Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Preparation of a ABC Tricyclic Model Representative of the Cylindrospermopsin Alkaloids via a Biomimetically Inspired Pathway

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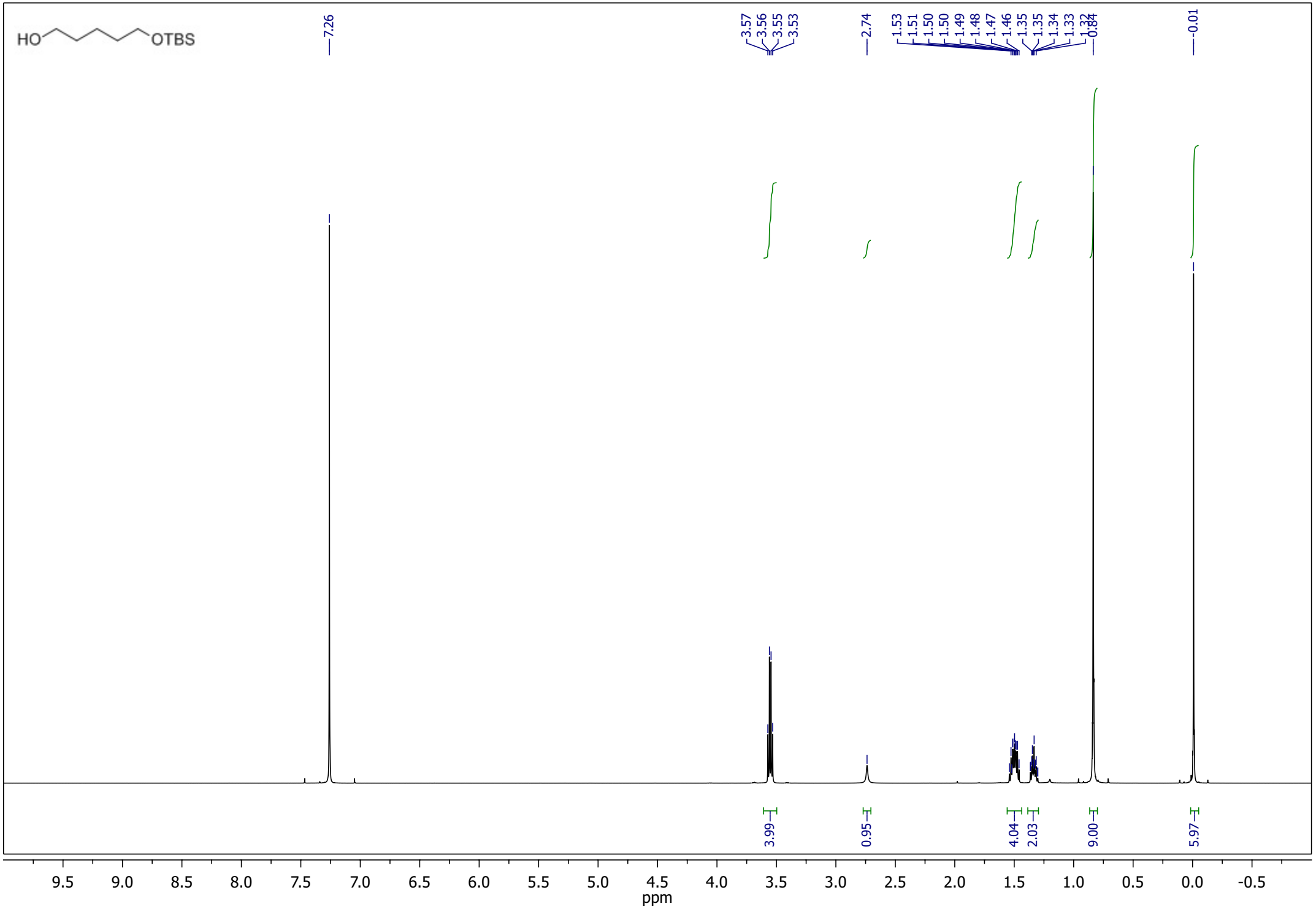
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1.48
1.47
1.46
1.35
1.35
1.34
1.33
1.32
0.84
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0.95
4.04
2.03
9.00
5.97
9.5
9.0
8.5
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6.0
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5.0
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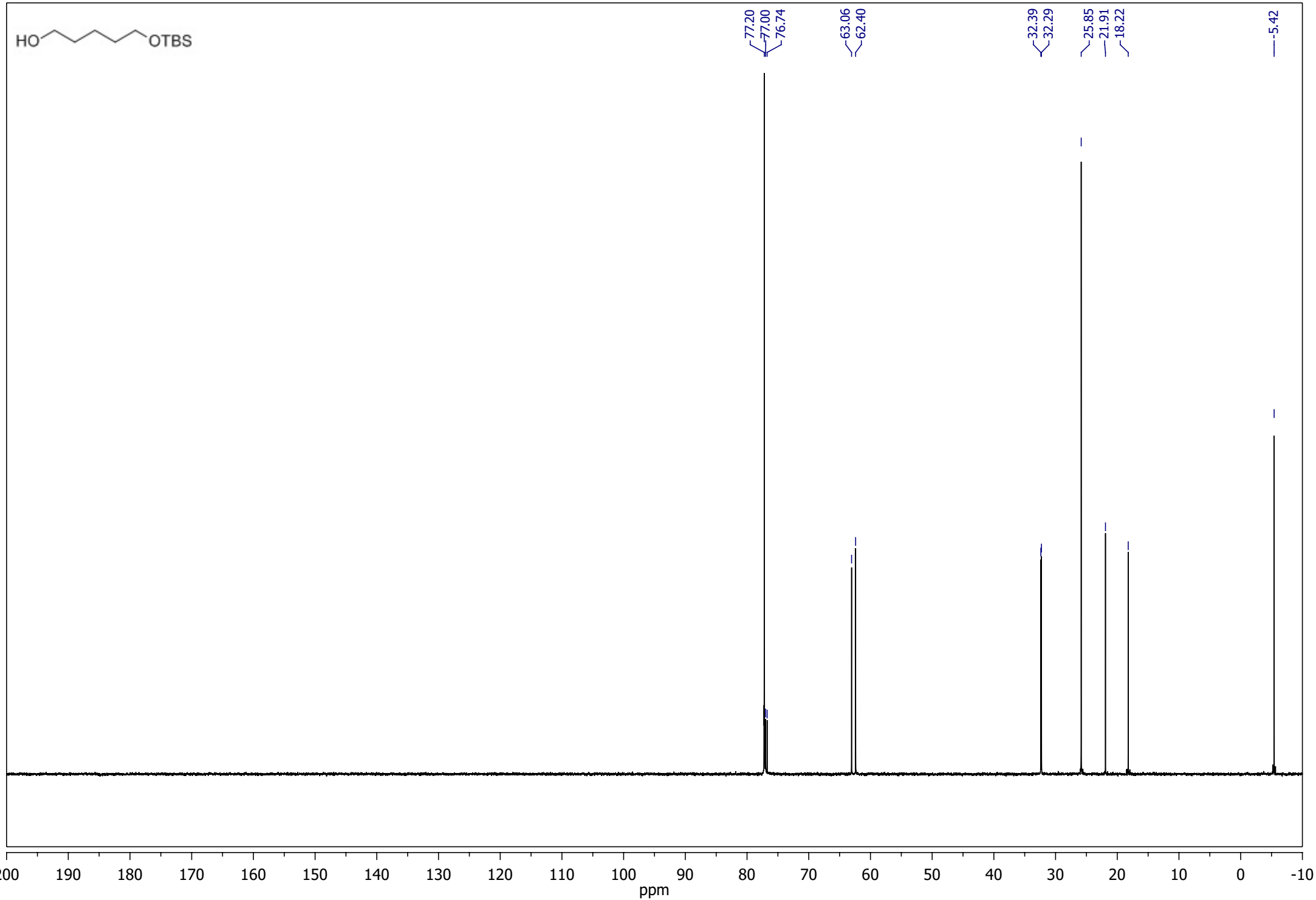
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200
190
180
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50
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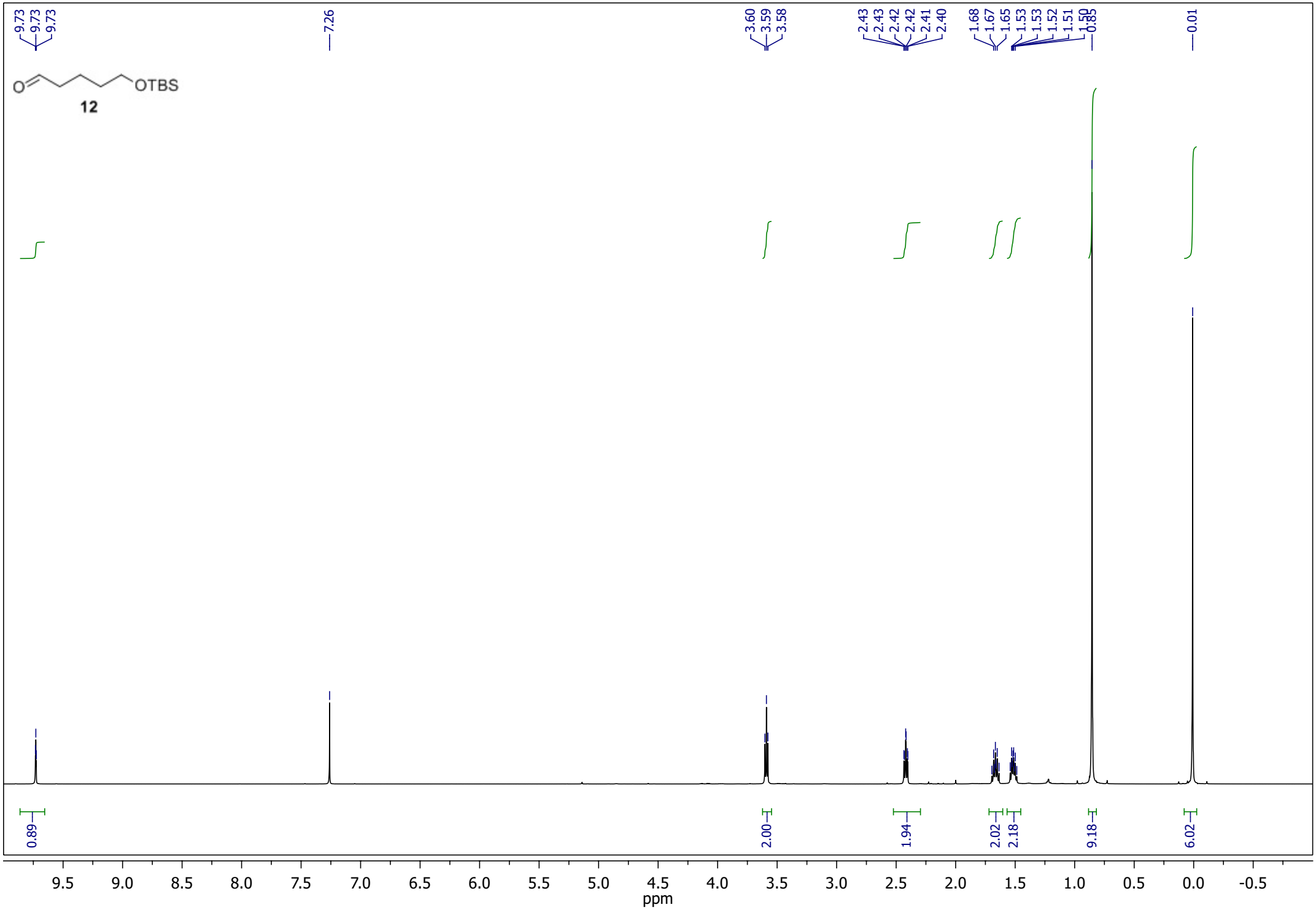
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1.68
1.67
1.65
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1.53
1.52
1.51
1.50
0.85
0.01
O
OTBS
12
0.89
2.00
1.94
2.02
2.18
9.18
6.02
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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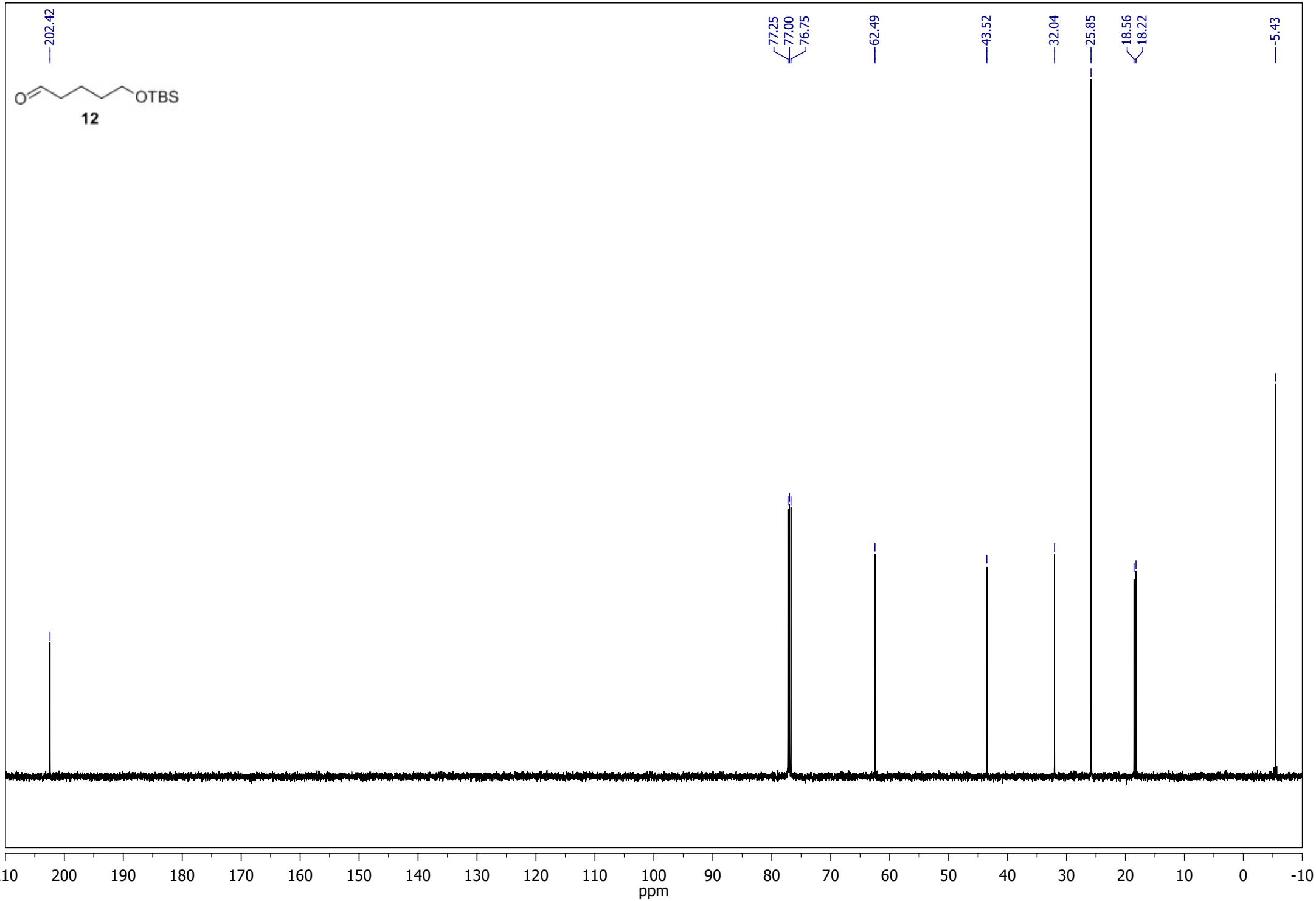
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12
