was purified by flash chromatography on silica gel (ethyl acetate/hexane/methylene chloride : 1/3/1, v/v/v) to afford 3,5-dinitroanilide of (S)-naproxen. The spectroscopic (^{1}H NMR and IR) and melting point data of this compound were consistent with those reported previously.[8]

All other derivatization reactions of (S)-naproxen were performed via the same procedure as described above for 3, 5-dinitroanilide of (S)-naproxen except for the use of 2 N HCl solution instead of 6 N HCl solution to wash the reaction mixture.

Derivatization of (S)-naproxen with various nucleophiles in the presence of a coupling agent such as EEDQ or DCC was performed as following. (S)-Naproxen (0.20 g, 0.87 mmole) and EEDQ (0.26 g, 1.05 mmole, 1.2 eq.) or DCC (0. 22 g, 1.06 mmole, 1.2 eq.) dissolved in 20 mL of methylene chloride was stirred for 20 min at room temperature and then a nucleophile (1.0 eq.) was added. The whole mixture was stirred at room temperature for 12 hr and then washed successively with 60 mL of saturated $NaHCO_3$ solution, 50 mL of 2 N HCl solution and brine. The organic solution was dried over anhydrous $MgSO_4$, filtered and then evaporated. The residue was purified by flash chromatography on silica gel (ethyl acetate/hexane/methylene chloride : 1/3/1, v/v/v) to afford a derivative of (S)-naproxen.

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Asymmetrically Substituted Calix[5]arene Derivatives

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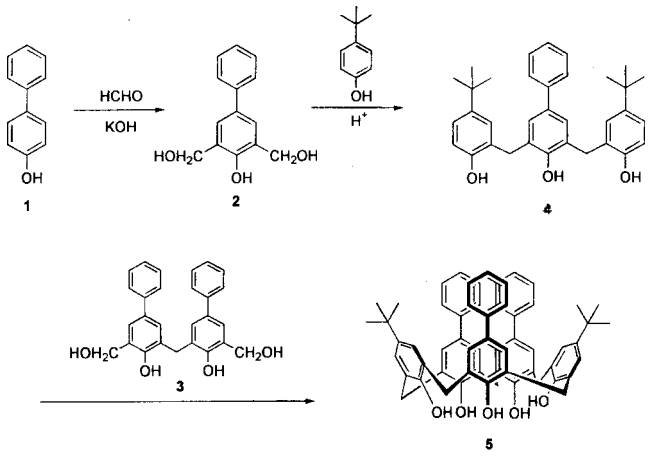
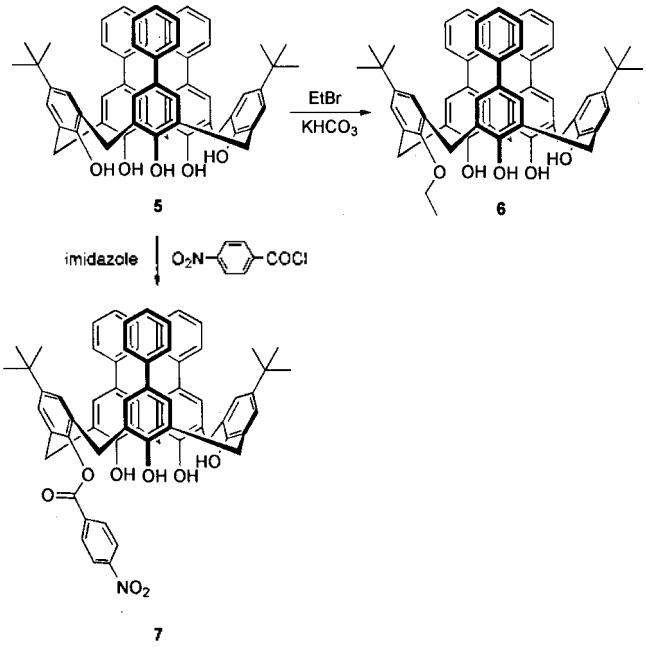
Calixarenes are macrocyclic compounds available in a variety of ring sizes and are of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures.[1-3] One of the main features of naturally occurring host molecules is their capacity for enantioselective recognition. Various attempts have therefore been made to obtain chiral host molecules based on calixarenes. The most simple method to convert calixarene into chiral derivatives is the introduction of chiral substituent at the lower[4,5] or upper[3,6] rim of calixarene skeleton. More interest has been focused on the possibility of synthesizing "inherently" chiral calixarenes, which are built up of nonchiral subunits and consequently owe their chirality to the fact that the calixarene molecule is not planar and several procedures for the inherently chiral calix[4]arene were reported.[7-20] However only one article was published by Böhmer and Pappalardo[21] for the preparation of chiral *p-t*-butylcalix[5]arene. They treated *p-t*-butylcalix[5]arene with suitable oligoethylene glycol ditosylate in the presence of CaF_2 to produce 1,2- or 1,3-isomer of calix[5]crownether, which was desymmetrized by O-alkylation of one of the two adjacent hydroxy groups to afford asymmetrically substituted calix[5]arenes. Recently we reported the facile preparation of calix[5]arene which have different substituents at the upper



