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## SELECTIVE SYNTHESIS OF MONOSUBSTITUTED *p*-*tert*-BUTYLTHIACALIX[4]ARENE UNDER PHASE TRANSFER CATALYSIS

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**Abstract** – Phase transfer catalysis (PTC) technique for lower rim alkylation of *p*-*tert*-butylthiacalix[4]arene (TCA) with diethyl bromomalonate, phenacyl bromide, *N,N*-diethylchloroacetamide, ethyl bromoacetate and chloroacetonitrile using K<sub>2</sub>CO<sub>3</sub>, CsOH or Na<sub>2</sub>CO<sub>3</sub> as a base and tetraethylammonium bromide (TEAB) as catalyst in benzene has been employed. Selective synthesis of monosubstituted *p*-*tert*-butylthiacalixarene using K<sub>2</sub>CO<sub>3</sub> or CsOH as base has been elaborated. Unprecedented alkylation cyclization as well as arene oxidation by using of Na<sub>2</sub>CO<sub>3</sub> as a base for alkylation of *p*-*tert*-butylthiacalix[4]arene under PTC conditions led to the synthesis of two new *p*-*tert*-butylthiacalix[4]arene derivatives with heterocyclic bridging rings. The structures of the newly synthesized compounds were characterized by different spectroscopy methods IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and single crystal X-ray diffraction.

