Supporting Information

Cation induced conformational and self-assembly transitions in designer peptides

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1. General Information

1.1 Materials

All reagents were used as such and solvents used in the reactions were dried before use. Amino acids used were of L-configuration and were purchased from SRL India or Sigma-Aldrich. Reactions were monitored by silica gel (Silica gel G, Merck) thin layer chromatography (TLC) and purifications were done by column chromatography (Silica gel 100-200 mesh). Fisher-Scientific melting point apparatus were used for recording melting points. IR spectra were recorded as KBr pellets using Nicolet, Protégé 460 spectrometer. ^{1}H NMR (Brucker-DPX-300/500) spectrometers were used and tetramethylsilane was used as an internal standard. Coupling constants are recorded in Hz, and the ^{1}H NMR data are reported as s (singlet), d (doublet), br (broad), t (triplet) and m (multiplet), dd (double doublet). All compounds were characterized by high-resolution mass spectrometry analysis (HRMS) on Bruker MicrO-TOF-QII model using ESI-technique. Optical rotation was recorded on Rudolph Research Analytical Autopol® V Polarimeter where concentrations are given in gram/100 mL. Circular dichroism (CD) spectra were recorded on AVIV Model 410 spectrometer using a quartz cell of 1 mm path length. The samples were prepared in acetonitrile with a concentration of 500 μM. The CD spectra were recorded with a scan speed of 1 nm/min and averaged over 3 scans. UV-visible spectra were recorded in Shimadzu (UV-2400 double beam spectrophotometer). The emission spectra were recorded in FluoroMax-4 spectrofluorometer (HORIBA JOBIN YVON Scientific), using a 3 mL quartz cuvette with slit width of 5 nm.

1.2 Methods

1.2.1 Scanning Electron Microscopy (SEM)

Solutions of compounds were prepared by dissolving 1 mg of each compound in 1 mL of MeOH. A glass coverslip was attached to a stub using carbon tape. About 10 µL of the solution was drop-casted onto the coverslip, and left to dry at room temperature. Similarly, a solution of 1:1 compound:Cu^{2+} (1mM) was drop casted on to the coverslip attached on the stub. Further, it was coated with gold (~10 nm) and analyzed by ZEISS EVO 50 Scanning Electron Microscope. The images captured at room temperature were processed using Image J software.

1.2.2 Atomic Force Microscopy (AFM)

Solution of compounds were prepared by dissolving 1 mg of each compound per mL of the solvent. About 5µL of this sample solution was deposited onto a freshly cleaned silicon wafer and allowed to dry at room temperature. Atomic force microscope (Bruker Dimension Icon) in tapping mode was used for imaging. The data obtained was analyzed using Nanoscope 5.31r software.

1.2.3 Transmission electron Microscopy (TEM)

Samples for TEM were prepared by dissolving the compound in methanol. About 2 µL aliquot of the sample solution was placed on a 200 mesh copper grid and allowed to dry at room temperature. Samples were viewed using a TECHNAI G2 (20S-TWIN) electron microscope and were processed using Image J software.

1.2.4 NMR titration study

All the compound **CW-CL** solutions were made of 10 mM concentration in the DMSO-d_6 and metal ions solutions of concentration 100 mM were prepared by dissolving the perchlorate salts of the respective metal ions and added to the host solution 0-2 equivalent and recorded the NMR spectrum.

1.2.5 Selectivity analysis

a) UV-visible Experiment:

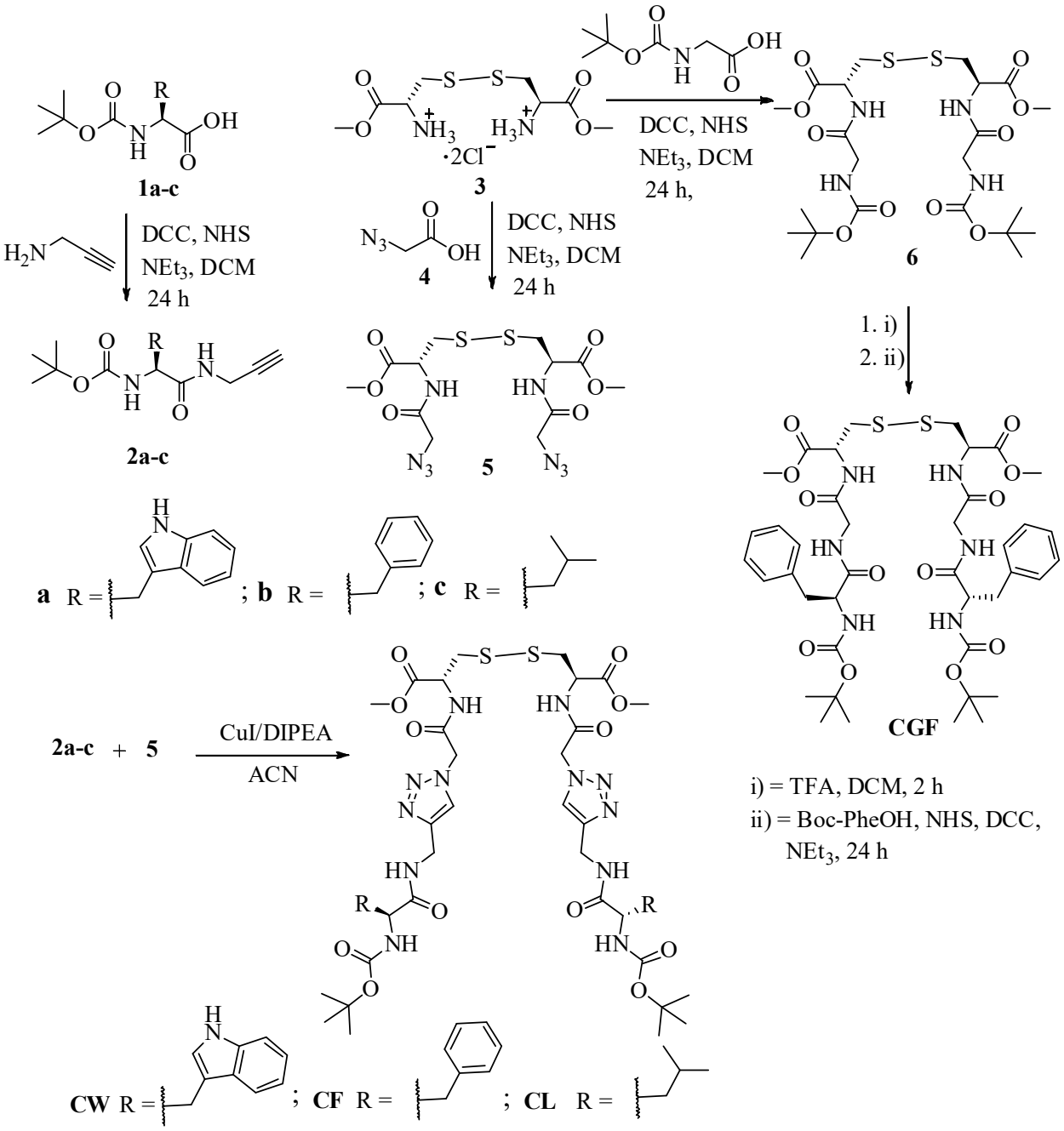
Each metal ion solution (Cu^{2+}, Na^{+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) is added to **CW** solution. The UV-visible spectra were recorded.

To a solution of **CW** in acetonitrile/chloroform (95/5) Cu^{2+} (10 equiv.) in (acetonitrile) and another metal ion (100 equiv. each) in (acetonitrile) was added and the UV spectra were recorded. Metal ions such as (Na^{+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) were used as the interfering cations.

b) ESI-Mass analysis:

Compounds **CW**, **CF** and **CL** (2 mM) were made in acetonitrile/chloroform(95/5%) solvent, and 2 equivalent of various metal ions (Cu^{2+}, Na^{+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) as perchlorate salts were added to the solution of compound. Further the mixture solution was diluted 10 times and the resulting solution was analysed by ESI technique.

***1.2.6 Scheme* S1**: *Synthesis of compound* **CW**, **CF**, **CL** and **CGF**.



1.3 General Synthetic Procedure

1.3.1 Preparation of 2a

To an ice-cooled solution of Boc-Tryptophan **1a** (500 mg, 1.65 mmol) in dry CH_2Cl_2 was added N-hydroxysuccinimide (NHS) (228 mg, 1.98 mmol) and dicyclohexylcarbodiimide (DCC) (408 mg, 1.98 mmol) and stirred. After 5 minutes, propargylamine (109 mg, 1.98 mmol) in 10 mL CH_2Cl_2 and triethylamine (0.27 mL, 1.98 mmol) were added and the reaction mixture was stirred for 24 h. The reaction mixture was filtered, and the clear filtrate obtained was washed sequentially with 0.2N H_2SO_4, aq. $NaHCO_3$ solution and water. The organic part was dried over anhydrous Na_2SO_4 and purified by silica gel column chromatography using ethyl acetate and hexane as eluents to afford about 76% yield of **2a**.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (s, 9H), 2.15 (br s, 1H), 3.24 (br d, *J* = 15.3 Hz, 2H), 3.90 (br s, 2H), 4.46 (br s, 1H), 5.21 (br s, 1H), 6.23 (br s, 1H), 7.01 (br s, 1H), 7.07-7.30 (m, 2H) 7.35 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 6.5 Hz, 1H), 8.40 (s, 1H).

^{13}C NMR ($CDCl_3$ 75 MHz) δ 28.3, 29.1, 29.7, 55.1, 71.6, 79.2, 80.3, 110.2, 111.3, 118.8, 119.8, 122.2, 123.4, 127.5, 136.2, 155.6, 171.7

IR (KBr): 3392, 3342, 3297, 2976, 2919, 1684, 1641, 1526, 1386, 1249, 1168 cm^{-1}.

HRMS: Calcd. for $C_{19}H_{23}N_3O_3Na$ m/z = 364.1632, found m/z = 364.1647

1.3.2 Preparation of 2b[1]

To an ice-cooled solution of Boc-phenylalanine **1b** (500 mg, 1.88 mmol) in dry CH_2Cl_2 was added NHS (260 mg, 2.26 mmol) and DCC (466 mg, 2.26 mmol) and stirred. After 5 minutes, propargylamine (124 mg, 2.26 mmol) in 10 mL dry CH_2Cl_2 and NEt_3 (0.31 ml, 2.26 mmol) were added, and the reaction mixture was stirred for 24 h. The reaction mixture was stirred for 24 h. The reaction mixture was filtered, and the clear filtrate obtained was washed sequentially with

0.2N H_2SO_4, aq. $NaHCO_3$ solution and finally with water. The organic part was dried over anhydrous Na_2SO_4, evaporated, and purified by silica gel column chromatography using ethyl acetate and hexane as eluents to afford about 86% yield of **2b**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 9H), 2.19 (t, *J* = 2.4 Hz, 1H), 3.06 (m, 2H), 3.98 (br s, 2H), 4.36 (br s, 1H), 5.10 (br s, 1H), 6.31 (br s, 1H), 7.16-7.37 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.2, 29.0, 38.6, 55.6, 71.6, 79.0, 80.2, 126.9, 128.6, 129.3, 136.5, 155.5, 177.2

IR (KBr): 3326, 2673, 2925, 1691, 1655, 1530, 1447, 1390, 1368, 1170 cm^{-1}.

1.3.3 Preparation of 2c[2]

To an ice-cooled solution of Boc-Leucine, **1c** (500 mg, 2.16 mmol) in dry CH_2Cl_2 was added NHS (298 mg, 2.59 mmol) and DCC (534 mg, 2.59 mmol) and stirred. After 5 minutes, propargylamine (143 mg, 2.59 mmol) in 10 mL dry CH_2Cl_2 and NEt_3 (0.36 ml, 2.59 mmol) were added. The reaction mixture was stirred for 24 h. The reaction mixture was filtered, and the clear filtrate obtained were washed sequentially with 0.2N H_2SO_4, aq. $NaHCO_3$ solution and finally with water. The organic part was dried over anhydrous Na_2SO_4, evaporated, and purified by silica gel column chromatography using ethyl acetate and hexane as eluents to afford about 82% yield of **2c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94 (d+d, *J* = 6.0, 5.5 Hz, 6H), 1.41-1.55 (s+m, 10H), 1.66 (m, 2H), 2.22 (br t, 1H), 4.04 (br d, 2H), 4.14 (br s, 1H). 4.96 (d, *J* = 8.4 Hz, 1H), 6.63 (br s, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.9, 22.9, 24.7, 28.3, 29.0, 41.3, 52.8, 71.5, 79.4, 80.0, 155.9, 172.7

IR (KBr): 3316, 2963, 2933, 2873, 1684, 1659, 1529, 1369, 1278, 1245, 1171 cm^{-1}.

1.3.4. Preparation of 5

To an ice-cooled solution of azidoacetic acid **4** (300 mg, 2.97 mmol) in dry CH_2Cl_2 was added NHS (342 mg, 2.97 mmol) and DCC (612 mg, 2.97 mmol) and stirred. After 5 minutes, a solution

of cystine dimethyl ester dihydrochloride (460 mg, 1.35 mmol) was neutralized by NEt_3 (0.75 mL, 5.39 mmol) in 20 mL CH_2Cl_2 was added. The reaction mixture was left of stirred for 24 h. The reaction mixture was filtered, and the clear filtrate obtained were washed sequentially with 0.2N H_2SO_4, aq. $NaHCO_3$ solution and finally with water. The organic part was dried over anhydrous Na_2SO_4, evaporated, and purified by silica gel column chromatography using ethyl acetate and hexane as eluent to afford 401mg of **5**.

Yield: 68%

MP: 106-108 °C

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.22 (br dd, 4H), 3.80 (s, 6H), 4.05 (d, J = 2.6 Hz, 4H), 4. 90 (m, 2H), 7.17 (d, J = 7.6 Hz, 2H).

^{13}C NMR ($CDCl_3$ 75 MHz) δ 40.3, 51.7, 52.4, 53.0, 166.9, 170.3

IR (KBr): 3332, 3069, 2998, 2953, 2102, 1731, 1658, 1547, 1439, 1326, 1236, 1215, 1171 cm^{-1}.

HRMS: Calcd. for $C_{12}H_{18}N_8O6S_2Na$ m/z = 457.0683, found m/z = 457.0678.

***1.3.5 Preparation of* CW**

To a solution of **2a** (460 mg, 1.35 mmol) in 10 mL acetonitrile was added diisopropyl ethylamine (0.24 mL, 1.35 mmol), followed by compound **5** (280 mg, 0.65 mmol) and stirred under argon atmosphere. After 15 minutes CuI (26 mg, 0.14 mmol) was added and stirred for ~24 h under argon atmosphere. Filtered the reaction mixture, and the residue obtained was taken in sintered funnel and washed with NH_4Cl: NH_4OH (9:1), 0.2N H_2SO_4, saturated solution of $NaHCO_3$ and water. It was then dried. The obtained crude products were purified by silica gel column chromatography using $CHCl_3$/CH_3OH to afford **CW**

Yield: 87%

MP: 146-148 °C

$[\alpha]_D$: -24.1 (c 0.102 in MeOH)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.30 (s, 18H), 2.89 (dd, J = 14.2, 9.6 Hz, 2H) 3.03 (m, 4H), 3.18 (dd, J = 14.2, 5.0 Hz, 2H), 3.66 (s, 6H), 4.20 (m, 2H), 4.33 (m, 4H), 4.64 (m, 2H), 5.14 (s, 4H), 6.83 (d, J = 7.3 Hz, 2H), 6.96 (t, J = 7.4 Hz, 2H), 7.05 (t, J = 7.4 Hz, 2H), 7.12 (br s, 2H), 7.31 (d, J = 8.0 Hz, 2H) 7.60 (d, J = 7.8 Hz, 2H), 7.72 (s, 2H), 8.53 (br t, 2H), 9.04 (d, J = 7.5 Hz, 2H), 10.79 (s, 2H),

^{13}C NMR (DMSO-d_6, 75 MHz) δ 28.3, 28.6, 29.4, 31.8, 34.8, 51.6, 51.9, 52.9, 55.6, 78.4, 110.6, 111.7, 118.6, 119.0, 121.2, 124.2, 127.8, 136.5, 145.2, 155.6, 166.3, 170.9, 172.5

IR (KBr): 3376, 3061, 2929, 1740, 1688, 1532, 1367, 1247, 1168 cm^{-1}.

