Supporting information

Characterization of an unprecedented organomercury adduct *via* Hg(II)-mediated cyclization of 9-propargylguanine

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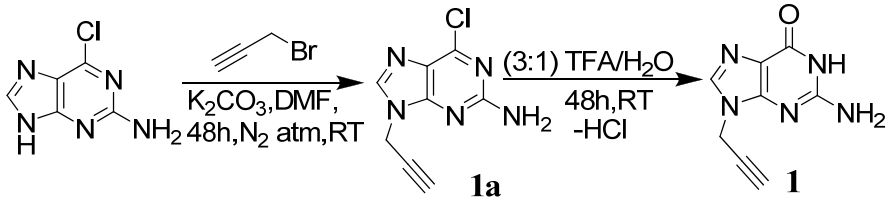
General procedures: ^{1}H and ^{13}C NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer operating at 500MHz. The spectra were recorded in DMSO-d_6 solution and the chemical shifts were referenced with respect to tetramethylsilane. High resolution (ESI^+ mode) mass spectra were obtained on WATERS HAB 213 machine, Department of Chemistry, IIT Kanpur. Infrared spectra were obtained (KBr disk, 400–4000 cm^{-1}) on a Perkin-Elmer Model 1320 spectrometer. All solvents were distilled prior to use using standards procedures. Solvents were evaporated using rotary evaporator under reduce pressure.

SCHEME 1:



Synthesis of 9-propargyl-2-amino-6-chloropurine (1a): The compound **1**a was synthesized based on literature procedure.[1] 2-amino-6-chloropurine (3.0g, 1eq) was suspended in DMF (50mL) followed by addition of anhydrous K_2CO_3 (2.934g, 1.2eq) and stirring under N_2 atmosphere for 1hr, after this propargyl bromide (1.894g, 0.9eq) is added and stirred for 48 hours under N_2 atmosphere at room temperature. After this time DMF was evaporated at 60 $^{\circ}C$ under high vacuum and compound was purified by column chromatography eluting with methanol/chloroform to afford yellowish-white powder (2.58g, 70% Yield). HRMS: $(M+H)^+$ calculated: 208.0390, found: 208.0395; ^{1}H NMR (500 MHz, DMSO-d_6, 25 $^{\circ}C$, TMS): δ (ppm) 3.43 (s, 1H, Acetylenic C-H), 4.89(s, 2H, CH_2), 6.97 (s, 2H, NH_2), 8.13 (s, 1H, C8-H); ^{13}C NMR (125 MHz, DMSO-d_6, 25 $^{\circ}C$, TMS): δ (ppm) 32.47, 76.16, 77.98, 123.12, 142.45, 149.61, 153.62, 159.99.

Synthesis of 9-propargylguanine (1): The title compound was synthesized based on literature procedure.[2] Compound **1a** (1g) was dissolved in 3:1 mixture of TFA-H_2O (10ml) and then stirred for 48hrs at ambient temperature. The reaction mixture was evaporated and washed well with diethylether to afford compound **1** as a white solid (0.873g, 96% Yield). HRMS: $(M+H)^+$ calculated: 190.0729, found: 190.0728; M.P. >240 $^{\circ}$C (decomposed); IR (KBr): 2131 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 3.55 (s, 1H, Acetylenic C-H), 4.90(s, 2H, CH_2), 7.12 (s, 2H, NH_2), 8.64 (s, 1H, C8-H), 11.42 (s,1H, N1-H); ^{13}C NMR (125 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 33.76, 76.83, 77.41, 109.64, 136.79, 149.71, 154.10, 155.43.

Synthesis of Complex 2: Compound **1** (0.01g, 0.053 mmol) and $HgCl_2$ (0.007g, 0.026 mmol) were suspended in 5 ml methanol/water mixture (4:1). This solution was kept in 10 ml Teflon bomb and sealed and then heated at 140 $^{\circ}$C for 2 days under hydrothermal conditions and cooled down to room temperature for 1 day. Few crystals of complex **2** were obtained and then dried. (0.006g, 30% Yield); HRMS: $(L+Hg+Cl+H_2O)^+$ calculated: 444.0151, 442.0128, 441.0127, 443.0148, 440.0112, 446.0122, found: 444.0179, 442.0163, 441.0165, 443.0178, 440.0147, 446.0191; ^{1}H NMR (500 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 2.28 (s, 1H, H11), 5.13(s, 2H, CH_2), 6.87 (s, 2H, NH_2), 8.52 (s, 1H, C8-H); ^{13}C NMR (125 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 27.29, 53.21, 109.70, 139.32, 149.90, 154.43, 155.11, 200.09.

Isolation of Compound 3: Compound **1** (0.01g, 0.053 mmol) was suspended in aqueous methanolic mixture. The pH of the above solution was adjusted around 1-2 by dropwise addition of conc. $HClO_4$. The obtained acidic solution was filtered and kept for slow evaporation. After few days, the crystals of compound **3** (0.007, 44%) were obtained.

Crystal structure refinement details for 1, 2 and 3: Single Crystal of **1, 2** and **3** were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo KR radiation. The data integration and reduction were processed with the SAINT software.[3] An absorption correction was applied.[4] Structures were solved by the direct method using SHELXS-97 and refined on *F*2 by a full-matrix least-squares technique using the SHELXL-97 program package.[5] Non-hydrogen

atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. Crystal structure refinement parameters are given in Table S1 whereas H-bonding parameters are provided in Table S2. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC **778729**, **778728**, **778730** for **1**, complex **2** and **3** respectively. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. [Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. The overall quality of the data for **1** is poor because of weakly diffracted crystals.

Table S1: Crystallographic data for **1,** complex **2** and **3**.

Identification code	**1**	**Complex 2**	**3**
Empirical formula	$C_8H_7N_5O$	$C_8H_6ClHgN_5O$	$C_8H_{10}ClN_5O_6$
*M*r	189.19	424.22	307.66
crystal system	Monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	P-1
a/Å	4.011(2)	3.8929(13)	7.4810(18)
b/Å	11.194(6)	12.593(4)	13.111(3)
c/Å	19.934(10)	19.667(6)	13.431(3)
α/°	90	90	72.577(4)
β/°	92.72(2)	94.034(5)	84.086(5)
γ/°	90	90	76.667(4)
Volume/ Å^3	894.0(8)	961.8(6)	1222.2(5)
Z	4	4	4
Dx /Mg m^{-3}	1.406	2.930	1.672
F(000)	392	776	632
μ/ mm^{-1}	0.102	16.264	0.350
θ range for data collection/ °	2.05 to 25.48	2.08 to 28.38	2.61 to 28.35
Limiting indices	-4<=h<=4, -13<=k<=13, -16<=l<=24	-5<=h<=4, -16<=k<=16, -26<=l<=24	-9<=h<=9, -11<=k<=17, -17<=l<=17
Reflections collected	4459	6115	7842
unique reflections	1602	2359	5671
R(int)	0.0331	0.0677	0.0243
Completeness to *θ*	96.3	99.5	97.9
T_{max} / T_{min}	0.9800/0.9770	0.1394/0.1177	0.9333/0.9238
Data / restraints / parameters	1602/0/128	2359/0/145	5671/3/369
Goodness-of-fit on F^2	1.052	1.115	1.148
*R*1 and *R*2 [$I>2\sigma(I)$]	0.0769, 0.1984	0.0408, 0.0898	0.0597, 0.1608
*R*1 and *R*2 (all data)	0.0942, 0.2243	0.0673, 0.1219	0.0818, 0.2393
Largest diff. peak and hole/e.A^{-3}	0.784and -0.386	3.349 and -3.229	0.726 and -0.899
CCDC No.	**778729**	**778728**	**778730**

Table S2: Selected hydrogen bonding distances and bond angles in **1**, complex **2** and **3**.

