

Supporting Information

***ent*-Kaurane-Based Regio- and Stereoselective Inverse Electron Demand Hetero-Diels-Alder Reactions: Synthesis of Dihydropyran-Fused Diterpenoids**

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Table of Content

Experimental Procedure-----	S2-14
Key HMBC and NOESY correlations of compounds 8 and 9 -----	S15
Copies of ¹ H, ¹³ C NMR spectra of compound 3 -----	S16-17
Copies of ¹ H, ¹³ C NMR, HMBC and HMQC spectra of compound 4 -----	S18-21
Copies of ¹ H, ¹³ C NMR spectra of compounds 5 and 7 -----	S22-25
Copies of ¹ H, ¹³ C NMR, HMBC, HMQC and NOESY spectra of compounds 8 and 9 ----	S16-35
Copies of ¹ H, ¹³ C NMR spectra of compounds 11 – 18 -----	S36-51
Copies of ¹ H, ¹³ C NMR, NOESY, HMQC and HMBC spectra of compounds 19 and 20 --	S52-61
Copies of ¹ H, ¹³ C NMR spectra of compounds 21 – 22 , 24 – 27 and 29 -----	S62-75
Copies of ¹ H, ¹³ C NMR, HMBC, HMQC and NOESY spectra of compound 31 -----	S76-81
Copies of thermal ellipsoid plots (ORTEPs) for the crystal structures 5 and 20 -----	S82-83

EXPERIMENTAL PROCEDURE

General. All commercially available starting materials and solvents were reagent grade, and used without further purification. Oridonin was purchase from Shanxi Huike, China. Reactions were performed under a nitrogen atmosphere in dry glassware with magnetic stirring. Preparative column chromatography was performed using silica gel 60, particle size 0.063-0.200 mm (70-230 mesh, flash). Analytical TLC was carried out employing silica gel 60 F254 plates (Merck, Darmstadt). Visualization of the developed chromatograms was performed with detection by UV (254 nm). NMR spectra were recorded on a Bruker-600 (¹H, 600 MHz; ¹³C, 150 MHz) spectrometer or Bruker-300 (¹H, 300 MHz; ¹³C, 75 MHz). ¹H and ¹³C NMR spectra were recorded with TMS as an internal reference. Chemical shifts were expressed in ppm, and *J* values were given in Hz. High-resolution mass spectra (HRMS) were obtained from Thermo Fisher LTQ Orbitrap Elite mass spectrometer. Parameters include the following: Nano ESI spray voltage was 1.8 kV; Capillary temperature was 275 °C and the resolution was 60,000; Ionization was achieved by positive mode. Melting points were measured on a Thermo Scientific Electrothermal Digital Melting Point Apparatus. Purity of final compounds was higher than 95%, and determined by analytical HPLC, which was carried out on a Shimadzu HPLC system (model: CBM-20A LC-20AD SPD-20A UV/VIS).

Synthesis of

(2*R*,4*aR*,4*a'R*,5'*S*,6*aR*,6'*S*,6*a'R*,7*S*,8*S*,8*aR*,9'*S*,11*S*,11*a'S*,11*b'S*,13*aS*,13*bS*,13*cR*,14'*R*,17*R*)-5',6',7,8,14',17-hexahydroxy-4',4',6,6-tetramethyl-8',10-dimethylenehexadecahydro-3*H*-spiro[4*a*,13*c*-epoxy-8,13*b*-(epoxymethano)-8*a*,11-methanocyclohepta[3,4]benzo[1,2-*h*]chromene-2,2'-6,11*b*-(epoxymethano)-6*a*,9-methanocyclohepta[*a*]naphthalene]-1',7',9(3'*H*,4*H*,5*H*,8'*H*,10*H*)-trione (5).

To a solution of **4** (15 mg, 0.02 mmol) in dichloromethane (2 mL) was added ~70% *m*-CPBA (5.0 mg, 0.02 mmol) at 0 °C. The resulting mixture was stirred at rt for 24 h. The reaction mixture was then diluted with 3 mL of water and extracted with 10 mL of dichloromethane three times. The extract was washed with saturated NaHCO₃ (aq) solution (5 mL) and brine (5 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 60% EtOAc in hexanes to afford the desired product **5** as a colorless solid (12 mg, 80%). The chemical structure and absolute configurations of **5** were determined by X-ray analysis of its single crystal. $[\alpha]_D^{25} +62$ (*c* 0.10, CH₂Cl₂/CH₃OH = 10:1). ¹H NMR (600 MHz, CDCl₃/CD₃OD = 12:1) δ 6.49 (s, 1H), 6.18 (s, 1H), 5.82 (s, 1H), 5.59 (s, 1H), 4.89 (s, 1H), 4.80 (s, 1H), 4.35 (d, 1H, *J* = 10.2 Hz), 4.31 (s, 1H), 4.21 (d, 1H, *J* = 9.6 Hz), 4.15 (d, 1H, *J* = 10.2 Hz), 3.99 (d, 1H, *J* = 10.2 Hz), 3.73 (d, 2H, *J* = 7.8 Hz), 3.12 (d, 1H, *J* = 9.0 Hz), 2.95 (d, 1H, *J* = 9.6 Hz), 2.63 (dd, 1H, *J* = 13.2 Hz, 5.4 Hz), 2.51 (dt, 1H, *J* = 13.8 Hz, 8.4 Hz), 2.46 (d, 1H, *J* = 7.8 Hz), 2.37 (m, 1H), 2.19 (m, 1H), 2.11 (m, 1H), 2.01 (d, 1H, *J* = 15.0 Hz), 1.89 (m, 3H), 1.72 (t, 2H, *J* = 13.8 Hz), 1.58 (m, 5H), 1.52 (m, 1H), 1.27 (m, 2H), 1.22 (s, 3H), 1.20 (s, 3H), 1.06 (s, 3H), 0.93 (s, 3H). ¹³C NMR (150 MHz, CDCl₃/CD₃OD = 12:1) δ 207.5 (2C), 206.1, 151.7, 151.5, 122.2, 121.5, 98.4, 97.7, 86.0, 80.5, 73.1, 73.0, 72.9, 72.8, 66.2, 66.0, 64.1, 61.7 (2C), 57.8, 57.4, 52.3, 47.0, 43.8, 43.4, 41.9, 33.1, 32.5, 31.1, 30.8, 30.2, 30.0, 29.4, 27.3, 25.6, 25.4, 22.5, 19.3, 18.6. HRMS Calcd for C₄₂H₅₂O₁₃: [M + H]⁺ 765.3481; found 765.3476.

Synthesis of (3*S*,3*aR*,3*a*¹*R*,6*aR*,7*S*,7*aR*,11*aS*,11*bS*)-7-hydroxy-5,5,8,8-tetramethyl-15-methyleneoctahydro-1*H*-6*a*,11*a*-(epoxymethano)-3,3*a*¹-ethanophenanthro[1,10-*de*][1,3]dioxine-11,14(2*H*)-dione (6**).**

To a solution of **2** (400 mg, 0.9 mmol) in acetone (20 mL) were added *p*-TsOH (20 mg) and 2,2-dimethoxypropane (1.6 mL) at room temperature. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with saturated NaHCO₃ aqueous solution and brine, dried over anhydrous Na₂SO₄, filtered, and evaporated to afford compound **6** (416 mg, 95%) as a colorless gel.¹

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-ethoxy-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (11) and (2*S*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-ethoxy-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (12).

A mixture of **6** (50 mg, 0.12 mmol), dimethylammonium chloride (21 mg, 0.26 mmol), and paraformaldehyde (8 mg) in 1,4-dioxane (2 mL) was refluxed for 4 h. The reaction mixture was then diluted with 3 mL of water and extracted with 10 mL of dichloromethane three times. The extract was washed with saturated NaHCO₃ (aq) solution (5 mL) and brine (5 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated to give an oily residue. Without any purification, the residue was directly dissolved in *n*-butyl vinyl ether (1 mL) in the presence of Yb(fod)₃ (11 mg, 0.01 mmol). The resulting mixture was stirred at 32 °C for 72 h. The reaction mixture was then diluted with 3 mL of water and extracted with 10 mL of dichloromethane three times. The extract was washed with brine (5 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 15%

EtOAc in hexanes to afford the desired product **11** (3.7 mg) and **12** (34.0 mg) as colorless amorphous gel in total 59% yield (2 steps).

11: $[\alpha]_D^{25} +8$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.54 (s, 1H), 5.30 (d, 1H, *J* = 12.0 Hz), 4.91 (m, 1H), 4.85 (d, 1H, *J* = 1.2 Hz), 4.23 (dd, 1H, *J* = 9.3 Hz, 1.2 Hz), 4.00 (d, 1H, *J* = 9.3 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.60 (dq, 1H, *J* = 9.3 Hz, 6.9 Hz), 3.44 (dq, 1H, *J* = 9.3 Hz, 6.9 Hz), 3.03 (d, 1H, *J* = 9.6 Hz), 2.48 (m, 1H), 1.86 (m, 9H), 1.65 (s, 3H), 1.51 (m, 2H), 1.34 (s, 3H), 1.16 (s, 3H), 1.14 (t, 3H, *J* = 7.2 Hz), 1.01 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 140.8, 119.9, 108.9, 100.9, 95.4, 95.2, 72.1, 70.1, 64.1, 62.9, 59.1, 56.5, 50.1, 45.2, 40.6, 40.3, 32.9, 30.8, 30.6, 30.2, 26.9, 25.3, 22.1, 21.0, 20.6, 15.1. HRMS Calcd for C₂₈H₃₈O₇: [M + H]⁺ 487.2690; found 487.2682.

12: $[\alpha]_D^{25} +102$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.54 (s, 1H), 5.34 (d, 1H, *J* = 12.0 Hz), 4.86 (d, 1H, *J* = 1.8 Hz), 4.60 (dd, 1H, *J* = 8.7 Hz, 1.8 Hz), 4.18 (d, 1H, *J* = 9.3 Hz), 3.99 (d, 1H, *J* = 9.3 Hz), 3.86 (dd, 1H, *J* = 12.0 Hz, 8.7 Hz), 3.83 (dq, 1H, *J* = 9.6 Hz, 6.9 Hz), 3.53 (dq, 1H, *J* = 9.6 Hz, 7.2 Hz), 2.50 (m, 1H), 1.97 (m, 7H), 1.67 (m, 2H), 1.65 (s, 3H), 1.54 (m, 2H), 1.34 (s, 3H), 1.22 (t, 3H, *J* = 7.2 Hz), 1.17 (s, 3H), 1.03 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 142.7, 120.0, 107.5, 100.9, 99.7, 95.4, 72.0, 70.1, 64.4, 63.9, 58.6, 56.4, 49.7, 44.7, 40.6, 40.3, 32.9, 30.8 (2C), 30.1, 28.4, 25.9, 25.3, 21.2, 20.4, 15.2. HRMS Calcd for C₂₈H₃₈O₇: [M + H]⁺ 487.2690; found 487.2684.

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-7-hydroxy-2-isobutoxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (13) and (2*S*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-7-hydroxy-2-isobutoxy-6,6,9,9-tetramethyl-

16-methylene-2,3,4,5,6,6a,7,10a,11,12,13,13a-dodecahydro-7a,13b-(epoxymethano)-7a¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (14).

Compounds **13** (3.6 mg) and **14** (31.0 mg) were prepared in 54% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compounds were obtained as colorless amorphous gel.

13: $[\alpha]_D^{25} +8$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.54 (s, 1H), 5.32 (d, 1H, *J* = 12.0 Hz), 4.88 (m, 1H), 4.85 (d, 1H, *J* = 0.9 Hz), 4.23 (d, 1H, *J* = 10.2 Hz), 4.01 (d, 1H, *J* = 9.9 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.25 (dd, 1H, *J* = 8.7 Hz, 7.2 Hz), 3.15 (dd, 1H, *J* = 8.7 Hz, 6.0 Hz), 3.03 (d, 1H, *J* = 9.0 Hz), 2.48 (m, 1H), 1.83 (m, 9H), 1.66 (s, 3H), 1.56 (m, 3H), 1.35 (s, 3H), 1.16 (s, 3H), 1.00 (s, 3H), 0.85 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 140.7, 119.9, 108.8, 100.9, 95.5, 95.4, 74.4, 72.0, 70.1, 64.2, 59.0, 56.5, 50.1, 45.2, 40.6, 40.3, 32.8, 30.8, 30.6, 30.1, 28.5, 26.8, 25.3, 21.8, 20.9, 20.6, 19.5, 19.3. HRMS Calcd for C₃₀H₄₂O₇: [M + H]⁺ 515.3003; found 515.3011.

14: $[\alpha]_D^{25} +90$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.54 (s, 1H), 5.34 (d, 1H, *J* = 12.0 Hz), 4.87 (d, 1H, *J* = 1.2 Hz), 4.57 (d, 1H, *J* = 9.0 Hz), 4.17 (d, 1H, *J* = 9.0 Hz), 3.99 (d, 1H, *J* = 9.3 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.53 (dd, 1H, *J* = 9.3 Hz, 6.6 Hz), 3.20 (dd, 1H, *J* = 9.3 Hz, 6.6 Hz), 3.03 (d, 1H, *J* = 8.4 Hz), 2.50 (m, 1H), 1.94 (m, 9H), 1.66 (s, 3H), 1.53 (m, 3H), 1.34 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H), 0.91 (dt, 6H, *J* = 0.6 Hz, 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 142.7, 120.0, 107.4, 100.9, 100.0, 95.4, 75.8, 72.0, 70.1, 63.9, 58.6, 56.5, 49.8, 44.7, 40.5, 40.3, 32.8, 30.8 (2C), 30.1, 28.5, 28.3, 25.8, 25.4, 21.2, 20.4, 19.3 (2C). HRMS Calcd for C₃₀H₄₂O₇: [M + H]⁺ 515.3003; found 515.2992.

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(*tert*-butoxy)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6a,7,10a,11,12,13,13a-dodecahydro-7a,13b-

(epoxymethano)-7a¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (15)
and **(2*S*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(*tert*-butoxy)-7-hydroxy-6,6,9,9-**
tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-

(epoxymethano)-7a¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (16).

Compounds **15** (3.5 mg) and **16** (29.6 mg) were prepared in 52% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compounds were obtained as colorless amorphous gel.

15: $[\alpha]_{\text{D}}^{25} +10$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.13 (s, 1H), 5.53 (s, 1H), 5.31 (d, 1H, *J* = 11.7 Hz), 5.19 (s, 1H), 4.84 (s, 1H), 4.18 (d, 1H, *J* = 9.6 Hz), 3.98 (d, 1H, *J* = 9.6 Hz), 3.87 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.03 (d, 1H, *J* = 9.0 Hz), 2.48 (m, 1H), 2.02 (m, 2H), 1.86 (m, 3H), 1.66 (s, 3H), 1.64 (m, 4H), 1.53 (m, 2H), 1.34 (s, 3H), 1.68 (s, 9H), 1.15 (s, 3H), 1.01 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 151.0, 141.2, 119.8, 108.1, 100.8, 95.3, 89.8, 73.9, 72.0, 70.1, 64.4, 59.1, 56.6, 50.2, 45.4, 40.3 (2C), 32.9, 30.8, 30.5, 30.1, 28.8 (3C), 28.4, 25.4, 21.6, 20.8, 20.6. HRMS Calcd for C₃₀H₄₂O₇: [M + H]⁺ 515.3003; found 515.3005.

16: $[\alpha]_{\text{D}}^{25} +96$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.13 (s, 1H), 5.54 (s, 1H), 5.34 (d, 1H, *J* = 12.0 Hz), 4.86 (d, 1H, *J* = 1.5 Hz), 4.75 (dd, 1H, *J* = 2.1 Hz, 9.0 Hz), 4.14 (d, 1H, *J* = 9.6 Hz), 3.98 (d, 1H, *J* = 9.9 Hz), 3.88 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.03 (d, 1H, *J* = 9.6 Hz), 2.48 (m, 1H), 1.92 (m, 7H), 1.66 (s, 3H), 1.64 (m, 2H), 1.52 (m, 2H), 1.34 (s, 3H), 1.23 (s, 9H), 1.17 (s, 3H), 1.04 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 143.2, 119.9, 107.0, 100.9, 95.4, 94.7, 75.0, 72.0, 70.1, 64.2, 58.5, 56.5, 49.9, 44.7, 40.3, 40.3, 32.8, 30.9, 30.7, 30.1, 29.9, 28.8 (3C), 26.7, 25.3, 21.2, 20.7. HRMS Calcd for C₃₀H₄₂O₇: [M + H]⁺ 515.3003; found 515.3004.

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(allyloxy)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (17) and (2*S*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(allyloxy)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (18)

Compounds **17** (3.5 mg) and **18** (31.8 mg) were prepared in 57% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compounds were obtained as colorless amorphous gel.

17: $[\alpha]_D^{25} -12$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.83 (m, 1H), 5.54 (s, 1H), 5.32 (d, 1H, *J* = 12.0 Hz), 5.24 (dd, 1H, *J* = 17.1 Hz, 1.8 Hz), 5.15 (dd, 1H, *J* = 10.2 Hz, 1.5 Hz), 4.96 (t, 1H, *J* = 1.2 Hz), 4.85 (d, 1H, *J* = 1.2 Hz), 4.23 (dd, 1H, *J* = 9.9 Hz, 0.6 Hz), 4.08 (m, 1H), 4.01 (d, 1H, *J* = 9.9 Hz), 3.95 (m, 1H), 3.90 (dd, 1H, *J* = 12.0 Hz, 8.7 Hz), 3.04 (d, 1H, *J* = 9.0 Hz), 2.49 (m, 1H), 1.86 (m, 9H), 1.65 (s, 3H), 1.52 (m, 2H), 1.34 (s, 3H), 1.16 (s, 3H), 1.00 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 140.7, 134.1, 120.0, 116.7, 109.1, 100.9, 95.4, 94.6, 72.0, 70.1, 67.9, 64.1, 59.0, 56.5, 50.0, 45.2, 40.6, 40.3, 32.9, 30.7, 30.6, 30.1, 26.7, 25.3, 21.9, 21.0, 20.5. HRMS Calcd for C₂₉H₃₈O₇: [M + H]⁺ Exact Mass: 499.2690; found 499.2681.

18: $[\alpha]_D^{25} +106$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.89 (m, 1H), 5.54 (s, 1H), 5.34 (d, 1H, *J* = 12.0 Hz), 5.28 (dd, 1H, *J* = 17.1 Hz, 1.5 Hz), 5.21 (dd, 1H, *J* = 10.8 Hz, 1.2 Hz), 4.86 (d, 1H, *J* = 0.3 Hz), 4.64 (d, 1H, *J* = 8.4 Hz), 4.27 (dd, 1H, *J* = 12.6 Hz, 5.1 Hz), 4.18 (d, 1H, *J* = 9.3 Hz), 4.05 (dd, 1H, *J* = 12.9 Hz, 6.0 Hz), 3.99 (d, 1H, *J* = 9.9 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.04 (d, 1H, *J* = 9.3 Hz), 2.49 (m, 1H), 1.95 (m, 7H), 1.71 (m, 2H),

1.66 (s, 3H), 1.54 (m, 2H), 1.34 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 150.9, 142.6, 134.1, 120.0, 117.4, 107.7, 100.9, 99.0, 95.4, 72.0, 70.1, 69.6, 63.9, 58.6, 56.5, 49.7, 44.8, 40.6, 40.3, 32.9, 30.8 (2C), 30.1, 28.2, 25.8, 25.4, 21.3, 20.4. HRMS Calcd for $\text{C}_{29}\text{H}_{38}\text{O}_7$: $[\text{M} + \text{H}]^+$ 499.2690; found 499.2691.

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(2-chloroethoxy)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (19) and (2*S*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(2-chloroethoxy)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (20).

Compounds **19** (3.5 mg) and **20** (31.4 mg) were prepared in 54% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compounds were obtained as colorless amorphous gel.

19: $[\alpha]_{\text{D}}^{25} -14$ (*c* 0.10, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3): δ 6.14 (s, 1H), 5.54 (s, 1H), 5.31 (d, 1H, $J = 12.0$ Hz), 4.98 (t, 1H, $J = 2.1$ Hz), 4.84 (d, 1H, $J = 1.5$ Hz), 4.21 (dd, 1H, $J = 9.6$ Hz, 1.2 Hz), 4.02 (d, 1H, $J = 9.3$ Hz), 3.89 (dd, 1H, $J = 12.0$ Hz, 8.7 Hz), 3.77 (dt, 1H, $J = 10.8$ Hz, 5.4 Hz), 3.67 (m, 1H), 3.56 (t, 2H, $J = 5.7$ Hz), 3.04 (d, 1H, $J = 9.3$ Hz), 2.49 (m, 1H), 1.87 (m, 9H), 1.65 (s, 3H), 1.52 (m, 2H), 1.34 (s, 3H), 1.16 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 150.9, 140.6, 120.0, 109.3, 100.9, 95.6, 95.4, 72.0, 70.1, 67.7, 64.0, 59.0, 56.5, 50.0, 45.2, 42.7, 40.5, 40.3, 32.9, 30.7, 30.6, 30.1, 26.5, 25.3, 21.6, 21.0, 20.6. HRMS Calcd for $\text{C}_{28}\text{H}_{37}\text{ClO}_7$: $[\text{M} + \text{H}]^+$ 521.2301; found 521.2296.

20: $[\alpha]_{\text{D}}^{25} +96$ (*c* 0.10, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3): δ 6.14 (s, 1H), 5.55 (s, 1H), 5.34 (d, 1H, $J = 12.0$ Hz), 4.86 (d, 1H, $J = 1.2$ Hz), 4.66 (dd, 1H, $J = 9.0$ Hz, 1.8 Hz), 4.16 (dd, 1H, J

= 9.6 Hz, 0.9 Hz), 4.01 (m, 2H), 3.89 (dd, 1H, $J = 12.3$ Hz, 9.0 Hz), 3.76 (m, 1H), 3.63 (t, 2H, $J = 6.0$ Hz), 3.04 (d, 1H, $J = 9.3$ Hz), 2.49 (m, 1H), 1.96 (m, 7H), 1.68 (m, 2H), 1.66 (s, 3H), 1.54 (m, 2H), 1.34 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 150.9, 142.6, 120.1, 107.9, 100.9, 100.1, 95.4, 72.0, 70.1, 69.0, 63.9, 58.6, 56.4, 49.7, 44.7, 42.8, 40.5, 40.3, 32.9, 30.8 (2C), 30.1, 28.1, 25.6, 25.4, 21.2, 20.5. HRMS Calcd for $\text{C}_{28}\text{H}_{37}\text{ClO}_7$: $[\text{M} + \text{H}]^+$ 521.2301; found 521.2291.

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-7-hydroxy-2-(4-hydroxybutoxy)-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (21) and (2*S*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-7-hydroxy-2-(4-hydroxybutoxy)-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (22)

Compounds **21** (22.3 mg) and **22** (17.9 mg) were prepared in 61% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compounds were obtained as colorless amorphous gel.

21: $[\alpha]_D^{25} +8$ (c 0.10, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3): δ 6.14 (s, 1H), 5.54 (s, 1H), 5.32 (d, 1H, $J = 12.0$ Hz), 4.91 (t, 1H, $J = 2.1$ Hz), 4.84 (s, 1H), 4.22 (d, 1H, $J = 8.4$ Hz), 4.00 (d, 1H, $J = 9.3$ Hz), 3.89 (dd, 1H, $J = 12.0$ Hz, 8.4 Hz), 3.62 (m, 3H), 3.44 (m, 1H), 3.03 (d, 1H, $J = 9.3$ Hz), 2.49 (m, 1H), 1.87 (m, 9H), 1.65 (s, 3H), 1.62 (m, 5H), 1.52 (m, 2H), 1.34 (s, 3H), 1.16 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 150.9, 140.7, 120.0, 108.9, 100.9, 95.5, 95.4, 72.0, 70.1, 67.6, 64.1, 62.6, 59.0, 56.5, 50.0, 45.2, 40.6, 40.3, 32.9, 30.7, 30.6, 30.1, 30.0, 26.7, 26.4, 25.3, 21.8, 21.0, 20.6. HRMS Calcd for $\text{C}_{30}\text{H}_{42}\text{O}_8$: $[\text{M} + \text{H}]^+$ 531.2952; found 531.2944.

22: $[\alpha]_D^{25} +72$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.55 (s, 1H), 5.35 (d, 1H, *J* = 12.0 Hz), 4.86 (d, 1H, *J* = 0.9 Hz), 4.60 (dd, 1H, *J* = 9.0 Hz, 1.2 Hz), 4.17 (d, 1H, *J* = 9.6 Hz), 3.99 (d, 1H, *J* = 9.9 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.83 (m, 1H), 3.66 (m, 2H), 3.50 (m, 1H), 3.04 (d, 1H, *J* = 9.3 Hz), 2.50 (m, 1H), 1.94 (m, 8H), 1.66 (m, 9H), 1.54 (m, 2H), 1.34 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.8, 150.9, 142.7, 120.1, 107.6, 100.9, 99.8, 95.4, 72.0, 70.1, 68.9, 63.9, 62.6, 58.6, 56.5, 49.7, 44.7, 40.6, 40.3, 32.9, 30.8 (2C), 30.1, 29.8, 28.3, 26.4, 25.8, 25.4, 21.2, 20.5. HRMS Calcd for C₃₀H₄₂O₈: [M + H]⁺ 531.2952; found 531.2943.

When the reaction was catalyzed by Eu(fod)₃ at rt, **21** (43.4 mg) was obtained in 70% yield (2 steps) as the sole product.

Synthesis of (2*R*,6*aR*,7*S*,7*aR*,7*a*¹*R*,10*aR*,11*S*,13*aS*,13*bS*)-2-(ethylthio)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6*a*,7,10*a*,11,12,13,13*a*-dodecahydro-7*a*,13*b*-(epoxymethano)-7*a*¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (24**)**

Compound **24** (45 mg) was prepared in 72% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compound was obtained as a colorless amorphous gel. $[\alpha]_D^{25} +112$ (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.14 (s, 1H), 5.55 (d, 1H, *J* = 0.3 Hz), 5.34 (d, 1H, *J* = 12.0 Hz), 4.86 (d, 1H, *J* = 1.2 Hz), 4.75 (dd, 1H, *J* = 9.9 Hz, 1.8 Hz), 4.16 (dd, 1H, *J* = 9.6 Hz, 1.5 Hz), 3.99 (d, 1H, *J* = 9.6 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 8.7 Hz), 3.03 (dd, 1H, *J* = 9.6 Hz, 0.9 Hz), 2.67 (m, 2H), 2.50 (m, 1H), 1.97 (m, 9H), 1.65 (s, 3H), 1.55 (m, 2H), 1.34 (s, 3H), 1.28 (t, 3H, *J* = 7.2 Hz), 1.17 (s, 3H), 1.04 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 150.9, 144.6, 120.0, 107.8, 100.8, 95.4, 80.1, 72.0, 70.0, 63.8, 58.7, 56.4, 49.7, 45.0, 40.6, 40.3, 32.8, 30.8, 30.7, 30.1, 28.8, 26.7, 25.3, 24.7, 21.2, 20.4, 15.0. HRMS Calcd for C₂₈H₃₈O₆S: [M + H]⁺ 503.2462; found 503.2449.

Synthesis of (3aR,3a¹R,4S,4aR,7aS,11aR,12bS,12cS,15S,15aR)-4-hydroxy-2,2,5,5-tetramethyl-16-methylene-4a,5,6,7,7a,8,9,10,11a,12c,13,14,15,15a-tetradecahydro-4H-3a,12b-(epoxymethano)-3a¹,15-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]pyrano[2,3-b]chromen-17-one (27)

Compound **27** (21 mg) was prepared in 35% yield (2 steps) by a procedure similar to that used to prepare compounds **11** and **12**. The title compound was obtained as a colorless amorphous gel. [α]_D²⁵ +8 (*c* 0.10, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.15 (d, 1H, *J* = 0.6 Hz), 5.55 (d, 1H, *J* = 0.6 Hz), 5.34 (d, 1H, *J* = 12.0 Hz), 4.88 (d, 1H, *J* = 2.1 Hz), 4.85 (d, 1H, *J* = 1.2 Hz), 4.29 (dd, 1H, *J* = 9.9 Hz, 1.5 Hz), 3.99 (d, 1H, *J* = 9.6 Hz), 3.89 (dd, 1H, *J* = 12.0 Hz, 9.0 Hz), 3.75 (m, 1H), 3.65 (dt, 1H, *J* = 11.1 Hz, 4.2 Hz), 3.04 (d, 1H, *J* = 9.6 Hz), 2.52 (m, 1H), 2.01 (m, 6H), 1.65 (m, 7H), 1.51 (m, 4H), 1.34 (s, 3H), 1.17 (s, 3H), 1.02 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 204.8, 150.9, 142.0, 120.0, 106.1, 100.9, 96.5, 95.3, 72.1, 70.1, 64.0, 62.6, 58.9, 56.6, 50.0, 44.8, 40.6, 40.4, 32.9, 32.8, 32.1, 30.8 (2C), 30.2, 25.4, 24.3, 24.0, 21.1, 20.7. HRMS Calcd for C₂₉H₃₈O₇: [M + H]⁺ 499.2690; found 499.2686.

Synthesis of (2R,6aR,7S,7aR,7a¹R,10aR,11S,13aS,13bS)-2-(4-azidobutoxy)-7-hydroxy-6,6,9,9-tetramethyl-16-methylene-2,3,4,5,6,6a,7,10a,11,12,13,13a-dodecahydro-7a,13b-(epoxymethano)-7a¹,11-ethano[1,3]dioxino[4',5',6':4,5]naphtho[2,1-*h*]chromen-17-one (26)

To a solution of compound **21** (61 mg, 0.12 mmol) in dichloromethane was added Et₃N (35 mg, 0.35 mmol) and MsCl (20 mg, 0.17 mmol) dropwise at 0 °C. The mixture was stirred at rt overnight, and diluted with water and extracted with dichloromethane. The organic extract was washed with brine, dried over anhydrous Na₂SO₄, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 25% EtOAc in hexanes to afford the desired product **25** as a colorless gel (62 mg, 86%). ¹H NMR (300 MHz, CDCl₃): δ

6.14 (s, 1H), 5.54 (s, 1H), 5.32 (d, 1H, $J = 12.0$ Hz), 4.89 (t, 1H, $J = 2.1$ Hz), 4.85 (d, 1H, $J = 1.5$ Hz), 4.23 (m, 3H), 3.98 (d, 1H, $J = 9.3$ Hz), 3.88 (dd, 1H, $J = 12.0$ Hz, 9.0 Hz), 3.58 (dt, 1H, $J = 9.3$ Hz, 6.3 Hz), 3.44 (dt, 1H, $J = 9.3$ Hz, 5.7 Hz), 3.01 (d, 1H, $J = 6.3$ Hz), 3.00 (s, 3H), 2.48 (m, 1H), 1.90 (m, 9H), 1.66 (m, 8H), 1.52 (m, 2H), 1.34 (s, 3H), 1.16 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 150.9, 140.7, 120.0, 108.9, 100.9, 95.5, 95.4, 72.0, 70.1, 69.7, 66.8, 64.1, 59.0, 56.5, 50.0, 45.2, 40.6, 40.3, 37.4, 32.9, 30.8, 30.6, 30.1, 26.7, 26.4, 25.7, 25.3, 21.9, 21.0, 20.6. HRMS Calcd for $\text{C}_{31}\text{H}_{44}\text{O}_{10}\text{S}$: $[\text{M} + \text{H}]^+$ 609.2728; found 609.2717.

A mixture of **25** (30 mg, 0.05 mmol) and NaN_3 (10 mg, 0.15 mmol) in the dried DMF (2 mL) was stirred at 65 °C under N_2 for 16 h. After the completion of the reaction, which was monitored by TLC, the mixture was diluted with water and extracted with dichloromethane. The organic extract was washed with brine, dried over anhydrous Na_2SO_4 , filtered, and evaporated to give an oily residue, which was further purified using preparative TLC developed by 20% EtOAc in hexanes to afford the desired product **26** (16.8 mg, 63%) as a colorless amorphous gel. ^1H NMR (300 MHz, CDCl_3): δ 6.14 (s, 1H), 5.54 (d, 1H, $J = 0.3$ Hz), 5.32 (d, 1H, $J = 12.0$ Hz), 4.90 (t, 1H, $J = 2.1$ Hz), 4.84 (d, 1H, $J = 1.5$ Hz), 4.22 (dd, 1H, $J = 9.3$ Hz, 1.2 Hz), 3.99 (d, 1H, $J = 9.6$ Hz), 3.89 (dd, 1H, $J = 9.0$ Hz, 12.0 Hz), 3.56 (m, 1H), 3.42 (m, 1H), 3.27 (m, 2H), 3.04 (d, 1H, $J = 9.6$ Hz), 2.49 (m, 1H), 1.88 (m, 9H), 1.64 (m, 8H), 1.52 (m, 2H), 1.34 (s, 3H), 1.16 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 150.9, 140.7, 120.0, 109.0, 101.0, 95.5, 95.4, 72.1, 70.1, 67.0, 64.2, 59.0, 56.5, 51.3, 50.1, 45.2, 40.6, 40.3, 32.9, 30.8, 30.6, 30.2, 26.9, 26.8, 26.1, 25.4, 21.9, 21.0, 20.6. HRMS Calcd for $\text{C}_{30}\text{H}_{41}\text{N}_3\text{O}_7$: $[\text{M} + \text{H}]^+$ 556.3017; found 556.3010.

***In Vitro* Determination of Effects of Synthesized Diterpenoids on Cancer Cell Proliferation.**

Breast cancer cell lines MCF-7, MDA-MB-231, MDA-MB-486 and MCF/ADR were seeded in

96-well plates at a density of 1×10^4 cells/well and treated with DMSO and 0.125, 0.625, 1.25, 2.5, 5, 10, and 50 μM of individual compound for 48 h, and then 20 μL of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) (5 mg/mL in PBS) was added to each well and further incubated for another 4 h. Then MTT solution was removed, and 150 μL of DMSO was added to each well. Absorbance of all wells was determined by measuring OD at 550 nm after a 10 min incubation on a 96-well GlowMax absorbance reader (Promega, Madison, WI). Each individual compound was tested in quadruplicate wells for each concentration.

Reference:

1. W. Zhou, Y. Cheng, *Acta Chim. Sinica* 1990, **48**, 1185–1190.

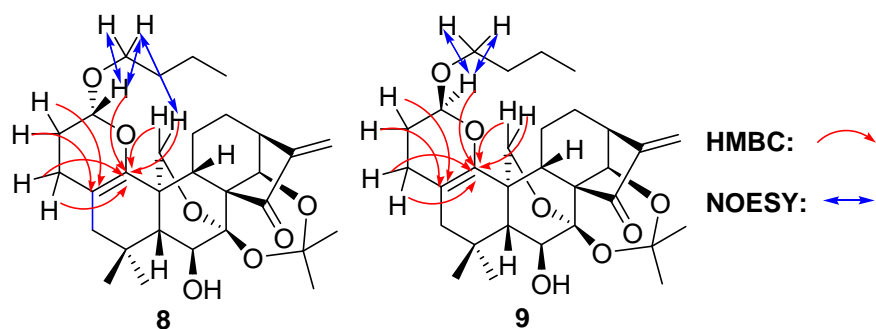
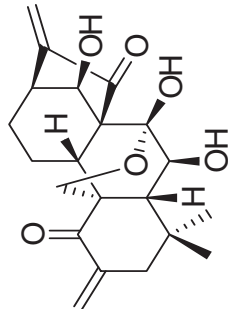
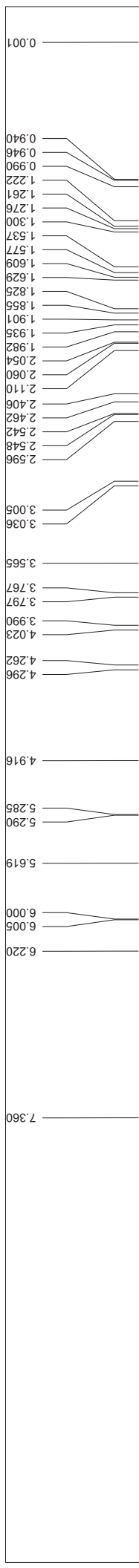
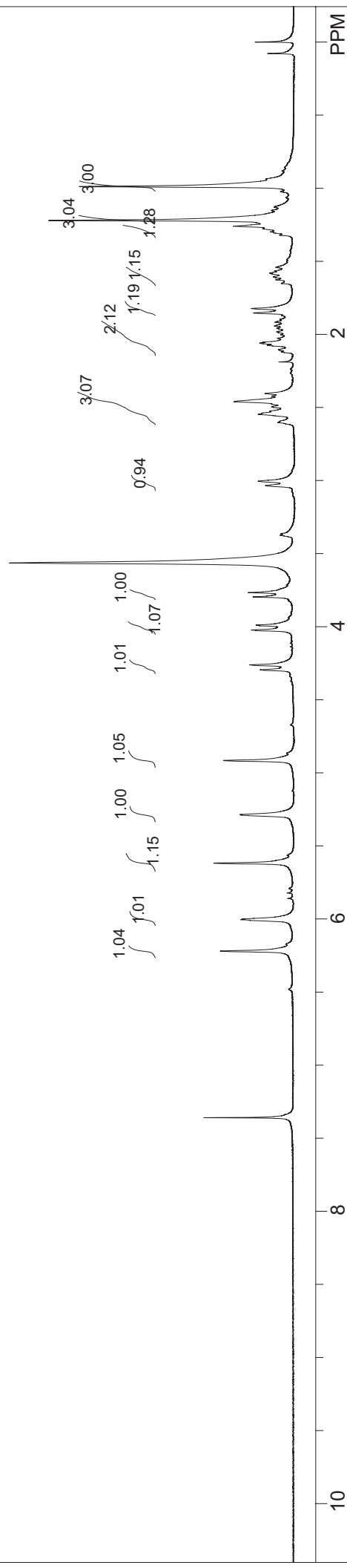


Figure 1S. Key HMBC and NOESY correlations of compounds **8** and **9**. Characteristic HMBC correlations indicate the presence of the pyran moiety fused into the A-ring of **8** and **9**. The stereochemistry of C-2 was determined by NOESY experiments, in which the cross peaks for H-23 and H-1' of **8** indicated that C-2 had *R* configuration, and its appended ethereal C-O bond was assigned as α -oriented; on the contrary, no similar cross peaks for H-23 and H-1' of **9** were observed, suggesting C-2 had *S* configuration, and its ethereal C-O bond was on the β -face. The conformations of the dihydropyran rings in **8** and **9** were also deduced from chemical shift values and coupling constants of protons attached to C-2. ^1H NMR spectra of **8** reveal the signals of proton on C-2 as a triplet at 4.89 ppm with a small coupling constant of 2.1 Hz. Thus, the proton at C-2 in **8** is equatorial, while the *n*-butoxy group occupies the axial position. For diastereoisomer **9**, the proton at C-2 resonates as a doublet of doublets at 4.58 ppm with two coupling constants of 1.5 Hz and 9.0 Hz, respectively, due to coupling with two protons at C-3. Thus, the proton at C-2 in **9** is axial.



