

Supporting information

Adenine containing architectures from silver supported dimeric units

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General procedures: ^1H and ^{13}C NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer operating at 500MHz. The spectra were recorded in methanol- d_4 solution and the chemical shifts were referenced with respect to tetramethylsilane. Elemental analyses of the compounds were obtained on a thermoquest CE instrument CHNS-O EA/110 model High resolution (ESI⁺ mode) mass spectra were obtained on WATERS HAB 213 machine, Department of Chemistry, IIT Kanpur.

Synthesis of N9-propyladenine (9-PA): The synthesis of 9-PA was reported earlier from our lab.¹ A similar protocol was followed and the purity of the product was further confirmed by spectroscopic techniques.

Synthesis of 8-bromo-N9-propyladenine: The title compound was synthesized by following a literature procedure with little modification.² 9-PA (2.0 g, 1.0 eq) was refluxed with 10 mL of bromine solution for 24 hours under nitrogen atmosphere. After this, excess bromine was quenched with aqueous sodium hydrogen sulphite solution. 8-bromo-N9-propyladenine was separated from the aqueous layer using CHCl_3 . The organic layer was separated, dried over Na_2SO_4 and evaporated under high vacuum. Finally, the compound was purified by column chromatography eluting with MeOH/ CHCl_3 (2:98) to afford brown colour powder. (1.62 g, 56% Yield). HRMS: $(\text{M}+\text{H})^+$ calculated: 256.0198, found: 256.0191; ^1H NMR (500 MHz, CD_3OD , 25 °C, TMS): δ (ppm) 0.94 (t, 3H, CH_3), 1.86 (m, 2H, CH_2), 4.17 (t, 2H, CH_2), 8.14 (s, 1H, C2-H); ^{13}C NMR (125 MHz, CD_3OD , 25 °C, TMS): δ (ppm) 11.20, 23.81, 30.77, 120.52, 128.68, 151.9377, 153.75, 156.14.

Synthesis of 8-N, N-dimethylamino-N9-propyladenine (1): The compound **1** was prepared by following the modified literature procedure.³ 8-bromo-N9-propyladenine (1.62 g, 1.0 eq) was refluxed with 5 mL of N, N-dimethylamine under nitrogen atmosphere for 24 hours. The reaction mass was dried under high vacuum and subjected for column chromatography eluting

with MeOH/CHCl₃ (2.5:97.5) to afford the desired compound as a white powder. (0.84 g, 60% Yield). Anal. Calculated for C₁₀H₁₆N₆ (**1**): C, 54.53; H, 7.32; N, 38.15. Found: C, 54.88; H, 7.20; N, 37.36. HRMS: (M+H)⁺ calculated: 221.1515, found: 221.1511; ¹H NMR (500 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 0.87 (t, 3H, CH₃), 1.83 (m, 2H, CH₂), 2.98 (s, 6H, 2[N-CH₃]), 4.08 (t, 2H, CH₂), 8.04 (s, 1H, C2-H); ¹³C NMR (125 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 11.21, 22.88, 42.07, 46.15, 117.37, 151.48, 151.97, 154.50, 157.64.

Synthesis of silver complex (2): In a 25 mL round bottom flask which was wrapped with aluminum foil, 50 mg of **1** was dissolved in 5 mL methanol and a freshly prepared aqueous AgClO₄ (1.0 eq.) solution was added with stirring. The complex **2** started precipitating out immediately. Stirring was continued for 2 hours. The precipitate was filtered carefully in dark, washed with methanol (4 x 5 mL) to remove any traces of unreacted metal salt and ligand. The white precipitate was collected and dried under high vacuum (50 mg, 52% Yield). Anal. Calculated for C₁₀H₁₆N₆AgClO₄ (**2**): C, 28.09; H, 3.77; N, 19.65. Found: C, 27.72; H, 3.71; N, 18.99. HRMS: [L+Ag]⁺ calculated: 327.0487, 329.0484, found: 327.0533, 329.0544; [2L+Ag]⁺ calculated: 547.1924, 549.1920, found: 547.1924, 549.1933.

Synthesis of silver complex (3): Complex **3** was prepared following the same procedure as described above for complex **2** using AgNO₃ instead of AgClO₄. The white precipitate was collected and dried under high vacuum (53 mg, 55% Yield). Anal. Calculated for C₁₀H₂₀N₇AgO₅ (**3**): C, 28.18; H, 4.73; N, 23.01. Found: C, 28.39; H, 3.92; N, 22.68. HRMS: [L+Ag]⁺ calculated: 327.0487, 329.0484, found: 327.0483, 329.0498; [2L+Ag]⁺ calculated: 547.1924, 549.1920 found: 547.1747, 549.1770.

