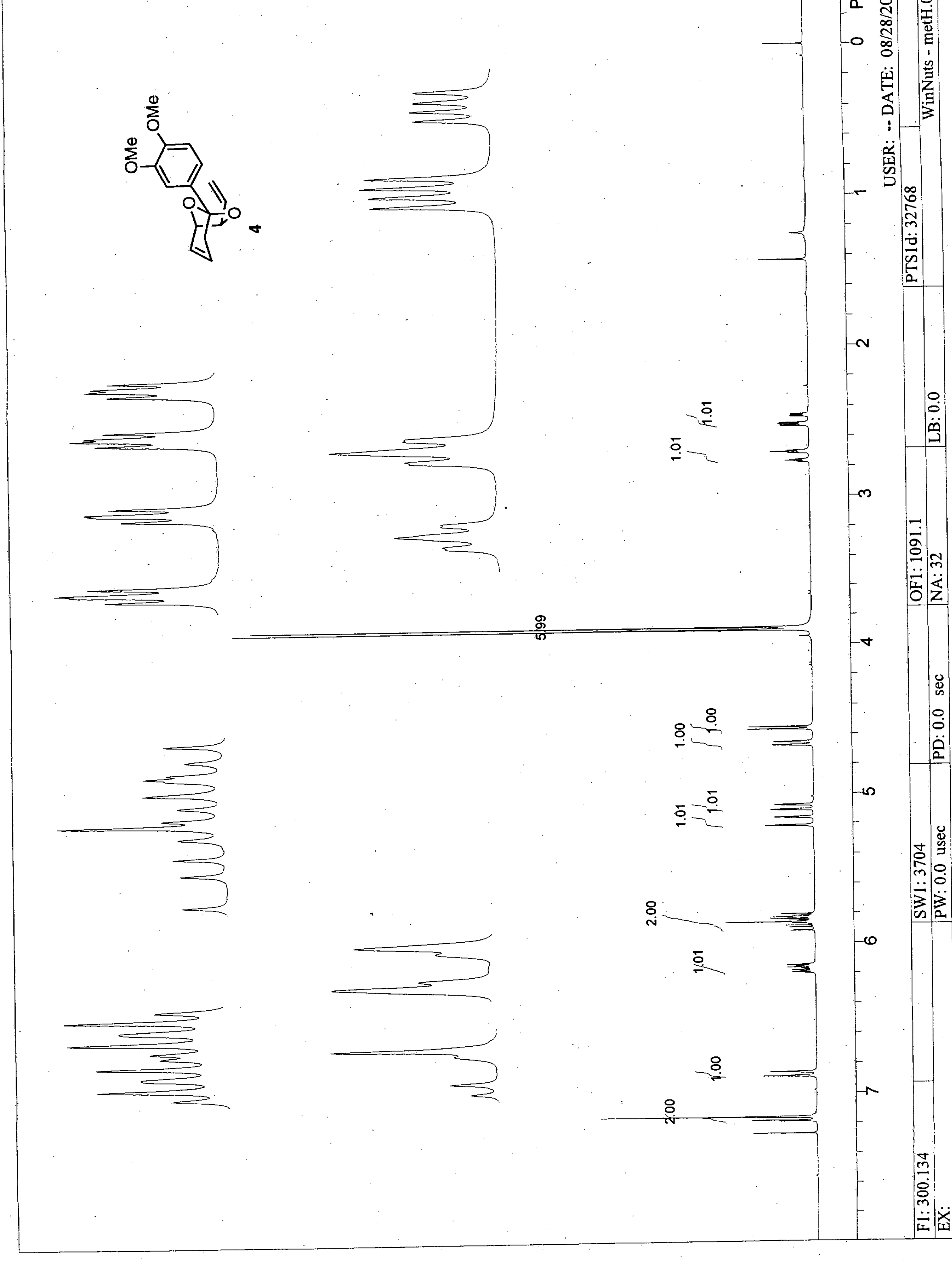

OMe
MeO
Br
8
4.01
1.99
6.00
1.00
1.01
3.01
1.00
1.01
1.01
1.00
1.01
1.01
0
1
2
3
4
5
6
7
P
USER: -- DATE: 09/05/20
WinNuts - brketH.001
PTS1d: 32768
LB: 0.0
OF1: 1101.8
NA: 32
PD: 0.0 sec
SW1: 3676
PW: 0.0 usec
F1: 300.134
EX:

