Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Removal of Au^{3+} and Ag^{+} from aqueous media with Magnetic Nanoparticles functionalized with squaramide derivatives

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SEM Microphotographs

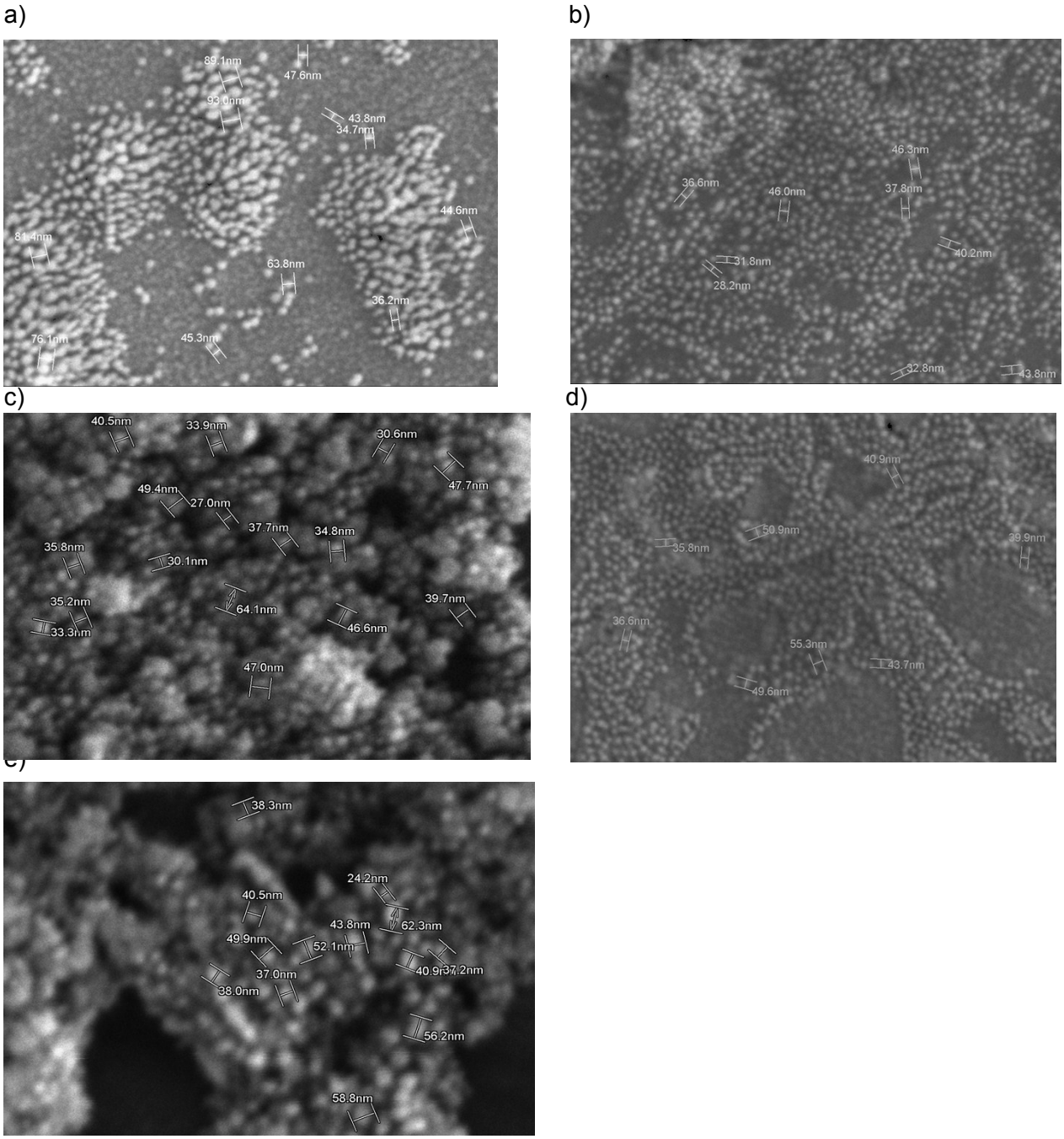
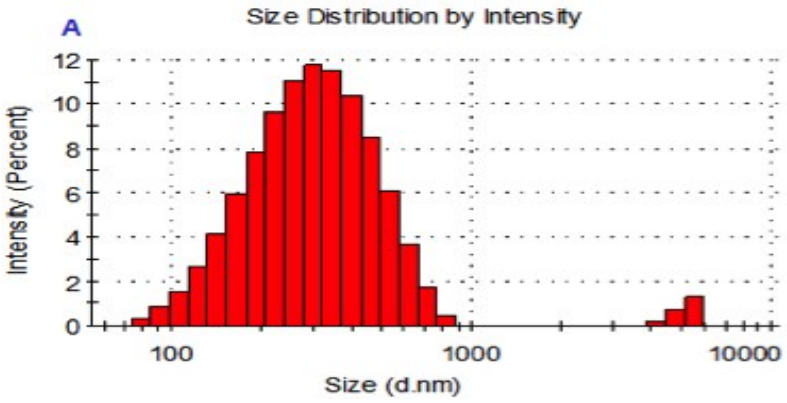


Figure SI-1A. SEM microphotographs of: a) FeNP, b) FeNP-SQ1, c) FeNP-SQ2, d) FeNP-SQ3, e) FeNP-SQ4.

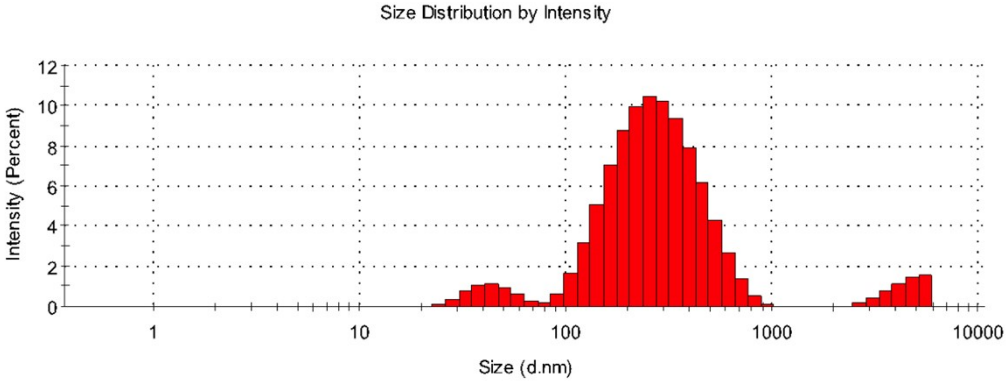
Dynamic Light Scattering

a)



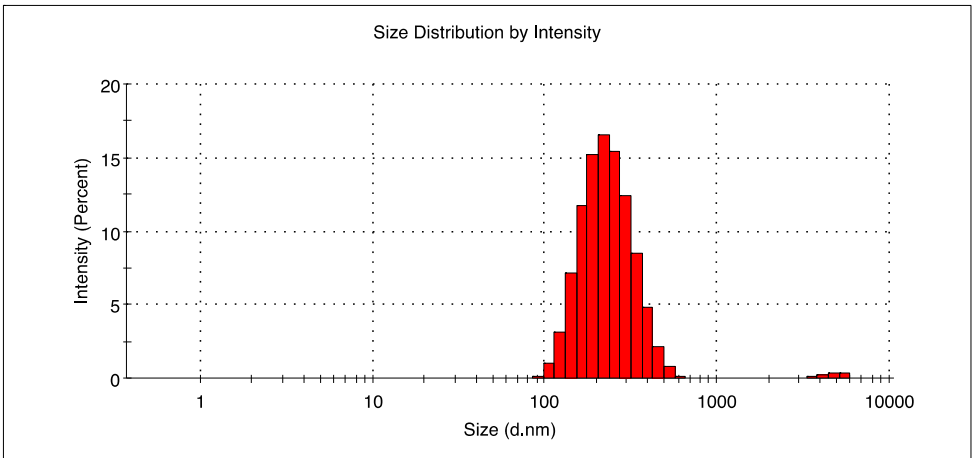
b)

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 229.0	Peak 1:	297.4	89.1	141.5
PdI: 0.378	Peak 2:	4480	5.6	889.3
Intercept: 0.922	Peak 3:	44.69	5.3	11.96
Result quality : Good				



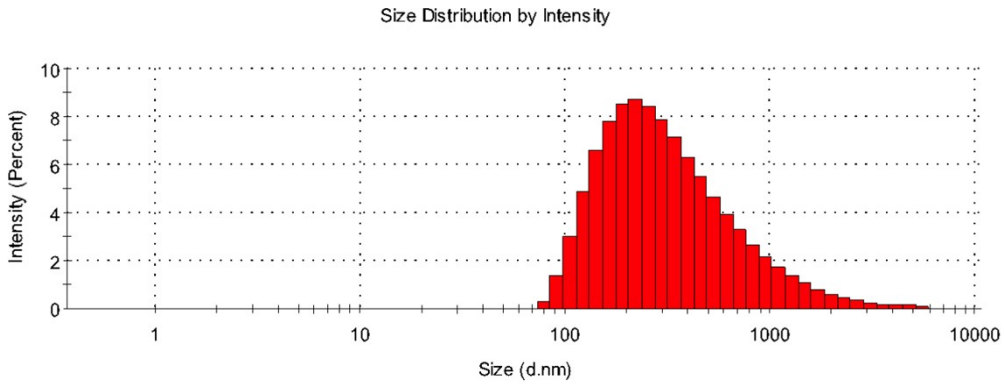
c)

