Electronic Supporting Information (ESI)

An Unprecedented Intramolecular to Intermolecular Mechanistic Switch in 1,1-Diaminoazines Leading to Differential Product Formation during the I_2-Induced Tandem Oxidative Transformation

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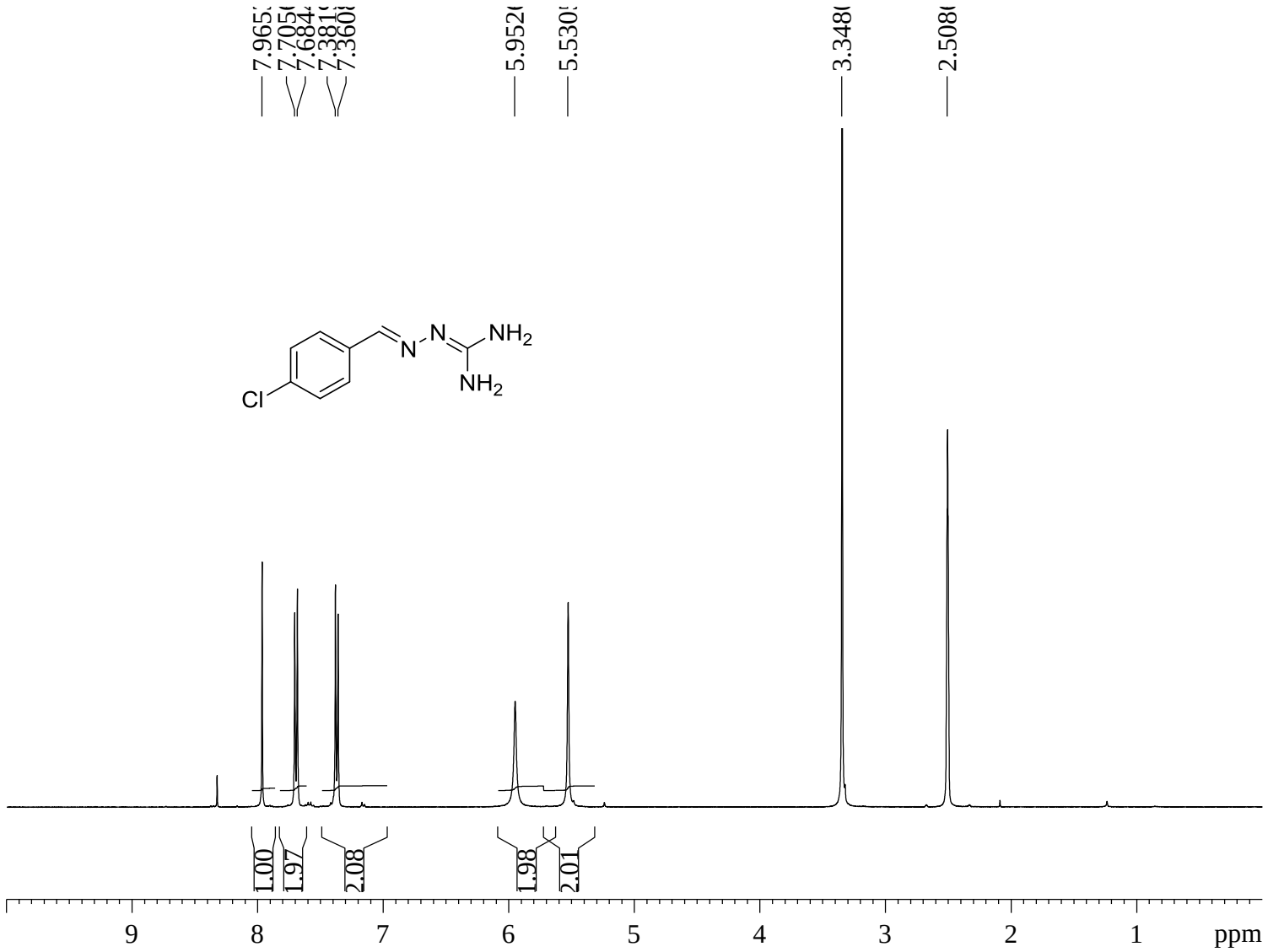
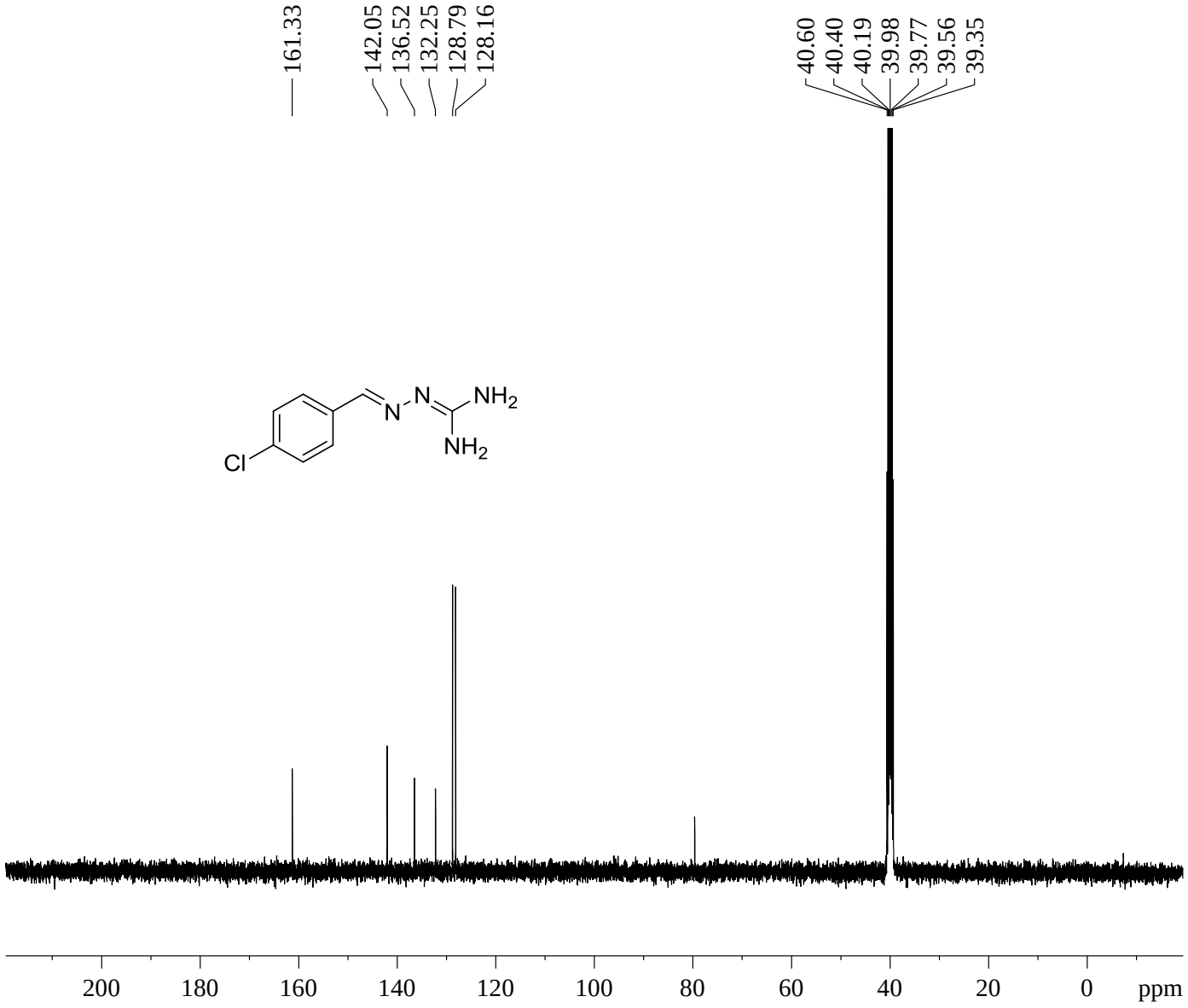
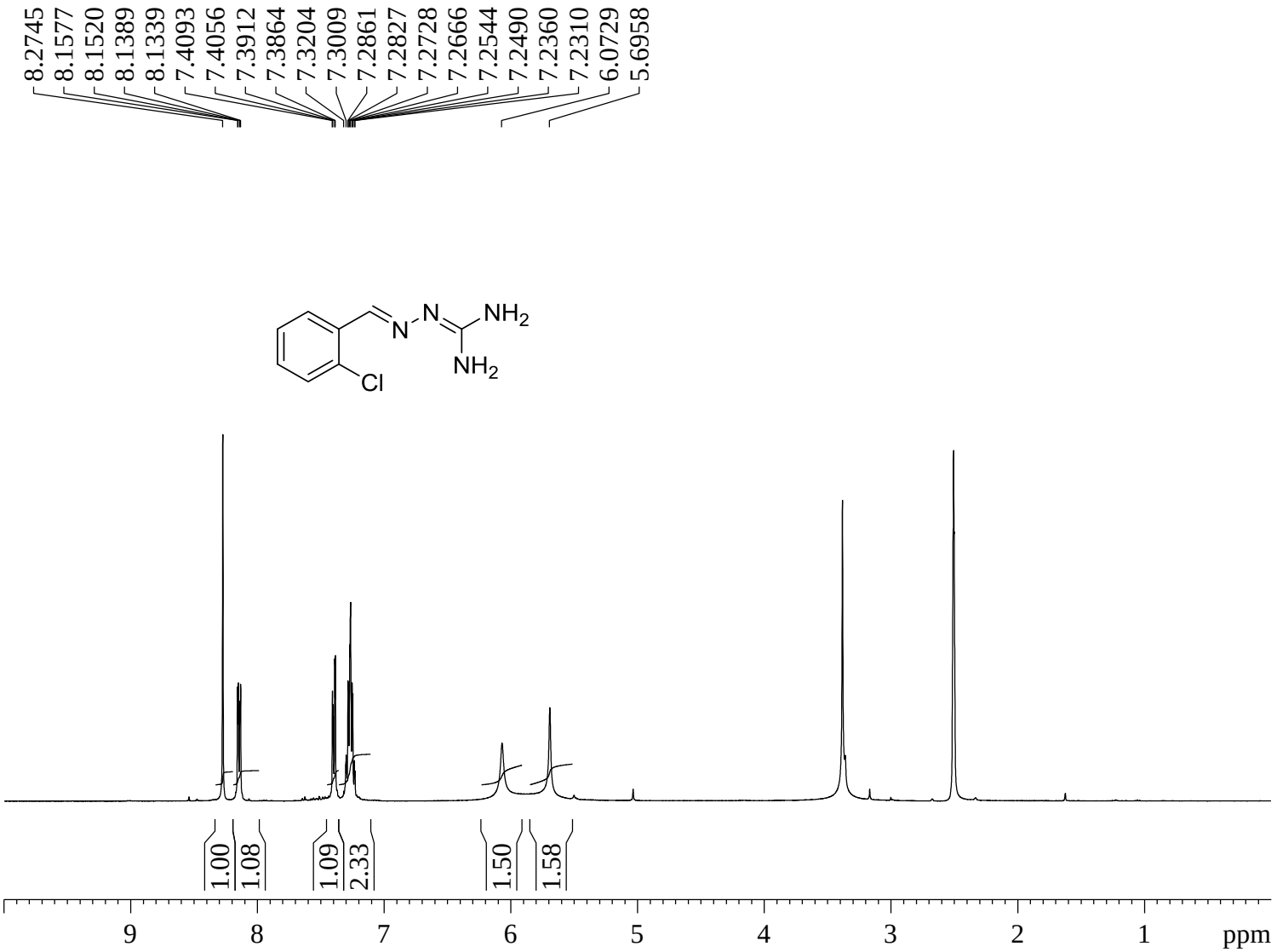


^{13}C spectra of compound 1a



^{1}H spectra of compound 1b



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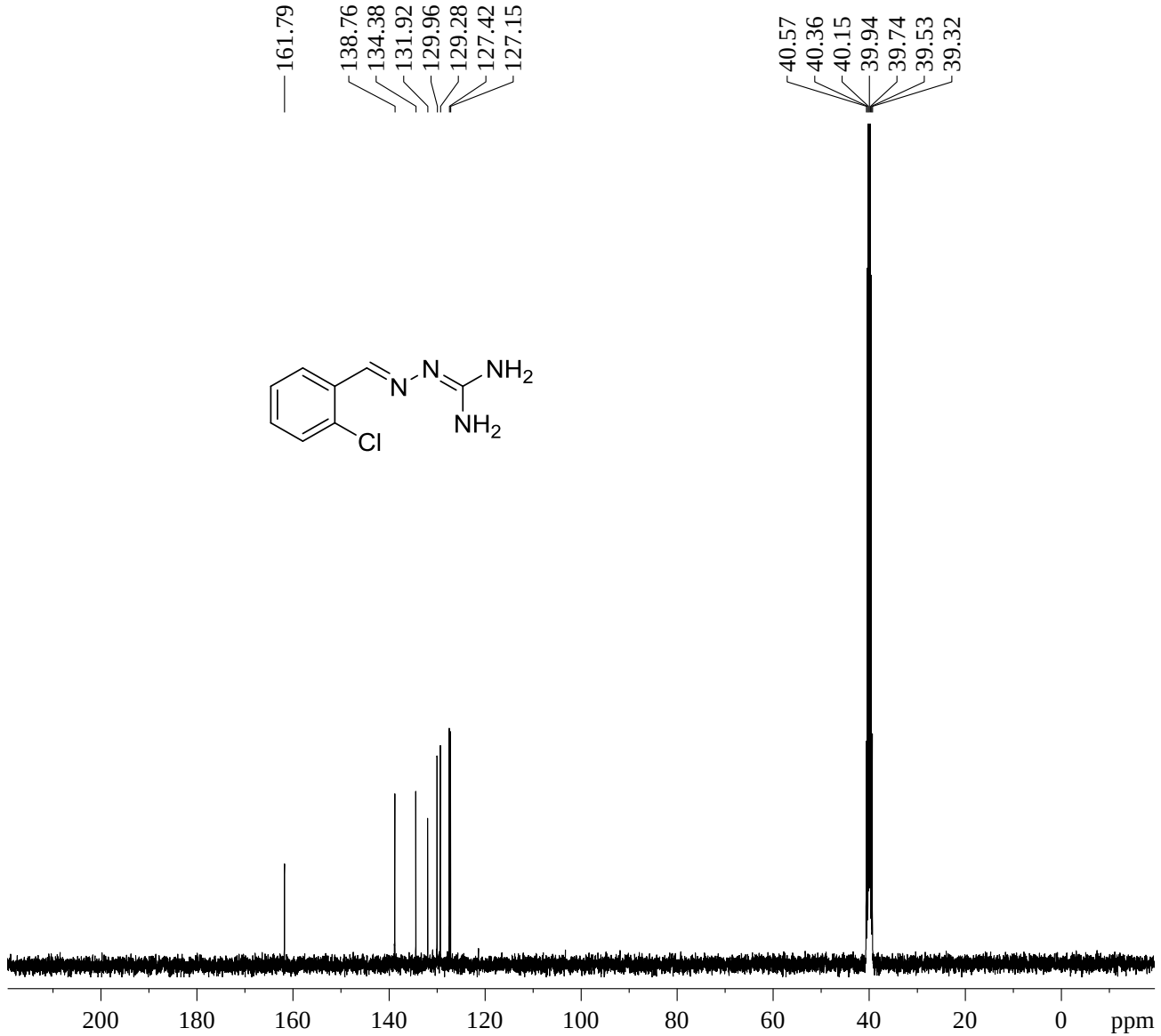

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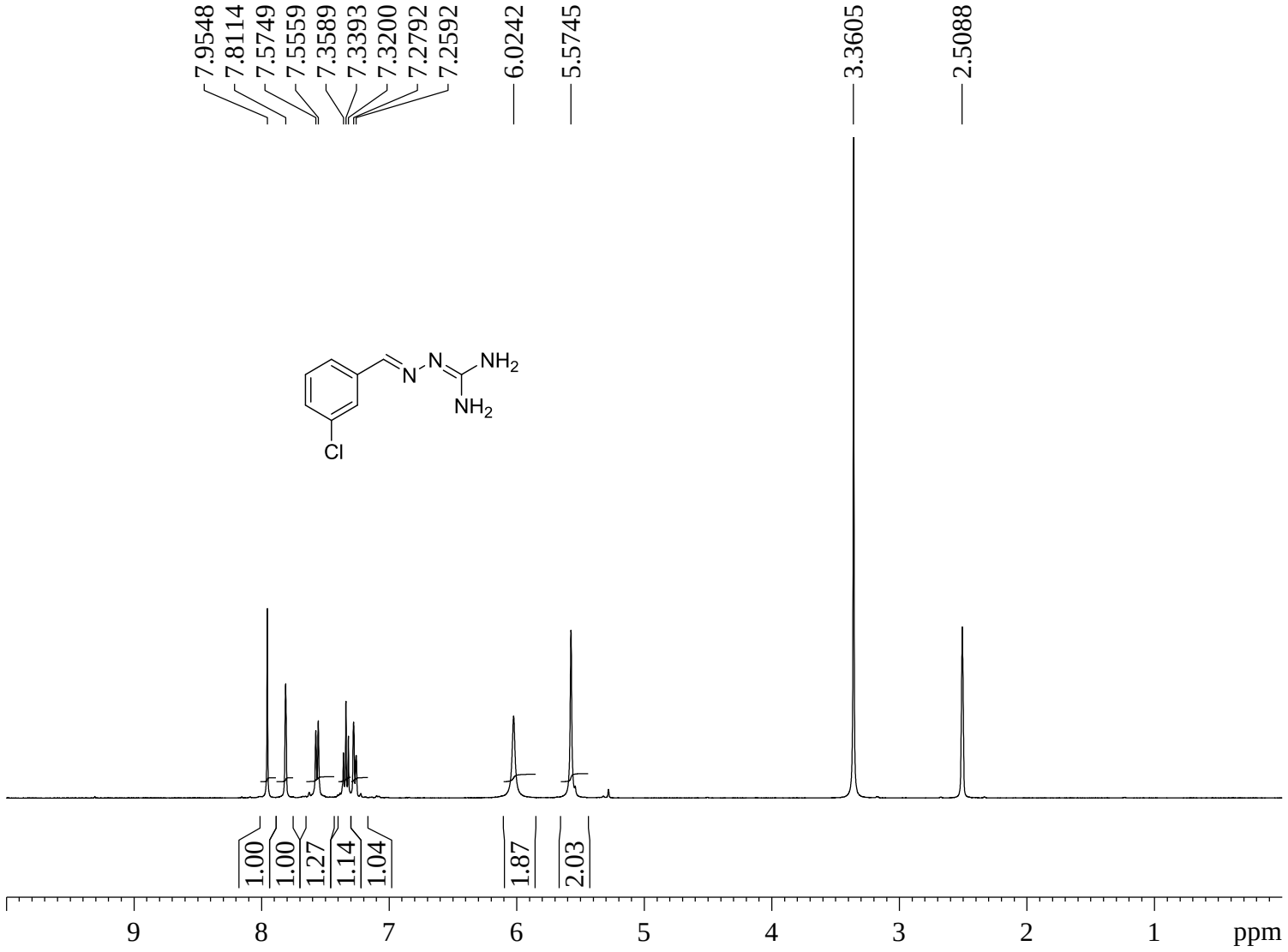

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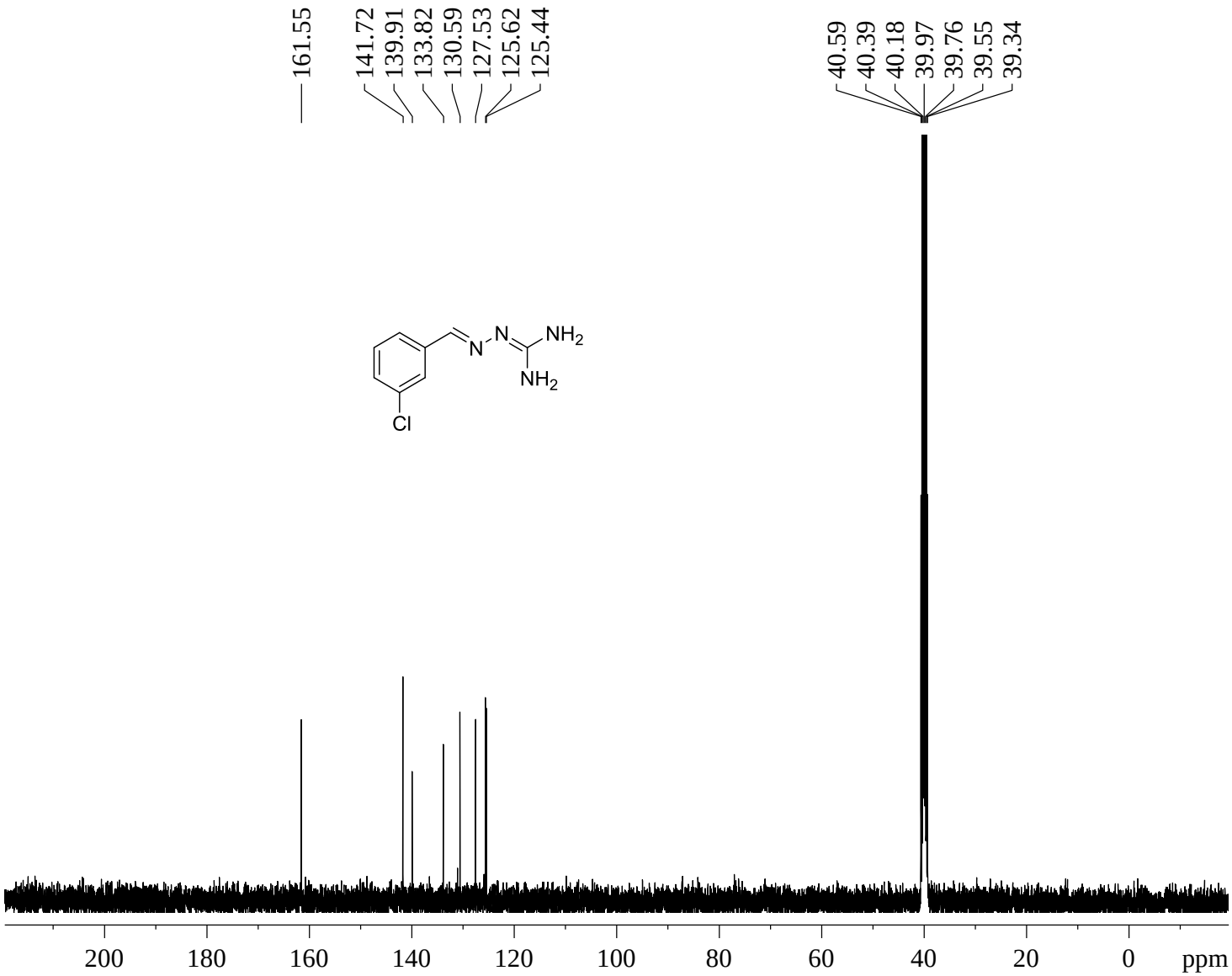

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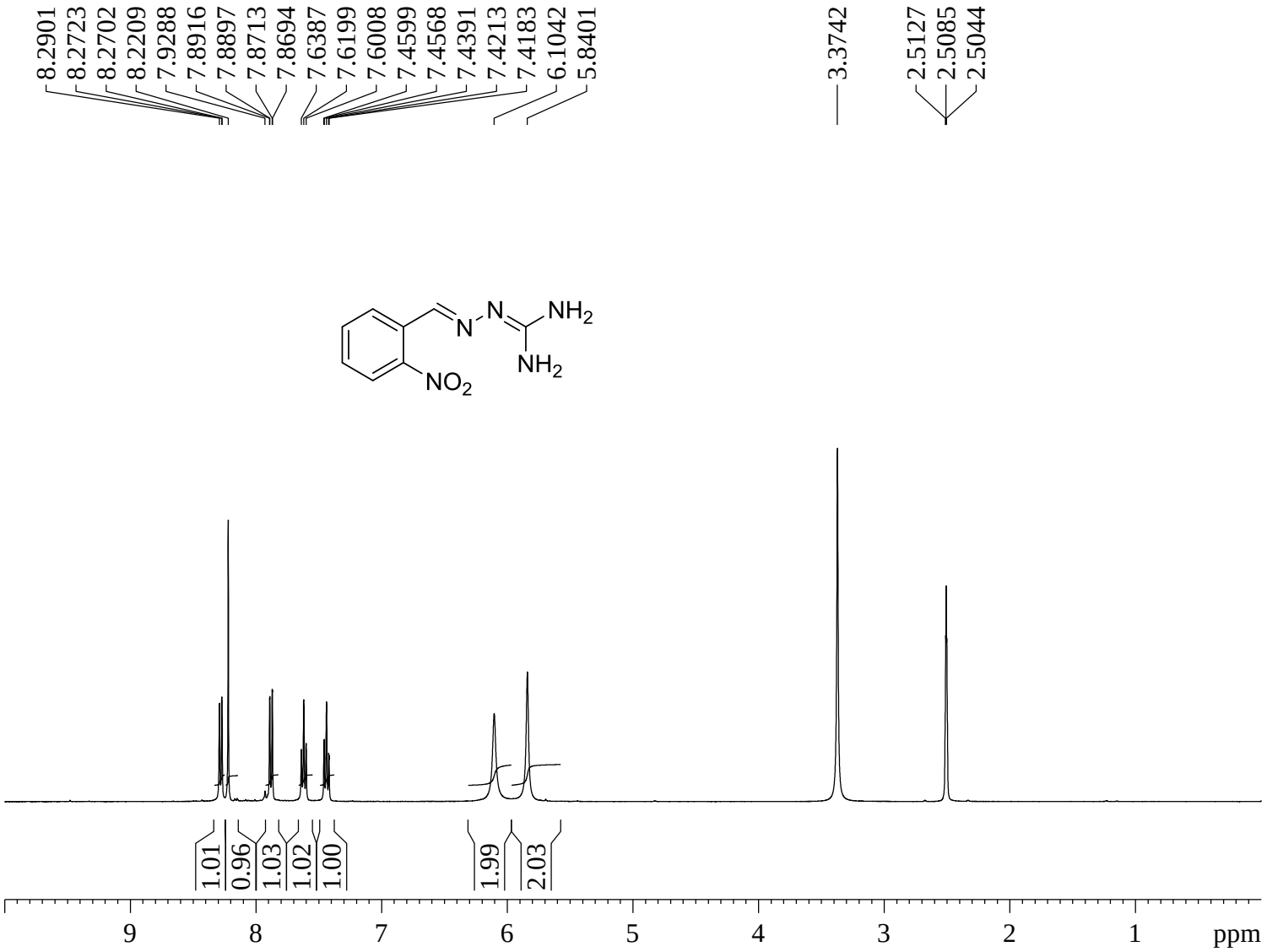

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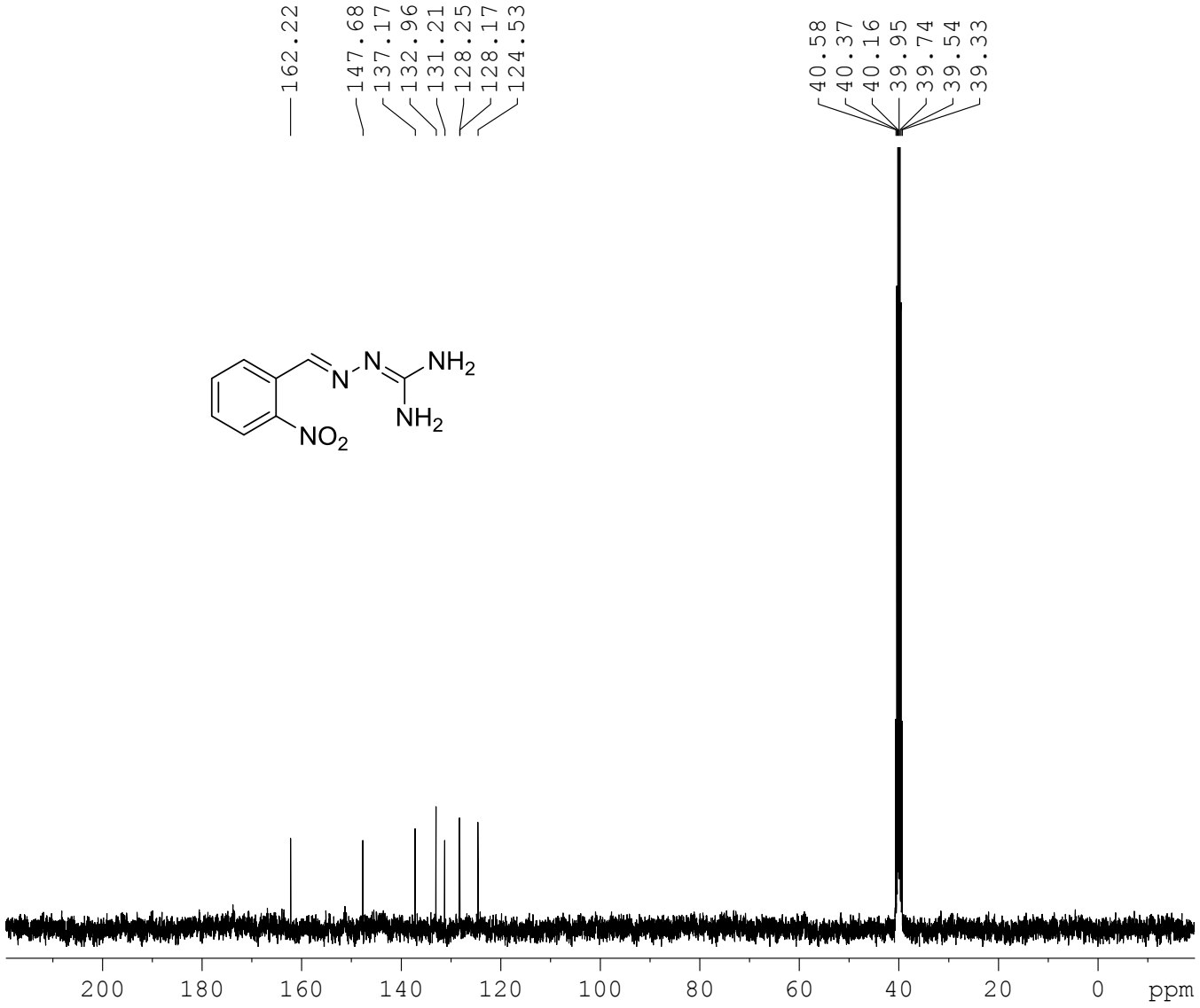

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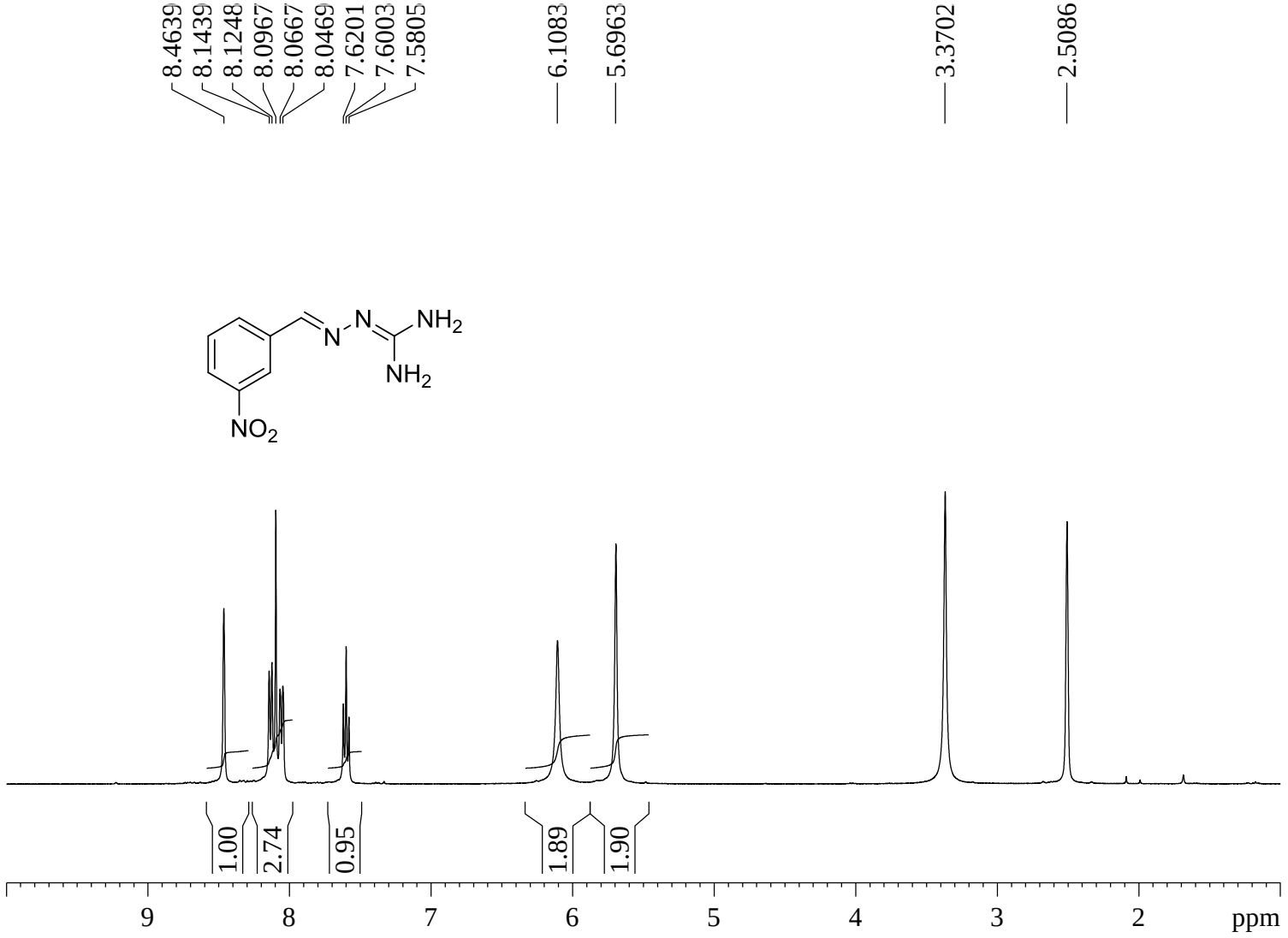

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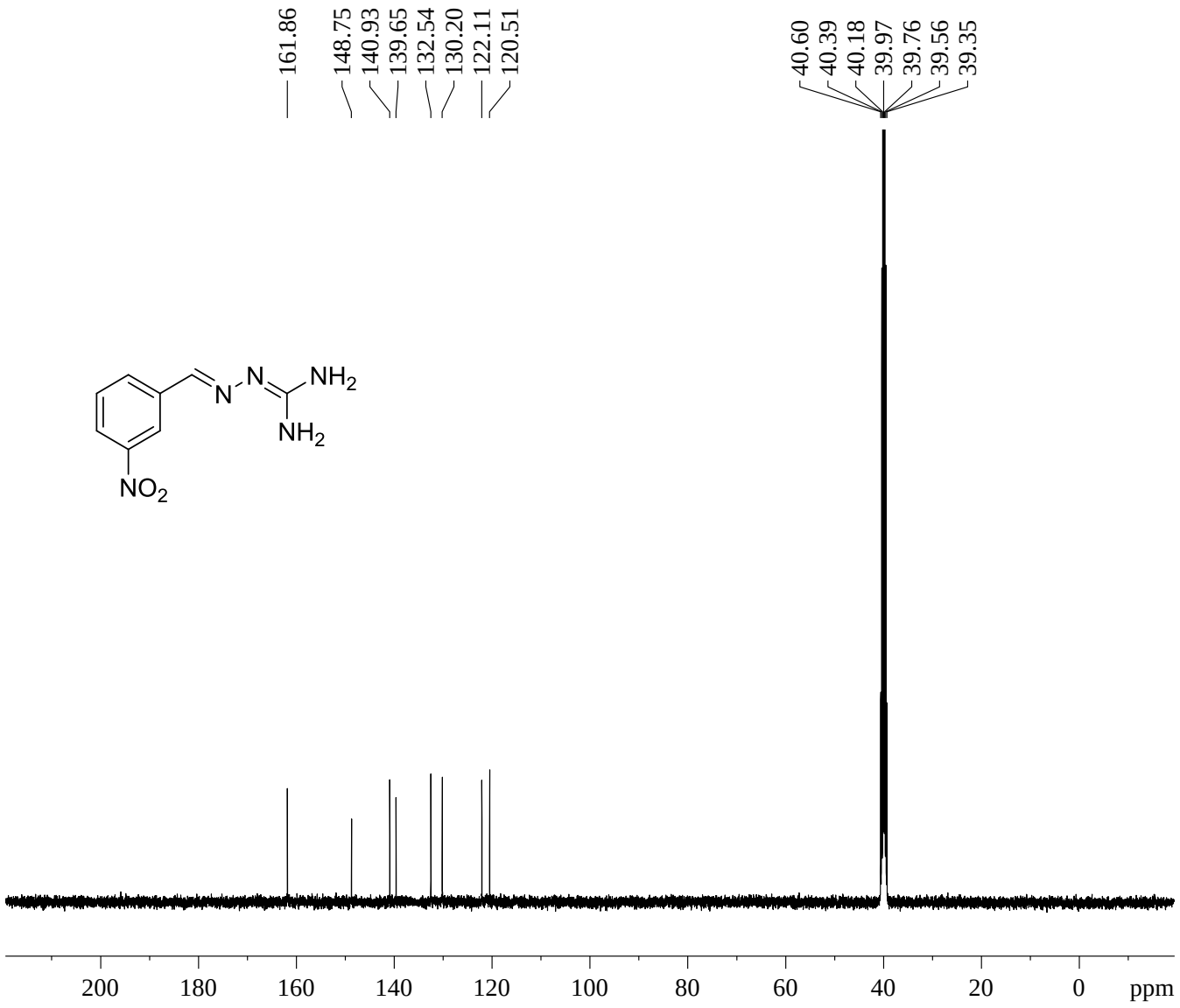

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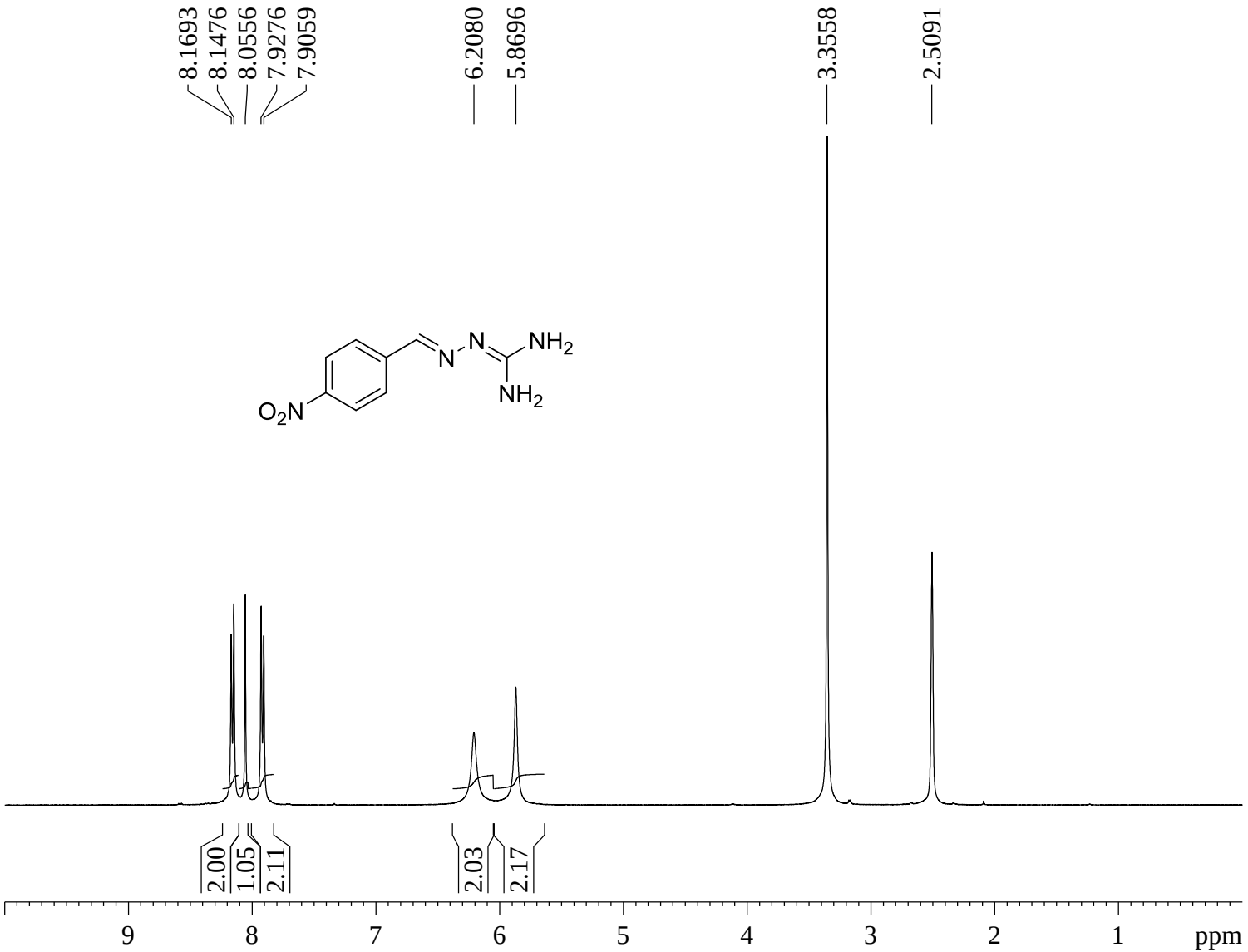

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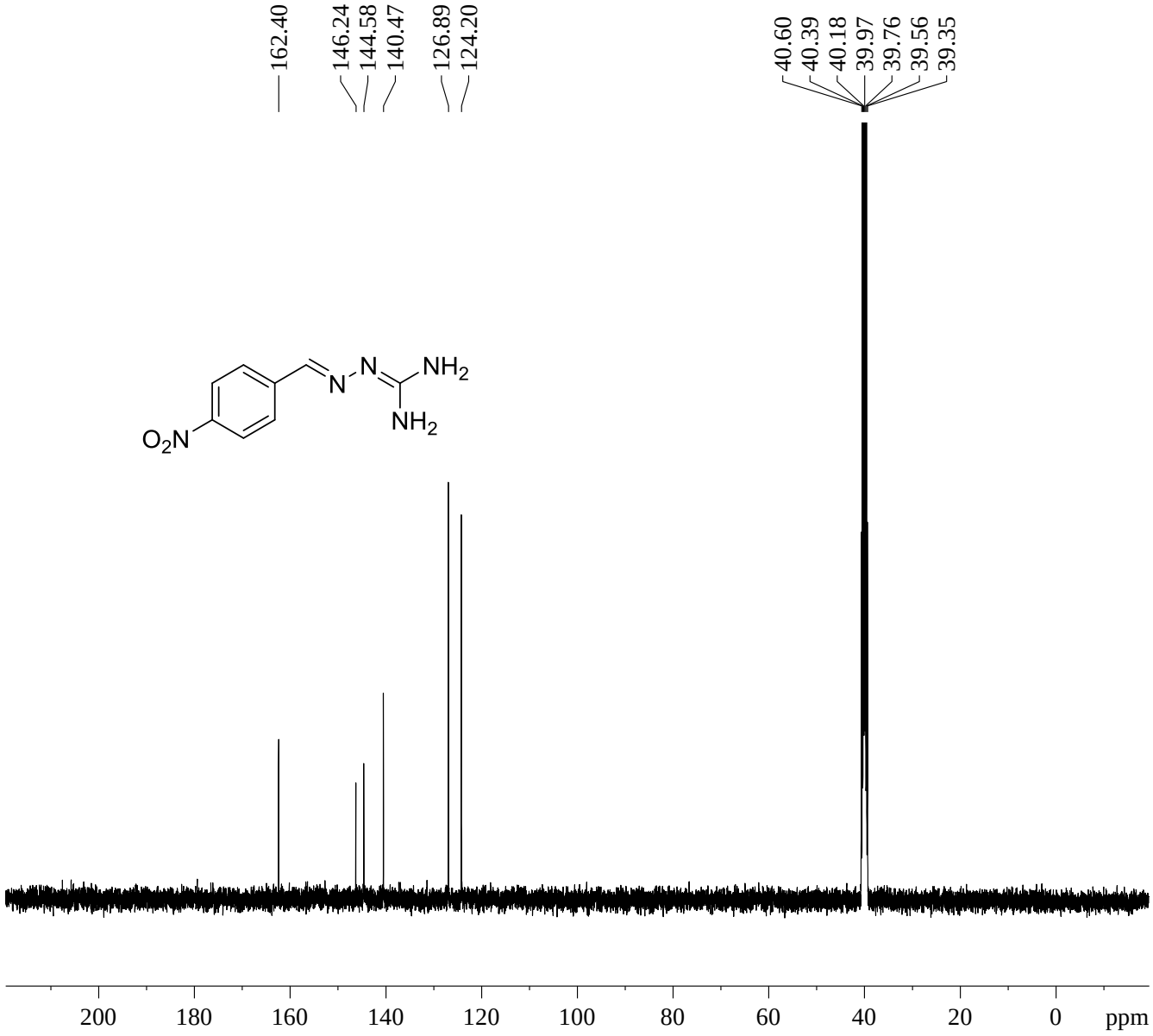

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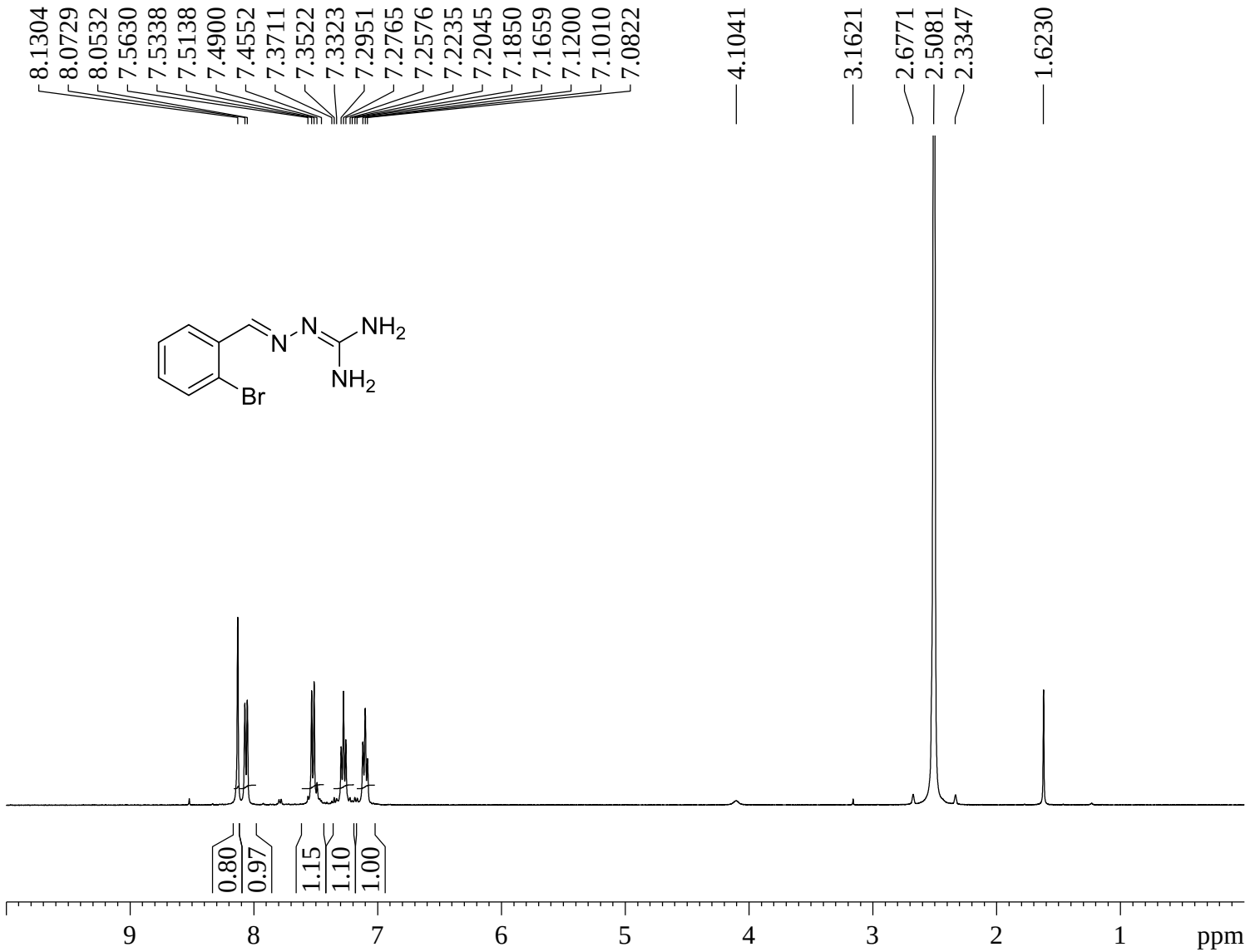

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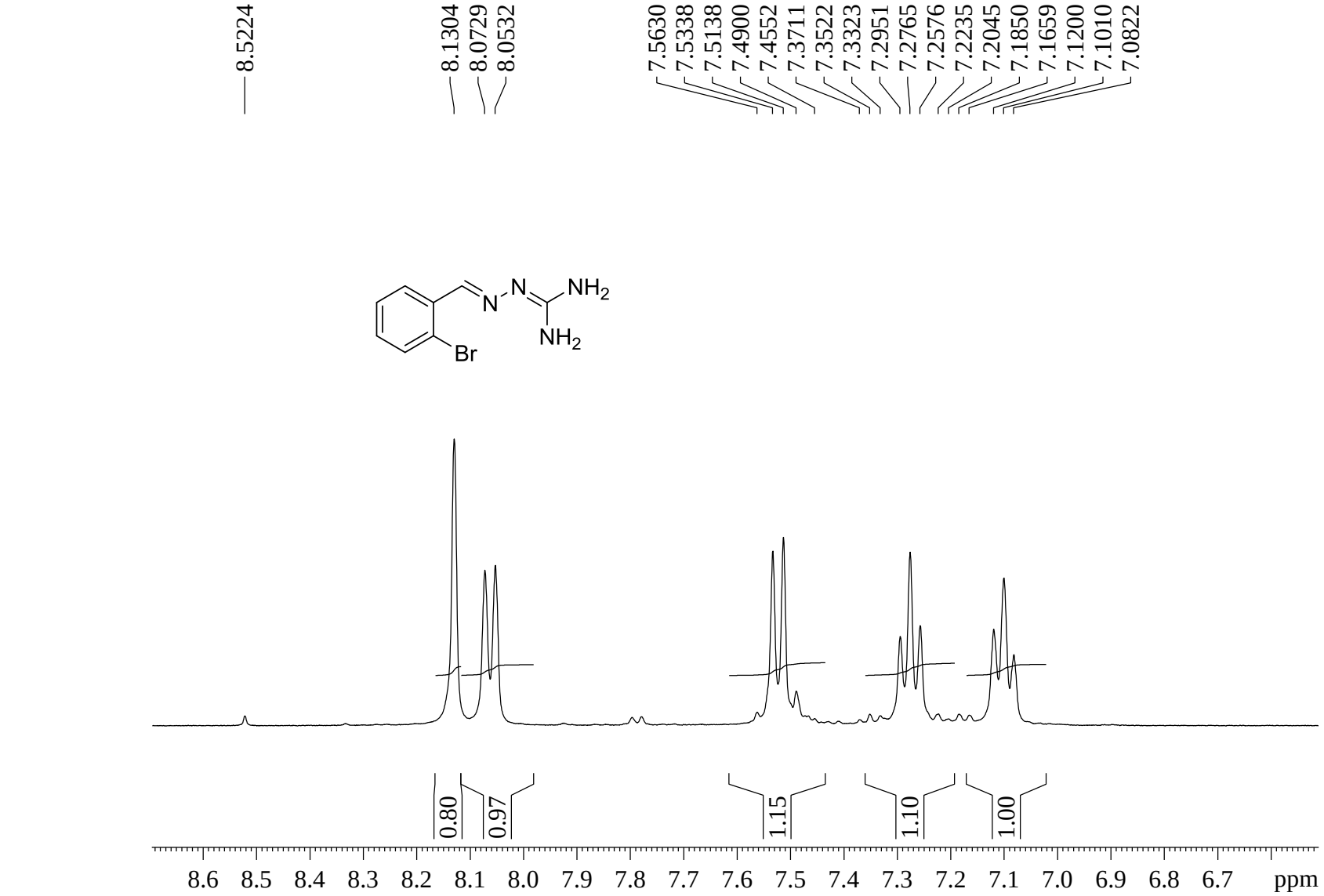

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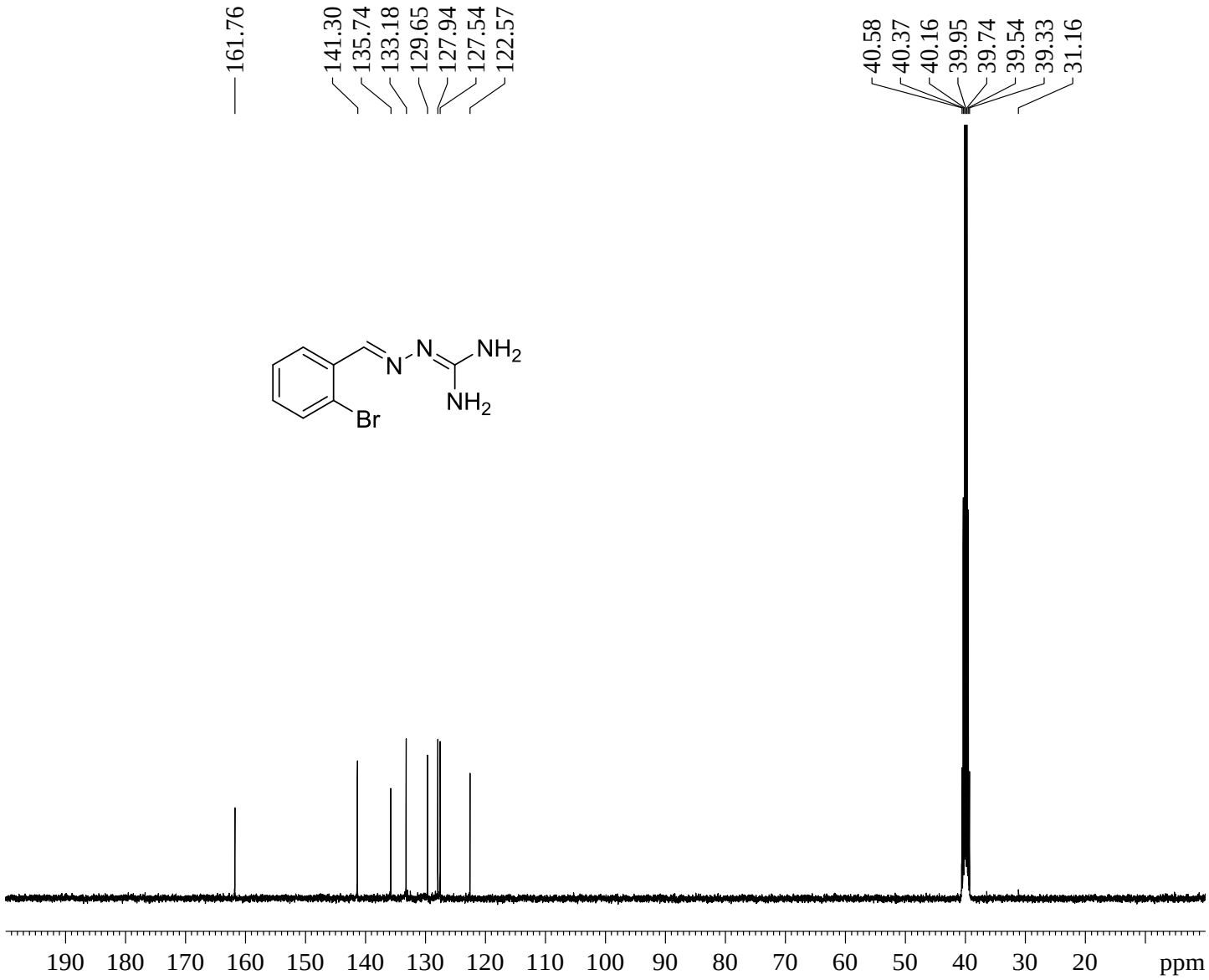

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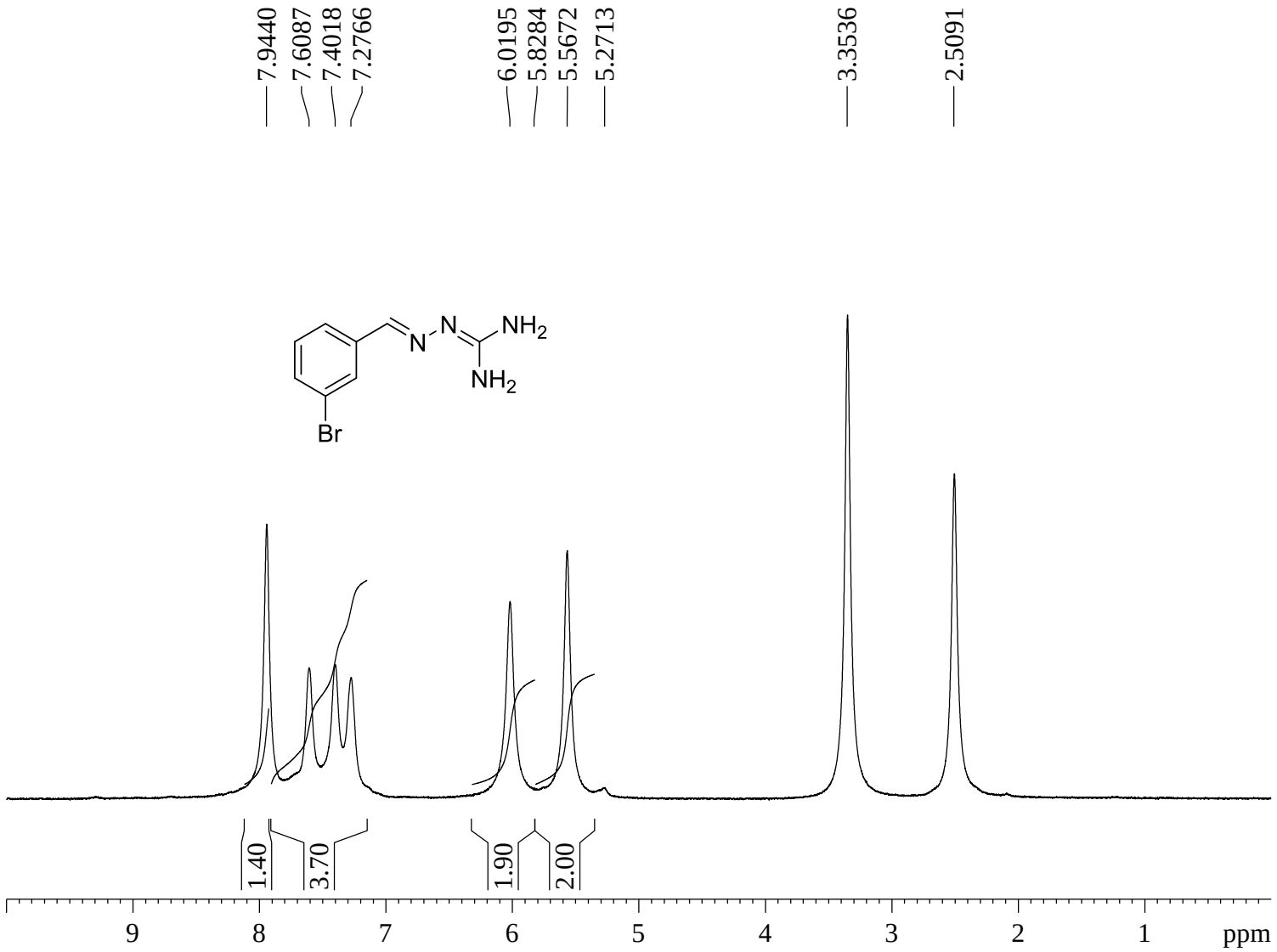

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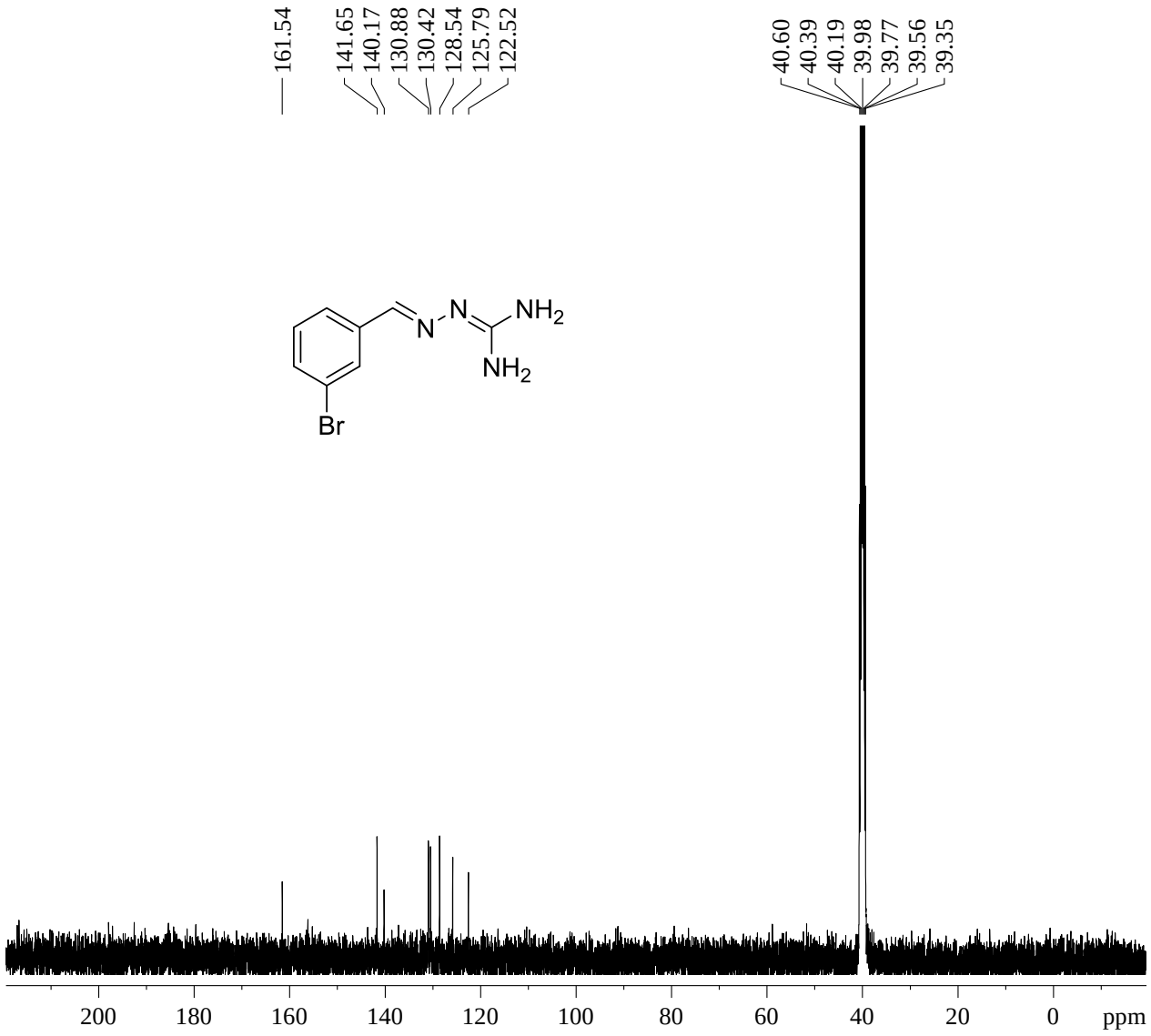

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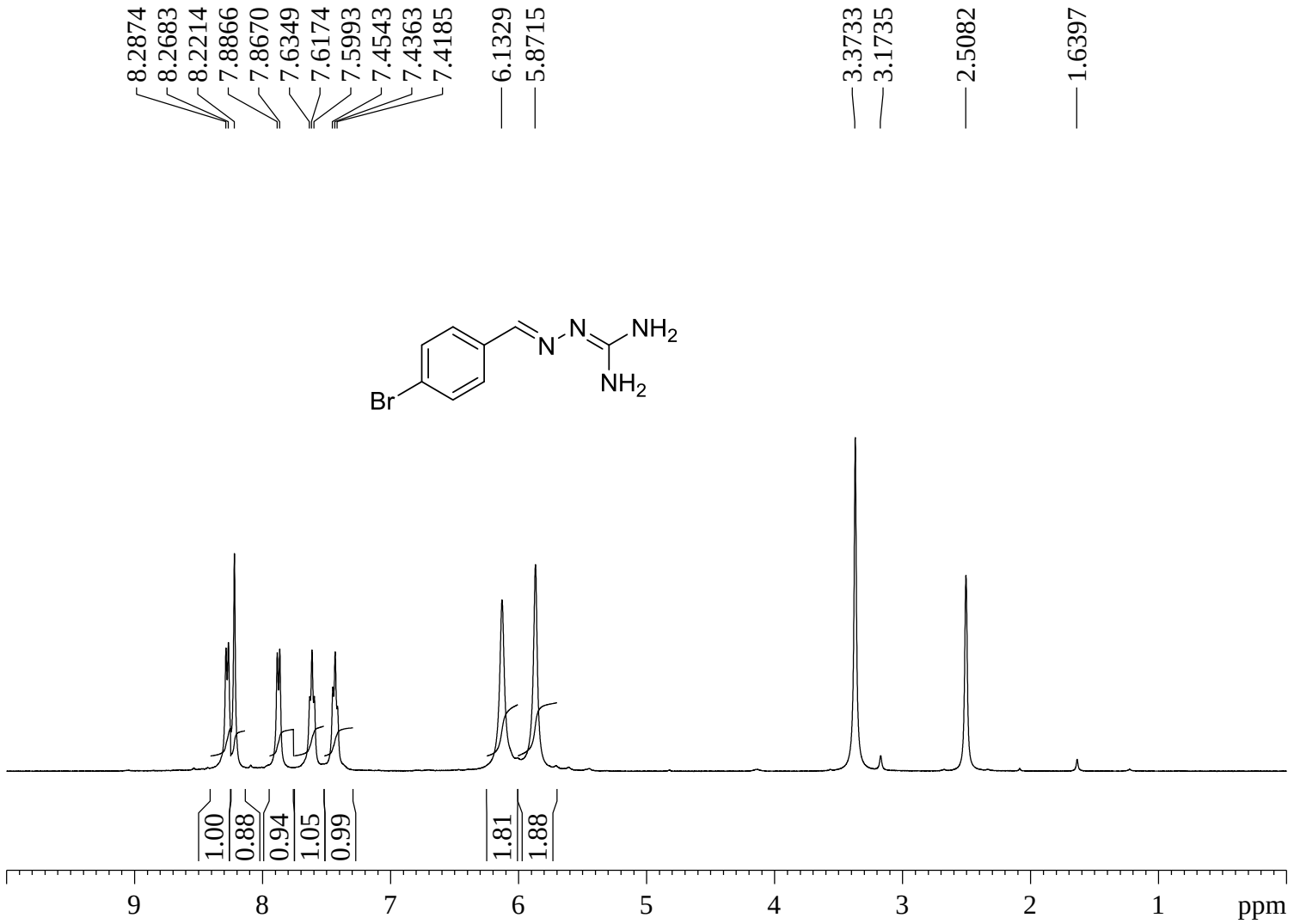

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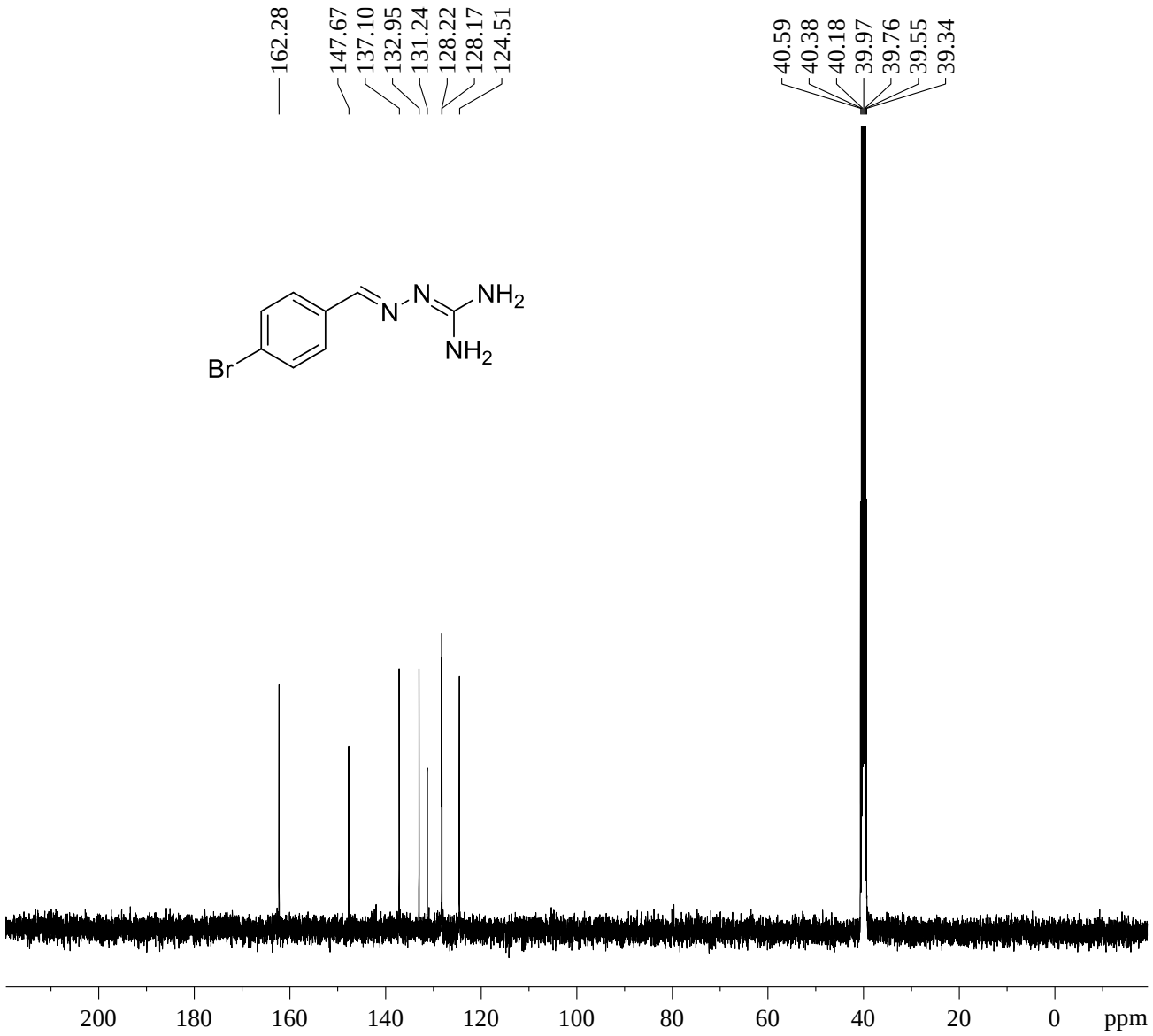

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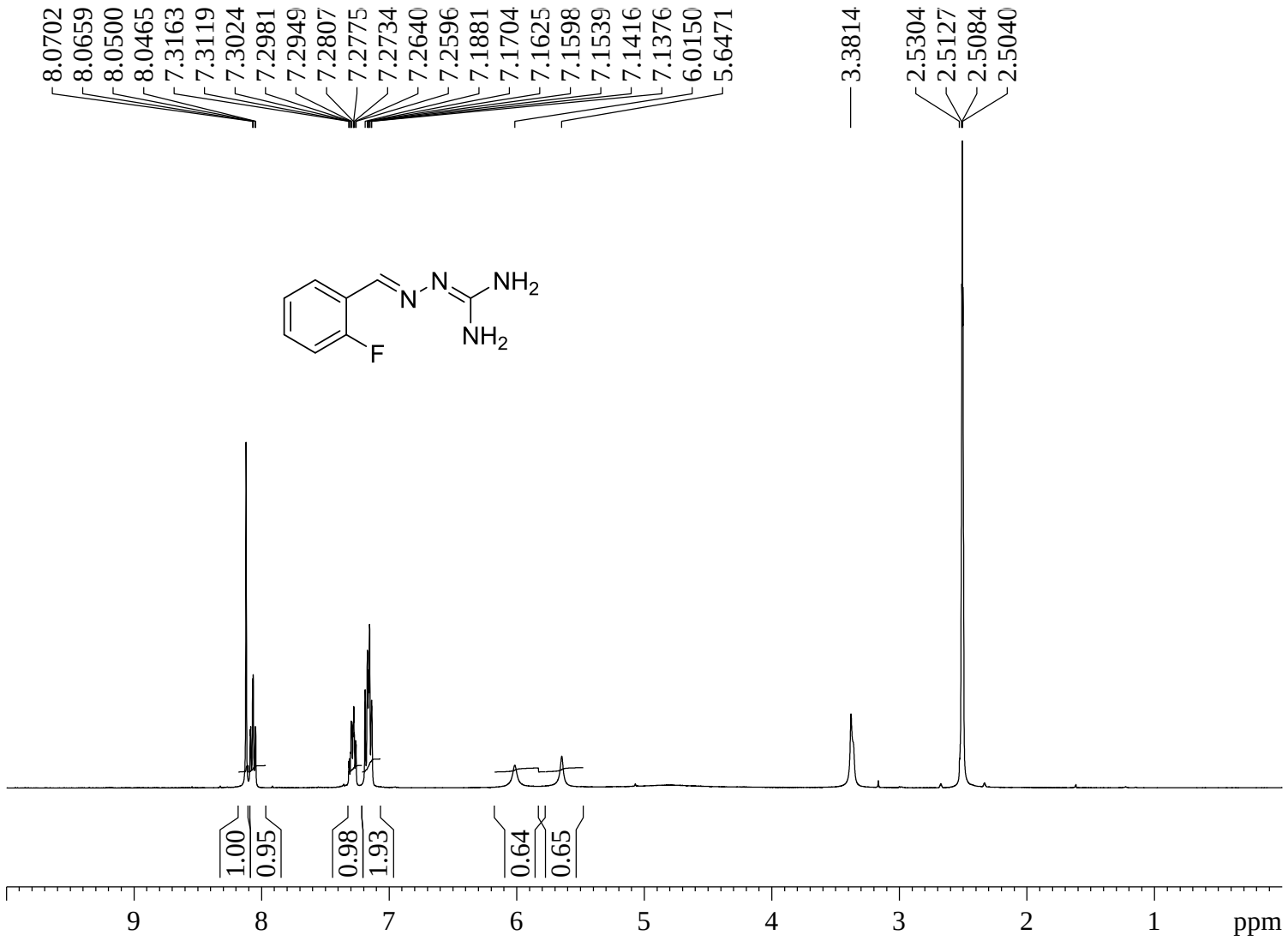