Scheme 1

rim.[22] These kind of calix[5]arenes have reduced symmetry, usually have only one plane of symmetry, therefore can be used as starting material for the preparation of chiral calixarene. As shown on following schemes, this paper deals with the synthesis of two chiral calix[5]arenes starting from the calix[5]arene **5**, which has three phenyls and two *t*-butyl groups in AABAB pattern at upper rim of calix. Calix[5] arene **5** was synthesized by the "3+2" fragmentation condensation reaction between bishydroxymethylated dimer of *p*-phenylphenol (AA) and *p*-substituted phenol trimer (BAB) as shown in following Scheme 1.

Following the published procedure,[23,24] a mixture of *p*-phenylphenol, formaldehyde and large excess KOH was heated at 45-50 °C for 4 days to produce 2,6-bishydroxymethyl-4-phenylphenol **2** and its dimer diol **3** in 35 and 55% yield respectively. Compound **2** was treated with excess *p-t*-butylphenol in the presence of a catalytic amount of *p*-toluenesulfonic acid in benzene and the unreacted excess *p-t*-butylphenol and solvent were removed by steam distillation. The crude product was recrystallized from hexane to afford the corresponding trimers **4** in 95% yield. Using this trimer **4** and dimer diol **3** as coupling components, calix[5]arene **5** was prepared by "3+2" fragmentation condensation route similar to that developed by Böhmer and coworkers.[25,26] An equimolar mixture of trimer **4** and bishydroxymethyl dimer **3** in xylene was refluxed for 3 days under nitrogen atmosphere. After removal of solvent, the residue was purified to afford the calix[5]arene **5** in 32% yield. The structure of calix[5] arene **5** was established by elemental analysis, ^{1}H NMR/^{13}C NMR spectroscopy and mass spectrometry. In ^{1}H NMR spectrum of **5**, the OH resonance peak appears as three singlets in the 1 : 2 : 2 ratio, and the resonances arising from the $ArCH_2Ar$ methylene hydrogens of the calix show temperature dependent spectral patterns. At room temperature the pattern is two broad singlets in the ratio of 1 : 4, while at lower temperature (−20 °C) it is a set of AB quartet. The presence of three $ArCH_2Ar$ methylene carbon resonance peaks at 31-29 ppm in the ^{13}C NMR spectrum of compound **5** indicates a cone conformation, but the conformational interconversion is fast on the ^{1}H NMR time scale at room temperature. The only symmetry element in calix[5]arene **5** is a mirror plane and therefore it can be desymmetrized by O-alkylation or O-acylation of one hydroxy group of the two



Scheme 2

t-butyl phenol rings (B) or adjacent two *p*-phenylphnol rings (AA). To explore this possibility, we tried selective ethylation and benzoylation and prepared two chiral calix[5] arenes **6** and **7** as shown in Scheme 2.