210
200
190
180
170
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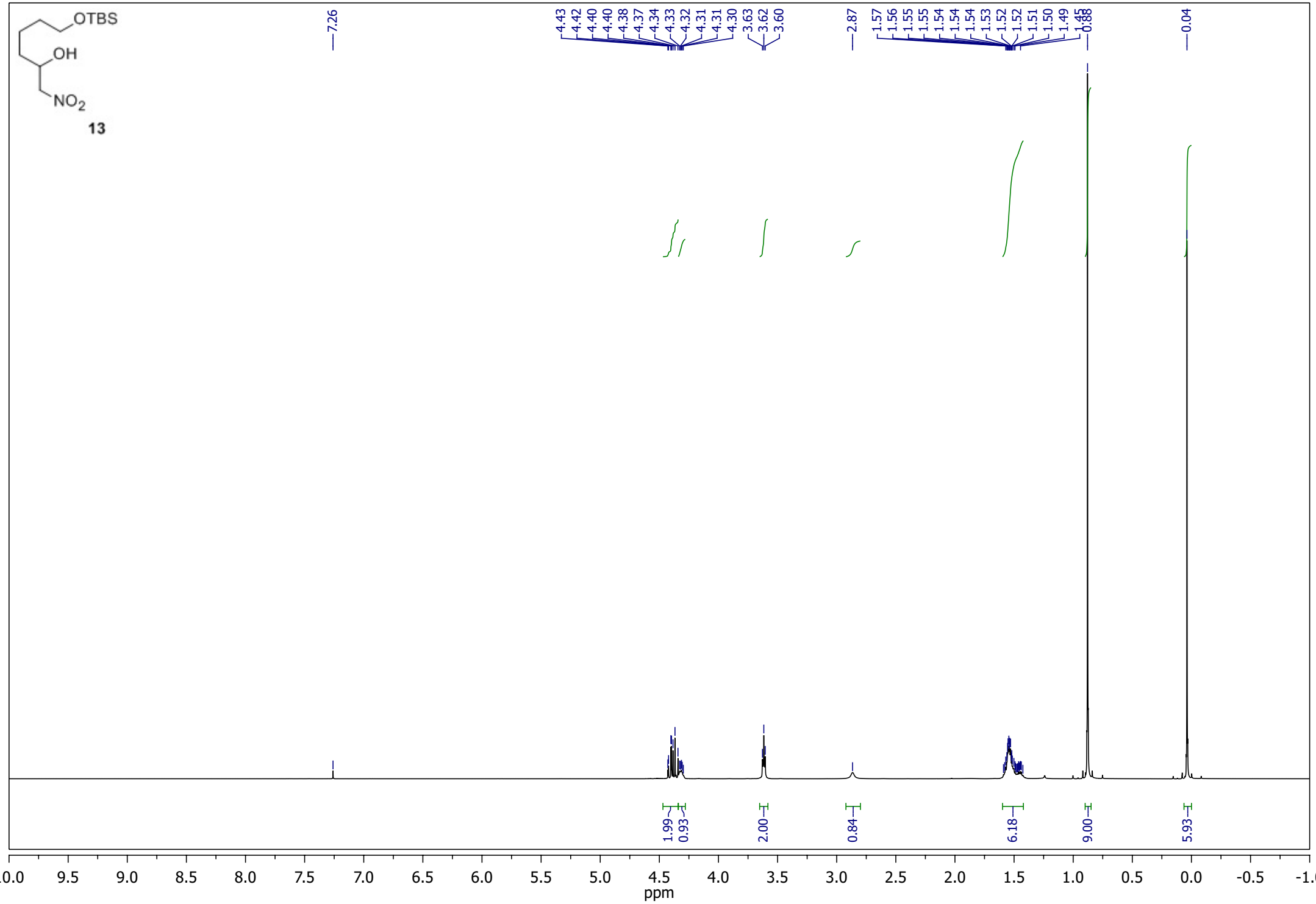
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4.40
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4.32
4.31
4.31
4.30
3.63
3.62
3.60
2.87
1.57
1.56
1.55
1.55
1.54
1.54
1.53
1.52
1.52
1.51
1.50
1.49
1.45
0.88
0.04
1.99
0.93
2.00
0.84
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9.00
5.93
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5.0
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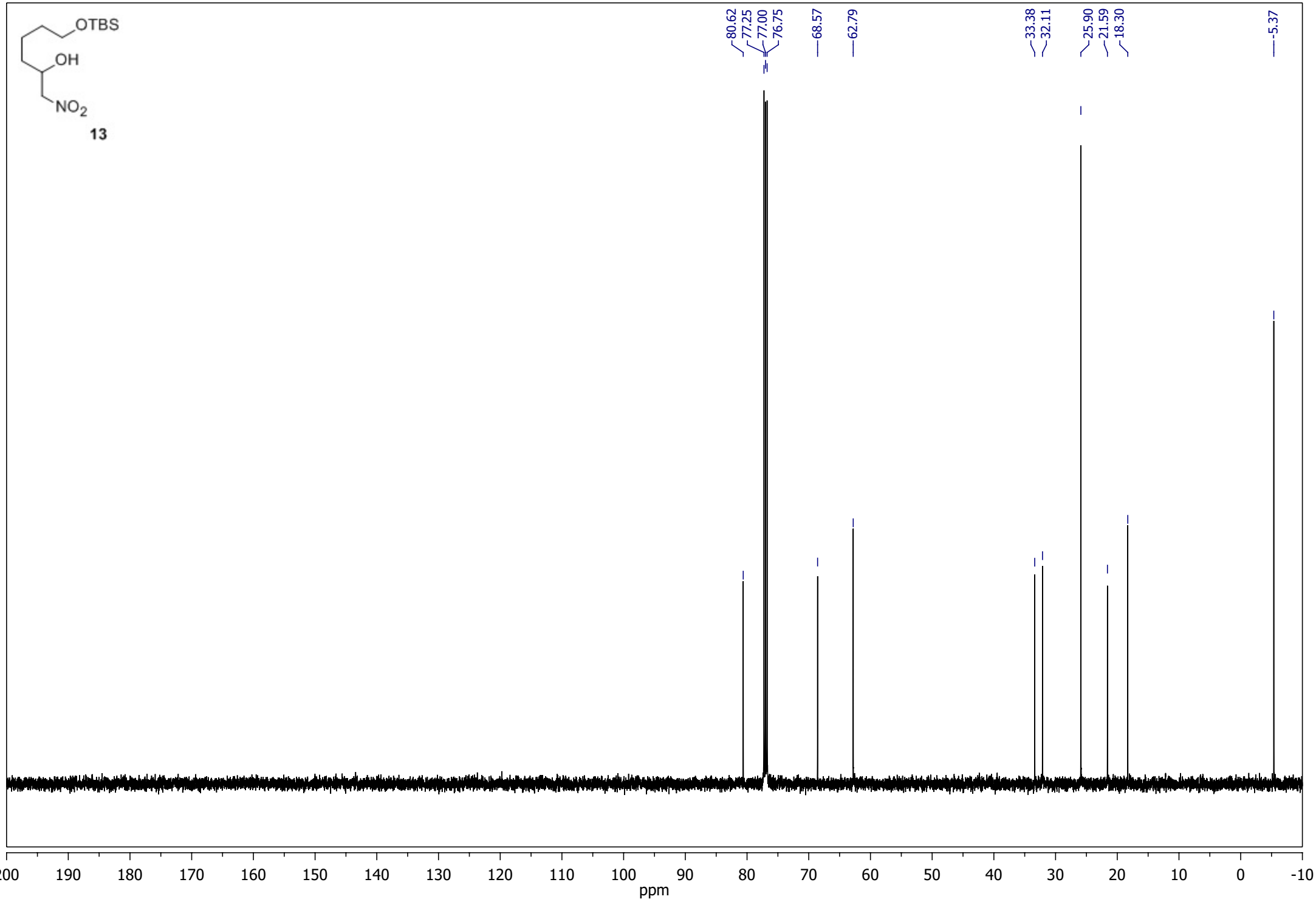
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180
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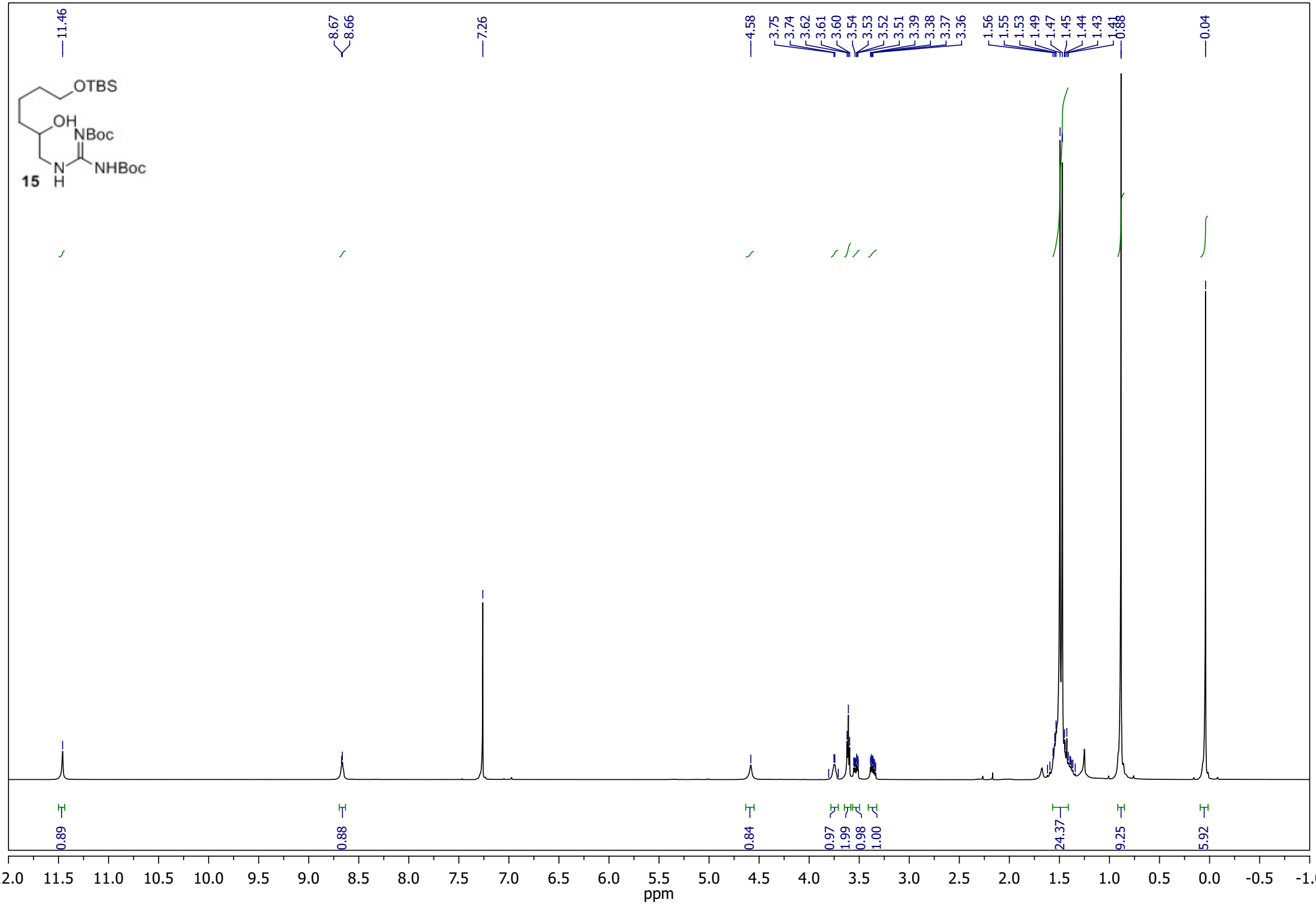
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3.37
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1.53
1.49
1.47
1.45
1.44
1.43
1.41
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0.04
OTBS
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NHBoc
N
H
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0.84
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0.98
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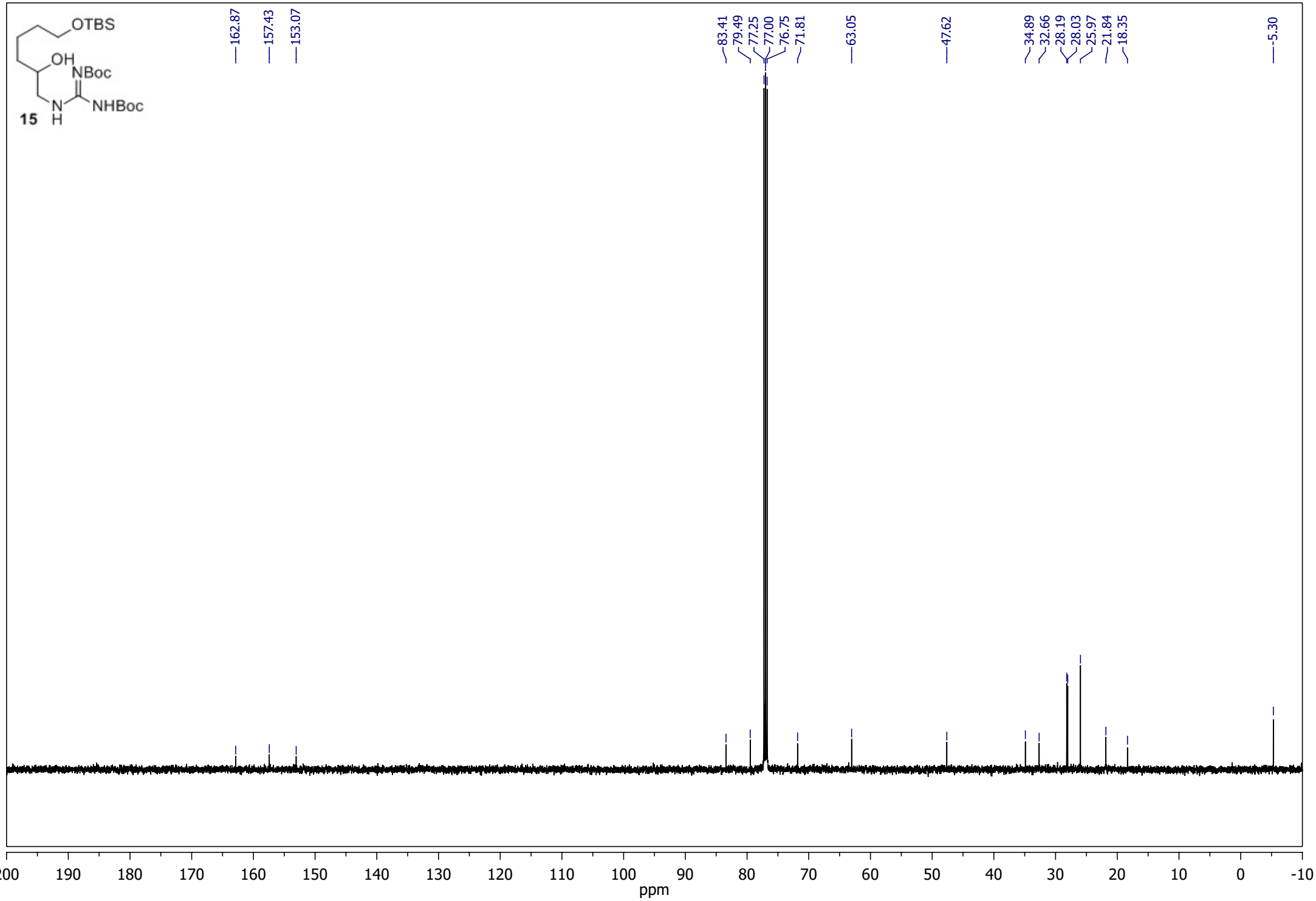
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32.66
