Novel ring chemistry of Vitamin B_6 with singlet oxygen and an activated ene: Isolated products and identified intermediates suggesting an operable [3+2] cycloaddition

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Supporting Information

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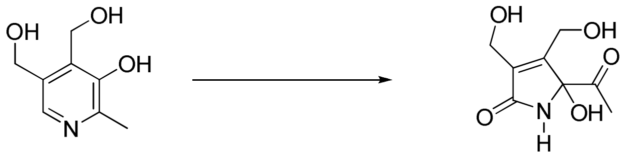
1. General Methods

Phosphate buffers were prepared through the mixing of 1M solutions of Na_2HPO_4 and NaH_2PO_4 (prepared from commercially obtained salts). The desired pH was determined by EMD® colorphast™ pH strips, range 5-10, and the buffer diluted to the appropriate concentration. Deuterium buffers were prepared as outlined in the experimental section. Water was purified by an Elix 5® system. Pyridoxine, pyridoxine hydrochloride, pyridoxal hydrochloride, and pyridoxamine dihydrochloride were obtained from commercial sources (Acros Organics® and Sigma-Aldrich®) and used as received. Pyridoxal and pyridoxamine free bases were prepared by treatment of the corresponding salts with 10% Na_2CO_3 followed by filtration and air drying. Oxygen was used directly without treatment from a compressed cylinder and introduced by bubbling through reaction mixtures via syringe. The light source used was a combination of three 23W green-filtered Phillips® Par38 compact fluorescent floodlights. TLC was performed on EMD 60 F254 silica gel plates on glass backing and visualized by UV light (254 nm). Flash chromatography was performed on Silicycle® SiliaFlash™ P60 230-400 mesh silica gel. Deuterium-labeled solvents were used as received from Cambridge Isotopes or Acros Organics®. Solvents for chromatography were used as received from Pharmco-Aaper®. NMR experimentation was performed on a JEOL ECS 400 NMR, in the deuterated solvents stated and processed using Delta™ NMR software. The field was locked by external referencing to the relevant deuteron resonance. ^{1}H NMR spectra were recorded at 400 MHz and data are reported as follows: chemical shift in parts per million, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant), integration. ^{13}C NMR spectra were recorded at 100 MHz and data were reported as follows: chemical shift in parts per million. 2D NMR (COSY, HMQC, HMBC) and variable temperature NMR studies were performed on the ECS 400MHz NMR using Delta™ software. LRMS was performed on a Finnigan LCQ Deca and standardized (caffeine/resperine) prior to use. Infrared spectroscopy was performed on a Nicolet Nexus 670 FT-IR as a thin film using SpectulATR™ with a ZnSe sample plate. Data was processed using OMNIC software and selected characteristic peaks are reported in cm^{-1}.

2. Experimental

Pyridoxine Oxidation. 3,4-Bis-hydroxymethyl-5-hydroxy-5-(1-oxoethyl)-1,6-dihydropyrrole-2-one (4)

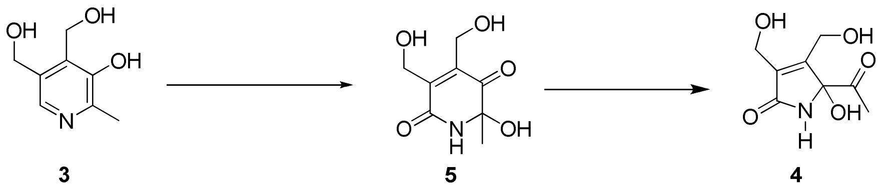


Pyridoxine hydrochloride (2.10 g, 10.2 mmol) and Rose Bengal (17 mg) were dissolved in phosphate buffer (280 mL, 0.25 M, pH 7.5). The resulting solution was sparged with oxygen and irradiated with light (see General Methods) for 4 hours at room temperature. The mixture of products was lyophilized and purified via column chromatography on silica gel (15% MeOH in CH_2Cl_2). The fractions containing the major product yielded a white solid (0.89 g, 43%). The product was recrystallized from ethanol. mp 161-163 ^{o}C; ^{1}H NMR (DMSO-D_6, 400 MHz) δ: 11.24 (br s, 1H), 8.16 (br s, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.09 (d, *J* = 7.4 Hz, 2H), 4.89 (dd, *J* = 14.2 Hz, 1H), 4.73 (d, *J* = 14.2 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (DMSO-D_6, 100 MHz) δ: 203.7, 172.9, 155.9, 133.4, 89.8, 54.7, 53.6, 24.2. IR (thin film, cm^{-1}) 3293 (br), 2938, 1693, 1356; LRMS (m/z) M^{+}+1 : 202.1. X ray data provided on page S24.

Preparation of Deuterated Phosphate Buffer

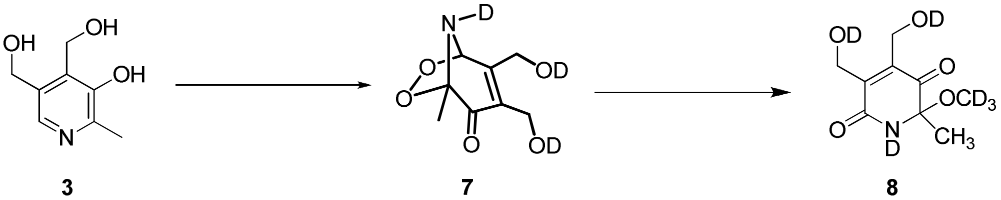
Disodium phosphate heptahydrate (27 mg) and monosodium phosphate monohydrate (3.3 mg) were dissolved in deuterated water (50 mL) to produce a 0.25M, 7.5 pH phosphate buffer. The buffer was lyophilized and redissolved in additional 30 mL D_2O. After a second lyophilization, 50 mL of deuterated water was added. pH was checked following this process and recorded.

Time-course Pyridoxine Oxidation. 3,4-Bis-hydroxymethyl-6-hydroxy-6-methyl-1,6-dihydropyridine-2,5-dione (5)



Pyridoxine hydrochloride (75 mg, 0.36 mmol) and Rose Bengal (2 mg) were dissolved in deuterated phosphate buffer (10 mL, 0.25M, 7.5 pH). The resulting solution was sparged with oxygen and irradiated (See Methods) for 4 hours. Reaction progress was tracked hourly via ^{1}H NMR producing both product **4** and the unstable intermediate **5**. The reaction proceeded to 100% total conversion providing **5** and **4** after 3 hr. **5** was characterized by additional NMR spectroscopy (^{13}C NMR via HMQC and HMBC). ^{1}H NMR (D_2O, 400 MHz) δ: 4.58 (s, 2H, CH_2), 4.55 (s, 2H, CH_2), 1.58 (s, 3H, CH_3). ^{13}C NMR (methanol-d_4, 100 MHz by HMBC) δ: 196.2, 163.9, 144.9, 140.6, 81.9, 55.9, 54.7, 25.2; LRMS (m/z)- M^++1: 202.1.

Low-temperature Studies of Pyridoxine oxidation intermediate. 3,4-Bis-hydroxymethyl-1 -methyl-6,7-dioxa—8-aza-bicyclo[3.2.1]oct-3-ene-2-one (7)

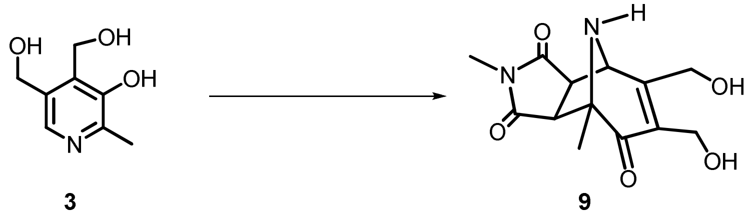


Pyridoxine (20 mg, 0.097 mmol) and Rose Bengal (1 mg) were dissolved in methanol-d_4 (1 mL) in an NMR tube. The tube was placed under a balloon of oxygen and cooled in a -78 ºC bath. After 4 hours of light irradiation (see General Methods), the reaction was characterized using low temperature (-78 ºC) ^{1}H NMR, ^{13}C NMR, HMQC, and HMBC. A 60% conversion of **1** was observed after 4 hours of reaction. Reaction run in CH_3OH produced identical ^{1}H NMR and ^{13}C NMR spectra (see page S20 and S21).

For **7**. ^{1}H NMR (methanol-d_4, 400 MHz) δ: 5.96 (s, 1H), 4.75 (d obscured by starting material, 1H), 4.40 (d, J = 15.1 Hz, 1H), 4.31(d, J = 11.9 Hz, 1H), 4.22 (d, J = 11.9 Hz, 1H) 1.59 (s, 3H, CH_3). ^{13}C NMR (methanol-d_4, 100 MHz) δ: 190.4, 157.2, 131.2, 98.4, 89.2, 57.7, 51.9, 14.3.

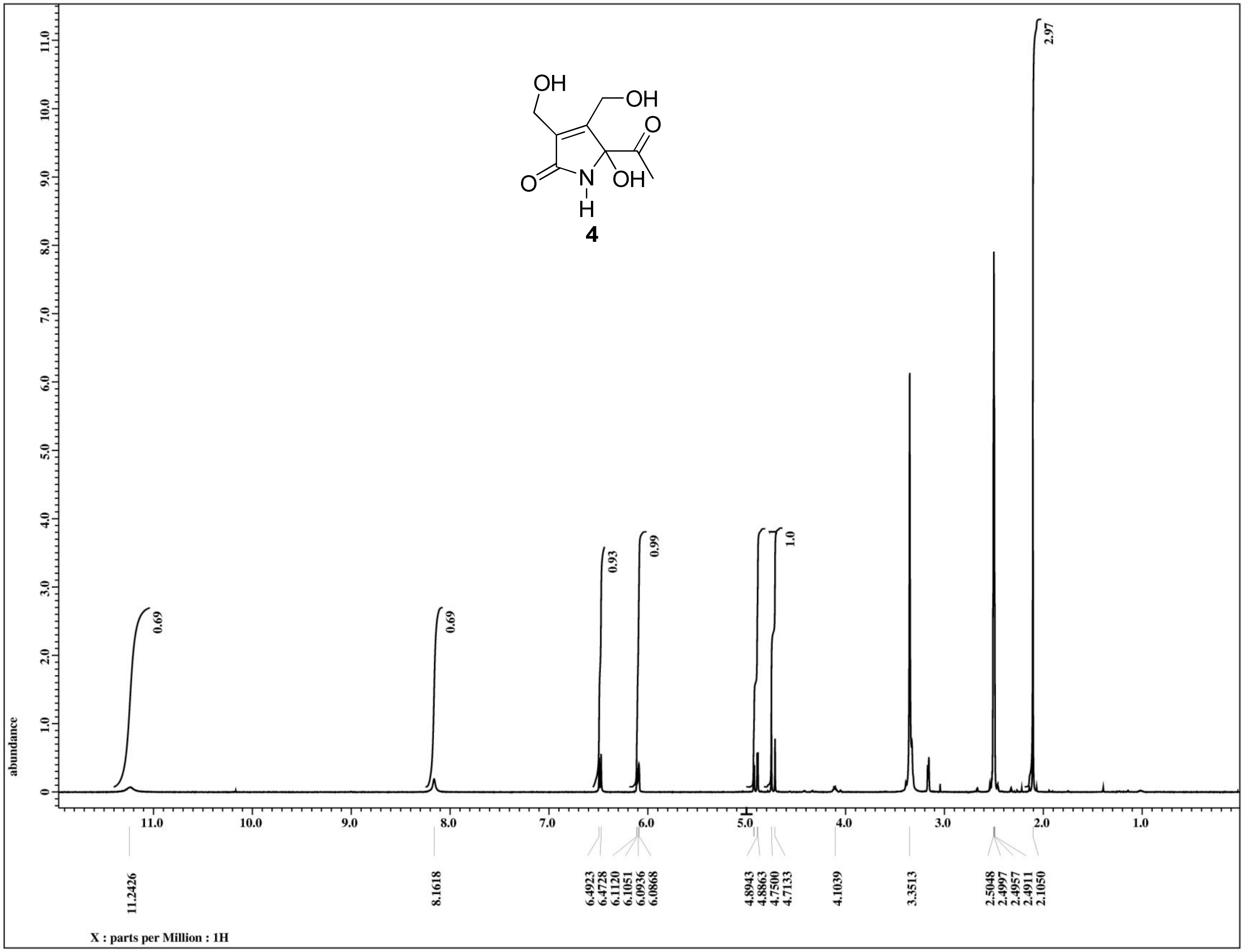
For **8**. After warming to room temperature, ^{1}H NMR (methanol-D$_4$, 400 MHz) δ: 4.63 (s, 1H, CH$_2$), 4.54 (s, 2H, CH$_2$), 1.50 (s, 3H, CH$_3$). ^{13}C NMR (methanol-d$_4$, 100 MHz) δ: 195.3, 164.8, 146.4, 143.0, 87.1, 57.1, 55.3, 24.7. NMR matches previously published data of non-deuterium labeled product.

