Supporting Information of

Site-Selective Conversion of Azido Groups at Carbonyl α-Positions into Oxime Groups Leading Triazide to Triple Click Conjugation Scaffold

Taiki Yokoi, Tomomi Ueda, Hiroki Tanimoto,* Tsumoru Morimoto, and Kiyomi Kakiuchi

Division of Materials Science, Graduate School of Science and Technology
Nara Institute of Science and Technology (NAIST)

E-mail: tanimoto@ms.naist.jp

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[1] General Information Including Important Notices

Caution!: Organic azides, especially multiple azido compounds as well as diazo compounds are potentially hazardous and explosive. Although we have never experienced such an explosion with those used in this study, all manipulation should be carefully conducted behind a safety shield in a hood. Sodium azide should be handled with plastic spatula. At azidation stage of azido compound preparation, complete removal of residual halogenated solvent used in the last steps or extractions should be in mind to avoid generation of explosive species such as diazidomethane from dichloromethane.[1]

Storage of TBAF: Tetrabutylammonium fluoride (TBAF) was purchased from TCI (Tokyo Chemical Industry, Co. Ltd) as 1 mol/L solution of THF. Because we encountered irreproducible results when we used old solution, probably due to the decomposition of TBAF by the reagent itself or contaminated water from moisture,[2] the newly purchased bottle of TBAF solution was repacked in small subsection vial bottles. These were filled with nitrogen gas, and were stored in the refrigerator. With these small batch bottles, we successfully obtained reproducible results as described both in the manuscript and this supporting information.

Analysis and Reagents: ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR, and 126 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak ($CDCl_3$: δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR, CD_3OD: δ 3.30 for ^{1}H NMR and δ 49.0 for ^{13}C NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), and m (multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a JASCO FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStaion [EI-magnetic sector (70 eV), CI-magnetic sector, and ESI-TOF], and Bruker Autoflex II (MALDI-spiral TOF). All measurements of single crystal X-ray diffraction analysis were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-Kα radiation. The data were collected at a temperature of -150 or -170 °C. UV-visible spectra were recorded using JASCO V-630. The progress of the reactions was monitored by silica gel thin layer chromatography (TLC) (Merck TLC Silica gel 60 F_{254}). Phosphomolybdic acid-cerium(IV) sulfate sulfuric acid solution was used for the TLC stains, and TLC was also monitored with UV lamp. Flash column chromatography was performed using neutral silica gel N60 from Kanto Chemical Co. Inc. If not specified as neutral silica gel column chromatography, Merck Silica gel 60 and packed column of Biotage® SNAP Ultra with HP-Sphere™ 25μm were used. If necessary, further purification of the crude materials was performed using a LC-908 recycling gel permeation chromatography (GPC) equipped with a JAIGEL 2H-40 column (chloroform elution) made by Japan Analytical Industry Co., Ltd. All reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd, TCI (Tokyo Chemical Industry, Co. Ltd), Kanto Chemical Co. Inc., and Nacalai Tescque. Anhydrous solvents such as tetrahydrofuran (THF), toluene, acetonitrile, and dichloromethane were purchased from Kanto Chemical and Wako Pure Chemical. Dimethyl sulfoxide (DMSO) was distilled under reduced pressure after refluxing in the presence of calcium hydride.

[2] Synthesis of Oxime Compounds

Preparation of Azido Substrates

Mono-, di-, and triazides **1a**–**l**, **3a**–**d**, **5a**,**b** were prepared in accordance with our previous report.[3]

General Procedure for Synthesis of Oximes

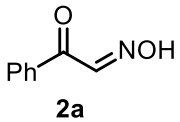
Stereochemistry of oximes (*E*/*Z*) was not determined. However, the products were obtained as a single stereoisomer unless otherwise noted. Chloroform-*d* should be passed through alumina prior to NMR experiments, otherwise the products isomerized to *E*/*Z* mixtures.

From ketones: TBAF (1.8 equiv, 1.0 M in THF) was added dropwise to a stirred solution of α-azido ketone (1.0 equiv) and hydroxylammonium chloride (1.2 equiv) in DMSO (0.1 M based on azido substrate) at 25 °C (set by water bath) under the nitrogen gas atmosphere. After completion of the reaction checked by TLC, the mixture was diluted with ether and quenched with water. The solution was extracted three times with ether, and was washed with water and brine. The collected organic layer was dried over sodium sulfate. Concentration and purification by flash neutral silica gel column chromatography gave the oxime product.

From amides: TBAF (3.2 equiv, 1.0 M in THF) was added to a stirred solution of α-azido amide (1.0 equiv) and hydroxylammonium chloride (1.2 equiv) in DMSO (0.1 M based on azido substrate) at 25 °C (set by water bath) under the nitrogen gas atmosphere. After completion of the reaction checked by TLC, the mixture was diluted with ether and quenched with water. The solution was extracted three times with ether, and was washed with water and brine. The collected organic layer was dried over sodium sulfate. Concentration and purification by flash neutral silica gel column chromatography gave the oxime product.

NOTE: Volume and the ratio of DMSO solvent in the reaction mixture is very important to succeed. However, we still used THF solution of TBAF, because use of commercial solid TBAF hydrate or removal of THF from the reagent solution prior to use gave low yields or irreproducible results. For storage of used TBAF, see General Information section.

2-Oxo-2-phenylacetaldehyde oxime (2a)

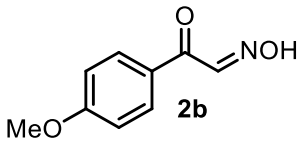


2a

A total of 11.9 mg of **2a** (80%) was obtained from the reaction with azide **1a** (16.1 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.18 mL, 1.0 M in THF, 0.18 mmol, 1.8 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 15/1 to 8/1).

Yellow powder ; R_f value 0.60 (hexane/ethyl acetate = 1/1); m.p. 124–125 °C; IR (NaCl, neat) ν_{max} 3272, 2893, 1676, 1594, 1460, 1240 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09–8.03 (m, 4H), 7.61 (t, 1H, *J* = 7.3 Hz), 7.48 (dd, 2H, *J* = 8.0, 8.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.6, 148.4, 135.7, 133.7, 129.9, 128.5; LRMS (EI, M = $C_8H_7NO_2$) *m*/*z* 149 (M^+, 36%), 105 (100), 77 (63); HRMS (EI) calcd for $C_8H_7NO_2$ [M^+] 149.0477, found 149.0475.

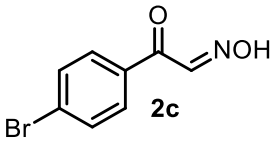
2-(4-Methoxyphenyl)-2-oxoacetaldehyde oxime (2b)



A total of 15.3 mg of **2b** (86%) was obtained from the reaction with azide **1b** (19.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.18 mL, 1.0 M in THF, 0.18 mmol, 1.8 equiv) in DMSO (1.0 mL, 1.0 M) for 5 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 10/1 to 5/1).

Yellow powder; R_f value 0.50 (hexane/ethyl acetate = 1/1); m.p. 119–121 °C; IR (NaCl, neat) ν_{max} 3225, 3176, 3044, 2984, 1597, 1571, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.09–8.05 (m, 3H), 6.95 (d, 2H, J = 8.5 Hz), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.6, 164.1, 148.7, 132.4, 128.6, 113.8, 55.5; LRMS (EI, M = $C_9H_9NO_3$) m/z 179 (M^+, 28%), 135 (100%); HRMS (EI) calcd for $C_9H_9NO_3$ [M^+] 179.0582, found 179.0582.

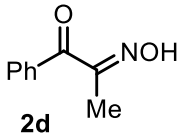
2-(4-Bromophenyl)-2-oxoacetaldehyde oxime (2c)



A total of 14.9 mg of **2c** (65%) was obtained from the reaction with azide **1c** (24.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.18 mL, 1.0 M in THF, 0.18 mmol, 1.8 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 15/1 to 8/1).

Pale yellow powder; R_f value 0.5 (hexane/ethyl acetate = 2/1); m.p. 155–156 °C; IR (KBr, disc) ν_{max} 3242, 3092, 1673, 1583, 1248 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.95 (d, 2H, J = 9.0 Hz), 7.62 (d, 2H, J = 9.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 148.9, 134.3, 131.7, 131.5, 129.0; LRMS (EI, M = $C_8H_6BrNO_2$) m/z 229 (23%, M^+ of ^{81}Br), 227 (24, M^+ of ^{79}Br), 185 (96), 183 (100), 157 (37), 155 (37), 84 (84); HRMS (EI) calcd for $C_8H_6{}^{79}BrNO_2$ (M^+) 226.9582, found 226.9588.

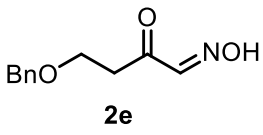
2-(Hydroxyimino)-1-phenylpropan-1-one (2d)



A total of 11.8 mg of **2d** (73%) was obtained from the reaction with azide **1d** (17.4 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.18 mL, 1.0 M in THF, 0.18 mmol, 1.8 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 15/1 to 8/1).

White solid; R_f value 0.50 (hexane/ethyl acetate = 2/1); m.p. 113–114 °C; IR (NaCl, neat) ν_{max} 3252, 2925, 1661, 1447, 1365, 1000 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.89 (d, 2H, J = 7.0 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.45 (dd, 2H, J = 7.0, 7.5 Hz), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 156.9, 136.3, 132.8, 130.2, 128.2, 10.2; LRMS (EI, M = $C_9H_9NO_2$) m/z 163 (M^+, 30%), 105 (100), 77 (78); HRMS (EI) calcd for $C_9H_9NO_2$ (M^+) 163.0633, found 163.0624.

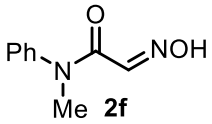
4-(Benzyloxy)-2-oxobutanal oxime (2e)



A total of 11.2 mg of **2e** (54%) was obtained from the reaction with azide **1e** (21.9 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.20 mL, 1.0 M in THF, 0.20 mmol, 2.0 equiv) in DMSO (1.0 mL, 1.0 M) for 2 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 10/1 to 6/1).

Colorless oil; R_f value 0.33 (hexane/ethyl acetate = 2/1); IR (NaCl, neat) ν_{max} 3270, 3209, 3061, 2871, 1684, 1454 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.64 (br, 1H), 7.56 (s, 1H), 7.37–7.31 (m, 5H), 4.58 (s, 2H), 3.87 (t, 2H, J = 7.0 Hz), 3.22 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 149.0, 137.0, 128.5, 128.1, 73.6, 65.0, 38.0; HRMS (ESI) calcd for $C_{11}H_{12}NO_3$ $[M–H]^-$ 206.0817, found 206.0812.

2-(Hydroxyimino)-*N*-methyl-*N*-phenylacetamide (2f)

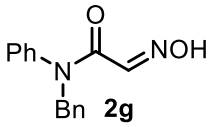


2f

A total of 16.1 mg of **2f** (91%) was obtained from the reaction with azide **1f** (19.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 10/1 to 3/1 to 1/1 to 1/2).

White solid; R_f value 0.20 (hexane/ethyl acetate = 1/1); m.p. 168–170 °C; IR (NaCl, neat) ν_{max} 3165, 1654, 1590, 1474, 1389, 1065 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.48 (s, 1H), 7.43 (dd, 2H, J = 7.5, 7.5 Hz), 7.37 (t, 1H, J = 7.3 Hz), 7.19 (d, 2H, J = 7.5 Hz), 3.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 142.2, 141.8, 130.0, 128.3, 127.0, 37.5; LRMS (EI, M = $C_9H_{10}N_2O_2$) m/z 178 (M^+, 69%), 161 (70), 106 (100); HRMS (EI) calcd for $C_9H_{10}N_2O_2$ (M^+) 178.0742, found 178.0736.

N-Benzyl-2-(hydroxyimino)-*N*-phenylacetamide (2g)

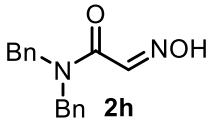


2g

A total of 25.1 mg of **2g** (99%) was obtained from the reaction with azide **1g** (26.5 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.27 mL, 1.0 M in THF, 0.27 mmol, 2.7 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 10/1 to 3/1 to 1/1).

Colorless amorphous solid; R_f value 0.4 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3298, 3063, 1656, 1593, 1495, 1454, 1253 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.34–7.32 (m, 3H), 7.26–7.24 (m, 3H), 7.21–7.19 (m, 2H), 6.99–6.47 (m, 2H), 4.98 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 142.4, 140.1, 136.3, 129.8, 128.9, 128.5, 128.4, 128.2, 127.6, 53.1; HRMS (CI) calcd for $C_{15}H_{15}N_2O_2$ $[M+H]^+$ 255.1134, found 255.1140.

N,*N*-Dibenzyl-2-(hydroxyimino)acetamide (2h)

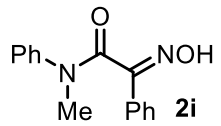


2h

A total of 25.8 mg of **2h** (96%) was obtained from the reaction with azide **1h** (28.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 10/1 to 3/1).

White amorphous solid; R_f value 0.53 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3061, 3030, 2925, 1644, 1604, 1496, 1454 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.38–7.26 (m, 7H), 7.26–7.18 (m, 3H), 4.60 (s, 2H), 4.59 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 143.4, 136.1, 135.8, 128.9, 128.7, 128.5, 127.9, 127.7, 127.0, 50.0, 48.0; HRMS (CI) calcd for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1290, found 269.1295.

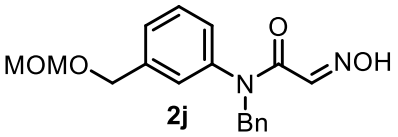
2-(Hydroxyimino)-*N*-methyl-*N*,2-diphenylacetamide (2i)



Total of 23.2 mg of **2i** (91%) was obtained from the reaction with azide **1i** (26.6 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 0.1 M) for 2 h. However in this case, the reaction mixture was diluted with diethyl ether and quenched with saturated aqueous solution of sodium bicarbonate. This quenching method was important to prevent the generation of hydrolyzed material of oxime **2i**. The mixture were extracted three times with ether and was washed with water and brine. The collected organic layer was dried over sodium sulfate. Concentration and purification by neutral silica gel column chromatography (hexane/ethyl acetate = 5/1 to 2/1 with 1% of triethylamine) afforded the product as above.

Colorless oil; R_f value 0.4 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3238, 3061, 1649, 1594, 1496 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.60 (br, 1H), 7.66 (br, 1H), 7.55–7.41 (m, 2H), 7.40 (dd, 1H, J = 7.5, 7.0 Hz), 7.33 (dd, 1H, J = 7.5, 7.5 Hz), 7.20–7.15 (m, 3H), 7.01 (br, 2H), 3.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 167.8, 141.8, 134.9, 131.1, 129.4, 129.3, 128.4, 127.8, 127.3, 126.5, 36.7; HRMS (EI) calcd for $C_{15}H_{14}N_2O_2$ (M^+) 254.1055, found 254.1055.

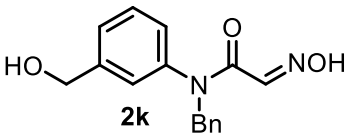
***N*-Benzyl-2-(hydroxyimino)-*N*-(3-((methoxymethoxy)methyl)phenyl)acetamide (2j)**



A total of 31.5 mg of **2j** (96%, ratio of isomers = 6.3 : 1 based on ^1H NMR) as isomeric mixture was obtained from the reaction with azide **1j** (34.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 6/1 to 2/1 to 1/2).

Colorless amorphous solid; R_f value 0.33 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3316, 2935, 2887, 1660, 1453, 1047 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) peaks from major isomer are listed. δ 7.45 (s, 1H), 7.30 (d, 2H, J = 5.0 Hz), 7.26–7.18 (m, 5H), 7.02 (s, 1H), 6.88 (m, 1H), 4.97 (s, 2H), 4.65 (s, 2H), 4.53 (s, 2H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) Peaks from major isomer are listed. δ 161.5, 142.1, 140.2, 140.1, 136.3, 129.7, 128.9, 128.4, 127.6, 127.4, 127.1, 95.7, 68.1, 55.4, 53.1; LRMS (EI, M = $C_{18}H_{20}N_2O_4$) m/z 328 (M^+, 2%), 311 (9), 194 (16), 91 (100); HRMS (EI) calcd for $C_{18}H_{20}N_2O_4$ (M^+) 328.1423, found 328.1427.

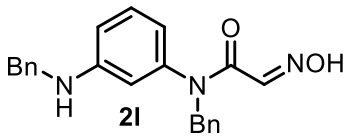
***N*-Benzyl-2-(hydroxyimino)-*N*-(3-(hydroxymethyl)phenyl)acetamide (2k)**



A total of 25.5 mg of **2k** (90%) as single isomer was obtained from the reaction with azide **1k** (29.5 mg, 0.10 mmol), hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 2/1 to 1/1 to 1/2 with 2% methanol).

White powder; R_f value 0.3 (hexane/ethyl acetate = 1/2); m.p. 137–138 °C; IR (NaCl, neat) ν_{max} 2870, 1655, 1602, 1586, 1453 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 7.36–7.32 (m, 3H), 7.28–7.20 (m, 5H), 7.14 (s, 1H), 6.95–6.94 (m, 1H), 5.01 (s, 2H), 4.56 (s, 2H); ^{13}C NMR (126 MHz, CD_3OD) δ 163.9, 145.2, 143.0, 141.7, 138.0, 130.7, 129.7, 129.5, 128.7, 128.2, 127.9, 127.4, 64.3, 54.0; HRMS (CI) calcd for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1239, found 285.1230.

N-Benzyl-*N*-(3-(benzylamino)phenyl)-2-(hydroxyimino)acetamide (2l)

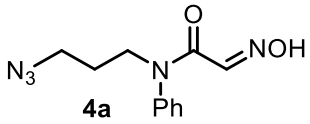


2l

A total of 34.4 mg of **2l** (96%, isomeric ratio = 4.9 : 1 based on ^{1}H NMR) as isomeric mixture was obtained from the reaction with azide **1l** (37.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 2 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 5/1 to 3/1 to 2/1 to 1/1).

Yellow amorphous solid; R_f value 0.3 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3354, 3061, 6029, 1656, 1602, 1495, 1453 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) Peaks from major isomer are listed. δ 10.7 (br, 1H), 7.54 (s, 1H), 7.35 (dd, 2H, J = 7.5, 6.5 Hz), 7.31–7.26 (m, 3H), 7.25–7.19 (m, 5H), 7.07 (dd, 1H, J = 8.0, 8.0 Hz), 6.54 (dd, 1H, J = 8.0, 1.5 Hz), 6.30 (d, 1H, J = 6.5 Hz), 6.20 (s, 1H), 4.90 (s, 2H), 4.20 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) Peaks from major isomer are listed. δ 161.4, 149.1, 142.4, 141.4, 138.4, 136.7, 130.3, 128.9, 128.7, 128.3, 127.45, 127.42, 127.39, 116.7, 112.9, 111.9, 52.9, 47.9; HRMS (MALDI-TOF) calcd for $C_{22}H_{21}N_3O_2Na$ $[M+Na]^+$ 382.1531, found 382.1526.

N-(3-Azidopropyl)-2-(hydroxyimino)-*N*-phenylacetamide (4a)

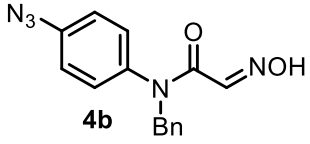


4a

A total of 22.7 mg of **4a** (92%) as single isomer was obtained from the reaction with azide **3a** (25.9 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 5/1 to 1/1).

White solid; R_f value 0.15 (hexane/ethyl acetate = 1/1); m.p. 98–100 °C; IR (NaCl, neat) ν_{max} 3260, 2936, 2098, 1659, 1593, 1493, 1254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.45–7.37 (m, 4H), 7.16 (d, 2H, J = 7.5 Hz), 3.87 (t, 2H, J = 7.5 Hz), 3.34 (t, 2H, J = 7.0 Hz), 1.85 (tt, 2H, J = 7.5, 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 142.2, 140.2, 130.1, 128.6, 127.8, 49.0, 47.2, 27.0; LRMS (EI, M = $C_{11}H_{13}N_5O_2$) *m*/*z* 247 (M^+, 5%), 164 (26), 147 (21), 119 (28), 106 (100); HRMS (EI) calcd for $C_{11}H_{13}N_5O_2$ $[M^+]$ 247.1069, found 247.1078.

N-(4-Azidophenyl)-*N*-benzyl-2-(hydroxyimino)acetamide (4b)

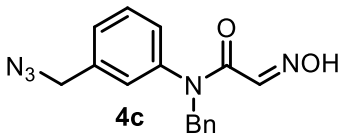


4b

A total of 27.4 mg of **4b** (93%) was obtained from the reaction with azide **3b** (30.6 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 6/1 to 3/1 to 1/1).

Pale yellow amorphous solid; R_f value 0.43 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3298, 3063, 2930, 2122, 1663, 1505, 1298, 1280 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.26–7.25 (m, 3H), 7.19 (dd, 2H, J = 7.5, 3.5 Hz), 6.99–6.94 (m, 4H), 4.96 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 142.5, 140.4, 136.6, 136.1, 129.7, 129.0, 128.6, 127.8, 120.2, 53.1; LRMS (EI, M = $C_{15}H_{13}N_5O_2$) *m*/*z* 295 (2%, M^+), 282 (9), 267 (38), 223 (11), 91 (100); HRMS (EI) calcd for $C_{15}H_{13}N_5O_2$ (M^+) 295.1069, found 295.1078.

***N*-(3-(Azidomethyl)phenyl)-*N*-benzyl-2-(hydroxyimino)acetamide (4c)**

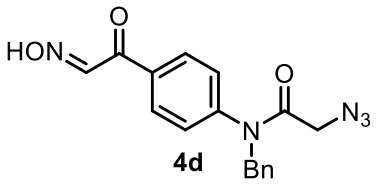


4c

A total of 28.9 mg of **4c** (94%) was obtained from the reaction with azide **3c** (32.0 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 5/1 to 3/1 to 1/1).

Colorless amorphous solid; R_f value 0.43 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3298, 3062, 2932, 2101, 1656, 1451, 1258 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.4 (br, 1H), 7.44 (s, 1H), 7.35 (dd, 1H, J = 8.5, 7.5 Hz), 7.29–7.26 (m, 3H), 7.26–7.24 (m, 2H), 7.20–7.15 (m, 2H), 6.95–6.94 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 142.2, 140.6, 137.4, 136.1, 130.2, 128.9, 128.51, 128.46, 128.14, 128.11, 127.77, 127.67, 53.8, 53.1; LRMS (EI, M = $C_{16}H_{15}N_5O_2$) m/z 309 (7%, M^+), 292 (20), 237 (19), 209 (30), 91 (100); HRMS (EI) calcd for $C_{16}H_{15}N_5O_2$ (M^+) 309.1226, found 309.1225.

2-Azido-*N*-benzyl-*N*-(4-(2-(hydroxyimino)acetyl)phenyl)acetamide (4d)

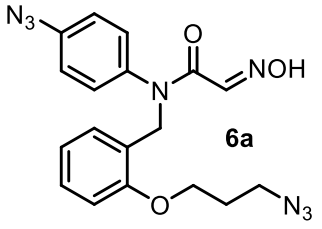


4d

A total of 21.8 mg of **4d** (65%) was obtained from the reaction with azide **3d** (34.9 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.18 mL, 1.0 M in THF, 0.18 mmol, 1.8 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 10/1 to 6/1 to 2/1).

Yellow oil; R_f value 0.55 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 3282, 3060, 2107, 1657, 1600, 1426, 1260 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.38 (br, 1H), 8.06 (d, 2H, J = 8.5 Hz), 7.96 (s, 1H), 7.26–7.25 (m, 3H), 7.17–7.15 (m, 2H), 7.06 (d, 2H, J = 8.0 Hz), 4.92 (s, 2H), 3.62 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.1, 167.5, 148.4, 144.0, 135.8, 135.5, 131.8, 128.7, 128.6, 127.9, 127.8, 53.3, 50.9; HRMS (CI) calcd for $C_{17}H_{16}N_5O_3$ $[M+H]^+$ 338.1253, found 338.1255.

***N*-(4-Azidophenyl)-*N*-(2-(3-azidopropoxy)benzyl)-2-(hydroxyimino)acetamide (6a)**

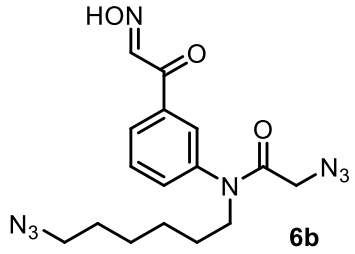


6a

A total of 33.0 mg of **6a** (84%) was obtained from the reaction with azide **5a** (40.6 mg, 0.10 mmol), *N*-hydroxylammonium chloride (8.3 mg, 0.12 mmol, 1.2 equiv), and TBAF (0.32 mL, 1.0 M in THF, 0.32 mmol, 3.2 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 6/1 to 3/1 to 2/1 to 1/1).

Pale yellow amorphous solid; R_f value 0.3 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 2932, 2877, 2099, 1663, 1505, 1297, 1247 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.0 (br, 1H), 7.43 (s, 1H), 7.21 (dd, 1H, J = 7.5, 7.0 Hz), 7.17 (d, 1H, J = 7.5 Hz), 6.97–6.93 (m, 4H), 6.85 (dd, 1H, J = 7.5, 7.5 Hz), 6.78 (d, 1H, J = 8.0 Hz), 5.03 (s, 2H), 3.91 (t, 2H, J = 5.5 Hz), 3.40 (t, 2H, J = 6.5 Hz), 1.89 (t, 2H, J = 6.5, 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 156.5, 142.5, 140.2, 136.7, 130.9, 129.7, 129.2, 124.0, 120.8, 119.9, 110.9, 64.2, 48.0, 47.6, 28.6; LRMS (EI, M = $C_{18}H_{18}N_8O_3$) m/z 394 (M^+, 2%), 366 (9), 162 (23), 134 (100), 105 (35); HRMS (EI) calcd for $C_{18}H_{18}N_8O_3$ (M^+) 394.1502, found 194.1505.

2-Azido-*N*-(6-azidohexyl)-*N*-(3-(2-(hydroxyimino)acetyl)phenyl)acetamide (6b, CCDC 1879115)



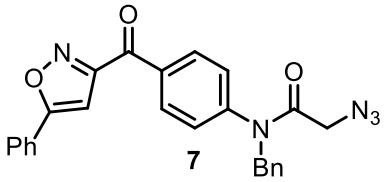
6b

A total of 1.12 g of **6b** (65%) as single isomer was obtained from the reaction with azide **5b** (1.78 g, 4.64 mmol), hydroxylammonium chloride (387.4 mg, 5.57 mmol, 1.2 equiv), and TBAF (8.4 mL, 1.0 M in THF, 8.40 mmol, 1.8 equiv) in DMSO (1.0 mL, 1.0 M) for 1 h followed by neutral silica gel chromatography (hexane/ethyl acetate = 4/1 to 3/1). Recrystallization for X-ray analysis was performed with hexane/dichloromethane.

Pale yellow solid; R_f value 0.2 (hexane/ethyl acetate = 2/1); m.p. 85–86 °C; IR (NaCl, neat) ν_{max} 3265, 2935, 2861, 2105, 1655, 1444, 1256 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.1 (s, 1H), 8.05 (d, 1H, J = 8.0 Hz), 7.98 (s, 1H), 7.95 (s, 1H), 7.59 (dd, 1H, J = 8.5, 7.0 Hz), 7.42–7.40 (m, 1H), 3.76 (t, 2H, J = 7.5 Hz), 3.66 (s, 2H), 3.26 (t, 2H, J = 7.0 Hz), 1.55 (tt, 4H, J = 7.0, 7.0 Hz), 1.40–1.32 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.0, 167.6, 149.0, 139.8, 137.6, 131.9, 130.7, 130.4, 130.0, 51.5, 51.3, 49.7, 28.6, 27.2, 26.3, 26.1; HRMS (CI) calcd for $C_{16}H_{21}N_8O_3$ $[M+H]^+$ 373.1737, found 373.1729.

Chemoselective conjugation with azido oxime 4d

2-Azido-*N*-benzyl-*N*-(4-(5-phenylisoxazole-3-carbonyl)phenyl)acetamide (7)



7

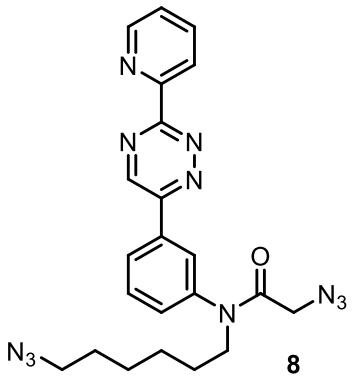
To a solution of **4d** (16.9 mg, 0.050 mmol) and phenyl acetylene (27.5 μL, 0.25 mmol, 5.0 equiv) in methanol/water (0.50 mL, 5/1, 0.1 M) was added [bis(trifluoroacetoxy)iodo]benzene (33.2 mg, 0.075 mmol, 1.5 equiv) at room temperature. After 1 h, the solvent was removed under reduced pressure to obtained crude material, which was purified by neutral silica gel column chromatography (hexane/ethyl acetate = 8/1 to 5/1) followed by GPC purification to afford 9.1 mg of **7** (42%).

Colorless oil; R_f value 0.57 (hexane/ethyl acetate = 2/1); IR (NaCl, neat) ν_{max} 2105, 1669, 1600, 1441, 1251 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, 2H, J = 7.0, 6.5 Hz), 7.85 (dd, 2H, J = 8.0, 3.0 Hz), 7.54–7.51 (m, 3H), 7.30–7.28 (m, 3H), 7.21 (dd, 2H, J = 7.5, 7.0 Hz), 7.17 (d, 2H, J = 8.0 Hz), 7.06 (s, 1H), 4.96 (s, 2H), 3.67 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 171.1, 166.9, 162.1, 145.3, 136.1, 135.6, 132.4, 130.9, 129.2, 128.9, 128.7, 128.3, 128.0, 126.4, 126.0, 100.1, 53.3, 50.9; LRMS (EI, M = $C_{25}H_{19}N_5O_3$) *m*/*z* 437 (M^+, 1%), 353 (17), 277 (11), 208 (10), 146 (20), 91 (100); HRMS (EI) calcd for $C_{25}H_{19}N_5O_3$ (M^+) 437.1488, found 437.1485.

[3] Synthesis of 1,2,4-Triazines

Synthesis of 3-(2-pyridyl)-1,2,4-triazines from α-hydroxyimino ketones was performed in accordance with Vrabel's report.[4]

2-Azido-*N*-(6-azidohexyl)-*N*-(3-(3-(pyridin-2-yl)-1,2,4-triazin-6-yl)phenyl)acetamide (8)

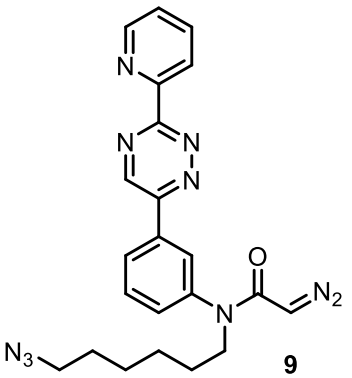


8

To a stirred solution of oxime **6b** (933 mg, 2.5 mmol) and hydrazine monohydrate (0.12 mL, 2.5 mmol, 1.0 equiv) in ethanol (3.8 mL, 0.67 M) was added one drop of acetic acid, and the mixture was heated at 45 °C for 16 h. Then, concentration of the reaction mixture *in vacuo* gave crude hydrazone (1.10 g) which was submitted to the next step without further purification.

To a stirred solution of crude hydrazone and 2-pyridinecarboxaldehyde (0.29 mL, 3.0 mmol, 1.2 equiv) in ethanol (16.7 mL, 0.15 M) was added three drops of acetic acid. After 23 h, the reaction mixture was concentrated *in vacuo*. The obtained crude material was dissolved in acetic acid (4.2 mL, 0.60 M), and the mixture stirred was heated at 100 °C. After 1 h, the reaction mixture was diluted with water, and was quenched with saturated aqueous solution of sodium bicarbonate. The organic components were extracted three times with dichloromethane and washed with brine, and then was dried over sodium sulfate. Concentration of the organic layer followed by purification by silica gel column chromatography (hexane/ethyl acetate = 1/1 to 1/2 with 2% methanol to dichloromethane/methanol = 20/1) gave 959 mg of **8** (84% for 3 steps). Brown oil; R_f value 0.13 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 2934, 2103, 1669, 1584, 1403, 1258 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.21 (s, 2H), 8.91 (d, 1H, J = 4.0 Hz), 8.75 (d, 1H, J = 8.0 Hz), 8.14–8.13 (m, 2H), 7.96 (ddd, 1H, J = 8.0, 7.5, 2.0 Hz), 7.69 (dd, 1H, J = 8.0, 8.0 Hz), 7.51 (dd, 1H, J = 7.5, 7.0 Hz), 7.38 (d, 1H, J = 8.5 Hz), 3.80 (t, 2H, J = 8.0 Hz), 3.64 (s, 2H), 3.23 (t, 2H, J = 7.0 Hz), 1.58 (tt, 4H, J = 7.5, 7.5 Hz), 1.36 (t, 4H, J = 3.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 162.2, 154.6, 152.0, 150.6, 147.0, 142.0, 137.3, 135.2, 131.2, 130.6, 126.8, 126.5, 125.9, 124.1, 51.2, 50.9, 49.7, 28.6, 27.4, 26.3, 26.2; HRMS (MALDI-TOF) calcd for $C_{22}H_{23}N_{11}ONa$ $[M+Na]^+$ 480.1983, found 480.1973.

N-(6-Azidohexyl)-2-diazo-*N*-(3-(3-(pyridin-2-yl)-1,2,4-triazin-6-yl)phenyl)acetamide (9)

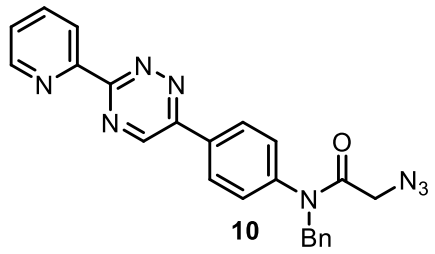


9

To a stirred solution of diazide **8** (666 mg, 1.46 mmol), 4-toluenesulfonyl hydrazide (1.36 g, 7.28 mmol, 5.0 equiv), and pyrrolidine (0.61 mL, 7.28 mmol, 5.0 equiv) in DMSO (15 mL, 0.1 M) was added TBAF (8.7 mL, 8.74 mmol, 6.0 equiv) dropwise at 25 °C. After 4 h, the resulting mixture was diluted with dichloromethane and was quenched with water. Organic components were extracted 3 times with dichloromethane and washed twice with water. Drying collected organic layer over sodium sulfate followed by concentration *in vacuo* and purification by neutral silica gel column chromatography (hexane/ethyl acetate = 1/1 to dichloromethane elution to dichloromethane/methanol = 20/1) and GPC gave 256 mg of **9** (40%).