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3



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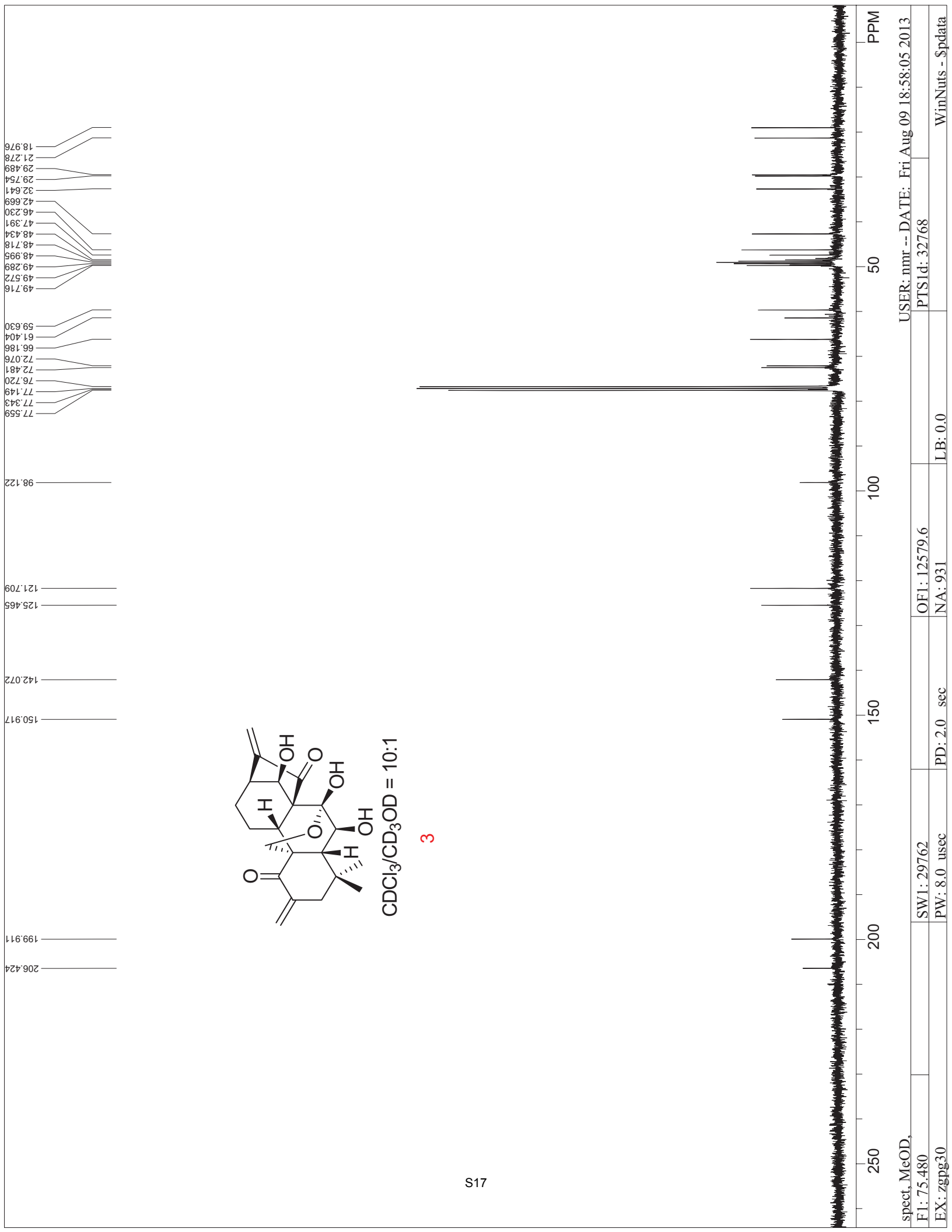
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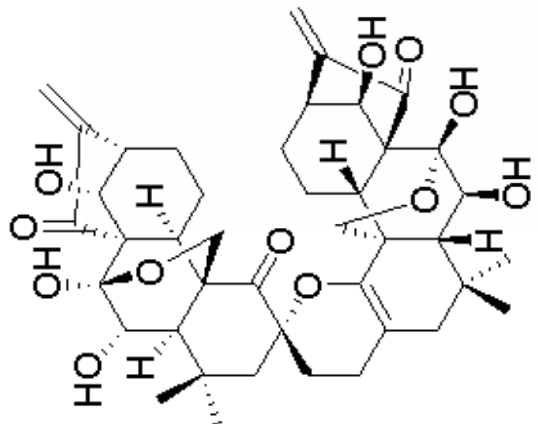
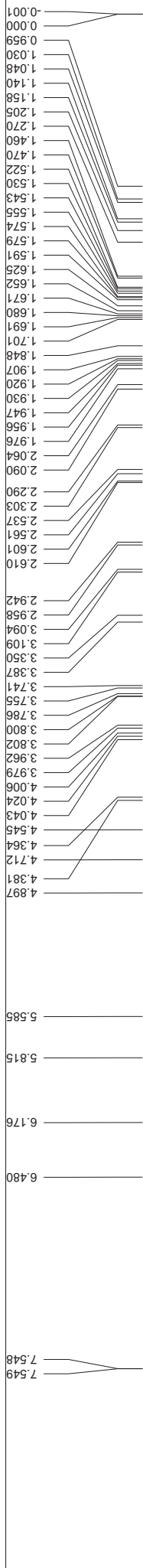
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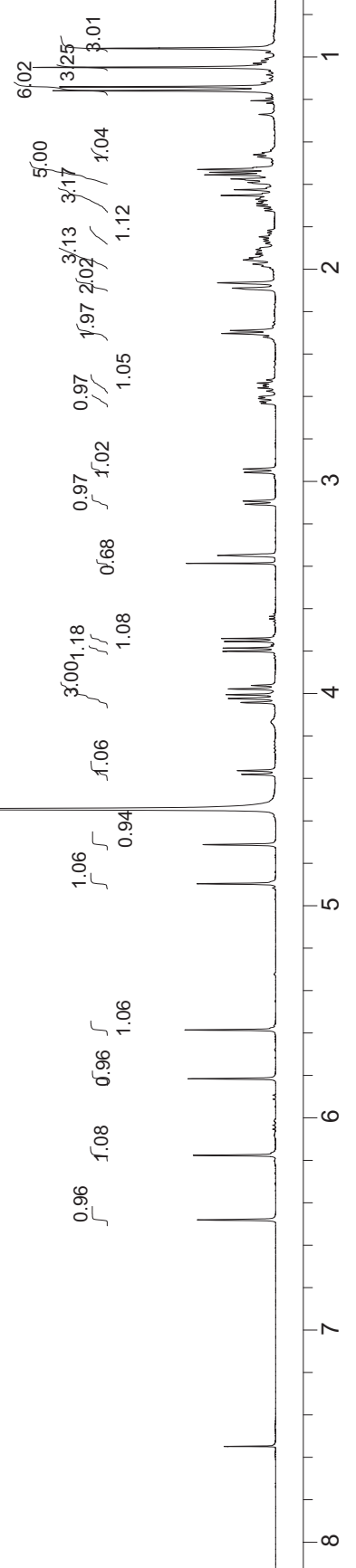
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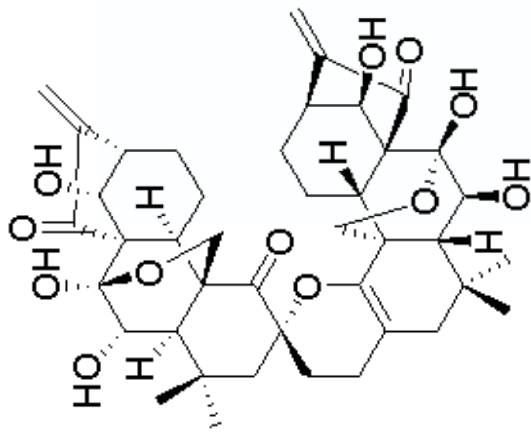




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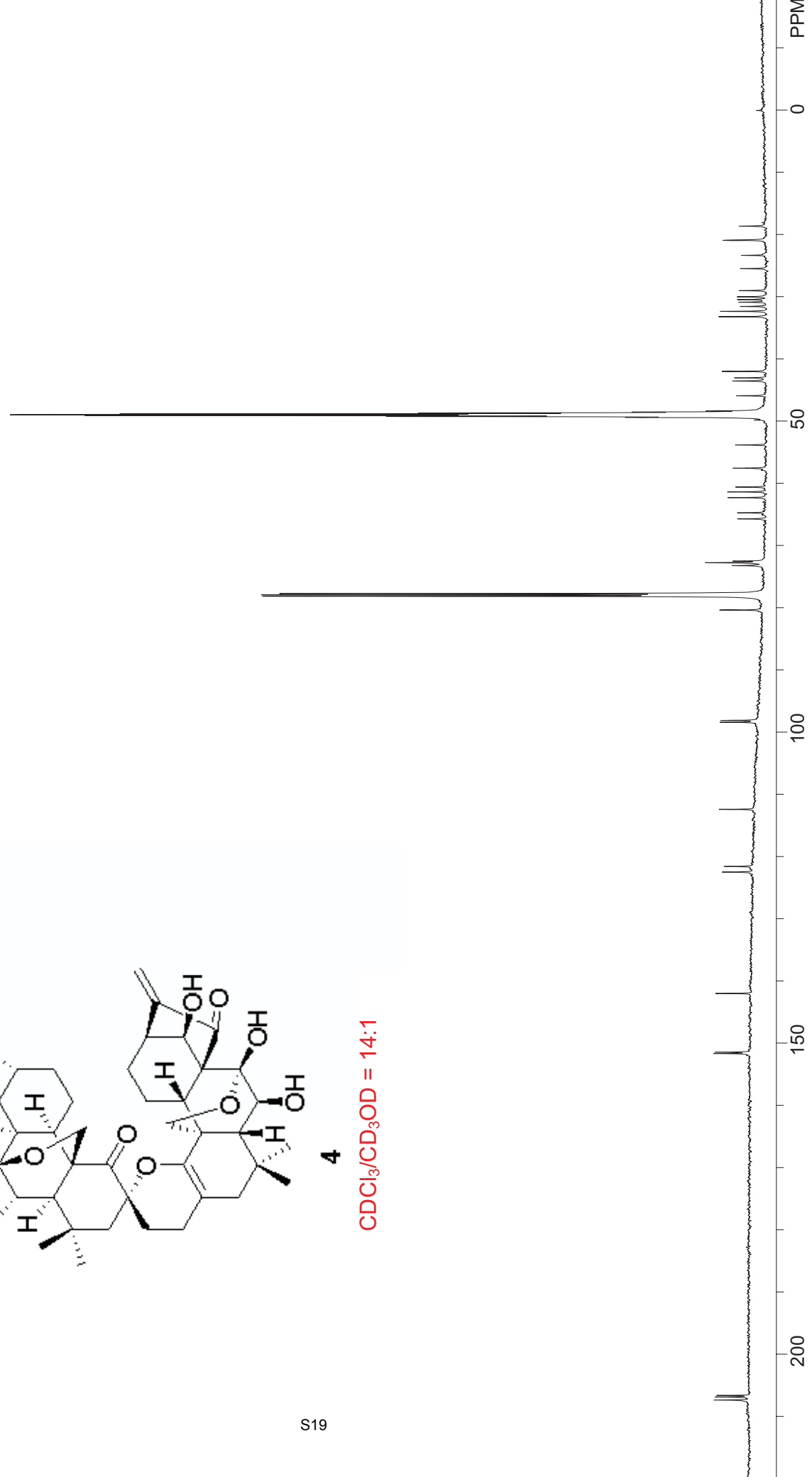
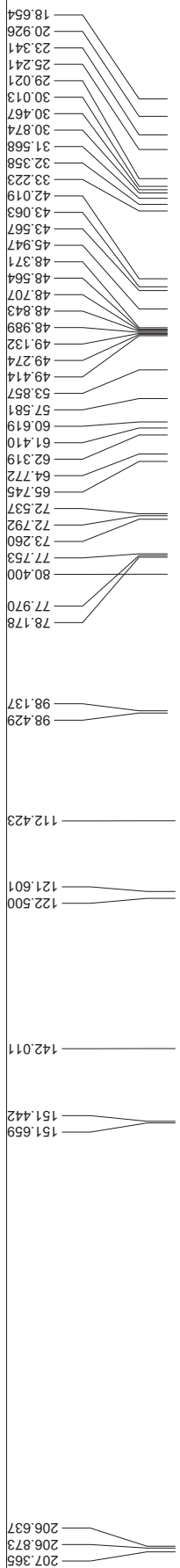
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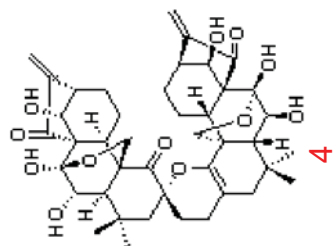
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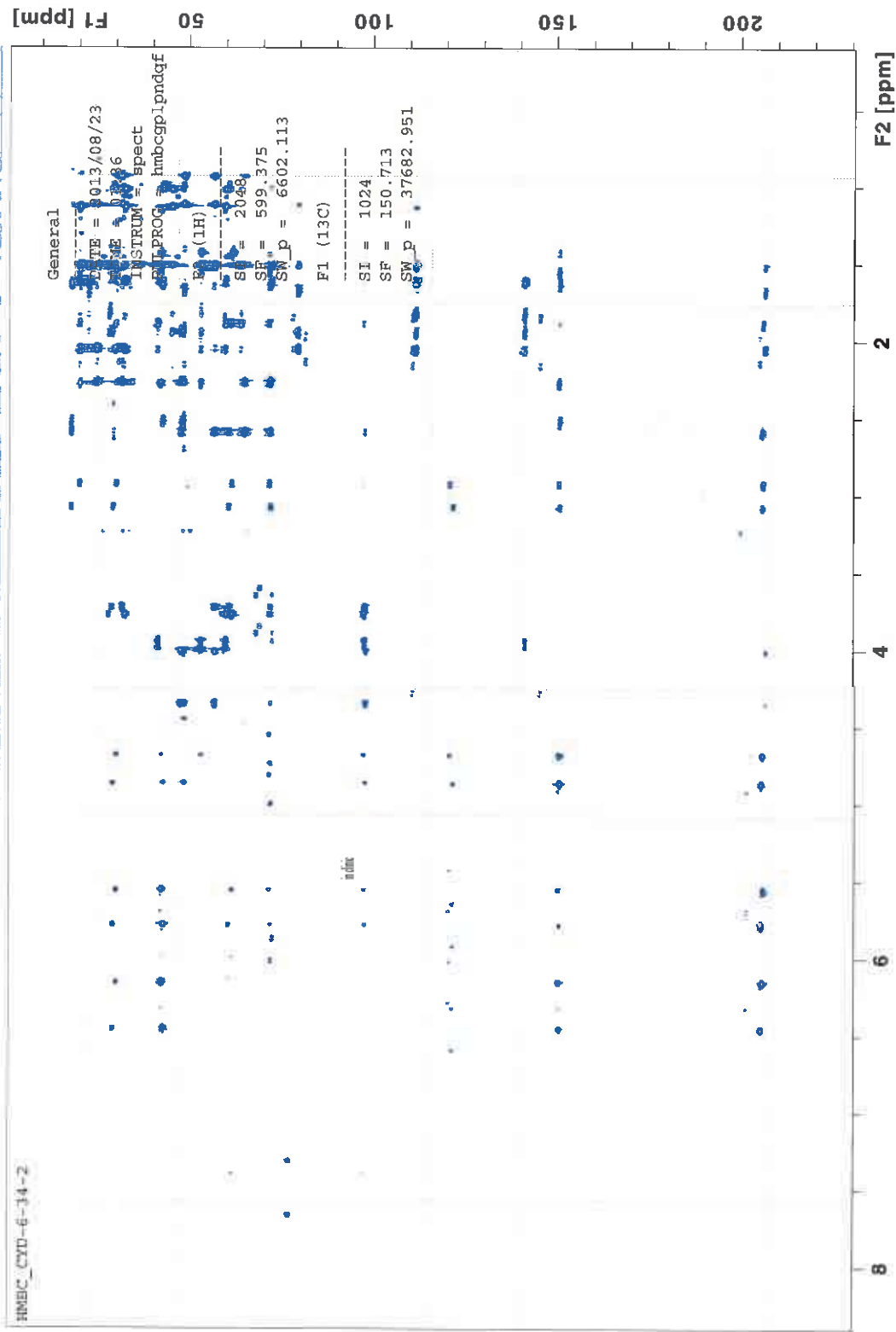


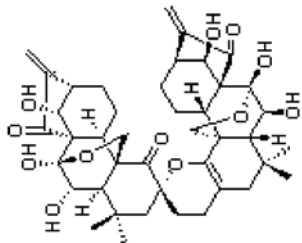
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CDCl₃/CD₃OD = 14:1

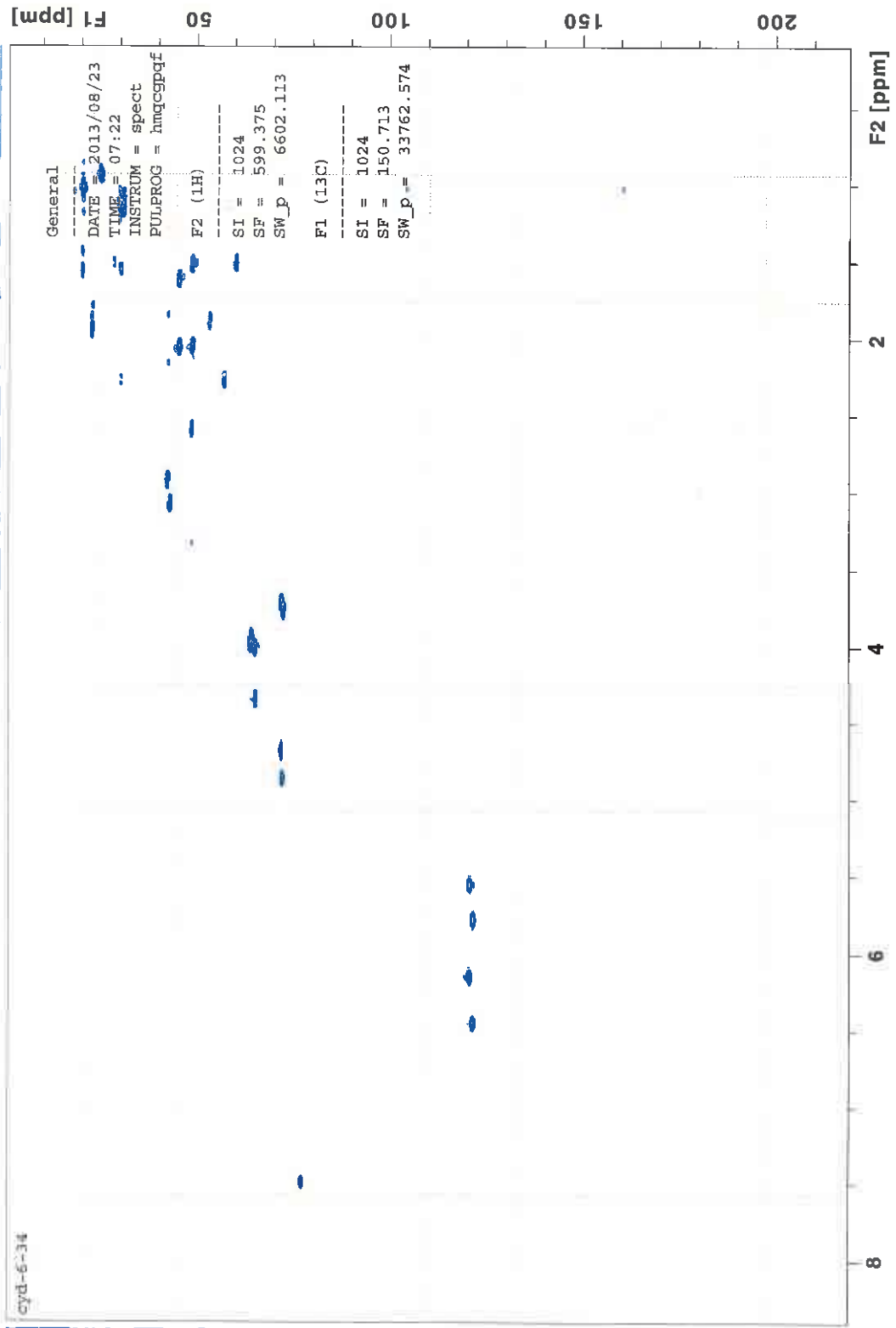


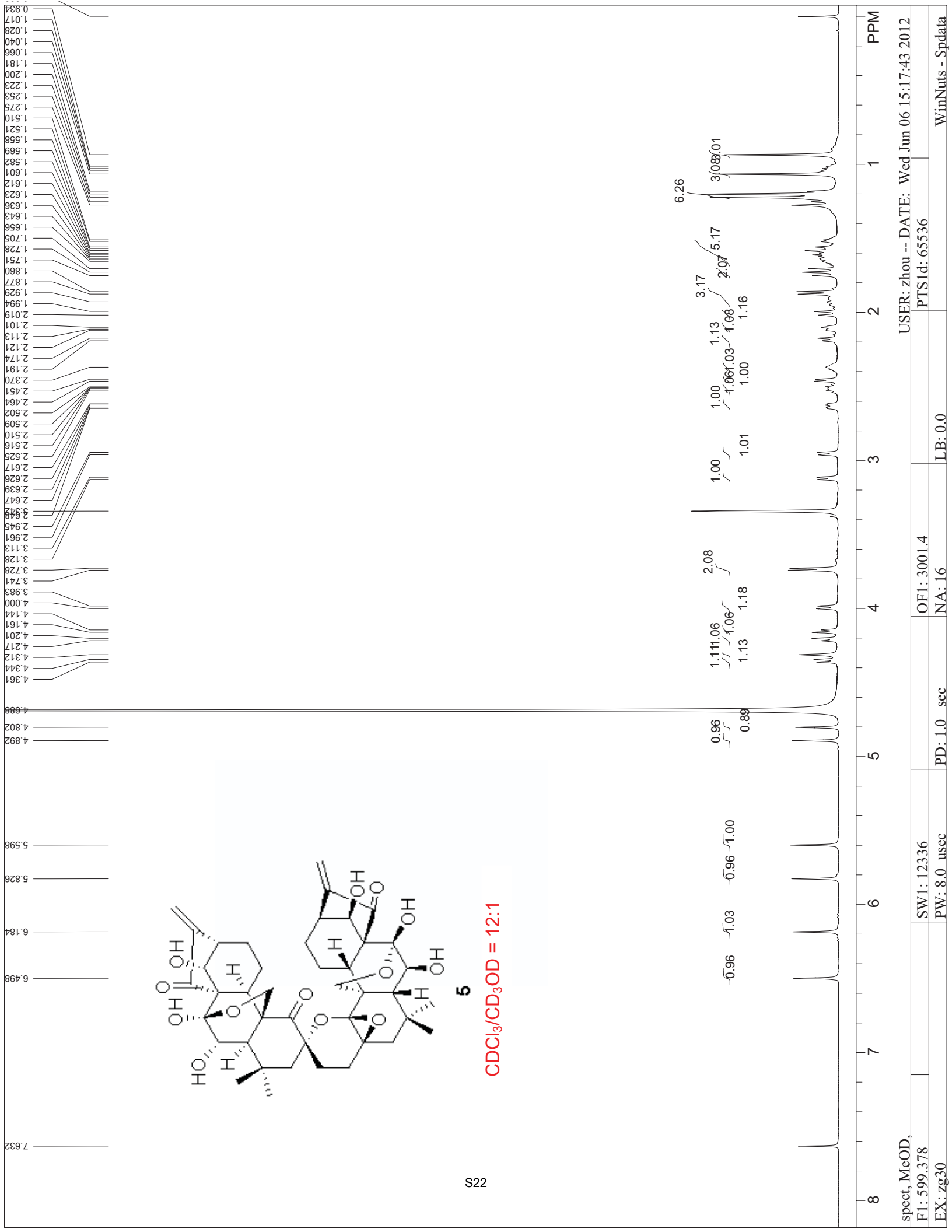


HMQC

hmqc 16 1 /opt/topspin3.0/data/zhou/nmr

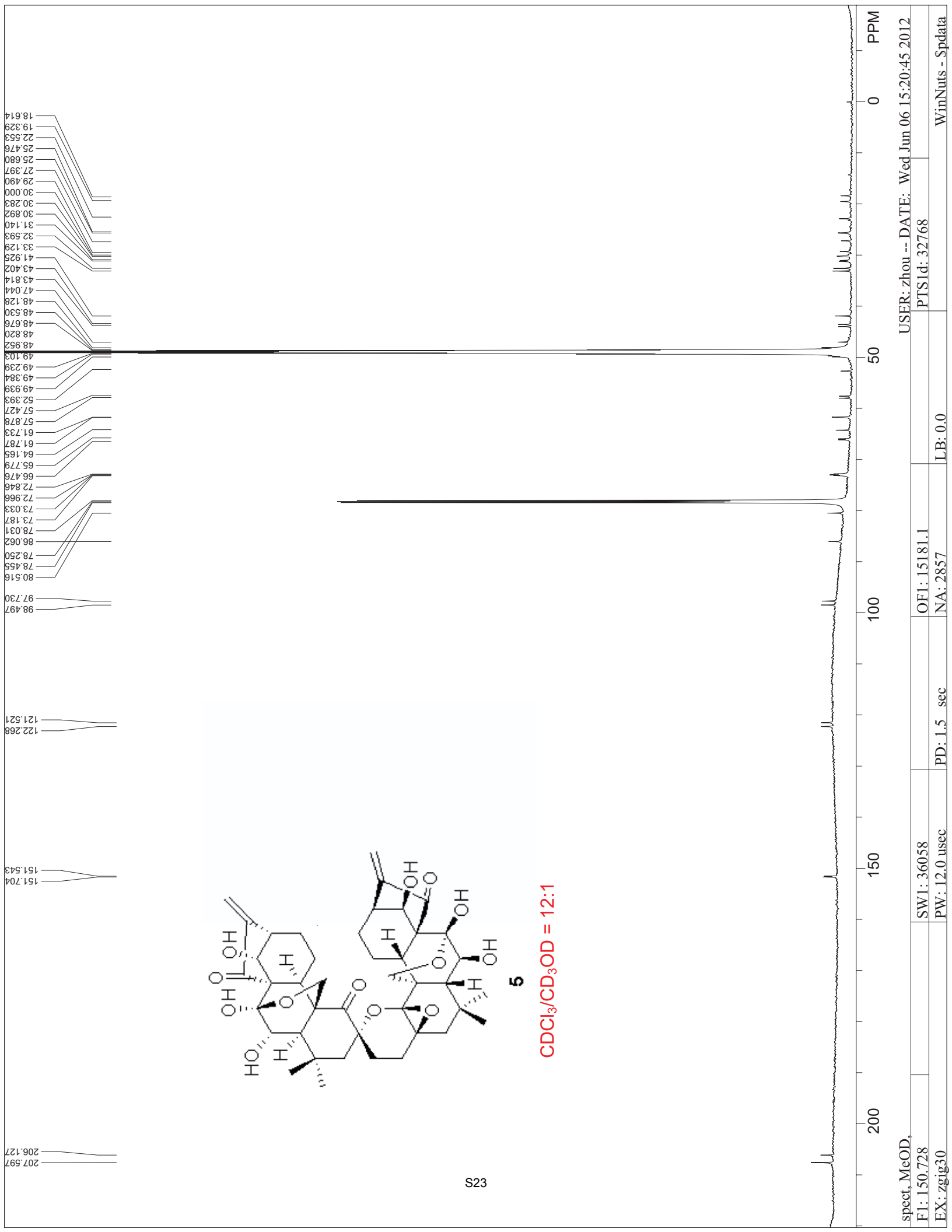
4
 CDCCl₃/CD₃OD = 14:1

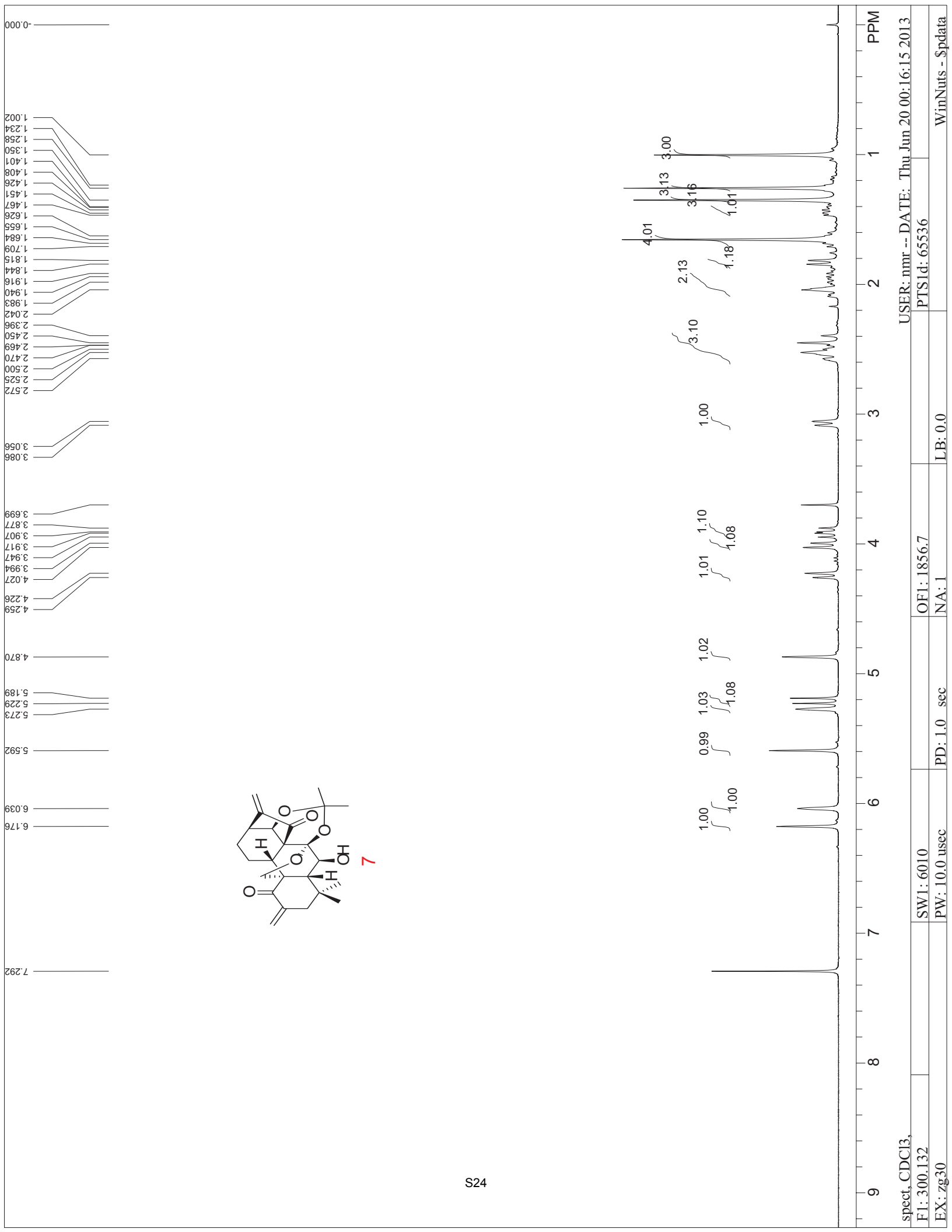


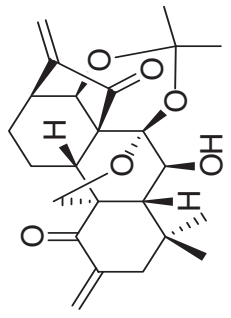
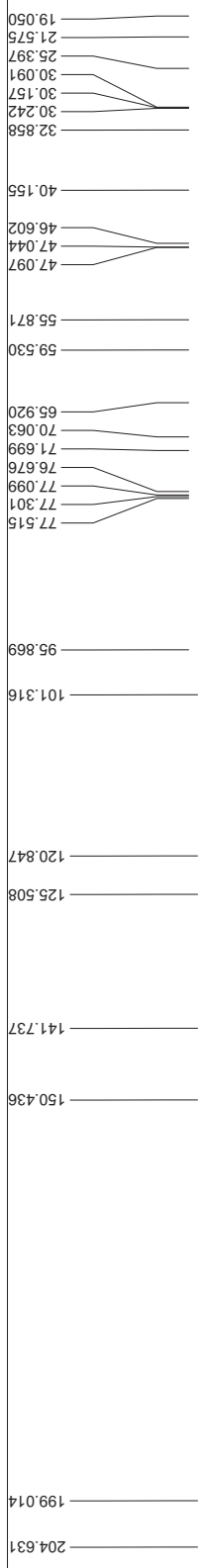


0.834	1.017	1.028	1.040	1.066	1.181	1.200	1.223	1.253	1.275	1.510	1.521	1.558	1.569	1.582	1.601	1.612	1.623	1.636	1.643	1.656	1.705	1.728	1.751	1.860	1.877	1.929	1.994	2.019	2.101	2.113	2.121	2.174	2.191	2.370	2.451	2.464	2.502	2.509	2.510	2.516	2.525	2.617	2.626	2.639	2.647	3.542	3.548	2.945	2.961	3.113	3.128	3.728	3.741	3.983	4.000	4.144	4.161	4.201	4.217	4.312	4.344	4.361	4.698	4.802	4.892	5.598	5.826	6.184	6.498	7.632
																																	PPM																																					

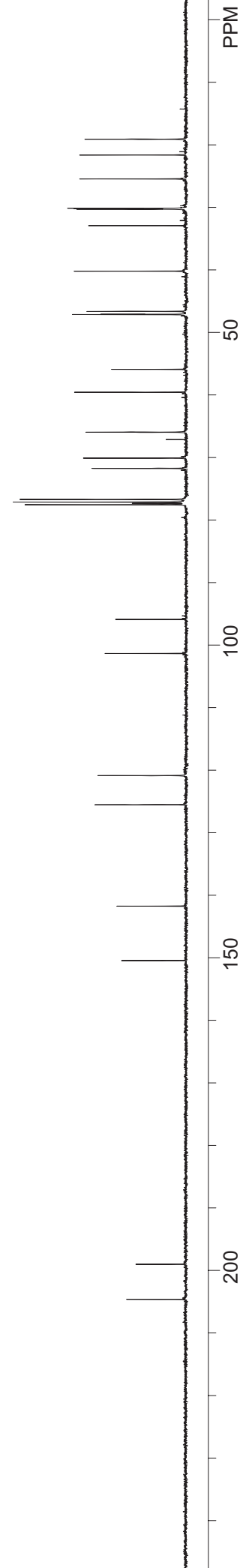
USER: zhou	DATE: Wed Jun 06 15:17:43 2012
PTSI: 65536	
OFI: 3001.4	
NA: 16	
LB: 0.0	
PD: 1.0 sec	
PW: 8.0 usec	
SW1: 12336	
EX: zg30	



