Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information
(Experimental Procedures and NMR Spectra Data)

Stereoselective Construction of 2-Vinyl 3-Hydroxybenzopyran Rings: Total Syntheses of Teadenols A and B

Ryunosuke Yoshida, Hitoshi Ouchi, Atsushi Yoshida, Tomohiro Asakawa, Makoto Inai
Masahiro Egi, Yoshitaka Hamashima* and Toshiyuki Kan*

School of Pharmaceutical Sciences
University of Shizuoka, 52-1 Yada, Suruga-ku, Shizuoka, 422-8526, Japan

Fax: (+81) 54-264-5745
E-mail: kant@u-shizuoka-ken.ac.jp, hamashima@u-shizuoka-ken.ac.jp

Analysis Instruments

Nuclear magnetic resonance [^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz)] spectra were determined on JEOL ECA-500 instrument. Chemical shifts for ^{1}H NMR were reported in parts per million downfields from tetramethylsilane (δ) as the internal standard and coupling constants were in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts for ^{13}C NMR were reported in ppm relative to the centerline of a triplet at 77.0 ppm for deuteriochloroform.

High-resolution mass spectra (HRMS) were obtained on a BRUKER DALTONICS micrOTOF (ESI).

Infrared (IR) spectra were recorded on a SHIMADZU IRPrestige-21.

Optical rotations were measured on a JASCO P-1030 Polarimeter at RT using the sodium D line.

Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F_{254}. Preparative TLC separations were made on 7 x 20 cm plates prepared with a 0.25 mm layer of Merck silica gel 60 F_{254}. Compounds were eluted from the adsorbent with 10% methanol in chloroform. Column chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical) 40–50 μm, Silica Gel 60 (spherical) 63–210 μm or Silica Gel 60 N (spherical, neutral) 63–210 μm.

Reagents and solvents were commercial grades and were used as supplied with the following exceptions.

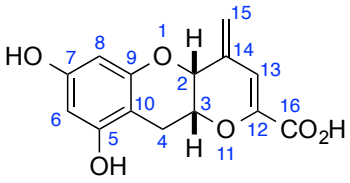
1) Dichloromethane, tetrahydrofuran and toluene: dried over molecular sieves 4A.

2) Methanol and acetonitrile: dried over molecular sieves 3A.

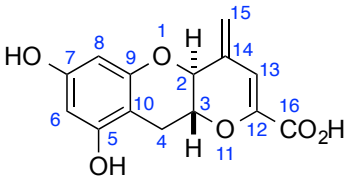
All reactions sensitive to oxygen and/or moisture were conducted under an argon atmosphere.

Numbering System

Based on a numbering system employed in Ishimaru's paper,[1] we employ the following numbering system in the main text and Supporting Information. The numbers assigned for early synthetic intermediates to specify positions of interest are in accord with the corresponding carbons in Teadenol A and B.



Teadenol A (**1**)



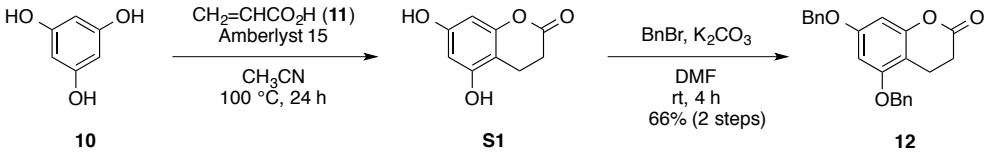
Teadenol B (**2**)

1. Wulandari, R. A.; Amano, M.; Yanagita, T.; Tanaka, T.; Kouno, I.; Kawamura, D.; Ishimaru, K. *J. Nat. Med.* **2011** *65*, 594.

Table of Contents

I. Synthesis of Common Intermediate **9**

Synthesis of Lactone **12**



To a solution of phloroglucinol (**10**, 100 g, 793 mmol) in CH_3CN (800 mL) were added acrylic acid (**11**, 60 mL, 872 mmol) and Amberlyst 15 (32 g) at room temperature. The resulting mixture was stirred at 100 °C for 24 hours. Then the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including **S1** was applied to the following reaction without further purification.

To a solution of the crude material including **S1** in DMF (800 mL) were added K_2CO_3 (329 g, 2.38 mol) and benzyl bromide (283 mL, 2.38 mol) at 0 °C. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 20/1) to afford **12** (188 g, 66%, 2 steps) as a colorless solid.

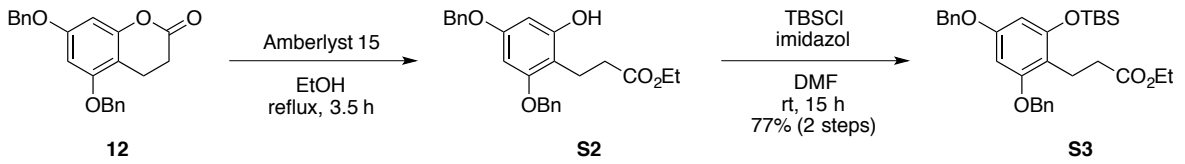
IR (film, cm^{-1}): 3032, 2912, 1770, 1624, 1595.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.32 (m, 10H), 6.41 (d, J = 2.3 Hz, 1H), 6.32 (d, J = 2.3 Hz, 1H), 5.03 (s, 2H), 5.02 (s, 2H), 2.93 (t, J = 7.7 Hz, 2H), 2.72 (t, J = 7.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.6, 159.0, 156.3, 153.1, 136.4, 136.3, 128.61, 128.57, 128.11, 128.09, 127.5, 127.2, 104.0, 96.7, 95.2, 70.31, 70.26, 28.7, 17.2.

HRMS (ESI): Calcd for $C_{23}H_{20}O_4Na$ [$(M+Na)^+$] 383.1259, found 383.1253.

Synthesis of Ester **S3**



To a solution of **12** (188 g, 26.4 mmol) in EtOH (1.0 L) was added Amberlyst 15 (10 g) at room temperature. The resulting mixture was refluxed for 3.5 hours. After cooling, the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including **S2** was applied to the following reaction without further purification.

To a solution of the crude material including **S2** in DMF (1.0 L) were added imidazole (53.3 g, 783 mmol) and TBSCl (94.4 g, 626 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 15 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 19/1) to afford **S3** (209 g, 77%, 2 steps) as a colorless oil.

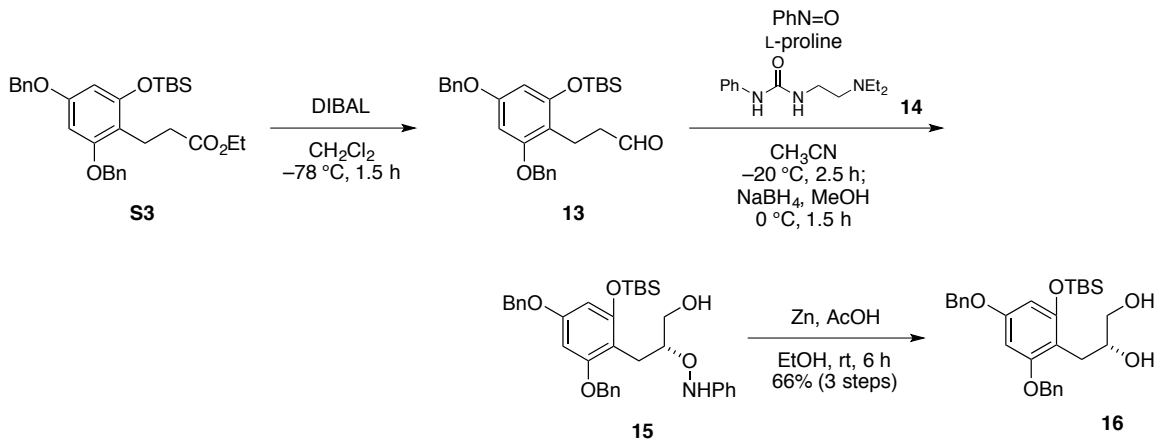
IR (ATR, cm^{-1}): 2953, 2930, 2859, 1732, 1605, 1586, 1431.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.42-7.35 (m, 8H), 7.28-7.24 (m, 2H), 6.25 (d, J = 2.3 Hz, 1H), 6.07 (d, J = 2.3 Hz, 1H), 5.02 (s, 2H), 4.98 (s, 2H), 4.10 (q, J = 7.4 Hz, 2H), 2.94 (t, J = 8.2 Hz, 2H), 2.46 (t, J = 8.2 Hz, 2H), 1.22 (t, J = 7.4 Hz, 3H), 0.99 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 173.4, 158.1, 158.0, 154.7, 137.1, 136.9, 128.5, 128.4, 127.9, 127.6, 127.3, 126.8, 112.6, 98.3, 93.7, 70.0, 69.9, 59.9, 34.0, 25.6, 19.3, 18.1, 14.2, –4.3.

HRMS (ESI): Calcd for $C_{31}H_{40}O_5SiNa$ [$(M+Na)^+$], 543.2558, found 543.2537.

Synthesis of Diol **16**



To a solution of **S3** (106 g, 203 mmol) in CH_2Cl_2 (1.0 L) was added DIBAL (239 mL, 244 mmol, 1.02 M solution in *n*-hexane) over 1 hour at –78 °C. The resulting mixture was stirred at the same temperature for 1.5 hours. Then the reaction mixture was quenched with MeOH (6.0 mL). The resulting mixture was diluted with 1 M HCl (1.4 L) and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **13** was applied to the following reaction without further purification.

To a solution of the crude material including **13** in CH_3CN (660 mL) were added nitrosobenzene (21.7 g, 203 mmol), L-proline (5.85 mg, 50.8 mmol) and urea **14**[2] at –20 °C. After 2.5 hours, MeOH (35 mL) and $NaBH_4$ (2.37 g, 81.3 mmol) were added at the same temperature. The resulting mixture was stirred at –20 °C for 1.5 hours. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **15** was applied to the following reaction without further purification.

To a solution of the crude material including **15** in EtOH (500 mL) were added AcOH (500 mL) and zinc powder (133 g, 2.03 mol). The resulting mixture was stirred at room temperature for 6 hours. Then the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 4/1 to 2/1) to afford diol **16** (66 g, 66% 3 steps, 98% ee) as a yellow oil. The enantiomeric excess value (ee) of **16** was determined by chiral HPLC analysis.

HPLC: (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA = 10/1, 1.0 mL/min, 254 nm, τ_{major} 11.7 min, τ_{minor} 8.6 min).

$[\alpha]_D^{25}$ +2.2 (*c* 1.00, $CHCl_3$, 98% ee).

IR (film, cm^{-1}): 3412, 2954, 2930, 2884, 2859, 1608, 1586, 1431, 1387.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.30 (m, 10H), 6.32 (d, *J* = 2.3 Hz, 1H), 6.11 (d, *J* = 2.3 Hz, 1H), 5.01 (s, 2H), 5.00 (s, 2H), 3.86 (quintet, *J* = 2.8 Hz, 1H), 3.52 (dd, *J* = 11.3, 2.8 Hz, 1H), 3.42 (dd, *J* = 11.3, 6.2 Hz, 1H), 2.87 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.83 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.63 (brs, 1H), 2.21 (brs, 1H), 0.99 (s, 9H), 0.192 (s, 3H), 0.186 (s, 3H).

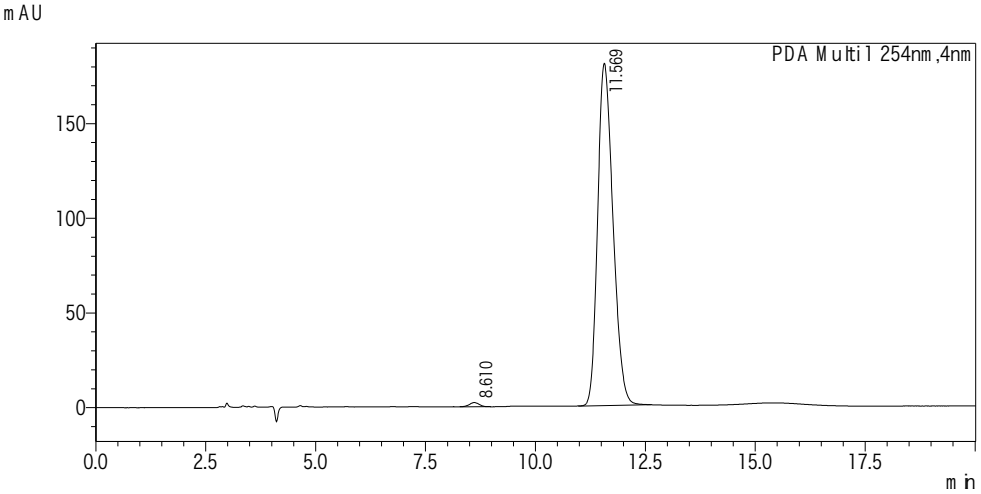
^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.3, 158.2, 155.1, 136.8, 136.3, 128.7, 128.6, 128.1, 128.0, 127.4, 127.2, 126.8, 109.7, 98.7, 94.0, 72.1, 70.5, 70.1, 65.9, 27.2, 25.7, 18.2, –4.17, –4.25.

HRMS (ESI): Calcd for $C_{29}H_{38}O_5SiNa$ $[(M+Na)^+]$ 517.2399, found 517.2381.

2. Poe, S. L.; Bogdan, A. R.; Mason, B. P.; Steinbacher, J. L.; Opalka, S. M.; McQuade, D. T. *J. Org. Chem.* **2009**, *74*, 1574–1580.

The racemic diol (±)-**16** was prepared by similar procedure to prepare optical active compound exception for employment with racemic catalyst.

Optically Active: Diol (+)-**16**



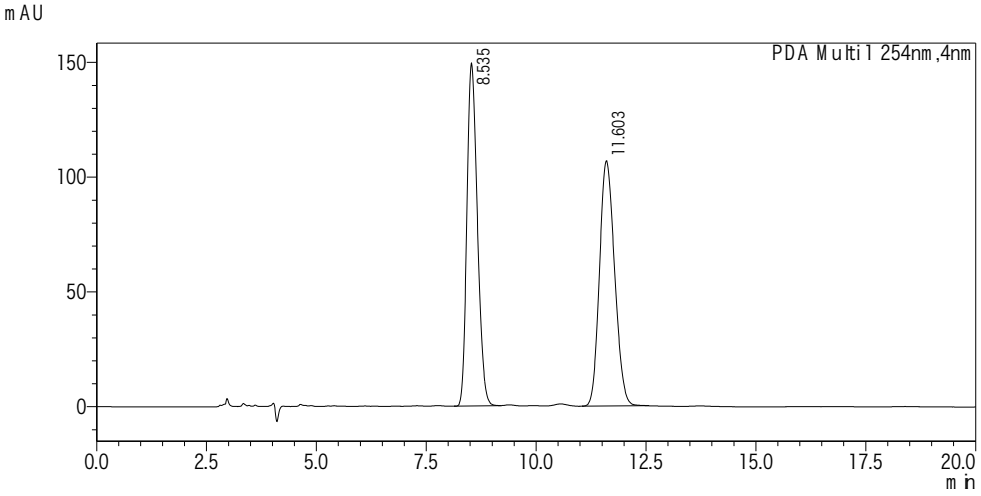
<Peak Report>

PDA Ch1 254nm

Peak#	Retention time	Area	Hight	Area%
1	8.610	34058	2111	0.770
2	11.569	4388208	176669	99.230

DAICEL CHIRALCEL OD-H, *n*-hexane/*i*-PrOH = 10/1, Flow rate 1.0 mL/min, 254 nm

Racemic: Diol (±)-**16**



<Peak Report>

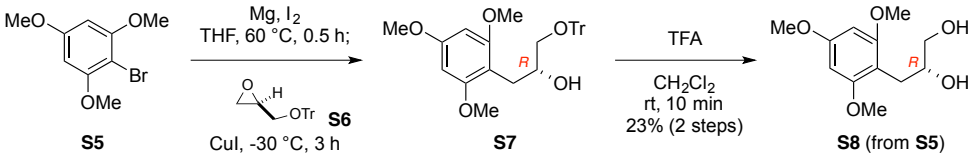
PDA Ch1 254nm

Peak#	Retention time	Area	Hight	Area%
1	8.535	2478814	143174	49.142
2	11.603	2565397	105373	50.858

DAICEL CHIRALCEL OD-H, *n*-hexane/*i*-PrOH = 10/1, Flow rate 1.0 mL/min, 254 nm

Since a determination of the absolute configuration of **16** by the modified Mosher method was difficult, we decided to prepare the authentic sample (*R*)-**S8** from chiral epoxide **S6** as shown in the following scheme. After transmetalation of bromide **S5**, copper catalyzed epoxide opening reaction of **S6** with the Grignard reagent proceeded smoothly to provide **S6**. Removal trityl group by TFA, the desired diol **S8** was obtained in optical active form.

Synthesis of (*R*)-**S8** from **S5**



To a suspension of magnesium ribbon (29 mg, 1.2 mmol) in THF (1.3 mL) were added I_2 (1 small amount) and a solution of **S5** (300 mg, 1.21 mmol) in THF (0.5 mL). After 0.5 hours, CuI (23 mg, 0.12 mmol) and a solution of **S6** (383 mg, 1.21 mmol) in THF (0.5 mL) were added at –30 °C. The resulting mixture was stirred at the same temperature for 3 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S7** was applied to the following reaction without further purification.

To a solution of the crude material including **S7** in CH_2Cl_2 (1.0 mL) was added TFA (0.1 mL) at room temperature. The resulting mixture was stirred at the same temperature for 10 minutes. Then the reaction mixture was quenched with Et_3N and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/4) to afford (*R*)-**S8** (from **S5**, 30 mg, 23% 2 steps, 99% ee) as a colorless solid. The enantiomeric excess value (ee) of (*R*)-**S8** was determined by chiral HPLC analysis.

HPLC: (DAICEL CHIRALCEL AS-H, *n*-hexane/IPA = 9/1, 1.0 mL/min, 254 nm, τ_{major} 18.5 min, τ_{minor} 16.7 min).

$[\alpha]_D^{25}$ –1.7 (*c* 1.00, $CHCl_3$, 99% ee).

IR (film, cm^{-1}): 3311, 2941, 2890, 2837, 1594, 1495, 1452, 1415.

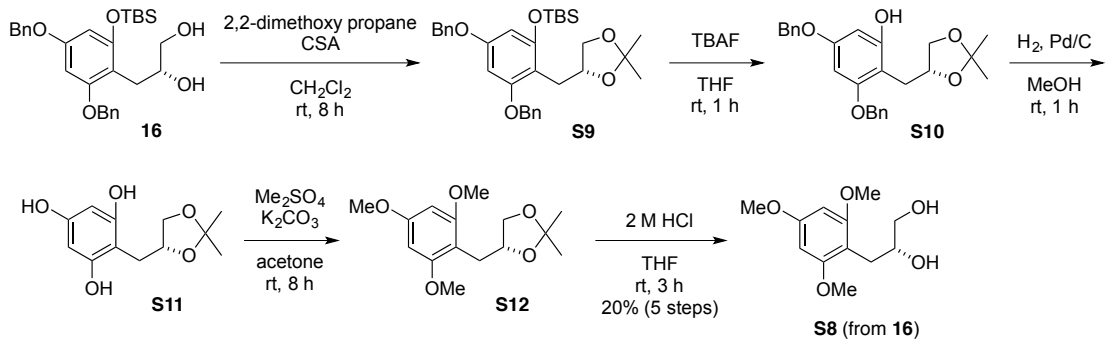
^{1}H NMR (500 MHz, CDCl3, δ): 6.16 (s, 2H), 3.87 (quintet, *J* = 4.5 Hz, 1H), 3.82 (s, 6H), 3.81 (s, 3H), 3.51 (dd, *J* = 11.3, 3.4, 1H), 3.44 (dd, *J* = 11.3, 5.1 Hz, 1H), 2.88 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.83 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.60 (brs, 1H), 2.39 (brs, 1H).

^{13}C NMR (125 MHz, CDCl3, δ): 159.8, 158.8, 106.3, 90.7, 72.0, 65.8, 55.6, 55.3, 26.3.

HRMS (ESI): Calcd for $C_{12}H_{18}O_5Na$ [$(M+Na)^+$] 265.1052, found 265.1046.

Conversion from our synthetic intermediate **16** to the diol **S8** was performed by changing the protecting group from benzyl and TBS to the methyl ethers as shown in the following scheme.

Synthesis of **S8** from **16**



To a solution of **16** (1.00 g, 2.02 mmol) in CH_2Cl_2 (20 mL) were added 2,2-dimethoxy propane (0.37 mL, 3.0 mmol) and 10-camphor sulfonic acid (CSA, 47 mg, 0.20 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 8 hours. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was filtered through a pad of silica gel (Eluted with EtOAc) and evaporated under reduced pressure. The crude material including **S9** was applied to the following reaction without further purification.

To a solution of the crude material including **S9** in THF (10 mL) was added TBAF (2.0 mL, 2.0 mmol, 1 M solution in THF) at room temperature. The resulting mixture was stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was filtered through a pad of silica gel (Eluted with EtOAc) and evaporated under reduced pressure. The crude material including **S10** was applied to the following reaction without further purification.

To a solution of the crude material including **S10** in MeOH (20 mL) was added 5% Pd/C (215 mg) at room temperature. The resulting mixture was stirred at the same temperature under ordinary hydrogen pressure (balloon) for 1 hour. Then the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including **S11** was applied to the following reaction without further purification.

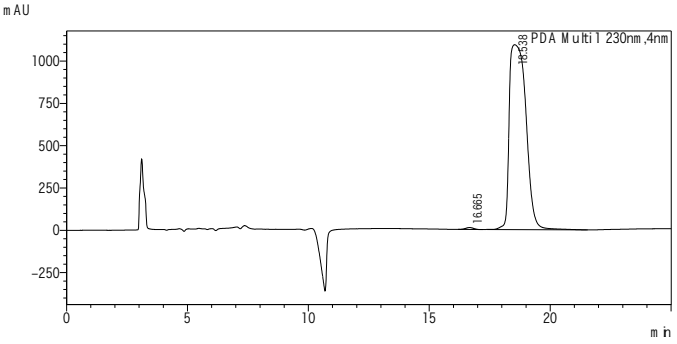
To a solution of the crude material including **S11** in acetone (10 mL) were added K_2CO_3 (838 mg, 6.06 mmol) and Me_2SO_4 (0.57 mL, 6.1 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 8 hours. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S12** was applied to the following reaction without further purification.

To a solution of the crude material including **S12** in THF (10 mL) was added 2 M HCl (2.0 mL) at room temperature. The resulting mixture was stirred at the same temperature for 3 hours. Then the reaction mixture was diluted with H_2O and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/4) to afford **S8** (from **16**, 97 mg, 20% 5 steps, 98% ee) as a colorless solid.

Since the all spectral data ($[\alpha]_D$, ^1H NMR, ^{13}C NMR, IR, HRMS and HPLC) of **S8** derived from **16**, were in full agreement with (*R*)-**S8**, which was prepared from **S5** and **S6**, the absolute configuration of **16** was concluded to 3*R*.

According to the preparation of optical active **S8**, racemic diol **S8** was synthesized from racemic **16**, described in above. Confirmation of the absolute configuration and enantio excess of **16** was accomplished by comparison with the chiral HPLC analysis of racemic as well as optical active **S8** derived from **16** and **6S**, as shown in the following.

Optically Active: Diol (*R*)-**S8** Derived from **5S** and **6S**

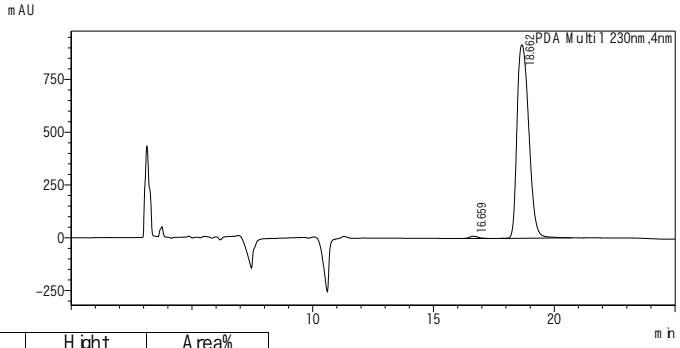


PDA Ch1 230nm

Peak#	Retention time	Area	Hight	Area%
1	16.665	274272	11415	0.519
2	18.538	52522682	1091014	99.481

DAICEL CHIRALCEL AS-H, *n*-hexane/*i*-PrOH = 9/1, Flow rate 1.0 mL/min, 230 nm

Optically Active: Diol **S8** Derived from **16**

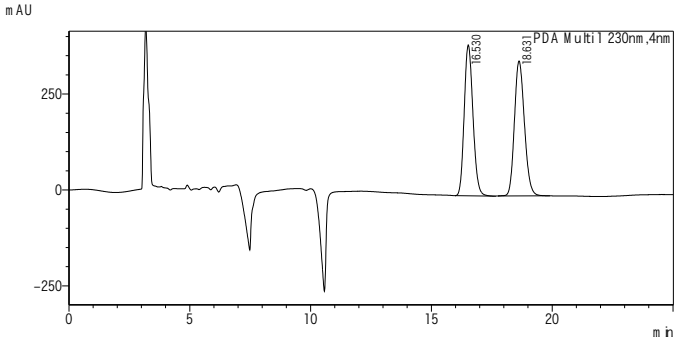


PDA Ch1 230nm

Peak#	Retention time	Area	Hight	Area%
1	16.659	259271	10171	0.825
2	18.662	31184263	910372	99.175

DAICEL CHIRALCEL AS-H, *n*-hexane/*i*-PrOH = 9/1, Flow rate 1.0 mL/min, 230 nm

Racemic: Diol (±)- **S8**

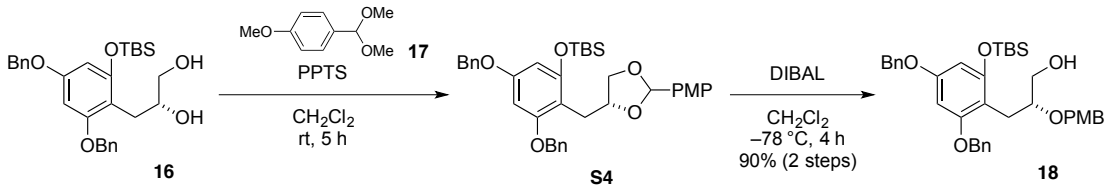


PDA Ch1 230nm

Peak#	Retention time	Area	Hight	Area%
1	16.530	9906921	388437	49.458
2	18.631	10124111	349706	50.542

DAICEL CHIRALCEL AS-H, *n*-hexane/*i*-PrOH = 9/1, Flow rate 1.0 mL/min, 230 nm

Synthesis of PMB Ether **18**



To a solution of **16** (23.9 g, 48.3 mmol) in CH_2Cl_2 (120 mL) were added *p*-anisaldehyde dimethyl acetal (**17**, 12.3 mL, 72.5 mmol) and PPTS (1.21 g, 4.83 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 5 hour. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S4** was applied to the following reaction without further purification.

To a solution of the crude material including **S4** in CH_2Cl_2 (500 mL) was added DIBAL (104 mL, 106 mmol, 1.02 M solution in CH_2Cl_2) over 1 hour at –78 °C. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was quenched with MeOH (10 mL). The resulting mixture was diluted with 1 M HCl (1.0 L) and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 9/1) to afford **18** (26.6 g, 90%, 2 steps) as a colorless oil.

$[\alpha]_D^{24}$ –5.8 (*c* 1.05, $CHCl_3$).

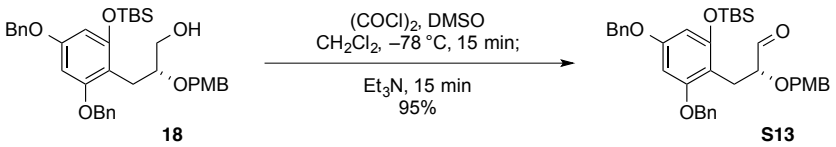
IR (film, cm^{-1}): 2955, 2932, 2859, 1605, 1587, 1512, 1431.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.45-7.30 (m, 10H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.08 (d, *J* = 2.3 Hz, 1H), 5.02-4.95 (m, 4H), 4.49 (d, *J* = 11.3 Hz, 1H), 4.30 (d, *J* =11.3 Hz, 1H), 3.78 (s, 3H), 3.67 (m, 1H), 3.52 (m, 1H), 3.44 (m, 1H), 2.98 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.74 (dd, *J* = 13.0, 9.3 Hz, 1H), 2.17 (m, 1H), 0.98 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.9, 158.3, 158.1, 155.0, 136.8, 136.6, 130.9, 129.1, 128.50, 128.46, 128.0, 127.8, 127.6, 127.2, 113.5, 109.6, 98.4, 93.6, 79.4, 70.8, 70.3, 70.0, 64.1, 55.0, 25.8, 24.8, 18.2, –4.14, –4.22.

HRMS (ESI): Calcd for $C_{37}H_{46}O_6SiNa$ $[(M+Na)^+]$ 637.2975, found 637.2956

Synthesis of Aldehyde **S13**



To a solution of oxalyl chloride (0.70 mL, 8.2 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of DMSO (0.86 mL, 12 mmol) in CH_2Cl_2 (10 mL) at –78 °C. After 15 minutes, a solution of **18** (3.36 g, 5.47 mmol) in CH_2Cl_2 (10 mL) was added at –78 °C. After 15 minutes, Et_3N (4.6 mL, 33 mmol) was added at –78 °C. The resulting mixture was stirred at the same temperature for 15 minutes. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 9/1) to afford **S13** (3.17 g, 95%) as a colorless oil.

$[\alpha]_D^{24}$ +22.5 (*c* 0.96, $CHCl_3$).

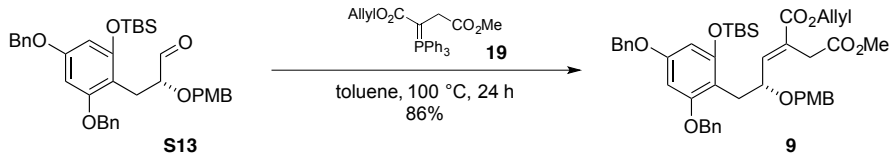
IR (film, cm^{-1}): 2955, 2932, 2859, 1734, 1609, 1589, 1512, 1431.

^1H NMR (500 MHz, $CDCl_3$, δ): 9.48 (d, *J* = 2.8 Hz, 1H), 7.42-7.28 (m, 10H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.24 (d, *J* = 2.3 Hz, 1H), 6.06 (d, *J* = 2.3 Hz, 1H), 4.98 (s, 2H), 4.96 (d, *J* = 11.3 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.46 (d, *J* = 11.3 Hz, 1H), 4.36 (d, *J* = 11.3 Hz, 1H), 3.96-3.91 (m, 1H), 3.77 (s, 3H), 3.08-2.98 (m, 2H), 0.97 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H).

^{13}C NMR (125 MHz, CDCl3, δ): 202.4, 159.1, 158.5, 158.3, 155.1, 136.8, 136.7, 129.5, 129.4, 128.5, 128.4, 127.9, 127.8, 127.2, 113.6, 107.5, 98.2, 93.5, 82.3, 71.8, 70.0, 69.9, 55.0, 25.7, 24.7, 18.1, –4.28, –4.32.

HRMS (ESI): Calcd for $C_{37}H_{44}O_6SiNa$ $[(M+Na)^+]$ 635.2794, found 635.2799.

Synthesis of Diester **9**

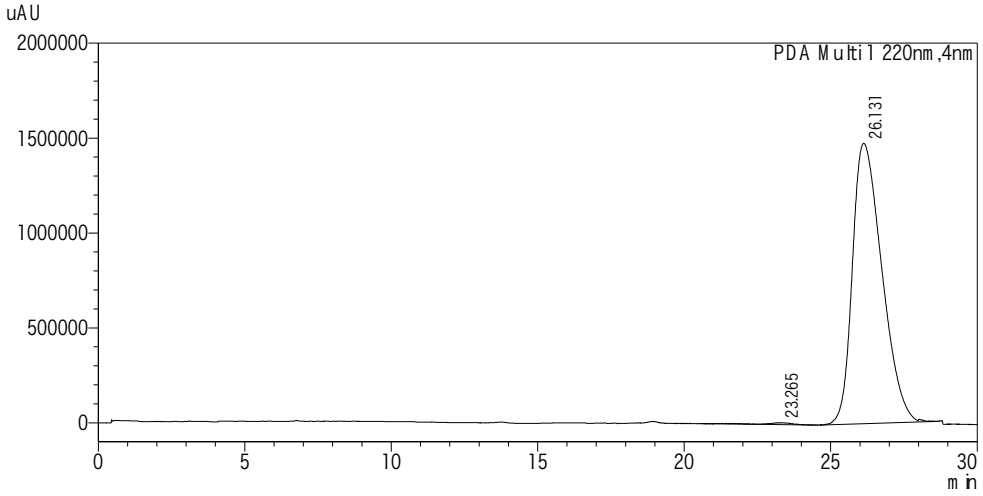


To a solution of **S13** (2.56 g, 4.18 mmol) in toluene (4.0 mL) was added **19**[3] (5.09 g, 12.5 mmol). The resulting mixture was stirred at 100 °C for 24 hours. Then the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 9/1) to afford **9** (2.74 g, 86%, 98% ee) as a colorless oil. The enantiomeric excess value (ee) of **9** was determined by chiral HPLC analysis.

