Electronic Supporting Information

Azulene tethered *N*-aryl nucleobases: synthesis, morphology and biochemical evaluations

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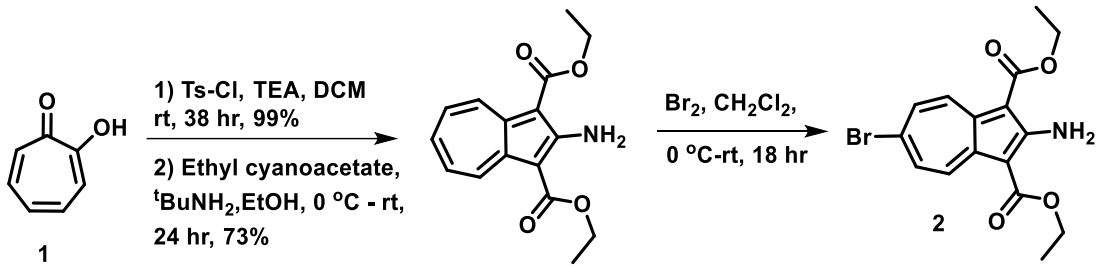
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and were used as received. DMF was distilled over CaH_2 and stored over 4Å molecular sieves. Reactions were monitored by thin layer chromatography, visualized by UV and Ninhydrin. Column chromatography was performed in 100-200 mesh silica. Mass spectra (HRMS) were obtained from Bruker microTOF-Q II and Waters Spectrometer and the samples were prepared in methanol and injected in methanol and water mixture. NMR spectra were recorded on Bruker 400 MHz and Bruker 700 MHz NMR spectrometer at room temperature and processed using Mnova software from Mestrelab Research. The crystal data were collected on a Rigaku Oxford diffractometer. Absorption spectra were obtained using Jasco V-730 spectrometer. The surface morphologies of compounds were studied with field emission scanning electron microscopy (FESEM, Merlin Compact with a GEMINI-I/ GEMINI-II electron column, Zeiss Pvt. Ltd., Germany) and high-resolution transmission electron microscopy (HRTEM, JEOL 2100F). FTIR analysis of the samples was carried out by the PerkinElmer FTIR spectrometer equipped with an attenuated total reflectance accessory.

2. Synthesis of Diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (2)

Diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (**2**) was synthesized from commercially available Tropolone by following the reported procedure.[1, 2]



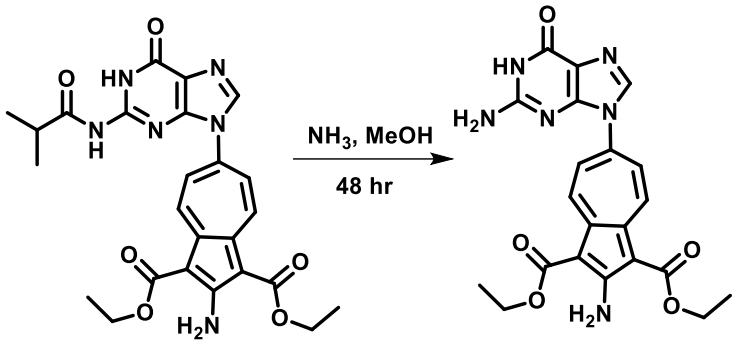
3. General procedure for the preparation of N-Azulenyl Nucleobases

In a round bottom flask a mixture of Nucleobase (1 equiv.) (Thymine/ Cytosine/ Adenine/ *N*-isobutyryl-Guanine), Diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (1.2 equiv.), K_2CO_3 (4 equiv.) and 18-C-6 (0.02 equiv.) in anh. DMF was stirred and heated in an oil bath at 80 ^oC for 72 h. After cooling it to room temperature the mixture was filtered through a pad of celite and the solution was evaporated in reduced pressure. The residue

was subjected to column chromatography using 100-200 mesh silica gel and MeOH: DCM as solvent system to get the desired products. . In case of guanine, we didn't get regioselectivity unlike in other cases. All the compounds were completely soluble in DMSO but Az-A wasn't, when concentration was high.

Deprotection of Isobutyryl group:

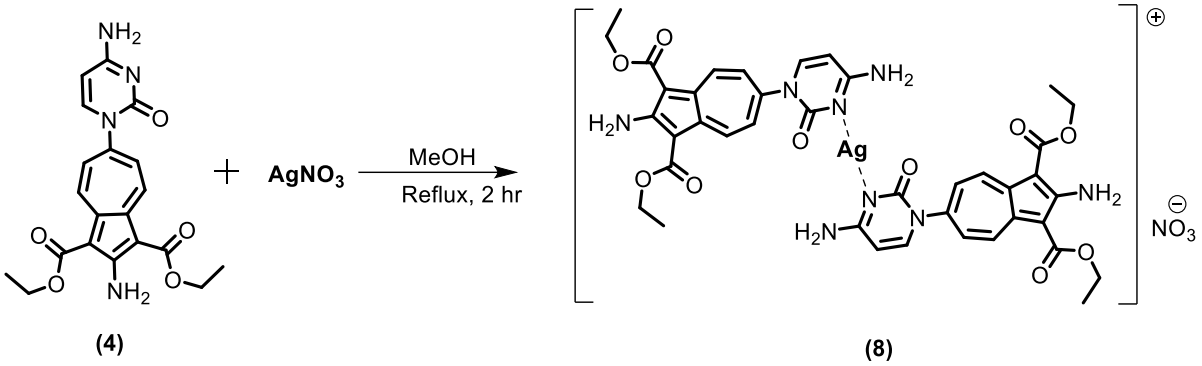
To the solution of compound **^{i}Bu-6** (N^9 derivative) (**7**) (.04 mmol) in MeOH, ammonia solution (7N methanolic ammonia) was added and the resulting solution was stirred for 48 h at room temperature. After completion the reaction mixture was evaporated in reduced pressure. The residue was washed with n-pentane thrice. To the residue small amount of MeOH was added followed by addition of excess diethyl ether solution resulting in precipitation of product. The solution was decanted and the precipitate was dried in rota vapour under reduced pressure to get the product compound **6** in 87 % yield.



^{i}Bu-6 6

4. Procedure for the preparation of Silver complex Az-C-Ag (8)

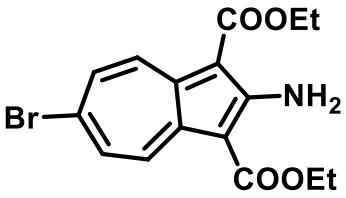
Az-C (**4**) (.025 mmol, 2.0 equiv.) was dissolved in MeOH (2 ml). To this solution, another solution (0.5 ml) of $AgNO_3$ (0.12 mmol, 1.0 equiv.) was added slowly. The mixture was heated under reflux (77 °C) for 2 h in the dark. The solution was filtered while still warm. After cooling it to room temperature diethyl ether solution was added to precipitate the compound. The compound was dried under reduced pressure, washed with n-pentane and dried again, giving the product (**8**) in 62% yield.



(4) (8)

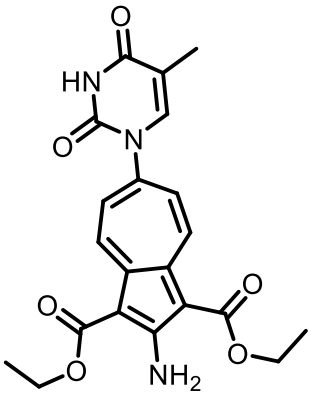
5. Characterization data of products

Diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate(**2**): Following the reported procedure the



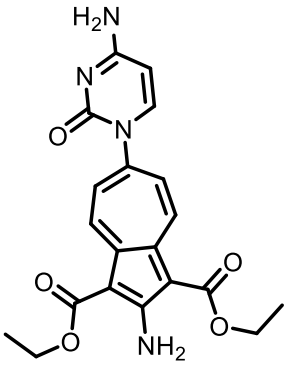
title compound was synthesized and obtained as a deep purple solid.[1,2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 11.5 Hz, 2H), 7.81 (s, 2H), 7.78 (d, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.23, 162.34, 144.33, 135.31, 129.45, 128.37, 101.00, 60.07, 14.61. HRMS (ESI) calcd for $C_{16}H_{16}BrNO_4$: $[M+Na]^+$ 388.0155, found 388.0135.

Diethyl 2-amino-6-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)azulene-1,3-



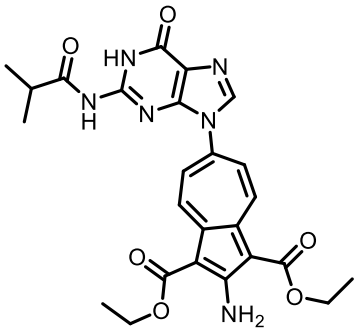
dicarboxylate(**3**): Following the general procedure the title compound was isolated by column chromatography (eluent: dichloromethane) as a yellow solid in 35% yield (46 mg).^{1}H NMR (400 MHz, DMSO) δ 11.53 (s, 1H), 9.05 (d, *J* = 11.5 Hz, 2H), 7.94 (s, 2H), 7.76 (s, 1H), 7.71 (d, *J* = 11.5 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 4H), 1.83 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 165.75, 164.83, 161.98, 151.07, 145.07, 141.81, 141.48, 132.91, 128.96, 110.00, 100.39, 60.28, 14.87, 12.33, HRMS (ESI) calcd for $C_{21}H_{21}N_3O_6$: $[M+Na]^+$ 434.1323, found 434.1309, FT-IR (cm^{-1}) 3497, 3374, 3168, 3061, 2972, 2954, 2922, 2849, 2818, 2377, 2332, 2322, 1701, 1678, 1647, 1597, 1560, 1532, 1507, 1492, 1456, 1427, 1376, 1302, 1283, 1233, 1188, 1151, 1115, 1073, 1039, 986, 931, 854, 819, 790, 753, 686, 640, 613, 592, 560.

Diethyl 2-amino-6-(4-amino-2-oxopyrimidin-1(2H)-yl)azulene-1,3-dicarboxylate (**4**) : Following the general procedure the title compound was isolated by column chromatography



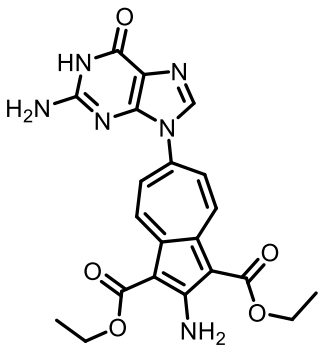
(eluent: dichloromethane) as a yellow solid in 34% yield (49 mg).^{1}H NMR (700 MHz, DMSO) δ 9.05 (d, *J* = 10.6 Hz, 2H), 7.90 (s, 2H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 10.6 Hz, 2H), 7.51 (s, 1H), 7.40 (s, 1H), 5.86 (d, *J* = 7.1 Hz, 1H), 4.41 (q, *J* = 13.2, 6.1 Hz, 4H), 1.40 (t, *J* = 7.0 Hz, 6H).^{13}C NMR (176 MHz, DMSO) δ 166.38, 166.11, 165.79, 161.80, 155.10, 146.18, 144.88, 144.35, 132.83, 129.13, 100.14, 94.84, 60.19, 14.88. HRMS (ESI) calcd for $C_{20}H_{20}N_4O_5$: $[M+H]^+$ 397.1506, found 397.1501, FT-IR (cm^{-1}), 3512, 3394, 3332, 3278, 3162, 3085, 3054, 2954, 2921, 2859, 2366, 2343, 1692, 1673, 1628, 1596, 1544, 1510, 1495, 1442, 1429, 1382, 1371, 1315, 1278, 1237, 1222, 1183, 1139, 1121, 1104, 1027, 988, 928, 865, 805, 780, 765, 650, 604.

Diethyl 2-amino-6-(2-isobutyramido-6-oxo-1,6-dihydro-9H-purin-9-yl)azulene-1,3-dicarboxylate (**^{i}Bu-6**): Following the general procedure the title compound was isolated by column chromatography (eluent: dichloromethane) as a yellow solid in 7% yield (7 mg).



^{1}H NMR (700 MHz, $CDCl_3$) δ 12.25 (s, 1H), 9.60 (s, 1H), 8.87 (d, *J* = 11.0 Hz, 2H), 8.03 (s, 1H), 7.76 (s, 2H), 7.46 (d, *J* = 11.0 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 4H), 2.93 – 2.82 (m, 6.9 Hz, 1H), 1.46 (t, *J* = 7.1 Hz, 6H), 1.27 (d, *J* = 6.8 Hz, 6H), ^{13}C NMR (176 MHz, $CDCl_3$) δ 179.19, 165.89, 162.47, 155.56, 148.37, 148.25, 144.27, 138.91, 135.81, 128.90, 127.85, 121.58, 101.37, 60.25, 36.41, 19.03, 14.63, HRMS (ESI) calcd for $C_{21}H_{21}N_3O_6$: $[M+H]^+$ 507.1951, found 507.1992.

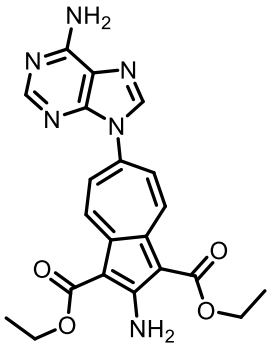
Diethyl 2-amino-6-(2-amino-6-oxo-1,6-dihydro-9H-purin-9-yl)azulene-1,3-dicarboxylate (**6**):



Following the procedure for deprotection of isobutyryl group, the title compound was isolated as a yellow solid in 87% yield (15 mg). ^{1}H NMR (700 MHz, DMSO) δ 9.12 (d, *J* = 11.5 Hz, 2H), 8.40 (s, 1H), 8.12 (s, 1H), 7.98 (s, 1H), 7.94 (s, 1H), 7.93 (d, *J* = 3.7 Hz, 2H), 6.65 (s, 2H), 4.44 – 4.40 (m, *J* = 11.4, 5.7 Hz, 4H), 1.41 (t, *J* = 7.1 Hz, 6H), ^{13}C NMR (176 MHz, DMSO) δ 165.79, 161.84, 157.33, 154.58, 151.70, 144.52, 137.87, 137.46, 130.73, 130.32,

129.43, 117.50, 100.52, 60.29, 14.93, HRMS (ESI) calcd for $C_{21}H_{20}N_6O_5$: $[M+H]^+$ 437.1573, found 437.1571, FT-IR (cm^{-1}), 3487, 3451, 3338, 3169, 3117, 2979, 2904, 2839, 2726, 2198, 2108, 1940, 1720, 1667, 1630, 1584, 1534, 1510, 1483, 1431, 1378, 1353, 1278, 1169, 1115, 1070, 1028, 963, 835, 776, 684, 624, 590, 553.

