# CHAPTER II

# EXPERIMENTAL SECTION

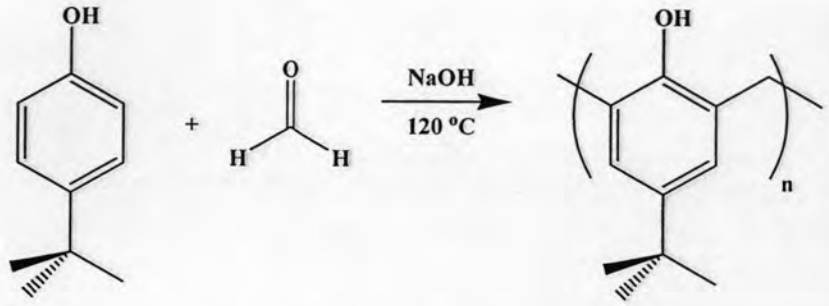
## 2.1 Synthesis

**Materials:** Propargyl bromide, propargyl alcohol, iodine, bromine, morpholine, *p*-toluenesulfonyl chloride, copper(I) iodide, copper(I) chloride, pyrrolidine, propyl bromide, *tert*-butyldimethylsilyl chloride (TBDMSCl), imidazole, sodium hydride, potassium carbonate, barium oxide, barium hydroxide octahydrate, triethylamine, pyridine, ethylamine solution (70% aq.), hydroxylamine hydrochloride, butylamine, ammonium chloride, sodium thiosulphate, potassium hydroxide, sodium hydroxide, sodium sulphate, *p-tert*-butylphenol, formaldehyde, and diphenyl ether were purchased from Fluka (Switzerland). Dibutyltindilaurate, 4-dimethylaminopyridine (DMAP), benzyl bromide, 4-pentyn-1-ol, 3-butyn-1-ol, butylamine, hexyl isocyanate, phenyl isocyanate, butyl isocyanatoacetate, triphosgene and potassium bromide were purchased from Aldrich (USA). Butyl isocyanate was purchased from Merck (Germany) and used without further purification. *tert*-Butylcalix[4]arene was prepared according to the literature [99]. Tetrahydrofuran was distilled over sodium and benzophenone, acetonitrile was distilled over calcium hydride and stored over molecular sieves. Other analytical grade solvents were used as received without further distillation. For extraction and chromatography, solvents were commercial grade and they were distilled prior to use. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Column chromatography was performed using Merck silica gel 60 (70-230 mesh).

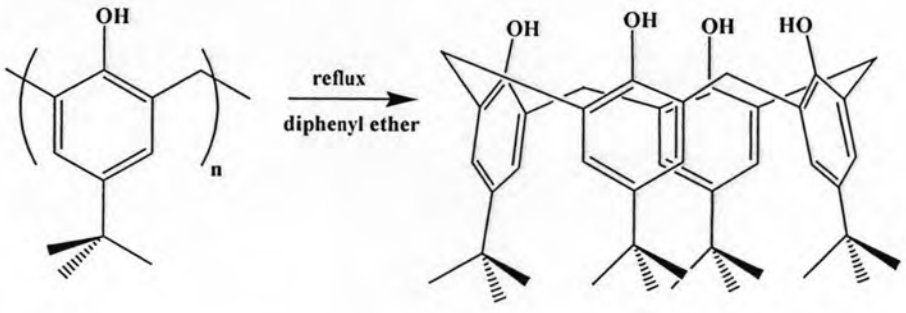
**Analytical instruments:** $^{1}H$ and $^{13}C$ NMR spectra were recorded on Varian Mercury 400 MHz NMR spectrometer (Varian, USA) and AC Bruker 200, 250 and 500 MHz NMR spectrometer (Bruker, USA) using the residual solvent proton resonance of $CDCl_3$ at 7.26 ppm as the reference. Elemental analysis was performed on PE 2400 Series II (Perkin-Elmer, USA). Infrared spectra were measured from KBr pellets on a Nicolet Impact 410 FT-IR spectrophotometer (Thermo Nicolet, USA). UV/vis spectra were recorded on Varian Cary 100 Bio UV-Visible spectrophotometer (Varian, USA). The melting points were recorded on Mettler Toledo DSC 823e (Mettler Toledo, USA) in aluminium standard cell (40 $\mu$L) as a holder at the heating rate of 10 °C/min. Raman spectra were performed on a Perkin-Elmer 1760 FT-IR spectrophotometer (Thermo Fisher Scientific company, USA) with an Nd:YAG laser source and a Raman sample compartment attached to the FT-IR instrument. GPC analysis was measured on a Water system (Waters, USA), with a Water 600 pump, a Water 2414 refractive index detector and a set of Styragel® columns (HR1, HR3 and HR4) at 35 °C using tetrahydrofuran as an eluent at the flow rate of 1.00 mL/min. TEM images were recorded on a JEOL JEM-2100 transmission electron microscope (JEOL, Japan). AFM images were taken on a SPA 400 atomic force microscope (Seiko, Japan). Mass analysis was conducted with a Microflex MALDI-TOF MS (Bruker Daltonics, Germany). The particle size measurements were made by a dynamic light scattering using a Nanosizer (Malvern instruments, England). UV-irradiation was performed by UV light source (TUV 15W/G15 T18 lamp; Philips, Holland).

### 2.1.1 Preparation of calix[4]arene

**Polymerization**




**Cracking**

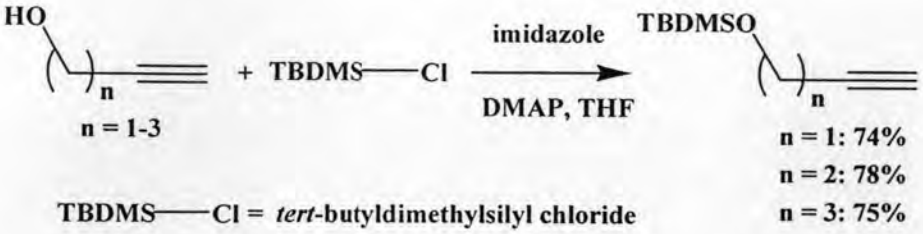



**Polymerization step:** In a 1 L, a round bottomed flask equipped with a magnetic stirring bar a mixture of *tert*-butylphenol (0.17 mmol, 25.00 g), 37% formaldehyde in ethanol (0.20 mmol, 15.50 mL) and sodium hydroxide (4 pellets) was stirred. The flask was left opened and stirred during heating at 100-120 °C on a heating mantle to allow the water by-product to escape from the reaction mixture. The stirring and heating was continued until a colorless liquid turned to spongy yellow solid as the water had evaporated. Then the reaction was cool down to room temperature. Over heating resulted in a low yield of the desired product in the following step due to the formation of green polymeric materials. The small amount of green polymer by-product, if formed, was disposed and only the yellow part of the precursor was brought to the next cracking step. The prepared precursor should be used within a few days to assure the high yield of *tert*-butylcalix[4]arene.

**Cracking step:** Two batches of the yellow polymer from the first step was crushed to powder and combined. In a 2 L, round bottomed flask equipped with a magnetic stirring bar, condenser, and a Dean-Stark trap, the precursor from polymerization process (25.00 g) was stirred in diphenyl ether (250 mL). The reaction flask and the Dean-Stark side arm were wrapped with heating jacket and cotton wool in aluminium foil in order to maintain the temperature. Then the mixture was refluxed on a heating mantle. The cracking process produced "pop" sound as the water was removed to from the highly viscous mixture. When the "pop" sound was completely subsided, the reaction was allowed to cool to room temperature. The pale brown color product was precipitated out by addition of ethyl acetate (400 mL). The product was washed stepwise with ethyl acetate (2×100 mL), acetic acid (50 mL), water (100 mL) and acetone (2×50 mL) yielding a white solid (82% yield).

### 2.1.2 Preparation of *tert*-butyldimethylsilyloxy alkyne

**General procedure**




To a stirred solution of alkynyl alcohol and DMAP in tetrahydrofuran was added *tert*-butyldimethylsilyl chloride followed by imidazole. The mixture was stirred at room temperature for 1 hr. The reaction mixture was concentrated by a rotary evaporator. The concentrated reaction mixture was added with $H_2O$ and extracted with dichloromethane. The combined organic extract was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and evaporated to dryness *in vacuo*. The residue was isolated by column chromatography with hexane.

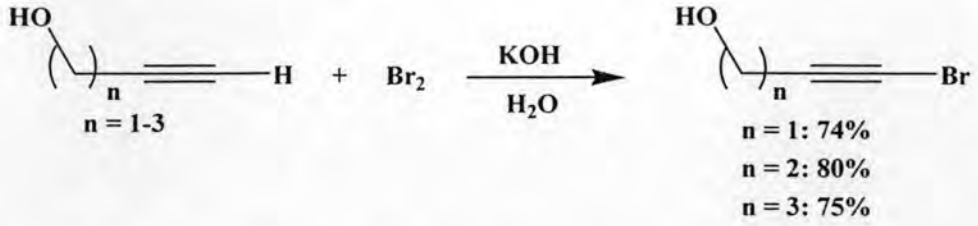
***tert*-butyldimethylsilyloxy-2-propyne:** According to urethane formation above, the compound was synthesized from propargyl alcohol (3.11 g, 55.48 mmol), *tert*-butyldimethylsilyl chloride (10.03 g, 66.57 mmol) and imidazole (6.42 g, 94.31mmol) in 200 mL of tetrahydrofuran. The residue was isolated by column chromatography with hexane as an eluent to afford colorless oil (6.99 g, 74% yield). $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 4.19 (d, 2H, $J$ = 4.0 Hz, $C\underline{H}_2CC$), 2.26 (t, 1H, $J$ = 2.0 Hz, $CC\underline{H}$), 0.79 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

***tert*-butyldimethylsilyloxy-3-butyne:** The compound was synthesized from 3-butynol (3.05 g, 43.52 mmol), *tert*-butyldimethylsilyl chloride (10.03 g, 52.22 mmol) and imidazole (6.42 g, 73.9 mmol) in 200 mL of tetrahydrofuran. The residue was isolated by column chromatography with hexane as an eluent to afford colorless oil (6.26 g, 78% yield). $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 3.67 (t, 2H, $J$ = 6.8 Hz, $OC\underline{H}_2$), 2.33 (t, 2H, $J$ = 4.0 Hz $C\underline{H}_2CC$), 1.89 (br, 1H, $CC\underline{H}$), 0.82 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

***tert*-butyldimethylsilyloxy-4-pentyne:** The compound was synthesized from 4-pentynol (2.75 g, 28.02 mmol), *tert*-butyldimethylsilyl chloride (5.07 g, 33.63 mmol) and imidazole (3.24 g, 47.64 mmol) in 100 mL of tetrahydrofuran. The residue was isolated by column chromatography with hexane as an eluent to afford colorless oil (4.46 g, 75% yield). $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 3.62 (t, 2H, $J$ = 6.4 Hz, $OC\underline{H}_2$), 2.29 (m, 2H, $C\underline{H}_2CC$), 2.12 (t, 1H, $J$ = 2.4 Hz, $CC\underline{H}$), 1.67 (m, 2H, $C\underline{H}_2$), 0.84 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

### 2.1.3 Preparation of bromo alkynol

**General procedure**




Bromine was added dropwise to KOH in $H_2O$ (500 mL) under stirring 0-5 °C. A pale yellow solution of KOBr was observed to form immediately. Propargyl alcohol was added to 1,4-dioxane to increase the solubility of the compound. The KOBr solution was added dropwise to the above mixture over 30 min at 5-10 °C and vigorously stirred for 30 min. This mixture was extracted with diethyl ether, the organic layers were separated, dried over $Na_2SO_4$ anhydrous, filtered, concentrated and isolated by column chromatography (dichloromethane) to afford bromo alkyn-1-ol.

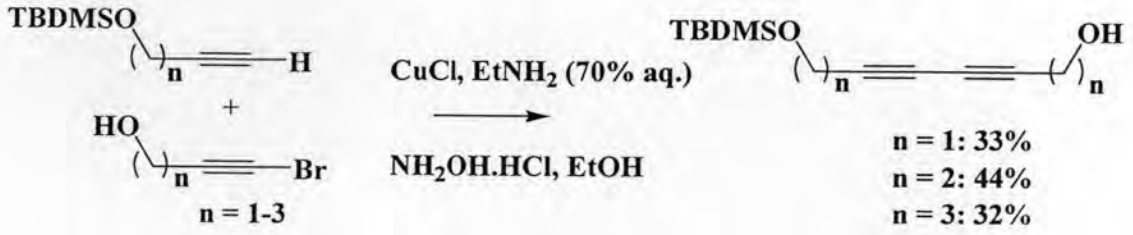
**3-Bromo-2-propynol:** The compound was synthesized from propargyl alcohol (9.80 g, 0.17 mol), bromine (83.81 g, 0.52 mol), KOH (78.47g, 1.40 mol) in 500 mL of $H_2O$. The residue was isolated by column chromatography with dichloromethane as an eluent to afford light yellow oil (17.46 g, 74% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.34 (s, 2H, C<u>H</u>$_2$), 1.72 (s, 1H, O<u>H</u>)

**4-Bromo-3-butynol:** The compound was synthesized from 3-butynol (4.00 g, 0.06 mol), bromine (27.36 g, 0.17 mol), KOH (25.62 g, 0.46 mol) in 200 mL of $H_2O$. The residue was isolated by column chromatography with dichloromethane as an eluent to afford light yellow oil (6.78 g, 80% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.77 (t, 2H, $J$ = 6 Hz, HOC<u>H</u>$_2$), 2.52 (t, 2H, $J$ = 10 Hz, C<u>H</u>$_2$CC), 2.21 (s, 1H, O<u>H</u>)

**5-Bromo-4-pentynol:** The compound was synthesized from 4-pentynol (3.41 g, 0.03 mmol), bromine (16.66 g, 0.10 mol), KOH (15.60 g, 0.28 mol) in 200 mL of $H_2O$. The residue was isolated by column chromatography with dichloromethane as an eluent to afford light yellow oil (4.92 g, 75% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ

(ppm): 3.78 (t, 2H, $J$ = 6.4 Hz, HOC$\underline{H}_2$), 2.53 (t, 2H, $J$ = 6.0 Hz, C$\underline{H}_2$CC), 1.80 (m, 2H, HOCH$_2$C$\underline{H}_2$), 1.61 (s, 1H, O$\underline{H}$)

### 2.1.4 Preparation of diacetylene by Cadiot-Chodkiewicz coupling




To a stirred solution of a mixture containing copper(I) chloride, hydroxylamine hydrochloride, and *tert*-butyldimethylsilyloxy alkyne in ethanol was added ethylamine (70% in water) 0 °C and the reaction mixture was allowed to stir at room temperature. Then the reaction mixture was added a degassed solution of bromo alkynol over a period of 30 min. After stirring at room temperature for 2 hr, solvents was removed under reduced pressure in *in vacuo* and the orange residue was poured into cold water then extract with diethyl ether. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed *in vacuo*. The crude product was isolated by column chromatography (ethyl acetate/hexane).