HPLC: (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA = 100/1, 1.0 mL/min, 220 nm, τ_{major} 26.1 min, τ_{minor} 23.3 min).
$[\alpha]_D^{24}$ +11.9 (*c* 1.05, $CHCl_3$, 98% ee).
IR (film, cm^{-1}): 2953, 2932, 2859, 1742, 1719, 1609, 1587, 1512, 1436.
^1H NMR (500 MHz, $CDCl_3$, δ): 7.40-7.29 (m, 10H), 7.12 (d, *J* = 9.1 Hz, 1H), 6.88 (d, *J* = 9.1 Hz, 2H), 6.78 (d, *J* = 9.1 Hz, 2H), 6.19 (d, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.3 Hz, 1H), 5.85 (ddt, *J* = 17.0, 10.2, 5.7 Hz, 1H), 5.26 (ddd, *J* = 17.0, 1.7, 1.1 Hz, 1H), 5.19 (ddd, *J* = 10.2, 1.7, 1.1 Hz, 1H), 4.99 (s, 2H), 4.91 (d, *J* = 11.9 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.59 (ddt, *J* = 13.0, 5.7, 1.1 Hz, 1H), 4.53 (ddt, *J* = 13.0, 5.7, 1.1 Hz, 1H), 4.44 (d, *J* = 11.3 Hz, 1H), 4.41 (td, *J* = 9.1, 6.2 Hz, 1H), 4.23 (d, *J* = 11.3 Hz, 1H), 3.77 (s, 3H), 3.55 (s, 3H), 3.04 (dd, *J* = 13.0, 5.7 Hz, 1H), 2.91 (dd, *J* = 13.0, 9.1 Hz, 1H), 2.81 (s, 2H), 0.98 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.8, 166.1, 159.0, 158.5, 158.3, 155.3, 145.8, 136.9, 136.8, 132.1, 130.4, 129.3, 128.6, 128.4, 127.9, 127.7, 127.3, 127.1, 117.9, 113.6, 108.5, 98.2, 93.4, 74.2, 70.6, 70.0, 65.4, 55.2, 55.1, 51.7, 31.8, 28.8, 25.8, 18.2, –4.29, –4.37.
HRMS (ESI): Calcd for $C_{45}H_{54}O_9SiNa$ [$(M+Na)^+$] 789.3401, found 789.3429.

3. (a) Castaneda, F.; Silva, P.; Acuna, C.; Garland, M. T.; Bunton, C. A. *J. Mol. Struct.* **2013**, *1034*, 51–56. (b) Bacaloglu, R.; Blasko, A.; Bunton, C. A.; Cerichelli, G. F.; Rivera, C. E. *J. Chem. Soc. Perkin Trans. 2* **1995**, 965–972. (c) Cameron, A. F.; Duncanson, F. D.; Freer, A. A.; Armstrong, V. W.; Ramage, R. *J. Chem. Soc. Perkin Trans. 2* **1975**, 1030–1036.

Optically Active: Diester (+)-**9**



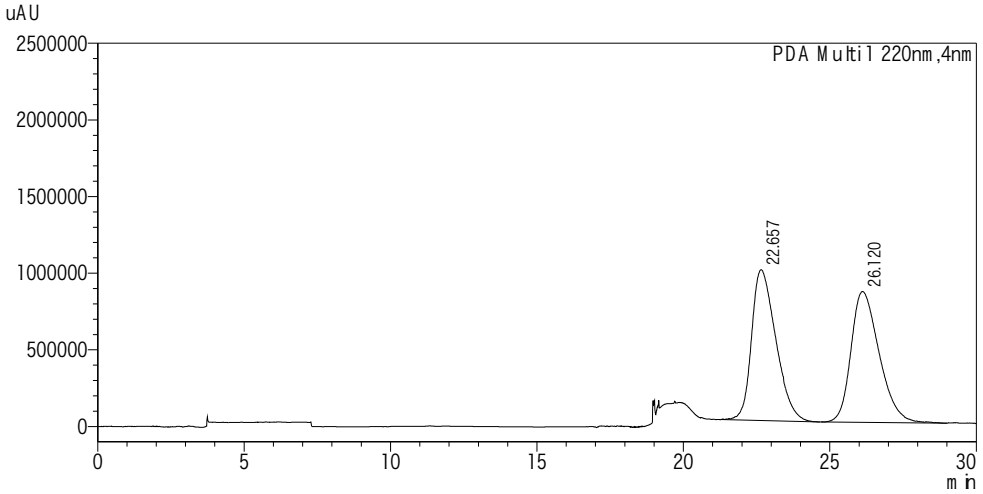
<Peak Report>

PDA Ch1 220nm

Peak#	Retention time	Area	Hight	Area%
1	23.265	642276	9432	0.617
2	26.131	103514073	1472524	99.383

DAICEL CHIRALCEL OD-H, *n*-hexane/*i*-PrOH = 100/1, Flow rate 1.0 mL/min, 220 nm

Racemic: Diester (±)-**9**



<Peak Report>

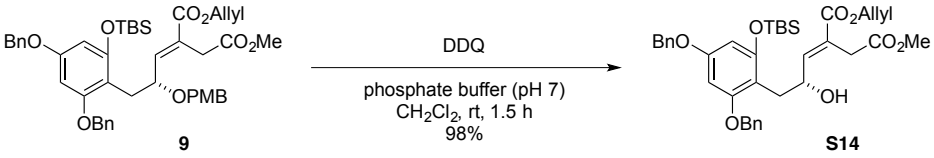
PDA Ch1 220nm

Peak#	Retention time	Area	Hight	Area%
1	22.657	56836440	981596	49.816
2	26.120	57256638	851929	50.184

DAICEL CHIRALCEL OD-H, *n*-hexane/*i*-PrOH = 100/1, Flow rate 1.0 mL/min, 220 nm

II. Total Synthesis of Teadenol A (**1**)

Synthesis of Alcohol **S14**



To a solution of **9** (7.00 mg, 9.13 mmol) in a mixture of CH_2Cl_2 (180 mL) and phosphate buffer (pH 7, 60 mL) was added DDQ (4.14 g, 18.3 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1.5 hours. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 4/1 to 3/1) to afford **S14** (760 mg, 98%) as a colorless oil.

$[\alpha]_D^{25}$ –13.1 (*c* 1.05, $CHCl_3$).

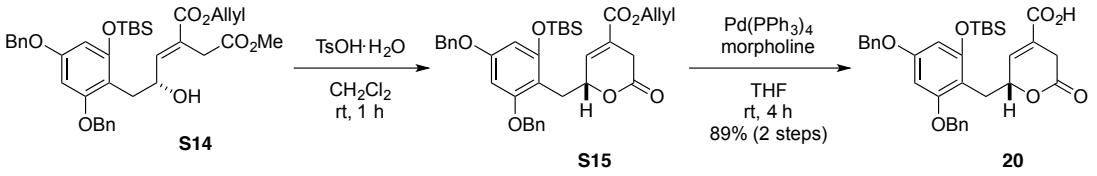
IR (film, cm^{-1}): 2953, 2932, 2859, 1742, 1719, 1701, 1605, 1589, 1431.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.29 (m, 10H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 6.07 (d, *J* = 2.3 Hz, 1H), 5.87 (ddt, *J* = 11.3, 10.2, 5.7 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.1 Hz, 1H), 4.99 (s, 2H), 4.98 (s, 2H), 4.67-4.51 (m, 3H), 3.59 (s, 3H), 3.21 (d, *J* = 16.4 Hz, 1H), 3.16 (d, *J* = 16.4 Hz, 1H), 2.96 (dd, *J* = 13.0, 6.5 Hz, 1H), 2.92 (dd, *J* = 13.0, 5.7 Hz, 1H), 2.63 (brs 1H), 0.99 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 171.3, 166.4, 158.5, 158.4, 155.3, 146.81, 146.75, 136.8, 136.6, 132.0, 128.6, 127.9, 127.2, 125.6, 117.9, 117.8, 108.6, 98.2, 93.4, 70.2, 70.1, 68.9, 68.8, 65.4, 52.0, 51.9, 32.1, 30.4, 25.7, 18.2, –4.14, –4.30.

HRMS (ESI): Calcd for $C_{37}H_{46}O_8SiNa$ $[(M+Na)^+]$ 669.2864, found 669.2854.

Synthesis of Dihydropyranone **20**



To a solution of **S14** (11.1 g, 17.2 mmol) in CH_2Cl_2 (340 mL) was added $TsOH \cdot H_2O$ (326 mg, 1.72 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S15** was applied to the following reaction without further purification.

To a solution of the crude material including **S15** in THF (170 mL) were added $Pd(PPh_3)_4$ (1.99 g, 1.72 mmol) and morpholine (1.6 mL, 19 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction mixture was quenched with 2 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 3/1 to 3/2) to afford carboxylic acid **20** (8.80 g, 89%, 2 steps) as a colorless solid.

$[\alpha]_D^{25}$ –45.6 (*c* 1.13, $CHCl_3$).

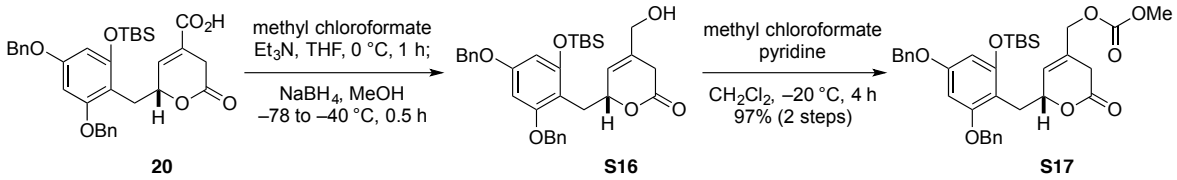
IR (film, cm^{-1}): 3034, 2955, 2932, 2885, 1742, 1719, 1605, 1589, 1431.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.29 (m, 10H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.09 (d, *J* = 2.3 Hz, 1H), 5.30-5.24 (1H, m), 5.00 (s, 2H), 4.99 (s, 2H), 3.23-3.14 (m, 2H), 3.11-3.03 (m, 2H), 0.96 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 169.5, 168.1, 159.1, 158.6, 155.5, 138.8, 136.7, 136.6, 128.63, 128.57, 128.04, 127.97, 127.3, 127.2, 123.8, 106.2, 98.20, 98.18, 93.6, 93.5, 78.4, 70.20, 70.17, 70.13, 29.1, 28.6, 25.7, 18.2, –4.28.

HRMS (ESI): Calcd for $C_{33}H_{38}O_7SiNa$ $[(M+Na)^+]$ 597.2304, found 597.2279.

Synthesis of Allyl Carbonate **S17**



20 **S16** **S17**

To a solution of **20** (8.80 g, 15.3 mmol) in THF (150 mL) were added Et_3N (3.2 mL, 17 mmol) and methyl chloroformate (1.3 mL, 17 mmol) at 0 °C. After 1 hour, the reaction mixture was filtered through a pad of Celite and washed with THF (50 mL). To the resulting filtrate was added MeOH (50 mL) and $NaBH_4$ (2.32 g, 61.2 mmol) at –78 °C. After 0.5 hours, the resulting mixture was warn up to –40 °C and stirred at the same temperature for 0.5 hours. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S16** was applied to the following reaction without further purification.

To a solution of the crude material including **S16** in CH_2Cl_2 (150 mL) were added pyridine (7.4 mL, 92 mmol) and methyl chloroformate (3.5 mL, 46 mmol) at –20 °C. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 4/1) to afford **S17** (9.20 g, 97%, 2 steps) as a colorless oil.

$[\alpha]_D^{26}$ –21.5 (*c* 1.18, $CHCl_3$).

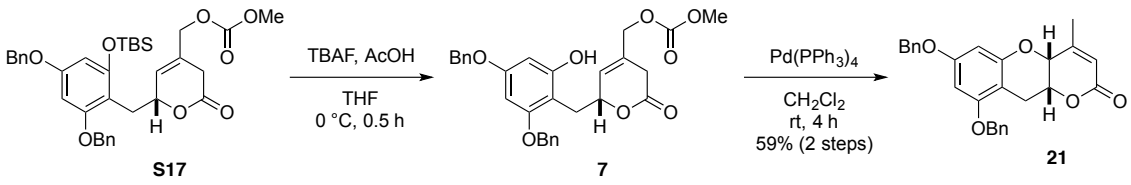
IR (film, cm^{-1}): 2955, 2932, 2859, 1742, 1605, 1589, 1431.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.42-7.30 (m, 10H), 6.28 (d, *J* = 2.3 Hz, 1H), 6.08 (d, *J* = 2.3 Hz, 1H), 5.86-5.82 (m, 1H), 5.17 (brs, 1H), 5.00 (s, 2H), 4.98 (s, 2H), 4.47 (d, *J* = 13.0 Hz, 1H), 4.41 (d, *J* = 13.0 Hz, 1H), 3.76 (s, 3H), 2.96 (dd, *J* = 13.0, 6.2 Hz, 1H), 3.00 (dd, *J* = 13.0, 8.5 Hz, 1H), 2.94 (d, *J* = 21.0 Hz 1H), 2.83 (d, *J* = 21.0 Hz 1H), 0.96 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.6, 158.8, 158.6, 155.4, 155.3, 136.8, 136.7, 128.6, 128.5, 127.95, 127.86, 127.3, 127.2, 124.9, 107.1, 98.2, 93.5, 78.2, 70.1, 68.4, 54.9, 30.6, 29.5, 25.6, 18.1, –4.23, –4.33.

HRMS (ESI): Calcd for $C_{35}H_{42}O_8SiNa$ $[(M+Na)^+]$ 641.2511, found 641.2541.

Synthesis of Lactone **21**



S17 **7** **21**

To a solution of **S17** (980 mg, 1.58 mmol) in THF (16 mL) were added AcOH (0.18 mL, 3.2 mmol) and TBAF (1.7 mL, 1.7 mmol, 1 M solution in THF) at 0 °C. The resulting mixture was stirred at the same temperature for 0.5 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with 1 M HCl, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **7** was applied to the following reaction without further purification.

To a solution of the crude material including **7** in CH_2Cl_2 (80 mL) was added $Pd(PPh_3)_4$ (183 mg, 0.158 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/$CHCl_3$/EtOAc = 5/4/1) to afford **21** (400 mg, 59%, 2 steps) as a colorless solid.

$[\alpha]_D^{25}$ +88.8 (*c* 0.94, $CHCl_3$).

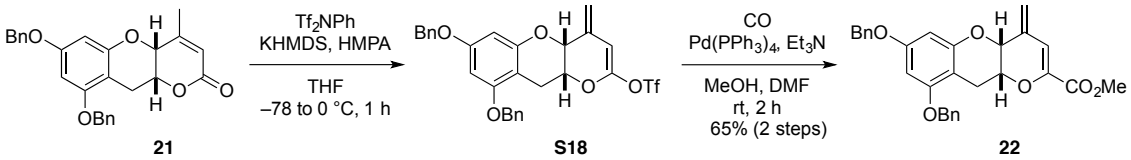
IR (ATR, cm^{-1}): 1725, 1621, 1594, 1500.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.43-7.29 (m, 10H), 6.25 (d, *J* = 2.3 Hz, 1H), 6.14 (d, *J* = 2.3 Hz, 1H), 5.93 (d, J = 1.7 Hz, 1H), 5.01 (s, 2H), 4.98 (s, 2H), 4.08 (quintet, *J* = 2.8 Hz, 1H), 4.34 (d, *J* = 1.7 Hz, 1H), 3.16 (dd, *J* = 17.6, 2.3 Hz, 1H), 2.97 (dd, *J* = 17.6, 5.7 Hz, 1H), 2.16 (d, *J* = 1.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 163.6, 158.7, 157.8, 154.5, 154.1, 136.7, 128.54, 128.52, 128.0, 127.9, 127.5, 127.2, 119.3, 99.7, 94.4, 94.2, 71.1, 70.1, 70.0, 69.1, 23.9, 20.7.

HRMS (ESI): Calcd for $C_{27}H_{24}O_5Na$ $[(M+Na)^+]$ 451.1521, found 451.1516.

Synthesis of Ester **22**



To a solution of **21** (450 mg, 1.05 mmol) in THF (10 mL) were added HMPA (0.37 mL, 2.1 mmol) and KHMDS (4.2 mL, 2.1 mmol, 0.5 M solution in toluene) at –78 °C. After 1 hour, Tf_2NPh (563 mg, 1.58 mmol) was added at –78 °C. After 1 hour, the resulting mixture was warm up to 0 °C and stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S18** was applied to the following reaction without further purification.

To a solution of the crude material including **S18** in a 9:1 mixture of MeOH and DMF (total 10 mL) were added $Pd(PPh_3)_4$ (121 mg, 0.105 mmol) and Et_3N (440 μL, 3.15 mmol) at room temperature. The resulting mixture was stirred at the same temperature under ordinary carbon monooxide pressure (balloon) for 2 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/$CHCl_3$/EtOAc = 50/50/1 to 10/10/1) to afford **22** (323 mg, 65%) as a colorless solid.

$[\alpha]_D^{22}$ +320.5 (*c* 0.50, $CHCl_3$).

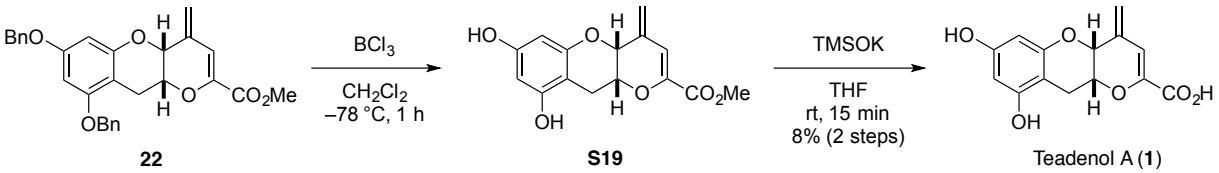
IR (film, cm^{-1}): 2922, 2851, 1734, 1719, 1618, 1595, 1499, 1458.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.46-7.28 (m, 10H), 6.64 (s, 1H), 6.24 (d, *J* = 2.3 Hz, 1H), 6.17 (d, *J* = 2.3 Hz, 1H), 5.38 (s, 1H), 5.31 (s, 1H), 4.99 (s, 2H), 4.96 (s, 2H), 4.56 (brs, 1H), 4.50-4.46 (m, 1H), 3.79 (s, 3H), 3.18 (dd, *J* = 17.8, 2.3 Hz, 1H), 2.94 (dd, *J* = 17.8, 5.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 163.6, 158.7, 157.8, 154.5, 154.1, 136.7, 128.54, 128.52, 128.0, 127.9, 127.5, 127.2, 119.3, 99.7, 94.4, 94.2, 71.1, 70.1, 70.0, 69.1, 23.9, 20.7.

HRMS (ESI): Calcd for $C_{29}H_{26}O_6Na$ [$(M+Na)^+$] 493.1627, found 493.1621.

Synthesis of Teadenol A (**1**)



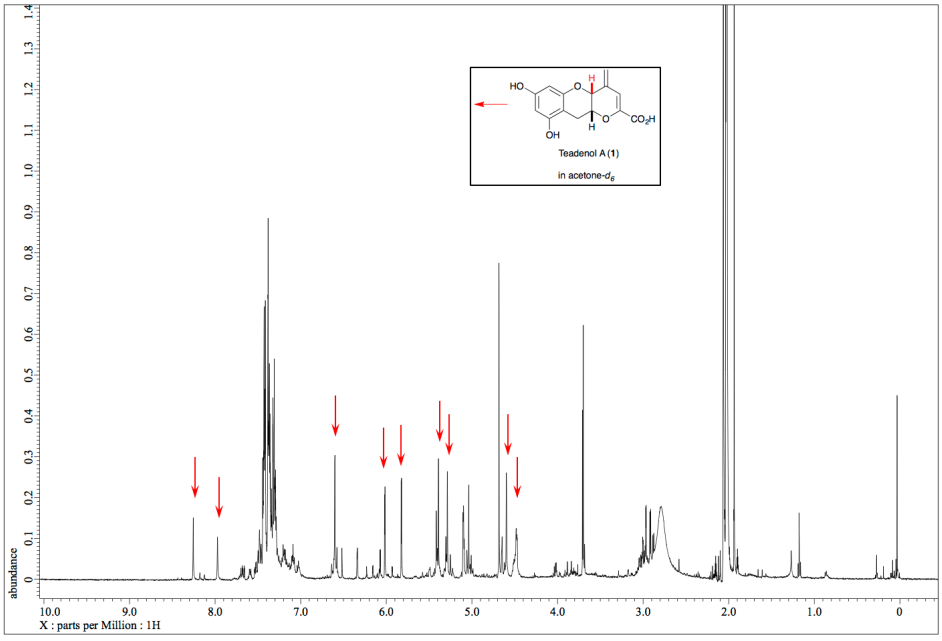
To a solution of **22** (160 mg, 0.340 mmol) in CH_2Cl_2 (10 mL) was added BCl_3 (1.4 mL, 1.4 mmol, 1 M solution in CH_2Cl_2) at –78 °C. The resulting mixture was stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S19** was applied to the following reaction without further purification.

To a solution of the crude material including **S19** in THF (3.5 mL) was added TMSOK (131 mg, 1.02 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 15 minutes. Then the reaction mixture was quenched with 1 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue (124 mg) was purified by column chromatography (ODS, H_2O/CH_3CN = 1/0 to 1/1) and preparative HPLC (Cosmosil 20D x 250 mm, gradient, 0% to 50% MeOH in H_2O, for 120 min, minute ramp, λ = 254 nm, flow rate; 3 mL/min) to afford **1** (7.3 mg, 8%, 2 steps) as a colorless solid.

$[\alpha]_D^{22}$ +451 (*c* 0.12, DMSO). Lit: $[\alpha]_D^{21}$ +468 (*c* 0.15, DMSO)[4].
IR (ATR, cm^{-1}): 3608, 3496, 3261, 1721, 1623, 1613, 1525, 1476.
^1H NMR (500 MHz, DMSO-d_6, δ): 9.37 (s, 1H), 9.03 (s, 1H), 5.69 (s, 1H), 6.57 (s, 1H), 5.97 (d, J = 2.3 Hz, 1H), 5.70 (d, J = 2.3 Hz, 1H), 5.45 (brs, 1H), 5.33 (brs, 1H), 4.63 (s, 1H), 4.43 (t, J = 3.4 Hz, 1H), 2.81 (d, J = 3.4 Hz, 2H).
^{13}C NMR (125 MHz, DMSO-d_6, δ): 163.1, 156.5, 156.3, 154.6, 144.0, 136.5, 118.0, 110.1, 96.8, 95.5, 94.2, 70.9, 70.8, 24.0.
HRMS (ESI): Calcd for $C_{14}H_{13}O_6$ [(M+H)$^-$] 277.0712, found 277.0707.

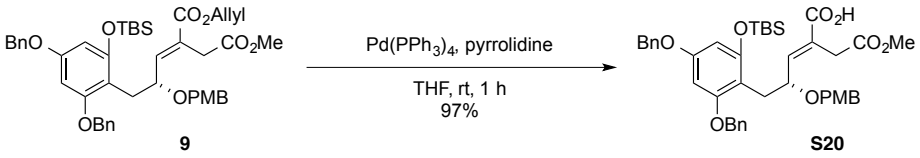
4. Wulandari, R. A.; Rani, A.; Amano, M.; Yanagita, T.; Tanaka, T.; Kouno, I.; Kawamura, D.; Ishimaru, K. *J. Nat. Med.* **2011**, *65*, 594–597.

500 MHz NMR spectrum of crude material of teadenol A (**1**)



III. Total Synthesis of Teadenol B (**2**)

Synthesis of Carboxylic Acid **S20**



To a solution of **9** (19.5 g, 25.4 mmol) in THF (100 mL) were added $Pd(PPh_3)_4$ (2.94 g, 2.54 mmol) and pyrrolidine (2.3 mL, 28 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1 hour. Then the reaction mixture was quenched with 1 M HCl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1) to afford **S20** (18.0 g, 97%) as a yellow amorphous.

$[\alpha]_D^{24}$ +15.9 (*c* 1.12, $CHCl_3$).

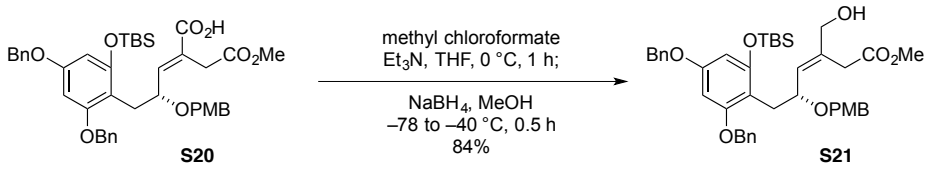
IR (ATR, cm^{-1}): 2950, 2929, 2855, 1739, 1690, 1701, 1603, 1584, 1511, 1432.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.29 (m, 10H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 9.1 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.20 (d, *J* = 2.3 Hz, 1H), 6.03 (d, *J* = 2.3 Hz, 1H), 4.99 (s, 2H), 4.89 (q, *J* = 11.3 Hz, 2H), 4.44 (d, *J* = 11.3 Hz, 1H), 4.50-4.39 (m, 1H), 4.23 (d, *J* = 11.3 Hz, 1H), 3.76 (s, 3H), 3.55 (s, 3H), 3.06 (dd, *J* = 13.0, 5.7 Hz, 1H), 2.91 (dd, *J* = 13.0, 9.1 Hz, 1H), 2.80 (s, 2H), 0.98 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 171.9, 170.7, 159.0, 158.5, 158.3, 155.3, 148.2, 136.9, 136.8, 130.3, 129.3, 128.6, 128.5, 127.94, 127.85, 127.4, 127.3, 126.6, 113.6, 108.4, 98.2, 93.4, 74.3, 70.7, 70.1, 70.0, 55.2, 51.8, 31.4, 28.7, 25.8, 18.2, –4.25, –4.38.

HRMS (ESI): Calcd for $C_{42}H_{50}O_9SiNa$ $[(M+Na)^+]$ 749.3095, found 749.3116.

Synthesis of Alcohol **S21**



To a solution of **S20** (18.0 g, 1.95 mmol) in THF (250 mL) were added Et_3N (5.2 mL, 37 mmol) and methyl chloroformate (2.1 mL, 27 mmol) at 0 °C. The resulting mixture was stirred at the same temperature for 1hour. The reaction mixture was filtered through a pad of Celite and washed with THF (100 mL). To the resulting filtrate was added MeOH (80 mL) and $NaBH_4$ (3.75 g, 99.2 mmol) at –78 °C. After 0.5 hours, the resulting mixture was warn up to –40 °C and stirred at the same temperature for 0.5 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 3/1) to afford **S21** (14.9 g, 84%) as a colorless oil.

$[\alpha]_D^{25}$ +39.3 (*c* 1.26, $CHCl_3$).

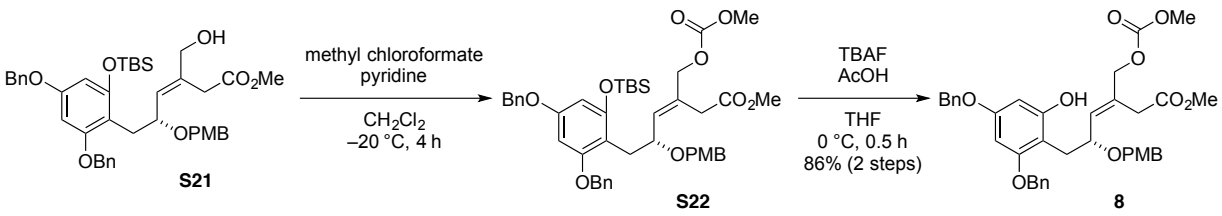
IR (film, cm^{-1}): 3450, 3032, 2953, 2930, 2859, 1736, 1605, 1589, 1512, 1435.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.29 (m, 10H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.22 (d, *J* = 2.3 Hz, 1H), 6.03 (d, *J* = 2.3 Hz, 1H), 5.58 (d, *J* = 9.1 Hz, 1H), 4.99 (s, 2H), 4.95 (d, *J* = 11.3 Hz, 1H), 4.91 (d, *J* = 11.3 Hz, 1H), 4.40 (d, *J* = 11.3 Hz, 1H), 4.32 (ddd, *J* = 9.3, 9.1, 5.1 Hz, 1H), 4.22 (d, *J* = 11.3 Hz, 1H), 3.97 (s, 2H), 3.76 (s, 3H), 3.53 (s, 3H), 3.01 (dd, *J* = 13.0, 5.1 Hz, 1H), 2.83 (dd, *J* = 13.0, 9.3 Hz, 1H), 2.73 (d, *J* = 16.2 Hz, 1H), 2.55 (d, *J* = 16.2, Hz, 1H), 0.99 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 172.1, 158.8, 158.5, 158.1, 155.2, 137.0, 136.9, 134.3, 132.5, 130.9, 129.2, 128.5, 128.4, 127.9, 127.8, 127.25, 127.17, 113.5, 109.6, 98.3, 93.6, 74.1, 70.1, 70.0, 69.9, 67.4, 55.1, 51.7, 33.0, 29.3, 25.8, 18.1, –4.29, –4.34.

HRMS (ESI): Calcd for $C_{42}H_{52}O_8SiNa$ $[(M+Na)^+]$ 735.3353, found 735.3324.

Synthesis of Phenol **8**



To a solution of **S21** (14.9 g, 20.9 mmol) in CH_2Cl_2 (200 mL) were added pyridine (10.0 mL, 125 mmol) and methyl chloroformate (4.8 mL, 63 mmol) at –20 °C. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S22** was applied to the following reaction without further purification.

To a solution of crude material including **S22** in THF (200 mL) were added AcOH (2.3 mL, 39 mmol) and TBAF (22.0 mL, 22 mmol, 1 M solution in THF) at 0 °C. The resulting mixture was stirred at the same temperature for 0.5 hours. Then the reaction mixture was quenched with 1 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 4/1 to 3/2) to afford **8** (11.1 g, 86%, 2 steps) as a colorless oil.

$[\alpha]_D^{25}$ +57.4 (*c* 1.20, $CHCl_3$).

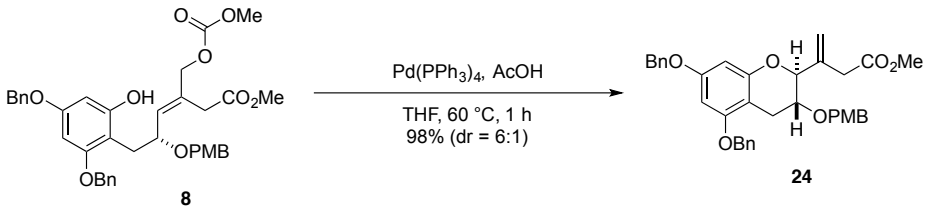
IR (film, cm^{-1}): 3290, 2955, 2395, 1736, 1611, 1589, 1512, 1456.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.93 (s, 1H), 7.41-7.29 (m, 10H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.27 (d, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 5.75 (d, *J* = 8.5 Hz, 1H), 5.00 (s, 2H), 4.95 (s, 2H), 4.63 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.5 Hz, 1H), 4.51 (d, *J* = 11.3 Hz, 1H), 4.33 (ddd, *J* = 8.5, 8.5, 2.3 Hz, 1H), 4.27 (d, *J* = 11.3 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.57 (s, 3H), 3.09 (d, *J* = 15.9 Hz, 1H), 2.97 (dd, *J* = 13.0, 2.3 Hz, 1H), 2.84 (dd, *J* = 13.0, 8.5 Hz, 1H), 2.80 (d, *J* = 15.9, Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.4, 159.2, 159.1, 157.8, 157.4, 155.3, 136.93, 136.89, 133.6, 130.2, 129.5, 129.0, 128.5, 128.4, 127.9, 127.8, 127.5, 127.2, 113.7, 106.2, 95.8, 93.0, 70.74, 70.68, 70.0, 69.9, 55.1, 54.8, 51.9, 33.2, 29.4.