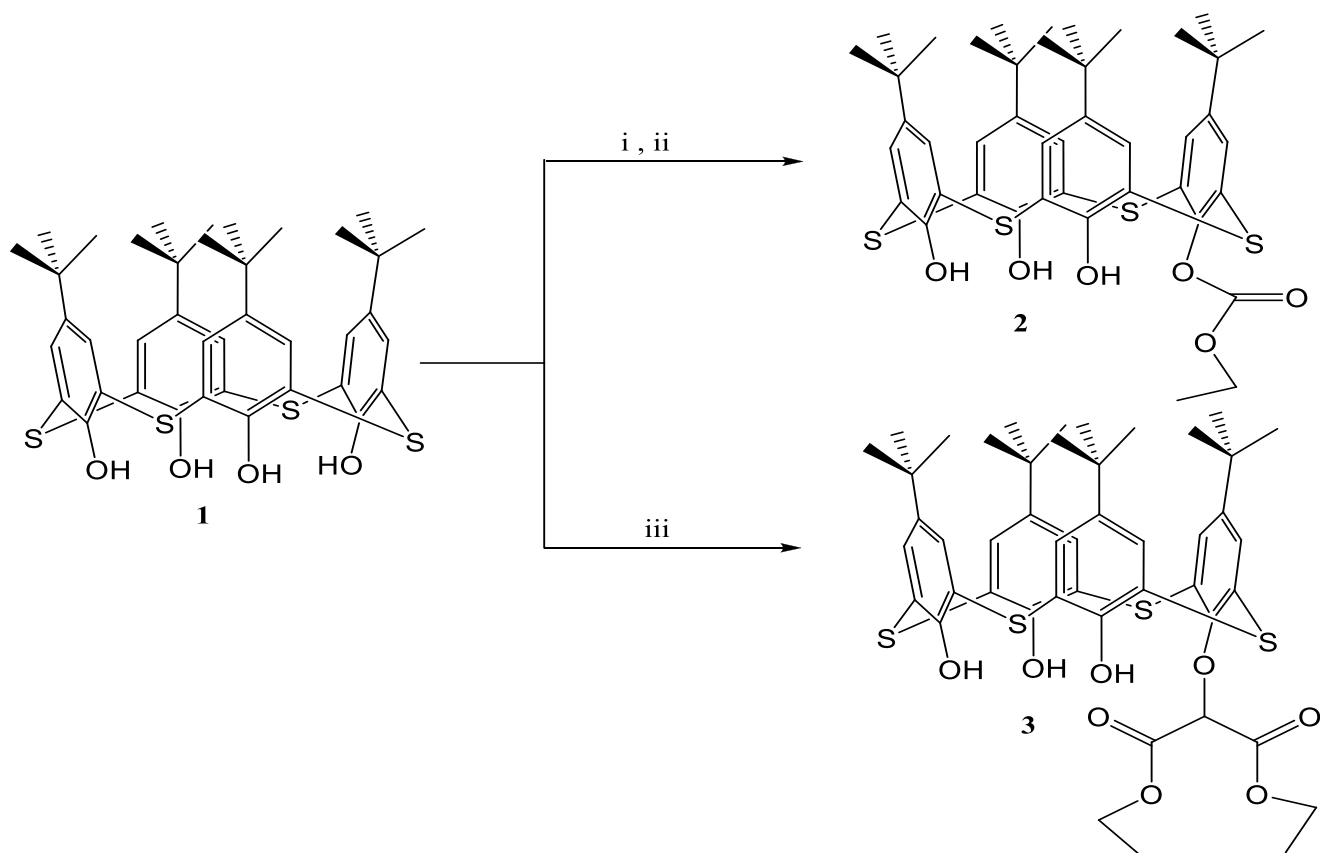
## INTRODUCTION

Calixarenes have been found to be an outstanding platform for creating attractive host molecules and have prominent host–guest recognition ability towards different ions.<sup>1-3</sup> In 1997, *p*-*tert*-butylthiacalix[4]arene has been reported by Miyano et al.<sup>4</sup> as a calixarenes analogy with some additional features because of sulfur bridging atom in its skeleton structure attracted much attention in research rather than the classical calixarenes. Thiocalixarenes recognition ability as well as their selectivity alkylation has been improved by the introduction of new functional groups at its active sites upper, lower rims and bridges groups.<sup>5</sup> The lower rim of *p*-*tert*-butylthiacalix[4]arene which contains four hydroxyl groups are considered the most important active sites for introduction of new functional groups. The mono, di, tri or tetra-alkylated derivatives are all the possible products prepared by alkylation of *p*-*tert*-butylthiacalixarene at the lower rim

hydroxyl groups. Literatures showed that di and tetra-alkylated thiacalixarenes are the most common products rather than mono and tri-alkylated thiacalixarenes. The monosubstituted thiacalixarenes, the lowest degree of alkylation of thiacalix[4]arenes at lower rim are considered the biggest lower rim thiacalix[4]arenes modification. These lower rim thiacalixarene modifications are very necessary for improved their metal ion recognition ability but still no much work has been reported in literature.<sup>6-8</sup> Few related reactions to the synthesis of mono or tri-substituted of thiacalix[4]arenes were recently presented researchers.<sup>6-8</sup> The majority of the lower rim alkylation reactions of *p-tert*-butylthiacalixarene have been carried out in aprotic polar solvents such as acetone, acetonitrile or dimethylformamide in the presence of alkali metal carbonate, hydroxide or hydride with alkylating reagents.<sup>9-11</sup> In my previous work,<sup>7</sup> I have studied the alkylation of *p-tert*-butylthiacalix[4]arene with diethyl bromomalonate using the above conditions formed mono, di and tri-alkylated *p-tert*-butylthiacalix[4]arene derivatives at lower rim as a mixture products. The above study<sup>7</sup> showed also some of these products were formed through the decomposition of diethyl bromomalonate like the formation of monosubstituted thiacalixarenes **2** ethoxycarbonyl fragment. Looking for an alternative reaction condition to avoid the decomposition of diethyl bromomalonate during the reaction with *p-tert*-butylthiacalix[4]arene, we found phase transfer catalysis conditions and also the best way for selective synthesis of monosubstituted *p-tert*-butylthiacalix[4]arene. In current study, we present a selective synthesis of monosubstituted *p-tert*-butylthiacalix[4]arene derivatives containing different alkylating groups.