		Size (d.nm...	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 224.5	Peak 1:	240.6	99.0	82.53
PdI: 0.169	Peak 2:	4797	1.0	725.5
Intercept: 0.958	Peak 3:	0.000	0.0	0.000
Result quality Good				



d)

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 255.0	Peak 1:	427.8	100.0	484.3
PdI: 0.258	Peak 2:	0.000	0.0	0.000
Intercept: 0.931	Peak 3:	0.000	0.0	0.000
Result quality : Good				



e)

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 321.9	Peak 1:	392.2	96.3	181.2
PdI: 0.266	Peak 2:	4667	3.7	798.7
Intercept: 0.944	Peak 3:	0.000	0.0	0.000
Result quality : Good				

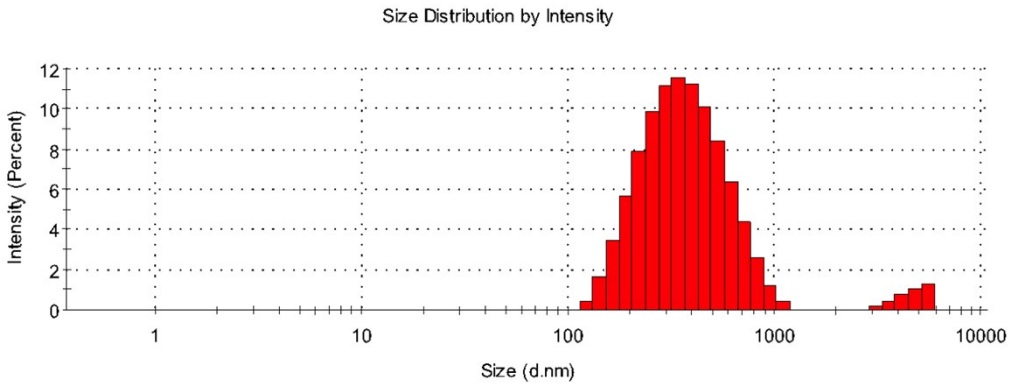


Figure SI-1B. DLS in water (pH= 6.5) of: a) FeNP, b) FeNP-SQ1, c) FeNP-SQ2, d) FeNP-SQ3, e) FeNP-SQ4.

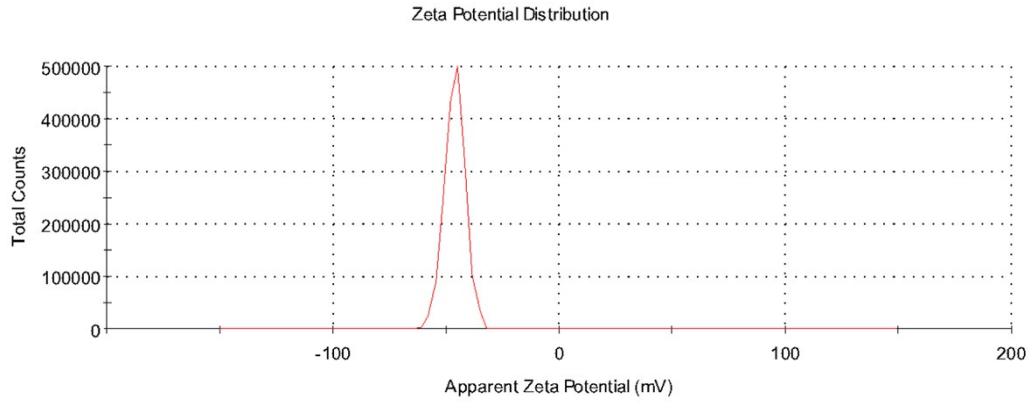
Z-Potential

a)

b)

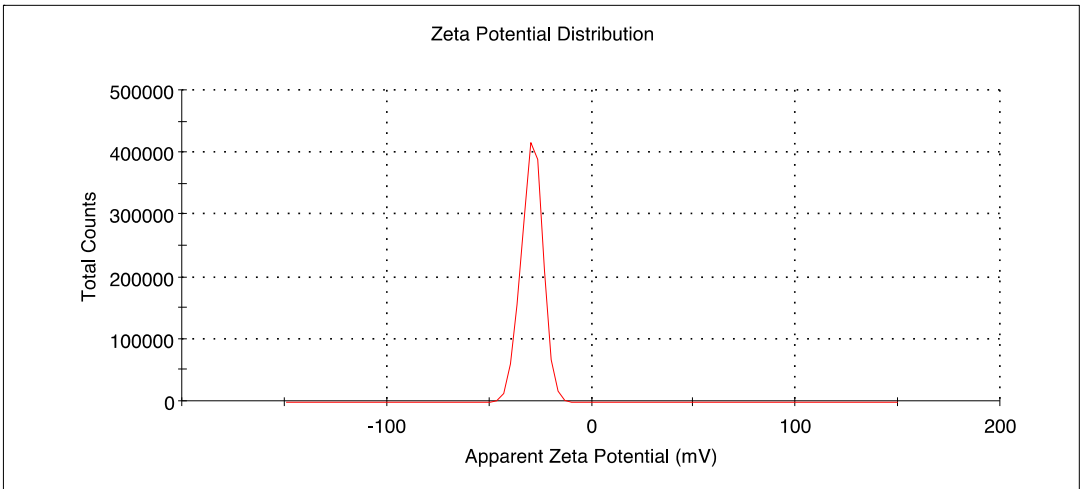
		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -46.0	Peak 1:	-46.0	100.0	4.62
Zeta Deviation (mV): 4.62	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.429	Peak 3:	0.00	0.0	0.00

Result quality : Good



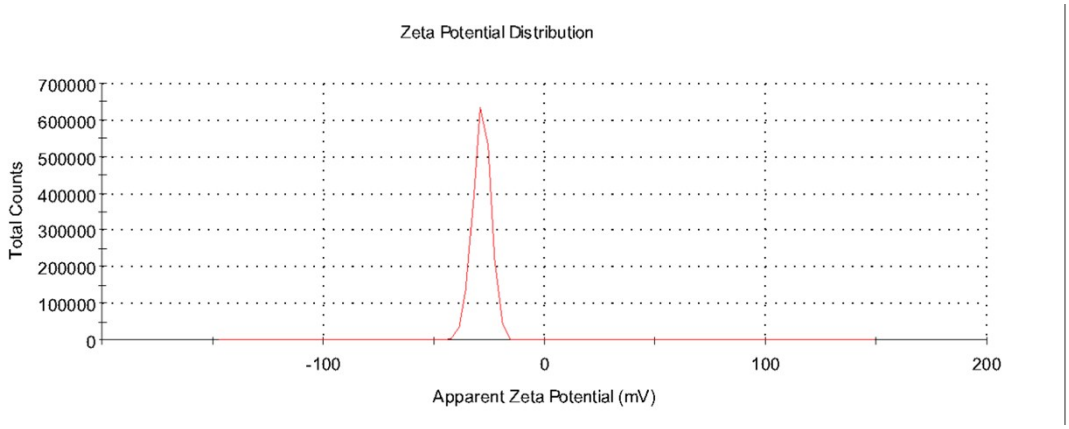
c)

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-29.3	**Peak 1:**	-29.3	100.0	5.14
Zeta Deviation (mV):	4.87	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.0103	**Peak 3:**	0.00	0.0	0.00
Result quality	Good				



d)

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-28.2	**Peak 1:**	-28.2	100.0	4.06
Zeta Deviation (mV):	4.06	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.0197	**Peak 3:**	0.00	0.0	0.00
Result quality :	Good				



e)

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -22.0	Peak 1:	-22.0	100.0	3.62
Zeta Deviation (mV): 3.62	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.00789	Peak 3:	0.00	0.0	0.00

Result quality : Good

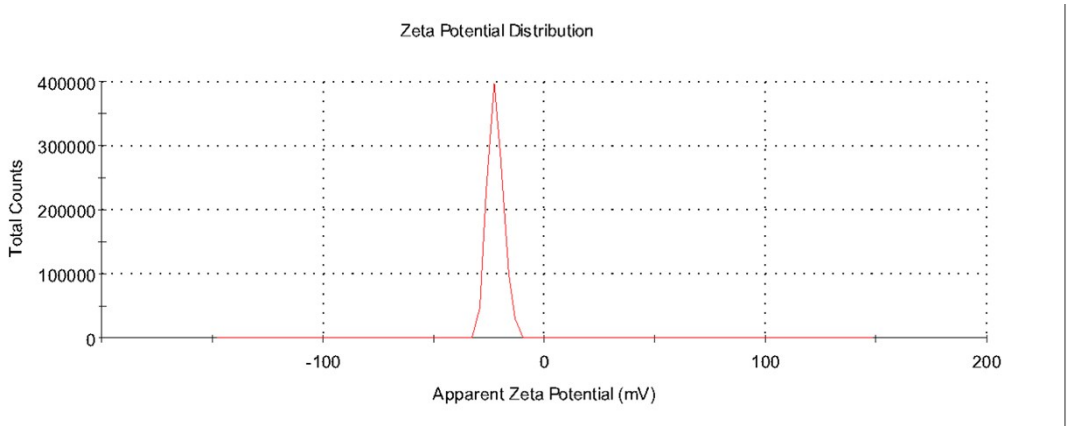


Figure SI-1C. Z-potential in water (pH= 6.5) of: a) FeNP, b) FeNP-SQ1, c) FeNP-SQ2, d) FeNP-SQ3, e) FeNP-SQ4.