**6-*tert*-butyldimethylsilyloxy-2,4-hexadiynol:** The compound was synthesized from 3-bromo-2-propynol (2.38 g, 17.63 mmol), copper(I) chloride (0.06 g, 0.61 mmol), hydroxylamine hydrochloride (4.90 g, 70.51 mmol), ethylamine (70% in water) (7.00 mL) and *tert*-butyldimethylsilyloxy-2-propyne (3.60 g, 14.45 mmol) in 20 mL of ethanol. The residue was isolated by column chromatography (ethyl acetate/hexane = 10/90) to afford light yellow oil (0.83 g, 33% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.26 (s, 2H, SiOC$\underline{H}_2$), 4.22 (s, 2H, C$\underline{H}_2$OH), 0.78 (s, 9H, C(C$\underline{H}_3$)$_3$), 0.00 (s, 6H, C$\underline{H}_3$)

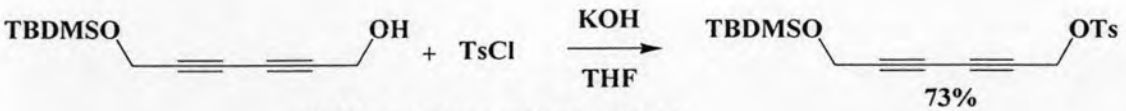
**8-*tert*-butyldimethylsilyloxy-3,5-octadiynol:** The compound was synthesized from 4-bromo-3-butynol (2.94 g, 19.73 mmol), copper(I) chloride (0.06 g, 0.66 mmol), hydroxylamine hydrochloride (2.52 g, 35.98 mmol), ethylamine (70% in water) (7.00 mL) and *tert*-butyldimethylsilyloxy-3-butyne (3.03 g, 16.44 mmol) in 20 mL of ethanol. The residue was isolated by column chromatography (ethyl

acetate/hexane = 15/85) to afford light yellow oil (1.83 g, 44% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.67 (m, 4H, $C\underline{H}_2OH$ and $C\underline{H}_2OSi$), 2.46 (t, 2H, $J$ = 6.4 Hz, $SiOCH_2C\underline{H}_2$), 2.40 (t, 2H, $J$ = 7.2 Hz, $HOCH_2C\underline{H}_2$), 0.82 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

**10-*tert*-butyldimethylsilyloxy-4,6-decadiynol:** The compound was synthesized from 5-bromo-4-hexynol (3.15 g, 17.80 mmol), copper(I) chloride (0.06 g, 0.66 mmol), hydroxylamine hydrochloride (2.5 g, 35.98 mmol), ethylamine (70% in water) (7.00 mL) and *tert*-butyldimethylsilyloxy-5-hexyne (3.15 g, 14.83 mmol) in 20 mL of ethanol. The residue was isolated by column chromatography (ethyl acetate/hexane = 13/87) to afford light yellow oil (1.46 g, 32% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.70 (t, 2H, $J$ = 5.2 Hz, $C\underline{H}_2OSi$), 3.62 (t, 2H, $J$ = 5.6 Hz, $HOC\underline{H}_2$), 2.34 (m, 2H, $C\underline{H}_2CC$), 2.29 (m, 2H, $C\underline{H}_2CC$), 1.73 (m, 2H, $CH_2CH_2C\underline{H}_2$), 1.66 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.12 (s, 1H, $O\underline{H}$), 0.84 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

### 2.1.5 Preparation of diacetylenic tosylate

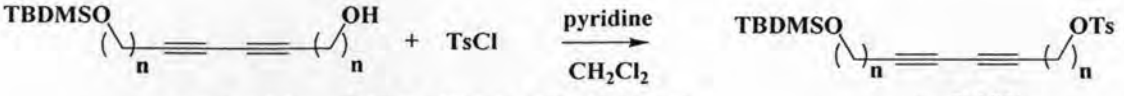
**6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate**




**TsCl = *p*-toluene sulfonyl chloride**

To a stirred solution of a mixture containing 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynol (1.31 g, 5.84 mmol) and potassium hydroxide (0.65 g, 11.68 mmol) in tetrahydrofuran (6 mL) was added dropwise the solution of tosyl chloride (1.67 g, 8.76 mmol) in tetrahydrofuran (4 mL) at 0 °C and the reaction mixture was allowed to stir at room temperature for 2 hr. The reaction mixture was concentrated by a rotary evaporator. The concentrated reaction mixture was added with 2 M HCl (50 mL) and extracted with dichloromethane (3×50 mL). The combined organic extract was washed with brine (100 mL), dried over anhydrous $Na_2SO_4$, filtered and evaporated to dryness *in vacuo*. The residue was isolated by column chromatography with ethyl acetate/hexane (3/97) as an eluent to yield 73% (1.61 g) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (d, 2H, $J$ = 7.2 Hz, $\underline{H}_{ortho}$-Ar), 7.26 (d, 2H, $J$ = 7.6 Hz, $\underline{H}_{meta}$-Ar), 4.67 (s, 2H, $SO_3C\underline{H}_2$), 4.25 (s, 2H, $C\underline{H}_2OSi$), 2.35 (s, 3H, $C\underline{H}_3$-Ar), 0.79 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

**General procedure for C6 and C10**




n = 2 and 3 TsCl = *p*-toluene sulfonyl chloride

n = 2: 78%
n = 3: 73%

To a stirred solution of a mixture containing diacetylenic alcohol and pyridine in dichloromethane was added dropwise the solution of tosyl chloride in dichloromethane at 0 °C and the reaction mixture was allowed to stir at room temperature for overnight. The reaction mixture was concentrated by a rotary evaporator. The concentrated reaction mixture was added with 2 M HCl and extracted with dichloromethane. The combined organic extract was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and evaporated to dryness *in vacuo*. The residue was isolated by column chromatography with ethyl acetate/hexane as an eluent.

**8-*tert*-butyldimethylsilyloxy-3,5-octadiynyl tosylate:** The compound was synthesized from 8-*tert*-butyldimethylsilyloxy-3,5-octadiynol (2.54 g, 10.06 mmol), pyridine (1.63 mL, 20.13 mmol) and tosyl chloride (2.30 g, 12.08 mmol) in 30 mL of dichloromethane. The residue was isolated by column chromatography (ethyl acetate/hexane = 10/90) to afford yellow solid (3.19 g, 78% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, 2H, $J$ = 7.6 Hz, $\underline{H}_{ortho}$-Ar), 7.29 (d, 2H, $J$ = 7.6 Hz, $\underline{H}_{meta}$-Ar), 4.01 (t, 2H, $J$ = 7.2 Hz, $SO_3C\underline{H}_2$), 3.65 (t, 2H, $J$ = 7.2 Hz, $C\underline{H}_2OSi$), 2.55 (t, 2H, $J$ = 7.2 Hz, $SO_3CH_2C\underline{H}_2$), 2.39 (t, 2H, $J$ = 7.2 Hz, $C\underline{H}_2CH_2OSi$), 2.39 (s, 3H, $C\underline{H}_3$-Ar), 0.82 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

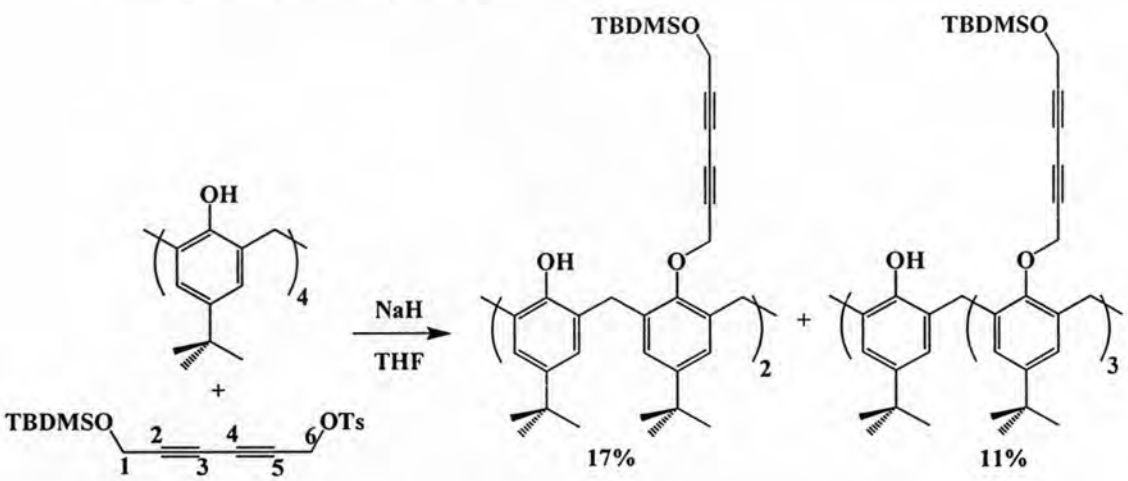
**10-*tert*-butyldimethylsilyloxy-4,6-decadiynyl tosylate:** The compound was synthesized from 10-*tert*-butyldimethylsilyloxy-4,6-decadiynol (2.31 g, 7.49 mmol), pyridine (1.21 mL, 14.97 mmol) and tosyl chloride (1.71 g, 8.98 mmol) in 250 mL of dichloromethane. The residue was isolated by column chromatography (ethyl acetate/hexane = 10/90) to afford yellow solid (2.53 g, 73% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, 2H, $J$ = 7.6 Hz, $\underline{H}_{ortho}$-Ar), 7.31 (d, 2H, $J$ = 7.6 Hz, $\underline{H}_{meta}$-Ar), 4.07 (t, 2H, $J$ = 7.2 Hz, $SO_3C\underline{H}_2$), 3.61 (t, 2H, $J$ = 7.2 Hz, $C\underline{H}_2OSi$), 2.41 (s, 3H, $C\underline{H}_3$-Ar), 2.27 (m, 4H, $C\underline{H}_2CCCC\underline{H}_2$), 1.80 (m, 2H, $CH_2C\underline{H}_2CH_2$), 1.66 (m, 2H, $CH_2CH_2C\underline{H}_2$), 0.82 (s, 9H, $C(C\underline{H}_3)_3$), 0.00 (s, 6H, $C\underline{H}_3$)

### 2.1.6 Alkylation of calix[4]arene with diacetylenic tosylate

**General procedure**

Calix[4]arene and sodium hydride which was washed by hexane were dissolved in tetrahydrofuran, and the solution was stirred at room temperature for 1 hr. Then the solution of diacetylenic tosylate in tetrahydrofuran was added by dropwise. After adding was complete, the reaction mixture was stirred, refluxed for 24 hr and monitored by thin layer chromatography method. The reaction mixture was allowed to cool to room temperature and quenched by ethanol to decompose sodium hydride. The solvent was removed *in vacuo* and then the residue was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ anhydrous, filtered and removed solvent *in vacuo*. The residue was isolated by column chromatography.

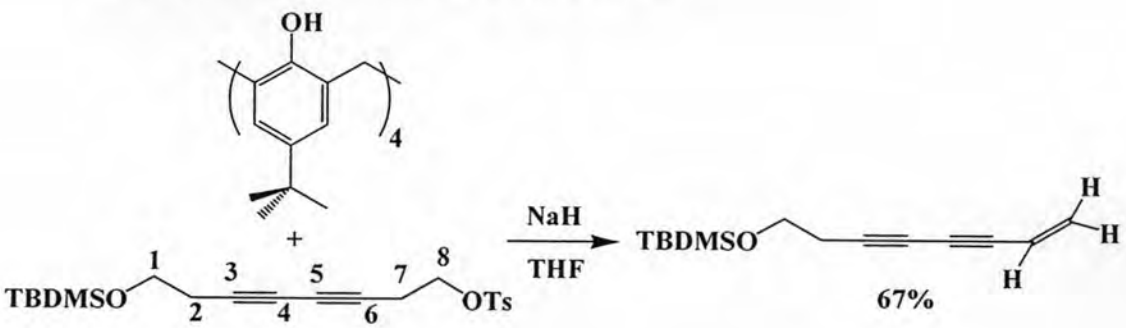
**Calix[4]arene containing C6 diyne units:**




The compound was synthesized from calix[4]arene (0.75 g, 1.16 mmol), sodium hydride (0.28 g, 11.56 mmol) and 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate (3.50 g, 9.25 mmol) in 30 mL of tetrahydrofuran. The residue was isolated by column chromatography (ethyl acetate/hexane = 3/97) to afford disubstituted as a white solid and trisubstituted calix[4]arene as a white solid (17% and 11% yield, respectively). $^1$H NMR (500 MHz, $CDCl_3$) δ (ppm) for disubstituted calix: 7.08 (s, 4H, Ar-H), 6.70 (s, 4H, Ar-H), 6.26 (s, 2H, O$\underline{H}$), 4.81 (s, 4H, OC$\underline{H_2}$), 4.39 (s, 4H, C$\underline{H_2}$OSi), 4.33 (d, 4H, $J$ = 13.2 Hz, ArC$\underline{H_2}$Ar), 3.34 (d, 4H, $J$ = 13.2 Hz, ArC$\underline{H_2}$Ar), 1.32 (s, 18H, (C$\underline{H_3}$)$_3$), 0.91 (s, 18H, (C$\underline{H_3}$)$_3$), 0.88 (s, 18H, C(C$\underline{H_3}$)$_3$), 0.13

