Electronic Supplementary Information (ESI)

Meso-functionalization of calix[4]arene with 1,3,7-triazapyrene in the design of novel fluorophores with the dual target detection of Al^{3+} and Fe^{3+} cations

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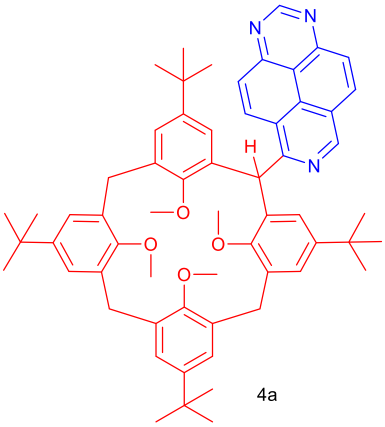
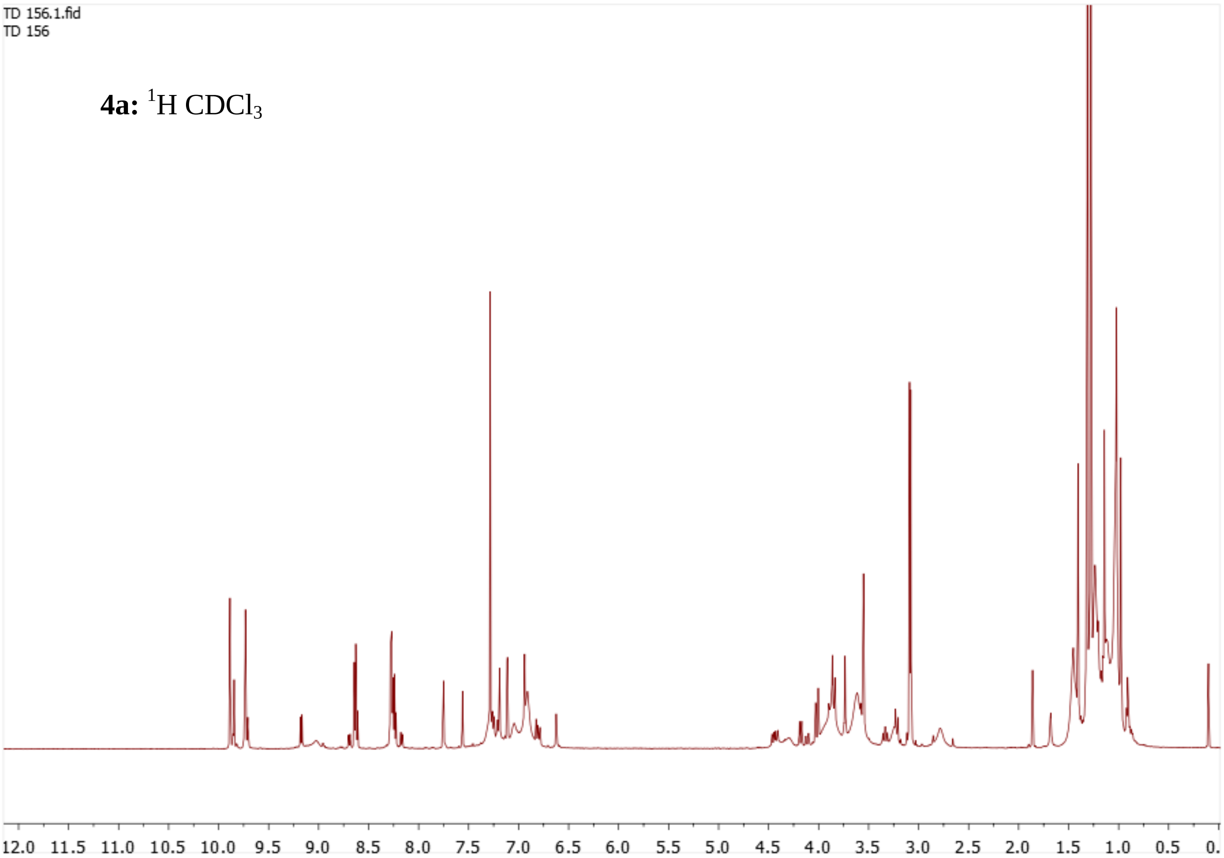
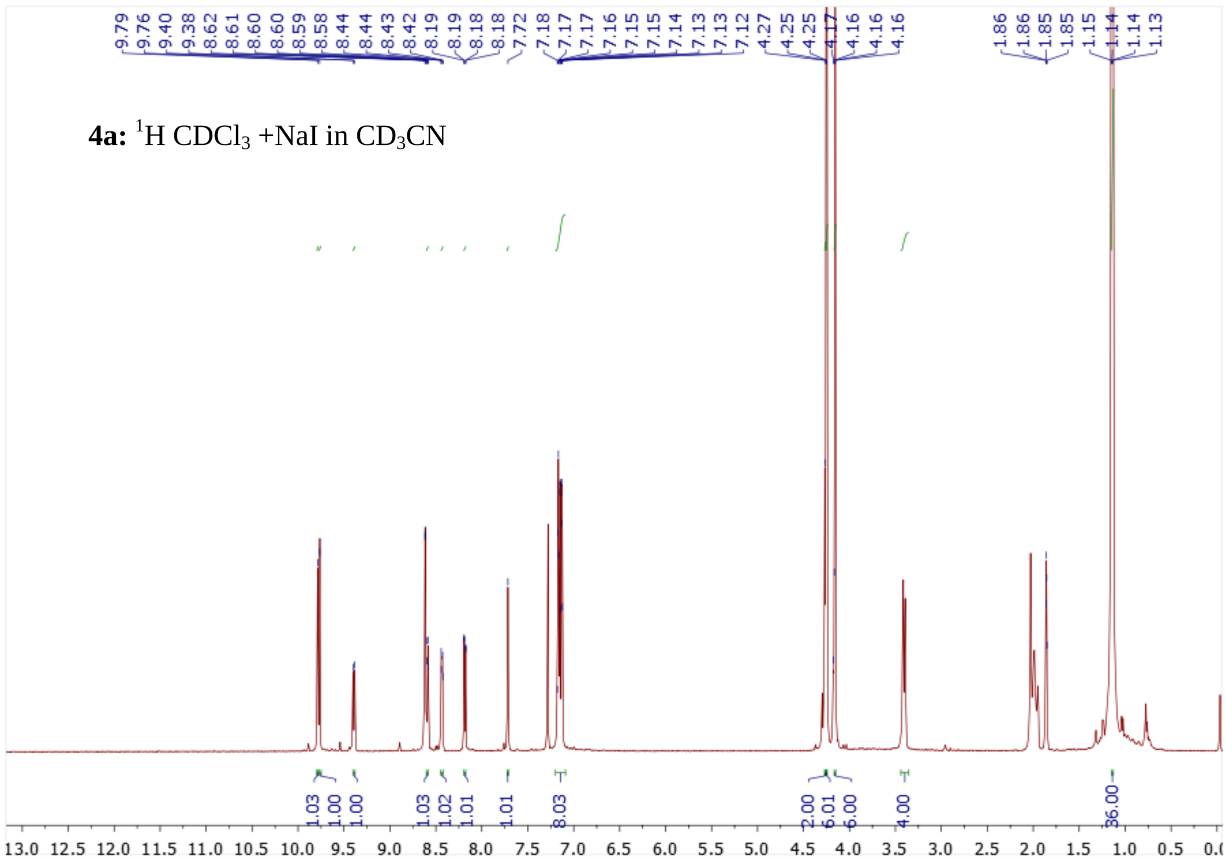


4a

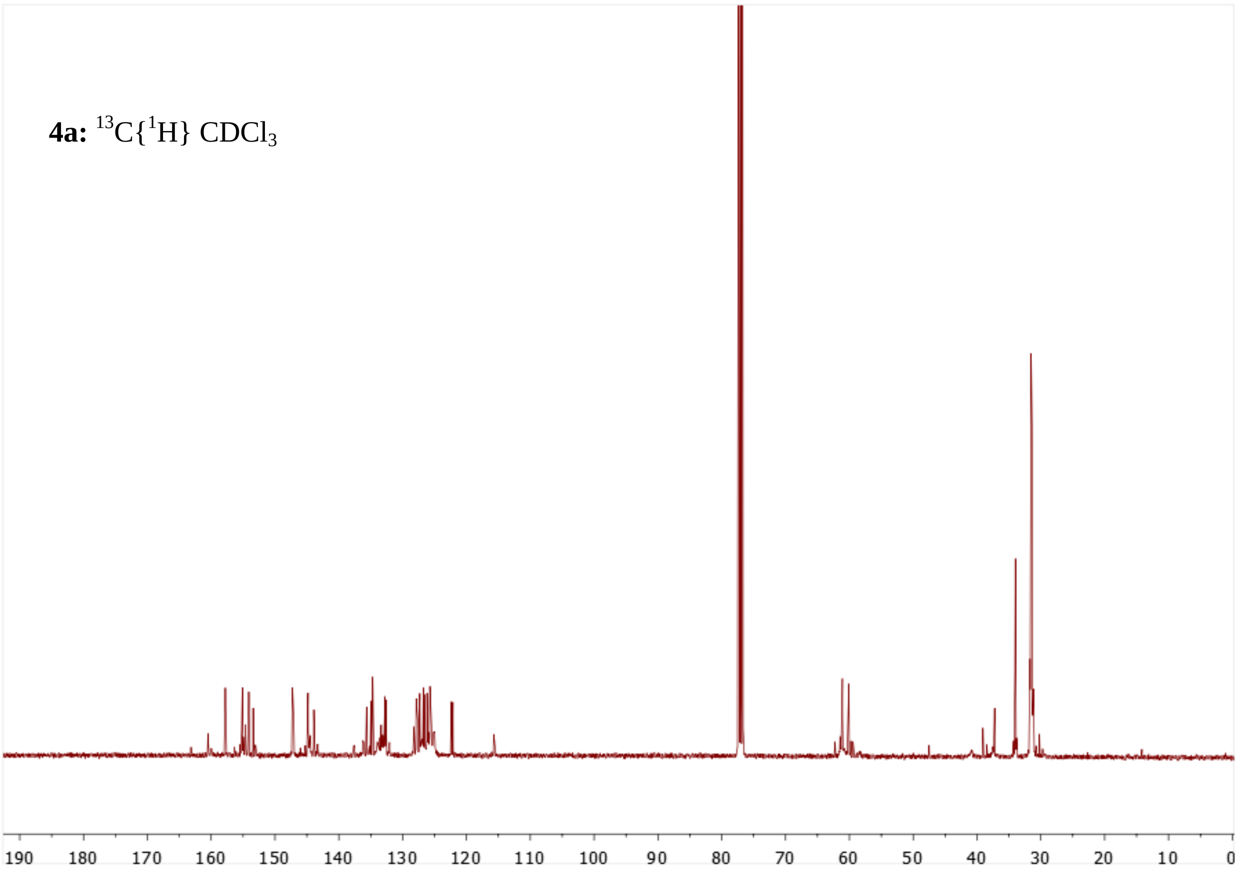
Spectrum S1. ^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



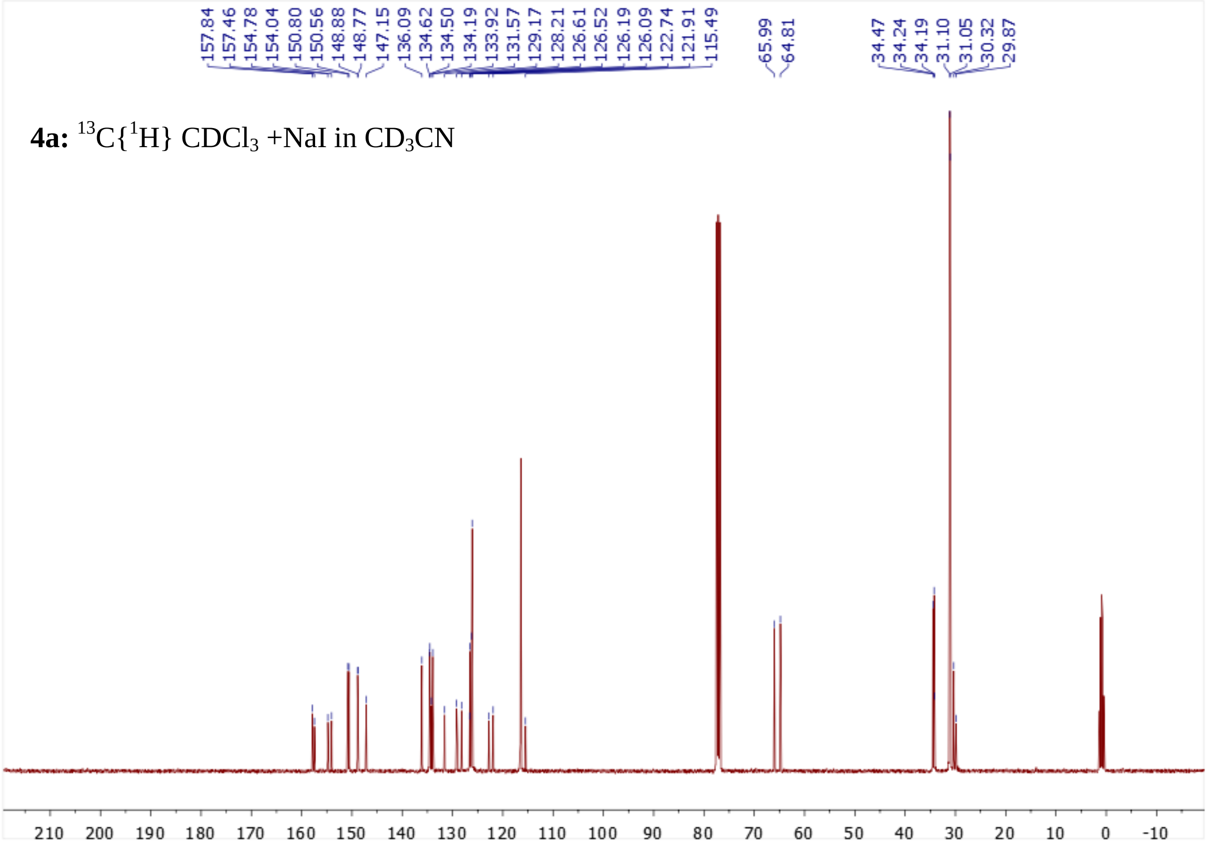
Spectrum S2. ^{1}H NMR (400 MHz, $CDCl_3$) of **4a** with addition of NaI



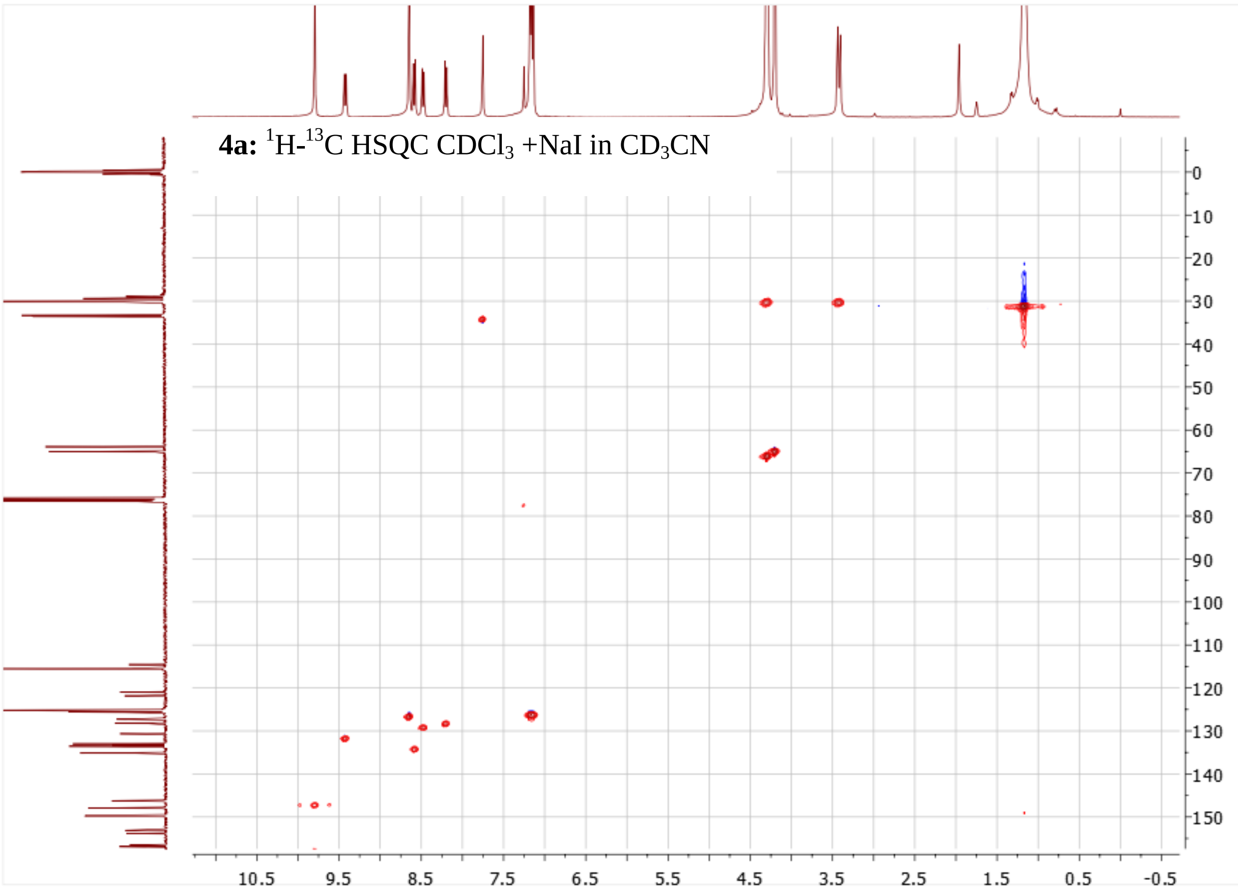
Spectrum S3. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **4a**



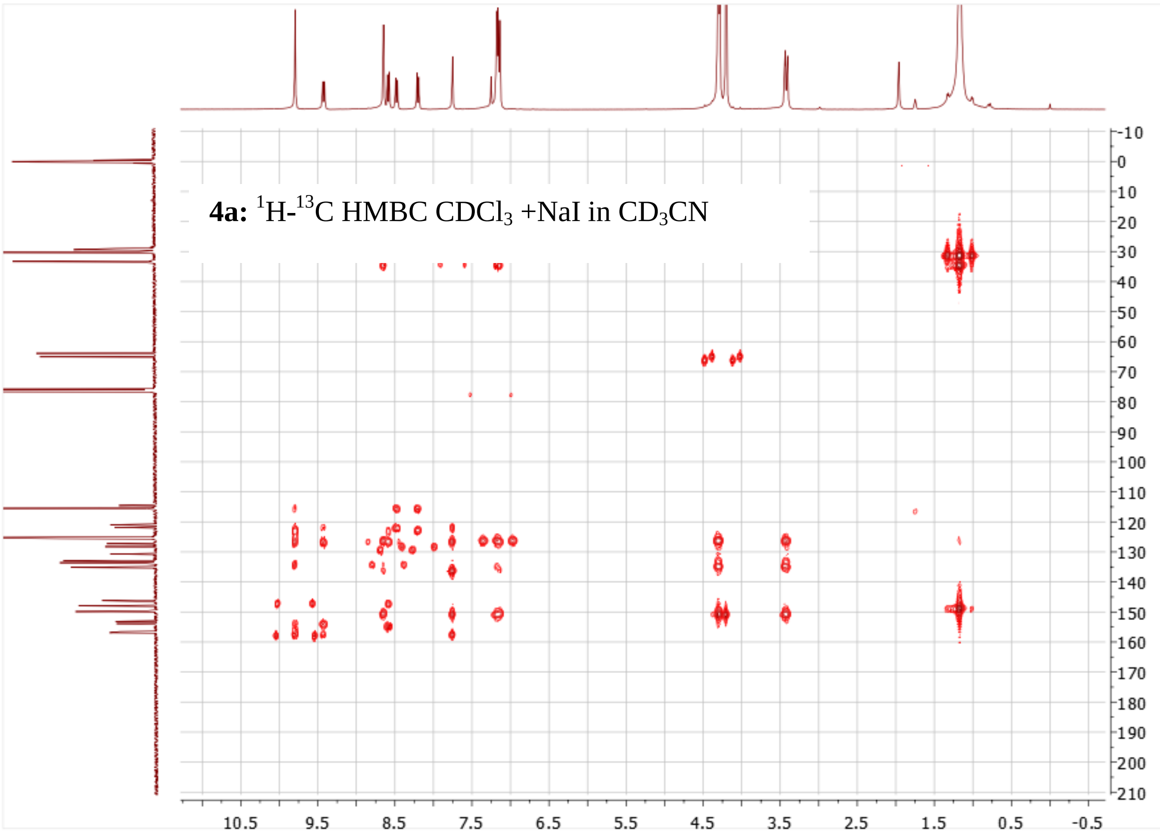
Spectrum S4. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **4a** with addition of NaI



