

Simple and novel synthetic method to mixed-donor podand

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Abstract: An efficient method for the synthesis of new compounds of dibenzo podand containing mixed-donor atom is described. The key starting materials for these podand was successfully prepared in 92% yield from 2-aminophenol and benzaldehyde in water. The structures of these new compounds were confirmed on the basis of IR, ^1H NMR and ^{13}C NMR and Ms spectroscopic data.

Keywords: Mix donor; Cesium carbonate; Podand; SDS; Amino phenol. © 2015 ACG Publications. All rights reserved.

1. Introduction

In recent years many advances have been made in the field of host-guest chemistry. Part of this progress is due to combinations of podand. These compounds, in addition to host-guest chemistry are also used in other fields of chemistry including catalysis and biological chemistry¹⁻⁵. Also podands have been widely used for transport of ionic species but the stability of the podand-metal ion complex is dependent on size of the cavity, number of donor atoms and number of benzo substituents⁶. Often podands containing oxygen atoms. Experience has shown that these podands has been used extensively to bind and isolate alkali and alkaline earth metal ions⁷⁻¹³. Podands containing only nitrogen or sulfur donor atoms strongly complex towards heavy transition metal ions. More recently, interest in change in the properties of metal complexes led to replacement of one or more oxygen with sulfurs and/or nitrogen¹⁴⁻¹⁶. They have complexation properties that are intermediate between those of all-oxygen and all-nitrogen or thia crown ethers. Such compounds have multiple complexation centers, which influence the rigidity of the compound, and modify the stability and selectivity of ligand metal cations extraction^{17, 18}.

The object of the present work is to offer a new and simple strategy to the formation of mixed N, O, S-donor podands in reasonable yields.

2. Results and discussion

Several synthetic methods have been developed for the synthesis podands. In this paper we intended to make podand with aminophenol and precursors which can be useful building block for macrocyclization.

Amino phenols have two functional groups, which needed to protect one of these groups. In orders to overcome difficulties in deprotection, we have chosen to use imine group to protect primary amines in cyclisation reactions. The advantages of imine groups are that: (i) they can be readily

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introduced into primary amines, (ii) imine-protected podand can be easily purified by recrystallization, (iii) imine groups are generally removed under mild acidic conditions without affecting the macrocycle and (iv) they can be readily prepared in green condition.

Previously, we reported the synthesis of β -amino carbonyl compounds, in micellar solution of sodium dodecylsulfate (SDS)¹⁹. Herein, we report a mild, simple, efficient, method for the preparation of imine compounds by the reaction of aminophenol with benzaldehyde (the click reaction) in the presence of SDS in water under neutral conditions. The reaction was preceded in less than one hour in good yield 92%. Imine was isolated by simple filtration and recrystallized from ethanol (Scheme 1). The IR spectrum of **2** showed characteristic absorption bands at 1624 cm^{-1} , which is due to the C=N functional group.

