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ORIGINAL ARTICLE

Synthesis and characterization of novel chiral calix[4]arene bearing (*R*)-(+)-1-phenylethylamine bonded silica particles

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Abstract Two novel chiral di- and tri-amide derivatives of *p-tert*-butylcalix[4]arene were synthesized by (*R*)-(+)-1-Phenylethylamine via convenient reactions and then immobilized on aminopropyl functionalized silica particles. The prepared chiral calix[4]arenes and their silica polymers (Calix-SP1 and Calix-SP2) were characterized using ^{1}H NMR, ^{13}C NMR, FT-IR, and thermal and elemental analysis techniques.

Keywords Calix[4]arene · Silica particles · Chiral · Immobilization · Amide

Introduction

A macrocyclic compound forms a stable complex with a guest molecule by entrapping it in its cavity. Since the 1980s, calixarene, which is formed by the condensation of *p*-alkyl phenol and formaldehyde under basic conditions, has attracted much attention as a macrocyclic platform. A number of books have been published concerning the synthesis, structural features and host–guest interactions of calixarenes (For general references on calixarenes, see [1–3]). More specifically, the subject of chemical recognition and separation of ions has been addressed in several publications [4–11]. On the other hand, only a few reviews of the biochemical recognition of calixarenes are available, for example, on peptido- and glycoconjugates and the role of hydrogen-bonding interactions [12], on neoglycoconjugates with large rigidified cavities [13] and on synthetic receptors [14]. Molecular recognition, and in particular chiral recognition, is one of the most fundamental and significant processes in living systems [15–18]. Chiral recognition can contribute to the understanding of biochemical systems and offer new perspectives on the development of pharmaceuticals, enantioselective sensors, catalysts and other molecular devices [19, 20]. Among the several types of host molecules that engage in recognition, calixarenes offer a number of advantages, in terms of their selectivity and efficiency of binding. The introduction of chiral substituents on the lower rim, through the phenolic oxygens or at the para positions of the calix[4]arene skeleton, or via the synthesis of 'inherently' chiral derivatives could, in turn, lead to the chirality of the artificial receptors. Chiral receptors that are based on the calixarene platform may have potential applications in the preparation, separation, and analysis of enantiomers [21, 22]. In this regard, investigations of the synthesis of chiral calix[4]arene derivatives have attracted considerable attention. Here, we wish to report the synthesis of new chiral calix[4]arene derivatives and their immobilization on silica particles, as well as the characterization of chiral calix[4]arene-anchored silica particles. Our findings may have important applications including in regard to the HPLC stationary phase materials used in the separation of various chiral molecules.

Experimental

Materials and methods

Silica gel (particle size 5 μm, pore size 100 Å and specific surface area 300–400 m^2/g) were obtained from Merck (Darmstadt, Germany) and used after drying in a vacuum at

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80 °C for 24 h. Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. Analytical grade solvents were used. Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Elemental analyses were performed on a Leco CHNS-932 analyzer. ^{1}H and ^{13}C-NMR spectra were recorded with a Varian 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hertz. Specific rotations were measured on A Krüss Optronic polarimeter. FT-IR spectra were recorded with a PerkinElmer spectrum 100. Thermal gravimetric analysis (TG) was carried out with Seteram thermogravimetric analyzer. Analysis was performed from room temperature to 900 °C at heating rate of 10 °C min^{-1} in argon atmosphere with a gas flow rate of 20 mL min^{-1}.

Synthesis

3-Aminopropyl silica gel

Silica gel (2 g) was suspended in 100 mL dry toluene and then, 3-aminopropyltrimethoxysilane (APTMS, 2 mL) was added upon this suspension. The mixture was stirred and heated to reflux under nitrogen atmosphere for 24 h. The solid was filtered and washed in sequence with toluene, MeOH and distilled water. The product (3-aminopropyl-bonded silica, APS) was dried at 100 °C under vacuum for 8 h. Elemental analysis: C, 5.68; H, 1.66; N, 1.96%.

*Compound **3***

(*R*)-(+)-1-Phenylethylamine (20.0 mmol) was dissolved in 1:2 toluene/MeOH mixture (60 mL) and added dropwise to a solution of 5,11,17,23-tert-butyl-25,27 methoxycarbonylmethoxy-26,28-hydroxycalix[4]arene **2** and (4.0 mmol) in 20 mL toluene with continuous stirring at room temperature for about 30 min. The reaction mixture was refluxed and the reaction was monitored by TLC. After the substrate had been consumed, the solvent was evaporated under reduced pressure and the residue triturated with MeOH to give a crude product. The crude products were purified by flash chromatography and recrystallized. Yield: 46%, mp: 251–253 °C. $[\alpha]_D^{20} = -19.1^o$ (c 0.5, $CHCl_3$); FT-IR: 3355 cm^{-1}(OH), 1680 cm^{-1} (NHCO); ^{1}H NMR ($CDCI_3$): δ 1.00 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$) 1.63 (d, 6H, J=7.0 Hz, $CHCH_3$), 3.29 (d, 2H, J= 13.4 Hz, $ArCH_2Ar$), 3.42 (d, 2H, J=13.5 Hz, $ArCH_2Ar$), 4.04 (d, 2H, J=13.4 Hz, $ArCH_2Ar$), 4.07 (d, 2H, J=13.6 Hz, $ArCH_2Ar$), 4.28 ve 4.62 (d, 2H, J= 15.4 Hz, OCH_2CO), 5.17 (p, 2H, J=7.0 Hz, NH-CH-CH_3), 6.85 (d, 4H, J=6.6 Hz, ArH), 7.06 (d, J=6.6 Hz, 4H, ArH), 7.19–7.27 (m, 10H, Ph-H), 7.44 (s, 2H, ArOH), 9.21 (d, 2H, NH). ^{13}C NMR ($CDCl_3$) δ 21.48, 31.15, 31.86, 32.35, 32.55, 34.17, 34.39, 49.71, 75.14, 125.64, 125.96, 126.14, 126.74, 126.87, 127.07, 127.55, 127.59, 128.69, 132.34, 132.46, 143.09, 143.41, 148.56, 149.43, 149.72,167.66. Calculated for $C_{64}H_{78}O_6N_2$: C, 79.16; H, 7.63; N, 2.89. Found: C, 73.75; H, 7.99; N, 2.91.