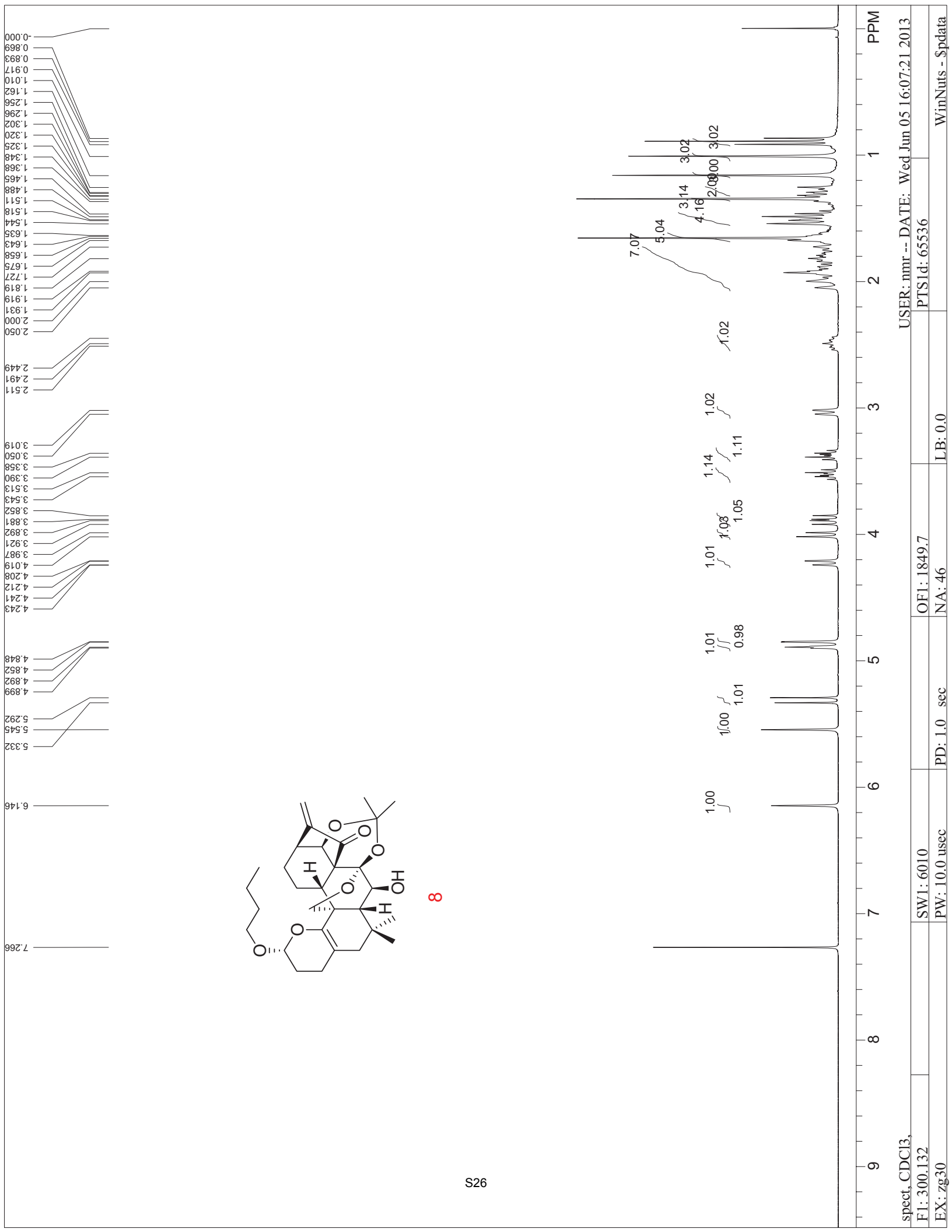




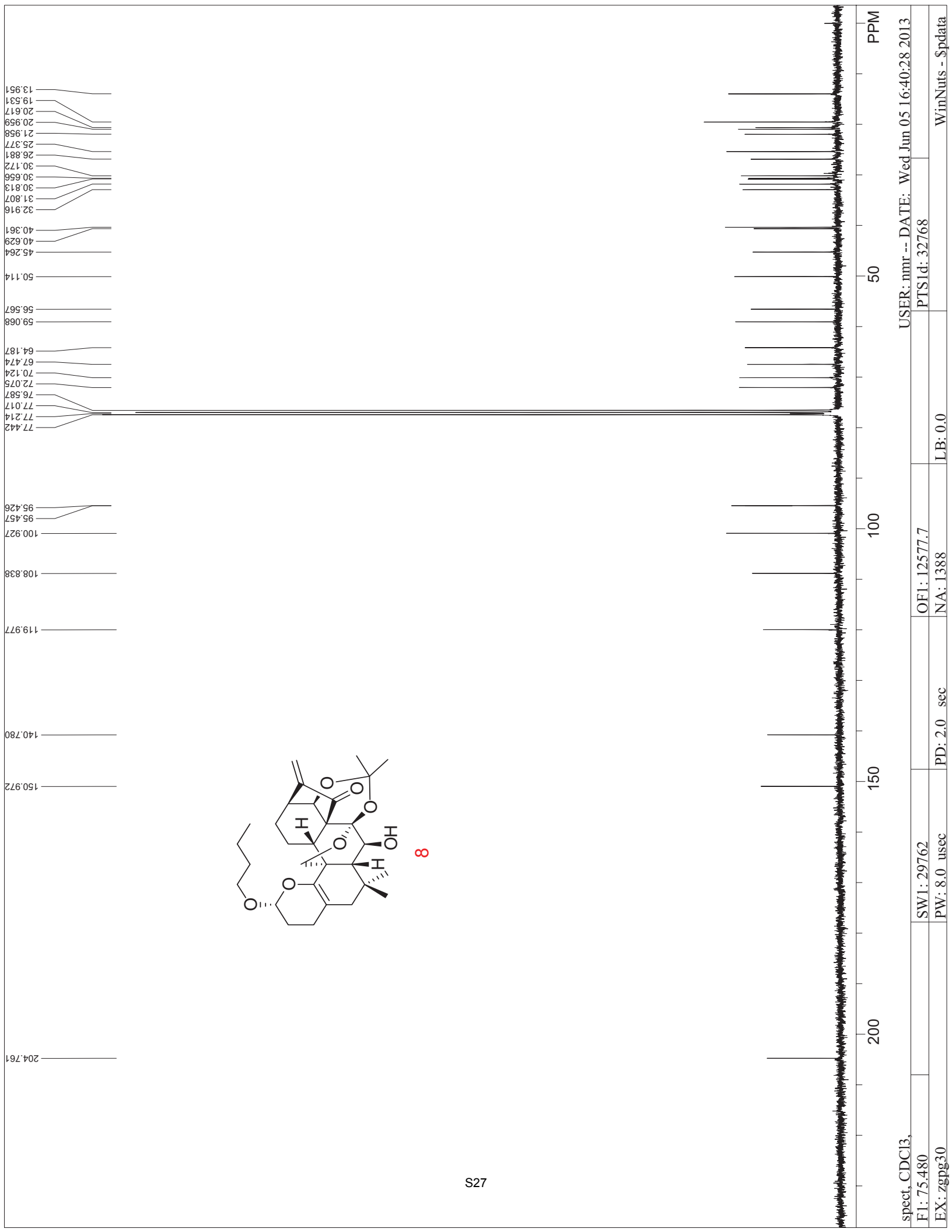
7



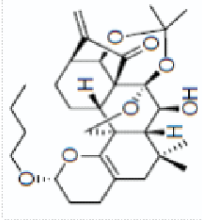
spect, CDCI3,	USER: nmr -- DATE: Thu Jun 20 00:22:08 2013
F1: 75.480	PTS1d: 32768
EX: zgpg30	LB: 0.0
	OF1: 12579.6
	NA: 625
	PD: 2.0 sec
	PW: 8.0 usec
	SW1: 29762
	WinNuts - \$pdata



spect, CDC13, USER: nmr --- DATE: Wed Jun 05 16:07:21 2013
 F1: 300.132 SW1: 6010 OF1: 1849.7 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec LB: 0.0 WinNuts - \$pdata



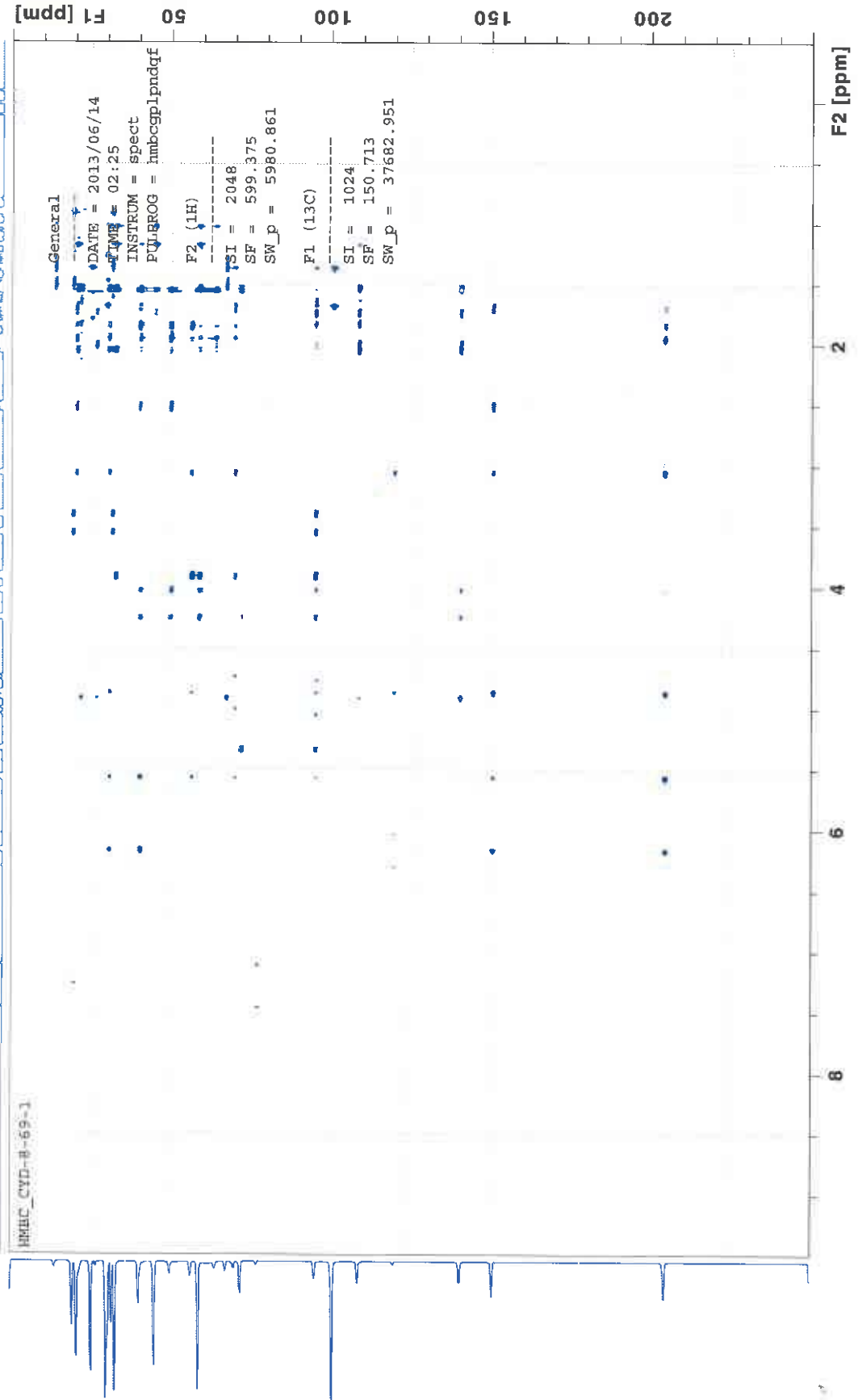
spect, CDCI3, USER: nmr -- DATE: Wed Jun 05 16:40:28 2013
 F1: 75.480 PTSId: 32768
 EX: zgpg30 WinNuts - \$pdata
 OF1: 12577.7 LB: 0.0
 NA: 1388
 PD: 2.0 sec
 SW1: 29762
 PW: 8.0 usec

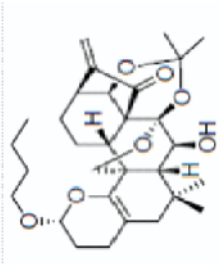


8

HMBC

hmbc 11 1 /opt/topspin3.0/data/zhou/nmr

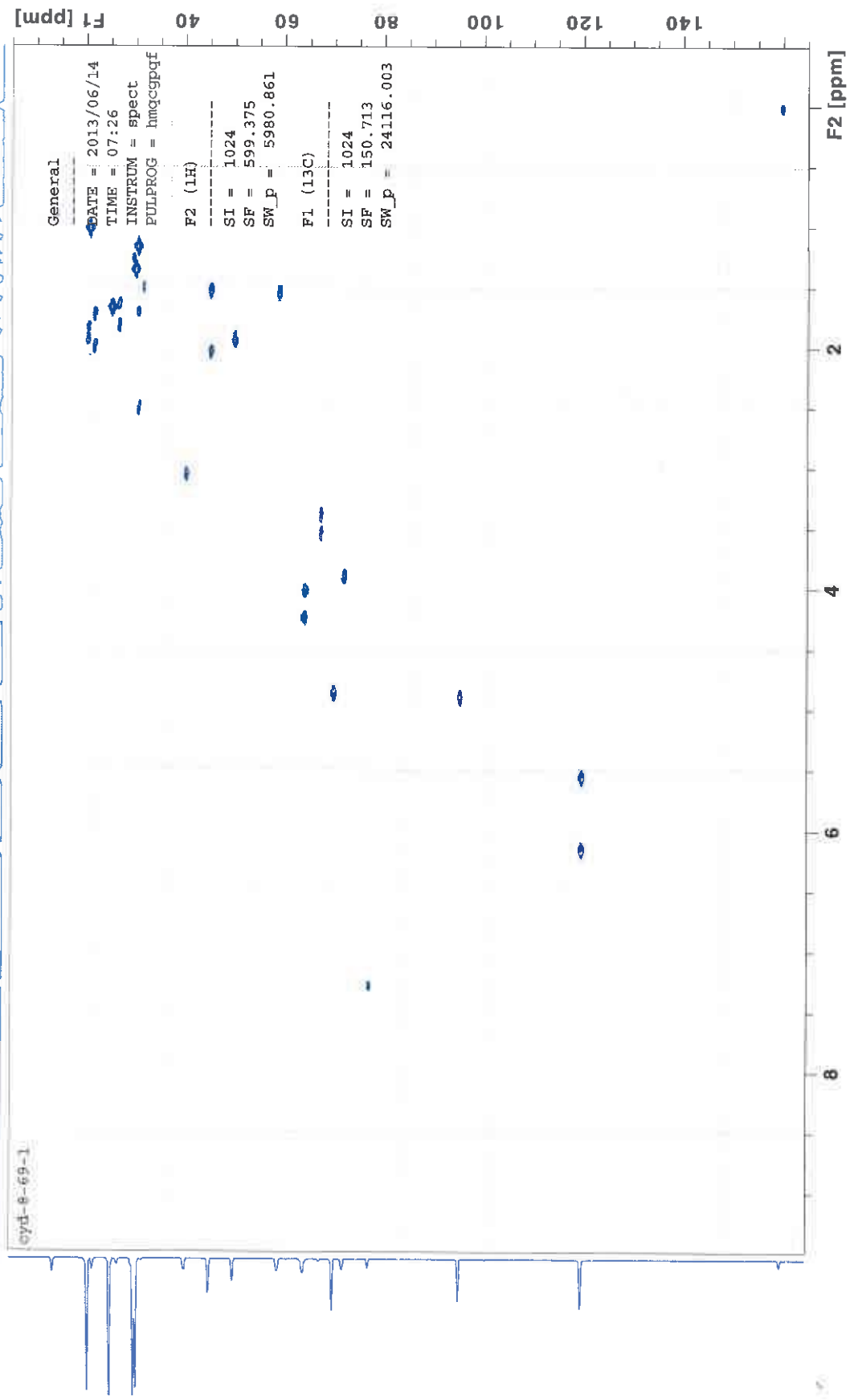




8

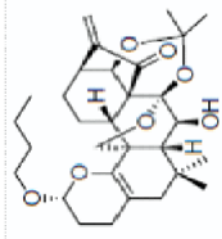
HMQC

hmqc 11 1 /opt/topspin3.0/data/zhou/nmr

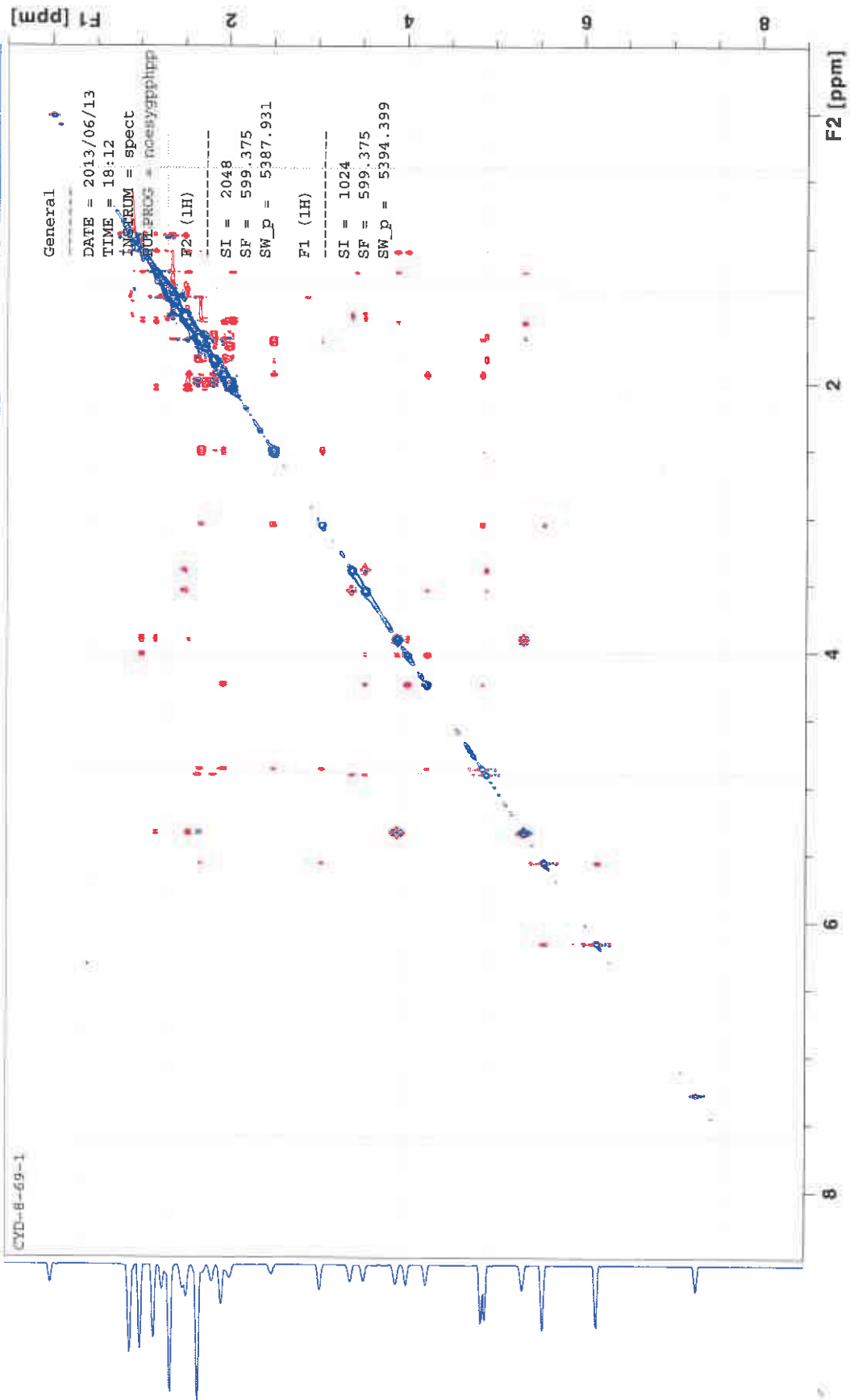


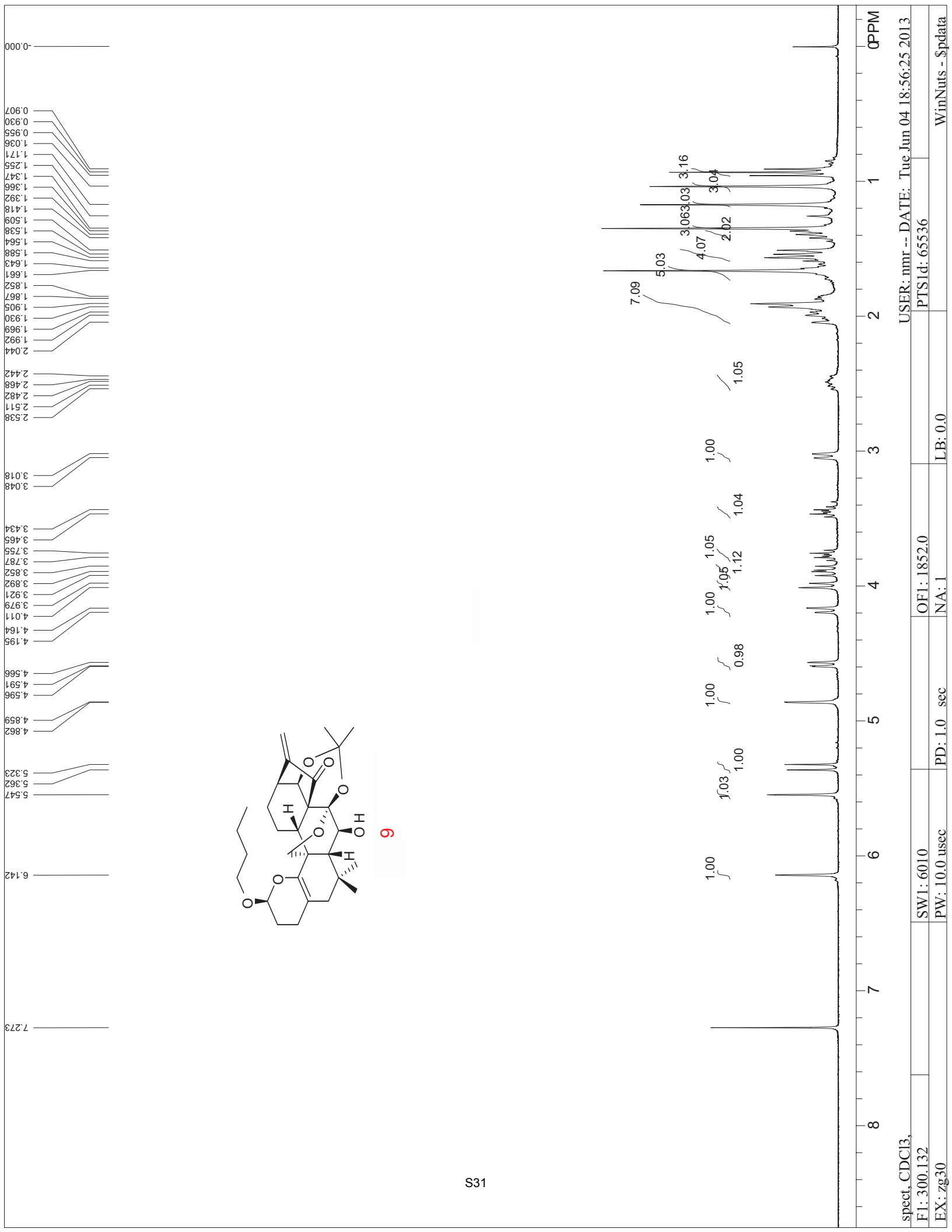
NOESY

noesy 8 1 /opt/topspin3.0/data/zhou/nmr

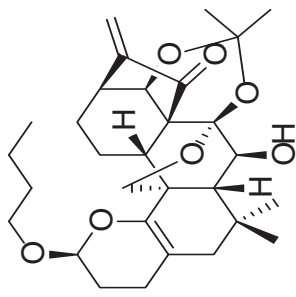


8

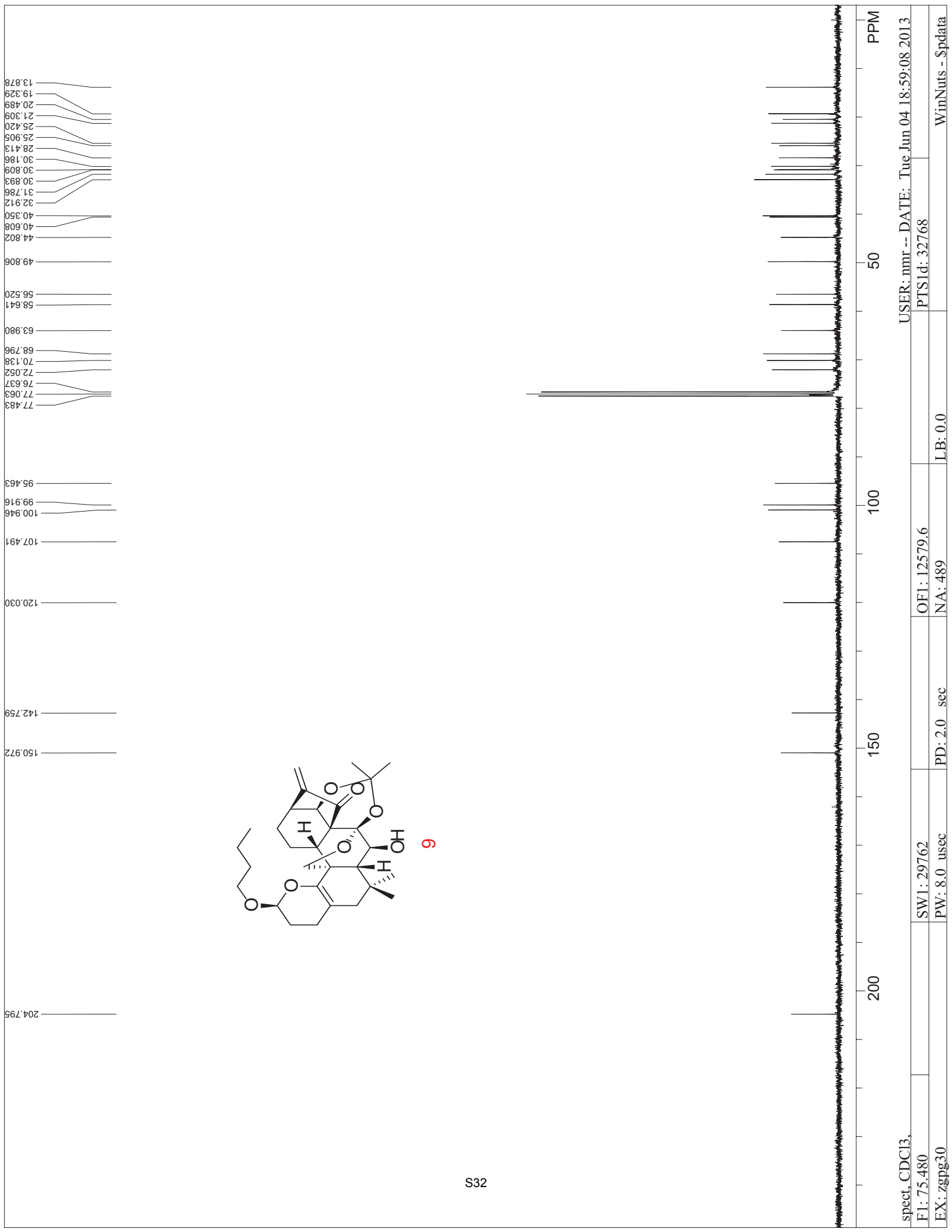




spect, CDC13, USER: nmr -- DATE: Tue Jun 04 18:56:25 2013
 F1: 300.132 SW1: 6010 OF1: 1852.0 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec NA: 1 LB: 0.0 WinNuts - \$pdata



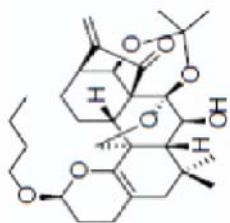
9



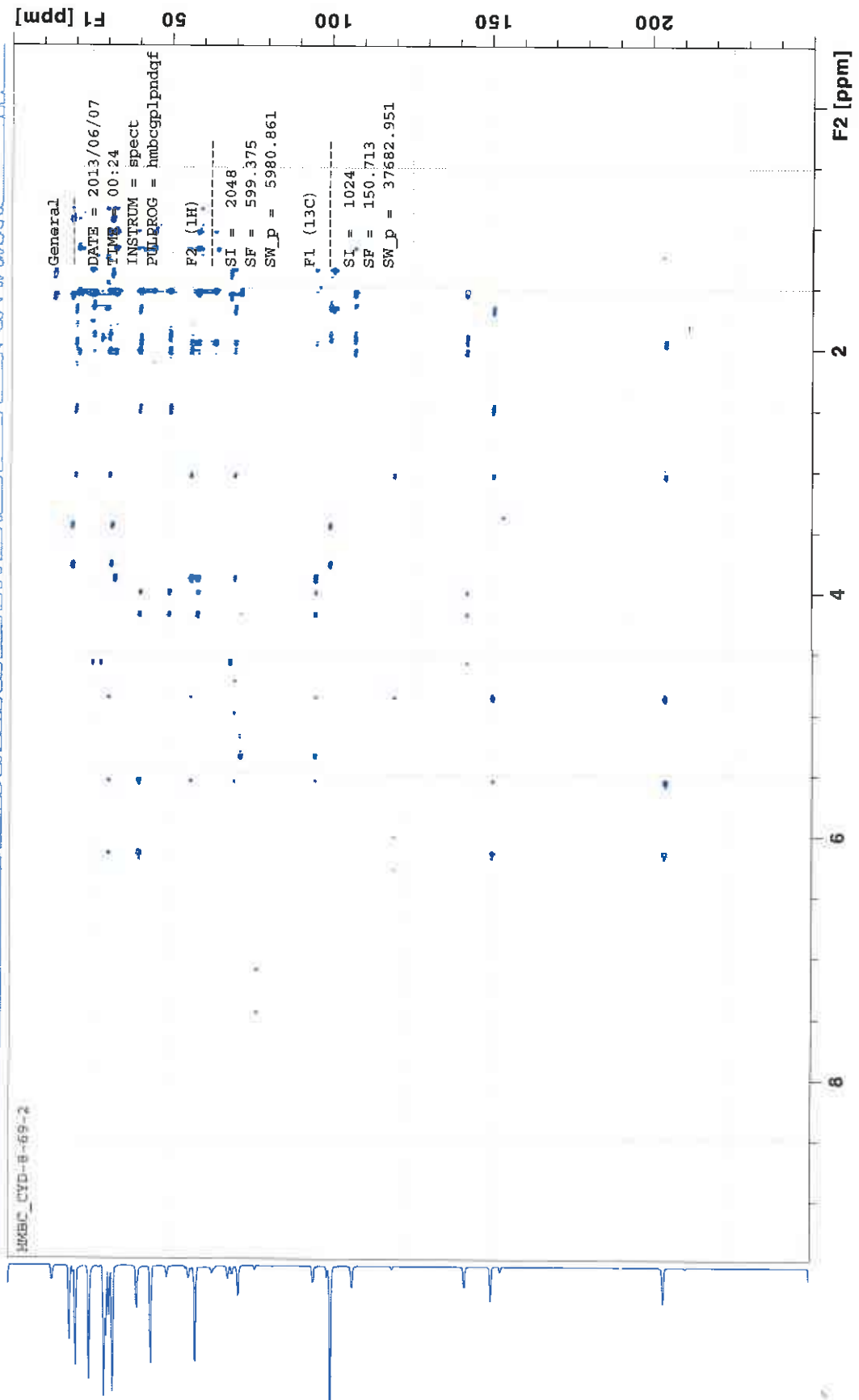
spect, CDCl3, USER: nmr -- DATE: Tue Jun 04 18:59:08 2013
 F1: 75.480 PTS1d: 32768
 EX: zgpg30 OF1: 12579.6 LB: 0.0
 PD: 2.0 sec NA: 489
 WinNuts - \$pdata

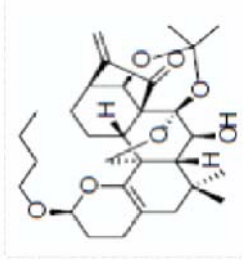
HMBC

hmbc 10 1 /opt/topspin3.0/data/zhou/nmr



9

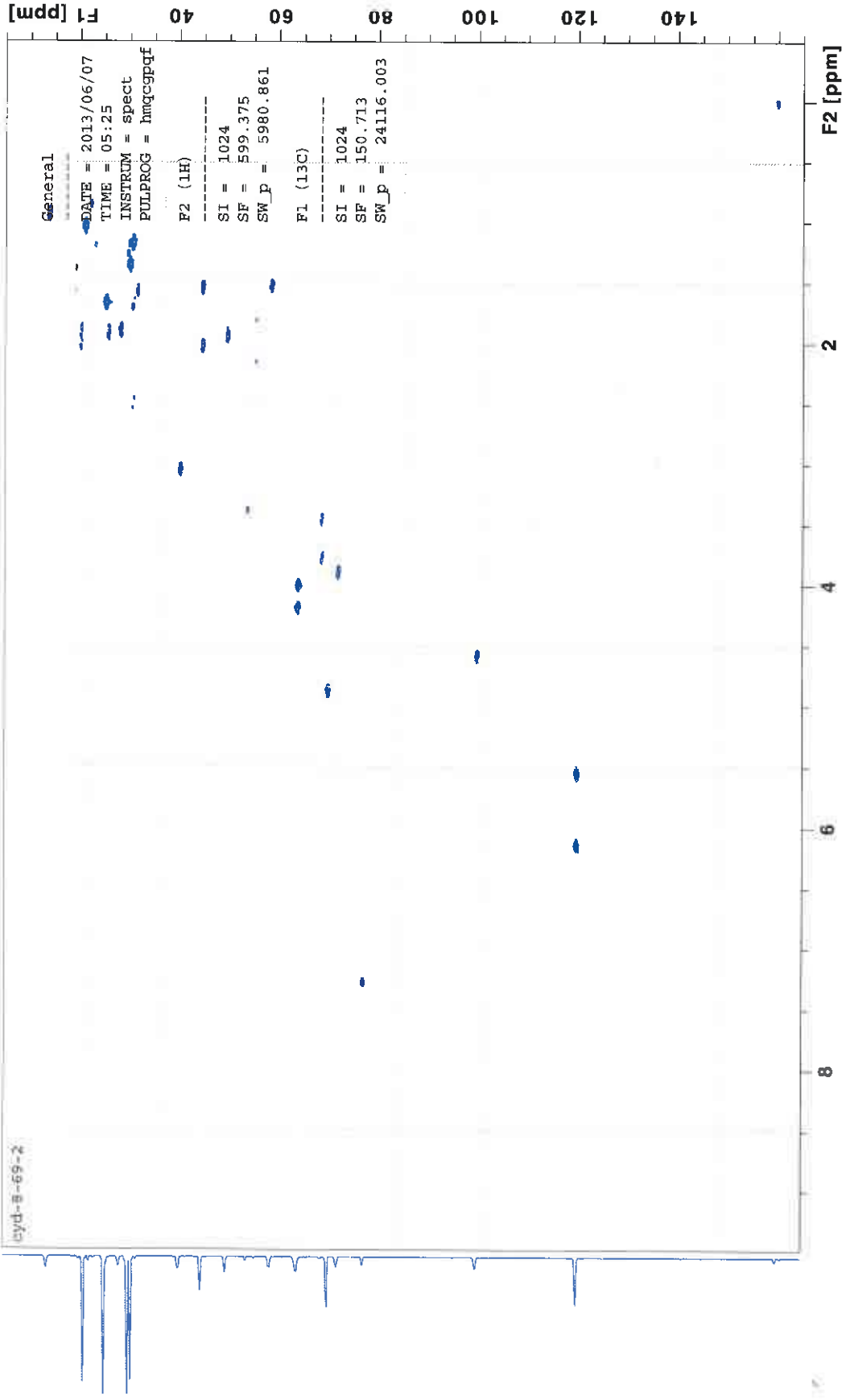




9

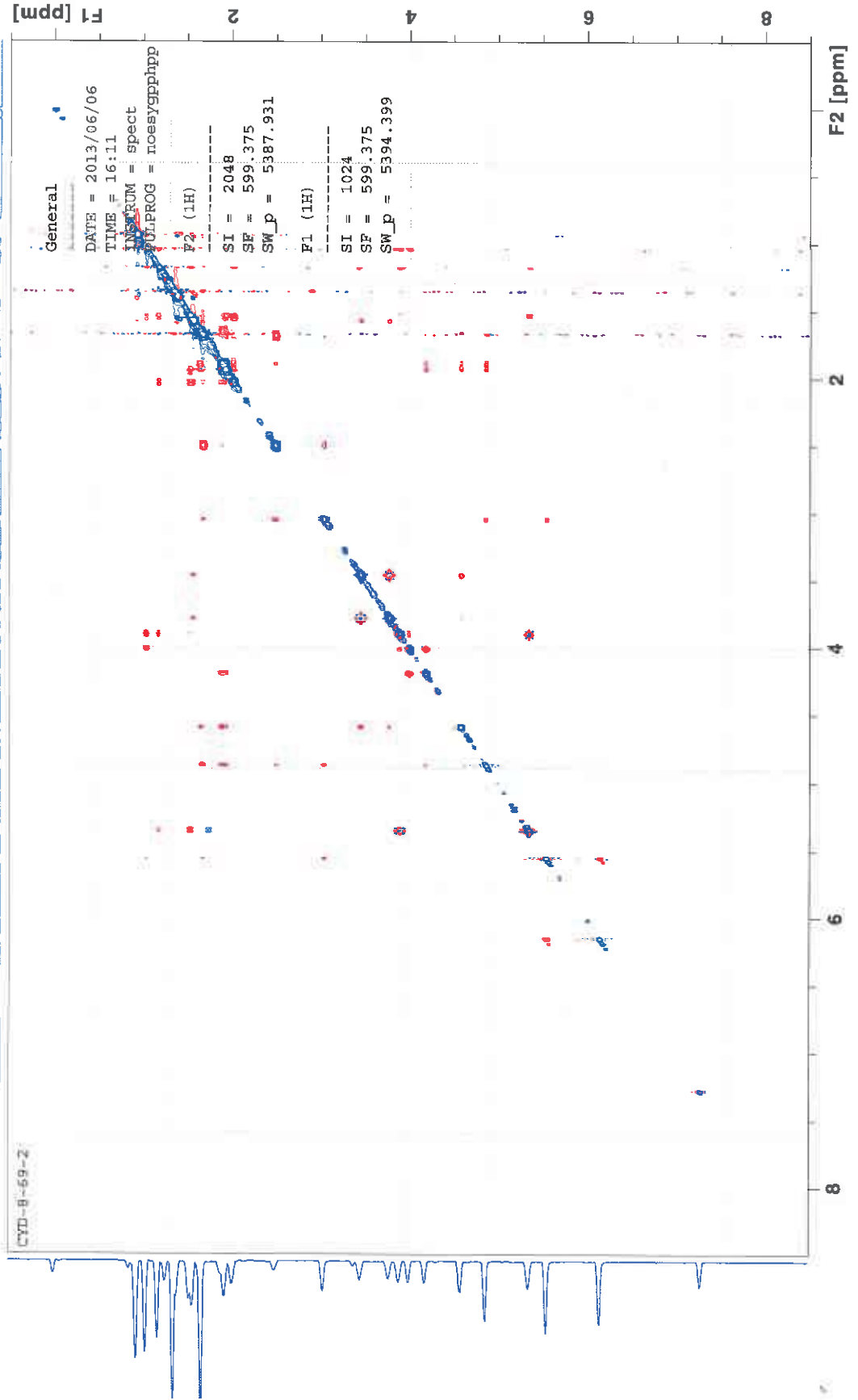
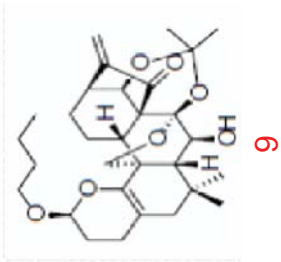
HMQC

