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FACILE SYNTHESES OF HOMOTHIACALIXARENES

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Abstract: Homothiacalixarenes were conveniently prepared from the reactions of bis(chloromethyl)phenol-formaldehyde trimers with alkanedithiols in good yields.

Calixarenes have attracted much interest as potential host compounds, because of their easy modification and their large variety.[1,2] Most derivatives of calixarenes are obtained by attaching functional groups to the phenol units. In contrast, our interest was focussed on the modification of methylene moiety of calixarenes, which were built up by changing the methylene unit to other group such as carbonyl, sulfur, and amino acids.[3]

Recently, Miyano et al. reported a convenient and easy synthesis of tetrathiacalix[4]arene in a satisfactory yield by simply heating a phenol with elemental sulfur in the presence of a base.[4] After this useful synthetic method of

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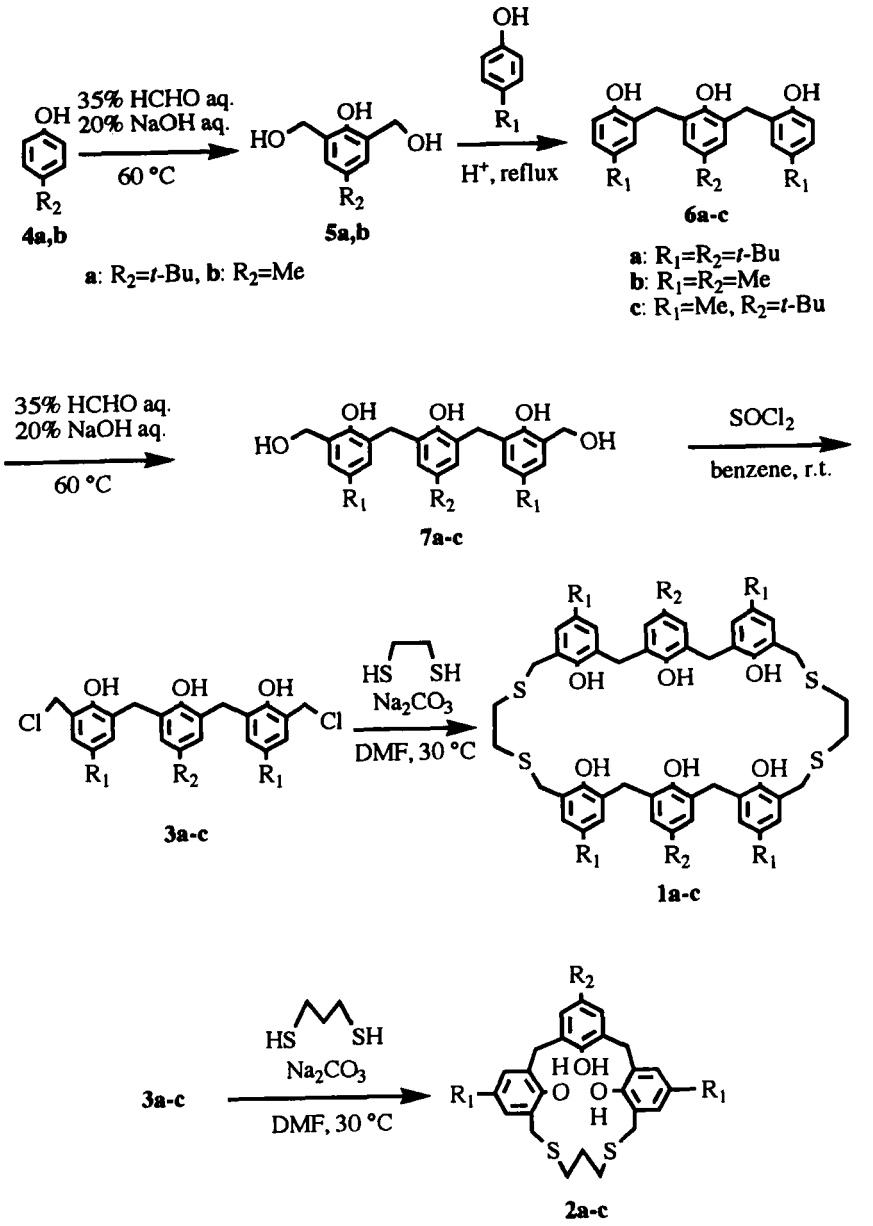
thiacalix[4]arene was reported, the increasing interest in the development of thiacalix[4]arenes is certainly due to the unique properties of sulfur atom in the macrocyclic ring.[5-10]

