Supplementary Material for

Anthrapyridone-based amino acids as colorimetric probes for Cu^{2+} ions determination

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A. NMR spectra

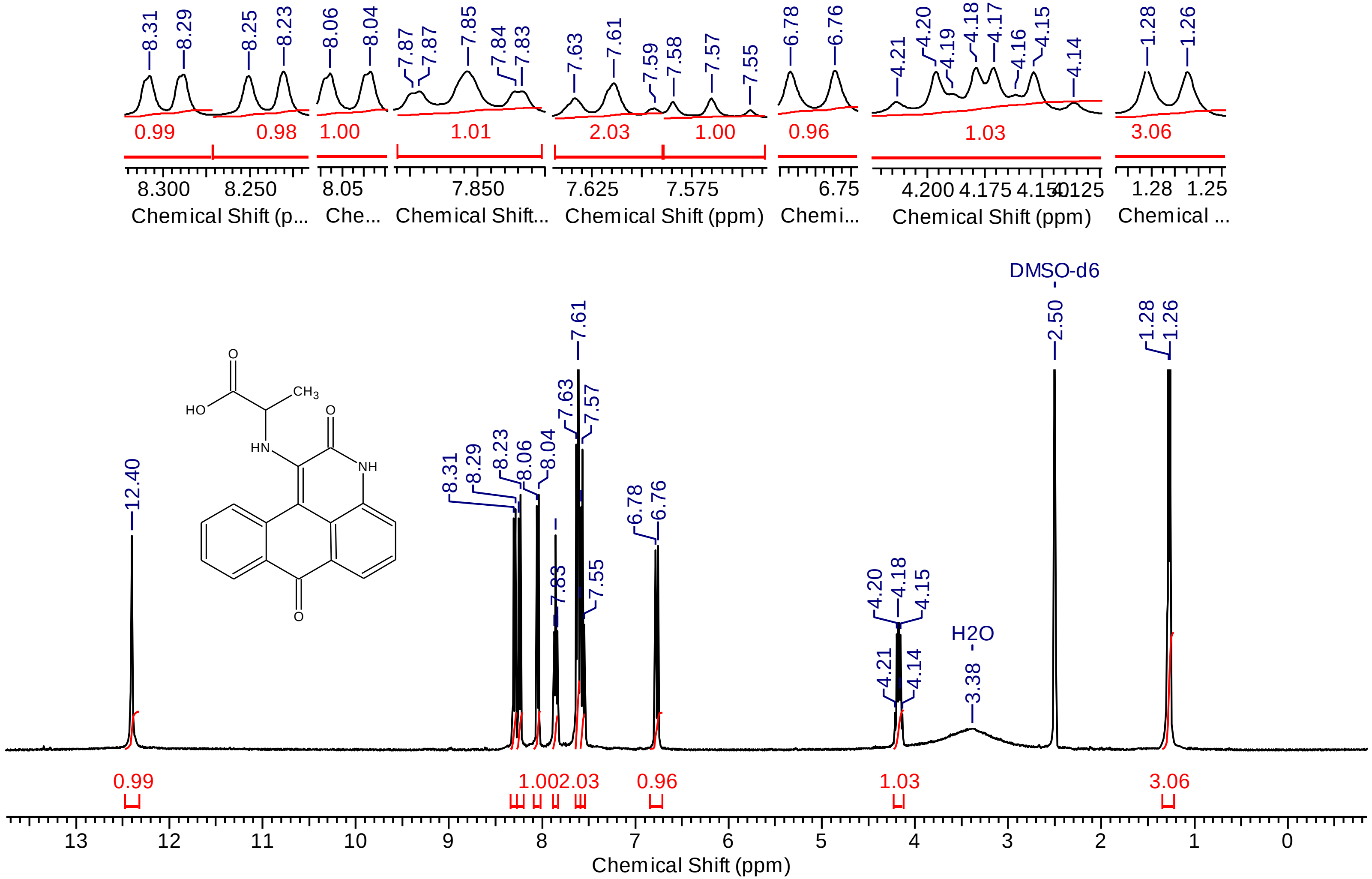

Fig. SA1. ^{1}H NMR spectrum of probe **4a** in DMSO-d_6.

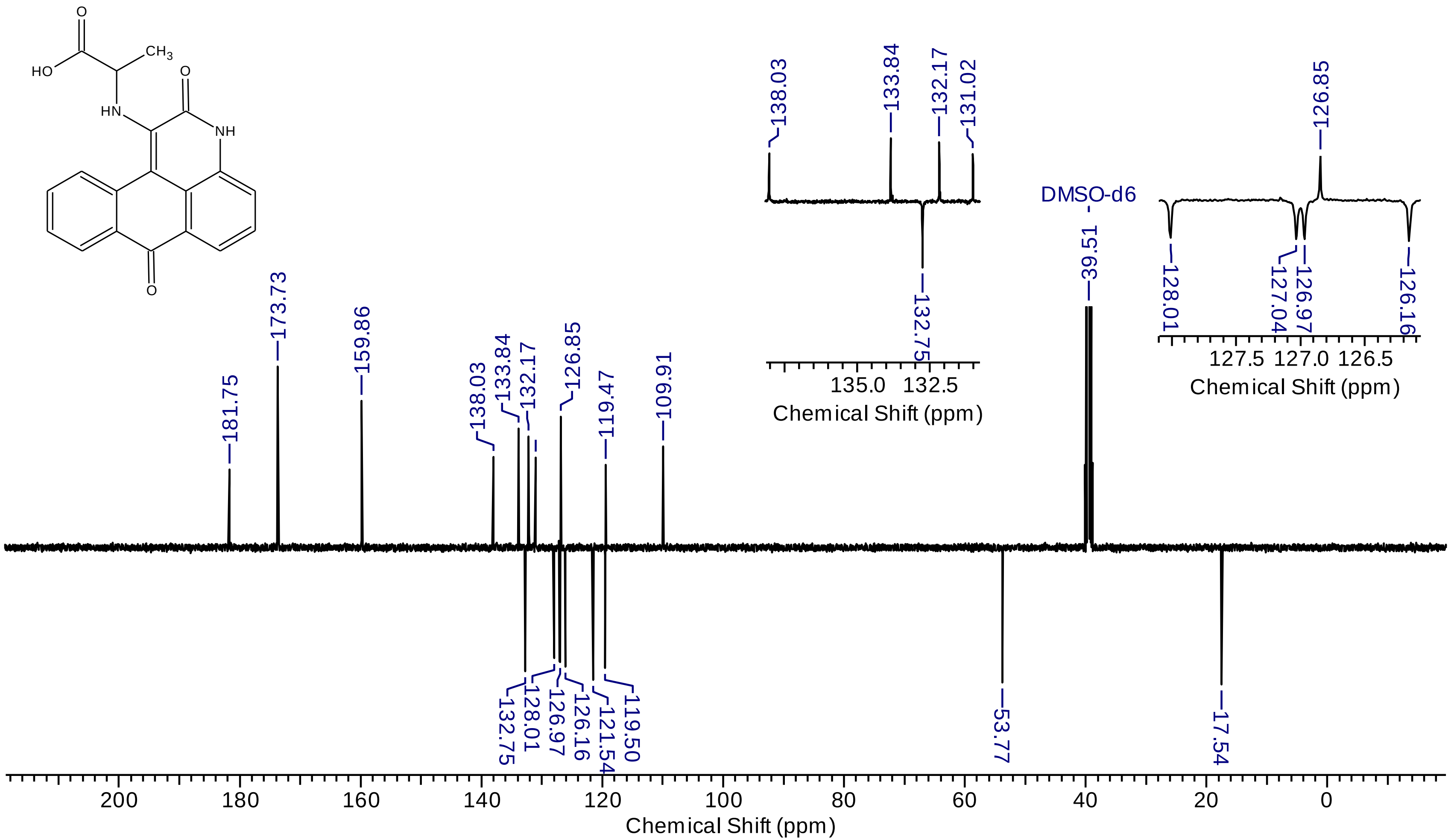

Fig. SA2. ^{13}C NMR spectrum of probe **4a** in DMSO-d_6.

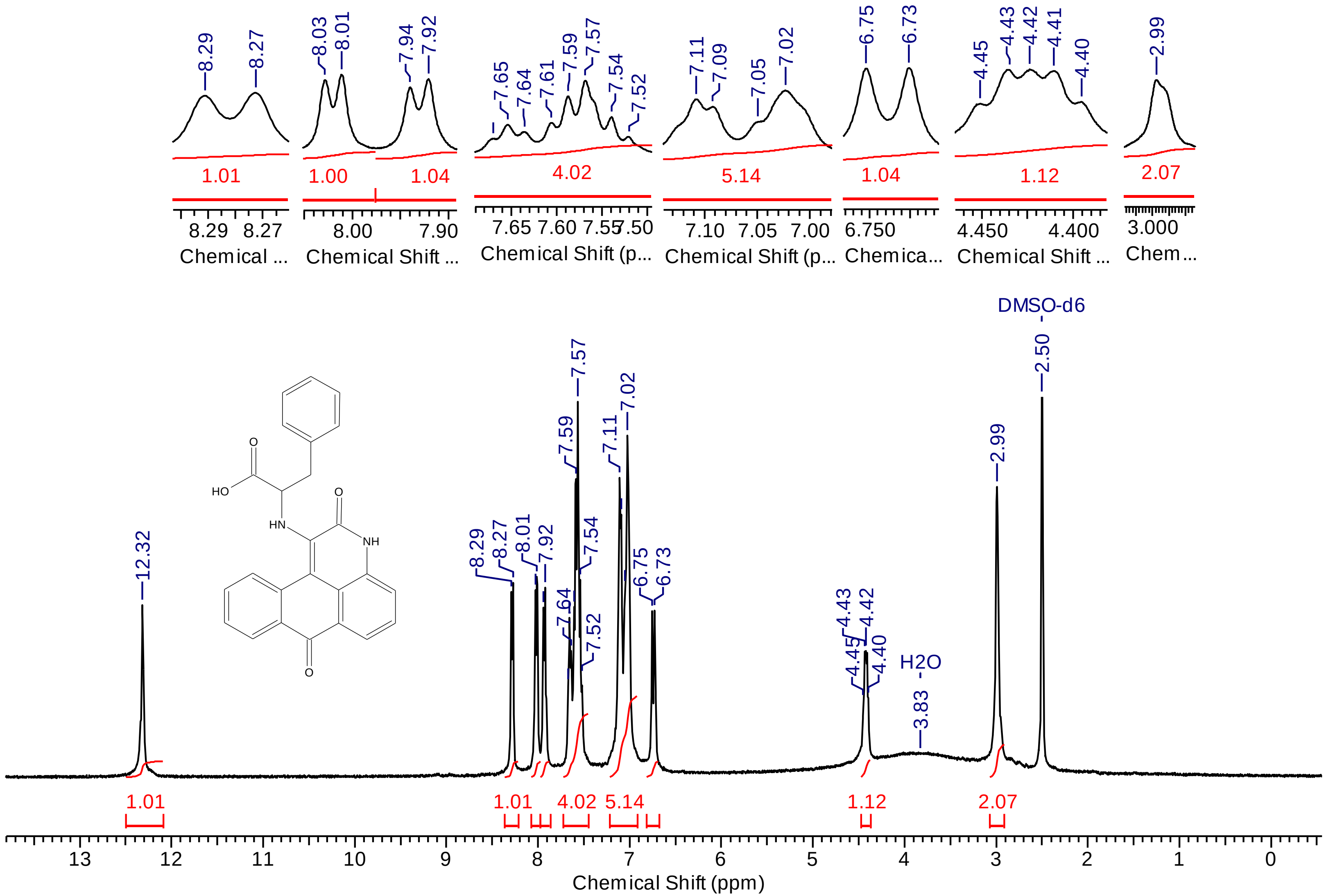

Fig. SA3. ^{1}H NMR spectrum of probe **4b** in DMSO-d_6.

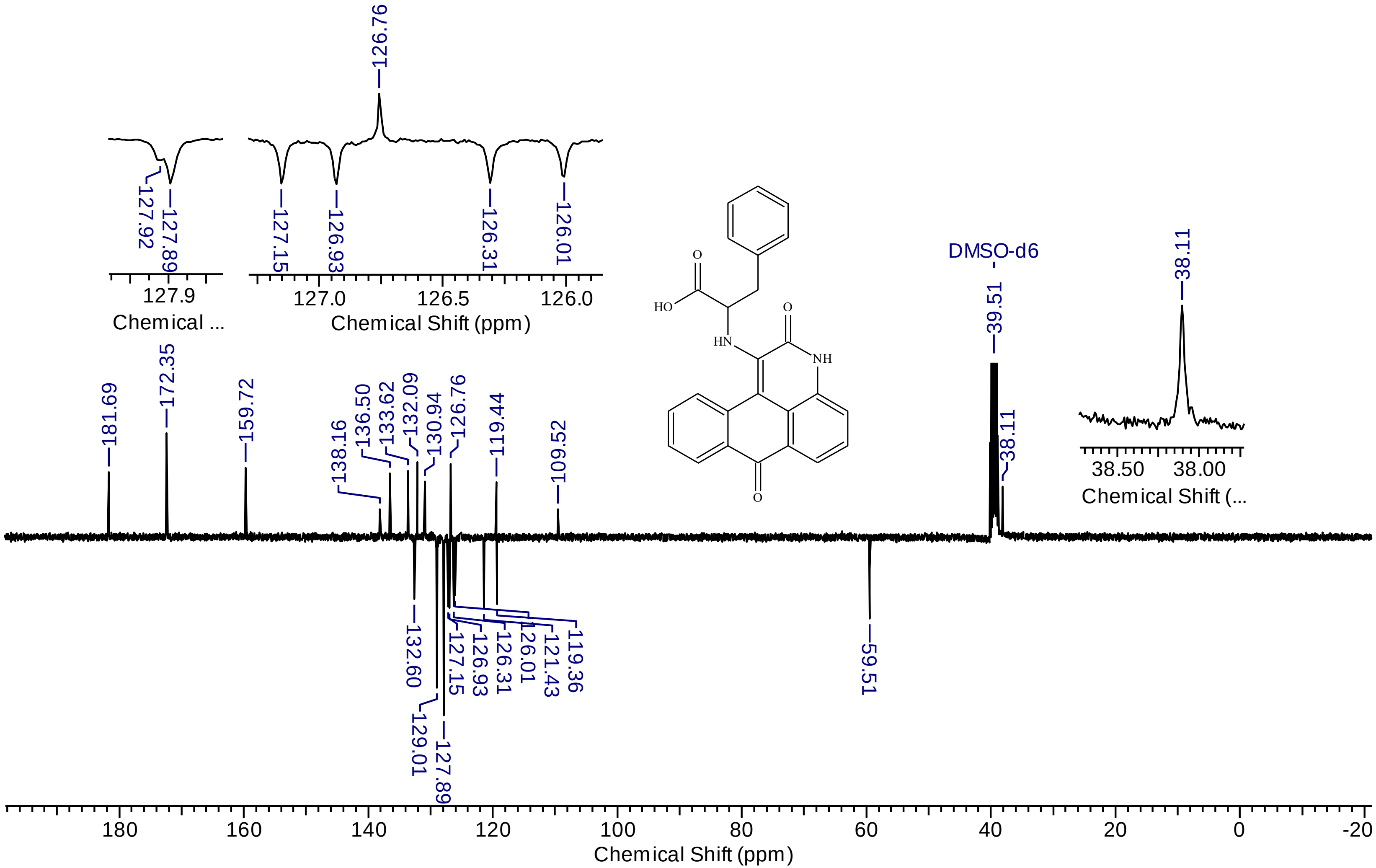

Fig. SA4. ^{13}C NMR spectrum of probe **4b** in DMSO-d$_6$.

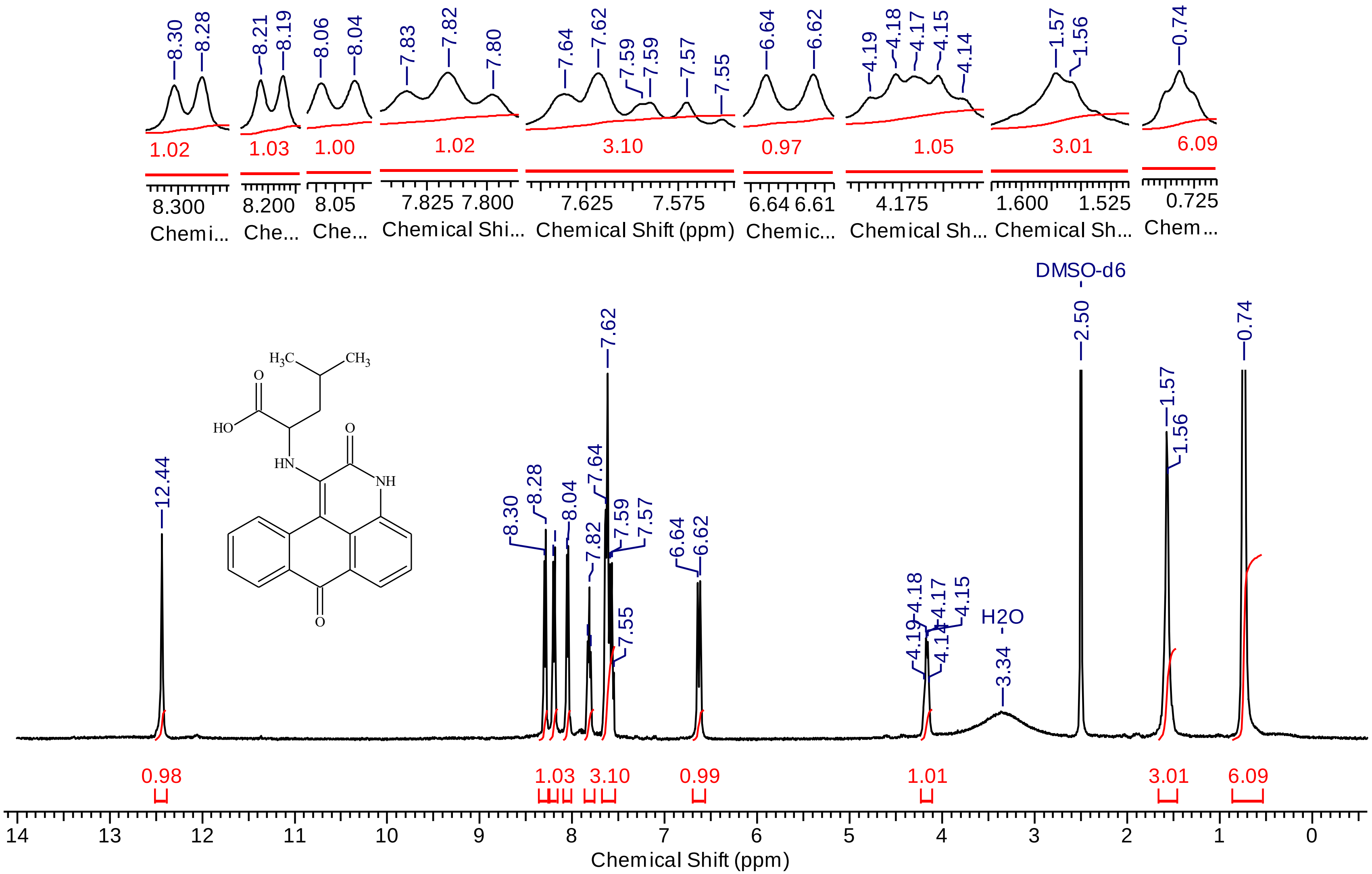

Fig. SA5. ^{1}H NMR spectrum of probe **4c** in DMSO-d_6.