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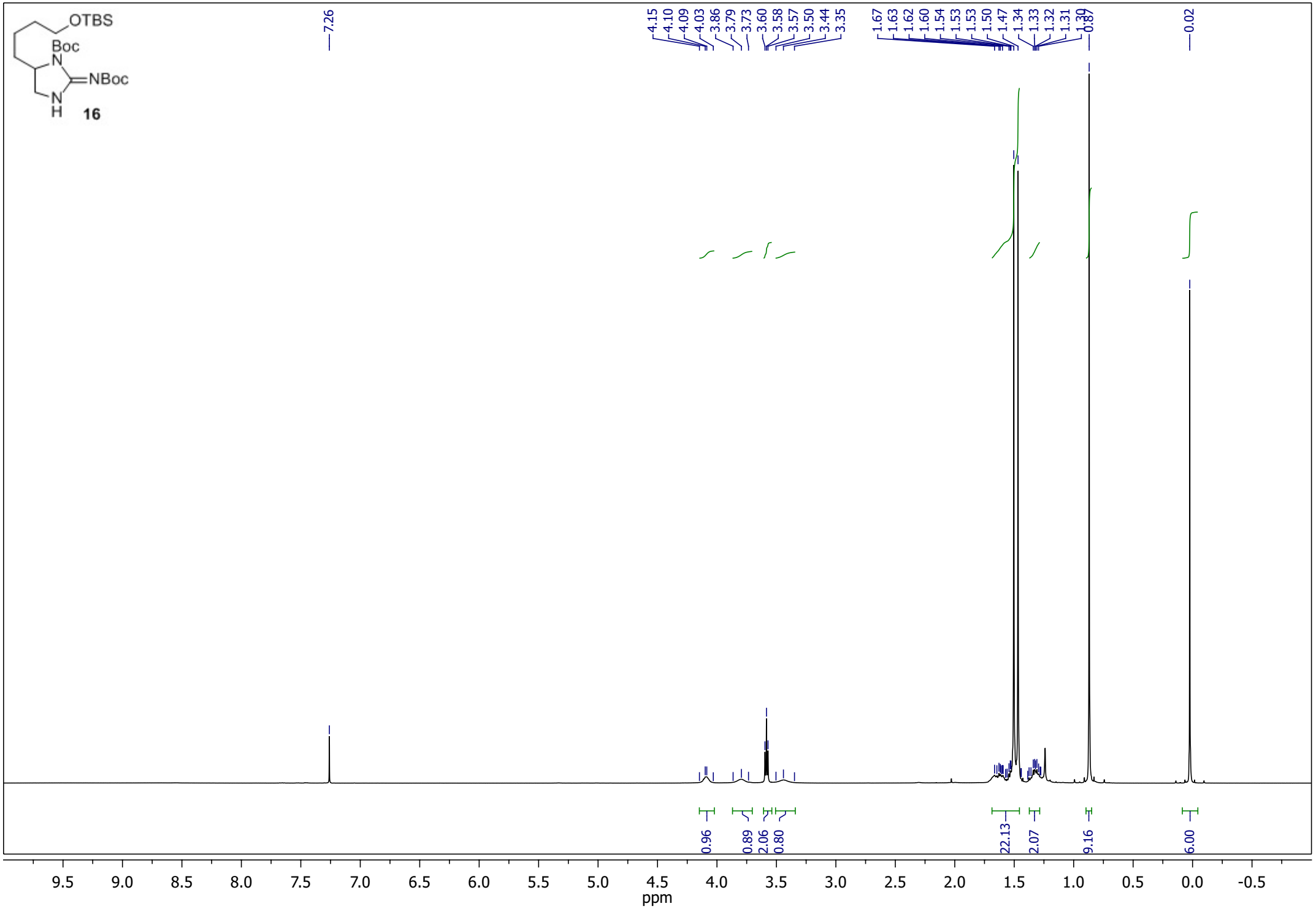
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1.62
1.60
1.54
1.53
1.53
1.50
1.47
1.34
1.33
1.32
1.31
1.30
0.87
0.02
0.96
0.89
2.06
0.80
22.13
2.07
9.16
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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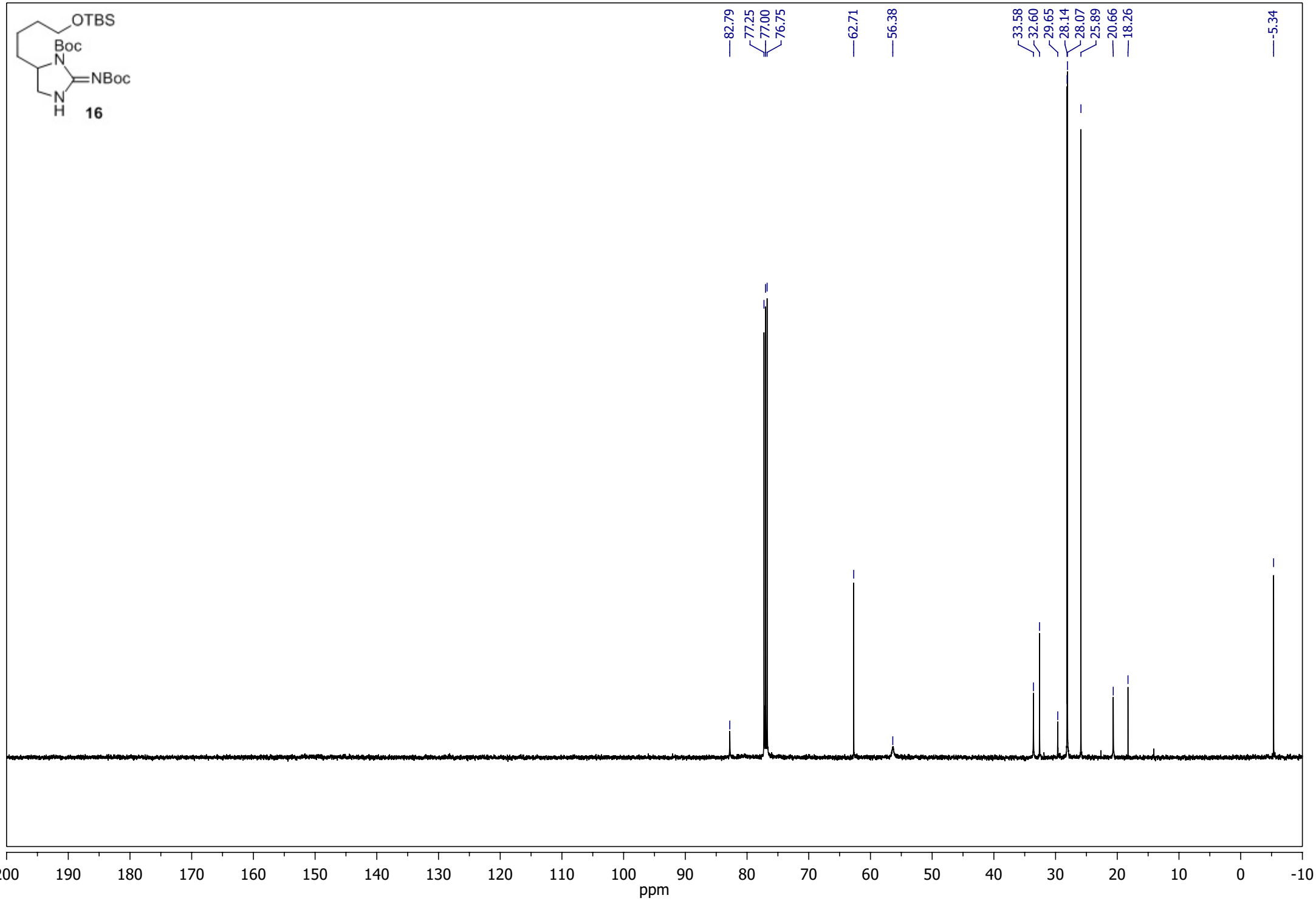
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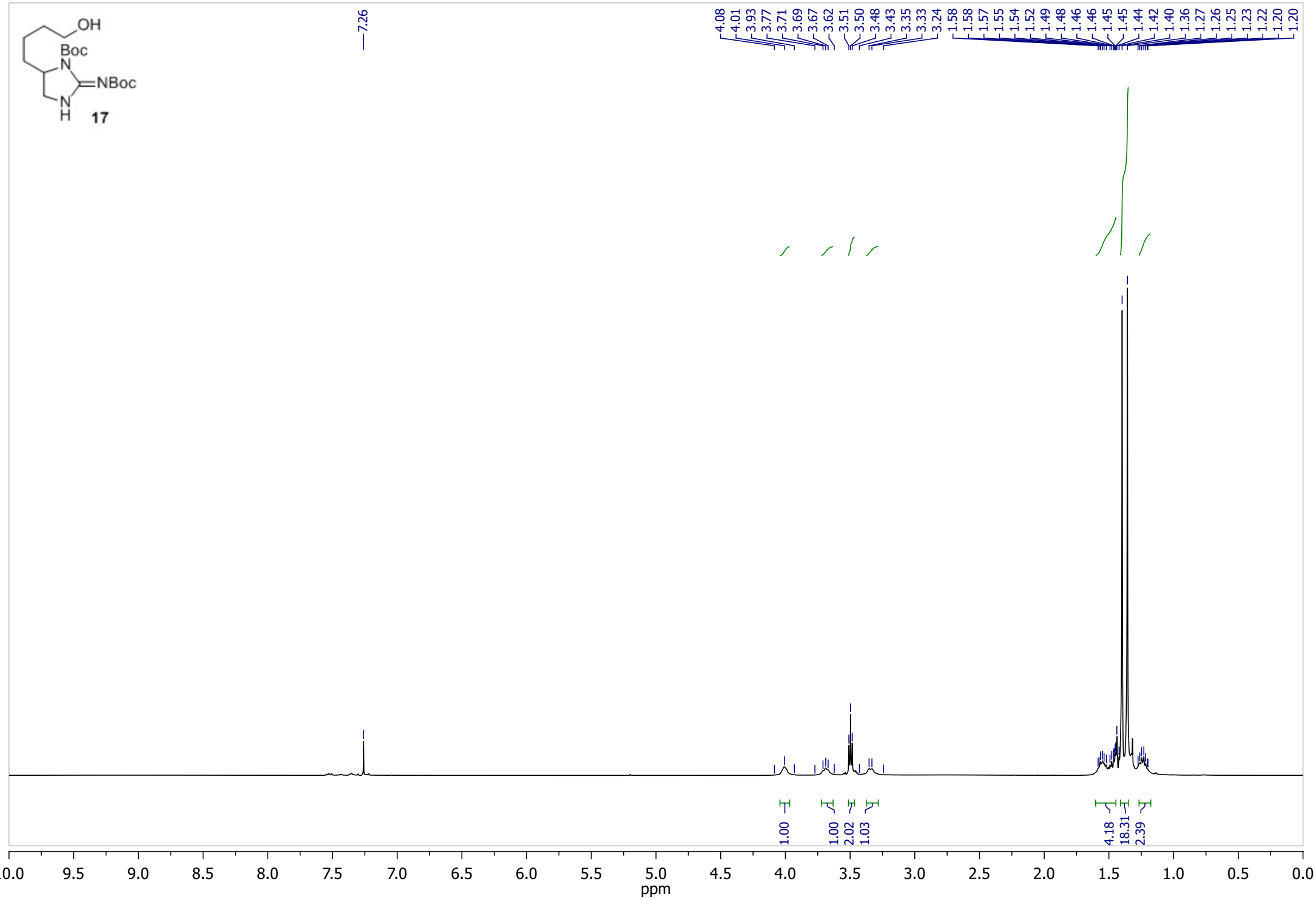
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1.55
1.54
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1.48
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1.46
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1.40
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1.22
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1.20
1.00
1.00
2.02
1.03
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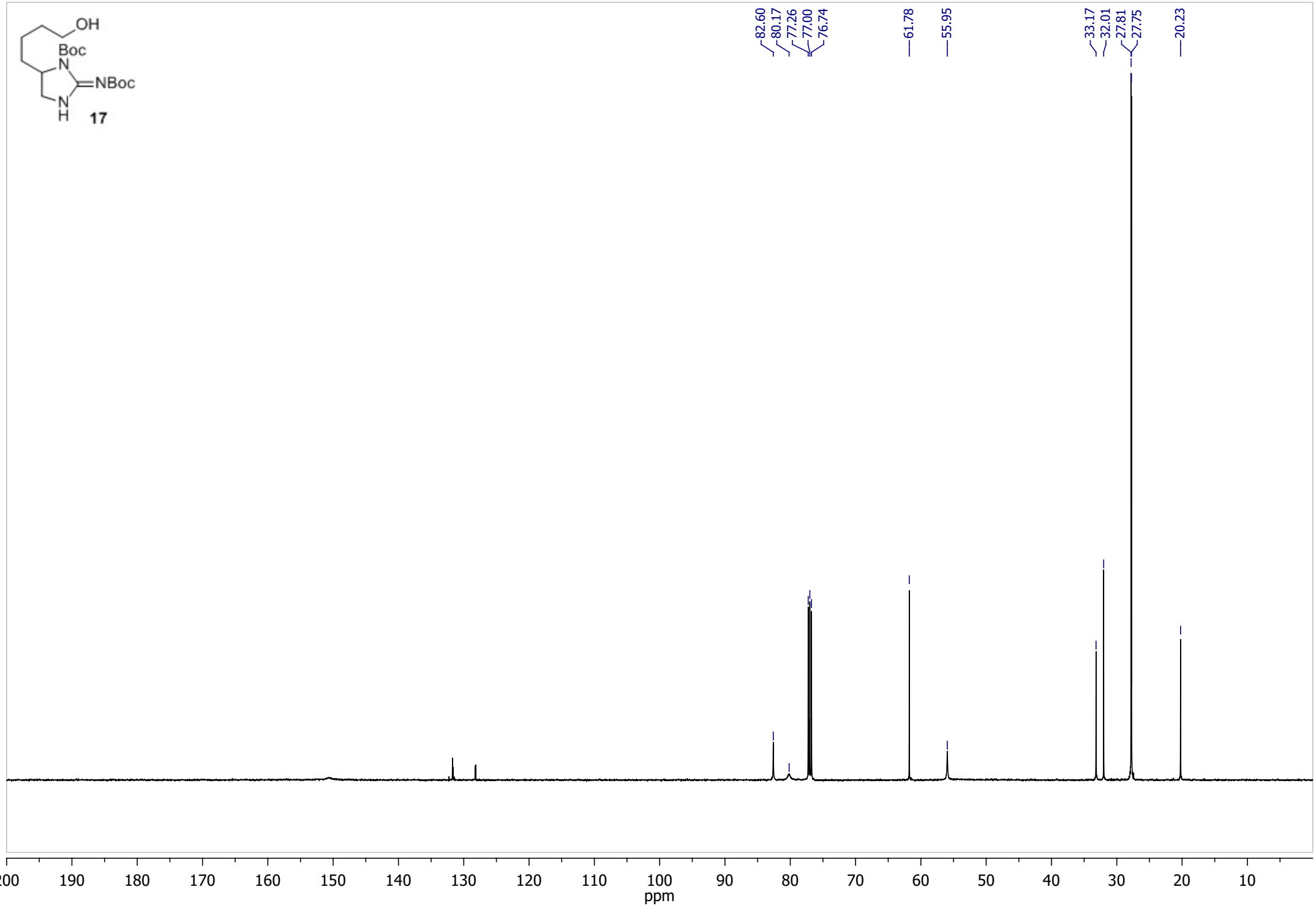
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H
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20.23
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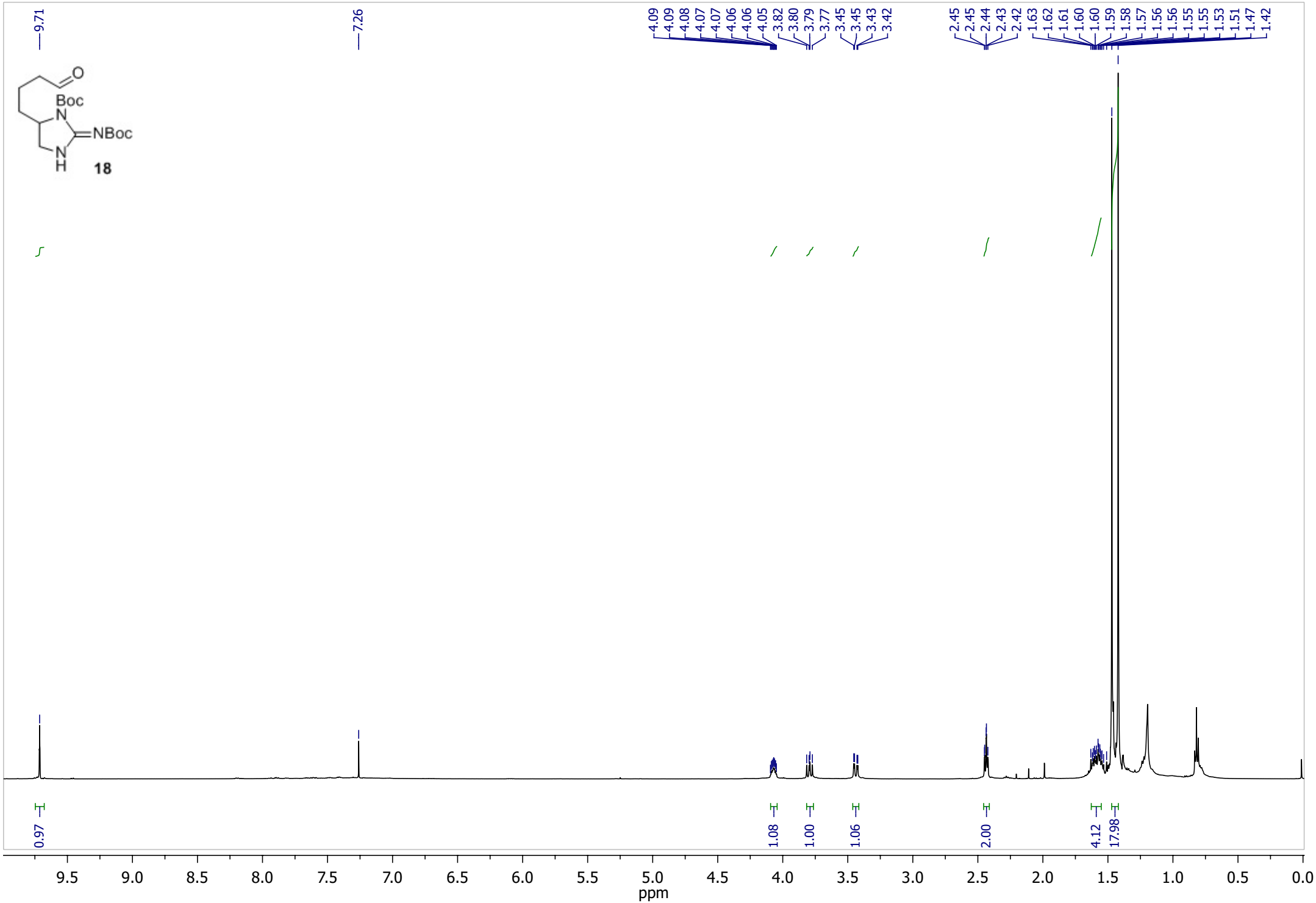
10
ppm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2.42
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1.56