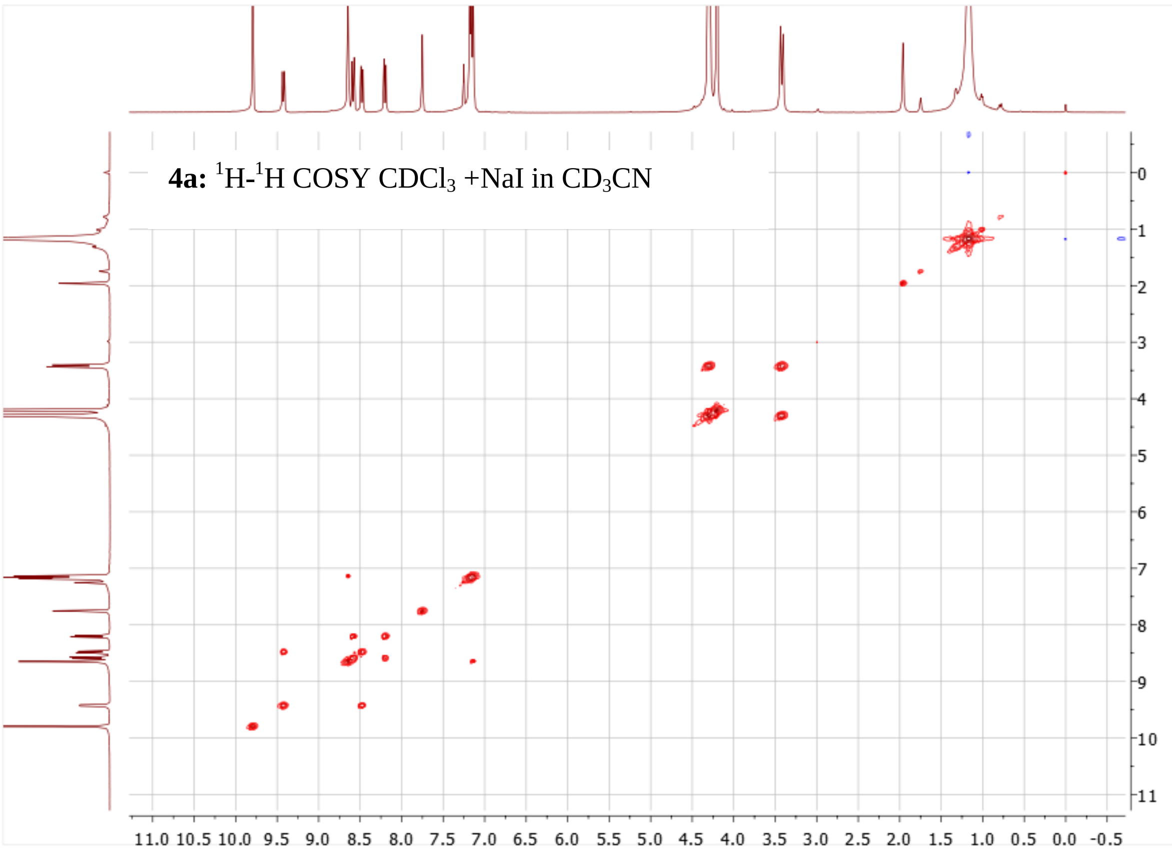
Spectrum S5. ^{1}H-^{13}C HSQC NMR ($CDCl_3$) of **4a** with addition of NaI



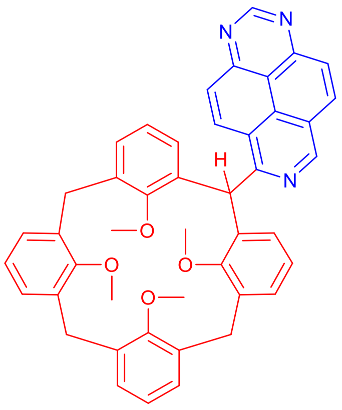
Spectrum S6. ^{1}H-^{13}C HMBC NMR ($CDCl_3$) of **4a** with addition of NaI



Spectrum S7. ^{1}H-^{1}H COSY NMR ($CDCl_3$) of **4a** with addition of NaI

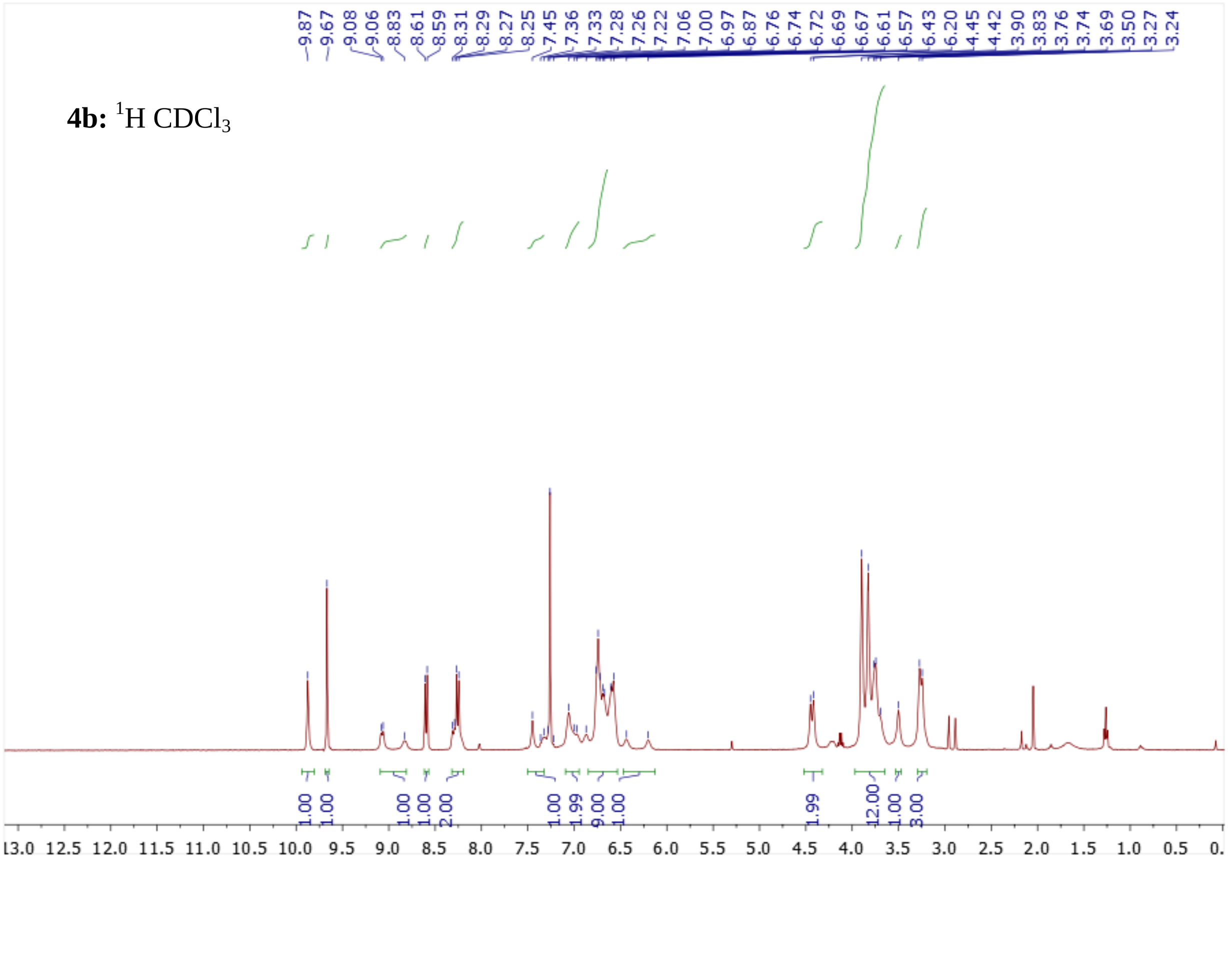


2. **Copies of ^{1}H, ^{13}C NMR spectra for 2-(1,3,7-triazapyrene-6-yl)-25,26,27,28-tetramethoxycalix[4]arene (4b)**

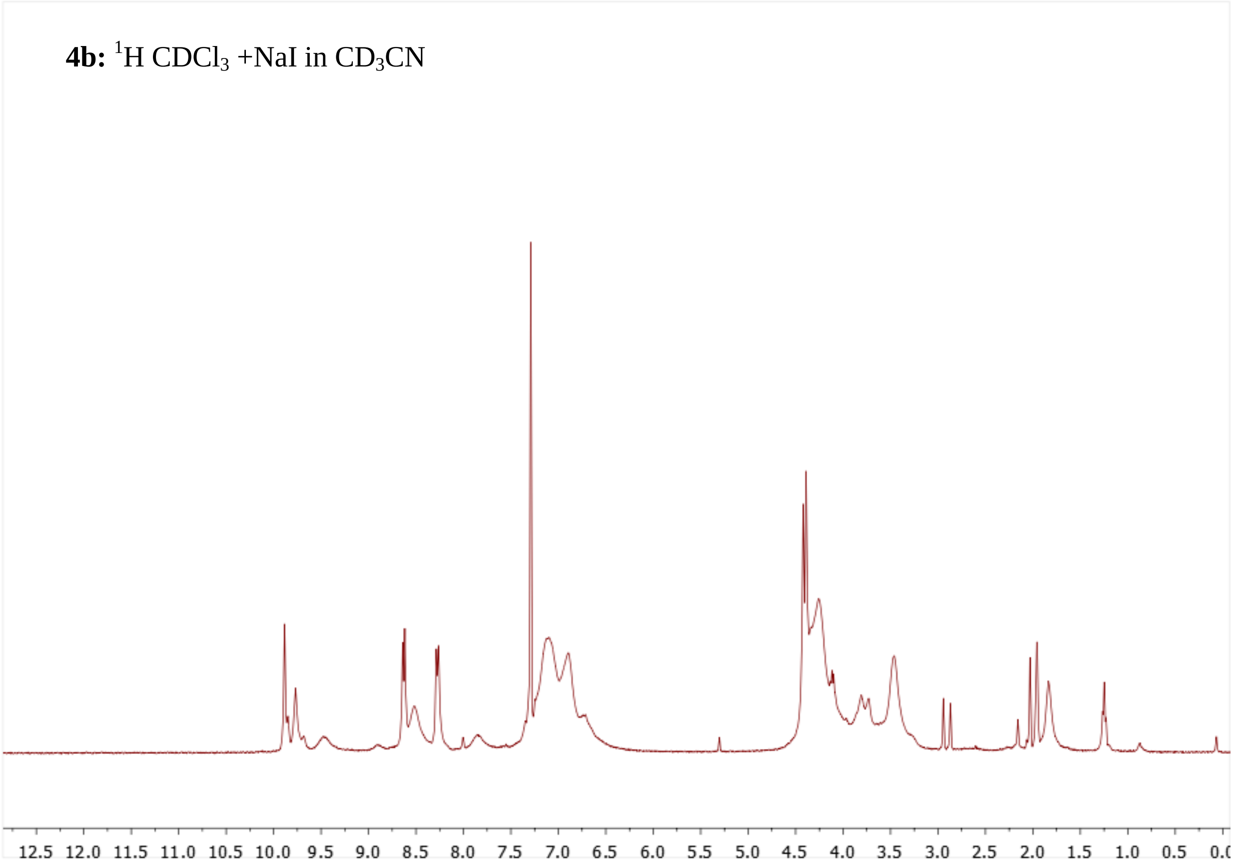


4b

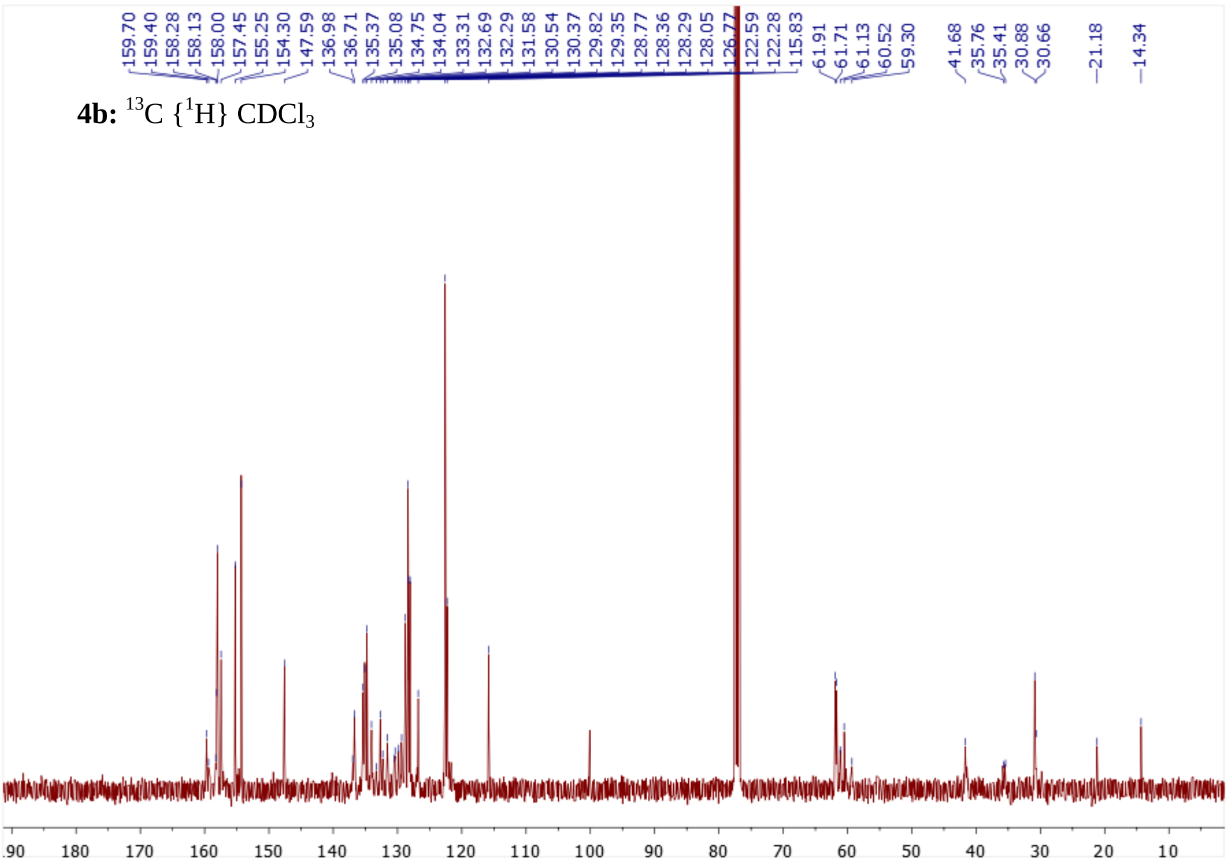
Spectrum S8. ^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



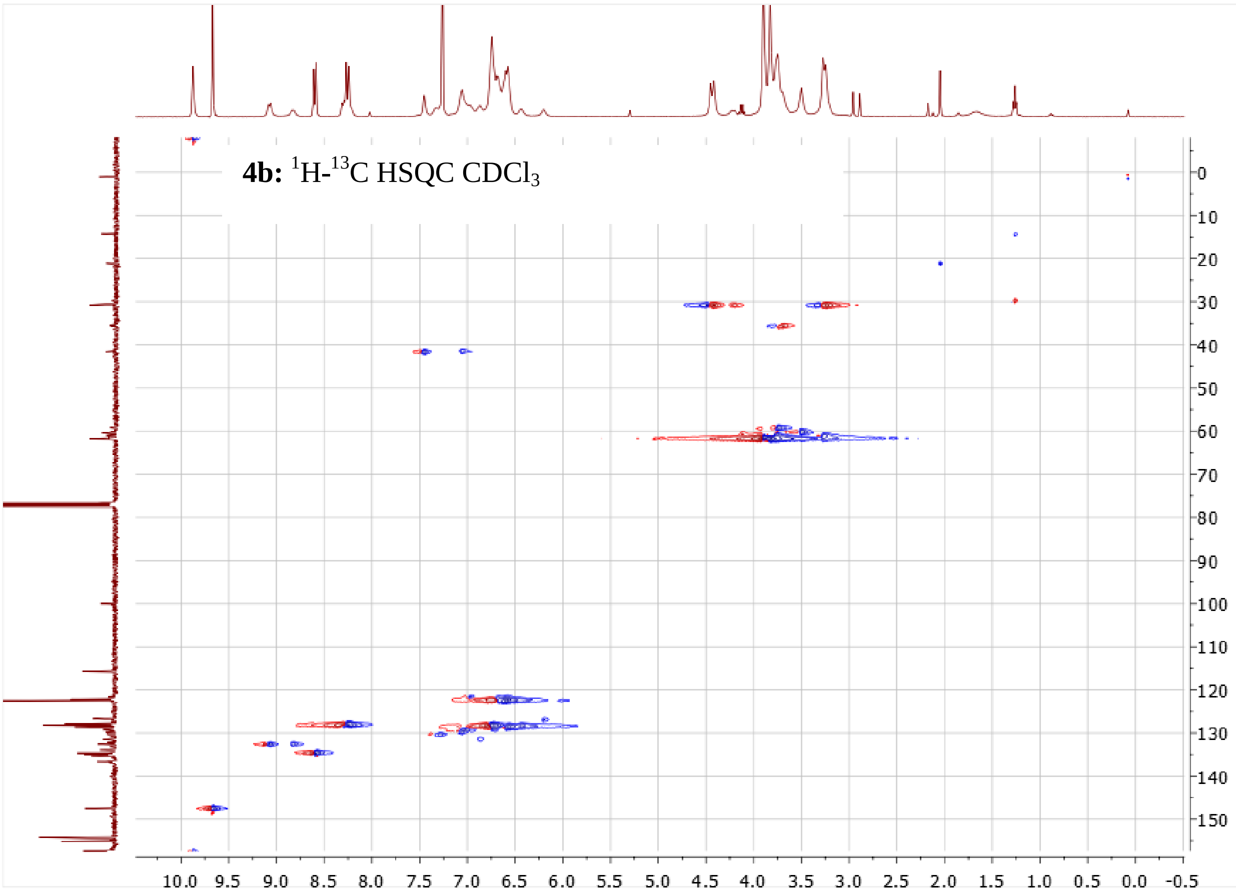
Spectrum S9. ^{1}H NMR (400 MHz, $CDCl_3$) of **4b** with addition of NaI



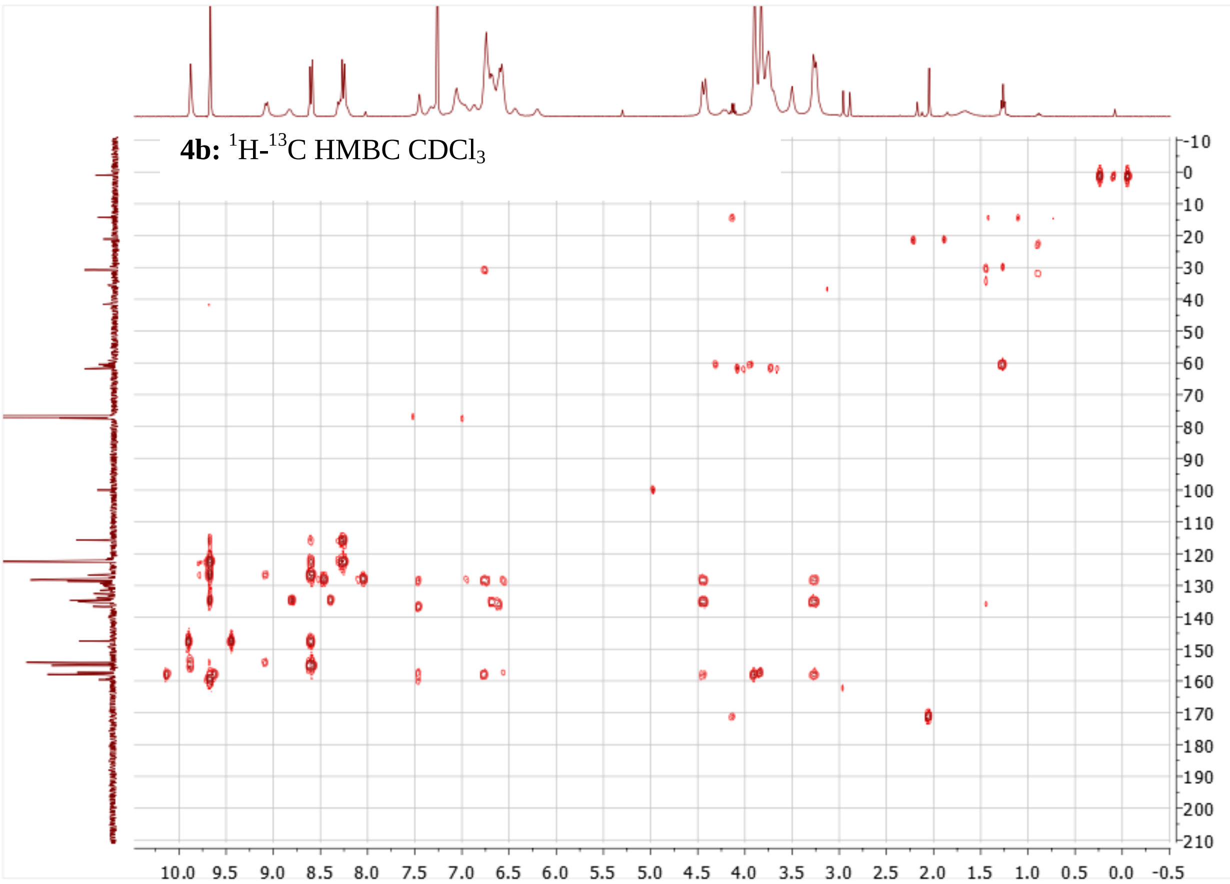
Spectrum S10. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **4b**



