Supporting Information

Overcoming Synthetic Challenges of Oridonin A-Ring Structural Diversification: Regio- and Stereoselective Installation of Azides and 1,2,3-Triazoles at the C-1, C-2, or C-3 Position

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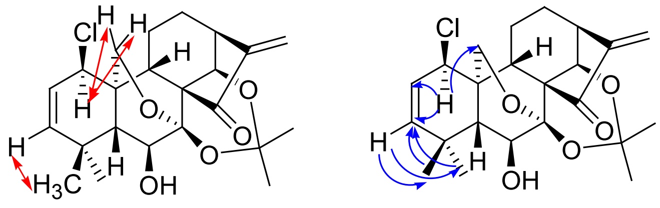
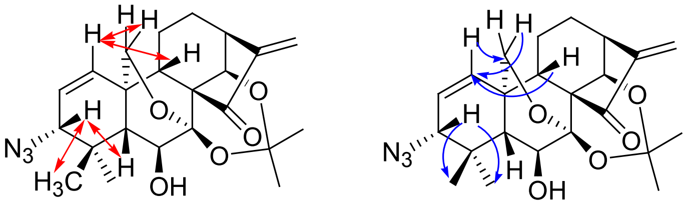


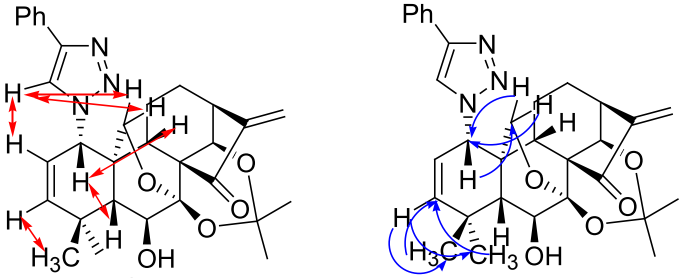
10 **10**

Figure S1. Selected ROESY correlations (H ⟷ H) and key HMBC correlations (H ⟶ C) of **10.** The ROESY correlations of H-1/H_2-20 indicated that H-1 was *α*-directed. 1-Allylic chloride was determined by the ROESY correlation of H-1/H_2-20 and the HMBC correlations of H-1/C-20, H-1/C-2 and H-1/C-3. The Δ^2 double bond was confirmed by the ROESY correlation of H-3/H_3-18 and the HMBC correlations of H-3/C-18, H-3/C-19, H_3-18/C-3 and H_3-19/C-3.



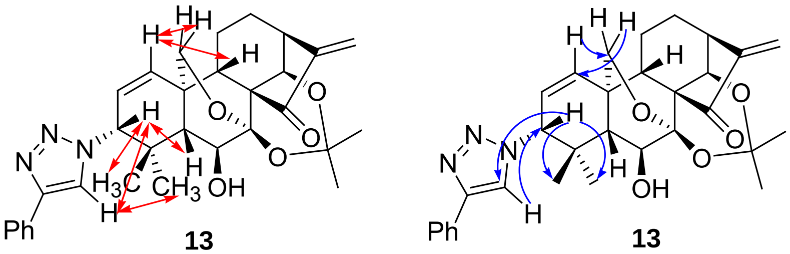
8 **8**

Figure S2. Selected ROESY correlations (H ⟷ H) and key HMBC correlations (H ⟶ C) of **8.** The ROESY correlations of H-3/H_3-18 and H-3/H-5 indicated that H-3 was *β*-directed. 3-Allylic azide was determined by the ROESY correlation of H-3/H_3-18 and the HMBC correlations of H-3/C-18 and H-3/C-19. The Δ^1 double bond was confirmed by the ROESY correlations of H-1/H_2-20 and H-1/H-9, and the HMBC correlations of H-1/C-20, H-9/C-1 and H_2-20/C-1.



12 **12**

Figure S3. Selected ROESY correlations (H ⟷ H) and key HMBC correlations (H ⟶ C) of **12.** The ROESY correlations of H-1/H-5, H-1/H-9 and H-5'/H_2-20 indicated that H-1 was *β*-directed. 1-Allylic 1,2,3-triazole was determined by the ROESY correlations of H-1/H-9 and H-5'/H_2-20, the HMBC correlations of H-1/C-20 and H_2-20/C-1. The Δ^2 double bond was confirmed by the ROESY correlations of H-3/H_3-18 and the HMBC correlations of H-3/C-18, H-3/C-19, H_3-18/C-3 and H_3-19/C-3.



13 **13**

Figure S4. Selected ROESY correlations (H ↔ H) and key HMBC correlations (H → C) of **13.** The ROESY correlations of H-3/H_3-18, H-5'/H_3-19 and H-3/H-5 indicated that H-3 was *β*-directed. 3-Allylic 1,2,3-triazole was determined by the ROESY correlations of H-3/H_3-18 and H-5'/H_3-19, and the HMBC correlations of H-3/C-18, H-3/C-19, H-5'/C-3 and H-3/C-5'. The Δ^1 double bond was confirmed by the ROESY correlations of H-1/H_2-20 and H-1/H-9, and the HMBC correlations of H-1/C-20 and H_2-20/C-1.

Table S1. Ring opening of 1*S*,2*R*-epoxide **20** with NaN_3[a]

Entry	Coordinating salt	Solvent	T (˚C)	Time (h)	Yield (%)[b]	Recovery of **20** (%)[b]
1	NH_4Cl (2 equiv.)	$MeOH/H_2O$ (1:1)	55	24	trace	90
2	NH_4Cl (2 equiv.)	$EtOH/H_2O$ (1:1)	85	24	52	31
3	NH_4Cl (2 equiv.)	$EtOH/H_2O$ (1:1)	85	48	40	24
4	NH_4Cl (2 equiv.)	CH_3CN/H_2O (1:1)	85	24	13	86
5	NH_4Cl (2 equiv.)	Acetone/H_2O (1:1)	85	24	8	82
6	NH_4Cl (2 equiv.)	DMF	100	24	20	32
7	$CeCl_3{\cdot}7H_2O$ (1.2 equiv.)	$EtOH/H_2O$ (1:1)	85	24	0	96
8	$Bi(OTf)_3$ (2 equiv.)	$EtOH/H_2O$ (1:1)	85	24	trace	90
9	$LiClO_4$ (2 equiv.)	$EtOH/H_2O$ (1:1)	85	24	60	20

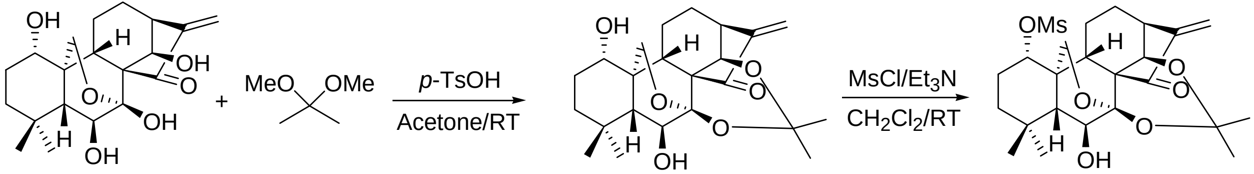
[a] Reactions were performed with epoxide **20** (0.062 mmol), NaN_3 (8 equiv.), and the coordinating salt in 2 mL of solvent. [b] Isolated yield.

***In Vitro* Determination of Proliferation Effects against Cancer cells.** Cancer cells (breast cancer cell lines MCF-7 and MDA-MB-231) were seeded in 96-well plates at a density of 1 × 10^4 cells/well and treated with DMSO, 0.01 µM, 0.1 µM , 1 µM, 5 µM, 10 µM, and 100 µM of individual compound for 48 h. Proliferation was measured by treating cells with the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) in a CellTiter 96t AQueous Non-Radioactive Cell Proliferation Assay kit (Promega, Madison, WI, USA). Absorbance of all wells was determined by measuring OD at 550 nm after 1 h incubation at 37 °C on a 96-well iMark^{TM} Microplate Absorbance Reader (BioRad, Hercules, CA). Each individual compound was tested in quadruplicate wells for each concentration.

Synthetic Experimental Procedures

General. All commercially available starting materials and solvents were reagent grade, and used without further purification. 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 Brucker-600 (^{1}H, 600 MHz; ^{13}C, 150 MHz) or Brucker-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometers. ^{1}H and ^{13}C 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 and uncorrected. Purity of final compounds was determined by analytical HPLC, which was carried out on a Shimadzu HPLC system (model: CBM-20A LC-20AD SPD-20A UV/VIS). HPLC analysis conditions: Waters μBondapak C18 (300 × 3.9 mm); flow rate 0.5 mL/min; UV detection at 270 and 254 nm; linear gradient from 30% acetonitrile in water (0.1% TFA) to 100% acetonitrile (0.1% TFA) in 20 min followed by 30 min of the last-named solvent.

Synthesis of (3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,11*S*,11a*S*,11b*S*)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-14-oxodecahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-11-yl methanesulfonate (2).

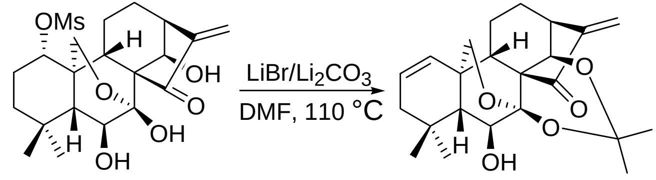


Oridonin (1)

2

To a solution of oridonin (500 mg, 1.36 mmol) in acetone (20 mL) was added TsOH (20 mg) and 2,2-dimethoxypropane (3.0 mL) at rt. The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to afford the acetonide intermediate (520 mg, 93%); To a solution of the acetonide intermediate (277 mg, 0.68 mmol) in dichloromethane was added Et_3N (138 mg, 1.37 mmol) and MsCl (94 mg, 0.82 mmol) slowly at 0 ˚C. The mixture was stirred at rt overnight, and diluted with water and extracted with dichloromethane. The organic extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The crude residue was further purified by silica gel column; elution with 50% EtOAc in hexane afforded the desired product **2** as a colorless gel (264 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.17 (s, 1H), 5.82 (d, 1H, *J* = 12.0 Hz), 5.58 (s, 1H), 4.75 (d, 1H, *J* = 1.2 Hz), 4.60 (dd, 1H, *J* = 6.0 Hz, 12.0 Hz), 4.14 (m, 2H), 3.92 (dd, 1H, *J* = 7.8 Hz, 12.0 Hz), 3.07 (d, 1H, *J* = 9.0 Hz), 2.99 (s, 3H), 2.53 (m, 1H), 2.08 (m, 1H), 1.89 (m, 2H), 1.77 (m, 3H), 1.63 (s, 3H), 1.52 (m, 1H), 1.38 (d, 1H, *J* = 7.2 Hz), 1.33 (s, 3H), 1.31 (m, 1H), 1.19 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.1, 150.4, 120.5, 101.1, 94.6, 84.8, 72.9, 69.9, 62.3, 59.5, 55.9, 50.1, 40.6, 40.1 (2C), 38.2, 33.2, 33.0, 30.1 (2C), 26.4, 25.4, 22.4, 18.8; HRMS Calcd for $C_{24}H_{36}O_8S$: $[M + H]^+$ 483.2047; found 483.2052.

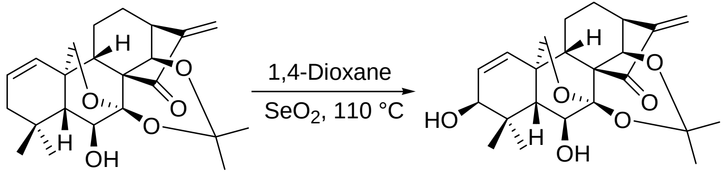
Synthesis of (3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,11a*R*,11b*S*)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,9,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (4).



2 **4**

To a solution of **2** (34 mg, 0.07 mmol) in DMF (5 mL) was added LiBr (18 mg, 0.21 mmol) and Li_2CO_3 (15 mg, 0.21 mmol) at rt. The resulting mixture was stirred at 115 ˚C for 2 h, and then diluted with water and extracted with EtOAc. The organic extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The crude residue was further purified by silica gel column; elution with 25% EtOAc in hexane afforded the desired product **4** as a colorless amorphous gel (25 mg, 84%). HPLC purity 99.8% (t_R = 18.30 min). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.16 (s, 1H), 5.77 (m, 1H), 5.56 (s, 1H), 5.41 (d, 1H, *J* = 12.0 Hz), 5.19 (dd, 1H, *J* = 3.0 Hz, 10.2 Hz), 4.82 (s, 1H), 3.99 (d, 1H, *J* = 10.2 Hz), 3.90 (dd, 1H, *J* = 8.4 Hz, 12.0 Hz), 3.81 (d, 1H, *J* = 9.6 Hz), 3.06 (d, 1H, *J* = 9.0 Hz), 2.53 (m, 1H), 1.95 (d, 1H, *J* = 17.4 Hz), 1.76 (m, 4H), 1.65 (s, 3H), 1.56 (m, 1H), 1.50 (d, 1H, *J* = 8.4 Hz), 1.35 (s, 3H), 1.18 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.5, 150.5, 130.3, 124.1, 120.4, 101.2, 95.4, 72.0, 70.1, 64.8, 57.9, 56.3, 49.1, 41.1, 40.3, 38.1, 32.2, 31.1, 30.3, 30.1, 25.5, 22.1, 17.3; HRMS Calcd for $C_{23}H_{31}O_5$: $[M + H]^+$ 387.2166; found 387.2169.

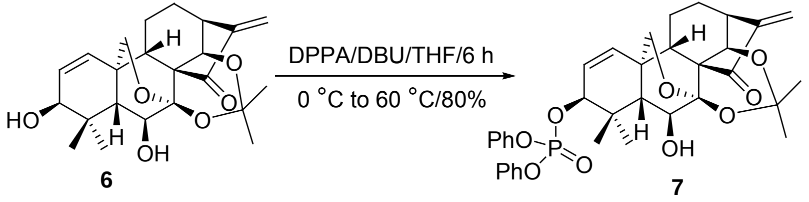
Synthesis of (3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*S*,9*S*,11a*R*,11b*S*)-7,9-dihydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,9,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (6).



4 **6**

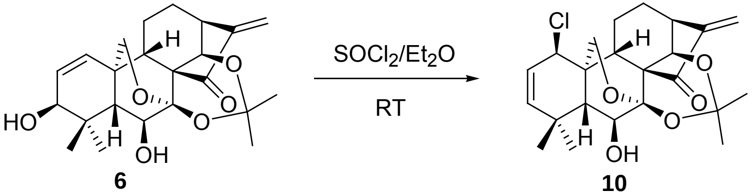
A mixture of **4** (20 mg, 0.05 mmol) and SeO_2 (16 mg, 0.15 mmol) in 1,4-dioxane (4 mL) was stirred at 100 ˚C for 16 h. After that, the reaction mixture was filtered, and the filtrate was diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 50% EtOAc in hexane to afford the desired product **6** as a colorless solid (16 mg, 76%). HPLC purity 99.7% (t_R = 17.31 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.16 (s, 1H), 6.00 (dd, 1H, *J* = 6.0 Hz, 10.2 Hz), 5.56 (s, 1H), 5.42 (m, 2H), 4.82 (s, 1H), 3.94 (m, 2H), 3.84 (d, 1H, *J* = 9.6 Hz), 3.06 (d, 1H, *J* = 9.6 Hz), 2.53 (m, 1H), 1.87 (d, 1H, *J* = 9.0 Hz), 1.82 (m, 2H), 1.71 (m, 2H), 1.65 (s, 3H), 1.57 (m, 1H), 1.35 (s, 1H), 1.24 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.1, 150.3, 130.9, 128.6, 120.6, 101.2, 95.5, 72.6, 71.5, 70.0, 64.5, 56.1, 51.0, 48.8, 40.3, 38.2, 36.7, 30.2, 30.1, 25.9, 25.4, 21.9, 17.3; HRMS Calcd for $C_{23}H_{31}O_6$: $[M + H]^+$ 403.2115; found 403.2118.

(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*S*,9*S*,11a*R*,11b*S*)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-14-oxo-2,3,3a,7,7a,8,9,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-9-yl diphenyl phosphate (7).



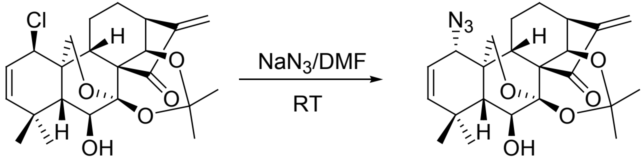
To a solution of **6** (25 mg, 0.062 mmol) in toluene (3 mL) was added DPPA (20.0 mg, 0.074 mmol) and DBU (11.0 mg, 0.074 mmol) at 0 ˚C. The resulting mixture was stirred at 60 ˚C for 6 h, and then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 30% EtOAc in hexane to afford the desired product **7** (31 mg, 80%) as a colorless amorphous gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.28 (m, 5H), 7.20 (m, 3H), 7.12 (m, 1H), 6.26 (s, 1H), 6.10 (m, 1H), 5.65 (s, 1H), 5.41 (m, 2H), 4.80 (s, 1H), 4.49 (t, 1H, *J* = 6.0 Hz), 3.89 (m, 2H), 3.82 (m, 1H), 3.09 (d, 1H, *J* = 9.0 Hz), 2.52 (m, 1H), 1.80 (d, 1H, *J* = 9.0 Hz), 1.75 (m, 1H), 1.70 (m, 1H), 1.65 (s, 3H), 1.45 (m, 1H), 1.37 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.0, 150.6, 150.5, 150.3, 131.3, 129.8, 129.5, 127.3, 125.3, 125.1, 120.6, 120.1, 120.0, 101.3, 95.4, 80.1, 71.2, 69.9, 64.3, 56.0, 51.2, 48.3, 40.3, 38.2, 36.6, 30.1, 29.9, 26.2, 25.4, 21.5, 17.2. HRMS Calcd for $C_{35}H_{40}O_9P$: $[M + H]^+$ 635.2404; found 635.2411.

(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,11*R*,11a*S*,11b*R*)-11-chloro-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,11,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (10).



To a solution of **6** (25 mg, 0.062 mmol) in anhydrous ether (3 mL) was added freshly distilled $SOCl_2$ (8 mg, 0.068 mmol) at ice-water bath. The resulting mixture was stirred at rt for 3 h, and then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 25% EtOAc in hexane to afford the desired product **10** (19 mg, 73%) as a colorless amorphous gel. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (s, 1H), 5.71 (m, 3H), 5.60 (s, 1H), 4.78 (s, 1H), 4.12 (dd, 1H, *J* = 7.2 Hz, 11.7 Hz), 4.00 (d, 1H, *J* = 6.0 Hz), 3.75 (m, 2H), 3.10 (d, 1H, *J* = 9.0 Hz), 2.52 (m, 1H), 2.33 (m, 1H), 1.92 (dd, 1H, *J* = 1.8 Hz, 6.9 Hz), 1.73 (m, 3H), 1.59 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8, 150.2, 143.6, 120.7 (2C), 101.4, 95.5, 73.0, 70.0, 65.6, 56.3, 54.9, 52.3, 44.8, 40.3, 39.6, 34.3, 33.8, 30.1, 29.9, 28.1, 25.6, 16.3. HRMS Calcd for $C_{23}H_{30}ClO_5$: $[M + H]^+$ 421.1776; found 421.1791.

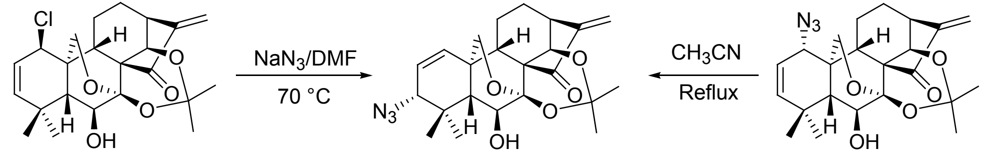
(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,11*S*,11a*R*,11b*S*)-11-azido-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,11,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (11).



10 **11**

A mixture of **10** (30 mg, 0.071 mmol) and NaN_3 (25 mg, 0.355 mmol) in the dried DMF (3 mL) was stirred at rt under N_2 for 16 h. After the completion of the reaction, which was monitored by TLC, the reaction solvent was evaporated under vacuum at 27 ˚C to give an oily residue. The residue was further purified using preparative TLC developed by 25% EtOAc in hexane to afford the desired product **11** (21 mg, 71%) as a colorless amorphous gel. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.91 (d, 1H, *J* = 11.7 Hz), 5.84 (dd, 1H, *J* = 2.1 Hz, 10.2 Hz), 5.59 (s, 1H), 5.44 (dd, 1H, *J* = 3.0 Hz, 10.2 Hz), 4.82 (d, 1H, *J* = 1.5 Hz), 4.18 (dd, 1H, *J* = 2.1 Hz, 10.2 Hz), 4.07 (m, 1H), 3.97 (dd, 1H, *J* = 1.2 Hz, 9.9 Hz), 3.97 (m, 1H), 3.12 (d, 1H, *J* = 9.6 Hz), 2.60 (m, 1H), 1.98 (m, 1H), 1.77 (m, 2H), 1.68 (s, 3H), 1.62 (m, 2H), 1.39 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.0, 150.4, 143.3, 120.4, 118.3, 101.2, 94.8, 72.8, 70.0, 63.2, 60.8, 56.6, 56.1, 49.6, 40.2, 38.6, 34.5, 32.4, 30.2, 30.1, 29.7, 26.2, 25.5, 18.2. HRMS Calcd for $C_{23}H_{30}N_3O_5$: $[M + H]^+$ 428.2180; found 428.2192.

(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,9*R*,11a*R*,11b*S*)-9-azido-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,9,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (8).

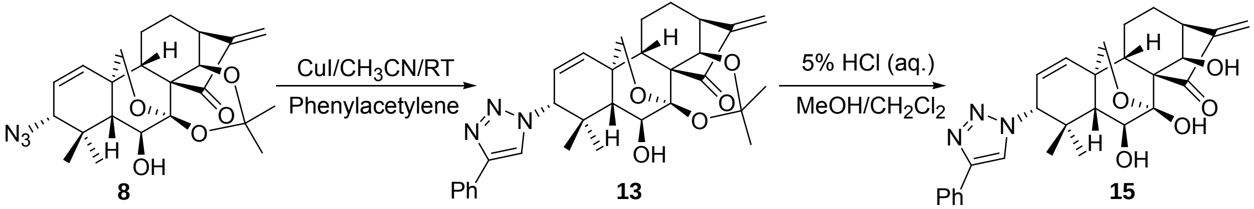


10 **8** **11**

A mixture of **10** (30 mg, 0.071 mmol) and NaN_3 (25 mg, 0.355 mmol) in the dried DMF (3 mL) was stirred at 70 ˚C under N_2 for 10 h. After that, the reaction mixture was diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 25% EtOAc in hexane to afford the desired product **8** (22 mg, 74%) as a colorless amorphous gel.

A solution of **11** (10 mg, 0.023 mmol) in the dried CH_3CN was refluxed at 85 ˚C for 8 h. After completion of the reaction, which was monitored by TLC, the reaction solvent was evaporated under vacuum at 27 ˚C to give an oily residue. The residue was further purified using preparative TLC developed by 25% EtOAc in hexane to afford the desired product **8** (9 mg, 90%) as a colorless amorphous gel. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.73 (dd, 1H, *J* = 1.8 Hz, 10.5 Hz), 5.59 (s, 1H), 5.48 (d, 1H, *J* = 12.0 Hz), 5.38 (dd, 1H, *J* = 2.7 Hz, 10.5 Hz), 4.81 (d, 1H, *J* = 1.2 Hz), 3.95 (m, 2H), 3.84 (m, 1H), 3.75 (dd, 1H, *J* = 1.8 Hz, 2.4 Hz), 3.08 (dd, 1H, *J* = 0.9 Hz, 8.7Hz), 2.54 (m, 1H), 1.76 (m, 3H), 1.64 (s, 3H), 1.53 (m, 2H), 1.35 (s, 3H), 1.28 (s, 3H), 1.01 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 150.2, 129.5, 127.3, 120.8, 101.3, 95.3, 71.3, 69.9, 68.4, 64.6, 57.3, 56.1, 48.8, 40.2, 38.5, 38.3, 30.1 (2C), 27.2, 25.4, 17.3, 16.9. HRMS Calcd for $C_{23}H_{30}N_3O_5$: $[M + H]^+$ 428.2180; found 428.2190.

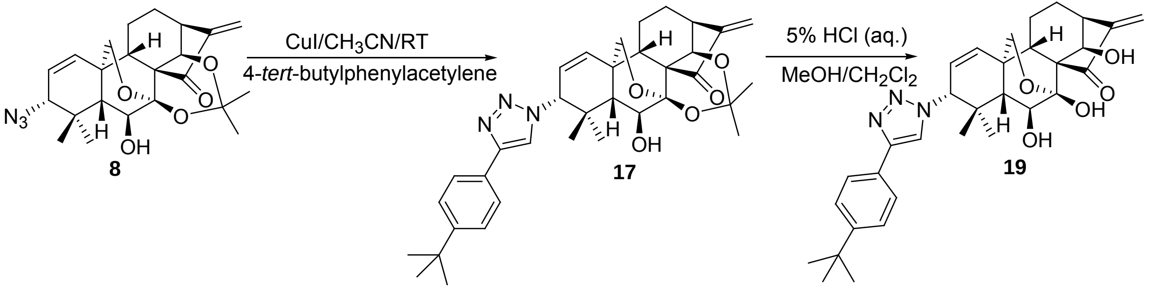
(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,9*R*,11a*R*,11b*S*)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-9-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2,3,3a,7,7a,8,9,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (13) and (3*R*,4a*R*,5*S*,6*S*,6a*R*,9*S*,11a*S*,11b*R*,14*R*)-5,6,14-trihydroxy-4,4-dimethyl-8-methylene-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-4,4a,5,6,9,10,11,11a-octahydro-3*H*-6,11b-(epoxymethano)-6a,9-methanocyclohepta[*a*]naphthalen-7(8*H*)-one (15).



A mixture of **8** (15.0 mg, 0.035 mmol), phenylacetylene (7.1 mg, 0.07 mmol) and copper (I) iodide (6.6 mg, 0.035 mmol) in the dried acetonitrile (2 mL) was stirred at rt for 24 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 30% ethyl acetate in hexane to afford the desired product **13** (14.0 mg, 78%) as a colorless amorphous gel. To a solution of **13** (10 mg, 0.018 mmol) in a mixture of MeOH (2.0 mL) and CH_2Cl_2 (1.0 mL) was added 5% HCl aqueous solution (0.5 mL) at rt. The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 2.5% methanol in dichloromethane to afford the desired product **15** (8.0 mg, 86%) as a colorless amorphous gel. **Compound 13**: HPLC purity 96.8% (t_R = 23.39 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, 2H, *J* = 7.2 Hz), 7.70 (s, 1H), 7.42 (m, 2H), 7.33 (t, 1H, *J* = 7.2Hz), 6.22 (s, 1H), 5.90 (d, 1H, *J* = 10.2 Hz), 5.62 (s, 1H), 5.61 (d, 1H, *J* = 11.4 Hz), 5.56 (d, 1H, *J* = 10.2 Hz), 5.10 (s, 1H), 4.85 (s, 1H), 4.10 (d, 1H, *J* = 9.6 Hz), 3.97 (m, 2H), 3.11 (d, 1H, *J* = 9.0 Hz), 2.58 (m, 1H), 1.86 (m, 2H), 1.76 (m, 2H), 1.66 (s, 3H), 1.63 (m, 1H), 1.36 (s, 3H), 1.24 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.4, 150.1, 147.1, 130.5, 129.1, 128.8 (2C), 128.1, 127.9, 125.7 (2C), 121.1, 119.9, 101.4, 95.3, 71.4, 69.9, 67.8, 64.7, 57.3, 56.1, 48.8, 40.2, 38.4, 38.1, 30.1, 27.0, 25.4, 17.8, 17.3. HRMS Calcd for $C_{31}H_{36}N_3O_5$: $[M + H]^+$ 530.2649; found 530.2667. **Compound 15**: $[\alpha]^{25}_D$ -72 (*c* 0.1, CH_2Cl_2); HPLC purity 96.8% (t_R = 17.23 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.69 (s, 1H), 7.42 (t, 2H, *J* = 7.5 Hz), 7.34 (m, 1H), 6.24 (br s, 2H), 5.91 (m, 1H), 5.63 (s, 1H), 5.61 (m, 1H), 5.10 (m, 1H), 4.93 (s, 1H), 3.99 (m, 3H), 3.07 (d, 1H, *J* = 8.7 Hz), 2.53 (m, 1H), 2.07 (m, 1H), 1.80 (m, 2H), 1.79 (d, 1H, *J* = 8.1 Hz), 1.63 (m, 2H), 1.21 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4, 150.8, 147.2, 130.4, 129.4, 128.9 (2C), 128.3, 128.2, 125.7 (2C), 122.0, 119.8, 97.6, 72.8, 72.1, 67.6, 65.3, 62.0, 56.8, 52.0, 42.6, 38.9, 38.2, 29.6, 26.7, 17.6, 17.5. HRMS Calcd for $C_{28}H_{32}N_3O_5$: $[M + H]^+$ 490.2336; found 490.2344.

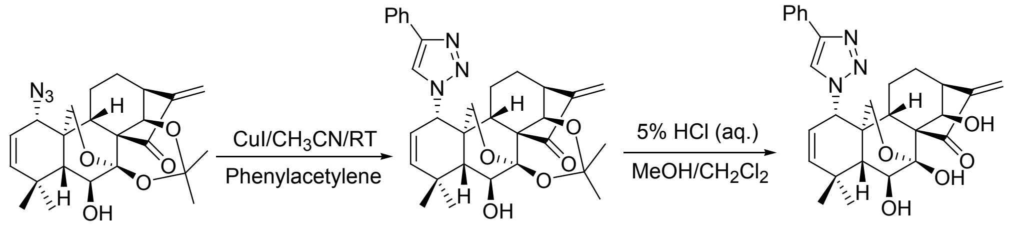
(3*S*,3a*R*,3a^1*R*,6aR,7*S*,7a*R*,9*R*,11a*R*,11b*S*)-9-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,9,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (17) and (3*R*,4a*R*,5*S*,6*S*,6a*R*,9*S*,11a*S*,11b*R*,14*R*)-3-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-

5,6,14-trihydroxy-4,4-dimethyl-8-methylene-4,4a,5,6,9,10,11,11a-octahydro-3*H*-6,11b-(epoxymethano)-6a,9-methanocyclohepta[*a*]naphthalen-7(8*H*)-one (19).



A mixture of **8** (13.6 mg, 0.032 mmol), 4-*tert*-butylphenylacetylene (10 mg, 0.064 mmol) and copper (I) iodide (6.0 mg, 0.032 mmol) in the dried acetonitrile (3 mL) was stirred at rt for 36 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 30% ethyl acetate in hexane to afford the desired product **17** (15 mg, 80%) as a colorless amorphous gel. To a solution of **17** (6.0 mg, 0.01 mmol) in a mixture of MeOH (2.0 mL) and CH_2Cl_2 (1.0 mL) was added 5% HCl aqueous solution (0.5 mL). The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 3% methanol in dichloromethane to afford the desired product **19** (4.7 mg, 85%) as a colorless amorphous gel. **Compound 17**: HPLC purity 96.8% (t_R = 23.39 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, 1H, *J* = 8.4 Hz), 7.66 (s, 1H), 7.45 (d, 1H, *J* = 8.4 Hz), 6.22 (s, 1H), 5.90 (dd, 1H, *J* = 1.8 Hz, 10.8 Hz), 5.62 (s, 1H), 5.61 (d, 1H, *J* = 12.0 Hz), 5.56 (m, 1H), 5.09 (m, 1H), 4.85 (d, 1H, *J* = 1.2 Hz), 4.10 (d, 1H, *J* = 10.2 Hz), 3.95 (m, 1H), 3.10 (d, 1H, *J* = 9.0 Hz), 2.08 (m, 1H), 1.86 (m, 2H), 1.77 (m, 2H), 1.66 (s, 3H), 1.64 (m, 1H), 1.36 (s, 3H), 1.34 (s, 9H), 1.23 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.4, 151.3, 150.1, 147.1, 129.2, 127.8, 127.7, 125.7 (2C), 125.4 (2C), 121.0, 119.6, 101.4, 95.3, 71.4, 69.9, 67.8, 64.7, 57.3, 56.1, 48.8, 40.2, 38.4, 38.1, 34.6, 31.2 (3C), 30.1, 29.7, 27.0, 25.4, 17.7, 17.3. HRMS Calcd for $C_{35}H_{44}N_3O_5$: $[M + H]^+$ 586.3275; found 586.3280. **Compound 19**: $[\alpha]^{25}_D$ -84 (*c* 0.1, MeOH/CH_2Cl_2 = 1:1); HPLC purity 96.5% (t_R = 20.82 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, 2H, *J* = 7.8 Hz), 7.65 (s, 1H), 7.45 (d, 2H, *J* = 7.8 Hz), 6.25 (s, 1H), 6.14 (d, 1H, *J* = 12.0 Hz), 5.92 (d, 1H, *J* = 10.2 Hz), 5.63 (s, 1H), 5.57 (d, 1H, *J* = 10.2 Hz), 5.19 (br s, 1H), 5.09 (s, 1H), 4.93 (s, 1H), 4.54 (br s, 1H), 4.10 (d, 1H, *J* = 10.2 Hz), 3.98 (d, 1H, *J* = 10.2 Hz), 3.88 (m, 1H), 3.10 (d, 1H, *J* = 9.0 Hz), 2.53 (m, 1H), 1.89 (m, 2H), 1.78 (d, 1H, *J* = 8.4 Hz), 1.66 (m, 2H), 1.34 (s, 9H), 1.21 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.2, 151.4, 150.8, 147.2, 129.5, 128.2, 127.5, 125.8 (2C), 125.4 (2C), 122.0, 119.5, 97.6, 72.9, 72.1, 67.5, 65.3, 62.1, 56.8, 51.9, 42.6, 38.9, 38.2, 34.6, 31.2 (3C), 29.6, 26.7, 17.6, 17.4. HRMS Calcd for $C_{32}H_{40}N_3O_5$: $[M + H]^+$ 546.2962; found 546.2976.

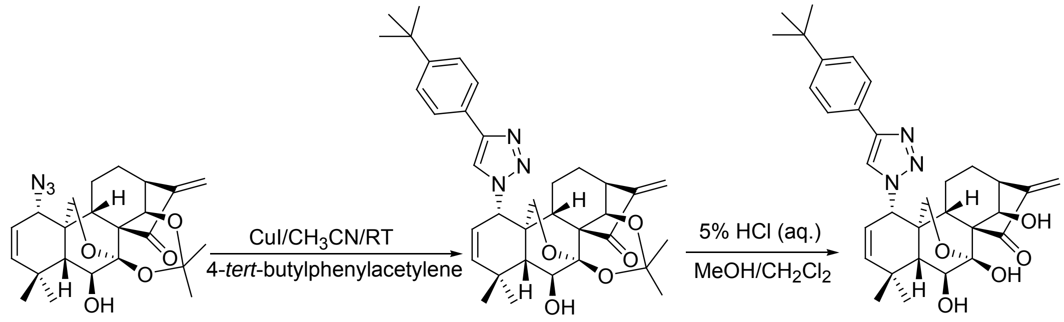
(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,11*S*,11a*R*,11b*S*)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-11-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2,3,3a,7,7a,8,11,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (12) and (1*S*,4a*R*,5*S*,6*S*,6a*R*,9*S*,11a*S*,11b*R*,14*R*)-5,6,14-trihydroxy-4,4-dimethyl-8-methylene-1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-4,4a,5,6,9,10,11,11a-octahydro-1*H*-6,11b-(epoxymethano)-6a,9-methanocyclohepta[*a*]naphthalen-7(8*H*)-one (14).