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NBoc
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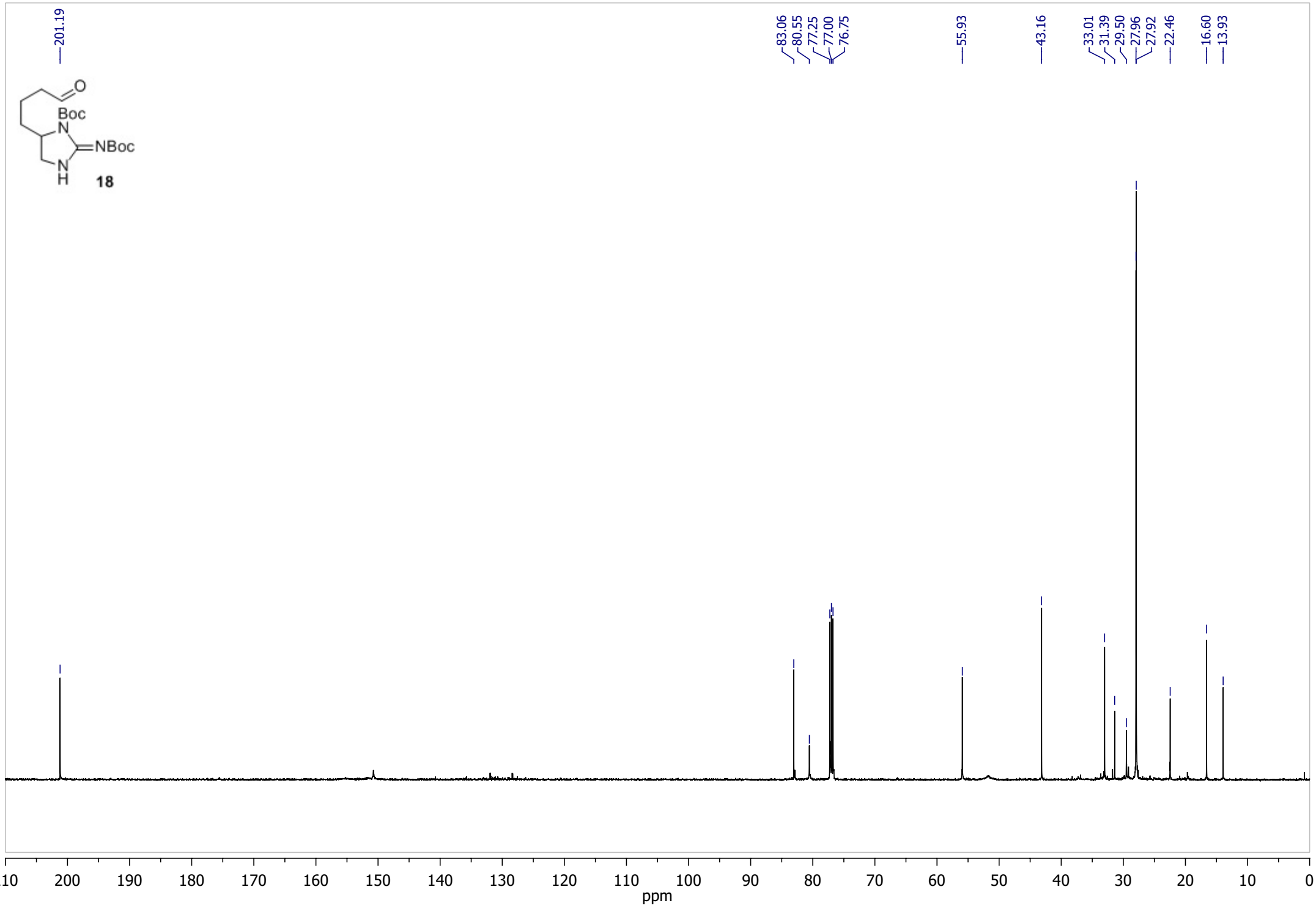
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22.46
16.60
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O
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NBoc
N
H
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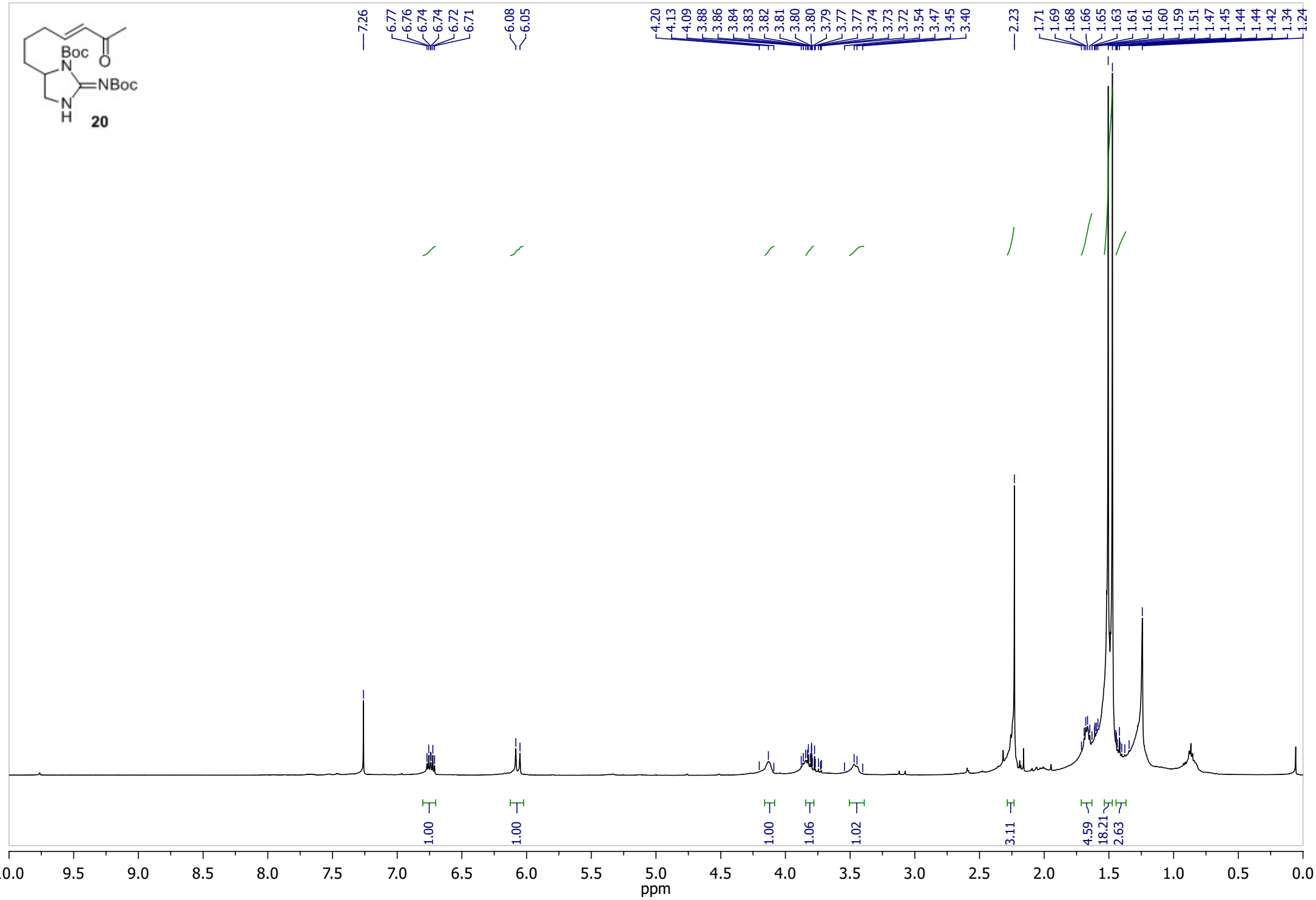
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1.63
1.61
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1.47
1.45
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1.00
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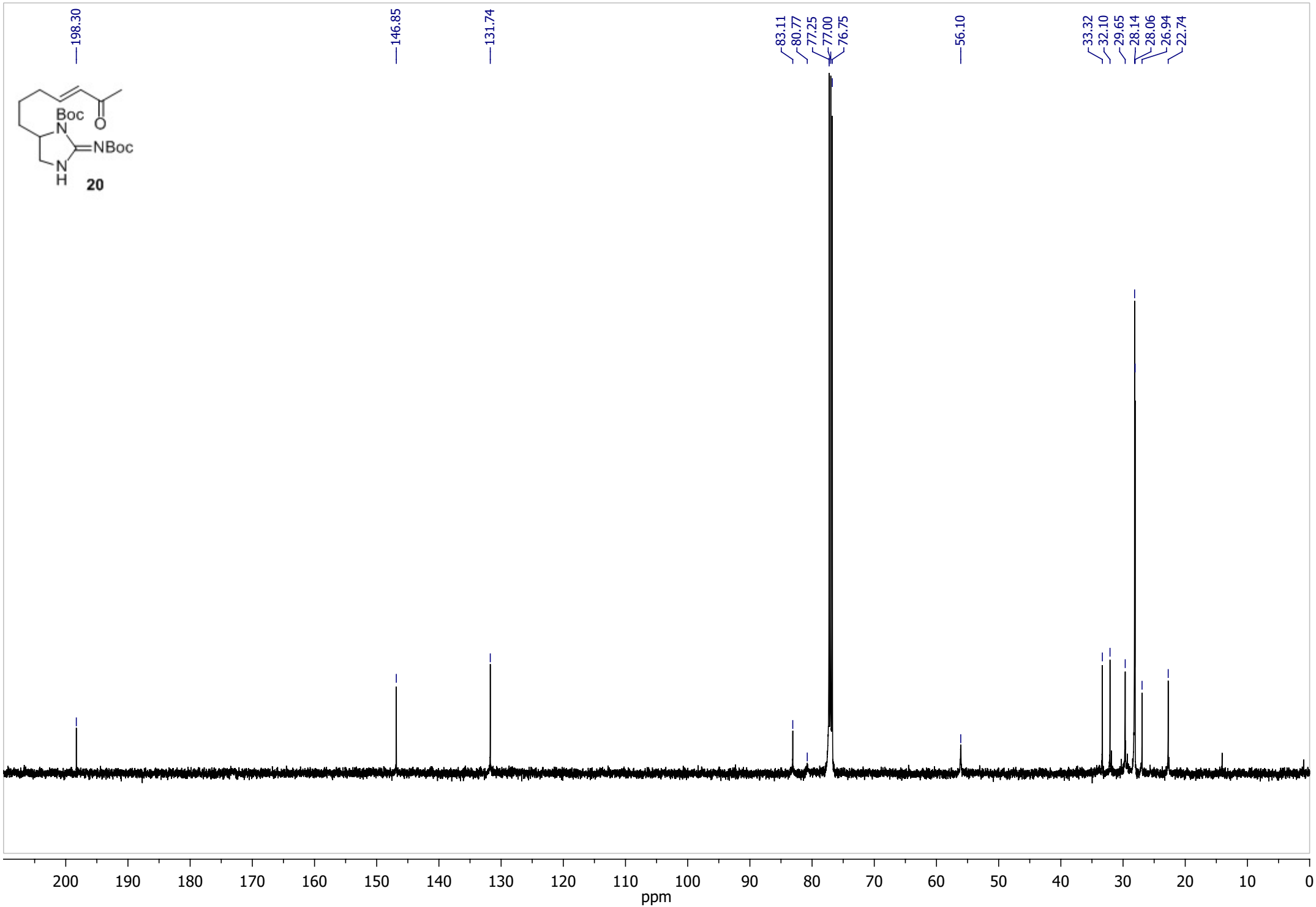
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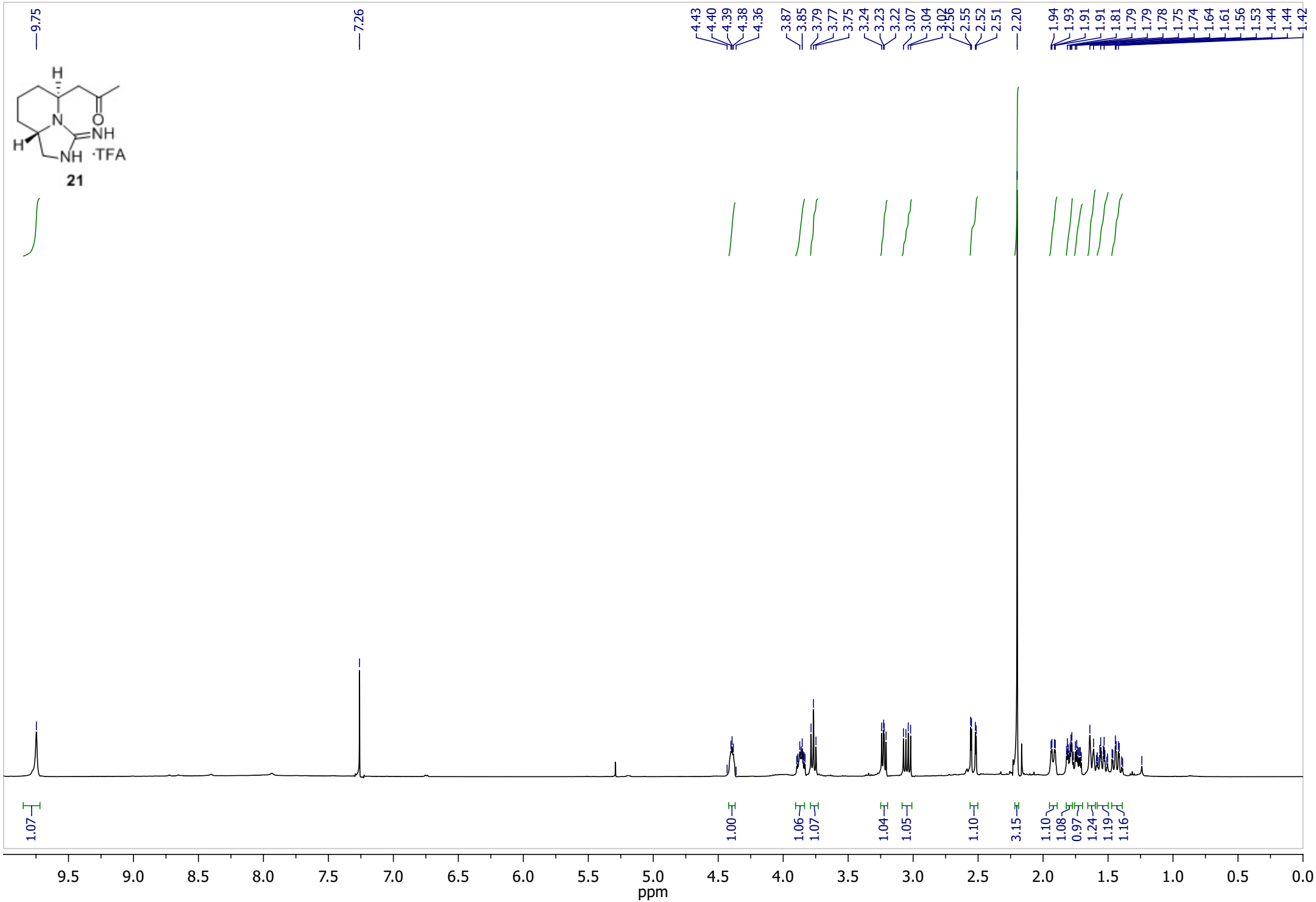
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O
NH
H
NH
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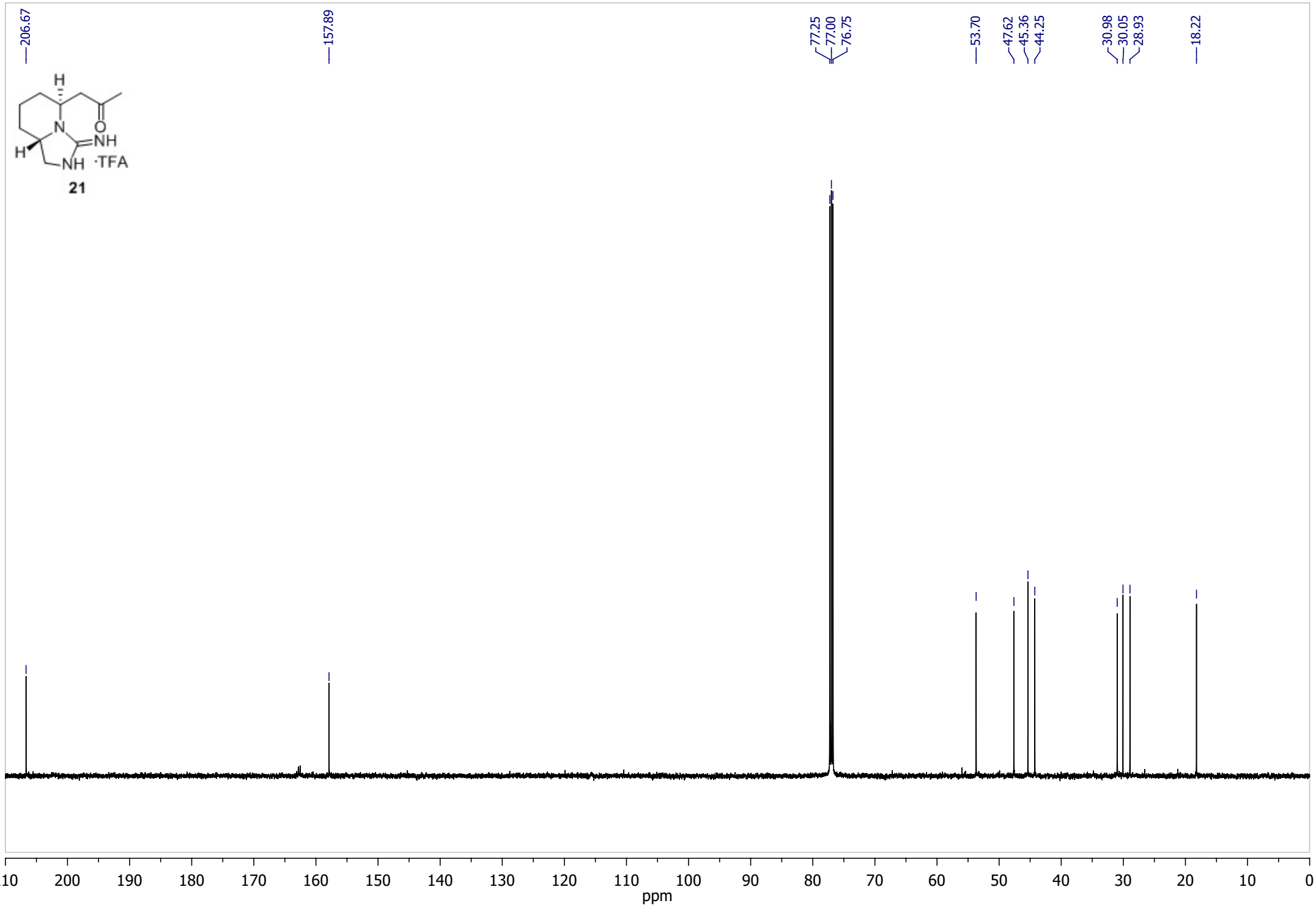
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30.05
28.93
18.22
H
N
O
NH
H
NH
·TFA
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200
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180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Table 1. Crystal data and structure refinement.