Diethyl 2-amino-6-(6-amino-9H-purin-9-yl)azulene-1,3-dicarboxylate (**5**) Following the general procedure the title compound was isolated by column chromatography (eluent: dichloromethane) as a yellow solid in 36% yield (46 mg). ^{1}H NMR (400 MHz, DMSO) δ 9.16 (d, *J* = 11.3 Hz, 2H), 8.61 (s, 1H), 8.24 (s, 1H), 8.08 (d, *J* = 11.3 Hz, 2H), 7.92 (s, 2H), 7.38 (s, 2H), 4.43 (q, *J* = 6.9 Hz, 4H), 1.42 (t, *J* = 7.0 Hz, 6H). HRMS (ESI) calcd for $C_{21}H_{20}N_6O_4$: $[M+H]^+$ 421.1619, found 421.1605, FT-IR (cm^{-1}) 3430, 3313, 3176, 3123, 2954, 2917, 2850, 2352, 2336, 2327, 2320, 2308, 1682, 1671, 1660, 1644, 1634, 1591, 1567, 1554, 1531, 1505, 1470, 1454, 1443, 1426, 1415, 1382, 1368, 1336, 1308, 1260, 1194, 1169, 1112, 1064, 1015, 967, 842, 796, 733, 691, 669, 646, 606.



6. ^{1}H, ^{13}C Spectra and HRMS

^{1}H, ^{13}C NMR (400MHz, $CDCl_3$) and HRMS of compound **2**

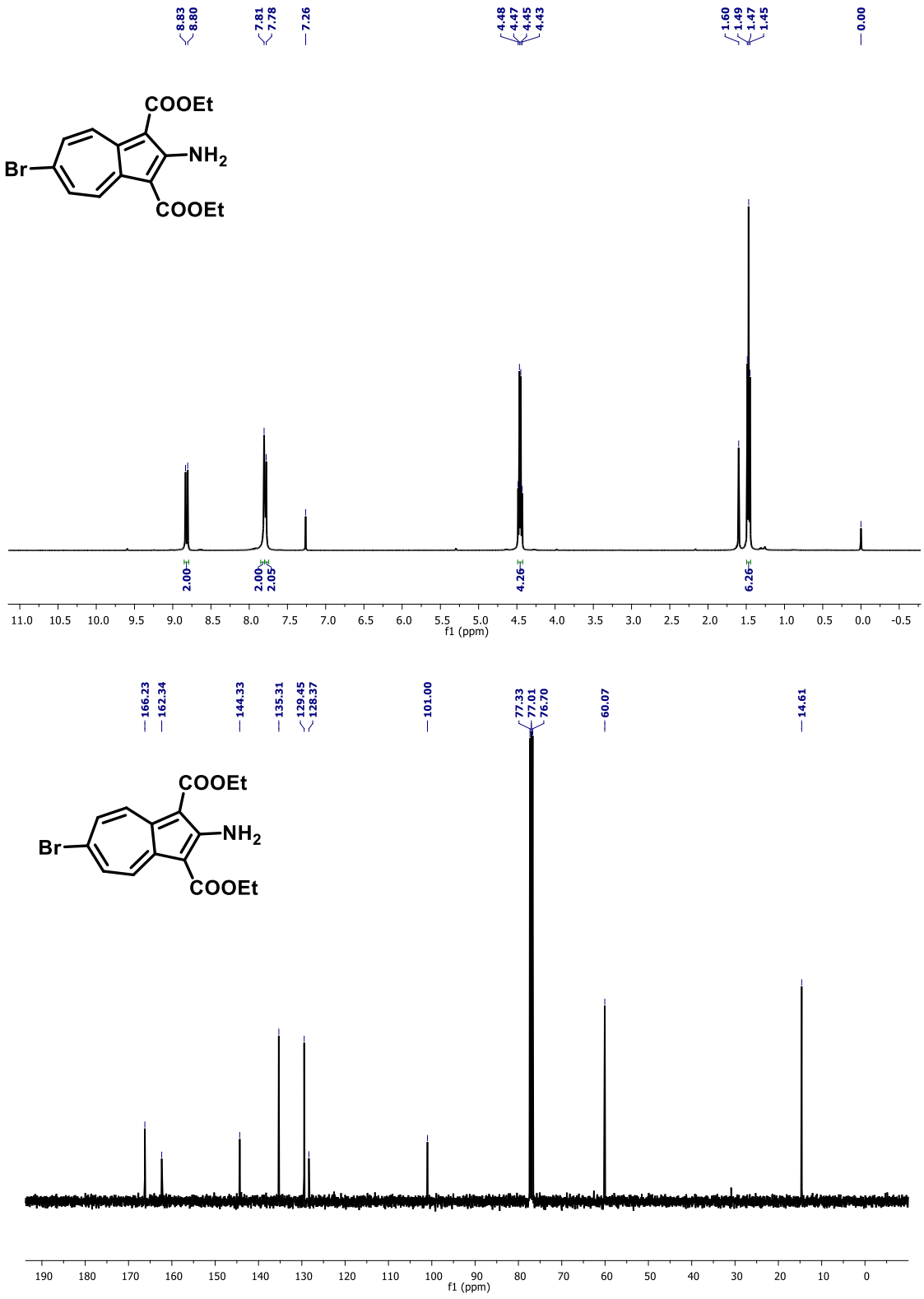


Figure S1. $^{1}H/^{13}C$ NMR (400MHz, $CDCl_3$) spectra of compound **2**.

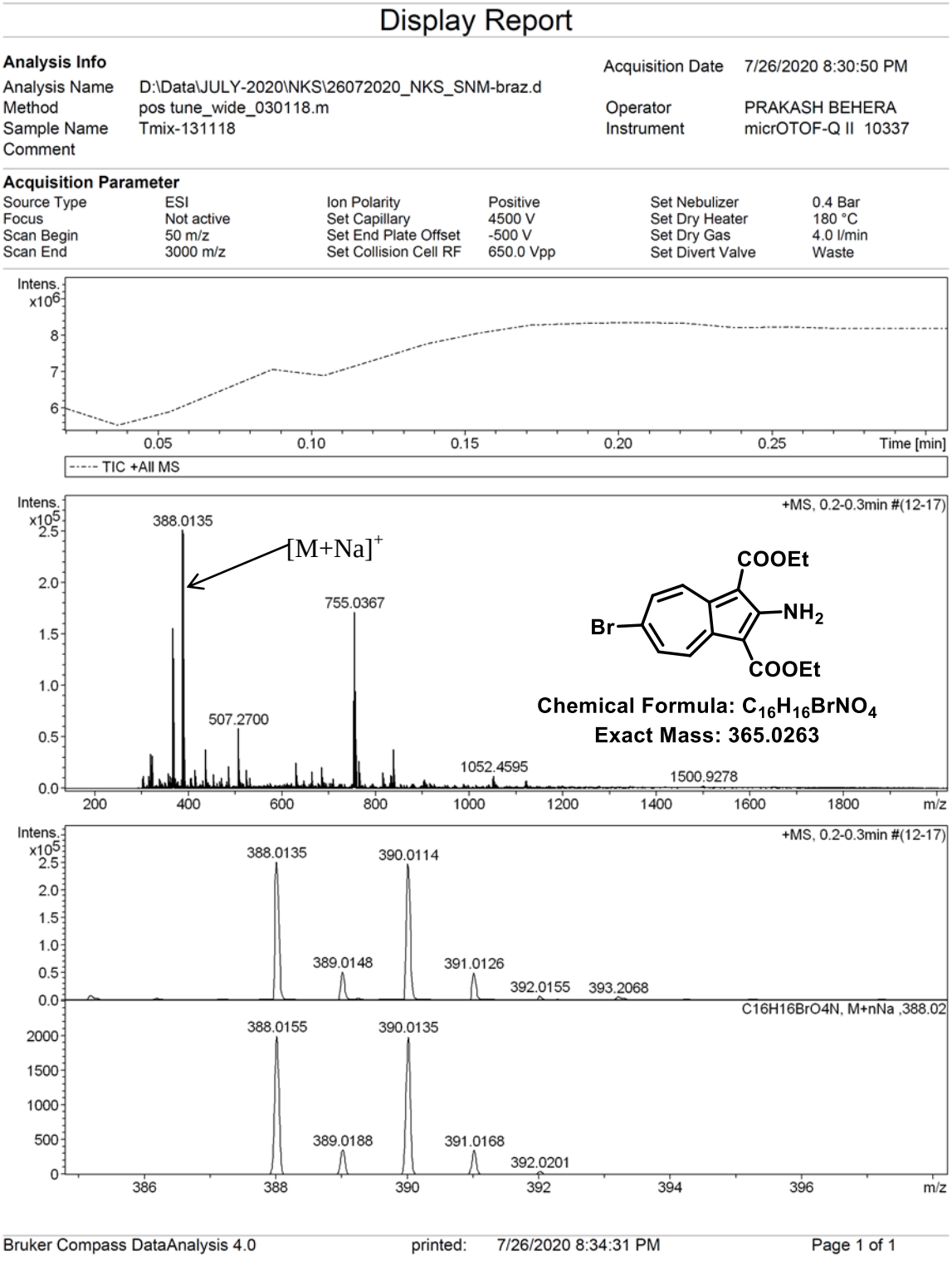


Figure S2. ESI-MS/HRMS spectra of compound **2.**

^{1}H, ^{13}C NMR (400MHz, DMSO) and HRMS of compound **3**

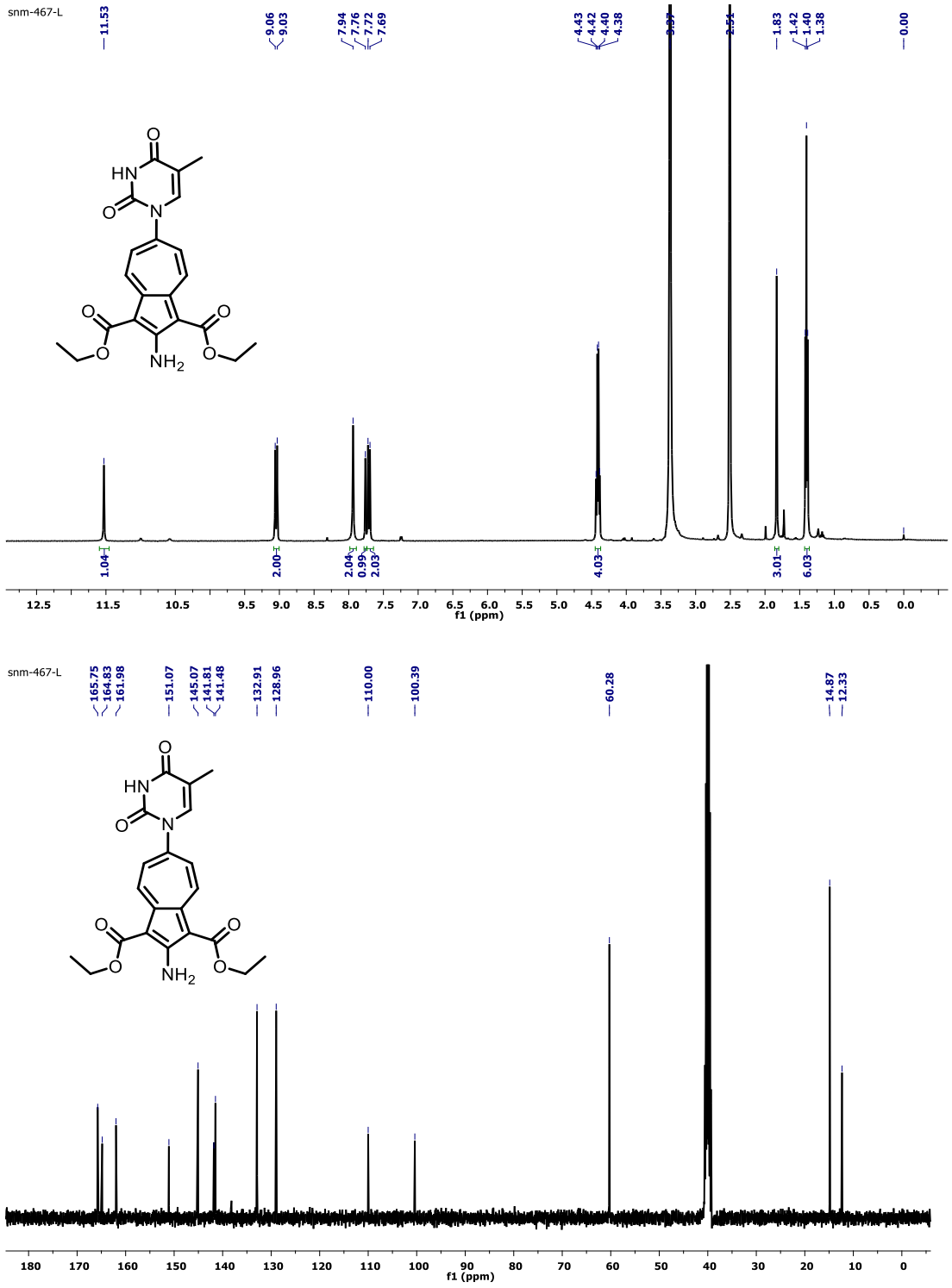


Figure S3. $^{1}H/^{13}C$ NMR (400MHz, DMSO) spectra of compound **3** in DMSO- d_6.