FTIR

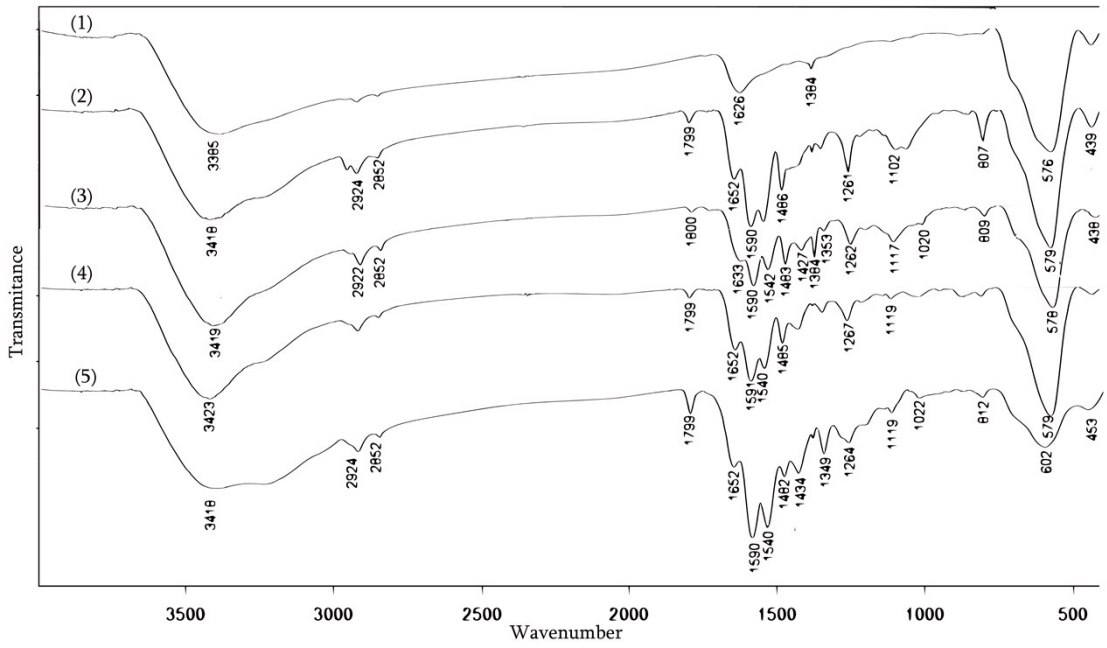
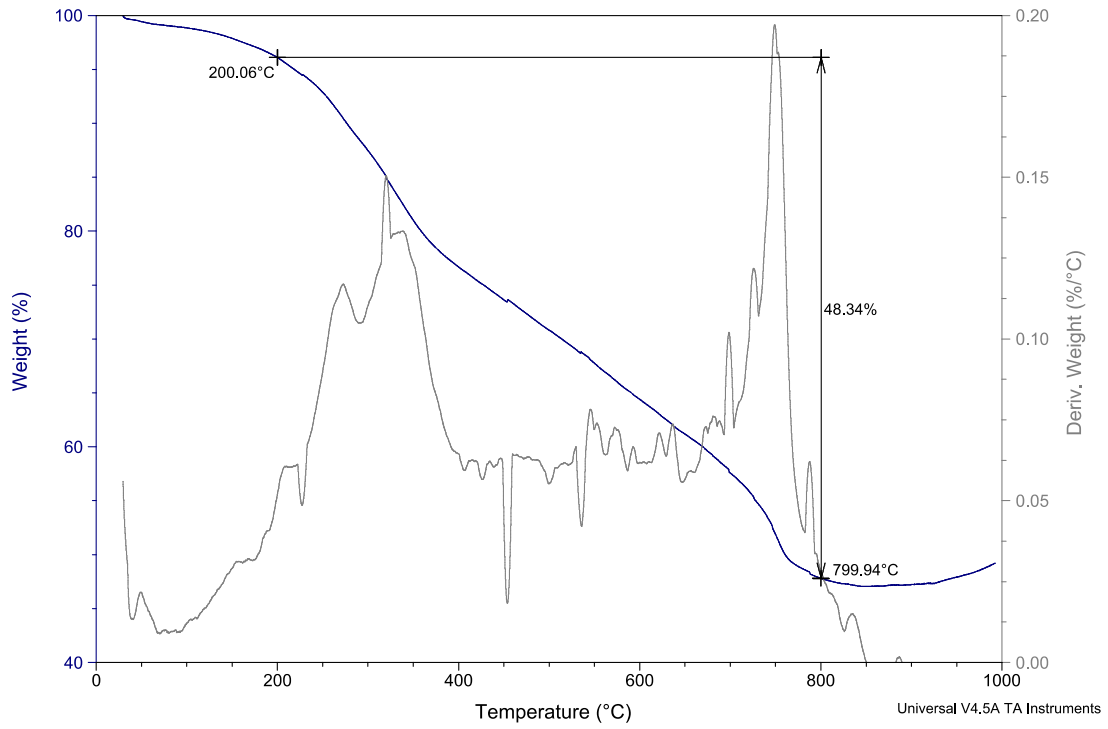


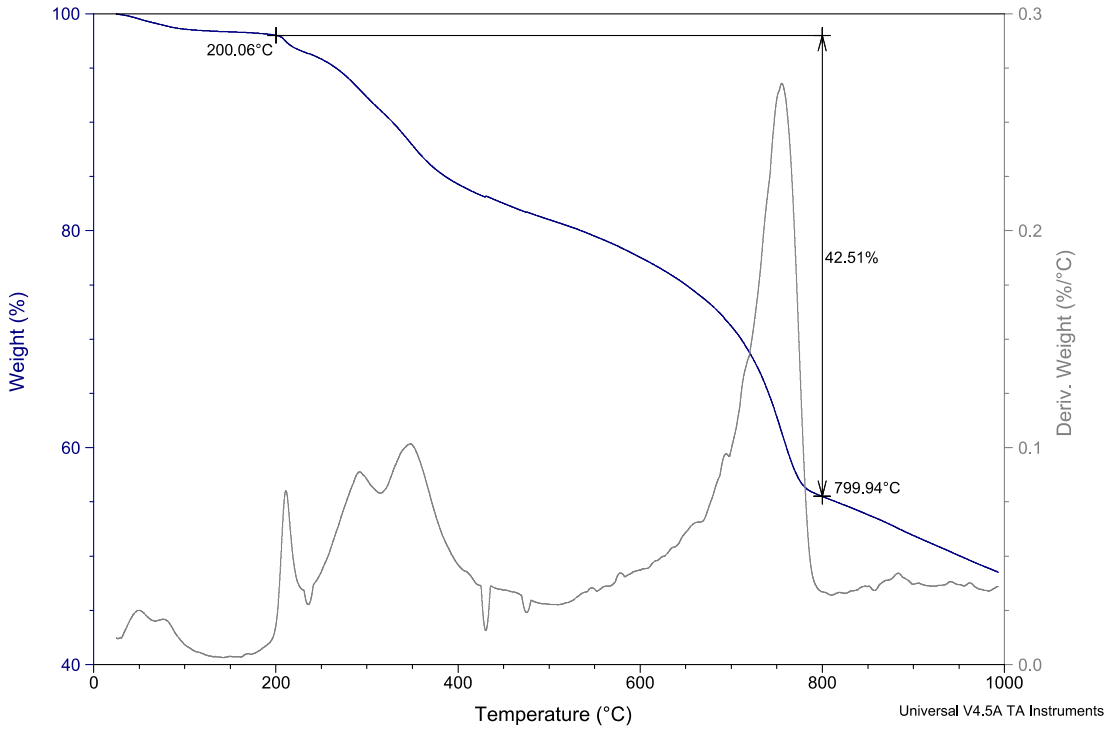
Figure SI-2. FTIR in KBr of: a) FeNP, b) FeNP-SQ1, c) FeNP-SQ2, d) FeNP-SQ3, e) FeNP-SQ4.