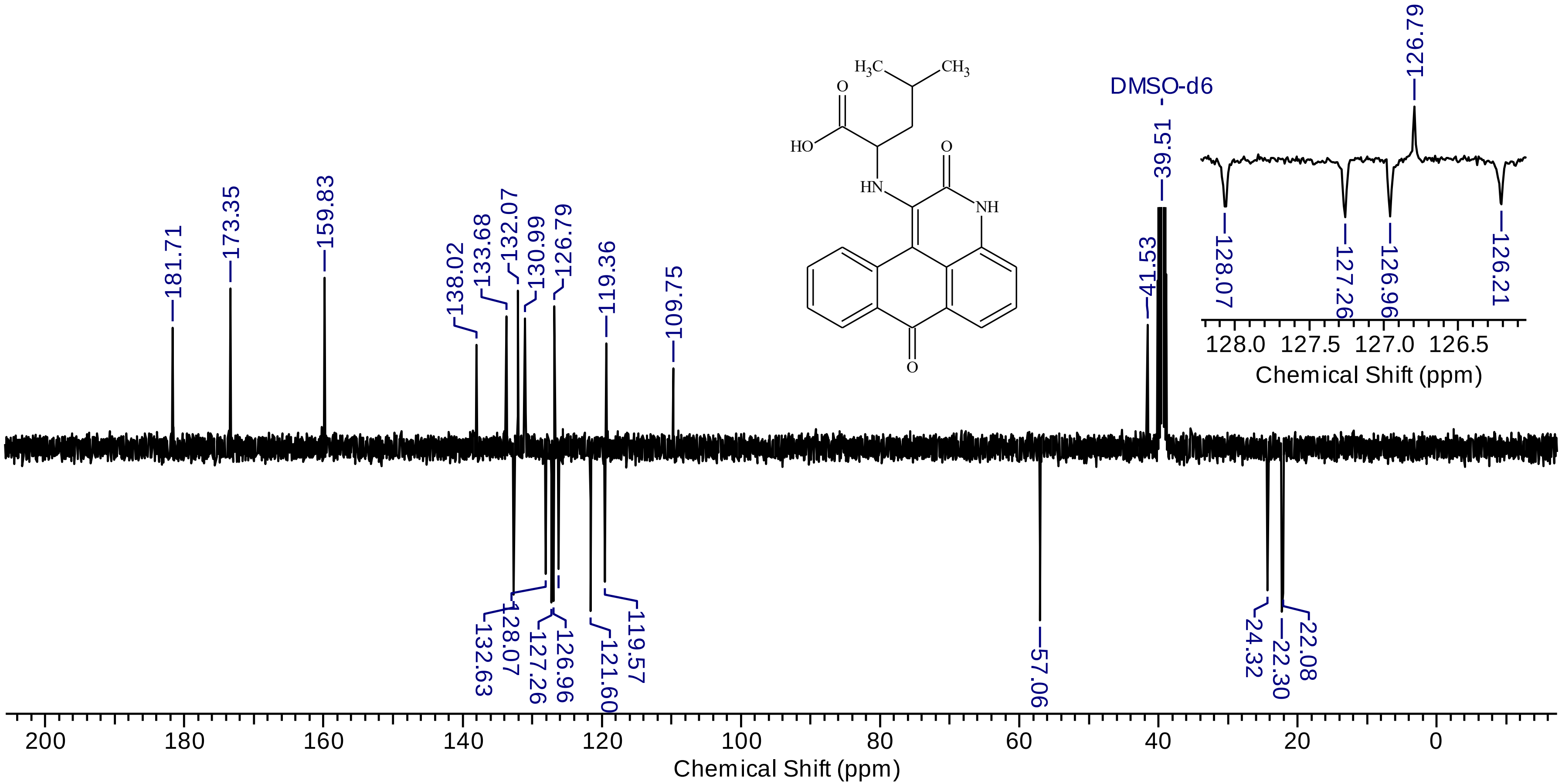

Fig. SA6. ^{13}C NMR spectrum of probe **4c** in DMSO-d_6.

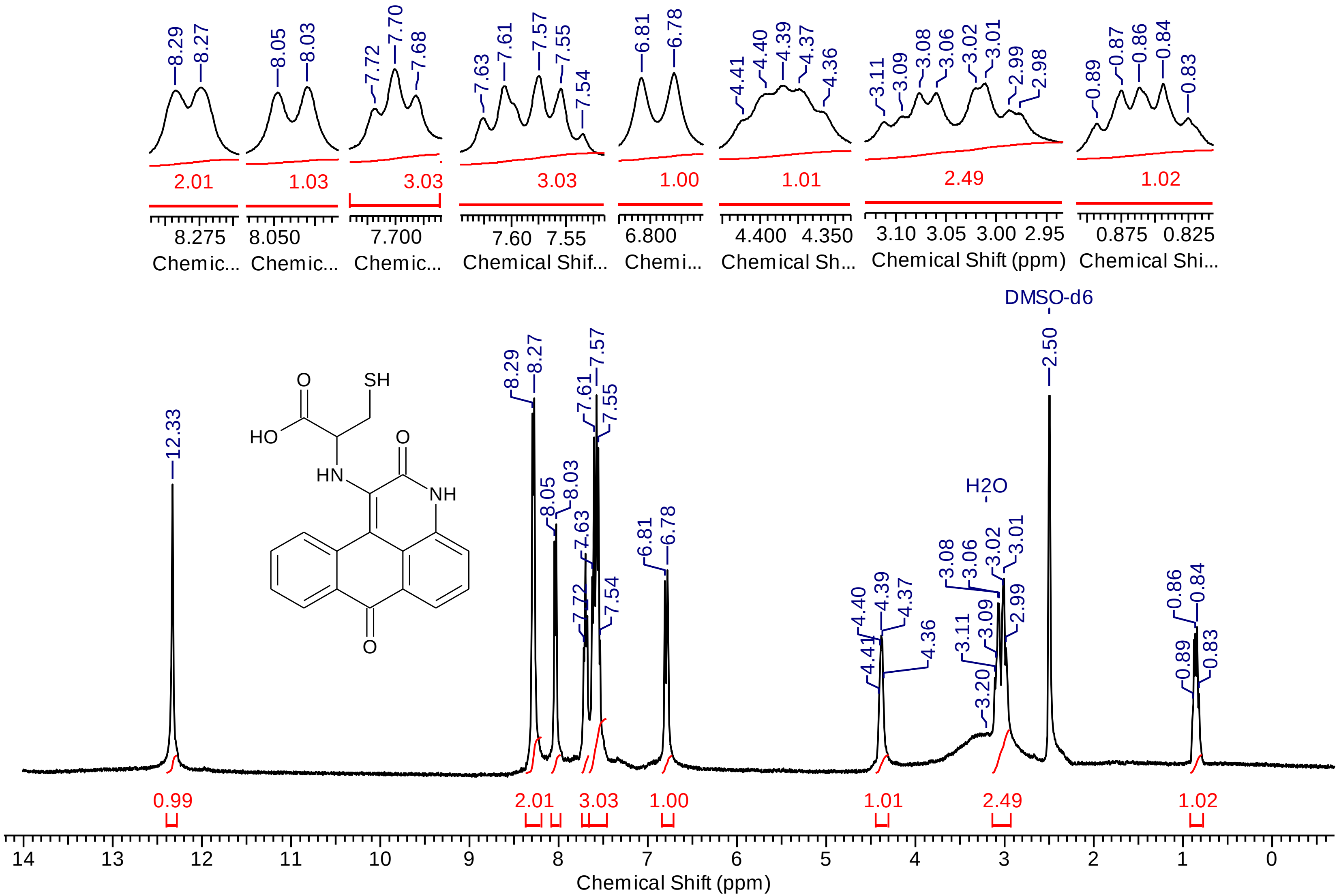

Fig. SA7. ^{1}H NMR spectrum of probe **4d** in DMSO-d_6.

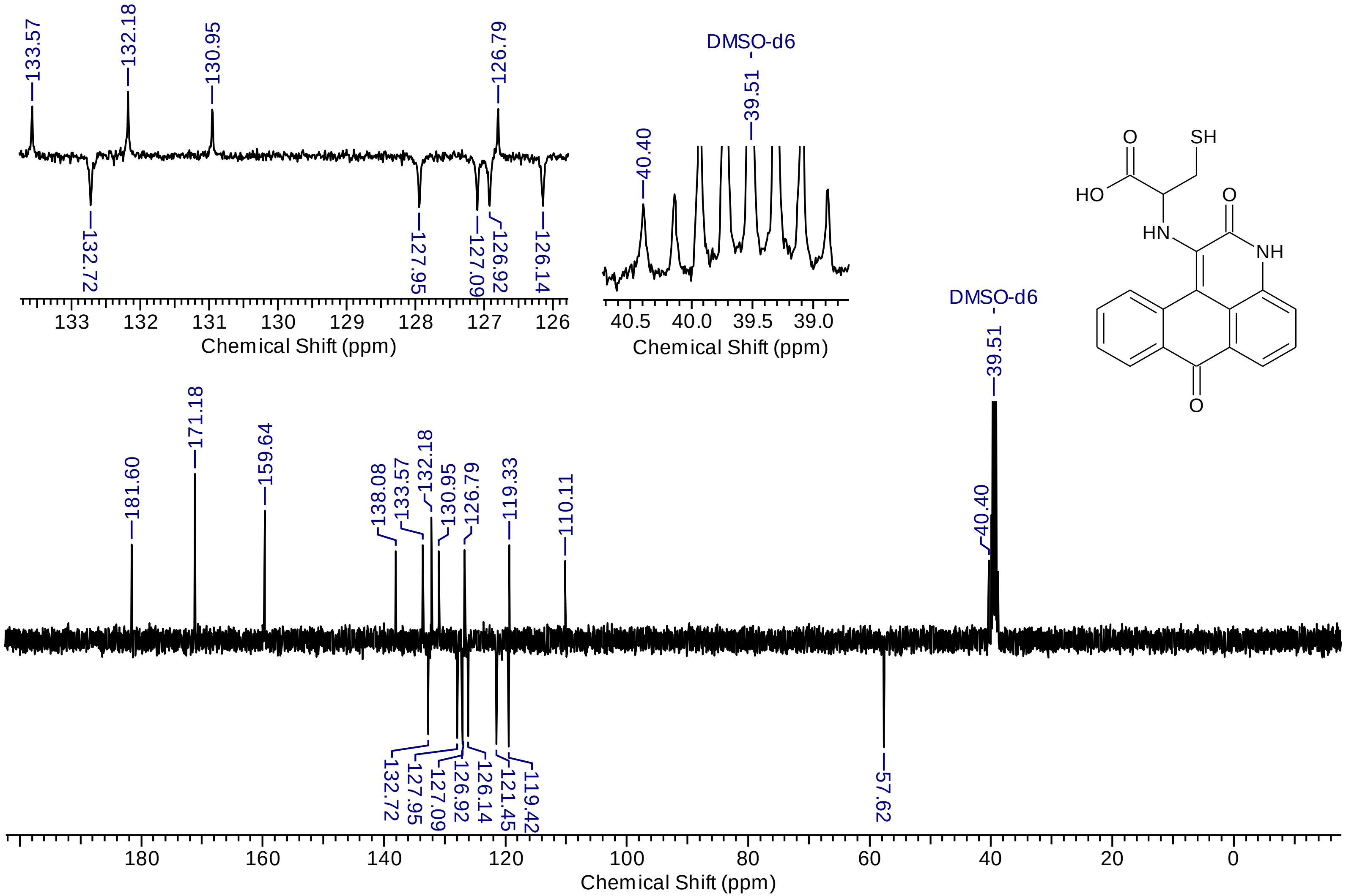

Fig. SA8. ^{13}C NMR spectrum of probe **4d** in DMSO-d$_6$.

B. Photos of solutions

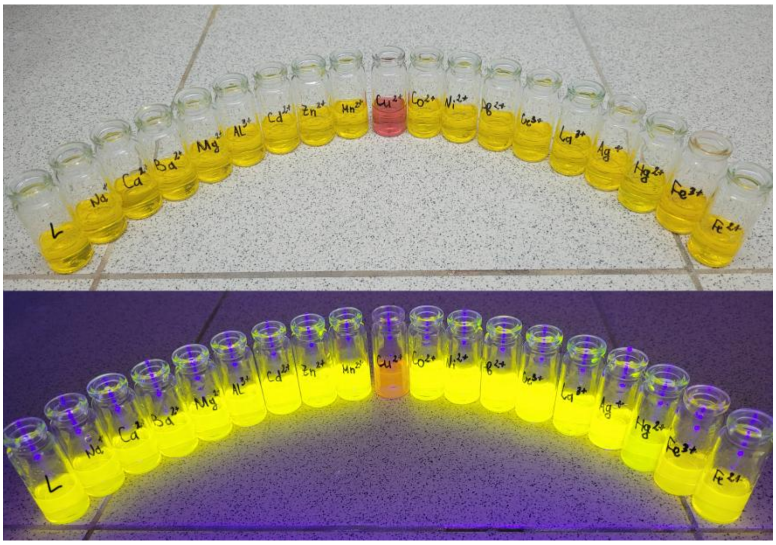

Fig. SB1. Color and fluorescence changes of **4b (**200 μM) upon the addition of various metal cations (200 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

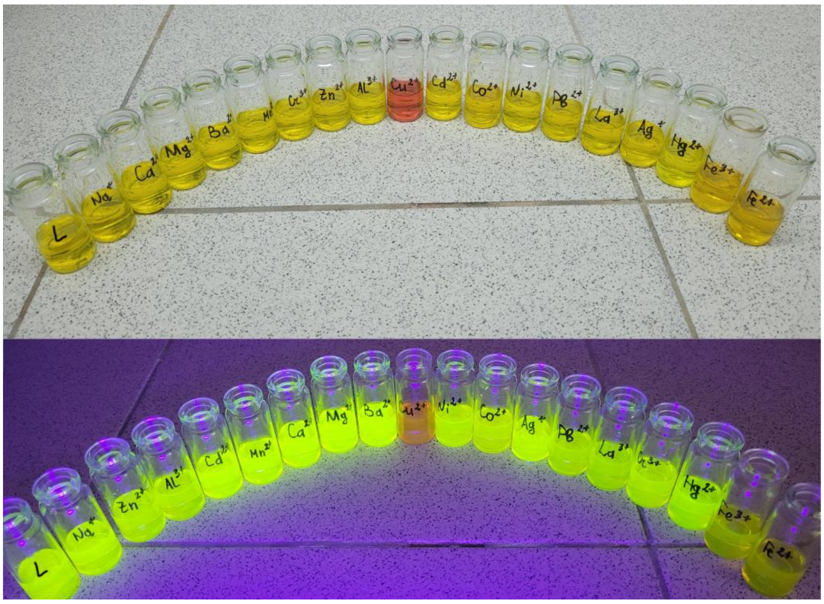

Fig. SB2. Color and fluorescence changes of **4c (**200 μM) upon the addition of various metal cations **(**200 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

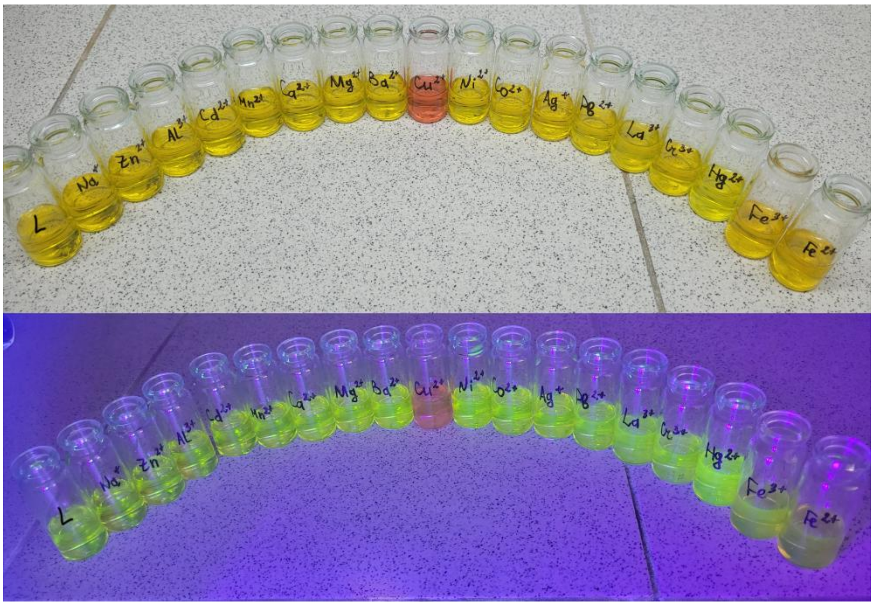

Fig. SB3. Color and fluorescence changes of **4d (**200 μM) upon the addition of various metal cations **(**200 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

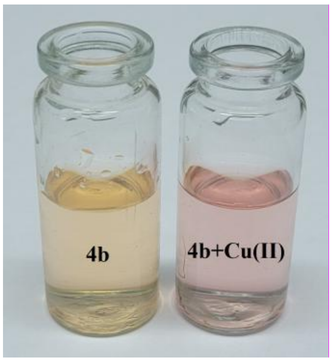

Fig. SB4. Solutions of amino acid **4b** (20 μM) in the absence and presence of Cu^{2+} (20 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

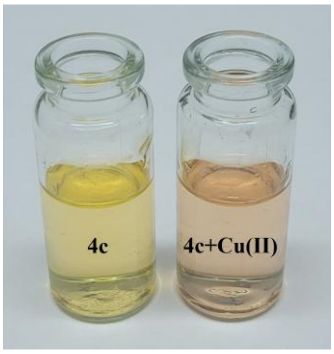

Fig. SB5. Solutions of amino acid **4c** (20 μM) in the absence and presence of Cu^{2+} (20 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

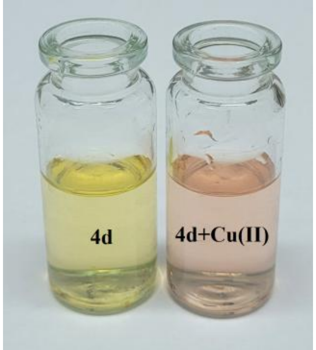

Fig. SB6. Solutions of amino acid **4d** (20 μM) in the absence and presence of Cu^{2+} (20 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