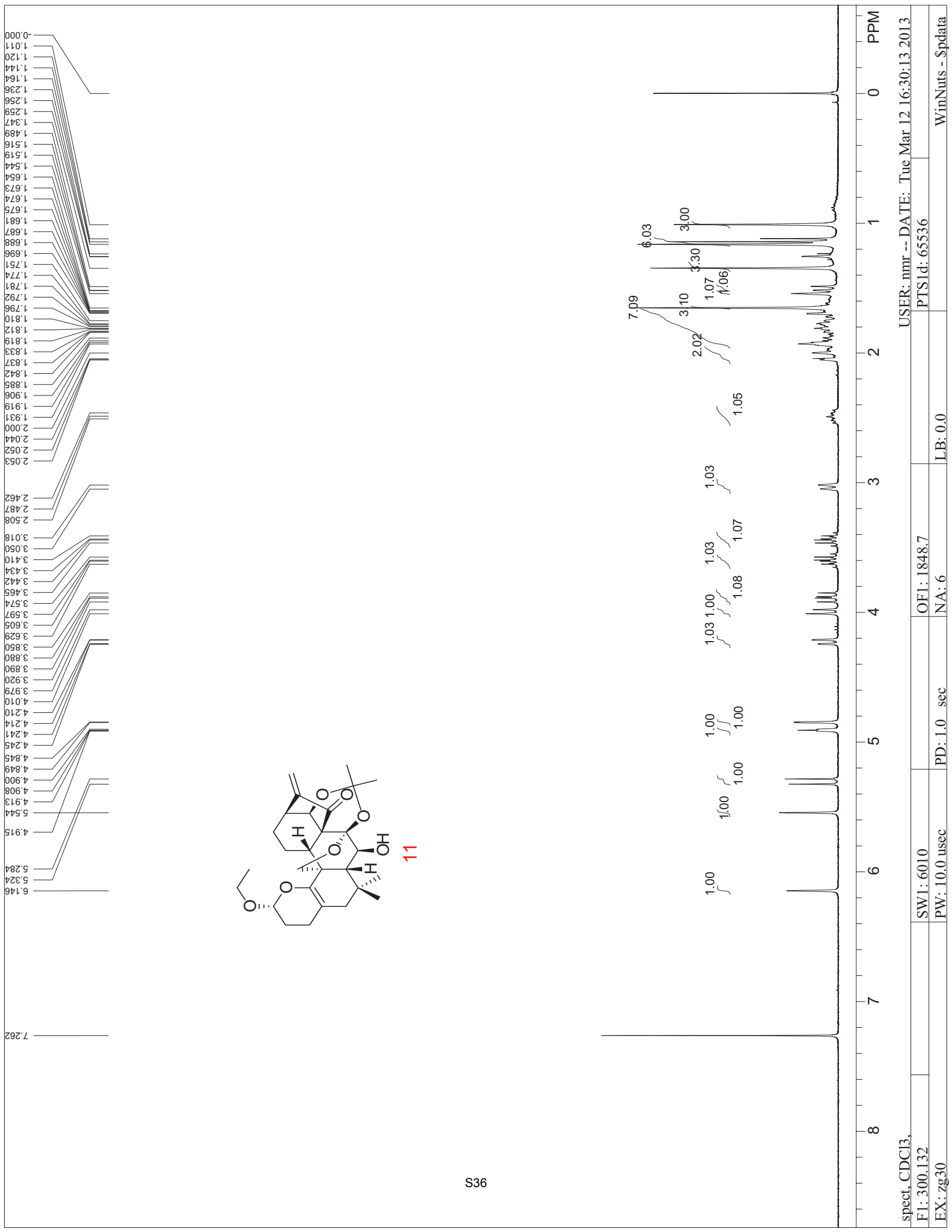
hmqc 1.0 1 /opt/topsp.in3.0/data/zhou/nmr



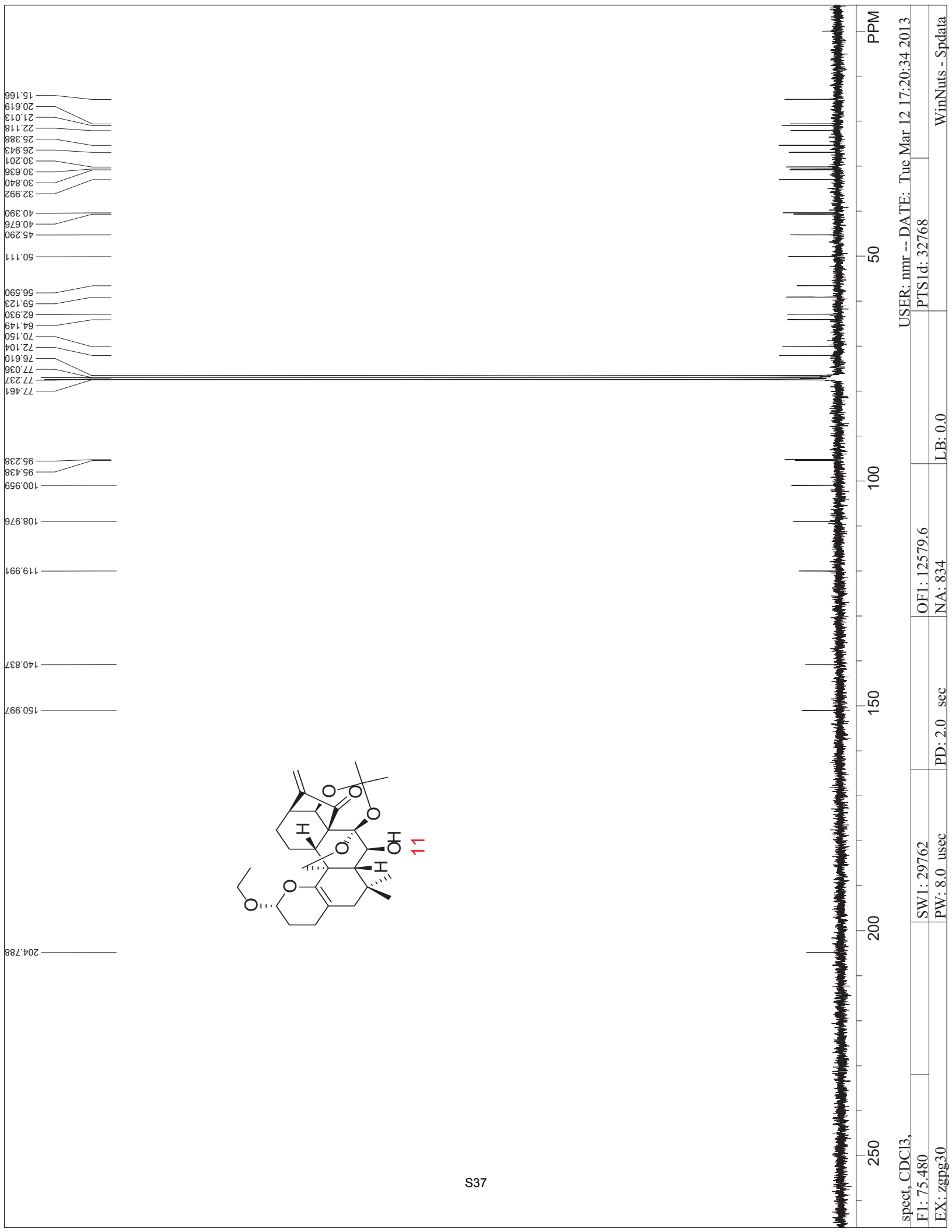
NOESY

noesy 1 /opt/topspin3.0/data/zhou/nmr

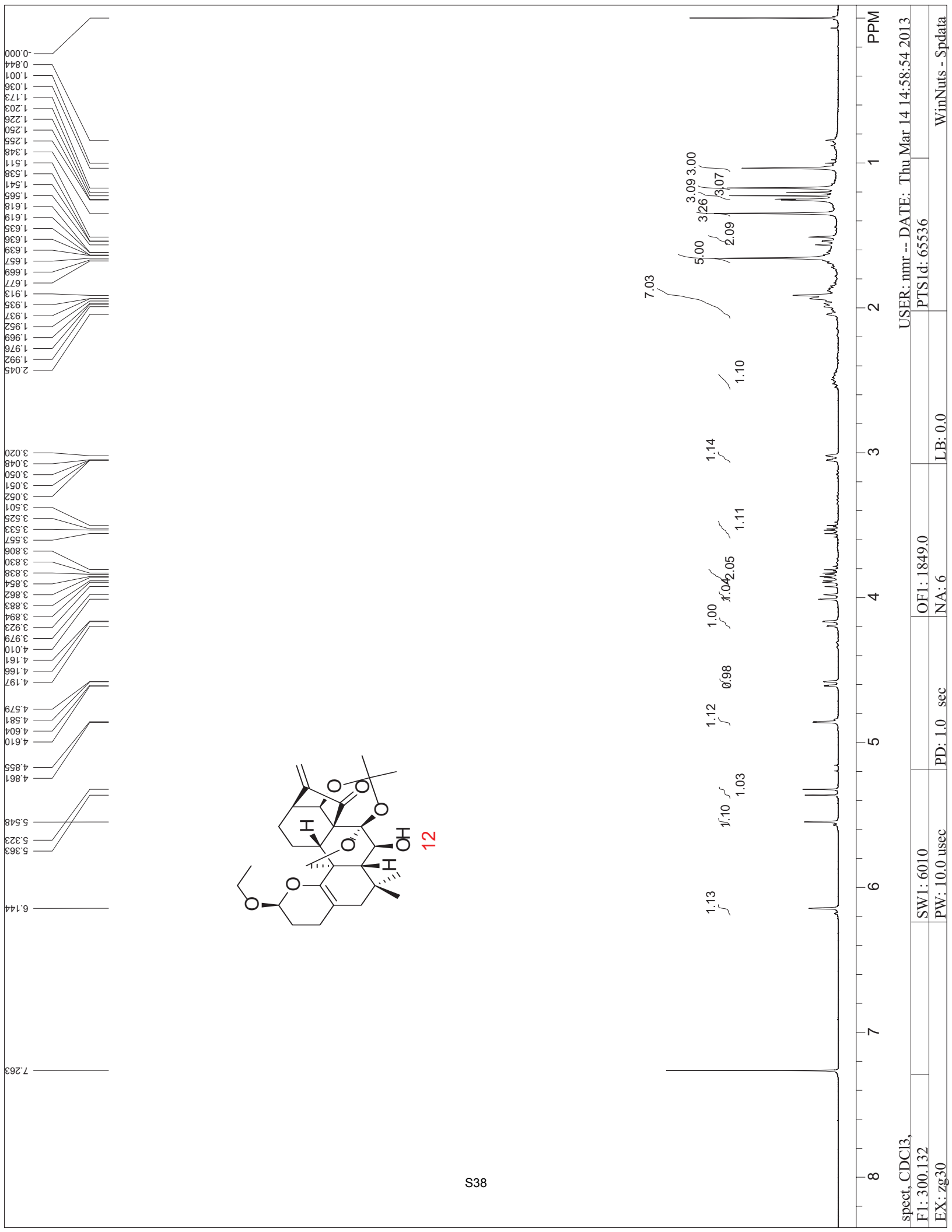




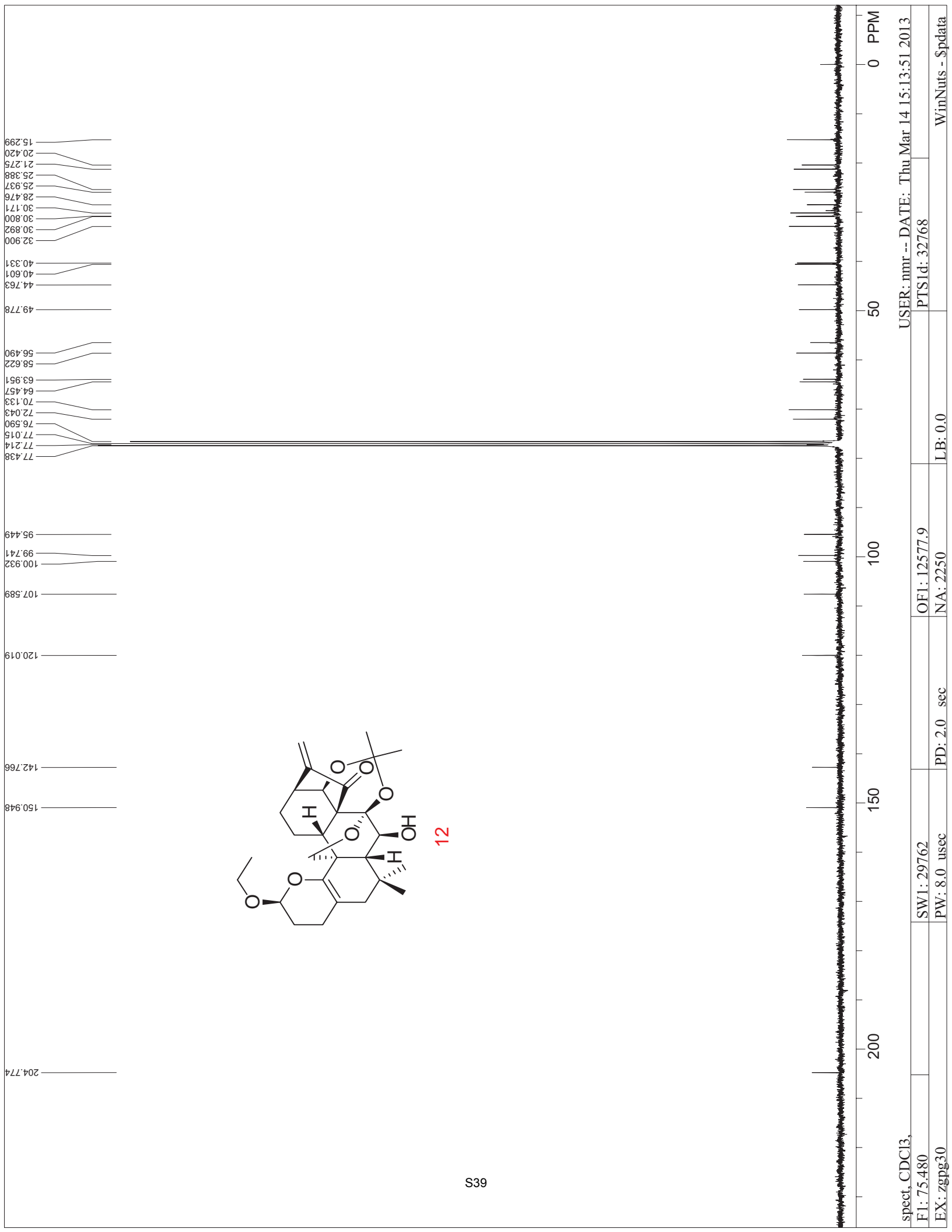
spect, CDCI3, USER: nmr --- DATE: Tue Mar 12 16:30:13 2013
 F1: 300.132 PTSId: 65536
 EX: zg30 WinNuts - \$pdata
 OF1: 1848.7 LB: 0.0
 NA: 6
 PD: 1.0 sec



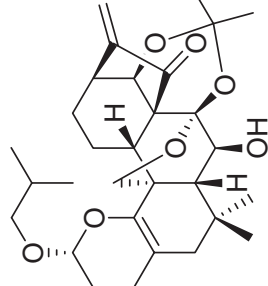
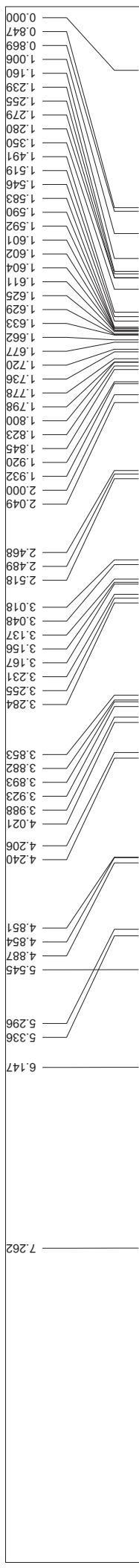
spect, CDCI3, USER: nmr --- DATE: Tue Mar 12 17:20:34 2013
 F1: 75.480 SW1: 29762 OF1: 12579.6 PTS1d: 32768
 EX: zgpg30 PW: 8.0 usec PD: 2.0 sec NA: 834 LB: 0.0 WinNuts - \$pdata



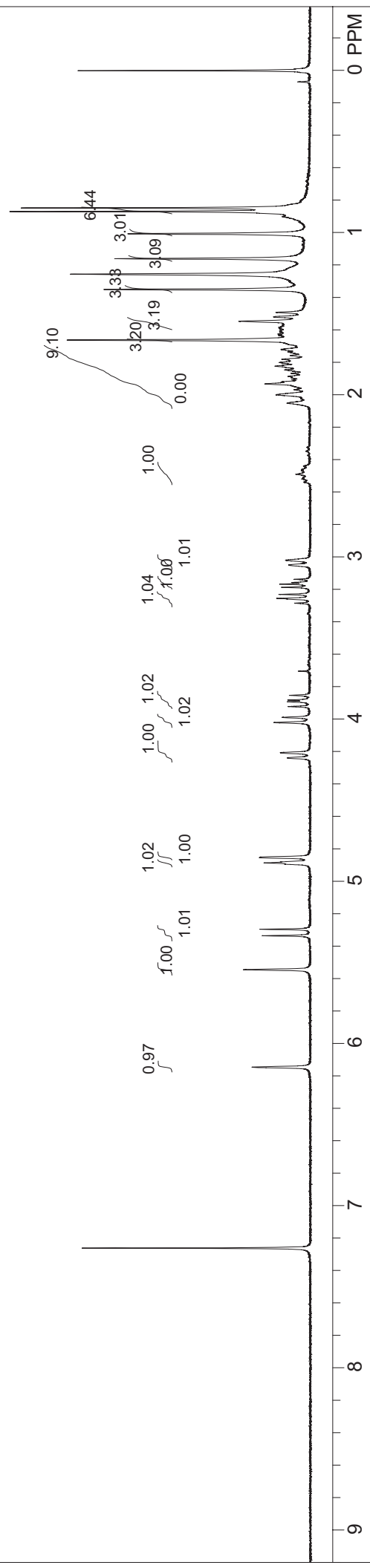
spect, CDCI3, USER: nmr --- DATE: Thu Mar 14 14:58:54 2013
 F1: 300.132 OF1: 1849.0 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec NA: 6 LB: 0.0 WinNuts - \$pdata

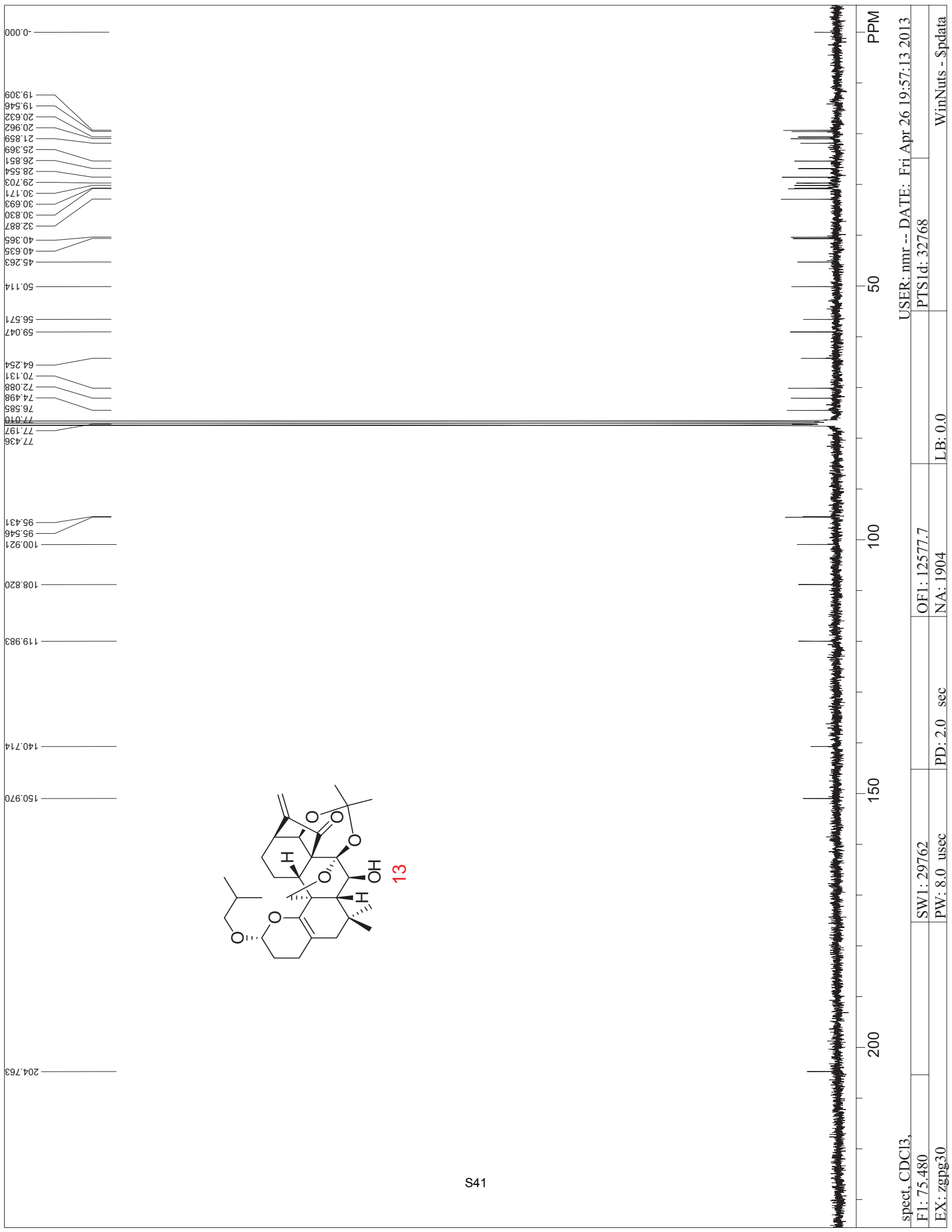


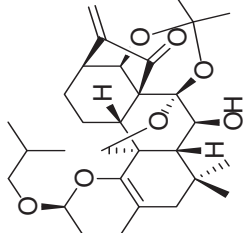
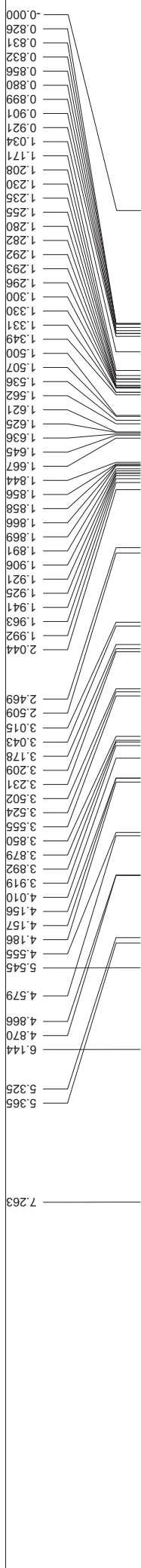
12



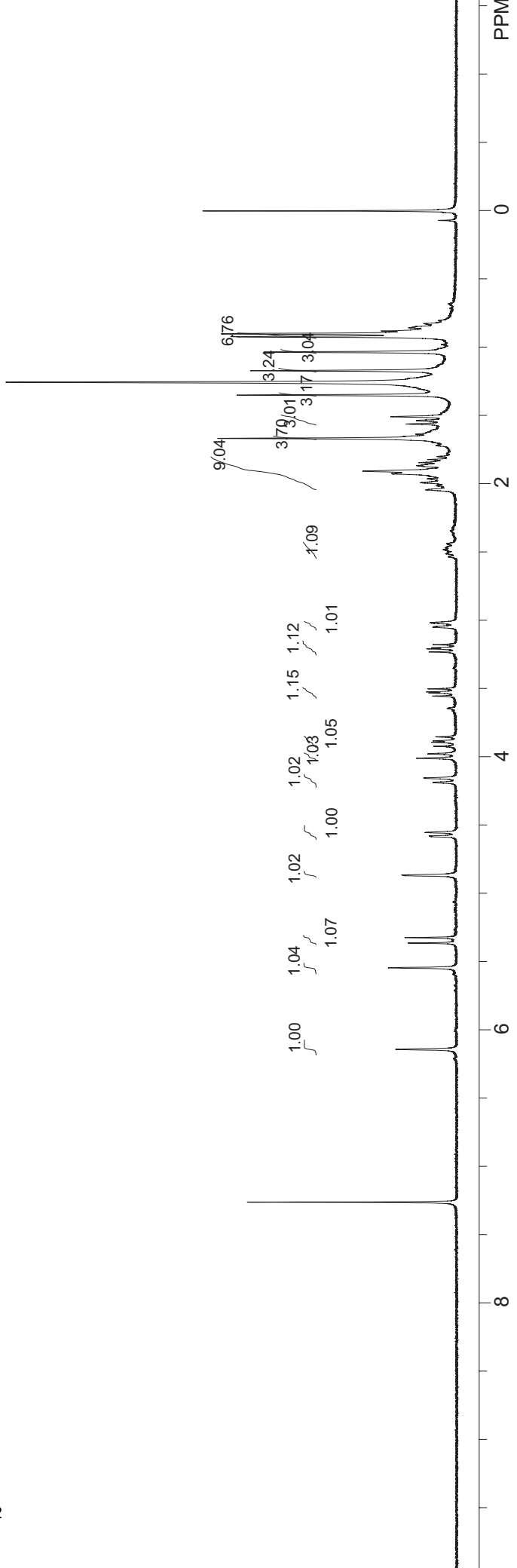
13



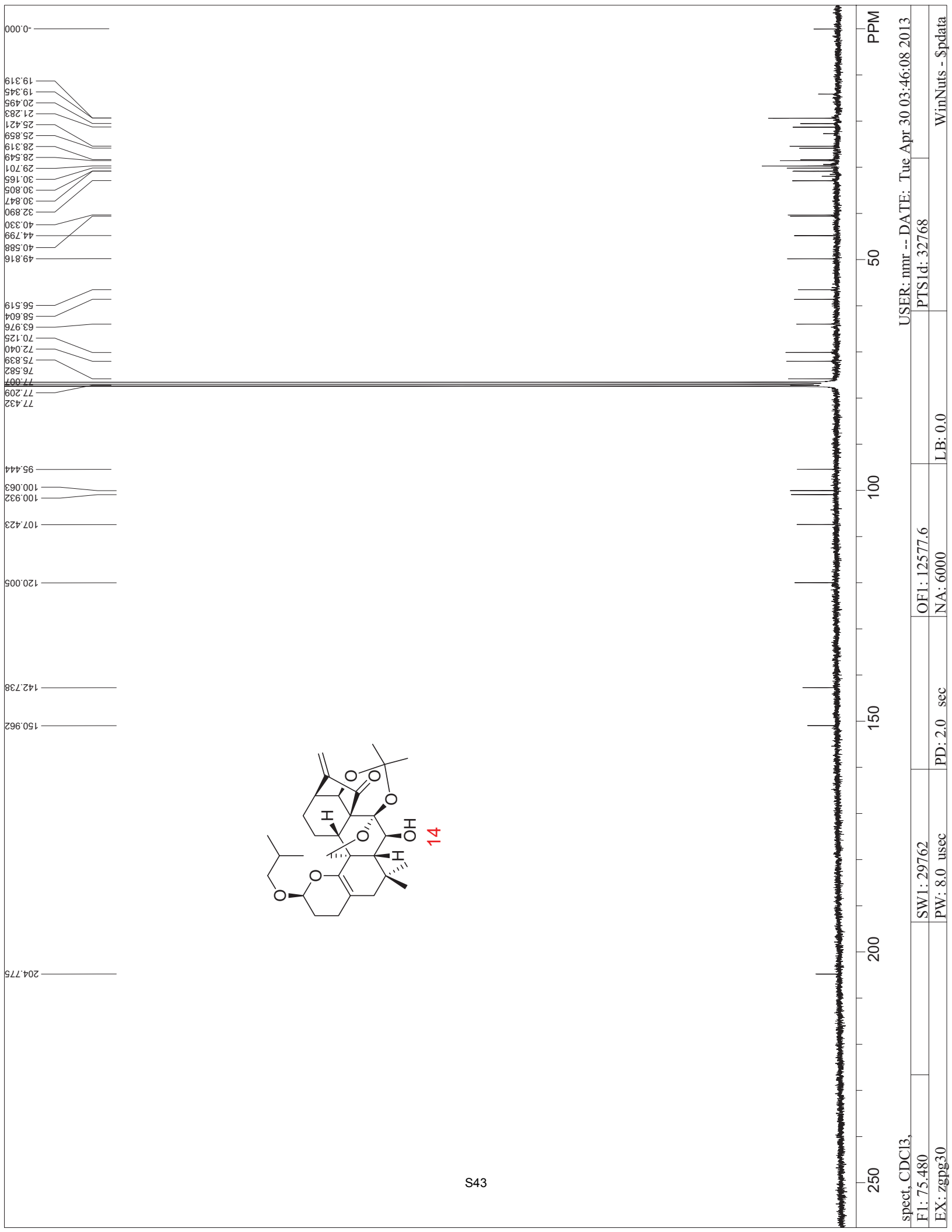




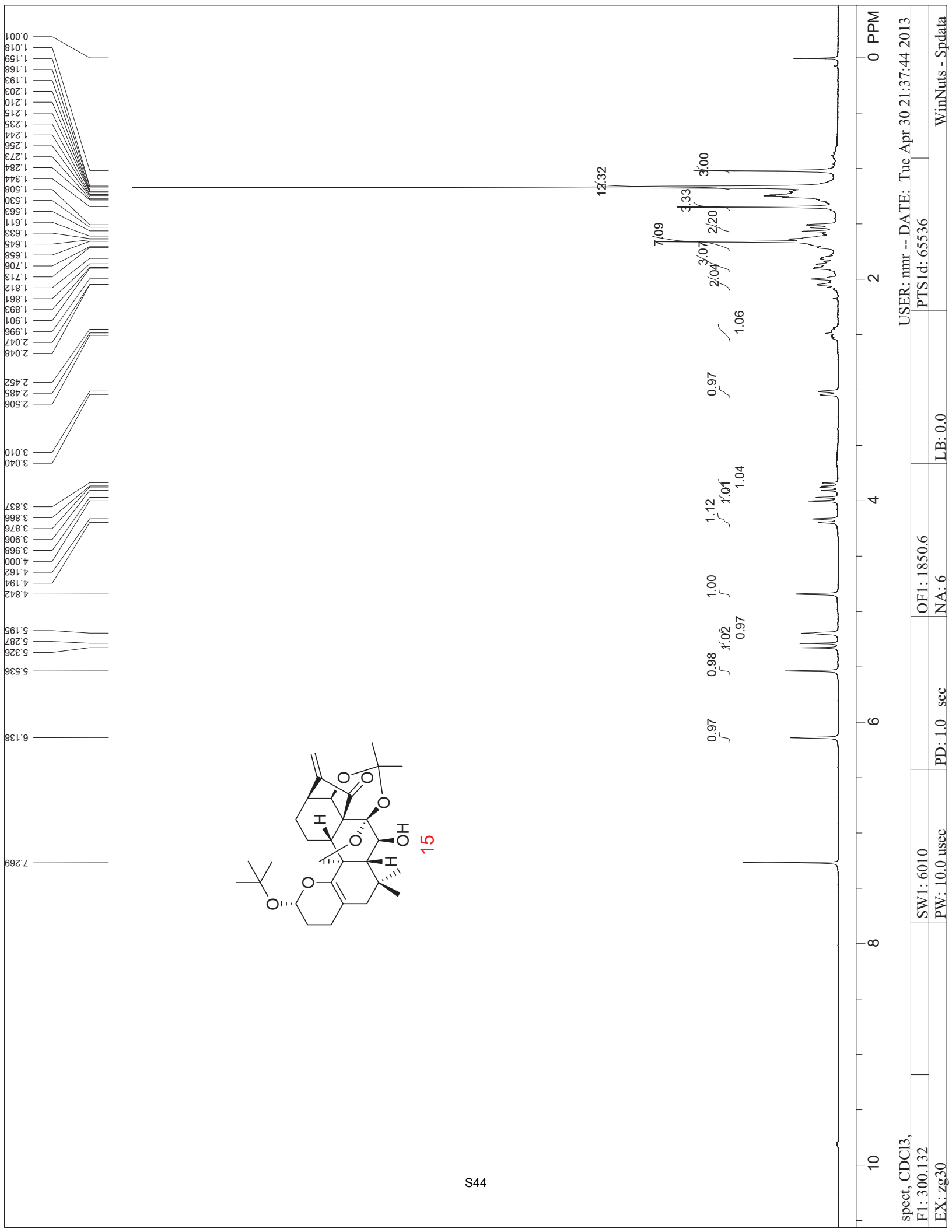
14



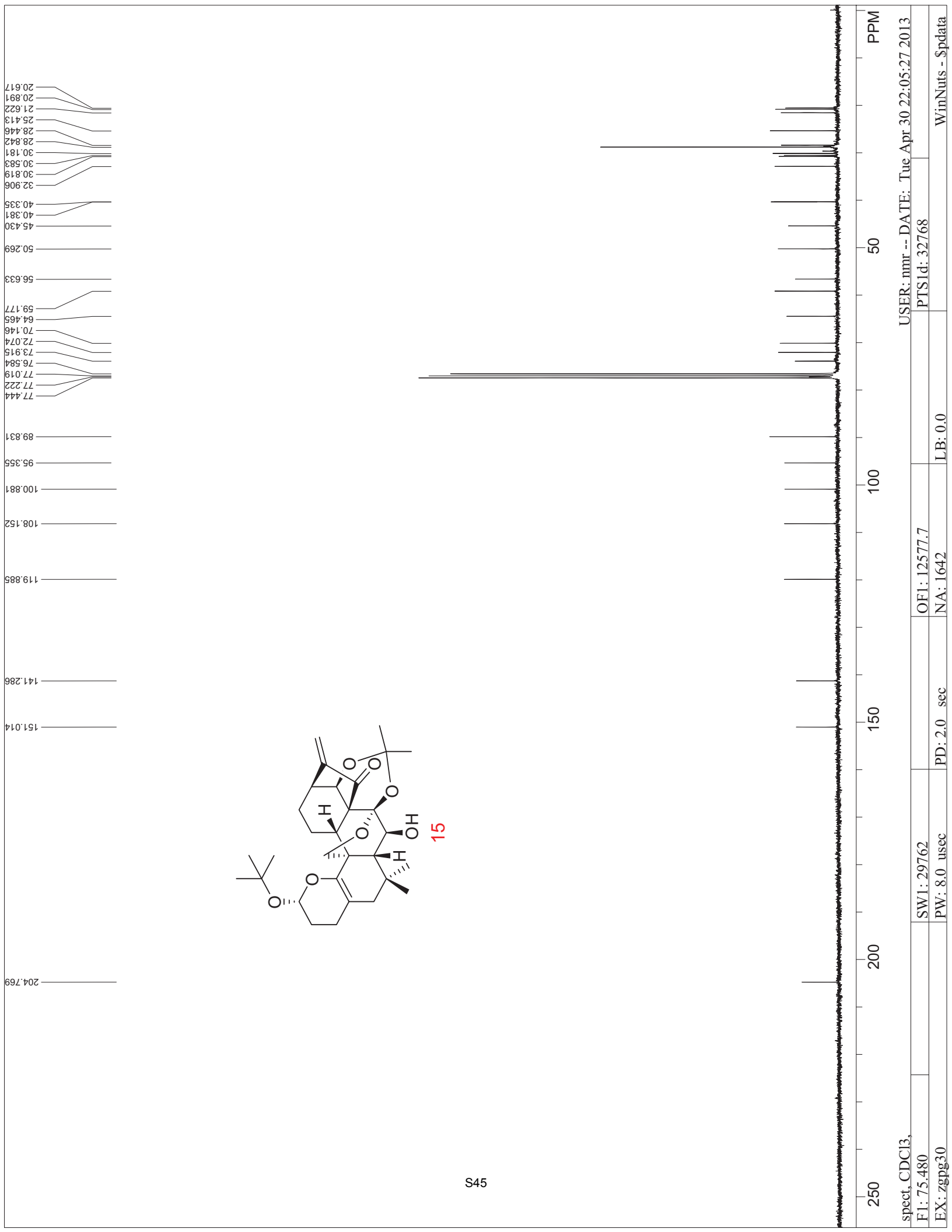
spect, CDC13,	USER: nmr -- DATE: Mon Apr 29 21:04:13 2013
F1: 300.132	PTS1d: 65536
EX: zg30	WinNuts - \$pdata
SW1: 6010	OF1: 1848.7
PW: 10.0 usec	NA: 9
PD: 1.0 sec	LB: 0.0