This situation inspired us to synthesize calixarene analogs containing sulfur atom into the macrocyclic ring.[11] Accordingly, we investigated the syntheses of homothiacalixarenes through the reactions of bis(chloromethyl)phenol-formaldehyde oligomers with alkanedithiols, and found the facile formation of decahomotetrathiacalix[6]arenes and hexahomodithiacalix[3]arenes in good yields. We now report the results.

Decahomotetrathiacalix[6]arenes (**1**) were synthesized from the 2:2 cyclization reactions of 1,2-ethanedithiol and bis(chloromethyl)-*p*-substituted phenol-formaldehyde trimers (**3**). Hydroxymethylation of *p*-substituted phenol with 35% formalin in the presence of base as a catalyst led to the bis(hydroxymethyl)phenols (**5**) in high yield. Condensation of **5** with excess of *p*-cresol or *p-tert*-butylphenol in the presence of acid as a catalyst gave the trimers (**6**) in good yields. Trimers (**6**) were hydroxymethylated again, followed by chlorination of the resulting alcohols (**7**) by thionyl chloride to yield **3** in high yields. The reaction of **3a** with 1,2-ethanedithiol in the presence of sodium carbonate in dry DMF at 30 ℃ under a nitrogen atmosphere gave **1a** in 90 % yield. The similar reactions using **3b** and **3c** gave the corresponding products (**1b** and **1c**) in 77 and 89 % yields, respectively. In contrast, the reactions using the corresponding bis(chloromethyl)-*p-tert*-butylphenol-formaldehyde monomer, dimer, and tetramer, which were prepared from the similar method as mentioned above, did not give any macrocyclic compound except polymeric materials. Reactions of **3a-3c** with 1,3-propanedithiol instead of 1,2-ethanedithiol gave 1:1 macrocycles (**2a-2c**), hexahomodithiacalix[3]arenes, in 73, 56, and 43 % yields, respectively. In this case, we did not obtain the corresponding 2:2 macrocycles.



Scheme 1

The strcuture of the macrocycles (**1** and **2**) was established on the bases of their NMR, IR, and mass spectra, and elemental analyses. The OH proton signals of **1** and **2** in the ^{1}H NMR spectra appear at the range of δ 8.4 - 8.8 ppm, indicating the existence of the intramolecular hydrogen bonding. In the variable temperature ^{1}H NMR spectra of the macrocycles, the signals of the methylene protons of the $ArCH_2Ar$ were observed as singlets at ambient temperature, and did not split at -60 °C in $CDCl_3$, indicating conformational flexibility of **1** and **2**. The methylene carbons of $ArCH_2Ar$ of the macrocycles (**1** and **2**) were observed at δ 31.3-31.6 ppm, suggesting that the adjacent phenol rings preferred to adopt *syn* orientation.[12,13] Therefore, major conformers of **1** and **2** are considered to be *syn*-cone/cone or *anti*-cone/cone like conformation[14] in **1** and cone like form in **2**.

In conclusion, we found facile syntheses of homothiacalixarenes through the cyclization reactions between bis(chloromethyl)phenol-formaldehyde trimers and alkanedithiols, and elucidated that the length of alkyl chain of alkanedithiols and the number of phenol units of phenol-formaldehyde oligomers play an important role in the formation of the macrocycles.

EXPERIMENTAL

All of the melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on Varian Mercury 200 or Varian INOVA 500 spectrophotometer using tetramethyl silane as an internal standard. IR spectra were taken on HORIBA FT-200 spectrophotometer. FAB-MS (*m*-nitrobenzylalcohol as a matrix) and EI-MS (70 eV) spectra were collected by JEOL JMS AX-505HA spectrometer. **3a**, m.p. 115-116 °C (lit. 115-116 °C)[15], **5a**, m.p. 66-69 °C (lit. 74.5 °C)[16], **5b**, m.p. 130-130.5 °C (lit. 133-134 °C)[17], **6a**, m.p. 220-221 °C (lit. 221-222 °C)[18], **6b**, m.p. 214-215 °C (lit. 215 °C)[19], **7a**, m.p. 140-145 ° C (lit. 143-145 °C)[20], **7b**, m.p. >300 °C (lit. >300 °C)[21] were prepared by reported methods in literatures.