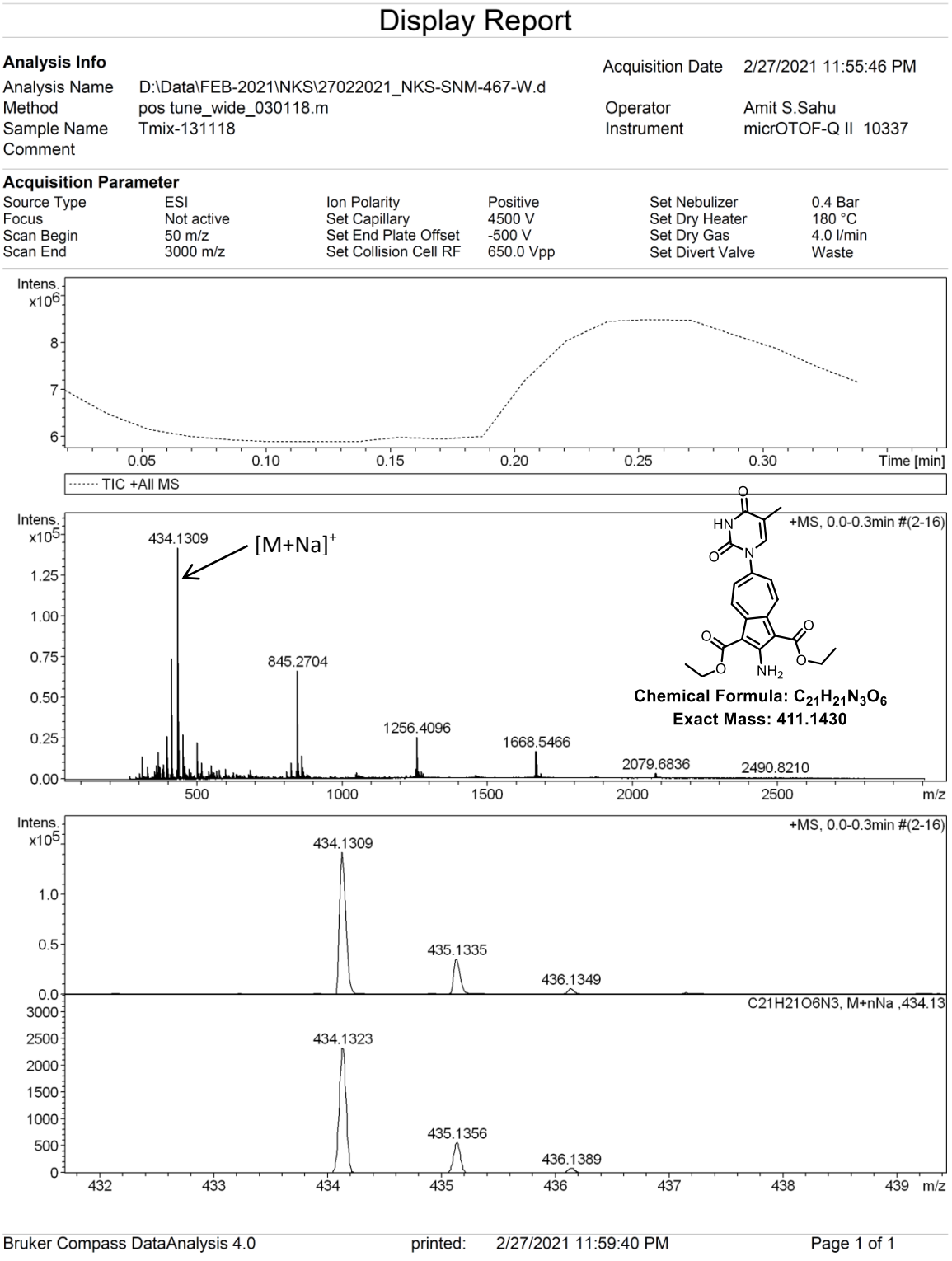


Figure S4. ESI-MS/HRMS spectra of compound **3.**

^{1}H, ^{13}C NMR (700MHz, DMSO) and HRMS of compound **4**

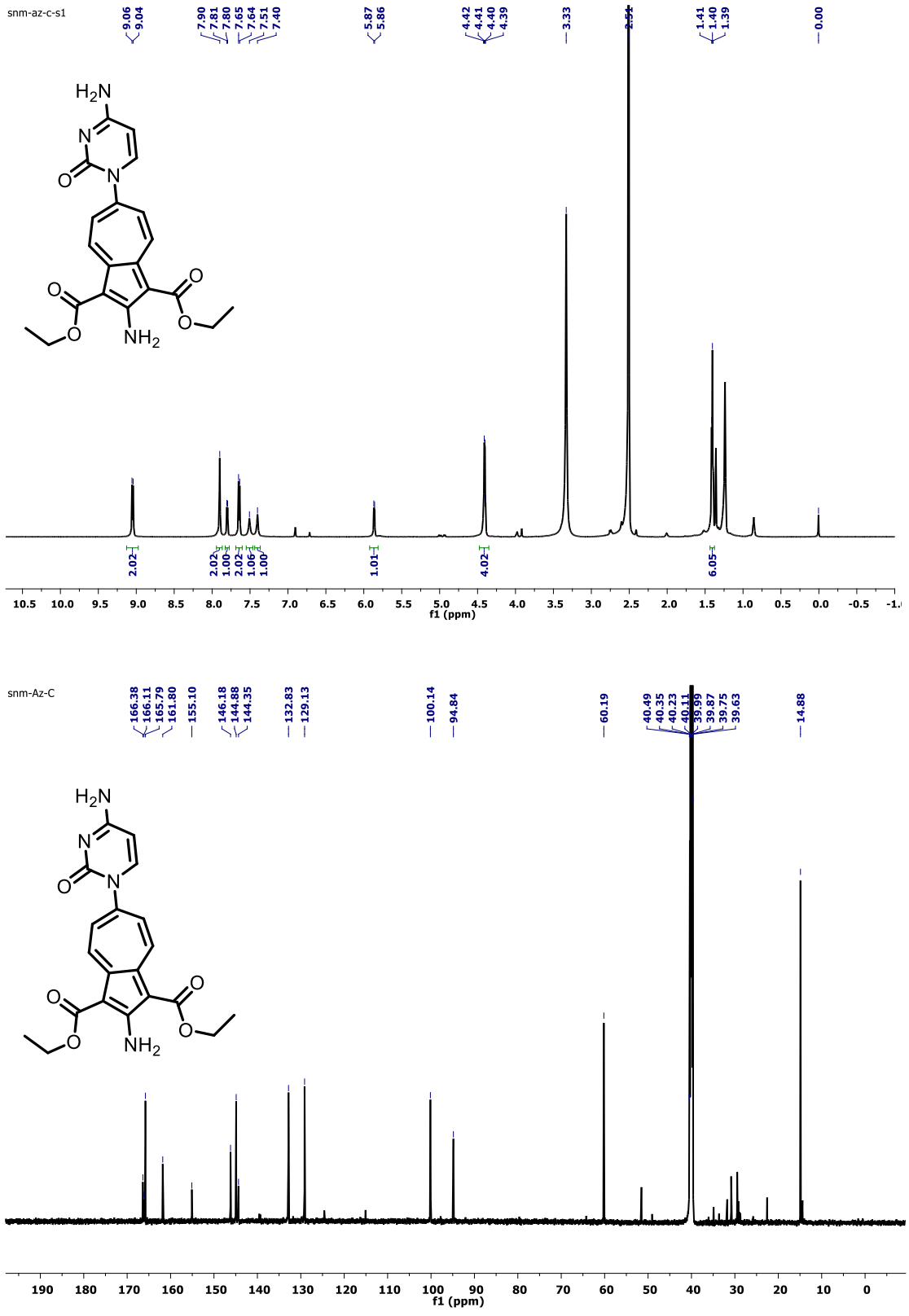


Figure S5. ^{1}H/^{13}C NMR (700MHz, DMSO) spectra of compound **4** in DMSO-d_6.

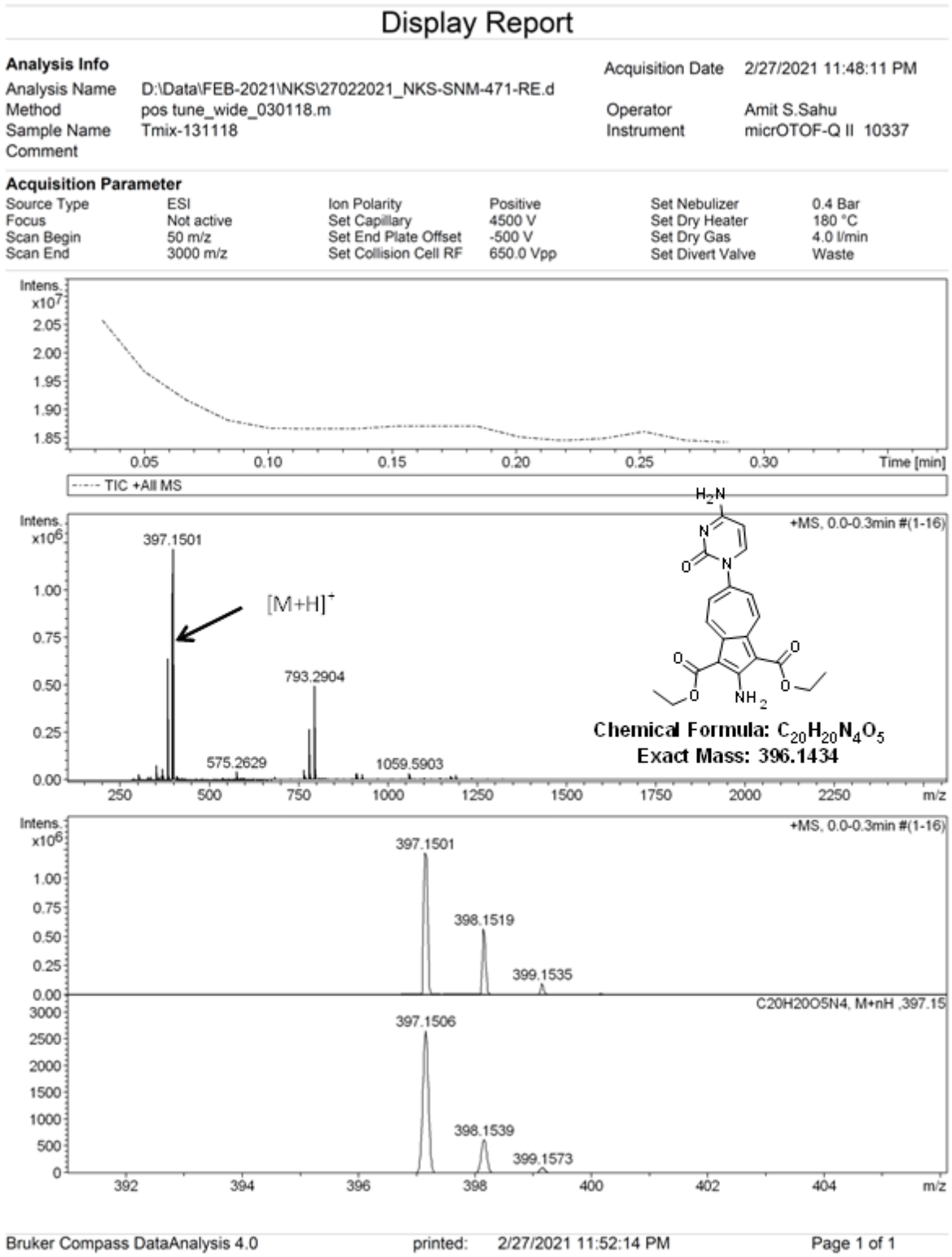


Figure S6. ESI-MS/HRMS spectra of compound **4.**

^{1}H, ^{13}C NMR (700MHz, $CDCl_3$) and HRMS of compound ^{i}**Bu-6**

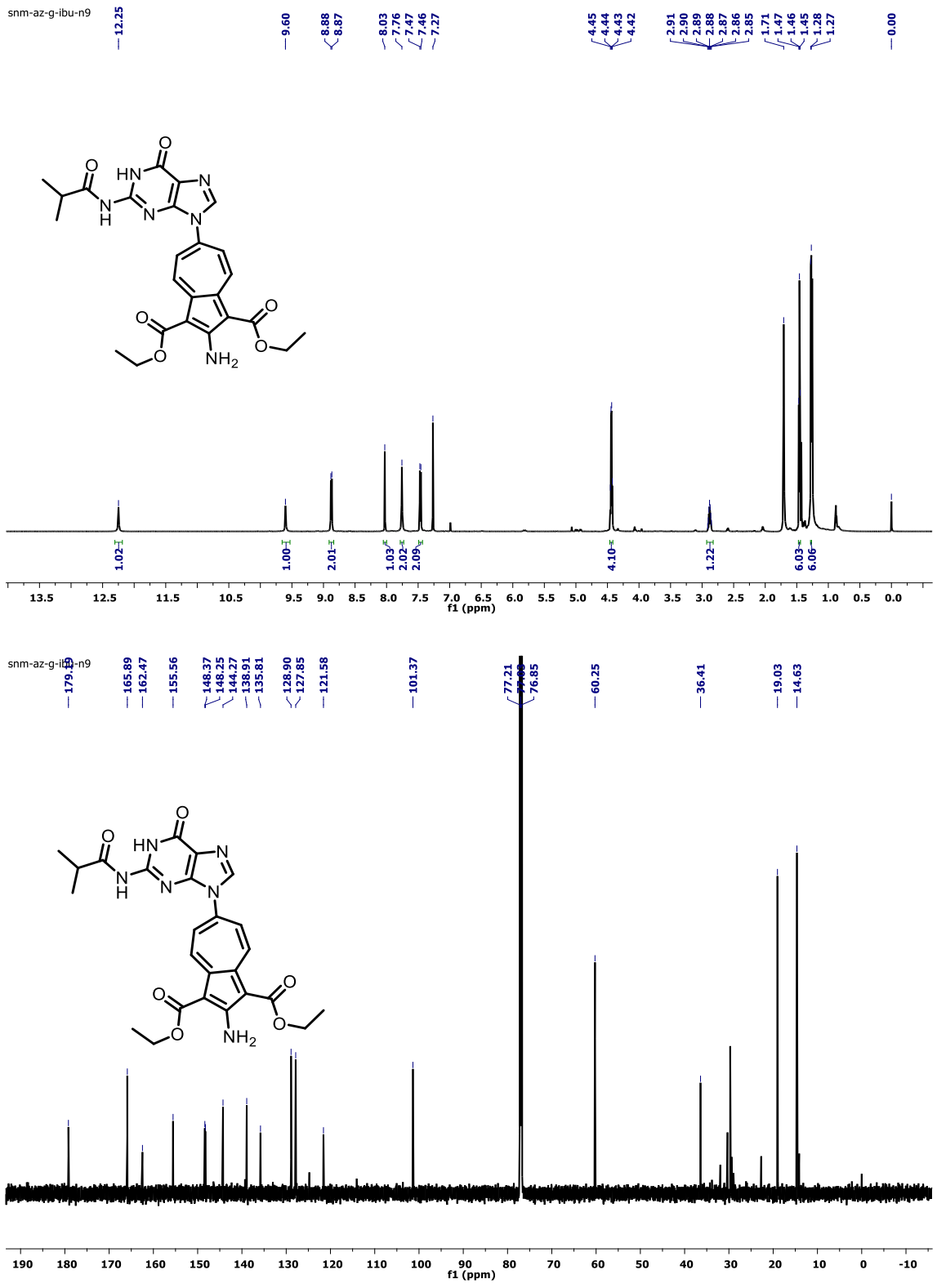


Figure S7. ^{1}H/^{13}C NMR (700MHz, $CDCl_3$) spectra of compound **7** in $CDCl_3$.