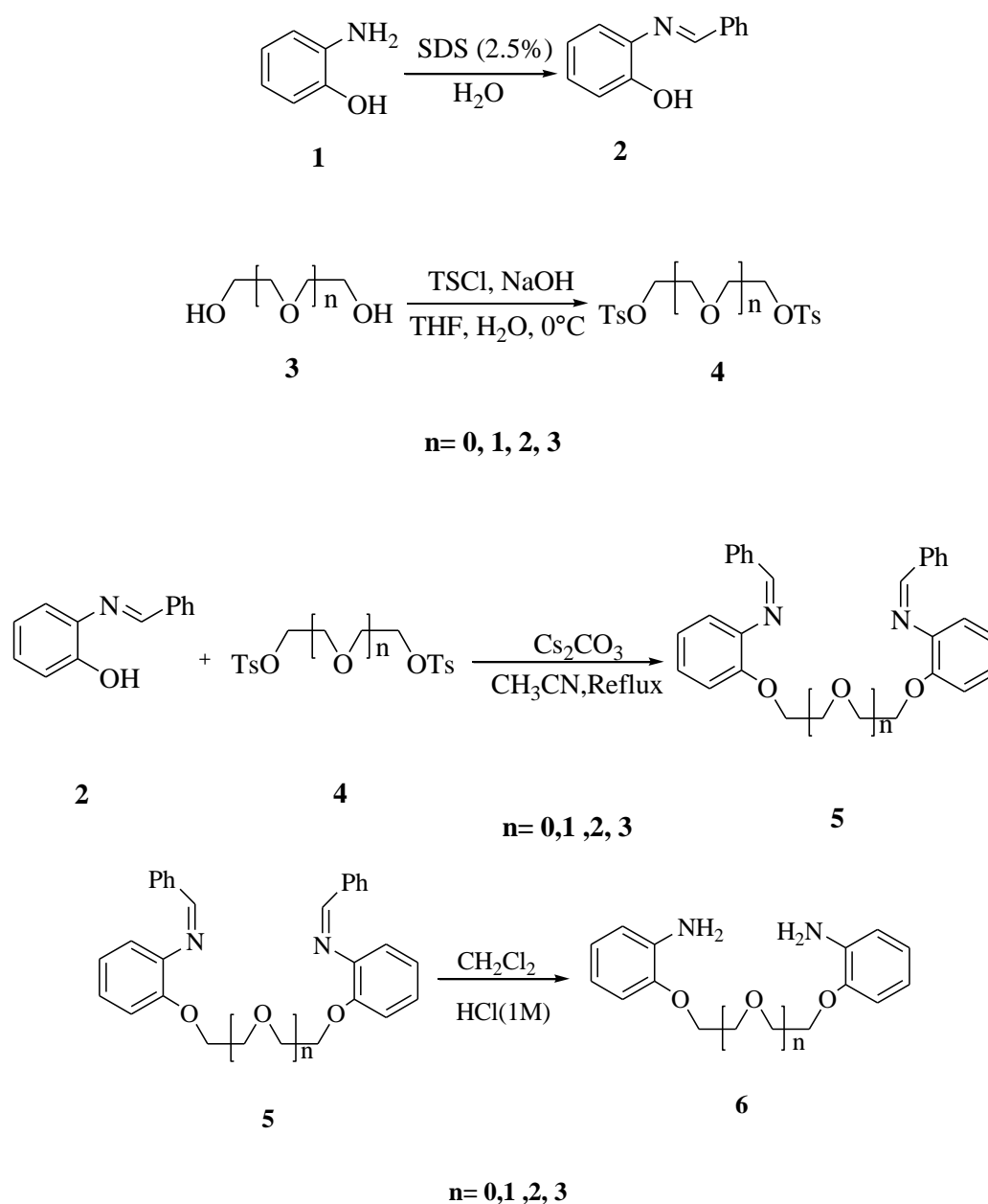


Figure 1. Synthesis of mixed N, O, S-donor podands derivatives

To develop an efficient procedure to prepare podand **6**, we needed oligoethylene ditosylate. We prepared 2, 2'-oxybis (ethane-2, 1-diyl) bis(4-methylbenzenesulfonate) **4b**, from diethylene glycol using sodium hydroxide and tosylchloride in the mixture of water/tetrahydrofurane. This product was obtained in good yield (90%) without any further purification. The IR spectrum of **4b** showed characteristic absorption bands at 1353 cm^{-1} and 1172 cm^{-1} , which are due to the S=O functional groups. The ^1H NMR (CDCl_3) spectrum of **4b** showed a singlet at δ 2.44 ppm for methyl proton. Aliphatic protons (CH_2) resonated as two triplets in 3.59 ppm and 4.08 ppm with coupling constant of $J = 4.5\text{ Hz}$ and $J = 4.5\text{ Hz}$ respectively. The four protons of the benzenesulfonate ring resonated as a pair of doublets centred at δ 7.32 and δ 7.77 with coupling constants of $J = 8.0\text{ Hz}$ and $J = 7.75\text{ Hz}$. Distinctive ^{13}C NMR signals of **4b** appeared at $\delta = 21.6$ for CH_3 , $\delta = 68.6, 69.0$ for four CH_2 aliphatic and $\delta = 127.8, 129.9, 132.7, 144.9$ for C aromatic.

