Chapter 2

Calix[4]resorcinarene and their Derivatives: 
Conventional and Microwave-Assisted Synthesis  
and Spectroscopic Characterization
Resume

This chapter deals with the rapid, eco-friendly and convenient method of synthesis of parent calix[4]resorcinarene (basic calix platforms) using microwave irradiation technique. The basic calix platform has been further functionalised as its ester and hydrazide derivatives. In effect, two calix[4]resorcinarene hydrazides i.e. one having twelve and other having four hydrazide groups on the periphery of basic calix platforms have been synthesized.

The structures of all basic calix platforms and their derivatives have been confirmed on the basis of various physico-chemical techniques such as elemental analysis, FT-IR, $^1$H NMR, ESI-MS and $^{13}$C NMR spectroscopy. Single crystal structure of basic calix platforms i.e. 5,11,17,23-tetra methyl calix[4]resorcinarene and octamethoxy calix[4]resorcinarene has also been reported.
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1. Introduction

Calix[4]resorcinarene have recently received considerable attention in recent times because of its wide range of applications e.g. HPLC stationary phases [1-5], for the separation of pyrimidine bases [3], racemic drugs [1] and isomers [4], the selective extractions of lanthanides and actinides [6-9], as molecular receptors [10-13], NMR chiral shift agents [14, 15], multifunctional antiradical and antioxidant agents [16], photo resist material [17], in GC separations [18, 19] and as starting materials for the synthesis of macrocyclic compounds (e.g. cavitands and carcerands) [20-22]. A few reviews on different aspects of these molecules have been published [23-26]. The early review of Timmerman provides a good general introduction to these molecules [27].

C-alkyl and C-aryl calix[4]resorcinarenes can be prepared not only from resorcinol but also from 2-hydroxy resorcinol and 2-alkyl resorcinol (Scheme 1(a) and 2(a)) [28]. New synthetic routes for various types of resorcinarenes have emerged over the years, which are somewhat different from the conventional mineral acid-catalyzed cyclo-oligomerization. The various derivatives of calix[4]resorcinarene obtained by the conventional method are reported in literature. Solvent-free synthesis of aryl calix[4]resorcinarene and C-methyl calix[4]resorcinarene [29, 30], solvent-free synthesis of novel calix[4]resorcinarene derivatives using tungstate sulfuric acid [31], synthesis of calix[4]resorcinarene based on fennel oil [32] have been reported in literature. A versatile route to a series of C-alkyl calix[4]resorcinarenes have been developed using the lewis acids, SOCl$_2$, POCl$_3$, AlCl$_3$, SiCl$_2$Me$_2$ and SnCl$_4$ to catalyze the condensative tetramerization of 1,3-dimethoxybenzene and 2,4-dimethoxycinnamates as starting material with aliphatic/aromatic aldehyde to give high yields of the resorcinarenes [33,
Novel calix[4]phloroglucinarene was synthesized from phloroglucinol as a starting material and trifluoroacetic acid as catalyst [35, 36]. Trifluoromethane sulfonate salts, also known as triflates, such as ytterbium(III)triflate [37] and bismuth(III)triflate [36], have been described as efficient catalysts for the synthesis of calix[4]resorcinarenes. Recently, lanthanide(III)tosylates and lanthanide(III)nitrobenzenesulfonates [38] have also been used as efficient, inexpensive, recyclable and environment friendly catalysts for the synthesis of calix[4]resorcinarenes. Tetrameric products are not obtained when the resorcinol involved has an electron withdrawing substituent, such as -NO$_2$ or -Br at the 2-position [39]. Under certain conditions, reactions of formaldehyde and 2-methyl resorcinol or Pyrrogallol yield isolable amounts of the tetrameric product [40]. In last decades, microwave irradiation technique has played an important role as a very effective and non-polluting method for activating reactions because it takes less time with improved yield, uses milder reaction conditions and are environment friendly [41].

Calix[4]resorcinarenes are three-dimensional, cyclic aromatic tetramers and are easily synthesized by a well-established one-pot procedures. Calix[4]resorcinarene derivatives are also readily obtainable with various substituent at the sites of the bridging methylene groups and by various functionalization of the hydroxy group on the upper rim. We exploited the -OH group and synthesized the ester and hydrazide derivatives. Hydrazides moieties are very versatile ligands and are found to be excellent reagents for reducing and stabilizing for the metal nanoparticles. Calix[4]resorcinarenes and other calixarene derivatives have been used both as a reducing as well stabilizing agent previously to enhance the dispersion of colloidal metal particles in various organic
solvents, as well as their self-assembly into well-defined nanostructures with novel collective properties [42-44].