## RESULTS AND DISCUSSION

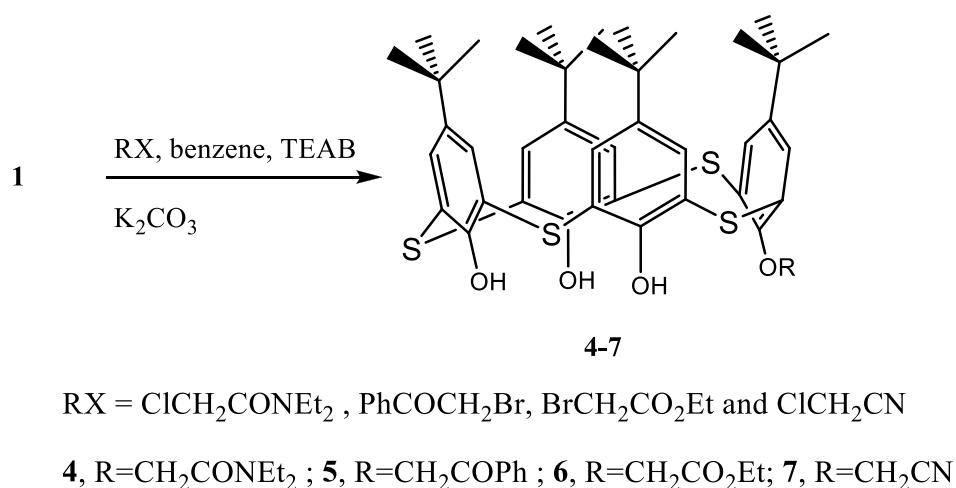
Some trials have been done before establishing the phase transfer catalysis as a best conditions for monosubstituted *p-tert*-butylthiacalix[4]arene selective synthesis. For instance, we carried out the reaction of *p-tert*-butylthiacalix[4]arene with diethyl bromomalonate with a variation of molar reactants ratio from 1:2 to 1:16 as well as shortening reaction time (approximately 10 hours) using different metal carbonate ( $K_2CO_3$ ,  $CS_2CO_3$ ) or metal hydroxide (KOH, CsOH) in acetone as a solvent, however only thiacalixarene **2** was formed as a result of diethyl bromomalonate decomposition as reported.<sup>7</sup> Continue appealing a new technique to optimize the reaction conditions to prevent the decomposition of diethyl bromomalonate during the alkylation of *p-tert*-butylthiacalix[4]arene, improving the yield of the alkylated product, shortening the reaction time and also perfecting the selectivity of thiacalixarenes alkylation reactions, we employed phase transfer catalysis technique. The reaction of *p-tert*-butylthiacalix[4]arene with diethyl bromomalonate under phase transfer catalysis condition (using  $K_2CO_3$  as a base and tetraethylammonium bromide (TEAB) as a catalyst in benzene), succeeded to avoid diethyl decomposition and as a result of monosubstituted *p-tert*-butylthiacalix[4]arene with diethyl malonate fragment **3** was prepared at the lower rim (Scheme 1).



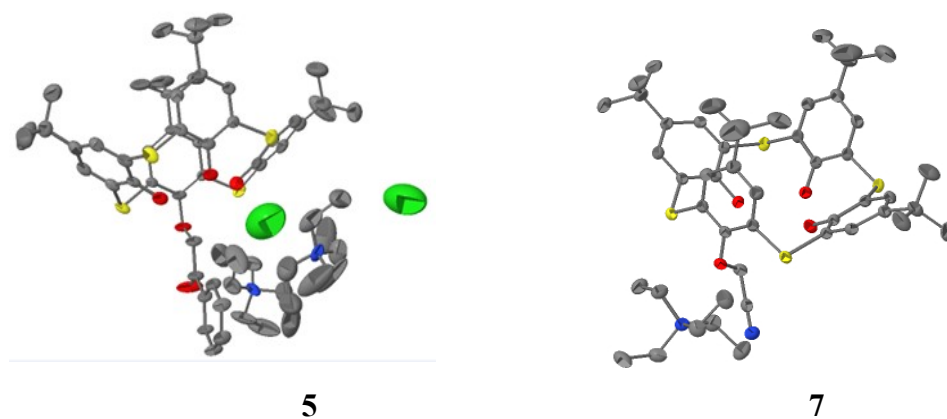
**Scheme 1.** i.  $\text{BrCH}(\text{CO}_2\text{Et})_2/\text{K}_2\text{CO}_3$ , acetone; ii.  $\text{BrCH}(\text{CO}_2\text{Et})_2/\text{Cs}_2\text{CO}_3$ , acetone, 85% yield; iii.  $\text{BrCH}(\text{CO}_2\text{Et})_2/\text{K}_2\text{CO}_3$  or  $\text{CsOH}$  /benzene/TEAB, 70% yield.