Recently, Xu and co-workers²⁰ reported the synthesis of alkoxyaniline by reacting imine with alkyl halide in acetone using potassium carbonate with the use of high dilution techniques. Attempt to employing the same methodology as used to prepare **6** was unsuccessful. Thus, imine was reacted with diethylene glycol ditosylate in the presence of caesium carbonate in acetonitrile for the synthesis of **5b** without any side product. The imine protecting groups were finally removed with aqueous hydrogen chloride readily afforded podand **6b**. We observed this reaction in acetonitrile in the presence of caesium carbonate producing the desired product of 2,2'-(2,2'-(1,2-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy)diethanol **6a** in 74% yield after 24 h. The IR spectrum of **6b** showed characteristic absorption bands at 3465 cm^{-1} and 3361 cm^{-1} for NH_2 and 1275 and 1126 cm^{-1} , which are due to the C-O functional groups. The ^1H NMR (CDCl_3) spectrum of **6b** showed a singlet at 3.82 ppm for NH_2 . Other aliphatic protons resonated in 3.93 ppm and 4.2 ppm with coupling constant of $J = 2.8\text{ Hz}$ and $J = 3.2\text{ Hz}$, respectively. The four protons of the aromatic ring resonated as a multiplet at δ (6.66-7.26). Distinctive ^{13}C NMR signals of **6b** appeared at $\delta = 69.61, 71.04, 69.3$ for four CH_2 aliphatic and $\delta = 114.23, 116.85, 119.92, 123.07, 137.56$ and 147.64 for C aromatic.

Synthetic routes towards preparation of these macrocycles are outlined in Figure 1.

After this success, we have developed this method for ethylene glycol, tri ethylene glycol and tetra ethylene glycol derivatives (Table 1).

In addition to the above oligoethylene glycol, we prepared ditosylates from diethanolamin and 1, 8-dihydroxy-3, 6-dithia octandiol. Tosylation of these compounds were carried out in the presence of tri ethylamine as a base and dichloromethane as a solvent (Figure 2).

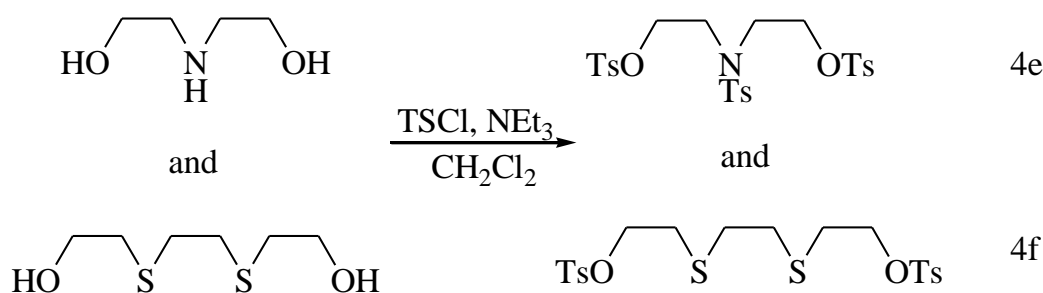
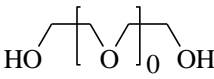
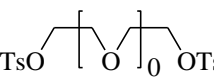
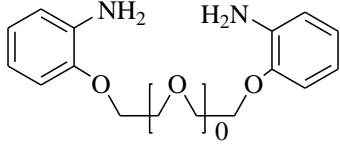
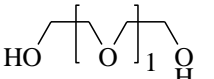
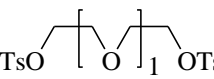
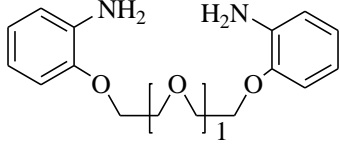
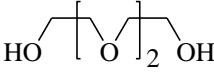
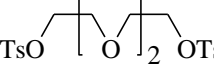
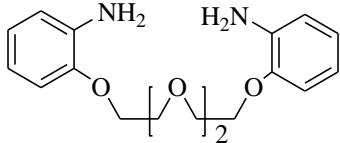
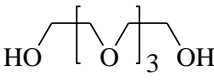
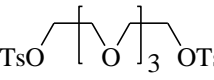
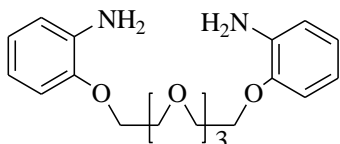
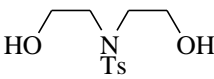
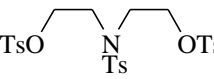
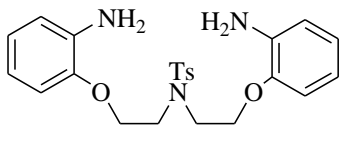
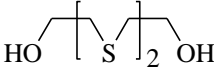
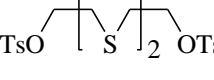
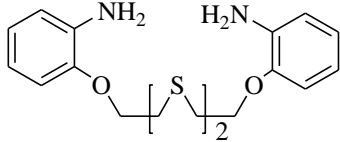


Figure 2. Tosylation of diethanolamin and 1, 8-dihydroxy-3, 6-dithia octandiol.