HRMS: Calcd. for $C_{50}H_{64}N_{14}O_{12}S_2Na$ m/z = 1139.4162, found m/z = 1139.4150.

***1.3.6 Preparation of* CF**

To a solution of **2b** (438 mg, 1.45 mmol) in 20 mL acetonitrile was added diisopropyl ethylamine (0.25 mL, 1.45 mmol), followed by compound **5** (300 mg, 0.69 mmol) under argon atmosphere and stirred. After 15 minutes CuI (28 mg, 0.15 mmol) was added into it and stirred it for ~24 h under argon atmosphere. Filtered the reaction mixture, and the residue obtained was taken in a sintered funnel, was washed with NH_4Cl: NH_4OH (9:1), 0.2N H_2SO_4, saturated solution of $NaHCO_3$ and water. The obtained crude products were purified by silica gel column chromatography using $CHCl_3$/CH_3OH to afford 480 mg of **CF**

Yield: 67 %

MP: 138-140 °C

$[\alpha]_D$: -25.1 (c 0.102 in MeOH)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.29 (s, 18H), 2.72 (dd, J = 14.3, 9.8 Hz, 2H), 2.94 (dd, J = 13.6, 3.5 Hz, 2H), 3.01 (dd, J = 13.2, 8.3 Hz, 2H), 3.18 (dd, J = 13.7, 4.0 Hz, 2H), 3.66 (s, 6H), 4.16

(m, 2H), 4.25-4.40 (m, 4H), 4.64 (m, 2H), 5.15 (s, 4H), 6.91 (d, *J* = 8.3 Hz, 2H), 7.18 (br s, 2H), 7.24 (s, 8H), 7.73 (s, 2H), 8.45 (br t, 2H), 9.01 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.3, 29.7, 34.9, 38.9, 39.9, 52.4, 53.0, 55.6, 80.1, 124.2, 126.8, 128.5, 129.4, 136.8, 145.0, 155.6, 165.6, 170.3, 171.9

IR (KBr): 3312, 3083, 2975, 1729, 1669, 1549 (br), 1453, 1368, 1244, 1171 cm^{-1}.

HRMS: Calcd. for $C_{46}H_{62}N_{12}O_{12}S_2Na$ m/z = 1061.3944, found m/z = 1061.3924.

***1.3.7 Preparation of* CL**

To a solution of **2c** (248 mg, 0.92 mmol) in 10 mL acetonitrile was added, diisopropylethylamine (0.16 mL, 0.92 mmol), followed by compound **5** (191 mg, 0.44 mmol) under argon atmosphere and stirred. After 15 minutes, CuI (18 mg, 0.09 mmol) was added to it and stirred it for ~24 h under argon atmosphere. Evaporated the reaction mixture, re-dissolved in dichloromethane, and washed with NH_4Cl:NH_4OH (9:1), 0.2N H_2SO_4, saturated solution $NaHCO_3$, and finally with water. The organic part was then dried over anhydrous Na_2SO_4 to yield the corresponding acyclic compound. The crude products were purified by silica gel column chromatography using $CHCl_3$/CH_3OH to afford 333 mg of **CL**

Yield: 78 %

MP: 130-132 °C

$[\alpha]_D$: -48.8 (c 0.107 in MeOH)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.85 (d+d, *J* = 6.6, 6.7 Hz, 12H), 1.28-1.46 (s + m, 22H), 1.56 (m, 2H), 3.01 (dd, *J* = 14.0, 8.5 Hz, 2H), 3.18 (dd, *J* = 14.0, 5.1 Hz, 2H), 3.67 (s, 6H), 3.97 (m, 2H), 4.30 (m, 4H), 4.63 (m, 2H), 5.15 (s, 4H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 2H), 8.32 (t, *J* = 5.6 Hz, 2H), 9.01 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR ($CDCl_3$ 75 MHz) δ 21.8, 23.1, 24.7, 28.3, 29.7, 34.9, 40.1, 41.7, 52.4, 53.0, 79.9, 124.4, 145.0, 155.9, 165.9, 170.4, 173.5

IR (KBr): 3309 (br), 3072, 2958 (br), 2872, 1745, 1690 (br), 1532, 1437, 1367, 1249 (br), 1168, 1050, cm^{-1}.

HRMS: Calcd. for $C_{40}H_{66}N_{12}O_{12}S_2Na$ m/z = 993.4257, found m/z = 993.4279

1.3.8 Preparation of CGF

To an ice cooled solution of **6** (300 mg, 0.52 mmol) in 2 mL CH_2Cl_2 was added trifluoroacetic acid (TFA) (1.19 mL, 15.45 mmol) and the reaction mixture was stirred for 4 h at room temperature. The reaction was monitored by TLC and after completion, the reaction mixture was evaporated under a high vacuum with a KOH trap to afford N-deprotected derivative of **6**.

To an ice cold solution of Boc–PheOH (300 mg, 1.13 mmol) in dry CH_2Cl_2 was added NHS (130 mg, 1.13 mmol), DCC (233 mg, 1.13 mmol). The N-deprotected **6**, NEt_3 (0.30 mL, 2.06 mmol) in CH_2Cl_2 were added and the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was filtered, and the clear filtrate obtained was washed sequentially with 0.2N H_2SO_4, aq. $NaHCO_3$ solution and water. The organic part was dried over anhydrous Na_2SO_4, evaporated and purified by silica gel column chromatography using ethyl acetate and hexane as eluent to afford 296 mg of **CGF**

Yield: 66%

MP: 122-124 °C

$[\alpha]_D$: -37.7 (c 0.104 in MeOH)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37 (s, 18H), 3.01 (m, 4H), 3.15 (m, 4H), 3.75 (s, 6H), 3.91 (m, 2H), 4.05 (m, 2H) 4.46 (m, 2H), 4.82 (m, 2H), 5.34 (br s, 2H), 7.16 (br t, 2H), 7.18-7.32 (m, 10H), 7.36 (d, J = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$ 125 MHz) δ 28.3, 38.5, 40.7, 43.2, 52.3, 52.8, 55.9, 80.2, 126.9, 128.6, 129.3, 136.7, 155.8 169.2, 170.6, 172.6

IR (KBr): 3319 (br), 2976, 2929, 1743, 1690, 1644, 1527, 1442, 1368, 1248, 1168 cm^{-1}.

HRMS: Calcd. for $C_{40}H_{56}N_6O_{12}S_2Na$ m/z = 899.3290, found m/z = 899.3314

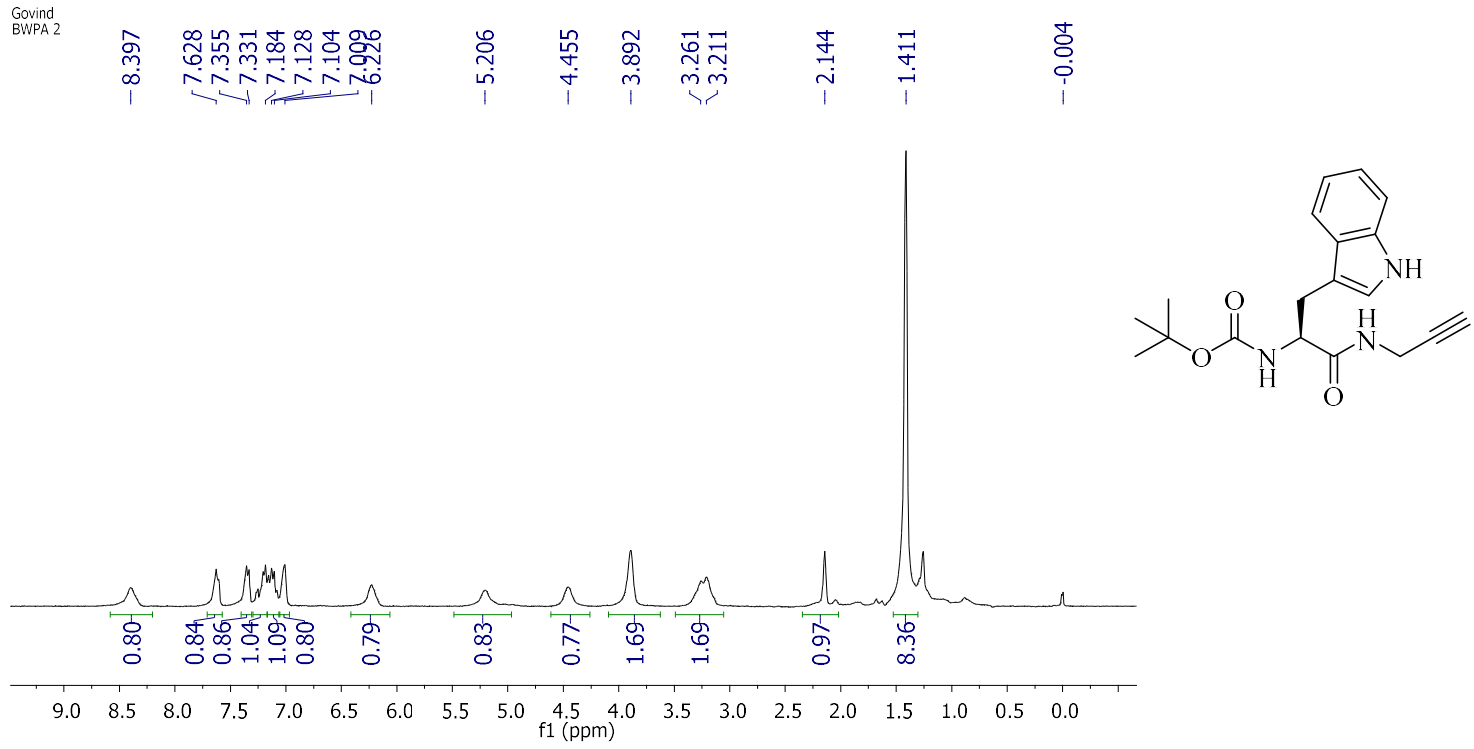
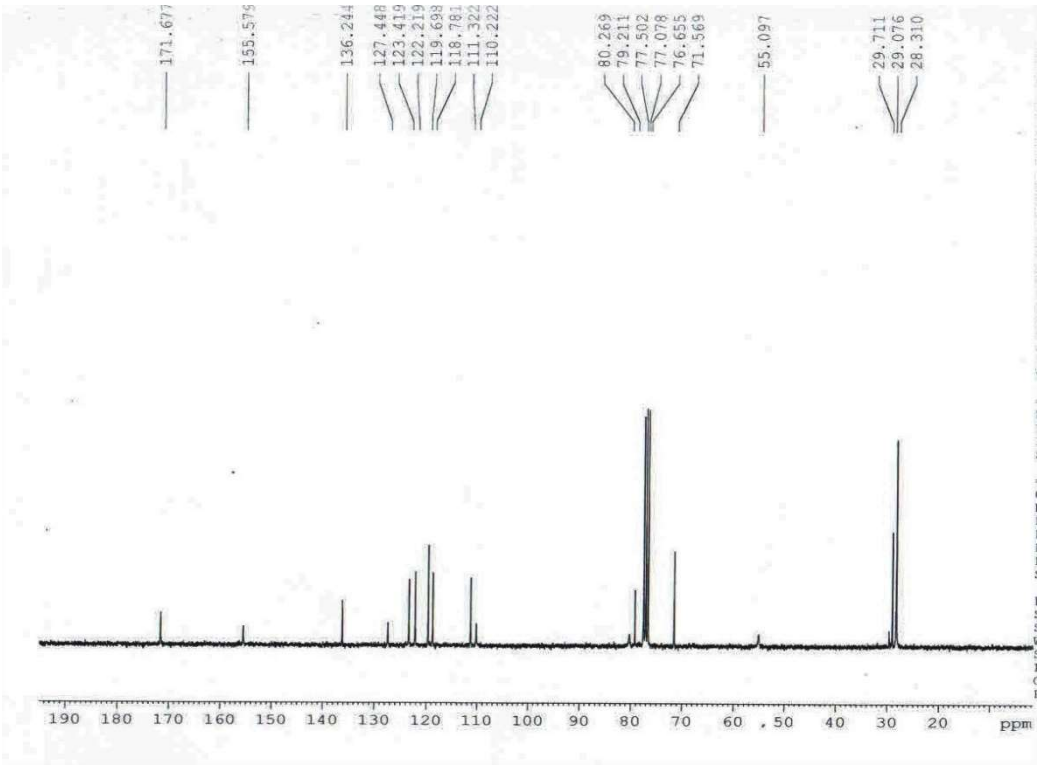


Fig S2: ^{1}H NMR ($CDCl_3$, 300 MHz) of **2a**



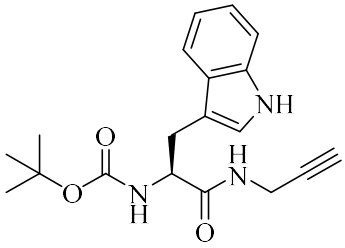
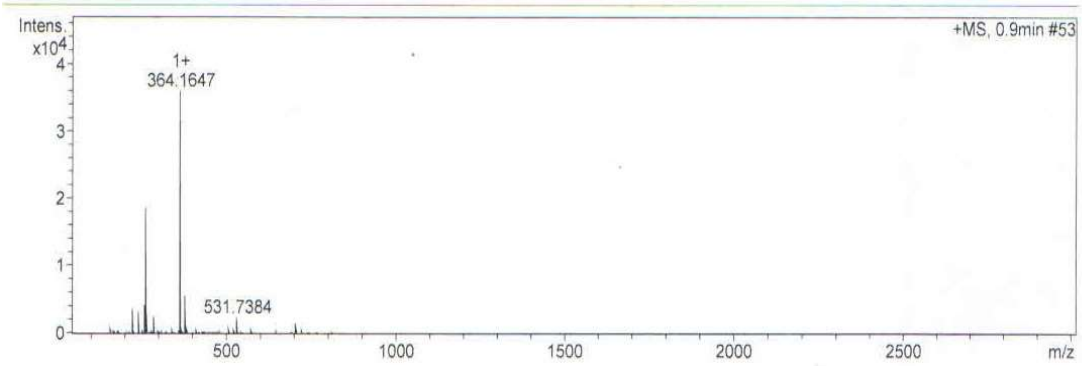


Fig **S3:** ^{13}C NMR ($CDCl_3$, 75 MHz) of **2a**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
364.164672	1	C19H23N3NaO3	364.163162	-4.1	-5.4	9.5	ok	even	10.4	16.2	n.a.	n.a.	n.a.	n.a.