11 **12** **14**

A mixture of **11** (9.0 mg, 0.021 mmol), phenylacetylene (4.3 mg, 0.042 mmol) and copper (I) iodide (4 mg, 0.021 mmol) in the dried acetonitrile (2 mL) was stirred at rt for 36 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 30% ethyl acetate in hexane to afford the desired product **12** (9 mg, 82%). To a solution of **12** (5 mg, 0.009 mmol) in a mixture of MeOH (2.0 mL) and CH_2Cl_2 (1.0 mL) was added 5% HCl aqueous solution (0.5 mL) at rt. The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 2.5% methanol in dichloromethane to afford the desired product **14** (4.0 mg, 86%) as a colorless solid. **Compound 12**: HPLC purity 98.7% (t_R = 21.52 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.55 (s, 1H), 7.42 (t, 2H, *J* = 7.8 Hz), 7.35 (m, 1H), 6.20 (s, 1H), 6.04 (m, 1H), 5.83 (d, 1H, *J* = 12.0 Hz), 5.60 (s, 1H), 5.40 (m, 2H), 4.71 (s, 1H), 4.07 (dd, 1H, *J* = 7.8 Hz, 12.0 Hz), 3.98 (d, 1H, *J* = 10.2 Hz), 3.35 (dd, 1H, *J* = 1.8 Hz, 10.2 Hz), 3.08 (d, 1H, *J* = 9.6 Hz), 2.55 (m, 1H), 2.27 (m, 1H), 2.09 (m, 1H), 1.82 (dd, 1H, *J* = 1.2 Hz, 7.2 Hz), 1.73 (m, 2H), 1.56 (s, 3H), 1.39 (s, 6H), 1.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.8, 150.3, 147.6, 144.7, 129.0, 128.9 (2C), 128.4, 125.7 (2C), 120.8, 120.0, 118.8, 101.2, 94.8, 72.6, 69.9, 63.8, 60.1, 57.4, 56.1, 50.6, 40.1, 38.3, 34.5, 32.2, 30.1, 30.0, 29.7, 25.4, 25.2, 18.6. HRMS Calcd for $C_{31}H_{36}N_3O_5$: $[M + H]^+$ 530.2649; found 530.2652. **Compound 14**: $[\alpha]^{25}_D$ +68 (*c* 0.1, MeOH/CH_2Cl_2 = 1:1); HPLC purity 99.4% (t_R = 18.44 min); ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 8.00 (s, 1H), 7.81 (m, 2H), 7.44 (m, 2H), 7.35 (m, 1H), 6.18 (s, 1H), 5.93 (dd, 1H, *J* = 2.1 Hz, 9.9 Hz), 5.59 (s, 1H), 5.46 (t, 1H, *J* = 2.7 Hz), 5.25 (dd, 1H, *J* = 3.3 Hz, 6.9 Hz), 4.79 (d, 1H, *J* = 1.2 Hz), 4.37 (m, 3H), 4.00 (d, 1H, *J* = 6.0 Hz), 3.78 (m, 1H), 3.37 (s, 1H), 3.02 (m, 1H), 2.46 (m, 1H), 2.28 (m, 1H), 2.01 (m, 1H), 1.90 (m, 1H), 1.65 (m, 1H), 1.47 (m, 1H), 1.40 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 208.6, 151.6, 148.3, 142.6, 130.6, 129.5 (2C), 129.0, 126.3 (2C), 121.8, 121.5, 121.0, 97.6, 73.7, 73.5, 64.7, 62.1, 61.8, 58.4, 52.6, 43.7, 39.8, 35.3, 31.8, 30.2 (2C), 25.2, 18.8. HRMS Calcd for $C_{28}H_{32}N_3O_5$: $[M + H]^+$ 490.2336; found 490.2344.

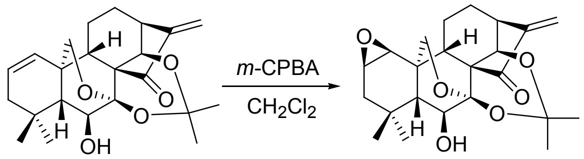
(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,11*S*,11a*R*,11b*S*)-11-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-7-hydroxy-5,5,8,8-tetramethyl-15-methylene-2,3,3a,7,7a,8,11,11b-octahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (16) and (1*S*,4a*R*,5*S*,6*S*,6a*R*,9*S*,11a*S*,11b*R*,14*R*)-1-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-5,6,14-trihydroxy-4,4-dimethyl-8-methylene-4,4a,5,6,9,10,11,11a-octahydro-1*H*-6,11b-(epoxymethano)-6a,9-methanocyclohepta[*a*]naphthalen-7(8*H*)-one (18).



11 **16** **18**

A mixture of **11** (17 mg, 0.039 mmol), 4-*tert*-butylphenylacetylene (12 mg, 0.078 mmol) and copper (I) iodide (7.4 mg, 0.039 mmol) in the dried acetonitrile (3 mL) was stirred at rt for 36 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 30% ethyl acetate in hexane to afford the desired product **16** (18 mg, 78%) as a colorless amorphous gel. To a solution of **16** (10 mg, 0.017 mmol) in a mixture of MeOH (2.0 mL) and CH_2Cl_2 (1.0 mL) was added 5% HCl aqueous solution (0.5 mL). The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 3% methanol in dichloromethane to afford the desired product **18** (8.4 mg, 91%) as a colorless amorphous gel. **Compound 16**: HPLC purity 98.2% (t_R = 24.06 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, 2H, *J* = 1.8 Hz, 6.6 Hz), 7.51 (s, 1H), 7.45 (dd, 1H, *J* = 1.8 Hz, 8.4 Hz), 6.19 (s, 1H), 6.04 (m, 1H), 5.82 (d, 1H, *J* = 12.0 Hz), 5.60 (s, 1H), 5.40 (m, 2H), 4.71 (d, 1H, *J* = 1.8 Hz), 4.07 (dd, 1H, *J* = 7.8 Hz, 12.0 Hz), 3.96 (dd, 1H, *J* = 1.2 Hz, 9.6 Hz), 3.35 (m, 1H), 3.08 (d, 1H, *J* = 9.6 Hz), 2.56 (m, 1H), 2.25 (m, 1H), 2.08 (m, 1H), 1.82 (dd, 1H, *J* = 1.8 Hz, 7.8 Hz), 1.71 (m, 2H), 1.56 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H), 1.34 (s, 9H), 1.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.9, 151.6, 150.3, 147.6, 144.6, 127.2, 125.8 (2C), 125.4 (2C), 120.8, 120.0, 118.5, 101.2, 94.8, 72.6, 69.9, 63.8, 60.0, 57.5, 56.1, 50.6, 40.1, 38.4, 34.7, 34.5, 32.2, 31.2 (3C), 30.1, 30.0, 29.7, 25.4, 25.2, 18.5. HRMS Calcd for $C_{35}H_{44}N_3O_5$: $[M + H]^+$ 586.3275; found 586.3284. **Compound 18**: $[\alpha]^{25}_D$ +48 (*c* 0.07, MeOH/CH_2Cl_2 = 1:1); HPLC purity 98.3% (t_R = 21.13 min); ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 7.72 (dd, 2H, *J* = 1.8 Hz, 6.6 Hz), 7.70 (s, 1H), 7.47 (dd, 2H, *J* = 1.8 Hz, 6.6 Hz), 6.20 (s, 1H), 5.97 (dd, 1H, *J* = 2.4 Hz, 10.2 Hz), 5.59 (s, 1H), 5.42 (m, 1H), 5.27 (dd, 1H, *J* = 3.3 Hz, 9.9 Hz), 4.77 (d, 1H, *J* = 1.5 Hz), 3.99 (d, 1H, *J* = 6.0 Hz), 3.84 (br s, 2H), 3.68 (m, 1H), 3.02 (d, 1H, *J* = 9.9 Hz), 2.47 (m, 1H), 2.23 (m, 1H), 2.06 (m, 1H), 1.87 (m, 1H), 1.64 (m, 1H), 1.51 (m, 1H), 1.38 (s, 3H), 1.35 (s, 9H), 1.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 207.8, 152.1, 151.0, 148.0, 142.9, 127.1, 126.1 (2C), 125.7 (2C), 121.1, 121.0, 119.9, 97.2, 73.1, 64.3, 61.7, 61.2, 57.9, 52.4, 43.1, 39.3, 34.9 (2C), 31.6, 31.3 (3C), 29.9, 25.0, 18.5. HRMS Calcd for $C_{32}H_{40}N_3O_5$: $[M + H]^+$ 546.2962; found 546.2980.

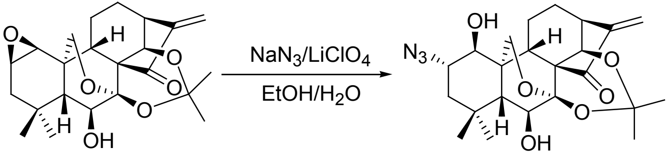
(1a*R*,3a*R*,4*S*,4a*R*,4a^1*R*,7a*R*,8*S*,10a*S*,10b*S*,10c*S*)-4-hydroxy-3,3,6,6-tetramethyl-13-methylenedecahydro-1a*H*-4a,10b-(epoxymethano)-4a^1,8-ethanooxireno[2',3':5,6]phenanthro[1,10-*de*][1,3]dioxin-14-one (20).



4 **20**

To a solution of **4** (16 mg, 0.04 mmol) in dichloromethane (4 mL) was added *m*-CPBA (9.0 mg, 0.04 mmol) at 0 ˚C. The resulting mixture was stirred at rt for 1 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was further purified using preparative TLC developed by 50% EtOAc in hexane to afford the desired product **20** as a colorless gel (14 mg, 86%). HPLC purity 96.0% (t_R = 19.21 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.90 (s, 1H), 5.58 (br s, 1H), 4.83 (s, 1H), 4.14 (d, 1H, *J* = 9.6 Hz), 4.02 (d, 1H, *J* = 9.6 Hz), 3.82 (br s, 1H), 3.25 (br s, 1H), 3.08 (d, 1H, *J* = 9.0 Hz), 2.58 (m, 1H), 2.55 (m, 1H), 2.09 (m, 1H), 1.83 (m, 3H), 1.72 (m, 1H), 1.65 (s, 3H), 1.52 (d, 1H, *J* = 15.0 Hz), 1.34 (s, 3H), 1.19 (d, 1H, *J* = 7.8 Hz), 1.08 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.4, 150.2, 120.7, 101.4, 95.3, 71.9, 70.0, 64.9, 55.7, 54.4, 53.1, 52.3, 45.5, 40.4, 40.2, 36.0, 32.4, 30.3, 30.1 (2C), 25.5, 23.5, 16.6. HRMS Calcd for $C_{23}H_{31}O_6$: $[M + H]^+$ 403.2115; found 403.2128.

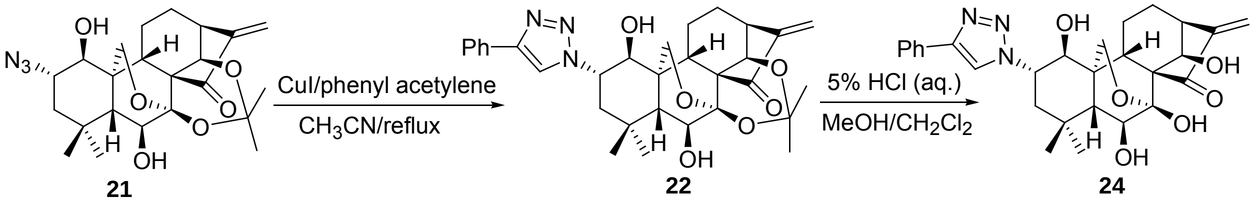
(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,10*S*,11*S*,11a*S*,11b*S*)-10-azido-7,11-dihydroxy-5,5,8,8-tetramethyl-15-methylenedecahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (21).



20 **21**

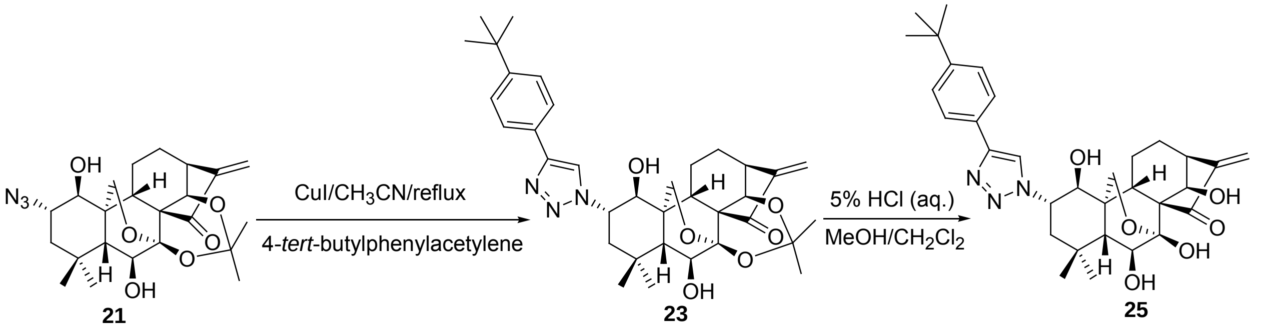
To a solution of **20** (25 mg, 0.062 mmol) in a mixture of ethanol (1 mL) and water (1 mL) was added $LiClO_4$ (13 mg, 0.124 mmol) and NaN_3 (32 mg, 0.496 mmol) at rt. The resulting mixture was stirred at 85˚C for 24 h, and then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 5% ethyl acetate in dichloromethane to afford the desired product **21** (16 mg, 60%) as a white solid, and 8 mg of **20** was recovered. HPLC purity 98.0% (t_R = 19.36 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.19 (s, 1H), 6.02 (d, 1H, *J* = 12.0 Hz), 5.59 (s, 1H), 4.78 (s, 1H), 4.48 (d, 1H, *J* = 10.2 Hz), 3.99 (dd, 1H, *J* = 7.2 Hz, 12.0 Hz), 3.83 (m, 2H), 3.36 (s, 1H), 3.09 (d, 1H, *J* = 9.0 Hz), 2.54 (m, 1H), 2.25 (m, 1H), 1.96 (m, 2H), 1.77 (m, 2H), 1.68 (m, 2H), 1.66 (s, 3H), 1.62 (d, 1H, *J* = 6.6 Hz), 1.37 (s, 3H), 1.35 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.2, 150.5, 120.3, 101.2, 94.7, 72.5, 70.2, 67.1, 64.8, 61.9, 55.7, 53.9, 44.0, 40.4, 39.4, 37.0, 34.7, 32.4, 30.2, 29.9, 25.6, 25.5, 16.3. HRMS Calcd for $C_{23}H_{32}N_3O_6$: $[M + H]^+$ 446.2286; found 446.2300.

(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,10*S*,11*S*,11a*S*,11b*S*)-7,11-dihydroxy-5,5,8,8-tetramethyl-15-methylene-10-(4-phenyl-1*H*-1,2,3-triazol-1-yl)decahydro-1*H*-6a,11a-(epoxymethano)-3,3a^1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (22) and (1*S*,2*S*,4a*R*,5*S*,6*S*,6a*R*,9*S*,11a*S*,11b*S*,14*R*)-1,5,6,14-tetrahydroxy-4,4-dimethyl-8-methylene-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)decahydro-1*H*-6,11b-(epoxymethano)-6a,9-methanocyclohepta[a]naphthalen-7(8*H*)-one (24).

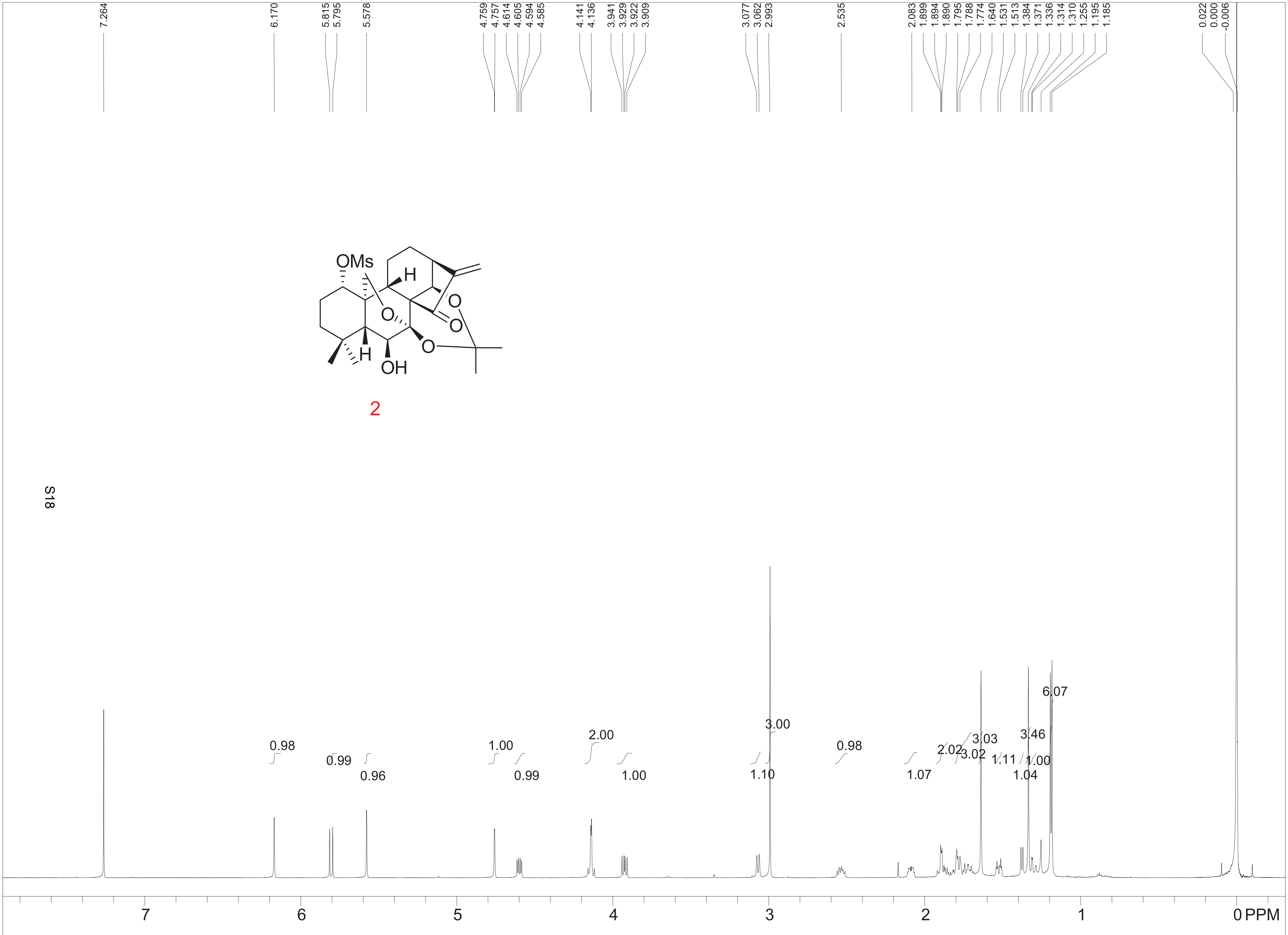


Copper (I) iodide (3.8 mg, 0.02 mmol) was added to a mixture of **21** (9 mg, 0.02 mmol) and phenyl acetylene (2.4 mg, 0.024 mmol) in acetonitrile (2 mL). The reaction mixture was stirred at 85 ˚C for 16 h, and then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 5% ethyl acetate in dichloromethane to afford the desired 1,2,3-triazole product **22** (6 mg, 60%), and 3 mg of **21** was recovered. To a solution of **22** (6 mg, 0.01 mmol) in a mixture of MeOH (2.0 mL) and CH_2Cl_2 (1.0 mL) was added 5% HCl aqueous solution (0.5 mL) at rt. The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 5% methanol in dichloromethane to afford the desired product **24** (5.5 mg, 98%) as a colorless amorphous gel. **Compound 22**: HPLC purity 95.6% (t_R = 19.78 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (m, 3H), 7.39 (m, 3H), 6.19 (s, 1H), 5.59 (s, 1H), 5.57 (d, 1H, *J* = 12.0 Hz), 4.82 (d, 1H, *J* = 1.2 Hz), 4.60 (m, 1H), 4.43 (m, 1H), 4.00 (m, 3H), 3.07 (d, 1H, *J* = 9.0 Hz), 2.99 (m, 1H), 2.50 (m, 1H), 2.33 (m, 1H), 2.18 (d, 1H, *J* = 7.2 Hz), 1.88 (m, 2H), 1.70 (m, 2H), 1.63 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H), 1.17 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 205.1, 150.6, 147.5, 130.1, 128.9 (2C), 128.4, 125.6 (2C), 120.4, 119.5, 101.1, 95.3, 72.4, 70.1, 68.7, 66.1, 62.0, 55.8, 54.4, 45.3, 40.8, 40.4, 33.9, 32.6, 30.4, 30.1, 29.7, 27.2, 25.4, 18.3. HRMS Calcd for $C_{31}H_{38}N_3O_6$: $[M + H]^+$ 548.2755; found 548.2775. **Compound 24**: $[\alpha]^{25}_D$ +12 (*c* 0.1, MeOH/CH_2Cl_2 = 1:1); HPLC purity 99.7% (t_R = 16.74 min); ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 8.22 (s, 1H), 7.80 (d, 2H, *J* = 7.2 Hz), 7.44 (m, 2H), 7.36 (m, 1H), 6.20 (s, 1H), 5.61 (s, 1H), 4.88 (s, 1H), 4.43 (s, 1H), 4.22 (m, 2H), 4.00 (d, 1H, *J* = 10.8 Hz), 3.85 (d, 1H, *J* = 10.8 Hz), 3.81 (d, 1H, *J* = 6.0 Hz), 3.05 (d, 1H, *J* = 9.6 Hz), 2.55 (m, 1H), 2.35 (m, 3H), 1.92 (m, 1H), 1.87 (m, 1H), 1.80 (d, 1H, *J* = 6.0 Hz), 1.72 (m, 1H), 1.28 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 207.9, 151.4, 147.8, 130.3, 129.2 (2C), 128.7, 125.9 (2C), 120.9, 120.3, 97.5, 73.3, 73.2, 66.3, 66.2, 62.6, 61.4, 53.7, 43.5, 41.1, 38.3, 33.6, 32.7, 30.1, 29.9, 26.0, 16.6. HRMS Calcd for $C_{28}H_{34}N_3O_6$: $[M + H]^+$ 508.2442; found 508.2457.

(3*S*,3a*R*,3a^1*R*,6a*R*,7*S*,7a*R*,10*S*,11*S*,11a*S*,11b*S*)-10-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-7,11-dihydroxy-5,5,8,8-tetramethyl-15-methylenedecahydro-1*H*-6a,11a-(epoxymethano)-3,3a1-ethanophenanthro[1,10-*de*][1,3]dioxin-14-one (23) and (1*S*,2*S*,4a*R*,5*S*,6*S*,6a*R*,9*S*,11a*S*,11b*S*,14*R*)-2-(4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)-1,5,6,14-tetrahydroxy-4,4-dimethyl-8-methylenedecahydro-1*H*-6,11b-(epoxymethano)-6a,9-methanocyclohepta[*a*]naphthalen-7(8*H*)-one (25).



Copper (I) iodide (10.0 mg, 0.05 mmol) was added to a mixture of **21** (22.0 mg, 0.05 mmol) and 4-*tert*-butylphenylacetylene (15.8 mg, 0.10 mmol) in acetonitrile (2 mL). The reaction mixture was stirred at 85 ˚C for 16 h, and then diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 33% ethyl acetate in hexane to afford the desired 1,2,3-triazole intermediate **23** (19 mg, 82%), and 5 mg of **21** was recovered. To a solution of **23** (8 mg, 0.013 mmol) in a mixture of MeOH (2.0 mL) and CH_2Cl_2 (1.0 mL) was added 5% HCl aqueous solution (0.5 mL) at rt. The resulting mixture was stirred at rt for 2 h, and then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ (aq.) solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give an oily residue. The residue was purified using preparative TLC developed by 3% methanol in dichloromethane to afford the desired product **25** (7.0 mg, 98%) as a colorless amorphous gel. **Compound 23**: HPLC purity 95.0% (t_R = 22.34 min); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.67 (d, 1H, J = 9.0 Hz), 7.44 (d, 1H, J = 8.4 Hz), 6.19 (s, 1H), 5.59 (s, 1H), 5.58 (d, 1H, J = 11.4 Hz), 4.82 (s, 1H), 4.57 (m, 1H), 4.44 (m, 1H), 3.97 (m, 3H), 3.08 (m, 2H), 2.48 (m, 1H), 2.34 (m, 1H), 2.17 (d, 1H, J = 7.2 Hz), 1.88 (m, 1H), 1.83 (m, 1H), 1.73 (m, 2H), 1.63 (s, 3H), 1.34 (s, 9H), 1.30 (s, 3H), 1.25 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.1, 151.8, 150.6, 147.2, 127.3, 125.8 (2C), 125.3 (2C), 120.4, 118.8, 100.8, 95.0, 72.3, 70.1, 68.5, 66.1, 62.0, 55.8, 54.3, 45.3, 40.7, 40.3, 34.7, 33.9, 32.5, 31.2 (3C), 30.4, 30.1, 29.7, 27.1, 25.4, 18.1. HRMS Calcd for $C_{35}H_{46}N_3O_6$: $[M + H]^+$ 604.3381; found 604.3378. **Compound 25**: $[\alpha]^{25}_D$ +10 (c 0.1, $MeOH/CH_2Cl_2$ = 1:1); HPLC purity 99.9% (t_R = 19.40 min); ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 6.18 (s, 1H), 7.73 (d, 1H, J = 8.4 Hz), 7.48 (d, 1H, J = 8.7 Hz), 6.20 (s, 1H), 5.60 (s, 1H), 4.89 (d, 1H, J = 1.2 Hz), 4.44 (d, 1H, J = 2.1 Hz), 4.22 (br s, 3H), 4.00 (d, 1H, J = 9.0 Hz), 3.81 (m, 2H), 3.04 (d, 1H, J = 9.6 Hz), 2.54 (m, 1H), 2.33 (m, 3H), 1.84 (m, 4H), 1.35 (s, 9H), 1.28 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3/CD_3OD$ = 10:1) δ 208.3, 152.1, 151.8, 148.0, 127.7, 126.3 (2C), 125.9 (2C), 121.0, 120.5, 97.7, 73.6, 73.5, 66.4, 66.3, 62.7, 61.6, 54.1, 43.8, 41.3, 38.3, 35.0, 33.8, 32.9, 31.4 (3C), 30.4, 30.1, 26.0, 16.7. HRMS Calcd for $C_{32}H_{42}N_3O_6$: $[M + H]^+$ 564.3068; found 564.3073.



2

spect, CDCl3,
USER: zhou -- DATE: Thu Dec 13 20:23:50 2012

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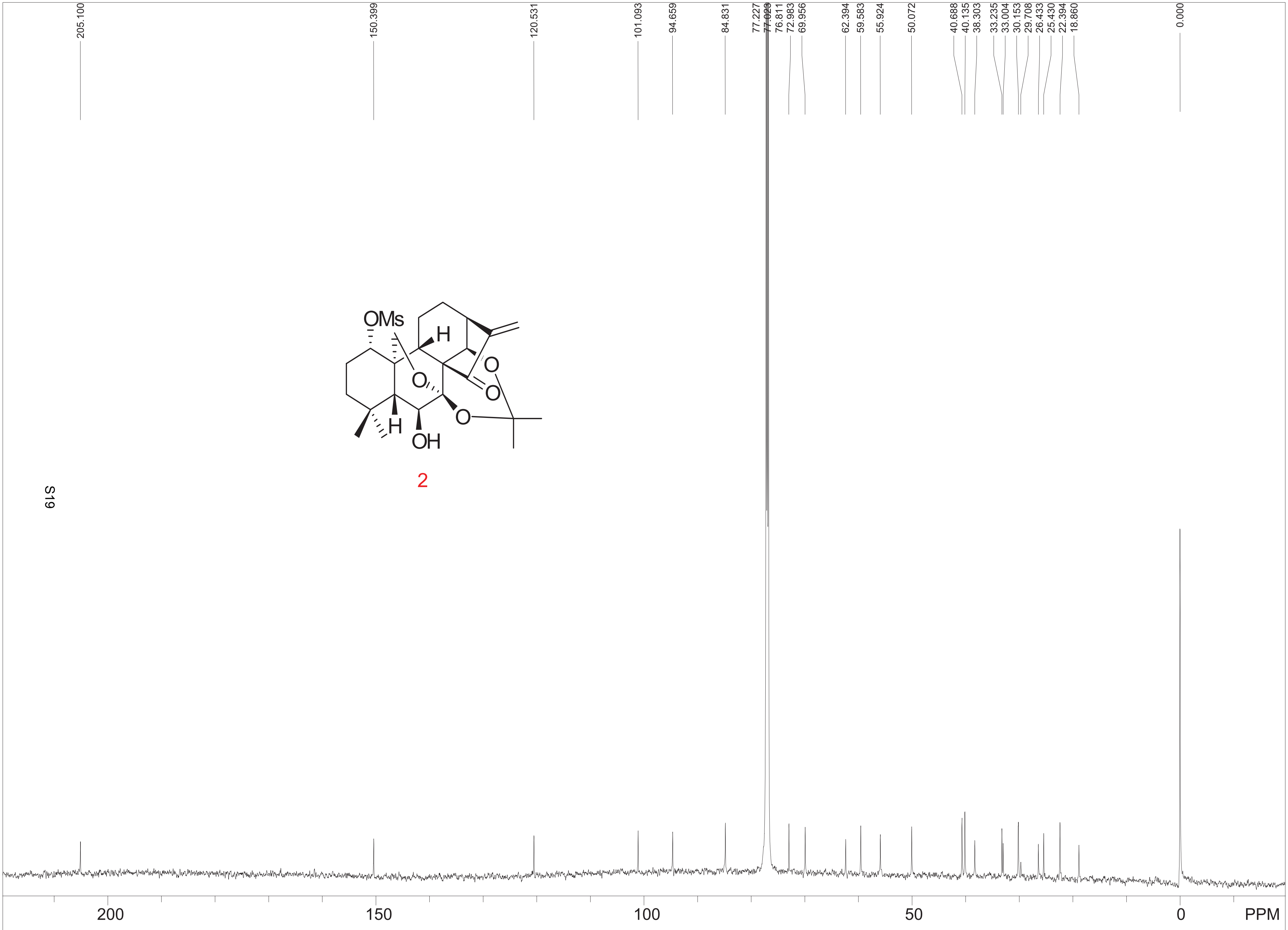

2

spect, CDCl3, USER: zhou -- DATE: Thu Dec 13 20:29:20 2012

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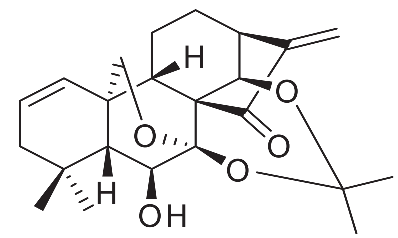

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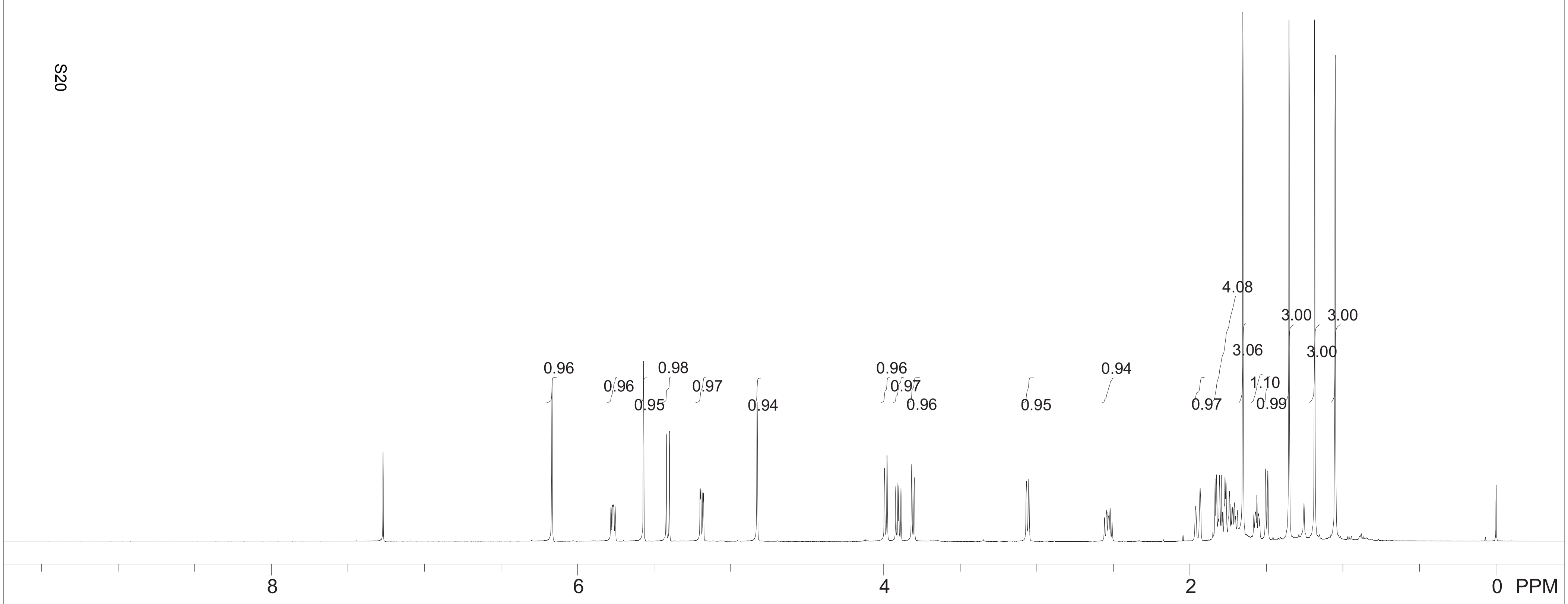

spect, CDCl3,

USER: zhou -- DATE: Thu Jul 05 21:06:02 2012

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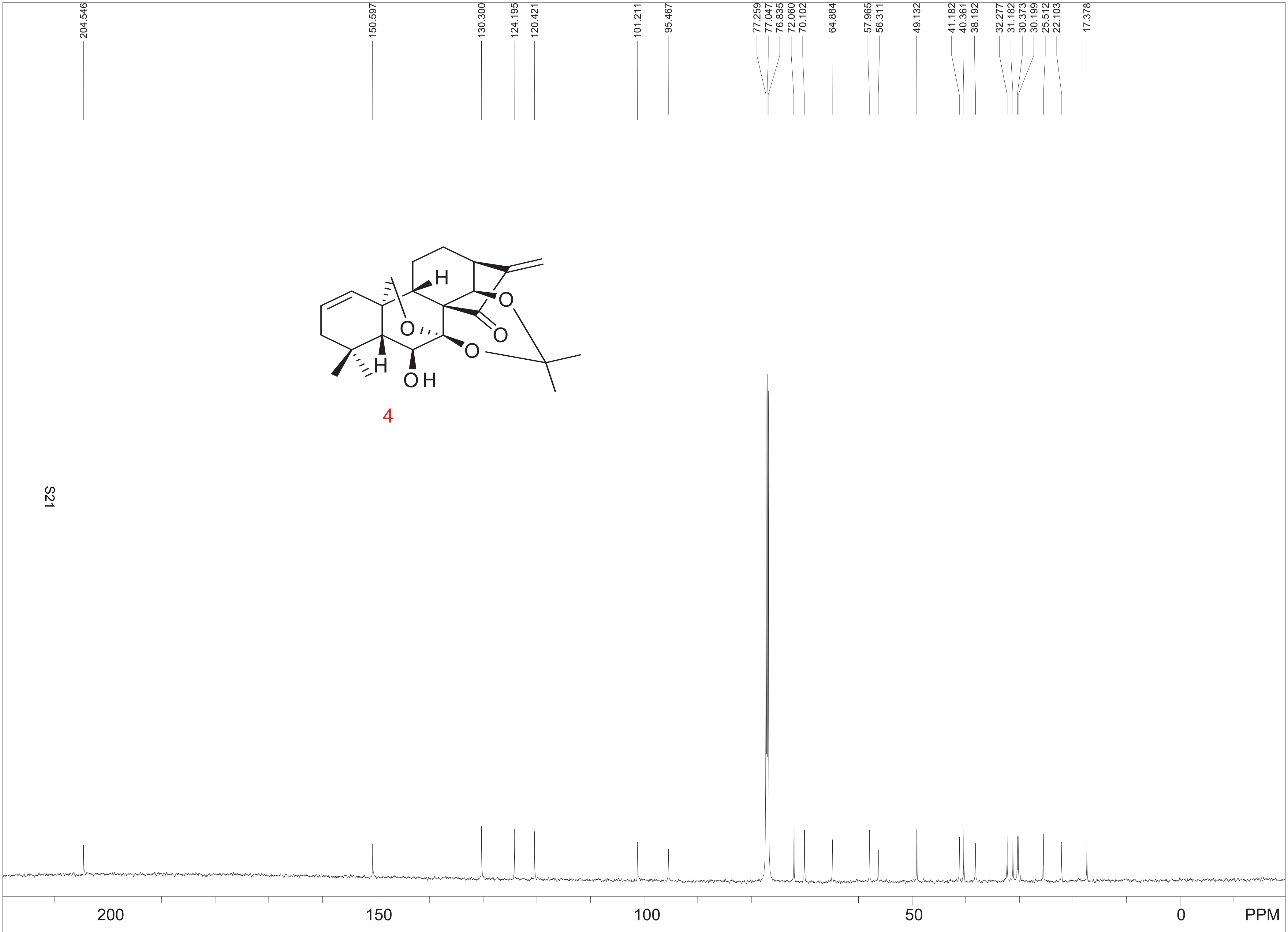

