Synthesis of Calixsalen : A Route to Azacalixarene Analogue

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Received November 18, 2006

Key Words : Calixarene, Azacalixarene, Calixsalen

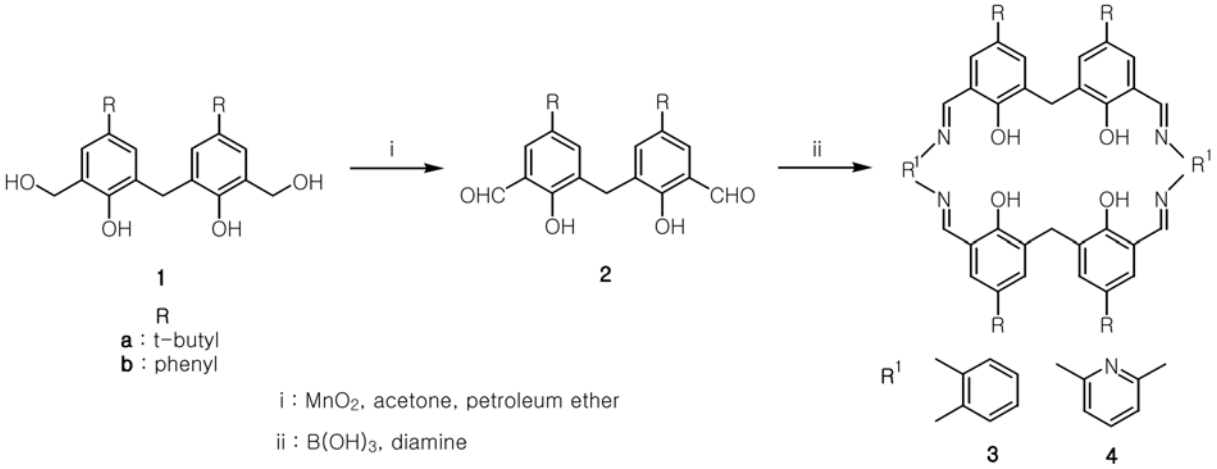
Calixarenes are synthetic macrocyclics available in a variety of ring sizes and of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures and have received a great deal of attention in recent years.[1-4] Chemical modification of calixarene represents an effective and versatile way of producing receptors with highly selective binding properties. Even minor changes in the functionalization or conformation of chemically modified calixarenes can lead to drastic changes in the complexation behaviour. Although main chemical modifications have been made on the upper (after removal of *tert*-butyl groups or *ipso* substitution) and lower rims (by reaction at the OH groups), modifications have been also done at the level of the linking methylene groups. Azacalixarene, which is derived from calixarenes by the replacement of at least one methylenic carbon atom by a methyleneaza link, has been the subject of relatively few investigations up to now.[5] In particular, in spite of their potential richness and versatility as ligands, the structural studies of their complexes are scarce compared to those of calixarenes and even oxacalixarenes, which are another closely related family of expanded calixarenes. The presence of a soft nitrogen atom in azacalixarenes is envisioned to bind soft cations like ion metals according to Hard Soft Acid and Base Principle (HSAB) as well as other specific features such as building sophisticated receptors, metal ligand systems etc. Therefor during the last few years, we reported the preparation and characterization of the oxacalix[4]arene and azacalix[4]arene and their derivatives.[6,7]

Calixarene-like salen (calixsalen) ligands which contain salen structure in the macrocyclic ring of calixarene structure have attracted considerable attention due to formation of a variety of multi-metal complexes, which exhibit catalytic activity for epoxidation of olefins, asymmetric ring-opening of epoxides, NLO behavior, etc.[8,9] Furthermore, metallohosts bearing a salen analogue provide a unique and cooperative binding site for both neutral guests and cations.[10,11] In addition the reduction of C=N group of calixsalen provides a new route to the preparation of azacalixarene analogue.