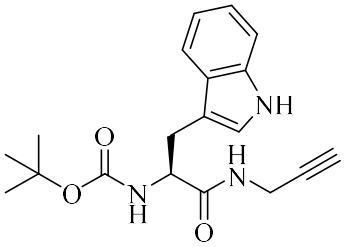


Fig S4: ESI-HRMS of **2a**

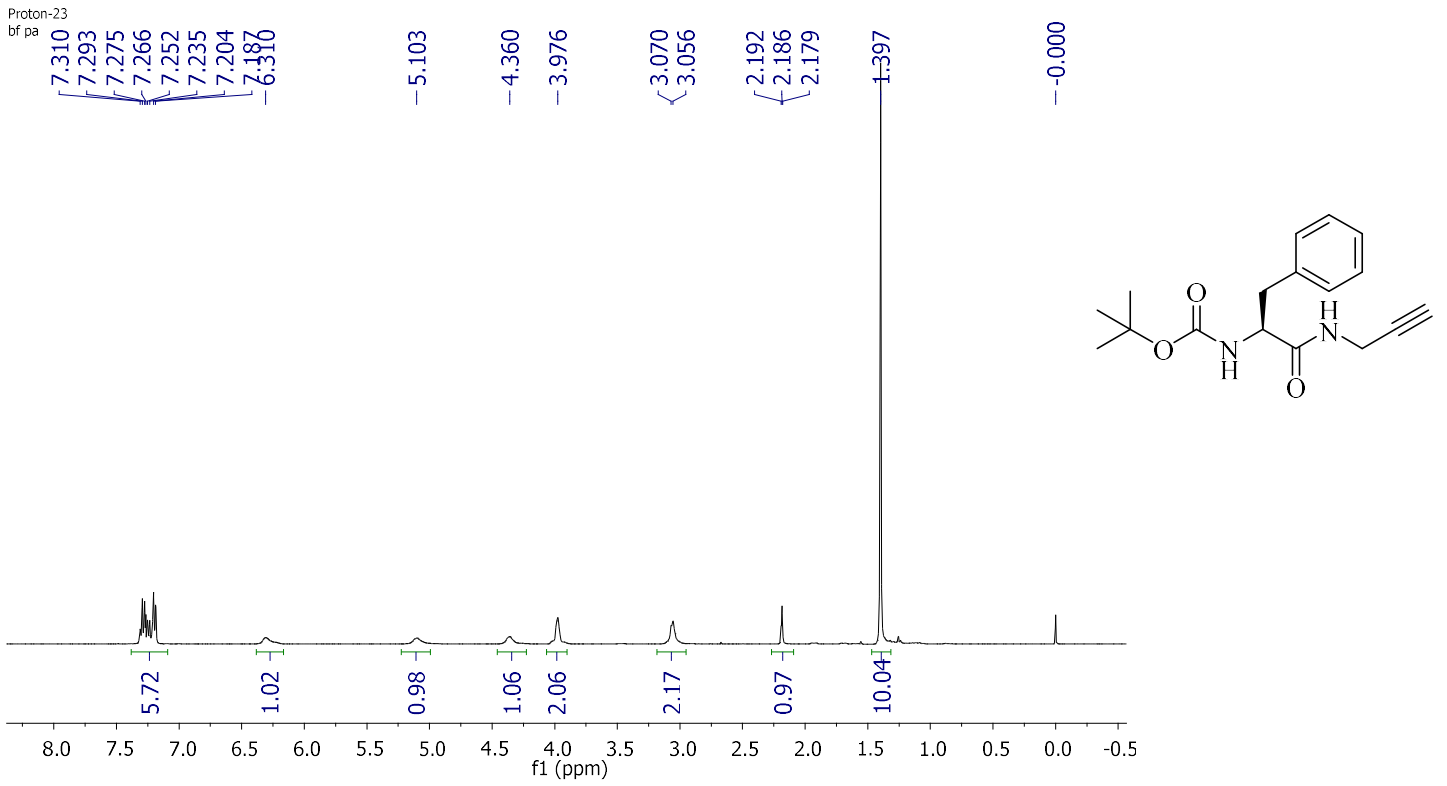


Fig S5: ^{1}H NMR ($CDCl_3$, 400 MHz) of **2b**

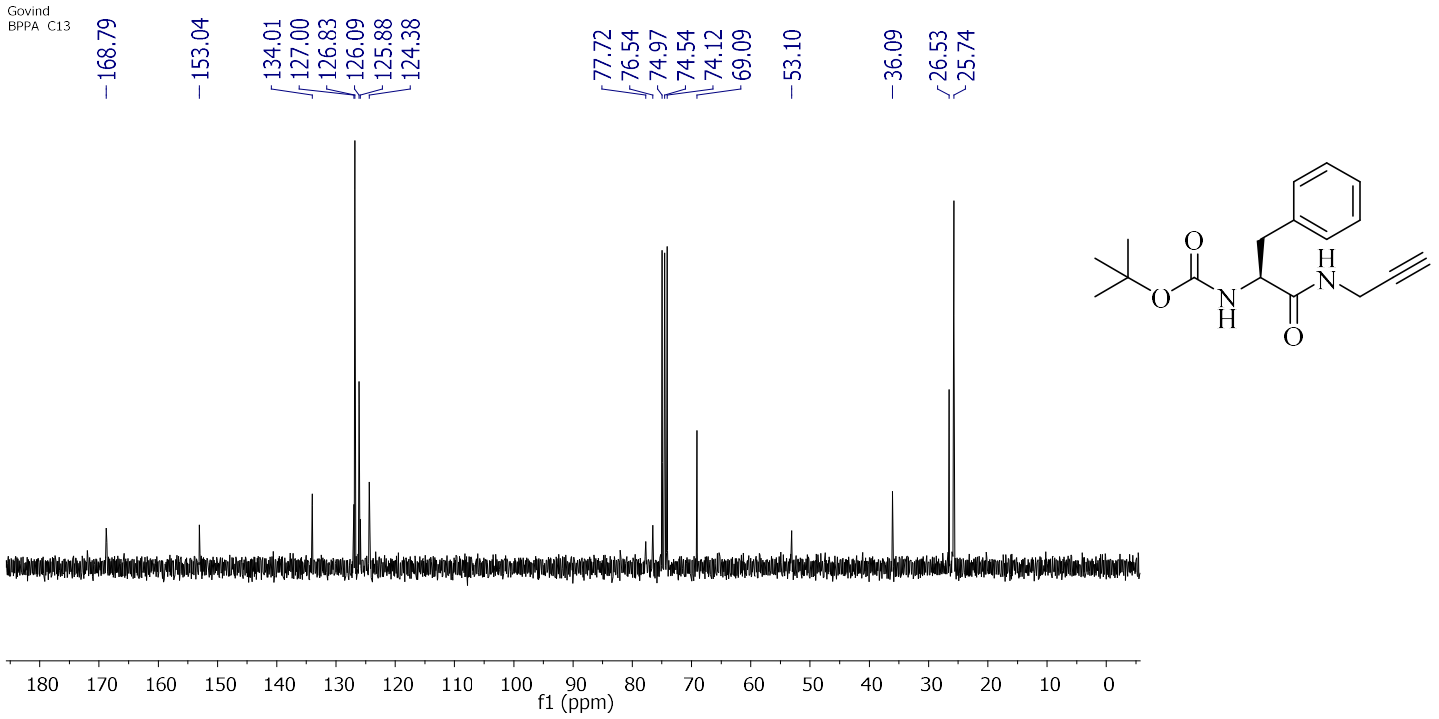


Fig **S6:** ^{13}C NMR ($CDCl_3$, 75 MHz) of **2b**

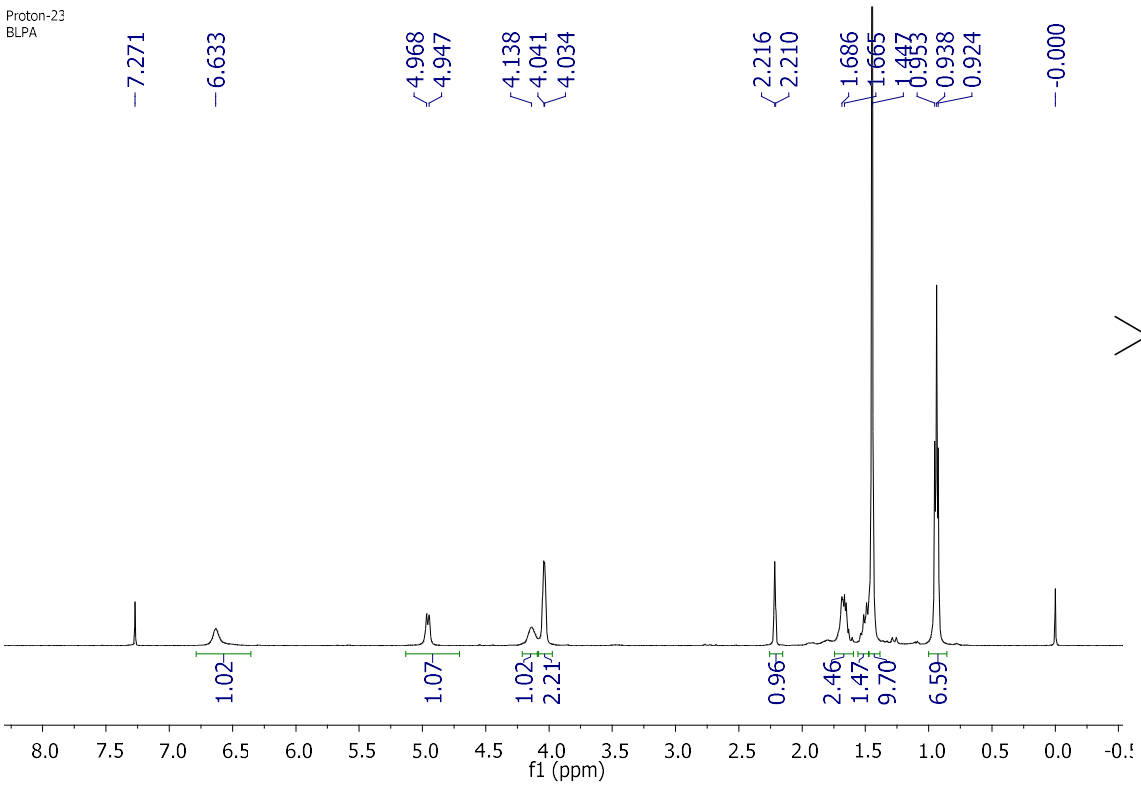


Fig S7: ^{1}H NMR ($CDCl_3$, 400 MHz) of **2c**

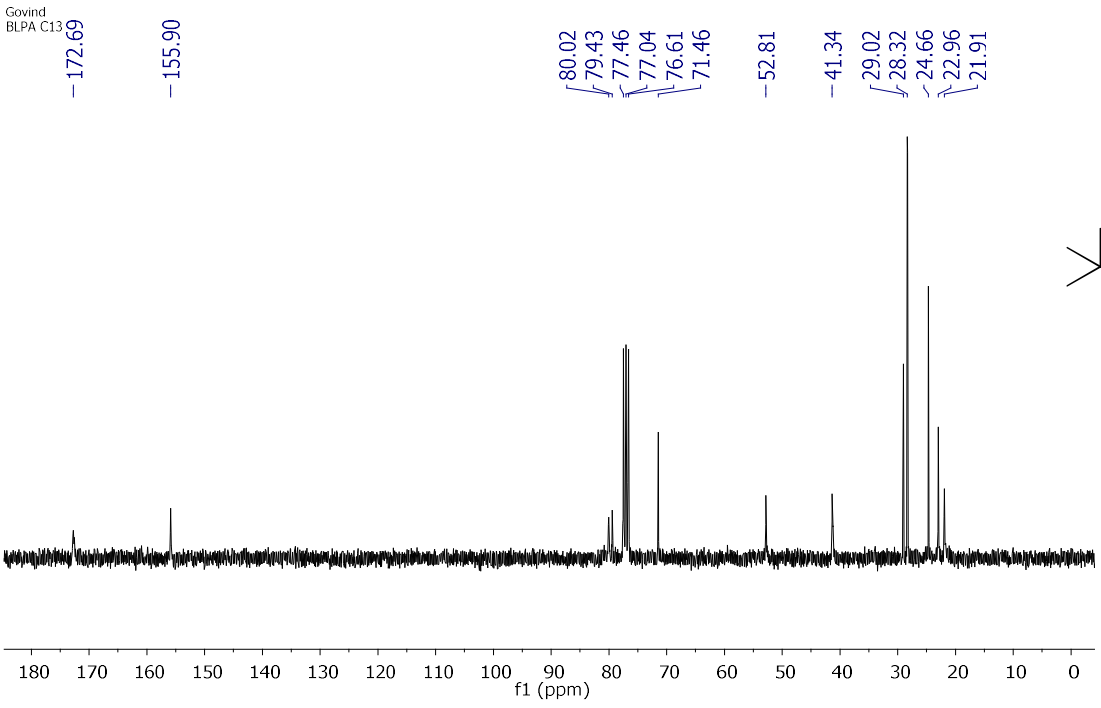
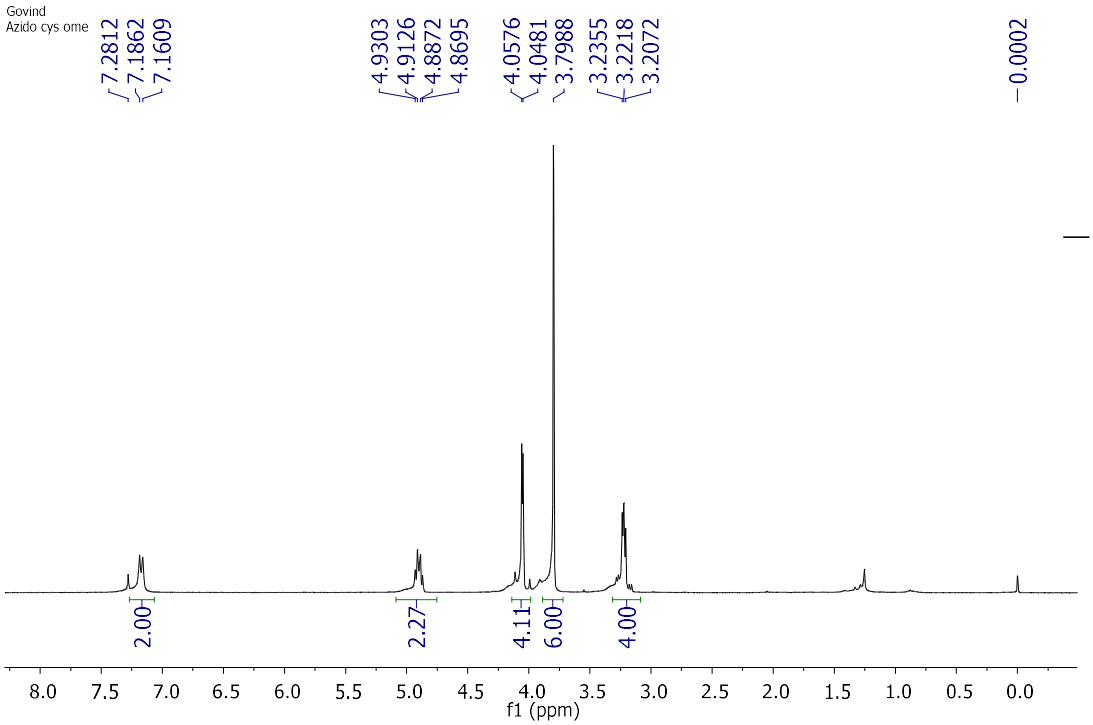


Fig **S8:** ^{13}C NMR ($CDCl_3$, 75 MHz) of **2c**



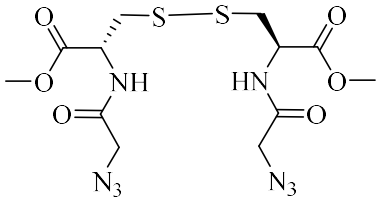
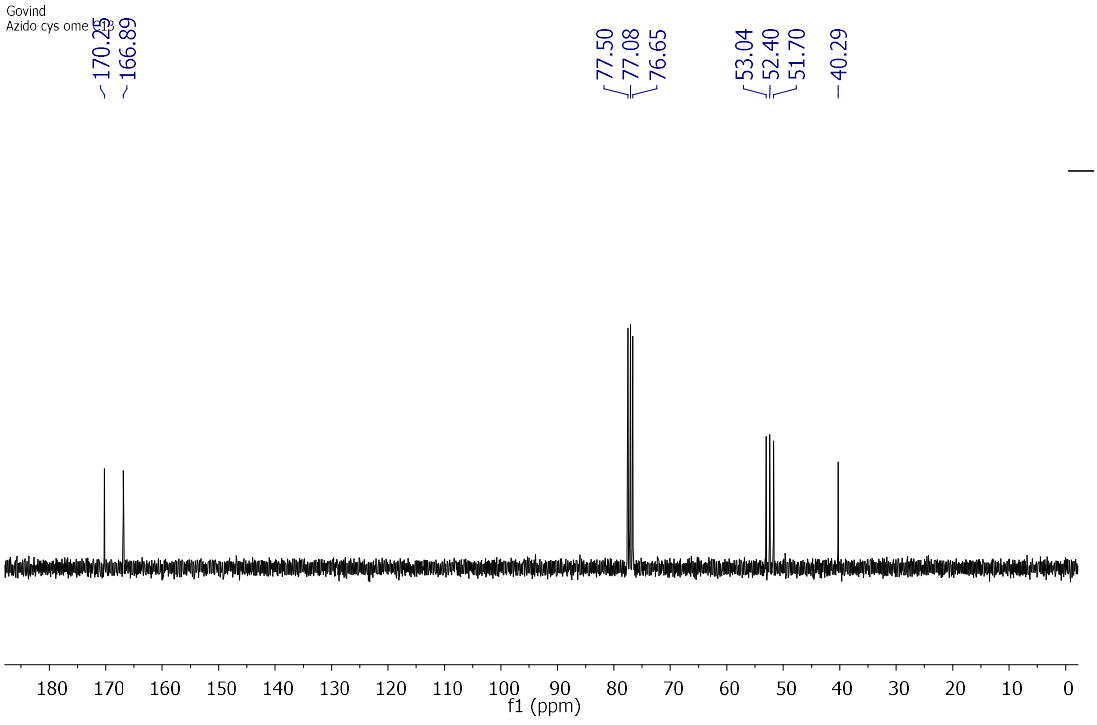