HRMS (ESI) Calcd for $C_{38}H_{40}O_{10}Na$ [$(M+Na)^+$] 679.2505, found 679.2514.

Synthesis of Chromane **24**



To a solution of **8** (9.20 g, 14.0 mmol) in THF (280 mL) were added AcOH (0.80 mL, 14 mmol) and $Pd(PPh_3)_4$ (1.62 g, 1.40 mmol) at room temperature. The resulting mixture was stirred at 60 °C for 1 hour. Then the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 4/1) to afford **24** (7.94 g, total 98%, dr = 6:1) as a colorless solid. The diastereomer ratio (dr) of **24** was determined by ^{1}H NMR spectrum.

$[\alpha]_D^{24}$ –45.6 (*c* 0.78, $CHCl_3$).

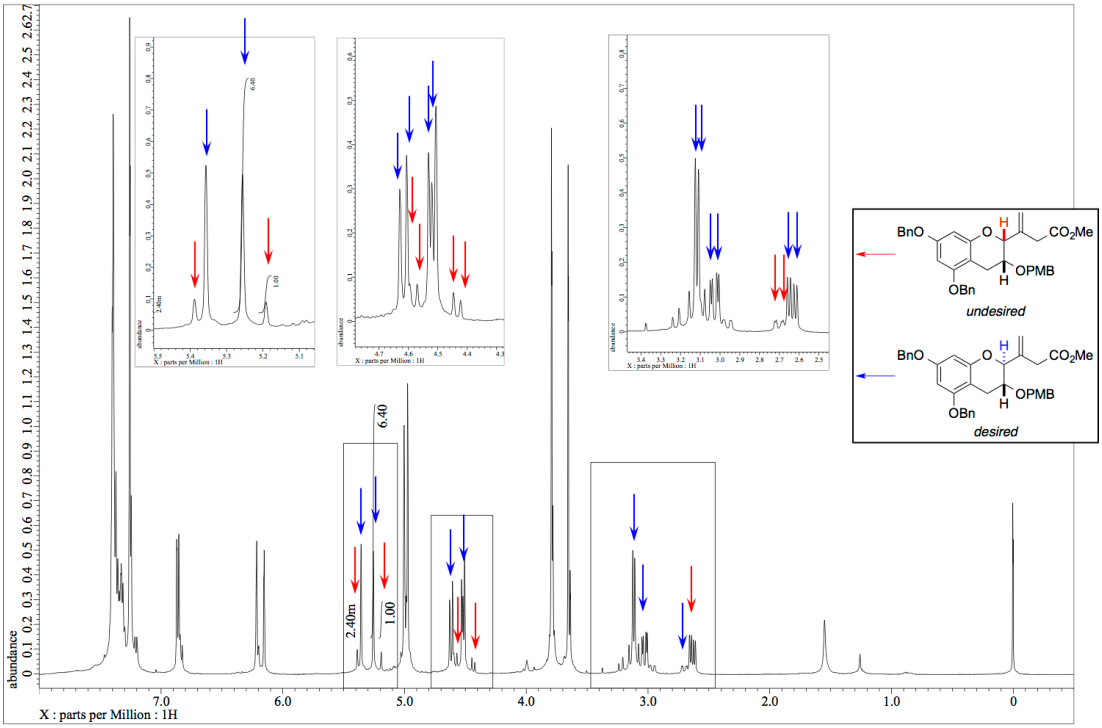
IR (film, cm^{-1}): 2920, 2853, 2395, 1736, 1612, 1593, 1508, 1431.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.41-7.30 (m, 10H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.21 (d, *J* = 2.3 Hz, 1H), 6.15 (d, *J* = 2.3 Hz, 1H), 5.35 (s, 1H), 5.25 (s, 1H) 5.00 (d, *J* = 1.1 Hz, 2H), 4.97 (s, 2H), 4.62 (d, *J* = 11.3 Hz, 1H), 4.52 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 6.8 Hz, 1H), 3.79 (ddd, *J* = 7.9, 6.8, 5.1 Hz, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 3.14 (d, *J* = 15.6 Hz, 1H), 3.09 (d, *J* = 15.6 Hz, 1H), 3.03 (dd, *J* = 16.4, 5.1 Hz, 1H), 2.63 (dd, *J* = 16.4, 7.9 Hz, 1H).

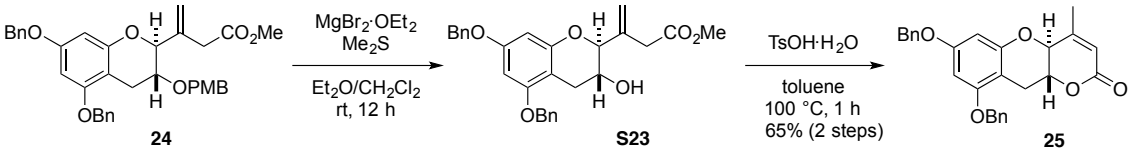
^{13}C NMR (125 MHz, $CDCl_3$, δ): 171.5, 159.2, 158.7, 157.6, 154.7, 139.3, 137.0, 136.9, 130.1, 129.4, 128.6, 128.5, 127.95, 127.86, 127.5, 127.2, 117.9, 113.8, 101.7, 94.3, 93.6, 79.8, 71.3, 70.6, 70.1, 69.9, 55.3, 51.9, 38.3, 24.9.

HRMS (ESI) Calcd for $C_{36}H_{36}O_7Na$ [$(M+Na)^+$] 603.2351, found 603.2364.

500 MHz NMR spectrum of Chromane **26** (dr = 6:1)



Synthesis of Lactone **25**



To a suspension of $MgBr_2 \cdot OEt_2$ (8.89 g, 34.4 mmol) in a mixture of Et_2O (25 mL) and CH_2Cl_2 (10 mL) were added a solution of **24** (2.00 g, 3.44 mmol) and Me_2S (7.5 mL, 100 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 12 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S23** was applied to the following reaction without further purification.

To a solution of the crude material including **S23** in toluene (20 mL) was added $TsOH \cdot H_2O$ (65.0 mg, 0.344 mmol). The resulting mixture was stirred at 100 °C for 1hour. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 4/1) to afford **25** (965 mg, 65%, 2 steps) as a colorless solid.

$[\alpha]_D^{24}$ –139.9 (*c* 0.68, $CHCl_3$).

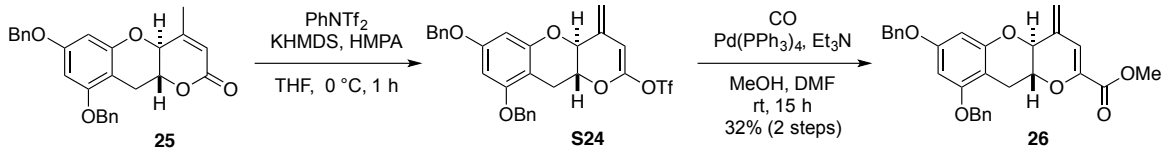
IR (ATR, cm^{-1}): 1720, 1585, 1489, 1435, 1381.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.30-7.24 (m, 10H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 1.7 Hz, 1H), 5.89 (t, *J* = 1.7 Hz, 1H), 5.05 (d, *J* = 11.9 Hz, 1H), 5.02 (d, *J* = 11.9 Hz, 1H), 5.01 (s, 2H), 4.50 (td, *J* = 10.8, 5.7 Hz, 1H), 4.23 (d, *J* = 10.8 Hz, 1H), 3.29 (dd, *J* = 15.9, 6.2 Hz, 1H), 2.83 (dd, *J* = 15.9, 10.8 Hz, 1H), 2.17 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 162.7, 159.1, 157.8, 157.3, 154.4, 136.60, 136.58, 128.6, 128.5, 128.0, 127.9, 127.4, 126.9, 116.8, 101.6, 94.6, 94.5, 74.0, 72.3, 70.1, 69.9, 26.5, 17.5.

HRMS (ESI) Calcd for $C_{27}H_{25}O_5$ [$(M+H)^+$] 429.1702, found 429.1697.

Synthesis of Methyl Ester **26**



To a solution of HMPA (0.78 mL, 4.5 mmol) in THF (20 mL) were added KHMDS (9.0 mL, 4.5 mmol, 0.5 M solution in toluene) and a solution of **25** (965 mg, 2.25 mmol) in THF (20 mL) at –78 °C. After 1 hour, a solution of $PhNTf_2$ (1.21 g, 3.38 mmol) in in THF (5 mL) was added at –78 °C. After 1 hour, the resulting mixture was worm up 0 °C and stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with phosphate buffer (pH 6.4) and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S24** was applied to the following reaction without further purification.

To a solution of the crude material including **S24** in a 9:1 mixture of MeOH and DMF (total 20 mL) were added $Pd(PPh_3)_4$ (260 mg, 0.225 mmol) and Et_3N (0.94 mL, 0.68 mmol) at room temperature. The resulting mixture was stirred at the same temperature under ordinary hydrogen pressure (balloon) for 15 hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/$CHCl_3$/EtOAc = 1/1/0.1) to afford **26** (338 mg, 32%, 2 steps) as a colorless solid.

$[\alpha]_D^{22}$ –16.9 (*c* 0.42, $CHCl_3$).

IR (ATR, cm^{-1}): 2921, 2852, 1720, 1618, 1592, 1500, 1434.

^1H NMR (500 MHz, $CDCl_3$, δ): 7.45-7.30 (m, 10H), 6.65 (s, 1H), 6.29 (d, *J* = 2.3, 1H), 6.25 (d, *J* = 2.3 Hz, 1H), 5.60 (brs, 1H), 5.25 (brs, 1H), 5.02 (s, 2H), 5.02 (d, *J* = 11.3 Hz, 1H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.43 (dt, *J* = 10.8, 2.3 Hz, 1H), 4.12 (td, *J* = 10.2, 6.2 Hz, 1H), 3.84 (s, 3H), 3.40 (dd, *J* = 16.5, 6.2 Hz, 1H), 2.83 (dd, *J* = 16.5, 10.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 162.8, 159.0, 157.7, 154.6, 143.0, 136.8, 136.7, 136.3, 128.6, 128.5, 128.0, 127.9, 127.5, 127.2, 113.7, 112.9, 101.8, 94.5, 94.1, 73.5, 72.0, 70.2, 70.0, 52.5, 26.2.

HRMS (ESI) Calculated for $C_{29}H_{26}O_6Na$ $[(M+Na)^+]$ 493.1627, found 493.1633.

Synthesis of Teadenol B (**2**)

To a solution of **26** (300 mg, 0.638 mmol) in CH_2Cl_2 (30 mL) were added $PhMe_5$ (567 mg, 3.83 mmol) and BCl_3 (2.6 mL, 2.6 mmol, 1 M solution in CH_2Cl_2) at –78 °C. The resulting mixture was stirred for 5 hours at the same temperature. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$, acidified with 2 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude material including **S25** was applied to the following reaction without further purification.

To a solution of the crude material including **S25** in MeOH (15 mL) was added a solution of $LiOH{\cdot}H_2O$ (268 mg, 6.38 mmol) in H_2O (15 mL) at room temperature. The resulting mixture was stirred at the same temperature for 15 minutes. The reaction mixture was quenched with 2 M HCl and extracted with EtOAc. The residue (202 mg) was purified by preparative HPLC (Cosmosil 20D x 250 mm, gradient, 20% to 80% MeOH in H_2O, for 120 min, minute ramp, λ = 254 nm, flow rate; 3 mL/min) to afford **2** (8.4 mg, 5%, 2 steps) as a colorless solid.

$[\alpha]_D^{22}$ –27.0 (*c* 0.20, $CHCl_3$). Lit: $[\alpha]_D^{20}$ –27.7 (*c* 0.18, MeOH)[4].

IR (ATR, cm^{-1}): 3431, 1677, 1598, 1454.

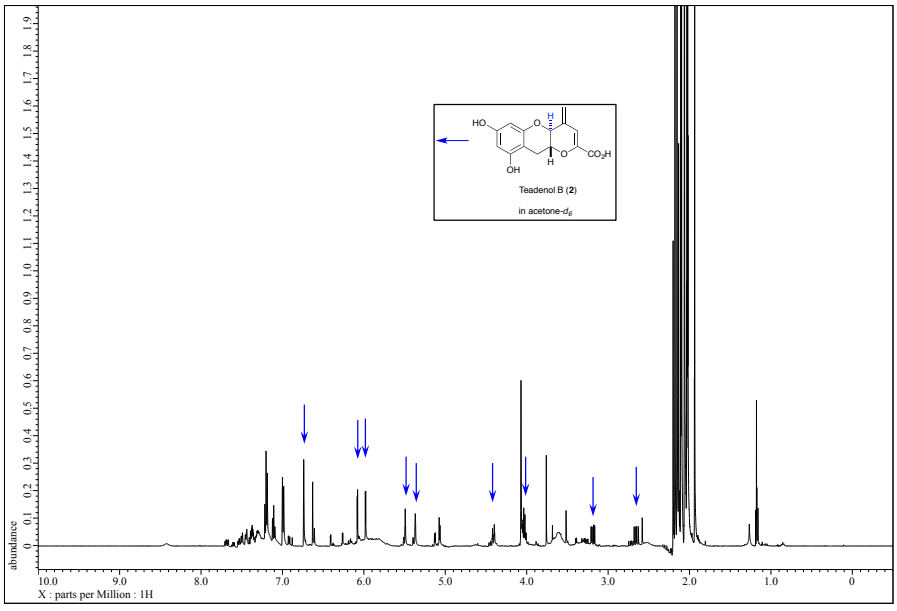
^{1}H NMR (500 MHz, CD_3OD, δ): 6.62 (s, 1H), 5.95 (d, *J* = 2.3, 1H), 5.90 (d, *J* = 2.3 Hz, 1H), 5.51 (brs, 1H), 5.32 (brs, 1H), 4.43 (dt, *J* = 10.8, 2.3 Hz, 1H), 4.35 (td, *J* = 10.8, 2.3 Hz, 1H), 4.00 (td, *J* = 10.2, 6.2 Hz, 1H), 3.19 (dd, *J* = 15.9, 6.2 Hz, 1H), 2.65 (dd, *J* = 15.9, 10.2 Hz, 1H).

^{13}C NMR (125 MHz, CD_3OD, δ): 164.2, 156.9, 156.5, 154.7, 143.2, 137.3, 112.2, 112.1, 98.7, 95.6, 94.3, 73.7, 71.9, 25.7.

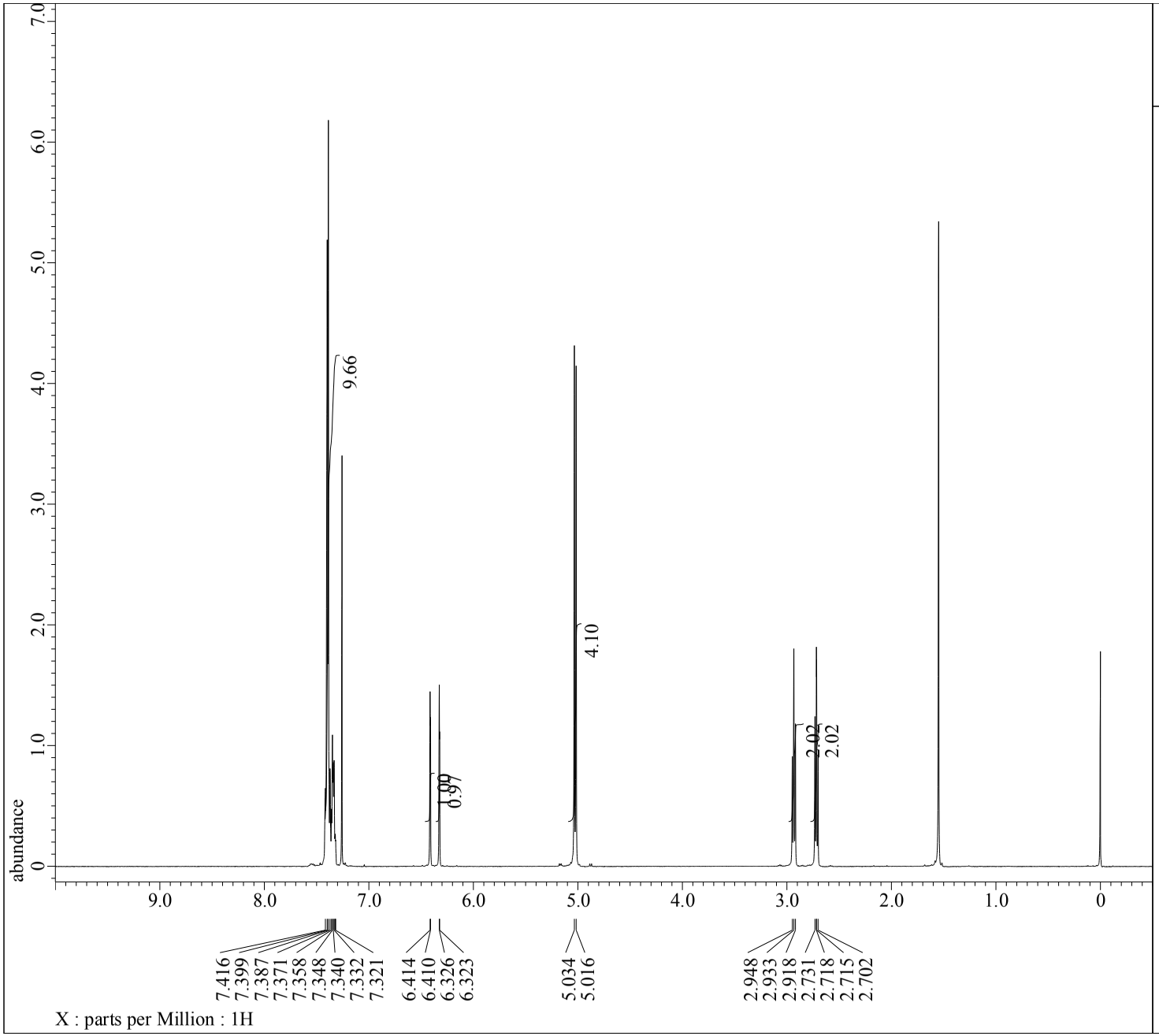
HRMS (ESI) Calculated for $C_{14}H_{12}O_6Na$ [$(M+Na)^+$] 299.0532, found 299.0526.

¥4. Wulandari, R. A.; Rani, A.; Amano, M.; Yanagita, T.; Tanaka, T.; Kouno, I.; Kawamura, D.; Ishimaru, K. *J. Nat. Med.* **2011**, *65*, 594–597.

500 MHz NMR spectrum of crude material of teadenol B (**2**)

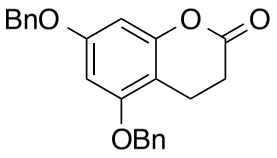


IV. NMR Spectra Data

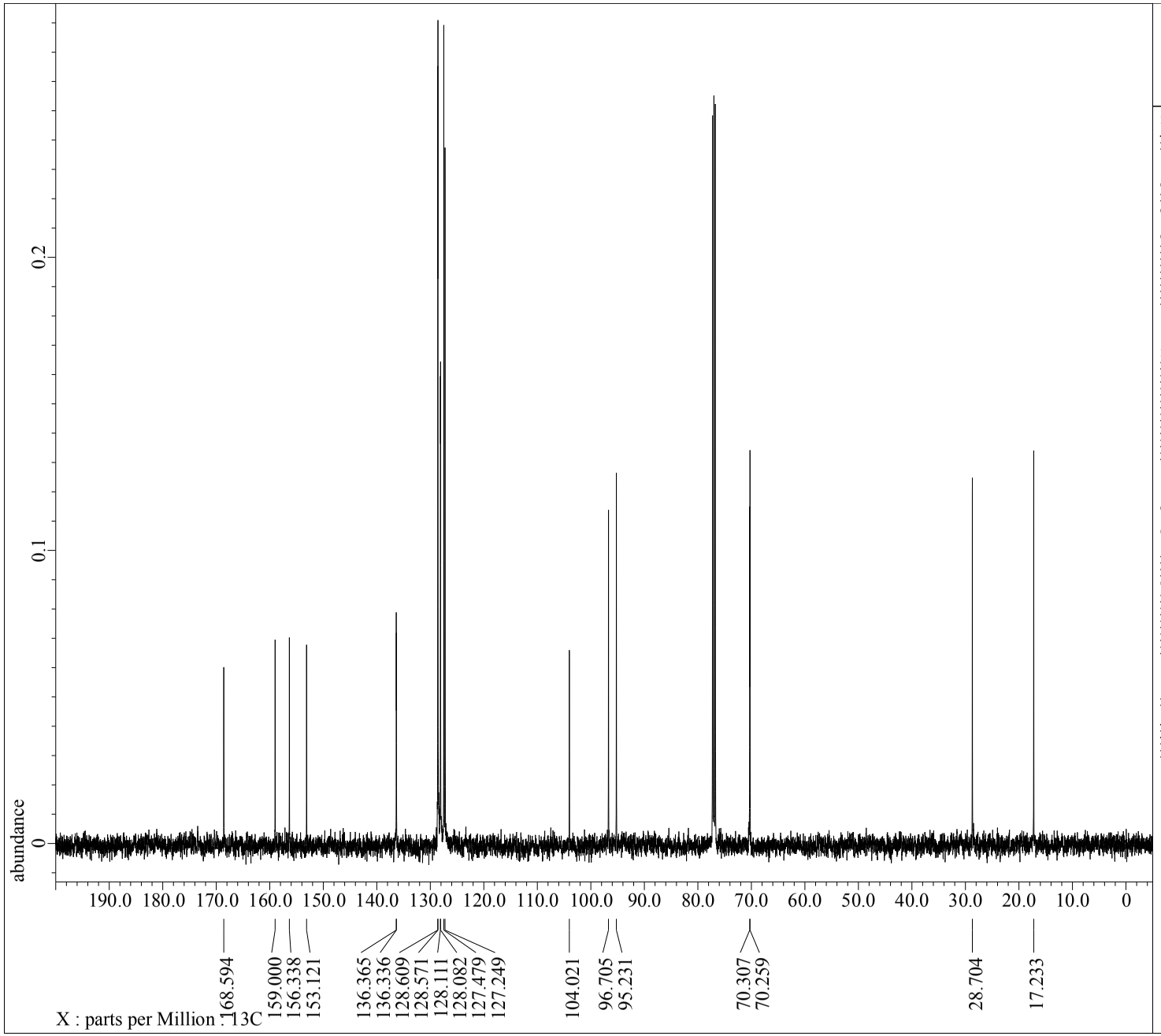


JEOL RESONANCE

```
Filename          = HOo-140528-1-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#522745
Solvent           = CHLOROFORM-D
Creation_Time     = 28-MAY-2014 14:20:15
Revision_Time     = 10-SEP-2015 11:25:08
Current_Time      = 10-SEP-2015 11:33:49

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 50
Temp_Get          = 27.3[dC]
X_90_Width        = 7.36[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.68[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

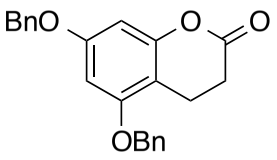


12

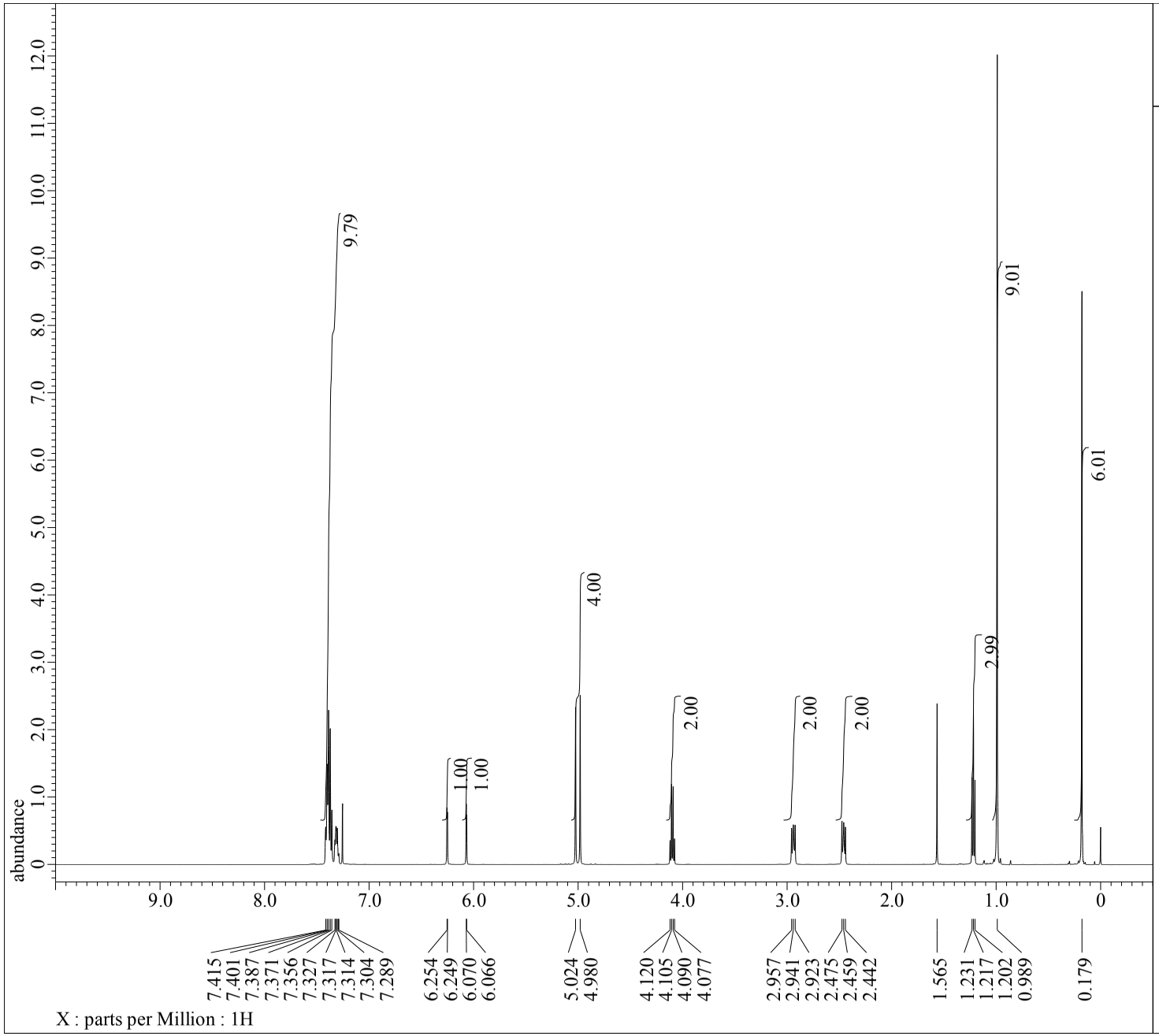


JEOL RESONANCE

```
Filename          = RY-121119-5-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#480657
Solvent           = CHLOROFORM-D
Creation_Time     = 19-NOV-2012 13:39:36
Revision_Time     = 10-SEP-2015 13:20:23
Current_Time      = 10-SEP-2015 13:21:17

Comment           = Bn
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 500
Total_Scans       = 500

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 20.6[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

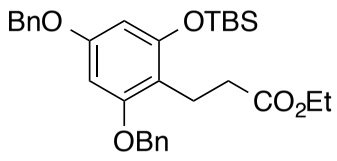


12

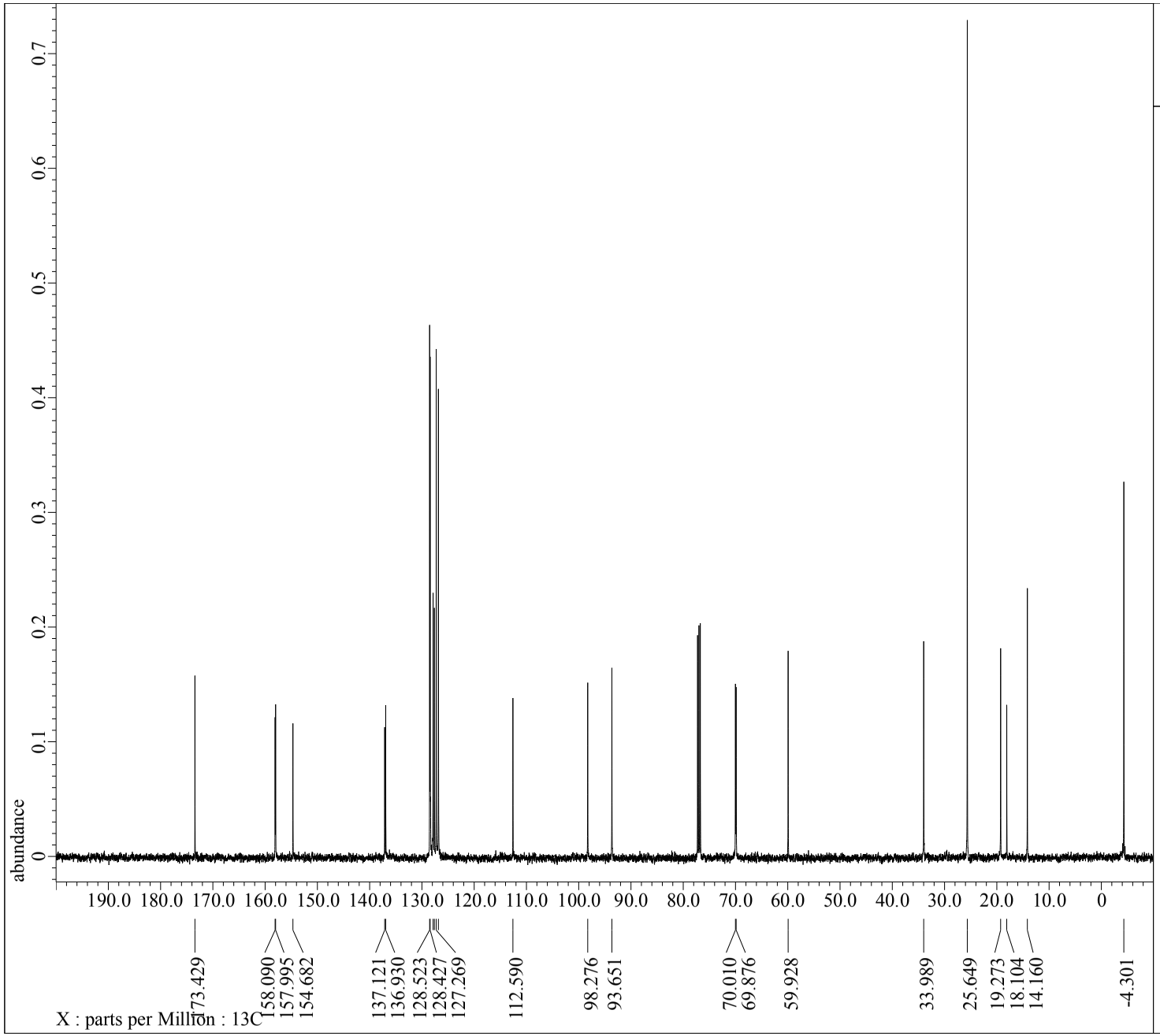


JEOL RESONANCE

Filename	= HOo-140604-2-6.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_Id	= 1
Solvent	= CHLOROFORM-D
Creation_Time	= 4-JUN-2014 23:30:39
Revision_Time	= 10-SEP-2015 13:56:58
Current_Time	= 10-SEP-2015 13:57:09
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
Dim_Title	= 1H
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 1.76422912[s]
X_Domain	= 1H
X_Freq	= 495.13191398[MHz]
X_Offset	= 5[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.5668198[Hz]
X_Sweep	= 9.28677563[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= 1H
Tri_Freq	= 495.13191398[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 38
Temp_Get	= 24.5[dC]
X_90_Width	= 7.36[us]
X_Acq_Time	= 1.76422912[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 3.68[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Repetition_Time	= 6.76422912[s]

