Journal of Fluorescence (2019) 29:375–385
https://doi.org/10.1007/s10895-018-02345-1

ORIGINAL ARTICLE

Carboxamide-Based Tripodal Fluororeceptors for Cations: Preparation, Characterization and Spectroscopic Studies

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Received: 22 October 2018 / Accepted: 28 December 2018 / Published online: 19 January 2019

Abstract

Tripodal receptors, N-1,3,5-tris[2-(ethylamino)ethyl]benzene-1,3,5-tricarboxylamide (L1), N-1,3,5-tris[2-(phenylamino)ethyl]benzene-1,3,5tricarboxylamide (L2) and highly fluorescent N-1,3,5-tris[2(naphthalene-2-ylamino)-ethyl]benzene-1,3,5,tricarboxyl-amid)) (L3) were synthesized by the reaction of 1,3,5-benzene-tricarbonylchloride and different amine groups originally. Sensitivity measurements were performed with the addition of Fe(II), Cu(II), Hg(II), Zn(II), Ni(II), Mn(II), Cd(II), Ga(III), Co(II), Yb(III), Cr(III) and Ag(I) metals to the receptor solutions. According to the absorption and emission studies, these receptors show fluorescent property and Fe(II) ion quenches their fluorescence effectively.

Keywords Fluororeceptor · Metal · Tripodal · Carboxamide · Fe(II) · Cations

Introductıon

The carboxamide [–C(O)NH–] group is an essential ligand unit for coordination chemistry [1–3]. They are preferable in dendrimer formation, asymmetric catalysis, molecular sensing, antitumour studies, protein binding, drug synthesis [4–6]. In general, carboxamides are prepared in good yields by acylation of amines with acyl halides by the help of DIPEA [7–9]. DIPEA is nucleophilic compound with its two isopropyl groups, ethyl group and central nitrogen. Isopropyl and ethyl groups occupy much of the space surrounding the nitrogen, because of that just small electrophiles can react with DIPEA. So, it is preferred as a hindered base in amide-forming reactions of amine groups and acyl chloride groups in our study.

The behaviour of carboxamides towards d-block metals has been widely investigated [10–13]. Tri-carboxamide receptors supports excellent space for metal targets with their high coordination numbers, good geometries with three arms. Fluorescence property makes tricarboxamide ligand an effective fluororeceptors for sensing metal ions in systems. Selectivity property for the target metals generally requires efficient binding sites and suitable signalling unit. This signalling unit is helpful for both qualitative and quantitative estimation of the target metal ion for which the chelate is designed. Firstly, the target metal is recognized by the receptor, the fluorescence signalling unit observed in the form of quenching, enhancement or shift in the fluorescence maxima due to either electron transfer (ET), charge transfer (CT) or energy transfer (ET) mechanisms [14–16].

The importance of iron in biological and environmental systems has led to big interest in recent years. Iron is the most abundant transition metal for all living systems, and it plays an important role in cellular metabolism, enzyme catalysis, and, as an oxygen carrier in hemoglobin, environmental studies [17, 18]. Both irons' deficiency and excess from the normal permissible limit can induce serious disorders. Therefore, developing receptors capable of qualitative and quantitative determining both Fe(II) and Fe(II) is very valuable and still regarded as a challenge. Fe(II) and Cu(II) is spectroscopically and magnetically silent because of its d^{10} electron configuration. So, sensitive and noninvasive fluorescence-based techniques stand out as a method of choice for iron (or copper)

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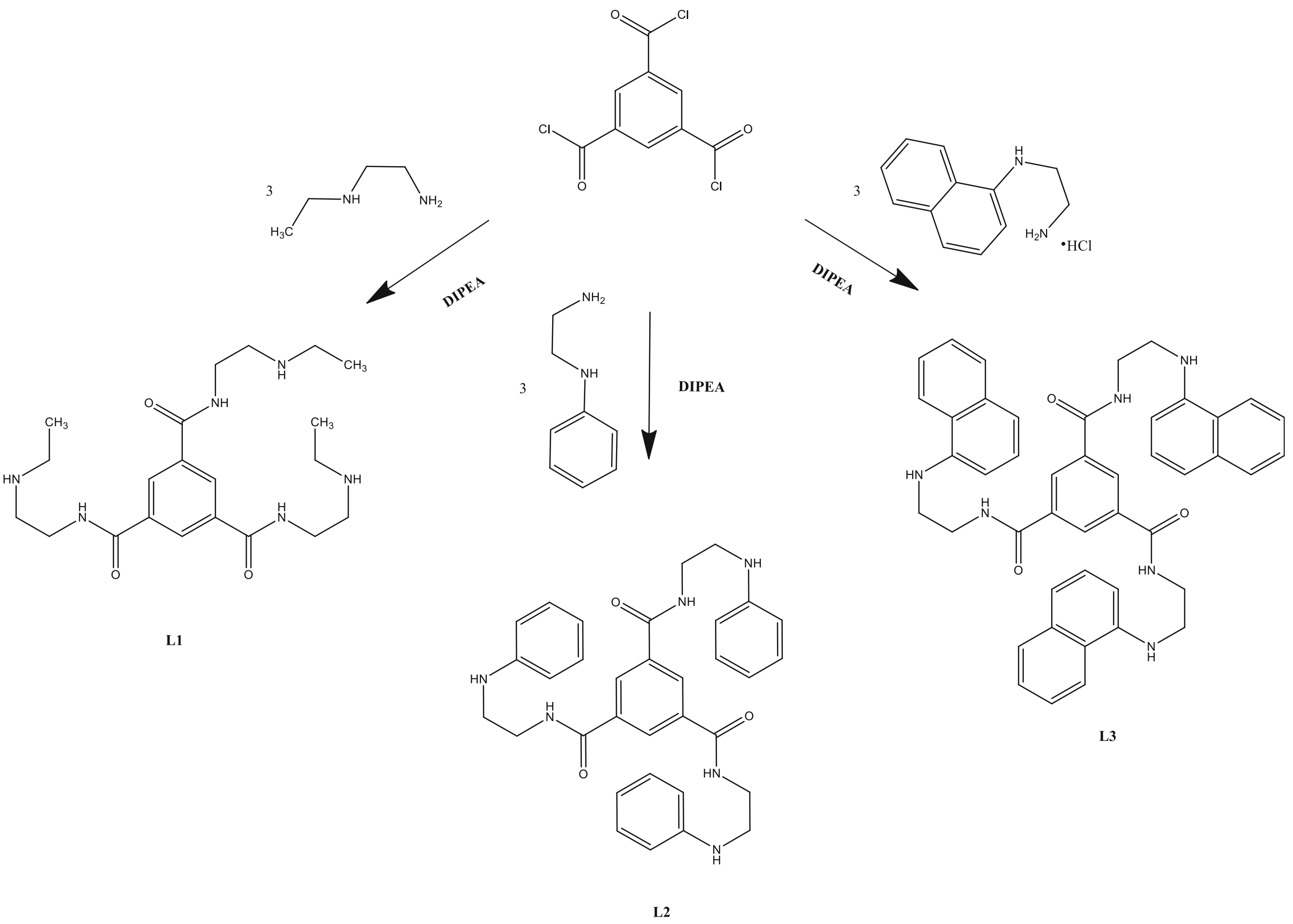