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 K α radiation. The data integration and reduction were processed with the SAINT software.⁴ An absorption correction was applied.⁵ 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.⁶ Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters however in case of complex **3**, the hydrogen atoms of

water molecules present in the lattice are located on Fourier map and refined with restraints like DFIX and DANG to fix the H—O distance and H—O—H angle, respectively. Crystal structure refinement parameters and H-bonding parameters are given as Table S1 and Table S2, respectively. CCDC contains the supplementary crystallographic data for this paper with a deposition numbers of CCDC **803419**, **803420** and **807830**. 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].

Table S1. Crystal structure refinement parameters for **1–3**.

Identification code	Ligand 1	Complex 2	Complex 3
Empirical formula	C ₁₀ H ₁₆ N ₆	C ₁₀ H ₁₆ N ₆ AgClO ₄	C ₁₀ H ₂₀ N ₇ AgO ₅
<i>Mr</i>	220.29	427.61	426.20
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.9530(19)	12.4905(17)	8.7996(13)
<i>b</i> /Å	11.212(3)	11.1849(15)	12.9830(19)
<i>c</i> /Å	12.307(3)	11.9231(16)	13.942(2)
<i>α</i> /°	90	90	90
<i>β</i> /°	103.187(4)	117.768(2)	101.802(2)
<i>γ</i> /°	90	90	90
Volume/ Å ³	1068.5(4)	1473.9(3)	1559.1(4)
<i>Z</i>	4	4	4
<i>D_x</i> /Mg m ⁻³	1.369	1.927	1.816
<i>F</i> (000)	472	856	864
<i>μ</i> / mm ⁻¹	0.091	1.577	1.331
<i>θ</i> range for data collection/ °	2.49 to 26.00	2.59 to 28.29	2.17 to 28.38
Limiting indices	-9 → <i>h</i> → 9, -13 → <i>k</i> → 7, -14 → <i>l</i> → 15	-16 → <i>h</i> → 7, -14 → <i>k</i> → 14, -14 → <i>l</i> → 15	-11 → <i>h</i> → 11, -13 → <i>k</i> → 17, -18 → <i>l</i> → 18
Reflections collected	5700	9243	9956
unique reflections	2084	3599	3813
<i>R</i> (int)	0.0625	0.0621	0.0500
Completeness to <i>θ</i>	= 26.00, 99.6	= 28.29, 99.8	= 28.38, 99.4
Data / restraints / parameters	2084 / 0 / 147	3599 / 0 / 201	3813 / 6 / 225
Goodness-of-fit on <i>F</i> ²	1.130	1.187	1.139
<i>R</i> 1 and <i>R</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0626, 0.1522	0.0513, 0.1429	0.0532, 0.1482
<i>R</i> 1 and <i>R</i> 2 (all data)	0.0821, 0.1749	0.0738, 0.2353	0.0807, 0.2324
Largest diff. peak and hole/e.Å ⁻³	0.556 and -0.507	2.789 and -2.167	2.926 and -1.979
CCDC No.	803419	803420	807830

Table S2. Hydrogen bond and short contact parameters for **1–3**.[#]

D—H...A[#]	<i>d</i>_{H...A}	<i>d</i>_{D...A}	∠D—H...A
Ligand 1			
N(6)—H(6A)···N(1) ⁱ	2.22	3.077(3)	179
N(6)—H(6B)···N(3) ⁱⁱ	2.26	3.096(3)	164
C(2)—H(2)···N(7) ⁱⁱⁱ	2.62	3.419(3)	145
Complex 2			
N(6)—H(6A)···O(4) ^{iv}	2.53	3.128(9)	128
N(6)—H(6A)···N(3) ^v	2.50	3.228(8)	143
N(6)—H(6B)···O(3) ^{vi}	2.24	3.045(7)	156
C(2)—H(2)···O(3) ^{vii}	2.44	3.339(8)	164
C(2)—H(2)···O(4) ^{viii}	2.46	3.209(7)	138
Complex 3			
N(6)—H(6A)···O(1) ^{viii}	2.14	2.935(6)	153
N(6)—H(6B)···O(1W)	2.06	2.837(7)	150
O(1W)—H(1W1)···O(3) ^{ix}	2.02(5)	2.785(7)	150(7)
O(1W)—H(1W2)···O(2W) ^x	1.86(5)	2.718(6)	174(12)
O(2W)—H(2W1)···O(2)	2.06(10)	2.844(7)	153(12)
O(2W)—H(2W1)···O(3)	2.50(14)	3.207(7)	140(12)
O(2W)—H(2W2)···N(3) ^{xi}	2.09(8)	2.871(6)	152(7)
C(2)—H(2)···O(3) ^{xi}	2.54	3.347(8)	145
C(10)—H(10A)···O(2) ^{xii}	2.53	3.416(7)	152

[#]Symmetry of A: (i) 2-x, 1-y, 2-z; (ii) -1/2+x, 1/2-y, -1/2+z; (iii) 1/2+x, 1/2-y, 1/2+z; (iv) -x, 1/2+y, 3/2-z; (v) x, 1/2-y, -1/2+z; (vi) x, 1/2-y, -1/2+z; (vii) -x, -y, 2-z; (viii) 3/2-x, -1/2+y, 3/2-z; (ix) 1/2+x, 3/2-y, -1/2+z (x) 1+x, y, z; (xi) 1-x, 1-y, 2-z; (xii) 1/2+x, 3/2-y, 1/2+z where A= acceptor and D=donor; all the distances are in Å and bond angles are in degree.