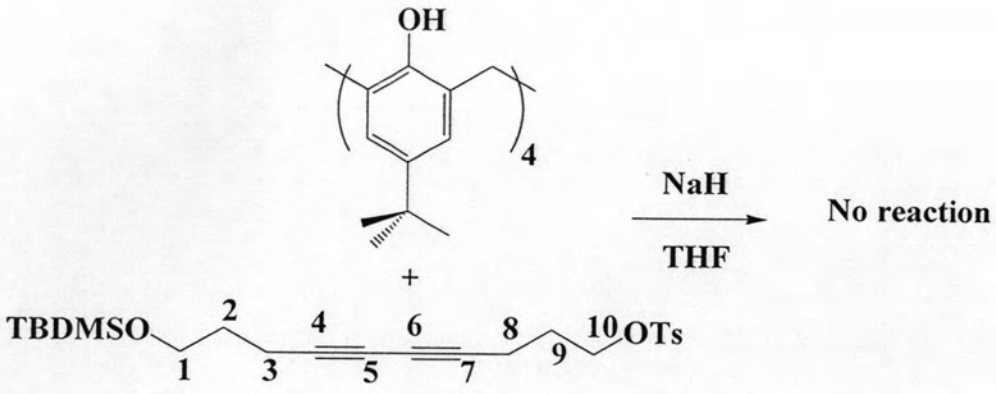
(s, 12H, C$\underline{H}_3$), for trisubstituted calix: 7.01 (s, 2H, Ar-H), 6.96 (s, 2H, Ar-H), 6.44 (s, 2H, Ar-H), 6.40 (s, 2H, Ar-H), 4.88 (s, 1H, OH), 4.50 (d, 4H, $J$ = 11.2 Hz, OC$\underline{H}_2$), 4.41 (d, 2H, $J$ = 13.6 Hz, ArC$\underline{H}_2$Ar), 4.27 (m, 8H, 3×C$\underline{H}_2$OSi and OC$\underline{H}_2$), 4.22 (d, 2H, $J$ = 13.6 Hz, ArC$\underline{H}_2$Ar), 3.18 (d, 2H, $J$ = 13.6 Hz, ArC$\underline{H}_2$Ar), 3.11 (d, 2H, $J$ = 13.6 Hz, ArC$\underline{H}_2$Ar), 1.22 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.21 (s, 9H, C(C$\underline{H}_3$)$_3$), 0.79 (s, 18H, SiC(C$\underline{H}_3$)$_3$), 0.78 (s, 9H, SiC(C$\underline{H}_3$)$_3$), 0.71 (s, 18H, C(C$\underline{H}_3$)$_3$), 0.02 (s, 12H, SiC$\underline{H}_3$), 0.00 (s, 6H, SiC$\underline{H}_3$)

**Calix[4]arene containing C8 diyne units:**




The compound was synthesized from calix[4]arene (0.48 g, 0.74 mmol), sodium hydride (0.18 g, 7.40 mmol) and 8-*tert*-butyldimethylsilyloxy-3,5-octadiynyl tosylate (2.41 g, 5.92 mmol) in 25 mL of tetrahydrofuran. The residue was isolated by column chromatography (ethyl acetate/hexane = 10/90) to afford *tert*-butyldimethyl(octa-7-en-3,5-diynyloxy)silane as yellow oil (0.93 g, 67% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.70 (d, 2H, $J$ = 3.2 Hz, C=C$\underline{H}_2$), 5.52 (dd, 1H, $J$ = 3.6 and 2.8 Hz, $\underline{H}$C=C), 3.67 (t, 2H, $J$ = 6.8 Hz, SiOC$\underline{H}_2$), 2.46 (t, 2H, $J$ = 6.8 Hz, C$\underline{H}_2$CC), 0.82 (s, 9H, SiC(C$\underline{H}_3$)$_3$), 0.00 (s, 6H, SiC$\underline{H}_3$)

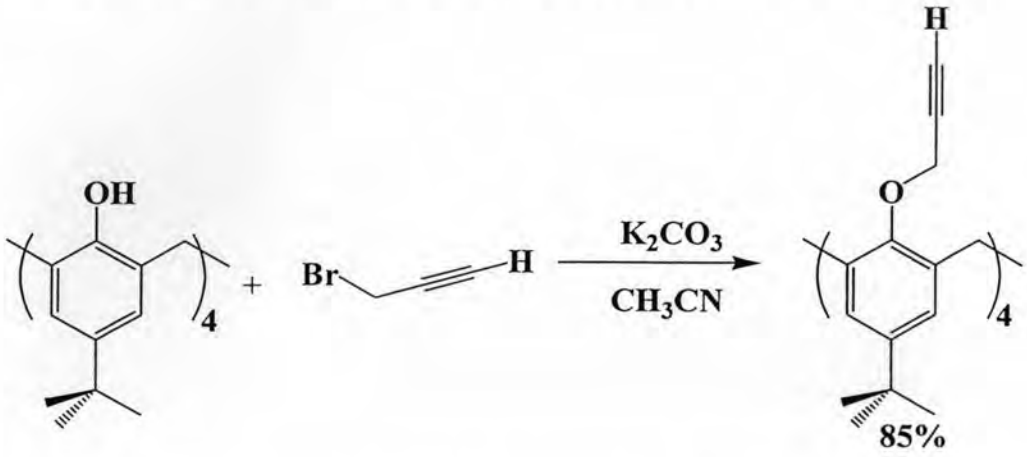
**Calix[4]arene containing C10 diyne units:**




The compound was synthesized from calix[4]arene (0.27 g, 0.42 mmol), sodium hydride (0.12 g, 4.20 mmol) and 10-*tert*-Butyldimethylsilyloxy-4,6-decadiynyl tosylate (1.80 g, 4.16 mmol) in 25 mL of tetrahydrofuran. The TLC trace did not show any products but only the unreacted starting material.

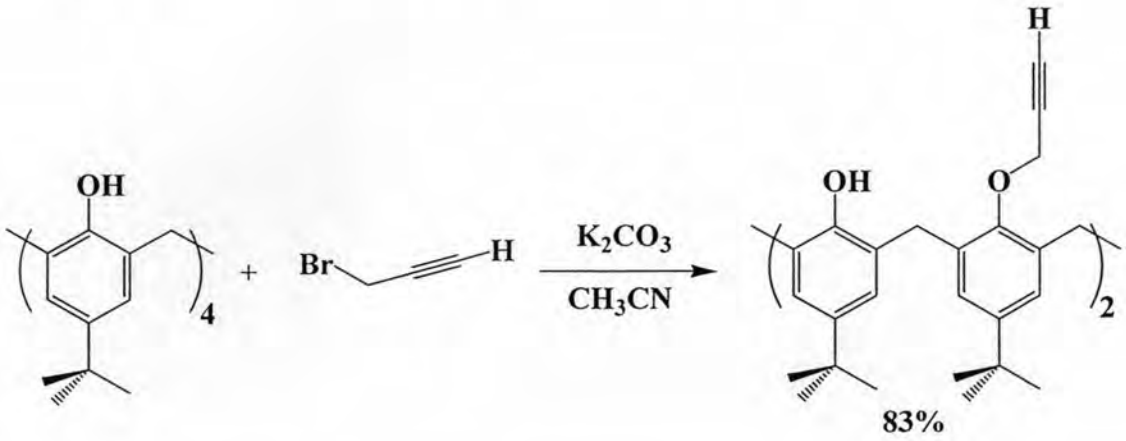
### 2.1.7 Alkylation of calix[4]arene with propargyl bromide

**Preparation of 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]arene**



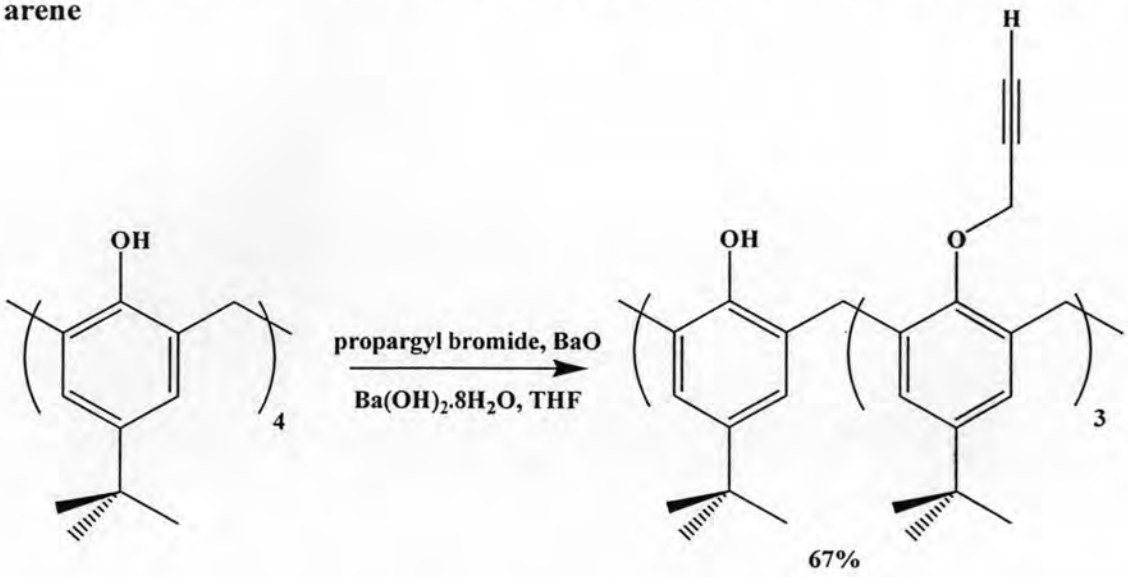

To a solution of *tert*-butylcalix[4]arene (10.18 g, 15.68 mmol) in acetonitrile (300 mL), potassium carbonate (43.37 g, 313.76 mmol) was stirred at room temperature for 1 hr under $N_2$. A solution of propargyl bromide (23.33 g, 156.88 mmol) in acetonitrile (50 mL) was added dropwise at room temperature over 30 min. The reaction mixture was allowed to reflux for 5 days, the cooled reaction mixture was filtered to remove insoluble particles and solvent was removed *in vacuo*. The reaction mixture was quenched with 2 M HCl (100 mL), extracted with dichloromethane (3×200 mL), combined organic layers were washed with brine (100 mL), dried over $Na_2SO_4$ anhydrous, filtered and removed solvent *in vacuo*. The crude mixture was crystallized from $CH_2Cl_2$/MeOH to afford white solid (10.68 g, 85% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.78 (s, 8H, Ar-H), 4.80 (s, 8H, $OCH_2$), 4.60 (d, 4H, $J$= 13.2 Hz, $ArCH_2Ar$), 3.16 (d, 4H, $J$= 13.2 Hz, $ArCH_2Ar$), 2.48 (t, 3H, 2.4 Hz, CCH), 1.07 (s, 36H, $(CH_3)_3$). $^{13}$C NMR ($CDCl_3$) δ(ppm): 152.4 ($C_{ipso}$-Ar), 145.5 ($C_{para}$-Ar), 134.3 ($C_{ortho}$-Ar), 124.9 ($C_{meta}$-Ar), 81.2 (CCH), 74.3 (CCH), 61.0 ($OCH_2$), 33.9 ($C(CH_3)_3$), 32.3 ($ArCH_2Ar$), 31.3 ($(CH_3)_3$).

**Preparation of 25,27-dipropargyloxy-26,28-dihydroxy-*tert*-butylcalix[4]-arene**




A mixture of potassium carbonate (1.71 g, 12.34 mmol), *tert*-butylcalix[4]arene (4.01 g, 6.18 mmol) in acetonitrile (200 mL) was stirred at room temperature for 1 hr. A solution of propargyl bromide (1.24 g, 12.98 mmol) in acetonitrile (50 mL) was added dropwise into the stirred mixture over 30 min. The reaction mixture was refluxed for 48 hr and was then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles and the filtrate was concentrated by a rotary evaporator. The concentrated reaction mixture was added with 2 M HCl (100 mL) and extracted with dichloromethane (3×100 mL). The combined organic extract was washed with brine (100 mL), dried over anhydrous $Na_2SO_4$, filtered and evaporated to dryness *in vacuo*. The crude mixture was crystallized from $CH_2Cl_2/CH_3OH$ to afford white solid (3.72 g, 83% yield). $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.13 (s, 4H, Ar-H), 6.78 (s, 4H, Ar-H), 6.55 (s, 2H, OH), 4.80 (d, $J$ = 4.0 Hz, 4H, $OCH_2$), 4.42 (d, $J$= 14.0 Hz, 4H, $ArCH_2Ar$), 3.38 (d, $J$ = 14.0 Hz, 4H, $ArCH_2Ar$), 2.58 (t, $J$ = 4.0 Hz, 2H, C≡CH), 1.35 (s, 18H, $(CH_3)_3$), 0.94 (s, 18H, $(CH_3)_3$).

**Preparation of 25,26,27-tripropargyloxy-28-hydroxy-*tert*-butylcalix[4]-arene**

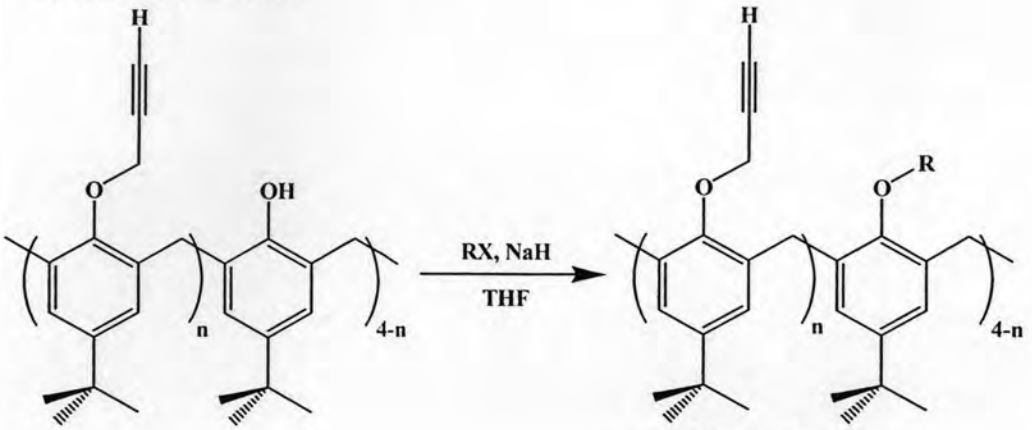



67%

A mixture of $Ba(OH)_2.8H_2O$ (3.66 g, 11.60 mmol), BaO (1.02 g, 6.63 mmol) and *tert*-butylcalix[4]arene (2.15 g, 3.31 mmol) were dissolved in tetrahydrofuran (50.0 mL) and the solution was stirred at room temperature for 1 hr. A solution of propargyl bromide (4.93 g, 33.0 mmol) in tetrahydrofuran (30 mL) was added dropwise into the stirred mixture over 30 min. The reaction mixture was refluxed for 48 hr and was then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles and the filtrate was concentrated by a rotary evaporator. The concentrated reaction mixture was added with 2 M HCl (50 mL) and extracted with dichloromethane (3×60 mL). The combined organic extract was dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed to give a brown oil residue. The residue was isolated by column chromatography with dichloromethane/hexane (15/85) to give white solid (67% yield, 1.69 g). $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.18 (s, 2H, Ar-H), 7.13 (s, 2H, Ar-H), 6.63 (s, 2H, Ar-H), 6.59 (s, 2H, Ar-H), 5.83 (s, 1H, OH), 5.08 (d, $J$ = 2.5 Hz, 2H, $OCH_2$), 4.70 (d, $J$ = 3.0 Hz, 4H, $OCH_2$), 4.66 (d, $J$ = 14.0 Hz, 2H, $ArCH_2Ar$), 4.43 (d, $J$ = 14.0 Hz, 2H, $ArCH_2Ar$), 3.36 (d, $J$ = 14.0 Hz, 2H, $ArCH_2Ar$), 3.27 (d, $J$ = 14.0 Hz, 2H, $ArCH_2Ar$), 2.56 (t, $J$ = 3.0 Hz, 2H, C≡CH), 2.50 (t, $J$ = 2.5 Hz, 1H, C≡CH), 1.37 (s, 18H, $(CH_3)_3$), 0.90 (s, 9H, $(CH_3)_3$) , 0.89 (s, 9H, $(CH_3)_3$).