Fig. 1 Synthesis route of the tripodal receptors; N-1,3,5-tris[2-(ethylamino)ethyl]benzene-1,3,5-tricarboxylamide(L1), N-1,3,5-tris[2-(phenylamino)ethyl]benzene-1,3,5tricarboxylamide (L2) and N-1,3,5-tris[2(naphthalene-2-ylamino)-ethyl]benzene-1,3,5,tricarboxyl-amid)) (L3)

analysis. In our study, tri-carboxamide fluororeceptors can selectively bind to Fe(II) with efficient quenching with electron transfer (ET) mechanisms. Cu(II) also makes spectacular changes with the tri-carboxamide fluororeceptors with increase/quench the fluorescence intensity [19–22].

Experimental Section

Materials and Methods

The reagents and solvents employed for synthesis were commercially available and used without further purification. ^{1}H-NMR spectra were measured on a Varian 400-MHz Spectrometer. FT-IR spectra were recorded by Perkin Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were carried out using a LECO-CHNS- 932 elementel analyser. The absorption spectra were recorded using a Perkin Elmer Lambda 25 UV–Vis Spectrometer. The fluorescence measurements were made on a Perkin Elmer LS 55 Luminescence Spectrometer.

Syntheses of the Ligands

Preparation of N-1,3,5-Tris[2-(Ethylamino)Ethyl]Benzene-1,3,5-Tricarboxylamide, L1 Ethylethylenediamine (3 mmol, 0.31 mL) was dissolved in 5 mL DCM and added drop by drop into the solution of 1,3,5-benzenetricarbonyltrichloride (1 mmol, 0.26 g) in 5 mL DCM with effective stirring in ice-bath. Then n-ethyldiisopropylamine (3 mmol, 0.51 mL) was added into the reaction medium and the reaction mixture was stirred for 3 h. Yellow oily product was obtained. M.P.: 219 °C, Elemental analysis Calculated (Found): C: 59.98 (59.94), H: 8.63 (8.59), N: 19.98 (19.75). FT-IR (cm^{-1}): (2944, Ar C-H), (2700–2800, C-H), (3270, N-H), (1281 N-H), (1641 C=O). ^{1}H-NMR (DMSO-d6): δ 9.1 (s, CH, 3H), 8.1

