electrical conductivity and catalytic activity indicate that the oxygen vacancies formed by Sr-doping into neodymium oxide play an important role on the enhancement of catalytic activity in the oxidative coupling of methane. In Table 1, the Sr-doped Nd_2O_3 shows higher C_n selectivity and methane conversion than Mn^- and Ni-doped Nd_2O_3 systems. Therefore, it is obvious that in the present catalysts, the Sr-doping effect on the production of higher hydrocarbons is more significant than Ni- and Mn-doping effects. Since Ni and Sr have the same valency of 2+ in their oxides, we can not exclude a chemical effect on the catalytic activity of impurity-doped neodymium oxide as well as an electronic effect. Ni/Nd_2O_3 and Mn/Nd_2O_3 systems prepared in this work were found to be complete solid solutions up to the doping level of 5 mol% Ni and 8 mol% Mn, respectively. Considering the metal ion solubilities and catalytic activities, it is believed that strontium is better promotor than nickel or manganese. Otsuka *et al.*[15] carried out the kinetic studies on the oxidative coupling of methane over samarium oxide catalyst. They obtained the apparent activation energies for the formation of C_2H_6 from CH_4 and the formation of C_2H_4 from C_2H_6 in the temperature range of 873 to 999 K and the values were 135 kJ/mol and 173 kJ/mol, respectively. Since the apparent activation energy for the formation of C_2H_4 from C_2H_6 is higher than that for the formation of C_2H_6 from CH_4, the ratio of $[C_2H_4]/[C_2H_6]$ will be increased with increasing temperature. As shown in Figure 1, the ratio of $[C_2H_4]/[C_2H_6]$ increases with increasing the reaction temperature up to 850 ℃. The result enable us to consider that ethylene is stepwise produced. Namely, methane is activated *via* abstraction of a hydrogen atom by active oxygen species on the surface of catalyst and the resultant methyl radicals are coupled to form ethane. Ethylene is subsequently produced by dehydrogenation of ethane, not directly produced from methane.

Work is currently in progress to attempt to increase the C_n selectivity and the ratio of $[C_2H_4]/[C_2H_6]$. Studies on the surface chemistry and the mechanism of this reaction are also under way.

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Synthesis of a Novel Basket-Shaped C_3 Receptor

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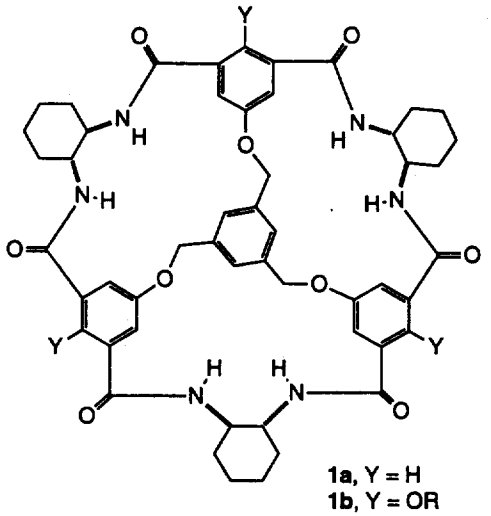
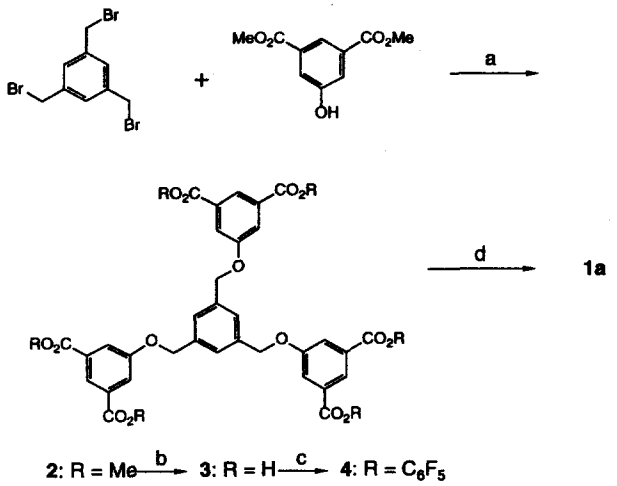
A major problem in the production of new molecular receptors is the design of structures which form well-defined cavities of dimensions sufficient to encapsulate polyatomic substrates. While monocyclic large ring compounds are generally better hosts than their acyclic counterparts, most of them exist as a multitude of conformations. This conformational flexibility leads not only to reduced binding constants but also to poor selectivities among substrates. To further limit the number of accessible, low energy conformations, bridged macrocyclic systems may be used. While many such molecules having small cavities have been described, only a few structures have been reported with the large binding sites close to those of the active sites of biopolymers.[1]