### 2.1.8 Alkylation of the remaining phenolic groups of calix[4]arene

**General procedure**




**R = -$CH_3$, X = -I, n = 2: -**
**n = 3: -**
**R = -$CH_2C_6H_5$, X = -Br, n = 2: 48%**
**n = 3: 90%**
**R = -$CH_2CH_2CH_3$, X = -Br, n = 2: 62%**
**n = 3: 82%**

Calix[4]arene derivatives containing the remaining free phenolic groups and sodium hydride which was washed by hexane were dissolved in tetrahydrofuran and the solution was stirred at room temperature for 1 hr. Then the solution of alkyl halide in tetrahydrofuran was added by dropwise. After adding was complete, the reaction mixture was stirred, refluxed for 24 hr and monitored by a TLC method. The reaction mixture was allowed to cool to room temperature and quenched by ethanol to decompose sodium hydride. The solvent was removed *in vacuo* to obtain yellow residue and then the residue was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ anhydrous, filtered and removed solvent *in vacuo* to give yellow-brown residue. The residue was isolated by column chromatography to afford desired product.

**25,27-dipropargyloxy-26,28-dimethyl-*tert*-butylcalix[4]arene:**

The compound was synthesized from 25,27-dipropargyloxy-26,28-dihydroxy-*tert*-butylcalix[4]arene (0.53 g, 0.73 mmol), methyl iodide (2.08 g, 14.69 mmol) and sodium hydride (0.17 g, 7.34 mmol) in tetrahydrofuran (30 mL). The residue was isolated by column chromatography with dichloromethane/hexane (10/90) as an eluent. The obtained white solid (one spot on TLC plate) shows the mixture of conformers by $^1$H NMR measurement.

**25,27-dipropargyloxy-26,28-dibenzyloxy-*tert*-butylcalix[4]arene:**

The compound was synthesized from 25,27-dipropargyloxy-26,28-dihydroxy-*tert*-butylcalix[4]arene (0.67 g, 0.93 mmol), benzyl bromide (0.79 g, 4.62 mmol) and sodium hydride (0.22 g, 9.30 mmol) in tetrahydrofuran (30 mL). The residue was isolated by column chromatography with dichloromethane as an eluent to yield 48% (0.40 g) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.53 (d, 4H, 10 Hz, $\underline{H}_{ortho}$-Ar), 7.36 (m, 6H, $\underline{H}_{meta}$-Ar and $\underline{H}_{para}$-Ar), 7.09 (s, 4H, Ar-$\underline{H}$), 6.44 (s, 4H, Ar-$\underline{H}$), 4.78 (s, 4H, OC$\underline{H}_2$Ar), 4.75 (d, 4H, $J$= 4.0 Hz, OC$\underline{H}_2$CCH), 4.49 (d, 4H, $J$= 15.0 Hz, ArC$\underline{H}_2$Ar), 3.08 (d, 4H, $J$= 15.0 Hz, ArC$\underline{H}_2$Ar), 2.20 (t, 3H, 3.0 Hz, CC$\underline{H}$), 1.33 (s, 18H, (C$\underline{H}_3$)$_3$), 0.83 (s, 18H, (C$\underline{H}_3$)$_3$).

**25,26,27-tripropargyloxy-28-benzyloxy-*tert*-butylcalix[4]arene:**

The compound was synthesized from 25,26,27-tripropargyloxy-28-hydroxy-*tert*-butylcalix[4]arene (0.25 g, 0.33 mmol), benzyl bromide (0.17 g, 0.33 mmol) and sodium hydride (0.03 g, 0.33 mmol) in tetrahydrofuran (30 mL). The residue was isolated by column chromatography with dichloromethane as an eluent to yield 90% (0.25 g) as a white solid. $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.65 (d, 4H, $J$ = 6.0 Hz, $\underline{H}_{ortho}$-Ar), 7.43 (m, 6H, $\underline{H}_{meta}$-Ar and $\underline{H}_{para}$-Ar), 7.05 (s, 2H, Ar-$\underline{H}$), 7.02 (s, 2H, Ar-$\underline{H}$), 6.62 (s, 2H, Ar-$\underline{H}$), 6.59 (s, 2H, Ar-$\underline{H}$), 4.85 (m, 6H, OC$\underline{H}_2$Ar, ArC$\underline{H}_2$Ar, C$\underline{H}_2$CC), 4.58 (m, 6H, ArC$\underline{H}_2$Ar, C$\underline{H}_2$CC), 3.20 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 3.14 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 2.49 (t, 2H, $J$ = 3.0 Hz, CC$\underline{H}$), 2.40 (t, 1H, $J$ = 2.0 Hz, CC$\underline{H}$), 1.28 (s, 18H, (C$\underline{H}_3$)$_3$), 0.96 (s, 9H, (C$\underline{H}_3$)$_3$), 0.94 (s, 9H, (C$\underline{H}_3$)$_3$).

**25,27-dipropargyloxy-26,28-dipropyl-*tert*-butylcalix[4]arene:**

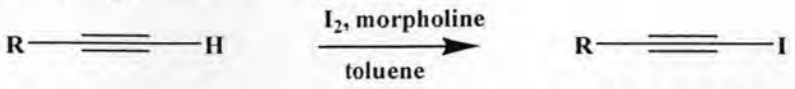
The compound was synthesized from 25,27-dipropargyloxy-26,28-dihydroxy-*tert*-butylcalix[4]arene (1.03 g, 1.42 mmol), propyl bromide (1.74 g, 14.16 mmol) and sodium hydride (0.40 g, 14.16 mmol) in tetrahydrofuran (20 mL). The residue was isolated by column chromatography with dichloromethane as an eluent to yield 62% (0.71 g) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09 (s, 4H, Ar-$\underline{H}$), 6.45 (s, 4H, Ar-$\underline{H}$), 5.02 (s, 4H, OC$\underline{H}_2$Ar), 4.52 (d, 4H, $J$= 12.0 Hz, ArC$\underline{H}_2$Ar), 3.71 (t, 4H, $J$ = 6.0 Hz, C$\underline{H}_2$CH$_2$CH$_3$), 3.14 (d, 4H, $J$= 12.0 Hz, ArC$\underline{H}_2$Ar), 2.39 (t, 3H, 4.0 Hz, CC$\underline{H}$), 2.00 (m, 4H, CH$_2$C$\underline{H}_2$CH$_3$), 1.33 (s, 18H, (C$\underline{H}_3$)$_3$), 1.05 (t, $J$ = 6.0 Hz, 6H, CH$_2$CH$_2$C$\underline{H}_3$), 0.83 (s, 18H, (C$\underline{H}_3$)$_3$).

**25,26,27-tripropargyloxy-28-propyl-*tert*-butylcalix[4]arene:**

The compound was synthesized from 25,26,27-tripropargyloxy-28-hydroxy-*tert*-butylcalix[4]arene (0.93 g, 1.22 mmol), propyl bromide (0.75g, 6.08 mmol) and sodium hydride (0.15 g, 6.08 mmol) in tetrahydrofuran (20 mL). The residue was isolated by column chromatography with dichloromethane as an eluent to yield 82% (0.80 g) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.00 (s, 2H, Ar-H), 6.98 (s, 2H, Ar-H), 6.60 (s, 2H, Ar-H), 6.54 (s, 2H, Ar-H), 4.98 (d, $J$ = 2.4 Hz, 2H, $CH_2C{\equiv}C$), 4.89 (d, $J$ = 2.4 Hz, 2H, $CH_2C{\equiv}C$), 4.63 (d, $J$ = 2.0 Hz, 2H, $CH_2C{\equiv}C$), 4.59 (d, $J$ = 12.5 Hz, 2H, $ArCH_2Ar$), 4.51 (d, $J$ = 12.5 Hz, 2H, $ArCH_2Ar$), 3.76 (t, $J$ = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 3.17 (d, $J$ = 5.6 Hz, 2H, $ArCH_2Ar$), 3.13 (d, $J$ = 5.6 Hz, 2H, $ArCH_2Ar$), 2.4 (t, $J$ = 2.0 Hz, 1H, $C{\equiv}CH$), 2.44 (t, $J$ = 2.4 Hz, 2H, $C{\equiv}CH$), 2.00 (m, 2H, $CH_2CH_2CH_3$), 1.28 (s, 18H, $(CH_3)_3$), 1.07 (t, $J$ = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 0.96 (s, 9H, $(CH_3)_3$) , 0.94 (s, 9H, $(CH_3)_3$).

### 2.1.9 Preparation of iodo alkyne

**General procedure**




**R = -$CH_2CH_2OH$: 85%**
**-$CH_2CH_2CH_2OH$: 87%**
**-$(CH_2)_9CH_3$: 92%**

A solution of morpholine in toluene at 45 °C under $N_2$ was treated with iodine, shielded from light and stirred for 1 hr. A solution of alkyne in toluene was added and the reaction was stirred at 45-50 °C for 1 hr. The reaction mixture was cooled at room temperature and filtered to remove salt. The filtrate was poured over diethyl ether and saturated aqueous $Na_2S_2O_3$ solution and shaken vigorously until the organic layer was colorless. The organic layers were separated, washed with $Na_2S_2O_3$, dried over $Na_2SO_4$ anhydrous, filtered, concentrated and isolated by column chromatography with ethyl acetate/hexane.

**4-iodo-3-butynol:** The compound was synthesized from 3-butyn-1-ol (1.03 g, 14.70 mmol), morpholine (12.80 mL, 146.95 mmol) and iodine (5.22 g, 20.57 mmol) in 100 mL of toluene. The residue was isolated by column chromatography (ethyl acetate/hexane = 7/93) to afford 4-iodo-3-butynol as a light yellow oil (2.45 g, 85% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.77 (t, 2H, $J$ = 6.4 Hz, OC$\underline{H}_2$), 2.68 (t, 2H, $J$ = 6.4 Hz, C$\underline{H}_2$CC), 1.73 (s, 1H, O$\underline{H}$)

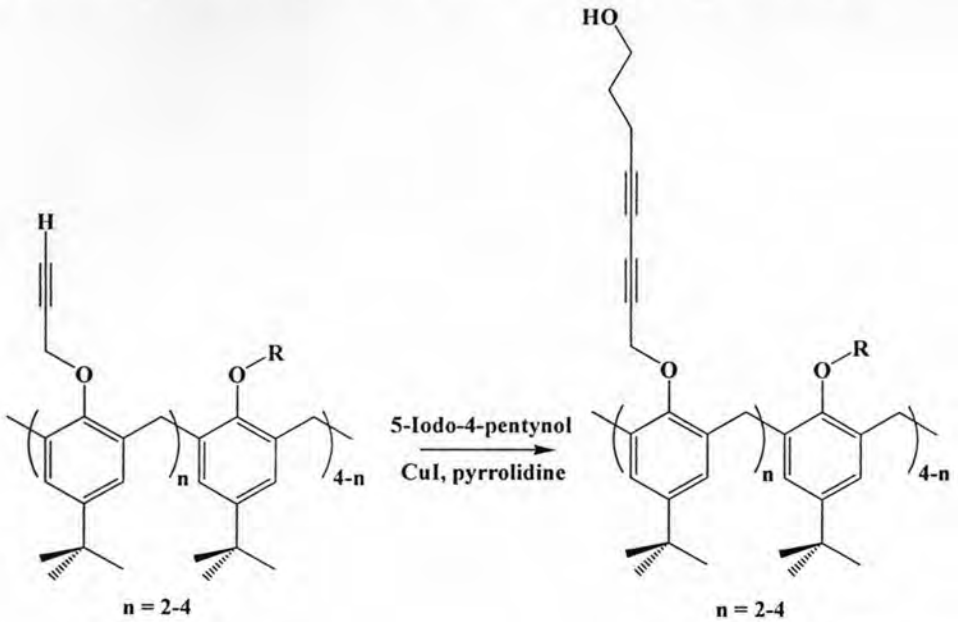
**5-Iodo-4-pentynol:** The compound was synthesized from 4-pentyn-1-ol (3.21 g, 38.16 mmol), morpholine (33.25 mL, 381.60 mmol) and iodine (13.56 g, 53.42 mmol) in 350 mL of toluene. The residue was isolated by column chromatography (ethyl acetate/hexane = 10/90) to afford 5-iodo-4-pentynol as a light yellow oil (6.97 g, 87% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.78 (t, 2H, $J$ = 5.8 Hz C$\underline{H}_2$OH), 2.53 (t, 2H, $J$ = 6.4 Hz, CCC$\underline{H}_2$), 1.80 (q, 2H, $CH_2C\underline{H}_2CH_2$), 1.61 (bs, 1 O$\underline{H}$).

**1-iodo-1-dodecyne:** The compound was synthesized from dodec-1-yne (7.17 g, 43.11 mmol), morpholine (37.56 mL, 431.12 mmol) and iodine (15.32 g, 60.35 mmol) in 250 mL of toluene. The residue was isolated by column chromatography (hexane) to afford 1-iodo-1-dodecyne as colorless oil (11.51 g, 92% yield). $^1$H NMR

(400 MHz, $CDCl_3$) δ (ppm): 2.35 (t, 2H, $J$ = 6.8 Hz, $C\underline{H}_2CC$), 1.50 (quin, 2H, $C\underline{H}_2CH_2CC$), 1.26 (m, 14H, $CH_3(C\underline{H}_2)_7$), 0.88 (t, 3H, $J$ = 7.2 Hz, $C\underline{H}_3$).