Pyridoxine Cycloaddition with *N*-methylmaleimide. 3,4-Bis-hydroxymethyl-1-methyl-6,7-(1-methylpyrrolidine-2,5-dione)-8-aza-bicyclo[3.2.1]oct-3-ene-2-one



3 **9**

Pyridoxine hydrochloride (105 mg, 0.51 mmol) was added to 0.25 M phosphate buffer (4 mL). *N*-methylmaleimide (170 mg, 1.53 mmol) was then added to the solution and the reaction mixture was stirred for 36 hr. The solvent was removed under high vacuum and the residual solid was redissolved in minimal methanol and subjected to column chromatography on silica gel (10% CH$_3$OH/CH$_2$Cl$_2$). The white solid product was isolated in 63% yield (90 mg). mp 139-142 °C (decomp); ^{1}H NMR (CD$_3$OD, 400 MHz) δ: 4.57(d, 1H, J = 15.1 Hz), 4.50 (d, J = 15.1 Hz, 1H), 4.49 (s, 1H), 4.31 (d, J = 11.9 Hz, 1H), 4.22 (d, J = 11.9 Hz, 1H), 3.46 (d, J = 7.3 Hz, 1H), 3.35 (s, 1H), 2.96 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (CD$_3$OD, 100 MHz) δ:198.2, 178.6, 176.6, 165.5, 131.1, 70.8, 60.0, 59.0, 54.5, 53.8, 50.0, 25.4, 17.5. IR (thin film, cm^{-1}) 3284 (br), 2953, 1776, 1693; LRMS (m/z) : M$^+$+1: 281.1, Xray data provided on page S34.