Yellow amorphous solid; R_f value 0.33 (dichloromethane/methanol = 15/1); IR (NaCl, neat) ν_{max} 2934, 2860, 2102, 1621, 1584, 1402 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.92 (d, 1H, J = 4.5 Hz), 8.76 (d, 1H, J = 8.5 Hz), 8.12–8.10 (m, 2H), 7.97 (ddd, 1H, J = 8.0, 8.0, 2.0 Hz), 7.66 (dd, 1H, J = 8.5, 8.0 Hz), 7.52 (ddd, 1H, J = 7.5, 7.5, 1.0 Hz), 7.42–7.40 (m, 1H), 4.50 (s, 1H), 3.83 (t, 2H, J = 7.5 Hz), 3.23 (t, 2H, J = 7.0 Hz), 1.60–1.56 (m, 4H), 1.37 (t, 4H, J = 4.0, 3.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 162.0, 154.9, 152.0, 150.6, 147.0, 142.9, 137.3, 134.8, 131.1, 130.9, 126.8, 126.2, 125.9, 124.0, 51.2, 49.1, 47.7, 28.7, 28.0, 26.4, 26.2; HRMS (ESI) calcd for $C_{22}H_{23}N_{11}ONa$ $[M+Na]^+$ 465.1876, found 465.1857.

2-Azido-*N*-benzyl-*N*-(4-(3-(pyridin-2-yl)-1,2,4-triazin-6-yl)phenyl)acetamide (10)



10

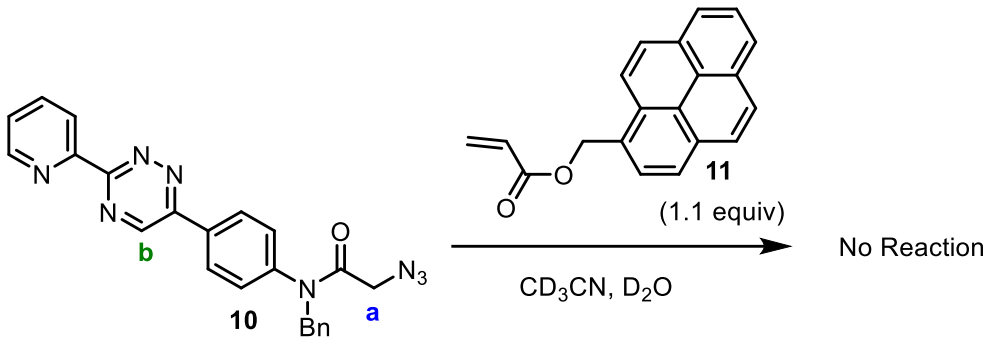
To a stirred solution of azido oxime **4d** (101 mg, 0.30 mmol) and hydrazine monohydrate (14.6 μL, 0.30 mmol, 1.0 equiv) in ethanol (0.45 mL, 0.67 M) was added one drop of acetic acid, and the mixture was heated at 45 °C for 16 h. Then, concentration of the reaction mixture *in vacuo* gave crude hydrazone (110 mg) which was submitted to the next step without further purification.

To a stirred solution of crude hydrazone and 2-pyridinecarboxaldehyde (34.5 μL, 0.359 mmol, 1.2 equiv) in ethanol (2.0 mL, 0.15 M) was added three drops of acetic acid. After 23 h, the reaction mixture was concentrated *in vacuo*. The obtained crude material was dissolved in acetic acid (0.50 mL, 0.60 M), and the stirred mixture was heated at 100 °C. After 1 h, the reaction mixture was diluted with water, and was quenched with saturated aqueous solution of sodium bicarbonate. The organic components were extracted three times with dichloromethane and washed with brine, and then was dried over sodium sulfate. Concentration of the collected organic layer *in vacuo* and purification by silica gel column chromatography (hexane/ethyl acetate = 1/1 to 1/2 with 2% methanol to dichloromethane/methanol = 20/1) gave 119 mg of **10** (94% for 3 steps).

Brown amorphous solid; R_f value 0.13 (hexane/ethyl acetate = 1/1); IR (NaCl, neat) ν_{max} 2105, 1670, 1402, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.90 (m, 1H), 8.74 (d, 1H, J = 8.0 Hz), 8.19 (ddd, 2H, J = 9.5, 2.5, 2.5 Hz), 7.96 (ddd, 1H, J = 8.0, 7.5, 2.0 Hz), 7.52–7.50 (m, 1H), 7.32–7.28 (m, 3H), 7.24–7.21 (m, 4H), 4.97 (s, 2H), 3.68 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 162.0, 154.8, 152.0, 150.6, 146.9, 143.0, 137.3, 136.1, 133.4, 129.3, 129.0, 128.7, 128.5, 128.0, 125.9, 124.0, 53.4, 51.0; LRMS (EI, M = $C_{23}H_{18}N_8O$) m/z 422 (M^+, 2%), 394 (12), 338 (23), 206 (26), 91 (100); HRMS (EI) calcd for $C_{23}H_{18}N_8O$ (M^+) 422.1604, found 422.1602.

[4] Model Study on Chemoselectivity

•Azido triazine 10 with acrylate 11



Azido triazine **10** (15.5 mg, 0.0375 mmol) was dissolved in acetonitrile-d_3 / D_2O (0.75 mL, 1:1, 0.05 M). Then, 1-pyrenemethyl acrylate **11**[5] (11.2 mg, 0.041 mmol, 1.1 equiv) was added to the mixture. The reaction was monitored for 5 h by ^{1}H NMR (Figure S1).

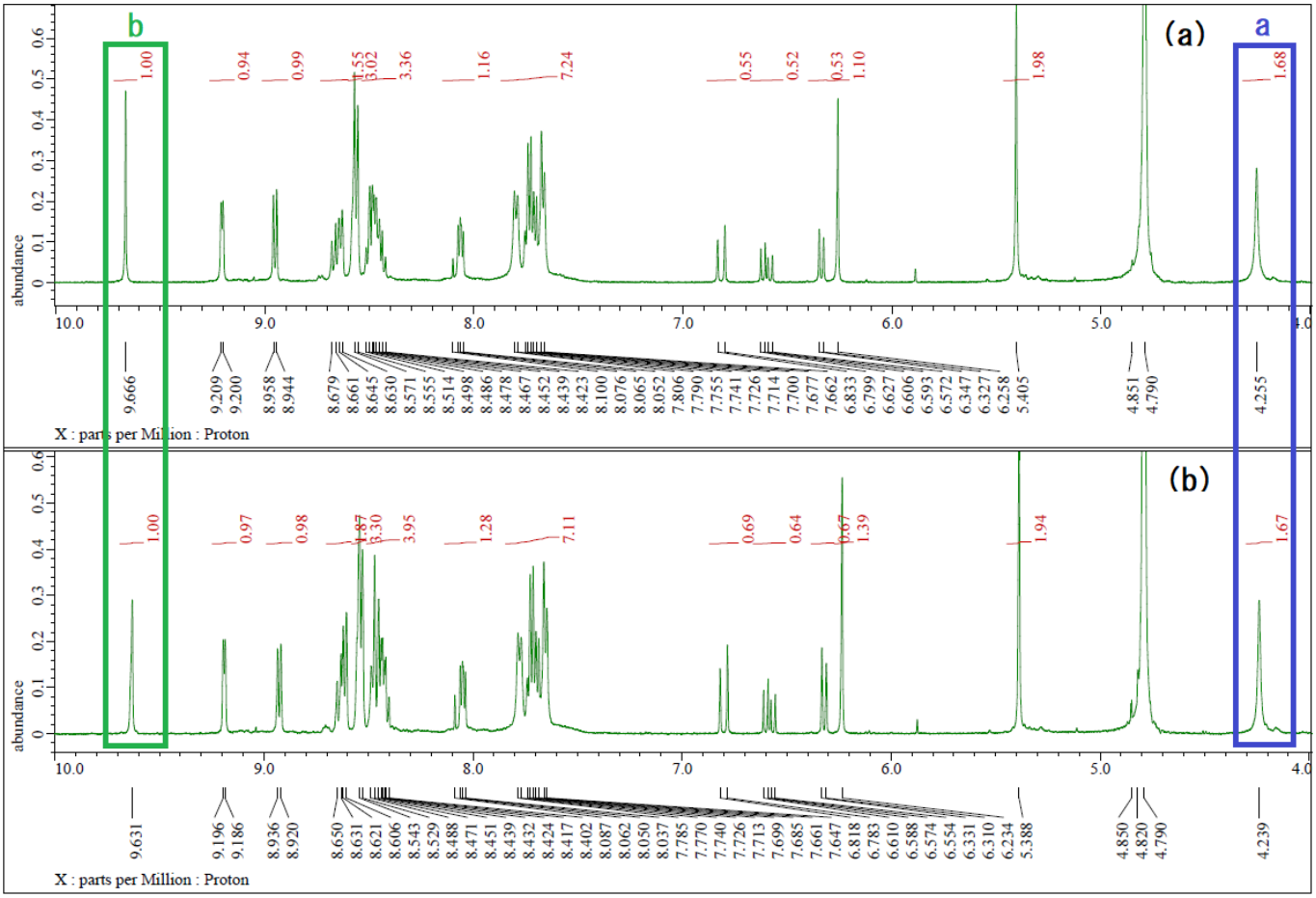
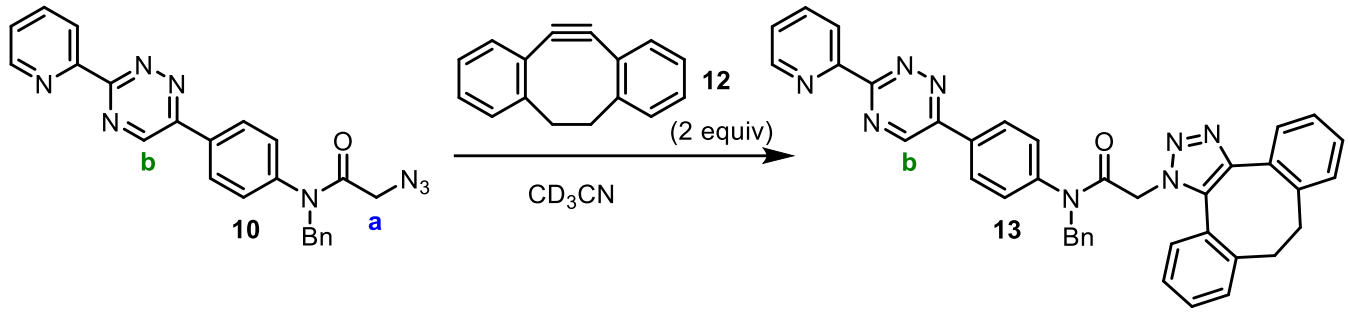


Figure S1. Comparison of NMR charts of the reaction (a) just after addition of **11** (0 h), and (b) 5 h after addition of **11** in CD_3CN / D_2O (1:1). Molecular ratio which is not identical to the reaction conditions is due to the insufficient solubility of the substrates in the aqueous solvent.

•Azido triazine 10 with dibenzocyclooctyne 12



Azido triazine **10** (15.2 mg, 0.0375 mmol) was dissolved in acetonitrile-d_3 (0.75 mL, 0.05 M) in an NMR tube (Figures S2a and S3a). And then, dibenzocyclooctyne **12**[6] (15.3 mg, 0.075 mmol, 2.0 equiv) was added to the mixture (Figure S1b). The reaction was monitored the disappearance of the peaks of the protons on each click functional groups (protons **a** and **b**) by ^{1}H NMR after 40 min (Figure S2c) and 7 h (Figures S2d, and S3b).

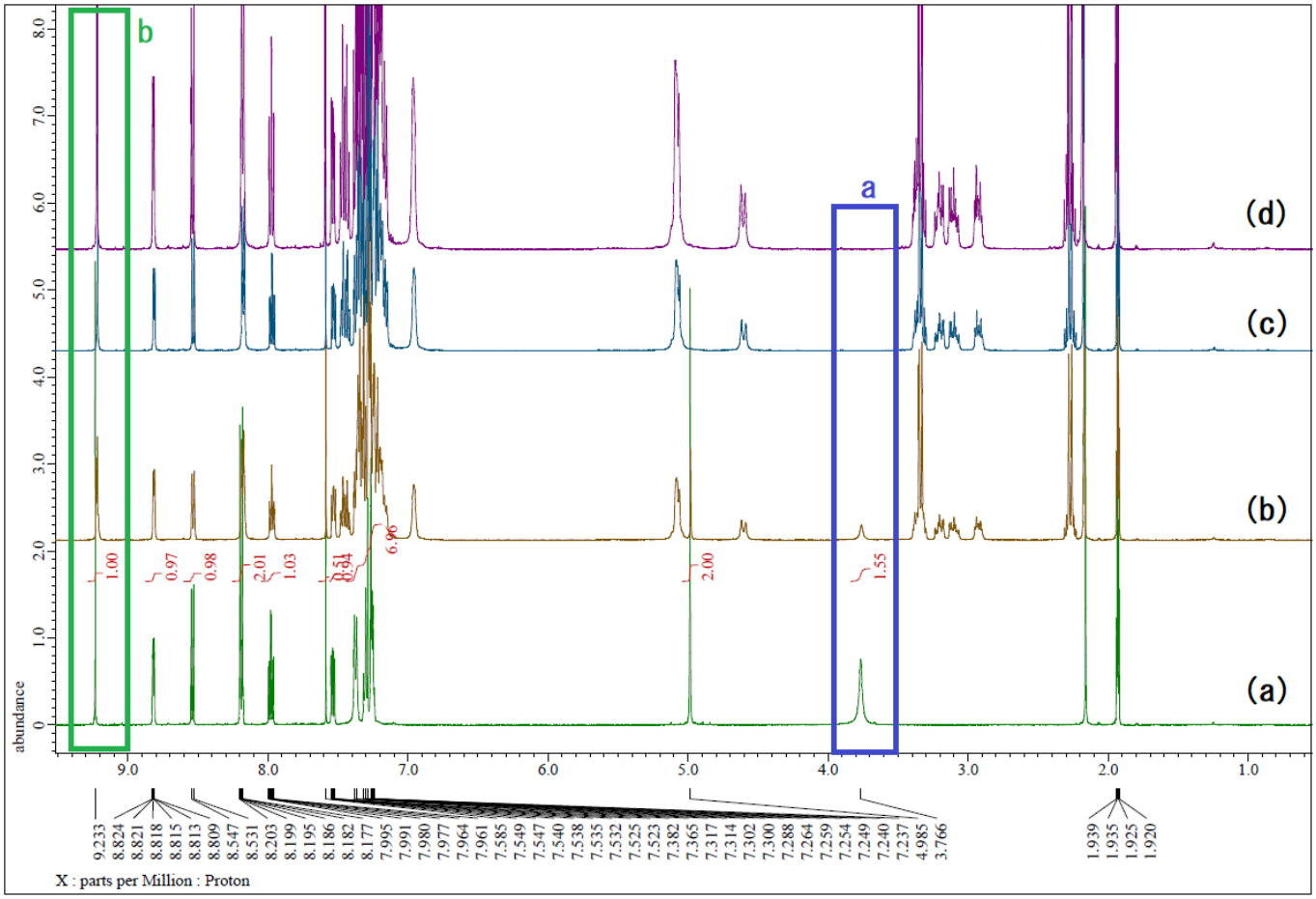


Figure S2. ^{1}H NMR experiments (a) **10** in CD_3CN, (b) soon after addition of **11**, (c) after 40 min, and (d) after 7 h.

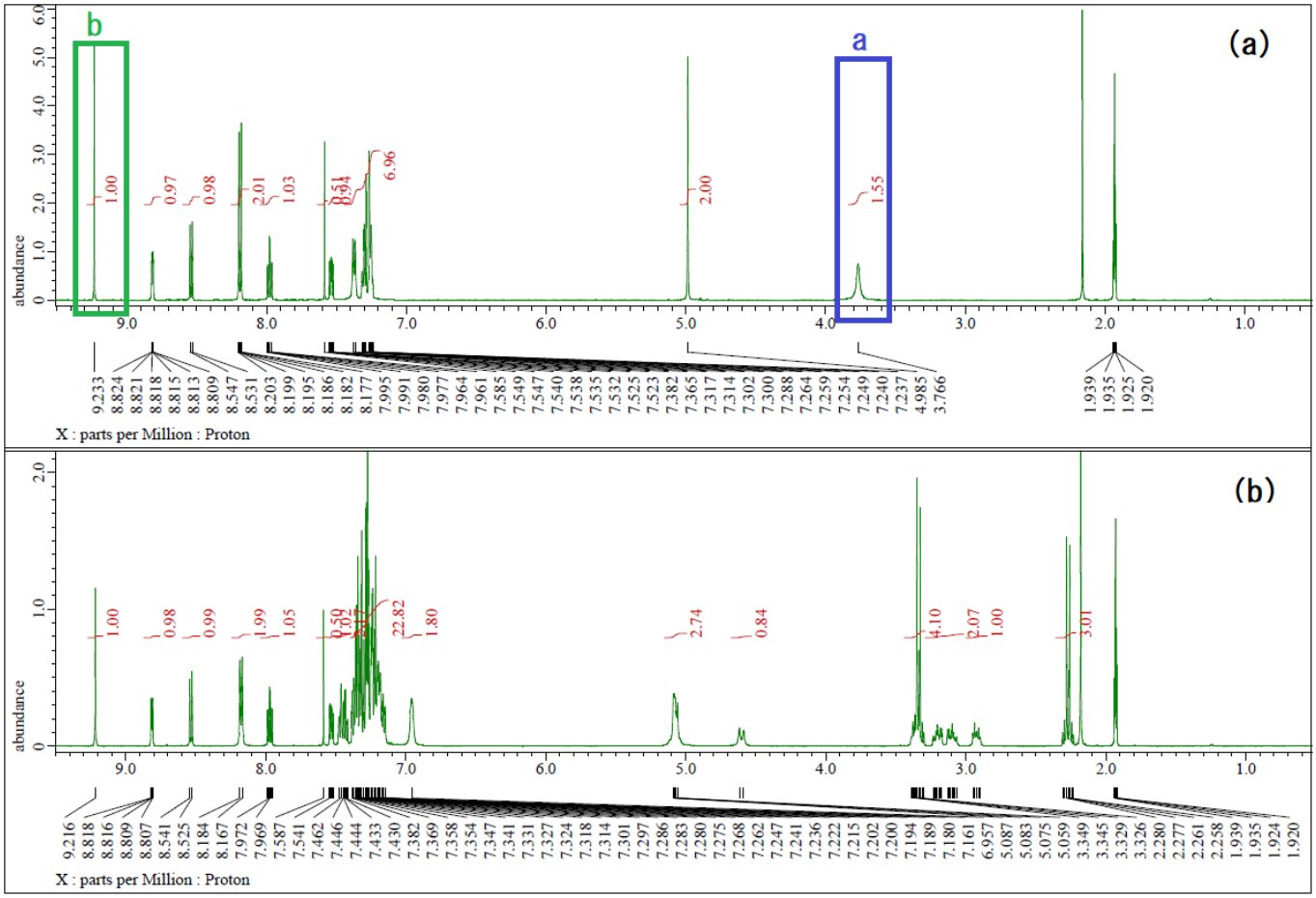
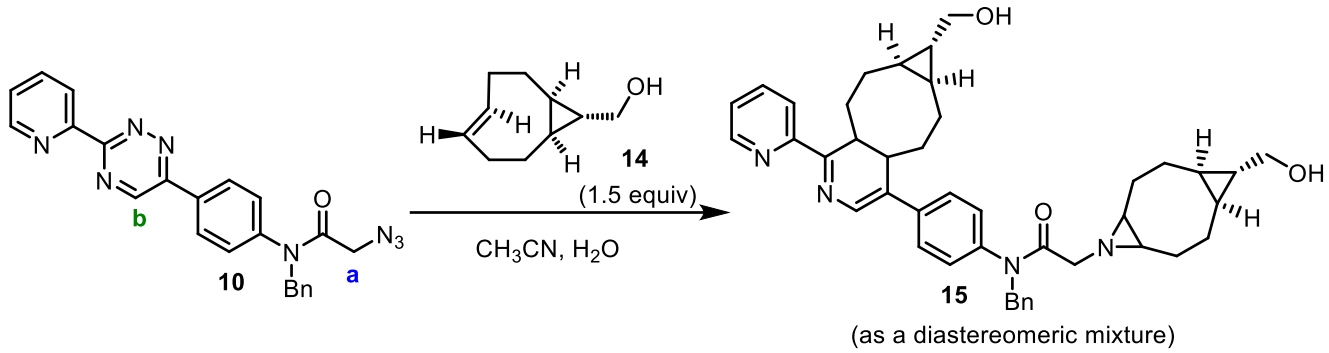


Figure S3. Comparison of NMR charts of the reaction (a) before addition of **12**, and (b) 7 h after addition of **12**.

•Azido triazine 10 with cyclopropane-fused *trans*-cyclooctene 14



To a solution of azido triazine **10** (20.8 mg, 0.05 mmol) in acetonitrile/water (1.0 mL, 1/1 vol., 0.05 M) was added *trans*-cyclooctene **14**[7] (11.1 mg, 0.075 mmol, 1.5 equiv) at room temperature. After 30 min, concentration and purification by silica gel column chromatography (hexane/ethyl acetate = 1/1 to dichloromethane to dichloromethane/methanol = 20/1) followed by GPC to afford 12.5 mg of **15** (50% based on **14**) as stereomixture. Loss of triazine and azido structures were confirmed by ^{1}H NMR (Figure S4), and IR spectra as well as HRMS.

Compound **15**: Pale yellow amorphous solid; R_f value 0.17 (dichloromethane/methanol = 15/1); IR (NaCl, neat) ν_{max} 2925, 2856, 1662, 1509 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{18}N_8O$ $[M+H]^+$ 671.3961, found 671.3910.

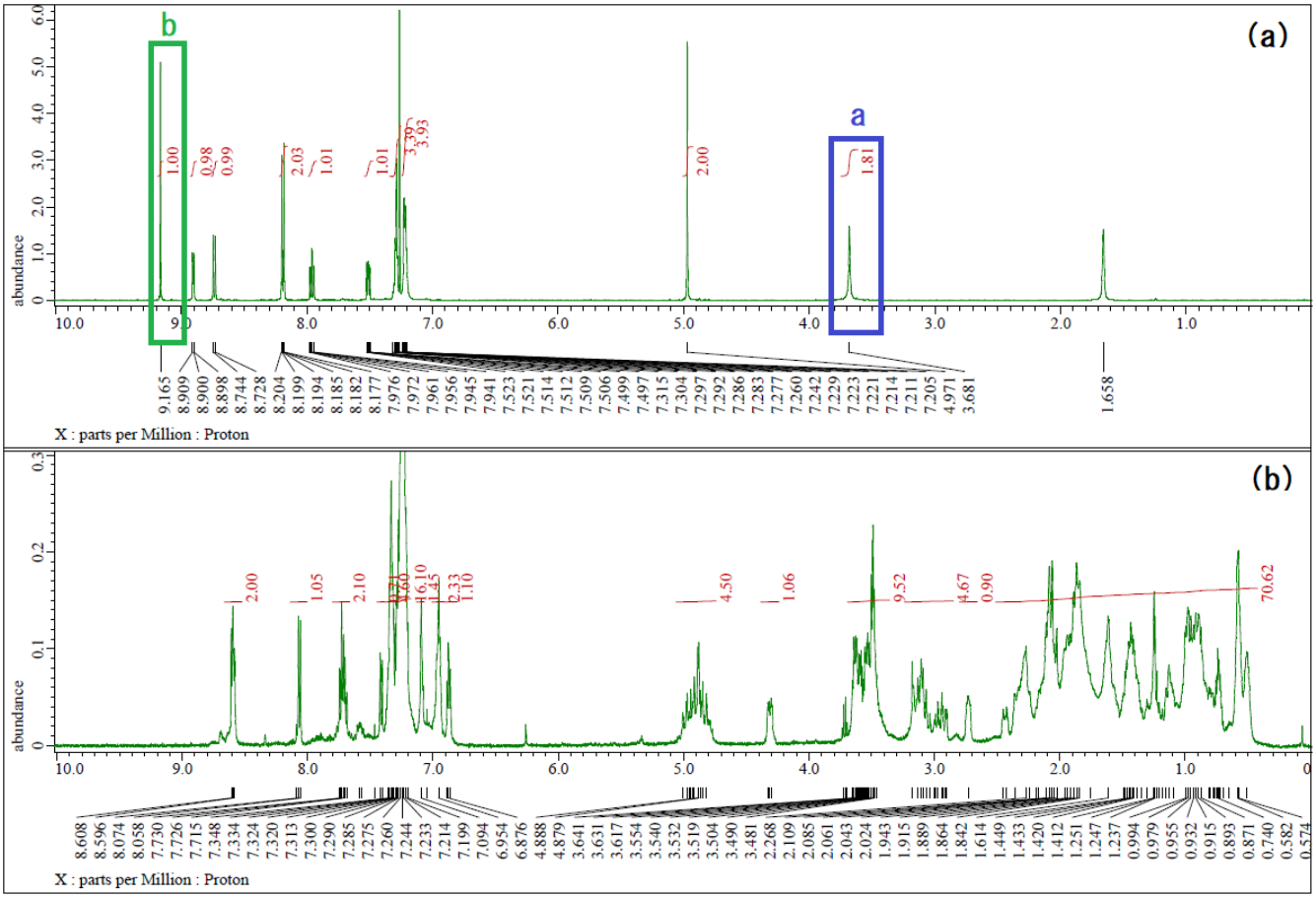
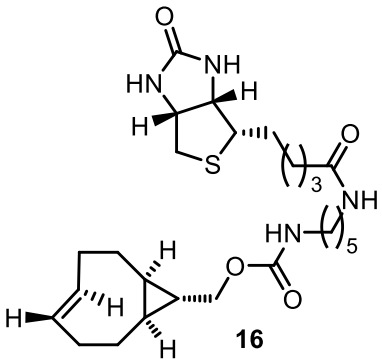


Figure S4. Comparison of NMR charts of (a) starting material **10**, and (b) addition product **15** as a diastereomeric mixture in $CDCl_3$.

[5] One-pot sequential triple click conjugation reaction

Biotin-conjugated *trans*-cyclooctene (16)

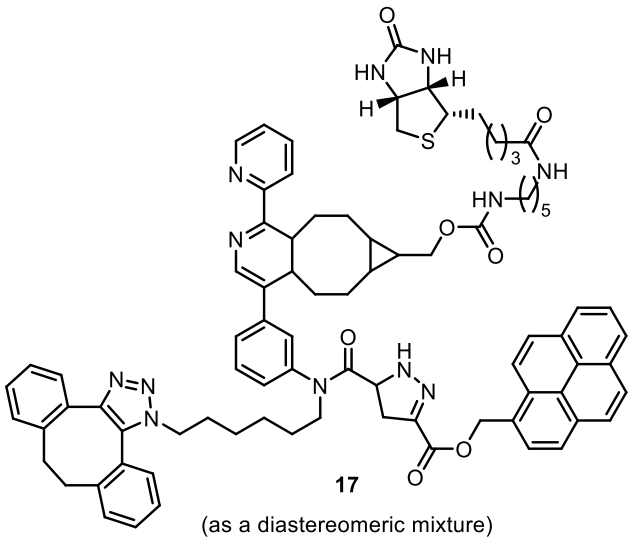


(as a diastereomeric mixture at *trans*-cyclooctene position)

To a solution of 5-((+)-biotinamido)pentylamine trifluoroacetic acid salt[8] (264 mg, 0.596 mmol) and racemic (*rel*-1*R*,8*S*,9*R*,4*E*)-bicyclo[6.1.0]non-4-ene-9-ylmethyl (4-nitrophenyl) carbonate[7] (227 mg, 0.716 mmol, 1.2 equiv) in DMF (60 mL, 0.01 M) was added triethylamine (0.25 mL, 1.79 mmol, 3.0 equiv) at room temperature. After 24 h, to the mixture was added triethylamine (0.25 mL, 1.79 mmol, 3.0 equiv) again. After 24 h, the resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (dichloromethane elution to dichloromethane/methanol = 15/1) gave **16** (157 mg, 0.310 mmol, 52%). Although residual nitrophenol was inseparable even after GPC purification, which also ended large loss of the product (down to ca. 5%), the obtained material was used in the next reaction without further purification.

White amorphous solid; R_f value 0.17 (dichloromethane/methanol = 10/1); IR (NaCl, neat) ν_{max} 3301, 2926, 2854, 1702, 1642, 1545, 1267 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.49–6.41 (br, 1H), 6.22 (br, 1H), 5.85 (ddd, 1H, *J* = 17, 8.0, 6.5 Hz), 5.62–5.55 (br, 1H), 5.12 (ddd, 1H, *J* = 14.0, 10.0, 3.5 Hz), 4.88 (br, 1H), 4.51 (dd, 1H, *J* = 7.0, 5.0 Hz), 4.31 (dd, 1H, *J* = 4.5, 2.0 Hz), 3.91 (d, 2H, *J* = 8.0 Hz), 3.22–3.20 (m, 2H), 3.15 (m, 4H), 2.90 (dd, 1H, *J* = 8.0, 5.0 Hz), 2.73 (d, 1H, *J* = 13.0 Hz), 2.35 (d, 1H, *J* = 14.0 Hz), 2.27–2.24 (m, 2H), 2.21–2.18 (m, 2H), 1.95–1.87 (m, 2H), 1.73–1.65 (m, 4H), 1.52–1.41 (m, 6H), 1.34 (m, 2H), 0.87–0.81 (m, 2H), 0.55–0.51 (m, 2H), 0.41 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 163.9, 157.0, 138.3, 131.2, 70.5, 69.4 (assigned to diastereomer), 61.8, 60.2, 55.6, 40.5, 39.2, 38.7, 35.9, 33.8, 32.6, 29.7, 29.6, 29.0, 28.1, 28.0, 27.6, 25.6, 24.7, 23.8, 21.9, 20.9; HRMS (ESI) calcd for $C_{22}H_{23}N_{11}ONa$ $[M+Na]^+$ 529.2824, found 529.2821.

Four-component coupling product (17)



(as a diastereomeric mixture)

To a solution of azido-diazo-triazine **9** (16.4 mg, 0.0361 mmol) in acetonitrile-water (2.9 mL, 1:1, 0.013 M) was added 1-pyrenemethyl acrylate **11**[5] (52.4 mg, 0.181 mmol, 5.0 equiv) at room temperature. After 24 h, dibenzocyclooctyne **12**[6] (9.1 mg, 0.0433 mmol, 1.2 equiv) was added to the resulting mixture at same temperature. Then after 2 h, *trans*-alkene-biotin tag **16** (18.3 mg, 0.0361 mmol, 1.0 equiv) dissolved in acetonitrile-water (1.0 mL + rinsed with 0.5 mL×2, 1:1) at same temperature. After 1 h, the solvent was removed under reduced pressure followed by silica gel column chromatography (hexane/ethyl acetate = 1/1 to dichloromethane elution to dichloromethane/methanol = 20/1 to 15/1 to 10/1)

gave **17** (22.1 mg, 0.0157 mmol, 44%) as diastereomeric mixture.

Yellow amorphous solid; R_f value 0.3 (dichloromethane/methanol = 10/1); IR (NaCl, neat) ν_{max} 3309, 2930, 1699, 1654, 1460, 1245 cm^{-1}; UV-vis ($CHCl_3$) λ_{max} = 267, 278, 302(sh), 315, 329, 346, 376(sh); ^1H NMR (500 MHz, $CDCl_3$) See NMR spectra section; HRMS (MALDI-TOF) calcd for $C_{84}H_{90}N_{12}O_7SNa$ $[M+Na]^+$ 1433.6668, found 1433.6659.

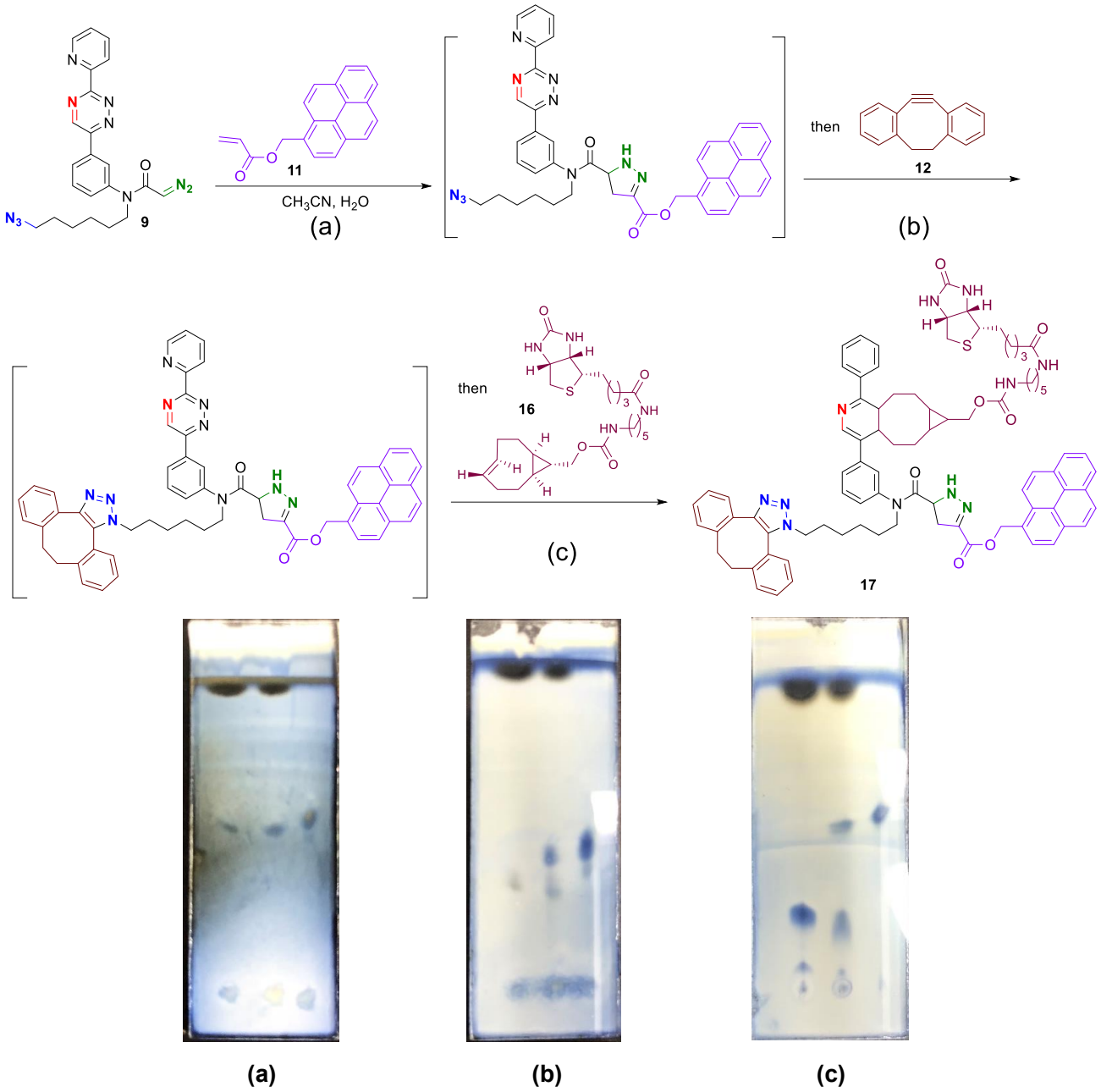


Figure S5. TLC analysis of the progress of four-component coupling reaction (left: reaction mixture, middle: reaction mixture + starting material scaffold **9**; right: reference sample of **9**) (a) 24 h after addition of acrylate **11** [(dichloromethane/methanol = 20/1)×2], (b) 2 h after addition of dibenzocyclooctyne **12** [(dichloromethane/methanol = 20/1)×2], (c) 1 h after addition of biotin-connected *trans*-cyclooctene **16** (dichloromethane/methanol = 10/1).