D—H…A[#]	D…A	H…A	D—H…A
1			
N(1)—H(1)…N(7)^{i}	2.839(3)	1.99	169
N(2) —H(2B)...O(1)^{i}	2.947(3)	2.13	159
C(11)—H(11)...O(1)^{ii}	3.162(4)	2.24	171
Complex 2			
N(2)—H(2A)...N(1)^{iii}	2.786(12)	1.91	173
C(9)—H(9A) ...O(1)^{iv}	3.191(13)	2.29	151
C(9) —H(9B)...O(1)^{v}	3.051(13)	2.33	129
C(11)—H(11)...Cl(1)^{vi}	3.571(11)	2.68	157
3			
N(1)—H(1)...O(1')^{vii}	2.809(5)	1.97	165
N(1')—H(1')...O(1) ^{vii}	2.825(4)	1.99	163
O2W—H2W1...O(5) ^{viii}	2.901(4)	2.06	168
O2W—H2W2...O1W^{ix}	2.783(4)	2.07	149
N(2)—H(2B)...O(5)^{x}	3.127(4)	2.44	138
N(2')—H(2D)...O(5')	3.031(5)	2.35	136
N(2')—H(2D)...O(2')^{ix}	2.979(6)	2.53	113
O1W—H1W1...O(5')	2.917(4)	2.32(5)	131(4)
O1W—H1W1...O(3')^{ix}	2.796(4)	2.19(4)	132(5)
O1W—H1W2...O(1)	2.765(4)	1.92(8)	151(7)
N7—H7...O(1W) ^{vii}	2.716(4)	1.86	176
N(7')—H(7')...O(2W) ^{xi}	2.610(4)	1.75	175
C(8)—H(8)...O(3)	3.049(5)	2.27	141
C(8')—H(8')...O(2') ^{xii}	3.178(5)	2.48	132
C(9)—H(9B)...O(2) ^{xiii}	3.415(5)	2.53	152
C(9')—H(9C)...O(5) ^{viii}	3.416(5)	2.48	162
C(9')—H(9D)...O(2)	3.171(5)	2.41	135
C(11)—H(11')...O(4) ^{xiv}	3.342(5)	2.49	153

[#]Symmetry of A: (*i*) –x,1/2+y,1/2-z (*ii*) x,1/2-y,-1/2+z (*iii*) 2-x,1-y,-z (*iv*) 3/2-x,-1/2+y,1/2-z (*v*) 5/2-x,-1/2+y,1/2-z (*vi*) -x,-y,-z (*vii*) -x,1-y,1-z (*viii*) 1+x,y,z (*ix*) 1-x,1-y,1-z (*x*) x,y,1+z (*xi*) 1-x,1-y,-z (*xii*) x,y,-1+z (*xiii*) 1-x,-y,1-z (*xiv*) 1-x,-y,-z; where A= acceptor and D= donor

Table S3: Observed bond lengths between constituent atoms for **1,** complex **2** and **3**.

Bond	**1**	**2**	**3**
C2-N1	1.369	1.384	1.365
C2-N2	1.335	1.220	1.329
C2-N3	1.319	1.402	1.324
C4-C5	1.387	1.336	1.387
C4-N9	1.362	1.349	1.367
C4-N3	1.351	1.372	1.343
C5-N7	1.390	1.402	1.366
C5-C6	1.408	1.436	1.420
C6-O1	1.241	1.201	1.239
C6-N1	1.393	1.421	1.392
C8-N7	1.304	1.303	1.327
C8-N9	1.380	1.372	1.358
C9-N9	1.467	1.447	1.481
C9-C10	1.456	1.494	1.459
C10-C11	1.183	1.362	1.182
N3-C11	------	1.423	------

Figure S1: Hydrogen bonding interactions between guanine moieties in **1,** complex **2** and **3**.

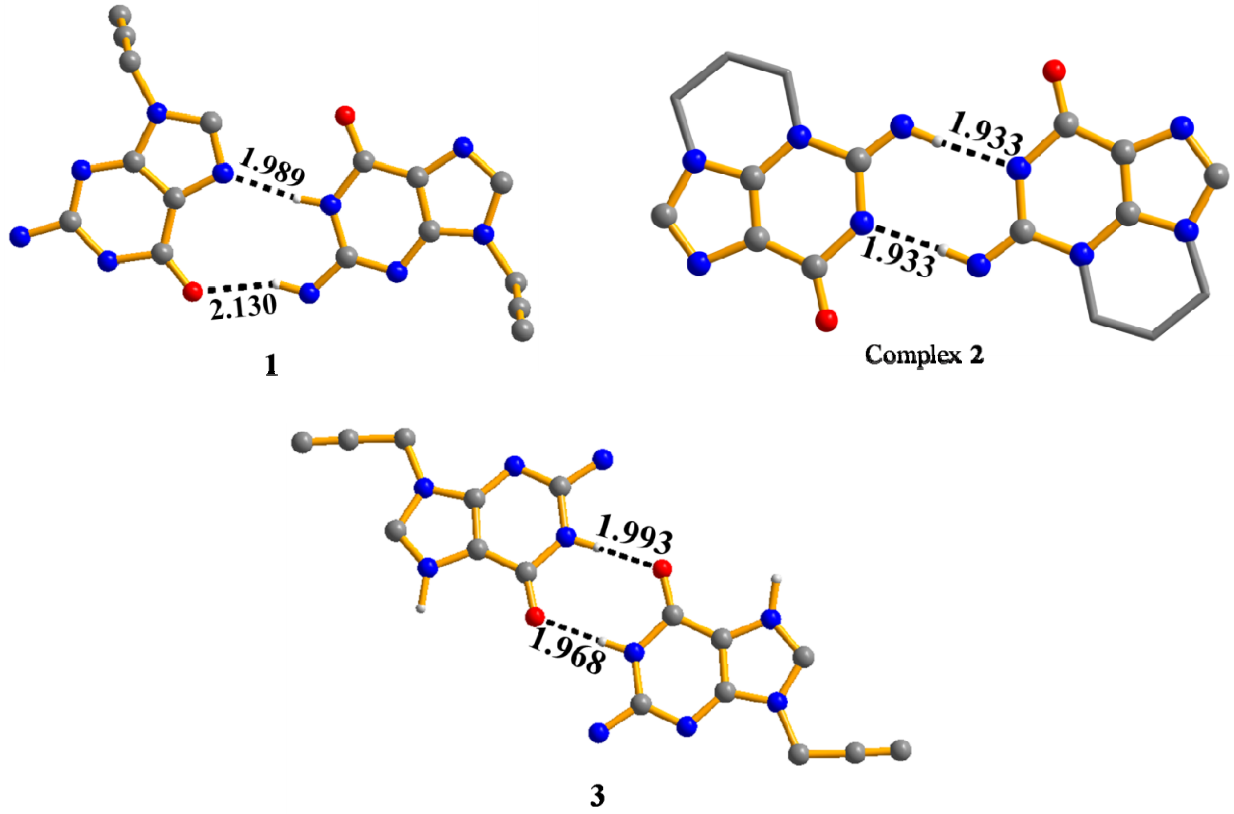


Figure S2: Different views (a and b) of crystal lattice of complex **2**.