C. UV-Vis spectra of amino acids

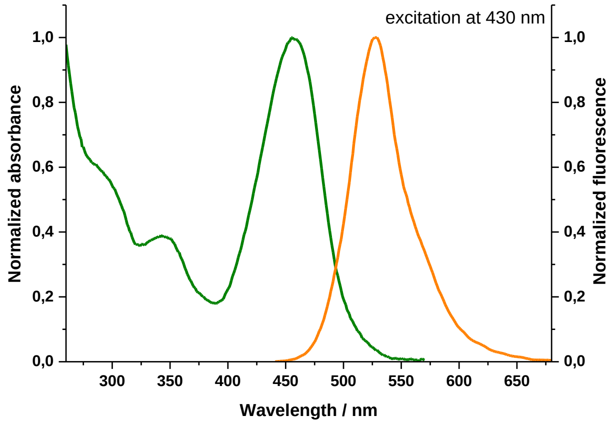

Fig. SC1. Normalized absorption and emission spectra of **4a** in ethanol

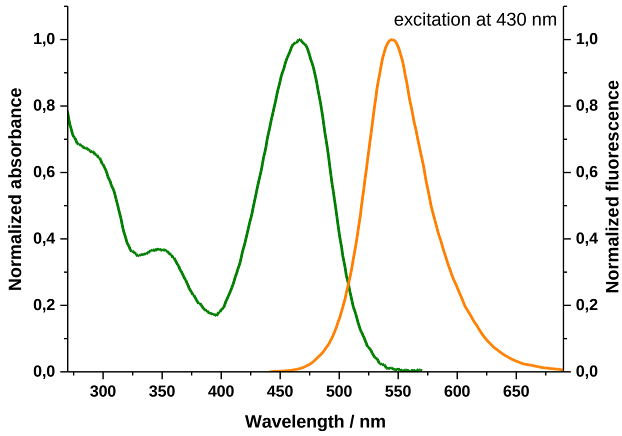

Fig. SC2. Normalized absorption and emission spectra of **4b** in ethanol

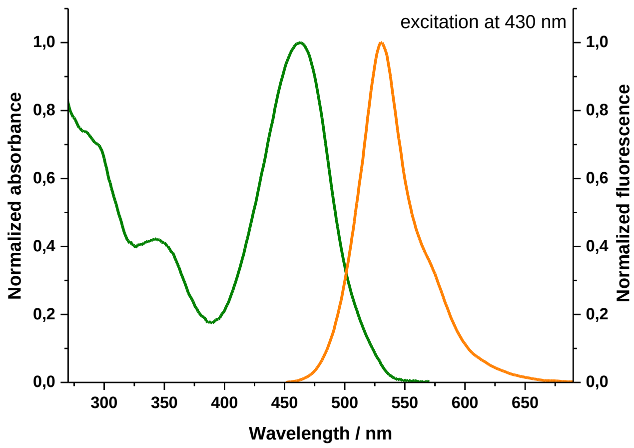

Fig. SC3. Normalized absorption and emission spectra of **4c** in ethanol

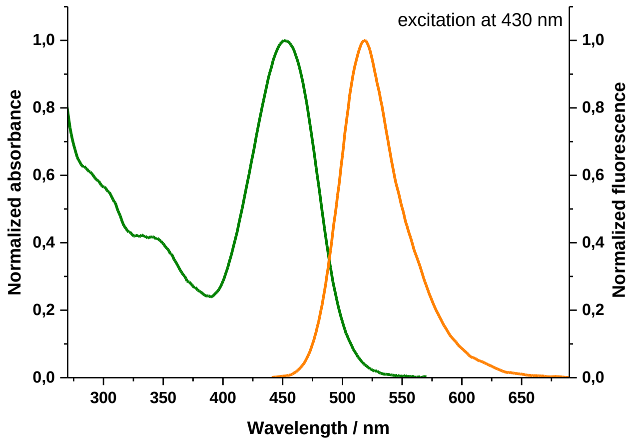

Fig. SC4. Normalized absorption and emission spectra of **4d** in ethanol

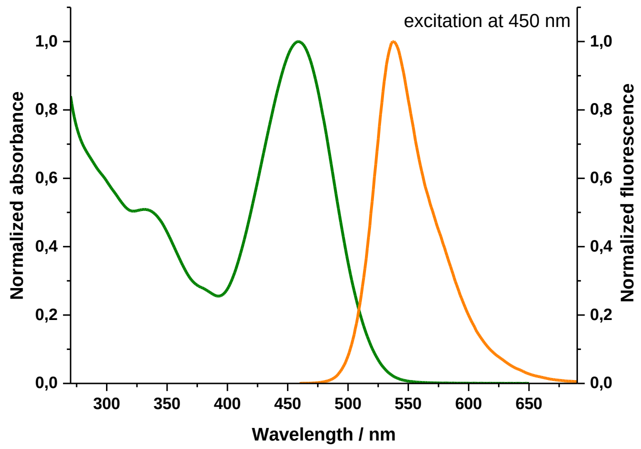

Fig. SC5. Normalized absorption and emission spectra of **4a** in H_2O/DMSO (9:1 v/v)

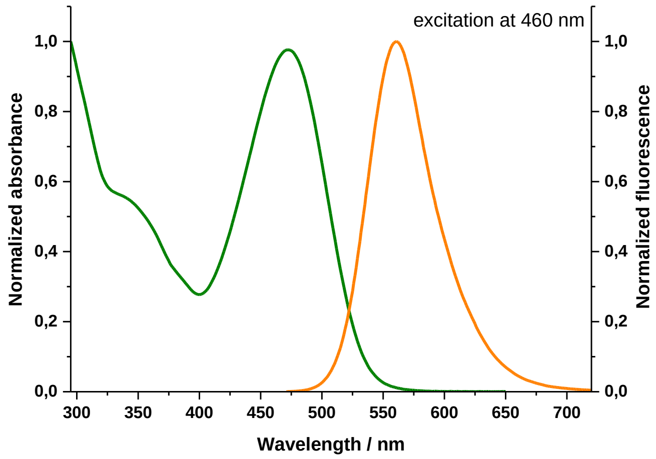

Fig. SC6. Normalized absorption and emission spectra of **4b** in H_2O/DMSO (9:1 v/v)

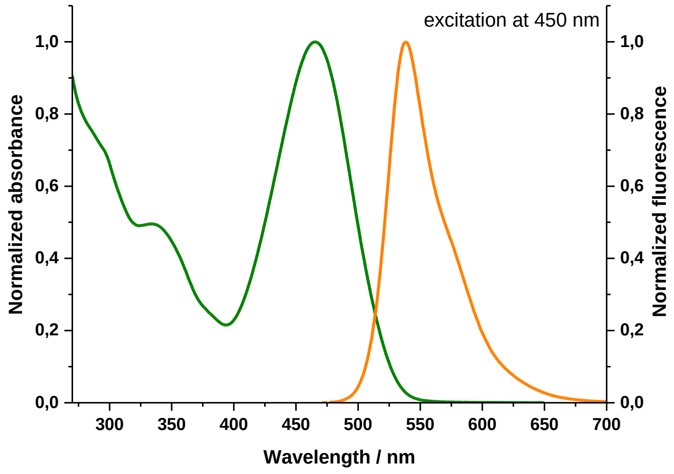

Fig. SC7. Normalized absorption and emission spectra of **4c** in H_2O/DMSO (9:1 v/v)

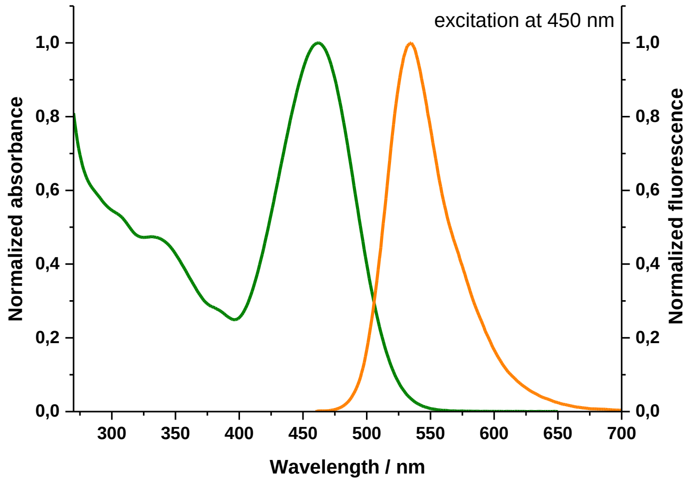

Fig. SC8. Normalized absorption and emission spectra of **4d** in H_2O/DMSO (9:1 v/v)

D. Study of Complex Formation

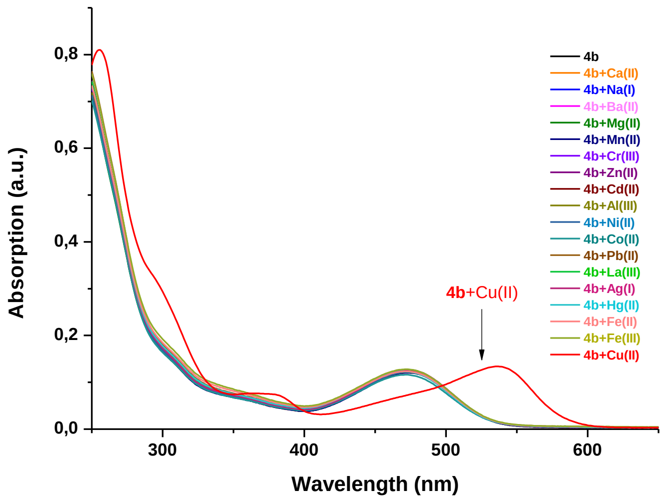

Fig. SD1. Absorption spectra of **4b** (10µM) in H_2O/DMSO (9:1 v/v) upon addition of different cations (10µM) at a pH of 7.4.

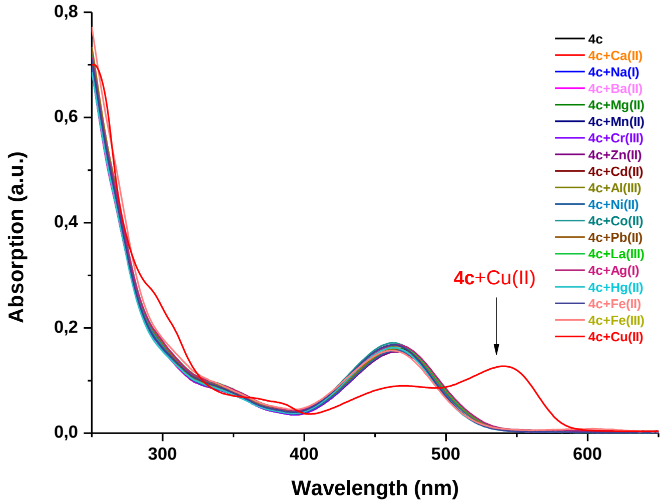

Fig. SD2. Absorption spectra of **4c** (10µM) in H_2O/DMSO (9:1 v/v) upon addition of different cations (10µM) at a pH of 7.4.

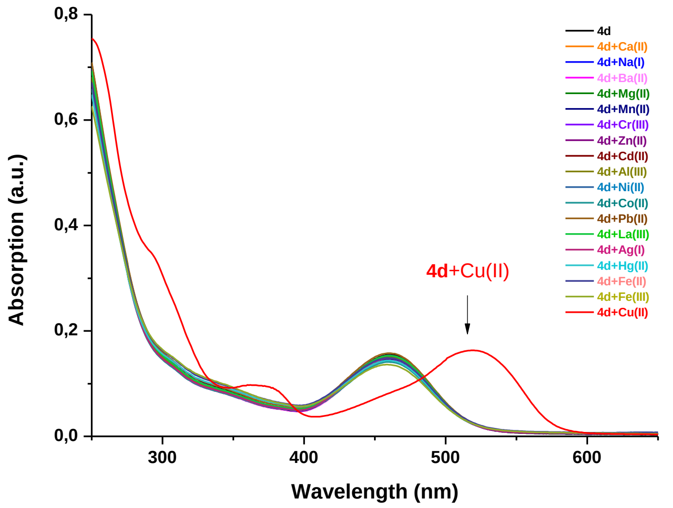

Fig. SD3. Absorption spectra of **4d** (10µM) in H_2O/DMSO (9:1 v/v) upon addition of different cations (10µM) at a pH of 7.4.

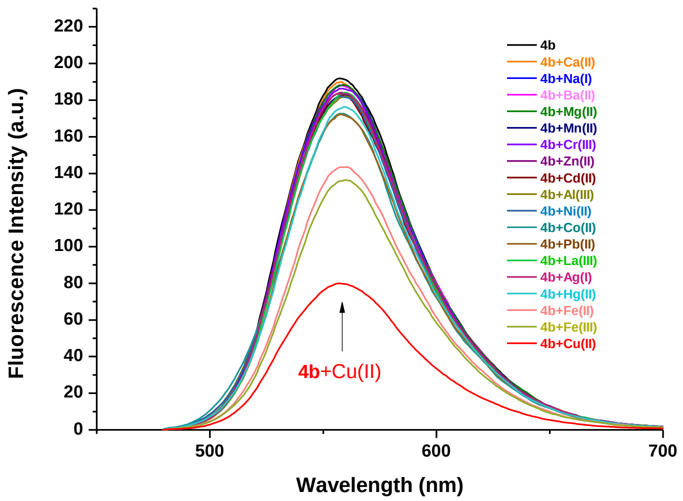

Fig. SD4. Fluorescence spectra of **4b** (10µM) in H_2O/DMSO (9:1 v/v) upon addition of different cations (10µM) at a pH of 7.4.

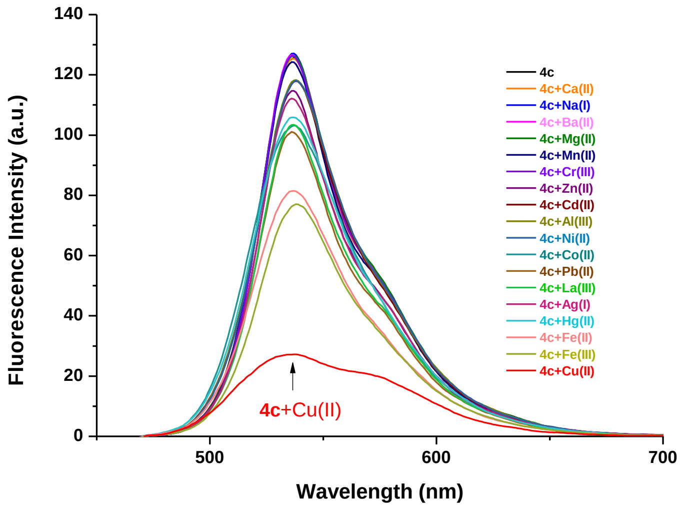

Fig. SD5. Fluorescence spectra of **4c** (10μM) in H_2O/DMSO (9:1 v/v) upon addition of different cations (10μM) at a pH of 7.4.

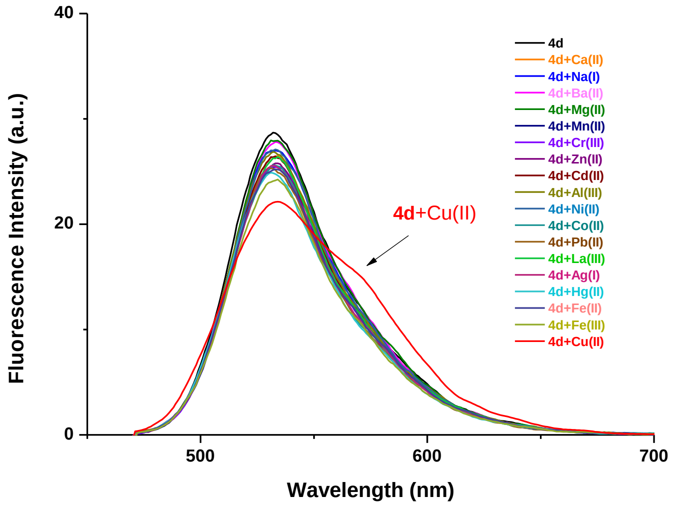

Fig. SD6. Fluorescence spectra of **4d** (10μM) in H_2O/DMSO (9:1 v/v) upon addition of different cations (10μM) at a pH of 7.4.

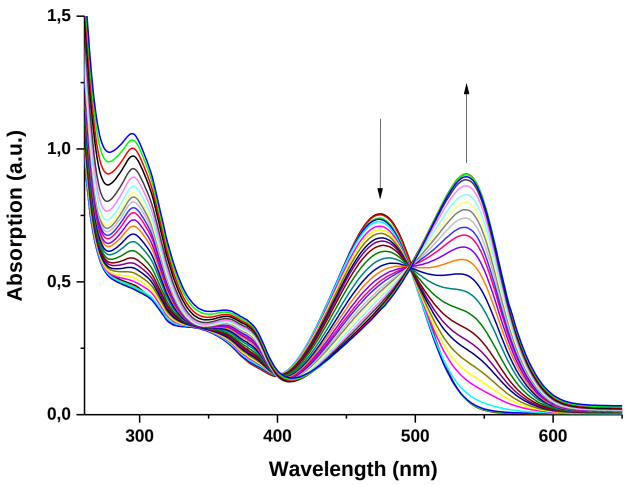

Fig. SD7. Absorption spectra of **4b** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

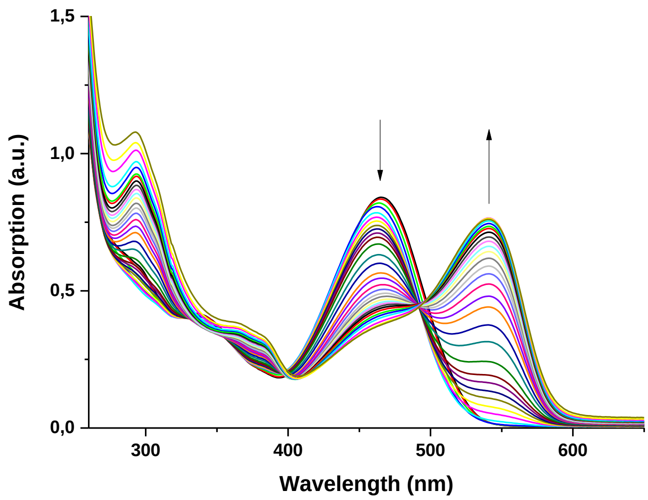

Fig. SD8. Absorption spectra of **4c** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

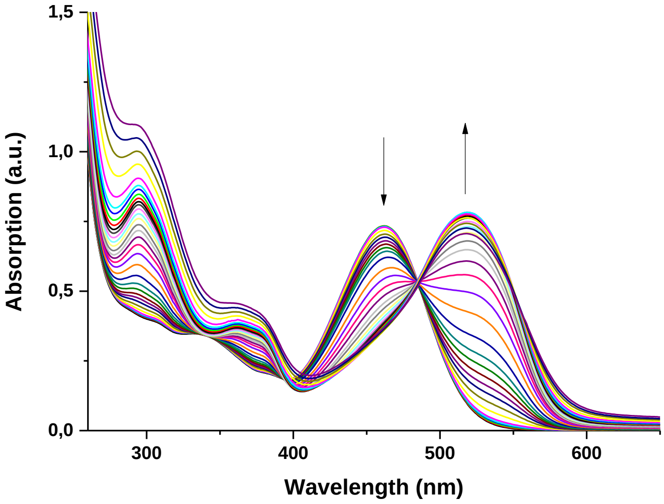

Fig. SD9. Absorption spectra of **4d** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

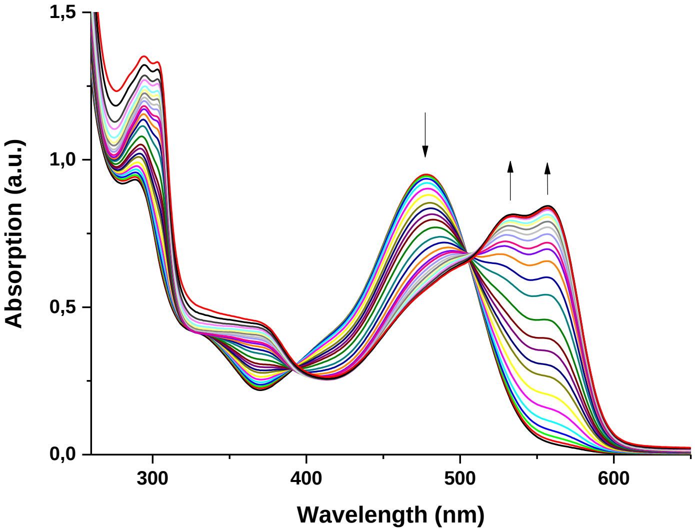

Fig. SD10. Absorption spectra of **4a** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

