Supporting information

Hippuric acid–appended aminothiazole derivatives as ion-responsive metallogelators for visual detection of Ce(III)

Priyanka Yadav[a]* Mahammdmahir M. Saiyed[a] and Vinay S. Sharma[b]

[a]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Anand, 388120 Gujarat, India.

[b]Department of Chemistry, Parul institute of applied science, research and development cell, Parul university, Vadodara, Gujarat, 391760, India.

Materials.

All reagent grade materials were purchased from Sigma-Aldrich and used as received**.** The solvents used for the preparation of gels were purified, dried and distilled as required.

Instrumentation.

FTIR spectroscopy: FTIR Spectra were recorded on a Bruker –ALPHA II, FTIR instrument. Solid samples were recorded as an intimate mixture with powdered KBr.

NMR *spectroscopy*: The ^{1}H- NMR spectra were measured by using a Bruker AVANCE, 400MH_Z for ^{1}H-NMR with TMS as internal standard and $CDCl_3$/DMSO as solvent.

Scanning Electron Microscopic Study: Morphologies of all reported gel materials were investigated using scanning electron microscopy (SEM). For SEM study, solution of a gelator is placed on a SEM sample holder and allowed to form gel, which was then dried under vacuum to give xerogel, and then the micrographs were taken in a SEM apparatus (FEI Nova NanoSEM 450 microscope)

Rheometer. The rheological experiments were carried out with a Anton paar - MCR102 Rheometer with a parallel plate configuration.

X-ray Photoelectron Spectroscopy (**XPS**). The XPS study were carried out with Thermo Scientific K-Alpha class or equivalent.

Table S1. Comparison of Ce^{3+} detection methods

Method	Detection Principle	Detection Limit (LOD)	Linear Range	Practicality/ Application	Trade-off Highlighted
ICP-MS[1]	Mass spectrometry of ions		Wide (ppb–ppm)	Highly sensitive, precise	Requires expensive instrumentation, trained personnel
UV-Vis Spectroscopy[2]	Absorbance of Ce^{3+} complexes	~0.1–1 ppm	ppm range	Moderate sensitivity, lab-based	Needs sample preparation, less portable
Electrochemical Sensors[3]	Redox response of Ce^{3+}	~0.01–0.1 ppm	ppm range	Sensitive, portable options	Requires calibration, interference possible
Fluorescence Probes[4]	Quenching/enhancement by Ce^{3+}	~0.1 ppm	ppm range	Sensitive, selective	Probe synthesis, stability issues
Thiazole-based Metallogel (this work)	Visual gel formation (qualitative)	~1000 ppm	Not established	Rapid, on-site, simple screening	Low sensitivity; suitable for highly contaminated samples

Table S2- ^{1}H and ^{13}C NMR chemical shift changes of ligand 2a upon complexation with Ce^{3+} ion.

Proton/Carbon Type	Free Ligand (ppm)	Metal Complex (ppm)	Typical Shift Direction	Reason
Methyl protons (C-4)	2.00	2.05	Slight downfield	Inductive deshielding, minor effect.
CH_2 (Near carboxylic group)	3.90	4.14	Downfield	deshielding and line broadening
NH of amide group	8.81	9.02	Downfield	deshielding and line broadening
-CH of thiozole ring	6.06	6.10	Slight downfield	deshielding, minor effect.
-CH benzene ring near to amide group	7.84	7.91	Slight downfield	deshielding, minor effect.
Carbon of carboxylic group (C=O)	171.46	172.49	Downfield	Direct coordination site →strong deshielding.
carbon attached to NH_2 and ring N-atom	168.33	168.77	Slight downfield	π-electron withdrawal by metal center.
Carbon of amide group attached to aromatic ring	166.09	167.01	Downfield	Direct coordination site →strong deshielding.
Carbon attached to ring sulphur atome (C-S)	100.10	101.156	Downfield	site for hydrogen bonding →strong deshielding.

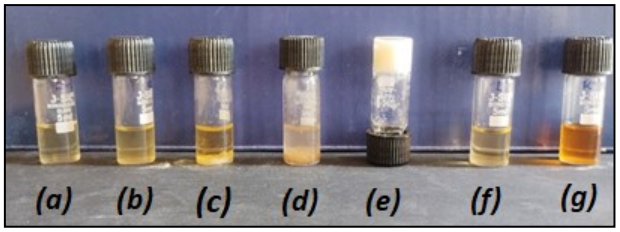

Fig.S1 photograph of ion selective response of ligand 2a with (a) Zn^{+2}, (b) Cd^{+2}, (c) Pb^{+2}, (d) Ag^{+}, (e) Ce^{3+}, (f) Li^{+}, and (g) K^{+}

Analytical data

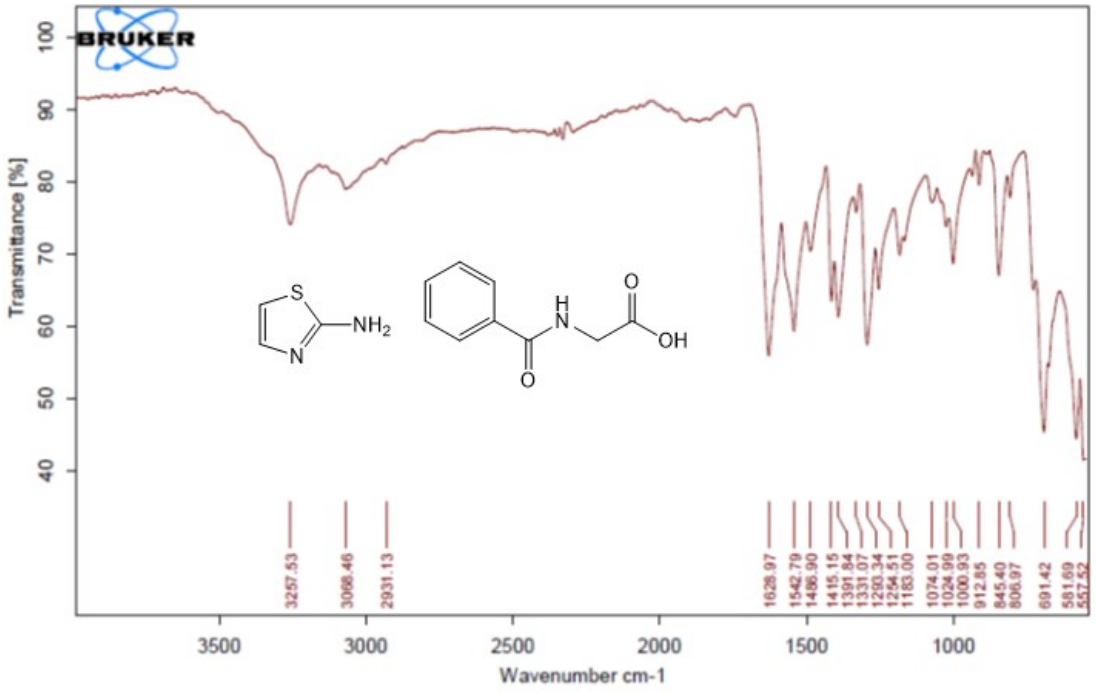

Fig.S2 IR spectra of compound-1a.

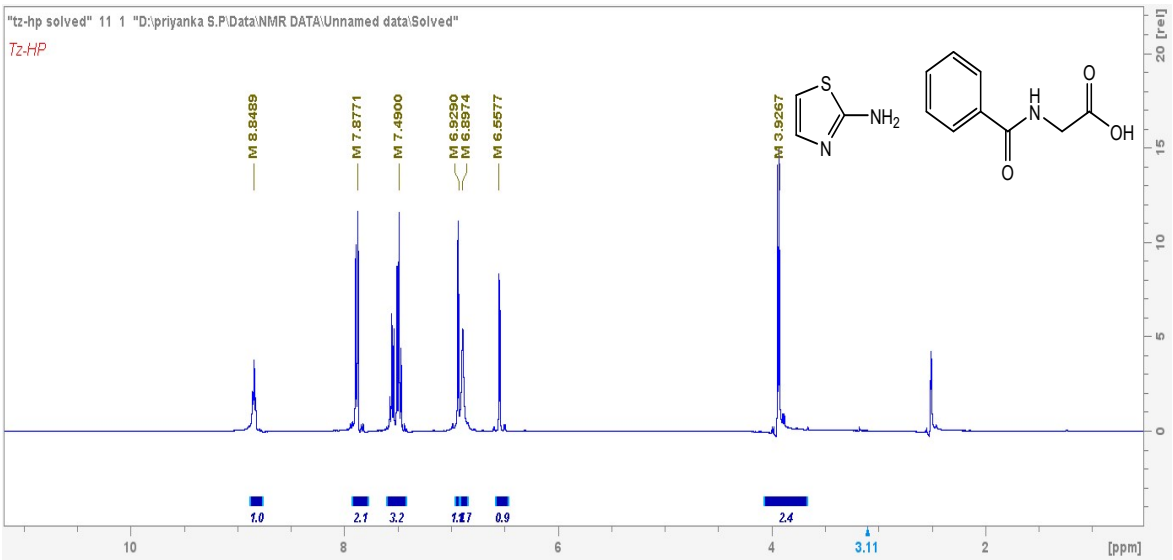

Fig.S3 ^{1}HNMR spectra of compound-1a.

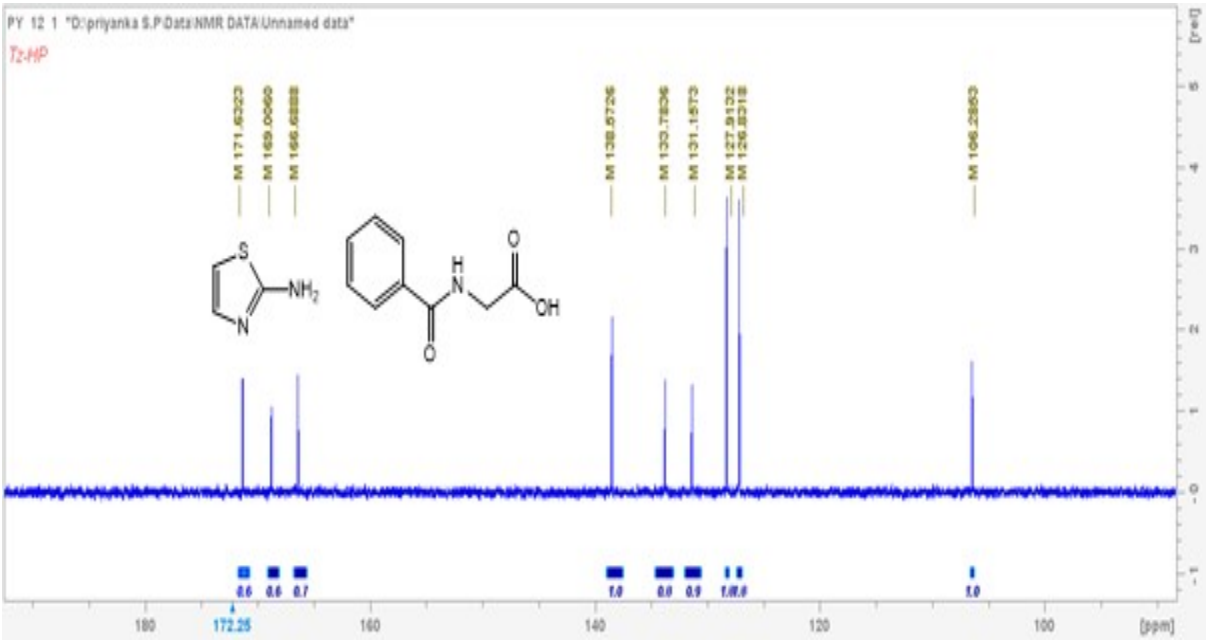

Fig.S4 ^{13}CNMR spectra of compound-1a.