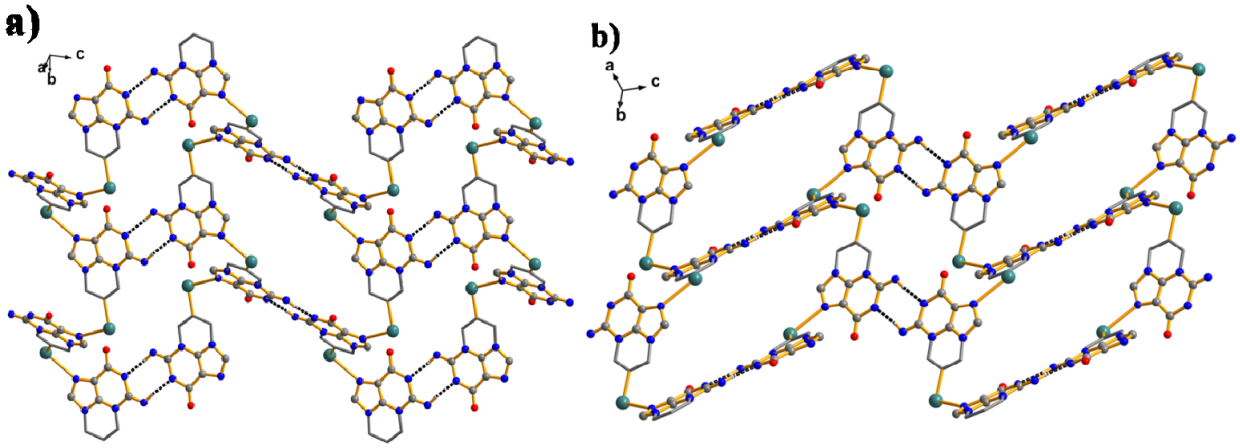


Figure S3: ^{1}H NMR of 9-propargyl-2-amino-6-chloropurine (**1a**).

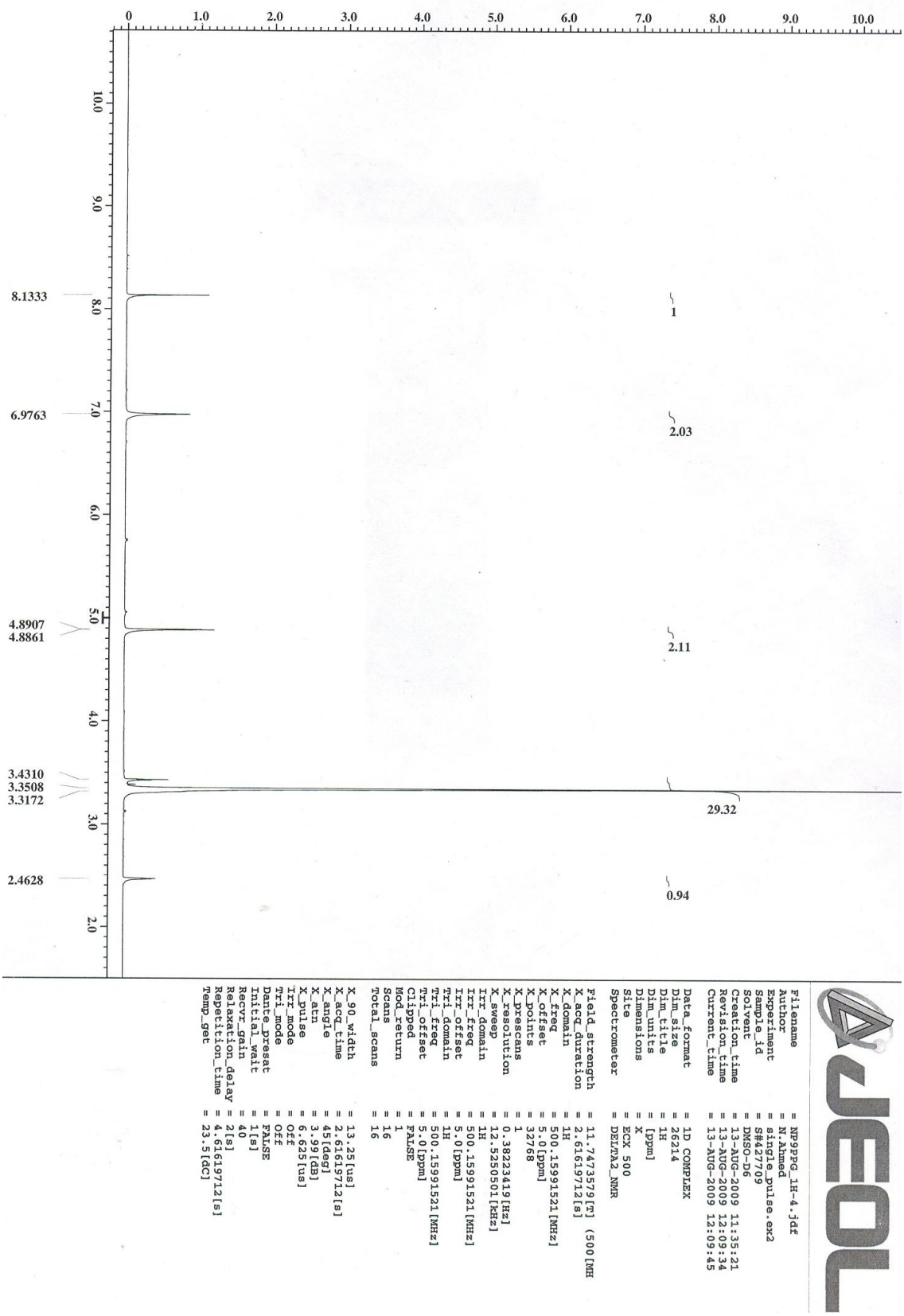


Figure S4: ^{13}C NMR of 9-propargyl-2-amino-6-chloropurine (**1a**).