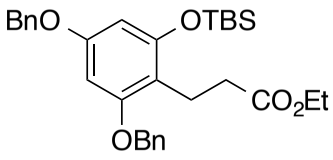


S3

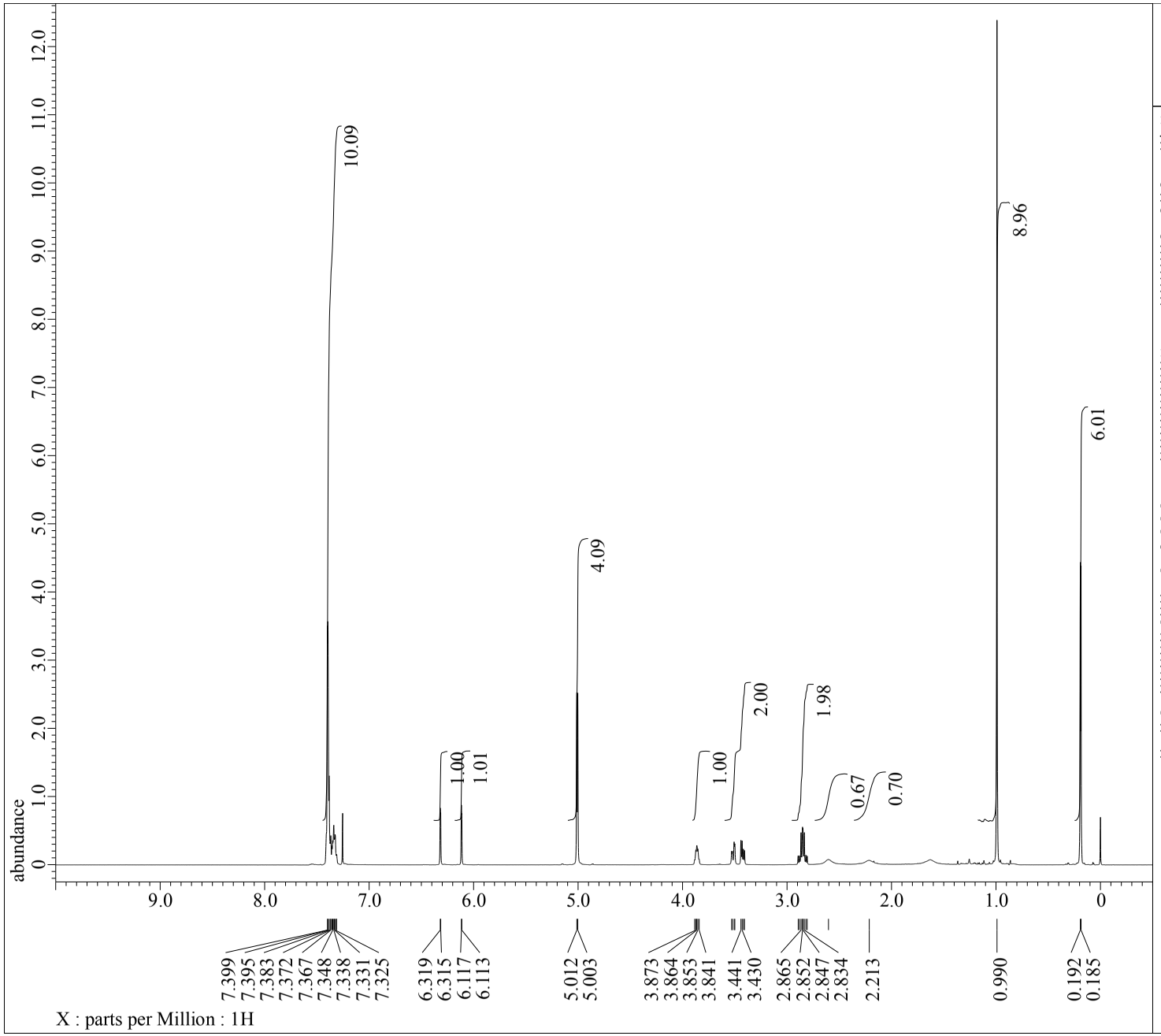


JEOL RESONANCE

```
Filename          = RY-121204-7-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     =  4-DEC-2012 17:15:25
Revision_Time     = 10-SEP-2015 13:58:54
Current_Time      = 10-SEP-2015 14:00:29

Comment           = TBS
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T]  (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 320
Total_Scans       = 320

Relaxation_Delay  = 2[s]
Recvr_Gain        = 48
Temp_Get          = 20.6[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

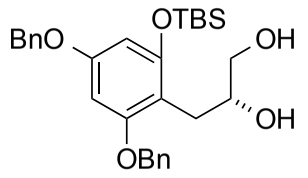


S3

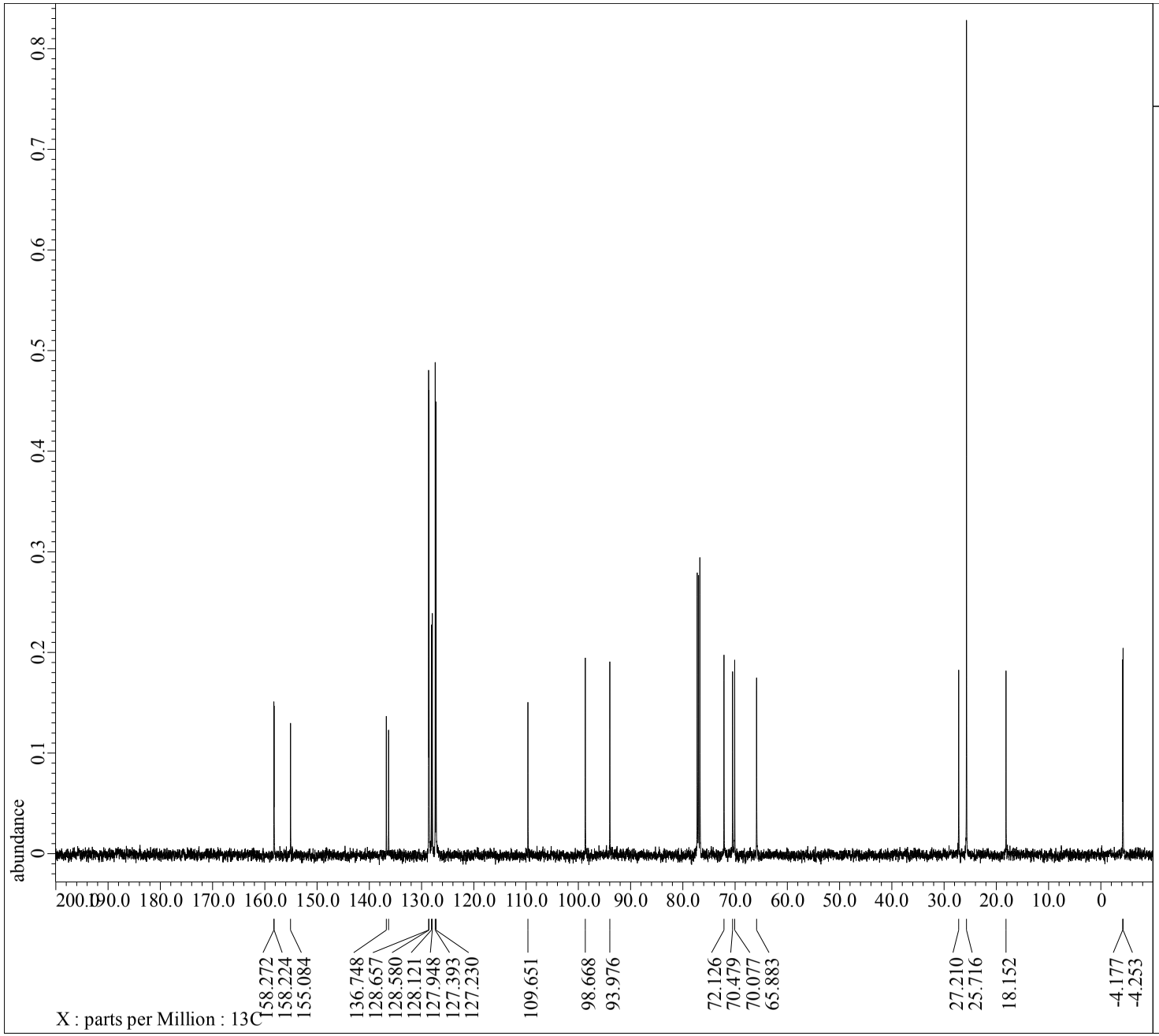


JEOL RESONANCE

```
Filename          = HOo-140702-1-H-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 1
Solvent           = CHLOROFORM-D
Creation_Time     =  2-JUL-2014 13:05:25
Revision_Time     = 10-SEP-2015 17:37:30
Current_Time      = 10-SEP-2015 17:38:24

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 36
Temp_Get          = 23.2[dC]
X_90_Width        = 7.36[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.68[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

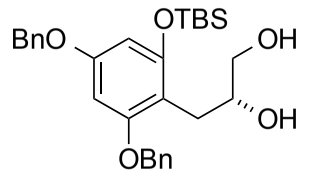


16

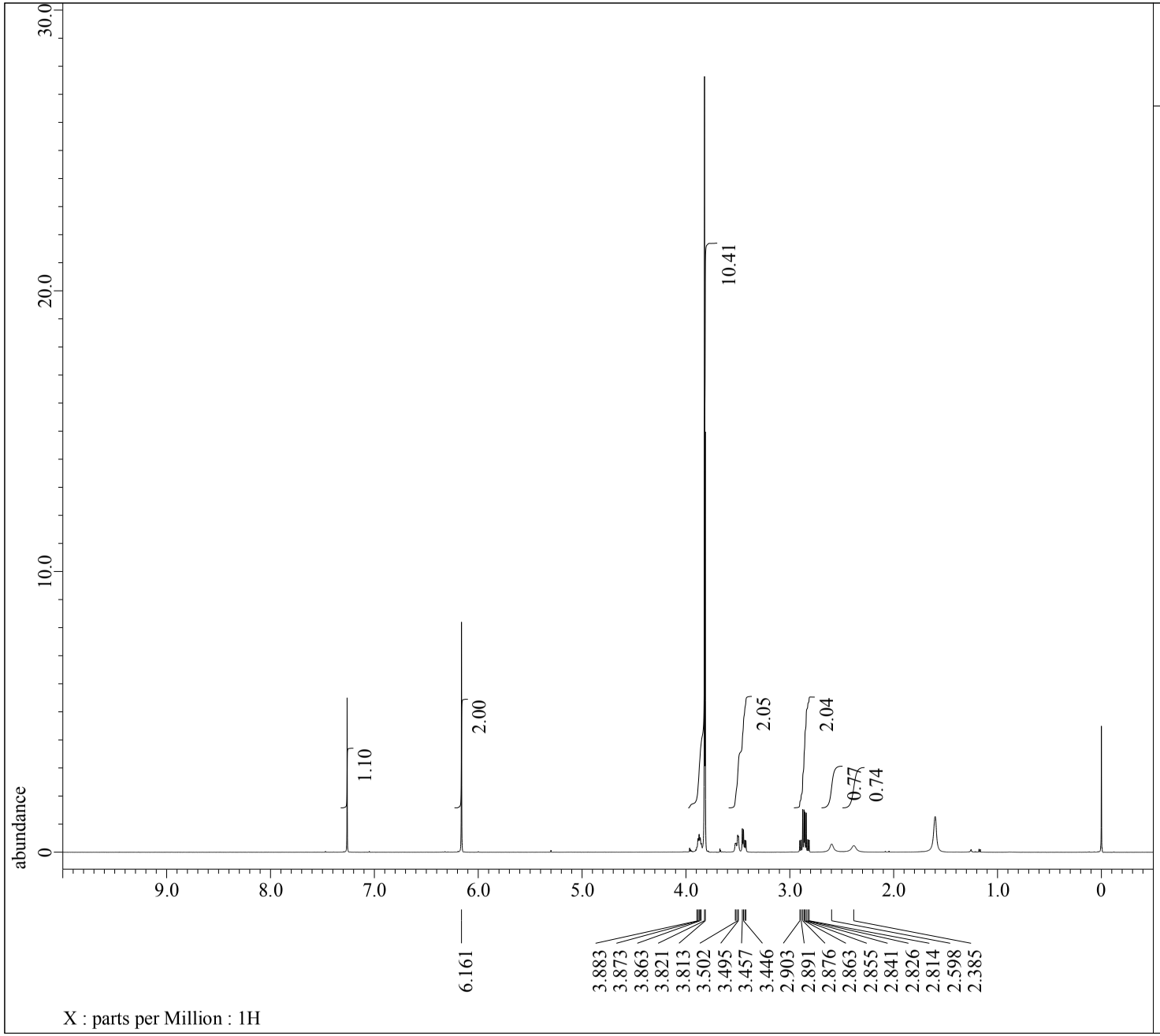


JEOL RESONANCE

```
Filename          = RY-121129-2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#472436
Solvent           = CHLOROFORM-D
Creation_Time     = 29-NOV-2012 13:16:48
Revision_Time     = 10-SEP-2015 22:16:53
Current_Time      = 10-SEP-2015 22:17:42

Comment           = diol
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 300
Total_Scans       = 300

Relaxation_Delay  = 2[s]
Recvr_Gain        = 52
Temp_Get          = 21.1[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

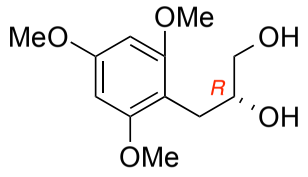


16

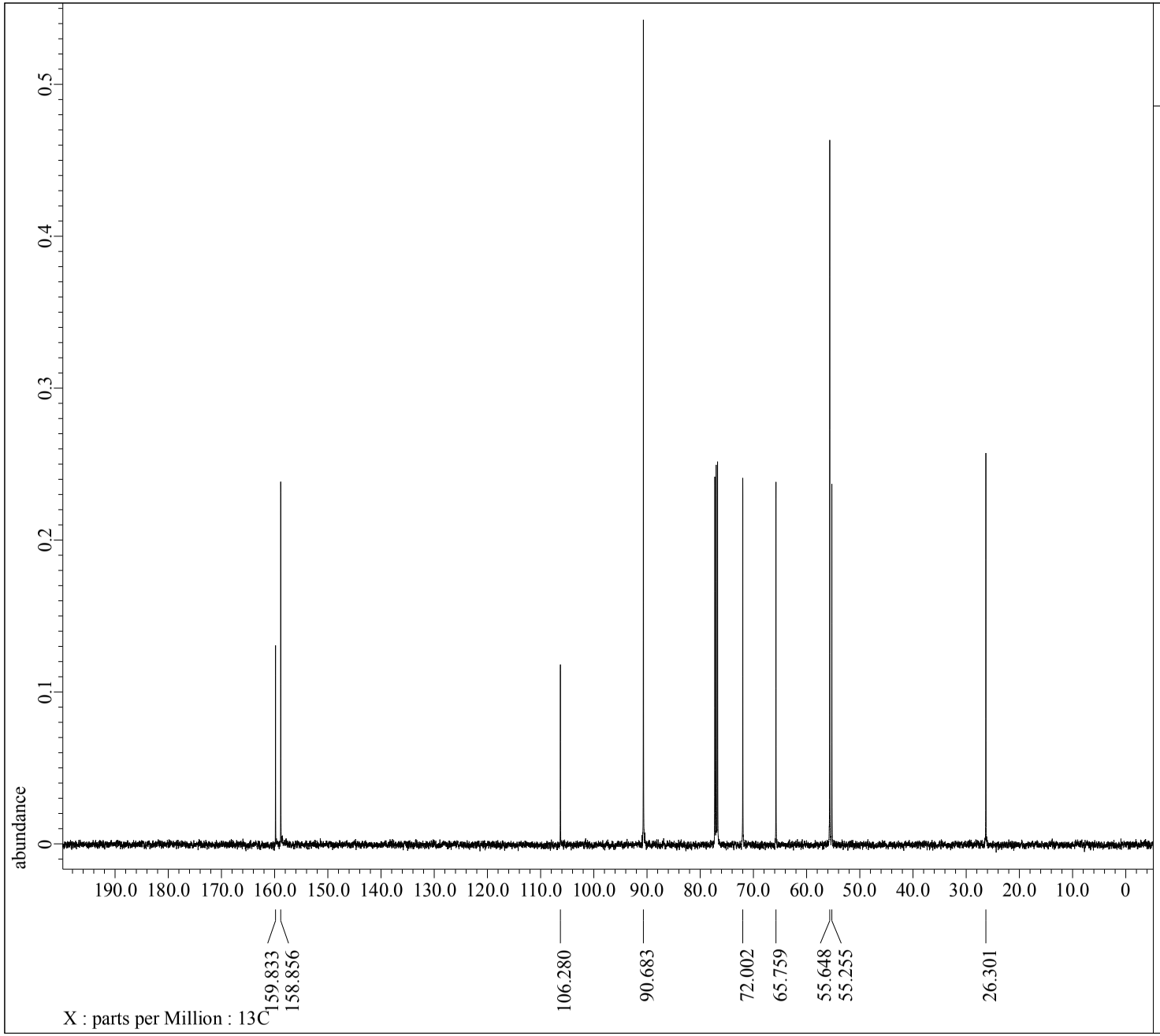


JEOL
Solutions for Innovation

```
Filename          = HOo-140830-1-7.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#823783
Solvent           = CHLOROFORM-D
Creation_Time     = 30-AUG-2014 22:41:06
Revision_Time     = 29-DEC-2015 12:57:44
Current_Time      = 29-DEC-2015 12:58:10

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 50
Temp_Get          = 24.2[dC]
X_90_Width        = 7.36[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.68[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

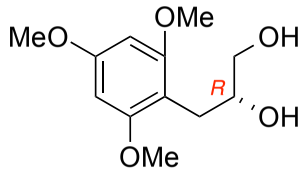


S8 (from **S5**)

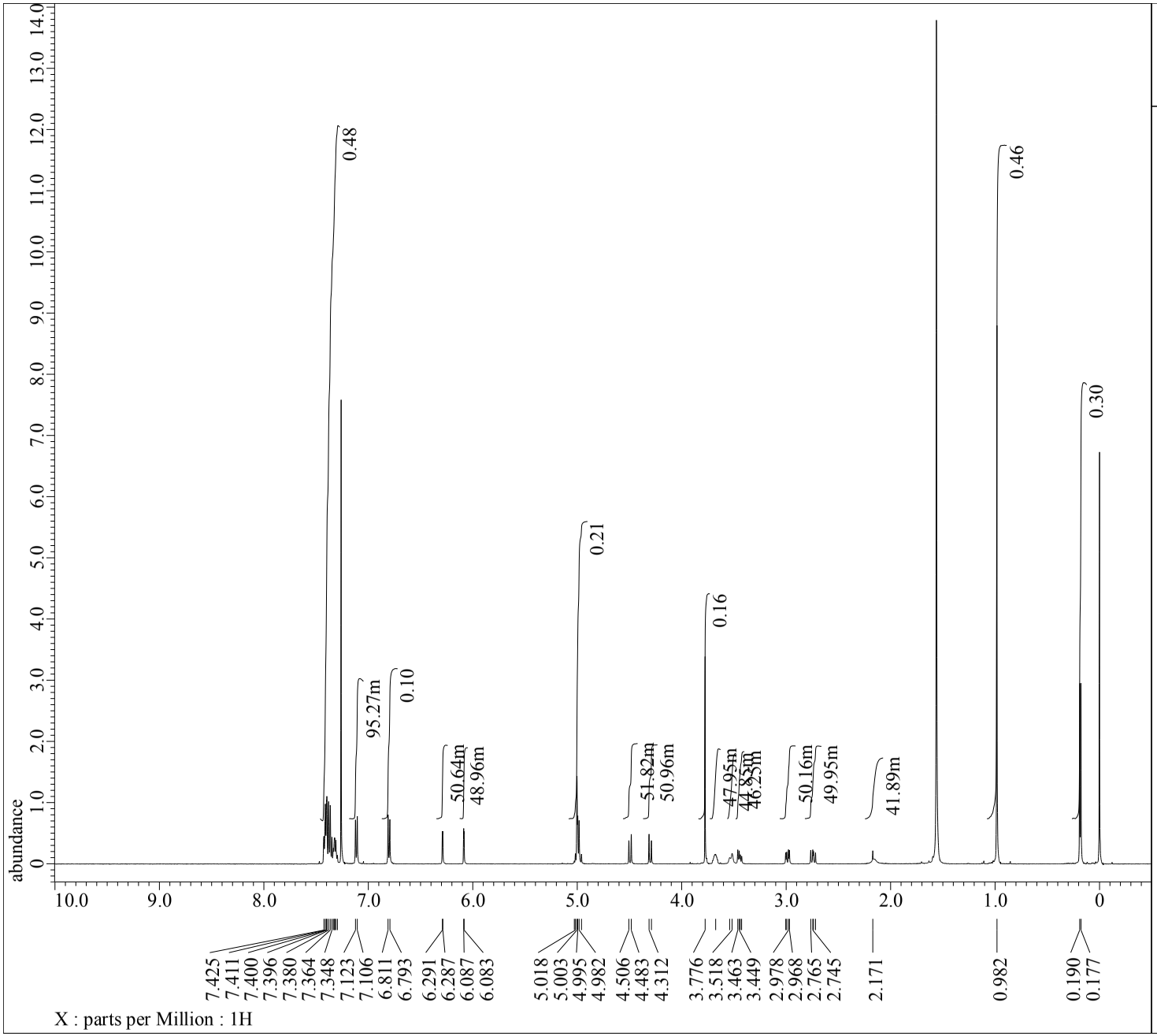


JEOL
Solutions for Innovation

```
Filename          = HOo-140827-1-C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = 1
Solvent           = CHLOROFORM-D
Creation_Time     = 27-AUG-2014 14:17:05
Revision_Time     = 29-DEC-2015 12:59:55
Current_Time      = 29-DEC-2015 13:00:08

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 24.5[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.434[dB]
Irr_Atn_Noe       = 25.434[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

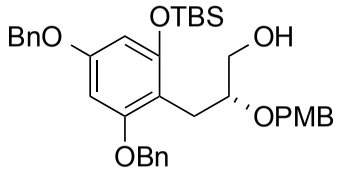


S8 (from **S5**)

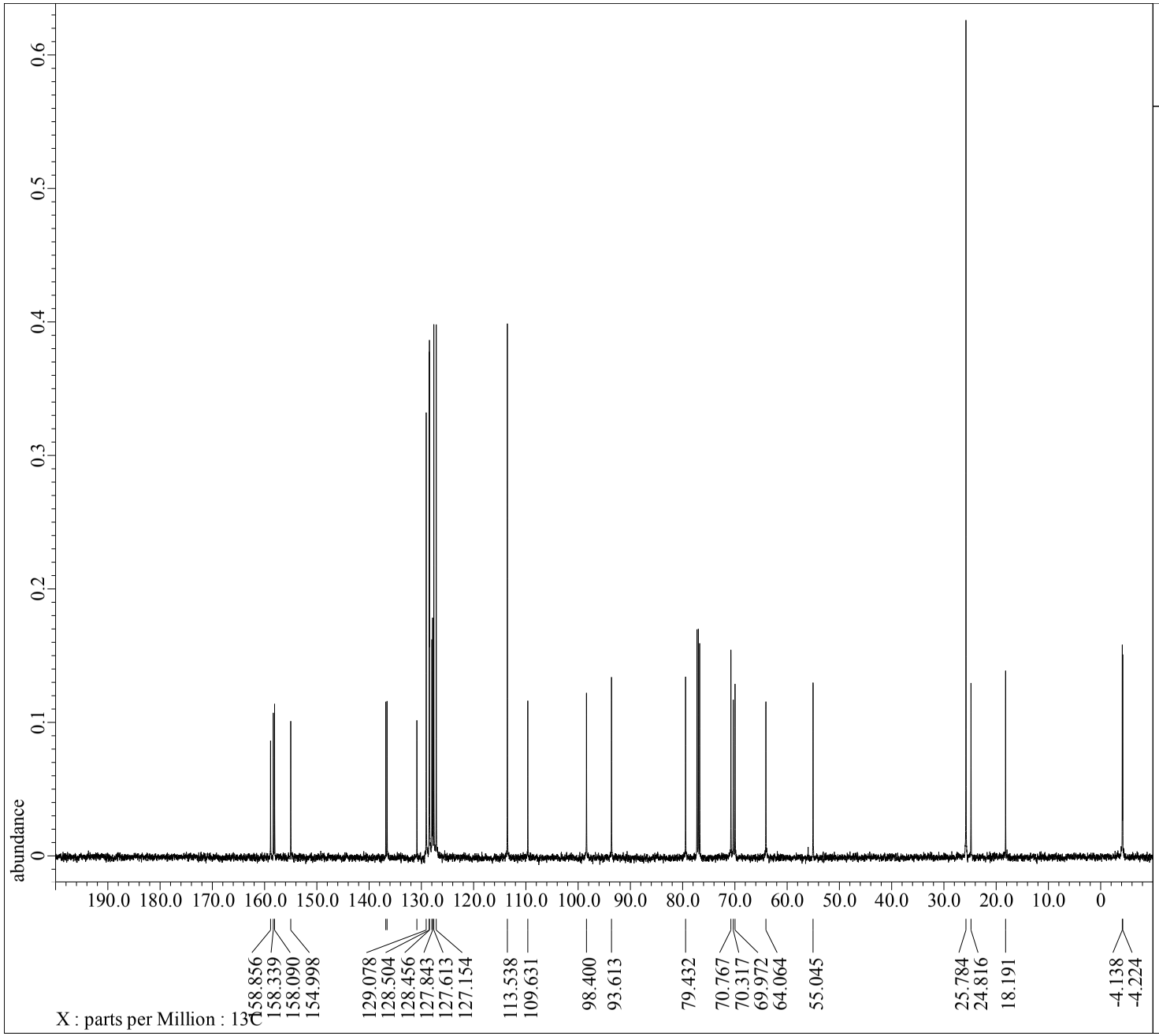


JEOL RESONANCE

```
Filename          = HOo-140723-1-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#354264
Solvent           = CHLOROFORM-D
Creation_Time     = 23-JUL-2014 09:37:18
Revision_Time     = 11-SEP-2015 14:29:47
Current_Time      = 11-SEP-2015 14:30:58

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 56
Temp_Get          = 26.1[dC]
X_90_Width        = 7.36[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.68[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

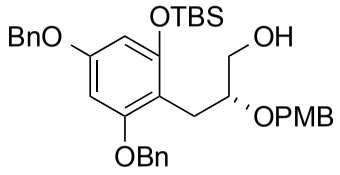


18

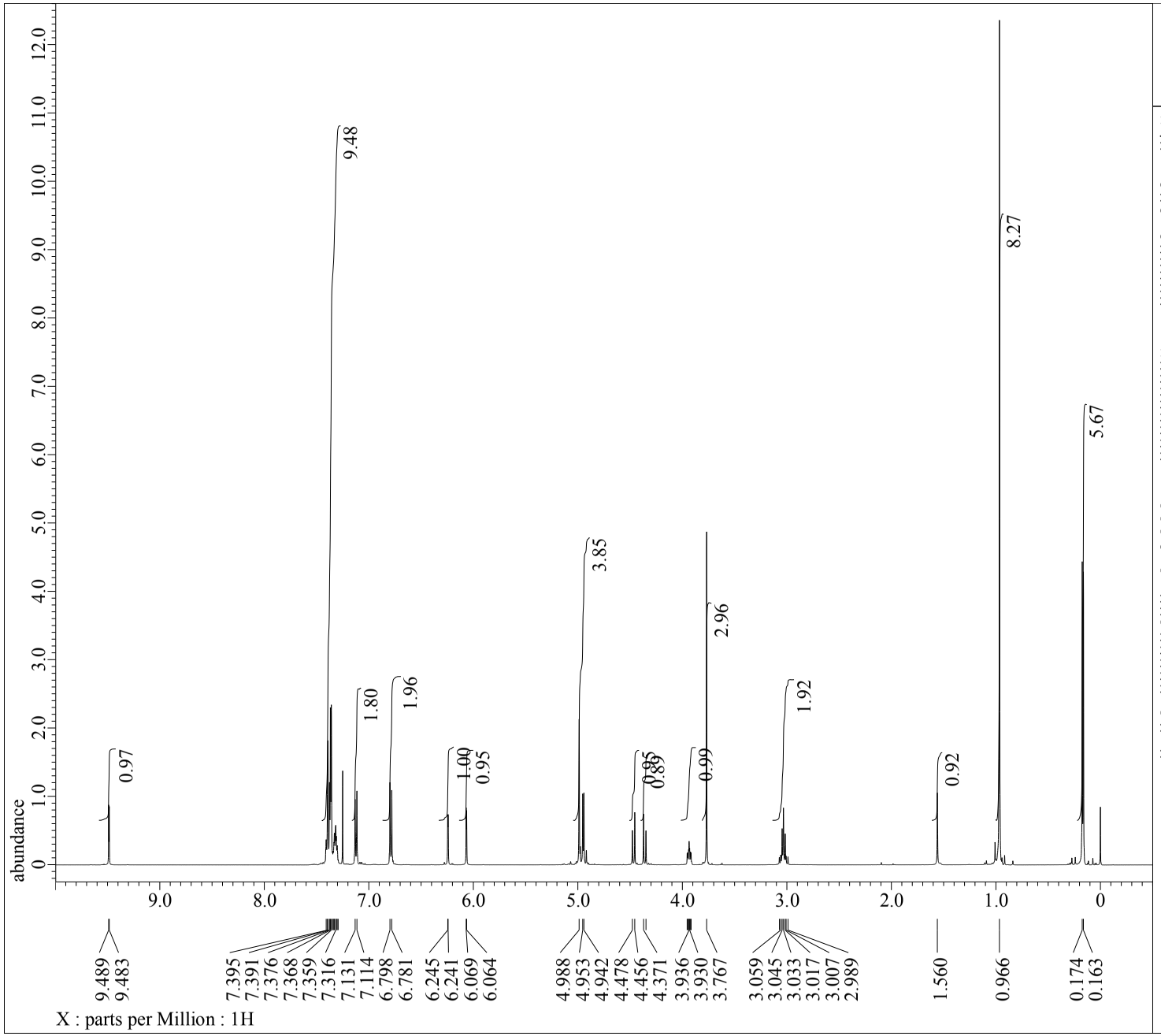


JEOL RESONANCE

```
Filename          = RY-121205-2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     =  5-DEC-2012 13:34:14
Revision_Time     = 11-SEP-2015 14:44:29
Current_Time      = 11-SEP-2015 14:45:36

Comment           = PMB OH
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 320
Total_Scans       = 320

Relaxation_Delay = 2[s]
Recvr_Gain        = 46
Temp_Get          = 20.6[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

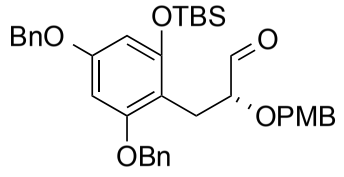


18

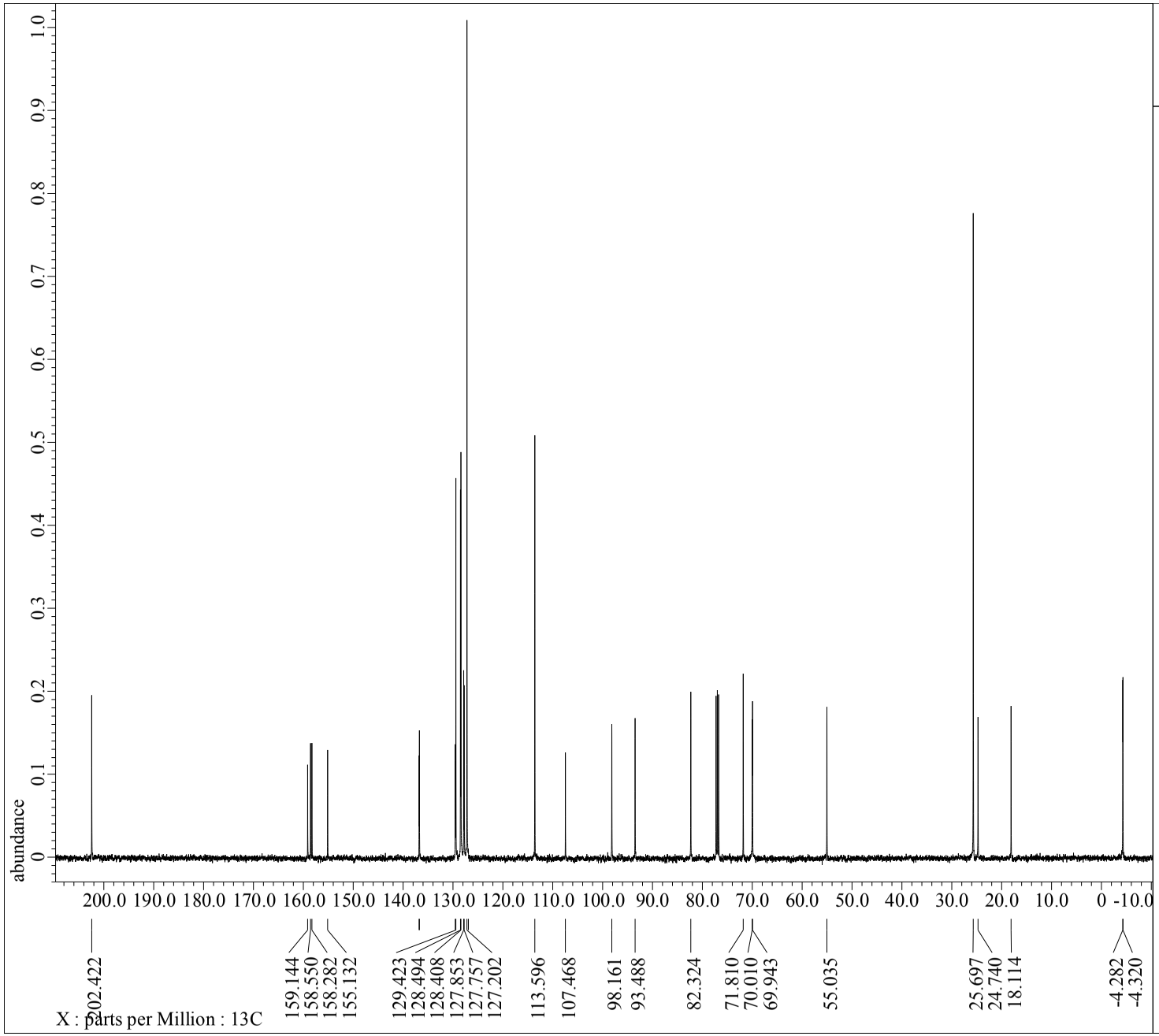


JEOL RESONANCE