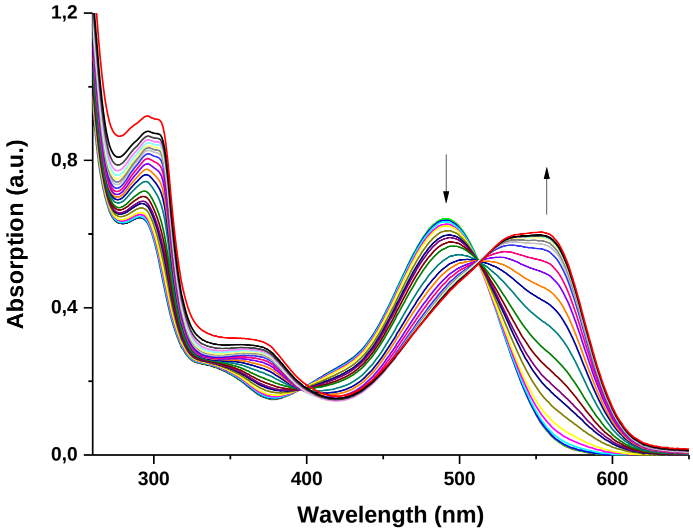

Fig. SD11. Absorption spectra of **4b** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

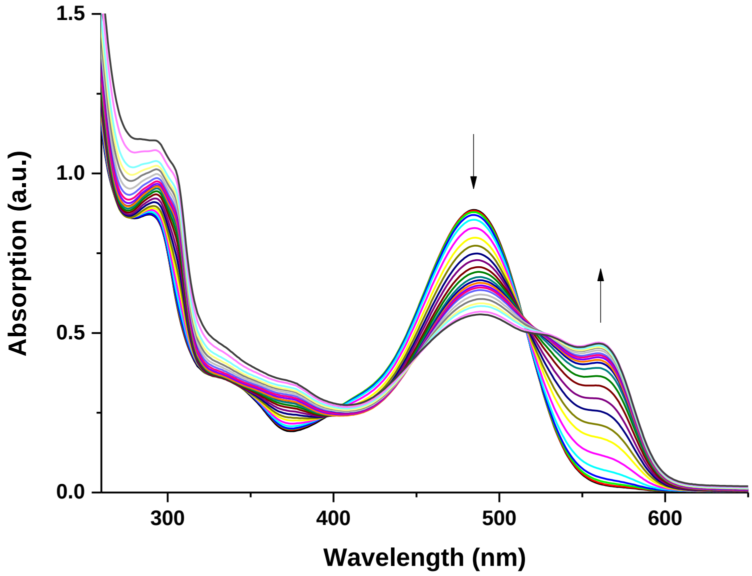

Fig. SD12. Absorption spectra of **4c** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

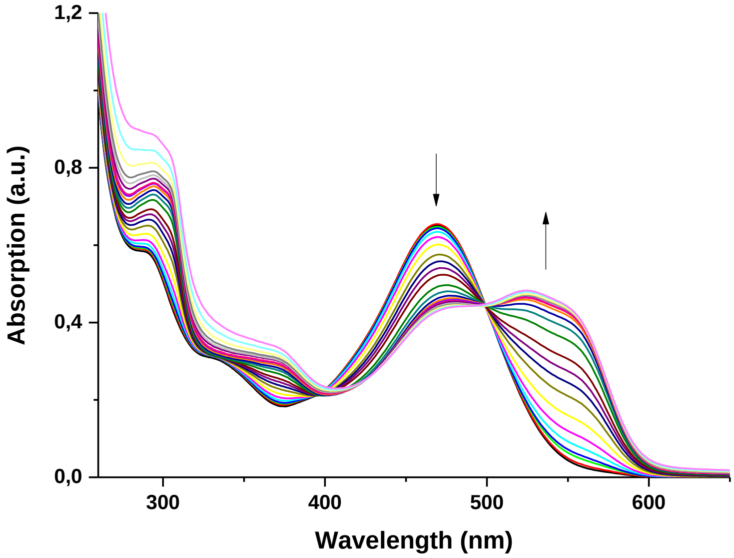

Fig. SD13. Absorption spectra of **4d** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

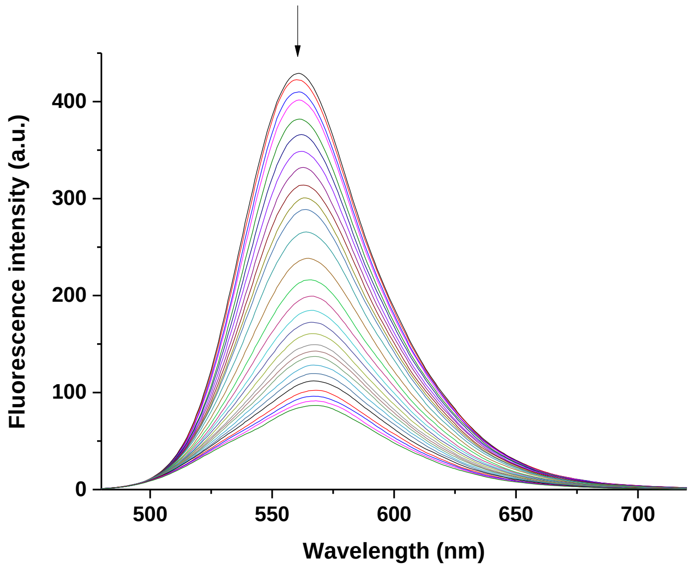

Fig. SD14. Fluorescence spectra of **4b** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

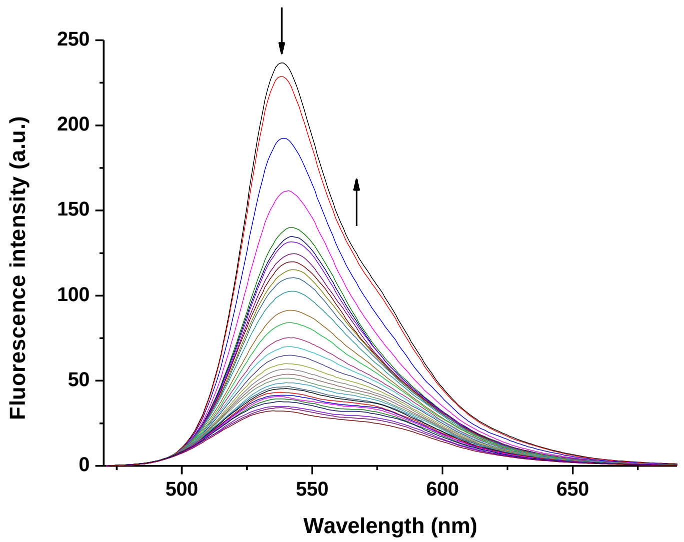

Fig. SD15. Fluorescence spectra of **4c** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

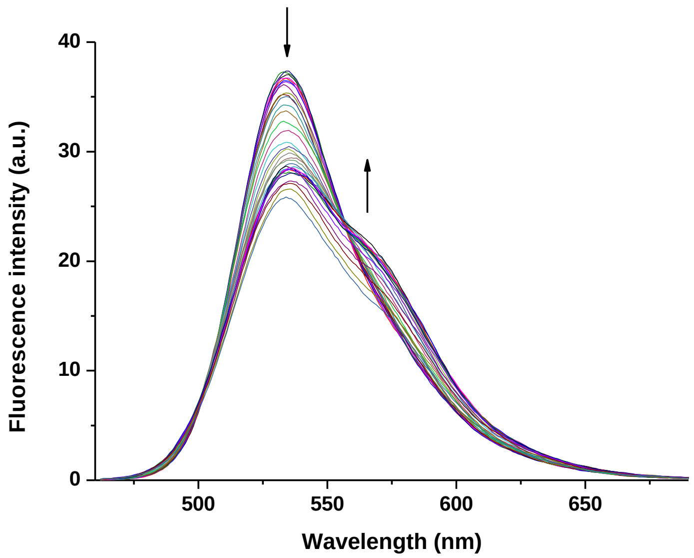

Fig. SD16. Fluorescence spectra of **4d** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

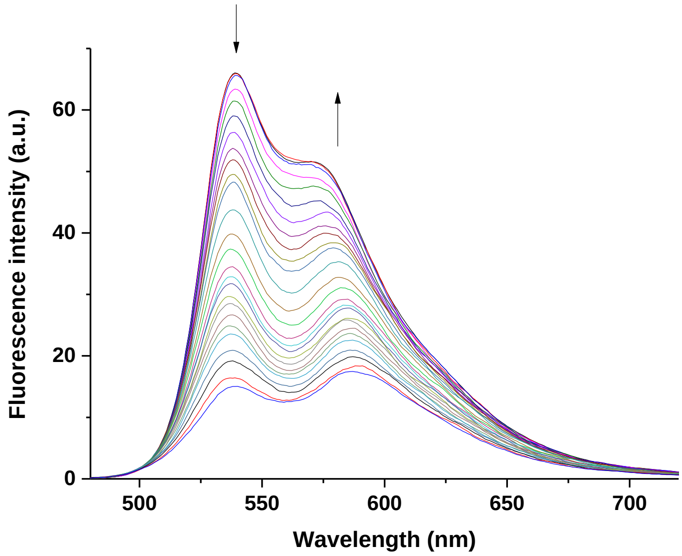

Fig. SD17. Fluorescence spectra of **4a** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

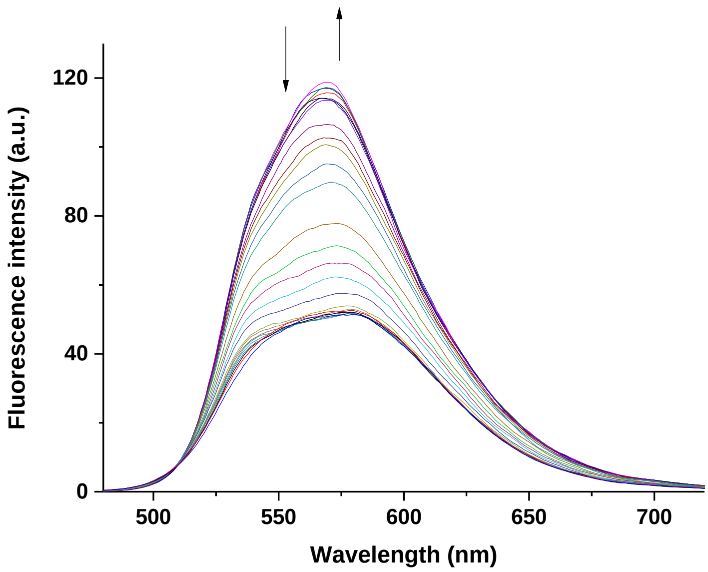

Fig. SD18. Fluorescence spectra of **4b** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

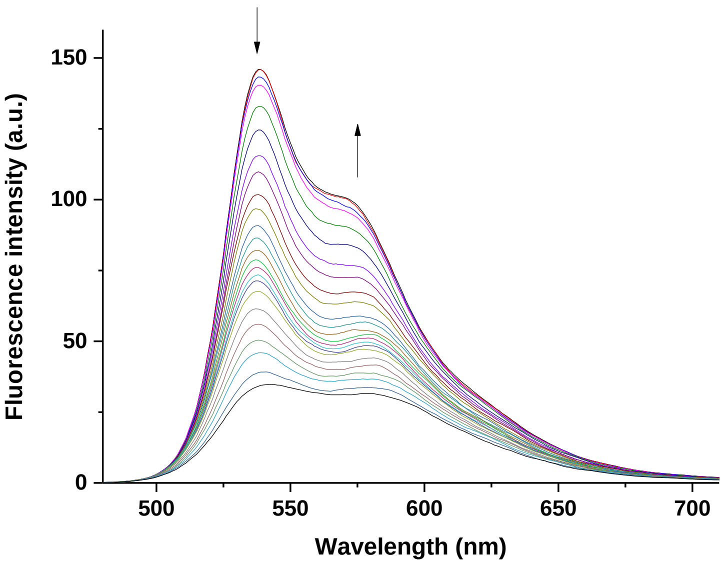

Fig. SD19. Fluorescence spectra of **4c** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

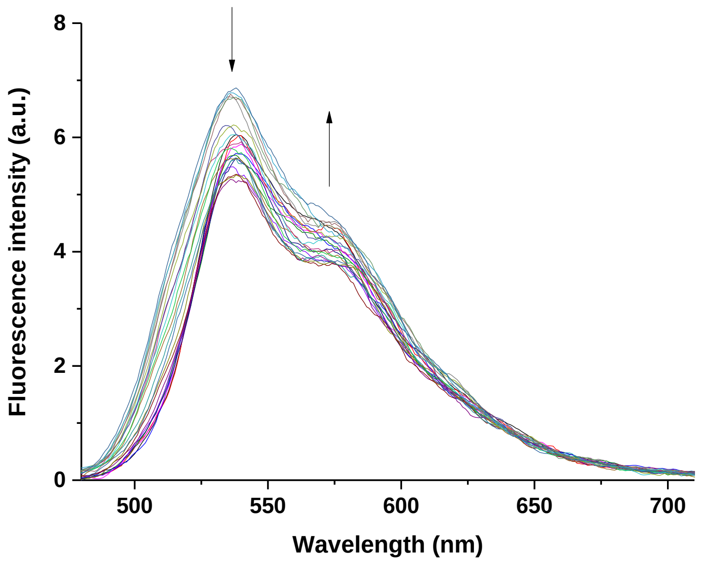

Fig. SD20. Fluorescence spectra of **4d** (60 μM) upon the addition of Cu^{2+} (0–200 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

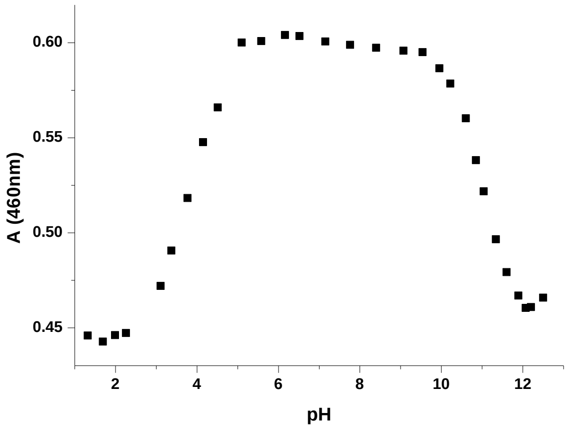

Fig. SD21. Effect of the pH on the absorbance of **4a** (50.0 μM) in the presence of Cu^{2+} (50.0 μM), H_2O/DMSO (9:1 v/v)

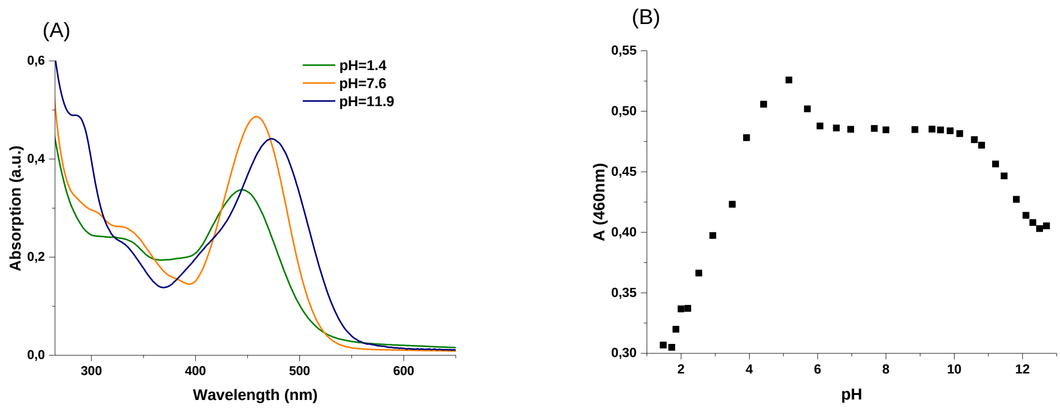

Fig. SD22. (A) Effect of the pH on the absorption spectrum of **4d** (50.0 μM). (B) Effect of pH on the absorbance of **4d** (50.0 μM). H_2O/DMSO (9:1 v/v)

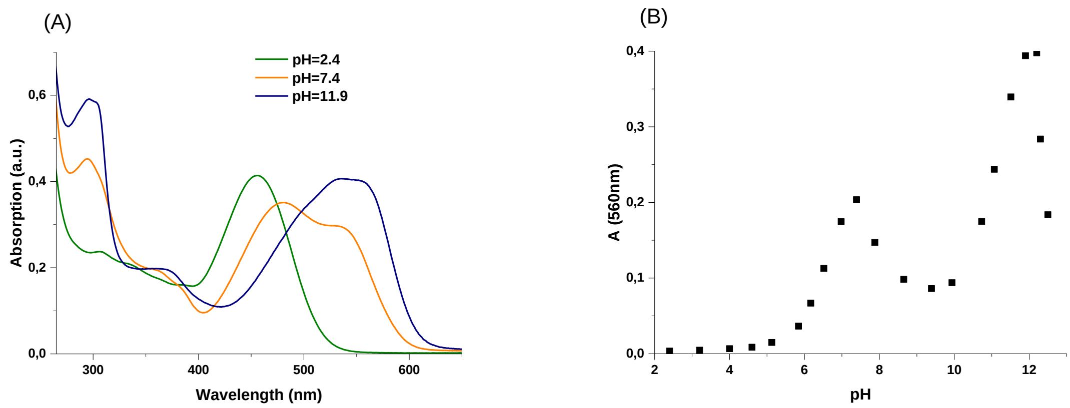

Fig. SD23. (A) Effect of the pH on the absorption spectrum of **4b** (50 μM) in the presence of Cu^{2+} (50 μM). (B) Effect of pH on the absorbance of **4b** (50 μM) in the presence of Cu^{2+} (50 μM). H_2O/DMSO (9:1 v/v)

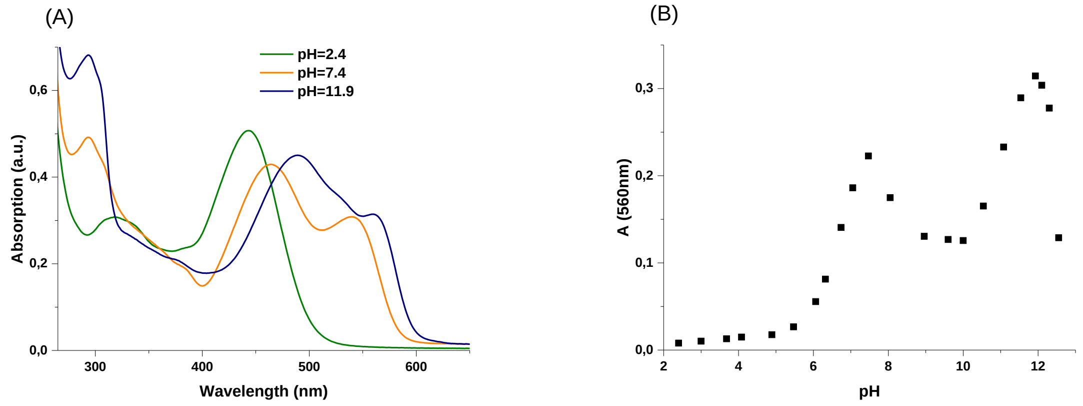

Fig. SD24. (A) Effect of the pH on the absorption spectrum of **4c** (50 μM) in the presence of Cu^{2+} (50 μM). (B) Effect of pH on the absorbance of **4c** (50 μM) in the presence of Cu^{2+} (50 μM). H_2O/DMSO (9:1 v/v)

