A rhodamine based chemodosimeter for the detection of Group 13 metal ions

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Experimental Section

Material & physical measurements

Rhodamine 6G, trans cinnamaldehyde, nitrates of Al^{3+}, Cr^{3+},Ga^{3+}, In^{3+}, Fe^{3+}, Tl^{3+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, *etc.* were procured from Sigma Aldrich and used as received. All other reagents for synthesis or measurements were obtained from commercial sources and used them as received. N-(rhodamine-6G)lactam-ethylenediamine (L_1) has been synthesized following a published method [S1]. Solvents for obtaining different spectra were purified and dried by following published methods before use [S2]. FT-IR spectra of HL-CIN and HL-CIN with different Group 13 metal ions were recorded by ATR technique on a Perkin Elmer spectrometer (Spectrum Two). Elemental analysis of the probe and its metal complexes was performed on a 2400 Perkin Elmer Series-II CHN analyzer.^{1}H and ^{13}C NMR spectra of HL-CIN and HL-CIN with different Group 13 metal ions were obtained on a Bruker 300 MHz spectrometer with tetramethylsilane (δ = 0) as the internal standard. The ESI-MS spectra of HL-CIN and HL-CIN with different Group 13 metal ions were recorded in methanol on Qtof Micro YA263 mass spectrometer. Absorption spectra of HL-CIN and HL-CIN with different Group 13and other relevant metal ions were obtained with a Shimadzu UV 1900 spectrophotometer whereas the corresponding emission spectra were measured on a Horiba Duetta Fluorescence and Absorbance Spectrometer. Luminescence lifetime measurements of HL-CIN and HL-CIN with different Group 13 metal ions were performed using a TCSPC setup from Horiba Jobin Yvon. The luminescence decay data collection was done on a Hamamatsu MCP photomultiplier (R3809) and the data were processed using the IBH DAS6 software.

Emission quantum yields (Φ) of HL-CIN and HL-CIN with different Group 13 metal ions were determined by using the following formula:

$$\Phi_{sample} = [(OD_{standard} \times A_{sample} \times \eta^2_{sample})/(OD_{sample} \times A_{standard} \times \eta^2_{standard})] \times \Phi_{standard}$$

where OD is the optical density of HL-CIN and HL-CIN with different Group 13 metal ions at the excitation wavelength i.e. 495 nm, A represents the area under the fluorescence emission curve, and η is the refractive index of the media in which spectra were recorded. Rhodamine- 6G is considered as the standard to determine the quantum yields (quantum yield of Rhodamine- 6G is 0.94 in ethanol) [S3].

Fluorescence and UV-vis spectral experiments

The absorption and fluorescence spectra of *HL-CIN* were obtained in absence and in the presence of different metal ions in 10 mM HEPES buffer in H_2O/ethanol = 1:9 (v/v) (pH 7.4) at room temperature. Generally, nitrate salts of different metal ions were used in the spectral measurements where concentration of the probe was fixed as 40 μM and concentrations of different metal ions were varied. Excitation wavelength for fluorescence measurement was 495 nm.

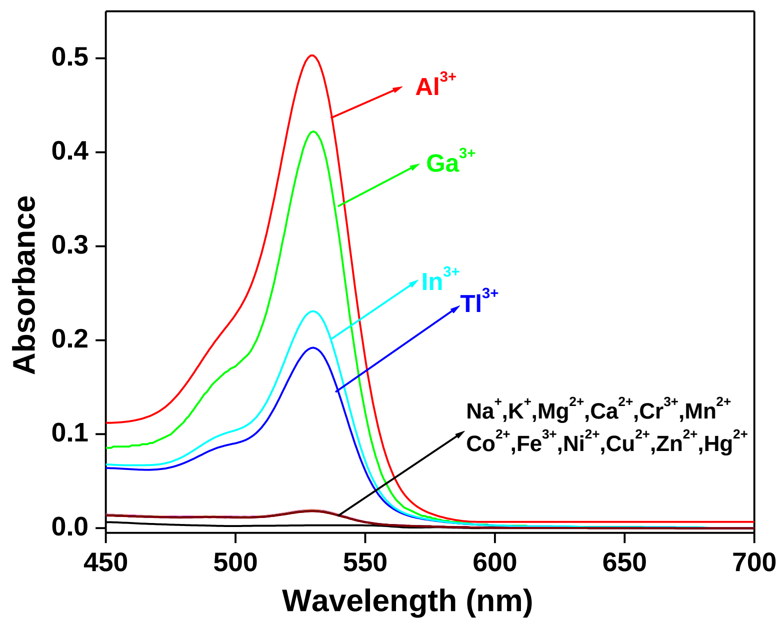


Fig. S1 Absorption spectra of HL-CIN (40 μM) in the presence of 40 μM of different metal ions in 10 mM HEPES buffer in H_2O/ethanol = 1:9 (v/v; pH = 7.4) at room temperature.

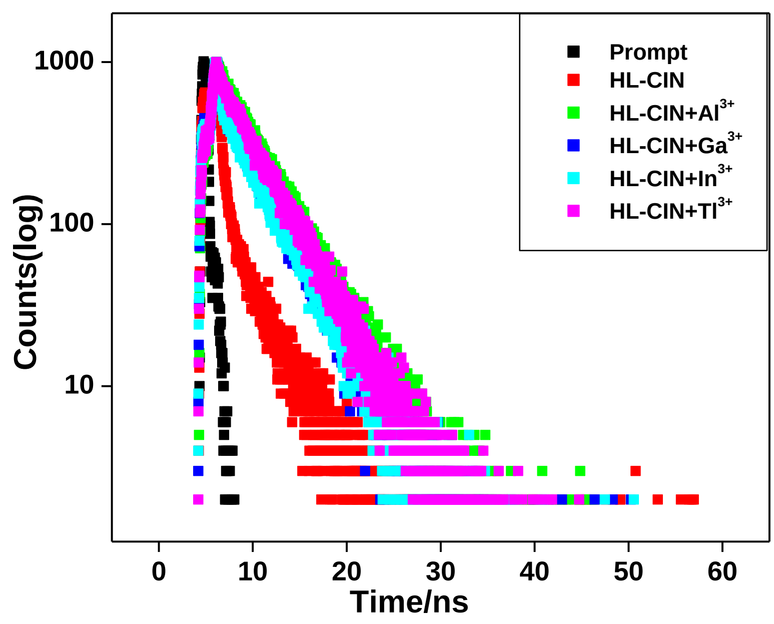


Fig. S2 Excited state fluorescence decay behavior of HL-CIN and HL-CIN in the presence of Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+} in 10 mM HEPES buffer in H_2O/CH_3OH = 1:9 (v/v; pH = 7.4) at room temperature.

Determination of LOD of HL-CIN for Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+}

Limit of detection (LOD) for HL-CIN has been determined by 3σ method [S4] by following equation:

LOD = K*Sb1/S

where K = 2 or 3 (3 in this case); here Sb1 is the standard deviation of the blank solution; and S is the slope of the calibration curve obtained from Linear dynamic plot of Fluorescence Intensity vs [metal ion] M.

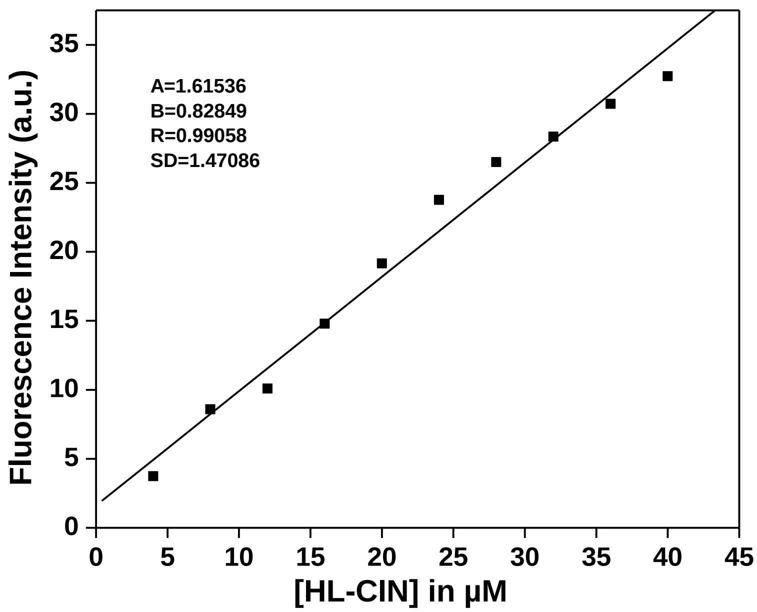


Fig. S3 Determination of Sb1 of the blank, HL-CIN solution.