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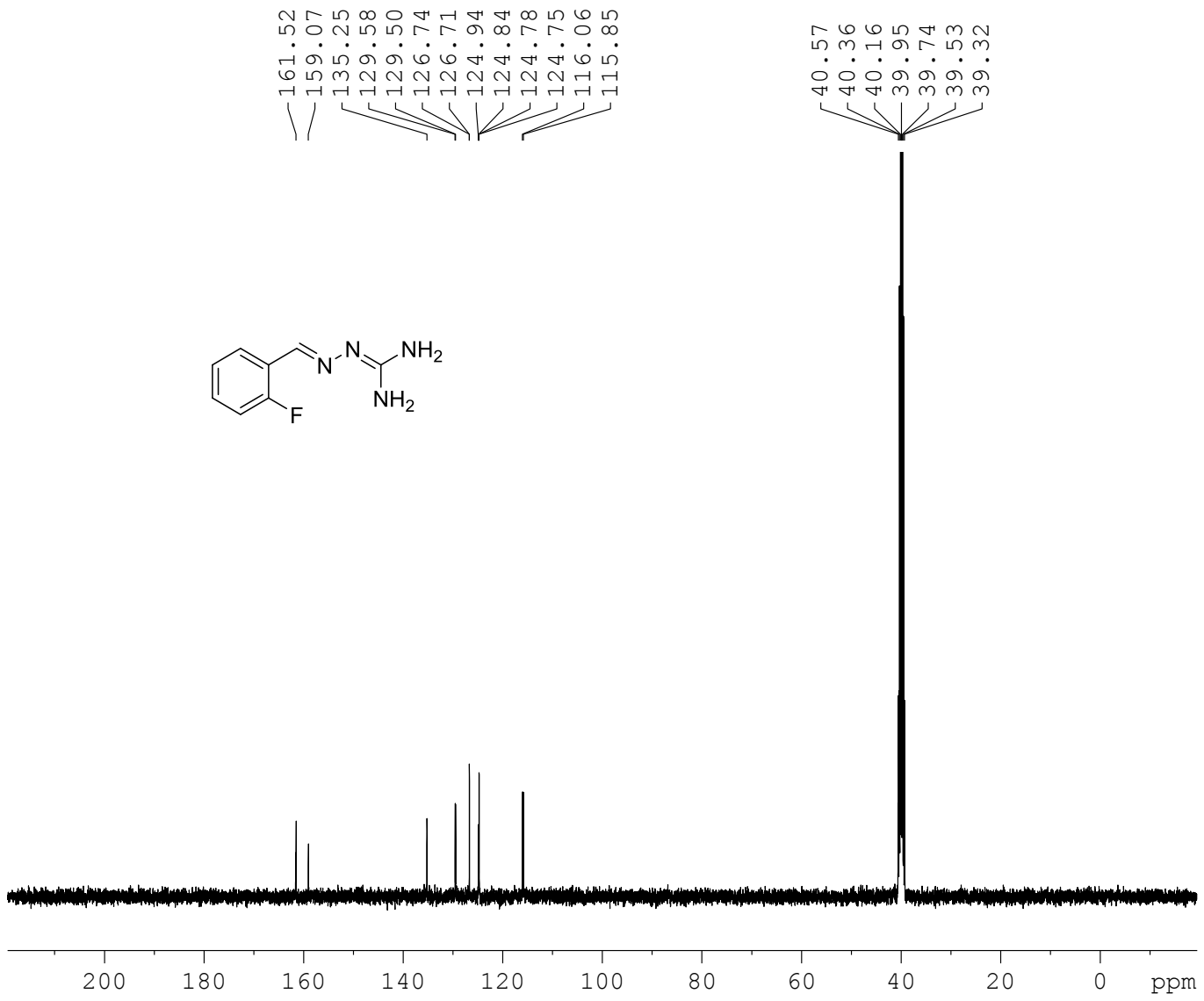
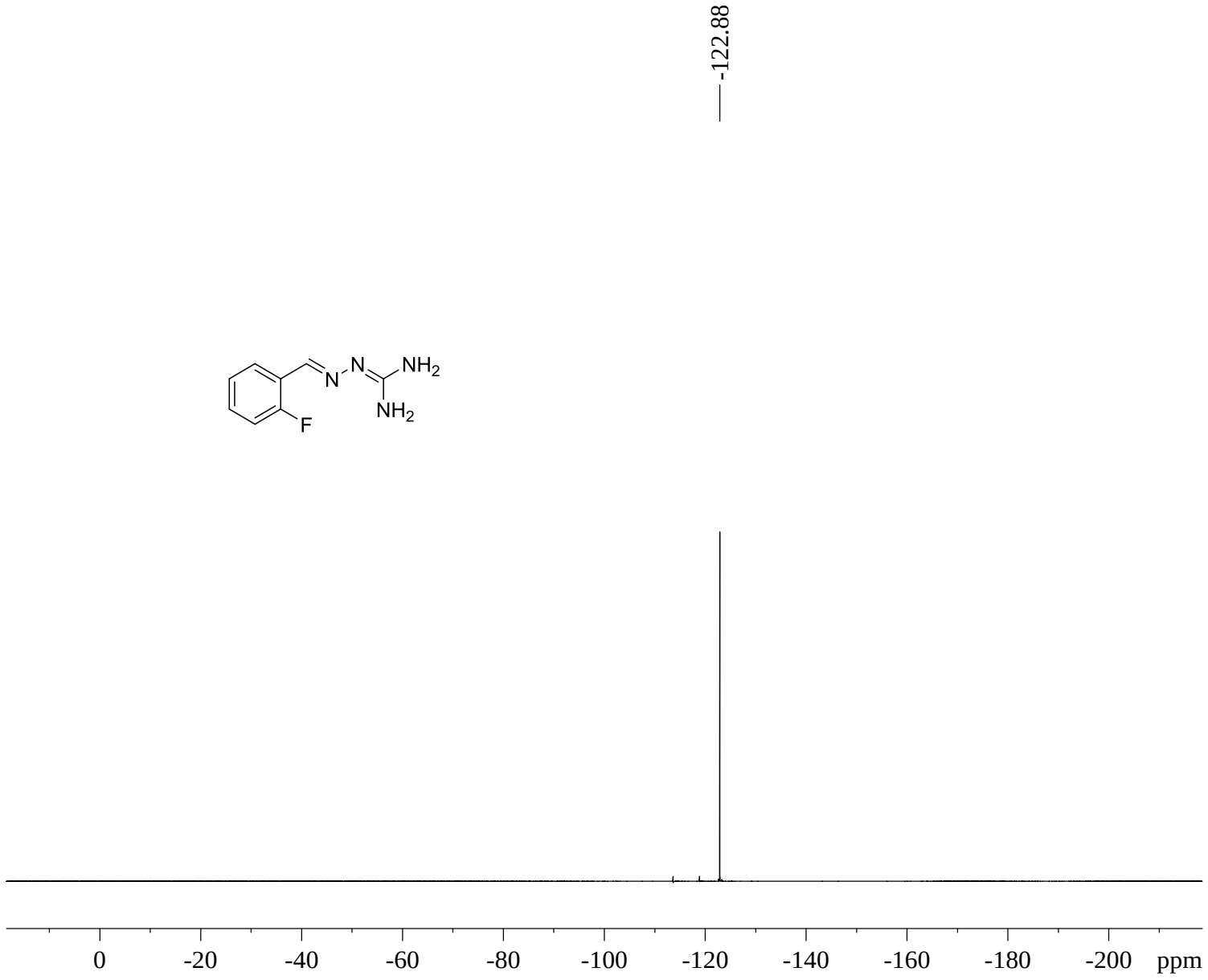


^{19}F spectra of compound 1j



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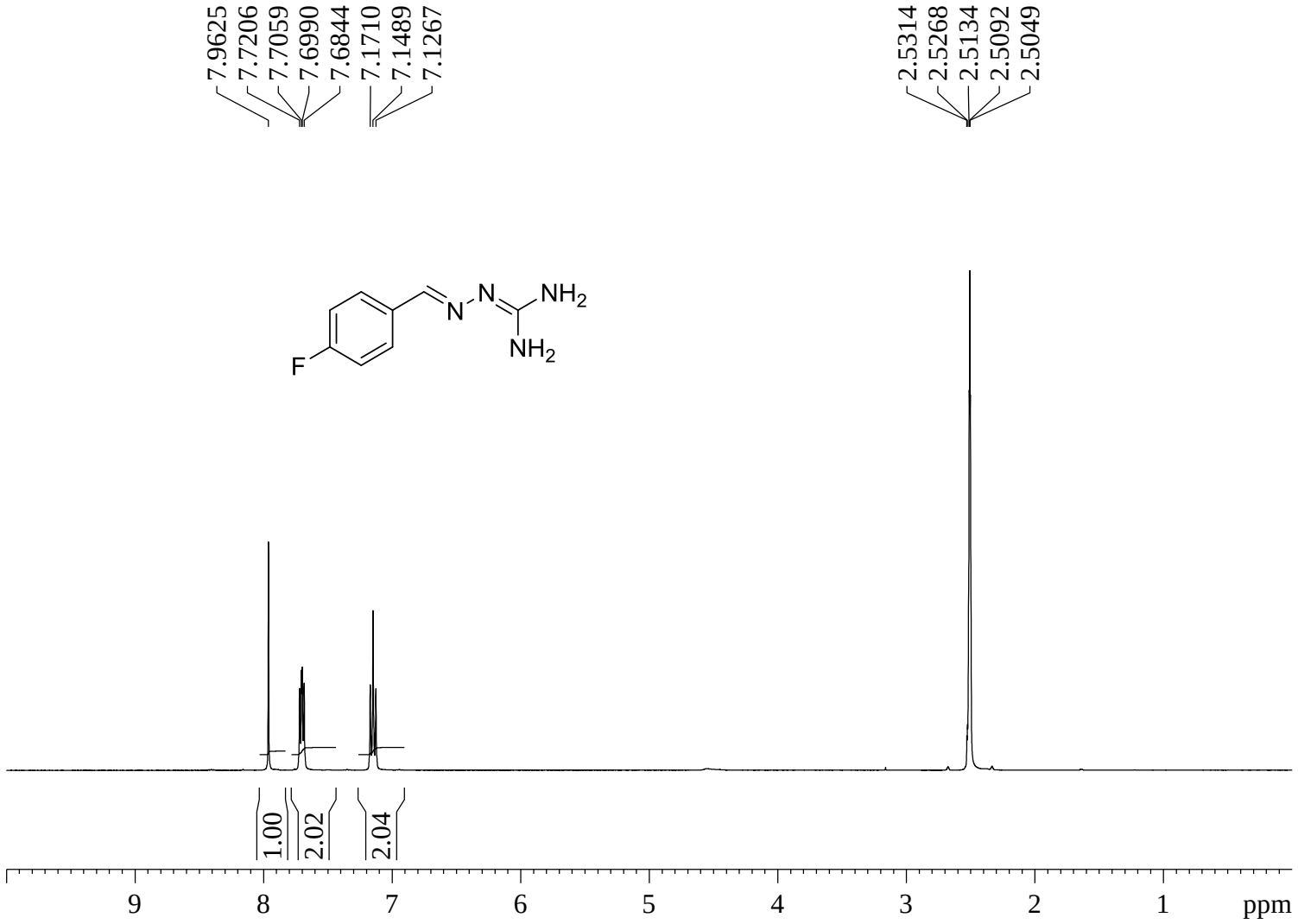

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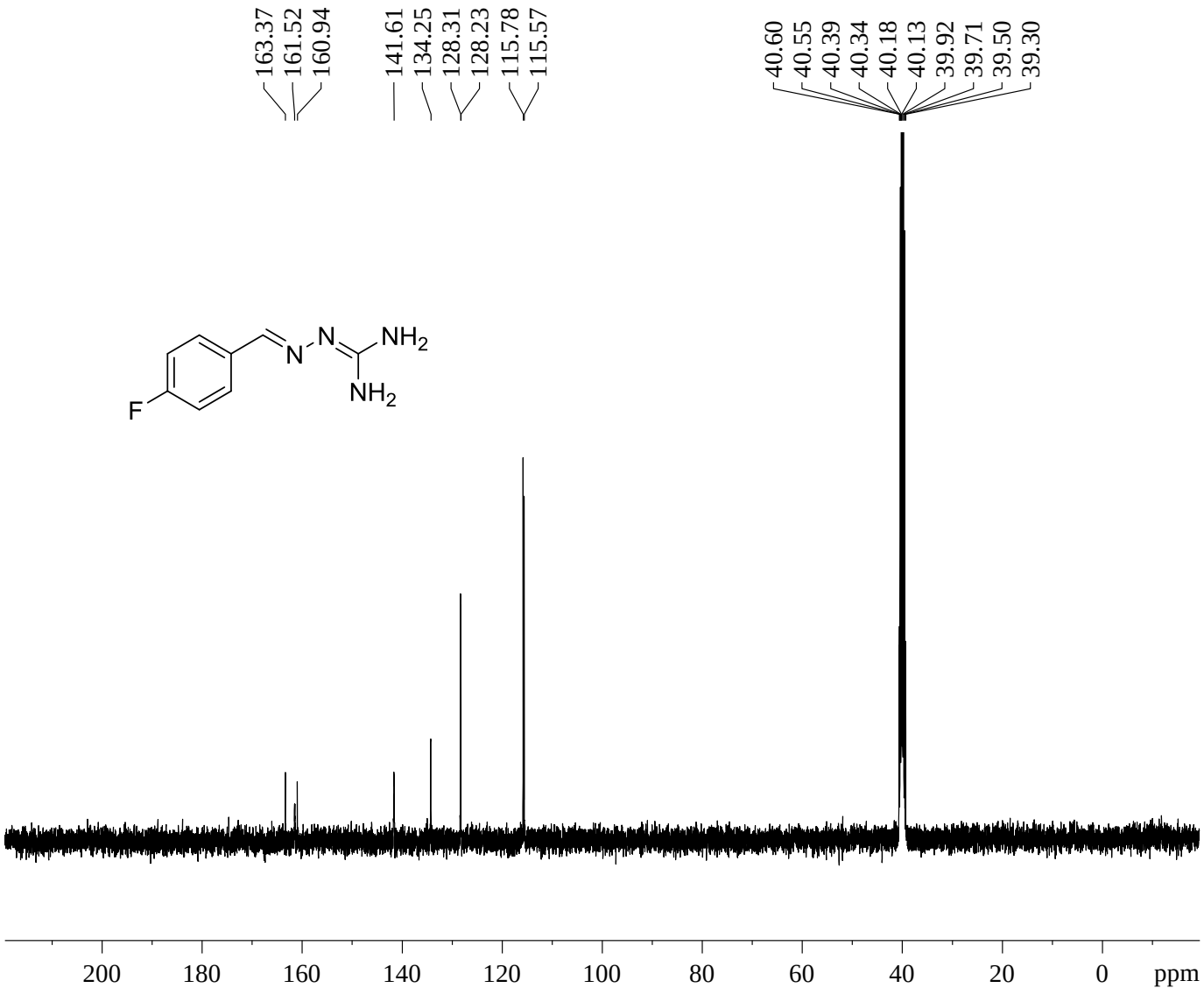

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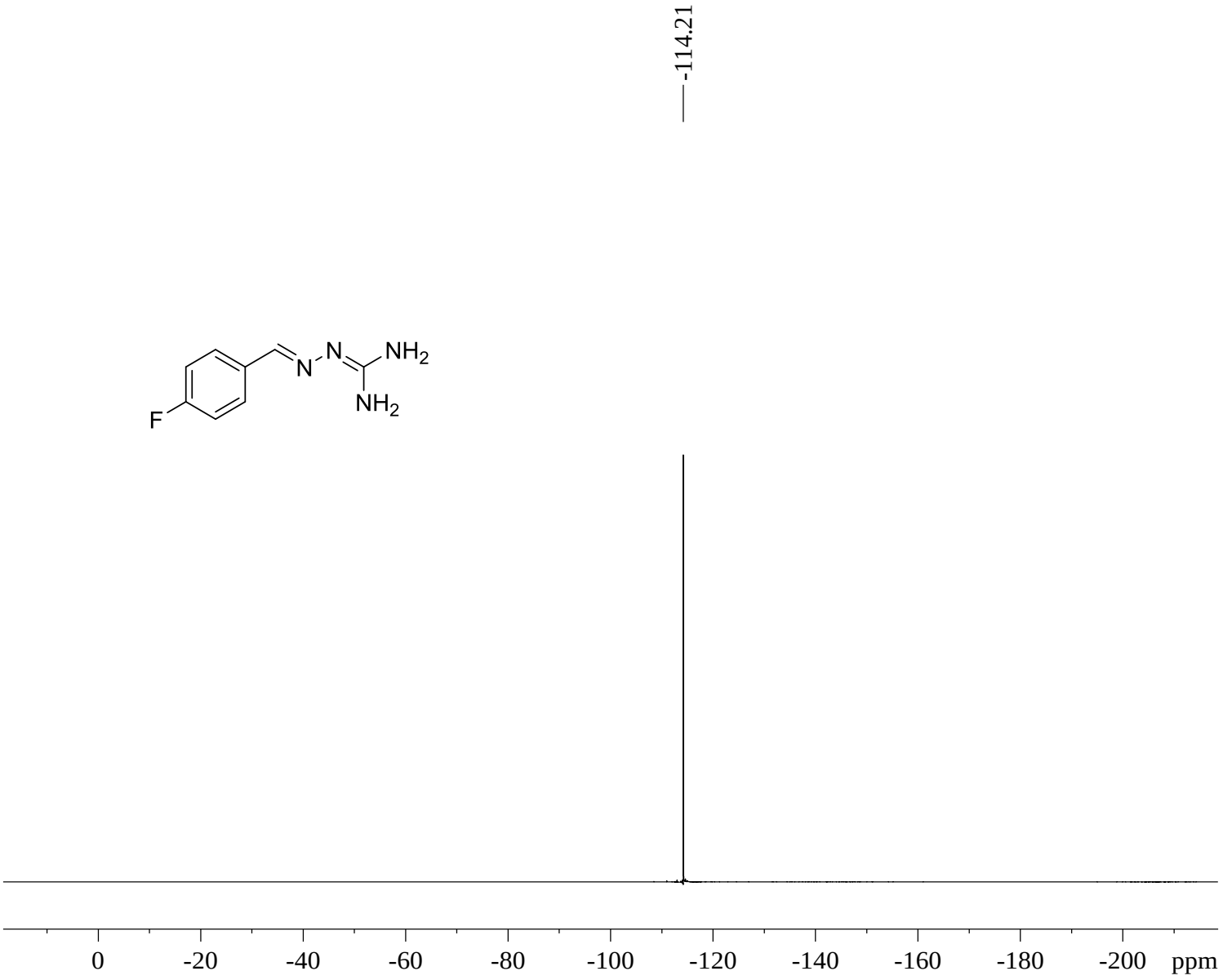

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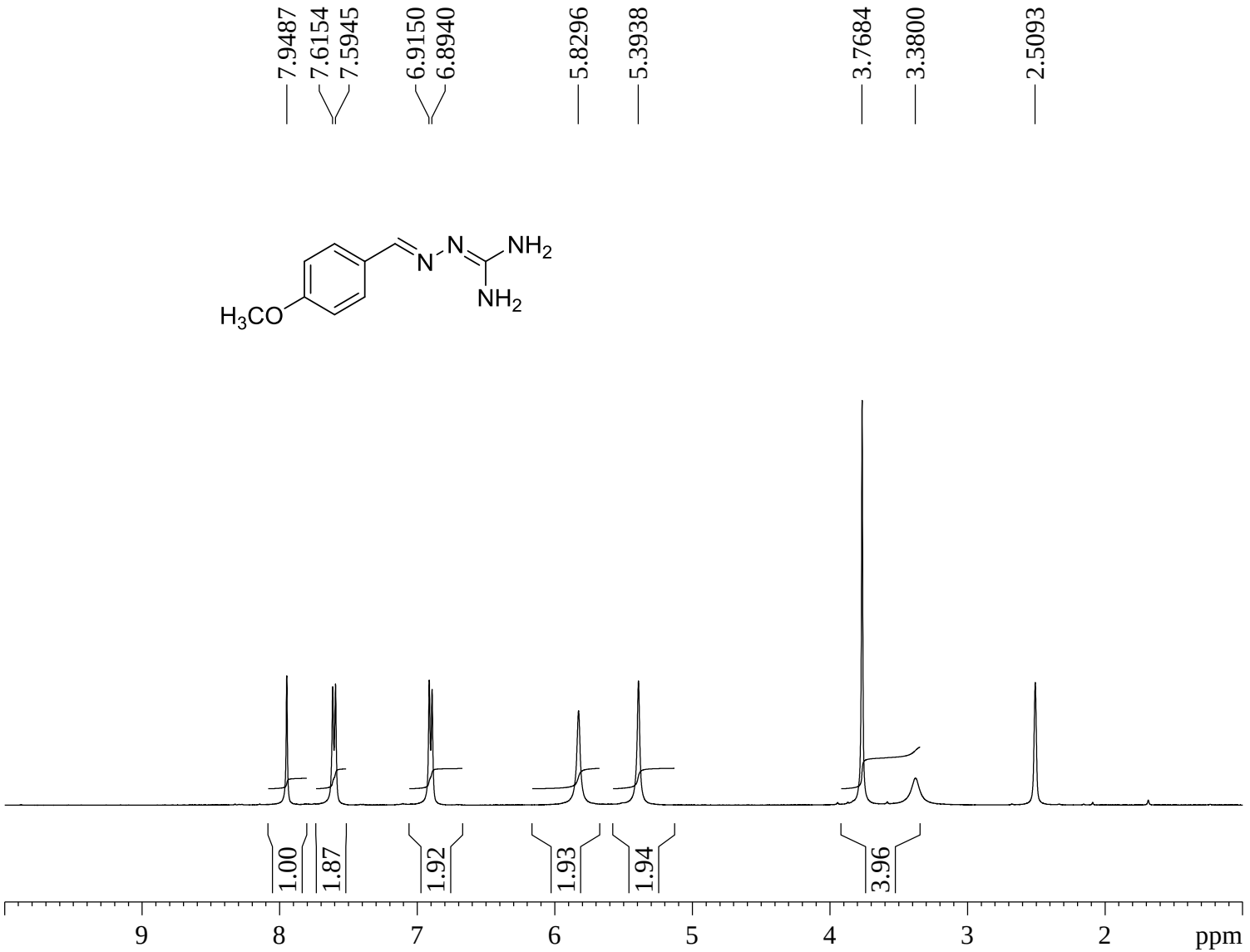

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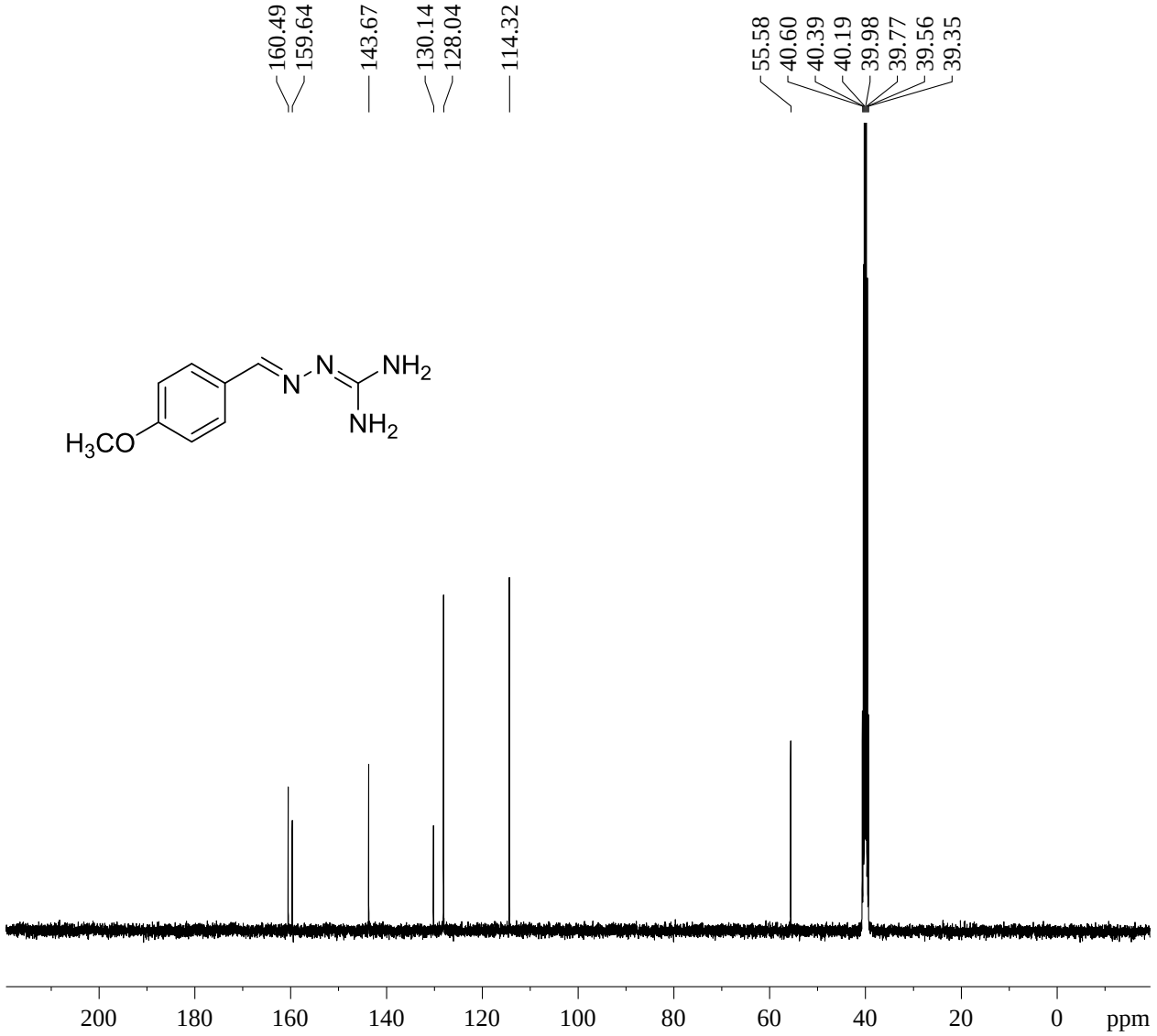

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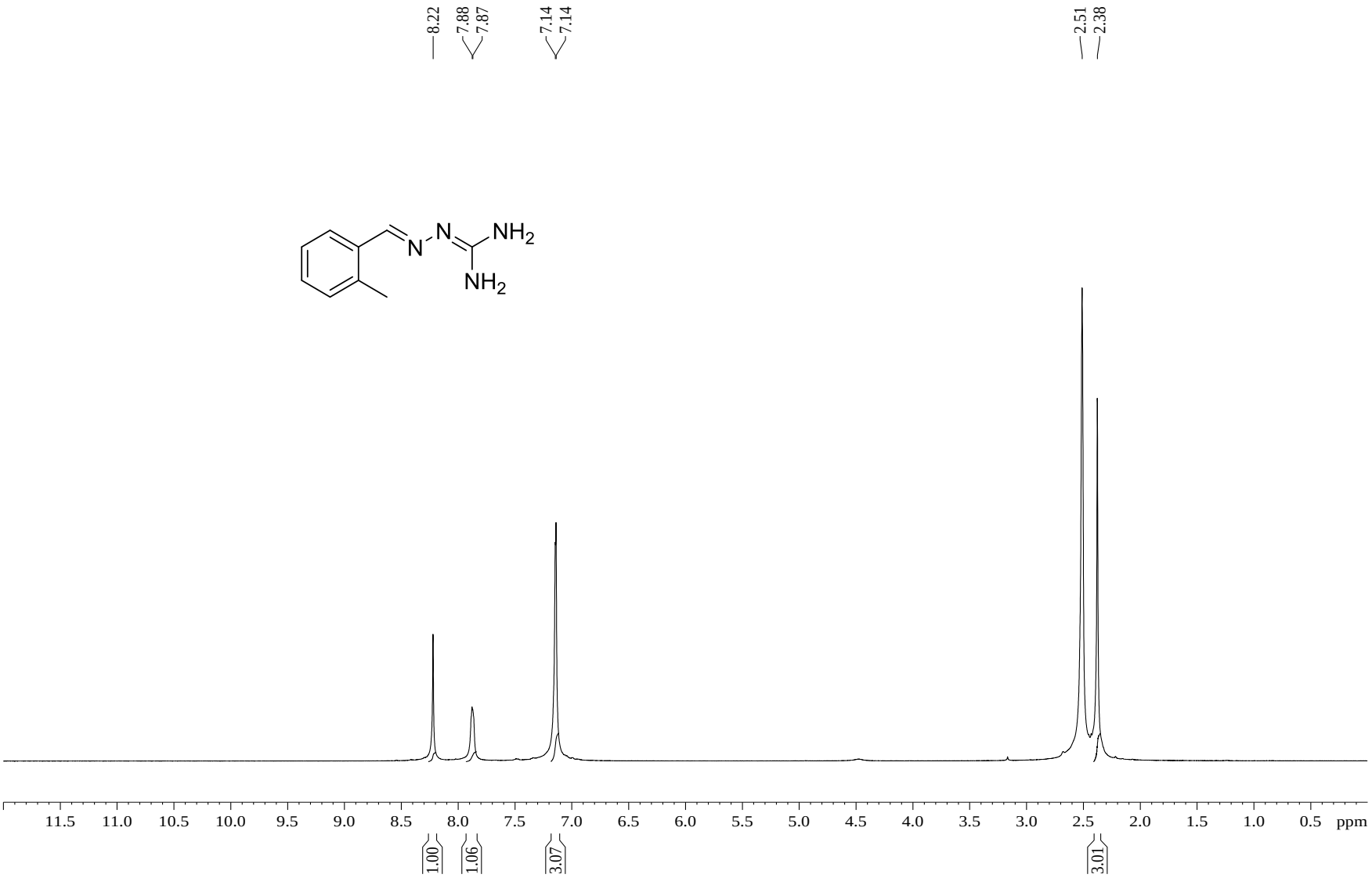

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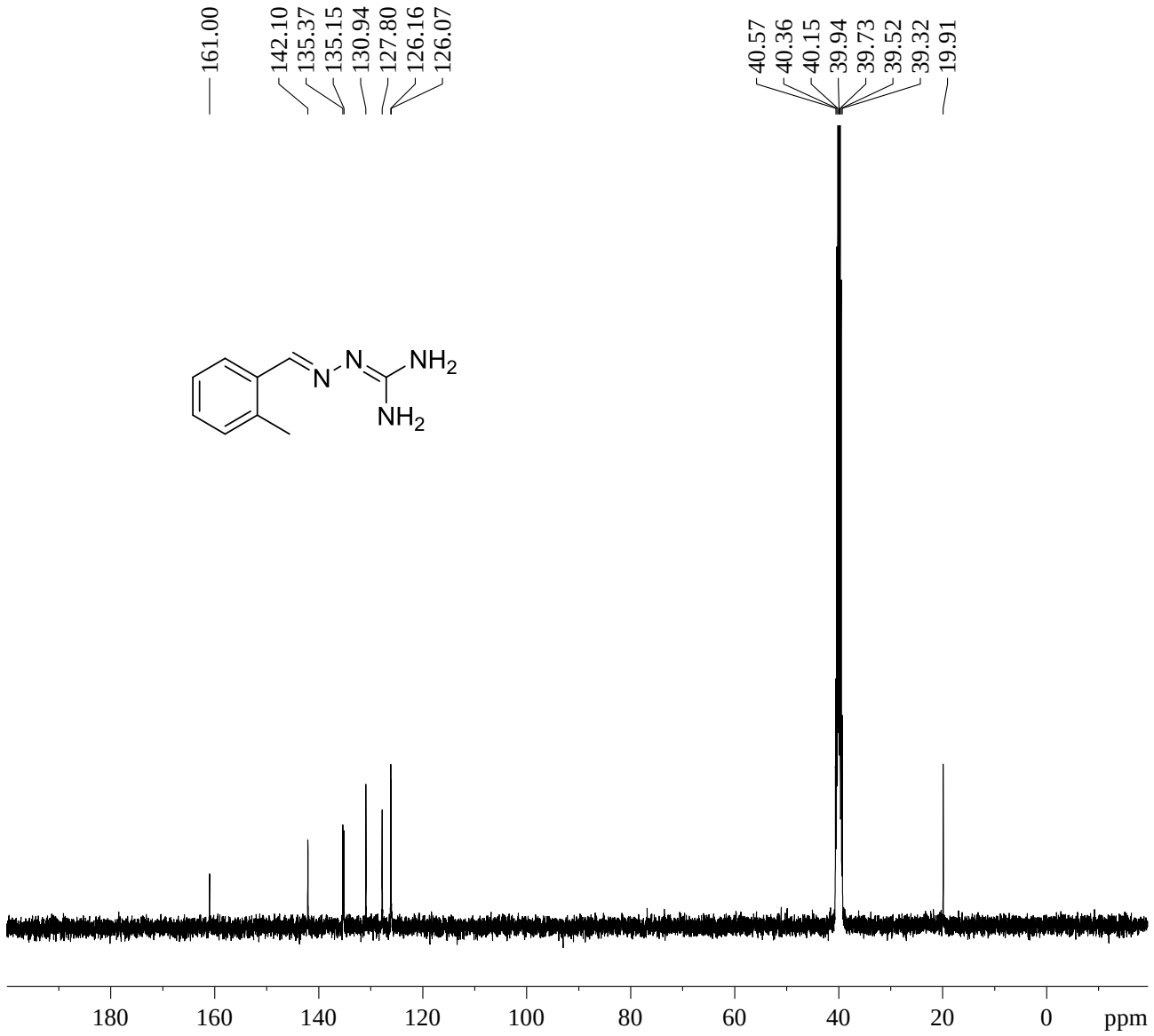

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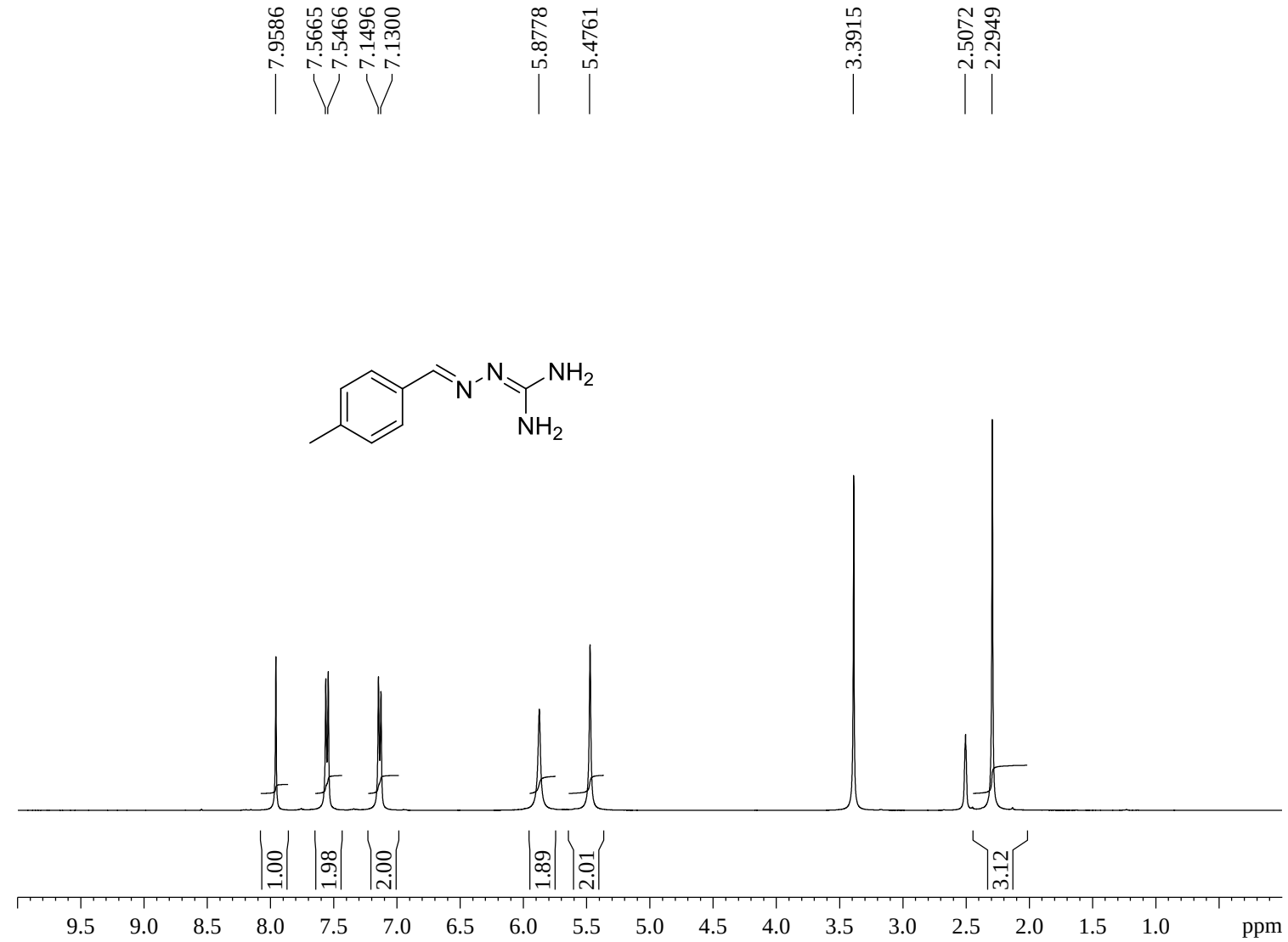

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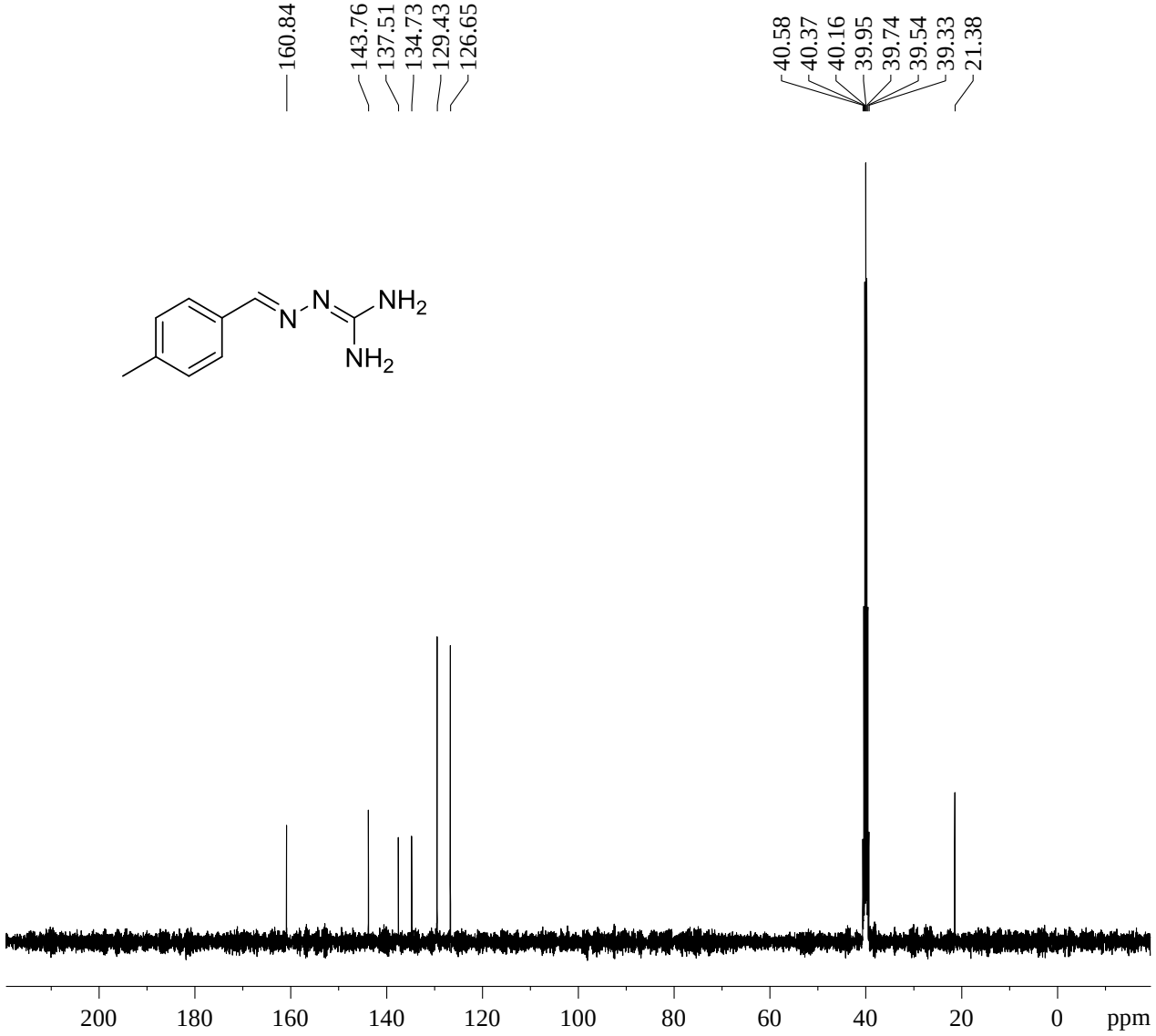

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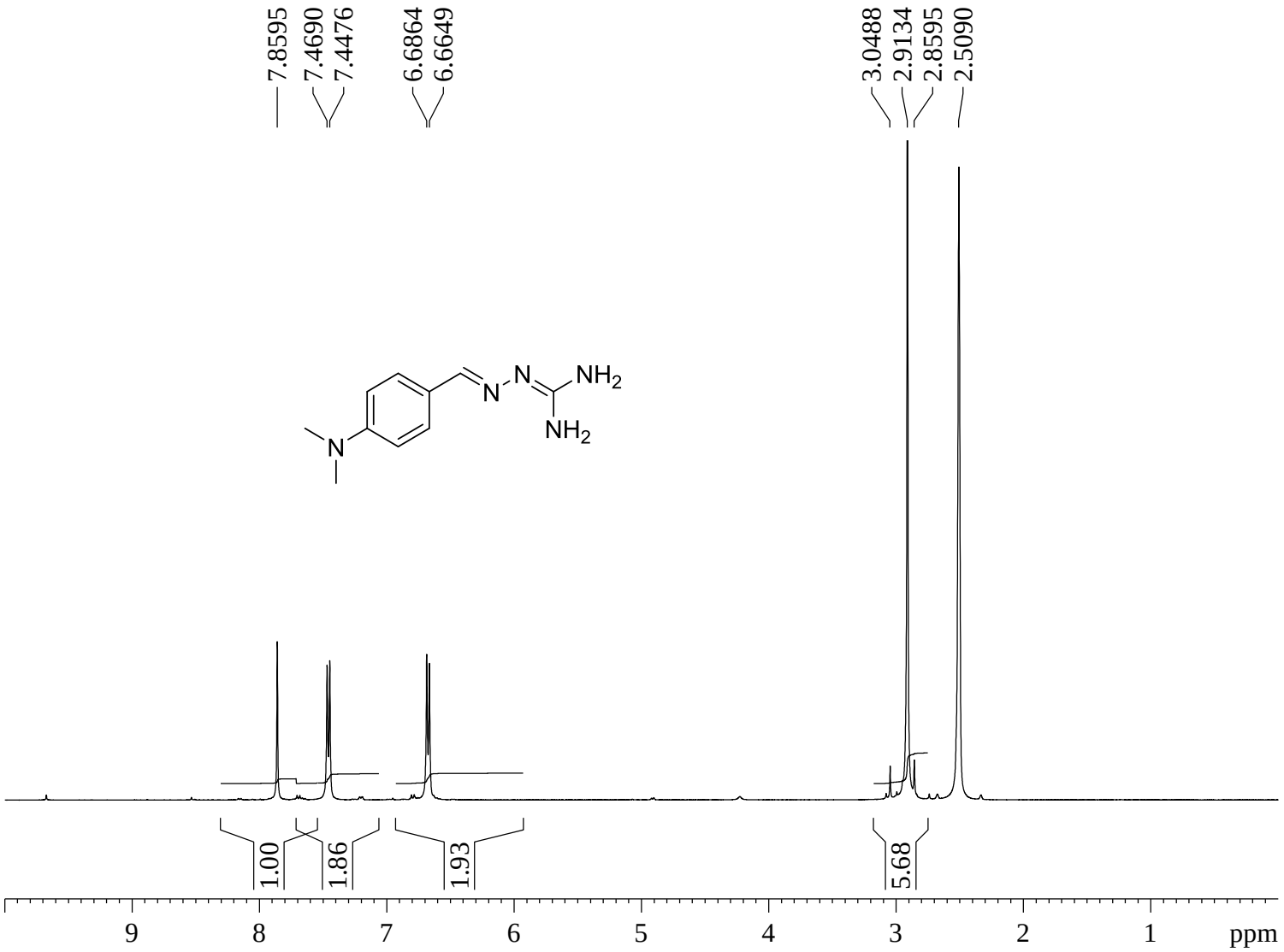

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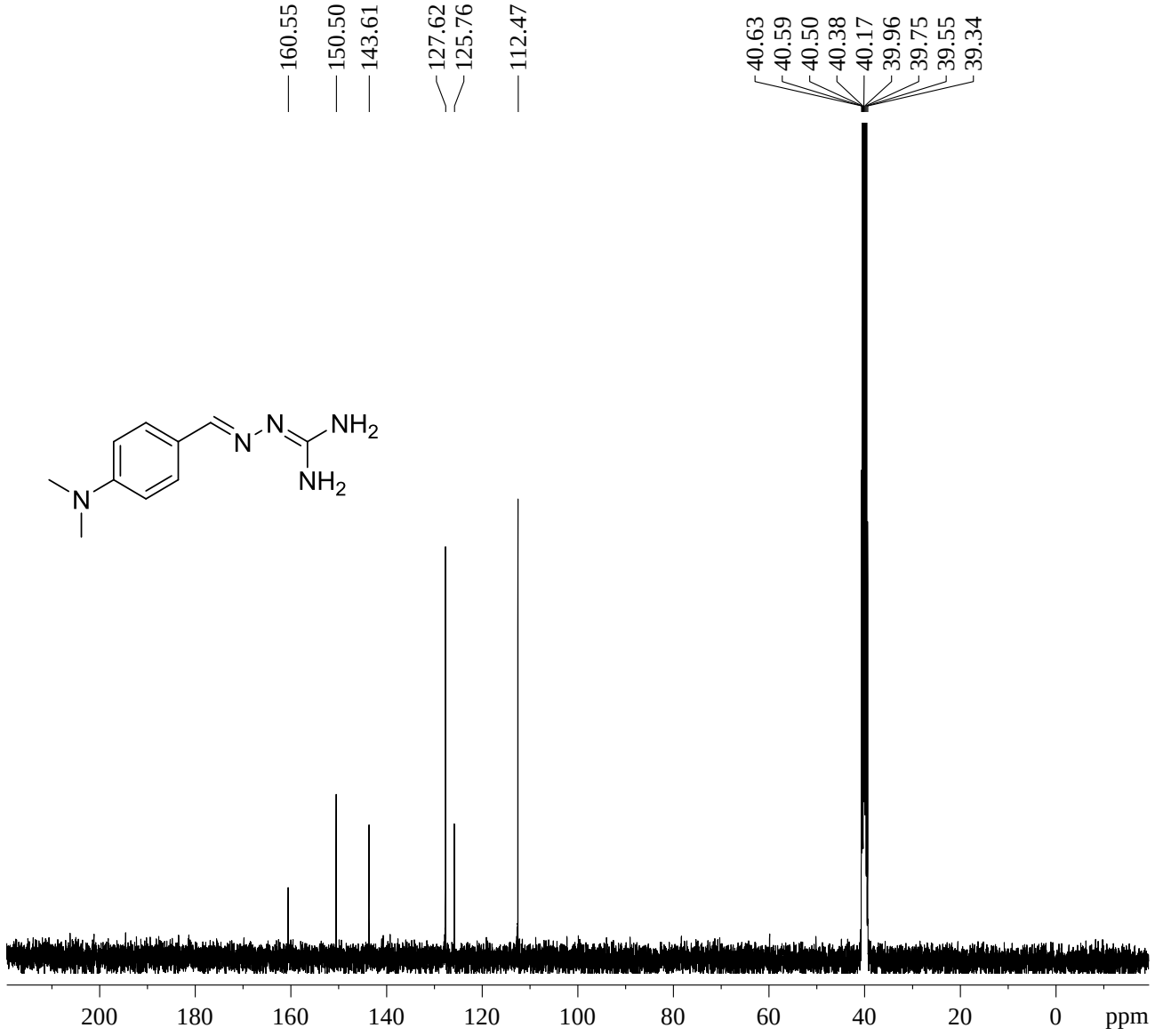

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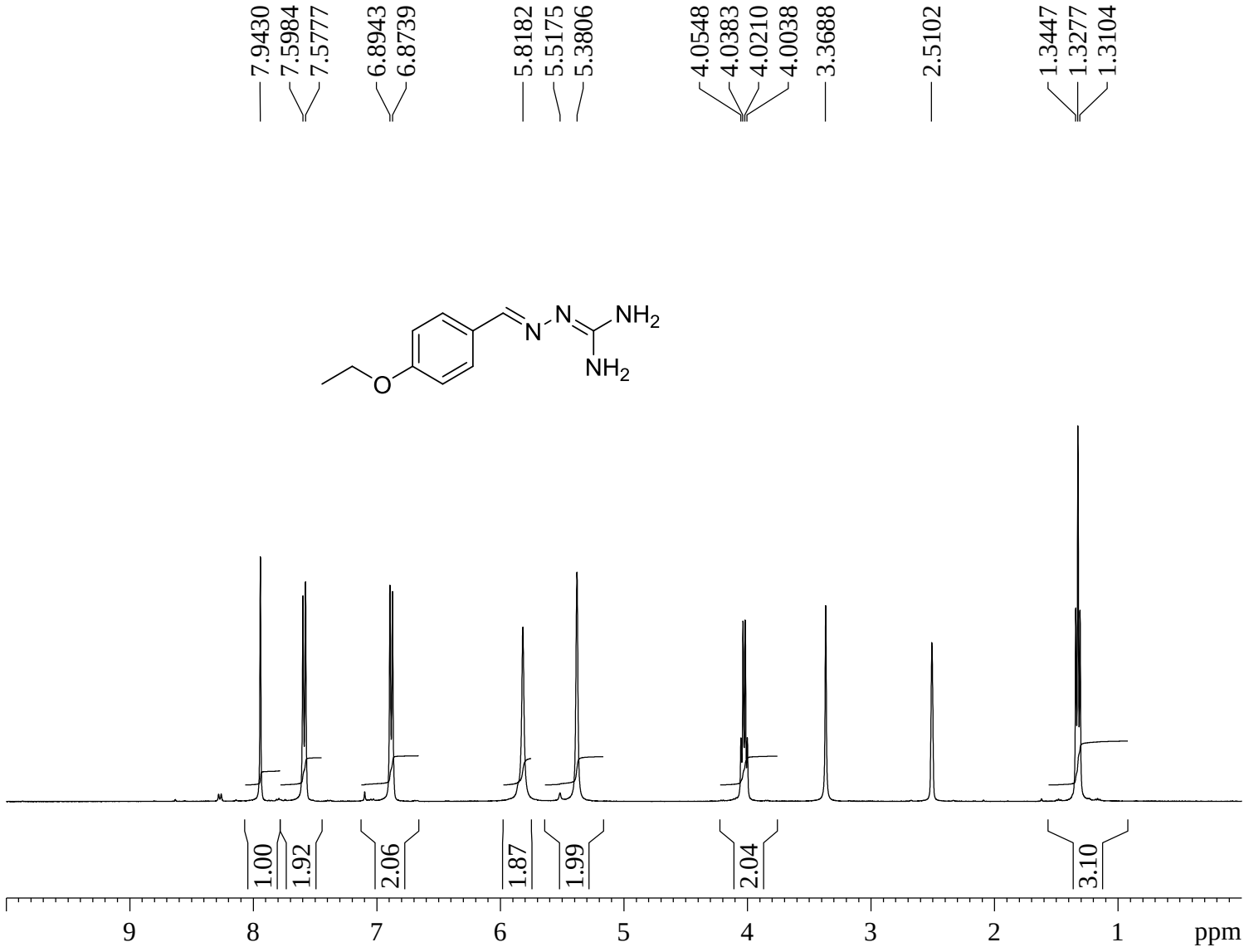

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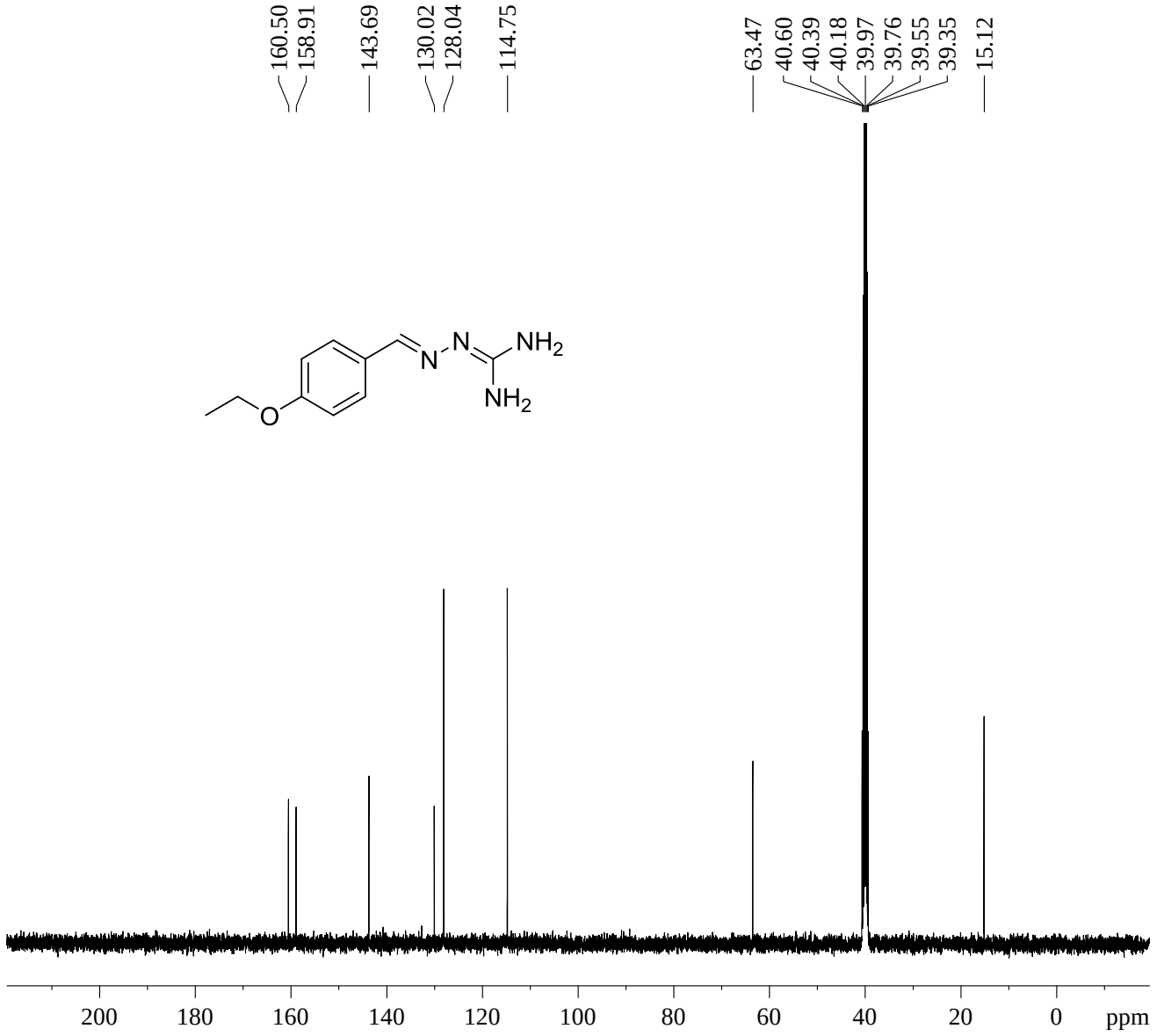
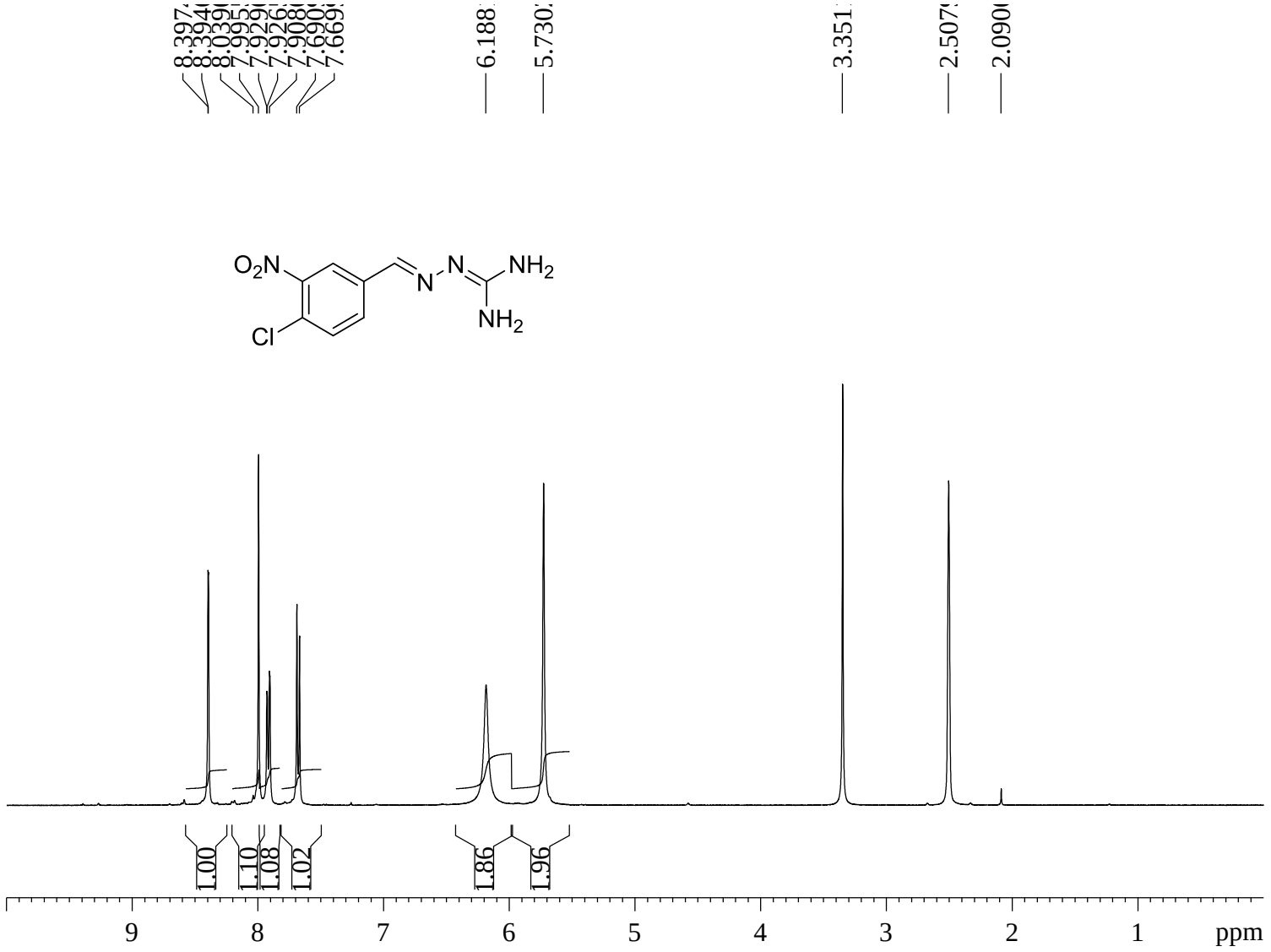


^{1}H spectra of compound 1q



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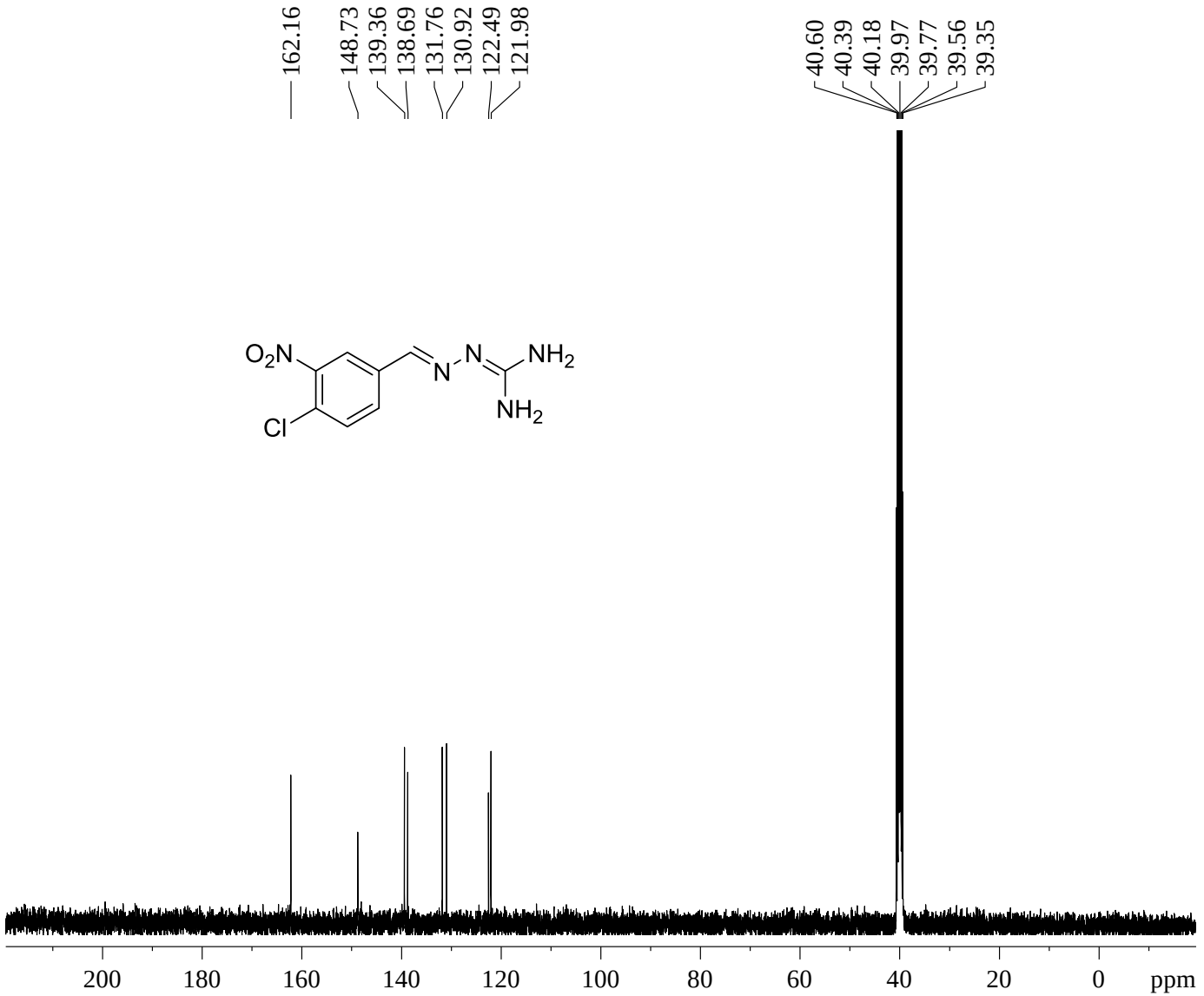

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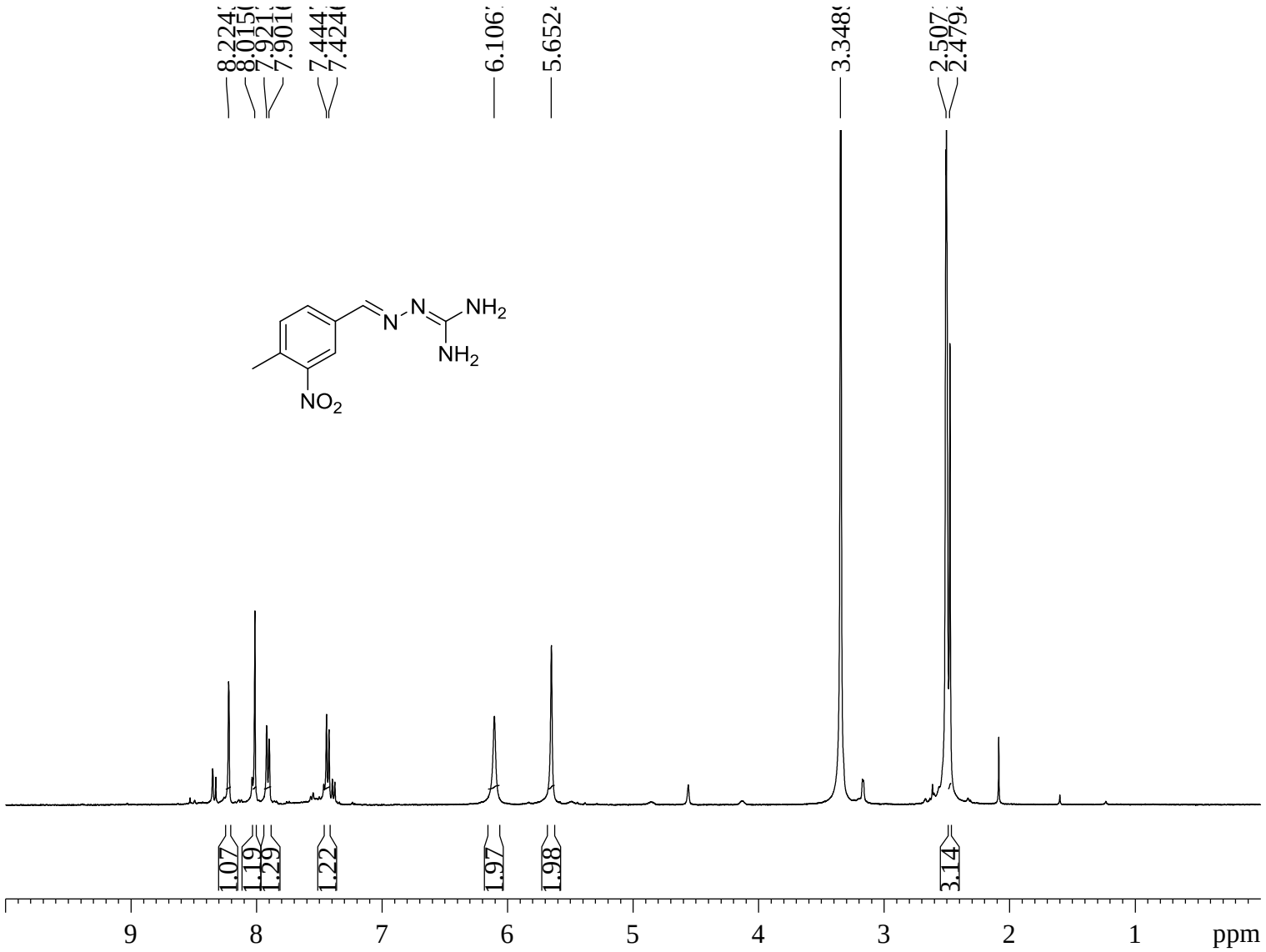

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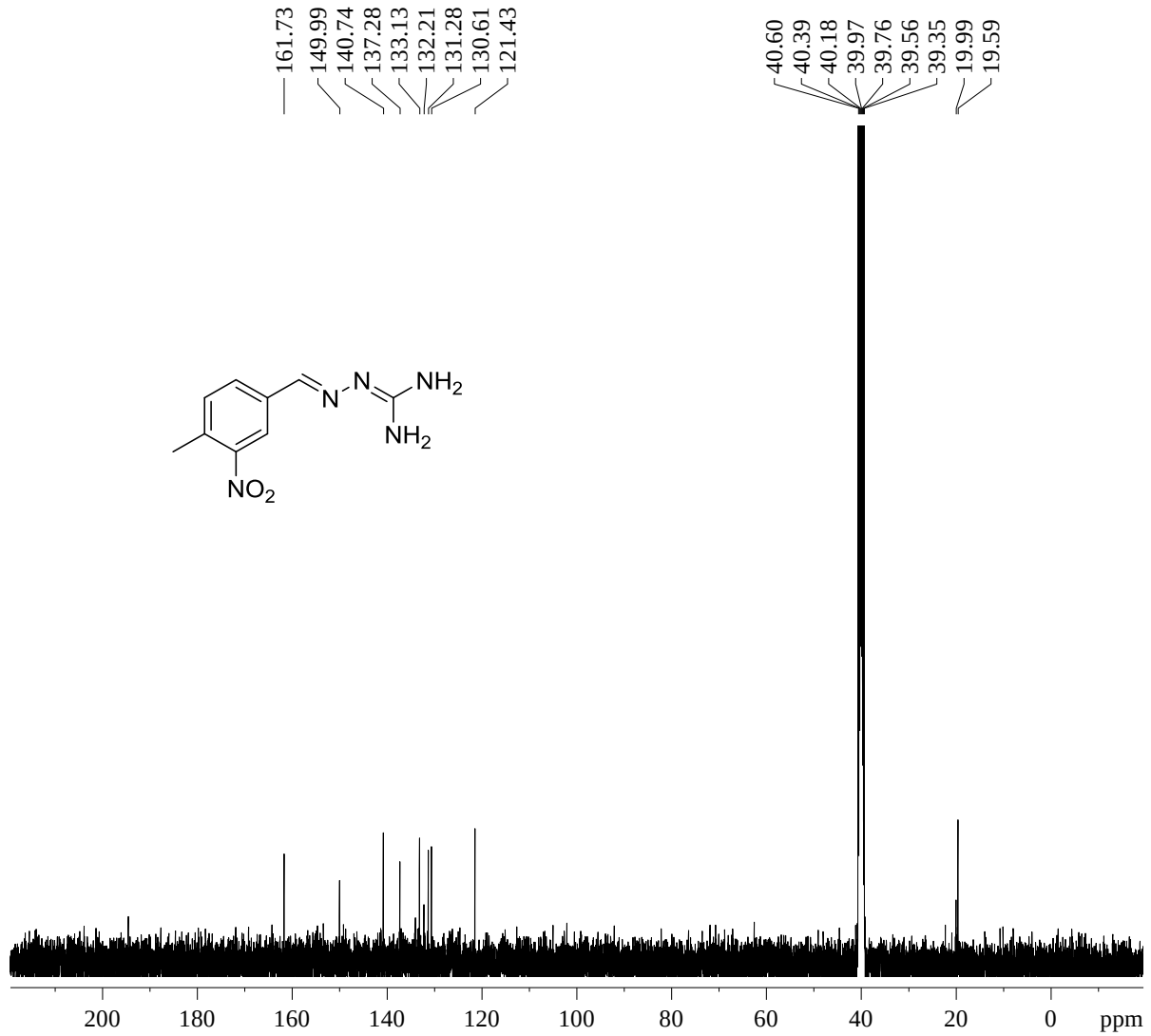

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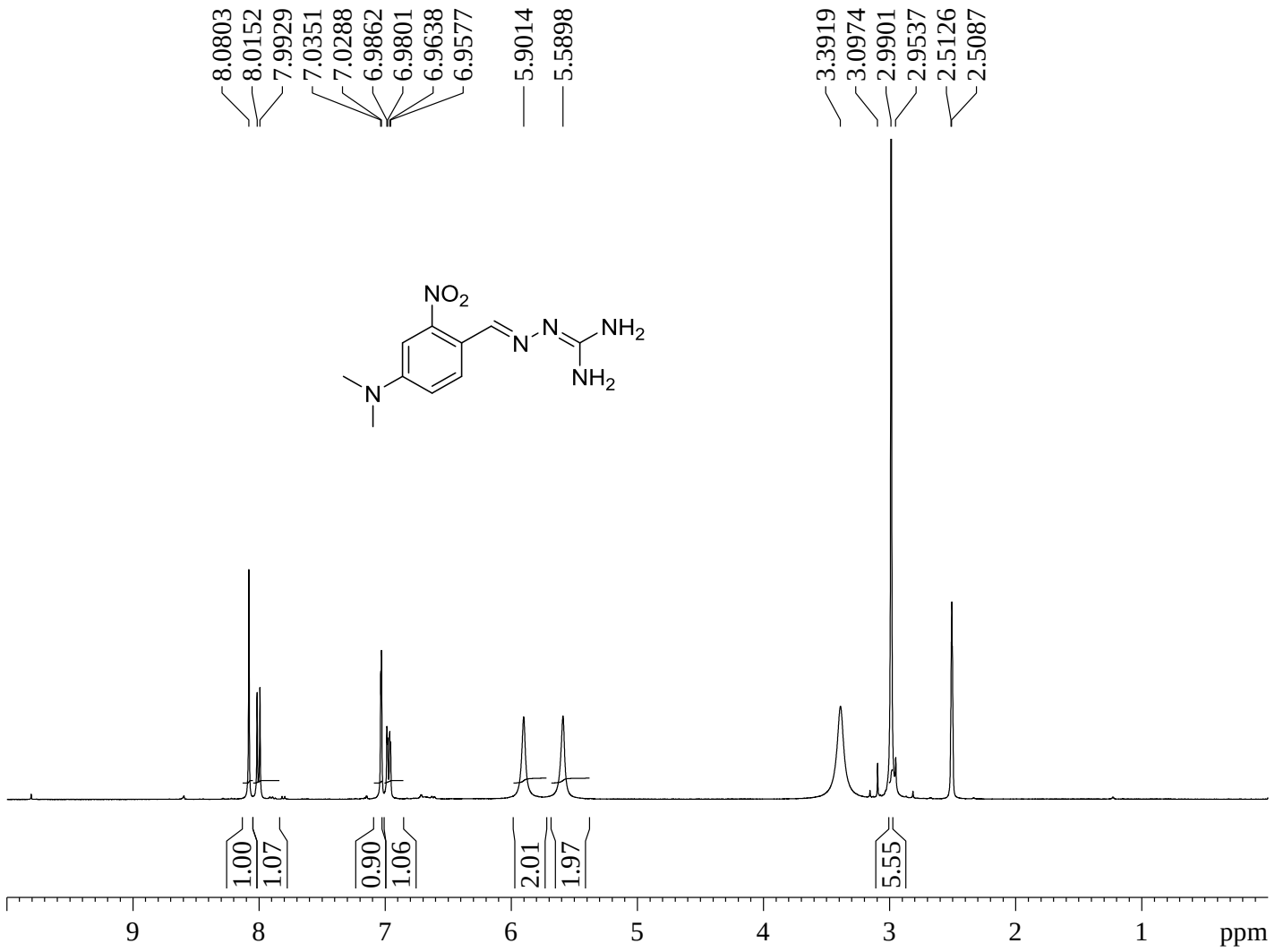

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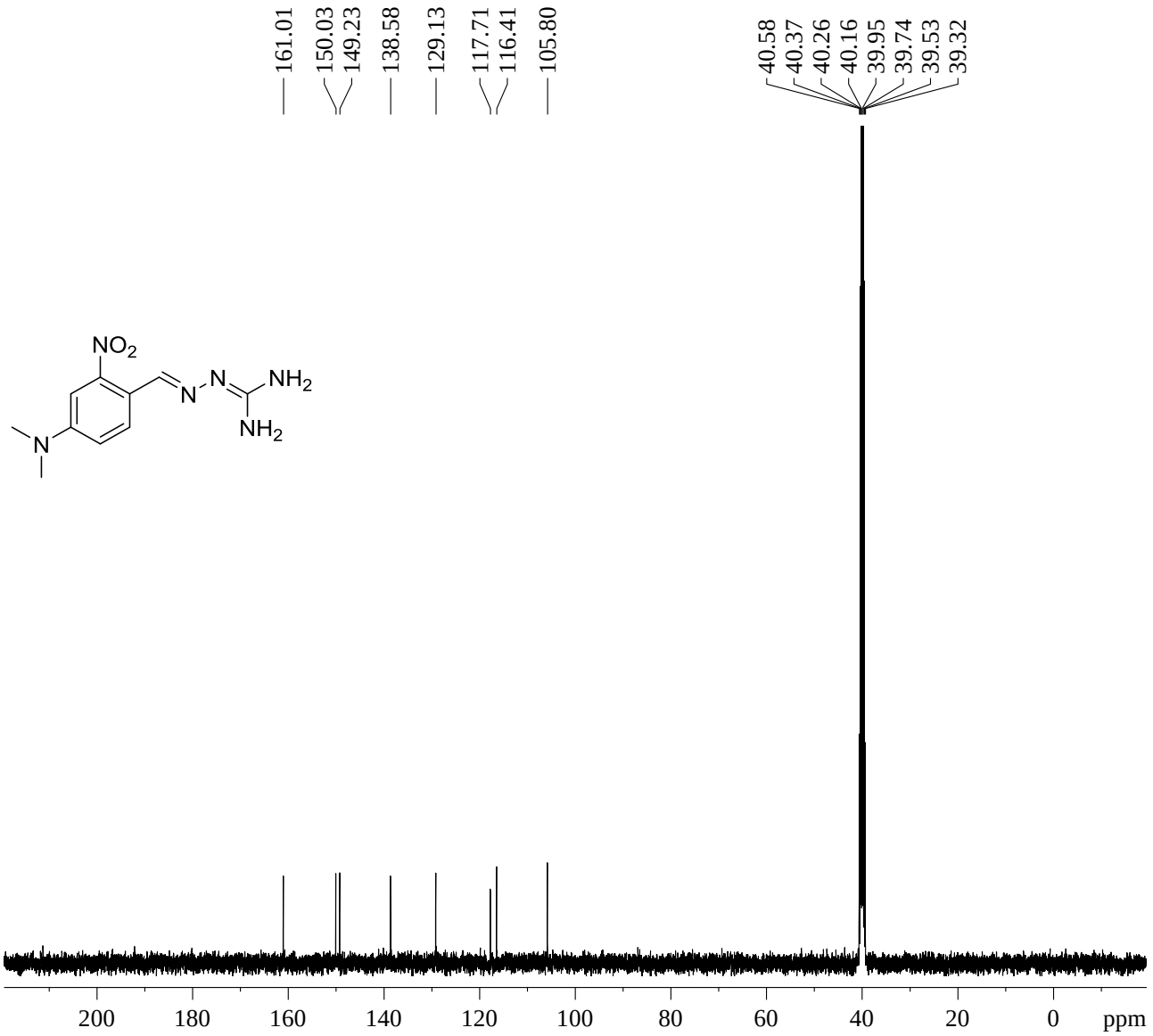