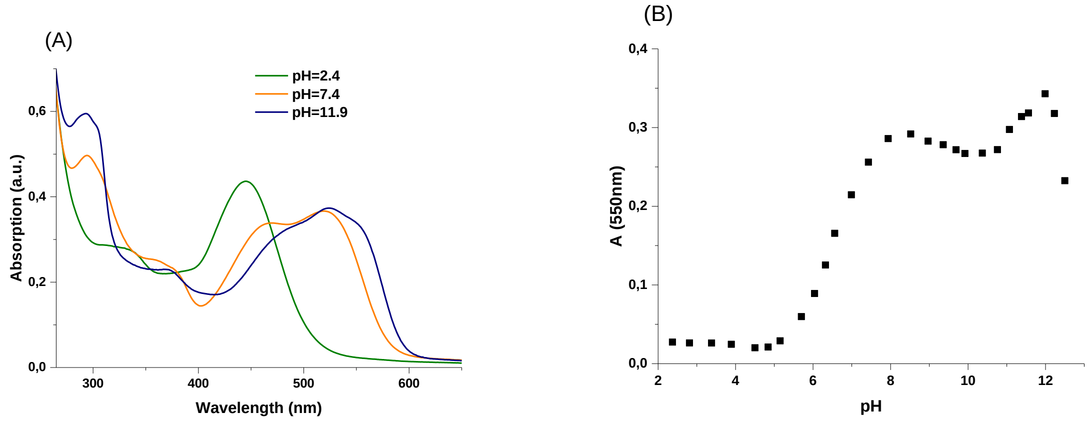

Fig. SD25. (A) Effect of the pH on the absorption spectrum of **4d** (50 μM) in the presence of Cu^{2+} (50 μM). (B) Effect of pH on the absorbance of **4d** (50 μM) in the presence of Cu^{2+} (50 μM). H_2O/DMSO (9:1 v/v)

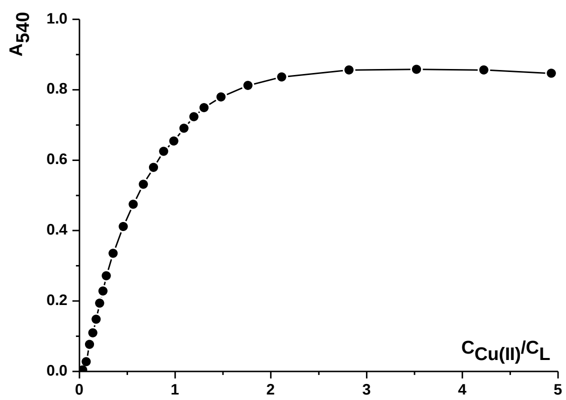

Fig. SD26. Absorption changes of compound **4b** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

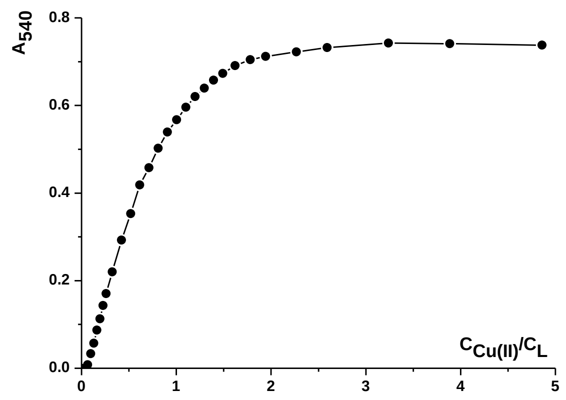

Fig. SD27. Absorption changes of compound **4c** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

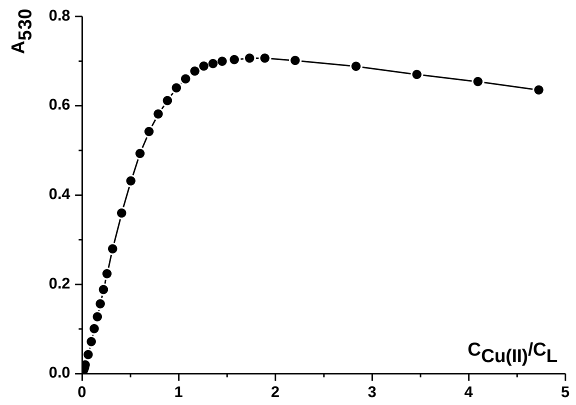

Fig. SD28. Absorption changes of compound **4d** (60 μM) upon the addition of Cu^{2+} (0–300 μM), pH=7.4, H_2O/DMSO (9:1 v/v)

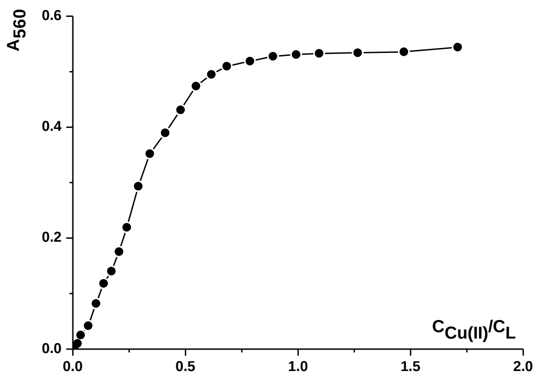

Fig. SD29. Absorption changes of compound **4b** (60 μM) upon the addition of Cu^{2+} (0–160 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

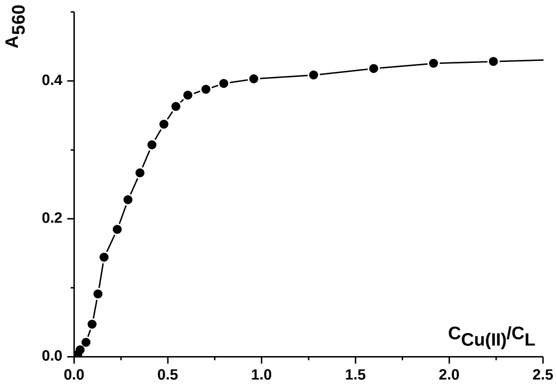

Fig. SD30. Absorption changes of compound **4c** (60 μM) upon the addition of Cu^{2+} (0–220 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

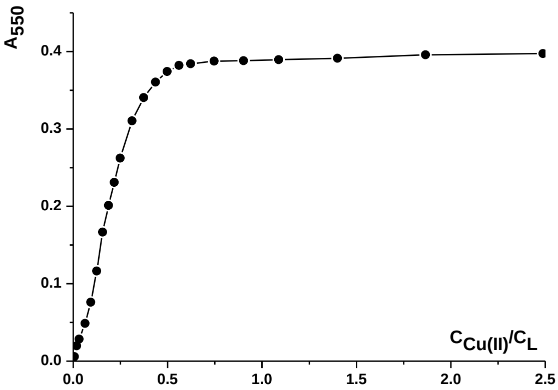

Fig. SD31. Absorption changes of compound **4d** (60 μM) upon the addition of Cu^{2+} (0–160 μM), pH=11.9, H_2O/DMSO (9:1 v/v)

Photometric titration of probe **4d** at pH 11.9 did not unambiguously establish the stoichiometry of its Cu^{2+} complex, suggesting a Cu^{2+}: ligand ratio between 1 : 2 and 1 : 3. To clarify the composition, we constructed a Job plot (Fig. SD26), which clearly indicates a 1 : 2 stoichiometry.

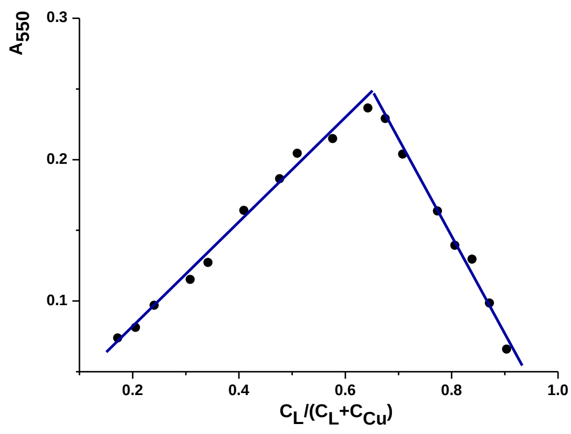

Fig. SD32. Job's plot for determining the stoichiometry of **4d** and Cu^{2+}. The total concentration of **4d** and Cu^{2+} 60 μM. pH=11.9, H_2O/DMSO (9:1 v/v)

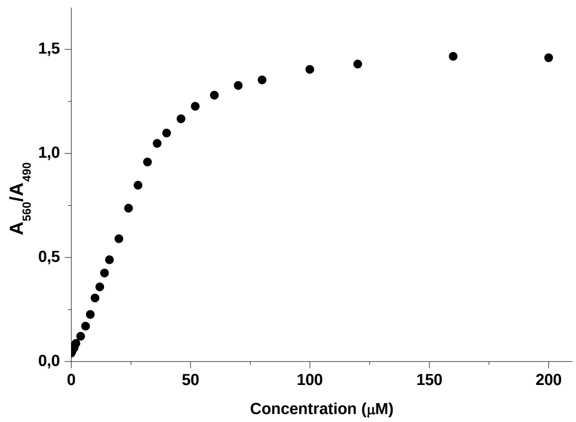

Fig. SD33. Absorption ratio of **4a** (60 μM) versus [Cu^{2+}], pH 7.4, H_2O/DMSO (9:1 v/v)

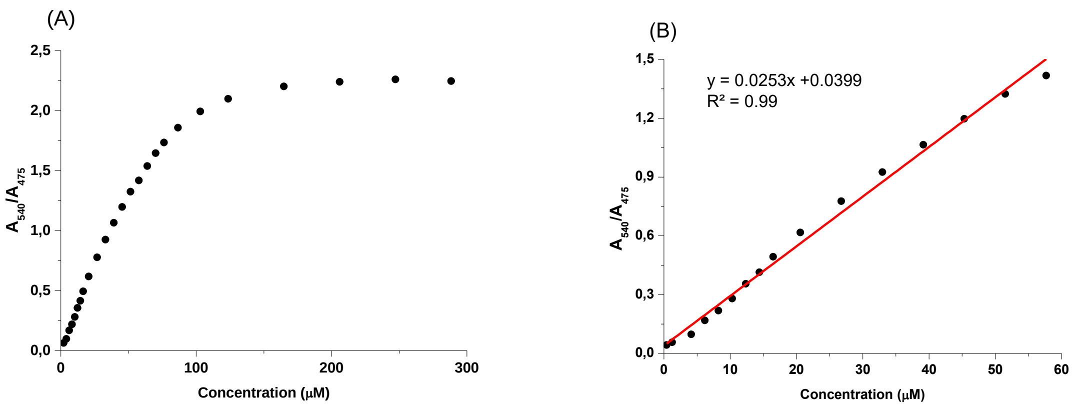

Fig. SD34. (A) Absorption ratio of **4b** (60 μM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4b** and increasing concentrations of Cu^{2+} (0–60 μM). pH 7.4, H_2O/DMSO (9:1 v/v)

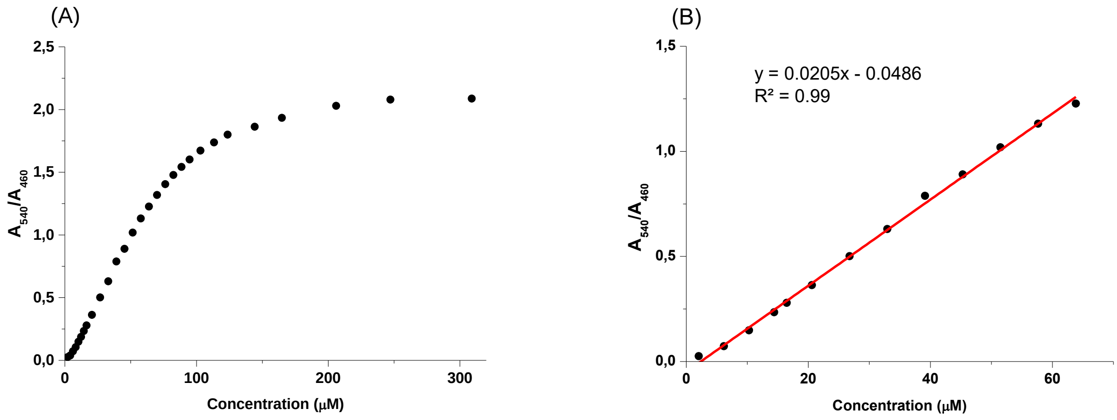

Fig. SD35. (A) Absorption ratio of **4c** (60 µM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4c** and increasing concentrations of Cu^{2+} (0–60 µM). pH 7.4, H_2O/DMSO (9:1 v/v)

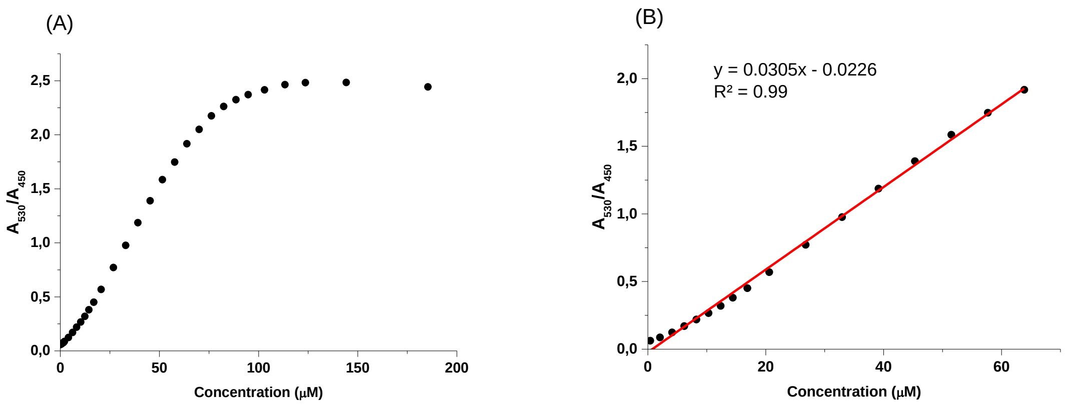

Fig. SD36. (A) Absorption ratio of **4d** (60 µM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4d** and increasing concentrations of Cu^{2+} (0–60 µM). pH 7.4, H_2O/DMSO (9:1 v/v)

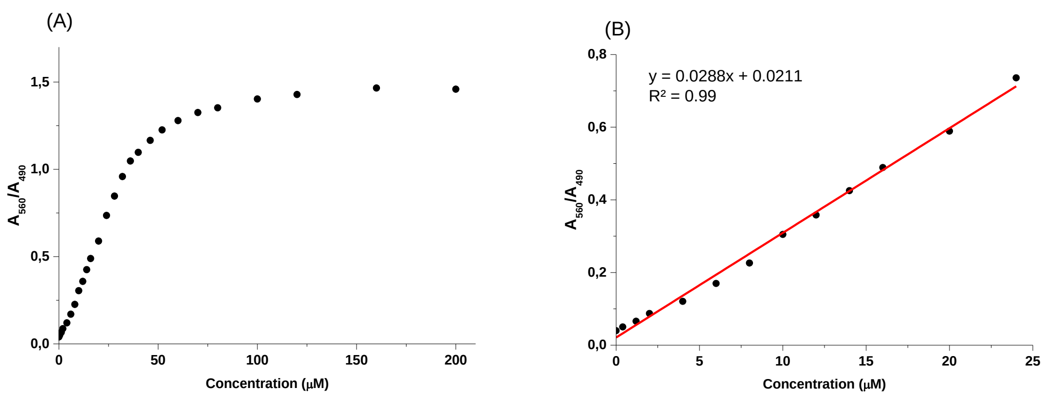

Fig. SD37. (A) Absorption ratio of **4a** (60 µM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4a** and increasing concentrations of Cu^{2+} (0–25 µM). pH=11.9, H_2O/DMSO (9:1 v/v)

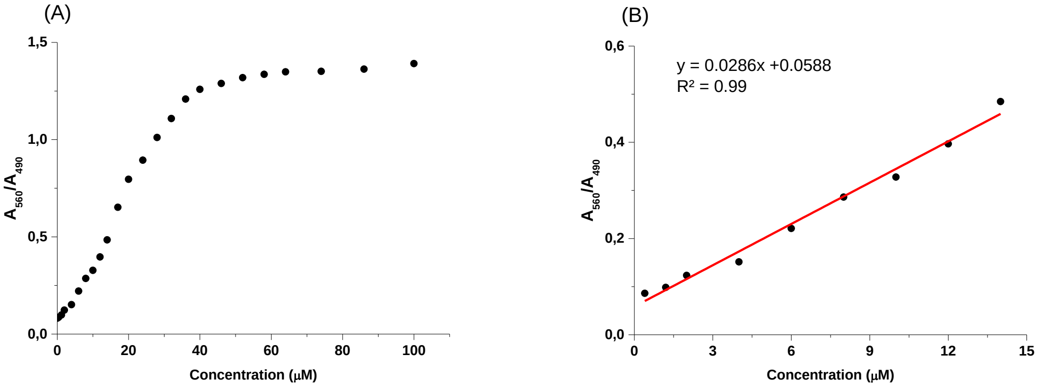

Fig. SD38. (A) Absorption ratio of **4b** (60 μM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4b** and increasing concentrations of Cu^{2+} (0–15 μM). pH=11.9, H_2O/DMSO (9:1 v/v)

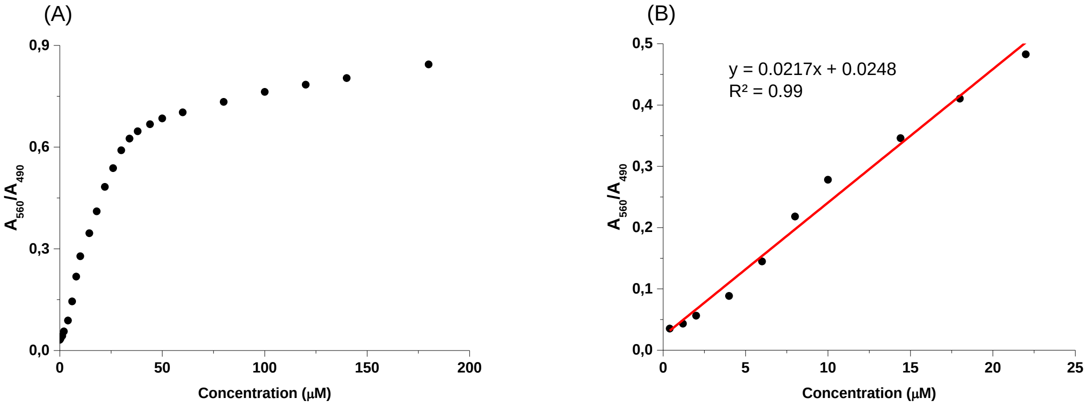

Fig. SD39. (A) Absorption ratio of **4c** (60 μM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4c** and increasing concentrations of Cu^{2+} (0–20 μM). pH=11.9, H_2O/DMSO (9:1 v/v)

