Supporting Information for:

Selectivity as a Determining Factor in Peroxidative Methane Oxidation by Multi-metallic Copper Complexes

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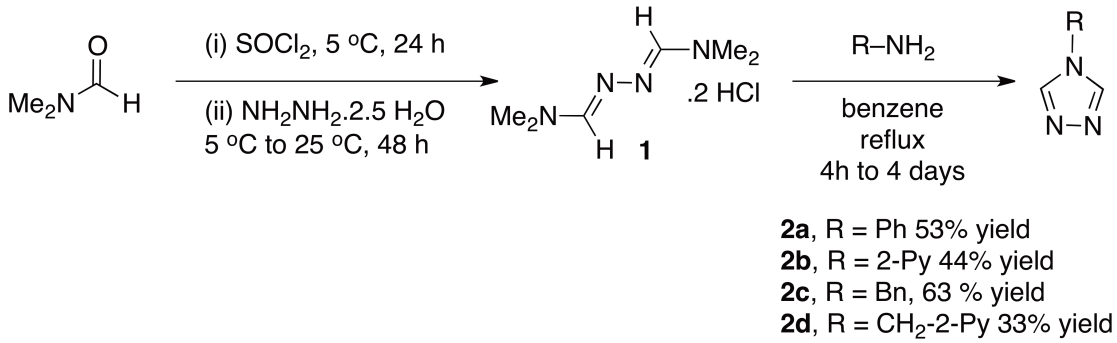
1. General Experimental

Glassware was dried for 12 hours at 120 ^{o}C prior to use. d_6-Benzene and d_8-toluene were dried over molten K, distilled, and stored over molecular sieves prior to use. D_3-MeCN and d_6-dmso were used as received. NMR spectra were obtained on Bruker 300, 400 or 500 MHz machines, all peaks are referenced against residual solvent and values are quoted in ppm. Data were processed in Topspin or MestReNova. Infrared spectra were obtained from solids on an ATR cell. GC-FID measurements were made with an Agilent 7820 GC equipped with a DB-WAX column. Elemental Analyses were performed by Stephen Boyer of London Metropolitan University. **4** was prepared according to the literature procedure.[4]

2.1 Preparation of 4-susbtituted triazoles

Scheme S1. Synthesis of 4-substituted Triazoles



Synthesis of N,N-Dimethylformamide Azine Dihydrochloride **(1):**[1] DMF was dried over $MgSO_4$ and freshly distilled before use. Stirred DMF (150 mL) in a two-necked flask was purged with Ar and cooled to 5 ^oC with a water ice mixture. Thionyl chloride (28.6 mL, 0.4 mol) was added to the mixture slowly by a dropping funnel. The solution was allowed to slowly warm to room temperature and stirred for 24 h. After which point the mixture was again cooled to 5 ^oC and $H_2N–NH_2$ dissolved in DMF (50 mL) was added dropwise. After stirring for 48 h, the precipitate was isolated by filtration. The salt, $C_6H_{14}N_4.2HCl$, was washed with DMF (20 mL) and Et_2O (2x20 mL) and used without further purification (5.9 g, 27.6 mmol, 28 %; Lit.[1] yield = 91 %).

Synthesis of 4-phenyl-4H-1,2,4-triazole (**2a**):[1] A mixture of aniline (1.02 g, 10.9 mmol) and the azine (**1**) (2.35 g, 10.9 mmol, 1 equiv.) were refluxed in benzene for 4 h. A sticky precipitate gradually formed over time. Following cooling to room temperature, the solvent was removed and the crude dissolved in DCM (100 mL) and washed with 30 % NaOH (2 x 50 mL). The organic layer was dried with $MgSO_4$ and the solvent removed to give the crude product. The material was sublimed twice at 1 x 10^{-2} mbar using a heatgun without careful control of the temperature (<350 ^oC) to give 4-phenyl-4H-1,2,4-triazole as a colorless solid (0.84g, 5.8 mmol, 53 %, Lit[1] 60%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ : 7.38 - 7.43 (m, 2H), 7.47 - 7.53 (m, 1H), 7.54 - 7.58 (m, 2H), 8.94 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz, 298 K) δ : 122.3, 129.2, 130.4, 133.9, 141.5. Infrared (ATR cell, cm^{-1}) 3120 (s), 1658, 1590, 1520 (s), 1495, 1267, 1222, 1092, 770.

Synthesis of 4−(pyridin−2−yl)−4H−1,2,4−triazole (**2b**): 2-aminopyridine (0.88 g, 9.3 mmol) was added dropwise to a slurry of the azine (**1**) (2.0 g, 9.3 mmol, 1 equiv.) in benzene (20 mL). The mixture was warmed gently and then heated to reflux for 2 days. ^{1}H NMR analysis of an aliquot showed a mixture of starting material and product. Additional **1** (1.0 g, 0.5 equiv.) was added and the reaction mixture refluxed for an additional 4 days. The solvent was removed and the crude purified by flash column chromatography on silica gel using a DCM to DCM:MeOH gradient of 100:0 to 95:5. Isolation and recrystallization from hot n-hexane:DCM gave the product as colorless needles (0.598 g, 4.1 mmol, 44%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.35 (dd, 1H, J = 8.0 and 4.8 Hz), 7,45 (d, 1H, J = 8.0 Hz), 7.91 (ddd, 1H, J = 8.0, 8.0 and 2.0 Hz), 8.51 (dd, 1H, J = 4.8 and 2.0 Hz), 8.90 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 113.2, 123.5, 139.7, 139.9, 146.6, 149.7. Infrared (ATR cell, cm^{-1}) 3123, 1594, 1503, 1444, 1241, 1222, 1095, 787.

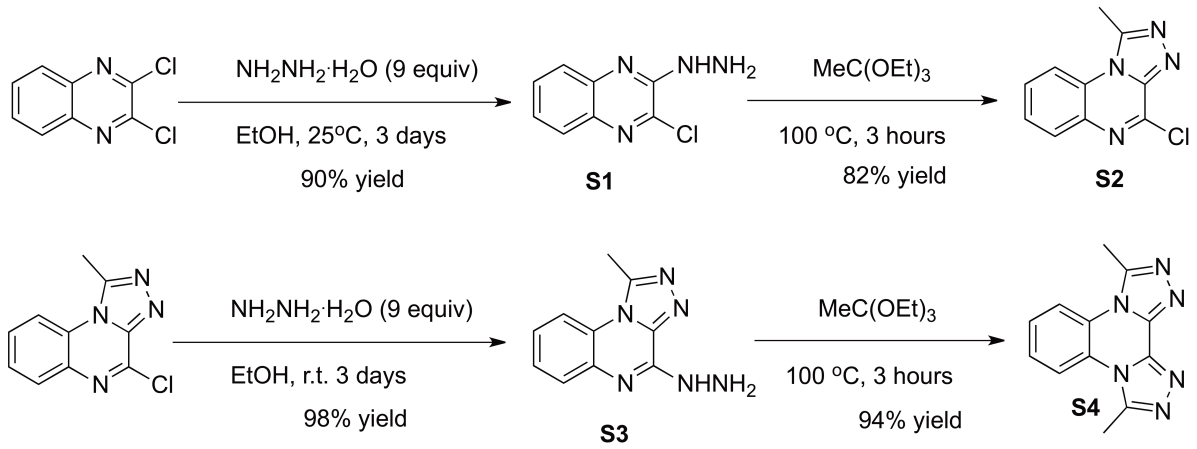
Synthesis of 4-benzyl-4H-1,2,4-triazole (**2c**):[2] Benzylamine (0.51 mL, 4.7 mmol) was added dropwise to a slurry of the azine (**1**) (2.0 g, 9.3 mmol, 2 equiv.) in toluene (20 mL). The mixture was heated gently to aid dissolution and then refluxed. After 48 h at reflux the mixture was cooled to room temperature and the solvent removed under reduced pressure, DCM (100 mL) was added and the mixture washed with sat. aqueous K_2CO_3 (2 x 50 mL). The aqueous phase was extracted with DCM (100 mL), the organic phases combined and dried over $MgSO_4$. The mixture was filtered and the solvent removed. The crude product was purified by recrystallization from a n-hexane:DCM mixture to give **2c** as large colourless neeedles. Isolated as two crops (0.46 g, 2.88 mmol, 61 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 5.20 (s, 2H), 7.19 - 7.21 (m, 2H), 7.39 - 7.41 (m, 3H), 8.19 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 49.1, 127.7, 128.9, 129.3, 134.1, 142.9. Infrared (ATR cell, cm^{-1}) 3130, 3084, 3029, 1679, 1533, 1519, 1454, 1181, 1075, 711.

Synthesis of 4-(pyridine-2-yl-methyl)-4H-1,2,4-triazole (**2d**):[1] A mixture of 2-(aminomethylpyridine) (1.29 g, 11.9 mmol) and the azine (**1**) (2.56 g, 11.9 mmol, 1 equiv.) were dissolved in benzene (20 mL) and gently warmed to aid dissolution and then heated to reflux for 14h. The solvent was removed and the crude material purified using flash column chromatography on silica. The column was first

flushed with dichloromethane then a 90:10:1 mixture of DCM:MeOH:Et_3N. The product was isolated as an off-white solid which could be further purified by hot recyrstallization from n-hexane:DCM (0.64 g, 4.0 mmol, 33 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 5.29 (s, 2H), 7.14 (d, 1H, J = 7.6 Hz), 7.26-7.29 (m, 1H), 7.70 (ddd, 1H, J = 7.6, 7.6 and 1.6 Hz), 8.29 (s, 2H), 8.59 (d, 1H, J = 4.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 50.2, 121.8, 123.6, 137.5, 143.1, 150.2, 154.0. Infrared (ATR cell, cm^{-1}) 3108, 1601, 1573, 1480, 1429, 1295, 1186, 1080, 749.

2.2 Preparation of a bis(triazole) 1,6-dimethyl-bis[1,2,4]triazolo[4,3-a:3',4'-c]quinoxaline (S4)

Scheme S2. Synthesis of the bis(triazole) **S4**



*Synthesis of 4-chloro-1-methyl-[1,2,4]Triazolo[4,3-a]quinoxaline **S2**:*[3] 2,3-dichloroquinoxaline (4.85 g, 24.3 mmol) was suspended in ethanol and hydrazine hydrate (9.4 mL, 200 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 3 days and the product was isolated by filtration and washed with ethanol and hexane to afford 4.2 g of 2-Chloro-3-hydrazinoquinoxaline **S1** as a white solid (90% yield). This material was used directly without further purification or analysis. A mixture of 2-Chloro-3-hydrazinoquinoxaline (0.610 g, 3.12 mmol) and triethyl ortoformate (10 mL) was stirred at 100 ^{0}C for 3 hours, cooled to room temperature and filtered. The solid obtained was isolated by filtration, washed with cyclohexane and dried under vacuum to yield 4-chloro-1-methyl-[1,2,4]triazolo[4,3-a]quinoxaline **S2** as a white solid (82%). ^{1}H NMR (dmso-d_6, 400 MHz, 298 K) δ

3.12 (s, 3H), 7.75 (t, 1H, *J* = 7.5 Hz), 7.83 (t, 1H, *J* = 8.0 Hz), 8.06 (d, 1H, *J* = 5.0 Hz),8.39 (d, 1H, *J* = 7.4 Hz); ^{13}C NMR (dmso-d^{6}, 100 MHz, 298 K) δ 14.5, 116.5, 126.3, 127.7, 129.1, 130.0, 134.8, 141.2, 142.6, 149.5. Infrared (ATR cell, cm^{-1}): 3108, 1517, 1492, 1409, 1141. Mass Spec. (ESI, +ve): 219 [M+]. High-resolution mass spec. calc. for $C_{10}H_8N_4Cl$ 219.0437 found 219.0446.

Synthesis of 4-hydrazino-1-methyl-[1,2,4]Triazolo[4,3-a]quinoxaline ***S3***:[3] 4 (0.215 g, 0.99 mmol) was suspended in ethanol and hydrazine hydrate (0.430 mL, 8.9 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 3 days and the product was isolated by filtration, washed with ethanol and hexane and dried under vacuum to yield **S3** as a white solid (98%). ^{1}H NMR (dmso-d_6, 400 MHz, 298 K) δ 9.43 (bs, 1H), 8.12 (bs, 1H), 7.64 (bs, 1H), 7.47 (bs, 1H), 7.33 (bs, 1H), 4.68 (bs, 2H), 3.04 (s, 3H); 13C NMR (dmso-d6, 100 MHz, 298 K) δ 148.2, 146.5, 138.7, 137.4, 127.1, 126.0, 123.6, 122.9, 115.9, 14.5. Infrared (ATR cell, cm^{-1}): 3260, 1551, 1149. Mass Spec. (ESI, +ve): 215 [M+H].