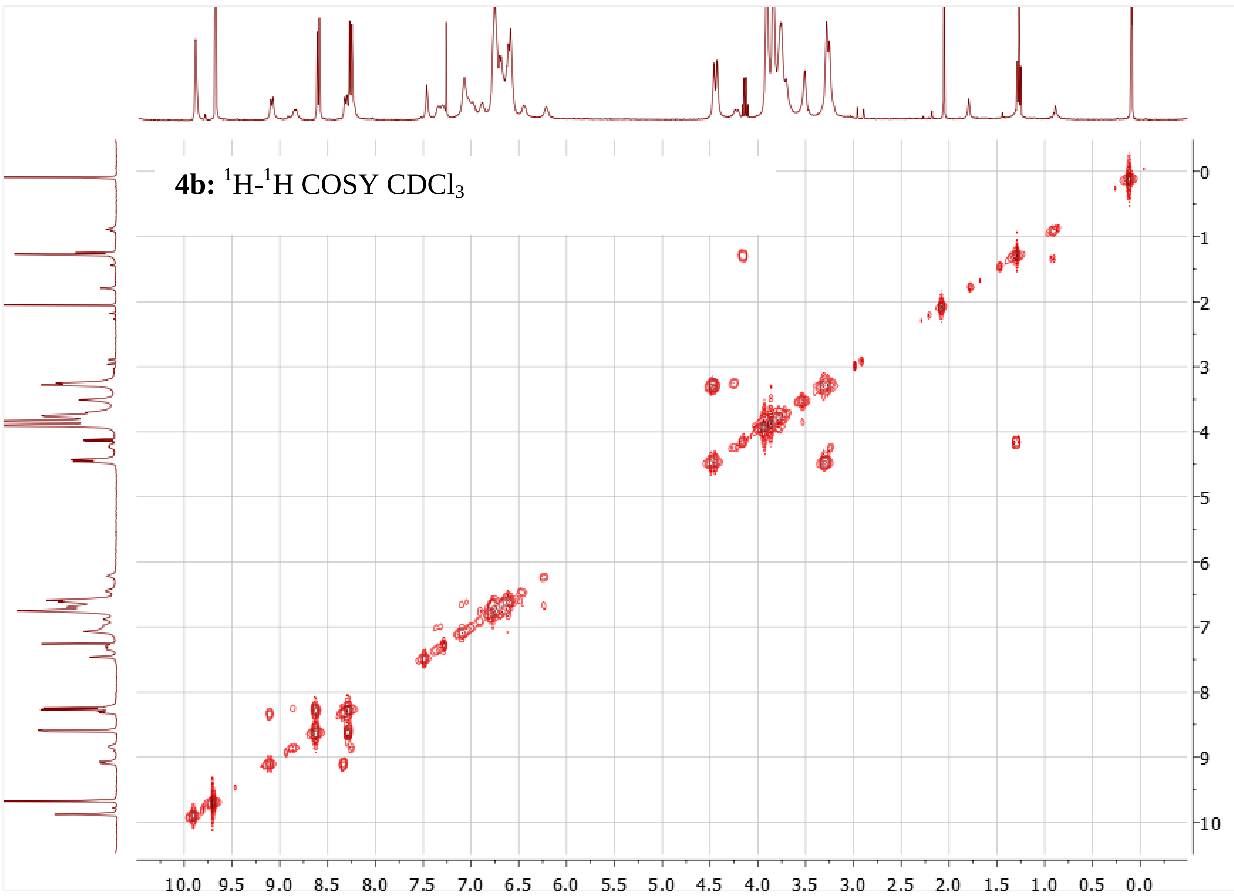
Spectrum S11. ^{1}H-^{13}C HSQC NMR ($CDCl_3$) of **4b**



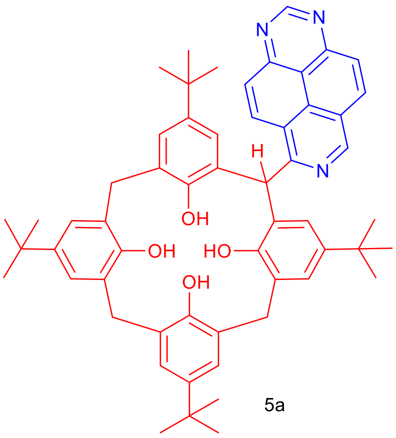
Spectrum S12. ^{1}H-^{13}C HMBC NMR ($CDCl_3$) of **4b**



Spectrum S13. ^{1}H -^{1}H COSY NMR ($CDCl_3$) of **4b**

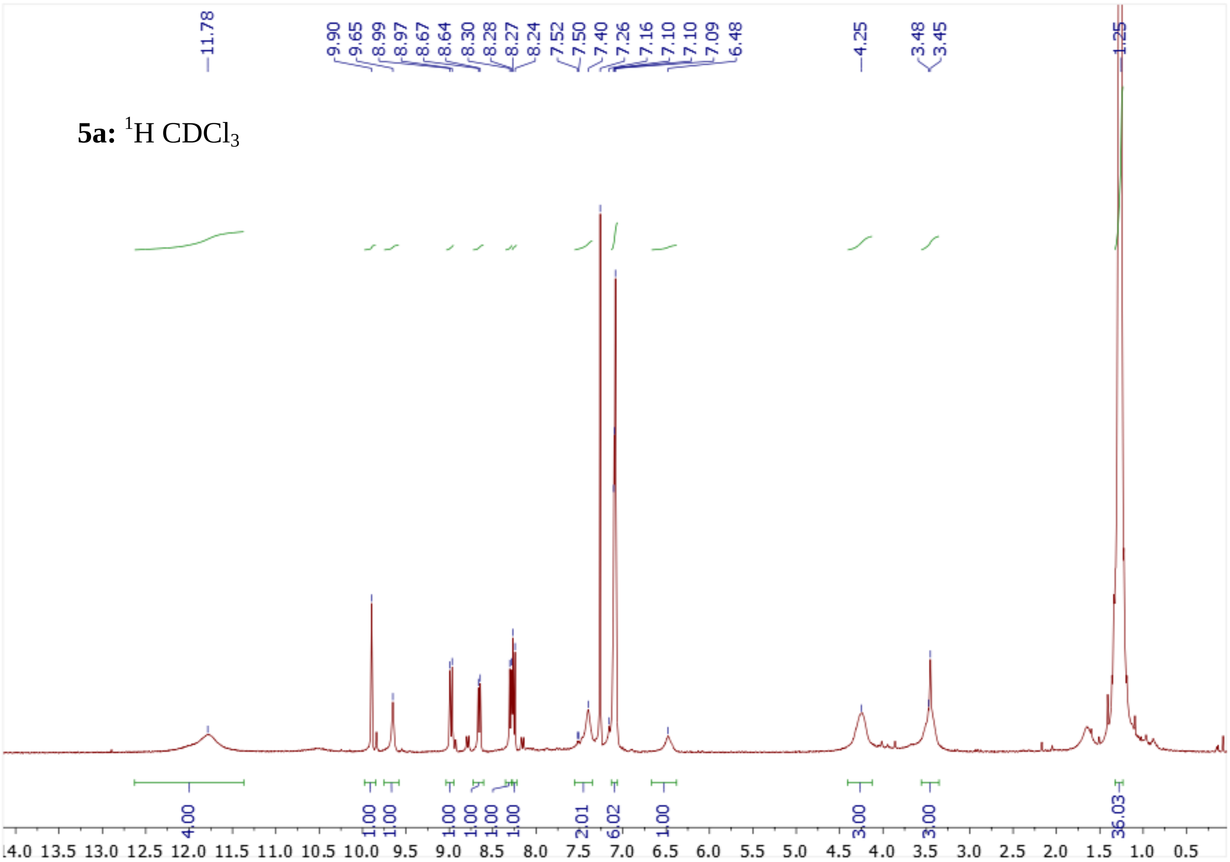


3. **Copies of ^{1}H, ^{13}C NMR spectra for 2-(1,3,7-triazapyrene-6-yl)-5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (5a)**

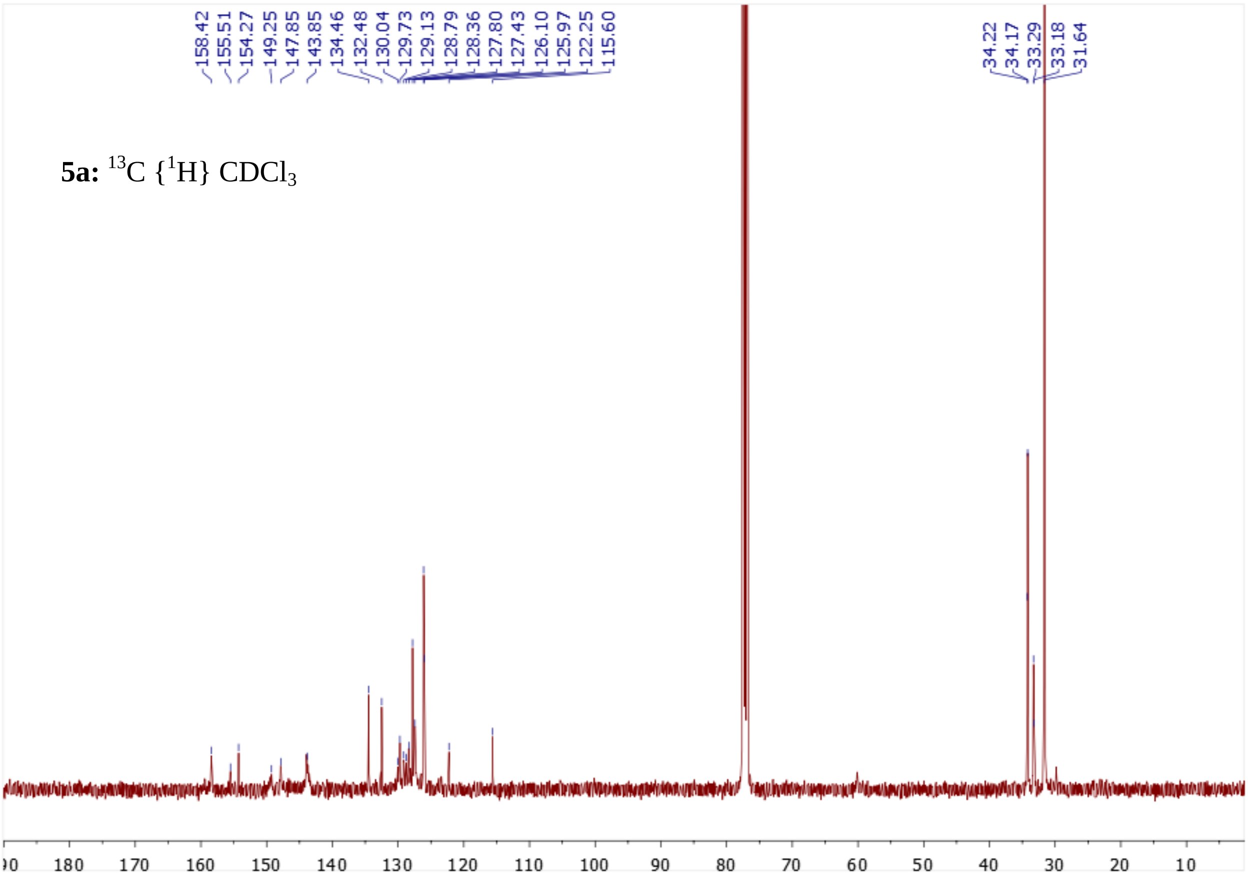


5a

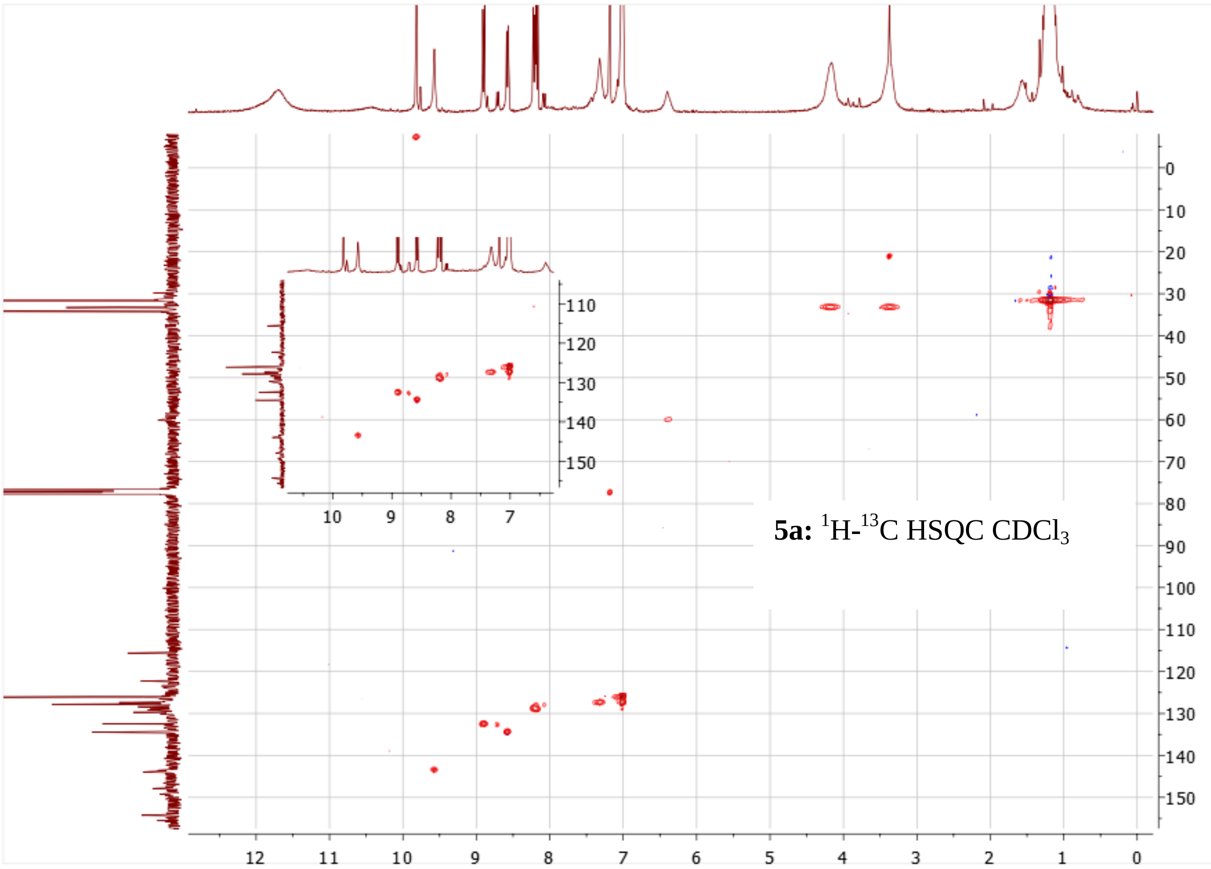
Spectrum S14. ^{1}H NMR (400 MHz, $CDCl_3$) of **5a**



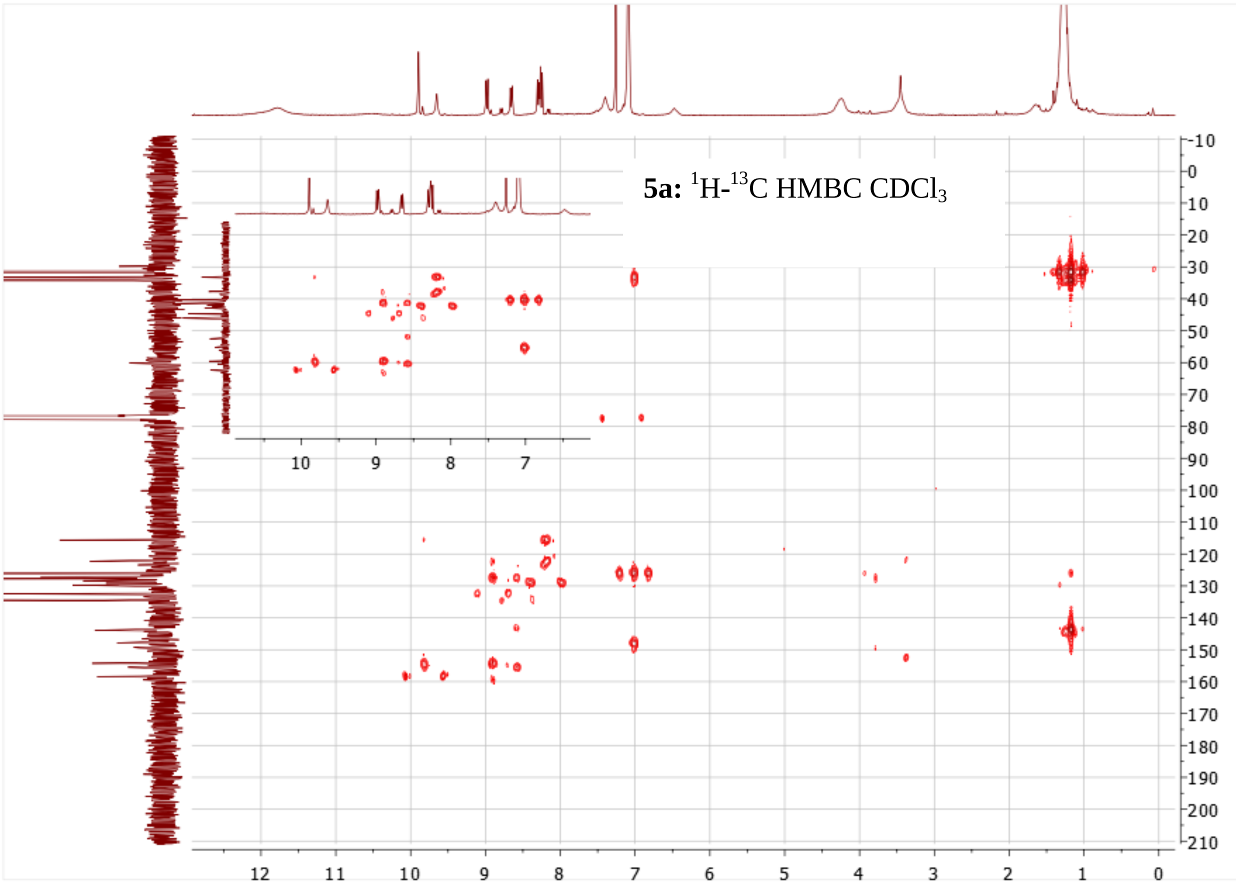
Spectrum S15. $^{13}C\ \{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **5a**