Thermogravimetric analysis

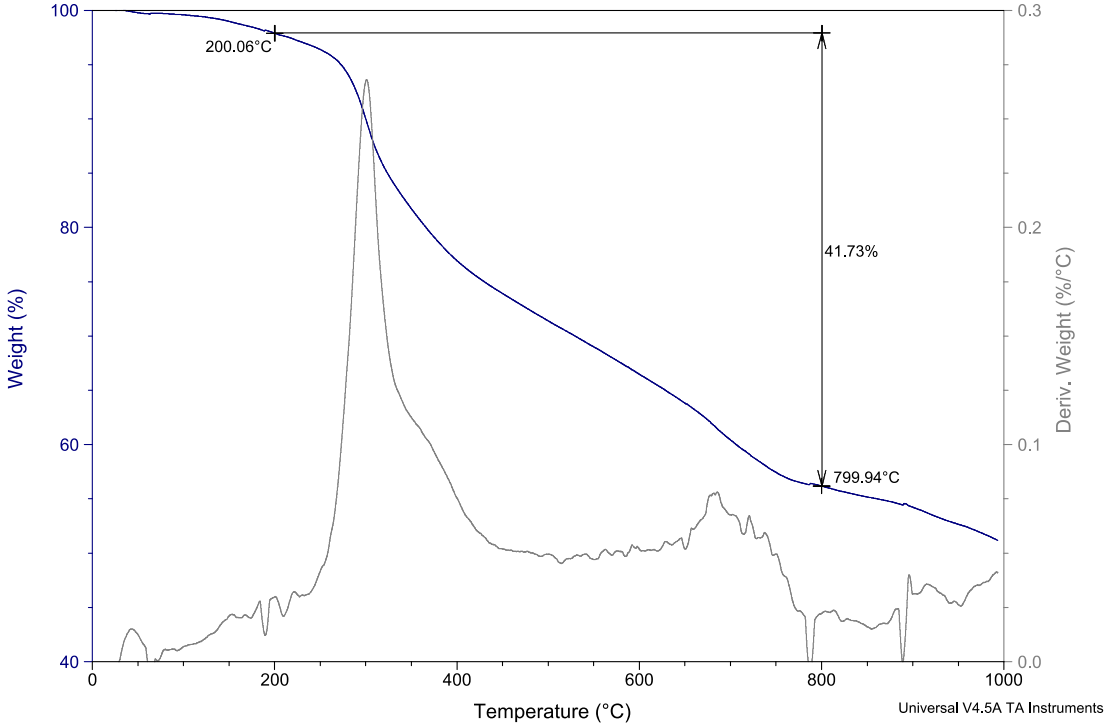
a)



b)



c)



d)

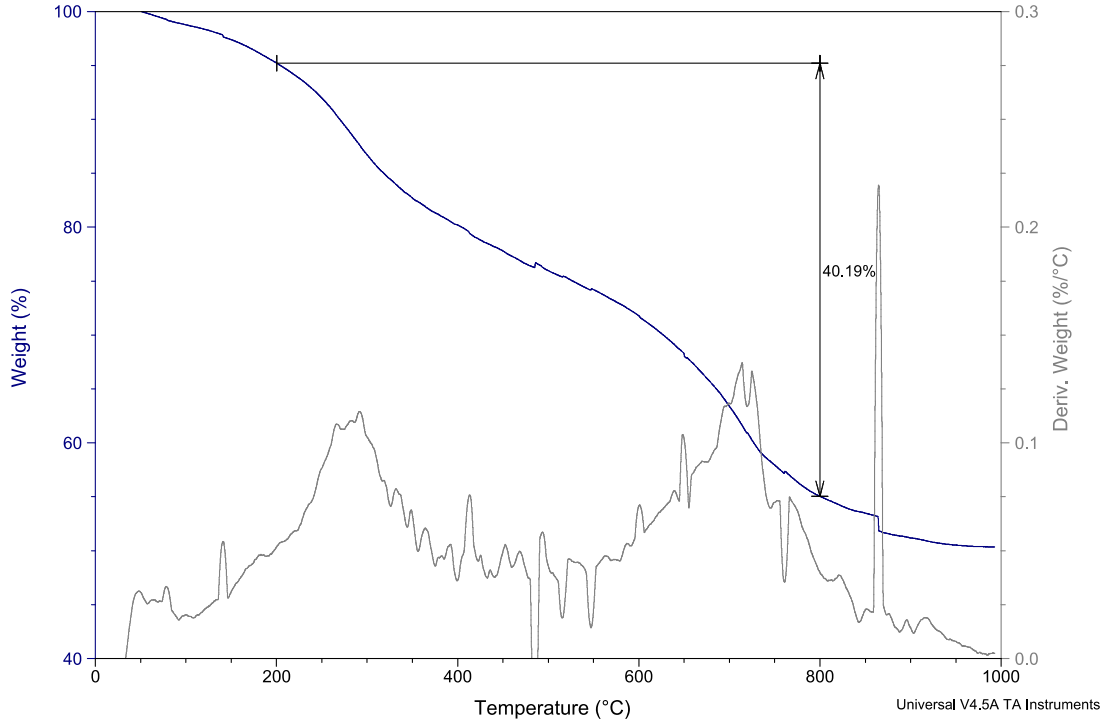


Figure SI-3. Thermogravimetric analysis (TGA) of: a) FeNP-SQ1, b) FeNP-SQ2, c) FeNP-SQ3, d) FeNP-SQ4.

Determination of number of molecules on FeNP-SQs surface.

The Thermogravimetric Analysis (TGA) shows a single weight loss, between 200 and 800 ºC. This value is used to determine the total number of molecules on the surface. Applying the following equations, the number of molecules on a FeNP-SQs surface can be determined:

$$N = \frac{\pi D^3 \rho}{6mw}$$

$$\frac{1}{N} = \frac{nanoparticles}{mol\ Fe_3O_4}$$

Where *1/N* refers to the number of FeNP-SQ for each mol of Fe_3O_4. *D* is the average diameter of FeNP-SQ in cm (provided by SEM micrographs), *ρ* is Fe_3O_4 density (5.196 g/cm^3) and *mw* is the molecular weight of Fe_3O_4 (231.53 g/mol). In order to improve and clarify the number of substituents, we chose TGA method to determine conjugation rate against mass loss due to decomposition. Experiments were performed with constant heating rate of 10 ºC/min from room temperature (25 ºC) to 1000 ºC. Using weight loss percentage values it is possible to quantify the number of molecules on FeNP-SQ surface applying previous equations.

RMN

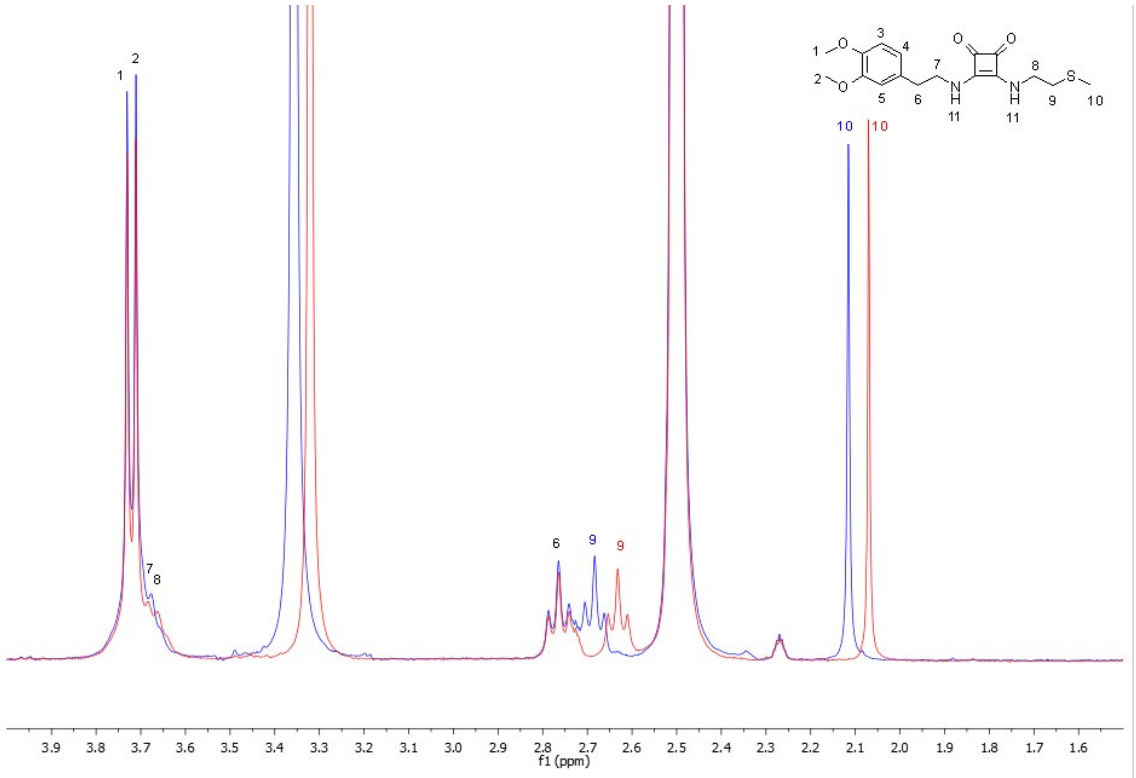


Figure SI-4A. ^{1}H RMN spectra, in DMSO-d_6, of SQ5 before (red) and after (blue) adding 1 equivalent of $Hg(ClO_4)_2$.