Depending on the above reaction results, *p*-*tert*-butylthiacalix[4]arene **1** was subjected to further alkylation with different alkylating agents such as *N,N*-diethylchloroacetamide, phenacyl bromide, ethyl bromoacetate and chloroacetonitrile using the above PTC condition and as a result monosubstituted *p*-*tert*-butylthiacalixarenes **4-7** were obtained in good yields (Scheme 2). Although compound **6** has been reported by Lamouchi et al.<sup>8</sup> through two reaction steps, first, by synthesis of 1,3-distal dialkylated thiacalixarene, and second by catalytic dealkylation of one of the two alkyl groups. This work showed a fast and direct production of monosubstituted *p*-*tert*-butylthiacalixarene **6** in an excellent yield (90%). Also monosubstituted thiacalix[4]arene with cyanomethoxy fragment **7** has been synthesized by Kovalev et al.<sup>12</sup> in 36% yield using the reported method, while when we applied our PTC technique the yield increased to more than 90%. The structure of the products was characterized by different physical methods IR, NMR and elemental analysis. All the above monosubstituted thiacalixarenes **2-7** have unsymmetrical structures which should contain three non-equivalent *tert*-butyl groups which should give a 2:1:1 ratio of resonance patterns, the splitting pattern of the calixarene aromatic protons appeared as two doublets and two singlets in the proton spectrum and also three phenolic hydroxyl groups give two different peaks in 2:1 ratio as described in the experimental part. For example, in thiacalixarene **3** have

Bu<sup>t</sup> peaks at  $\delta$  1.08 (9H, s) and 1.20-1.23 (27H, 2s), two doublets and two singlets at 7.47 (2H, s), 7.57 (2H, d), 7.61 (2H, s) and 7.63 (2H, d). The phenolic hydroxyl groups at 9.11 (2H, s) and 9.72 (1H, s). In addition, the structure determination of monosubstituted thiacalixarenes **5** and **7** were confirmed by its molecular salt with tetraethylammonium chloride by X-ray crystallography (Figure 1) under CCDC reference: 1429489<sup>13</sup> and CCDC reference: 1448429,<sup>14</sup> respectively. The selective synthesis of monosubstituted *p-tert*-butylthiacalix[4]arenes **4-7** using potassium carbonate as a base and tetraethylammonium bromide as a catalyst is explained by the stabilization of the *p-tert*-butylthiacalix[4]arenes with tetraethylammonium bromide salt which have registered by X-ray investigation of the their molecular salt structure in Figure 1 for monosubstituted *p-tert*-butylthiacalix[4]arenes **5** and **7**. Also, the molecular salt of the monosubstituted *p-tert*-butylthiacalix[4]arene **6** with tetraethylammonium bromide is under investigation by X-ray diffraction.