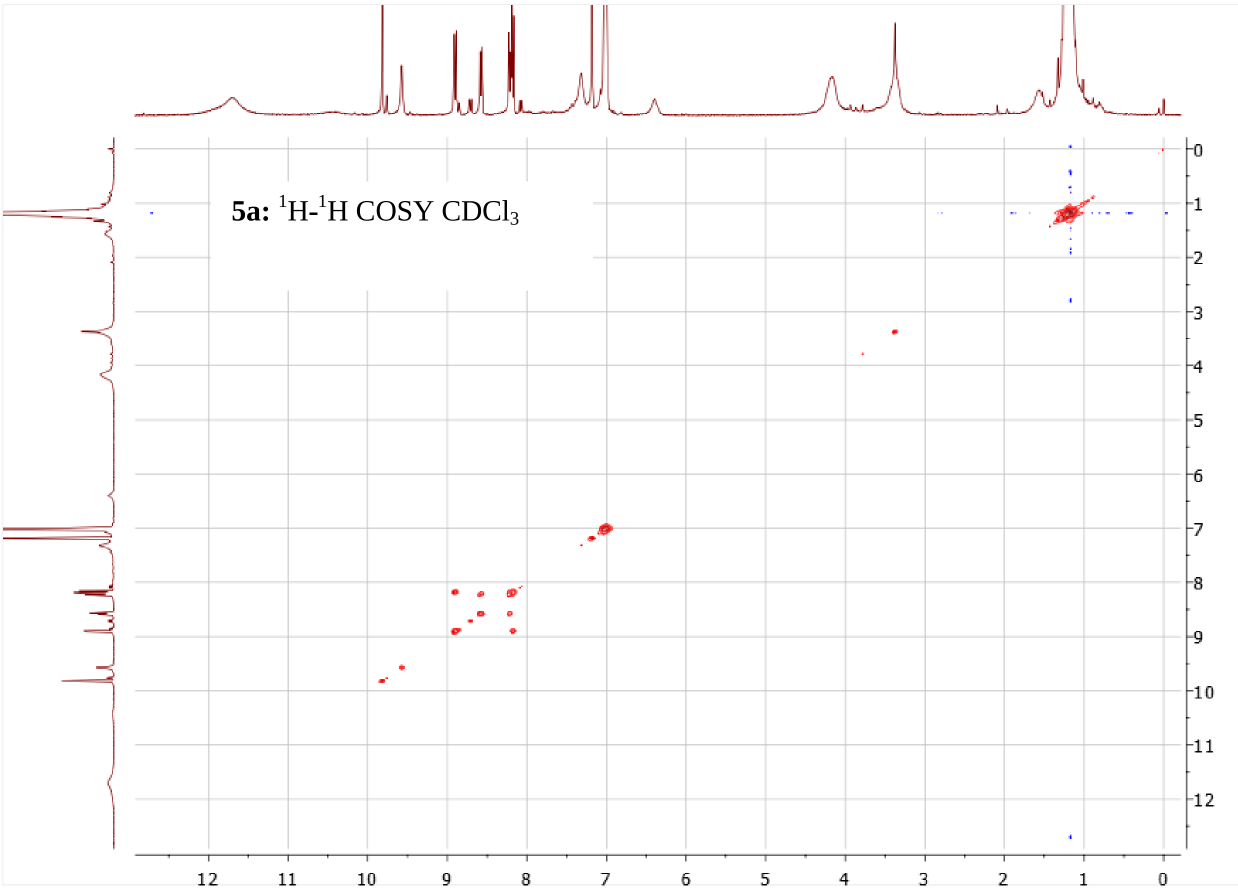
Spectrum S16. ^{1}H-^{13}C HSQC NMR ($CDCl_3$) of **5a**



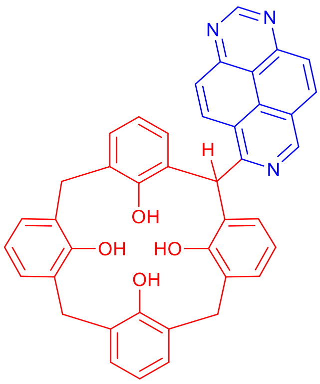
Spectrum S17. ^{1}H-^{13}C HMBC NMR ($CDCl_3$) of **5a**



Spectrum S18. ^{1}H-^{1}H COSY NMR ($CDCl_3$) of **5a**

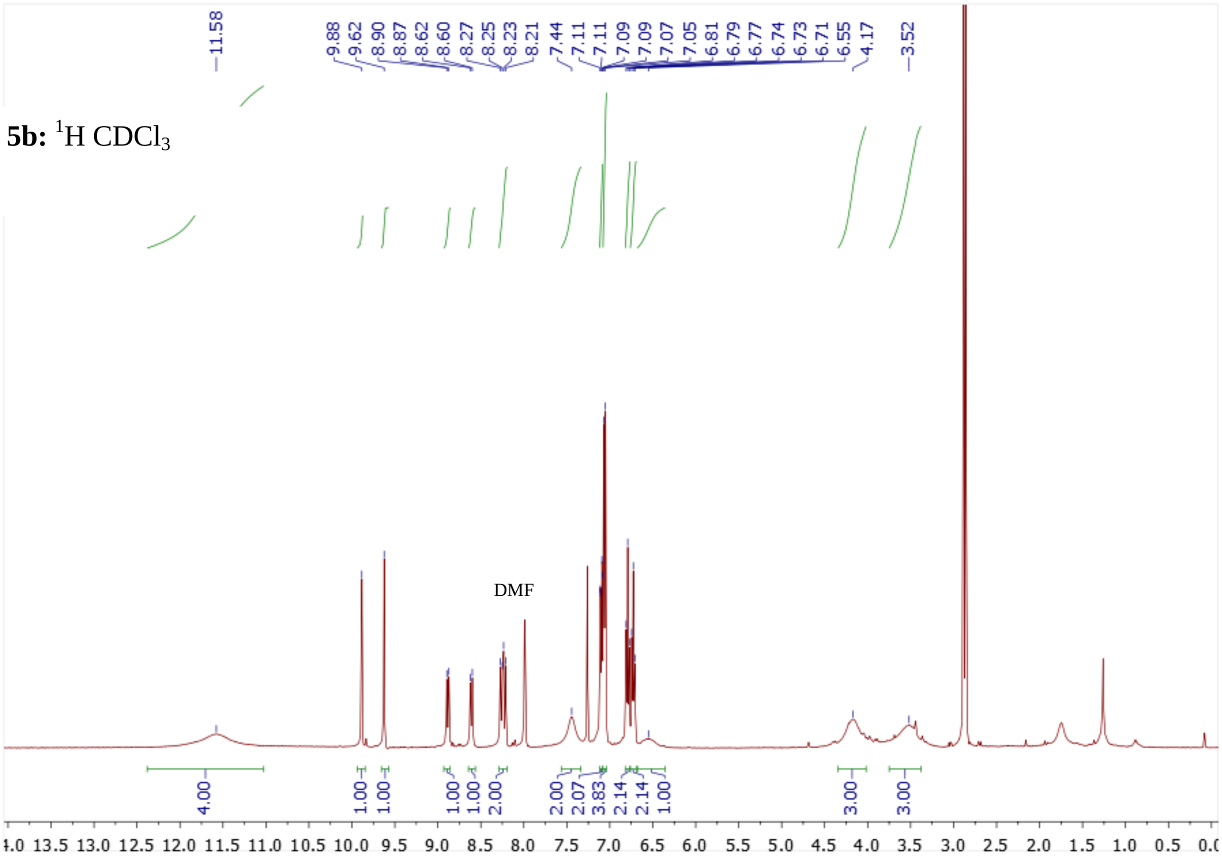


4. **Copies of ^{1}H, ^{13}C NMR spectra for 2-(1,3,7-triazapyrene-6-yl)-25,26,27,28-tetrahydroxycalix[4]arene (5b)**

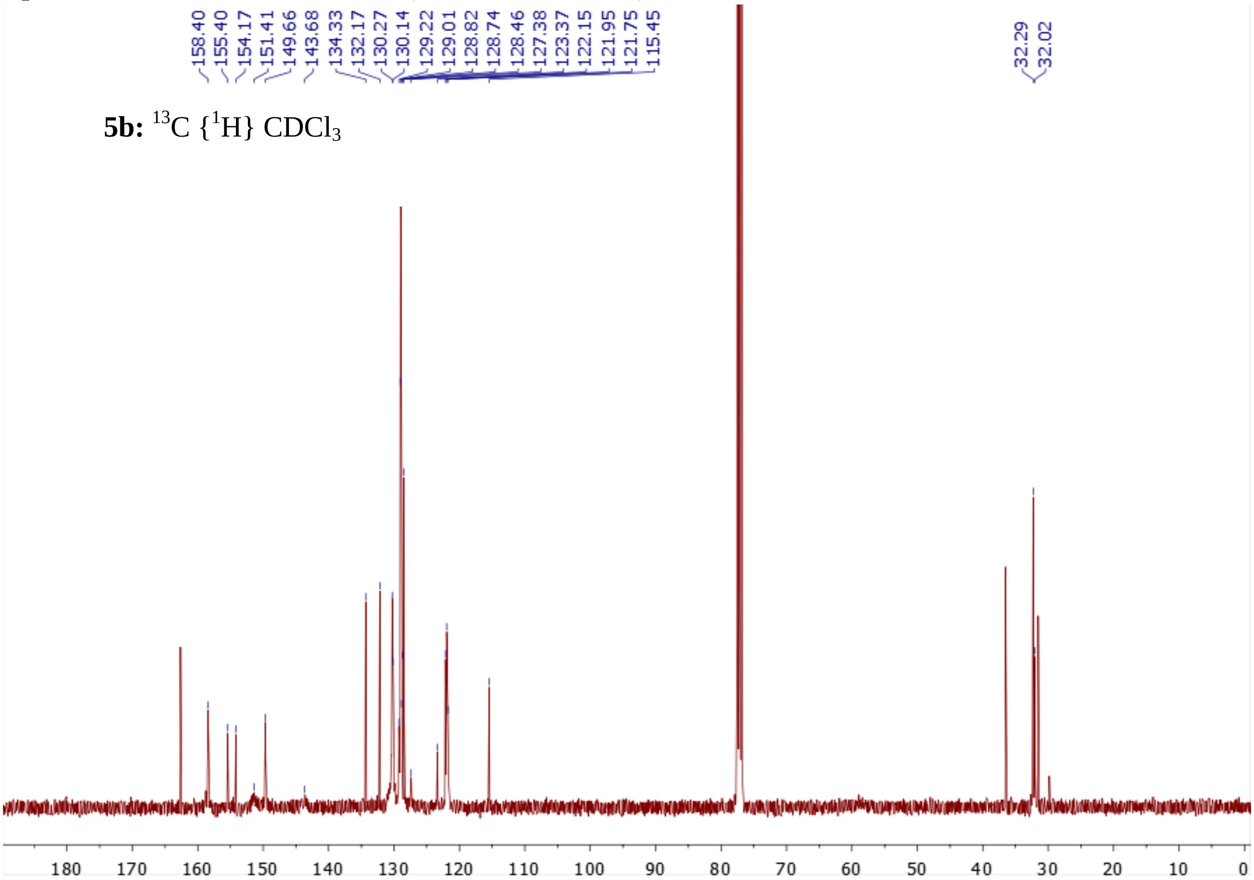


5b

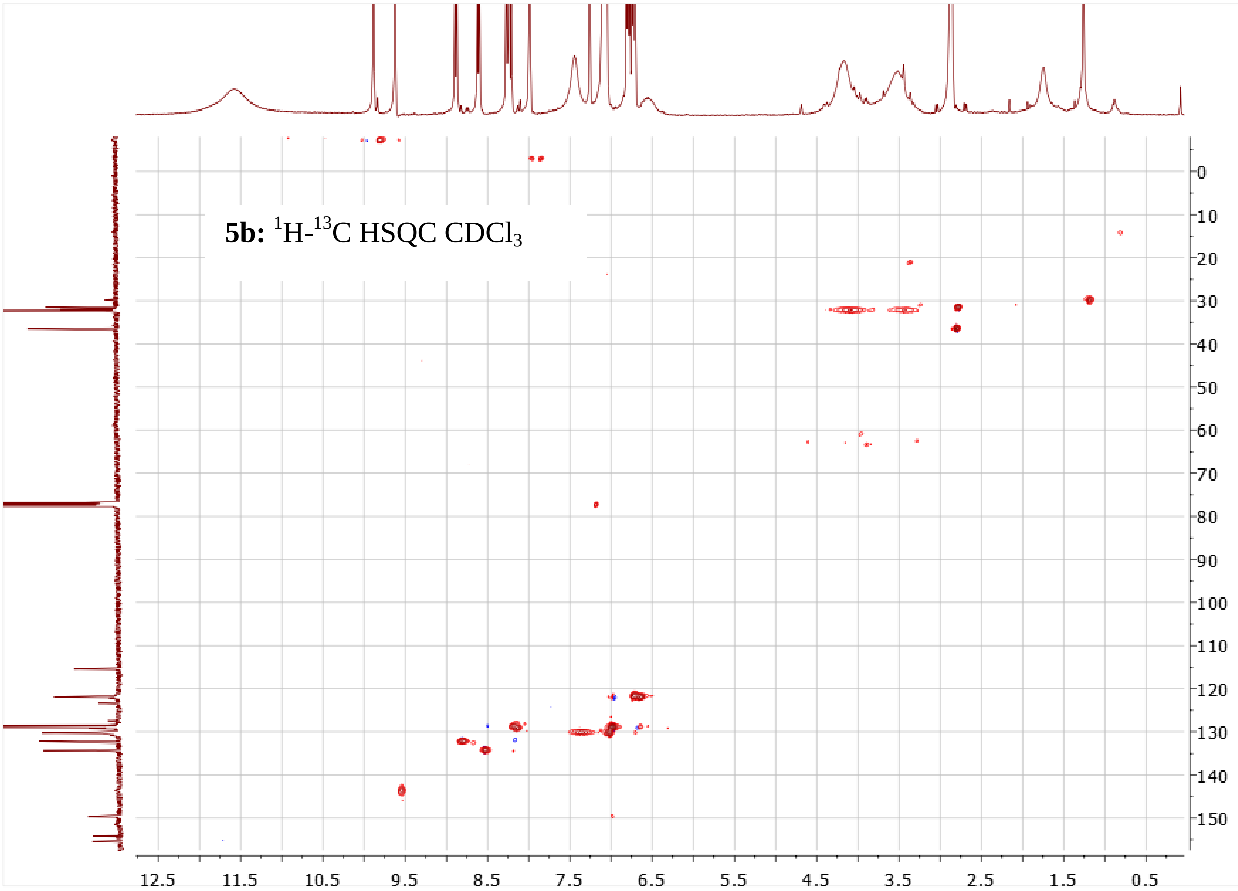
Spectrum S19. ^{1}H NMR (400 MHz, $CDCl_3$) of **5b**



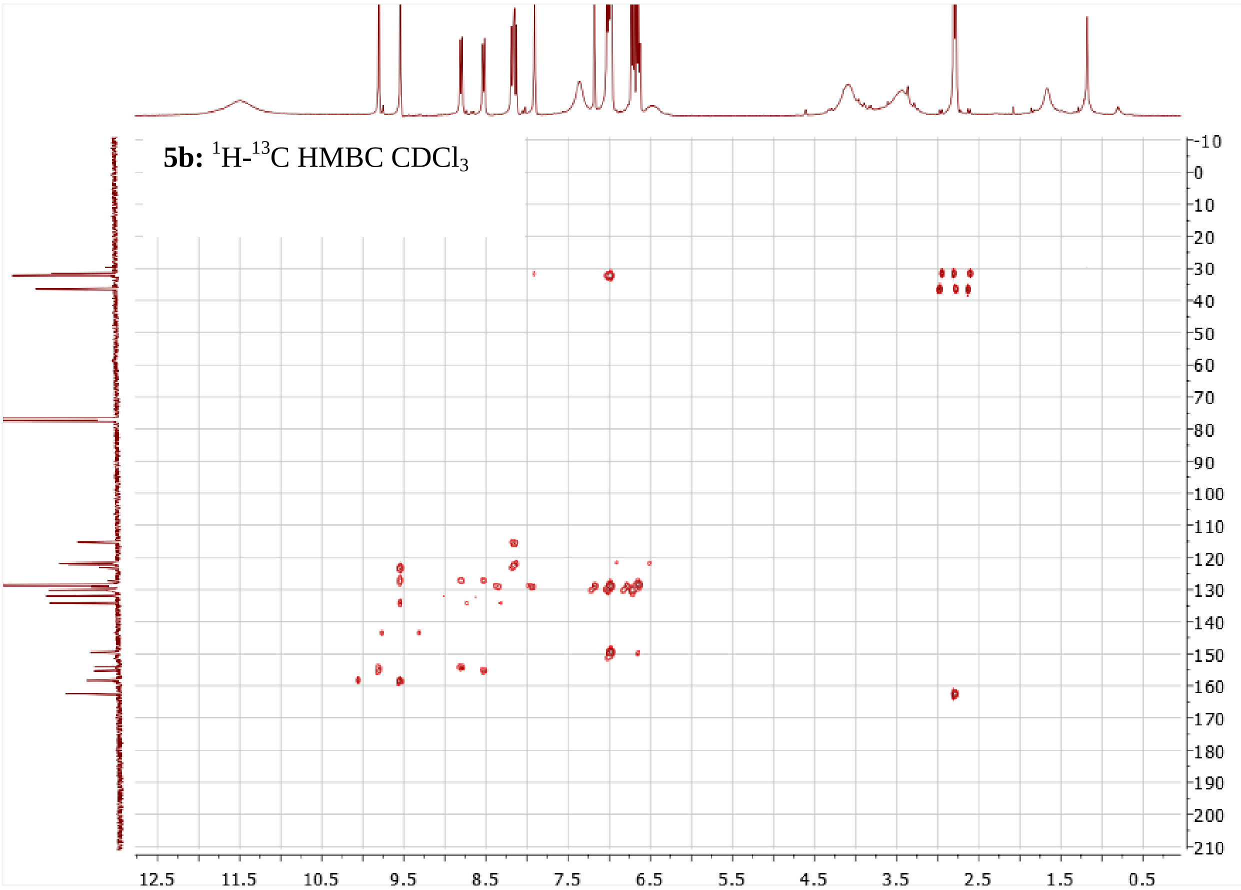
Spectrum S20. $^{13}C\ \{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **5b**



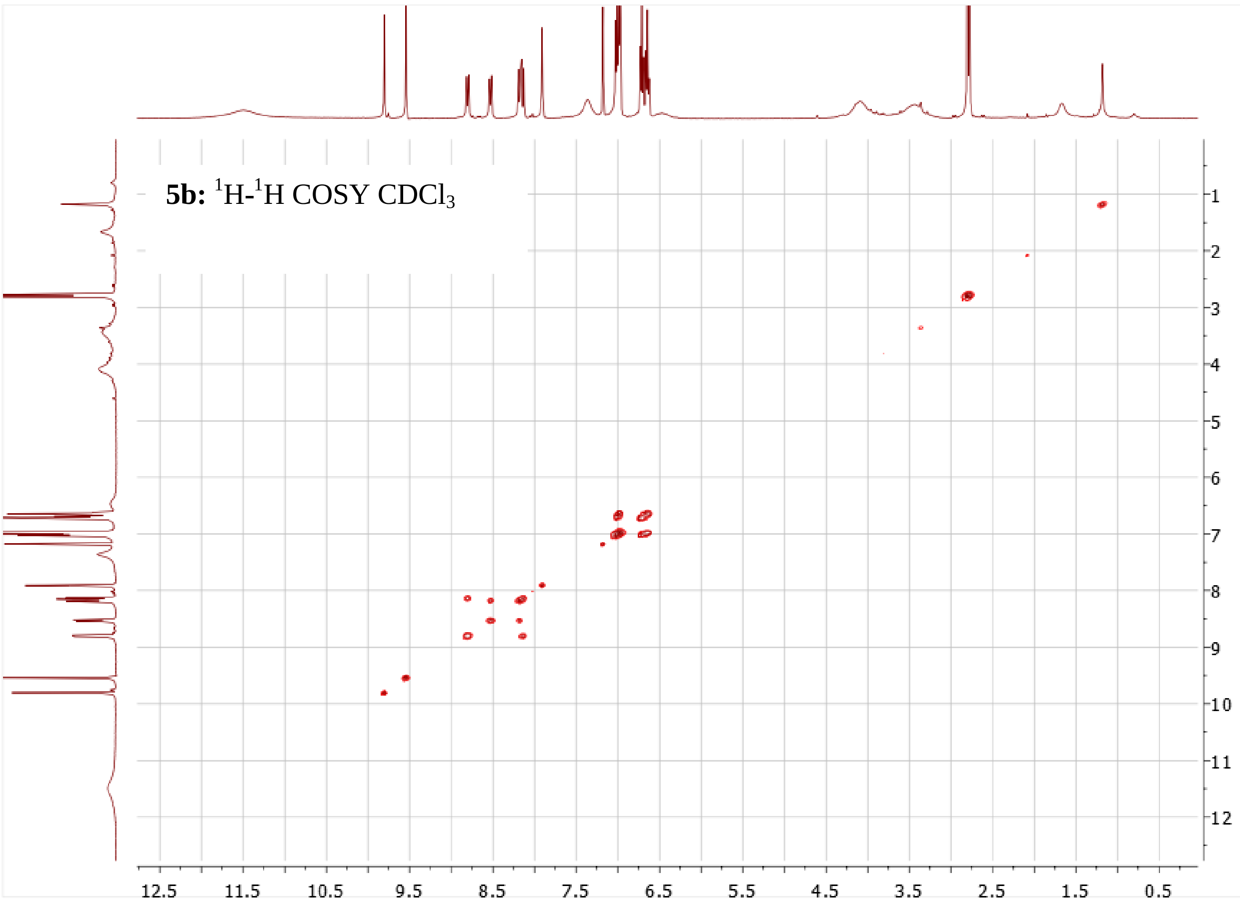
Spectrum S21. ^{1}H-^{13}C HSQC NMR ($CDCl_3$) of **5b**