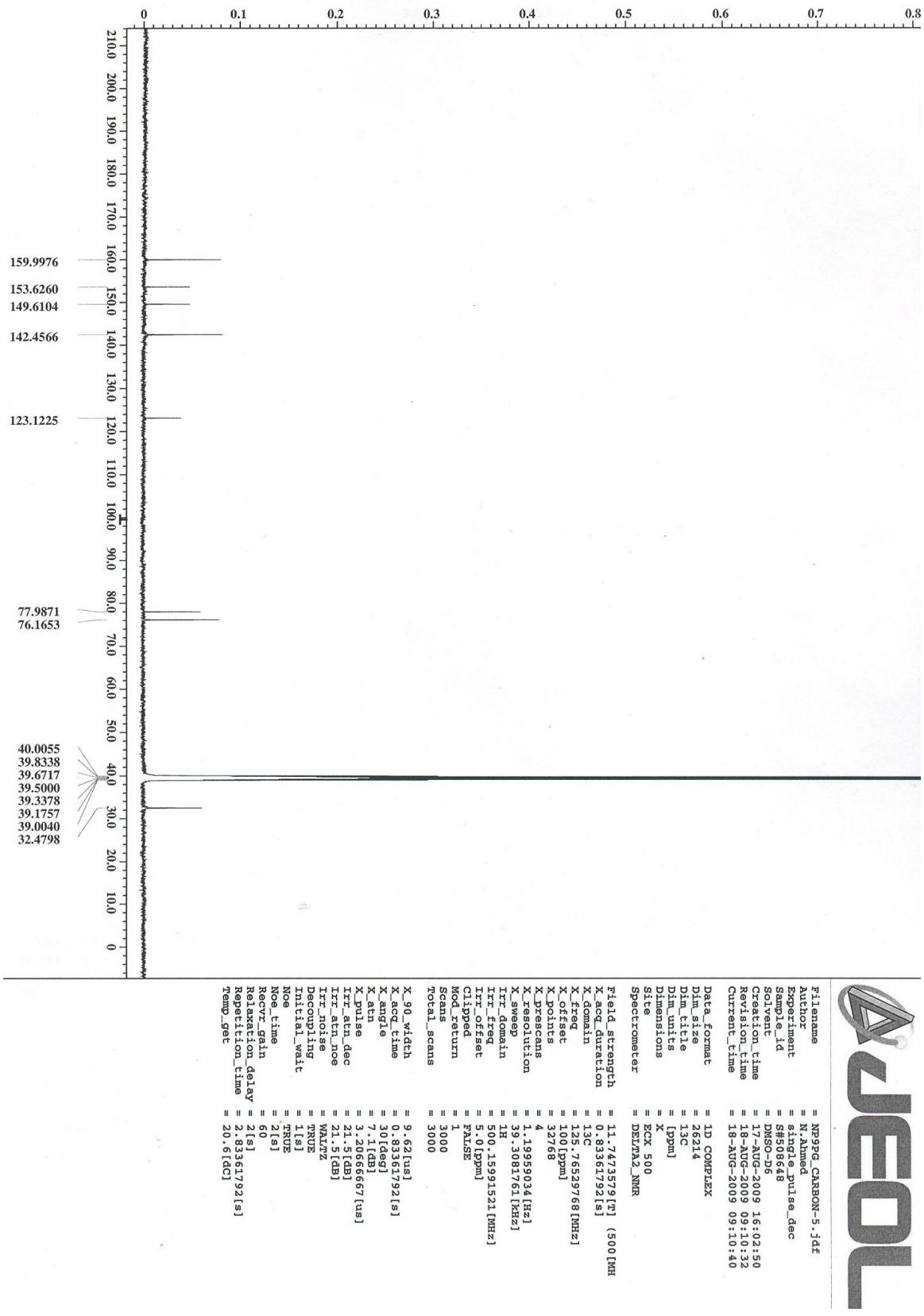


Figure S5: ESI-HRMS of 9-propargyl-2-amino-6-chloropurine (**1a**).

Figure S6: ^{1}H NMR of 9-propargylguanine (**1**).

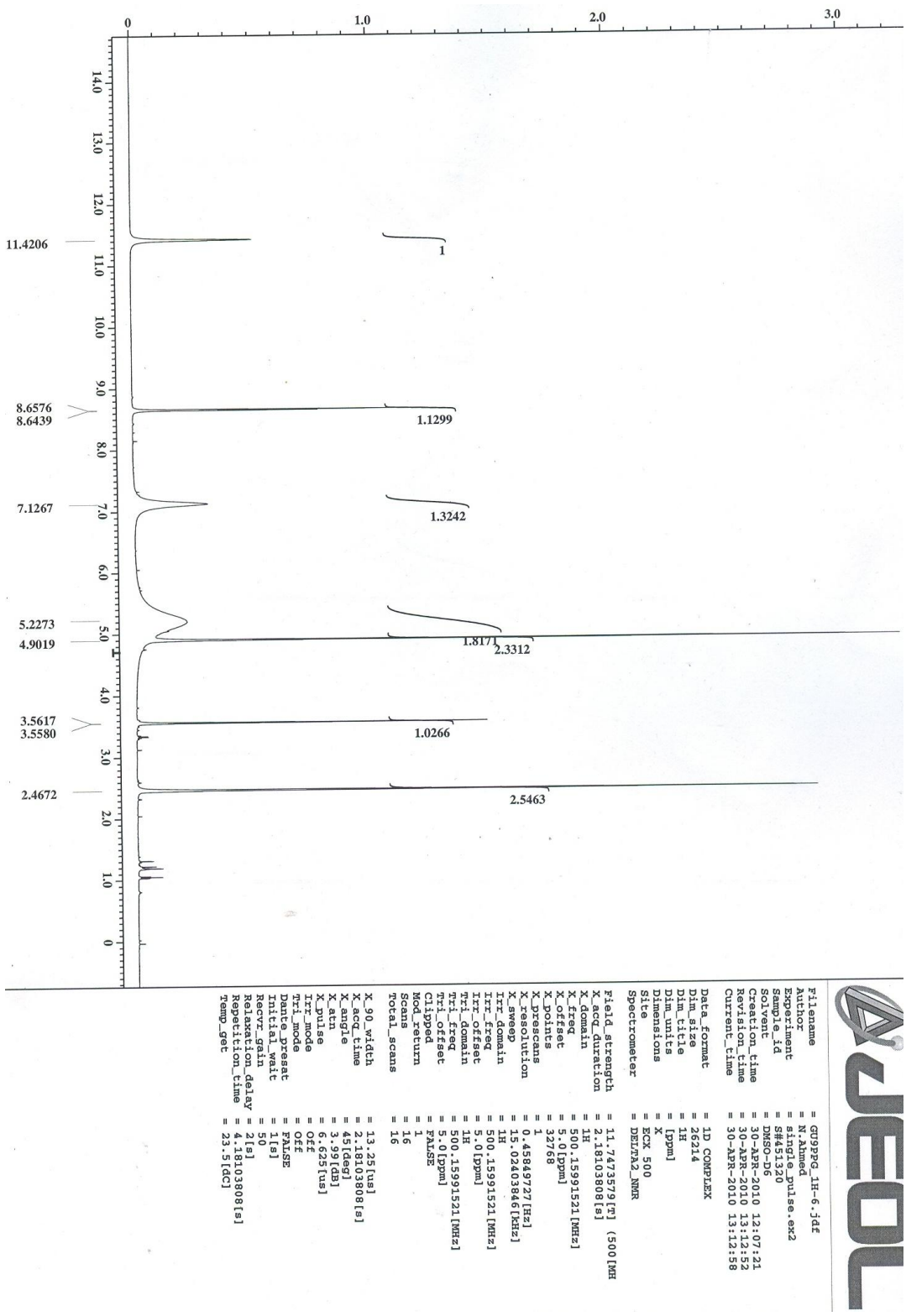


Figure S7: ^{13}C NMR of 9-propargylguanine (**1**).