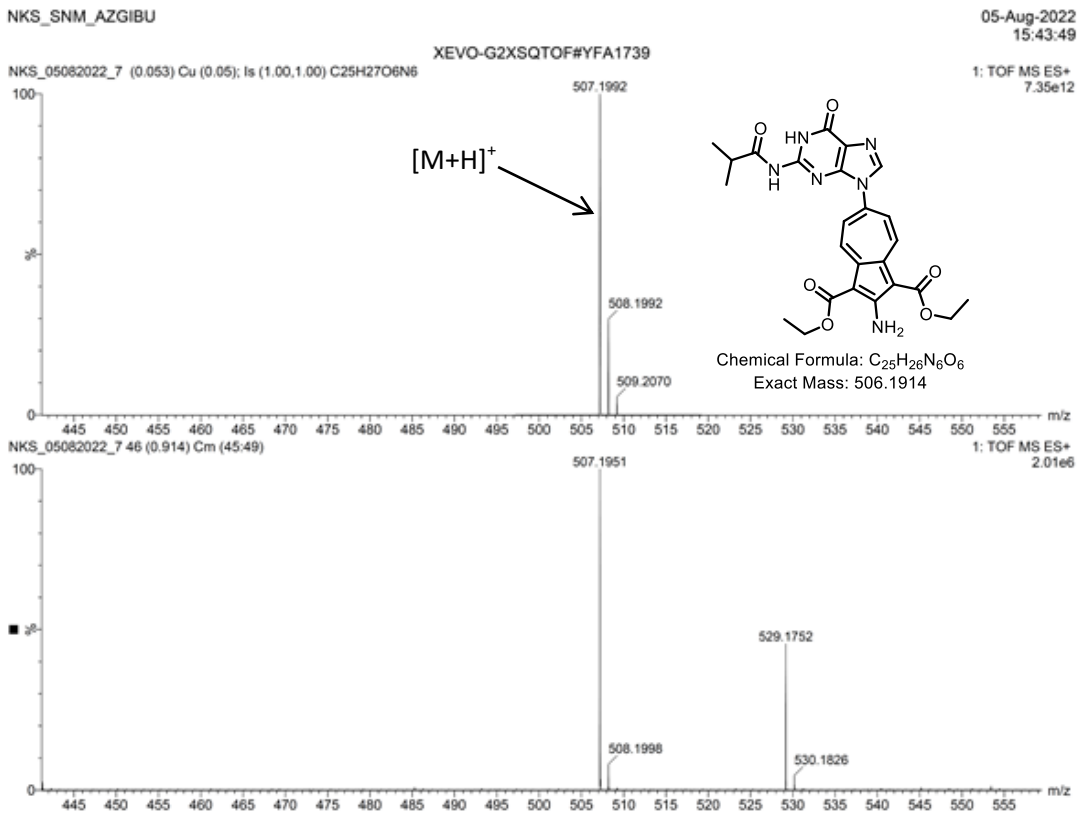


Figure S8. ESI-MS/HRMS spectra of compound **^{i}Bu-6**

^{1}H NMR (400MHz, $CDCl_3$) and HRMS of compound **5**

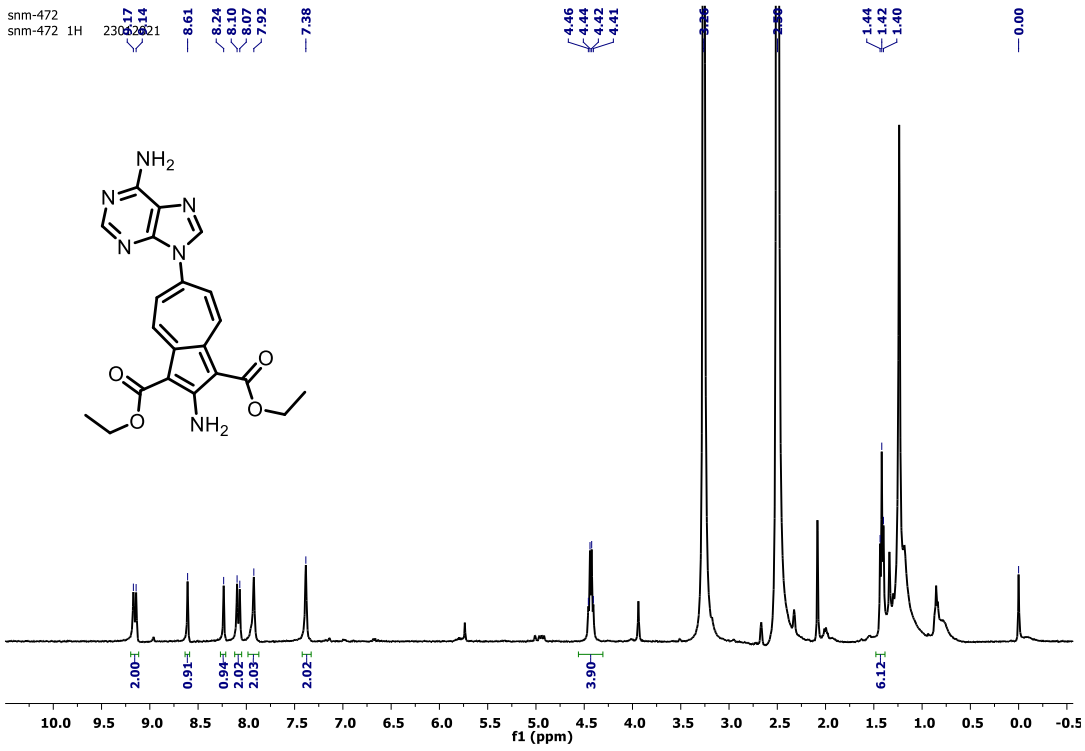


Figure S9. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **5** in DMSO-d_6.

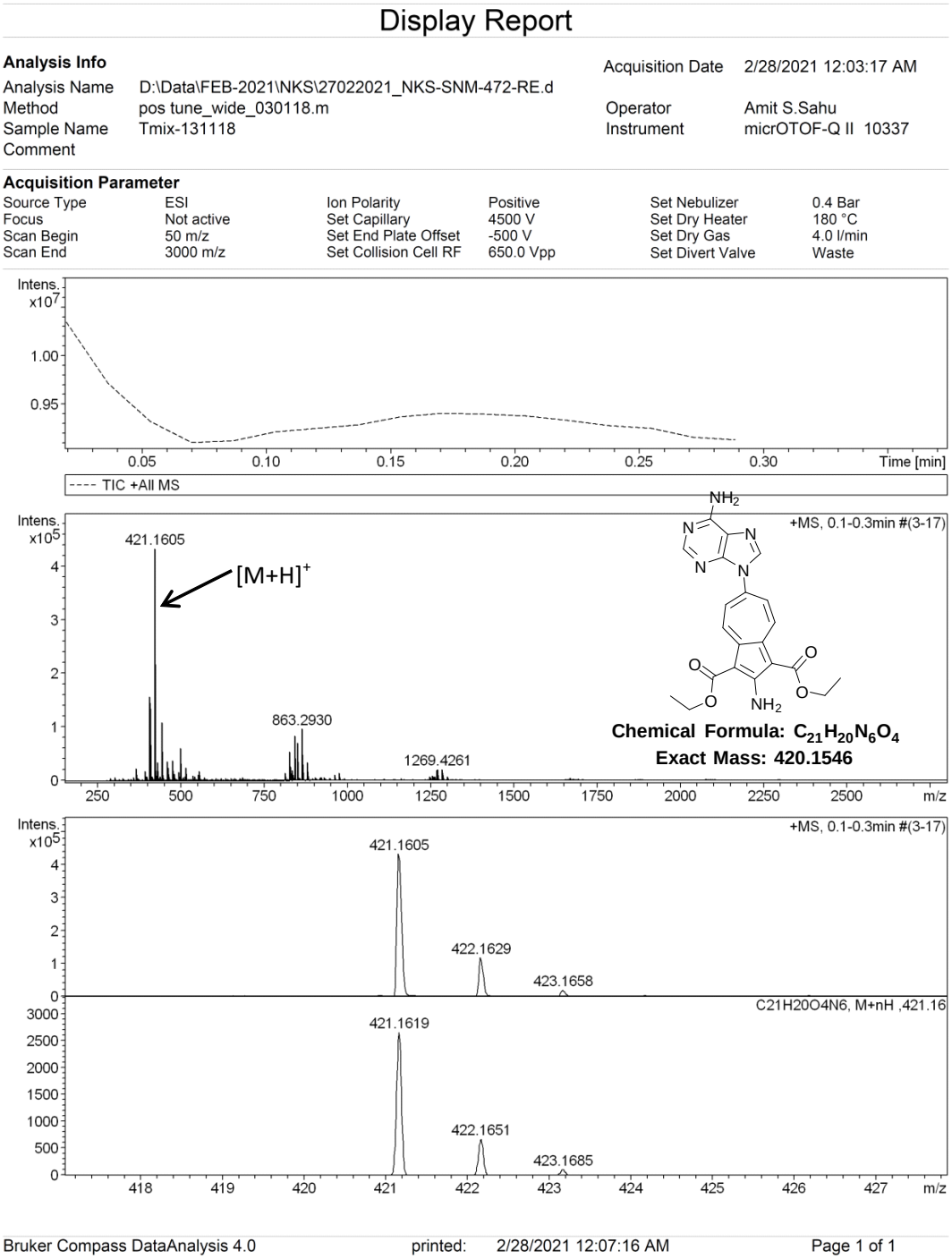


Figure S10. ESI-MS/HRMS spectra of compound **5.**

^{1}H, ^{13}C NMR (700MHz, $CDCl_3$) and HRMS of compound **6**

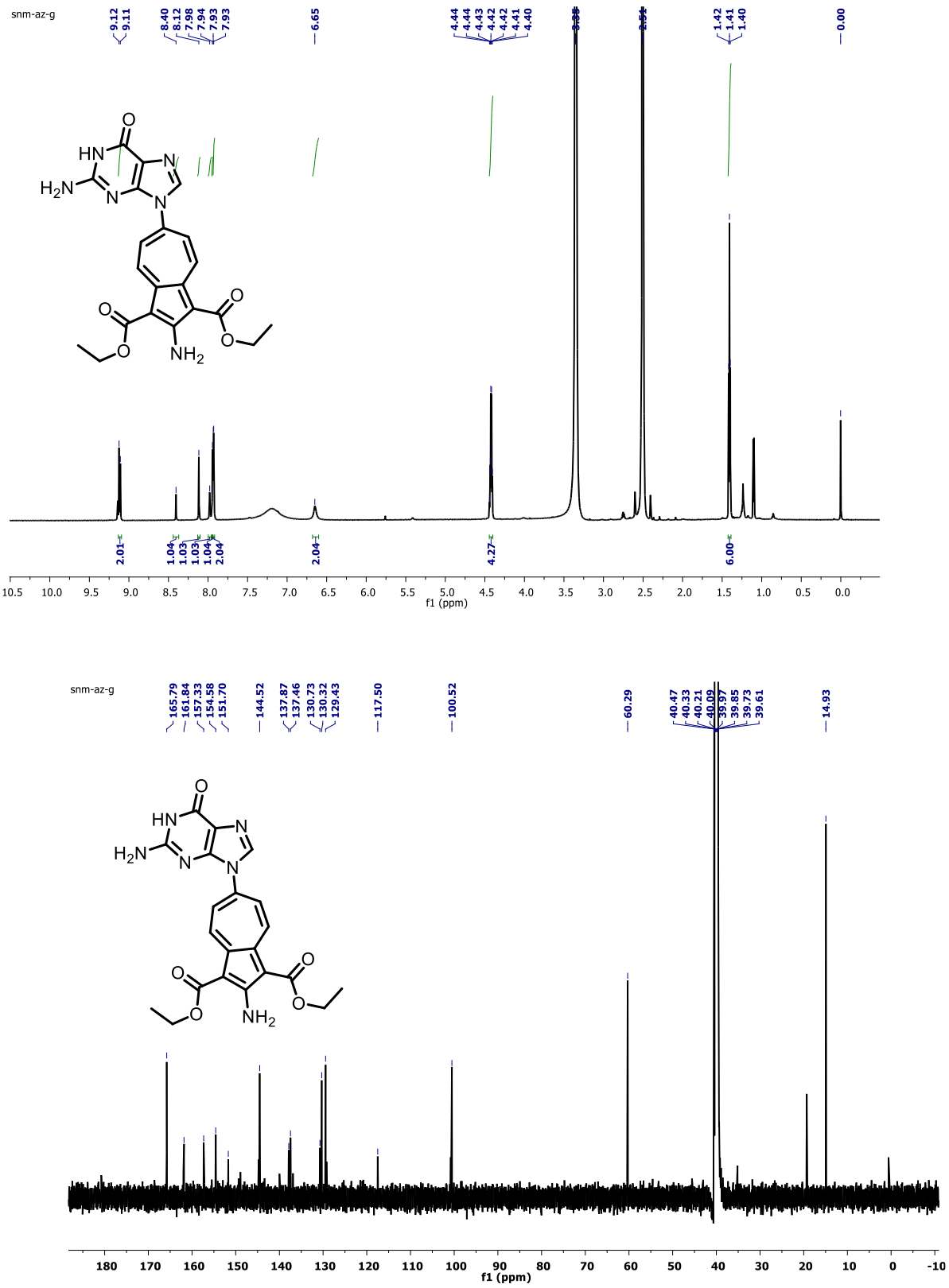


Figure S11. ^{1}H/^{13}C NMR (700MHz, DMSO) spectra of compound **6** in DMSO-d_6.