Recently, the synthesis of novel calixsalen ligand with well-defined and rigid cavity was reported.[12-15] Robson and coworkers prepared a calixsalen by treatment of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol in the presence of excess nickel(II) acetate as a template ion and investigated the X-ray crystal structure.[12] Hisaeda and coworkers reported the preparation of macrocyclic ligands by Schiff-base condensation reaction with 3,3-methylenebis(salicylaldehyde) and phenylenediamine using the boric ion template method. Neither the metal-templated method, such as Ni^{2+} and La^{3+}, nor high dilution method formed the pure desired product.[13] Zhu and coworkers reported the synthesis of a new chiral calixarene-like salen ligand by the condensation of p-*tert*-butylphenol timer bisaldehyde and (*1R,2R*)-1,2-diaminocyclohexane and examined the enantioselective Friedel-Craft reaction of aromatic compounds with glyoxylate.[14] However, the complexation properties of these calixsalen derivatives have not been published except the transition metals which are used as template ion in the synthesis.

In a continuation of constructing hetero atom containing calixarene receptors, in this paper the synthesis of calixsalens and the upper rim modification to explore the possibility of these molecules as a host ligand are reported.

2-(5-*Tert*-butylsalicyl)-4-*tert*-butylphenol was treated with 25% NaOH solution and 35% formaldehyde in methanol to produce Compound **1a** in 73% yield. Compound **1b** was prepared in 55% yield via the published method.[16] And then the dimer diol **1** and the activated manganese dioxide were reacted in acetone and petroleum ether. After the solid MnO_2 was separated through a short column of silica gel, the resulting dark colored residue was purified with column chromatography to afford the bisaldehyde **2**. The macrocyclic ligand **3** and **4** were prepared by the published method,[13] in which a boric ion was used as a template as shown Scheme 1. To a solution of bisaldehyde **2** in $CHCl_3$ was added a methanol solution of boric acid and stirred for 0.5 h. Then a methanol solution of corresponding diamine was added and stirring was continued for 7-40 hr at room temperature. The precipitates were collected by filtration, washed with methanol and dried in *vacuo*, which gave satisfactory elemental analyses without further purification. The structures of calixsalen ligand **3** and **4** were identified by ^{1}H NMR, ^{13}C NMR, IR spectrum and the elemental analysis. Due to the symmetry of the calixsalens **3** and **4**, ^{1}H NMR spectra reveal singlets corresponding to hydroxy protons, C*H*=N protons, methyl protons of *tert*-butyl groups. The aromatic protons are also appear as singlet. These NMR patterns indicate the free interconversion between conformational isomers at room temperature. The ^{13}C NMR specturm of **3** and **4** shows one peak at around 30 ppm for the Ar*C*H_2Ar bridge carbons implying that two adjacent benzene ring are in a *syn* orientation. The X-ray crystal structure of **3a** was reported by Hisaeda *et al*.[13] Compound **3a** has a macro-cyclic structure and has two N2O2 metal binding



Scheme 1

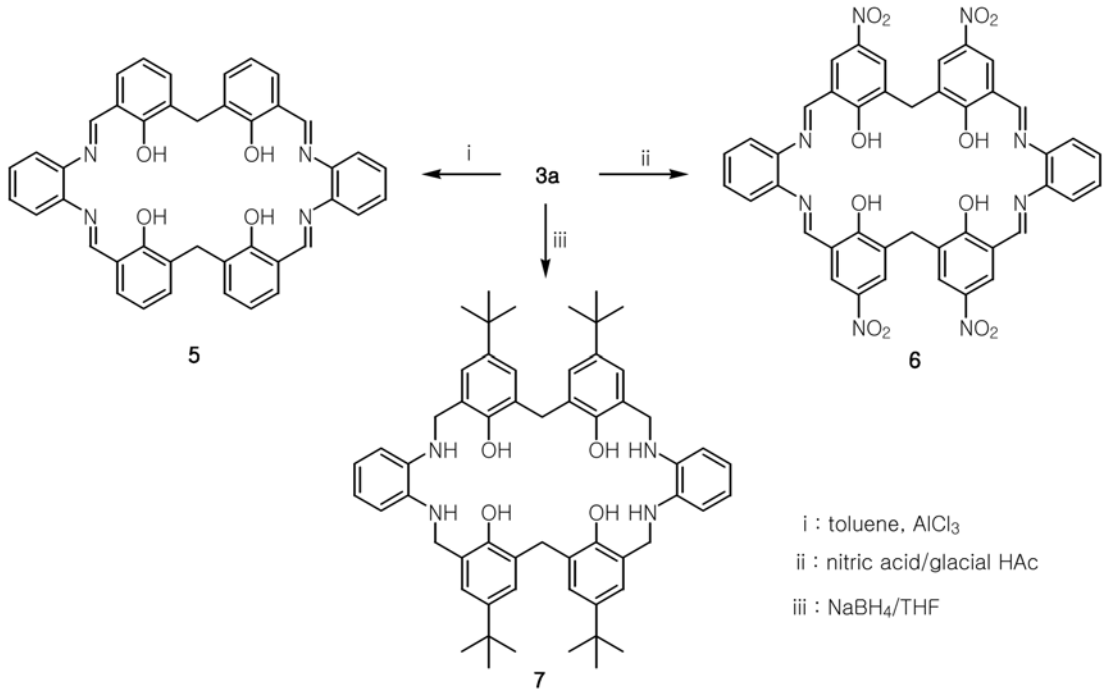
sites and the overall structure is similar to the distorted 1,2-alternate conformation of calix[4]arene.