Table 1. Reactions of amino phenol with ditosylates

Entry	diol	Ditosylate	product
1	 3a	 4a	 6a
2	 3b	 4b	 6b
3	 3c	 4c	 6c
4	 3d	 4d	 6d
5	 3e	 4e	 6e
6	 3f	 4f	 6f

3. Experimental Section:

General: Chemicals were purchased from Merck and Fluka. Chemical Companies. All the products are known and were characterized by comparison of their physical data with those reported in the literature. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were reported on a 70ev (EI) Ms Model: 5973 Network Mass Selective Detector (Agilent Technology (HP)). The purity of the products and the progress of the reactions were measured by TLC on silica-gel polygram SILG/UV254 plates.

Melting Points were reported with Electro thermal 9100 apparatus. Elemental analysis was performed on a Thermo Finnigan (San Jose, CA, USA) Flash EA micro analyzer.

3.1. General procedure for synthesis of 4- Synthesis of Imine(2-(benzylideneamino) phenol):

To a solution of SDS (2.5 mol%) in H₂O (20 mL) was added 2-aminophenol (1 eq, 10 mmol), and benzaldehyde (1eq, 10 mmol). The mixture was stirred at the room temperature for 1h. Water (10 mL) was added to the reaction mixture, and the precipitated imine was separated with a simple filtration. The filtered solid was washed with H₂O and dried to afford the product in good yield. This compound was obtained in 92% yield as yellow crystal. mp: 94-95. IR (KBr, cm⁻¹) ν_{\max} : 3332(OH), 1624(C=N).

4.2. General procedure for the synthesis of Ditosylates 4 (a, b, c, d) from Diols 3(a, b, c, d):

For ditosylation of the diols, to a solution of oligo ethylene glycol (1eq, 20 mmol) tetrahydrofuran (15 mL) was added sodium hydroxide (3.5eq, 70 mmol) in H₂O (15 mL) and the reaction mixture was stirred at room temperature until a homogeneous solution was achieved. A solution of p-toluenesulfonyl chloride (2.5eq, 50 mmol) in 25 mL of tetrahydrofuran was added drop wise to the stirred mixture at 0° C. Upon completion of the addition, HCl (15 mL, 10% aqueous solution) and ice were added to the reaction mixture, and the precipitated was separated with a simple filtration. The filtered solid was washed with H₂O and dried to afford the pure products in good to excellent yields.

4.2.1. *Ethylene glycol di p-toluene sulphonate (4a)*. 85% yield as colourless crystal. mp: 126.6-127.8(lit²³: 88-89.1). IR (KBr, cm⁻¹) ν_{\max} : 1361 and 1180 (SO); ¹H NMR (250MHz, CDCl₃): δ 2.41 (s, 6H), 3.68 (s, 2H), 7.41 (d, J = 8.1 Hz, 4H), 7.8 (d, J = 8 Hz, 4H) ppm.

4.2.2. *2, 2'-oxybis (ethane-2, 1-diyl) bis(4-methylbenzenesulfonate)(4b)*. 90% yield as colourless crystal. mp: 87.5-89.0 (lit²¹: 87-87.8). IR (KBr, cm⁻¹) ν_{\max} : 1353 and 1172 (SO); ¹H NMR (250MHz, CDCl₃): δ 2.44 (s, 6H), 3.59 (t, J = 4.5 Hz, 4H), 4.08 (t, J = 4.5 Hz, 4H), 7.32 (d, J = 8 Hz, 4H), 7.77 (d, J = 7.75 Hz, 4H) ppm. ¹³C NMR (62.5 MHz, CDCl₃) δ : 12.61, 68.66, 69.05, 127.88, 129.90, 132.78, 144.98.

4.2.3. *Triethylene glycol di p-toluene sulphonate (4c)*. 83% yield as white crystal. mp: 81-83 (lit²³: 80-81). IR (KBr, cm⁻¹) ν_{\max} : 1353 and 1191 (SO); ¹H NMR (250MHz, CDCl₃): δ 2.39 (s, 6H), 3.6 (s, 6H), 3.68 (t, J = 4.3 Hz, 4H), 4.18(t, J = 4.3 Hz, 4H), 7.33 (d, J = 8 Hz, 4H), 7.79 (d, J = 8 Hz, 4H) ppm.