Table S3: Various silver coordination bond lengths and angles for complexes **2** and **3**.[#]

Bond length (Å)		Bond angles (°)	
Complex 2			
Ag1–N1 ⁱ	2.1845(67)	N1 ⁱ –Ag1–N3 ⁱⁱ	103.298(183)
Ag1–N3 ⁱⁱ	2.6500(49)	N1 ⁱ –Ag1–N7	156.854(194)
Ag1–N7	2.1754(55)	N1 ⁱ –Ag1–O4 ⁱⁱⁱ	86.644(162)
Ag1–O4 ⁱⁱⁱ	2.6974(49)	N3 ⁱⁱ –Ag1–N7	85.905(175)
		N3 ⁱⁱ –Ag1–O4 ⁱⁱⁱ	78.490(138)
		N7–Ag1–O4 ⁱⁱⁱ	116.205(154)
Complex 3			
Ag1–N1	2.1705(40)	N1–Ag1–N7 ^{iv}	178.40(15)
Ag1–N7 ^{iv}	2.1807(40)	N1–Ag1–O1W ^{iv}	94.820(139)
Ag1–O1W ^{iv}	2.7319(45)	N1–Ag1–O2 ^{iv}	95.845(150)
Ag1–O2 ^{iv}	2.7650(57)	N7 ^{iv} –Ag1–O1W ^{iv}	85.288(139)
		N7 ^{iv} –Ag1–O2 ^{iv}	83.210(149)
		O1W ^{iv} –Ag1–O2 ^{iv}	145.871(142)

[#]Symmetry element: (i) -x, 0.5+y, 1.5-z; (ii) -x, 1-y, 2-z; (iii) x, 1+y, z; (iv) 1.5-x, -0.5+y, 1.5-z.

Figure S1: Hydrogen bonded crystal lattice of ligand **1** when viewed along *a*-axis (C8 and N9-substituen has been removed for clarity; color code: C, gray; N, blue and H light gray).

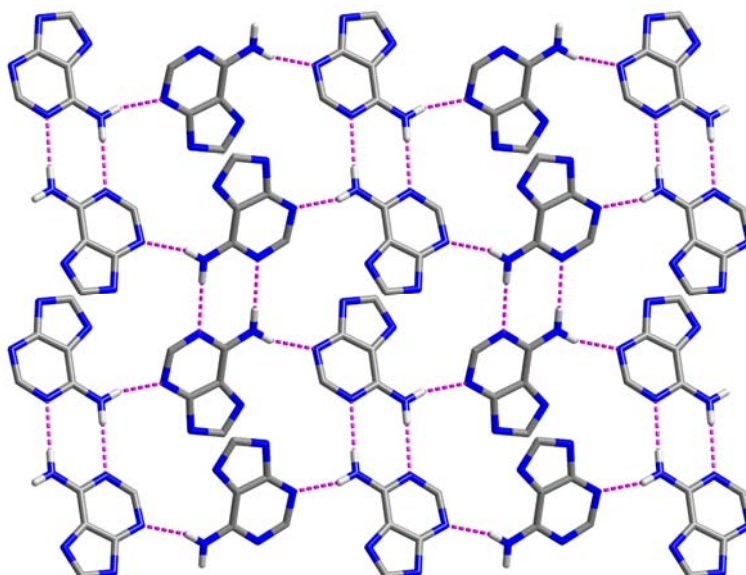


Figure S1 shows the formation of hexameric assembly as a result of intricate hydrogen bonding.

Figure S2: π -stacking interaction in the crystal lattice of complex **2**.

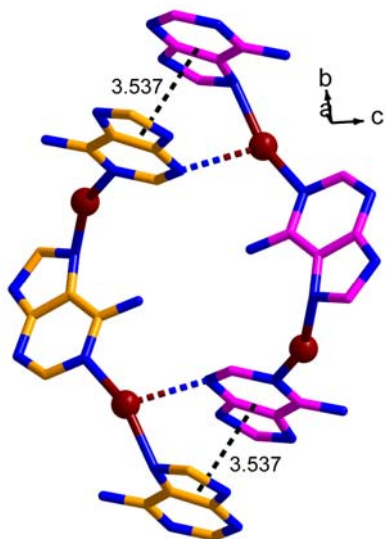


Figure S2 shows the π -stacking interaction between adenine residues stabilizes the metallacycle formation from 1D polymeric chain in the crystal lattice of complex **2**.