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spect, CDCl3,

USER: zhou -- DATE: Thu Jul 05 21:08:38 2012

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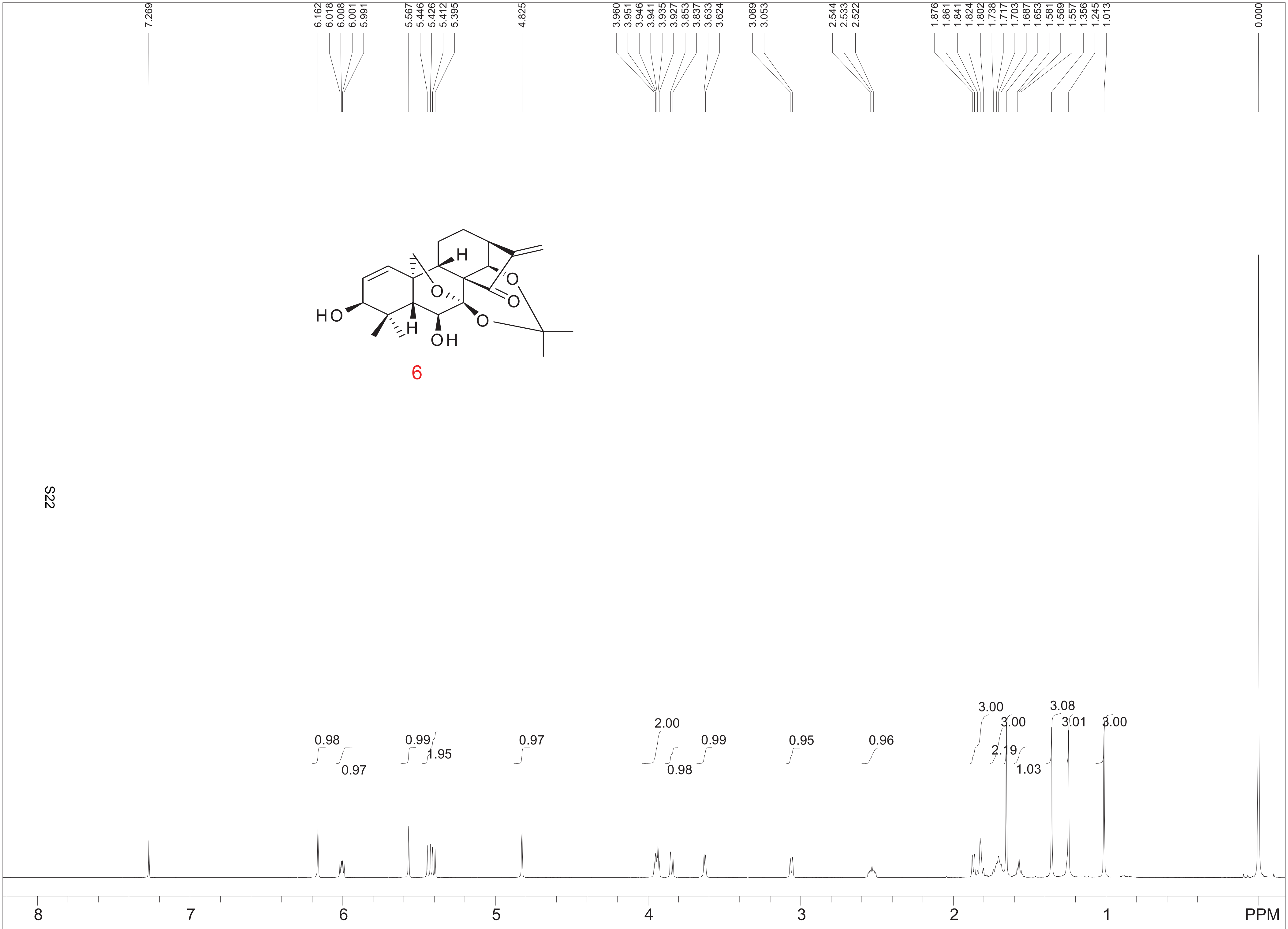

6

spect, CDCl3,					USER: zhou -- DATE: Thu Jul 19 17:03:13 2012	
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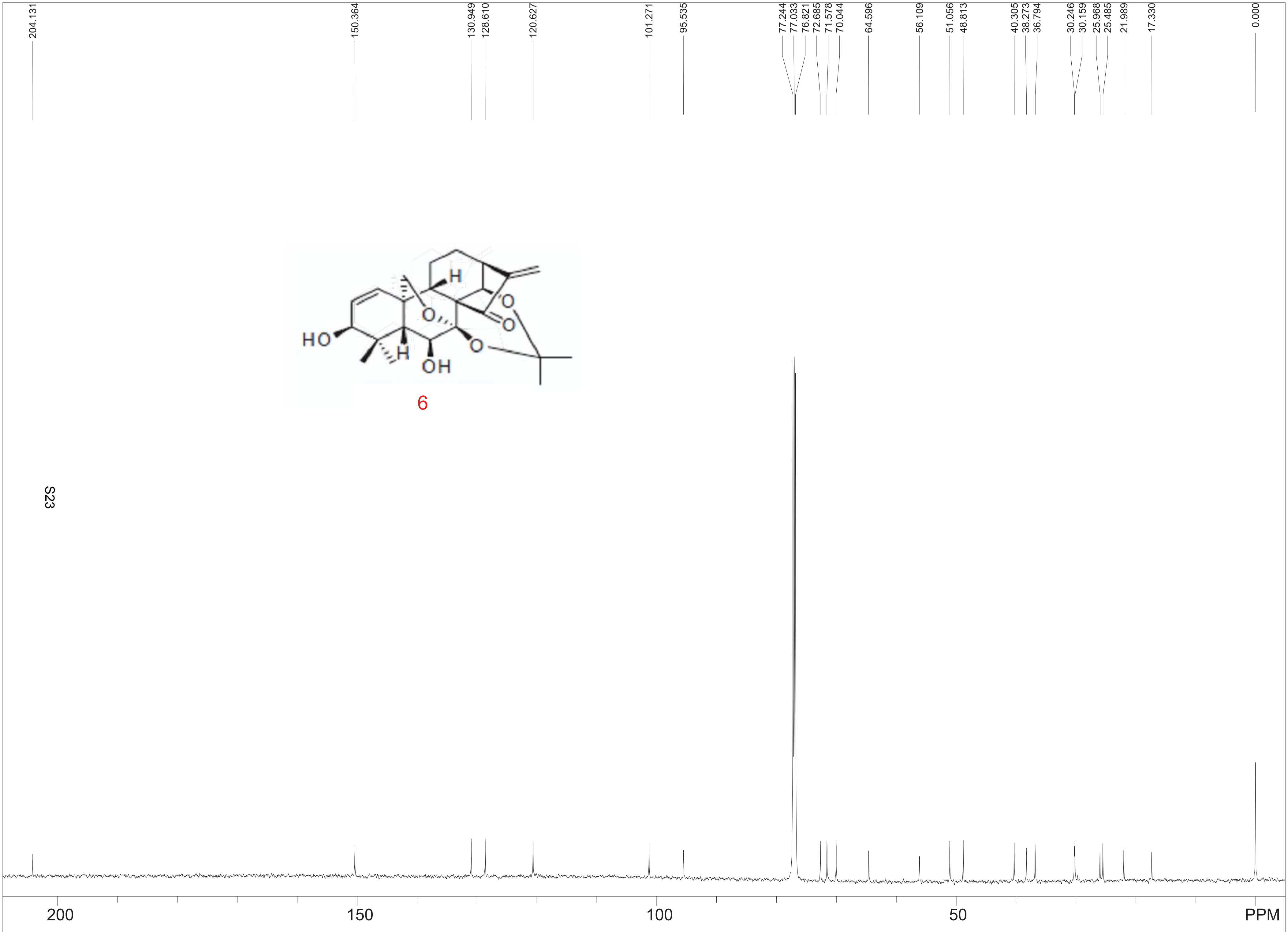

spect, CDCl3,
USER: zhou -- DATE: Thu Jul 19 17:05:41 2012
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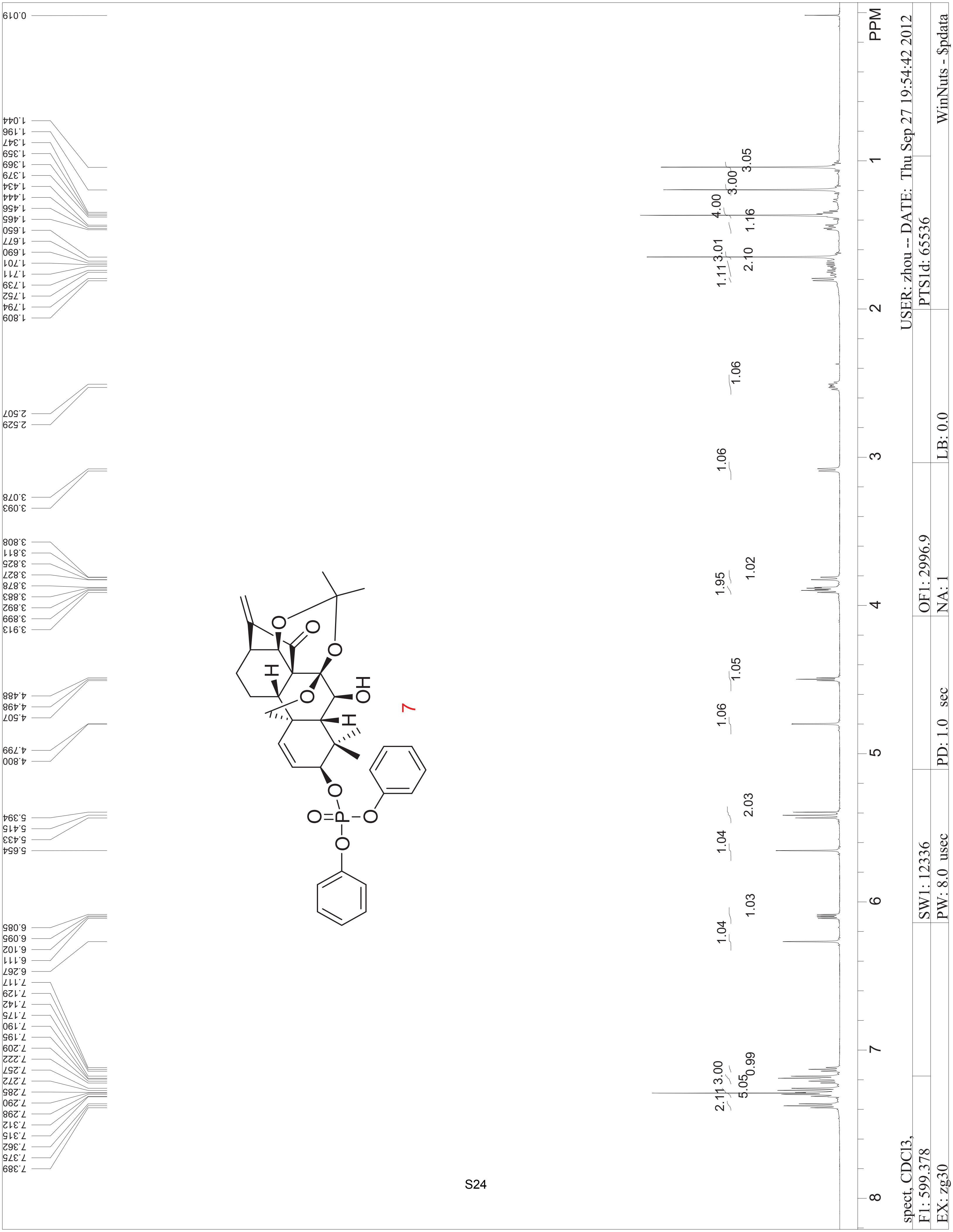
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USER: zhou -- DATE: Thu Sep 27 19:54:42 2012
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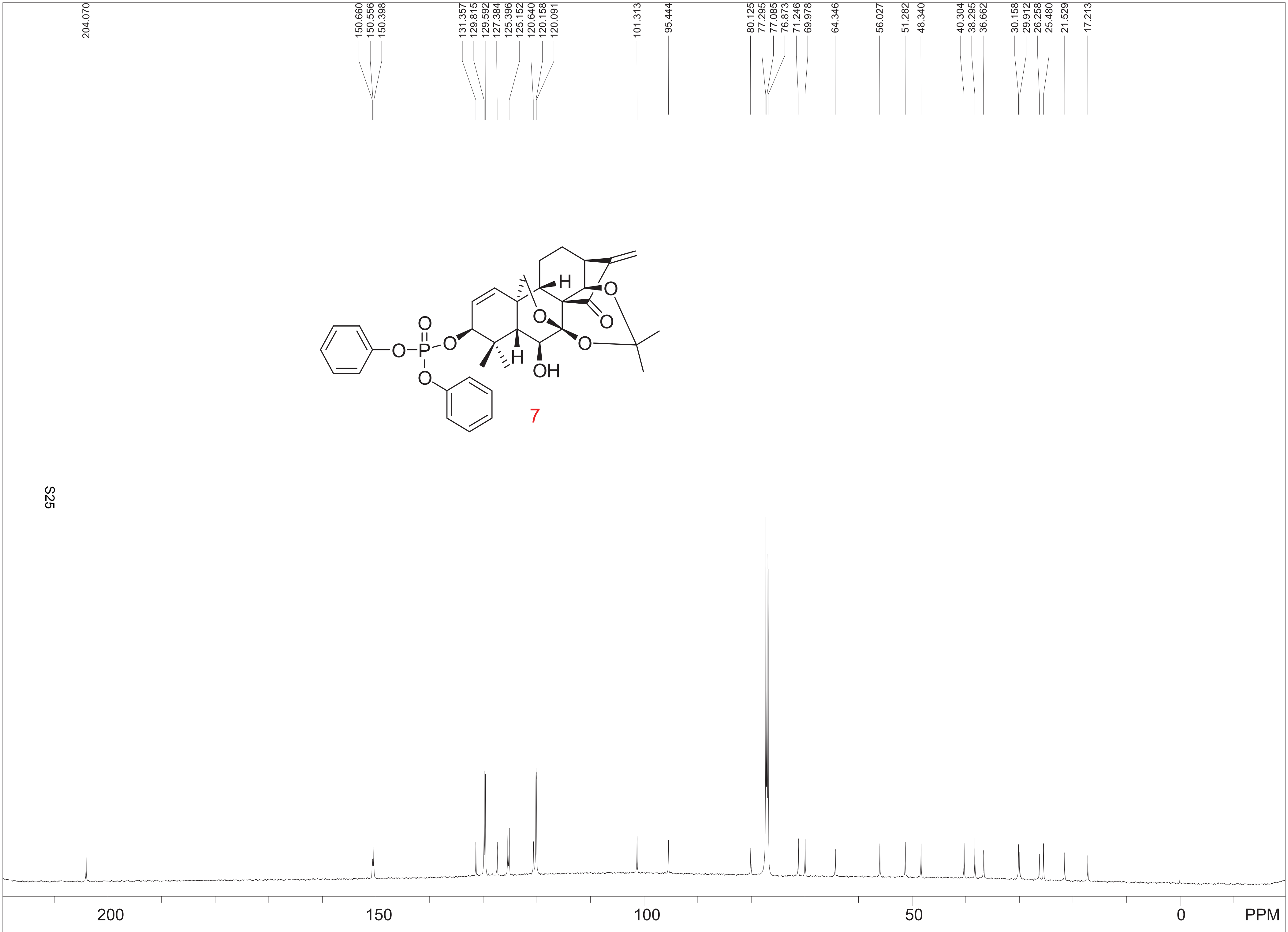
7



7

spect, CDCl3, USER: zhou -- DATE: Thu Sep 27 20:00:05 2012

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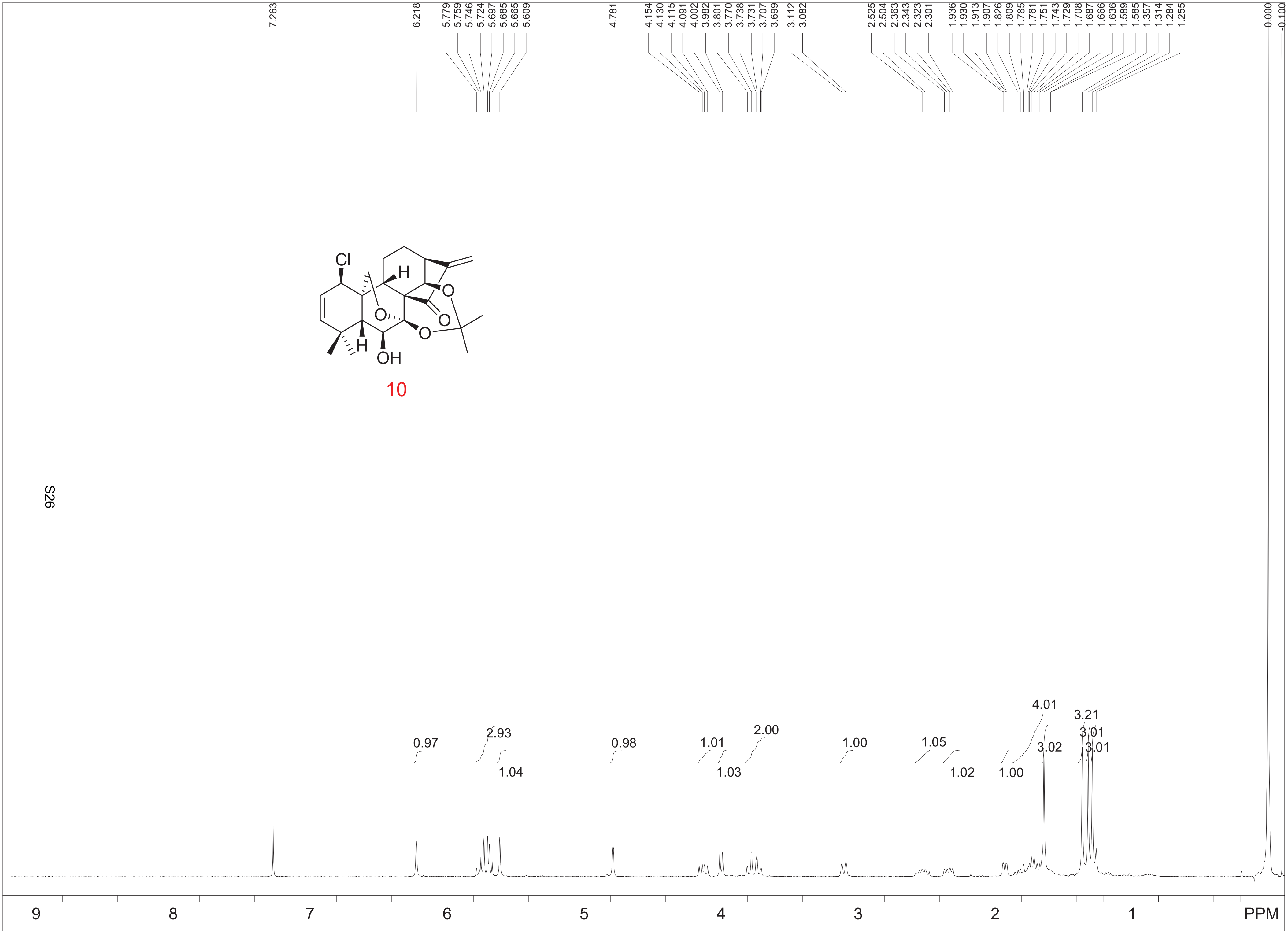

spect, CDCl3, USER: nmr -- DATE: Mon Nov 12 21:04:06 2012

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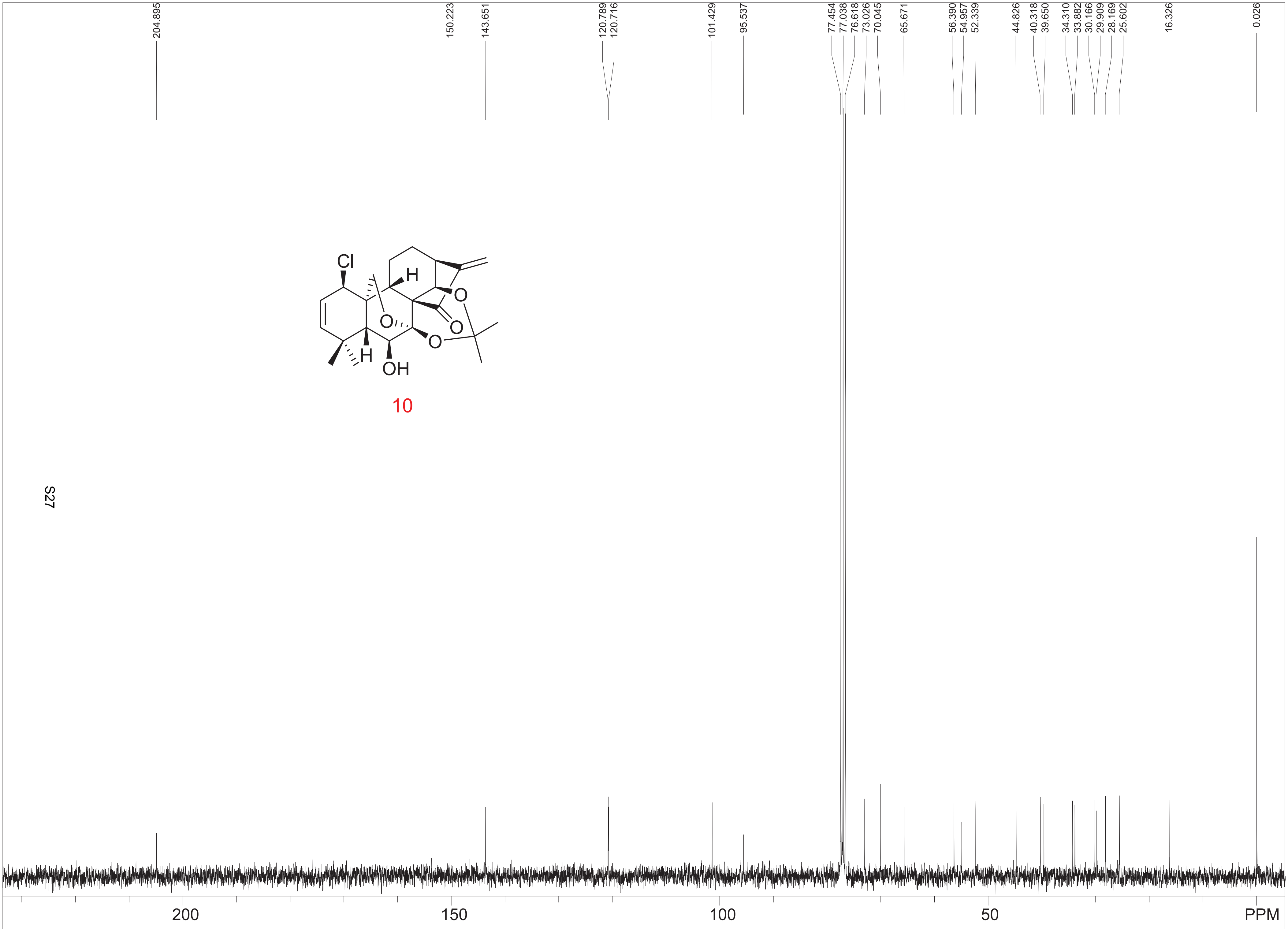

10

spect, CDCl3,
USER: nmr -- DATE: Mon Nov 12 21:08:15 2012

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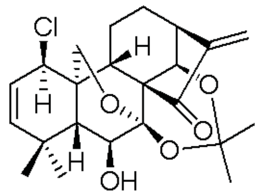

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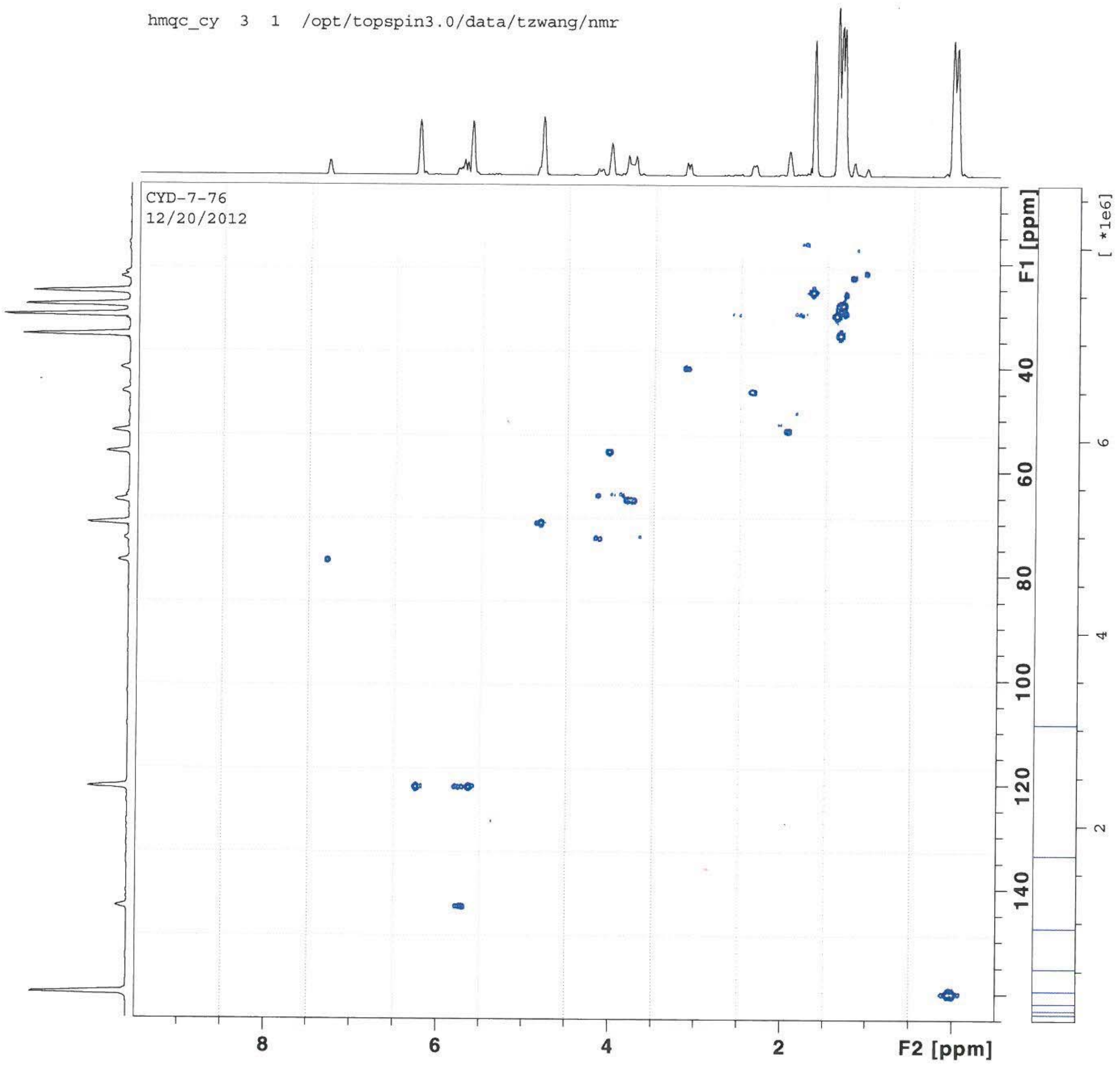
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12/20/2012
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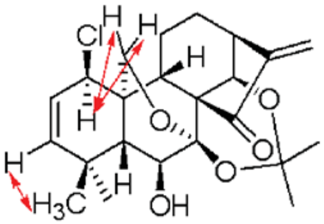
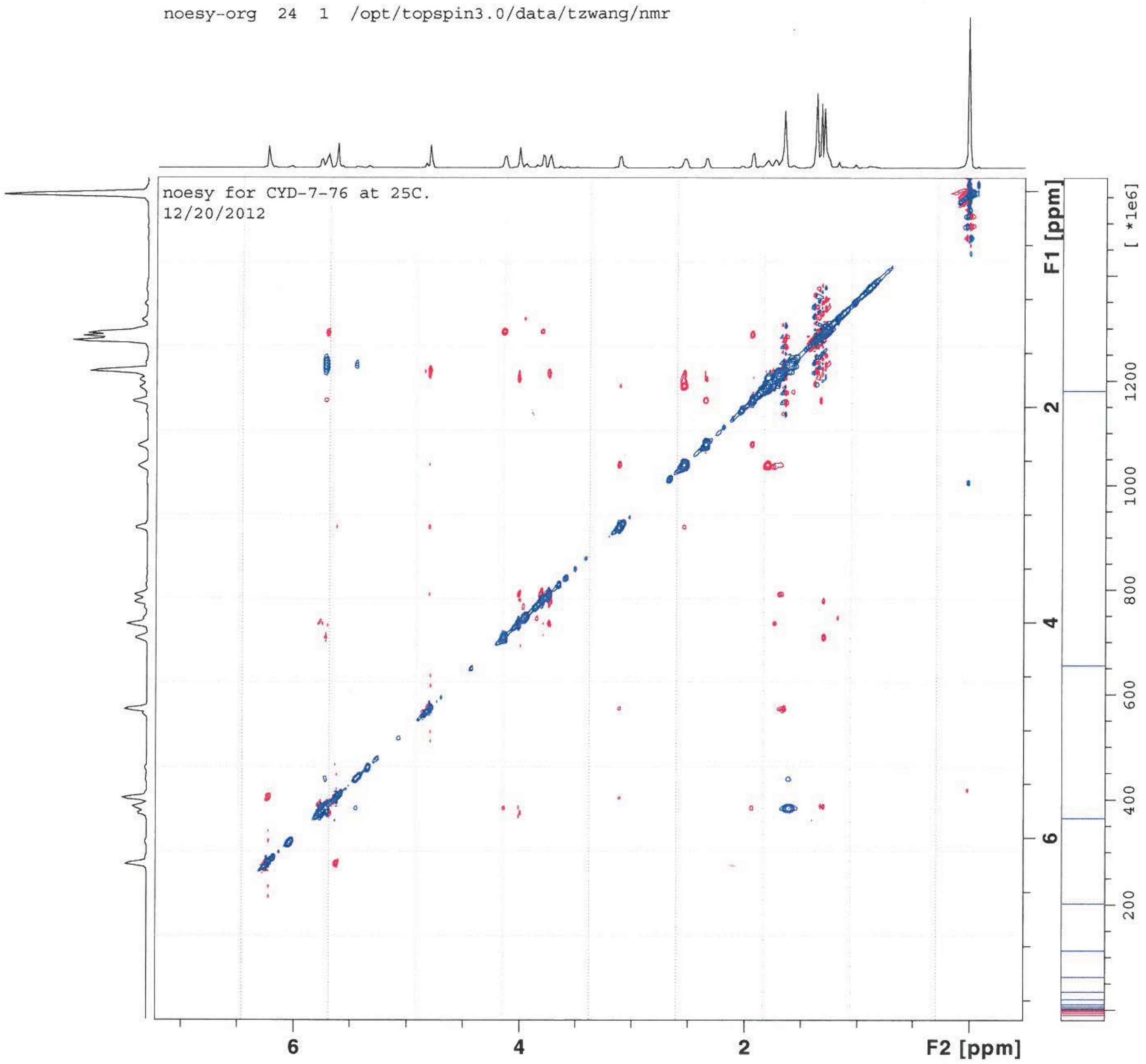