The most pronounced features of calixarenes are the relatively simple modification at both the lower rim and the upper rim. To explore these possibilities of the upper rim modification of calixsalen, de-*tert*-butylation and *ipso*-nitration of **3a** was investigated. And the reduction of C=N was also investigated to prepare the azacalixarene analogue **7**.

Tert-butyl group must be removed prior to the introduction of functional groups into the para position of phenol rings of calixarene, therefor dealkylation of **3a** was tried. When the **3a** was treated with $AlCl_3$ in the presence of phenol in toluene, the dealkylated compound **5** was obtained in 64.5% yield. In the ^1H and ^{13}C NMR spectrum, the peak for the 36 protons peak of at 1.25 ppm and carbon peaks at 33.93 and 31.39 ppm of *tert*-butyl groups were disappeared, which supported the reaction. The introduction of various founctional groups into the para position is now under investigation.

Nitro group can serve as admirable precursors for functional group introduction after reduction to amino groups, so various research groups reported the procedures for the introduction of nitro group into the upper rim of calixarenes.[17] Therefor we tried to introduce nitro group into the para position of **3a** using *ipso* nitration procedure.[18] Compound **3a** was treated with glacial acetic acid and 100% nitric acid in methylene chloride to afford the para nitrated compound **6** in 65% yield. The nitro group stretching band at 1530 and 1360 cm^{-1} in the IR spectrum of **6** support the introduction of nitro group.

In spite of their potential richness and versatility as ligands, Azacalixarene have been the subject of relatively few



Scheme 2

investigations up to now. Therefor in this study we tried to reduce CH=N group of **3a** to CH_2NH group using $NaBH_4$ as reducing agent for the preparation of novel azacalix[4]arene derivative **7**. To the suspension of $NaBH_4$ in methanol was added a THF solution of **3a** and then the reaction mixture was refluxed for 3 h. From the residue obtained after removal of the solvent, **7** was produced in 40.5% yield. Reduction of CH=N to CH_2NH was conformed by IR and NMR spectrum. In IR spectrum the C=N band at 1618 cm^{-1} was disappeared and N-H stretching band at 3350 cm^{-1} was appeared. In ^1H NMR spectrum four proton of the N=C*H* singlet peak at 8.64 ppm was replaced by the eight proton singlet peak of the ArCH_2N at 4.28 ppm and four proton singlet peak of the N*H* at 4.24 ppm. ^{13}C NMR also confirmed the reduction.

In conclusion, novel ligands with a macrocyclic structure have been synthesized by a convenient method. To explore the possibility of these compounds as a calixarene analogous host molecule, reduction of C=N, de-*tert*-butylation of *t*-butyl group and *ipso* nitration reaction were investigated. Detailed property and reactivity of these new derivatives are now under investigation in our laboratory.