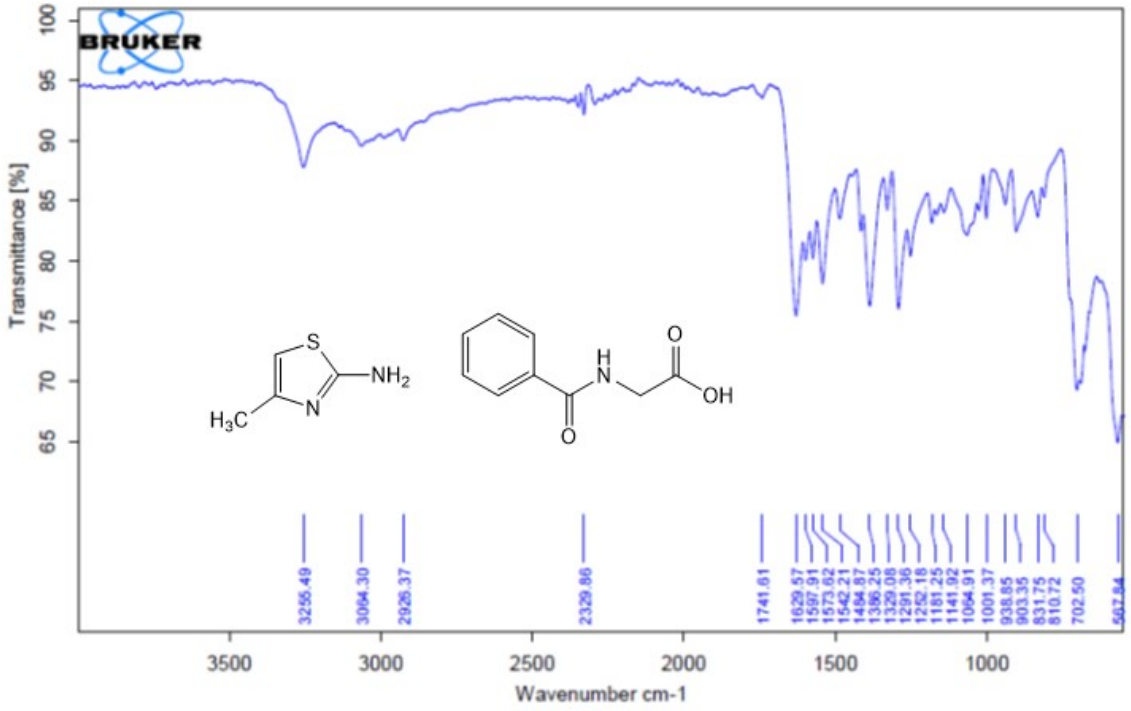

Fig.S5 IR spectra of compound-2a.

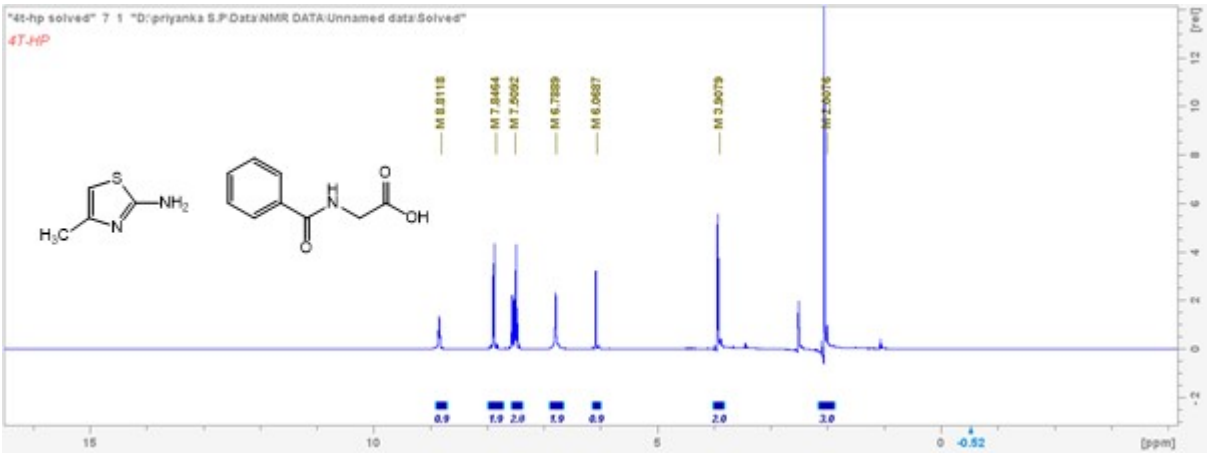

Fig.S6 [1]HNMR spectra of compound-2a.

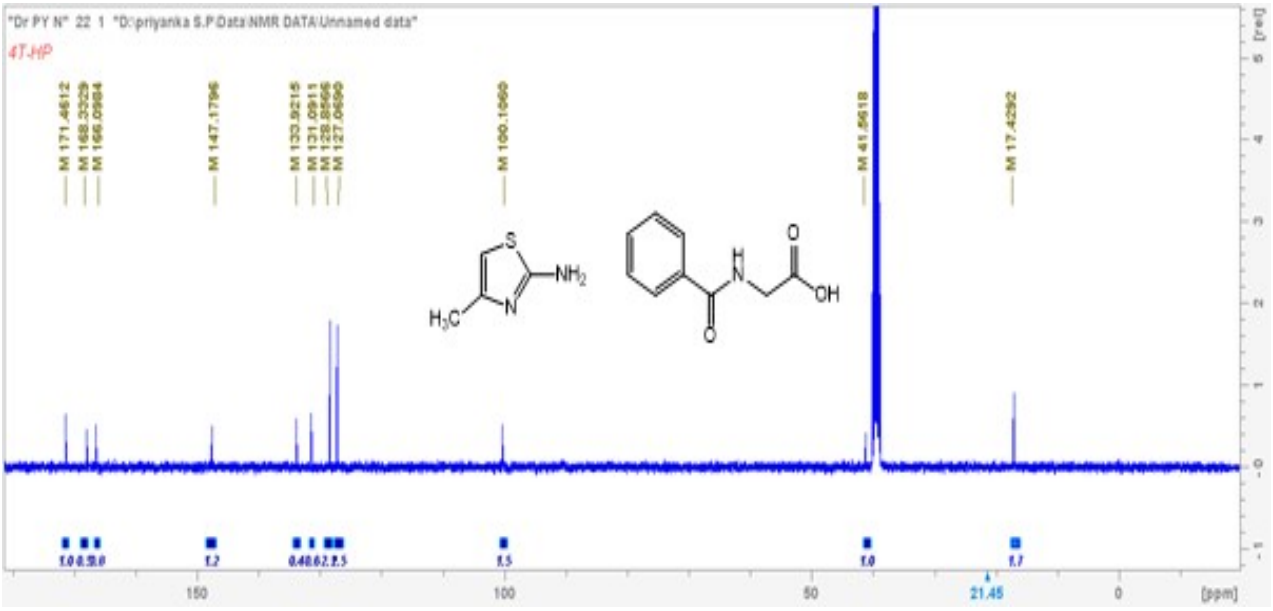

Fig.S7 [13]C NMR spectra of compound-2a.