10, NOESY



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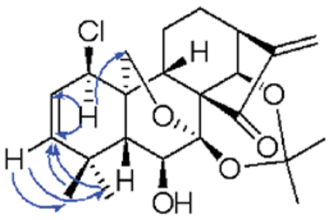
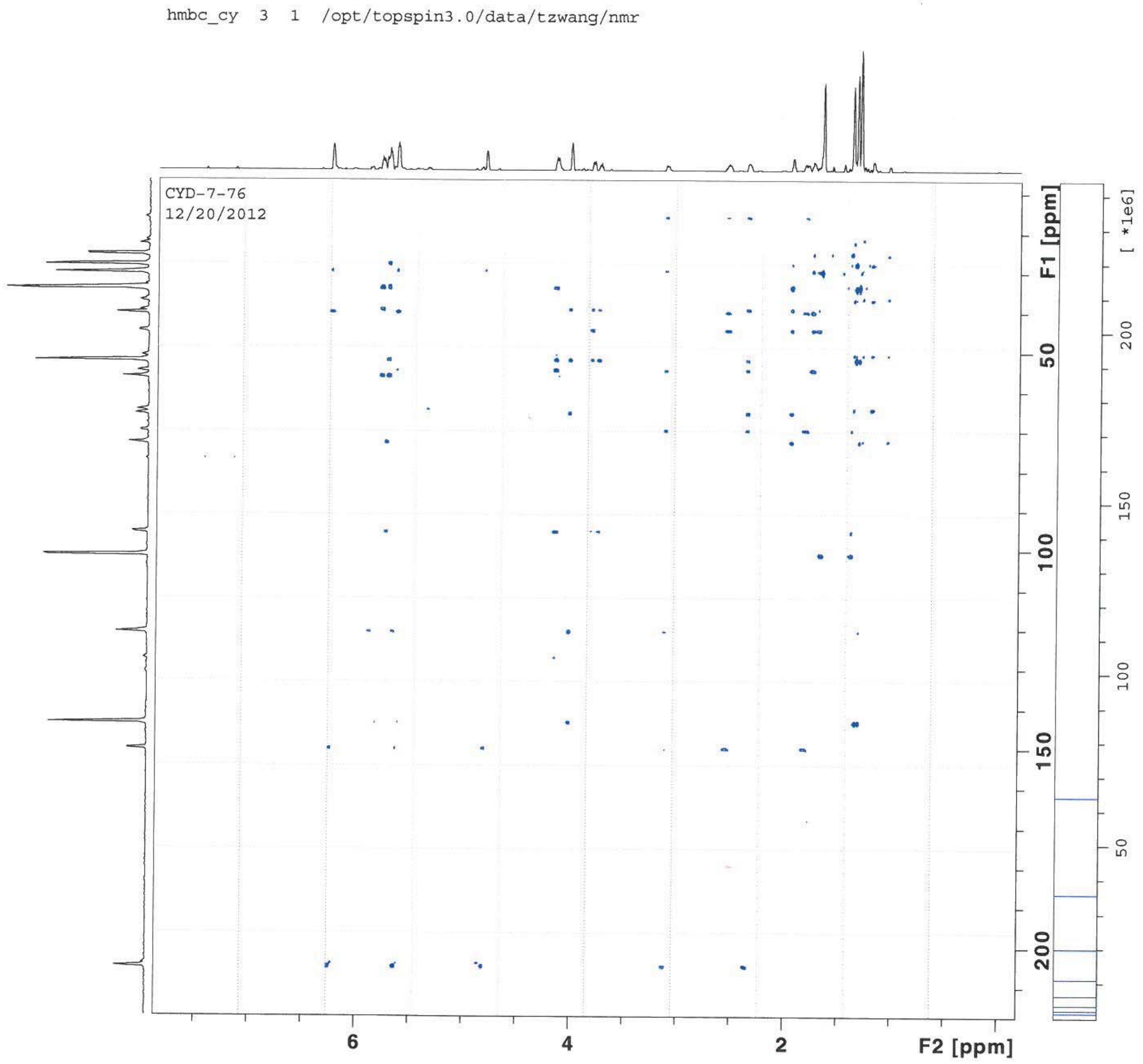
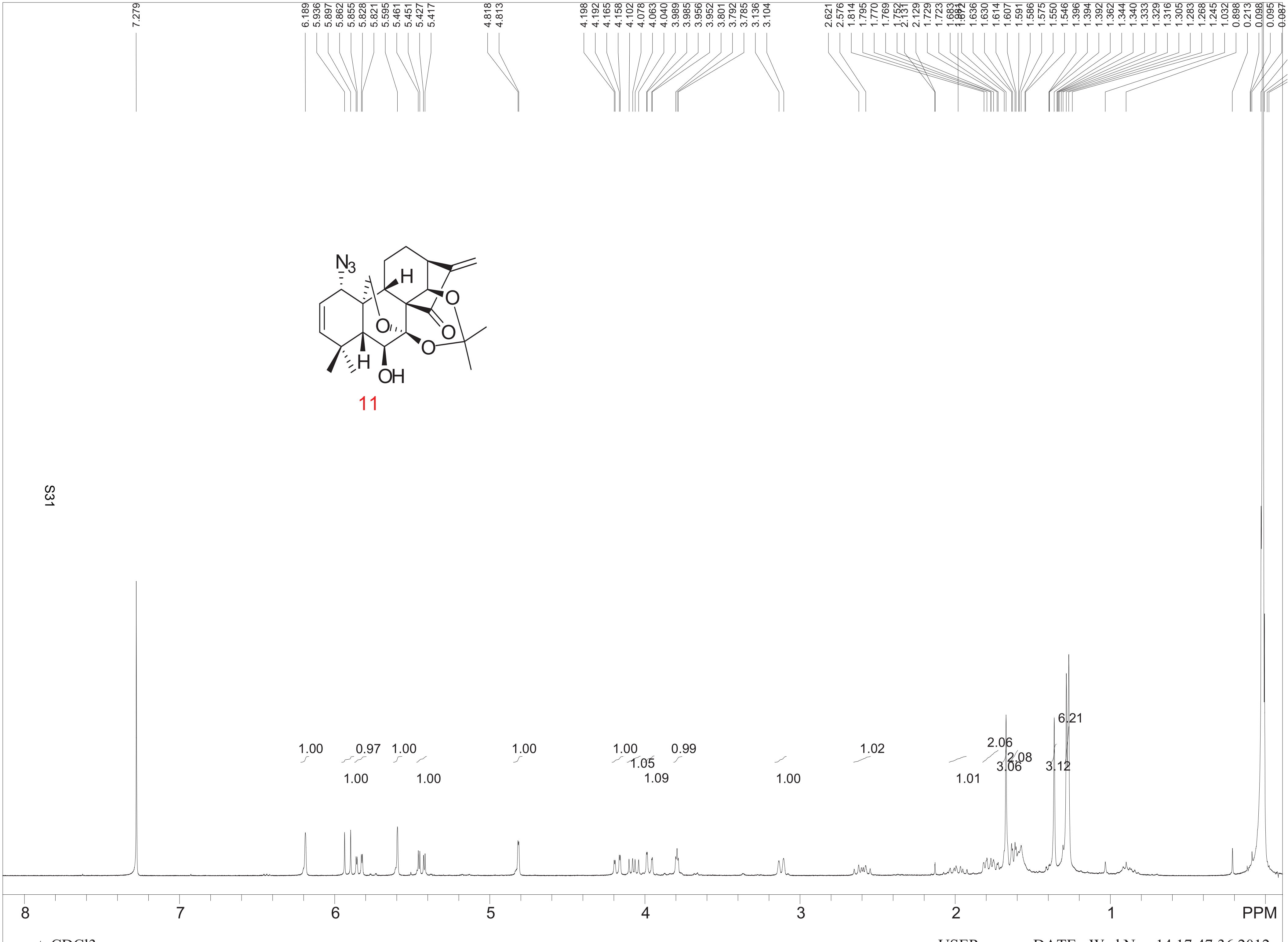
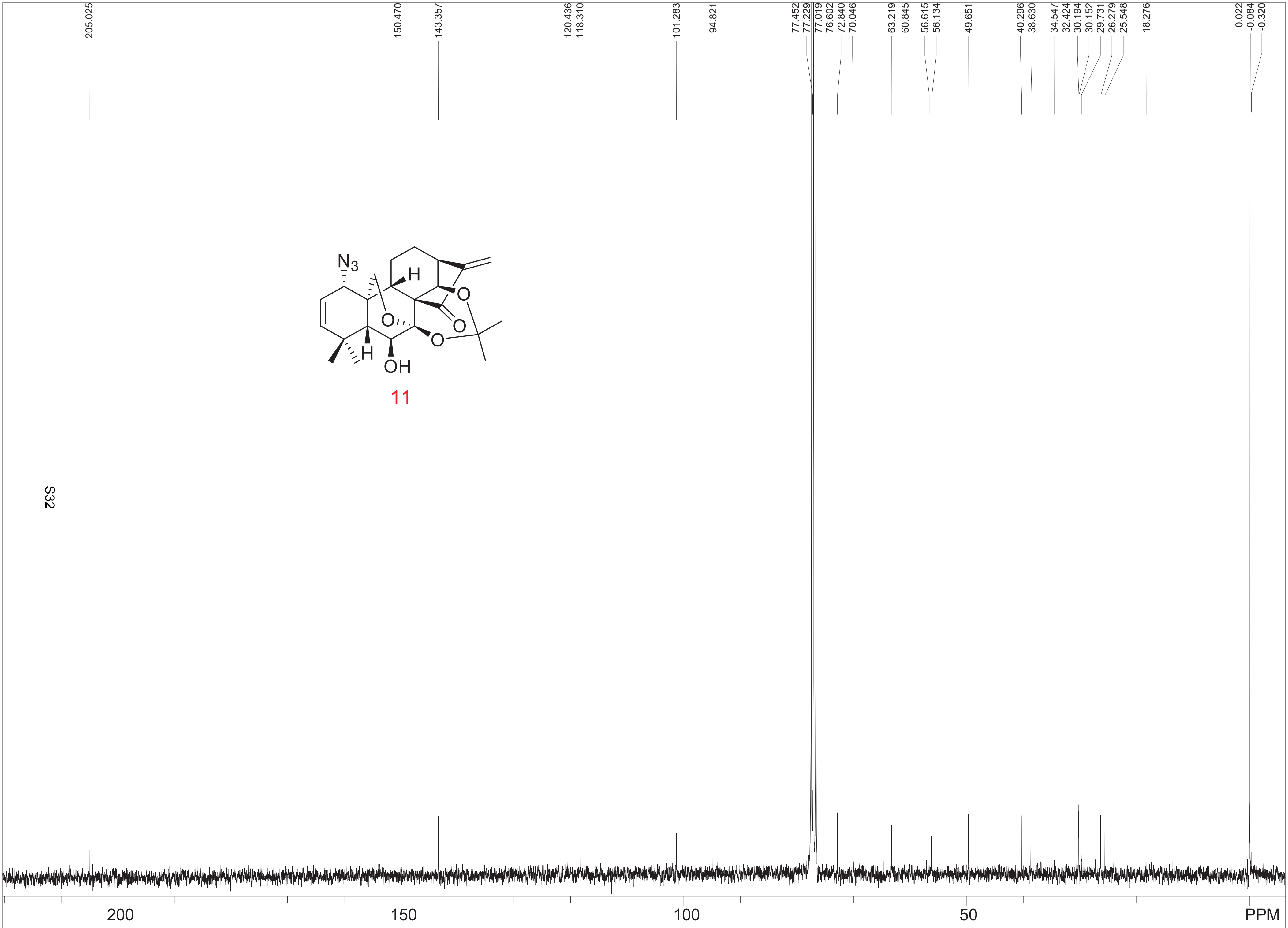


10, HMBC





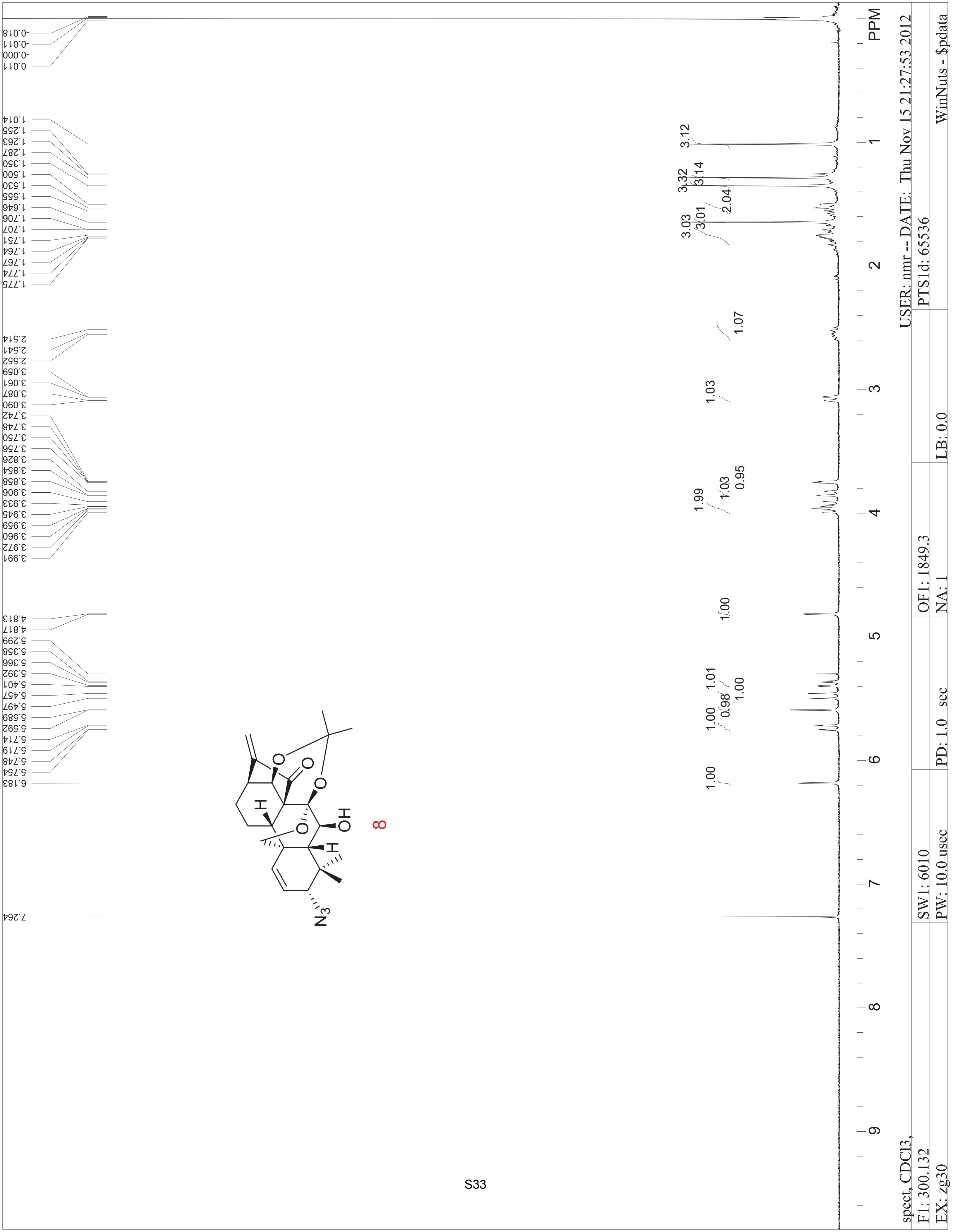
spect, CDCl3,					USER: nmr -- DATE: Wed Nov 14 17:47:36 2012
F1: 300.132	SW1: 6010		OF1: 1853.5		PTS1d: 65536
EX: zg30	PW: 10.0 usec	PD: 1.0 sec	NA: 64	LB: 0.0	WinNuts - $pdata



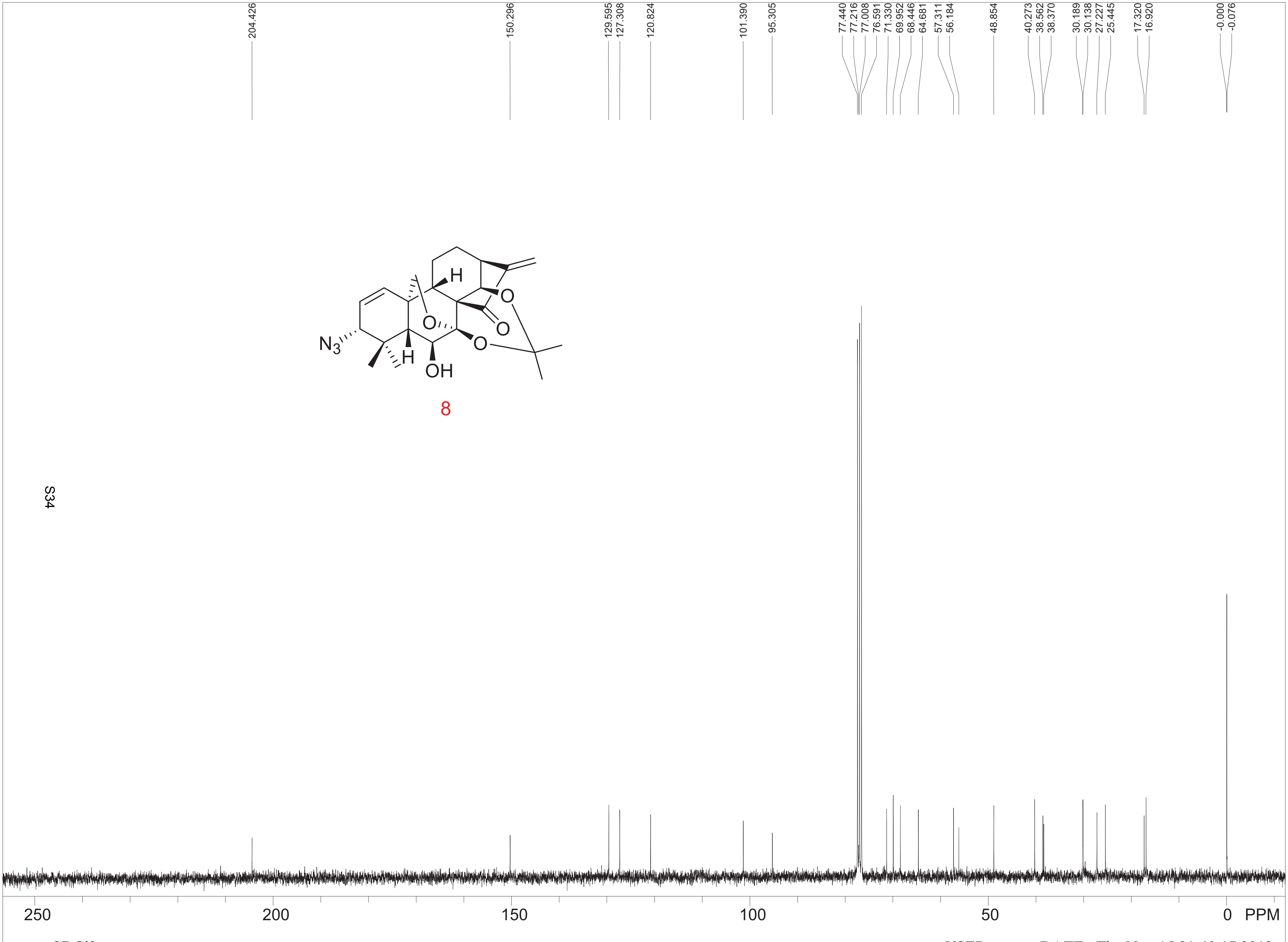
spect, CDCl3,

USER: nmr -- DATE: Wed Nov 14 18:49:05 2012

F1: 75.480	SW1: 29762		OF1: 12579.6		PTS1d: 32768
EX: zgpg30	PW: 8.0 usec	PD: 2.0 sec	NA: 2793	LB: 0.0	WinNuts - $pdata



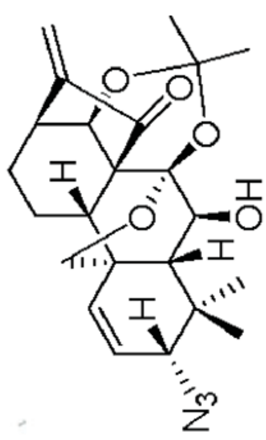
-0.018
-0.011
-0.000
0.011
1.014
1.255
1.263
1.287
1.350
1.500
1.530
1.555
1.646
1.706
1.707
1.751
1.764
1.767
1.774
1.775
2.514
2.541
2.552
3.059
3.061
3.087
3.090
3.742
3.748
3.750
3.756
3.826
3.854
3.858
3.906
3.933
3.945
3.959
3.960
3.972
3.991
4.813
4.817
5.299
5.358
5.366
5.392
5.401
5.457
5.497
5.589
5.592
5.714
5.719
5.748
5.754
6.183
7.264
3.12
3.32
3.14
2.04
3.03
3.01
1.07
1.03
1.99
1.03
0.95
1.00
1.01
1.00
0.98
1.00
1.00
O
O
O
O
H
OH
H
N3
8
PPM
1
2
3
4
5
6
7
8
9
USER: nmr -- DATE: Thu Nov 15 21:27:53 2012
PTS1d: 65536
OF1: 1849.3
SW1: 6010
spect, CDCl3,
F1: 300.132
LB: 0.0
NA: 1
PD: 1.0 sec
PW: 10.0 usec
EX: zg30
WinNuts - $pdata



8

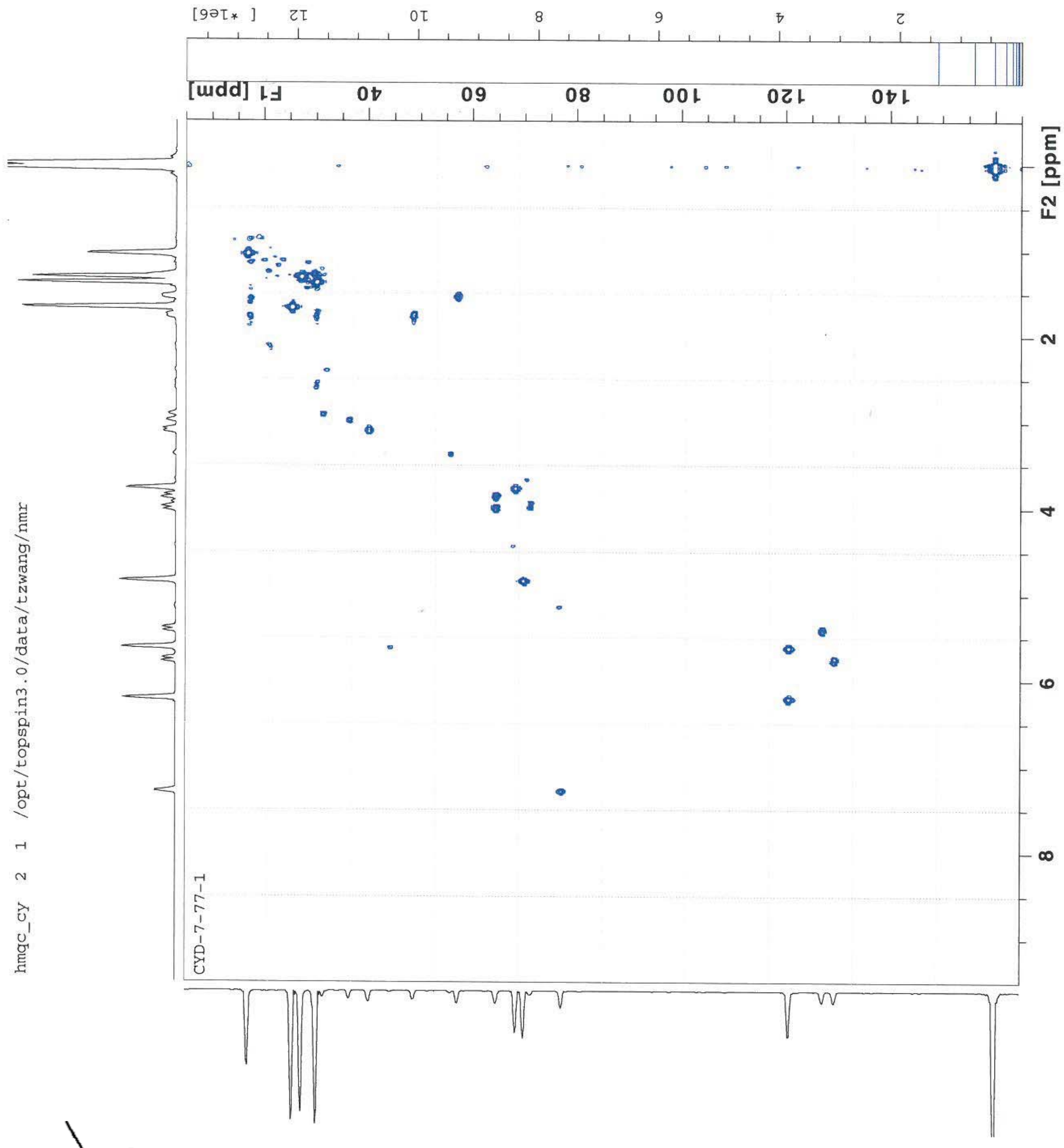
spect, CDCl3, USER: nmr -- DATE: Thu Nov 15 21:40:17 2012

F1: 75.480	SW1: 29762		OF1: 12577.8		PTS1d: 32768	
EX: zgpg30	PW: 8.0 usec	PD: 2.0 sec	NA: 407	LB: 0.0		WinNuts - $pdata

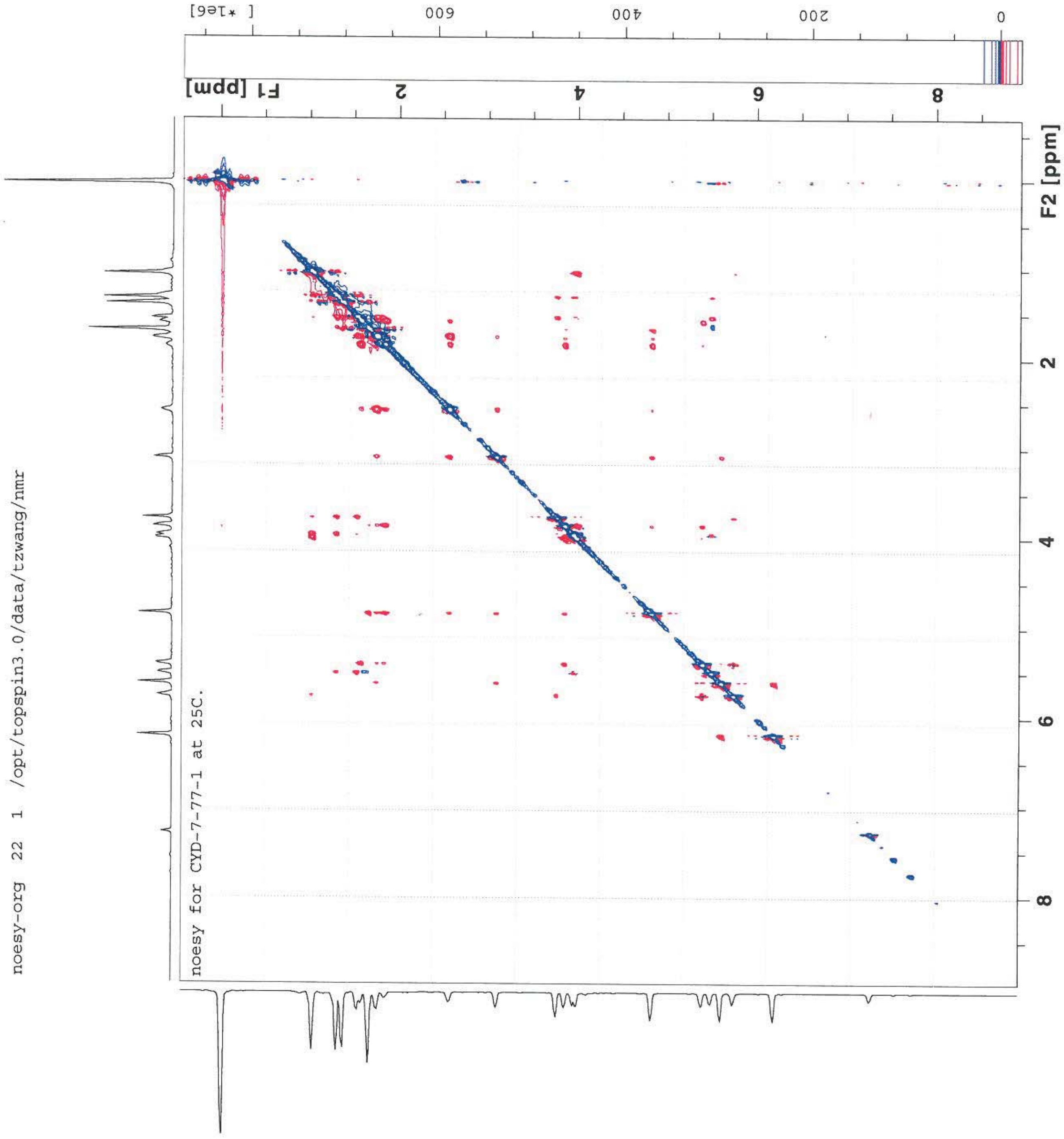


N3
H
H
OH
O
O
O
O

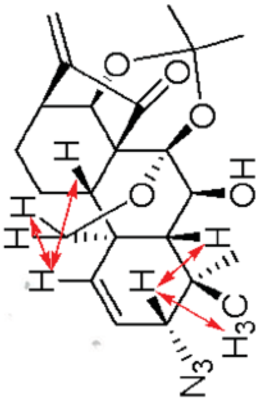
8, HMQC



hmqc_cy 2 1 /opt/topspin3.0/data/tzwang/nmr
CYD-7-77-1
F1 [ppm]
40
60
80
100
120
140
F2 [ppm]
2
4
6
8
[*1e6]
12
10
8
6
4
2

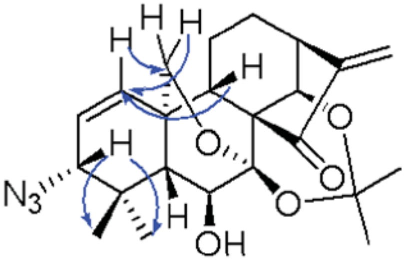


noesy-org 22 1 /opt/topspin3.0/data/tzwang/nmr
noesy for CYD-7-77-1 at 25C.
F1 [ppm]
2
4
6
8
F2 [ppm]
2
4
6
8
[*1e6]
600
400
200
0