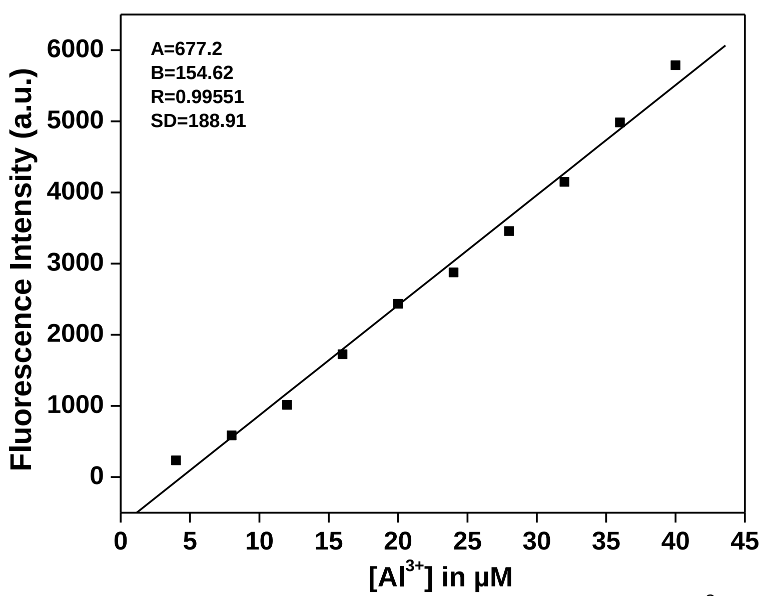


Fig. S4 Linear dynamic plot of Fluorescence Intensity vs. [Al^{3+}] for the determination of S (slope); [HL-CIN] = 40 μM

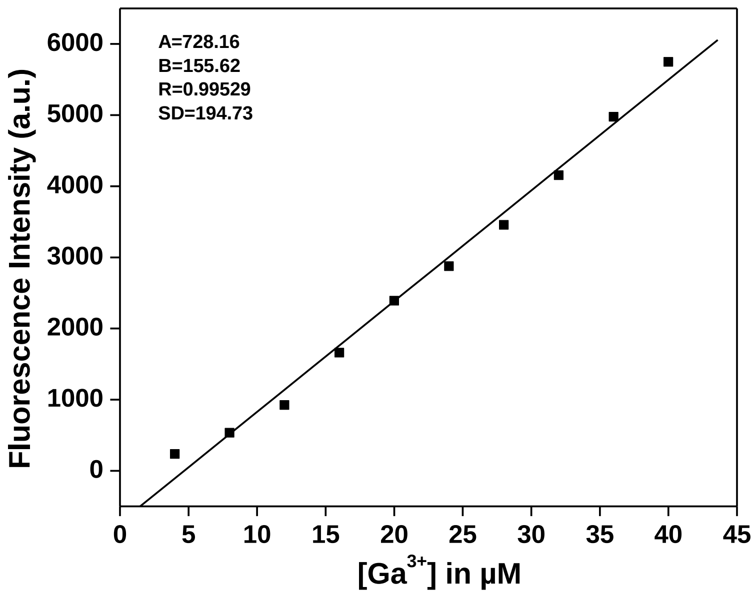


Fig. S5 Linear dynamic plot of Fluorescence Intensity vs. [Ga^{3+}] for the determination of S (slope); [HL-CIN] = 40 μM

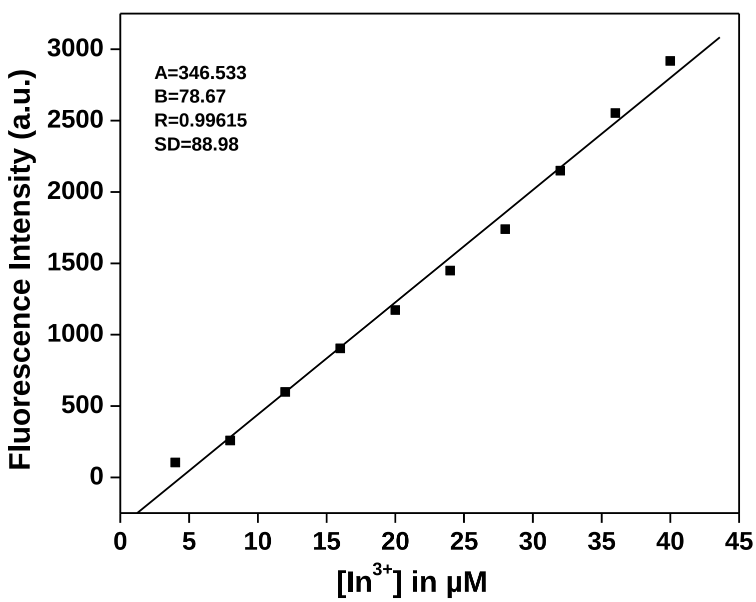


Fig. S6 Linear dynamic plot of Fluorescence Intensity vs. [In^{3+}] for the determination of S (slope); [HL-CIN] = 40 μM

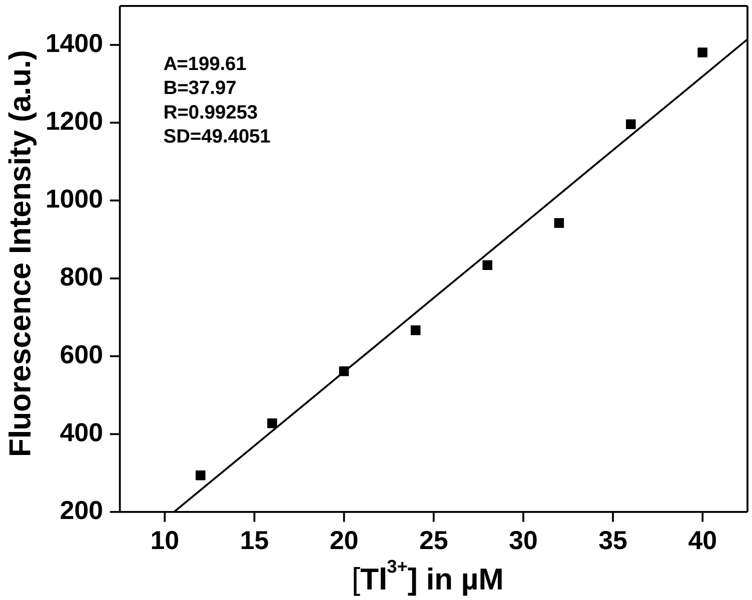


Fig. S7 Linear dynamic plot of Fluorescence Intensity vs. [Tl^{3+}] for the determination of S (slope); [HL-CIN] = 40 μM

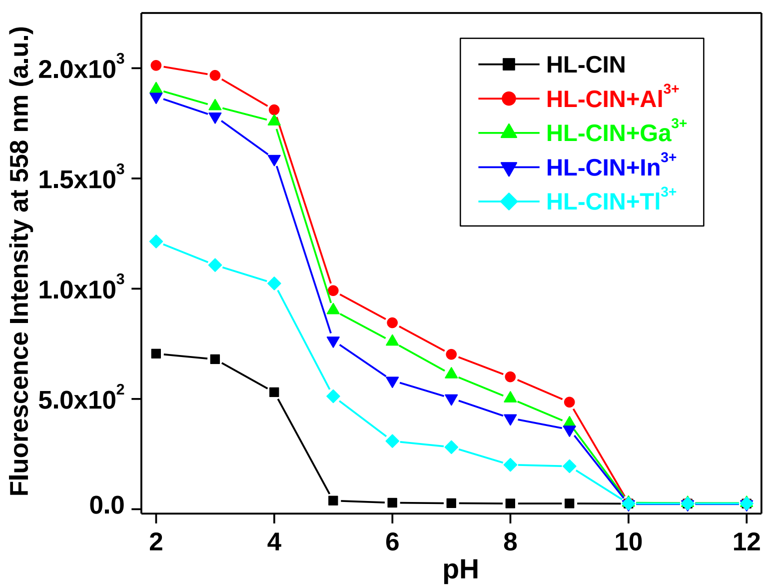


Fig. S8 Fluorescence intensity of HL-CIN (40 μM) and HL-CIN in the presence of one equivalent of Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+} at different pH.

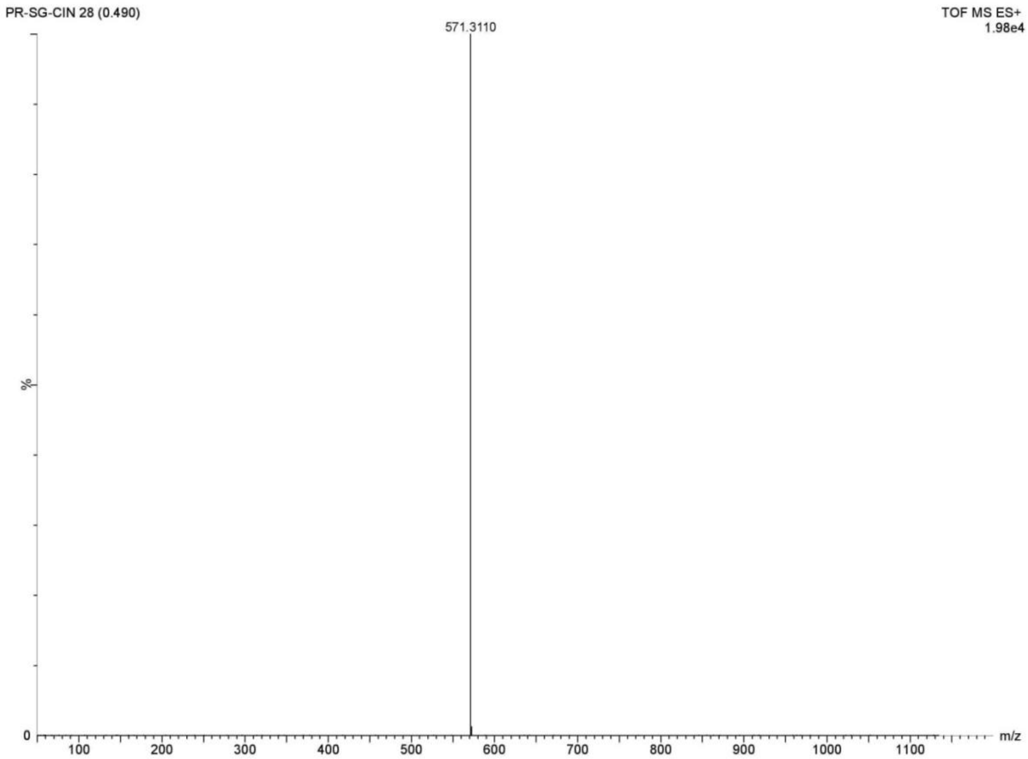


Fig. S9 ESI mass spectrum of HL-CIN in methanol.