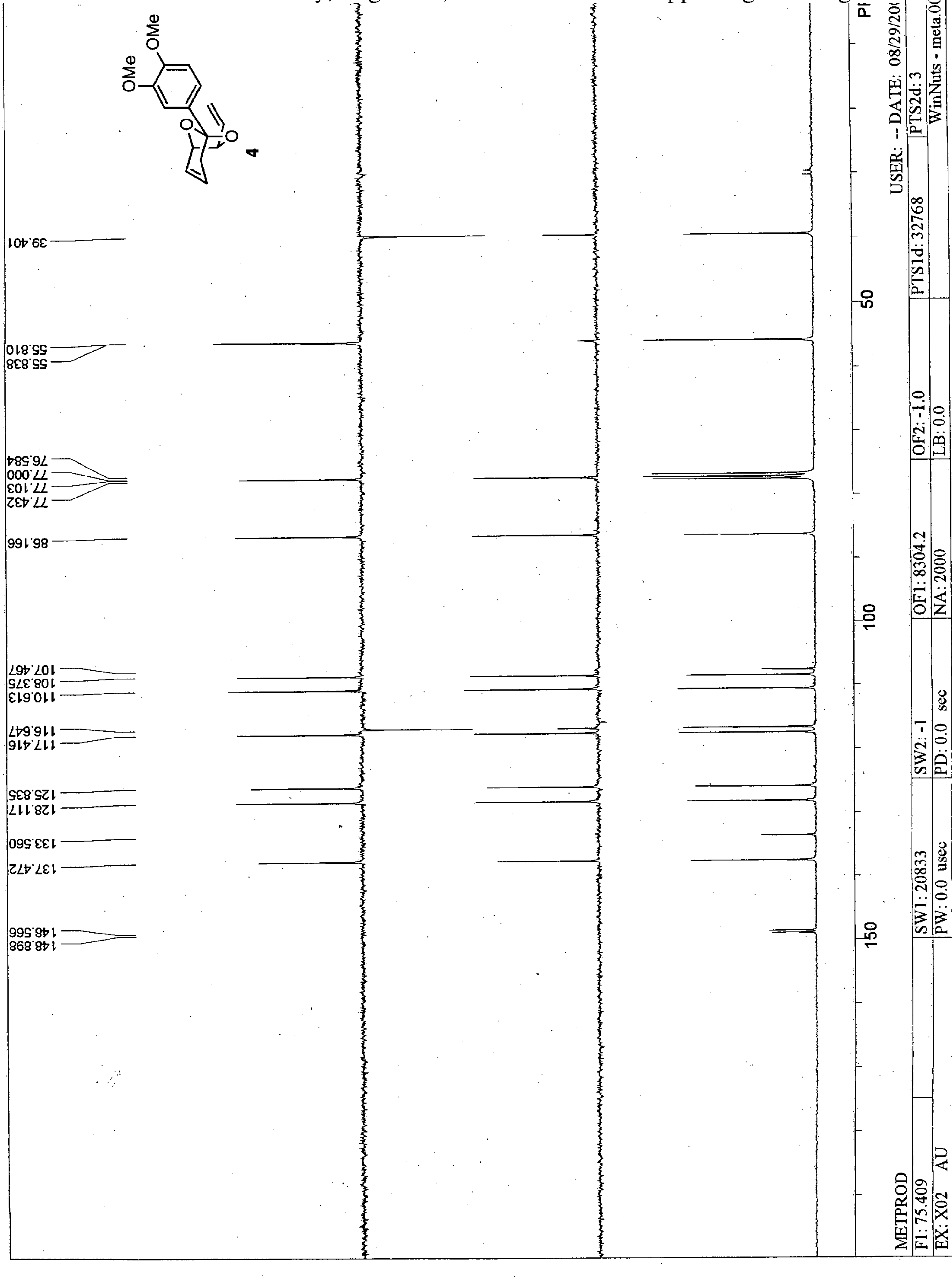

MeO
OMe
Br
8
27.157
33.752
40.034
55.825
55.905
76.580
77.000
77.418
81.809
83.948
108.777
110.303
110.471
117.725
119.120
119.381
133.023
134.414
136.136
148.556
PP
0
50
100
150
BROMOKETAL
F1: 75.409
EX: X02 AU
SW1: 20833
PW: 0.0 usec
SW2: -1
PD: 0.0 sec
OF1: 8304.6
NA: 2048
OF2: -1.0
LB: 0.0
PTS1d: 32768
USER: -- DATE: 09/06/200
PTS2d: 3
WinNuts - brketa.001