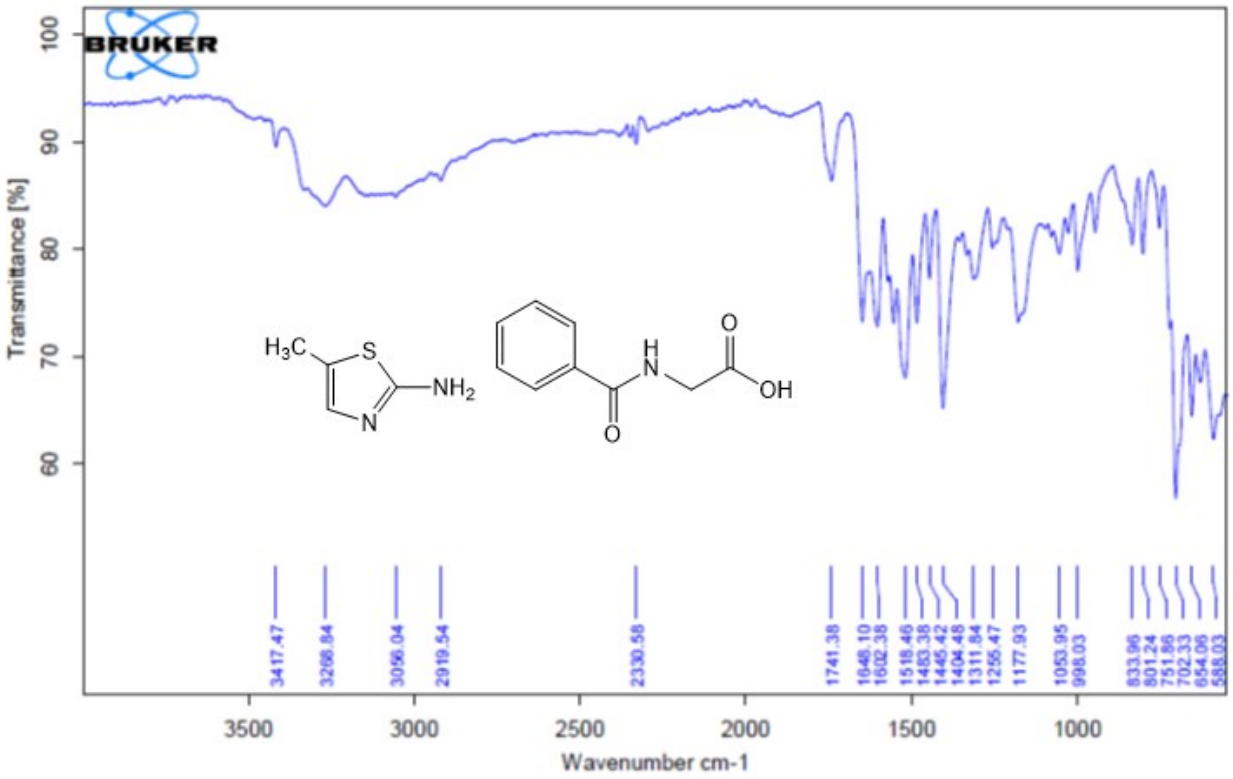

Fig.S8 IR spectra of compound-3a

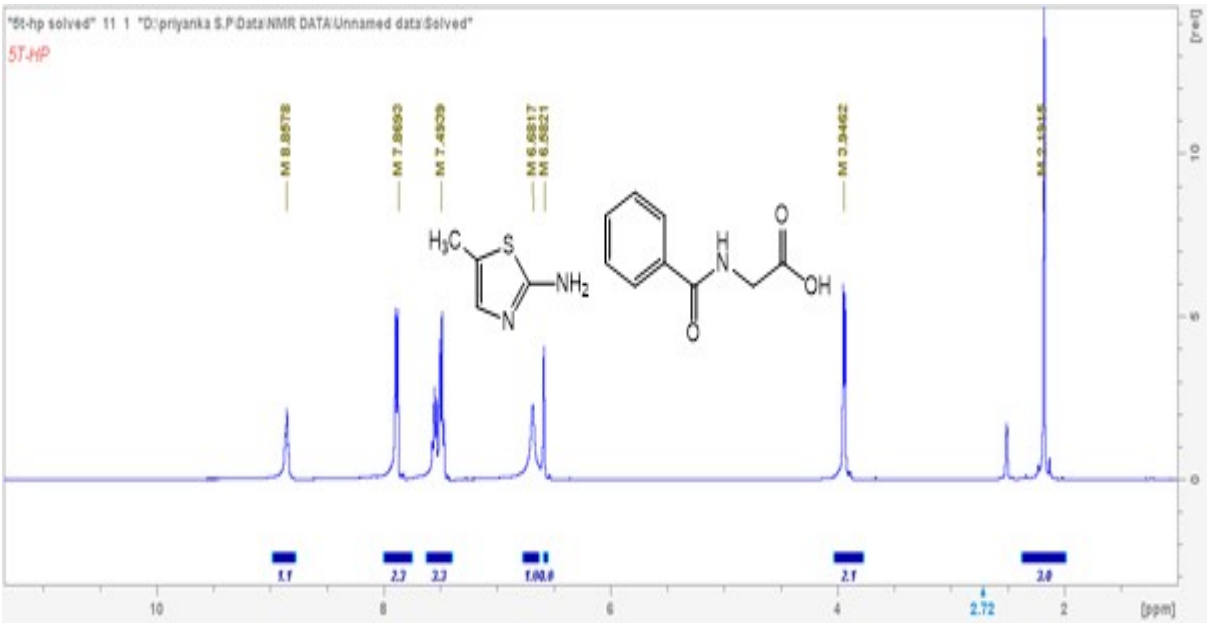

Fig.S9 [1]HNMR spectra of compound-3a.

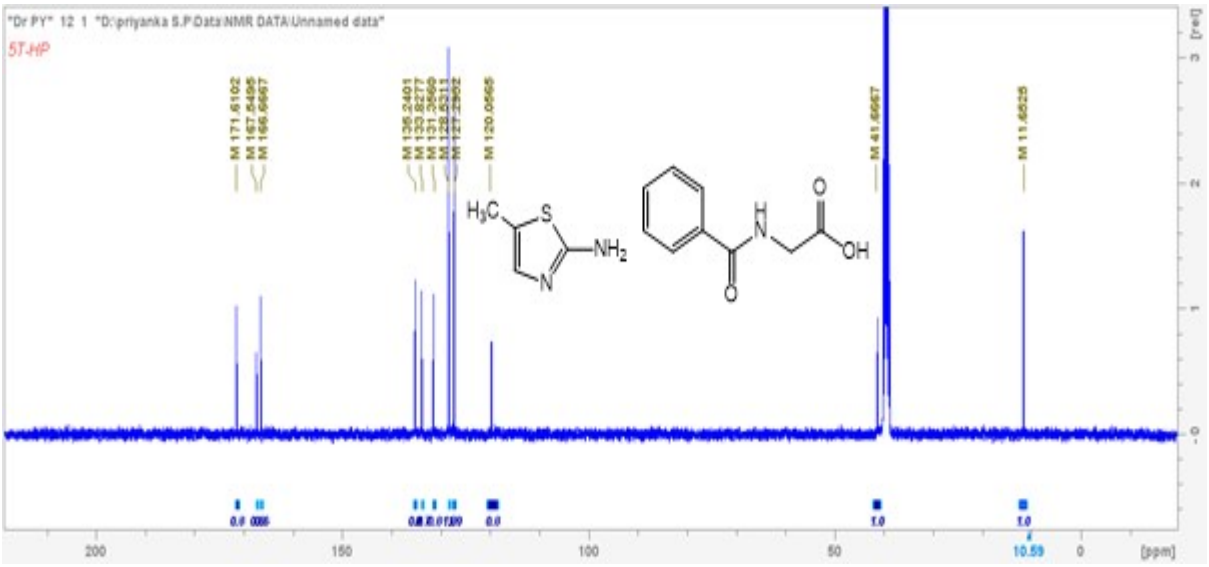

Fig.S10 [13]C NMR spectra of compound-3a.

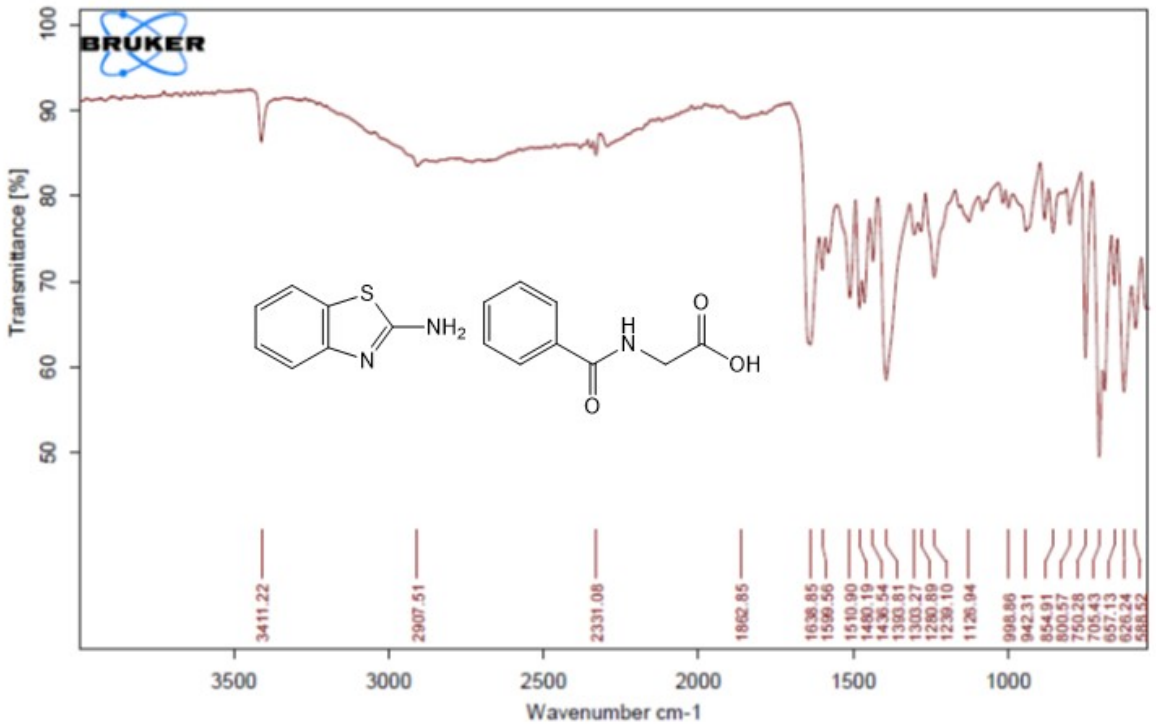

Fig.S11 IR spectra of compound-4a

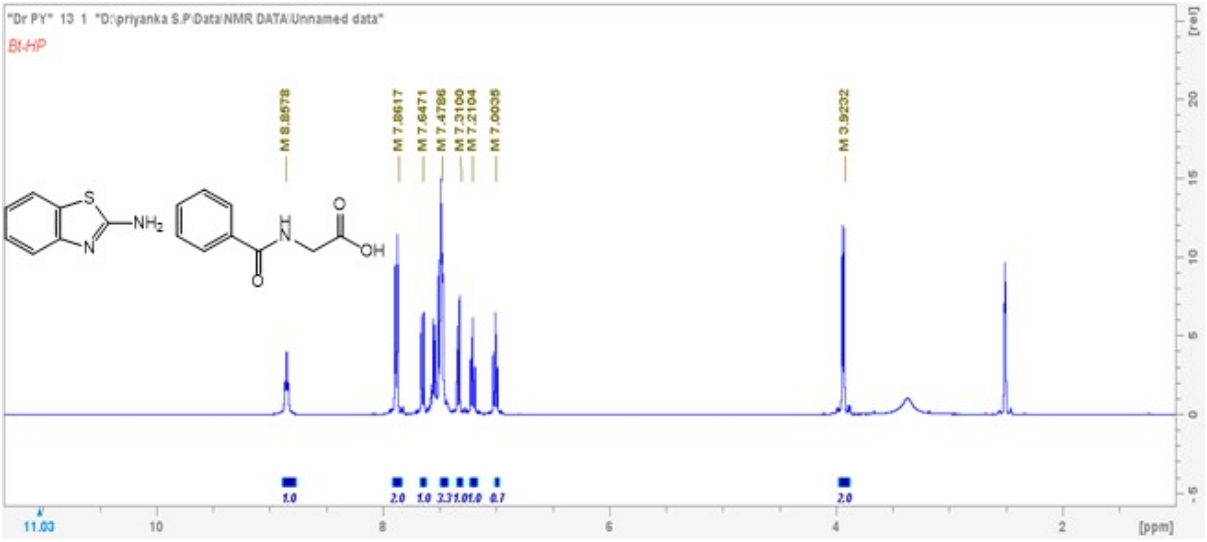

Fig.S12 [1]HNMR spectra of compound-4a.