A recent study has shown that monoalkylation of *p-t*-butylcalix[5]arene with alkyl tosylate can be achieved with high yield in the presence of $KHCO_3$.[27] Pappalardo[28] also reported the selective partial alkylation of *p-t*-butylcalix[5] arene using the similar method reported by Gutsche. Following the Gutsche procedure, calix[5]arene **5** was refluxed with ethyl bromide in the presence of anhyd. $KHCO_3$ in acetonitrile under nitrogen atmosphere. Purification of the resulting crude product by column chromatography afforded the desired chiral calixarene **6** in 43% yield as a racemate. The structure of calix[5]arene **6** was established by elemental analysis, ^{1}H NMR/^{13}C NMR spectroscopy and mass spectrometry. In ^{1}H NMR spectrum of **6**, the OH resonance peak appears as four singlets and the resonances arising from the *t*-butyl group appear as two singlets. The resonance peaks from methylene bridge protons appear as very complex pattern which supports the lack of symmetry of this compound. ^{13}C NMR spectrum of compound **6** has 33 peaks (44 expected) from aromatic carbons and five peaks from $ArCH_2Ar$ methylene carbons at 32-30 ppm. The quarternary carbon and methyl carbon of the *t*-butyl groups appear as two peaks respectively. Both of the ^{1}H and ^{13}C NMR spectra support the cone conformation and chirality of calixarene **6**. The position of ethyl group can not be definitely determined by the ordinary NMR spectrum data only. The detailed regioselectivity of single O-ethylation was confirmed by the preliminary X-ray diffraction study which will be published after more data refinement. We also tried to introduce benzoyl group and the compound **5** was stirred with 4-nitrobenzoyl chloride using imidazole as base in acetonitrile for 1 day at room temperature under nitrogen atmosphere. The obtained residue was purified by flash chromatography to afford the compound **7** in 46% yield. IR spectrum of **7**

shows stretching vibration bands of ester carbonyl and nitro groups. NMR and mass spectra of compound **7** also support the structure of this compound. In ^{1}H NMR spectrum of **7**, the proton resonance peaks appear as similar patterns with compound **6**. ^{13}C NMR spectrum of compound **6** has 43 peaks (48 expected) from aromatic carbons and five peaks from $ArCH_2Ar$ methylene carbons at 32-31 ppm. The quarternary carbon and methyl carbon of the t-butyl groups appear as two peaks respectively, which commensurated with the asymmetric structure of compound **7**. In this work we have demonstrated that asymmetrically substituted calix [5]arene is readily available by the selective O-alkylation or O-benzoylation of calix[5]arene which has two different substituents in AABAB pattern.

Experimental

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points of all compounds were taken in sealed and evacuated capillary tubes on an Syblon thermolyne apparatus with polarizing microscope and were not corrected. IR spectra were determined on a Nicolet Impact 400 FT-IR spectrometer as KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 300 (300 and 75 MHz) and Bruker AMX 500 instrument. Chemical shifts are recorded as δ values in parts per million relative to TMS (δ 0.0) as an internal standard. Elemental analyses were carried out at Organic Chemistry Research Center (OCRC). TLC analyses were carried out on silica gel plates (absorbent thickness 250 μm). Flash chromatography was carried out with E. Merck silica gel (230-400 mesh ASTM). Elution rate were 2 in/min.

2,6-Bishydroxymethyl-4-phenylphenol 2 and 3-(3-Hydroxymethyl-5-phenyl-salicyl)-5-phenyl-2-hydroxybenzyl alcohol 3. were prepared in 35% and 55% yields respectively following the published procedure.[18]