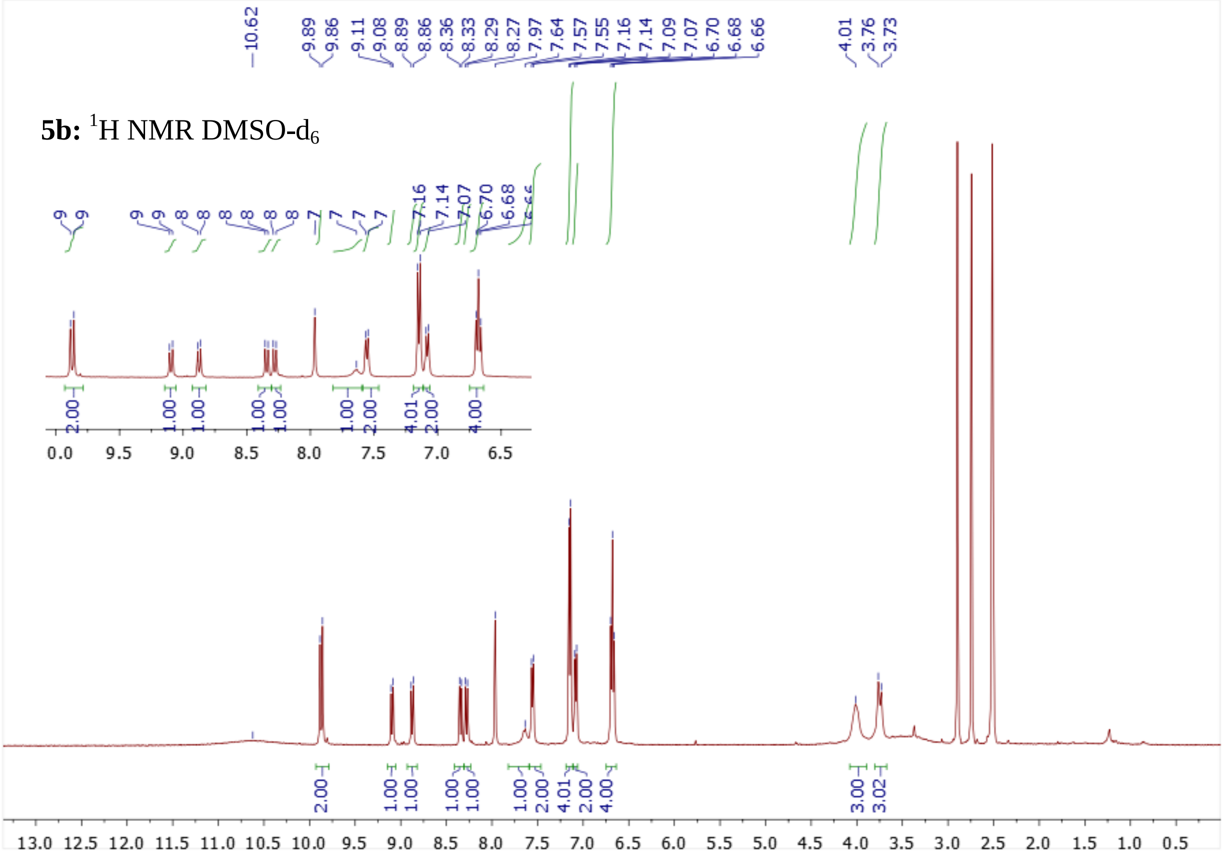
Spectrum S22. ^{1}H-^{13}C HMBC NMR ($CDCl_3$) of **5b**



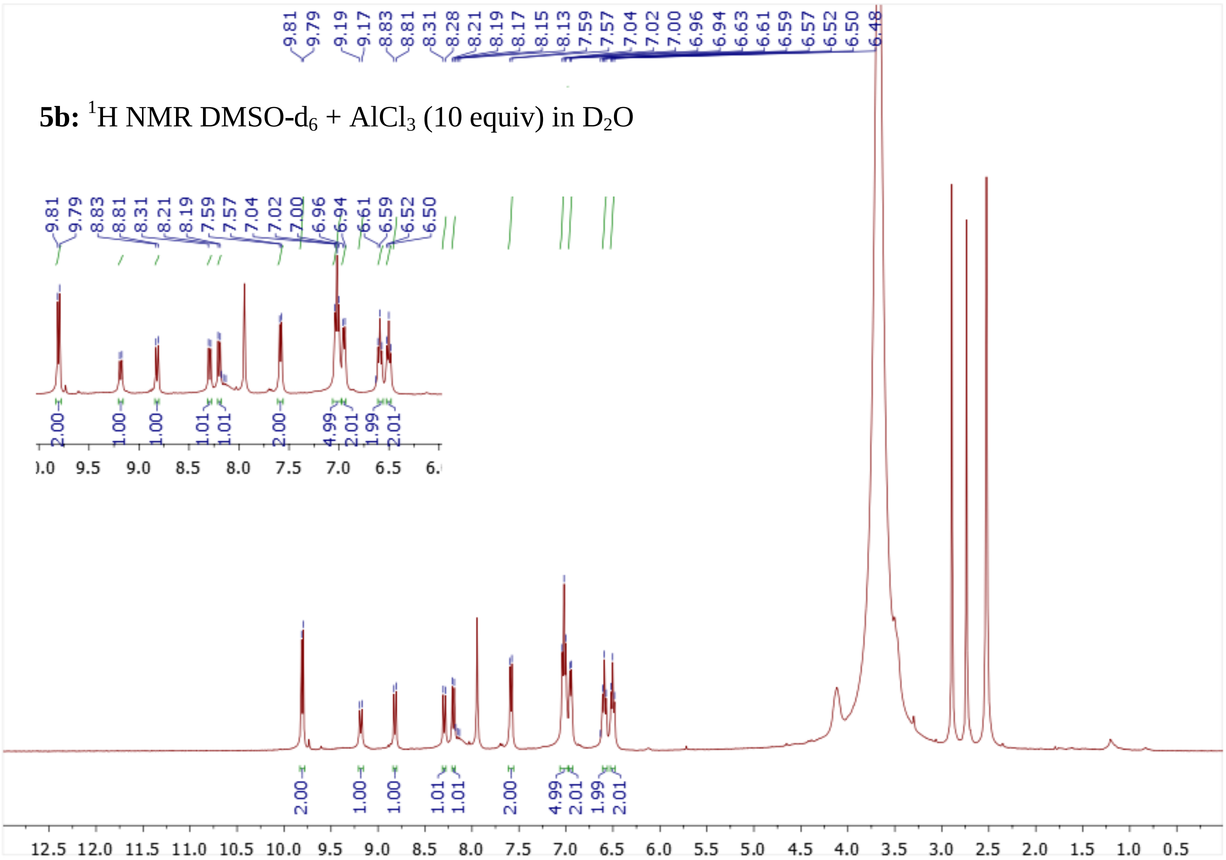
Spectrum S23. ^{1}H-^{1}H COSY NMR ($CDCl_3$) of **5b**



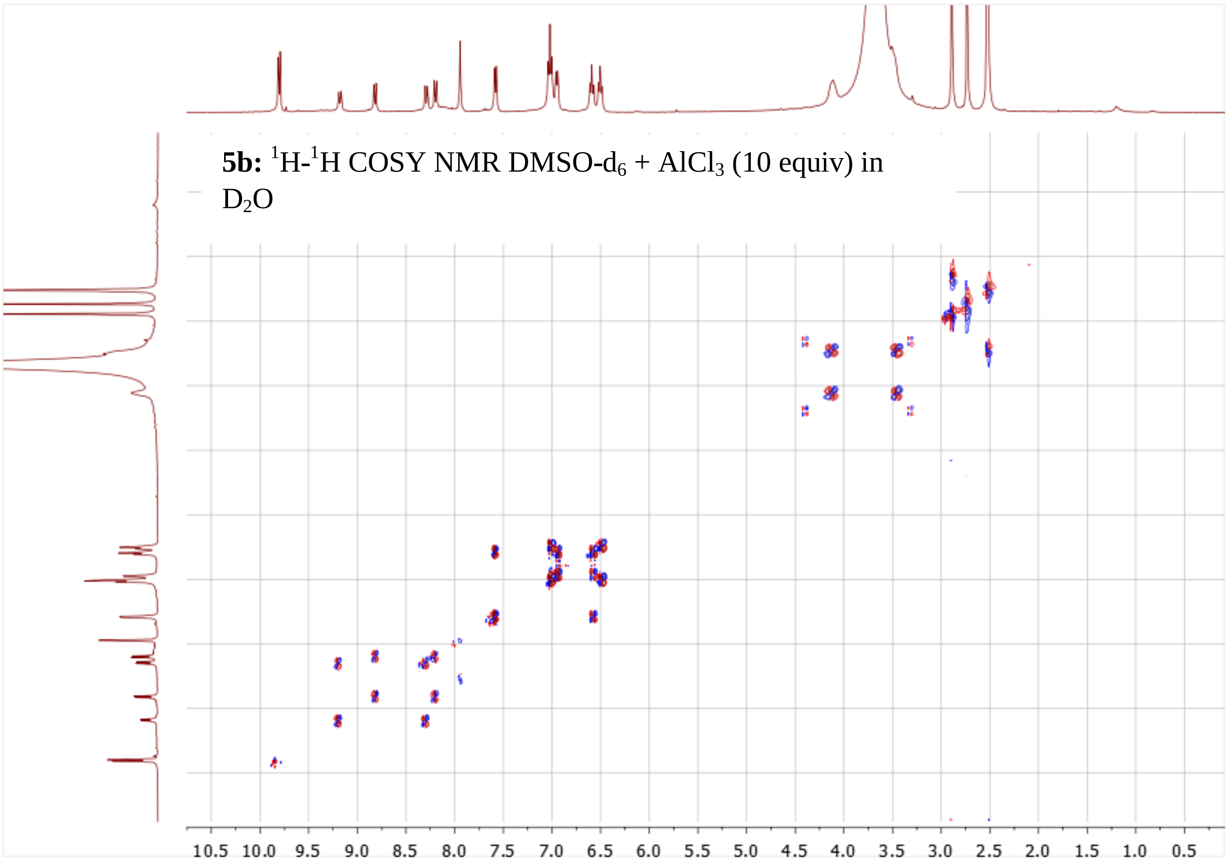
Spectrum S24. ^{1}H NMR (400 MHz, DMSO-d_6) of **5b**



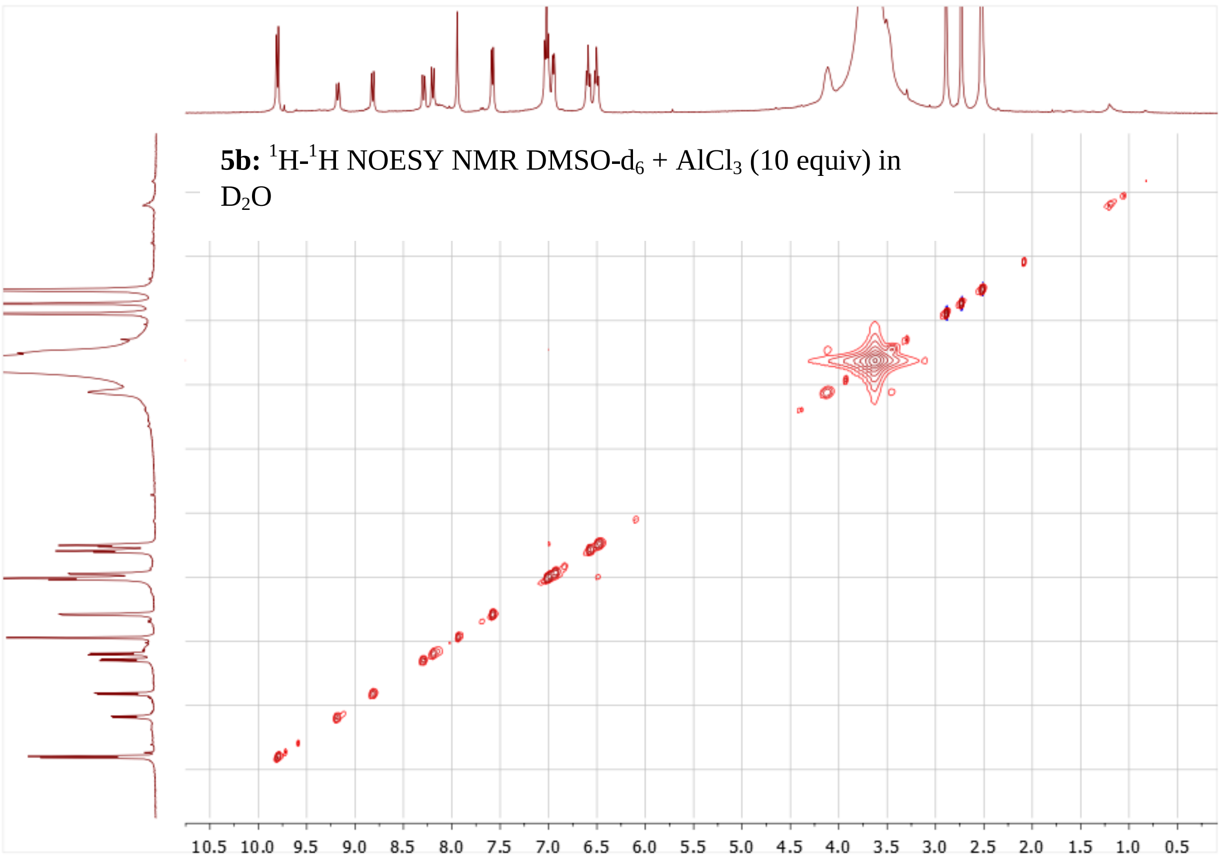
Spectrum S25. ^{1}H NMR (400 MHz, DMSO-d6) of **5b** with addition of $AlCl_3$ (10 equiv) in D_2O



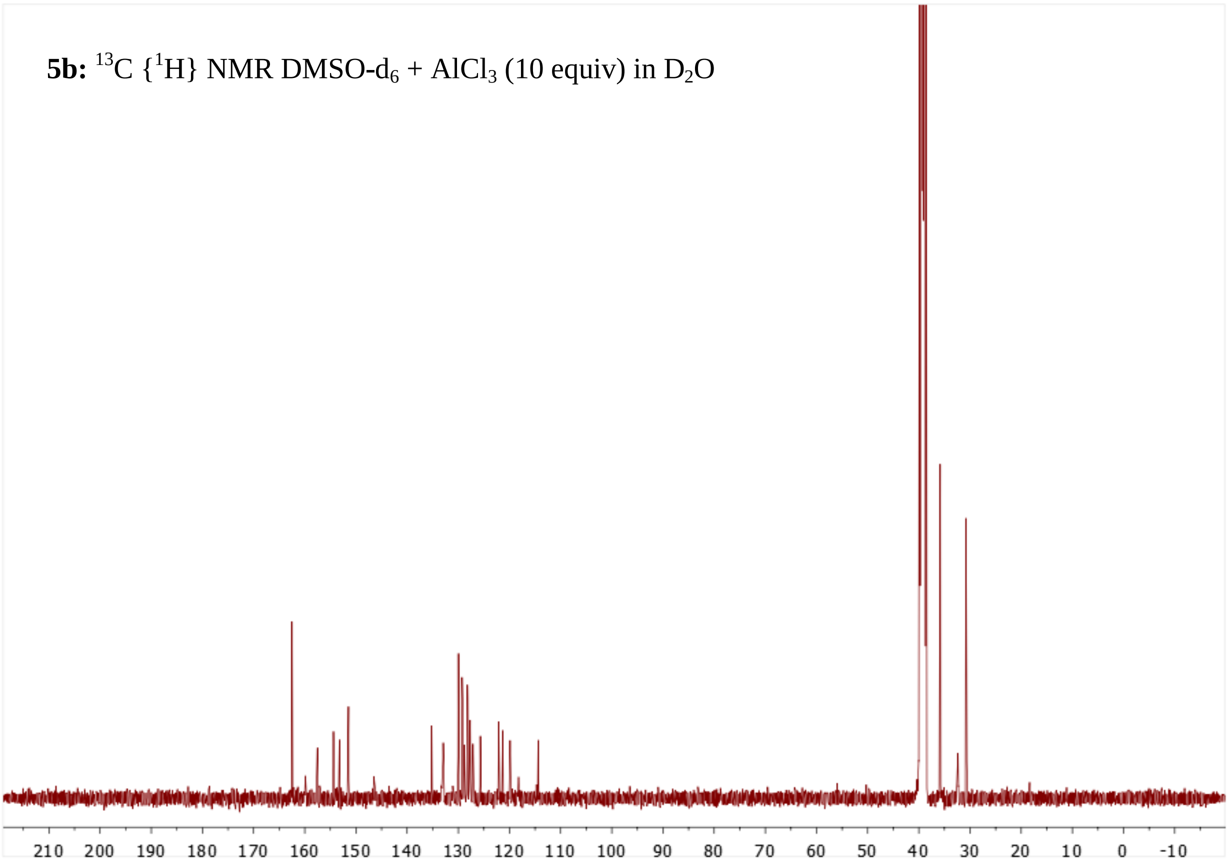
Spectrum S26. ^{1}H-^{1}H COSY NMR (DMSO-d6) of **5b** with addition of $AlCl_3$ (10 equiv) in D_2O



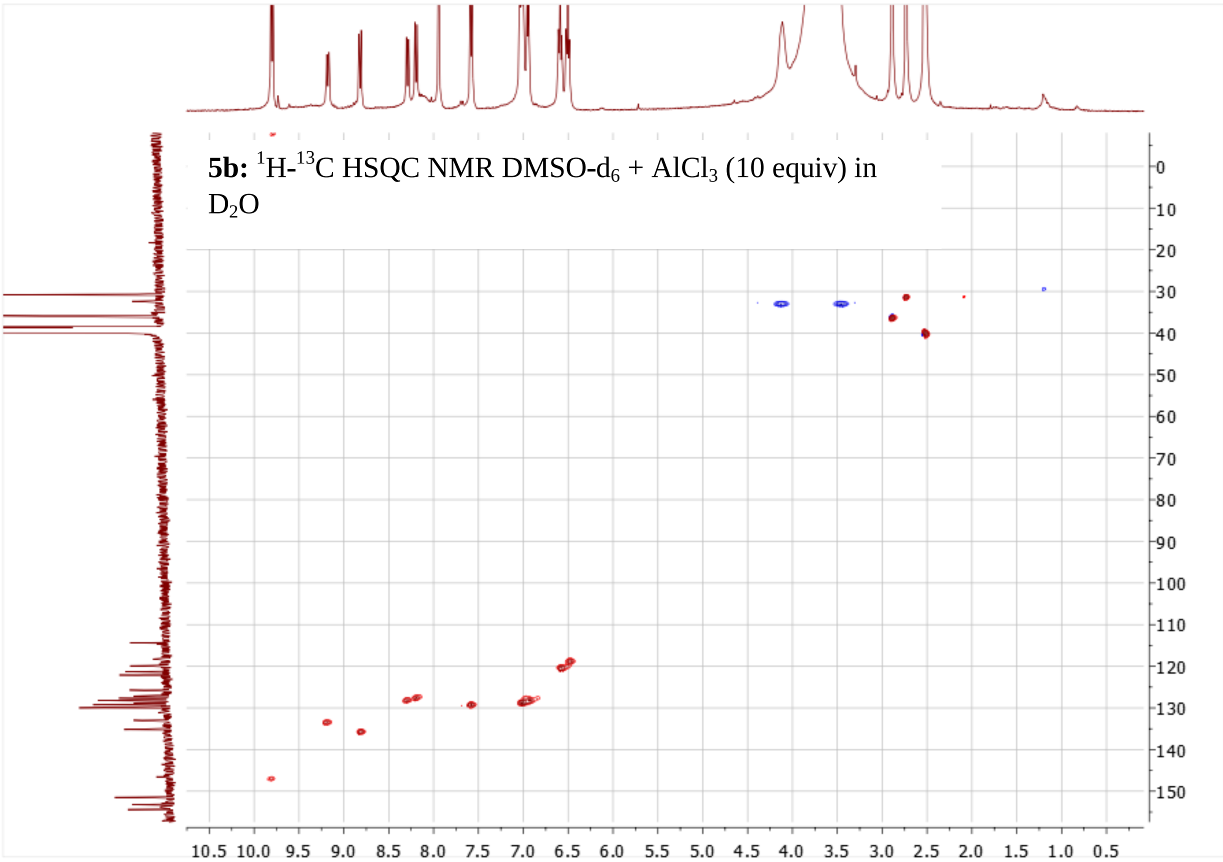
Spectrum S27. ^{1}H-^{1}H NOESY NMR (DMSO-d6) of **5b** with addition of $AlCl_3$ (10 equiv) in D_2O