Preparation of 2-[3-(5-methylsalicyl)-5-*tert*-butylsalicyl]-4-methylphenol (**6c**).

A mixture of *p*-cresol (8.86g, 82 mmol), **5a** (1.72 g, 8.2 mmol), *p*-toluenesulfonic acid (50 mg, 0.26 mmol) in benzene (50 ml) was refluxed for 2 h. Removal of excess *p*-cresol by steam distillation gave white powder, which was recrystallized from benzene to give **6c** (2.01g, 63 %) as colorless crystals. m.p. 231-232 °C (from benzene), ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 9H, *t*-Bu), 2.23 (s, 6H, CH_3 x 2), 3.85 (s, 4H, $ArCH_2Ar$ x 2), 6.68 (d, 2H, Ar-H x 2, J=8.0Hz), 6.87 (dd, 2H, Ar-H x 2, J=2.2, 8.0Hz), 7.06 (d, 2H, Ar-H x 2, J=2.2Hz), 7.16 (s, 2H, Ar-H x 2); ^{13}C NMR ($CDCl_3$): δ 19.3, 29.9, 30.5, 32.7, 114.1, 124.4, 125.8, 126.0, 126.5, 127.6, 127.6, 129.7, 141.3, 148.3, 150.4; MS (m/z), 390 (M^+). Anal. Calcd for $C_{26}H_{30}O_3$: C, 79.97; H, 7.74. Found: C, 80.02; H, 7.70.

Preparation of 3-[3-[3-(hydroxymethyl)-5-methylsalicyl]-5-*tert*-butylsalicyl]-2-hydroxy- 5-methylbenzyl alcohol (**7c**). To a mixture of **6c** (1.0 g, 2.6 mmol), 25 % potassium hydroxide aqueous solution (5 ml), and 1,4-dioxane (5 ml) was added 35 % formalin (20 ml, 230 mmol) at 0 °C over 30 min. After the addition was complete, the mixture was allowed to stir at 60 °C for 20 h. After cooling to room temperature, the mixture was acidified by 10 % HCl aqueous solution to give white precipitates, which were collected by filtration, and then dissolved with chloroform. The solution was washed with water three times and dried over anhydrous sodium sulfate. Removal of chloroform gave colorless oily residue, which was subjected to column chromatography on silica gel using hexane : ethyl acetate 2:1 as an eluent to give **7c** (0.6 g, 53 %) as colorless crystals, m.p. 144-146 °C (from ethyl acetate-hexane), ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, *t*-Bu), 2.19 (s, 6H, CH_3 x 2), 3.85 (s, 4H, $ArCH_2Ar$ x 2), 4.68 (s, 4H, $ArCH_2OH$ x 2), 6.66 (d, 2H, Ar-H x 2, J=2.0Hz), 6.98 (d, 2H, Ar-H x 2, J=2.0Hz), 7.13 (s, 2H, Ar-H x 2); ^{13}C NMR ($CDCl_3$): δ 20.4, 31.4, 31.5, 34.0, 63.7, 125.5, 125.9, 127.0, 127.1, 127.7,

129.7, 130.5, 144.1, 147.4, 149.9; MS (FAB, m/z), 451 $(M+H)^+$. Anal. Calcd for $C_{28}H_{34}O_5$: C, 74.64; H, 7.61. Found: C, 74.88; H, 7.72.

General procedure of the preparation of bis(chloromethyl)phenol-formaldehyde trimers (**3**). To a solution of **7** (1.1 mmol) in dry benzene (10 ml) was added a solution of thionyl chloride (1.0 g, 8 mmol) in dry benzene (10 ml) over 30 min. After the addition was complete, the mixture was allowed to stir at room temperature for 3 h. Removal of benzene and excess thionyl chloride below 25 °C under a reduced pressure gave **3** as colorless powder, which was recrystallized from benzene to give pure crystals.