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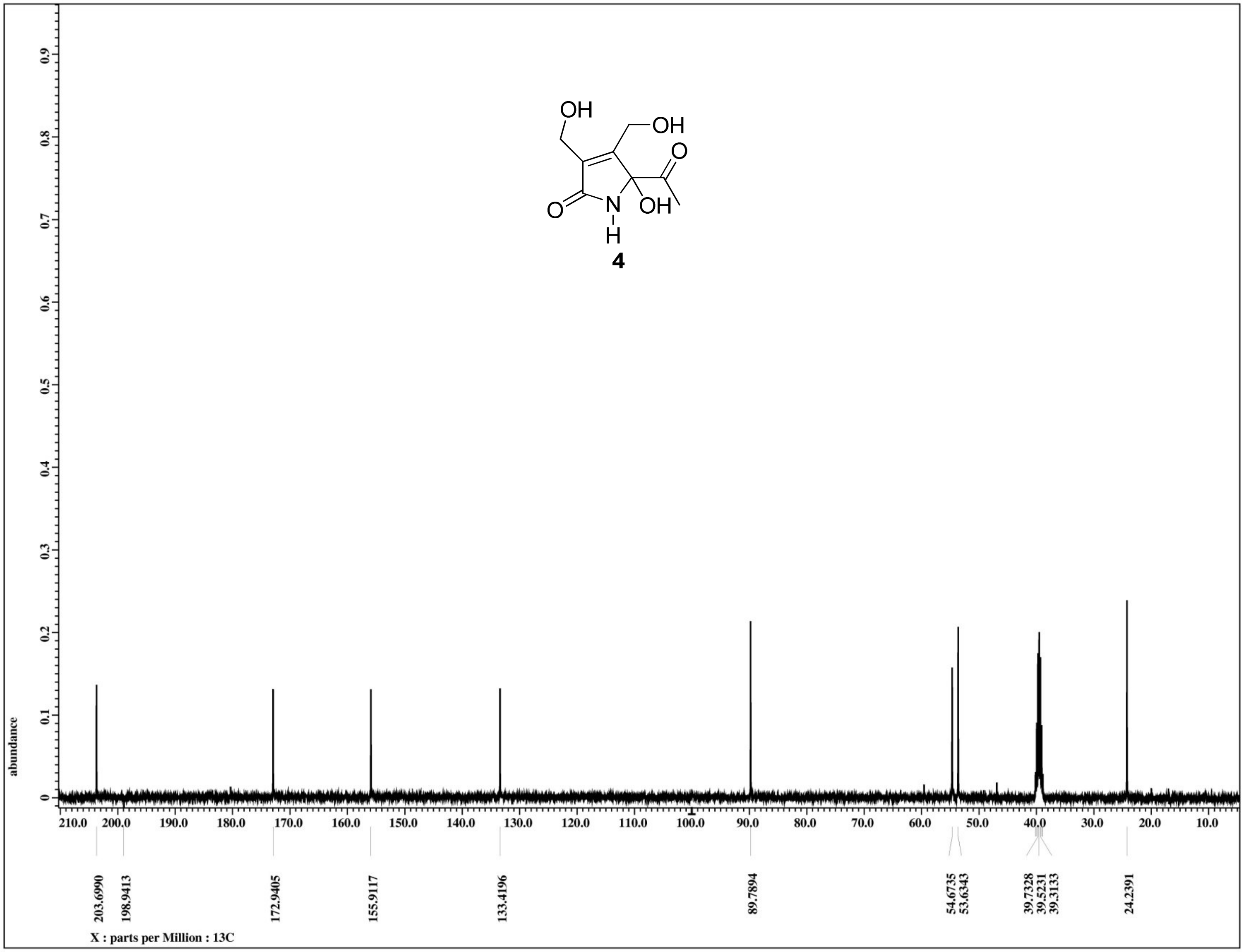
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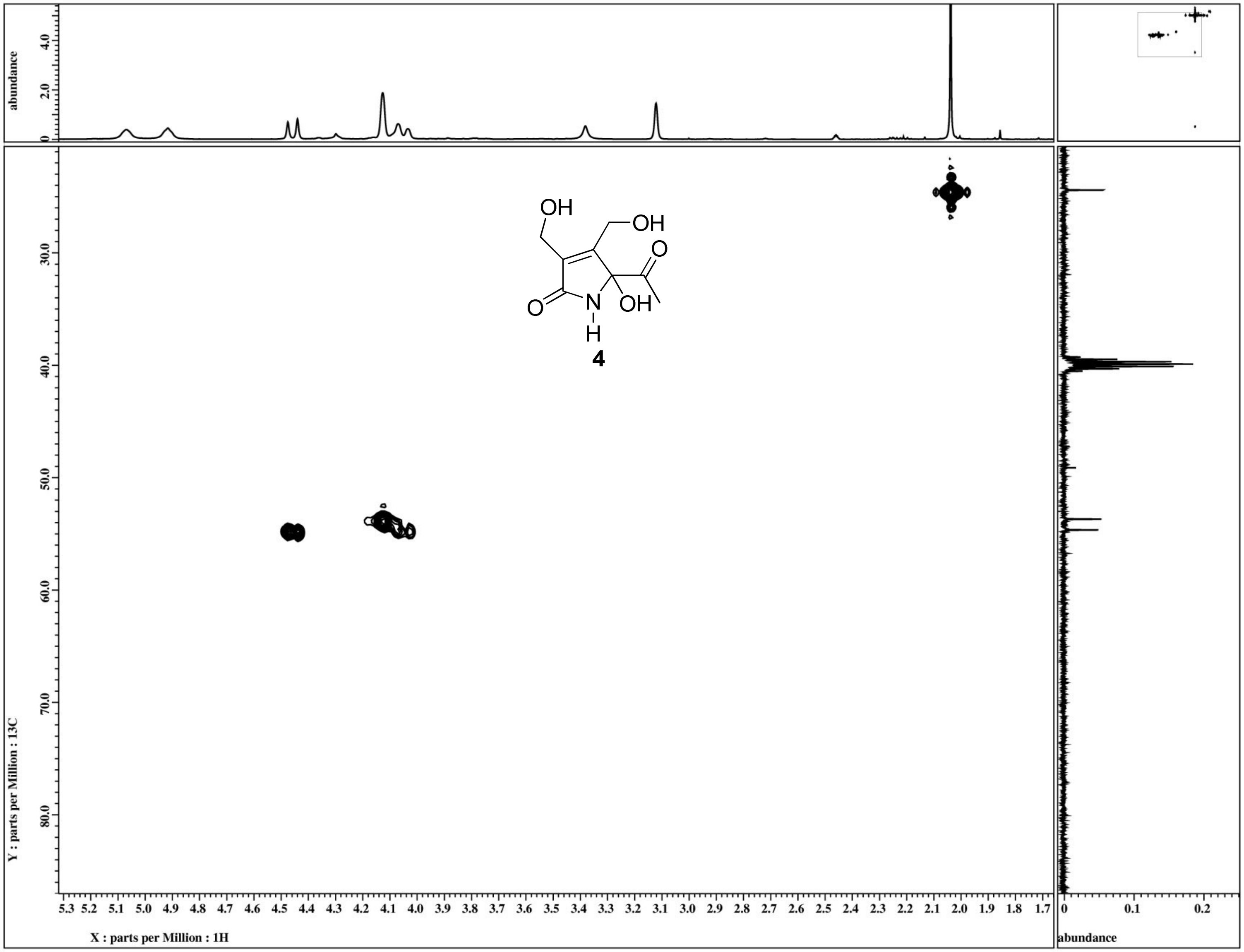
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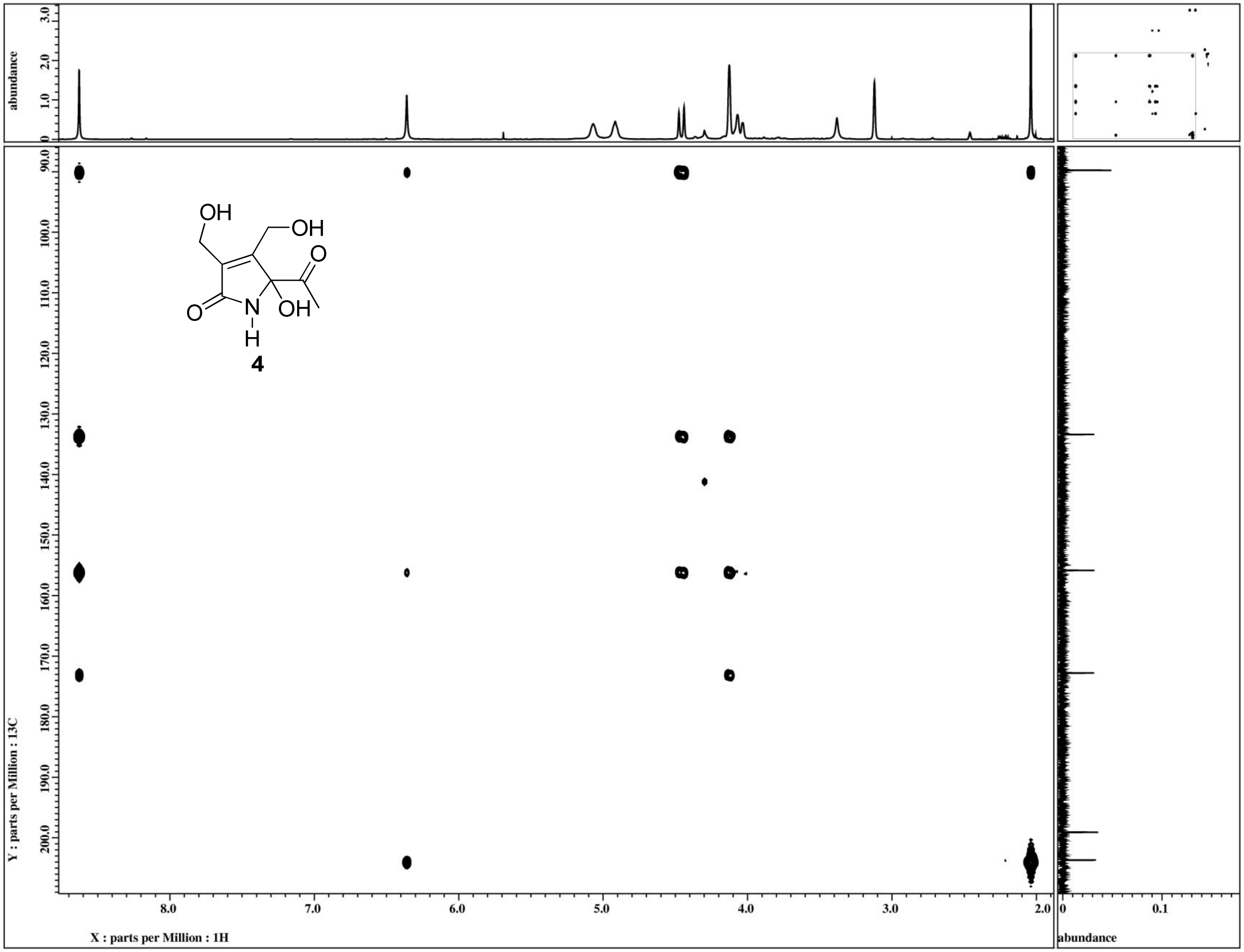
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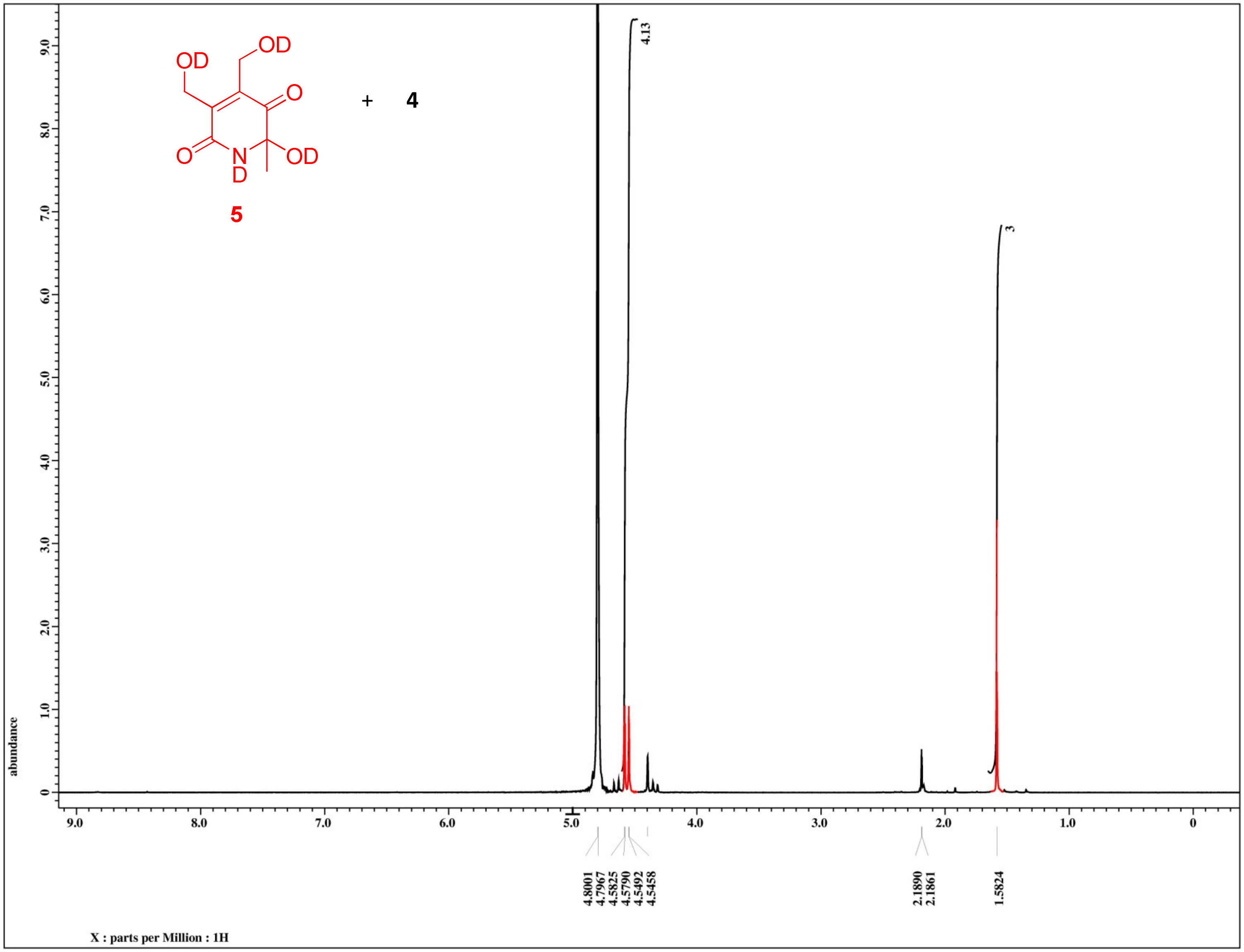
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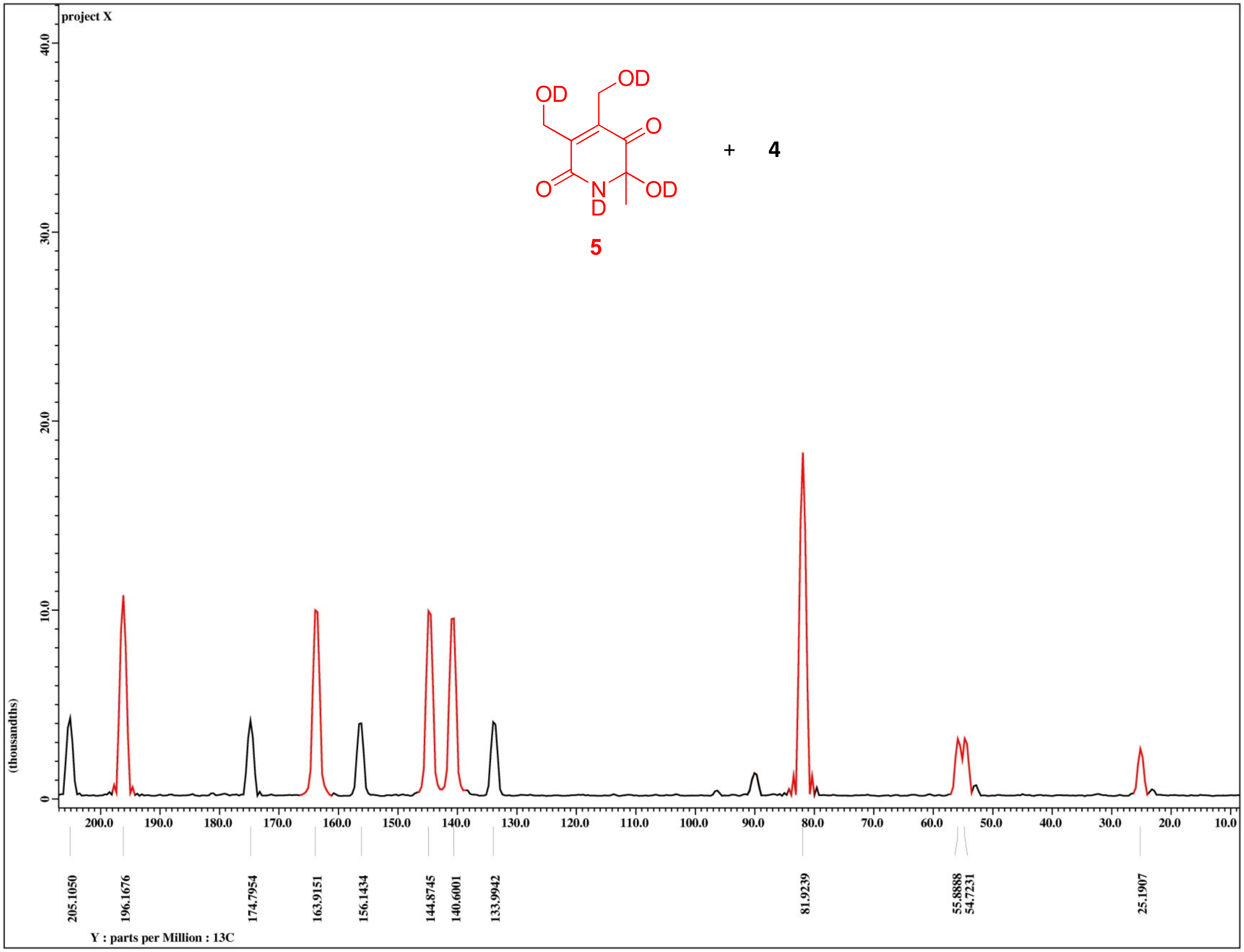
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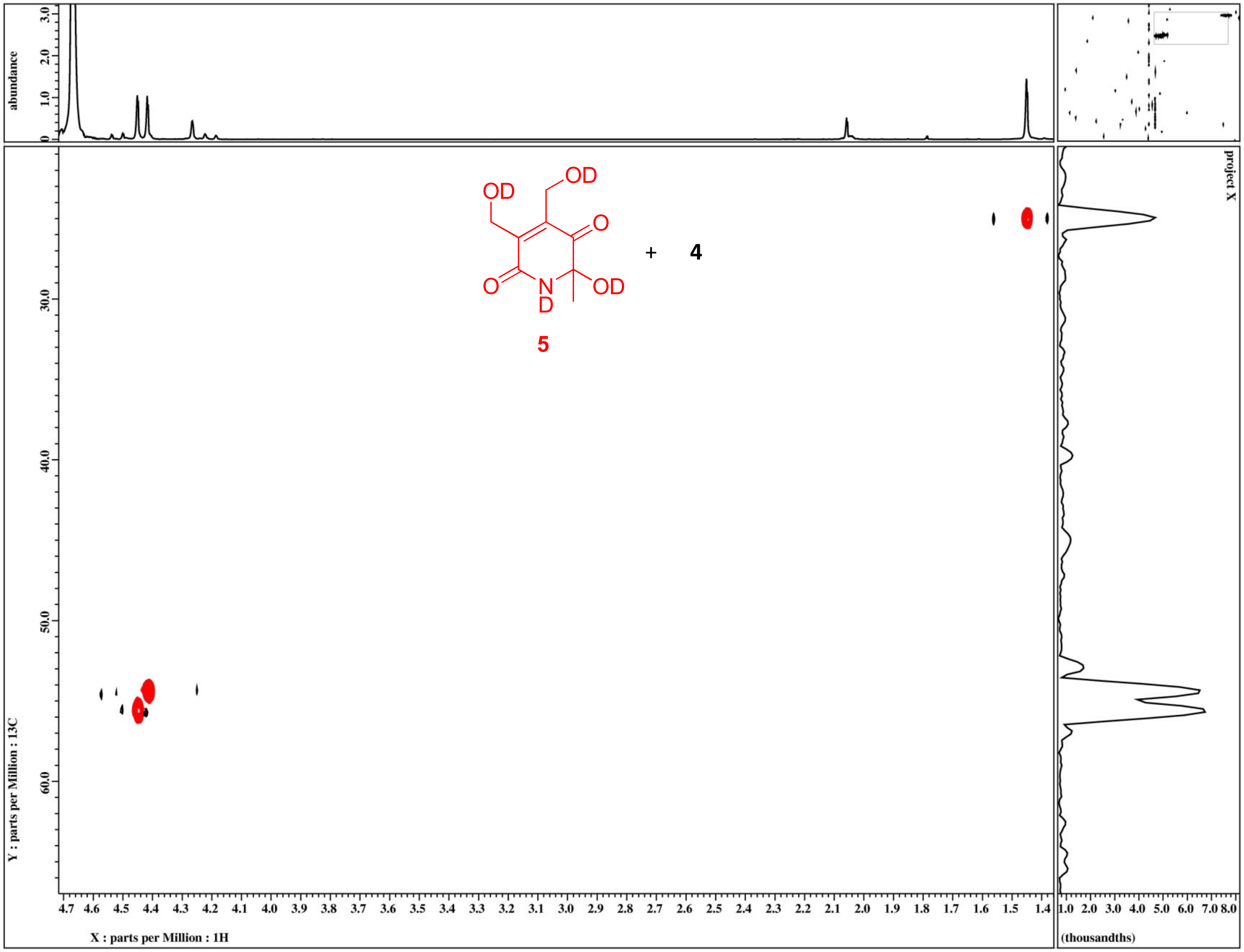
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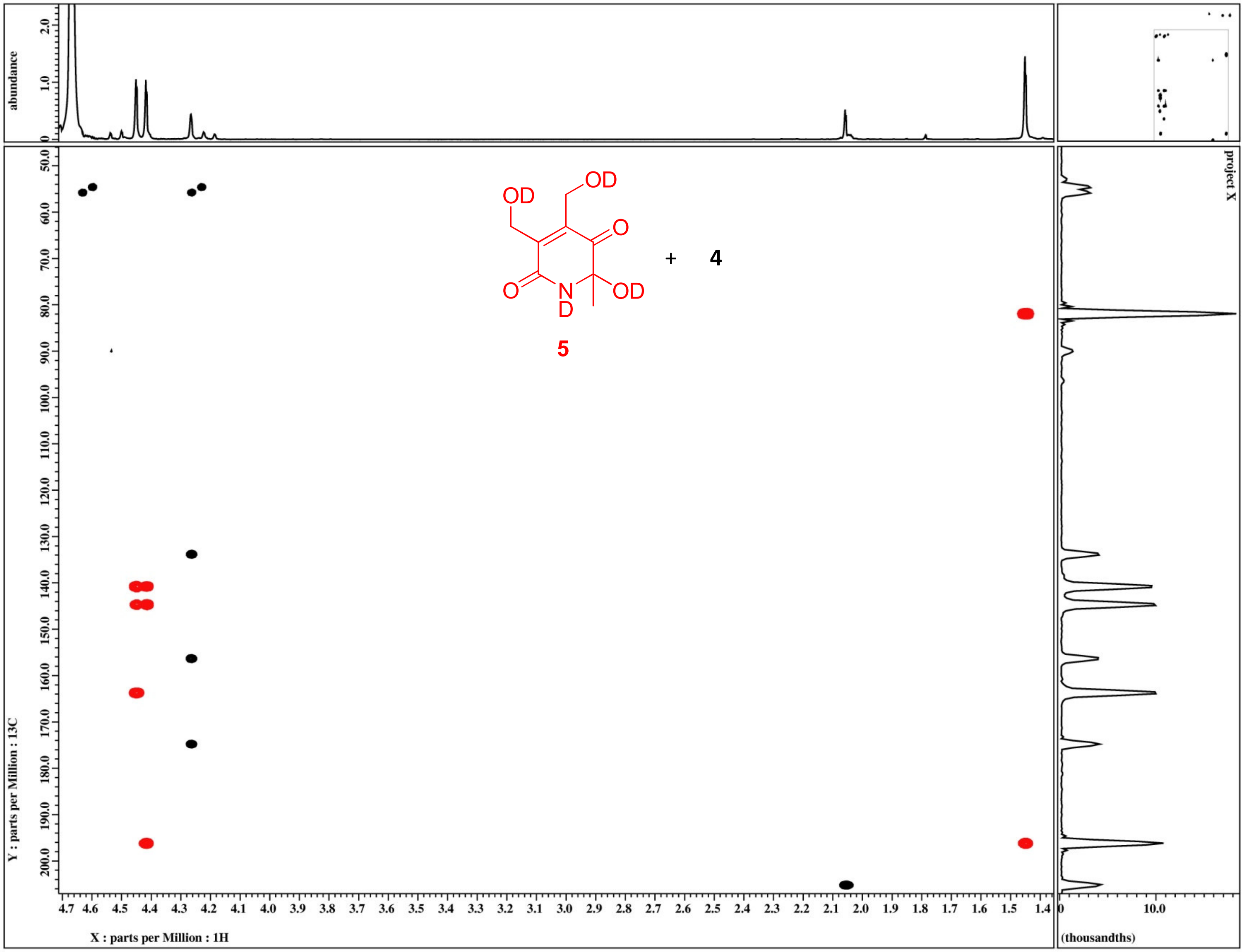
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Y : parts per Million : 13C
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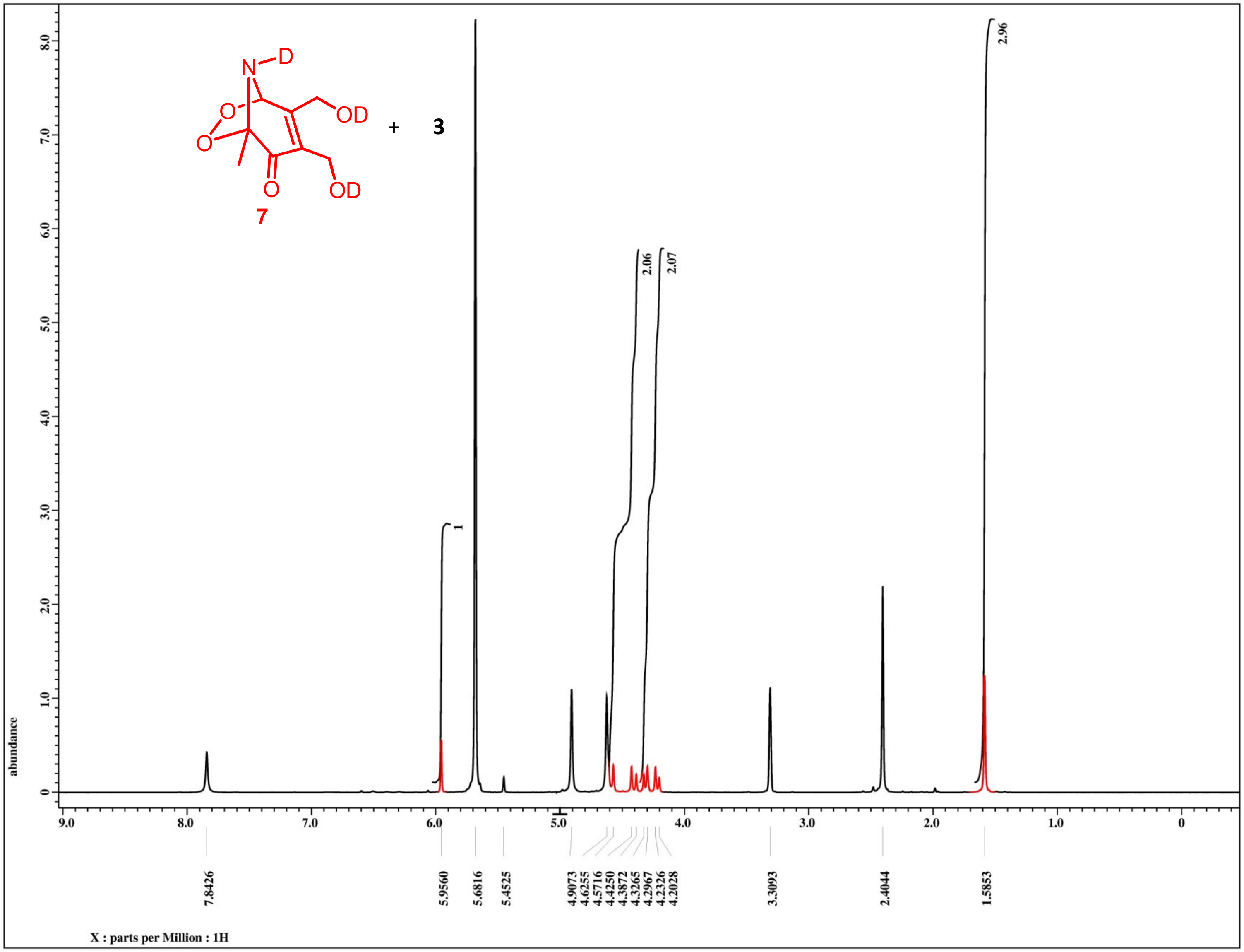