```
Filename          = HOo-140805-4-H-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 1
Solvent           = CHLOROFORM-D
Creation_Time     =  5-AUG-2014 12:57:48
Revision_Time     = 11-SEP-2015 15:50:48
Current_Time      = 11-SEP-2015 15:52:05

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 36
Temp_Get          = 24.3[dC]
X_90_Width        = 7.36[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.68[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

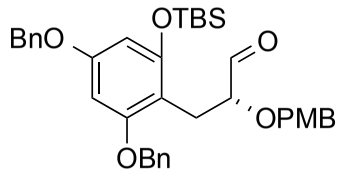


S13

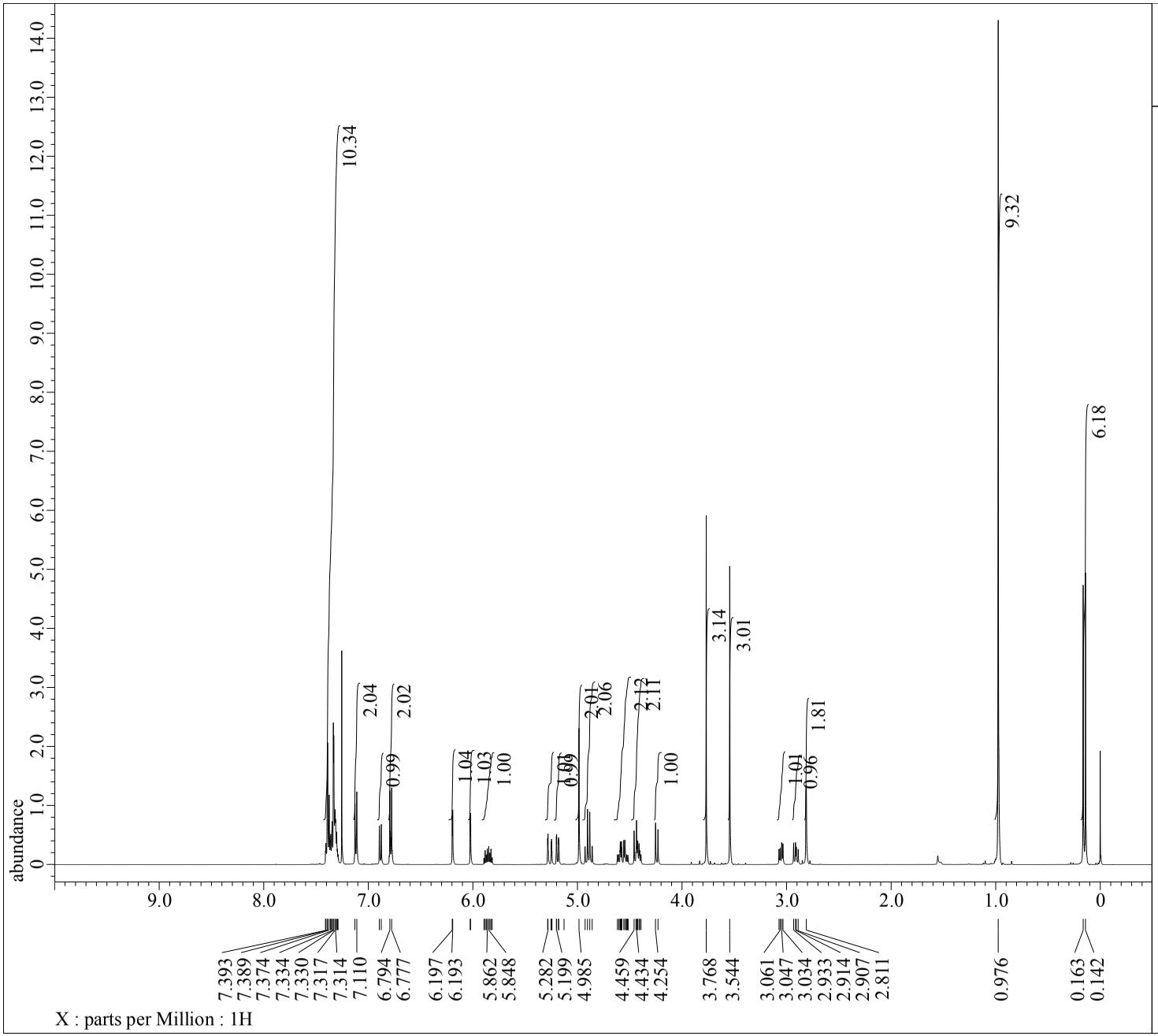


JEOL RESONANCE

```
Filename          = RY-121210-2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 10-DEC-2012 17:17:58
Revision_Time     = 11-SEP-2015 15:56:18
Current_Time      = 11-SEP-2015 15:56:55

Comment           = PMB aldehyde
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 320
Total_Scans       = 320

Relaxation_Delay = 2[s]
Recvr_Gain        = 48
Temp_Get          = 20.6[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

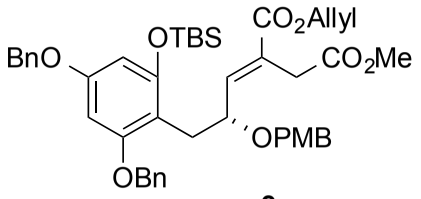


S13

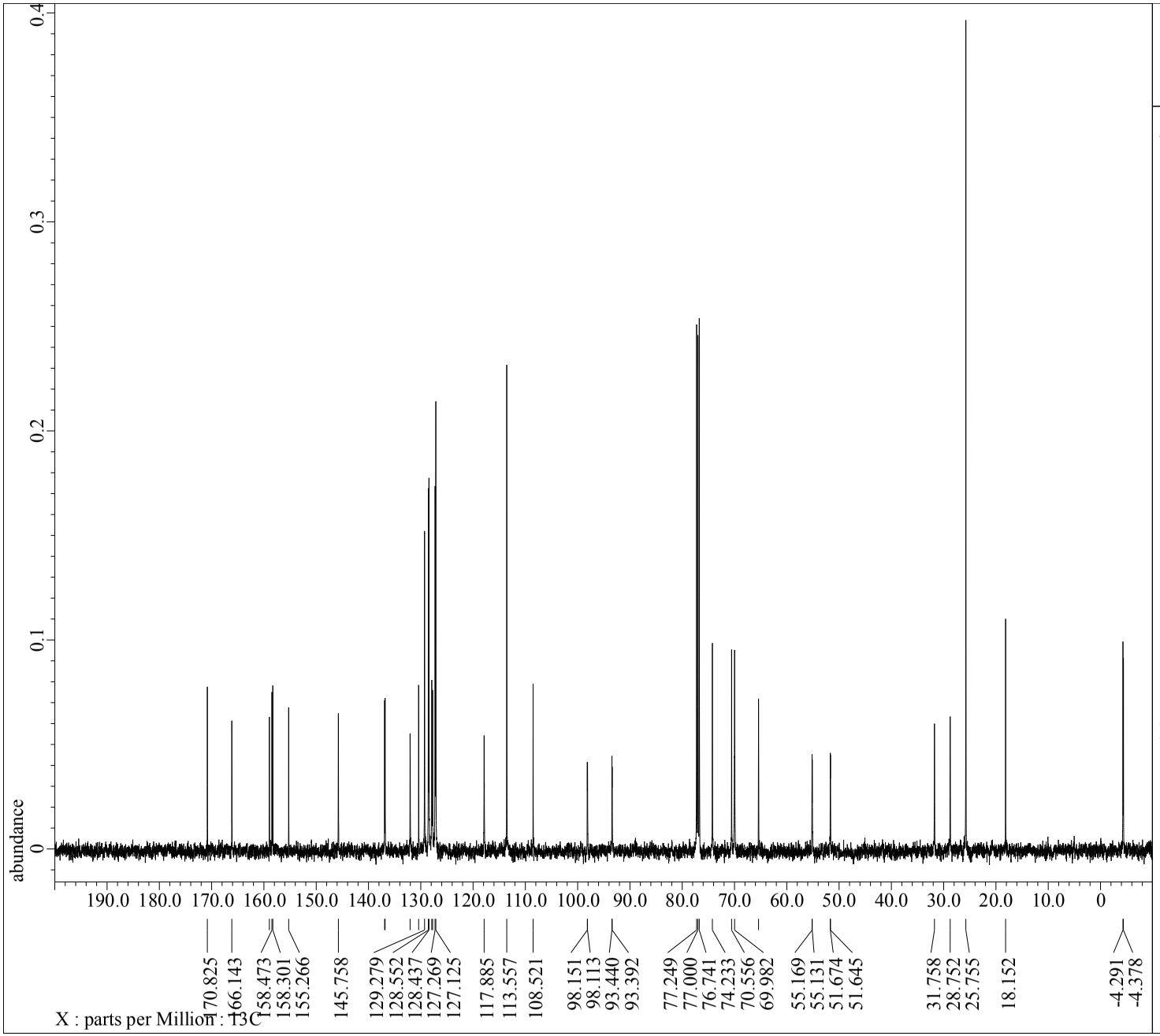


JEOL RESONANCE

```
Filename          = HOo-141202-1-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#811749
Solvent           = CHLOROFORM-D
Creation_Time     =  2-DEC-2014 22:20:03
Revision_Time     = 11-SEP-2015 21:53:00
Current_Time      = 11-SEP-2015 21:54:36

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 25[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

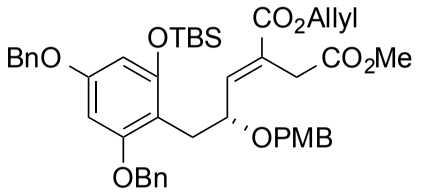


9

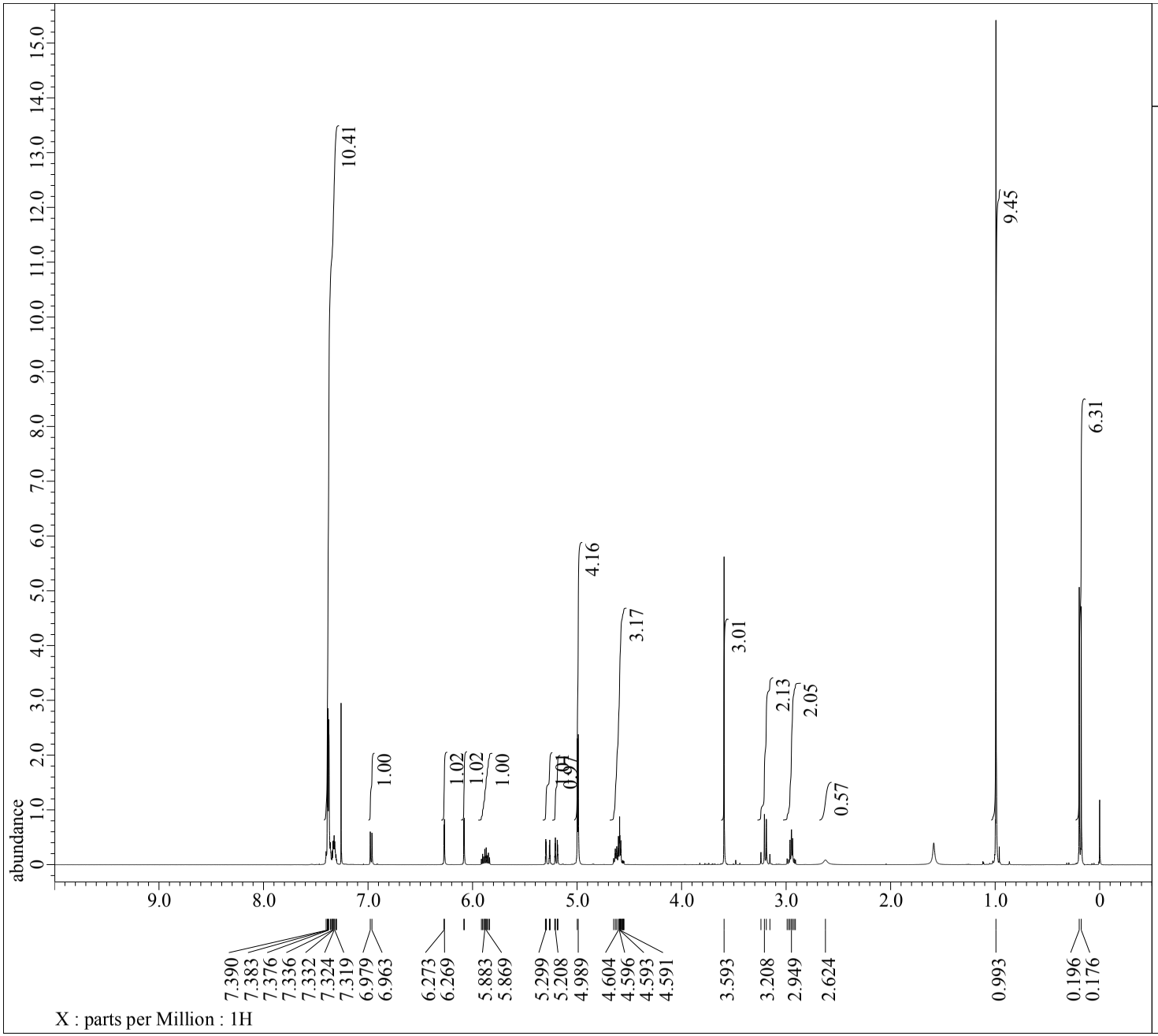


JEOL RESONANCE

```
Filename          = RY-121212-3-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 12-DEC-2012 14:56:51
Revision_Time     = 11-SEP-2015 23:31:22
Current_Time      = 11-SEP-2015 23:34:17

Comment           = Wittig
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 500
Total_Scans       = 500

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 20.7[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

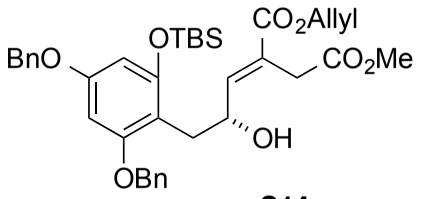


9

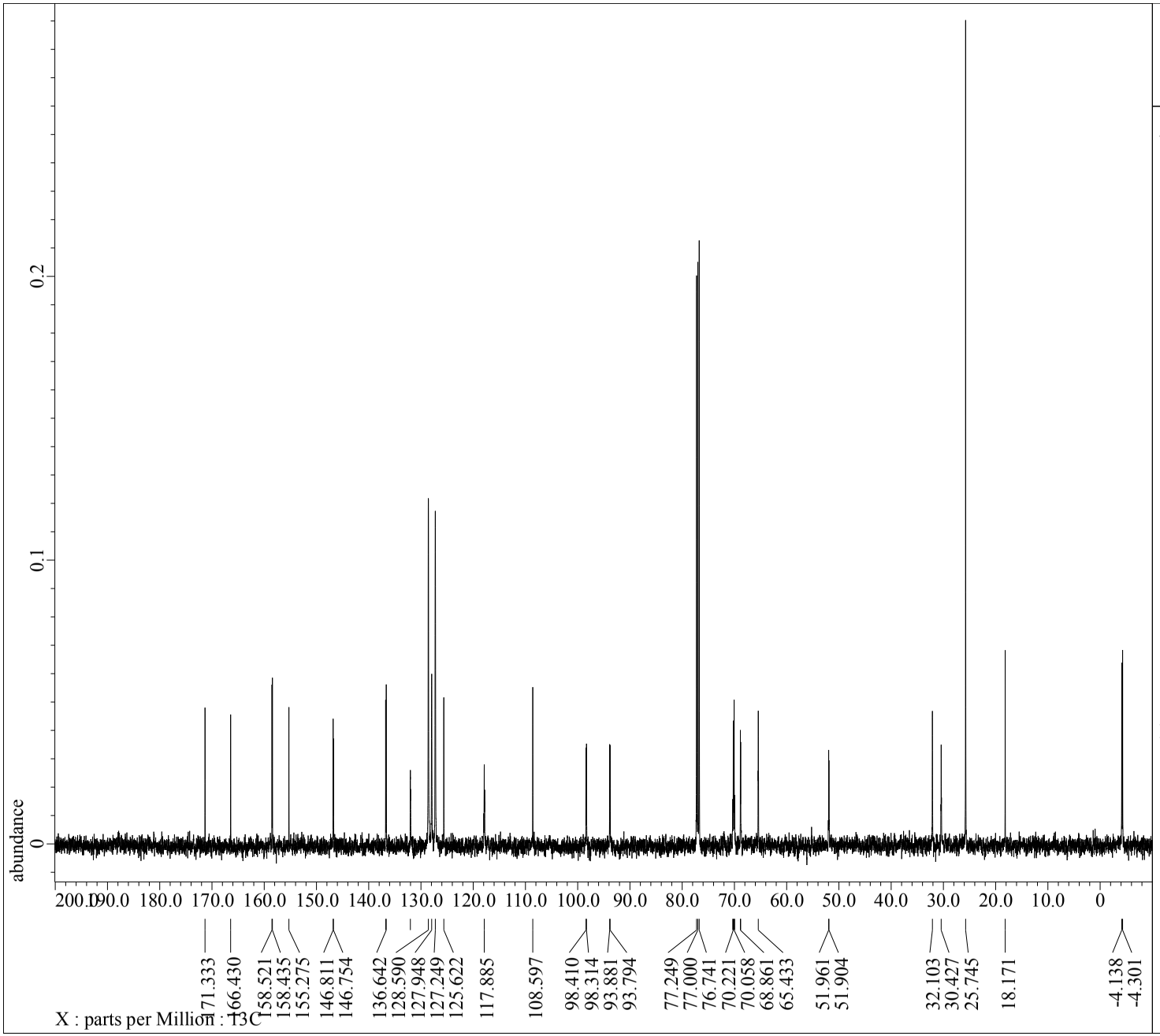


JEOL RESONANCE

```
Filename          = HOo-141010-3-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#725001
Solvent           = CHLOROFORM-D
Creation_Time     = 10-OCT-2014 19:53:49
Revision_Time     = 12-SEP-2015 11:46:25
Current_Time      = 12-SEP-2015 11:46:38

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 38
Temp_Get          = 24.9[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

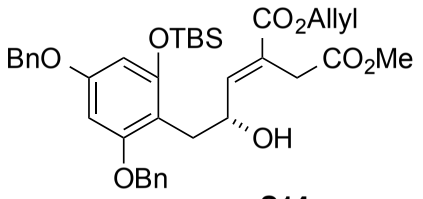


S14

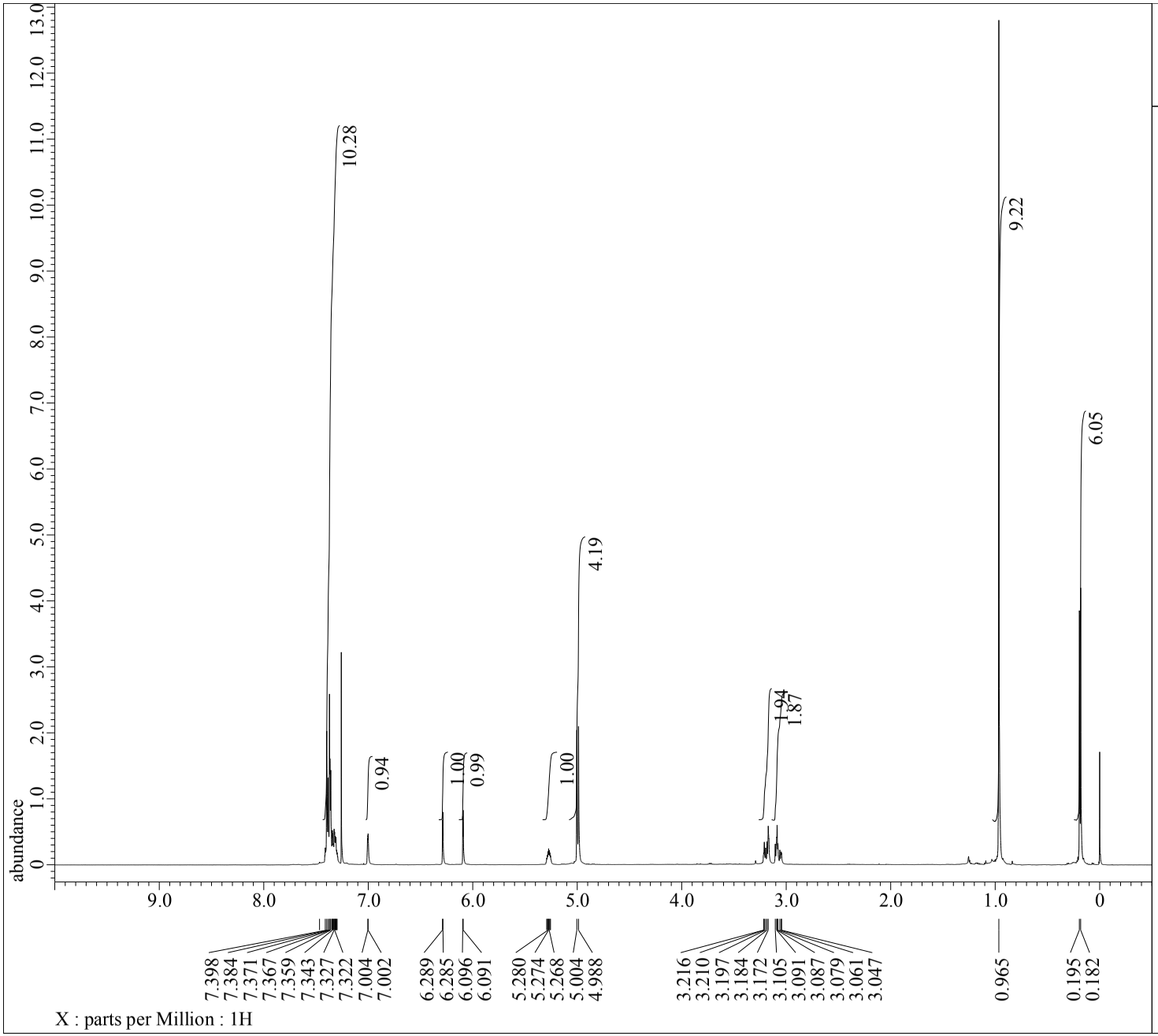


JEOL RESONANCE

Filename	= RY-121214-5-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_Id	= S#613852
Solvent	= CHLOROFORM-D
Creation_Time	= 14-DEC-2012 17:17:00
Revision_Time	= 12-SEP-2015 11:56:03
Current_Time	= 12-SEP-2015 11:56:15
Comment	= DDQ
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= 13C
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 0.8388608[s]
X_Domain	= 13C
X_Freq	= 124.5010059[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.1920929[Hz]
X_Sweep	= 39.0625[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 400
Total_Scans	= 400
Relaxation_Delay	= 2[s]
Recvr_Gain	= 48
Temp_Get	= 20.7[dC]
X_90_Width	= 17.2[us]
X_Acq_Time	= 0.8388608[s]
X_Angle	= 30[deg]
X_Atn	= 6[dB]
X_Pulse	= 5.73333333[us]
Irr_Atn_Dec	= 25.42[dB]
Irr_Atn_Noe	= 25.42[dB]
Irr_Noise	= WALTZ
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 2[s]
Repetition_Time	= 2.8388608[s]

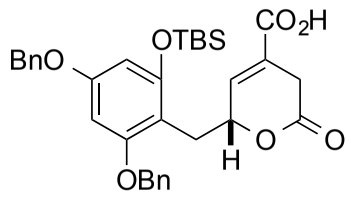


S14

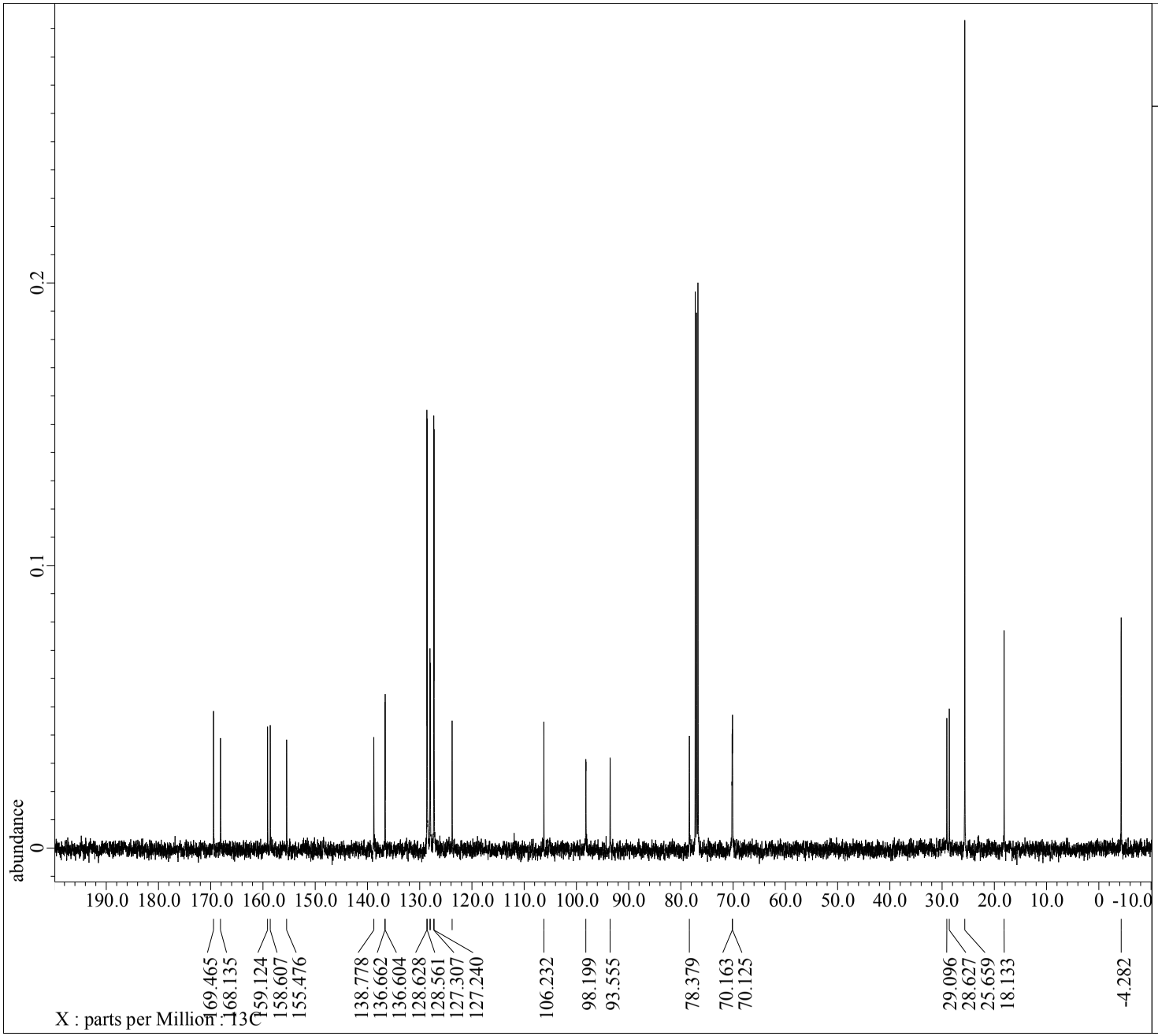


JEOL RESONANCE

```
Filename          = HOo-141020-2-H-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 1
Solvent           = CHLOROFORM-D
Creation_Time     = 20-OCT-2014 16:07:57
Revision_Time     = 14-SEP-2015 11:03:43
Current_Time      = 14-SEP-2015 11:04:21

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 25.3[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

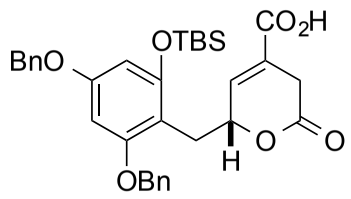


20

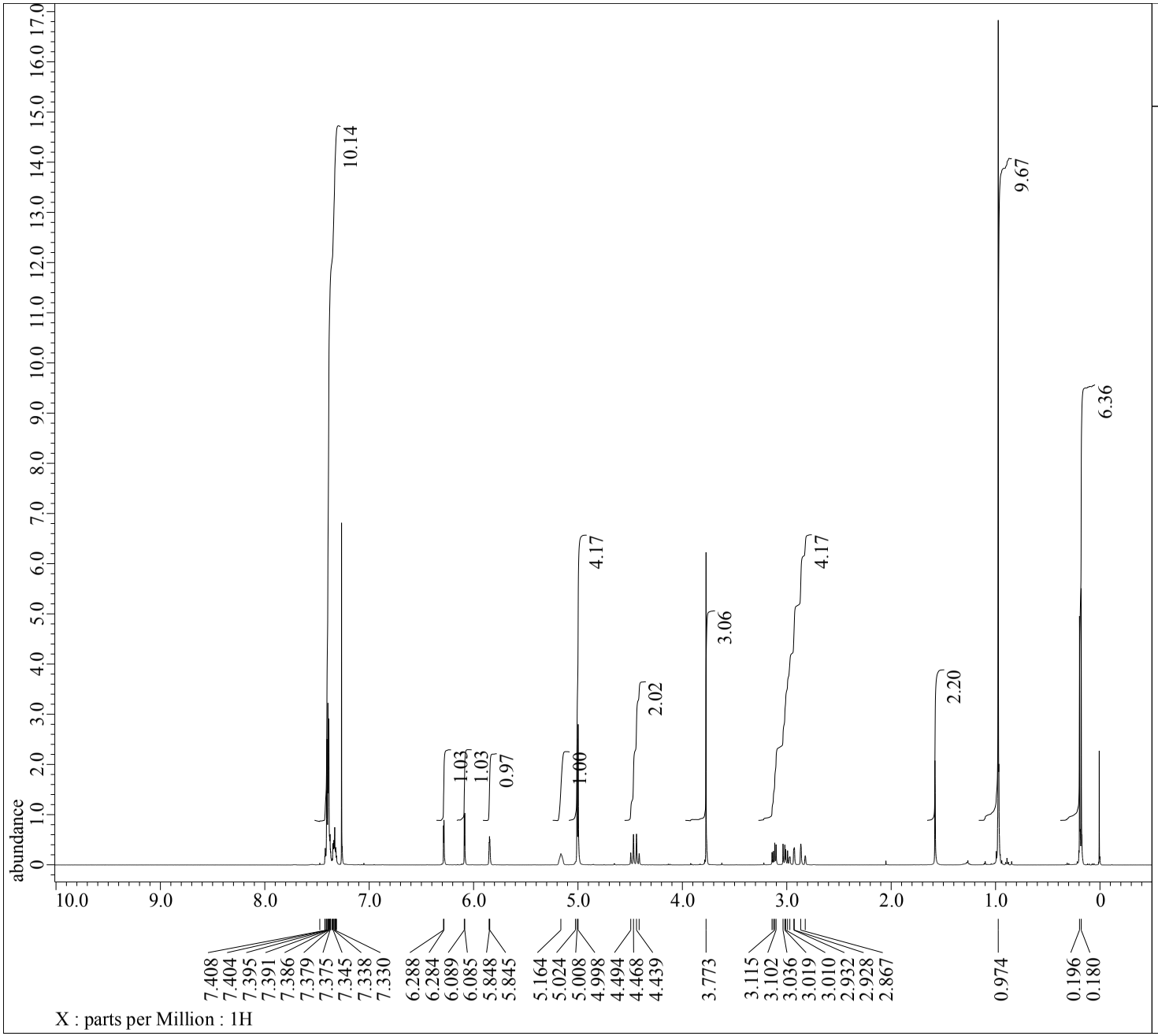


JEOL RESONANCE