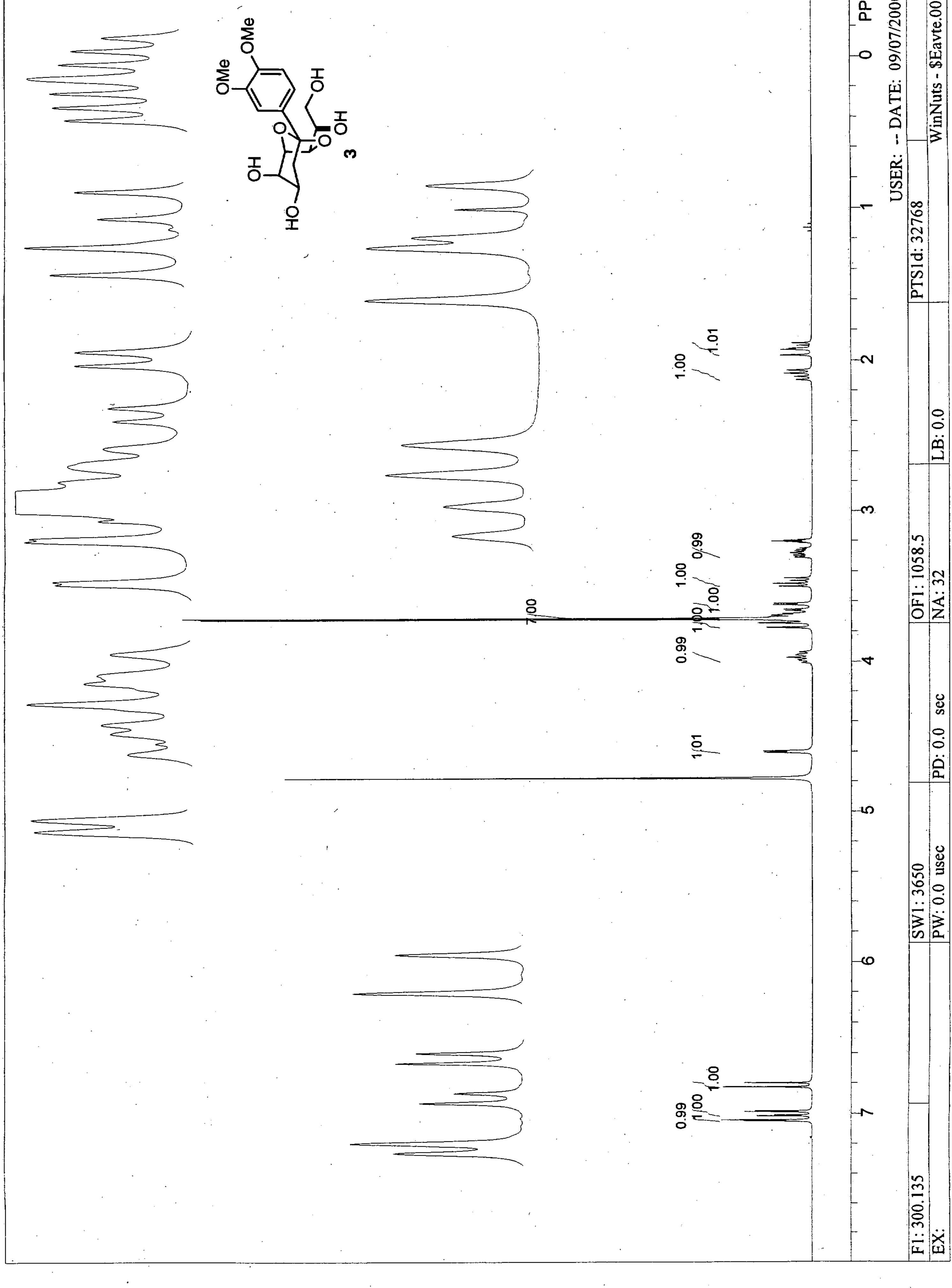

5

MeO
OMe
O
O
PPM
0
1
2
3
4
5
6
7
2.01
6.00
1.00
1.00
3.01
2.00
0.99
2.01
1.01
1.00
1.01
1.00
USER: -- DATE: 08/16/200
WinNuts - $Eav3112.001
PTS1d: 32768
LB: 0.0
OF1: 1088.1
NA: 16
PD: 0.0 sec
SW1: 3704
PW: 0.0 usec
F1: 300.134
EX:

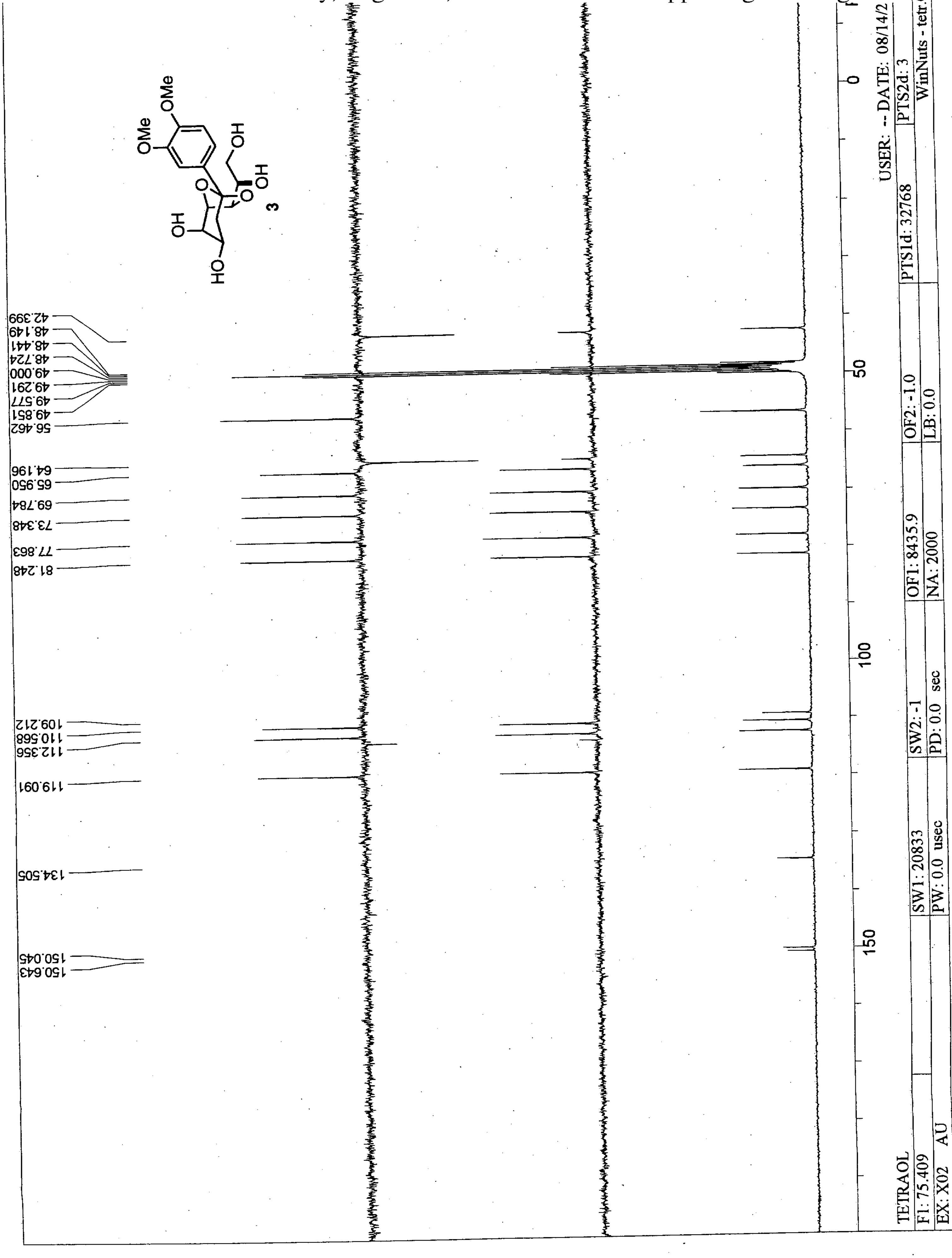

MeO
OMe
O
O
5
46.104
55.844
55.934
76.572
77.000
77.203
77.425
81.949
84.020
108.998
110.086
110.405
117.865
118.351
119.083
119.439
132.381
133.164
134.440
136.302
148.444
148.513
P
0
50
100
150
USER: --DATE: 08/16/20
PTS2d: 3
WinNuts - trien.001
PTS1d: 32768
OF2: -1.0
LB: 0.0
OF1: 8308.0
NA: 2000
SW2: -1
PD: 0.0 sec
SW1: 20833
PW: 0.0 usec
TRIENE1
F1: 75.409
EX: X02 AU