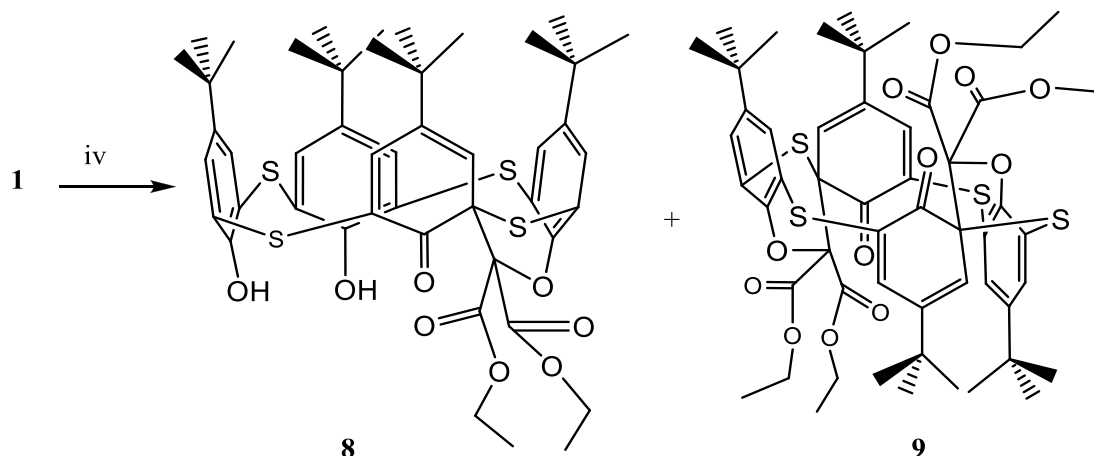


**Scheme 2.** Synthesis of monosubstituted *p-tert*-butylthiacalix[4]arene at lower rim, 90% yield

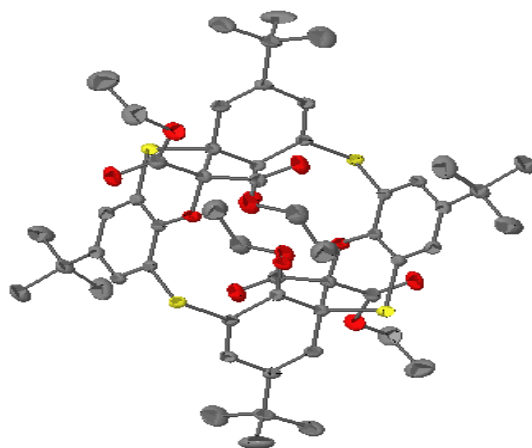


**Figure 1.** X-Ray structures of **5** and **7**, hydrogen atom omitted for clarity

Unprecedented *p-tert*-butylthiacalix[4]arene, alkylation, ring cyclization and arene ring oxidation by the reaction with diethyl bromomalonate under PTC reaction condition (benzene/ Na<sub>2</sub>CO<sub>3</sub>/ TEAB) afforded thiacalixarenes **8** and **9**. The X-ray structure investigation<sup>15</sup> of compound **9** (Figure 2) supports us to determine the structures of both **8** and **9** products (Scheme 3).

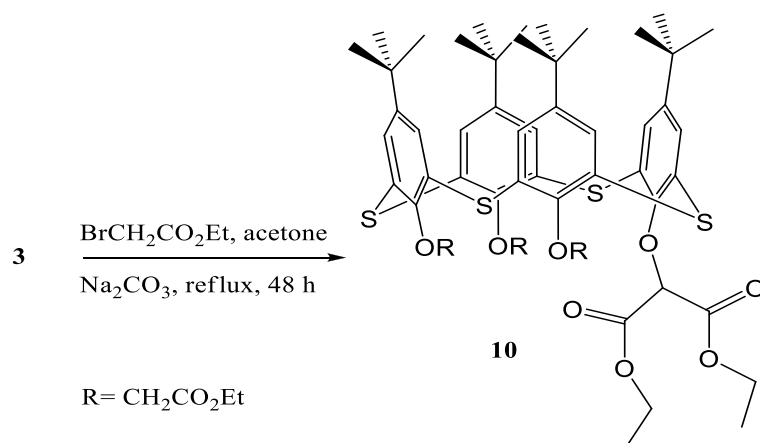


**Scheme 3.** (iv) BrCH(CO<sub>2</sub>Et)<sub>2</sub> / Na<sub>2</sub>CO<sub>3</sub>/ TEAB / benzene, synthesis of thiacalixarene **8** in 40% yield and thiacalixarene **9** in 45% yield.



**Figure 2.** X-Ray structure of **9** with CCDC reference: 1425819, hydrogen atom omitted for clarity

The synthesis of *p-tert*-butylthiacalix[4]arene **10** containing five coordination carbonyl groups reflects lower rim modification possibility through using monosubstituted thiacalix[4]arene **3** (Scheme 4). Its structure was determined by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. Although compound **10** is synthesized in the cone conformer as shown in Scheme 4 its proton NMR analysis is similar to partial cone because of the presence of one different substituent between three similar substituents at the lower rims as describing in the experimental section.



**Scheme 4.** Synthesis of *p-tert*-butylthiacalix[4]arene **10** with five carbonyl groups at lower rim, 60% yield

## CONCLUSION

Phase transfer catalysis reaction technique using benzene as a solvent, potassium carbonate as a base and tetraethylammonium bromide as catalyst showed a suitable condition for selective synthesis of monosubstituted *p-tert*-butylthiacalix[4]arene. The unprecedented products obtained from the reaction of *p-tert*-butylthiacalix[4]arene with diethyl bromomalonate in the presence of sodium carbonate as a catalyst through thiacalixarene's phenolic ring oxidation as well as bridging ring cyclization will be our soon coming study.

## EXPERIMENTAL

Chemicals were used without more purification. Melting points (C, uncorrected) were measured in open glass capillaries using a Thermo Scientific IA 9100 melting point apparatus. FT-IR Spectrometer, Thermo Scientific, model: Nicolet iS5 was used for recording infrared (IR) spectra of the prepared compounds as KBr pellets.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of compounds were run on JEOL ECP-400 MHz and 500 MHz NMR spectrometer, in  $\text{CDCl}_3$  at room temperature. The chemical shifts are expressed in  $\delta$  7.24 (ppm) downfield from chloroform ( $\text{CDCl}_3$ ) used as reference.

### Synthesis of 5,11,17,23-tetra-*tert*-butyl-25-[(ethoxycarbonyl)oxy]-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene **2**.