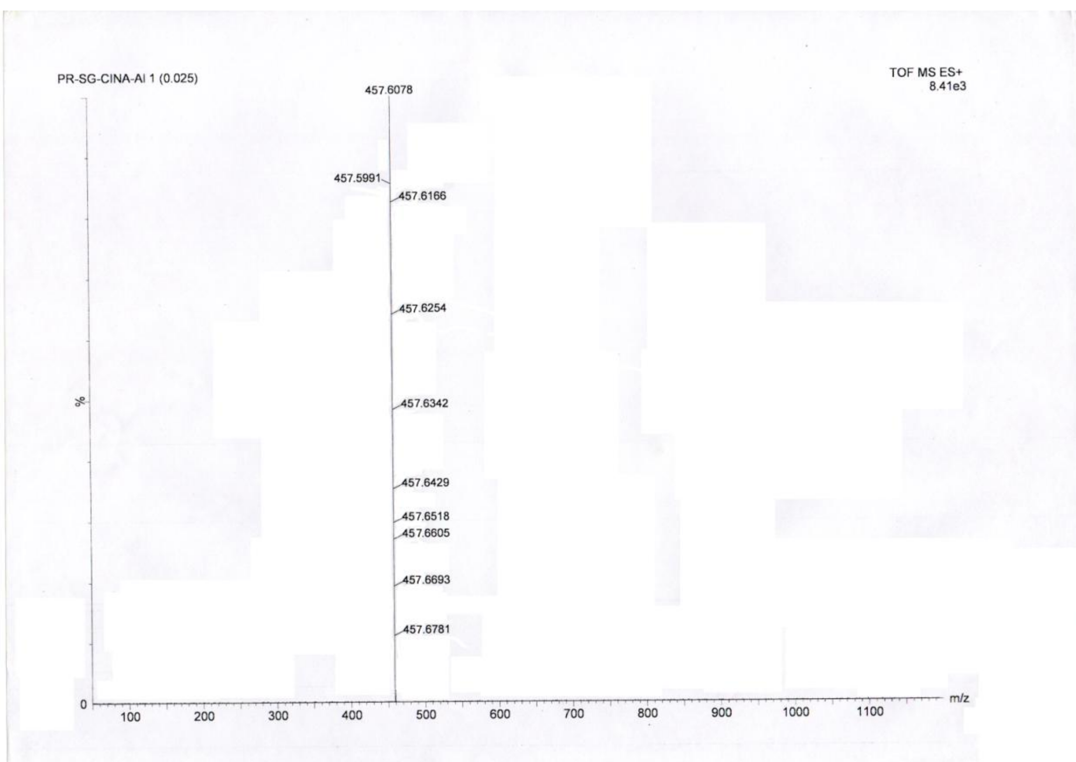


Fig. S10 ESI mass spectrum of HL-CIN in the presence of Al^{3+} in methanol.

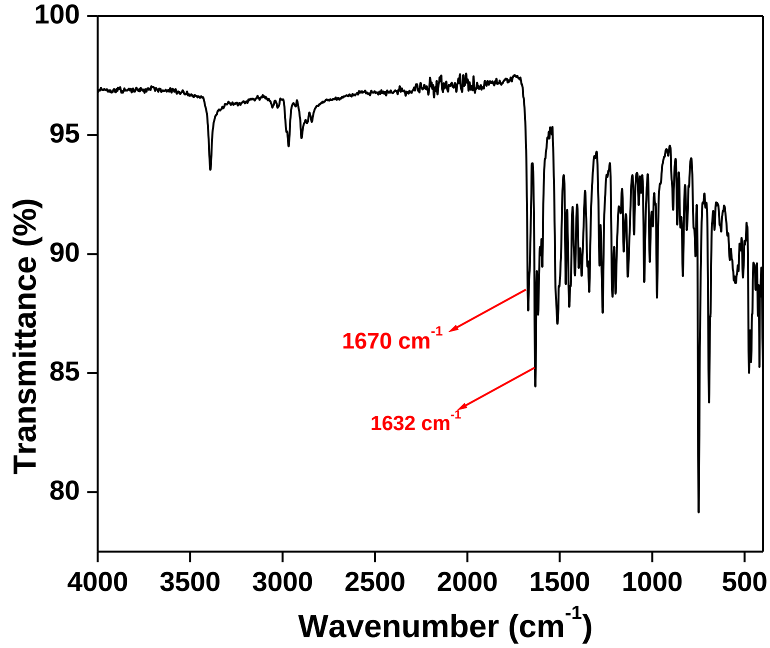


Fig. S11 FT-IR spectrum of HL-CIN.

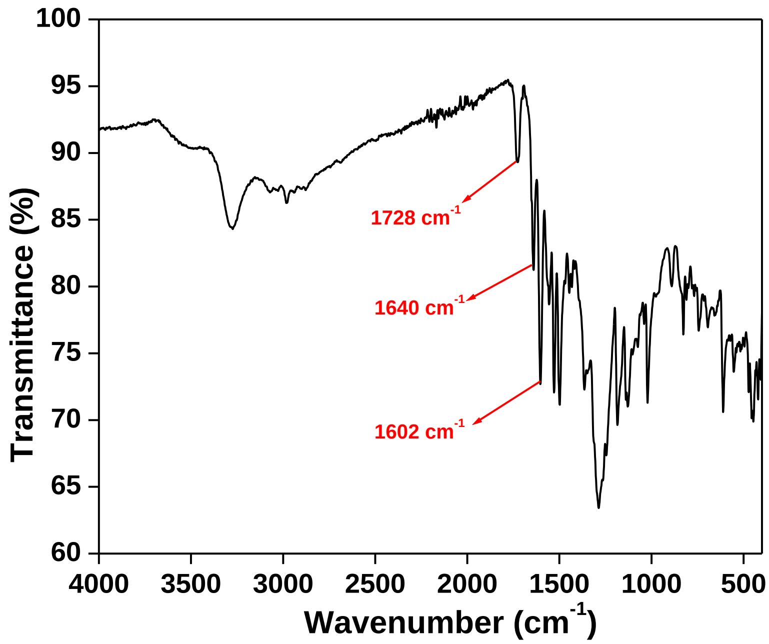


Fig. S12 FT-IR spectrum of HL-CIN in the presence of Al^{3+}.