Synthesis 1,6-dimethyl-Bis[1,2,4]triazolo[4,3-a:3',4'-c]quinoxaline S**4**:[3] A mixture of 4-hydrazino-1-methyl-[1,2,4]Triazolo[4,3-a]quinoxaline (0.279 g, 1.3 mmol) and triethyl orthoformate (4 mL, large excess) was stirred at 100 ^{o}C for 3 hours, and cooled to room temperature. The product was isolated by filtration, was washed with cyclohexane and dried under vacuum to obtain **S4** as a white solid in 94% yield. ^{1}H NMR (dmso-d_6, 400 MHz, 298 K) δ 8.34 (dd, 2H, *J* = 6.4 and 2.9 Hz), 7.70 (dd, 2H, *J* = 6.4 and 3.0 Hz), 3.06 (s, 6H); ^{13}C NMR (dmso-d_6, 100 MHz, 298 K) δ 148.5, 140.2, 127.5, 124.1, 118.0, 14,9. Infrared (ATR cell, cm^{-1}): 3137, 2993, 1491, 1407, 1149. Mass spec. (ES): 239 [M+H]. High-resolution mass spec. calc. for $C_{12}H_{11}N_6$ 239.1045 found 239.1056.

All attempts to generate copper(II) and copper(I) complexes from **S4** failed due to its low solubility in common solvents.

3.1 Cyclohexane Oxidation

General procedure: Experiments were carried out in a 20 mL sealed vial. The vial was charged with the catalyst (0.01 mmol), CH_3CN (3 mL), cyclohexane (0.54 mL, 5 mmol), an aqueous solution of H_2O_2 (30% wt. in H_2O, 0.5 mL, 5 mmol) and HNO_3 (70% wt. in H_2O, 13 μL, 0.2 mmol, when specified). After sealing the vial, the whole mixture was stirred at 30 ^{0}C for the reaction time. Then a known amount of a solution of ISTD in ether was added and the whole mixture stirred for 10 more minutes. A 1 mL aliquot was taken and filtered before being analysed in the GC.

Table S1. Oxidation of Cyclohexane catalysed by copper complexes[a]

Entry	Catalyst	n (H_2O_2)/ n (catalyst)	t (h)	TON[f]		
				Cyclohexanol	Cyclohexanone	Total[g]
1	**3a**	500	2	10.4	4.8	15.2
2	**3a**/HNO_3[c]	500	2	4	3	7
3	**3a**	500	20	11.3	4.5	15.8
4	**3a**/HNO_3[c]	500	20	12.7	4.2	16.9
5[b]	**3a**	5000	2	0	0	0
6[b]	**3a**/HNO_3[d]	5000	2	0	0	0
7[b]	**3a**	5000	20	15.9	27.2	43.1
8[b]	**3a**/HNO_3[d]	5000	20	49.8	30.8	80.6
9	**3b**	500	2	10.9	3.9	14.8
10	**3b**/HNO_3[c]	500	2	1.7	0	1.7
11	**3b**	500	20	10	3.9	13.9
12	**3b**/HNO_3[c]	500	20	13.5	4.0	17.5
13[b]	**3b**	5000	2	0	0	0
14[b]	**3b**/HNO_3[d]	5000	2	0	0	0
15[b]	**3b**	5000	20	16.4	27.3	43.7
16[b]	**3b**/HNO_3[d]	5000	20	54.1	36.5	90.6
17	**3c**/HNO_3[c]	500	20	7.1	3.2	10.3
18[b]	**3c**/HNO_3[d]	5000	20	0	0	0
19	**3d**/HNO_3[c]	500	20	7.5	3.5	11
20[b]	**3d**/HNO_3[d]	5000	20	0	0	0
21	**4**/ HNO_3	500	72	11.4	3.8	15.2
22[e]	**4**/ HNO_3	400	72	1.1	1.9	3
23	$Cu(NO_3)_2$	500	2	0	0	0
24	$Cu(NO_3)_2$	500	20	1.5	0	1.5
25[b]	$Cu(NO_3)_2$ HNO_3[c]	5000	2	0	0	0
26[b]	$Cu(NO_3)_2$ HNO_3[c]	5000	20	0	0	0

[a] Reaction Conditions: Catalyst (0.01 mmol), H_2O_2 (5 mmol), cyclohexane (5 mmol). [b] Catalyst (0.001 mmol). [c] HNO_3 (0.2 mmol). [d] HNO_3 (0.02 mmol). [e] Reaction conditions taken from Ref 4. Catalyst (0.0125 mmol), H_2O_2 (5 mmol), cyclohexane (0.63 mmol), HNO_3 (0.12 mmol), 25 ^{o}C. Results obtained by Pombeiro and coworkers Ref. 4 TON: Cyclohexanol (10.5), Cyclohexanone (4.9), Total (15.3). [f] Turnover number (moles of product per mol of catalyst). Analyzed by GC-FID using chlorobenzene as internal standard [g] Cyclohexanol + Cyclohexenone.

3.2 Methane Oxidation

Table S2. Oxidation of methane catalysed by copper complexes[a]

Entry	Catalyst	Solvent	n (H_2O_2)/ n (catalyst)	Amount MeOH				Amount of CO_2 (μmol)
				GC method[f]		NMR method[g]		
				μmol	TON[h]	μmol	TON[h]	
1	**3b**	H_2O	1000	11.5	0.12	-	-	
2	**3b**	CH_3CN/H_2O	1000	50.3	0.50	-	-	
3[b]	**3b**/HNO_3	CH_3CN/H_2O	1000	131.9	1.32	-	-	
4[b][c]	**3a**/HNO_3	CH_3CN/H_2O	3000	94.6	2.86	104.6	3.17	
5[b][c]	**3b**/HNO_3	CH_3CN/H_2O	3000	102.1	3.09	108.0	3.27	
6[d]	**3a**/HNO_3	CH_3CN/H_2O	3000	64.0	3.8	57.1	3.4	3700
7[d]	**3b**/HNO_3	CH_3CN/H_2O	3000	73.5	4.3	77.9	4.6	3900
8[e]	**4**/HNO_3	CH_3CN/H_2O	1000	69.4	1.4	71.6	1.4	3650
9	$Cu(NO)_3$	CH_3CN/H_2O	1000	21.9	0.22	-	-	-
10[b]	$Cu(NO)_3$/ HNO_3	H_2O	1000	12.1	0.18	-	-	-
11[b]	$Cu(NO)_3$/ HNO_3	CH_3CN/H_2O	1000	138.4	1.38	-	-	-
12[d]	$Cu(NO)_3$/ HNO_3	CH_3CN/H_2O	3000	43.8	2.6	34.9	2.1	3000

[a] Reaction Conditions: Catalyst (0.1 mmol), H_2O_2 (100 mmol), methane (30 bar). [b] HNO_3 (2 mmol). [c] Reaction conditions: Catalyst (0.03 mmol), H_2O_2 (100 mmol), methane (30 bar). [d] Reaction conditions: Catalyst (0.017 mmol), H_2O_2 (50 mmol), HNO_3 (1 mmol), methane (30 bar), V= 20mL. [e] Reaction conditions from Ref. 4 scaled up to V=20 mL, Catalyst (0.05 mmol), H_2O_2 (50 mmol), HNO_3 (1 mmol), methane (30 bar). [f] Analyzed by GC-FID. [g] Analyzed by 1H-NMR following a solvent suppression protocol, DMSO as internal standard. [h] Turnover number (moles of product per mol of catalyst).

4. X-ray Crystallographic Data

The X-ray crystal structure of 3b

The hydrogen atoms of the four coordinated water molecules in the structure of **3b** were all located from Δ*F* maps and refined freely subject to an O–H distance constraint of 0.90 Å. Those of the included 50% occupancy water molecule could not be located and were omitted from the atom list; this water molecule was assigned as being 50% occupancy based on its thermal parameter.

The location of the nitrogen atom in each of the C(6)-, C(26)-, C(46)-, C(66)-, C(86)-, C(106)-, C(126)- and C(146)-based pyridyl rings was unambiguously determined in every case on the basis of (i) the thermal parameters of the two possible positions when both were refined as carbon atoms, (ii) the location from a ΔF map of the C–H hydrogen atom on one of the possible positions, and (iii) consideration of the bond lengths involving the two possible positions.

The X-ray crystal structure of 4

The cation in the structure of **4** was found to have crystallographic C_2 symmetry about an axis that passes through O(23) and bisects the Cu(1)–O(23)–Cu(1A) and Cu(2)–O(23)–Cu(2A) angles. The encapsulating triethanolamine-based ligand was found to be highly disordered with two orientations for each of the six unique $–CH_2–CH_2–O$ arms being identified. This disorder can be seen as corresponding to rotations of *ca*. 33 and 34° about the N(1)–Cu(1) and N(11)–Cu(2) vectors respectively, and as such all of the disorder is linked. The two orientations were found to have occupancies of *ca*. 52 and 48%, their geometries were restrained to be similar, the thermal parameters of adjacent atoms were likewise restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). Given the extensive nature of this disorder, and the C_2 symmetry of the complex, the possibility of the disorder being a consequence of approximate rather than perfect C_2 symmetry was investigated. This was done by solving and refining the structure using the lower symmetry space group without the 2-fold axis (space group *Cc*, no. 9). The resulting structure was found to have no reduction in the amount of disorder, and so the higher symmetry version presented here was preferred.

Both of the BF_4 anions were found to be disordered across C_2 axes. For the B(10)-based anion two unique orientations were identified of *ca*. 35 and 15% occupancy, whilst for the B(20)-based anion three unique orientations were identified of *ca*. 21, 21 and 8% occupancy. The geometries of all the orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

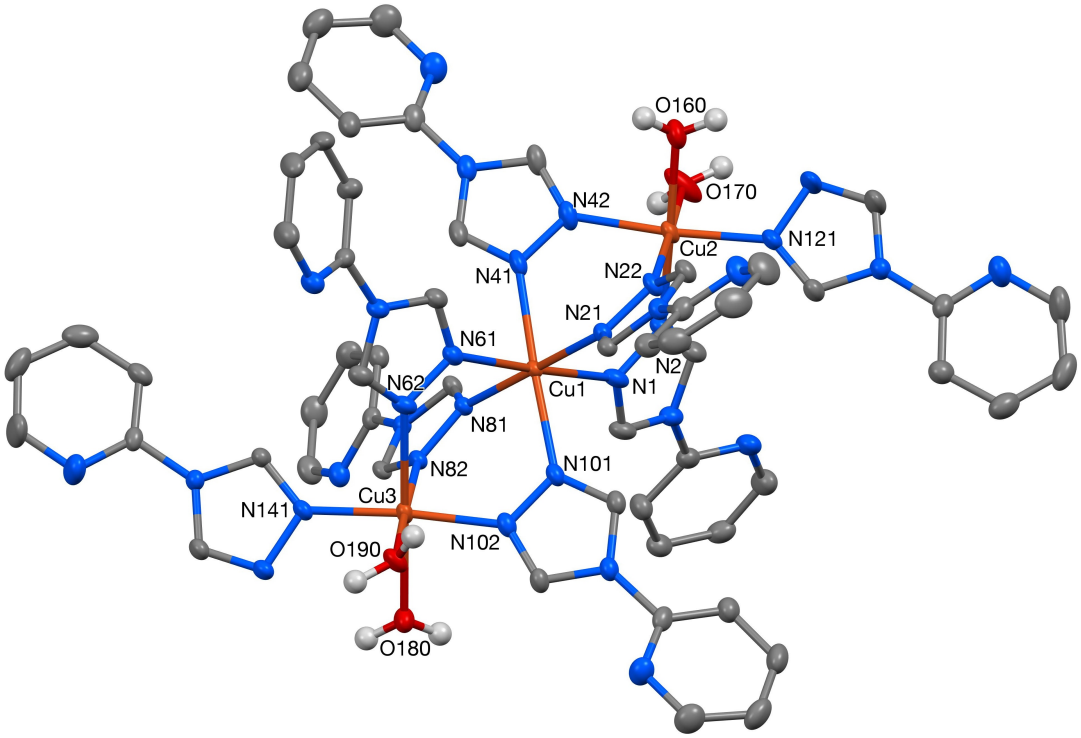


Figure. S1 The structure of the cation present in the crystal of **3b** (50% probability ellipsoids).

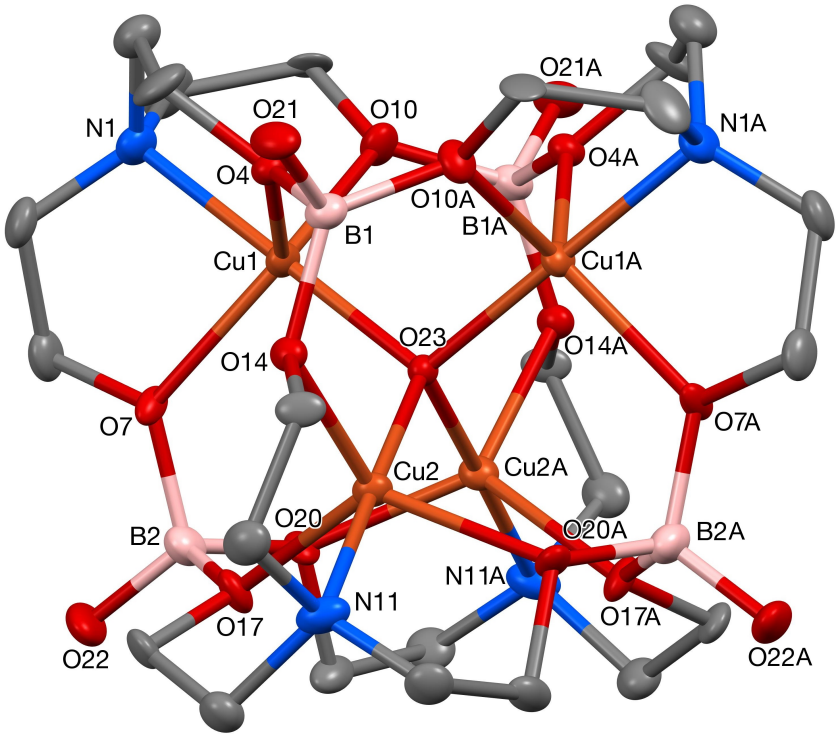


Figure. S2 The structure of the C_2-symmetric cation present in the crystal of **4** (50% probability ellipsoids).