*Compound **4***

To a mixture of **3** (2 g, 2.06 mmol) and K_2CO_3 (0.71 g, 5.15 mmol) in acetone (200 mL), methylbromoacetate (1 mL, 8.24 mmol) was added and the reaction mixture was stirred at reflux for 24 h. After cooling, the solvent was removed under reduced pressure. The remaining solid was taken up CH_2Cl_2 and washed with 1 M HCl and water. The organic layer was dried over $MgSO_4$ and evaporated to give a white powder. The product was crystallized from methylene chloride and hexane to obtain pure 4. Yield: %90, m.p: 175–177 °C, $[\alpha]_D^{20} = -9.7^o$ (c 0.5, $CHCl_3$); FT-IR; 1765 cm^{-1} (CO), 1682 cm^{-1} (NHCO); ^{1}H NMR ($CDCI_3$): δ 0.87 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$) 1.62 (d, 6H, J=7.0 Hz, $CHCH_3$), 3.16 (d, 2H, J =13.4 Hz, $ArCH_2Ar$), 3.25 (d, 2H, J=13.5 Hz, $ArCH_2Ar$), 3.55 (s,6H, OCH_3), 4.20 (s, 4H, OCH_2), 4.53 (d, 2H, J= 13.1 Hz, $ArCH_2Ar$), 4.59 (d, 2H, J=13.1 Hz, $ArCH_2Ar$), 4.61 ve 4.79 (d, 2H, J= 15.4 Hz, OCH_2CO), 5.36 (p, 2H, J=7.0 Hz, NH-CH-CH_3), 6.48 (m, 4H, ArH), 7.06 (m, 4H, ArH), 7.20–7.43 (m, 10H, Ph-H), 8.02 (d, 2H, NH). ^{13}C NMR ($CDCl_3$) δ= 21.28, 31.36, 31.42, 31.47, 31.77, 31.82, 31.91, 33.91, 34.32, 48.27, 51.86, 71.54, 75.35, 125.40, 126.58, 127.25, 128.62, 131.10, 131.23, 134.51, 134.58, 143.07, 145.36, 146.20, 152.73, 153.85, 169.02, 171.33. Calculated for $C_{70}H_{86}O_6N_2$: C, 80.00; H, 8.19; N, 2.66. Found: C, 80.09; H, 8.17; N, 2.61.

*Immobilization of compound **3** onto APS (Calix-SP1)*

Compound **4** (1.0 g) was dissolved in dry toluene (50 mL) and APS (1.5 g) was added to this solution. The mixture was refluxed under nitrogen atmosphere for 48 h and the product was filtered and washed in sequence with toluene, CH_2Cl_2, MeOH and distilled water. Subsequently, Calix-SP1 was obtained, and dried at 100 °C under vacuum for 8 h, then cooled to room temperature in a desiccator. Elemental analysis: C, 15.71; H, 1.96; N, 1.25%.

*Compound **6***

A solution of the tetraester (**5**) (2 g, 2.14 mmol) in CH_2Cl_2 (100 ml) was treated with acetic acid (4 ml, 100%) and HNO_3 (6.7 mL, 65%). The solution was stirred at room

temperature for 45 min and then washed with water. The dried solution was concentrated to leave a white solid which on recrystallisation from ethanol–water furnished (**6**) (4.8 g, 88%) as white crystals. Yield: 91%, mp: 146–148 °C. FT-IR: 3435 cm^{-1} (OH), 1765 cm^{-1} (CO), 1740 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ 0.83 (s, 18H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$), 3.20 (d, 2H, *J*=13.1 Hz, $ArCH_2Ar$), 3.27(d, 2H, *J*=12.9 Hz, $ArCH_2Ar$), 3.77 (s, 3H, OCH_3), 3.81 (s, 6H, OCH_3), 4.36 (d, 2H, *J*=15.6 Hz, OCH_2), 4.56 (d, 2H, *J*=13.4 Hz, $ArCH_2Ar$), 4.60 (s, 2H, OCH_2), 4.86 (d, 2H, *J*=15.6 Hz, OCH_2), 4.94 (d, 2H, *J*=12.9 Hz, $ArCH_2Ar$), 4.98 (s, 2H, OCH_2), 6.54 (d, 2H, *J*=2.1 Hz, ArH), 6.63 (d, 2H, *J*=2.1 Hz, ArH), 7.15 (s, 2H, ArH), 7.16 (s, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 31.19, 31.82, 31.88, 33.94, 34.33, 34.47, 51.85, 52.26, 71.27, 72.72, 73.28, 125.34, 125.75, 126.14, 126.22, 132.32, 132.38, 134.71, 135.58, 146.09, 146.30, 147.68, 151.12, 151.32, 155.02, 170.17, 170.40, 171.99. Calculated for $C_{55}H_{69}O_{12}$: C, 71.66; H, 7.49. Found: C, 71.63; H, 7.51.