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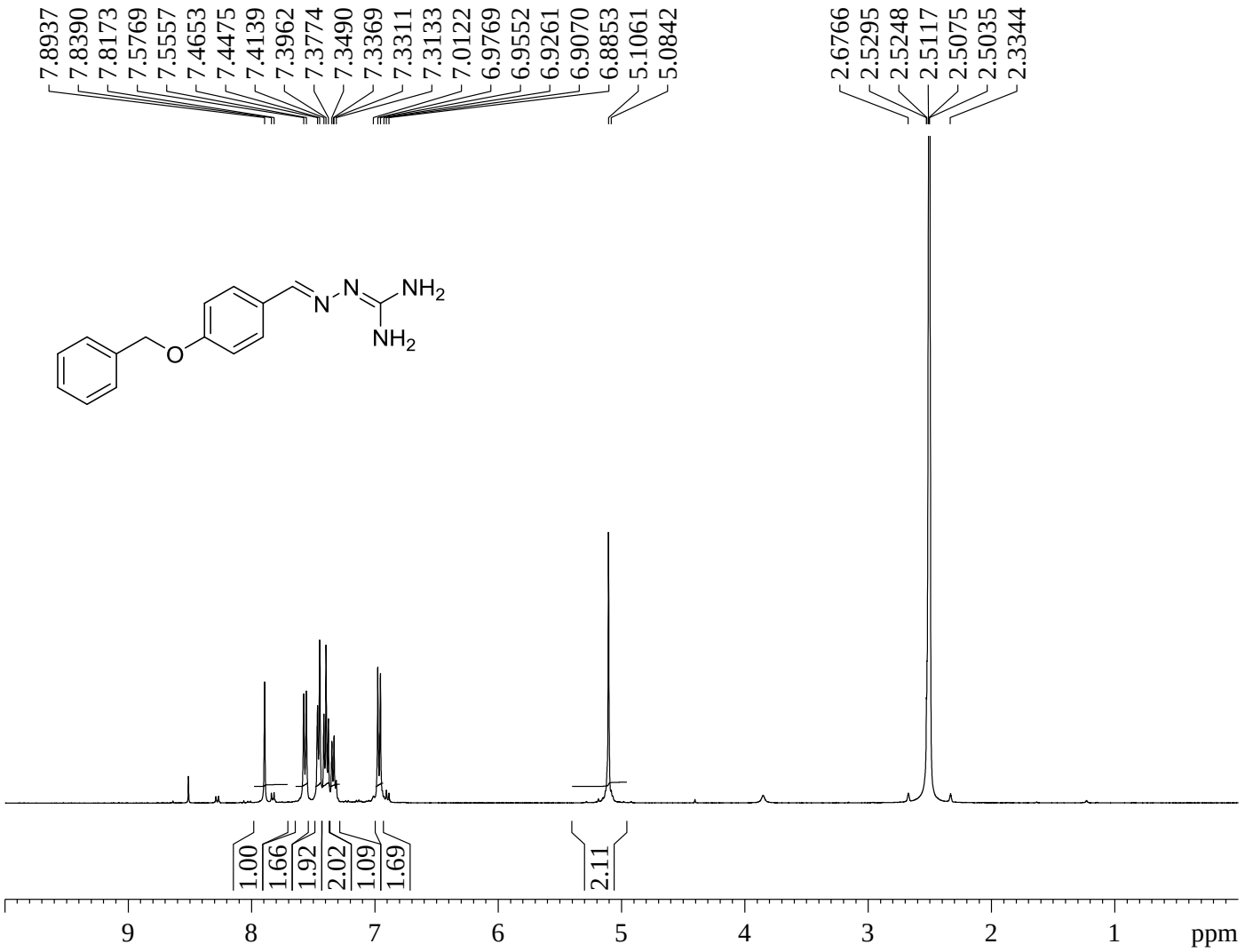

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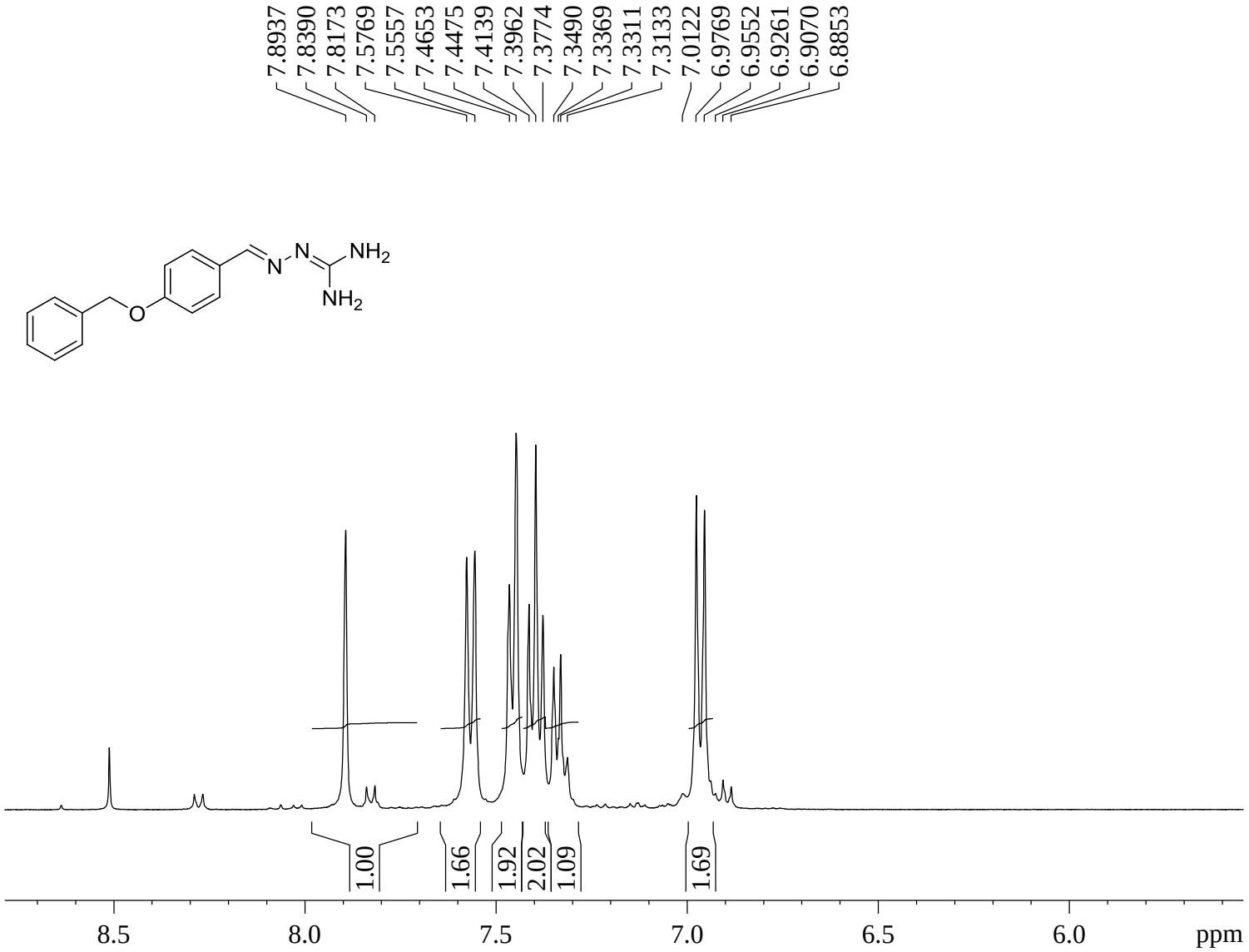

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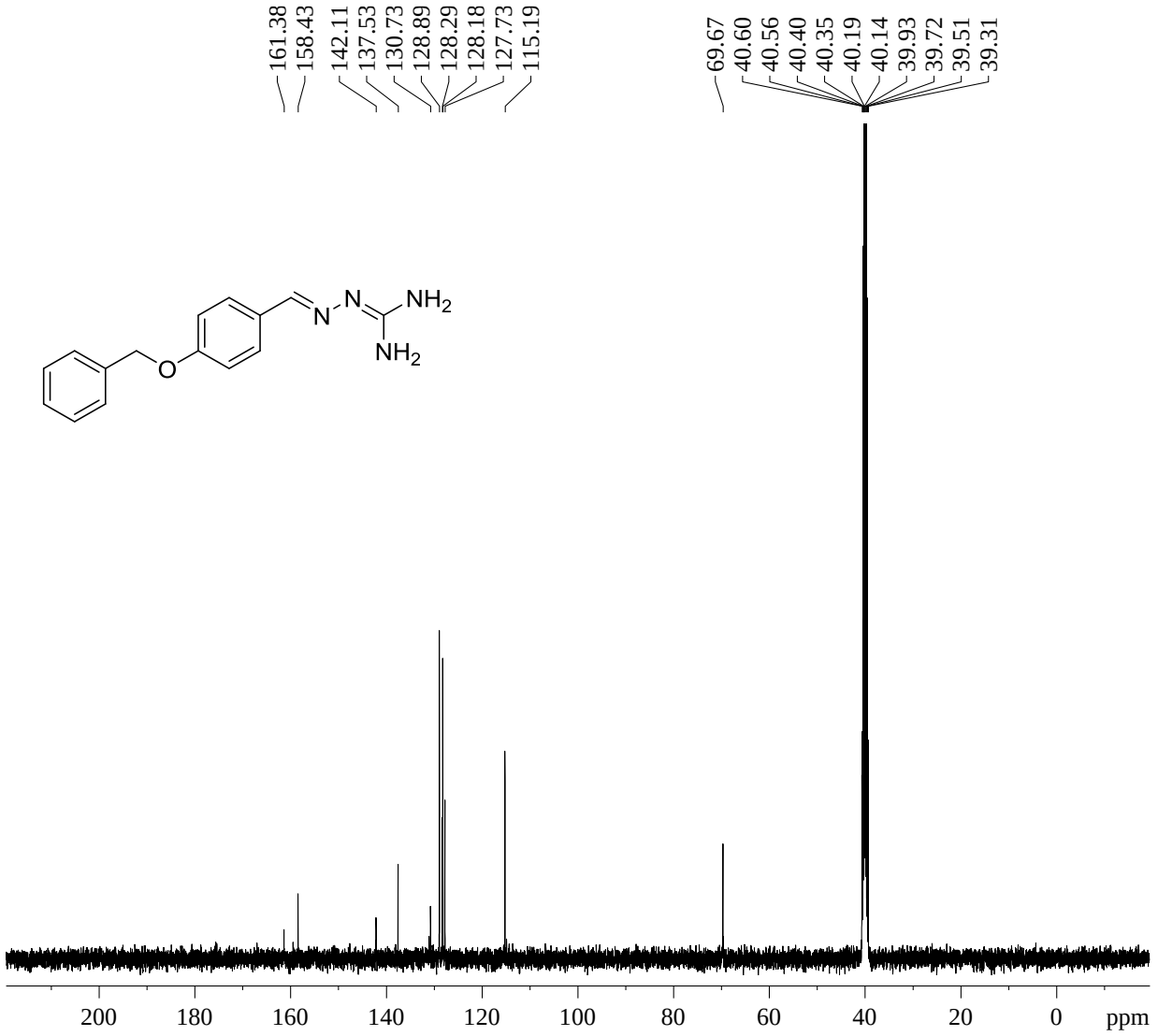
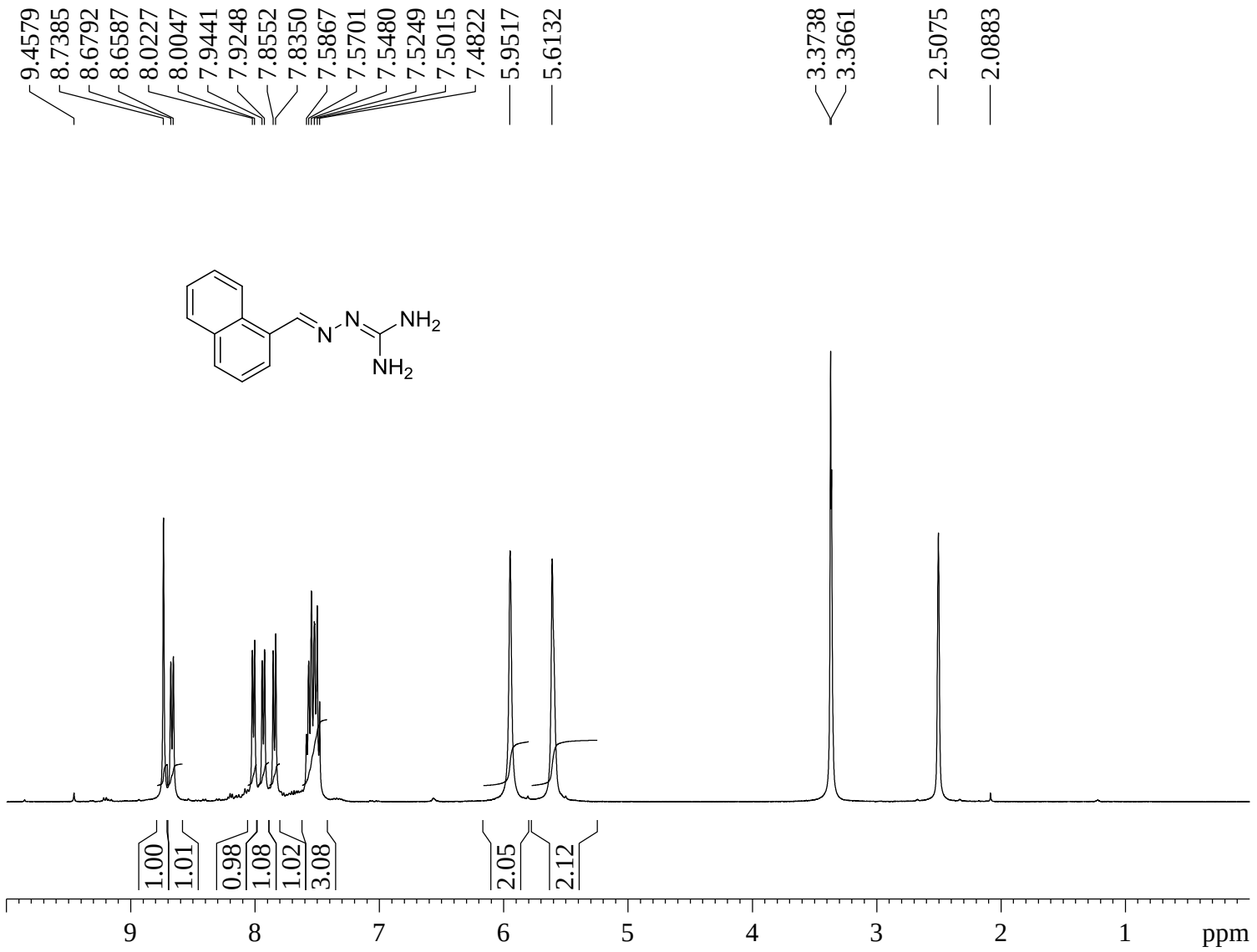


^{1}H spectra of compound 1u



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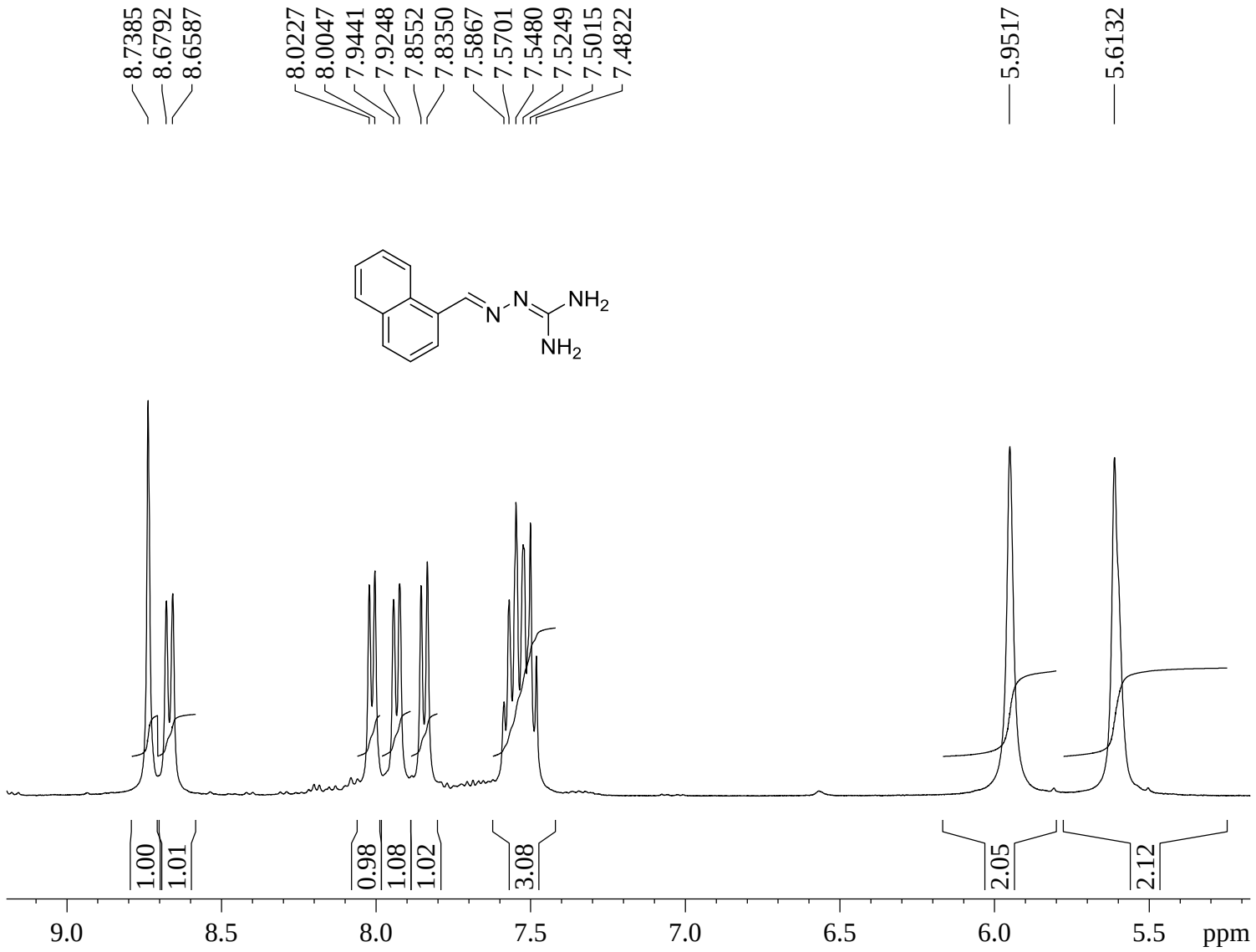

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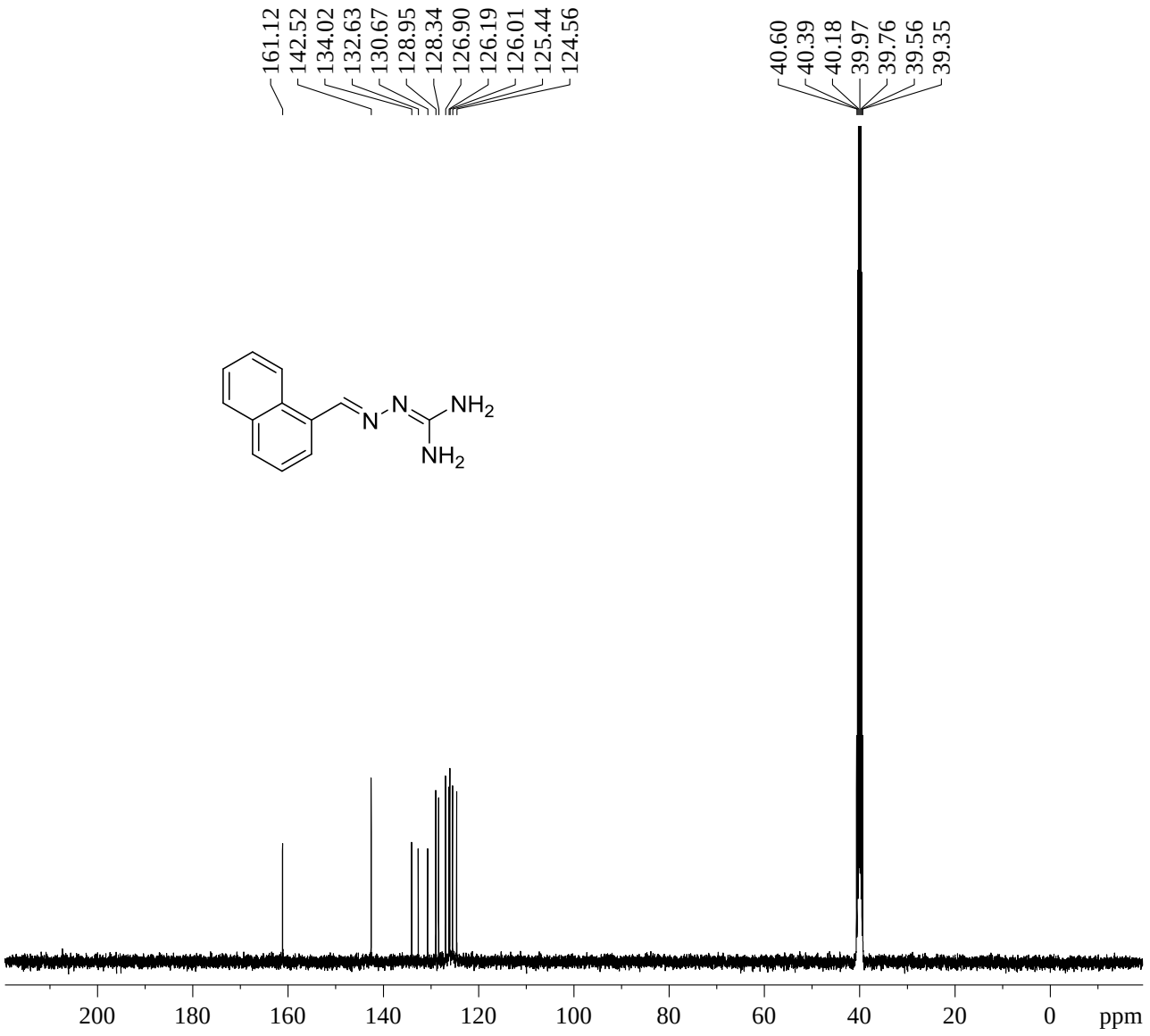

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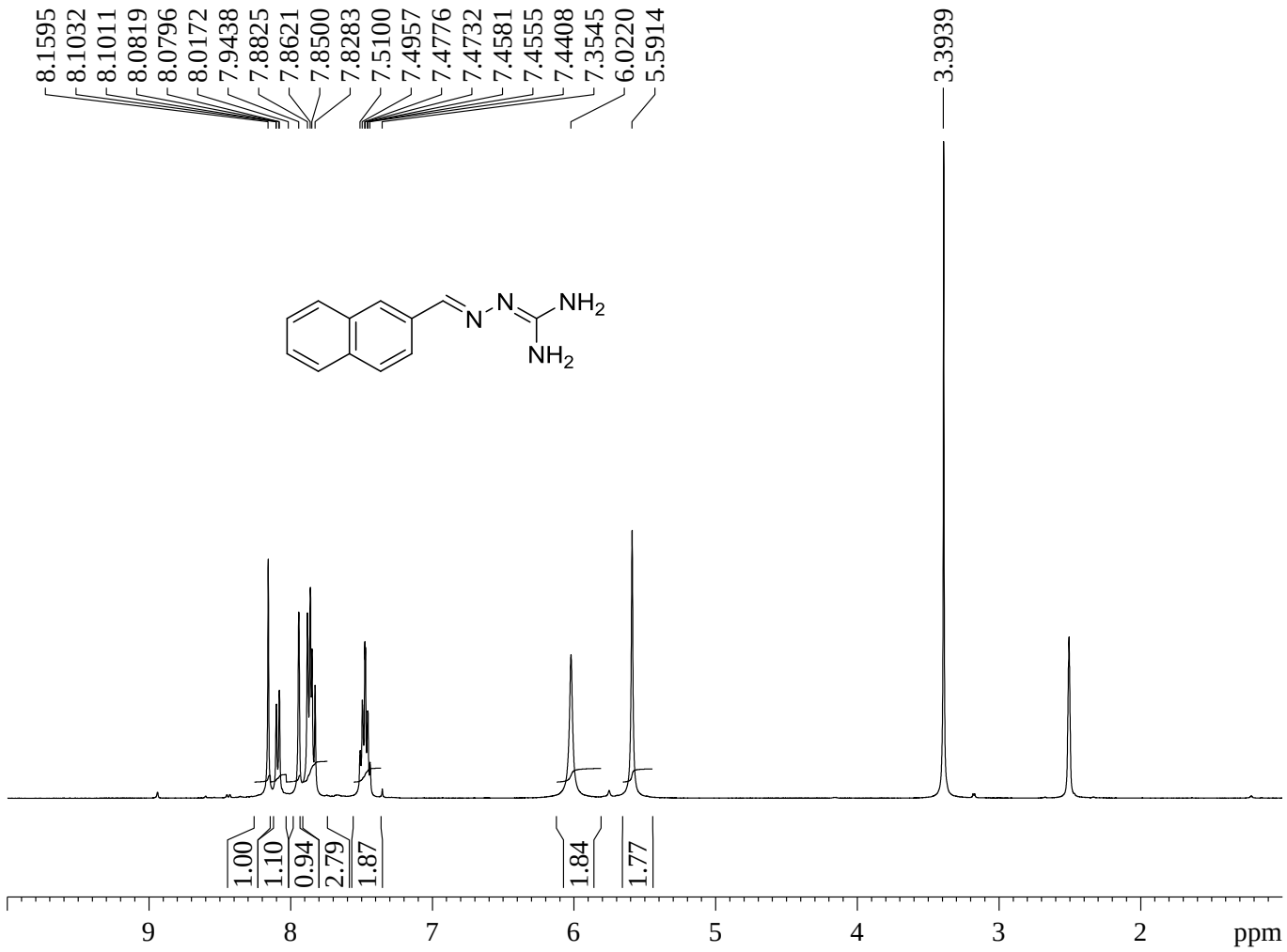

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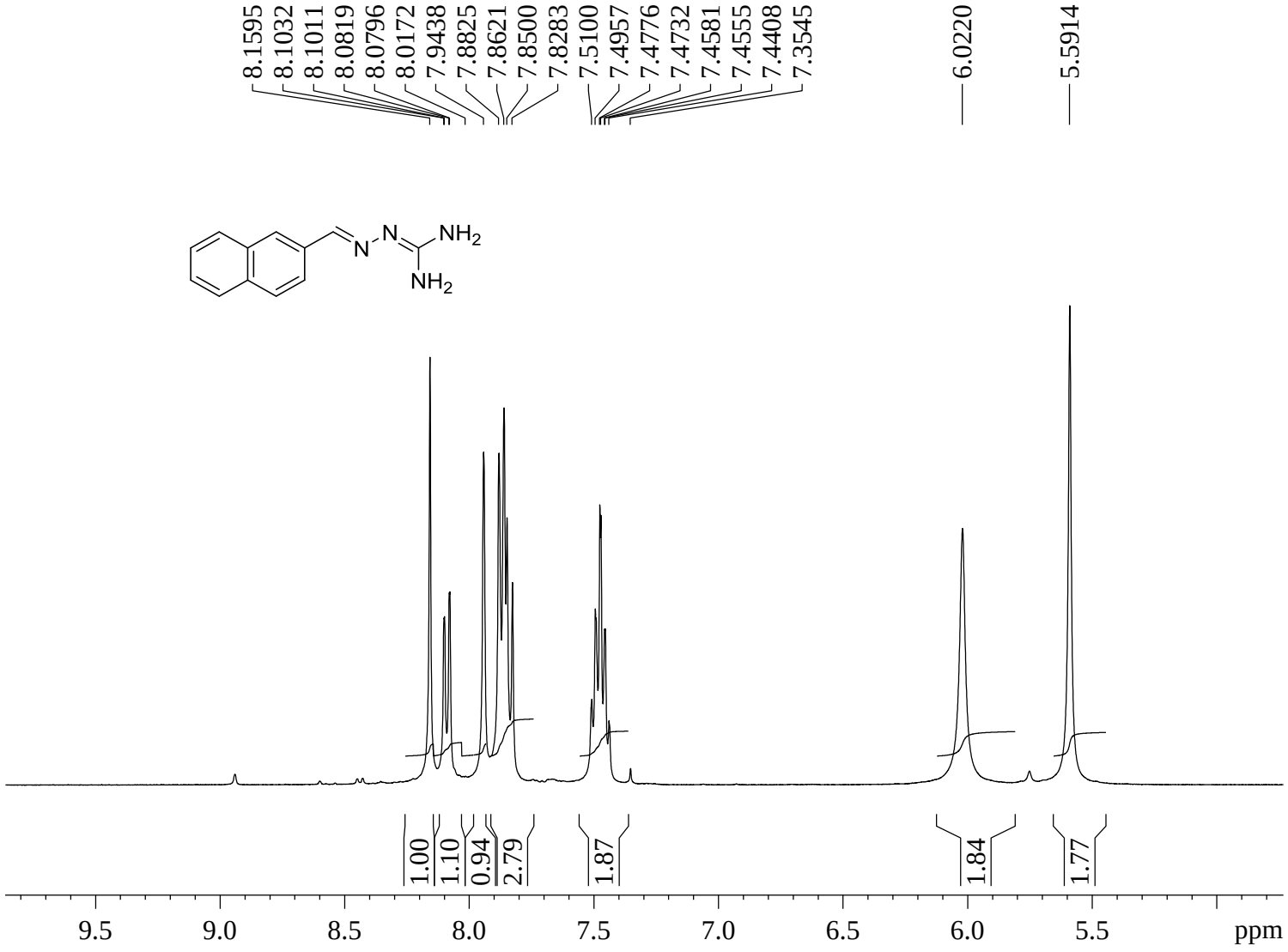

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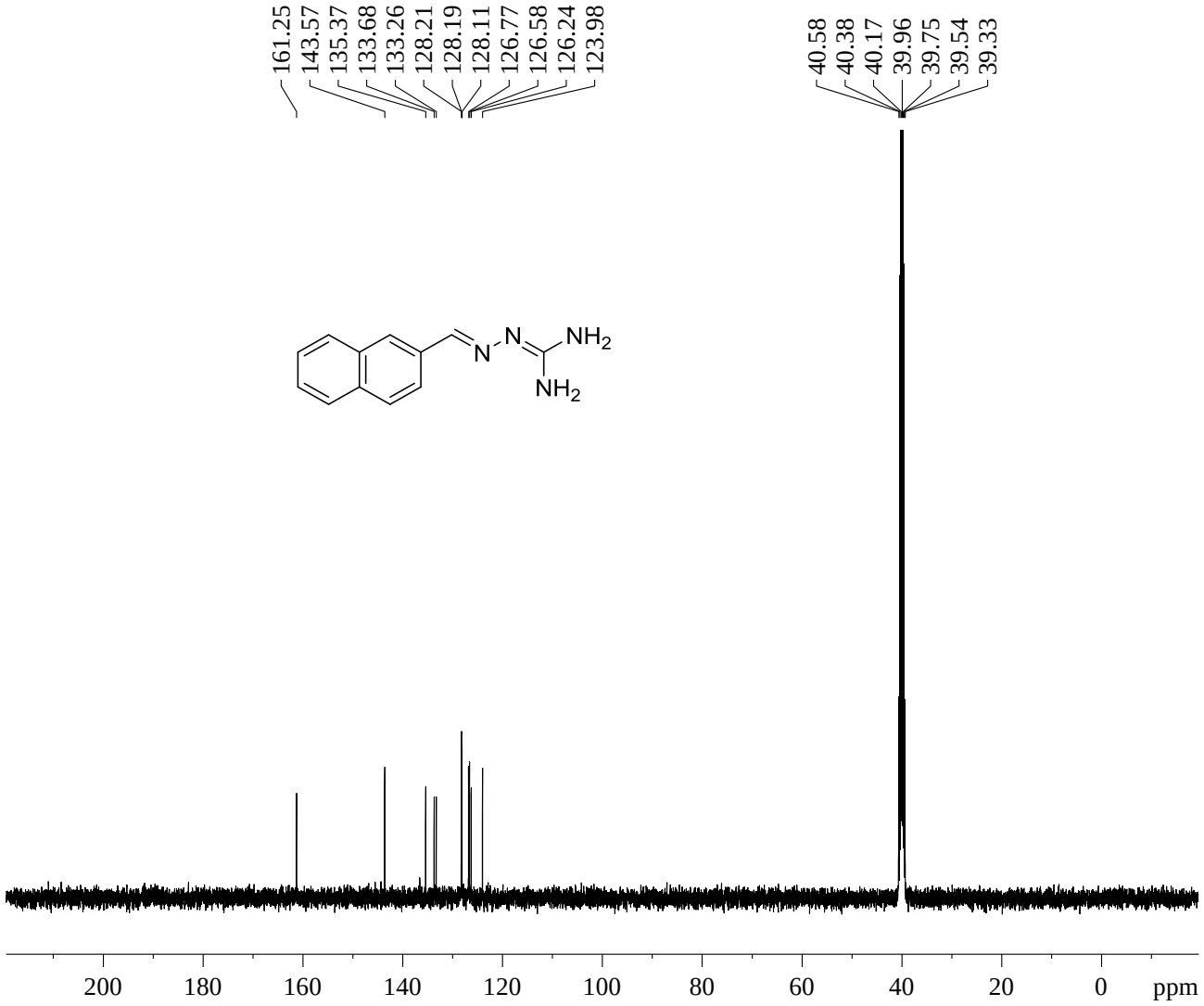
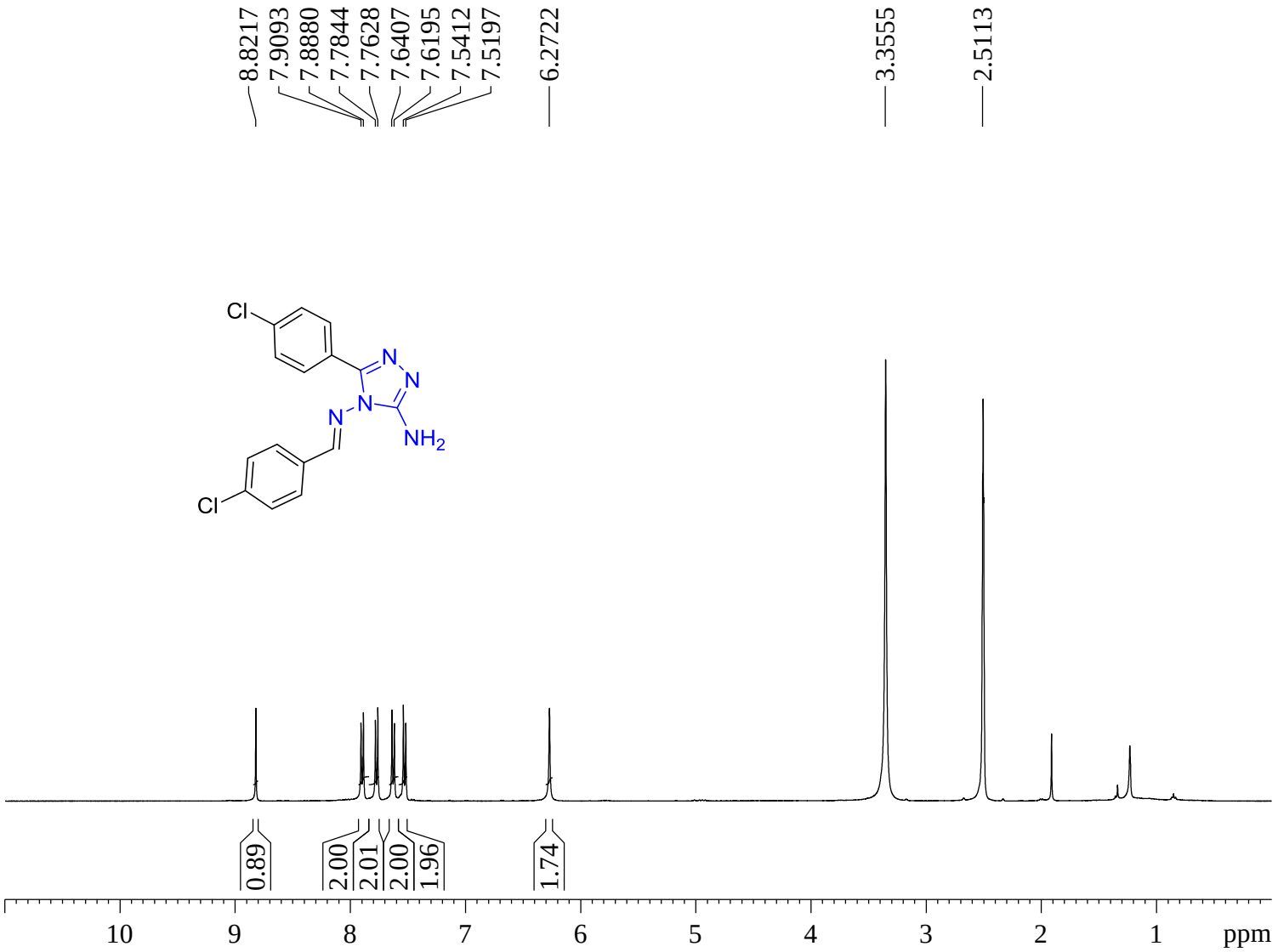


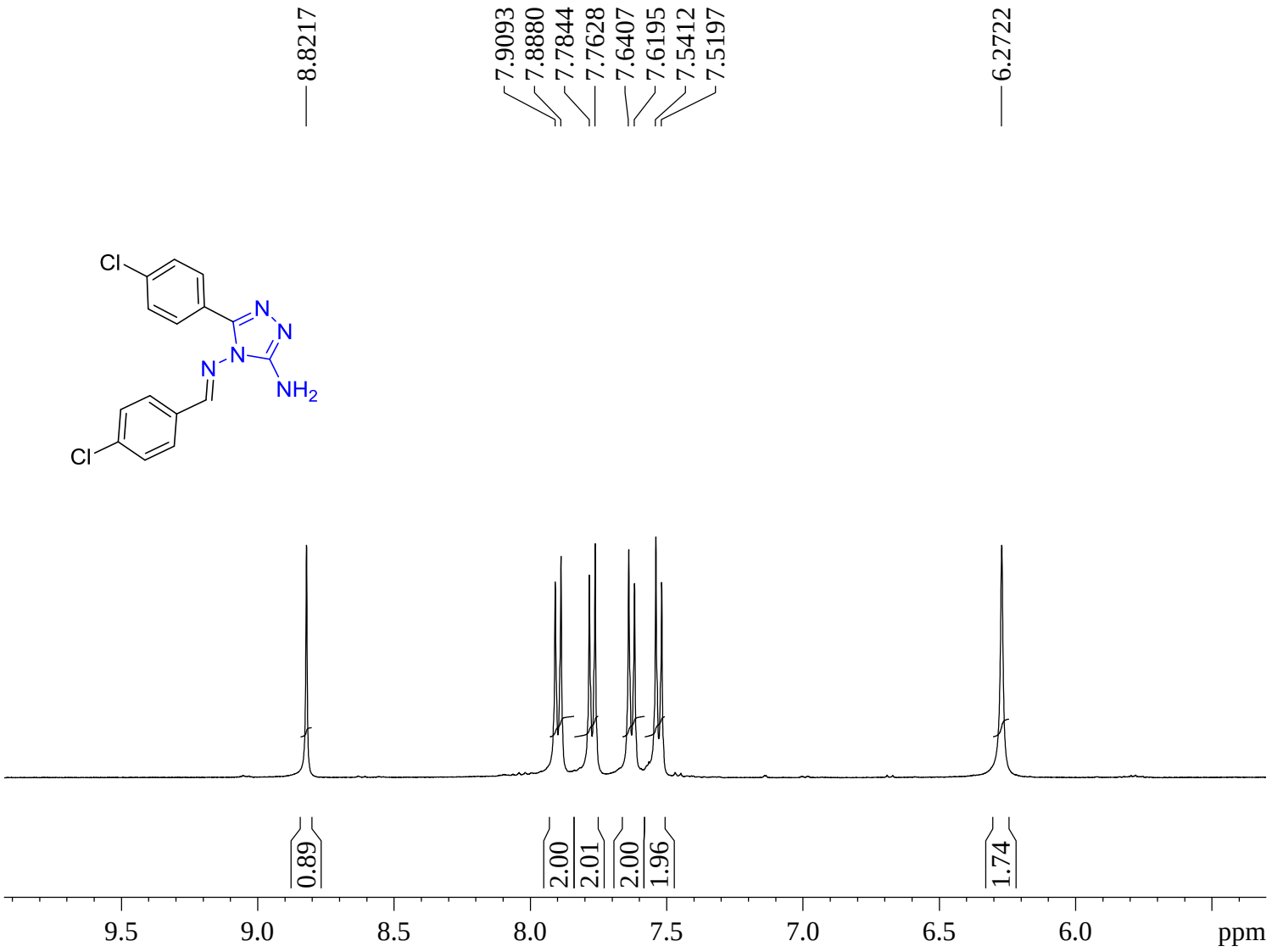
^{1}H and ^{13}C NMR spectra of compounds 5a-v

