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Synthesis of Thia-calix[4]arene Hydroxamic Acids by Microwave Irradiation

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Abstract: Thia-calix[4]arene hydroxamic acids have been synthesized by partial reduction of nitro-thia-calix[4]arenes with hydrazine hydrate, Rn/Ni, and their coupling with benzoyl chloride under the influence of microwave irradiation with 90–95% yield and 3–6 min reaction time.

Keywords: Microwave irradiation; thia-calix[4]arene

INTRODUCTION

Thiacalixarenes are a new class of calixarene with sulfur atoms[1] in place of the usual methylene. Their chemical modification leads to a great variety of derivatives with modified solubility, conformational mobility, and complexing abilities. These compounds have emerging applications as sensors,[2] catalysts,[3] stationary phases for gas chromatography,[4] chelating adsorbents for heavy metal ions,[5] highly selective means for the luminescence determination of terbium,[6] and components in the construction of ionsensors.[7] In recent decades, microwave technology has taken an important place in chemical laboratory practice as a very effective, nonpolluting method for activating reactions. The use of microwaves provide fast heating of the chemicals, thus enhancing reaction rates and significantly shortening preparation time.[8]

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Herein, we report microwave-irradiated synthesis of thia-calix[4]-arene, biphenylthia-calix[4]arene, and their nitro and hydroxamic acid derivatives for the first time.

p-tert-Butylthiacalix[4]arene **(3)** is conveniently synthesized using *p-tert*-butylphenol **(1)**, elemental sulfur S_8 **(2)**, and NaOH in tetraethylene glycol dimethyl ether (TEGDME).[9] As nitration of *p-tert*-butylthiacalix[4]arene cannot be carried out by reaction conditions normally used in classical calixarene chemistry, which lead to only the oxidation of the bridging sulphur atoms.[10] we have synthesized it using $KNO_3/AlCl_3$ in the presence of TEGDME[11] followed by de-*t*-butylation[12] to get compound **(5)**, which is partially reduced to obtain the corresponding hydroxylamine **(6)**, whose condensation with benzoyl chloride yields thiacalix[4]arene hydroxamic acid (TC4HA)[13] **(7)** (Fig. 1).

Thia-biphenylcalix[4]arene **(9)** has been synthesized by 9 h of reflux of biphenyl-4-ol, S_8. diphenylether (DPE), and NaOH,[14] which is nitrated with $KNO_3/AlCl_3$ in the presence of TEGDME to obtain compound **10**. Compound **10** is partially reduced with hydrazin hydrate in the presence of Raney Ni (W-4) to give the corresponding hydroxylamine **(11)**. Compound **11** is reacted with benzoyl chloride, which gives thiabiphenyl-calix[4]arene hydroxamic acid (TBPC4HA) **(12)** (Fig. 2).

Compound **16** has been synthesized to investigate how its ion extraction properties changed compared to methylene-bridged calixcrowns. Compound **9** was refluxed in the presence of ditosylate of tetraethyleneglycol, K_2CO_3, and CH_3CN for 3 days to obtain thiacalix[4]monocrown[15] **(13)**, whose nitration with $KNO_3/AlCl_3$ in the presence of TEGDME gives compound **14**, which is partially reduced with Raney Ni and hydyrazin hydrate to the corresponding hydroxylamine **(15)**. Further, compound **15** is condensed with benzoyl chloride to form thiabiphenyl-calix[4]monocrown hydroxamic acid (TBPC4MCHA) **(16)** (Fig. 3).

These conventional syntheses have three major disadvantages: longer reaction time, large amount of solvents (which is not eco friendly), and very poor yield. To overcome these, we have developed a synthesis under microwave irradiation in the absence of solvent. The reaction time is 3–6 min with 90% to 95% yield depending on the compounds to be synthesized.

The structural identification and composition of newly synthesized thia-calix[4]arene hydroxamic acids (TCHAs) have been confirmed by Fourier transform infrared spectrometer (FT-IR), ^{1}H NMR, ^{13}C NMR, and C, H, N analysis.