Compound 7

(*R*)-(+)-1-Phenylethylamine (20.0 mmol) was dissolved in 1:2 toluene/MeOH mixture (60 mL) and added dropwise to a solution of compound **6** (4.0 mmol) in 20 mL toluene with continuous stirring at room temperature for about 30 min. The reaction mixture was refluxed and the reaction was monitored by TLC. After the substrate had been consumed, the solvent was evaporated under reduced pressure and the residue triturated with MeOH to give a crude product. The crude products were purified by flash chromatography and recrystallized. Yield; 85%, mp: 140–141 °C, $[\alpha]_D^{20} = -9.9^o$ (*c* 0.5, $CHCl_3$); FT-IR: 3435 cm^{-1}(OH), 1740 cm^{-1} (CO), 1685 cm^{-1} (NHCO); ^1H NMR ($CDCl_3$): δ 0.81 (s, 9H, $C(CH_3)_3$), 0.83 (s, 9H, $C(CH_3)_3$), 1.20-1.40 (m, 21H, $C(CH_3)_3$, $NHCH\mathit{CH_3}$), 1.65 (d, 3H, *J* =7.0 Hz, $NHCH\mathit{CH_3}$), 1.70 (d, 3H, *J* =7.0 Hz, $NHCH\mathit{CH_3}$), 3.11-3.31 (m, 4H, $ArCH_2Ar$), 4.10-4.29 (m, 6H, $ArCH_2Ar$, $COCH_2$), 4.41-4.63 (m, 6H, $ArCH_2Ar$, $COCH_2$), 5.01 (p, 1H, *J* =7.0 Hz, $NH\mathit{CH}CH_3$), 5.20, 5.26 (2xp, 2H, *J* =7.0 Hz, $NH\mathit{CH}CH_3$), 5.90 (d, 1H, *J* =7.8 Hz, CONH), 6.43-6.57 (m, 4H, ArH), 7.05-7.47 (m, 19H, ArH, Ph-H), 7.96 (d, 2H, *J* =7.8 Hz, CONH). ^{13}C NMR ($CDCl_3$): δ 21.22, 21.59, 21.65, 31.28, 31.73, 31.79, 31.82, 33.96, 34.28, 34.41, 48.97, 49.06, 49.64, 75.35, 75.57, 75.69, 75.75, 125.76, 126.19, 126.20, 126.59, 126.63, 126.79, 126.92, 127.25, 128.61, 128.66, 128.70, 128.73, 129.03, 143.04, 143.54, 143.81, 145.87, 145.93,1 45.96, 146.02, 146.46, 147.43, 151.18, 151.33, 151.78, 153.43, 168.25, 168.42, 168.46. Calculated for $C_{76}H_{90}O_9N_3$: C, 76.76; H, 7.57; N, 3.53. Found: C, 76.63; H, 7.61; N, 3.57.

Compound 8

A solution of compound **7** (1.0 g, 0.82 mmol) in dry THF (50 mL) containing oxalyl chloride (0.20 mL, 2.56 mmol) was heated under reflux under nitrogen for ca. 3 h. Removal of the solvent and residual oxalyl chloride under reduced pressure furnished compound **8**. The product was used in subsequent preparations without purification**.**

Immobilization of compound 8 onto APS (Calix-SP2)

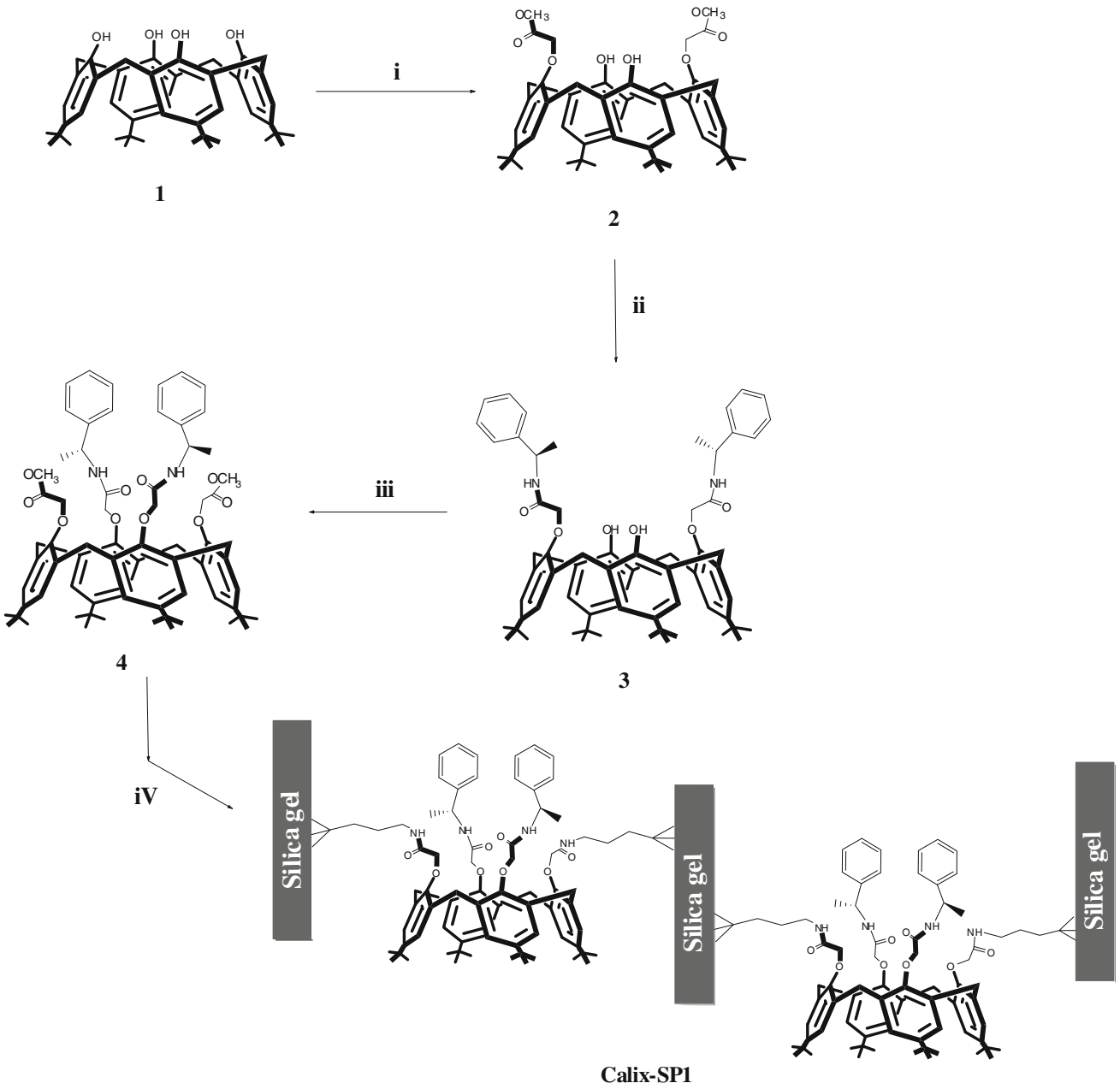
Compound **8** (0.80 g; 0.64 mmol), APS (1.5 g), and dry toluene (25 mL) were added to a 50 mL round-bottomed flask equipped with a magnetic stirrer, and stirred at room temperature for 5 h under nitrogen atmosphere and then refluxed for 5 h. The cooled mixture was filtered and washed in sequence three times with warm toluene, acetone, methanol, and distilled water. The product was dried at 100 °C to give Calix-SP2, under vacuum, for 3 h and kept in a desiccator before use.