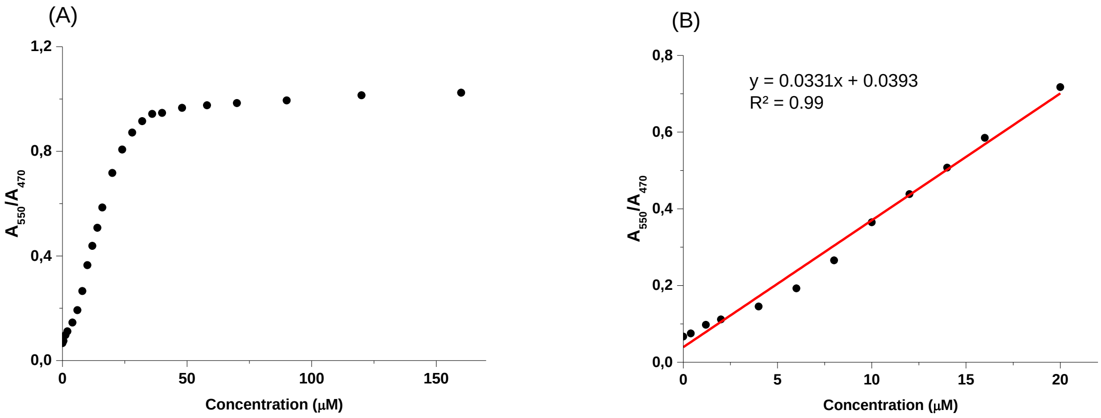

Fig. SD40. (A) Absorption ratio of **4d** (60 μM) versus [Cu^{2+}]; (B) Calibration curve between absorption ratio of **4d** and increasing concentrations of Cu^{2+} (0–20 μM). pH=11.9, H_2O/DMSO (9:1 v/v)

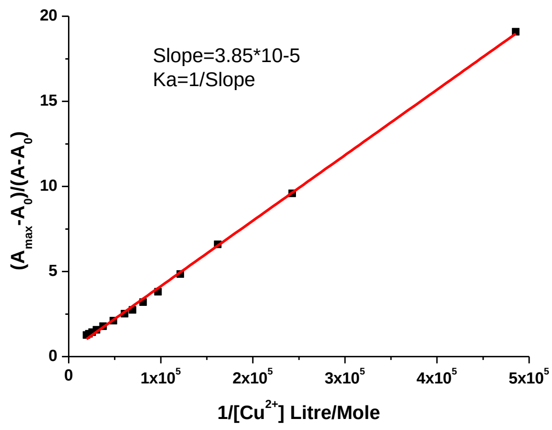

Fig. SD41. Benesi-Hildebrand plot to calculated the association constant of **4b** (60 µM) towards Cu^{2+} ions, pH 7.4, H_2O/DMSO (9:1 v/v)

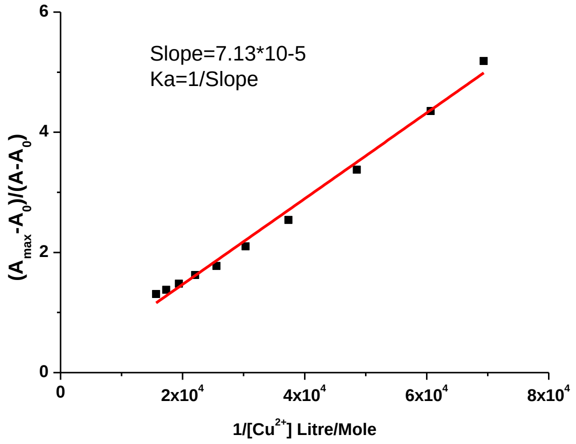

Fig. SD42. Benesi-Hildebrand plot to calculated the association constant of **4c** (60 µM) towards Cu^{2+} ions, pH 7.4, H_2O/DMSO (9:1 v/v)

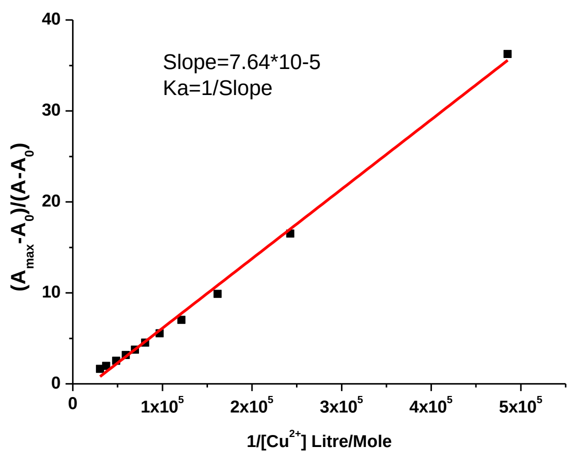

Fig. SD43. Benesi-Hildebrand plot to calculated the association constant of **4d** (60 µM) towards Cu^{2+} ions, pH 7.4, H_2O/DMSO (9:1 v/v)

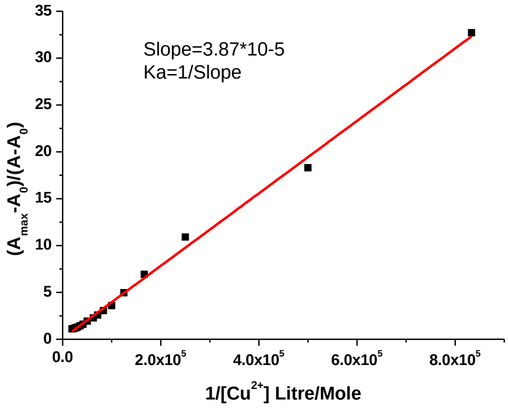

Fig. SD44. Benesi-Hildebrand plot to calculated the association constant of **4a** (60 µM) towards Cu^{2+} ions. pH=11.9, H_2O/DMSO (9:1 v/v)

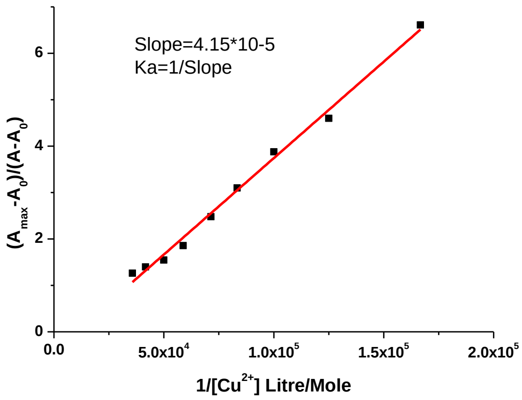

Fig. SD45. Benesi-Hildebrand plot to calculated the association constant of **4b** (60 µM) towards Cu^{2+} ions. pH=11.9, H_2O/DMSO (9:1 v/v)

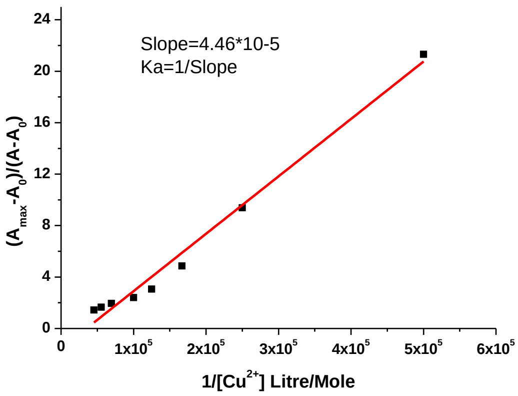

Fig. SD46. Benesi-Hildebrand plot to calculated the association constant of **4c** (60 µM) towards Cu^{2+} ions. pH=11.9, H_2O/DMSO (9:1 v/v)

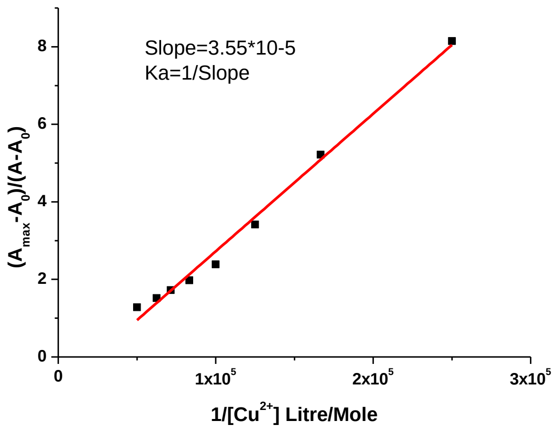

Fig. SD47. Benesi-Hildebrand plot to calculated the association constant of **4d** (60 μM) towards Cu^{2+} ions. pH=11.9, H_2O/DMSO (9:1 v/v)

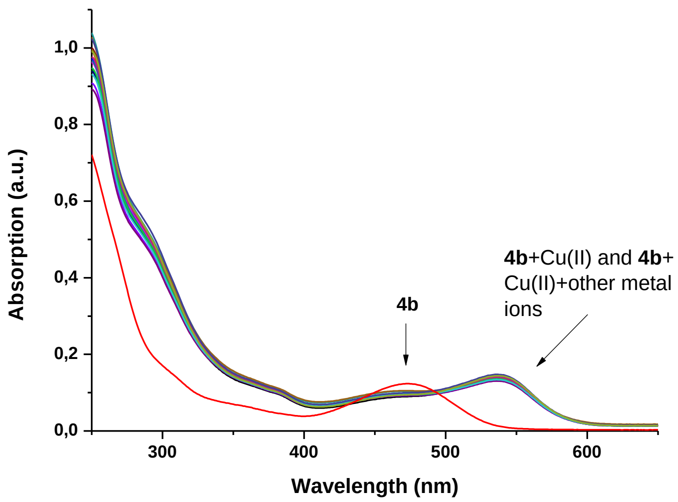

Fig. SD48. Absorption spectra of **4b** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 7.4, [**4b**] = 10 μM, [Cu^{2+}] = 100 μM, [metal ions] = 500 μM, H_2O/DMSO (9:1 v/v).

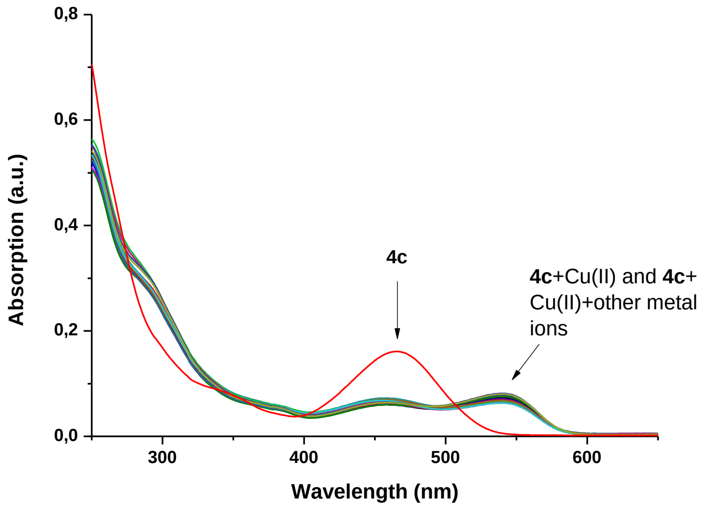

Fig. SD49. Absorption spectra of **4c** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 7.4, [**4c**] = 10 μM, [Cu^{2+}] = 100 μM, [metal ions] = 500 μM, H_2O/DMSO (9:1 v/v).

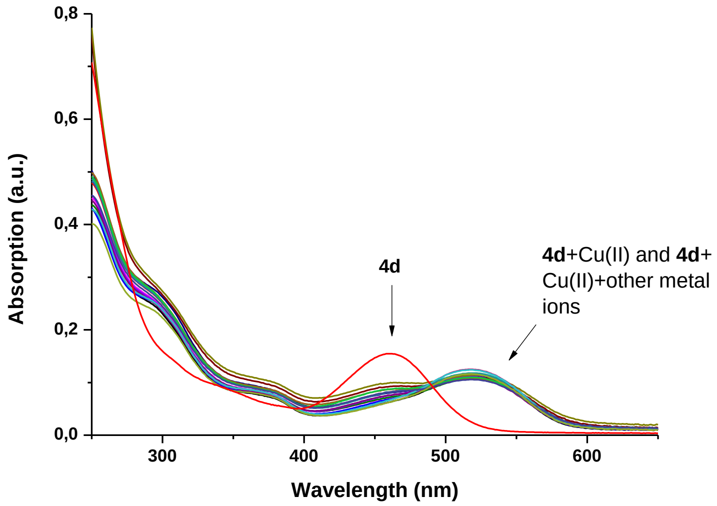

Fig. SD50. Absorption spectra of **4d** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 7.4, [**4d**] = 10 μM, [Cu^{2+}] = 100 μM, [metal ions] = 500 μM, H_2O/DMSO (9:1 v/v).

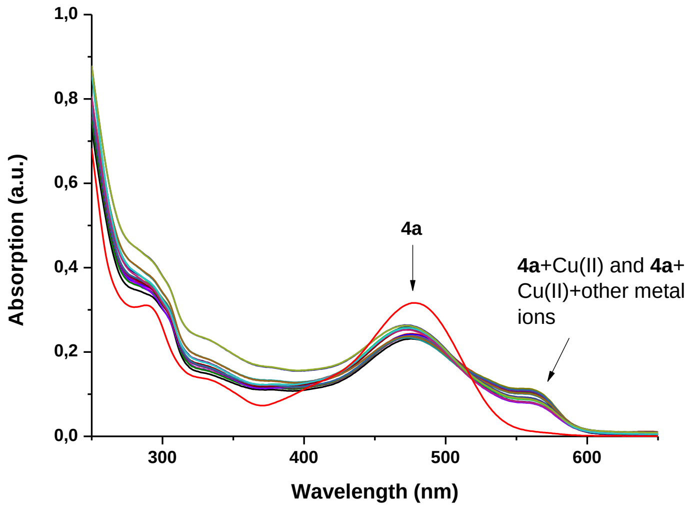

Fig. SD51. Absorption spectra of **4a** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4a**] = 10 µM, [Cu^{2+}] = 10 µM, [metal ions] = 10 µM, H_2O/DMSO (9:1 v/v).

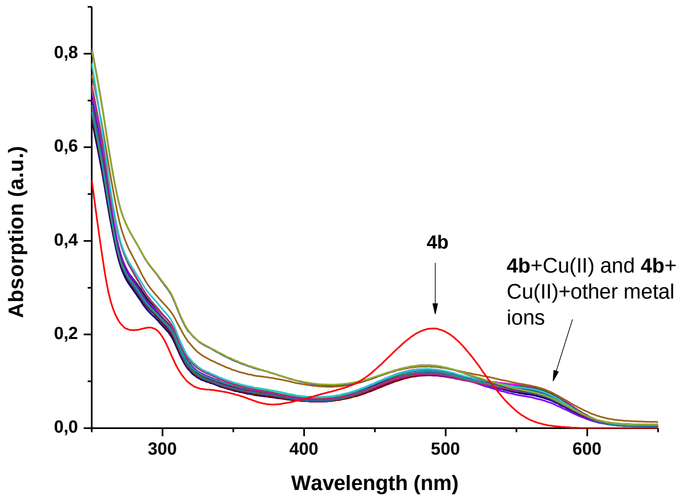

Fig. SD52. Absorption spectra of **4b** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4b**] = 10 µM, [Cu^{2+}] = 10 µM, [metal ions] = 10 µM, H_2O/DMSO (9:1 v/v).

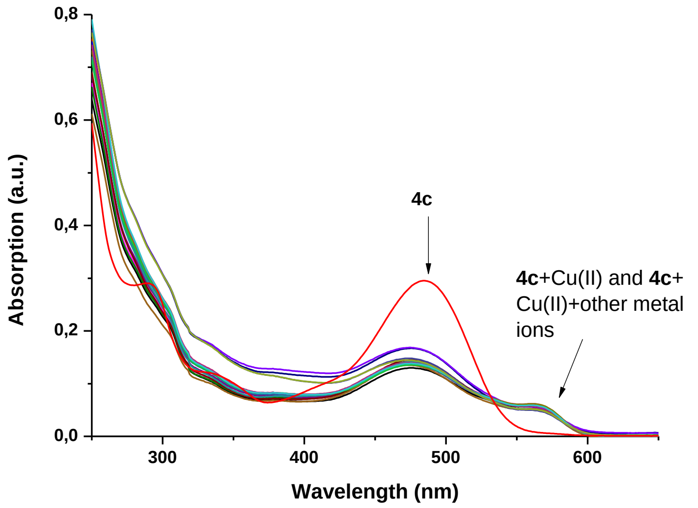

Fig. SD53. Absorption spectra of **4c** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4c**] = 10 μM, [Cu^{2+}] = 10 μM, [metal ions] = 10 μM, H_2O/DMSO (9:1 v/v).

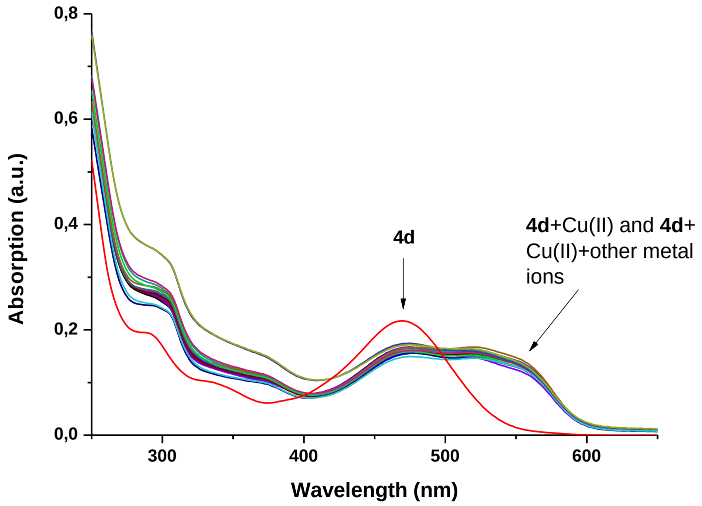

Fig. SD54. Absorption spectra of **4d** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4d**] = 10 μM, [Cu^{2+}] = 10 μM, [metal ions] = 10 μM, H_2O/DMSO (9:1 v/v).

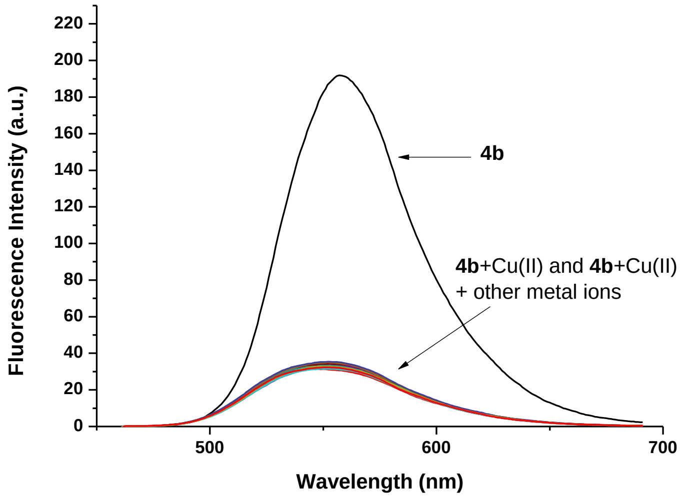

Fig. SD55. Fluorescence spectra of **4d** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 7.4, [**4b**] = 10 μM, [Cu^{2+}] = 100 μM, [metal ions] = 500 μM, H_2O/DMSO (9:1 v/v).