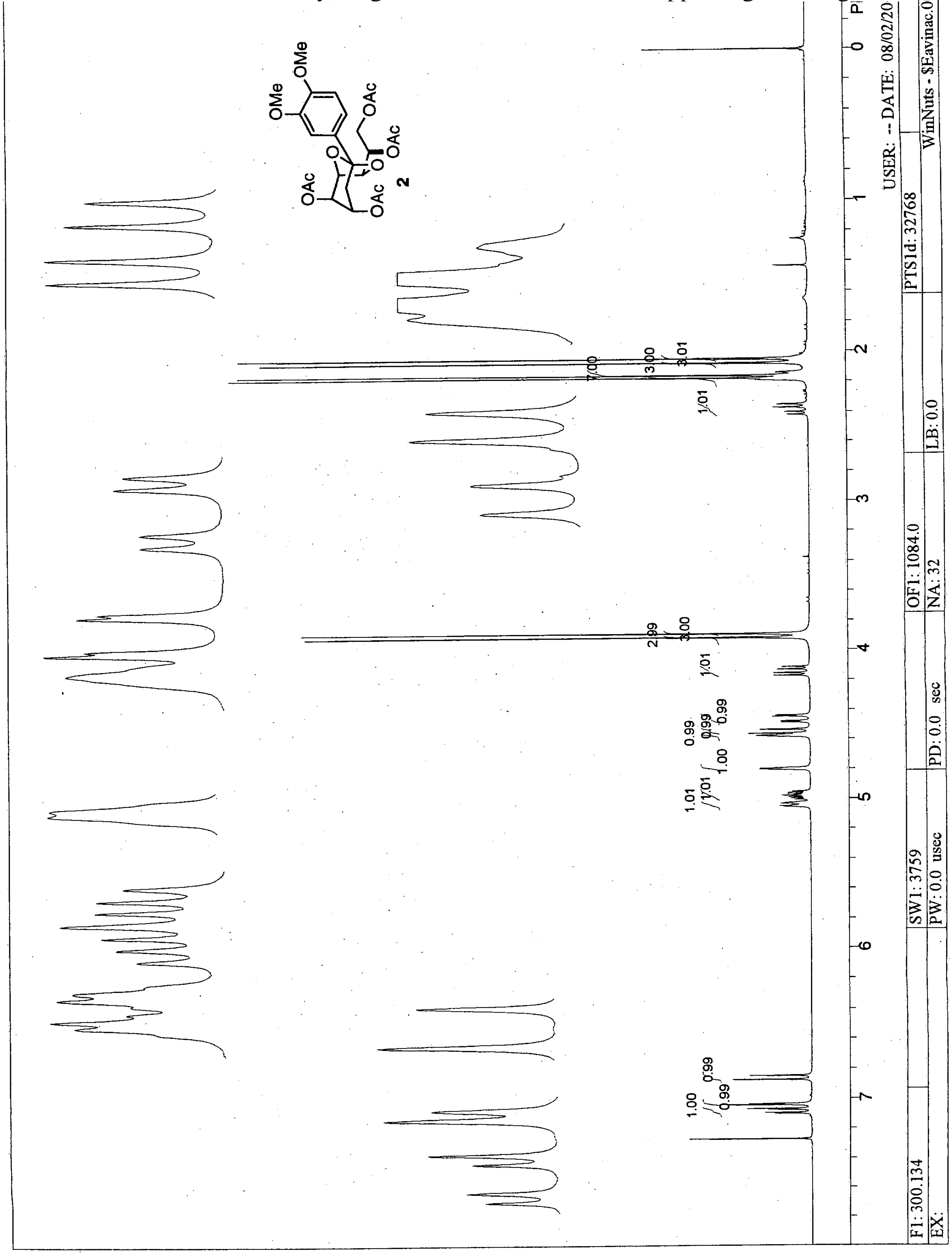

OMe
OMe
O
O
4
1.01
1.01
5.99
1.00
1.00
1.01
1.01
2.00
1.01
1.00
2.00
0
1
2
3
4
5
6
7
P
USER: -- DATE: 08/28/2C
WinNuts - metH.001
PTS1d: 32768
LB: 0.0
OF1: 1091.1
NA: 32
PD: 0.0 sec
SW1: 3704
PW: 0.0 usec
F1: 300.134
EX:

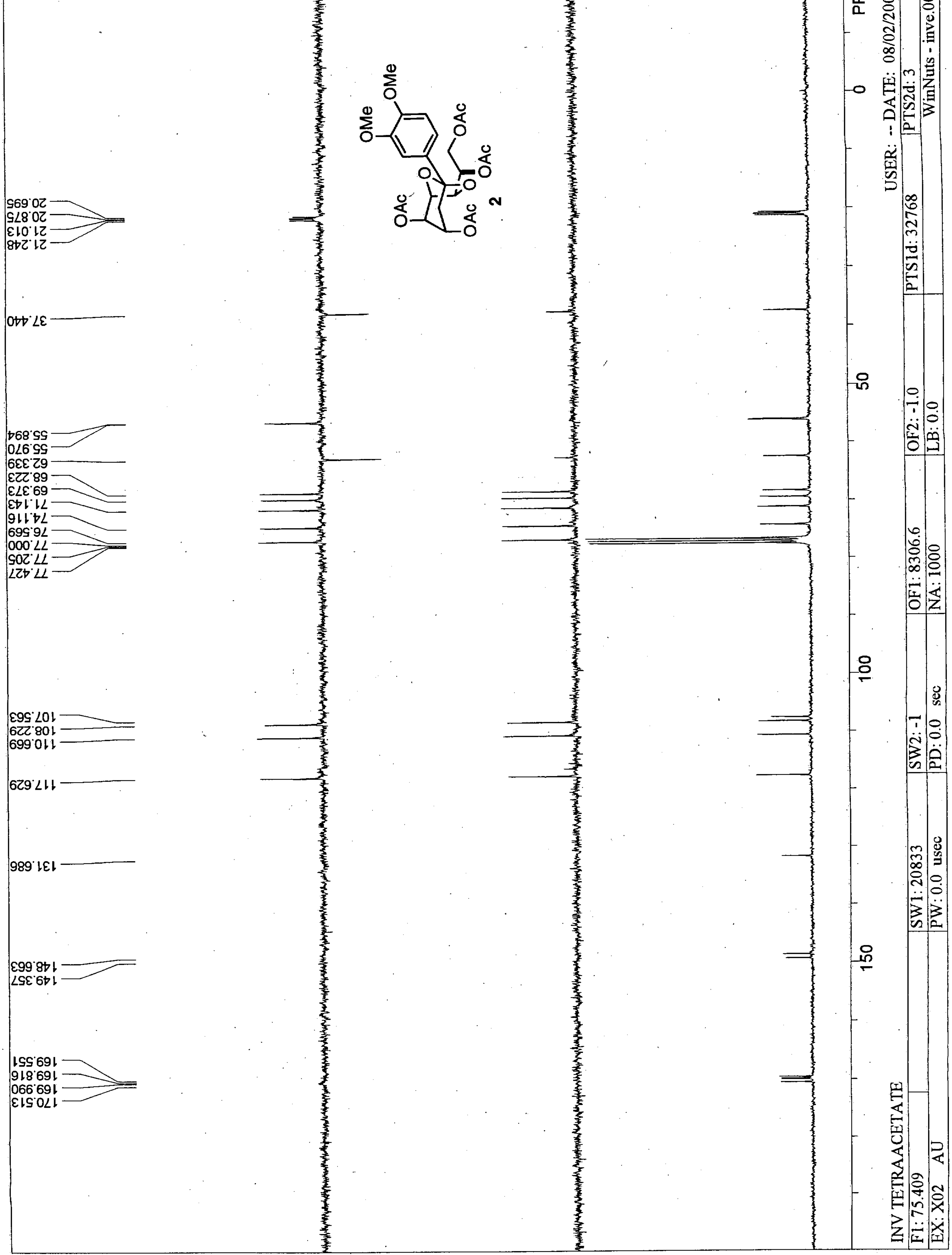

OMe
OMe
O
O
4
39.401
55.810
55.838
76.584
77.000
77.103
77.432
86.166
107.467
108.375
110.613
116.647
117.416
125.835
128.117
133.560
137.472
148.566
148.898
50
100
150
USER: --DATE: 08/29/20(
PTS1d: 32768
PTS2d: 3
WinNuts - meta.001
OF2: -1.0
LB: 0.0
OF1: 8304.2
NA: 2000
SW2: -1
PD: 0.0 sec
SW1: 20833
PW: 0.0 usec
METPROD
F1: 75.409
EX: X02 AU