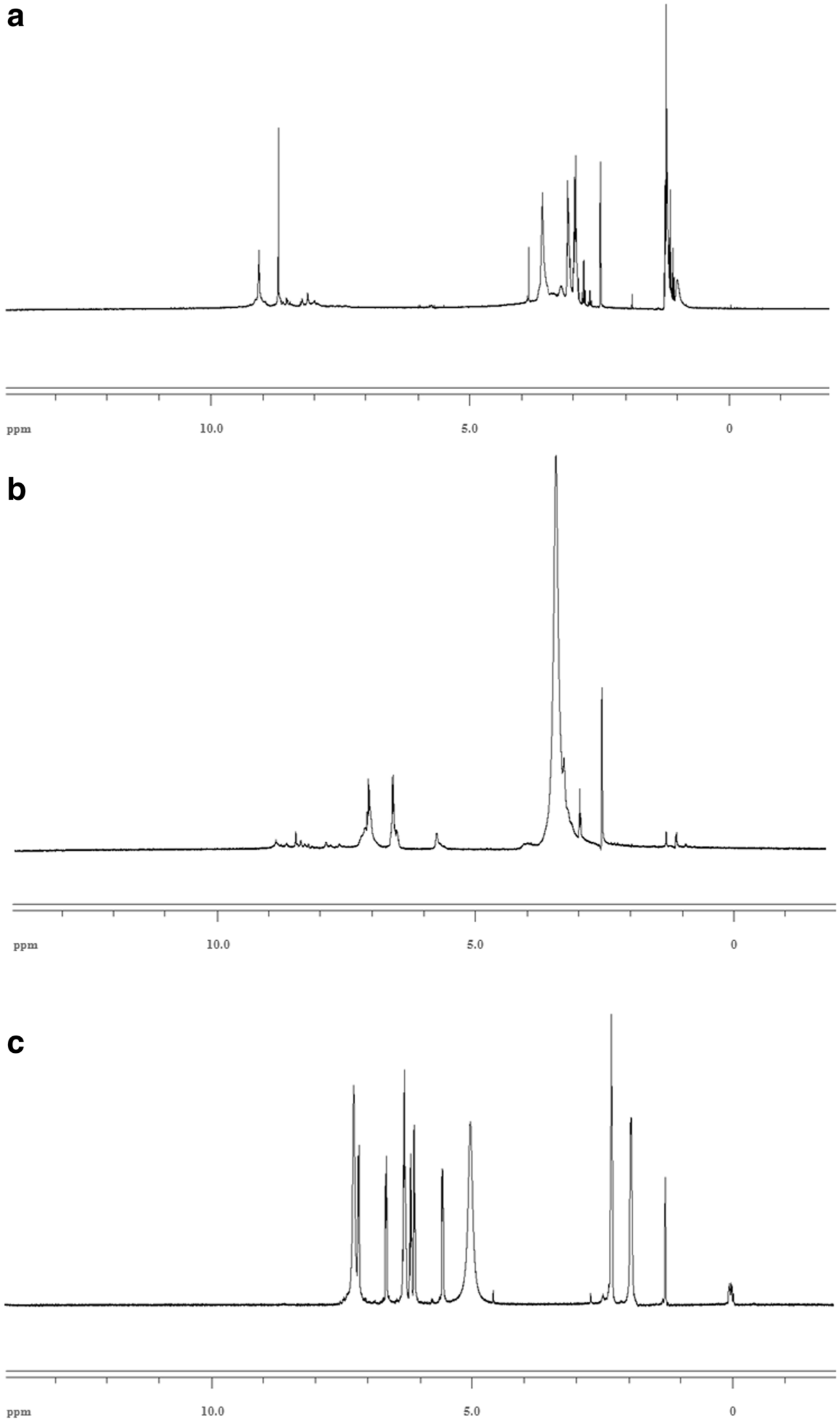


Fig. 2 ^{1}H-NMR spectra of the tripodal carboxylamide-based receptors; **a**) L1, **b**) L2, **c**) L3

(s, R-CONH, 3H), 5.9 (t, R-NH, 3H), 2.5 (d, CH_2, 6H), 2.9–4.0 (t, CH_2, 12H), 0.9 (t, CH_3, 9H).

Preparation of N-1,3,5-Tris[2-(Phenylamino)Ethyl]Benzene-1,3,5tricarboxylamide, L2 Phenylethylenediamine (3 mmol, 0.39 mL) was dissolved in 5 mL DCM and added drop by drop into the solution of 1,3,5-benzenetricarbonyltrichloride (1 mmol, 0.26 g) in 5 mL DCM with effective stirring. Then n-ethyldiisopropylamine (3 mmol, 0.51 mL) was added into the reaction medium and stirred for 3 h. After being soaked in an

Fig. 3 FT-IR spectra of the tripodal carboxylamide-based receptors; **a**) L1, **b**) L2, **c**) L3

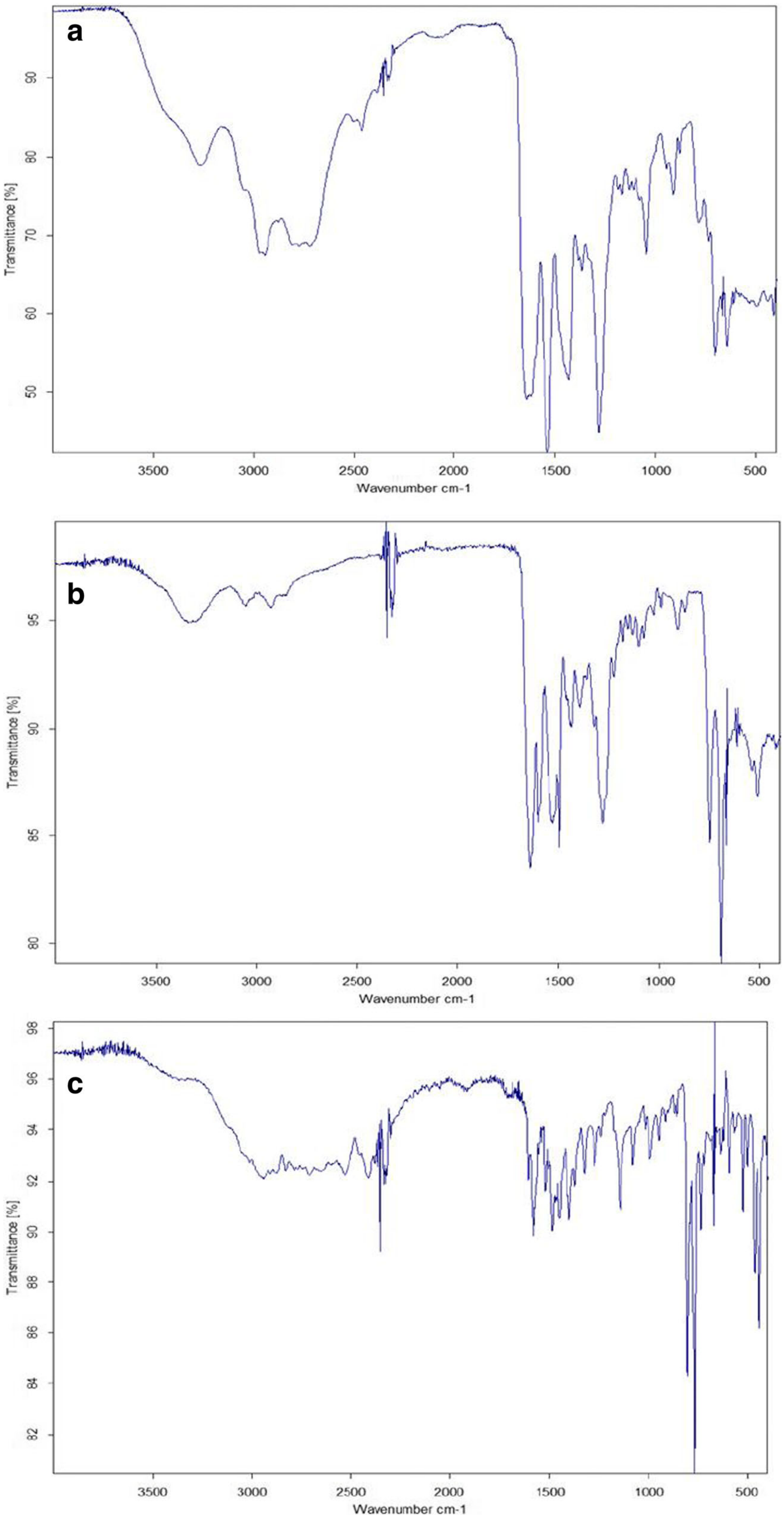


Fig. 4 Absorption changes of the receptors and cation targets in acetonitrile medium (1×10^{-4}M)