2-[3-[3-(Chloromethyl)-5-methylsalicyl]-5-methylsalicyl]-6-(chloromethyl)-4-methylphenol (**3b**). The yield of **3b** was 95 % as colorless crystals, m.p. 110-111 °C (from benzene), ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 3H, CH_3), 2.24 (s, 6H, CH_3 x 2), 3.84 (s, 4H, $ArCH_2Ar$ x 2), 4.62 (s, 4H, CH_2Cl x 2), 6.92 (d, 2H, Ar-H x 2, J=2.0Hz), 6.94 (s, 2H, Ar-H x 2), 7.07 (d, 2H, Ar-H x 2, J=2.0Hz) 7.12 (br s, 2H, OH x 2), 8.00 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 31.2, 43.2, 123.9, 127.1, 128.0, 128.3, 129.0, 129.2, 129.7, 132.1, 147.3, 149.3; MS (FAB, m/z), 445 $(M+H)^+$. Anal. Calcd for $C_{25}H_{26}Cl_2O_3$: C, 67.42; H, 5.88. Found: C, 67.44; H, 5.99.

2-[3-[3-(Chloromethyl)-5-methylsalicyl]-5-*tert*-butylsalicyl]-6-(chloromethyl)-4-methylphenol (**3c**). The yield of **3c** was 90 % as colorless crystals, m.p. 134 ° C (decomp.) (from benzene), ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, *t*-Bu), 2.19 (s, 6H, CH_3 x 2), 3.85 (s, 4H, $ArCH_2Ar$ x 2), 4.67 (s, 4H, $ArCH_2Cl$ x 2), 6.65 (d, 2H, Ar-H x 2, J=2.2 Hz), 6.98 (d, 2H, Ar-H x 2, J=2.2 Hz), 7.13 (s, 2H, Ar-H x 2); ^{13}C NMR ($CDCl_3$): δ 20.4, 30.5, 31.6, 34.1, 43.2, 123.9, 126.2, 126.6, 128.0, 129.2, 130.7, 132.1, 144.5, 147.4, 149.4; MS (FAB, m/z), 487 $(M+H)^+$. Anal. Calcd for $C_{28}H_{32}Cl_2O_3$: C, 68.99; H, 6.62. Found: C, 68.88; H, 6.82.

General procedure for the preparation of decahomotetrathiacalix[6]arenes (**1**).

To a suspension of sodium carbonate (212 mg, 2.0 mmol) in dry DMF (5 ml) were added a solution of bis(chloromethyl)phenol-formaldehyde trimer (**3**) (0.5 mmol) in dry DMF (5 ml) and a solution of 1,2-ethanedithiol (47 mg, 0.5 mmol) in DMF (5 ml) over 1 h. After the addition was complete, the mixture was allowed to stir at 30 °C for 2h. Removal of solvent under a reduced pressure gave pale yellow oily residue, which was subjected to column chromatography on silica gel using hexane : ethyl acetate, 4 : 1 as an eluent to give **1** as white powder.

5,11,22,28,34,45-Hexa-*tert*-butyl-15,18,38,41-tetrathiaheptacyclo[41.3.1.1^{3,7}.1^{9,13}.1^{20,24}.1^{26,30}.1^{32,36}]dopentaconta-1(46),3(48),4,6,9(49),10,12,20(50),21,23,25(51),27,29,32(52),33,35,43(47),44-octadecaene-47,48,49,50,51,52-hexaol (**1a**), m.p. 105-110 °C (from dichloromethane-hexane), ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 36H, *t*-Bu x 4), 1.29 (s, 18H, *t*-Bu x 2), 2.82 (s, 8H, SCH_2 x 4), 3.79 (s, 8H, $ArCH_2S$ x 4), 3.87 (s, 8H, $ArCH_2Ar$ x 4), 6.85 (d, 4H, Ar-H x 4, J= 2.4Hz), 7.17 (s, 4H, Ar-H x 4), 7.19 (d, 4H, Ar-H x 4, J=2.4 Hz), 8.77 (bs, 6H, OH x 6); ^{13}C NMR ($CDCl_3$): δ 31.3, 31.4, 31.6, 32.5, 33.9, 34.2, 123.8, 125.4, 125.9, 126.6, 126.9, 127.5, 143.5, 144.1, 147.2, 149.1; MS (FAB, m/z), 1185 $(M+H)^+$. Anal. Calcd for $C_{72}H_{96}O_6S_4$: C, 72.93; H, 8.16. Found: C, 72.99; H, 8.22.

