

# Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

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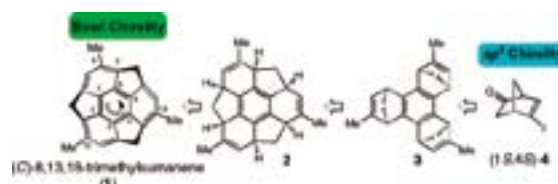
Bowl-shaped  $\pi$ -conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. Heteroatom-containing buckybowls (heterobuckybowls) have also been expected to exhibit unique physical characters. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiralbowls has appeared. In the present project, we develop the rational route to the various kinds of buckybowls/heterobuckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly- functionalized protective polymers: Catalytic activity of metal nanoclusters under the laser-irradiated conditions.

## 1. Asymmetric Synthesis of a Chiral Buckybowl, Trimethylsumanene<sup>1)</sup>

Many buckybowls possess “bowl chirality” derived from their three-dimensional geometry, similar to chiral fullerenes and carbon nanotubes. Methods to control the bowl chirality can potentially be applied to the related chiral fullerenes and carbon nanotubes as well. In addition, chiral aromatic com-

pounds are expected to contribute to a variety of applications such as asymmetric molecular recognition, homochiral crystal organic materials, and chiral ligands for organometallic catalysis. Asymmetric synthesis of chiral buckybowls is challenging since synthetic strategies have not yet been established. We developed the first rational asymmetric synthesis of a  $C_3$  symmetric chiral buckybowl, (C)-8,13,18-trimethylsumanene (**1**).



Scheme 1. Strategy for the asymmetric synthesis of (C)-1.

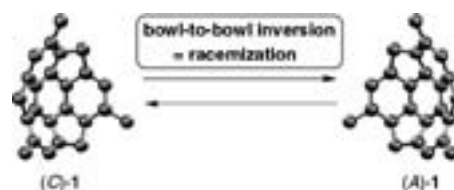
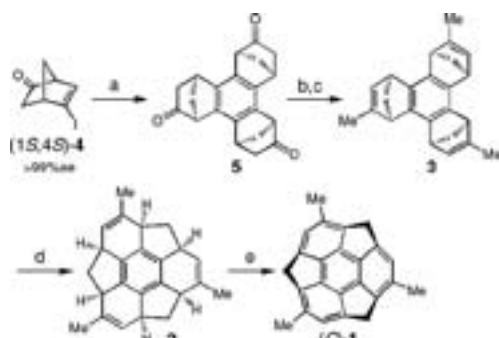


Figure 1. Racemization of **1** through a bowl-to-bowl inversion.

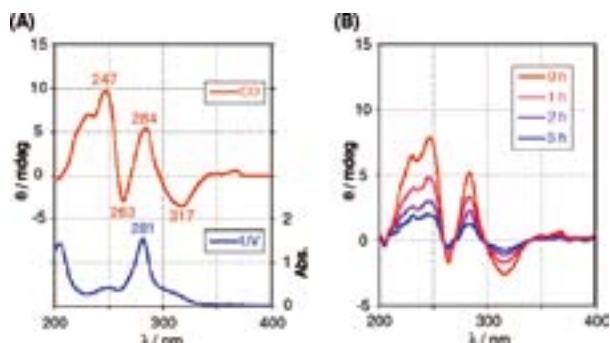
The bowl-to-bowl inversion energy barrier must be taken into account at this step, because this inversion corresponds to a racemization process for a chiral buckybowl (Figure 1). The bowl-to-bowl inversion energy barrier of **1** is estimated to be ca. 21 kcal/mol. Since the energy barrier corresponds to ca. 2 h half-life time of racemization at 0 °C, the aromatization step must be carried out at a low temperature. The bowl-shaped structure of **2** could be constructed from a benzonorbornene derivative **3** utilizing a tandem ring-opening/closing olefin metathesis approach. The benzonorbornene derivative **3** could be obtained by cyclotrimerization of a chiral halonorbornene derivative (1*S*,4*S*)-**4**. By adopting this approach, the bowl

chirality of **1** is controlled by the  $sp^3$  chirality of the starting norbornene derivative. Synthetic route to (C)-**1** is listed in Scheme 2.



(a) Pd(OAc)<sub>2</sub> 5 mol%, PPh<sub>3</sub> 10 mol%, Bu<sub>4</sub>NOAc 1000 mol%, Na<sub>2</sub>CO<sub>3</sub>, MS 4 Å, 1,4-dioxane, 100 °C, 2 h, 55%; (b) NaN(SiMe<sub>3</sub>)<sub>2</sub> 350 mol%, (2,6-diMePhO)<sub>2</sub>P(O)Cl 350 mol%, P(O)(NMe<sub>2</sub>)<sub>3</sub> 350 mol%, THF, -80 °C, 75%; (c) Pd(OAc)<sub>2</sub> 5 mol%, PCy<sub>3</sub>•HBF<sub>4</sub> 10 mol%, MeMgI 400 mol%, THF, 40 °C, 2 h, 72%; (d) Grubbs 1st generation catalyst 50 mol%, CH<sub>2</sub>Cl<sub>2</sub>, under ethylene, 40 °C, 6 h, then Grubbs 2nd generation catalyst 50 mol%, CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 12 h, 24%; (e) DDQ 600 mol%, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 1 min 68%.