Results and discussion

Silica gel (particle size 5 μm, pore size 100 A° and a specific surface area 300–400 m^2/g) was treated with 3-(aminopropyl)-trimethoxysilane in toluene, and under nitrogen atmosphere to yield aminopropyl functionalized silica particles (APS) which was characterized by elemental and thermal analysis [23].

Scheme 1 shows the synthesis of chiral calix[4]arene di-amide bonded silica particles (Calix-SP1). Compounds **1** and **2** were prepared according to the reported procedure [24]. The chiral calix[4]arene derivative **3** was synthesized by refluxing **2** with (*R*)-(+)-1-phenylethylamine in toluen:MeOH (1:1). Compound **3** was obtained in pure form as a white solid, via chromatography on SiO_2 with EtOAc/Hexane (1:7) as eluent in 46% yield. Then, compound **3** was reacted with $BrCH_2CO_2CH_3$ in the presence of K_2CO_3 in acetone, for 24 h, to afford **4** in 90% yield. ^1H NMR spectra of **3** showed amide protons at 9.21 ppm while FT-IR spectra showed only a characteristic amide band at about 1680 cm^{-1}. ^1H NMR spectra of **4** showed amide protons at 8.02 and methoxy protons at 3.55 ppm while FT-IR spectra showed characteristic amide bands at about 1682 cm^{-1} and the appearance of an ester carbonyl band at 1765 cm^{-1}. Also, the synthesis of **4** was supported by the appearance of carbon signals at 169.0 and 171.3 ppm belong to C=O groups of amide and ester in ^{13}C-NMR (Fig. 2), respectively. The ^1H NMR and ^{13}C NMR spectra of **4** were depicted in Figs. 1 and 2.

As shown in Scheme 1, the immobilization of chiral calix[4]arene di-amide derivative **4** on aminopropyl



Scheme 1 The preparation of Calix-SP1. *Reagents and conditions*: (i) $BrCH_2CO_2CH_3$, K_2CO_3, acetone, reflux, 90%; (ii) (*R*)-(+)-1-phenylethylamine, toluen:MeOH, reflux, 46%; (iii) $BrCH_2CO_2CH_3$, K_2CO_3, acetone, reflux, 90%; (iv) APS, toluen, reflux, 48 h

functionalized silica particles (APS) was made in dry toluene over the course of 48 h. The product was filtered and washed in sequence with toluene, CH_2Cl_2, methanol and distilled water. Subsequently, Calix-SP1 was obtained, and dried at 100 °C under vacuum for 8 h, then cooled to room temperature in a desiccator. The chiral calix[4]arene diamide anchored silica gel (Calix-SP1) was characterized using FT-IR, thermal and elemental analyses. The FT-IR spectrum of Calix-SP1 showed strong absorption bands at 1659 and 1050 cm^{-1} attributed to the carbonyl groups of 4 and Si–O–Si units of silica gel, respectively. A broad band between 3650 and 3150 cm^{-1} was assigned to the OH groups of the silica gel and adsorbed water (Fig. 3). The total losses in the temperature range of 40–900 °C were 5.2 and 16.3% for APS and Calix-SP1, respectively, due to the breakage of **4** anchored on the silica-gel surface together with the condensation of the remaining silanol groups, which produced siloxane (Fig. 4). Also, the elemental analysis results were summarized in Table 1. Elemental analysis (based on carbon content) revealed that 0.947 mmol of aminopropyl and 0.177 mmol of **4** were attached per gram of the silica support.