Fig S9: ^{1}H NMR ($CDCl_3$, 300 MHz) of **5**



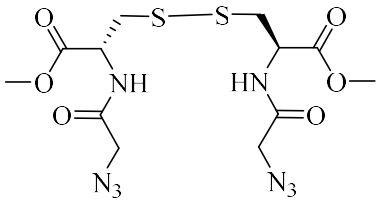


Fig **S10:** ^{13}C NMR ($CDCl_3$, 75 MHz) of **5**

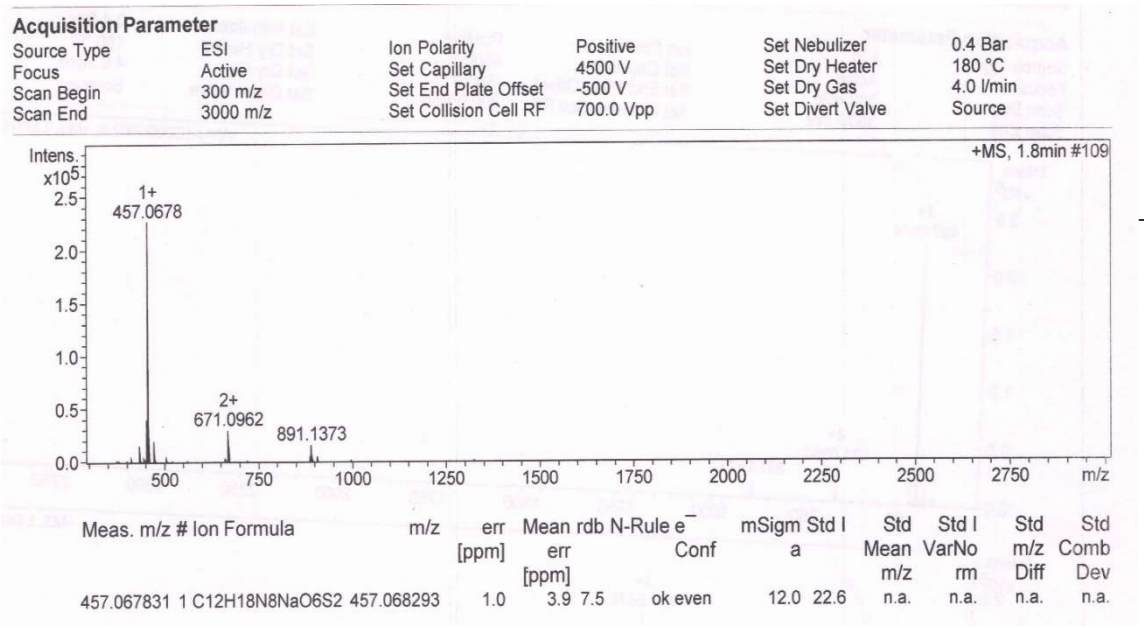


Fig S11: ESI-HRMS of **5**

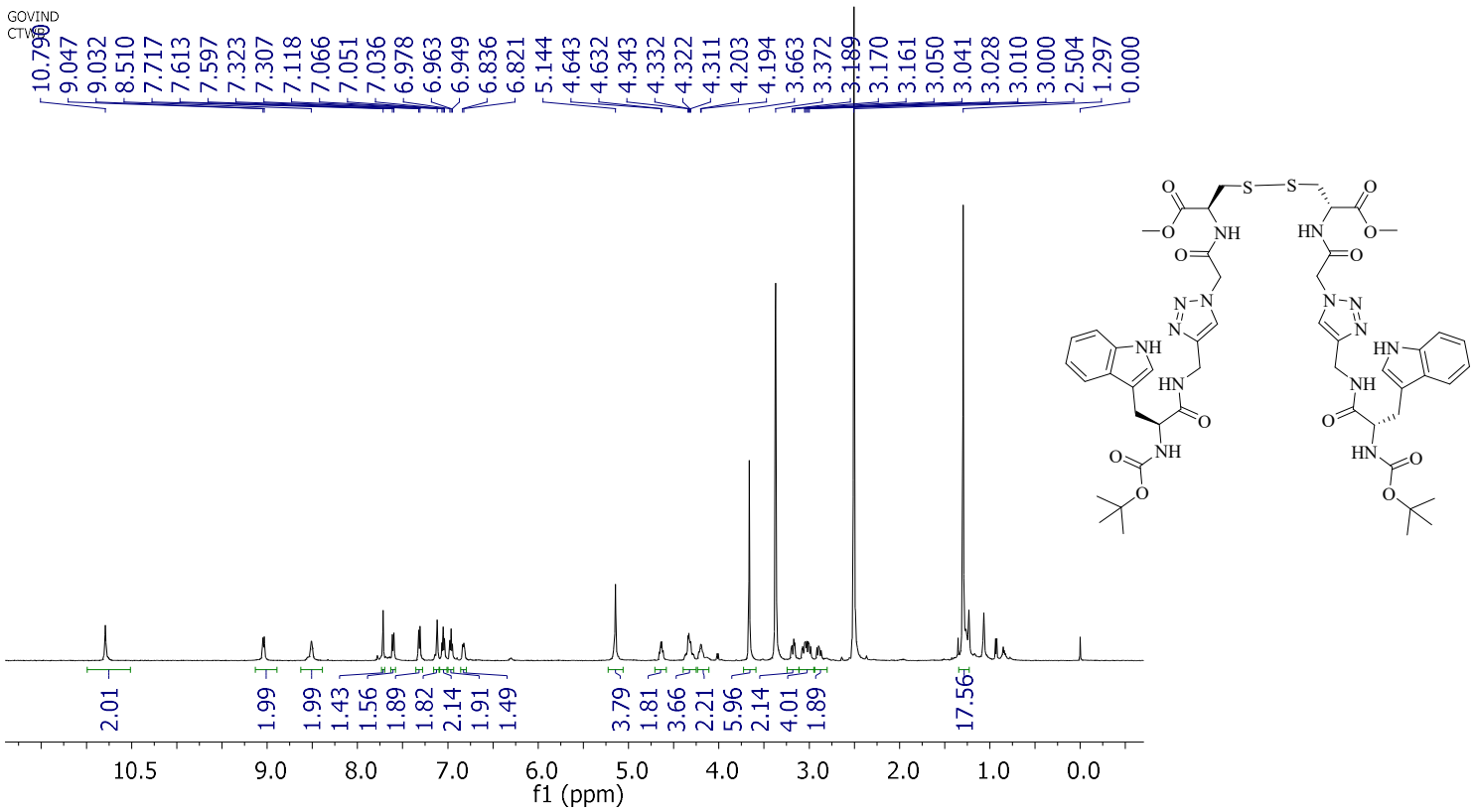


Fig S12: ^{1}H NMR (DMSO-d_6, 500 MHz) of **CW**

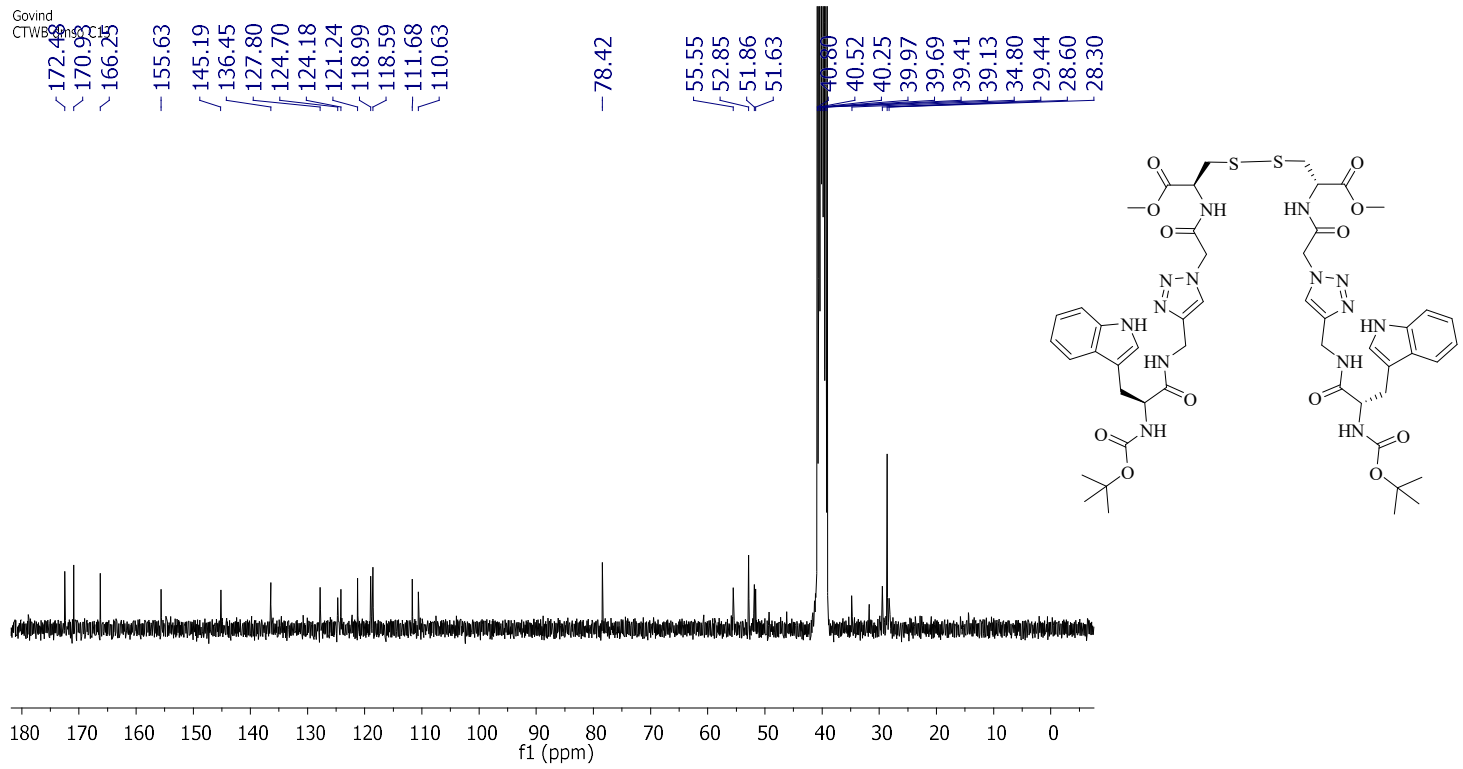
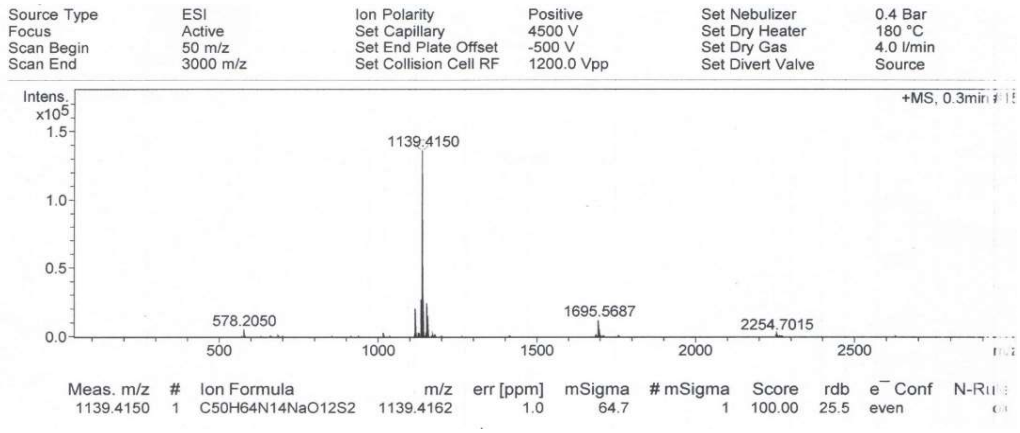