^{19}F NMR spectra of compounds 5j and 5k

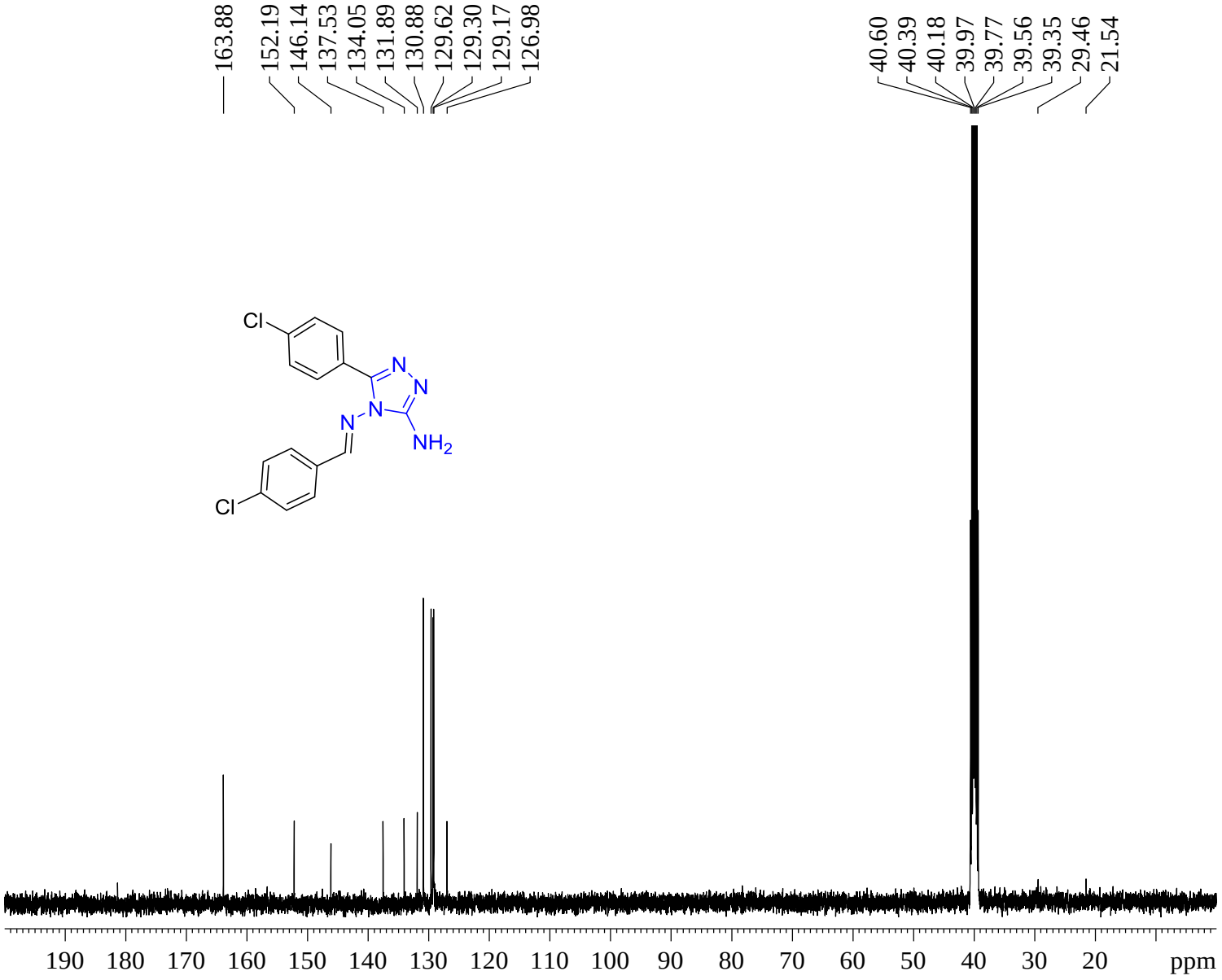
^{1}H spectra of compound 5a



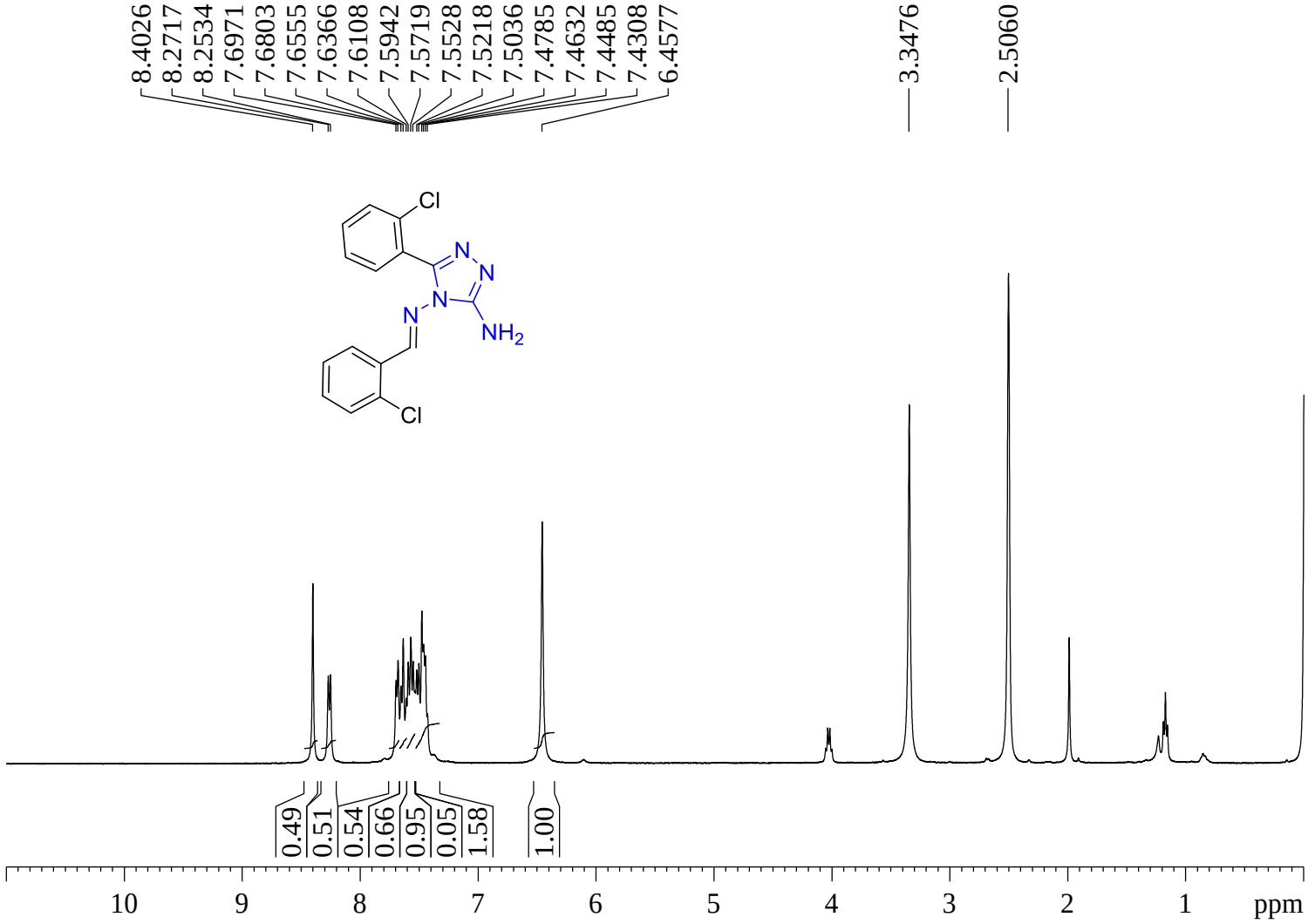
^{1}H spectra of compound 5a_expanded



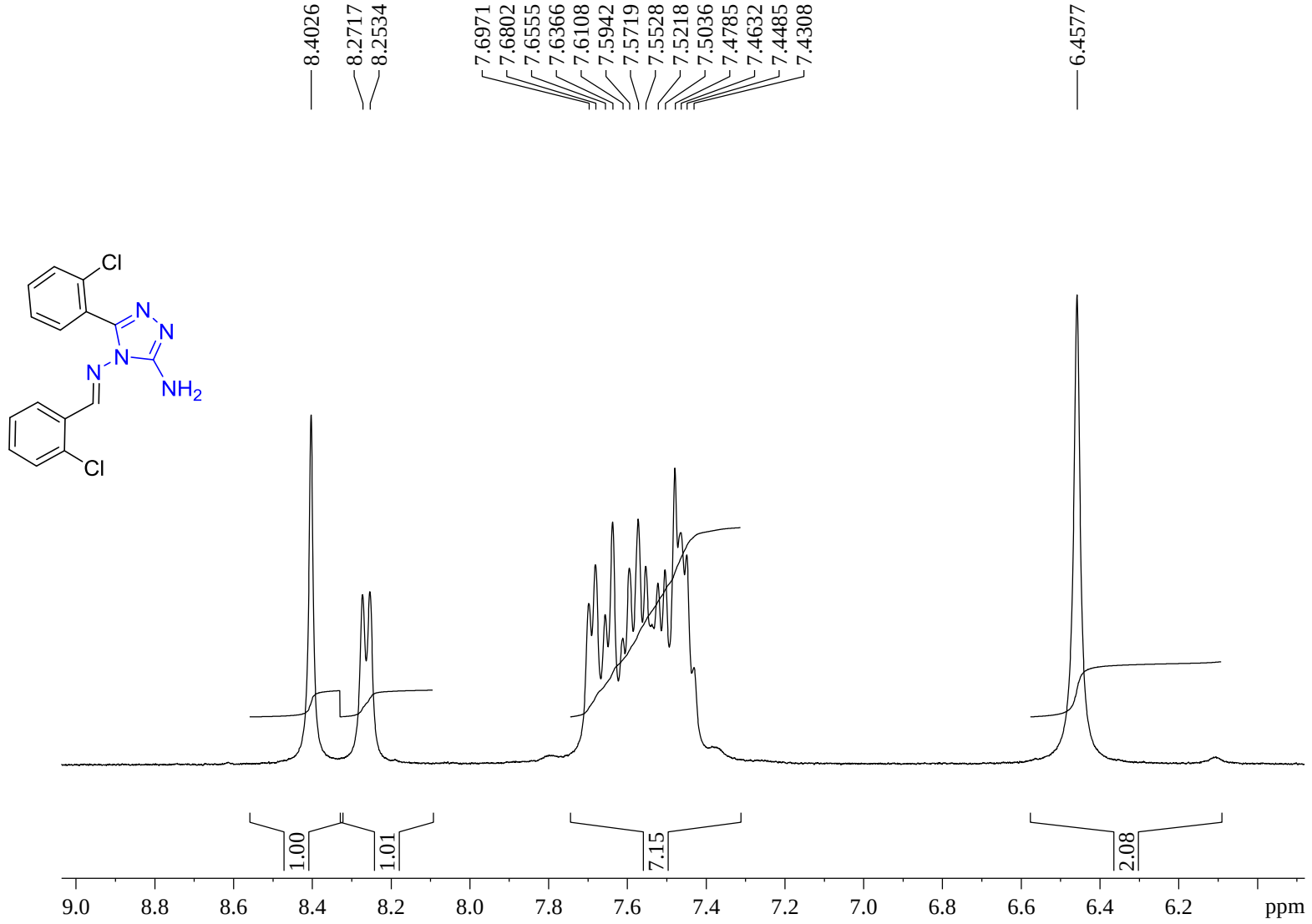
^{13}C spectra of compound 5a



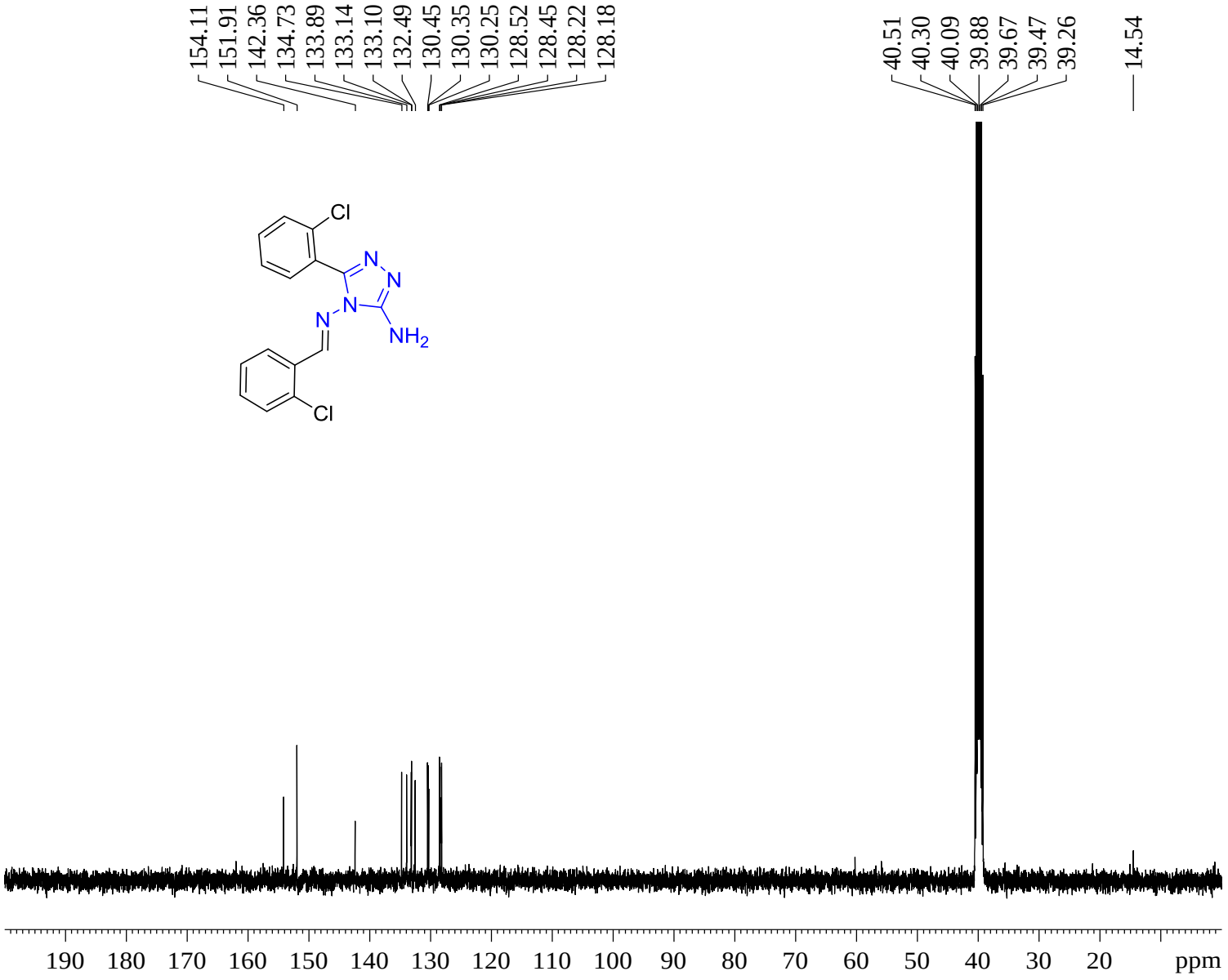
^{1}H spectra of compound 5b



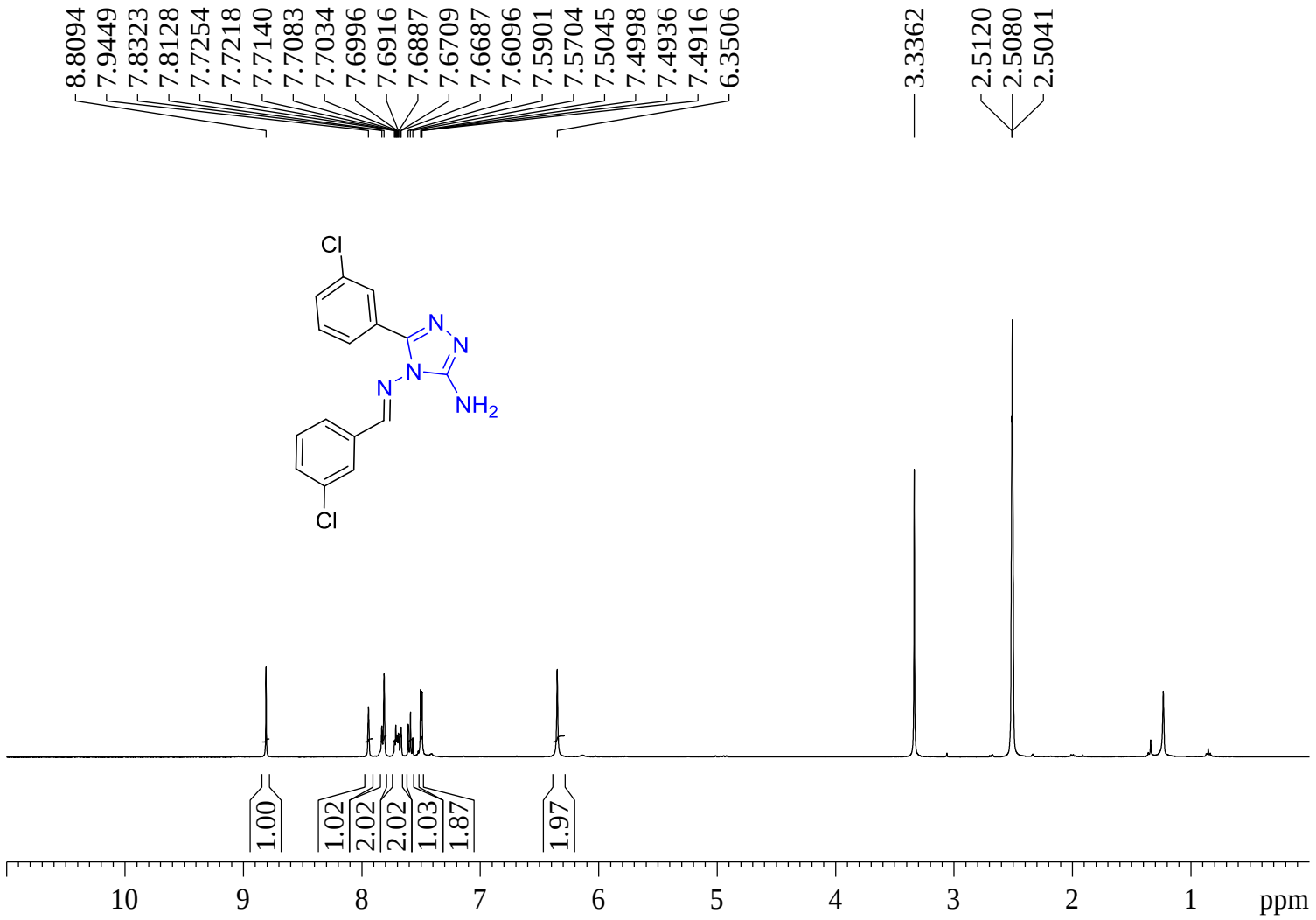
^{1}H spectra of compound 5b_expanded



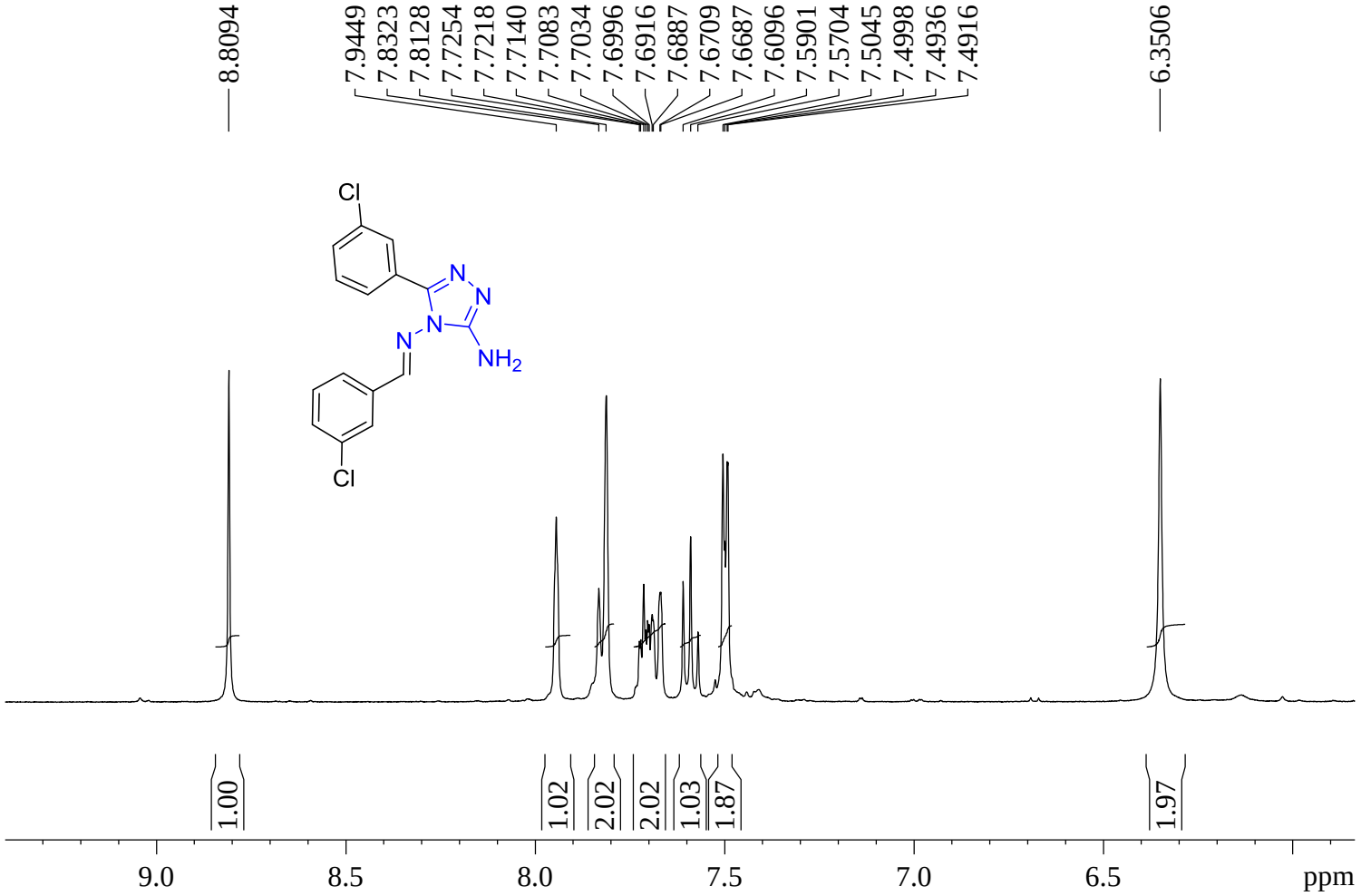
^{13}C spectra of compound 5b



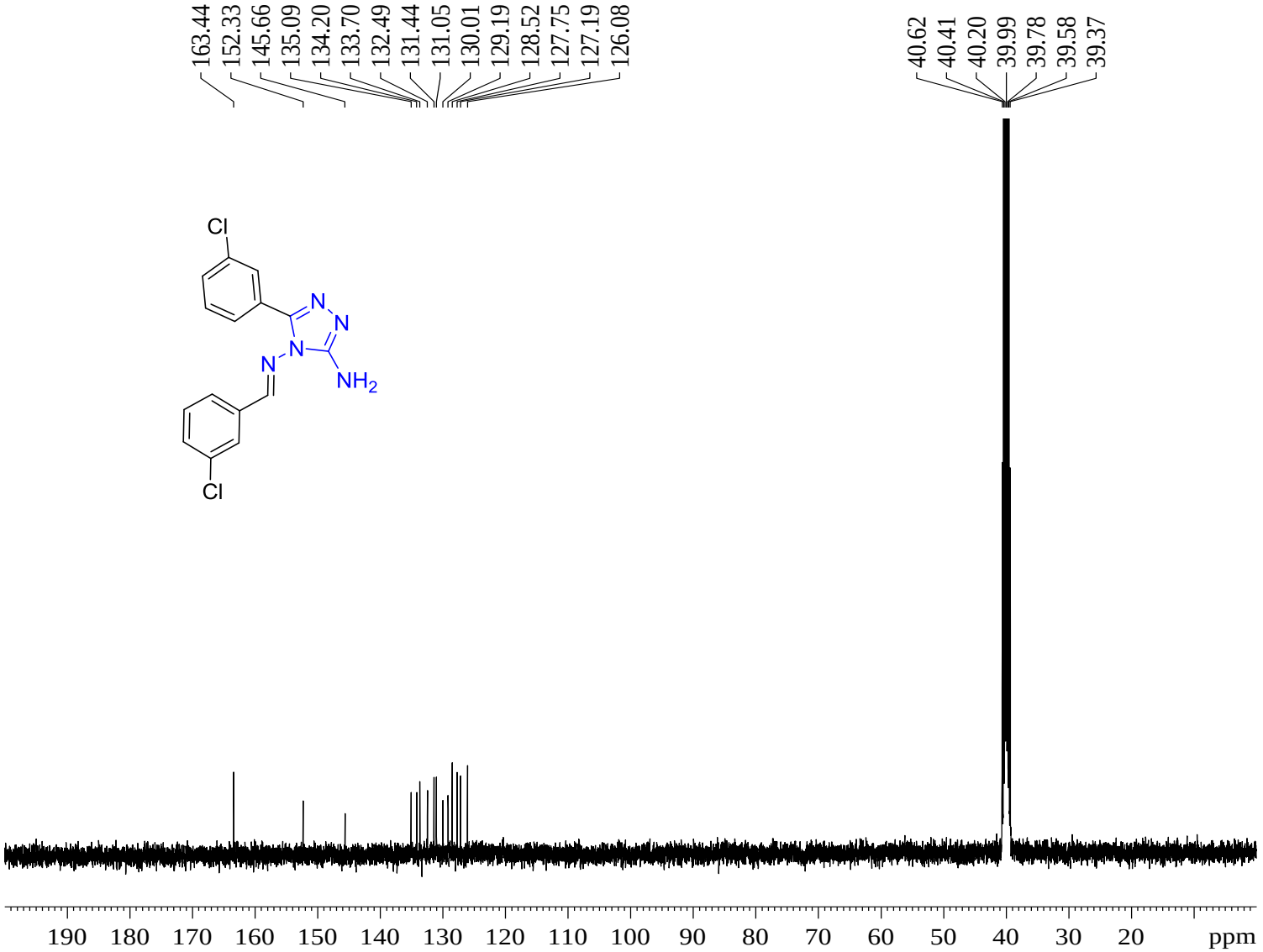
^{1}H spectra of compound 5c



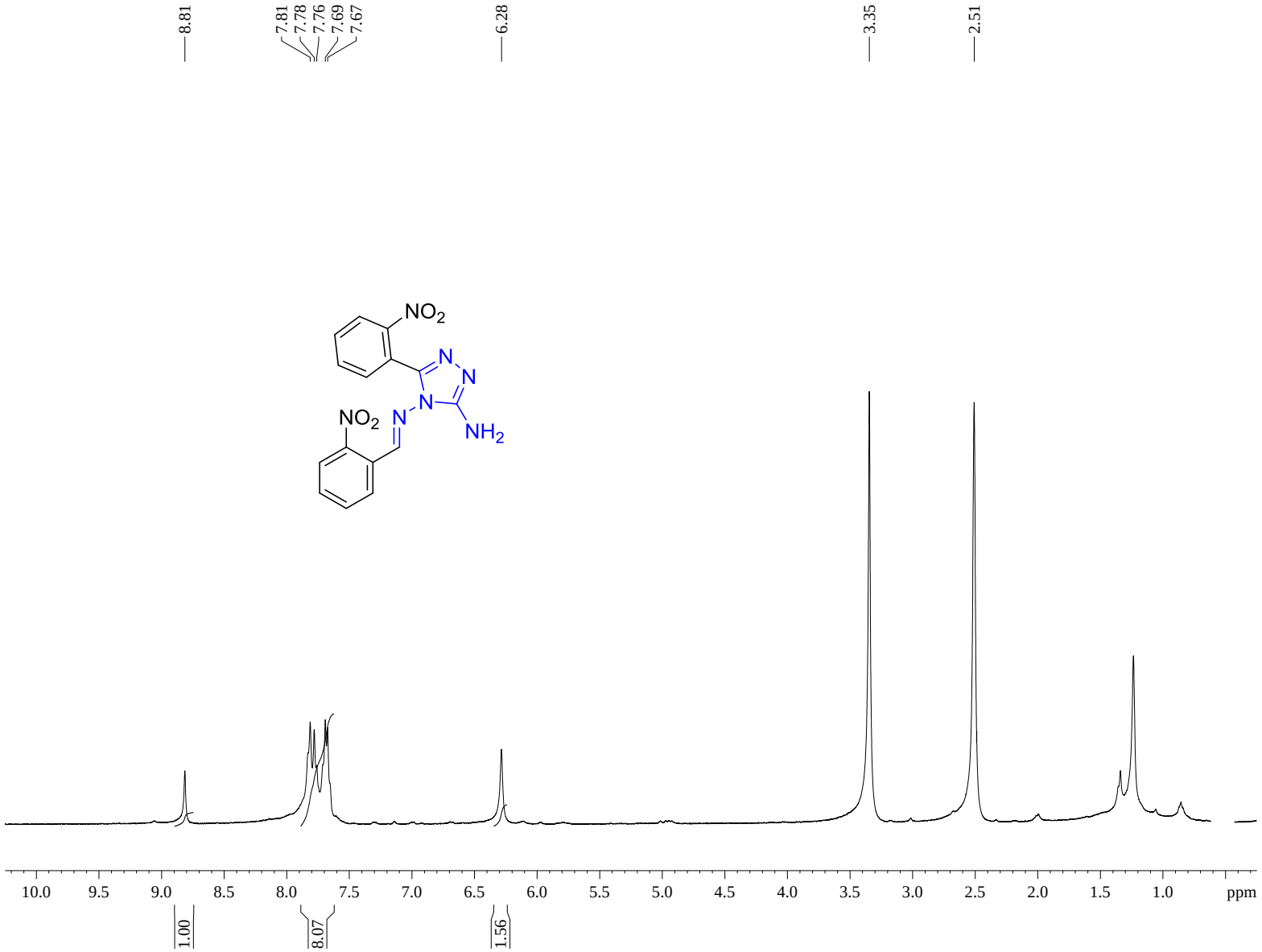
^{1}H spectra of compound 5c_expanded



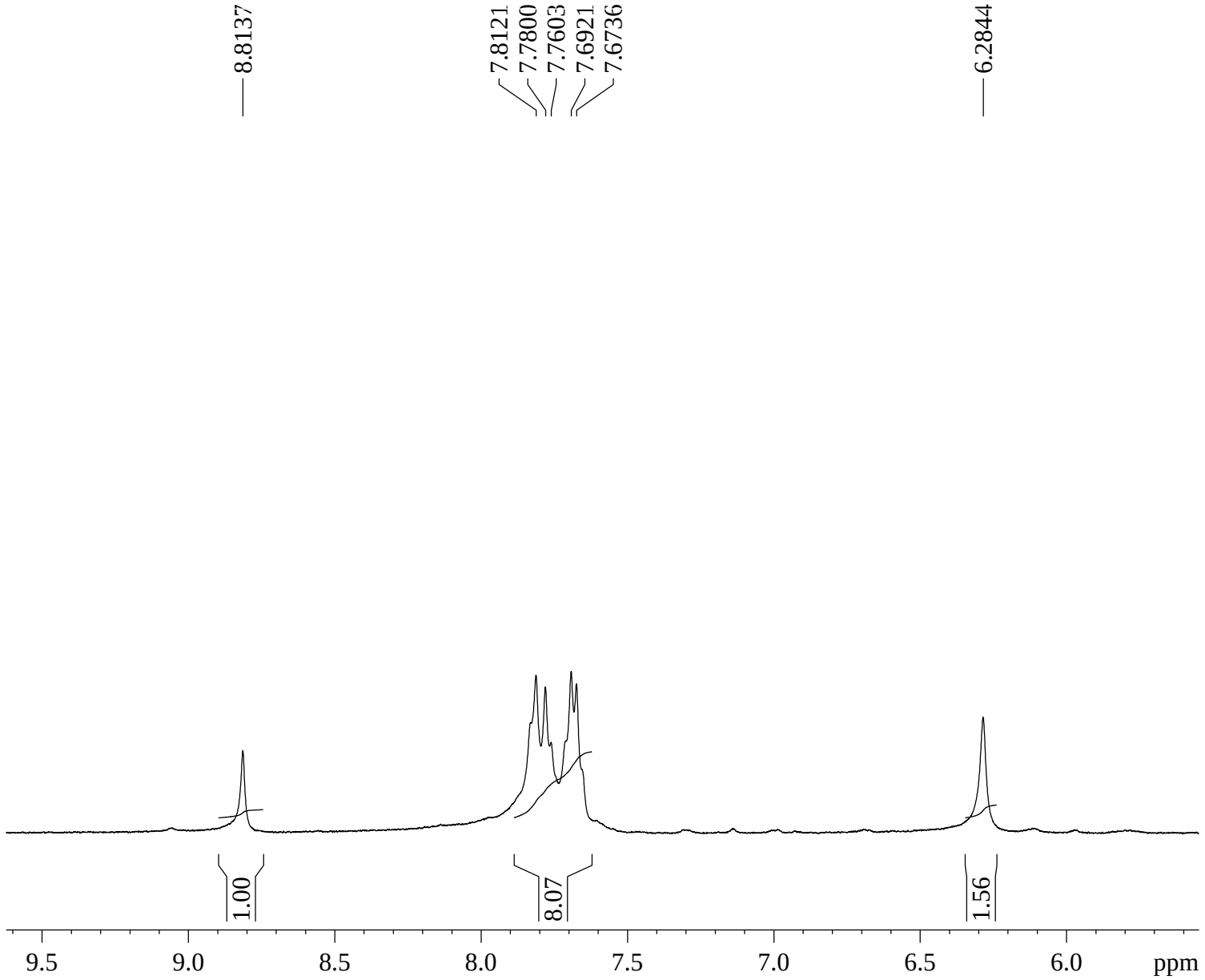
^{13}C spectra of compound 5c



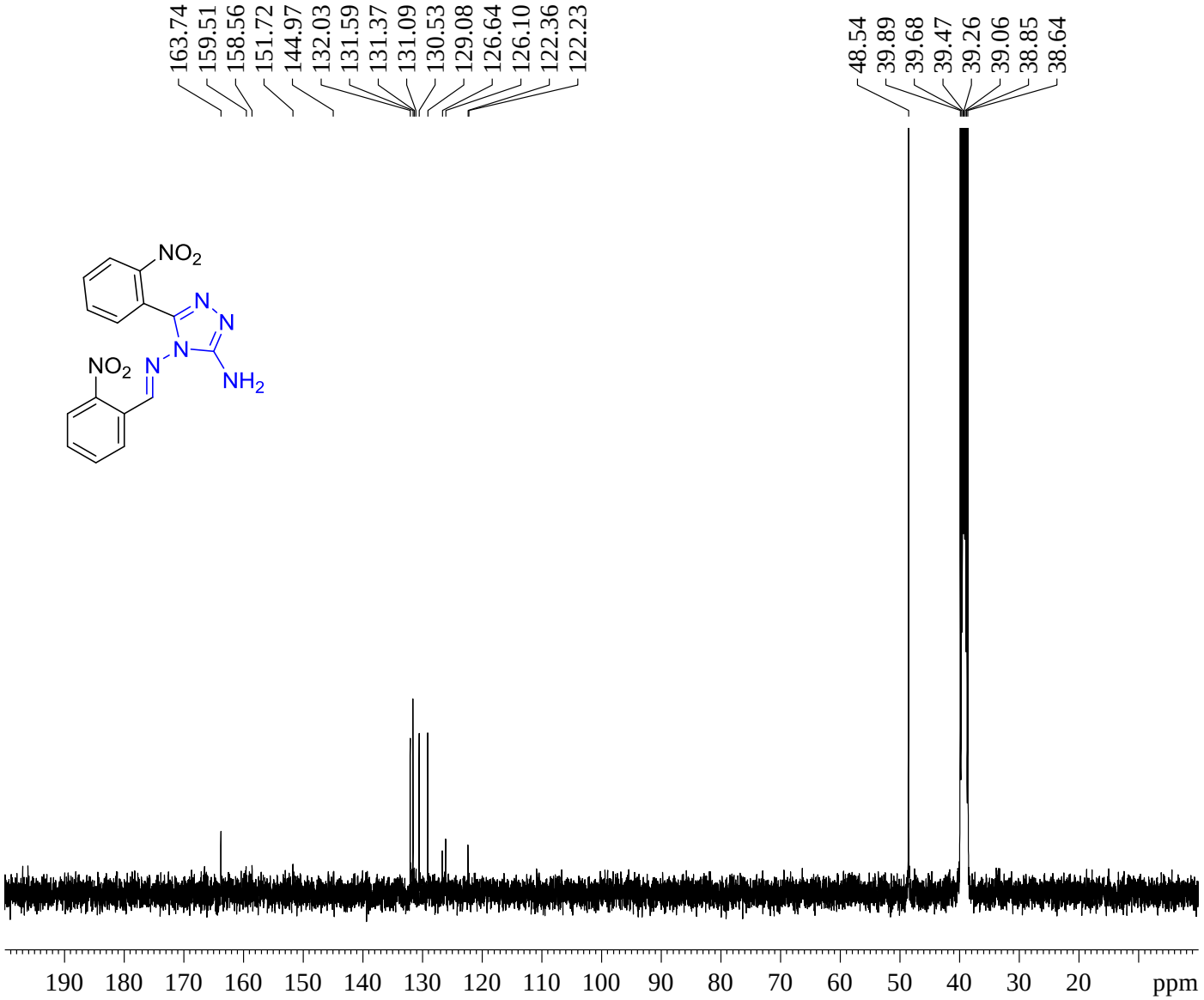
^{1}H spectra of compound 5d



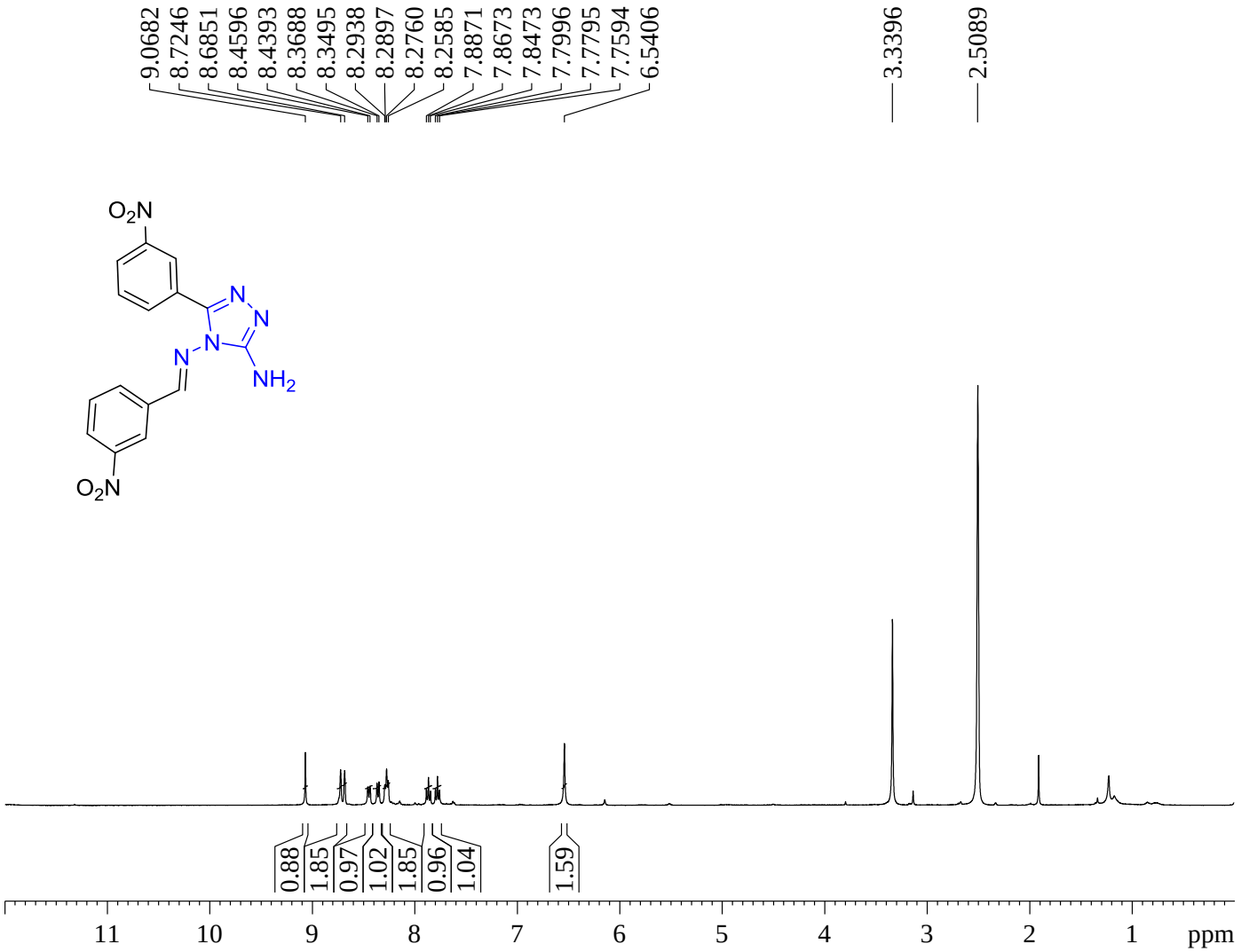
^{1}H spectra_expanded of compound 5d



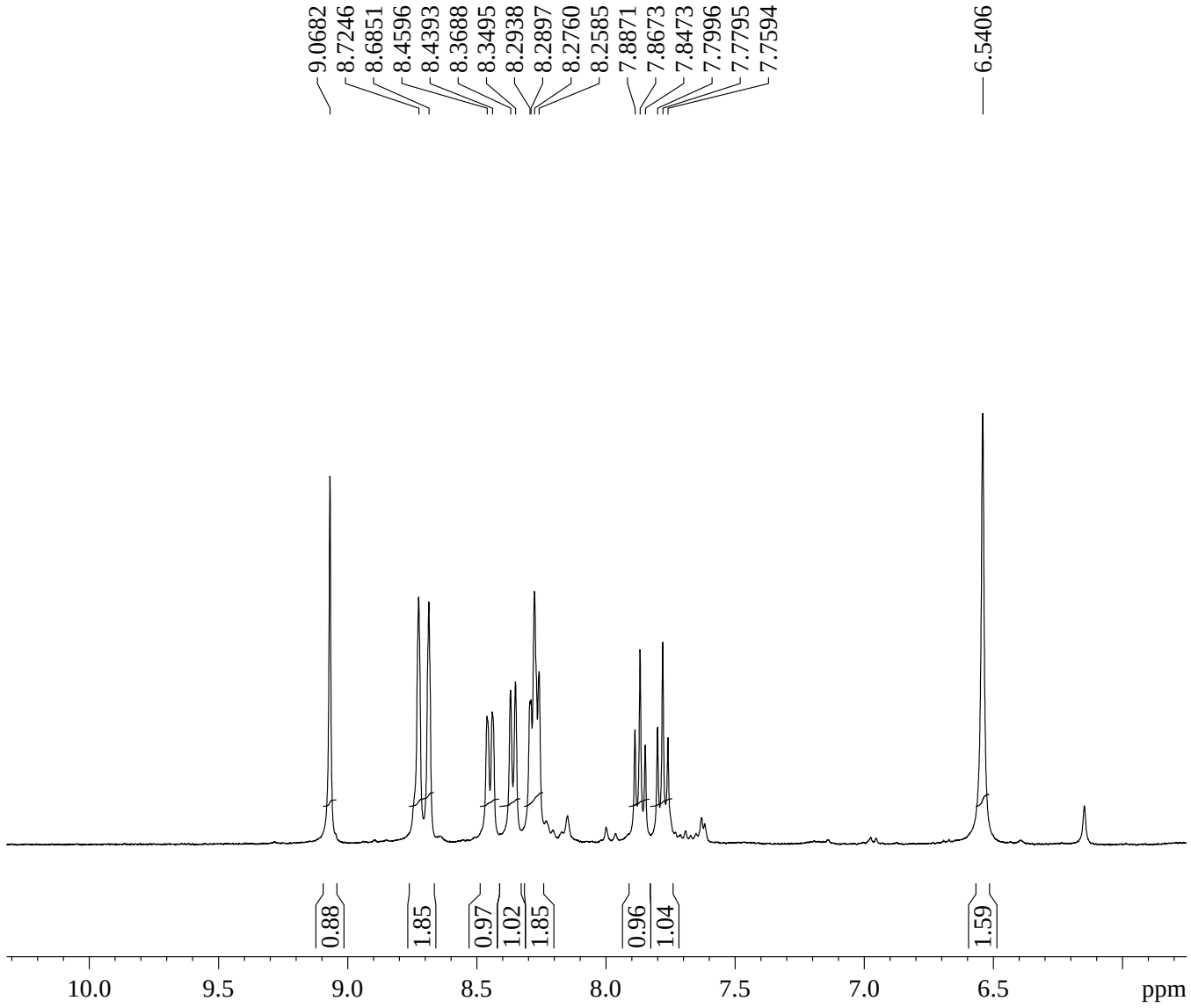
^{13}C spectra of compound 5d



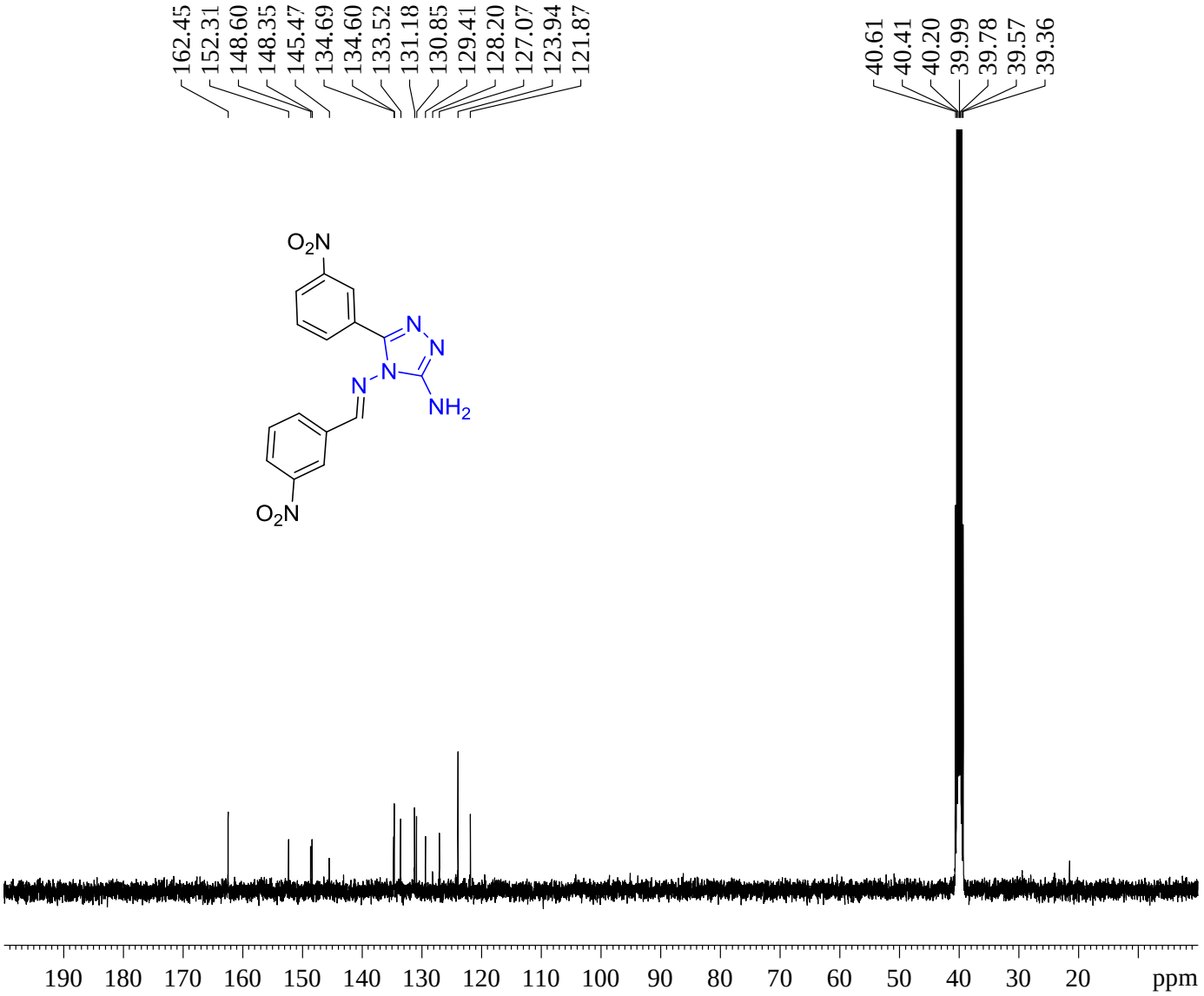
^{1}H spectra of compound 5e



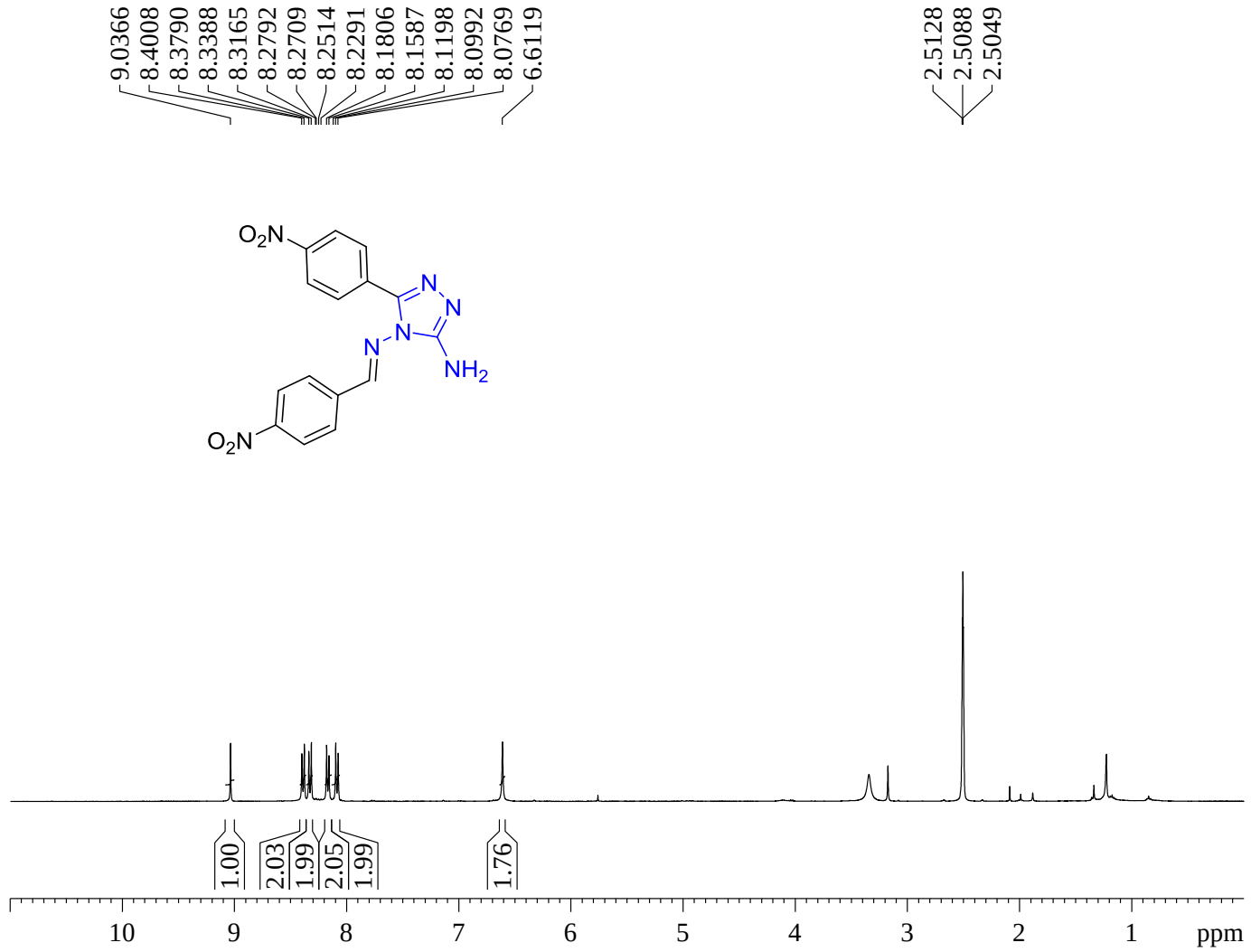
^{1}H spectra_expanded of compound 5e



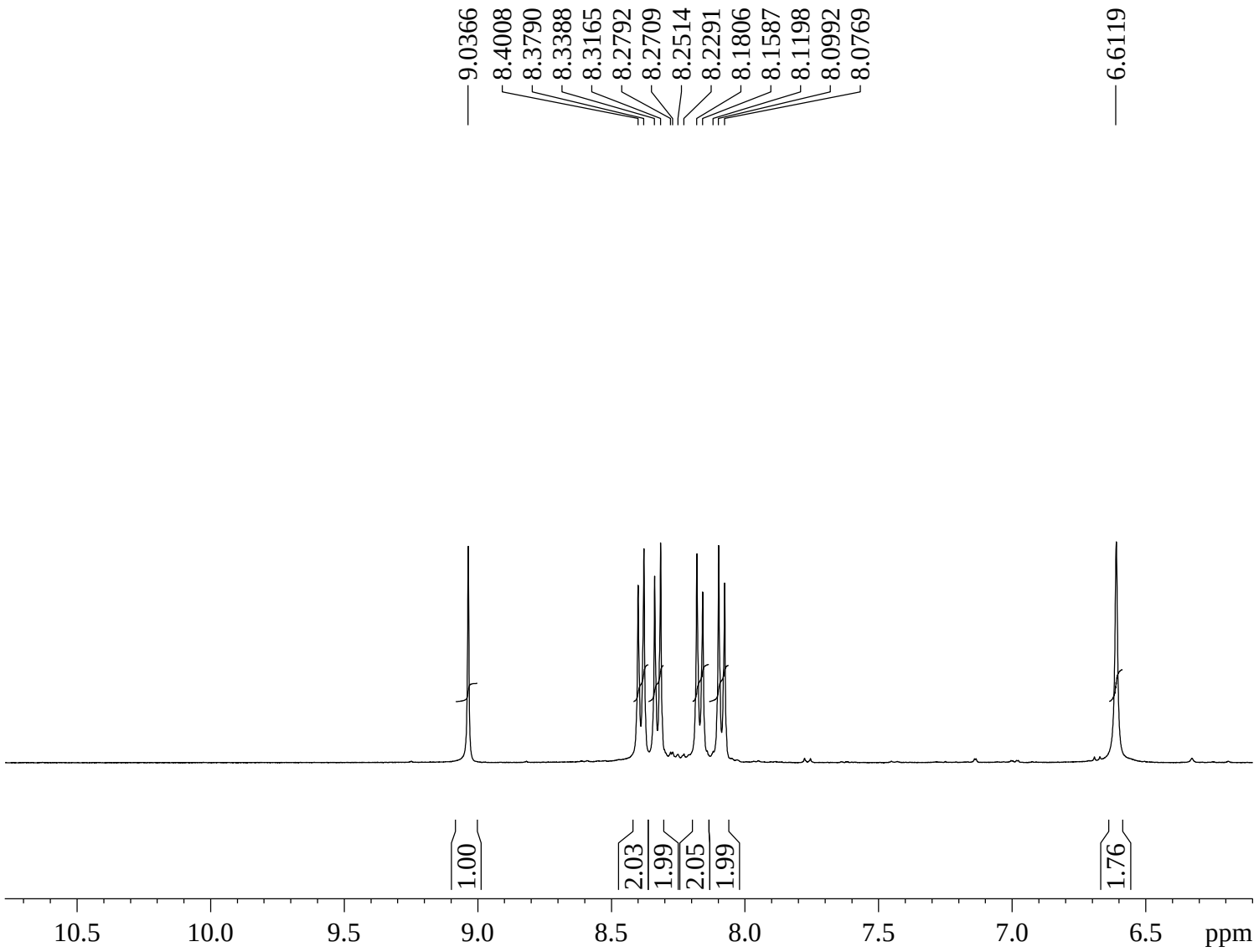
^{13}C spectra of compound 5e



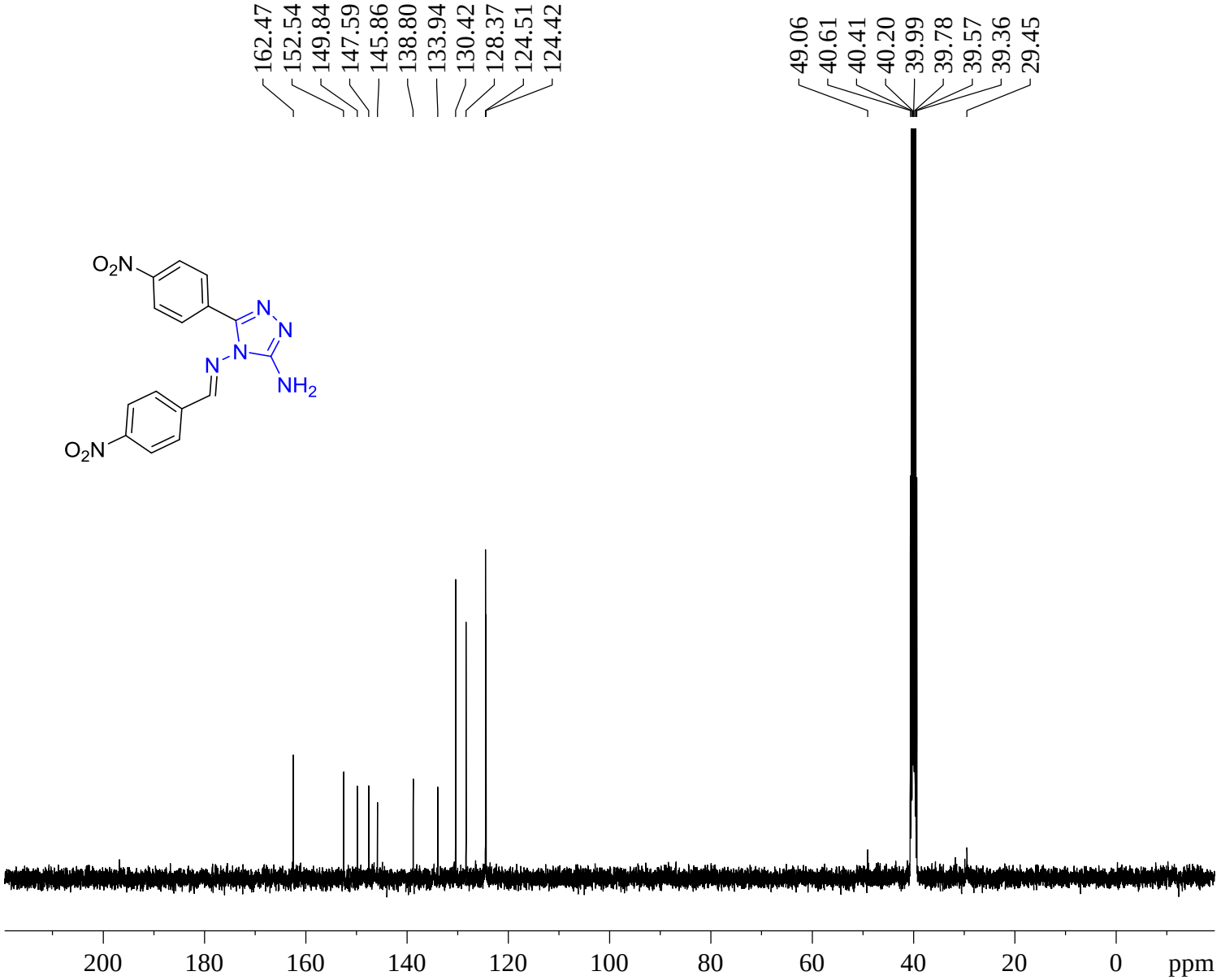
^{1}H spectra of compound 5f



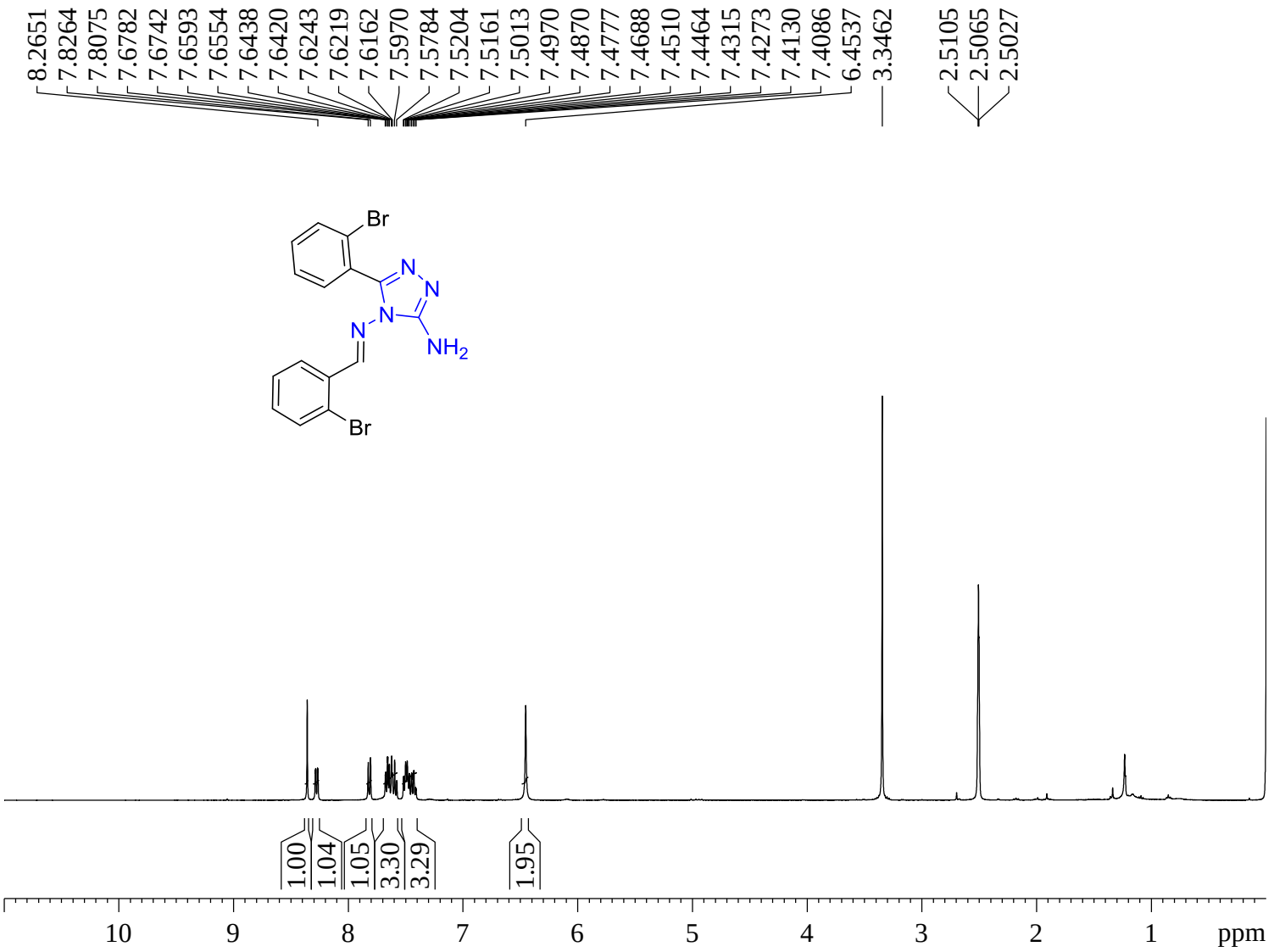
^{1}H spectra of compound 5f_expanded



^{13}C spectra of compound 5f



^{1}H spectra of compound 5g



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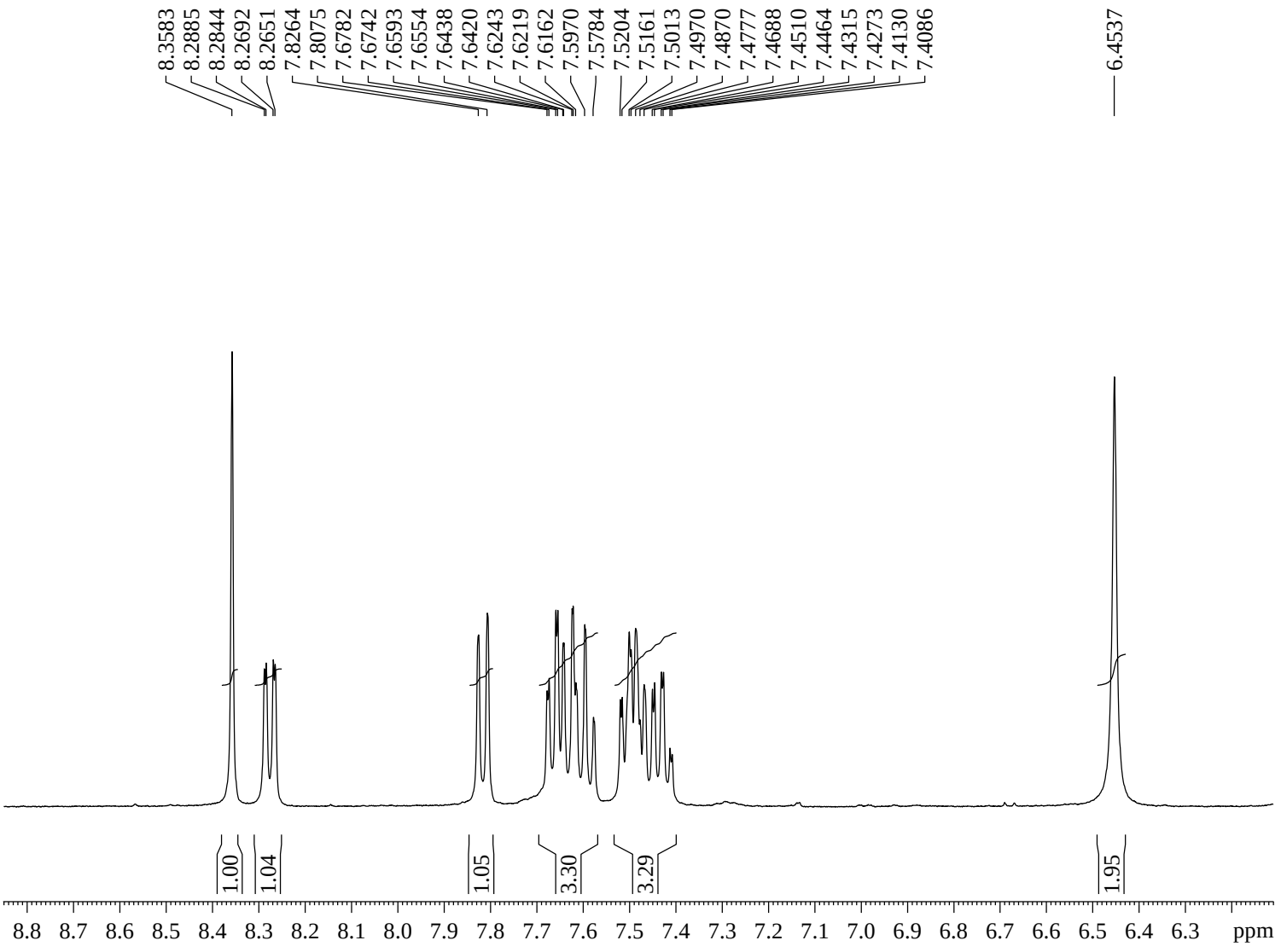
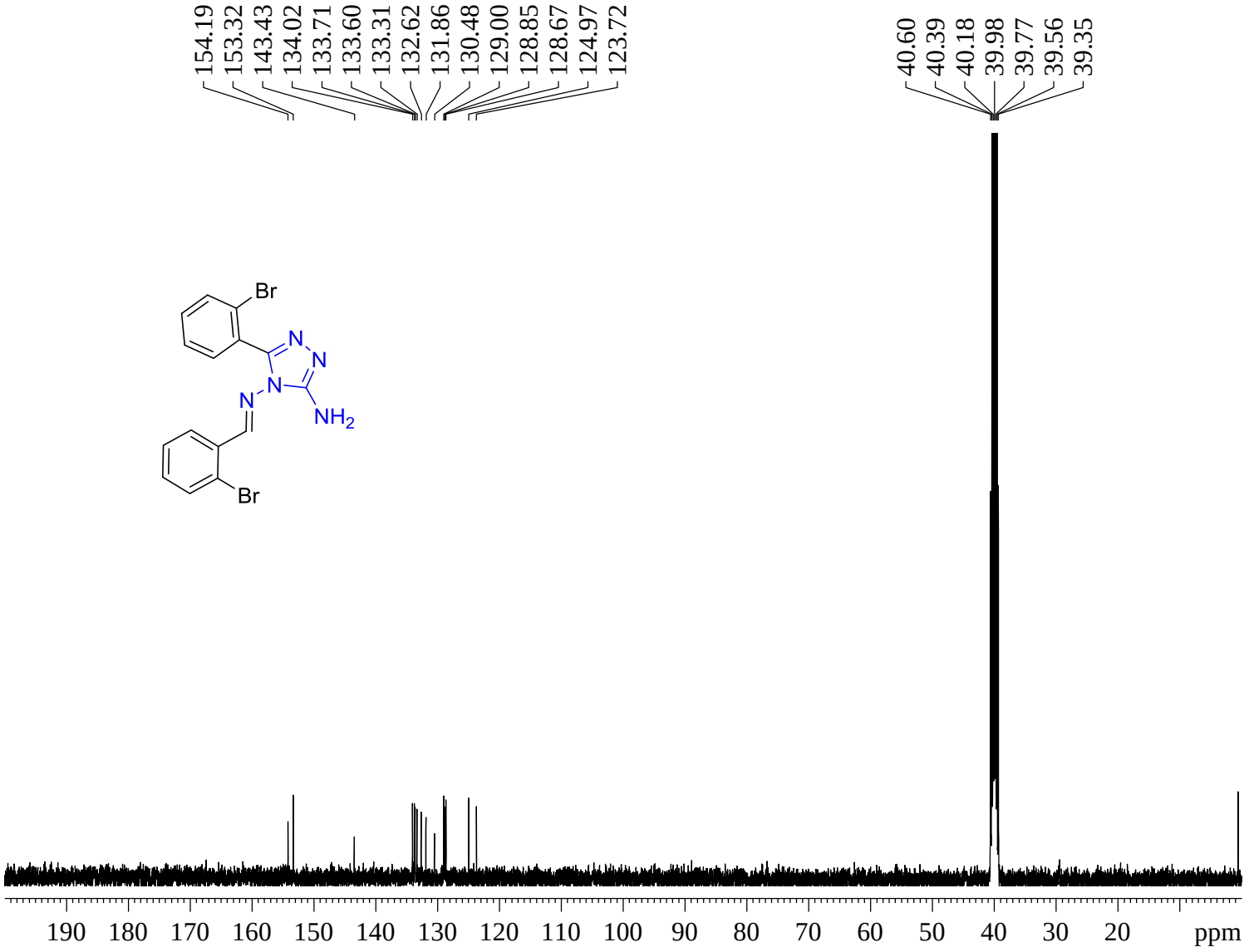
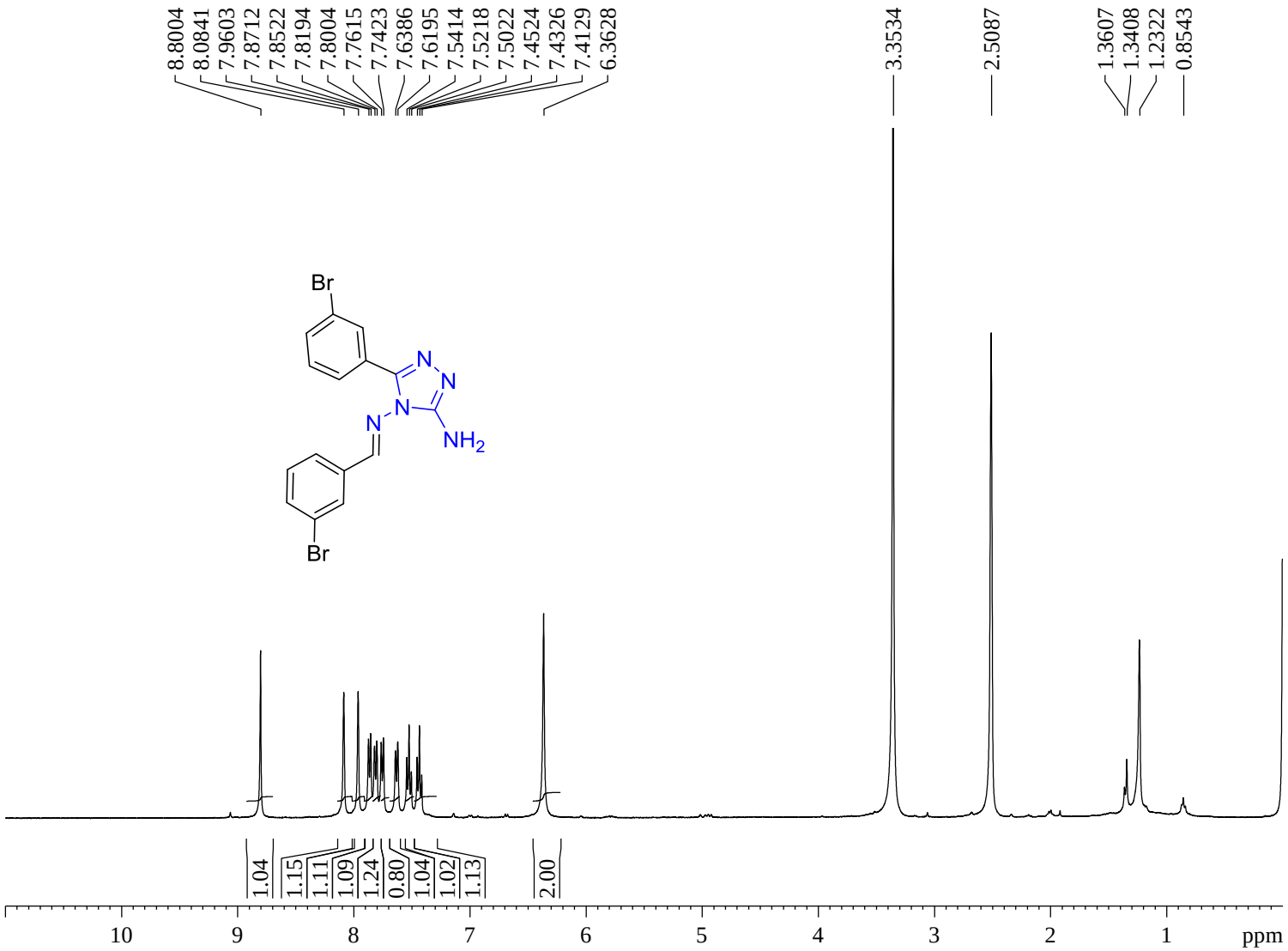
^{1}H spectra of compound 5g