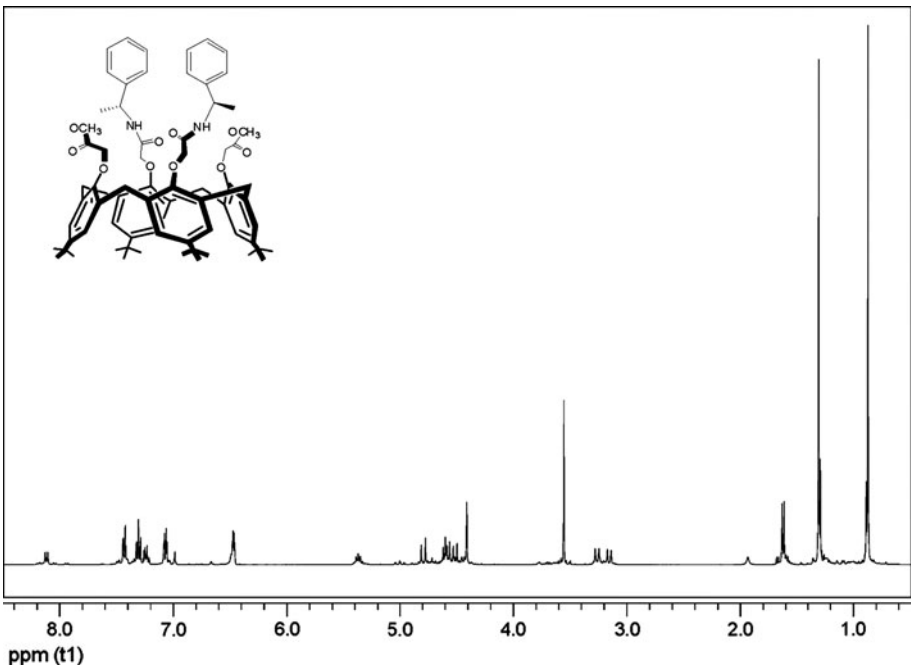


Fig. 1 ^{1}H-NMR spectrum in $CDCl_3$ for structure **4**

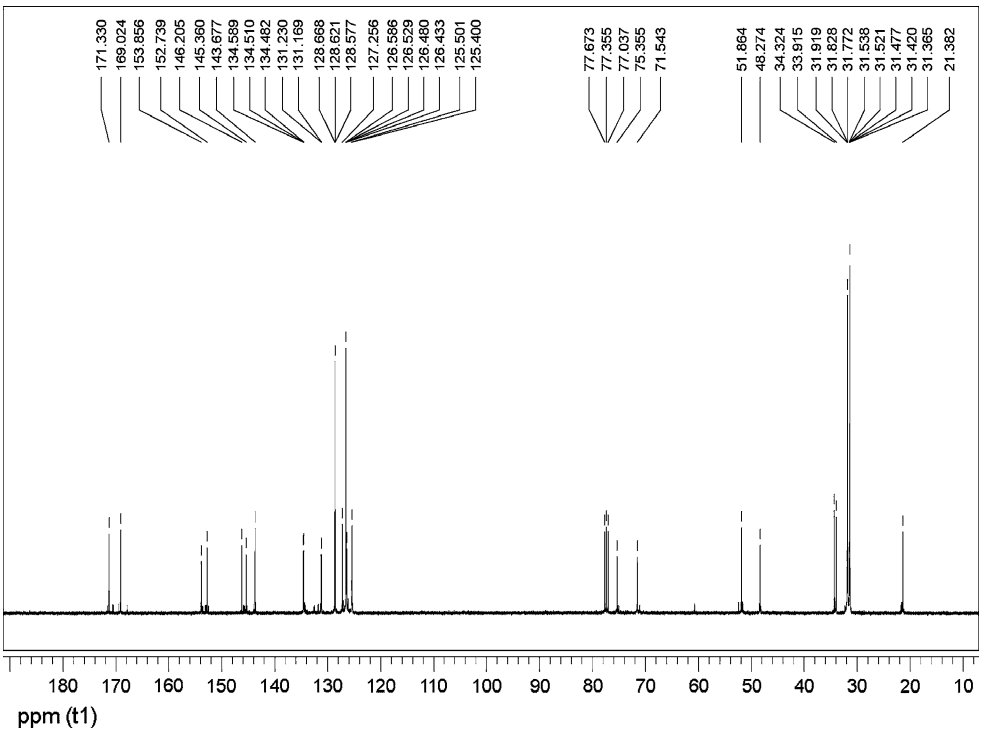


Fig. 2 ^{13}C-NMR spectrum in $CDCl_3$ for structure **4**

The synthetic route of chiral calix[4]arene tri-amide bonded silica particles was depicted in Scheme 2. The tetra methylester derivative of calix[4]arene **5** was prepared according to a known procedure [25]. The selective hydrolysis of **5** was achieved with HNO_3-AcOH (1:1.7) in CH_2Cl_2, to give the triester monoacid **6** in 91% yield. To prepare *p*-tert-butyl-calix[4]arene tri-amide derivative **7**, 1-phenylethylamine was dissolved in a 1:2 toluene–MeOH mixture and added dropwise to a solution of compound **6** in toluene, which was continuously stirred at room temperature for about 30 min. Then, the reaction mixture was refluxed for 3d and the tri-amide monoacid derivative **7** was isolated in 85% **y**ield.

The formation of the chiral tri-amide derivative of *p-tert*-butyl calix[4]arene **7** was confirmed by the appearance of the characteristic amide band at 1685 cm^{-1} and by the