1a, Y = H
1b, Y = OR

As new structures which are capable of encapsulating large, functionalized substrates (e.g., alanine, serine, valine,



Scheme 1. (a) Cs_2CO_3, Bu_4NI, DMF, 50℃ (89%). (b) 1 M NaOH, THF-MeOH-H_2O (88%). (c) C_6F_5OH, EDC, DMF (26%). (d) (1R,2R)-1,2-diaminocyclohexane, THF (27%).

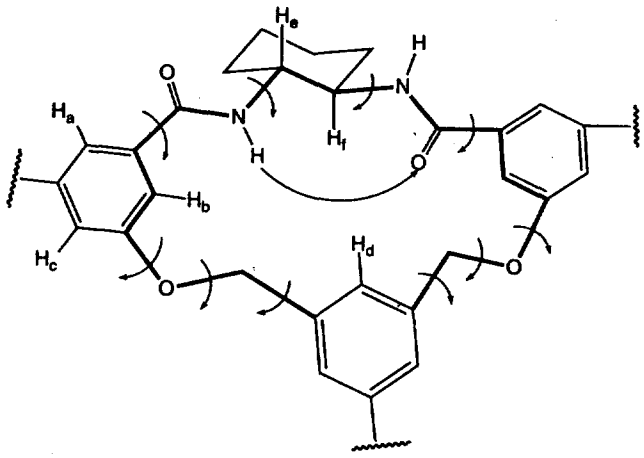


Figure 1. The longer arrow (NH to O=C) indicates the 7-membered intramolecular hydrogen-bond and the shorter arrows indicate selected rotatable bonds.

threonine, or leucine dipeptides), a series of the basket-shaped, 3-fold symmetric host compounds were designed[1h-1j] (**1a** and **1b**). They show the following features:

1. A binding cavity formed by meta-substituted aromatics may function as a hydrophobic pocket (van der Waals or aromatic stacking interaction site) for appropriately sized solvent molecule or nonpolar part of a substrate.

2. Hydrogen bond donor and acceptor functionalities[2] are arranged on an external surface of the upper rim of the basket-shaped host for recognizing rather complex substrates.

3. C_3 symmetric structures can take advantage of an efficient tri-directional synthesis.

4. The host structure has a bridged macrotricyclic framework incorporating meta-substituted aromatics as spacers to disfavor interchain association and chiral 1,2-diamine as enantiomerically pure linker.

From these structural features, the designed C_3 hosts (**1a** and **1b**) could act as specific and selective binders for polyatomic substrates (especially, dipeptides).

The synthesis of the receptor **1a** starts from the trialkylation of dimethyl 5-hydroxyisophthalate with 1,3,5-tris(bromomethyl)benzene[3] as shown in Scheme 1. Ester hydrolysis and subsequent EDC coupling with pentafluorophenol furnished the cyclization precursor **4**. The final step is an intermolecular macrolactamization between a hexakis(pentafluorophenyl)ester **4** and (1R,2R)-1,2-diaminocyclohexane.[4] A solution of the active ester **4** in THF and a solution of chiral 1,2-diamine in THF were separately added *via* syringe pumps over 12 hr to a large amount of THF (final concentration=0.26 mM). Purification by flash chromatography furnished the macrotricycle **1a** in 27% yield as a white solid.