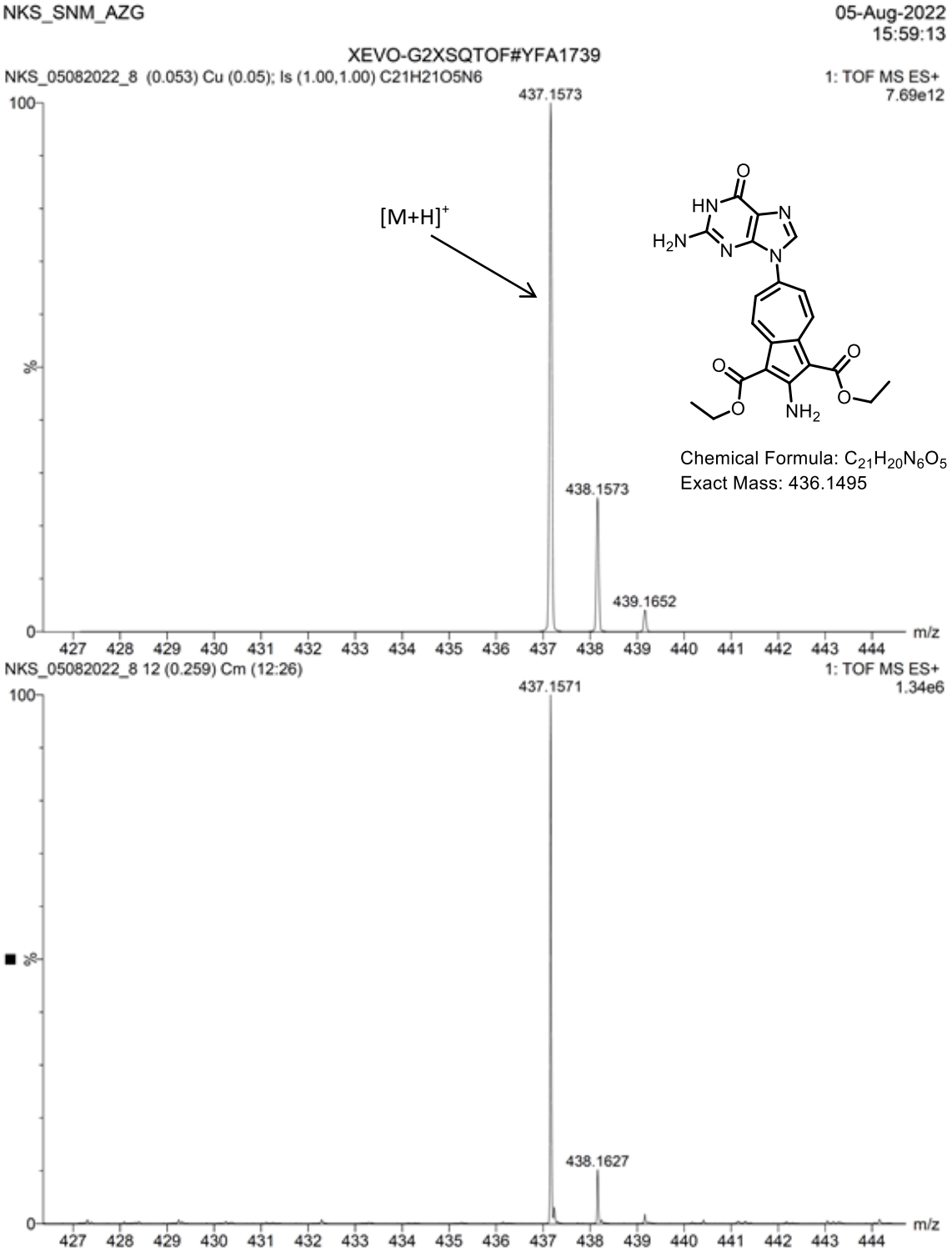


Figure S12. ESI-MS/HRMS spectra of compound **6.**

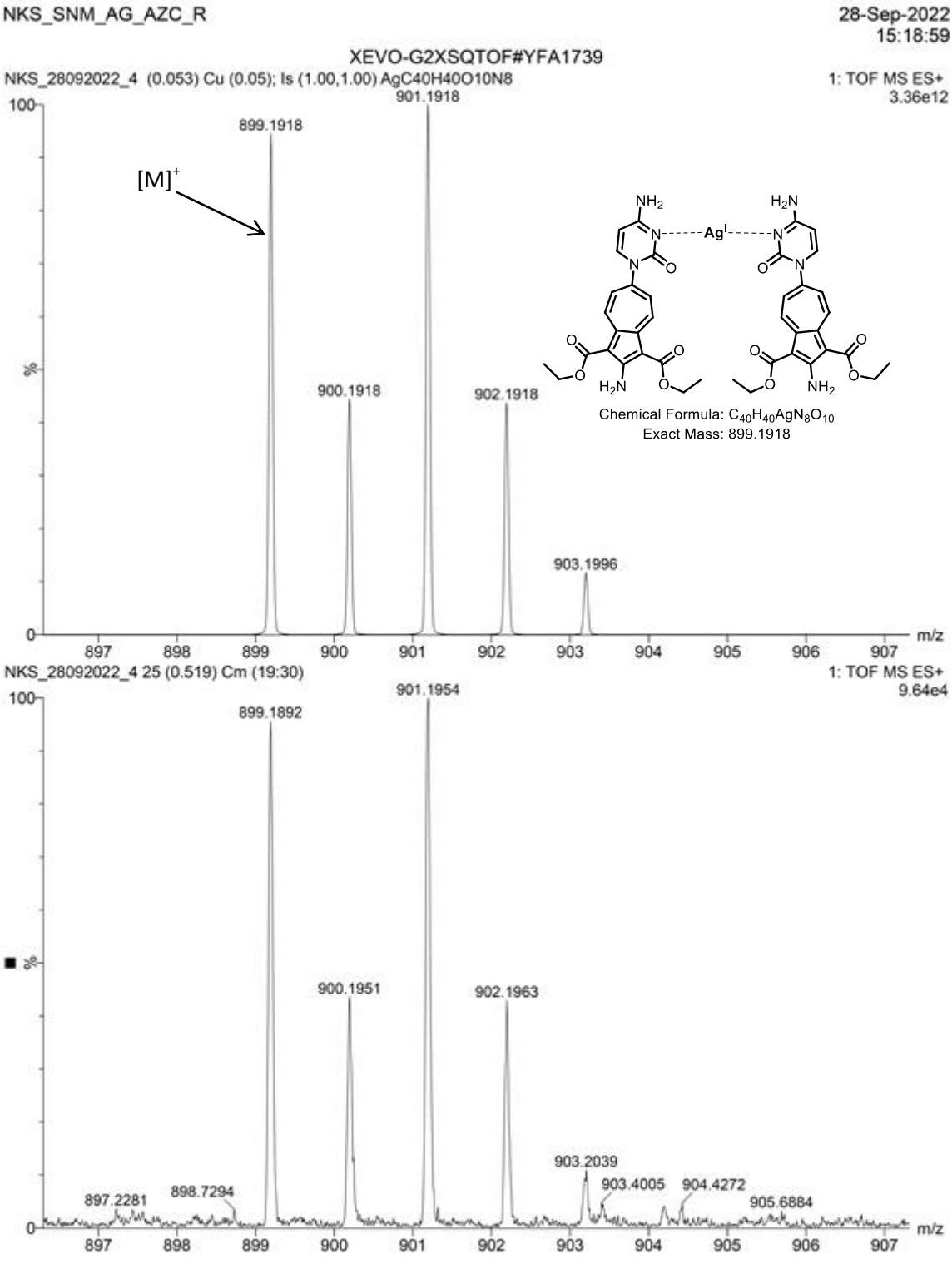


Figure S13. ESI-MS/HRMS spectra of compound **8.**

7. FT-IR Spectra

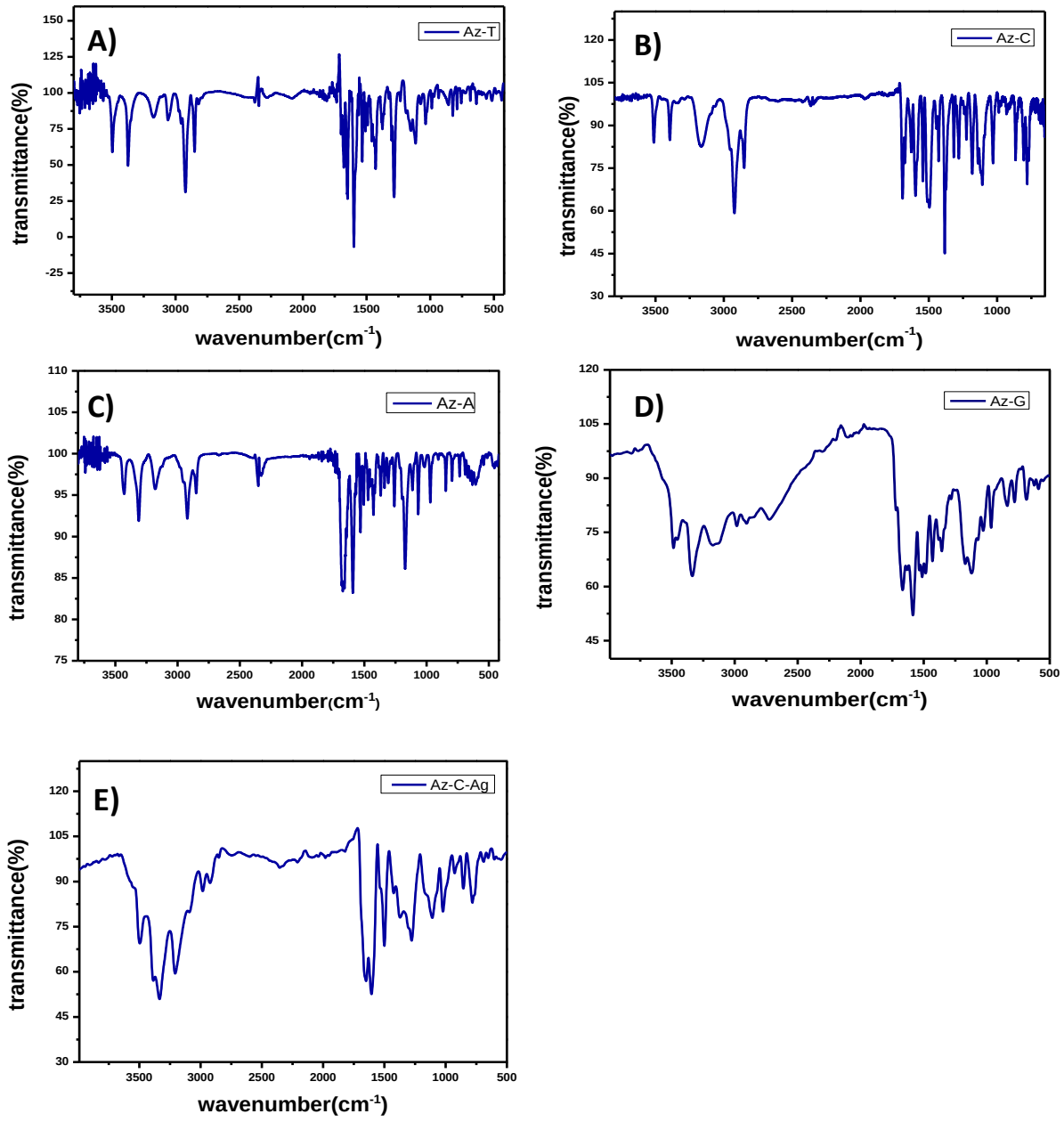


Figure S14. FT-IR spectra of compounds **3** (A), **4** (B), **5** (C), **6** (D) and **8** (E)**.**

8. Cell proliferation assay

The cytotoxicity analysis of compounds Az-T (**3**), Az-C (**4**), Az-A (**5**), Az-G (**6**) and Az-C-Ag complex (**8**) on HEK293T cells derived from human embryonic kidney was performed using MTS CellTiter 96® AQueous One Solution Reagent (Promega, WI, USA) as per the manufacturer's protocol. 20000 cells/ well were seeded in a 96 well plate for 16h followed by treatment with defined range of concentrations (0 to 100 µM) of selected compounds for 18 h. After incubation cell cytotoxicity was measured in terms of cell viability by addition of MTS reagent. The final absorbance was taken at 490 nm using Varioskan Flash multimode reader (Thermo Scientific).

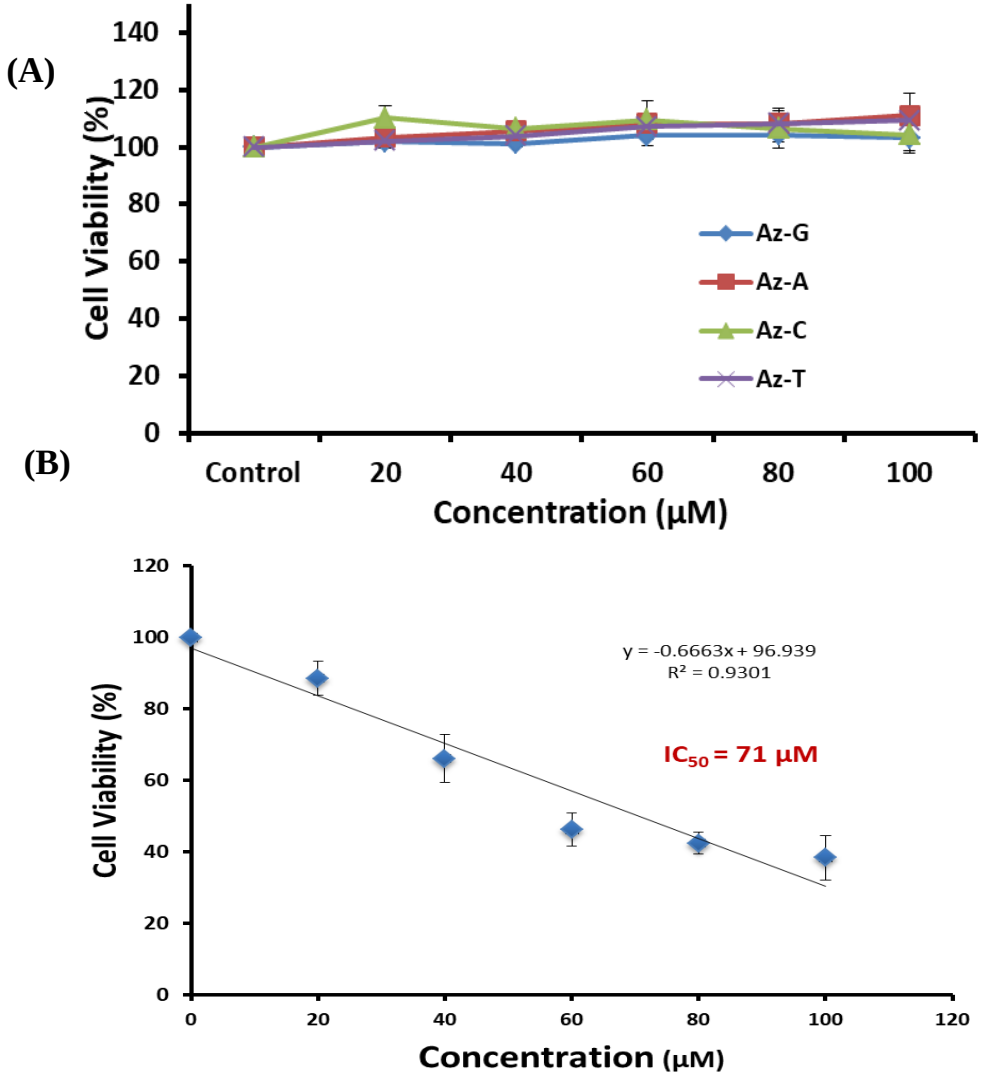


Figure S15. Plots for Cell viability assay of compounds Az-T (**3**), Az-C (**4**), Az-A (**5**), Az-G (**6**) (A); and Az-C-Ag complex (**8**) (B) for HEK293T cell line.