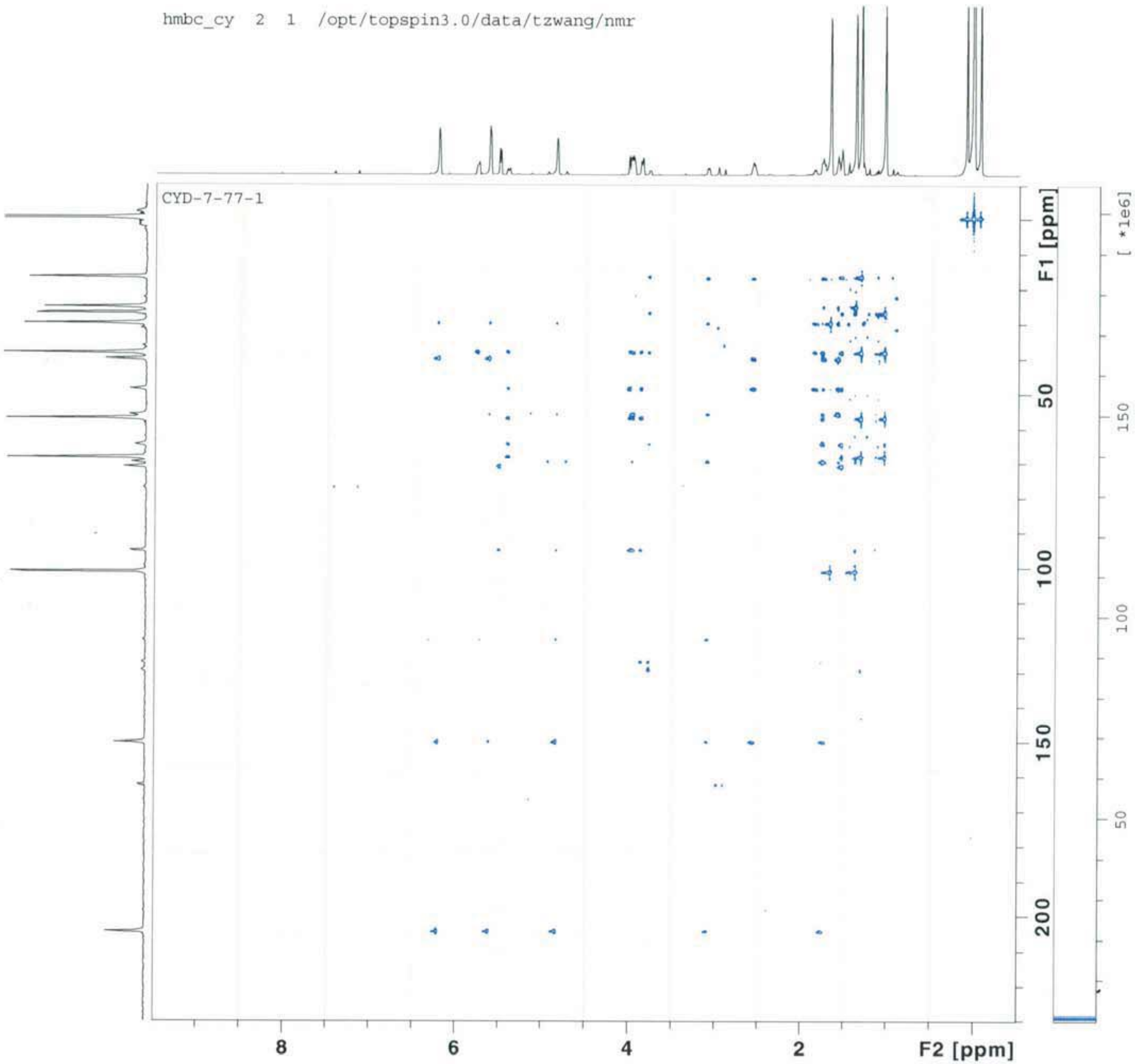


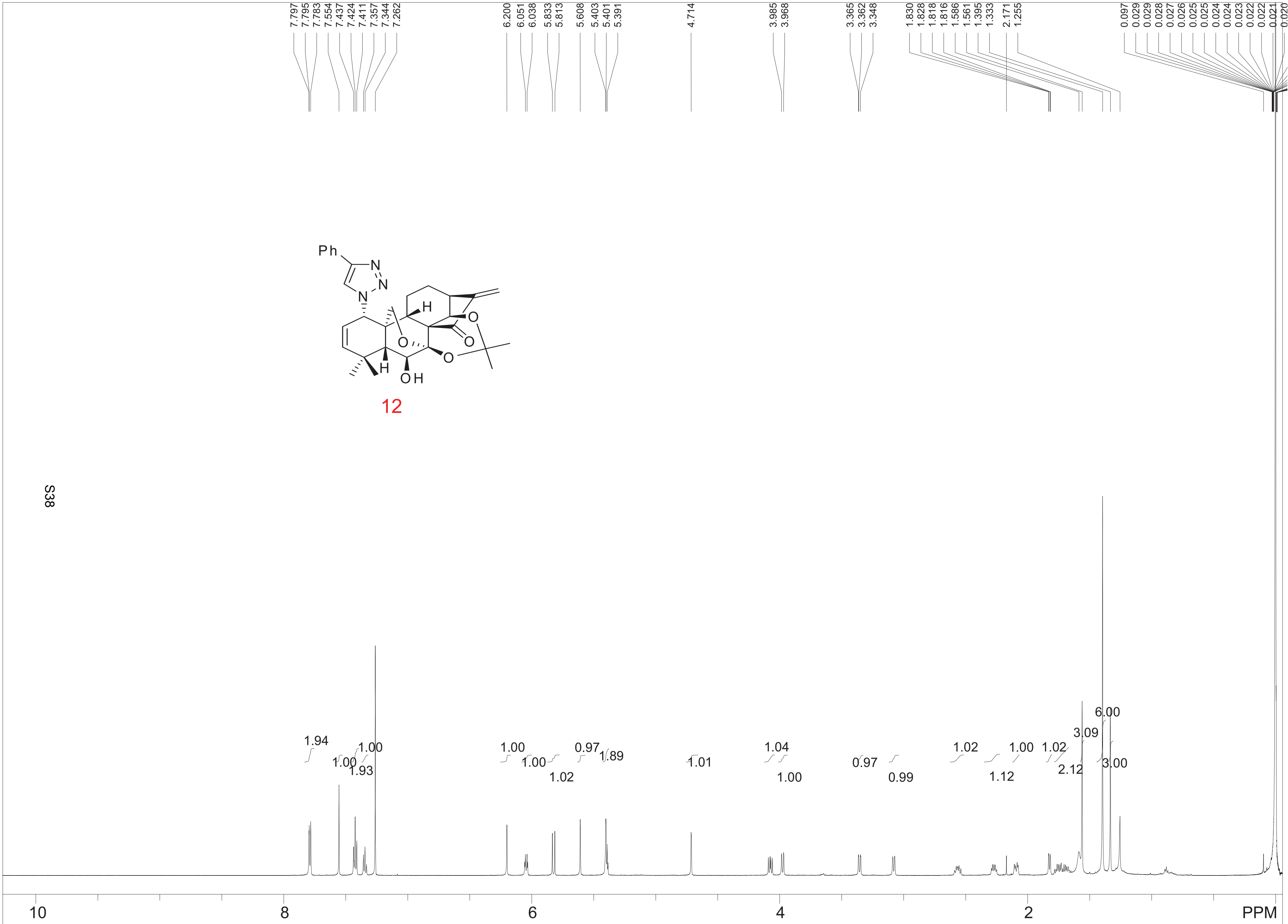
H
H
H
H
O
O
O
OH
H
H
H3C
N3

8, NOESY



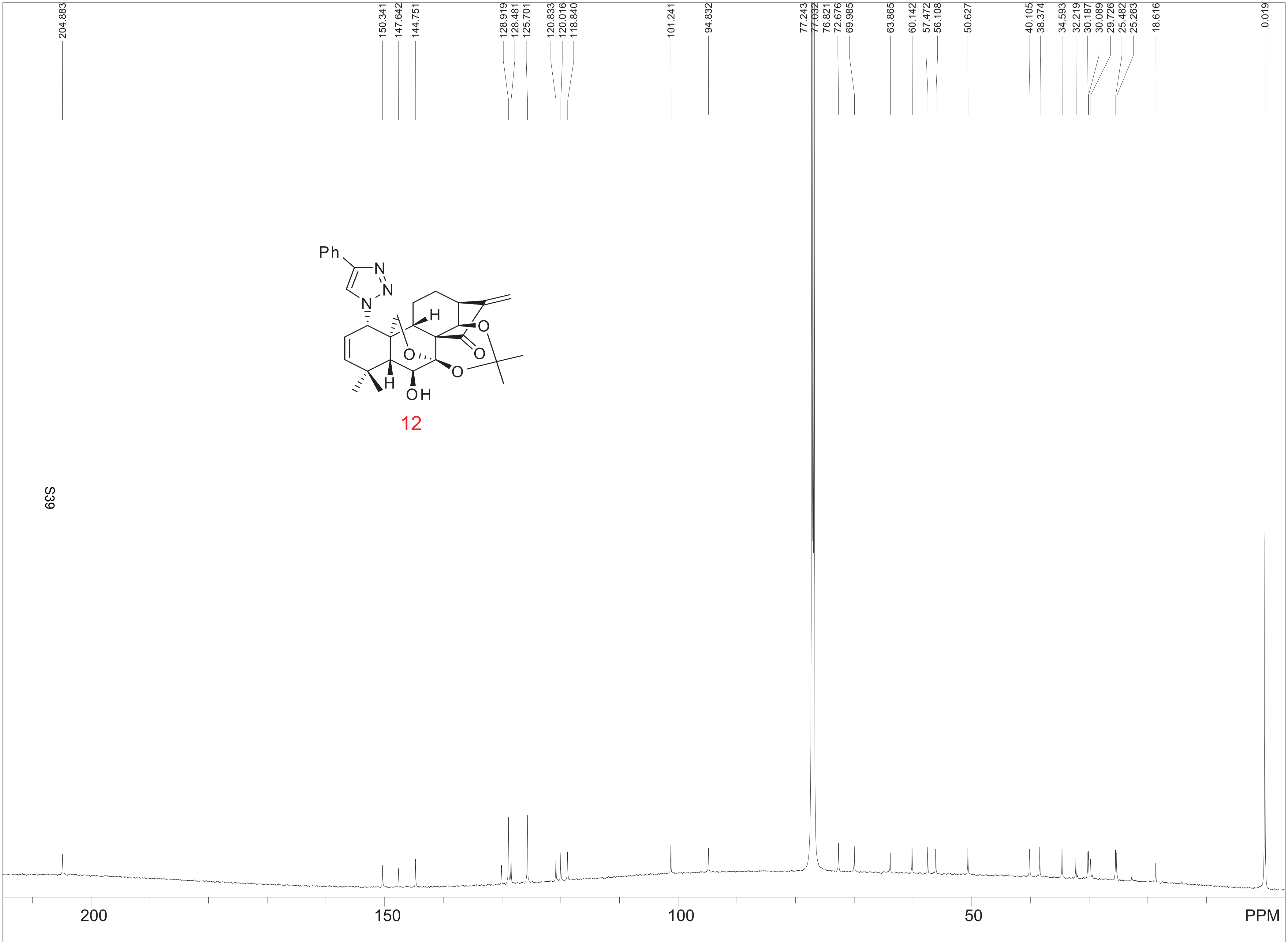
8, HMBC


hmbc_cy 2 1 /opt/topspin3.0/data/tzwang/nmr
CYD-7-77-1
F1 [ppm]
50
100
150
200
F2 [ppm]
8
6
4
2
[*1e6]
150
100
50

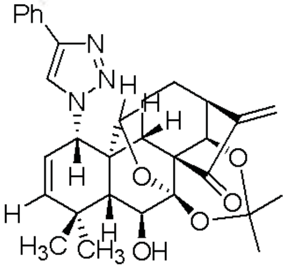


spect, CDCl3, USER: zhou -- DATE: Thu Dec 06 20:50:02 2012

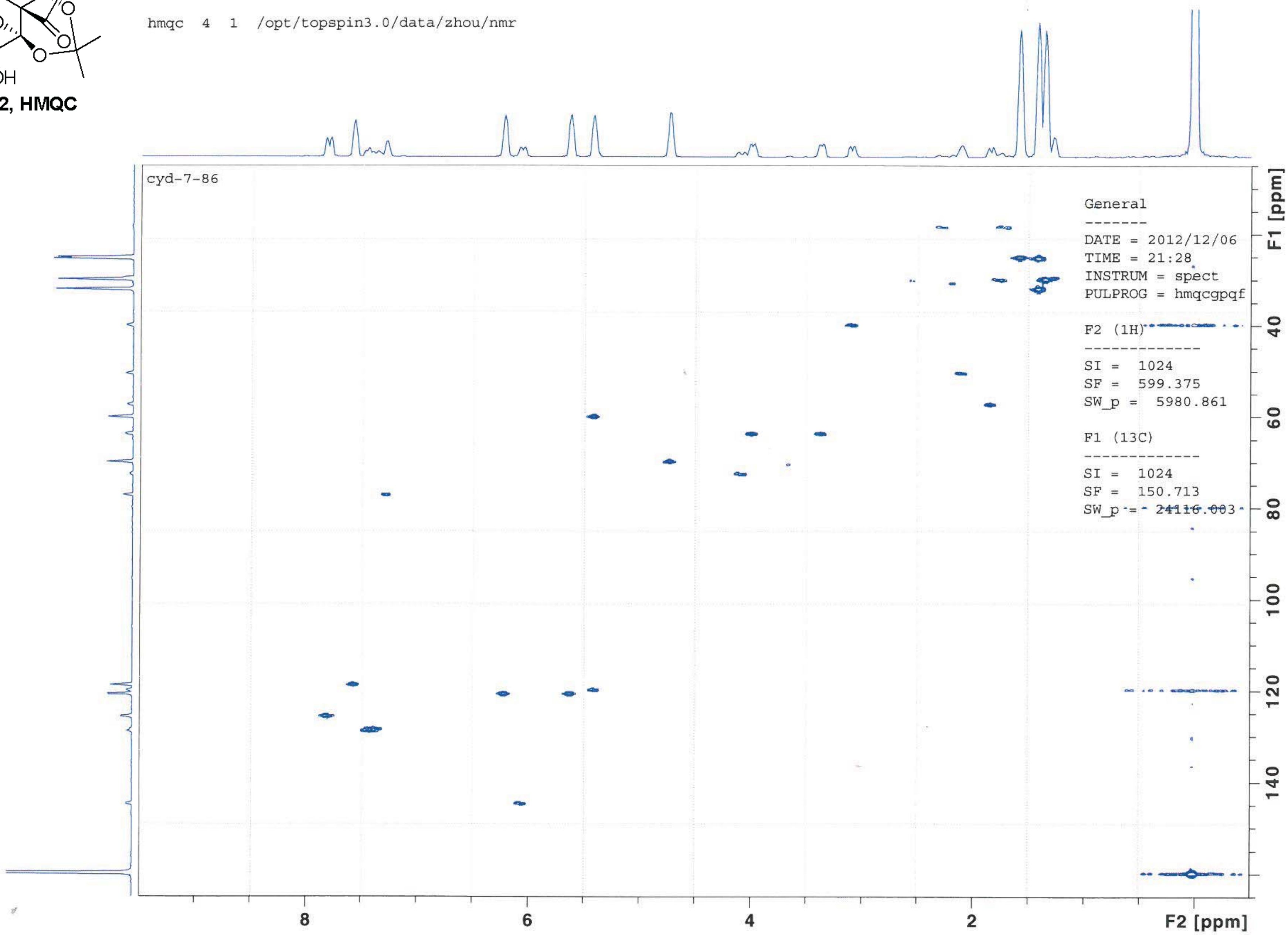
F1: 599.378		SW1: 12336		OF1: 2979.9		PTS1d: 65536	
EX: zg30		PW: 8.0 usec	PD: 1.0 sec	NA: 1	LB: 0.0		WinNuts - $pdata



spect, CDCl3,				USER: zhou -- DATE: Fri Dec 07 12:49:45 2012
F1: 150.728	SW1: 36058		OF1: 15071.4	PTS1d: 32768
EX: zgig30	PW: 12.0 usec	PD: 1.5 sec	NA: 4000	LB: 0.0	WinNuts - $pdata



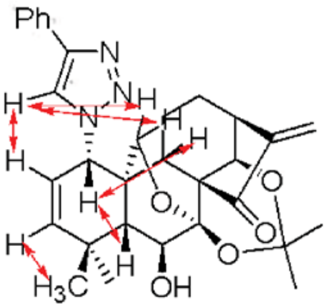
12, HMQC


hmqc 4 1 /opt/topspin3.0/data/zhou/nmr
cyd-7-86
General

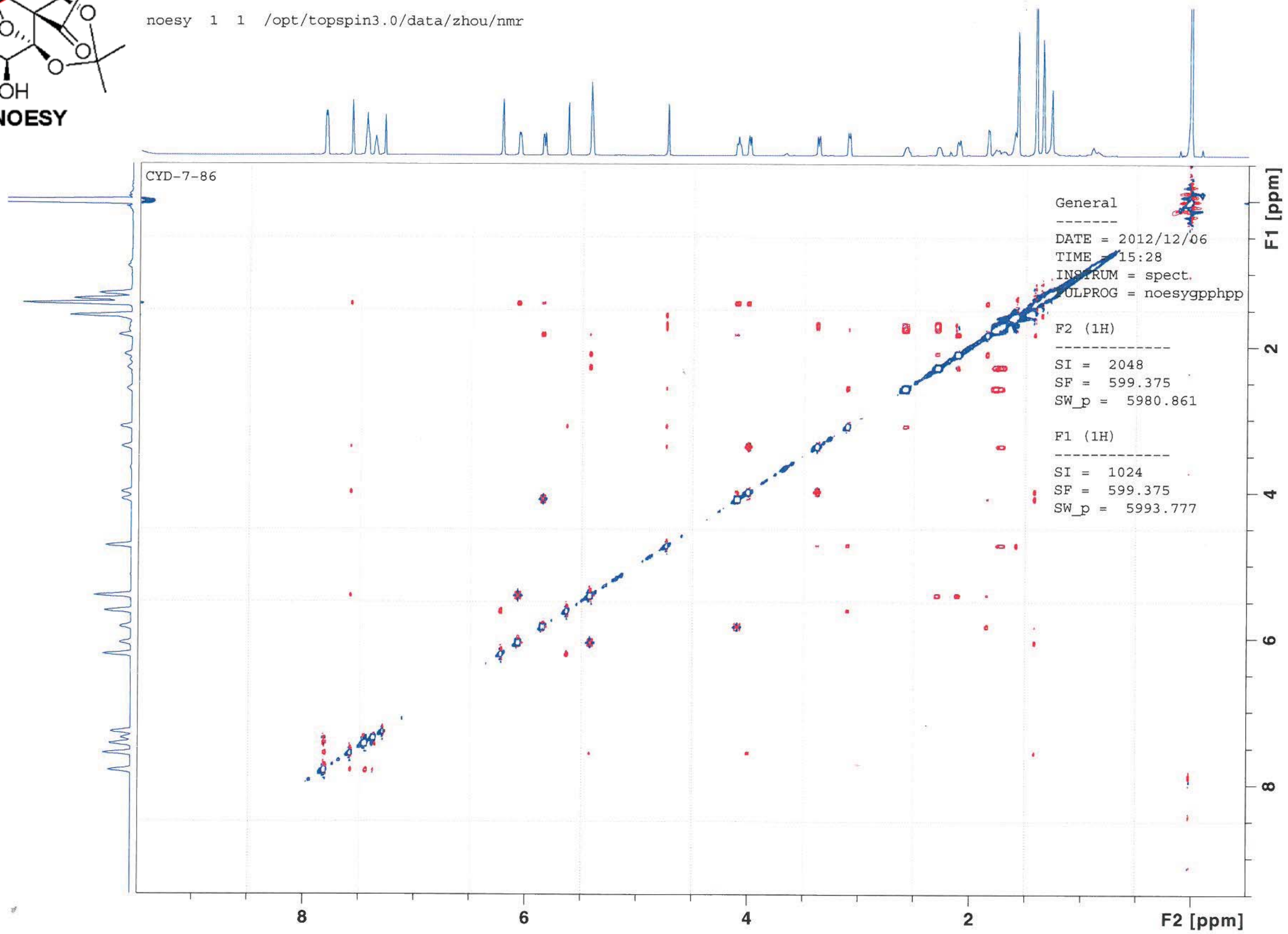
DATE = 2012/12/06
TIME = 21:28
INSTRUM = spect
PULPROG = hmqcgpqf
F2 (1H)

SI = 1024
SF = 599.375
SW_p = 5980.861
F1 (13C)

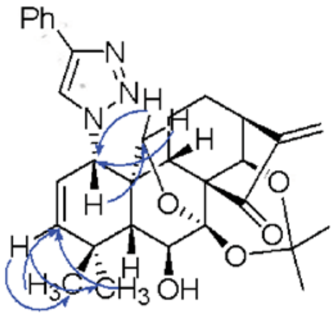
SI = 1024
SF = 150.713
SW_p = 24116.003
F1 [ppm]
40
60
80
100
120
140
8
6
4
2
F2 [ppm]



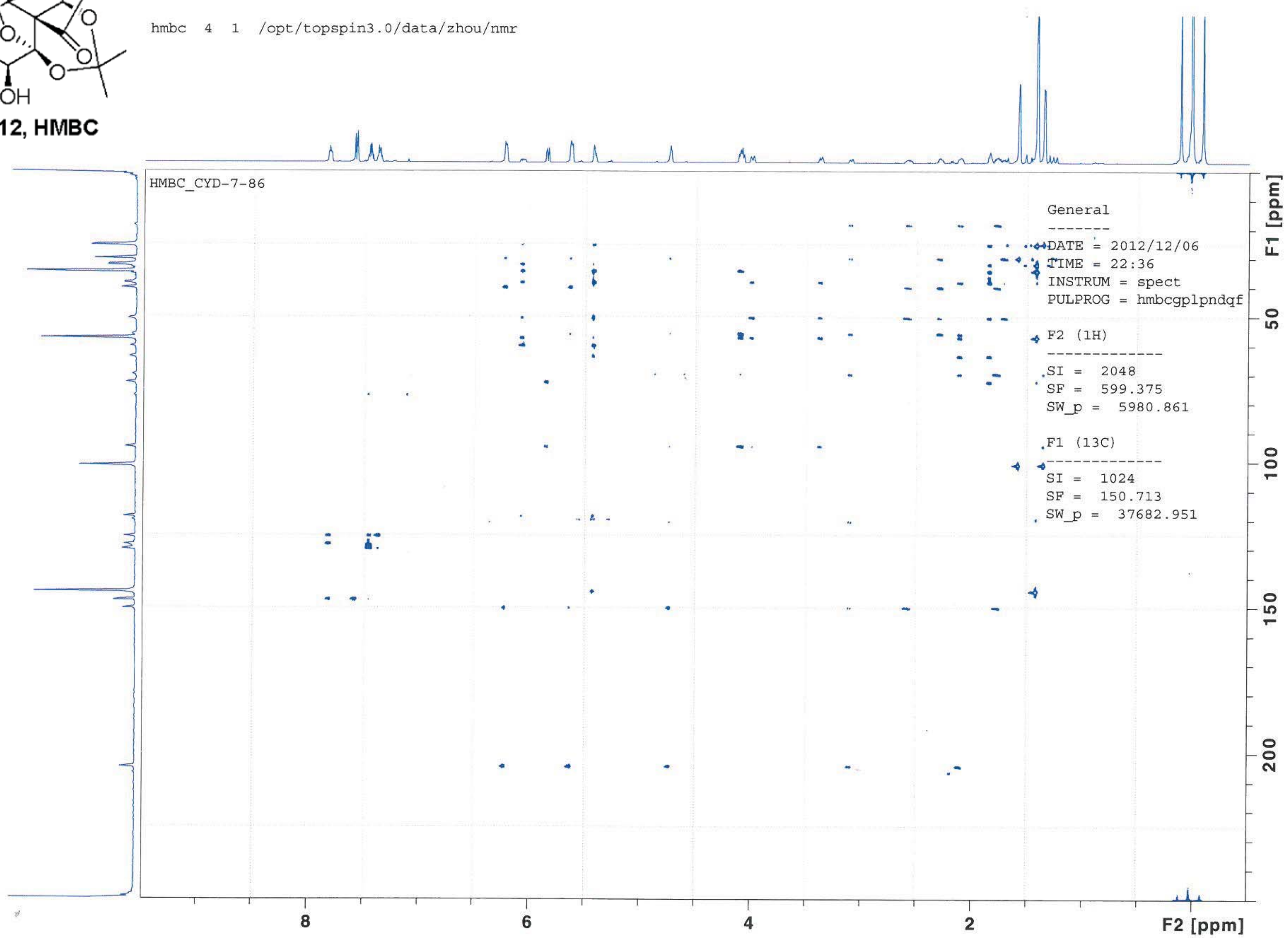
12, NOESY


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

```
General
-------
DATE = 2012/12/06
TIME = 15:28
INSTRUM = spect.
PULPROG = noesygpphpp

F2 (1H)
-------------
SI =   2048
SF =   599.375
SW_p =   5980.861

F1 (1H)
-------------
SI =   1024
SF =   599.375
SW_p =   5993.777
```


Ph
N
NH
N
H
H
H
O
O
O
O
H
H
H₃C
CH₃
OH

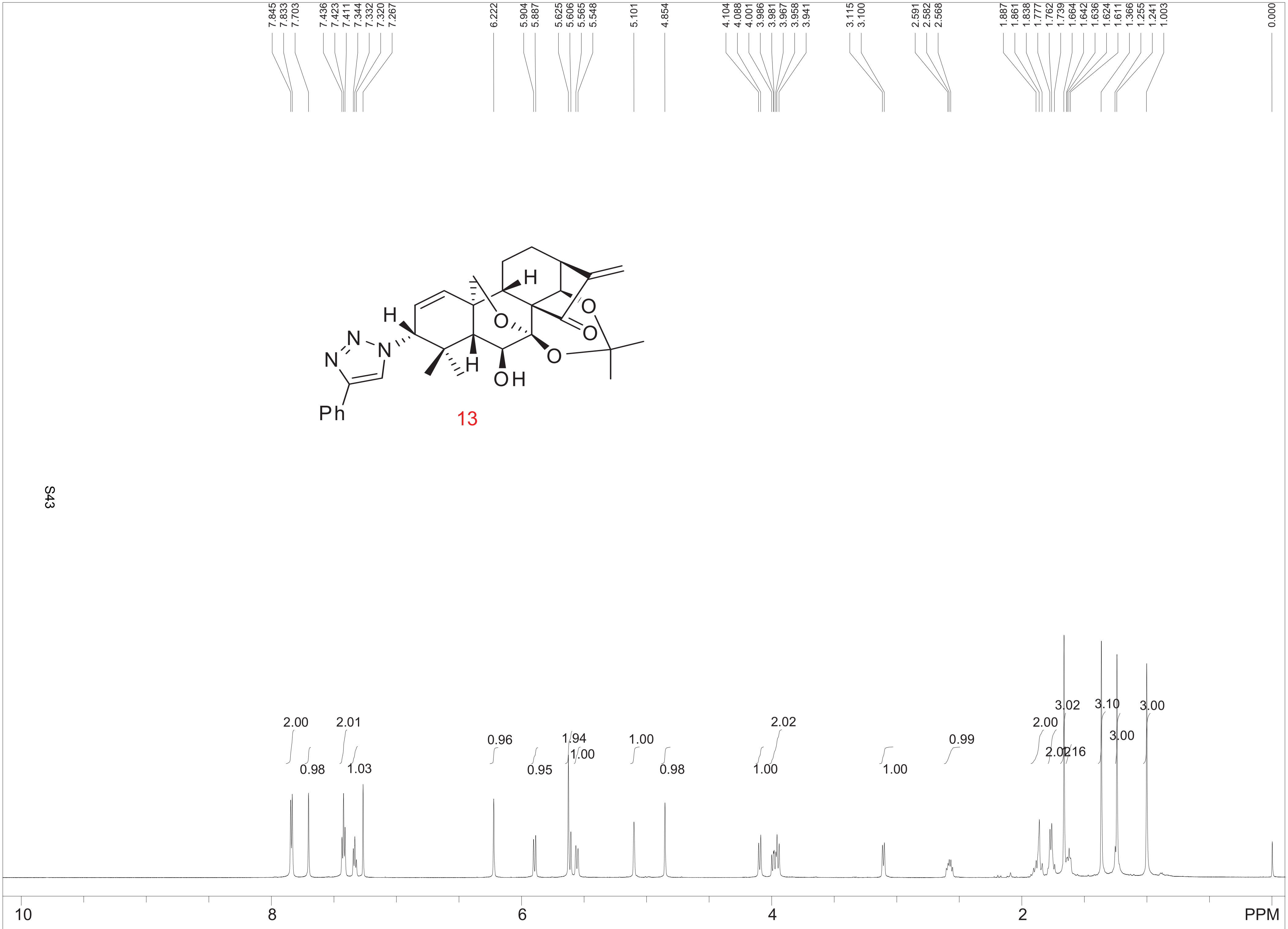
12, HMBC


hmbc 4 1 /opt/topspin3.0/data/zhou/nmr
HMBC_CYD-7-86
General

DATE = 2012/12/06
TIME = 22:36
INSTRUM = spect
PULPROG = hmbcgplpndqf
F2 (1H)

SI = 2048
SF = 599.375
SW_p = 5980.861
F1 (13C)

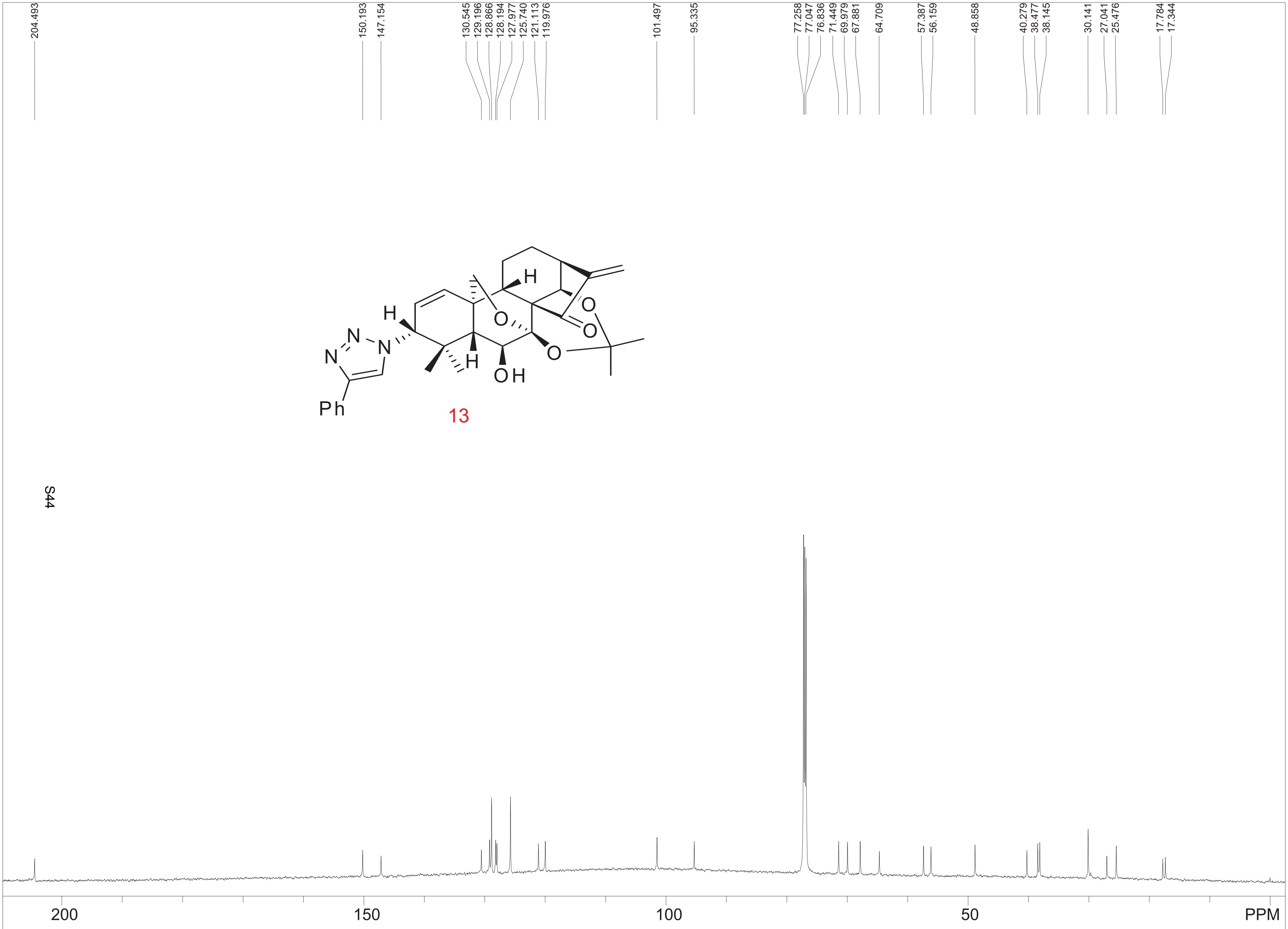
SI = 1024
SF = 150.713
SW_p = 37682.951
F1 [ppm]
50
100
150
200
8
6
4
2
F2 [ppm]



13

spect, CDCl3,
USER: zhou -- DATE: Wed Nov 21 21:00:58 2012

F1: 599.378	SW1: 12336		OF1: 2983.9		PTS1d: 65536
EX: zg30	PW: 8.0 usec	PD: 1.0 sec	NA: 1	LB: 0.0	WinNuts - $pdata

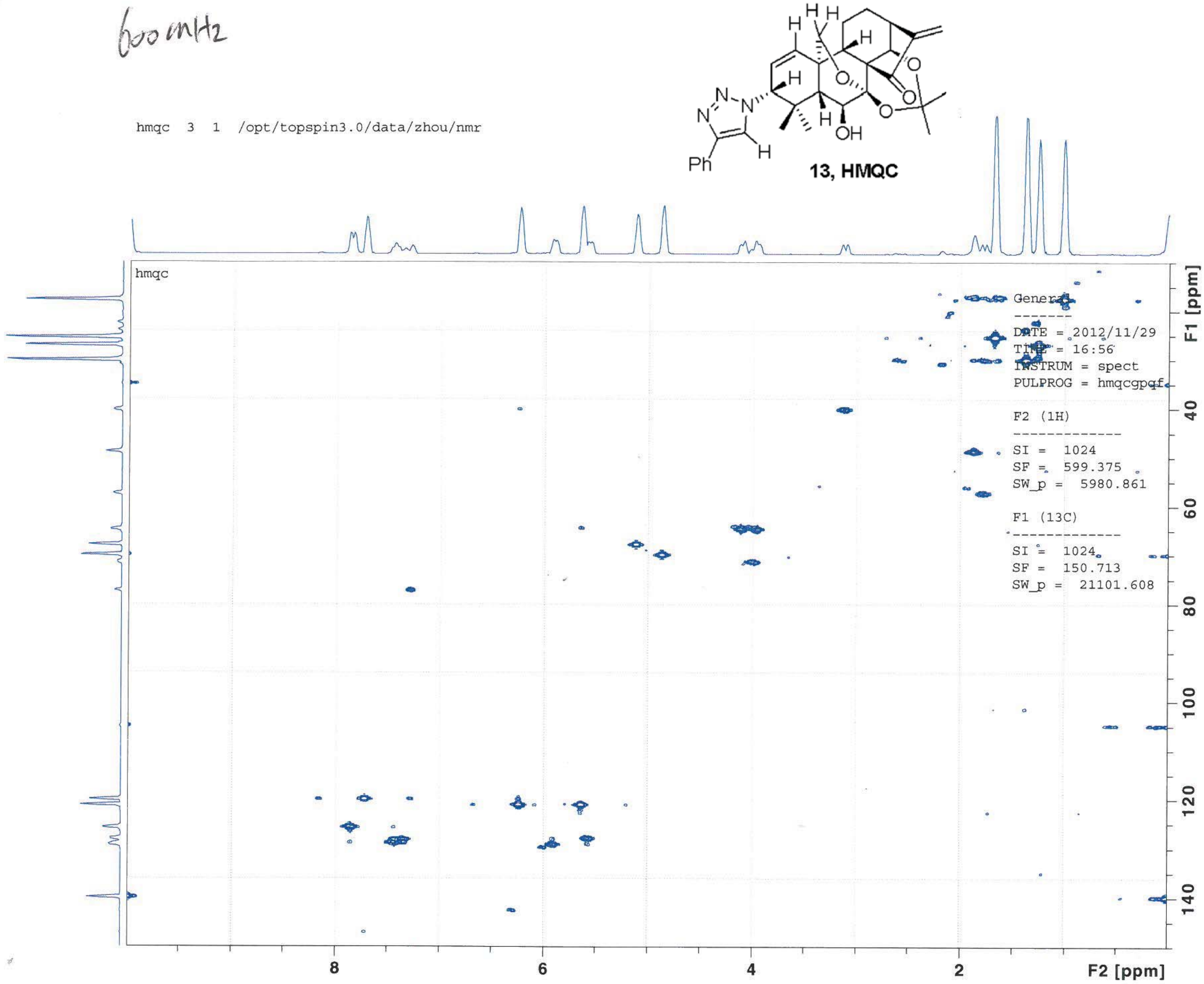


13

spect, CDCl3,				USER: zhou -- DATE: Wed Nov 21 21:04:30 2012	
F1: 150.728	SW1: 36058		OF1: 15074.2	PTS1d: 32768	
EX: zgig30	PW: 12.0 usec	PD: 1.5 sec	NA: 236	LB: 0.0	WinNuts - $pdata