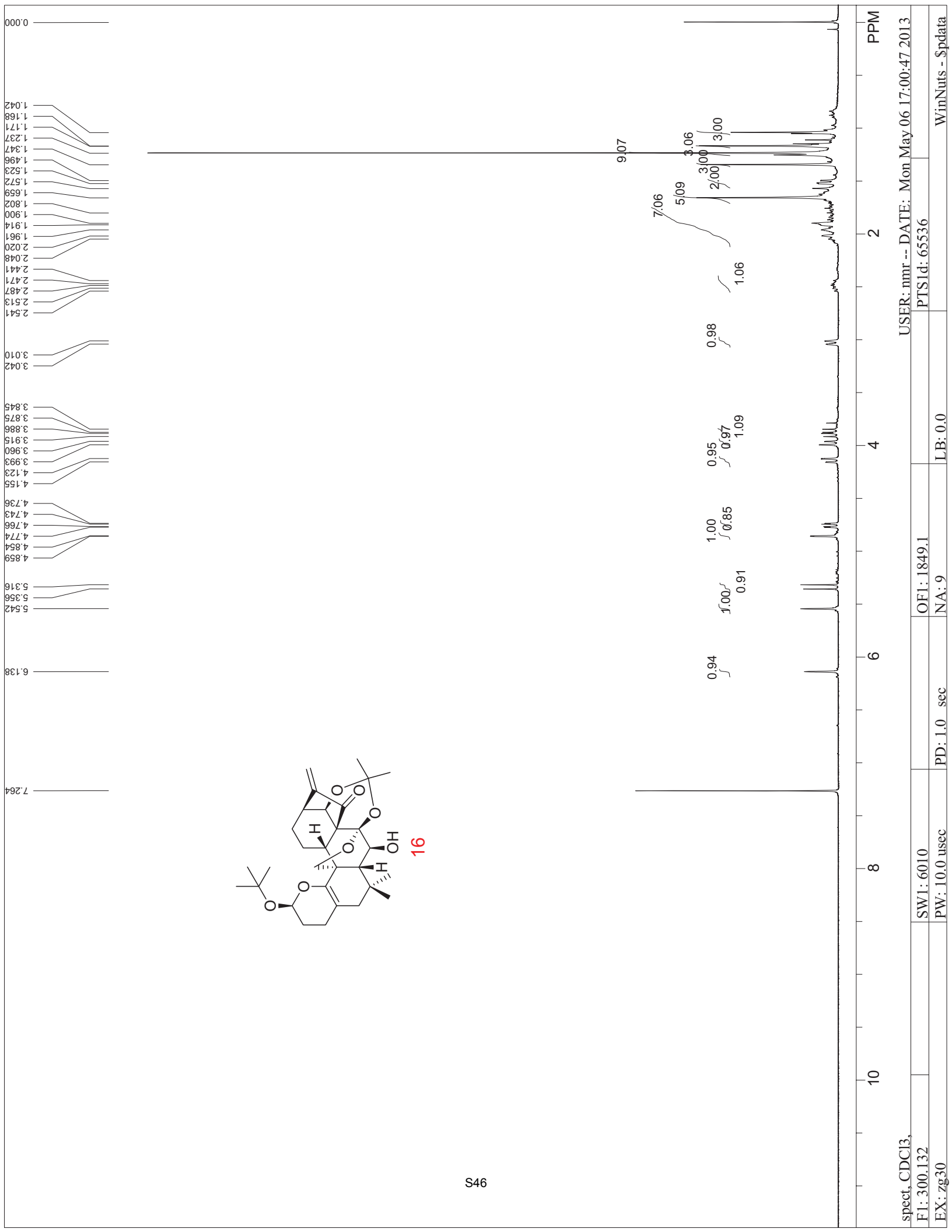
spect, CDCl3, USER: nmr -- DATE: Tue Apr 30 03:46:08 2013
 F1: 75.480 OF1: 12577.6 PTS1d: 32768
 EX: zgpg30 PD: 2.0 sec NA: 6000 LB: 0.0 WinNuts - \$pdata



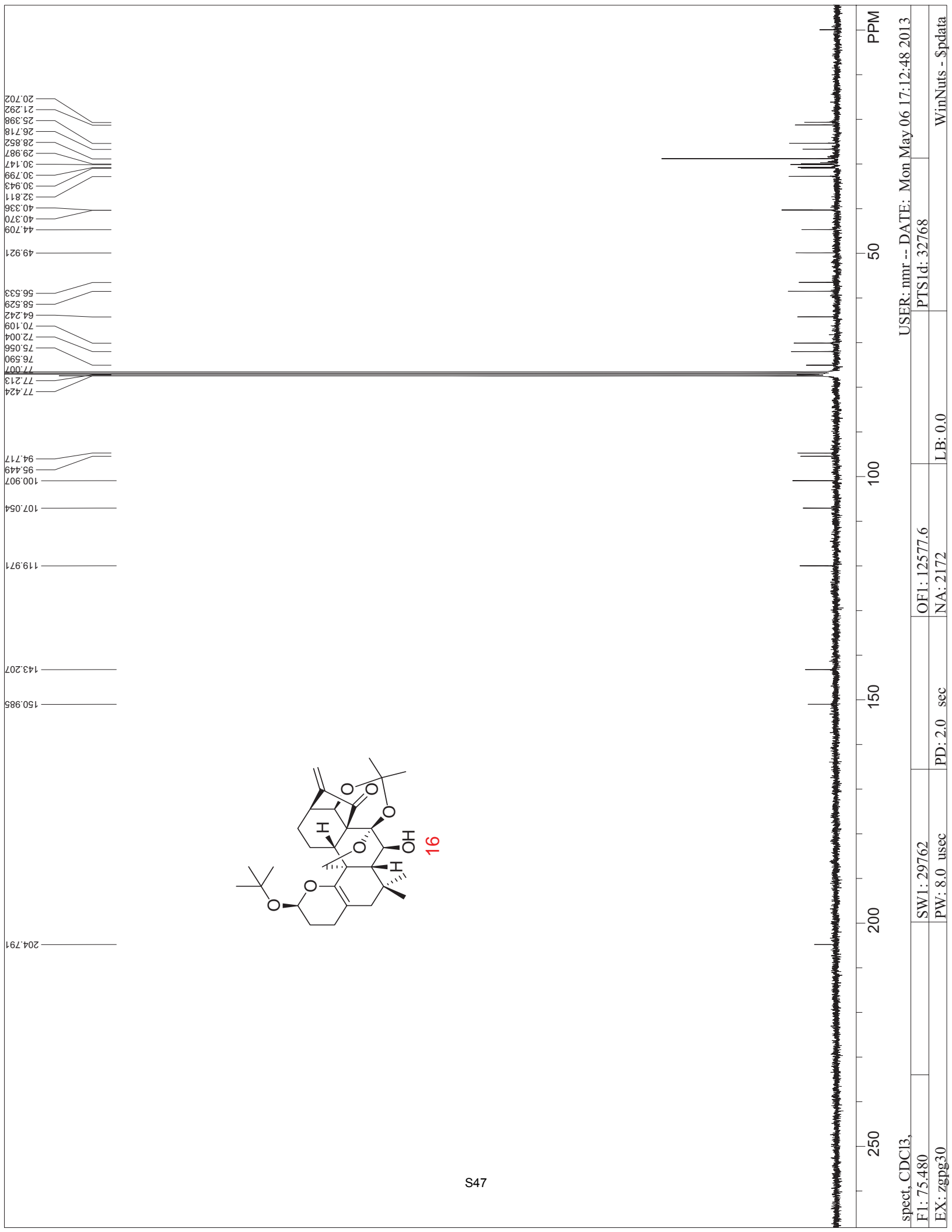
spect: CDCI3, USER: nmr -- DATE: Tue Apr 30 21:37:44 2013
 F1: 300.132 SW1: 6010 OF1: 1850.6 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec NA: 6 LB: 0.0 WinNuts - \$pdata



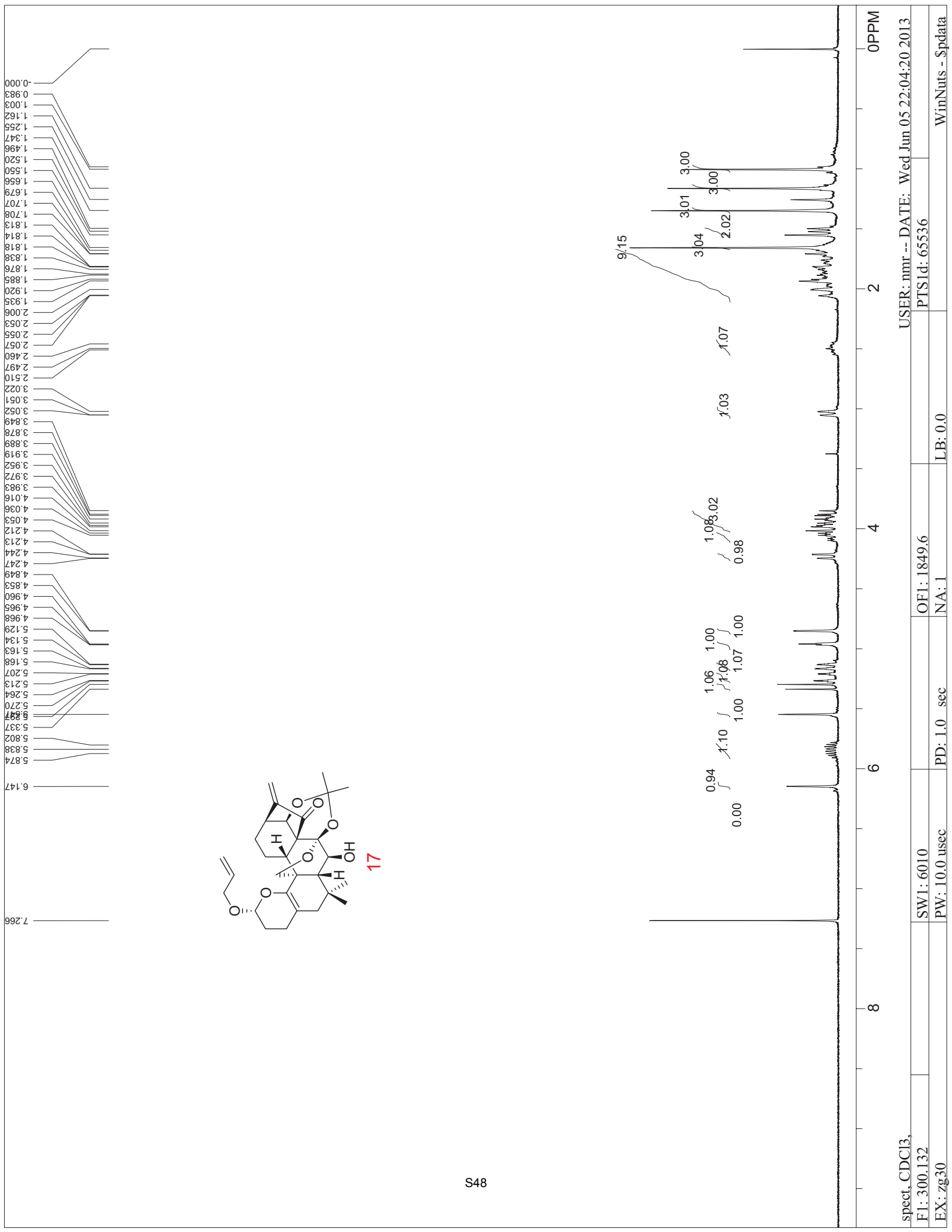
spect, CDCl3, USER: nmr -- DATE: Tue Apr 30 22:05:27 2013
 F1: 75.480 PTS1d: 32768
 EX: zgpg30 OF1: 12577.7 LB: 0.0
 PD: 2.0 sec NA: 1642
 WinNuts - \$pdata



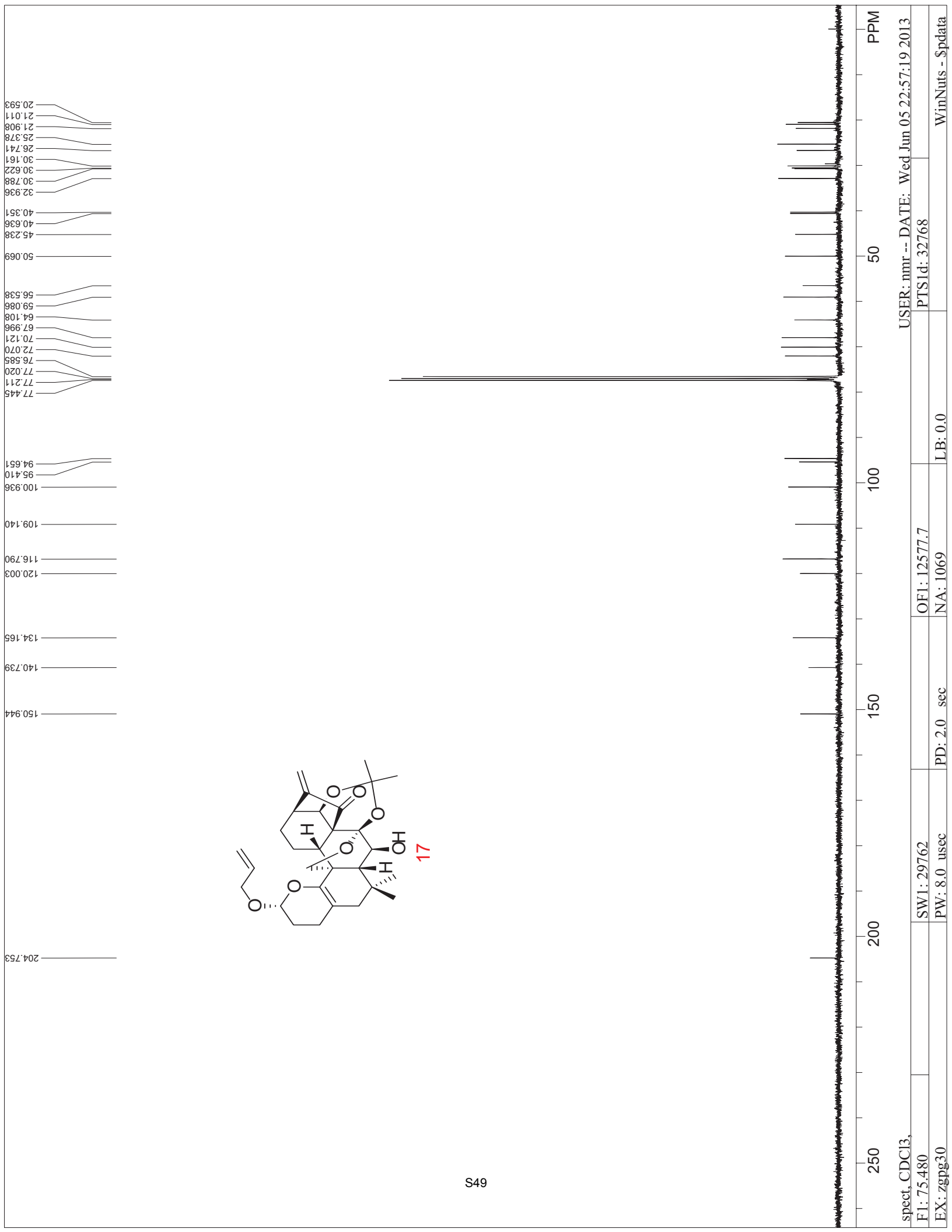
spect, CDC13, USER: nmr -- DATE: Mon May 06 17:00:47 2013
 F1: 300.132 OF1: 1849.1 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec NA: 9 LB: 0.0 WinNuts - \$pdata



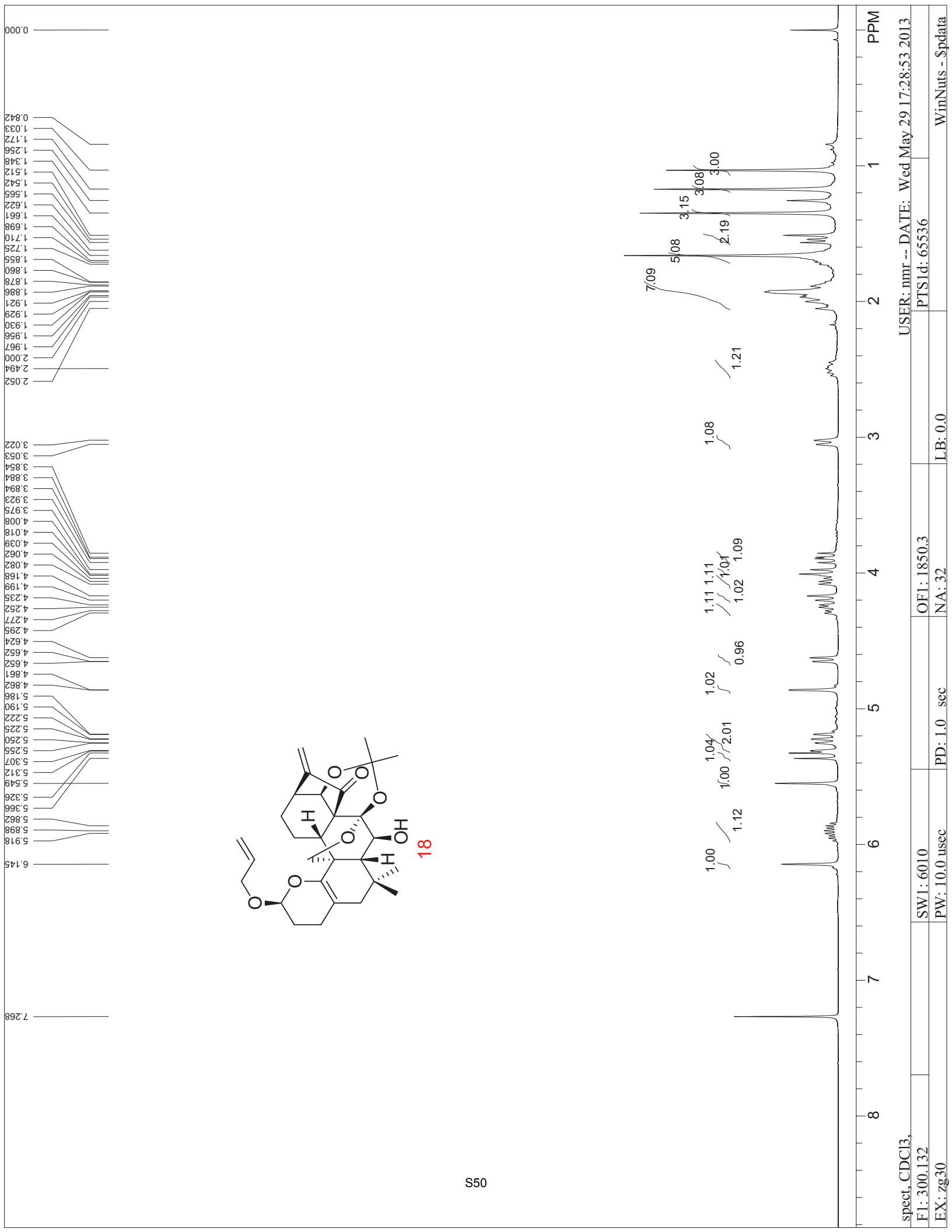
spect, CDCI3, USER: nmr -- DATE: Mon May 06 17:12:48 2013
 F1: 75.480 SW1: 29762 OF1: 12577.6 PTS1d: 32768
 EX: zgpg30 PW: 8.0 usec PD: 2.0 sec NA: 2172 LB: 0.0 WinNuts - \$pdata



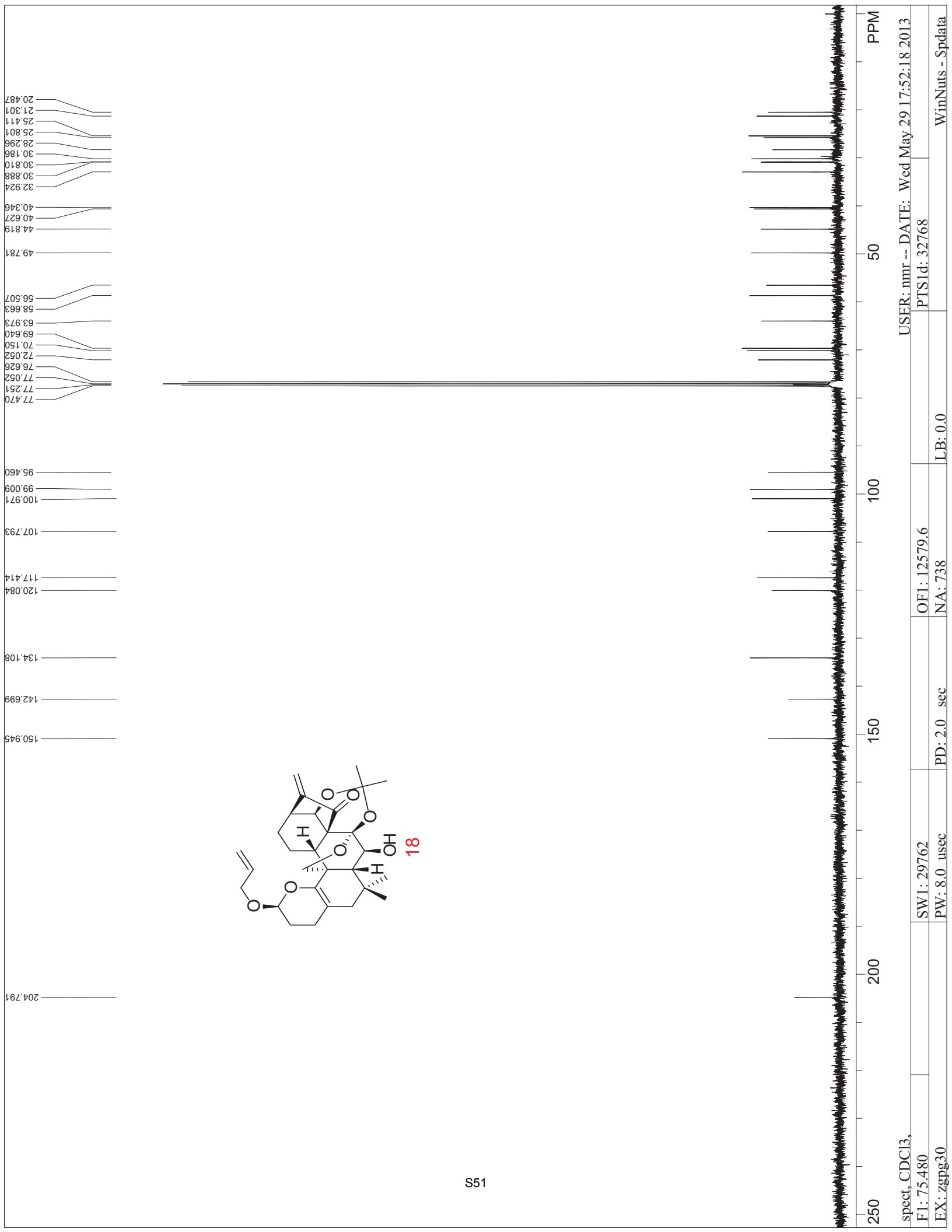
spect, CDC13, USER: nmr --- DATE: Wed Jun 05 22:04:20 2013
 F1: 300.132 OF1: 1849.6 PTS1d: 65536
 EX: zg30 PD: 1.0 sec LB: 0.0 WinNuts - \$pdata



spect, CDCl3, USER: nmr --- DATE: Wed Jun 05 22:57:19 2013
 F1: 75.480 SW1: 29762 OF1: 12577.7 PTS1d: 32768
 EX: zgpg30 PW: 8.0 usec PD: 2.0 sec NA: 1069 LB: 0.0 WinNuts - \$pdata



spect, CDCI3, USER: nmr -- DATE: Wed May 29 17:28:53 2013
 F1: 300.132 OF1: 1850.3 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec LB: 0.0 WinNuts - \$pdata



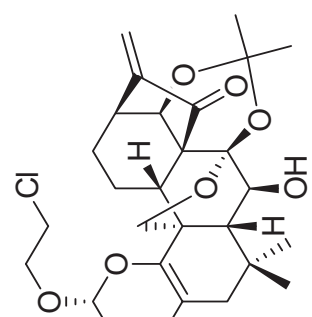
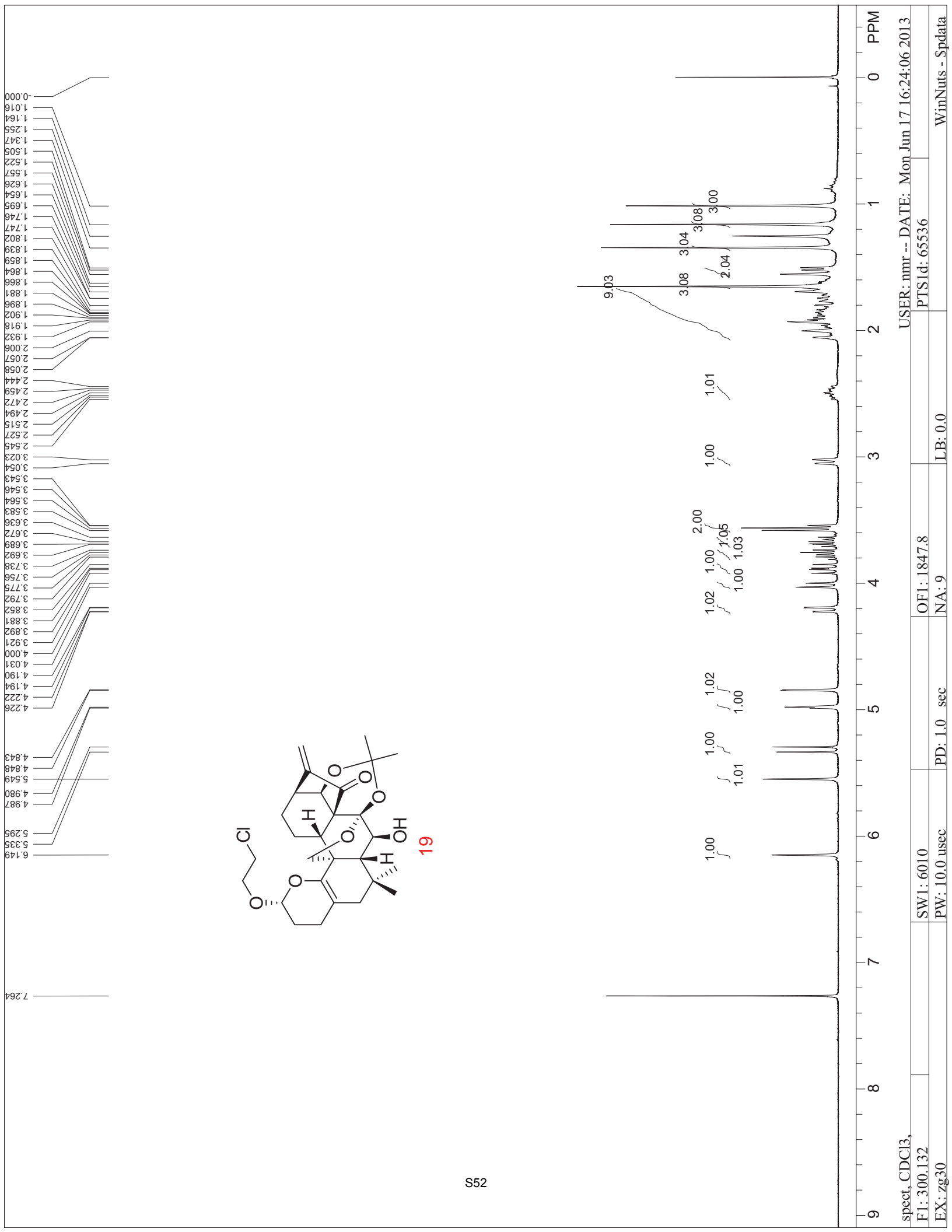
USER: nmr -- DATE: Wed May 29 17:52:18 2013
 PTSId: 32768

OF1: 12579.6
 NA: 738

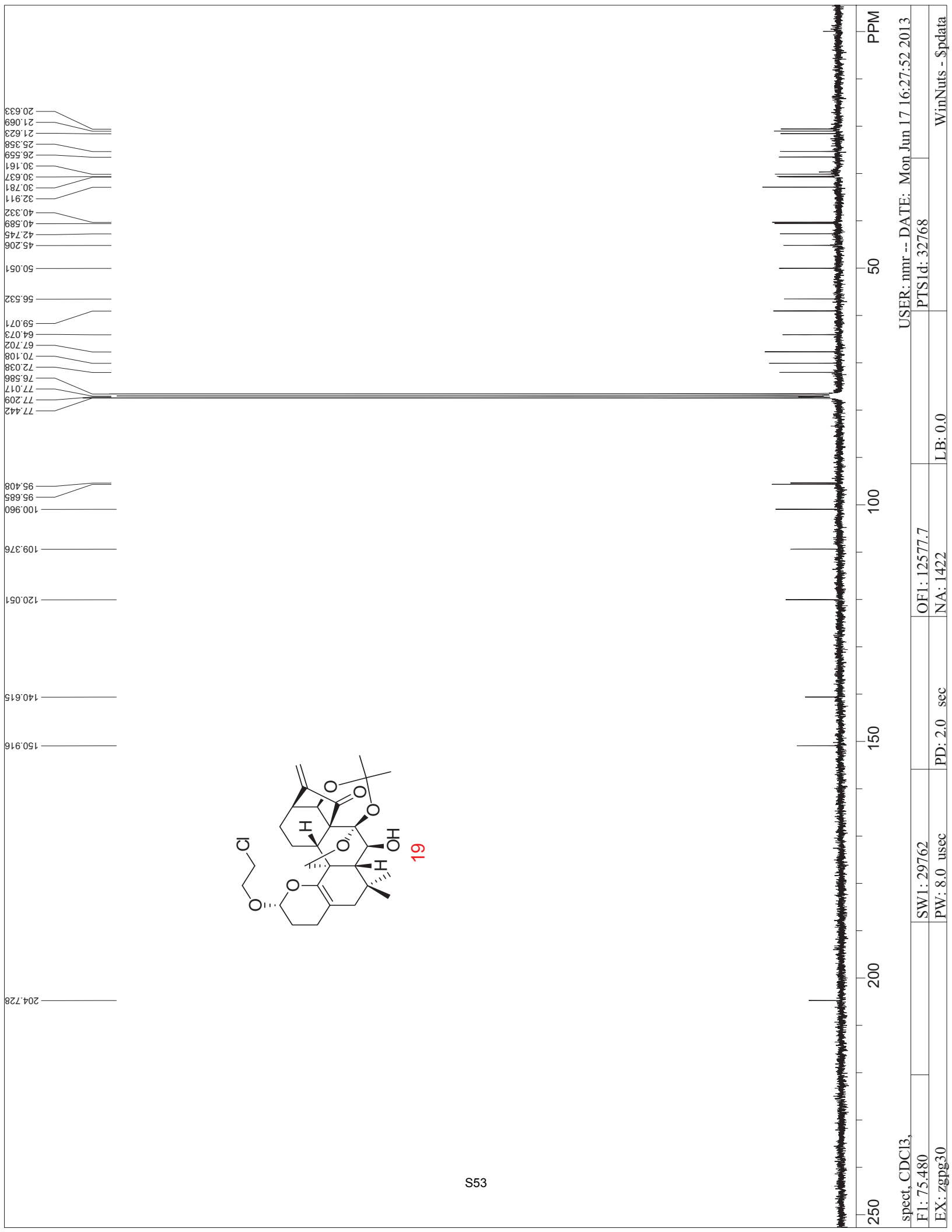
LB: 0.0
 PD: 2.0 sec

SW1: 29762
 PW: 8.0 usec

EX: zgpg30
 WinNuts - \$pdata

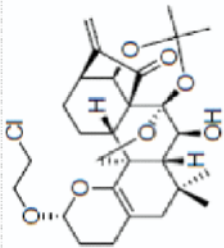


19



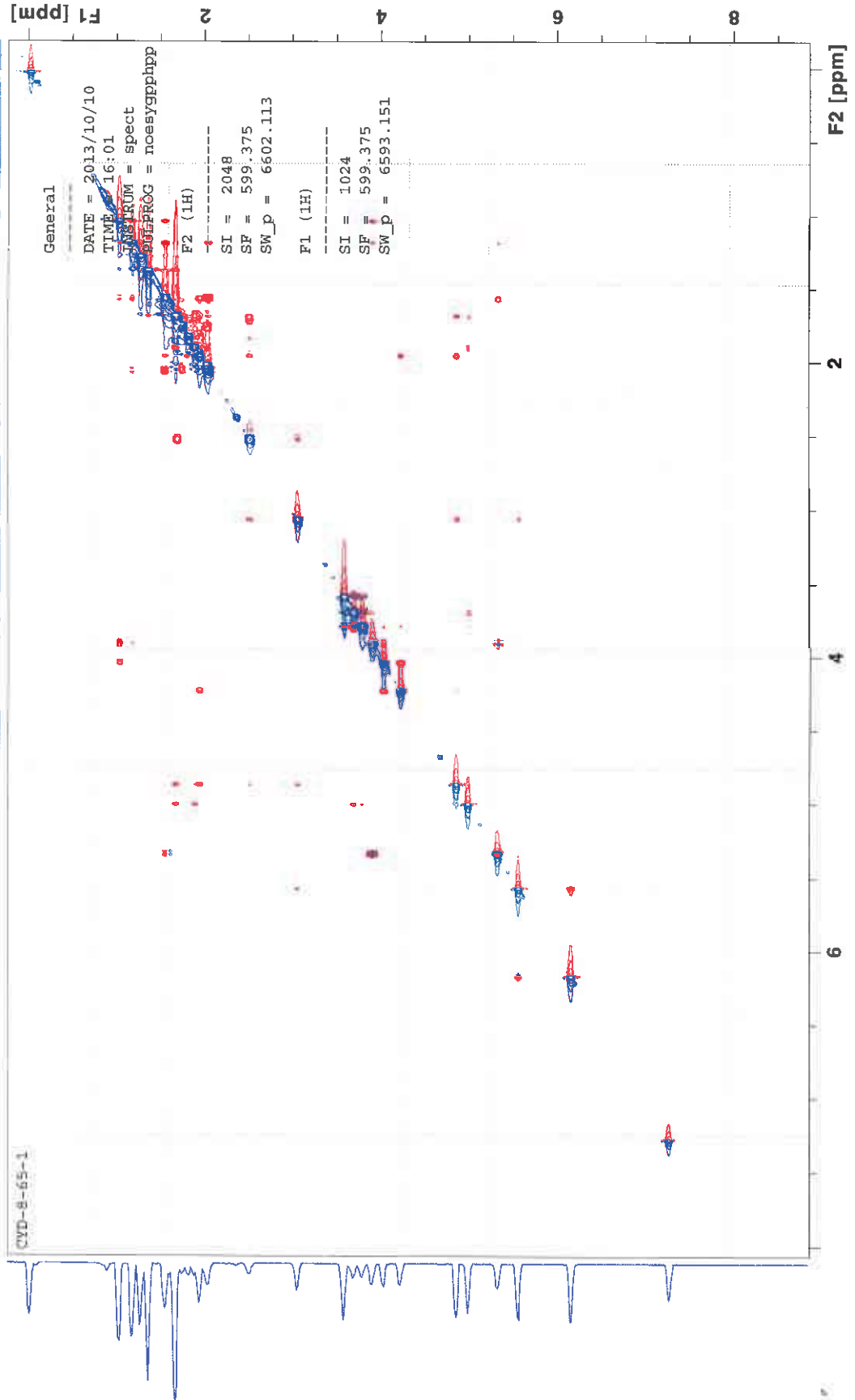
spect, CDCl3, USER: nmr -- DATE: Mon Jun 17 16:27:52 2013
 F1: 75.480 PTS1d: 32768
 EX: zgpg30 OF1: 12577.7 LB: 0.0
 PD: 2.0 sec NA: 1422
 WinNuts - \$pdata