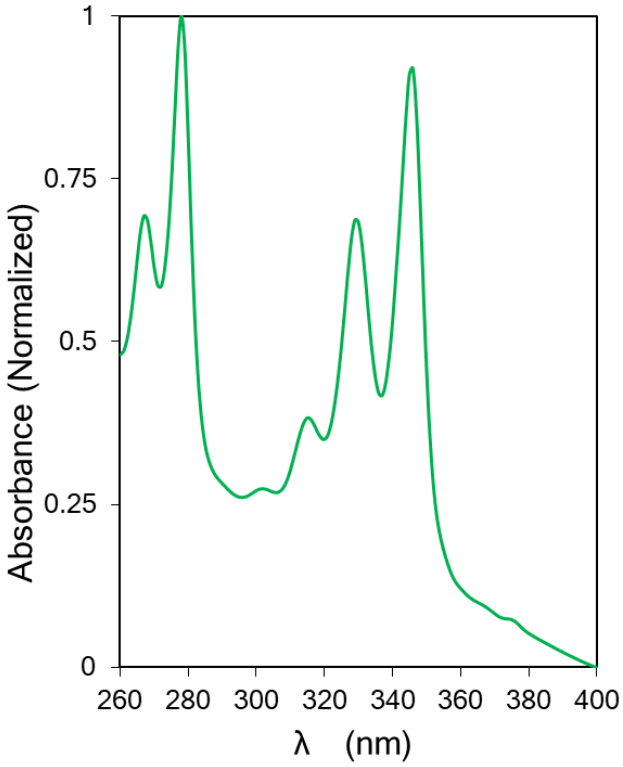


Figure S6. UV-vis spectrum of **17** (0.019 μM in chloroform)

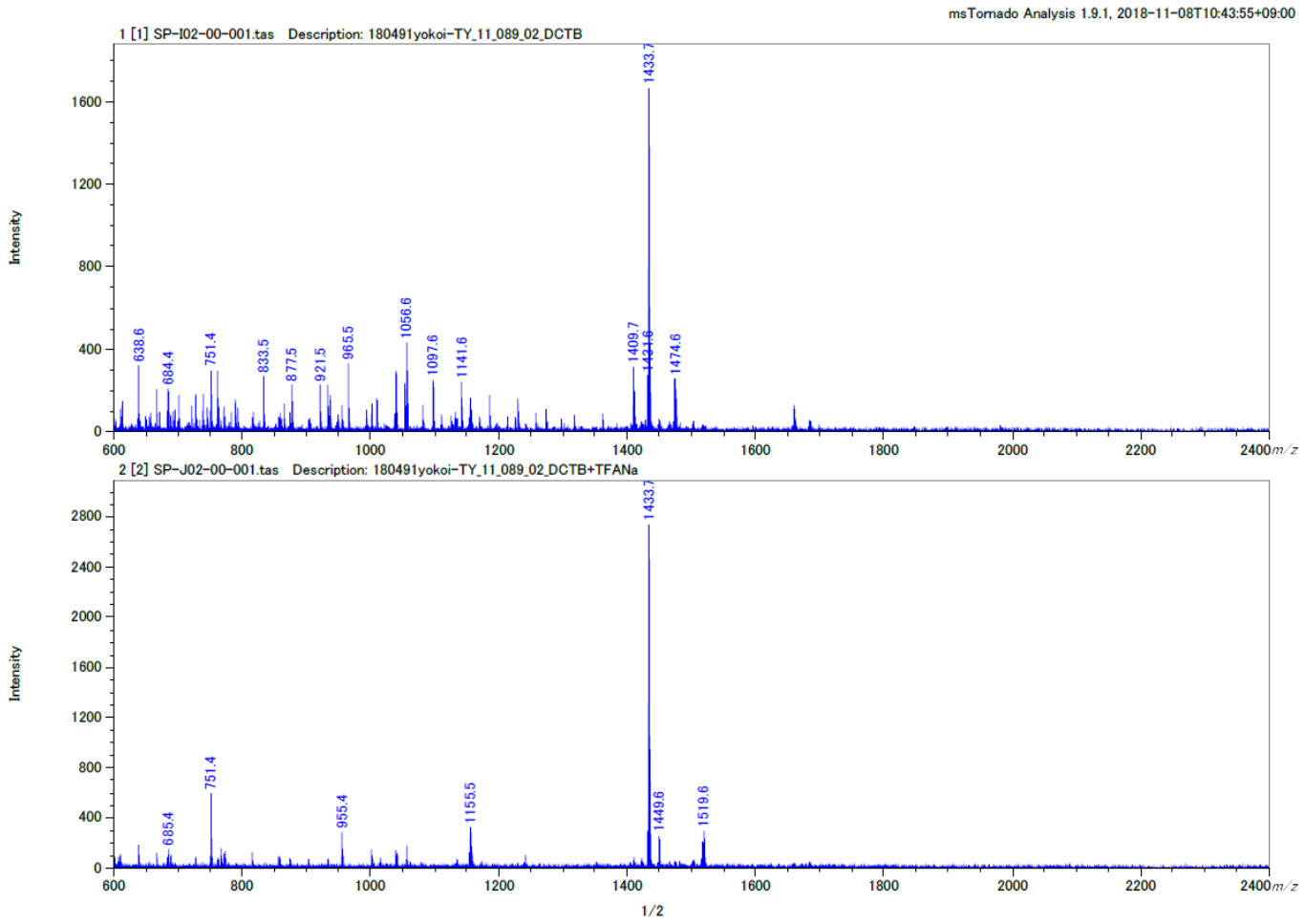


Figure S7. Mass spectra of **17** by MALDI-Spiral TOFMS: (top) with DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), (bottom) with DCTB + sodium trifluoroacetate.

[6] References

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(5) S. Amemori, K. Kokado, and K. Sada, *Angew. Chem. Int. Ed.* 2013, **52**, 4174.

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(7) M. Royzen, G. P. A. Yap, and J. M. Fox, *J. Am. Chem. Soc.*, 2008, **130**, 3760.

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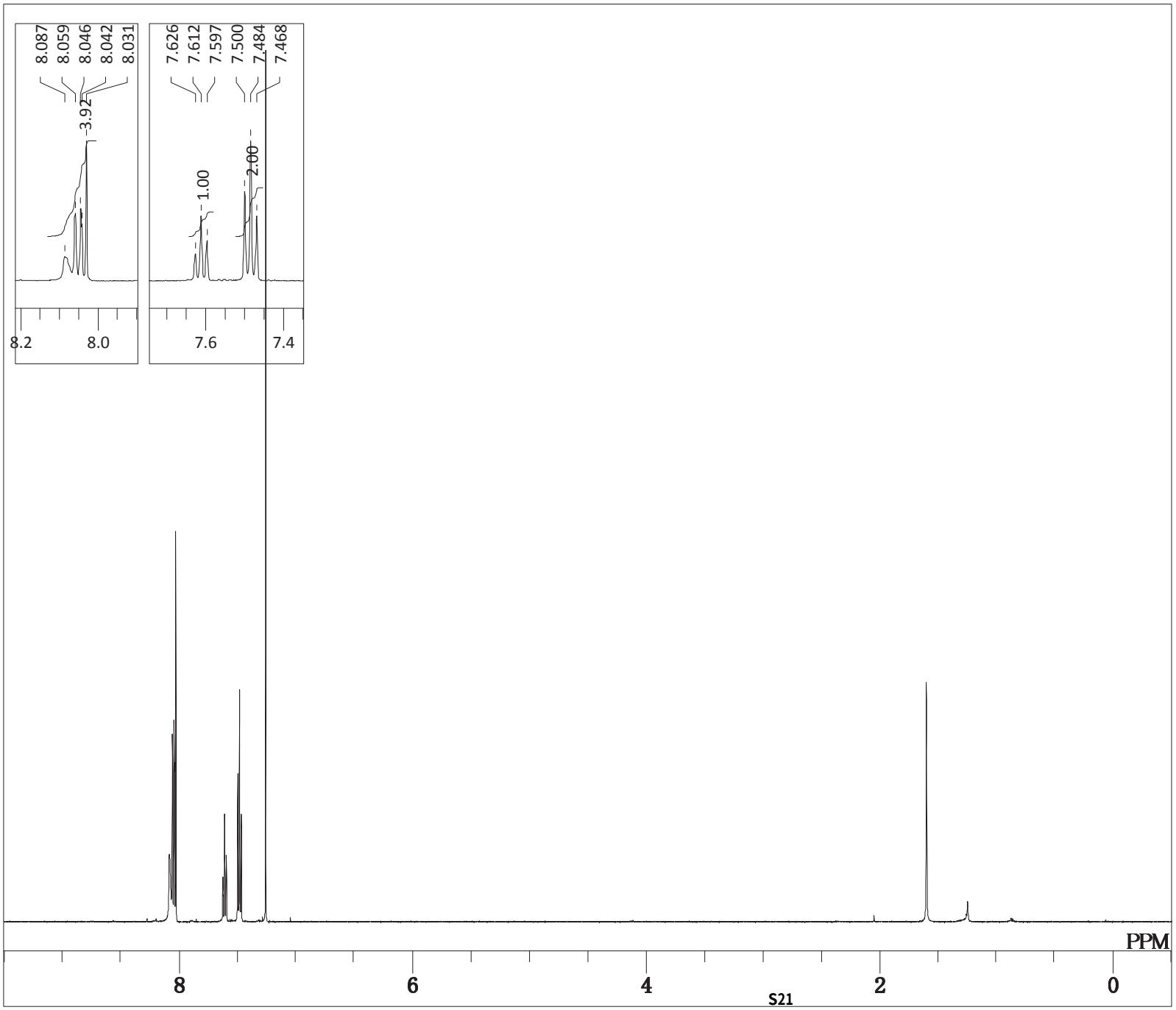
[7] ^{1}H, and ^{13}C NMR Spectra

See next pages.



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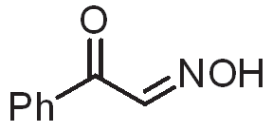

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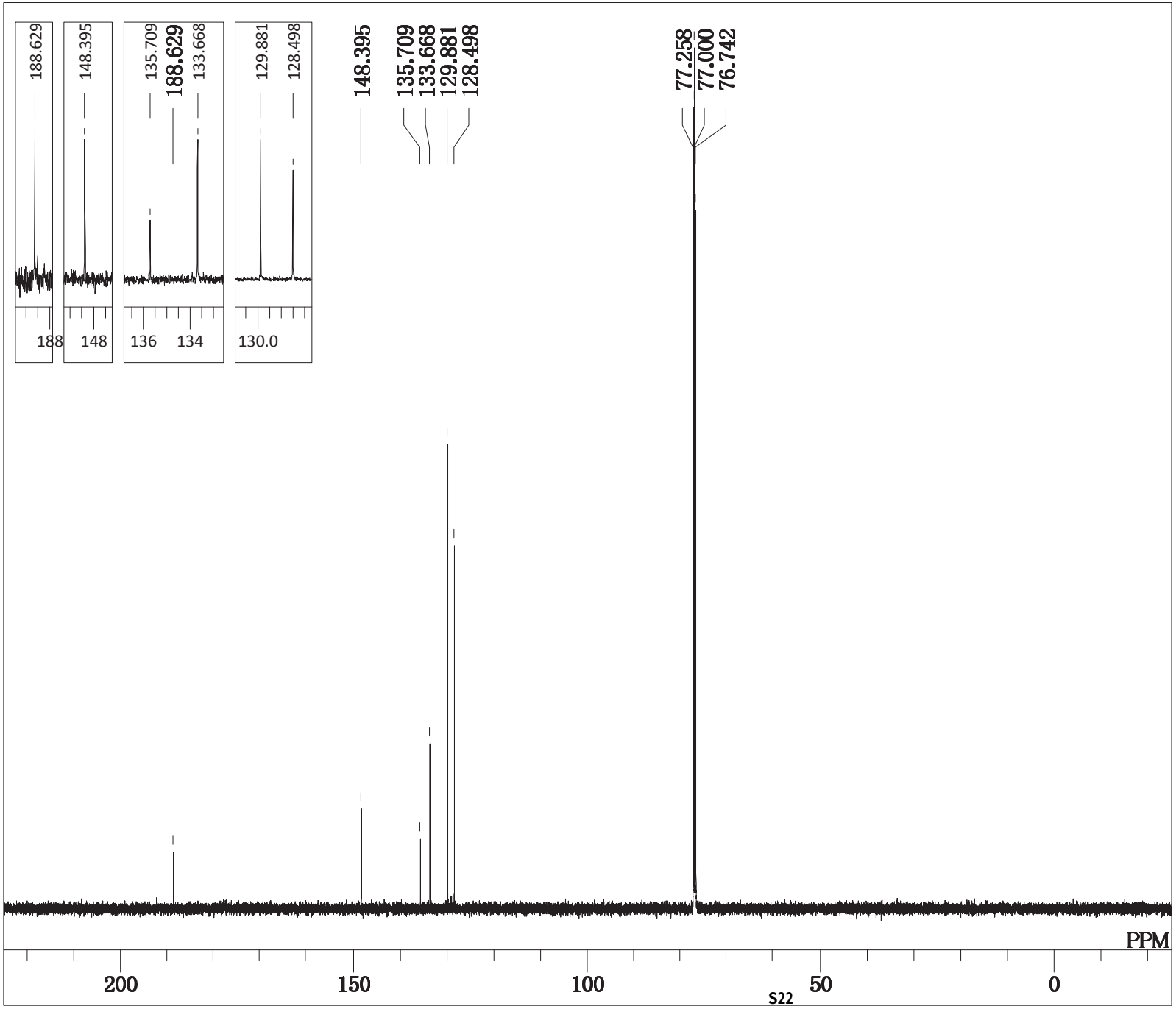

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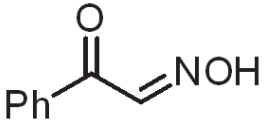

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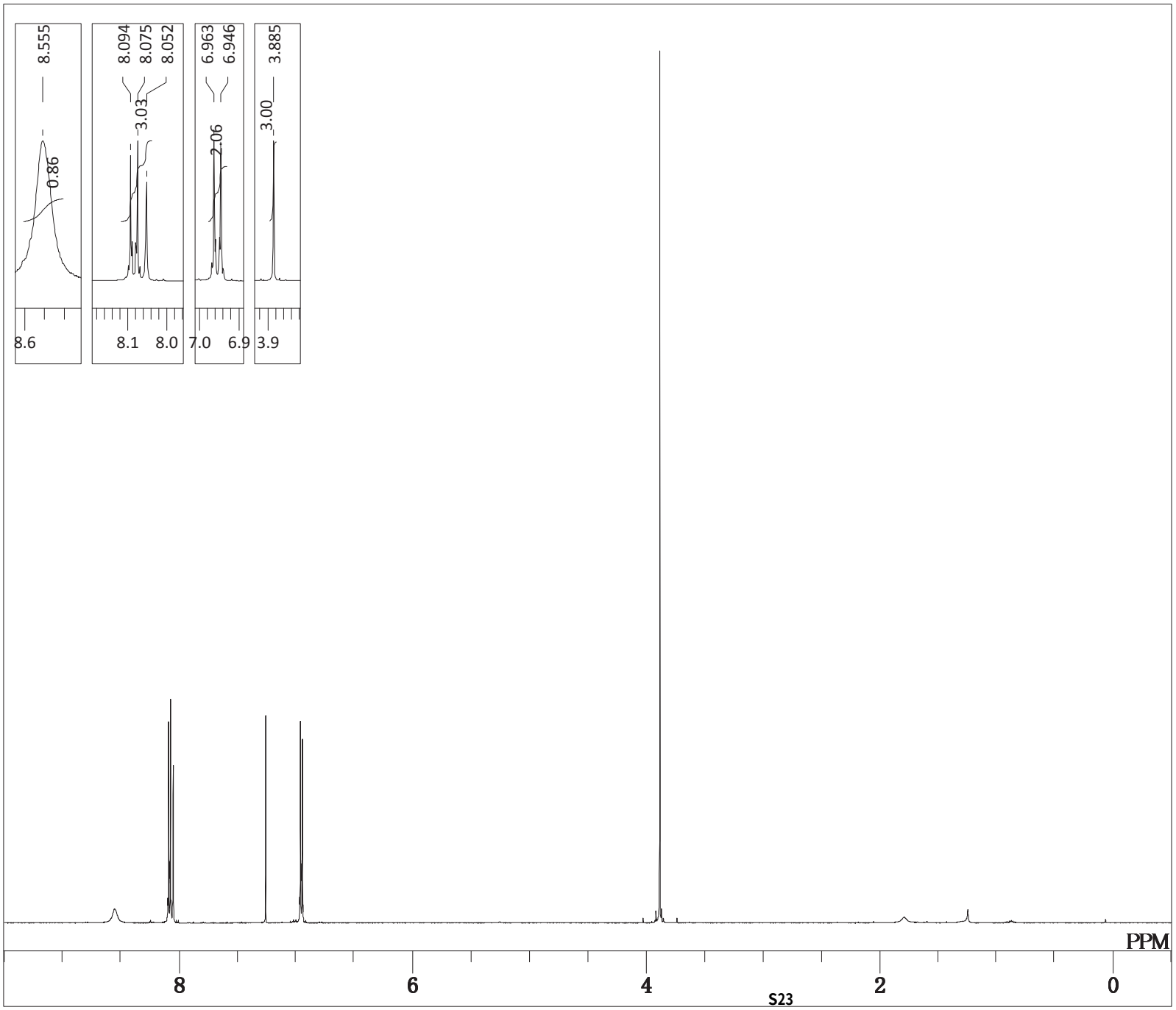

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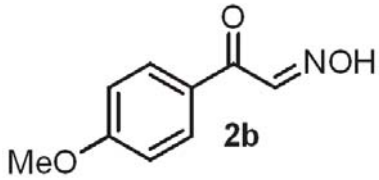

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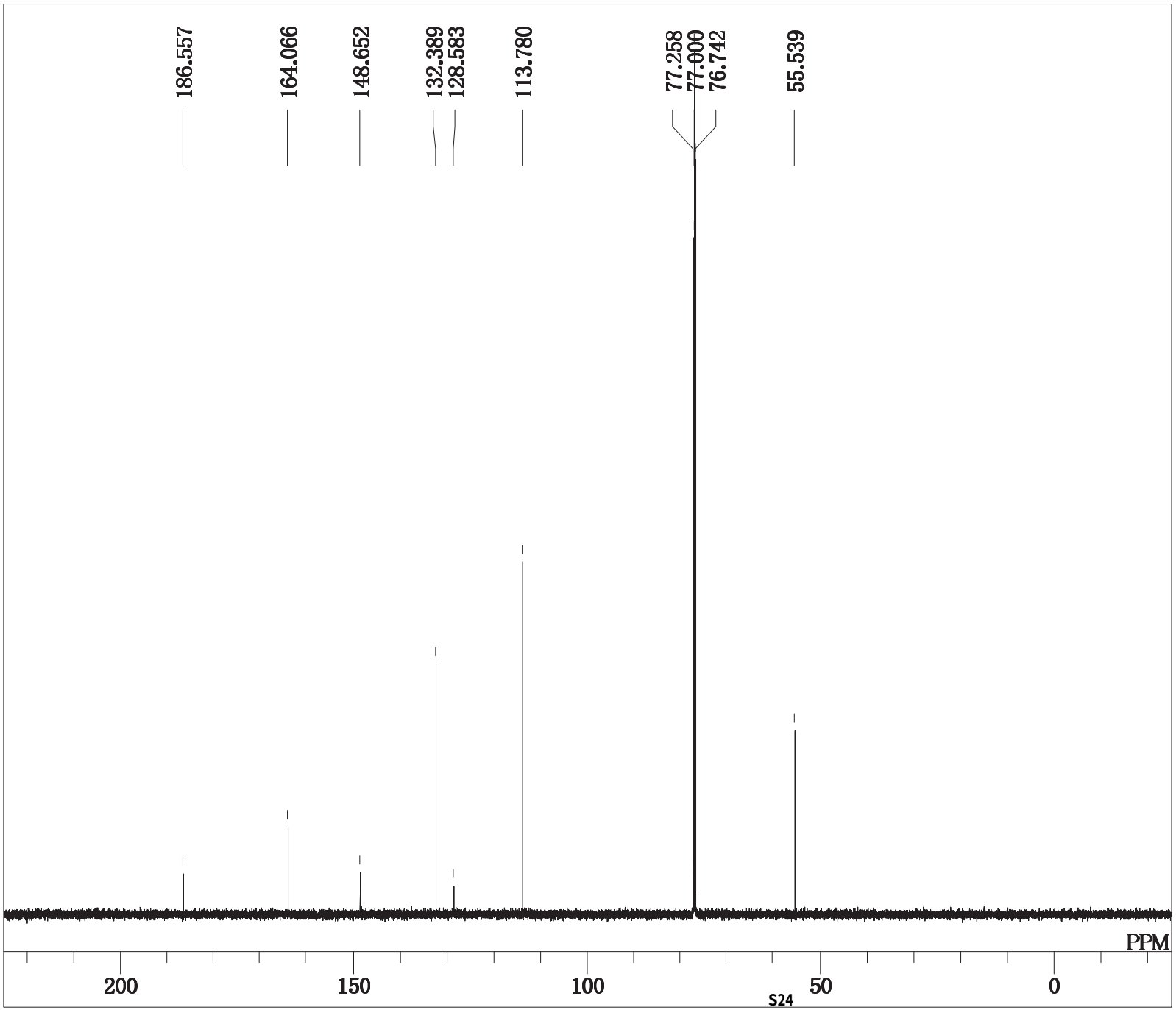

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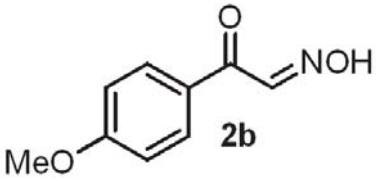

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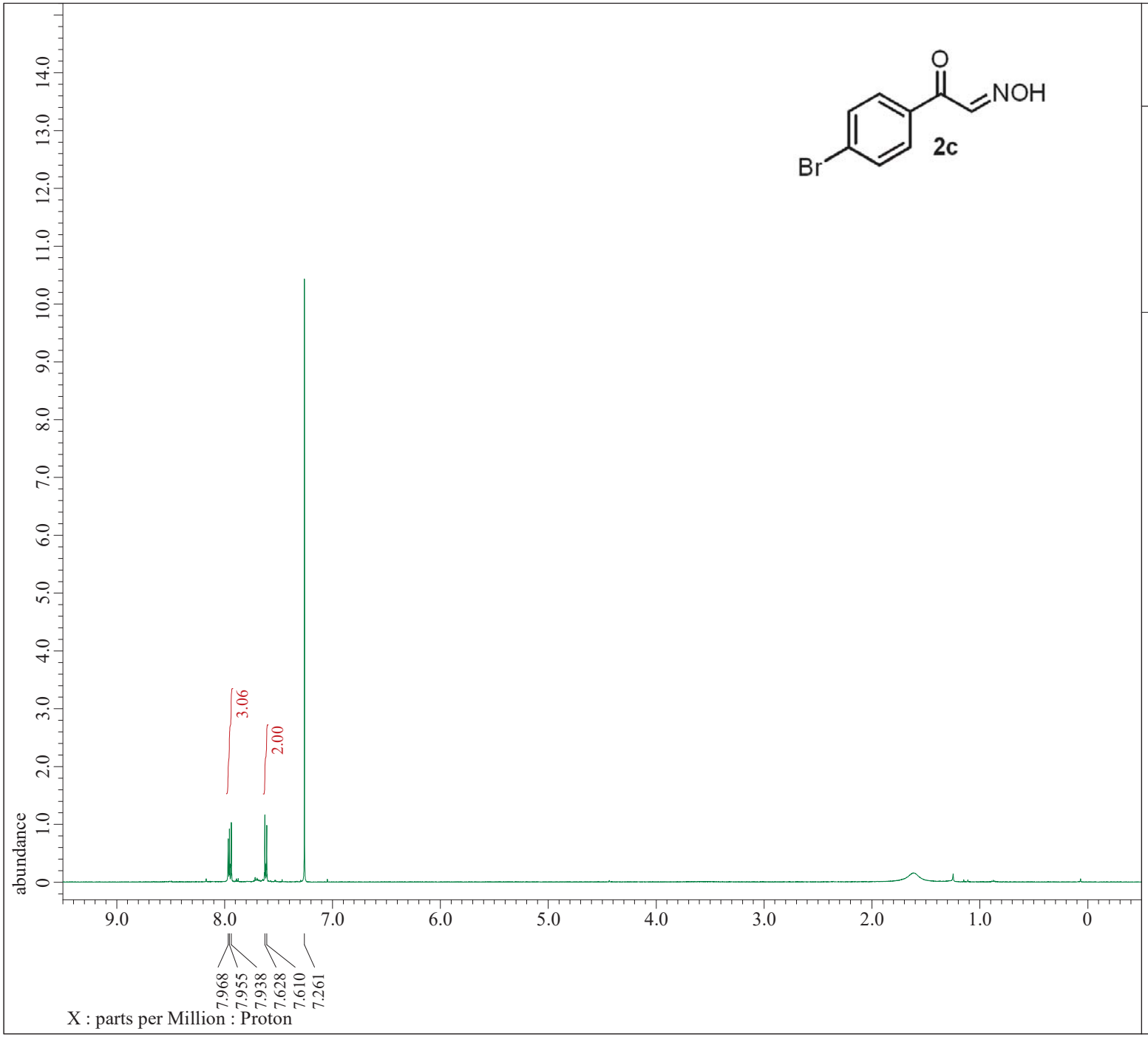


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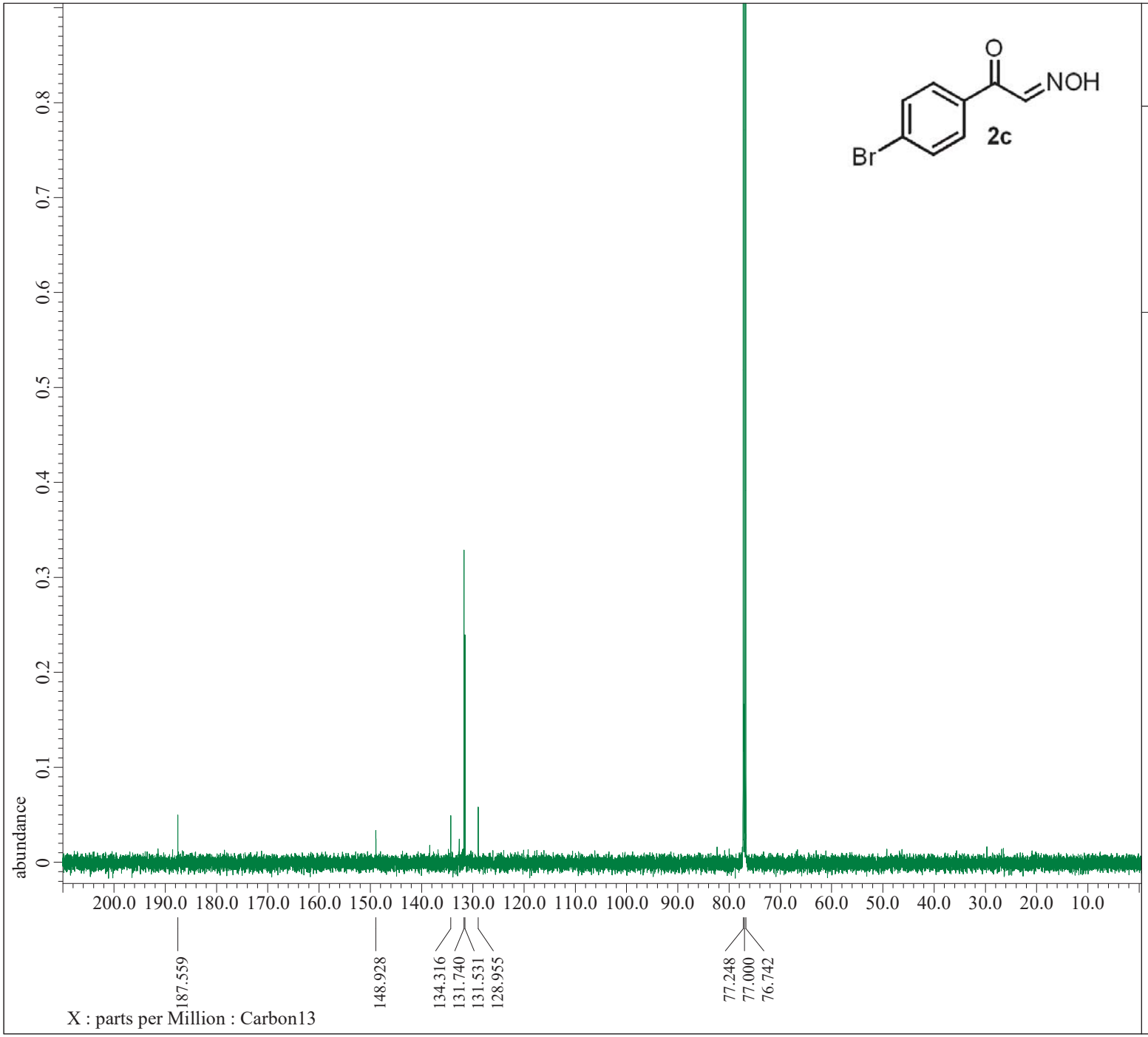


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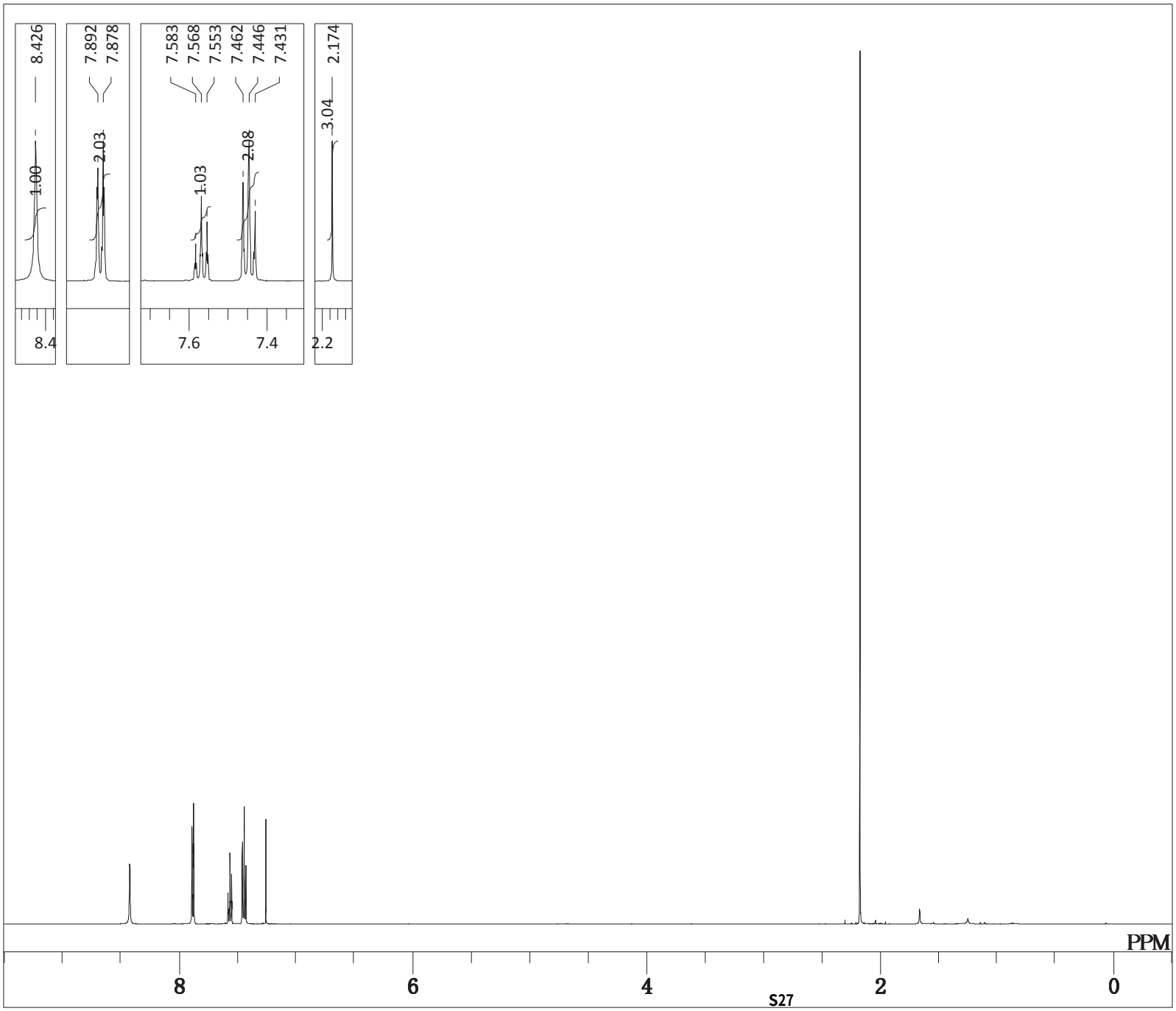
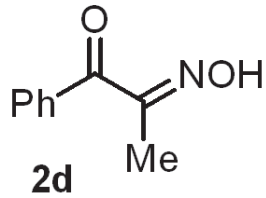
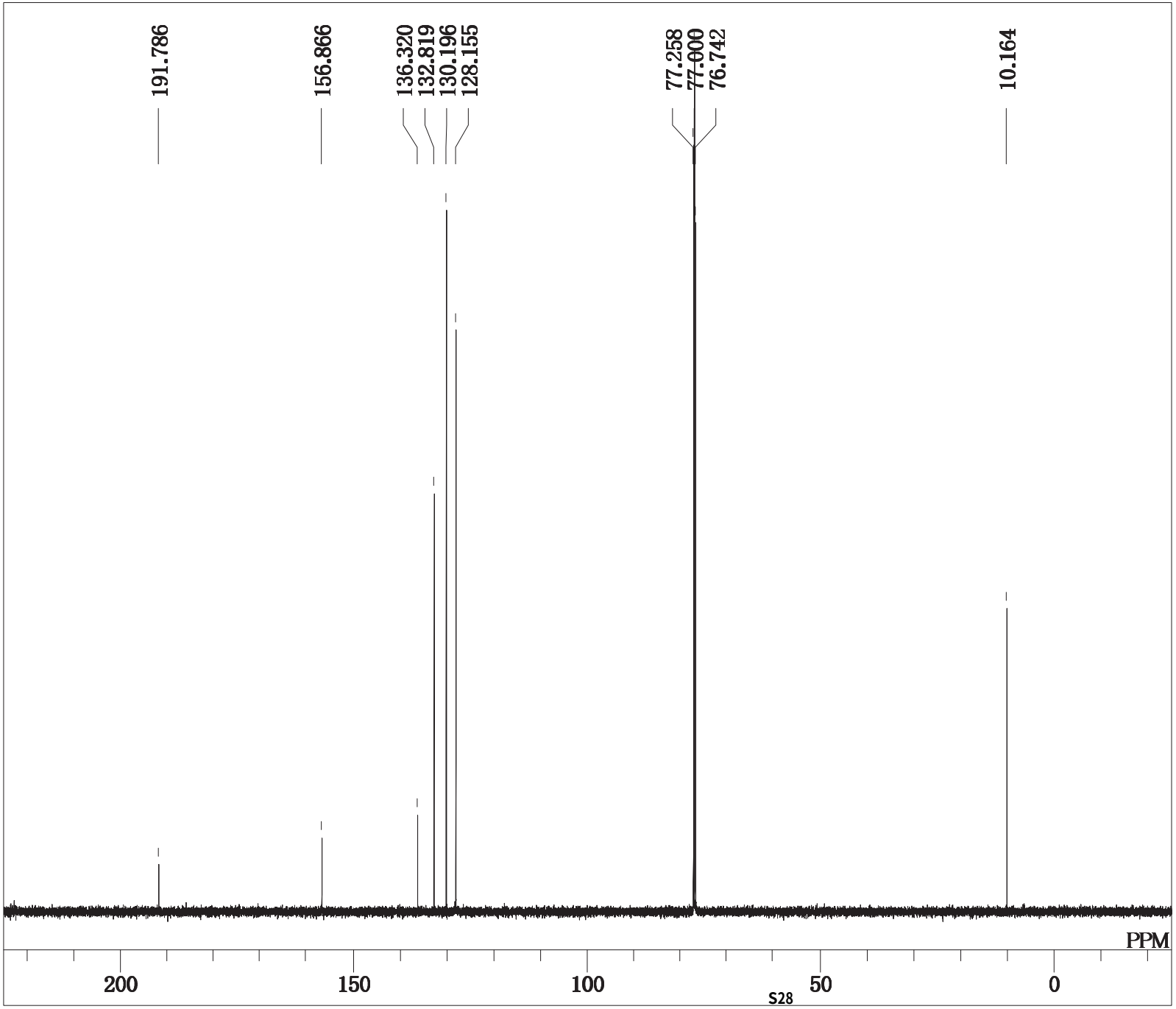