600 mHz

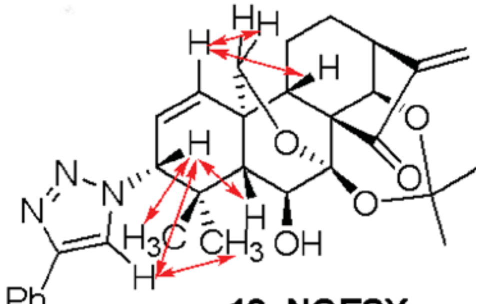
hmqc 3 1 /opt/topspin3.0/data/zhou/nmr


13, HMQC

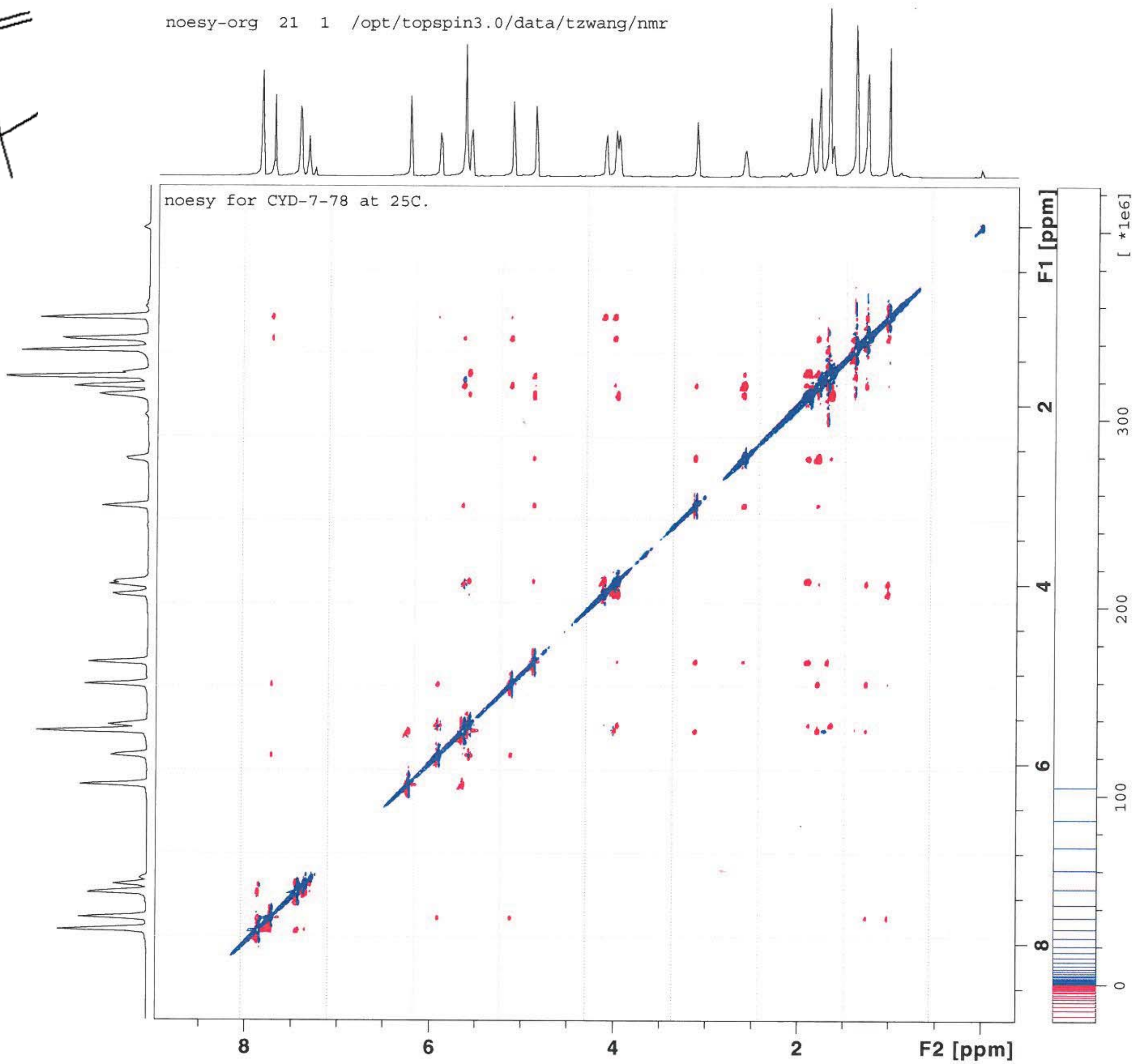
```
General
-------
DATE = 2012/11/29
TIME = 16:56
INSTRUM = spect
PULPROG = hmqcgpqf

F2 (1H)
-------------
SI =   1024
SF =   599.375
SW_p =   5980.861

F1 (13C)
-------------
SI =   1024
SF =   150.713
SW_p =   21101.608
```

cYD-7-78 750m HZ

c

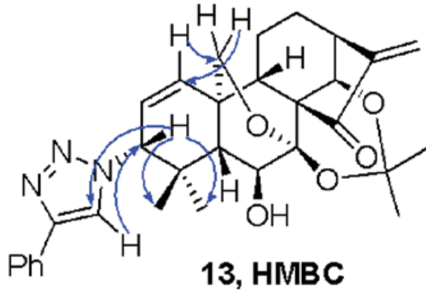


13, NOESY

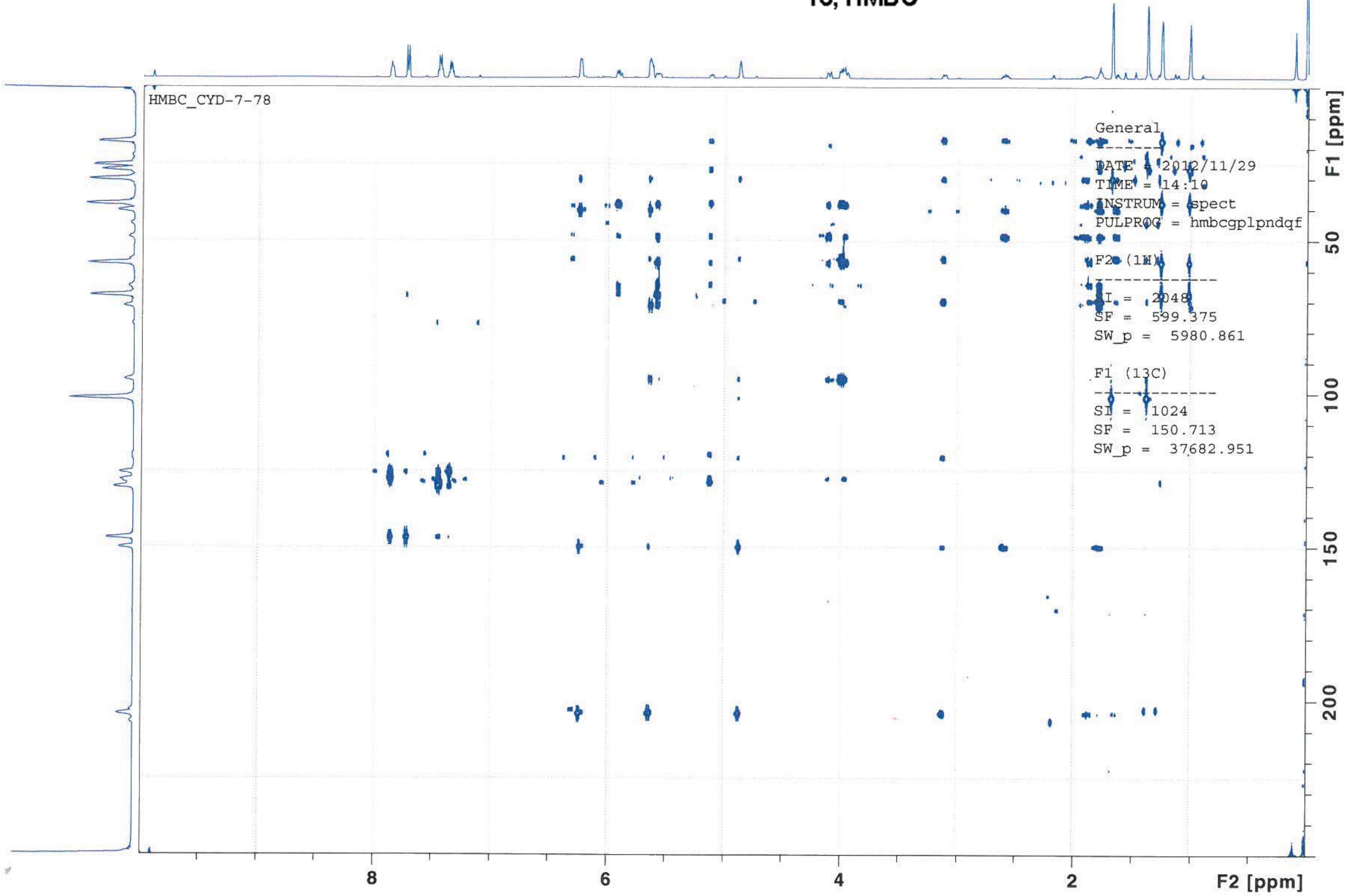


600MHz

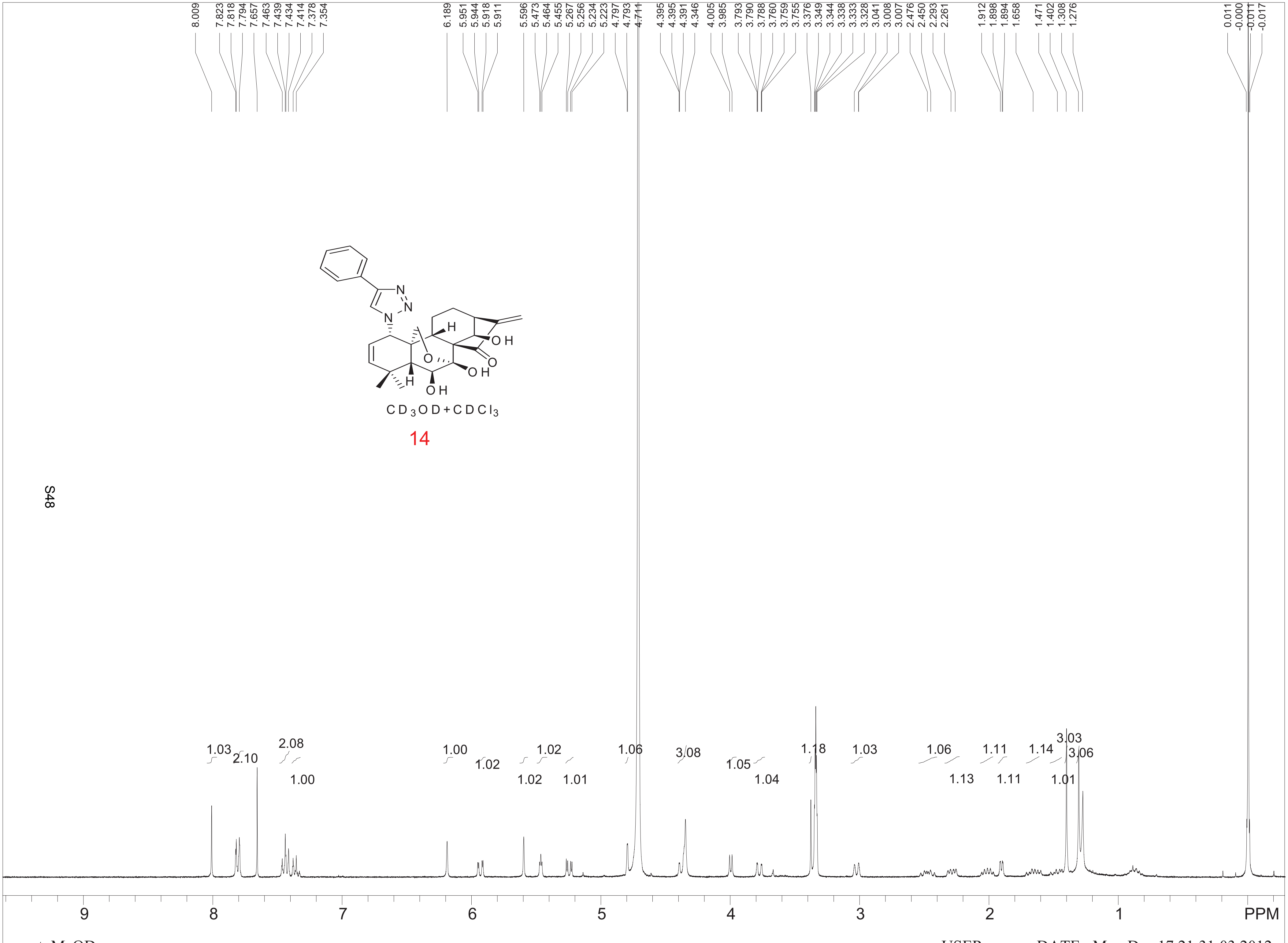
hmbc 3 1 /opt/topspin3.0/data/zhou/nmr



13, HMBC



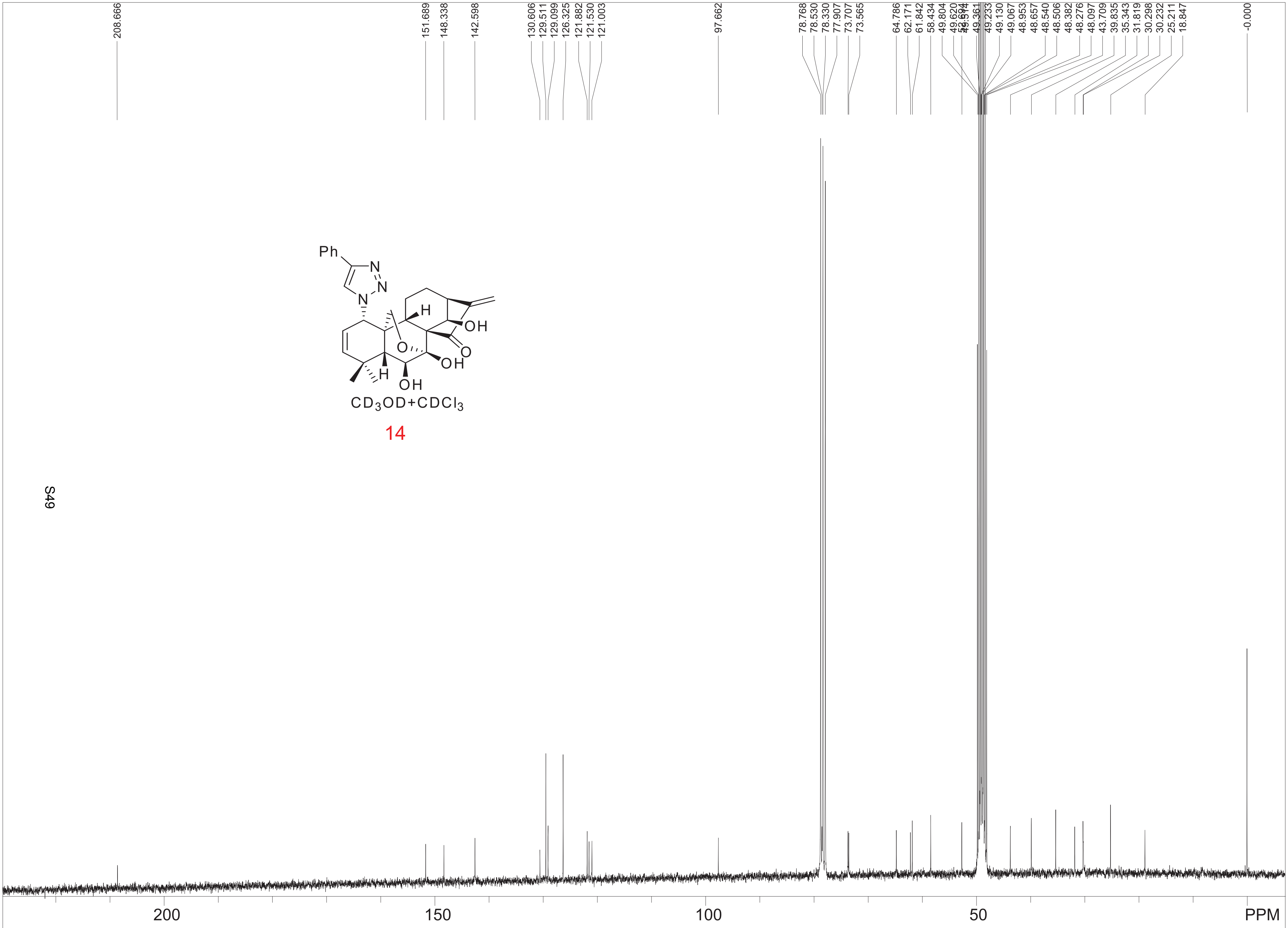
```
General
----------
DATE = 2012/11/29
TIME = 14:10
INSTRUM = spect
PULPROG = hmbcgplpndqf

F2 (1H)
----------
SI = 2048
SF = 599.375
SW_p = 5980.861

F1 (13C)
----------
SI = 1024
SF = 150.713
SW_p = 37682.951
```



14

spect, MeOD,
USER: nmr -- DATE: Mon Dec 17 21:31:03 2012

F1: 300.132	SW1: 6010		OF1: 1857.7		PTS1d: 65536
EX: zg30	PW: 10.0 usec	PD: 1.0 sec	NA: 16	LB: 0.0	WinNuts - $pdata



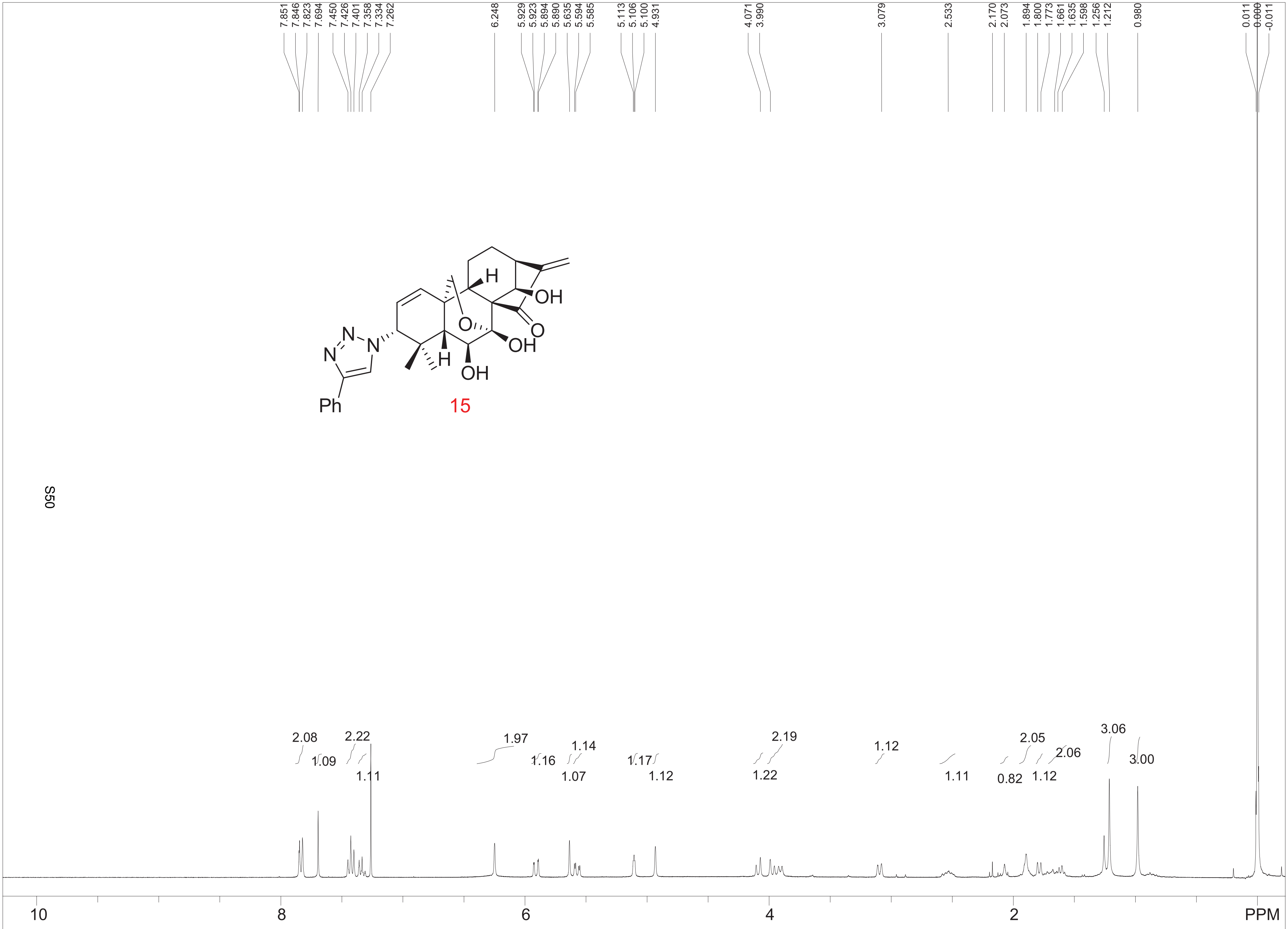
$CD_3OD+CDCl_3$

14

spect, MeOD,
USER: nmr -- DATE: Mon Dec 17 22:13:27 2012

F1: 75.480
SW1: 29762
OF1: 12636.7
PTS1d: 32768

EX: zgpg30
PW: 8.0 usec
PD: 2.0 sec
NA: 20000
LB: 0.0
WinNuts - $pdata

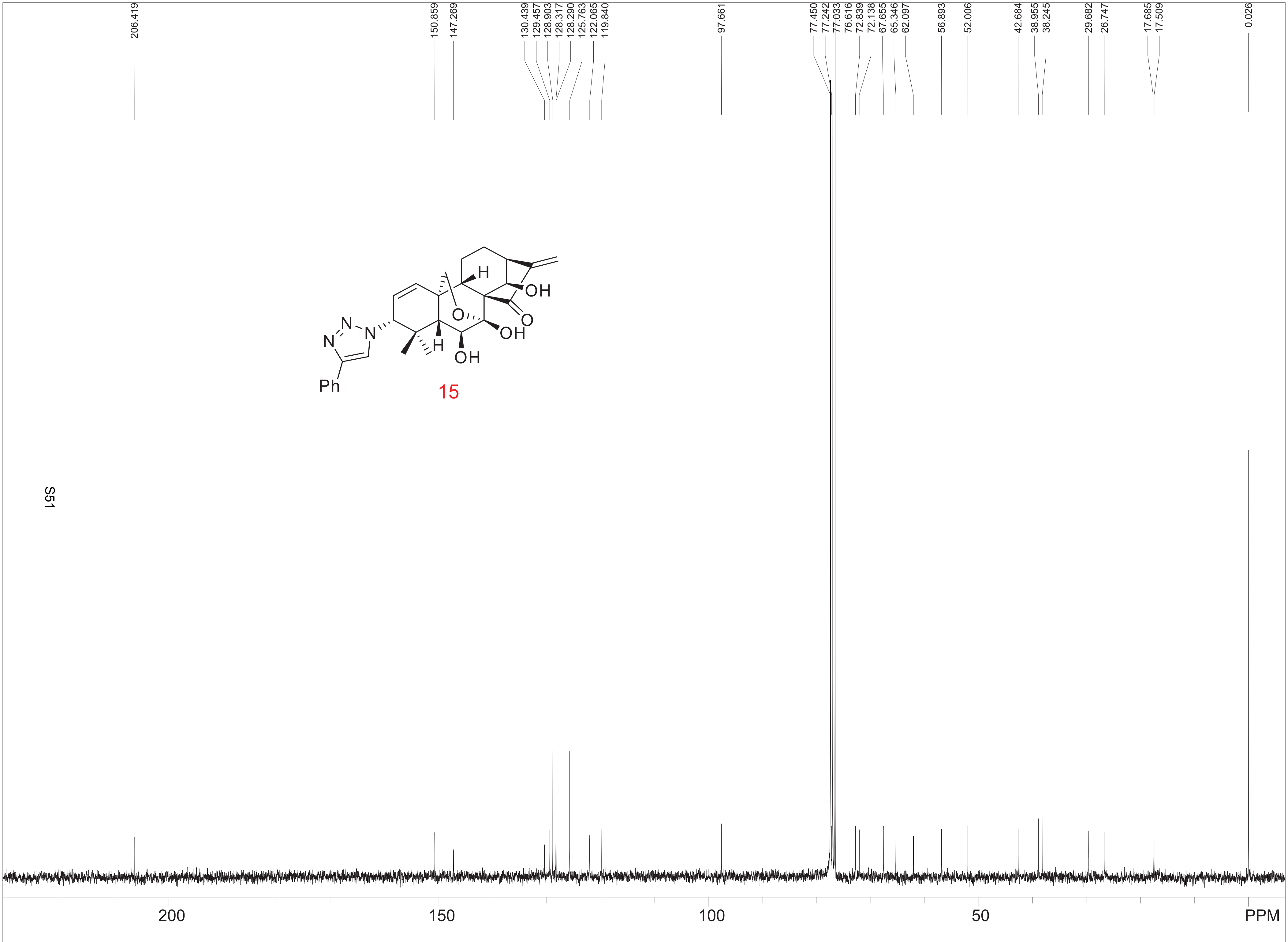


15

spect, CDCl3, USER: nmr -- DATE: Wed Nov 28 21:22:13 2012

F1: 300.132 SW1: 6010 OF1: 1848.6 PTS1d: 65536

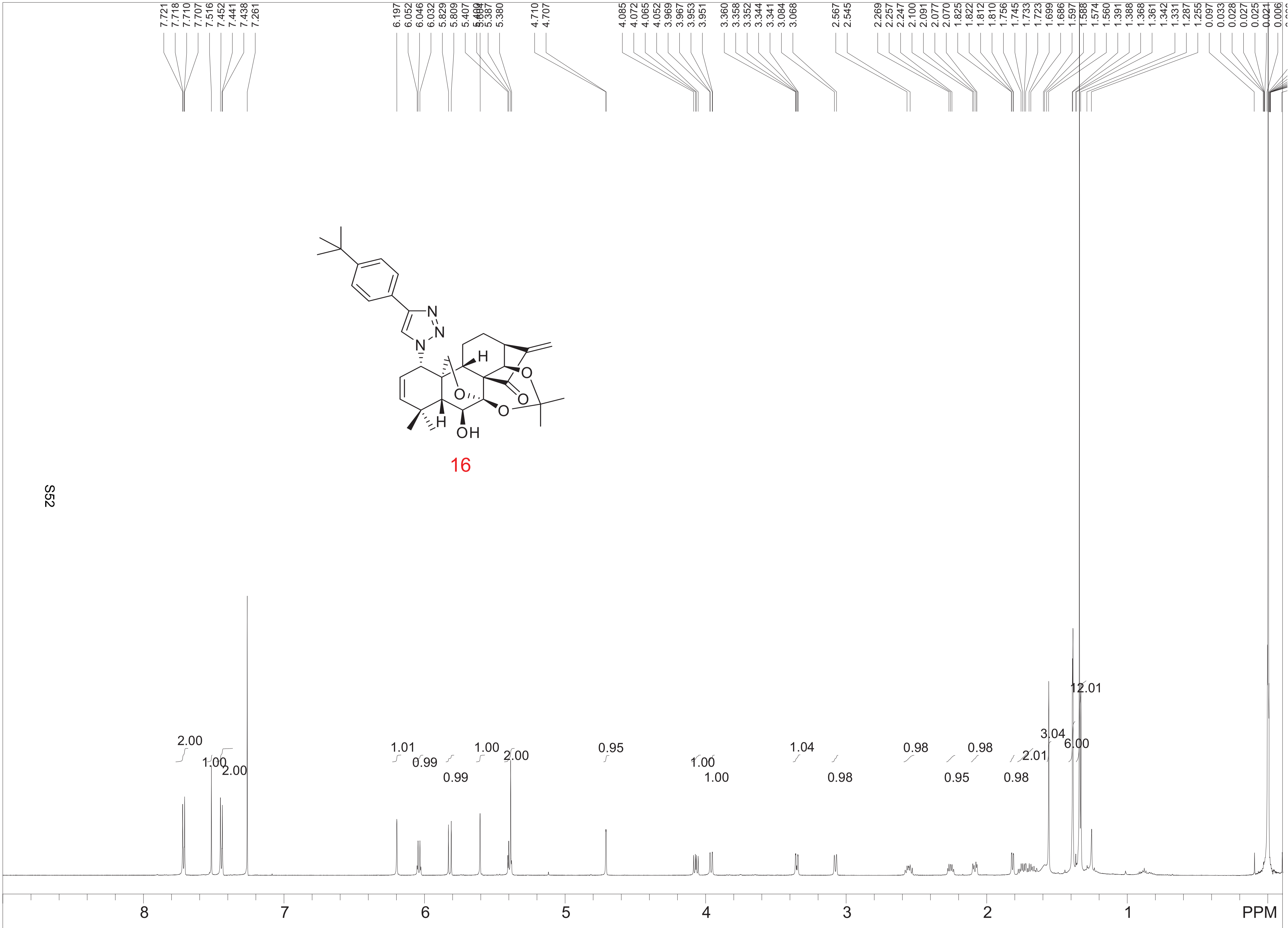
EX: zg30 PW: 10.0 usec PD: 1.0 sec NA: 16 LB: 0.0 WinNuts - $pdata



15

spect, CDCl3,
USER: nmr -- DATE: Wed Nov 28 22:01:45 2012

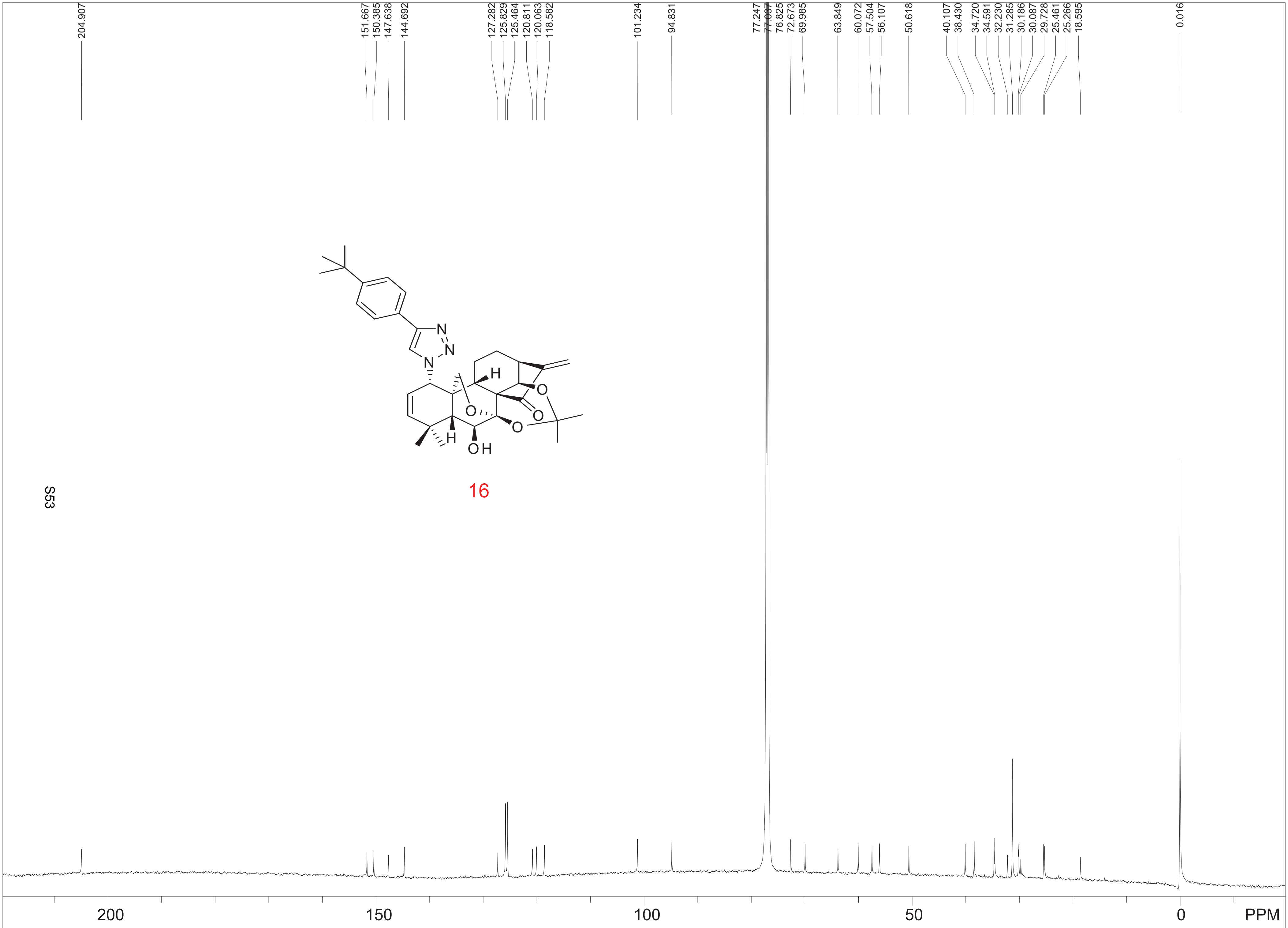
F1: 75.480		SW1: 29762		OF1: 12579.6		PTS1d: 32768
EX: zgpg30		PW: 8.0 usec	PD: 2.0 sec	NA: 1117	LB: 0.0	WinNuts - $pdata



16

spect, CDCl3,
USER: zhou -- DATE: Thu Dec 13 21:23:36 2012

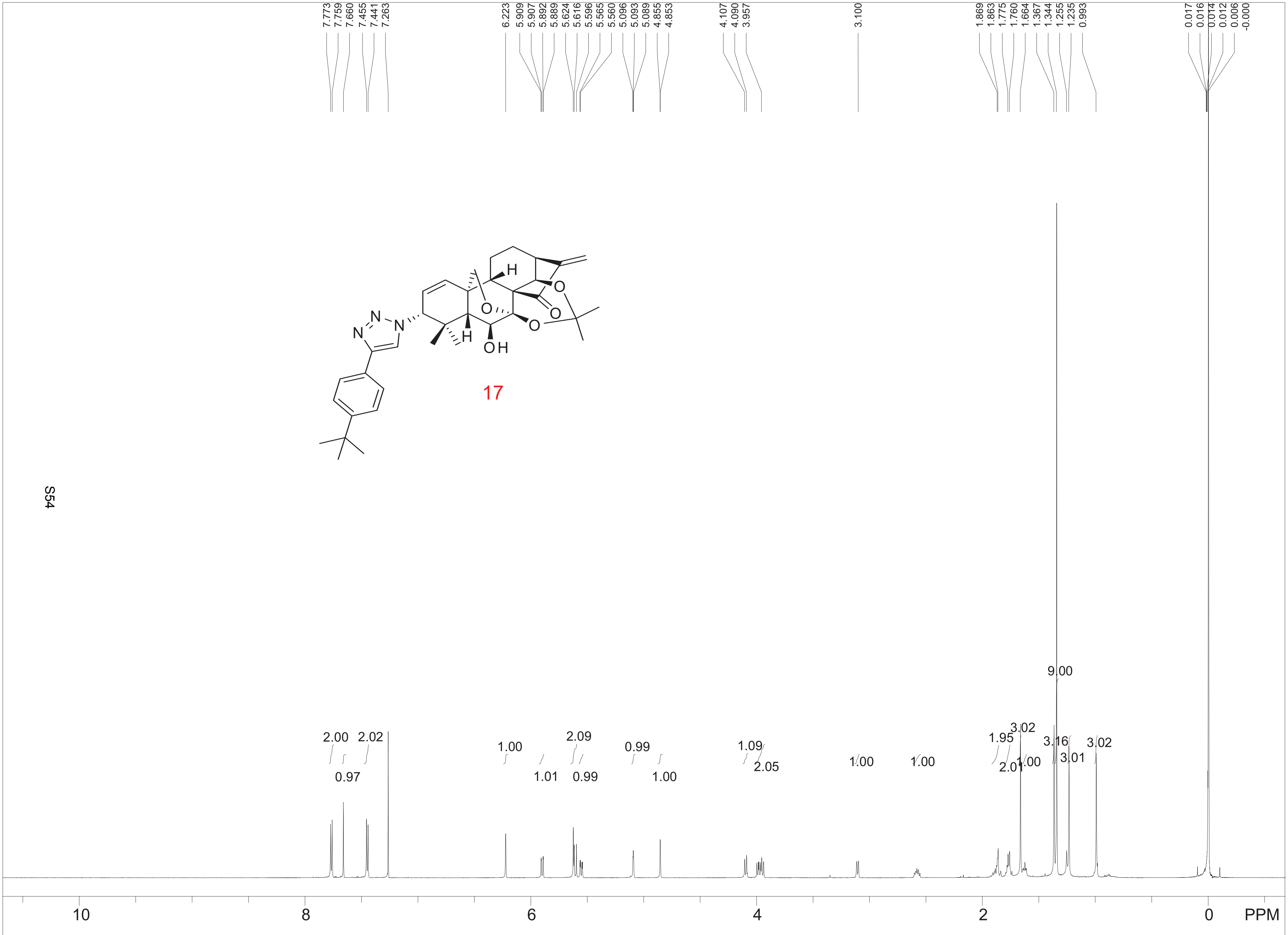
F1: 599.378	SW1: 12336		OF1: 2979.3		PTS1d: 65536
EX: zg	PW: 8.0 usec	PD: 1.0 sec	NA: 1	LB: 0.0	WinNuts - $pdata