noesy 15 1 /opt/topspin3.0/data/zhou/nmr

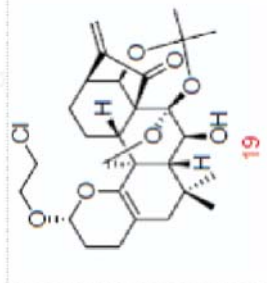


19

NOESY

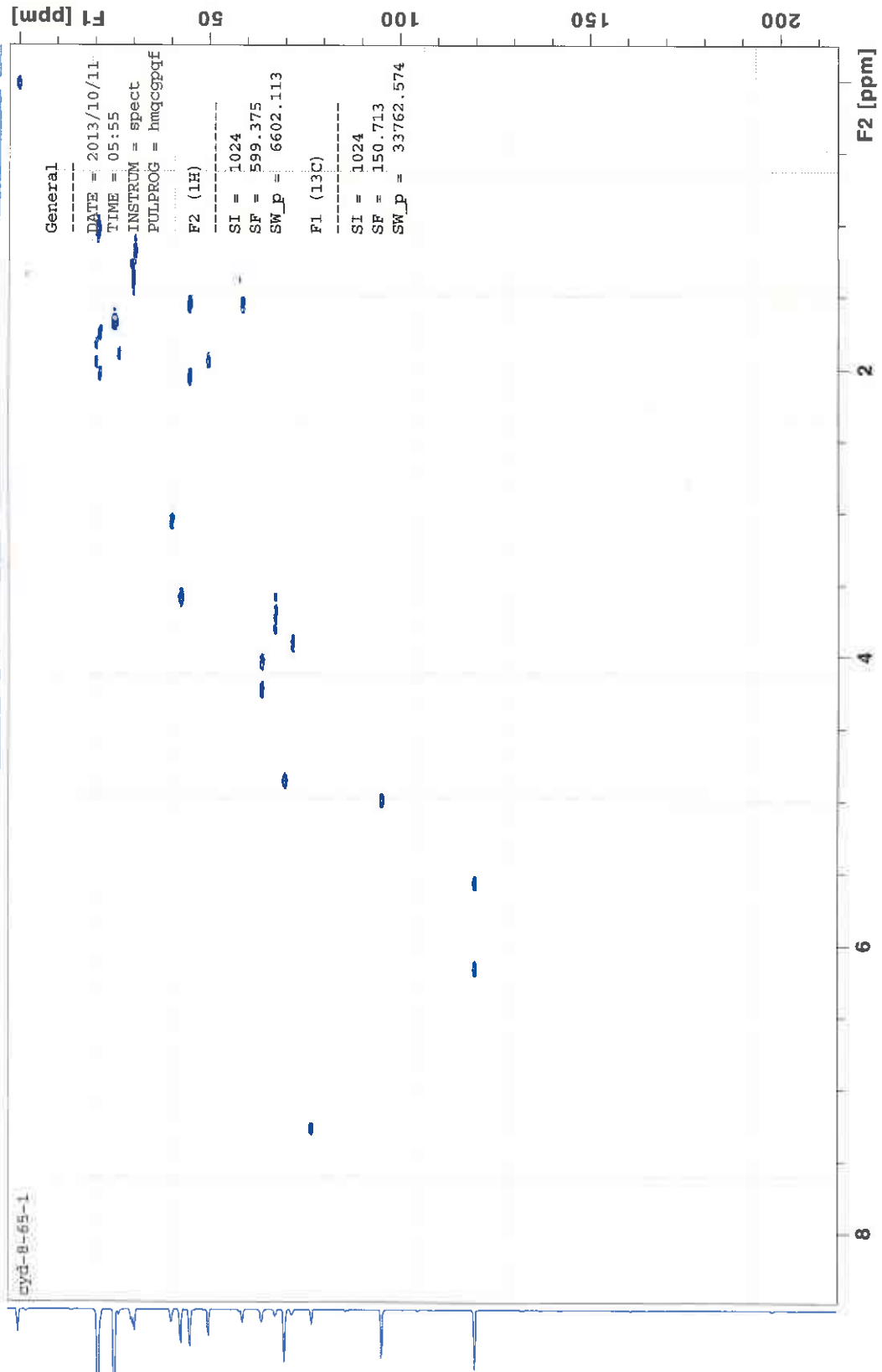


hmqc 18 1 /opt/topspin3.0/data/zhou/nmr

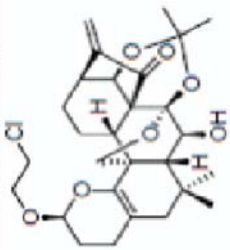


19

HMQC

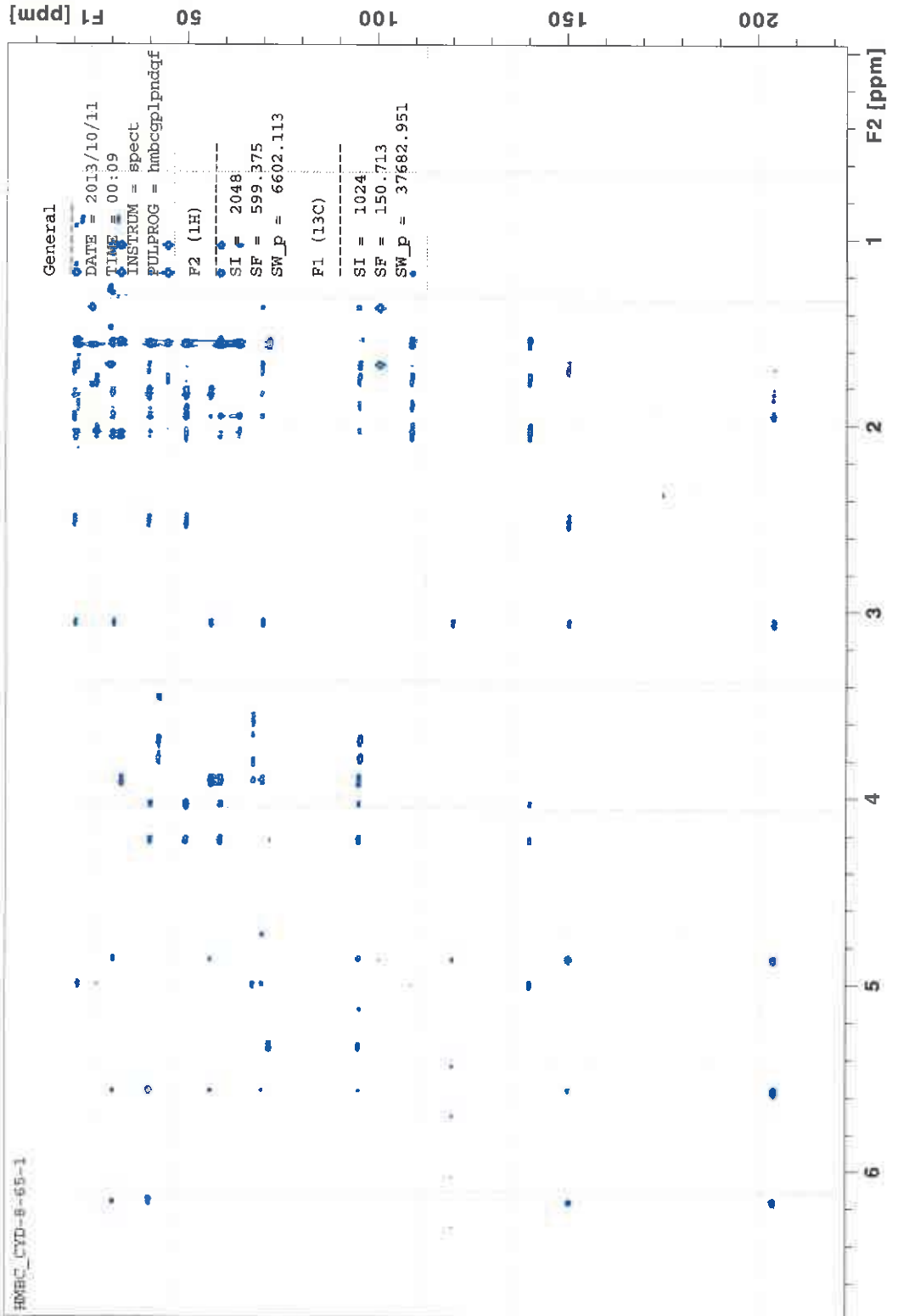


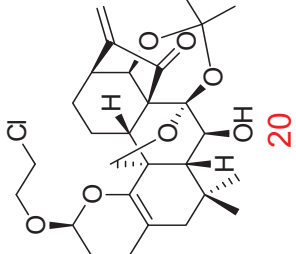
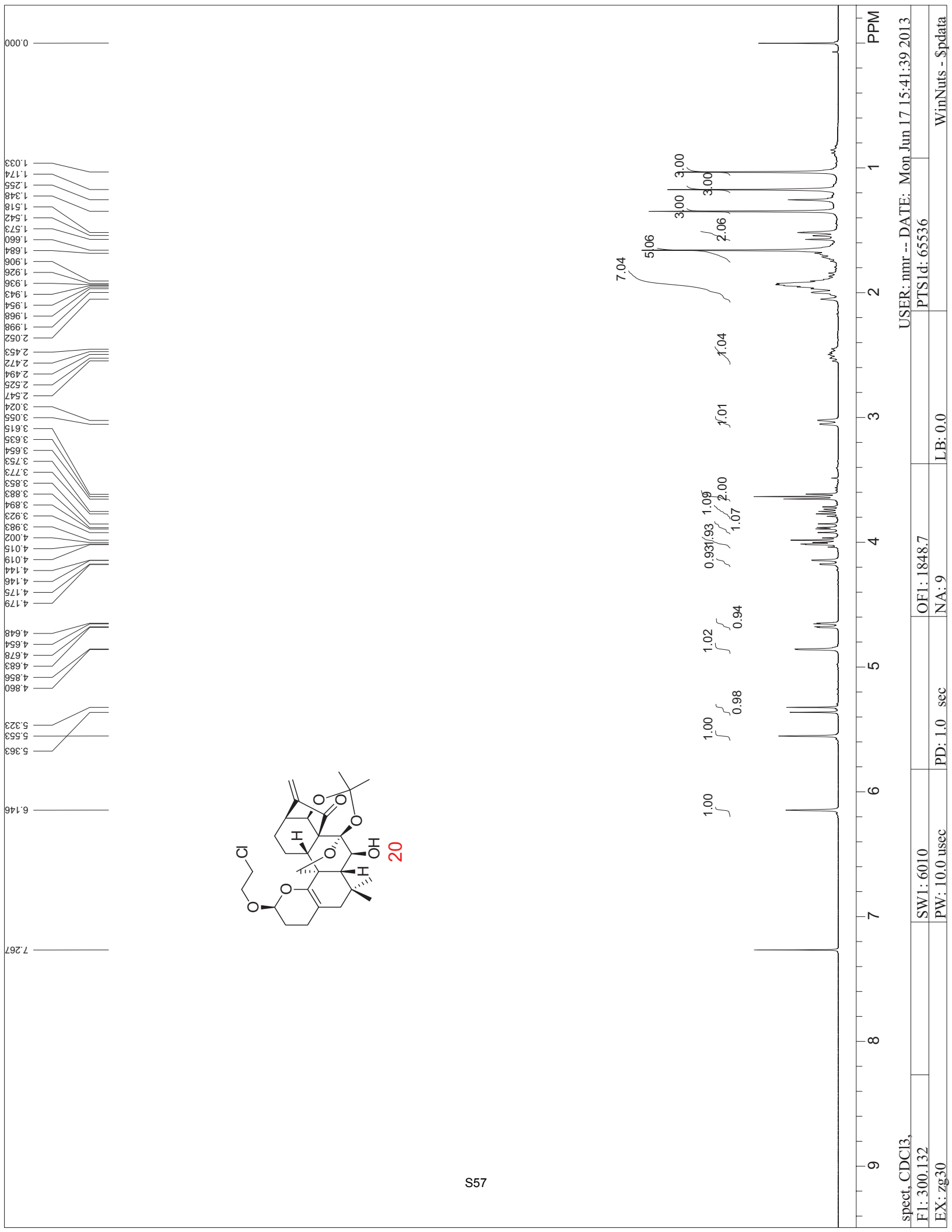
hmbc 18 1 /opt/topspin3.0/data/zhou/nmr



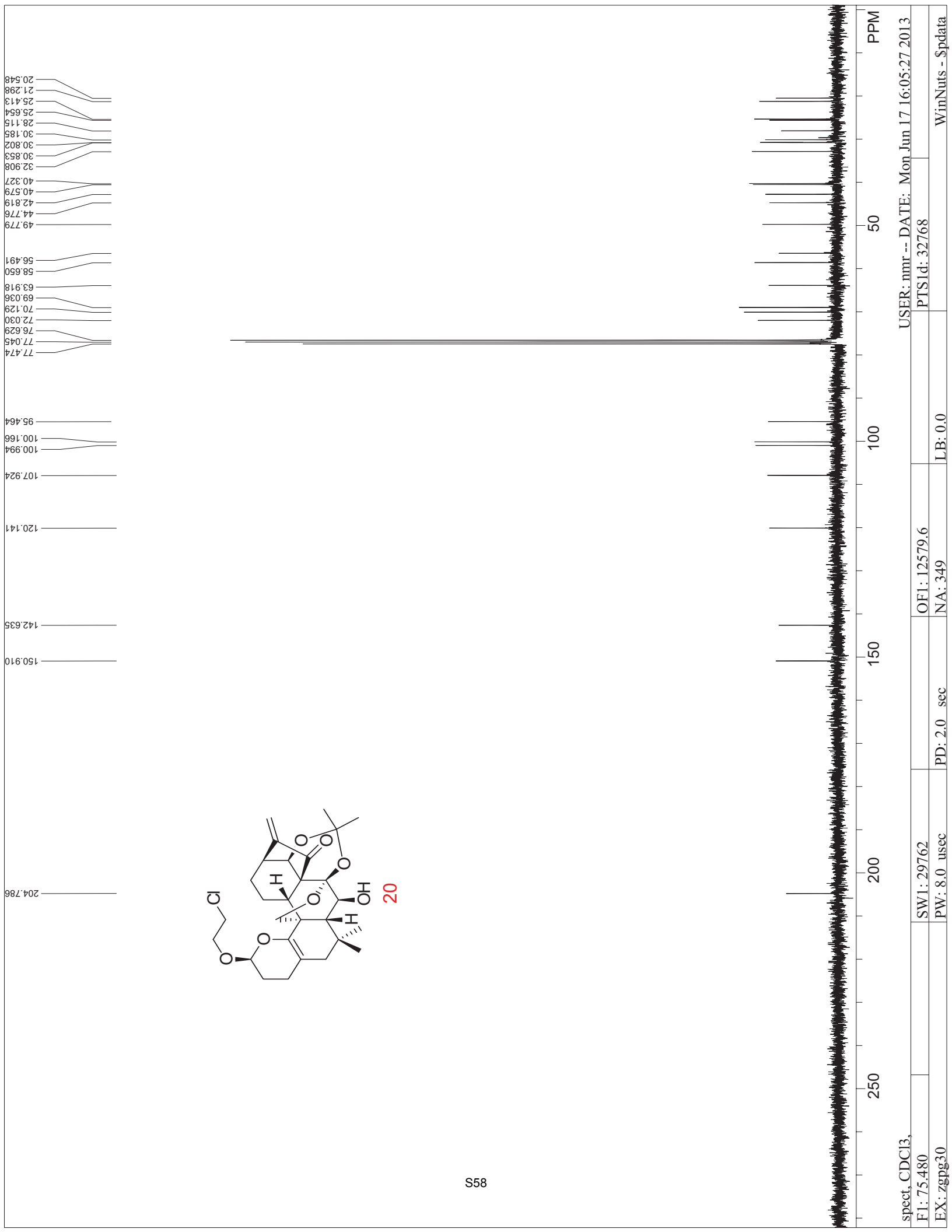
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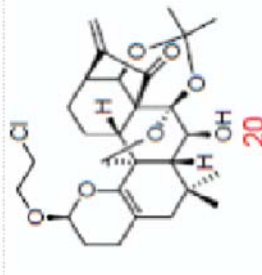
HMBC





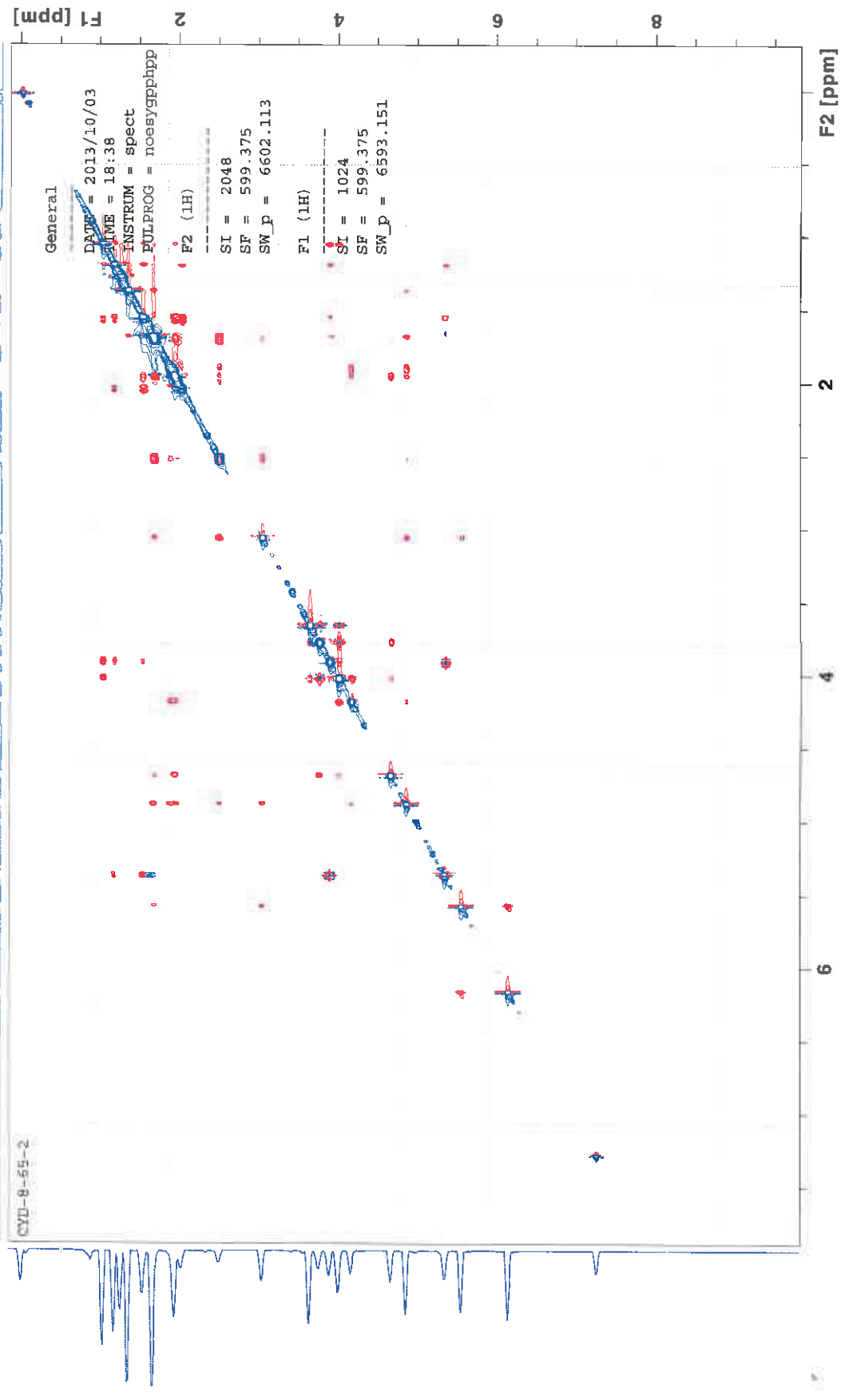
spect, CDCI3, USER: nmr --- DATE: Mon Jun 17 15:41:39 2013
 F1: 300.132 OF1: 1848.7 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec LB: 0.0 WinNuts - \$pdata

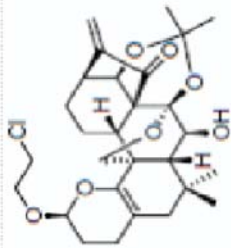




noesy 14 1 /opt/topspin3.0/data/zhou/nmr

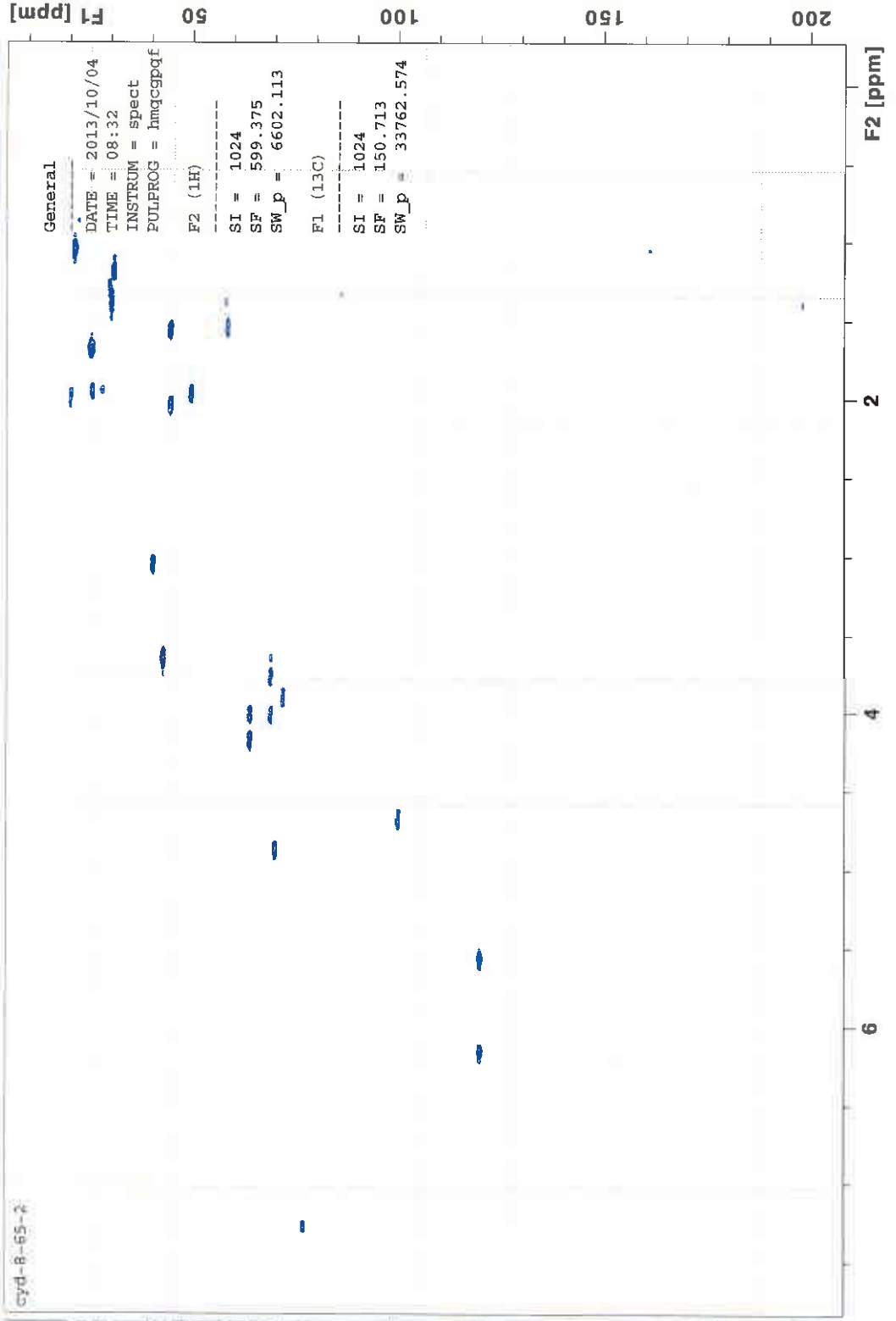
20
NOESY

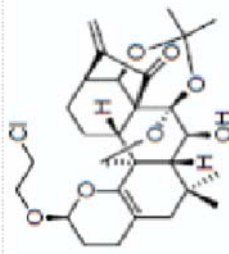




20
HMOC

hmqc 17 1 /opt/topspin3.0/data/zhou/nmr

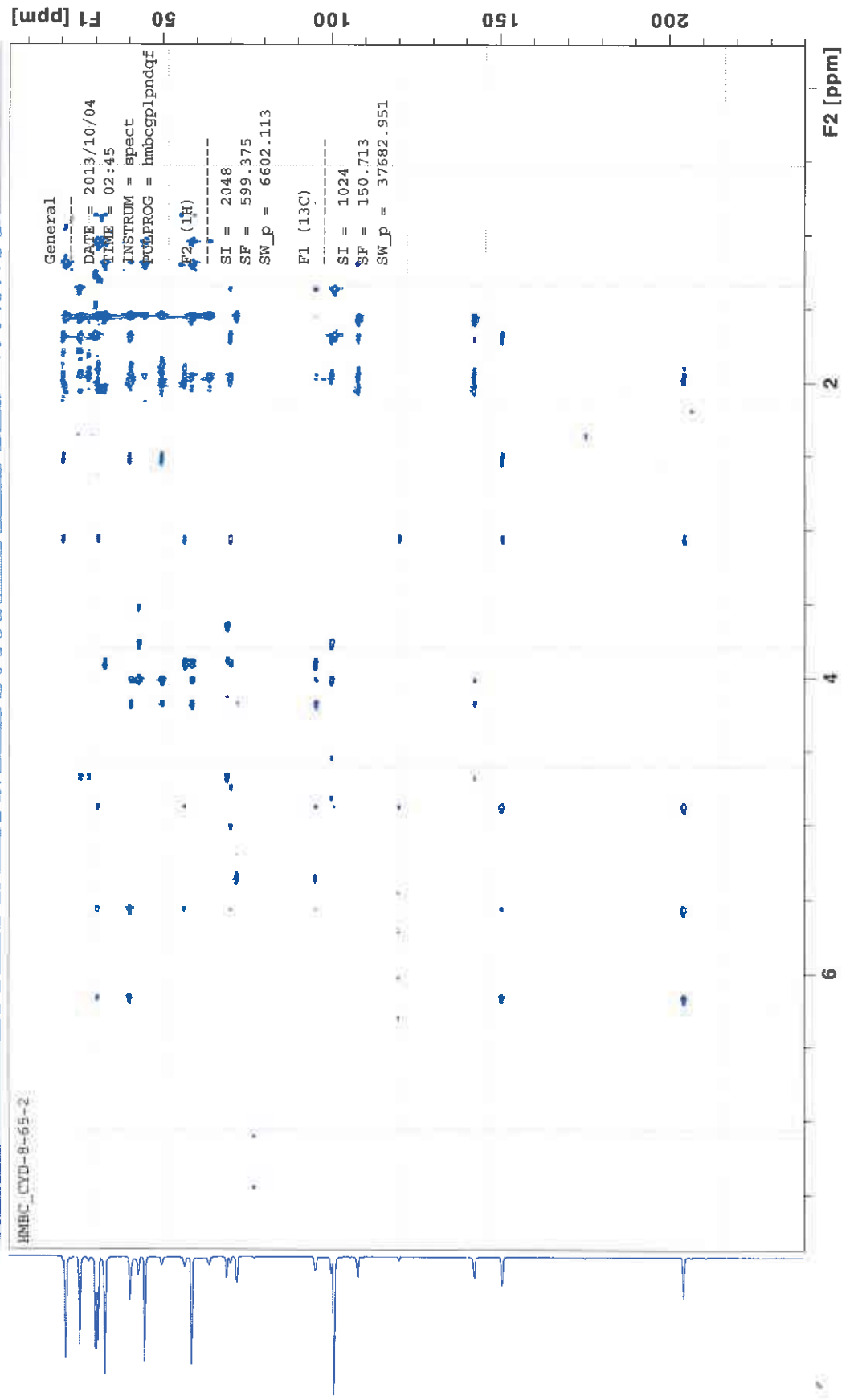


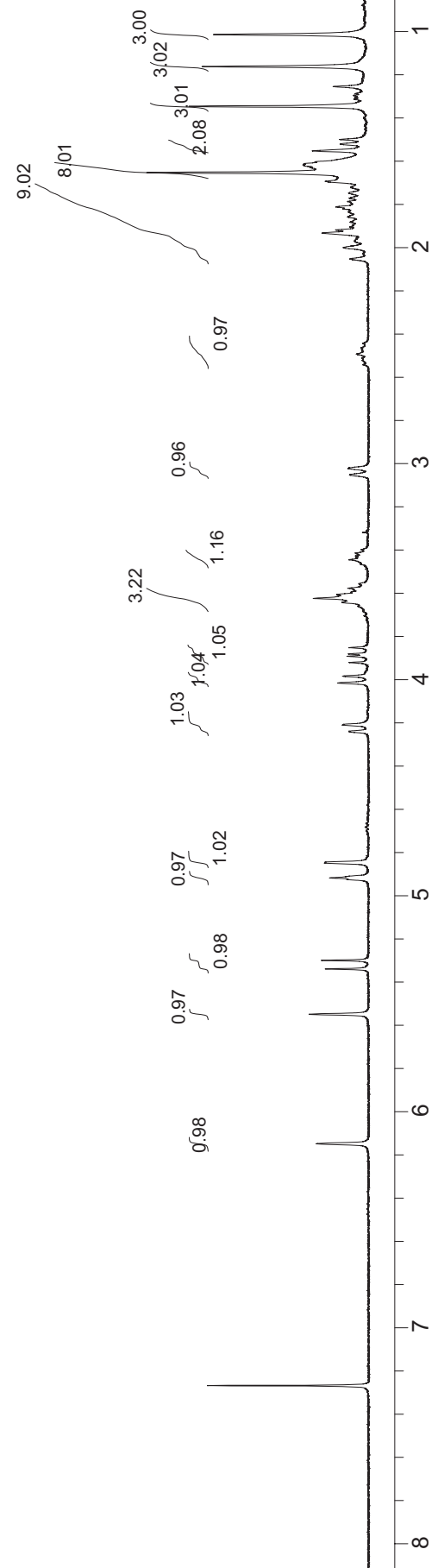
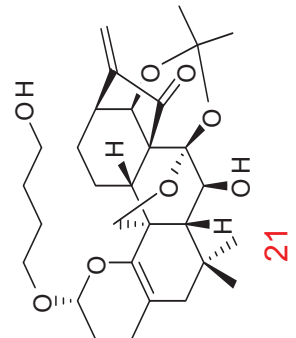
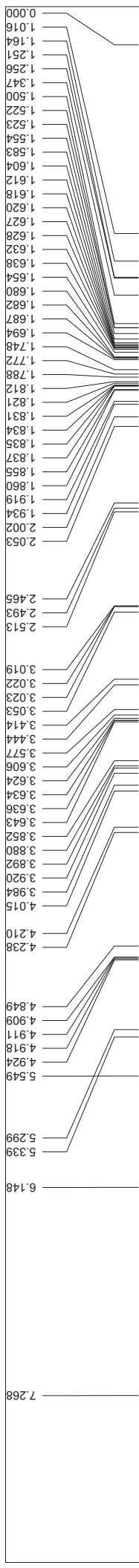


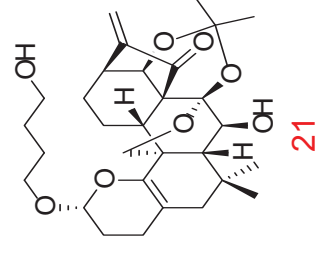
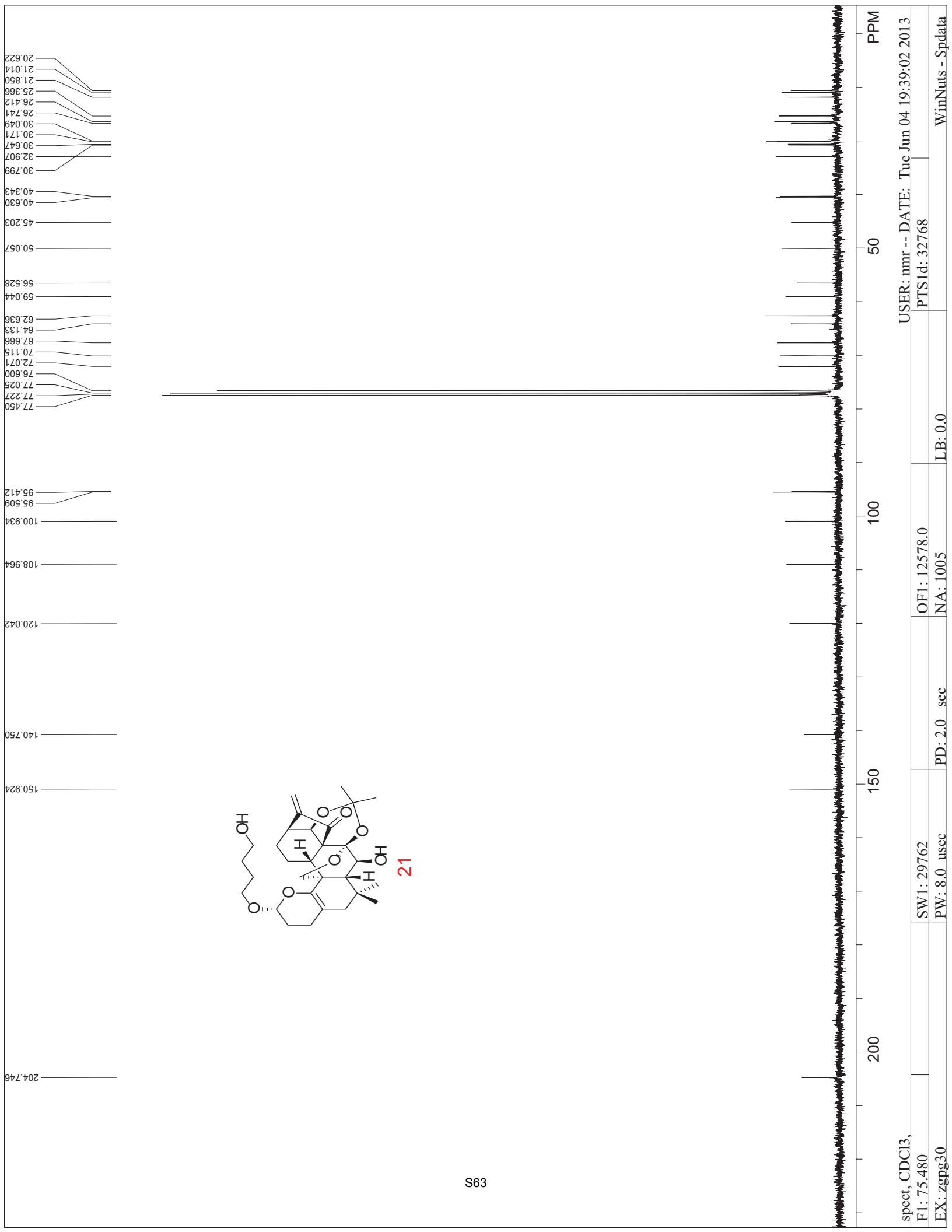
hmbc 17 1 /opt/topspin3.0/data/zhou/mmr