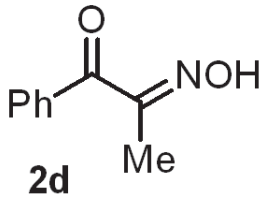
DFILE	TU-02-133-2_proton-1-1.als
COMNT	single_pulse
DATIM	2018-01-22 16:15:54
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.85 usec
IRNUC	1H
CTEMP	16.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	42



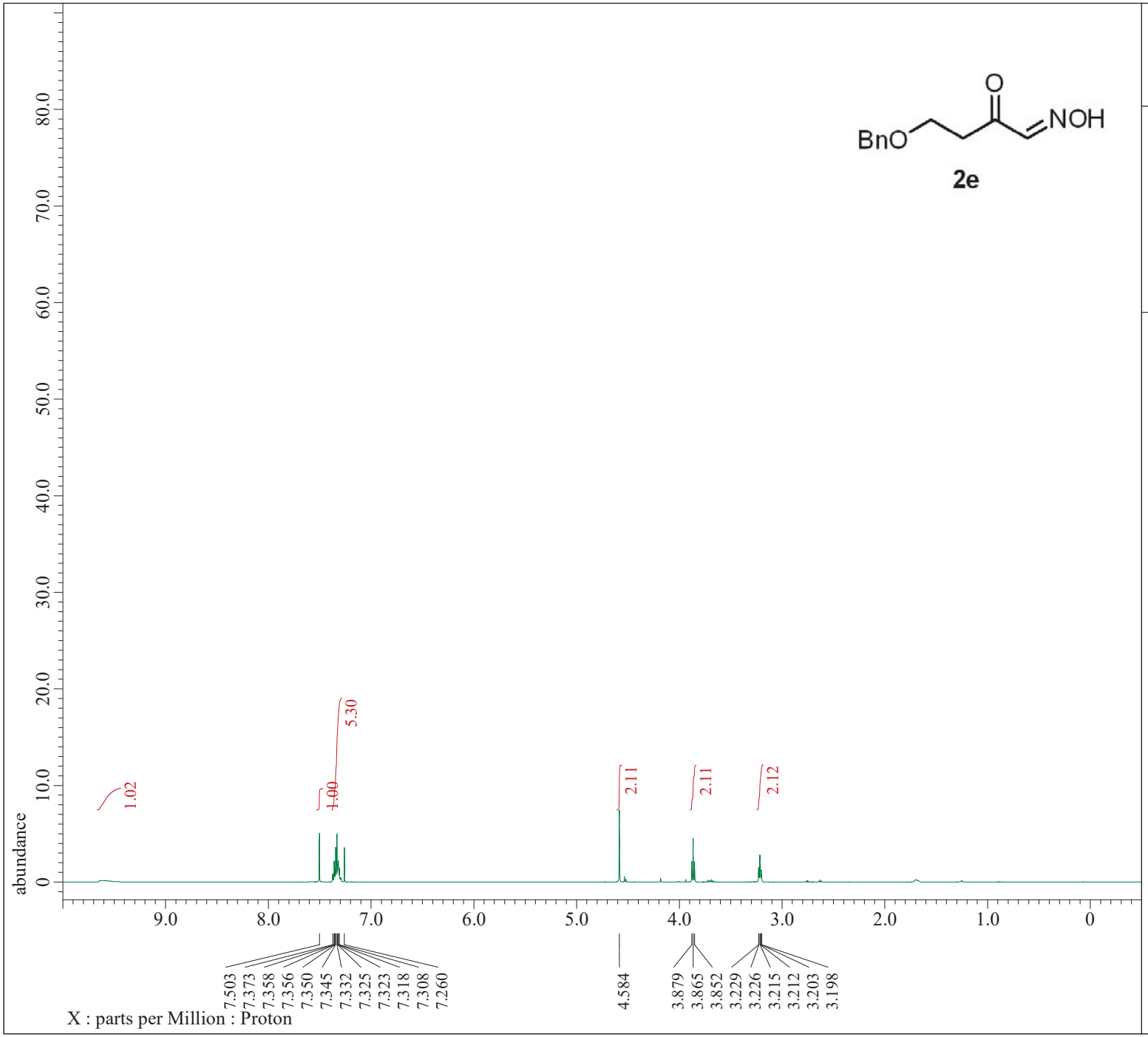
2d



DFILE	TU-02-133-2 180122_carbon-1-
COMNT	single pulse decoupled gated NO
DATIM	2018-01-22 17:27:53
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	16.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60

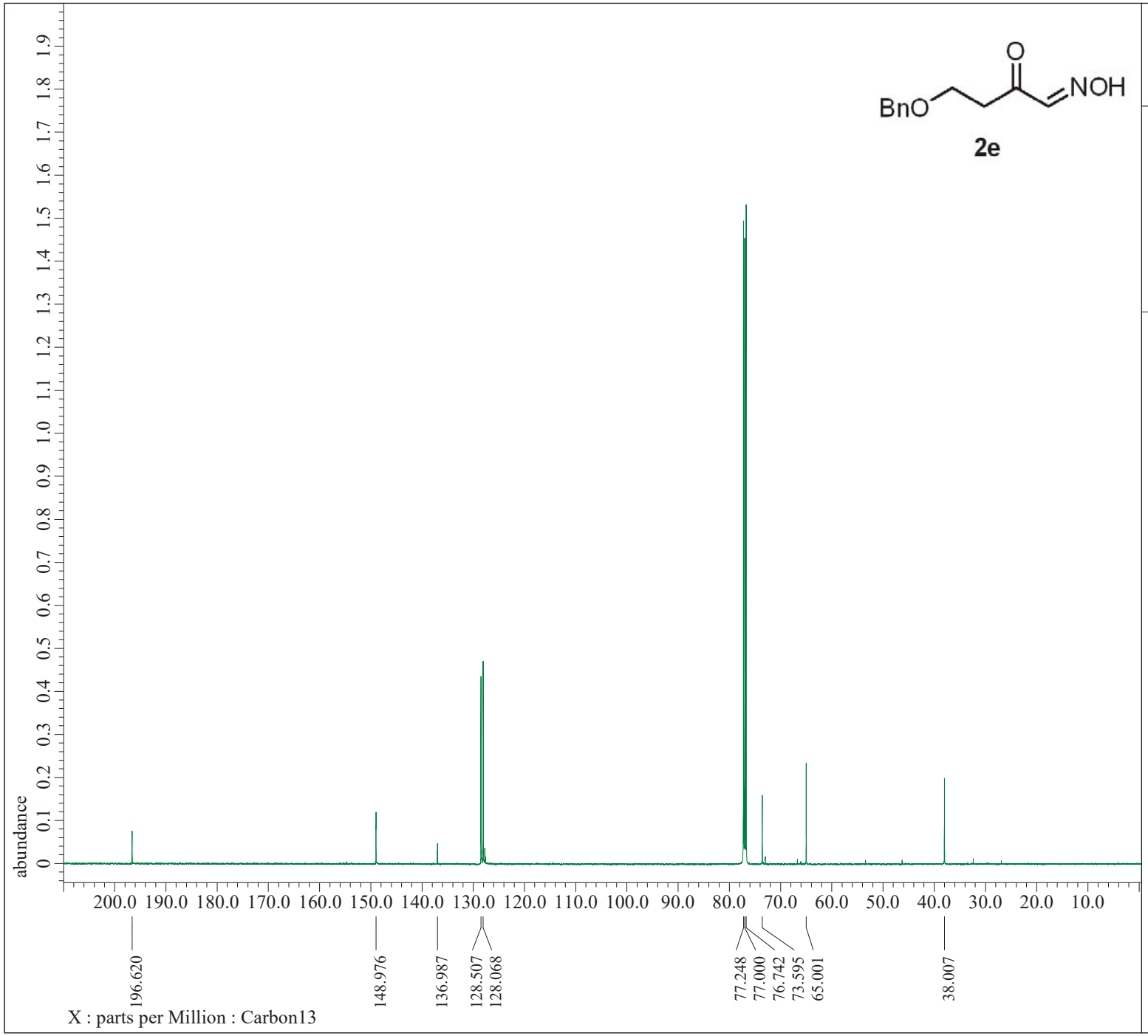


2d



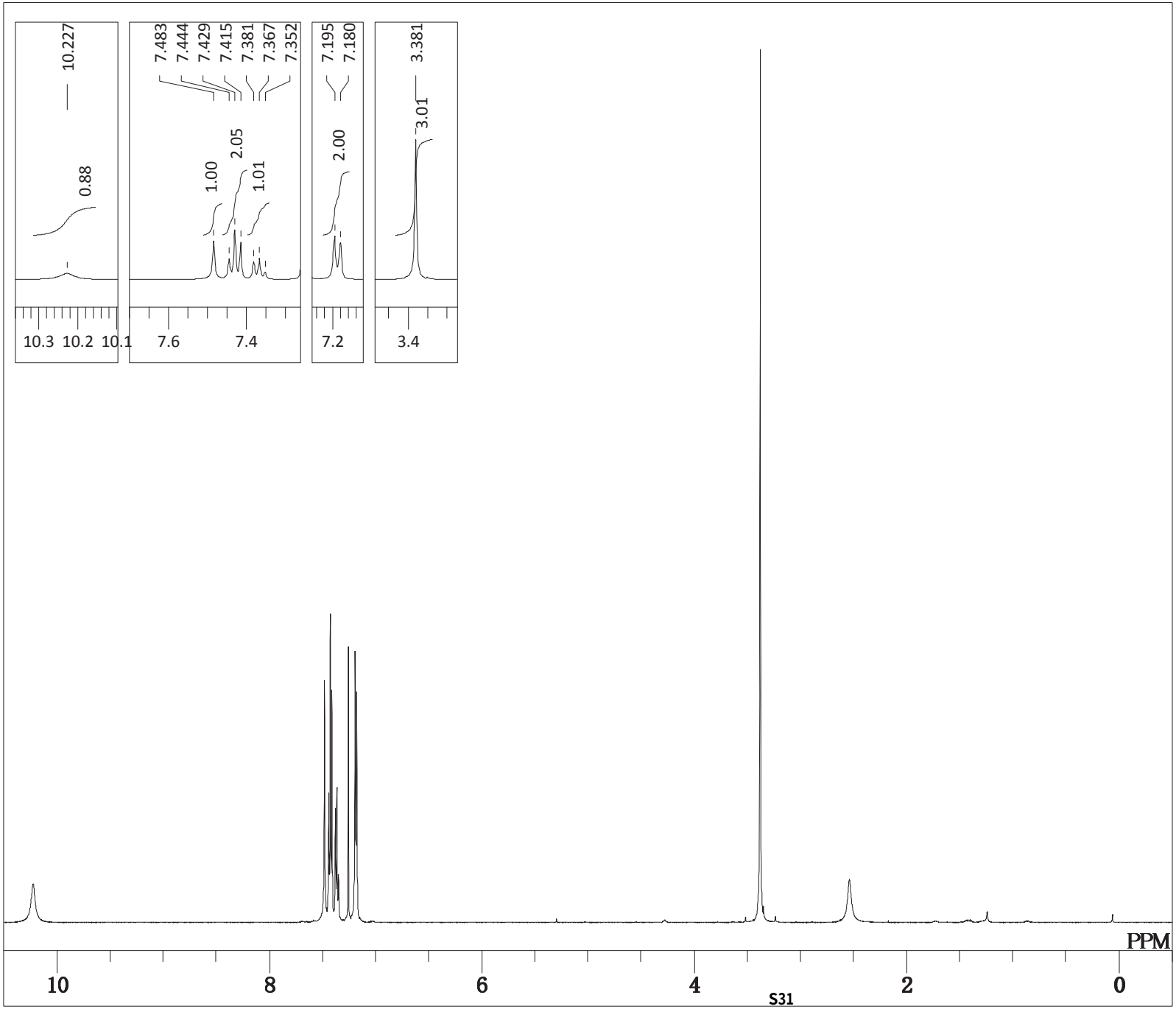

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_112_02_proton-1_Ana-2.jdf
```

```
Filename           = TY_10_112_02_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_10_112_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 31-MAY-2018 23:19:16
Revision_Time      = 21-AUG-2018 21:00:02

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 40
Temp_Get           = 15.6[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```

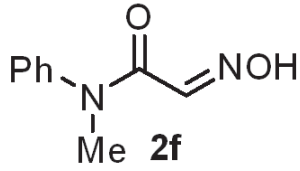



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_112_02_carbon-1_Ana-1.jdf
```

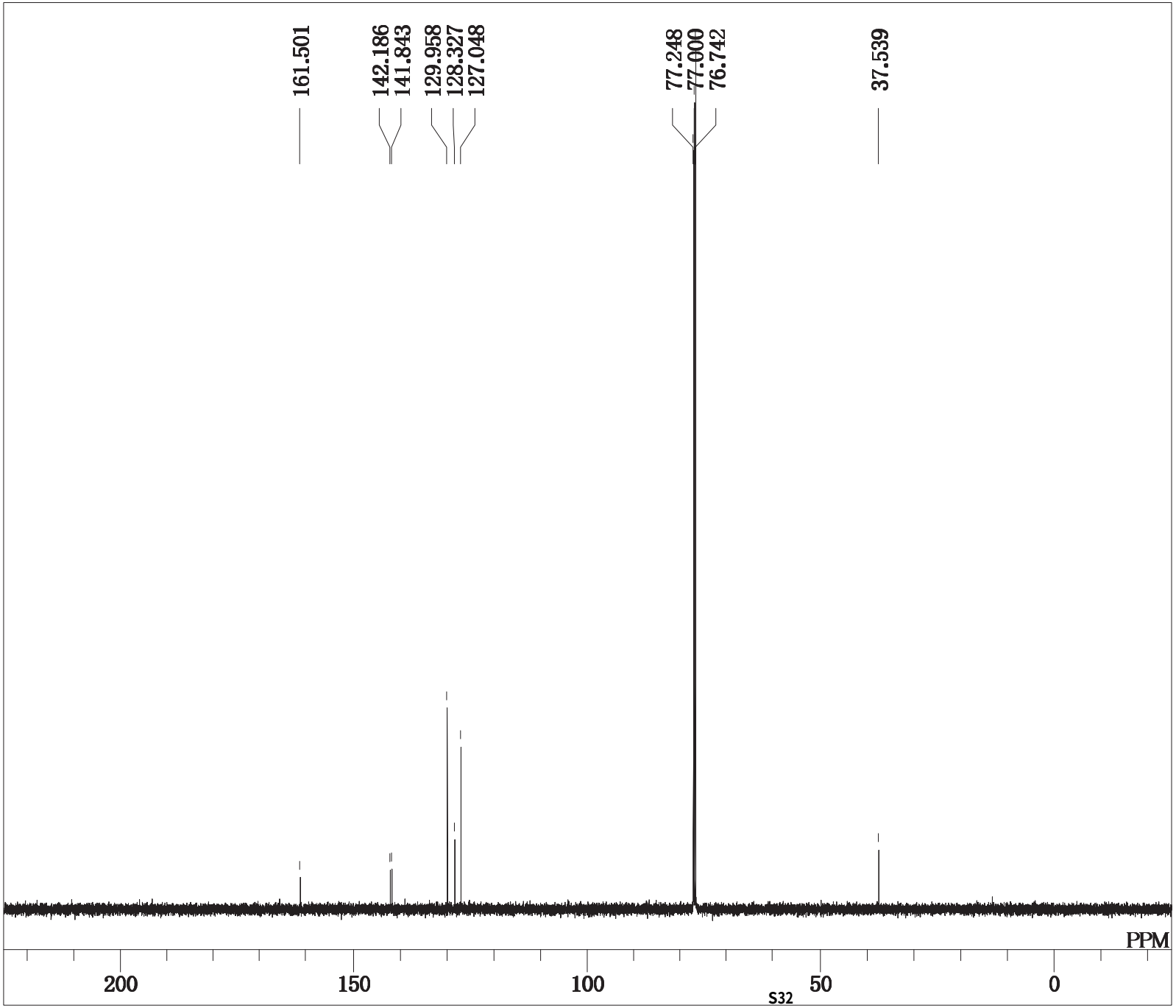
```
Filename           = TY_10_112_02_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_112_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 31-MAY-2018 23:21:13
Revision_Time      = 21-AUG-2018 21:00:55

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 9620
Total_Scans        = 9620

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 16.8[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



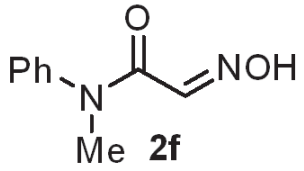
DFILE	TU-02-037-2 170614_proton-1-
COMNT	single_pulse
DATIM	2017-06-14 19:32:21
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.85 usec
IRNUC	1H
CTEMP	13.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	42



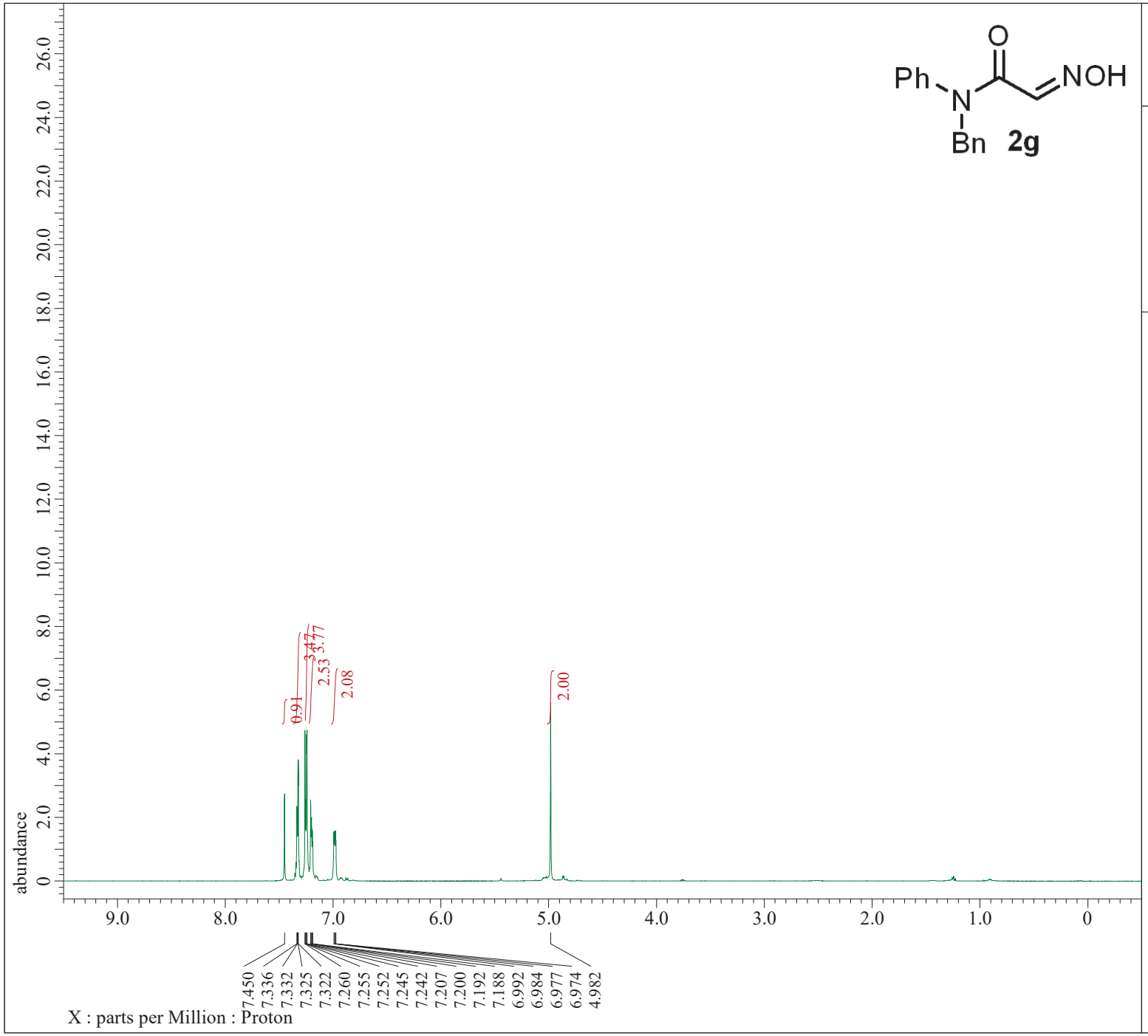
2f



DFILE	TU-02-037-2 170614_carbon-1-
COMNT	single pulse decoupled gated NO
DATIM	2017-06-14 19:33:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	13.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60

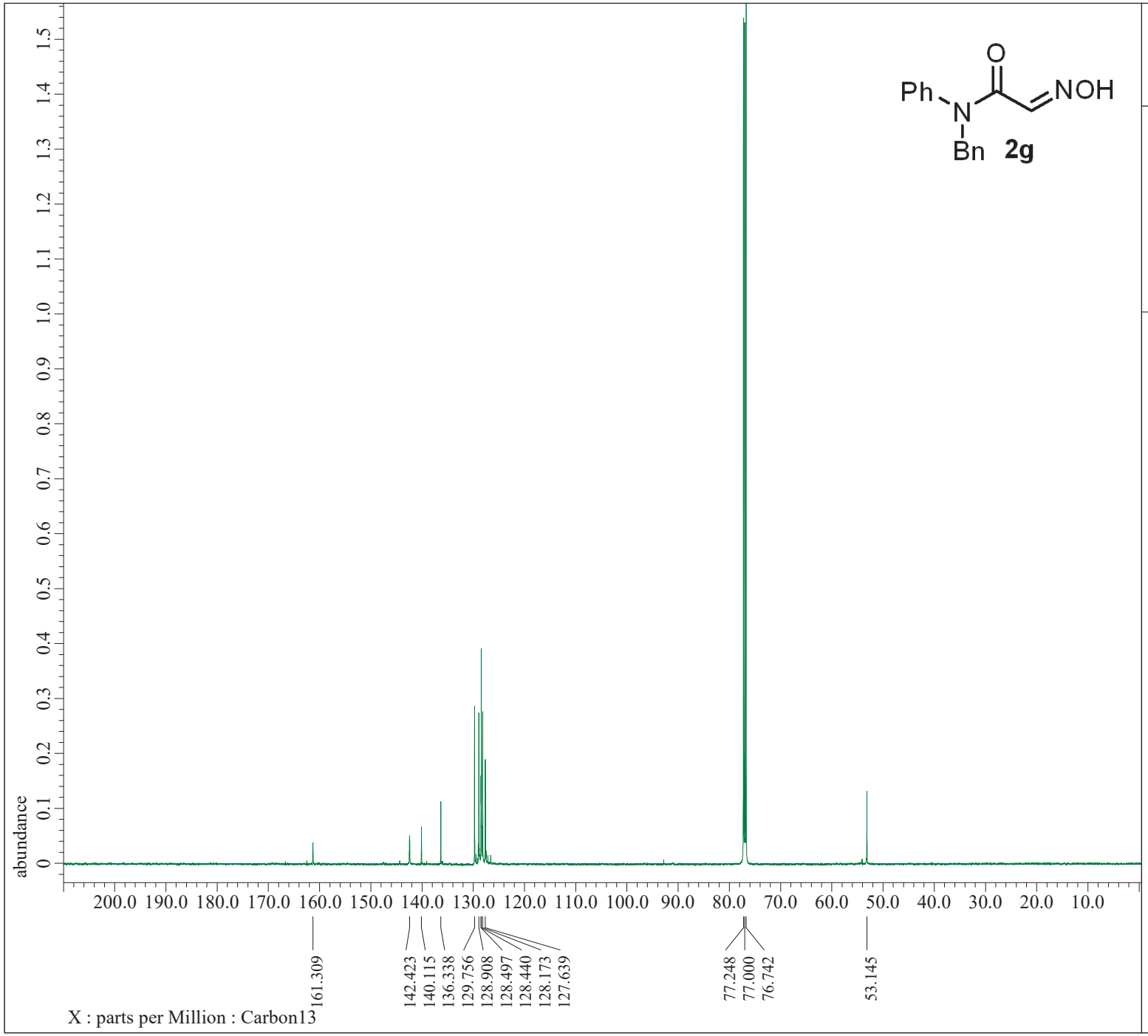


2f



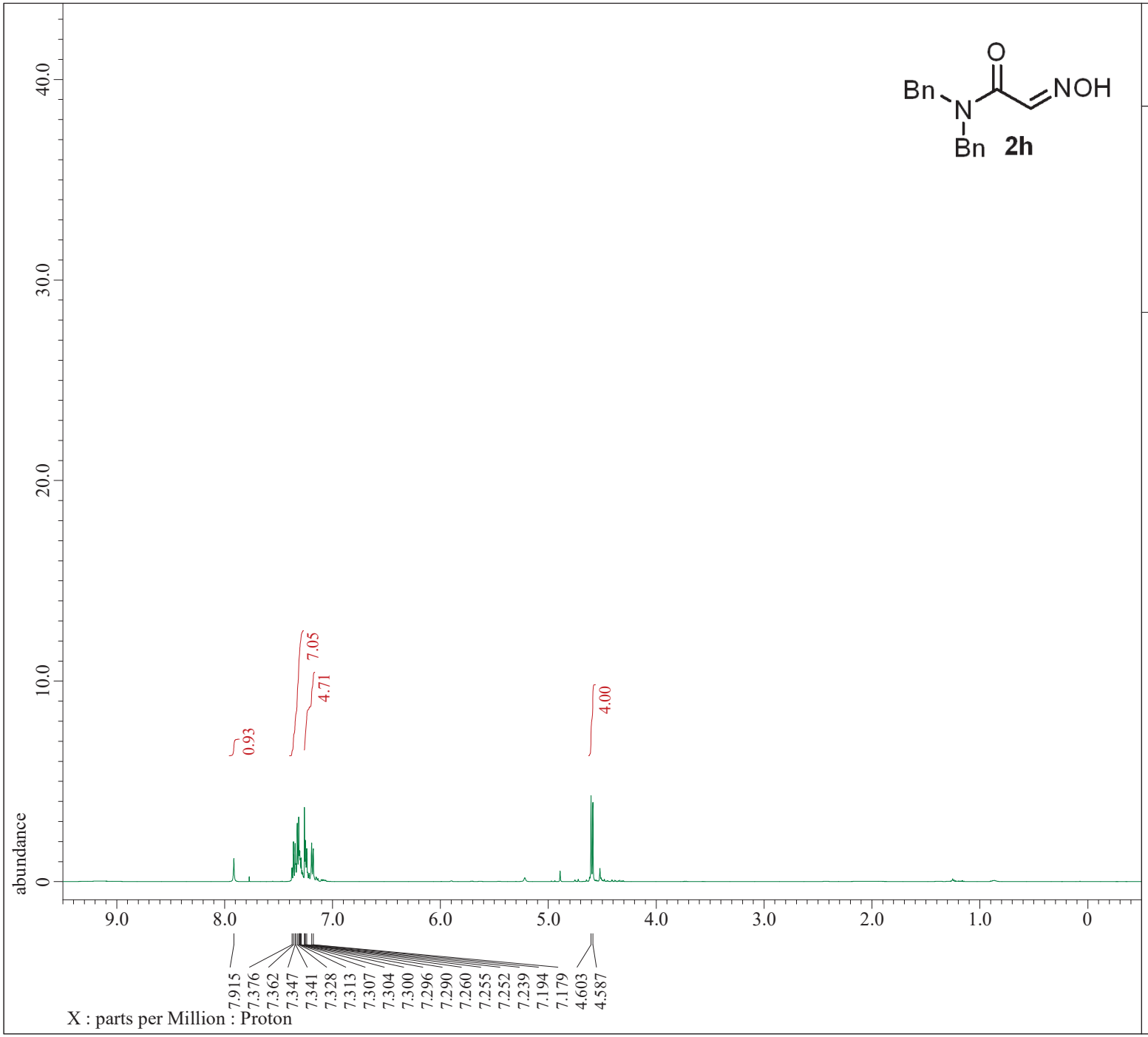

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_110_01_proton-1_Ana-1.jdf
```

```
Filename           = TY_10_110_01_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_10_110_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 30-MAY-2018 23:13:45
Revision_Time      = 15-NOV-2018 12:21:05

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 40
Temp_Get           = 14.7[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



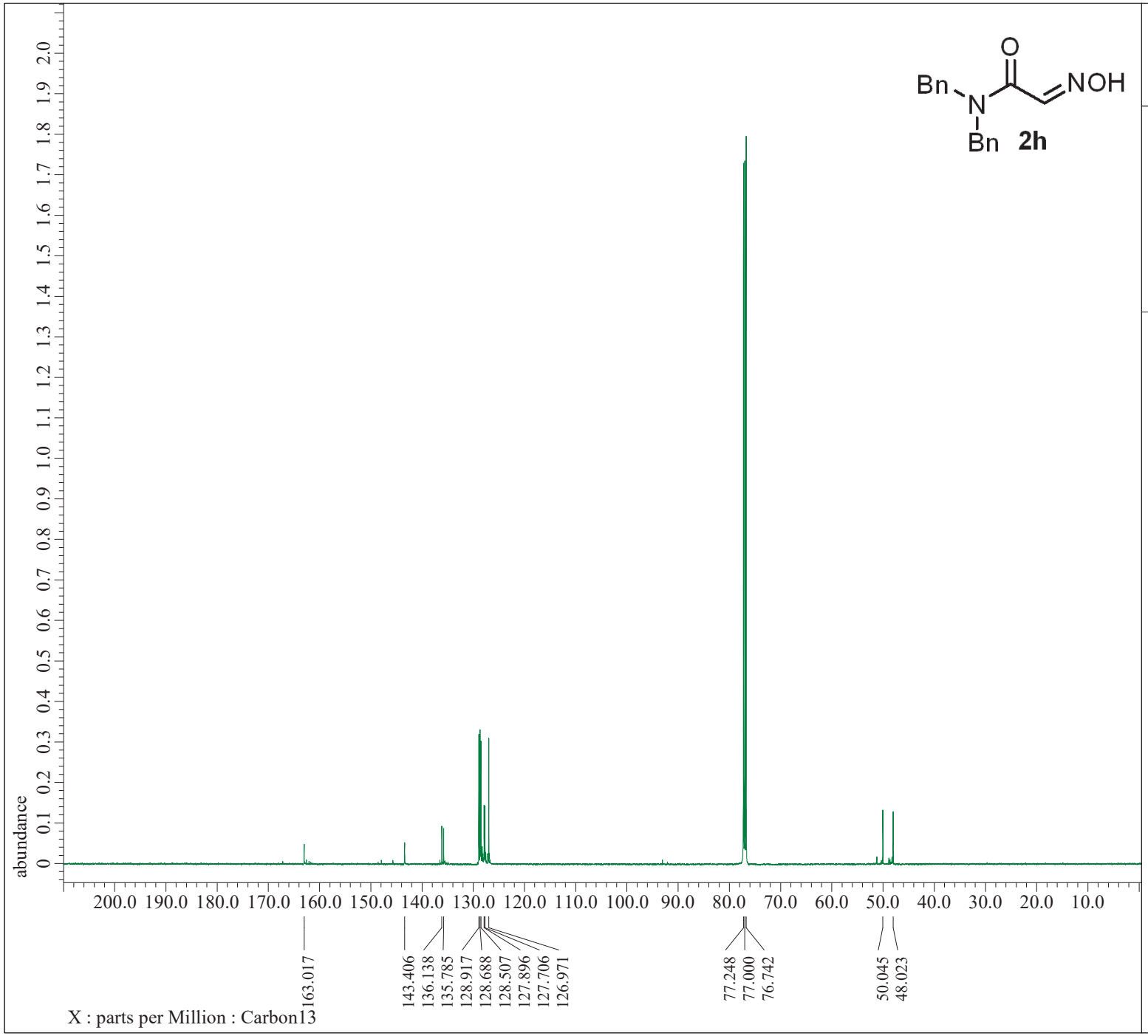

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_110_01_carbon-1-1.jdf
```

```
Filename           = TY_10_110_01_carbon-1-2.j
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_110_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 30-MAY-2018 23:15:32
Revision_Time      = 21-AUG-2018 20:53:27