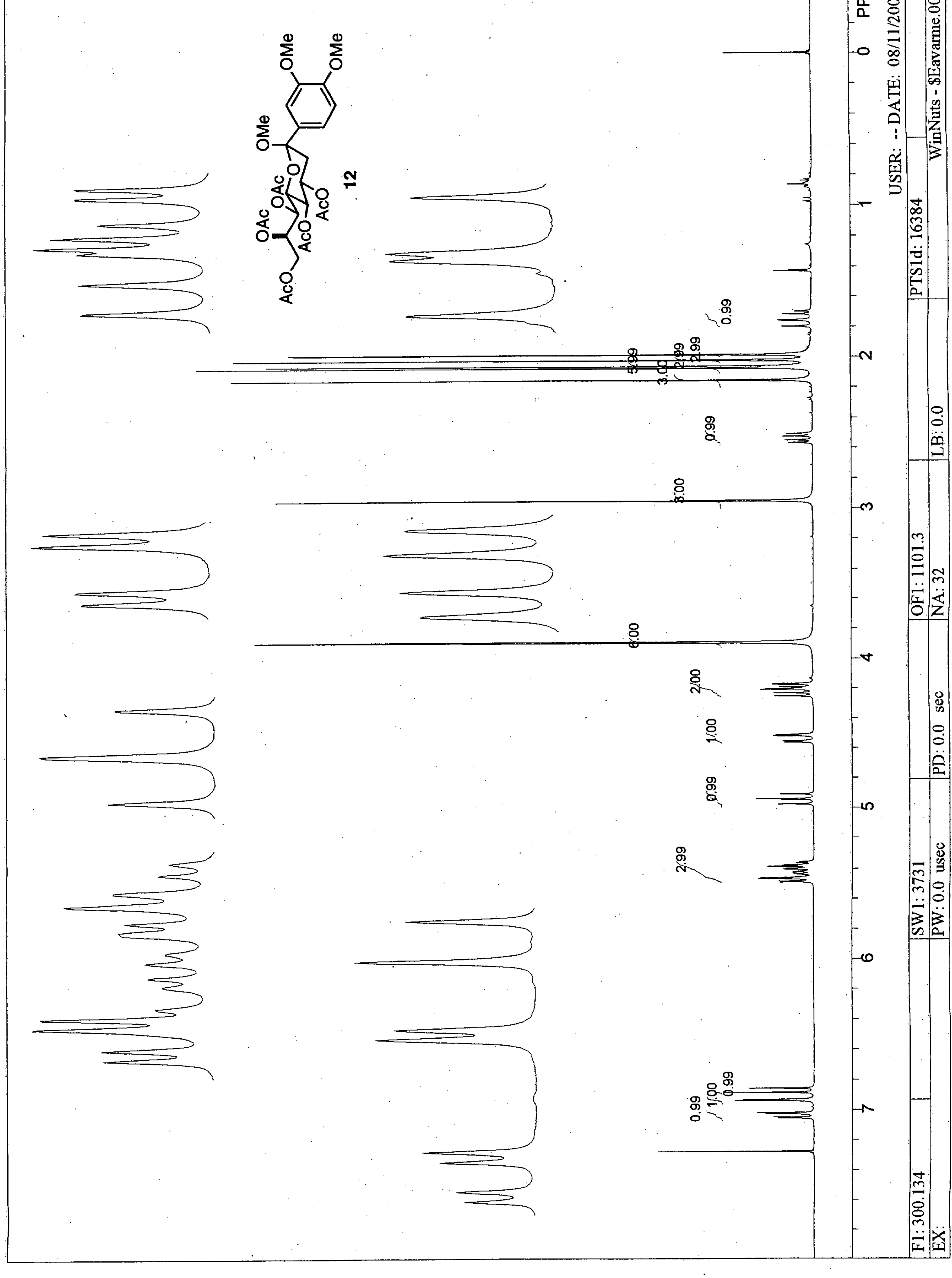


OMe
OMe
HO
OH
O
O
OH
OH
3
0.99
1.00
1.00
0.99
1.01
7.00
0.99
1.00
1.00
1.00
0.99
1.00
1.01
1.00
PPM
0
1
2
3
4
5
6
7
USER: -- DATE: 09/07/200
PTS1d: 32768
OF1: 1058.5
SW1: 3650
F1: 300.135
WinNuts - $Eavte.001
LB: 0.0
NA: 32
PD: 0.0 sec
PW: 0.0 usec
EX:

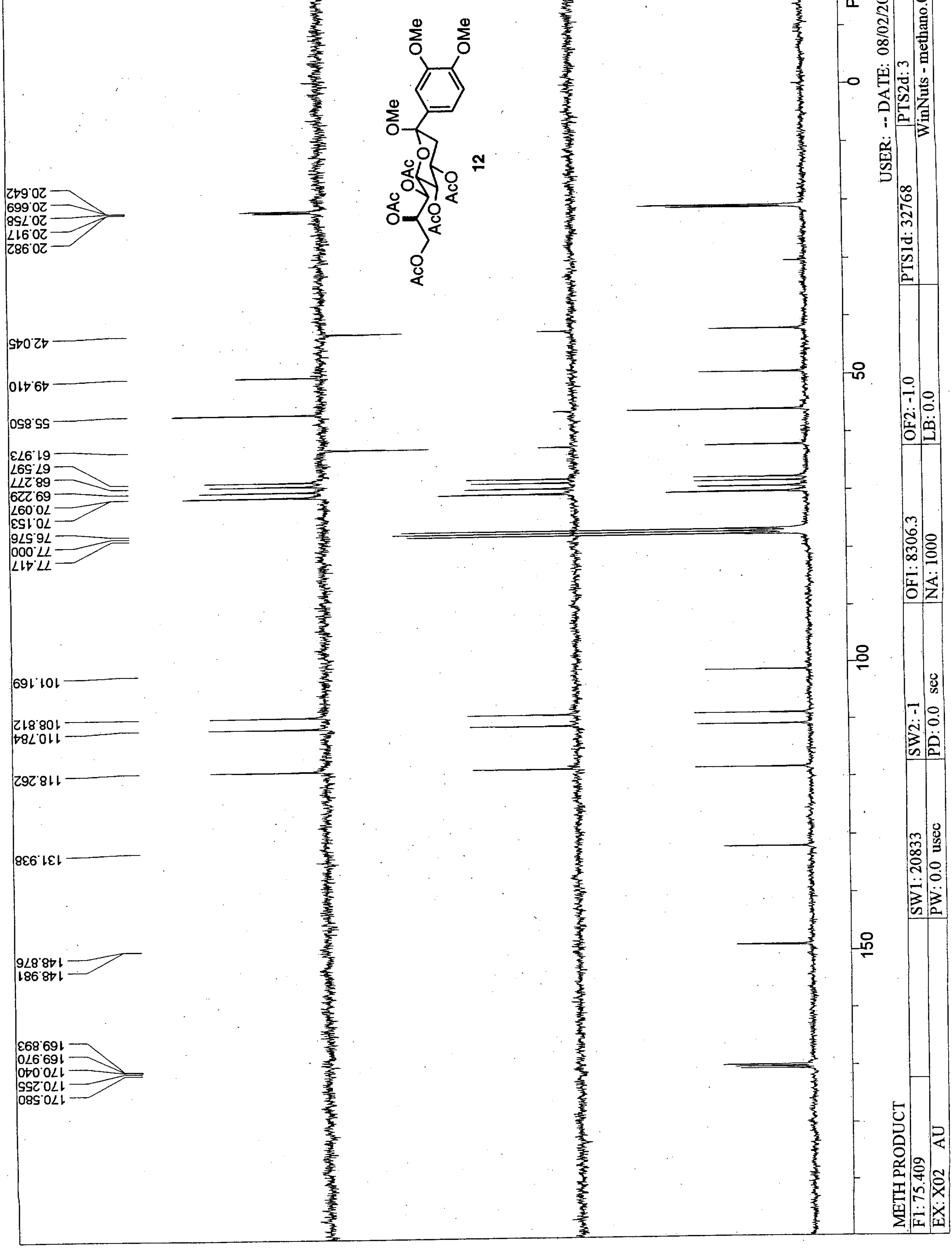

OMe
OMe
OH
HO
OH
HO
O
O
3
42.399
48.149
48.441
48.724
49.000
49.291
49.577
49.851
56.462
64.196
65.950
69.784
73.348
77.863
81.248
109.212
110.568
112.356
119.091
134.505
150.045
150.643
0
50
100
150
USER: -- DATE: 08/14/2
PTS2d: 3
WinNuts - tetr.001
PTS1d: 32768
OF2: -1.0
LB: 0.0
OF1: 8435.9
NA: 2000
SW2: -1
PD: 0.0 sec
SW1: 20833
PW: 0.0 usec
TETRAOL
F1: 75.409
EX: X02 AU