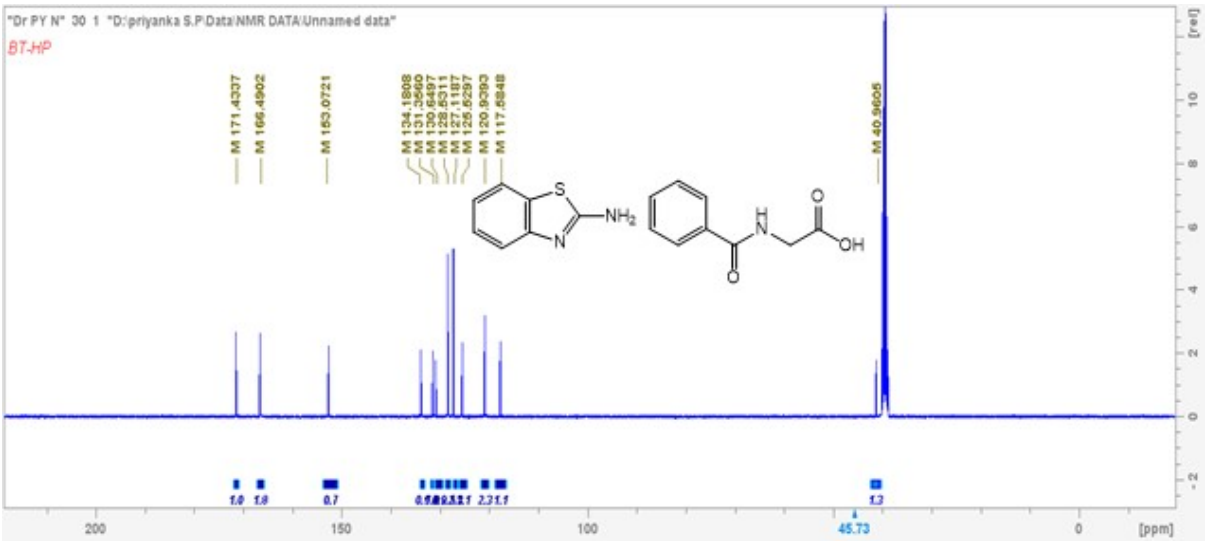

Fig.S13 ^{13}C NMR spectra of compound-4a.

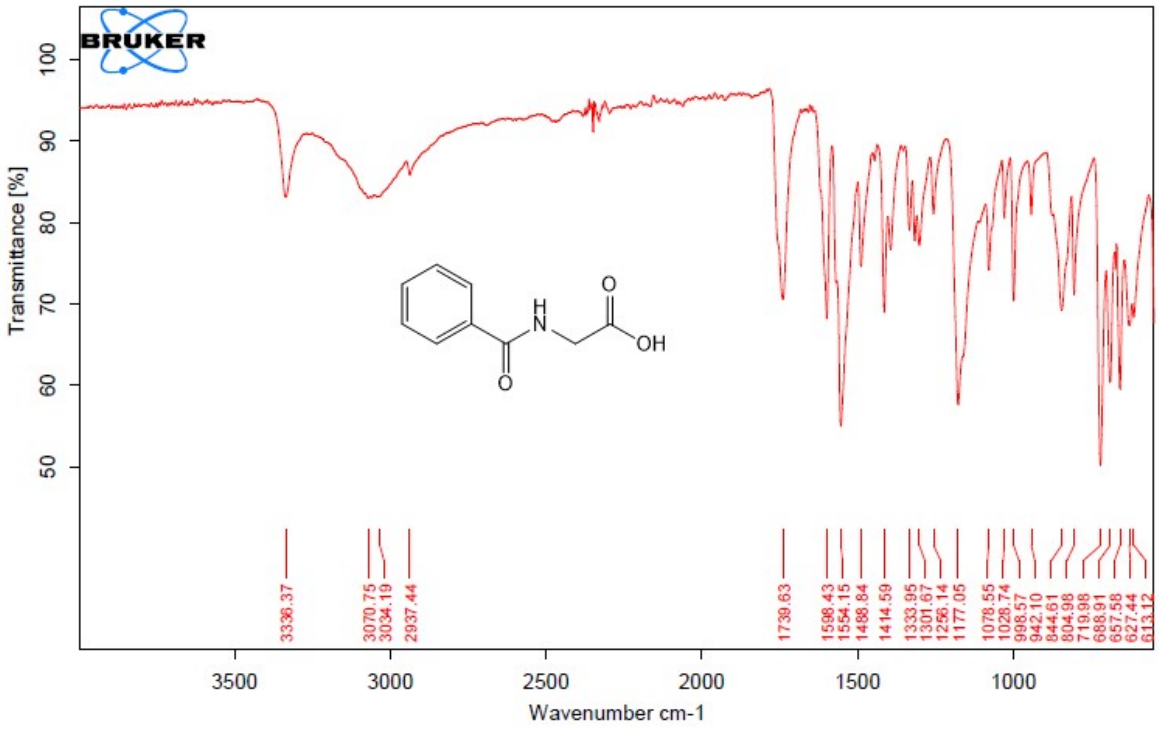

Fig.S14 IR spectra of hippuric acid compound-a.

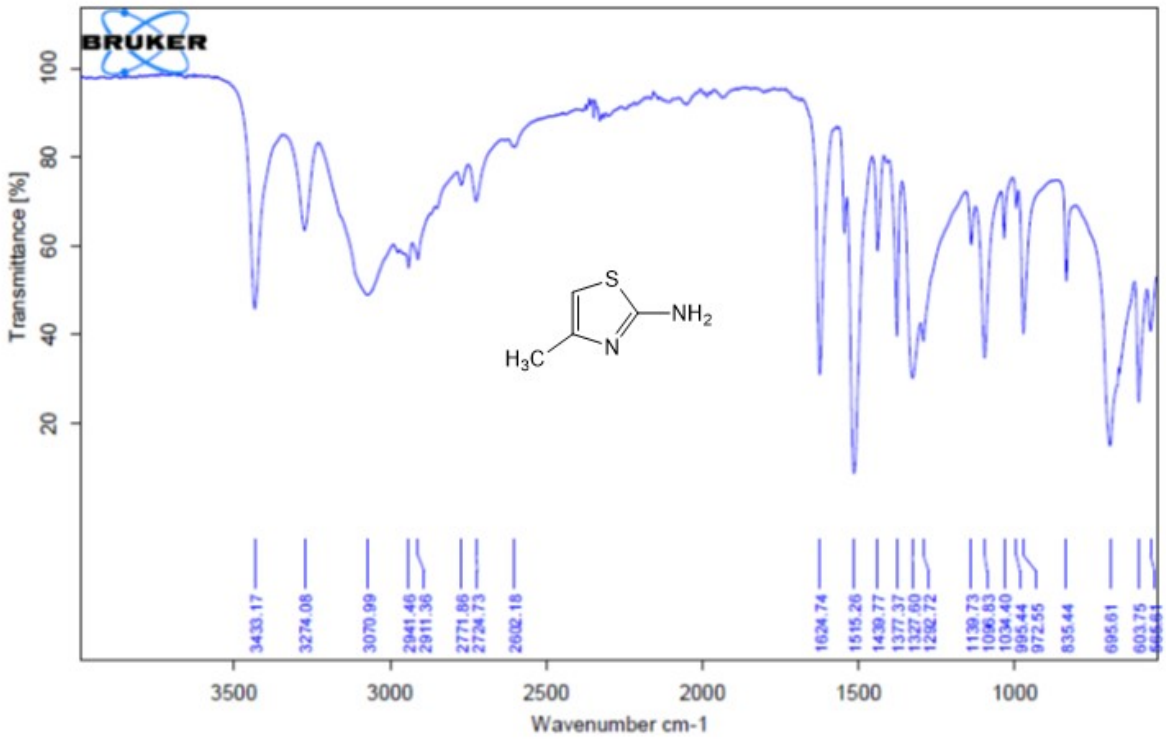

Fig.S15 IR spectra of 2-amino-4-methylthiazole compound-2.

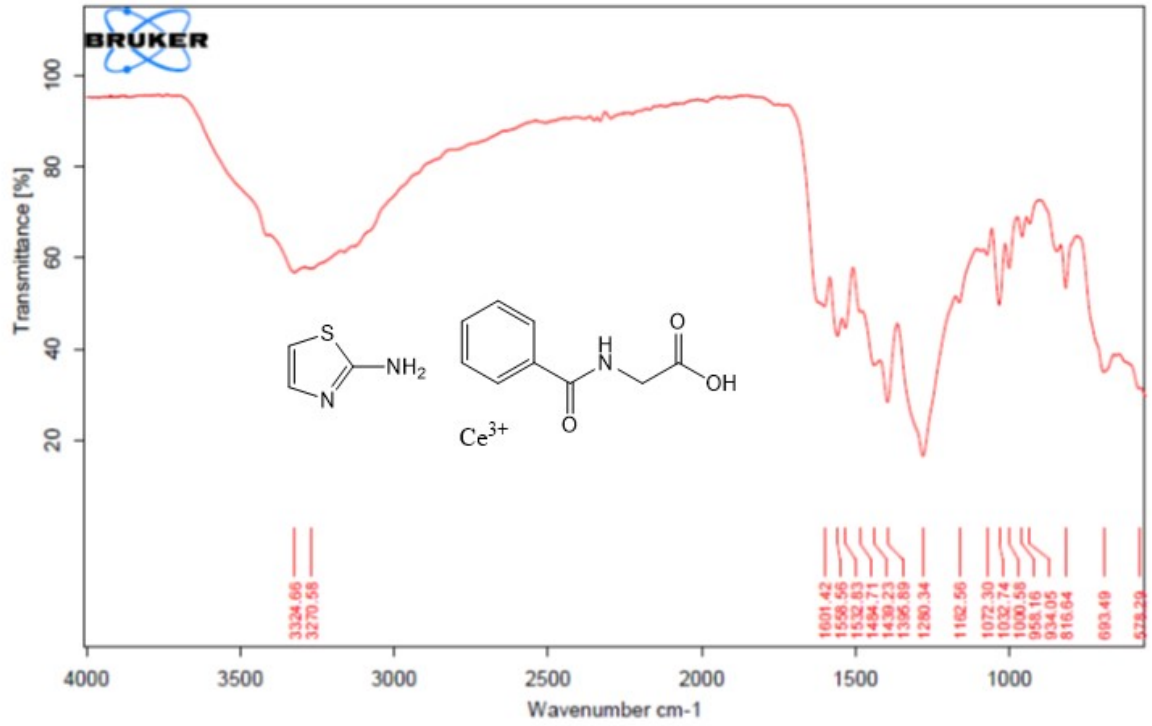

Fig.S16 IR spectra of 1a-Ce.