Fig **S13:** ^{13}C NMR (DMSO-d_6, 75 MHz) of **CW**



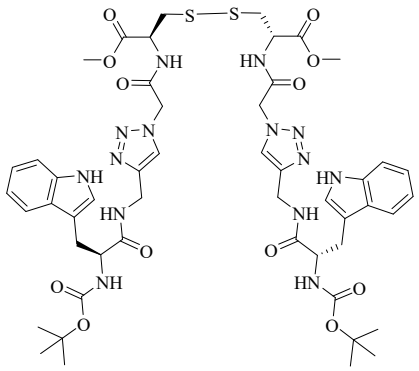


Fig S14: ESI-HRMS of **CW**

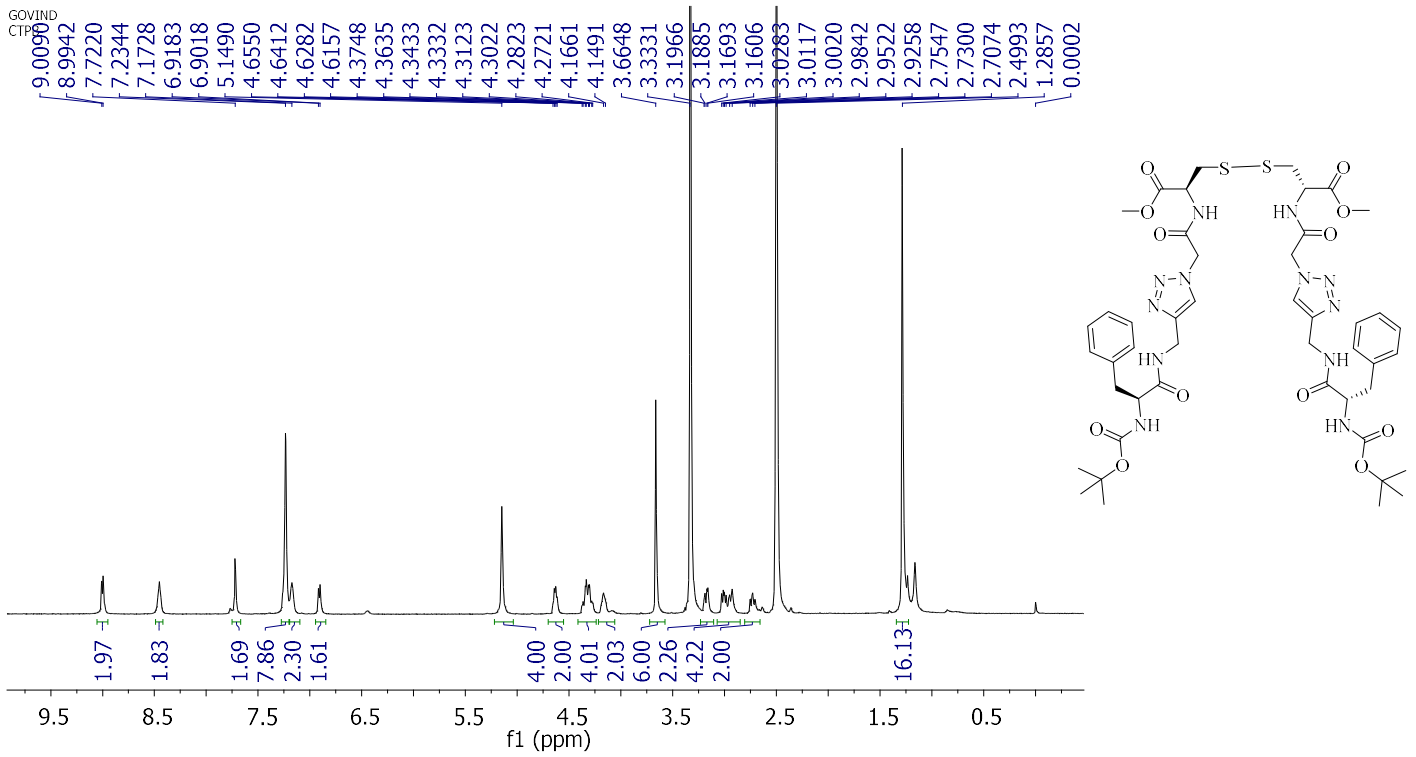


Fig S15: ^{1}H NMR (DMSO-d_6, 500 MHz) of **CF**

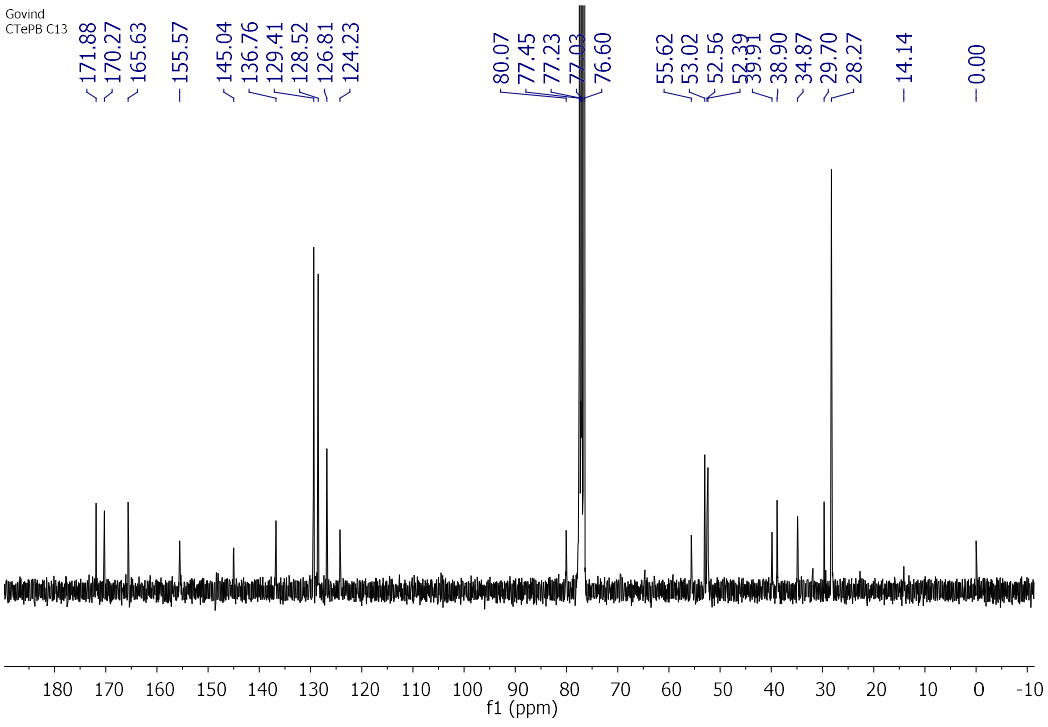
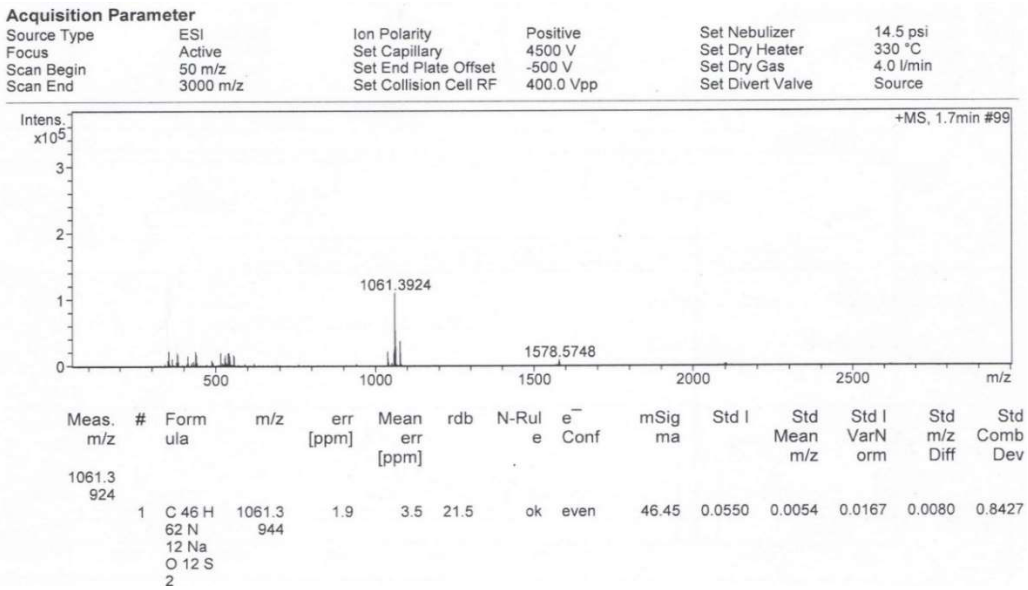


Fig **S16:** ^{13}C NMR ($CDCl_3$, 75 MHz) of **CF**



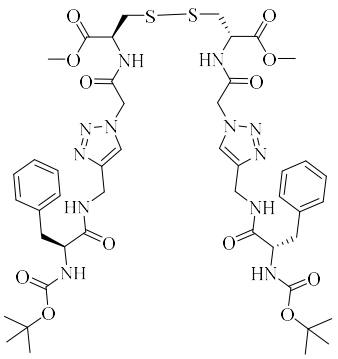
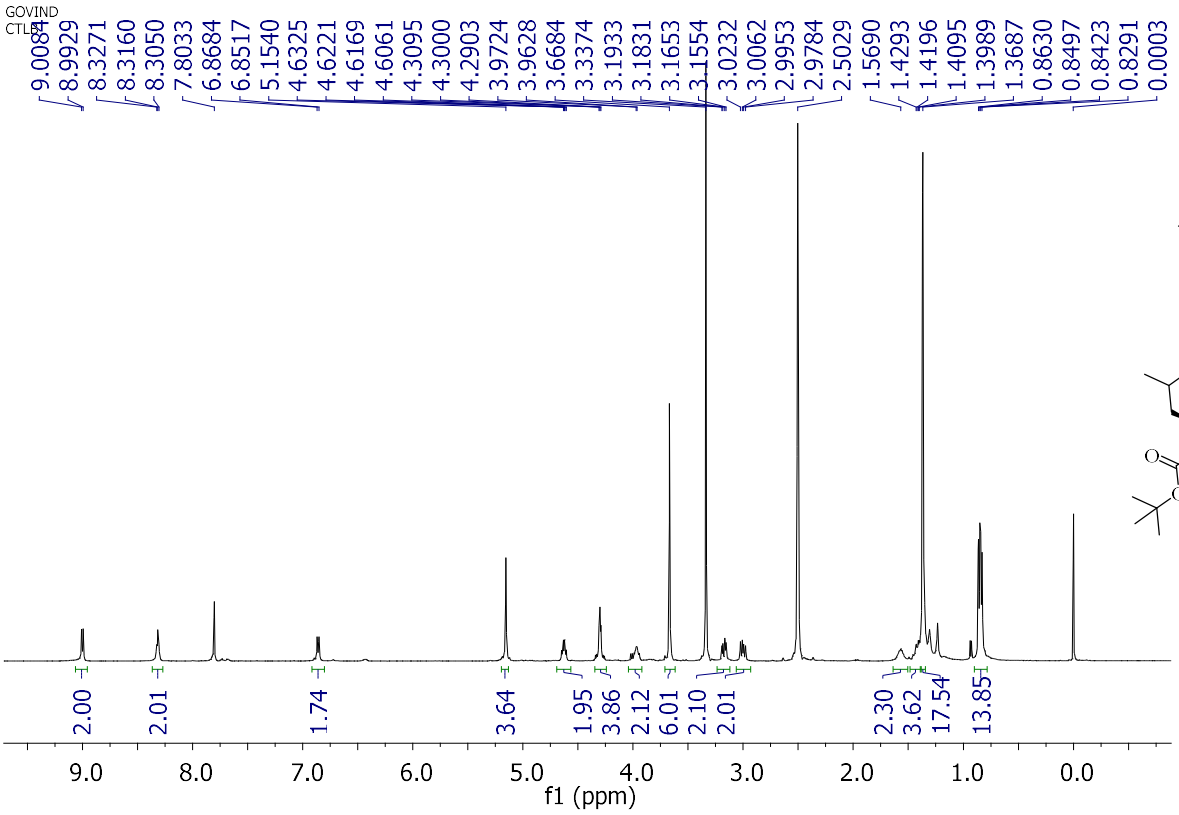