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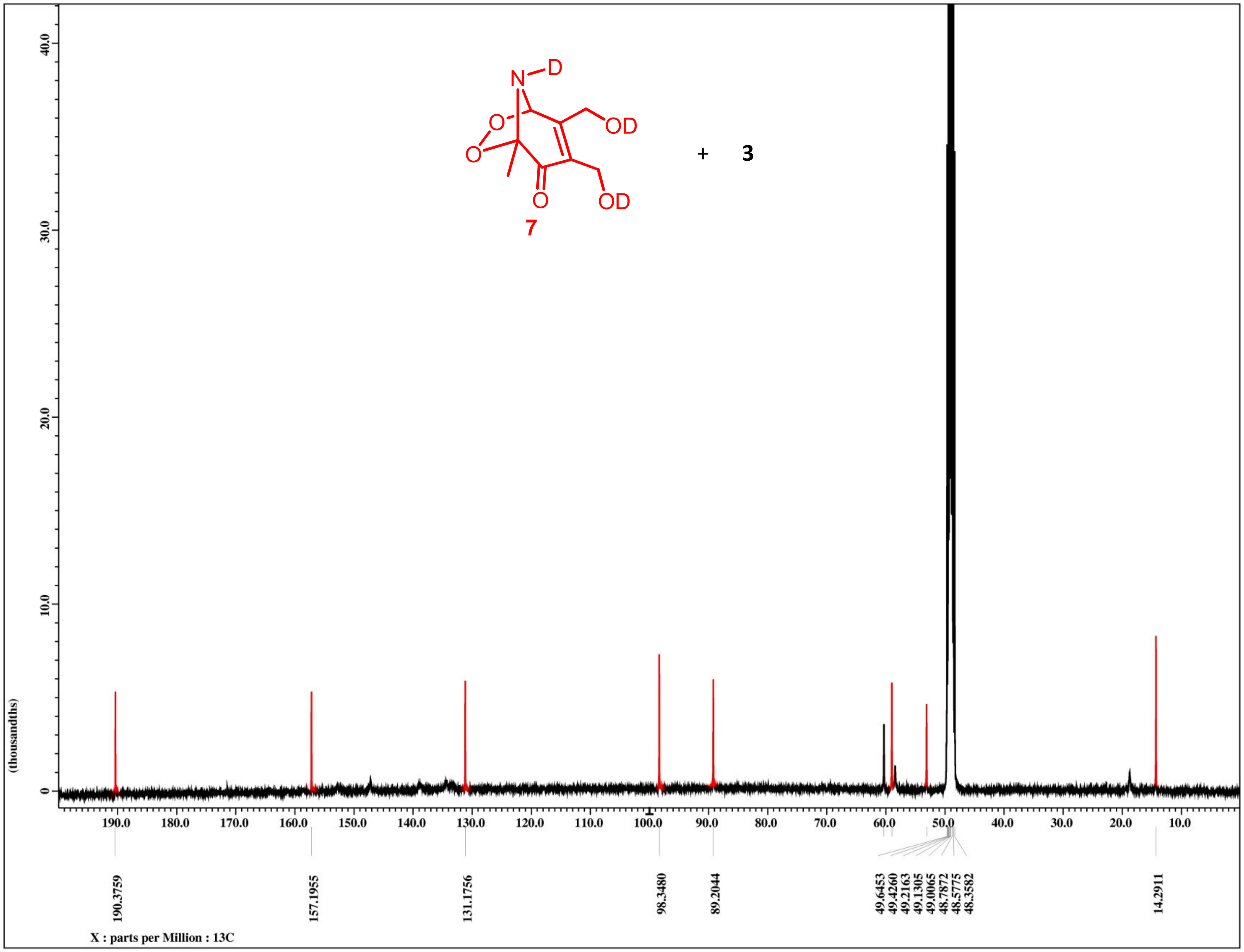
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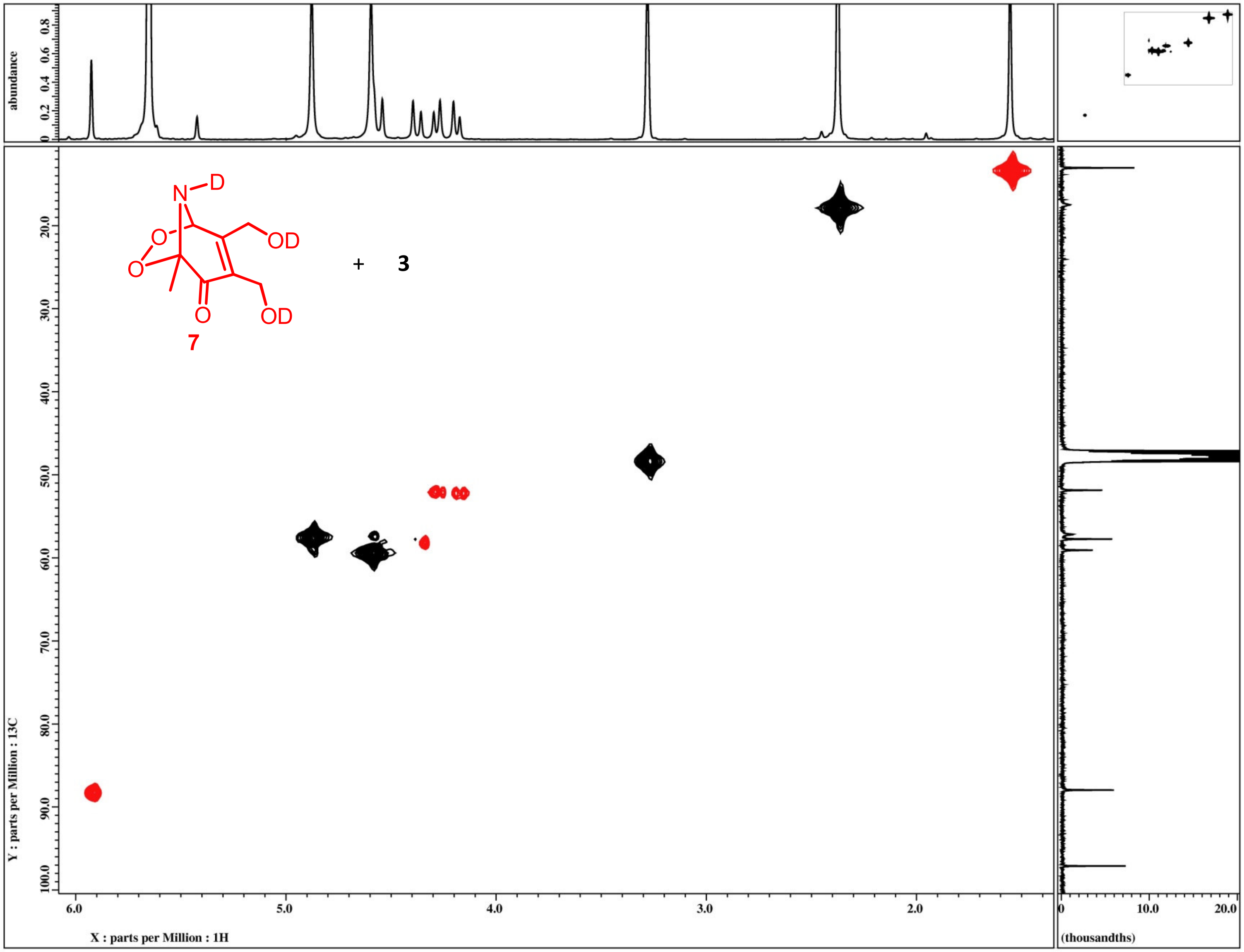
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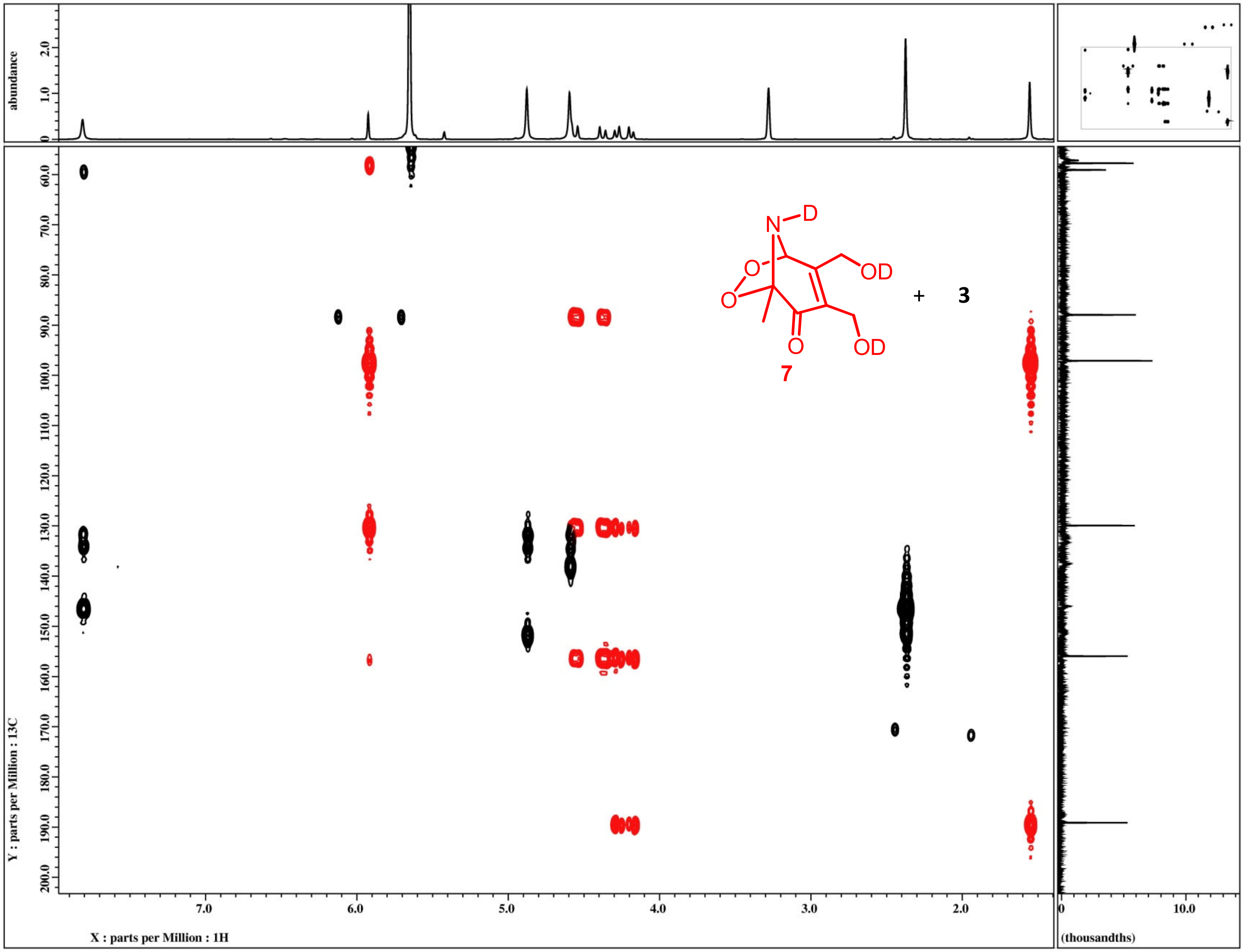
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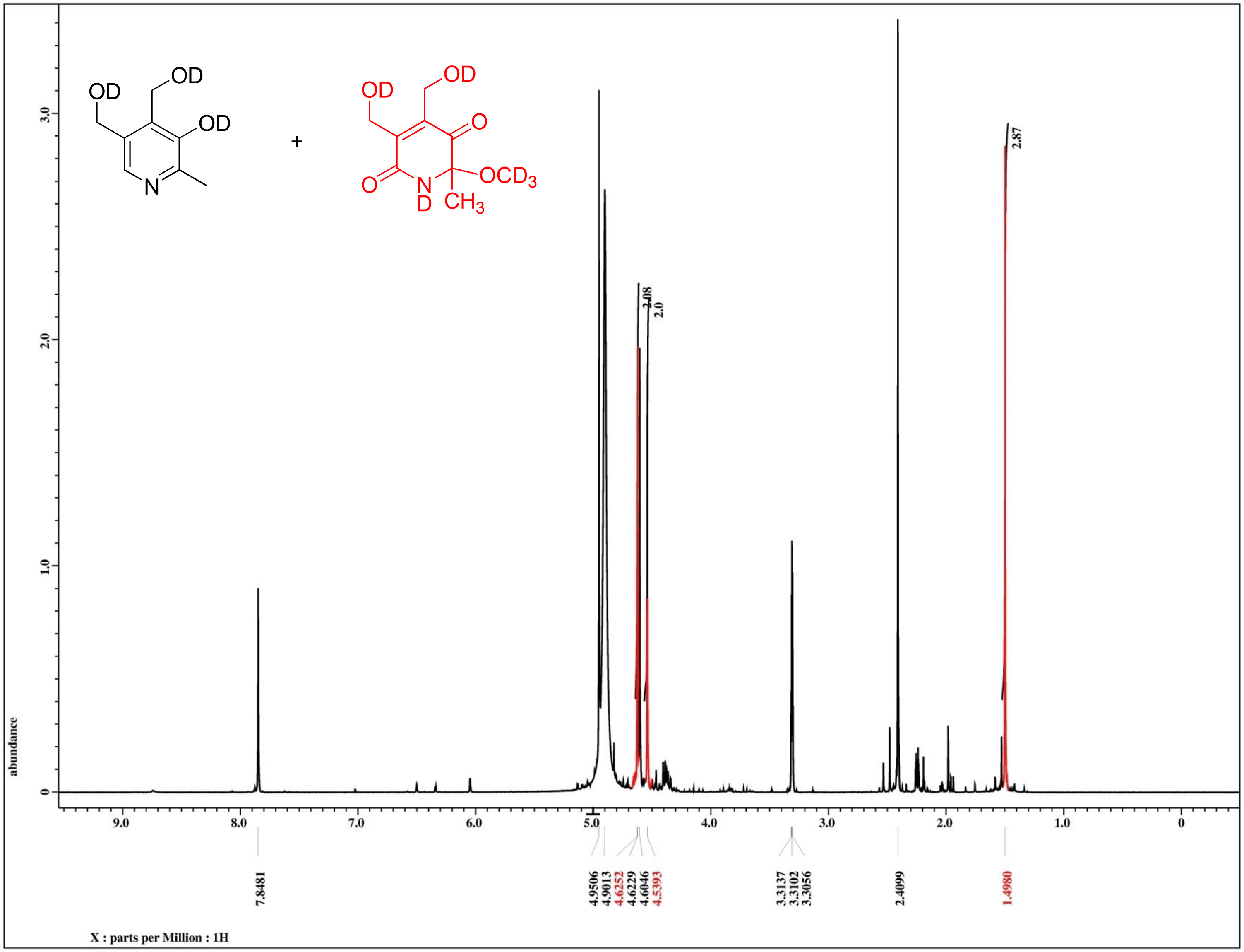
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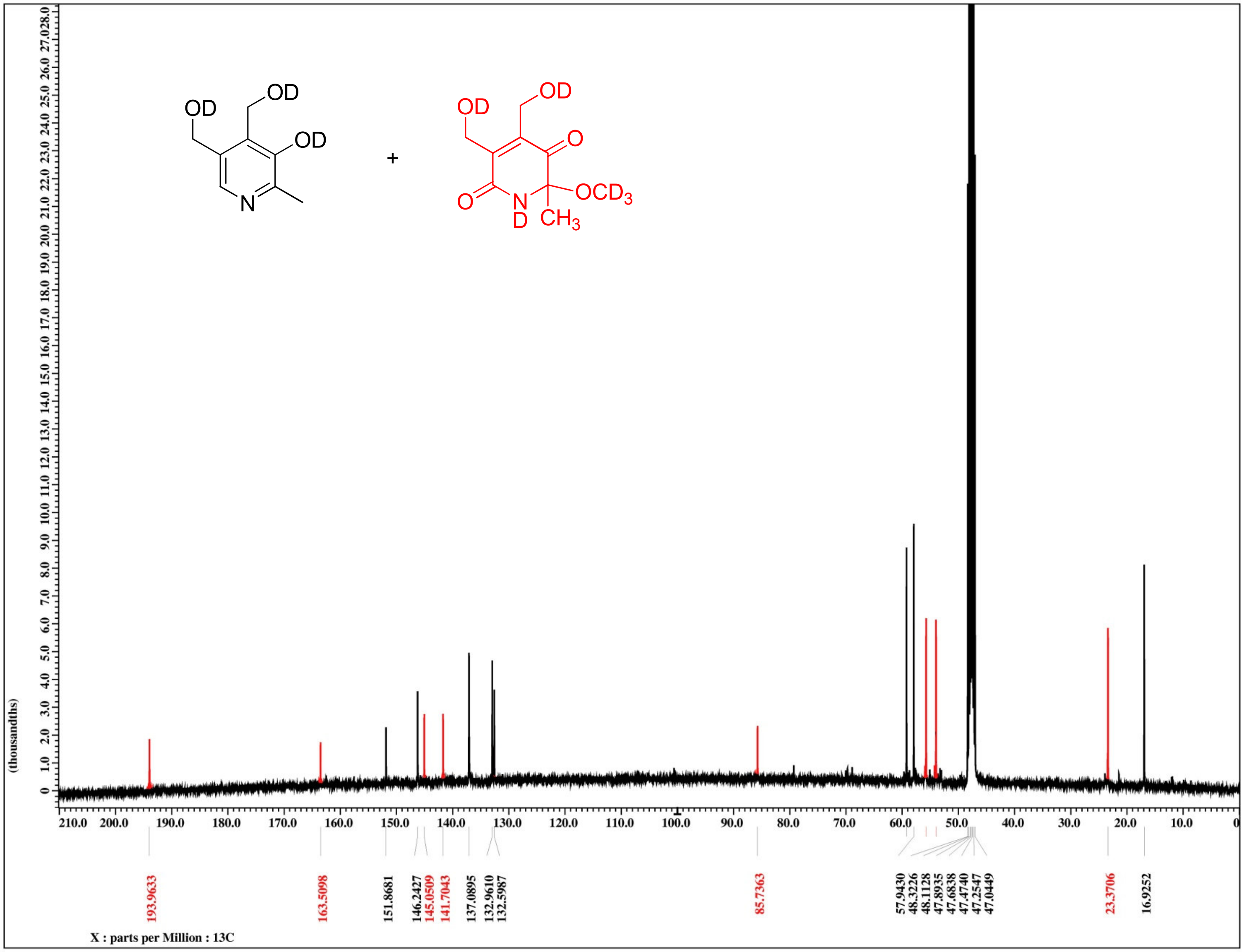
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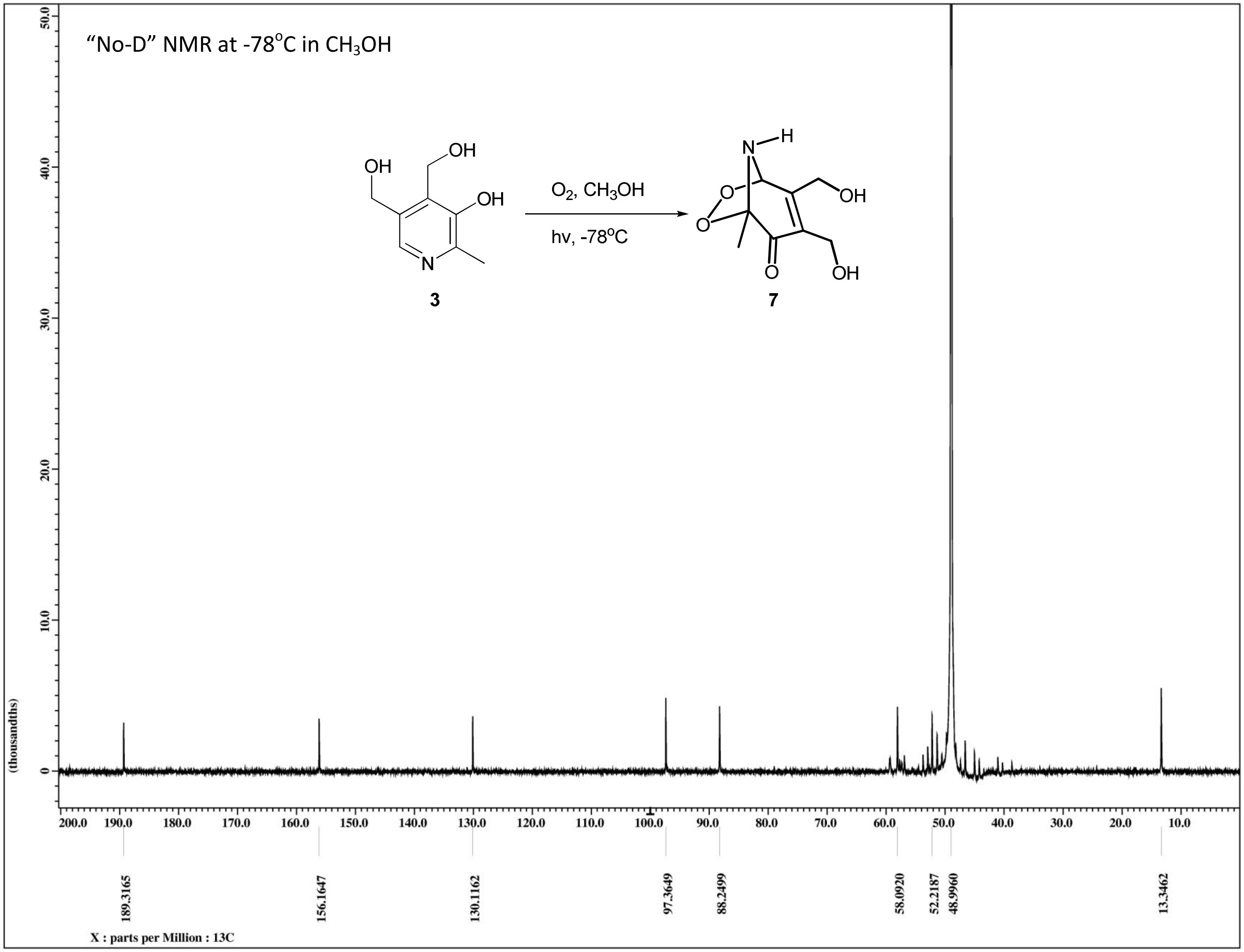
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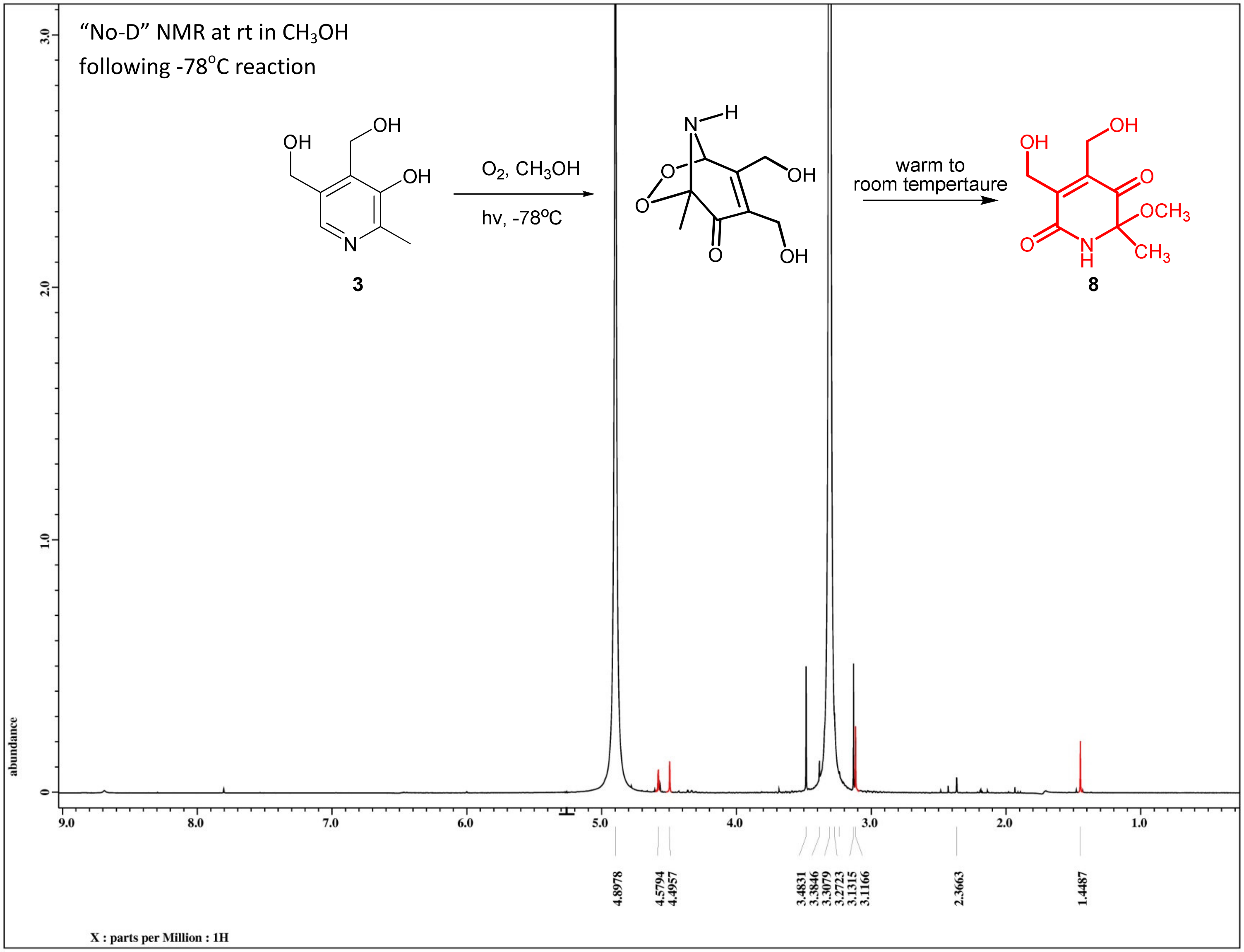
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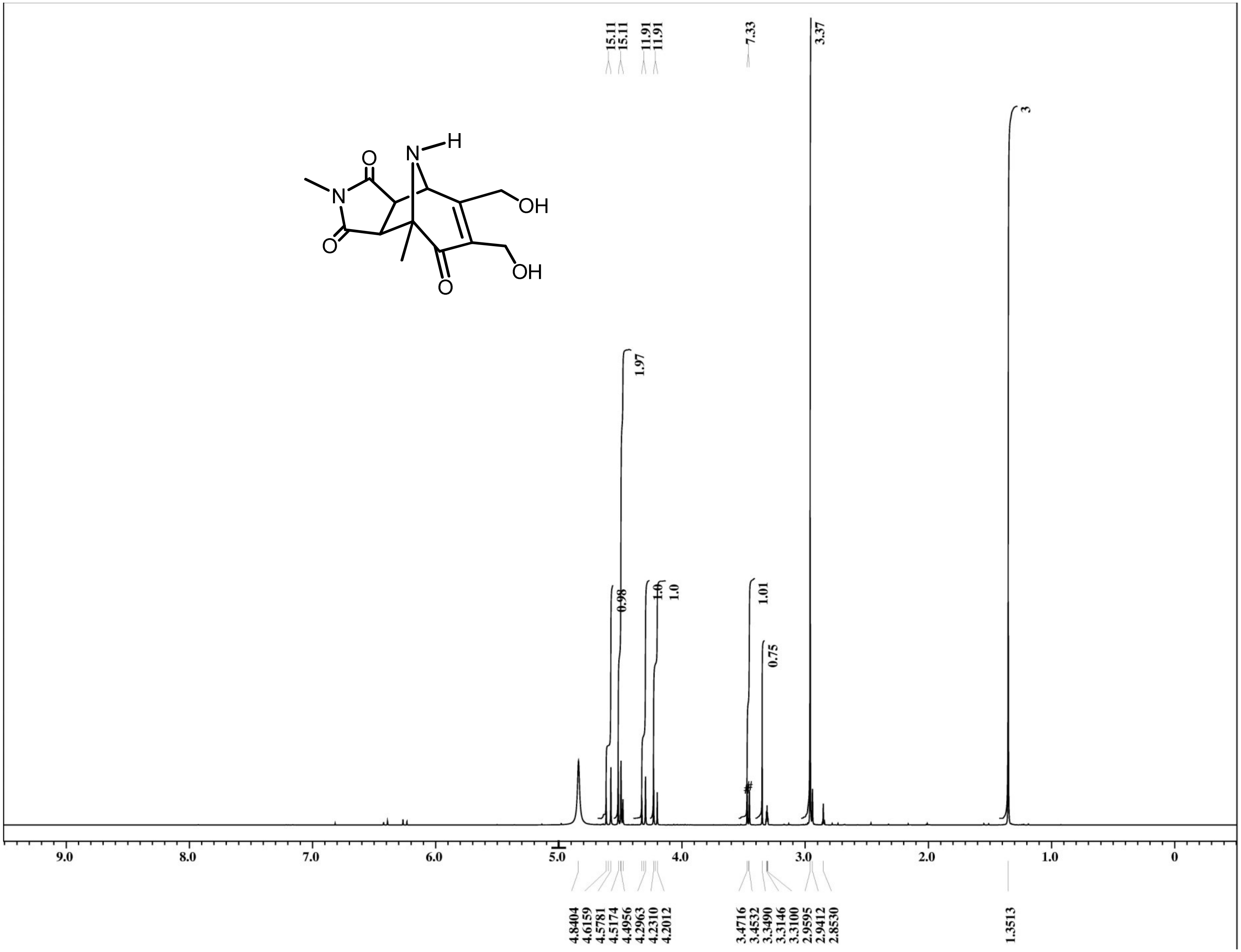
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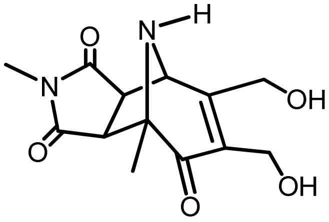
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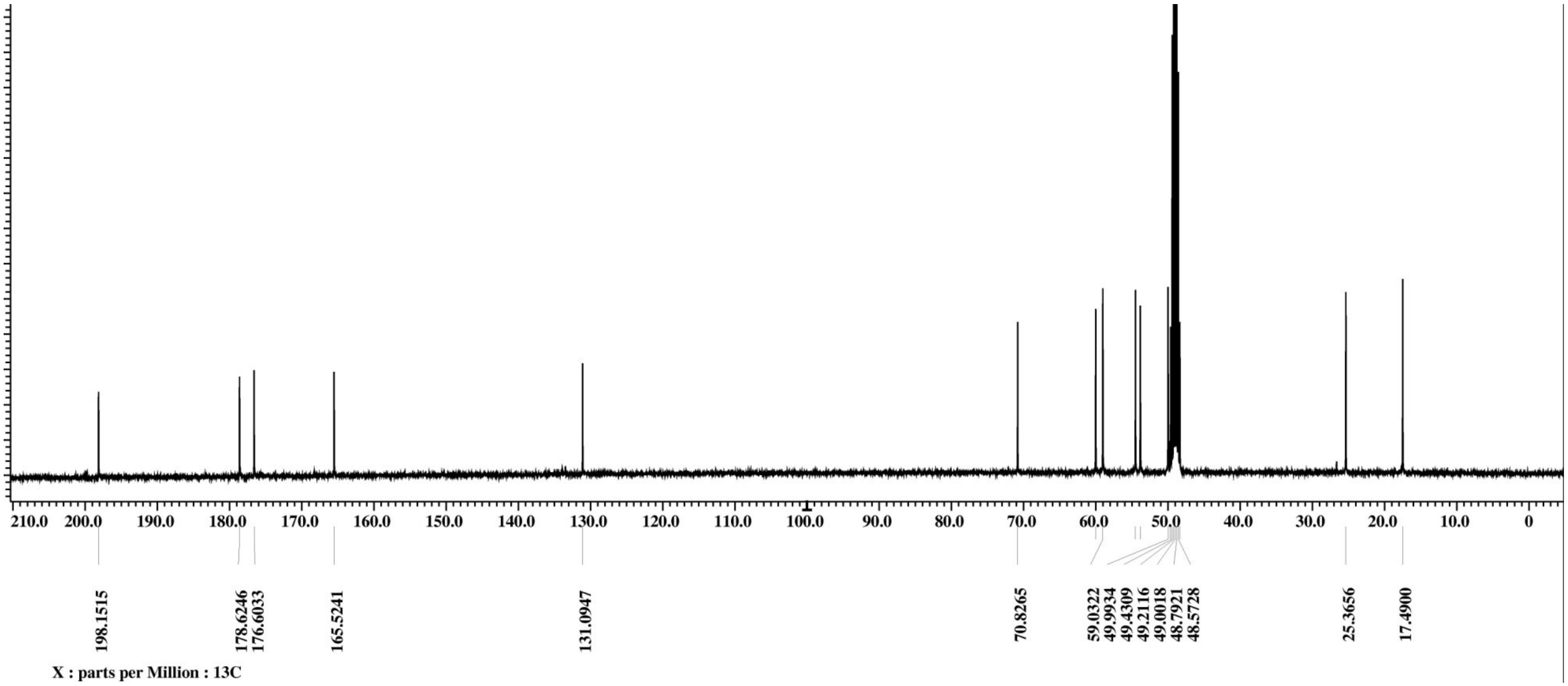
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17.4900
X : parts per Million : 13C