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 9850
Total_Scans        = 9850

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 16[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



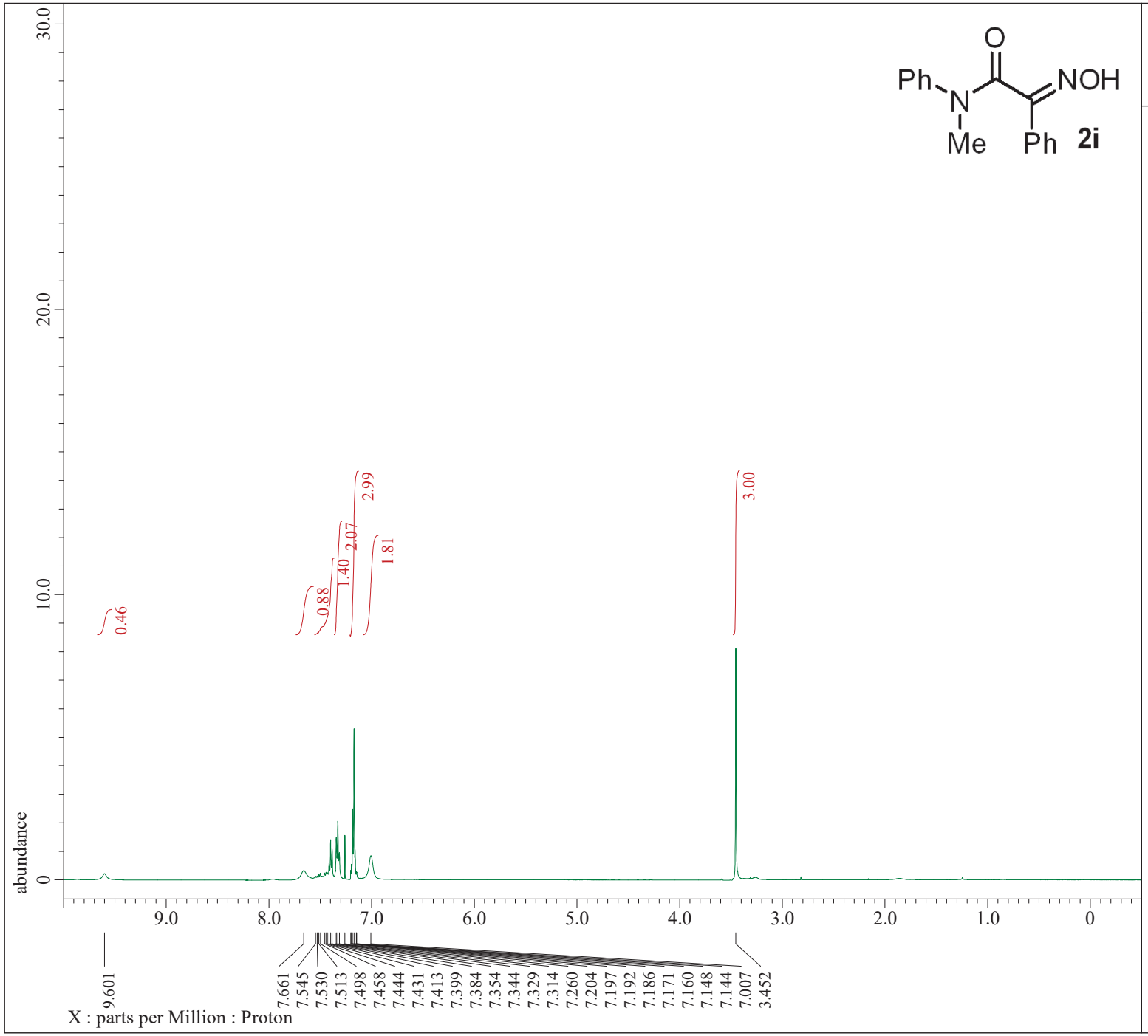

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_121_02_proton-1_Ana-1.jdf
```

```
Filename           = TY_10_121_02_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_10_121_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  7-JUN-2018 23:35:50
Revision_Time      = 21-AUG-2018 20:35:18

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 40
Temp_Get           = 14.3[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



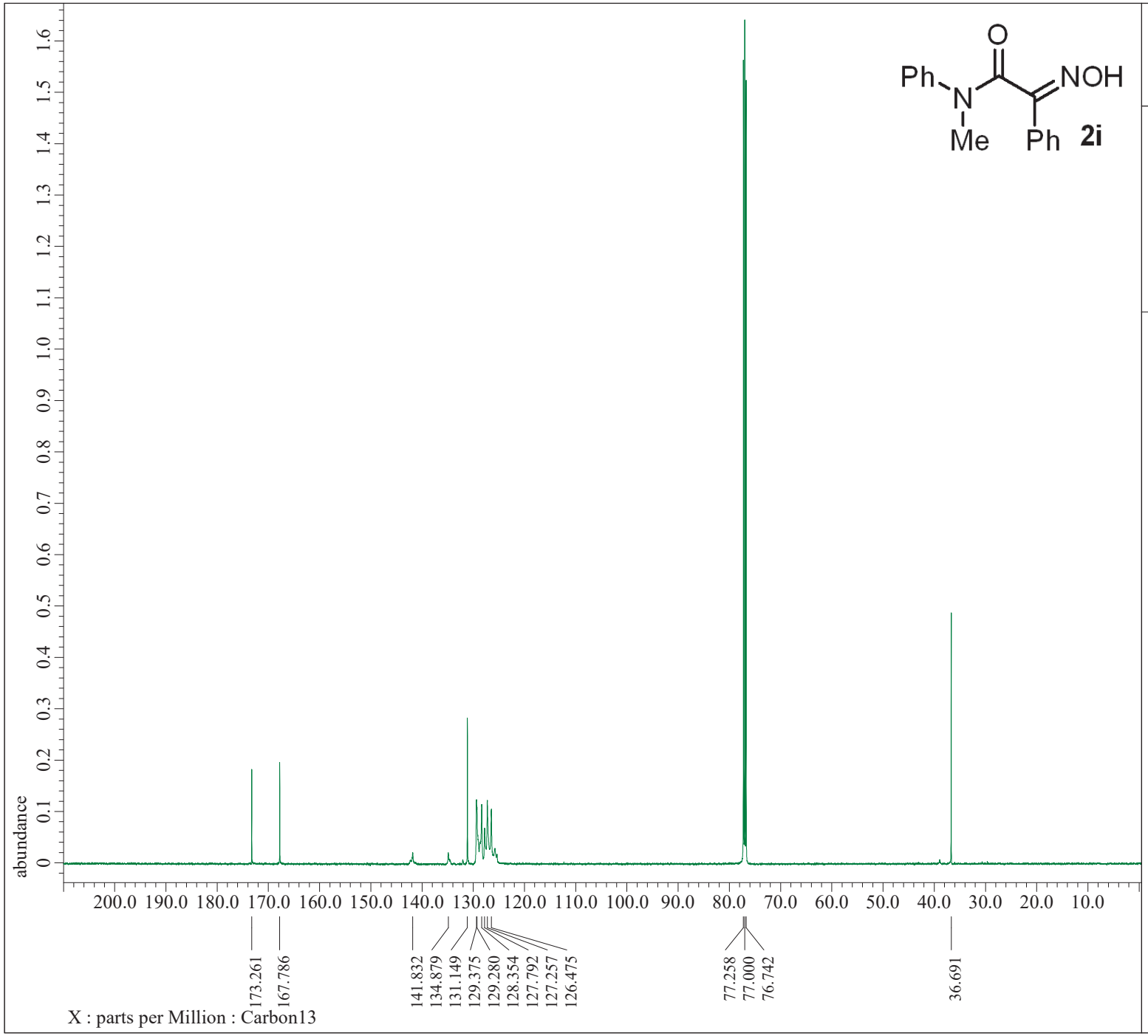

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_121_02_carbon-1_Ana-1.jdf
```

Filename	= TY_10_121_02_carbon-1_Ana
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= TY_10_121_02
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 7-JUN-2018 23:37:34
Revision_Time	= 21-AUG-2018 20:36:38
Comment	= single pulse decoupled ga
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 0.83361792[s]
X_Domain	= 13C
X_Freq	= 125.76529768[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.19959034[Hz]
X_Sweep	= 39.3081761[kHz]
X_Sweep_Clipped	= 31.44654088[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Clipped	= TRUE
Scans	= 9800
Total_Scans	= 9800
Relaxation_Delay	= 2[s]
Recvr_Gain	= 58
Temp_Get	= 14.7[dC]
X_90_Width	= 9.36[us]
X_Acq_Time	= 0.83361792[s]
X_Angle	= 30[deg]
X_Atn	= 3[dB]
X_Pulse	= 3.12[us]
Irr_Atn_Dec	= 20.54[dB]
Irr_Atn_Noe	= 20.54[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 92[us]
Decoupling	= TRUE



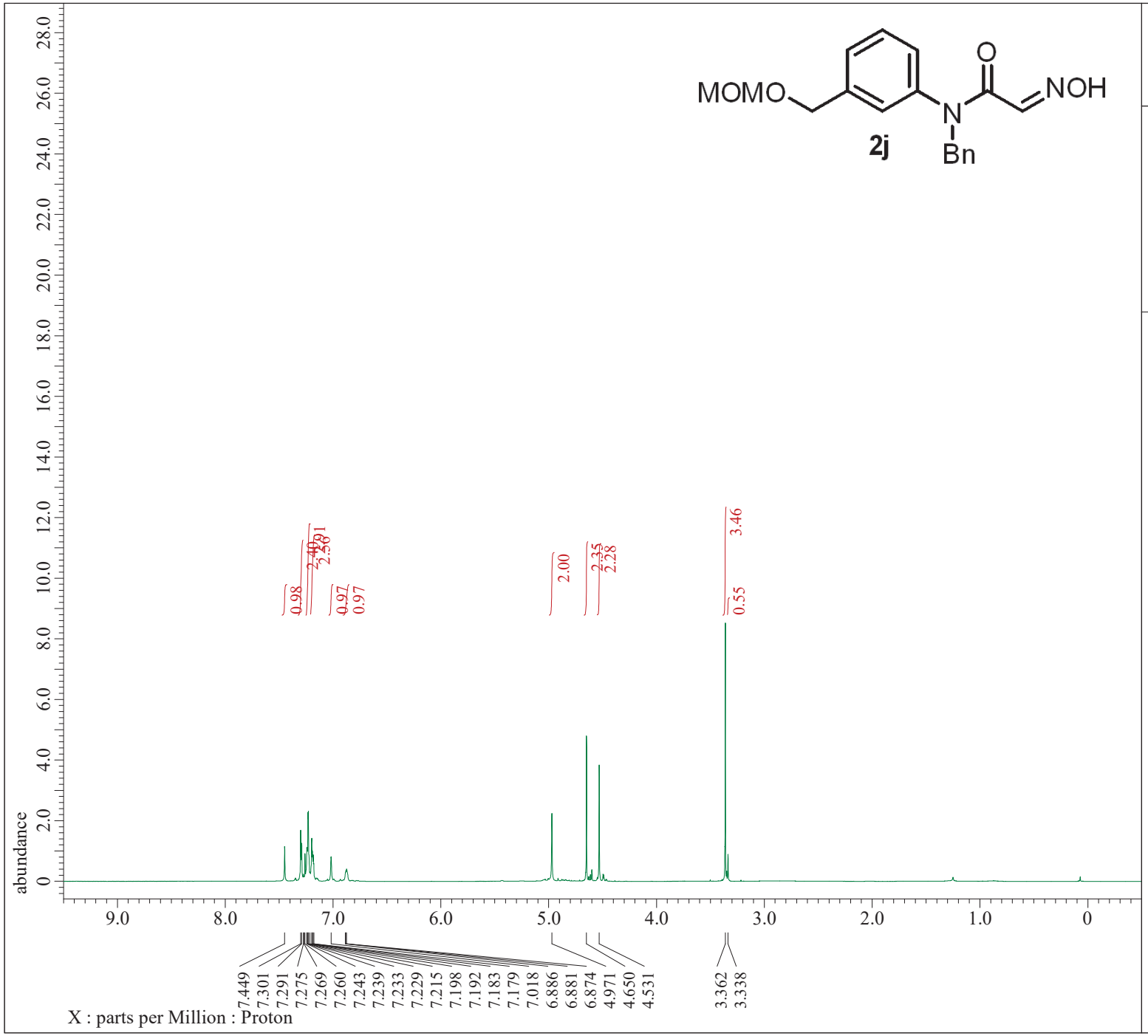

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_119_01_proton-1_Ana-1.jdf
```

```
Filename           = TY_10_119_01_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_10_119_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  6-JUN-2018 23:19:36
Revision_Time      = 21-AUG-2018 20:55:41

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 34
Temp_Get           = 14.5[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_119_01_carbon-1_Ana-1.jdf
```

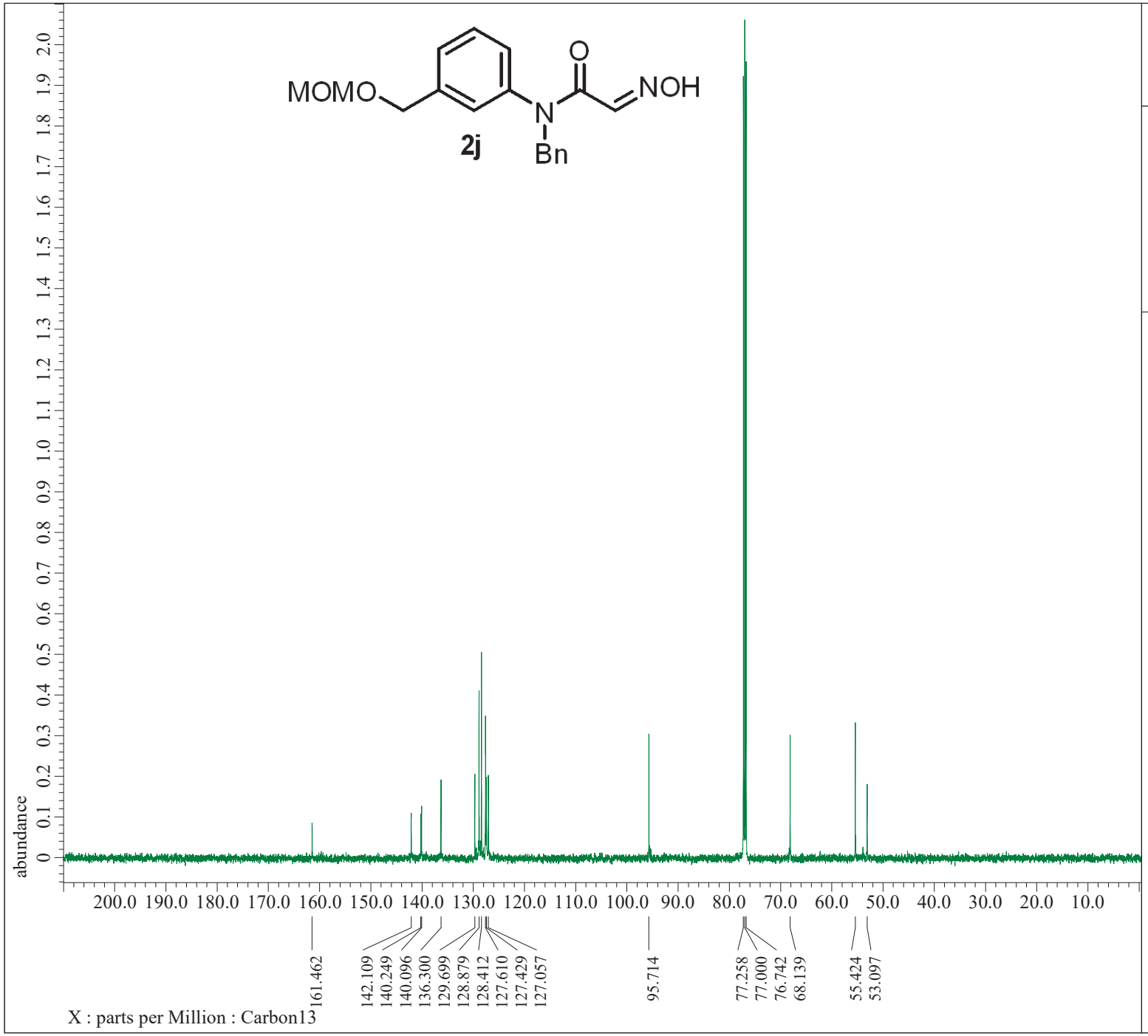
```
Filename           = TY_10_119_01_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_119_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  6-JUN-2018 23:21:21
Revision_Time      = 21-AUG-2018 20:57:01

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 9800
Total_Scans        = 9800

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 15.7[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



JEOL

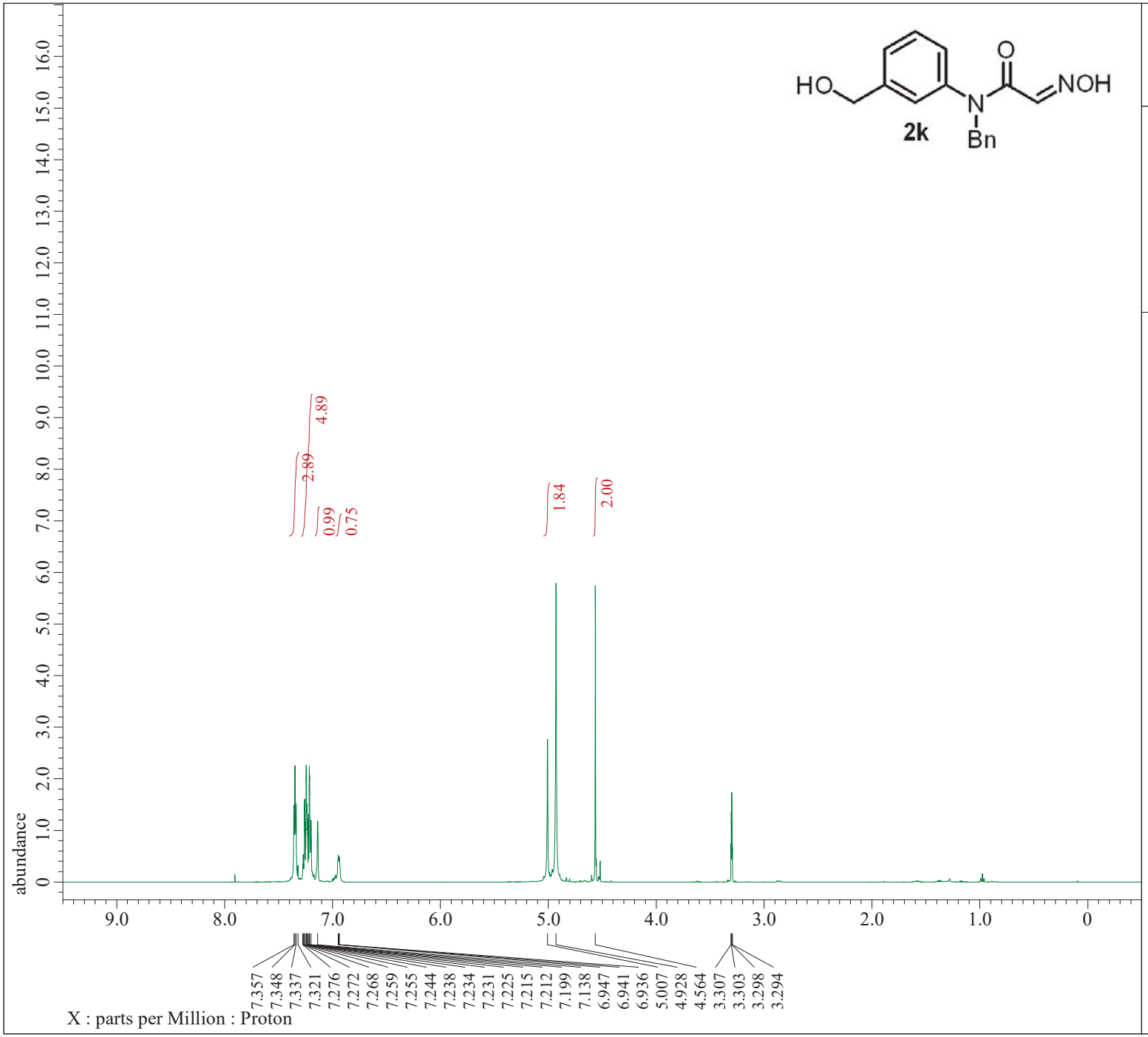
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_017_01_proton-1_Ana-3.jdf
```

```
Filename           = TY_11_017_01_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_11_017_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  5-JUL-2018 20:21:22
Revision_Time      = 21-AUG-2018 20:44:54

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T]  (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 30
Temp_Get           = 17.1[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



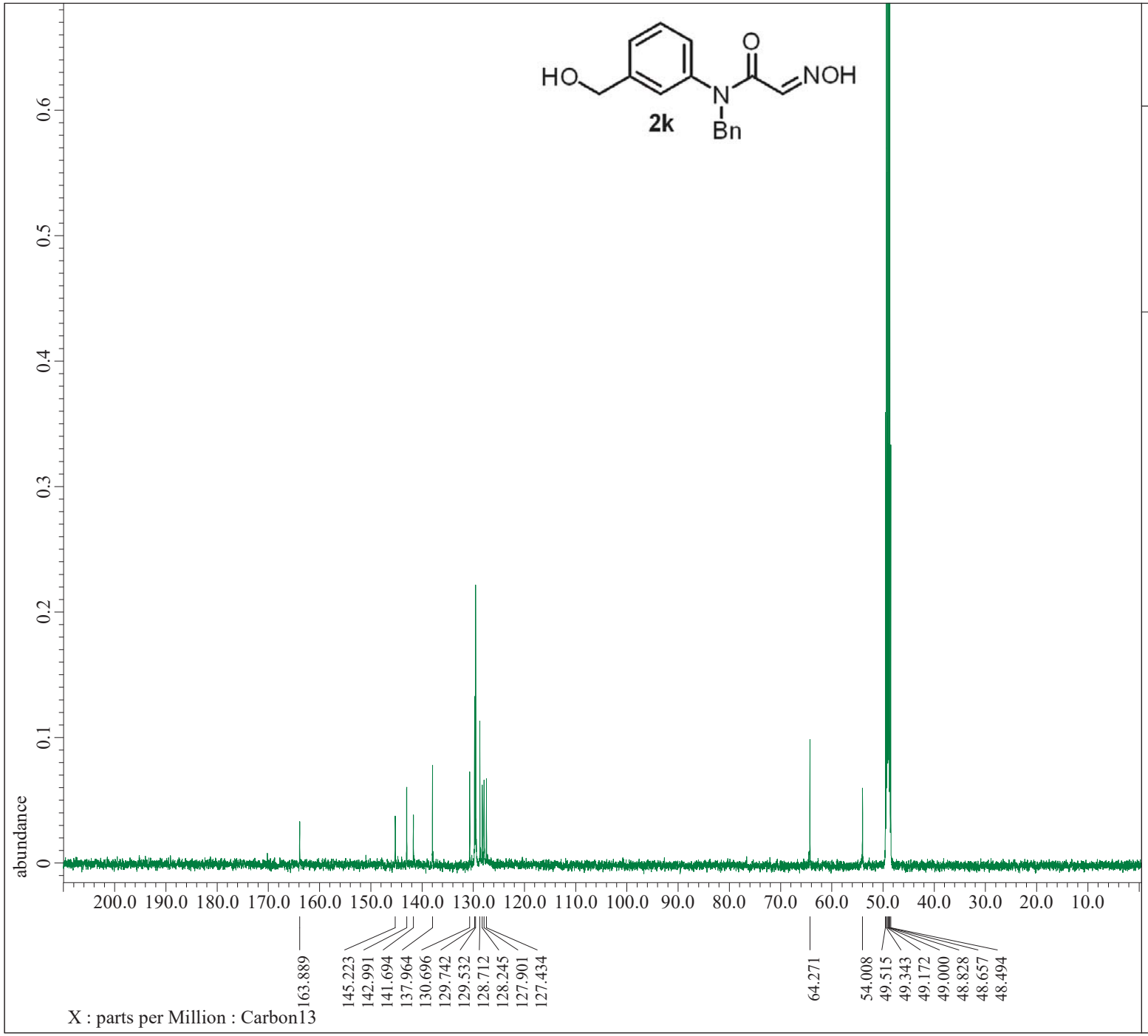

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_017_01_carbon-1_Ana-1.jdf
```

```
Filename           = TY_11_017_01_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_11_017_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  5-JUL-2018 20:23:43
Revision_Time      = 21-AUG-2018 20:45:23

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 414
Total_Scans        = 414

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 17.4[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



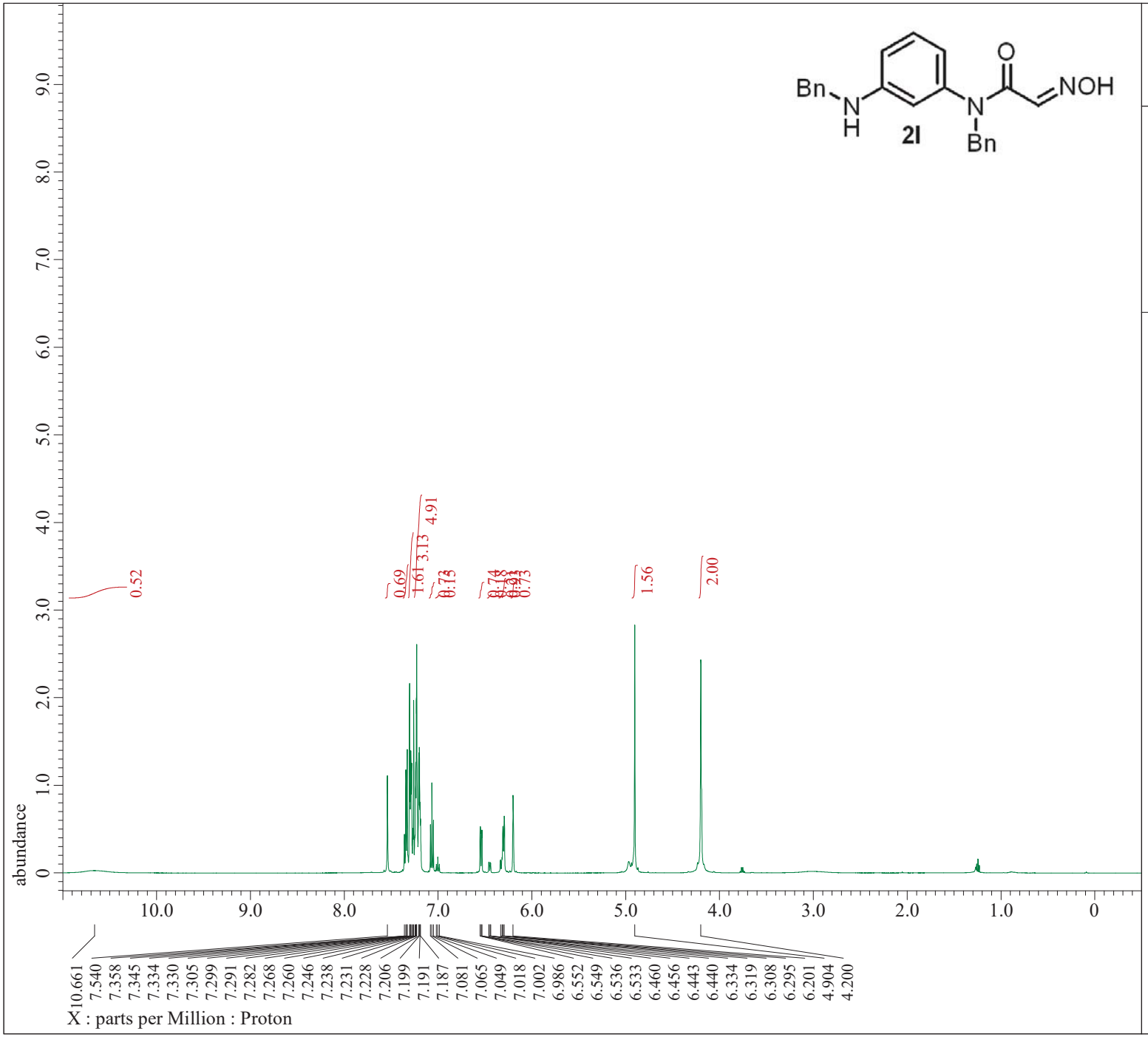

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_146_02_proton-1_Ana-1.jdf
```

```
Filename           = TY_10_146_02_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_10_146_02
Solvent            = METHANOL-D4
Actual_Start_Time  = 23-JUN-2018 15:03:09
Revision_Time      = 21-AUG-2018 20:39:36

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 36
Temp_Get           = 15.1[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



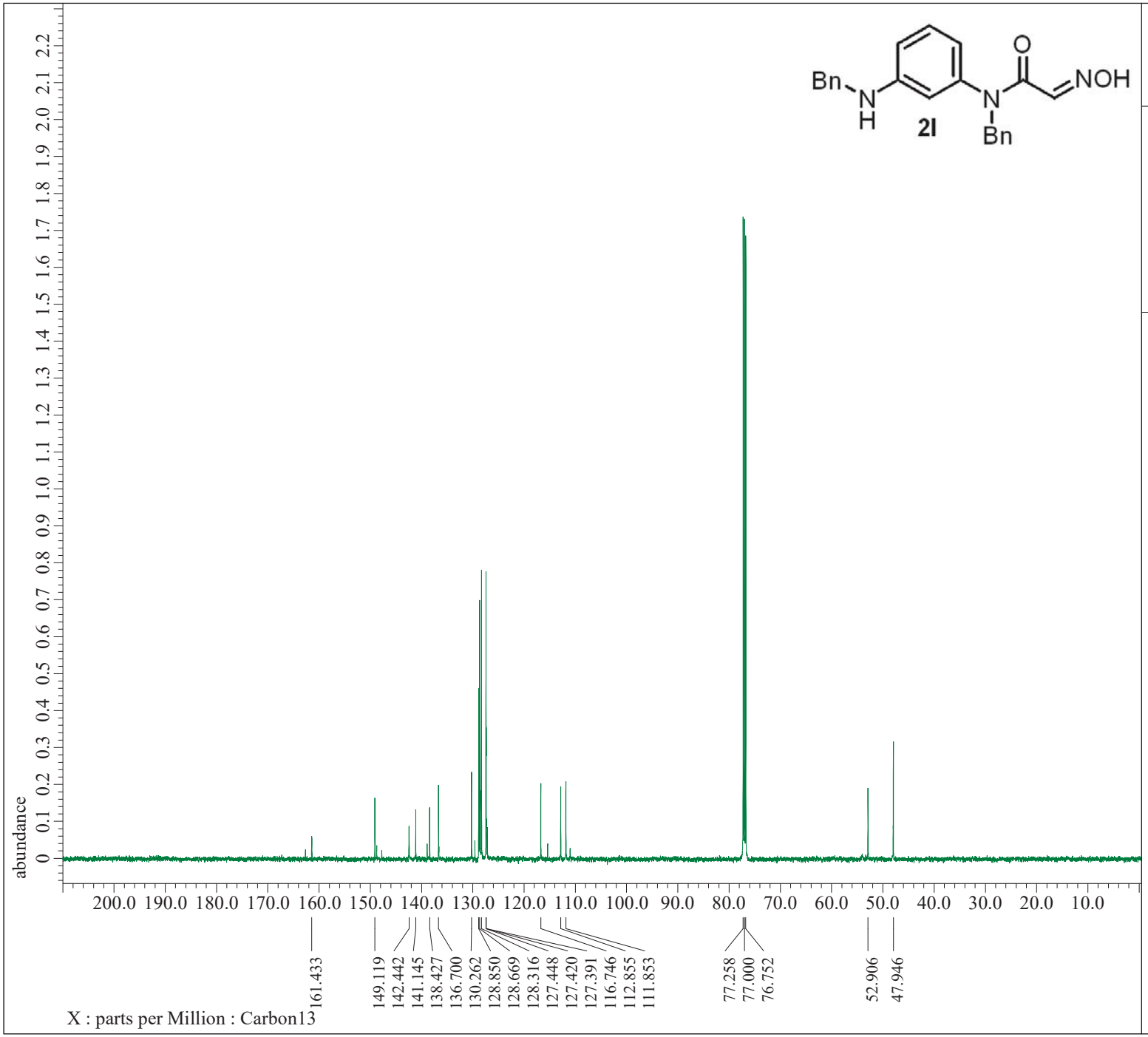

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_146_02_carbon-1_Ana-1.jdf
```

```
Filename           = TY_10_146_02_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_146_02
Solvent            = METHANOL-D4
Actual_Start_Time  = 23-JUN-2018 15:04:48
Revision_Time      = 21-AUG-2018 20:40:34

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 1720
Total_Scans        = 1720

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 15.1[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



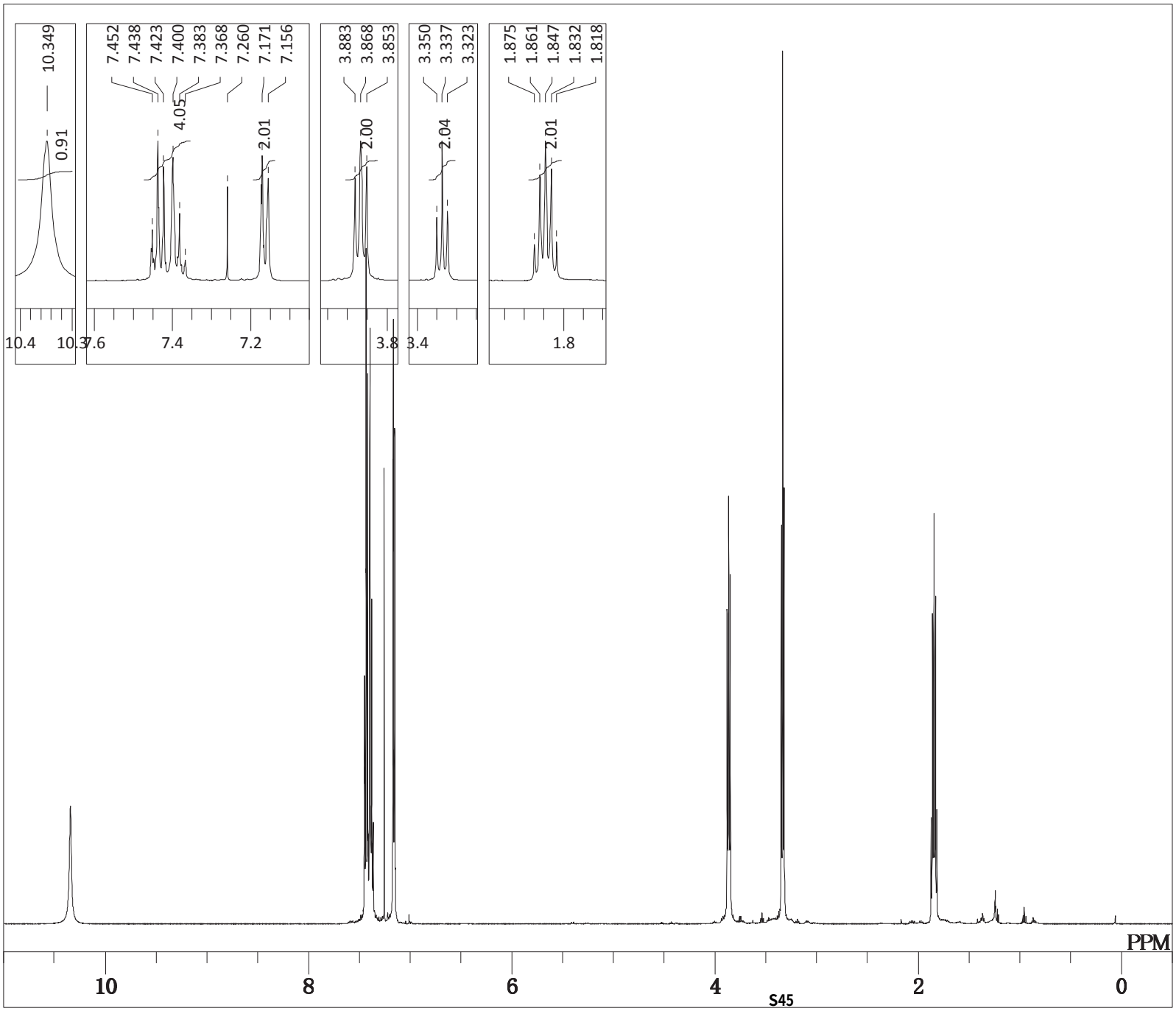

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_006_02_proton-1_Ana-2.jdf
```

```
Filename            = TY_11_006_02_proton-1_Ana
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TY_11_006_02
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  1-JUL-2018 13:48:14
Revision_Time       = 21-AUG-2018 20:31:48

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 30
Temp_Get            = 18.1[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```

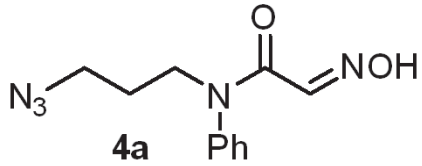



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_006_02_carbon-1_Ana-1.jdf
```