Fig S17: ESI-HRMS of **CF**



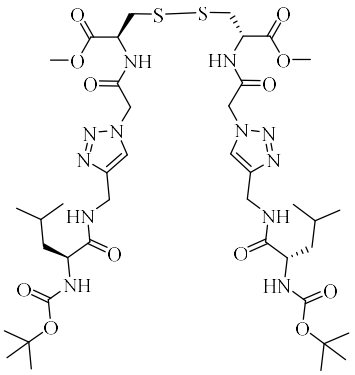


Fig S18: ^{1}H NMR (DMSO-d_6, 500 MHz) of **CL**

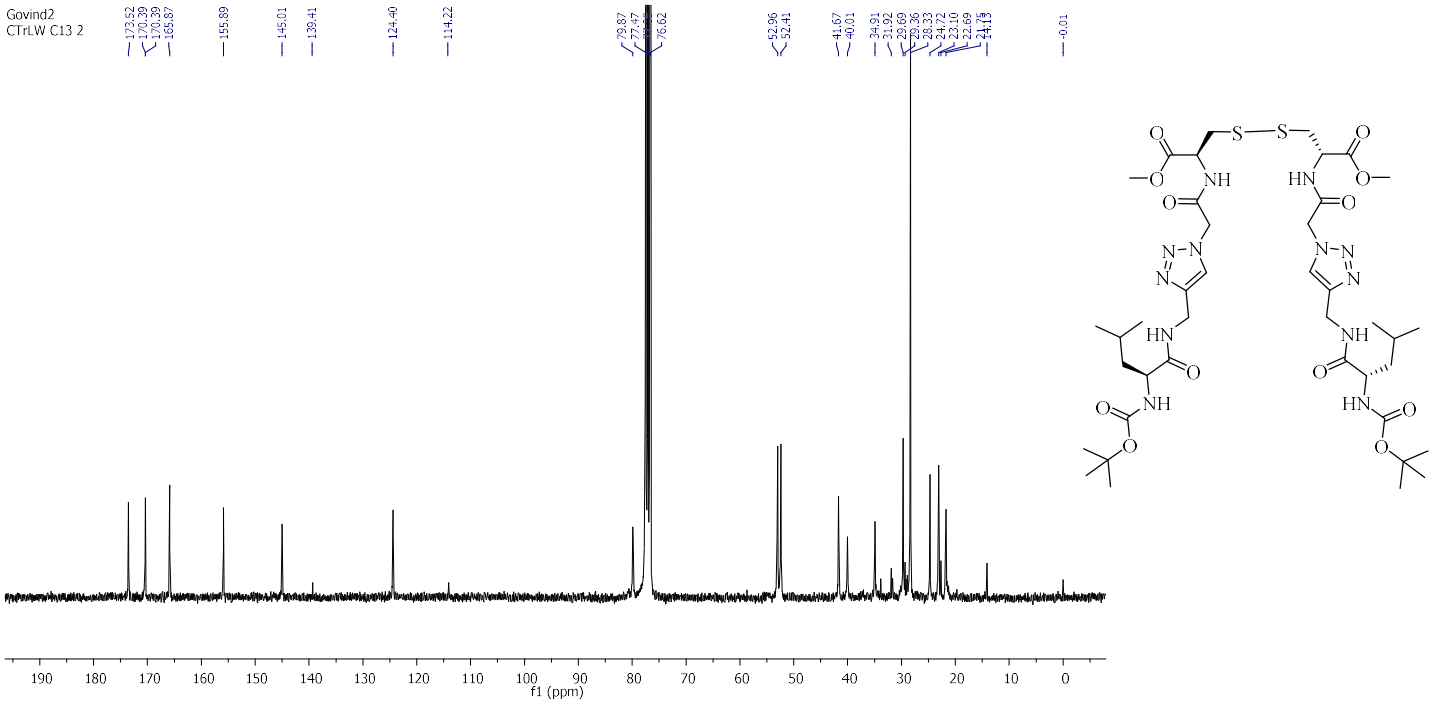


Fig S19: ^{13}C NMR ($CDCl_3$, 75 MHz) of **CL**

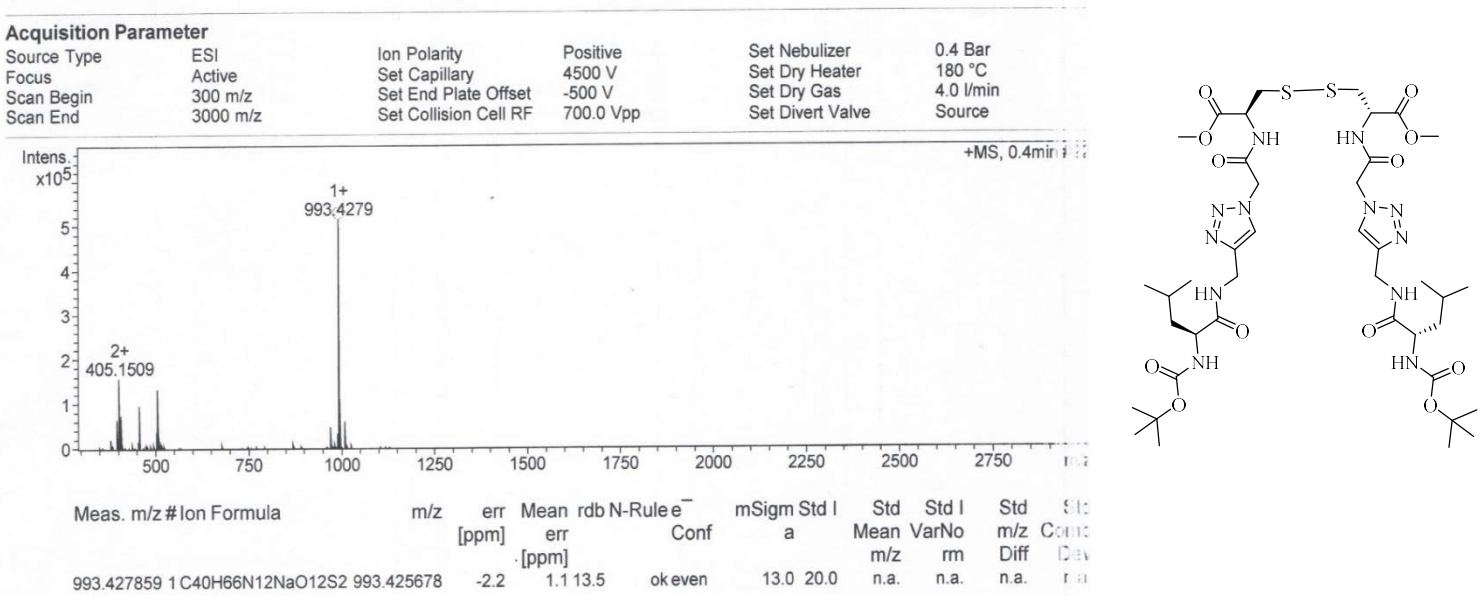


Fig S20: ESI-HRMS of **CL**

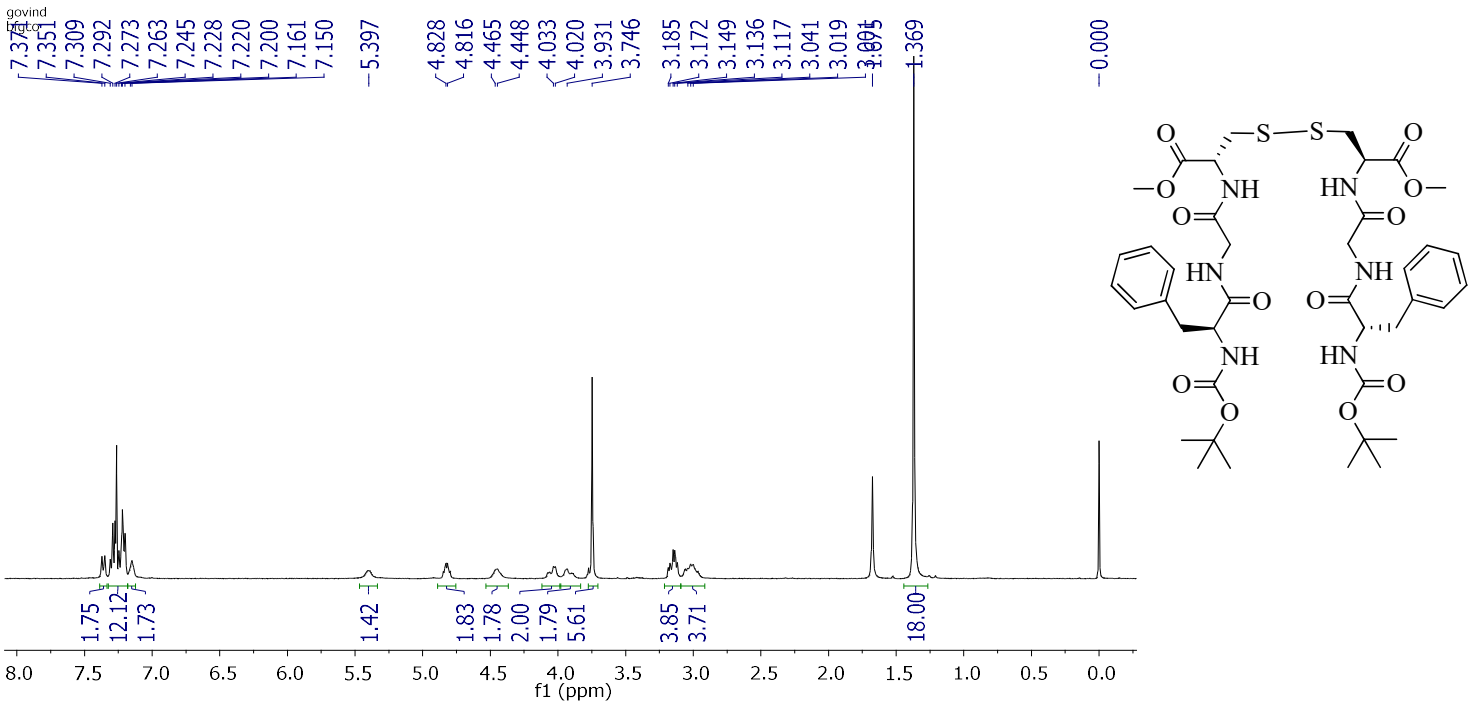


Fig S21: ^{1}H NMR ($CDCl_3$, 500 MHz) of **CGF**

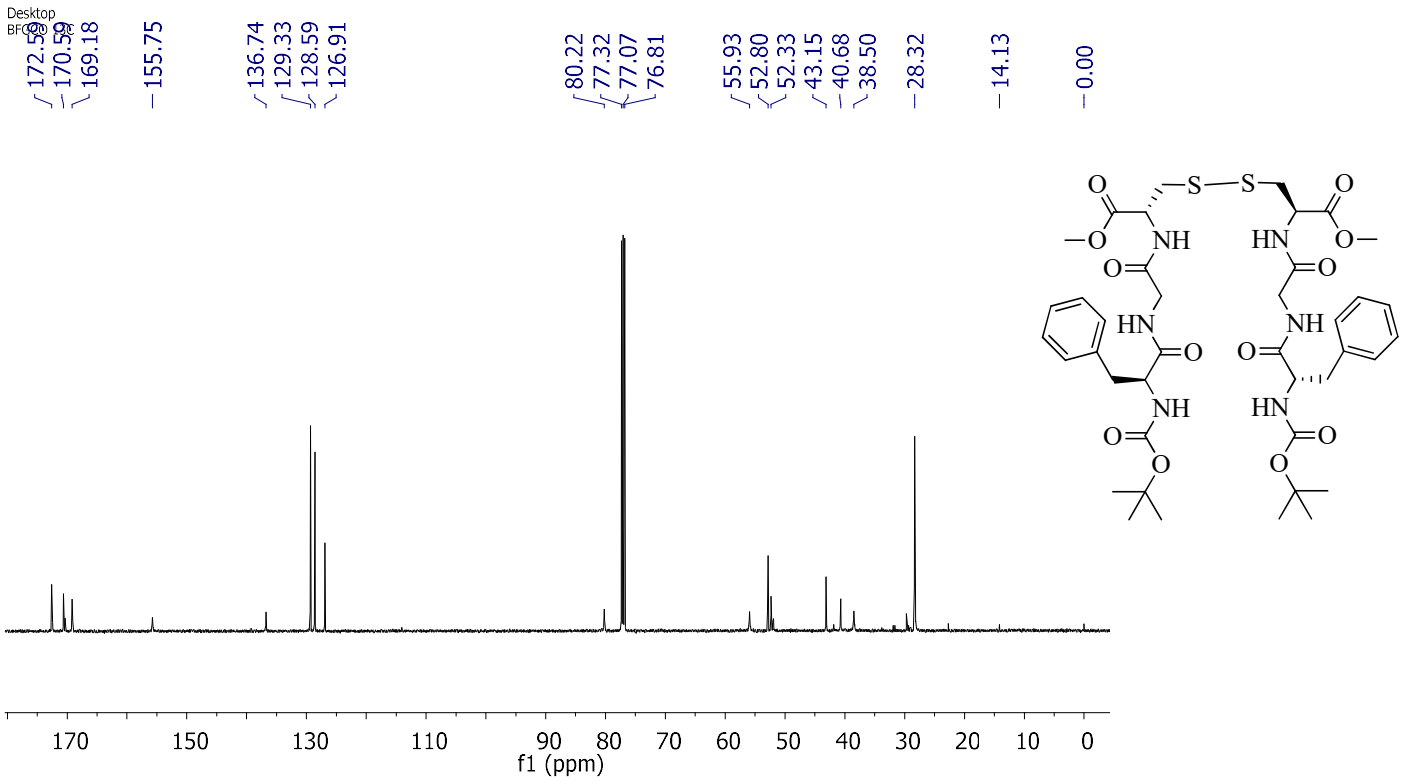
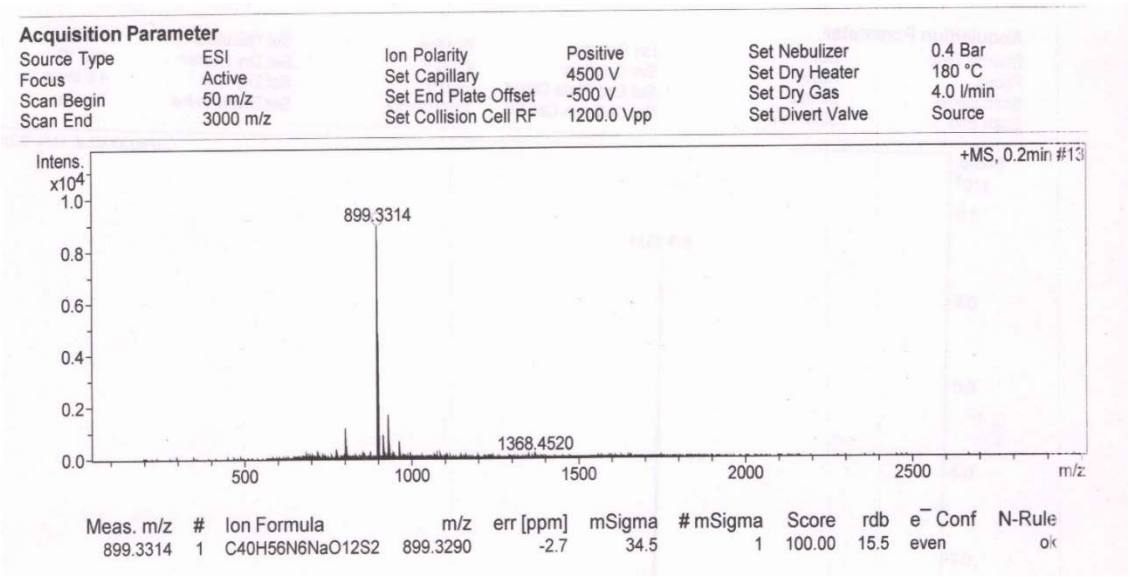


Fig S22: ^{13}C NMR ($CDCl_3$, 125 MHz) of **CGF**



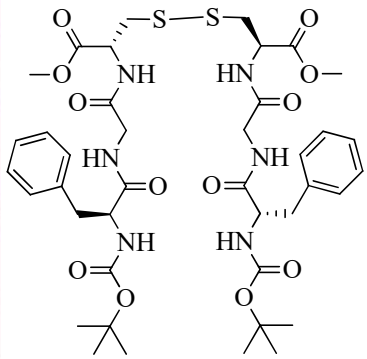


Fig S23: ESI-HRMS of **CGF**

1.4 Cation Binding Studies

1.4.1 Cation binding studies using UV-vis spectroscopy

Stock solutions of compounds **CW**, **CF** and **CL** with a concentration of 10^{-4} M were made in acetonitrile/chloroform (95/5%). Stock solutions of cation salts (10^{-3} M) were made in acetonitrile. The compounds were titrated against the cation solutions and the UV-vis and fluorescence spectra were recorded. The titration was continued till a saturation point was observed.

1.4.2 Job plot calculation

Stoichiometry of binding was calculated by Job plot from UV-vis. absorbance data:

A series of solutions containing compounds (**CW**, **CF**, **CL**) ($1x10^{-5}$ M) and cations ($1x10^{-5}$ M) were prepared in ACN/$CHCl_3$ (95/5%). The mole fraction of the receptors were varied from 0.1 to 1 and the absorbance of each solution is measured at a suitable wavelength and a graph is made showing the corrected absorbance versus mole fraction of X or P. Maximum absorbance/fluorescence is reached at the composition corresponding to the stoichiometry of the predominant complex.

1.4.3 Calculation of binding constant using Bindfit software

The binding constants were calculated by a non-linear fitting using Bindfit (http://www.supramolecular.org). UV fitting for 1:1 model was done using the Nelder-Mead method.

1.4.4 Limit of detection (LOD) calculation

The plot of concentration of cations against A/A_0 gave a straight line with a linear equation $A/A_0 = mx + C$. Then limit of detection was calculated using equation:

$$LOD = 3\sigma/S$$

Where σ is the standard deviation of blank measurements and was measured for 10 blank measurements, S is the slope of the straight line.

1.4.5 UV-visible spectroscopic studies

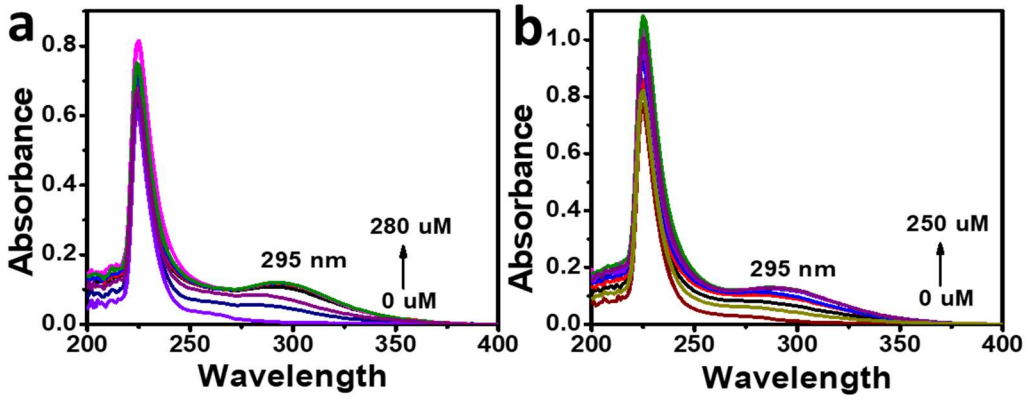


Figure S24. UV-visible studies of a) **CF** and b) **CL** [1X10^{-4} M] in ACN/$CHCl_3$ (95/5) alone and with addition of $Cu(ClO_4)_2$

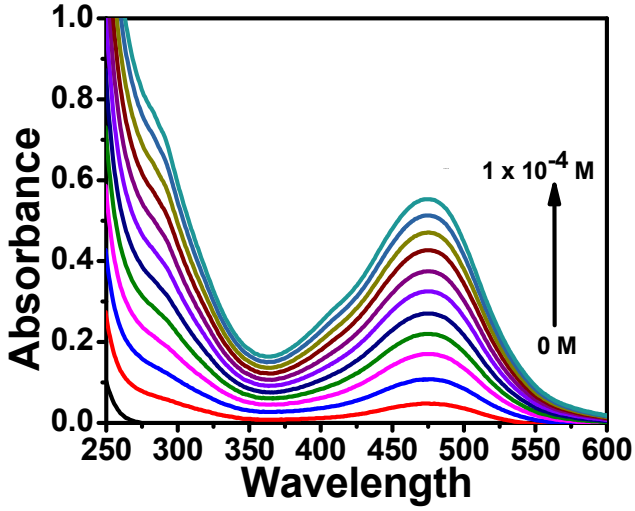


Figure S25. UV-visible studies of $Cu(ClO_4)_2$ [1X10^{-3} M] in ACN/$CHCl_3$ (95/5) alone and with addition of different amounts **CW** [0-1X10^{-4} M].

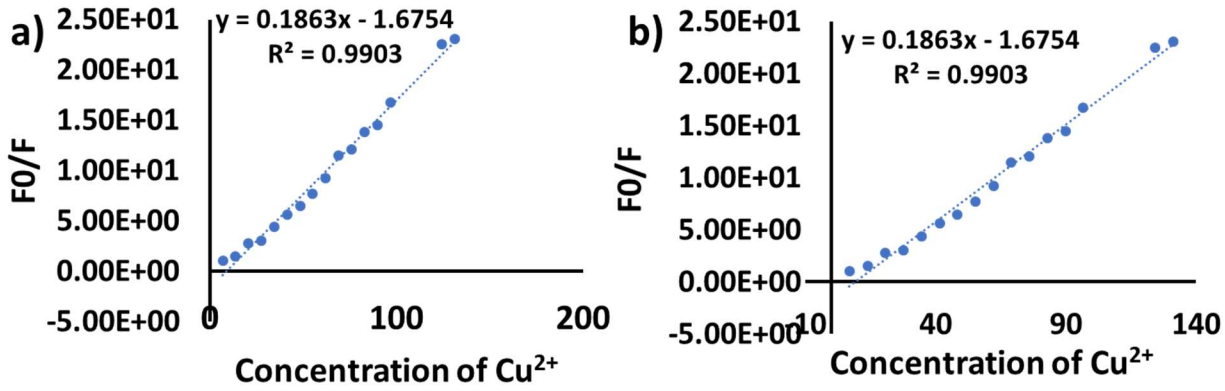


Figure S26. a) Stern-volmer quenching constant and b) Limit of detection of **CW** [1X10^{-4} M] in ACN/$CHCl_3$ (95/5) upon addition of $Cu(ClO_4)_2$.