The best evidence for the successful macrocyclization was provided by several informative differences between the ^1H NMR spectrum of **1a** and that of its acyclic precursor **4**. Although **1a** was sparingly soluble in $CDCl_3$, it could be characterized by several spectroscopic methods. Mass spectrum showed an M+1 signal at m/z 896, and the 500 MHz ^1H NMR in 2% $CD_3OD/CDCl_3$ displayed a simple spectrum as would be expected for the symmetrical structure. Two different aromatic proton peaks (H_b and H_c) and two different methine proton signals (H_e and H_f) in a cyclohexane part presumably result from breaking C_2 symmetry of the partial structure of overall C_3 symmetric receptor *via* 7-membered intramolecular hydrogen bond as shown in Figure 1. Two different carbonyl carbon signals of the ^{13}C NMR spectrum appeared at 156.8 and 166.5 ppm (see the Experimental section). Lower field ^{13}C peak should be of carbonyl groups participating in the intramolecular hydrogen bonding. More direct evidence comes from the presence of both free and hydrogen-bonded N-H infrared stretching bands (3427, 3292 cm^{-1}).

It is expected from the CPK models that the 3-dimensional structure of the receptor **1a** is similar to that of the C_3 receptor previously synthesized by Still and coworkers.[1g] However, it has fewer rotatable bonds between meta-substituted aromatics on the cavity wall (see the shorter arrows in Figure 1). As in the Still's receptor, **1a** also has three 7-membered intramolecular hydrogen bonds between three sets of two amide groups around the periphery of a binding cavity which may further limit the number of accessible low energy conformations (see the longer arrow in Figure 1). Therefore, **1a** will have the significant conformational homogeneity and is likely to have highly selective binding properties with various dipeptide substrates. The receptor **1a** will use hydogen bonds as major driving force for binding dipeptide substrates in nonpolar solvents. Since **1a** was sparingly soluble in $CDCl_3$, it was not possible to study complexation properties of **1a** in $CDCl_3$. Synthesis of $CDCl_3$ soluble C_3 receptor is necessary for efficient binding of peptide substrates.

In summary, we synthesized a chiral, C_3-symmetric receptor having limited conformational flexibility, deep basket-shaped three-dimensional binding cavity and appropriately positioned hydrogen bond donor and acceptor functionalities. NMR studies and CPK models suggest that the receptor might be preorganized into a conformation suitable for binding with small peptide molecules. We will report on the synthesis of $CDCl_3$-soluble binder (e.g., **1b**) and its binding properties with small peptide substrates in due course.

Experimental

Hexakis(methyl)ester (2). To a solution of 1,3,5-tris (bromomethyl)benzene (1.75 g, 4.90 mmol) and dimethyl 5-hydroxyisophthalate (3.09 g, 14.7 mmol) in 20 mL of DMF were added Cs_2CO_3 (9.55 g, 29.3 mmol) and n-Bu_4NI (185 mg, 0.50 mmol). The mixture was stirred at 50 ℃ for 3 days and poured into 200 mL of water. The resulting mixture was extracted three times with $CHCl_3$. The combined organic extracts were washed three times with water and then with brine. Drying ($MgSO_4$) and solvent removal were followed by trituration with ether to give a white solid (3.23 g, 89% yield).

IR (KBr) 2950, 1730, 1600, 1430, 1335, 1245, 1120, 1055, 1050, 880 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.90 (s, 18H, $ArCO_2CH_3$), 5.20 (s, 6H, Ar'CH_2OAr), 7.52 (s, 3H, Ar'H), 7.84 (s, 6H, ArH_a), 8.30 (s, 3 H, ArH_b).