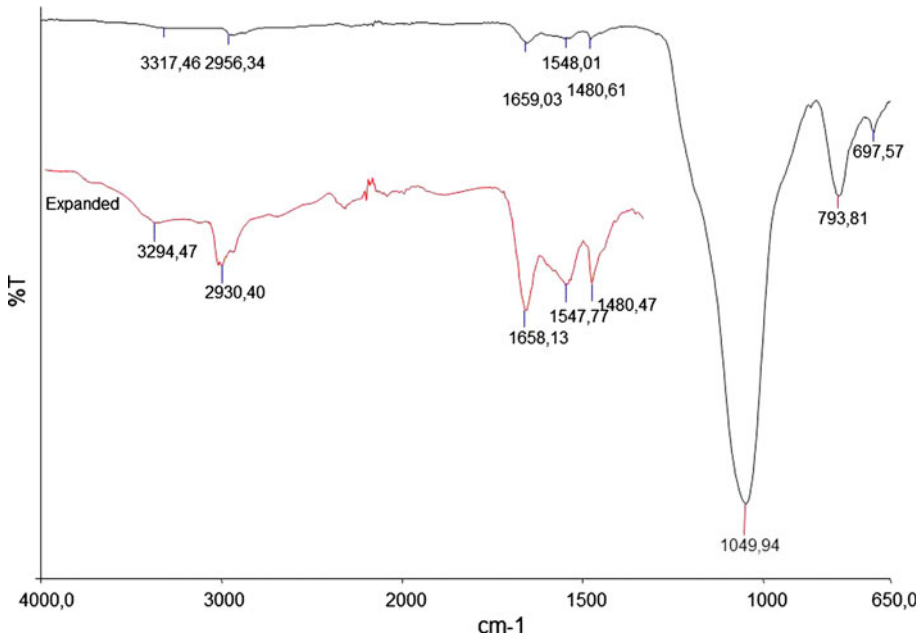


Fig. 3 FT-IR spectra of Calix-SP1

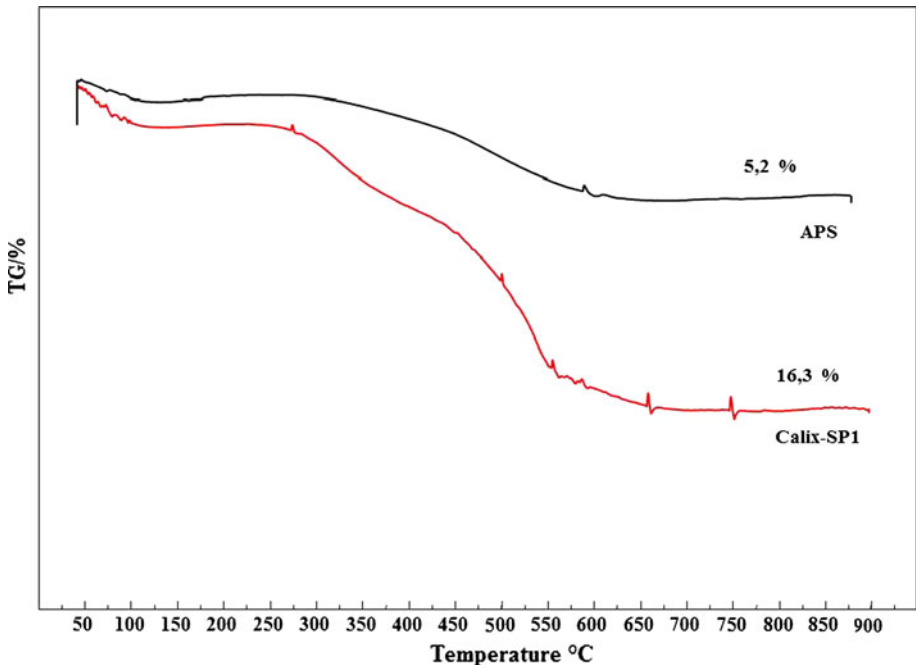


Fig. 4 TG curve of APS and Calix-SP1

disappearance of the ester carbonyl band at about 1765 cm^{-1} in its FT-IR spectra. The characteristic conformations of calix[4]arenes were conveniently estimated using the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^1H NMR spectroscopy. ^1H NMR data showed that compound **7** had a cone conformation. A typical AB pattern was observed for the methylene bridge $ArCH_2Ar$ protons at 3.22 (J = 13 Hz), 4.19 (J = 13 Hz), 4.50 (J = 13 Hz) for **7** in ^1H NMR**.** Also, compound **6** displayed truly dramatic asymmetry because the *tert*-butyl groups appeared as four signals in the ^1H NMR spectrum. The ^1H NMR and ^{13}C NMR spectra of **7** were depicted in Figs. 5 and 6. The tri-amide monoacid **7** obtained was converted to tri-amide monoacid chloride derivative **8** using oxalyl chloride in dry THF. The product was used unpurified, so as to be immobilized on aminopropyl silica particles.

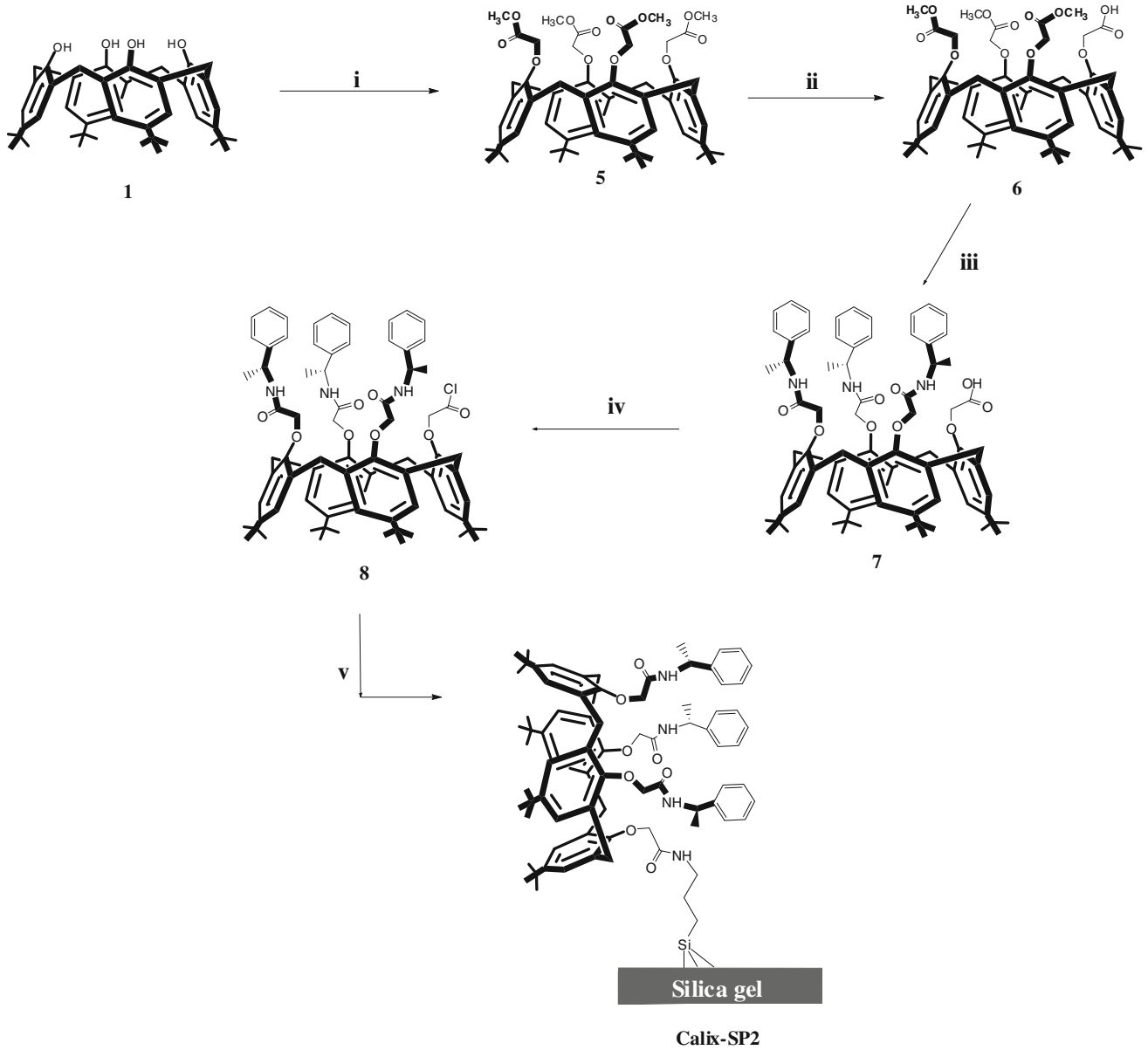
To prepare chiral calix[4]arene tri-amide bonded silica particles (Calix-SP2), a mixture of **8** and aminopropyl silica gel in toluene were stirred at room temperature for 5 h under nitrogen atmosphere and then refluxed for 5 h, as in Scheme 2. The cooled mixture was filtered and washed