Identification code	**2009src1065 / DME-176-8-10**	
Empirical formula	$C_{12}H_{18}F_3N_3O_3$	
Formula weight	309.29	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*–1	
Unit cell dimensions	a = 7.9832(6) Å	α = 95.866(3)°
	b = 8.8773(7) Å	β = 107.215(4)°
	c = 12.1929(10) Å	γ = 114.500(4)°
Volume	725.49(10) Å^3	
Z	2	
Density (calculated)	1.416 Mg / m^3	
Absorption coefficient	0.127 mm^{-1}	
F(000)	324	
Crystal	Cut Blade; Colourless	
Crystal size	0.12 × 0.08 × 0.05 mm^3	
θ range for data collection	2.93 – 27.48°	
Index ranges	$-10 \le h \le 9$, $-11 \le k \le 11$, $-15 \le l \le 15$	
Reflections collected	12761	
Independent reflections	3301 [R_{int} = 0.0487]	
Completeness to θ = 27.48°	99.1 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.9937 and 0.9849	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3301 / 124 / 222	
Goodness-of-fit on F^2	1.151	
Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0792, *wR2* = 0.1219	
R indices (all data)	*R1* = 0.1279, *wR2* = 0.1416	
Largest diff. peak and hole	0.319 and –0.254 e Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426). S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** *ORTEP3 for Windows* (L. J. Farrugia, J. Appl. Crystallogr. 1997, 30, 565).