5. References

1. a) A. D. Naik, J. Marchand-Brynaert, Y. Garcia, *Synthesis* **2008**, *1*, 149. B) S. B. Muñoz, III, W. K. Foster, H.-J. Lin, C. G. Margarit, D. A. Dickie, J. M. Smith, *Inorg. Chem.* **2012**, *51*, 12660.

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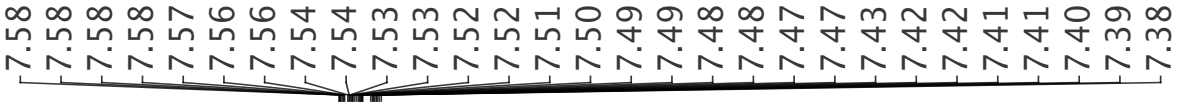
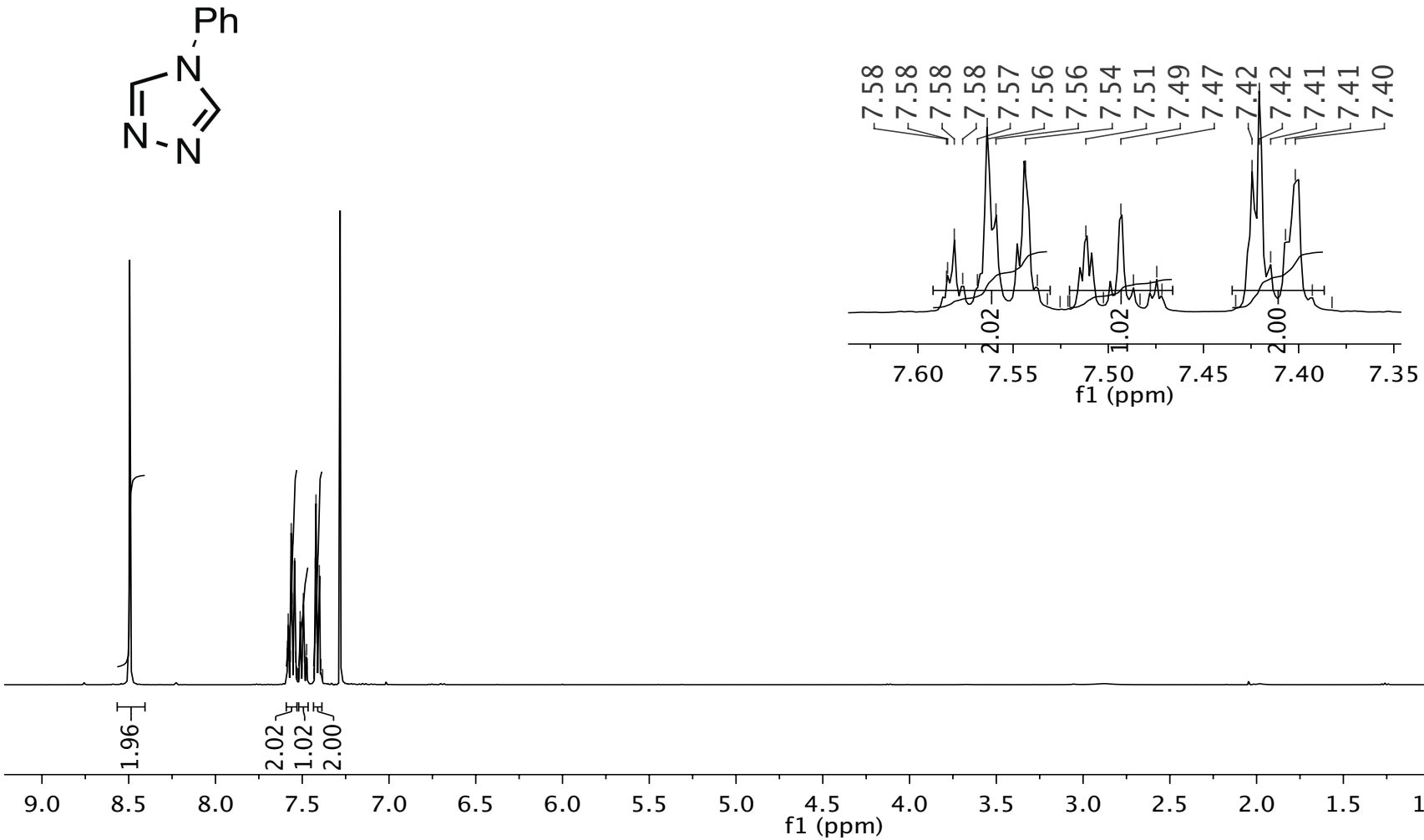


^{1}H NMR ($CDCl_3$, 298 K, 400 MHz)



141.5
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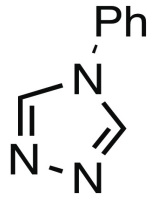
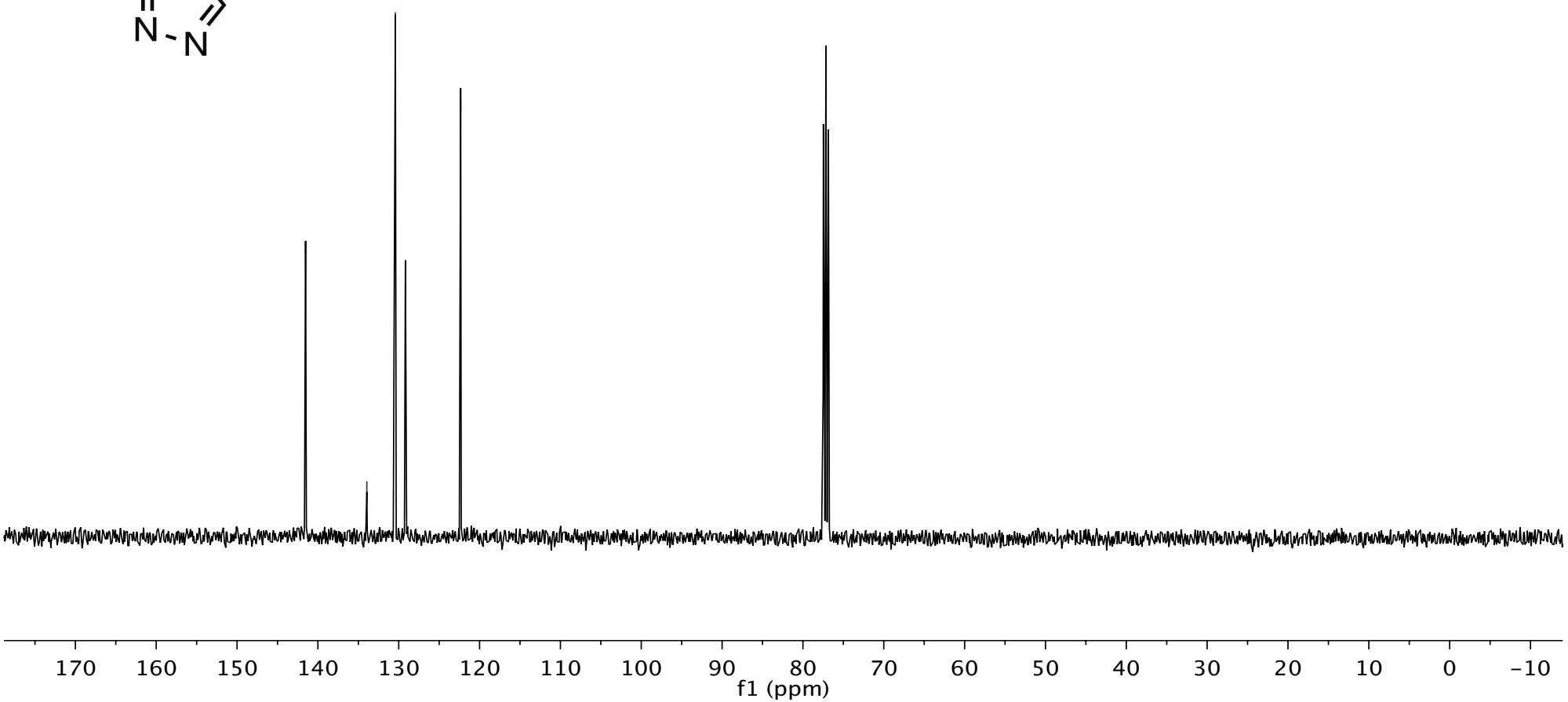
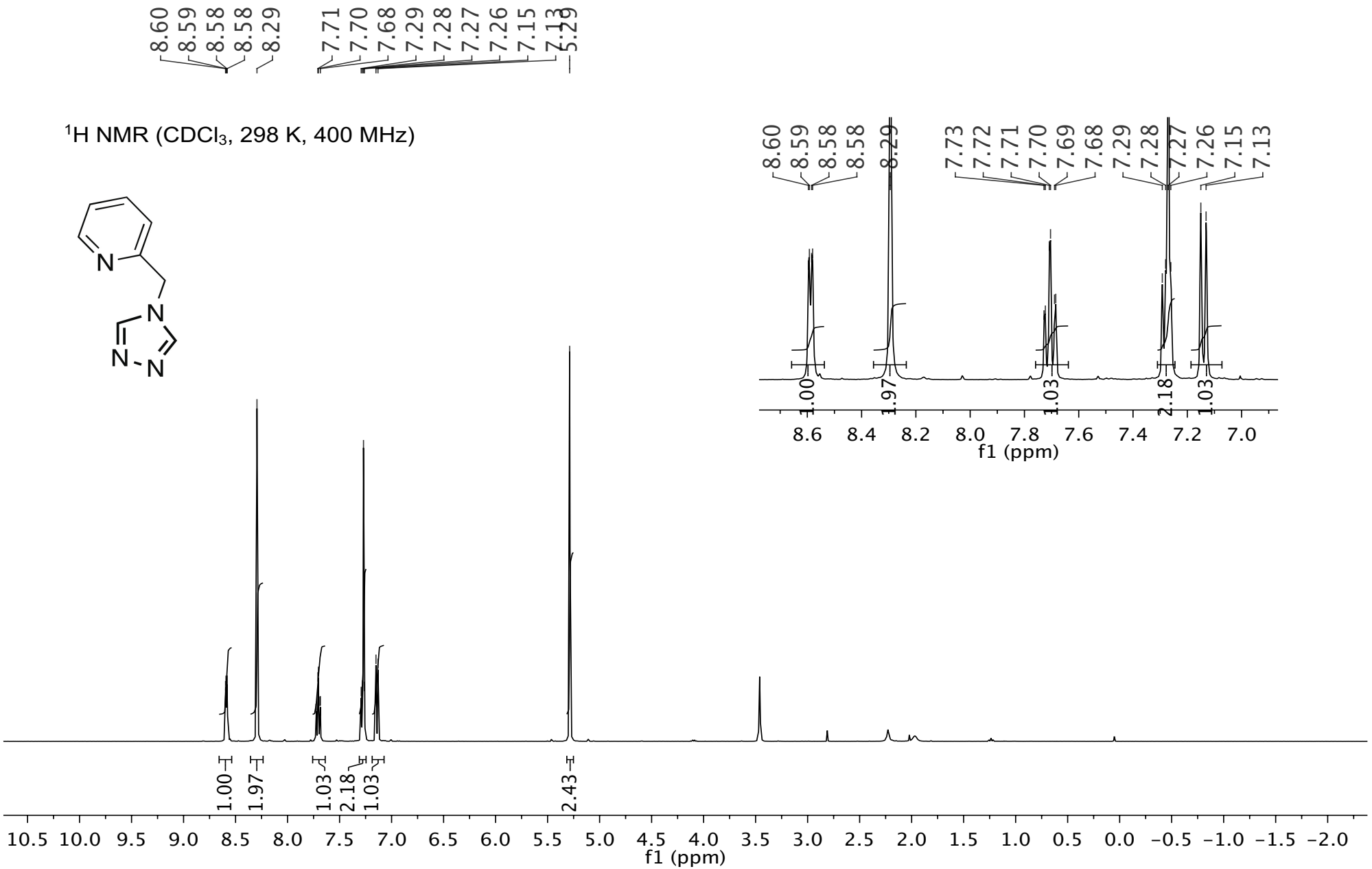
130.4
129.2
122.3

^{13}C NMR ($CDCl_3$, 298 K, 100 MHz)