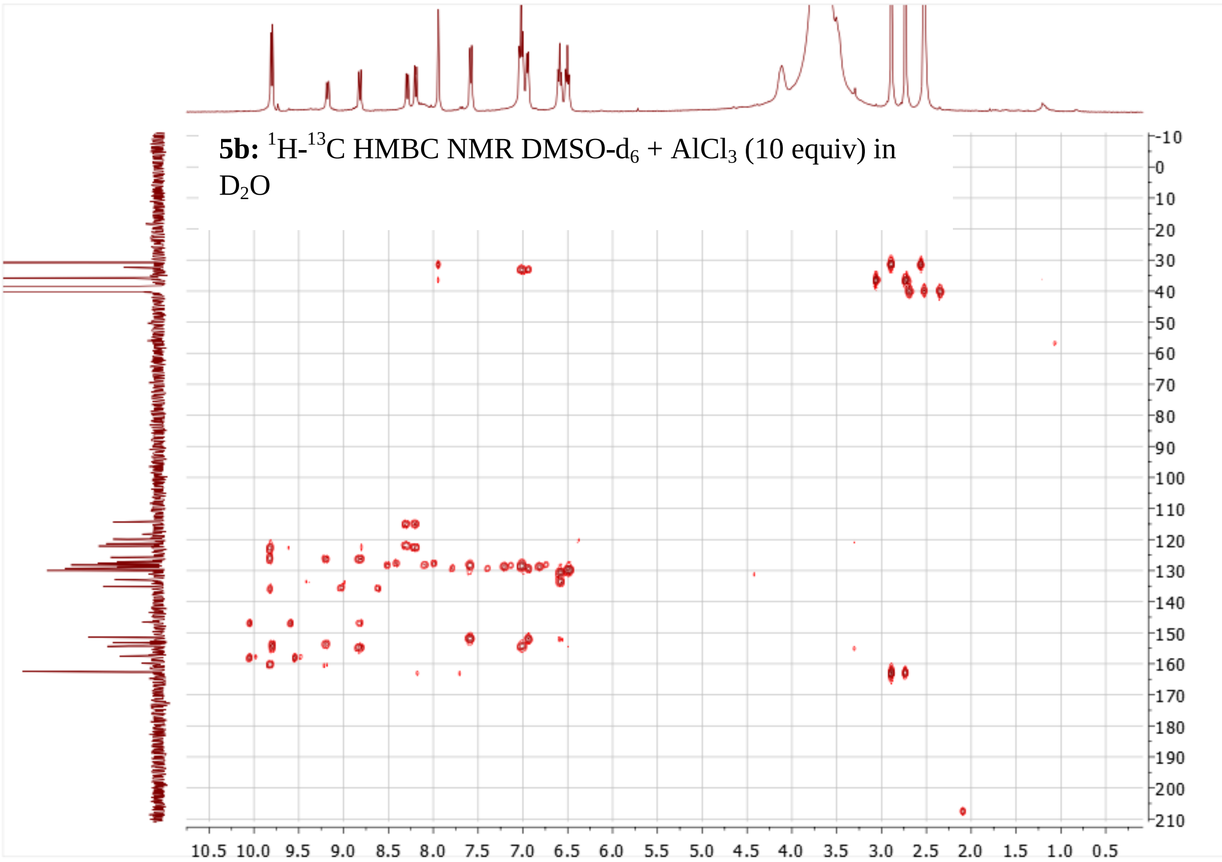
Spectrum S28. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6) of **5b** with addition of $AlCl_3$ (10 equiv) in D_2O



Spectrum S29. ^1H-^{13}C HSQC NMR (DMSO-d6) of **5b** with addition of $AlCl_3$ (10 equiv) in D_2O

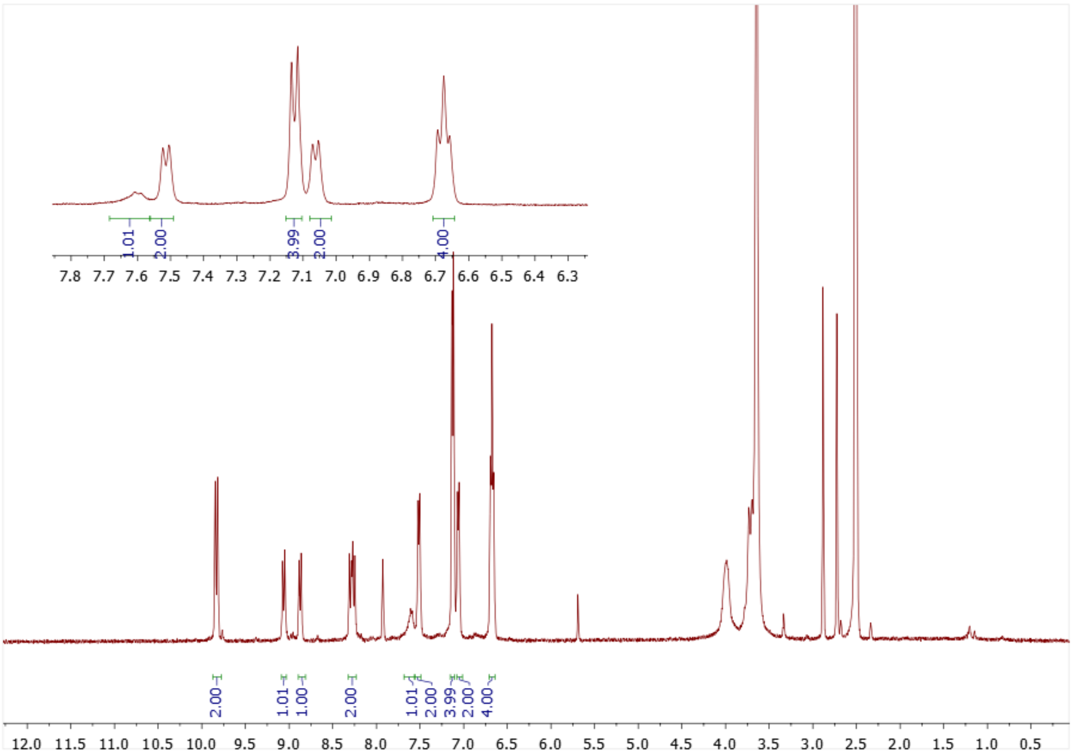


Spectrum S30. ^{1}H-^{13}C HMBC NMR (DMSO-d_6) of **5b** with addition of $AlCl_3$ (10 equiv) in D_2O



In order to clarify the reasons of changes in the NMR spectra (complex formation or conformational transformation), the control ^{1}H NMR experiment without Al^{3+} ions in the DMSO-d_6/D_2O mixture was carried out

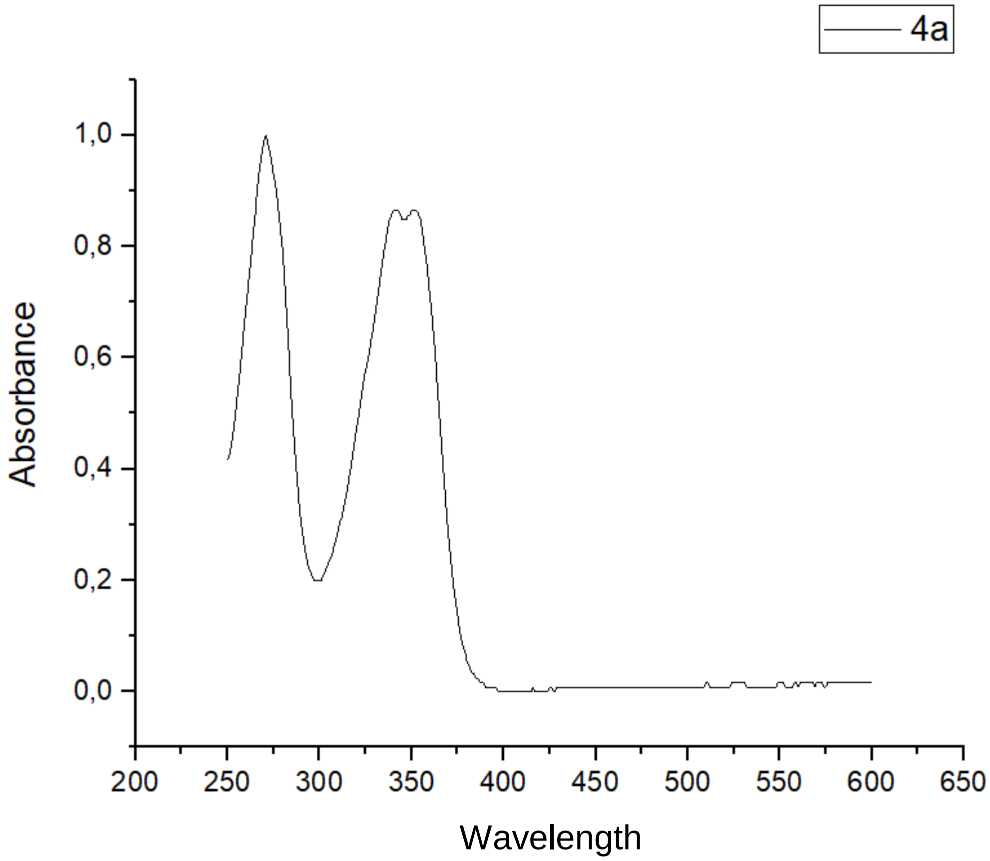
Spectrum S31. ^{1}H NMR (DMSO-d_6/D_2O mixture) of **5b**



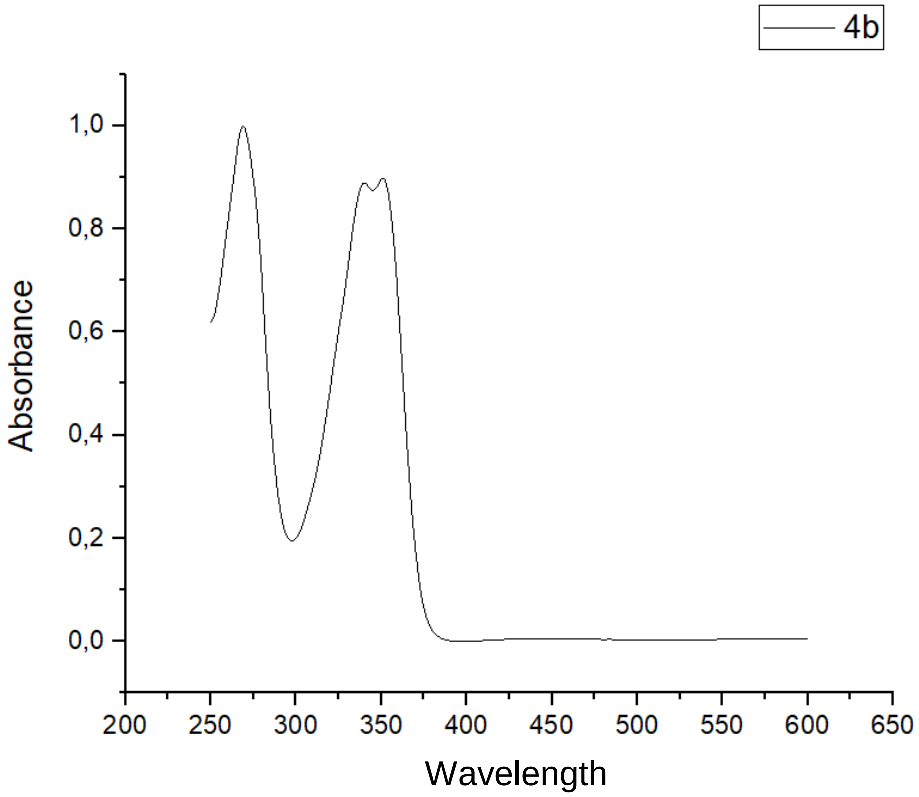
5. Photophysical studies

5.1. Absorbance spectra

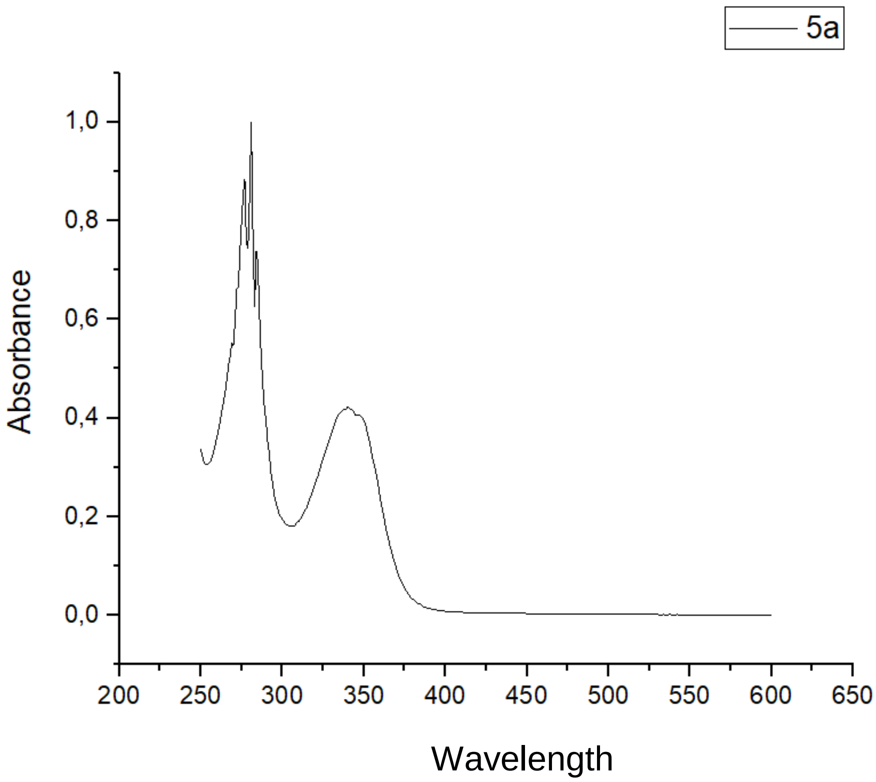
Spectrum S32. Absorbance of **4a** (C = 10^{-5} M in THF)



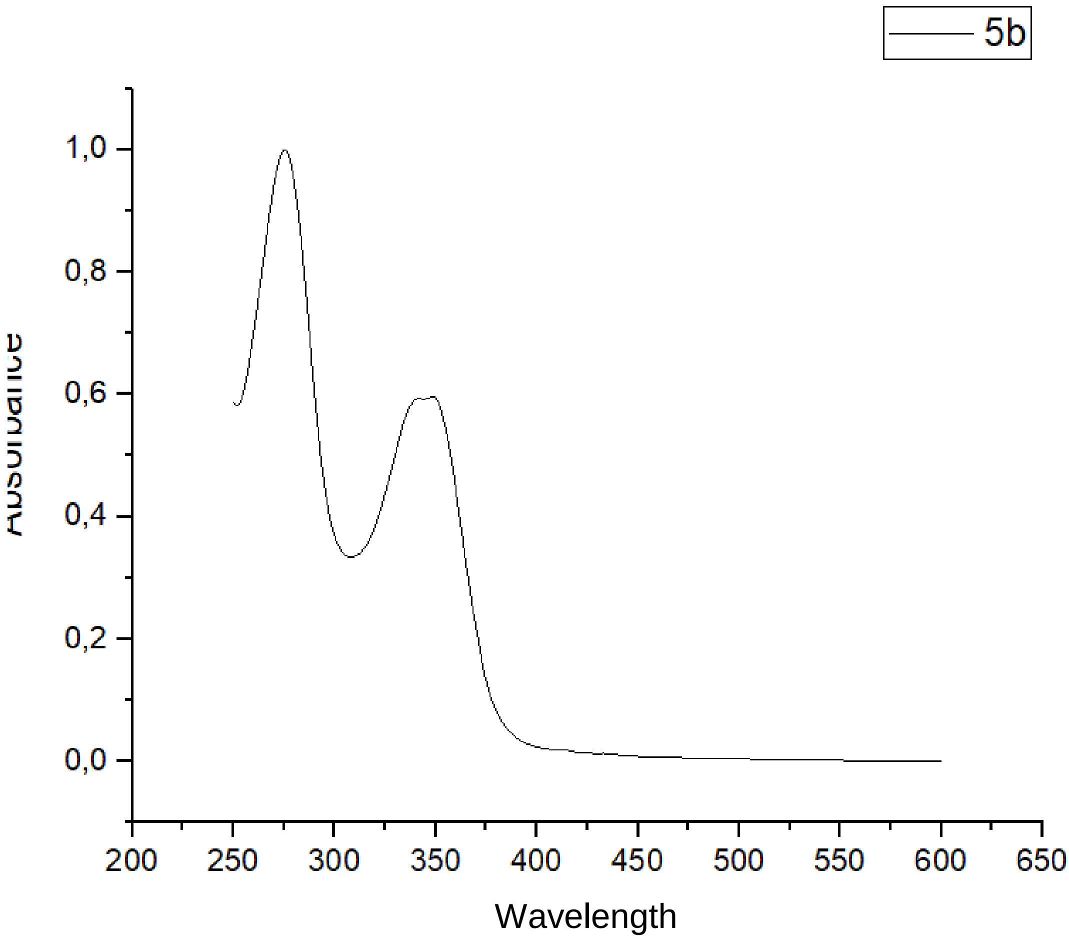
Spectrum S33. Absorbance of **4b** (C = 10^{-5} M in THF)



Spectrum S34. Absorbance of **5a** (C = 10^{-5} M in THF)

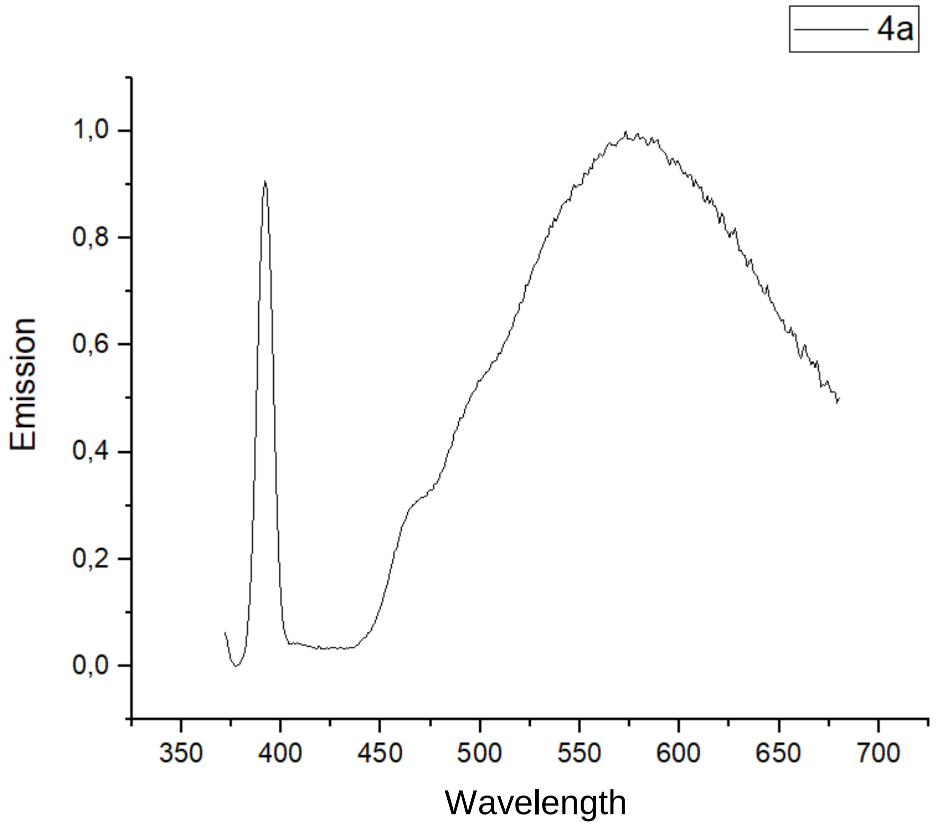


Spectrum S35. Absorbance of **5b** (C = 10^{-5} M in THF)