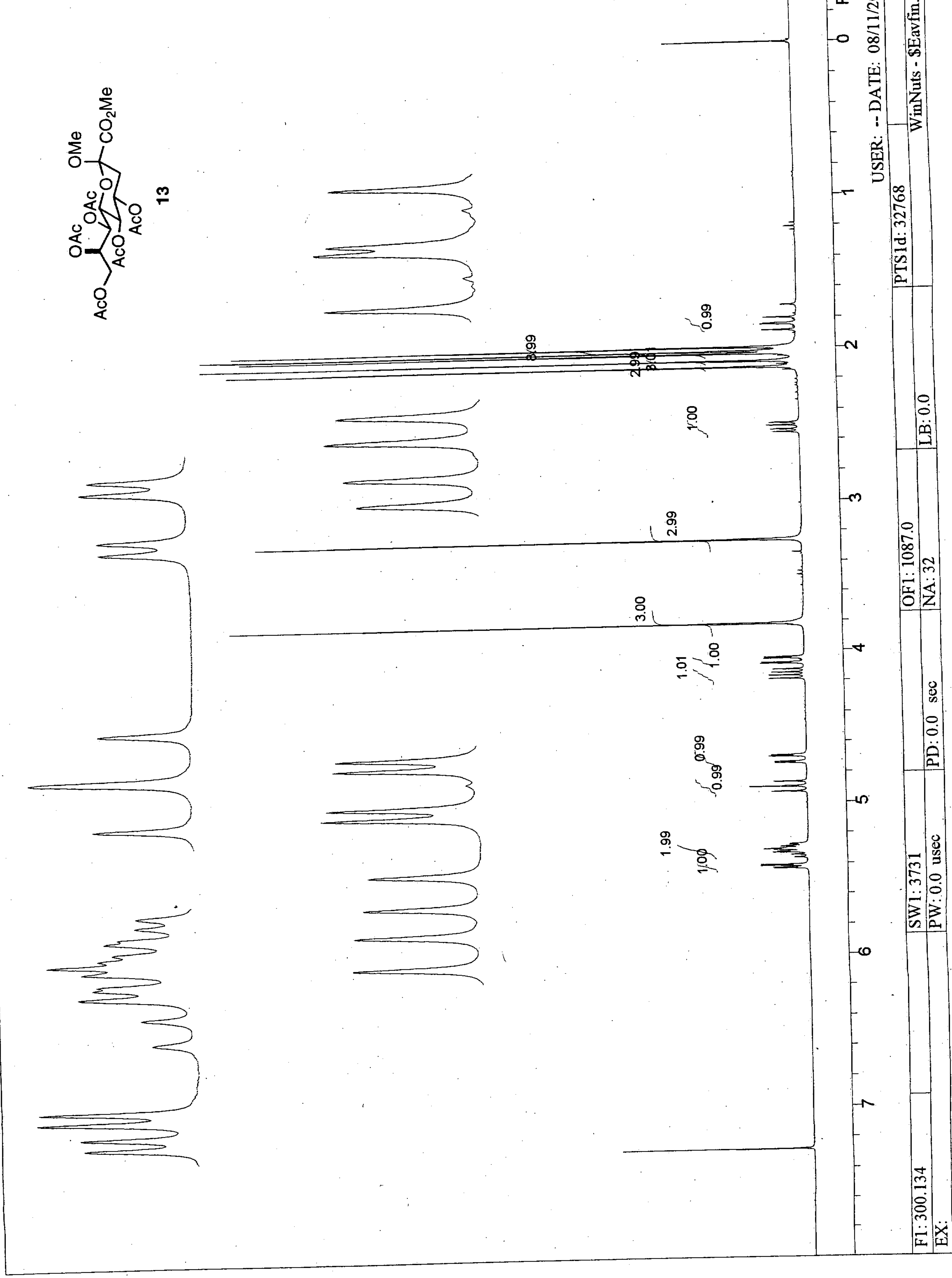

OMe
OMe
OAc
OAc
O
OAc
OAc
O
2
7.00
3.00
3.01
1.01
2.99
3.00
1.01
0.99
0.99
0.99
1.00
1.01
1.01
1.00
0.99
0.99
0
1
2
3
4
5
6
7
USER: -- DATE: 08/02/20
PTS1d: 32768
WinNuts - $Eavinac.001
LB: 0.0
OF1: 1084.0
NA: 32
PD: 0.0 sec
SW1: 3759
PW: 0.0 usec
F1: 300.134
EX:

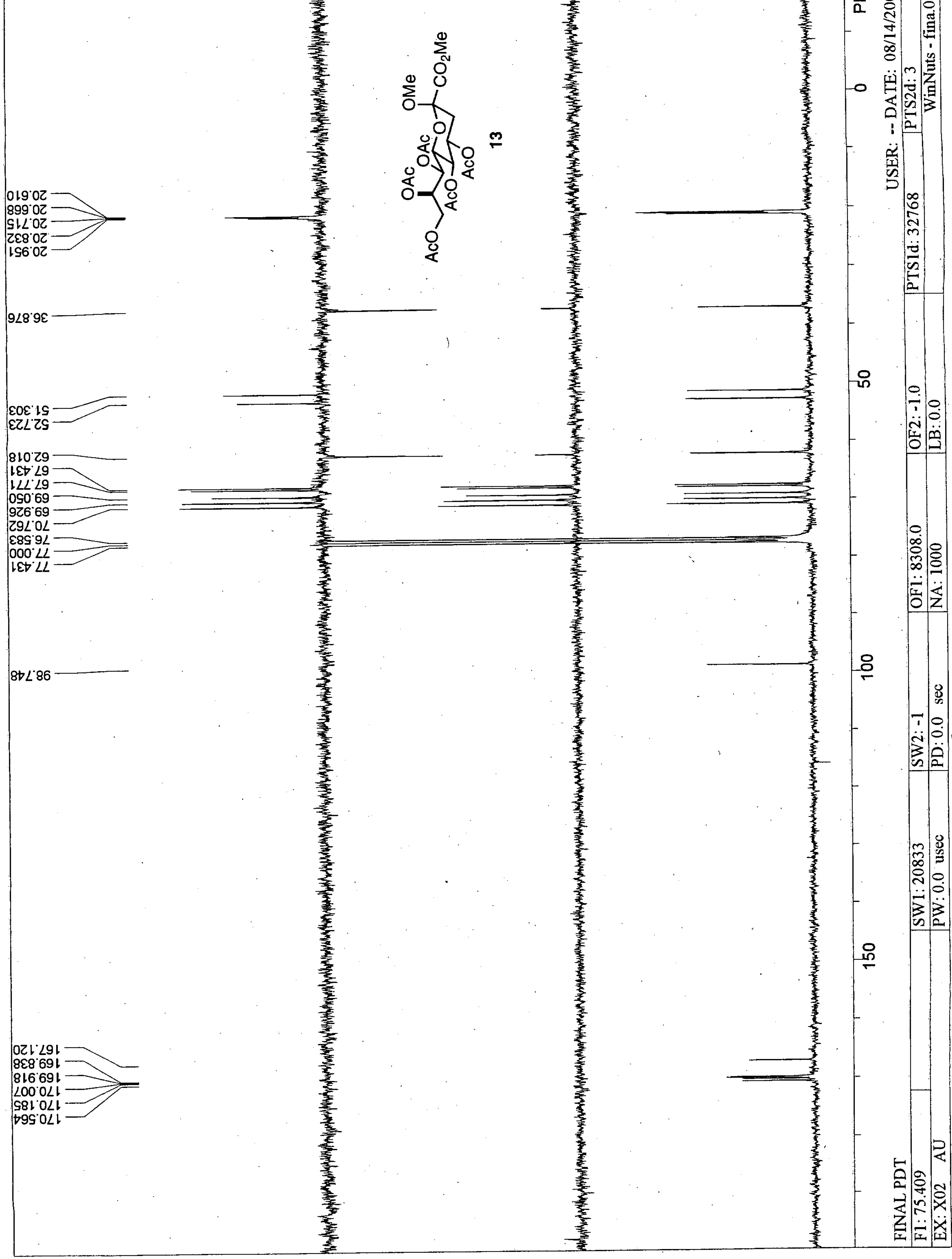

20.695
20.875
21.013
21.248
37.440
55.894
55.970
62.339
68.223
69.373
71.143
74.116
76.569
77.000
77.205
77.427
107.563
108.229
110.669
117.629
131.686
148.663
149.357
169.551
169.816
169.990
170.513
OMe
OMe
OAc
OAc
OAc
OAc
O
O
2
0
50
100
150
PP
INV TETRAACETATE
F1: 75.409
EX: X02 AU
SW1: 20833
PW: 0.0 usec
SW2: -1
PD: 0.0 sec
OF1: 8306.6
NA: 1000
OF2: -1.0
LB: 0.0
PTS1d: 32768
PTS2d: 3
USER: -- DATE: 08/02/20
WinNuts - inve.001


OMe
OMe
OMe
OAc
OAc
AcO
AcO
AcO
PF
0
1
2
3
4
5
6
7
0.99
5.99
3.00
2.99
2.99
0.99
3.00
6.00
2.00
1.00
0.99
2.99
0.99
1.00
0.99
USER: --DATE: 08/11/200
WinNuts - $Eavarme.001
PTS1d: 16384
LB: 0.0
OF1: 1101.3
NA: 32
PD: 0.0 sec
SW1: 3731
PW: 0.0 usec
F1: 300.134
EX:

**12**


20.642
20.669
20.758
20.917
20.982
42.045
49.410
55.850
61.973
67.597
68.277
69.229
70.097
70.153
76.576
77.000
77.417
101.169
108.812
110.784
118.262
131.938
148.876
148.981
169.893
169.970
170.040
170.255
170.580
OMe
OMe
OMe
OAc
OAc
AcO
AcO
AcO
O
12
F1
0
50
100
150
USER: -- DATE: 08/02/2(
PTS2d: 3
WinNuts - methano.001
PTS1d: 32768
OF2: -1.0
LB: 0.0
OF1: 8306.3
NA: 1000
SW2: -1
PD: 0.0 sec
SW1: 20833
PW: 0.0 usec
METH PRODUCT
F1: 75.409
EX: X02 AU


AcO
OAc
OAc
AcO
AcO
OMe
CO2Me
13
0.99
3.99
2.99
3.01
1.00
2.99
3.00
1.01
1.00
0.99
0.99
1.99
1.00
0
1
2
3
4
5
6
7
USER: -- DATE: 08/11/2
PTS1d: 32768
WinNuts - $Eavfm.001
LB: 0.0
OF1: 1087.0
NA: 32
PD: 0.0 sec
SW1: 3731
PW: 0.0 usec
F1: 300.134
EX:


20.610
20.668
20.715
20.832
20.951
36.876
51.303
52.723
62.018
67.431
67.771
69.050
69.926
70.762
76.583
77.000
77.431
98.748
167.120
169.838
169.918
170.007
170.185
170.564
OMe
$CO_2Me$
OAc
OAc
O
AcO
AcO
AcO
13
0
50
100
150
Pl
USER: -- DATE: 08/14/20
PTS1d: 32768
PTS2d: 3
WinNuts - fina.001
OF2: -1.0
LB: 0.0
OF1: 8308.0
NA: 1000
SW2: -1
PD: 0.0 sec
SW1: 20833
PW: 0.0 usec
FINAL PDT
F1: 75.409
EX: X02 AU