2. Experimental section

2.1. Materials and methods

All the reagents and metal salts of AR grade were purchased from Sigma-Aldrich and used without further purification. Solvents used for spectroscopic studies were
purified and dried before use. All aqueous solutions were prepared from quartz distilled deionized water which was further purified by a Millipore Milli-Q water purification system (Millipack 20, Pack name: Simpak 1, Synergy). Melting points (uncorrected) were taken in a single capillary tube using a VEEGO (Model No: VMP-DS, India) melting point apparatus. FT-IR spectra were recorded on Bruker, Tensor 27Infrared spectrophotometer as KBr pellets. H NMR spectra were recorded on a Bruker-ARX 500MHz instrument, using tetramethylsilane as internal standard. Mass Spectra were recorded on MICROMASS QUATTRO II triple quadruple mass spectrometer using ESI capillary (3.5 KV, 40 V). The spectra were recorded at room temperature. Absorption spectra were studied on a Jasco V-570 UV-Vis recording spectrophotometer. A single crystal data and X-ray structure analysis were done using a Bruker Smart-CCD diffractometer.

3. Synthesis


3.1.1 Conventional method

5,11,17,23 tetramethyl calix[4]resorcinarene 1(a) was synthesized with the help of the reported procedure [45] as follows: 2-methyl resorcinol (5 g, 0.040 mol) in 5 mL hydrochloric acid was added to 15 mL solution of p-hydroxy benzaldehyde (4.88 g, 0.040 mol) in methanol containing 5 mL of hydrochloric acid with constant stirring and then refluxed for 4-5 hours at 75°C. Pink coloured precipitate was obtained which was washed with cold methanol and further recrystallized in DMF- methanol mixture.

Octamethoxy calix[4]resorcinarene 2(a) was synthesized with the help of reported procedure [46] as follows. Aqueous hydrochloric acid (9 M, 0.8 mL) was added dropwise
to a stirring solution of 1,3-dimethoxy benzene (0.528 g, 3.82 mmol) and p-hydroxy benzaldehyde (0.46 g, 3.82 mmol) in ethanol (62.5 mL), the reaction mixture was refluxed with constant stirring for about for 7-8 hours. The mixture was allowed to cool at room temperature and then filtered to yield the crude mixture of isomers as a purple powder, which were washed with cold methanol and further recrystallized in DMF-methanol mixture.

3.1.2. Microwave irradiation method

A mixture of 2-methyl resorcinol (5 g, 0.040 mol), p-hydroxy benzaldehyde (4.88 g, 0.040 mol), concentrated HCl in water-methanol (30 mL) were kept under microwave irradiation for 3-5 minutes at 20% output with a break of 30 seconds each, for the purpose of stirring, after regular interval of 2 minutes. After completion of the reaction, a solid was obtained which was washed with water and little amount of methanol. The pink solid was recrystallized with appropriate solvent to give a pure product 1(a) for analysis.

To a mixture of 1,3-dimethoxy benzene (0.528 g, 3.82 mmol) and p-hydroxy benzaldehyde (0.46 g, 3.82 mmol) in ethanol (62.5 mL), aqueous hydrochloric acid (9 M, 0.8 mL) was added dropwise. The reaction mixture was subjected to microwave irradiation for approximately 10-12 minutes with a break of one minute each, for the purpose of stirring, after regular interval of 2 minutes. The reaction mixture was filtered to get the crude mixture as a purple powder which was washed with little amount of methanol. The purple solid was recrystallized with appropriate solvent to give a pure product 2(a) for analysis.


To a 500 mL three neck round bottom flask, equipped with a mechanical stirrer, reflux condenser and dropping funnel, 5, 11, 17, 23 methyl calix[4]resorcinarene 1(a) (4.5 g, 5.0 mmol), anhydrous potassium carbonate (13.6 g, 90 mmol), and potassium iodide (0.8 g, 5.0 mmol) in dry acetone (150 mL) was heated to reflux under nitrogen for at least 0.5 hour. Then ethyl bromoacetate (13.16 mL, 78 mmol) was added to the reaction mixture and refluxed for 5 days. After removal of acetone, the residue was dissolved in water, acidified with HCl and extracted with CHCl₃. The yellow organic layer was separated and dried with MgSO₄. Red oil yielded after evaporation of the solvent, was treated with alcohol to give yellow product and was further recrystallized from ethanol to give pure white solid compound 1(b) [48, 49].