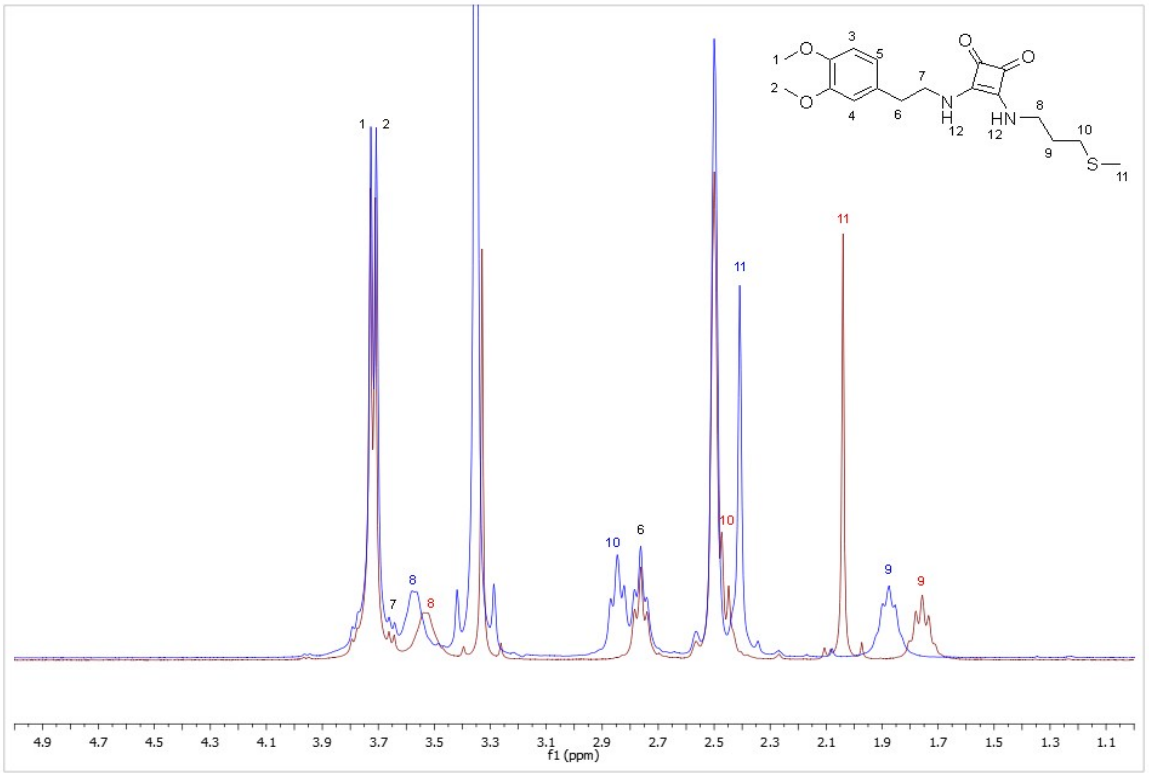


Figure SI-4B. ^{1}H RMN spectra, in DMSO-d_6, of SQ6 before (red) and after (blue) adding 1 equivalent of $Hg(ClO_4)_2$.

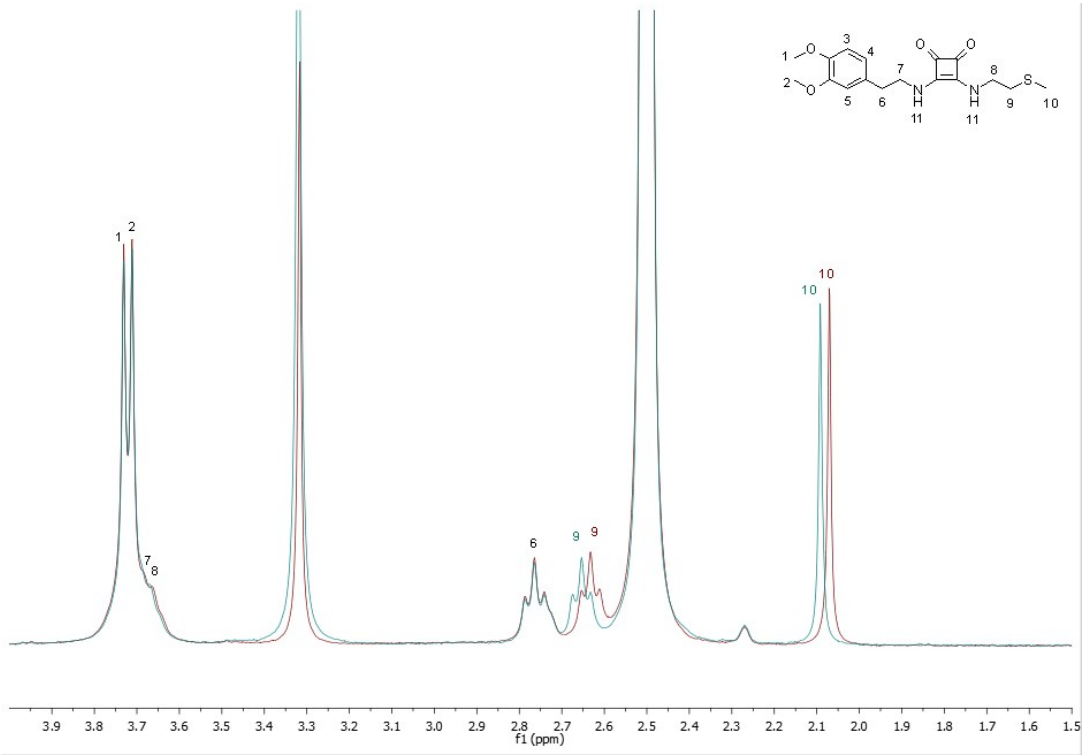


Figure SI-5A. ^{1}H RMN spectra, in DMSO-d_6, of SQ5 before (red) and after (blue) adding 1 equivalent of $AgNO_3$.

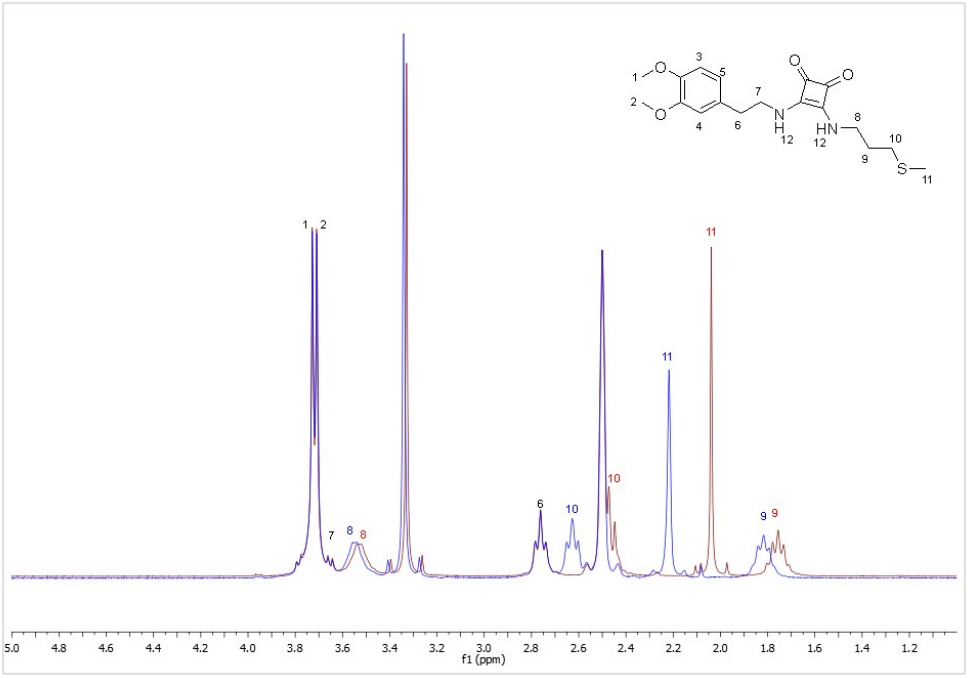


Figure SI-5B. ^{1}H RMN spectra, in DMSO-d_6, of SQ6 before (red) and after (blue) adding 1 equivalent of $AgNO_3$.