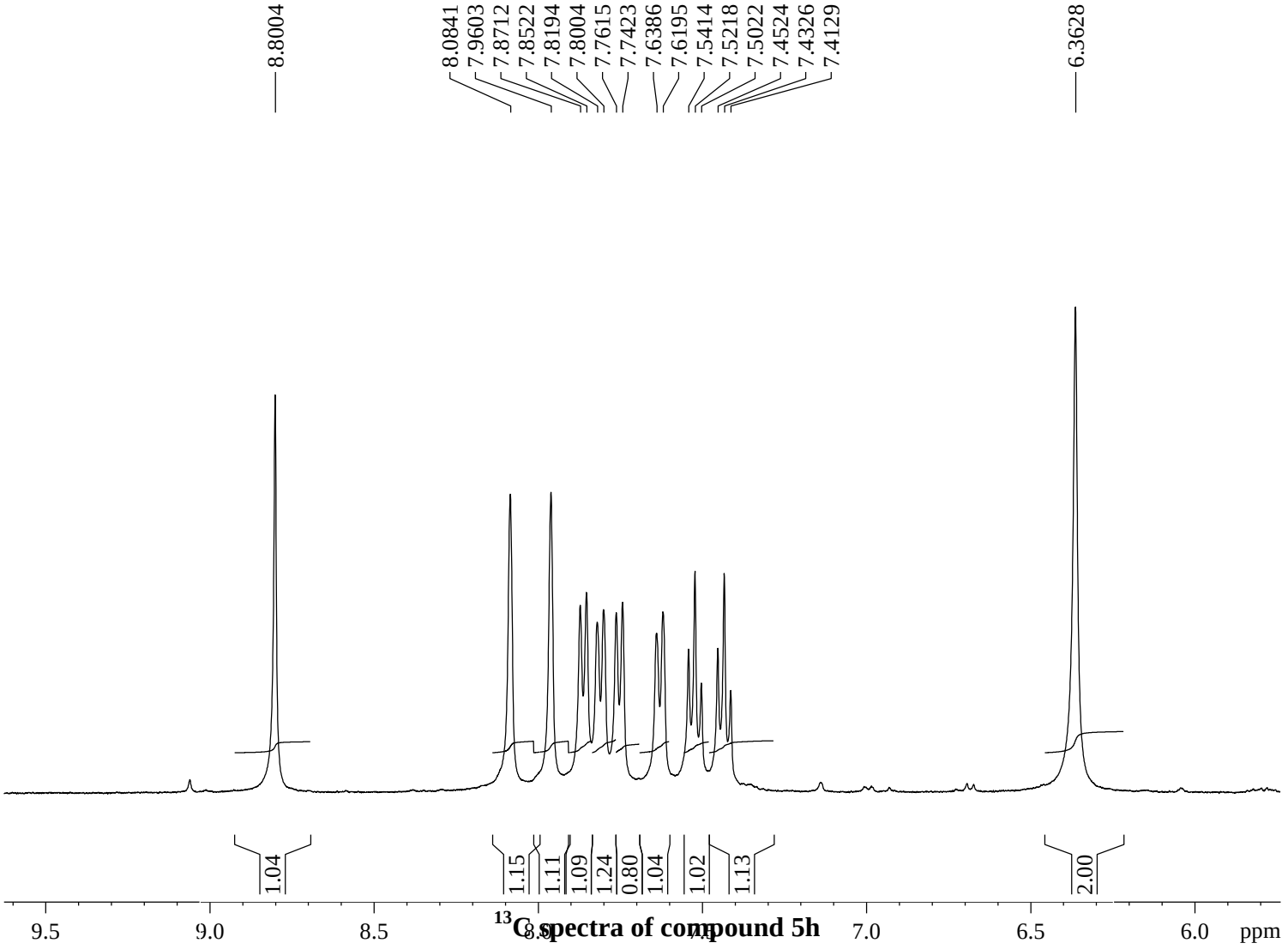
^{13}C spectra of compound 5g



^{1}H spectra of compound 5h

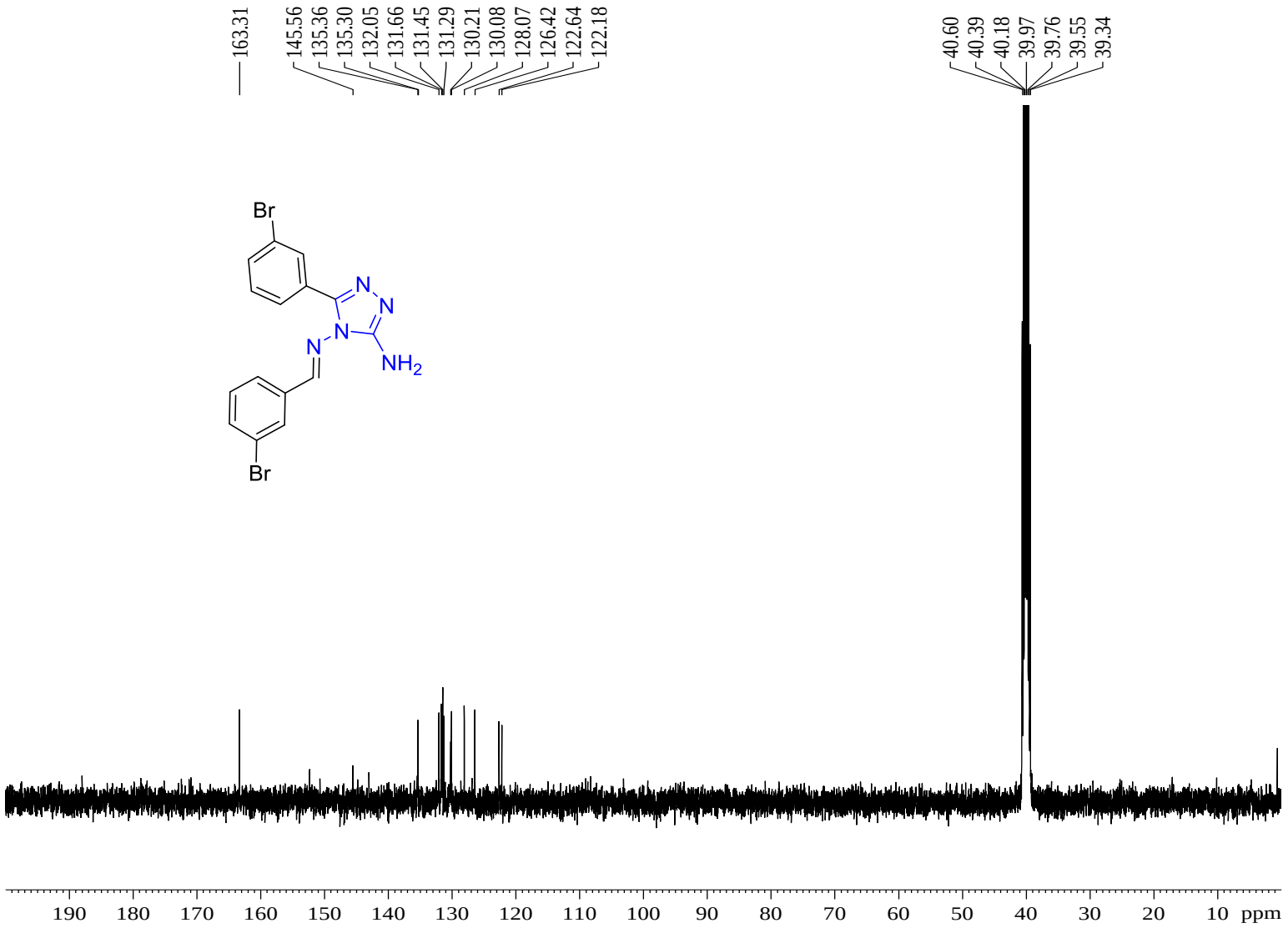


^{1}H spectra of compound 5h_expanded

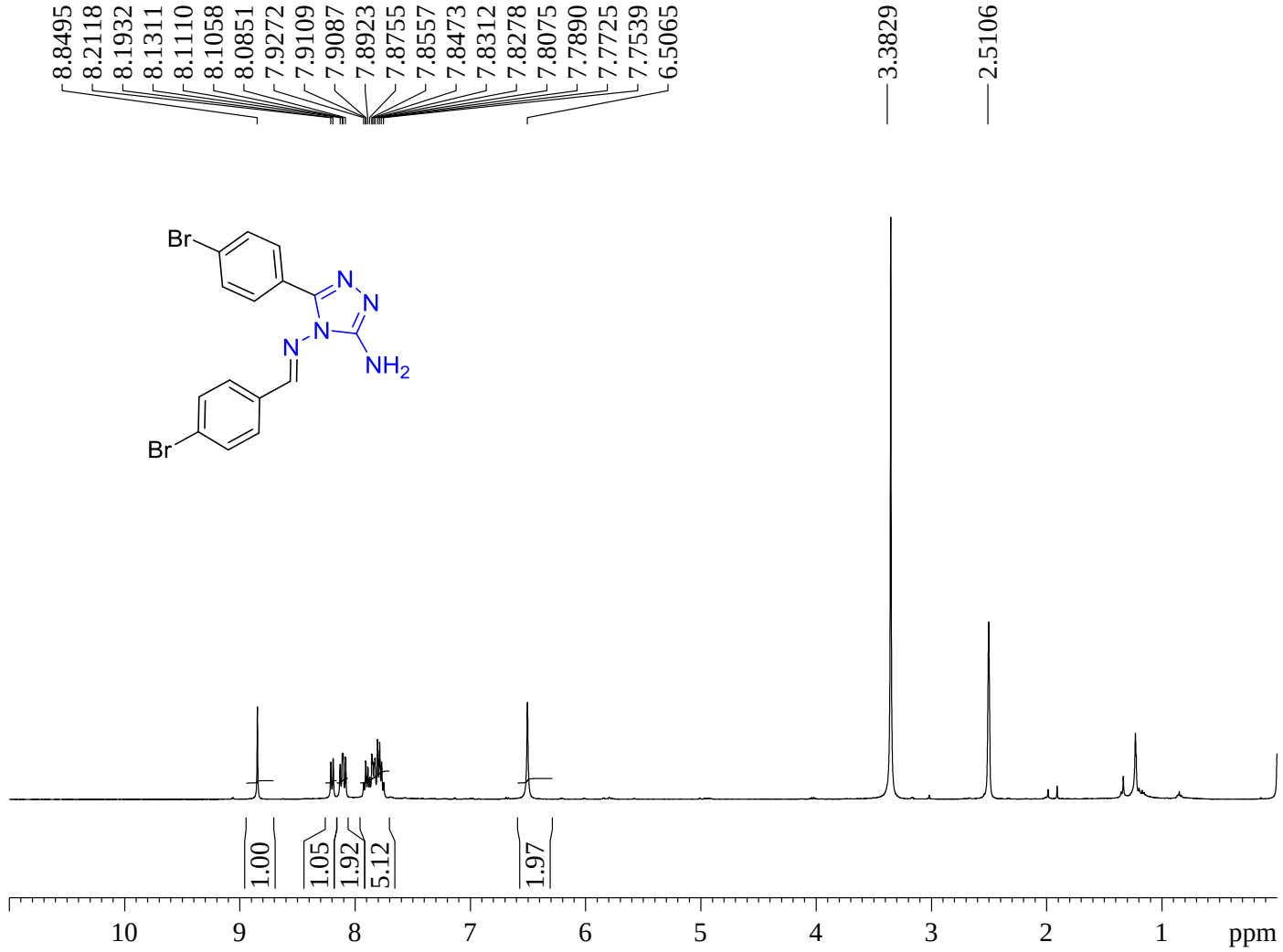


^{13}C spectra of compound 5h

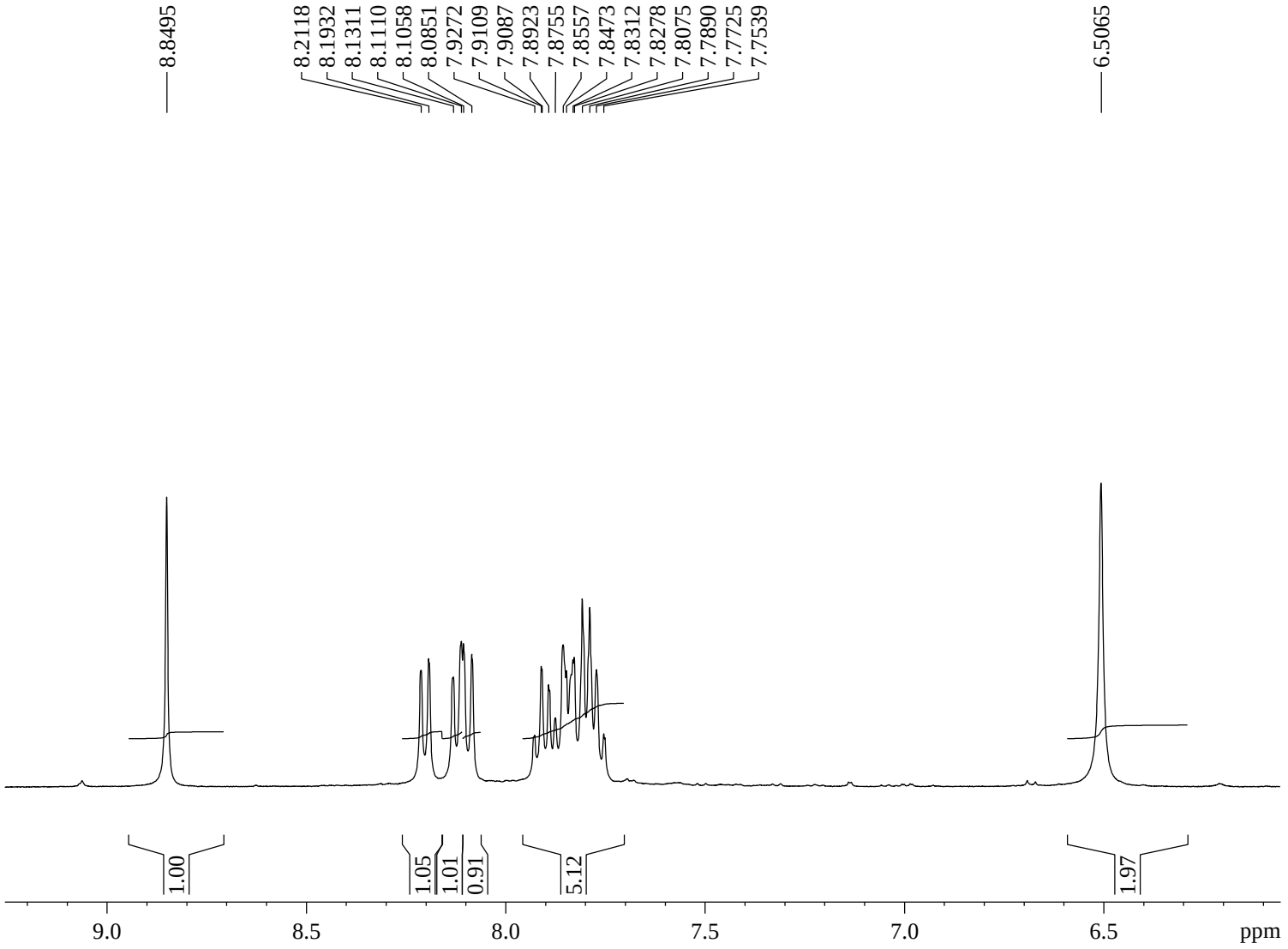
^{13}C spectra of compound 5h



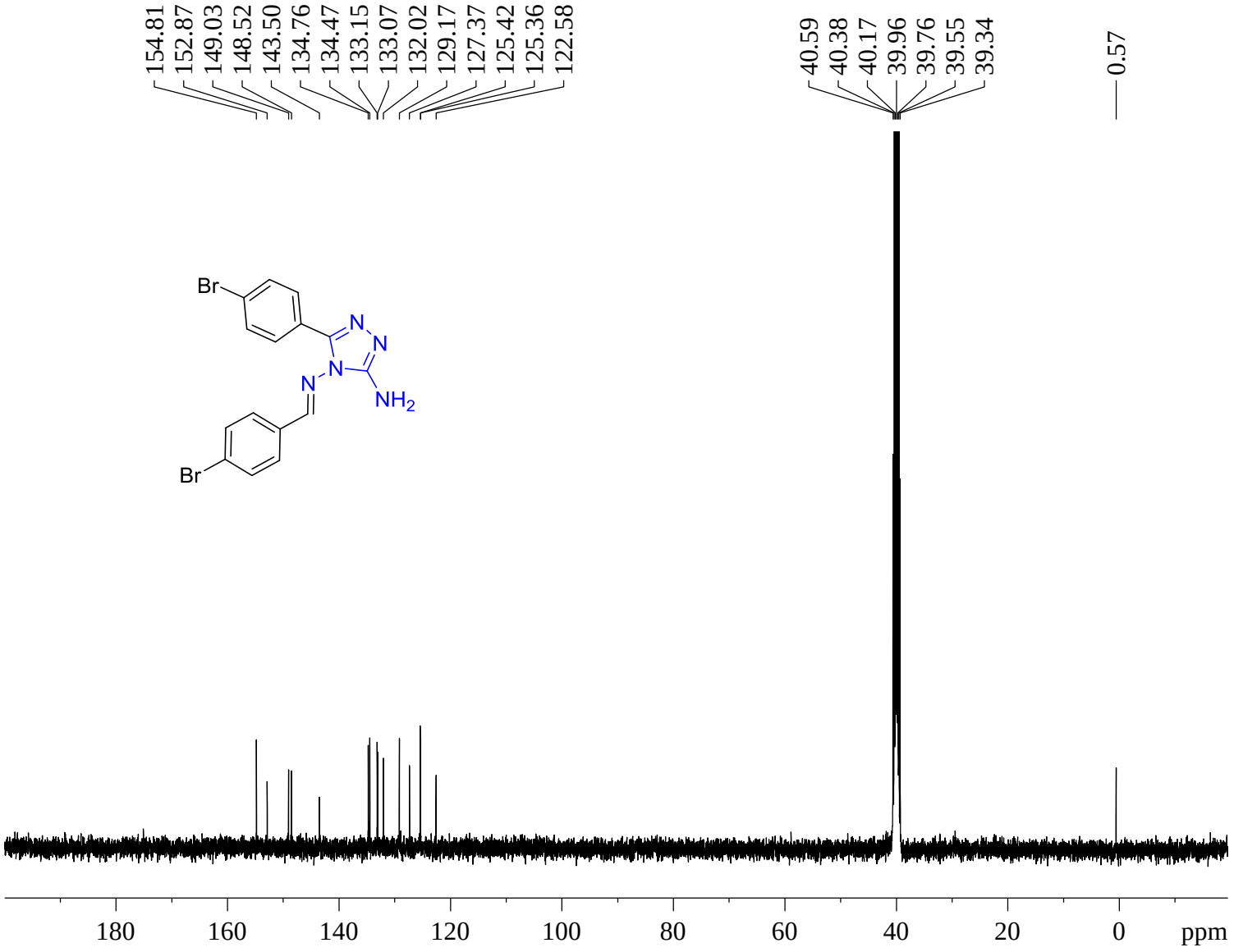
^{1}H spectra of compound 5i



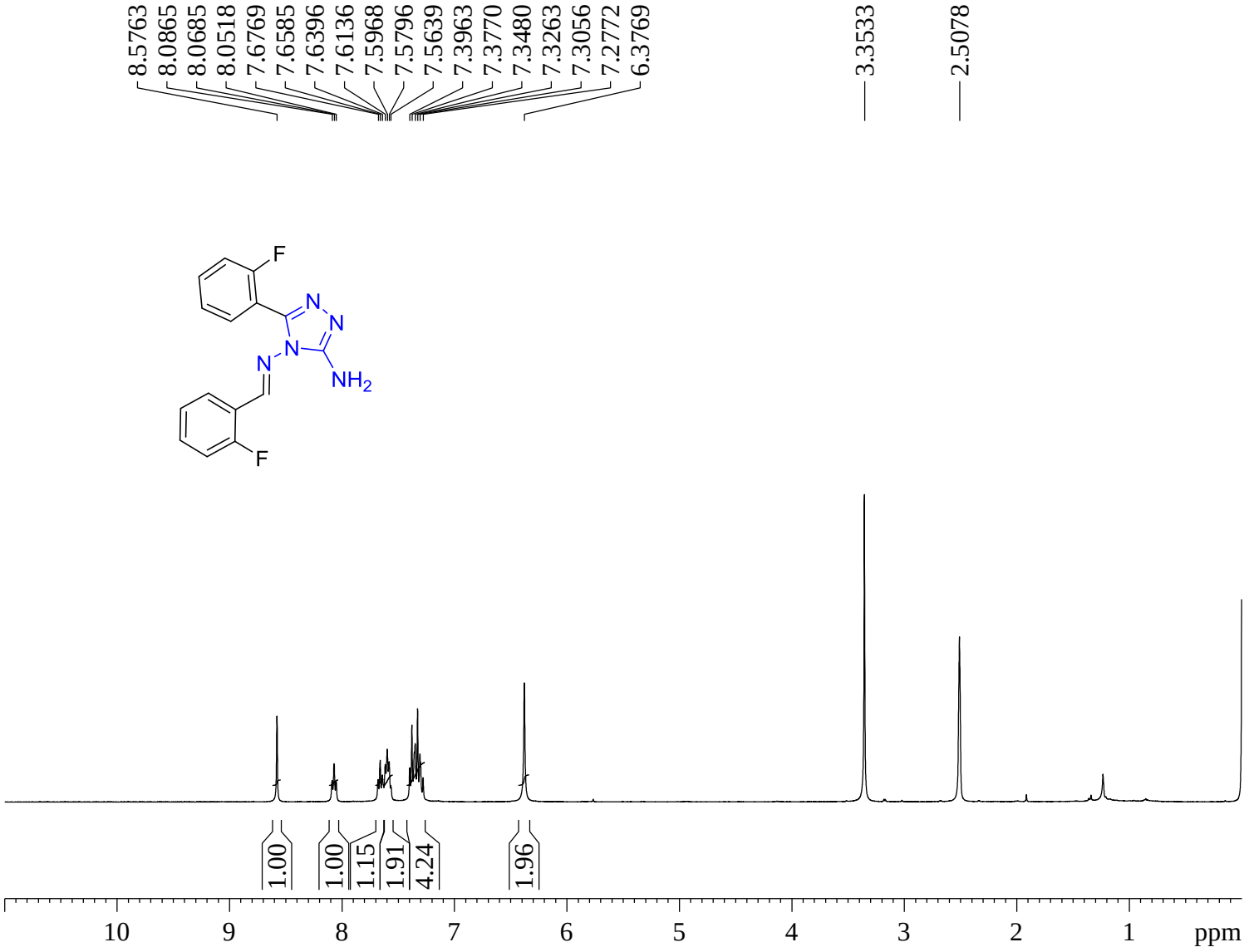
^{1}H spectra of compound 5i



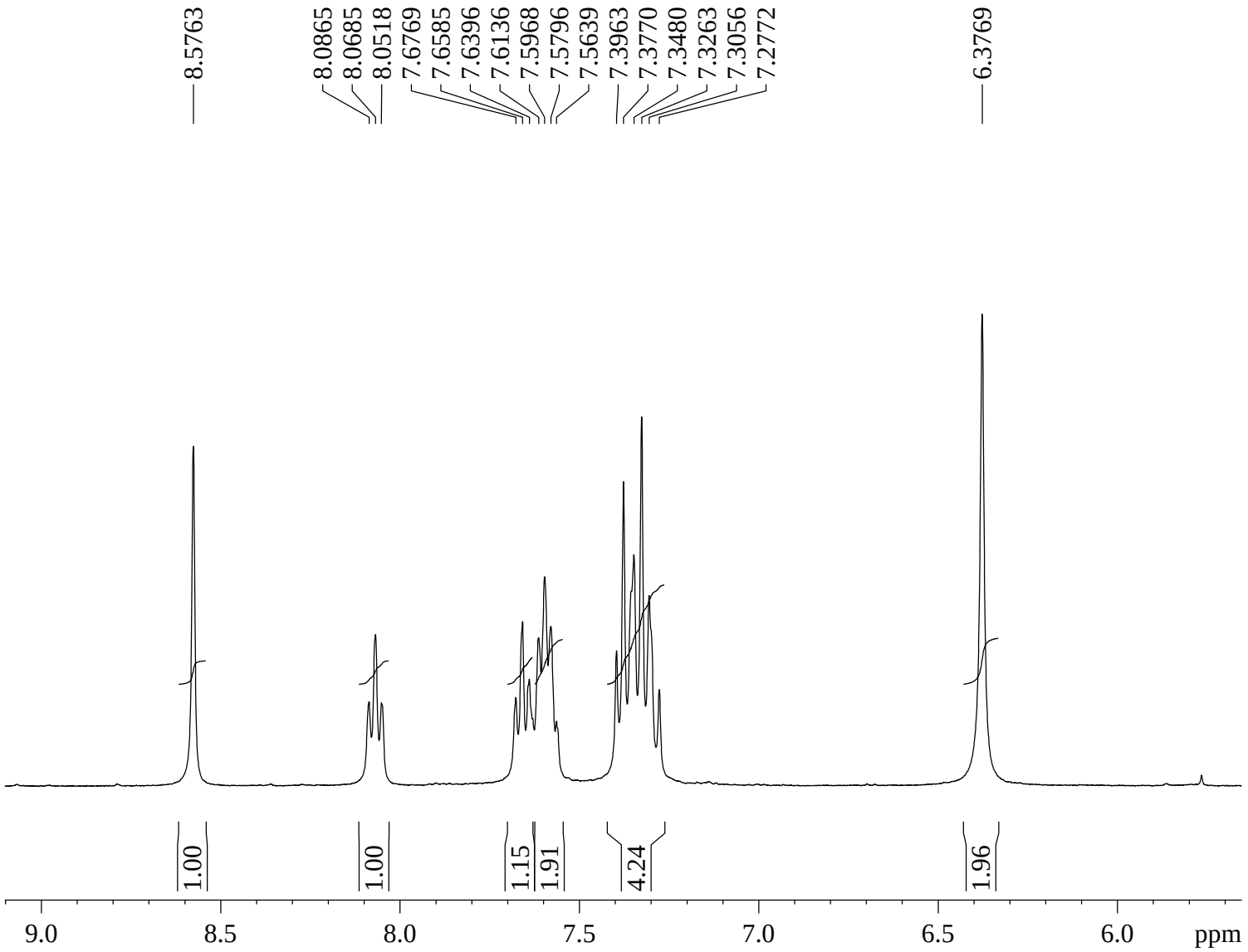
^{13}C spectra of compound 5i



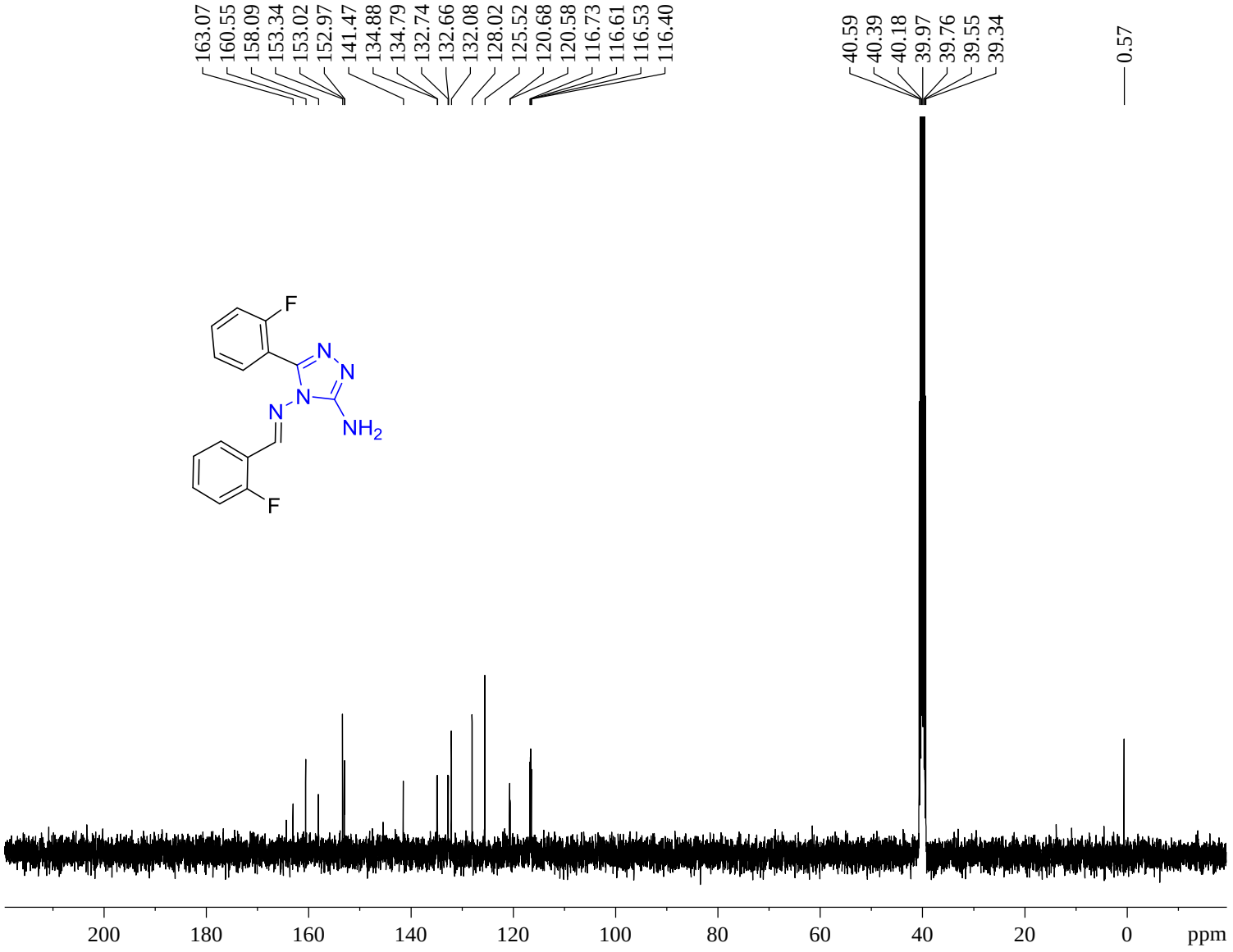
^{1}H spectra of compound 5j



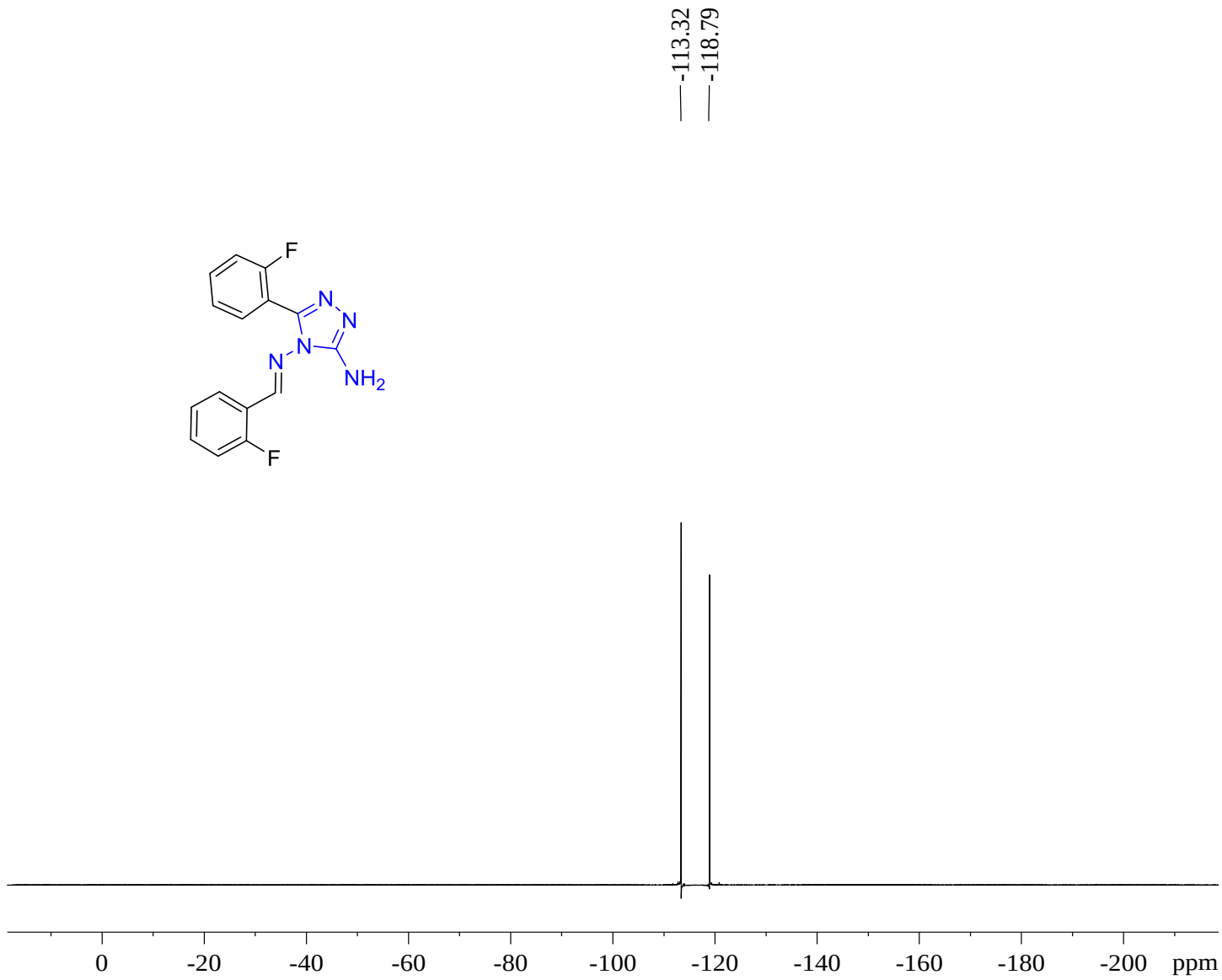
^{1}H spectra of compound 5j



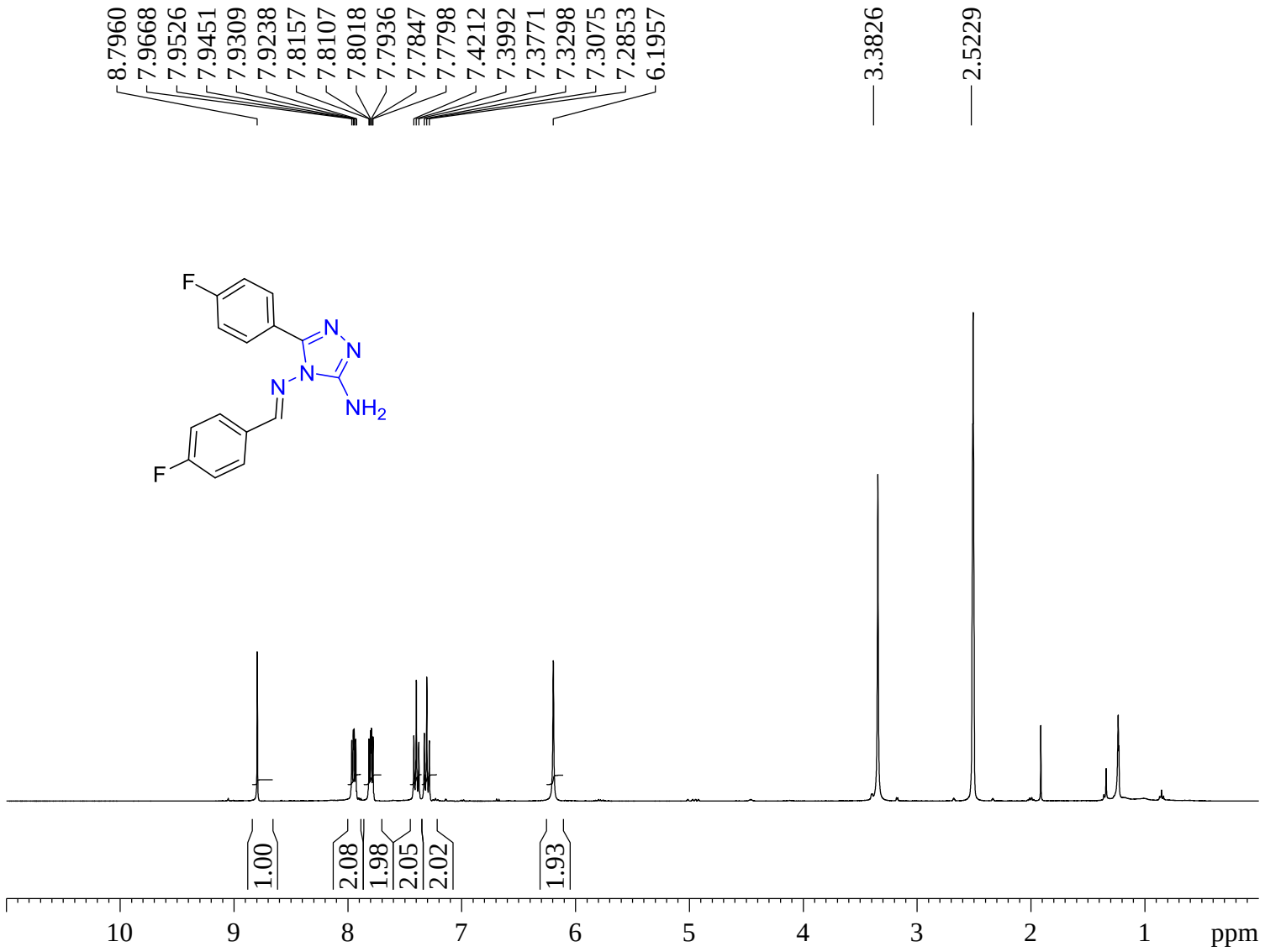
^{13}C spectra of compound 5j



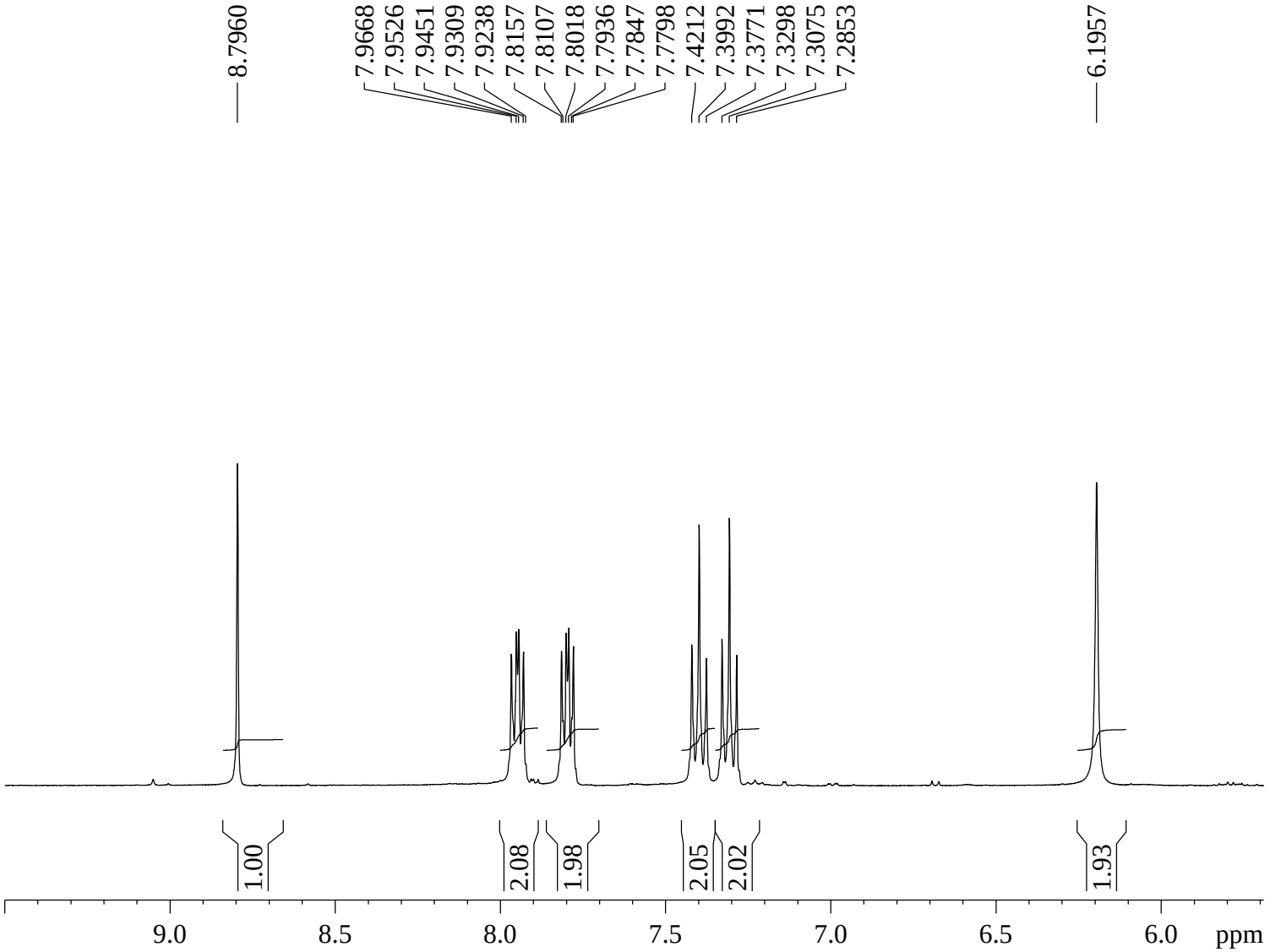
^{19}F spectra of compound 5j



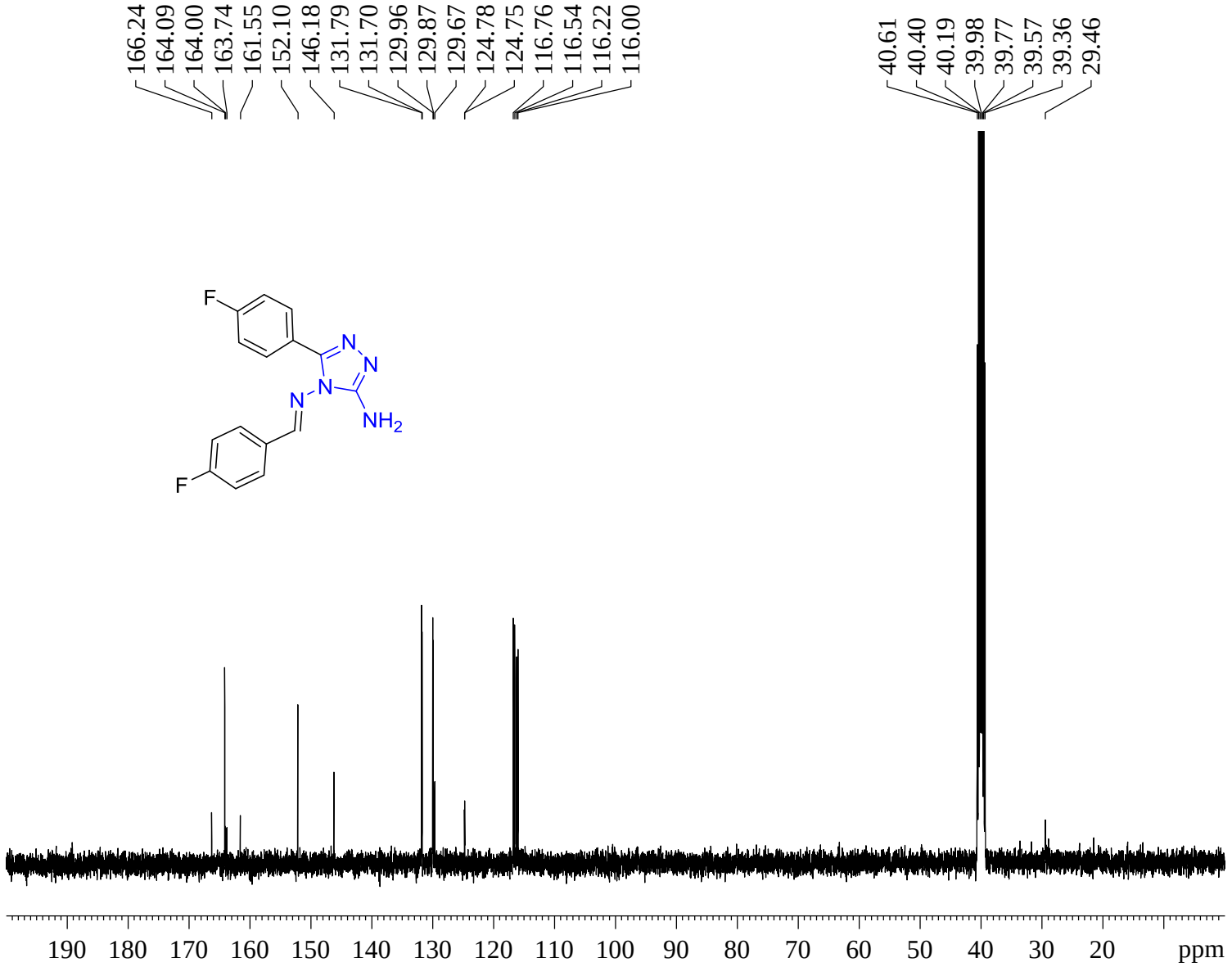
^{1}H spectra of compound 5k



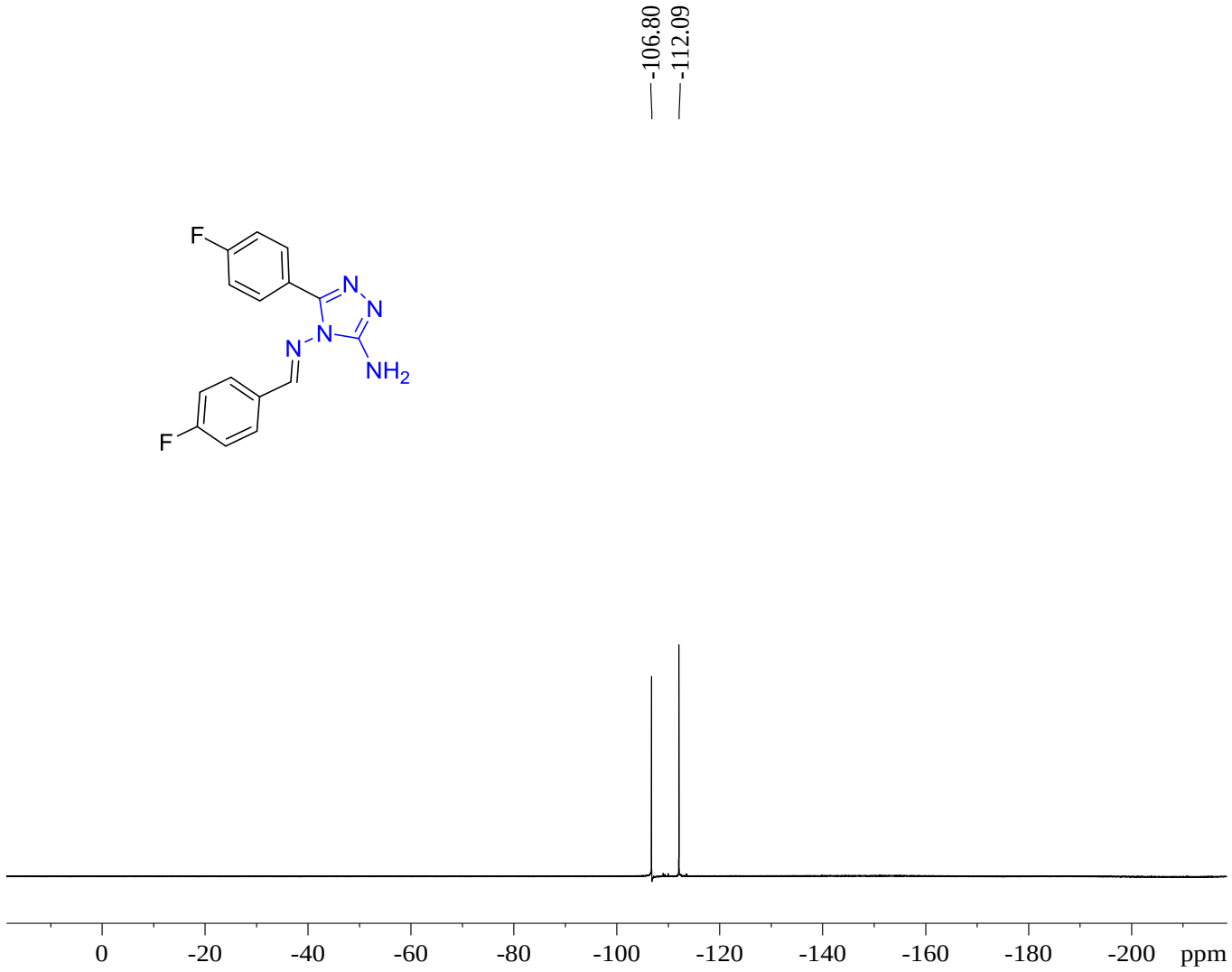
^{1}H spectra of compound 5k_expanded



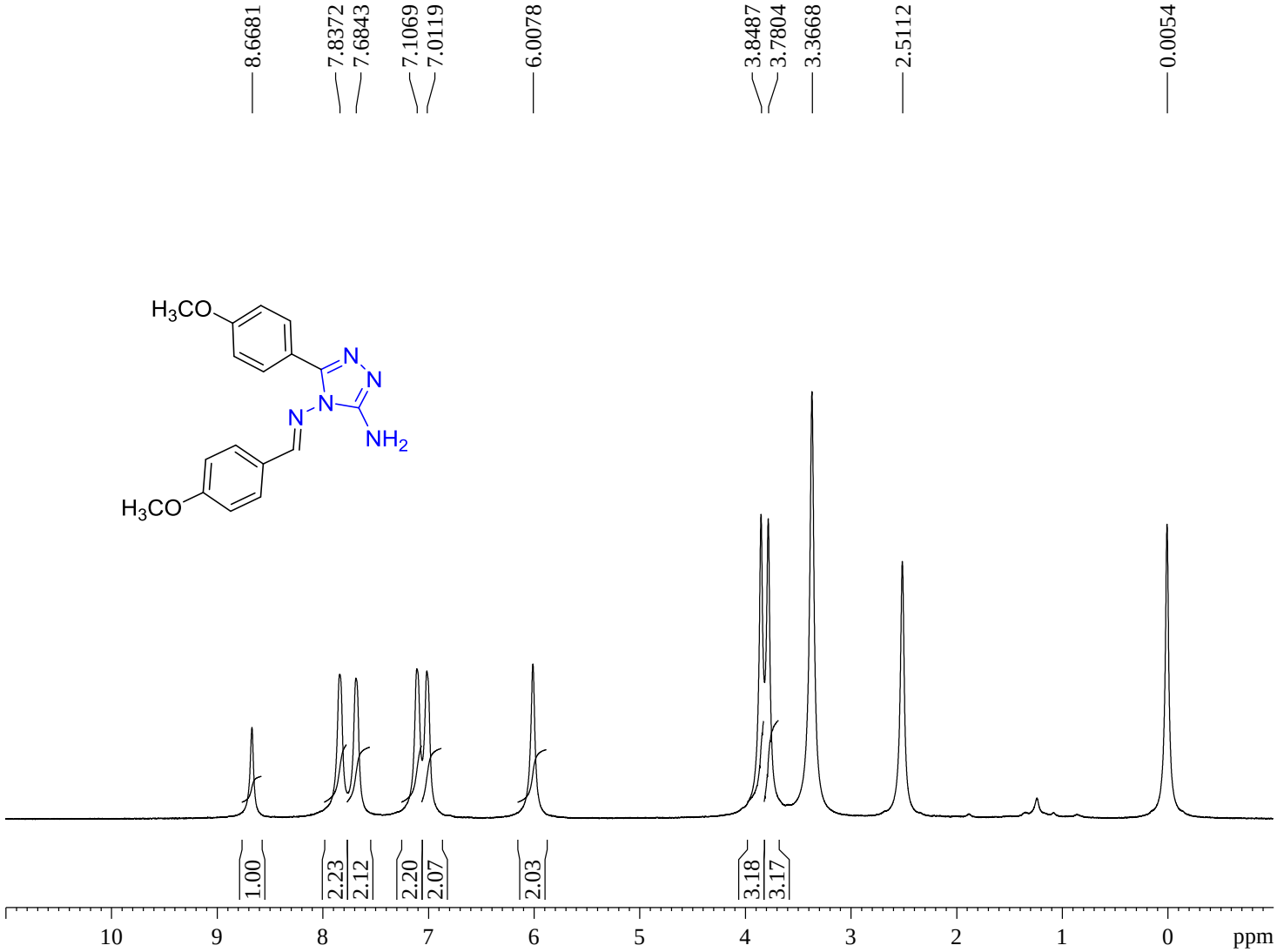
^{13}C spectra of compound 5k



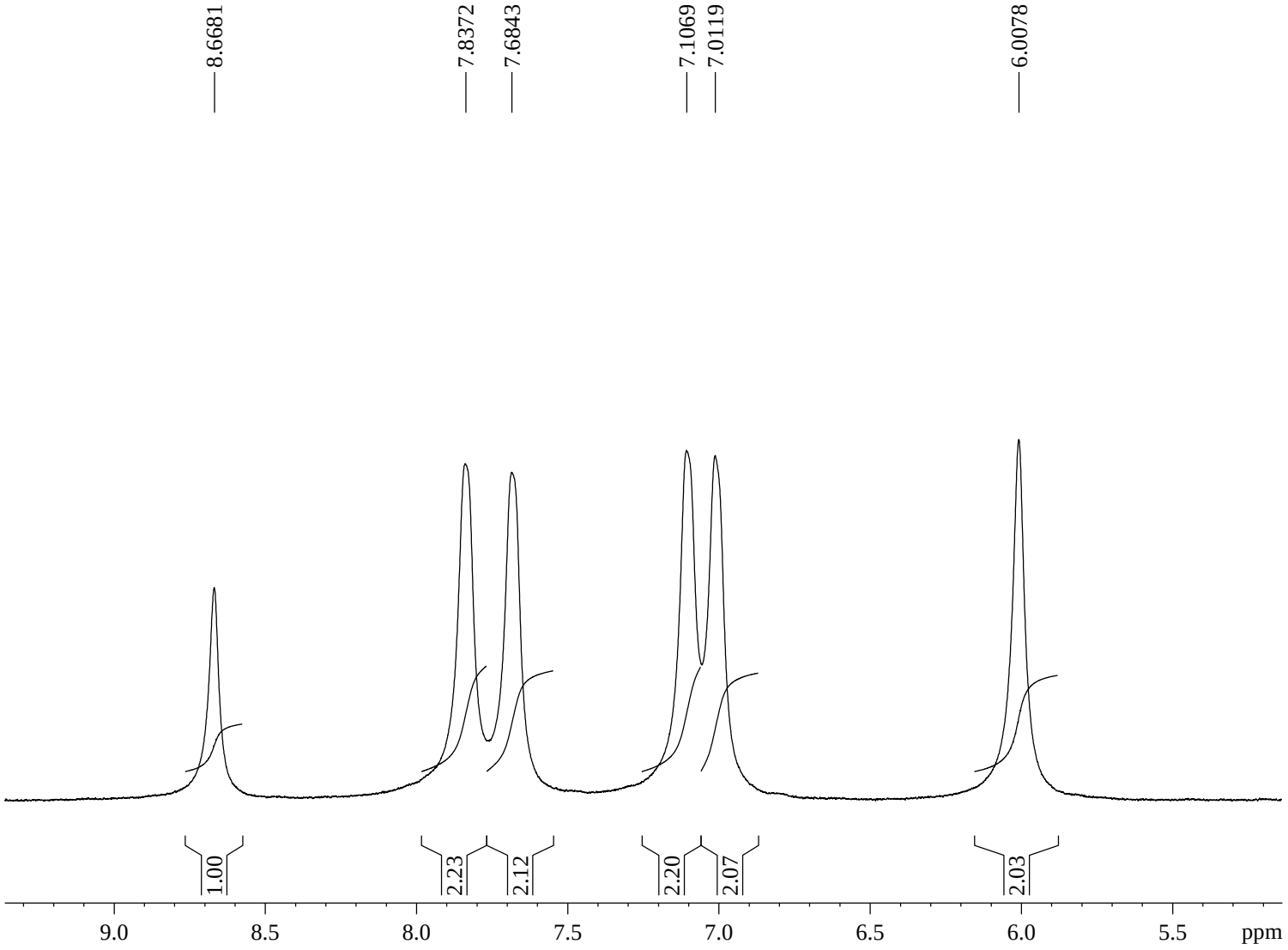
^{19}F spectra of compound 5k



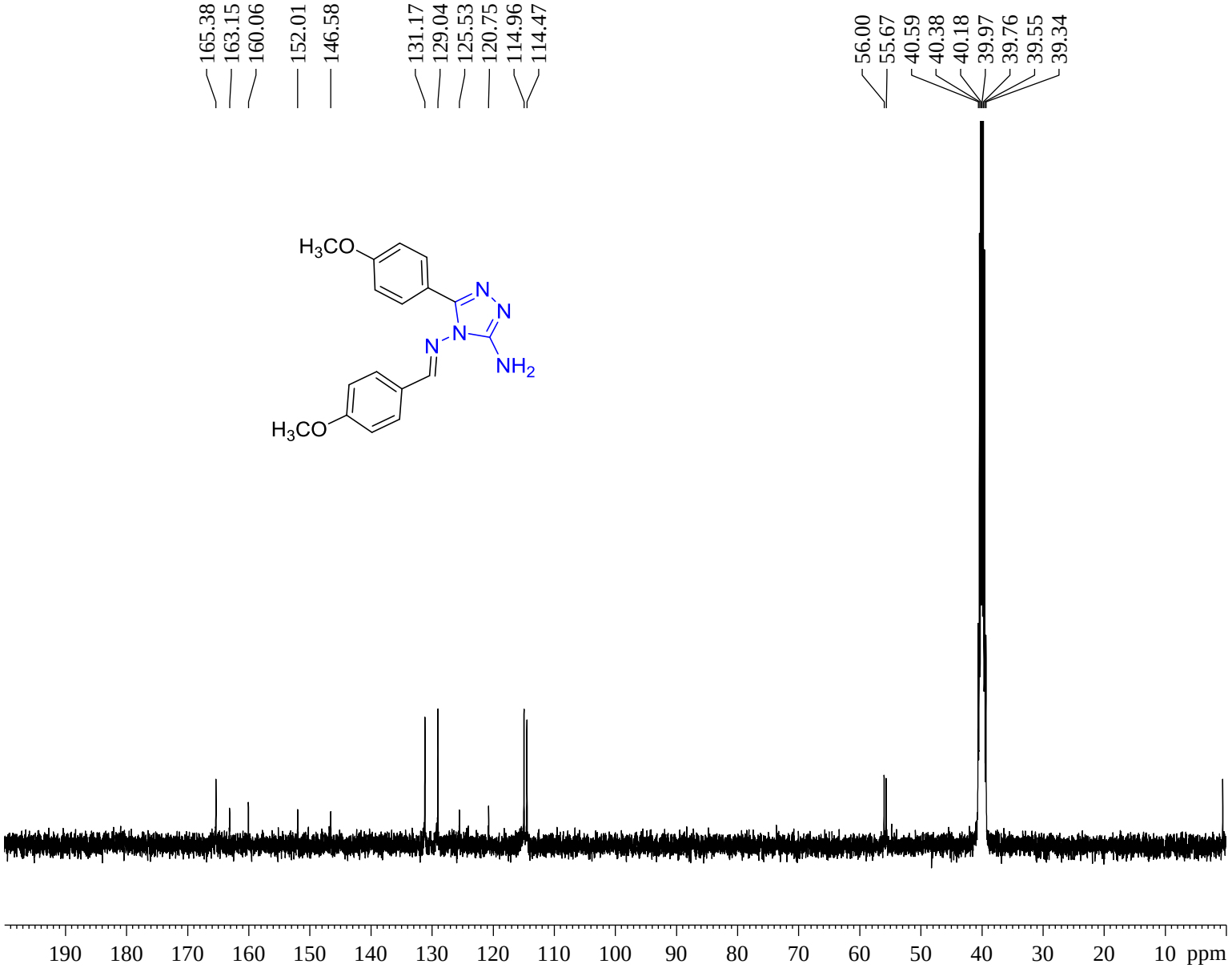
^{1}H spectra of compound 5l



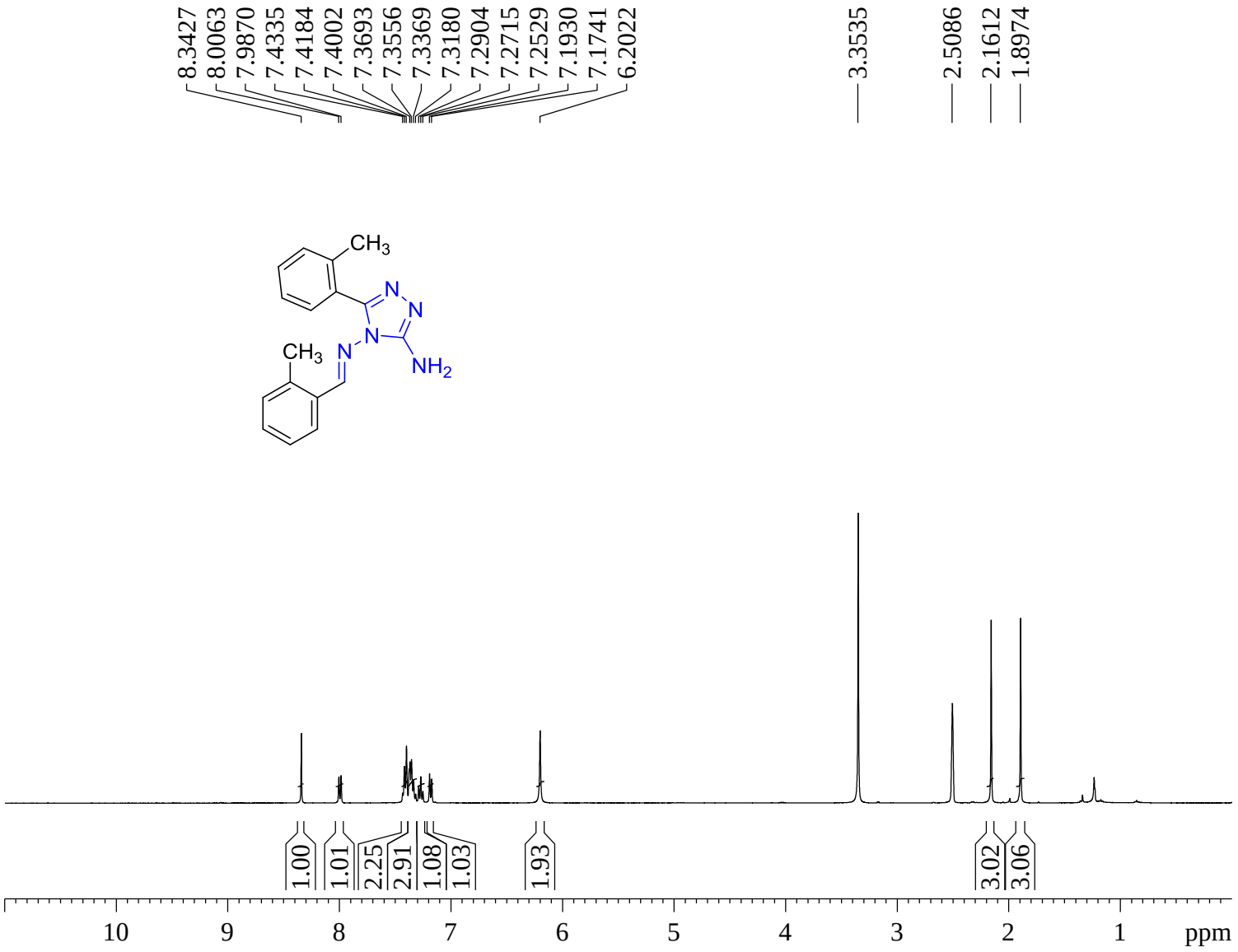
^{1}H spectra of compound 5l_expanded



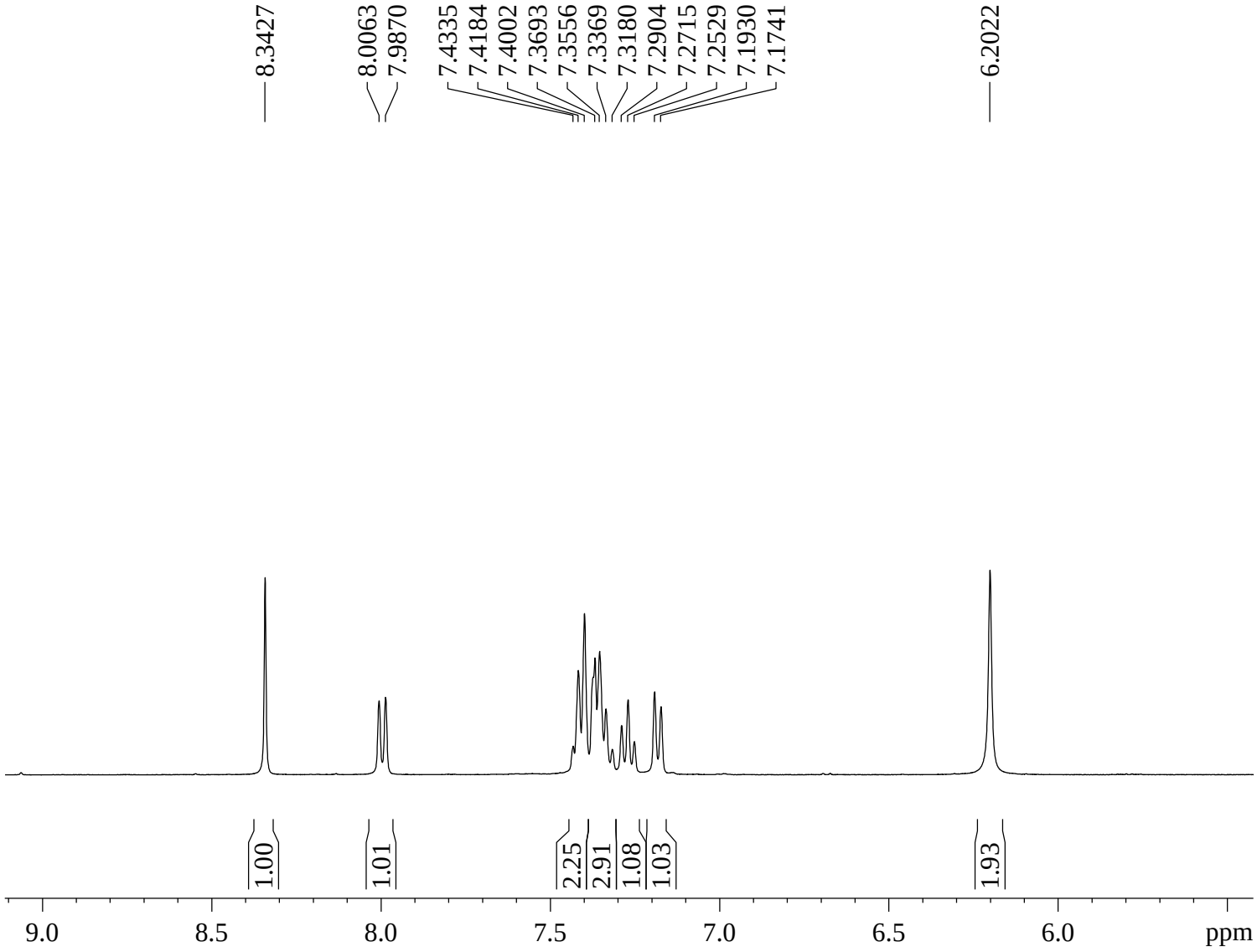
^{13}C spectra of compound 5l



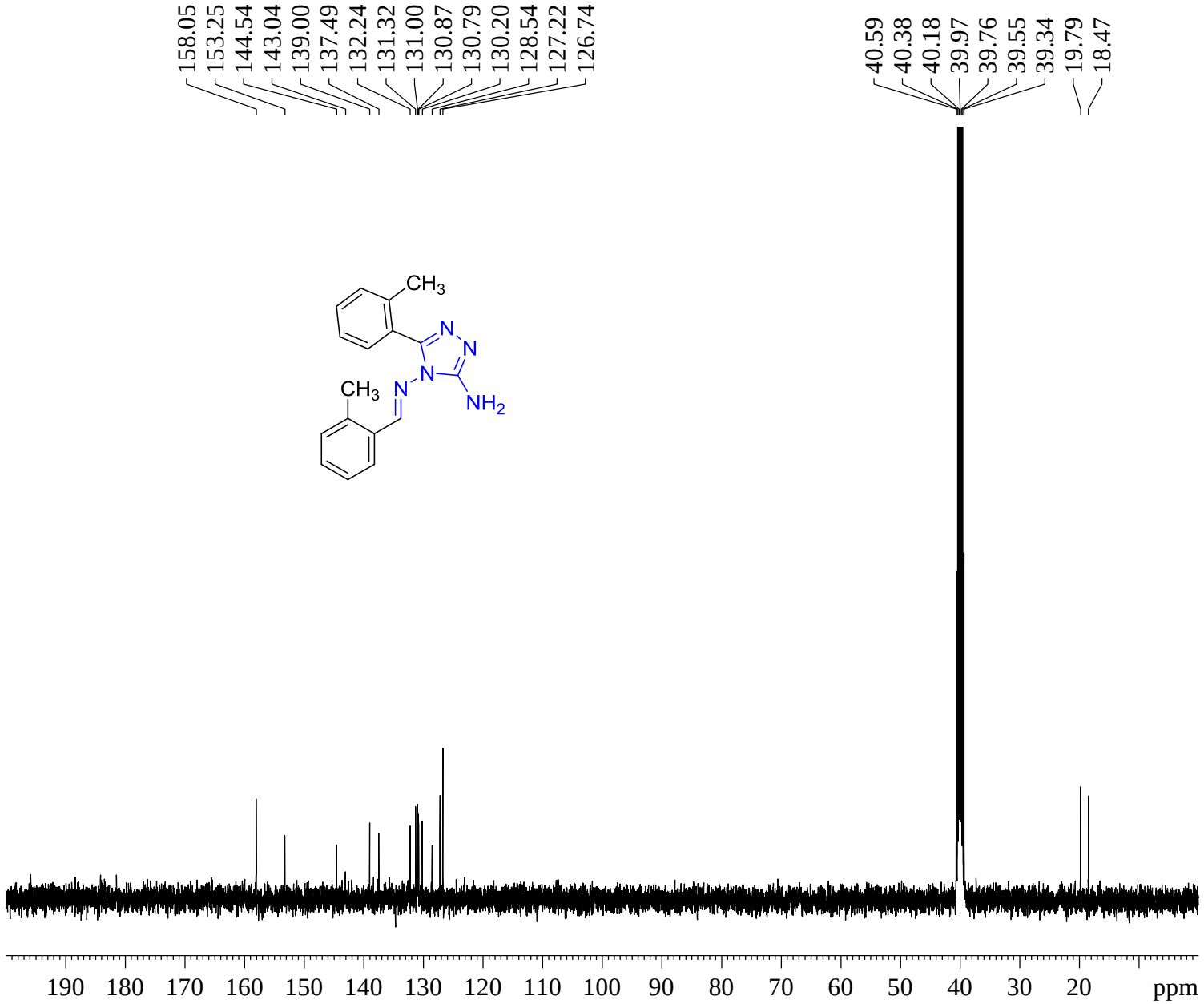
^{1}H spectra of compound 5m



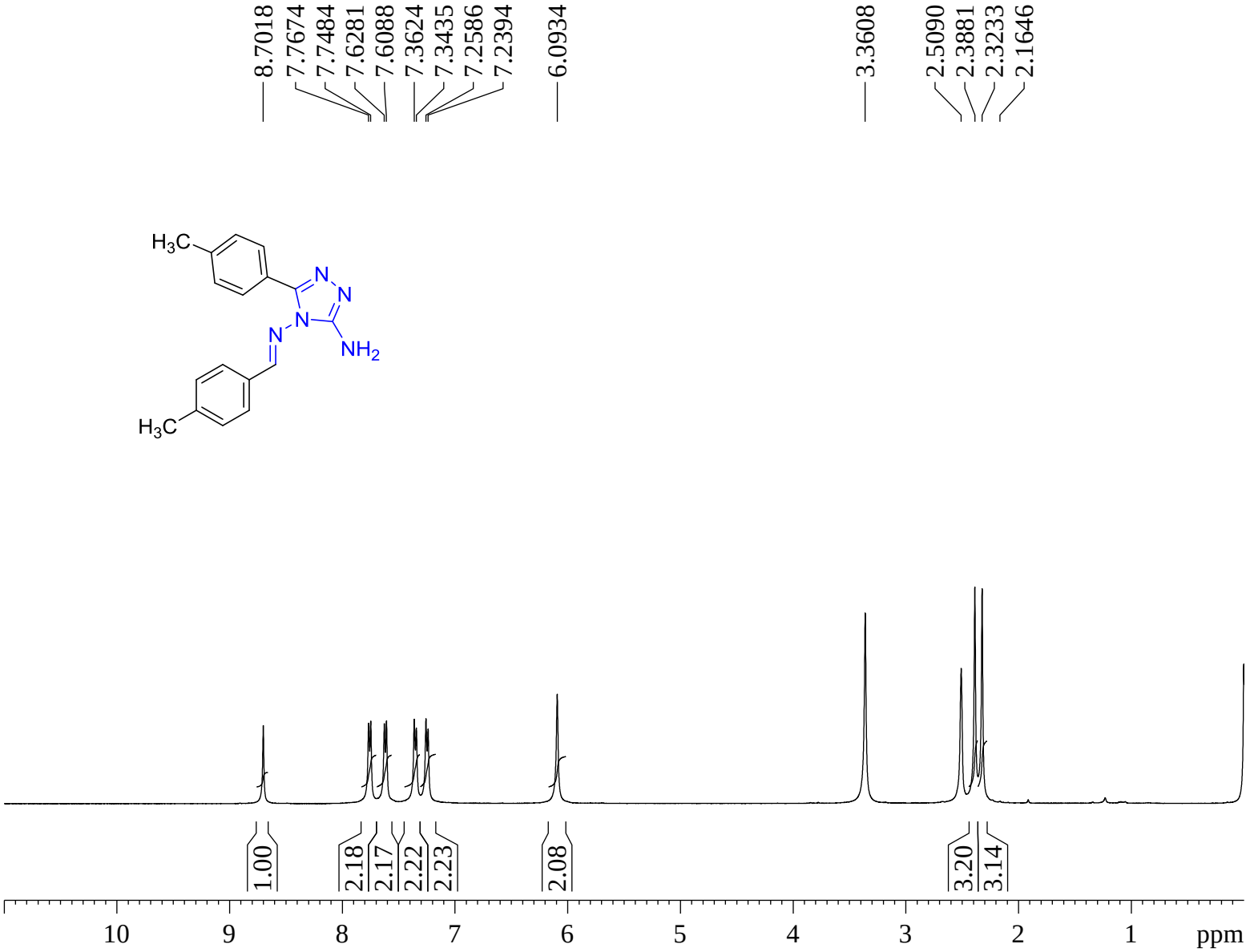
^{1}H spectra of compound 5m_expanded



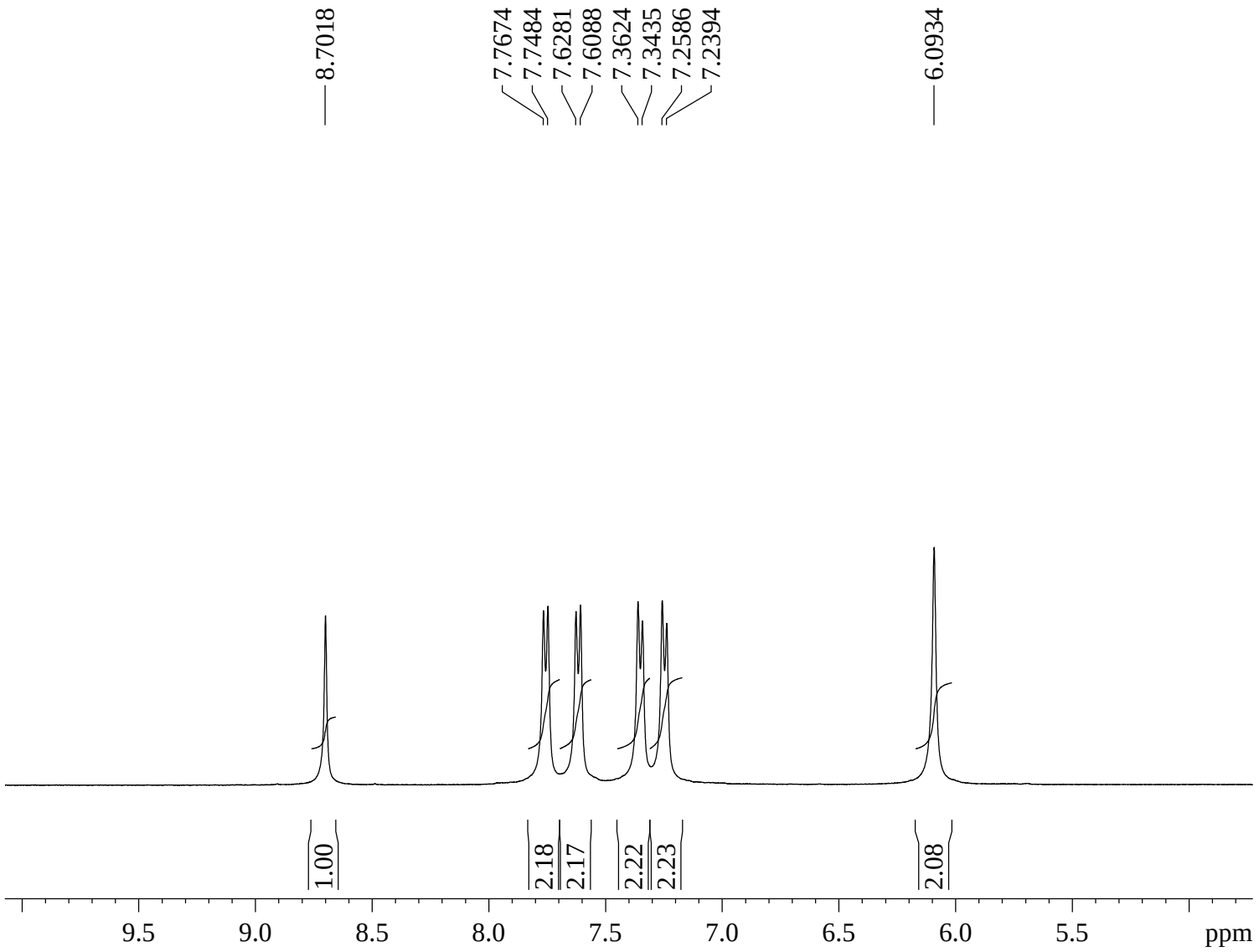
^{13}C spectra of compound 5m



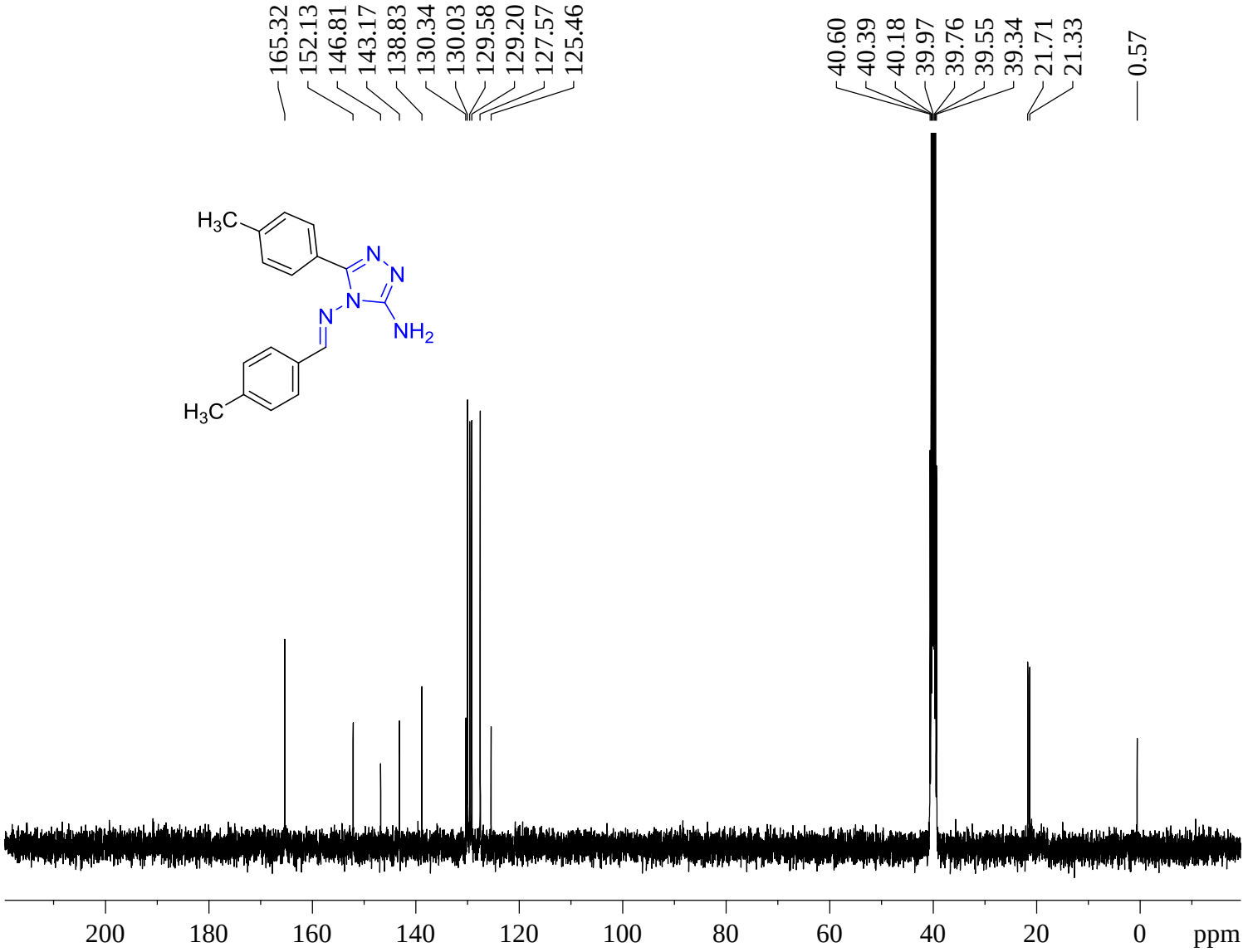
^{1}H spectra of compound 5n



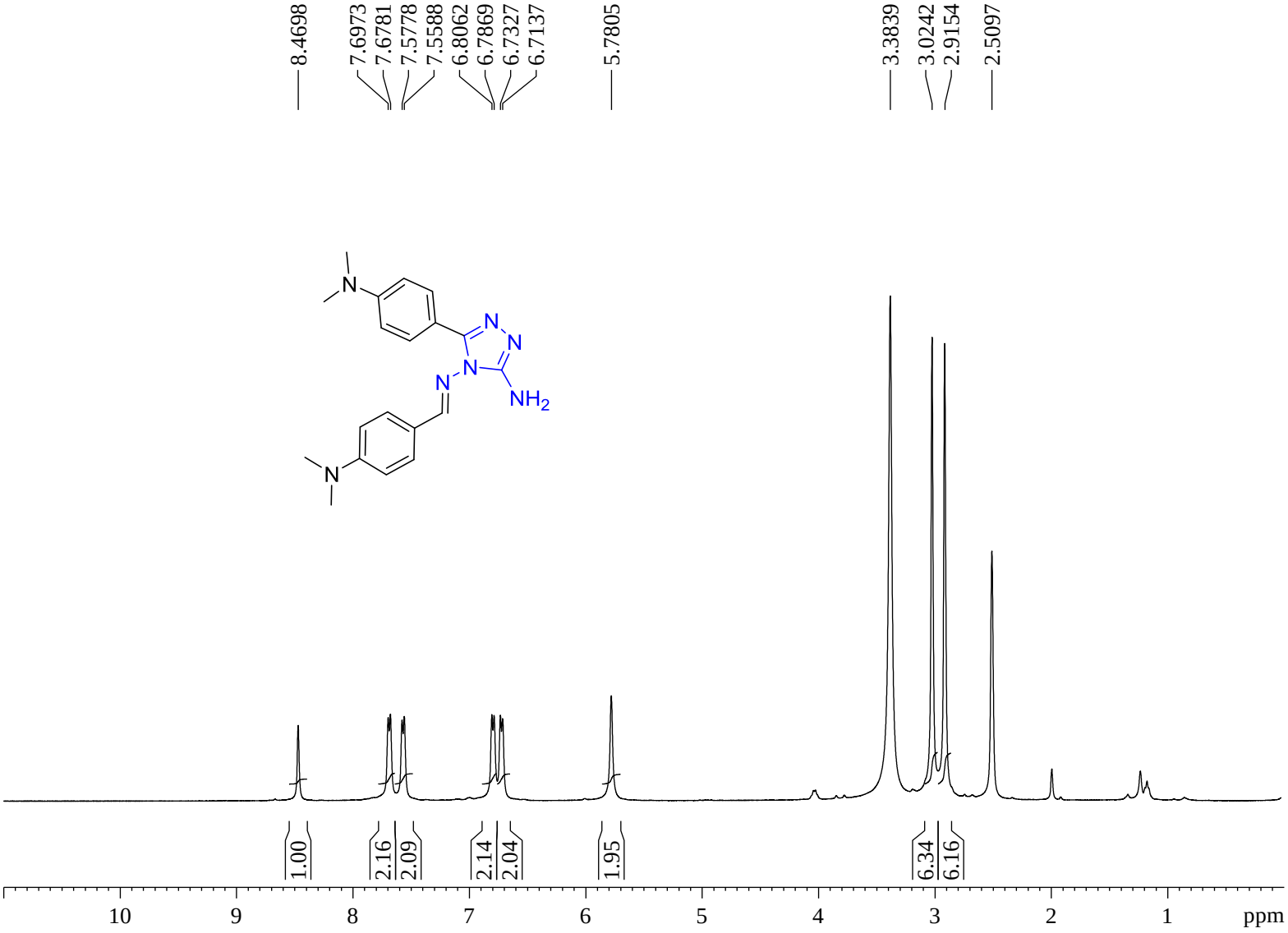
^{1}H spectra of compound 5n



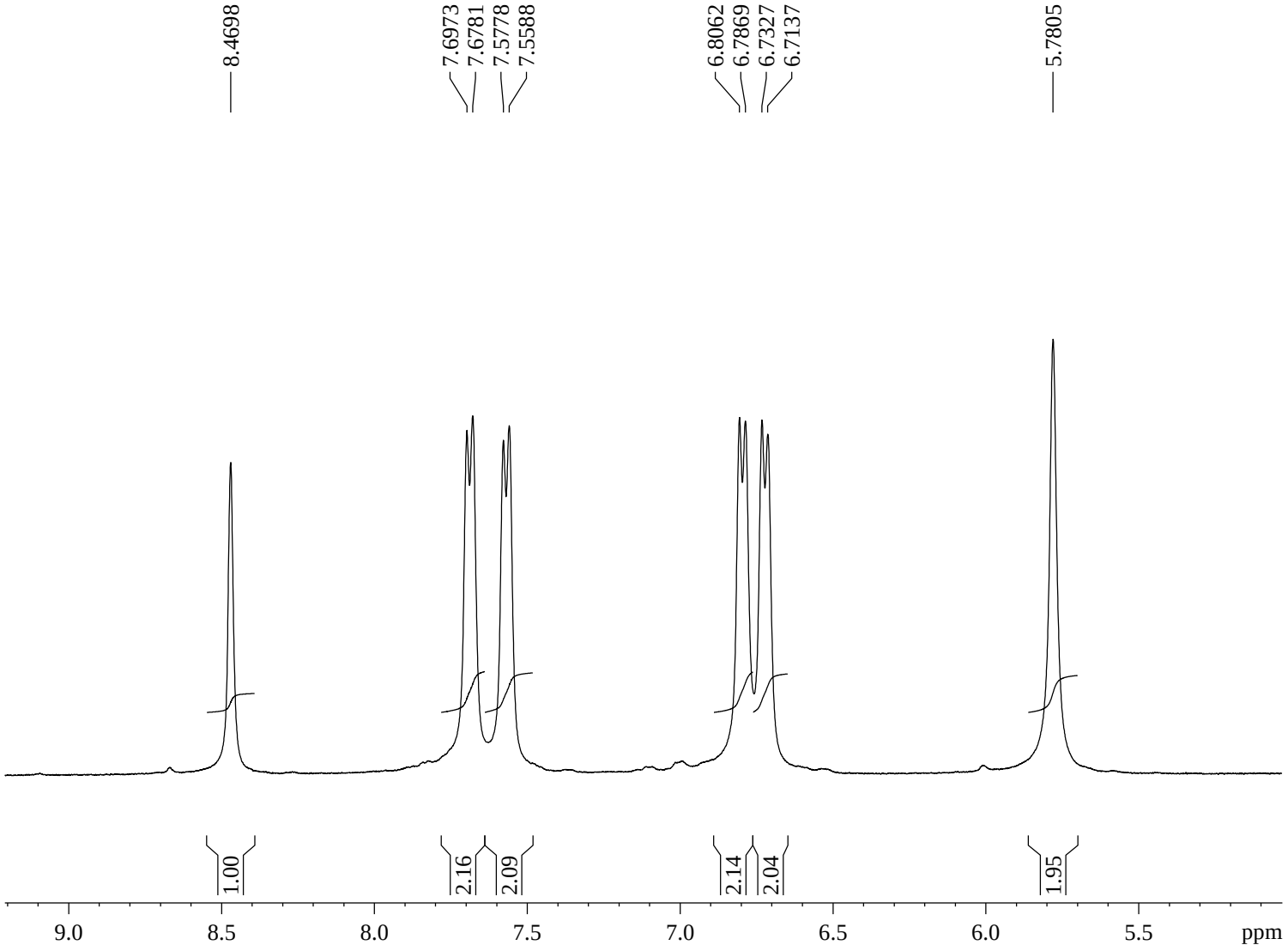
^{13}C spectra of compound 5n



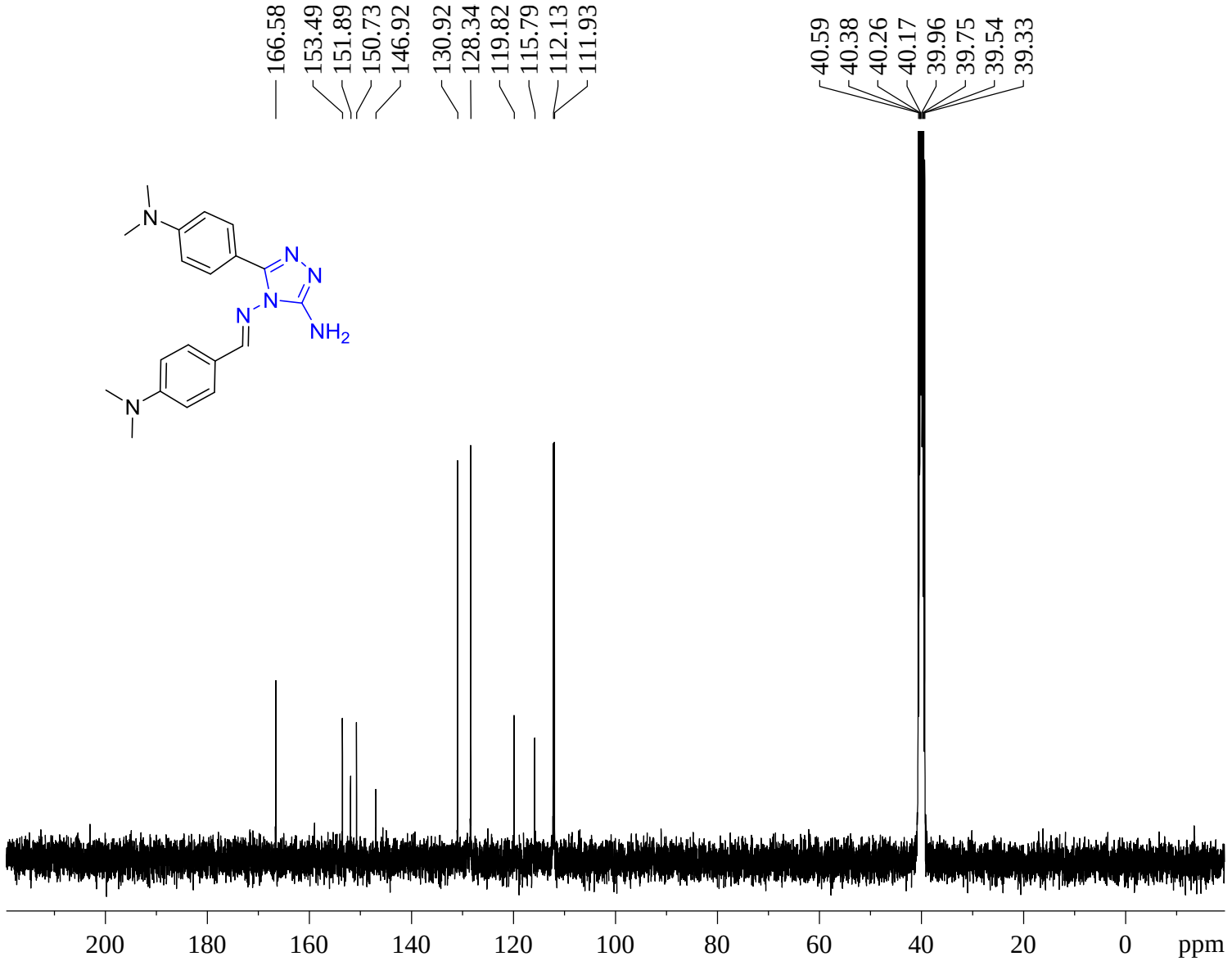
^{1}H spectra of compound 5o



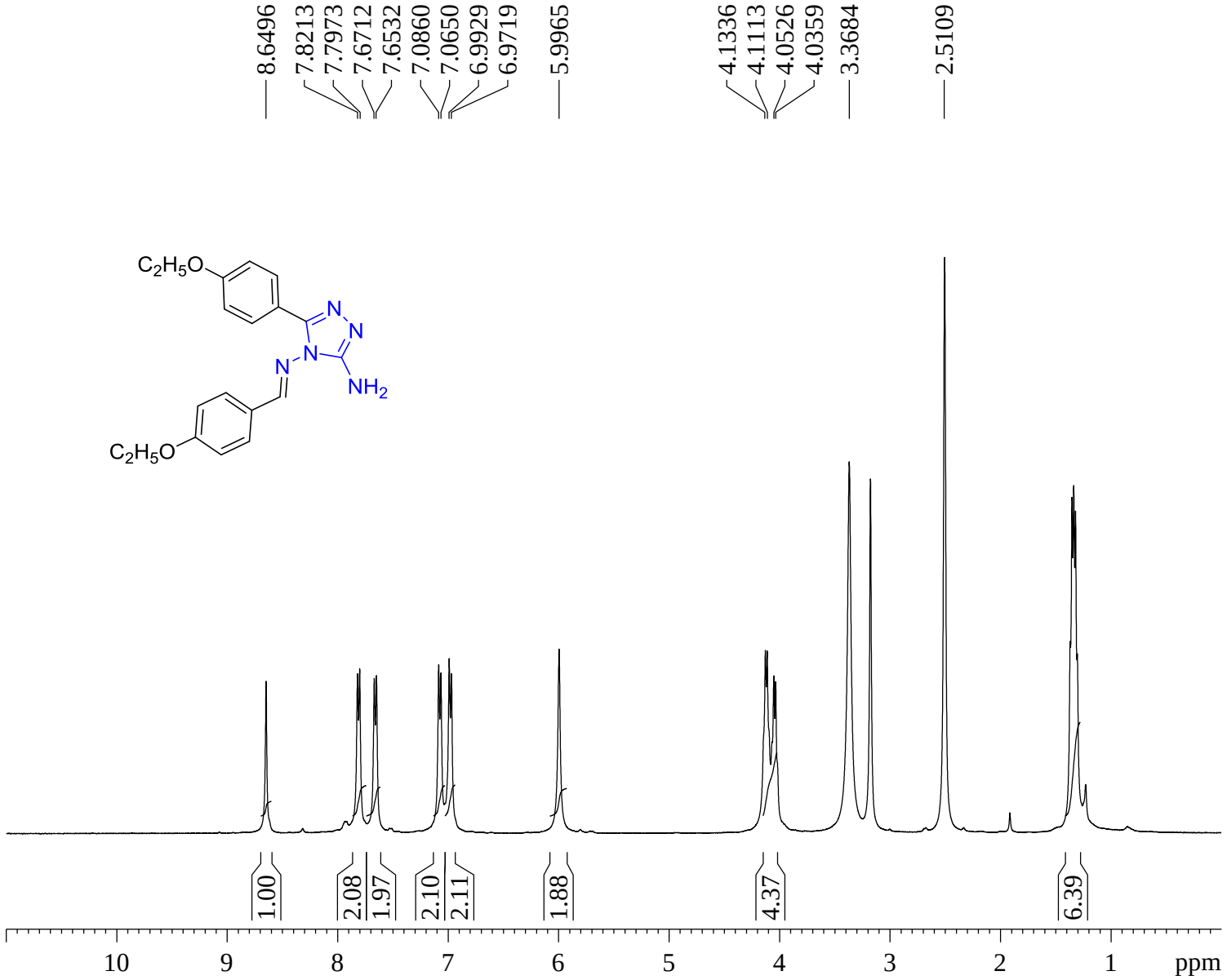
^{1}H spectra of compound 5o_expanded



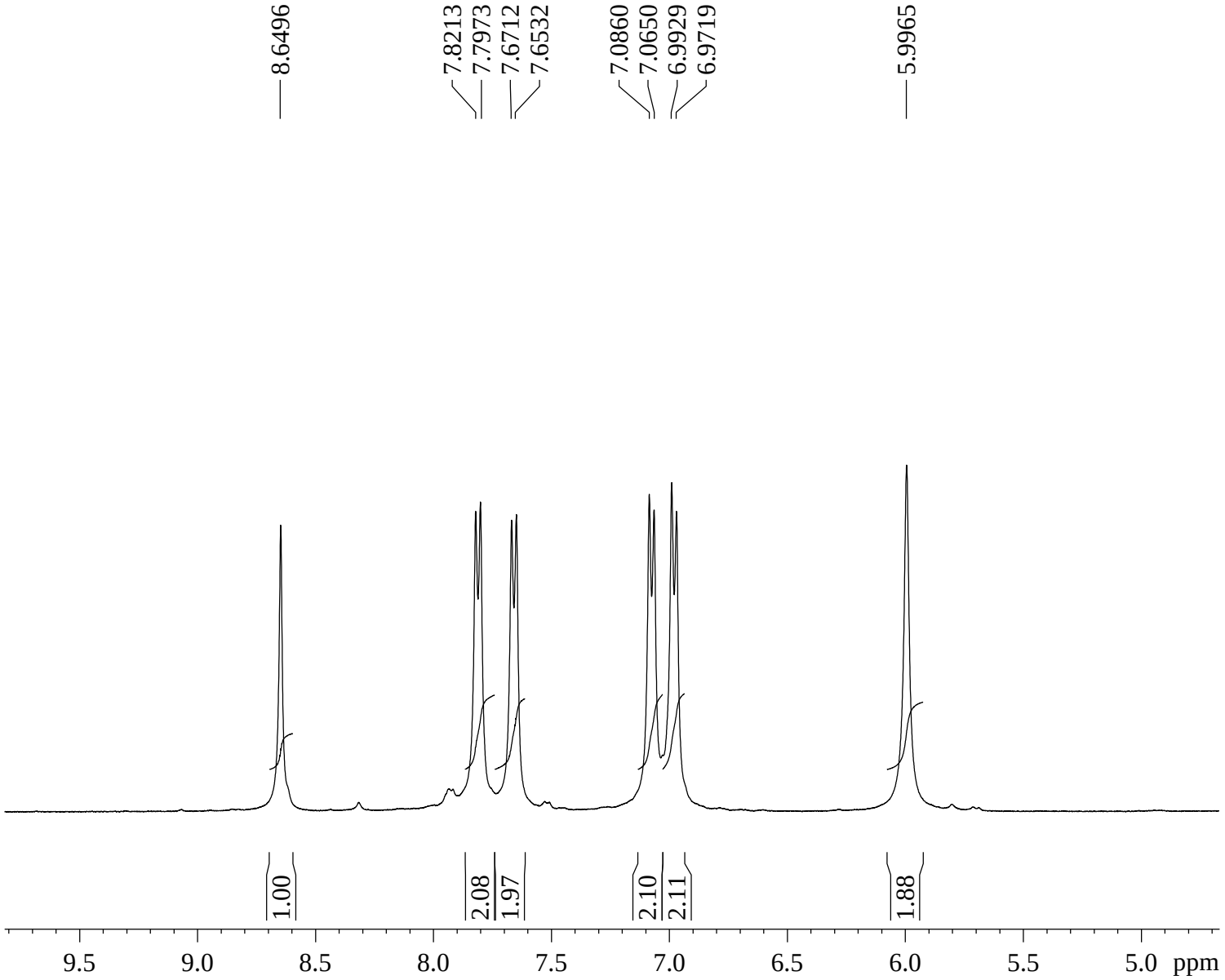