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7.27
7.26
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7.13
5.29
1H NMR (CDCl3, 298 K, 400 MHz)
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N
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N
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1.97
1.03
2.18
1.03
2.43
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8.58
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7.15
7.13
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8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
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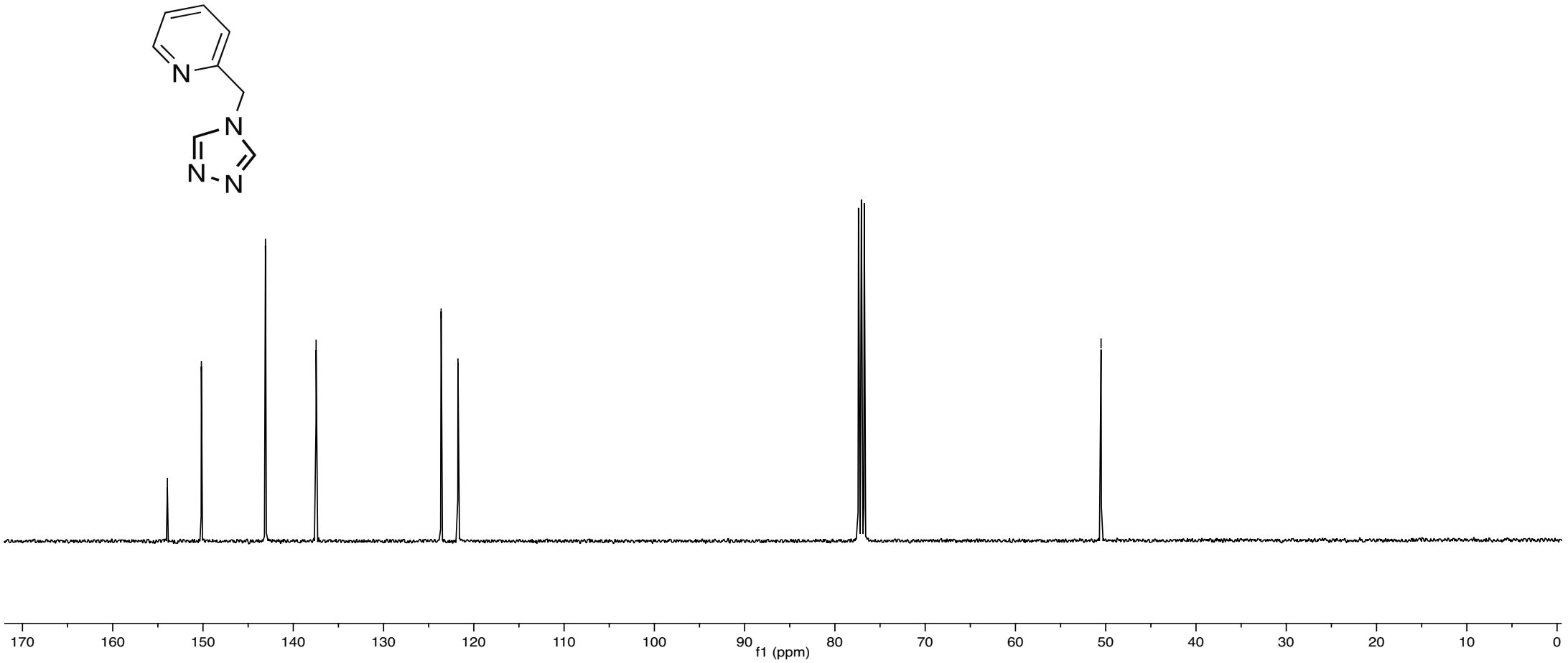
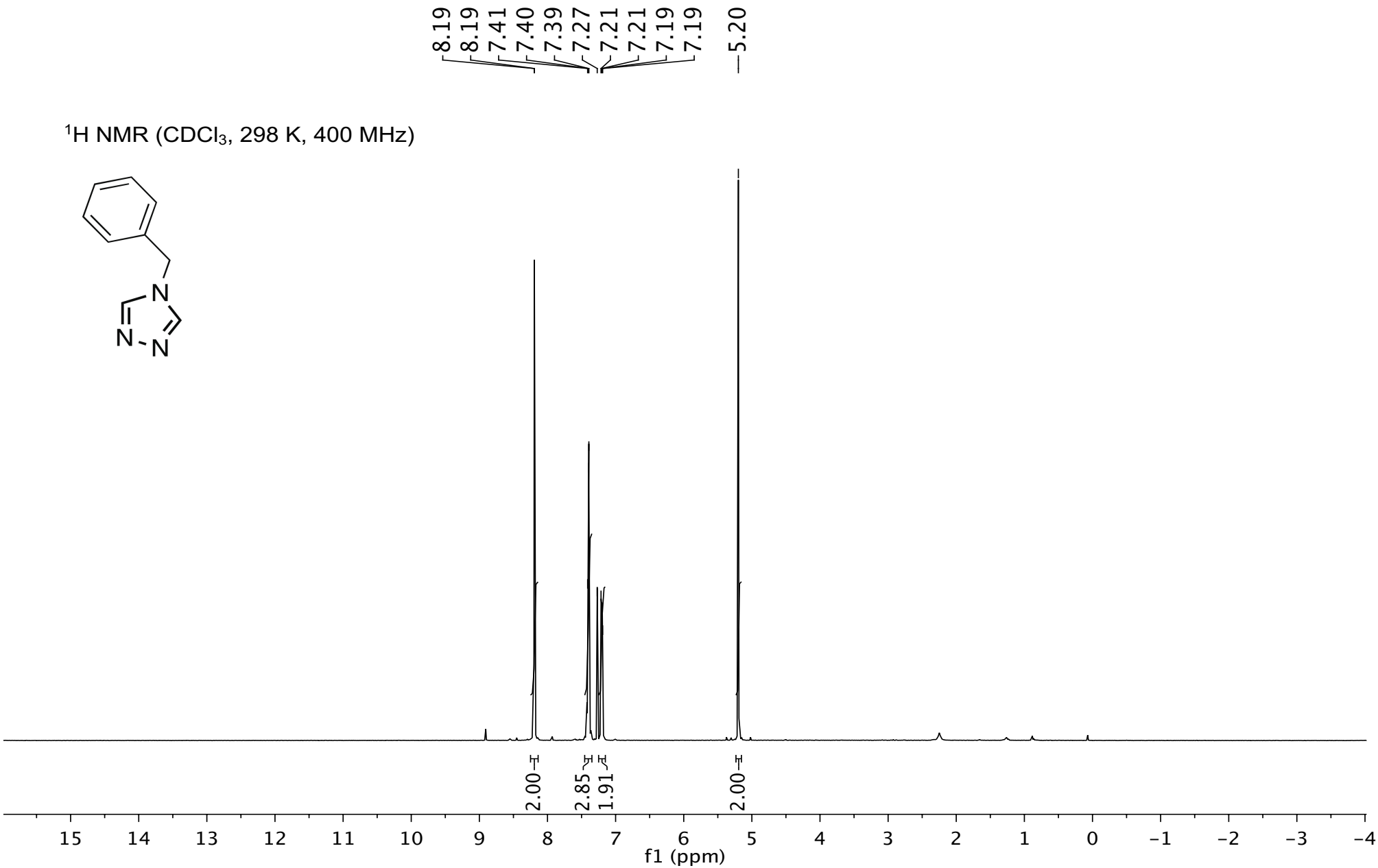
50.52

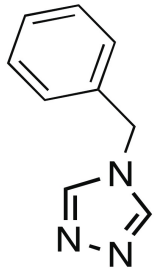
^{13}C NMR ($CDCl_3$, 298 K, 100 MHz)

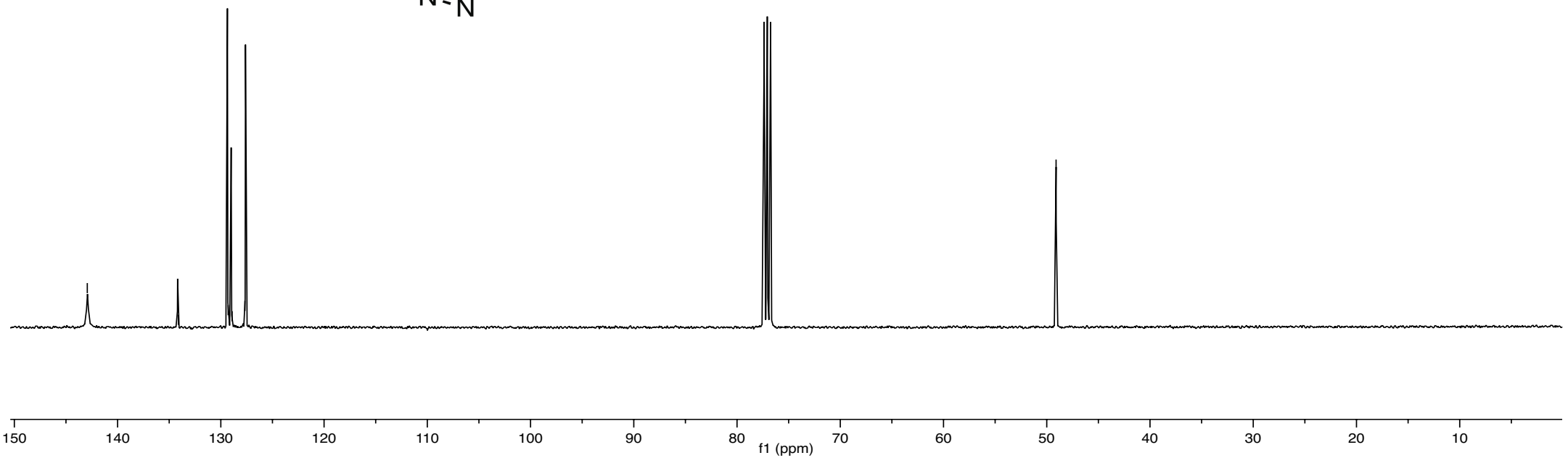


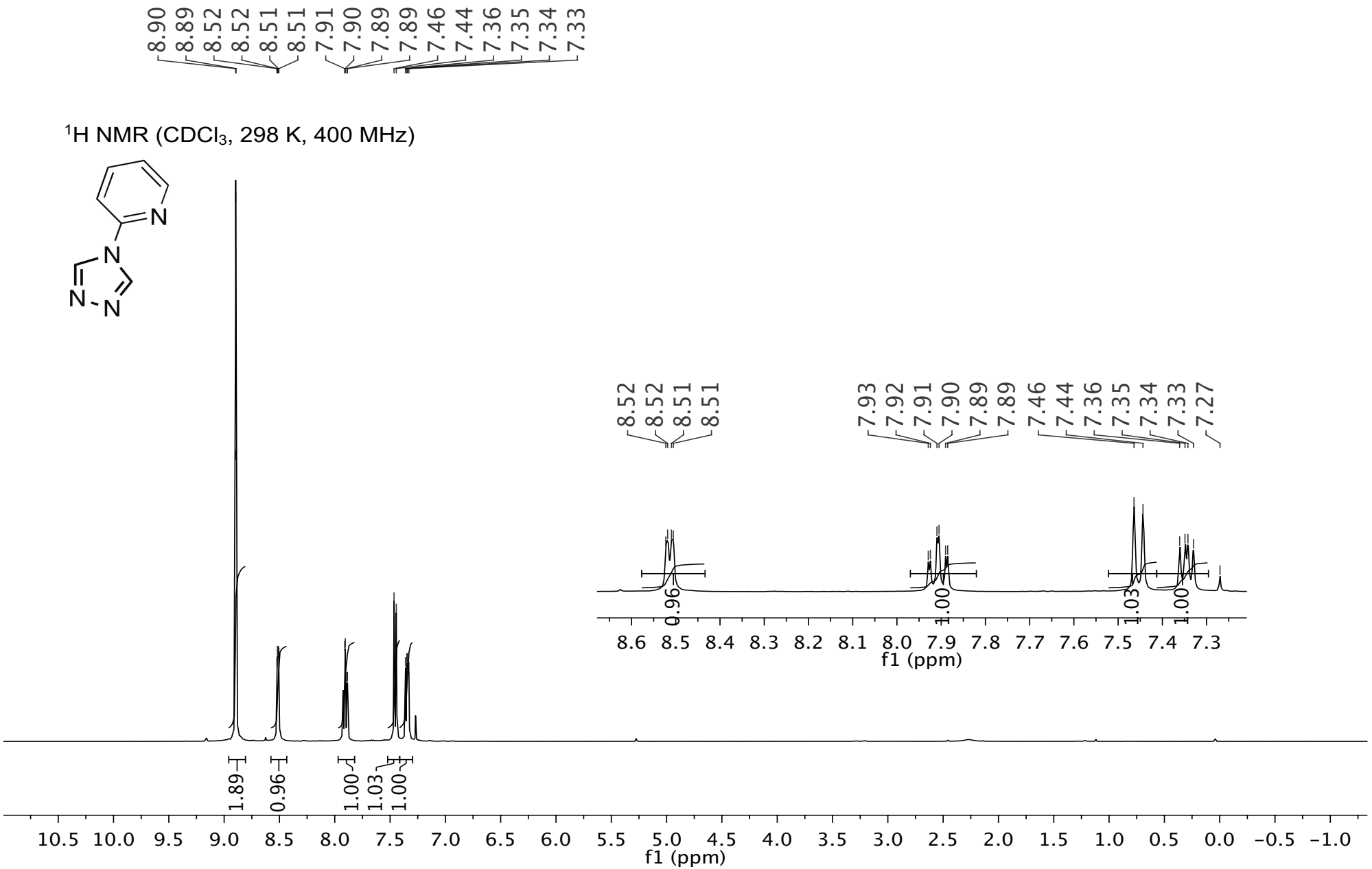

8.19
8.19
7.41
7.40
7.39
7.27
7.21
7.21
7.19
7.19
5.20
^{1}H NMR ($CDCl_3$, 298 K, 400 MHz)
N
N
N
2.00
2.85
1.91
2.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)