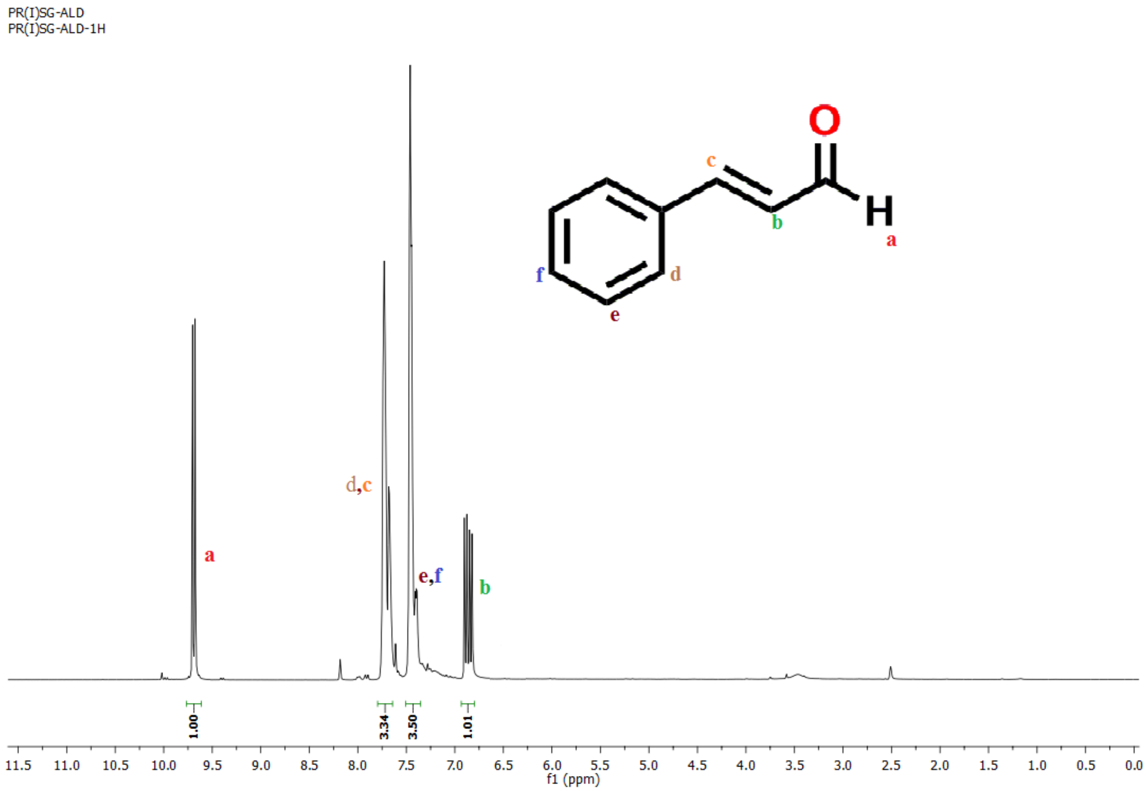


Fig. S13 ^{1}H NMR spectra of *trans* cinnamaldehyde in DMSO-d_6.

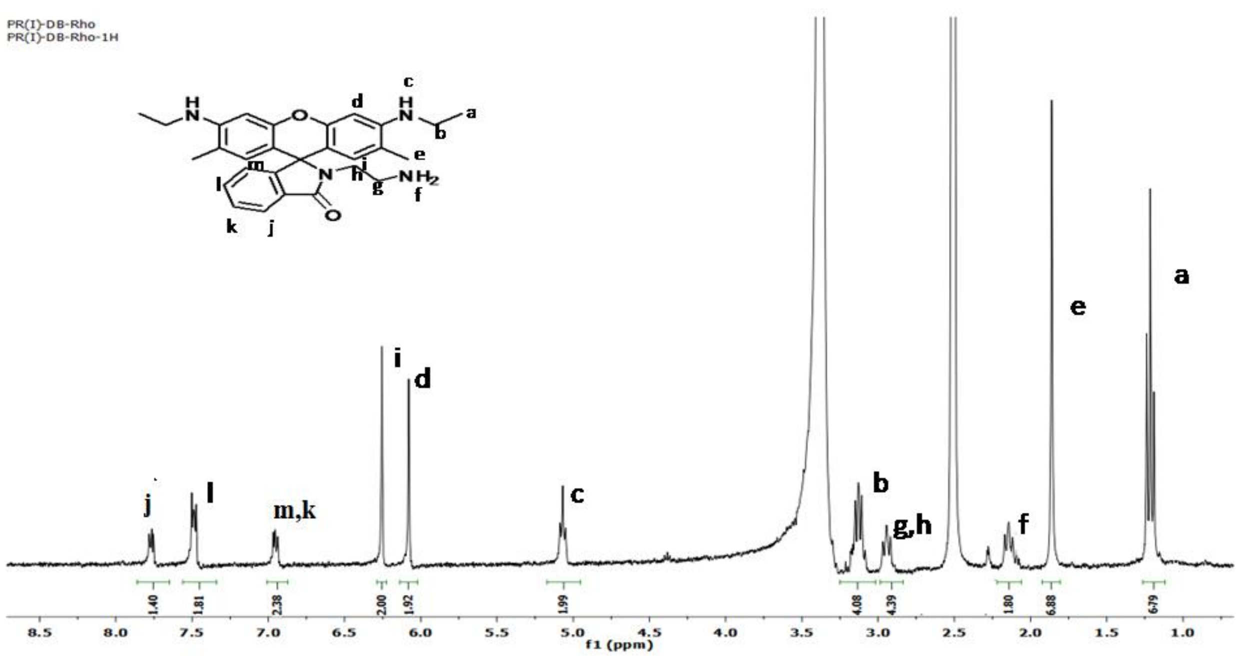


Fig. S14 ^{1}H NMR spectra of L_1 in DMSO-d_6.

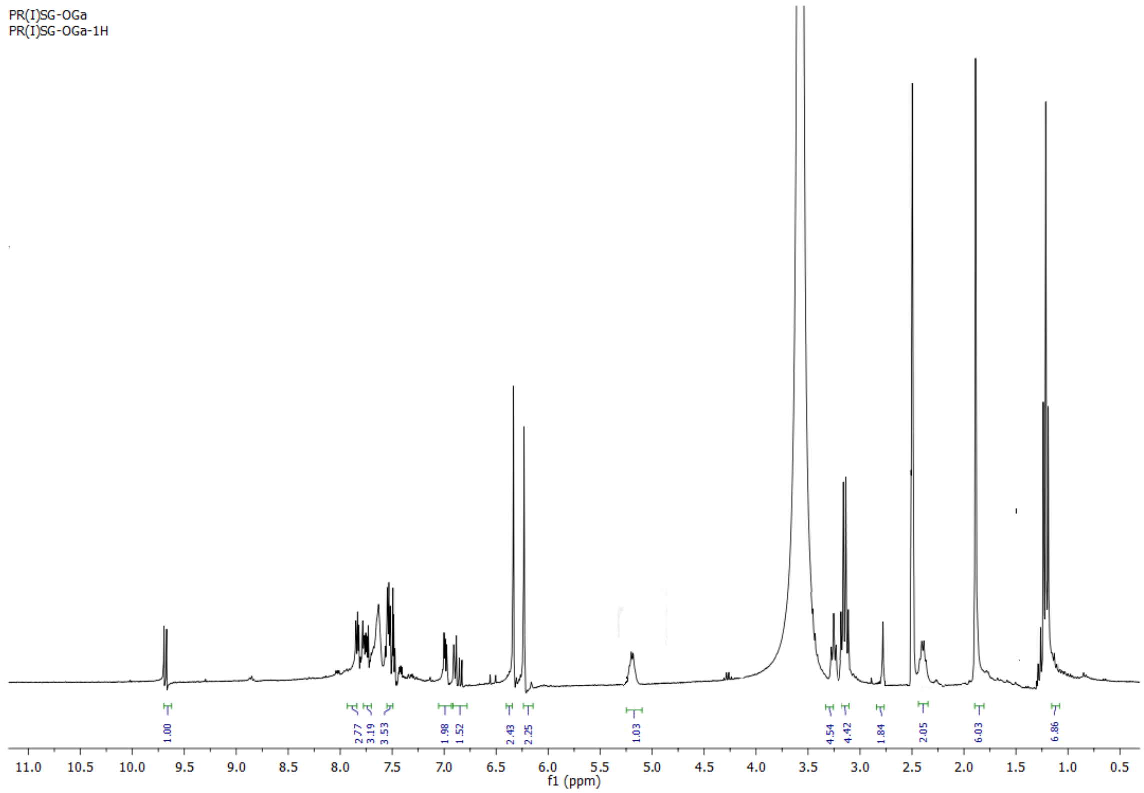


Fig. S15 ^{1}H NMR spectra of HL-CIN in the presence of Ga^{3+} in DMSO-d_6.

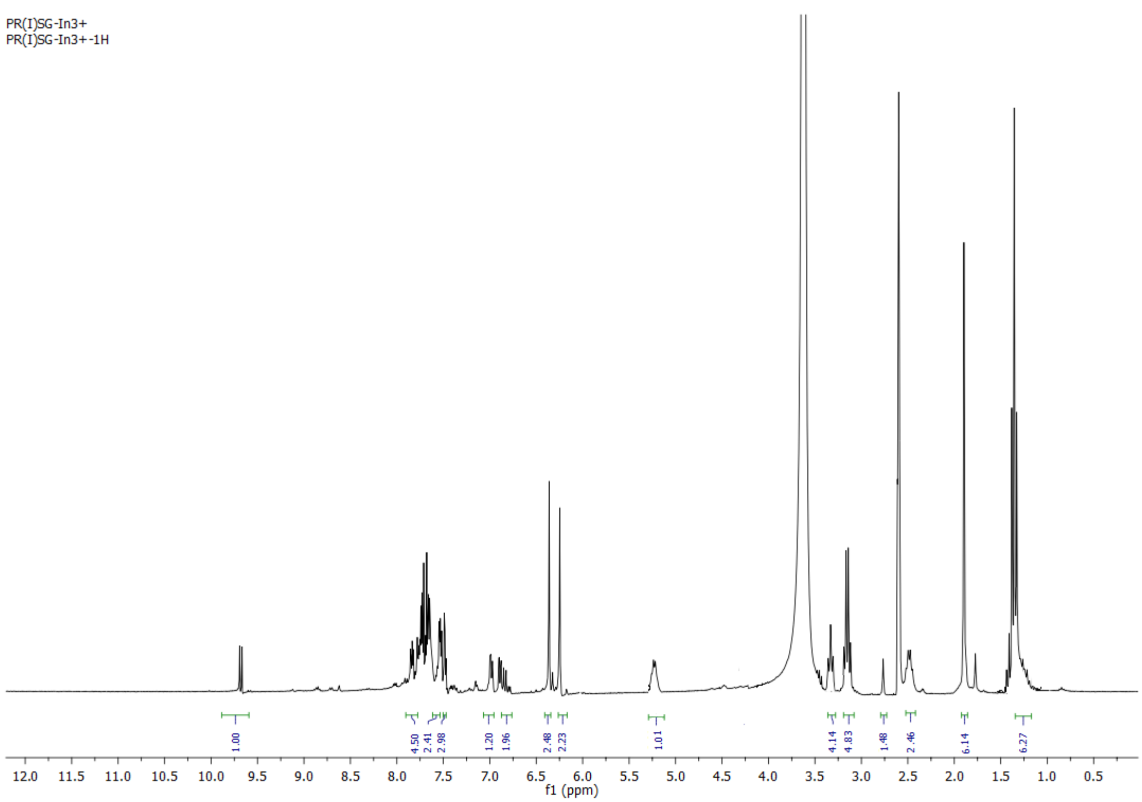


Fig. S16 ^{1}H NMR spectra of HL-CIN in the presence of In^{3+} in DMSO-d_6.