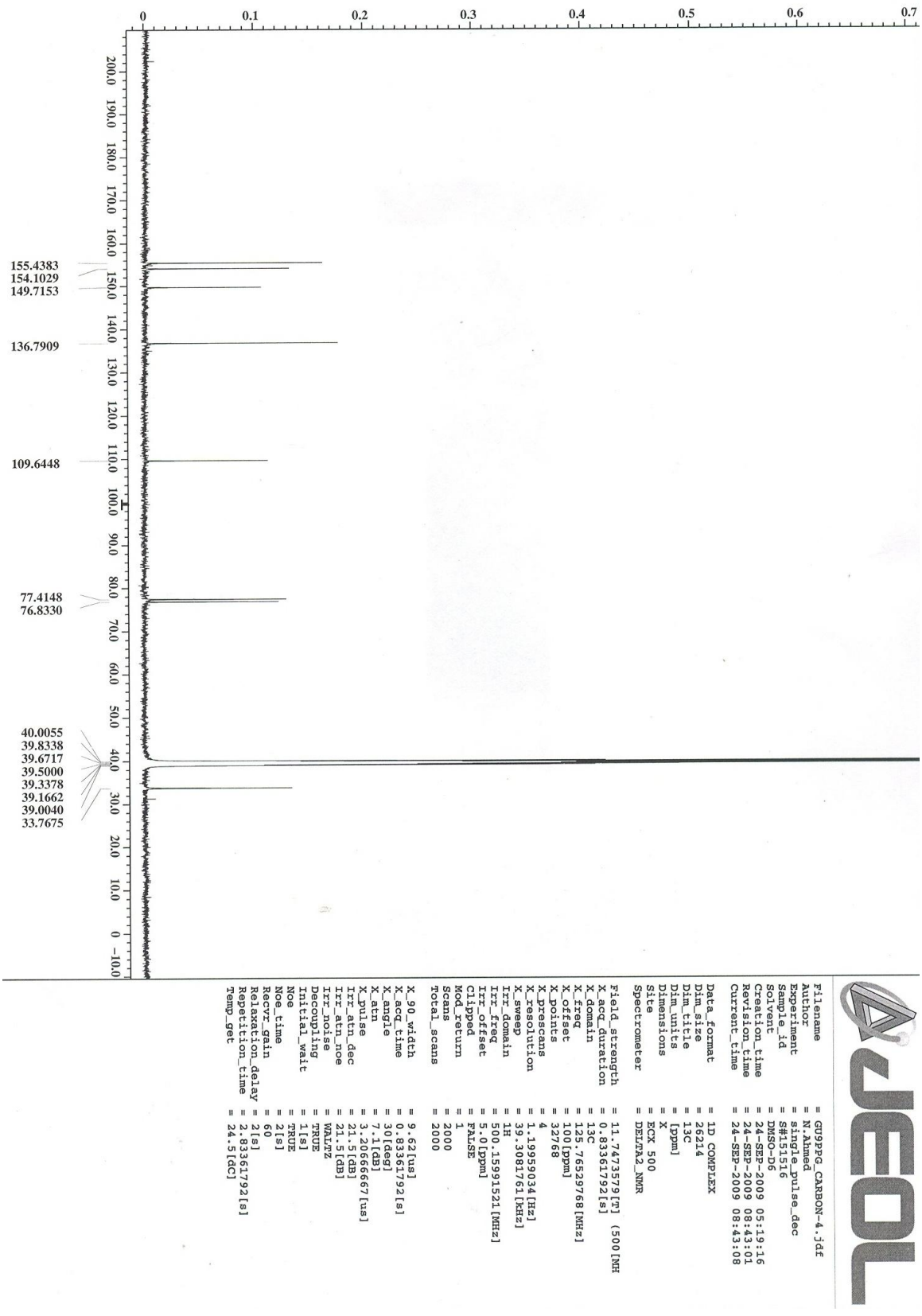


Figure S8: ESI-HRMS of 9-propargylguanine (**1**).