The FT-IR (KBr) spectrum of compounds **7, 12**, and **16** displayed three sharp bands at 920, 1600, and 3300 cm^{-1}. The band at 3300 cm^{-1} is due to O-H stretching vibration. It is known that O-H stretching vibration bands occur at around 3600 cm^{-1}, but this band shifts to lower frequencies because hydrogen bonding. Particularly in hydroxamic acids, the $-$OH group is

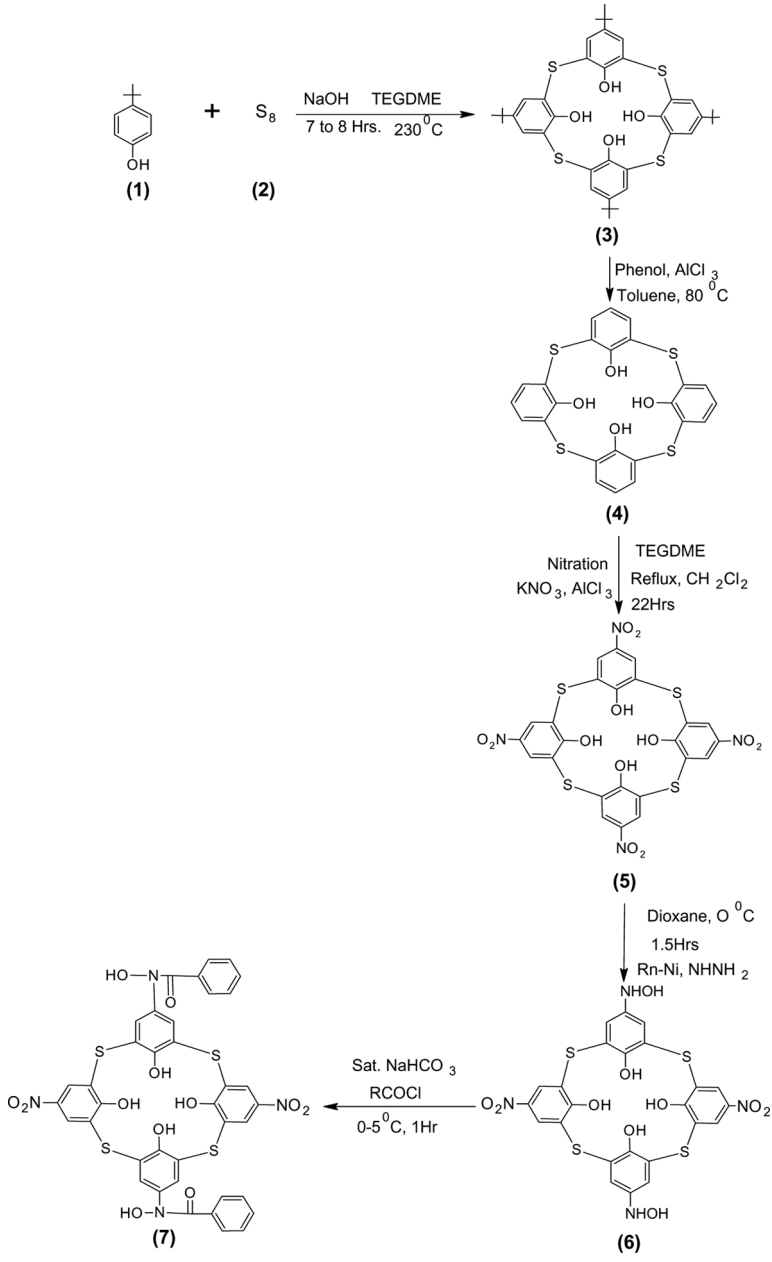

Figure 1. Synthetic scheme for compound **7**.