Experimental Section

Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Melting points were taken in evacuated and sealed capillary tubes with a Mel-Temp apparatus. IR spectra were determined with a Nicolet Impact 400 FT-IR spectrometer as KBr pellets. ^1H and ^{13}C NMR spectra were recorded with Bruker AMX 400 spectrometer. Chemical shifts are recorded in parts per million relative to TMS as an internal standard. **2-**(5-*Tert*-butylsalicyl)-4-*tert*-butylphenol and 3-(3-hydroxylmethyl-5-phenylsalicyl)-5-phenyl-2-hydroxybenzyl alcohol **1b** were prepared following published procedures.[15]

3-[3-Hydroxymethyl)-5-*tert*-butylsalicyl]-5-*tert*-butyl-2-hydroxybenzyl Alcohol 1a. A mixture of 2-(5-*tert*-butylsalicyl)-4-*tert*-butylphenol (6.02 g, 19.3 mmol), 8.8 mL of 25% NaOH, 12 mL of CH_3OH, and 28 mL of 35% HCHO solution was heated at 50 °C for 24 h in an atmosphere of N_2. The mixture was cooled to room temperature, poured into 200 mL of ice cold water, acidified with 1 N HCl, and the precipitated white solid extracted into chloroform. The chloroform extract was washed with water several times, dried over anhydrous $MgSO_4$, and the solvent was removed by evaporation to leave a waxy residue that was triturated with petroleum ether to afford 5.26 g (73.3%) of the desired product as crystalline solid. mp 116-117 °C (lit.[19] mp 117-118 °C). ^1H NMR ($CDCl_3$) δ 8.45 (s, 2, OH), 7.26 (d, 2, Ar*H*, *J* = 2.4 Hz), 6.94 (d, 2, Ar*H*, *J* = 2.4 Hz), 4.75 (s, 4, CH_2O), 3.90 (s, 2, CH_2), 2.87 (br. s, 2, O*H*), 1.26 ppm (s, 18, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 150.22, 143.56, 127.52, 127.33, 125.39, 123.57 (*Ar*), 64.67 (ArCH_2O), 34.21 (*C*(CH$_3$)$_3$), 31.69 (C(*C*H$_3$)$_3$), 31.05 (*C*H$_2$).

3,3'-Methylenebis(salicylaldehyde) 2a and 2b. The mixed solution of **1** (8.05 mmol) in acetone (15 mL) and petroleum ether 20 (mL) was added into the petroleum ether solution (150 mL) of the activated manganese dioxide (7.0 g, 80.5 mmol) with stirring. After 3 days stirring, the solid MnO_2 was separated from the reaction mixture through a short column of silica gel and washed with petroleum ether two times. The combined filtrate and washing were concentrated to dark colored residue which was separated with column chromatography to afford the desire product **2** as crystalline solid.

2a. Eluent (1 : 30 mixture of acetone and hexane), 36.0% yield, mp 178 °C; ^1H NMR ($CDCl_3$) δ 11.12 (s, 2, C*H*O), 9.79 (s, 2, O*H*), 7.57 (s, 2, Ar*H*), 7.30 (s, 2, Ar*H*), 3.96 (s, 2, CH_2), 1.21 ppm (s, 18, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 197.11 (*C*O), 158.00, 142.48, 136.57, 128.19, 128.03, 119.89 (*Ar*), 34.34 (*C*(CH$_3$)$_3$), 31.40 (C(*C*H$_3$)$_3$), 29.17 (*C*H$_2$). Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.65; H, 7.39.

2b. Eluent (1 : 15 mixture of acetone and hexane), 51.6% yield, mp 202 °C; ^1H NMR ($CDCl_3$) δ 11.36 (s, 2, C*H*O), 9.96 (s, 2, O*H*), 7.84 (d, 2, Ar*H*, *J* = 2.2 Hz), 7.64 (d, 2, Ar*H*, *J* = 2.2 Hz), 7.53 (d, 4, Ar*H*, *J* = 6.8 Hz), 7.44 (t, 4, Ar*H*, *J* = 7.8 Hz), 7.34 (t, 2, Ar*H*, *J* = 76.8 Hz) 4.18 ppm (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 197.00 (*C*O), 159.37, 139.70, 137.21, 133.22, 130.52, 129.16, 129.00, 127.53, 126.87, 120.71 (*Ar*), 28.95 (*C*H$_2$). Anal. Calcd for $C_{27}H_{20}O_4$: C, 79.40; H, 4.94. Found: C, 79.25; H, 4.82.