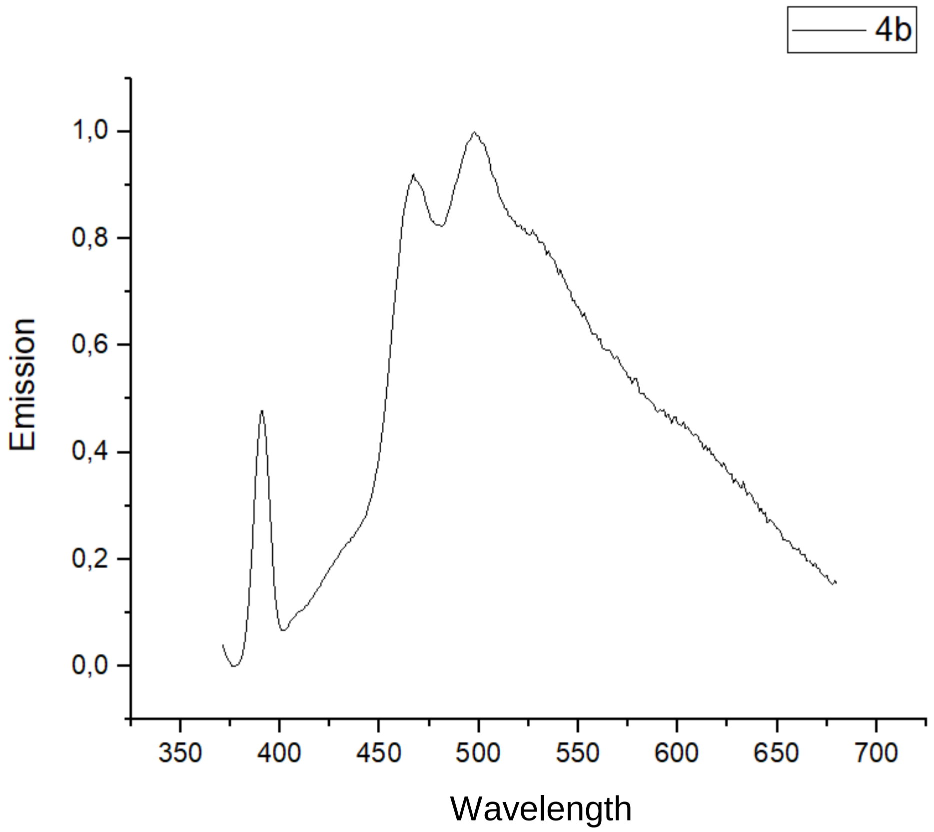


5.2. Emission spectra

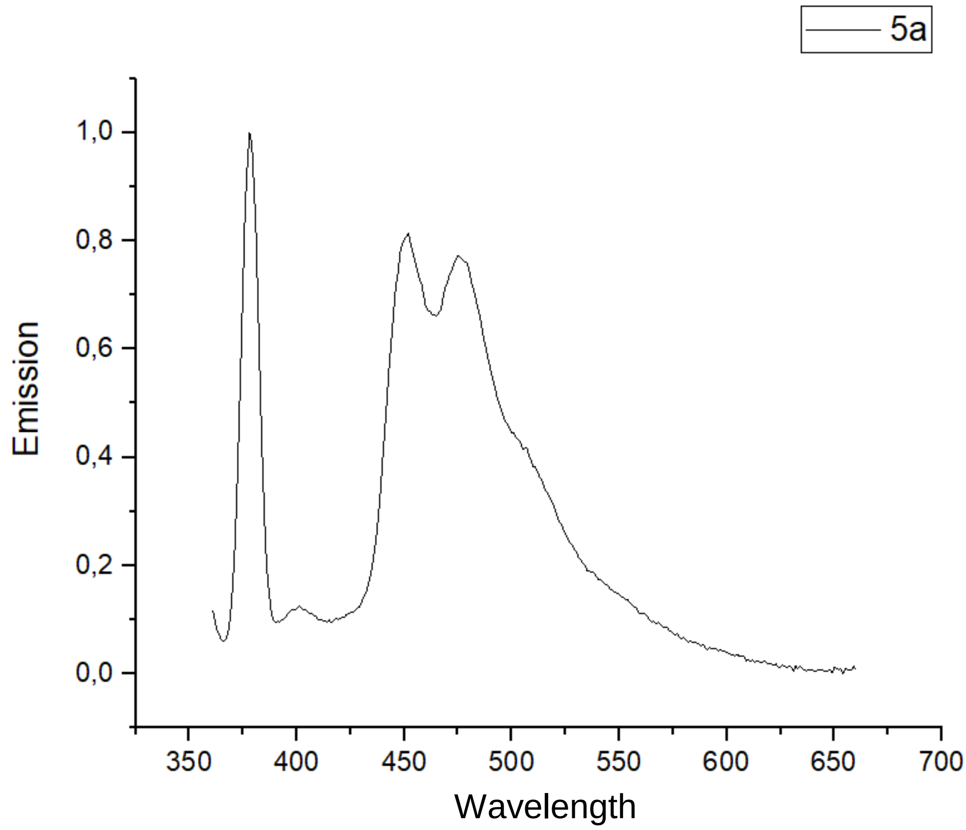
Spectrum S36. Emission of **4a** (C = 10^{-5} M in THF) λ_{ex} = 352 nm



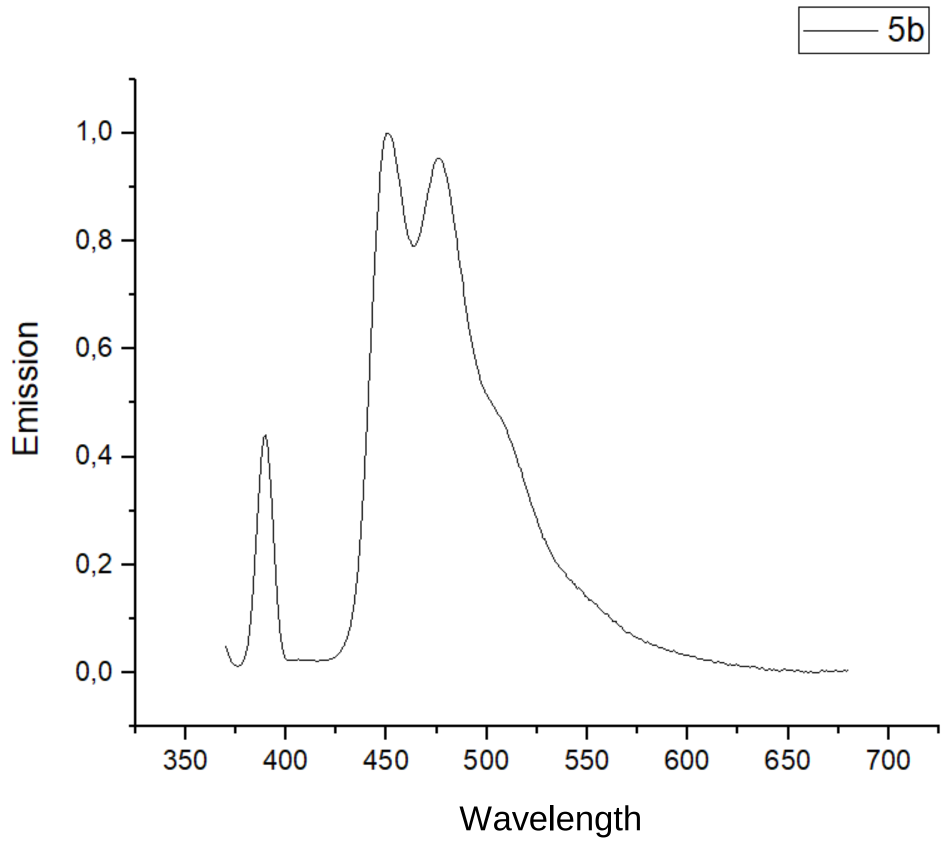
Spectrum S37. Emission of **4b** (C = 10^{-5} M in THF) λ_{ex} = 351 nm



Spectrum S38. Emission of **5a** (C = 10^{-5} M in THF) λ_{ex} = 341 nm

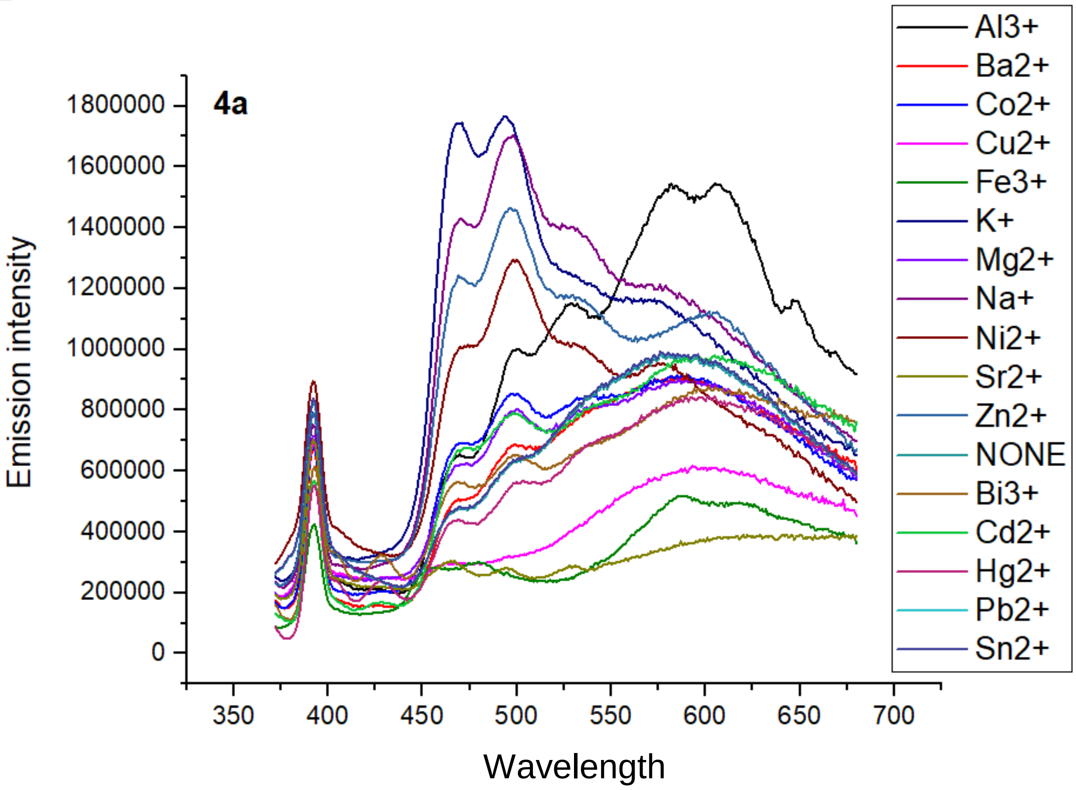


Spectrum S39. Emission of **5b** (C = 10^{-5} M in THF) λ_{ex} = 350 nm

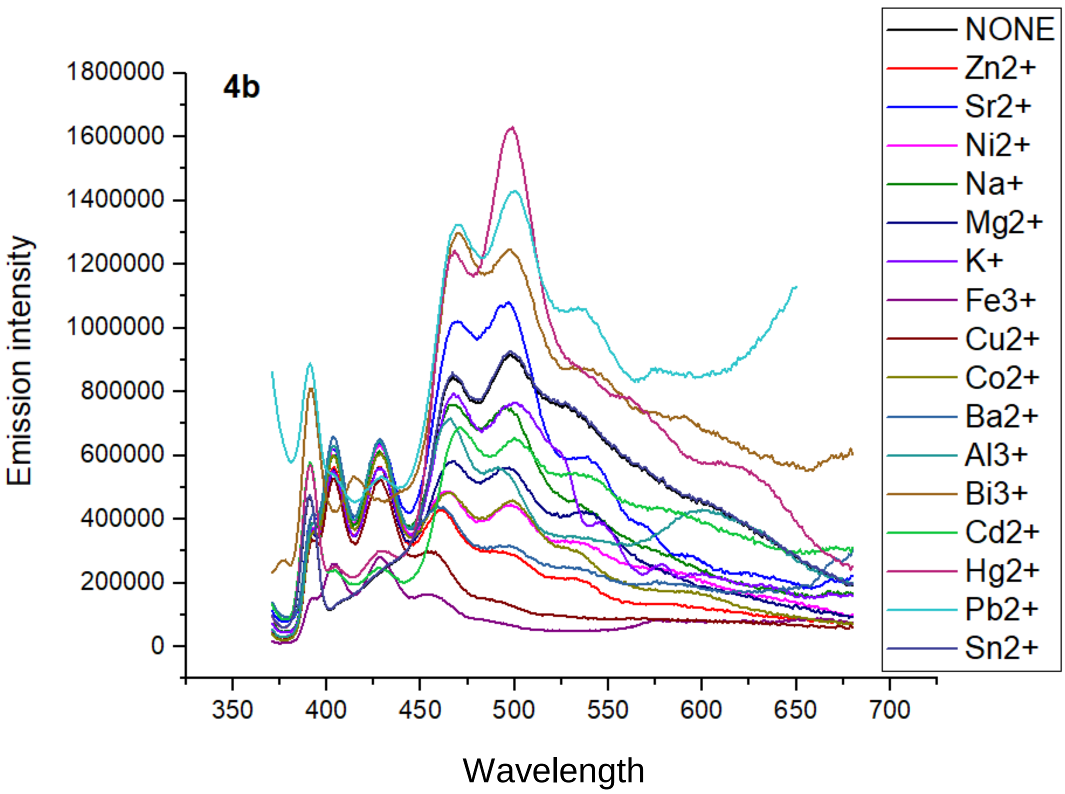


5.3. Emission spectra in the presence of various metal ions

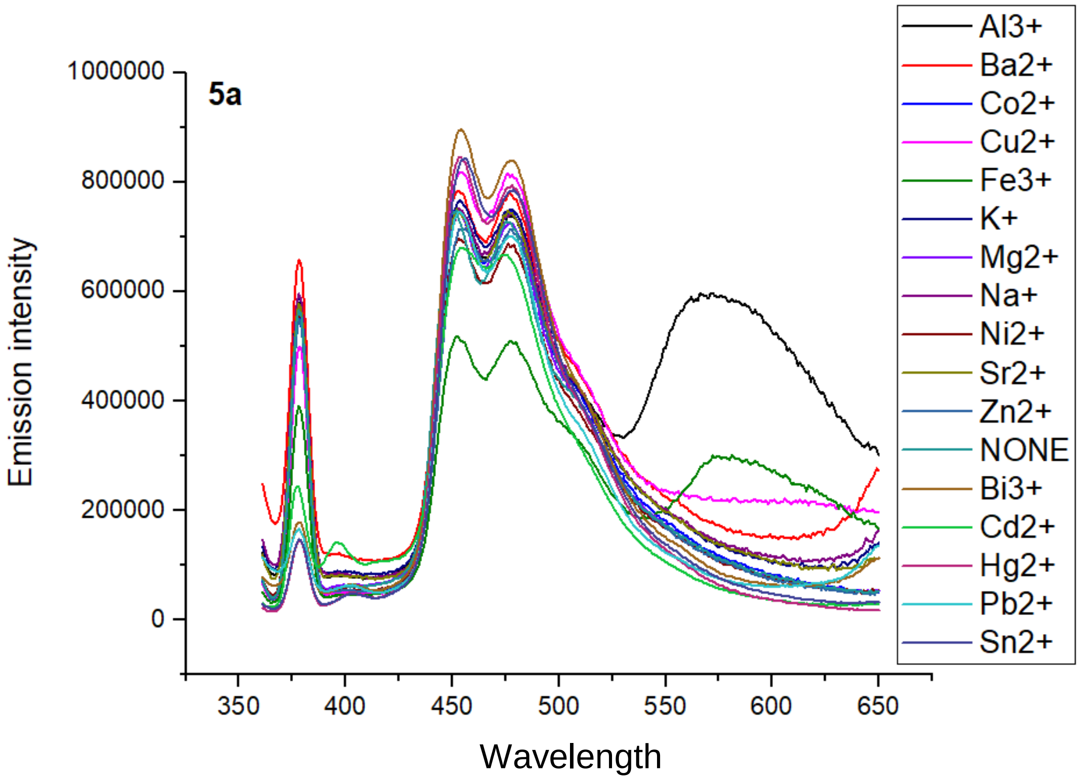
Spectrum S40. Emission of **4a** (C = 10^{-5} M in THF) with the presence of various metal ions (10 equiv in H_2O) λ_{ex} = 352 nm



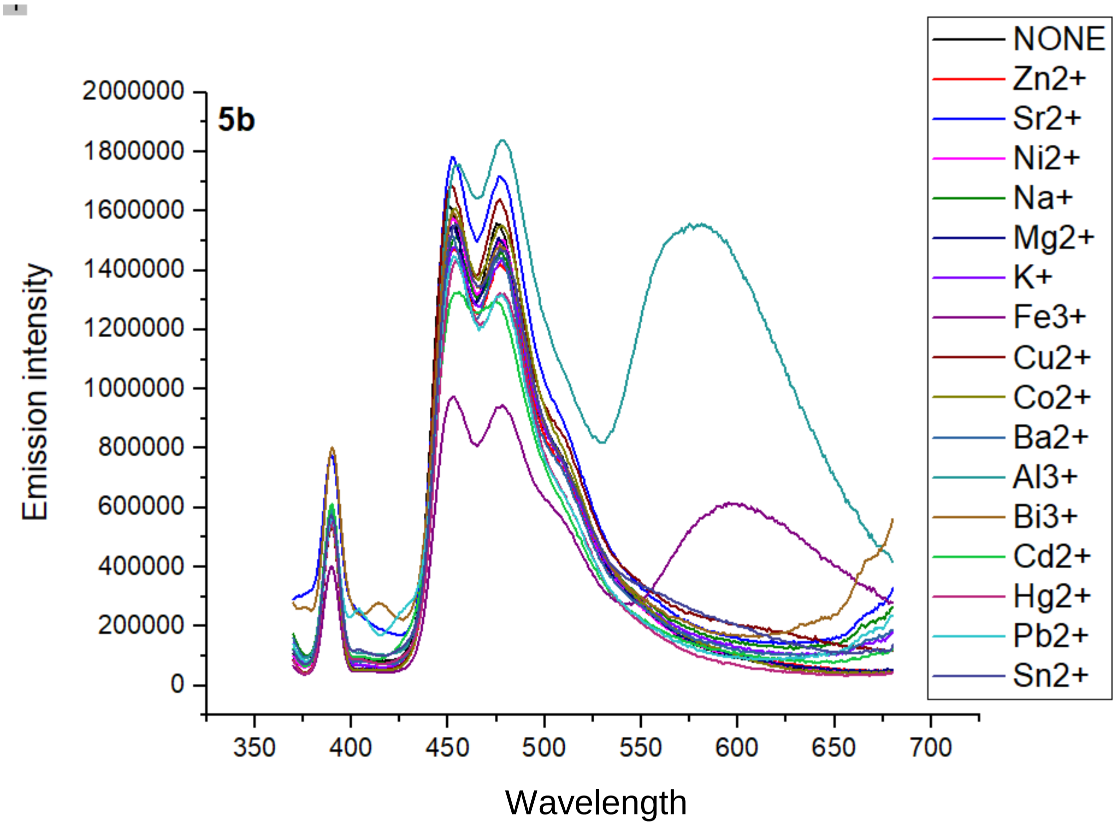
Spectrum S41. Emission of **4b** (C = 10^{-5} M in THF) with the presence of various metal ions (10 equiv in H_2O) λ_{ex} = 351 nm



Spectrum S42. Emission of **5a** (C = 10^{-5} M in THF) with the presence of various metal ions (10 equiv in H_2O) λ_{ex} = 341 nm



Spectrum S43. Emission of **5b** (C = 10^{-5} M in THF) with the presence of various metal ions (10 equiv in H_2O) λ_{ex} = 350 nm



6. Determining the stoichiometry of ligand: metal complex

The Job's method[1] was applied to determine the stoichiometry of **5b**:Al^{3+} and **5b**:Fe^{3+} complexes.

Figure S1. Job's plot for stoichiometry determination of **5b**:Al^{3+}complex, λ_{ex} = 350 nm, λ_{em} = 570 nm.

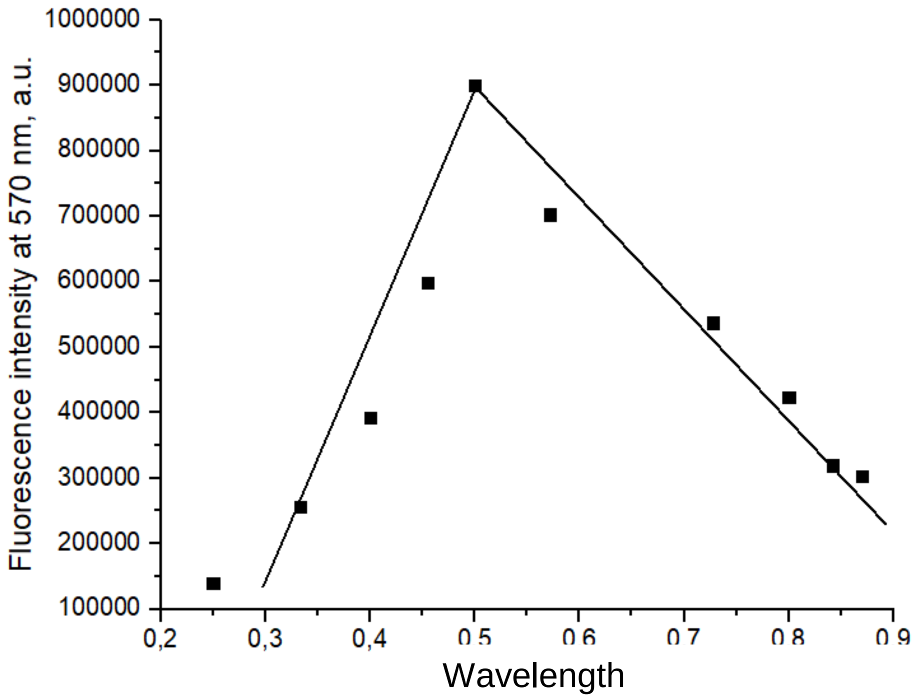
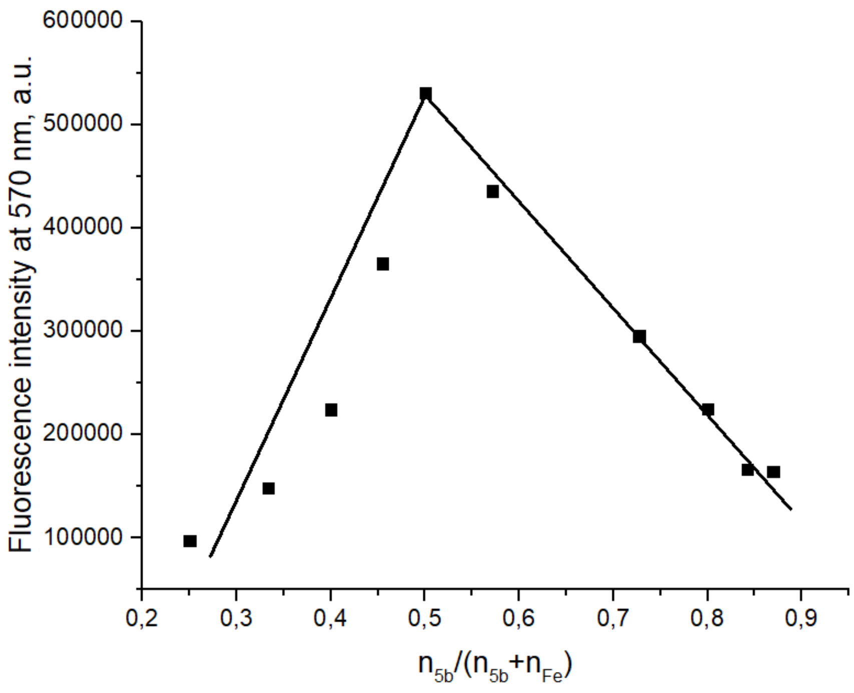


Figure S2. Job's plot for determination stoichiometry of **5b**:Fe^{3+} complex, λ_{ex} = 350 nm, λ_{em} = 570 nm.