Hexakisacid (3). To a solution of **2** (1.56 g, 2.10 mmol) in 200 mL of THF-methanol-water (v/v, 3 : 1 : 1) was added dropwise 25 mL of 1 N aqueous NaOH solution (25 mmol). The resulting solution was stirred at room temperature and concentrated to 1/5 of the original volume. The residue was diluted with 50 mL of water and treated with $BaCl_2$ (dihydrate, 2.97 g, 12.1 mmol). After the mixture had been stirred for 1 h at room temperature, the white barium salt was filtered. The dried barium salt was dissolved in water and acidified with 3 N aqueous HCl solution (pH 2-3). The resulting acid was filtered to give a white solid (1.22 g, 88% yield).

IR (KBr) 3100, 1700, 1600, 1420, 1270, 1130, 1070, 890 cm^{-1}; ^1H NMR (80 MHz, DMSO-d_6) δ 5.30 (s, 6H, Ar'CH_2OAr), 7.62 (s, 3H, Ar'H), 7.80 (s, 6H, ArH_a), 8.18 (s, 3H, ArH_b).

Hexakis(pentafluorophenyl)ester (4). To a solution of **3** (74 mg, 0.11 mmol) in 3 mL of dry DMF was added pentafluorophenol (138 mg, 0.75 mmol) followed by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (140 mg, 0.73 mmol). The solution was stirred at room temperature for 24 h. Solvent removal followed by chromatographic purification (silica gel, CH_2Cl_2) produced the desired product **4** (48 mg, 26% yield) as a white solid.

IR (neat) 1765, 1595, 1520, 1340, 1300, 1190, 1145, 1090, 1000 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 5.31 (s, 6H, Ar'CH_2 OAr), 7.66 (s, 3H, Ar'H), 8.08 (s, 6H, ArH_a), 8.61 (s, 3H, ArH_b).

C_3 receptor (1a). A solution of the active ester **4** (95 mg, 0.057 mmol) in 10 mL of dry THF and a solution of (1R,2R)-1,2-diaminocyclohexane (21 mg, 0.18 mmol) in 10 mL of dry THF were separately added with sirring to 200 mL of dry THF at room temperature over 12 h *via* syringe pumps. After the solution was stirred for an additional 12 h, the solvent was evaporated and 30 mL of 1 N aqueous HCl solution was added. The mixture was extracted three times with 30 mL of 4% MeOH/$CHCl_3$. The combined ogranic extracts were washed successively with saturated $NaHCO_3$ solution and brine. Drying ($MgSO_4$) followed by chromatographic purification (silica gel, 10% MeOH/CH_2Cl_2) furnished the macrotricycle **1a** (14 mg, 27% yield) as a white solid.

IR (KBr) 3427, 3292, 2980, 1645, 1595, 1540, 1265, 1100, 1030, 805 cm^{-1}; ^1H NMR (2% $CD_3OD/CDCl_3$, 500 MHz) δ 1.23-2.07 (m, 24H, aliphatic CH_2's), 3.69 (br, 3H, CH_eNH), 4.03 (dt, J=3.7, 11.4 Hz, 3H, CH_fNH), 5.16 (s, 6H, ArCH_2 OAr'), 7.11 (s, 3H, ArH), 7.34 (s, 3H, ArH), 7.56 (s, 3H, ArH), 7.63 (s, 3H, ArH); ^{13}C NMR (2% $CD_3OD/CDCl_3$, 125 MHz) δ 24.5, 25.0, 31.3, 32.0, 52.5, 56.0, 67.9, 116.6, 118.2, 118.8, 128.5, 133.4, 136.6, 156.8, 166.5; MS (FAB, glycerol) m/z 896 (M+1).

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Trialkylsilyl Triflate Promoted Conjugate Addition of Alkynylcuprates to α,β-Enones

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Organocuprates are the most commonly used reagents for 1,4-addition of alkyl and alkenyl groups to α,β-enones.[1] However, they cannot be employed in alkynylation reactions due to their inability to transfer alkynyl groups.[2] Therefore, the conjugate addition of alkynyl groups to α,β-enones has been a synthetic challenge. Dialkylalkynylalanes undergo 1,4-addition reactions with α,β-enones to give β-alkynyl ketones.[3]