^{13}C spectra of compound 5o



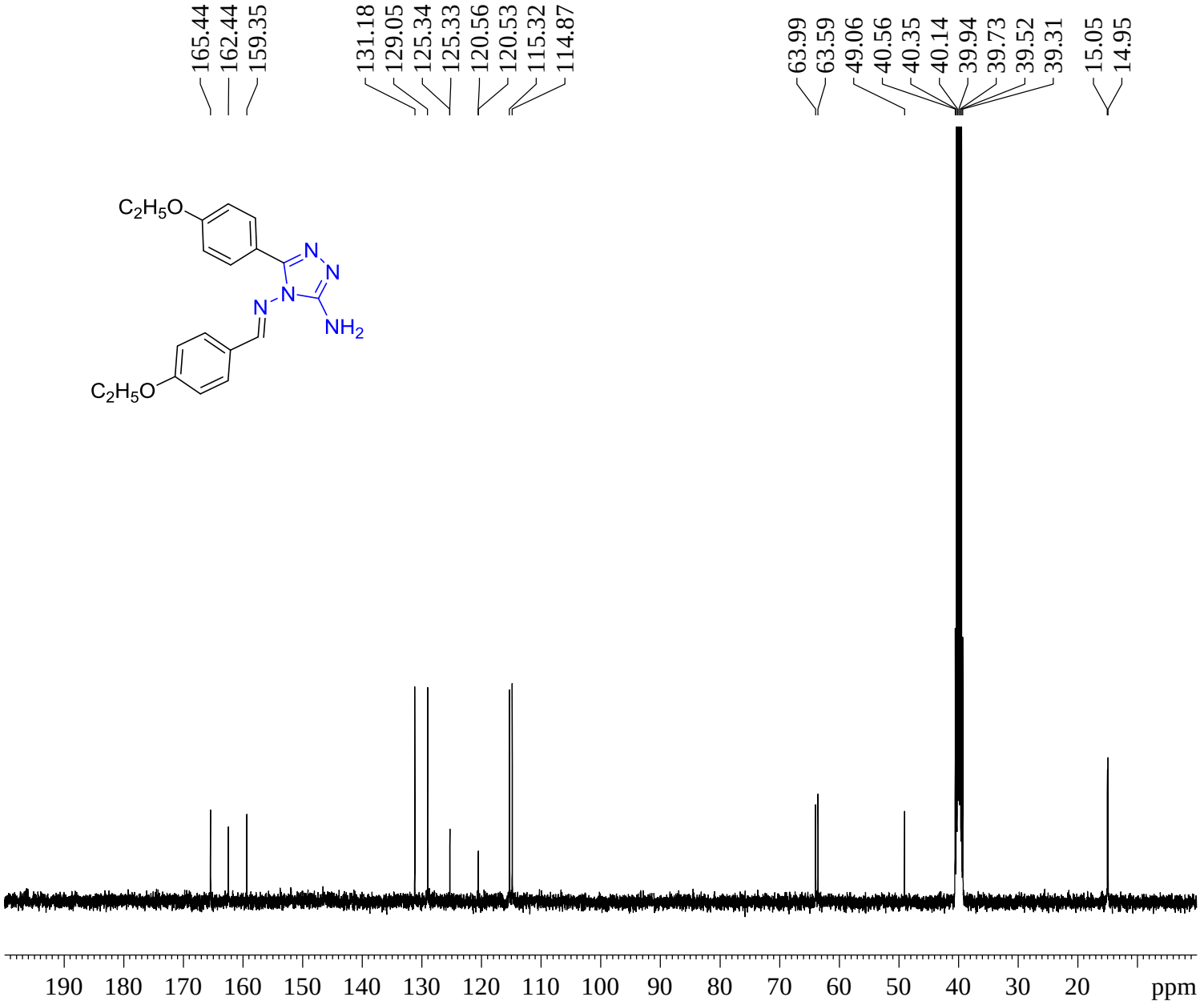
^{1}H spectra of compound 5p



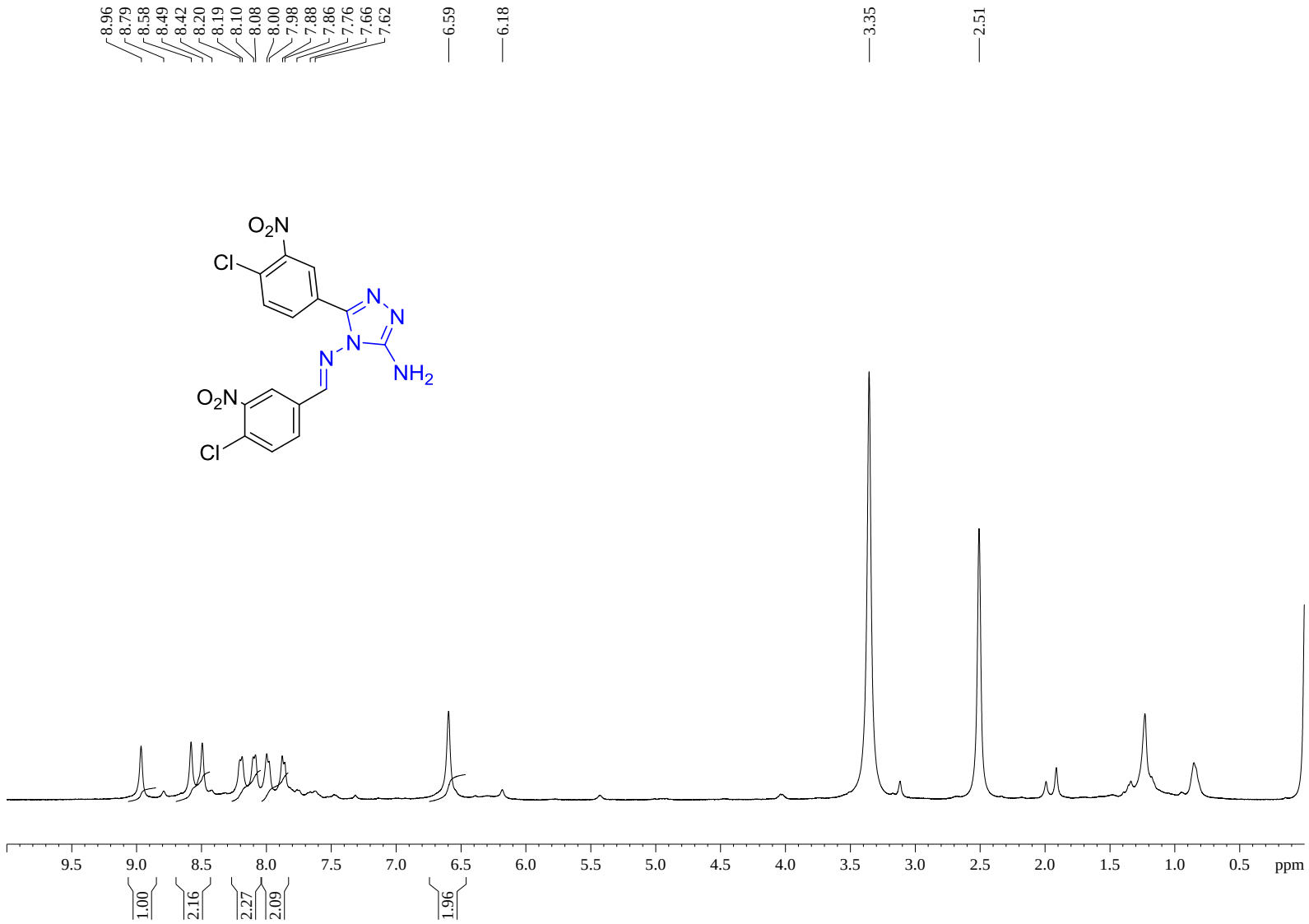
^{1}H spectra of compound 5p_expanded



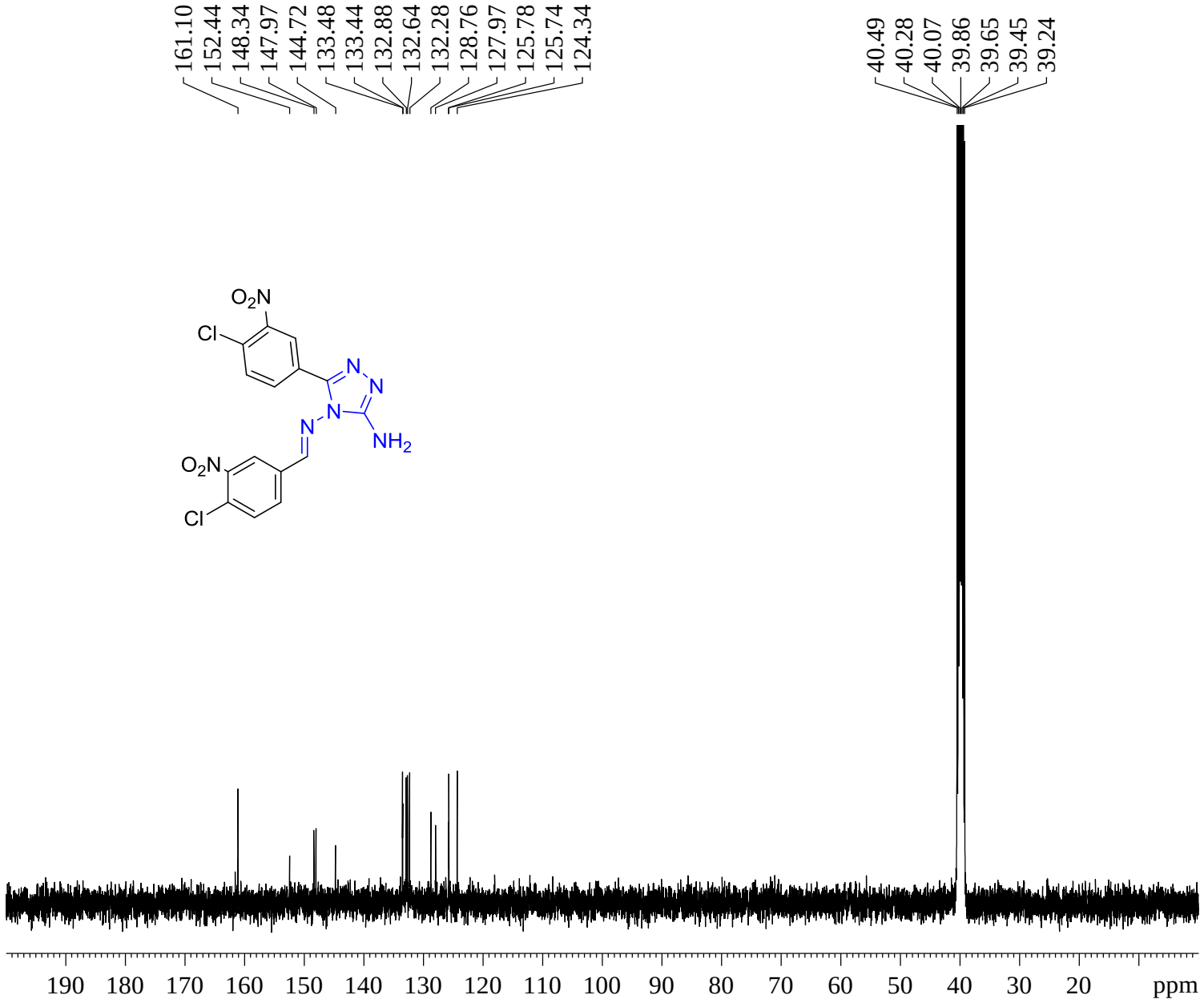
^{13}C spectra of compound 5p



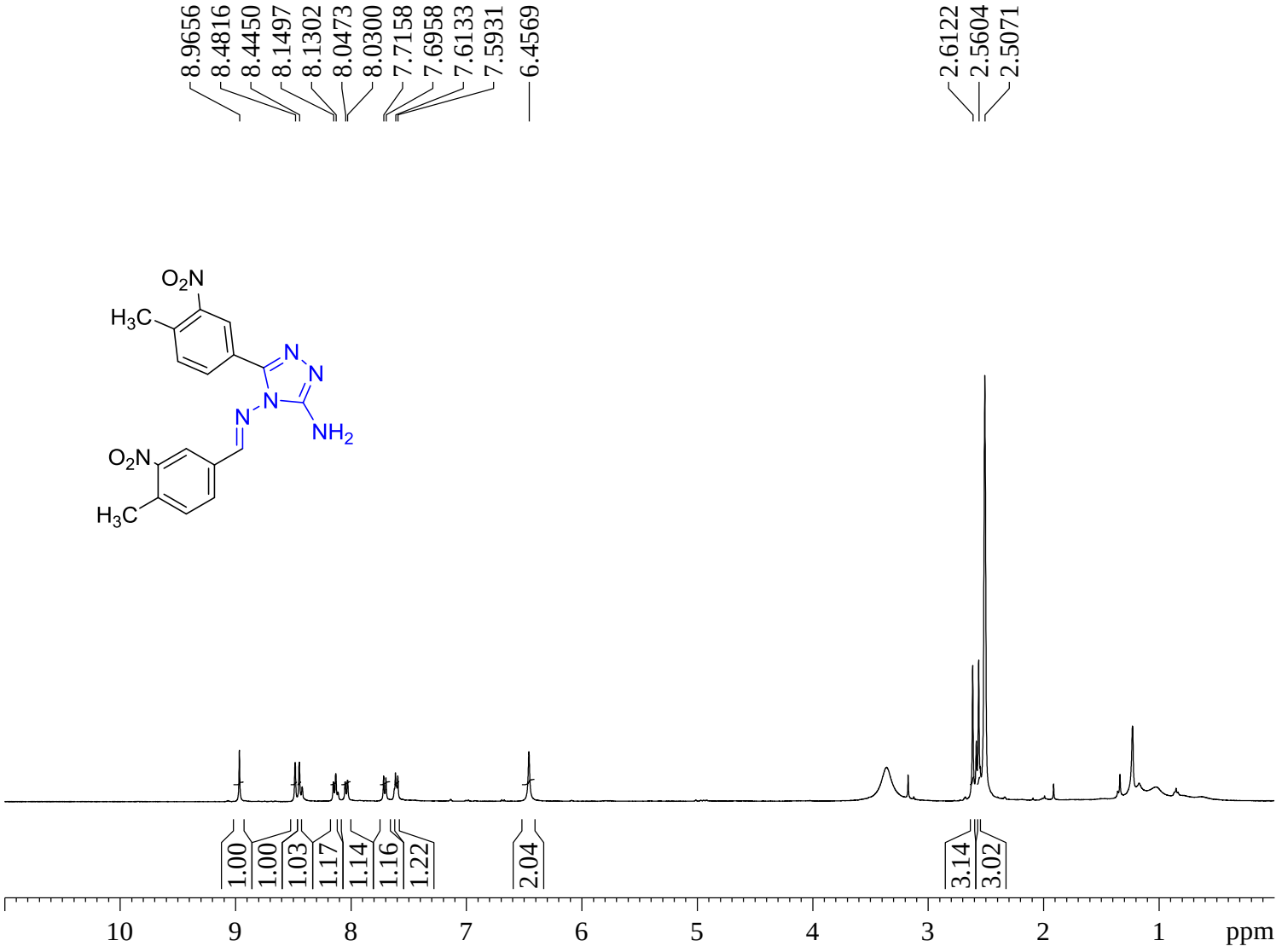
^{1}H spectra of compound 5q



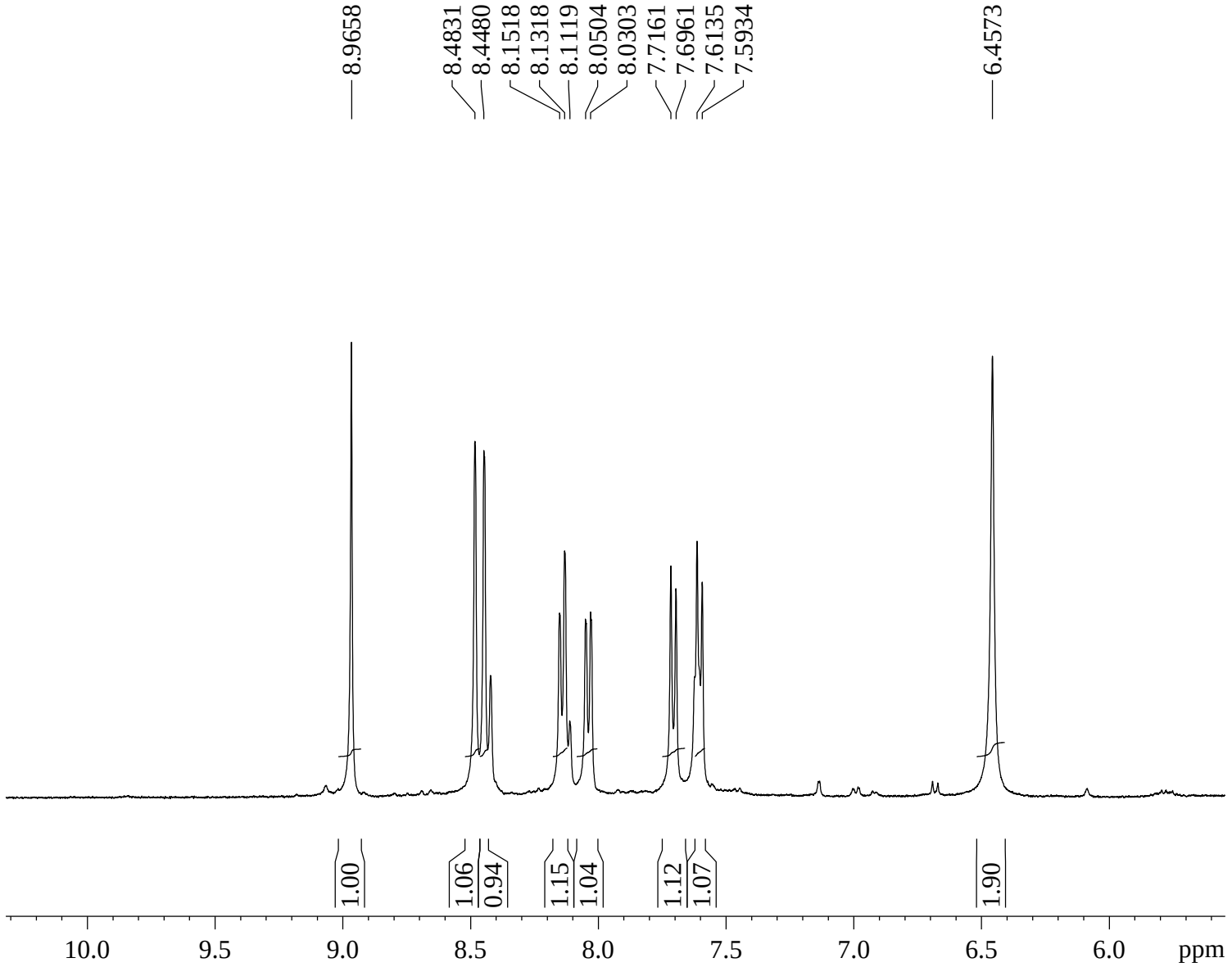
^{13}C spectra of compound 5q



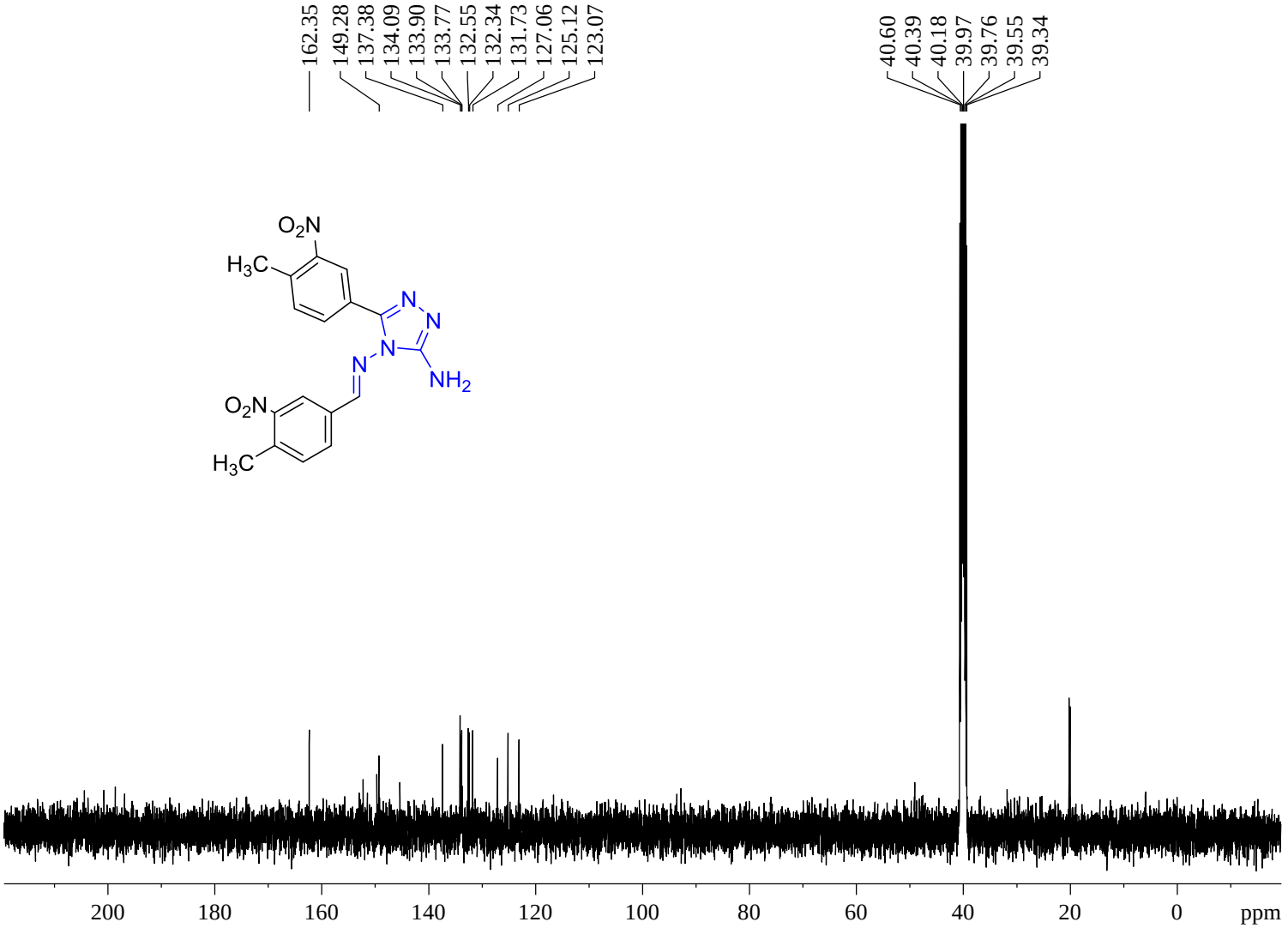
^{1}H spectra of compound 5r



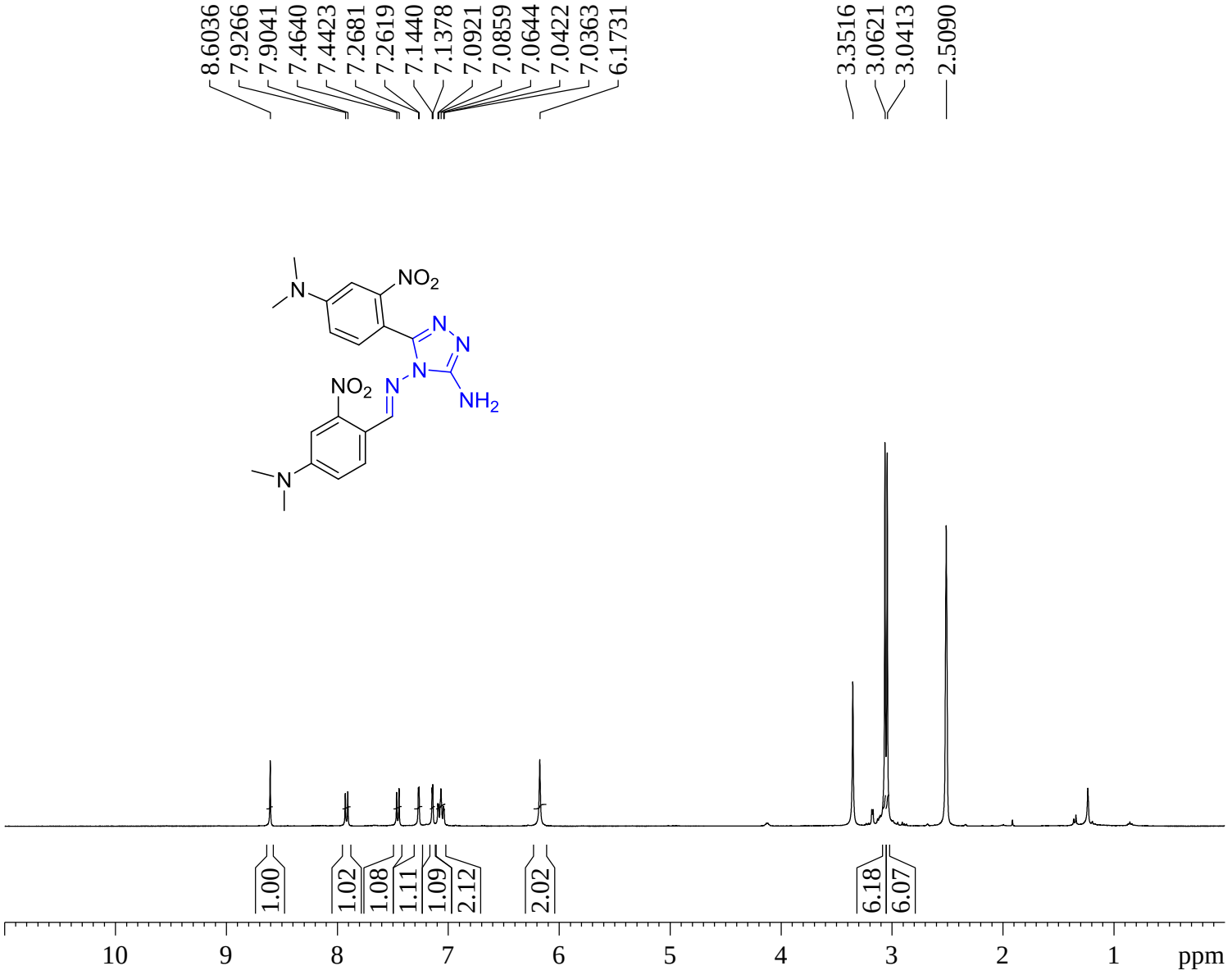
^{1}H spectra of compound 5r_expanded



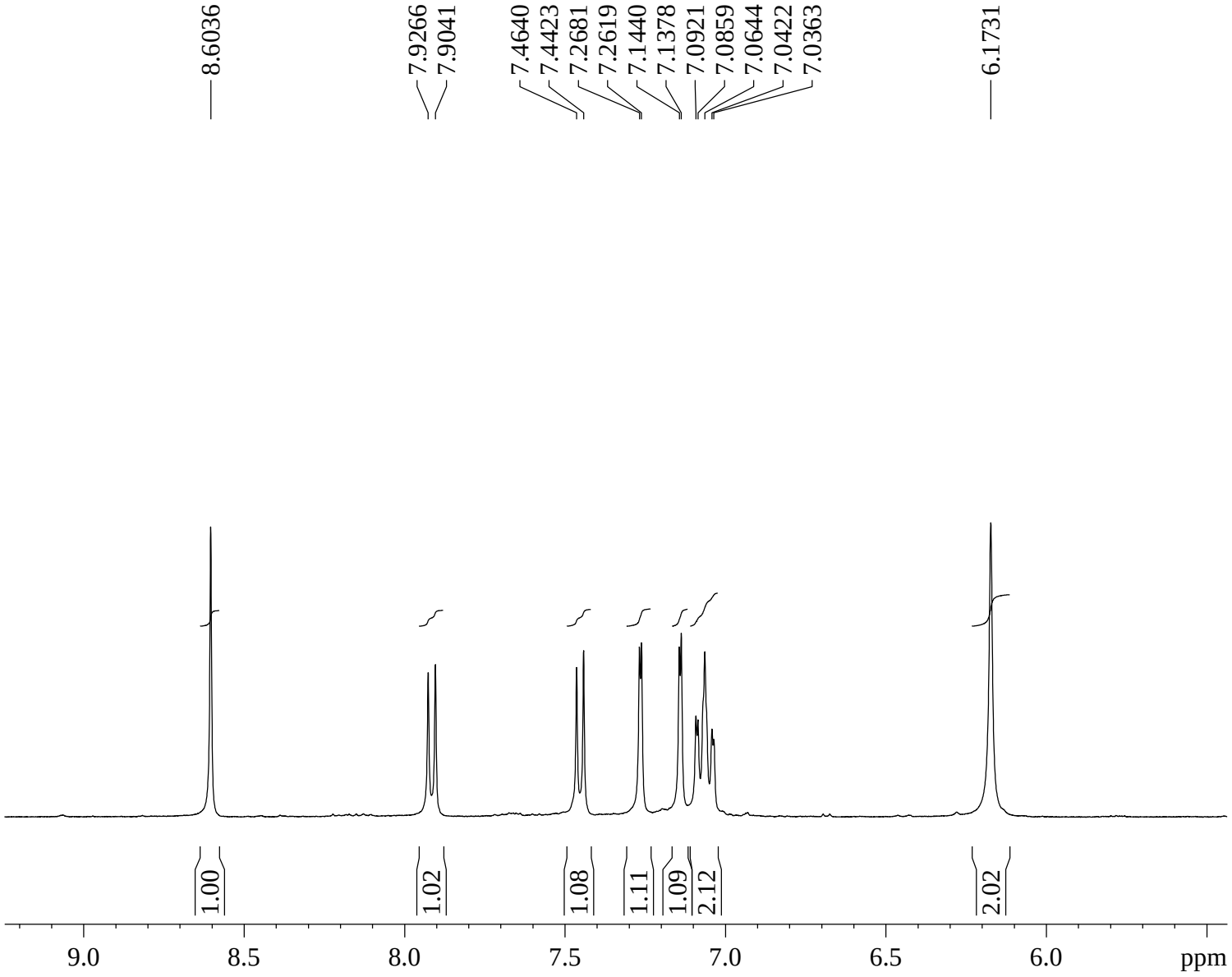
^{13}C spectra of compound 5r



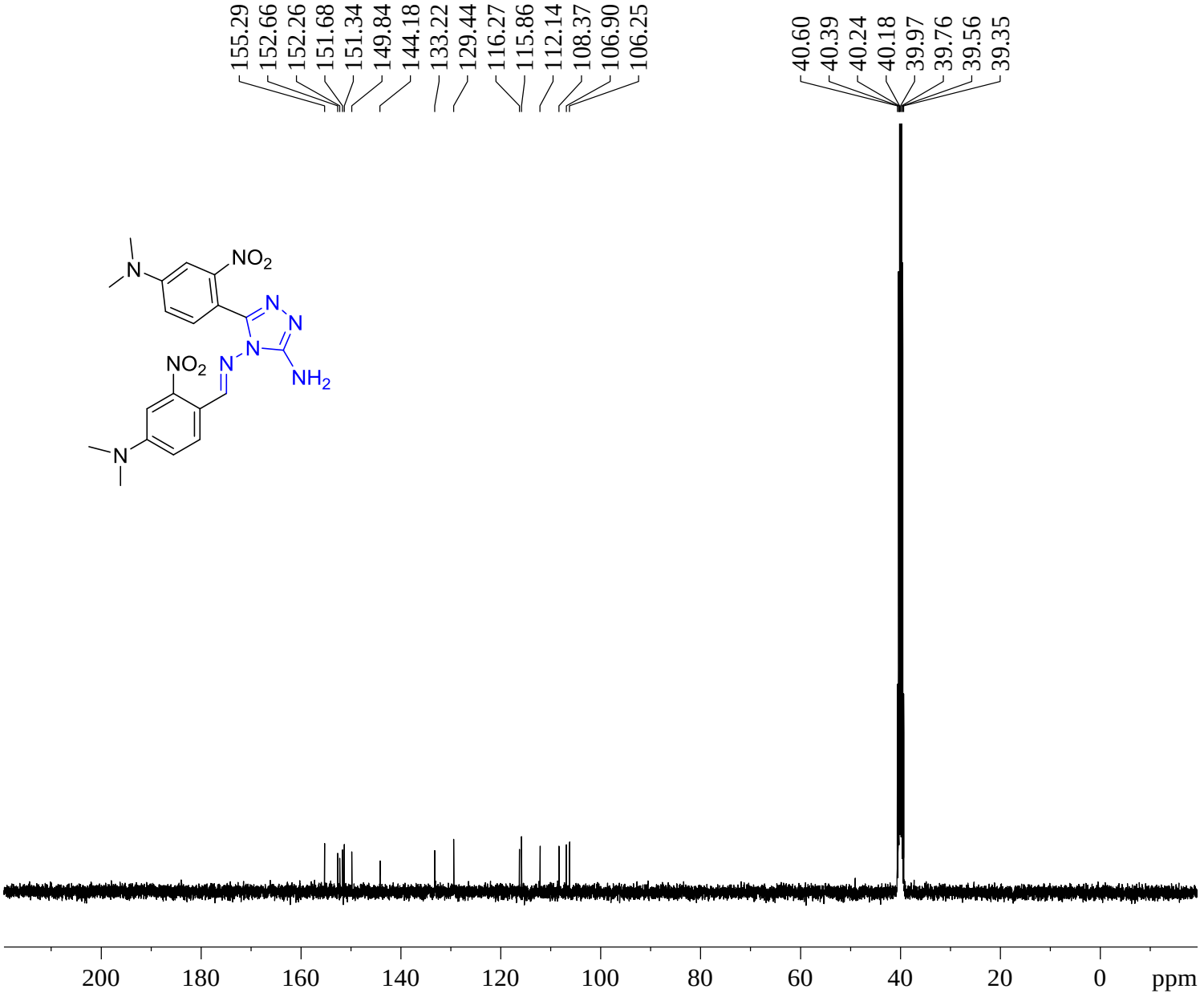
^{1}H spectra of compound 5s



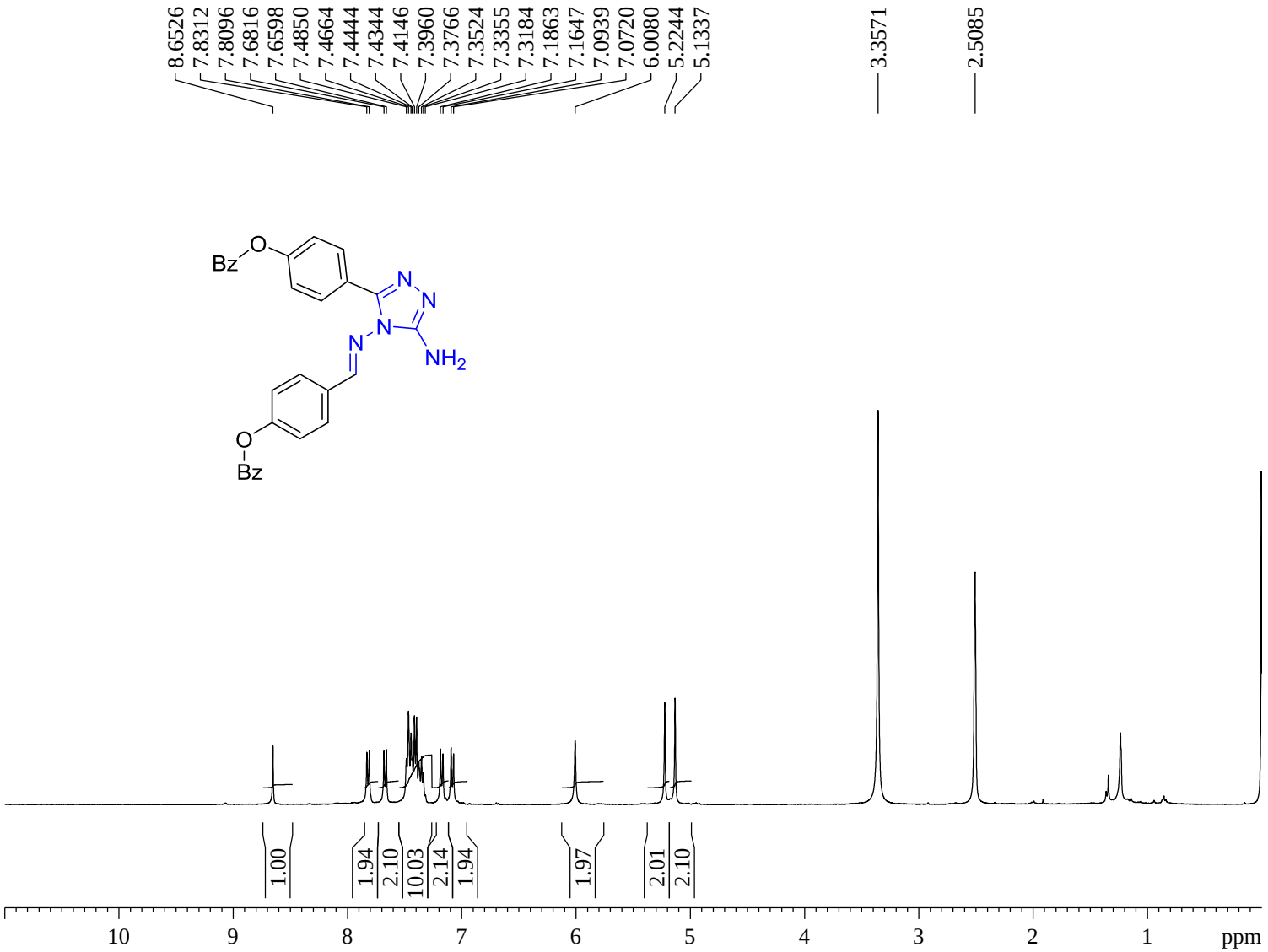
^{1}H spectra of compound 5s_expanded



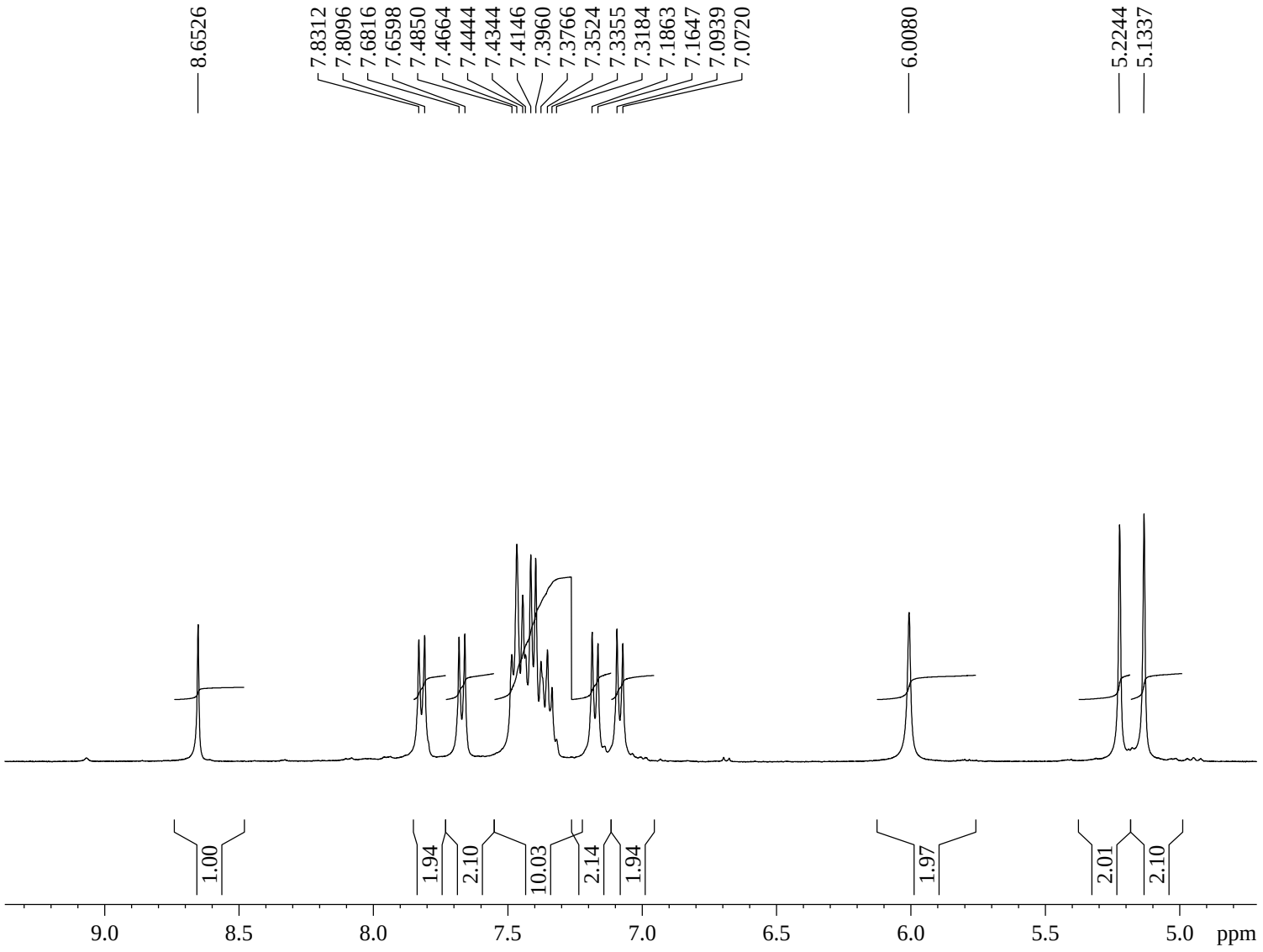
^{13}C spectra of compound 5s



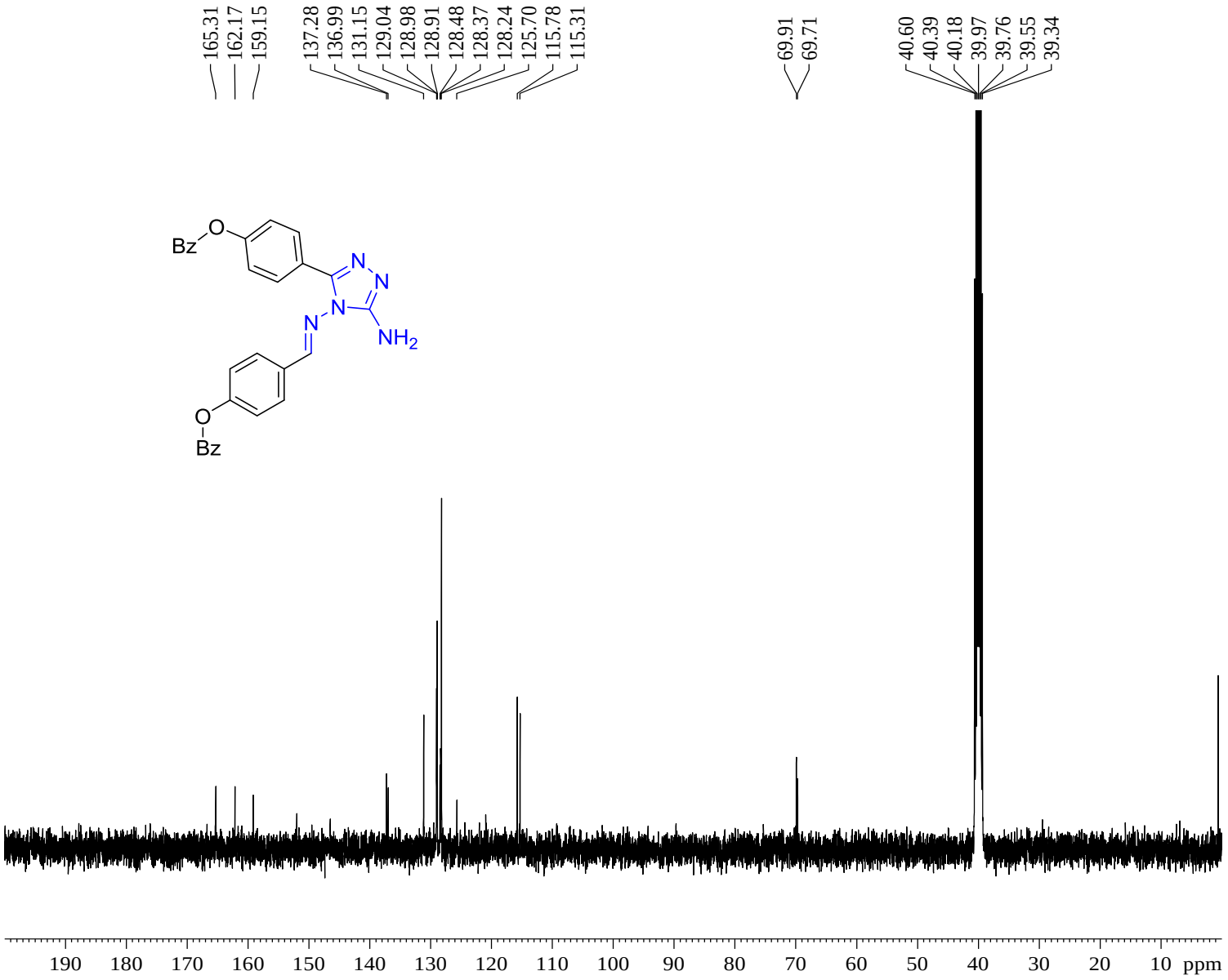
^{1}H spectra of compound 5t



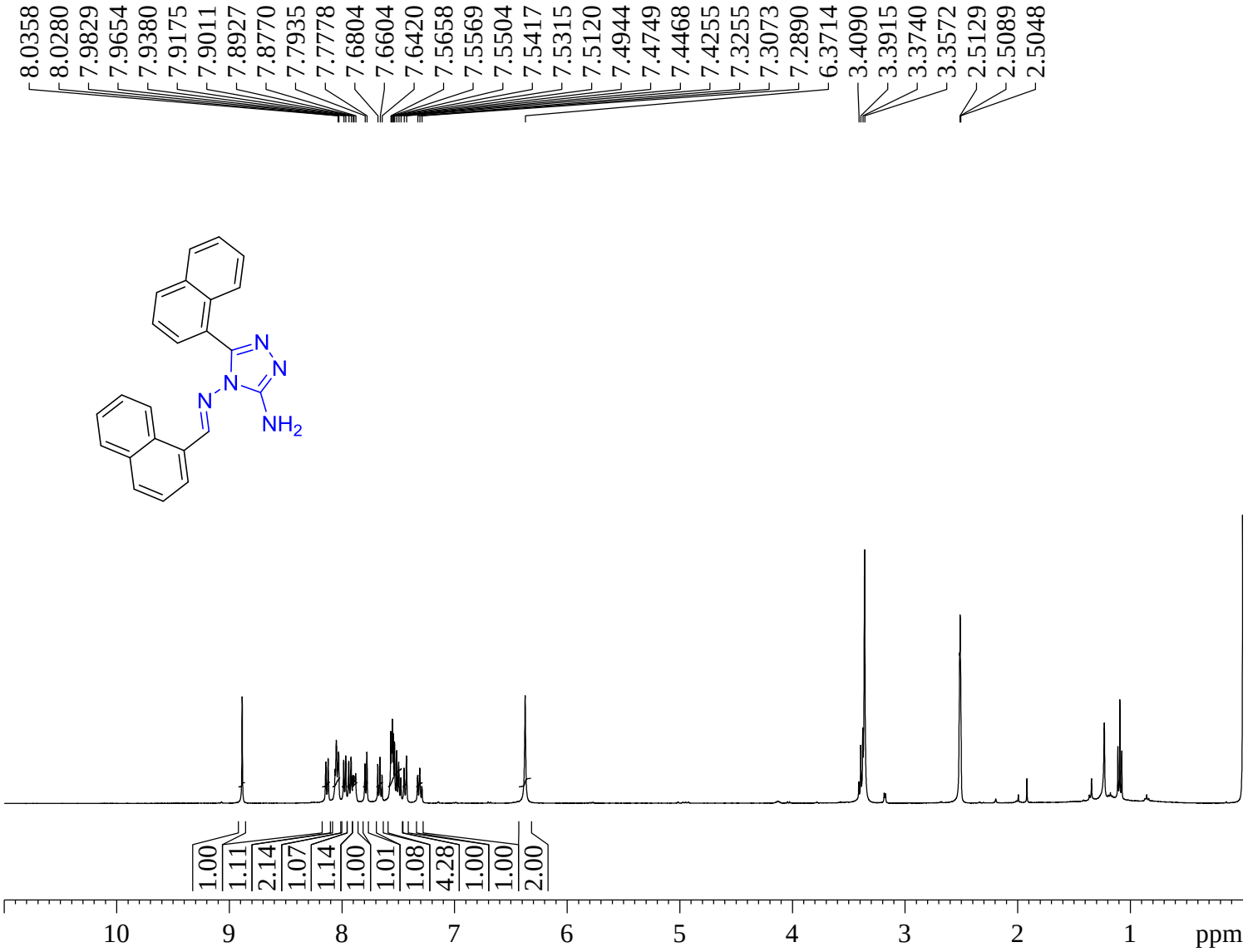
^{1}H spectra of compound 5t_expanded



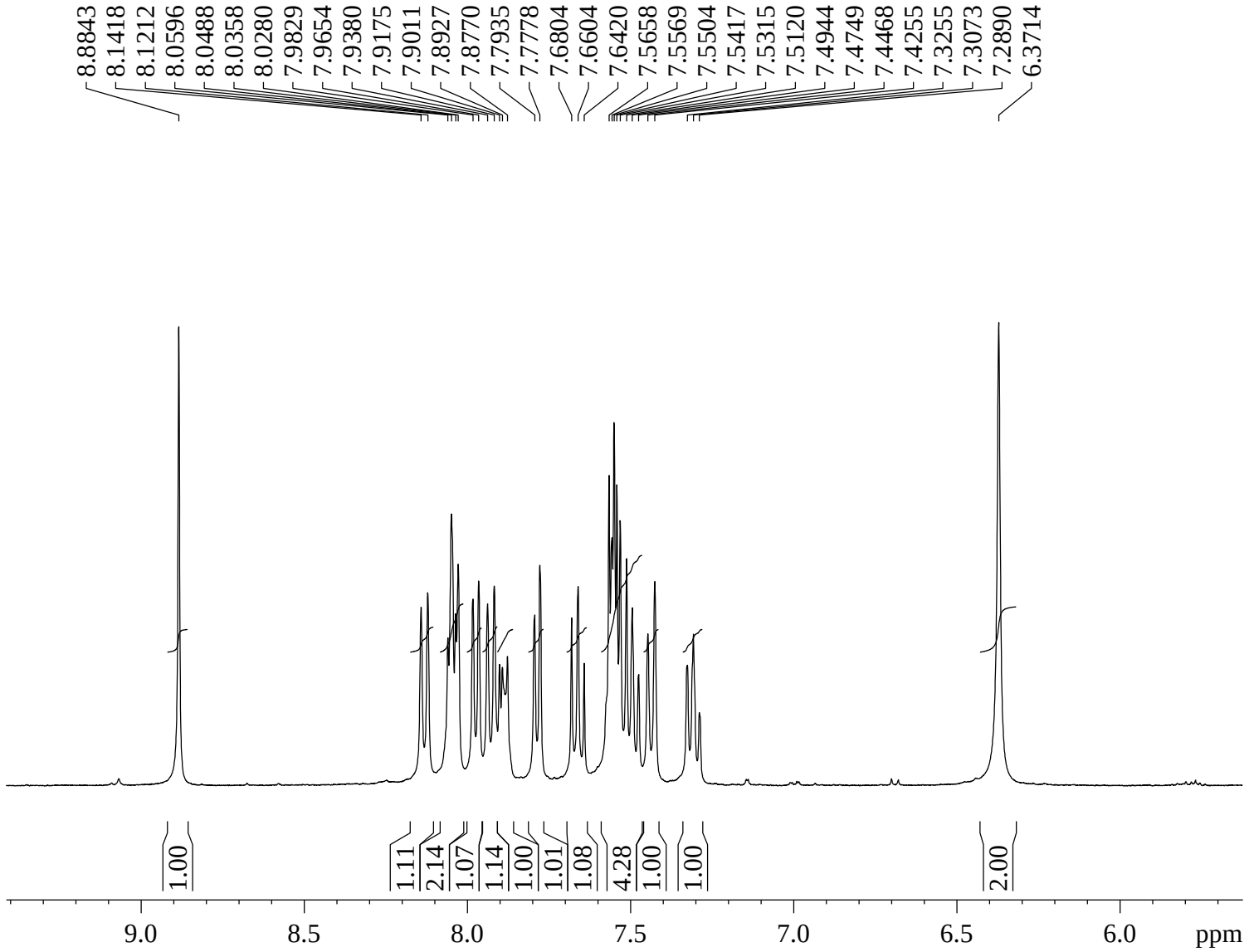
^{13}C spectra of compound 5t



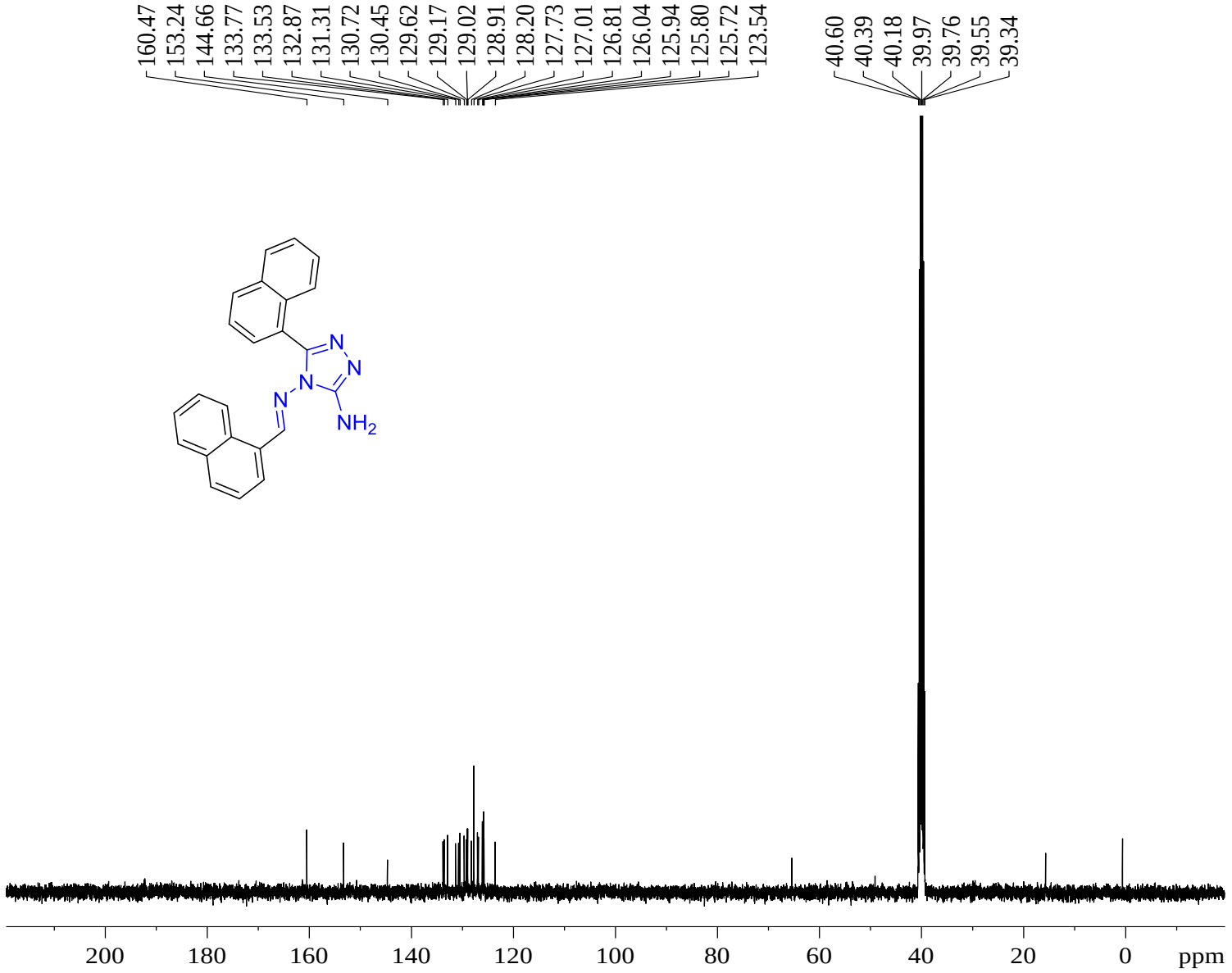
^{1}H spectra of compound 5u



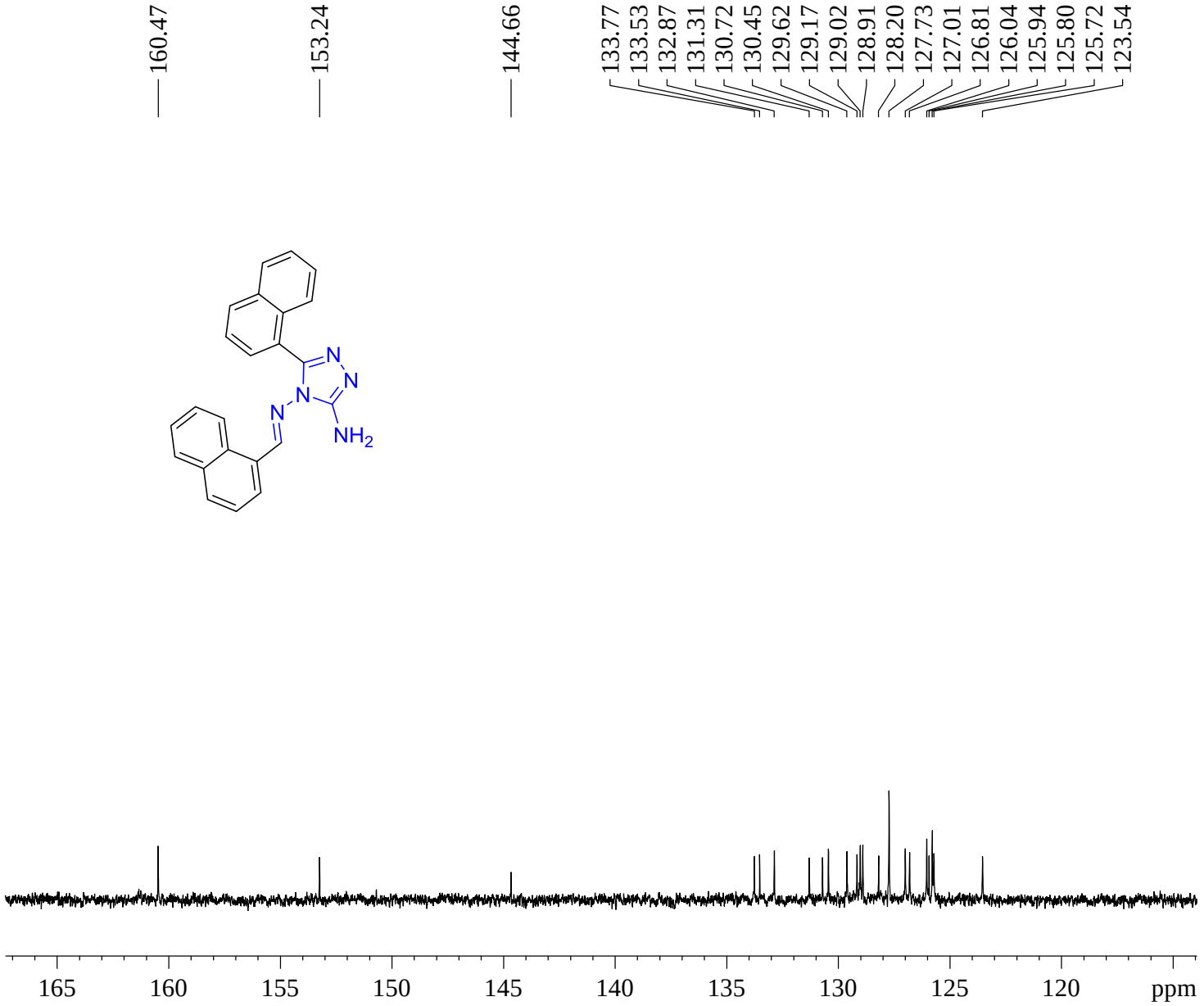
^{1}H spectra of compound 5u_expanded



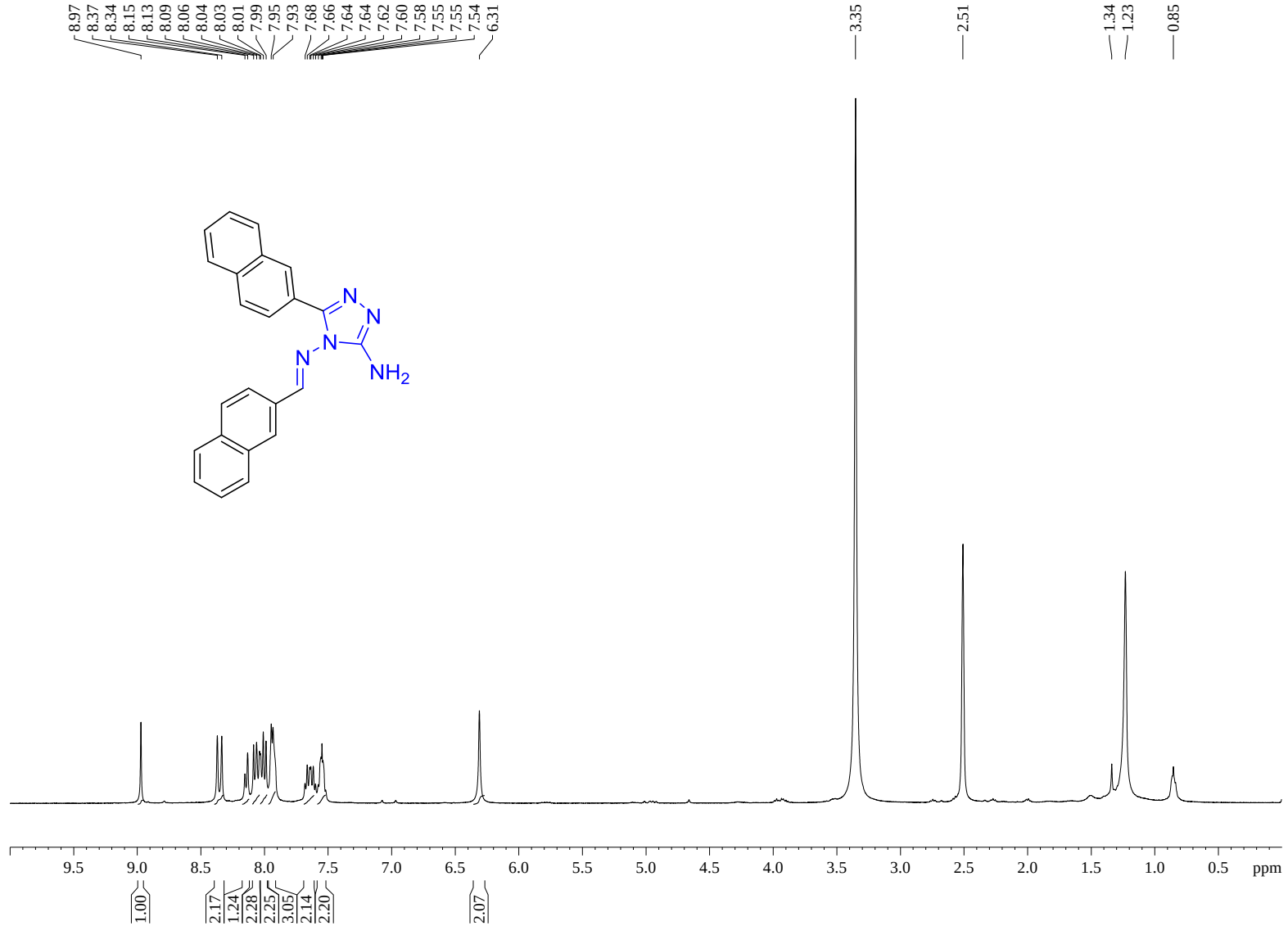
^{13}C spectra of compound 5u



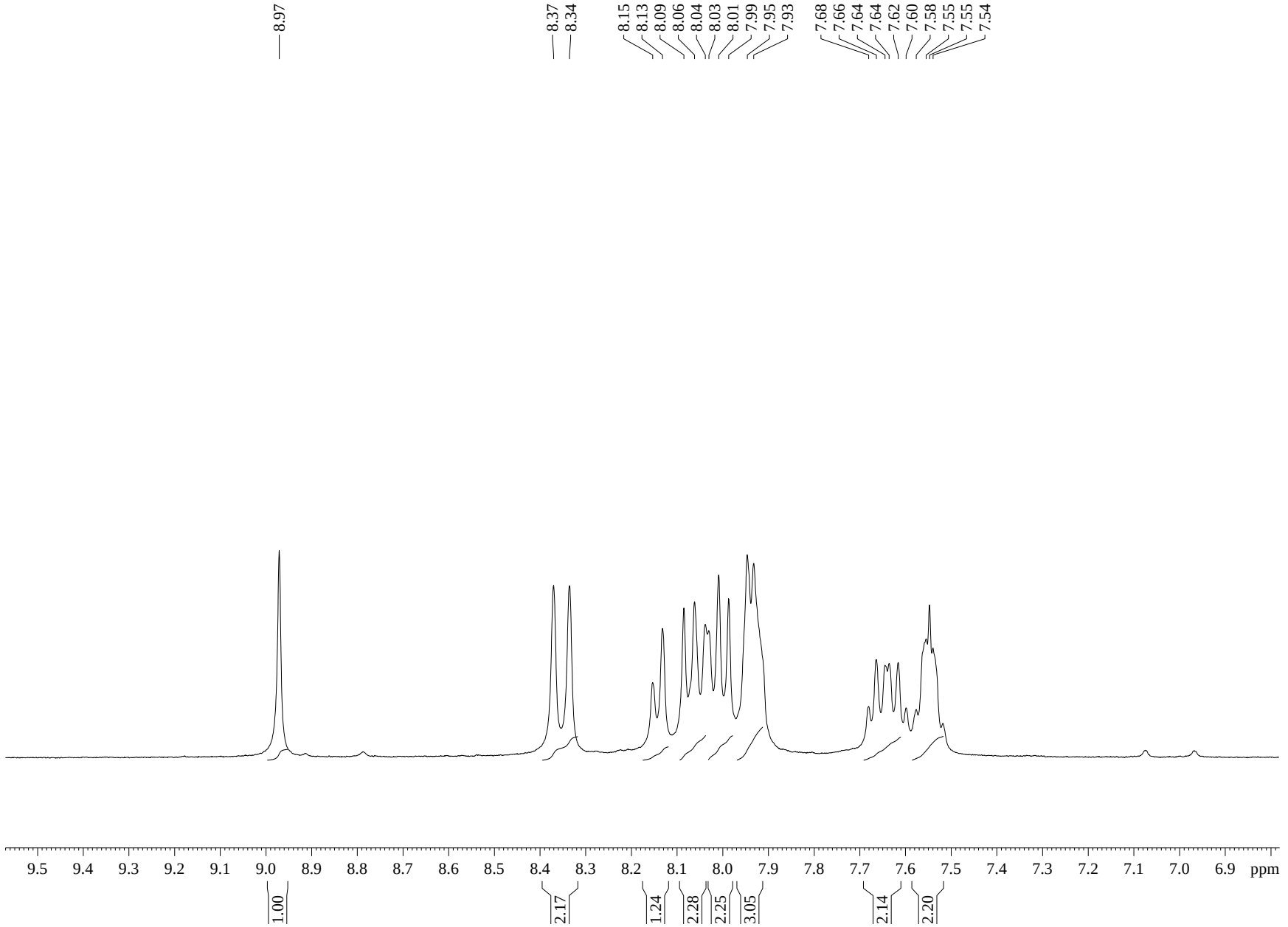
^{13}C spectra of compound 5u_expanded



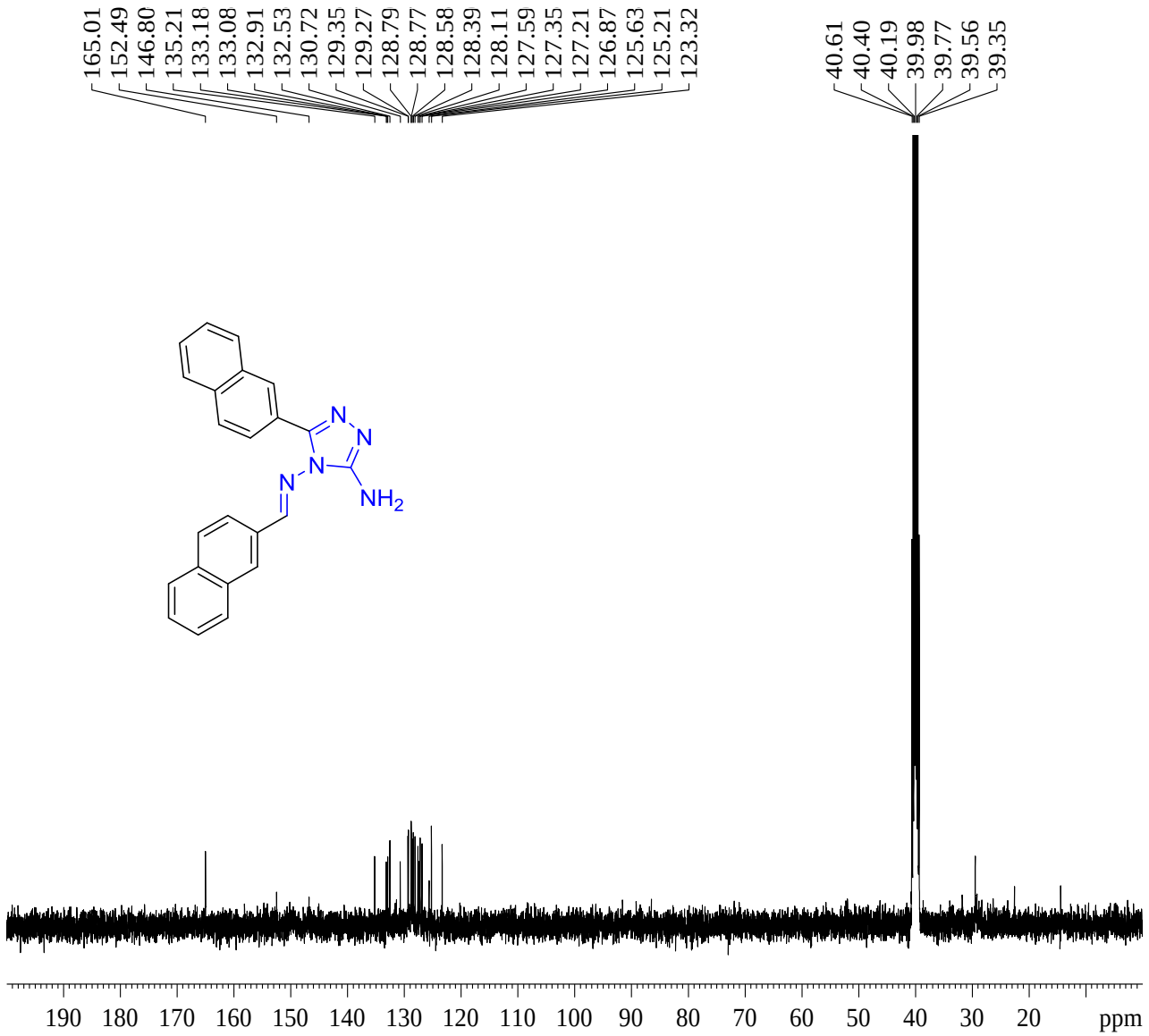
^{1}H spectra of compound 5v



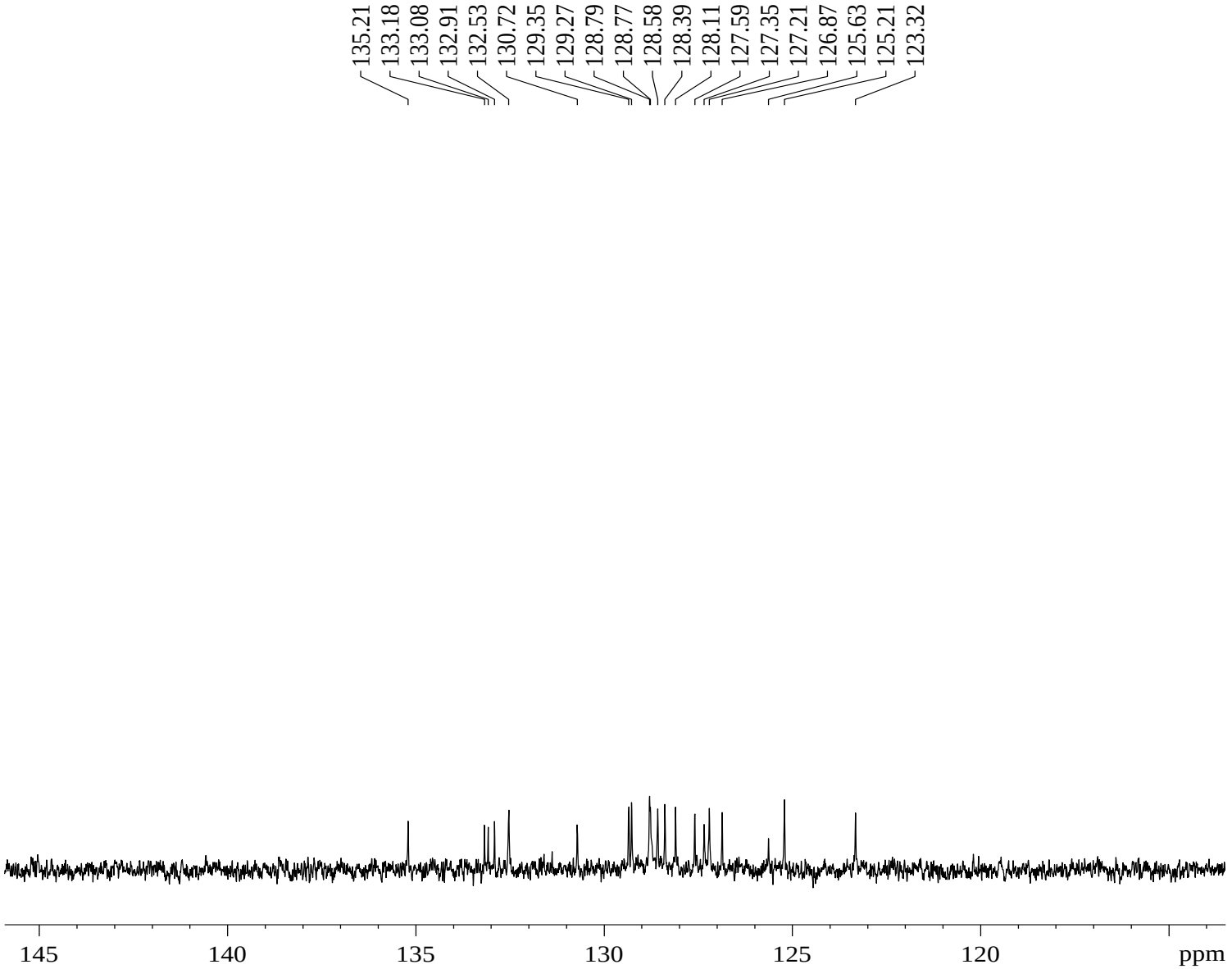
^{1}H spectra of compound 5v_expanded



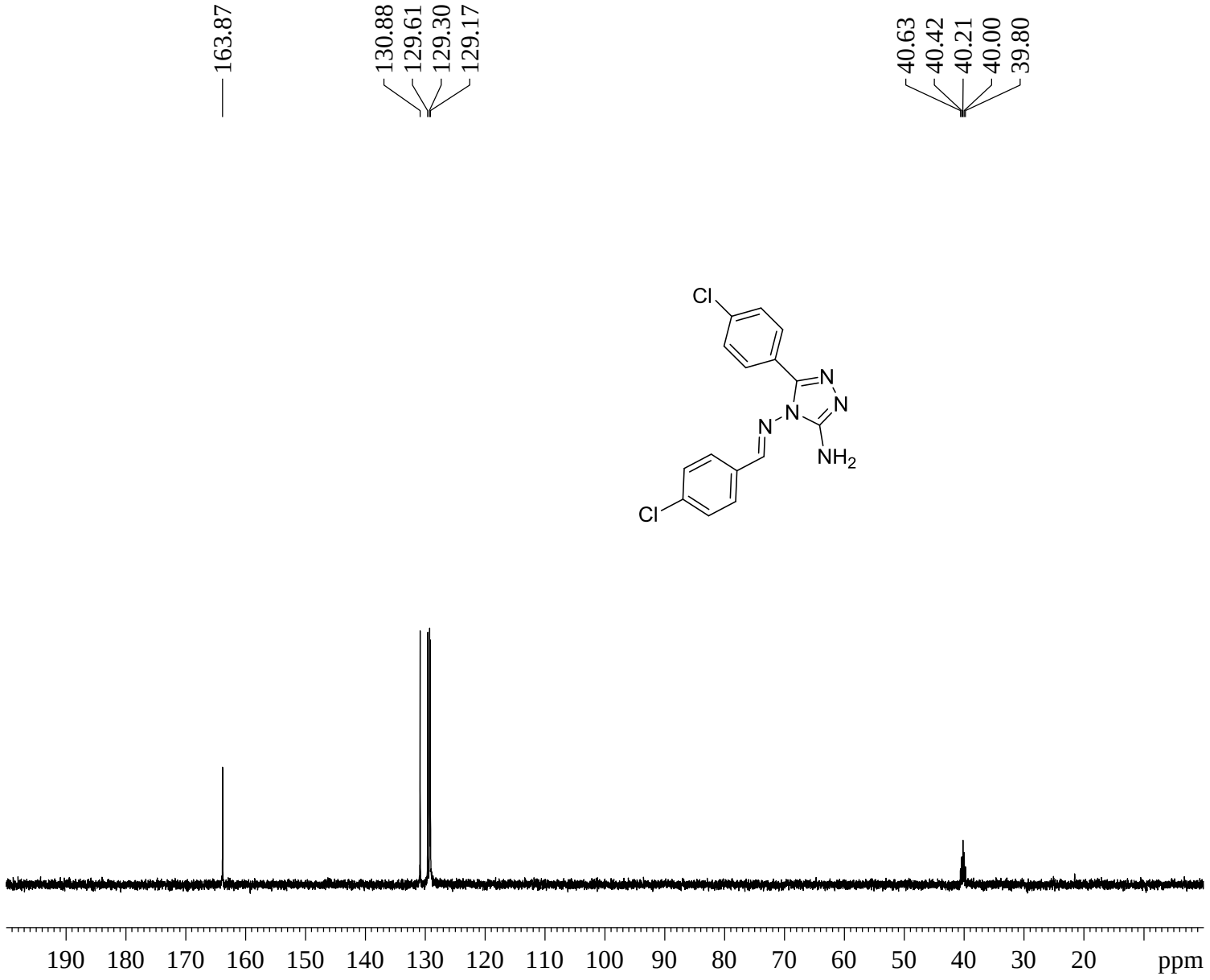
^{13}C spectra of compound 5v



^{13}C expanded spectra of compound 5v

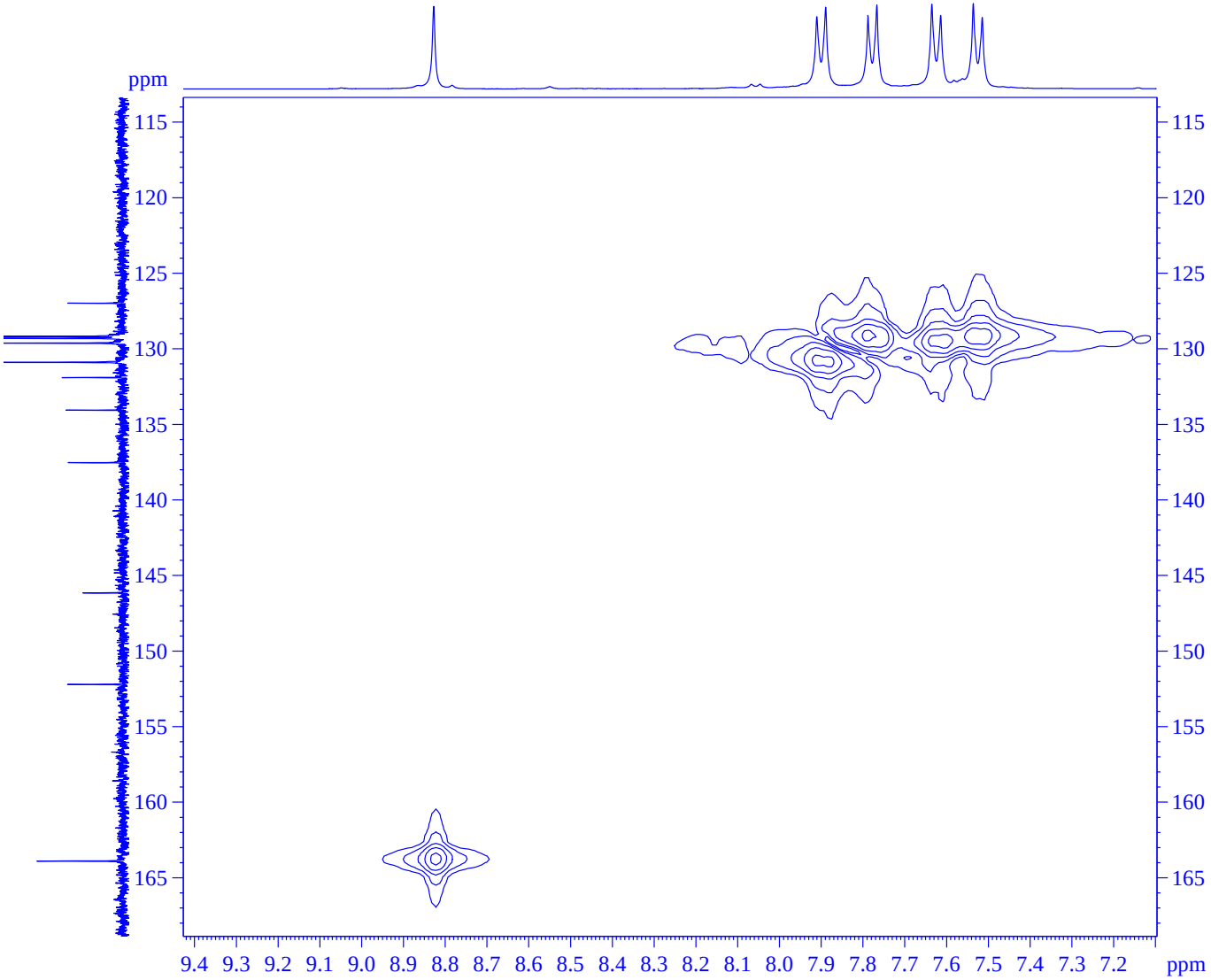


4. DEPT-135 spectra of compound 5a

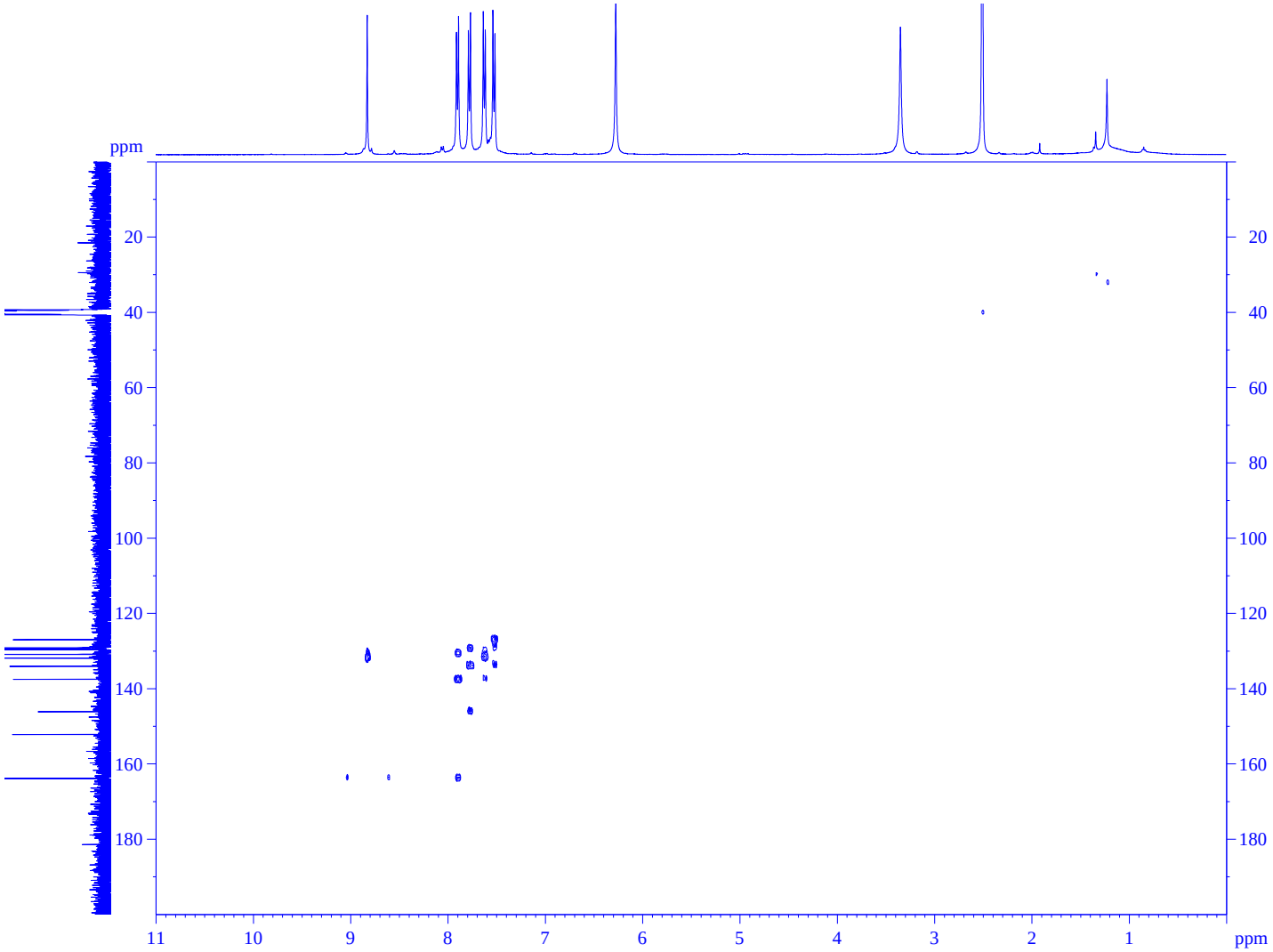


5. HSQC and HMBC spectra of 5a:

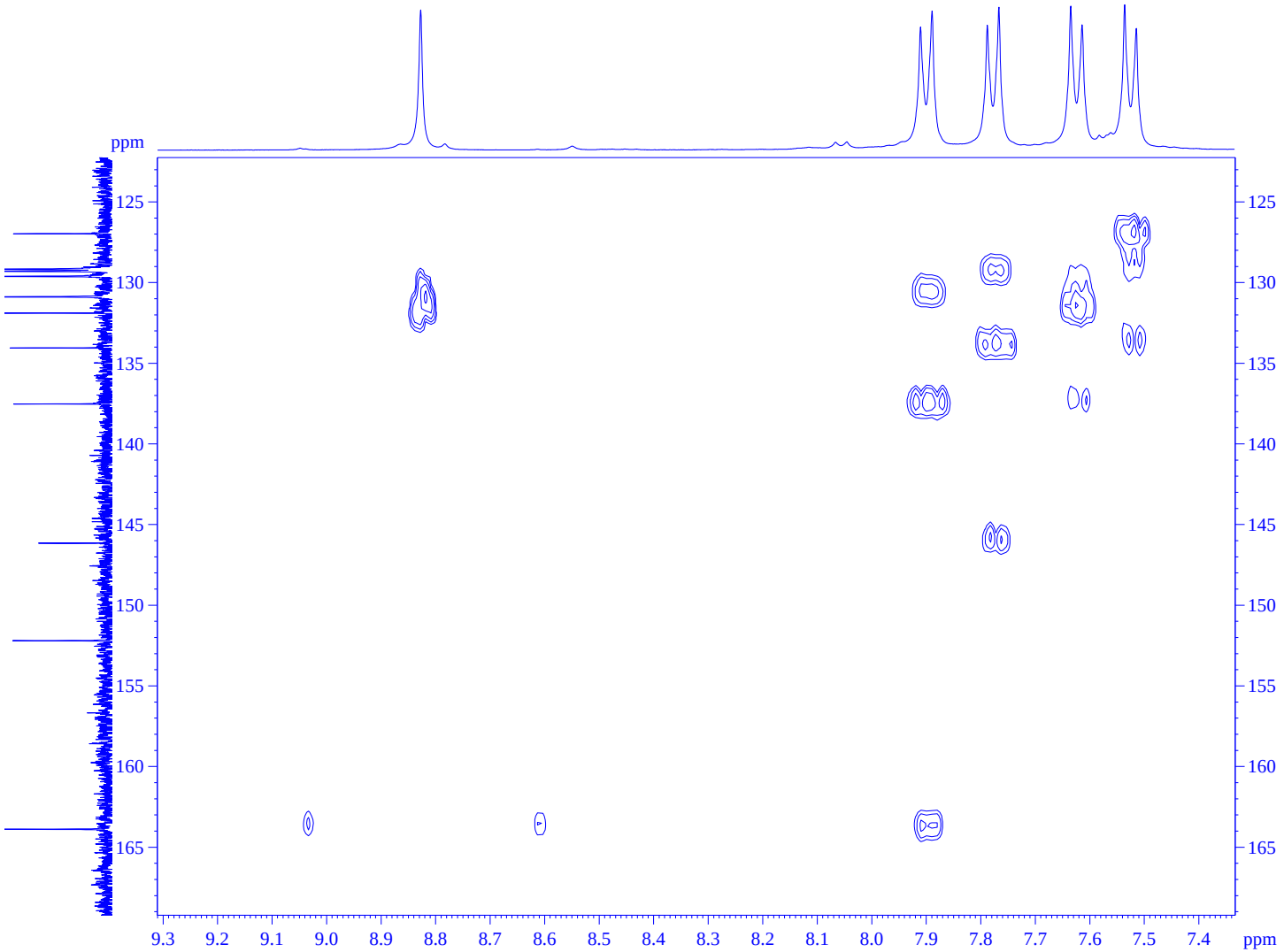
5.1. HSQC Correlations of (*E*)-4-((4-chlorobenzylidene)amino)-5-(4-chlorophenyl)-4*H*-1,2,4-triazol-3-amine (**5a**).