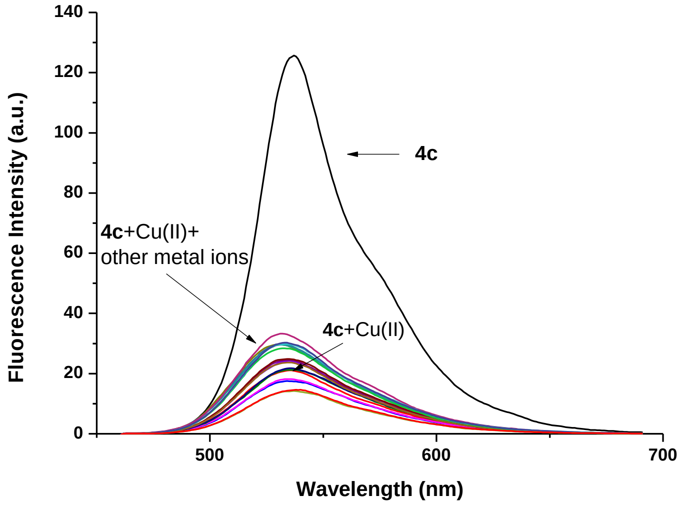

Fig. SD56. Fluorescence spectra of **4c** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 7.4, [**4c**] = 10 μM, [Cu^{2+}] = 100 μM, [metal ions] = 500 μM, H_2O/DMSO (9:1 v/v).

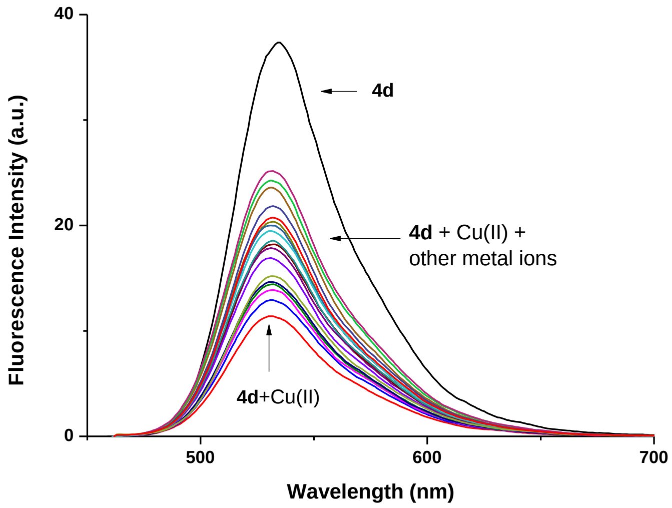

Fig. SD57. Fluorescence spectra of **4d** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 7.4, [**4b**] = 10 μM, [Cu^{2+}] = 100 μM, [metal ions] = 500 μM, H_2O/DMSO (9:1 v/v).

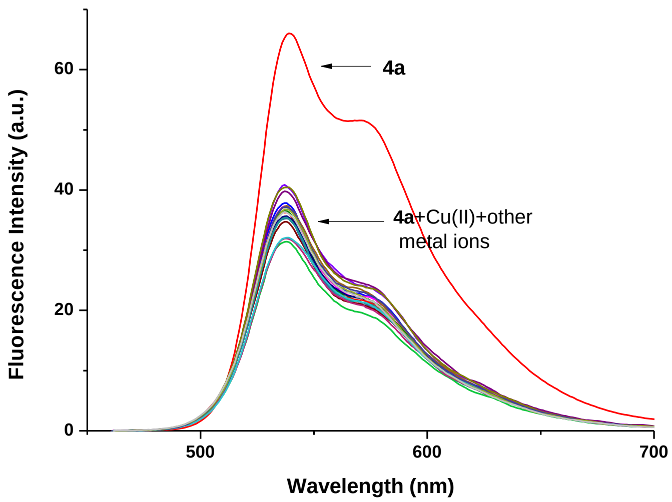

Fig. SD58. Fluorescence spectra of **4a** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4a**] = 10 μM, [Cu^{2+}] = 10 μM, [metal ions] = 10 μM, H_2O/DMSO (9:1 v/v).

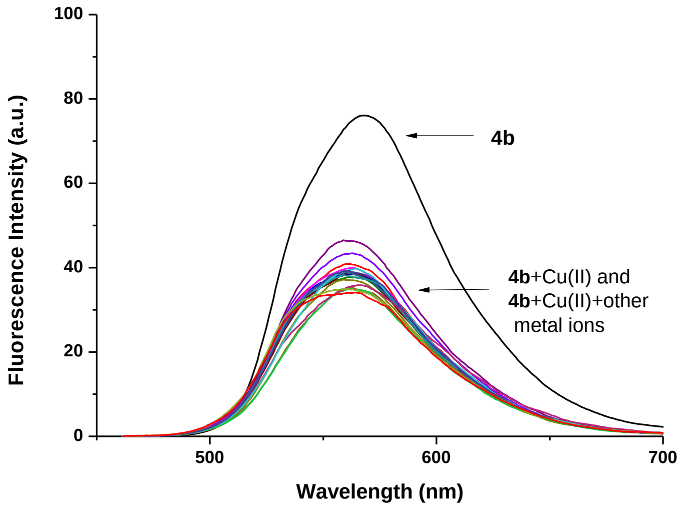

Fig. SD59. Fluorescence spectra of **4b** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4b**] = 10 μM, [Cu^{2+}] = 10 μM, [metal ions] = 10 μM, H_2O/DMSO (9:1 v/v).

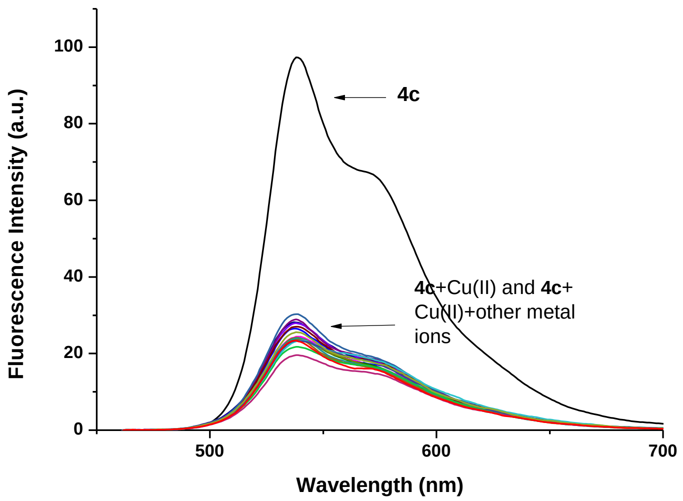

Fig. SD60. Fluorescence spectra of **4c** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4c**] = 10 μM, [Cu^{2+}] = 10 μM, [metal ions] = 10 μM, H_2O/DMSO (9:1 v/v).

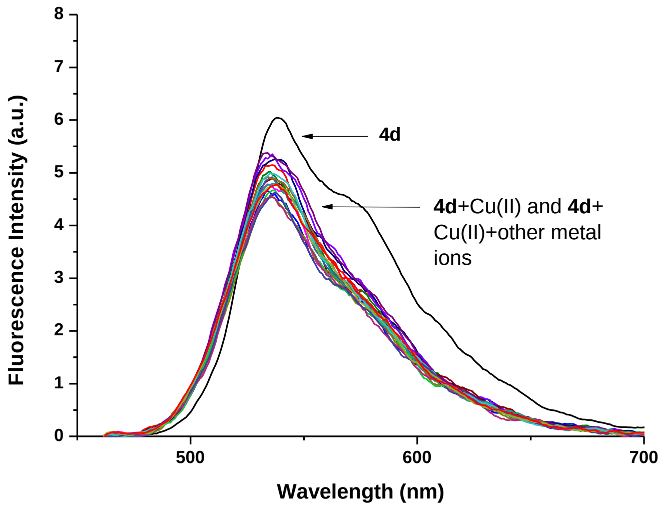

Fig. SD61. Fluorescence spectra of **4d** upon interaction with Cu^{2+} ions in the presence of competing metal ions. pH 11.9, [**4d**] = 10 µM, [Cu^{2+}] = 10 µM, [metal ions] = 10 µM, H_2O/DMSO (9:1 v/v).

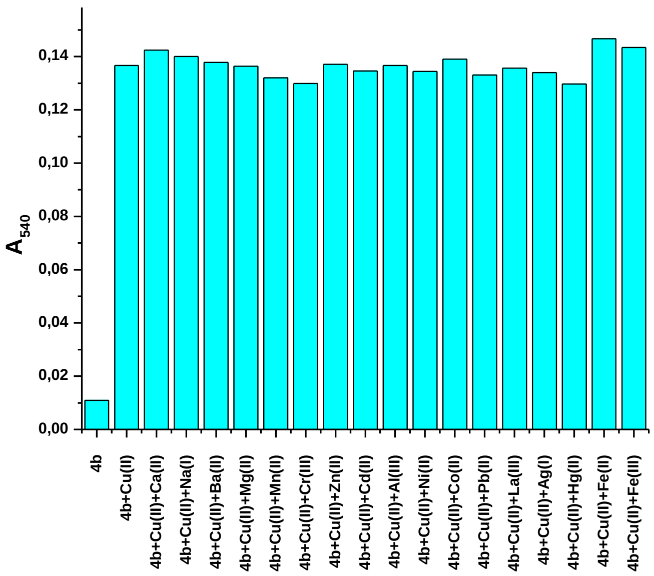

Fig. SD62. Absorption change of **4b** (10 µM**)** by Cu^{2+} ion (100 µM) in presence of competing metal ions (500 µM), pH 7.4, H_2O/DMSO (9:1 v/v)

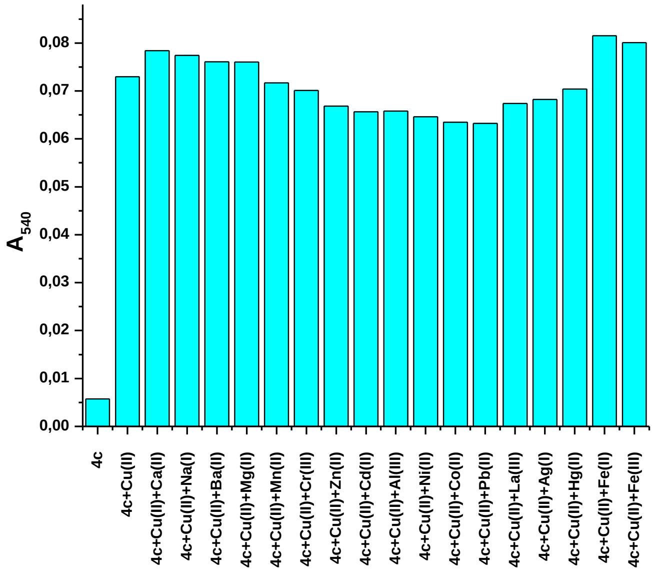

Fig. SD63. Absorption change of **4c** (10 μM**)** by Cu^{2+} ion (100 μM) in presence of competing metal ions (500 μM), pH 7.4, H_2O/DMSO (9:1 v/v)

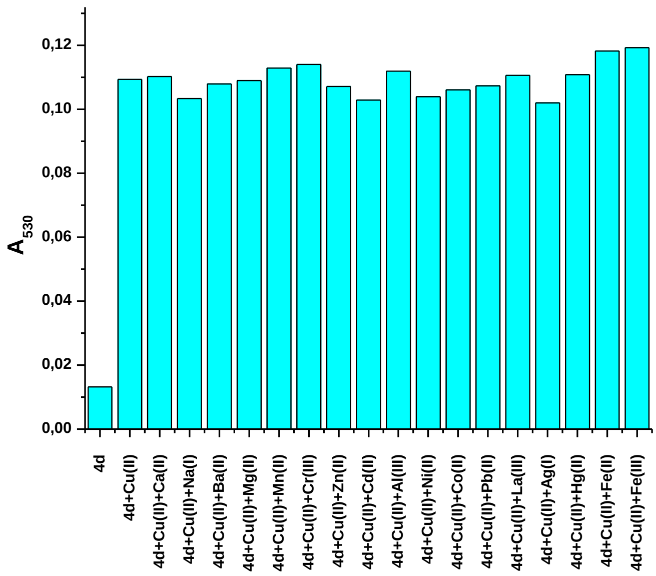

Fig. SD64. Absorption change of **4d (**10 μM**)** by Cu^{2+} ion (100 μM) in presence of competing metal ions (500 μM), pH 7.4, H_2O/DMSO (9:1 v/v)

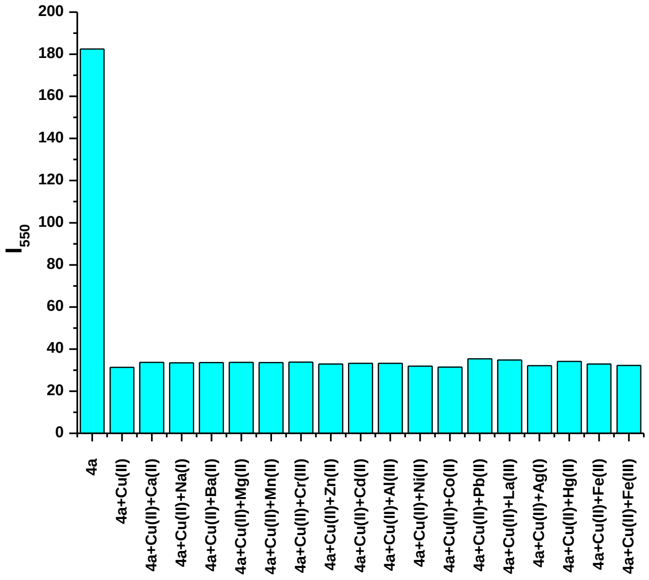

Fig. SD65. Fluorescence change of **4b (**10 μM**)** by Cu^{2+} ion (100 μM) in presence of competing metal ions (500 μM), pH 7.4, H_2O/DMSO (9:1 v/v)

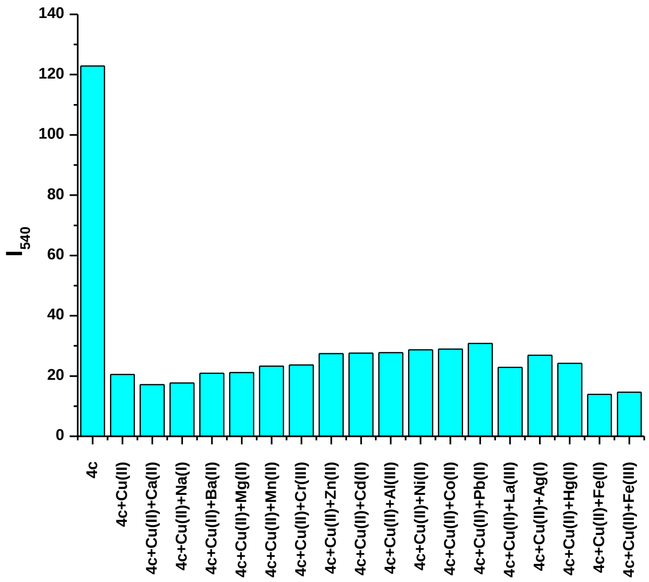

Fig. SD66. Fluorescence change of **4c (**10 μM**)** by Cu^{2+} ion (100 μM) in presence of competing metal ions (500 μM), pH 7.4, H_2O/DMSO (9:1 v/v)

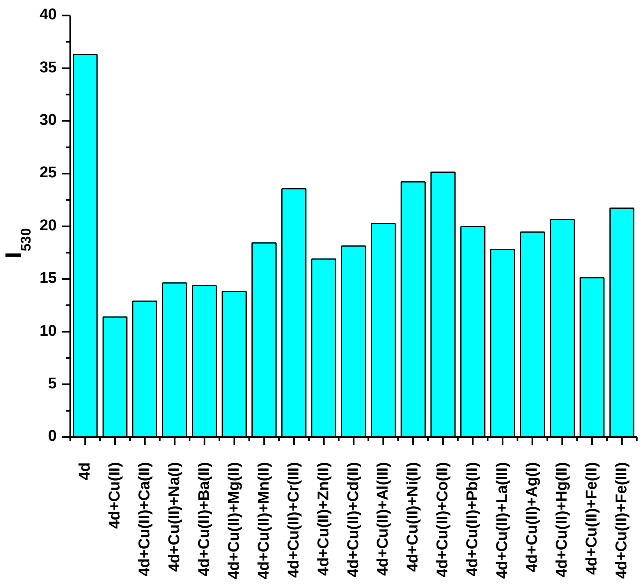

Fig. SD67. Fluorescence change of **4d (**10 μM**)** by Cu^{2+} ion (100 μM) in presence of competing metal ions (500 μM), pH 7.4, H_2O/DMSO (9:1 v/v)

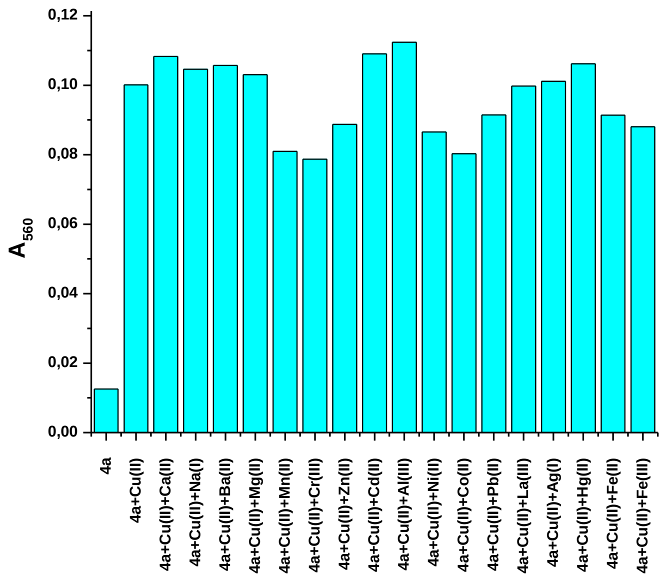

Fig. SD68. Absorption change of **4b (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

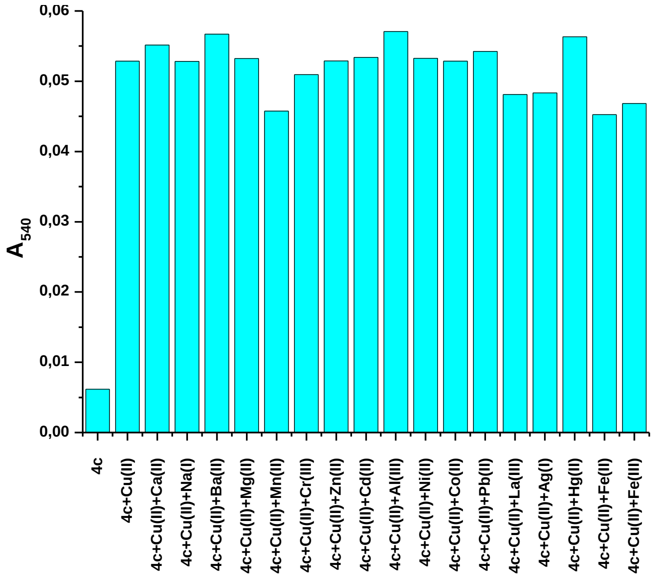

Fig. SD69. Absorption change of **4c (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