Syntheses of Calixsalen 3 and 4. To a solution of bisaldehyde (0.39 mmol) in 3 mL of $CHCl_3$ was added a boric acid (12.0 mg, 0.20 mmol) in methanol (3 mL) and stirred for 0.5 h. Then a methanol solution (7.5 mL) of corresponding diamine (0.39 mmol) was added and stirring was continued for 7-40 hr at room temperature. The precipitates were collected by filtration, washed with methanol and dried *in vacuo*, which gave satisfactory elemental analyses without further purification.

3a: reaction time 7 h; yield 85%; mp 278-279 °C; IR (KBr) 3410, 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.27 (s, 4, O*H*), 8.64 (s, 4, N=C*H*), 7.31 (br, 8, Ar*H*), 7.24 (s, 4, Ar*H*), 7.17 (s, 4, Ar*H*), 4.20 (s, 4, CH_2), 1.25 ppm (s, 36, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 163.49, 157.77, 143.08, 140.49, 131.39, 127.72, 127.37, 126.37, 118.79, 117.86 (*Ar* & *C*=N), 33.93 (*C*(CH$_3$)$_3$), 31.39 (C(*C*H$_3$)$_3$), 29.14 (*C*H$_2$). Anal. Calcd for $C_{58}H_{64}N_4O_4$: C, 79.06; H, 7.32; N, 6.36. Found: C, 78.90; H, 7.29; N, 6.26.

4a: reaction time 40 h; yield 75%; mp 290 °C (decompose); IR (KBr) 3398, 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.15 (s, 4, O*H*), 9.54 (s, 4, N=C*H*), 7.45 (s, 8, Ar*H*), 7.26 (s, 6, Ar*H*), 4.21 (s, 4, CH_2), 1.31ppm (s, 36, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 166.21, 158.40, 157.52, 141.67, 133.71, 128.25, 117.78 (*Ar* & *C*=N), 34.24 (*C*(CH$_3$)$_3$), 31.60 (C(*C*H$_3$)$_3$), 31.41 (*C*H$_2$). Anal. Calcd for $C_{56}H_{62}N_6O_4$: C, 73.82; H, 6.86; N, 12.30. Found: C, 73.59; H, 6.94; N, 12.18.

3b: reaction time 24 h; yield 69%; mp > 350 °C; IR (KBr) 3450, 1618 cm^{-1}; ^1H NMR (DMSO d_6) δ 13.21 (br. s, 4, O*H*) 9.07 (s, 4, N=C*H*), 7.90-7.29 (m, 36 Ar*H*), 4.21 ppm (s, 4, CH_2); ^{13}C NMR (DMSO d_6) δ 197.00 (*C*O), 159.27, 142.63, 140.19, 132.31, 131.24, 130.00, 128.91, 129.63, 128.54, 127.51, 126.70, 120.99, 119.48 (*Ar* & *C*=N), 31.27 (*C*H$_2$). Anal. Calcd for $C_{66}H_{48}N_4O_4$: C, 82.48; H, 5.03; N, 6.66.

Found: C, 82.70; H, 5.29; N, 6.36.