5,11,22,28,34,45-Hexamethyl-15,18,38,41-tetrathiaheptacyclo[41.3.1.1^{3,7}.1^{9,13}.1^{20,24}.1^{26,30}.1^{32,36}]dopentaconta-1(46),3(48),4,6,9(49),10,12,20(50),21,23,25(51),27,29,32(52),33,35,43(47),44-octadecaene-47,48,49,50,51,52-hexaol (**1b**), m.p. 140-145 °C (from dichloromethane-hexane), ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 12H, CH_3 x 4), 2.26 (s, 6H, CH_3 x 2), 2.74 (s, 8H, SCH_2 x 4), 3.73 (s, 8H, $ArCH_2S$ x 4), 3.81 (s, 8H, $ArCH_2Ar$ x 4), 6.68 (d, 4H, Ar-H x 4, J=2.4Hz), 6.94 (d, 4H, Ar-H x 4, J=2.4Hz), 6.96 (s, 4H, Ar-H x 4), 8.47 (bs, 4H, OH x 4), 8.59 (bs, 2H, OH x 2); ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 30.8, 32.1, 33.0, 124.7, 127.2, 127.8, 129.1, 129.6, 130.3, 130.5, 130.7, 147.5, 149.0; MS (FAB, m/z), 933

$(M+H)^+$. Anal. Calcd for $C_{54}H_{60}O_6S_4$: C, 69.49; H, 6.48. Found: C, 69.71; H, 6.32.

5,28-Di-*tert*-butyl-11,22,34,45-tetramethyl-15,18,38,41-tetrathiaheptacyclo[41.3.1.$1^{3,7}$.$1^{9,13}$.$1^{20,24}$.$1^{26,30}$.$1^{32,36}$]dopentaconta-1(46),3(48),4,6,9(49),10,12,20(50),21,23,25(51),27,29,32(52),33,35,43(47),44-octadecaene-47,48,49,50,51,52-hexaol (**1c**), m.p. 130-140 °C (from dichloromethane-hexane), ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 18H, *t*-Bu x 2), 2.15 (s, 12H, CH_3 x 4), 2.75 (s, 8H, SCH_2 x 4), 3.74 (s, 8H, $ArCH_2S$ x 4), 3.84 (s, 8H, $ArCH_2Ar$ x 4), 6.67 (d, 4H, Ar-H x 4, J= 2.4Hz), 6.94 (d, 4H, Ar-H x 4, J=2.4 Hz), 7.17 (s, 4H, Ar-H x 4), 8.47 (bs, 4H, OH x 4), 8.59 (bs, 2H, OH x 2); ^{13}C NMR ($CDCl_3$): δ 20.4, 31.4, 31.5, 32.3, 33.1, 34.0, 124.8, 126.0, 126.6, 127.8, 129.0, 130.3, 130.6, 144.0, 147.6, 148.9; MS (FAB, m/z) 1017 $(M+H)^+$. Anal. Calcd for $C_{60}H_{72}O_6S_4$: C, 70.83; H, 7.13. Found: C, 70.89; H, 7.33.

General procedure for the preparation of hexahomodithiacalix[3]arenes (**2**).

To a suspension of sodium carbonate (245 mg, 2.31 mmol) in dry DMF (10 ml) were added a solution of bis(chloromethyl)phenol-formaldehyde trimer (**3**) (0.385 mmol) in dry DMF (10 ml) and a solution of 1,3-propanedithiol (42 mg, 0.385 mmol) in dry DMF (10 ml) over 1 h. After the addition was complete, the mixture was allowed to stir at 30 °C for 2h. Removal of the solvent under a reduced pressure gave pale yellow oily residue, which was subjected to column chromatography on silica gel using hexane : ethyl acetate, 3 : 1 as an eluent to give **2** as white powder.