A mixture of octamethoxy calix[4]resorcinarene 2(a) (4.8 g, 5.0 mmol) and anhydrous potassium carbonate (10.6 g, 70 mmol), and potassium iodide (1.3 g, 8.0 mmol) in dry acetone (150 mL) was heated to reflux under nitrogen for at least 30 minutes. Then ethyl bromoacetate (8.4 mL, 50 mmol) was added and the reaction mixture was refluxed for 7 days. After removal of acetone, the residue was dissolved in water, acidified with HCl and extracted with CHCl₃. The yellow organic layer was separated and dried with MgSO₄. Red oil was yielded after evaporation of the solvent, which was treated with alcohol to give yellow product and was further recrystallized from ethanol to give pure white solid compound 2(b).

A mixture of compound 1(b) (4.0 g, 2 mmol) and hydrazine hydrate (15 mL, 80%) in 20 mL of ethanol was refluxed for 24 hours and was then allowed to cool at room temperature. Pink coloured solid precipitated out which was washed with absolute alcohol to get pure compound 1(c).


A mixture of compound 2(b) (5.0 g, 3.9 mmol) and hydrazine hydrate (20 mL, 80%) in 25 mL of ethanol was refluxed for 24 hours and was then allowed to cool at room temperature. The organic solvent and excessive amine were removed under vacuum. The residue was crystallized in ethanol to give white solid 2(c).

Microwave assisted synthesis of 5, 11, 17, 23 tetramethyl calix[4]resorcinarene hydrazide

A mixture of compound 5, 11, 17, 23 tetramethyl calix[4]resorcinarene acetate 1(b) (4.0 g, 2 mmol) and hydrazine hydrate (15 mL, 80%) in 10 mL of ethanol was placed in Kenstar domestic microwave oven at 10% output for 10-15 minutes. The reaction was done immediately and the pink residue was obtained, which was filtered and dried in oven and then the residue was crystallized in ethanol to give white solid 1(c).

Microwave assisted synthesis of octamethoxy calix[4]resorcinarene hydrazide

A mixture of compound octamethoxy resorcin[4]arene acetate 2(b) (5.0 g, 3.9 mmol) and hydrazine hydrate (20 mL, 80%) in 20 mL of ethanol was placed in microwave at 20% for 10 minutes and was then allowed to cool at room temperature. The organic solvent and excessive amine were removed under vacuum. The residue was crystallized in ethanol to give white solid 2(c).

4. Results and discussion

4.1. Synthesis and spectroscopic characterization

4.1.1 Conventional and microwave assisted synthesis of calix[4]resorcinarene derivatives

A new modified protocol has been developed for the synthesis of 1(a) and 2(a), Scheme 1 and 2, which represents conventional and microwave irradiation method of synthesis involving acid catalyzed cyclo-condensation of 2-methyl resorcinol 1(a) and 1,3 dimethoxy benzene 2(a) with p-hydroxy benzaldehyde. The reaction time and yield obtained are compared in table 1. The physical properties and spectroscopic characterisation of the products obtained by both the methods are same. Physical properties and spectroscopic characterisation were carried out by FT-IR, $^{13}$C NMR, $^1$H NMR and ESI -MS are presented in table 2 and 3, respectively.

The $^{13}$C NMR spectra of compound 1(a) displayed a peak at 9.79, 34.56 ppm for -CH$_3$, 111.14, 125.75 ppm for aromatic ring and 162.58 ppm for -OH containing carbon Fig. 1 and $^{13}$C NMR spectra of compound 2(a) displayed a peak at 39.63, 55.69 ppm for -OCH$_3$, 113.78, 130.02 ppm for Ar and 154.3 for -OH containing carbon Fig. 2. The $^1$H NMR spectra of compound 1(a) displayed a peak at 8.7-7.6 ppm, for phenolic -OH, and one singlet at 5.48 for -Ar$_2$CH. In addition, compound 1(a) showed overlapping of two doublets around 6.49 and 6.37 ppm for aromatic -CH as shown in Fig. 3. The $^1$H NMR spectra of compound 2(a) displayed in Fig. 4, showed singlet peak at 8.79 ppm for -OH, 5.49 ppm for -Ar$_3$CH and 3.64 ppm, 3.59 ppm for -OCH$_3$. The FT-IR spectra of compound 1(a) and 2(a) displayed a band within the range of 3345 cm$^{-1}$ to 3150 cm$^{-1}$ corresponding to -OH.
The FT-IR, $^1$H NMR, $^{13}$C NMR, elemental analysis and ESI-MS (table 2 and 3) of 5,11,17,23 tetramethyl calix[4]resorcinarene 1(a) and octamethoxy calix[4]resorcinarene 2(a). Microwave irradiation method is in agreement with reported data of these macrocycles synthesized by conventional method. With the reduced reaction time and high yield, microwave irradiation method for the synthesis was found to be a useful alternative to conventional methods [19-25]. ESI-MS of 1(a) and 2(a) is shown in Fig. 5 and 6.