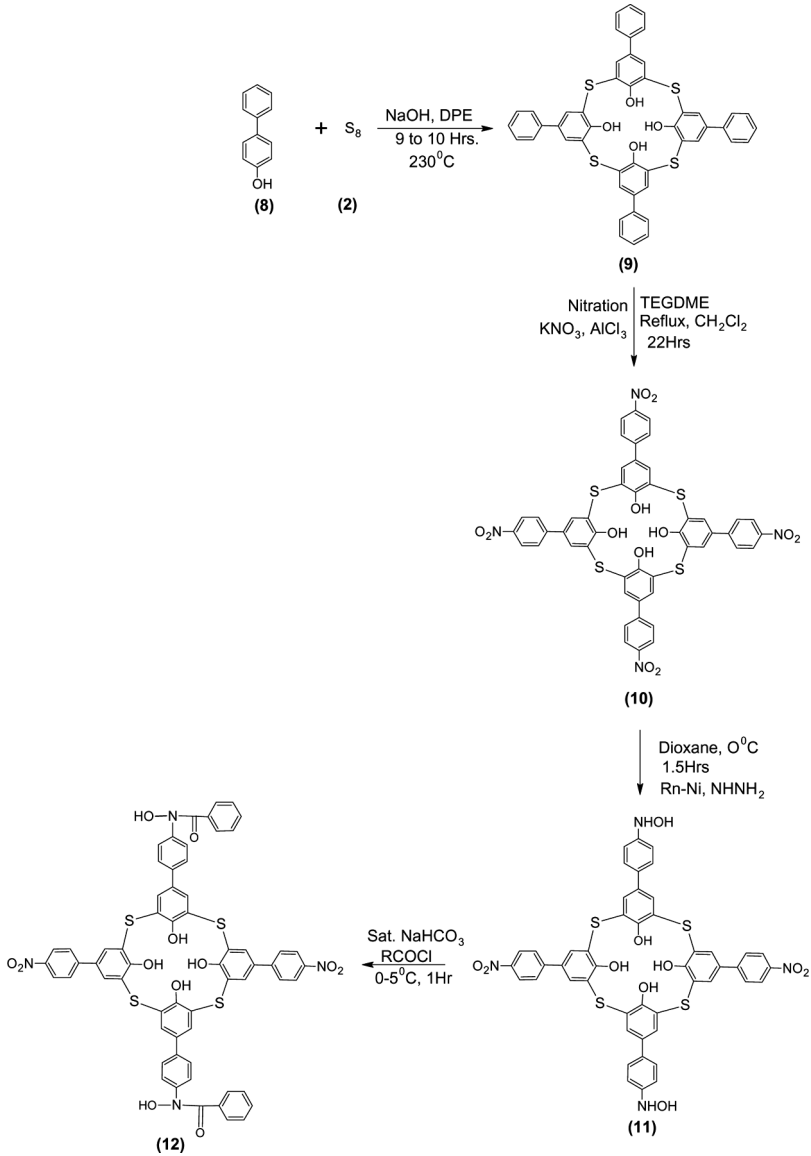

Figure 2. Synthetic scheme for compound **12**.

placed very close to the polar carbonyl C=O group. The band at 1600 cm^{-1} is assigned to the C=O of the hydroxamic acid group. The position of the C=O stretching band is highly influenced by the surrounding groups and mostly shifted to lower frequencies. Thus hydrogen bonding again lowers the