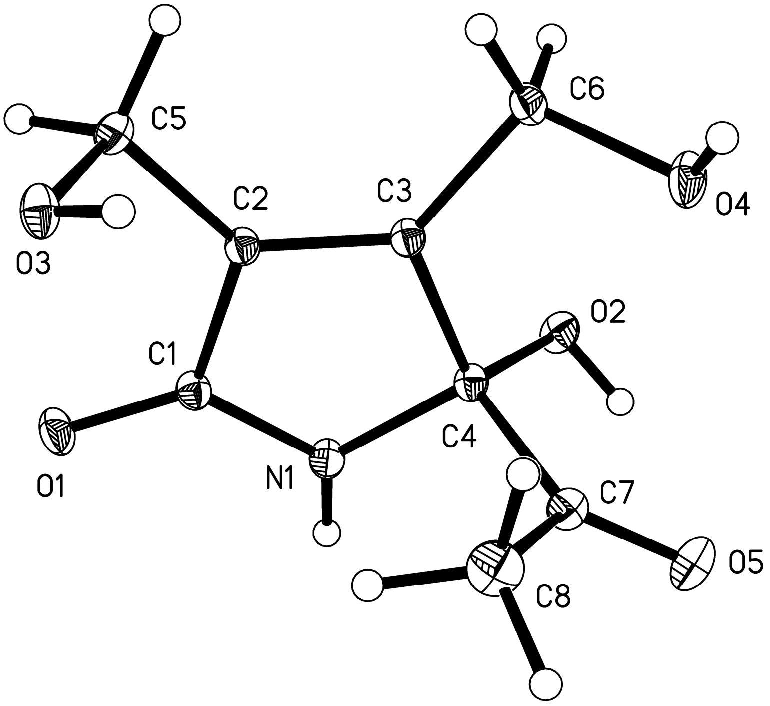
CRYSTAL STRUCTURE REPORT for compound **4**