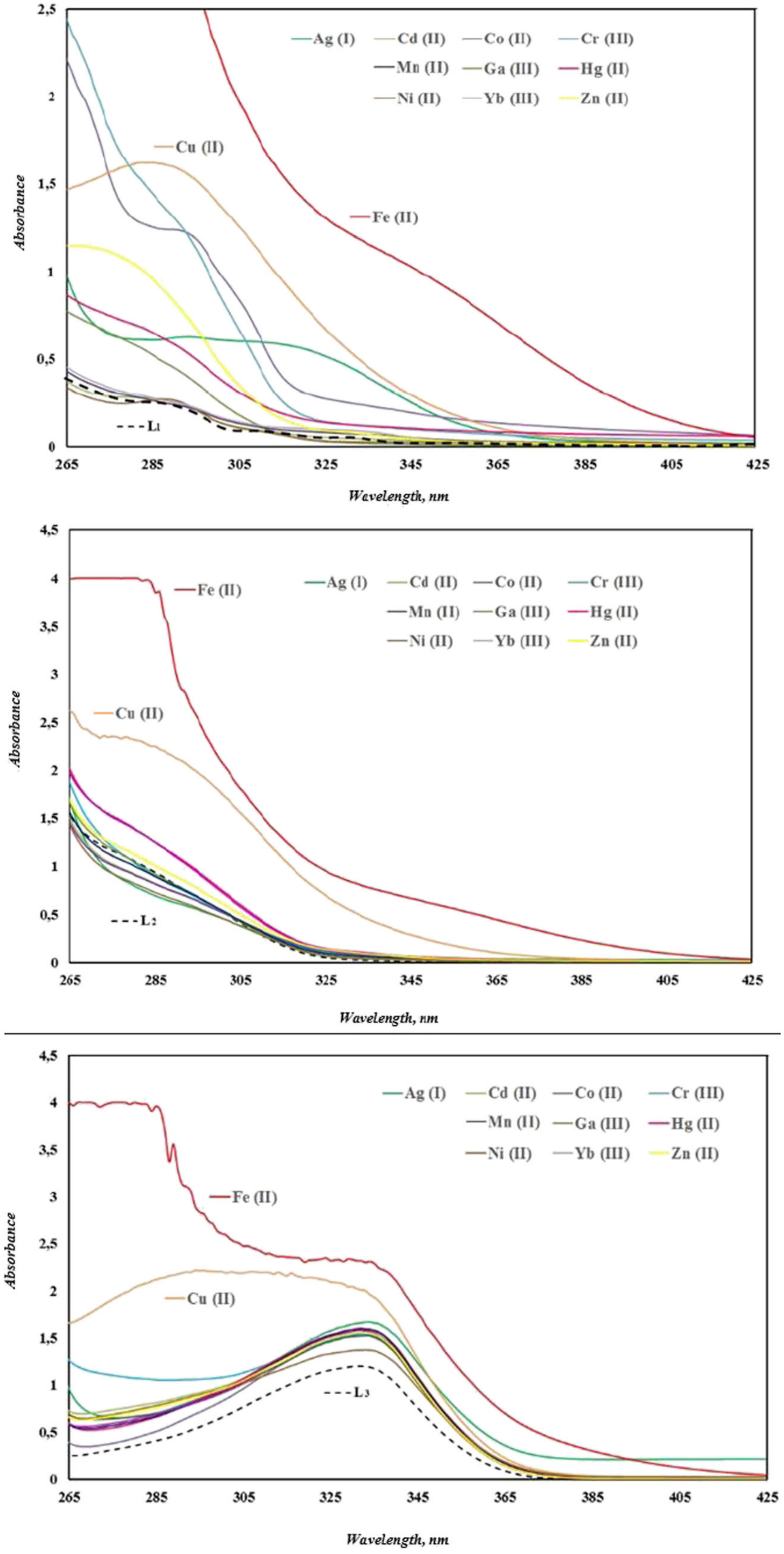


Table 1 Maximum wavelenghts (λ_{max}) and maximum absorbance values (A_{max}) and calculated molar absorptivity values (ε) of the receptors L1, L2, L3 and some metal ions (1×10^{-4} M) in acetonitrile medium

Sample	λ_{max} (nm)	A_{max} (A)	ε ($M^{-1}.cm^{-1}$)
L1	285	0.25	2.500
L1 + Fe(II)	295	2.8	28.000
L1 + Cu(II)	290	1.7	17.000
L2	280	1.25	12.500
L2 + Fe(II)	290	3.7	37.000
L2 + Cu(II)	296	2.4	24.000
L3	335	1.25	12.500
L3 + Fe(II)	295	3.5	35.000
L3 + Cu(II)	290	2.1	21.000

ice-cold bath overnight, obtained white solid was filtered and washed with DCM and then with distilled water to remove impurities and dried with anhydrous magnesium sulphate in a vacuum desiccator. Melting point identification was done. M.P.: 213 °C, Elemental analysis Calculated (Found): C: 70.19 (70.02), H: 6.43 (6.32), N: 14.88 (14.73). FT-IR (cm^{-1}): (3052, Ar C-H), (2930, C-H), (3324, N-H), (1279 N-H), (1641 C=O). ^{1}H-NMR (DMSO-d6): δ 8.2 (s, CH, 3H), 7.2–6.7 (d, CH, 15H), 8.1 (t, R-CONH, 3-H), 5.8 (t, R-NH, 3H), 3.6–2.4 (d, CH_2, 12H).