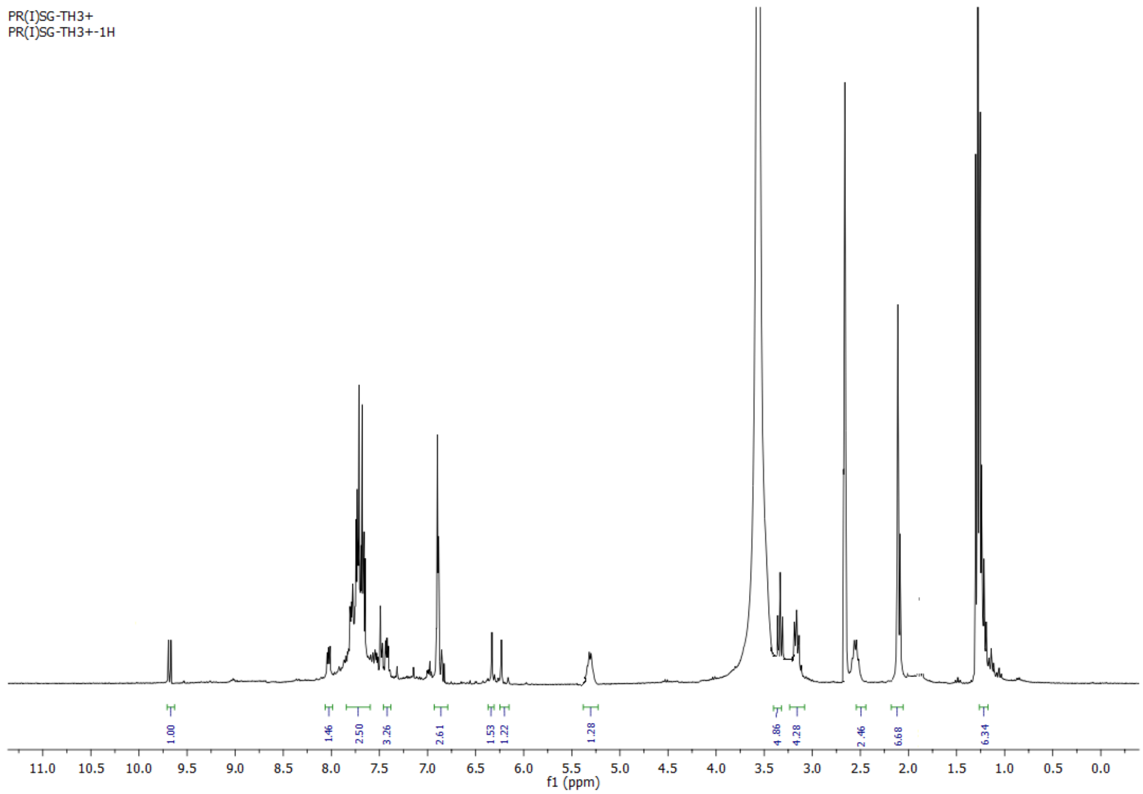


Fig. S17 ^{1}H NMR spectra of HL-CIN in the presence of Tl^{3+} in DMSO-d_6.

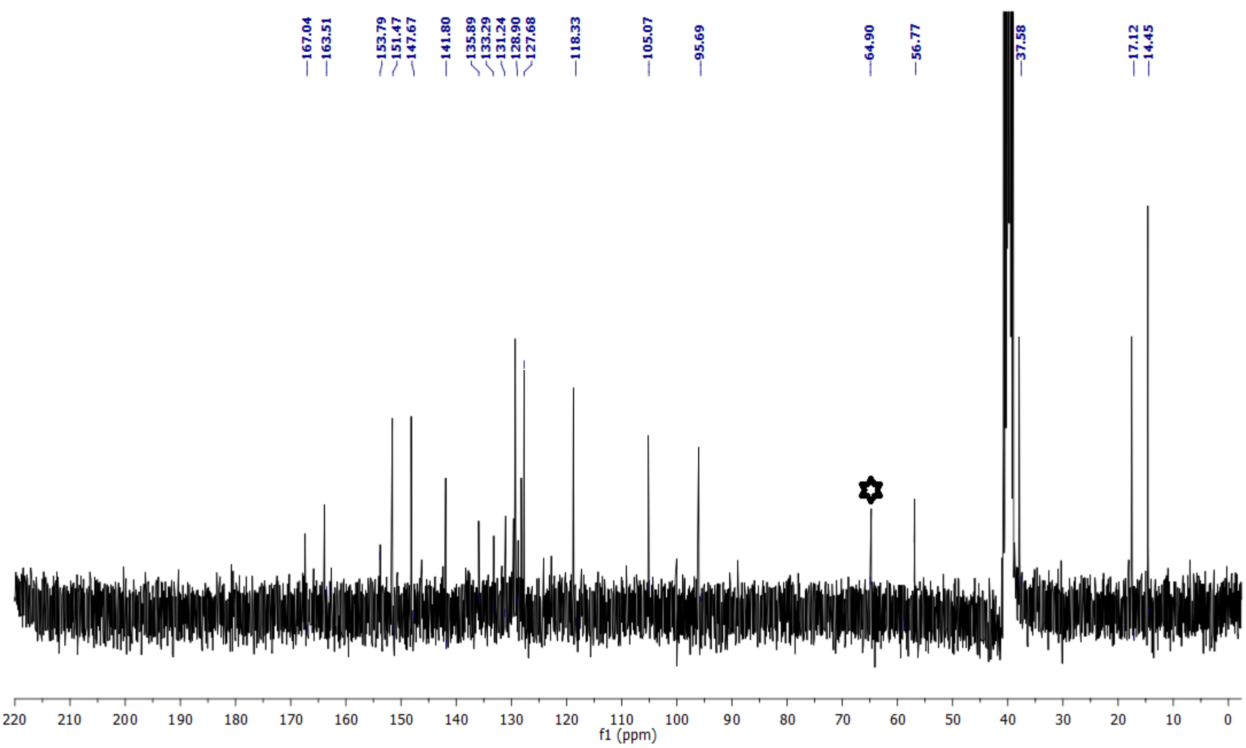


Fig. S18 ^{13}C NMR spectrum of f HL-CIN in DMSO-d_6.