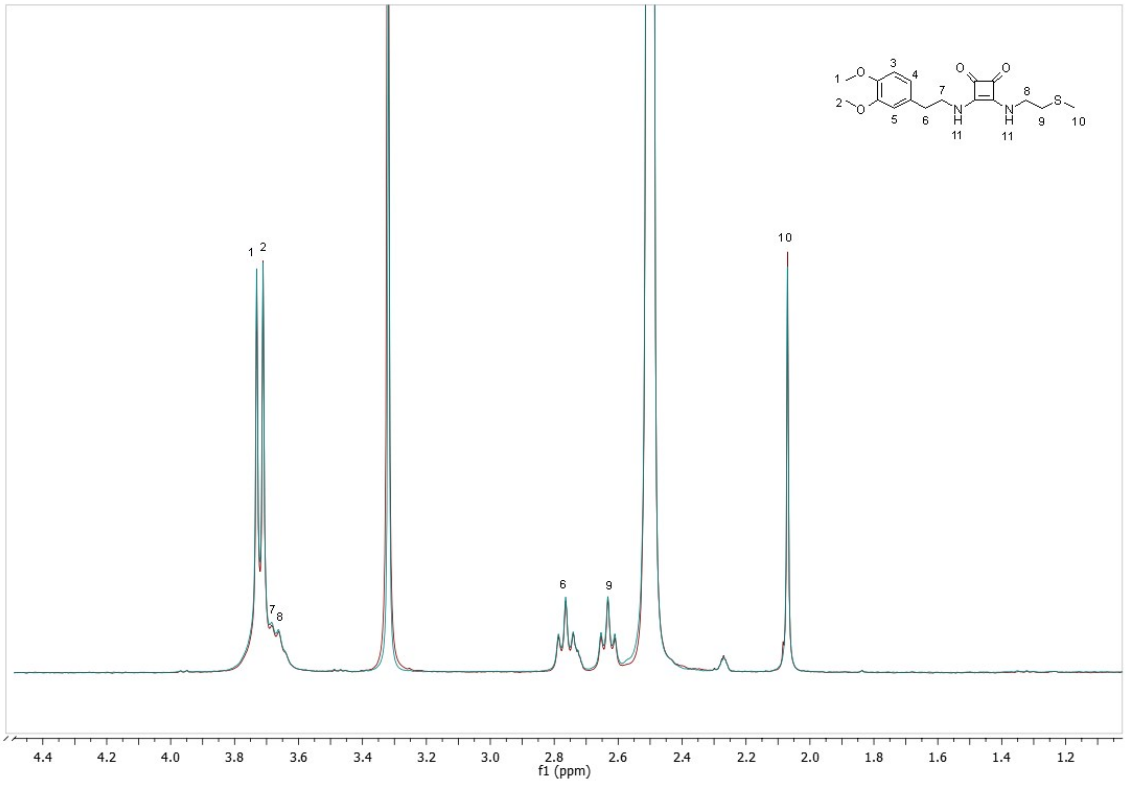


Figure SI-6A. ^{1}H RMN spectra, in DMSO-d_6, of SQ5 before (red) and after (blue) adding 1 equivalent of $Pb(ClO_4)_2$.

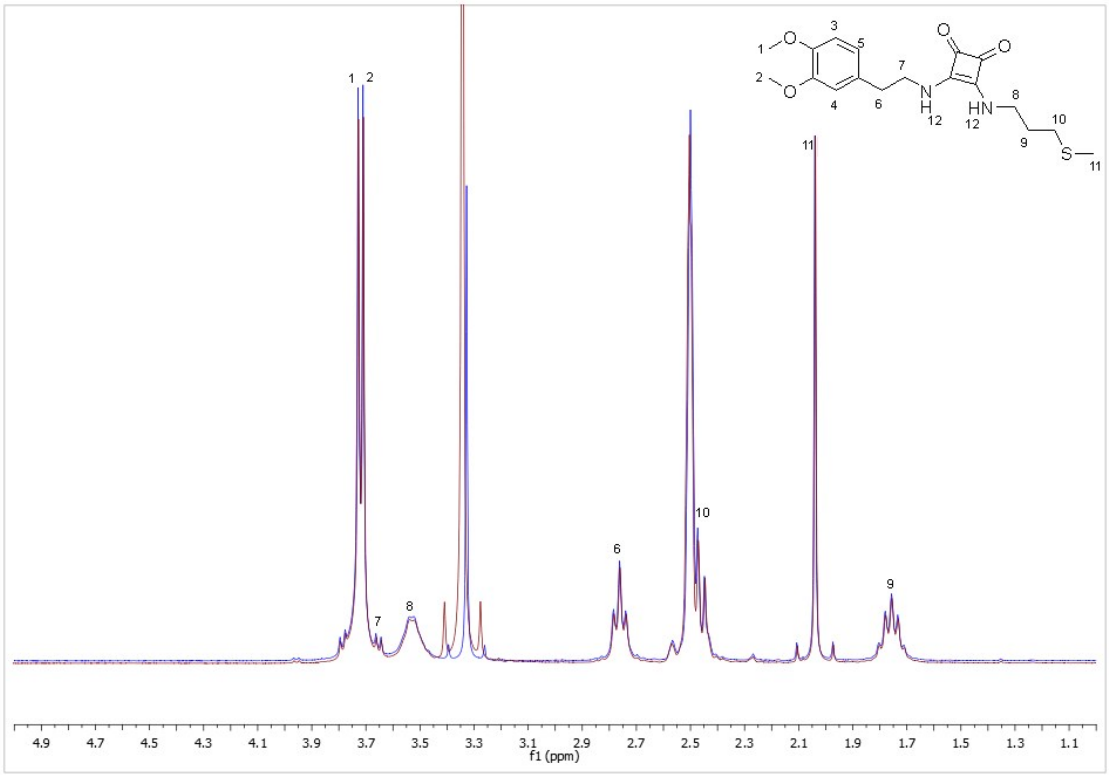


Figure SI-6B. ^{1}H RMN spectra, in DMSO-d_6, of SQ6 before (red) and after (blue) adding 1 equivalent of $Pb(ClO_4)_2$.

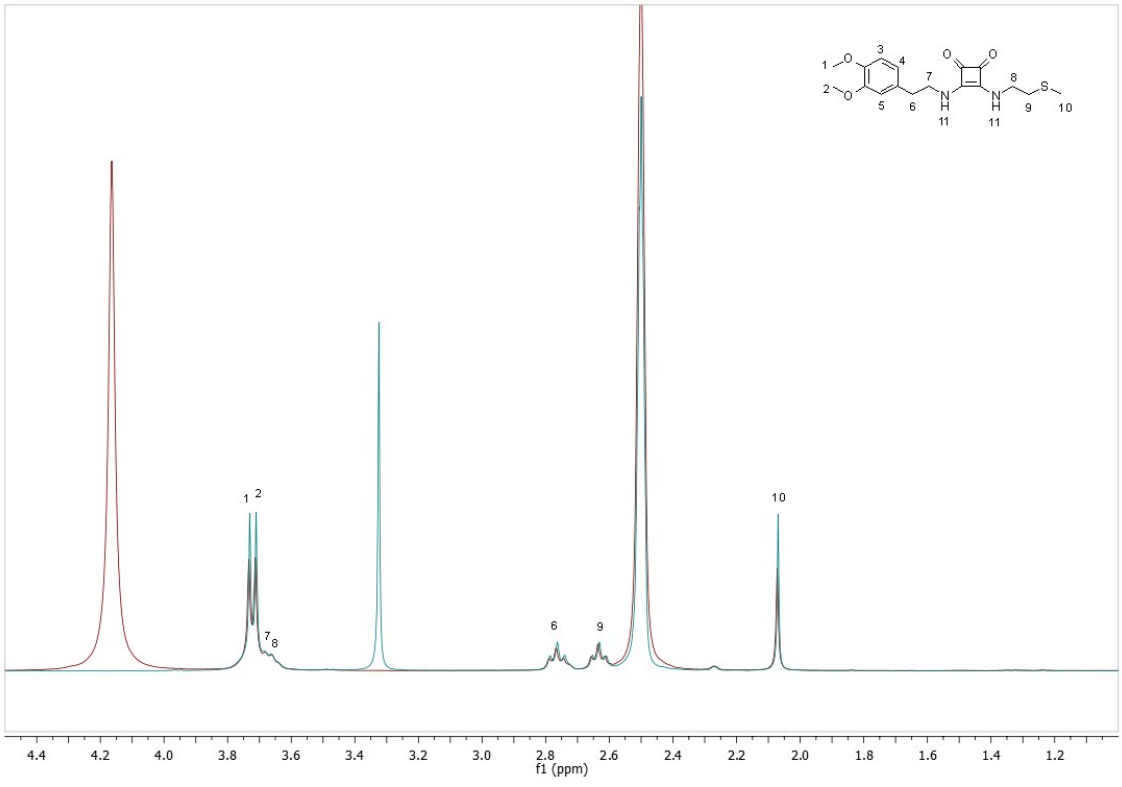


Figure SI-7A. ^{1}H RMN spectra, in DMSO-d_6, of SQ5 before (red) and after (blue) adding 1 equivalent of $AuCl_3 \cdot 3H_2O$.