Preparation of N-1,3,5-Tris[2(Naphthalene-2-Ylamino)-Ethyl]Benzene-1,3,5,Tricarboxyl-amid, L3 N1-Naphthalenethenylamine (3 mol, 0.66 g) was dissolved in 7 mL of DCM-methanol solvent mixture (5:2) and added added drop by drop into the solution of 1,3,5-benzenetricarbonyltrichloride (1 mmol, 0.26 g) in 5 mL DCM with effective stirring. Then n-ethyldiisopropylamine (3 mmol, 0.51 mL) was added into the reaction medium and the reaction mixture was stirred for 3 h. A precipitated pink color was formed and then washed with DCM to remove the impurities and dried with anhydrous megnesium sulfate in a vacuum desiccator and the melting point was determined. M.P.: 204 °C, Elemental analysis Calculated (Found): C: 75.19 (74.98), H: 5.92 (5.56), N: 11.76 (11.44). FT-IR (cm^{-1}): (2943, Ar C-H), (2711, C-H), (1141 N-H), (1603 C=O), (767 C-Cl). ^{1}H-NMR (DMSO-d6): δ 8.6 (s, CH, 3H), 7.7–7.16 (dd, CHN, 21H), 5.8 (t, R-CONH, 3H), 5.1(t, R-NH, 3H), 3.5–3.4 (t, CH_2, 12H).

Result and Dıscussıon

Synthesis and Characterization

Synthesis of the receptors are performed by the reaction of 1,3,5-benzenetricarbonyltrichloride and amine compunds as; ethylethylenediamine, phenylethylenediamine, N1-naphthalenethenylamine in organic solvent medium (Fig. 1). Also, DIPEA was used as a base to make carboxamide formation faster. So, the yields were above %60 in this method. These receptors were synthesized originally and their characterization were performed by spectroscopic techniques as FT-IR, ^{1}H-NMR. The ^{1}H-NMR and FT-IR spectra of the synthesized products are given in the experimental section, where only comments on the characteristic peaks are given. According to the ^{1}H-NMR data, the C-H aromatics of L1, L2 and L3 tricarboxylamide derivatives show singlets at 9,1-8,2–8,6 ppm, respectively. The amide NH bands, which form the synthesis feature, which were observed at L1 at 5.9 ppm and L2, L3 at 5.8–5.9 ppm (Fig. 2). From the FT-IR spectra, the stretching bands of Ar-CONH amide were observed moderately at 3270 cm^{-1}. NH bands at ligands of about 2944, 3324 and 2943 cm^{-1}. Amide C = O bands are observed at 1641, 1641 and 1603 cm^{-1} (Fig. 3).