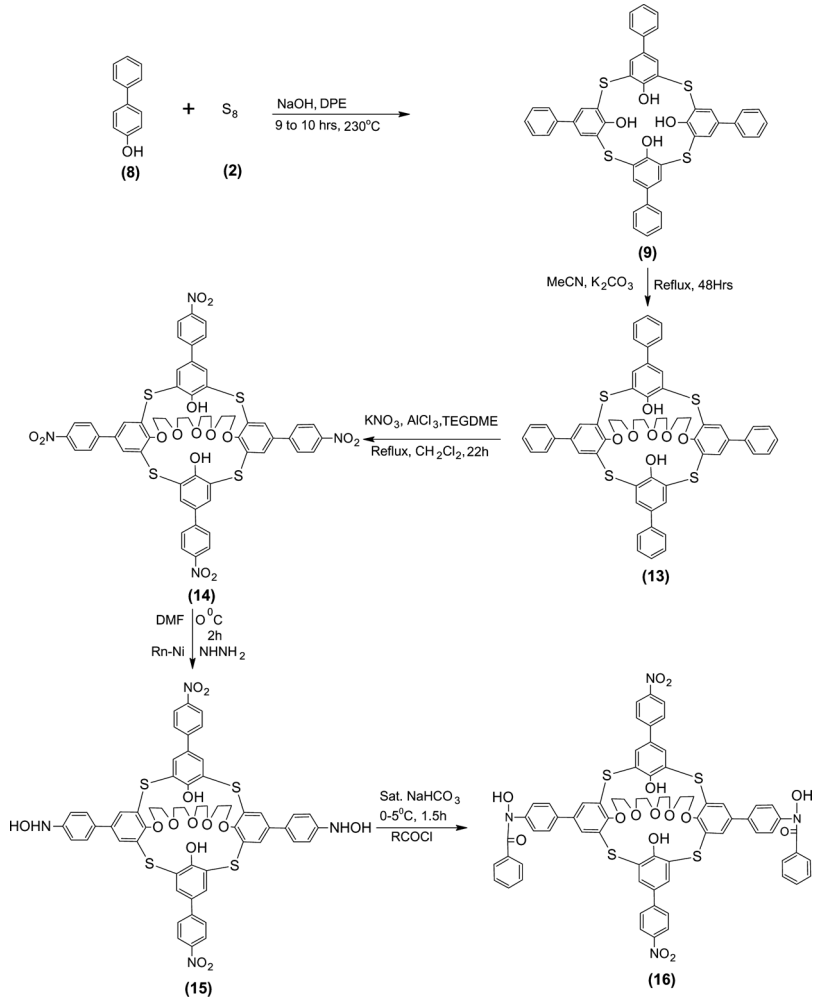

Figure 3. Synthetic scheme for compound **16**.

frequencies. N-O stretching gives a sharp band at 920 cm^{-1}. In addition, compounds **7, 12**, and **16** give sharp bands at 680 cm^{-1} for C-S stretching vibrations and a band at 1370 cm^{-1} for NO_2 stretching vibrations.

The ^1H NMR dimethyl sulfoxide (DMSO) spectrum of compounds **7, 12**, and **16** shows five singlets at 7.0–7.5 ppm for aromatic protons, 8.05 and 8.3 ppm for hydroxyl groups, and 8.5 ppm for hydroxamic acid groups. In addition, compound **7** shows a singlet at 10.0 ppm for the hydroxyl group. Compound **12** displayed multiples at 8.0 ppm for

aromatic hydrogens, and compound **16** shows a singlet at 3.01 ppm for methylene of crown ether.

The ^{13}C NMR (DMSO) spectrum of compounds **7, 12**, and **16** displayed singlets at 120–130 and 140–160 ppm for aromatic carbons and a singlet at 165–175 ppm for ketone groups. Compound **7** shows a singlet at 167.69 for the CO-N(OH) group. Compound **12** shows a singlet at 146.6 ppm for the CH-N group, and compound **16** shows a triplet at 73.8 ppm for methylene of crown moieties.

The presence of a hydroxamic acid group is proved by the results obtained and also from elemental analysis carried out in our laboratory.

EXPERIMENTAL

Melting points were uncorrected. FT-IR spectra were recorded on Jasco FT-IR 6100 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II spectrometer operating at 400 MHz in dimethyl sulfoxide (DMSO) with trimethyl selane (TMS) as an internal standard. An elemental analysis has been carried out in the analytical laboratory of the institute. The de-*tert*-butylation and nitration of *P*-*tert*-butyl thiacalix[4]arene have been carried out according to reported procedures. Moreover, biphenyl thiacalix[4]arene monocrown and biphenyl thia-calix[4]arene were also prepared from reported procedures.

Synthesis of Compound 3

Conventional Method

A mixture of *t*-butyl phenol (20.0 g, 0.1333 M), elemental sulfur S_8 (8.848 g, 0.2765 M), and TEGDME (6 ml) was stirred under inert nitrogen to remove the evolving H_2S gas. Solid NaOH (2.64 g, 0.0660 M) was added to this yellow solution, and the mixture was maintained for 2 h at a temperature of 145–145 °C. During this time, the reaction mixture changed from yellowish to red and finally to almost a black color. The temperature was elevated to 170 °C over the next 30 min and maintained at 170 °C–180 °C for another 2 h. The reaction mixture was warmed up to 230 °C over 1 h and maintained at this temperature for a further 3 h. During this time, the reaction mixture is converted to a black slurry. It was cooled to room temperature, diluted with $CHCl_3$, and acidified by 2 M HCl. The organic fraction was collected and washed with water, and chloroform was removed in a rotary evaporator. We got a liquid light-brown color residue. The final off-white compound **7** is obtained by stirring this residue overnight in ethyl acetate (100 ml). Mp: 318 °C.

Microwave-Assisted Method

We took a mixture of *t*-butylphenol (2.0 g, 0.01333 M), elemental sulfur S_8 (0.8848 g, 0.02765 M), and TEGDME (1 ml) in a 50-ml beaker and placed it in a microwave oven for 1 min at 60% output. Then we added NaOH (0.264 g, 0.0066 M) and again put it in the oven for 2 min at 60% output to get a blackish slurry. We added 20 ml of chloroform and 2 M HCl, separated the organic layer, and allowed it to concentrate. Stirring it in ethyl acetate gave an off-white compound **7**. Mp: 318 °C.