Figure S3: Hydrogen bonding pattern of complex **2**

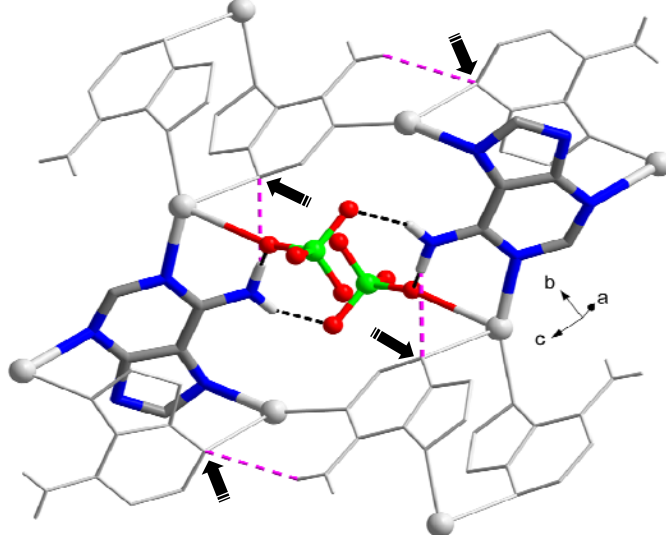


Figure S3 Shows Hydrogen bonding in case of complex **2** as striped lines; arrows highlight involvement of weakly coordinated N3 nitrogens in H-bonding with N6 protons.

Figure S4: ORTEP diagram of complex **3** at 35% probability level.

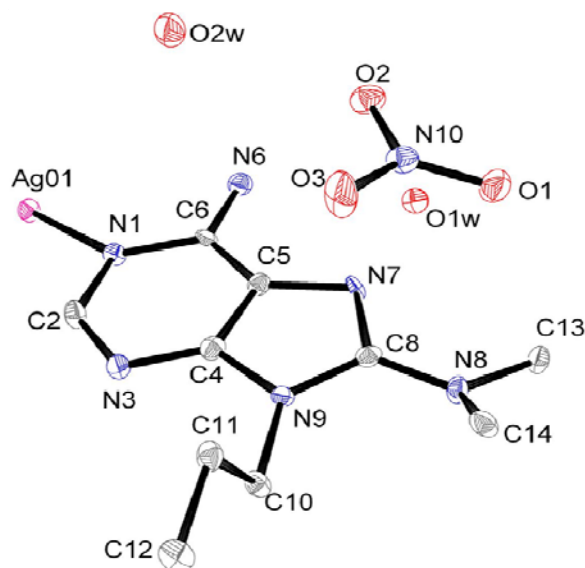


Figure S4 shows the ORTEP representation of complex **3** consisting one molecule of ligand **1** coordinated with one silver ion which is neutralized with nitrate ion along with two water molecules.

Figure S5: View of crystal lattice of complex **3**.

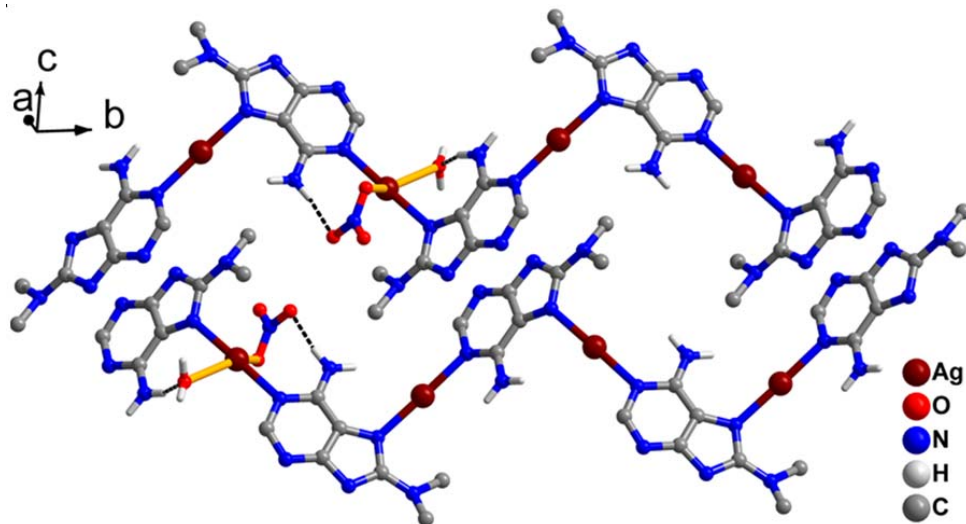


Figure S5 shows 1D coordination polymer as a result of bidentate coordination mode (N7, N1) rendered by adenine.

Figure S6: ¹H NMR spectrum of 1.