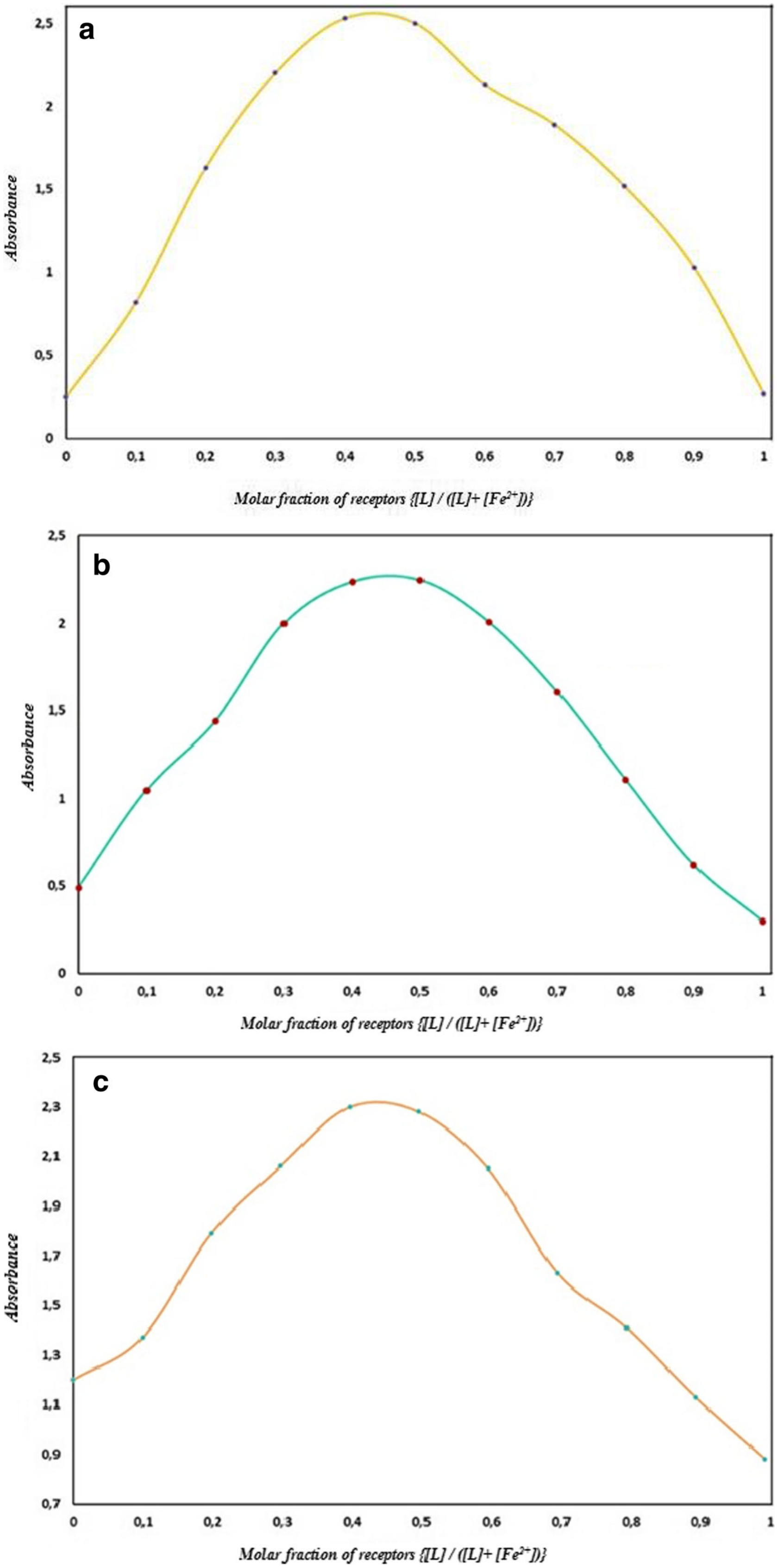
Absorption Studies

Uv-vis absorption spectrum of the ligands (L1, L2, L3) and target cations (Fe(II), Cu(II), Hg(II), Zn(II), Ni(II), Mn(II), Cd(II), Ga(III), Co(II), Yb(III), Cr(III), Ag(I)) were recorded in acetonitrile solution (1×10^{-4} M) (Fig. 4). L1 and L2 exhibited dual $\pi \rightarrow \pi^*$ absorption bands at 285–310 nm and 280–295 nm, respectively. Addition of the cations to the L1 resulted higher absorption band intensities and bathochromic shift to 295–345 (Fe(II)) and 290–355 nm (Cu(II)). L2 ligand also resulted higher absorption band intensities and bathochromic shift to 290–355 (Fe(II)) and 296–335 nm (Cu(II)). L3 ligand exhibited a single absorption band at 335 nm. After the addition of Fe (II), Cu (II) cations, absorption band intensity gets higher and hypsochromic shift to 295 nm (Fe(II)) and 290 nm (Cu(II)). Maximum wavelenghts (λ_{max}) and maximum absorbance values (A_{max}) and calculated molar absorptivity values (ε) are given in Table 1, ($\varepsilon = A_{max}$/ l.C (l = 1 cm) for the receptors and metal ions**.** According to the molar absorptivity values, the receptors have lower molar absorptivities than their metal binding forms. Additionally, Fe(II) ion binding forms of the receptors have highest molar absorptivities.

Binding Stoichiometry Determination

The job plot technique was used for the complex stoichiometry for the receptors L1, L2, L3 and Fe(II) ion. The maximum plots of the absorbance were recorded on 295 nm for Fe(II)-bindings. The concentrations of L-Fe(II) complexes approach a maximum plot when $\{[L] / ([L] + [Fe^{2+}])\}$ is about ≈ 0.50. The reaction stoichiometry of the receptors and Fe(II) is 1:1 according to Job's plot studies (Fig. 5). These results showed that the Fe (II) ions at a concentration of (1.10^{-4} M) interacted

Fig. 5 Job's plots for the receptors/Fe(II) ion. **a**)N-1,3,5-tris[2-(ethylamino)ethyl]benzene-1,3,5-tricarboxylamide(L1), **b**) N-1,3,5-tris[2-(phenylamino)ethyl]benzene-1,3,5-tricarboxyl amide (L2) and **c**) N-1,3,5-tris[2(naphthalene-2-ylamino)-ethyl]benzene-1,3,5,tricarboxyl-amid)) (L3)



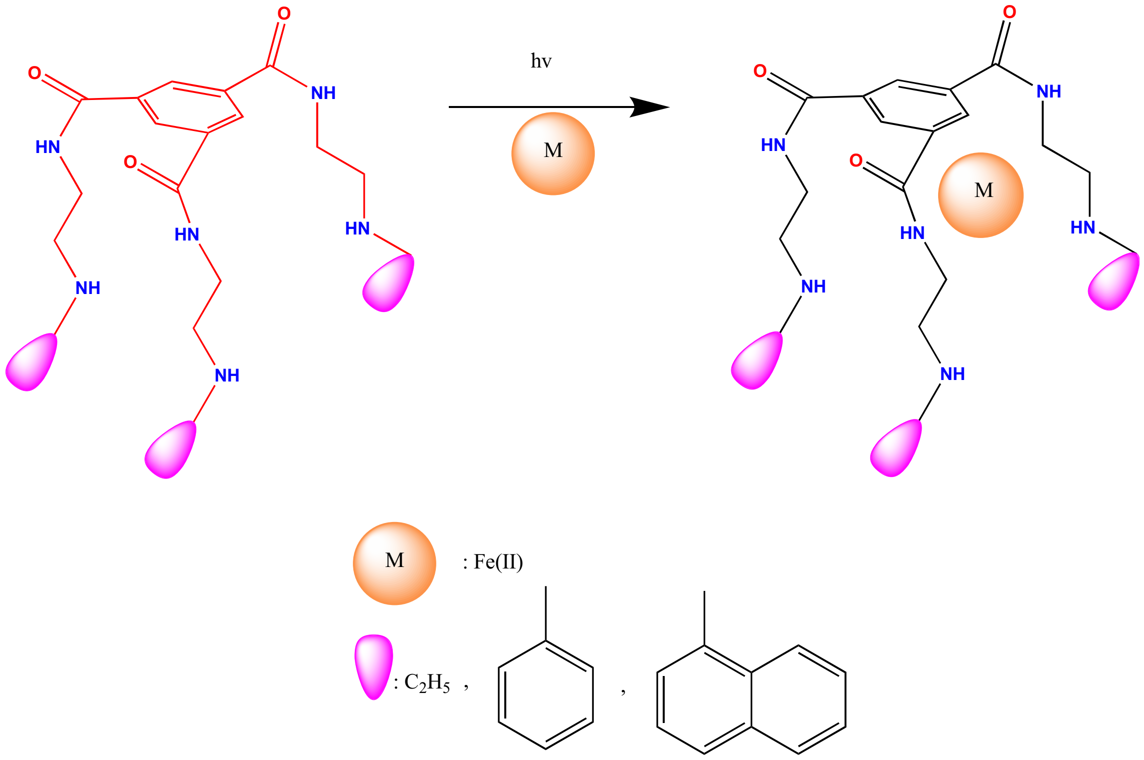


Fig. 6 Estimated perspective of the complex formation and quenching with the Fe(II) ion

with the three arms of the ligand and were trapped between these arms. Figure 6 illustrates binding stoichiometry and geometry of the -NH units of the receptors and Fe(II) ion.