Analysis of the data obtained for compound 1(a) and 2(a) confirms the following facts:

i. One of the goals of “green chemistry” is to avoid or to reduce the use of solvents in organic chemistry. When microwave method was applied, less solvent was required for acid catalyzed cyclo-condensation reaction.

ii. 5,11,17,23 tetramethyl calix[4]resorcinarene 1(a) was synthesized in 4-5 hours and 2(a) was synthesized in 6-8 hours by the conventional method with a yield of 65-70%, whereas with microwave irradiation technique, it took only 5-10 minutes with a yield of 80-90% [50, 51].

iii. There is a rudimentary difference between microwave irradiation and conventional heating. The conventional method is an inward heat transfer (from the heating device, e.g., the wall of the reactors for jacketed vessels, to the medium) while in microwave irradiation, the thermal power is generated in situ due to the interaction of polar molecules or ionic species with the electric field. Physical acceleration (higher temperature) and chemical activation (enhancement in dipole moment) happens using microwave irradiation, which reduces the reaction time and enhances the yield.
4.1.2. Functionalization with ester moiety

In order to design new types of valuable receptor molecules and supramolecular structures, various methods have been developed for complete and selective modification on the upper rim and lower rim of resorcinarenes. The study was initiated on the possibility of introducing nitrogen containing functional groups to aryl resorcinarenes, which can be potentially used in supramolecular chemistry [48].

The O-alkylation of phenolic hydroxyl groups is the first choice for the modification at the upper rim of resorcinarenes, and have been used in the no. of synthesis of alkyl resorcinarenes [52, 53], but aryl resorcinarenes, have much lower solubility in common organic solvents such as chloroform, ethanol, acetonitrile, etc. Compound 1(a) and 2(a) can still be fully O-alkylated with ethyl bromoacetate in presence of K$_2$CO$_3$, KI and dry acetone system for relatively longer times (5-7 days) to give ester derivative 1(b) and 2(b) in 50-60 % yield, which makes it possible to modify resorcinarene on the upper rim.

The formation of 5,11,17,23 tetramethyl resorcinaryl acetate 1(b) and octamethoxy calix[4]resorcinarene tetra acetate 2(b) derivatives were characterized by FT-IR, $^1$H NMR Fig. 9 and 10, $^{13}$C NMR Fig. 7 and 8 and ESI-MS Fig. 11 and 12 are reported in table 3. The FT-IR spectra of compound (1b) showed C=O stretching at band 1762 cm$^{-1}$ Fig. 18 and $^1$H NMR showed a peak at 4.3-4.5 ppm for -OCH$_2$, 1.1-1.3 for CH$_3$ and compound (2b) showed C=O stretching at band 1755cm$^{-1}$ Fig. 19, $^1$H NMR spectra showed a peak at 4.4-4.6 ppm for -OCH$_2$, 1.29-1.3 for CH$_3$ respectively.
4.1.3. Functionalization with hydrazide moiety

The preparation of calix[4]resorcinarene hydrazide derivative, 1(c) and 2(c), from ethyl calix[4]resorcinarene acetate 1(b) and 2(b) was easily achieved by refluxing 1(b) and 2(b) in excess of hydrazine hydrate for 24 hours to yield 95% of 1(c) and 80% of 2(c). 1(c) and 2(c) were duly characterized by FT-IR, $^1$H NMR, $^{13}$C NMR and ESI-MS. The spectroscopic data is presented in table 3. FT-IR spectra of compound 1(a), 1(b), 1(c) and 2(a), 2(b), 2(c) have been compared in Fig. 13 and F14, respectively. Compound 1(c) gives water dispersible colloidal solution, which has been used effectively to reduce the gold and silver ions to yield gold and silver nanoparticles, respectively. It may be noted that $^1$H NMR and likewise, $^{13}$C NMR of compound 1(c) could not be obtained, which may be due to its poor solubility in any solvent. However, a clear mass spectrum (ESI-MS) of compound 1(c) was observed, Fig.17. $^{13}$C NMR, $^1$H NMR, and ESI-MS of compound 2(c) are shown in Fig.15, Fig.16 and Fig. 18, respectively. Poor solubility of compound 1(c) in comparison to compound 2(c) may be attributed to 12 hydrazide group present on its periphery. These hydrazide groups may be forming strong intermolecular and intramolecular hydrogen bond to yield only a colloidal solution rather than clear solution.