7. Binding constants measurement

Figure S3. Plot of emission intensity of **5b** with increasing concertation of Al^{3+} in THF, λ_{ex} = 350 nm, λ_{em} = 570 nm

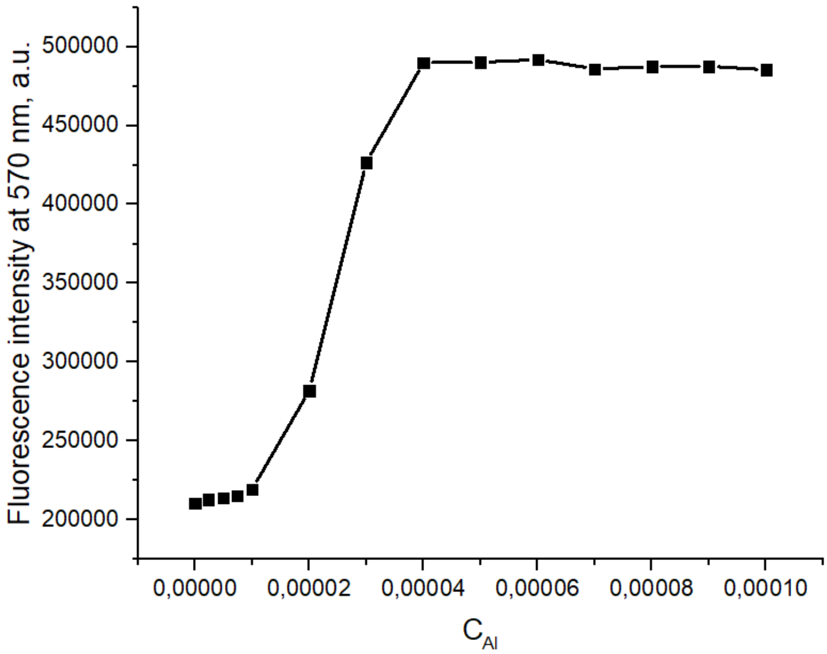
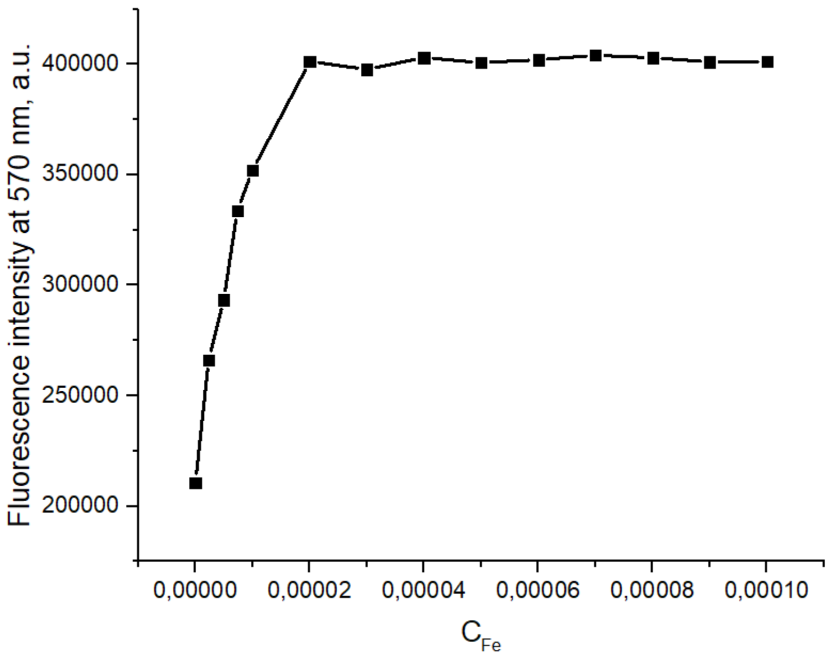


Figure S4. Plot of emission intensity of **5b** with increasing concertation of Fe^{3+} in THF, λ_{ex} = 350 nm, λ_{em} = 570 nm



Binding interactions of **5b** with Al^{3+} and Fe^{3+} cations in THF with addition of various concertation of guests in H_2O have been estimated using the modified Benesi–Hildebrand equation.[2]

$(F_{max} - F_0) / (F_x - F_0) = 1 + (1/K) (1/[M]^n)$, where F_0, F_x and F_{max} are the emission intensities of **5b** in the absence of Al^{3+} or Fe^{3+}, at an intermediate Al^{3+} and Fe^{3+}, and at a concentration of complete interaction, respectively, where K is the binding constant, M is the concentration of Al^{3+} or Fe^{3+} and n is the number of Al^{3+} or Fe^{3+} ions bound per **5b** (here, n = 1).

Emission intensities of **5b** (10 μM) in presence of different Al^{3+} or Fe^{3+} concentrations, namely 2.33, 5, 7.33, 10, 30, 50, 70, 90 μM have been used for calculation of binding constant.

The equation (example for Al^{3+}) used is:

$(F_{max} - F_0) / (F_x - F_0) = 1+ (1/K[M]^n)$, where F_{max} = 492880 a.u., F_0 = 210512 a.u., n = 1.

When 30 μM Al^{3+} is added to **5b** (10 μM), Fx = 426766 a.u.,

Now, $(F_{max}-F_0) / (F_x-F_0)$ = (492880 - 210512) / (426766- 210512) and 1/ [M] = 1/(30)

or, 1.3057 = 1 + 1/ 30K

Similar calculations were performed to other concentrations.

Thus, plot of $(F_{max} - F_0) / (F_x - F_0)$ *vs.* 1/ [M] based on Y = 1+ P × X, yields the slope, P = 439.97 for Al^{3+} and 6.13 for Fe^{3+}.

So, $K(Al^{3+}) = 2.27 \cdot 10^3\ M^{-1}$; $K(Fe^{3+}) = 1.63 \cdot 10^5\ M^{-1}$.

Figure S5. Benesi–Hildebrand equation for determining the binding constant of **5b** with Al^{3+} using the fluorescent titration, λ_{ex} = 350 nm, λ_{em} = 570 nm

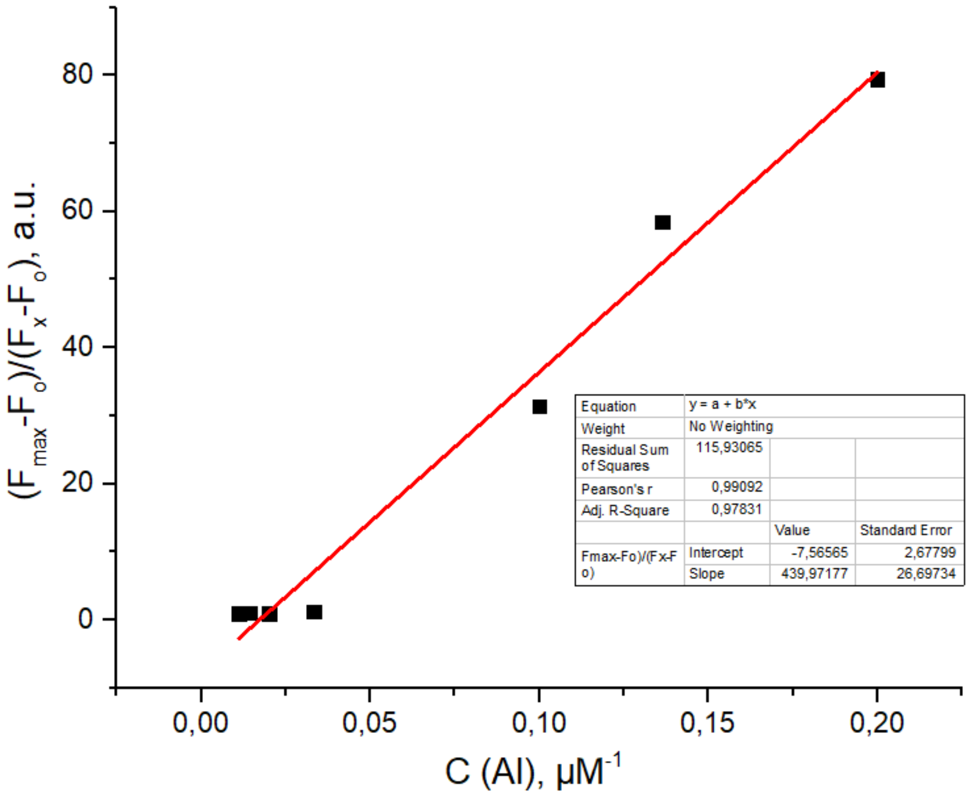
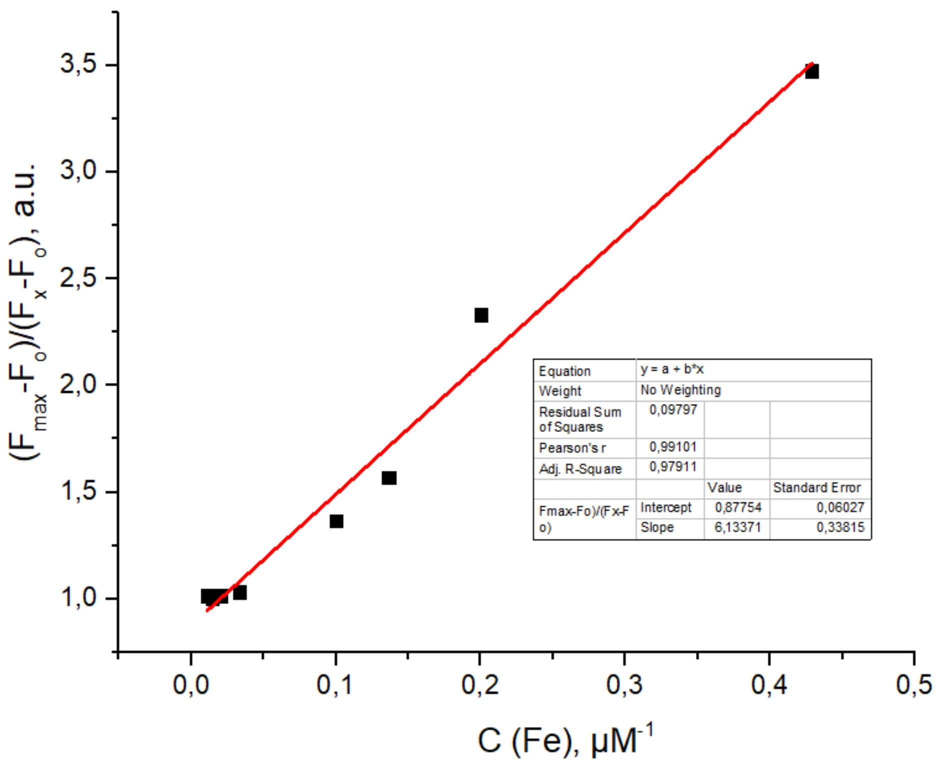
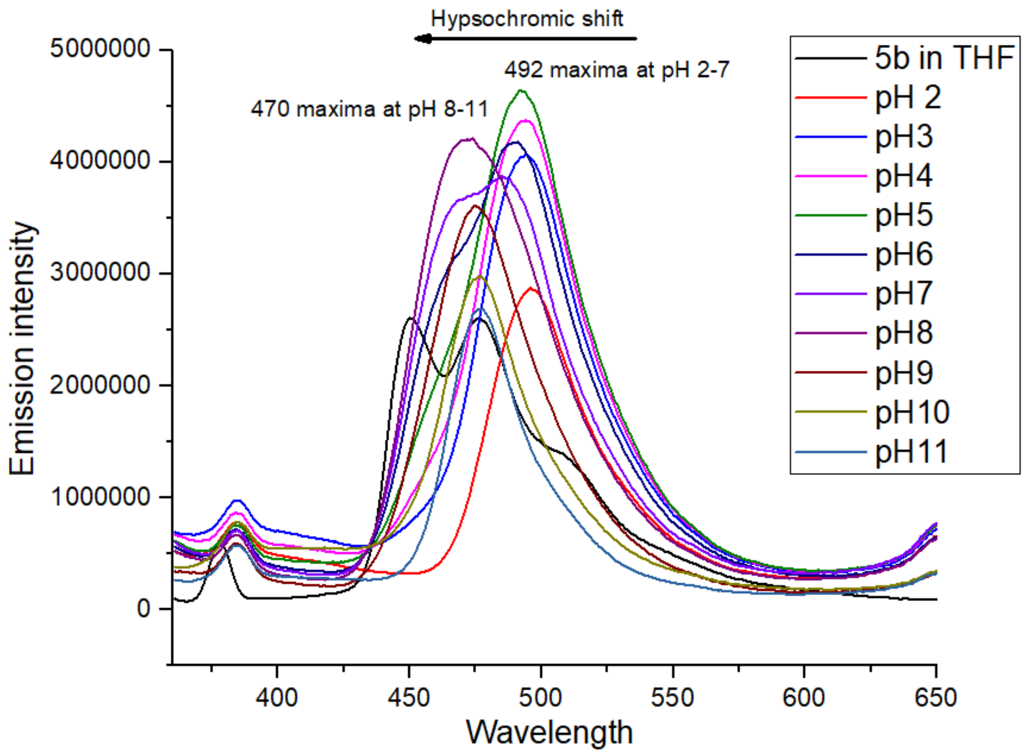


Figure S6. Benesi–Hildebrand equation for determining binding constant of **5b** with Fe^{3+} using the fluorescent titration, λ_{ex} = 350 nm, λ_{em} = 570 nm

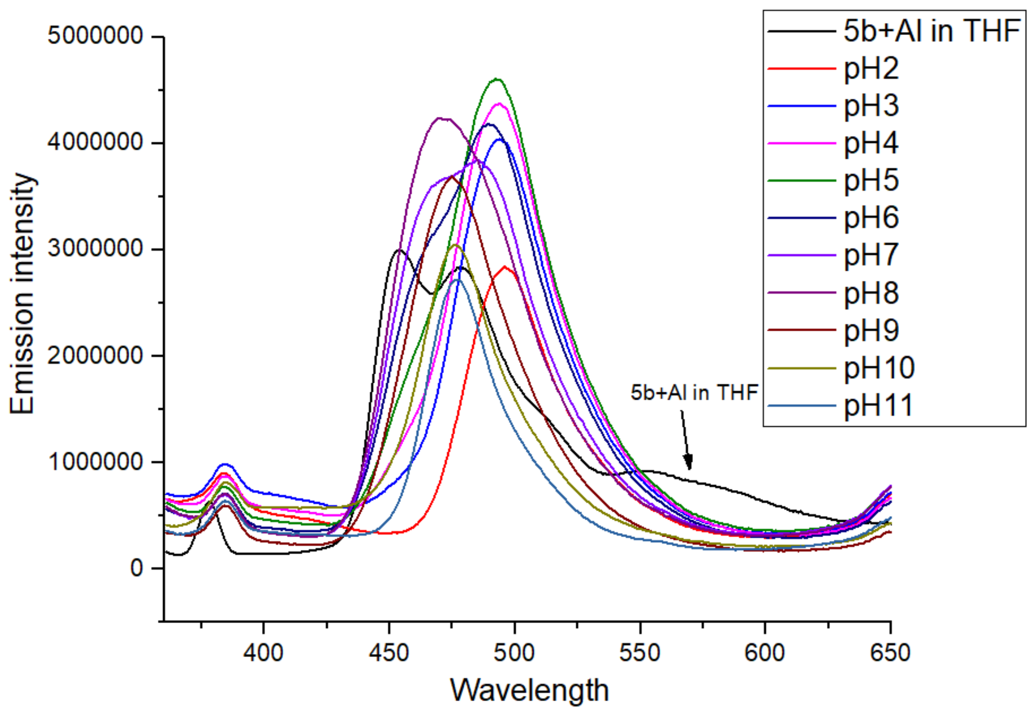


8. Emission spectra depending on pH

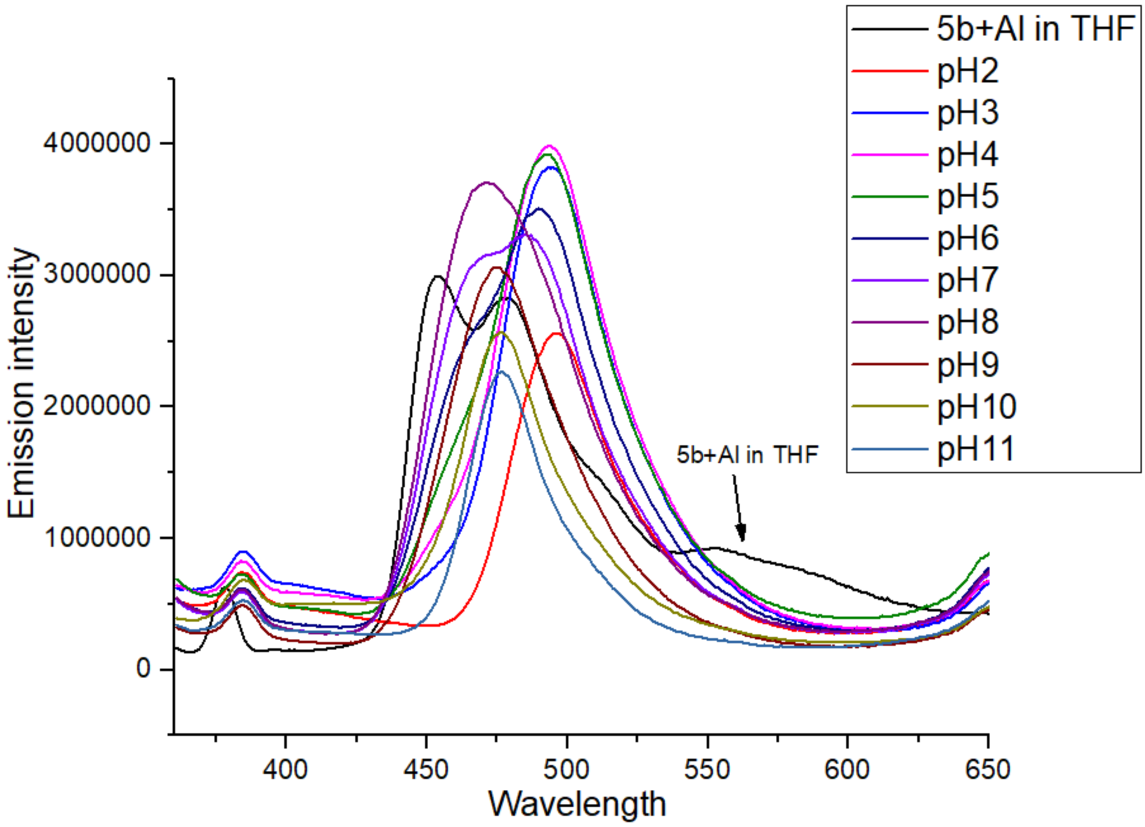
Spectrum S44. Emission intensity of **5b** in different pH, λ_{ex} = 350 nm, λ_{em} = 570 nm



Spectrum S45. Emission intensity of **5b** in different pH with addition of 10 equiv of Al^{3+}, λ_{ex} = 350 nm, λ_{em} = 570 nm



Spectrum S46. Emission intensity of **5b** in different pH with addition of 10 equiv of Al^{3+} and Fe^{3+}, λ_{ex} = 350 nm, λ_{em} = 570 nm



9. References

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