REFERENCE NUMBER: sbudh01

$C_8 H_{11} N O_5$

Report prepared for:
Prof. D. Hilmey

June 22, 2011



William W. Brennessel
X-ray Crystallographic Facility
Department of Chemistry, University of Rochester
120 Trustee Road
Rochester, NY 14627

Data collection

A crystal (0.45 x 0.40 x 0.36 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 3.97 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50º steps in ω at six different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3949 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_1/n$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found from the difference Fourier map and their positional and isotropic displacement parameters were refined independently from those of all other atoms. The final full matrix least squares refinement converged to $R1 = 0.0322$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0954$ (F^2, all data).

Structure description

The structure is the one suggested with all atoms in general positions. Intermolecular and intramolecular hydrogen bonding is observed (see diagram and Table 7).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

---

[1] *APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011.

[2] Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

[3] *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] Sheldrick, G. M. *Acta. Cryst.* **2008**, *A64*, 112-122.

Some equations of interest:

$$R_{\text{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max\,(0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

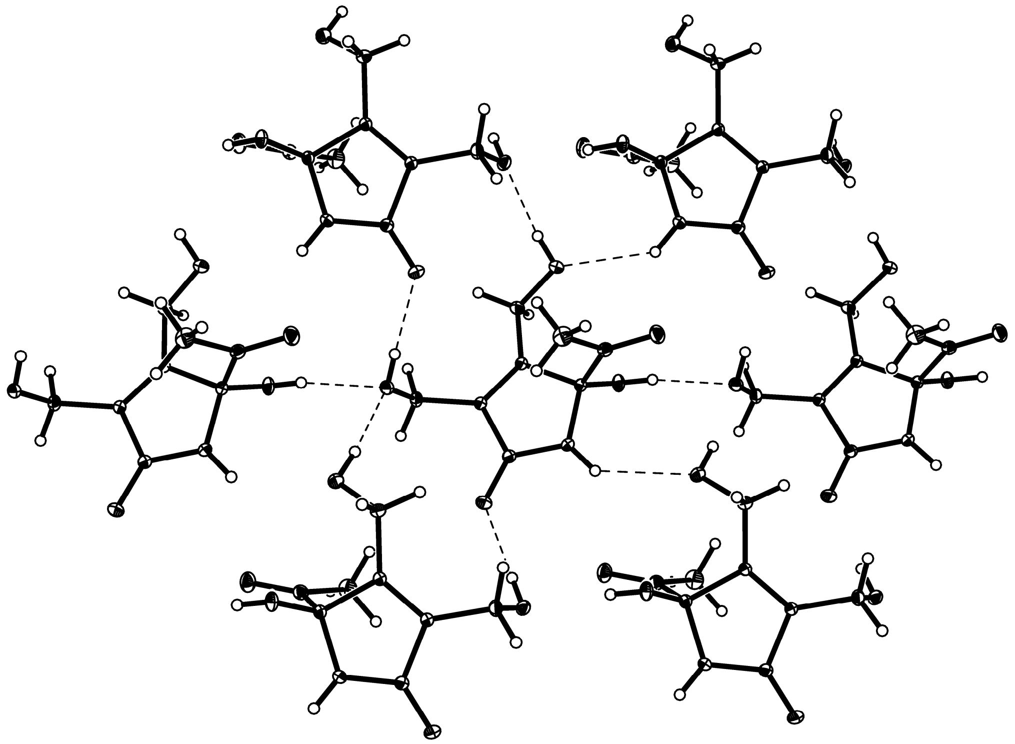


Table 1. Crystal data and structure refinement for Compound **4.**

Identification code	sbudh01	
Empirical formula	C8 H11 N O5	
Formula weight	201.18	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.1570(6) Å	α = 90°
	b = 10.1367(7) Å	β = 101.185(1)°
	c = 10.8698(8) Å	γ = 90°
Volume	881.70(11) $Å^3$	
Z	4	
Density (calculated)	1.516 Mg/m^3	
Absorption coefficient	0.127 mm^{-1}	
$F(000)$	424	
Crystal color, morphology	colorless, block	
Crystal size	0.45 x 0.40 x 0.36 mm^3	
Theta range for data collection	2.77 to 37.78°	
Index ranges	$-13 \leq h \leq 14, -17 \leq k \leq 17, -18 \leq l \leq 18$	
Reflections collected	31864	
Independent reflections	4711 [R(int) = 0.0256]	
Observed reflections	4303	
Completeness to theta = 37.78°	99.4%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9555 and 0.9449	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4711 / 0 / 171	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	$R1$ = 0.0322, $wR2$ = 0.0931	
R indices (all data)	$R1$ = 0.0351, $wR2$ = 0.0954	
Largest diff. peak and hole	0.723 and -0.220 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	6418(1)	11664(1)	6954(1)	14(1)
O2	2047(1)	8869(1)	6324(1)	12(1)
O3	9109(1)	9084(1)	7172(1)	12(1)
O4	4049(1)	6276(1)	6942(1)	15(1)
O5	2297(1)	8233(1)	8729(1)	16(1)
N1	4123(1)	10431(1)	7234(1)	11(1)
C1	5623(1)	10624(1)	6901(1)	10(1)
C2	6150(1)	9331(1)	6453(1)	9(1)
C3	4958(1)	8437(1)	6516(1)	9(1)
C4	3594(1)	9052(1)	7094(1)	9(1)
C5	7800(1)	9158(1)	6075(1)	11(1)
C6	4784(1)	7036(1)	6086(1)	12(1)
C7	3616(1)	8512(1)	8438(1)	11(1)
C8	5272(1)	8392(1)	9317(1)	17(1)

Table 3. Bond lengths [Å] and angles [°] for **4**.

O(1)-C(1)	1.2332(6)	C(3)-C(2)-C(1)	108.67(4)
O(2)-C(4)	1.3850(6)	C(3)-C(2)-C(5)	129.50(4)
O(2)-H(2)	0.846(15)	C(1)-C(2)-C(5)	121.77(4)
O(3)-C(5)	1.4403(7)	C(2)-C(3)-C(6)	130.79(5)
O(3)-H(3)	0.800(15)	C(2)-C(3)-C(4)	109.92(4)
O(4)-C(6)	1.4270(7)	C(6)-C(3)-C(4)	119.26(4)
O(4)-H(4)	0.859(14)	O(2)-C(4)-N(1)	114.05(4)
O(5)-C(7)	1.2127(7)	O(2)-C(4)-C(3)	110.54(4)
N(1)-C(1)	1.3556(7)	N(1)-C(4)-C(3)	102.21(4)
N(1)-C(4)	1.4621(7)	O(2)-C(4)-C(7)	111.28(4)
N(1)-H(1)	0.881(13)	N(1)-C(4)-C(7)	106.76(4)
C(1)-C(2)	1.4901(7)	C(3)-C(4)-C(7)	111.65(4)
C(2)-C(3)	1.3408(7)	O(3)-C(5)-C(2)	109.96(4)
C(2)-C(5)	1.4915(7)	O(3)-C(5)-H(5A)	109.7(7)
C(3)-C(6)	1.4932(7)	C(2)-C(5)-H(5A)	110.0(7)
C(3)-C(4)	1.5143(7)	O(3)-C(5)-H(5B)	106.7(6)
C(4)-C(7)	1.5571(7)	C(2)-C(5)-H(5B)	110.9(6)
C(5)-H(5A)	0.973(13)	H(5A)-C(5)-H(5B)	109.6(10)
C(5)-H(5B)	0.978(12)	O(4)-C(6)-C(3)	109.63(4)
C(6)-H(6A)	1.002(11)	O(4)-C(6)-H(6A)	108.0(6)
C(6)-H(6B)	0.982(11)	C(3)-C(6)-H(6A)	108.4(7)
C(7)-C(8)	1.5005(8)	O(4)-C(6)-H(6B)	109.2(7)
C(8)-H(8A)	0.970(13)	C(3)-C(6)-H(6B)	110.3(7)
C(8)-H(8B)	0.979(14)	H(6A)-C(6)-H(6B)	111.3(9)
C(8)-H(8C)	0.961(14)	O(5)-C(7)-C(8)	123.32(5)
C(4)-O(2)-H(2)	108.1(10)	O(5)-C(7)-C(4)	118.53(5)
C(5)-O(3)-H(3)	108.8(10)	C(8)-C(7)-C(4)	118.13(5)
C(6)-O(4)-H(4)	108.5(10)	C(7)-C(8)-H(8A)	113.4(7)
C(1)-N(1)-C(4)	111.92(4)	C(7)-C(8)-H(8B)	107.2(8)
C(1)-N(1)-H(1)	124.1(8)	H(8A)-C(8)-H(8B)	108.8(11)
C(4)-N(1)-H(1)	123.9(8)	C(7)-C(8)-H(8C)	110.7(9)
O(1)-C(1)-N(1)	127.18(5)	H(8A)-C(8)-H(8C)	105.8(11)
O(1)-C(1)-C(2)	125.78(5)	H(8B)-C(8)-H(8C)	111.1(12)
N(1)-C(1)-C(2)	107.04(4)		