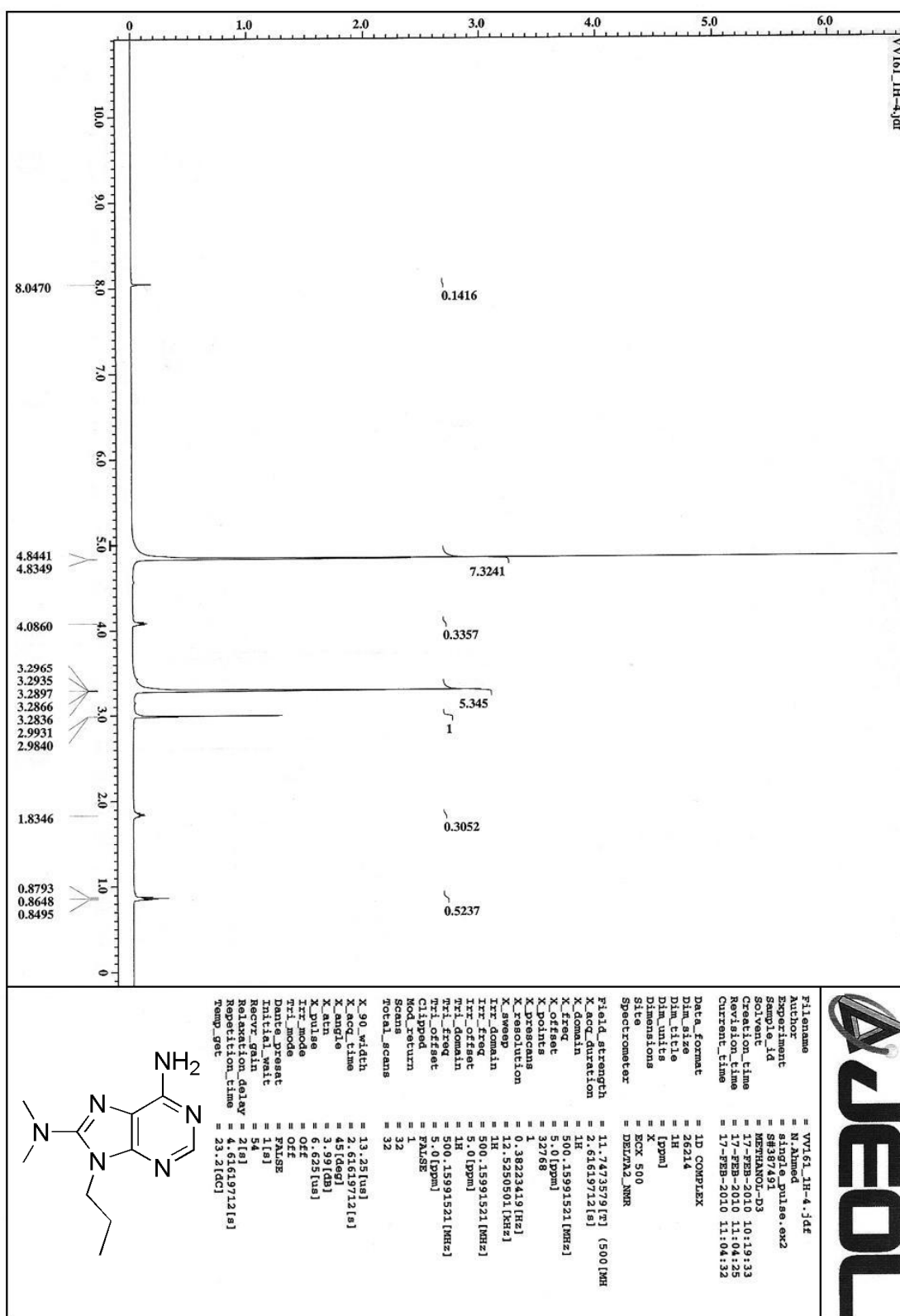


Figure S7: ^{13}C NMR spectrum of 1.