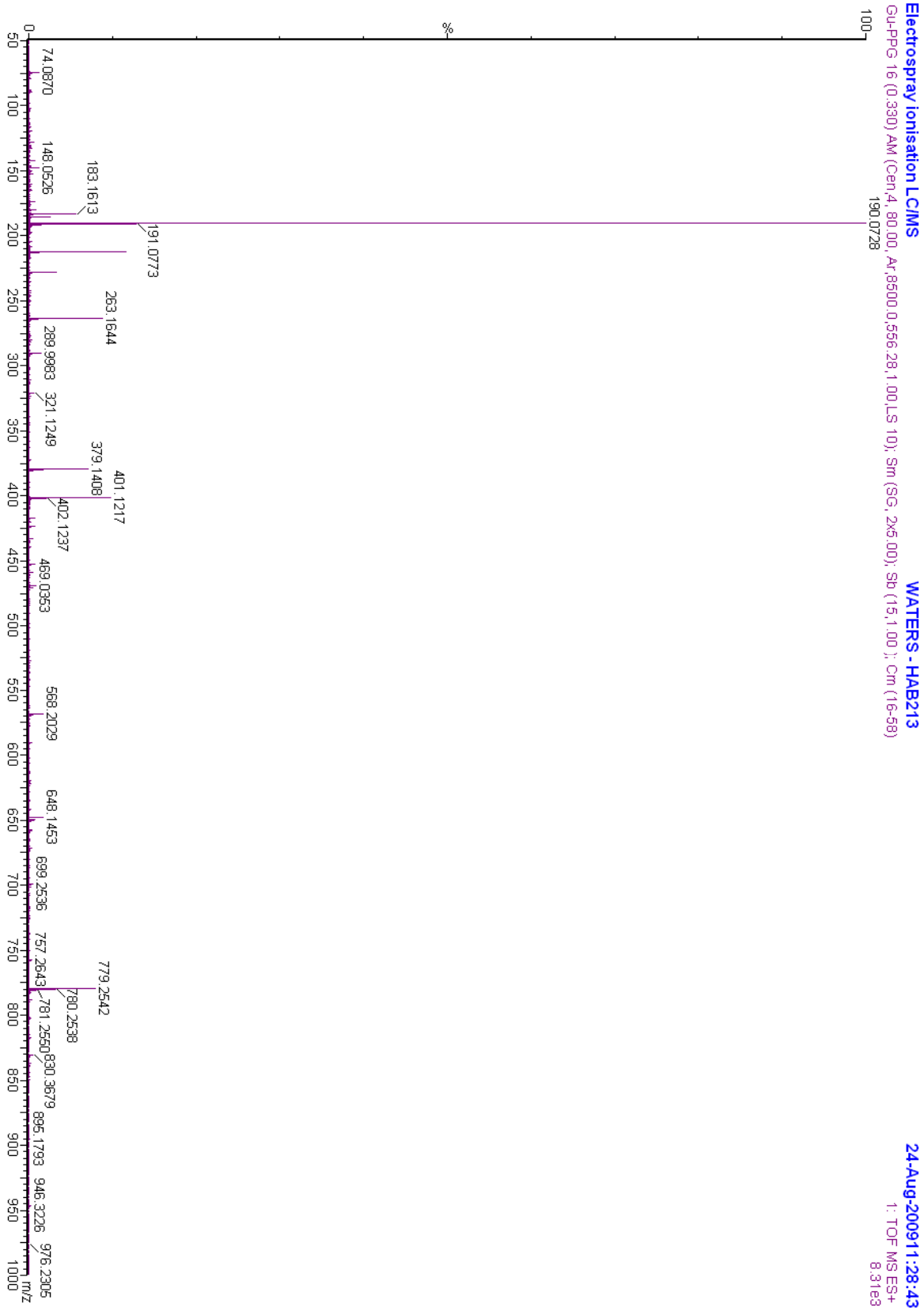


Figure S9: IR spectrum of 9-propargylguanine (**1**).

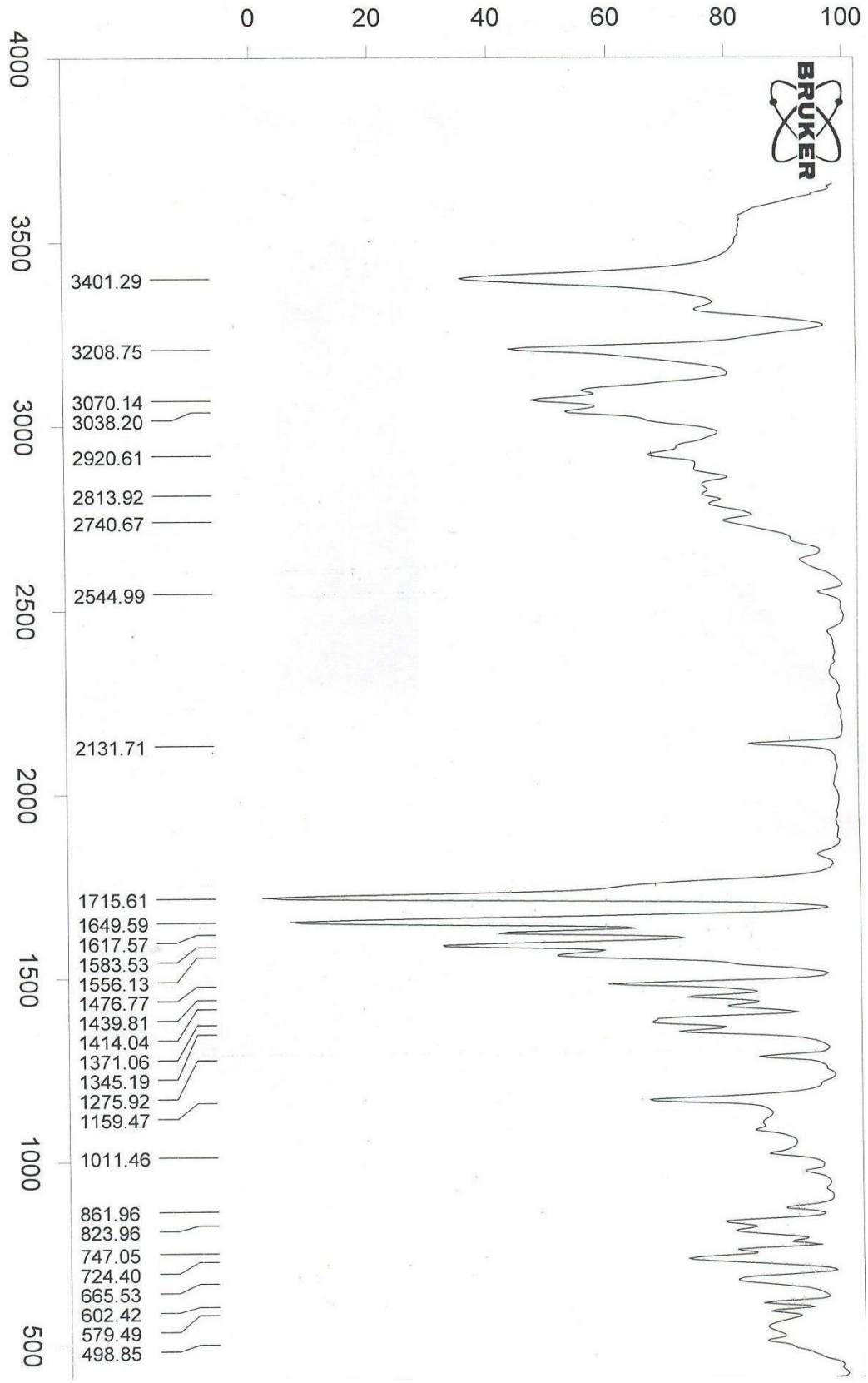


Figure S10: ^{1}H NMR spectrum of (a) **1** in DMSO-d_6 (b) **1**+ $HgCl_2$ in DMSO-d_6 after 2 days of heating at 75-80 $^{\circ}$C, showing near complete conversion to complex **2**. (note that the acetylenic H11 singlet at δ 3.59 ppm is converted to olefinic H11 proton).

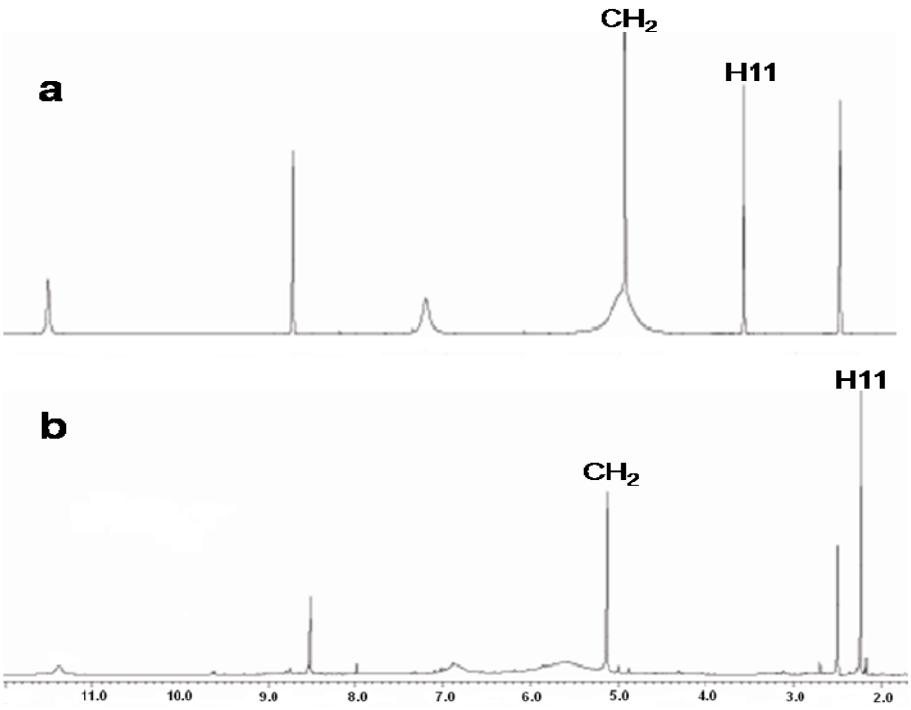


Figure S11: ^{13}C NMR spectrum of (a) **1** in DMSO-d_6 (b) **1**+ $HgCl_2$ in DMSO-d_6 after 2 days of heating at 75-80 $^{\circ}$C, showing near complete conversion to complex **2** (note that acetylenic C10/11 have shifted upon mercury coordination).