Table 1 Elemental analysis results

Bonded phase	C%	H%	N%	Bonded amount (mmol g^{-1})[a]
APS	5.68	1.66	1.96	0.947
Calix-SP1	15.71	1.96	1.25	0.177
Calix-SP2	16.01	1.72	1.35	0.169

[a] Bounded amount (mmol/g) = %C × 10/12n, where %C is the mass percentage of carbon in product and n is the number of carbon in the ligand

in sequence three times with warm toluene, acetone, methanol, and distilled water. The product was dried at 100 °C in a vacuum for 8 h, to give Calix-SP2 and, then cooled to room temperature in a desiccator. The characterization of Calix-SP2 was made using FT-IR, thermal and elemental analyses. The results of elemental analysis showed that the carbon content of APS and Calix-SP2 was 5.68 and 16.01%, respectively (Table 1). Depending on carbon content, the amount of **8** bonded onto APS was found to be approximately 0.169 mmolg^{-1}. Also, from the FT-IR results, it was observed that compound **8** was immobilized onto APS because the 3550–3150, 1666, and 1051 cm^{-1} bands in the FT-IR spectra corresponded to O–H, NH–C=O and Si–O–Si, respectively (Fig. 7). The total losses in the temperature range of 40–900 °C were 9.1 and 17.1% for APS and Calix-SP2, respectively. Thermal



Scheme 2 The preparation of Calix-SP2. *Reagents and conditions*: (i) $BrCH_2CO_2CH_3$, K_2CO_3, acetone, reflux, 90%; (ii) HNO_3-AcOH, CH_2Cl_2, rt, 91%; (iii) (*R*)-(+)-1-phenylethylamine, toluen:MeOH, reflux, 85%; (iv) oxalyl chloride, THF; (v) APS, toluen, reflux, 5 h