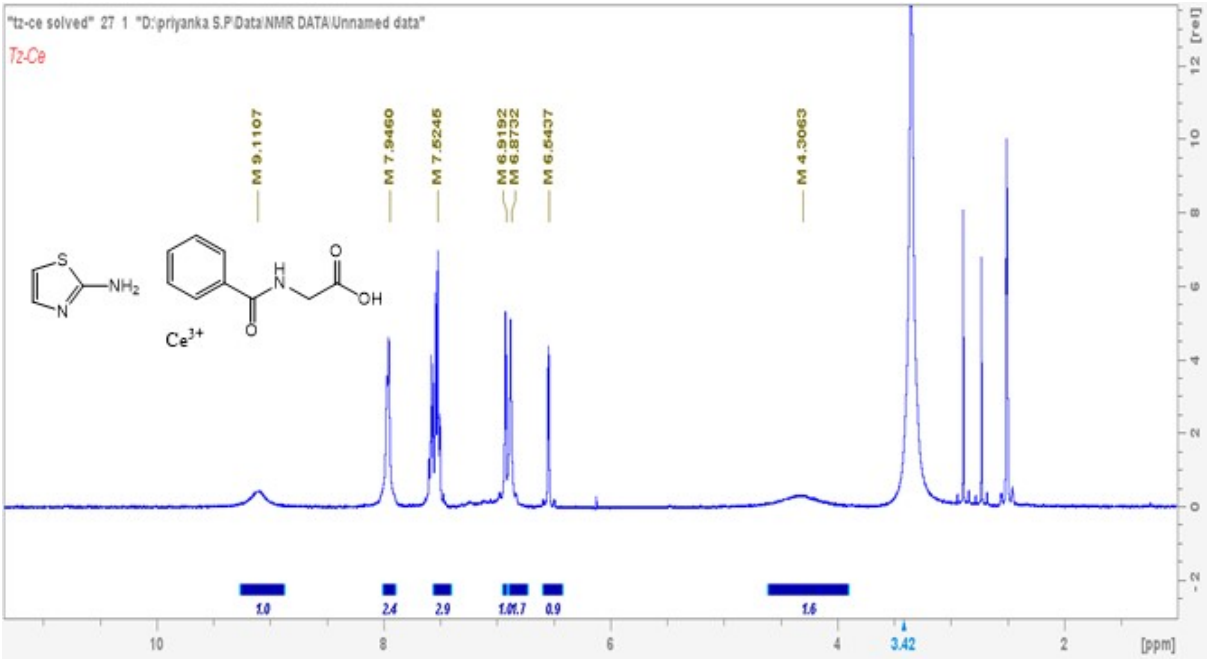

Fig.S17 [1]HNMR spectra of compound-1a-Ce.

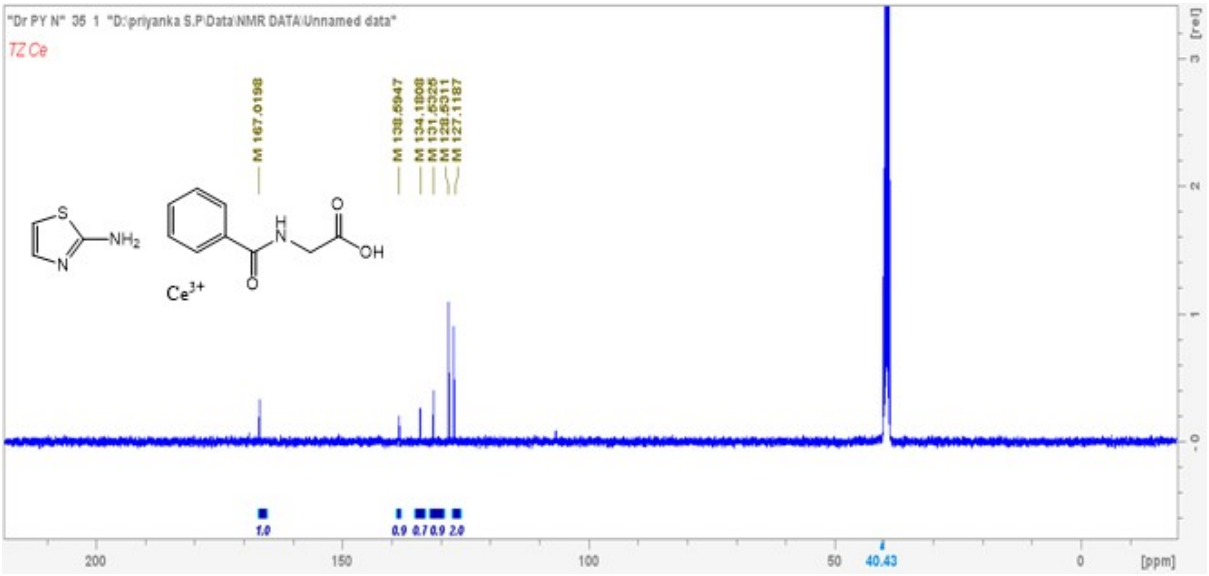

Fig.S18 [13]C NMR spectra of compound-1a-Ce.

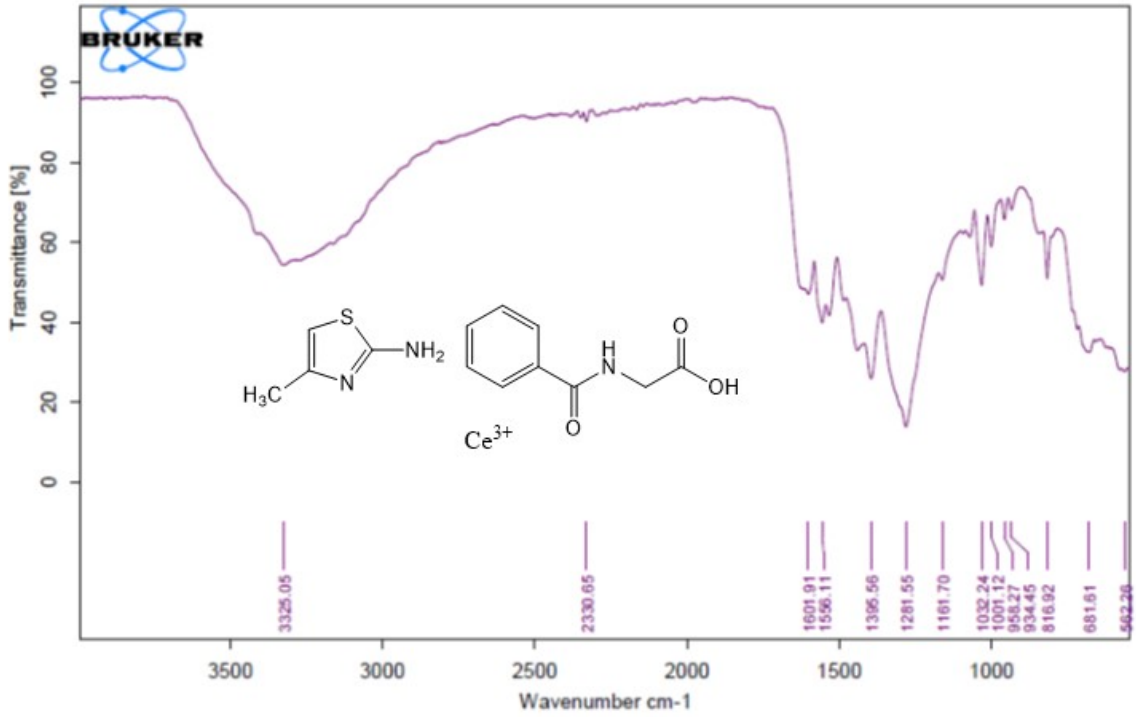

Fig.S19 IR spectra of compound-2a-Ce

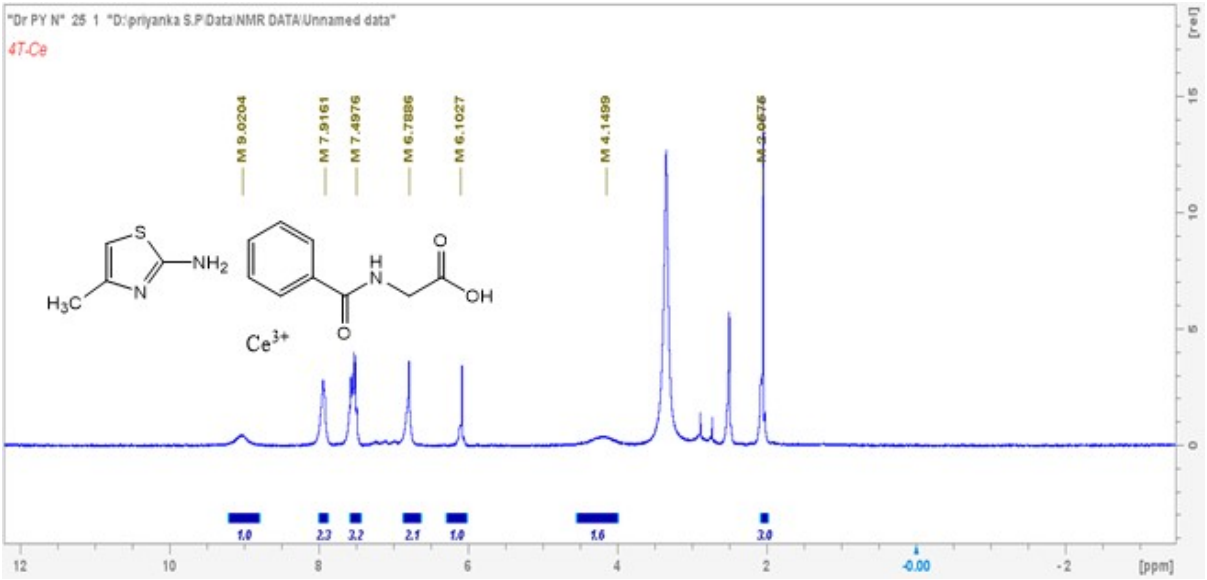

Fig.S20 [1]HNMR spectra of compound-2a-Ce.