```
Filename          = RY-121217-6-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 17-DEC-2012 16:47:29
Revision_Time     = 14-SEP-2015 13:52:31
Current_Time      = 14-SEP-2015 13:53:23

Comment           = morpho
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 500
Total_Scans       = 500

Relaxation_Delay  = 2[s]
Recvr_Gain        = 48
Temp_Get          = 20.4[dC]
X_90_Width        = 17.2[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.73333333[us]
Irr_Atn_Dec       = 25.42[dB]
Irr_Atn_Noe       = 25.42[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

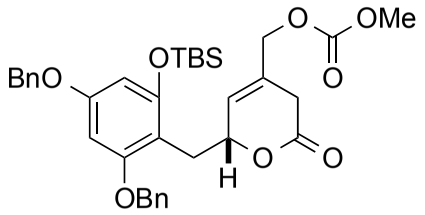


20

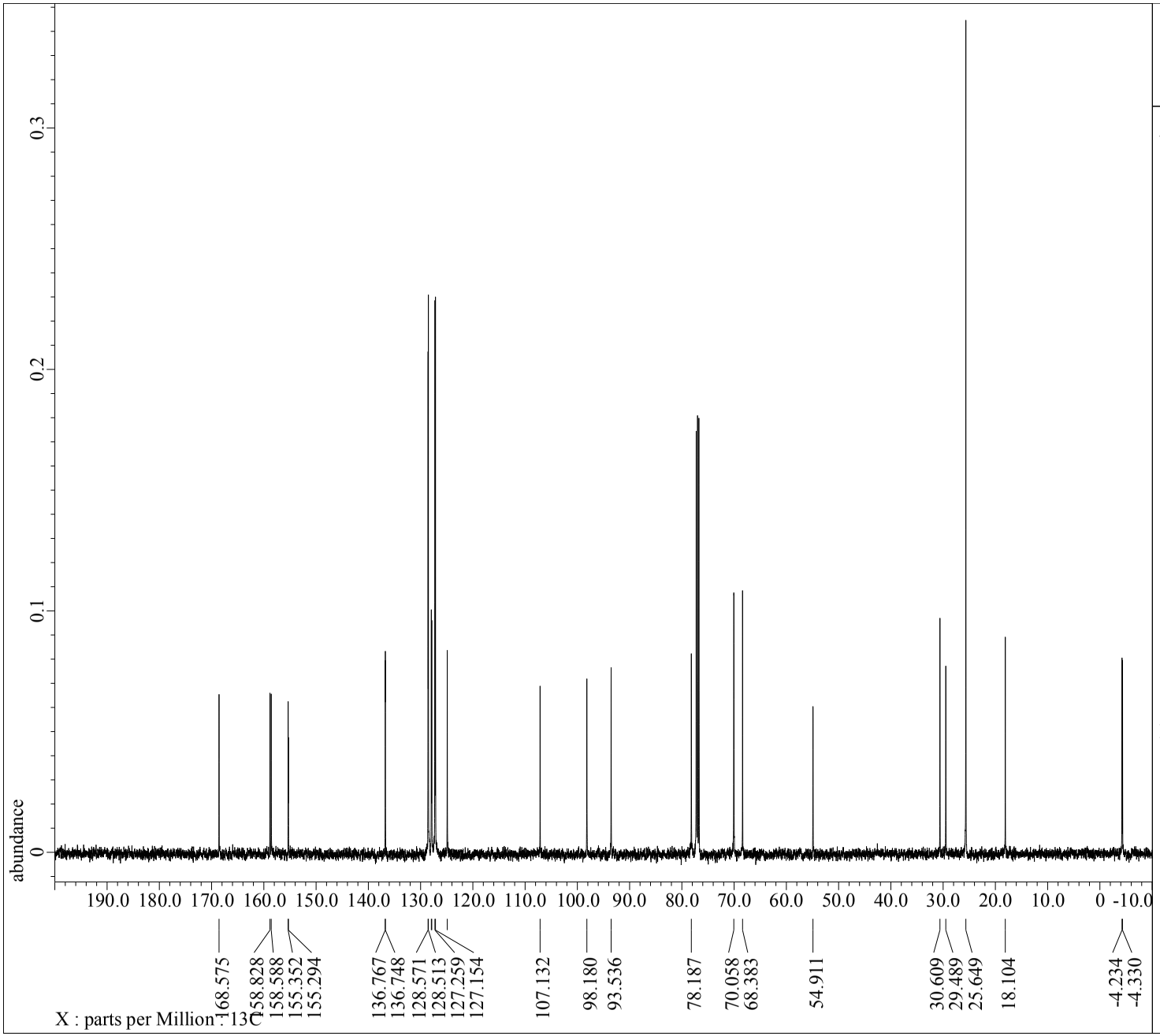


JEOL RESONANCE

Filename	= HOo-141022-2-5.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_Id	= S#702674
Solvent	= CHLOROFORM-D
Creation_Time	= 22-OCT-2014 19:16:38
Revision_Time	= 14-SEP-2015 14:23:07
Current_Time	= 14-SEP-2015 14:23:20
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
Dim_Title	= 1H
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 1.76422912[s]
X_Domain	= 1H
X_Freq	= 495.13191398[MHz]
X_Offset	= 5[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.5668198[Hz]
X_Sweep	= 9.28677563[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= 1H
Tri_Freq	= 495.13191398[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 40
Temp_Get	= 24.8[dC]
X_90_Width	= 8.16[us]
X_Acq_Time	= 1.76422912[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 4.08[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Repetition_Time	= 6.76422912[s]

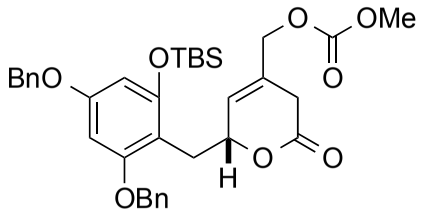


S17

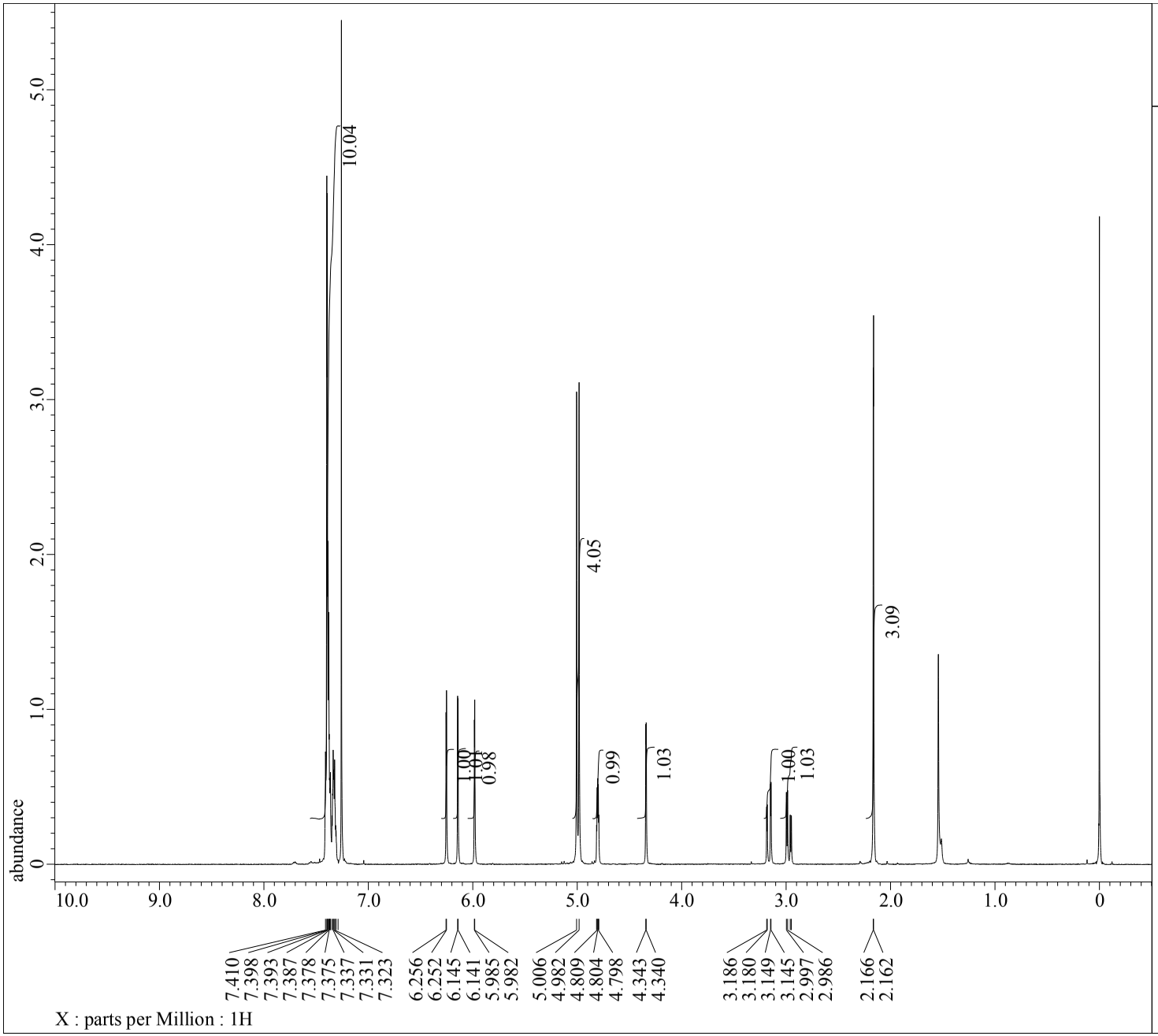


JEOL RESONANCE

Filename	= RY-121221-5-5.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_Id	= S#564312
Solvent	= CHLOROFORM-D
Creation_Time	= 21-DEC-2012 16:12:53
Revision_Time	= 14-SEP-2015 14:28:41
Current_Time	= 14-SEP-2015 14:28:57
Comment	= pyr
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= 13C
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 0.8388608[s]
X_Domain	= 13C
X_Freq	= 124.5010059[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.1920929[Hz]
X_Sweep	= 39.0625[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 800
Total_Scans	= 800
Relaxation_Delay	= 2[s]
Recvr_Gain	= 48
Temp_Get	= 21[dC]
X_90_Width	= 17.2[us]
X_Acq_Time	= 0.8388608[s]
X_Angle	= 30[deg]
X_Atn	= 6[dB]
X_Pulse	= 5.73333333[us]
Irr_Atn_Dec	= 25.42[dB]
Irr_Atn_Noe	= 25.42[dB]
Irr_Noise	= WALTZ
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 2[s]
Repetition_Time	= 2.8388608[s]

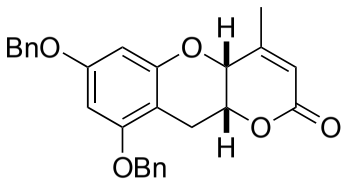


S17

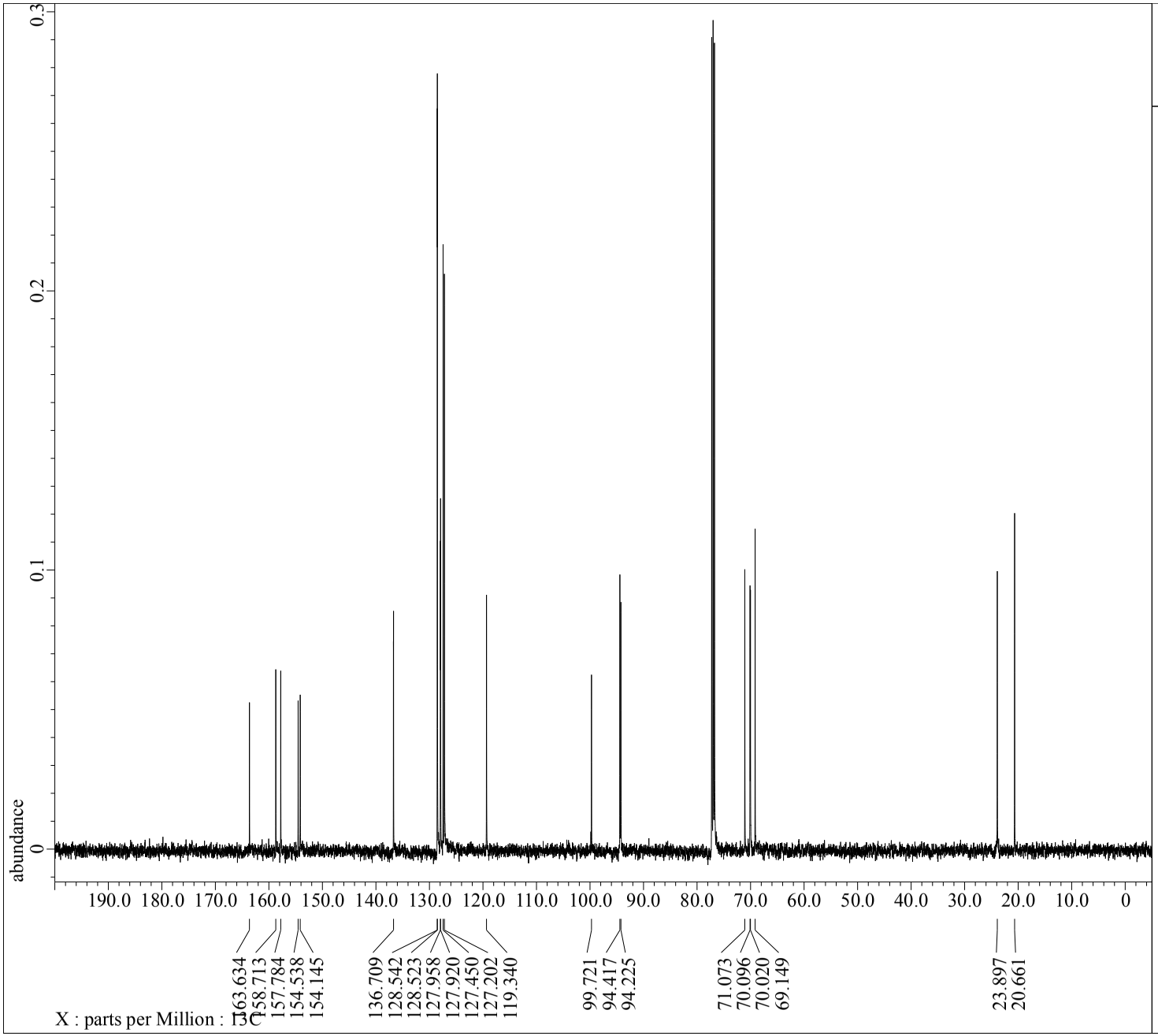


JEOL RESONANCE

```
Filename          = HOo-141128-3-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#788990
Solvent           = CHLOROFORM-D
Creation_Time     = 28-NOV-2014 21:41:43
Revision_Time     = 14-SEP-2015 15:53:42
Current_Time      = 14-SEP-2015 15:53:53

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 52
Temp_Get          = 25.4[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

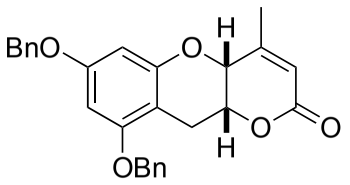


21

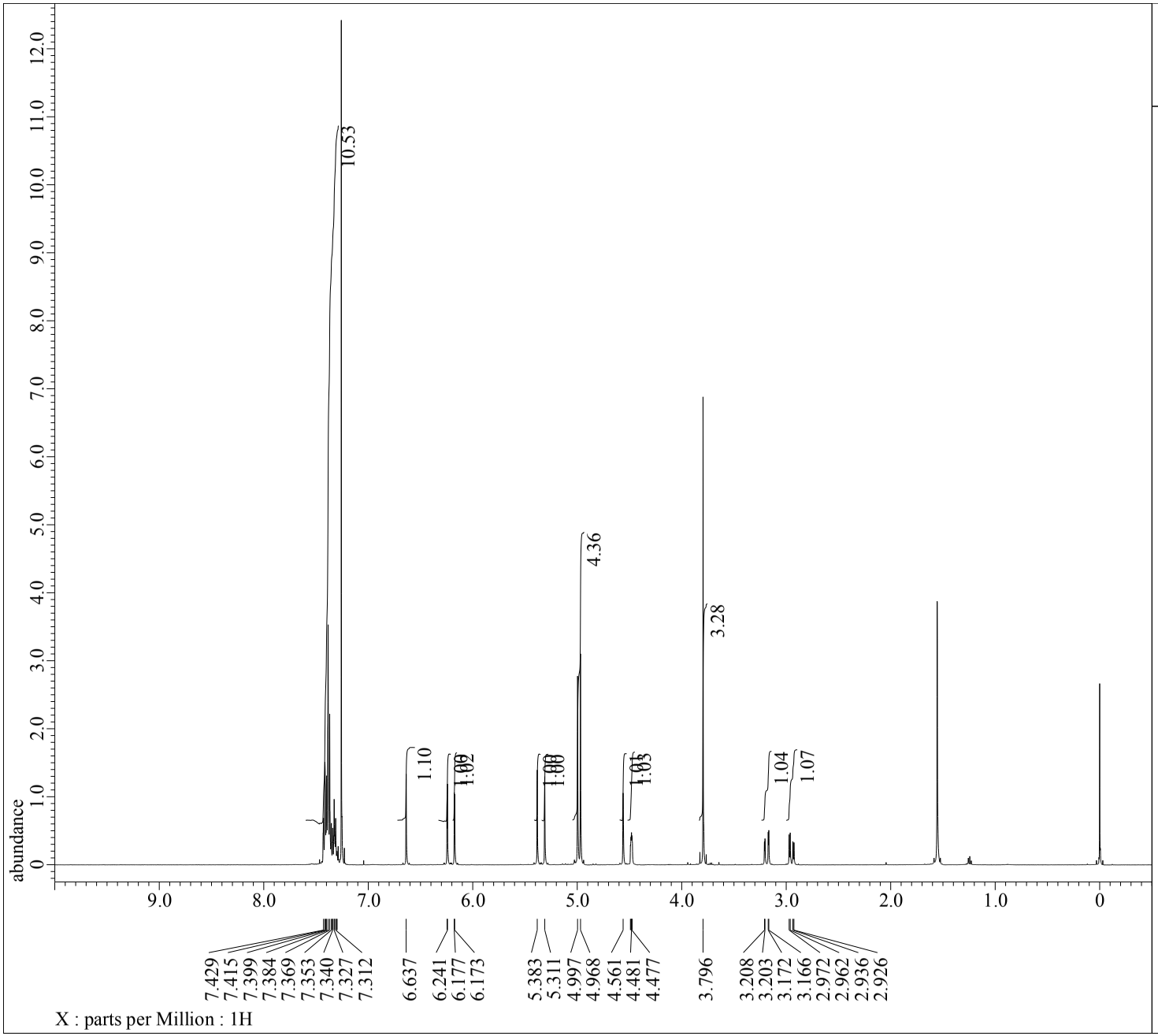


JEOL RESONANCE

```
Filename          = HOo-141128-3-C-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#793896
Solvent           = CHLOROFORM-D
Creation_Time     = 28-NOV-2014 22:39:49
Revision_Time     = 14-SEP-2015 16:07:20
Current_Time      = 14-SEP-2015 16:08:05

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 25.7[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

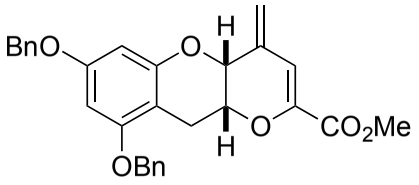


21

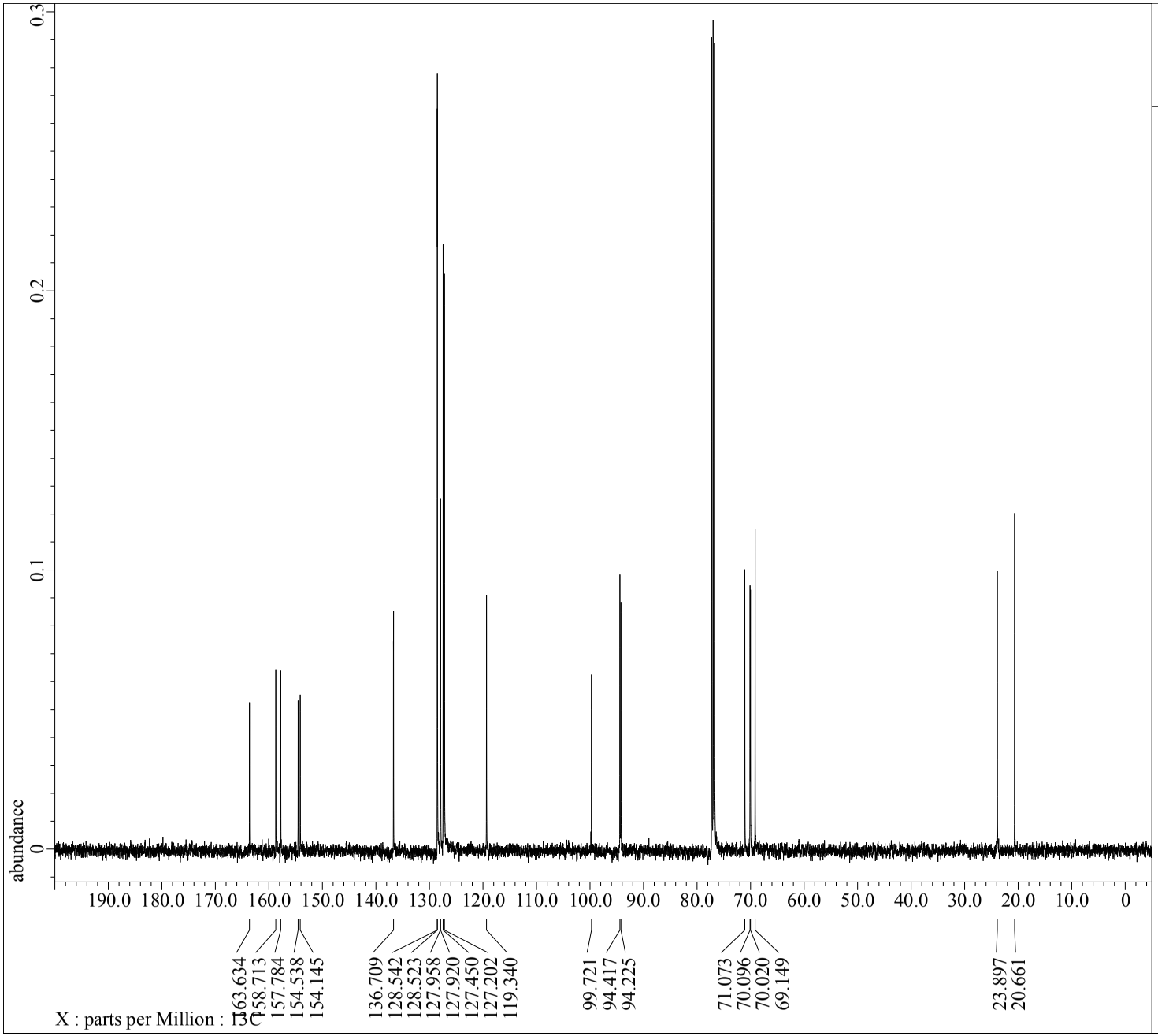


JEOL RESONANCE

```
Filename          = HOo-141103-1-H-10.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#598657
Solvent           = CHLOROFORM-D
Creation_Time     =  3-NOV-2014 16:23:31
Revision_Time     = 14-SEP-2015 16:30:43
Current_Time      = 14-SEP-2015 16:33:40

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 46
Temp_Get          = 24.8[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

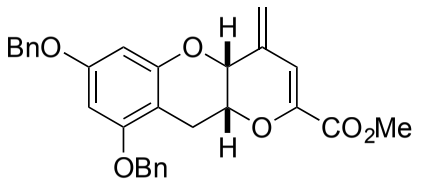


22

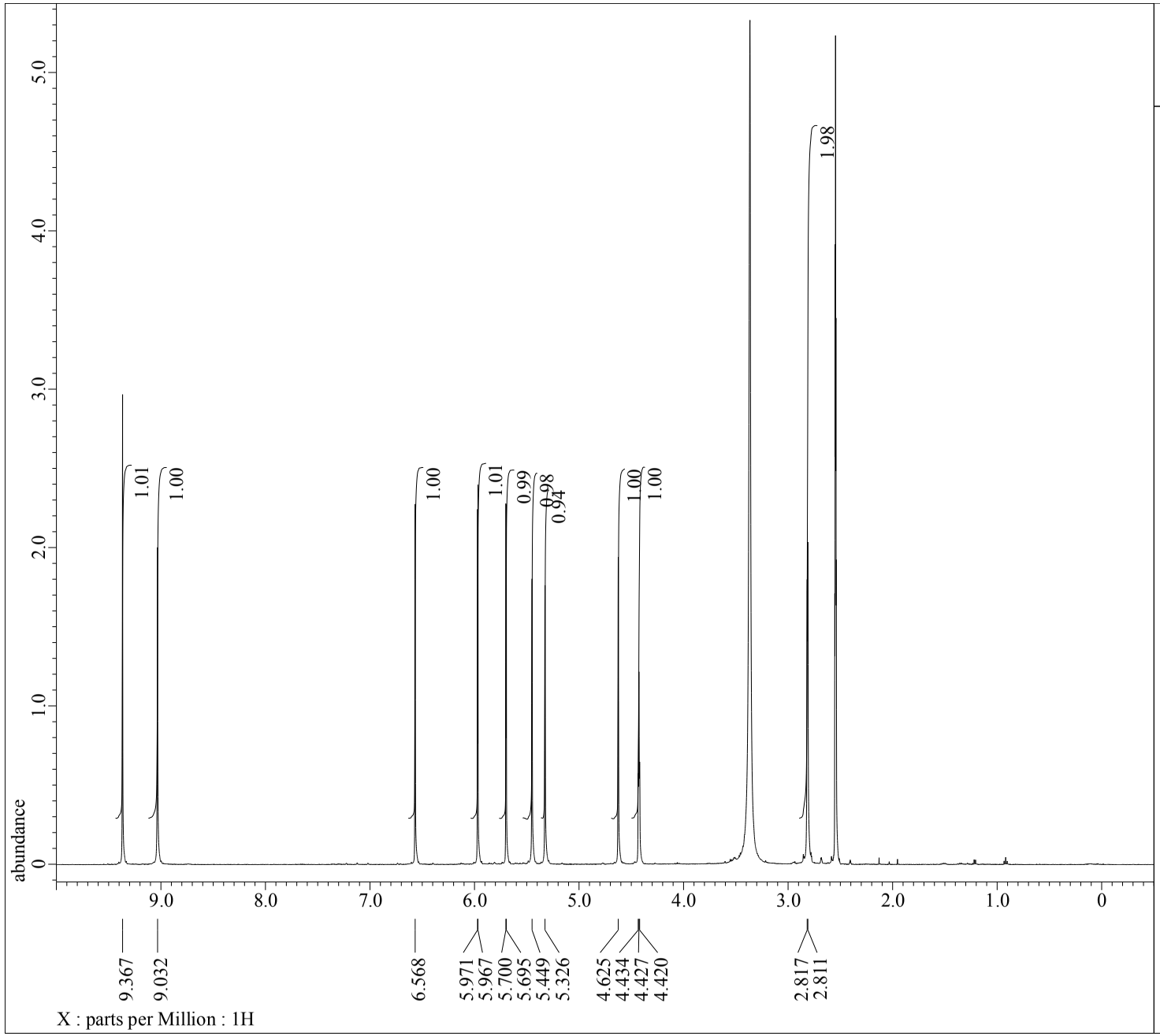


JEOL RESONANCE

```
Filename          = HOo-141128-3-C-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#793896
Solvent           = CHLOROFORM-D
Creation_Time     = 28-NOV-2014 22:39:49
Revision_Time     = 14-SEP-2015 16:42:35
Current_Time      = 14-SEP-2015 16:43:32

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 25.7[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