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U_{11}$ + ... + 2 h k a* b* U_{12}]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	13(1)	8(1)	21(1)	-2(1)	4(1)	-2(1)
O2	7(1)	17(1)	12(1)	1(1)	1(1)	0(1)
O3	8(1)	10(1)	16(1)	2(1)	1(1)	0(1)
O4	14(1)	9(1)	24(1)	4(1)	8(1)	0(1)
O5	14(1)	20(1)	17(1)	5(1)	6(1)	1(1)
N1	10(1)	8(1)	16(1)	0(1)	5(1)	1(1)
C1	9(1)	9(1)	12(1)	0(1)	2(1)	0(1)
C2	8(1)	8(1)	11(1)	0(1)	2(1)	0(1)
C3	8(1)	8(1)	11(1)	0(1)	2(1)	0(1)
C4	7(1)	9(1)	11(1)	1(1)	2(1)	0(1)
C5	9(1)	13(1)	12(1)	0(1)	3(1)	0(1)
C6	13(1)	8(1)	16(1)	-1(1)	5(1)	-1(1)
C7	11(1)	11(1)	11(1)	1(1)	2(1)	1(1)
C8	15(1)	20(1)	13(1)	2(1)	-2(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4**.

	x	y	z	U(eq)
H2	1314(18)	8881(14)	6778(14)	35(3)
H3	9019(18)	8403(14)	7527(14)	35(3)
H4	4681(18)	5609(14)	7180(14)	38(4)
H1	3516(16)	11066(13)	7471(13)	27(3)
H5A	7793(15)	8357(12)	5581(12)	23(3)
H5B	8057(13)	9916(12)	5588(11)	18(2)
H6A	4013(13)	7008(11)	5247(10)	18(2)
H6B	5884(14)	6666(11)	6042(11)	17(2)
H8A	6009(15)	9135(12)	9276(12)	26(3)
H8B	5807(17)	7590(14)	9086(13)	37(3)
H8C	5124(18)	8353(13)	10172(13)	32(3)

Table 6. Torsion angles [°] for **4**.

C4-N1-C1-O1	-177.56(5)	C2-C3-C4-N1	4.89(5)
C4-N1-C1-C2	2.38(6)	C6-C3-C4-N1	-173.29(4)
O1-C1-C2-C3	-179.12(5)	C2-C3-C4-C7	-108.89(5)
N1-C1-C2-C3	0.94(6)	C6-C3-C4-C7	72.93(6)
O1-C1-C2-C5	3.38(8)	C3-C2-C5-O3	-100.65(6)
N1-C1-C2-C5	-176.56(4)	C1-C2-C5-O3	76.28(6)
C1-C2-C3-C6	174.18(5)	C2-C3-C6-O4	144.33(5)
C5-C2-C3-C6	-8.58(9)	C4-C3-C6-O4	-37.93(6)
C1-C2-C3-C4	-3.72(5)	O2-C4-C7-O5	-12.89(7)
C5-C2-C3-C4	173.52(5)	N1-C4-C7-O5	112.14(5)
C1-N1-C4-O2	-123.67(5)	C3-C4-C7-O5	-136.93(5)
C1-N1-C4-C3	-4.35(5)	O2-C4-C7-C8	168.42(5)
C1-N1-C4-C7	112.99(5)	N1-C4-C7-C8	-66.55(6)
C2-C3-C4-O2	126.66(4)	C3-C4-C7-C8	44.38(6)
C6-C3-C4-O2	-51.52(6)		

Table 7. Hydrogen bonds and close contacts for **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O2-H2...O3#1	0.846(15)	1.940(15)	2.7384(6)	157.1(14)
O2-H2...O5	0.846(15)	2.216(15)	2.6617(6)	112.9(12)
O3-H3...O1#2	0.800(15)	1.906(15)	2.6943(6)	168.4(15)
O4-H4...O3#2	0.859(14)	1.896(15)	2.7501(6)	173.1(14)
N1-H1...O4#3	0.881(13)	2.312(13)	3.0211(6)	137.6(11)
N1-H1...O5#3	0.881(13)	2.575(13)	3.1678(7)	125.4(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+3/2,y-1/2,-z+3/2 #3 -x+1/2,y+1/2,-z+3/2

REFERENCE NUMBER: sbudh02

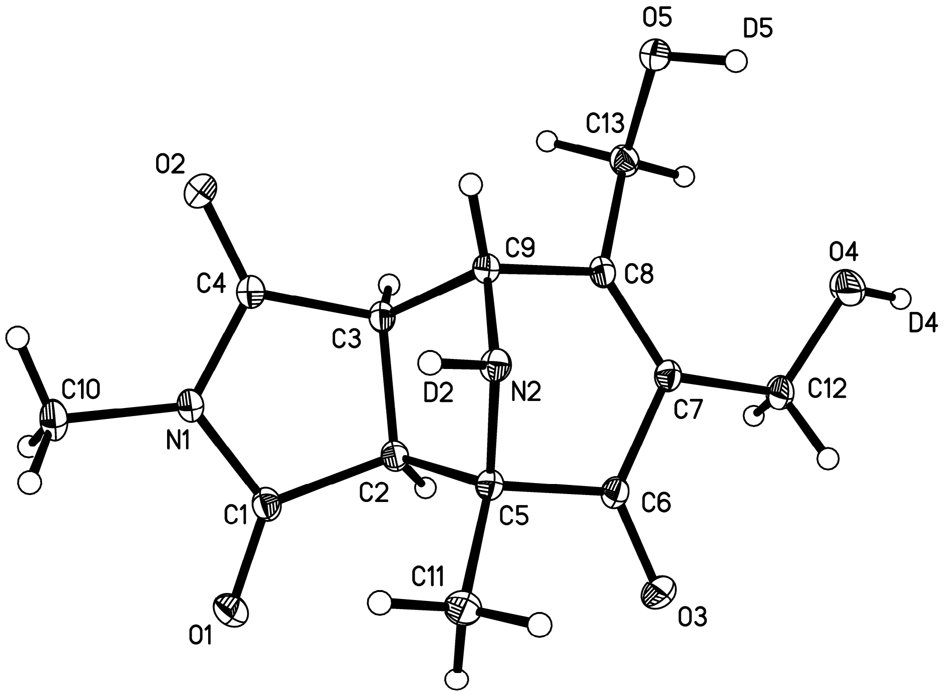
CRYSTAL STRUCTURE REPORT for compound **9**

$C_{13}H_{13}D_3N_2O_5$

Report prepared for:

Prof. D. Hilmey

May 10, 2012



William W. Brennessel
X-ray Crystallographic Facility
Department of Chemistry, University of Rochester
120 Trustee Road
Rochester, NY 14627

Data collection

A crystal (0.24 x 0.20 x 0.20 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(5) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 25 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50° steps in ω at six different ϕ settings and a detector position of -38° in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 4025 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

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Structure description

The structure is the one suggested, with all atoms in general positions. Hydrogen bonding links the molecules in two dimensional sheets, parallel to the *ab* plane (see diagrams and Table 7).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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[5] Sheldrick, G. M. *Acta. Cryst.* **2008**, *A64*, 112-122.

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\,|F_o^2 - \langle F_o^2\rangle| \,/\, \Sigma|F_o^2|$$

$$R1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

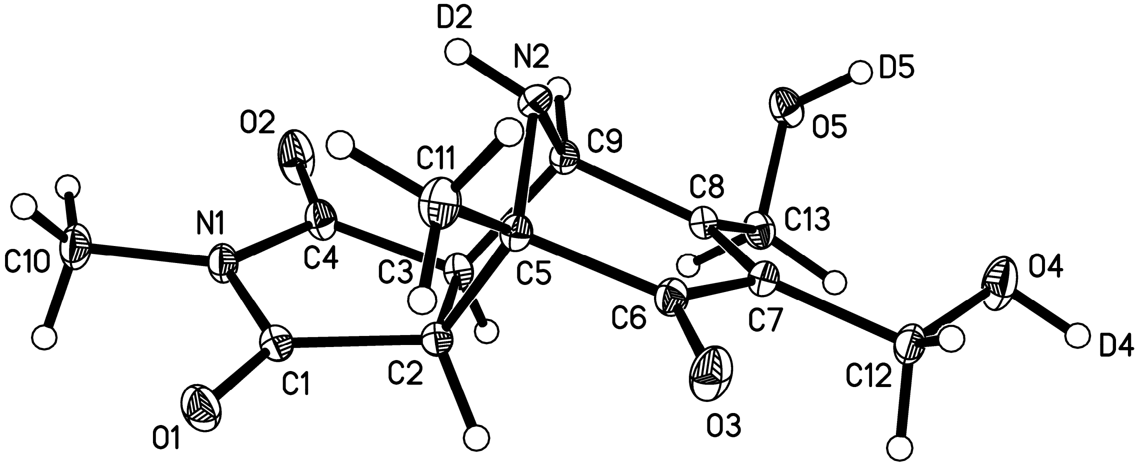
$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\,[w(F_o^2)^2]]^{1/2}$$

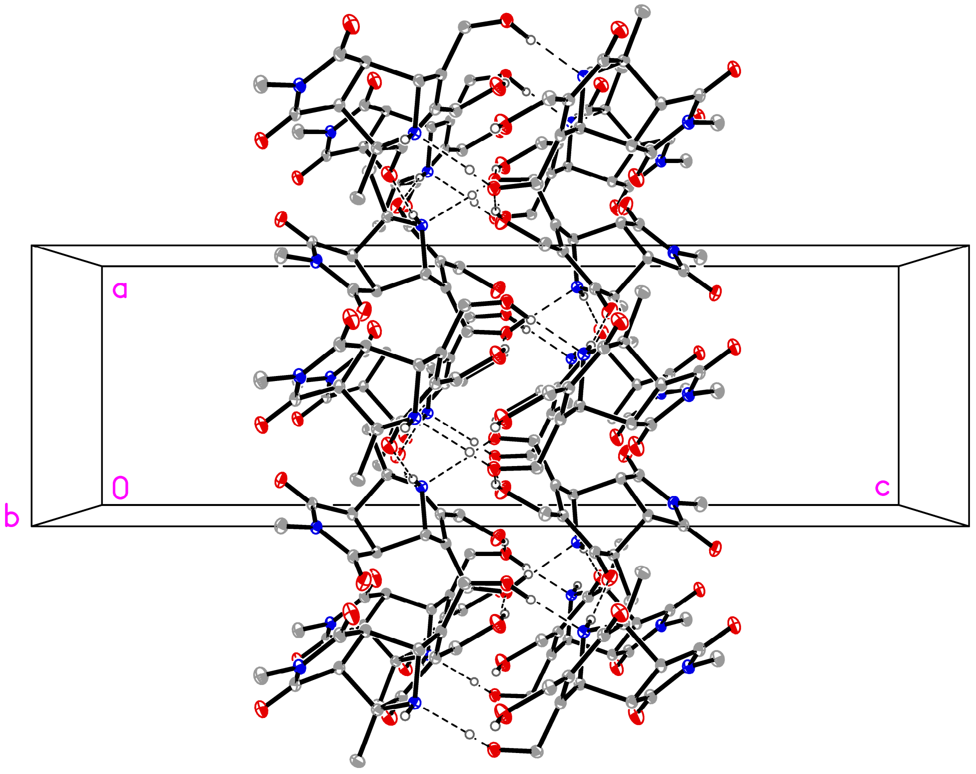
$$\text{where } w = 1 \,/\, [\sigma^2(F_o^2) + (aP)^2 + bP] \text{ and}$$

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

$$\mathrm{GOF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

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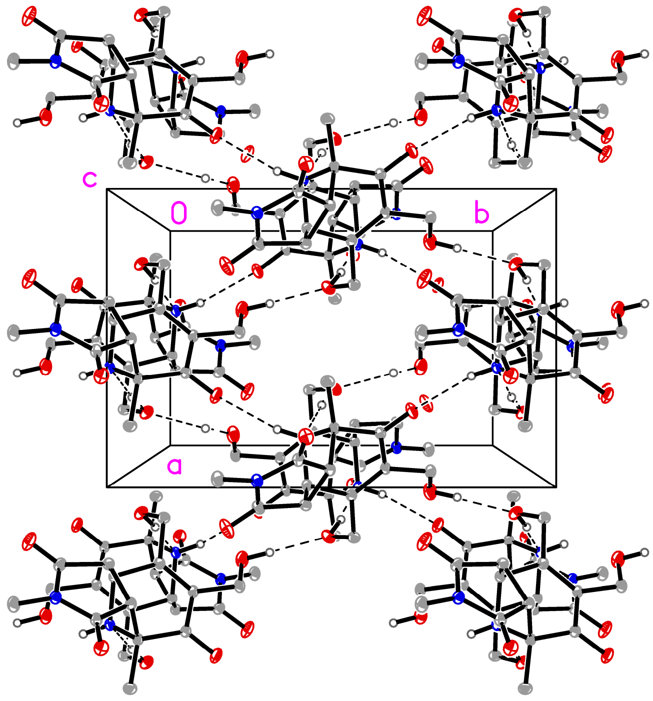
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Table 1. Crystal data and structure refinement for sbudh02.