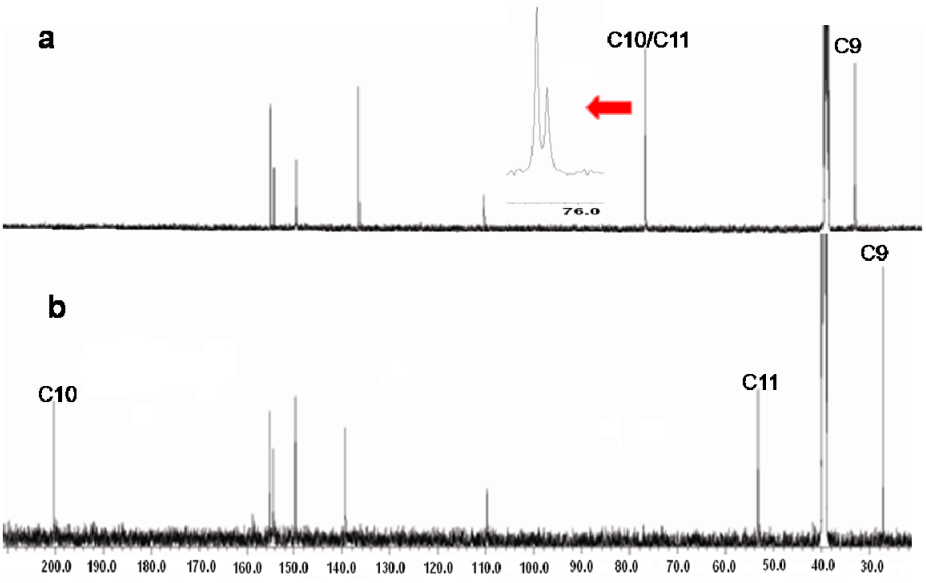
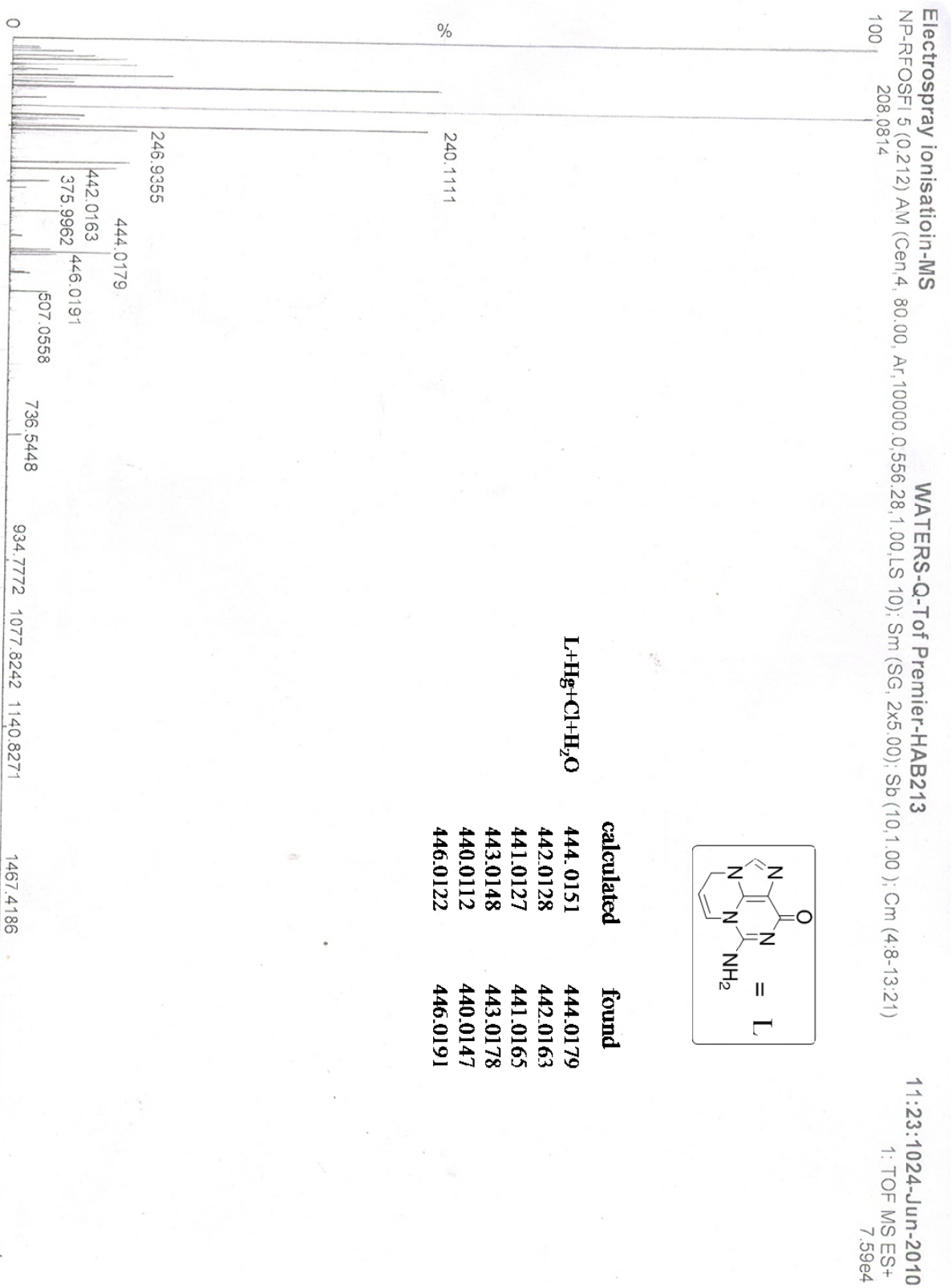


Figure S12: ESI-HRMS of complex **2**.



	calculated	found
L+Hg+Cl+H$_2$O	**444. 0151**	**444.0179**
	442.0128	**442.0163**
	441.0127	**441.0165**
	443.0148	**443.0178**
	440.0112	**440.0147**
	446.0122	**446.0191**

Figure S13: IR spectrum of complex **2**.