2-[3-(5-*t*-Butylsalicyl)-5-phenylsalicyl]-4-*t*-butylphenol 4. After a mixture of compound **2** (10.0 g, 43.5 mmol), *p*-*t*-butylphenol (60.0 g, 4 mole equivalent per hydroxymethyl group) and *p*-toluenesulfonic acid (130 mg) in benzene (200 mL) was refluxed for 20 h, excess *p*-*t*-butylphenol was removed by steam distillation. After the resulted solid material dissolved in $CHCl_3$ (100 mL), chloroform solution was washed with water several times, dried ($MgSO_4$) and then evaporated solvent to afford slightly brown colored residue. A recrystallization of the residue from hexane to produce 20.2 g (95%) of compound **4** as a colorless crystalline solid: mp 204-206 °C; IR (KBr) 3238 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.52 (s, 1, OH), 8.57 (s, 2, OH), 7.55-6.77 (m, 13, ArH), 4.02 (s, 4, CH_2), 1.31 (s, 18, CH_3); ^{13}C NMR ($CDCl_3$): δ 150.07, 149.89, 144.84, 141.43, 135.31, 128.90, 128.40, 128.19, 127.86, 127.15, 126.92, 126.46, 125.28, 115.89 (Ar), 33.97 ($\underline{C}(CH_3)_3$), 31.87 (CH_2), 31.40 (C($\underline{C}H_3)_3$);. Anal. Calcd. for $C_{34}H_{38}O_3$: C, 82.55; H, 7.74. Found: C, 82.43; H, 7.80.

11,29-Di-*t*-butyl-31,32,33,34,35-pentahydroxy-5,17,23-triphenylcalix[5]arene 5. A mixture of dimer diol **3** (2.06 g, 5.0 mmol) and trimer **4** (1.95 g, 5.0 mmol) in xylene (100 mL) was refluxed for 3 days under N_2. After removal of solvent, the residue was purified by column chromatography (eluent was 10 : 1 mixture of hexane and acetone) to afford the calix[5]arene **5** (800 mg, 32%) as a colorless crystalline solid: mp 225-226 °C; IR (KBr) 3272 cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 9.16 (s, 1, OH), 9.11 (s, 2, OH), 8.86 (s, 2, OH) 7.54-7.24 (m, 25, ArH), 3.95 (br, 10, CH_2) [(at 60 °C) 4.02 (s, 2, CH_2), 3.96 (s, 2, CH_2); (at 0 °C) 4.23 (br.s, 5, CH_2), 3.65 (br.s, 5, CH_2); (at −20 °C) 4.23 (d, 5, CH_2, J=14.1 Hz), 3.64 (d, 5, CH_2, J=14.1 Hz)], 1.29 (s, 18, tBu); ^{13}C NMR ($CDCl_3$) δ 149.82, 149.77, 147.68, 144.42, 140.86, 134.88, 128.69, 128.67, 128.06, 127.97, 127.94, 127.28, 127.23, 126.96, 126.92, 126.82, 126.77, 126.09, 125.86, 125.83 (Ar), 34.00 ($\underline{C}(CH_3)_3$), 31.83 ($ArCH_2Ar$), 31.53 ($C(\underline{C}H_3)_3$), 31.23, 29.70 ($ArCH_2Ar$); FAB MS 870 (M^+) (Calcd. M^+ 870); Anal. Calcd for $C_{61}H_{58}O_5$: C, 84.11; H, 6.71. Found: C, 84.28; H, 6.78.

11,29-Di-*t*-butyl-31-ethoxy-32,33,34,35-pentahydroxy-5,17,23-triphenylcalix[5]arene 6. After the mixture of calixarene **5** (1.00 g, 1.15 mmol) and anhyd. $KHCO_3$ (461 mg, 4.61 mmol) in MeCN (50 mL) was refluxed for 1h under N_2 atmosphere, a solution of C_2H_5Br (0.26 mL, 3,45 mmole) in MeCN (10 mL) was added and then refluxed for 36 h. After removal of solvent, the residue was extracted with chloroform (50 mL) and 1M HCl (20 mL). The organic layer was separated, washed with water, dried with $MgSO_4$ and then evaporated to dryness. The resulting pale yellow reside was purified by column chromatography (eluent was 9 : 1 mixture of hexane and acetone) to afford the desired compound **6** (430 mg, 43%) as a colorless crystalline solid; mp 196-198 °C; IR (KBr) 3387 cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.41 (b. s, 1, OH), 8.23 (b. s, 1, OH), 8.22 (b. s, 1, OH), 8.18 (br. s, 1, OH) 7.50-7.19 (m, 25, ArH), 4.16-3.59 (br. m, 10, $ArCH_2Ar$), 3.97 (q, 2, OCH_2, J=7 Hz), 1.32 (s, 9, tBu), 1.31 (s, 9, tBu), 1.27 (t, 3, CH_3, J=7 Hz); ^{13}C NMR ($CDCl_3$) δ 151.30, 150.90, 148.96, 148.58, 148.56, 146.80, 142.07, 141.95, 140.15, 140.00, 139.95, 139,70, 137.18, 137.09, 133.74, 133.65, 132.52, 132,36, 132.30, 127.62, 127.54, 127.16, 126.93, 126.87, 126.48, 126.26, 126.05, 125.92, 125.83, 125.67, 125.52, 125.09, 125.00 (Ar), 34.02, 33.82 ($\underline{C}(CH_3)_3$), 32.98, 31.31, 31.20, 30.70, 30.54 ($ArCH_2Ar$), 30.72, 30.63 ($C(\underline{C}H_3)_3$); FAB MS 898 (M^+) (Calcd. M^+ 898); Anal. Calcd for $C_{63}H_{62}O_5$: C, 84.15; H, 6.95. Found: C, 84.26; H, 7.04.