9. Crystal structures and data

Good quality crystals of compounds were obtained in solvent DMSO at 4 ^{0}C by slow evaporation method. The crystals data of compound **3** and **4** were collected on a Rigaku Oxford diffractometer at 293 K. Selected data collection parameters and other crystallographic results are summarized below. The program package SHELXTL1 and Olex2 was used for structure solution and packing diagram carried out by DIAMOND3.2 software.

CCDC **2224909** and **2224908** contains the supplementary crystallographic data for Az-T (**3**) and Az-C (**4**) respectively. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/data

Table S1. Crystal data and structure refinement for Az-C (4)

Identification code	NKS_SNM_AZ_C (1)
Empirical formula	$C_{20}H_{20}N_4O_5$
Formula weight	396.41
Temperature/K	303(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.8930(1)
b/Å	12.3968(2)
c/Å	15.7410(2)
α/°	99.503(1)
β/°	93.061(1)
γ/°	100.462(1)
Volume/Å^3	1299.74(3)
Z	2
ρ_{calc}g/cm^3	1.0128
μ/mm^{-1}	0.619
F(000)	417.5
Crystal size/mm^3	0.01 × 0.001 × 0.001
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.1 to 151.06
Index ranges	$-8 \leq h \leq 6$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$
Reflections collected	19861
Independent reflections	5195 [R_{int} = 0.2111, R_{sigma} = 0.2123]
Data/restraints/parameters	5195/0/264
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0694, wR_2 = 0.2080
Final R indexes [all data]	R_1 = 0.1022, wR_2 = 0.2215
Largest diff. peak/hole / e Å^{-3}	1.40/-1.20

Table S2. Crystal data and structure refinement for Az-T (3)

Identification code	SNM-T AZ
Empirical formula	$C_{23}H_{27}N_3O_7S$
Formula weight	489.55
Temperature/K	256(40)
Crystal system	triclinic
Space group	P-1
a/Å	8.7670(1)
b/Å	10.6359(2)
c/Å	14.1150(2)
α/°	108.665(1)
β/°	99.074(1)
γ/°	101.146(1)
Volume/Å^3	1188.79(3)
Z	2
ρ_{calc}g/cm^3	1.3675
μ/mm^{-1}	1.632
F(000)	518.4
Crystal size/mm^3	0.01 × 0.001 × 0.001
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.8 to 150.92
Index ranges	$-10 \leq h \leq 8$, $-13 \leq k \leq 12$, $-17 \leq l \leq 17$
Reflections collected	18490
Independent reflections	4820 [R_{int} = 0.0394, R_{sigma} = 0.0277]
Data/restraints/parameters	4820/0/312
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1372
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.50/-0.37

10. Photophysical studies

All the UV –Visible spectra of the compounds **3**, **4**, **5**, **6** and **8** (10 µM) were measured in MeOH solvent using a UV-Visible spectrophotometer with a cell of 1 cm path length. All spectroscopy samples were prepared from concentrated DMSO stock solutions; hence, all samples contain 0.4 v% or 0.2 v% DMSO.

Table S3. Photophysical parameters of compounds **3**, **4**, **5**, **7** and **8**

S. N.	Compound	λ_{abs}(nm)	Absorbance	ε_{331}(M^{-1} cm^{-1})
1	Az-T (**3**)	331	0.301	30100
2	Az-C (**4**)	331	0.532	53200
3	Az-A (**5**)	331	0.348	34800
4	Az-G (**6**)	331	0.301	30100
5	Az-C-Ag (**8**)	310	0.527	52700

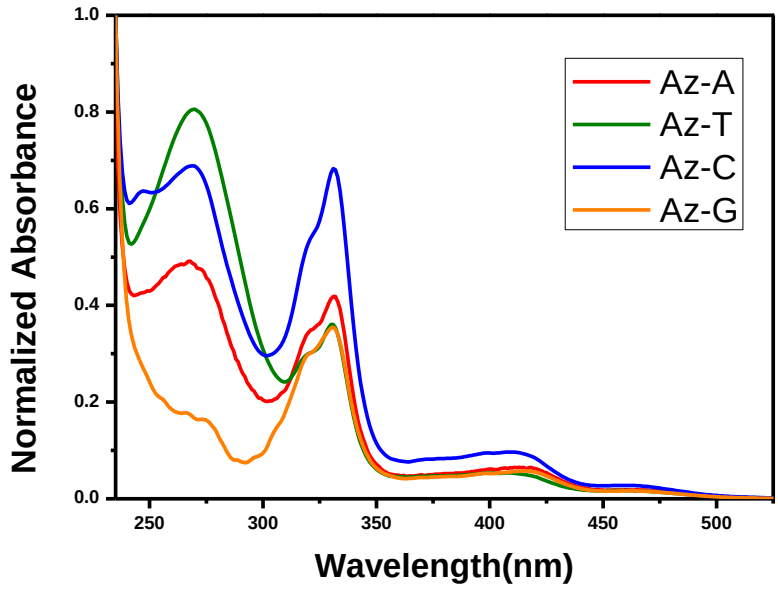


Figure S16. UV-Vis spectra of Az-T (**3**), Az-C (**4**), Az-A (**5**) and Az-G (**6**).

11. Optimized structure and HOMO- LUMO energy gap

The HOMO-LUMO energy gap for compounds Az-T (**3**), Az-C (**4**), Az-A (**5**) and Az-G (**6**) has been calculated using Gaussian 09 software and B3LYP/6-31+G* level of theory in vacuum.

Table S4. Calculated HOMO and LUMO gap at B3LYP/6-31+G* level of theory in vacuum

S.N.	Cpd	HOMO (eV)	LUMO (eV)	Δ (eV)
1	Az-C	-5.5488	-2.067	-3.482
2	Az-A	-5.6032	-2.122	-3.482
3	Az-T	-5.7664	-2.258	-3.509
4	Az-G	-6.0112	-2.502	-3.509

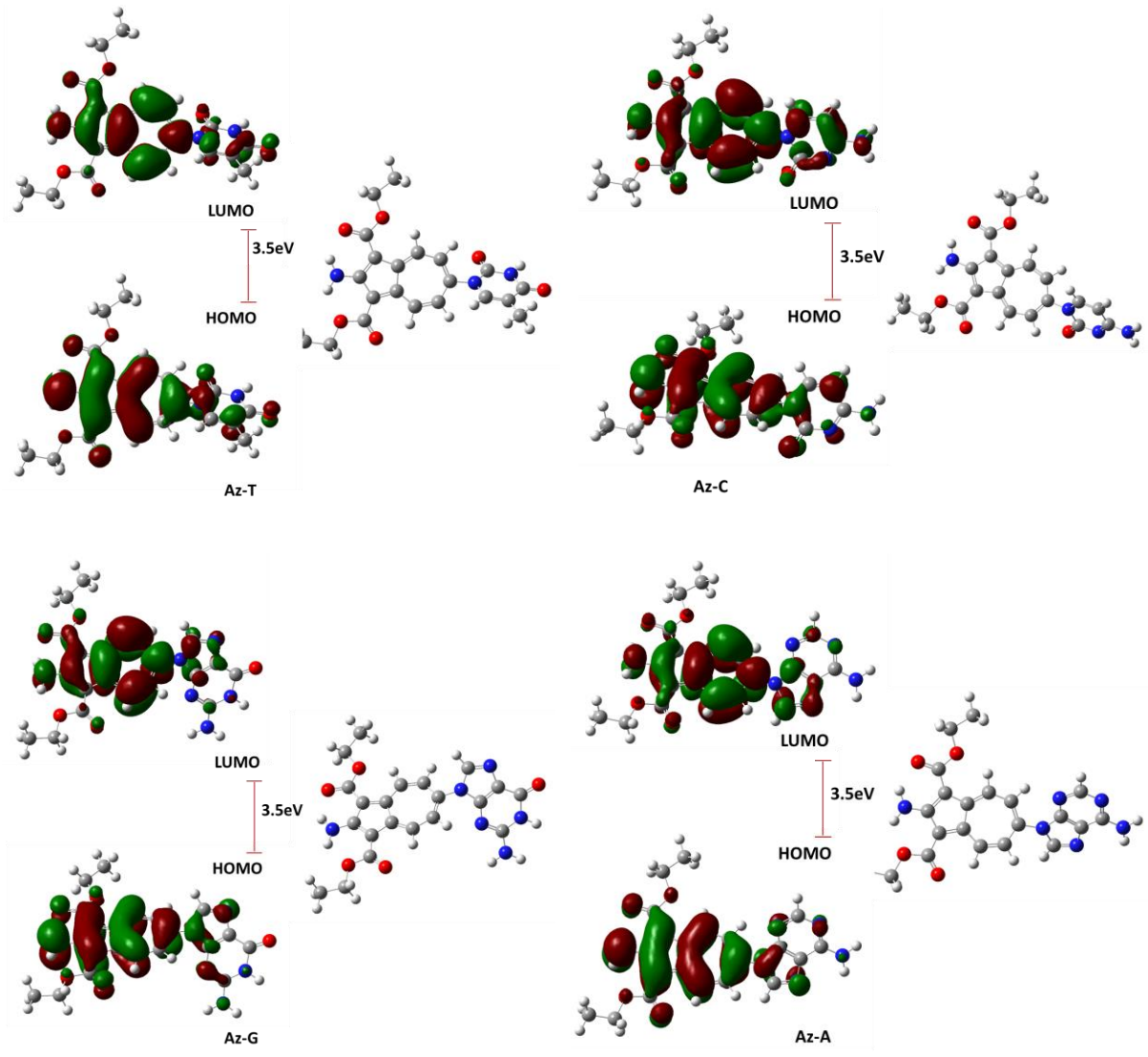


Figure S17. Optimized structure and HOMO- LUMO energy gap (atomic unit in eV) of compounds Az-T (**3**), Az-C (**4**), Az-A (**5**) and Az-G (**6**) at B3LYP/6-31+G* level of theory in vacuum

12. Disk diffusion test for concentration dependent antibiotic activity

The antimicrobial activity of silver nanoparticles (**8**) against pathogenic microorganism *Pseudomonas aeruginsa* (PA14) was measured on Luria-Bertani agar (LB) plates using the disc diffusion method. In this assay, the LB agar solution was poured into the disc while hot and is allowed to cool for gelation. Then PA14 was spread over the agar using a cotton swab. Small wells were made in the agar gel plate with the head of 1ml tip. 100 µl of sample (DMSO control, Az-C-Ag complex (**8**) in different concentration) was poured onto the agar plates. The plates were incubated at 37°C for 12 h. After the incubation period, the zones of inhibition around silver were measured, and compared with the zone of inhibition of each antibiotic disc.

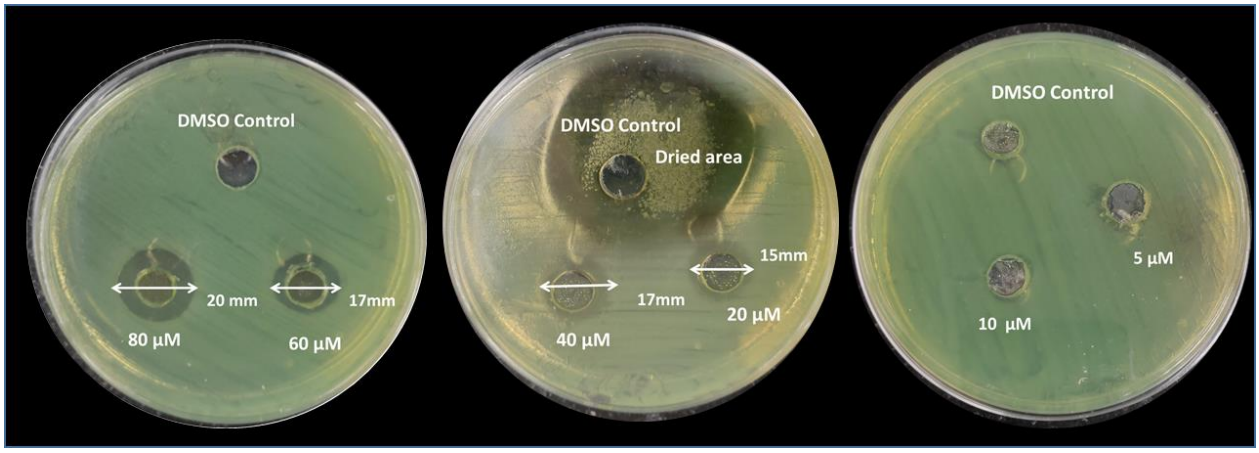


Figure S18. Concentration dependent antimicrobial activity of silver nanoparticles (Az-C-silver complex) (**8**) against *Pseudomonas aeruginosa* (PA14) by disc diffusion assay.

13. Field Emission Scanning Electronic Microscopy (FESEM) and High-Resolution Transmission Electron Microscopy (HRTEM)

Thin layer of samples of Az-T (**3**), Az-C (**4**), Az-A (**5**), Az-G (**6**) and Az-C-Ag complex (**8**) were prepared individually by drop casting EtOH solution of the samples on silicon wafer. These wafers were dried and kept under vaccum before recording their SEM-images. SEM images at nano-scales, at selectively resolutaion (~200 nm to ~2-10 µm) are illustrated along with Elemental mapping and EDAX spectrum in following Figures. For TEM images a dilute solution of the sample was prepared in ethanol solvent and drop casted onto a copper grid (200 mesh) and dried properly prior to the HRTEM analysis.