142.93
134.11
129.29
128.90
127.66
49.10

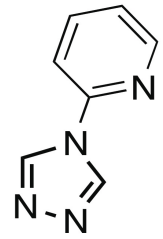
^{13}C NMR ($CDCl_3$, 298 K, 100 MHz)



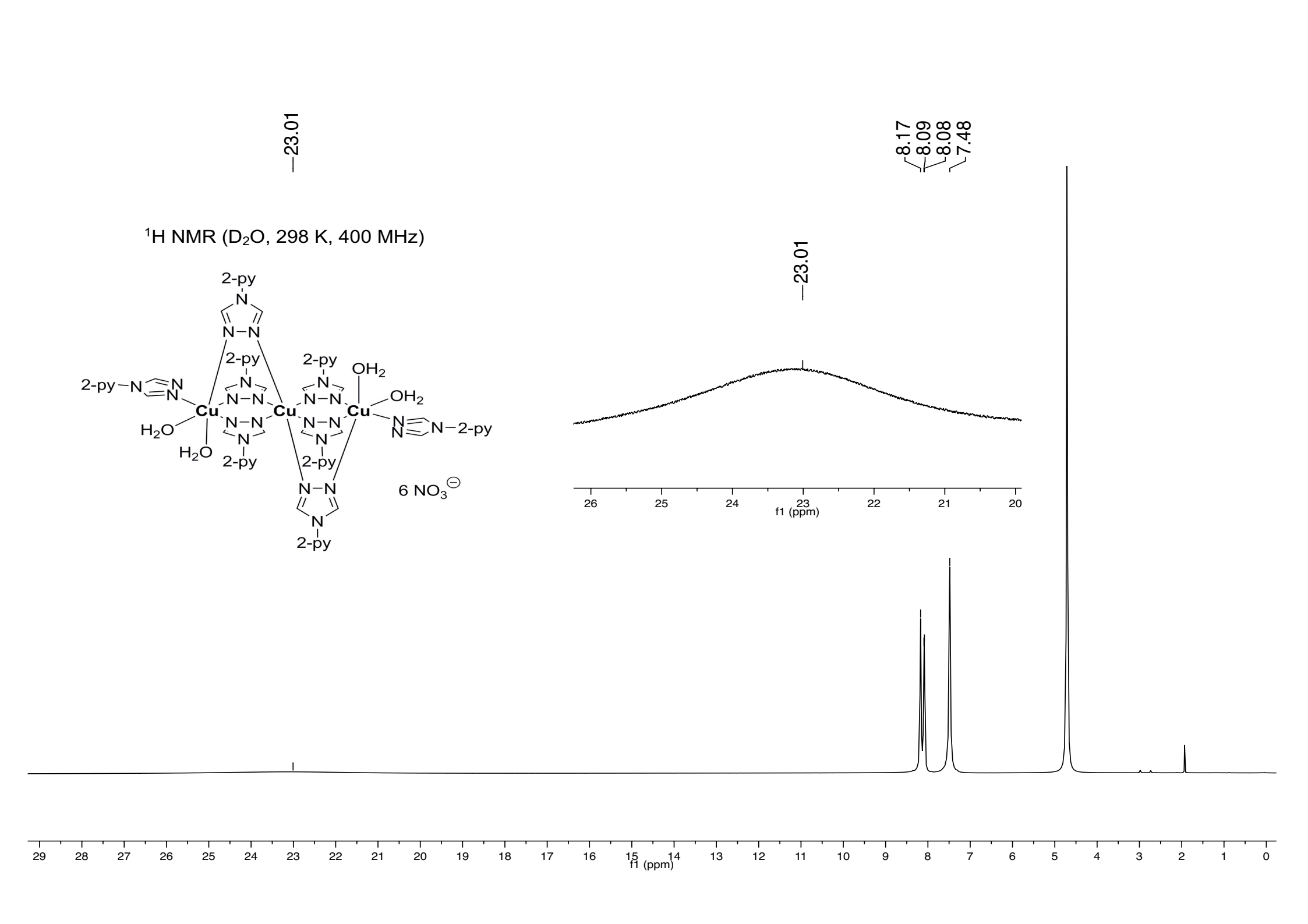



8.90
8.89
8.52
8.52
8.51
8.51
7.91
7.90
7.89
7.89
7.46
7.44
7.36
7.35
7.34
7.33
^{1}H NMR ($CDCl_3$, 298 K, 400 MHz)
N
N
N
N
8.52
8.52
8.51
8.51
7.93
7.92
7.91
7.90
7.89
7.89
7.46
7.44
7.36
7.35
7.34
7.33
7.27
0.96
1.00
1.03
1.00
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.89
0.96
1.00
1.03
1.00
10.5 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 −0.5 −1.0
f1 (ppm)

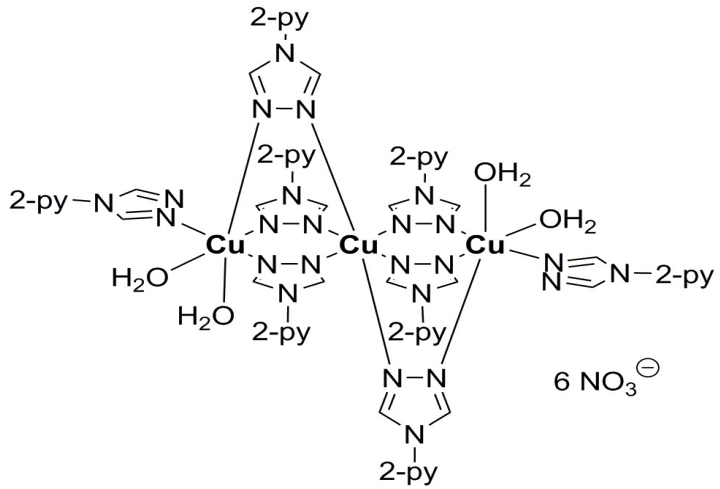
^{13}C NMR ($CDCl_3$, 298 K, 100 MHz)

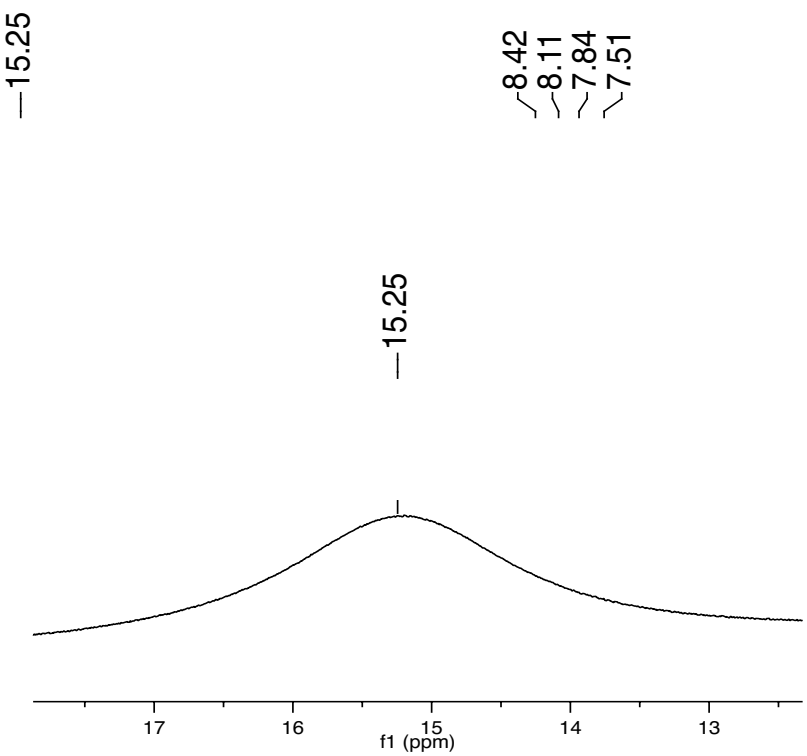


149.7
146.6
139.9
139.7
123.5
113.2

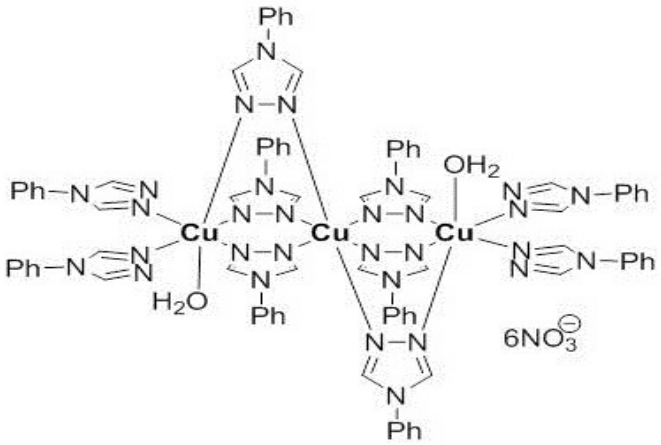

23.01
8.17
8.09
8.08
7.48
^{1}H NMR (D_2O, 298 K, 400 MHz)
2-py
Cu
OH_2
H_2O
6 $NO_3^{\ominus}$
f1 (ppm)

^{1}H NMR (DMSO-d^{6}, 298 K, 400 MHz)



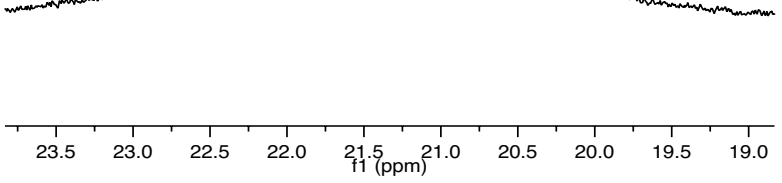


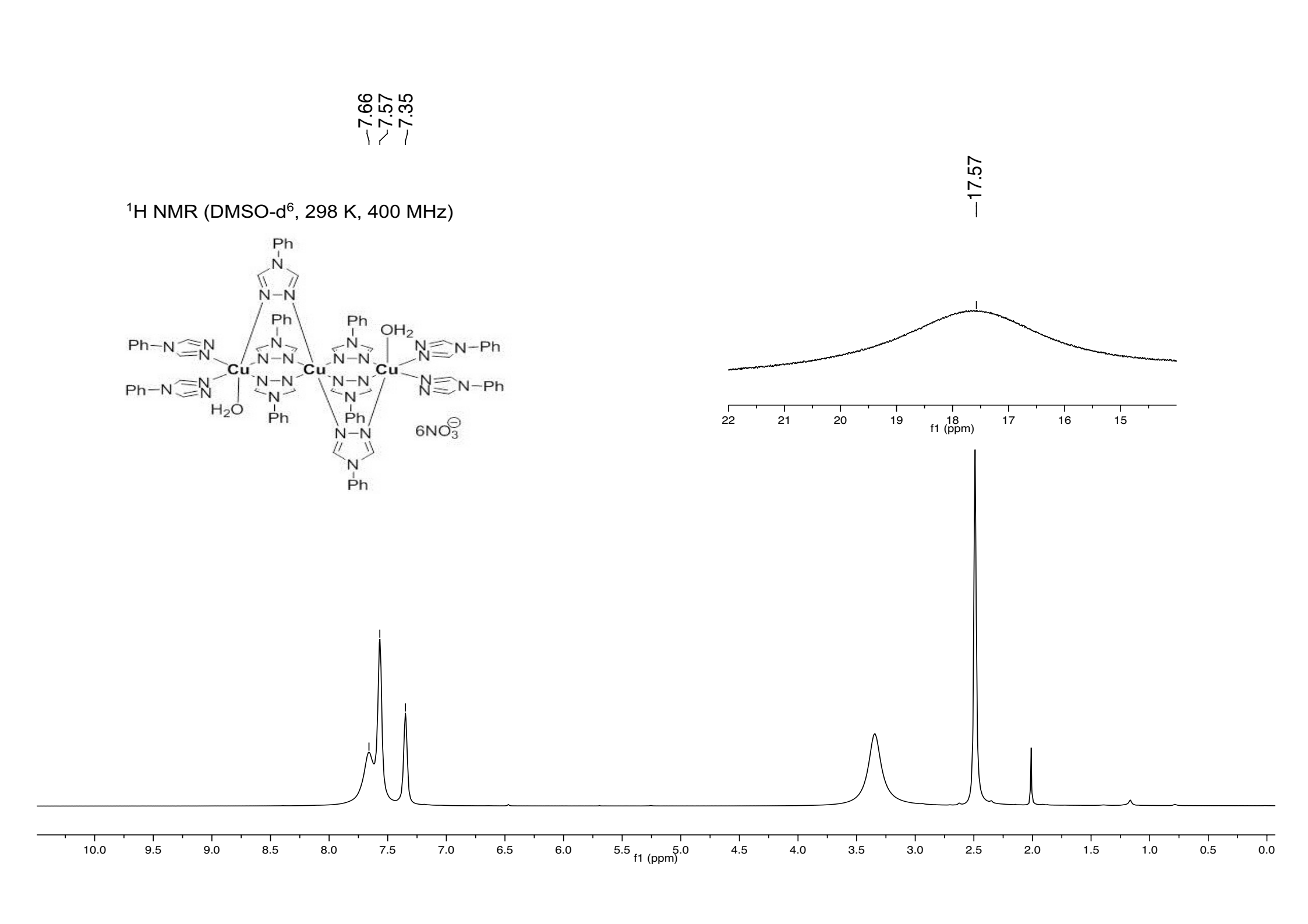
^{1}H NMR (D_2O, 298 K, 400 MHz)