A mixture of 1g (1.38 mmol) of *p-tert*-butylthiacalixarene, 0.5mL of diethyl bromomalonate and 0.5 g (3.59 mmol) of anhydrous  $\text{K}_2\text{CO}_3$  (0.2g KOH or 0.5g CsOH) in 50 mL of acetone was refluxed for 10 h and concentrated under vacuum. Diluted hydrochloric acid (30 mL) was added to the concentrated reaction mixture. The solid residue was extracted by  $\text{CH}_2\text{Cl}_2$ . The organic layer was concentrated dried over magnesium sulfate.  $\text{CH}_2\text{Cl}_2$  was evaporated under vacuum and the product was precipitated by treating the residue with MeOH. Yield  $\geq$  80%.

**Synthesis of 5,11,17,23-tetra-*tert*-butyl-25-[(diethoxycarbonyl)methoxy]-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene 3.**

A mixture of 1.5 g (2.08 mmol) of TCA, 10 g of anhydrous  $K_2CO_3$  and 0.5 g of TEAB and diethyl bromomalonate (3 mL, 8.23 mmol) in benzene (50 mL) was refluxed at 100 °C with stirring for 6 days. The reaction mixture was filtered off and the benzene layer was evaporated under reduced pressure to dryness. The solid residue was washed by diluted hydrochloric acid and extracted by  $CH_2Cl_2$ . The  $CH_2Cl_2$  layer was concentrated and MeOH was added. White solid product was precipitated, filtered and dried (yield 70%).

White crystals, MP > 350 °C, IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ), 3356.9 (OH), 2,964 (CH), 1742 (CO ester);  $^1H$  NMR (400 MHz and 500, MHz,  $CDCl_3$ ), 1.08 (9H, s,  $Bu^t$ ); 1.20-1.23 (27H, 2s,  $Bu^t$ ); 1.27-1.36 (6H, m,  $O(CH_2CH_3)_2$ ); 4.28-4.42 (4H, m,  $O(CH_2CH_3)_2$ ); 7.02 (1H, s,  $OCH(COOEt)_2$ ); 7.47 (2H, s, Ar-H); 7.57 (2H, d,  $J=3.0$  Hz, Ar-H); 7.61 (2H, s, Ar-H); 7.63 (2H, d,  $J=4.0$  Hz, Ar-H); 9.11 (2H, s, 2OH); 9.72 (1H, s, OH).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ), 13.80, 14.02, 30.91, 31.28, 34.10, 34.14, 34.22, 62.47, 62.54, 80.15, 120.19, 120.76, 121.17, 127.65, 136.09, 136.18, 136.22, 136.48, 143.64, 143.87, 148.52, 156.31, 156.63, 162.34, 165.80. Anal. Calcd for  $C_{48}H_{62}O_8S_4$ : C, 64.40%; H, 6.98%. Found: C, 64.38%; H, 6.78%.

**Synthesis 5,11,17,23-tetra-*tert*-butyl-25-[(*N,N*-diethylcarbamoyl)methoxy]-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene ; 5,11,17,23-tetra-*tert*-butyl-25-[(benzoyl)methoxy]-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene; 5,11,17,23-tetra-*tert*-butyl-25-[(ethoxycarbonyl)methoxy]-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene and 5,11,17,23-tetra-*p-tert*-butyl-25-[cyanomethoxy]-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene 4-7 respectively.**

General method: A mixture of TCA (1g, 1.38 mmol), anhydrous  $K_2CO_3$  (5.0 g), TEAB (0.4 g), *N,N*-diethylchloroacetamide (1.38-2.76 mmol), phenacyl bromide (0.28-0.55 g, 1.38-2.76 mmol), and ethyl bromoacetate (0.15 mL, 1.38 mmol) or chloroacetonitrile, (0.1 mL, 1.38 mmol) in benzene (50 mL) was refluxed at 100 °C for 2-3 days. The mixture was filtered off to remove any undesired material, and benzene layer was evaporated to dryness. The solid residue was washed by diluted hydrochloric acid solution and extracted with  $CH_2Cl_2$ . The  $CH_2Cl_2$  layer was concentrated and MeOH was added to afford a white solid precipitate Yield  $\geq 90\%$ .