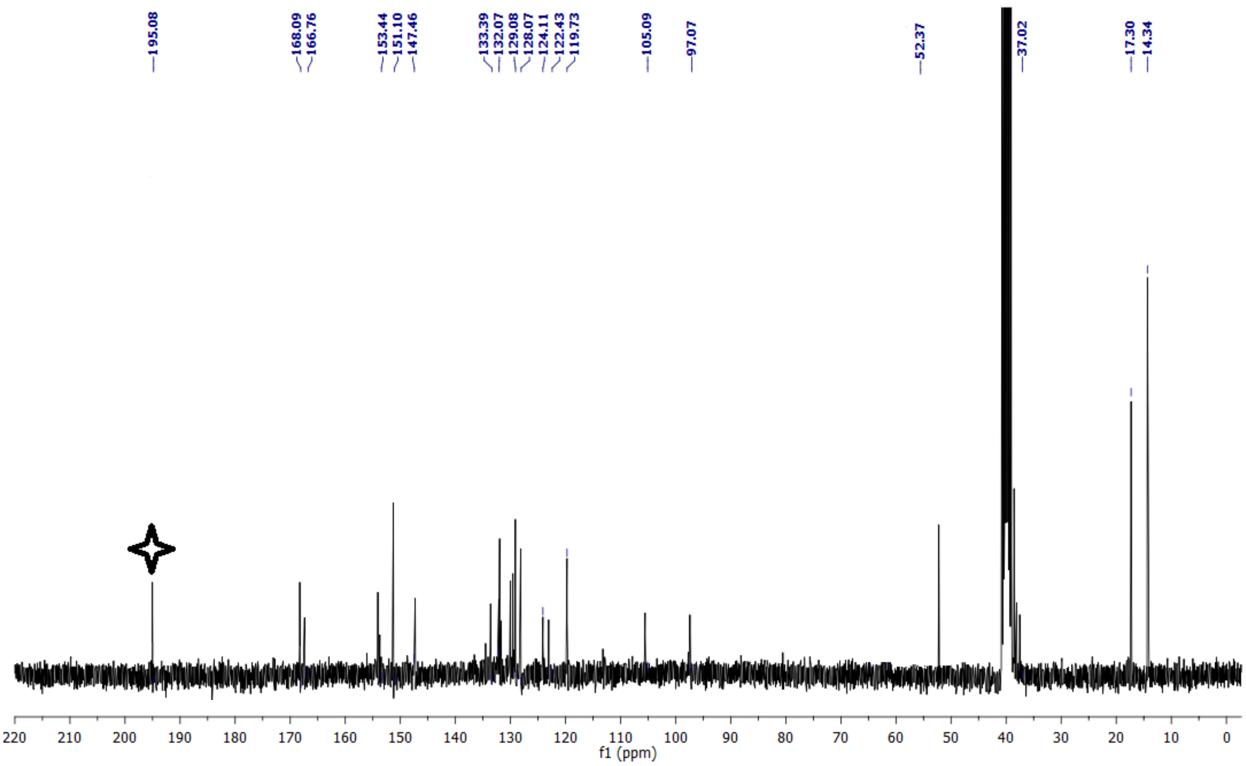


Fig. S19 ^{13}C NMR spectrum of HL-CIN in the presence of Al^{3+} in DMSO-d_6.

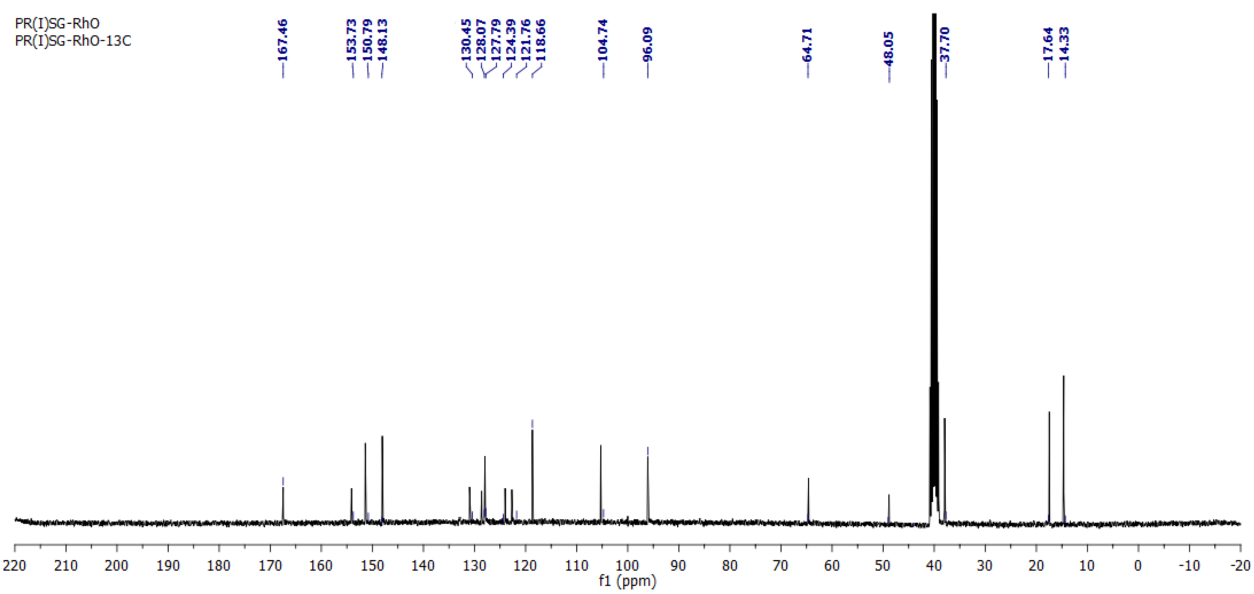


Fig. S20 ^{13}C NMR spectrum of L_1 in DMSO-d_6.

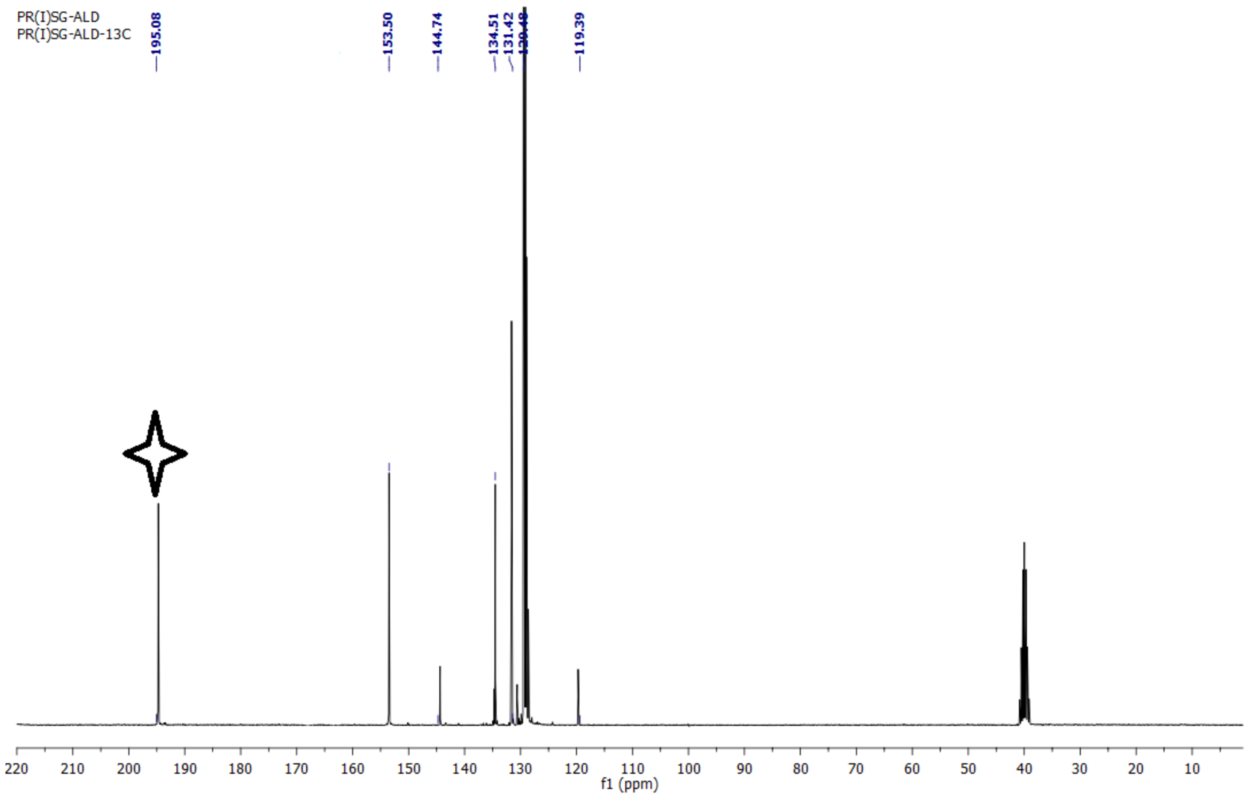


Fig. S21 ^{13}C NMR spectrum of *trans* cinnamaldehyde in DMSO-d_6.

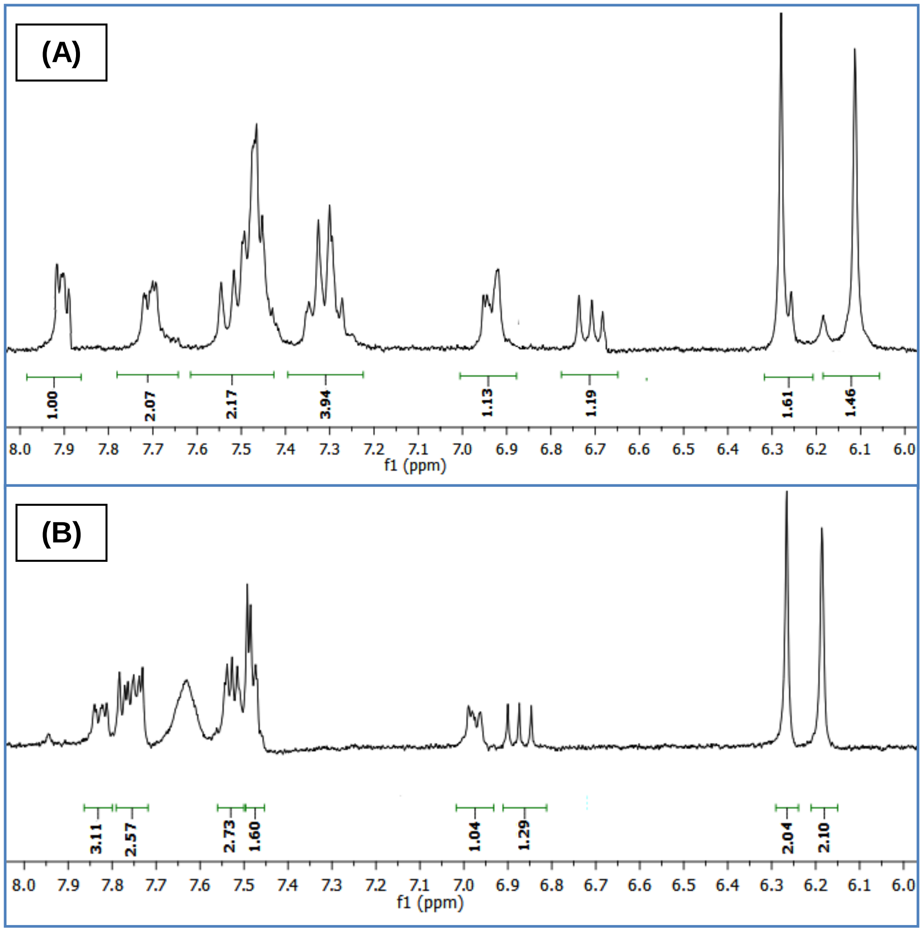


Fig. S22 ^{1}H NMR spectra of (A) HL-CIN and (B) HL-CIN in the presence of Al^{3+} showing the aromatic region in DMSO-d_6.