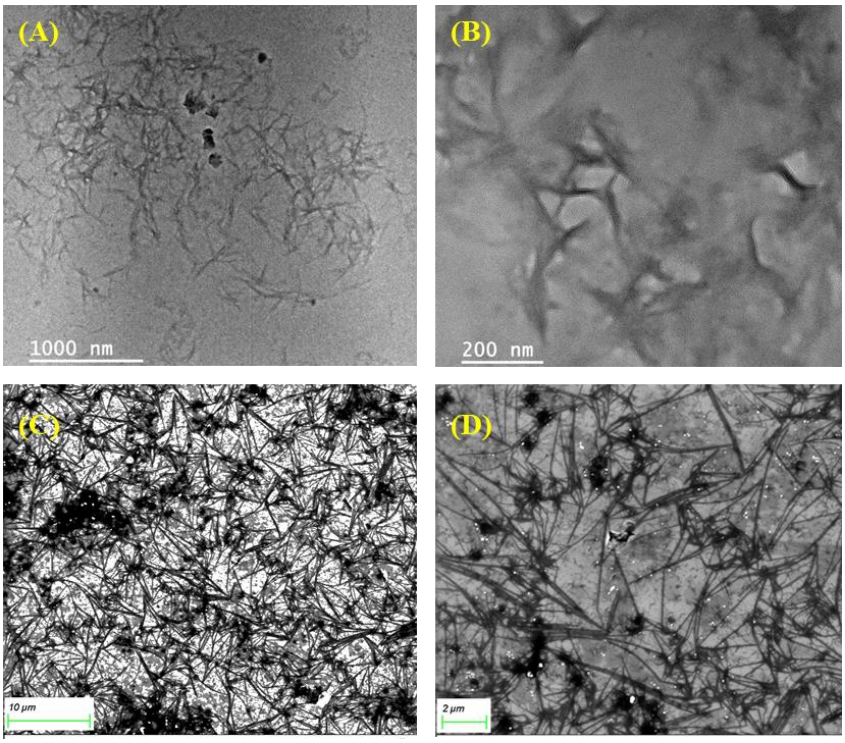


Figure S19. HRTEM images (A, B) and FESEM images (C, D) for compound **5** (Az-A) at different magnification.

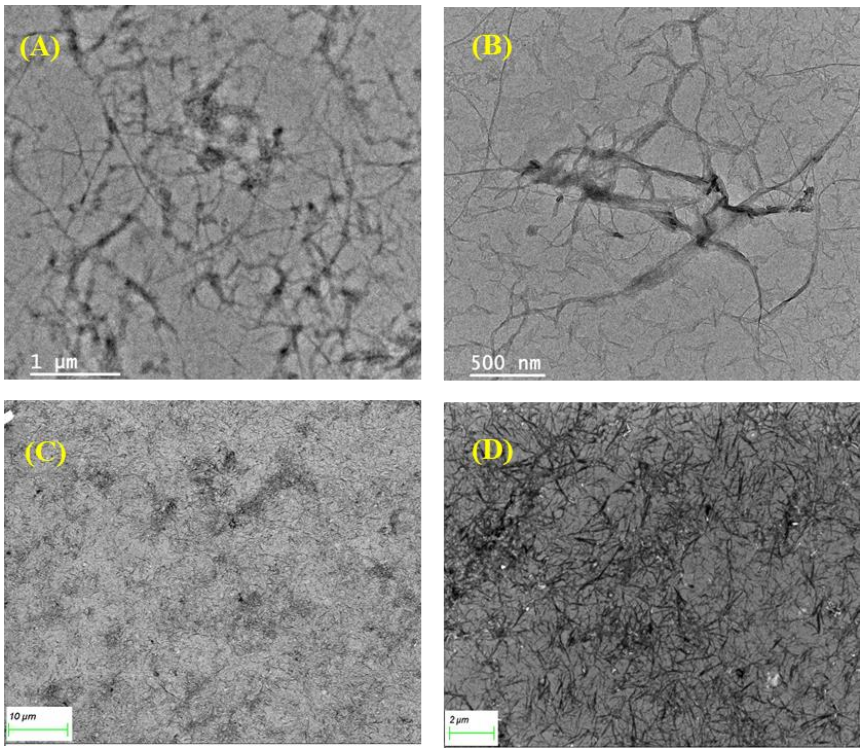
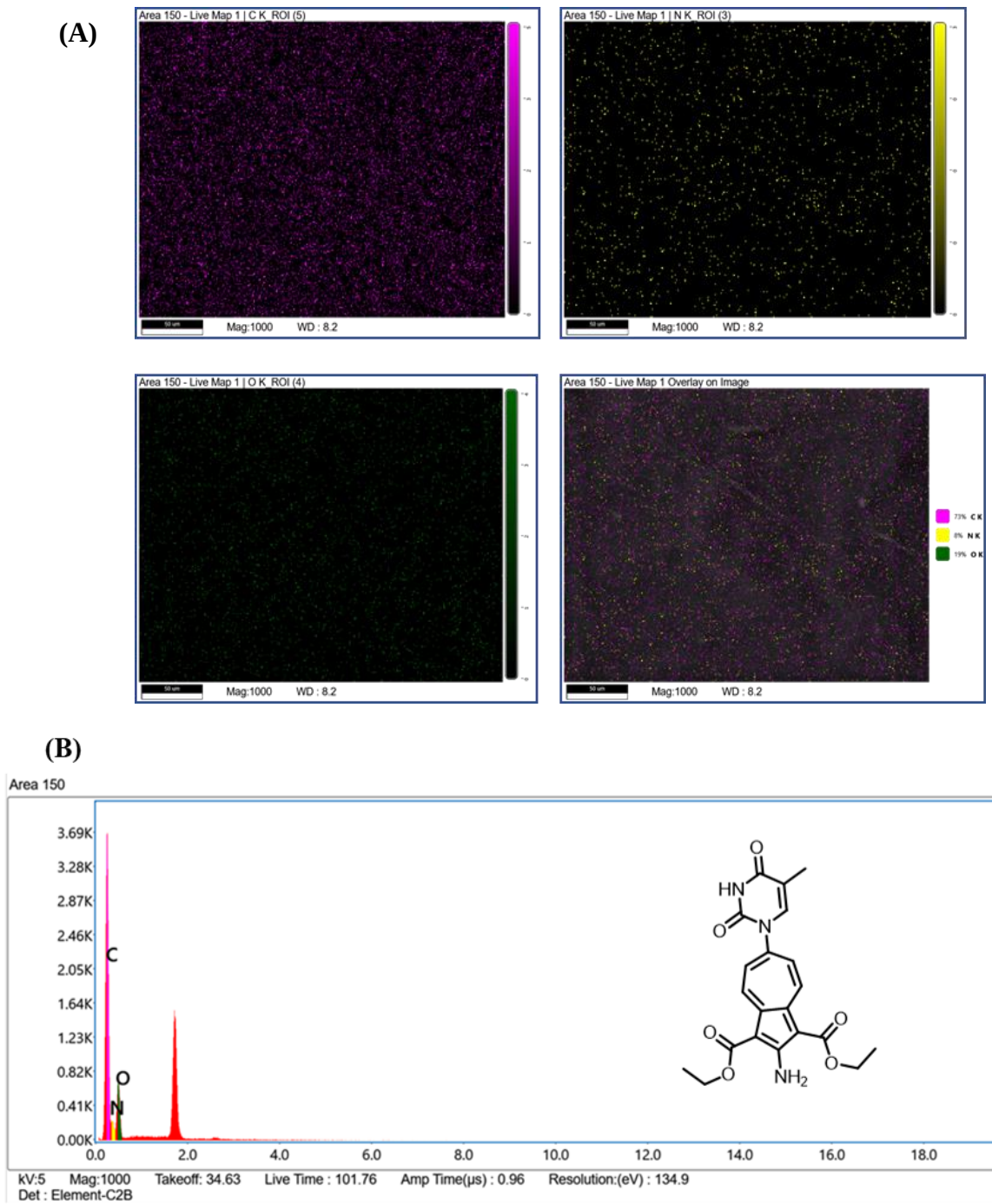
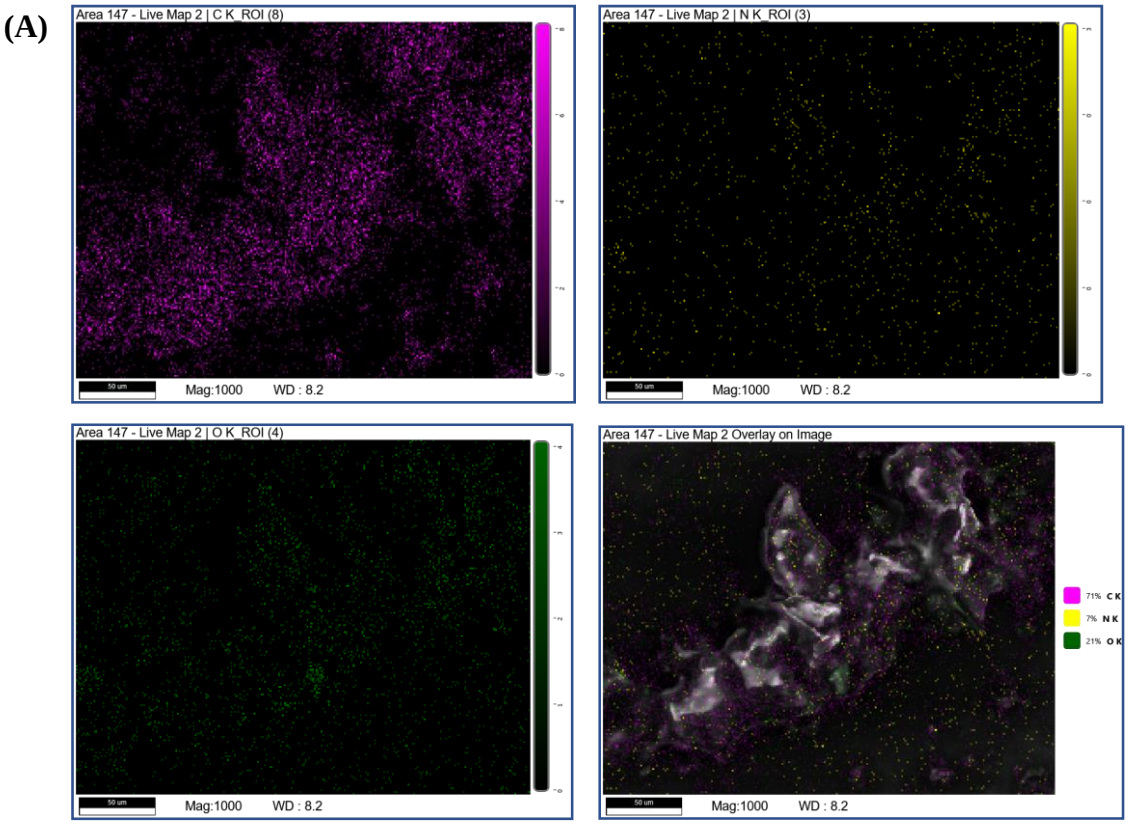


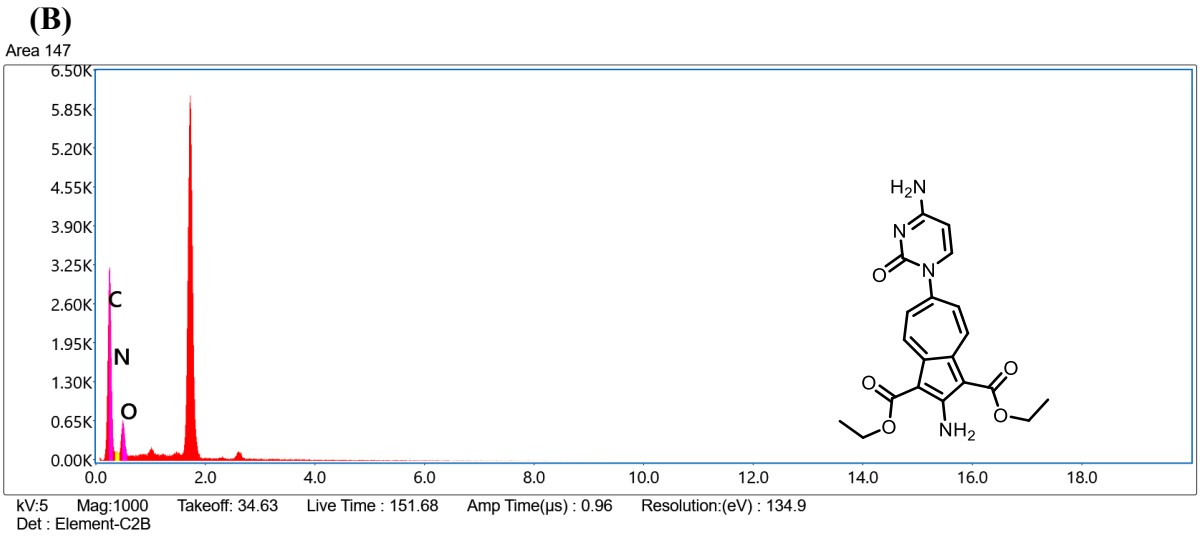
Figure S20. HRTEM images (A, B) and FESEM images (C, D) for compound **6** (Az-G) at different magnification.



Element	Weight %	Atomic %	Error %	Net Int.
C K	71.00	75.70	4.70	285.20
N K	9.10	8.30	14.70	14.30
O K	20.00	16.00	9.50	47.90

Figure S21. (A) Elemental mapping and (B) EDAX spectrum of compound **4** (Az-C) showing the presence of C, N and O.