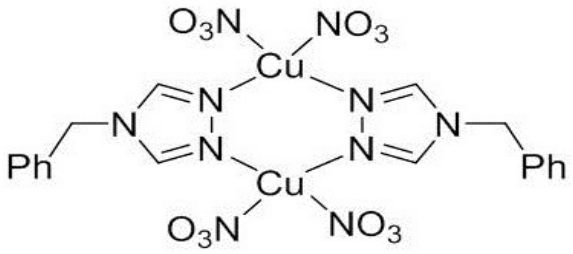
7.53
7.33
7.27

21.32

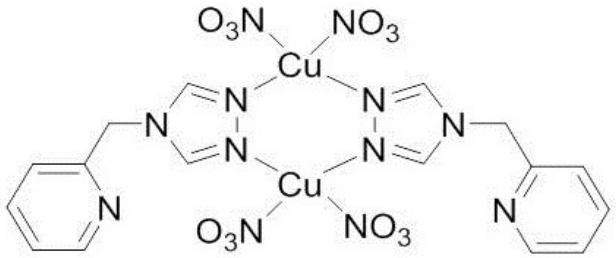



7.66
7.57
7.35
17.57
1H NMR (DMSO-d6, 298 K, 400 MHz)
Ph
N
N–N
Cu
OH2
H2O
6NO3
22
21
20
19
18
17
16
15
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

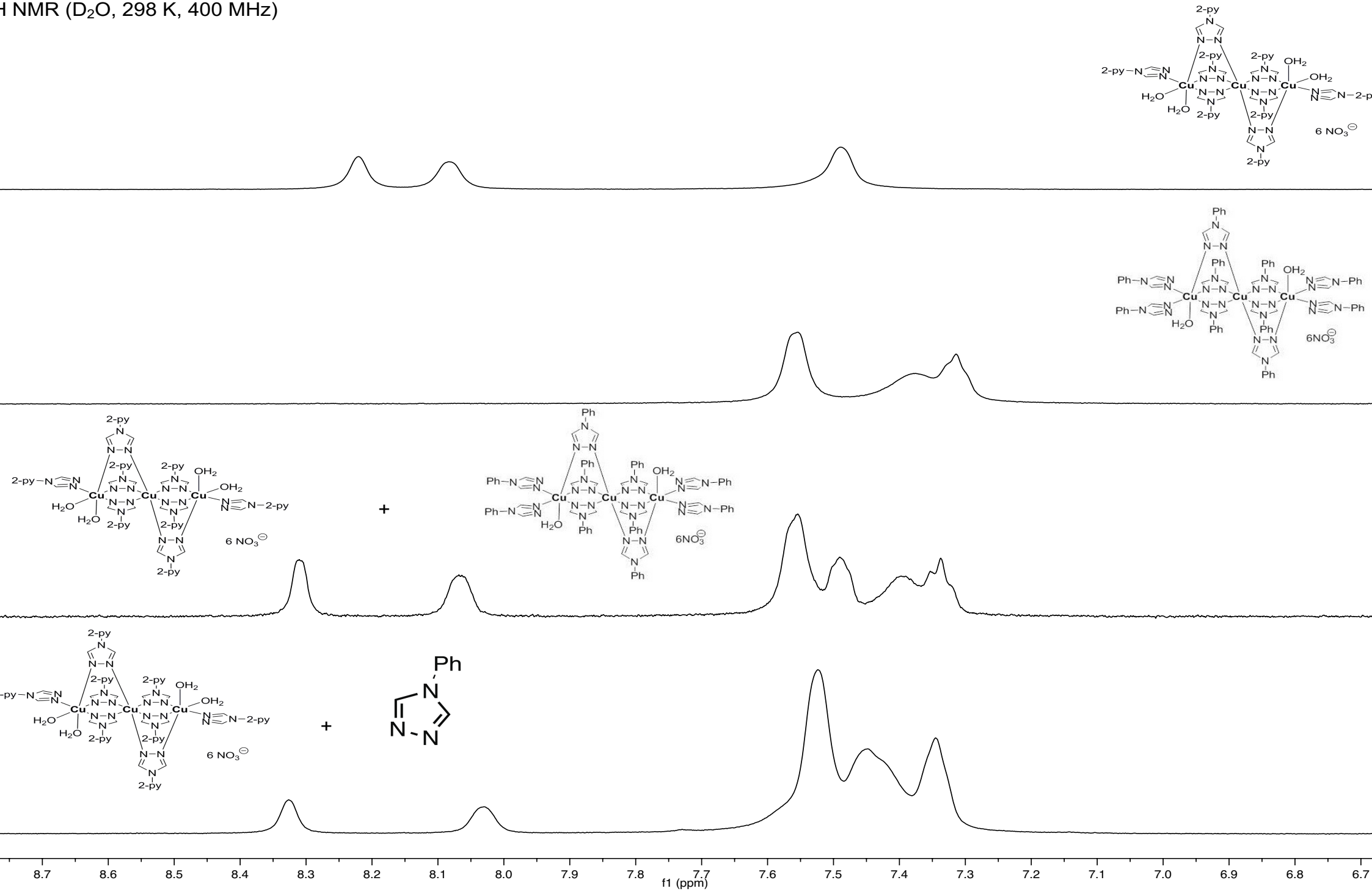
^{1}H NMR (DMSO-d^6, 298 K, 400 MHz)



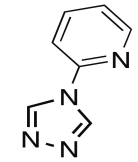
^{1}H NMR (DMSO-d^6, 298 K, 400 MHz)

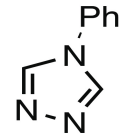


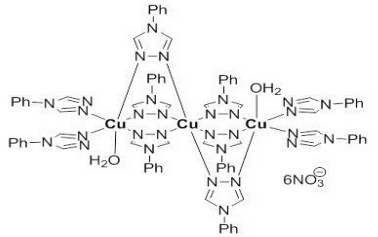
H NMR (D_2O, 298 K, 400 MHz)

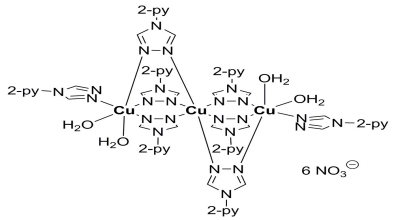


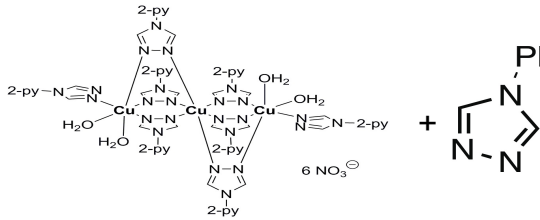
^{1}H NMR (DMSO-d^6, 298 K, 400 MHz)







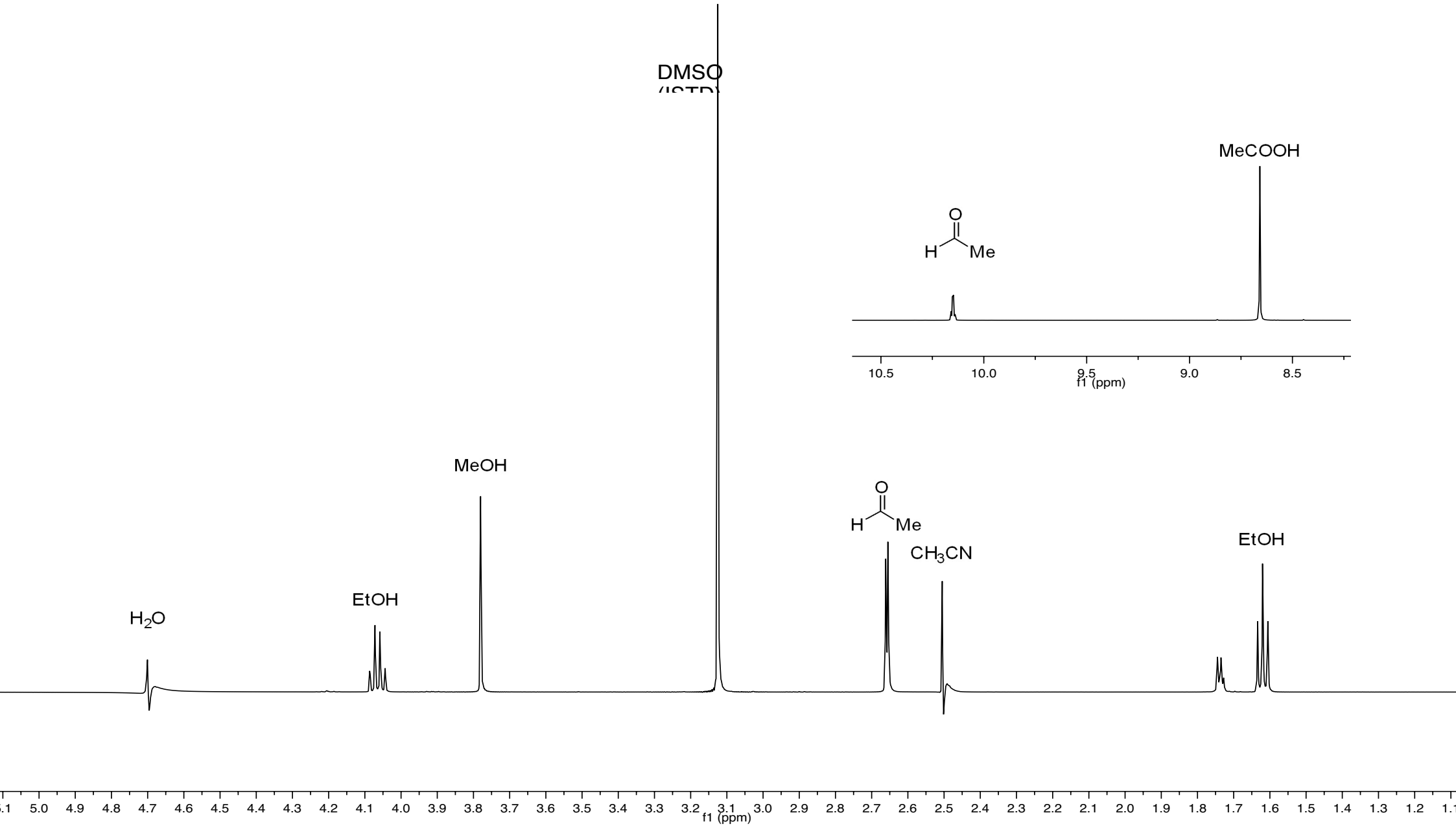




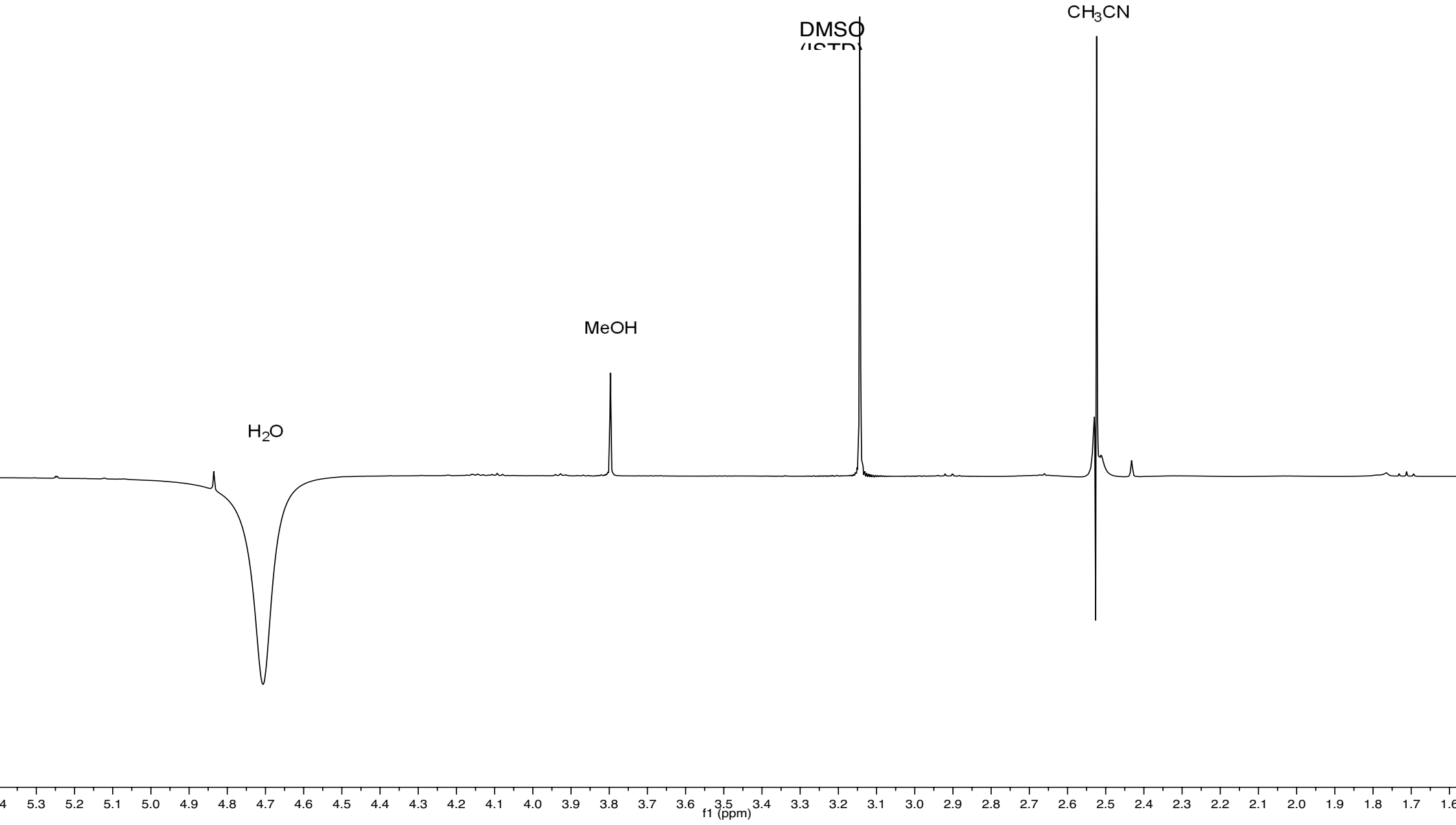
9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7