16

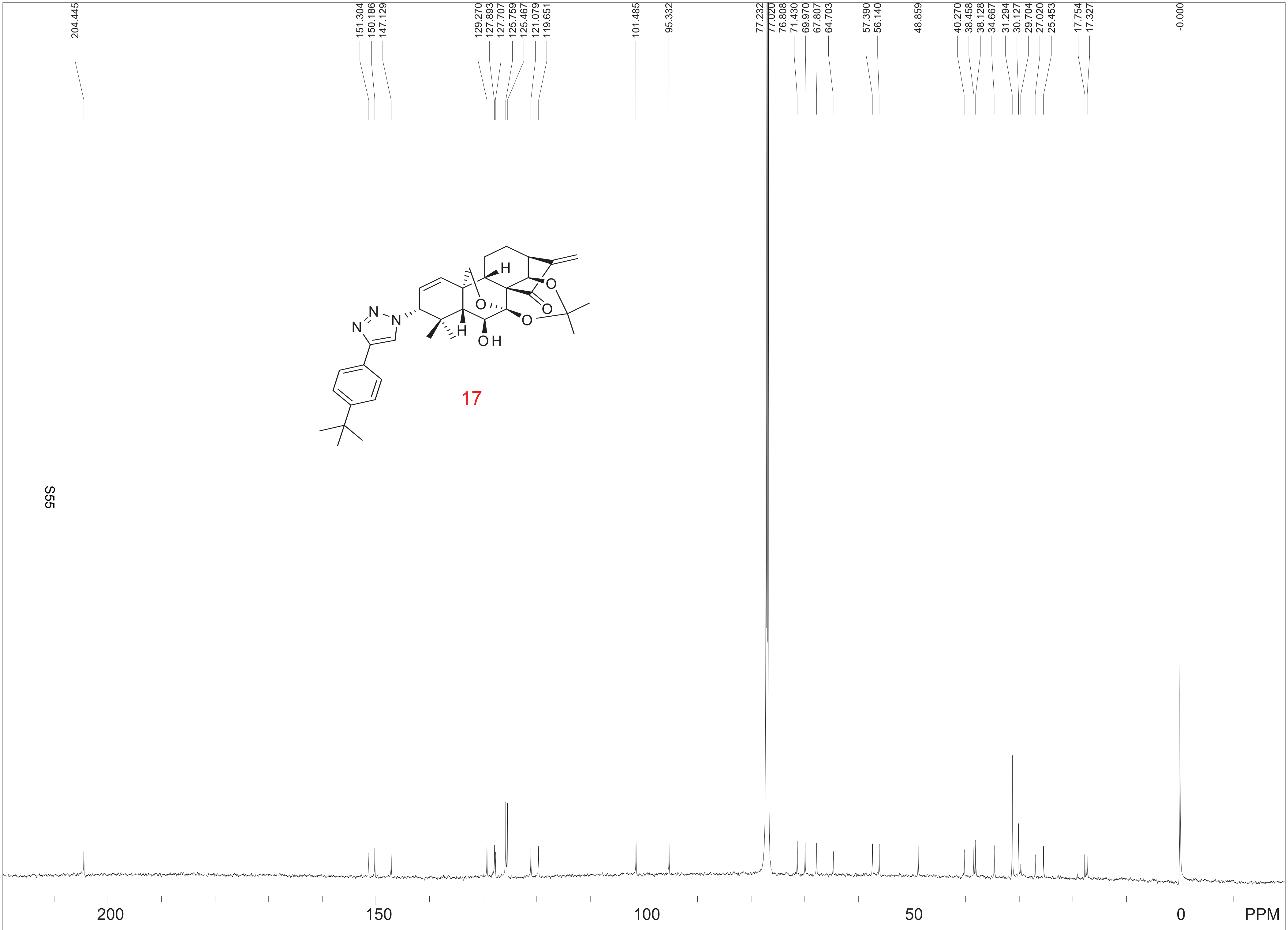
spect, CDCl3, USER: zhou -- DATE: Thu Dec 13 23:22:50 2012

F1: 150.728		SW1: 36058		OF1: 15074.2		PTS1d: 32768
EX: zgig30		PW: 12.0 usec	PD: 1.5 sec	NA: 2843	LB: 0.0	WinNuts - $pdata



17

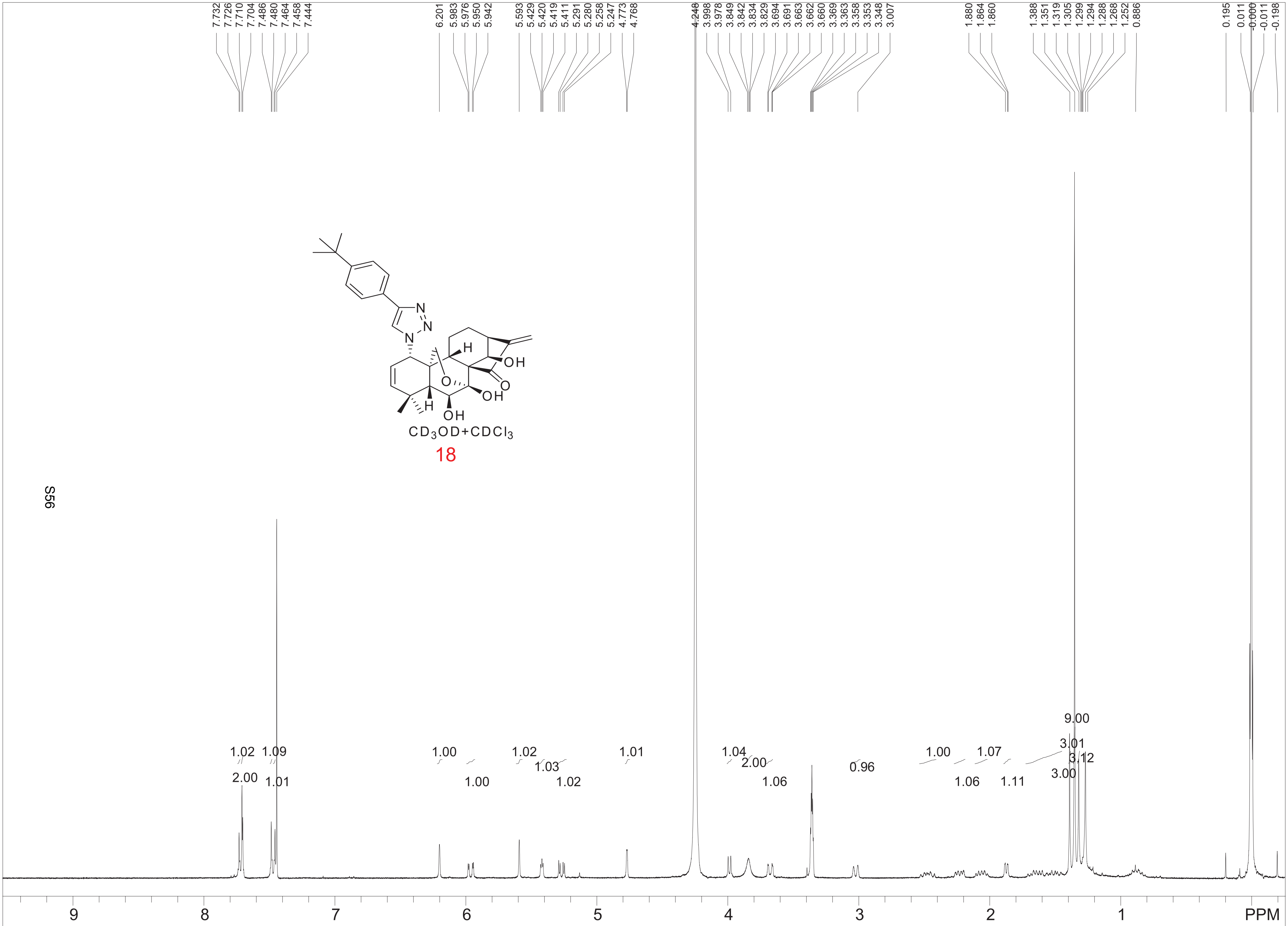
spect, CDCl3,				USER: zhou -- DATE: Thu Dec 13 20:57:50 2012	
F1: 599.378	SW1: 12336		OF1: 2980.4	PTS1d: 65536	
EX: zg	PW: 8.0 usec	PD: 1.0 sec	NA: 1	LB: 0.0	WinNuts - $pdata



17

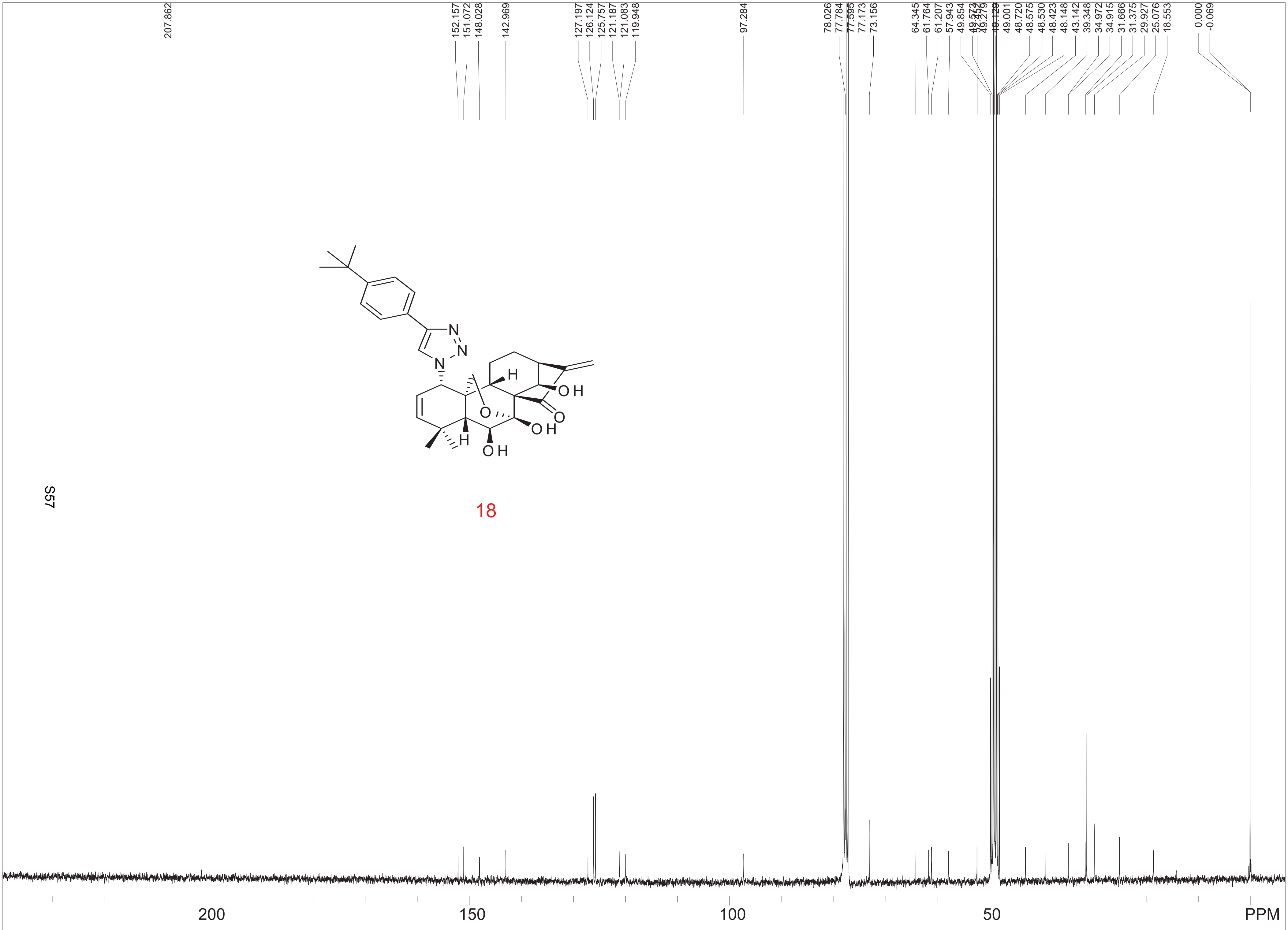
spect, CDCl3,
USER: zhou -- DATE: Thu Dec 13 21:03:32 2012

F1: 150.728	SW1: 36058	OF1: 15071.2	PTS1d: 32768	
EX: zgig30	PW: 12.0 usec	PD: 1.5 sec	NA: 402	LB: 0.0	WinNuts - $pdata



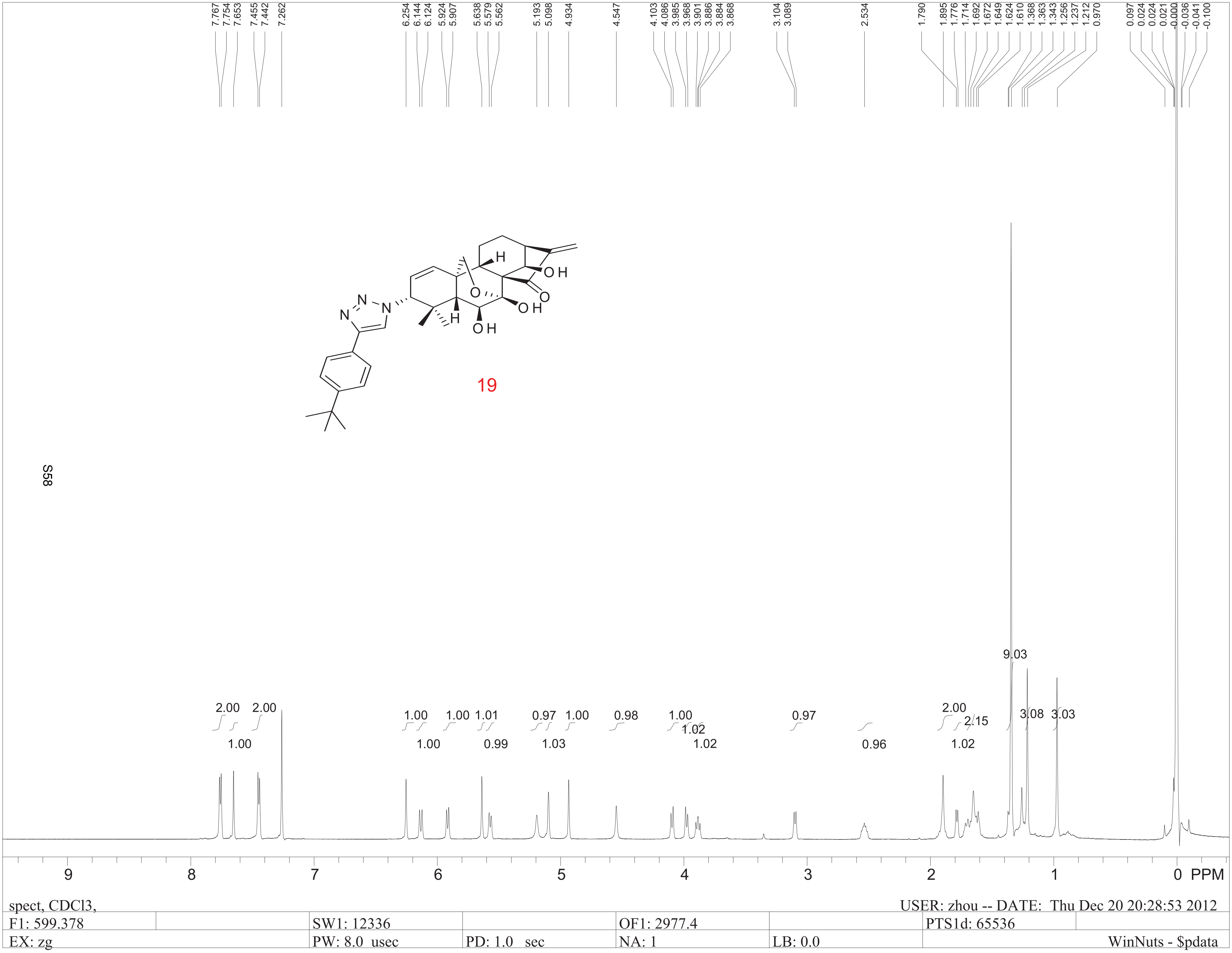
spect, MeOD,
USER: nmr -- DATE: Tue Dec 25 01:42:30 2012

F1: 300.132	SW1: 6010		OF1: 1863.5		PTS1d: 65536
EX: zg30	PW: 10.0 usec	PD: 1.0 sec	NA: 32	LB: 0.0	WinNuts - $pdata

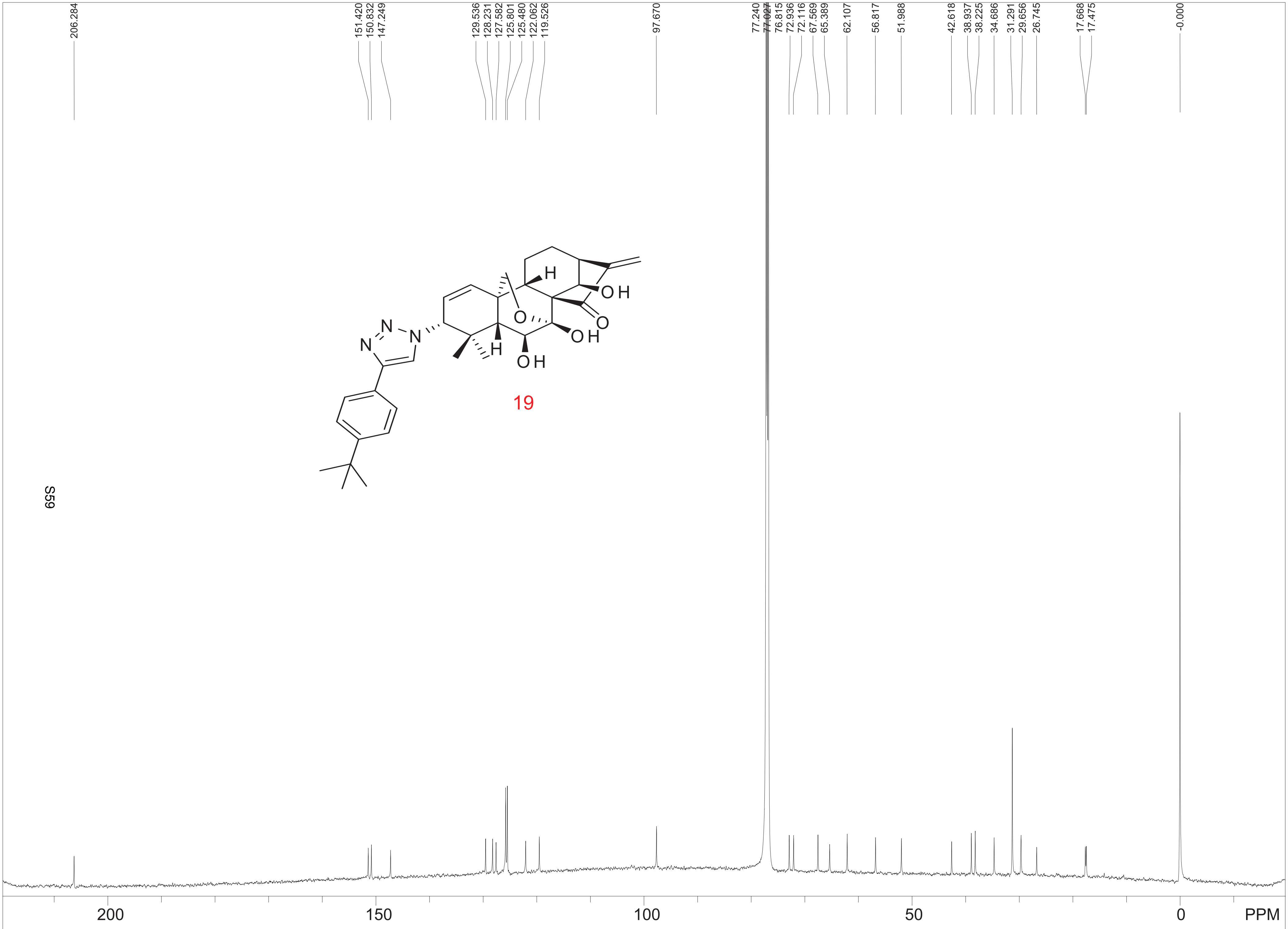


18

spect, MeOD,
USER: nmr -- DATE: Tue Dec 25 02:01:59 2012
F1: 75.480
SW1: 29762
OF1: 12603.6
PTS1d: 32768
EX: zgpg30
PW: 8.0 usec
PD: 2.0 sec
NA: 22000
LB: 0.0
WinNuts - $pdata

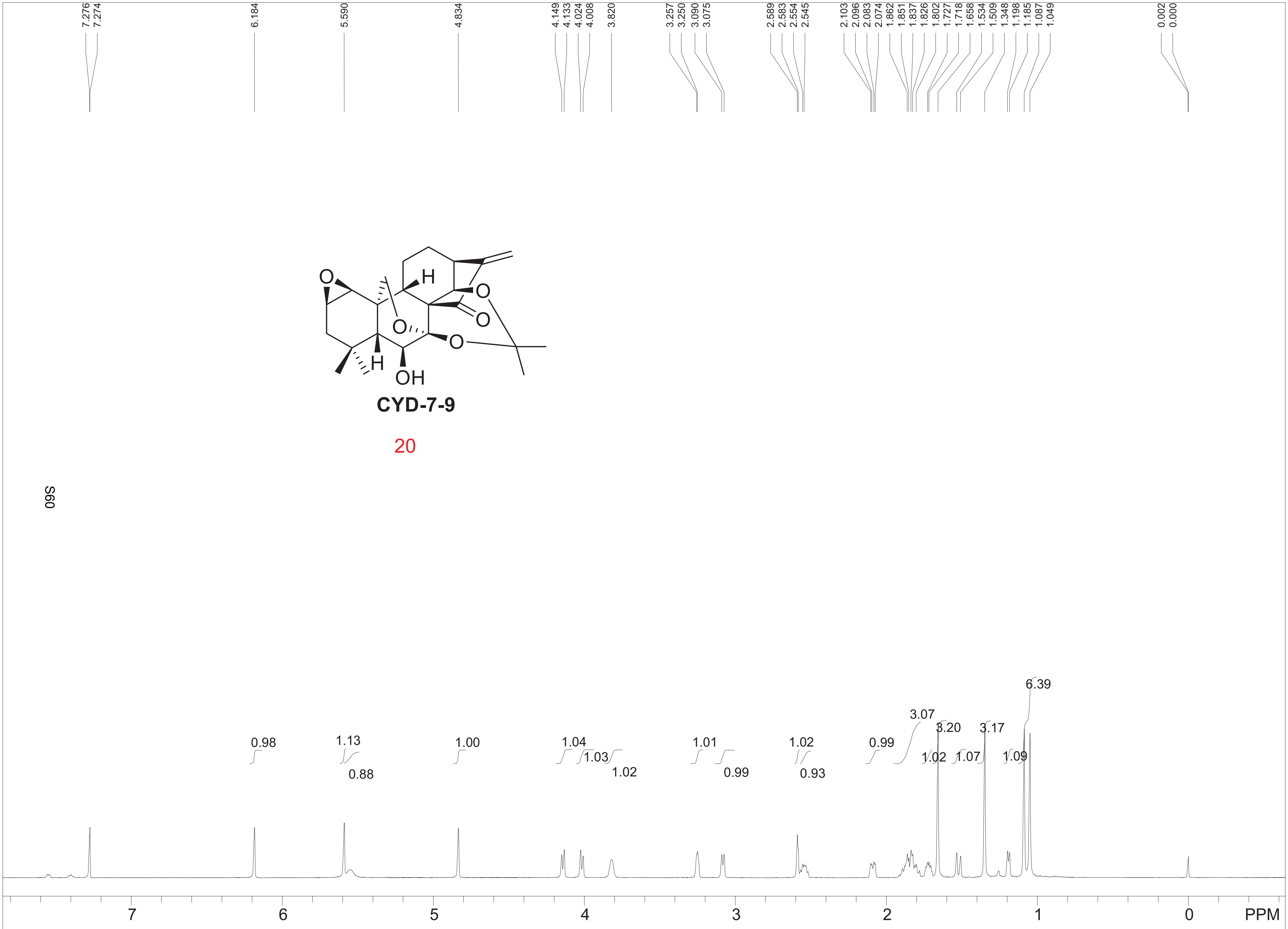


7.767
7.754
7.653
7.455
7.442
7.262
6.254
6.144
6.124
5.924
5.907
5.638
5.579
5.562
5.193
5.098
4.934
4.547
4.103
4.086
3.985
3.968
3.901
3.886
3.884
3.868
3.104
3.089
2.534
1.790
1.895
1.776
1.714
1.692
1.672
1.649
1.624
1.610
1.368
1.363
1.343
1.256
1.237
1.212
0.970
0.097
0.024
0.024
0.021
-0.000
-0.036
-0.041
-0.100
N
N
N
O
H
OH
O
OH
H
OH
19
2.00
1.00
2.00
1.00
1.00
1.00
1.01
0.99
0.97
1.03
1.00
0.98
1.00
1.02
1.02
0.97
0.96
2.00
2.15
1.02
9.03
3.08
3.03
9
8
7
6
5
4
3
2
1
0 PPM
spect, CDCl3,
USER: zhou -- DATE: Thu Dec 20 20:28:53 2012
F1: 599.378
SW1: 12336
OF1: 2977.4
PTS1d: 65536
EX: zg
PW: 8.0 usec
PD: 1.0 sec
NA: 1
LB: 0.0
WinNuts - $pdata



19

spect, CDCl3,					USER: zhou -- DATE: Thu Dec 20 20:47:50 2012
F1: 150.728	SW1: 36058		OF1: 15071.8		PTS1d: 32768
EX: zgig30	PW: 12.0 usec	PD: 1.5 sec	NA: 1449	LB: 0.0	WinNuts - $pdata


7.276
7.274
6.184
5.590
4.834
4.149
4.133
4.024
4.008
3.820
3.257
3.250
3.090
3.075
2.589
2.583
2.554
2.545
2.103
2.096
2.083
2.074
1.862
1.851
1.837
1.826
1.802
1.727
1.718
1.658
1.534
1.509
1.348
1.198
1.185
1.087
1.049
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0.000
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H
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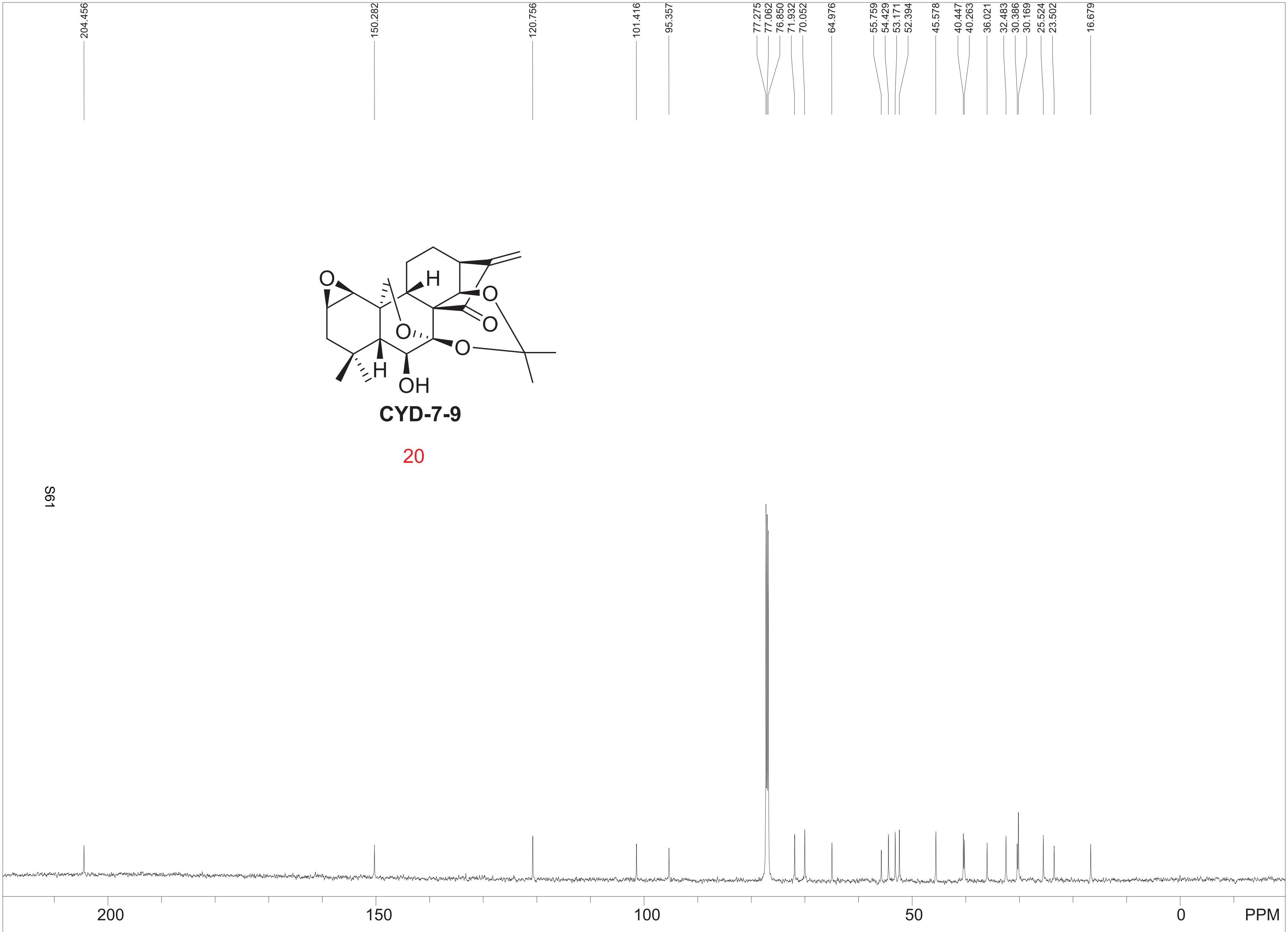
O
H
OH
0.98
1.13
0.88
1.00
1.04
1.03
1.02
1.01
0.99
1.02
0.93
0.99
3.07
1.02
3.20
1.07
3.17
1.09
6.39
7
6
5
4
3
2
1
0
PPM

CYD-7-9

20

spect, CDCl3,
USER: zhou -- DATE: Thu Aug 23 20:06:50 2012
F1: 599.378
SW1: 12336
OF1: 2988.2
PTS1d: 65536
EX: zg30
PW: 8.0 usec
PD: 1.0 sec
NA: 1
LB: 0.0
WinNuts - $pdata



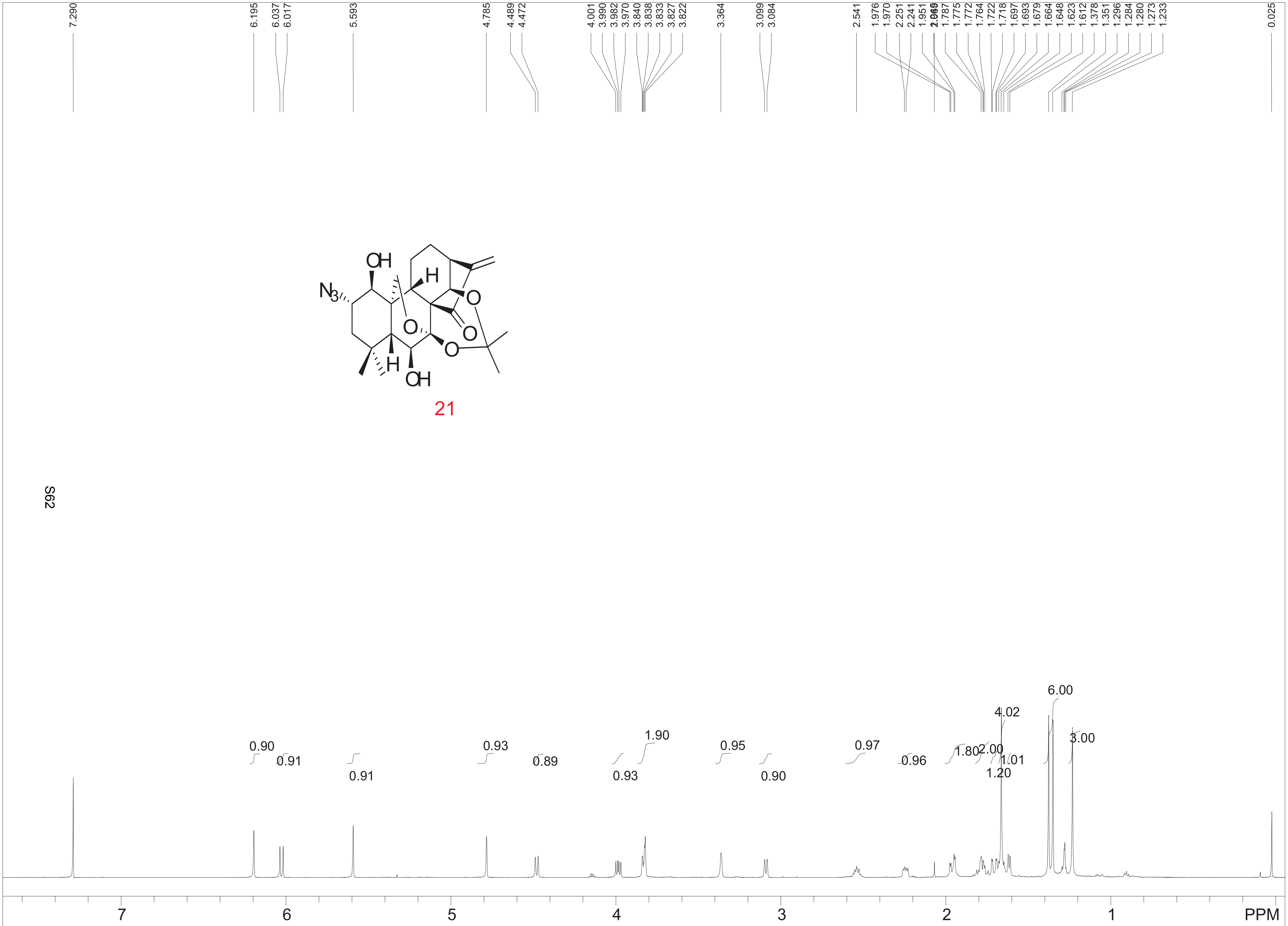
CYD-7-9

20

spect, CDCl3,
USER: zhou -- DATE: Thu Aug 23 20:13:24 2012

F1: 150.728
SW1: 36058
OF1: 15074.2
PTS1d: 32768

EX: zgig30
PW: 12.0 usec
PD: 1.5 sec
NA: 25
LB: 0.0
WinNuts - $pdata



spect, CDCl3,

USER: zhou -- DATE: Thu Oct 11 20:43:59 2012

F1: 599.378	SW1: 12336		OF1: 2996.9		PTS1d: 65536
EX: zg30	PW: 8.0 usec	PD: 1.0 sec	NA: 1	LB: 0.0	WinNuts - $pdata