### 2.1.10 Preparation of calix[4]arene containing diacetylenes

**General procedure (Cadiot-Chodkiewicz coupling reaction)**




**R = -$CH_2C_6H_5$, n = 2: 38%**
**n = 3: 46%**
**R = -$CH_2CH_2CH_3$, n = 2: 38%**
**n = 3: 58%**
**n = 4: 51%**

To a stirred solution of 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]-arene, and 5-iodo-4-pentynol in pyrrolidine was added copper(I) iodide. After stirring at room temperature for 2 hr under $N_2$, the mixture was hydrolyzed with saturated aqueous solution of ammonium chloride and extracted with diethyl ether. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed *in vacuo*. The crude product was isolated by column chromatography (ethyl acetate) to afford desired product.

**25,27-di(octa-4,6-diyn-1-ol)oxy-26,28-dibenzyloxy-*tert*-butylcalix[4]arene (BnC2A):** The compound was synthesized from 25,27-dipropargyloxy-26,28-dibenzyloxy-*tert*-butyl calix[4]arene (0.36 g, 0.39 mmol), 5-iodo-4-pentynol (0.49g, 2.35 mmol) and copper(I) iodide (0.02 g, 0.08 mmol) in pyrrolidine (2.00 mL). The residue was isolated by column chromatography with ethyl acetate/hexane (35/65) as an eluent to yield 38% (0.16 g) as a yellow solid. $^1$H NMR (200 MHz, $CDCl_3$) δ

(ppm): 7.82 (d, 4H, $J$ = 10 Hz, $\underline{H}_{ortho}$-Ar), 7.51 (m, 6H, $\underline{H}_{meta}$-Ar and $\underline{H}_{para}$-Ar), 7.11 (s, 4H, Ar-$\underline{H}$), 6.45 (s, 4H, Ar-$\underline{H}$), 4.78 (s, 4H, OC$\underline{H}_2$Ar), 4.75 (s, 4H, OC$\underline{H}_2$CC), 4.43 (d, 14H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 3.75 (t, 4H, $J$ = 6.0 Hz, C$\underline{H}_2$OH), 3.07 (d, 4H, $J$ = 15.0 Hz, ArC$\underline{H}_2$Ar), 2.46 (t, 4H, $J$ = 7 Hz, C$\underline{H}_2$CH$_2$CH$_2$ OH), 1.80 (quin, 4H, $J$ = 7 Hz, C$\underline{H}_2$CH$_2$OH), 1.36 (s, 18H, (C$\underline{H}_3$)$_3$), 0.85 (s, 18H, (C$\underline{H}_3$)$_3$).

**25,26,27-tri(octa-4,6-diyn-1-ol)oxy-28-benzyloxy-*tert*-butylcalix[4]arene (BnC3A):** The compound was synthesized from 25,26,27-tripropargyloxy-28-benzyloxy-*tert*-butylcalix[4]arene (0.24 g, 0.30 mmol), 5-iodo-4-pentynol (0.36 g, 1.79 mmol) and copper(I) iodide (0.02 g, 0.08 mmol) in pyrrolidine (2.0 mL). The residue was isolated by column chromatography (hexane/ethyl acetate = 50/50) gave desired product as a light yellow solid (0.14 g, 46% yield). $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.59 (d, 2H, $J$ = 6.0 Hz, $\underline{H}_{ortho}$-Ar), 7.43 (m, 6H, $\underline{H}_{meta}$-Ar and $\underline{H}_{para}$-Ar), 7.05 (s, 2H, Ar-$\underline{H}$), 7.02 (s, 2H, Ar-$\underline{H}$), 6.61 (s, 2H, Ar-$\underline{H}$), 6.57 (s, 2H, Ar-$\underline{H}$), 4.70 (m, 12H, OC$\underline{H}_2$Ar, ArC$\underline{H}_2$Ar, C$\underline{H}_2$CC ), 3.79 (t, 6H, $J$ = 6.0 Hz, C$\underline{H}_2$OH), 3.20 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 3.14 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 2.46 (t, 6H, $J$ = 7.0 Hz, C$\underline{H}_2$CH$_2$CH$_2$OH), 1.80 (quin, 6H, $J$ = 7.0 Hz, C$\underline{H}_2$CH$_2$OH), 1.28 (s, 18H, (C$\underline{H}_3$)$_3$), 0.97 (s, 9H, (C$\underline{H}_3$)$_3$), 0.96 (s, 9H, (C$\underline{H}_3$)$_3$).

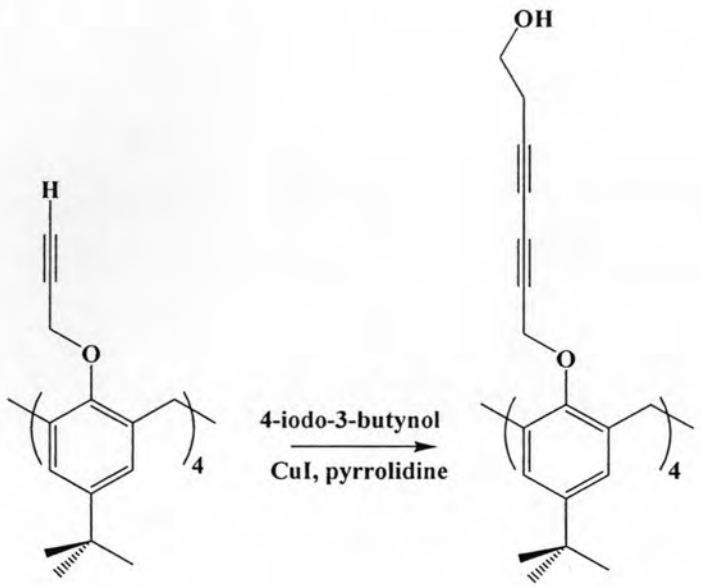
**25,27-di(octa-4,6-diyn-1-ol)oxy-26,28-dipropyl-*tert*-butylcalix[4]arene (PrC2A):** The compound was synthesized from 25,27-dipropargyloxy-26,28-dipropyl-*tert*-butyl calix[4]arene (0.22 g, 0.27 mmol), 5-iodo-4-pentynol (0.28 g, 1.34 mmol) and copper(I) iodide (0.01 g, 0.05 mmol) in pyrrolidine (1.0 mL). The residue was isolated by column chromatography (dichloromethane/ethyl acetate = 10/90) gave desired product as a light yellow solid (0.10 g, 38% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09 (s, 4H, Ar-$\underline{H}$), 6.43 (s, 4H, Ar-$\underline{H}$), 5.01 (s, 4H, OC$\underline{H}_2$CC), 4.48 (d, $J$ = 13.6 Hz, ArC$\underline{H}_2$Ar), 3.76 (t, 4H, $J$ = 6.0 Hz, C$\underline{H}_2$CH$_2$CH$_3$), 3.71 (t, 4H, $J$ = 7.4 Hz, C$\underline{H}_2$OH), 3.14 (d, 4H, $J$ = 13.6 Hz, ArC$\underline{H}_2$Ar), 2.43 (t, 4H, $J$ = 7.0 Hz, C$\underline{H}_2$CH$_2$CH$_2$ OH), 2.00 (m, 4H, CH$_2$C$\underline{H}_2$CH$_3$), 1.81 (quin, 4H, $J$ = 7.0 Hz, C$\underline{H}_2$CH$_2$OH), 1.33 (s, 18H, (C$\underline{H}_3$)$_3$), 1.05 (t, $J$ = 6.0 Hz, 6H, CH$_2$CH$_2$C$\underline{H}_3$), 0.82 (s, 18H, (C$\underline{H}_3$)$_3$).

**25,26,27-tri(octa-4,6-diyn-1-ol)oxy-28-propyl-*tert*-butylcalix[4]arene (PrC3A):** The compound was synthesized from 25,26,27-tripropargyloxy-28-benzyloxy-*tert*-butylcalix[4]arene (0.24 g, 0.30 mmol), 5-iodo-4-pentynol (0.36 g, 1.79 mmol) and copper(I) iodide (0.02 g, 0.08 mmol) in pyrrolidine (2.0 mL). The crude product was isolated by column chromatography (dichloromethane/ethyl acetate = 50/50) gave desired product as a light yellow solid (0.18 g, 58% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.00 (s, 4H, Ar-H), 6.58 (s, 2H, Ar-H), 6.51 (s, 2H, Ar-H), 5.01 (s, 2H, $CH_2C{\equiv}C$), 4.87 (s, 2H, $CH_2C{\equiv}C$), 4.71 (s, 2H, $CH_2C{\equiv}C$), 4.55 (d, $J$= 12.5 Hz, 2H, $ArCH_2Ar$), 4.46 (d, $J$ = 12.5 Hz, 2H, $ArCH_2Ar$), 3.76 (m, 8H, $CH_2CH_2CH_3$, and $CH_2OH$), 3.17 (d, $J$ = 6.4 Hz, 2H, $ArCH_2Ar$), 3.14 (d, $J$ = 6.4 Hz, 2H, $ArCH_2Ar$), 2.44 (t, $J$ = 6.6 Hz, 6H, $CH_2CH_2CH_2OH$), 2.00 (m, 4H, $CH_2CH_2CH_3$), 1.81 (m, 6H, $CH_2CH_2OH$), 1.25 (s, 18H, $(CH_3)_3$), 1.08 (t, $J$ = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 0.92 (s, 9H, $(CH_3)_3$), 0.87 (s, 9H, $(CH_3)_3$).

**25,26,27,28-tetra(octa-4,6-diyn-1-ol)oxy-*tert*-butylcalix[4]arene (C4A):**

The compound was synthesized from 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]arene (4.18 g, 5.22 mmol), 5-iodo-4-pentynol (10.96g, 52.18 mmol) and copper(I) iodide (0.40 g, 2.09 mmol) in pyrrolidine (40.00 mL). The residue was isolated by column chromatography (ethyl acetate) to afford a light yellow solid (2.73 g, 51% yield). Mp 100 °C, IR (KBr, $cm^{-1}$) ν 3386, 2965, 2905, 2868, 2254, 1688, 1603, 1480, 1362, 1196, $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.77 (s, 8H, Ar-H), 4.82 (s, 8H, $OCH_2$), 4.53 (d, $J$ = 13.2 Hz, 4H, $ArCH_2Ar$), 3.77 (t, $J$ = 7.0 Hz, 8H, $CH_2OH$), 3.17 (d, $J$ = 13.2 Hz, 4H, $ArCH_2Ar$), 2.45 (t, $J$ = 7.0 Hz, 8H, $C{\equiv}CCH_2$), 1.90 (bs, 1H, OH), 1.81 (qui, $J$ = 7.0 Hz, 8H, $CH_2CH_2CH_2$), 1.07 (s, 36H, $(CH_3)_3$), $^{13}$C NMR ($CDCl_3$) δ(ppm): 152.5 ($C_{ipso}$-Ar), 145.6 ($C_{para}$-Ar), 134.1 ($C_{ortho}$-Ar), 125.0 ($C_{meta}$-Ar), 79.9 ($C{\equiv}CC{\equiv}C$), 73.7($C{\equiv}CC{\equiv}C$), 71.0 ($C{\equiv}CC{\equiv}C$), 65.6 ($C{\equiv}CC{\equiv}C$), 61.9 ($CH_2OH$), 61.2 ($OCH_2$), 33.9 ($C(CH_3)_3$), 32.2 ($ArCH_2Ar$), 31.3 (($CH_3)_3$), 30.8 ($C{\equiv}CCH_2CH_2$), 15.9 ($C{\equiv}CCH_2$).

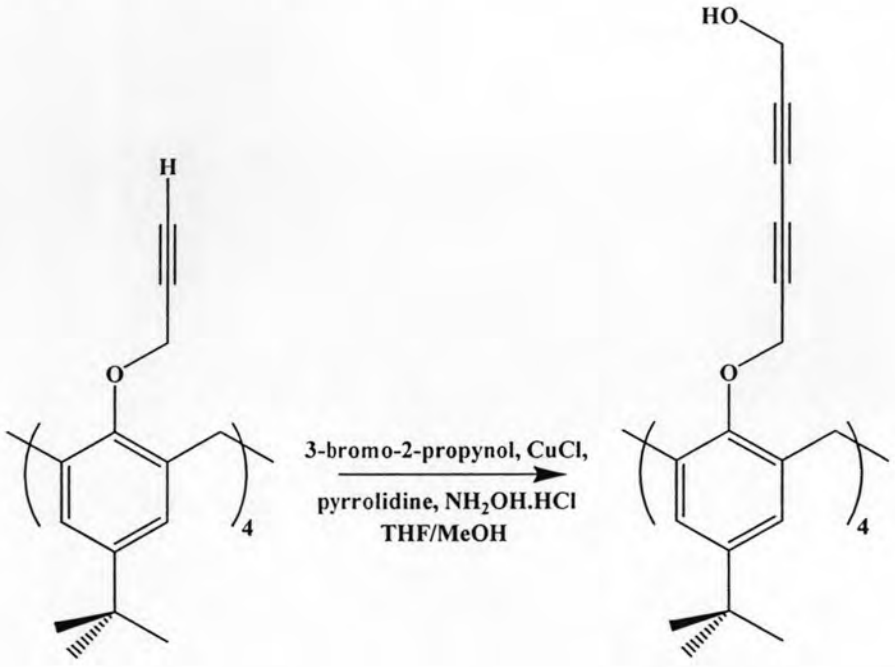
**Preparation of 25,26,27,28-tetra(hepta-4,6-diyn-1-ol)oxy-*tert*-butylcalix [4]arene (C4A″)**




46%

The compound was synthesized from 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]arene (2.35 g, 2.94 mmol), 4-iodo-3-butynol (4.60 g, 23.52 mmol) and copper(I) iodide (0.22 g, 1.18 mmol) in pyrrolidine (7.40 mL). The residue was isolated by column chromatography (5% ethyl acetate in hexane) to afford a light yellow solid (1.45 g, 46% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.78 (s, 8H, Ar-H), 4.83 (s, 8H, $OCH_2$), 4.51 (d, 4H, $J$ = 12.4 Hz, $ArCH_2Ar$), 3.78 (t, 8H, $J$ = 5.6 Hz, $CH_2OH$), 3.17 (d, 4H, $J$ = 12.4 Hz, $ArCH_2Ar$), 2.66 (br, 1H, OH), 2.59 (t, 4H, $J$ = 5.6 Hz, $CCCH_2$), 1.06 (s, 36H, $C(CH_3)_3$).