Fluorescence Studies

The changes in fluorescence intensities of the receptors upon addition of various metal ions were also recorded by the Fluorescence Spectrometer, with the concentration of 1 × 10^{-4} M in acetonitrile medium and the excitation at λ_{ex}: 270 nm (Table 2). The receptors L1, L2 and L3 exhibit emission bands at λ_{max}: 380, 375 and 415 nm, respectively. Upon addition of various metals to the receptor L1, quenching were seen. Mostly, Co(II) and Fe(II) quenched the fluorescence of L1. Cu(II), Co(II), Ni(II) and Hg(II) increased the fluorescence of L2 and Fe(II) quenced the fluorescence. L2 receptor has also red-shifted by the addition of Cu(II) ion from 375 nm to 400 nm. For the L3 receptor, Ag(I) and Co(II) increased the fluorescence and Cu(II) and Fe(II) quenched the fluorescence. As seen from the spectra (Fig. 7), Fe(II) quenches the fluorescences of all the receptors. Additionally, it causes red-shifts from 380 to 425 nm for L1, 375 to 425 nm for L2, from 415 to 425 nm for L3. As seen from the specta, tri-carboxamide fluororeceptors can also be effected by other metal ions but selectively bind to Fe(II) with efficient quenching with electron transfer mechanisms (ET). Cu(II) also makes spectacular changes with the tri-carboxamide fluororeceptors with increase/quench the fluorescence intensity [23, 24].

Table 2 Maximum fluorescence intensities of the receptors at their maximum wavelenghts

Sample	Intensity, I	λ_{max} (nm)
L1	220	380
L1 + Fe(II)	120	425
L1 + Co(II)	140	380
L2	230	375
L2 + Fe(II)	120	425
L2 + Cu(II)	280	400
L3	890	415
L3 + Fe(II)	130	425
L3 + Cu(II)	350	410

The emission spectra of the titration of receptors with Fe(II) were recorded in acetonitrile (1:10) (Fig. 8). When the changes in the fluorescence intensity were examined according to the increase of the Fe(II) ion concentration (0–50 equiv.), it was observed that the emission intensities were gradually decreased, more quenched. And they were red-shifted from 380 to 430 nm for L1, from 375 to 415 nm for L2 and from 415 to 425 nm for L3.