11,29-Di-*t*-butyl-32,33,34,35-pentahydroxy-31-(4-nitrobenzoyloxy)-5,17,23-triphenylcalix[5]arene 7. A mixture of compound **5** (1.00 g, 1.15 mmole), imidazole (1.20 g, 17.7 mmole) and 4-nitrobenzoyl chloride (280 mg, 1.53 mmole) in MeCN (25 mL) was stirred for 1 day at room temperature under N_2 atmosphere. After quenching the reaction by adding dil. HCl, the reaction mixture was extracted with chloroform. The organic layer was separated, washed with water several times, dried with $MgSO_4$ and then evaporated solvent. The resulting residue was triturated with methanol (15 mL) to produce precipitate, which was collected and purified by flash chromatography (eluent was 1 : 6 mixture of hexane and acetone) to afford the desired compound **7** (545 mg, 46%) as slightly yellow colored crystalline solid; mp 212-213 °C; IR (KBr) 3380, 1735, 1530, 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.59 (br. s, 2, OH), 8.31 (br. s, 2, OH), 7.83-6.94 (m, 29, ArH), 3.92-3.68 (m, 10, $ArCH_2Ar$), 1.25 (s, 9, tBu), 1.23 (s, 9, tBu); ^{13}C NMR ($CDCl_3$) δ 165.02 (C=O), 152.15, 151.78, 151.15, 151.08, 150.92, 150.72, 150.57, 150.45, 149.23, 148.44,

144.96, 144.51, 141.04, 140.52, 140.30, 140.23, 134.52, 133.47, 133.24, 132.62, 131.68, 131.50, 131.23, 131.03, 129.05, 128.93, 128.79, 128.61, 128.39, 128.15, 127.99, 127.87, 127.67, 127.52, 127.41, 127.33, 127.01, 126.92, 126.75, 126.60, 126.48, 126.40, 126.28, 126.15, 126.06, 123.35, 123.15 (Ar), 33.92, 33,59 ($\underline{C}(CH_3)_3$), 32.60, 32.11, 31.83, 31.34, 31.05 ($ArCH_2Ar$), 31.47, 30.82 ($C(\underline{CH}_3)_3$); FAB MS 1019 (M^+) (Calcd. M^+ 1019); Anal. Calcd. for $C_{68}H_{61}NO_8$: C, 80.05; H, 6.03. Found: C, 80.17; H, 6.09.

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Synthesis and Ceramic Conversion Reactions of Decaborane-CERASET Polymers: New Processable Precursors to $SiC/Si_3N_4/BN$ Ceramics

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There has been great recent interest in the development of new polymeric precursors to advanced silicon-based ceramic materials that enable their formation in technologically useful forms.[1] Polyborosilazanes polymers have been of particular interest since recent work has shown that they can serve as processable precursors to SiNCB ceramic materials that possess extraordinary properties.[2] Thus, these polyborosilazanes enable the homogeneous incorporation of boron into traditional silicon-based ceramics with the resulting amorphous SiNCB composites having greatly increased thermal and oxidative stabilities. The enhanced properties of these ceramics may now enable their use in many high temperature applications.

In this note, we report our preliminary studies of the