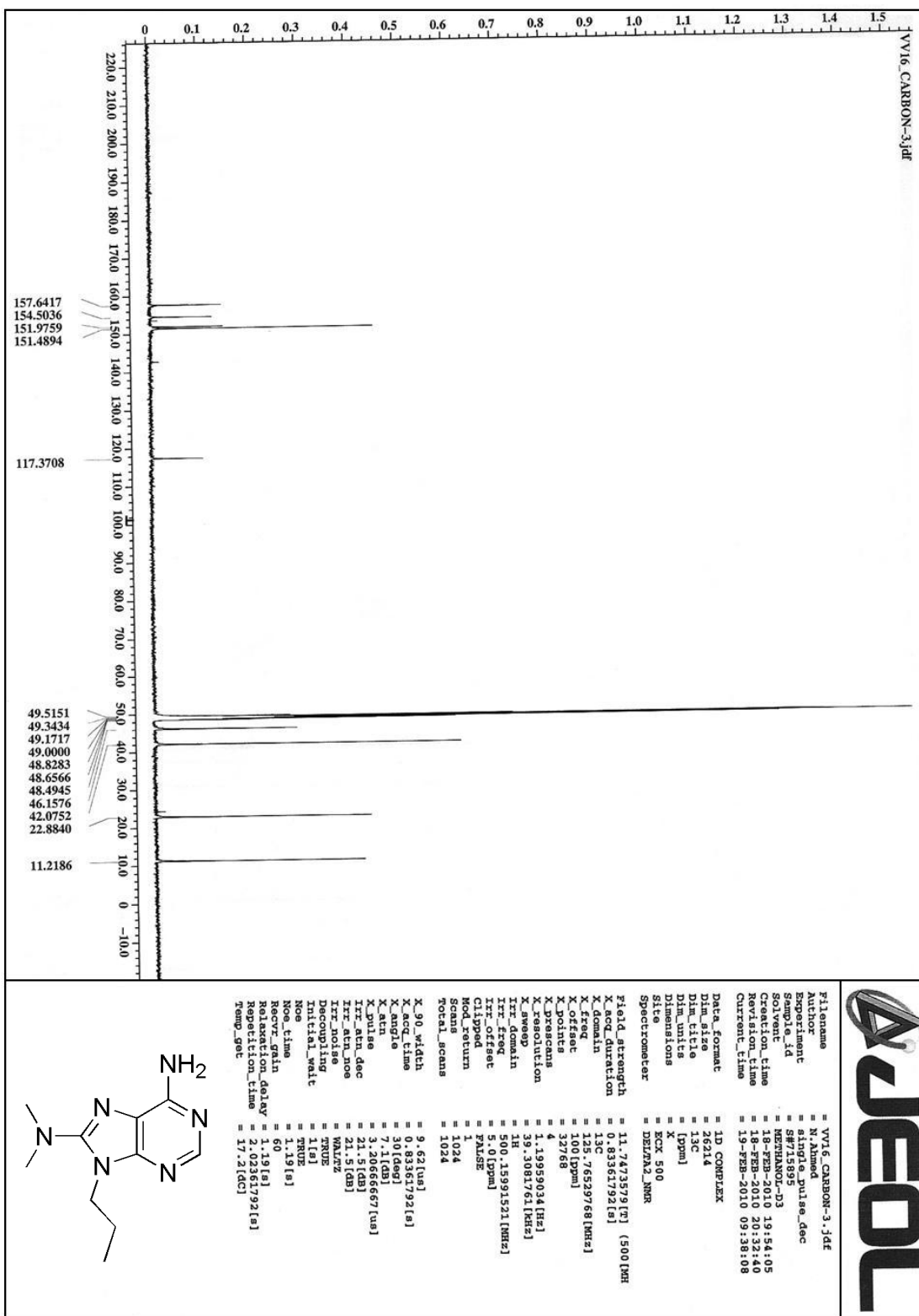


Figure S8: ESI–HRMS of ligand **1**.