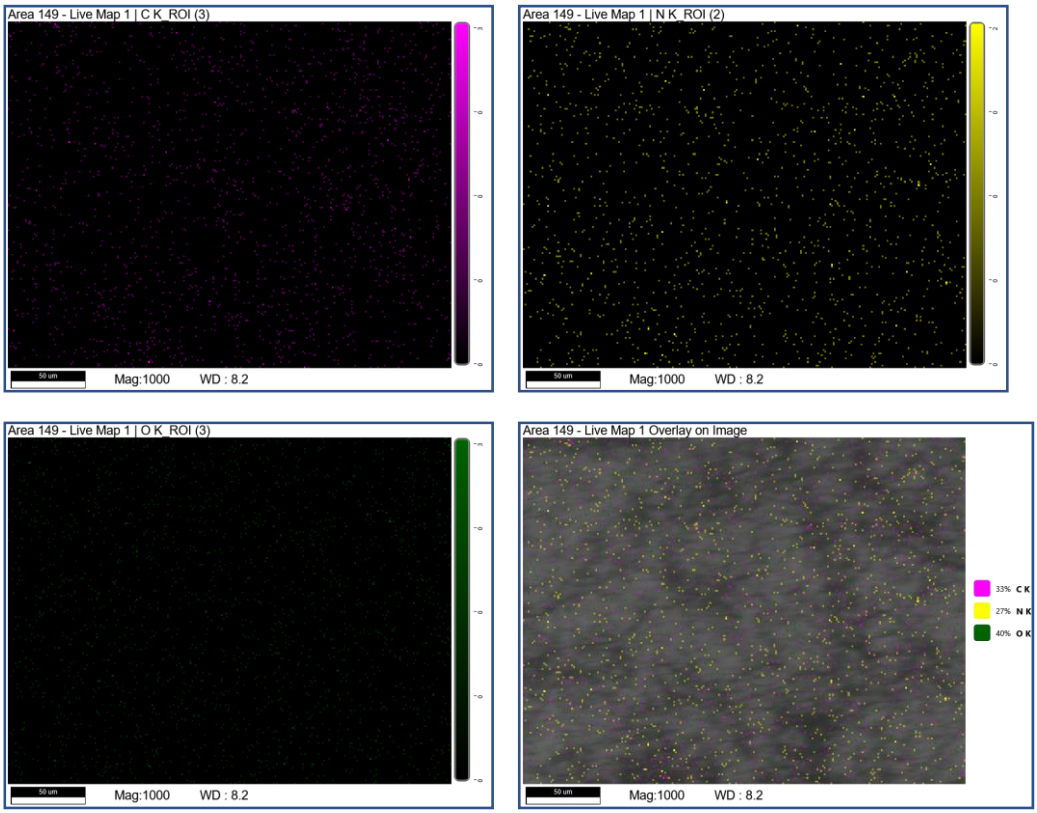




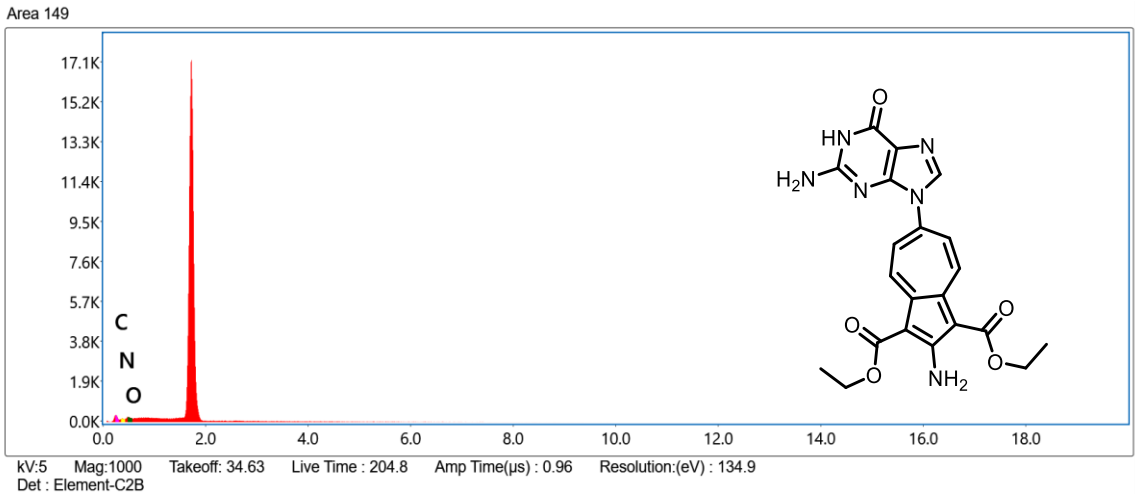
Element	Weight %	Atomic %	Error %	Net Int.
C K	72.90	77.60	4.80	165.00
N K	6.70	6.10	17.70	5.90
O K	20.40	16.30	9.80	27.70

Figure S22. (A) Elemental mapping and (B) EDAX spectrum of compound **3** (Az-T) showing the presence of C, N and O.

(A)



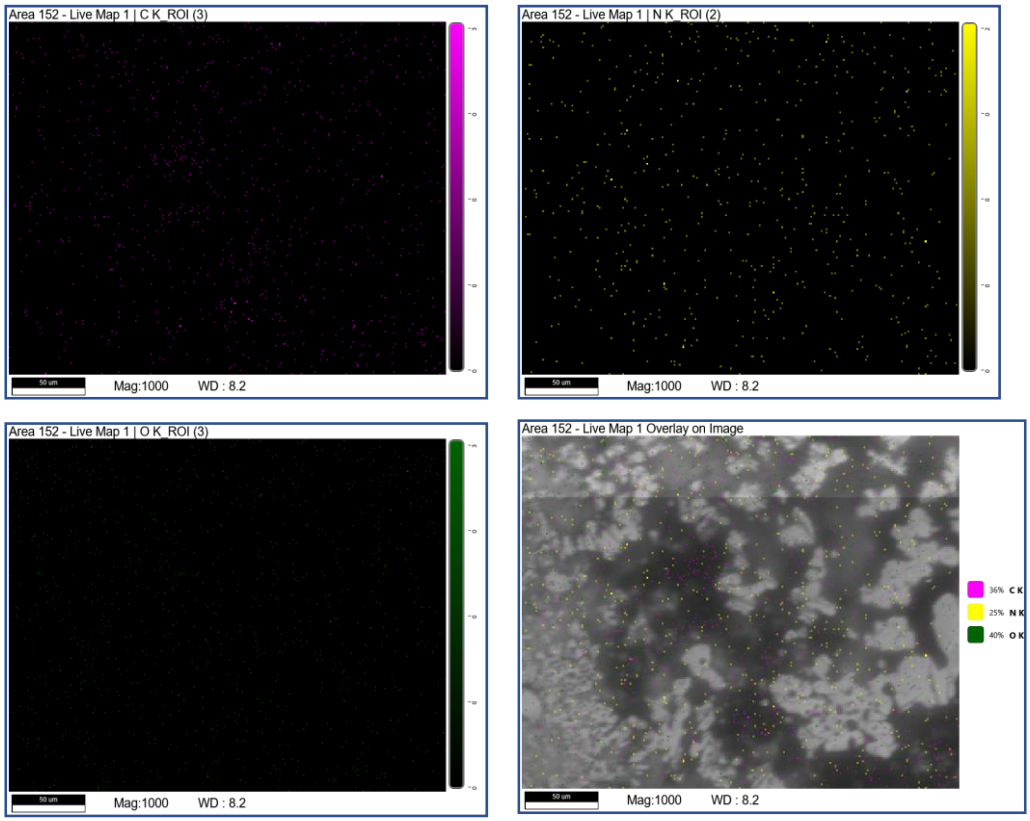
(B)



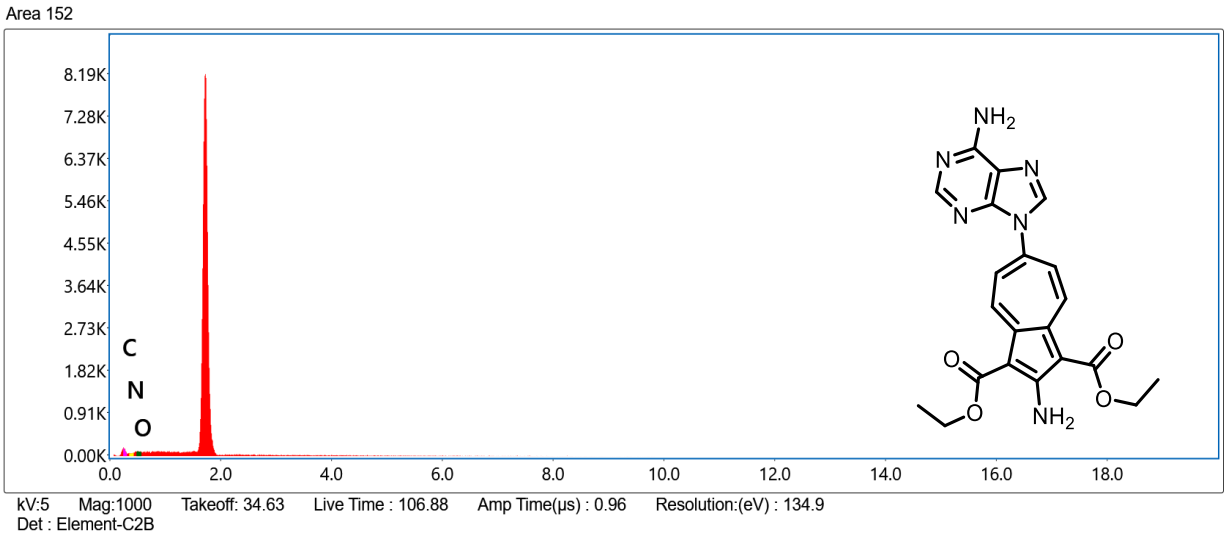
Element	Weight %	Atomic %	Error %	Net Int.
C K	42.70	48.40	7.90	11.70
N K	23.30	22.70	17.40	3.40
O K	34.00	28.90	14.30	6.00

Figure S23. (A) Elemental mapping and (B) EDAX spectrum of compound **6** (Az-G) showing the presence of C, N and O.

(A)



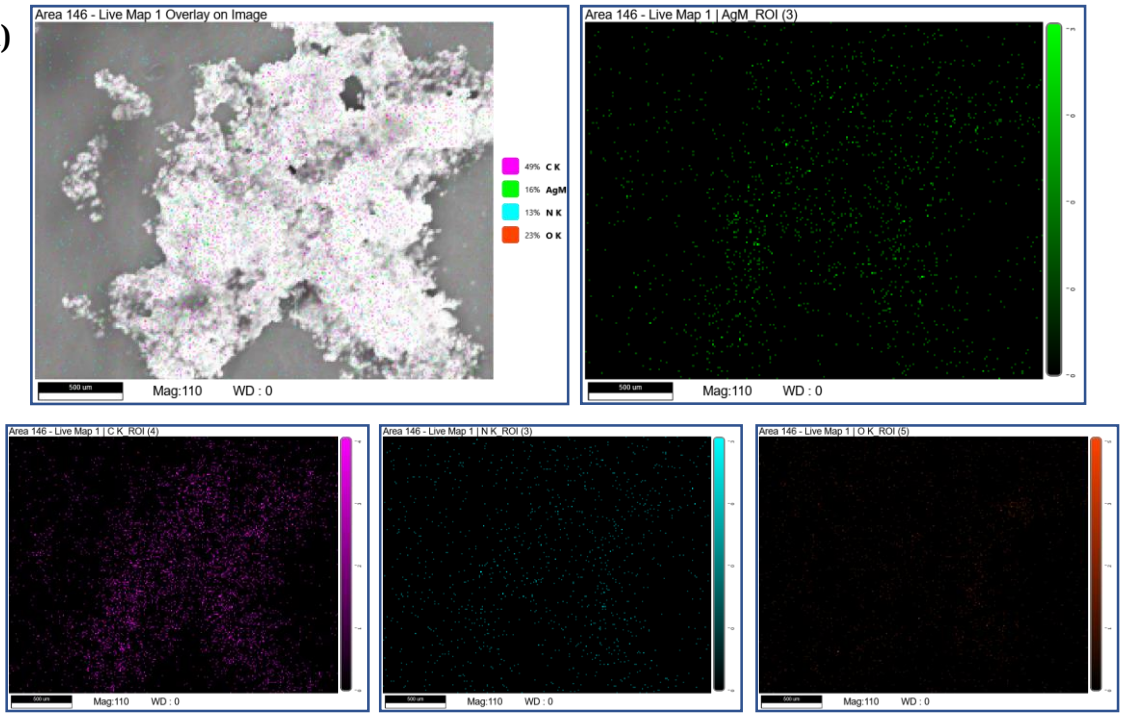
(B)



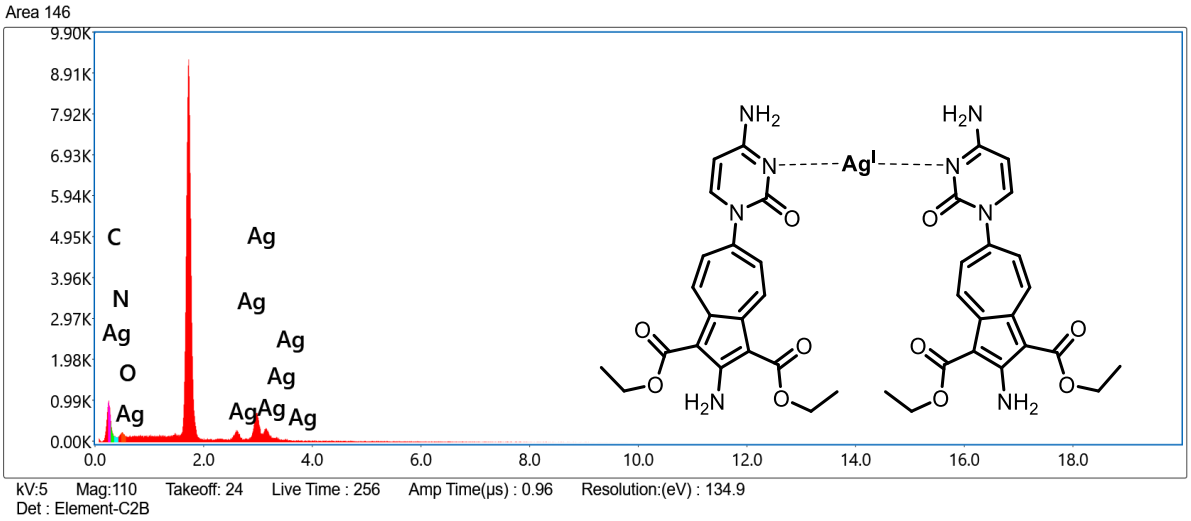
Element	Weight %	Atomic %	Error %	Net Int.
C K	46.30	52.30	8.60	12.80
N K	19.10	18.50	25.60	2.70
O K	34.60	29.30	15.50	6.20

Figure S24. (A) Elemental mapping and (B) EDAX spectrum of compound **5** (Az-A) showing the presence of C, N and O.

(A)



(B)



Element	Weight %	Atomic %	Error %	Net Int.
C K	31.70	45.20	8.10	13.10
N K	18.50	22.60	26.20	2.90
O K	26.60	28.50	22.20	4.80
Ag L	23.20	3.70	43.60	1.90

Figure S25. (A) Elemental mapping and (B) EDAX spectrum of compound **8** (Az-C-Ag complex) showing the presence of C, N, O and Ag.

14. References

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2 A. Ito, A. Ishii, T. Amaki, K. Fukuda, R. Yamasaki and I. Okamoto, *Tetrahedron Lett.*, 2019, **60**, 1929–1933.