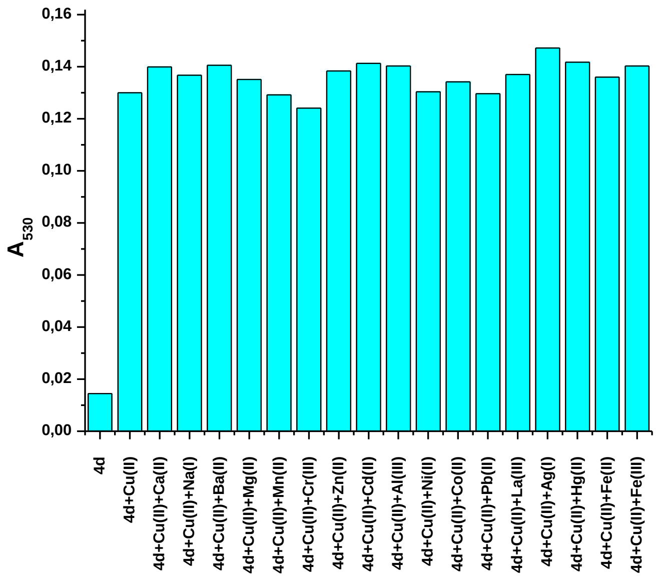

Fig. SD70. Absorption change of **4d (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

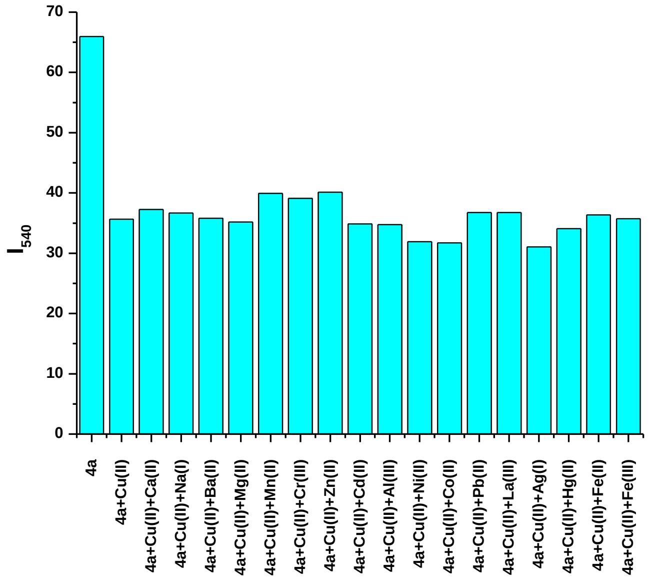

Fig. SD71. Fluorescence change of **4a (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

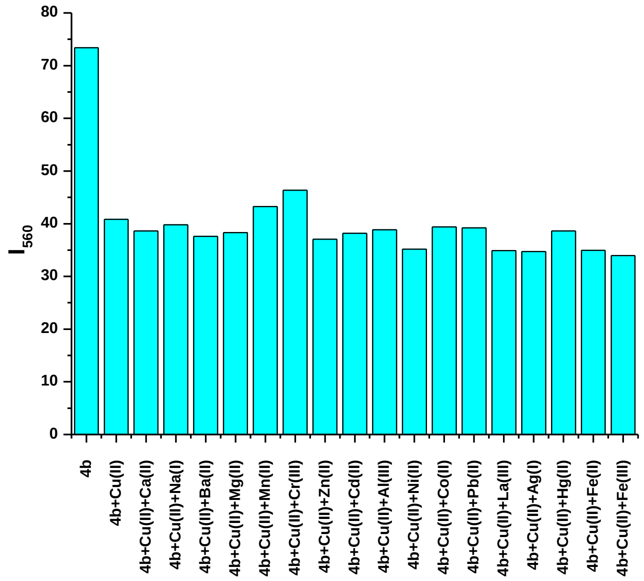

Fig. SD72. Fluorescence change of **4b (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

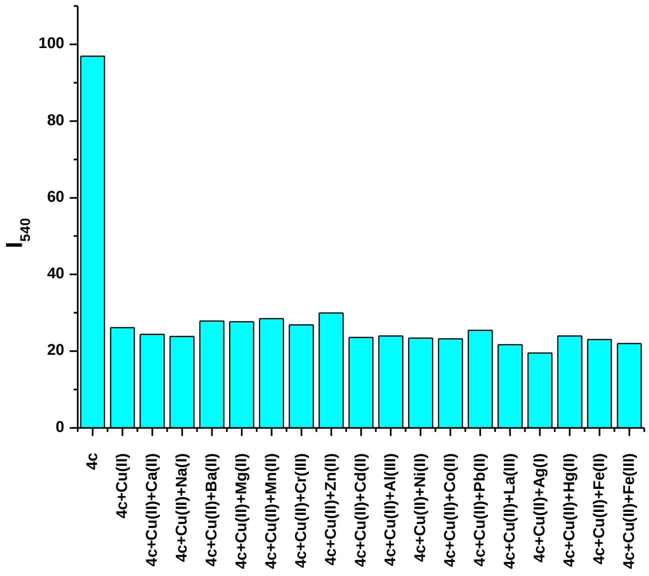

Fig. SD73. Fluorescence change of **4c (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

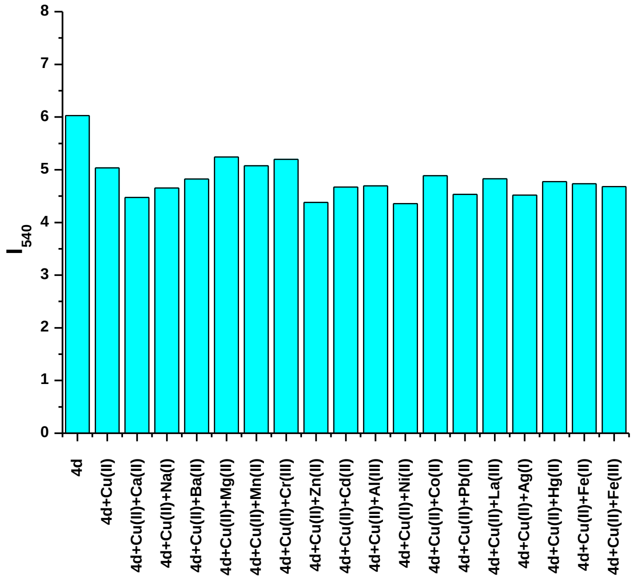

Fig. SD74. Fluorescence change of **4d (**10 μM**)** by Cu^{2+} ion (10 μM) in presence of competing metal ions (10 μM), pH 11.9, H_2O/DMSO (9:1 v/v)

E. Cartesian coordinates

4a neutral

Water CPCM. B3LYP-D4/def2-SVP

Atom	X	Y	Z
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6	-0.306500000	-0.147464000	-1.955976000
6	-0.296544000	-1.386828000	-1.209027000
6	-0.632494000	1.091062000	-1.348505000
6	-0.980656000	1.146260000	0.088022000
6	-0.708399000	-0.077704000	0.877950000
6	-0.326775000	-1.294150000	0.252691000
6	-0.019692000	1.038823000	-4.081800000
6	-0.650521000	2.272234000	-2.102136000
8	-1.413676000	2.173449000	0.611381000
6	-0.750154000	0.017885000	2.279572000
6	0.116163000	-2.346410000	1.084376000
6	0.097662000	-2.227376000	2.471306000
6	-0.367523000	-1.052087000	3.079674000
1	-1.066187000	0.966748000	2.717254000
1	0.522795000	-3.250848000	0.633529000
1	0.456533000	-3.057482000	3.085206000
1	-0.397952000	-0.968233000	4.168695000
6	-0.332439000	2.249047000	-3.459657000
1	0.221855000	1.002383000	-5.147030000
1	-0.916543000	3.203406000	-1.599475000
1	-0.334181000	3.172309000	-4.043588000
6	-0.262728000	-2.579409000	-1.927560000
6	0.129946000	-2.582171000	-3.366391000
7	0.259159000	-1.360192000	-3.954189000
8	0.319177000	-3.634186000	-3.979145000
7	-0.541677000	-3.835404000	-1.483683000
1	-0.365978000	-4.537019000	-2.207282000
6	-1.624389000	-4.211739000	-0.590802000
1	-1.351806000	-4.045573000	0.465147000
6	-2.941408000	-3.464946000	-0.859751000
1	-3.272724000	-3.630358000	-1.896628000
1	-3.719472000	-3.820394000	-0.170047000
1	-2.808623000	-2.386056000	-0.700584000
6	-1.817113000	-5.714921000	-0.746478000
8	-2.636781000	-6.202046000	0.182865000
8	-1.301909000	-6.384635000	-1.613962000
1	0.499067000	-1.366254000	-4.943965000
1	-2.756936000	-7.158553000	0.030427000

4a monoanion

Water CPCM. B3LYP-D4/def2-SVP

Atom	X	Y	Z
6	-0.020658000	-0.165981000	-3.351734000
6	-0.315812000	-0.156264000	-1.964628000
6	-0.289109000	-1.384546000	-1.207233000
6	-0.660079000	1.085580000	-1.371263000
6	-1.001529000	1.153901000	0.063957000
6	-0.714842000	-0.057688000	0.863487000
6	-0.322217000	-1.278104000	0.248408000
6	-0.039248000	1.011985000	-4.102857000
6	-0.695718000	2.258809000	-2.140513000
8	-1.441662000	2.185446000	0.579450000
6	-0.760510000	0.048762000	2.265595000
6	0.125997000	-2.320080000	1.092926000
6	0.101635000	-2.188930000	2.477187000
6	-0.373469000	-1.010589000	3.075745000
1	-1.085090000	0.999412000	2.693311000
1	0.539820000	-3.224791000	0.651075000
1	0.465062000	-3.010740000	3.099862000
1	-0.406974000	-0.918085000	4.164072000
6	-0.376984000	2.225999000	-3.495758000
1	0.209100000	0.968294000	-5.166406000
1	-0.975435000	3.191078000	-1.647185000
1	-0.393474000	3.141806000	-4.091206000
6	-0.240303000	-2.593124000	-1.915240000
6	0.198261000	-2.597787000	-3.345787000
7	0.298841000	-1.377502000	-3.943988000
8	0.439277000	-3.644875000	-3.946743000
7	-0.541499000	-3.828413000	-1.476617000
1	-0.364492000	-4.585032000	-2.151868000
6	-1.578972000	-4.260310000	-0.552373000
1	-1.222283000	-4.232901000	0.492148000
6	-2.860767000	-3.429112000	-0.637007000
1	-3.246357000	-3.417733000	-1.670031000
1	-3.614423000	-3.892083000	0.014852000
1	-2.710163000	-2.389238000	-0.312176000
6	-1.868268000	-5.771551000	-0.864255000
8	-2.707083000	-6.319701000	-0.120797000
8	-1.234428000	-6.277690000	-1.824484000
1	0.558345000	-1.387920000	-4.928583000

4a dianion

Water CPCM. B3LYP-D4/def2-SVP

Atom	X	Y	Z
6	-0.057195000	-0.226961000	-3.359690000
6	-0.328270000	-0.161019000	-1.950208000
6	-0.302845000	-1.377235000	-1.184745000
6	-0.643184000	1.091400000	-1.357685000
6	-0.949081000	1.178065000	0.079718000
6	-0.686373000	-0.037194000	0.881864000
6	-0.330307000	-1.271183000	0.267685000
6	-0.101071000	0.974999000	-4.098382000
6	-0.691755000	2.261083000	-2.137667000

1 Ligand $4a^{1-}$ + Cu^{2+} at pH = 7.3

Water CPCM. B3LYP-D4/def2-SVP

Atom	X	Y	Z
6	-0.326175000	0.032972000	-3.331896000
6	-0.220651000	-0.062690000	-1.925850000
6	-0.301339000	-1.357881000	-1.277912000
6	-0.134592000	1.137274000	-1.177848000
6	-0.165576000	1.094634000	0.305117000
6	-0.003756000	-0.241699000	0.935294000
6	0.026726000	-1.425000000	0.157188000
6	-0.245013000	1.278870000	-3.975864000
6	-0.087000000	2.372945000	-1.824539000

8	-1.351592000	2.225123000	0.606911000
6	-0.722754000	0.074092000	2.285320000
6	0.094140000	-2.320758000	1.119158000
6	0.077536000	-2.185281000	2.501932000
6	-0.362931000	-0.990936000	3.099222000
1	-1.020194000	1.035563000	2.709087000
1	0.483318000	-3.236436000	0.677692000
1	0.421440000	-3.014401000	3.126610000
1	-0.389758000	-0.893627000	4.187551000
6	-0.413311000	2.200343000	-3.501516000
1	0.119939000	0.913574000	-5.167666000
1	-0.949260000	3.202164000	-1.648576000
1	-0.440105000	3.109177000	-4.109744000
6	-0.239075000	-2.576473000	-1.909667000
6	0.202146000	-2.552426000	-3.352499000
7	0.256912000	-1.388101000	-4.005605000
8	0.468129000	-3.658673000	-3.889197000
7	-0.526304000	-3.820504000	-1.473507000
1	-0.342703000	-4.534482000	-2.190073000
6	-1.577426000	-4.270998000	-0.574888000
1	-1.246242000	-4.244979000	0.478169000
6	-2.866116000	-3.449772000	-0.676744000
1	-3.237887000	-3.442532000	-1.715217000
1	-3.627078000	-3.914569000	-0.034313000
1	-2.723859000	-2.407774000	-0.354704000
6	-1.861901000	-5.780405000	-0.889351000
8	-2.689447000	-6.335372000	-0.134269000
8	-1.246005000	-6.285785000	-1.860622000

8	-0.262504000	2.116536000	0.975901000
6	0.237551000	-0.295297000	2.315959000
6	0.452737000	-2.614121000	0.782442000
6	0.709141000	-2.651649000	2.152708000
6	0.566581000	-1.498507000	2.933616000
1	0.190196000	0.636070000	2.883020000
1	0.678823000	-3.502039000	0.190465000
1	1.040497000	-3.587455000	2.609280000
1	0.754626000	-1.533189000	4.009289000
6	-0.115630000	2.440294000	-3.222330000
1	-0.301323000	1.319390000	-5.066183000
1	-0.035278000	3.278144000	-1.217795000
1	-0.059364000	3.407765000	-3.726218000
6	-0.729538000	-2.420764000	-2.042729000
6	-0.749410000	-2.346185000	-3.509221000
7	-0.517547000	-1.123216000	-4.058029000
8	-0.918560000	-3.357755000	-4.205104000
7	-1.149468000	-3.689344000	-1.555322000
1	-0.872909000	-3.806752000	-0.585569000
6	-2.627203000	-4.000550000	-1.651368000
1	-2.861380000	-4.471106000	-0.681932000
6	-3.520507000	-2.779817000	-1.815502000
1	-3.365545000	-2.276721000	-2.781655000
1	-4.565637000	-3.114937000	-1.779381000
1	-3.354248000	-2.052195000	-1.007804000
6	-2.909407000	-5.114400000	-2.684386000
8	-4.049450000	-5.257471000	-3.113817000
8	-1.920392000	-5.895438000	-2.962118000
1	-0.521236000	-1.076012000	-5.076039000
29	-0.169135000	-5.129385000	-2.687053000
17	1.908181000	-4.374435000	-2.168330000
8	0.614093000	-6.622070000	-3.823124000
1	0.099452000	-7.441938000	-3.730671000
1	1.507912000	-6.828798000	-3.500198000

2 Ligands $4a^{2-}$ + Cu^{2+} at pH = 11.9

Water CPCM. B3LYP-D4/def2-SVP

Atom	X	Y	Z
6	-1.627641000	-1.258611000	-3.511683000
6	-1.690201000	-0.870258000	-2.139883000
6	-0.771845000	-1.457322000	-1.199653000
6	-2.681181000	0.065969000	-1.737528000
6	-2.786659000	0.478965000	-0.321237000
6	-1.662140000	0.083396000	0.561167000
6	-0.666228000	-0.828833000	0.130208000
6	-2.536964000	-0.687434000	-4.432639000
6	-3.577896000	0.592411000	-2.668575000
8	-3.722224000	1.165496000	0.089946000
6	-1.562332000	0.705723000	1.818462000
6	0.460224000	-1.008227000	0.958678000
6	0.566707000	-0.357196000	2.182895000
6	-0.460194000	0.485792000	2.634866000
1	-2.361375000	1.386675000	2.117221000
1	1.252111000	-1.677528000	0.629192000
1	1.457698000	-0.511794000	2.797288000
1	-0.383242000	0.980052000	3.606529000
6	-3.500567000	0.222189000	-4.018485000
1	-2.464065000	-0.990622000	-5.479904000

1	-4.334965000	1.297242000	-2.320227000
1	-4.199573000	0.646569000	-4.743453000
6	-0.003621000	-2.527316000	-1.652649000
6	0.060741000	-2.785917000	-3.093602000
7	-0.714266000	-2.166480000	-3.964611000
8	0.926333000	-3.666471000	-3.518542000
7	0.765044000	-3.386142000	-0.862966000
1	1.438611000	-3.835969000	-1.480259000
6	0.114331000	-4.424401000	-0.032511000
1	0.888653000	-5.204668000	0.077648000
6	-0.299018000	-3.998113000	1.373327000
1	-1.106658000	-3.253456000	1.355538000
1	-0.665210000	-4.879298000	1.916761000
1	0.555629000	-3.577587000	1.919159000
6	-1.044485000	-5.151003000	-0.759510000
8	-1.947755000	-5.676349000	-0.093022000
8	-1.016067000	-5.224191000	-2.045624000
6	-2.262269000	-8.534907000	-5.937244000
6	-1.474079000	-9.467797000	-6.672151000
6	-0.119360000	-9.730931000	-6.256677000
6	-2.044494000	-10.076736000	-7.822900000
6	-1.259603000	-11.036592000	-8.628296000
6	0.050854000	-11.451115000	-8.071754000
6	0.602389000	-10.838653000	-6.917534000
6	-3.578298000	-8.242452000	-6.363953000
6	-3.343268000	-9.762585000	-8.223292000
8	-1.687709000	-11.499742000	-9.684835000
6	0.713650000	-12.520830000	-8.699057000
6	1.792076000	-11.388001000	-6.394148000
6	2.421157000	-12.467557000	-7.005888000
6	1.896626000	-13.029506000	-8.179064000
1	0.258106000	-12.950135000	-9.593127000
1	2.223131000	-10.943578000	-5.499708000
1	3.336646000	-12.872735000	-6.566674000
1	2.403438000	-13.864870000	-8.668582000
6	-4.113433000	-8.847948000	-7.491500000
1	-4.158887000	-7.522936000	-5.781516000
1	-3.740685000	-10.243878000	-9.118411000
1	-5.131619000	-8.610777000	-7.809396000
6	0.392531000	-8.942101000	-5.227623000
6	-0.521580000	-8.105250000	-4.448764000
7	-1.784403000	-7.911165000	-4.817547000
8	-0.082925000	-7.541265000	-3.363475000
7	1.744439000	-8.877221000	-4.854505000
1	1.768228000	-8.515911000	-3.898914000
6	2.626807000	-7.973990000	-5.659000000
1	3.595908000	-7.984605000	-5.136433000
6	2.824654000	-8.375165000	-7.109962000
1	1.873272000	-8.396846000	-7.659217000
1	3.469874000	-7.628949000	-7.597766000
1	3.307304000	-9.357514000	-7.192909000
6	2.032753000	-6.553579000	-5.509457000
8	1.489967000	-5.991722000	-6.470964000
8	2.070878000	-6.101995000	-4.306696000
29	0.432053000	-5.576047000	-3.360217000
19	-2.510639000	-7.472354000	-2.046068000
19	0.319169000	-3.633349000	-6.216574000
8	-1.428735000	-5.146956000	-4.918681000
1	-1.975767000	-4.635095000	-4.302355000

1 -1.800877000 -6.061081000 -4.917083000