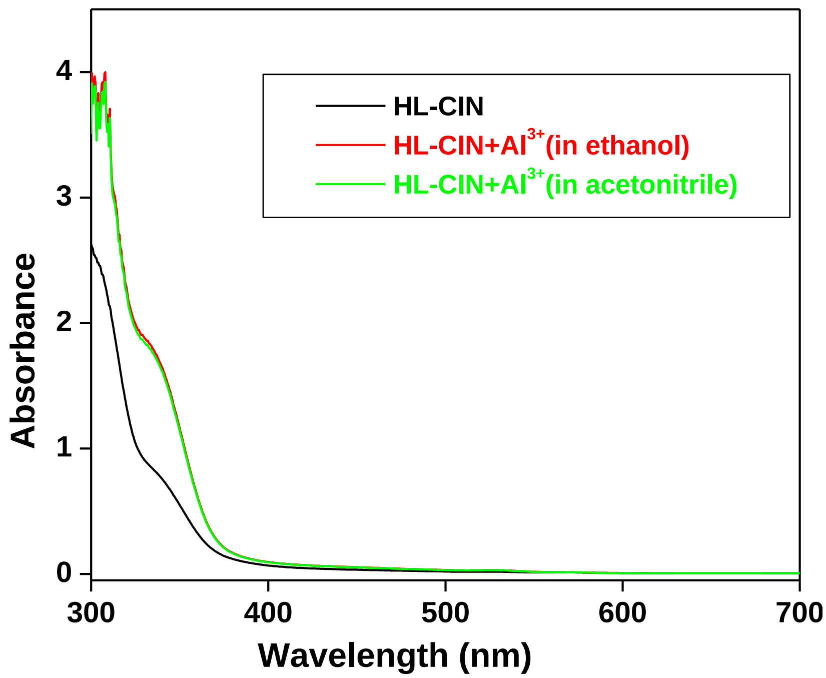


Fig. S23 Absorption spectra of HL-CIN (40 μM) in the presence of 40 μM of Al^{3+} ions in in ethanol and acetonitrile at room temperature.

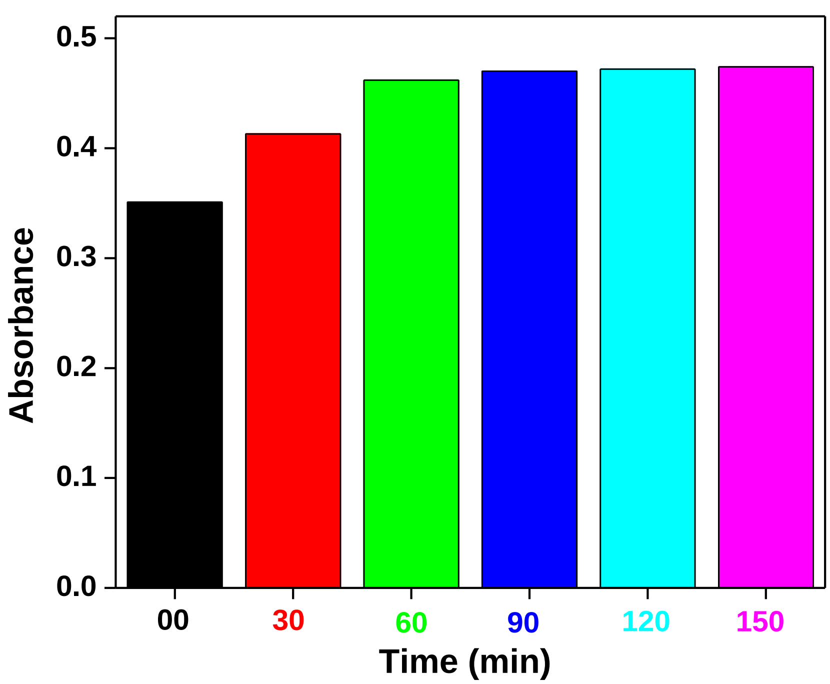


Fig. S24 Absorption spectra of HL-CIN (40 μM) in the presence of one equivalent Al^{3+} in 10 mM HEPES buffer in H_2O/CH_3OH = 1:9 (v/v; pH = 7.4) at room temperature in various time intervals.

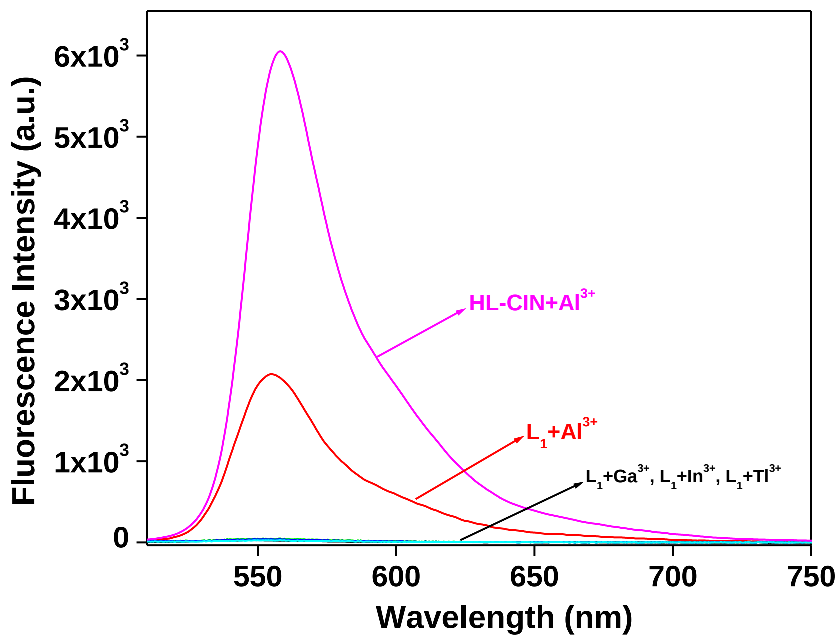


Fig. S25 Fluorescence spectra of L_1 in the presence of Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+} ions. Fluorescence spectrum of HL-CIN is given as a reference for comparison in changes in fluorescence intensity under the same experimental conditions.

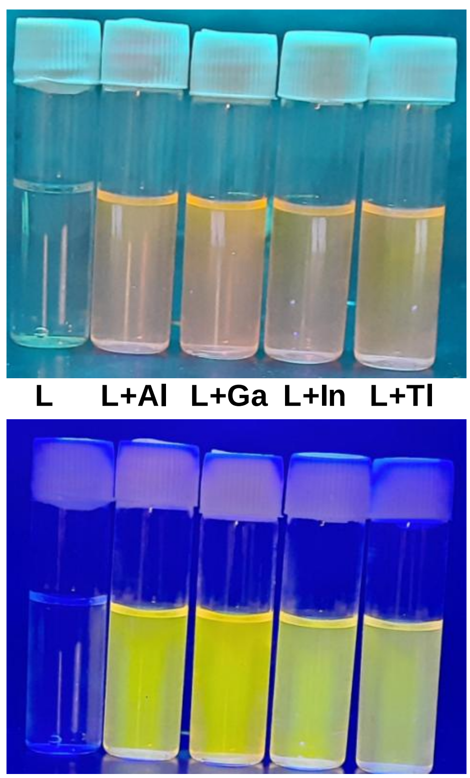


Fig. S26 Color of HL-CIN and HL-CIN in the presence of one equivalent of Group 13 metal ions in river water:ethanol (1:9, v/v) under visible light (upper row) and UV radiation (lower row).