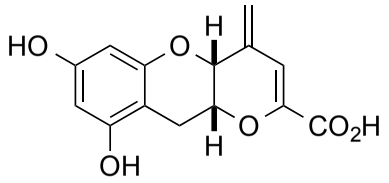


22

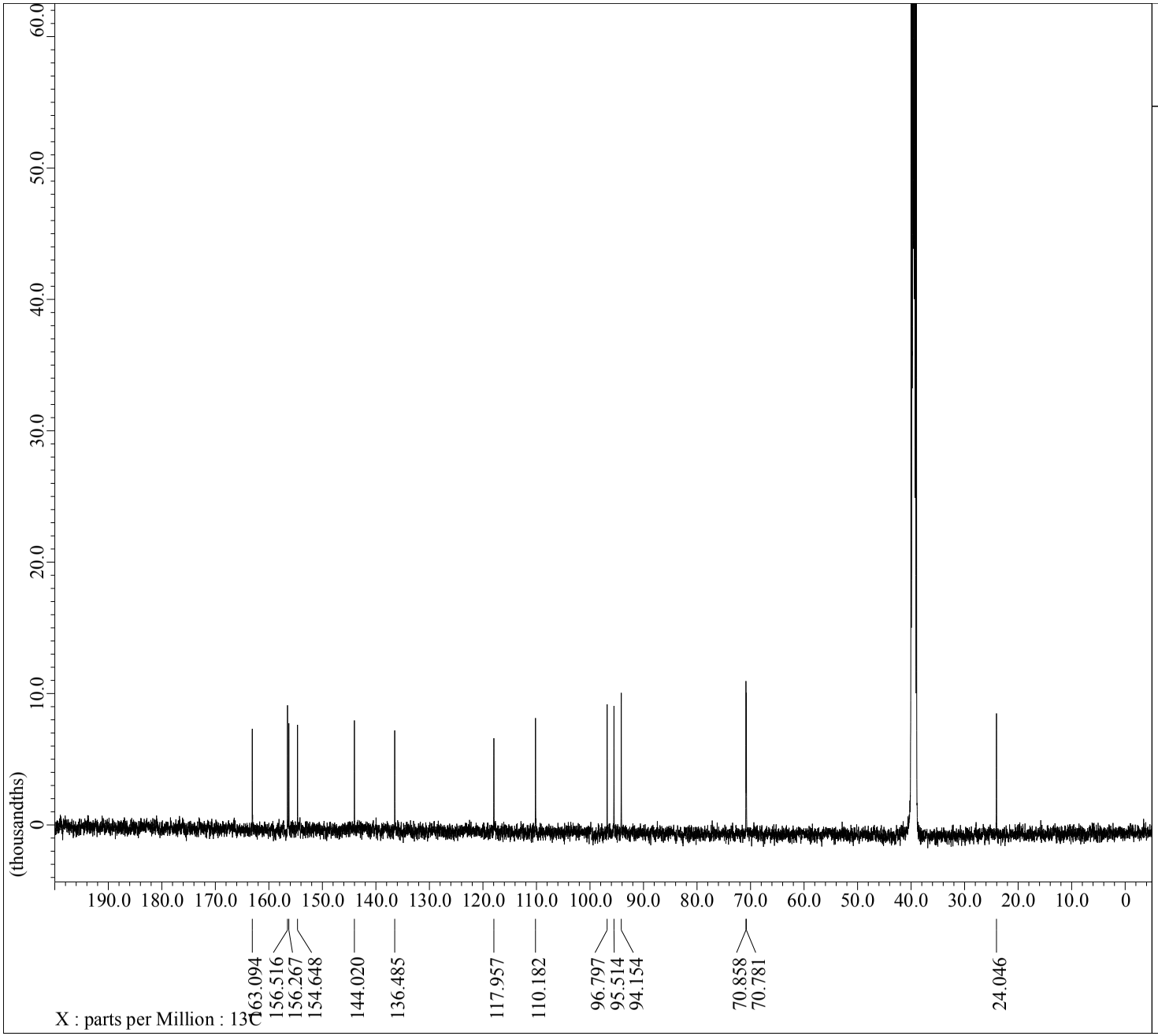


JEOL RESONANCE

```
Filename          = HOo-150305-1-7.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 1
Solvent           = DMSO-D6
Creation_Time     =  5-MAR-2015 23:28:23
Revision_Time     = 15-SEP-2015 12:00:51
Current_Time      = 15-SEP-2015 12:01:58

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 50
Temp_Get          = 27.3[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

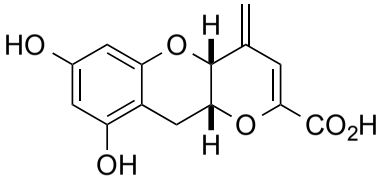


Teadenol A (**1**)

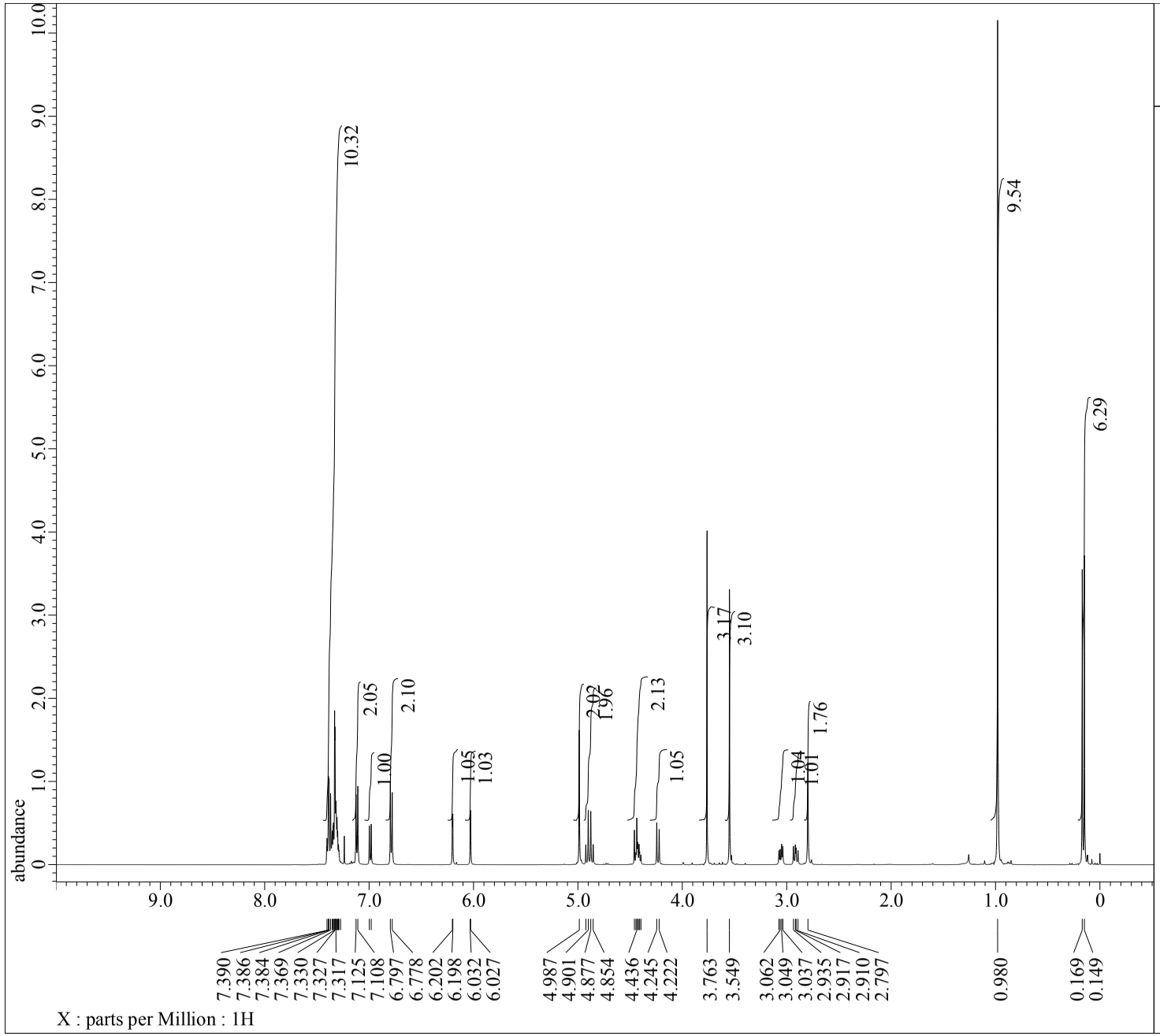


JEOL RESONANCE

```
Filename          = HOo-150305-1-C-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = 1
Solvent           = DMSO-D6
Creation_Time     =  6-MAR-2015 08:11:45
Revision_Time     = 15-SEP-2015 13:07:15
Current_Time      = 15-SEP-2015 13:07:44

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 11000
Total_Scans       = 11000

Relaxation_Delay = 2[s]
Recvr_Gain        = 48
Temp_Get          = 460.0[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

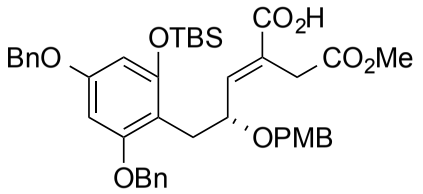


Teadenol A (**1**)

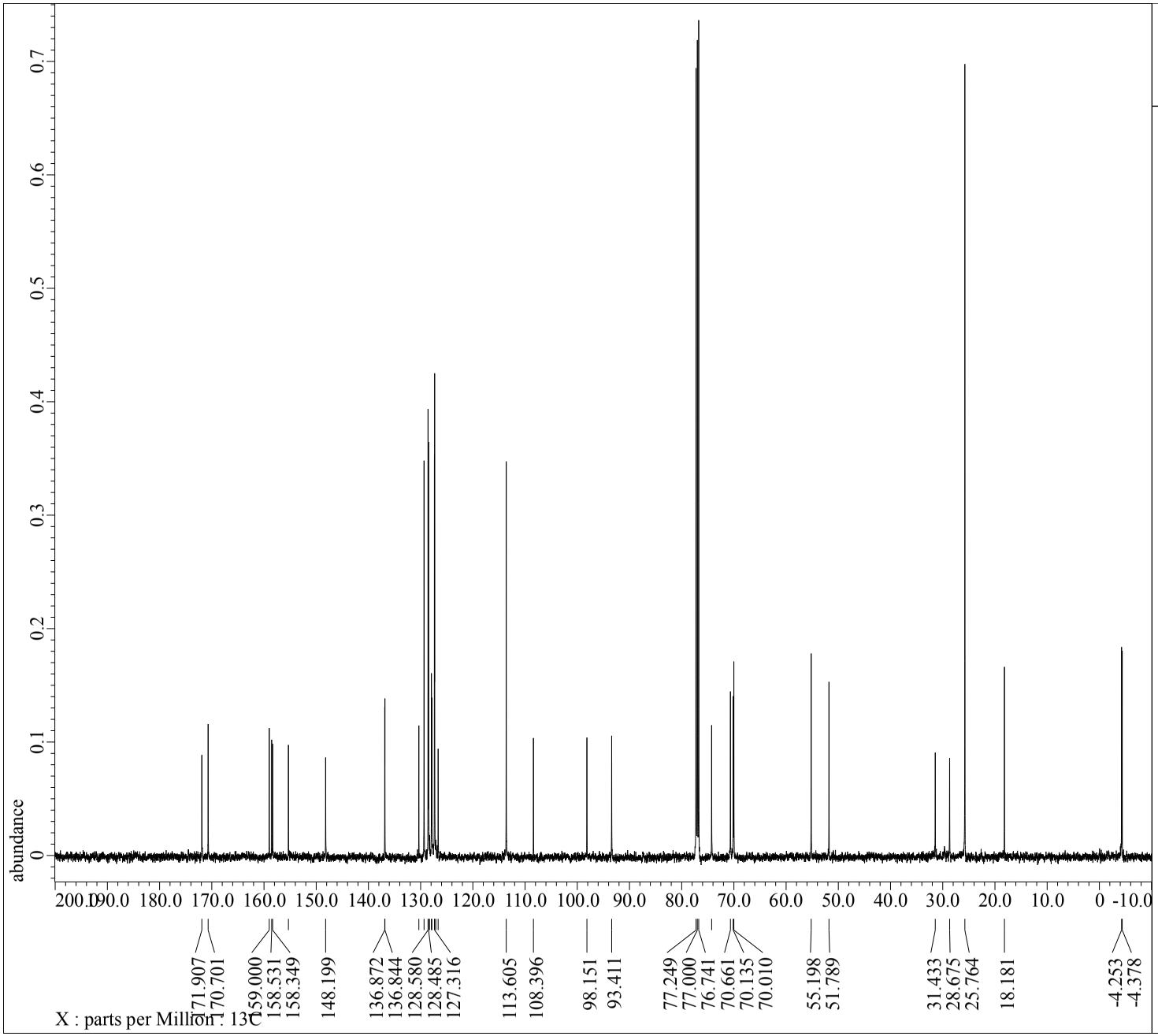


JEOL RESONANCE

Filename	= RY-130114-3-7.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_Id	= S#699734
Solvent	= CHLOROFORM-D
Creation_Time	= 14-JAN-2013 19:21:51
Revision_Time	= 15-SEP-2015 13:44:07
Current_Time	= 15-SEP-2015 13:44:36
Comment	= trans deallyl
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
Dim_Title	= 1H
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 1.76422912[s]
X_Domain	= 1H
X_Freq	= 495.13191398[MHz]
X_Offset	= 5[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.5668198[Hz]
X_Sweep	= 9.28677563[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= 1H
Tri_Freq	= 495.13191398[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 30
Temp_Get	= 21.7[dC]
X_90_Width	= 12.9[us]
X_Acq_Time	= 1.76422912[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 6.45[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Repetition_Time	= 6.76422912[s]

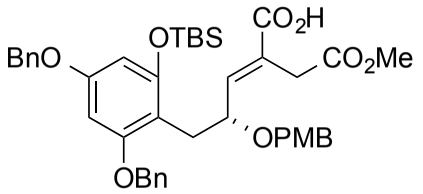


S20

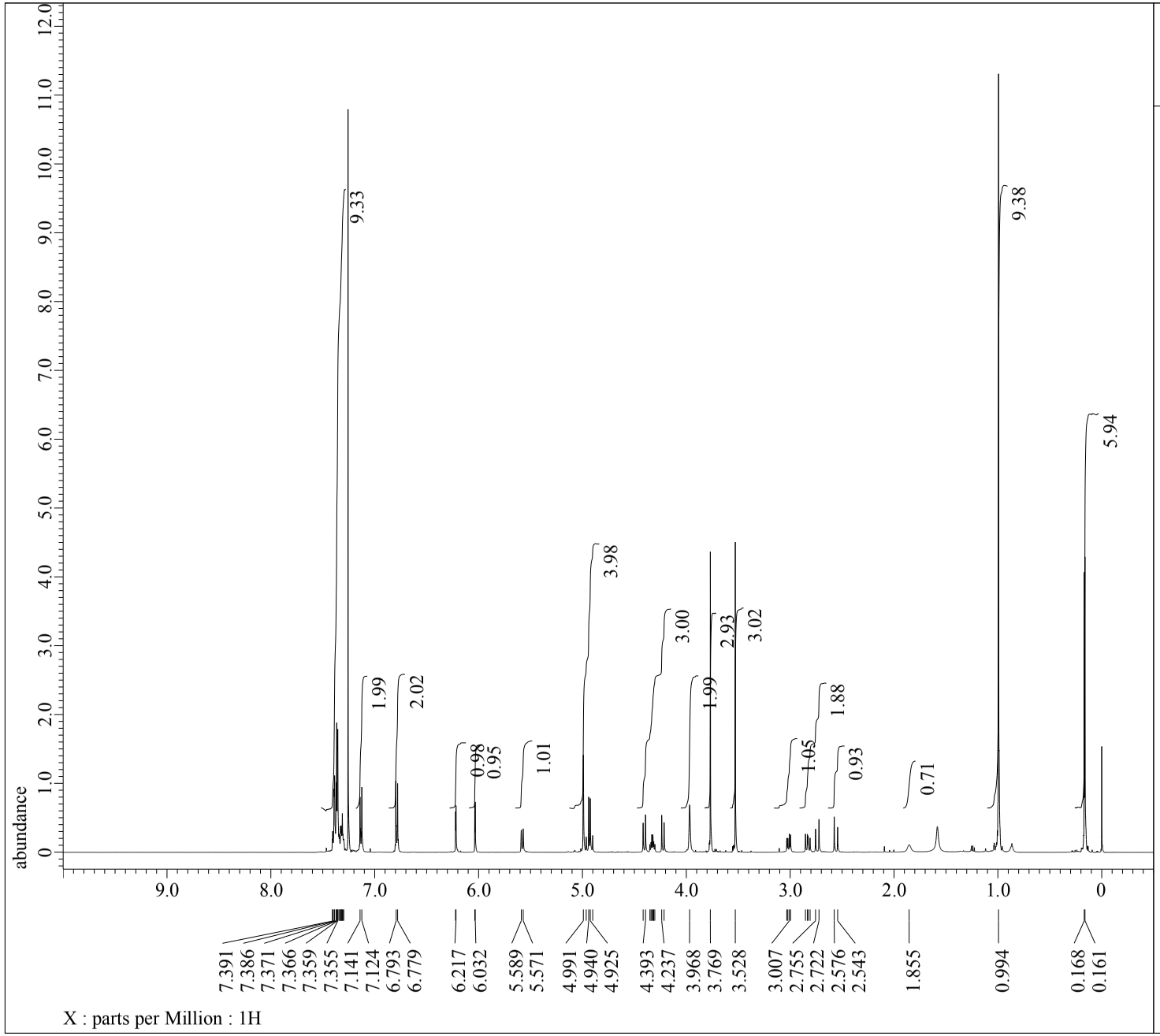


JEOL RESONANCE

```
Filename          = RY-130114-4-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#701478
Solvent           = CHLOROFORM-D
Creation_Time     = 14-JAN-2013 19:54:18
Revision_Time     = 15-SEP-2015 13:58:11
Current_Time      = 15-SEP-2015 13:58:44

Comment           = trans deallyl
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 640
Total_Scans       = 640

Relaxation_Delay = 2[s]
Recvr_Gain        = 52
Temp_Get          = 21.7[dC]
X_90_Width        = 10.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 8[dB]
X_Pulse           = 3.53333333[us]
Irr_Atn_Dec       = 21.06[dB]
Irr_Atn_Noe       = 21.06[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

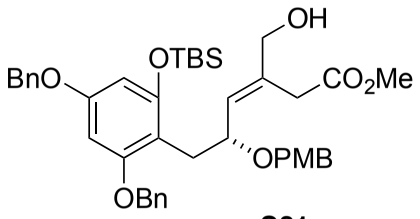


S20

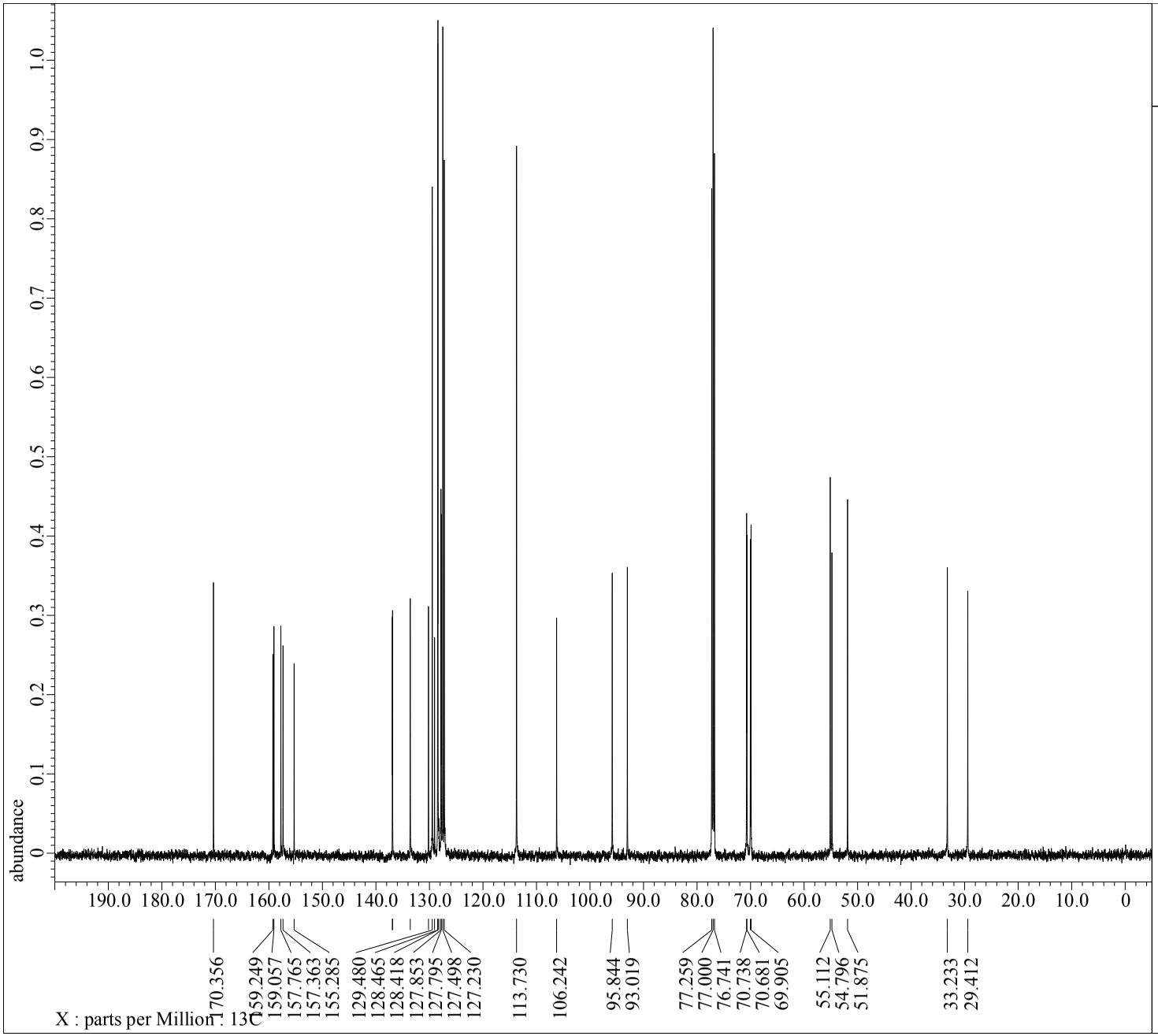


JEOL
Solutions for Innovation

```
Filename          = HOo-141121-3-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#630922
Solvent           = CHLOROFORM-D
Creation_Time     = 21-NOV-2014 17:18:13
Revision_Time     = 29-DEC-2015 17:55:44
Current_Time      = 29-DEC-2015 17:55:53

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 40
Temp_Get          = 24.7[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

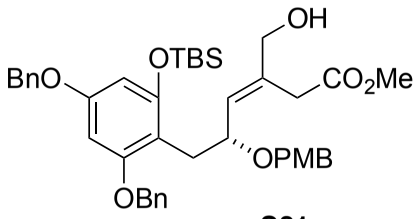


S21

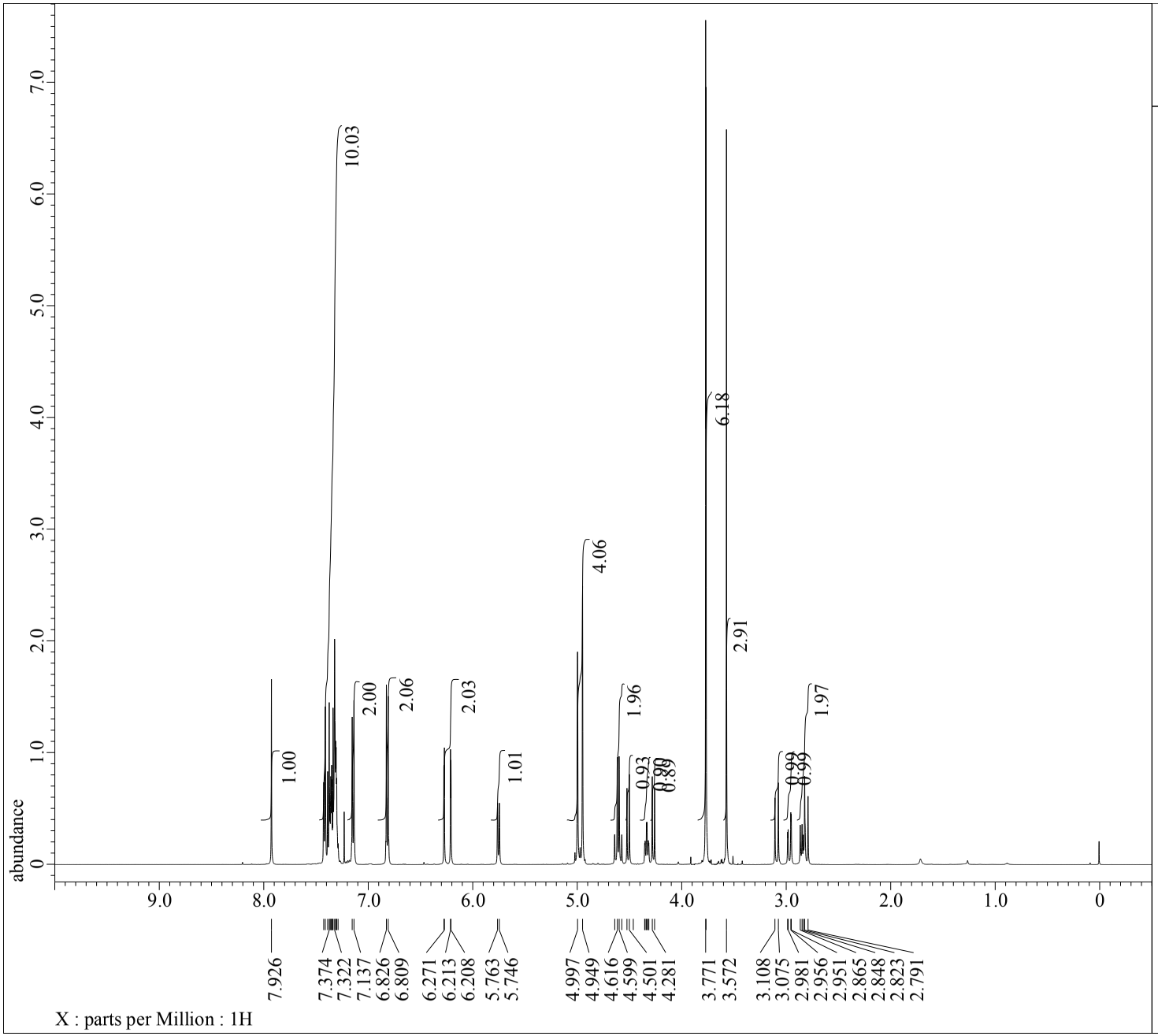


JEOL RESONANCE

```
Filename          = RY-130116-2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 16-JAN-2013 14:12:23
Revision_Time     = 16-SEP-2015 17:43:41
Current_Time      = 16-SEP-2015 17:44:09

Comment           = trans TBAF
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 400
Total_Scans       = 400

Relaxation_Delay = 2[s]
Recvr_Gain        = 54
Temp_Get          = 22.1[dC]
X_90_Width        = 10.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 8[dB]
X_Pulse           = 3.53333333[us]
Irr_Atn_Dec       = 21.06[dB]
Irr_Atn_Noe       = 21.06[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

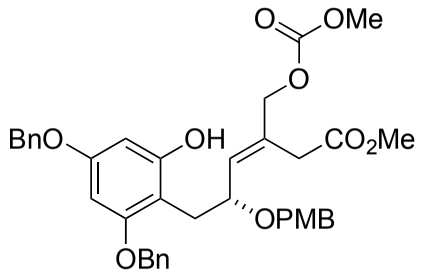


S21

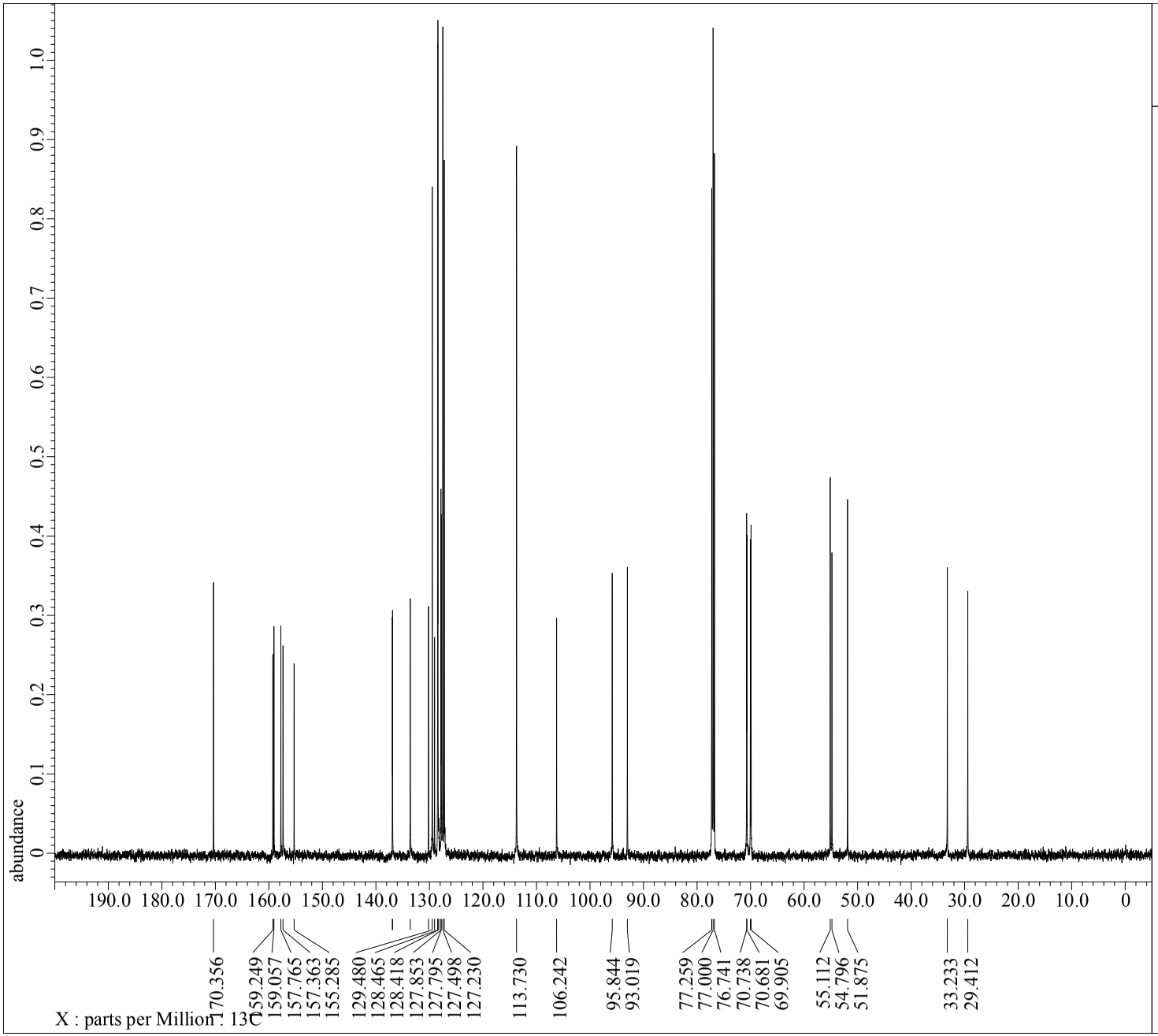


JEOL RESONANCE

```
Filename          = RY-130116-1-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 16-JAN-2013 13:52:51
Revision_Time     = 16-SEP-2015 16:53:53
Current_Time      = 16-SEP-2015 16:56:08

Comment           = trans TBAF
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 28
Temp_Get          = 21.6[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