4.3. Synthesis of Ditosylate from Diethanolamin:

Tosylation of diethanolamin were prepared according to Sasanuma et al., with minor modifications²². To a solution of diethanolamin (1 q, 10 mmol) in dichloromethane (15mL) was added of triethylamine (3eq, 30 mmol) and the reaction mixture was stirred at room temperature for 30 min. A solution of p-toluenesulfonyl chloride (3eq, 30 mmol) dichloromethane (40 mL) was added drop wise to the stirred mixture at 0° C during 2 hours. Upon completion of the addition, the reaction mixture was stirred for 2 h at room temperature. Afterward, the solvent were removed under reduced pressure, and white precipitated was obtained simply in good yield.

4.3.1. *(tosylazanediyl)bis(ethan-2,1-diyl)bis(4-methylbenzenesulfonate) (4e)*. 95% yield as white solid. IR (KBr, cm⁻¹) ν_{\max} : 1357 and 1176 (SO).

4.4. Synthesis of Ditosylate from 1, 8-dihydroxy-3, 6-dithia octandiol

To a solution of 1,8-dihydroxy-3, 6-dithia octandiol (1eq, 10 mmol) dichloromethane (15 mL) was added triethylamine(3eq, 30 mmol) and the reaction mixture was stirred at room temperature for 1 hours. A solution of p-toluenesulfonyl chloride (2eq, 20 mmol) dichloromethane (25 mL) was added drop wise to the stirred mixture during 4 hours. Upon completion of addition, the reaction mixture was stirred over night at room temperature. Afterward, the solvent were removed under reduced pressure, and yellowish liquid was obtained. The acetonitril was added to the crude product to precipitate unreacted starting material. Then, the mixture was filtered and washed. After removal of solvent in vacuo produced yellow sediment.

4.4.1. *(ethan-1,2-diylbis(sulfandiyl))bis(ethan-2,1-diyl)bis(4-methylbenzensulfonate) (4f)*: ¹H NMR (400 MHz, CDCl₃): δ 2.33(s, 6H), 2.72(t, J = 4 Hz, 4H), 2.88(s, 4H), 3.62 (t, J = 4 Hz, 4H), 7.16 (d, J

= 8 Hz, 4H), 7.71(d, J = 8 Hz, 4H) ppm. ^{13}C -NMR (100 MHz, CDCl_3): δ = 22.2, 33.4, 35.5, 62.3, 126.9, 130.1, 141.6, 142.6 ppm.

4.5. General Procedure for Synthesis of Bisanilines 6(a, b, c, d, e, f) from the 2-(benzylideneamino) phenol 8 and Ditosylates 4 (a, b, c, d, e, f):

To a solution of 2-(benzylideneamino) phenol (1eq, 5mmol) in anhydrous acetonitrile (15 mL) was added Cs_2CO_3 (2.1eq, 11mmol). The mixture was stirred for 30 min in reflux temperature. To this was added, ditosylate (0.5eq, 2.5mmol) and the reaction mixture was stirred for 48 hours. Upon cooling to room temperature, the mixture was filtered. To the resulting residue were added dichloromethane (20 mL) and HCl (50 mL, 1N) and the mixture was vigorously stirred for 4h. Two phases were separated and the aqueous layer was neutralized with NaHCO_3 , and then extracted with dichloromethane. The combined organic layer was dried over magnesium sulphate, and the solvent was removed in vacuo to afford podands as yellowish oil, or solid. After the solvent was evaporated, the residue was purified by column chromatography (ethyl acetate/n-hexane = 3:4v/v).

4.5.1. 2,2'-(ethane-1, 2-diylbis(oxy)) dianiline (6a). 78% yield yellow solid, FT-IR (KBr, cm^{-1}) ν_{max} : 3444 and 3363 (NH_2), 1272 and 1080 (CO); ^1H NMR (400 MHz, CDCl_3): δ 3.72 (s, 4H), 4.38 (s, 4H), 6.75 (d, J = 6.8 Hz, 4H), 6.82-6.84 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ : 68.56, 113.59, 116.51, 119.55, 123.04, 137.09, 147.38. Anal.calcd. for $\text{C}_{14}\text{O}_2\text{N}_2\text{H}_{16}$: C, 68.83; H, 6.59; N, 11.46. Found: C, 68.27; H, 7.11; N, 11.32. MS m/z ($\text{C}_{14}\text{O}_2\text{N}_2\text{H}_{12}$, 244) 244 (M^+).