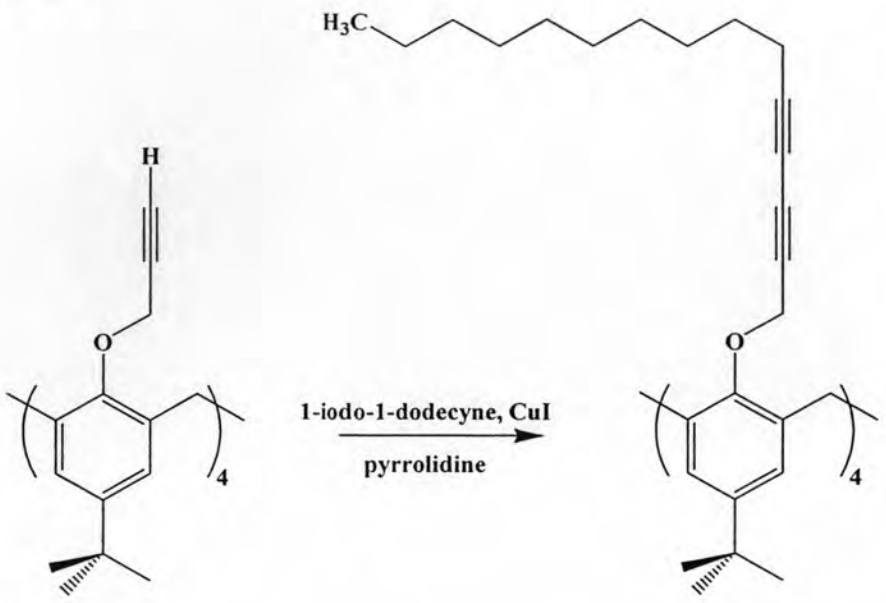
**Preparation of 25,26,27,28-tetra(hexa-2,4-diyn-1-ol)oxy-*tert*-butylcalix[4]-arene (C4A′)**




**C(6)4A: 55%**

To a stirred solution of a mixture containing copper(I) chloride (0.06 g, 0.59 mmol), hydroxylamine hydrochloride (0.10 g, 1.48 mmol), and 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]arene (1.18 g, 1.48 mmol) in tetrahydrofuran/ methanol (20 mL/5mL) was added pyrrolidine (3.70 mL) at 0 °C and the reaction mixture was allowed to stir at room temperature. Then the reaction mixture was added a degassed solution of 3-bromo-2-propynol (1.59 g, 11.8 mmol) over a period of 30 min. After stirring at room temperature for 2 hr, solvents was removed under reduced pressure in *in vacuo* and the orange residue was poured into ice cold water then extract with diethyl ether (3×50mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed *in vacuo*. The crude product was isolated by column chromatography (ethyl acetate/hexane = 80/20) to afford a light yellow solid (0.83 g, 55% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.79 (s, 8H, Ar-H), 4.83 (s, 8H, $OCH_2$), 4.49 (d, 4H, $J$ = 13.6 Hz, $ArCH_2Ar$), 4.39 (s, 8H, $CH_2OH$), 3.19 (d, 4H, $J$ = 13.6 Hz, $ArCH_2Ar$), 2.52 (br, 1H, OH), 1.09 (s, 36H, $C(CH_3)_3$).

**Preparation of 25,26,27,28-tetra(pentadeca-2,4-diyne)oxy-*tert*-butylcalix-[4]arene (C4PD)**

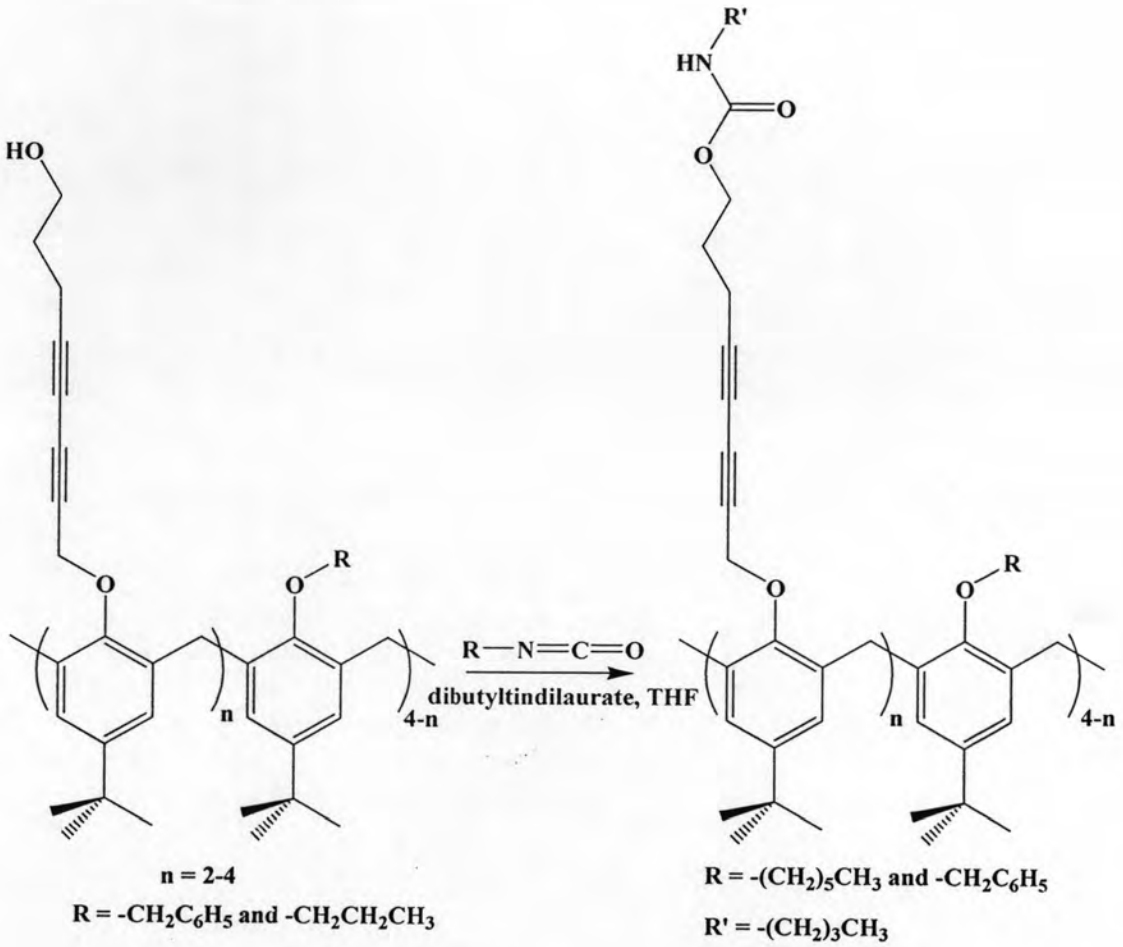



67%

To a stirred solution of 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4] arene (0.89 g, 1.11 mmol), and 1-iodo-1-dodecyne (3.24 g, 11.12 mmol) in pyrrolidine (2.80 mL) was added copper(I) iodide (0.08 g, 0.45 mmol). After stirring at room temperature for 2 hr, the mixture was hydrolyzed with saturated aqueous solution of ammonium chloride 50 mL) and extracted with diethyl ether (3×50mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed *in vacuo*. The crude product was isolated by column chromatography (dichloromethane/hexane = 6/94) to afford a light yellow gel (1.09 g, 67% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.77 (s, 8H, Ar-H), 4.83 (s, 8H, $OCH_2$), 4.57 (d, 4H, $J$ = 13.6 Hz, $ArCH_2Ar$), 3.17 (d, 4H, $J$ = 13.6 Hz, $ArCH_2Ar$), 2.29 (t, 8H, $J$ = 7.2 Hz, $CCCH_2$), 1.55 (quin, 8H, $J$ = 6.8 Hz, $CCCH_2CH_2$), 1.27 (s, 56H, $(CH_2)_7$), 1.07 (s, 36H, $C(CH_3)_3$), 0.88 (t, 12H, $J$ = 6.4 Hz, $CH_3$).

### 2.1.11 Urethane formation

**General procedure**




n = 2-4

R = -$CH_2C_6H_5$ and -$CH_2CH_2CH_3$

R = -$(CH_2)_5CH_3$ and -$CH_2C_6H_5$

R' = -$(CH_2)_3CH_3$

Diacetylenic alcohol-*tert*-butylcalix[4]arene derivatives and dibutyltindilaurate were dissolved in tetrahydrofuran, R-N=C=O (commercial available) was added dropwise in this solution with stirring at 0 °C. The mixture was allowed to warm to room temperature and the stirring was continued for 2 h before ice-water was added. Tetrahydrofuran was evaporated and the aqueous residue was extracted with $CH_2Cl_2$ several times and brine. The combined organic layers were dried over $Na_2SO_4$ anhydrous and the solvent was evaporated *in vacuo*. The crude product was eluted through a silica gel column by ethyl acetate/hexane to obtain the desired product.

**25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-*tert*-butylcalix[4]arene (C4BU′):** **C4BU′** was synthesized from **C4A′** (0.11 g, 0.11 mmol), butyl isocyanate (0.21 g, 2.16 mmol), and dibutyltindilaurate (0.27 g, 0.43 mmol) in tetrahydrofuran (30 mL) and isolated by column chromatography (2% ethyl acetate in dichloromethane) to give a white solid **C4BU′** in 65% yield (0.10 g): Mp 105 °C, IR (KBr, $cm^{-1}$) ν 3356, 2959, 2870, 2249, 1715, 1531, 1475, 1361, 1247, 1195, 1123, 1017, $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.78 (s, 8H, Ar-H), 5.33 (br, 4H, NH), 4.81 (s, 16H, $OCH_2$ and $CCCH_2$), 4.48 (d, 4H, $J$ = 13.2 Hz, $ArCH_2Ar$), 3.16 (m, 12H, $ArCH_2Ar$ and $NHCH_2$), 1.48 (m, 8H, $CH_2CH_2CH_3$), 1.35 (m, 8H, $CH_2CH_3$), 1.06 (s, 36H, $C(CH_3)_3$), 0.91 (t, 12H, $J$ = 7.2 Hz, $CH_3$), $^{13}$C NMR ($CDCl_3$) δ(ppm): 155.5 (CO), 152.4 ($C_{ipso}$-Ar), 145.8 ($C_{para}$-Ar), 133.9 ($C_{ortho}$-Ar), 125.1 ($C_{meta}$-Ar), 77.5 (CCCC), 73.3 (CCCC), 71.1 (CCCC), 70.2 (CCCC), 61.8 ($CH_2OCO$), 53.9 ($OCH_2$), 40.9 ($NHCH_2$), 33.9 ($C(CH_3)_3$), 32.2 ($ArCH_2Ar$), 31.8 ($NHCH_2CH_2$), 31.3 ($(CH_3)_3$), 19.9 ($CH_2CH_2CH_2$), 16.3 ($CH_2CH_3$), 13.7 ($CH_3$).

**25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-*tert*-butylcalix[4]arene (C4BU″):** **C4BU″** was synthesized from **C4A″** (0.45 g, 0.42 mmol), butyl isocyanate (0.42 g, 4.24 mmol), and dibutyltindilaurate (1.07 g, 1.69 mmol) in tetrahydrofuran (30 mL) and isolated by column chromatography (45-50% ethyl acetate in hexane) to give a white solid **C4BU″** in 89% yield (0.44 g): Mp 103 °C, IR (KBr, $cm^{-1}$) ν 3332, 2959, 2869, 2249, 1692, 1544, 1476, 1361, 1257, 1196, 1122, 1014, $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.78 (s, 8H, Ar-H), 4.90 (br, 4H, NH), 4.82 (s, 8H, $OCH_2$), 4.53 (d, 4H, $J$ = 13.6 Hz, $ArCH_2Ar$), 4.17 (t, 8H, $J$ = 6.0 Hz, $CH_2OCO$), 3.15 (m, 12H, $ArCH_2Ar$ and $CCCH_2$), 2.64 (t, 8H, $J$ = 6.4 Hz, $NHCH_2$), 1.48 (m, 8H, $CH_2CH_2CH_3$), 1.35 (m, 8H, $CH_2CH_3$), 1.07 (s, 36H, $C(CH_3)_3$), 0.91 (t, 12H, $J$ = 7.2 Hz, $CH_3$).

**25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-*tert*-butylcalix[4]arene C4BU:** **C4BU** was synthesized from **C4A** (0.85 g, 0.75 mmol), butyl isocyanate (0.75 g, 7.53 mmol), and dibutyltindilaurate (1.90 g, 3.01 mmol) in tetrahydrofuran (20 mL) and isolated by column chromatography (45-50% ethyl acetate in hexane) to give a white solid **C4BU** in 84% yield (0.96 g): Mp 103 °C, IR (KBr, $cm^{-1}$) ν 3332, 2956, 2930, 2872, 2261, 1690, 1543, 1481, 1362, 1273, 1199,

1155, 1122, $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.77 (s, 8H, Ar-H), 4.82 (s and bs ,8H, $OCH_2$ and NH, respectively), 4.53 (d, 4H, 13.2 Hz, $ArCH_2Ar$), 4.13 (t, 8H, 5.8 Hz, $OCOCH_2$), 3.17 (d, 4H, 13.2 Hz, $ArCH_2Ar$), 3.15 (t, 8H, $NCH_2$) 2.39 (t, 8H, 6.8 Hz, $CCCH_2$), 1.87 (q, 8H, $CCCH_2CH_2$), 1.47 (quin, 8H, $CH_2CH_2CH_3$), 1.33 (s, 8H, $CH_2CH_3$), 1.06 (s, 36H $(CH_3)_3$), 0.95 (t, 12H, 7.4 Hz, $CH_3$), $^{13}$C NMR ($CDCl_3$) δ(ppm): 156.5 (CO), 152.7 ($C_{ipso}$-Ar), 145.5 ($C_{para}$-Ar), 134.1 ($C_{ortho}$-Ar), 125.0 ($C_{meta}$-Ar), 79.4 (CCCC), 73.9 (CCCC), 71.0 (CCCC), 65.6 (CCCC), 63.2 ($CH_2OCO$), 61.9 ($OCH_2$), 40.7 ($NHCH_2$), 33.9 ($C(CH_3)_3$), 32.3 ($ArCH_2Ar$), 32.0 ($NHCH_2CH_2$), 31.3 ($(CH_3)_3$), 28.0 ($CCCH_2$), 19.9 ($CH_2CH_2CH_2$), 16.3 ($CH_2CH_3$), 13.7 ($CH_3$). Anal. calcd. for $C_{97}H_{128}N_4O_{12}$: C, 75.55; H, 8.37; N, 3.63. Found: C, 75.58; H, 8.39; N 3.65.