Synthesis of Compound 5

Conventional Method

TEGDME (6.0 ml, 0.0269 M) and KNO_3 (2.5 g, 0.0247 M) were added to a suspension of tetrahydroxythiacalix[4]arene (2.0 g, 0.0040 M) in CH_2Cl_2 (50 ml). This reaction mixture was stirred for 15 to 20 min at room temperature then cooled to 0 °C. $AlCl_3$ (3.0 g, 22.5 M) was added to this suspension. Slowly, a colorless mixture became orange; we refluxed it for another 22 h. We cooled the mixture at room temperature and added distilled water (50–70 ml) to hydrolyze it. The organic layer was further washed with water until it attained neutral pH; we separated it from aqueous media, dried it over Na_2SO_4, and evaporated the organic layer in a rotary evaporator to get slurry, from which compound **5** was precipitated out with diethyl ether in 60% yield. Mp: 260–262 °C.

Microwave-Assisted Method

Tetrahydroxythiacalix[4]arene (2.0 g, 0.0040 M) was added to a suspension of TEGDME (6.0 ml, 0.0269 M) and KNO_3 (2.5 g, 0.0247 M) in a 50-ml beaker. It was heated at 60% output for 1.5 min and cooled to 0 °C, then $AlCl_3$ (3.0 g, 0.0225 M) was added. The mixture was heated 2 min at 60% output to obtain a brown solution. Upon isolation of it from diethylether, we got a yellowish compound **5** at 90% of yield. Mp: 260–262 °C.

Synthesis of Compound 7

Conventional Method

In a 250-ml flat- bottomed flask equipped with magnetic stirrer, we added nitro-thiacalix[4]arene (1.2 g, 0.00177 M) in 15 ml of dioxane and Rn-Ni (0.6–0.8 g), then cooled the mixture to 0 °C. $NHNH_2$(1.0 ml, 0.0196 M) was added dropwise at 0 °C over 30 min. It was stirred for more 1 h then

filtered to give a hydroxyl amine. This solution in situ was used for hydroxamic acid preparation. It was kept below 0 °C and benzoyl chloride (0.5 ml, 0.00427 M) was added. The temperature of 0 °C was maintained. An aqueous suspension of sodium carbonate was added and stired for more 30 min while it warmed to room temperature. After filtering the solids, we obtained 0.80 g of cream-colored compound, thiacalil-x[4]arene hydroxamic acid. Mp: 110–115 °C.

Microwave-Assisted Method

Nitro-thiacalix[4]arene (1.2 g, 0.00177 M), Rn-Ni (0.6–0.8 g), and $NHNH_2$ (1.0 ml, 0.0196 M) were placed in a domestic Kenstar microwave oven at 0% output for 3.5 min to obtain hydroxyl amine, which was in situ condensed with benzoyl chloride (0.5 ml, 0.00427 M) in the presence of an aqueous suspension of Na_2CO_3 in the oven at 0% output for 2 min to obtain compound **7** with 89% yield. Mp: 110–115 °C.

Data

TC4HA (**3**): Yield 89%, mp 110–115 °C, IR (KBr): $\nu = 3300\,cm^{-1}$ (OH), $1600\,cm^{-1}$ (C=O), $1370\,cm^{-1}$ (-NO_2-), $680\,cm^{-1}$ (C-S). ^1H NMR (DMSO, δ): 10 (s, 4H, OH), 7.57 (m, Ar-H, 8H, $J = 6.84$), 8.05 (t, N-OH, 2H). ^{13}C NMR (DMSO, δ): 127.3 (s, 4C, Ar-S-Ar), 130 (t, Ar-H), 132.2 (m, 2C, ArC-NO_2), 167 (s, 2C, C=O). Anal. calcd. for $C_{38}H_{24}N_4O_{12}S_4$: C, 53.26; H, 2.82; N, 6.54; S, 14.97. Found: C, 53.25; H, 2.83; N, 6.57; S, 14.94.

Synthesis of Compound 9

Conventional Method

A mixture of biphenyl-4-ol (10 g, 0.0588 M), elemental sulfur S_8 (3.64 g, 0.1139 M), and diphenyl ether (8 ml) was stirred under N_2 to remove evolving H_2S gas. Solid NaOH (1.143 g, 0.0285 M) was added to this yellowish solution, and the mixture was maintained for 2 h at 145–145 °C. During this time, the reaction mixture changed from yellowish to red and finally to almost a black color. Temperature was elevated to 170 °C over the next 30 min and maintained at 170–180 °C for another 2 h. The reaction mixture was then warmed up to 230 °C over 1 h and maintained at this temperature for a further 3 h. During this time, the reaction mixture became thick, and a precipitate appeared, accompanied by color change from black to red to yellow.