**4**, white crystals, MP 150 °C, IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ), 3313 (OH), 2,963 (CH), 1661 (CO amide);  $^1H$  NMR (500 MHz and 500 MHz,  $CDCl_3$ ), 1.06 (9H, s,  $Bu^t$ ); 1.203 (9H, s,  $Bu^t$ ); 1.205 (18H, s,  $Bu^t$ ); 1.23-1.32 (6H, m,  $N(CH_2CH_3)_2$ ); 3.42 (2H, q,  $J=7.5$  Hz,  $NCH_2CH_3$ ); 3.57 (2H, q,  $J=7.5$  Hz,  $NCH_2CH_3$ ); 5.30 (2H, s,  $OCH_2$ ); 7.44 (2H, s, Ar-H); 7.56 (2H, d,  $J=2.0$  Hz, Ar-H); 7.58 (2H, s, Ar-H); 7.61 (2H, d,  $J=2.5$  Hz, Ar-H); 7.63 (1H, s, OH); 9.70 (2H, s, 2OH).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ), 13.13, 14.40, 31.05, 31.30, 31.40, 34.20, 34.35, 40.40, 41.30, 72.65, 120.60, 120.85, 120.93, 129.00, 135.60, 135.95, 136.10, 136.40,

143.30, 143.60, 148.40, 156.40, 156.97, 158.80, 158.10. Anal. Calcd for  $C_{46}H_{59}NO_5S_4$ : C, 66.34%; H, 7.03%, N, 1.72%. Found: C, 66.23%; H, 7.13%, N, 1.68%.

**5**, white crystals, MP 180 °C, IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ), 3320 (OH), 2,962 (CH), 1703 (CO);  $^1H$  NMR (400 MHz, and 500 MHz,  $CDCl_3$ ), 1.19 (9H, s,  $Bu^t$ ); 1.20 (18H, s,  $Bu^t$ ); 1.22 (9H, s,  $Bu^t$ ); 6.01 (2H, s,  $OCH_2CO-$ ); 7.52 (1H, t,  $J=2.0$  Hz, *p*-Ph-H); 7.55-7.65 (11H, m, Ar-H+ *m*-Ph-H); 7.68 (1H, s, OH); 8.09 (2H, d,  $J=2.5$  Hz, *o*-Ph-H); 9.54 (2H, s, 2OH).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ), 31.15, 31.36, 31.40, 34.18, 34.22, 34.29, 34.51, 50.97, 53.49, 120.54, 120.61, 120.81, 120.89, 128.13, 128.35, 128.98, 134.03, 136.04, 136.32, 136.34, 136.99, 143.63, 149.00, 156.60, 157.00, 158.04, 194.12. Anal. Calcd for  $C_{48}H_{54}O_5S_4$ : C, 68.70%; H, 6.49%. Found: C, 68.58%; H, 6.37%.

**6**, Spectral data, see reference No. 8. And for **7**, spectral data see reference No. 12.

Synthesis of thiacalix[4]arenes **8** and **9** in 40% and 45% yields respectively.

A mixture of 1.5 g (2.08 mmol) of *p*-*tert*-butylthiacalix[4]arene (TCA), 10 g of sodium carbonate, 0.5 g of tetraethylammonium bromide (TEAB) and diethyl bromomalonate (3 mL, 8.02 mmol) in 50 mL of benzene was refluxed at 100 °C with stirring for 6 days. The reaction mixture was filtered off and the benzene layer was evaporated under vacuum to dryness. The solid residue was washed by diluted hydrochloric acid and extracted by  $CH_2Cl_2$  (3 times). The  $CH_2Cl_2$  portions were concentrated then treated by MeOH. Yellow color of two solid mixture products were precipitated and filtered off. The mixture was separated by fractional crystallization by using a mixture of  $CH_2Cl_2$  / MeOH (1:1 v:v) to afford the two compounds as yellow crystals in 85% yield each.

**8**, yellow crystals, MP 312 °C IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ), 2,964 (CH), 1755 (CO ester), 1666 (CO, cyclic ketone), 3406 (OH);  $^1H$  NMR (500 MHz,  $CDCl_3$ ), 1.06-1.15 (6H, m,  $2CH_2CH_3$ ), 1.21 (9H, s,  $Bu^t$ ), 1.24 (9H, s,  $Bu^t$ ), 1.26 (9H, s,  $Bu^t$ ), 1.28 (9H, s,  $Bu^t$ ), 3.70-4.40 (4H, m,  $2CH_2CH_3$ ), 6.28 (1H, d,  $J=2.5$  Hz, Ar-H), 6.91 (1H, d,  $J=2.5$  Hz, Ar-H), 7.31 (1H, d,  $J=2.5$  Hz, Ar-H), 7.39 (1H, s, OH), 7.45 (1H, d,  $J=2.5$  Hz, Ar-H), 7.49 (1H, d,  $J=3.0$  Hz, Ar-H), 7.55 (1H, d,  $J=3.0$  Hz, Ar-H), 7.65 (1H, d,  $J=2.5$  Hz, Ar-H), 7.69 (1H, d,  $J=2.5$  Hz, Ar-H), 7.80 (1H, s, OH);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ), 13.77, 28.60, 31.20, 31.34, 31.38, 34.10, 34.98, 48.89, 53.40, 62.98, 63.32, 85.20, 112.97, 117.39, 120.09, 120.26, 122.31, 123.43, 124.72, 126.76, 130.74, 131.29, 132.03, 132.56, 133.63, 134.34, 142.74, 145.32, 145.72, 148.20, 154.73, 155.24, 162.60, 164.11, 190.47. TOF MS ES+, 877.35.