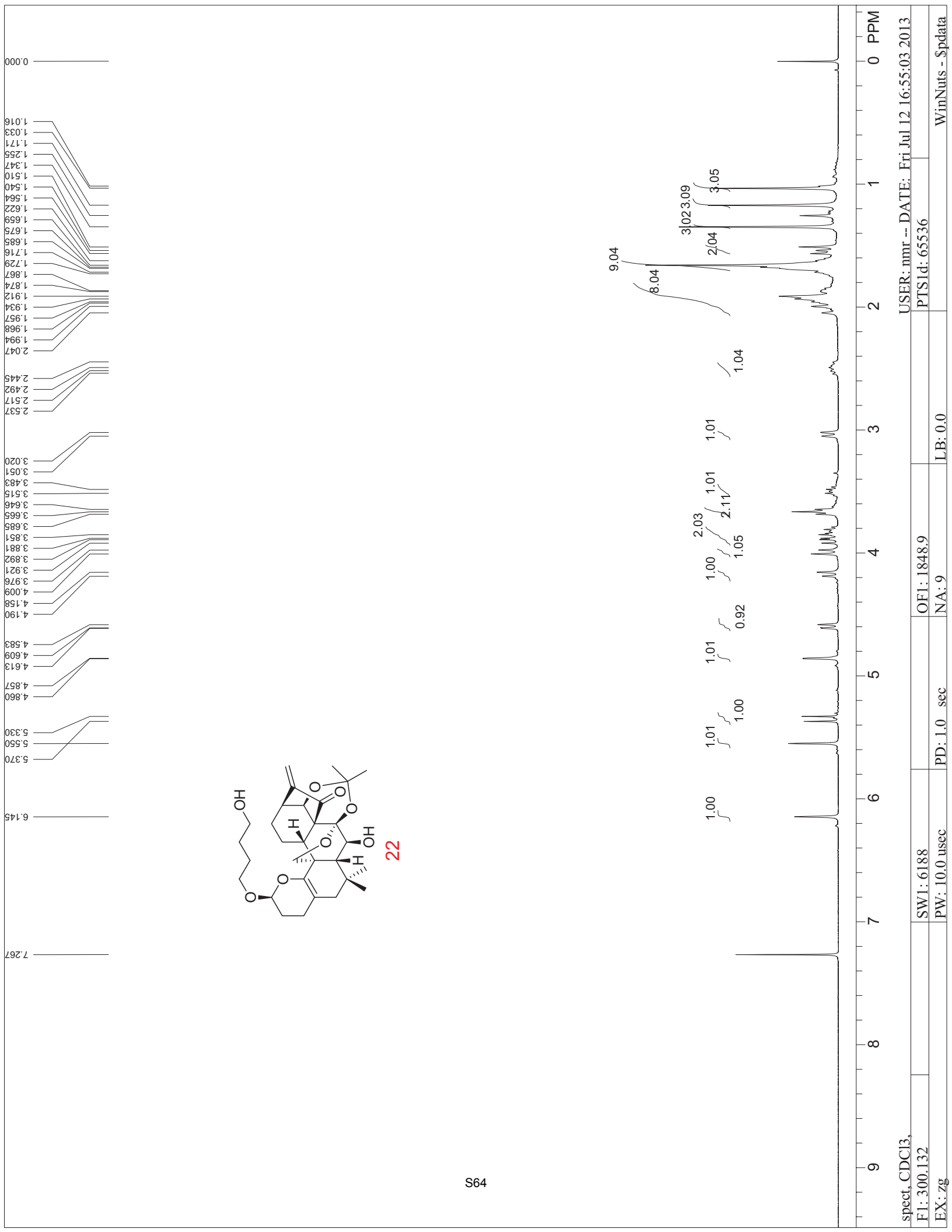
20

HMBC

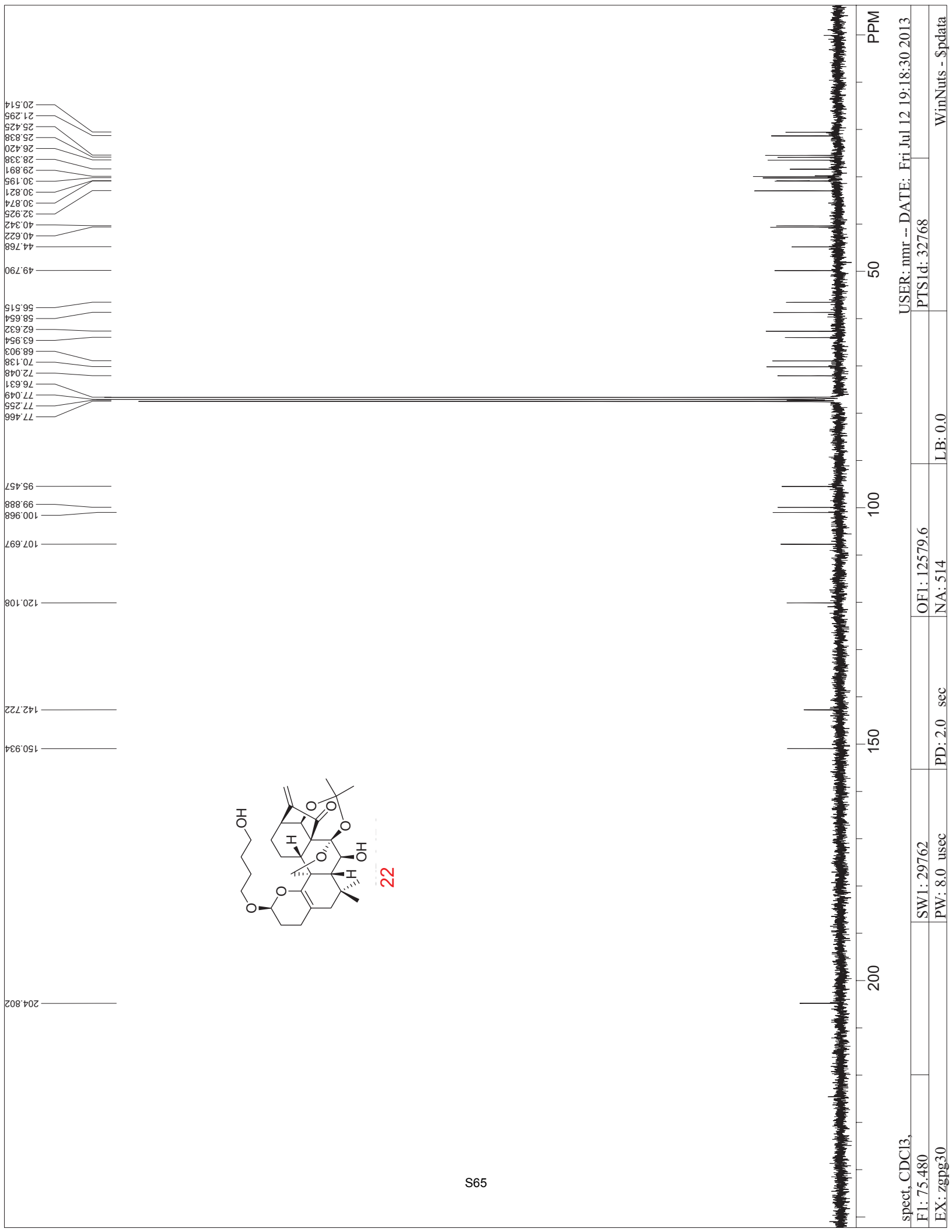




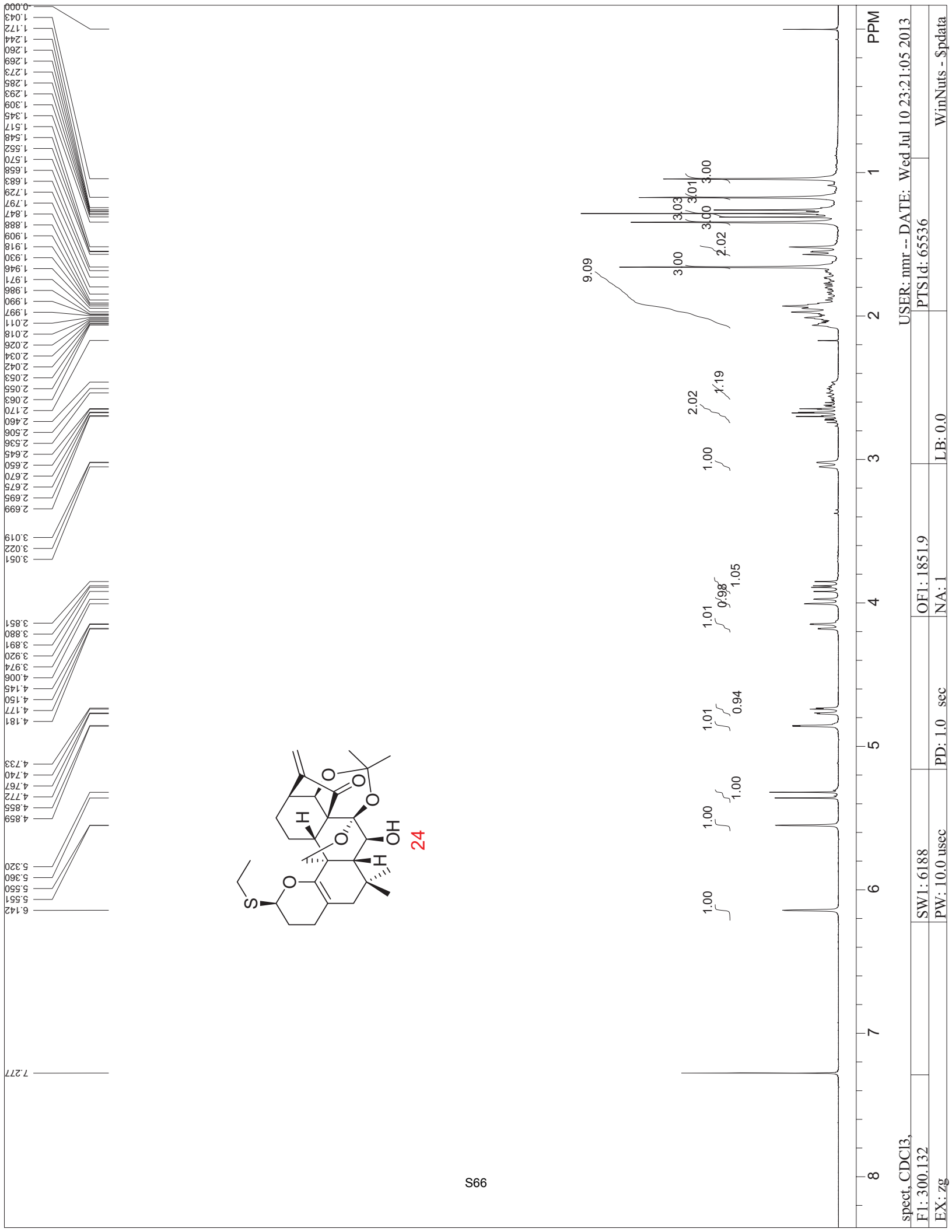




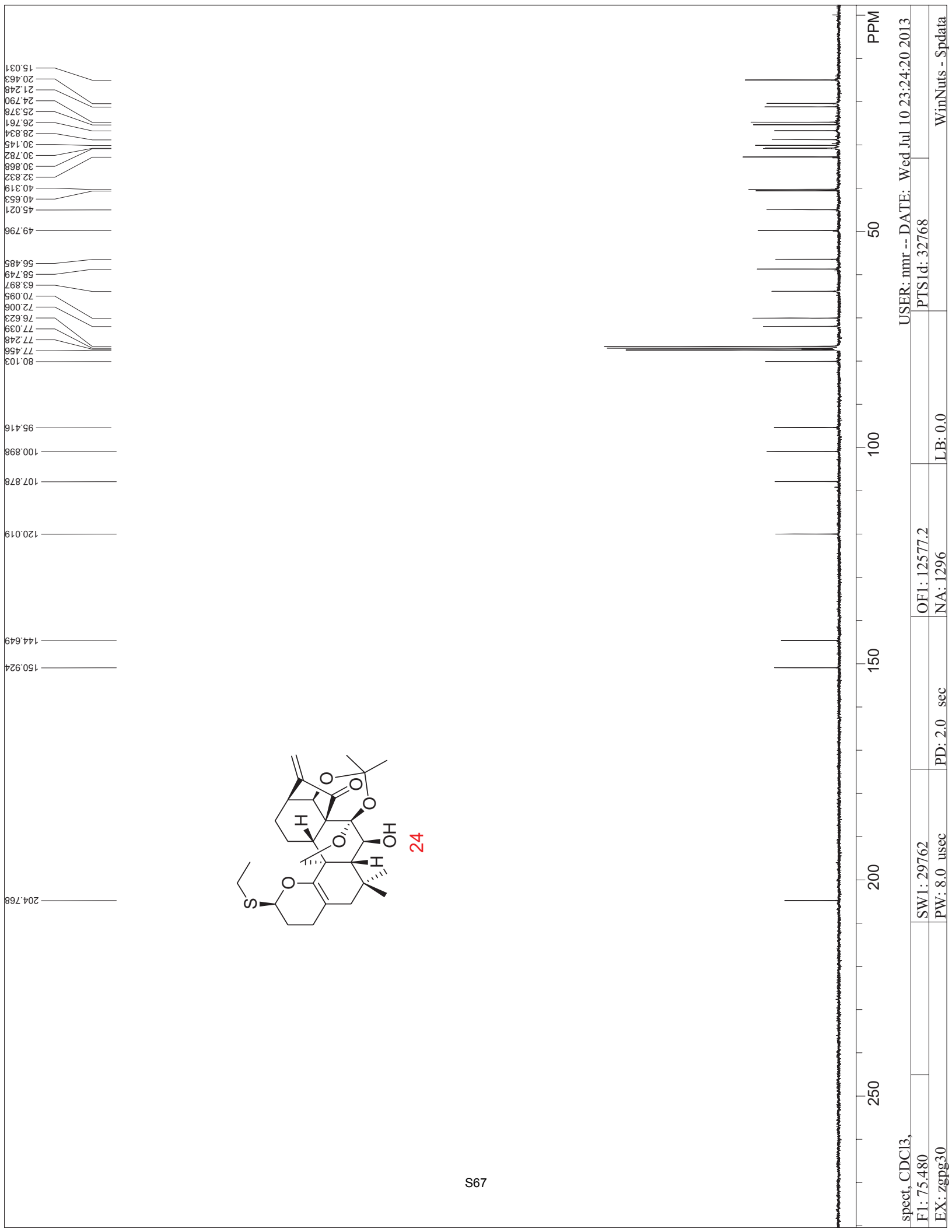
spect, CDC13, USER: nmr -- DATE: Fri Jul 12 16:55:03 2013
 F1: 300.132 SW1: 6188 OF1: 1848.9 PTS1d: 65536
 EX: zg PW: 10.0 usec PD: 1.0 sec LB: 0.0 WinNuts - \$pdata



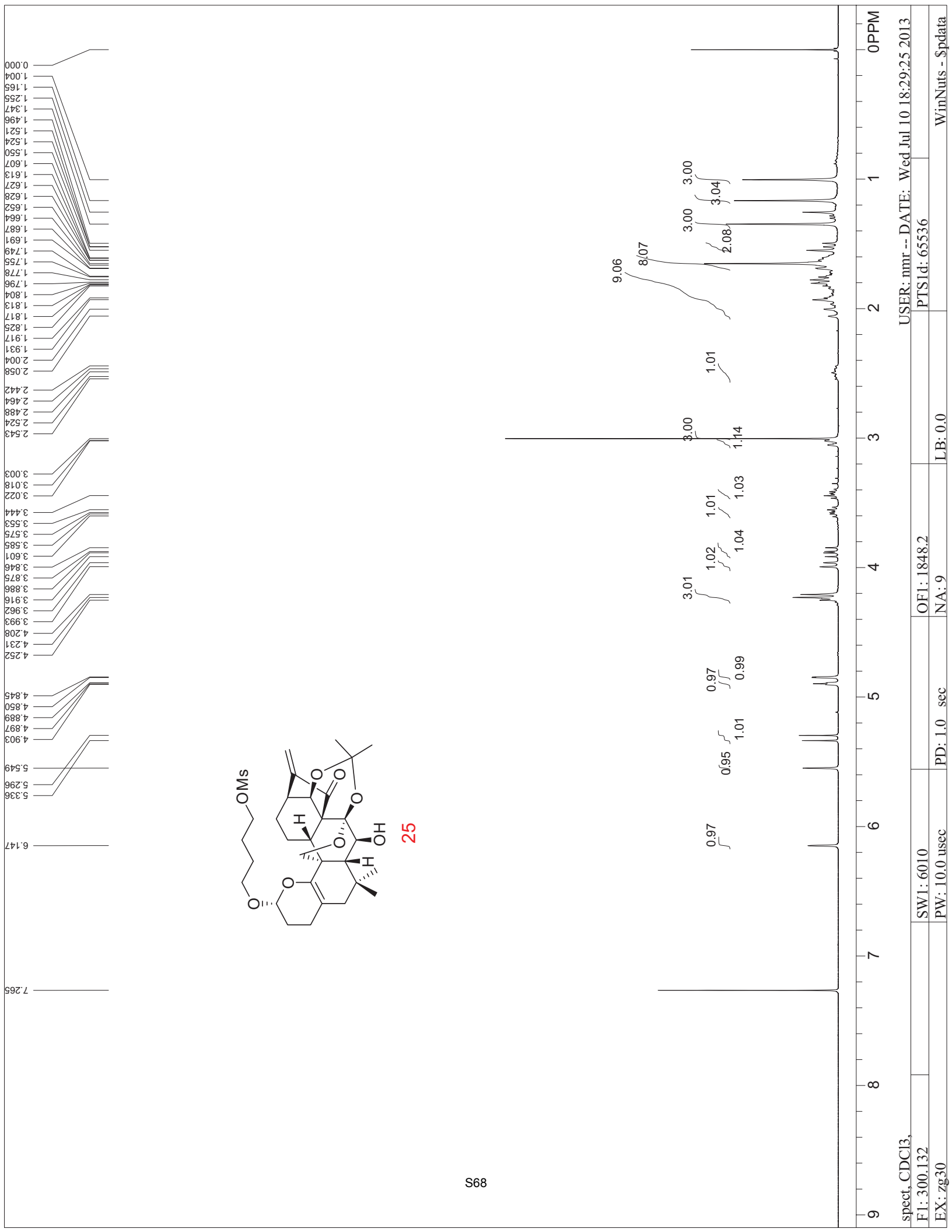
spect, CDCl3, USER: nmr -- DATE: Fri Jul 12 19:18:30 2013
 F1: 75.480 PTS1d: 32768
 EX: zgpg30 WinNuts - \$pdata
 OF1: 12579.6 LB: 0.0
 NA: 514
 PD: 2.0 sec



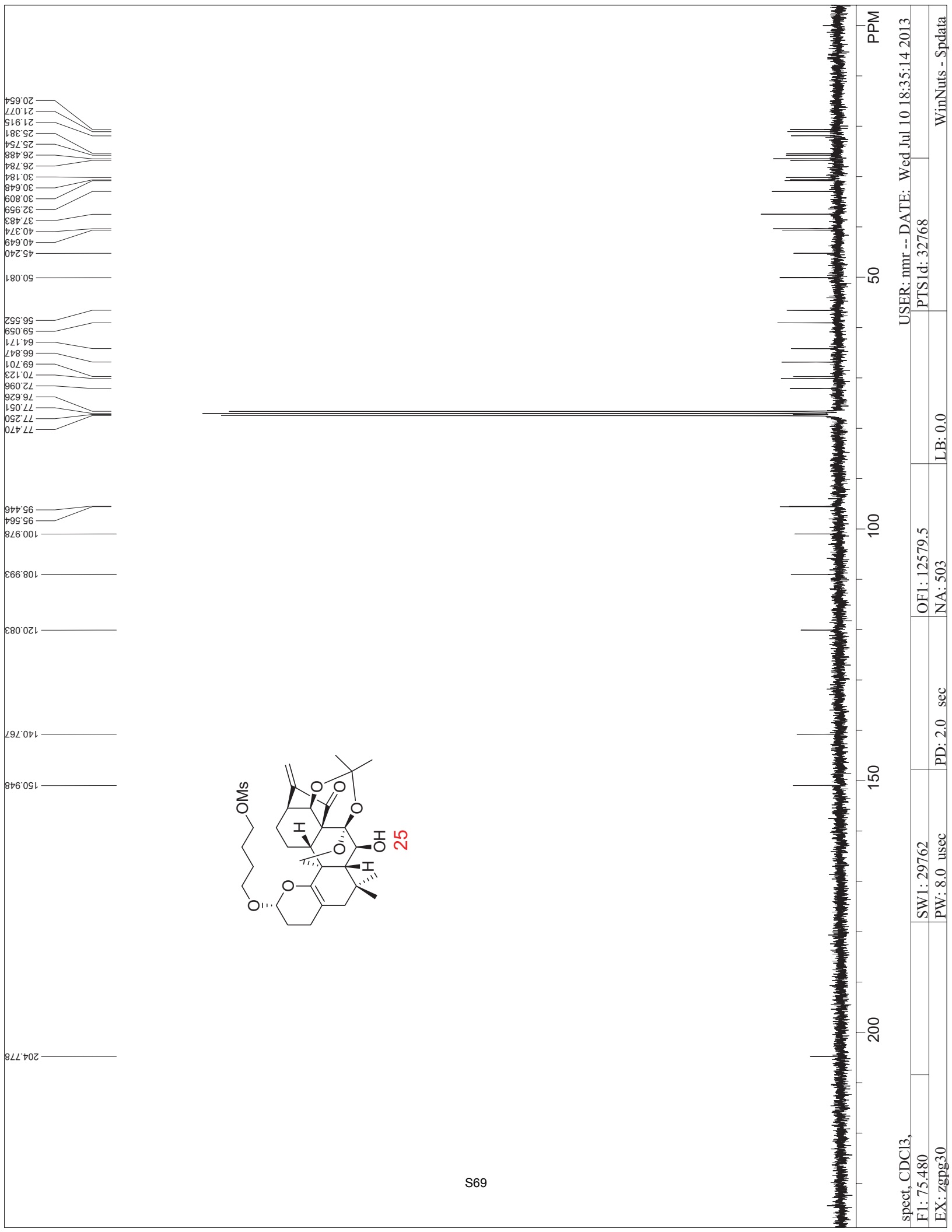
spect, CDCI3, USER: nmr -- DATE: Wed Jul 10 23:21:05 2013
 F1: 300.132 OF1: 1851.9 PTS1d: 65536
 EX: zg PW: 10.0 usec PD: 1.0 sec LB: 0.0 WinNuts - \$pdata



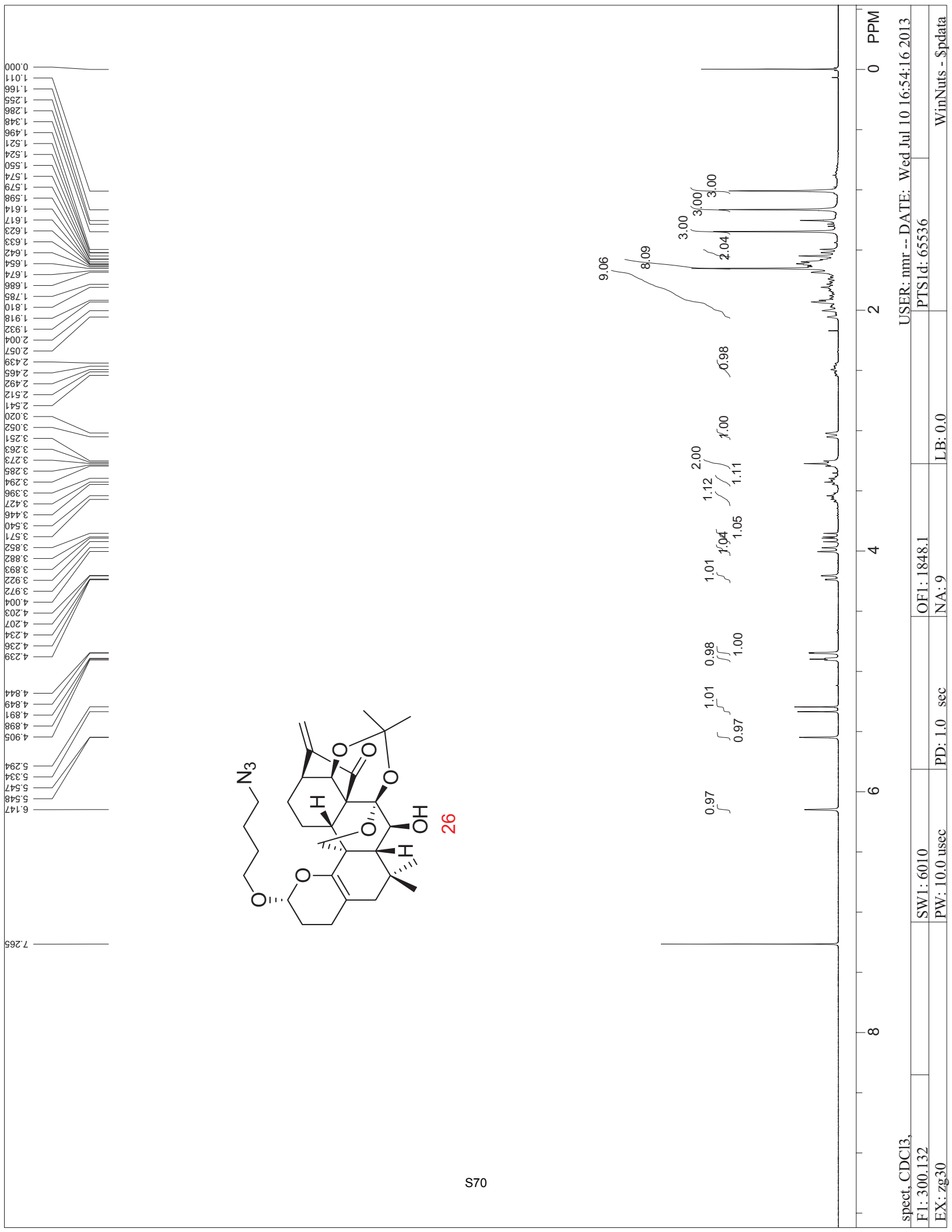
spect, CDCl3, USER: nmr -- DATE: Wed Jul 10 23:24:20 2013
 F1: 75.480 SW1: 29762 OF1: 12577.2 PTS1d: 32768
 EX: zgpg30 PW: 8.0 usec PD: 2.0 sec NA: 1296 LB: 0.0 WinNuts - \$pdata

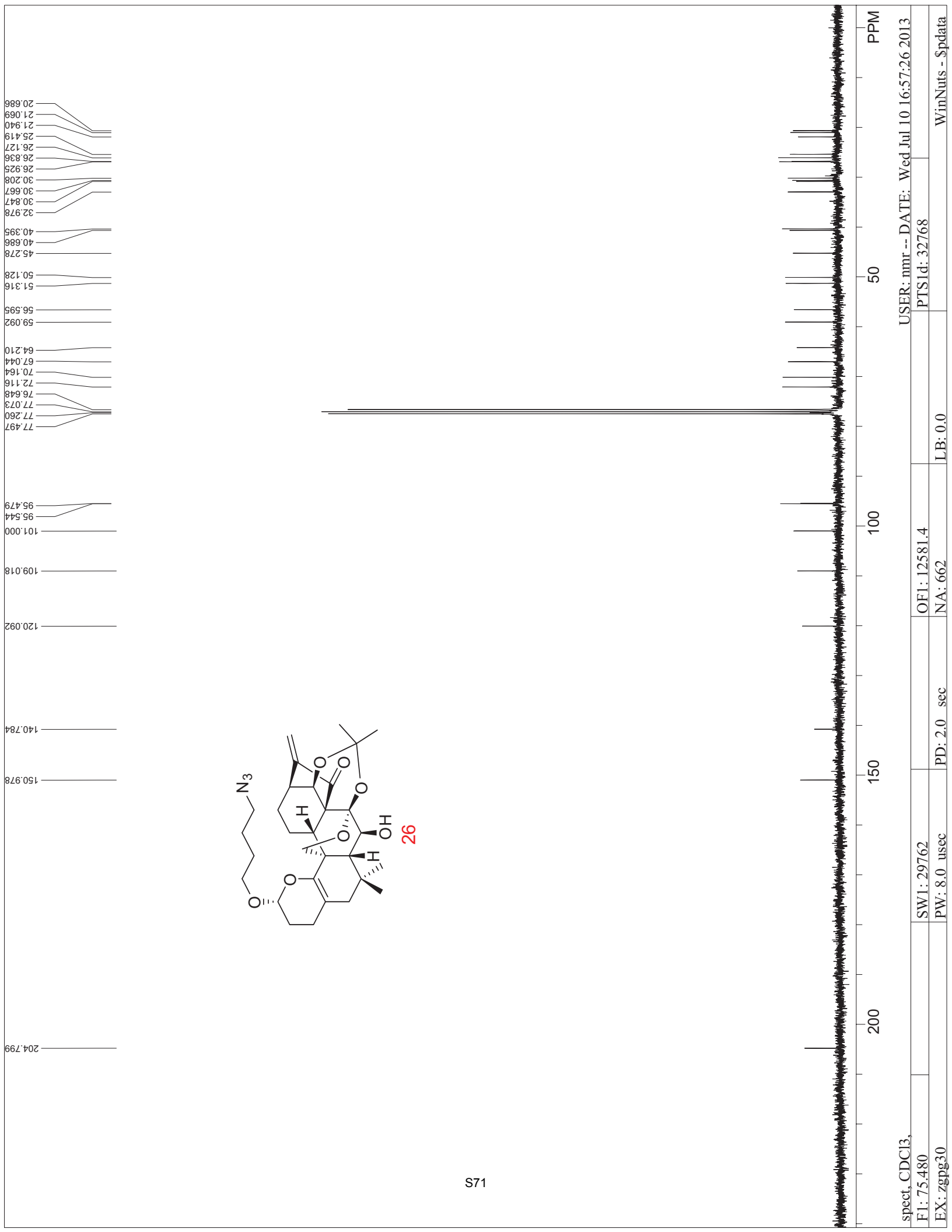


spect, CDC13, USER: nmr -- DATE: Wed Jul 10 18:29:25 2013
 F1: 300.132 OF1: 1848.2 PTS1d: 65536
 EX: zg30 PW: 10.0 usec PD: 1.0 sec NA: 9 LB: 0.0 WinNuts - \$pdata

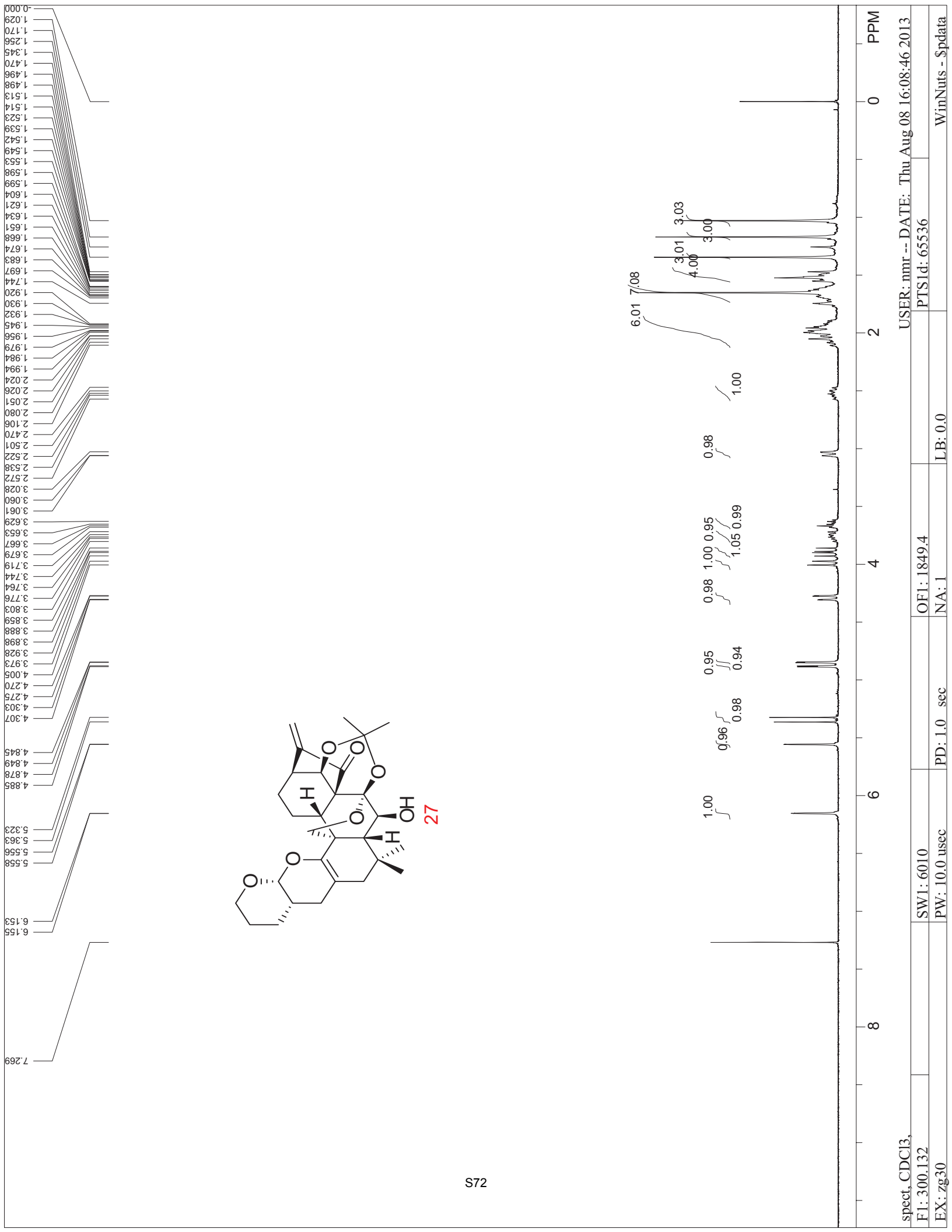


spect, CDC13, USER: nmr -- DATE: Wed Jul 10 18:35:14 2013
 F1: 75.480 OF1: 12579.5 PTS1d: 32768
 EX: zgpg30 PD: 2.0 sec NA: 503 LB: 0.0 WinNuts - \$pdata

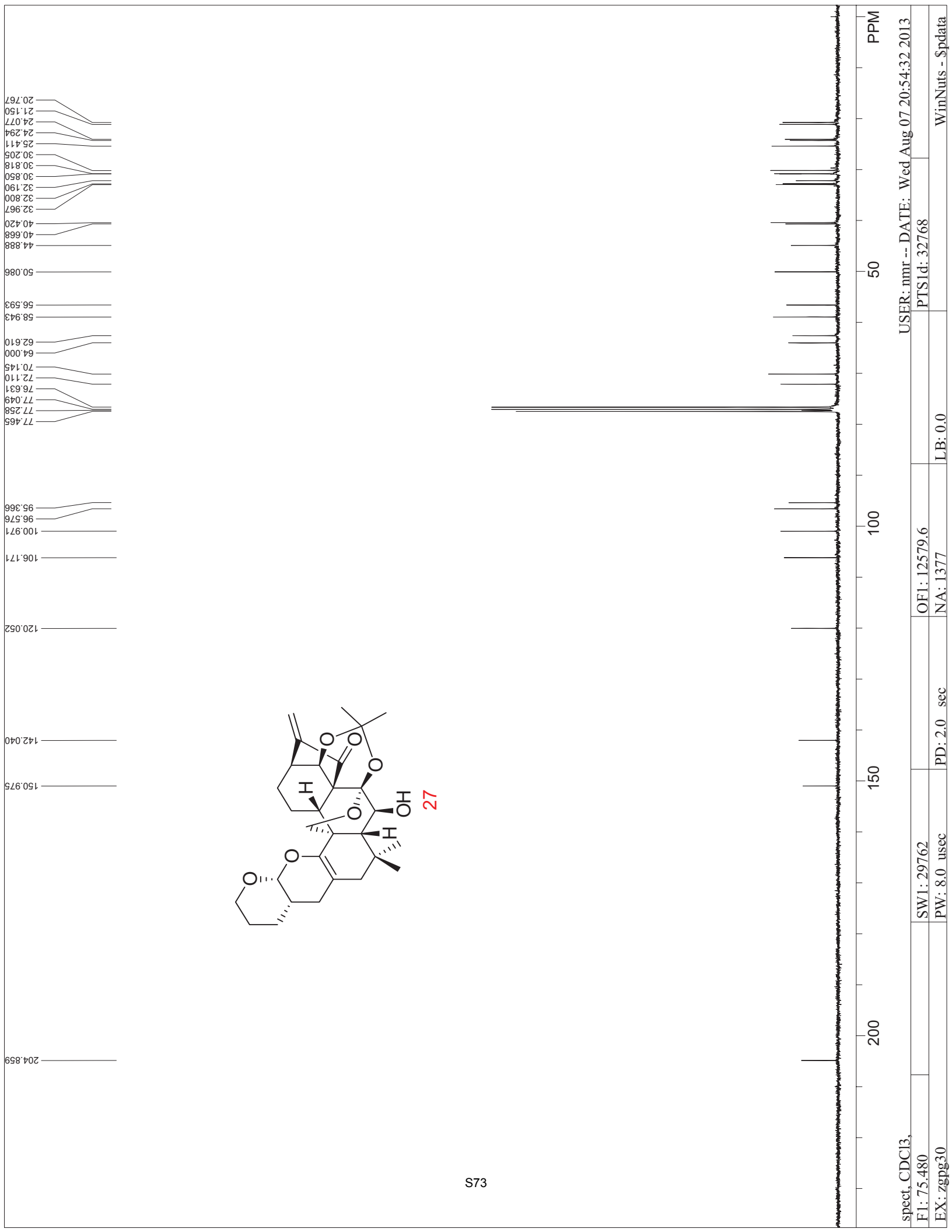




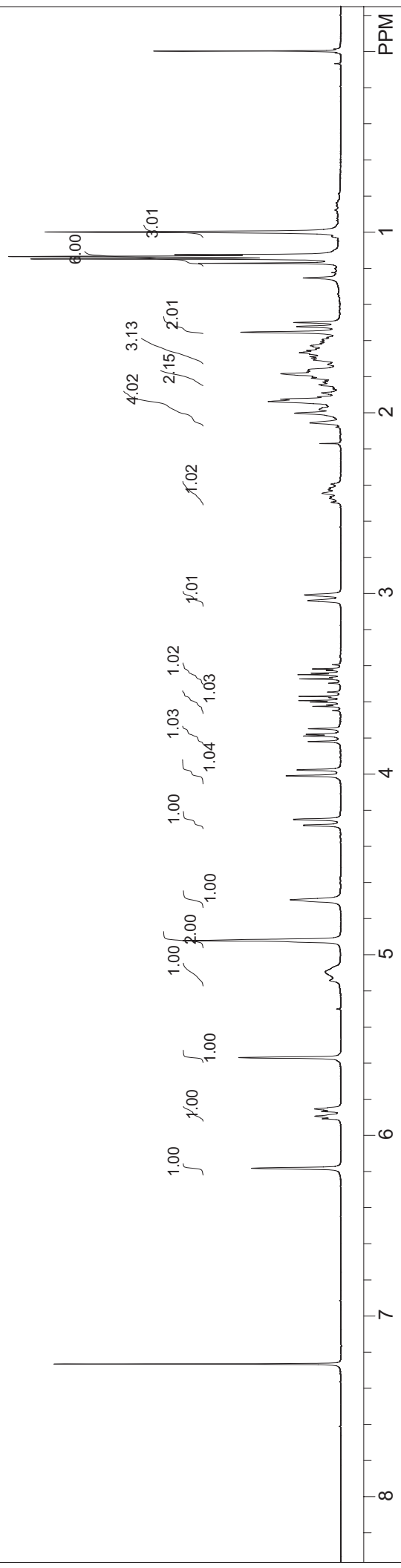
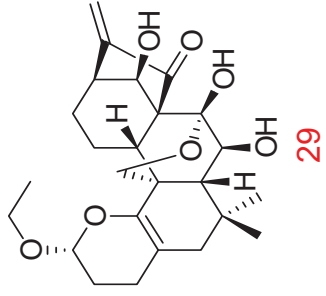
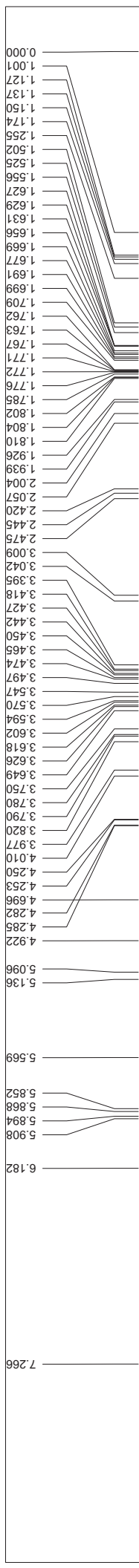
spect, CDCI3, USER: nmr -- DATE: Wed Jul 10 16:57:26 2013
 F1: 75.480 OF1: 12581.4 PTS1d: 32768
 EX: zgpg30 PD: 2.0 sec NA: 662 LB: 0.0 WinNuts - \$pdata