5,11,23-Tri-*tert*-butyl-15,19-dithiatetracyclo[19.3.1.1^{3,7}.1^{9,13}]heptacosa-1(24),3(26),4,6,9(27),10,12,21(25),22-nonaene-25,26,27-triol (**2a**), m.p. 104-105 °C (from dichloromethane-hexane), ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 18H, *t*-Bu x 2), 1.33 (s, 9H, *t*-Bu), 1.90 (quintet, 2H, CH_2, J=7.9 Hz), 2.30 (t, 4H, CH_2 x 2,

J=7.9 Hz), 3.75 (s, 4H, $ArCH_2S$ x 2), 3.85 (s, 4H, $ArCH_2Ar$ x 2), 7.00 (d, 2H, Ar-H x 2, J = 2.6 Hz), 7.20 (d, 2H, Ar-H x 2, J = 2.6 Hz), 7.26 (s, 2H, Ar-H x 2), 8.50 (bs, 2H, OH x 2), 8.70 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 28.1, 30.0, 31.4, 31.5, 31.7, 33.9, 122.8, 126.0, 126.1, 126.5, 126.6, 126.8, 143.5, 143.9, 147.7, 149.5; MS (FAB, m/z), 607 $(M+H)^+$. Anal. Calcd for $C_{37}H_{50}O_3S_2$: C, 73.22; H, 8.30. Found: C, 73.40; H,8.33.

5,11,23-Trimethyl-15,19-dithiatetracyclo[19.3.1.$1^{3,7}$.$1^{9,13}$]heptacosa-1(24),3(26),4,6,9(27),10,12,21(25),22-nonaene-25,26,27-triol (**2b**), m.p. 143-145 °C (from dichloromethane-hexane), ^1H NMR ($CDCl_3$): δ 1.83 (quintet, 2H, CH_2, J=8.0 Hz), 2.22 (s, 9H, 6H, CH_3 x 2), 2.25 (t, 4H, CH_2 x 2, J=8.0 Hz), 2.31 (s, 3H, CH_3), 3.79 (s, 4H, $ArCH_2S$ x 2), 3.83 (s, 4H, $ArCH_2Ar$ x 2), 6.85 (d, 2H, Ar-H x 2, J=2.0Hz), 7.03 (d, 2H, Ar-H x 2, J=2.0Hz), 7.05 (s, 2H, Ar-H x 2), 8.40 (bs, 2H, OH x 2), 8.62 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 28.2, 29.7, 30.9, 123.1, 126.8, 127.1, 1129.5, 129.8, 130.1, 130.2, 130.5, 147.7, 149.5; MS (FAB, m/z), 481 $(M+H)^+$. Anal. Calcd for $C_{28}H_{32}O_3S_2$: C, 69.96; H, 6.71. Found: C, 69.97; H, 6.73.

11,23-Dimethyl-5-*tert*-butyl-15,19-dithiatetracyclo[19.3.1.$1^{3,7}$.$1^{9,13}$]heptacosa-1(24),3(26),4,6,9(27),10,12,21(25),22-nonaene-25,26,27-triol (**2c**), m.p. 190.5-194 °C (from dichloromethane-hexane), ^1H NMR ($CDCl_3$): δ 1.28 (s, 9H, *t*-Bu), 1.82 (quintet, 2H, CH_2, J=7.9 Hz), 2.18 (s, 6H, CH_3 x 2), 2.30 (t, 4H, CH_2 x 2, J=7.9 Hz), 3.74 (s, 4H, $ArCH_2S$ x 2), 3.83 (s, 4H, $ArCH_2Ar$ x 2), 6.82 (d, 2H, Ar-H x 2, J = 2.6 Hz), 6.99 (d, 2H, Ar-H x 2, J = 2.6 Hz), 7.22 (s, 2H, Ar-H), 8.39 (bs, 2H, OH x 2), 8.61 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.4, 28.3, 29.7, 30.9, 31.4, 31.6, 34.0, 123.1, 126.3, 126.4, 127.1, 129.5, 130.2, 130.3, 143.9, 147.9, 149.5; MS (FAB, m/z), 523 $(M+H)^+$. Anal. Calcd for $C_{31}H_{38}O_3S_2$: C, 71.22; H, 7.33. Found: C, 71.32; H, 7.42.

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