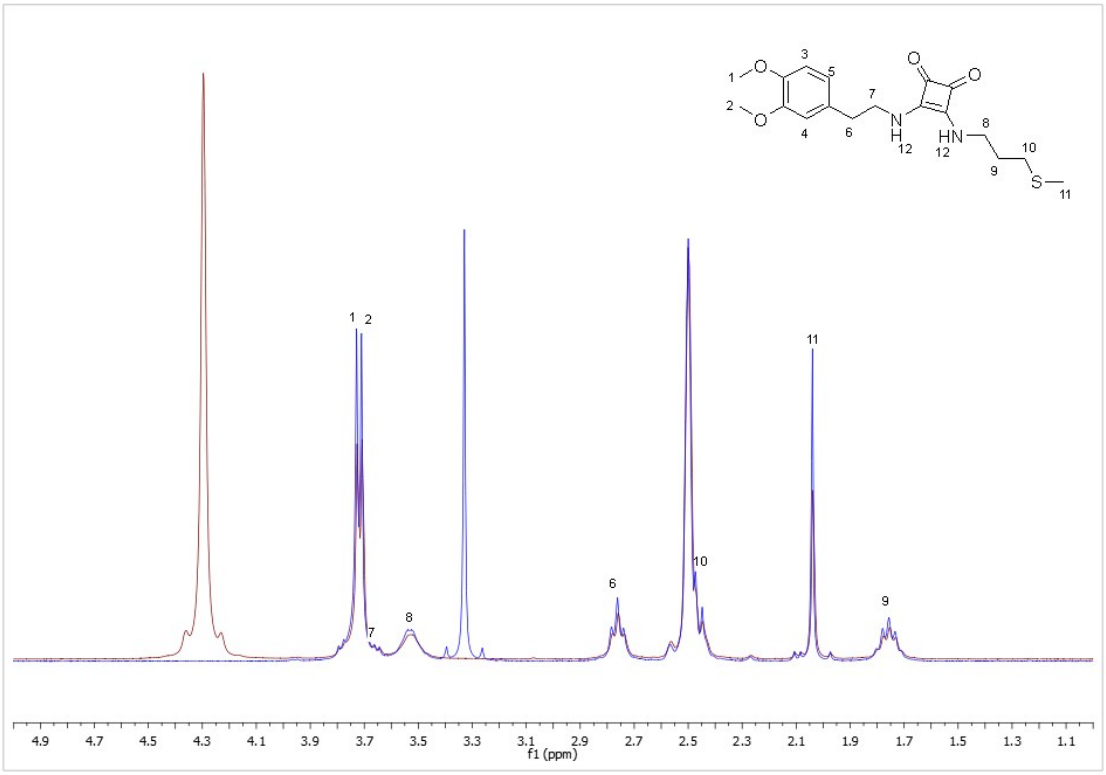


Figure SI-7B. ^{1}H RMN spectra, in DMSO-d_6, of SQ6 before (red) and after (blue) adding 1 equivalent of $AuCl_3 \cdot 3H_2O$.

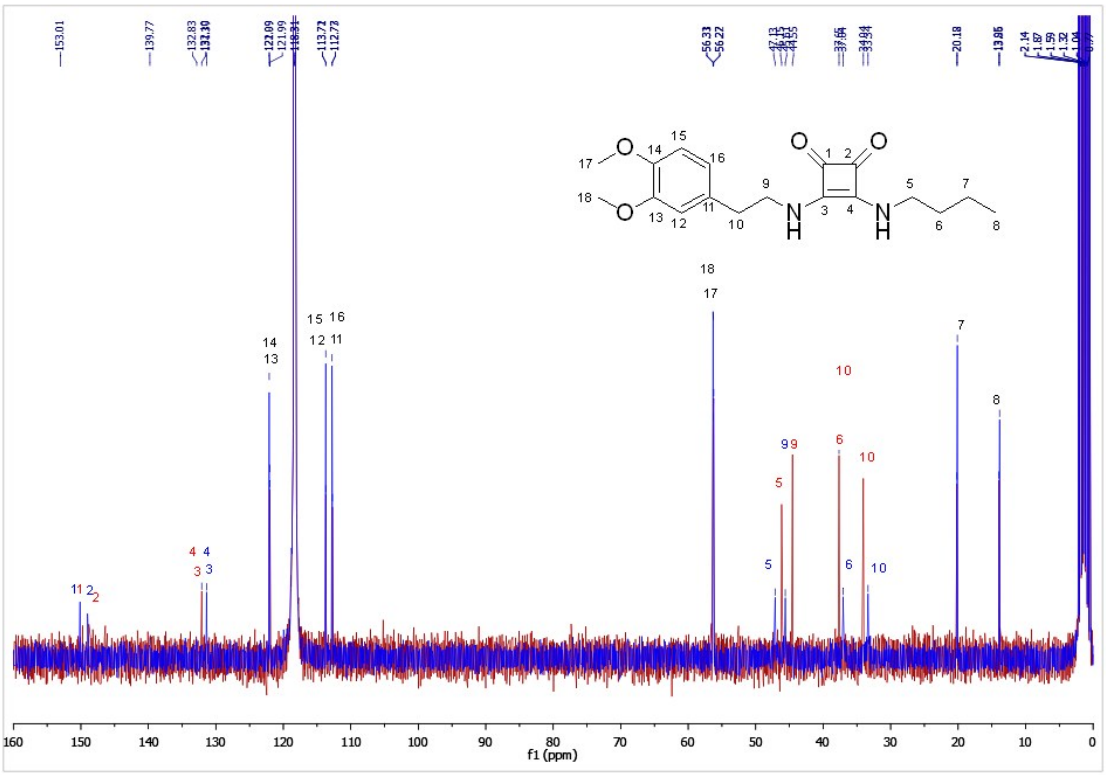


Figure SI-8 ^{13}C RMN spectra, in CD_3CN, of 3,4-dimethoxy-SQ1 before (red) and after (blue) adding 1 equivalent of $AuCl_3 \cdot 3H_2O$.

HRMS-ESI

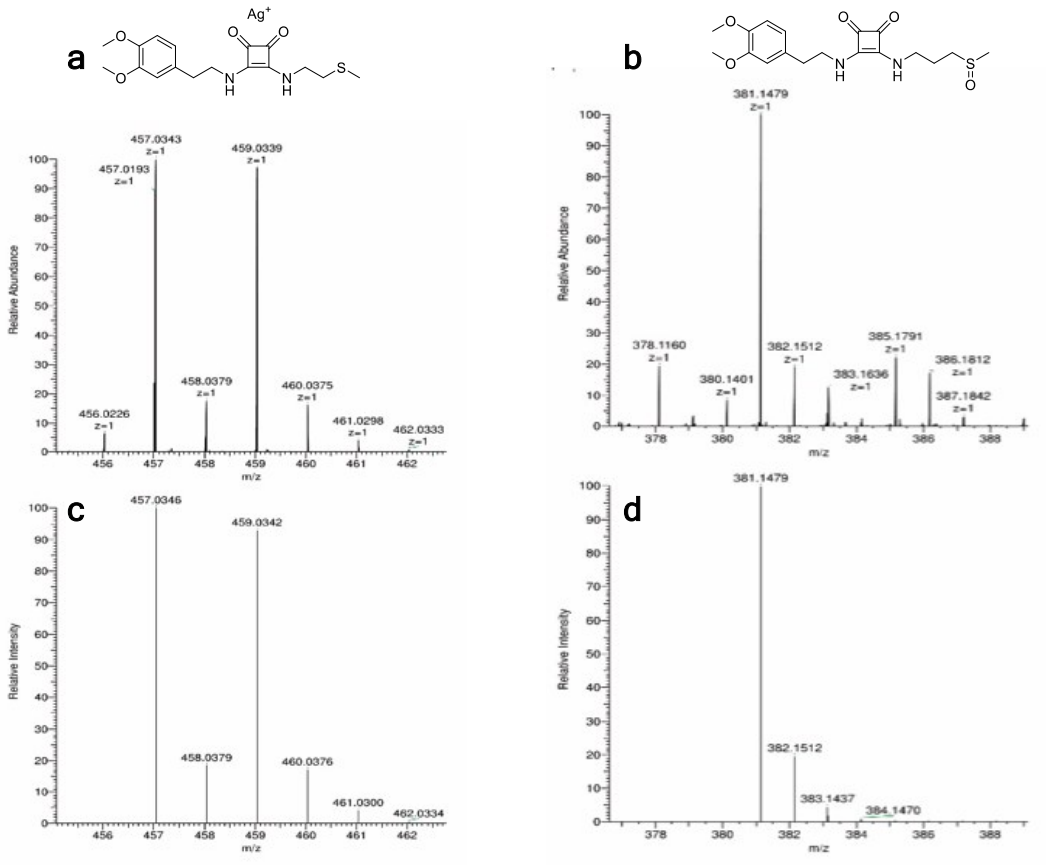


Figure SI-9A. a) HRMS-ESI(+) of a CH_3CN solution of SQ5 in presence of Ag^+. The signal at m/z 457.0343 corresponds to $[Ag{\cdot}SQ5]^+$. c) Calculated isotopic distributions for $[Ag{\cdot}SQ5]^+$. b) HRMS-ESI(+) of a CH_3CN solution of SQ6 in presence of Au^{3+}. The signal at m/z 341.1479 corresponds to sulfoxide of the starting SQ6. d) Calculated isotopic distributions for SQ6-sulfoxide. Note the excellent correlation between the recorded spectra and the calculated isotopic distributions.