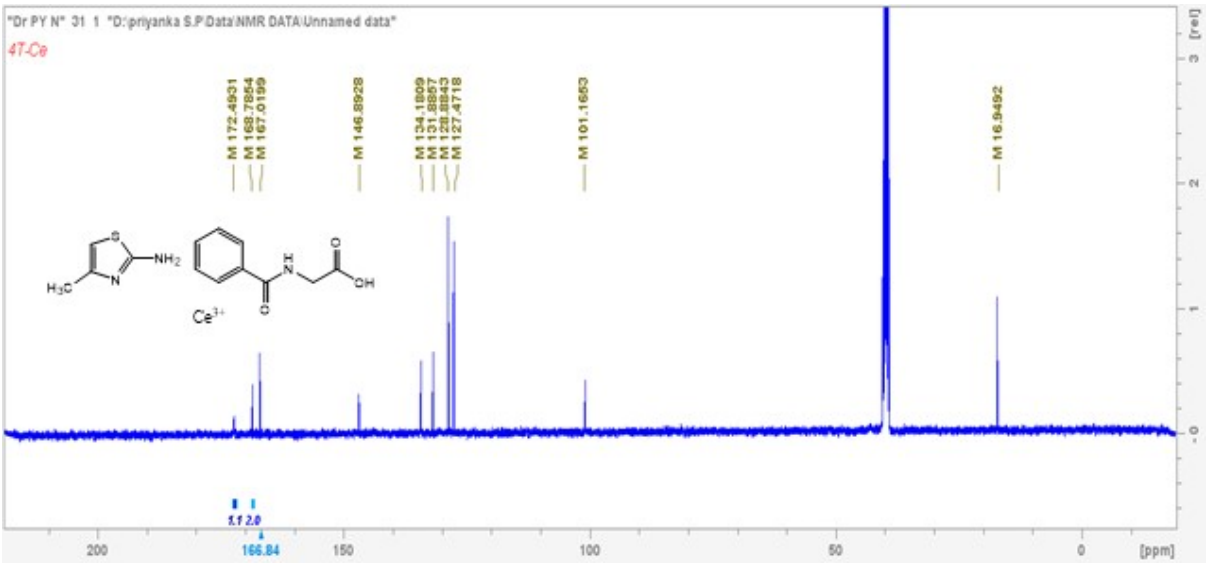

Fig.S21 ^{13}CNMR spectra of compound-2a-Ce.

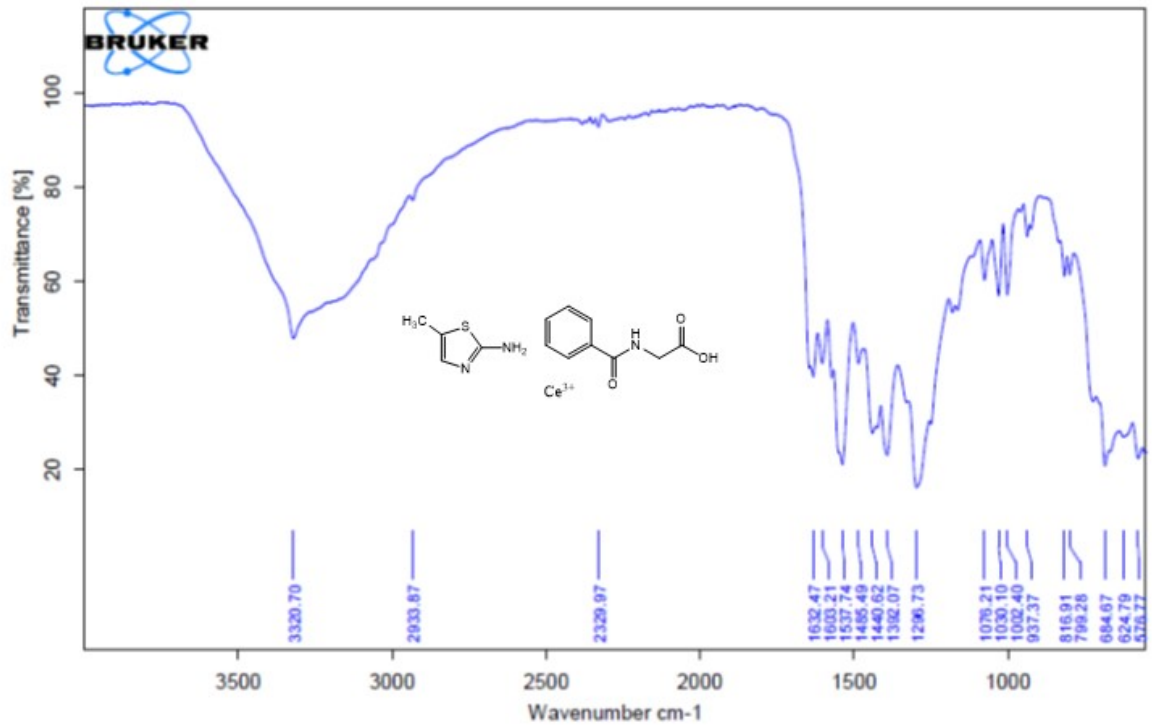

Fig.S22 IR spectra of compound-3a-Ce

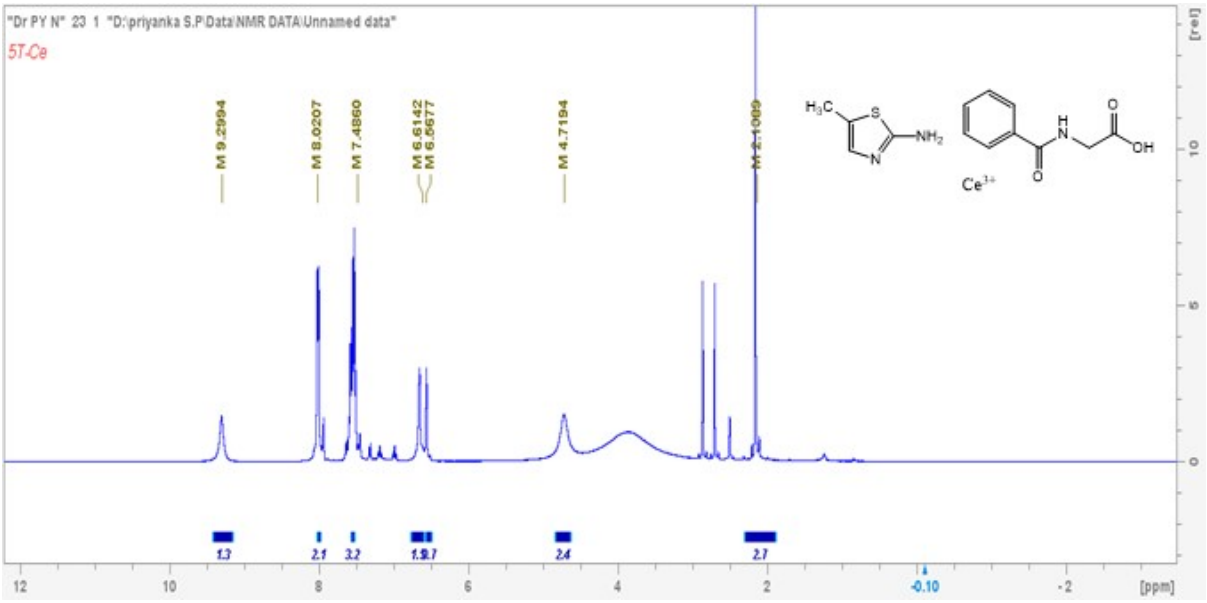

Fig.S23 [1]HNMR spectra of compound-3a-Ce

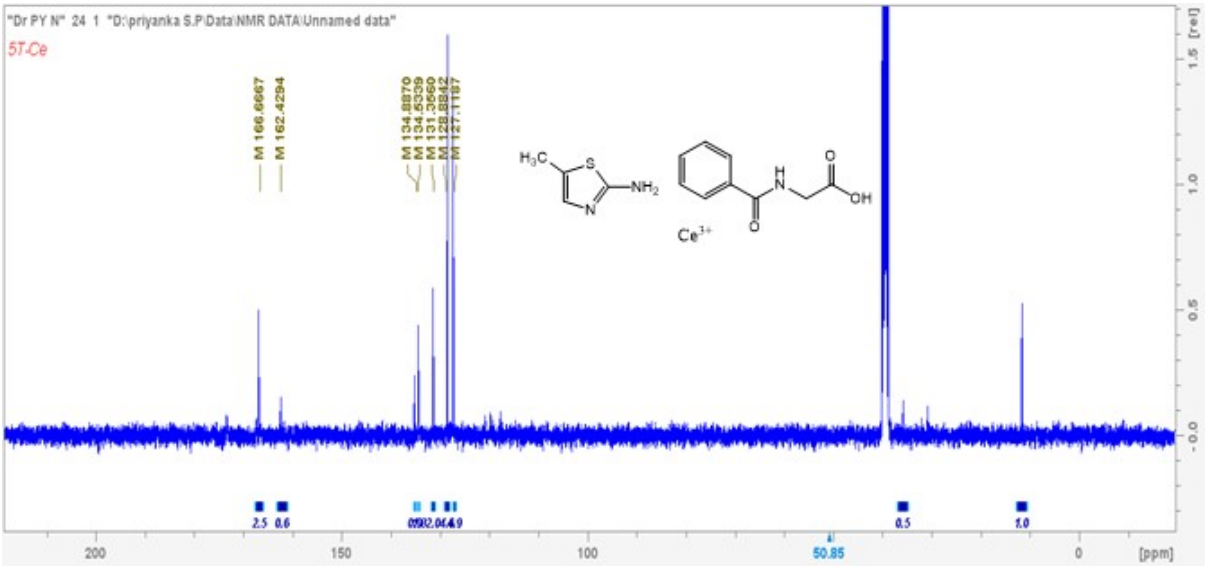

Fig.S24 [13]CNMR spectra of compound-3a-Ce.