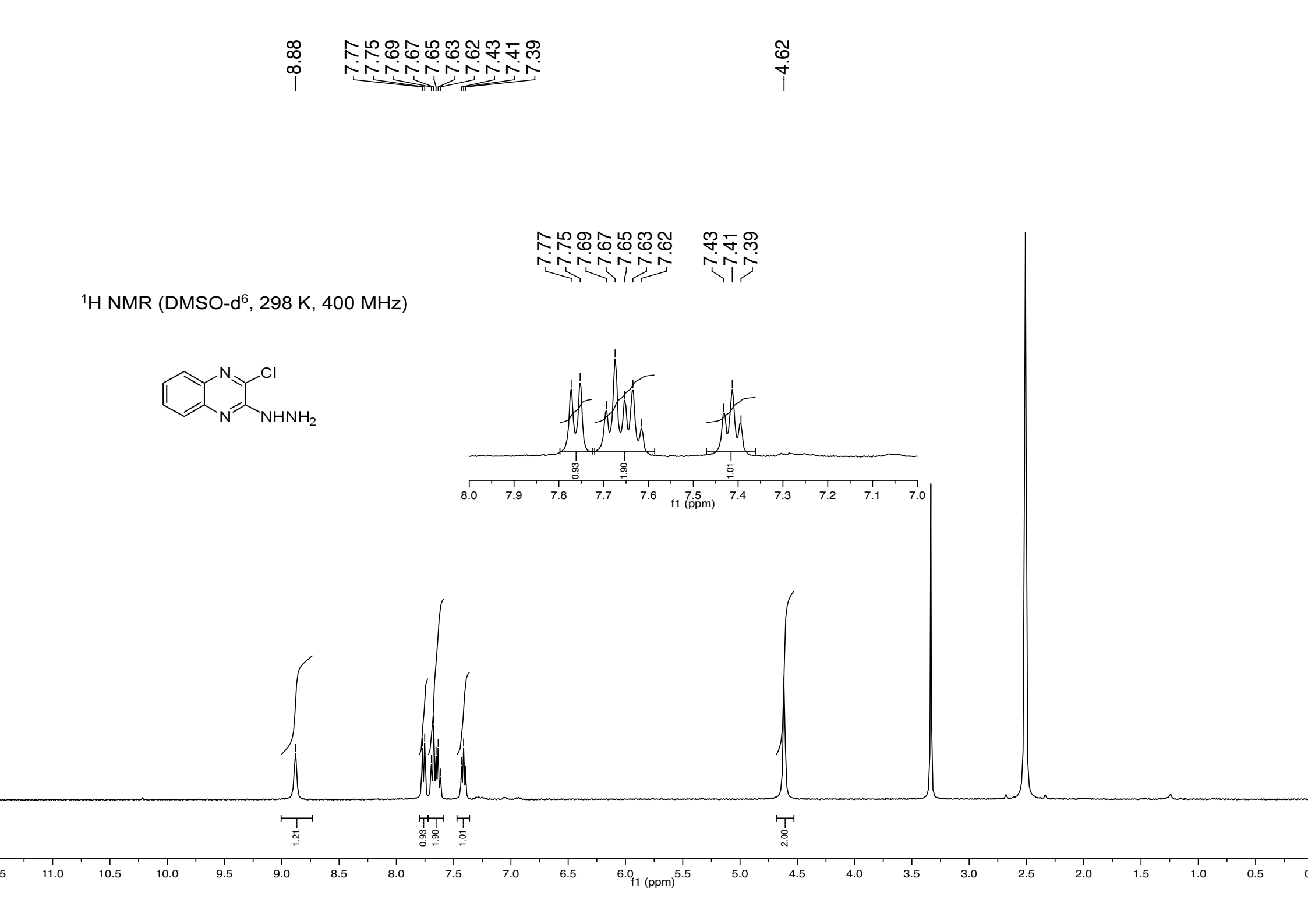
f1 (ppm)

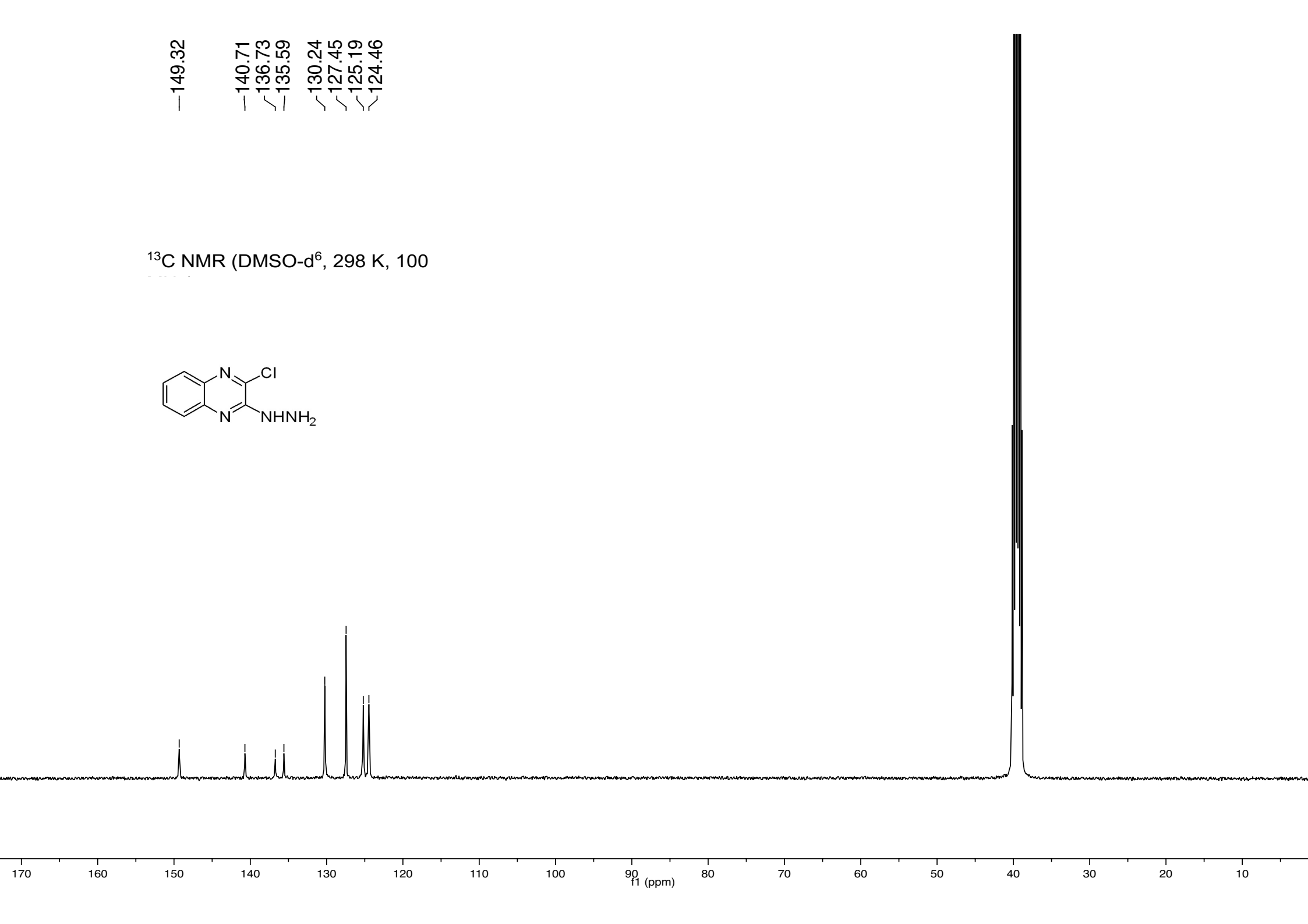
Solvent Suppression ^{1}H NMR of C1 and C2 oxidation products (D2O, 298 K, 400 MHz)



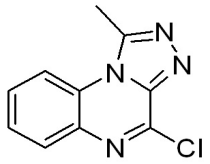
Solvent Suppression 1H NMR of a crude sample of methane oxidation catalysed by Pombeiro's catalyst (D2O, 298 K, 400 MHz)