Special details:
All hydrogen atoms were fixed using a standard riding model.
The trifluoroacetate anion was partially disordered over 2 main sites.

Table 2. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
C1	4244(4)	2482(3)	5322(2)	31(1)	1
C2	6691(4)	3793(4)	4599(3)	40(1)	1
C3	7655(4)	3769(4)	5891(3)	35(1)	1
C4	8778(5)	2735(5)	6039(3)	49(1)	1
C5	9250(5)	2444(5)	7283(3)	53(1)	1
C6	7341(5)	1520(4)	7504(3)	47(1)	1
C7	6139(4)	2501(4)	7370(3)	35(1)	1
C8	7074(4)	4085(4)	8405(3)	36(1)	1
C9	5787(5)	4930(4)	8424(3)	41(1)	1
C10	6677(5)	6527(5)	9402(3)	52(1)	1
N1	5920(3)	2964(3)	6237(2)	32(1)	1
N2	4575(4)	2911(3)	4366(2)	40(1)	1
N3	2431(3)	1646(3)	5322(2)	35(1)	1
O1	4109(3)	4335(3)	7697(2)	56(1)	1
C11	–525(4)	1369(4)	2489(3)	33(1)	1
O11	1134(3)	2274(3)	2477(2)	45(1)	1
O12	–974(3)	638(3)	3245(2)	48(1)	1
C12	–2358(17)	1175(16)	1479(10)	46(1)	0.441(10)
F11	–3441(14)	1720(16)	1852(5)	86(3)	0.441(10)
F12	–1907(10)	1943(14)	672(8)	83(3)	0.441(10)
F13	–3638(18)	–435(12)	938(10)	81(4)	0.441(10)
C212	–2217(14)	1185(13)	1387(8)	46(1)	0.559(10)
F211	–2359(11)	2600(8)	1443(8)	102(3)	0.559(10)
F212	–1949(10)	877(13)	386(5)	91(2)	0.559(10)
F213	–3920(11)	–103(12)	1200(8)	92(3)	0.559(10)

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

C1–N3	1.324(3)	C8–C9	1.506(4)
C1–N1	1.327(4)	C8–H8A	0.9900
C1–N2	1.328(4)	C8–H8B	0.9900
C2–N2	1.456(4)	C9–O1	1.214(4)
C2–C3	1.542(4)	C9–C10	1.502(5)
C2–H2A	0.9900	C10–H10A	0.9800
C2–H2B	0.9900	C10–H10B	0.9800
C3–N1	1.481(3)	C10–H10C	0.9800
C3–C4	1.517(4)	N2–H2	0.8800
C3–H3	1.0000	N3–H3A	0.8800
C4–C5	1.528(5)	N3–H3B	0.8800
C4–H4A	0.9900	C11–O12	1.234(3)
C4–H4B	0.9900	C11–O11	1.237(3)
C5–C6	1.523(5)	C11–C212	1.535(9)
C5–H5A	0.9900	C11–C12	1.540(11)
C5–H5B	0.9900	C12–F13	1.311(11)
C6–C7	1.529(4)	C12–F11	1.312(12)
C6–H6A	0.9900	C12–F12	1.305(11)
C6–H6B	0.9900	C212–F213	1.297(9)
C7–N1	1.463(3)	C212–F211	1.305(10)
C7–C8	1.528(4)	C212–F212	1.321(10)
C7–H7	1.0000		

N3–C1–N1	125.6(3)	N1–C7–H7	108.2
N3–C1–N2	122.4(3)	C8–C7–H7	108.2
N1–C1–N2	112.0(2)	C6–C7–H7	108.2
N2–C2–C3	103.3(2)	C9–C8–C7	114.7(2)
N2–C2–H2A	111.1	C9–C8–H8A	108.6
C3–C2–H2A	111.1	C7–C8–H8A	108.6
N2–C2–H2B	111.1	C9–C8–H8B	108.6
C3–C2–H2B	111.1	C7–C8–H8B	108.6
H2A–C2–H2B	109.1	H8A–C8–H8B	107.6
N1–C3–C4	109.7(2)	O1–C9–C10	121.9(3)
N1–C3–C2	102.5(2)	O1–C9–C8	121.7(3)
C4–C3–C2	114.9(3)	C10–C9–C8	116.4(3)
N1–C3–H3	109.8	C9–C10–H10A	109.5
C4–C3–H3	109.8	C9–C10–H10B	109.5
C2–C3–H3	109.8	H10A–C10–H10B	109.5
C3–C4–C5	110.5(3)	C9–C10–H10C	109.5
C3–C4–H4A	109.5	H10A–C10–H10C	109.5
C5–C4–H4A	109.5	H10B–C10–H10C	109.5
C3–C4–H4B	109.5	C1–N1–C7	127.3(2)
C5–C4–H4B	109.5	C1–N1–C3	110.6(2)
H4A–C4–H4B	108.1	C7–N1–C3	120.9(2)
C6–C5–C4	110.1(3)	C1–N2–C2	111.3(2)
C6–C5–H5A	109.6	C1–N2–H2	124.3
C4–C5–H5A	109.6	C2–N2–H2	124.3
C6–C5–H5B	109.6	C1–N3–H3A	120.0
C4–C5–H5B	109.6	C1–N3–H3B	120.0
H5A–C5–H5B	108.2	H3A–N3–H3B	120.0
C5–C6–C7	112.5(3)	O12–C11–O11	129.6(3)
C5–C6–H6A	109.1	O12–C11–C212	117.8(4)
C7–C6–H6A	109.1	O11–C11–C212	112.6(4)
C5–C6–H6B	109.1	O12–C11–C12	112.1(5)
C7–C6–H6B	109.1	O11–C11–C12	118.2(5)
H6A–C6–H6B	107.8	C212–C11–C12	6.7(8)
N1–C7–C8	111.1(2)	F13–C12–F11	101.7(9)
N1–C7–C6	108.4(2)	F13–C12–F12	107.6(11)
C8–C7–C6	112.6(2)	F11–C12–F12	108.4(10)

F13–C12–C11	112.2(10)	F211–C212–F212	105.6(8)
F11–C12–C11	113.4(8)	F213–C212–C11	113.9(8)
F12–C12–C11	112.8(8)	F211–C212–C11	110.7(7)
F213–C212–F211	110.3(9)	F212–C212–C11	113.1(7)
F213–C212–F212	102.8(8)		

Symmetry transformations used to generate equivalent atoms:

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

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	34(2)	27(2)	33(2)	9(1)	14(1)	14(1)
C2	38(2)	42(2)	45(2)	16(2)	23(2)	18(2)
C3	30(2)	33(2)	46(2)	13(1)	20(1)	14(1)
C4	49(2)	53(2)	61(2)	18(2)	29(2)	30(2)
C5	49(2)	65(2)	63(2)	25(2)	22(2)	40(2)
C6	52(2)	43(2)	51(2)	21(2)	17(2)	27(2)
C7	30(2)	37(2)	34(2)	16(1)	11(1)	11(1)
C8	32(2)	45(2)	32(2)	15(1)	12(1)	17(1)
C9	44(2)	51(2)	35(2)	17(2)	21(2)	24(2)
C10	58(2)	58(2)	47(2)	10(2)	26(2)	29(2)
N1	27(1)	36(1)	34(1)	14(1)	13(1)	13(1)
N2	33(1)	43(2)	32(1)	12(1)	11(1)	8(1)
N3	26(1)	39(1)	31(1)	13(1)	8(1)	9(1)
O1	44(1)	80(2)	45(1)	9(1)	12(1)	36(1)
C11	35(2)	29(2)	31(2)	9(1)	10(1)	12(1)
O11	33(1)	50(1)	41(1)	19(1)	12(1)	10(1)
O12	33(1)	58(2)	42(1)	28(1)	11(1)	10(1)
C12	42(2)	50(2)	40(2)	17(2)	12(2)	18(2)
F11	80(5)	132(6)	61(4)	6(4)	7(3)	80(5)
F12	51(3)	94(6)	56(5)	58(4)	–2(3)	–2(4)
F13	80(6)	49(4)	60(5)	–18(3)	–22(4)	22(4)
C212	42(2)	50(2)	40(2)	17(2)	12(2)	18(2)
F211	81(4)	73(4)	120(5)	10(4)	–24(4)	54(3)
F212	71(3)	128(6)	36(2)	11(3)	6(2)	23(4)
F213	31(3)	115(6)	68(4)	65(4)	–3(3)	–15(4)

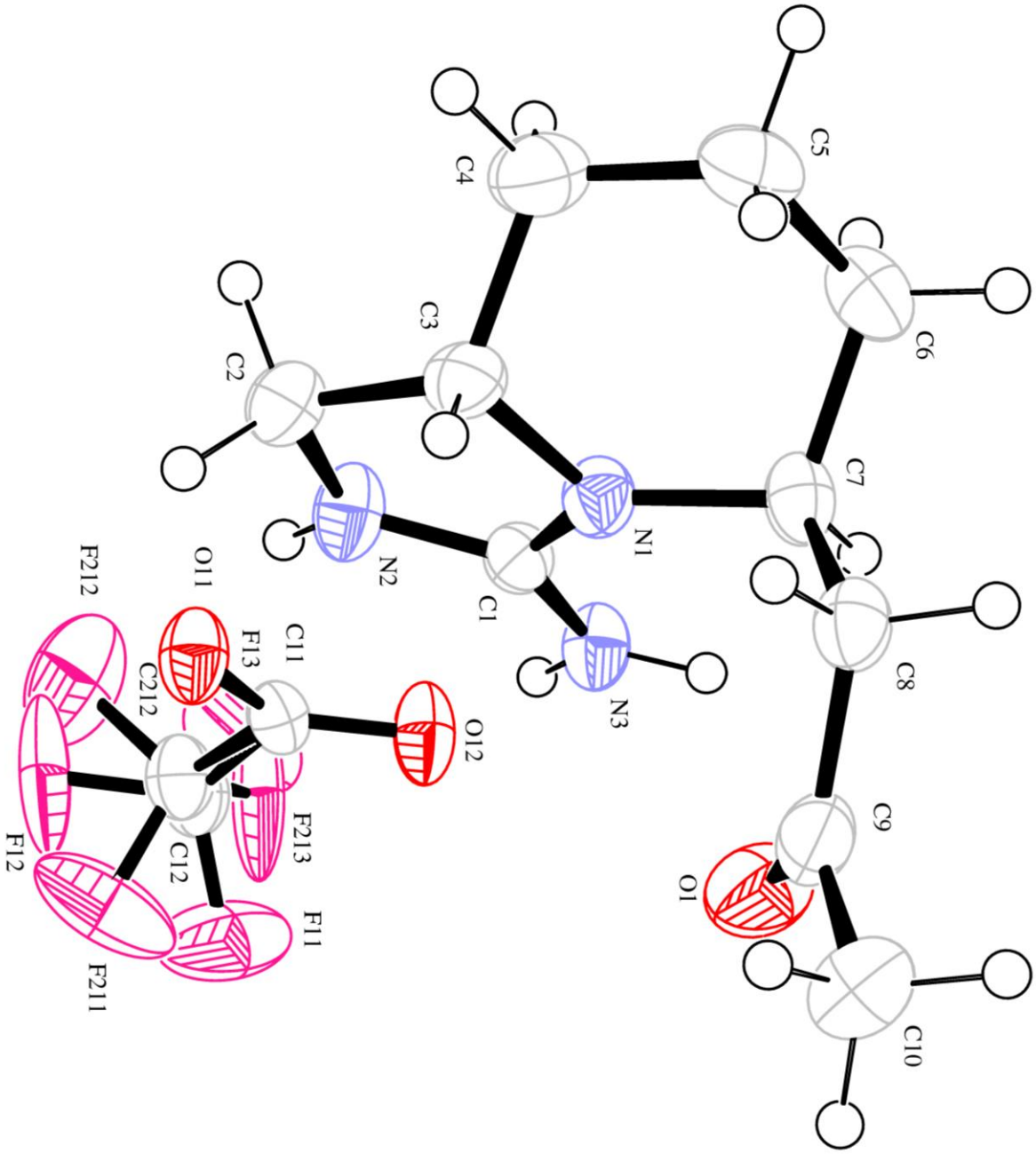
Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H2A	7117	4982	4522	48	1
H2B	7032	3178	4048	48	1
H3	8549	4969	6398	42	1
H4A	10028	3353	5908	59	1
H4B	7968	1616	5438	59	1
H5A	9961	1751	7363	63	1
H5B	10123	3560	7884	63	1
H6A	7674	1354	8317	56	1
H6B	6518	373	6935	56	1
H7	4788	1718	7343	42	1
H8A	7408	3752	9159	43	1
H8B	8331	4935	8372	43	1
H10A	5684	6918	9363	79	1
H10B	7824	7423	9310	79	1
H10C	7103	6281	10173	79	1
H2	3635	2691	3680	48	1
H3A	2265	1364	5967	42	1
H3B	1392	1372	4676	42	1

Table 6. Hydrogen bonds [Å and °].

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
N2–H2···O11	0.88	1.95	2.805(3)	162.4
N3–H3B···O12	0.88	1.96	2.836(3)	177.0
N3–H3A···O12^{i}	0.88	2.14	2.914(3)	147.1

Symmetry transformations used to generate equivalent atoms:
(i) –x,–y,–z+1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C6
C3
C2
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O12
C9
F213
C12
O1
F12
F11
F211
C10

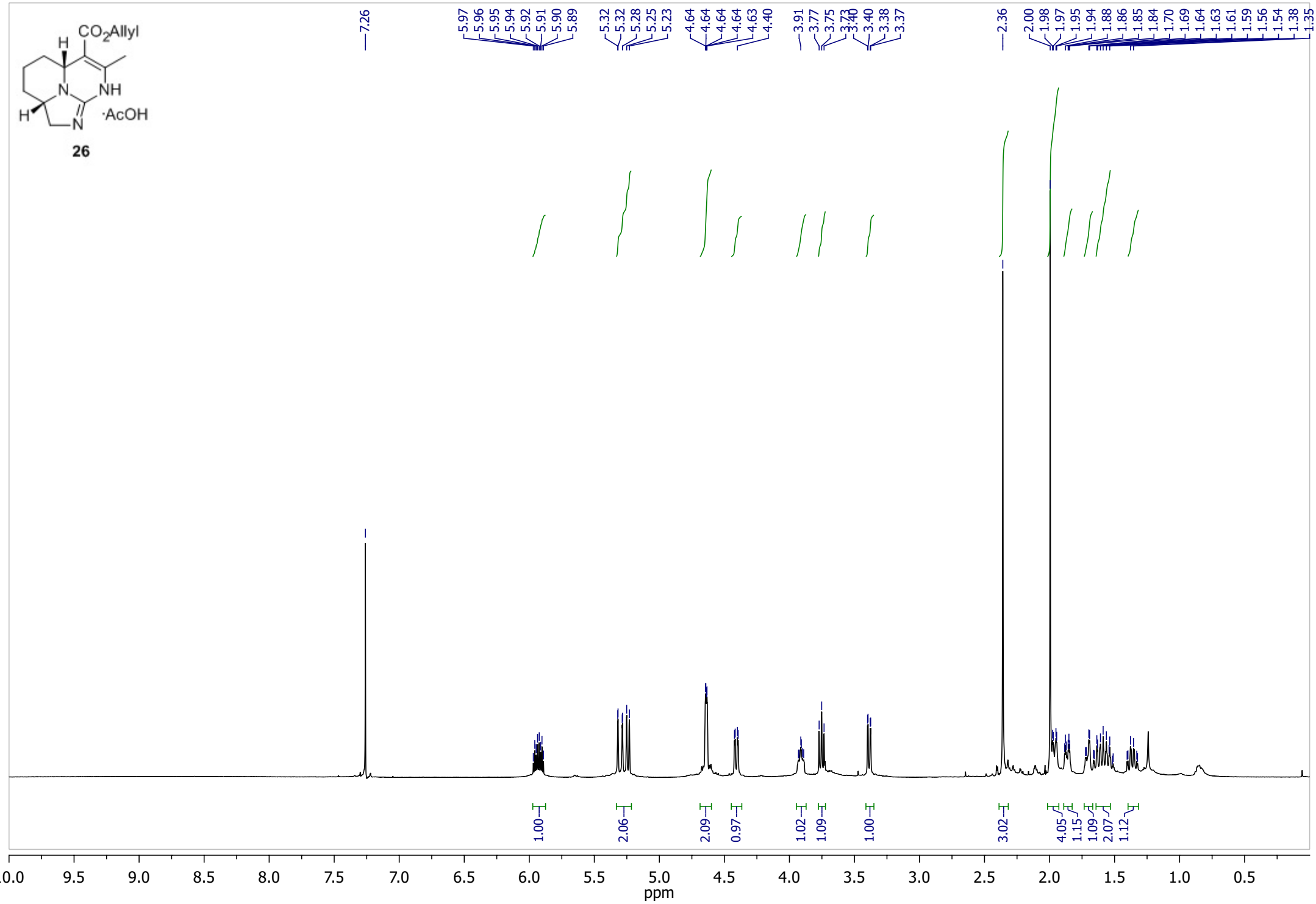
Crystal structure analysis (doi:10.5258/ecrystals/1048)

A crystal of **21** was selected and data collected on a Bruker Nonius KappaCCD Area Detector equipped with a Bruker Nonius FR591 rotating anode ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å) at 120K driven by COLLECT[1], processed by DENZO[2] software and corrected for absorption by using SADABS[3]. The structures were determined in SHELXS-97 and refined using SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically with hydrogen atoms included in idealized positions with thermal parameters riding on those of the parent atom. The fluorine atoms of the TFA anion were disordered over two sites, resulting in the use of both geometrical and anisotropic displacement restraints (SADI and SIMU) on these atoms.