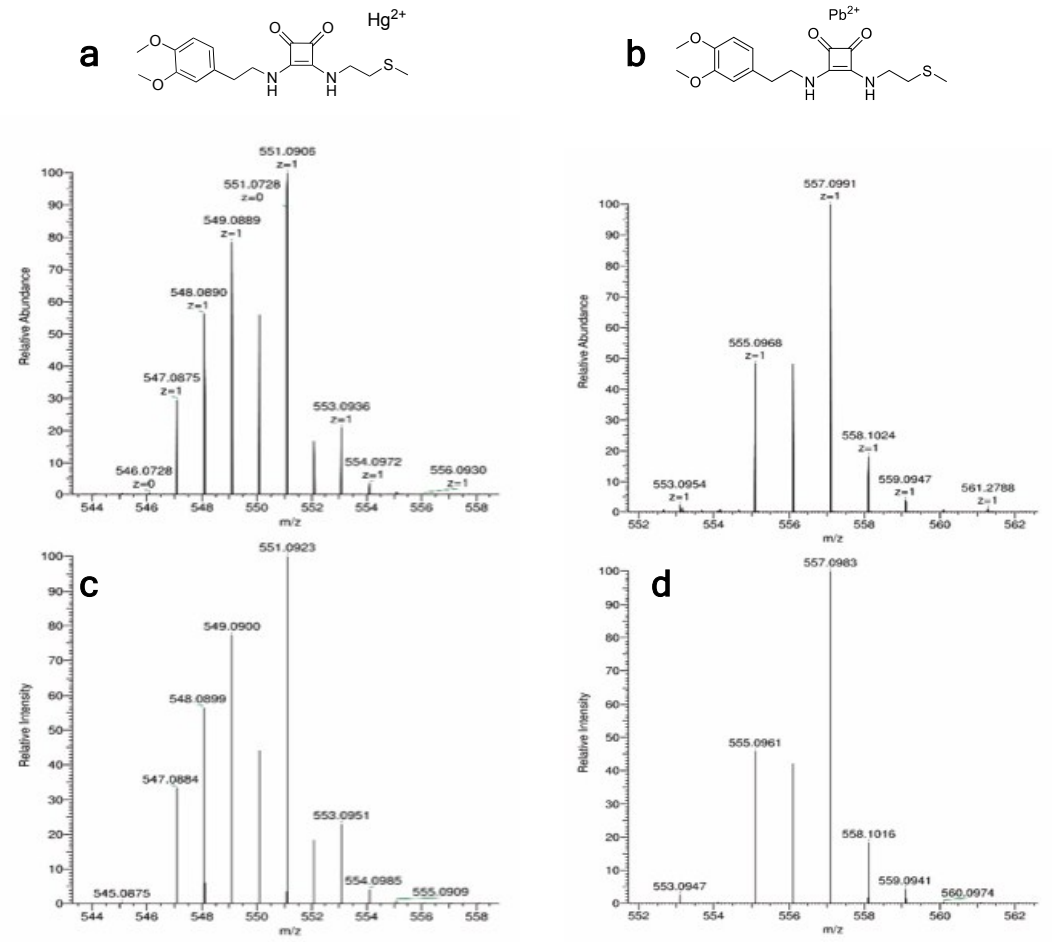


Figure SI-9B. a) HRMS-ESI(+) of a CH_3CN solution of SQ5 in presence of Hg^{2+}. The signal at m/z 551.0906 corresponds to $[Hg{\cdot}SQ5\text{-}H]^+$. c) Calculated isotopic distributions for $[Hg{\cdot}SQ5\text{-}H]^+$. b) HRMS-ESI(+) of a CH_3CN solution of SQ5 in presence of Pb^{2+}. The signal at m/z 557.0991 corresponds to $[Pb{\cdot}SQ5\text{-}H]^+$. d) Calculated isotopic distributions for $[Pb{\cdot}SQ5\text{-}H]^+$. Note the excellent correlation between the recorded spectra and the calculated isotopic distributions.

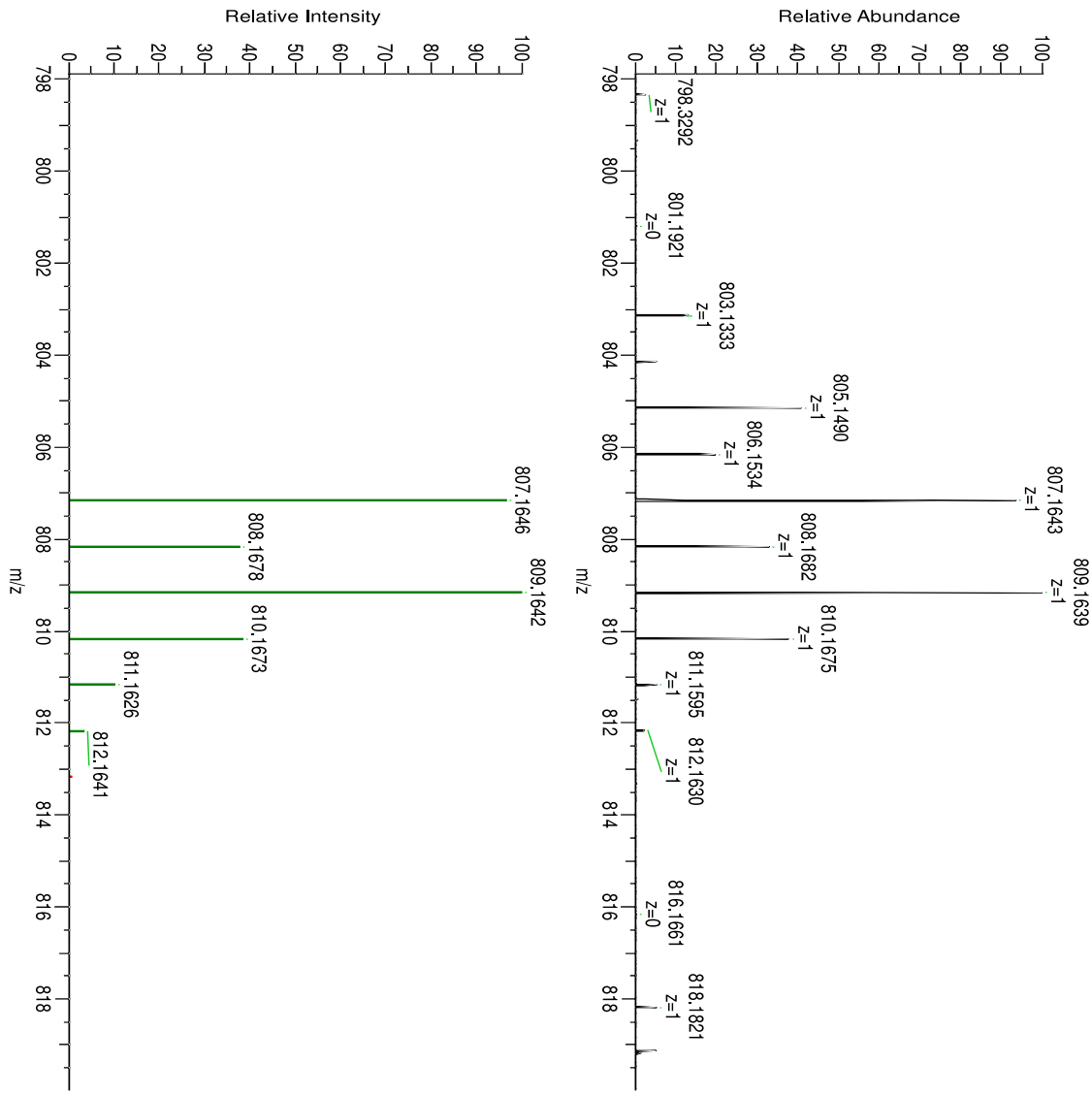


Figure SI-10. HRMS-ESI(+) of a CH_3CN solution of SQ5 in presence of Ag^+. The signal at m/z 807.1646 corresponds to $[Ag\cdot(SQ5)_2]^+$.

Removal procedure for each metal

In an illustrative removal procedure 5 mg of the hybrid-functionalized nanoparticles FeNP-SQX were suspended in 10 mL of a metal solution (5 ppm) in a 15 mL falcon tube. The suspension was irradiated with ultrasound for 10 minutes. The mixture was stirred for 2 hours. After that, the magnetic nanoparticles were isolated by magnetic filtration. The remaining solution was filtered by 0.45 µm Teflon filter and 2 mL of this solution was diluted with HNO_3 2.5% to a total of 10 mL to analyse by ICP-OES metal concentration remaining.