**25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-hexyl-urethane)]oxy-*tert*-butylcalix[4]arene C4HU: C4HU** was prepared from **C4A** (0.54 g, 0.48 mmol), butyl isocyanate (0.61 g, 4.78 mmol), and dibutyltindilaurate (1.21 g, 1.91 mmol) in tetrahydrofuran (15 mL) and isolated by column chromatography (23-27% ethyl acetate/hexane) to give a white solid in 45% yield (0.35 g): Mp 87 °C, IR (KBr, $cm^{-1}$) ν 3331, 2958, 2931, 2859, 2258, 1691, 1618, 1544, 1480, 1362, 1254, 1197, 1122, $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.76 (s, 8H, Ar-H), 4.91 (bs, NH), 4.80 (s, 8H, $OCH_2$), 4.53 (d, 4H, 12.8 Hz, $ArCH_2Ar$), 4.12 (t, 8H, 6.0 Hz, $CH_2OCO$), 3.16 (d, 4H, 12.8 Hz, $ArCH_2Ar$), 3.12 (t, 8H, 6.0 Hz, $NHCH_2$), 2.38 (t, 8H, $CCCH_2$), 1.85 (q, 8H, $CCCH_2CH_2$), 1.47 (m, 8H, $NHCH_2CH_2$), 1.27 (m, 24H, $CH_2CH_2CH_2CH_3$), 1.05 (s, 36H, $(CH_3)_3$), 0.87 (t, 12H, 6.2 Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$) δ(ppm): 156.4 (CO), 152.5 ($C_{ipso}$-Ar), 145.5 ($C_{para}$-Ar), 134.0 ($C_{ortho}$-Ar), 125.0 ($C_{meta}$-Ar), 79.3 (CCCC), 73.8 (CCCC), 71.0 (CCCC), 65.6 (CCCC), 63.1 ($CH_2OCO$), 61.8 ($OCH_2$), 40.9 ($NHCH_2$), 33.8 ($C(CH_3)_3$), 32.2 ($ArCH_2Ar$), 31.4 ($CH_2CH_2CH_3$), 31.2 ($(CH_3)_3$), 29.8 ($NHCH_2CH_2$), 27.9 ($CCCH_2CH_2$), 26.3 ($NHCH_2CH_2CH_2$), 22.5 ($CH_2CH_3$), 16.2 ($CH_3$), 13.9 ($CCCH_2$). Anal. calcd. for $C_{105}H_{144}N_4O_{12}$: C, 76.23; H, 8.77; N, 3.39. Found: C, 76.24; H, 8.64; N 3.76.

**25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-phenyl-urethane)]oxy-*tert*-butylcalix[4]arene C4PU: C4PU** was prepared from **C4A** (0.36 g, 0.32 mmol), phenyl isocyanate (0.38 g, 3.19 mmol), and dibutyltindilaurate (0.81 g, 1.27 mmol) in tetrahydrofuran (15 mL) and isolated by column chromatography (20-22% ethyl

acetate/hexane) to give a white solid in 65% yield (0.33 g): Mp 91 °C, IR (KBr, $cm^{-1}$) ν 3317, 2959, 2252, 1714, 1602, 1541, 1480, 1445, 1315, $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, 8H, 7.6 Hz, $H_{ortho}$-Ar), 7.28 (t, 8H, $H_{meta}$-Ar), 7.04 (t, 4H, $H_{para}$-Ar), 6.90 (bs, NH), 6.78 (s, 8H, H-$Ar_{calix}$), 4.82 (s, 8H, $OCH_2$), 4.54 (d, 4H, 12.8 Hz, $ArCH_2Ar$), 4.27 (t, 8H, 6.0 Hz, $OCOCH_2$), 3.18 (d, 4H, 12.8 Hz, $ArCH_2Ar$), 2.44 (t, 8H, 7.0 Hz, $CCCH_2$), 1.96 (q, 8H, $CH_2CH_2CH_2$), 1.06 (s, 36H, $(CH_3)_3$). $^{13}$C NMR ($CDCl_3$) δ(ppm): 158.3 (CO), 152.6 ($C_{ipso}$-$Ar_{calix}$), 145.6 ($C_{para}$-$Ar_{calix}$), 138.5 ($C_{ipso}$-Ar), 134.1 ($C_{ortho}$-$Ar_{calix}$), 129.0 ($C_{ortho}$-Ar), 125.0 ($C_{meta}$-$Ar_{calix}$), 123.4 ($C_{meta}$-Ar), 118.7 ($C_{para}$-Ar), 79.2 (CCCC), 74.0 (CCCC), 73.4 (CCCC), 65.9 (CCCC), 63.7 ($CH_2OCO$), 61.9 ($OCH_2$), 33.9 ($C(CH_3)_3$), 32.3 ($ArCH_2Ar$)), 31.3 (($CH_3)_3$), 27.8 ($CCCH_2CH_2$), 16.3 ($CCCH_2$). Anal. calcd. for $C_{105}H_{112}N_4O_{12}$: C, 77.75; H, 6.96; N, 3.45. Found: C, 77.39; H, 6.78; N 3.24.

**25,27-di[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-26,28-dibenzyl oxy-*tert*-butylcalix[4]arene (BnC2BU): BnC2BU** was prepared from **BnC2A** (0.19 g, 0.18 mmol), butyl isocyanate (0.18 g, 1.78 mmol), and dibutyltindilaurate (0.23, 0.36 mmol) in tetrahydrofuran (12 mL) and isolated by column chromatography in the presence of ethyl acetate/hexane (3/97) as eluent to obtain a yellow solid in 70% yield (0.16 g). Mp 95 °C, IR (KBr, $cm^{-1}$) ν 3347, 2958, 2868, 2252, 1713, 1527, 1476, 1363, 1247, 1196, 1120, 1006. $^1$H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.66 (d, 4H, $J$= 10.0 Hz, $H_{ortho}$-Ar), 7.43 (m, 6H, $H_{meta}$-Ar and $H_{para}$-Ar), 7.09 (s, 4H, Ar-H), 6.44 (s, 4H, Ar-H),4.83 (s, 4H, $OCH_2Ar$), 4.76 (s, 4H, $OCH_2CC$), 4.68 (s, 2H, NH), 4.43 (d, 4H, $J$= 14.0 Hz, $ArCH_2Ar$), 4.13 (t, 4H, $J$= 6.0 Hz, $CH_2OCO$), 3.18 (t, 4H, $J$= 10.0 Hz, $NCH_2$), 3.06 (d, 14H, $J$ = 14.0 Hz, $ArCH_2Ar$), 2.39 (t, 4H, $J$ = 7.0 Hz, $CH_2CH_2CH_2O$), 1.86 (quin, 4H, $J$= 7.0 Hz, $CH_2CH_2O$), 1.48 (m, 4H, $CH_2CH_2CH_3$), 1.35 (s, 18H, $(CH_3)_3$), 1.29 (m, 4H, $CH_2CH_3$), 0.91 (t, 6H, $J$= 7.4 Hz, $CH_3$), 0.84 (s, 18H, $(CH_3)_3$). $^{13}$C NMR ($CDCl_3$) δ(ppm): 156.8 (CO), 152.9 ($C_{ipso}$-Ar), 152.8($C_{ipso}$-Ar), 146.3 ($C_{para}$-Ar), 144.8 ($C_{para}$-Ar), 138.4 ($CH_2C_{ipso}$-Ar), 136.7 ($C_{ortho}$-Ar), 132.4 ($C_{ortho}$-Ar), 129.7 ($C_{meta}$-Ar), 128.7 ($C_{meta}$-Ar), 128.2 ($CH_2C_{meta}$-Ar), 125.8 ($CH_2C_{ortho}$-Ar), 124.8 ($CH_2C_{para}$-Ar), 79.5 ($CCCCCH_2CH_2$), 78.2 ($CH_2Ar$), 75.0 ($CCCCCH_2CH_2$), 71.3 ($CCCCCH_2CH_2$), 66.3 ($CCCCCH_2CH_2$), 63.6 ($CH_2OCO$), 60.6 ($OCH_2CC$), 41.1 ($NHCH_2$), 34.5 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 32.4 ($ArCH_2Ar$), 32.3 ($NHCH_2CH_2$), 32.1 (($CH_3)_3$), 31.5 (($CH_3)_3$), 28.4 ($CCCH_2CH_2$), 20.3 ($CH_2CH_3$), 16.6

(CC$\underline{C}H_2$), 14.1 ($\underline{C}H_3$). Anal. calcd. for $C_{84}H_{102}N_2O_8$: C, 79.58; H, 8.11; N, 3.01. Found: C, 74.65; H, 9.01; N 2.94.

**25,26,27-tri[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-28-benzyl-oxy-*tert*-butylcalix[4]arene (BnC3BU): BnC3BU** was synthesized from **BnC3A** (0.02 g, 0.02 mmol), butyl isocyanate (0.01 g, 0.16 mmol), and dibutyltindilaurate (0.03 g, 0.05 mmol) in tetrahydrofuran (10 mL) and isolated by column chromatography in the presence of ethyl acetate/dichloromethane (2/98) as eluent to obtain 47% (0.01 g) of (20) as a yellow solid. Mp 97 °C, IR (KBr, $cm^{-1}$) ν 3402, 2957, 2925, 2860, 2243, 1709, 1631, 1530, 1467, 1366, 1249, 1196, 1117. $^1$H NMR (500 MHz, CDCl3) δ (ppm): 7.59 (d, 2H, $J$ = 5.0 Hz, $\underline{H}_{ortho}$-Ar), 7.44 (t, 2H, $J$ = 7.5 Hz, $\underline{H}_{meta}$-Ar), 7.39 (d, 2H, $J$ = 10.0 Hz, $\underline{H}_{para}$-Ar), 7.00 (s, 2H, Ar-$\underline{H}$), 6.99 (s, 2H, Ar-$\underline{H}$), 6.60 (s, 2H, Ar-$\underline{H}$), 6.57 (s, 2H, Ar-$\underline{H}$), 4.88 (s, 2H, OC$\underline{H}_2$Ar), 4.86 (s, 2H, C$\underline{H}_2$CC), 4.67 (m, 4H, C$\underline{H}_2$CC), 4.55 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 4.44 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 4.15 (t, 6H, $J$ = 5.0 Hz, C$\underline{H}_2$OCO), 3.17 (m, 8H, NC$\underline{H}_2$, ArC$\underline{H}_2$Ar), 3.10 (d, 2H, $J$ = 14.0 Hz, ArC$\underline{H}_2$Ar), 2.38 (t, 6H, $J$ = 7.0 Hz, C$\underline{H}_2$CH$_2$CH$_2$O), 1.88 (quin, 6H, $J$ = 7.0 Hz, C$\underline{H}_2$CH$_2$OH), 1.51 (quin, 6H, C$\underline{H}_2$CH$_2$CH$_3$), 1.37 (s, 6H, C$\underline{H}_2$CH$_3$), 1.25 (s, 18H, (C$\underline{H}_3$)$_3$), 0.95 (m, 18H, (C$\underline{H}_3$)$_3$, C$\underline{H}_3$), 0.93 (s, 9H, (C$\underline{H}_3$)$_3$). $^{13}$C NMR ($CDCl_3$) δ(ppm): 158.9 ($\underline{C}$O), 156.9 ($\underline{C}$O), 153.3 ($\underline{C}_{ipso}$-Ar), 153.0 ($\underline{C}_{ipso}$-Ar), 152.4 ($\underline{C}_{ipso}$-Ar), 146.2 ($\underline{C}_{para}$-Ar), 145.6 ($\underline{C}_{para}$-Ar), 145.1 ($\underline{C}_{para}$-Ar), 138.5 (CH$_2\underline{C}_{ipso}$-Ar), 135.9 ($\underline{C}_{ortho}$-Ar), 135.8 ($\underline{C}_{ortho}$-Ar), 133.5 ($\underline{C}_{ortho}$-Ar), 133.1 ($\underline{C}_{ortho}$-Ar), 129.8 ($\underline{C}_{meta}$-Ar), 128.7 ($\underline{C}_{meta}$-Ar), 128.3 ($\underline{C}_{meta}$-Ar), 125.7 ($\underline{C}_{meta}$-Ar), 125.7 (CH$_2\underline{C}_{para}$-Ar), 125.1 (CH$_2\underline{C}_{ortho}$-Ar), 125.1 (CH$_2\underline{C}_{meta}$-Ar), 79.7 (C$\underline{C}$CC), 78.1 (C$\underline{C}$CC), 77.6 ($\underline{C}$CCC), 74.8 ($\underline{C}$CCC), 74.0 (CC$\underline{C}$C), 71.6 (CC$\underline{C}$C), 71.3 (CCC$\underline{C}$), 66.2 (CCC$\underline{C}$), 66.0 ($\underline{C}$H$_2$OCO), 63.6 ($\underline{C}$H$_2$OCO), 62.6 (O$\underline{C}$H$_2$), 61.4 (O$\underline{C}$H$_2$), 59.9 (O$\underline{C}$H$_2$-Ar), 41.1 (NH$\underline{C}$H$_2$), 40.8 (NH$\underline{C}$H$_2$), 34.4 (ArC$\underline{H}_2$Ar), 34.1 (ArC$\underline{H}_2$Ar), 32.5 (NHCH$_2\underline{C}$H$_2$), 32.3 (NHCH$_2\underline{C}$H$_2$), 32.0 ((C$\underline{H}_3$)$_3$), 31.6 ((C$\underline{H}_3$)$_3$), 31.5 ((C$\underline{H}_3$)$_3$), 30.1 (CC$\underline{C}$H$_2$), 28.4 (CC$\underline{C}$H$_2$), 23.1 (CH$_2\underline{C}$H$_2$CH$_2$), 20.4 (CH$_2\underline{C}$H$_2$CH$_2$), 20.3 ($\underline{C}$H$_2$CH$_3$), 20.3 ($\underline{C}$H$_2$CH$_3$), 16.7 ($\underline{C}$H$_2$CH$_3$), 14.5 ($\underline{C}$H$_3$), 14.1 ($\underline{C}$H$_3$). Anal. calcd. for $C_{90}H_{113}N_3O_{10}$: C, 77.38; H, 8.15; N, 3.01. Found: C, 78.23; H, 9.02; N 2.18.

**Urethane formation of PrC2BU, and PrC3BU**

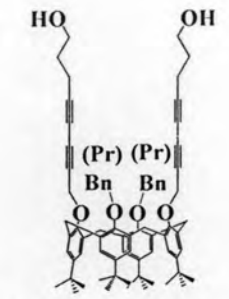
**General procedure**

Butylamine was dissolved in anhydrous chloroform. Triphosgene was gradually added to this solution with stirring. Triethylamine was added dropwise to this stirred mixture (a water bath may be needed to keep the temperature below 30 °C). The reaction mixture was refluxed for 2 hr before diacetylenic alcohol-*tert*-butylcalix[4]arene derivatives [**PrC2A**, or **PrC3A**] and dibutyltindilaurate were added. The stirring was continued for 10 hr at room temperature. The solvent was evaporated, and the residue was redissolved in hexane. The resulting solution was filtered, and the solid was washed several times with hexane. The filtrate was collected, and the solvent was evaporated. The residue was eluted through a silica gel column.