Identification code	sbudh02	
Empirical formula	C13 H13 D3 N2 O5	
Formula weight	283.30	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	*a* = 7.8267(6) Å	$\alpha = 90°$
	b = 11.7766(8) Å	$\beta = 90°$
	c = 26.1425(19) Å	$\gamma = 90°$
Volume	2409.6(3) $Å^3$	
Z	8	
Density (calculated)	1.562 Mg/m^3	
Absorption coefficient	0.120 mm^{-1}	
F(000)	1184	
Crystal color, morphology	colorless, block	
Crystal size	0.24 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.03 to 37.78°	
Index ranges	$-13 \le h \le 13$, $-20 \le k \le 20$, $-45 \le l \le 45$	
Reflections collected	83310	
Independent reflections	6466 [*R*(int) = 0.0644]	
Observed reflections	5075	
Completeness to theta = 37.78°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9764 and 0.9718	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6466 / 0 / 245	
Goodness-of-fit on F^2	1.053	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0434, *wR*2 = 0.1174	
R indices (all data)	*R*1 = 0.0577, *wR*2 = 0.1236	
Largest diff. peak and hole	0.621 and -0.236 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sbudh02. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	6383(1)	5621(1)	2522(1)	17(1)
O2	2746(1)	7650(1)	1517(1)	22(1)
O3	7206(1)	2949(1)	1227(1)	18(1)
O4	3866(1)	2378(1)	29(1)	21(1)
D4	3610(20)	1648(17)	-50(7)	42(5)
O5	2026(1)	5085(1)	-68(1)	15(1)
D5	2650(30)	4744(15)	-326(7)	44(5)
N1	4674(1)	6848(1)	2072(1)	13(1)
N2	6136(1)	5730(1)	903(1)	11(1)
D2	6462(17)	6395(12)	990(5)	15(3)
C1	5474(1)	5821(1)	2155(1)	12(1)
C2	5037(1)	5040(1)	1717(1)	11(1)
C3	3625(1)	5658(1)	1420(1)	11(1)
C4	3584(1)	6839(1)	1655(1)	14(1)
C5	6546(1)	4926(1)	1314(1)	11(1)
C6	6326(1)	3744(1)	1080(1)	11(1)
C7	4910(1)	3594(1)	709(1)	11(1)
C8	3832(1)	4480(1)	637(1)	10(1)
C9	4274(1)	5632(1)	857(1)	10(1)
C10	4810(1)	7789(1)	2428(1)	17(1)
C11	8336(1)	5097(1)	1520(1)	16(1)
C12	4756(1)	2406(1)	500(1)	13(1)
C13	2108(1)	4411(1)	384(1)	13(1)

Table 3. Bond lengths [Å] and angles [°] for sbudh02.

O(1)-C(1)	1.2160(10)	C(11)-H(11A)	1.003(16)
O(2)-C(4)	1.2127(10)	C(12)-H(12A)	0.967(15)
O(3)-C(6)	1.2241(10)	C(12)-H(12B)	1.010(13)
O(4)-C(12)	1.4155(11)	C(13)-H(13A)	0.946(13)
O(4)-D(4)	0.907(19)	C(13)-H(13B)	1.021(14)
O(5)-C(13)	1.4243(11)	C(12)-O(4)-D(4)	109.2(12)
O(5)-D(5)	0.927(19)	C(13)-O(5)-D(5)	109.9(11)
N(1)-C(1)	1.3797(10)	C(1)-N(1)-C(4)	113.37(7)
N(1)-C(4)	1.3853(11)	C(1)-N(1)-C(10)	122.36(7)
N(1)-C(10)	1.4507(11)	C(4)-N(1)-C(10)	123.83(7)
N(2)-C(9)	1.4671(10)	C(9)-N(2)-C(5)	103.08(6)
N(2)-C(5)	1.4683(10)	C(9)-N(2)-D(2)	112.9(9)
N(2)-D(2)	0.856(14)	C(5)-N(2)-D(2)	109.2(9)
C(1)-C(2)	1.5096(11)	O(1)-C(1)-N(1)	124.01(7)
C(2)-H(2)	1.004(14)	O(1)-C(1)-C(2)	127.79(7)
C(2)-C(3)	1.5342(11)	N(1)-C(1)-C(2)	108.19(6)
C(2)-C(5)	1.5874(11)	H(2)-C(2)-C(1)	109.9(8)
C(3)-H(3)	0.966(15)	H(2)-C(2)-C(3)	113.9(8)
C(3)-C(4)	1.5205(11)	C(1)-C(2)-C(3)	104.94(6)
C(3)-C(9)	1.5562(11)	H(2)-C(2)-C(5)	111.3(8)
C(5)-C(11)	1.5139(11)	C(1)-C(2)-C(5)	112.69(6)
C(5)-C(6)	1.5312(11)	C(3)-C(2)-C(5)	103.92(6)
C(6)-C(7)	1.4836(11)	H(3)-C(3)-C(4)	107.9(9)
C(7)-C(8)	1.3549(11)	H(3)-C(3)-C(2)	114.4(9)
C(7)-C(12)	1.5063(11)	C(4)-C(3)-C(2)	104.22(6)
C(8)-C(13)	1.5042(11)	H(3)-C(3)-C(9)	112.6(9)
C(8)-C(9)	1.5150(11)	C(4)-C(3)-C(9)	113.98(6)
C(9)-H(9)	0.953(13)	C(2)-C(3)-C(9)	103.53(6)
C(10)-H(10A)	0.965(17)	O(2)-C(4)-N(1)	124.03(8)
C(10)-H(10C)	0.960(15)	O(2)-C(4)-C(3)	127.77(8)
C(10)-H(10B)	0.972(17)	N(1)-C(4)-C(3)	108.19(7)
C(11)-H(11B)	0.960(16)	N(2)-C(5)-C(11)	112.16(7)
C(11)-H(11C)	1.006(17)	N(2)-C(5)-C(6)	105.56(6)

C(11)-C(5)-C(6)	111.55(6)	H(10A)-C(10)-N(1)	104.5(9)
N(2)-C(5)-C(2)	105.60(6)	H(10C)-C(10)-N(1)	108.1(9)
C(11)-C(5)-C(2)	116.21(7)	H(10B)-C(10)-N(1)	111.1(10)
C(6)-C(5)-C(2)	104.93(6)	H(11B)-C(11)-H(11C)	109.2(13)
O(3)-C(6)-C(7)	122.33(7)	H(11B)-C(11)-H(11A)	110.3(13)
O(3)-C(6)-C(5)	120.41(7)	H(11C)-C(11)-H(11A)	104.7(13)
C(7)-C(6)-C(5)	117.02(6)	H(11B)-C(11)-C(5)	110.6(9)
C(8)-C(7)-C(6)	117.67(7)	H(11C)-C(11)-C(5)	108.7(10)
C(8)-C(7)-C(12)	127.95(7)	H(11A)-C(11)-C(5)	113.1(9)
C(6)-C(7)-C(12)	114.04(7)	H(12A)-C(12)-H(12B)	106.5(12)
C(7)-C(8)-C(13)	125.32(7)	H(12A)-C(12)-O(4)	111.4(9)
C(7)-C(8)-C(9)	119.67(7)	H(12B)-C(12)-O(4)	108.8(8)
C(13)-C(8)-C(9)	114.84(6)	H(12A)-C(12)-C(7)	109.8(9)
H(9)-C(9)-N(2)	111.1(8)	H(12B)-C(12)-C(7)	108.0(8)
H(9)-C(9)-C(8)	111.2(8)	O(4)-C(12)-C(7)	112.10(7)
N(2)-C(9)-C(8)	109.13(6)	H(13A)-C(13)-H(13B)	112.9(11)
H(9)-C(9)-C(3)	113.3(8)	H(13A)-C(13)-O(5)	110.4(8)
N(2)-C(9)-C(3)	104.23(6)	H(13B)-C(13)-O(5)	105.3(8)
C(8)-C(9)-C(3)	107.60(6)	H(13A)-C(13)-C(8)	109.4(8)
H(10A)-C(10)-H(10C)	111.3(13)	H(13B)-C(13)-C(8)	106.8(8)
H(10A)-C(10)-H(10B)	112.5(14)	O(5)-C(13)-C(8)	112.02(7)
H(10C)-C(10)-H(10B)	109.2(13)		

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for sbudh02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	22(1)	18(1)	12(1)	-1(1)	-4(1)	2(1)
O2	31(1)	18(1)	19(1)	-5(1)	-7(1)	12(1)
O3	22(1)	12(1)	21(1)	-2(1)	-5(1)	6(1)
O4	28(1)	15(1)	20(1)	-6(1)	-9(1)	2(1)
O5	16(1)	17(1)	12(1)	-1(1)	0(1)	5(1)
N1	16(1)	11(1)	11(1)	-3(1)	-1(1)	1(1)
N2	12(1)	8(1)	12(1)	0(1)	0(1)	-1(1)
C1	15(1)	12(1)	10(1)	-1(1)	0(1)	0(1)
C2	14(1)	10(1)	10(1)	0(1)	0(1)	0(1)
C3	12(1)	12(1)	10(1)	-2(1)	0(1)	1(1)
C4	15(1)	14(1)	12(1)	-3(1)	-1(1)	3(1)
C5	11(1)	9(1)	11(1)	-1(1)	0(1)	0(1)
C6	12(1)	10(1)	12(1)	-1(1)	0(1)	1(1)
C7	13(1)	9(1)	11(1)	-1(1)	0(1)	0(1)
C8	12(1)	10(1)	9(1)	-1(1)	0(1)	0(1)
C9	12(1)	9(1)	10(1)	-1(1)	-1(1)	1(1)
C10	22(1)	14(1)	15(1)	-6(1)	-1(1)	0(1)
C11	13(1)	17(1)	18(1)	-3(1)	-3(1)	0(1)
C12	16(1)	10(1)	14(1)	-3(1)	-1(1)	0(1)
C13	12(1)	15(1)	12(1)	-2(1)	-1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for sbudh02.

	x	y	z	U(eq)
H2	4683(18)	4277(12)	1852(5)	17(3)
H3	2502(19)	5329(12)	1457(5)	20(3)
H9	3819(16)	6229(11)	652(5)	12(3)
H10A	4260(20)	7519(13)	2736(7)	32(4)
H10B	6000(20)	7997(14)	2484(6)	32(4)
H10C	4210(19)	8425(12)	2285(6)	23(3)
H11A	8570(20)	5899(14)	1628(7)	29(4)
H11B	8557(19)	4584(13)	1798(6)	25(4)
H11C	9180(20)	4948(14)	1237(6)	35(4)
H12A	5878(19)	2069(13)	469(6)	24(4)
H12B	4111(17)	1934(11)	758(5)	13(3)
H13A	1854(17)	3644(11)	308(5)	15(3)
H13B	1252(17)	4769(11)	630(5)	14(3)

Table 6. Torsion angles [°] for sbudh02.

C4-N1-C1-O1	-174.41(8)
C10-N1-C1-O1	-1.73(13)
C4-N1-C1-C2	6.38(9)
C10-N1-C1-C2	179.06(7)
O1-C1-C2-H2	47.9(8)
N1-C1-C2-H2	-132.9(8)
O1-C1-C2-C3	170.71(8)
N1-C1-C2-C3	-10.12(8)
O1-C1-C2-C5	-76.87(10)
N1-C1-C2-C5	102.30(7)
H2-C2-C3-H3	12.5(13)
C1-C2-C3-H3	-107.7(9)
C5-C2-C3-H3	133.8(9)
H2-C2-C3-C4	130.1(9)
C1-C2-C3-C4	9.85(8)
C5-C2-C3-C4	-108.66(7)
H2-C2-C3-C9	-110.5(9)
C1-C2-C3-C9	129.34(6)
C5-C2-C3-C9	10.82(7)
C1-N1-C4-O2	179.39(9)
C10-N1-C4-O2	6.83(14)
C1-N1-C4-C3	0.28(10)
C10-N1-C4-C3	-172.28(8)
H3-C3-C4-O2	-63.7(9)
C2-C3-C4-O2	174.35(9)
C9-C3-C4-O2	62.21(12)
H3-C3-C4-N1	115.4(9)
C2-C3-C4-N1	-6.58(9)
C9-C3-C4-N1	-118.72(7)
C9-N2-C5-C11	-165.44(6)
C9-N2-C5-C6	72.89(7)
C9-N2-C5-C2	-37.92(7)
H2-C2-C5-N2	138.9(9)
C1-C2-C5-N2	-97.08(7)
C3-C2-C5-N2	15.97(7)
H2-C2-C5-C11	-96.0(9)
C1-C2-C5-C11	27.96(9)
C3-C2-C5-C11	141.00(7)
H2-C2-C5-C6	27.7(9)
C1-C2-C5-C6	151.66(6)
C3-C2-C5-C6	-95.29(7)
N2-C5-C6-O3	148.75(8)
C11-C5-C6-O3	26.68(11)
C2-C5-C6-O3	-99.96(9)
N2-C5-C6-C7	-36.75(9)
C11-C5-C6-C7	-158.82(7)
C2-C5-C6-C7	74.54(8)
O3-C6-C7-C8	168.92(8)
C5-C6-C7-C8	-5.46(11)
O3-C6-C7-C12	-4.83(11)
C5-C6-C7-C12	-179.22(7)
C6-C7-C8-C13	-164.15(7)
C12-C7-C8-C13	8.61(13)
C6-C7-C8-C9	10.80(11)
C12-C7-C8-C9	-176.44(7)
C5-N2-C9-H9	167.6(8)
C5-N2-C9-C8	-69.45(7)
C5-N2-C9-C3	45.27(7)
C7-C8-C9-H9	149.7(8)
C13-C8-C9-H9	-34.8(8)
C7-C8-C9-N2	26.86(10)
C13-C8-C9-N2	-157.68(6)
C7-C8-C9-C3	-85.66(9)
C13-C8-C9-C3	89.80(8)
H3-C3-C9-H9	80.5(13)
C4-C3-C9-H9	-42.8(8)

C2-C3-C9-H9	-155.3(8)	C6-C5-C11-H11C	55.7(10)
H3-C3-C9-N2	-158.6(9)	C2-C5-C11-H11C	175.9(10)
C4-C3-C9-N2	78.09(8)	N2-C5-C11-H11A	53.3(11)
C2-C3-C9-N2	-34.46(7)	C6-C5-C11-H11A	171.5(11)
H3-C3-C9-C8	-42.8(9)	C2-C5-C11-H11A	-68.3(11)
C4-C3-C9-C8	-166.11(6)	C8-C7-C12-H12A	153.1(10)
C2-C3-C9-C8	81.33(7)	C6-C7-C12-H12A	-33.9(10)
C1-N1-C10-H10A	-64.5(11)	C8-C7-C12-H12B	-91.2(8)
C4-N1-C10-H10A	107.4(11)	C6-C7-C12-H12B	81.8(8)
C1-N1-C10-H10C	176.9(10)	C8-C7-C12-O4	28.68(12)
C4-N1-C10-H10C	-11.2(10)	C6-C7-C12-O4	-158.34(7)
C1-N1-C10-H10B	57.0(11)	C7-C8-C13-H13A	4.7(9)
C4-N1-C10-H10B	-131.1(11)	C9-C8-C13-H13A	-170.5(9)
N2-C5-C11-H11B	177.6(10)	C7-C8-C13-H13B	127.2(8)
C6-C5-C11-H11B	-64.2(10)	C9-C8-C13-H13B	-48.0(8)
C2-C5-C11-H11B	56.0(10)	C7-C8-C13-O5	-118.02(9)
N2-C5-C11-H11C	-62.5(10)	C9-C8-C13-O5	66.82(9)

Table 7. Hydrogen bonds and close contacts for sbudh02 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O4-D4...O5#1	0.907(19)	1.91(2)	2.8011(10)	168.0(18)
O5-D5...N2#2	0.927(19)	1.87(2)	2.7842(10)	171.0(17)
N2-D2...O3#3	0.856(14)	2.195(14)	3.0389(9)	168.8(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,z   #2 -x+1,-y+1,-z   #3 -x+3/2,y+1/2,z