The reaction mixture was cooled to room temperature, diluted with chloroform, and acidified by HCl. The organic fraction was collected and washed with water, and chloroform was removed in a rotary evaporator. We got a liquid light-brown residue. To this, ethyl acetate (100 ml) was added, and the mixture was stirred overnight. The precipitate was filtered to give compound **9** as a final product (almost 2.20 g). Mp: $>350\,^{\circ}C$.

Microwave-Assisted Method

A mixture of biphenyl-4-ol (1.0 g, 0.0588 M), elemental sulfur S_8 (3.64 g, 0.1139 M), and DPE (1 ml) in a 50-ml beaker was placed in a microwave oven for 1 min at 60% output. NaOH (1.143 g, 0.0285 M) was added, and the mixture was put in the oven for a further 2 min at 60% output. We got blackish slurry. Chloroform (20 ml) and 2 M HCl were added. The organic layer was separated and allowed it to concentrate. After stirring in ethylacetate, we obtained compound **9**. Mp: $>350\,^{\circ}C$.

Synthesis of Compound 10

Conventional Method

TEGDME (3.7 ml, 0.0165 M) and KNO_3 (1.54 g, 0.0152 M) were added to a suspension of biphenylthia-calix[4]arene (BPTC) (2.0 g, 0.0024 M) in CH_2Cl_2 (50 ml). This reaction mixture was stirred for 15 to 20 min at room temperature, then cooled to $0\,^{\circ}C$. $AlCl_3$ (1.85 g, 0.0138 M) was added to the suspension. Slowly the colorless mixture became orange; it was refluxed for 22 h. This mixture cooled to room temperature, and distilled water (50–70 ml) was added to hydrolyze it. The organic layer was further washed with water until it attained neutral pH then separated from the aqueous media and dried over Na_2SO_4. The organic layer was evaporated in a rotary evaporator to get slurry, from which product **10** was precipitated out with diethyl ether in 65% yield.

Microwave-Assisted Method

BPTC (2.0 g, 0.0024 M) was added to a suspension of TEGDME (3.7 ml, 0.0165 M) and KNO_3 (1.54 g, 0.0152 M) in a 50-ml beaker. This mixture was heated at 60% output for 1.5 min, then cooled to $0\,^{\circ}C$. $AlCl_3$ (1.85 g, 0.0138 M) was added heated up to 2 min at 60% output. We got a brown solution. Upon isolation of it from diethyl ether, we got a yellowish compound **10** at 90–95% yield.

Synthesis of Compound 12

Conventional Method

In a 250-ml flat-bottomed flask equipped with magnetic stirrer, nitro-BPTC (1.0 g, 0.0010 M) in 15 ml of dioxane and Rn-Ni (0.8–1.0 g) were added and cooled to 0 °C. Then $NHNH_2$ (0.7 ml, 0.0137 M) was added dropwise at 0 °C order 30 min. It was stirred for more than 1 h, then filtered to get a hydroxyl amine. This solution in situ is used for hydroxamic acid preparation. Again we brought the temperature of this solution below 0 °C and added benzoyl chloride (0.3 ml, 0.0025 M). It was stirred for 30 min and allowed it to warm to room temperature. After filtering the solids, we got 0.60 g of yellow-colored compound **12**.

Microwave-Assisted Method

Nitro-BPTC (1.0 g, 0.0010 M), Rn-Ni (0.8–1 g), and $NHNH_2$ (0.7 ml, 0.0137 M) were placed in a domestic Kenstar microwave oven at 0% output for 3.5 min. The hydroxyl amine was condensed with benzoyl chloride (0.3 ml, 0.0025 M) in the presence of an aqueous suspension of sodium carbonate in the oven at 0% output for 3 min to obtain compound **12** in 91% yield.