4.5.2. 2, 2'-(2, 2'-oxybis(ethane-2, 1-diyl))bis(oxy)dianiline(6b). This compound was obtained in 74% yield, yellow solid, FT-IR: (KBr, cm^{-1}) ν_{max} : 3465 and 3361(NH_2), 1275 and 1126 (CO); ^1H NMR (400 MHz, CDCl_3): δ 3.82 (s, 4H), 3.91-3.93 (m, 4H), 4.19-4.20 (m, 4H), 6.66-7.28 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3): δ : 69.61, 71.04, 114.23, 116.85, 119.92, 123.1, 137.5, 147.6. Anal.calcd. for $\text{C}_{16}\text{O}_3\text{N}_2\text{H}_{20}$: C, 66.65; H, 6.98, N; 9.71 Found: C, 65.99, H; 7.05, N; 9.93. MS m/z ($\text{C}_{16}\text{O}_3\text{N}_2\text{H}_{20}$, 288) 288 (M^+).

4.5.3. 2,2'-(2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy)diphenol(6c). 66% yield yellow oil, FT-IR (KBr, cm^{-1}) ν_{max} : 3450 and 3366 (NH_2), 1274 and 1124 (CO); ^1H NMR (400 MHz, CDCl_3): δ : 3.53-3.62 (m, 8H), 3.67 (s, 4H), 4.14(t, J = 4.8, 4H) 6.77-6.95 (m, 8H) ppm. Anal. calcd. for $\text{C}_{18}\text{O}_4\text{N}_2\text{H}_{24}$: C 65.04; H 7.27, N 8.42, Found: C 65.27, H 7.46, N 8.31. MS m/z ($\text{C}_{18}\text{O}_4\text{N}_2\text{H}_{24}$, 332) 332 (M^+).

4.5.4. 2,2'-(2,2'-(2,2'-oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy)dianiline (6d). 65% yield, yellow oil, FT-IR: (KBr, cm^{-1}) ν_{max} : 3460 and 3366 (NH_2), 1274 and 1080 (CO); ^1H NMR (400 MHz, CDCl_3): δ : 3.58-3.59 (m, 8H), 3.69-3.70 (m, 4H), 3.79-3.84 (m, 4H), 4.15 (s, 4H), 6.69-6.80 (m, 8H). Anal.calcd. for $\text{C}_{20}\text{O}_5\text{N}_2\text{H}_{28}$: C, 63.81; H, 7.49; N, 7.44. Found: C, 64.23; H, 7.87; N, 6.83. MS m/z ($\text{C}_{20}\text{O}_5\text{N}_2\text{H}_{28}$, 376) 376 (M^+).

4.5.6. *N, N*-bis(2-(2-aminophenoxy)ethyl)-4-methylbenzensulfonamid (6e). 71% yield, yellow solid, ^1H NMR (400 MHz, CDCl_3): δ : 2.01(s, 3H), 3.45(t, J = 4, 4H), 3.95 (s, 4H), 4.31(t, J = 4.4, 4H), 6.57-6.71(m, 8H), 7.37(d, J = 7.6, 2H), 7.96(d, J = 8, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ : 29.56, 34.56, 68.62, 113.67, 116.49, 119.52, 123.15, 128.52, 134.25, 137.46, 143.85, 149.33. Anal.Calcd. for $\text{C}_{23}\text{O}_2\text{N}_3\text{H}_{27}\text{S}$: C, 64.45; H, 6.63; N, 10.26; S, 7.83. Found: C, 64.66; H, 6.41; N, 9.73; S, 7.57. MS m/z ($\text{C}_{23}\text{O}_2\text{N}_3\text{H}_{27}\text{S}$, 409) 409 (M^+).

4.5.6. 2,2'-(((ethan-1,2-diylbis(sulfanediyl))bis(ethan-2,1-diyl))bis(oxy))dianiline (6f). 65% yield, yellow oil, FT-IR: (KBr, cm^{-1}) ν_{max} : 3444 and 3356 (NH_2), 1273 and 1012 (CO). Anal.Calcd. for $\text{C}_{18}\text{O}_2\text{N}_2\text{H}_{24}\text{S}_2$: C, 59.31; H, 6.63; N, 7.68; S, 17.59. Found: C, 59.34; H, 6.61; N, 7.65; S, 17.6. MS m/z ($\text{C}_{18}\text{O}_2\text{N}_2\text{H}_{24}\text{S}_2$, 364) 364 (M^+).

5. Conclusion

In conclusion, we have introduced very novel and efficient procedure for preparation of various hosts with diverse affinity towards the metal ions. In addition, we offer a simple and versatile synthetic strategy to protection amino phenols. This method has advantages such as using water as green solvent, high yield, and neutral reaction condition.

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