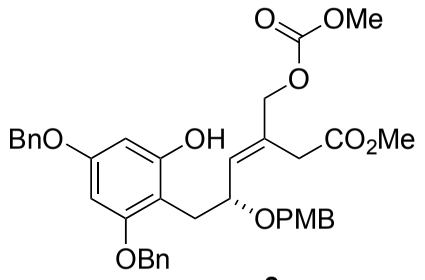


8

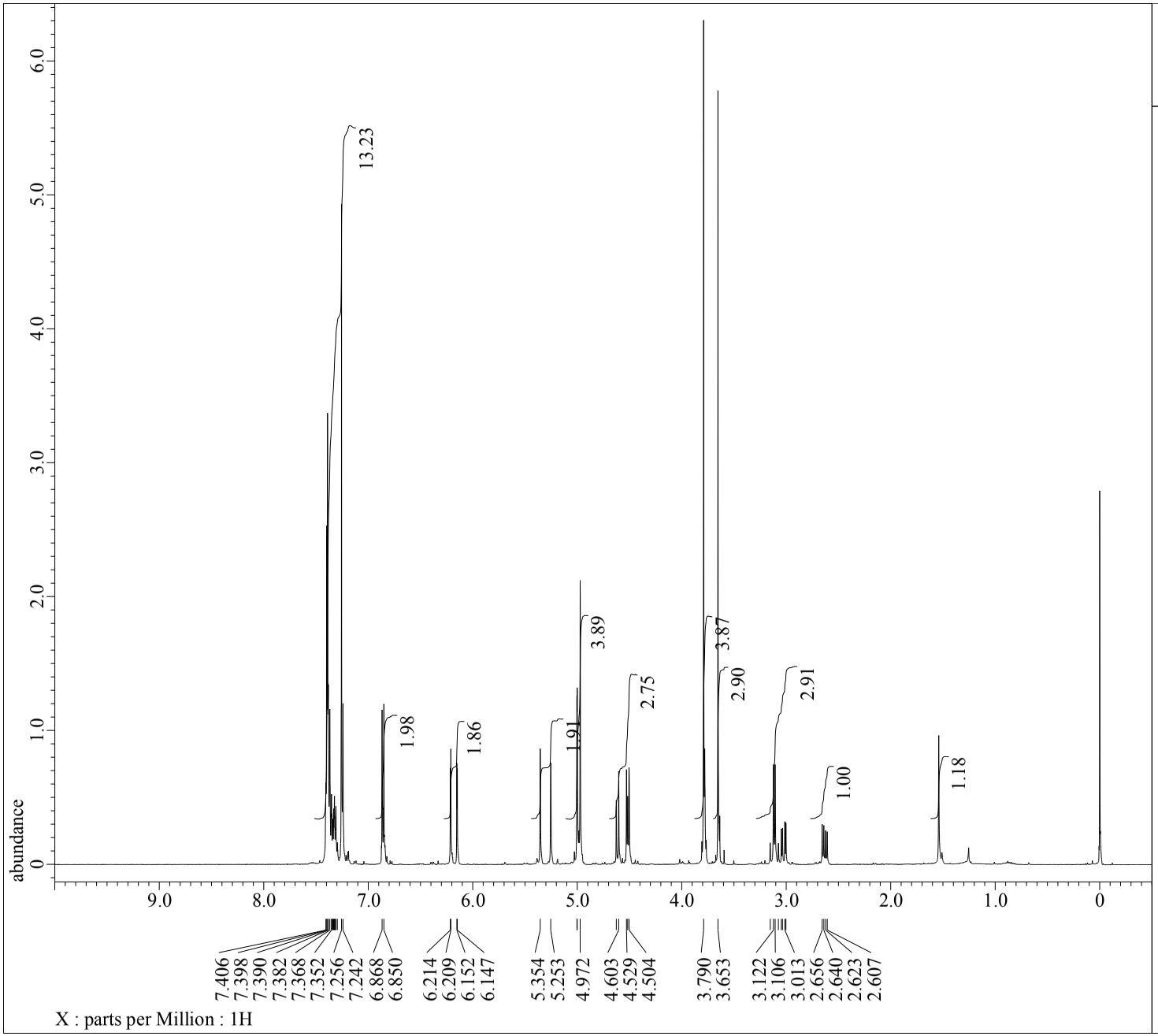


JEOL RESONANCE

```
Filename          = RY-130116-2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 16-JAN-2013 14:12:23
Revision_Time     = 16-SEP-2015 17:43:41
Current_Time      = 16-SEP-2015 17:44:09

Comment           = trans TBAF
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 400
Total_Scans       = 400

Relaxation_Delay = 2[s]
Recvr_Gain        = 54
Temp_Get          = 22.1[dC]
X_90_Width        = 10.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 8[dB]
X_Pulse           = 3.53333333[us]
Irr_Atn_Dec       = 21.06[dB]
Irr_Atn_Noe       = 21.06[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

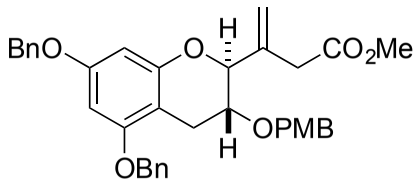


8

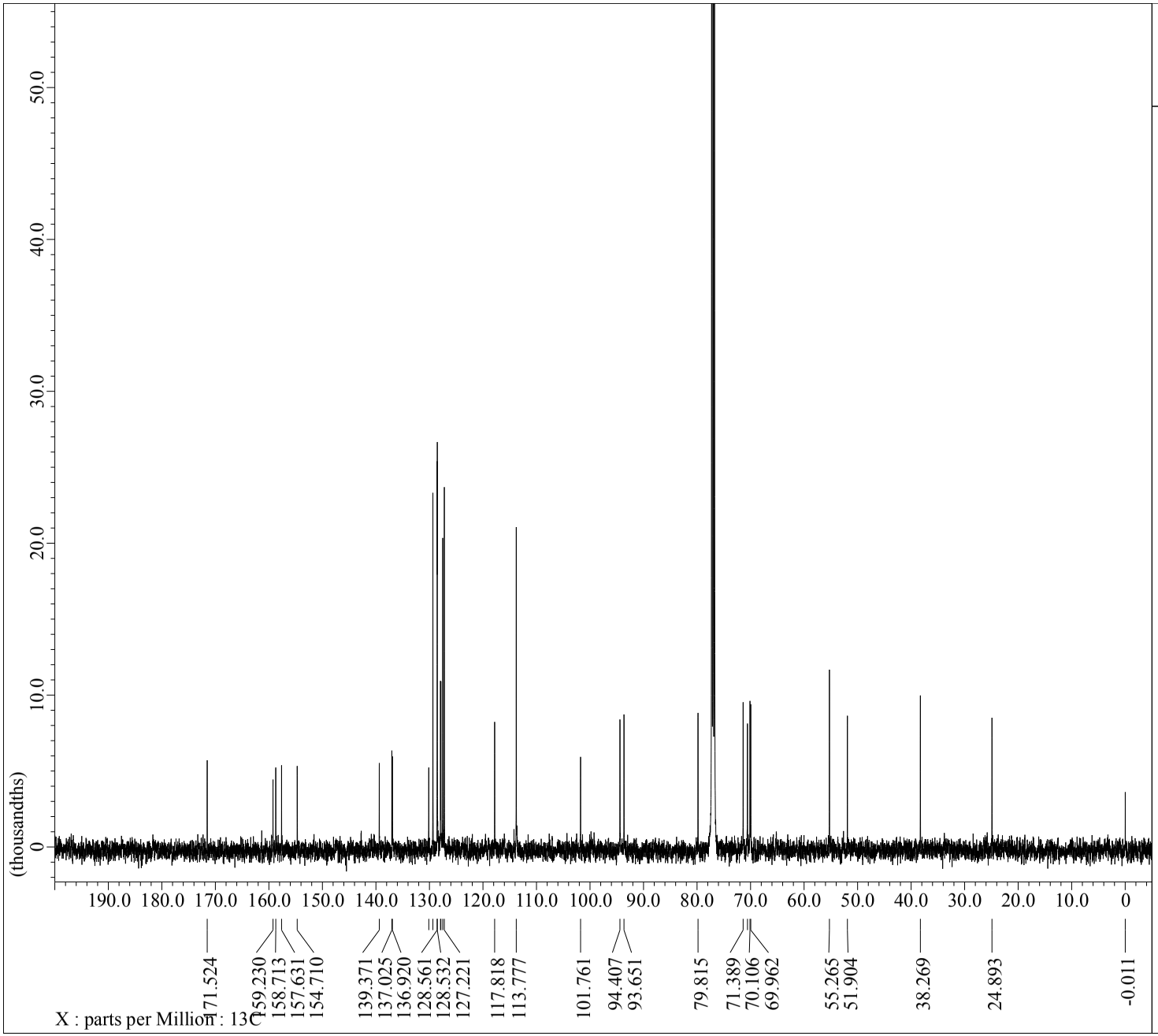


JEOL RESONANCE

```
Filename          = HOo-141225-1-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#596102
Solvent           = CHLOROFORM-D
Creation_Time     = 25-DEC-2014 16:16:56
Revision_Time     = 17-SEP-2015 15:46:37
Current_Time      = 17-SEP-2015 15:47:21

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 46
Temp_Get          = 24.9[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

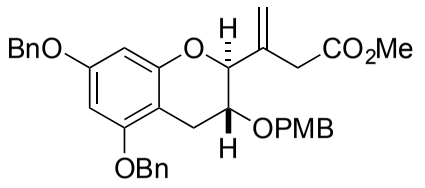


24

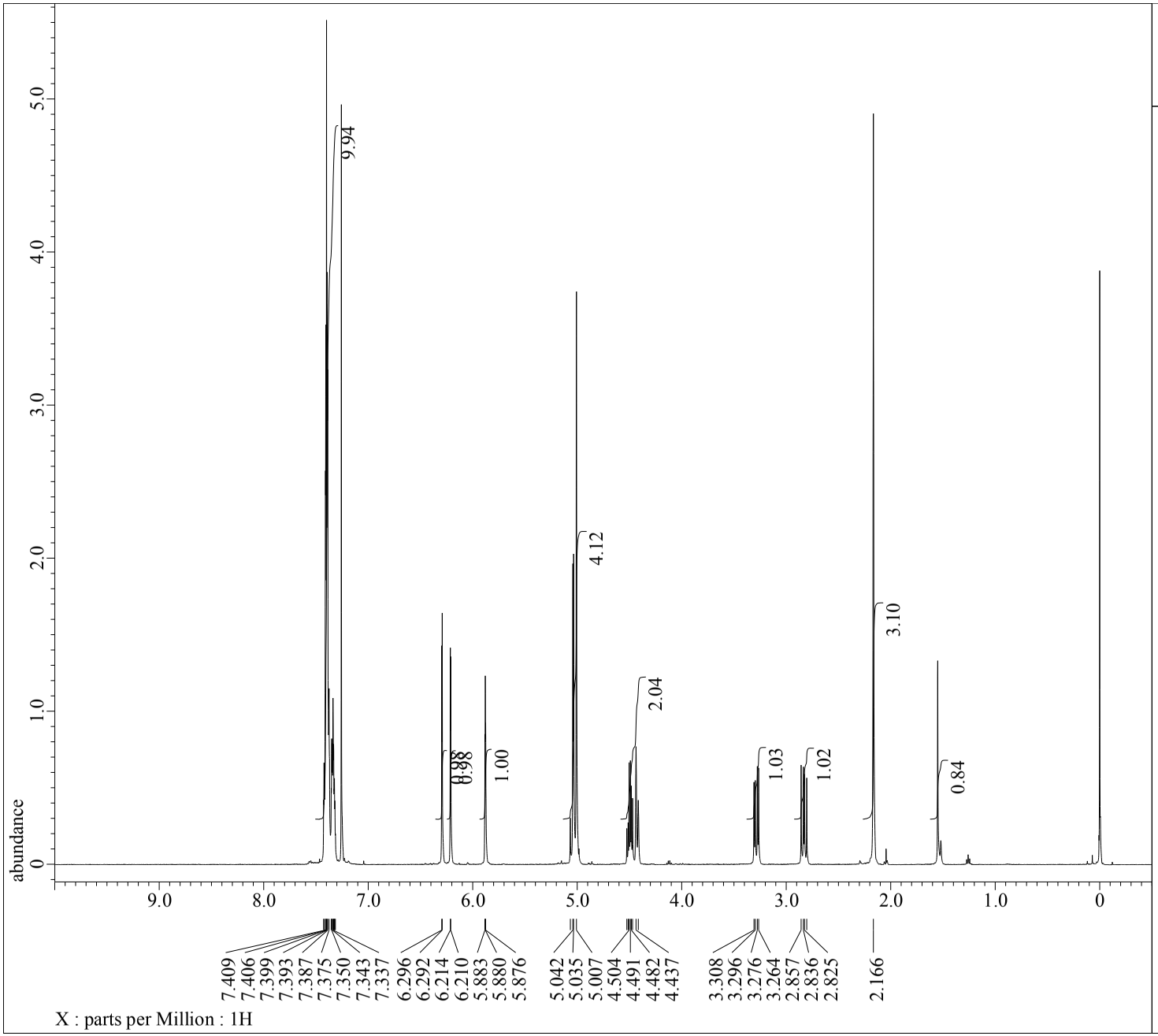


JEOL RESONANCE

```
Filename          = HOo-141225-2-8.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#813132
Solvent           = CHLOROFORM-D
Creation_Time     = 26-DEC-2014 08:11:24
Revision_Time     = 17-SEP-2015 15:10:40
Current_Time      = 17-SEP-2015 15:11:03

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 12500
Total_Scans       = 12500

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 24.3[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

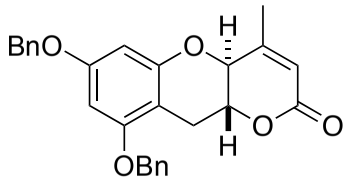


24

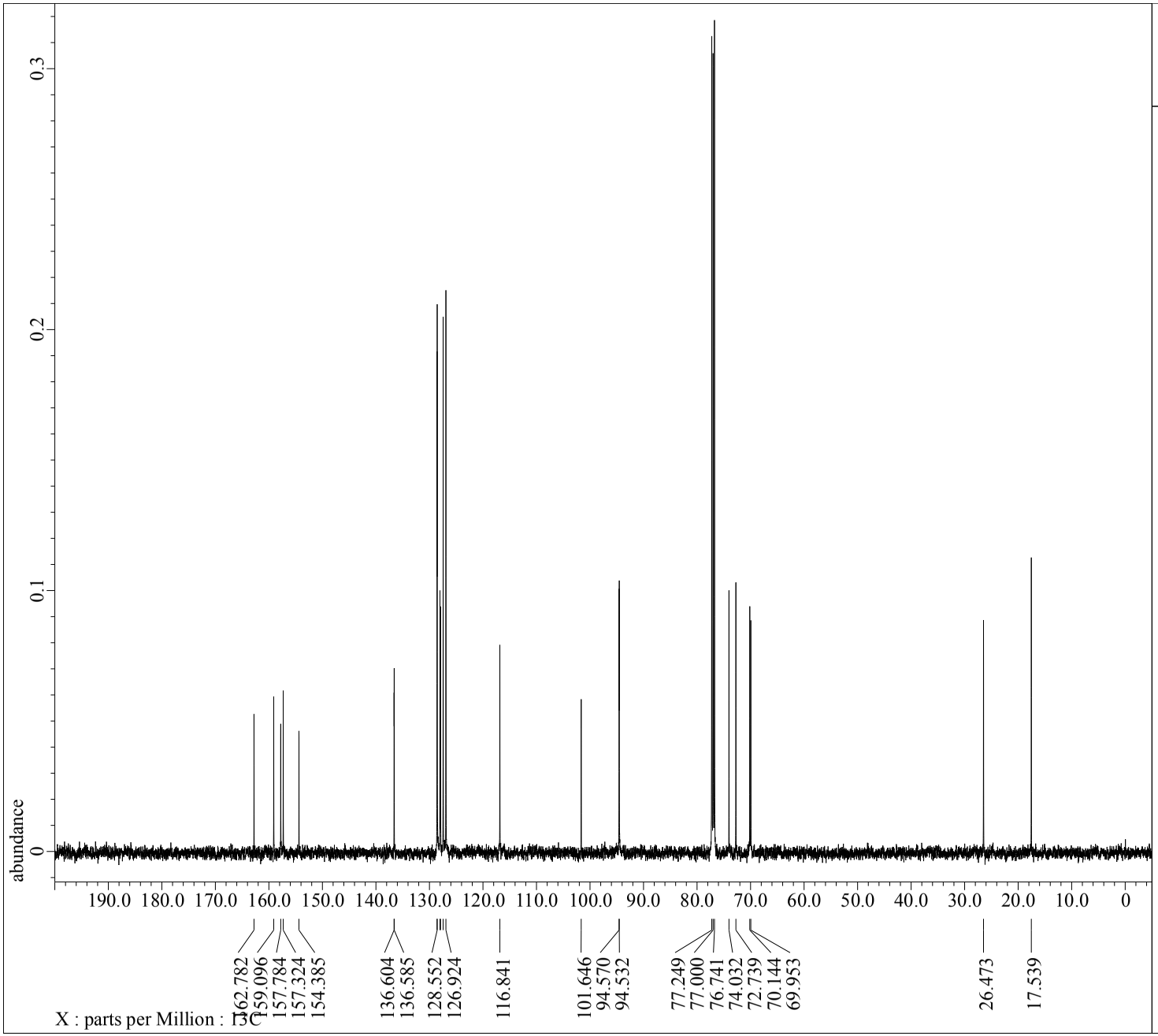


JEOL RESONANCE

```
Filename          = HOo-141223-3-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = S#780870
Solvent           = CHLOROFORM-D
Creation_Time     = 23-DEC-2014 21:25:08
Revision_Time     = 18-SEP-2015 14:59:33
Current_Time      = 18-SEP-2015 14:59:59

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 48
Temp_Get          = 24[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

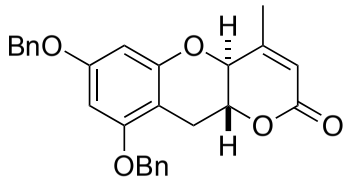


25

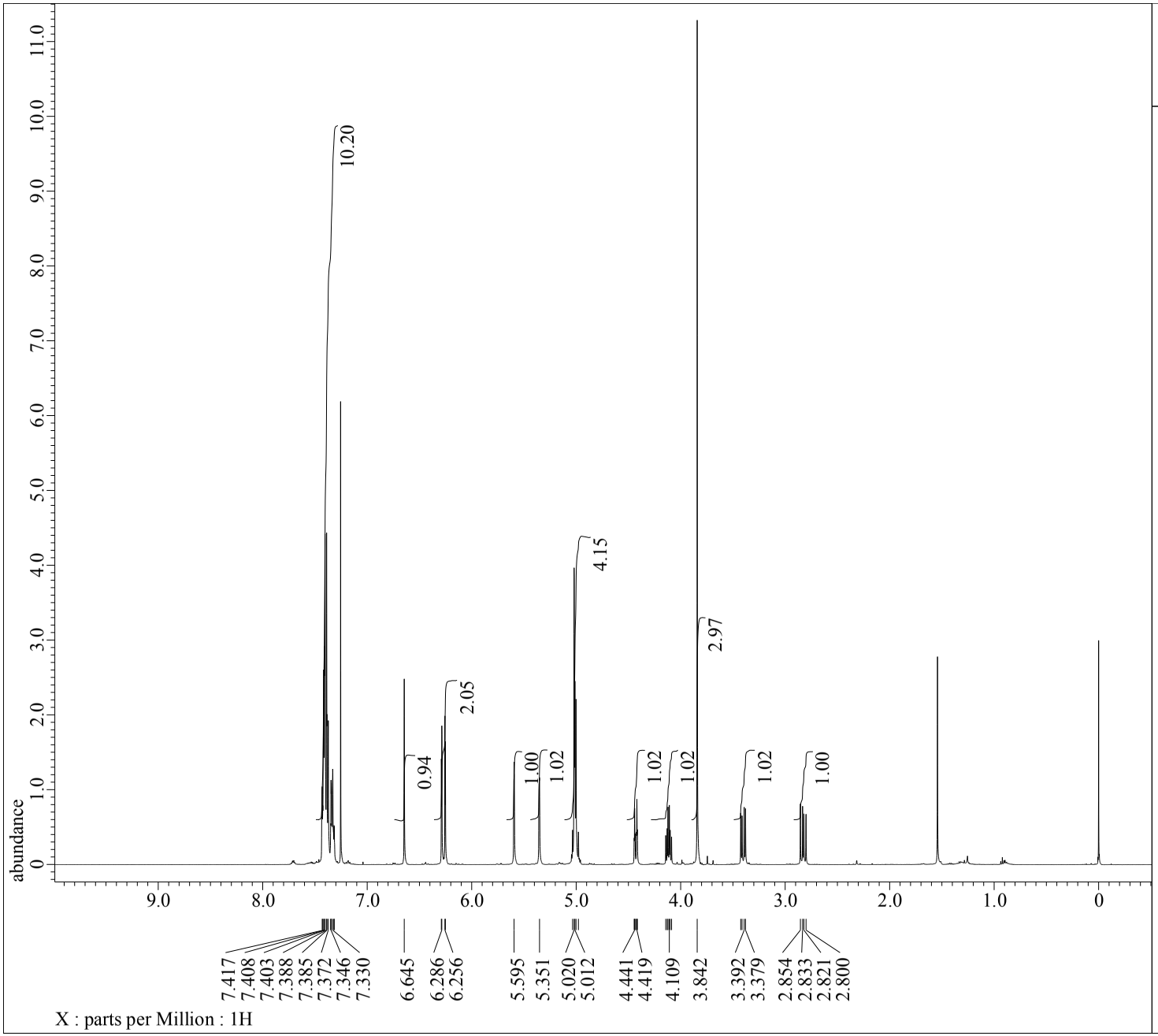


JEOL RESONANCE

```
Filename          = HOo-141224-1-C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#481318
Solvent           = CHLOROFORM-D
Creation_Time     = 24-DEC-2014 13:54:14
Revision_Time     = 18-SEP-2015 16:11:14
Current_Time      = 18-SEP-2015 16:11:49

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 24.3[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

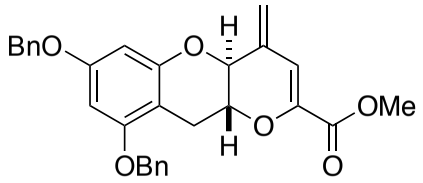


25

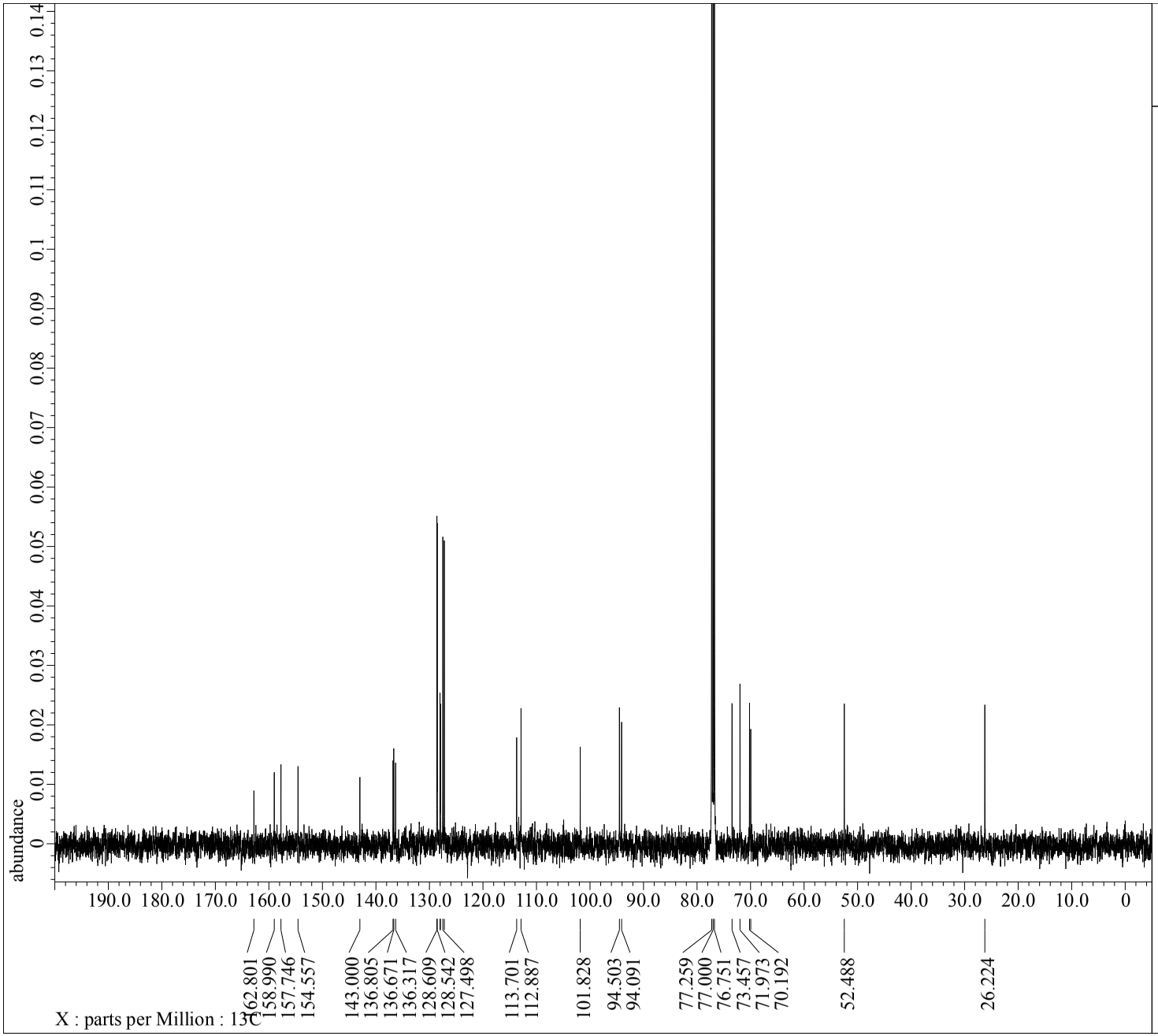


JEOL RESONANCE

```
Filename          = HOo-150218-1-13.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 1
Solvent           = CHLOROFORM-D
Creation_Time     = 18-FEB-2015 15:12:01
Revision_Time     = 18-SEP-2015 21:58:12
Current_Time      = 18-SEP-2015 21:58:33

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 46
Temp_Get          = 25.5[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

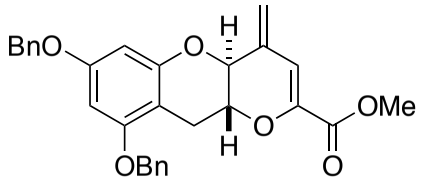


26

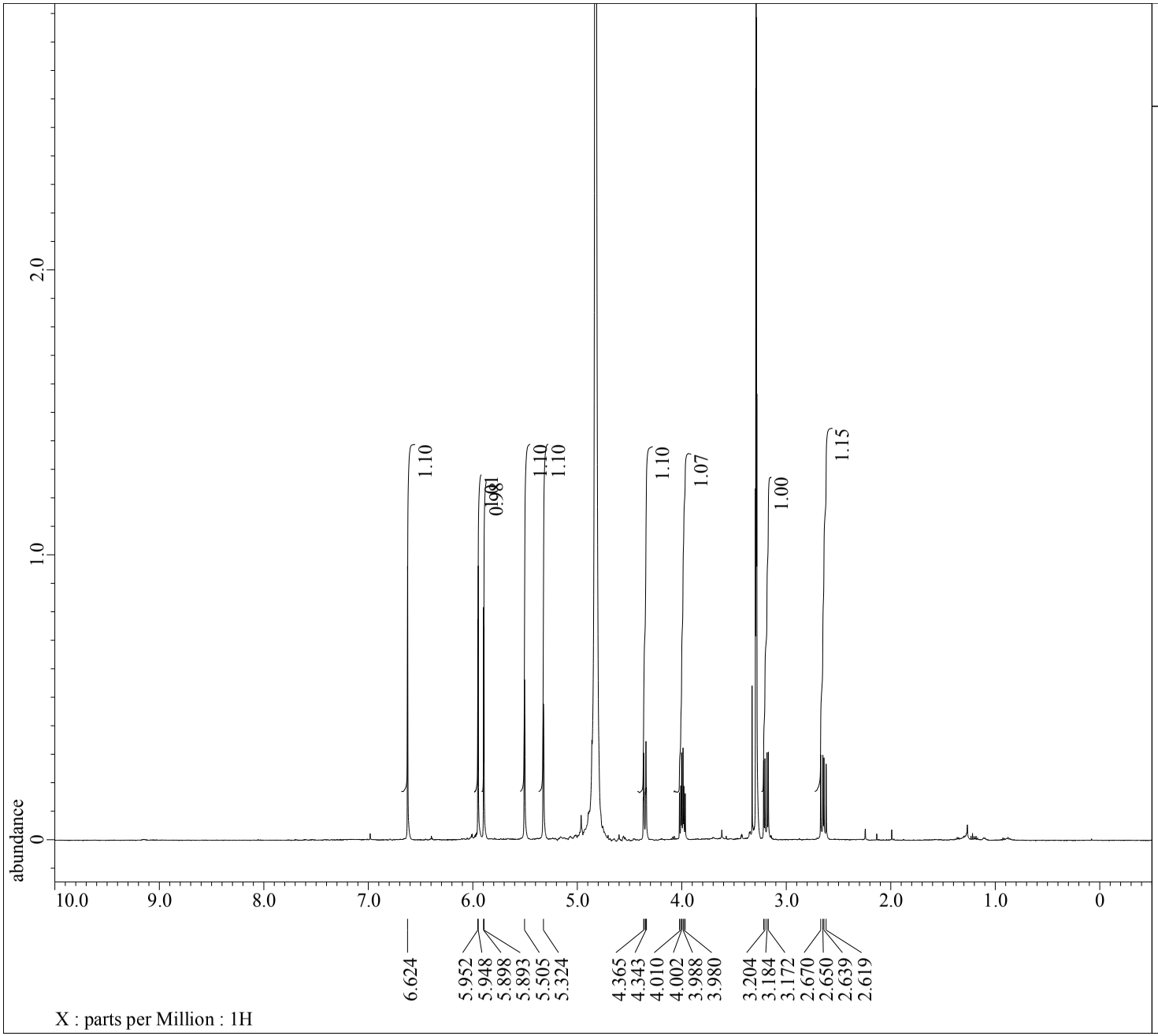


JEOL RESONANCE

```
Filename          = HOo-150218-1-C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = 1
Solvent           = CHLOROFORM-D
Creation_Time     = 18-FEB-2015 16:02:22
Revision_Time     = 18-SEP-2015 22:18:17
Current_Time      = 18-SEP-2015 22:19:06

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 25.5[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```

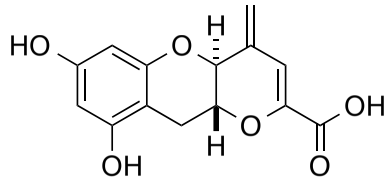


26

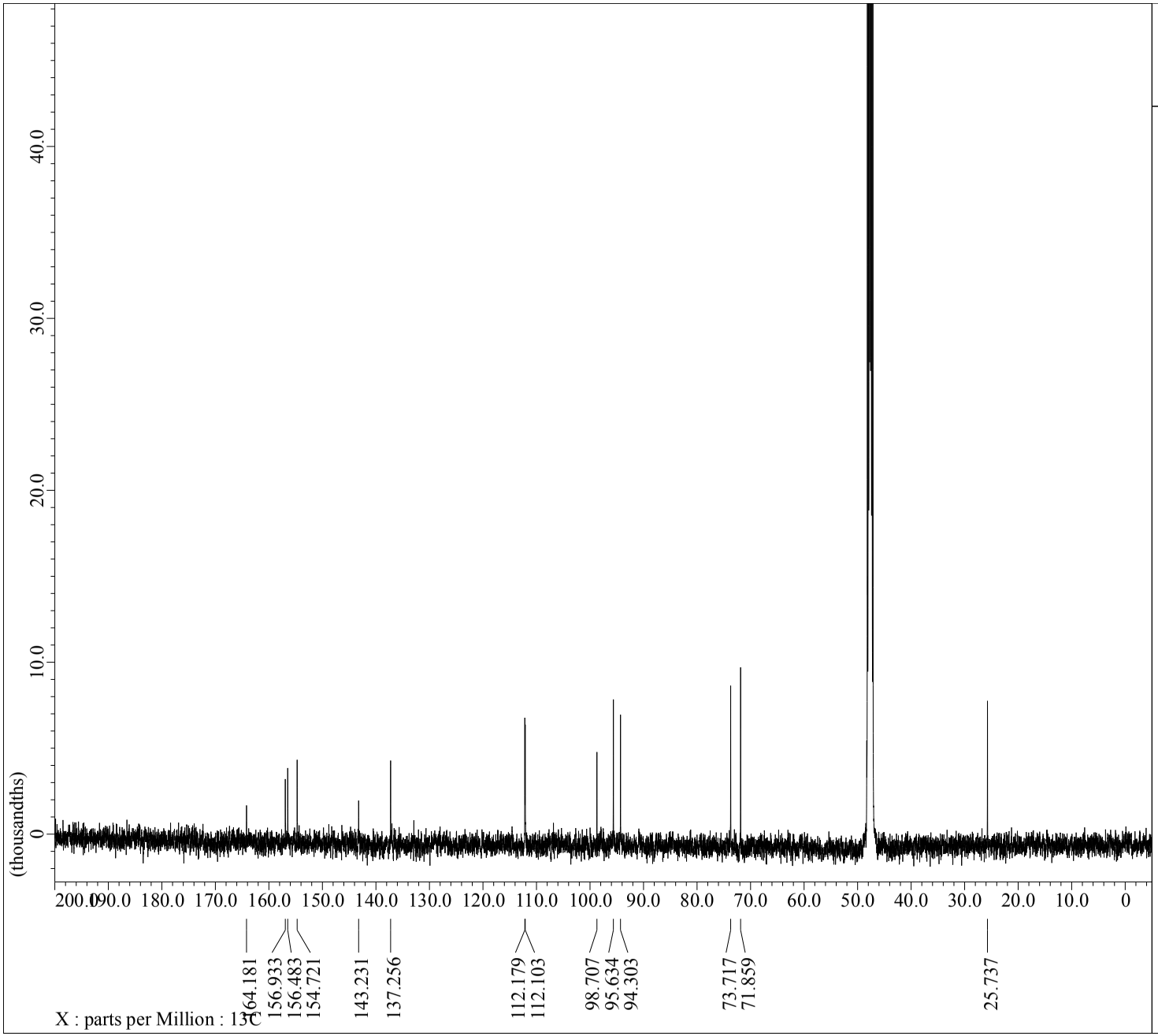


JEOL RESONANCE

```
Filename          = HOo-150319-2-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 1
Solvent           = METHANOL-D3
Creation_Time     = 19-MAR-2015 17:40:43
Revision_Time     = 25-SEP-2015 13:34:24
Current_Time      = 25-SEP-2015 13:34:48

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 1.76422912[s]
X_Domain          = 1H
X_Freq            = 495.13191398[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.5668198[Hz]
X_Sweep           = 9.28677563[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 495.13191398[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 46
Temp_Get          = 24.9[dC]
X_90_Width        = 8.16[us]
X_Acq_Time        = 1.76422912[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 4.08[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.76422912[s]
```

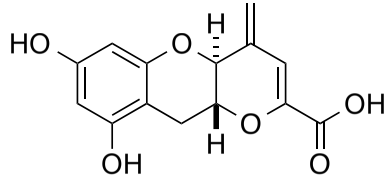


Teadenol B (**2**)



JEOL RESONANCE

```
Filename          = HOo-150322-2-C-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = S#815274
Solvent           = METHANOL-D3
Creation_Time     = 23-MAR-2015 07:53:03
Revision_Time     = 25-SEP-2015 13:46:53
Current_Time      = 25-SEP-2015 15:34:14

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 12000
Total_Scans       = 12000

Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 25.2[dC]
X_90_Width        = 15.6[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 5.2[us]
Irr_Atn_Dec       = 25.042[dB]
Irr_Atn_Noe       = 25.042[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.8388608[s]
```



Teadenol B (**2**)