Data

BPTC4HA (**12**): Yield 91%, mp 220–225 °C, IR (KBr): $\nu = 3300\,cm^{-1}$ (OH), $1600\,cm^{-1}$ (C=O), $1370\,cm^{-1}$ (-NO_2-), $680\,cm^{-1}$ (C-S). ^1H NMR (DMSO, δ): 9.66 (s, 4H, OH), 7.99 (m, Ar-H, 8H, $J = 4$), 7.65 (m, Ar-H, 20H), 8.0 (t, N-OH, 2H). ^{13}C NMR (DMSO, δ): 127.3 (s, 4 C, Ar-S-Ar), 130 (t, Ar-H), 132.2 (m, 2 C, ArC-NO_2), 167 (s, 2C, C=O). Anal. calcd. for $C_{62}H_{40}N_4O_{12}S_4$: C, 64.13; H, 3.47; N, 4.82; S, 11.05. Found: C, 64.13; H, 3.45; N, 4.83; S, 11.06.

Synthesis of Compound 14

Conventional Method

TEGDME (3.097 ml, 0.0138 M) and KNO_3 (1.28 g, 0.01273 M) were added to the suspension of TBPCMC (2.0 g, 0.0020 M) in CH_2Cl_2 (50 ml). This reaction mixture was stirred for 15 to 20 min at room temperature then cooled to 0 °C. $AlCl_3$ (1.54 g, 0.0116 M) was added to the

suspension. Slowly, a colorless mixture became orange. It was refluxed for 22 h and allowed to cool to room temperature. Distilled water (50–70 ml) was added to hydrolyze it. The organic layer was further washed with water until it attained neutral pH, separated from the aqueous media, and dried over Na_2SO_4. The organic layer was evaporated in a rotary evaporator to get a slurry, from which product **14** was precipitated out with diethyl ether in 60% yield.

Microwave-Assisted Method

BPTCMC (2.0 g, 0.0020 M) was added to a suspension of TEGDME (3.097 ml, 0.0138 M) and KNO_3 (1.28 g, 0.0127 M) in a 50-ml beaker and heated at 60% output for 1.5 min then cooled to 0°C. $AlCl_3$ (1.54 g, 0.0116 M) was added, and the mixture was heated up to 2 min at 60% output to get a brown solution. Upon isolation of it from diethyl ether, we got compound **14** in 92% yield.

Synthesis of Compound 16

Conventional Method

In a 250-ml flat-bottomed flask equipped with magnetic stirrer, nitro-BPTCMC (1.0 g, 0.0008 M) in 15 ml of dioxane and Rn-Ni (0.8–1.0 g) were added and cooled to 0 °C. Then $NHNH_2$ (0.60 ml, 0.012 M) was added dropwise at 0 °C over 30 min and stirred for more 1 h. The solution was filtered to get a hydroxyl amine. This solution in situ was used for hydroxamic acid preparation: again the solution was cooled below 0 °C, and benzoyl chloride (0.2 ml, 0.0017 M) was added. It was stirred for more than 30 min, then allowed to attain room temperature. After filtering the solids, we got 0.62 g of yellow-colored compound **16**.

Microwave-Assisted Method

Nitro-BPTCMC (1.0 g, 0.0008 M), Rn-Ni (0.8–1 g), and $NHNH_2$ (0.60 ml, 0.012 M) were placed in a domestic Kenstar microwave oven at 0% output for 3.5 min. The hydroxyl amine was condensed with benzoyl chloride (0.2 ml, 0.00170 M) in the presence of an aqueous suspension of sodium carbonate in an oven at 0% output for 3 min to obtain compound **16** in 90% yield.

Data

BPTCMC4HA (**16**): Yield 90%, mp > 300 °C, IR (KBr): $\nu = 3300\,cm^{-1}$ (OH), $1600\,cm^{-1}$ (C=O), $1370\,cm^{-1}$ (-NO_2-), $680\,cm^{-1}$ (C-S). ^1H NMR (DMSO, δ): 7.34 (s, Ar-H, 8H, $J = 8.9$), 8.3 (t, N-OH, 2H), 3.010 (t, -O$\underline{CH_2}$-, 8H). ^{13}C NMR (DMSO, δ): 73.8 (t, 8C, -O$\underline{CH_2}$-), 125.5 (s, 4C, Ar-S-Ar), 133 (m, 2C, ArC-NO_2), 170 (s, 2C, C=O). Anal. calcd. for $C_{70}H_{54}N_4O_{15}S_4$: C, 63.72; H, 4.13; N, 4.25; S, 9.72. Found: C, 63.75; H. 4.12; N, 4.22; S, 9.71.

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