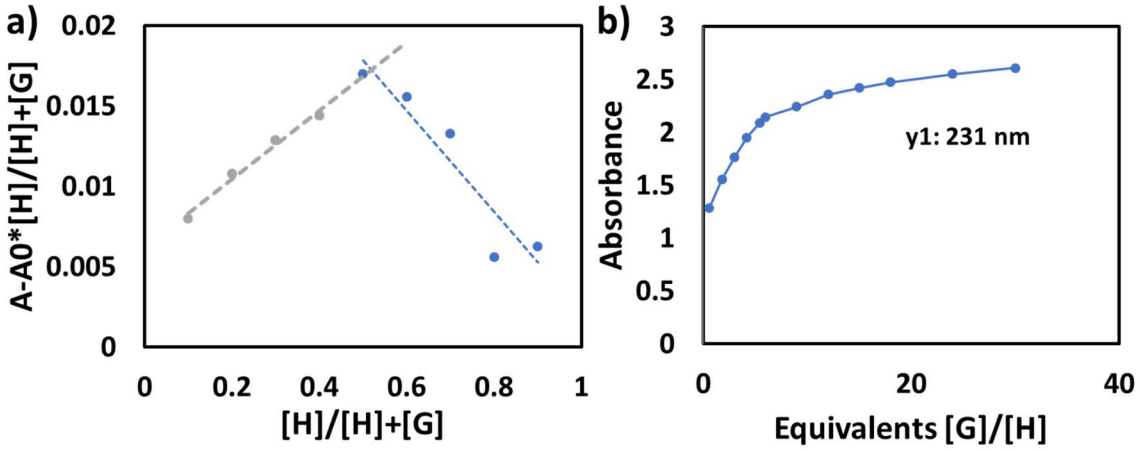


Figure S27. a) Job Plot; b) bindfit isotherm of **CW** [1X10^{-4} M] in ACN/$CHCl_3$ (95/5) on addition of $Cu(ClO_4)_2$

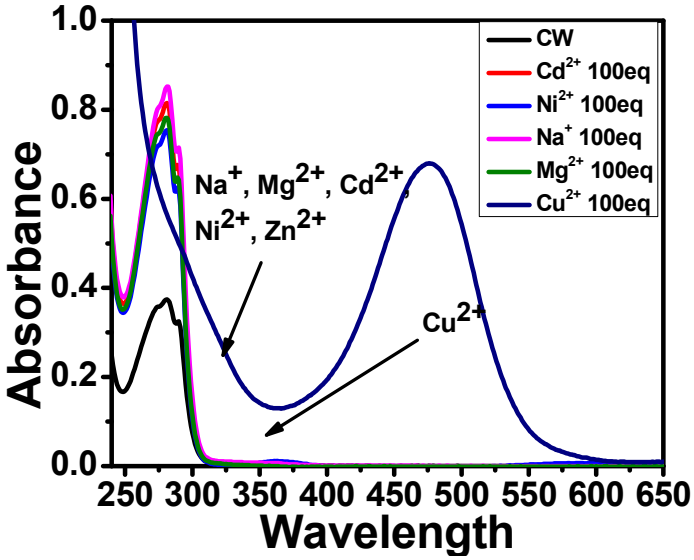


Figure S28: UV-visible studies showing selectivity of **CW** towards various metal ions (100equiv.).

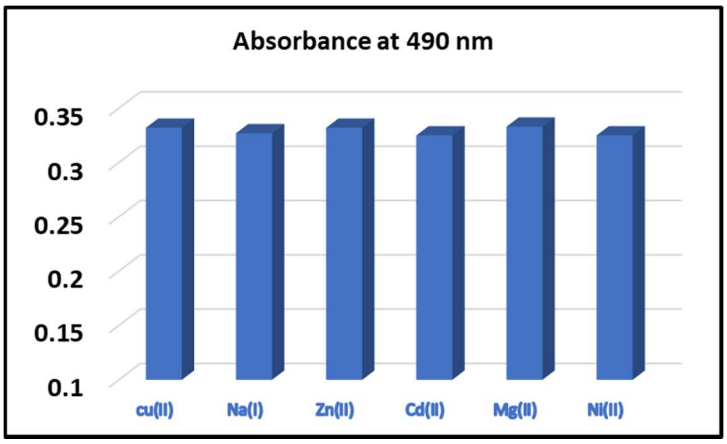


Figure S29: UV-vis studies on the interference of other metal ions towards the binding of Cu^{2+}:**CW**.

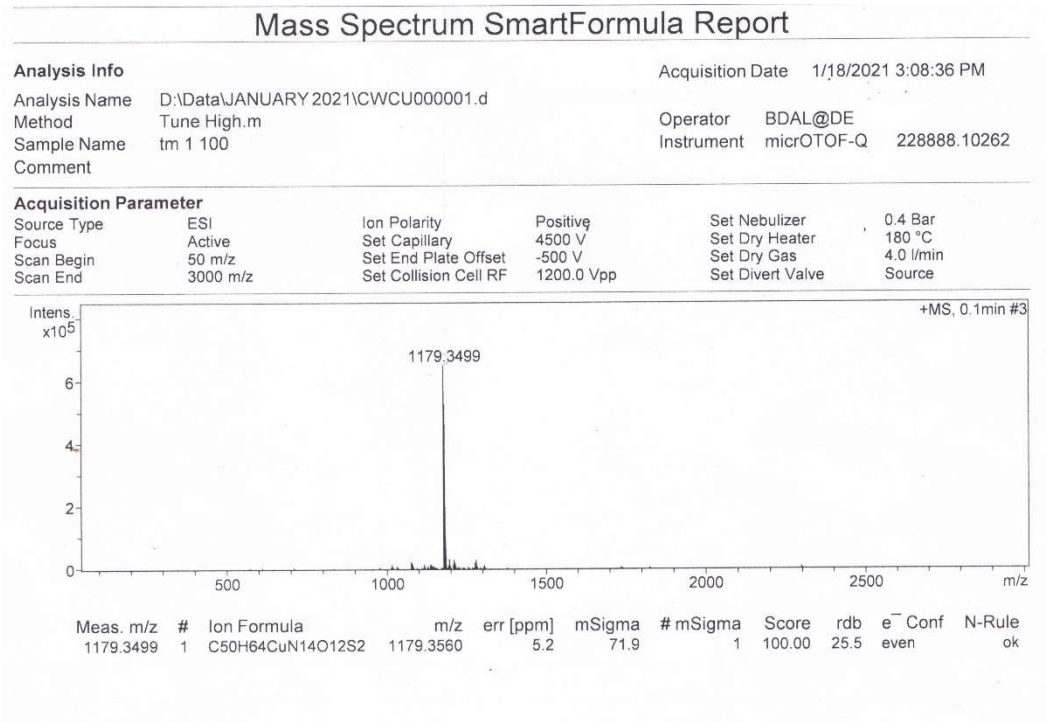


Fig S30: ESI-HRMS of **CW**:Cu^{2+} complex in presence of various metal ions

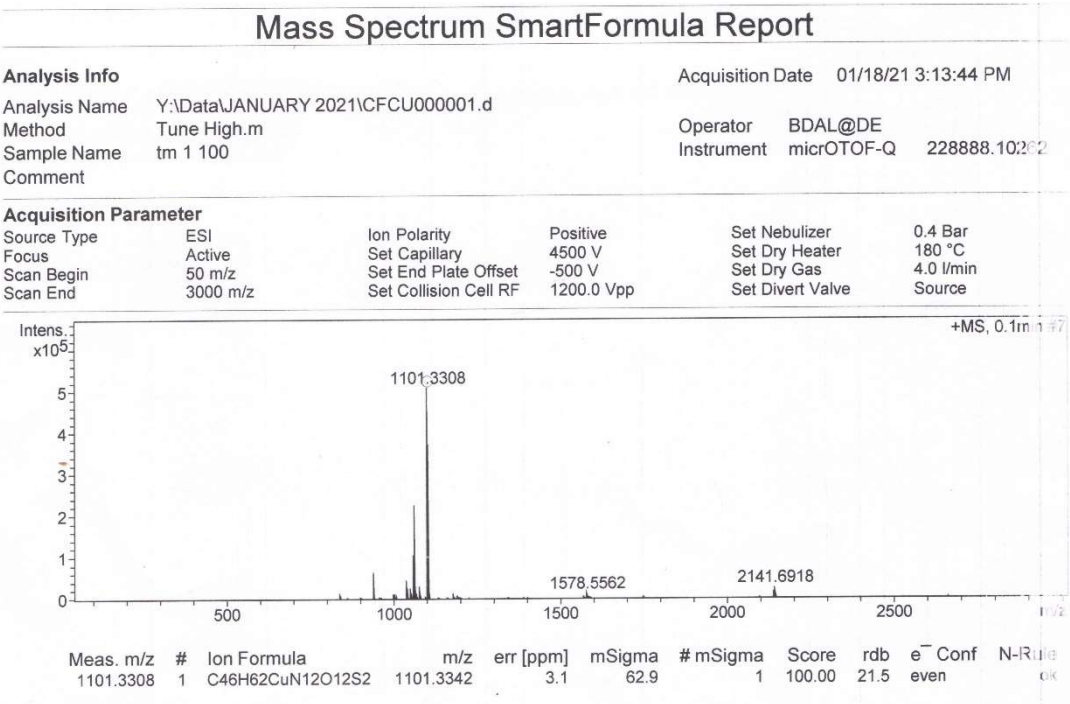


Fig S31: ESI-HRMS of **CF:**Cu^{2+} complex in presence of various metal ions

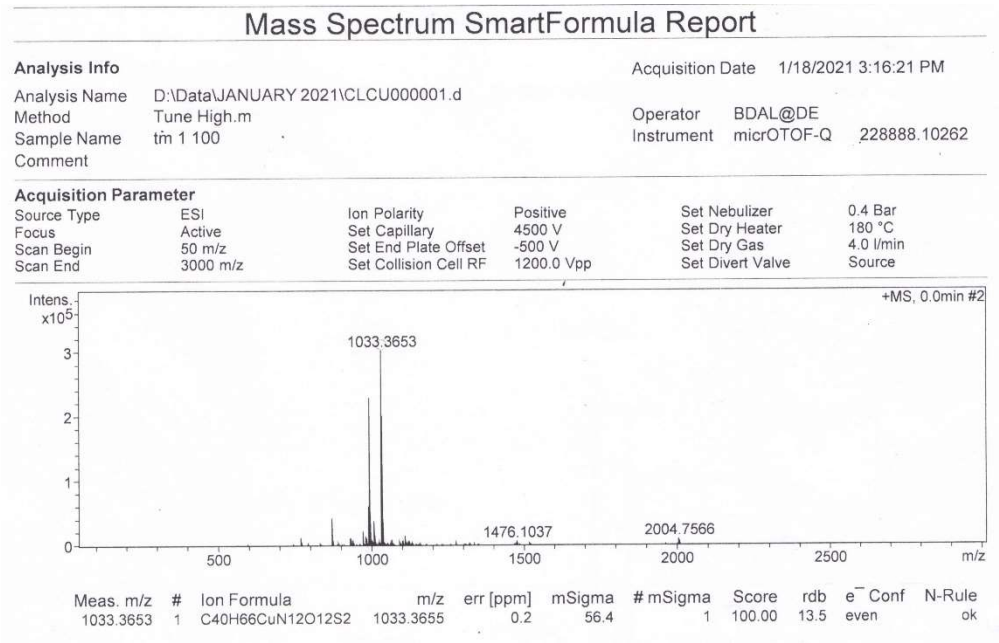


Fig S32: ESI-HRMS of **CL:**Cu^{2+} complex in presence of various metal ions

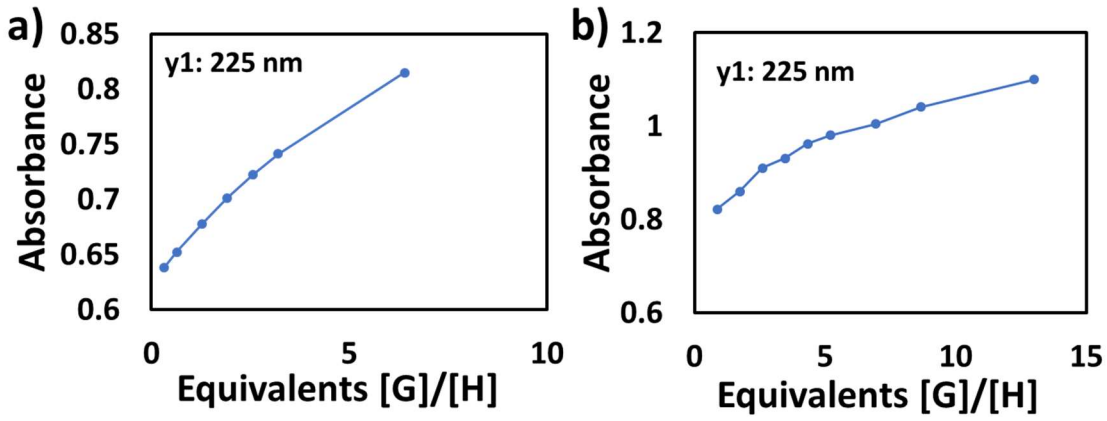


Figure S33. Bindfit isotherm of a) **CF** and b) **CL** in ACN/$CHCl_3$ (95/5) on addition of $Cu(ClO_4)_2$

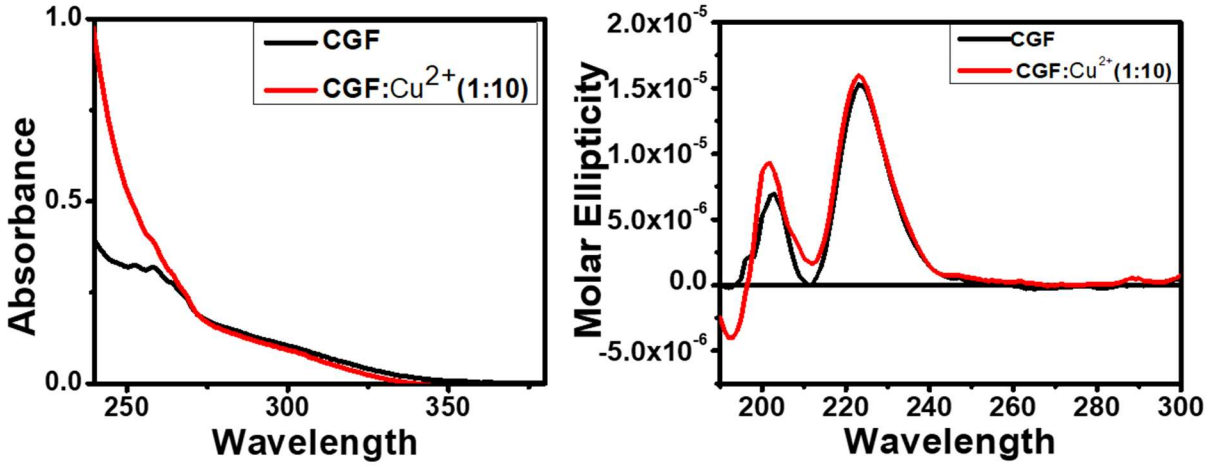


Figure S34. a) UV-visible and b) CD spectrum of **CGF** ($1X10^{-4}$ M) alone and with addition of $Cu(ClO_4)_2$ in acetonitrile