**9**, yellow crystals, MP 300 °C, IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ), 2,964 (CH), 1755 (CO ester), 1692 (CO, cyclic ketone);  $^1H$  NMR (500 MHz,  $CDCl_3$ ), 1.1 (3H, t,  $J=7.5$  Hz,  $COCH_2CH_3$ ), 1.16 (18H, s,  $Bu^t$ ), 1.22 (18H, s,  $Bu^t$ ), 1.12-1.26 (6H, m,  $2-COCH_2CH_3$ ), 1.28 (3H, t,  $J=7.5$  Hz,  $COCH_2CH_3$ ), 4.10-4.90 (8H, m,  $COCH_2CH_3$ ), 6.37 (2H, d,  $J=2.5$  Hz, Ar-H), 6.43 (2H, d,  $J=2.5$  Hz, Ar-H), 7.15 (2H, d,  $J=2.0$  Hz, Ar-H), 7.20 (2H, d,  $J=3.0$  Hz, Ar-H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ), 13.86, 14.00, 28.81, 31.47, 34.09, 34.92,



51.16, 62.39, 85.24, 112.83, 118.82, 122.74, 125.38, 133.75, 134.91, 135.49, 142.83, 144.12, 149.72, 164.66, 165.44, 186.24. TOF MS ES<sup>+</sup>, 1033.3.

**Synthesis of 5,11,17,23-tetra-*tert*-butyl-25-[(diethoxycarbonyl)methoxy]-26,27,28-tri-[(ethoxycarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene 10.**

Thiacalixarene **3** (0.5 g, 0.55 mmol) was suspended with 0.5 g of anhydrous Na<sub>2</sub>CO<sub>3</sub> and ethyl bromoacetate (0.5 mL, 4.4 mmol) in 50 mL of acetone. The reaction mixture was heated under reflux for 72 h then, concentrated. The residue was diluted with distilled water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was concentrated, and then treated with MeOH. The white solid product was collected and purified by column chromatography ((1v:1v) *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub> mixture), yield 60%.

White solid, MP 155 °C, IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>), 2962 (CH), 1765 (CO ester), 1738 (CO ester); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), 0.86 (3H, t, *J*=7.5 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.03 (9H, s, Bu<sup>t</sup>), 1.12 (3H, t, *J*=7.5 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.23 (27H, s, 3 Bu<sup>t</sup>). 1.25-1.42 (9H, m, 3-OCH<sub>2</sub>CH<sub>3</sub>), 3.7-4.3 (10H, m, 5-OCH<sub>2</sub>CH<sub>3</sub>), 4.6-4.8 (6H, m, 3-OCH<sub>2</sub>CO), 6.99 (2H, d, *J*=2.0 Hz, Ar-H), 7.49 (2H, s, Ar-H), 7.51 (2H, d, *J*=2.0 Hz, Ar-H), 7.53 (1H, s, OCH(COOEt)<sub>2</sub>), 7.84 (2H, s, Ar-H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 13.91, 14.03, 14.19, 14.24, 30.93, 31.05, 31.15, 31.20, 31.36, 34.02, 34.14, 34.20, 34.42, 59.69, 60.48, 60.57, 60.62, 66.01, 68.21, 69.36, 70.69, 126.66, 127.65, 128.00, 128.54, 129.32, 133.09, 133.95, 135.56, 145.02, 146.67, 156.71, 157.69, 158.66, 167.89, 168.52, 170.14. Anal. Calcd for C<sub>60</sub>H<sub>80</sub>O<sub>14</sub>S<sub>4</sub>: C, 62.47%; H, 6.99%. Found: C, 62.90%; H, 6.72%.

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