**Scheme 2.** Synthesis of (C)-8,13,18-trimethylsumanene (**1**).

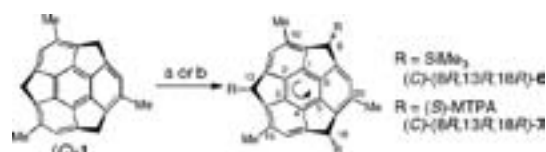


**Figure 2.** (A) CD spectra of (C)-**1** in CH<sub>3</sub>CN at -40 °C (red line) and UV spectra of (±)-**1** in CH<sub>3</sub>CN at rt (blue line); (B) decay of CD spectra of (C)-**1** in CH<sub>3</sub>CN at 10 °C for 3 h.

The chirality of thus-obtained (C)-**1** was confirmed by measurement of the circular dichroism (CD) spectra. The intensity of the CD spectra at -40 °C scarcely changed but gradually decreased at 10 °C (Figure 2). The bowl-to-bowl inversion energy barrier of **1** in CH<sub>3</sub>CN was determined to be 21.6 kcal/mol by tracing the decay of the CD spectra at 247 and 282 nm at 10 °C (Supporting Information). This value is in good accordance with the estimated one.

To determine the enantiomeric excess of synthetic **1**, we needed to derivatize **1** while avoiding racemization through a bowl-to-bowl inversion. Selective introduction of trimethylsilyl groups at the *exo* positions of the dibenzylic positions induces new  $sp^3$  chirality which prevents the enantiomers from racemizing (Scheme 3). However, we were unable to separate the enantiomers of **6** using chiral HPLC. Instead, (*S*)-Ph(CF<sub>3</sub>)(OMe)CCO groups were introduced to create diastereomers. Finally the enantiomeric excess of **1** was determined as 90%

ee based on the <sup>1</sup>H NMR analysis of the diastereomeric ratio of **7**.

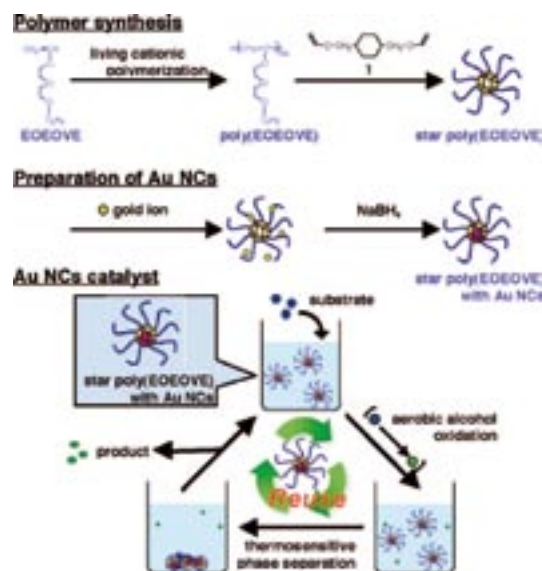


(a) (±)-**1**, LDA 1000 mol%, THF, 0 °C then Me<sub>3</sub>SiCl 1000 mol%, (±)-**6** 45%; (b) (C)-**1**, LDA 600 mol%, THF, -40 °C, then (*R*)-Ph(CF<sub>3</sub>)(MeO)CCOCl = (*R*)-MTPACl 1000 mol% 17%.

**Scheme 3.** Determination of the enantiomeric excess of **1**.

## 2. Thermosensitive Gold Nanoclusters Stabilized by Well-Defined Vinyl Ether Star Polymers: Reusable and Durable Catalysts for Aerobic Alcohol Oxidation<sup>2)</sup>

Au nanoclusters of less than 4 nm with a narrow size distribution were prepared and supported in thermosensitive vinyl ether star polymers (Au@star poly(EOEOVE)<sub>200</sub>) obtained by living cationic polymerization. The thermosensitivity of the star polymers permitted easy separation of the clusters from the reaction mixture without any negative aggregation. Thus, the Au clusters could be recovered for reuse several times to induce alcohol oxidation with similar reactivity in each run.



**Scheme 4.** Preparation and Catalytic Use of Au NCs.

## References

- 1) S. Higashibayashi and H. Sakurai, *J. Am. Chem. Soc.* **130**, 8592–8593 (2008).
- 2) S. Kanaoka, N. Yagi, Y. Fukuyama, S. Aoshima, H. Tsunoyama, T. Tsukuda, and H. Sakurai, *J. Am. Chem. Soc.* **129**, 12060–12061 (2007).