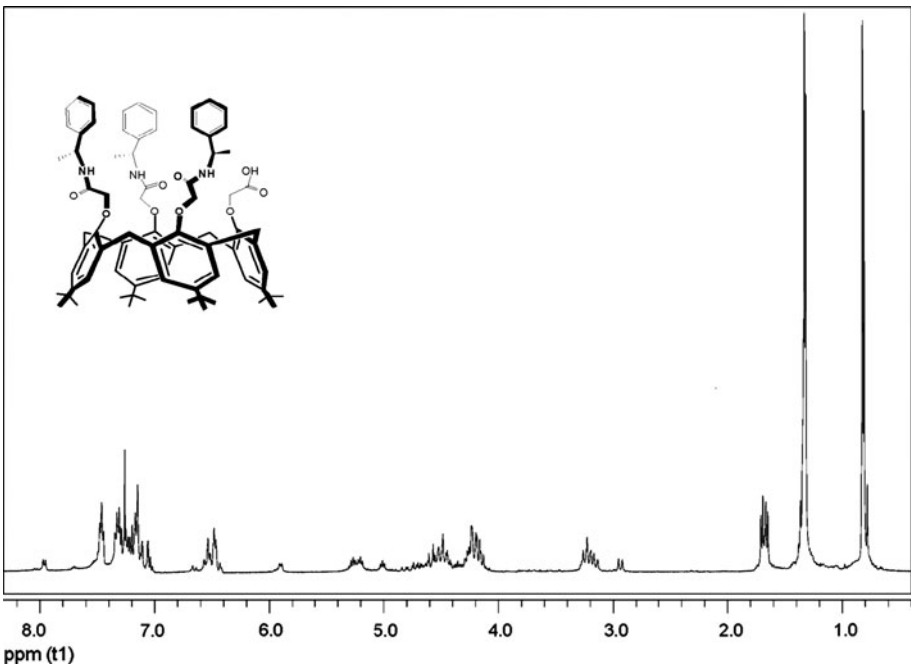


Fig. 5 ^{1}H-NMR spectrum in $CDCl_3$ for structure **7**

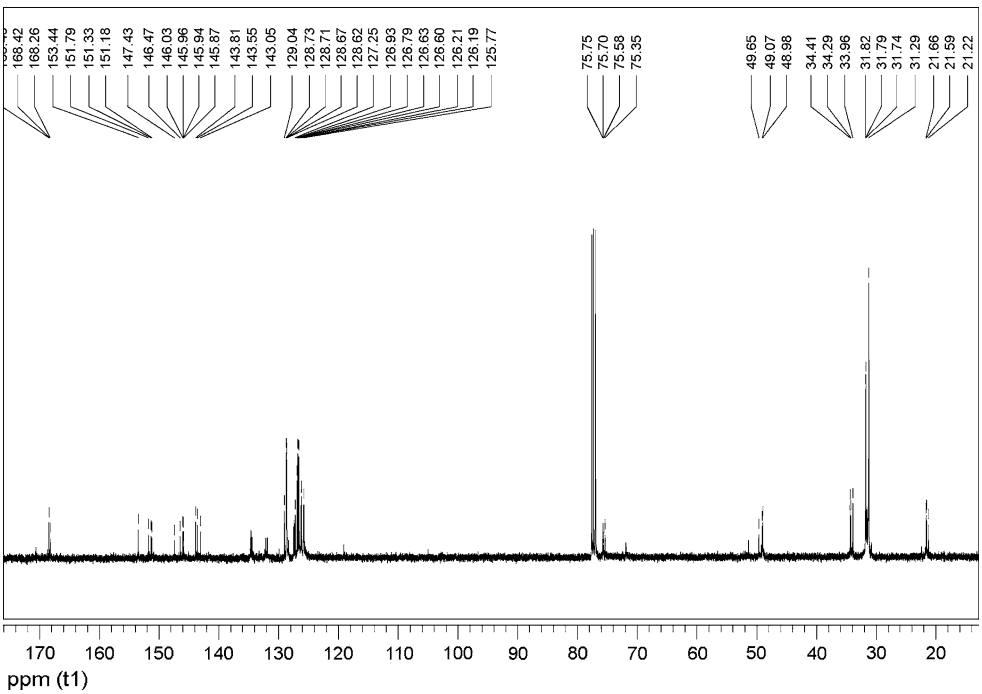


Fig. 6 ^{13}C-NMR spectrum in $CDCl_3$ for structure **7**

analysis showed a direct relationship of the loss of mass to the amount of the **8** anchored on the silica-gel surfaces (Fig. 8).

Conclusion

In conclusion, we synthesized two novel chiral calix[4]arene bearing (*R*)-(+)-1-phenylethylamine and immobilized them onto aminopropyl silica particles. The structures proposed for novel chiral calix[4]arenes were confirmed by ^{1}H-NMR, ^{13}C-NMR, FT-IR and elemental analysis. Also, the characterization of prepared chiral calix[4]arene anchored silica particles was made using thermal and elemental analysis techniques. Since chiral calixarenes have attracted increasing attention in recent years due to their potential as enantioselective artificial receptors and asymmetric catalysts, these novel chiral calix[4]

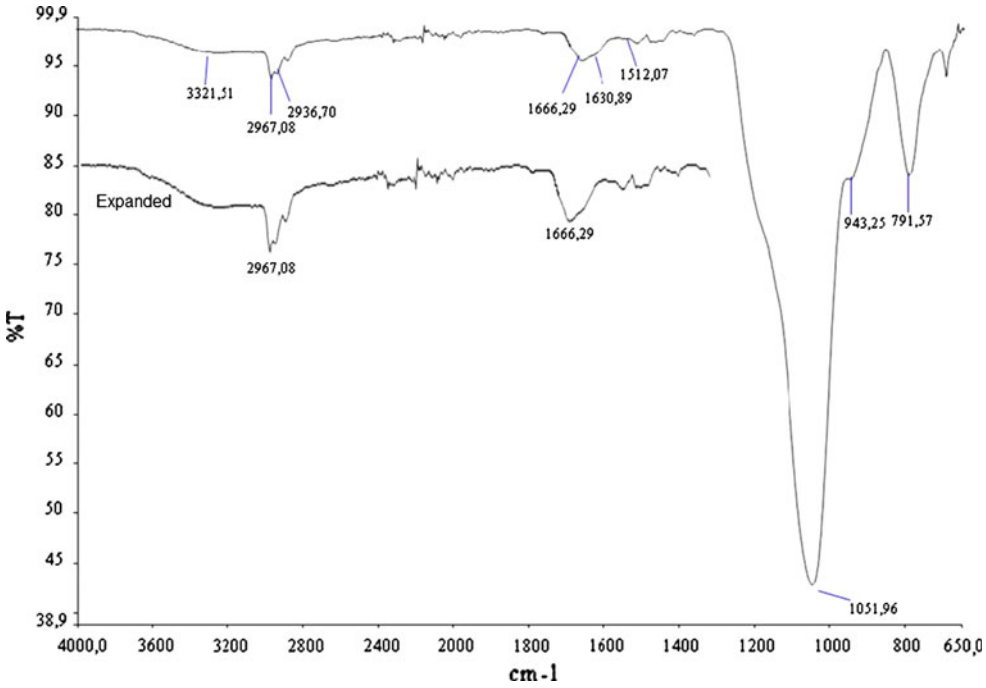


Fig. 7 FT-IR spectra of Calix-SP2

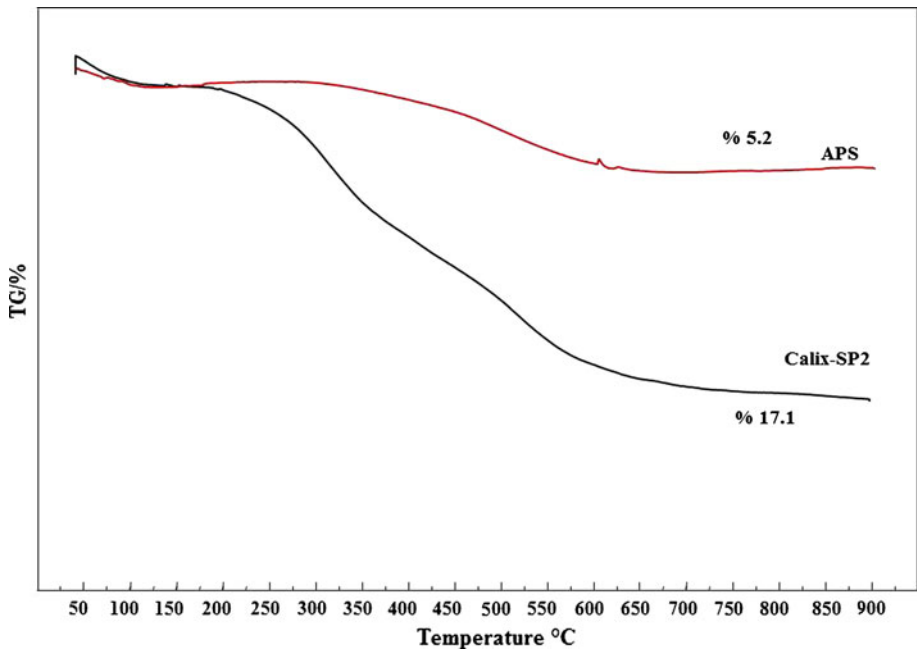


Fig. 8 TG curve of APS and Calix-SP2

arene bonded silica particles may be useful as HPLC stationary phase materials for the separation of various chiral molecules and catalyst in asymmetric synthesis.

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