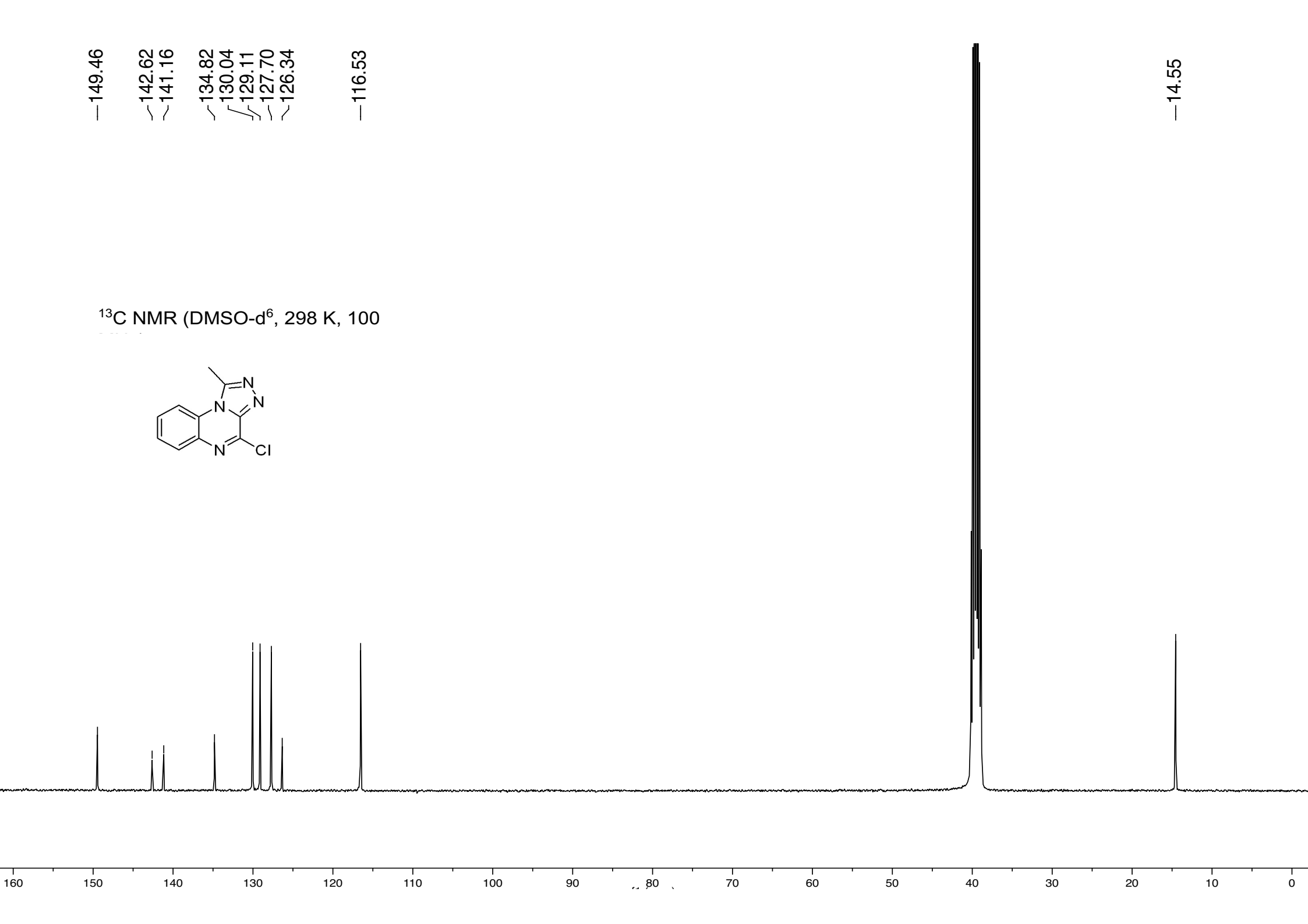


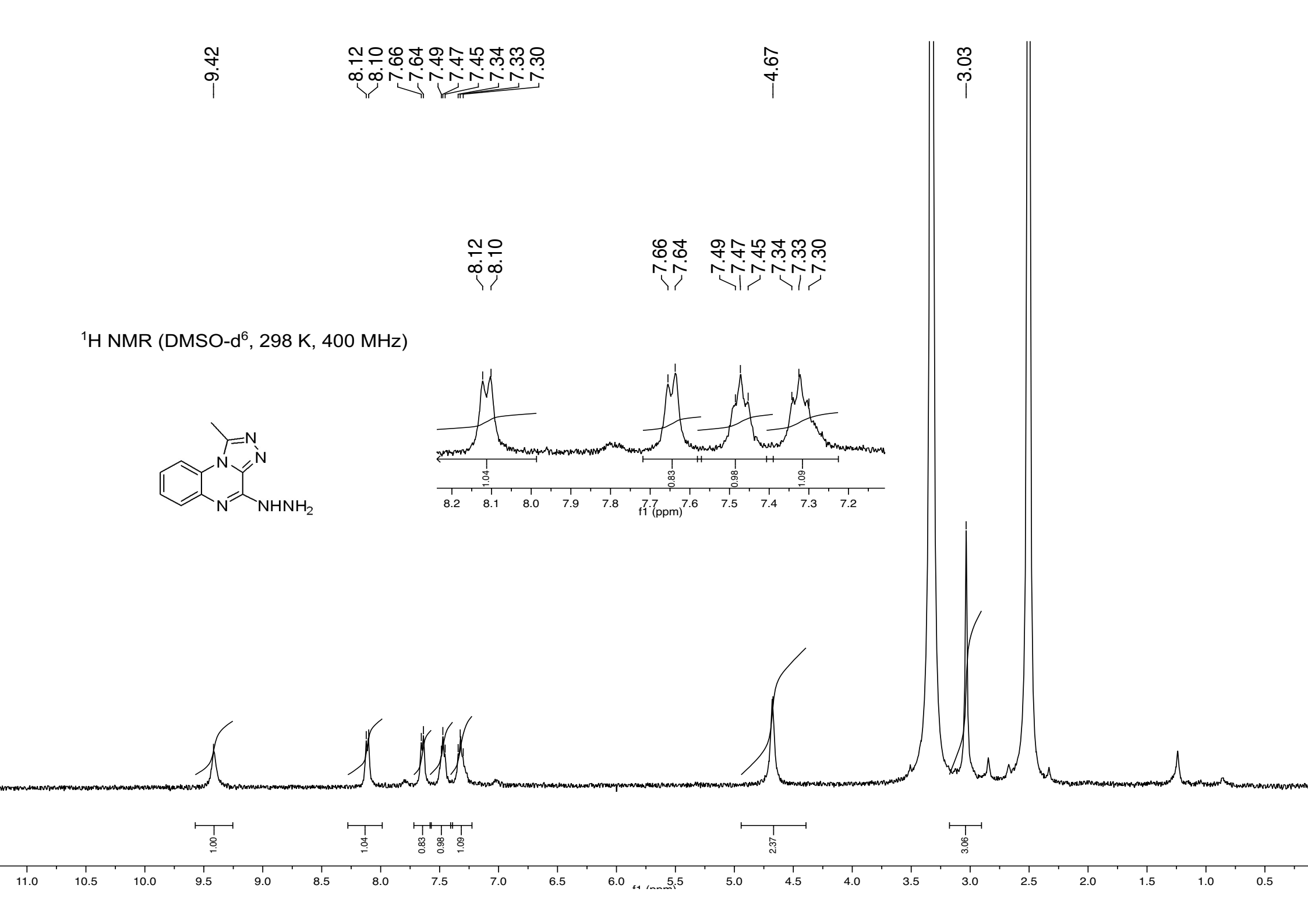

8.88
7.77
7.75
7.69
7.67
7.65
7.63
7.62
7.43
7.41
7.39
4.62
^{1}H NMR (DMSO-d^6, 298 K, 400 MHz)
N
Cl
N
NHNH$_2$
1.21
0.93
1.90
1.01
2.00
f1 (ppm)


149.32
140.71
136.73
135.59
130.24
127.45
125.19
124.46
13C NMR (DMSO-d6, 298 K, 100
N
Cl
N
NHNH2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR (DMSO-d^{6}, 298 K, 400 MHz)

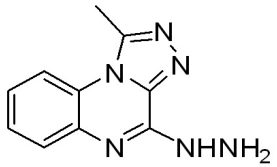


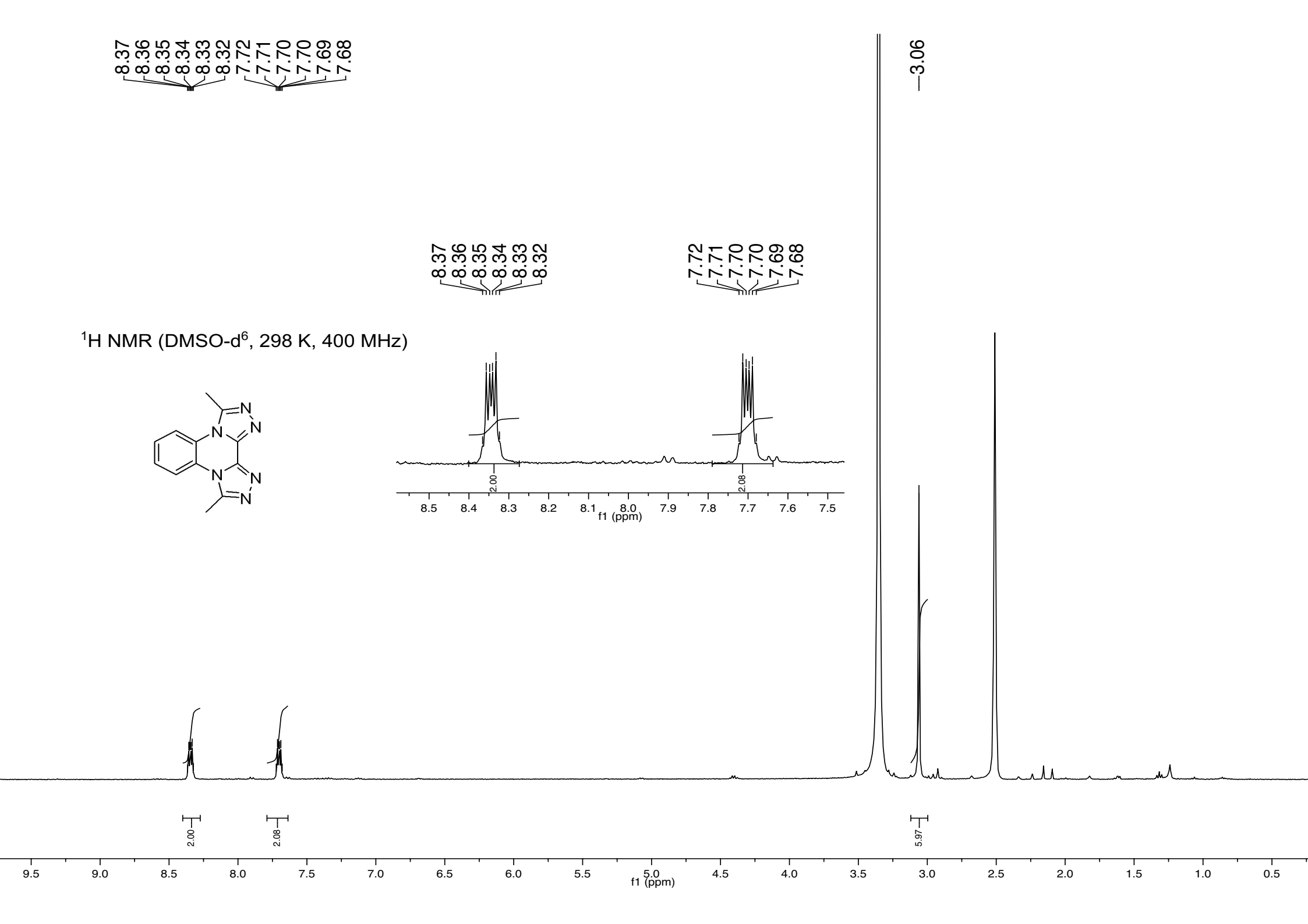

149.46
142.62
141.16
134.82
130.04
129.11
127.70
126.34
116.53
14.55
^{13}C NMR (DMSO-d^6, 298 K, 100
N
N
N
N
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

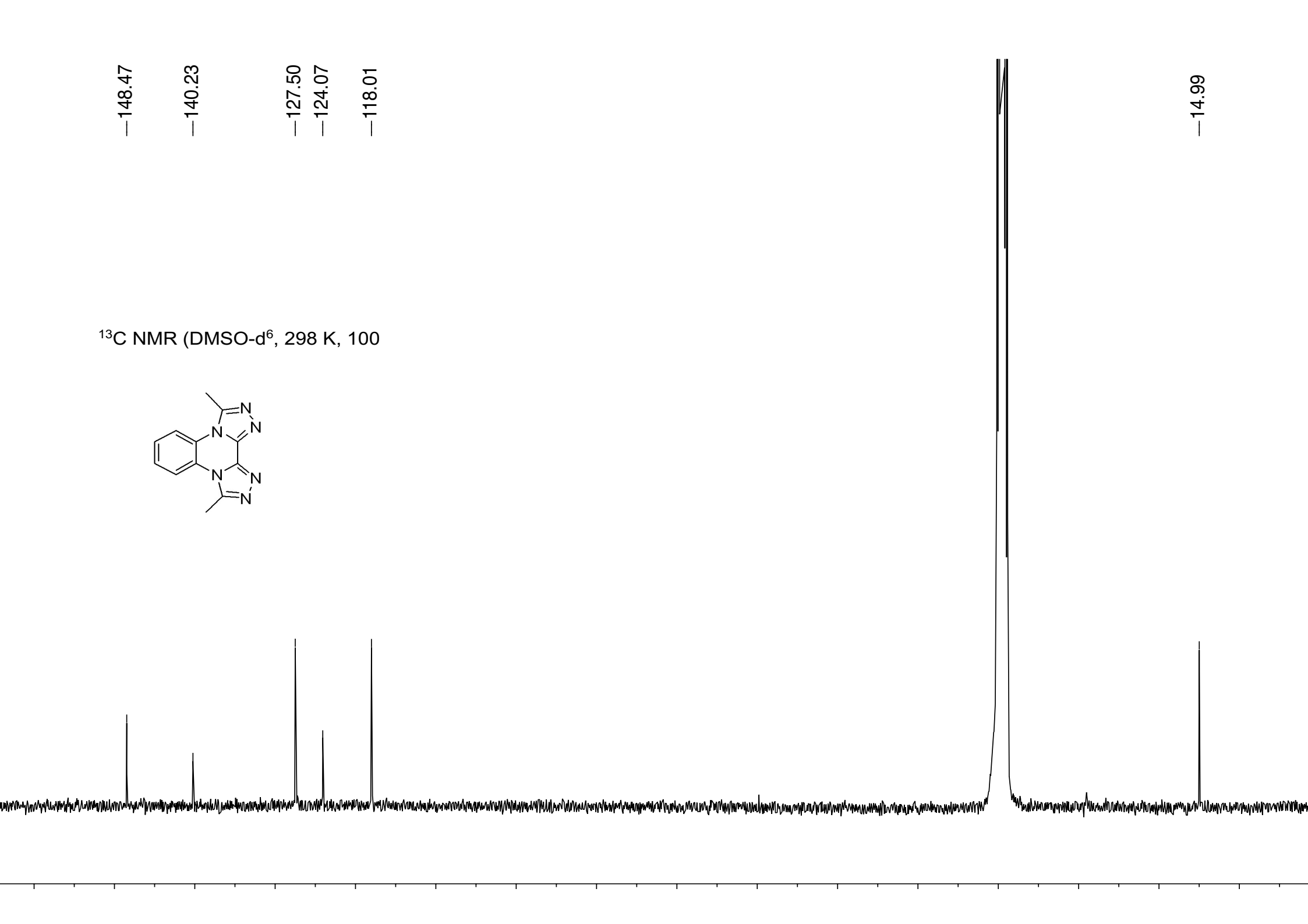

9.42
8.12
8.10
7.66
7.64
7.49
7.47
7.45
7.34
7.33
7.30
4.67
3.03
1H NMR (DMSO-d6, 298 K, 400 MHz)
NHNH2
f1 (ppm)
1.00
1.04
0.83
0.98
1.09
2.37
3.06

148.21
146.56
138.75
137.43
127.11
126.02
123.60
122.97
115.89
14.47

^{13}C NMR (DMSO-d^6, 298 K, 100




8.37
8.36
8.35
8.34
8.33
8.32
7.72
7.71
7.70
7.70
7.69
7.68
3.06
^{1}H NMR (DMSO-d^6, 298 K, 400 MHz)
2.00
2.08
f1 (ppm)
5.97
f1 (ppm)


148.47
140.23
127.50
124.07
118.01
14.99
13C NMR (DMSO-d6, 298 K, 100
N
N
N
N
N
N