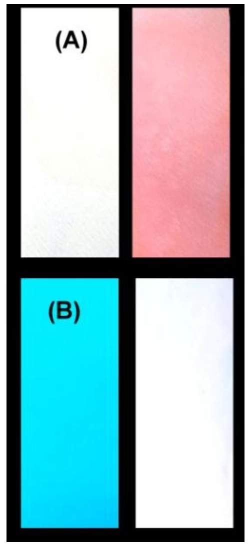
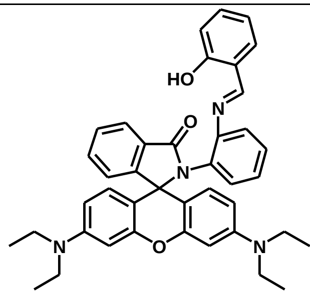
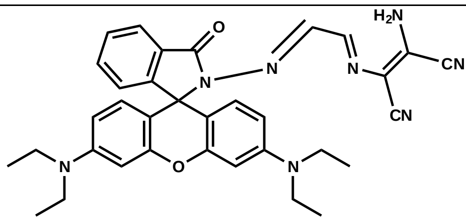
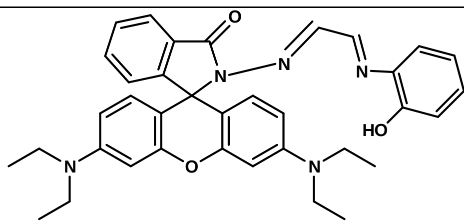
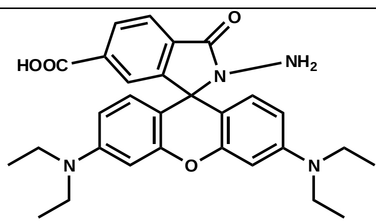
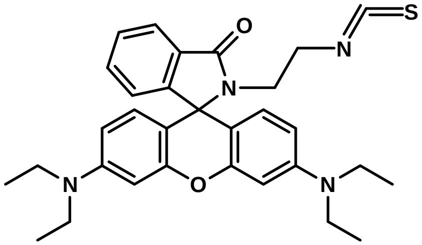
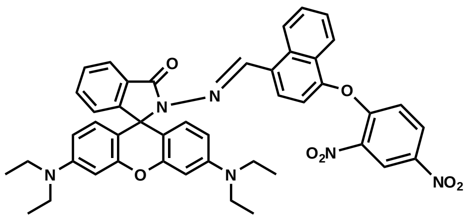
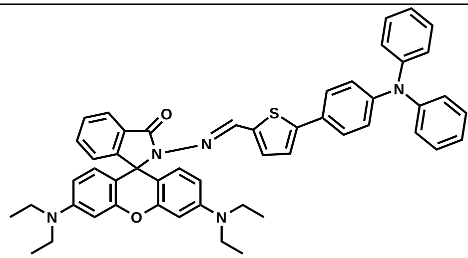
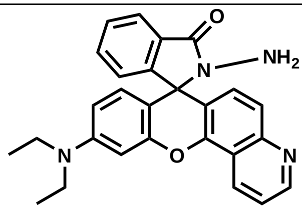
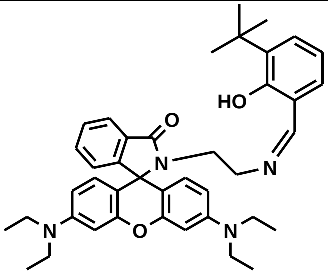
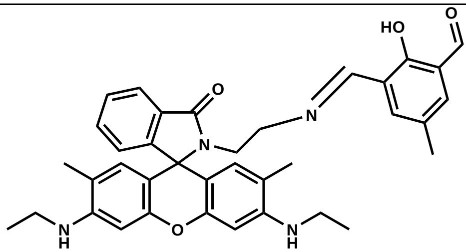
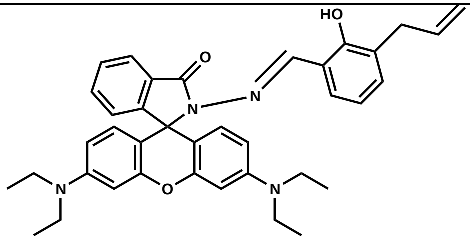
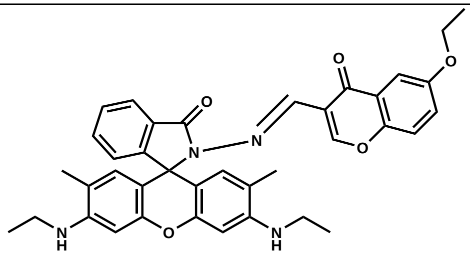


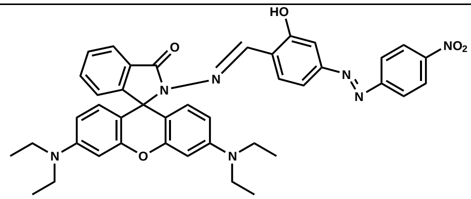
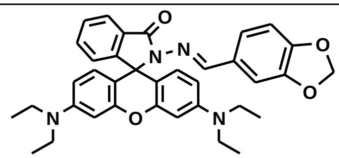
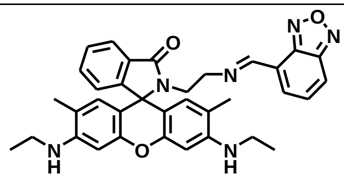
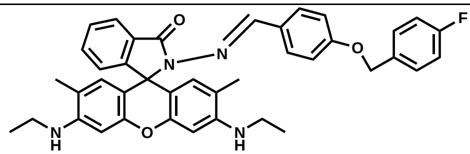
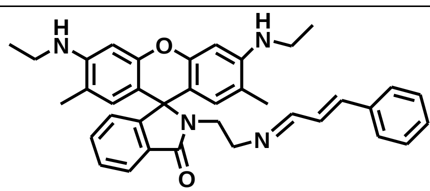
Fig. S27 Color of HL-CIN in and HL-CIN with saloon waste water under visible light (upper row, (A)) and UV radiation (lower row, (B)).

Table S2 Different parameters of recently published chemosensors for various metal ions.

Entry no.	Probes	Excitation (nm)/ Emission (nm)	LOD	Binding constant (K_a) (M^{-1})	Sensor for	Hydrolysis of occur?	Ref.
1		400/592	1.84 µM	4.39×10^{4}	Al^{3+}	No	43
2		525/585	3.52 nM	---	Ga^{3+} and Hg^{2+}	Yes	44
3		510/580	1.60×10^{-7} M	6.9×10^{4}	Al^{3+}	No	45
4		520/573	9.7×10^{-8} M	---	Hg^{2+}	Yes	46

5		554/583	11 nM (Al^{3+})	4.5×10^{4} (Al^{3+})	Al^{3+} and Hg^{2+}	No	47
6		560/588	1.51 µM	---	Au^{3+}	Yes	48
7		525/580	3.15×10^{-7} M	---	Au^{3+}	No	49
8		500/594	8.5 nM	---	Hg^{2+}	Yes	50

9		500/550 (Al^{3+}) 370/457 (Zn^{2+})	1.10 ×10^{-8} M (Al^{3+}) 7.69 ×10^{-8} M (Zn^{2+})	9.38 ×10^{3} (Al^{3+}) 4.75 ×10^{4} (Zn^{2+})	Al^{3+} And Zn^{2+}	No	35
10		500/550	6.97 nM (Al^{3+}) 15.80nM (Cr^{3+}) 14.00 nM (Fe^{3+})	1.47×10^{5} (Al^{3+}) 6.24×10^{4} (Cr^{3+}) 8.74×10^{4} (Fe^{3+})	Al^{3+}, Cr^{3+} and Fe^{3+}	No	36
11		---/559 (Al^{3+})	5.72 ×10^{-7} M (Al^{3+})	1.4×10^{4} (Al^{3+})	Al^{3+} and Cu^{2+}	No	51
12		500/550 (for $Al^{3+)}$	1.83×10^{-7} M (Al^{3+})	9.02×10^{4} (Al^{3+})	Al^{3+} and Zn^{2+}	No	52

13		500/582	1.10×10^{-7} M	7.033×10^{3}	Al^{3+}	No	53
14		535/576	1.2×10^{-8} M	-	Hg^{2+}	No	54
15		500/550	6.54nM(Al^{3+}) 16.0 nM(Hg^{2+})	4.44×10^{4} (Al^{3+}) 4.51×10^{4} (Hg^{2+})	Al^{3+} and Hg^{2+}	No	37
16.		495/555	2.66×10^{-8} M (Al^{3+}) 10.4×10^{-8} M (Ga^{3+}) 8.19×10^{-8} M (In^{3+}) 3.10×10^{-8} M (Tl^{3+})	5.01×10^{4} (Al^{3+}) 4.79×10^{4} (Ga^{3+}) 4.57×10^{4} (In^{3+}) 5.75×10^{4} (Tl^{3+}),	Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+}	No	13
17		495/558	2.8×10^{-8} M (Al^{3+}) 2.9×10^{-8} M (Ga^{3+}) 5.6×10^{-8} M (In^{3+}) 8.2×10^{-8} M (Tl^{3+})	---	Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+}	Yes	Present study

References

S1 J.-S. Wu, I.-C. Hwang, K. S. Kim, J. S. Kim Org. Lett. 9 (2007) 907.

S2 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, UK, 1980.

S3 A. M. Brouwer, Pure Appl. Chem. 83 (2011) 2213.

S4 V. Thomsen, D. Schatzlein, D. Mercuro, Spectroscopy 18 (2003) 112.