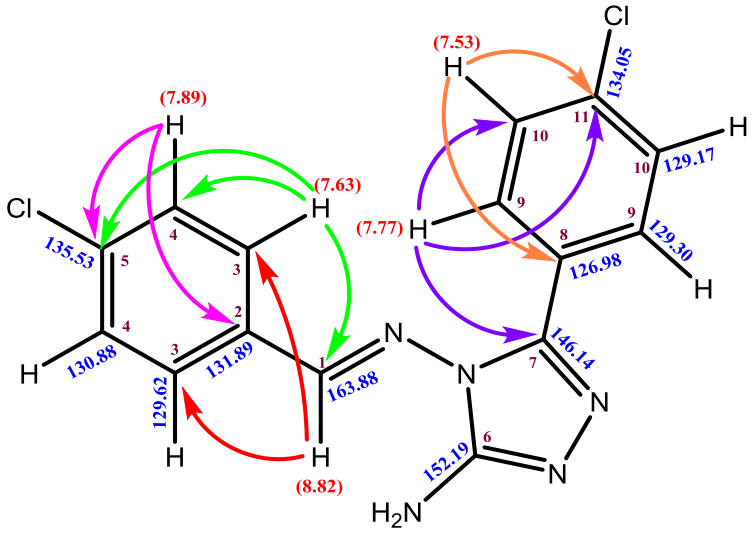
5.2. HMBC Correlations of (*E*)-4-((4-chlorobenzylidene)amino)-5-(4-chlorophenyl)-4*H*-1,2,4-triazol-3-amine (**5a**).



5.3. HMBC (expanded) Correlations of (*E*)-4-((4-chlorobenzylidene)amino)-5-(4-chlorophenyl)-4*H*-1,2,4-triazol-3-amine (**5a**).



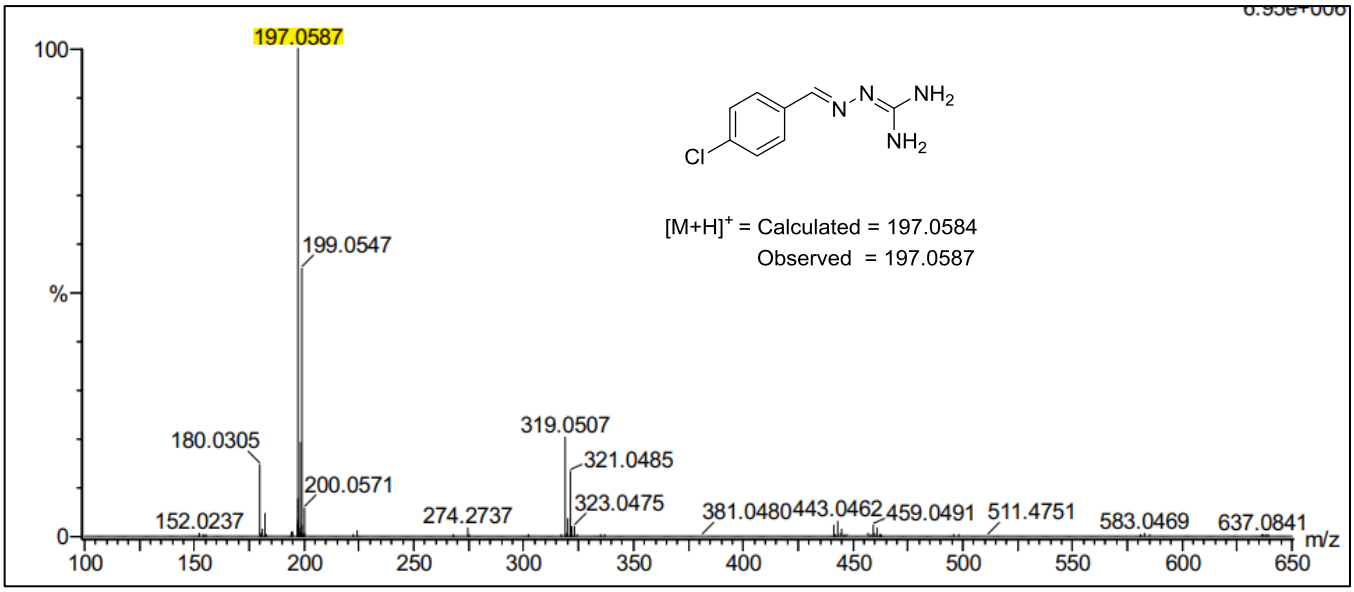
5.4. HSQC and HMBC correlation



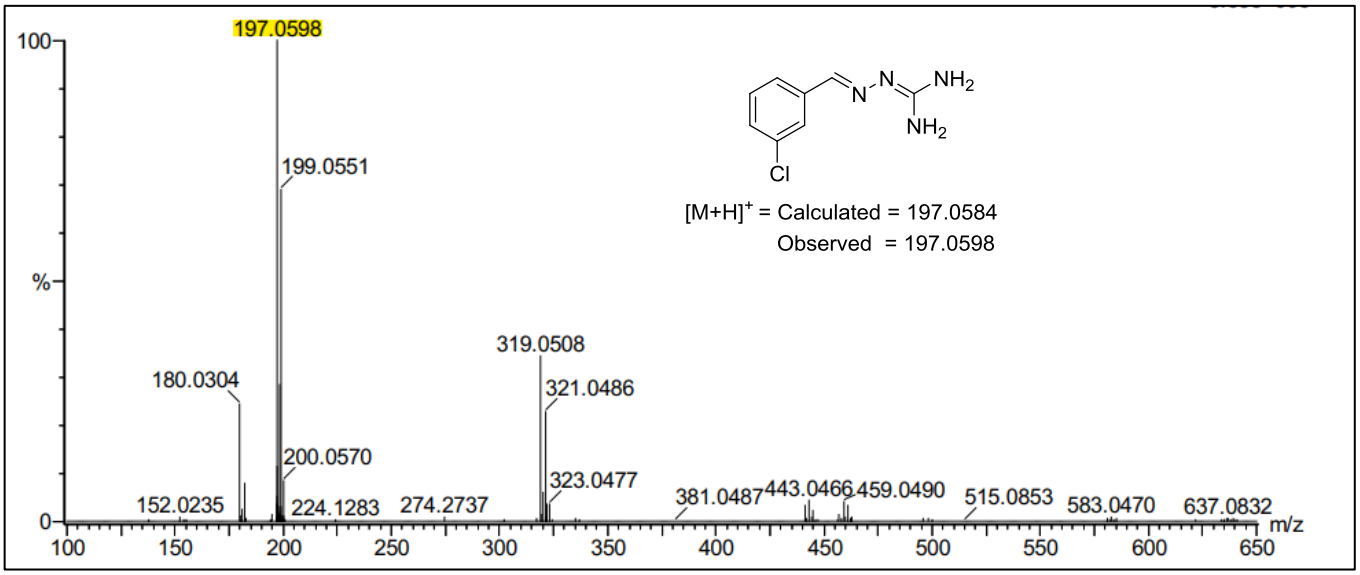
Carbon Label	^{1}H NMR	^{13}C NMR	HSQC	HMBC
C1	8.82	163.8	163.8	C3 (129.6)
C2	-	131.9	-	-
C3	7.63	129.6	129.6	C1 (163.9), C4 (130.9), C5 (135.5)
C4	7.89	130.9	130.9	C2 (131.9), C5 (135.5)
C5	-	135.5	-	-
C6	-	152.2	-	-
C7	-	146.1	-	-
C8	-	126.9	-	-
C9	7.77	129.3	129.3	C7 (146.1), C10 (129.2), C11 (134.1)
C10	7.53	129.2	129.2	C8 (126.9), C11 (134.1)
C11	-	134.1	-	-

6. HRMS Spectra of 1a, 1c, 1e-1v:

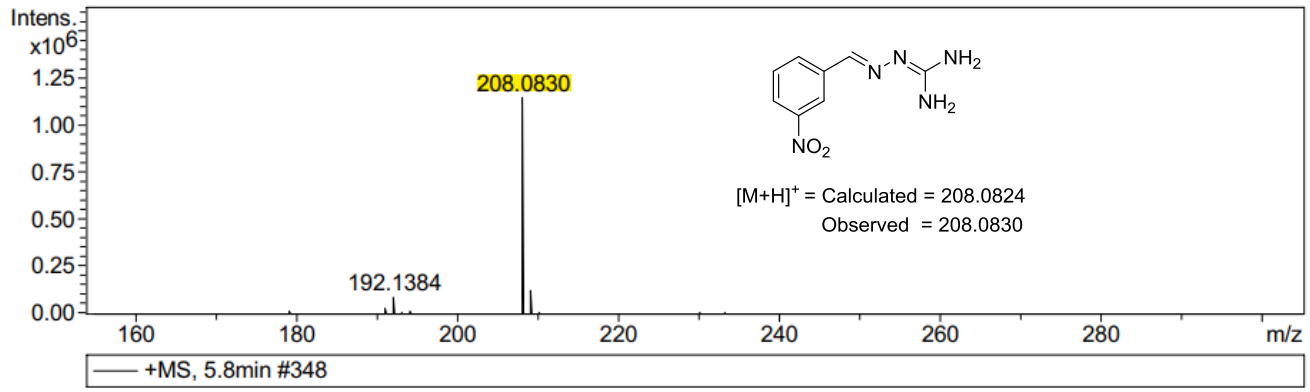
HRMS of 1a:



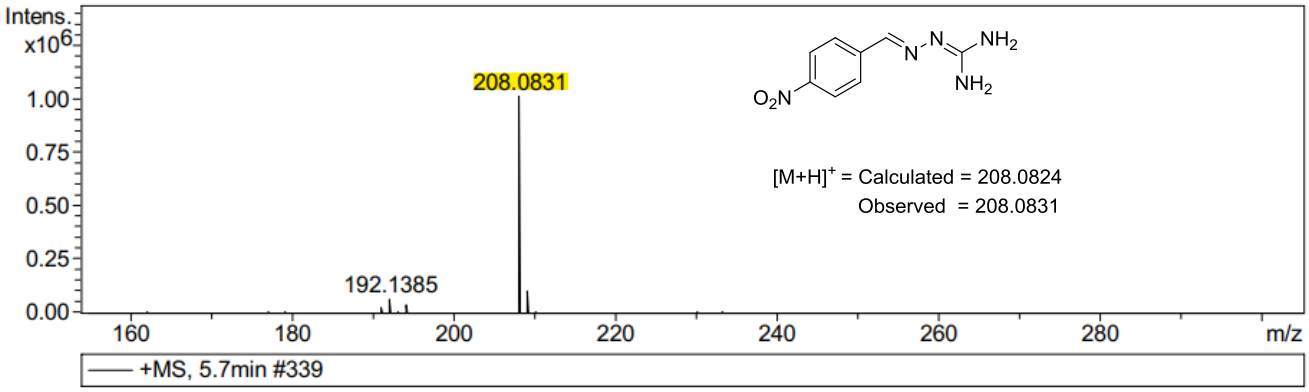
HRMS of 1c:



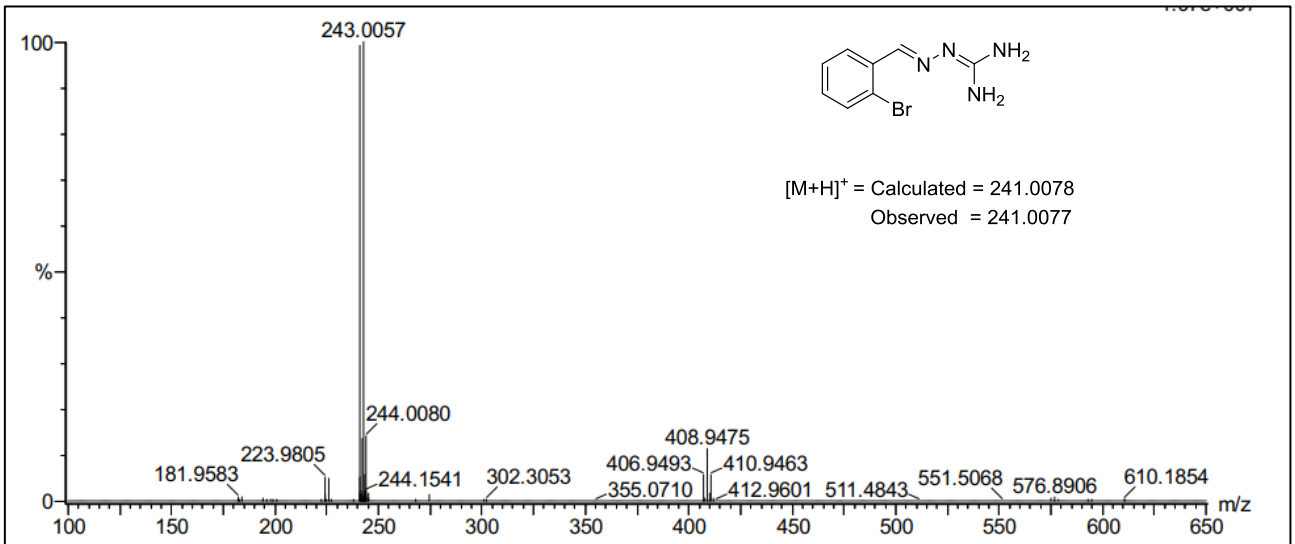
HRMS of 1e:



HRMS of 1f:

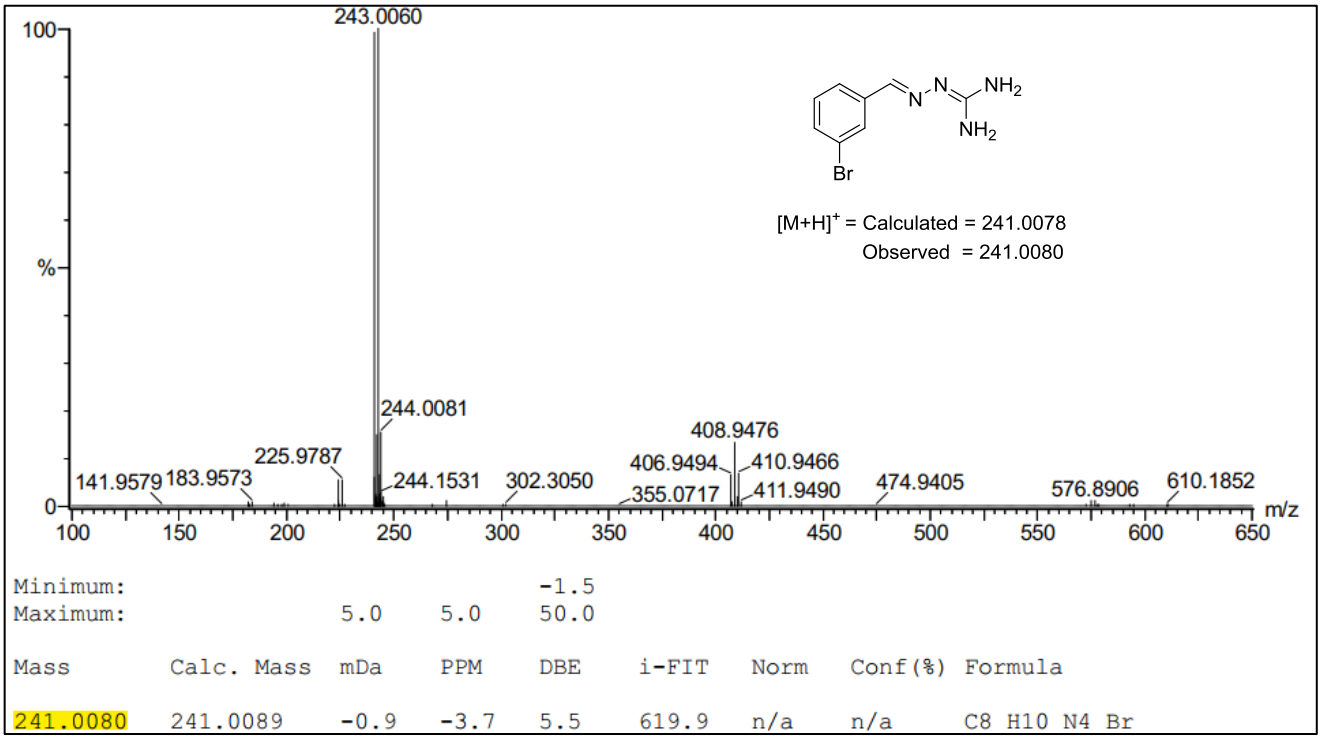


HRMS of 1g



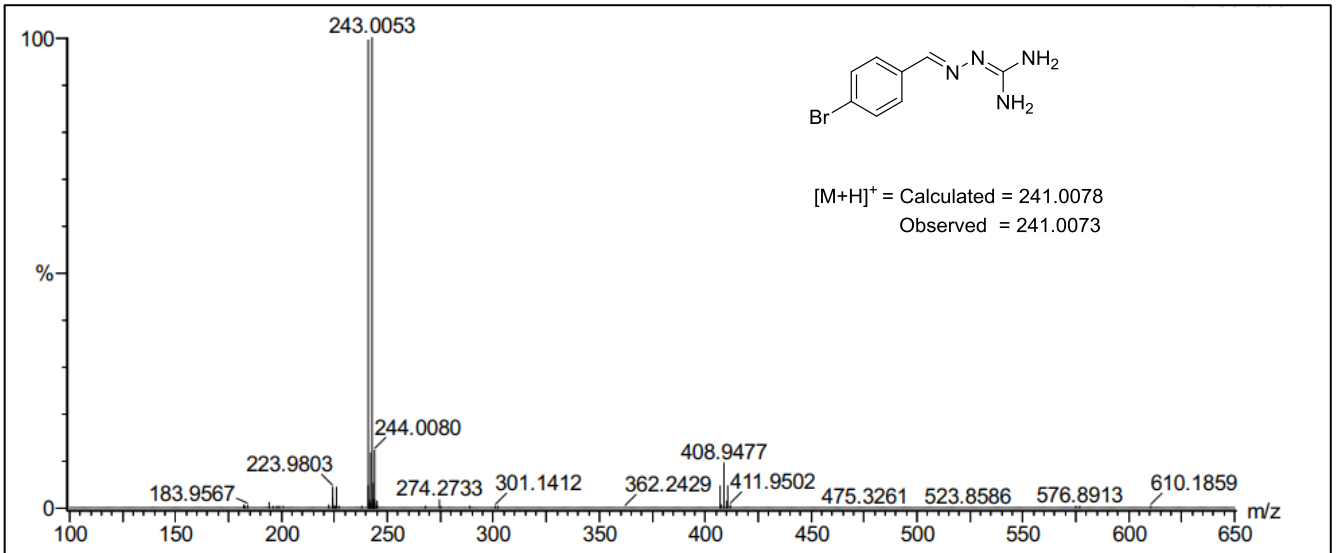
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
241.0077	241.0089	-1.2	-5.0	5.5	783.4	n/a	n/a	C8 H10 N4 Br

HRMS of 1h:



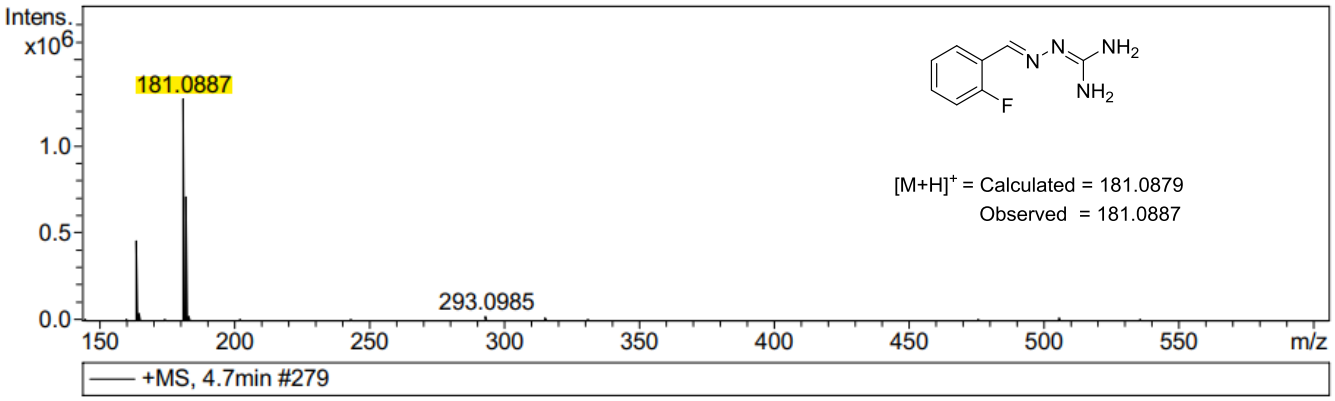
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
241.0080	241.0089	-0.9	-3.7	5.5	619.9	n/a	n/a	C8 H10 N4 Br

HRMS of 1i:

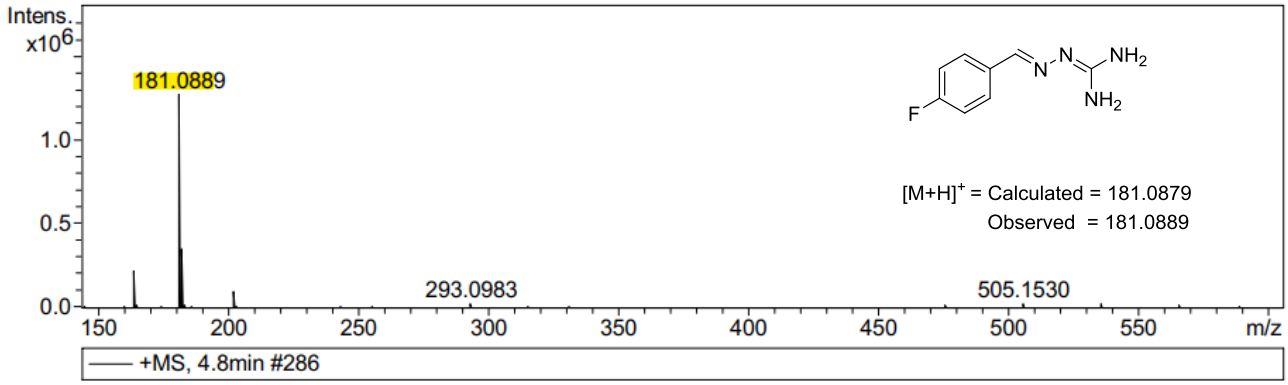


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
241.0073	241.0089	-1.6	-6.6	5.5	794.0	n/a	n/a	C8 H10 N4 Br

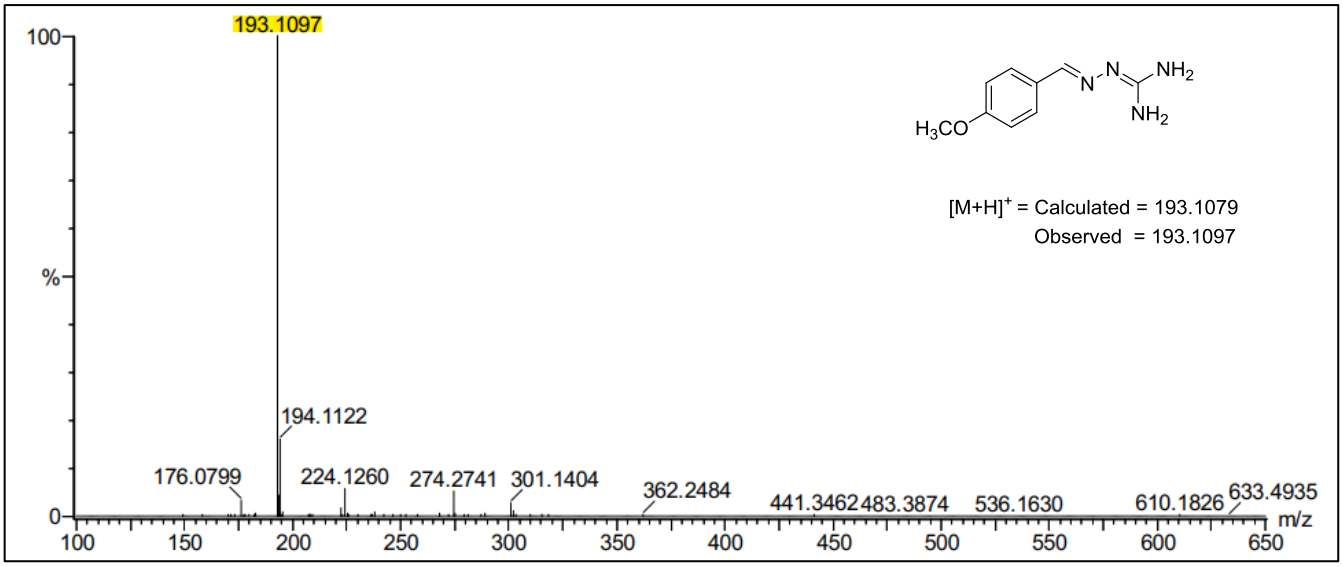
HRMS of 1j:



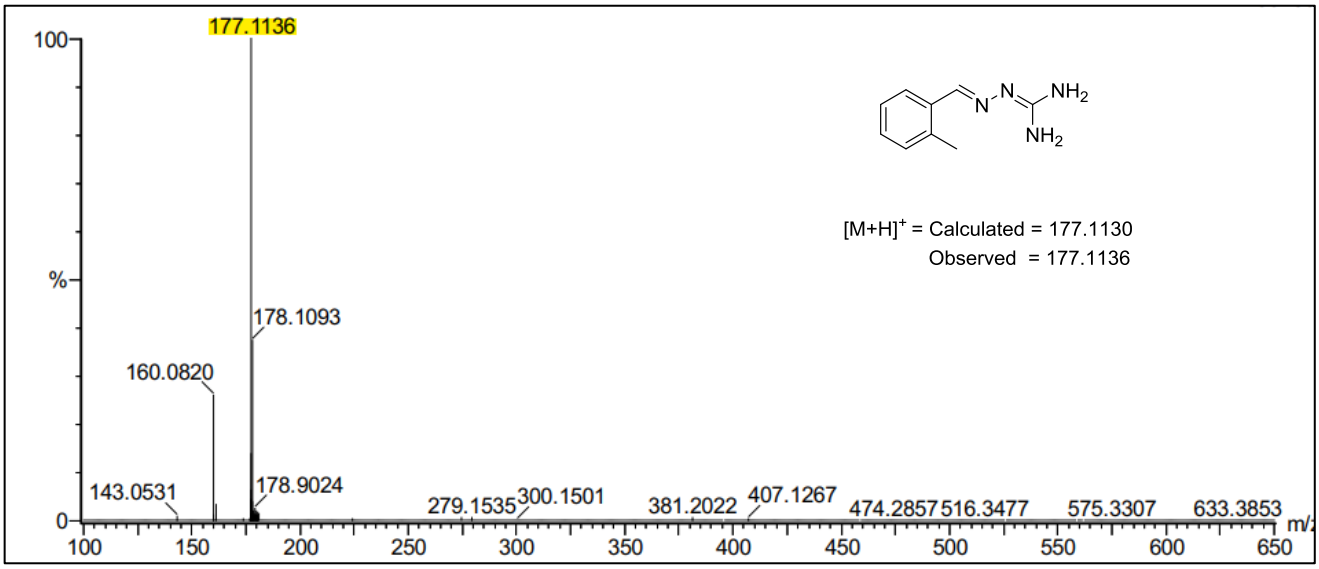
HRMS of 1k:



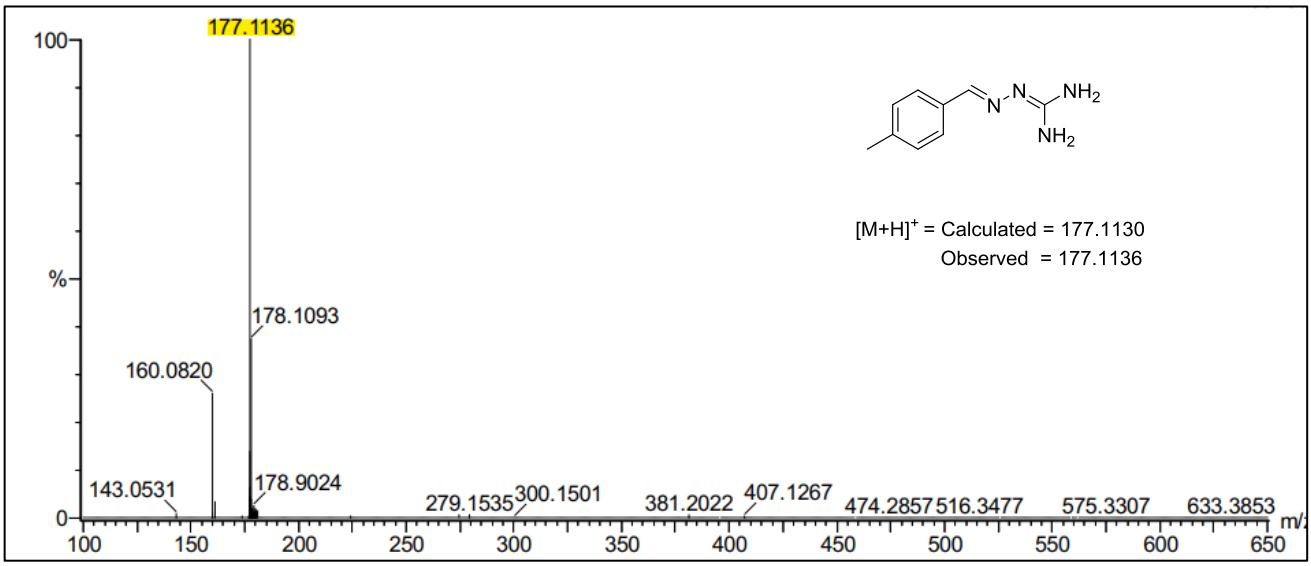
HRMS of 1l:



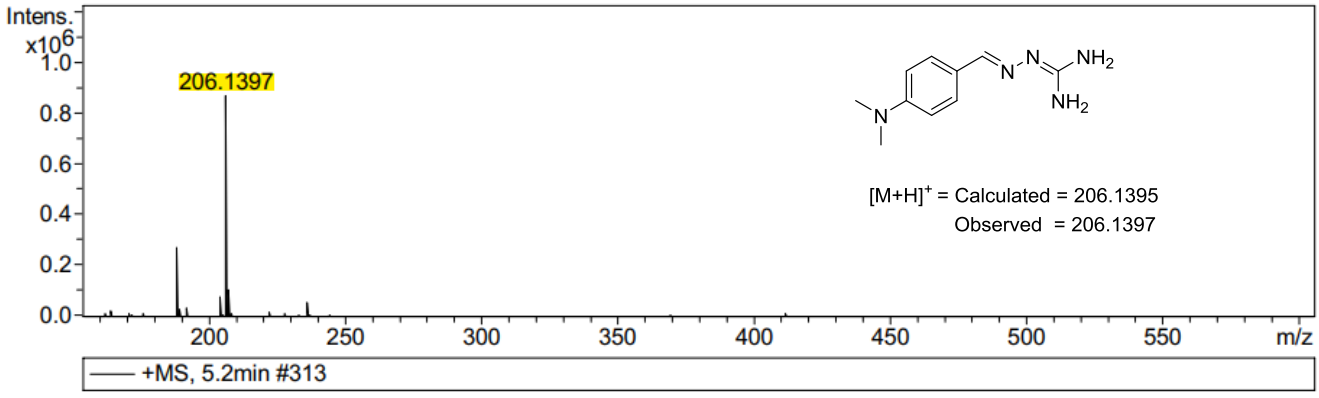
HRMS of 1m:



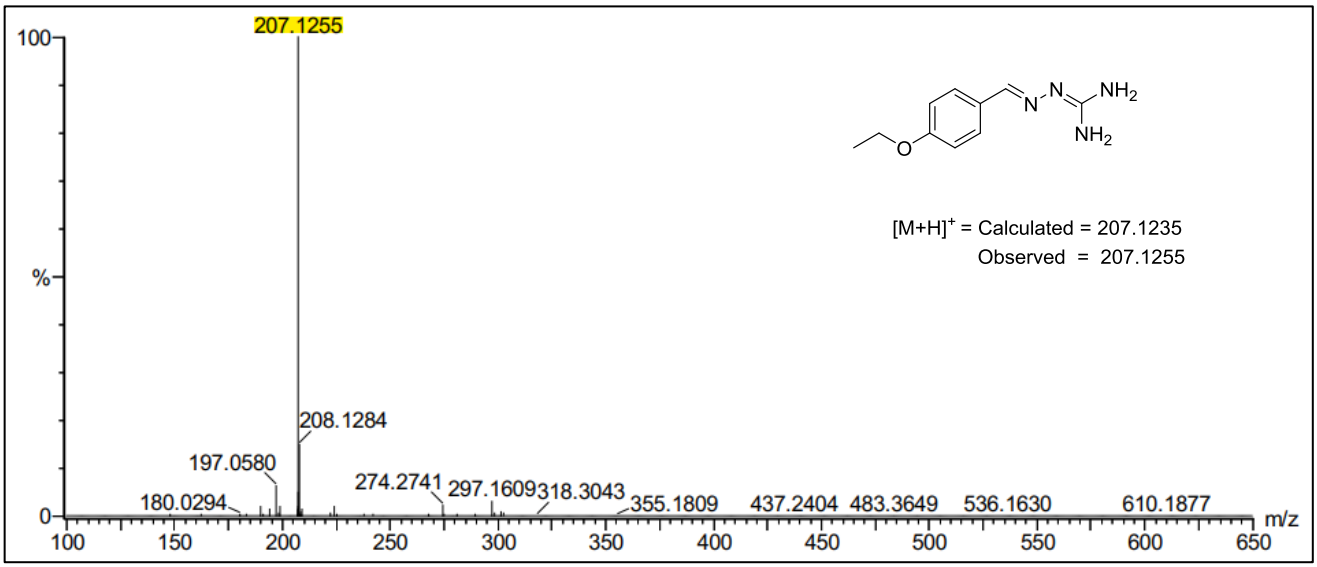
HRMS of 1n:



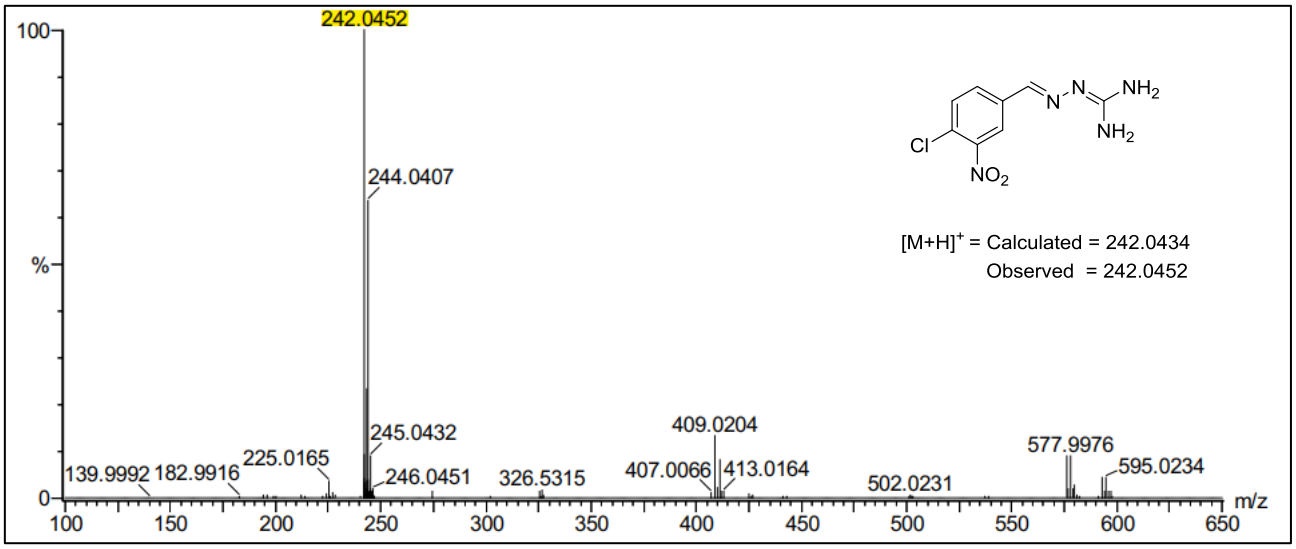
HRMS of 1o:



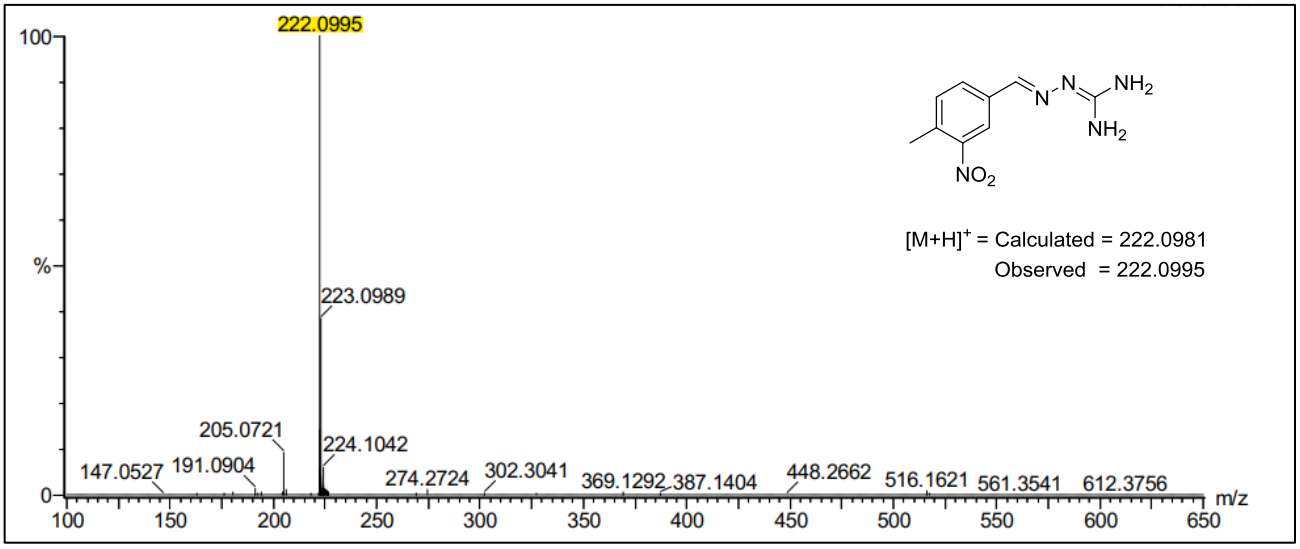
HRMS of 1p:



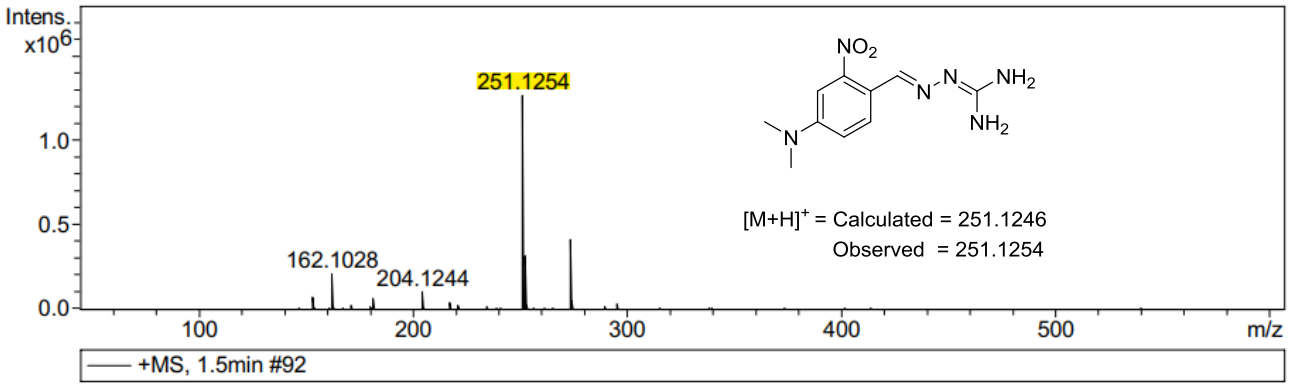
HRMS of 1q:



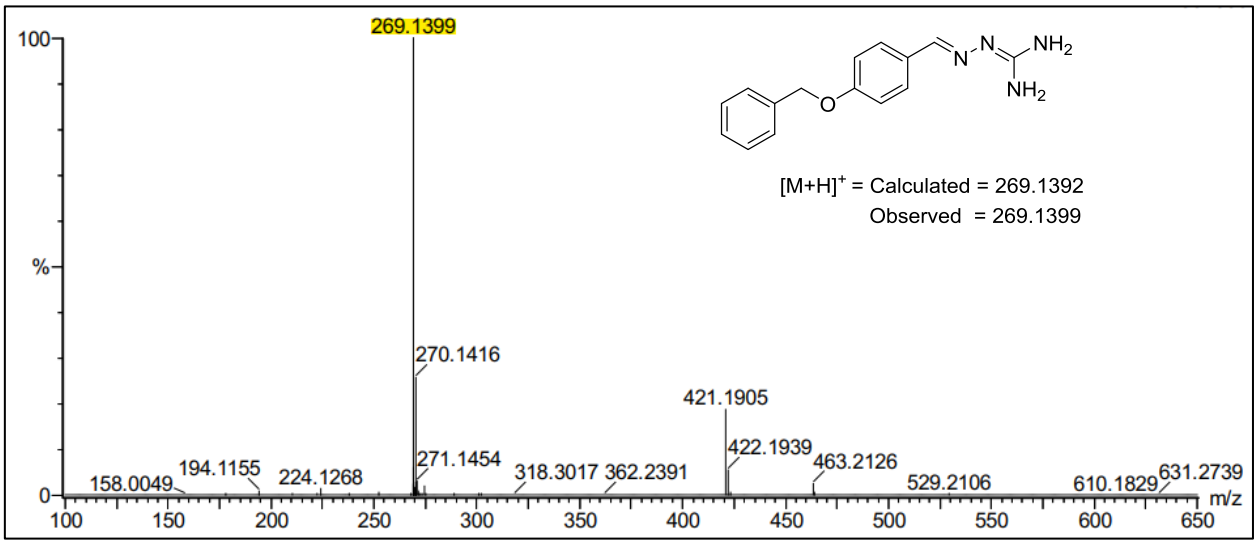
HRMS of 1r:



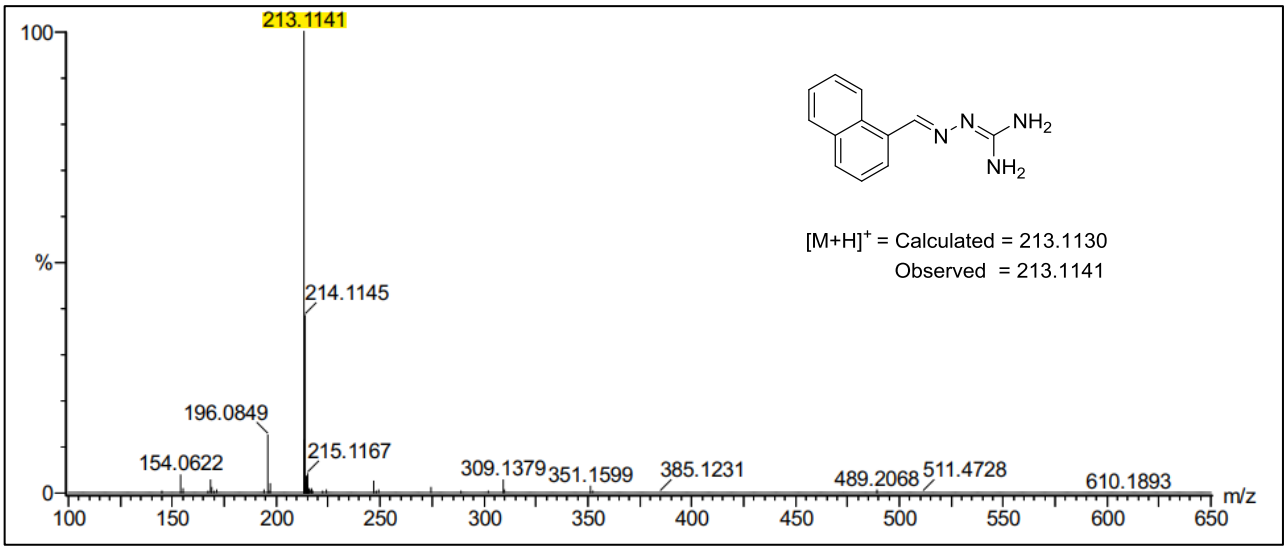
HRMS of 1s:



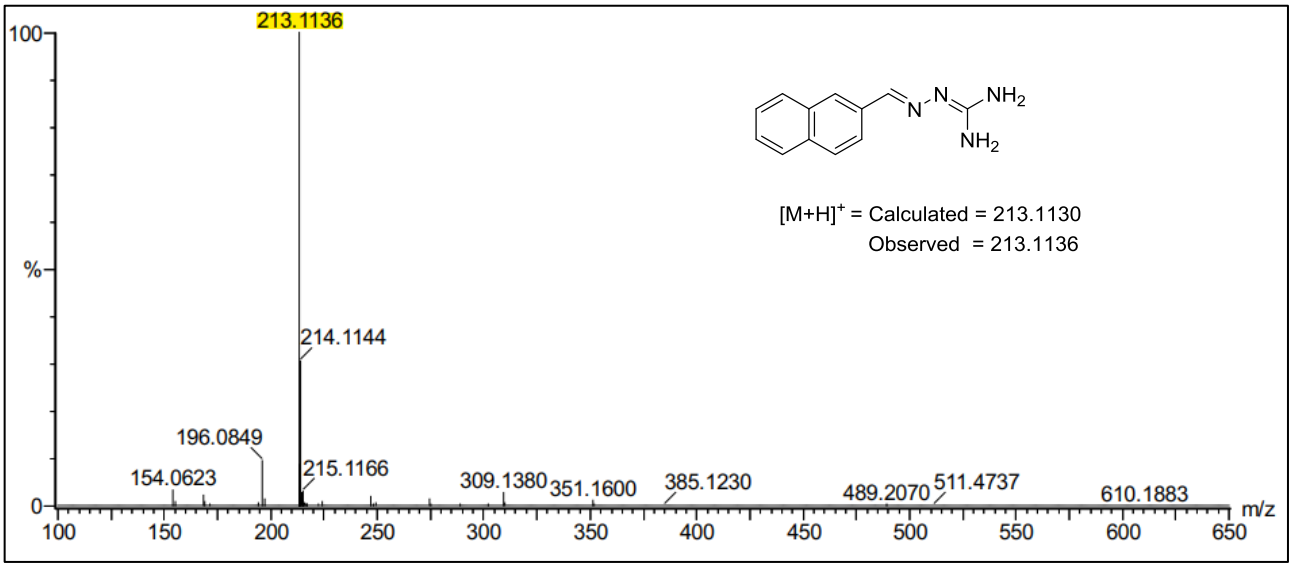
HRMS of 1t:



HRMS of 1u:

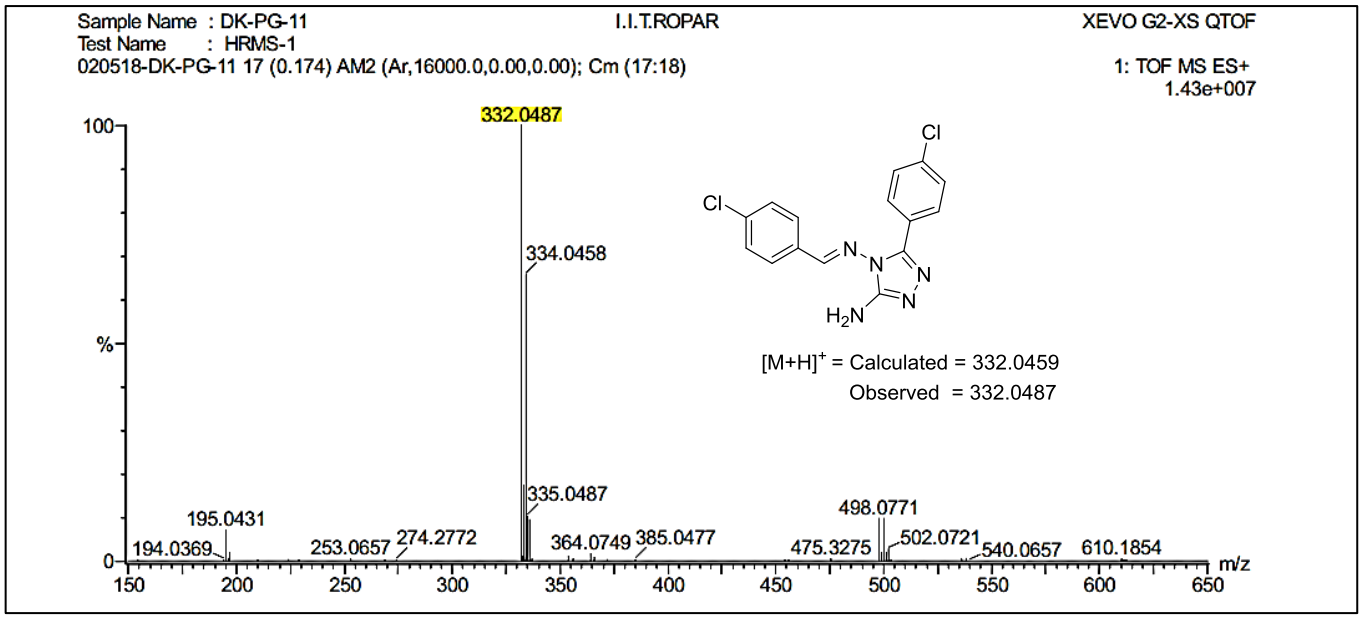


HRMS of 1v:

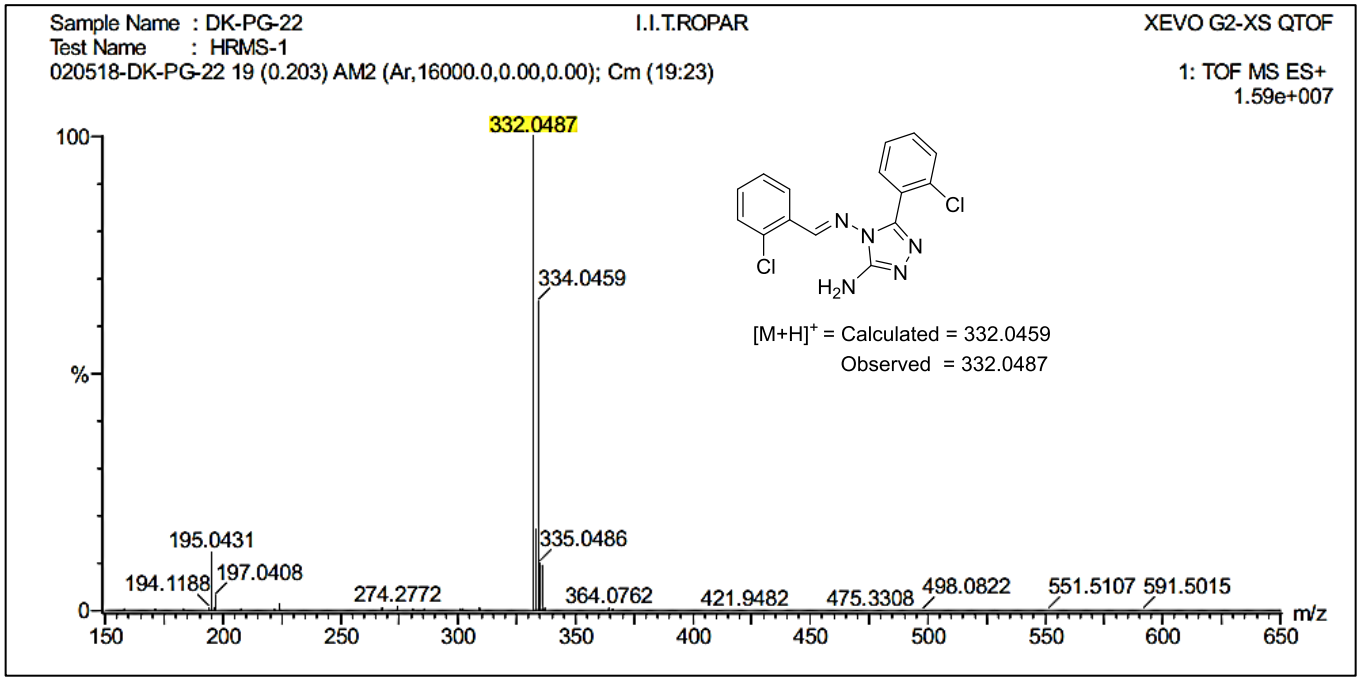

213.1136
100
%
0
214.1144
196.0849
154.0623
215.1166
309.1380
351.1600
385.1230
489.2070
511.4737
610.1883
m/z
100
150
200
250
300
350
400
450
500
550
600
650
NH2
NH2
[M+H]+ = Calculated = 213.1130
Observed = 213.1136

HRMS Spectra of 5a-v:

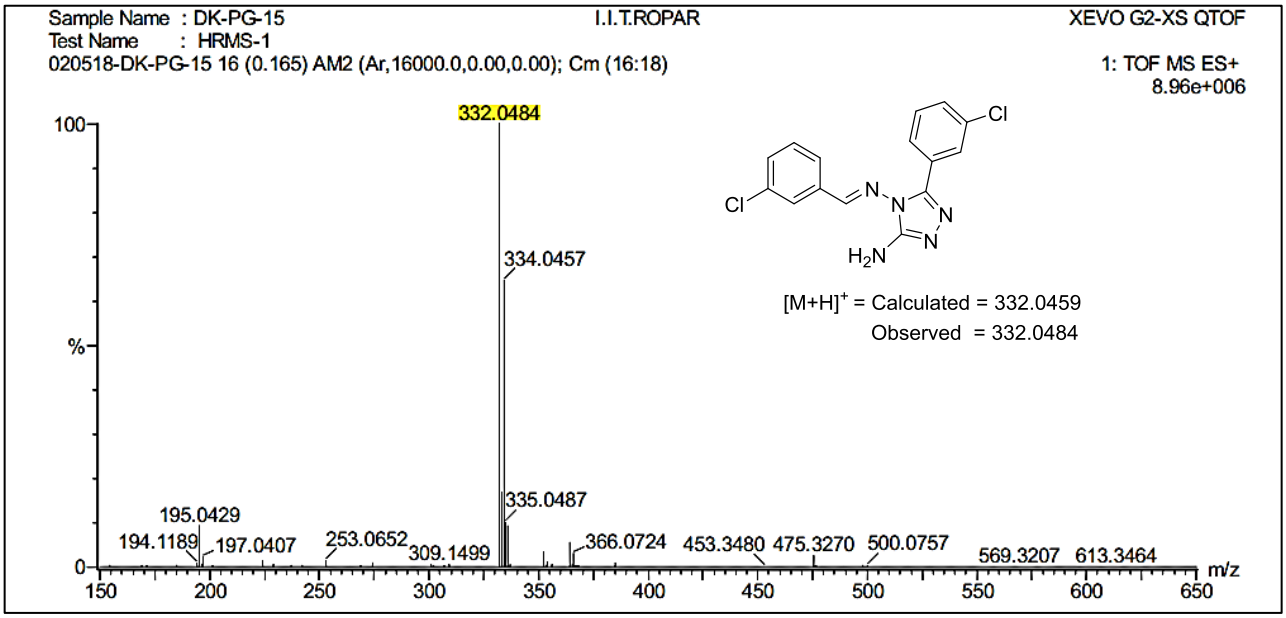
HRMS of 5a:



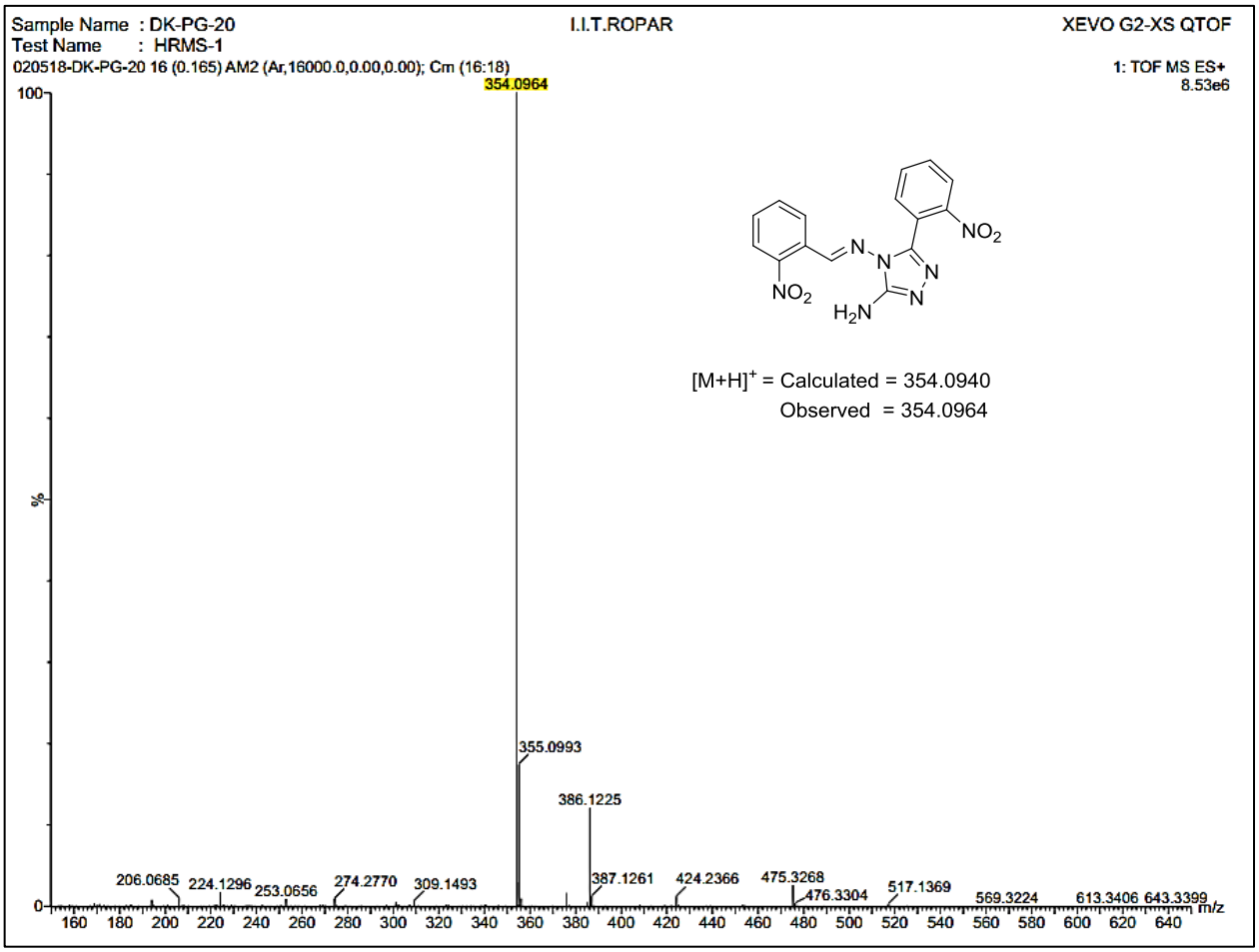
HRMS of 5b:



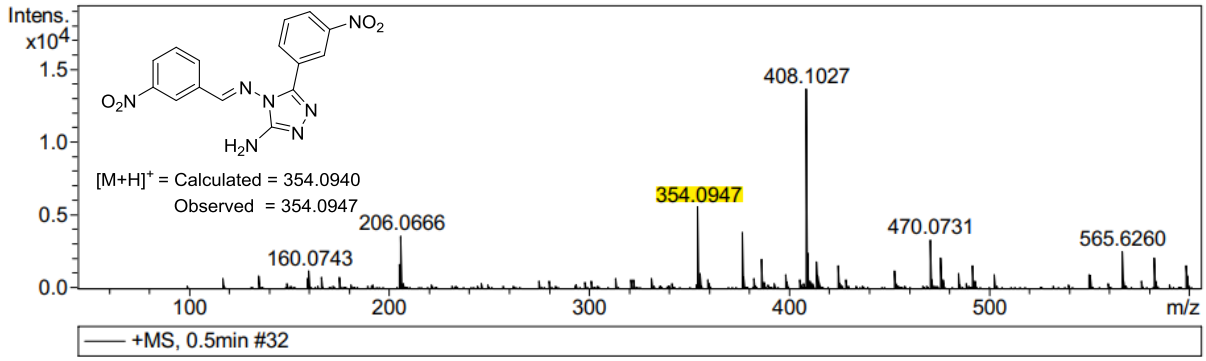
HRMS of 5c:



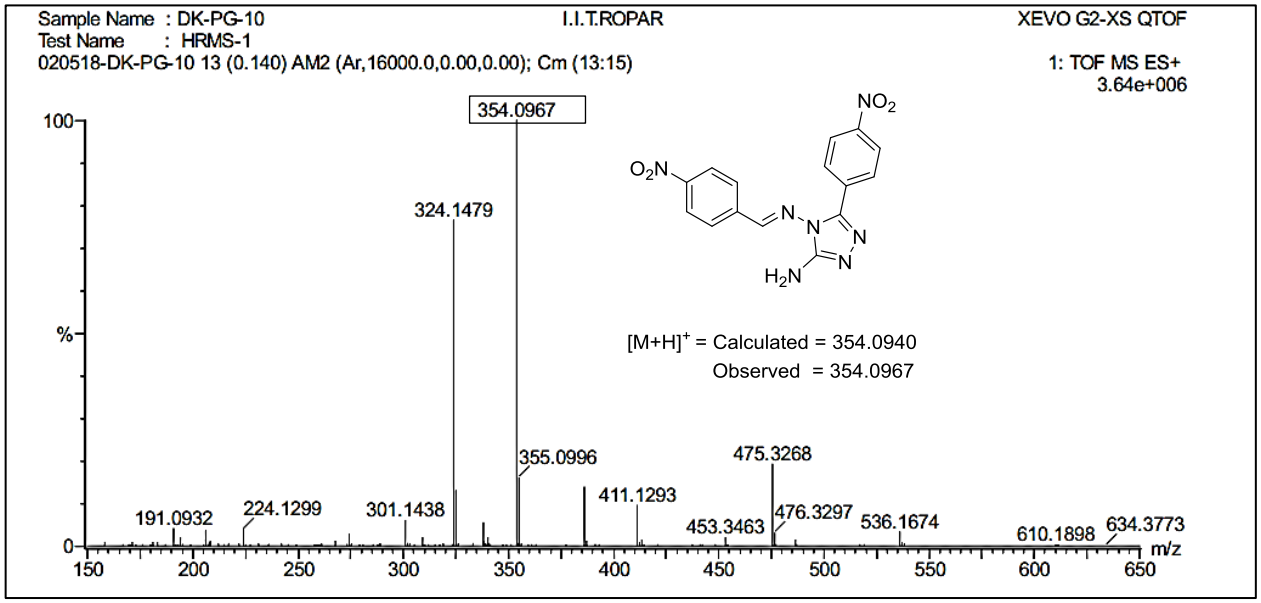
HRMS of 5d:



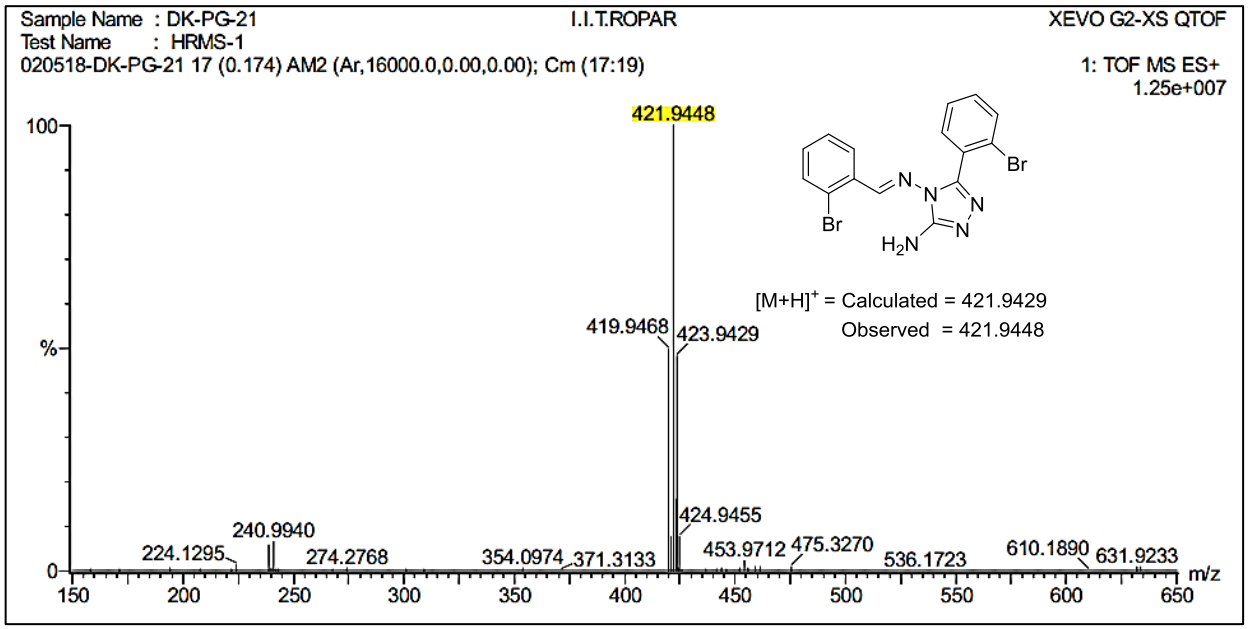
HRMS of 5e:



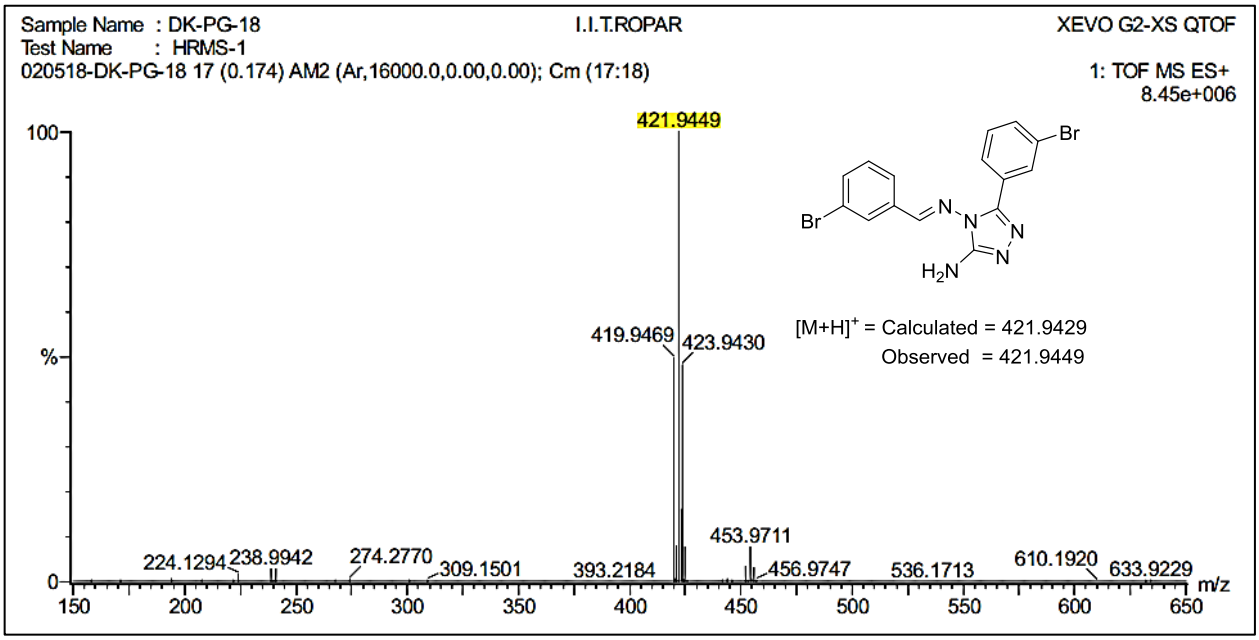
HRMS of 5f:



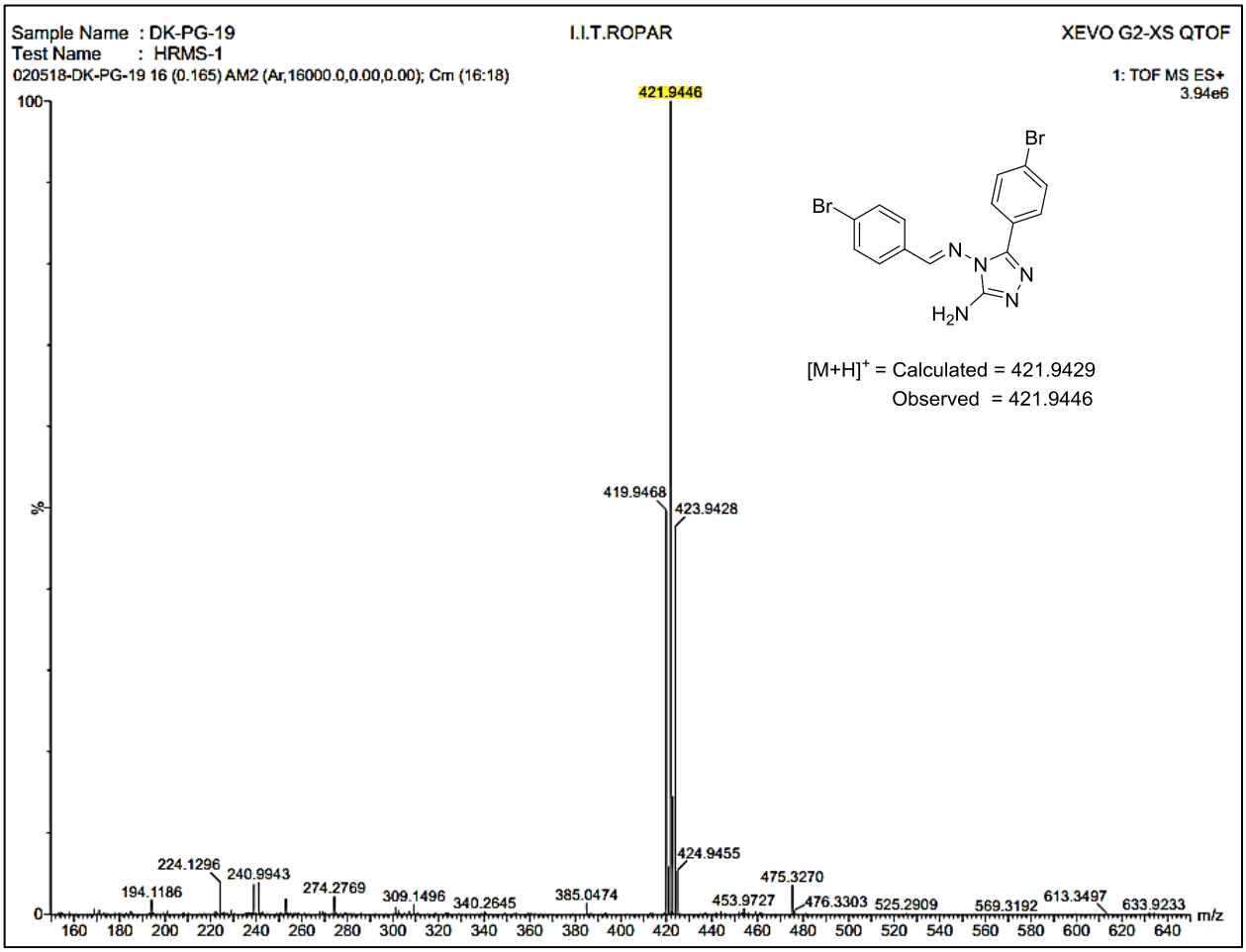
HRMS of 5g:



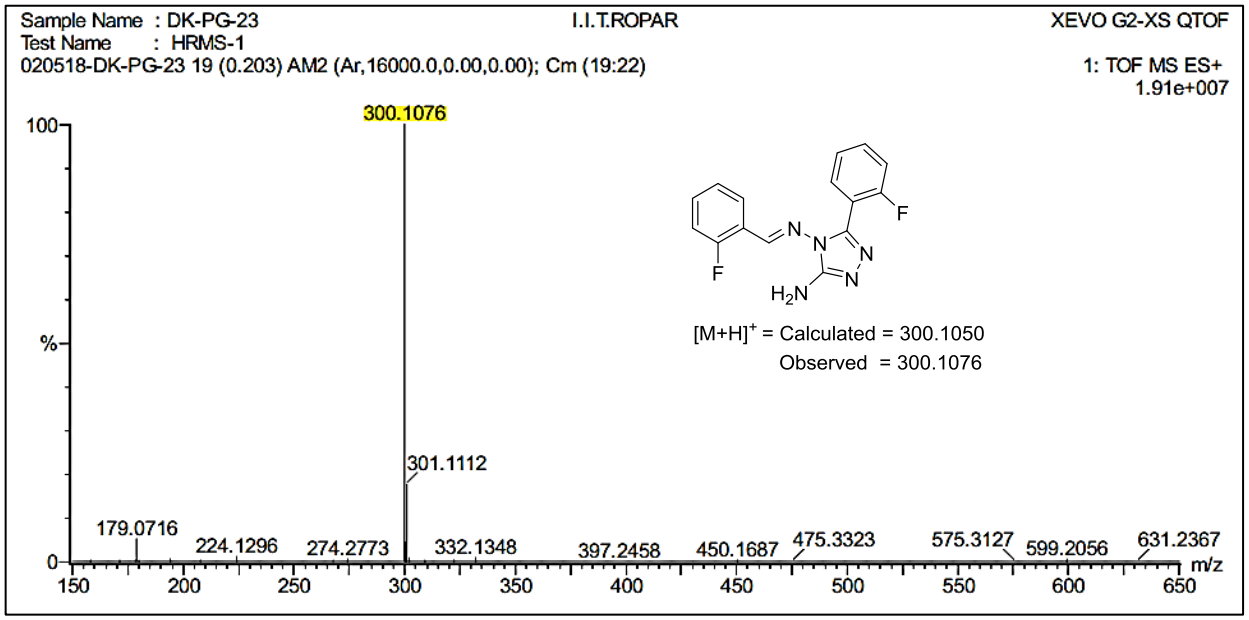
HRMS of 5h:



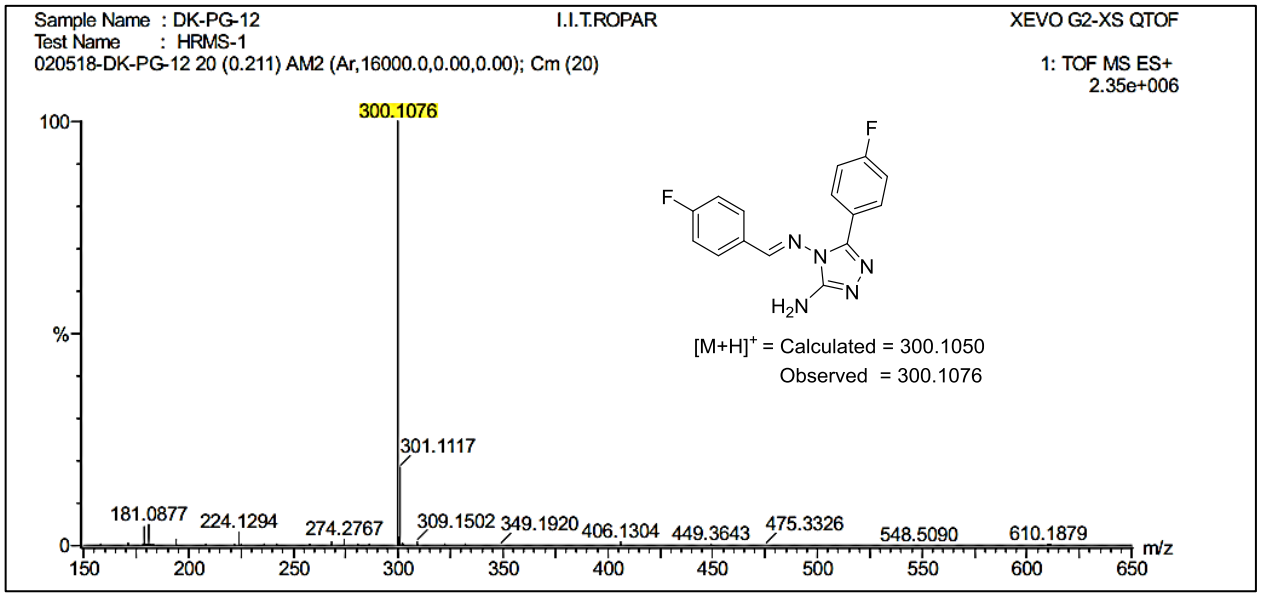
HRMS of 5i:



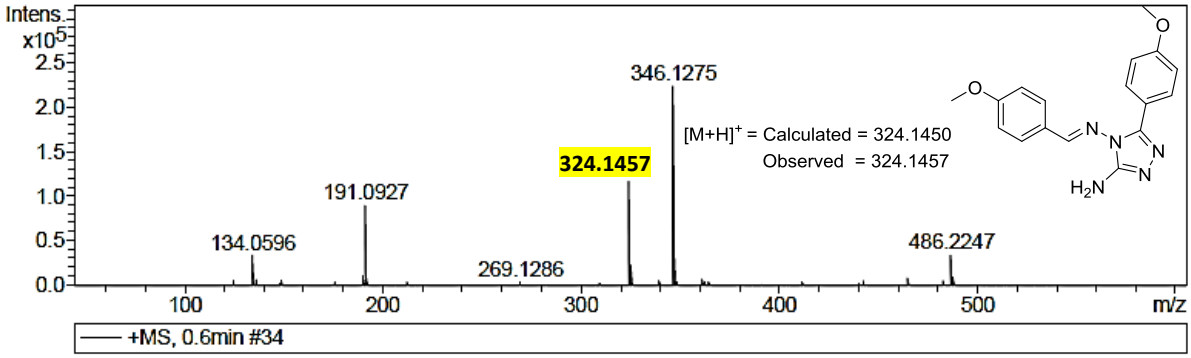
HRMS of 5j:



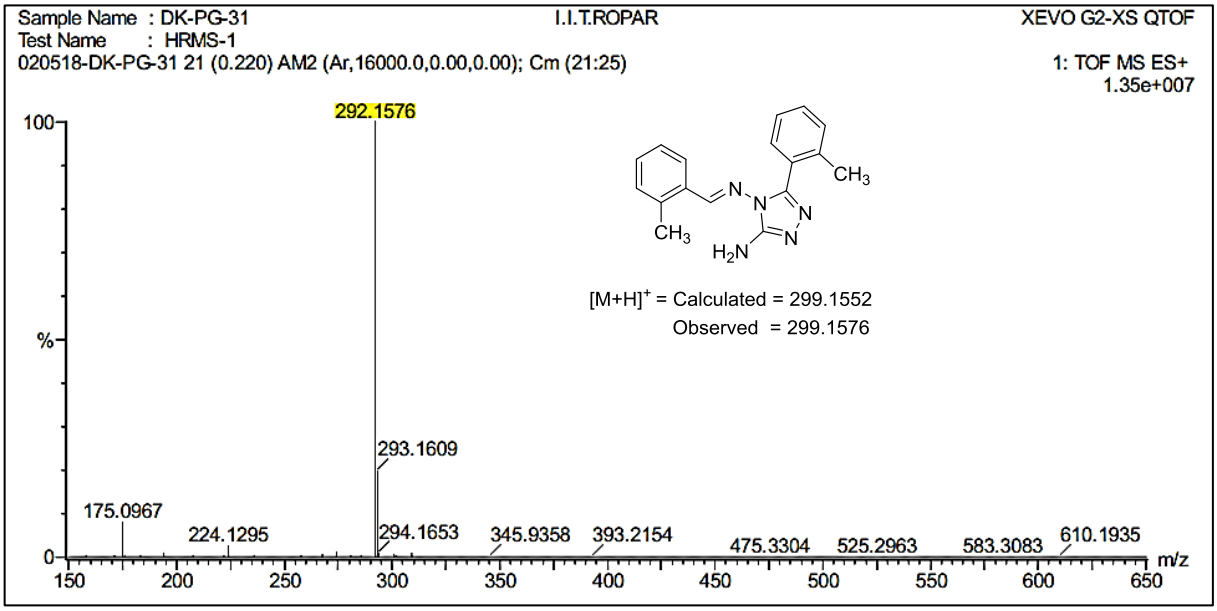
HRMS of 5k:



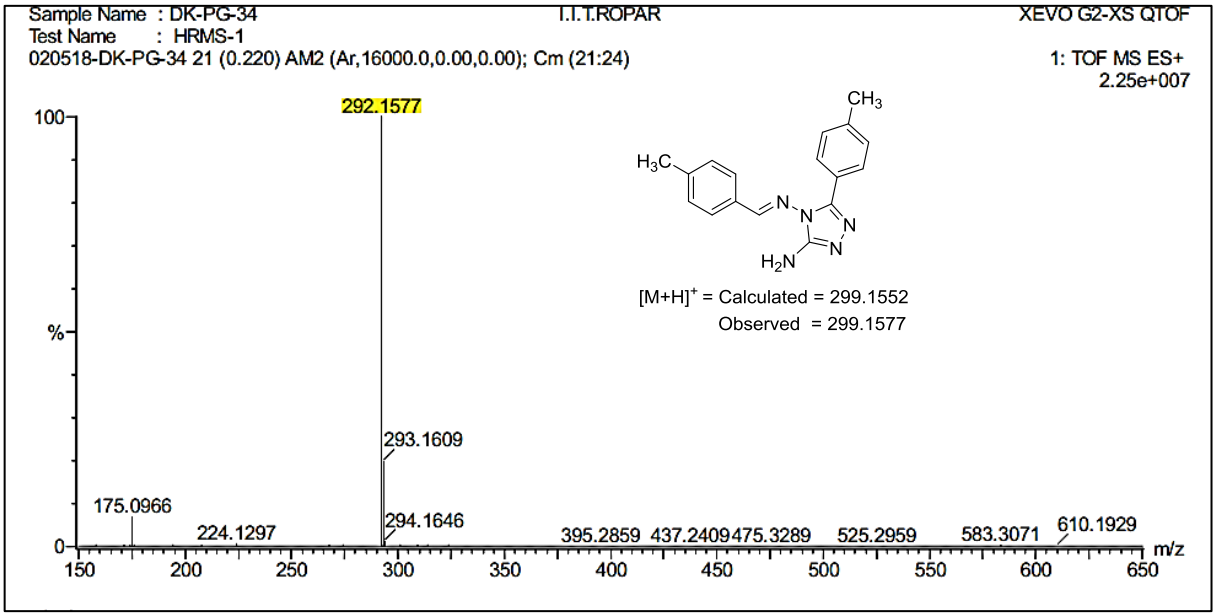
HRMS of 5l:



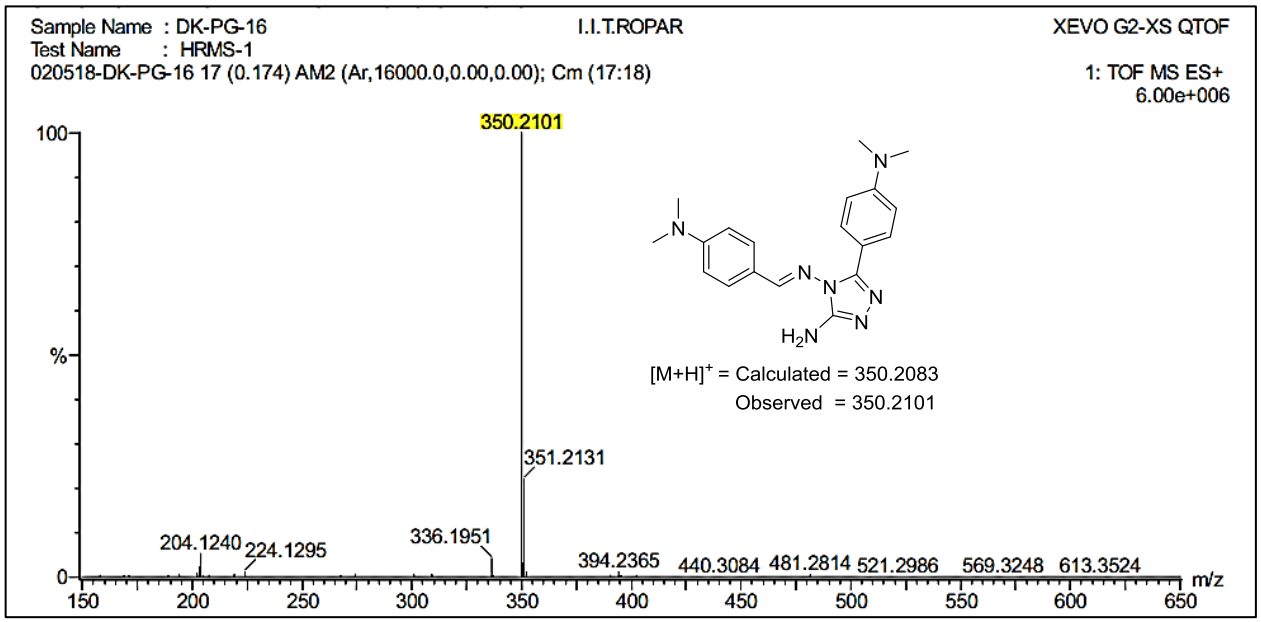
HRMS of 5m:



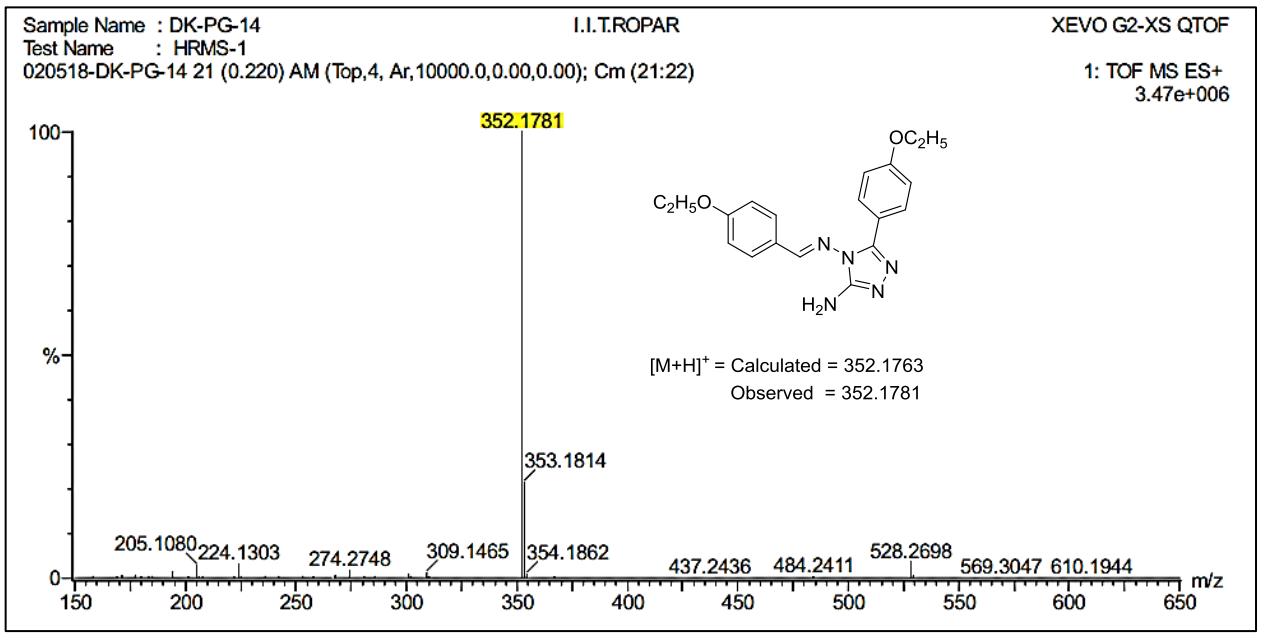
HRMS of 5n:



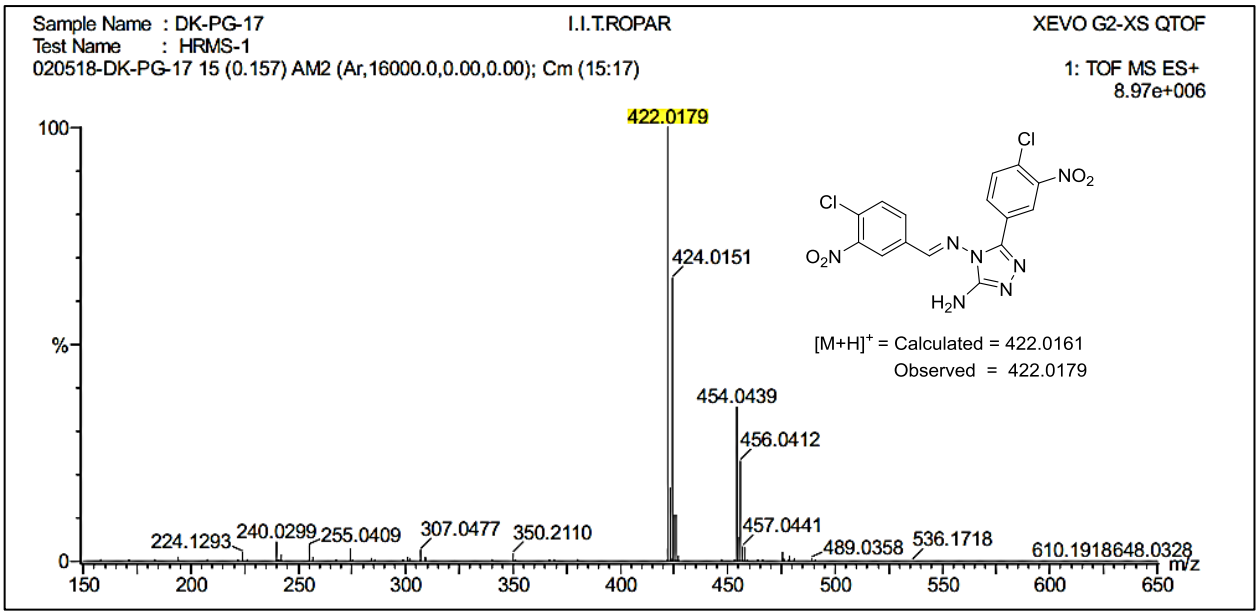
HRMS of 5o:



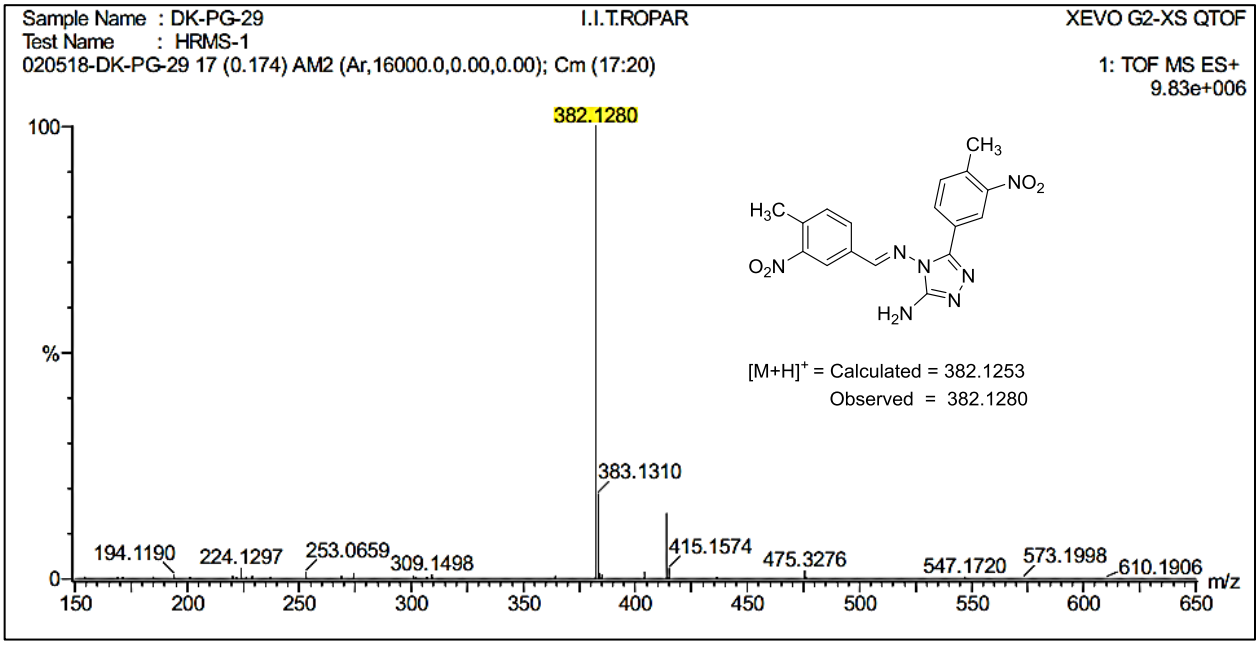
HRMS of 5p:



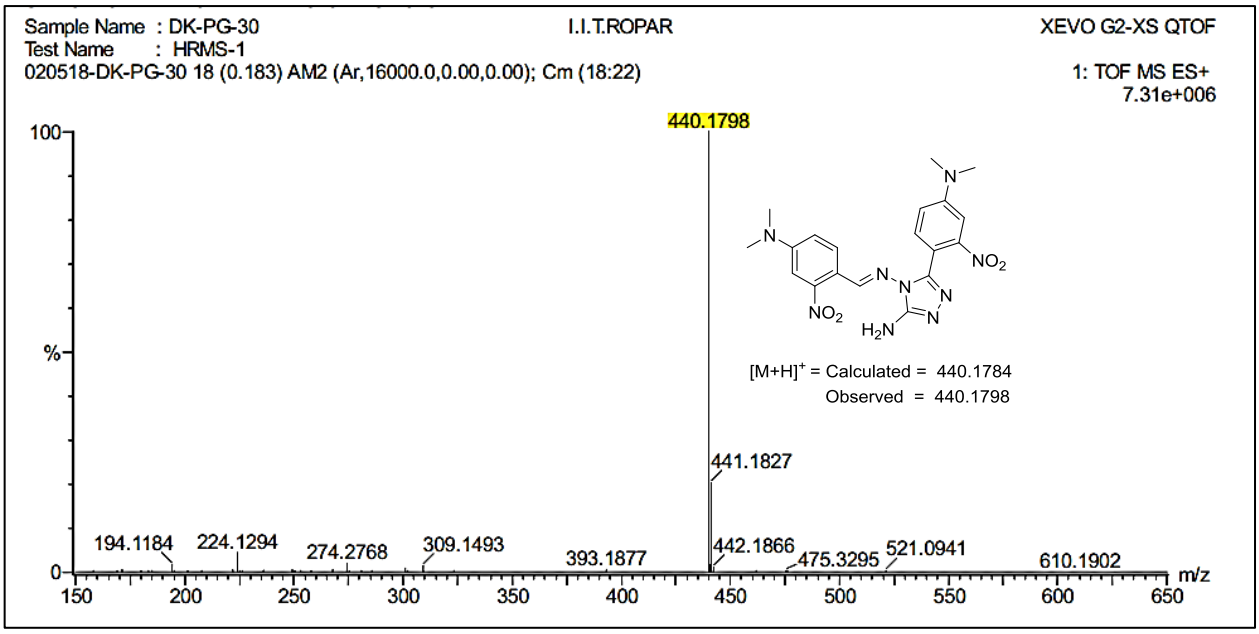
HRMS of 5q:



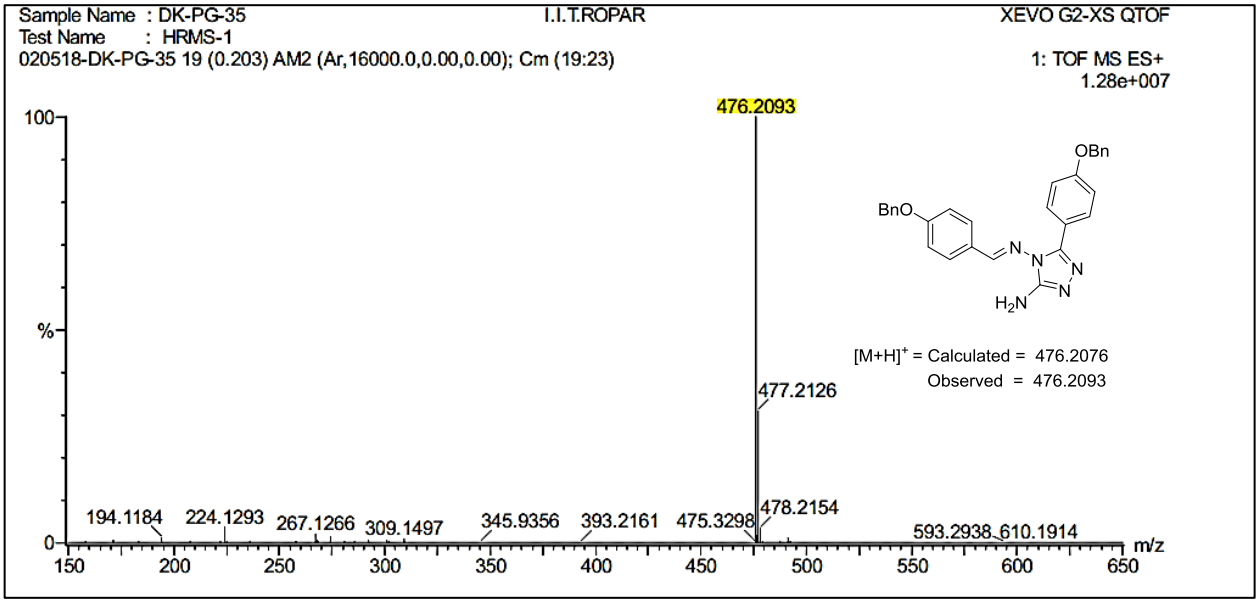
HRMS of 5r:



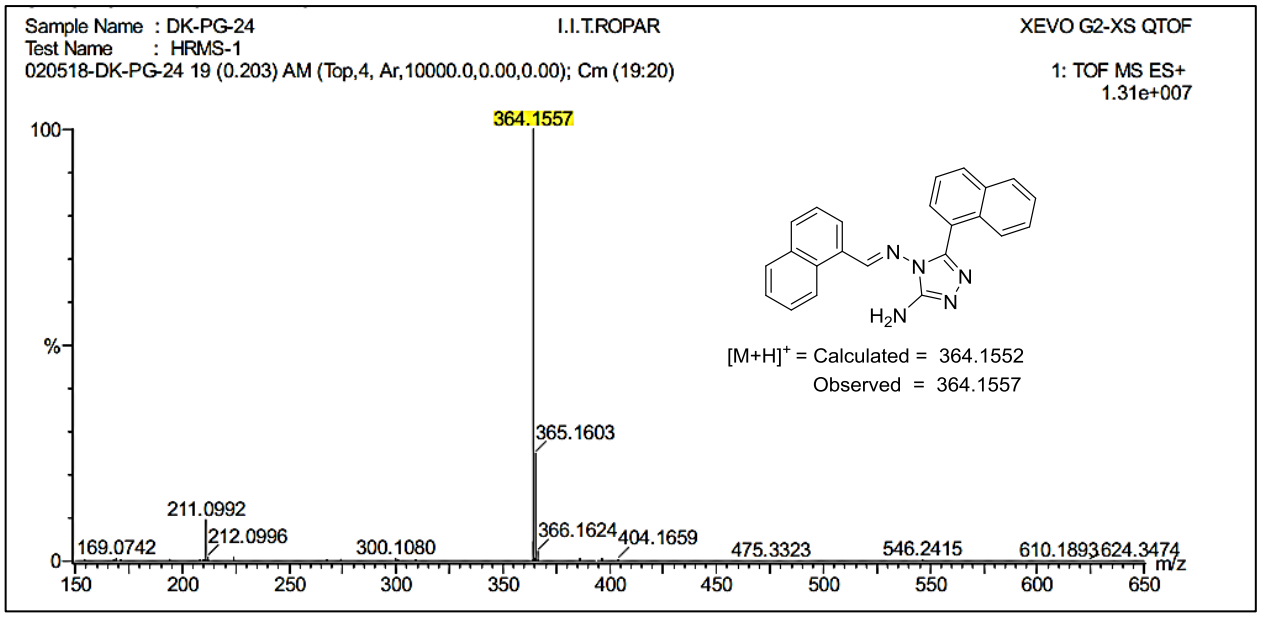
HRMS of 5s:



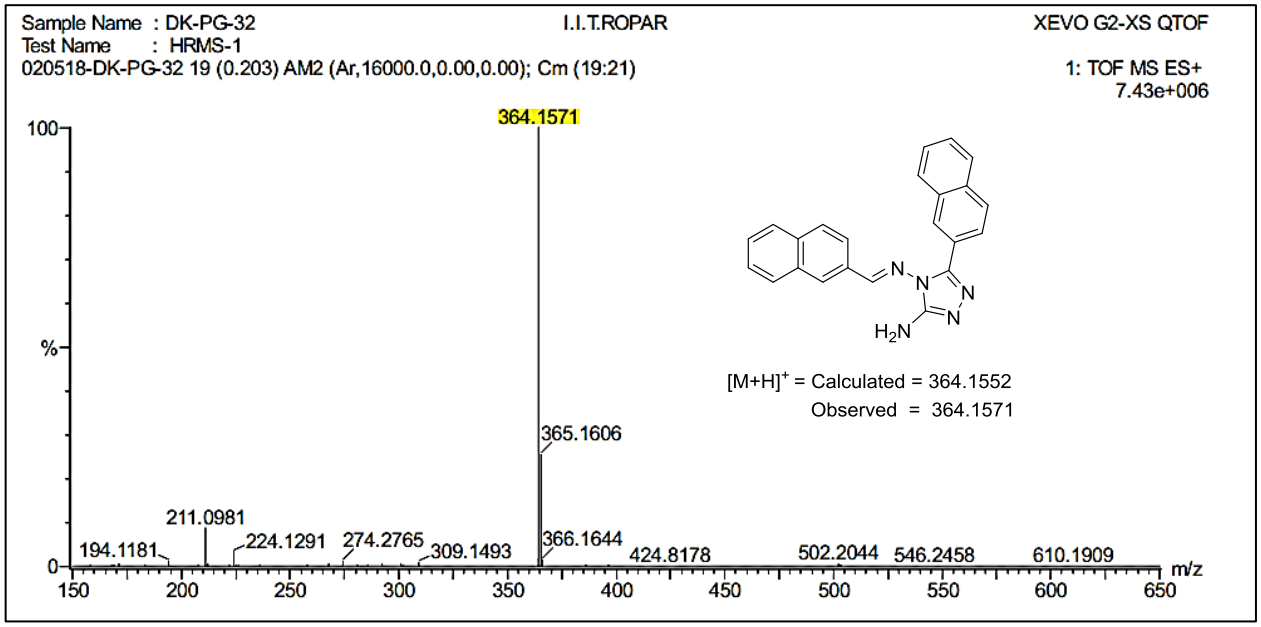
HRMS of 5t:



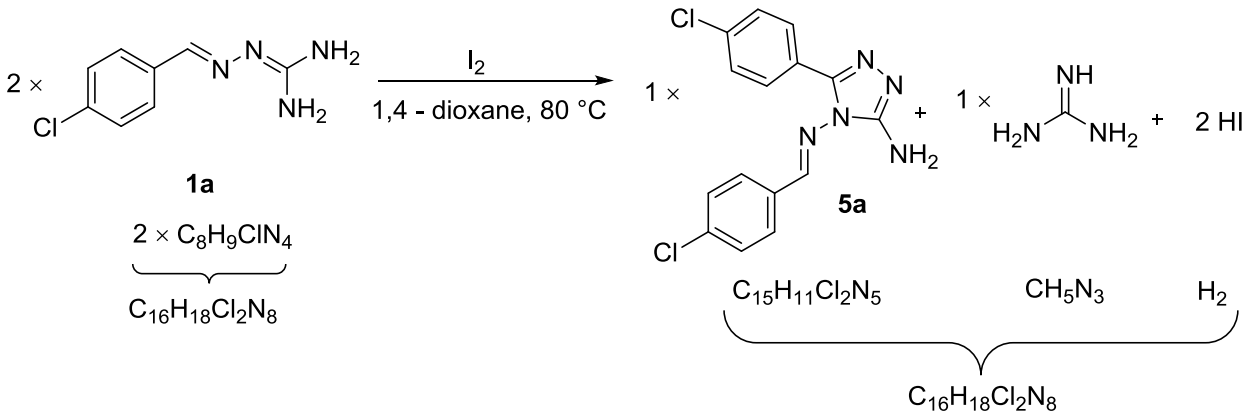
HRMS of 5u:



HRMS of 5v:



7. Yield calculation of observed product



2 mole of starting material **1a** gives 1 mole of product **5a**. Therefore, this fact was taken into consideration while calculating % yield of the product **5a**.[ref]

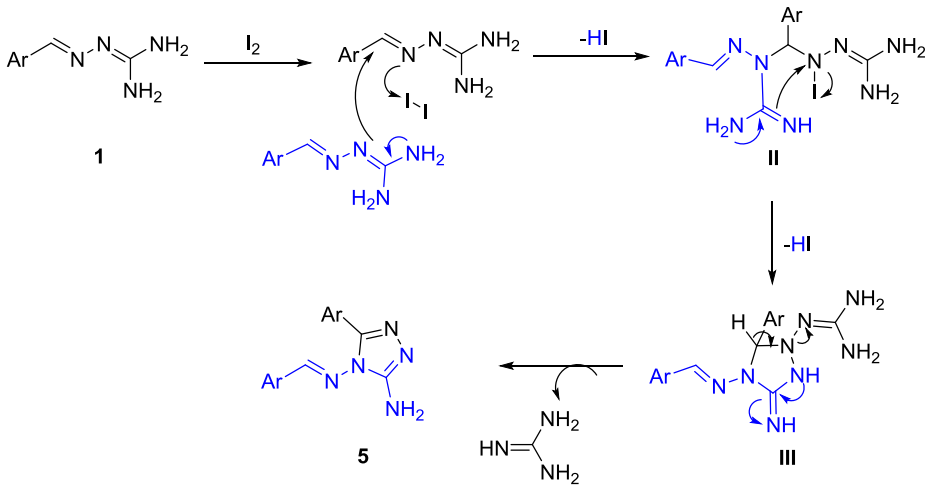
	1a	**5a**
Mol. wt.	196	332
Amount	0.1 g	0.062 g (isolated yield)
Theoretical yield	=	$= \frac{\text{Mol.wt. of } \mathbf{5a} \times \text{amount of } \mathbf{1a} \times \text{moles of } \mathbf{5a}}{\text{Mol.wt. of } \mathbf{1a} \times \text{moles of } \mathbf{1a}}$ $= \frac{332 \times 0.1 \times 1}{196 \times 2} = 0.085$ g
Practical yield (%)	=	Practical yield (%) $= \frac{\text{Isolated yield}}{\text{Theoretical yield}} \times 100$ $= \frac{0.061}{0.085} \times 100 = 72\%$

Ref:

Mudududdla, R.; Sharma, R.; Abbat, S.; Bharatam, P.V.; Vishwakarma, R.A.; Bharate, S.B.* Synthesis of 2-phenylnaphthalenes from styryl-2-methoxybenzenes. *Chem. Commun*. **2014**, *50*, 12076-12079.

8. Experimental Studies to Prove Mechanism:

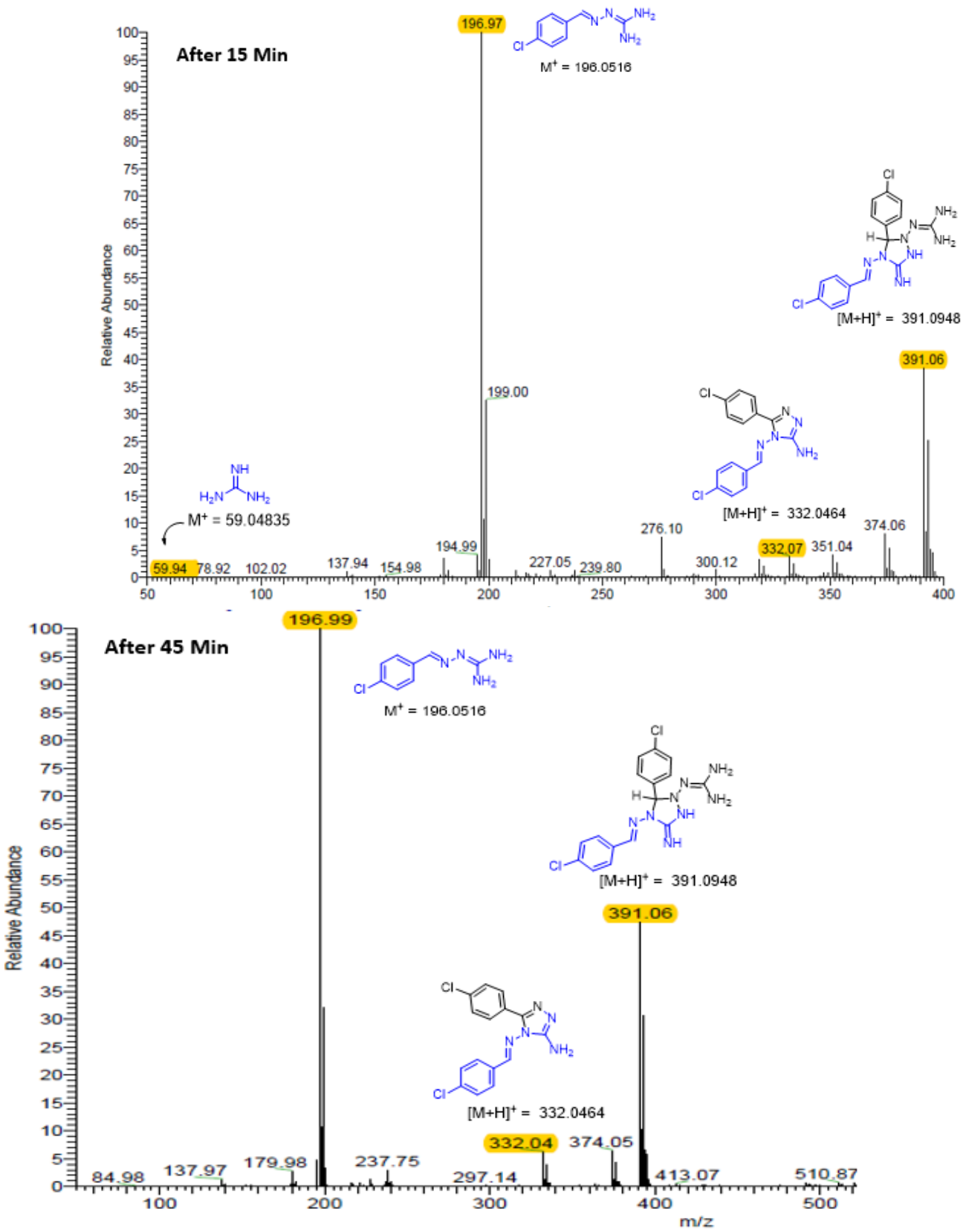
Plausible Mechanism



Mass study:

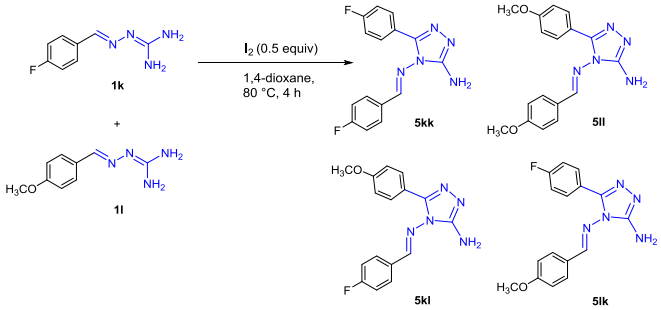
ESI-MS of crude mixtures obtained at intermediate time intervals from the onset of reaction for identifying the possible intermediates: Following the representative procedure, the reaction for the synthesis of compound **5a** was performed. Aliquots were withdrawn from resultant reaction mixture after interval times. The solvent and volatiles were completely evaporated under rotary evaporator. The crude reaction mixtures filtered and were subjected to mass spectrometry study. The mass spectrometry of crude mixture obtained at interval time for model reaction was studied and the characteristic peaks agreeably indicated the formation of intermediate **III**, where Ar = 4-chlorophenyl.

8.1. Identification of Intermediate by ESI-MS: From the synthesis of **5a**.



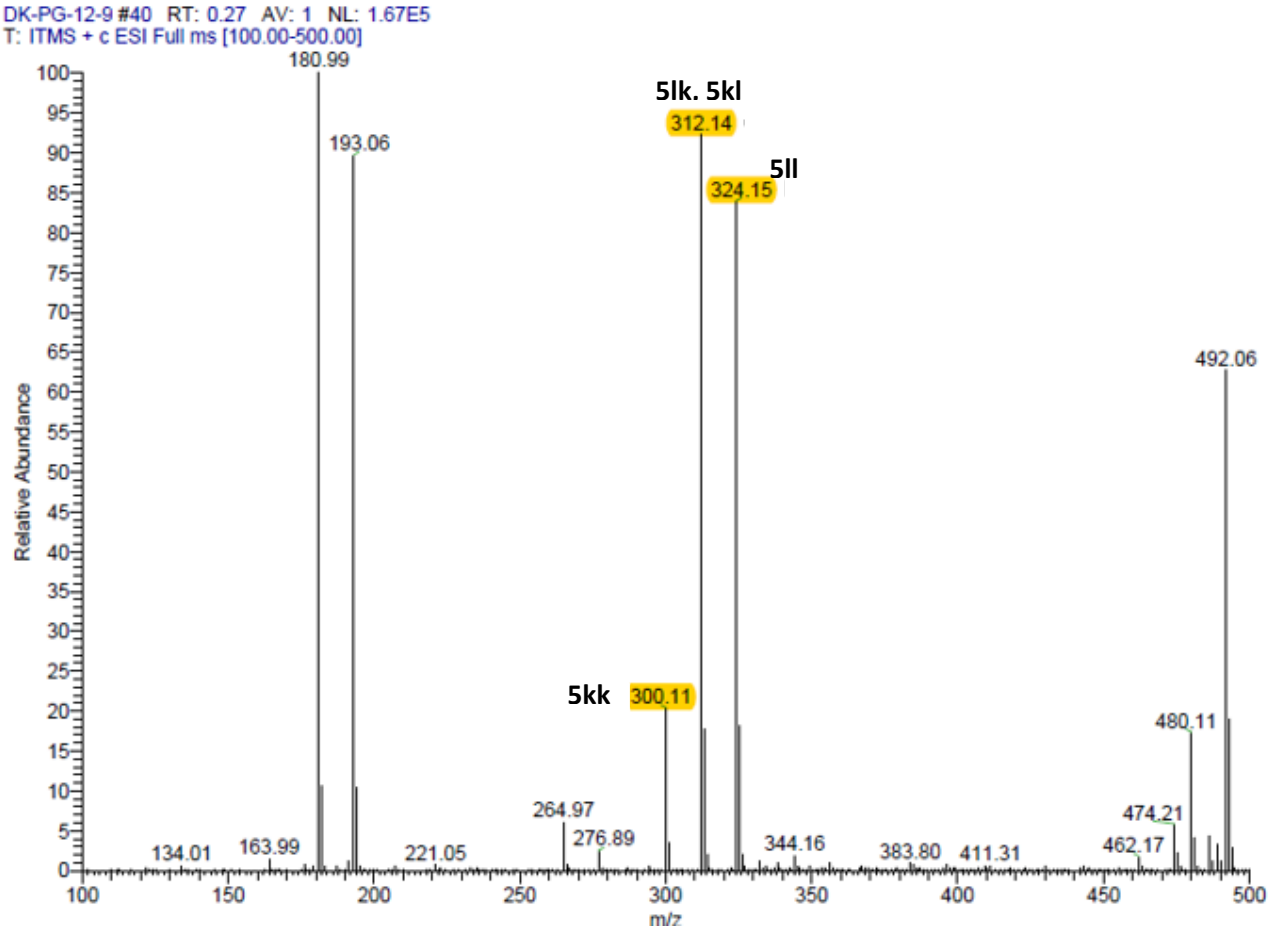
8.2. Evidence in Favor of Intermolecular Cyclization:

Scheme-SI-1: The I_2-catalyzed reaction of **1k** and **1l** under optimized conditions to form corresponding intermolecular cyclocondensation products.

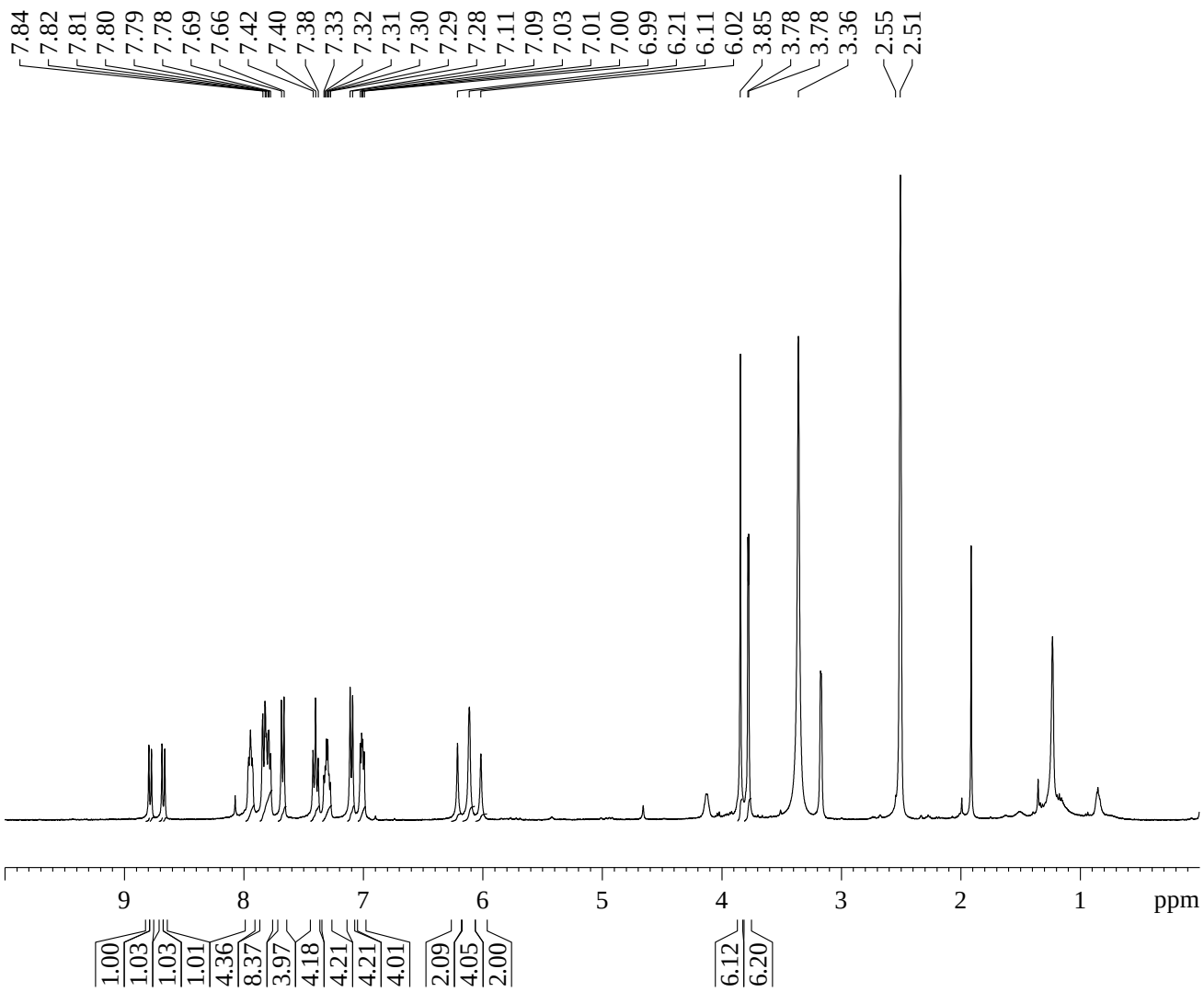


Following the representative procedure, the reaction of **1k** and **1l** was carried out for the identification of mechanism. Aliquots were withdrawn from resultant reaction mixture after interval times. The solvent and volatiles were completely evaporated under rotary evaporator. The crude reaction mixtures filtered and were subjected to mass spectrometry study. The mass spectrometry and ^{1}H NMR of crude mixture obtained at interval time for model reaction was studied and the formation of four different products (**5kk**, **5ll**, **5kl**, **5lk**) confirm the intermolecular mechanism,

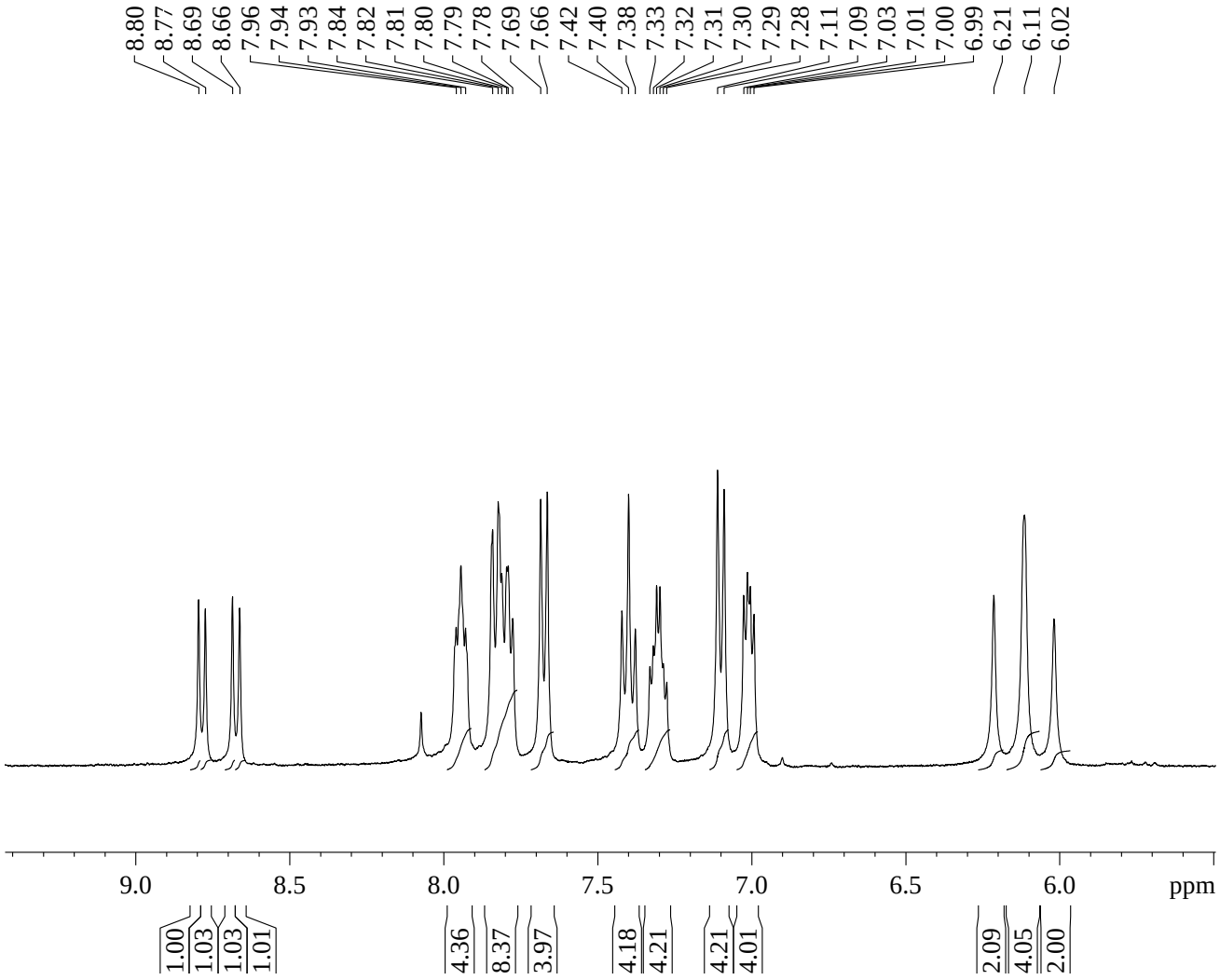
ESI-MS of 5k-5l



^{1}H NMR of 5k-5l (5kk, 5ll, 5kl, 5lk)



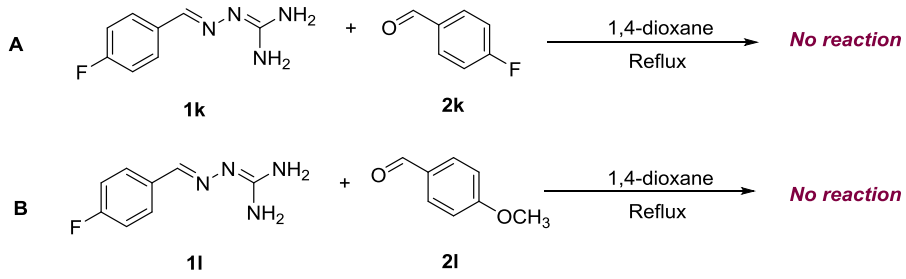
^{1}H NMR Expanded of 5k-5l
(5kk, 5ll, 5kl, 5lk)



8.3. Evidence in Favor of Intermolecular Cyclization: Reaction in Presence of Aldehyde:

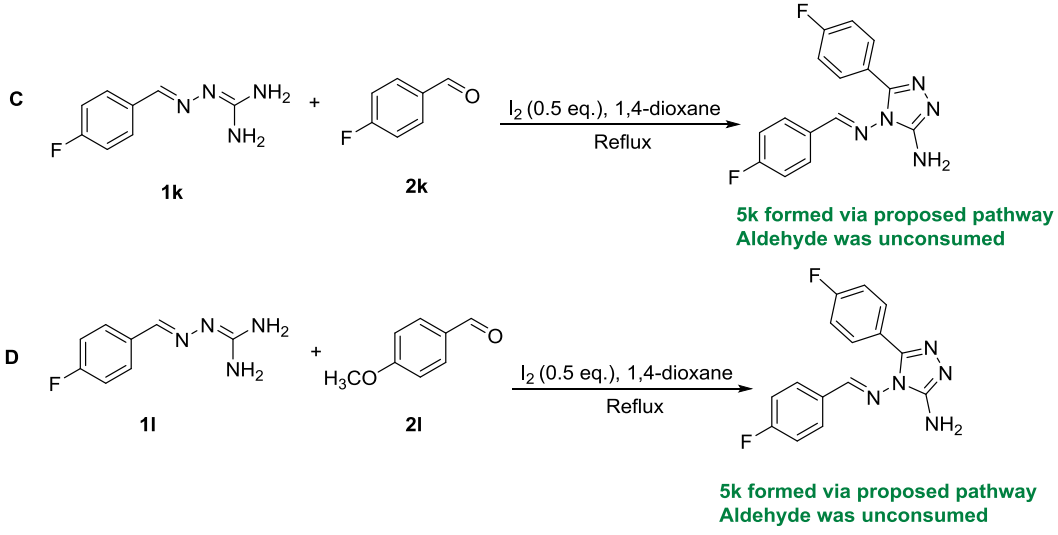
The reactions were carried out by treating **1k**/**1l** (100 mg, 0.5 mmol, 1 equiv) with **2k**/**2l** (100 mg, 0.5 mmol, 1 equiv) in 1,4-dioxane at 80 ˚C for 3 h. The reaction was monitored by TLC, but the formation of the product was not observed. Instead, both the starting materials were found to be intact even after 10 h (Scheme-SI-2).

Scheme-SI-2: The reaction of 1,1-diaminoazine (**1k**/**1l**) with aldehyde (**2k**/**2l**).



The reactions were carried out by treating **1k**/**1l** (100 mg, 0.5 mmol, 1 equiv) with **2k**/**2l** (100 mg, 0.5 mmol, 1 equiv) in the presence of I_2 (32mg, 0.25 mmol, 0.5 equiv) in 1,4-dioxane at 80 ˚C for 3 h. The progress of the reaction was monitored by TLC. After the completion of reaction, the solvent was evaporated under reduced pressure and the I_2 was quenched by aq. solution of $Na_2S_2O_8$. $5H_2O$ and the aqueous part was extracted with EtOAc (3 × 15 mL). The combined EtOAc extracts were dried (anh. Na_2SO_4), filtered, concentrated under vacuo, and the residue was subjected to column chromatography (eluent MeOH/DCM = 10:90). Aldehyde was found to be intact whereas, the 1,1-diaminoazine get reacted with iodine and gave the product formed by the reaction of intermolecular cyclization (Scheme-SI-3).

Scheme SI-3: The reaction of aldehyde (**1k**/**2l**) with **1k** to elucidate the mechanism.



9. Single crystal analysis of 5k (CCDC 1828789):

Experimental details:

A suitable single crystals of **5k** was selected and mounted using nylon loop on a SuperNova, Single source at offset/far, HyPix3000 diffractometer monochromated of MoKα radiation (λ = 0.71073 Å). The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the SIR2004[2] structure solution program using direct methods and refined with the olex2.refine[3] refinement package using Gauss-Newton minimisation. All nonhydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Two water molecules per molecule found to be highly disorder inside the cavity and could not able to model after several attempts so finally removed by solvent mask using Olex2.

1. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*., **2009**, *42*, 339-341.
2. Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D. Spagna, R. *J. Appl. Cryst.* **2007**, *40*, 609-613.
3. Bourhis, L .J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Acta Cryst*. **2015**, *A71*, 59-75.

Structural description

The molecule **5k** was crystalized in monoclinic space group of I2/*a* with one molecule per asymmetric unit. The two aromatic moieties stay one side of the triazole ring with almost a planner like structure (Figure SI-1, Table SI-1). In the lattice, two molecules approach each other on a head-to head dimeric arrangement through two strong H-bonds (2.965 Å) between $–NH_2$ group of one molecule with N-atom of other triazole moiety. Each dimer unit repeats in an alternate arrangement to form a sheet like architecture along *ac*-plane. As a result a small cavity (9x11 Å) is formed between two adjacent H-bonded dimes and may accommodate solvent molecules (Figure SI-2). Again the weak π-π interactions between the aromatic rings provides an additional expansion of packing the molecular alone *b*-axis. Detail crystallographic parameters including bond lengths and bond angles are listed in Table SI-1 and Table SI-2.

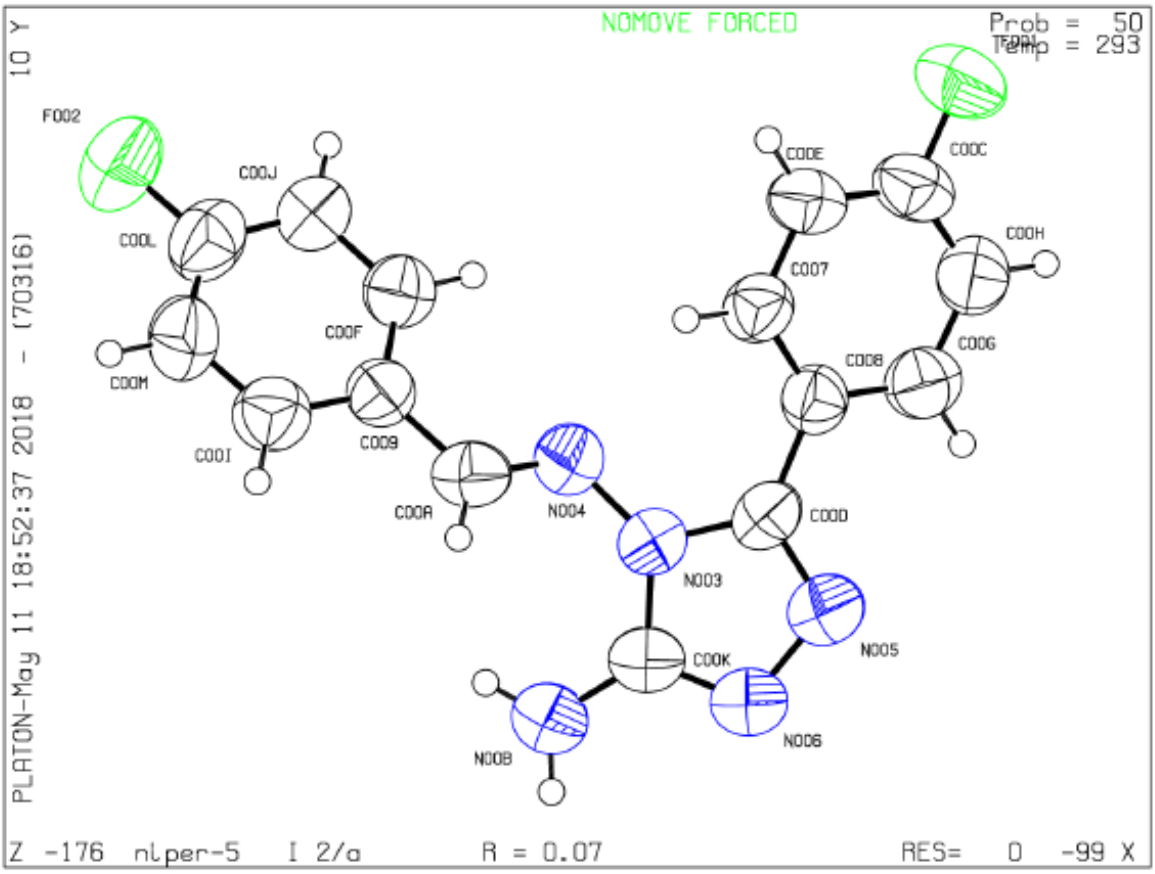


Figure SI-1: ORTEP diagram of **5k** with 50% thermal probability ellipsoids.

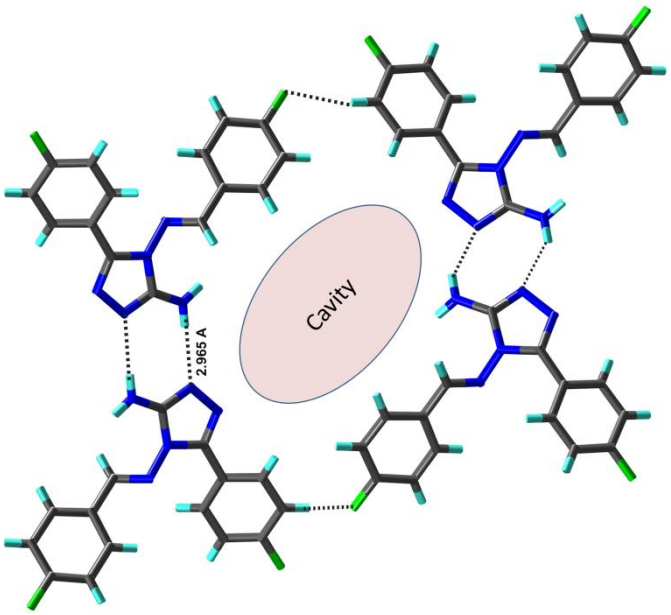


Figure SI-2: H-bonding and lattice arrangement along ac-plane. A small cavity has formed between the two adjacent dimes (color code: Green-F, Grey-C, Blue- N, light blue- H).

Table SI-2. Crystal data and structure refinement for **5k**.

CCDC	1828789
Empirical formula	$C_{15}H_{11}F_2N_5$
Formula weight	299.28
Temperature/K	293
Crystal system	monoclinic
Space group	I2/a
a/Å	25.282(2)
b/Å	3.7619(2)
c/Å	35.085(3)
α/°	90
β/°	92.481(7)
γ/°	90
Volume/Å^3	3333.7(4)
Z	8
ρcalcg/cm^3	1.1925
μ/mm^{-1}	0.091
F(000)	1232.6
Crystal size/mm^3	0.25 × 0.1 × 0.1
Radiation Mo Kα	0.71073
2Θ range for data collection/°	6.46 to 55.06
Index ranges	$-32 \leq h \leq 32$, $-4 \leq k \leq 4$, $-45 \leq l \leq 44$
Reflections collected	19238
Independent reflections	3650 [Rint = 0.1031, Rsigma = 0.1281]
Data/restraints/parameters	3650/0/199
Goodness-of-fit on	F2 0.920
Final R indexes	[I>=2σ (I)] R1 = 0.0700, wR2 = 0.1632

Table SI-3. Bond Length (Å) and bond angles (°)

Atom Atom	Length/Å	Atom Atom	Length/Å
F001 C00C	1.356(4)	C008 C00G	1.390(4)
F002 C00L	1.364(4)	C009 C00A	1.445(5)
N003 N004	1.396(4)	C009 C00F	1.373(5)
N003 C00D	1.374(4)	C009 C00I	1.379(5)
N003 C00K	1.384(4)	N00B C00K	1.342(4)
N004 C00A	1.268(4)	C00C C00E	1.365(5)
N005 N006	1.408(4)	C00C C00H	1.364(5)
N005 C00D	1.303(4)	C00F C00J	1.369(5)
N006 C00K	1.295(5)	C00G C00H	1.382(5)
C007 C008	1.380(4)	C00I C00M	1.381(5)
C007 C00E	1.371(4)	C00J C00L	1.366(5)
C008 C00D	1.468(5)	C00L C00M	1.344(5)
Bond angles (°)			
C00D N003 N004 121.9(3) N005 C00D N003 109.0(4)		C00D N003 N004 121.9(3) N005 C00D N003 109.0(4)	
C00K N003 N004 129.6(3) C008 C00D N003 125.5(4)		C00K N003 N004 129.6(3) C008 C00D N003 125.5(4)	
C00K N003 C00D 105.9(3) C008 C00D N005 125.5(4)		C00K N003 C00D 105.9(3) C008 C00D N005 125.5(4)	
C00A N004 N003 117.1(3) C00C C00E C007 118.6(4)		C00A N004 N003 117.1(3) C00C C00E C007 118.6(4)	
C00D N005 N006 108.1(3) C00J C00F C009 122.0(4)		C00D N005 N006 108.1(3) C00J C00F C009 122.0(4)	
C00K N006 N005 107.4(3) C00H C00G C008 120.0(4)		C00K N006 N005 107.4(3) C00H C00G C008 120.0(4)	
C00E C007 C008 120.8(4) C00G C00H C00C 118.6(4)		C00E C007 C008 120.8(4) C00G C00H C00C 118.6(4)	
C00D C008 C007 123.5(4) C00M C00I C009 121.5(4)		C00D C008 C007 123.5(4) C00M C00I C009 121.5(4)	
C00G C008 C007 119.4(4) C00L C00J C00F 117.5(4)		C00G C008 C007 119.4(4) C00L C00J C00F 117.5(4)	
C00G C008 C00D 117.1(4) N006 C00K N003 109.5(4)		C00G C008 C00D 117.1(4) N006 C00K N003 109.5(4)	
C00F C009 C00A 122.1(4) N00B C00K N003 124.3(4)		C00F C009 C00A 122.1(4) N00B C00K N003 124.3(4)	
C00I C009 C00A 120.2(4) N00B C00K N006 125.9(4)		C00I C009 C00A 120.2(4) N00B C00K N006 125.9(4)	
C00I C009 C00F 117.7(4) C00J C00L F002 118.5(5)		C00I C009 C00F 117.7(4) C00J C00L F002 118.5(5)	
C009 C00A N004 120.0(4) C00M C00L F002 118.1(5)		C009 C00A N004 120.0(4) C00M C00L F002 118.1(5)	
C00E C00C F001 118.1(4) C00M C00L C00J 123.4(4)		C00E C00C F001 118.1(4) C00M C00L C00J 123.4(4)	
C00H C00C F001 119.3(4) C00L C00M C00I 117.8(4)		C00H C00C F001 119.3(4) C00L C00M C00I 117.8(4)	
C00H C00C C00E 122.6(4)		C00H C00C C00E 122.6(4)	

10. Computational Methods:

Computational Methods

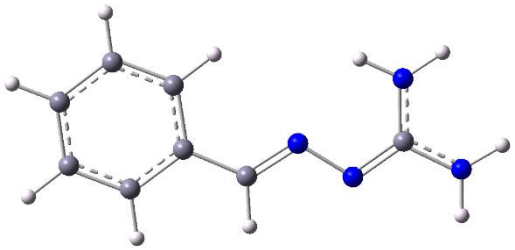
The quantum chemical calculations were performed using the Gaussian 09[1] suite of programs. Geometry optimization of compounds was performed by DFT[2] using B3LYP[3] method. The basis set used was 6-311++G(d,p). The frequency calculations were carried out on all the structures to verify stationary point with zero negative frequency. The NBO charges were calculated.[4]

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford CT, 2009.
2. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules* New York: Oxford University Press, 1989.
3. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, **1988**, *37*, 785-789.
4. Bamba, K.; Patrice, O. W.; Ziao N. *Computational Chem.*, **2016**, *5*, 51-64.

11. Cartesian Coordinates of 1a, 1a' and 1a-I_2

1w

Absolute Gibbs free energy = -529.870125



0 1

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H	-4.59934100	-1.48361700	0.00000200
H	-5.35510300	0.07964100	-0.00000100
N	-2.25386200	-0.77039600	0.00000000
N	-1.04670000	-0.10843300	-0.00000200
N	-3.16320300	1.41254900	0.00000000
H	-2.22678100	1.78501300	-0.00000200
H	-3.95866800	2.02385000	0.00000000
C	-3.26823100	0.05671000	0.00000000
C	-0.01564200	-0.87384100	-0.00000200
C	1.35585200	-0.36397200	-0.00000100
C	2.41909100	-1.28024400	0.00000000
H	2.20210100	-2.34363300	0.00000000
C	3.74153400	-0.84365800	0.00000100
H	4.54849000	-1.56802900	0.00000100
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C	1.65761400	1.00922800	-0.00000100
H	0.84381300	1.72349800	-0.00000100
C	2.97658600	1.44309100	0.00000000
H	3.19263900	2.50605100	0.00000000
H	5.05472600	0.86355600	0.00000200
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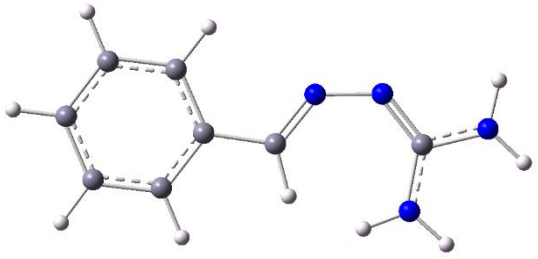
1w'

Absolute Gibbs free energy = - 529.835744



0 1

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N	-0.93988700	-0.84903500	-0.00013300
N	-3.01717600	1.37085900	-0.00006100
H	-2.11088100	1.79235700	-0.00007700
H	-3.81299800	1.98690700	-0.00004200
C	-3.17880200	0.01023400	0.00004800
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C	1.26121100	0.09272900	-0.00008200
C	2.03980600	1.25886700	0.00000100
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C	3.43129000	1.19059400	0.00008900
H	4.01683700	2.10339100	0.00014700
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C	1.91297500	-1.15190200	-0.00006100
H	1.30880200	-2.05039000	-0.00012800
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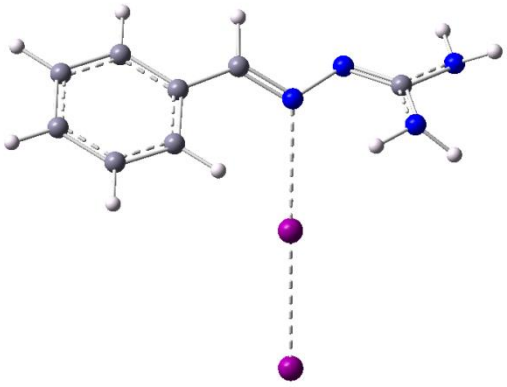
1w-I_2



Absolute Gibbs free energy = -552.661422

0 1

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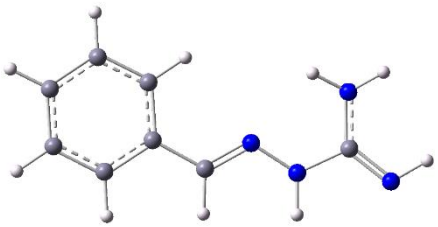
N	-1.82549000	2.65957200	-0.58512000
N	-1.86890900	1.36403600	-0.11856900
N	-0.73862800	3.24318100	1.45264600
H	-0.82496100	2.28052100	1.74738800
H	0.13016200	3.68037200	1.72553800
C	-1.16268100	3.48577100	0.17201500
C	-2.87767300	0.67480100	-0.52863900
C	-3.16182400	-0.71247900	-0.17569700
C	-4.12953400	-1.39505300	-0.93127800
H	-4.61965800	-0.88400700	-1.75335400
C	-4.45747000	-2.71578500	-0.64298700
H	-5.19974100	-3.23103600	-1.24168200
C	-3.83284600	-3.37136200	0.41629600
C	-2.54772700	-1.38142300	0.89629200
H	-1.81731800	-0.86487600	1.50346800
C	-2.88356300	-2.69685500	1.18728200
H	-2.40441500	-3.20068000	2.01892500
H	-4.08839200	-4.39937200	0.64674500
H	-3.59383200	1.17361500	-1.18537300
I	0.65052100	0.19633100	-0.04591400
I	3.35229700	-0.95728300	-0.10291500

1b



Absolute Gibbs free energy = -529.863074

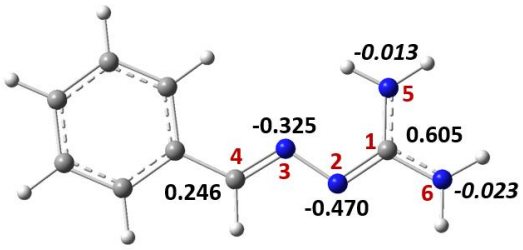
0 1

C	-4.01173500	0.54329500	0.04070400
C	-3.73913600	-0.82257100	0.03210400
C	-2.42096500	-1.27059900	0.00309700

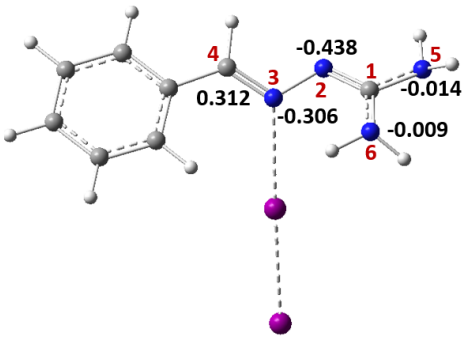
C	-1.35250400	-0.36161400	-0.01723700
C	-1.63999200	1.01403200	-0.00927300
C	-2.95512700	1.45792700	0.01946600
H	-5.03674100	0.89539700	0.06265000
H	-4.55157400	-1.54027800	0.04761700
H	-3.16199200	2.52242200	0.02427500
C	0.01442600	-0.88043000	-0.04723200
H	0.12591800	-1.97021300	-0.07282800
N	1.04758800	-0.11781500	-0.04349800
N	2.26612600	-0.68663800	-0.08217700
C	3.43718900	0.06148000	0.01176700
N	4.53194400	-0.59351900	0.13566400
H	5.34173400	0.02033600	0.14743900
N	3.24790600	1.42233800	-0.10246400
H	2.30283800	1.75276600	0.03315300
H	3.98025200	2.00586800	0.26733600
H	2.38927900	-1.69367500	-0.03054500
H	-0.82255900	1.72396200	-0.02818300
H	-2.21503100	-2.33626200	-0.00396000

12. NBO Charges on reactive centers in 1w, 1x and 1w-I_2

1w



1w-I_2



1w-HY

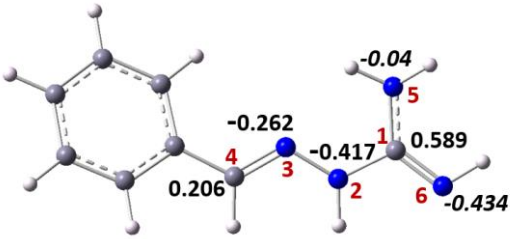


Figure-SI-3: The NBO charges at the various atoms in the azine (**1w**), Azine-I_2 complex (**1w-I_2**), and the hydrazone (**1w-HY**) forms.