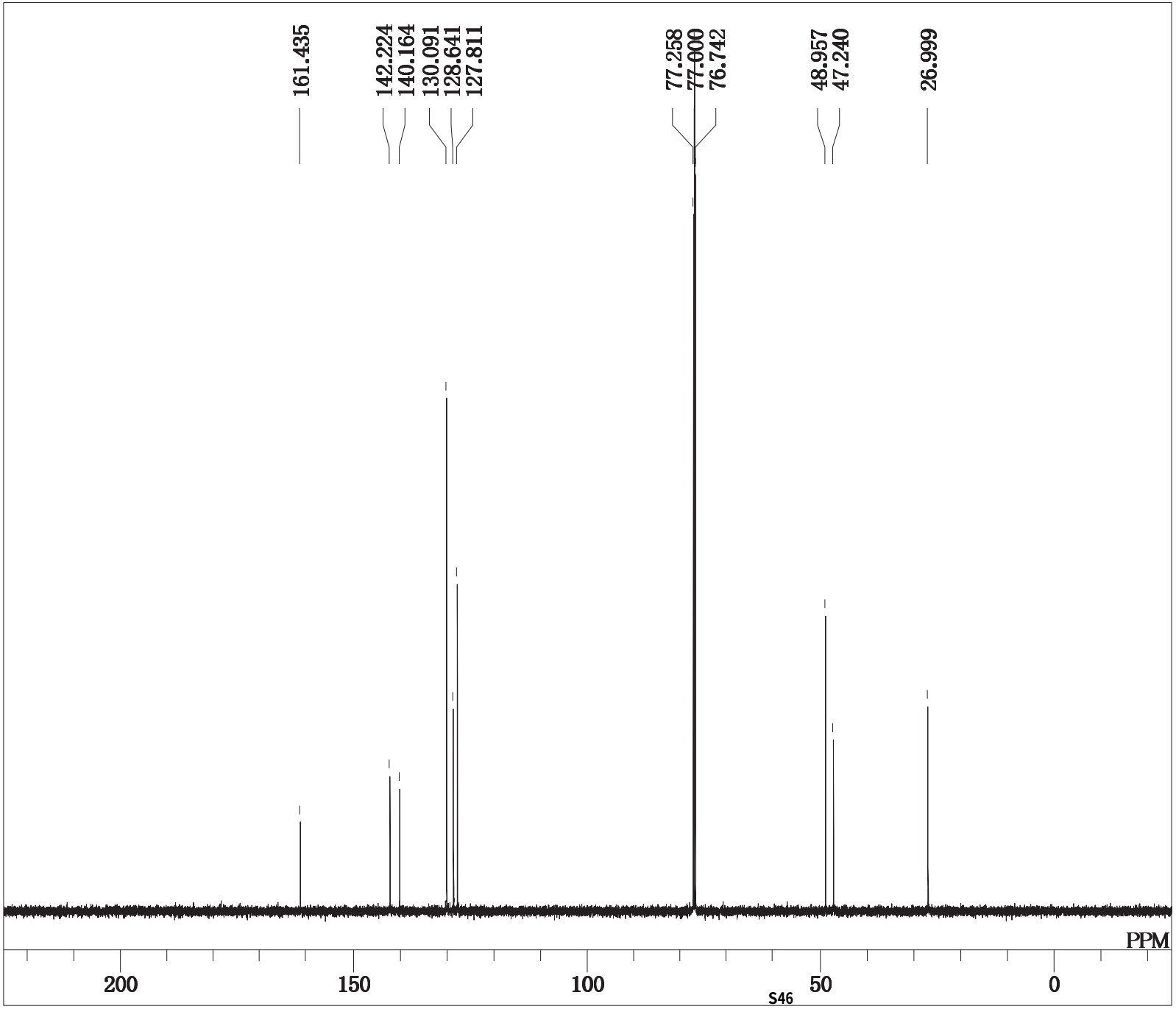
```
Filename           = TY_11_006_02_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_11_006_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  1-JUL-2018 13:49:58
Revision_Time      = 21-AUG-2018 20:32:34

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 900
Total_Scans        = 900

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 18.6[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



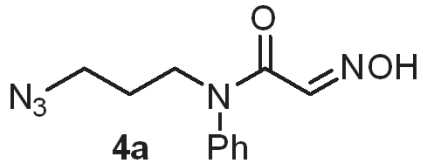
DFILE	TU-01-147-2 170126_proton-1-
COMNT	single_pulse
DATIM	2017-01-26 13:50:37
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.85 usec
IRNUC	1H
CTEMP	17.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	34



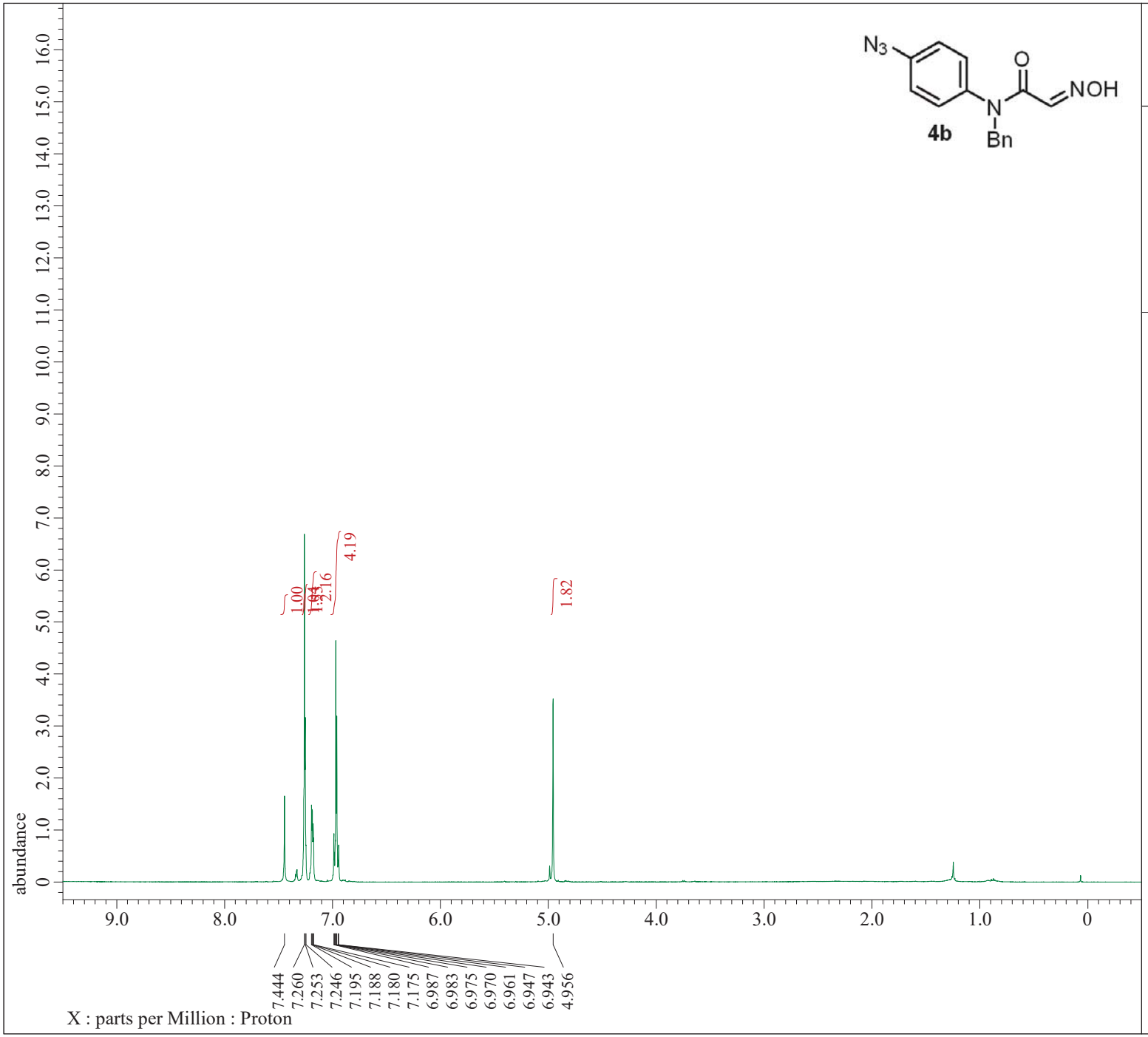
4a



DFILE	TU-01-147-2 170126_carbon-1-
COMNT	single pulse decoupled gated NO
DATIM	2017-01-26 13:52:28
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	18.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



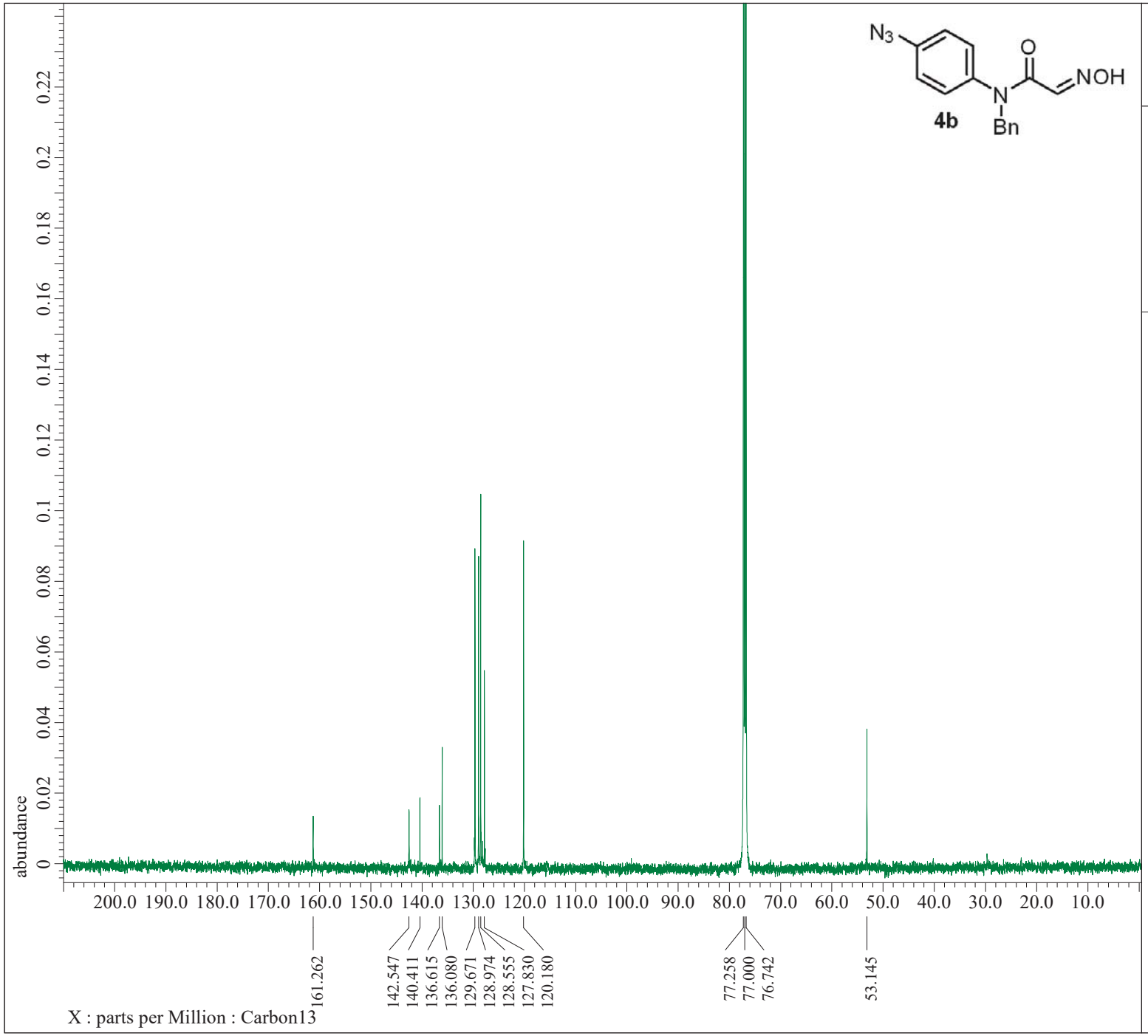
4a



JEOL

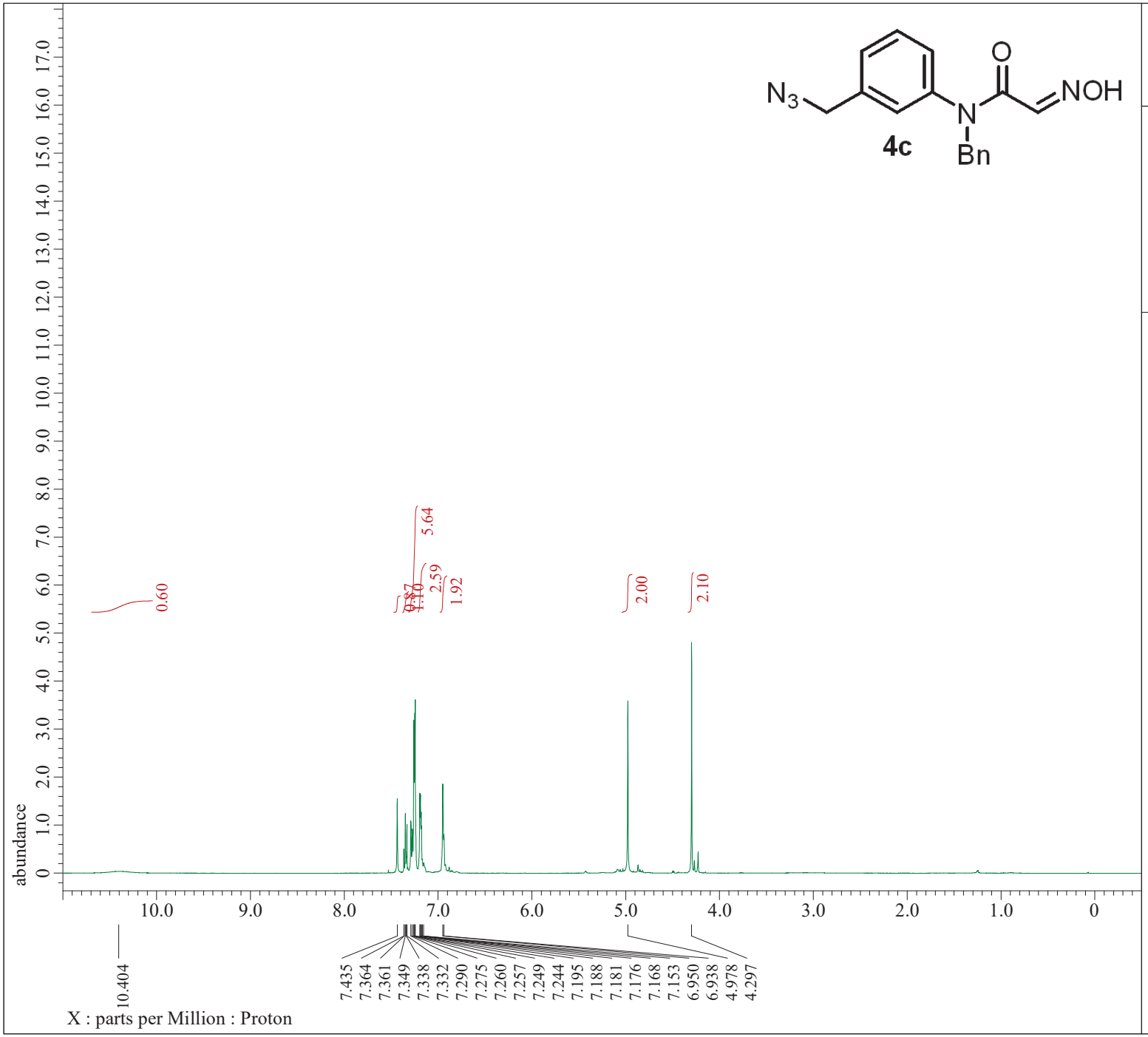
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_135_03_proton-1_Ana-1.jdf
```

```
Filename           = TY_10_135_03_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_10_135_03
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 13-JUN-2018 23:21:00
Revision_Time      = 22-AUG-2018 20:27:56

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 44
Temp_Get           = 12.8[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_135_03_carbon-1_Ana-1.jdf
```

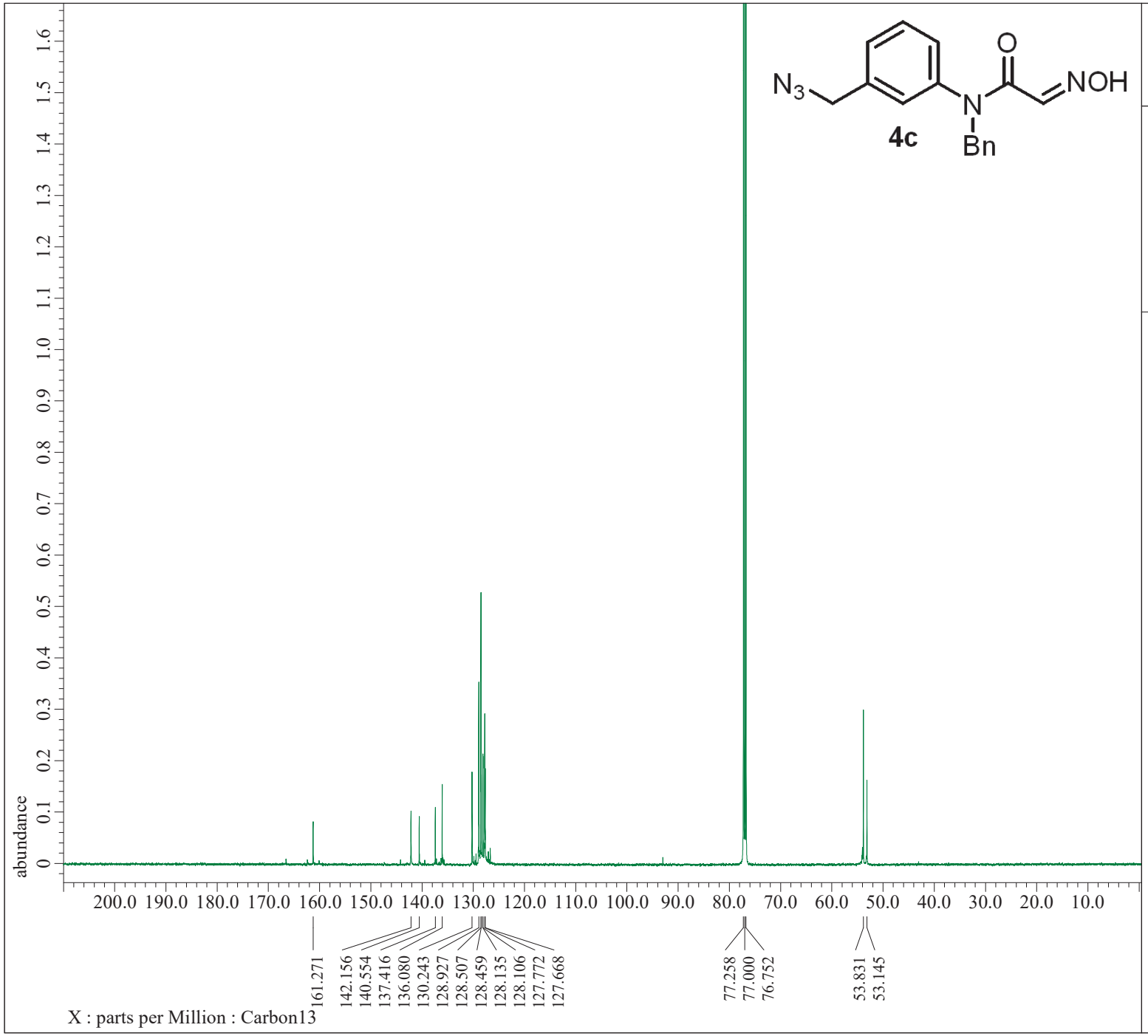
```
Filename           = TY_10_135_03_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_135_03
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 13-JUN-2018 23:22:39
Revision_Time      = 22-AUG-2018 20:28:53

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = TRUE
Scans              = 10000
Total_Scans        = 10000

Relaxation_Delay   = 2[s]
Recvr_Gain         = 56
Temp_Get           = 14.7[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



JEOL

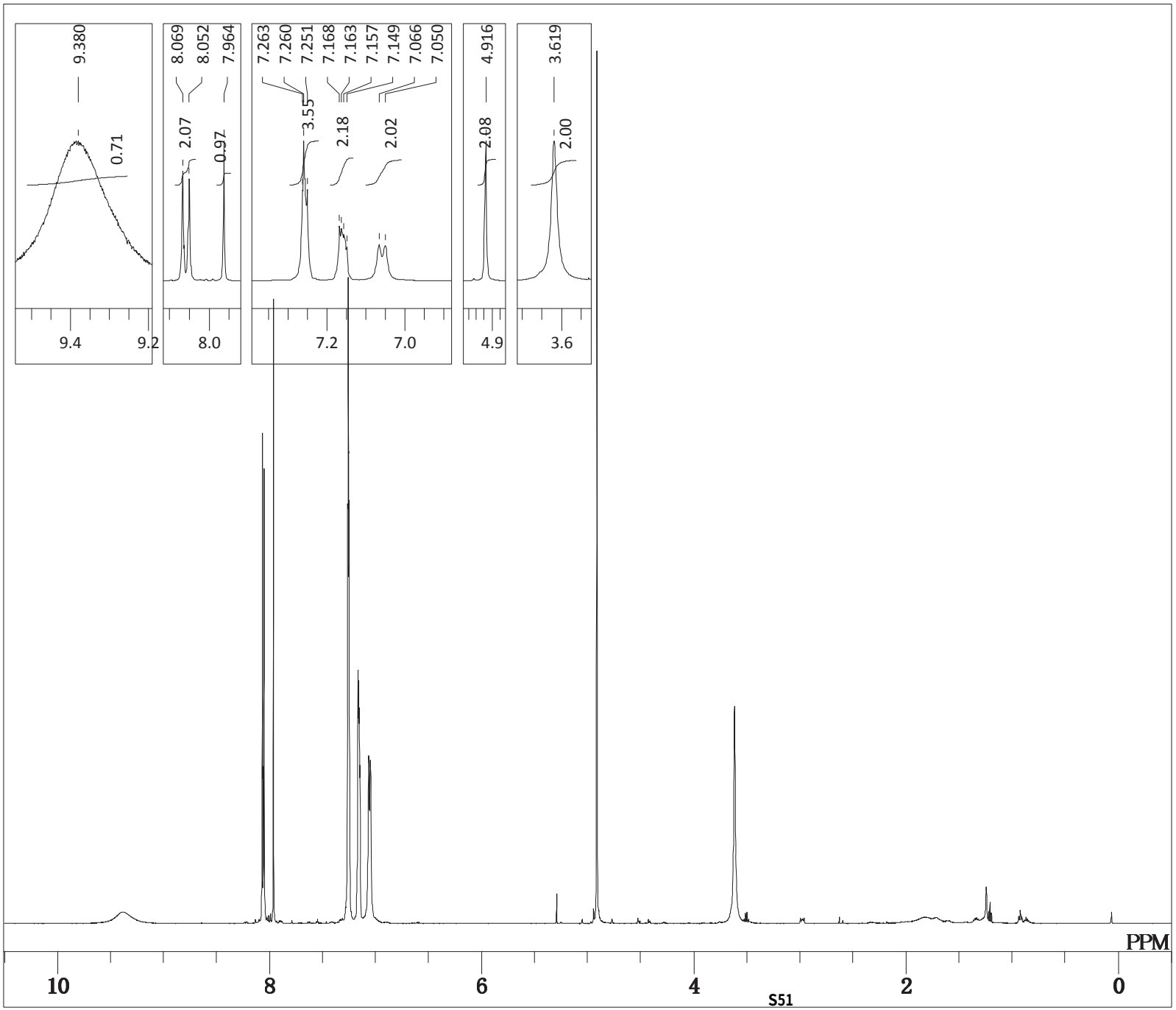
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_133_01_proton-1_Ana-2.jdf
```

```
Filename            = TY_10_133_01_proton-1_Ana
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TY_10_133_01
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 12-JUN-2018 23:12:27
Revision_Time       = 22-AUG-2018 20:34:42

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 34
Temp_Get            = 13.7[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```

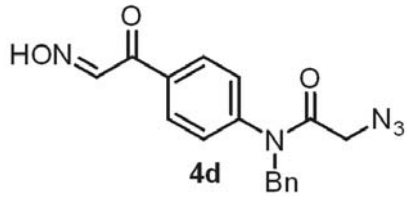



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_133_01_carbon-1Ana-1.jdf
```

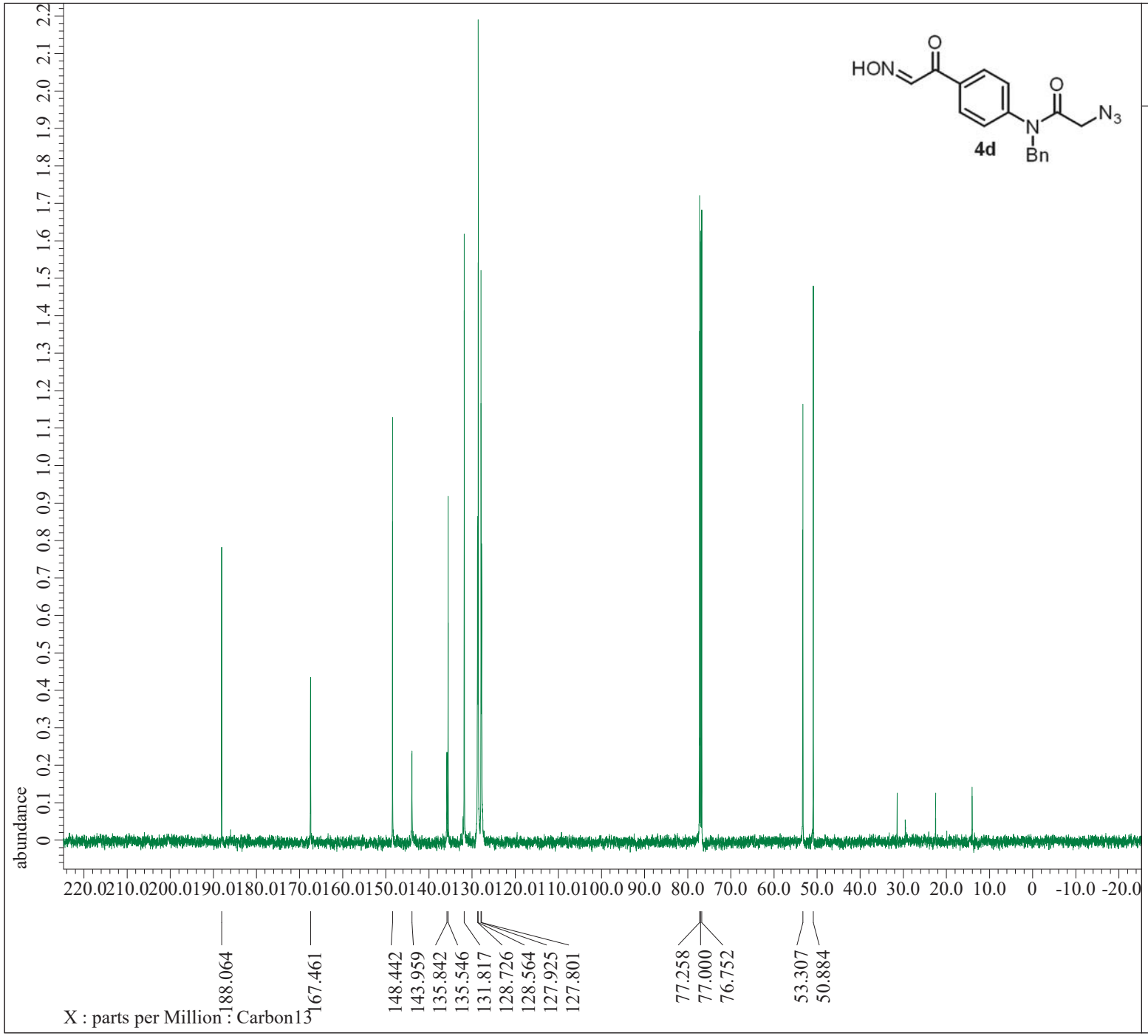
```
Filename           = TY_10_133_01_carbon-1Ana-
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_133_01
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 12-JUN-2018 23:14:17
Revision_Time      = 22-AUG-2018 20:36:03

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = TRUE
Scans              = 9800
Total_Scans        = 9800

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 14.9[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



DFILE	TU-02-045-2 170707_proton-1-
COMNT	single_pulse
DATIM	2017-07-07 13:16:27
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.85 usec
IRNUC	1H
CTEMP	17.3 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	38



4d



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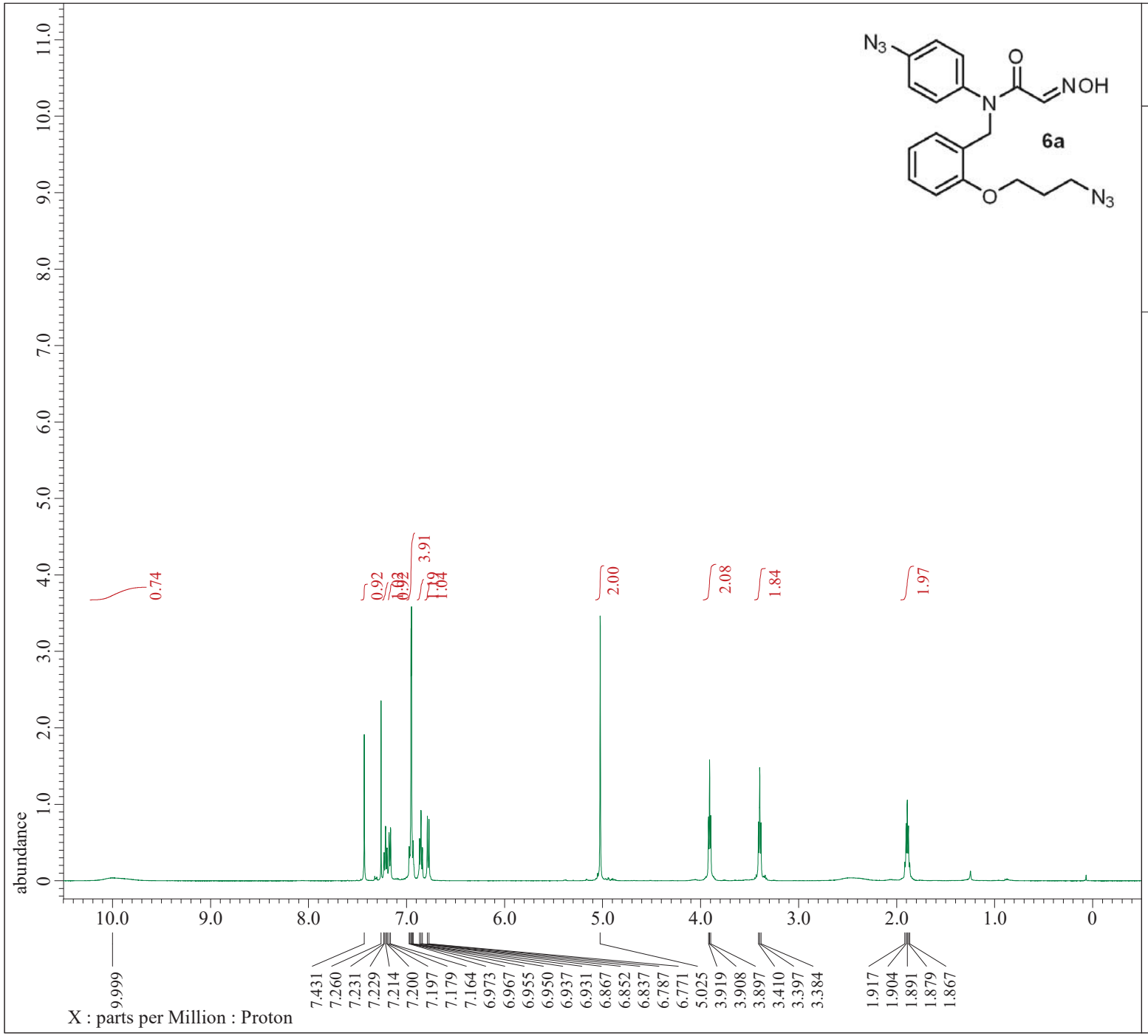
```
Filename          = TU-02-145-2 180310_carbon-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = TU-02-145-2 180310
Solvent           = CHLOROFORM-D
Creation_Time     = 10-MAR-2018 20:20:31
Revision_Time     =  1-NOV-2018 15:17:50
Current_Time      =  1-NOV-2018 15:18:19