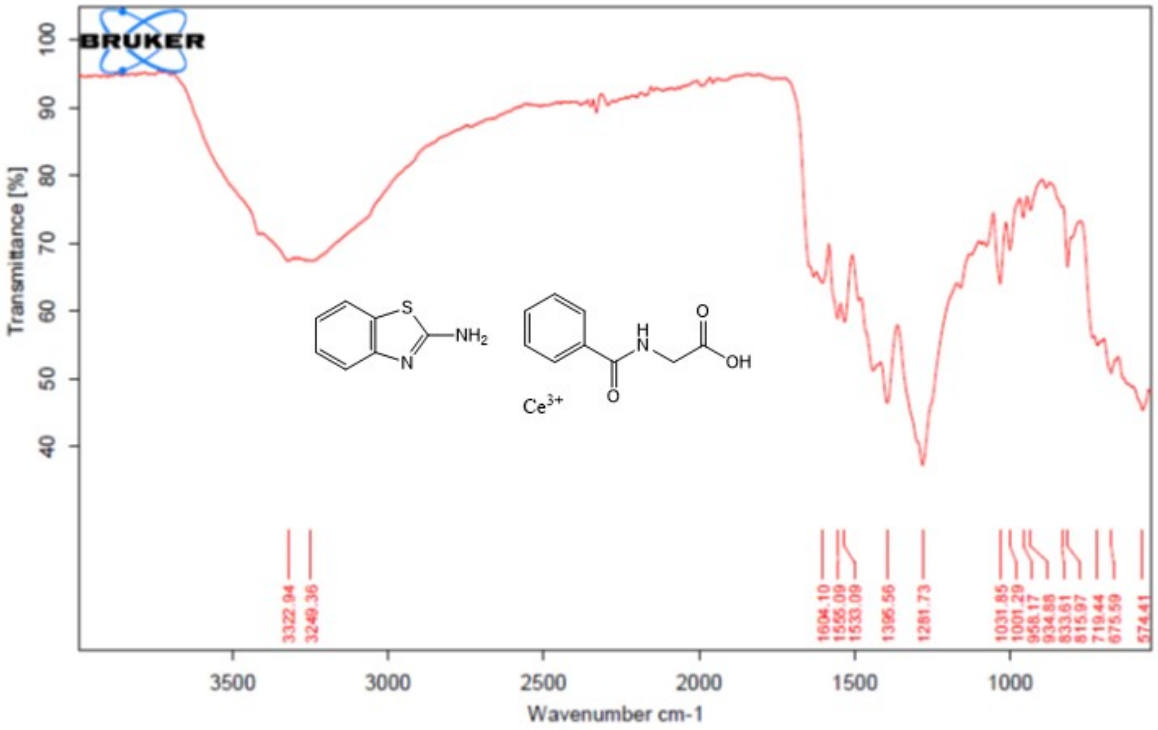

Fig.S25 IR spectra of compound-4a-Ce

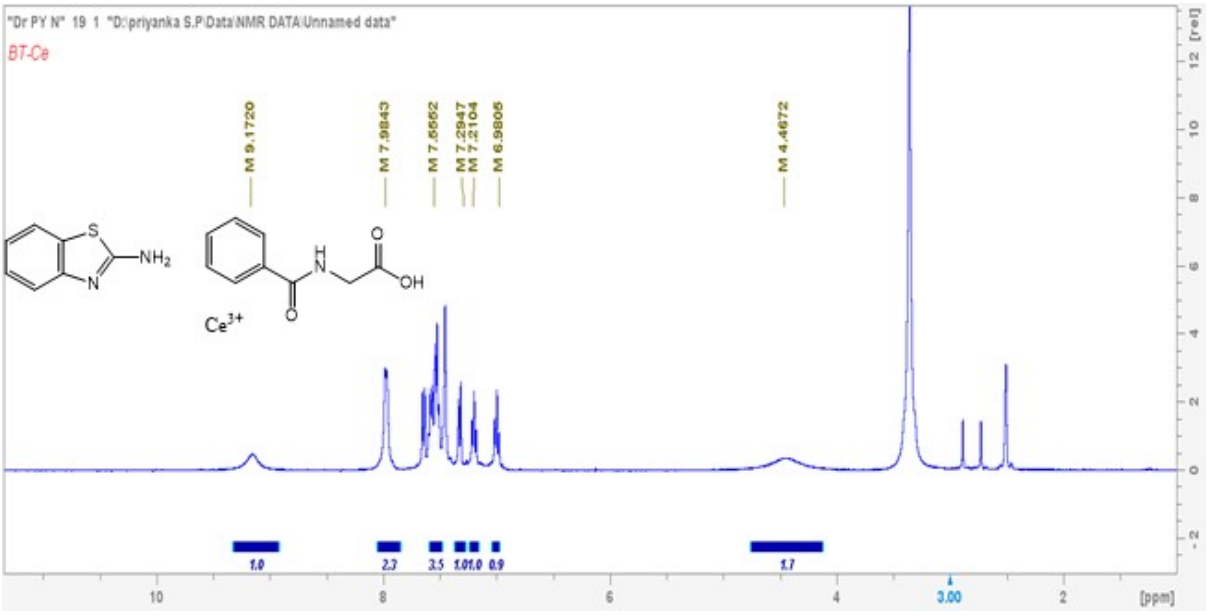

Fig.S26 [1]HNMR spectra of compound-4a-Ce

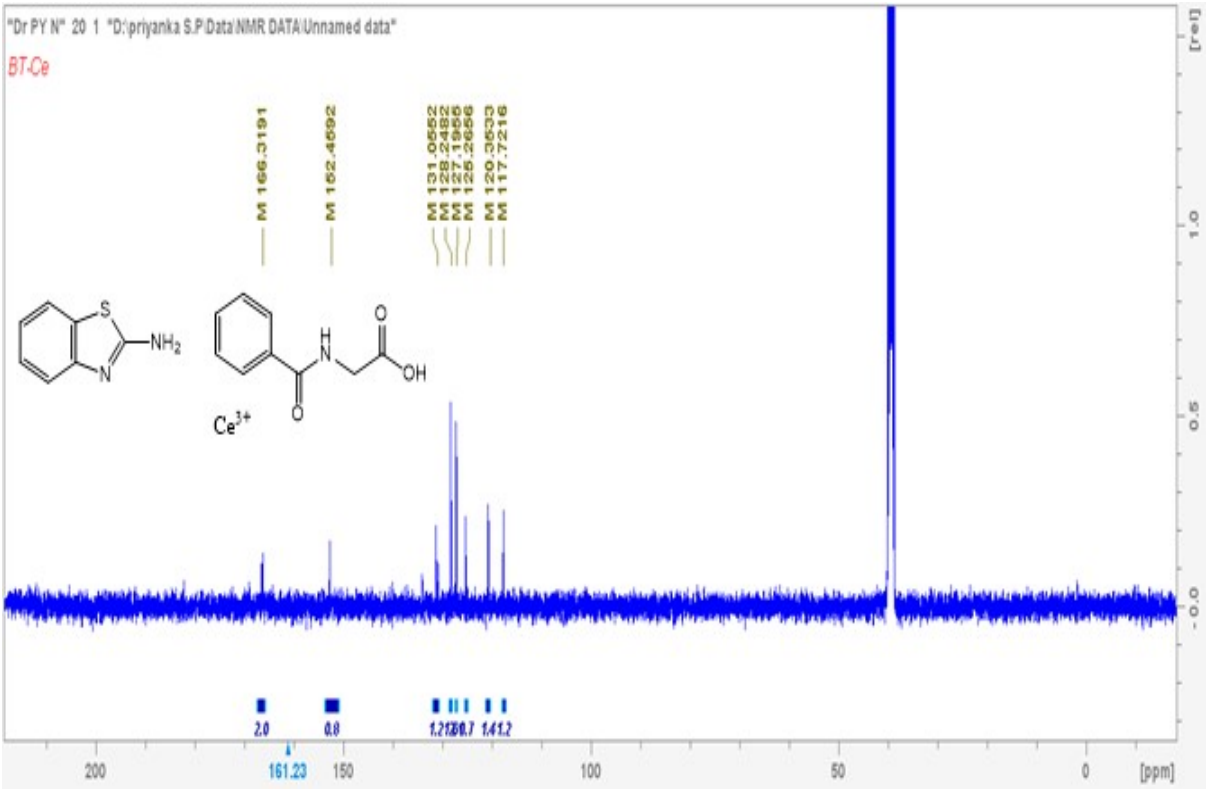

Fig.S27 ^{13}CNMR spectra of compound-4a-Ce.

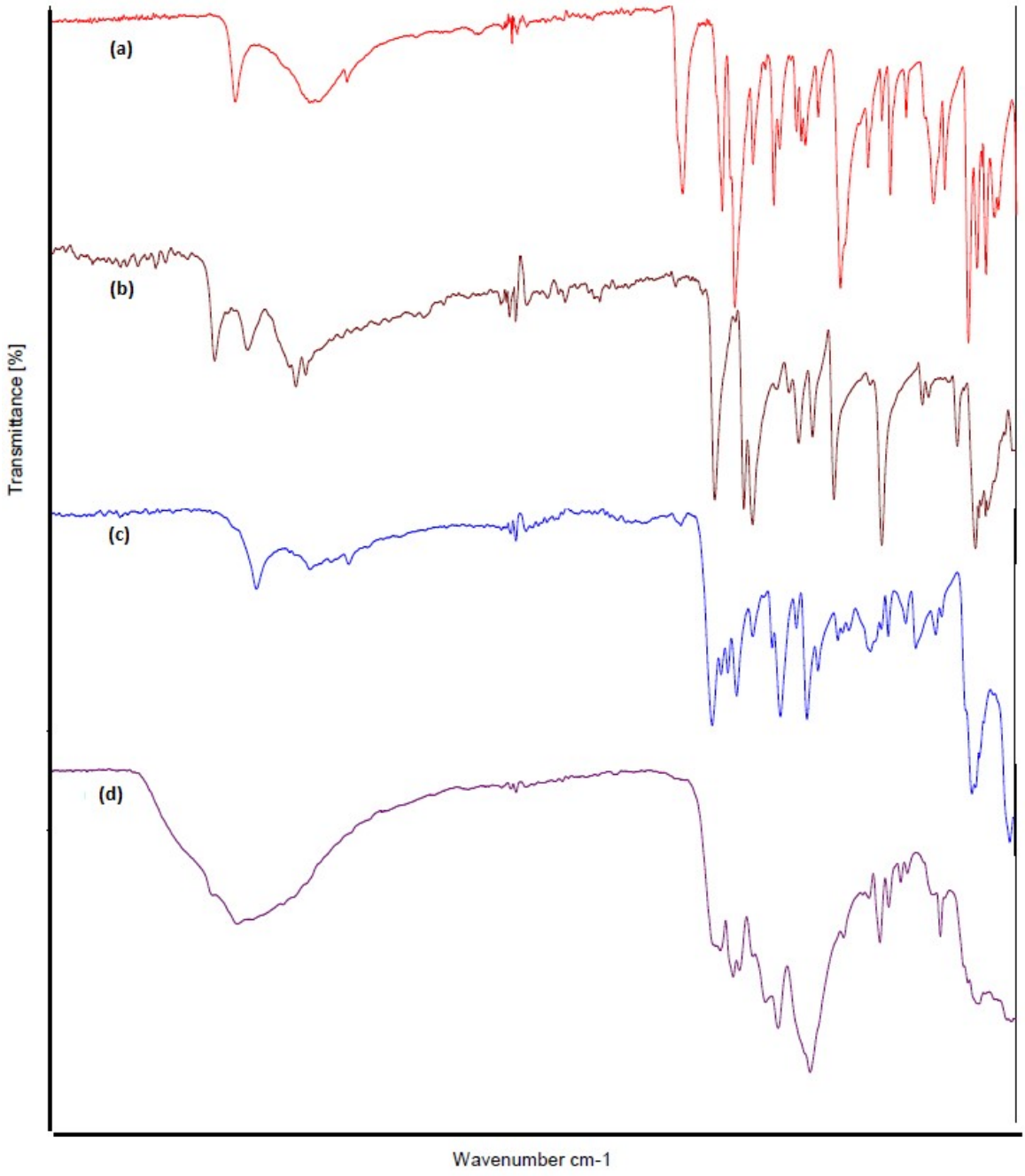

Fig.S28 Overlapping IR spectra of (a) Compound-a, (b) Compound-2, (c) Compound-2a, and (d) Compound-2a-Ce. The spectra illustrate the progressive changes in vibrational features upon structural modification and Ce^{3+} incorporation.