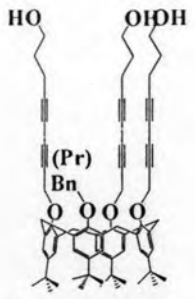
**25,27-di[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-26,28-dipropyl-*tert*-butylcalix[4]arene PrC2BU: PrC2BU** was synthesized from **PrC2A** (0.07 g, 0.07 mmol), butylamine (0.32 g, 4.32 mmol), triphosgene (0.43 g, 1.44 mmol), triethylamine (1.20 mL, 8.63 mmol), and dibutyltindilaurate (0.18 g, 0.29 mmol) in tetrahydrofuran (10 mL) and isolated by column chromatography (1% ethyl acetate in dichloromethane) to give a light yellow solid **C2BU** in 55% yield (0.05 g): Mp 81 °C, $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09 (s, 4H, Ar-H), 6.42 (s, 4H, Ar-H), 5.01 (s, 4H, $OCH_2CC$), 4.69 (bs, 2H, NH), 4.48 (d, 4H, $J$ = 13.6 Hz, $ArCH_2Ar$), 4.12 (t, 4H, $J$ = 5.8 Hz, $OCOCH_2$), 3.70 (t, 4H, $J$ = 6.0 Hz, $CH_2CH_2CH_3$), 3.14 (m, 8H, $J$ = 13.6 Hz, $ArCH_2Ar$, and $NCH_2$), 2.38 (t, 4H, $J$ = 6.6 Hz, $CCCH_2$), 2.00 (m, 4H, $CH_2CH_2CH_3$), 1.84 (q, 4H, $CCCH_2CH_2$), 1.47 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.32 (s, 18H, $(CH_3)_3$), 1.05 (t, $J$ = 6.0 Hz, 6H, $CH_2CH_2CH_3$), 0.92 (m, 6H, $CH_2CH_2CH_2CH_3$), 0.81 (s, 18H, $(CH_3)_3$), $^{13}$C NMR ($CDCl_3$) δ(ppm): 156.3 (CO), 153.0 ($C_{ipso}$-Ar), 152.6 ($C_{ipso}$-Ar), 145.8 ($C_{para}$-Ar), 144.0 ($C_{para}$-Ar), 136.3 ($C_{ortho}$-Ar),131.8 ($C_{ortho}$-Ar), 125.4 ($C_{meta}$-Ar), 124.3 ($C_{meta}$-Ar), 78.9 ($CCCCCH_2CH_2$), 77.4 ($OCH_2$), 74.6 ($CCCCCH_2CH_2$), 70.9 ($CCCCCH_2CH_2$), 65.7 ($CCCCCH_2CH_2$), 63.1 ($CH_2OCO$), 60.5 ($OCH_2CC$), 42.9 ($NHCH_2$), 40.4 ($ArCH_2Ar$), 34.1 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 31.7 ($NHCH_2CH_2$), 31.7 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 28.0 ($CH_2CH_2CH_2O$), 23.6 ($CH_2CH_3$), 20.1 ($CH_2CH_3$), 16.2 ($CCCH_2$), 13.8 ($CH_3$), 10.8 ($CH_3$). Anal. calcd. for $C_{76}H_{102}N_2O_8$: C, 77.91; H, 8.77; N, 2.89. Found: C, 76.28; H, 8.43; N, 3.19.

**25,26,27-tri[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-28-propyl-*tert*-butylcalix[4]arene PrC3BU: PrC3BU** was synthesized from **PrC3A** (0.07 g, 0.07 mmol), butylamine (0.07 g, 1.00 mmol), triphosgene (0.10 g, 0.30 mmol), triethylamine (0.28 mL, 2.00 mmol), and dibutyltindilaurate (0.13 g, 0.21 mmol) in tetrahydrofuran (10 mL) and isolated by column chromatography (15% ethyl acetate in hexane) to give a light yellow solid **PrC3BU** in 32% yield (0.03 g): Mp 85 °C, $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.00 (s, 4H, Ar-H), 6.56 (s, 2H, Ar-H), 6.50 (s, 2H, Ar-H), 4.99 (s, 2H, $CH_2CC$), 4.88 (s, 2H, $CH_2CC$), 4.80 (bs, 3H, NH), 4.70 (s, 2H, $CH_2CC$), 4.54 (d, 2H, $J$ = 12.8 Hz, $ArCH_2Ar$), 4.47 (d, 2H, $J$ = 13.2 Hz, $ArCH_2Ar$), 4.12 (t, 6H, $J$ = 5.6, $CH_2OCO$), 3.74 (t, 2H, $CH_2CH_2CH_3$), 3.15 (m, 10H, $ArCH_2Ar$ and $NHCH_2$), 2.39 (t, 6H, $J$ = 6.4 Hz, $CH_2CH_2CH_2OCO$), 2.03 (m, 4H, $CH_2CH_2CH_3$), 1.86 (m, 6H, $CH_2CH_2OCO$), 1.47 (m, 6H, $CH_2CH_2CH_3$), 1.34 (m, 6H, $CH_2CH_2CH_3$), 1.25 (s, 18H, $(CH_3)_3$), ), 1.07 (t, 3H, $J$ = 7.4, $CH_2CH_2CH_3$), 0.91 (s, 9H, $(CH_3)_3$), 0.86 (s, 9H, $(CH_3)_3$), $^{13}$C NMR ($CDCl_3$) δ(ppm): 156.5 (CO), 153.3 ($C_{ipso}$-Ar), 152.8 ($C_{ipso}$-Ar), 152.0 ($C_{ipso}$-Ar), 145.8 ($C_{para}$-Ar), 145.2 ($C_{para}$-Ar), 144.2 ($C_{para}$-Ar), 135.7 ($C_{ortho}$-Ar), 135.5 ($C_{ortho}$-Ar), 132.9 ($C_{ortho}$-Ar), 132.3 ($C_{ortho}$-Ar), 125.4 ($C_{meta}$-Ar), 125.2 ($C_{meta}$-Ar), 124.6 ($C_{meta}$-Ar), 124.5 ($C_{meta}$-Ar), 79.4 ($OCH_2CCCC$), 79.2 ($OCH_2CCCC$), 77.4 ($CH_2CH_2CH_3$), 74.4 ($OCH_2CCCC$), 73.3 ($OCH_2CCCC$), 71.2 ($OCH_2CCCC$), 70.8 ($OCH_2CCCC$), 65.7 ($OCH_2CCCC$), 65.6 ($OCH_2CCCC$), 63.2($CH_2OCO$), 62.4 ($ArOCH_2$), 61.1 ($ArOCH_2$), 40.7 ($NHCH_2$), 34.1 ($C(CH_3)_3$), 33.7 ($C(CH_3)_3$), 33.6 ($C(CH_3)_3$), 32.4 ($ArCH_2Ar$), 30.0 ($NHCH_2CH_2$), 31.7 ($ArCH_2Ar$), 31.6 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 29.7 ($CCCH_2CH_2$), 28.0 ($CCCH_2CH_2$), 27.9 ($CH_2CH_2CH_3$), 23.7 ($CH_2CH_3$), 19.9 ($CCCH_2CH_2$), 16.3 ($CCCH_2CH_2$), 13.7 ($CH_3$), 10.4 ($CH_3$). Anal. calcd. for $C_{86}H_{113}N_3O_{10}$: C, 76.58; H, 8.44; N, 3.12. Found: C, 74.40; H, 7.71; N 3.21.

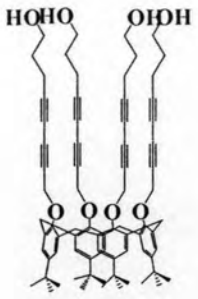
## 2.2 Polymerization by UV-irradiation



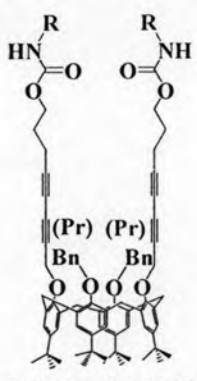

PrC2A and BnC2A



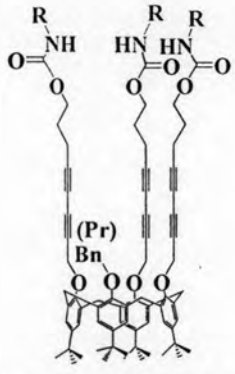

PrC3A and BnC3A



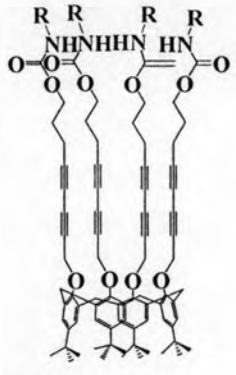

C4A



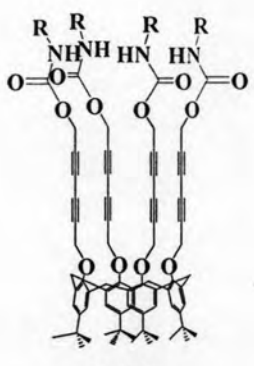

PrC2BU and BnC2BU



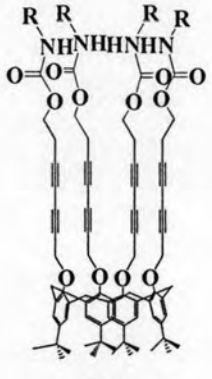

PrC3BU and BnC3BU




C4BU, C4HU, C4PU




C4BU'




C4BU''

**The letter Bn, Pr, B, H, P and U denote benzyl, propyl, butyl, hexyl, phenyl and urethane, respectively**

All calix[4]arenes containing diyne with hydroxyl and urethane units (**PrC2A**, **BnC2A**, **PrC3A**, **BnC3A**, **C4A**, **PrC2BU**, **BnC2BU**, **PrC3BU**, **BnC3BU**, **C4BU**, **C4HU**, **C4PU**, **C4BU′** and **C4BU″** as a solid were irradiated with UV light source (254 nm) at a distance of 30 cm for 30 min to observe the color change.

**2.3 Polymerization by gamma irradiation**

A Co-60 irradiator (Gamma beam 650) at Office of Atoms for Peace was used for this study. The dose rate determined with radiochromic film (FWT-60-00) dosimeter was 3.14 kGy/hr (kiloGray per hour). The polymerization was conducted by exposing **C4BU**, **C4BU″** and **C4HU** to 600 kGy of gamma radiation from $^{60}Co$.

**2.4 Purification of polymer**

**General procedure**

The resulting solid after gamma irradiation was dissolved in tetrahydrofuran with assistance of ultrasonication. The red solution was filtered through a 0.45 μm cellulose acetate filter, concentrated under vacuum until a little amount of tetrahydrofuran remained in a crude product, dropped into methanol and stirred for 2 hr at room temperature to give red insoluble precipitate. The precipitate was collected by filtration and dried under vacuum to obtain pure red polydiacetylene monitored by thin layer chromatography method.

**PC4BU:** The purification of polymerized solid (0.82 g) gave deep red polymer (0.61 g), 74.39% polymerization yield.

**PC4BU″:** The purification of polymerized solid (0.76 g) gave deep orange polymer (0.69 g), 90.79% polymerization yield.

**PC4HU:** The purification of polymerized solid (0.34 g) gave deep brown polymer (0.24 g), 70.59% polymerization yield.

**2.5 Polymer characterization**

- **UV/vis spectroscopy**

UV/vis measurement of polymers in solvent (tetrahydrofuran) and in the solvent (tetrahydrofuran)-cast film on the glass plate was performed in a quartz cuvette with 1.0 cm optical path length on a UV-Vis spectrometer.

- **Gel permeation chromatography (GPC)**

Molecular weights (MWs) and molecular weight distributions (MWDs) of the polymers were determined by GPC using a set of Styragel® columns (HR1, HR3 and HR4) at 35 °C. The mobile phase of tetrahydrofuran (flow rate of 1.00 mL $min^{-1}$) toward polystyrene standards, delivered using a Water 600 pump. The refractive index signal was measured using a Water 2414 refractive index detector.

- **Fourier transform infrared spectrometry (FT-IR)**

FT-IR spectroscopic studies were performed using a Nicolet Impact 410 FT-IR spectrophotometer. For the FT-IR measurement, 2 mg of each sample was mixed with 150 mg of potassium bromide powder (FT-IR grade) by grinding the two powders in a mortar. The mixtures were compressed into tablet casts with an internal diameter of 10 mm using a tablet machine. Then all the spectra were measured at room temperature (30 °C)

- **Fourier transform raman spectrometry (FT-Raman)**

FT-Raman spectroscopic studies were performed on a Perkin-Elmer 1760 FT-IR spectrophotometer with an Nd:YAG laser source and a Raman sample compartment attached to the FT-IR instrument. The sampling techniques consisted of mixing finely ground sample with a pure, dry spectroscopic grade of potassium bromide powder, usually at a concentration of about 1% sample in potassium bromide and all the spectra were measured at room temperature (30 °C).

- **Dynamic light scattering technique (DLS)**

The mean size of polymer and the size distribution were determined by nanosizer (Malvern Instruments). The polymer solution (5% v/v tetrahydrofuran dispersed in water) was sonicated for 1 min before measurement. Each measurement was repeated 3 times in order to acquire an average data.

- **Atomic force microscopy (AFM)**

Polymers were deposited on a freshly cleaved mica plate and dried at room temperature in desiccator for 4 hr. Seiko SPA 400 (SII Nanotechnology Inc.)

operating in non contact mode was used to observe the morphology and particle size of the deposited polymer

- **Transmission electron microscopy (TEM)**

TEM images were completed using a JEOL TEM-2100 electron microscope equipped with a CCD camera. The accelerating voltage was 200 KV. The polymer solution (5% v/v tetrahydrofuran dispersed in water) was deposited onto Formvar film coated copper grids (200 mesh), and stained with 2% uranyl acetate solution for 5 min and dried at room temperature in desiccator for 3 days.

## 2.6 Thermochromic study

### Visual observation

The polymers (1.0 mg) were dissolved in *N*,*N*-dimethylformamide (1.0 mL) in a test tube and heated in an oil bath from 30-140 °C. The color change and reversible color change of these samples were observed by naked eye. For UV/vis measurement, the polymer solutions in *N*,*N*-dimethylformamide was heated from 30-100 °C in a quartz cuvette with 1.0 cm optical path length on a temperature-controlled water UV/vis spectrometer in the kinetic mode.