spect, CDCl3,

USER: zhou -- DATE: Thu Oct 11 20:48:41 2012

F1: 150.728

SW1: 36058

OF1: 15074.2

PTS1d: 32768

EX: zgig30

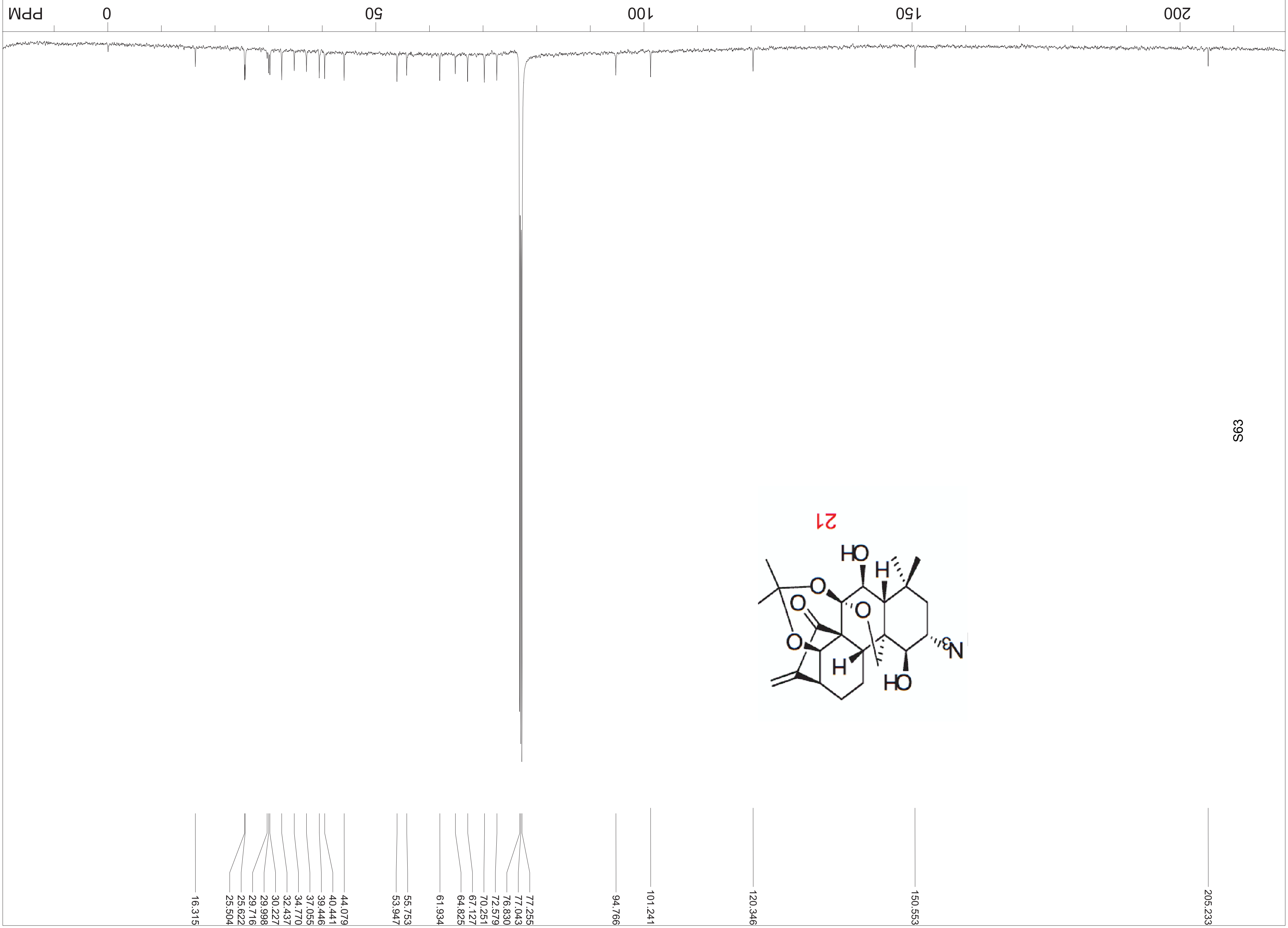
PW: 12.0 usec

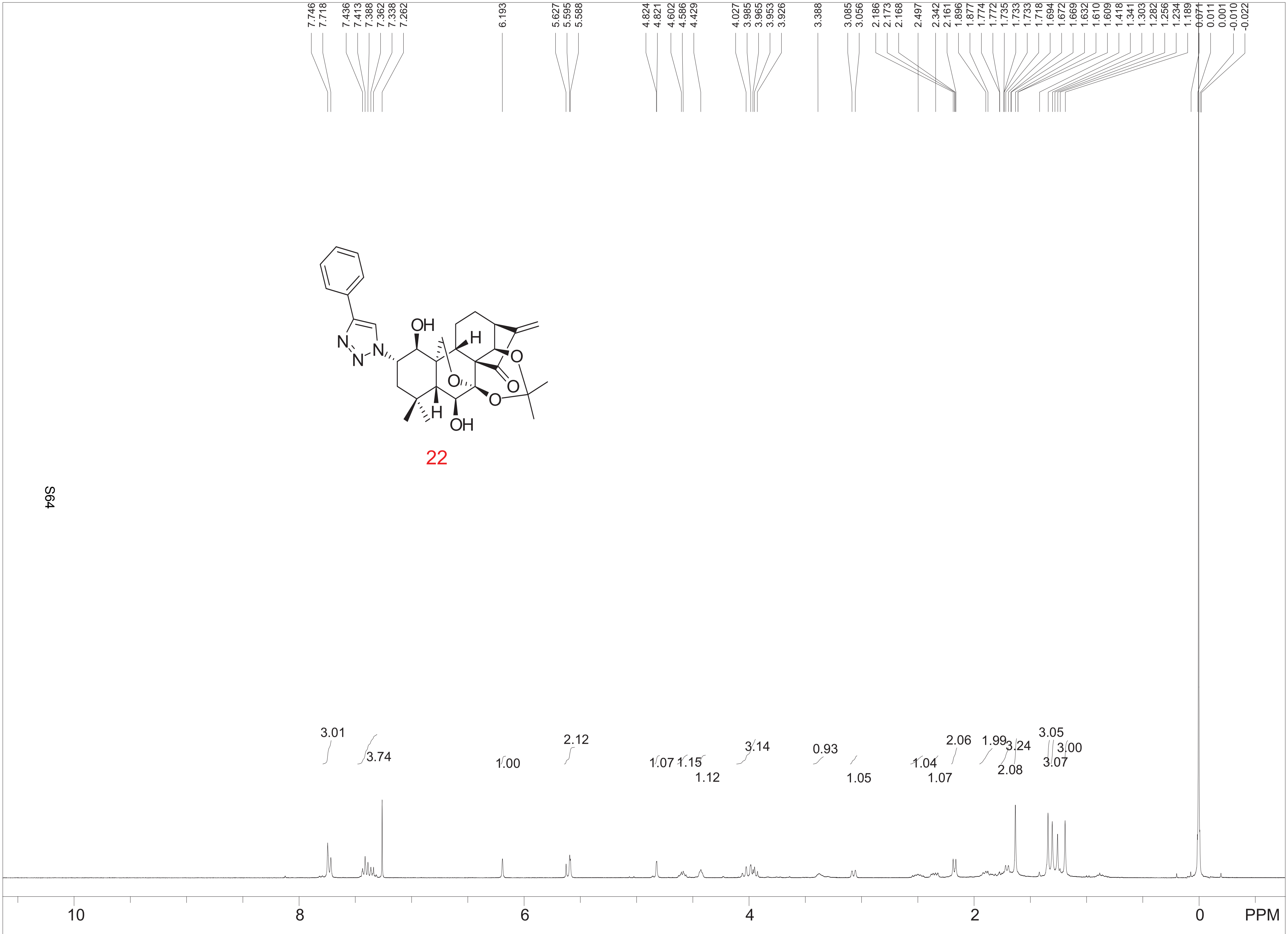
PD: 1.5 sec

NA: 131

LB: 0.0

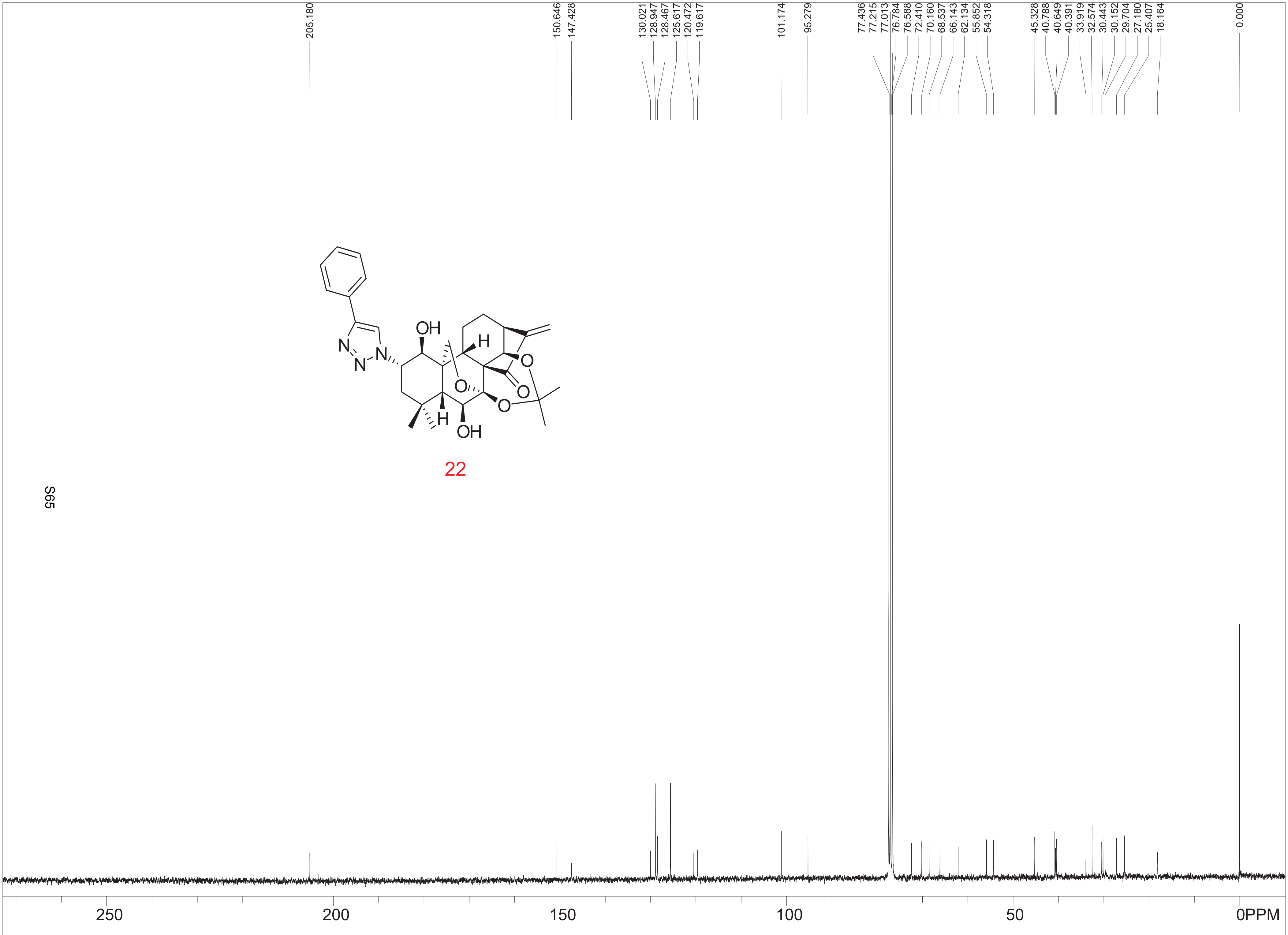
WinNuts - $pdata





22

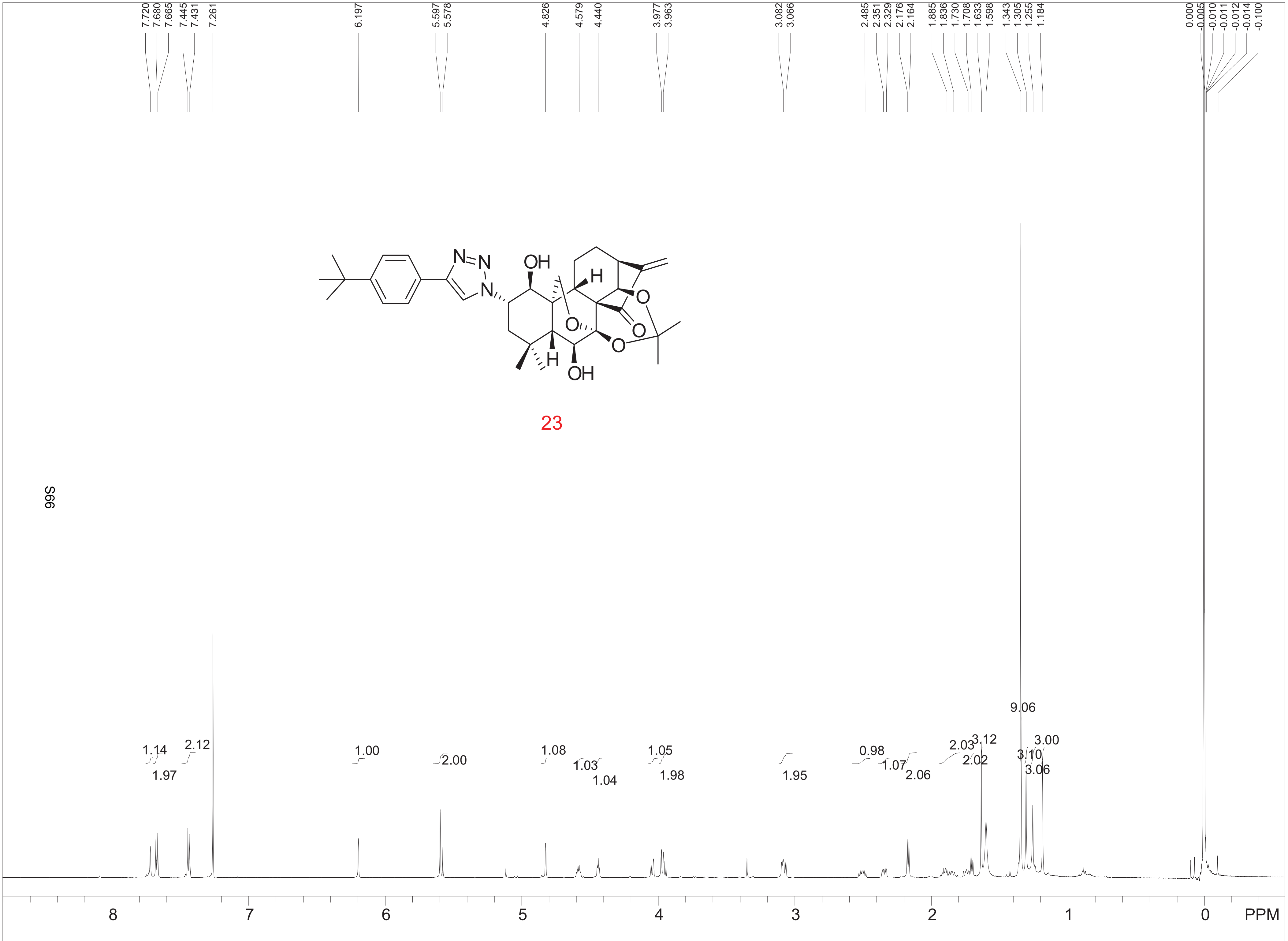
spect, CDCl3,
F1: 300.132
EX: zg30
SW1: 6010
PW: 10.0 usec
PD: 1.0 sec
OF1: 1848.6
NA: 16
LB: 0.0
USER: nmr -- DATE: Fri Nov 09 21:17:21 2012
PTS1d: 65536
WinNuts - $pdata



22

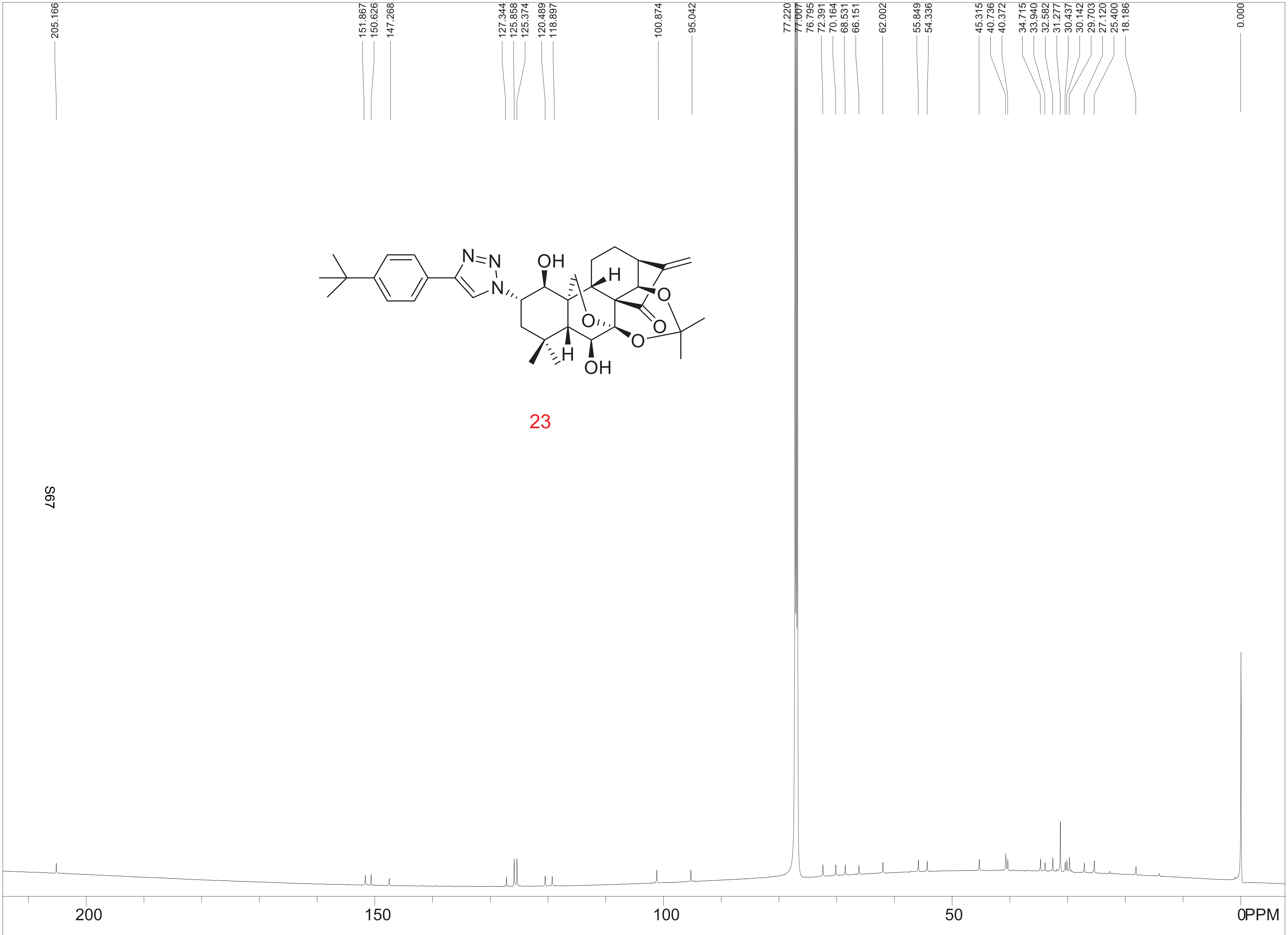
spect, CDCl3,
USER: nmr -- DATE: Fri Nov 09 22:18:43 2012

F1: 75.480		SW1: 29762		OF1: 12577.7		PTS1d: 32768
EX: zgpg30		PW: 8.0 usec	PD: 2.0 sec	NA: 4270	LB: 0.0	WinNuts - $pdata



spect, CDCl3, USER: zhou -- DATE: Thu Jan 10 20:49:12 2013

F1: 599.378	SW1: 12336		OF1: 2980.1		PTS1d: 65536	
EX: zg	PW: 8.0 usec	PD: 1.0 sec	NA: 1	LB: 0.0		WinNuts - $pdata

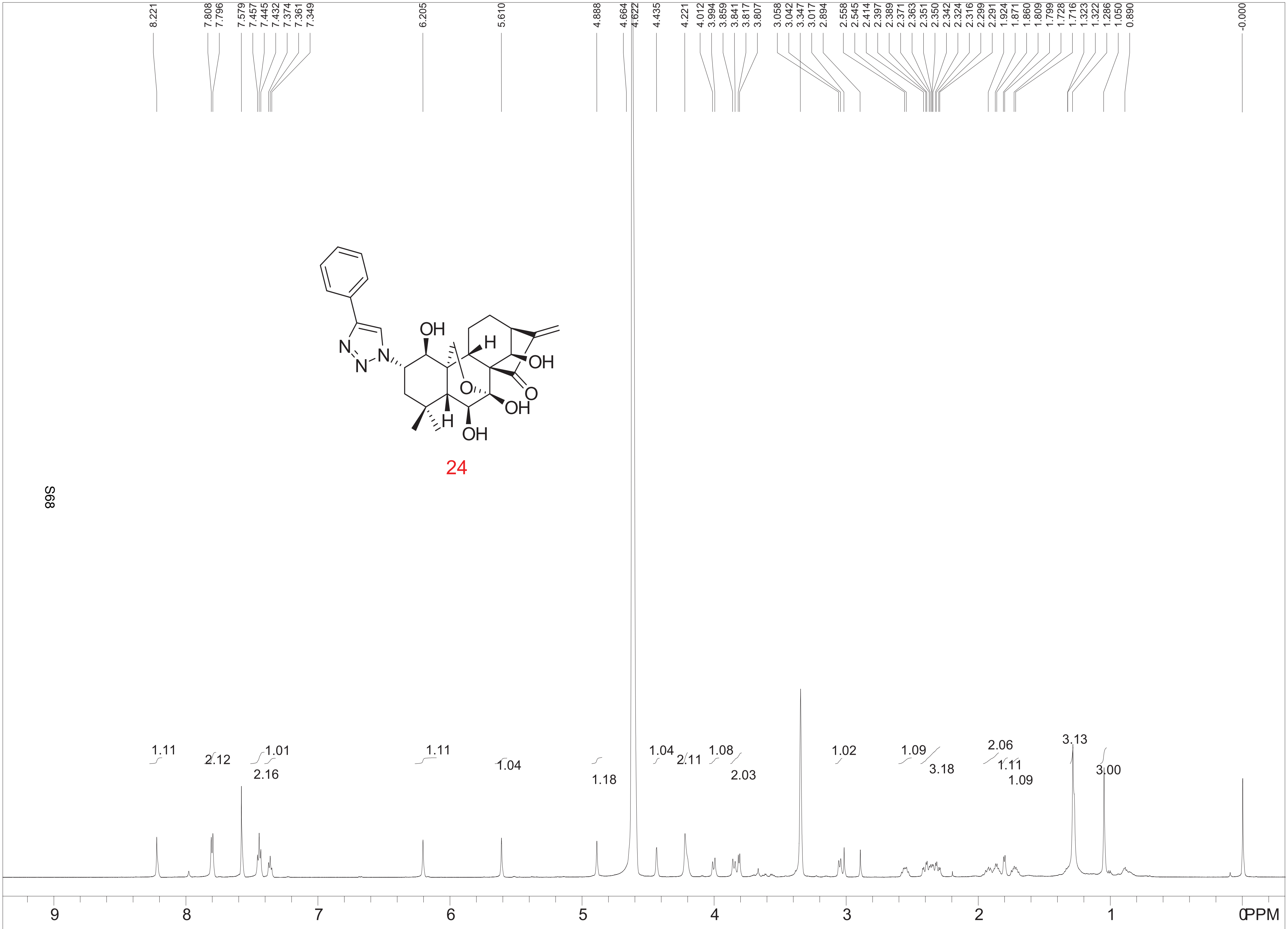


23

spect, CDCl3,

USER: zhou -- DATE: Fri Jan 11 14:53:22 2013

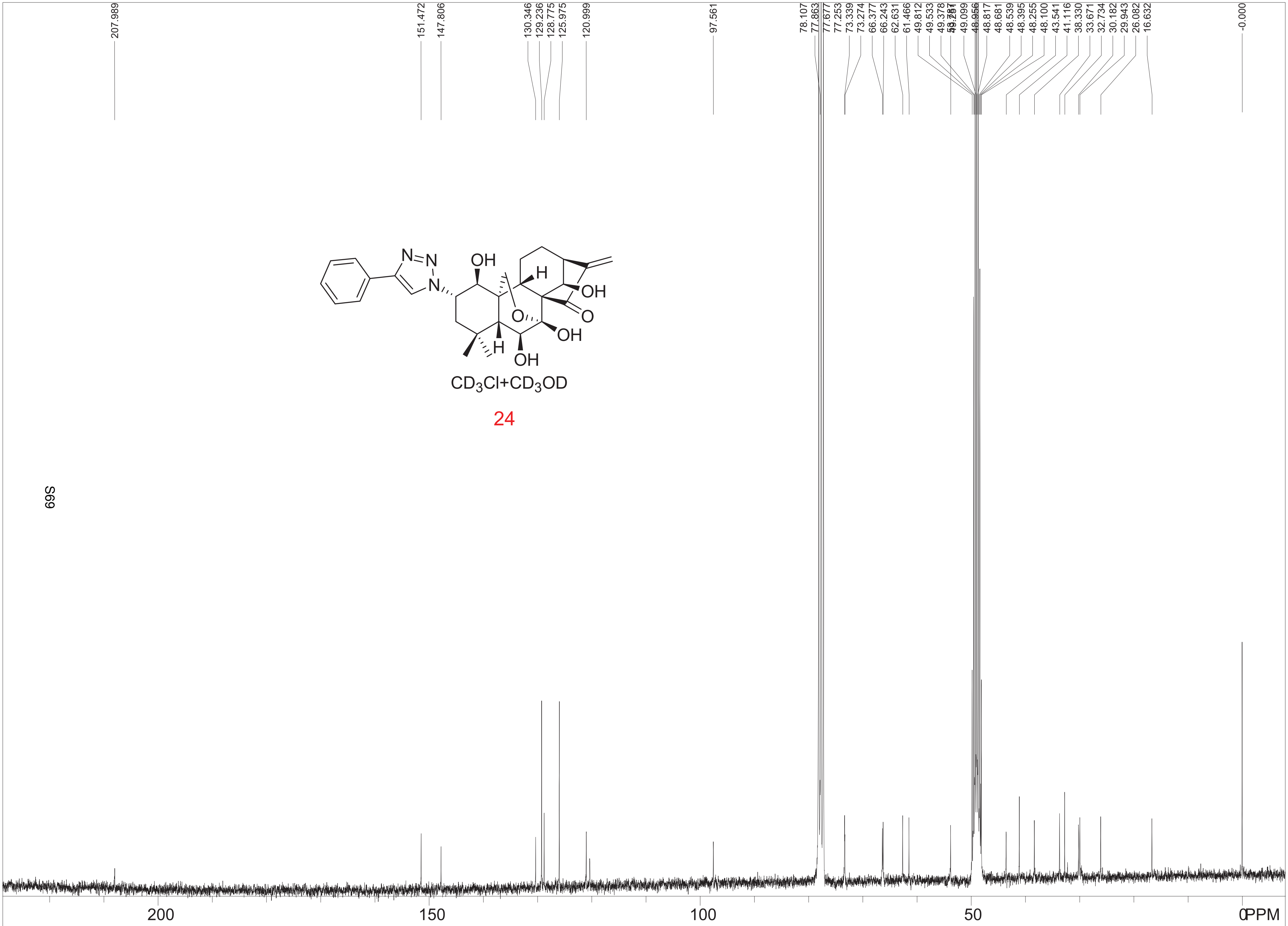
F1: 150.728	SW1: 36058		OF1: 15071.5		PTS1d: 32768
EX: zgig30	PW: 12.0 usec	PD: 1.5 sec	NA: 23121	LB: 0.0	WinNuts - $pdata



24

spect, MeOD, USER: zhou -- DATE: Thu Nov 08 19:57:40 2012

F1: 599.378		SW1: 12336		OF1: 3003.8		PTS1d: 65536	
EX: zg30		PW: 8.0 usec	PD: 1.0 sec	NA: 16	LB: 0.0		WinNuts - $pdata

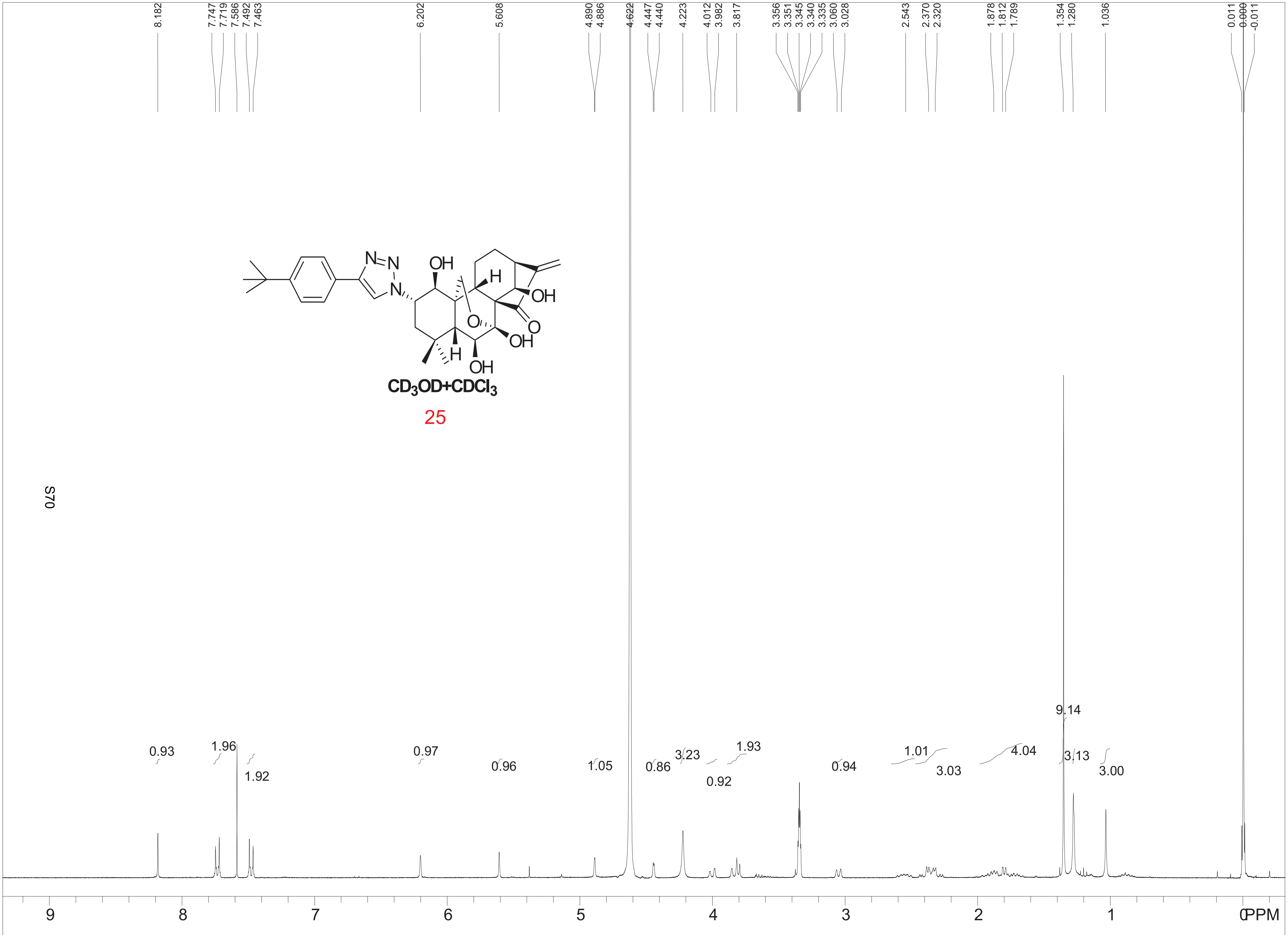


CD_3Cl+CD_3OD

24

spect, MeOD,
USER: nmr -- DATE: Mon Feb 04 23:22:30 2013

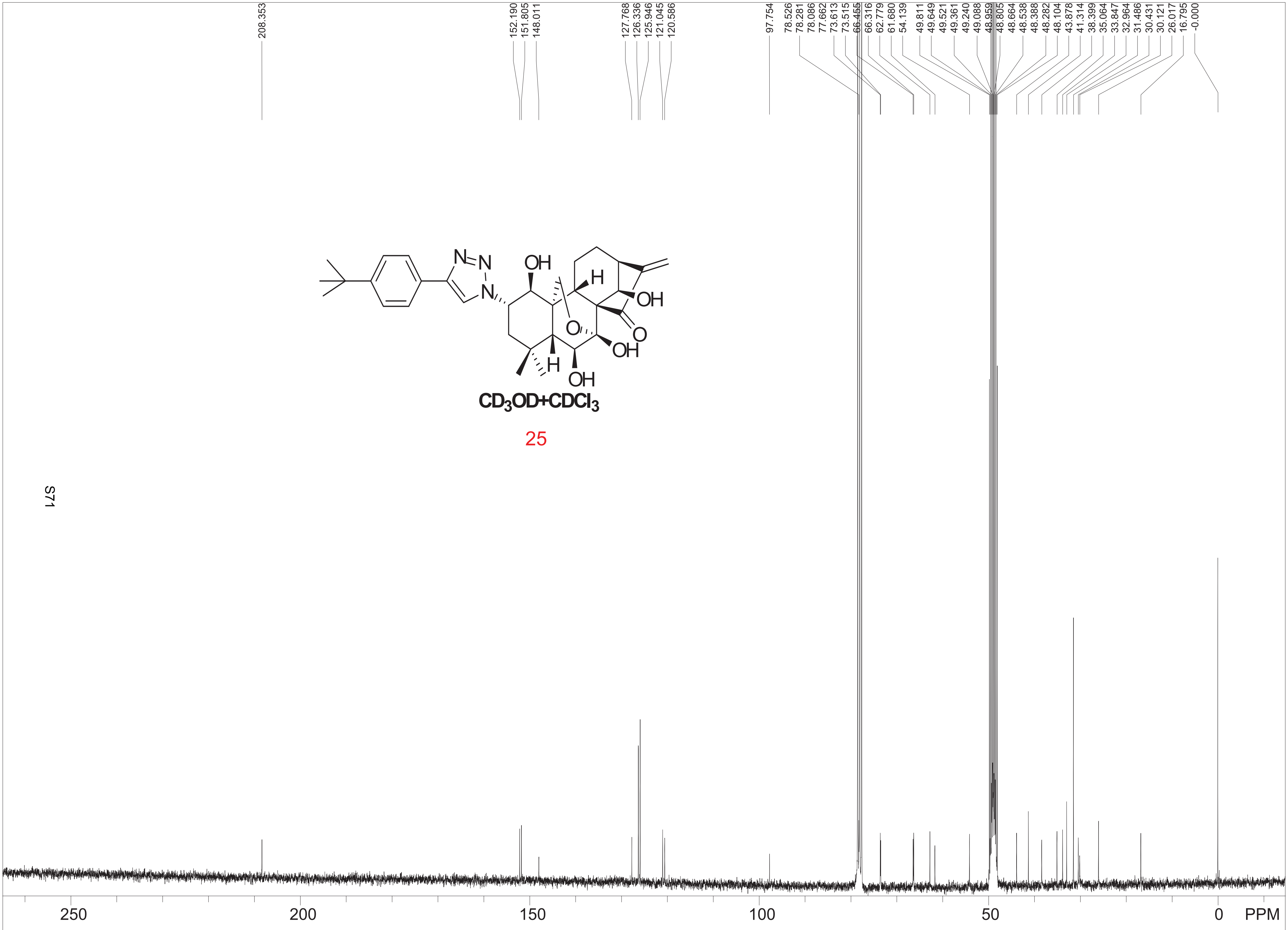
F1: 75.480	SW1: 29762		OF1: 12606.7		PTS1d: 32768
EX: zgpg30	PW: 8.0 usec	PD: 2.0 sec	NA: 20000	LB: 0.0	WinNuts - $pdata



CD_3OD+$CDCl_3$

25

spect, MeOD,
F1: 300.132
EX: zg30
SW1: 6010
PW: 10.0 usec
PD: 1.0 sec
OF1: 1859.7
NA: 16
LB: 0.0
USER: nmr -- DATE: Sat Jan 12 02:40:00 2013
PTS1d: 65536
WinNuts - $pdata



$CD_3OD+CDCl_3$

25

spect, MeOD,
USER: nmr -- DATE: Sat Jan 12 03:32:11 2013
F1: 75.480
SW1: 29762
OF1: 12625.4
PTS1d: 32768
EX: zgpg30
PW: 8.0 usec
PD: 2.0 sec
NA: 18993
LB: 0.0
WinNuts - $pdata