***p*-Hcalixsalen 5.** A slurry of 1.33 g (1.51 mmol) of *p-tert*-butylcalixsalen **3a**, 681 mg (7.25 mmol) of phenol and 1.06 g of $AlCl_3$ (7.93 mmol) was stirred in 50 mL of toluene at room temperature for 1 hr in an inert atmosphere. The mixture was poured into 50 mL of 0.2 N HCl, the organic phase was washed with water 3 times, dried with anhydrous $MgSO_4$ and then toluene was evaporated. Upon addition of methanol a precipitate formed, which was removed by filtration to give 640 mg (64.6%) of crystalline solid. mp 249 °C; IR (KBr) 3420, 1613 cm^{-1}; ^{1}H NMR (DMSO d_6) δ 13.12 (s, 4, O*H*), 8.91 (s, 4, N=C*H*), 7.51-7.48 (m, 6, Ar*H*), 7.41-7.38 (m, 6, Ar*H*), 7.05 (d, 4, Ar*H*, J = 7.2 Hz), 6.87 (t, 4, Ar*H*, J = 7.2 Hz), 3.79 (s, 4, CH_2); ^{13}C NMR (DMSO d_6) δ 165.53, 159.51, 142.70, 134.01, 131.86, 128.79, 127.94, 120.09, 119.26, 119.17 (*Ar* & *C*=N), 29.04 (*C*H_2). Anal. Calcd for $C_{42}H_{32}N_4O_4$: C, 76.81; H, 4.91; N, 9.75. Found: C, 76.92; H, 4.89; N, 9.56.

***p*-Nitrocalixsalen 6.** *p-Tert*-butylcalixsalen **3a** (250 mg, 0.283 mmol) was dissolved in 5 mL of dried CH_2Cl_2 under inert atmosphere and cooled to 0 °C. Glacial acetic acid (2.6 mL, 45.4 mmol) and 100% NHO_3 (0.91 mL, 22.7 mmol) were added. The solution was stirred for 1 h at 0 °C and 30 min at room temperature. The reaction mixture was slowly poured in 80 mL water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was triturated with methanol to afford 154 mg (65%) of the product as yellow solid. mp >350 °C; IR (KBr) 3430, 1618, 1530, 1360 cm^{-1}; ^{1}H NMR (DMSO d_6) δ 12.87 (s, 4, O*H*), 9.59 (s, 4, N=C*H*), 8.19 (s, 8, Ar*H*), 7.24 (s, 8, Ar*H*), 4.22 (s, 4, CH_2); ^{13}C NMR (DMSO d_6) δ 163.49, 163.17, 142.98, 140.49, 134.59, 127.72, 127.37, 126.17, 118.79, 117.86 (*Ar* & *C*=N), 30.44 (*C*H_2). Anal. Calcd for $C_{42}H_{28}N_8O_{12}$: C, 60.29; H, 3.37; N, 13.4. Found: C, 60.10; H, 3.19; N, 13.7.

***p-Tert*-butylazacalix[4]arene 7.** To the stirred suspension of $NaBH_4$ (206 mg, 5.45 mmol) in methanol (16 mL) was added a THF (4 mL) solution of **3a** (100 mg, 0.11 mmol) and then refluxed for 3 h. After removal of the solvent, the residue was extracted with CH_2Cl_2 (20 mL), washed with 0.1 N HCl (30 mL) and then with $NaHCO_3$ solution. The CH_2Cl_2 extract after treating with anhydrous $MgSO_4$ was evaporated to dryness on a rota-vap. The residue was triturated with methanol to afford a 45.0 mg (40.5%) of the desired product. mp 208-209 °C; IR (KBr) 3420, 3350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.56 (s, 4, O*H*), 7.30 (d, 4, Ar*H*, J = 2.4 Hz), 7.09 (d, 4, Ar*H*, J = 2.4 Hz), 6.86 - 6.81 (m, 8, Ar*H*), 4.28 (s, 8, ArCH_2N), 4.24 (br., 4, N*H*), 3.98 (s, 4, CH_2), 1.28 ppm (s, 36, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 150.75, 143.52, 137.25, 127.78, 127.18, 125.42, 123.82, 120.63, 113.08 (*Ar*), 48.32 (*C*H_2N) 34.23 (*C*(CH$_3$)$_3$), 31.75 (C(*C*H$_3$)$_3$), 31.70 (*C*H_2). Anal. Calcd for $C_{58}H_{72}N_4O_4$: C, 78.34; H, 8.16; N, 6.30. Found: C, 78.25; H, 8.29; N, 6.18.

Acknowledgment. This Research was supported by the Sookmyung Women's University Research Grants 2005.

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