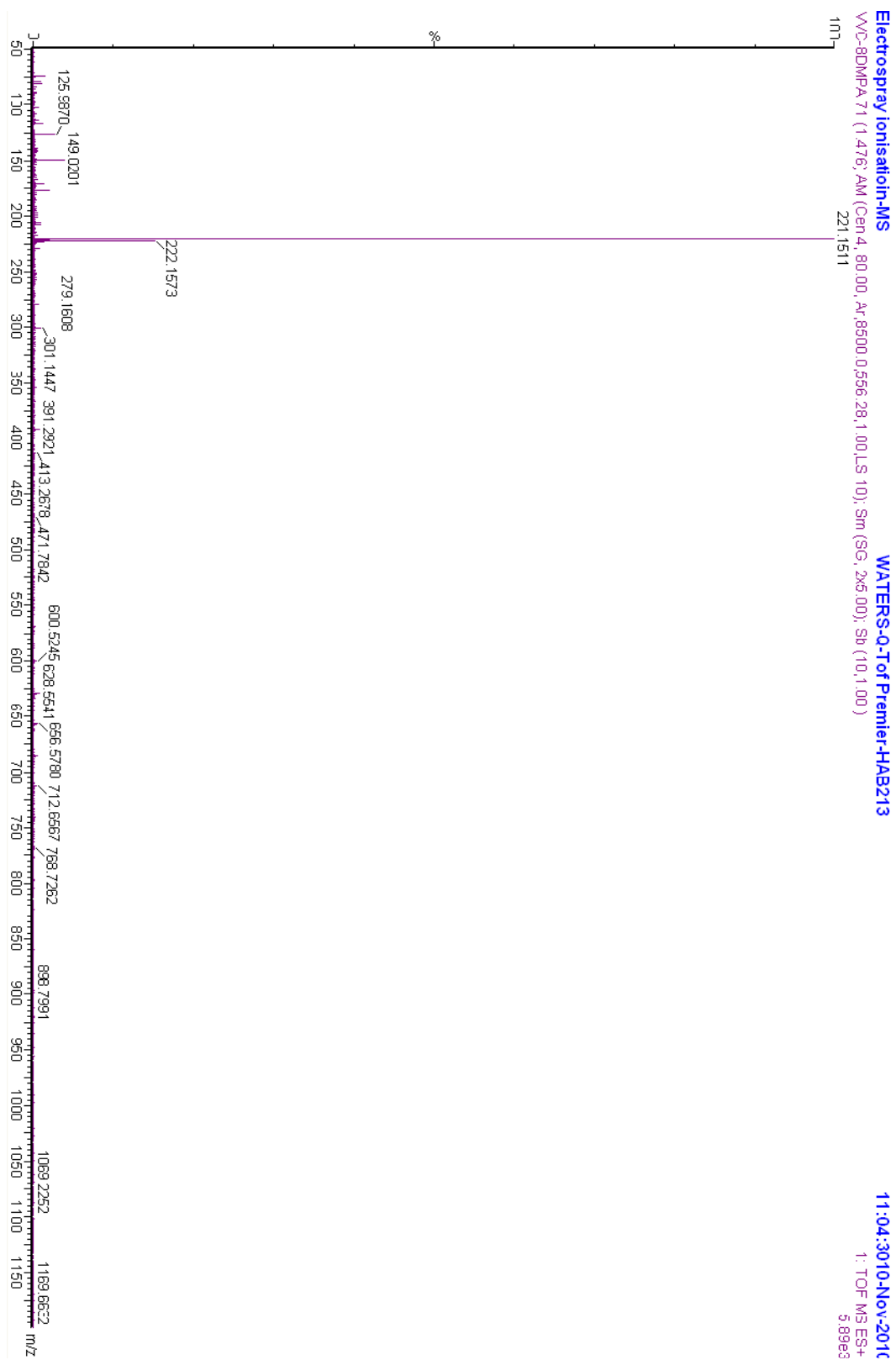


Figure S9: ESI-HRMS of complex 2.