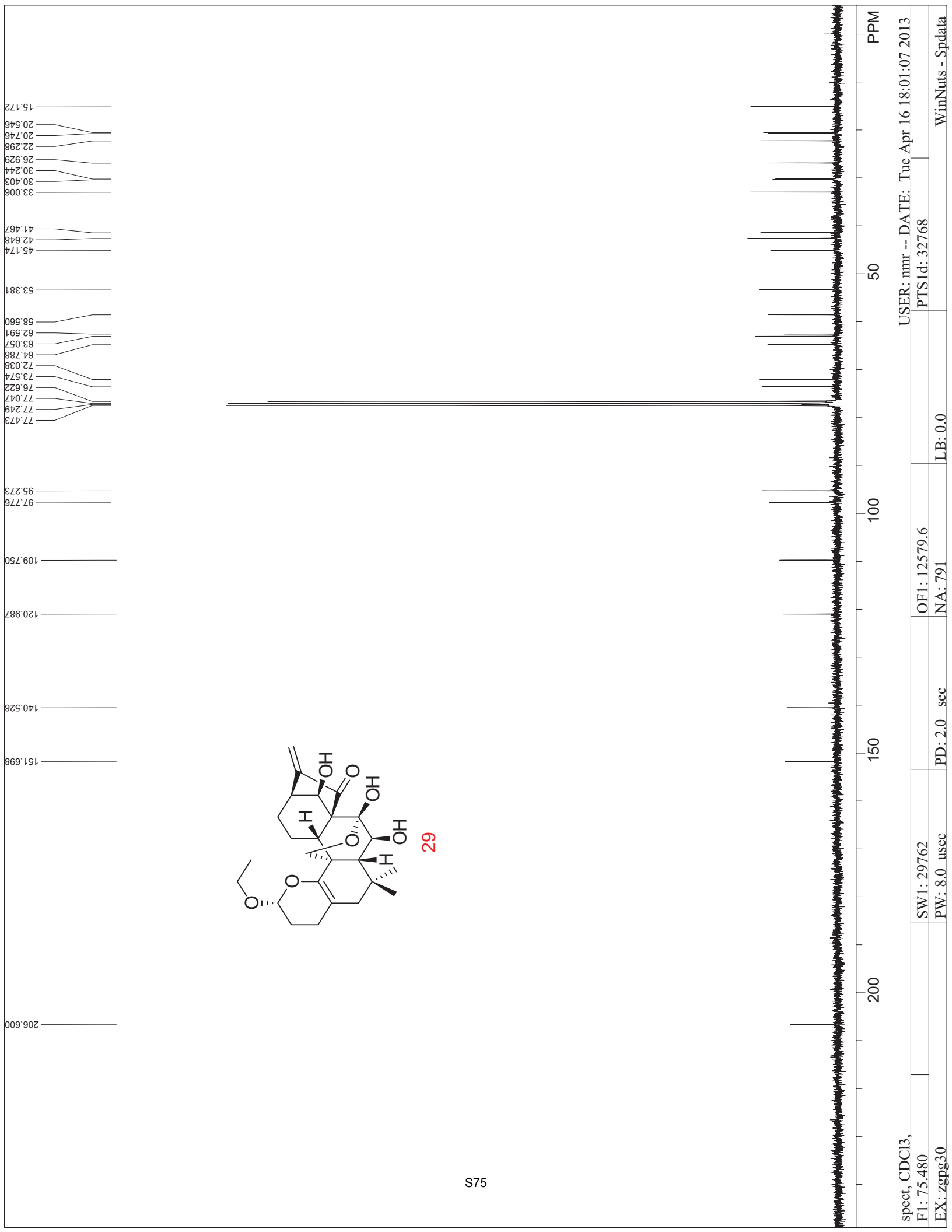
spect, CDC13, USER: nmr --- DATE: Thu Aug 08 16:08:46 2013
 F1: 300.132 PTS1d: 65536
 EX: zg30 WinNuts - \$pdata
 OF1: 1849.4 LB: 0.0
 SW1: 6010
 PW: 10.0 usec PD: 1.0 sec

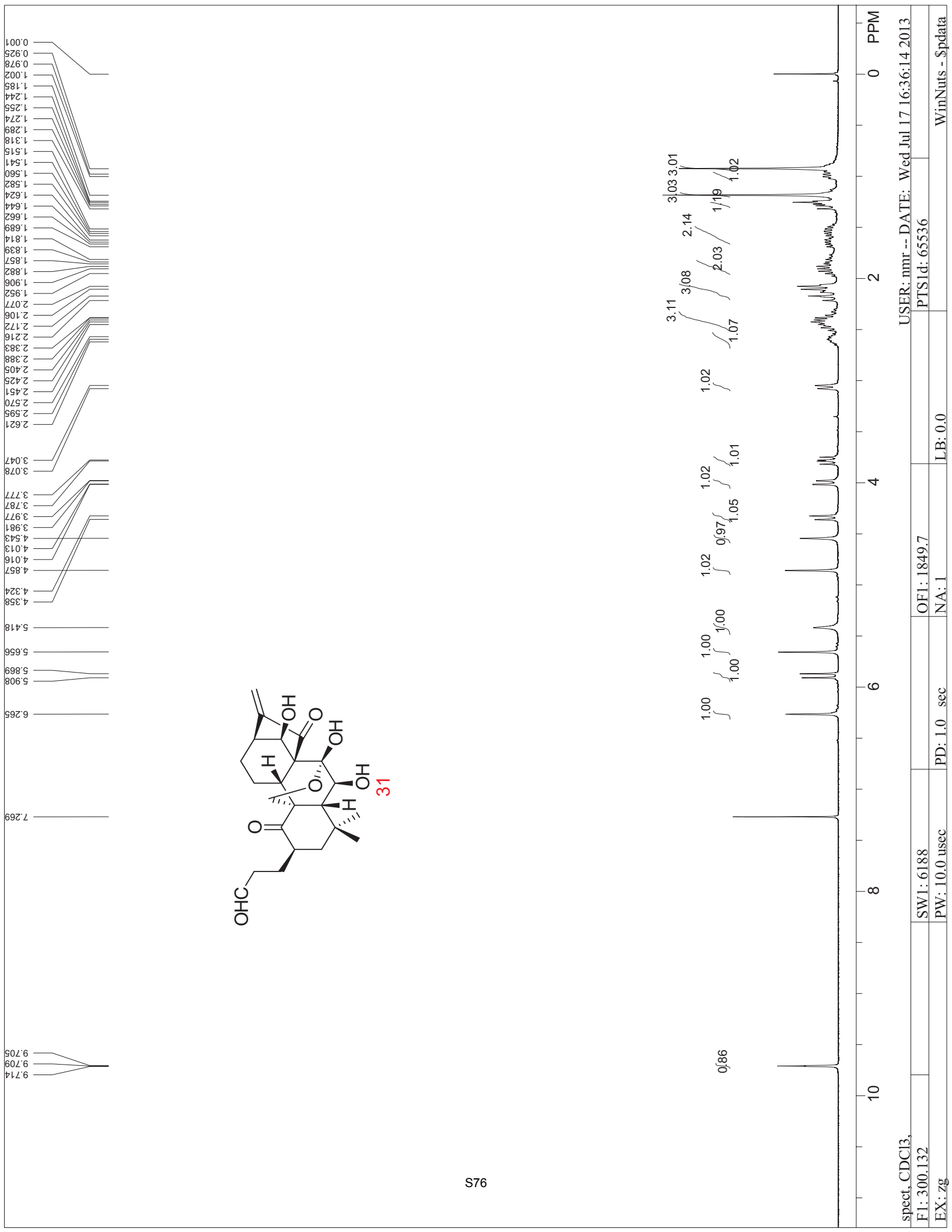


spect, CDCl3, USER: nmr -- DATE: Wed Aug 07 20:54:32 2013
 F1: 75.480 PTS1d: 32768
 EX: zgpg30 OF1: 12579.6 LB: 0.0
 NA: 1377 PD: 2.0 sec
 WinNuts - \$pdata

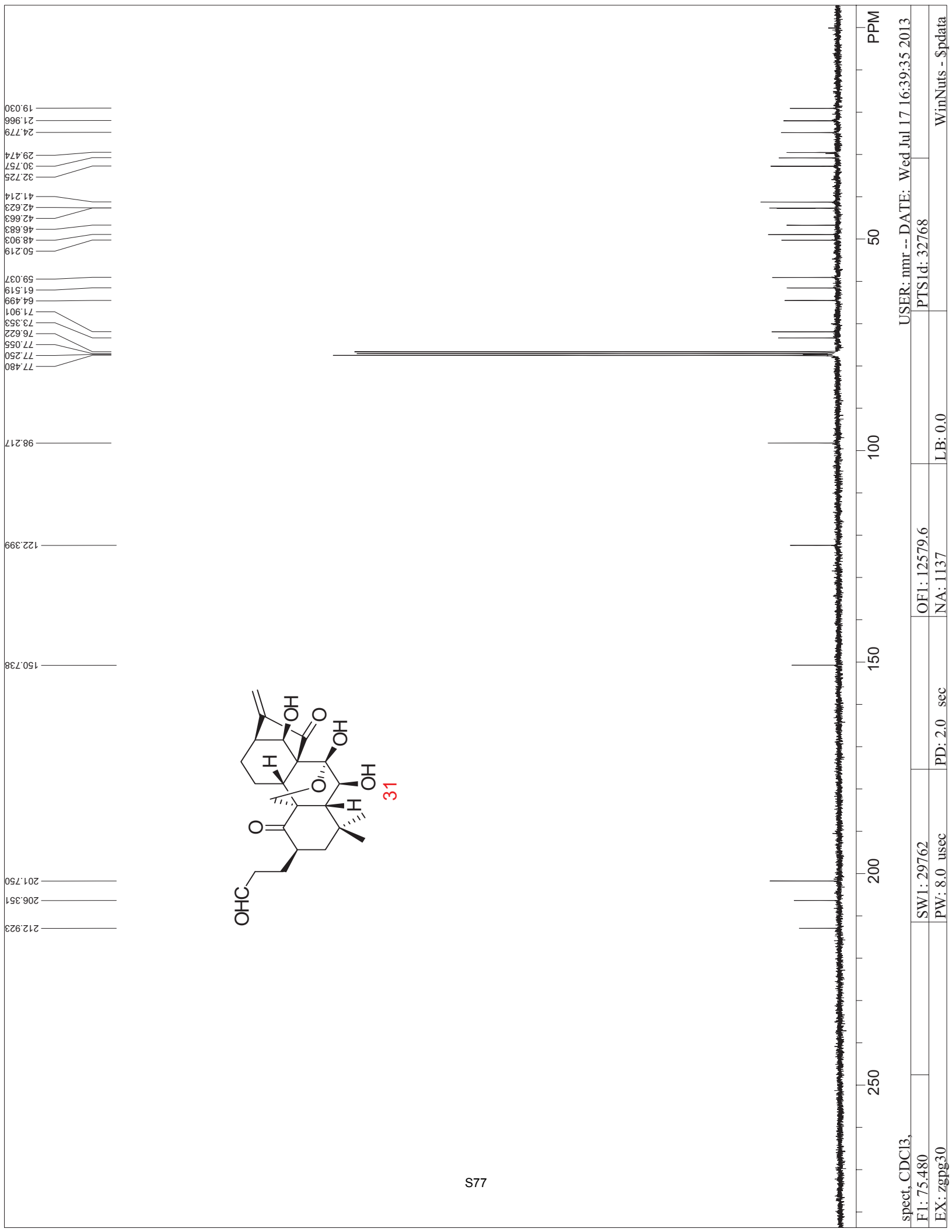


spect, CDC13,	USER: nmr -- DATE: Tue Apr 16 17:22:49 2013
F1: 300.132	PTS1d: 65536
EX: zg30	LB: 0.0
SW1: 6010	OF1: 1849.5
PW: 10.0 usec	NA: 9
PD: 1.0 sec	
	WinNuts - \$pdata

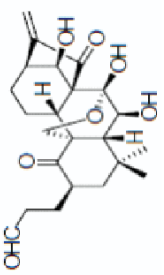




spect, CDC13, USER: nmr -- DATE: Wed Jul 17 16:36:14 2013
 F1: 300.132 PTS1d: 65536
 EX: zg SW1: 6188 OF1: 1849.7 LB: 0.0
 PW: 10.0 usec PD: 1.0 sec NA: 1
 WinNuts - \$pdata



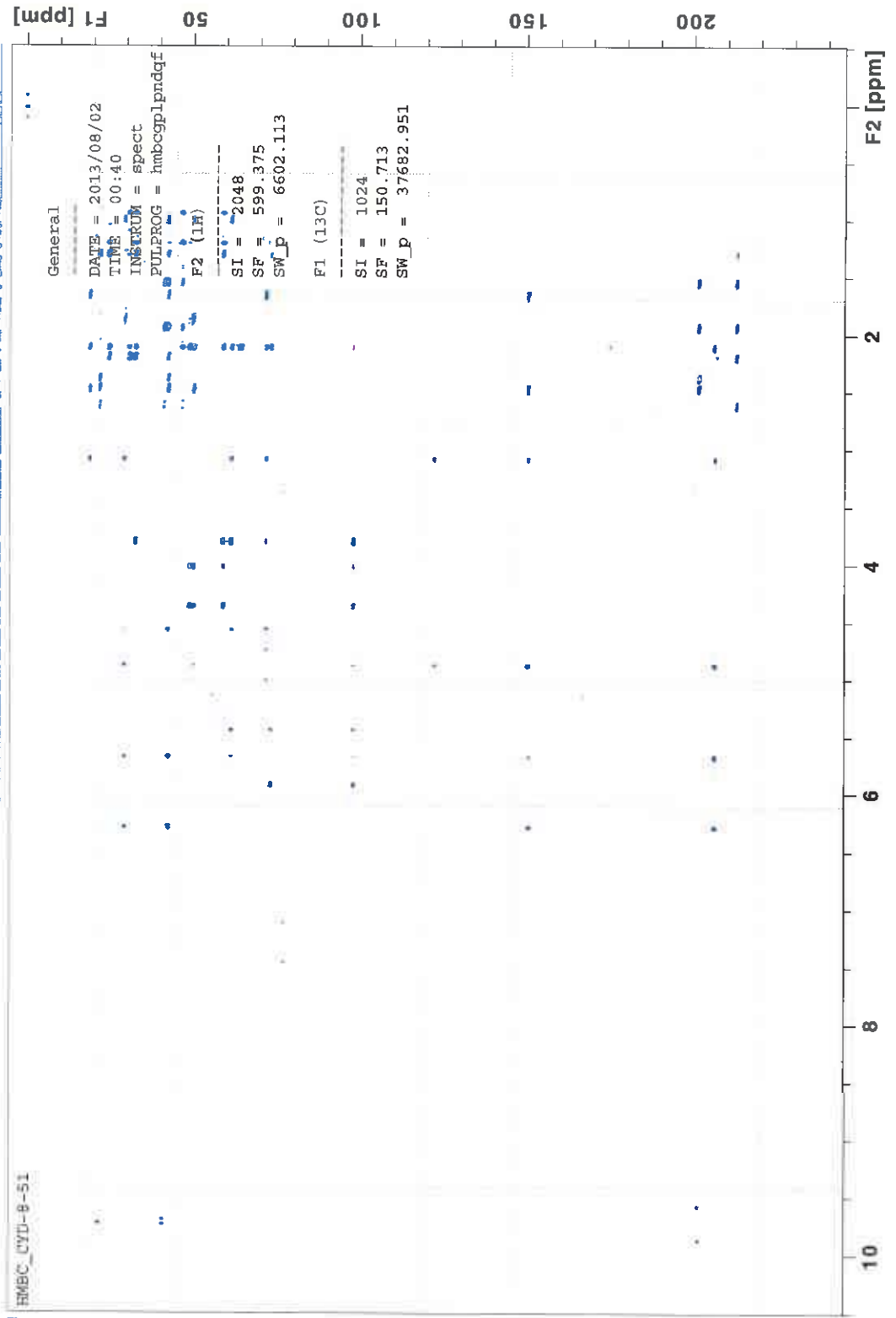
spect, CDCI3, USER: nmr -- DATE: Wed Jul 17 16:39:35 2013
 F1: 75.480 PTS1d: 32768
 EX: zgpg30 OF1: 12579.6 LB: 0.0
 SW1: 29762 PD: 2.0 sec NA: 1137
 PW: 8.0 usec
 WinNuts - \$pdata

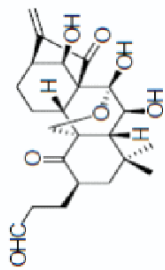


31

HMBC

hmbc 14 1 /opt/topspin3.0/data/zhou/mnr

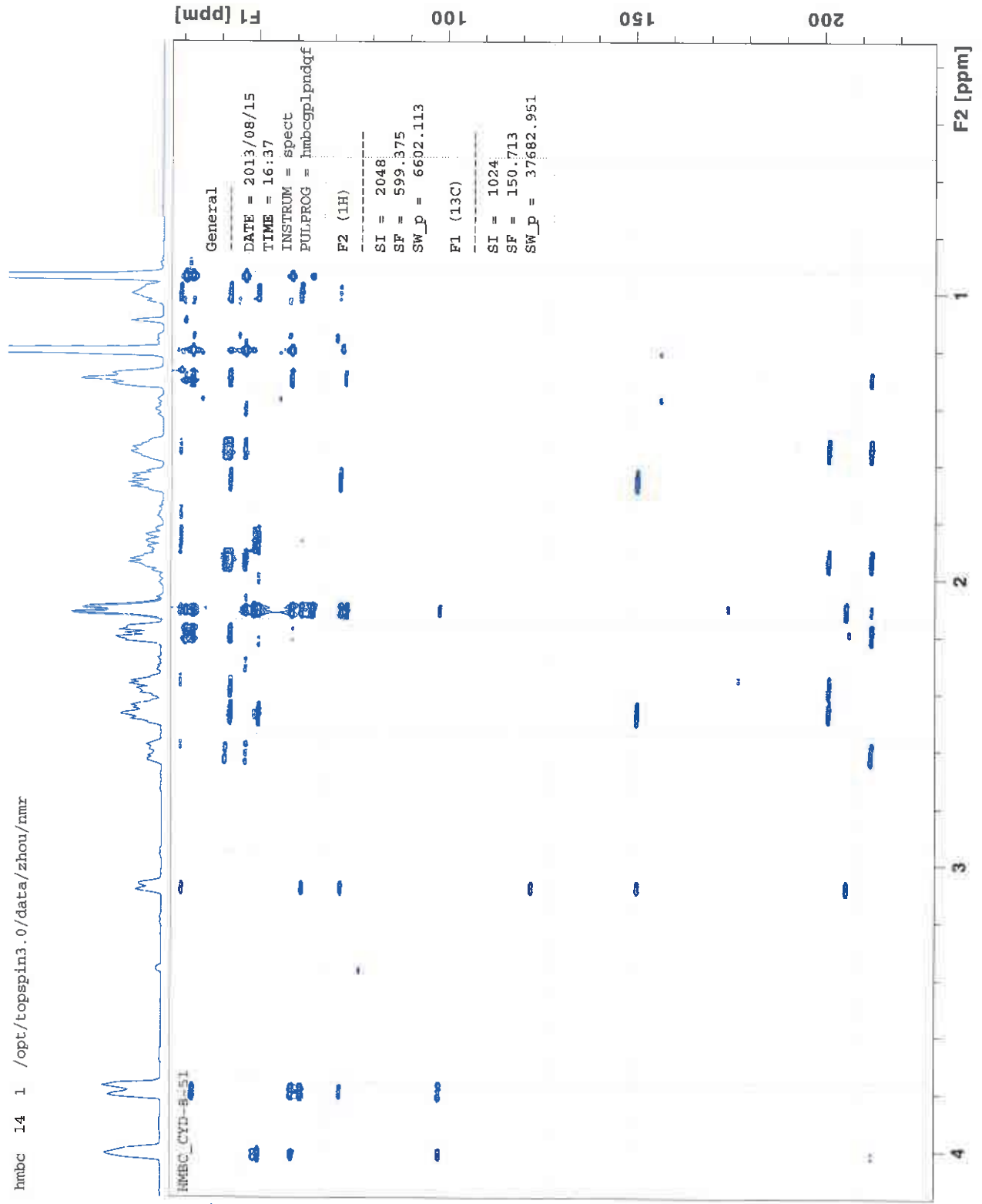


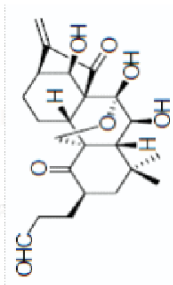


31

HMBC

hmbc 14 1 /opt/topspin3.0/data/zhou/mmr

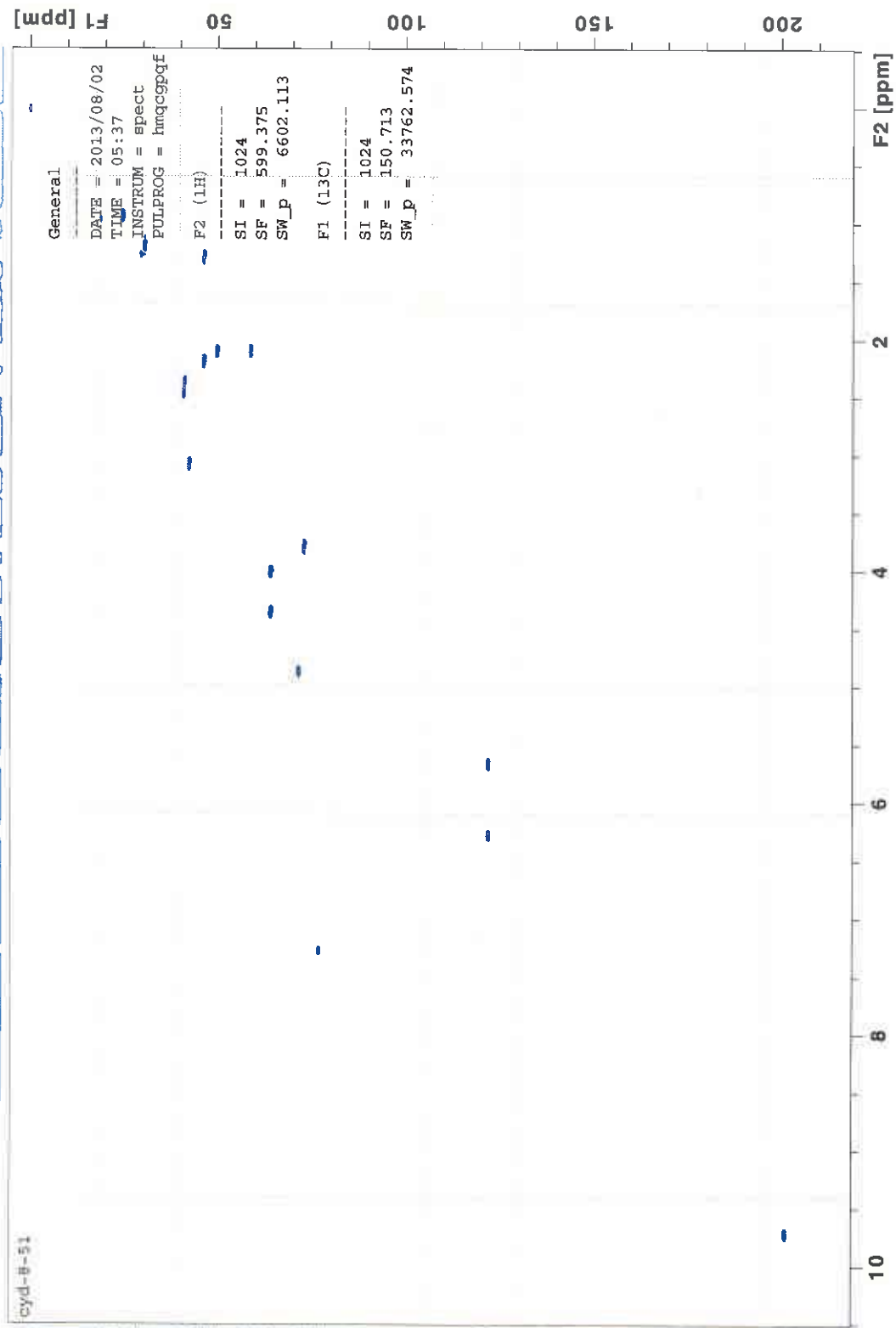




31

HMQC

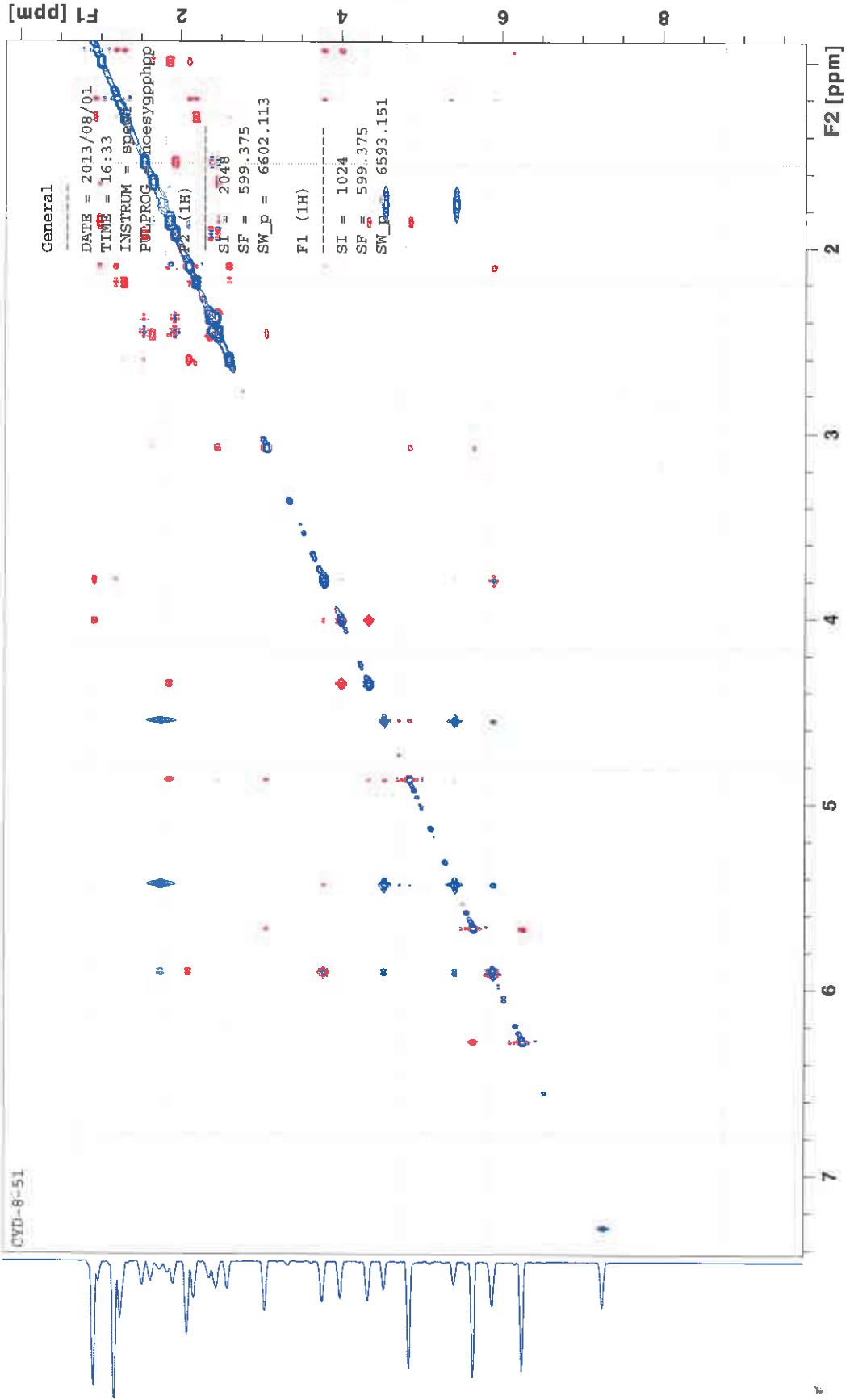
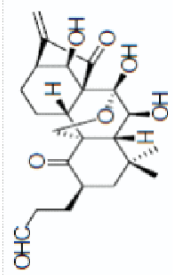
hmqc 14 1 /opt/topspin3.0/data/zhou/zmr

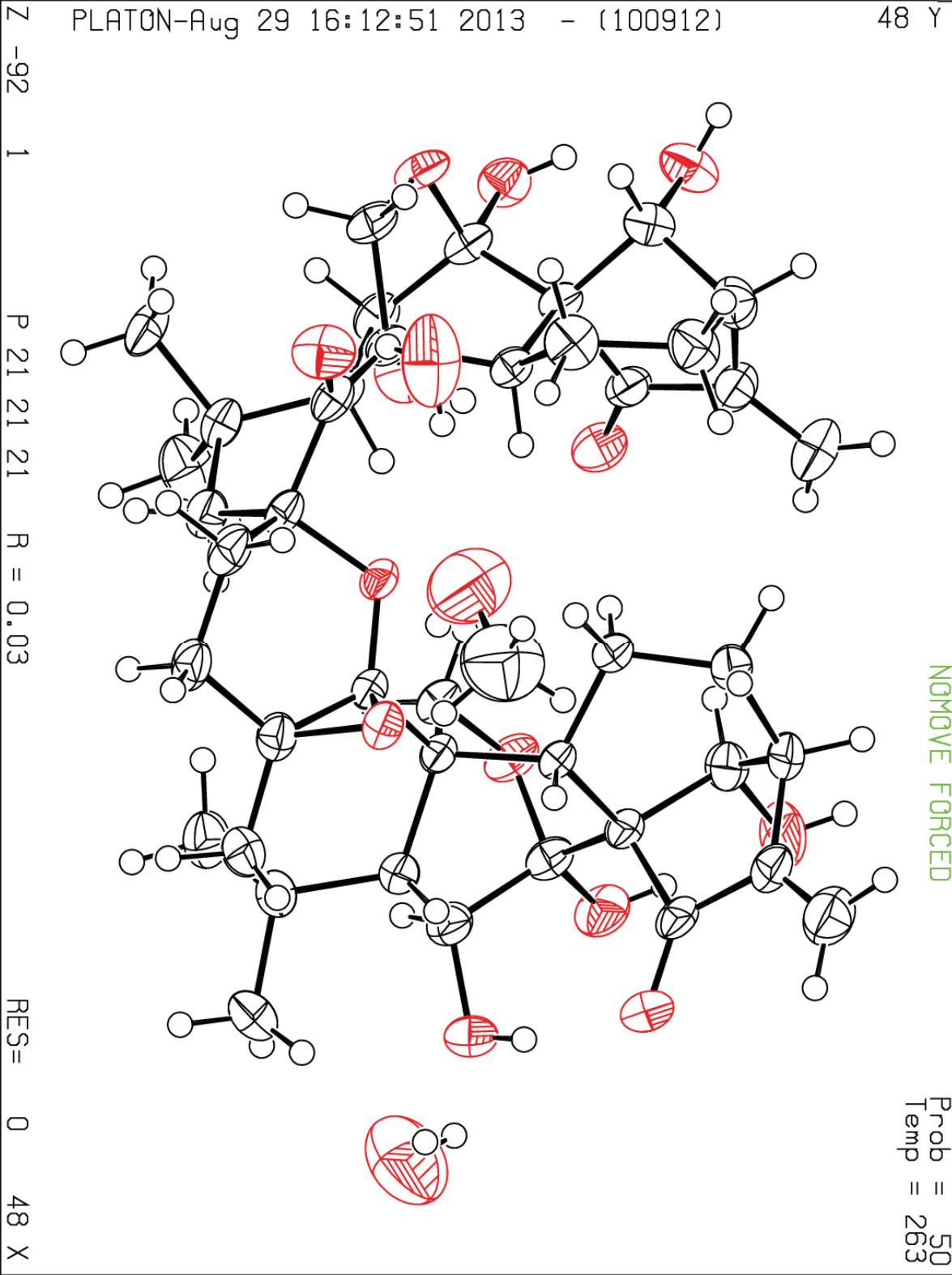
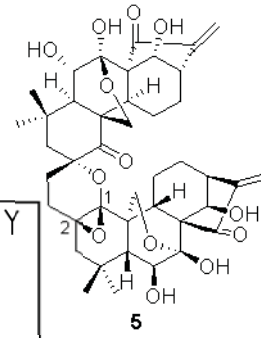


NOESY

noesy 11 1 /opt/topspin3.0/data/zhou/nmr

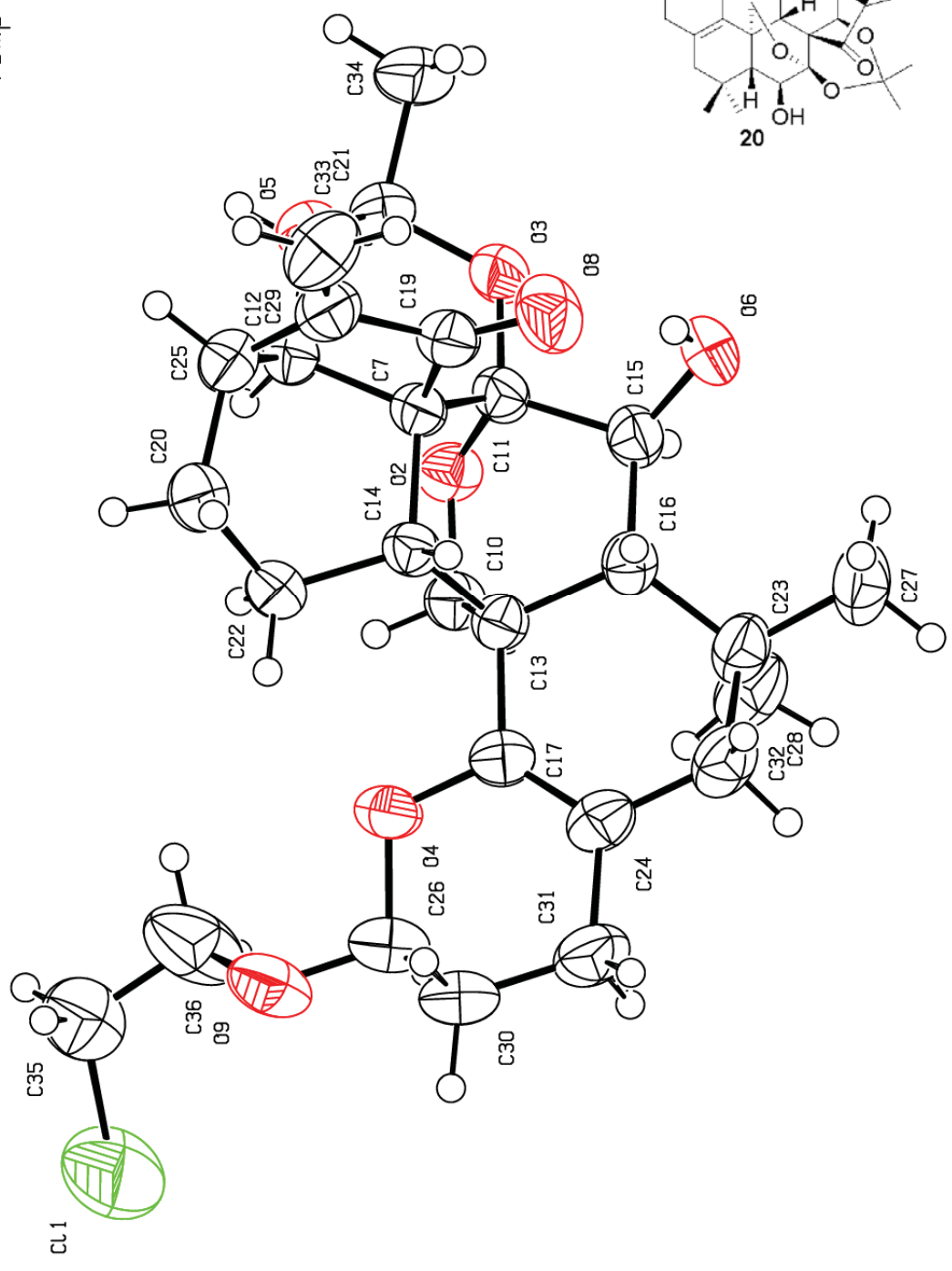
31





Prob = 50
Temp = 263

NOMOVE FORCED



PLATON-Aug 30 23:09:03 2013 - (100912) 23 Y

Z -142 1 P 21 21 21 R = 0.04 RES= 0 -64 X