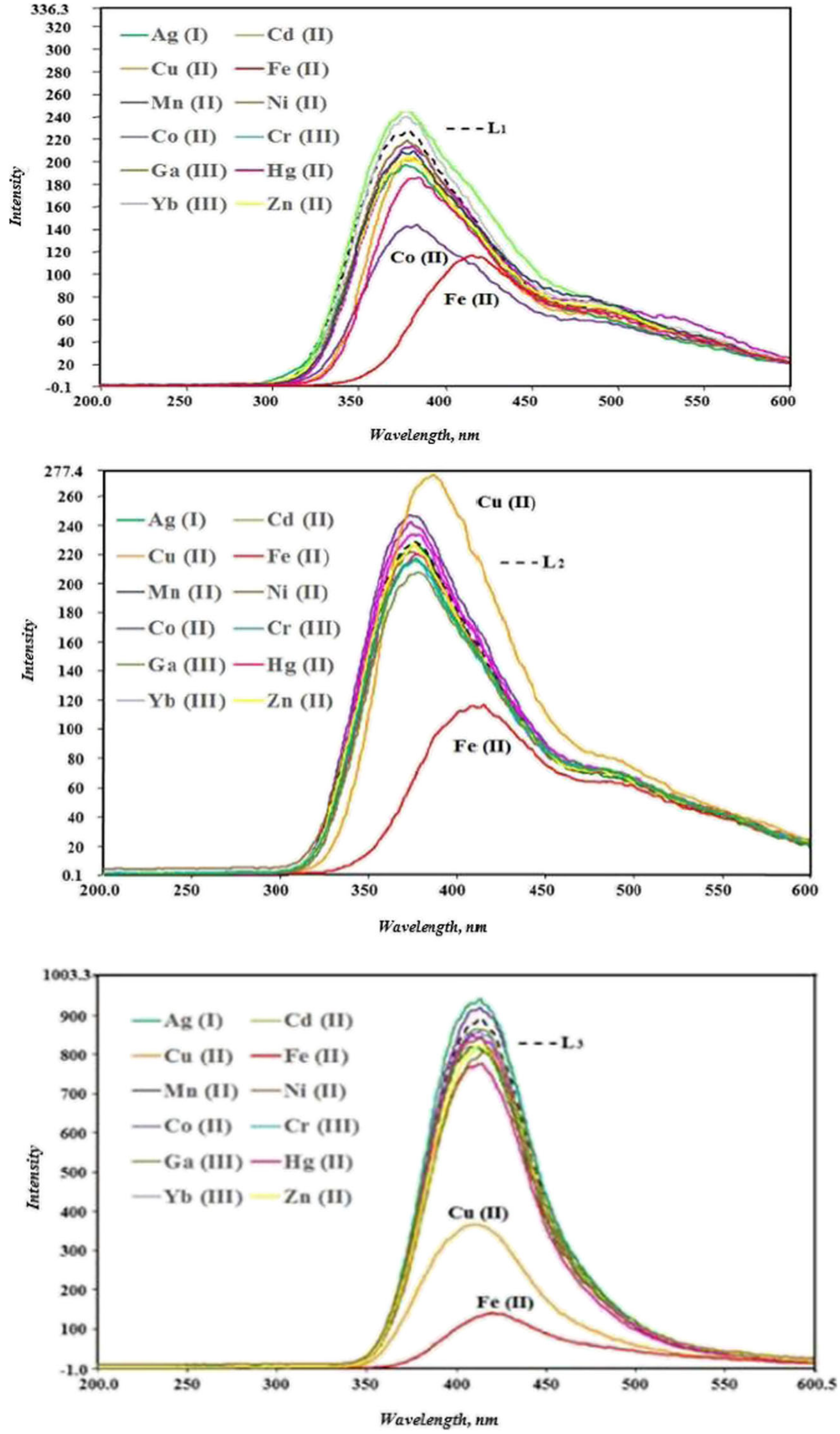
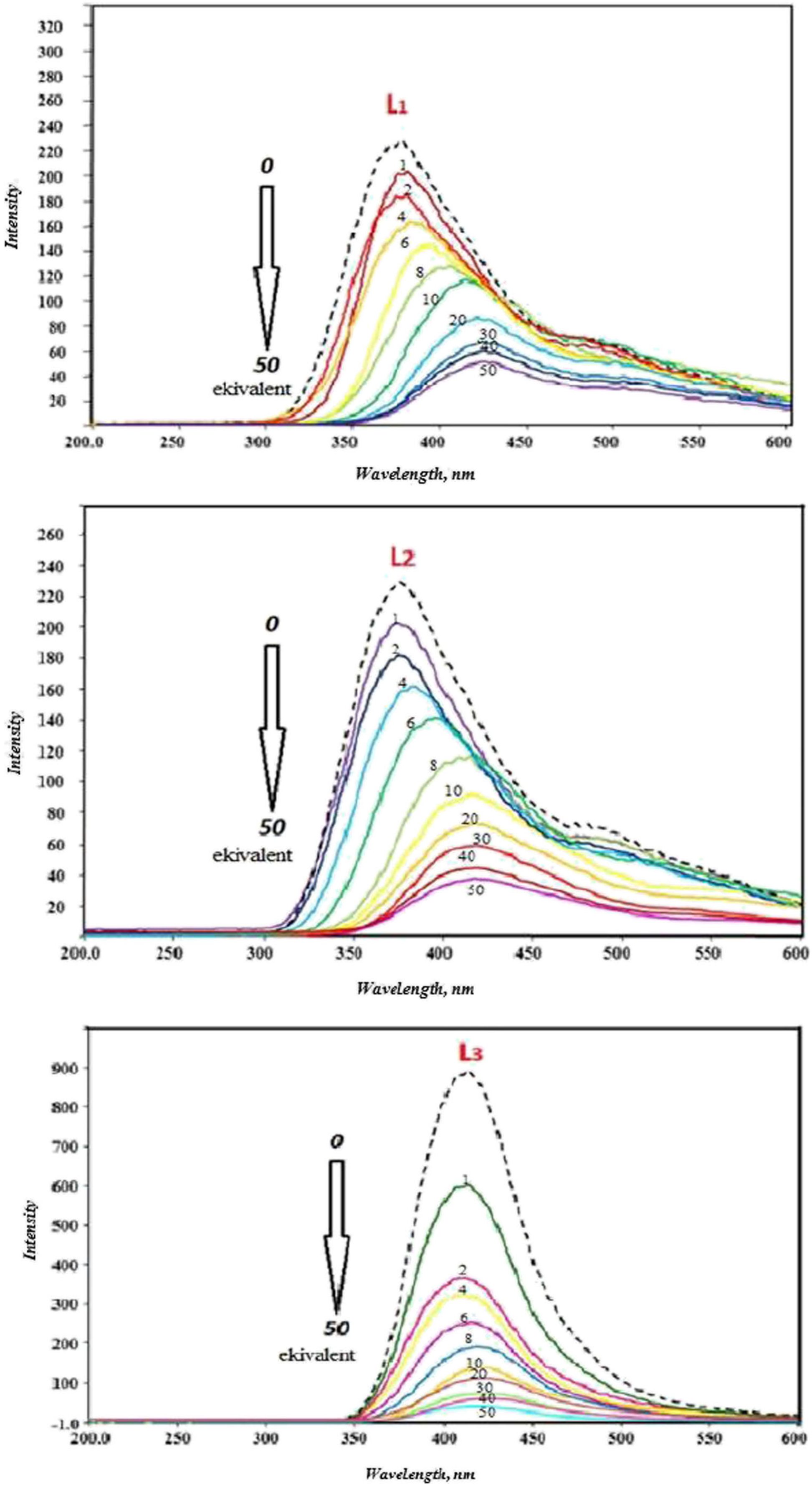


Fig. 7 Fluorescence changes of the receptors and cation targets in acetonitrile medium (1×10^{-4}M)

Conclusion

As a summary, tripodal carboxylamide-based receptors N-1,3,5-tris[2-(ethylamino)ethyl] benzene-1,3,5-tricarboxylamide (L1), N-1,3,5-tris[2-(phenylamino)ethyl]benzene-1,3,5-tricarboxylamide (L2) and N-1,3,5-tris[2(naphthalene-2-ylamino)-ethyl]benzene-1,3,5- tricarboxylamide (L3) were synthesized originally. Among the receptors, L3 is highly fluorescencent with the emission intensity of 890 at its max. Wavelenght 415 nm. Metal sensitivity measurements were performed by the various metal ions. Selective binding of Fe(II) ion by the -NH units of the receptors resulted in effective quenching. The ratio of the receptor:Fe(II) ion formations are found as 1:1 for all the receptors.

Fig. 8 Fe (II) titration of the receptors in acetonitrile. The metal concentration was taken as 0,2,4,6,8,10,20,30,40,50 equiv. in 1×10^{-4} M solutions



Acknowledgements We thank the Scientific Research Projects Foundation (BAP) of Selcuk University (Konya/TURKEY) for financial support of this work.

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