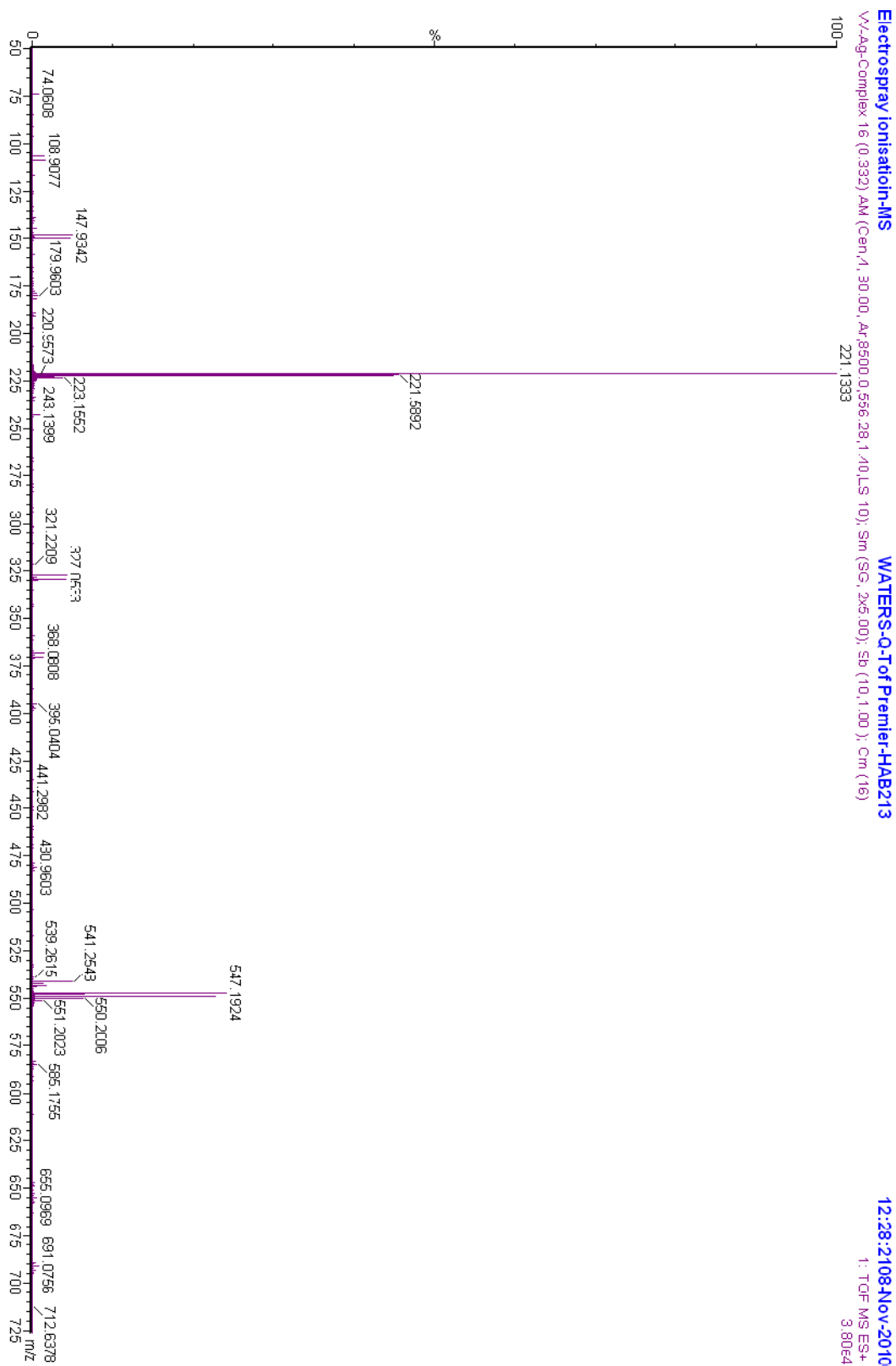
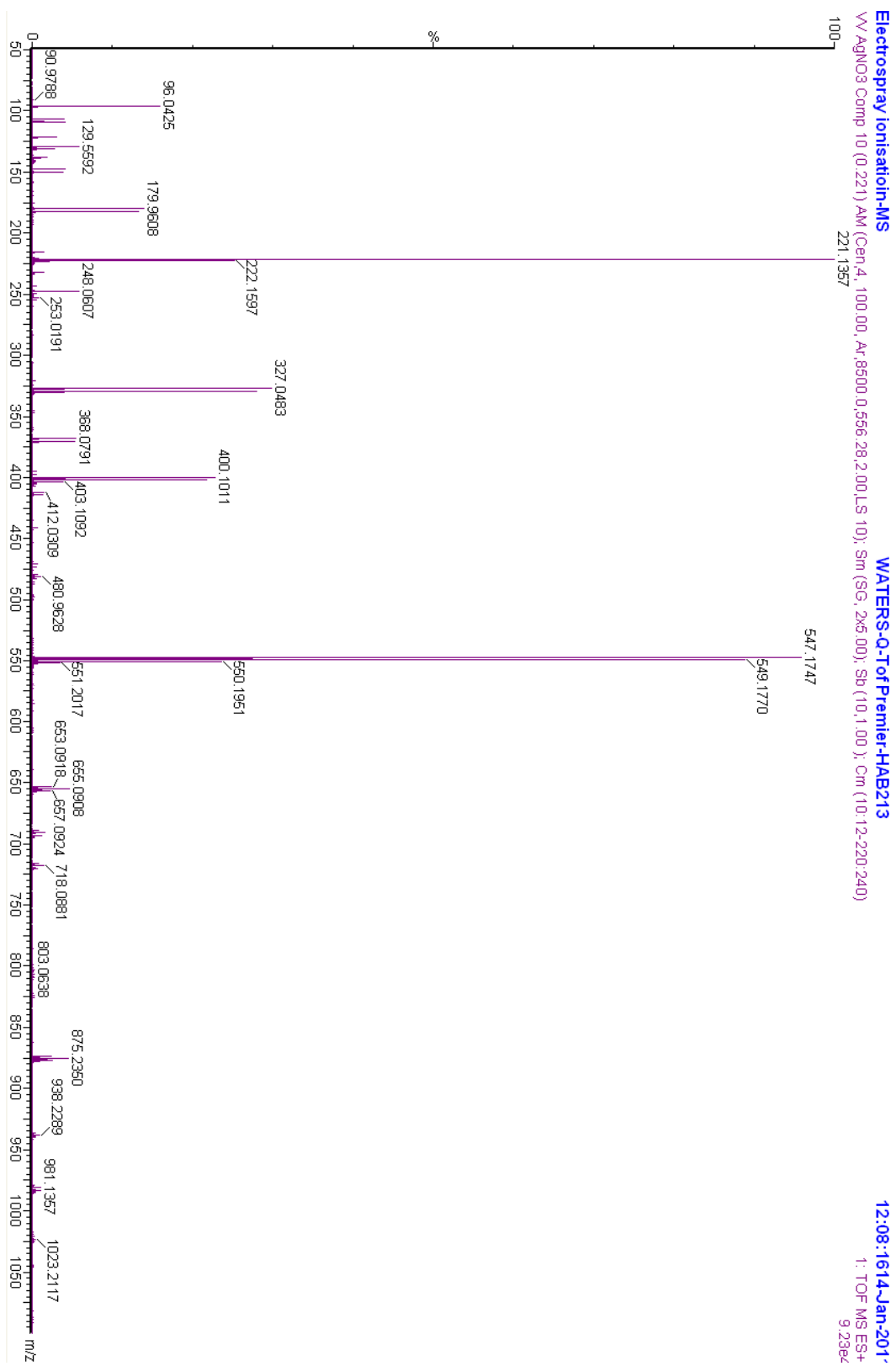


Figure S10: ESI-HRMS of complex 3.



Reference:

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