Crystal Data for **21**: $C_{12}H_{18}F_3N_3O_3$, M = 309.29, triclinic, a = 7.9832(6) Å, b = 8.8773(7) Å, c = 12.1929(10) Å, α = 95.866(3)°, β = 107.215(4)°, β = 114.500(4)°, U = 725.49(10) Å^3, T = 120(2) K, space group P-1, Z = 2, μ(Mo-K_a) = 0.127 mm^{-1}, 12761 reflections measured, 3301 unique (R_{int} = 0.0487) which were used in all calculations. Final R_1 = 0.0792, wR_2 = 0.1219 [$F^2 > 2\sigma(F^2)$], R_1 = 0.1279, wR_2 = 0.1416 (all data).

Crystallographic data for **21** has been deposited with the Cambridge Crystallographic Data Centre with CCDC971600. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax +44 1223 336033) or email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

[1] Collect: Data collection software, R. Hooft, Nonius B.V., 1998
[2] Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press (New York)
[3] G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473
[4] G. M. Sheldrick, Acta Cryst, (2008) A**64** 112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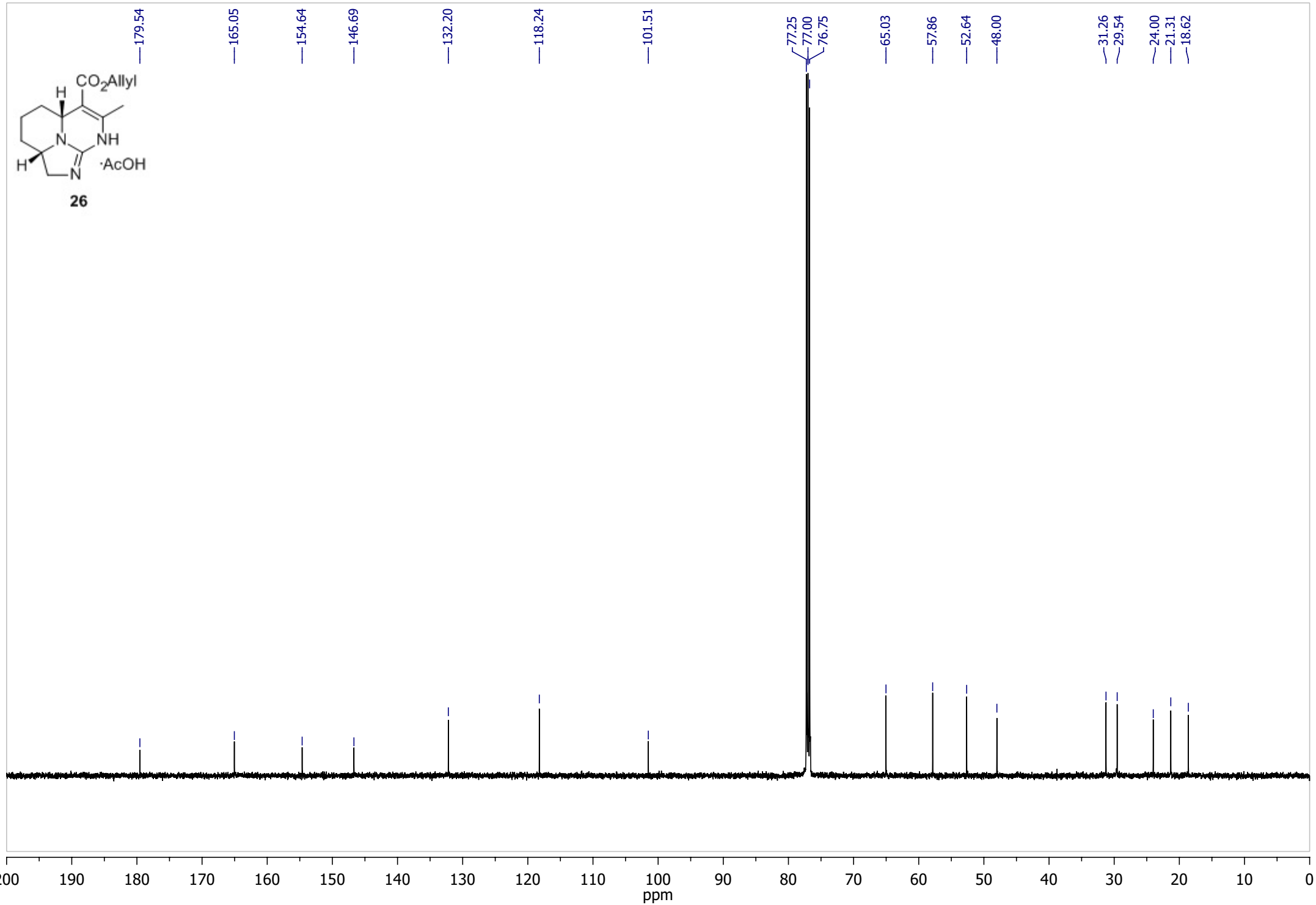
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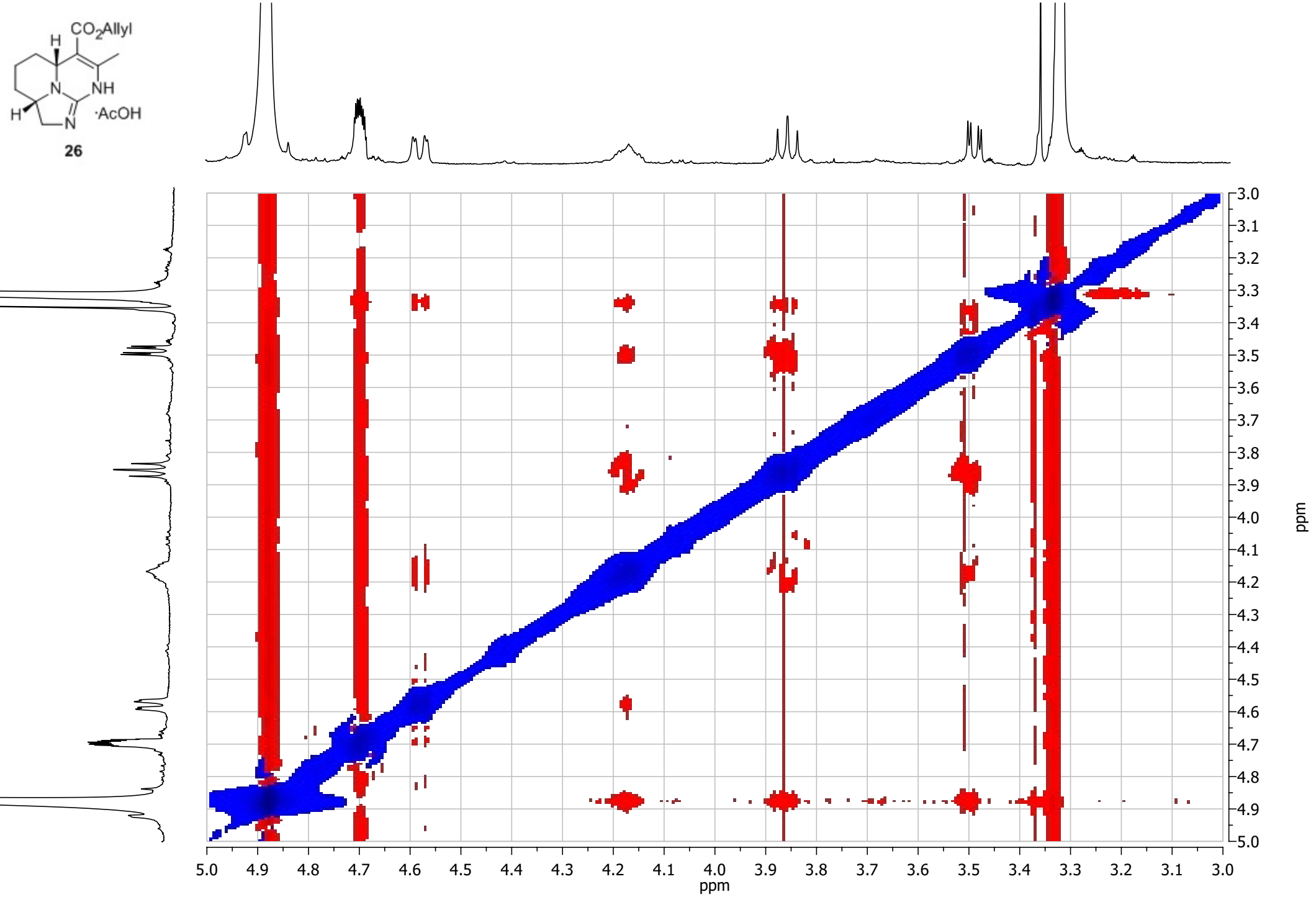
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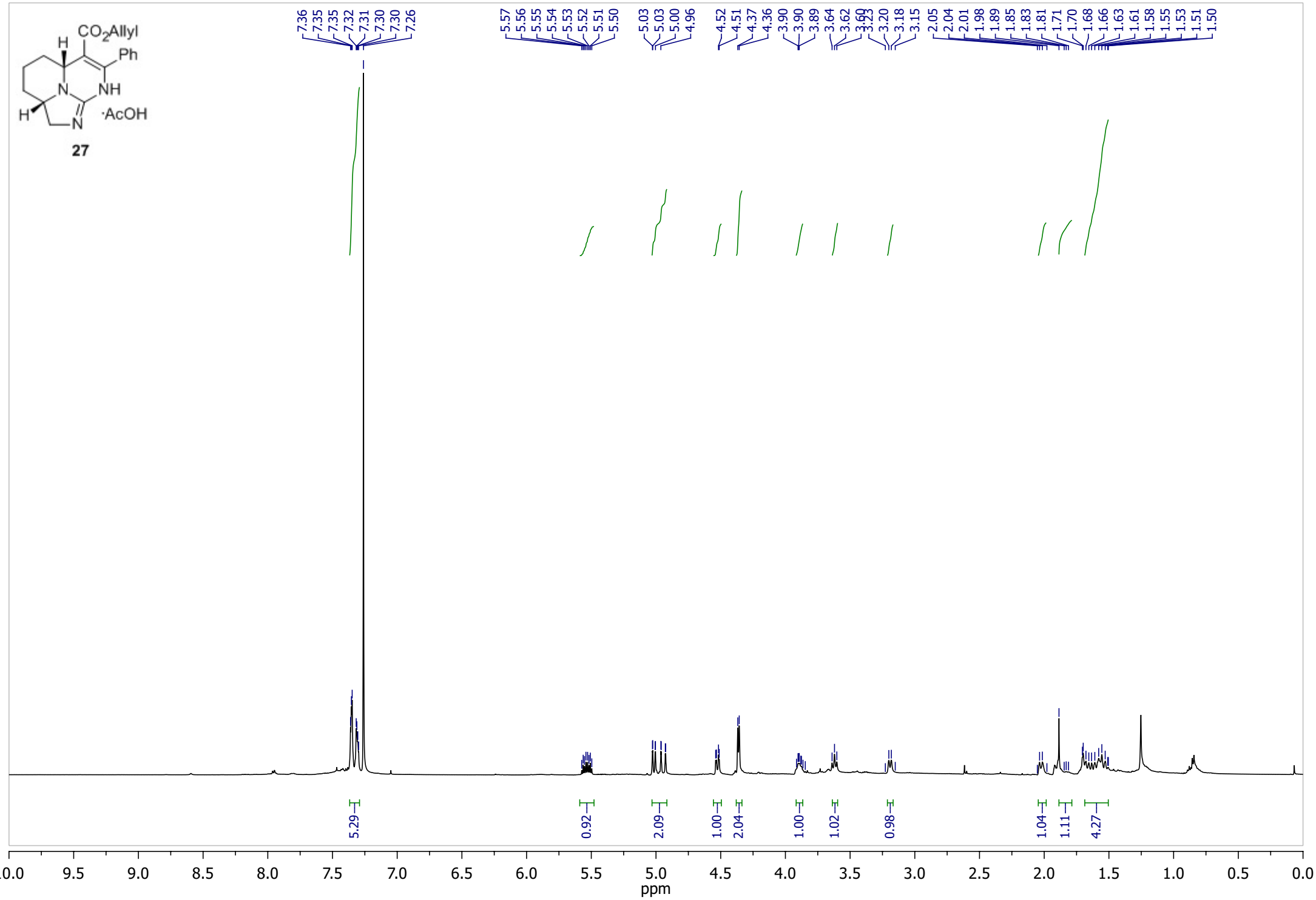
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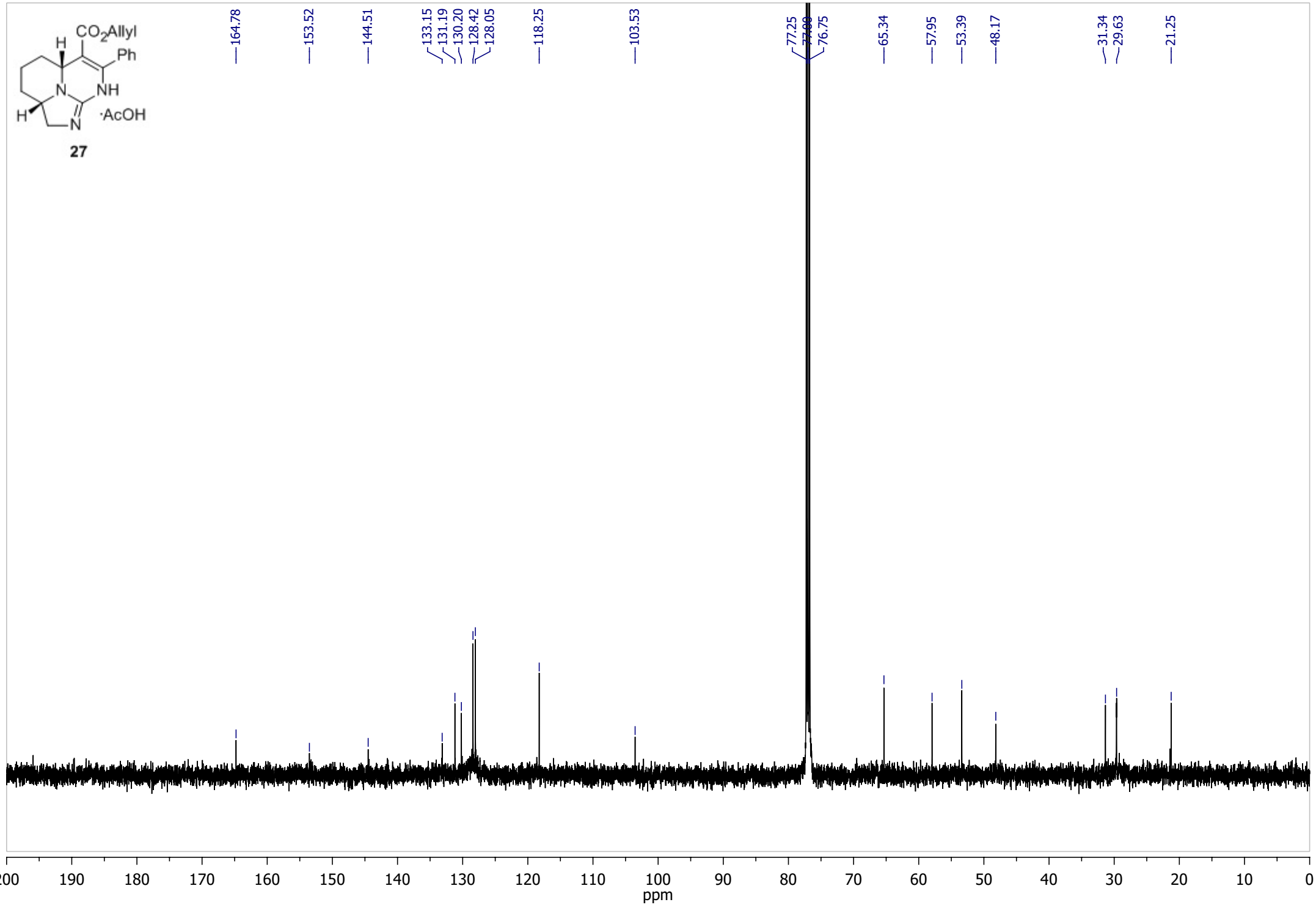
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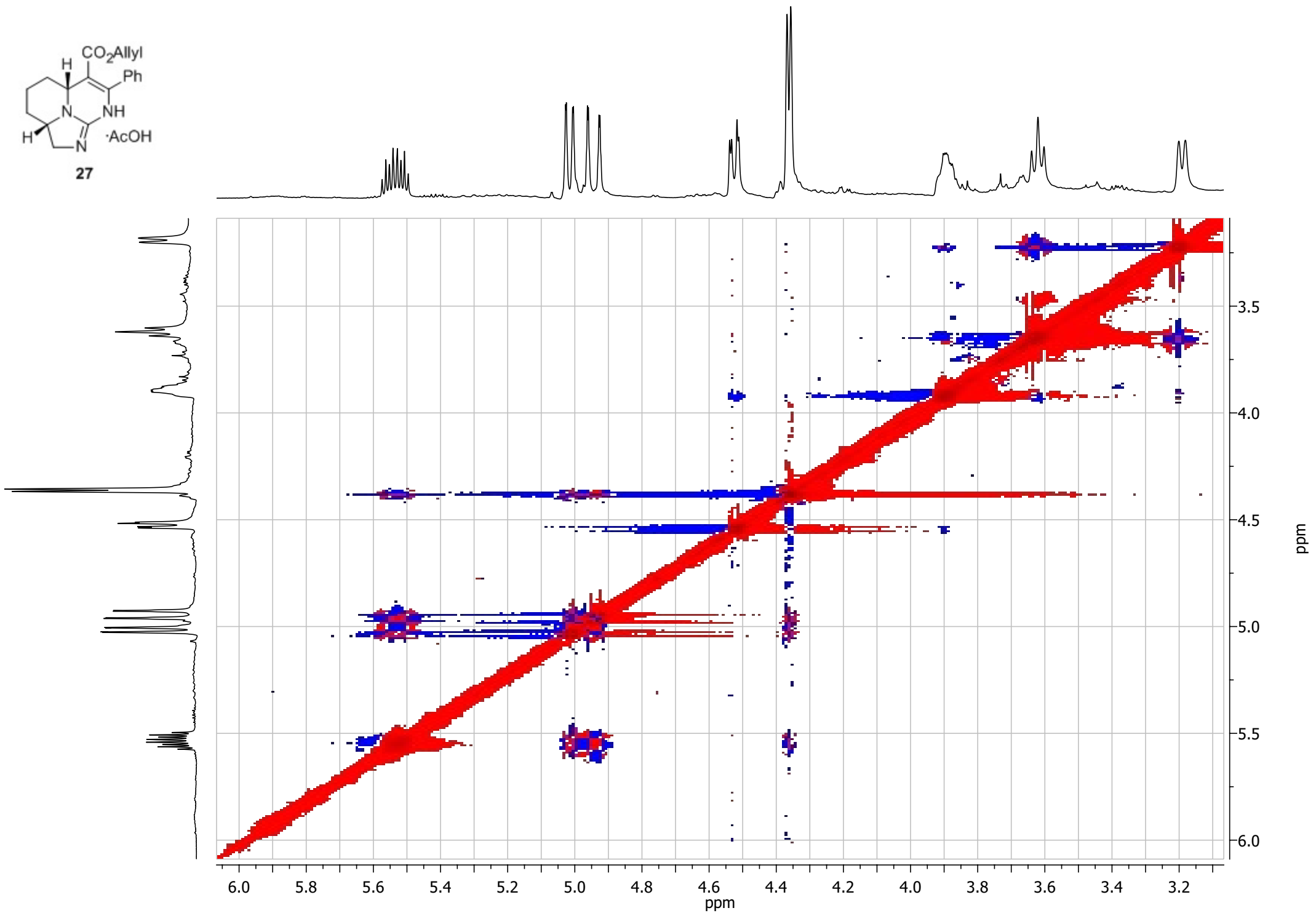
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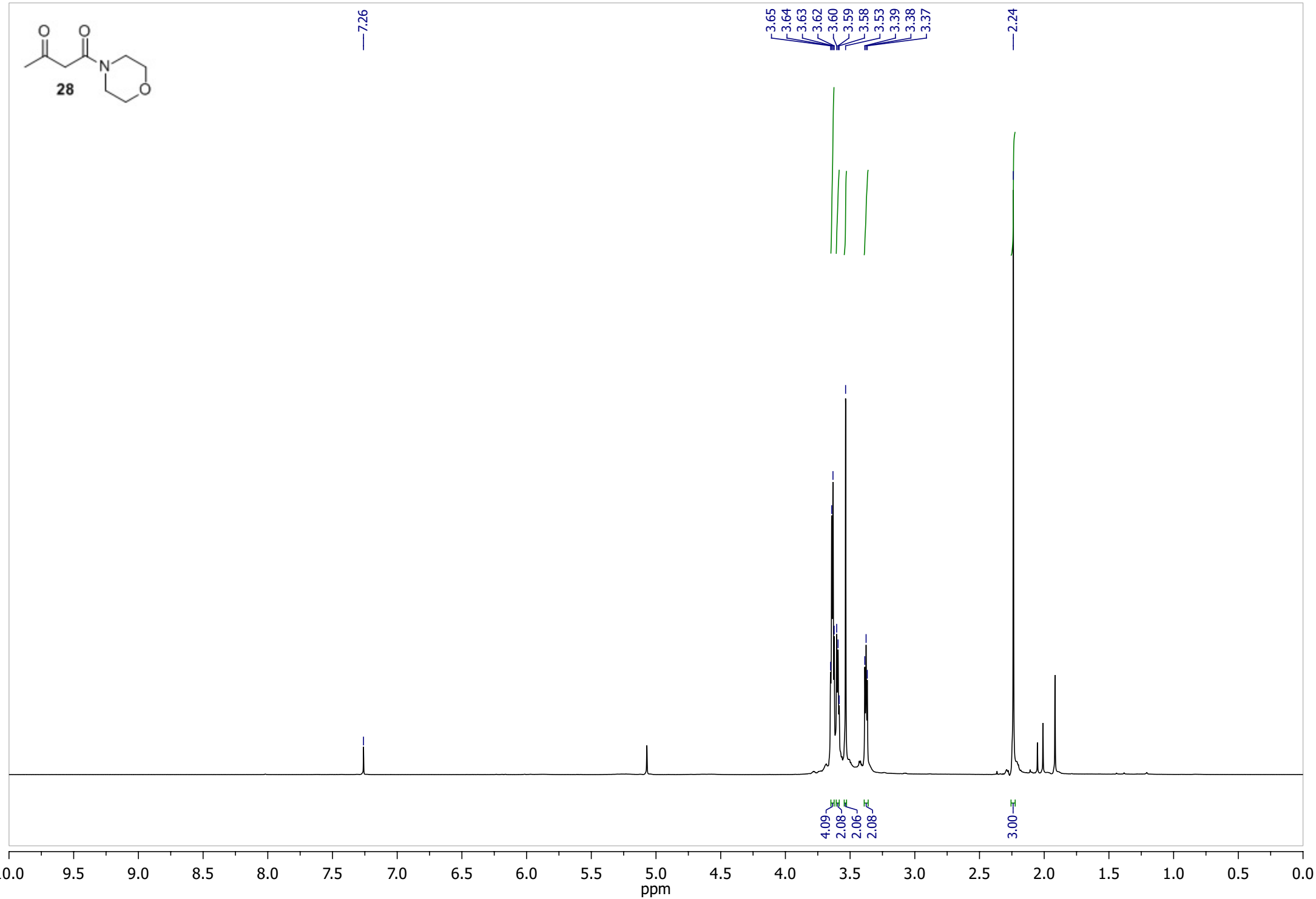