4.1.4. Determination of crystal structure

Single crystal structure study of compound 1(a) suitable for X-ray structure analysis was obtained from a solution of DMF and methanol and 2(a) from a solution of DMSO and methanol. The diffraction data was collected at 110.2 K using a Bruker Smart-CCD diffractometer (graphite-monochromated MO Ka radiation: A= 0.071073
nm). The structure was solved \textit{via} the direct method and refined by means of full-matrix least squares on $F^2$. All the calculations were performed using the SHELXTL crystallographic software package. A summary of crystallographic relevant data and molecular structure of compound (1a) is shown in supporting data, the four resorcinol units in the ring were divided into two groups with two resorcinol rings almost perpendicular to the other two resorcinol rings, which shows the resorcinarene in chair ($C_{2h}$) conformation.

\textbf{Crystal data and structure refinement of compound 1(a)}

\begin{itemize}
  \item Identification code: clxahm
  \item Empirical formula: C$_{74}$H$_{90}$N$_{5}$O$_{18}$
  \item Formula weight: 1351.52
  \item Temperature: 110(2) K
  \item Wavelength: 0.71073 Å
  \item Crystal system: Triclinic
  \item Space group: P-1

  \item Unit cell dimensions:
    \begin{align*}
      a &= 10.6640(12) \text{ Å} \quad \alpha = 75.923(2) \text{ deg.} \\
      b &= 11.4574(13) \text{ Å} \quad \beta = 78.762(2) \text{ deg.} \\
      c &= 14.7021(17) \text{ Å} \quad \gamma = 77.736(2) \text{ deg.}
    \end{align*}

  \item Volume: 1683.1(3) Å$^3$
  \item Density (calculated): 1.333 Mg/m$^3$
  \item Absorption coefficient: 0.096 mm$^{-1}$

  \item $F(000)$: 720
\end{itemize}
Crystal size 0.74 x 0.64 x 0.53 mm

Theta range for data collection 1.86 to 28.29 deg.

Index ranges -14 <= h <= 14, -14 <= k <= 15, -18 <= l <= 18

Reflections collected 13727

Independent reflections 7419 [R(int) = 0.0194]

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9511 and 0.9326

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 7419 / 0 / 456

Goodness-of-fit on F^2 1.041

Final R indices [I>2 sigma(I)] R1 = 0.0426, wR2 = 0.1171

R indices (all data) R1 = 0.0494, wR2 = 0.1225

Largest diff. peak and hole 0.435 and -0.235 eÅ^-3
ORTEP diagram of compound 1(a) with atom numbering scheme (50% probability factor for the thermal ellipsoids: lattice DMF molecules are omitted for clarity)

Pluto diagram of the compound 2(a) with atom numbering scheme
Conclusion

In recent years, microwave technology has created an undeniable place for itself in chemical laboratory practice as a very effective and non-polluting method for activating reactions. With this in view, a simple, fast, efficient, economical and green approach has been developed for the formation of parent calix[4]resorcinarenes and their derivatives based on microwave irradiation. The most important results of this approach when compared with the previously reported methods are the optimization of yield and reaction time. A new approach was developed to synthesize the hydrazide derivatives from the esterification of parent calix[4]resorcinarene. Two new calix[4]resorcinarene hydrazide were synthesized and characterized. The structures of all the synthesized compounds were confirmed on the basis of their elemental analysis, X-ray crystallography, FT-IR, ESI-MS, $^1$H NMR and $^{13}$C NMR spectroscopic techniques.
Table 1. Comparison of reaction time and yield obtained for calix[4]resorcinarene and its derivatives by conventional and microwave method