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 129
Total_Scans       = 129

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 13.4[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



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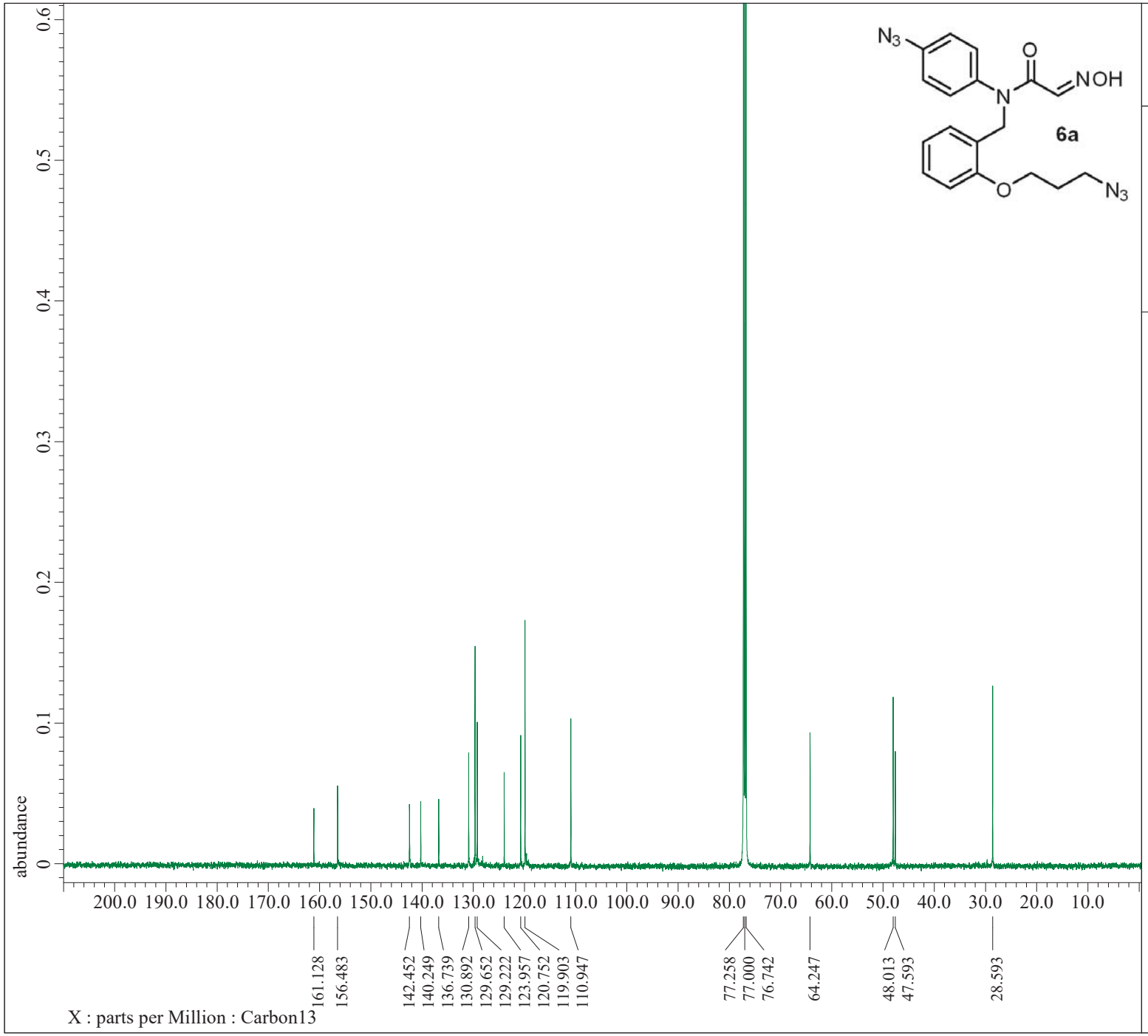
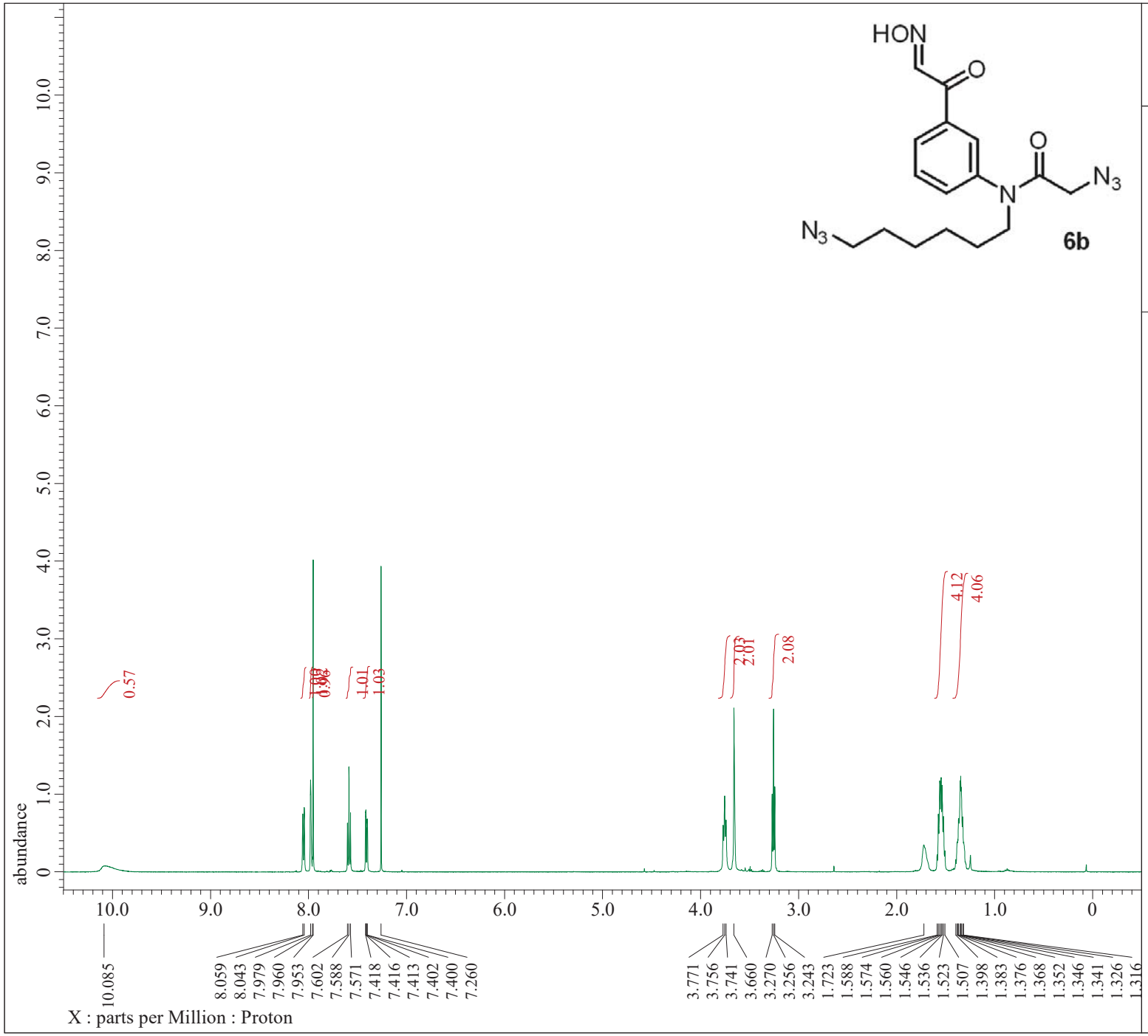
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_139_02_proton-1_Ana-3.jdf
```

```
Filename            = TY_10_139_02_proton-1_Ana
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TY_10_139_02
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 14-JUN-2018 23:13:53
Revision_Time       = 22-AUG-2018 20:45:57

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 40
Temp_Get            = 13.2[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```



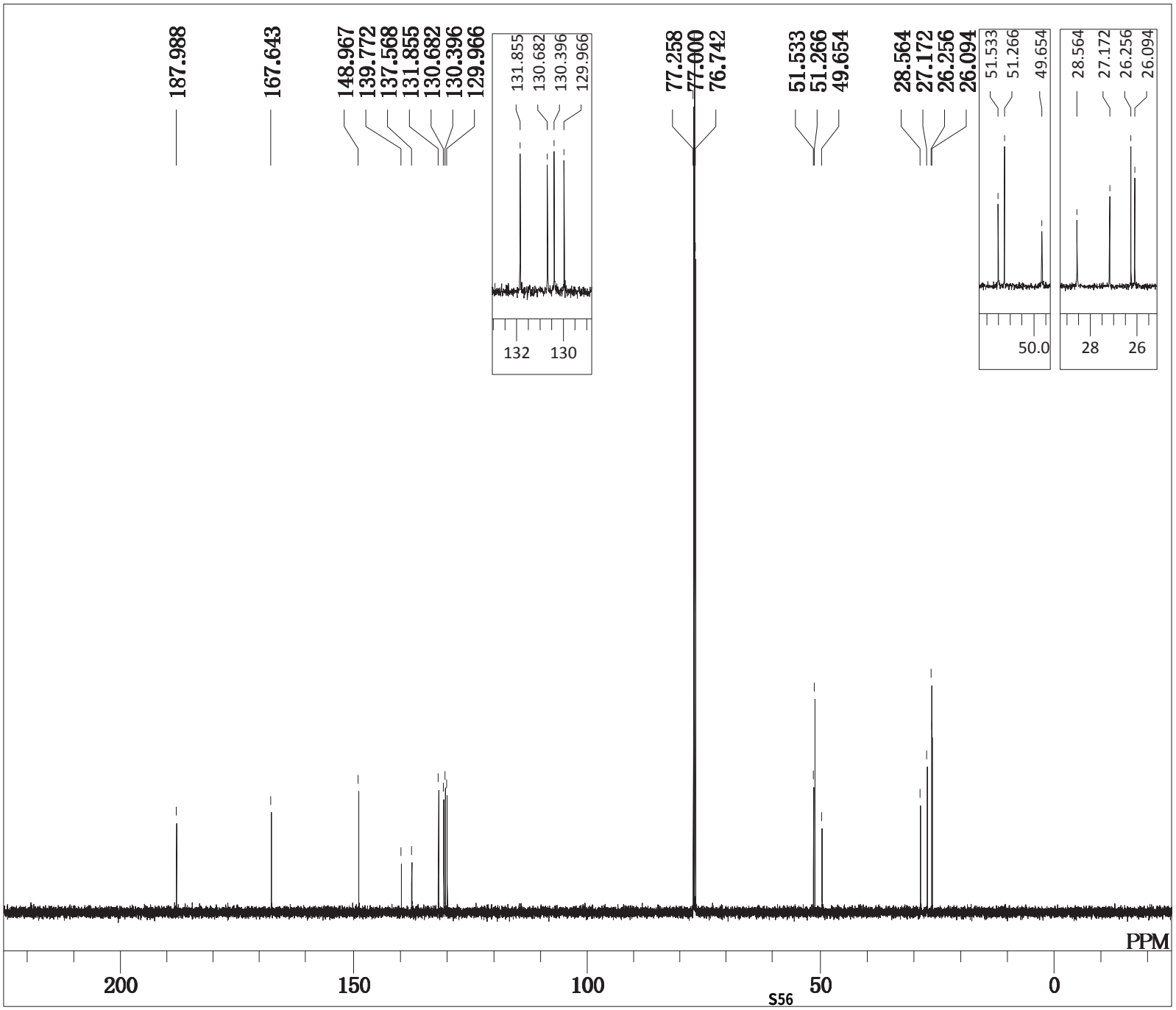

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_10_139_02_carbon-1_Ana-1.jdf
```

```
Filename           = TY_10_139_02_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_10_139_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 14-JUN-2018 23:15:38
Revision_Time      = 22-AUG-2018 20:46:54

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = TRUE
Scans              = 10000
Total_Scans        = 10000

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 13.9[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```

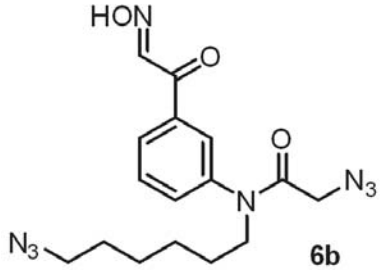



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_037_02-1_Ana-1.jdf
```

```
Filename           = TY_11_037_02-1_Ana-2.jdf
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_11_037
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 24-JUL-2018 20:31:17
Revision_Time      = 22-AUG-2018 20:39:43

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 44
Temp_Get           = 18.7[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



DFILE	TU-02-092-5 180308_carbon-1-
COMNT	single pulse decoupled gated NO
DATIM	2018-03-08 12:12:47
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32767
FREQU	39308.18 Hz
SCANS	366
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	15.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60



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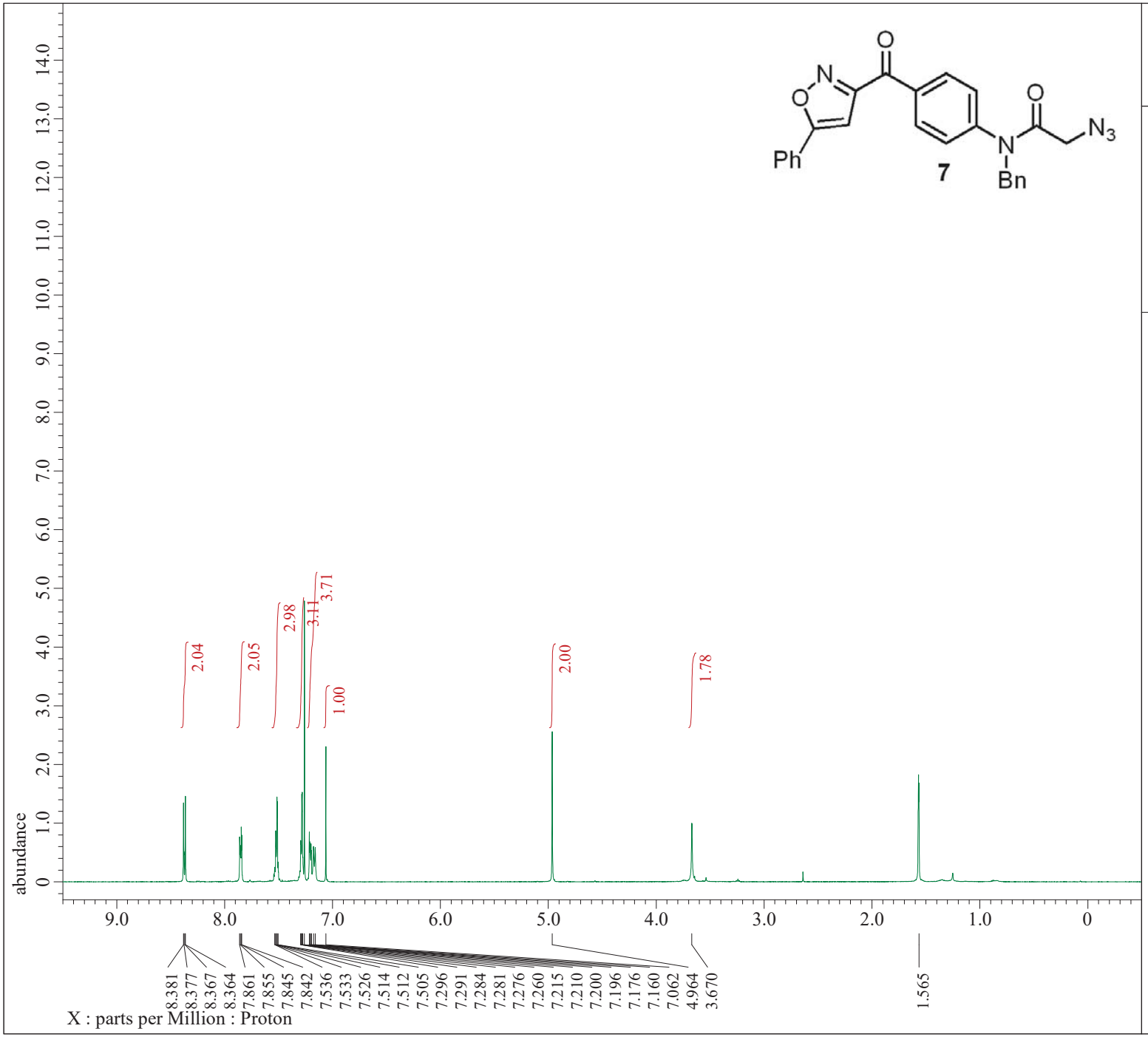
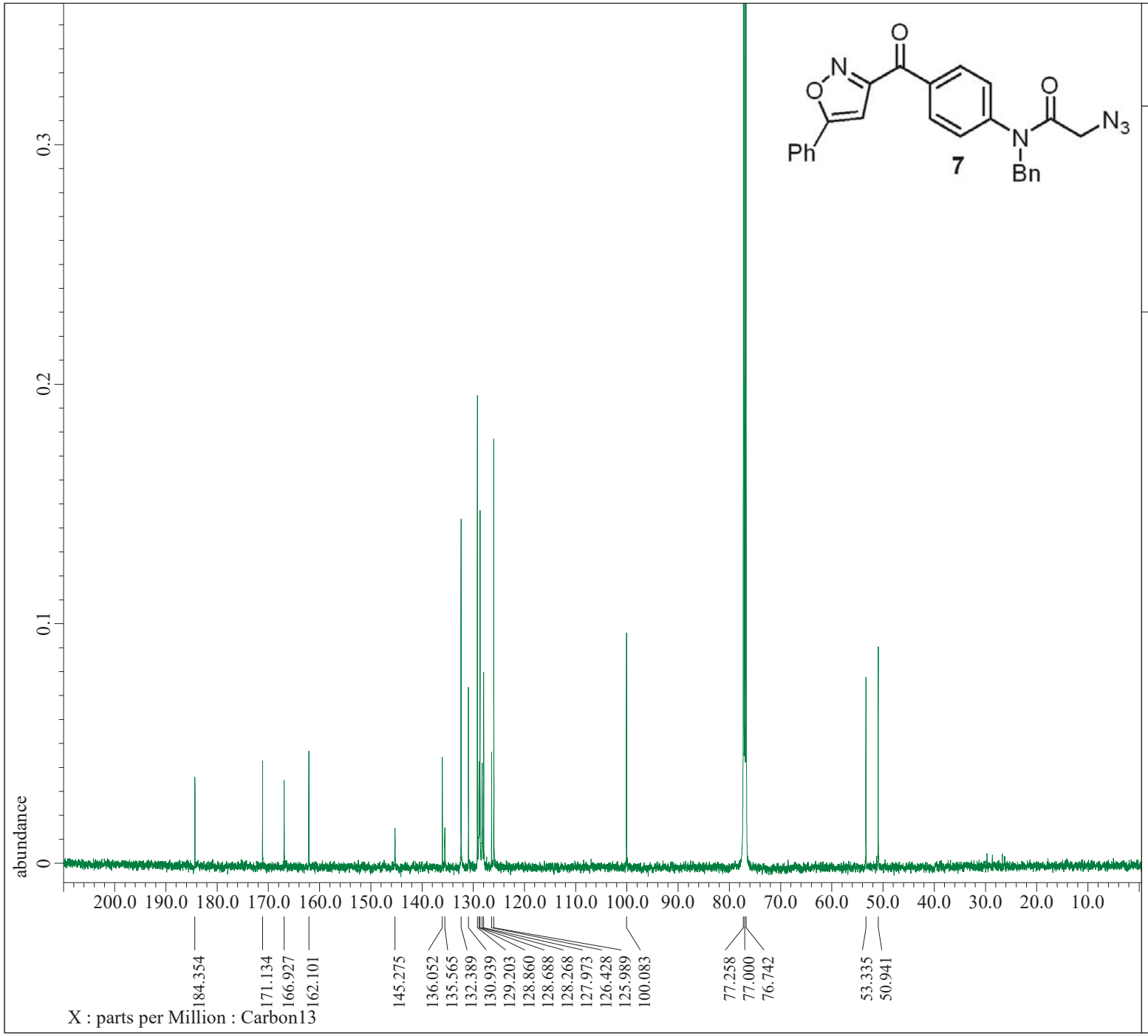



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_036_03-1_Ana-1.jdf
```

```
Filename           = TY_11_036_03-1_Ana-2.jdf
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_11_036
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 26-JUL-2018 10:08:41
Revision_Time      = 22-AUG-2018 20:52:33

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 46
Temp_Get           = 19[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



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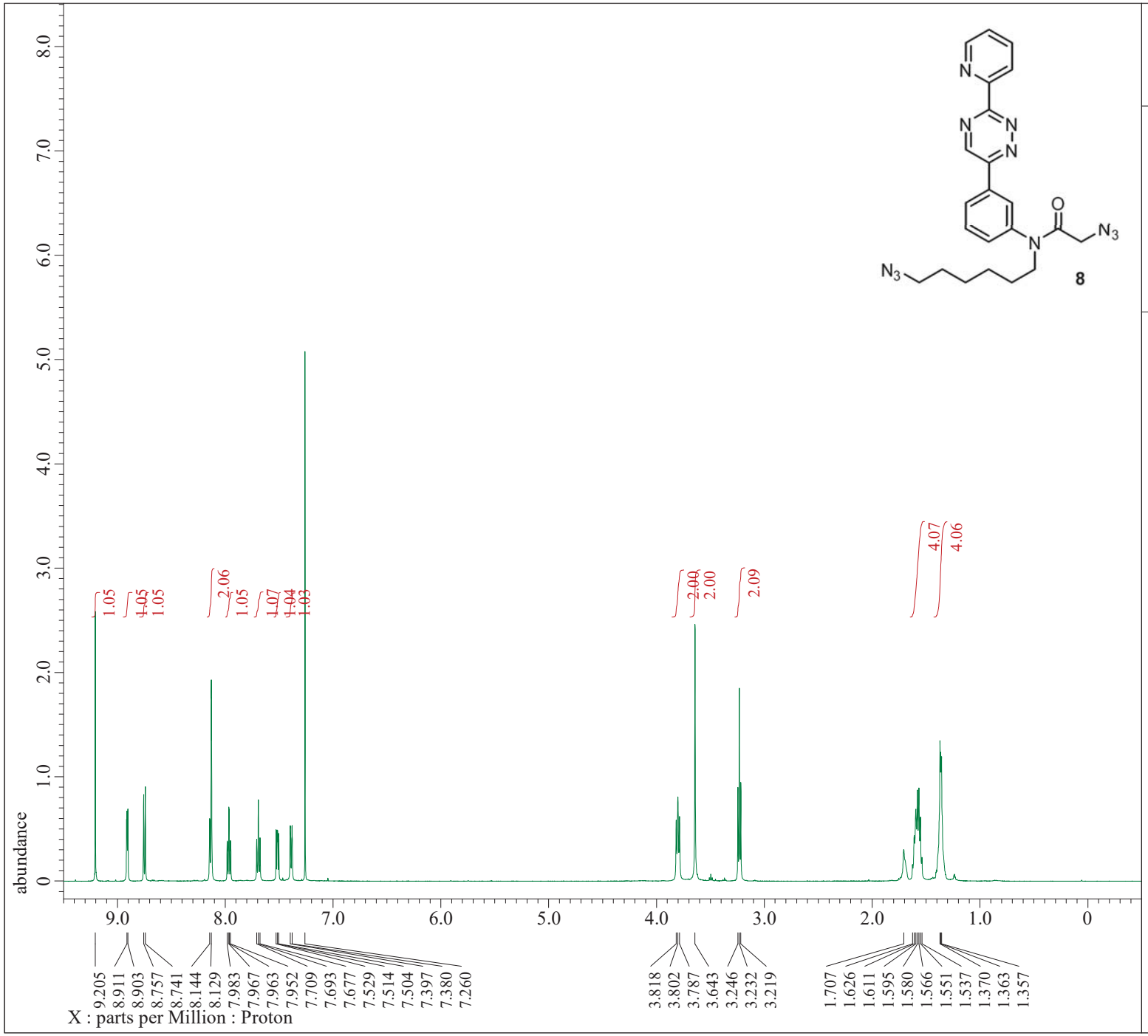
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_036_03_carbon-1_Ana-1.jdf
```

Filename	= TY_11_036_03_carbon-1_Ana
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= TY_11_036_03
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 27-JUL-2018 22:54:19
Revision_Time	= 22-AUG-2018 20:53:40
Comment	= single pulse decoupled ga
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 0.83361792[s]
X_Domain	= 13C
X_Freq	= 125.76529768[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.19959034[Hz]
X_Sweep	= 39.3081761[kHz]
X_Sweep_Clipped	= 31.44654088[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Clipped	= TRUE
Scans	= 9800
Total_Scans	= 9800
Relaxation_Delay	= 2[s]
Recvr_Gain	= 58
Temp_Get	= 18.1[dC]
X_90_Width	= 9.36[us]
X_Acq_Time	= 0.83361792[s]
X_Angle	= 30[deg]
X_Atn	= 3[dB]
X_Pulse	= 3.12[us]
Irr_Atn_Dec	= 20.54[dB]
Irr_Atn_Noe	= 20.54[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 92[us]
Decoupling	= TRUE



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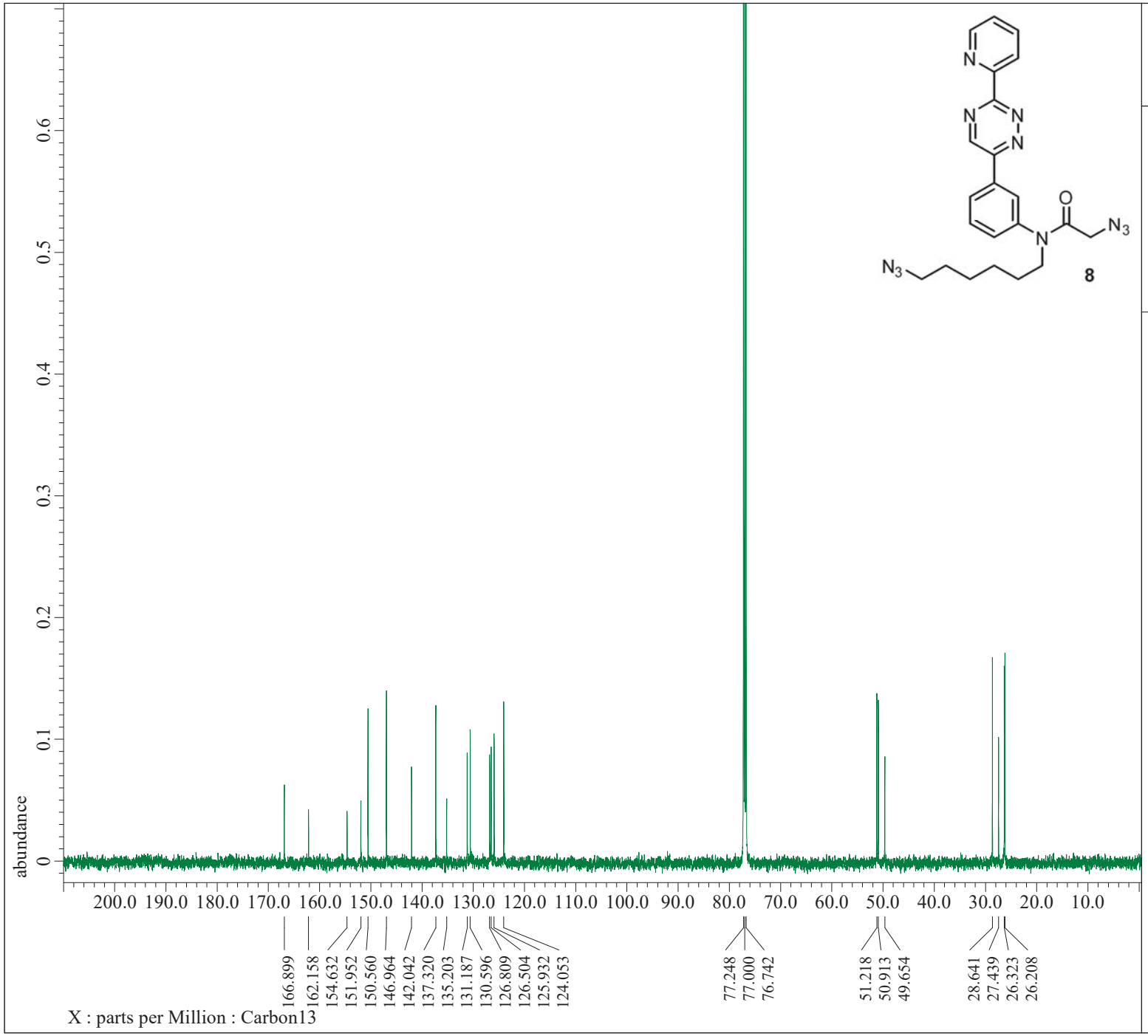
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_042_01_proton-1_Ana-1.jdf
```

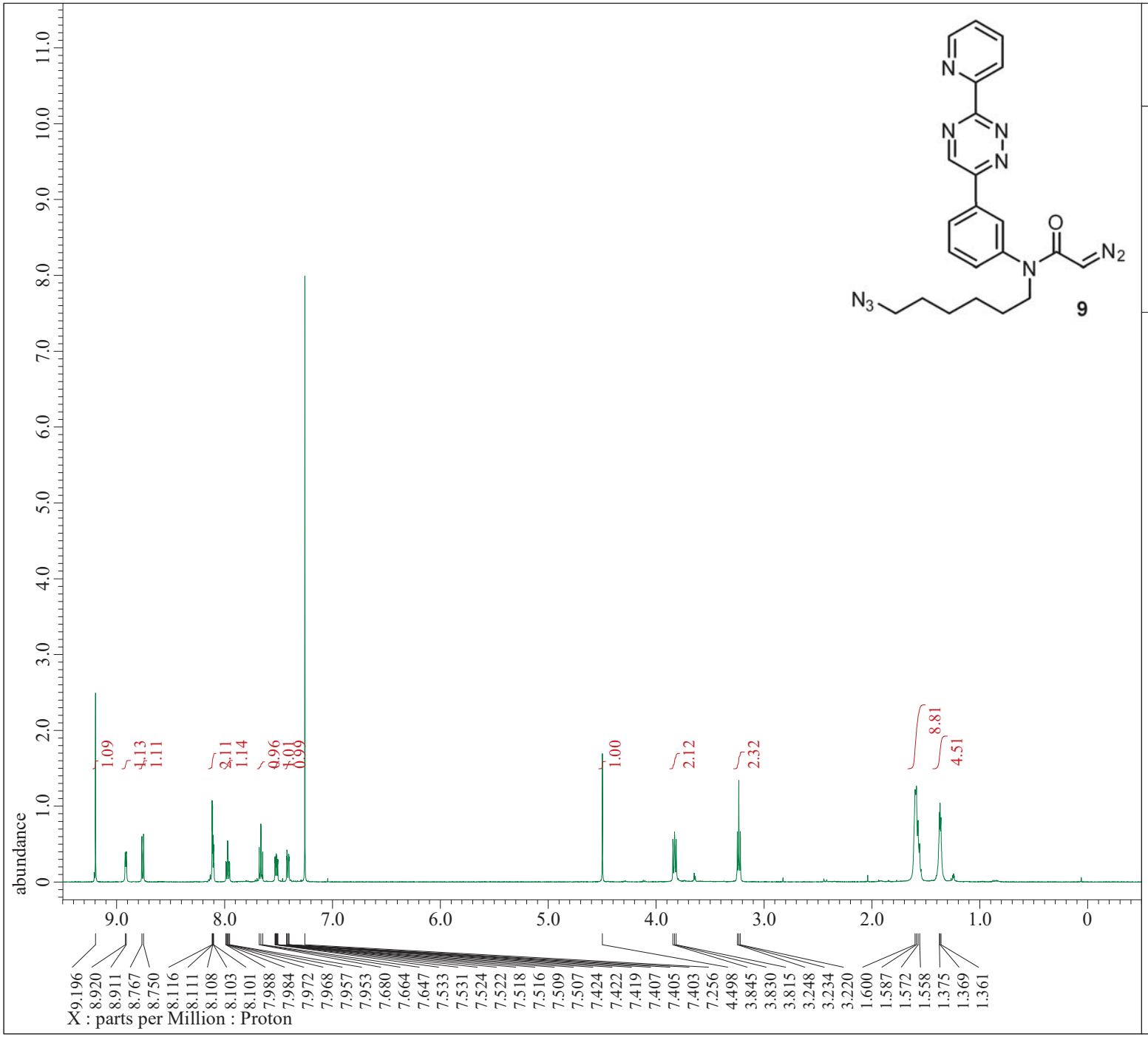
Filename	= TY_11_042_01_proton-1_Ana
Author	= delta
Experiment	= proton.jxp
Sample_Id	= TY_11_042_01
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 27-JUL-2018 16:26:19
Revision_Time	= 22-AUG-2018 20:41:23
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 1.74587904[s]
X_Domain	= 1H
X_Freq	= 500.15991521[MHz]
X_Offset	= 5.0[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.57277737[Hz]
X_Sweep	= 9.38438438[kHz]
X_Sweep_Clipped	= 7.50750751[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Tri_Domain	= Proton
Tri_Freq	= 500.15991521[MHz]
Tri_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 38
Temp_Get	= 18.9[dC]
X_90_Width	= 13.7[us]
X_Acq_Time	= 1.74587904[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 6.85[us]
Irr_Mode	= Off
Tri_Mode	= Off



8

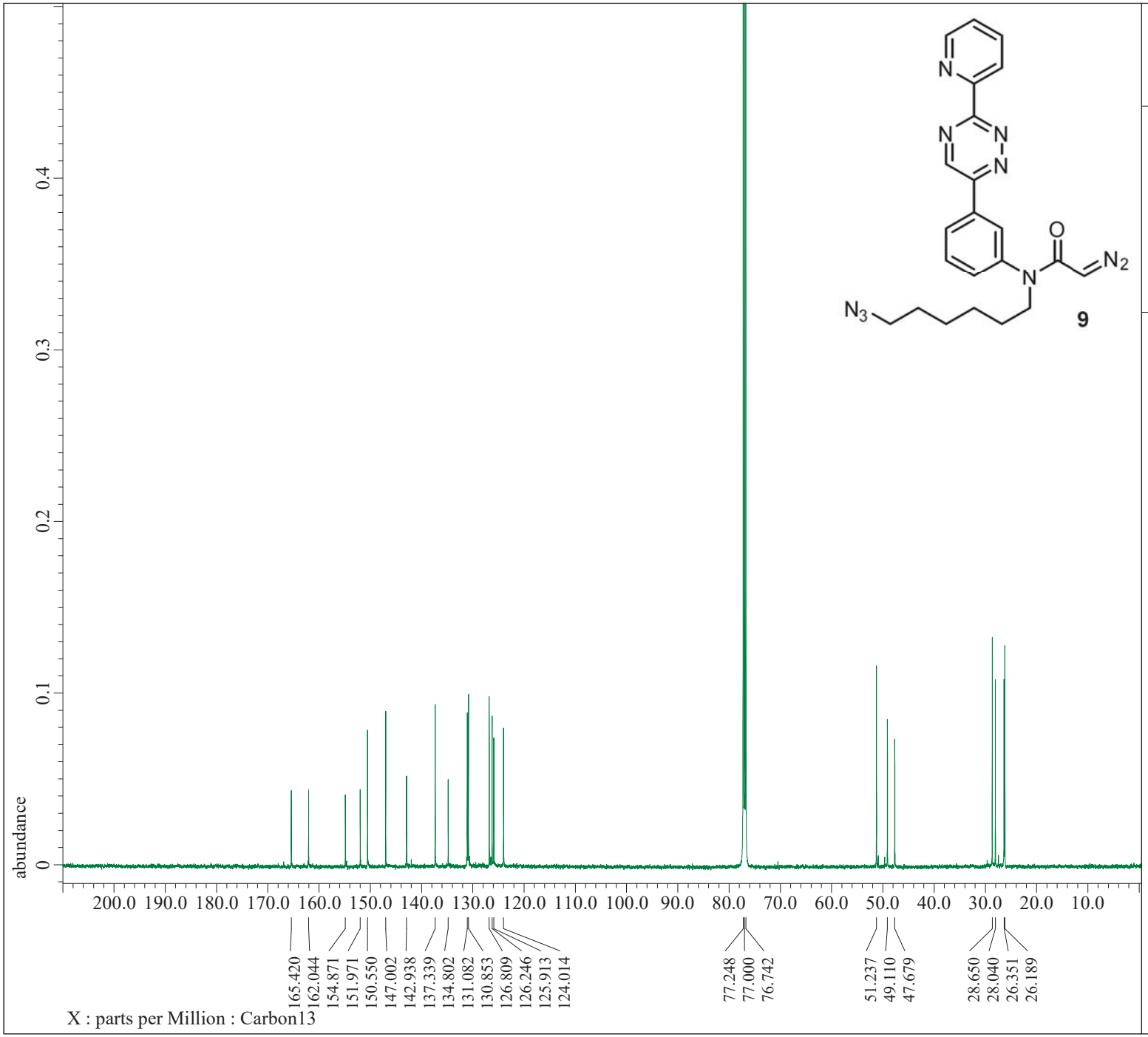
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_042_01_carbon-1_Ana-1.jdf
```

Filename	= TY_11_042_01_carbon-1_Ana
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= TY_11_042_01
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 27-JUL-2018 16:28:03
Revision_Time	= 22-AUG-2018 20:43:15
Comment	= single pulse decoupled ga
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 0.83361792[s]
X_Domain	= 13C
X_Freq	= 125.76529768[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.19959034[Hz]
X_Sweep	= 39.3081761[kHz]
X_Sweep_Clipped	= 31.44654088[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 1260
Total_Scans	= 1260
Relaxation_Delay	= 2[s]
Recvr_Gain	= 58
Temp_Get	= 19.3[dC]
X_90_Width	= 9.36[us]
X_Acq_Time	= 0.83361792[s]
X_Angle	= 30[deg]
X_Atn	= 3[dB]
X_Pulse	= 3.12[us]
Irr_Atn_Dec	= 20.54[dB]
Irr_Atn_Noe	= 20.54[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 92[us]
Decoupling	= TRUE




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_050_03-1-1.jdf
```

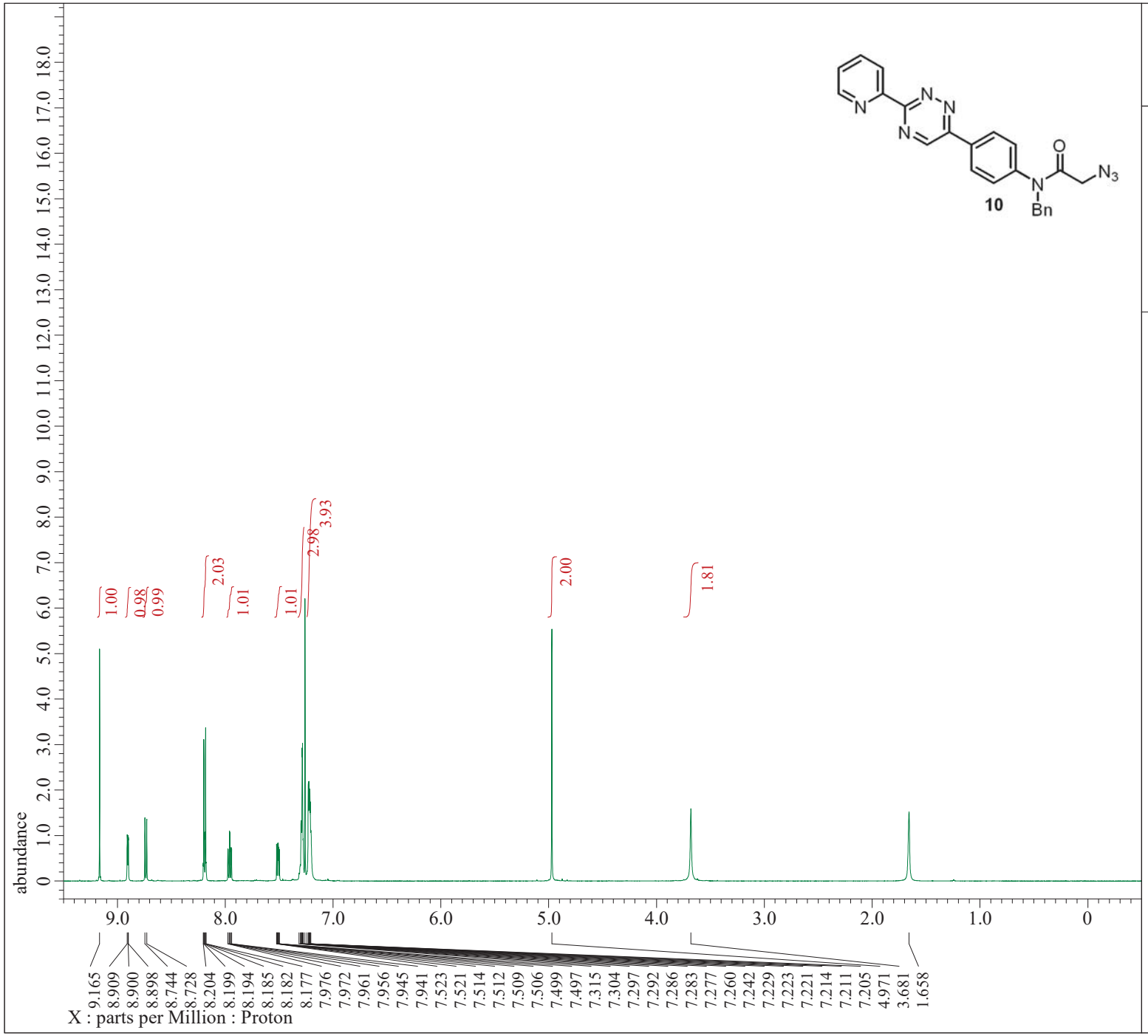
```
Filename            = TY_11_050_03-1-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TY_11_050
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  7-AUG-2018 10:46:32
Revision_Time       = 20-SEP-2018 20:10:57

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 17.9[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```



9

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_050_03_carbon-1-1.jdf
```

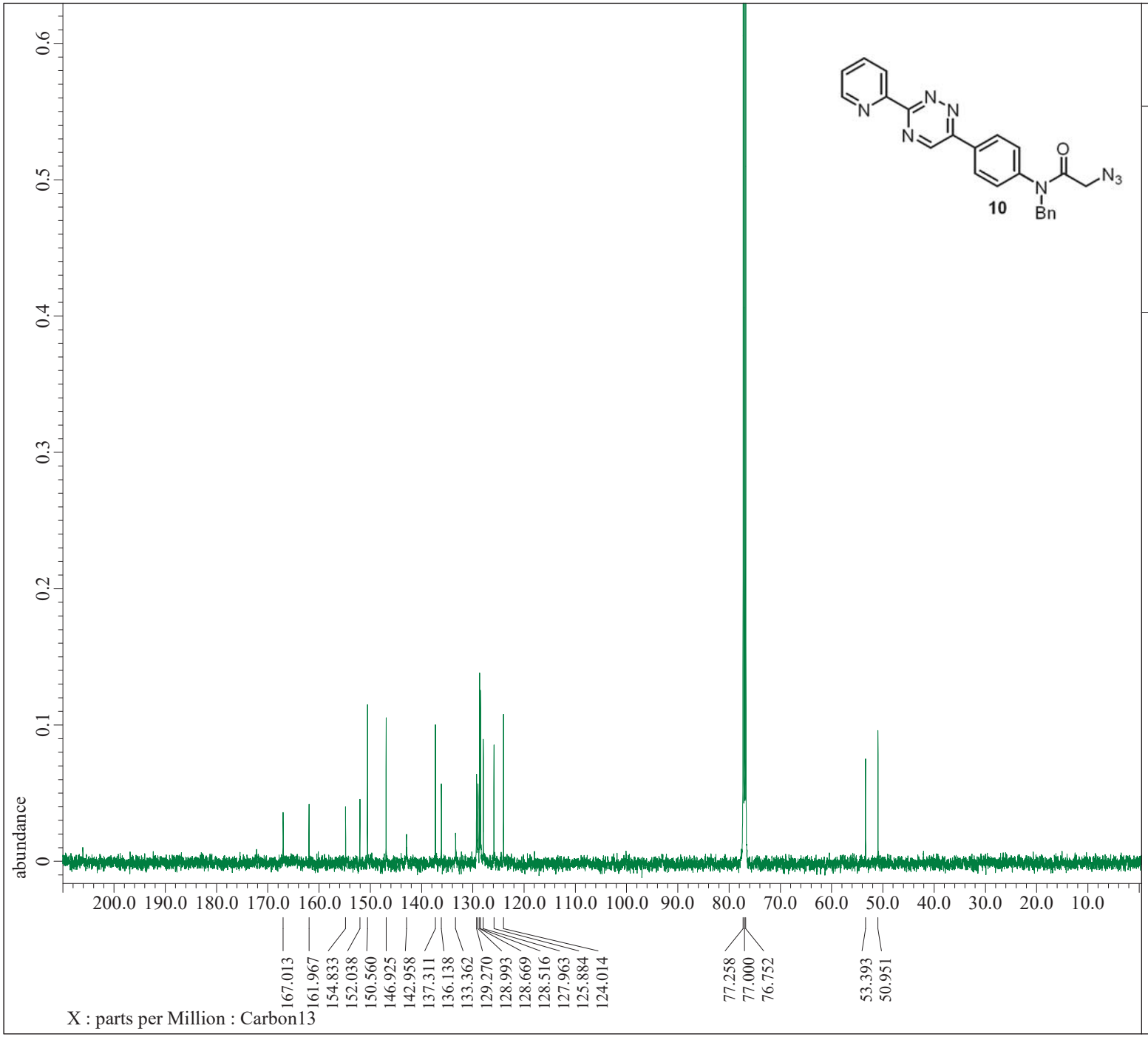
```
Filename           = TY_11_050_03_carbon-1-2.j
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_11_050_03
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 19-SEP-2018 22:23:42
Revision_Time      = 20-SEP-2018 20:00:31

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 11400
Total_Scans        = 11400

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 14.6[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



10

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_031_02_proton-1_Ana-1.jdf
```

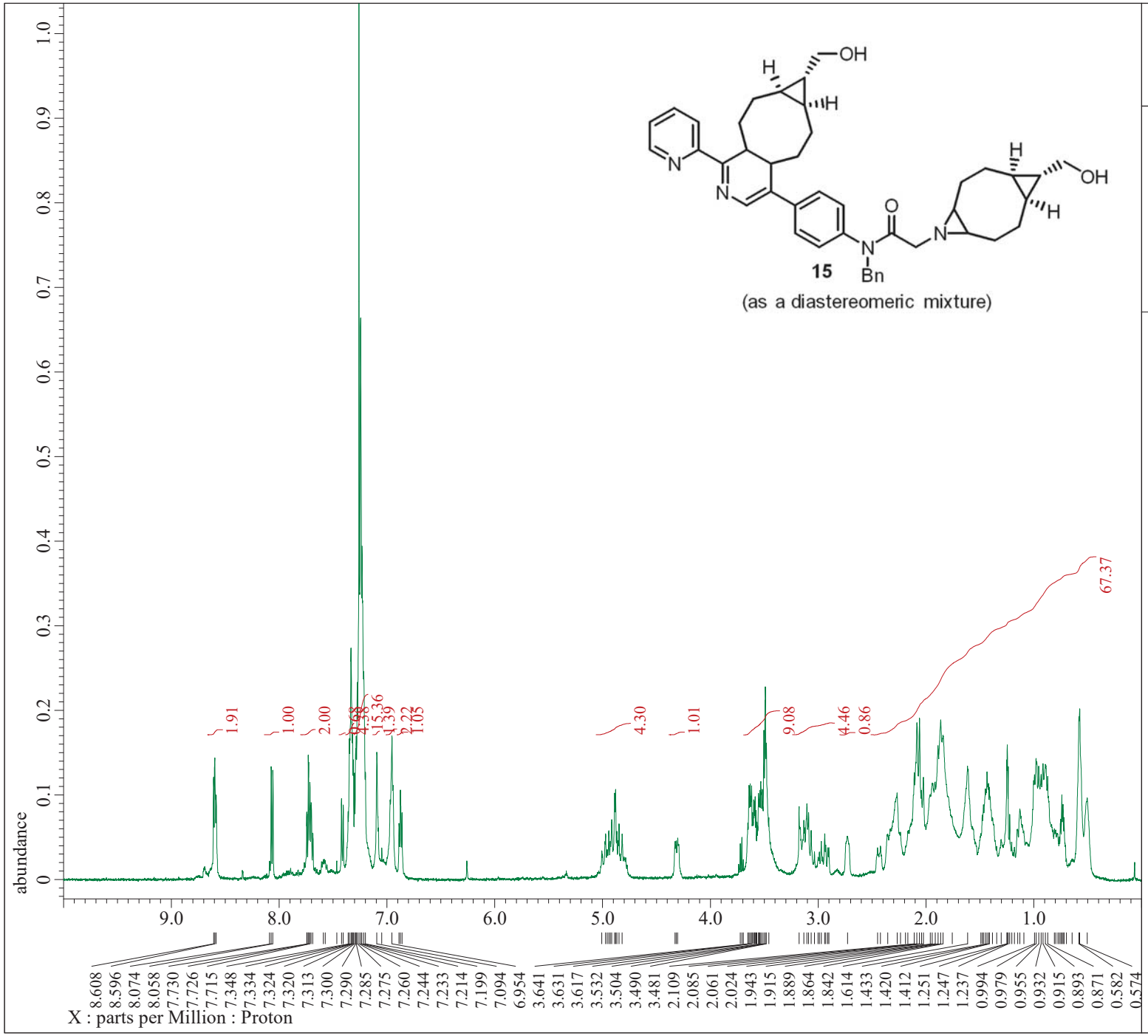
```
Filename           = TY_11_031_02_proton-1_Ana
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TY_11_031_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 21-JUL-2018 13:55:17
Revision_Time      = 22-AUG-2018 20:55:56

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 1.74587904[s]
X_Domain           = 1H
X_Freq             = 500.15991521[MHz]
X_Offset           = 5.0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.57277737[Hz]
X_Sweep            = 9.38438438[kHz]
X_Sweep_Clipped    = 7.50750751[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Tri_Domain         = Proton
Tri_Freq           = 500.15991521[MHz]
Tri_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 44
Temp_Get           = 19.8[dC]
X_90_Width         = 13.7[us]
X_Acq_Time         = 1.74587904[s]
X_Angle            = 45[deg]
X_Atn              = 4[dB]
X_Pulse            = 6.85[us]
Irr_Mode           = Off
Tri_Mode           = Off
```



JEOL

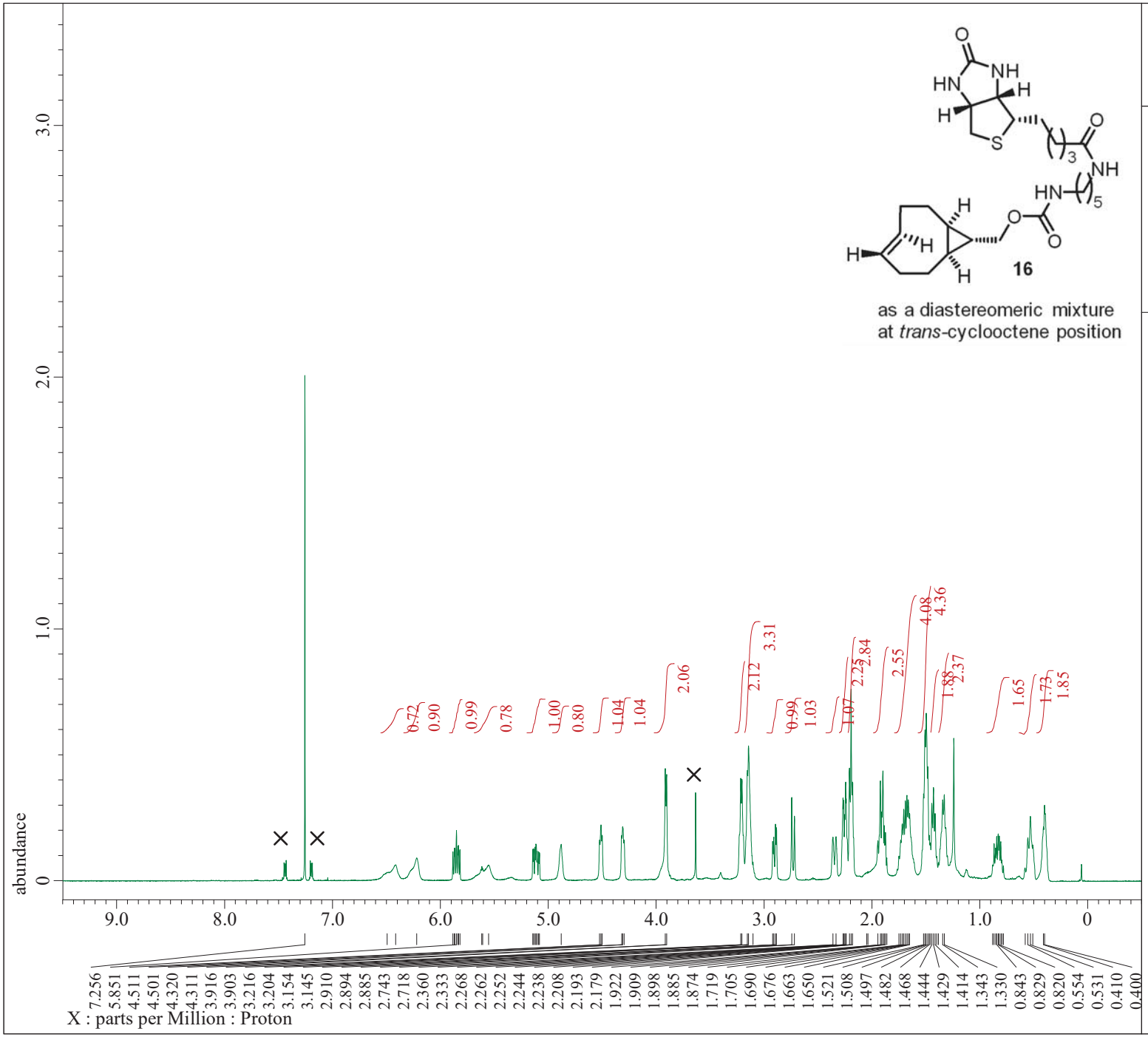
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_031_02_carbon-1_Ana-1.jdf
```

```
Filename           = TY_11_031_02_carbon-1_Ana
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TY_11_031_02
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 21-JUL-2018 13:57:06
Revision_Time      = 22-AUG-2018 20:57:10

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.7473579[T] (500[MHz])
X_Acq_Duration     = 0.83361792[s]
X_Domain           = 13C
X_Freq             = 125.76529768[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.19959034[Hz]
X_Sweep            = 39.3081761[kHz]
X_Sweep_Clipped    = 31.44654088[kHz]
Irr_Domain         = Proton
Irr_Freq           = 500.15991521[MHz]
Irr_Offset         = 5.0[ppm]
Clipped            = FALSE
Scans              = 1260
Total_Scans        = 1260

Relaxation_Delay   = 2[s]
Recvr_Gain         = 58
Temp_Get           = 20.4[dC]
X_90_Width         = 9.36[us]
X_Acq_Time         = 0.83361792[s]
X_Angle            = 30[deg]
X_Atn              = 3[dB]
X_Pulse            = 3.12[us]
Irr_Atn_Dec        = 20.54[dB]
Irr_Atn_Noe        = 20.54[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



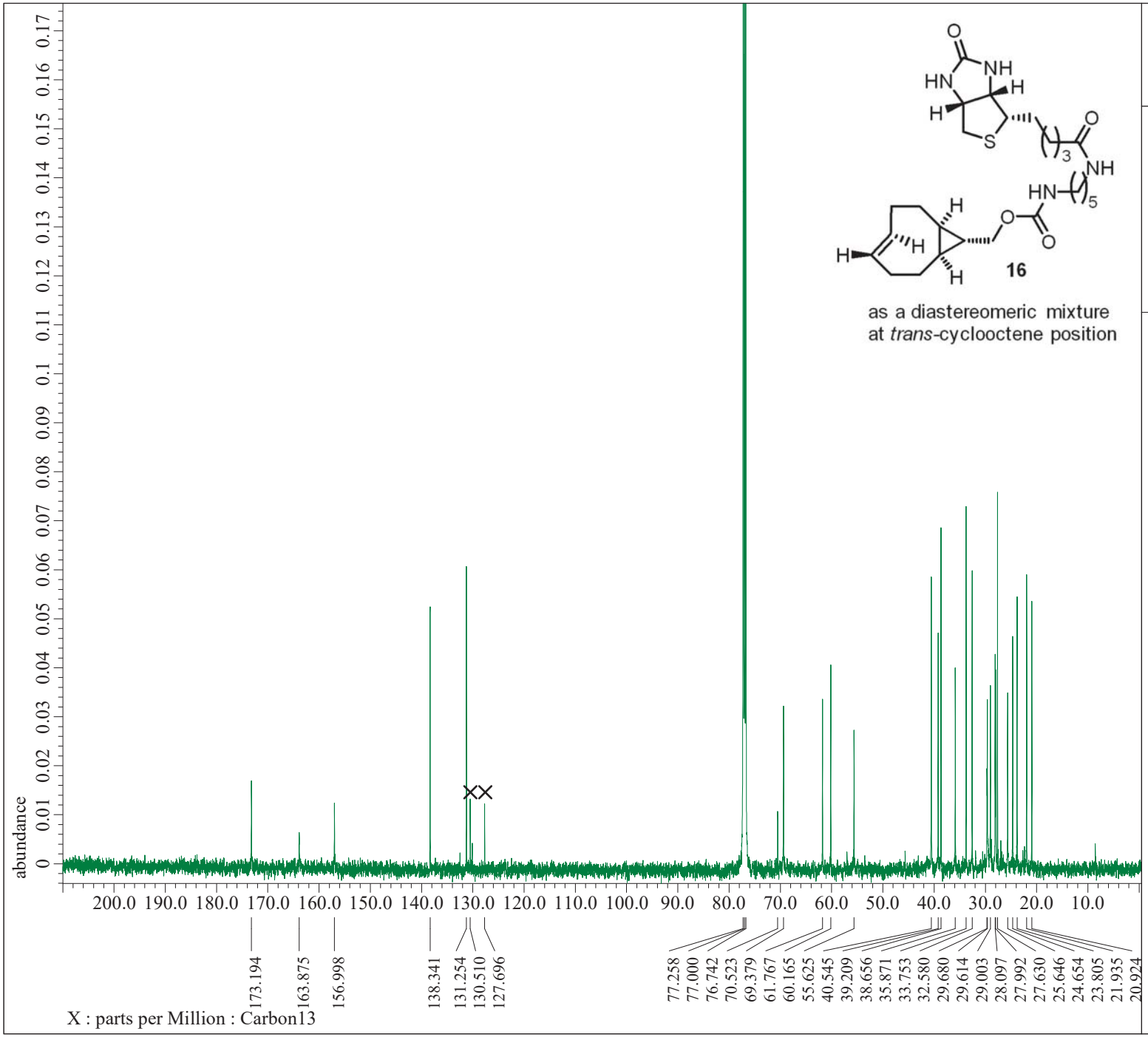

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_053_03-1_Ana-1.jdf
```

```
Filename            = TY_11_053_03-1_Ana-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TY_11_053
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  7-AUG-2018 19:05:39
Revision_Time       =  1-NOV-2018 11:10:26

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 18.4[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_088_02_proton-1_Ana-2.jdf
```

Filename	= TY_11_088_02_proton-1_Ana
Author	= delta
Experiment	= proton.jxp
Sample_Id	= TY_11_088_02
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 25-OCT-2018 22:13:37
Revision_Time	= 6-NOV-2018 16:12:49
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 1.74587904[s]
X_Domain	= 1H
X_Freq	= 500.15991521[MHz]
X_Offset	= 5.0[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.57277737[Hz]
X_Sweep	= 9.38438438[kHz]
X_Sweep_Clipped	= 7.50750751[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Tri_Domain	= Proton
Tri_Freq	= 500.15991521[MHz]
Tri_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 40
Temp_Get	= 17.7[dC]
X_90_Width	= 13.7[us]
X_Acq_Time	= 1.74587904[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 6.85[us]
Irr_Mode	= Off
Tri_Mode	= Off

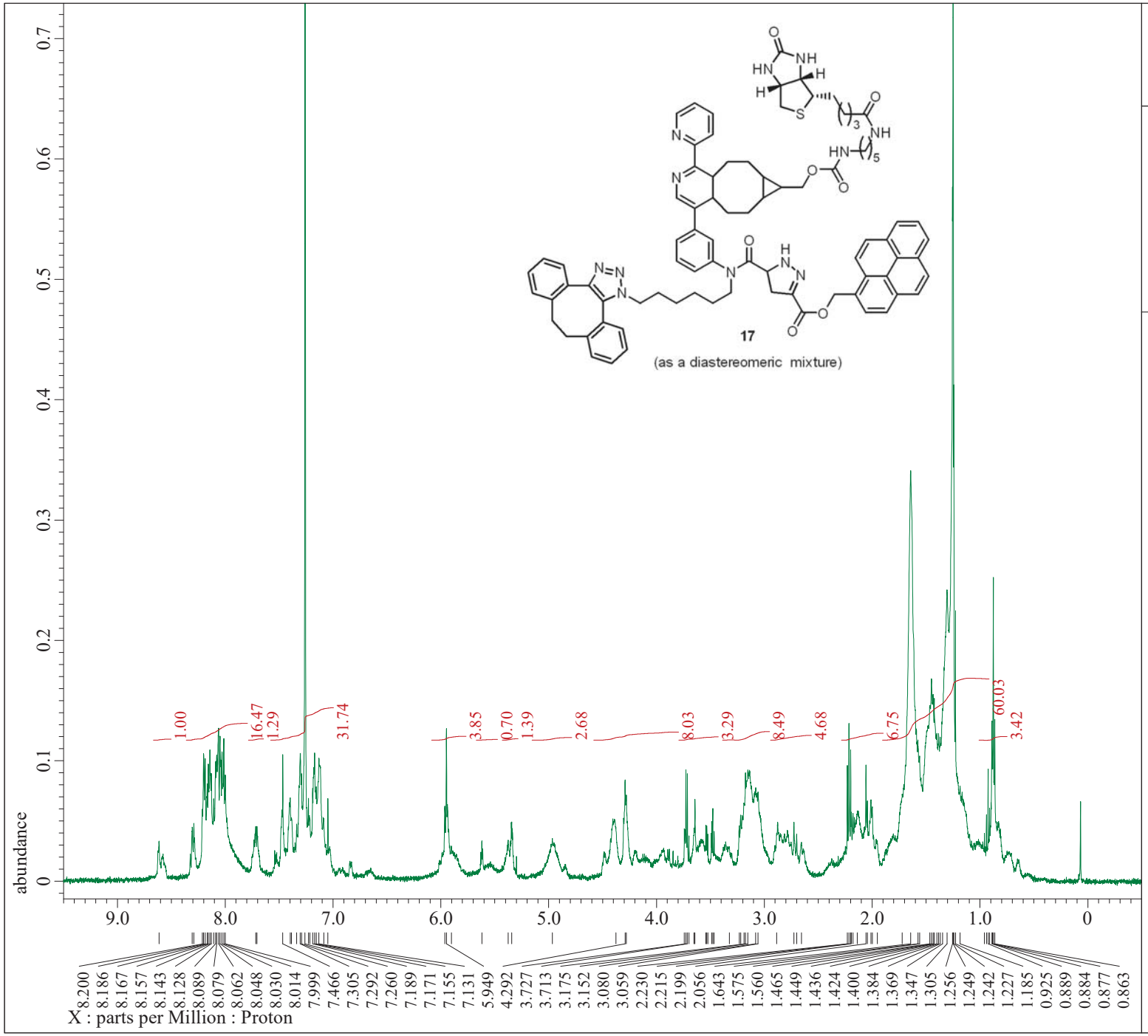


16

as a diastereomeric mixture
at *trans*-cyclooctene position

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_088_02_carbon-1_Ana-2.jdf
```

Filename	= TY_11_088_02_carbon-1_Ana
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= TY_11_088_02
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 25-OCT-2018 22:15:06
Revision_Time	= 6-NOV-2018 14:54:50
Comment	= single pulse decoupled ga
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 0.83361792[s]
X_Domain	= 13C
X_Freq	= 125.76529768[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.19959034[Hz]
X_Sweep	= 39.3081761[kHz]
X_Sweep_Clipped	= 31.44654088[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 10780
Total_Scans	= 10780
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 20.2[dC]
X_90_Width	= 9.36[us]
X_Acq_Time	= 0.83361792[s]
X_Angle	= 30[deg]
X_Atn	= 3[dB]
X_Pulse	= 3.12[us]
Irr_Atn_Dec	= 20.54[dB]
Irr_Atn_Noe	= 20.54[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 92[us]
Decoupling	= TRUE



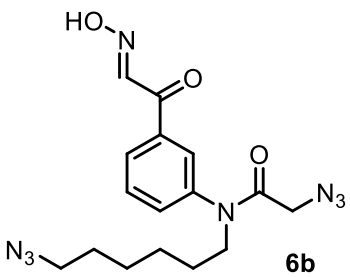
JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TY_11_089_02-1_Ana-1.jdf
```

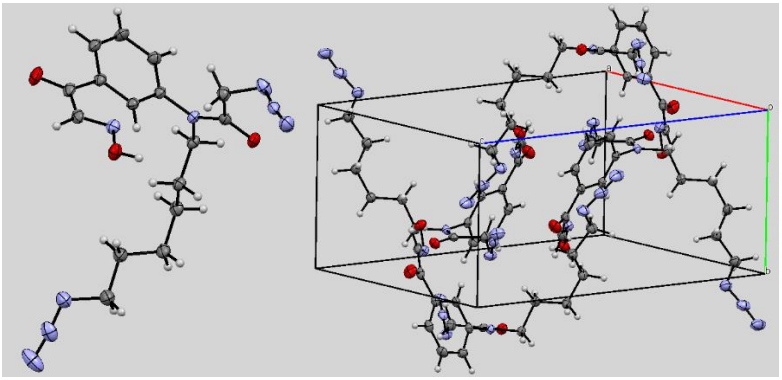
Filename	= TY_11_089_02-1_Ana-2.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= TY_11_089
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 6-NOV-2018 13:19:03
Revision_Time	= 7-NOV-2018 12:31:25
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 1.74587904[s]
X_Domain	= 1H
X_Freq	= 500.15991521[MHz]
X_Offset	= 5.0[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.57277737[Hz]
X_Sweep	= 9.38438438[kHz]
X_Sweep_Clipped	= 7.50750751[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Tri_Domain	= Proton
Tri_Freq	= 500.15991521[MHz]
Tri_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 44
Temp_Get	= 18.9[dC]
X_90_Width	= 13.7[us]
X_Acq_Time	= 1.74587904[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 6.85[us]
Irr_Mode	= Off
Tri_Mode	= Off

[8] X-ray Crystallographic Analysis Information
(ORTEP thermal ellipsoids at 50% probability)

(1) 6b (CCDC No. 1879115)



6b



Empirical formula	$C_{16}H_{20}N_8O_3$
Formula weight	372.39
Temperature	-150.0 °C
Wavelength	MoKα (λ = 0.71075 Å)
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 13.5247(4) Å
	b = 7.64772(17) Å β = 97.938(7) °
	c = 17.7480(5) Å
Volume	V = 1818.14(9) Å^3
Z	4
Density (calculated)	1.360 g/cm^3
$2\theta_{max}$	50.7 °
Absorption coefficient μ for Mo-Kα	0.992 cm^{-1}
F(000)	784.00
Crystal size	0.140 × 0.030 × 0.030 mm
No. of reflection collected	Total: 24512
	Unique: 3334 (R_{int} = 0.0332)
Transmission factor	min: 0.836, max: 0.997
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.046
Final R indices [I>2σ (I)]	R_1 = 0.0359
R indices (all data)	R_1 = 0.0454 wR_2 = 0.0822
Largest diff. peak and hole	-0.17 and 0.21 e•Å^{-3}