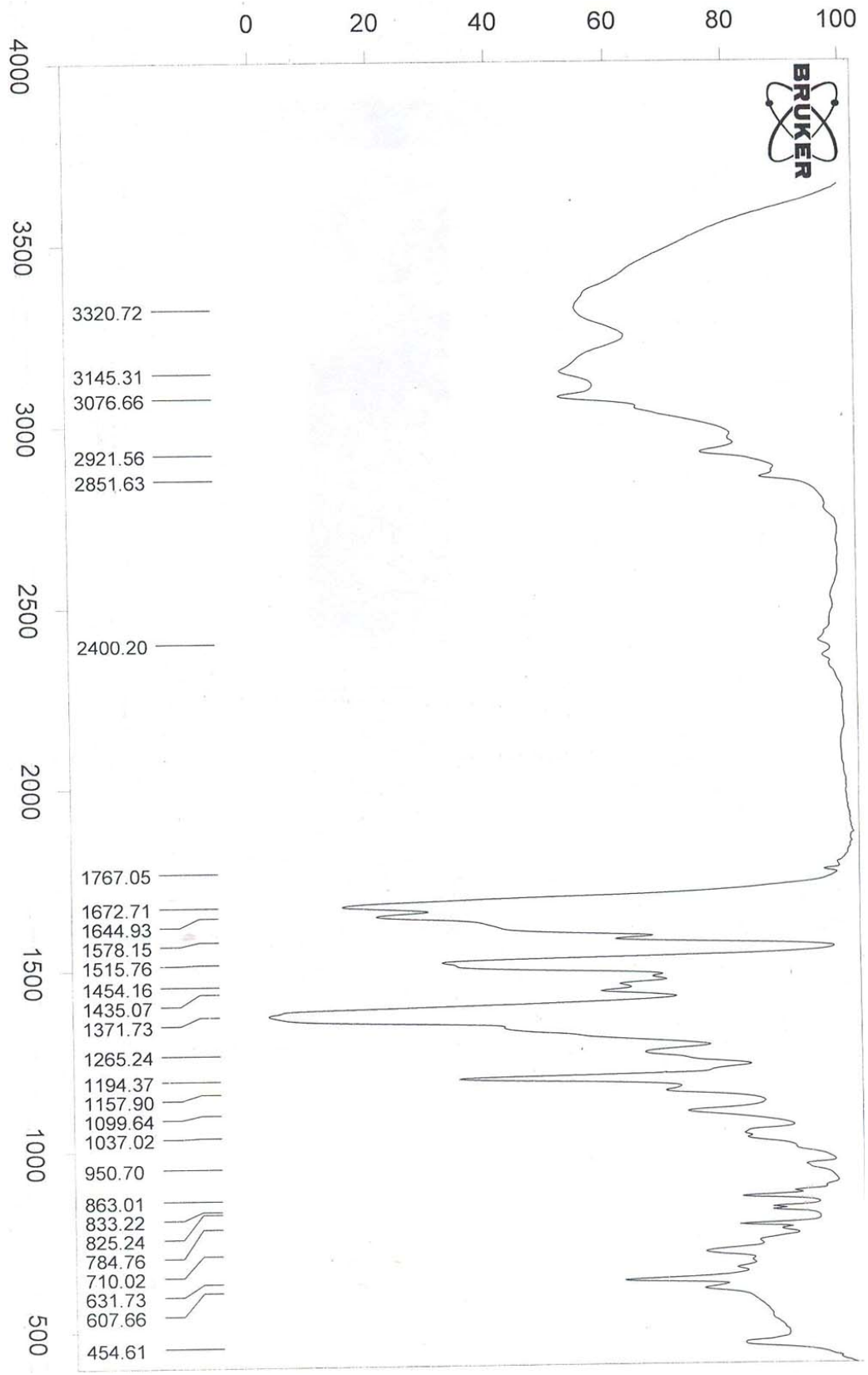
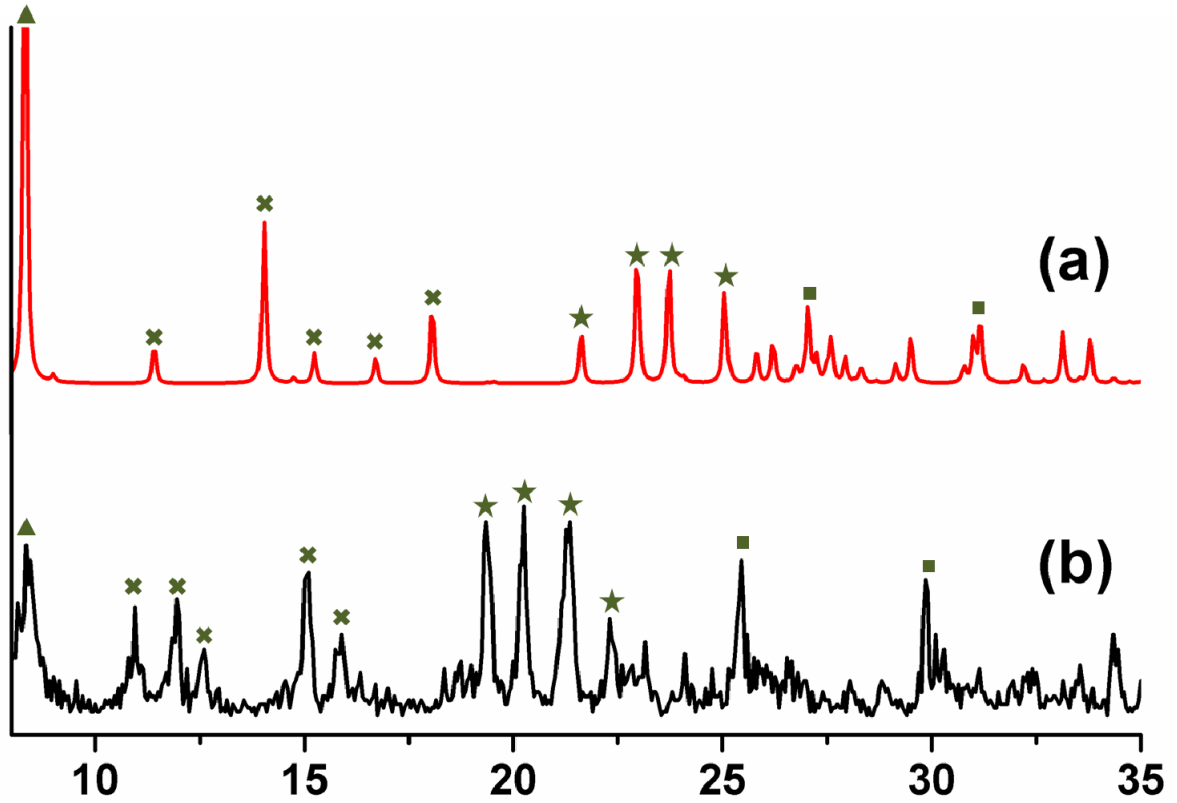


Figure S14: PXRD spectrum of complex **2.** (a) simulated pattern at 100 K (b) observed pattern at 298 K.



The peak correspondence is marked with symbols. The reason peaks are shifted may be attributed to difference in temperature for simulated and observed PXRD data, which causes a difference in the interplanar distances, thus changing the θ values.

References:

1. W. E. Lindsell, C. Murray, P. N. Preston and T. A. J. Woodman, *Tetrahedron*, 2000**, 56**, 1233.

2. S. Fletcher, V. M. Shahani and P. T. Gunning, *Tetrahedron Lett.*, 2009, **50**, 4258.

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