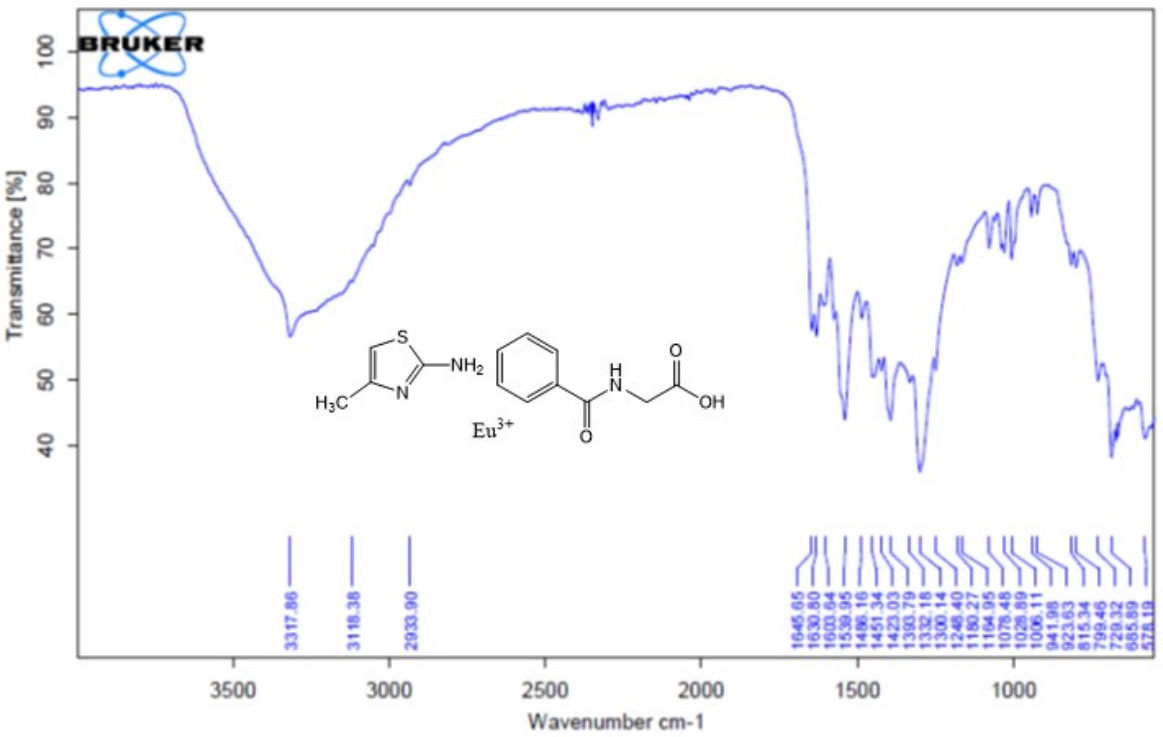

Fig.S29 IR spectra of compound-2a-Eu^{3+}

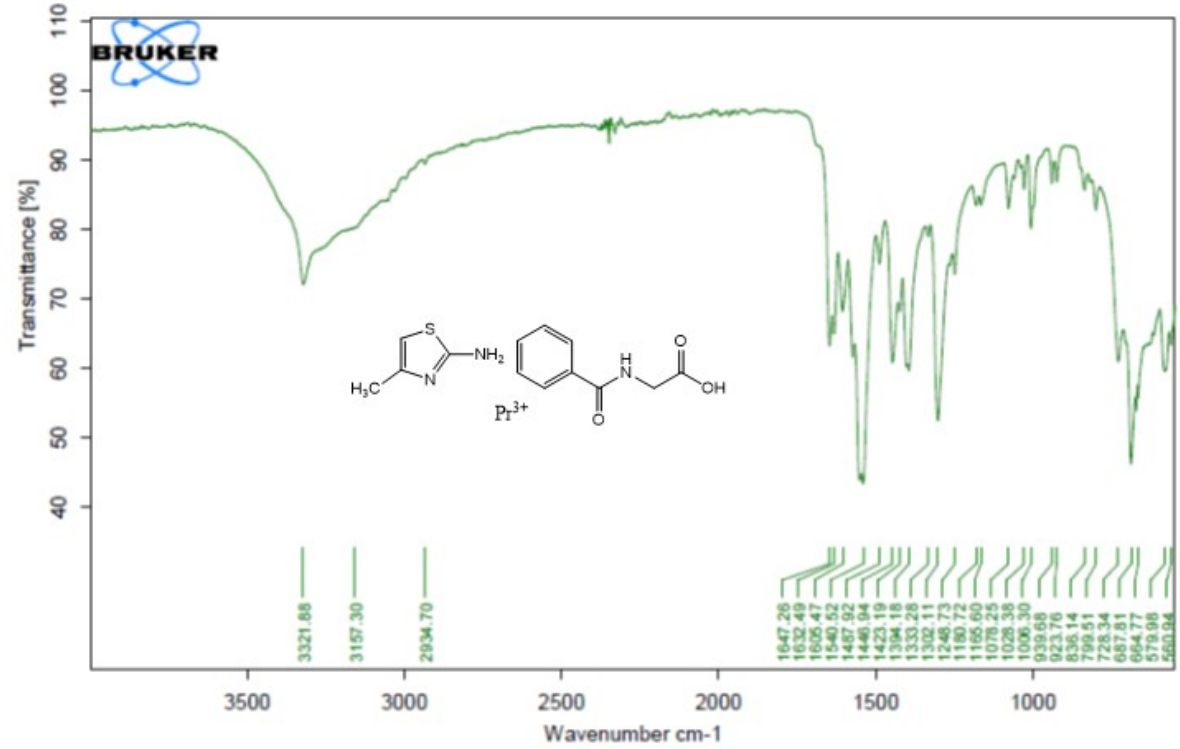

Fig.S30 IR spectra of compound-2a-Pr^{3+}

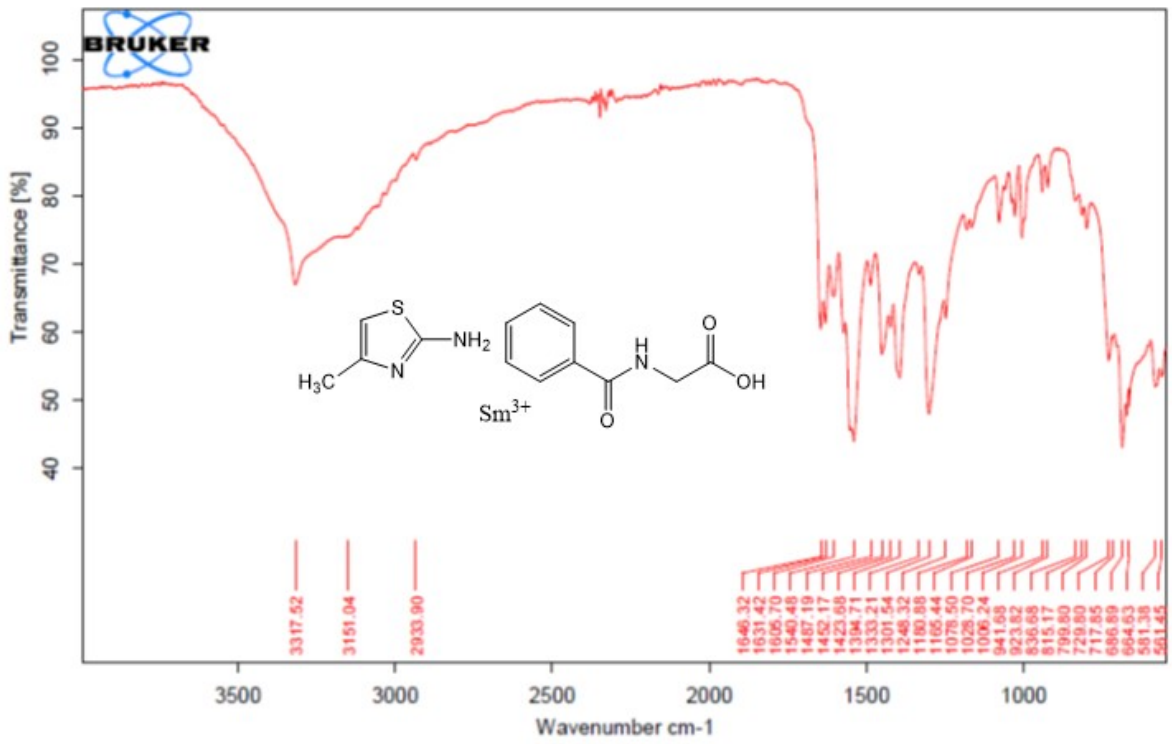

Fig.S31 IR spectra of compound-2a-Sm^{3+}

References

1. Y. Hua, ICP-MS determination of trace Ce(III) in environmental samples, *Anal. Methods*, **2021**, *13*, 4567–4574.

2. Quinoline-based probes for fluorescent and electrochemical sensing of Ce^{3+}, *J. Photochem. Photobiol. A: Chem.*, **2020**, *400*, 112706.

3. X. Luo, Spiropyran fluorescent probe for Ce^{3+} detection, *J. Rare Earths*, **2020**, *38*, 1234–1242.

4. Bio-inspired nanochannel/membrane for Ce^{3+} detection in wastewater, *Chem. Eng. J.,* **2023**, *456*, 132145.