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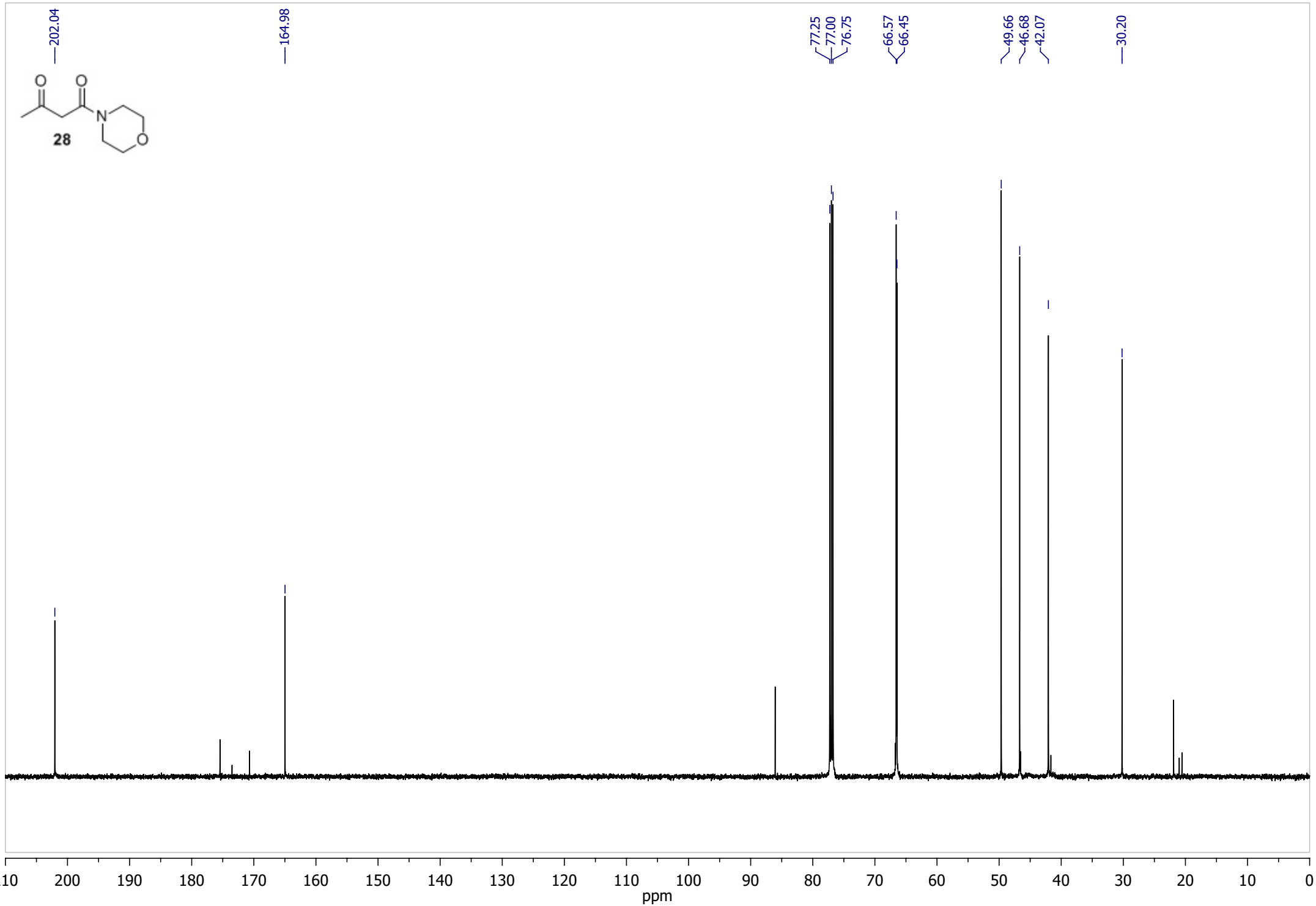
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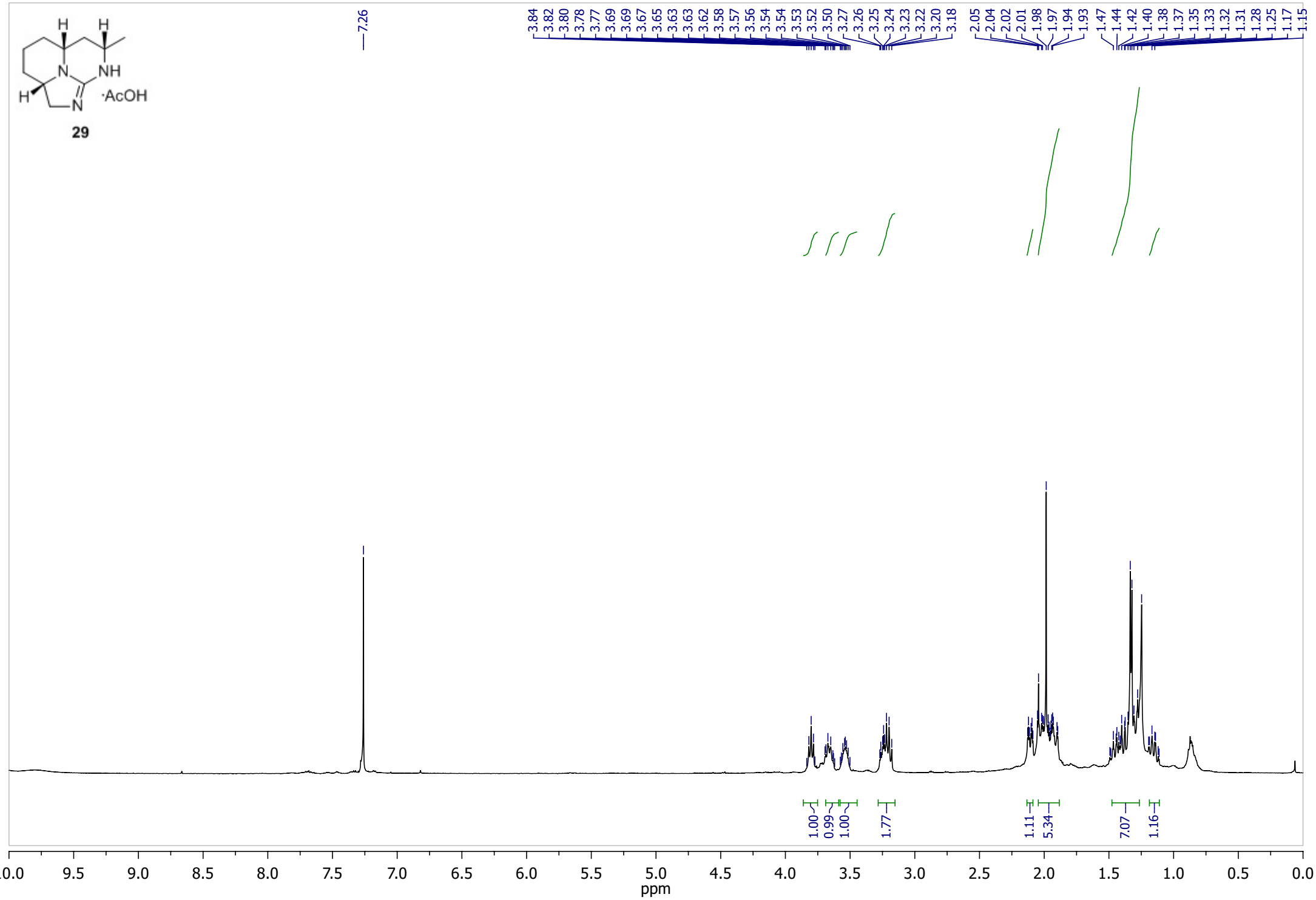
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0.99
1.00
1.77
1.11
5.34
7.07
1.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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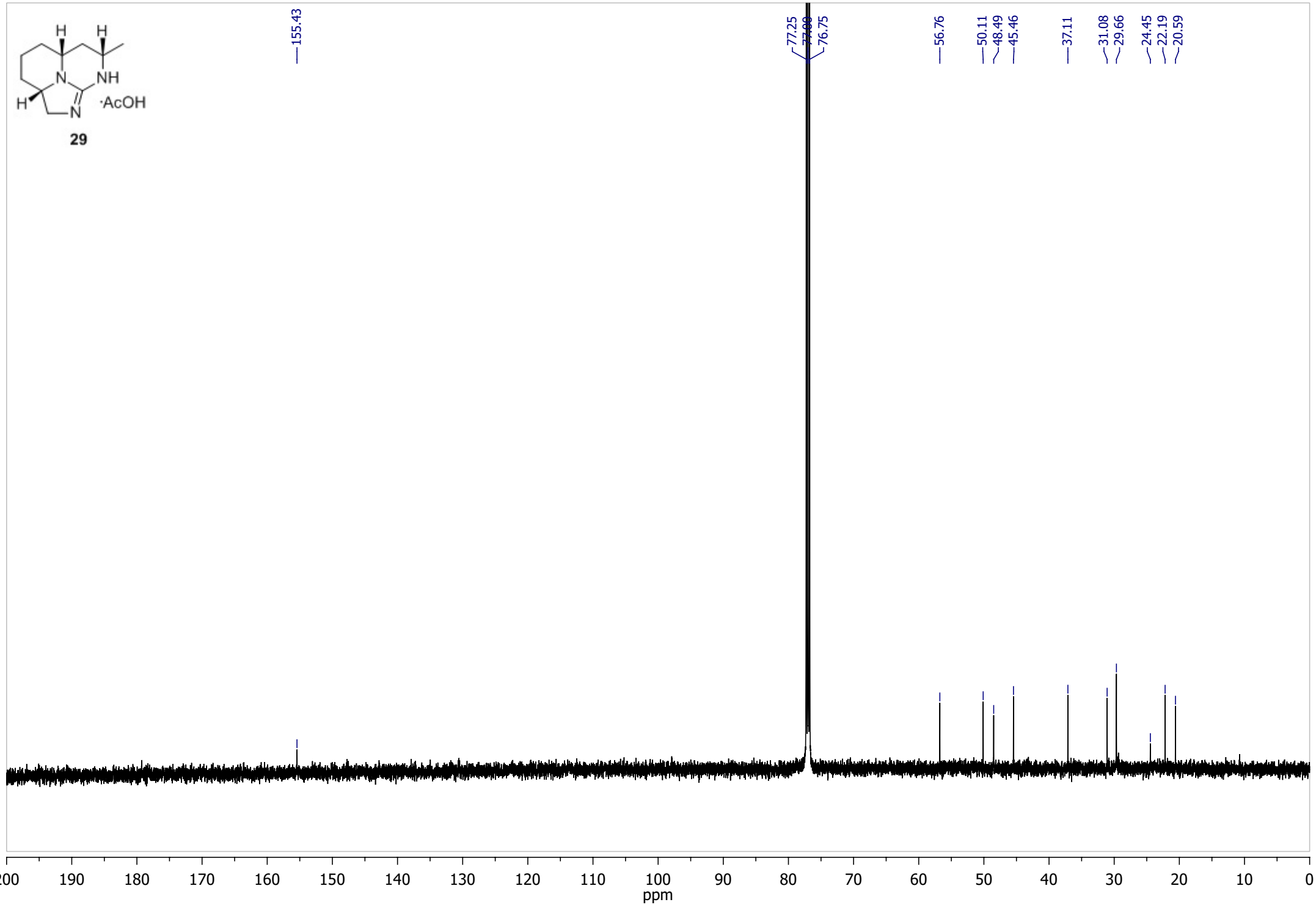
2.0
1.5
1.0
0.5
0.0
ppm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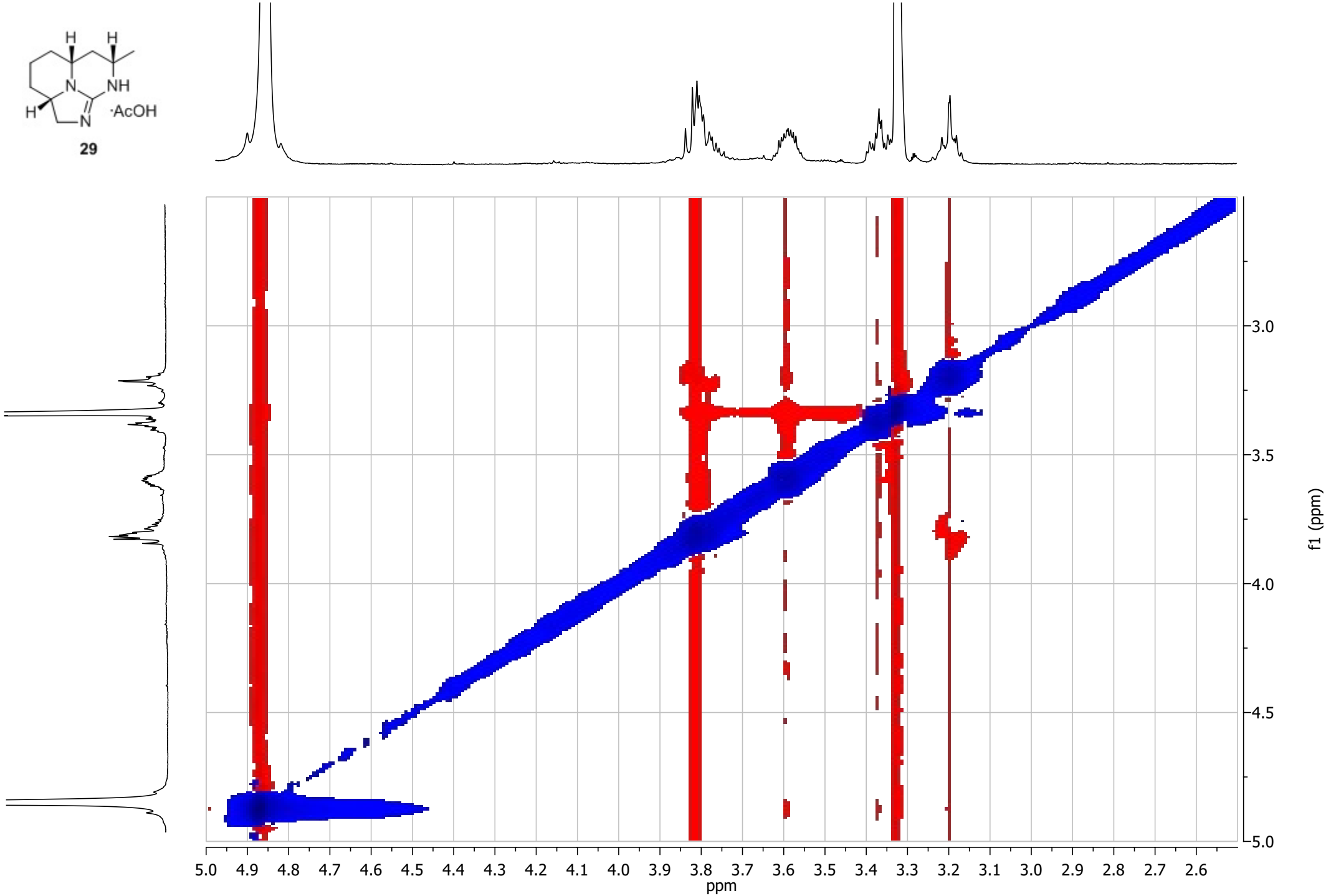
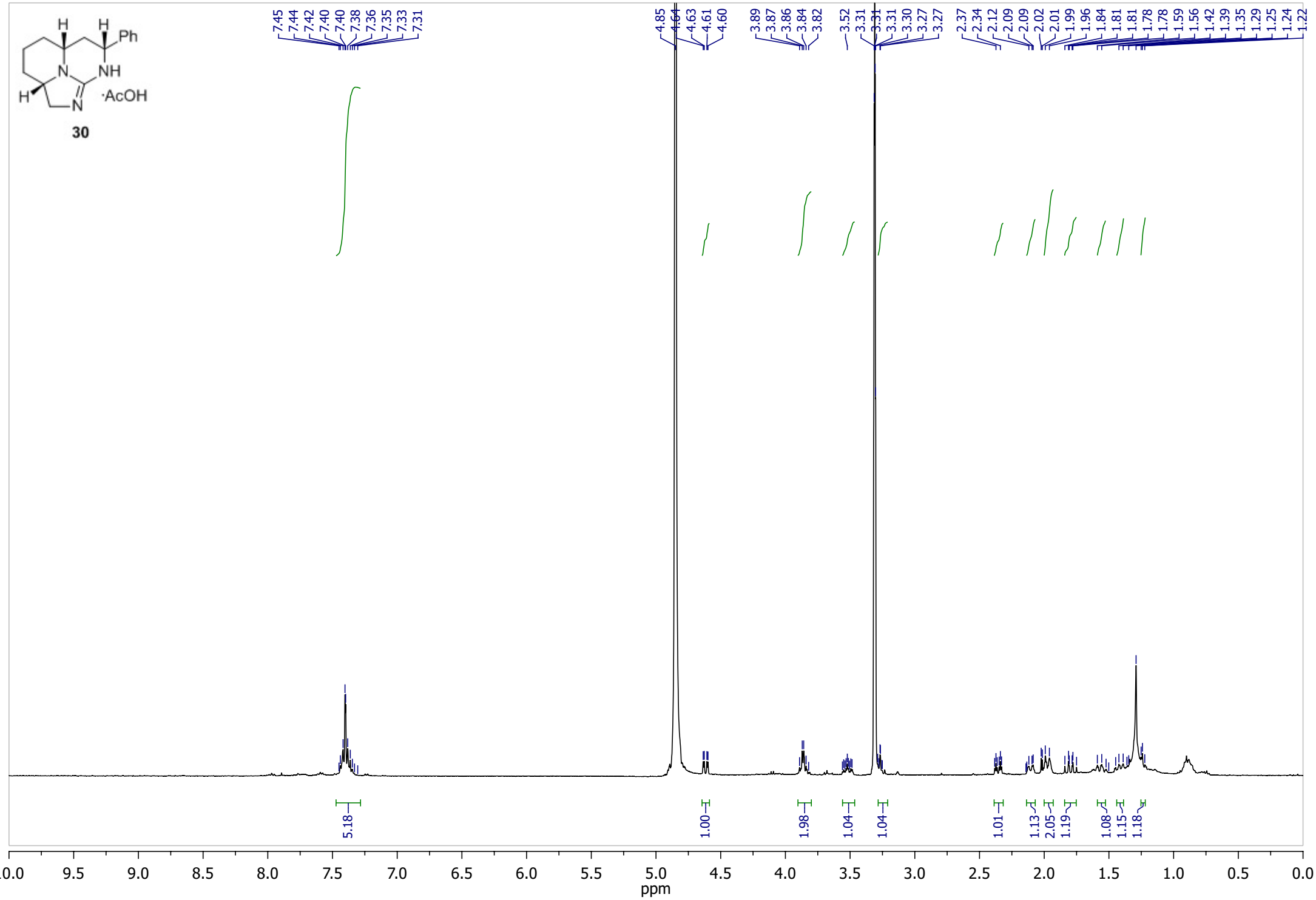
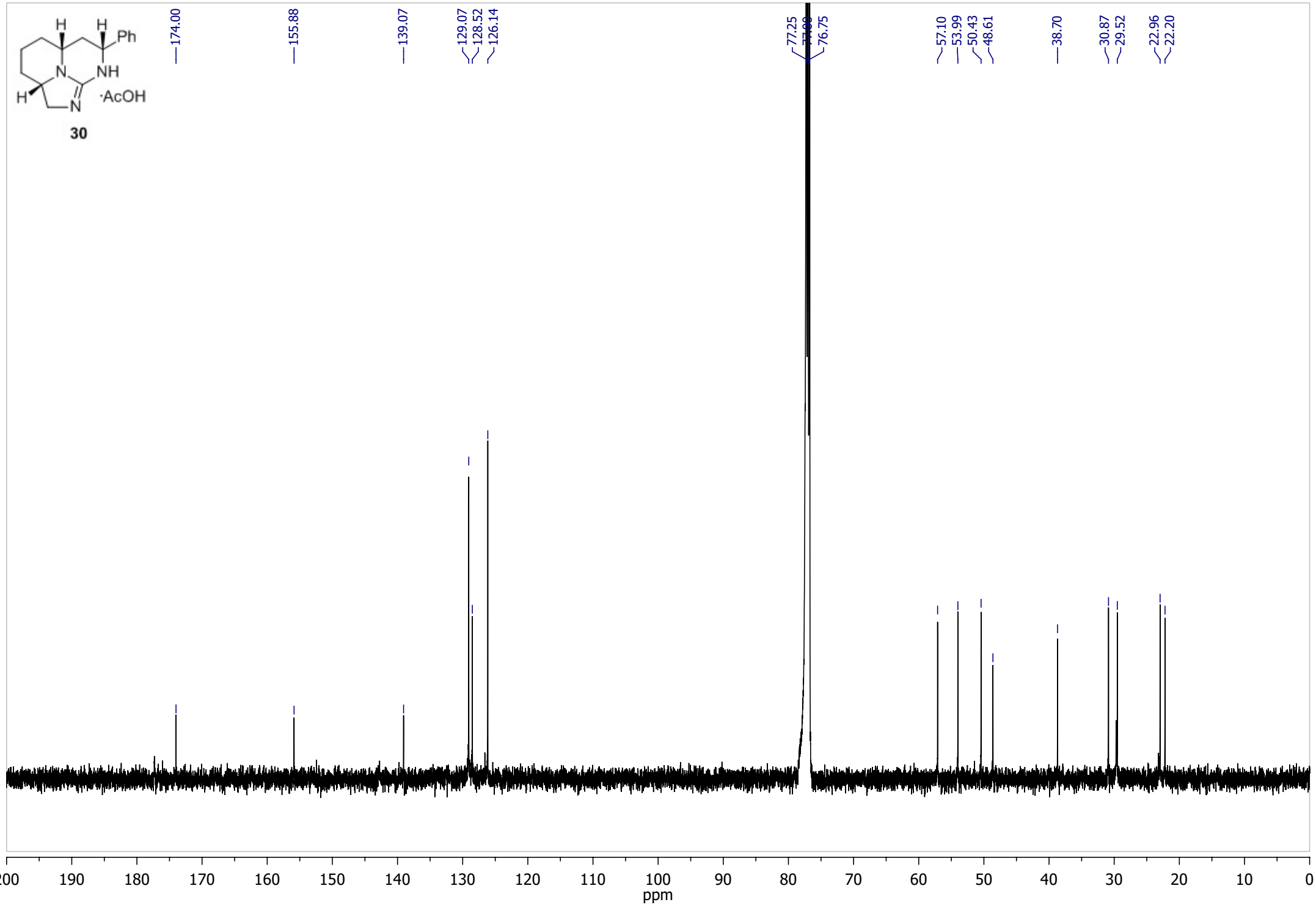
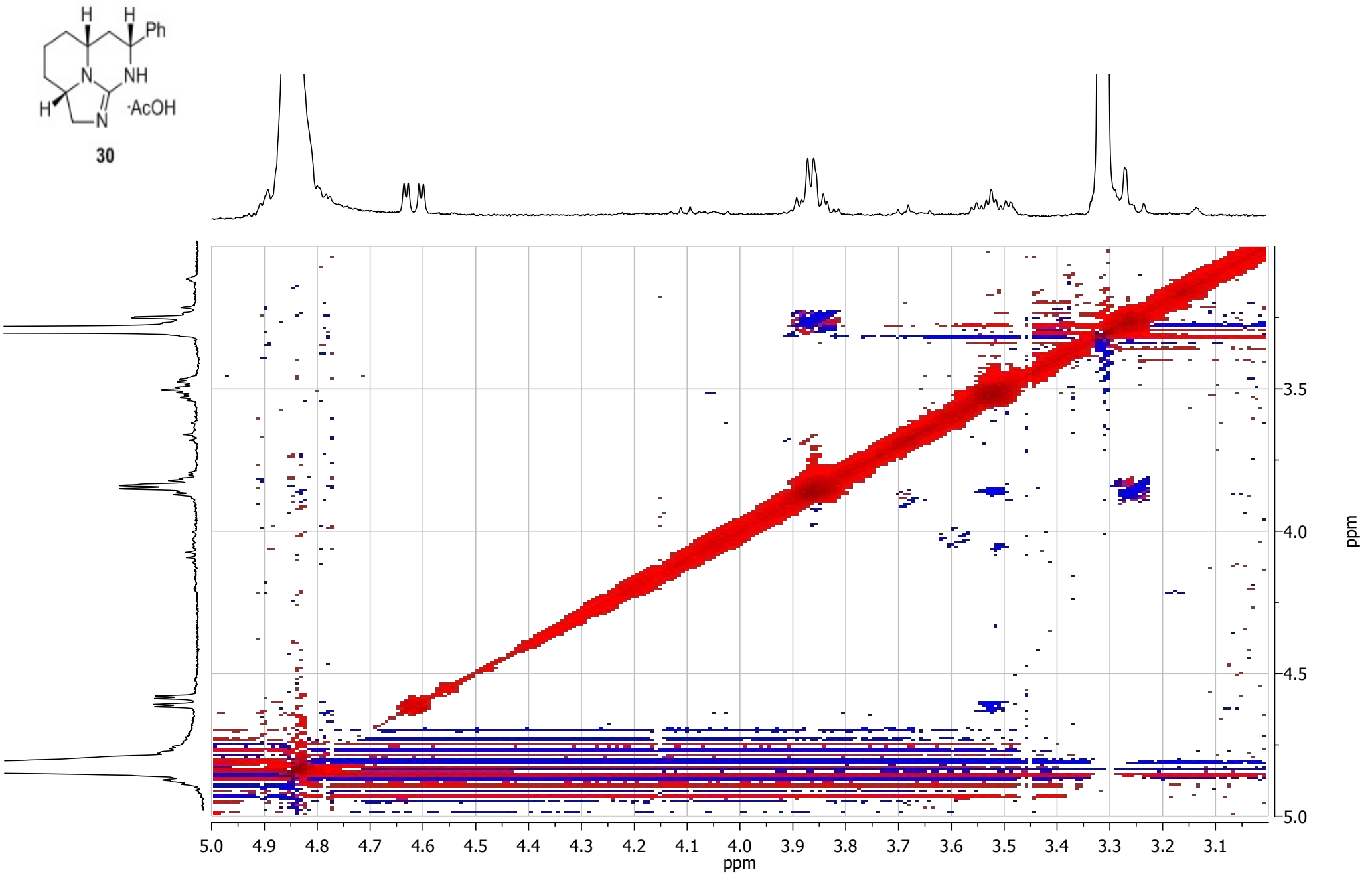
H
N
NH
H
N
·AcOH
29
155.43
77.25
77.00
76.75
56.76
50.11
48.49
45.46
37.11
31.08
29.66
24.45
22.19
20.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


H
H
N
NH
H
N
·AcOH
29
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
ppm
3.0
3.5
4.0
4.5
5.0
f1 (ppm)


H
H
Ph
N
NH
H
N
·AcOH
30
7.45
7.44
7.42
7.40
7.40
7.38
7.36
7.35
7.33
7.31
4.85
4.64
4.63
4.61
4.60
3.89
3.87
3.86
3.84
3.82
3.52
3.31
3.31
3.31
3.30
3.27
3.27
2.37
2.34
2.12
2.09
2.09
2.02
2.01
1.99
1.96
1.84
1.81
1.81
1.78
1.78
1.59
1.56
1.42
1.39
1.35
1.29
1.25
1.24
1.22
5.18
1.00
1.98
1.04
1.04
1.01
1.13
2.05
1.19
1.08
1.15
1.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


H
H
Ph
N
NH
H
N
·AcOH
30
174.00
155.88
139.07
129.07
128.52
126.14
77.25
77.00
76.75
57.10
53.99
50.43
48.61
38.70
30.87
29.52
22.96
22.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


H
H
Ph
N
NH
H
N
·AcOH
30
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
ppm
3.5
4.0
4.5
5.0
ppm