1.5 NMR titration Studies

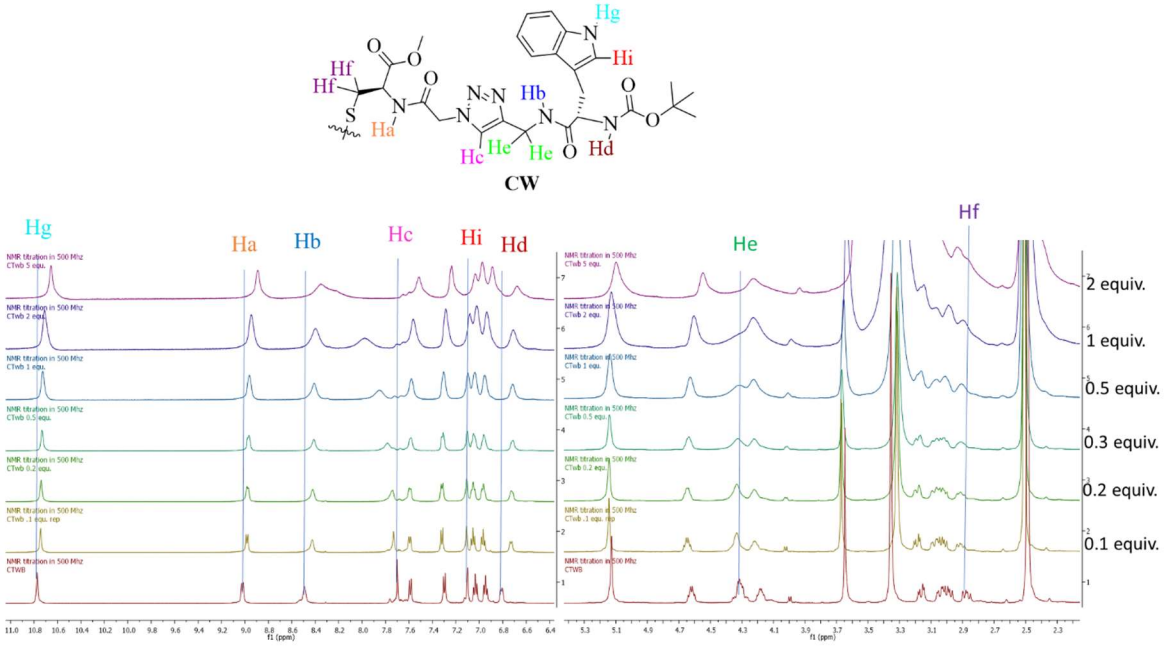
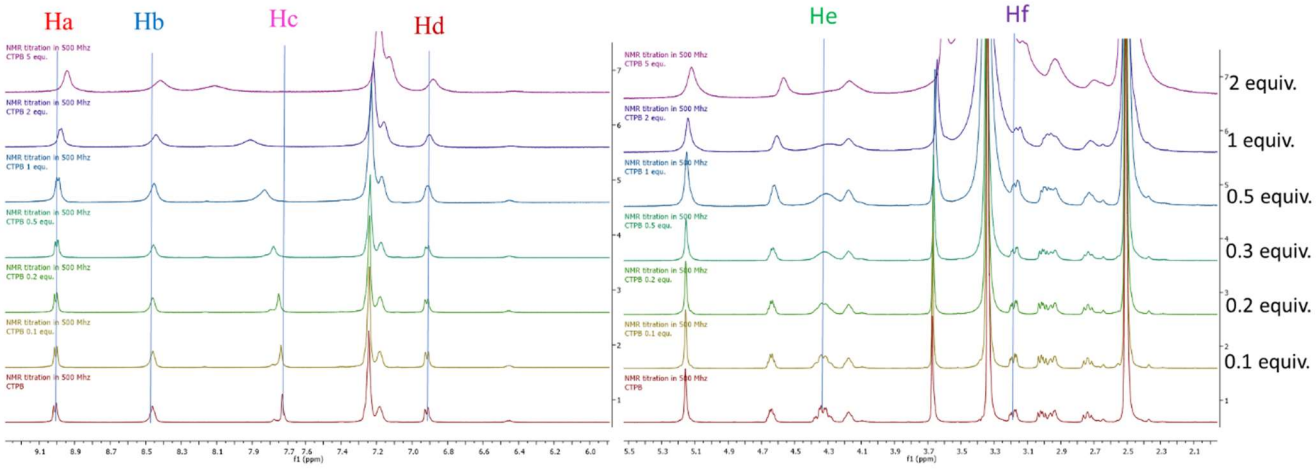
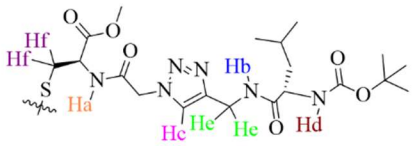


Figure S35. Partial ^{1}H NMR (DMSO-d_6, 500 MHz) spectra of **CW** in the presence of different amounts of $Cu(ClO_4)_2$

3b





3a

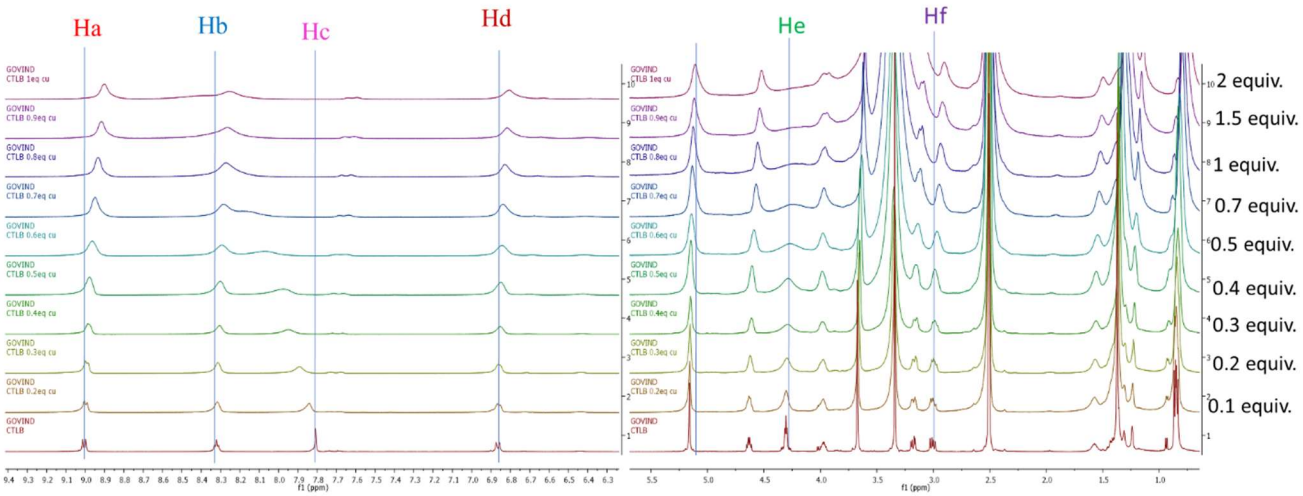


Figure S36. Partial ^{1}H NMR (DMSO-d_6, 500 MHz) spectra of **CF** and **CL** in the presence of different amounts of $Cu(ClO_4)_2$

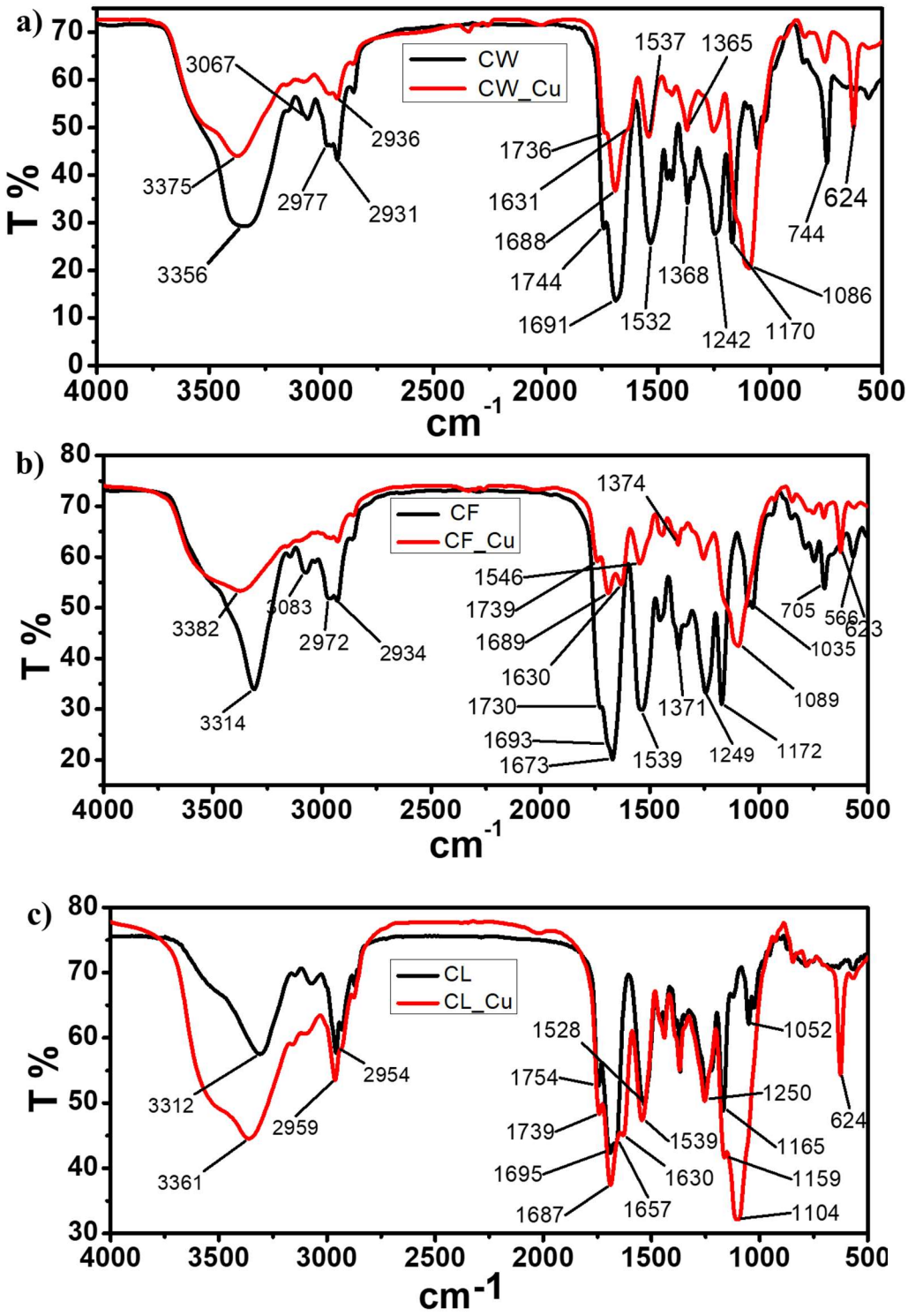


Figure S37. FT-IR spectra of a) **CW**, b) **CF** and c) **CL** alone and in the presence of $Cu(ClO_4)_2$

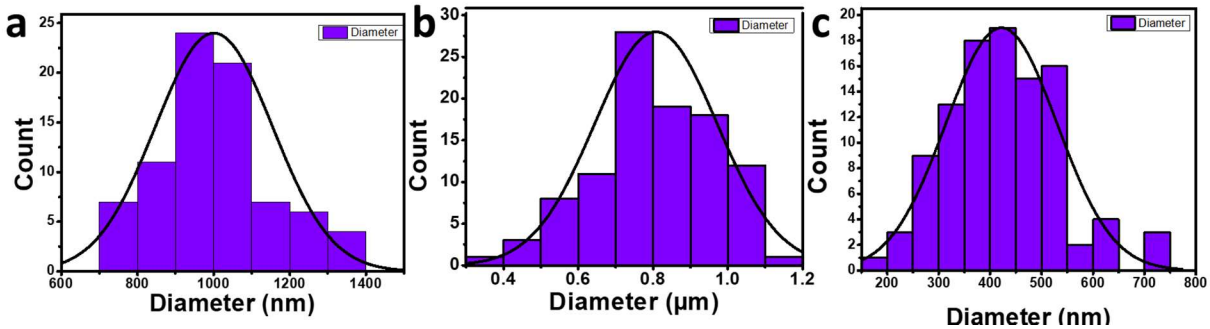


Figure S38. Histogram based on SEM images. Diameter of a) **CW**, b) **CF** and c) **CL**

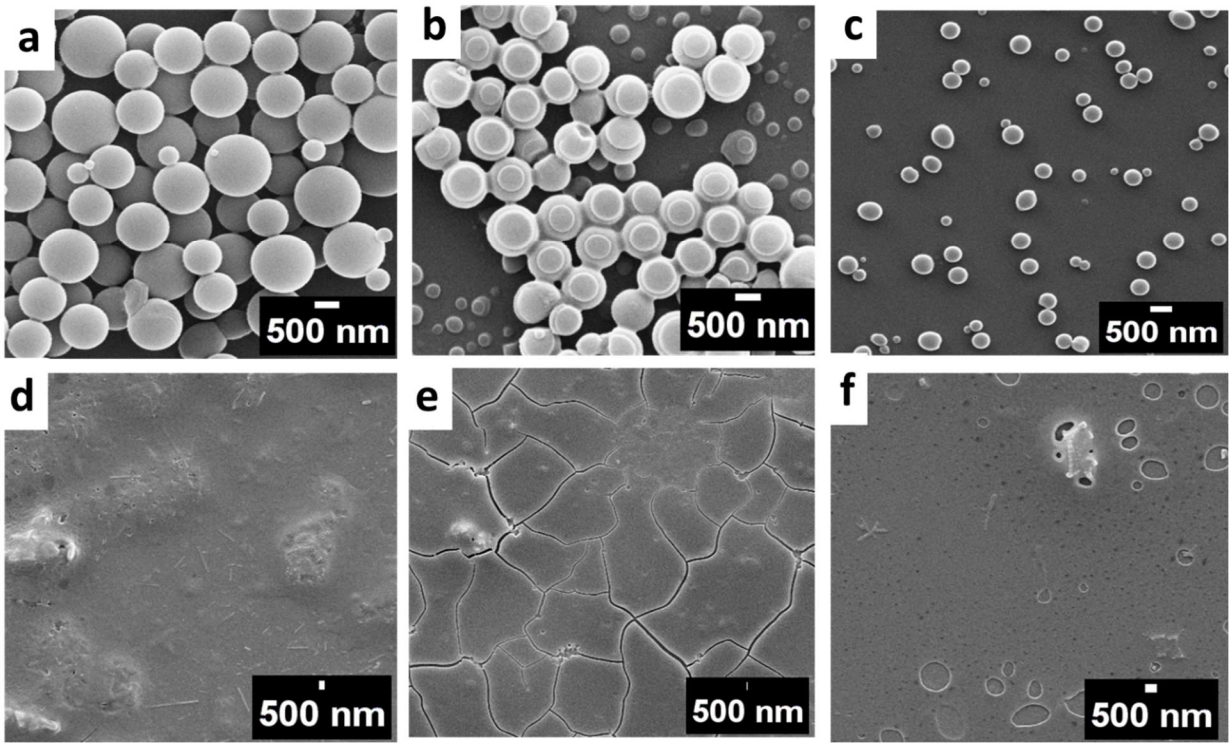


Figure S39: SEM images of (a) **CW** (b) **CF** (c) **CL** and (d) **CW** + Cu^{2+} (e) **CF** + Cu^{2+} (f) **CL** + Cu^{2+}

Table1. The binding constants of **CW**, **CF** and **CL** determined by UV-titrations and their percentage error.

S.N.	Compound	Binding Constant (M^{-1})	Error Factor (%)
1.	**CW**	$6.1x10^3$	±5.82646281
2.	**CF**	$4.2\ x10^3$	±6.61191872
3.	**CL**	$4.5x10^3$	±6.28645439

1.5 References:

1. S. Dhawan, A. Moudgil, H. Singh, S. Gahlawat, J. Babu, P. P. Ingole, S. Das and V. Haridas, *Mol. Syst. Des. Eng.*, 2020, **5**, 847–855.

2. V. Haridas, A. R. Sapala and J. P. Jasinski, *Chem. Commun.*, 2015, **51**, 6905–6908.