<table>
<thead>
<tr>
<th>Compound Code</th>
<th>Reaction time (hr/min)</th>
<th>Yield (%)</th>
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<td>Conventional method (hours)</td>
<td>Microwave method (minutes)</td>
<td>Conventional method</td>
<td>Microwave method</td>
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<tr>
<td>1a</td>
<td>4-5</td>
<td>3-5</td>
<td>65</td>
<td>80</td>
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<td>1b</td>
<td>-</td>
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<td>56</td>
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<tr>
<td>1c</td>
<td>24</td>
<td>10-15</td>
<td>85</td>
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<td>2a</td>
<td>7-8</td>
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<tr>
<td>2b</td>
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<tr>
<td>2c</td>
<td>24</td>
<td>10-12</td>
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<td>80</td>
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Table 2. Various physical properties of calix[4]resorcinarene and its functionalized derivative

<table>
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<tr>
<th>Compound Code</th>
<th>Molecular formula</th>
<th>Molecular weight (gm)</th>
<th>Melting point (°C)</th>
<th>Color</th>
<th>Analysis (%) (Practical)</th>
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<td>1a</td>
<td>C₅₆H₄₈O₁₂</td>
<td>913</td>
<td>&gt;300</td>
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<td>71.35, 5.01, -</td>
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<tr>
<td>1b</td>
<td>C₁₆₄H₁₂₀O₃₆</td>
<td>1964</td>
<td>151–153</td>
<td>white</td>
<td>63.21, 6.05, -</td>
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<td>1c</td>
<td>C₈₀H₉₆N₂₄O₂₄</td>
<td>1777</td>
<td>&gt;250</td>
<td>Pink-white</td>
<td>53.75, 5.38, 18.27</td>
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<tr>
<td>2a</td>
<td>C₆₀H₅₆O₁₂</td>
<td>969</td>
<td>320(decompose)</td>
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<td>74.50, 5.80</td>
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<td>2b</td>
<td>C₇₆H₆₀O₂₀</td>
<td>1313</td>
<td>165</td>
<td>Yellowish white</td>
<td>69.40, 6.24</td>
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<tr>
<td>2c</td>
<td>C₆₈H₇₂N₈O₁₆</td>
<td>1257</td>
<td>&gt;300</td>
<td>White</td>
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### Table 3. Spectroscopic characterization of compound

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<td>2b</td>
<td>56.1, 96.5, 156.3, 121.4,33.9</td>
<td>4.4-4.6 (-OCH$_3$)</td>
<td>3.4-3.6</td>
<td>6.6-6.1</td>
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<td></td>
<td>31, 155.3 65.3, 162.2, 61.3,</td>
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<td>2c</td>
<td>56.1, 96.5, 156.3, 121.4, 33.9</td>
<td>3.6-3.5</td>
<td>6.34-7.12</td>
<td>5.56</td>
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Fig. 1 $^{13}$C NMR of 5,11,17,23 tetramethyl calix[4]resorcinarene
Fig. 2 $^{13}$C NMR of octamethoxy calix[4]resorcinarene
Fig. 3 $^1\text{H}$ NMR of 5,11,17,23 tetramethyl calix[4]resorcinarene

Fig. 4 $^1\text{H}$ NMR of octamethoxy calix[4]resorcinarene
Fig. 5 Mass spectra of 5,11,17,23 tetramethyl calix[4]resorcinarene

Fig. 6 Mass spectra of octamethoxy calix[4]resorcinarene
Fig. 7 $^{13}$C NMR of 5,11,17, 23 tetramethyl calix[4]resorcinarene acetate
Fig. 8 $^{13}$C NMR of octamethoxy calix[4]resorcinarene tetraacetate
Fig. 9 $^1$H NMR of 5,11,17,23 tetramethyl calix[4]resorcinarene acetate
Fig. 10 $^1$H NMR of octamethoxy calix[4]resorcinarene tetraacetate
Fig. 11 Mass spectra of 5,11,17,23 tetramethyl calix[4]resorcinarene acetate

Fig. 12 Mass spectra of octamethoxy calix[4]resorcinarene tetraacetate
Fig. 15 $^{13}$C NMR of octamethoxy calix[4]resorcinarene tetrahydrazide
Fig. 16 $^1$H NMR of octamethoxy calix[4]resorcinarene tetrahydrazide
Fig. 17 Mass spectra of 5,11,17,23 tetramethyl calix[4]resorcinarene polyhydrazide
Fig. 18 Mass spectra of octamethoxy calix[4]resorcinarene tetrahydrazide
References:


