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# Efficient and Practical Arene Hydrogenation by Heterogeneous Catalysts under Mild Conditions

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**Abstract:** An efficient and practical arene hydrogenation procedure based on the use of heterogeneous platinum group catalysts has been developed. Rh/C is the most effective catalyst for the hydrogenation of the aromatic ring, which can be conducted in *i*PrOH under neutral conditions and at ordinary to medium $H_2$ pressures ($<10$ atm). A variety of arenes such as alkylbenzenes, benzoic acids, pyridines, furans, are hydrogenated to the corresponding cyclohexyl and heterocyclic compounds in good to excellent yields. The use of Ru/C, less expensive than Rh/C, affords an effective and practical method for the hydrogenation of arenes including phenols. Both catalysts can be reused several times after simple filtration without any significant loss of catalytic activity.

**Keywords:** arenes · heterogeneous catalysis · hydrogenation · rhodium · ruthenium

## Introduction

The cyclohexane moiety is an important structure in diverse organic compounds, such as natural products and functional materials including pharmaceuticals. The modification of cyclohexane rings is rather more difficult than that of aromatic rings, so the reduction of aromatic rings is a useful and important technique for obtaining a variety of cyclohexane derivatives. In addition, the reduction of aromatic rings in the structures of functional polymers, such as polycarbonates and epoxy resins, is effective for induction of yellowing resistance qualities, because the precursor aromatic rings can effectively absorb light energy, causing yellow discoloration of the polymers. Existing methods for aromatic ring reduction, however, require excess amounts of reagents and harsh reaction conditions because of the stabilization of the aromatic ring by resonance hybridization (151 kJ mol$^{-1}$ or 36 kcal mol$^{-1}$). Previously reported methods for construction of cyclohexane rings from arenes are classified into two types of reactions:

1) Reduction with a greater than stoichiometric amount of a reducing agent, such as $LiAlH_4$, a borane derivative,[1] or a dissolving metal (Birch reduction).[2] These reagents are moisture-sensitive and the reactions should be conducted under anhydrous and strongly reducing and basic conditions; some co-existing functional groups, such as esters and ketones, would not be tolerated under these conditions. Furthermore, these reactions produce large amount of metal waste from the reducing agents.
2) Hydrogenation with a transition-metal catalyst.[3,4] Catalytic hydrogenation is a simple, convenient, and sustainable method. Although some homogeneous catalysts do efficiently promote arene hydrogenation,[5] residual metal in the products makes industrial application difficult. On the other hand, the hydrogenation of arenes through the use of heterogeneous metals (Ni, Rh, Ru, Pt, and Pd)[4] has some advantages, such as easy handling, less metal contamination in the products, and reuse of the catalysts, which would make it suitable for industrial production. However, conventional methods using heterogeneous catalysts have required high pressures ($>10$ atm) and temperatures and/or strongly acidic or basic conditions. Only two mild hydrogenation methods, using active Rh nanoparticles, have been reported,[6] and only a few widely applicable hydrogenation methods for aromatic nuclei are reported.[4,7] Therefore, a simple,

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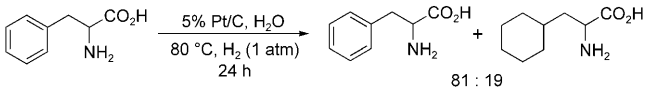
practical, and wide-ranging hydrogenation method is desirable.

We have recently developed facile and efficient methods for deuteration of various organic compounds through the use of Pd/C,[8] Pt/C,[9] Rh/C,[10] or Ru/C[11] in $D_2O$ in the presence of $H_2$ gas. During the course of our study of the deuteration of phenylalanine, we found that hydrogenation of the aromatic ring occurred under the stated conditions (Scheme 1).




Scheme 1. Pt/C-catalyzed (5%) hydrogenation of the aromatic ring of phenylalanine under the deuteration conditions.

Encouraged by this result, we speculated that this reaction might be developable into an efficient and general method for hydrogenation of aromatic nuclei by optimization of the reaction conditions. We have consequently developed an efficient hydrogenation method for diverse arenes in the presence of Rh/C in either $H_2O$ or *i*PrOH under ordinary to medium $H_2$ pressures ($<10$ atm). Furthermore, a practical and cost-effective method for hydrogenation of arenes, including phenol derivatives, in the presence of Ru/C as an inexpensive catalyst has also been achieved.

## Results and Discussion

### Rh/C catalysis

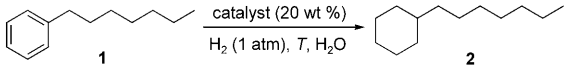
**Rh/C-catalyzed hydrogenation of arenes under ordinary $H_2$ pressure in $H_2O$**:[12] We first examined a variety of heterogeneous catalysts with *n*-heptylbenzene as a substrate (Table 1). Pt/C, Ru/C, and Rh/C all proved to be effective catalysts for arene hydrogenation in $H_2O$ (Table 1, entries 1–3), whereas Pd/C and Ir/C showed relatively poor catalyst activities (entries 4 and 5). Further investigation of the catalyst activity at 60°C indicated that Rh/C (10%) is a most suitable catalyst for the hydrogenation of aromatic nuclei (entry 9).

To examine the applicability of different substrates, we conducted some reactions with a selection of aromatic compounds under the conditions described above. Although alkylbenzenes were completely hydrogenated (Table 2, entries 1 and 2), the reactions of other substrates, such as diphenylmethane (**3a**), were incomplete under the same conditions (entries 3–5).

We then investigated the effects of reaction temperature and $H_2$ pressure with diphenylmethane (**3a**) as a substrate (Table 3). At 80°C the reaction was very effective for the hydrogenation of both nuclei (entry 3), whereas further heating caused a drop in the product ratio (entry 4). An increase in $H_2$ pressure up to 5 atm led to completion of the hydrogenation (entries 5 and 6) and the nuclei hydrogenation of both aromatic rings was completed within 2 h (entry 6).

The optimized reaction conditions were found to be applicable to a variety of aromatic compounds, with the corre-

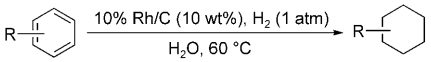
Table 1. Optimization of the heterogeneous catalyst for arene hydrogenation in $H_2O$.

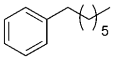
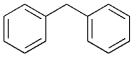
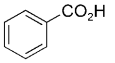



| Entry | Catalyst | $T$ [°C] | $t$ [h] | Ratio **1/2**[a] |
|---|---|---|---|---|
| 1 | Pt/C (5%) | 80 | 24 | 3:97 |
| 2 | Ru/C (5%) | 80 | 24 | 0:100 |
| 3 | Rh/C (5%) | 80 | 24 | 0:100 |
| 4 | Pd/C (5%) | 80 | 24 | 80:20 |
| 5 | Ir/C (5%) | 80 | 24 | 76:24 |
| 6 | Pt/C (5%) | 60 | 3 | 47:53 |
| 7 | Ru/C (5%) | 60 | 3 | 56:44 |
| 8 | Rh/C (5%) | 60 | 3 | 2:98 |
| 9[a] | Rh/C (10%) | 60 | 3 | 0:100 |

[a] Ratio was determined by $^1$H NMR. [b] Rh/C (10%, 10 wt%) was used as a catalyst.

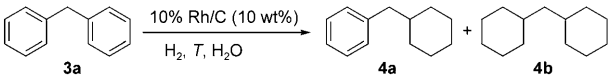
Table 2. Hydrogenation of aromatic compounds in the presence of Rh/C (10%) in $H_2O$ at 60°C under ordinary $H_2$ pressure.




| Entry | Substrate | $t$ [h] | Ratio **3/4**[a] |
|---|---|---|---|
| 1 |  | 3 | 0:100 |
| 2 |  | 6 | 0:100 |
| 3 |  | 24 | 24:58:18[b] |
| 4 |  | 24 | 48:52 |
| 5 |  | 24 | 45:55 |

[a] The ratio was determined by $^1$H NMR. [b] The ratio refers to diphenylmethane/cyclohexylmethylbenzene/dicyclohexylmethane.

Table 3. Effect of temperature and $H_2$ pressure.



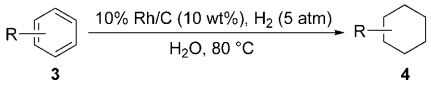

| Entry | $T$ [°C] | $H_2$ pressure [atm] | $t$ [h] | Ratio **3a/4a/4b**[a] |
|---|---|---|---|---|
| 1 | RT | 1 | 24 | 38:45:17 |
| 2 | 60 | 1 | 24 | 24:58:18 |
| 3 | 80 | 1 | 24 | 1:42:57 |
| 4 | 90 | 1 | 24 | 30:64:6 |
| 5[b] | 80 | 3 | 15 | 0:2:98 |
| 6[b] | 80 | 5 | 2 | 0:0:100 |

[a] The ratio was determined by $^1$H NMR. [b] The reaction was performed in a sealed tube.

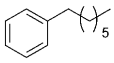
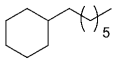
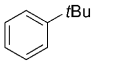
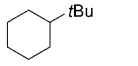
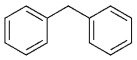
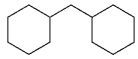
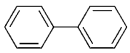
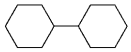
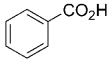
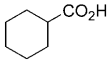
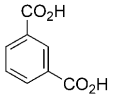
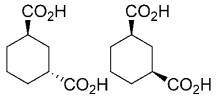
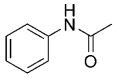
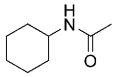
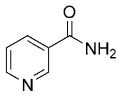
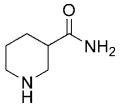
  

sponding cyclohexane derivatives being obtained in good to high yields (Table 4). The hydrogenations of alkylbenzene and diphenylmethane, as well as of biphenyl, stabilized by a stronger resonance hybridization, were complete within a few hours (entries 1–4). Electron-deficient aromatic rings were also hydrogenated (entries 5 and 6). Furthermore, heteroaromatic compounds were also reduced to the corresponding saturated heterocyclic compounds without any problems (entries 8–10). It is noteworthy that acetanilide and nicotinamide underwent the hydrogenation without their amide groups being affected (entries 7 and 10).

Table 4. Arene hydrogenation in $H_2O$ in the presence of Rh/C (10%) under $H_2$ (5 atm) at 80°C.




3 4

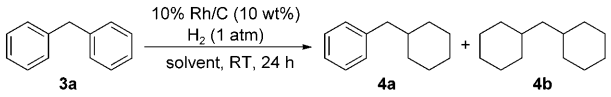
| Entry | Substrate **3** | $t$ [h] | Product **4** | Yield [%][a] |
|---|---|---|---|---|
| 1[b] |  | 3 |  | 96 |
| 2 |  | 2 |  | 73[c] |
| 3 |  | 2 |  | 86 |
| 4 |  | 3 |  | 93 |
| 5 |  | 2.5 |  | 95 |
| 6 |  | 6 |  | 91 (55:45)[d] |
| 7 |  | 3 |  | 90 |
| 8 |  | 0.5 |  | 90 |
| 9 |  | 2 |  | 96 |
| 10 |  | 1.5 |  | 97 |

[a] Isolated yield. [b] $H_2$ (1 atm). [c] The low yield is due to the volatile nature of the product. [d] The ratio of *cis*/*trans* isomers is indicated in the parentheses.

**The use of *i*PrOH for the hydrogenation**: Although the use of $H_2O$ as a solvent provides an environmentally friendly method in terms of cost and toxicity, the poor solubilities of organic compounds in $H_2O$ would be expected to suppress the reactions. The use of an appropriate organic solvent might therefore be helpful for efficient reaction progress under milder conditions.

Surprisingly, a significant enhancement of the reaction rate at RT was observed when *i*PrOH was used as a solvent (Table 5, entry 9). We then employed *i*PrOH as the most effective solvent for the arene hydrogenation and re-examined its scope and limitations in detail.

Table 5. Effect of solvent.



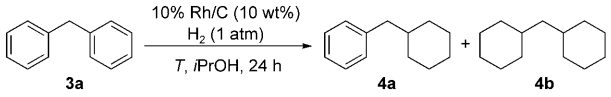

3a 4a 4b

| Entry | Solvent | Ratio **3a**/**4a**/**4b**[a] |
|---|---|---|
| 1 | $H_2O$ | 38:45:17 |
| 2 | cyclohexane | 2:47:51 |
| 3 | AcOEt | 1:35:64 |
| 4 | THF | 81:15:4 |
| 5 | $CH_3OH$ | 29:48:23 |
| 6 | EtOH | 45:45:10 |
| 7 | *n*BuOH | 44:43:13 |
| 8 | *t*BuOH | 7:51:42 |
| 9 | *i*PrOH | 0:26:74 |
| 10 | dodecan-1-ol | 52:30:18 |

[a] The ratio was determined by $^1H$ NMR.

Firstly, the reaction temperature in *i*PrOH under $H_2$ (1 atm) was investigated (Table 6). Complete hydrogenation of diphenylmethane was achieved when the reaction was performed at 60°C (entry 3), and the reaction was complete within 12 h rather than the standard 24 h (entry 7). Consequently, we employed 60°C as the optimal temperature in *i*PrOH.

Table 6. Effect of the reaction temperature in *i*PrOH under ordinary $H_2$ pressure.




3a 4a 4b

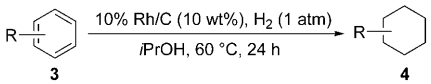
| Entry | $T$ [°C] | Ratio **3a**/**4a**/**4b**[a] |
|---|---|---|
| 1 | RT | 0:26:74 |
| 2 | 50 | 0:8:92 |
| 3 | 60 | 0:0:100 |
| 4 | 70 | 0:5:95 |
| 5 | 80 | 2:72:26 |
| 6 | 90 | 58:38:4 |
| 7[b] | 60 | 0:0:100 |
| 8[b] | 70 | 0:17:83 |

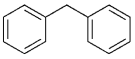
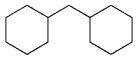
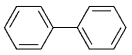
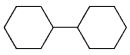
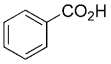
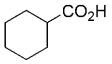
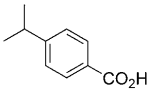
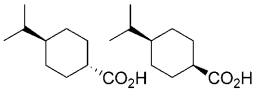
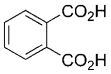
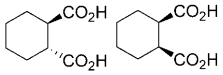
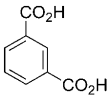
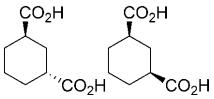
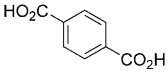
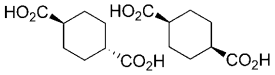
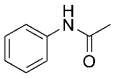
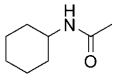
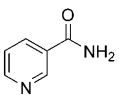
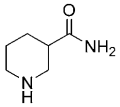
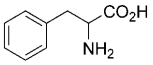
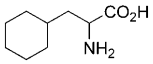
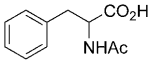
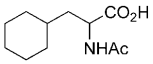
[a] The ratio was determined by $^1H$ NMR. [b] For 12 h.

We next conducted the hydrogenation of various arene derivatives in *i*PrOH (Table 7). Diverse arenes including heterocycles were hydrogenated under ordinary $H_2$ pressure at 60°C for 24 h to give the corresponding cyclohexane derivatives (entries 1–4, 8–10), as was also the case even for the highly electron-deficient isophthalic and terephthalic acids (entries 6 and 7). However, the hydrogenation of phthalic acid was incomplete (entry 5) because of reduced catalyst activity of the Rh/C (10%) due to the formation of a Rh-chelate with the *ortho*-carboxylic acid pair in the phthalic acid. The arene hydrogenation of phenylalanine was also incomplete, with 70% of the starting material remaining unchanged under the stated reaction conditions (entry 11); the amino moiety may act as a catalyst poison.

Table 7. Arene hydrogenation under ordinary $H_2$ pressure in *i*PrOH in the presence of Rh/C (10%) at 60°C.



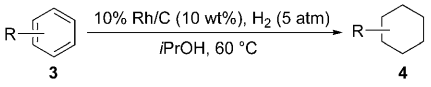

| Entry | Substrate **3** | Product **4** | Yield [%][a] |
|---|---|---|---|
| 1 |  |  | 96 |
| 2 |  |  | 97 |
| 3 |  |  | 91 |
| 4 |  |  | 99 (67:33)[b] |
| 5 |  |  | incomplete |
| 6 |  |  | 93 (60:40)[b] |
| 7 |  |  | 93 (83:17)[b] |
| 8 |  |  | 95 |
| 9 |  |  | 91 |
| 10 |  |  | 90 |
| 11 |  |  | (70:30)[c] |
| 12 |  |  | 97 |

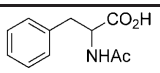
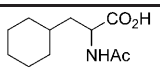
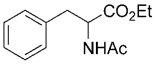
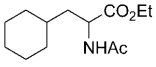
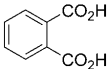
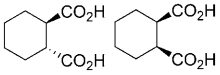
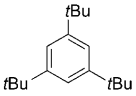
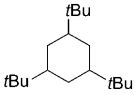
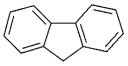
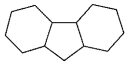
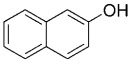
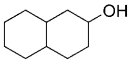
[a] Isolated yield. [b] The ratio of *cis*/*trans* isomers is indicated in the parentheses. [c] The parentheses indicate the ratio of **3**:**4** from $^1$H NMR.

Indeed, *N*-acetylphenylalanine was completely hydrogenated (97% yield) under the same reaction conditions (entry 12).

**Effect of $H_2$ pressure (5 atm)**: Increasing the $H_2$ pressure was effective for the progress of the reactions, with their rates being much improved (Table 8). The reactions of *N*-acetylphenylalanine and its ethyl ester were completed within 4 and 3 h under 5 atm $H_2$ pressure (entries 1 and 2). Phthalic acid could also be hydrogenated under $H_2$ (5 atm) to afford the two cyclohexene-1,2-dicarboxylic acid isomers (entry 3), whereas under ordinary pressure the reaction had not gone to completion (Table 7, entry 5). The arene hydrogenations of sterically hindered substrates, such as 1,2,4,5-tetramethylbenzene and 1,3,5-tri-*tert*-butylbenzene, were also successful, with the reactions being complete within 5 h (entries 4 and 5). Additionally, fluorene and 2-naphthol, polycyclic arenes, were also reduced to the corresponding poly-alicyclic products (entries 6 and 7). The hydrogenation of heteroaromatic compounds also proceeded easily under these conditions (entries 8 and 9); in particular, the hydrogenation of pyrrole-2-carboxylic acid gave racemic proline in good yield (entry 8). Many monomers of functional polymers possess aromatic rings as partial structures, and saturated monomers might function as modifiers of the original polymers to provide novel characteristic features. The hydrogenation of 4′-hydroxy-biphenylcarboxylic acid, a liquid-crystal material, was complete in 20 h, giving the corresponding bis-cyclohexane derivative (entry 10). It is note-

Table 8. Arene hydrogenation in *i*PrOH under $H_2$ (5 atm) at 60°C.



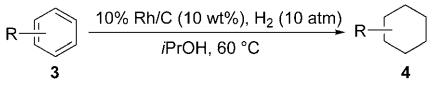

| Entry | Substrate **3** | *t* [h] | Product **4** | Yield [%][a] |
|---|---|---|---|---|
| 1 |  | 4 |  | 95 |
| 2 |  | 3 |  | 97 |
| 3 |  | 7 |  | 96 (85:15)[b] |
| 4 |  | 2 |  | 46[c,d] |
| 5 |  | 5 |  | 100[d] |
| 6 |  | 9 |  | 80[d] |
| 7 |  | 10 |  | 90[d] |
| 8 |  | 8 |  | 95 |
| 9 |  | 7 |  | 90 |
| 10 |  | 9 |  | 91[d] |
| 11 |  | 10 |  | 93 |
| 12 |  | 24 |  | incomplete |

[a] Isolated yield. [b] The ratio of *cis*/*trans* isomers is indicated in the parentheses. [c] The low yield is due to the volatile nature of the product. [d] It is hard to determine the *cis*/*trans* isomers.

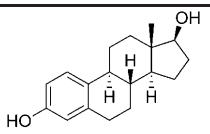
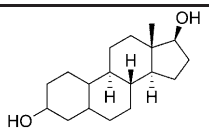
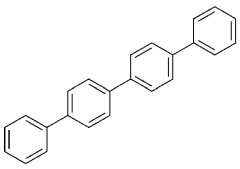
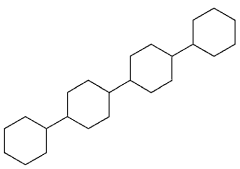
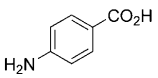
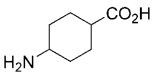
worthy that the partial reduction of binaphthol proceeded and racemic 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol (entry 11), the optically active isomers of which are used as chiral ligands, was obtained as the sole product. Unfortunately, estradiol, which possesses a highly rigid steroid skeleton, was not completely hydrogenated (entry 12).

**Effect of $H_2$ pressure (10 atm)**: Consequently, we decided to apply a higher $H_2$ pressure. As a result, the arene hydrogenation even of estradiol, with its robust and stable skeleton, was complete within 6 h under 10 atm of $H_2$ (Table 9, entry 1). 1-Naphthol was also hydrogenated under 10 atm of $H_2$, although under 5 atm of $H_2$ the reaction had been incomplete, unlike that of 2-naphthol (entry 2; see also Table 8, entry 7). Furthermore, polycyclic compounds, such as *p*-quaterphenyl, underwent hydrogenation to give the corresponding alicyclic compounds in high yields (entry 3). 4-Aminocyclohexanecarboxylic acid, which is a useful compound as an intermediate for pharmaceuticals and agrochemicals, was easily obtained from 4-aminobenzoic acid by arene reduction (entry 4).

Table 9. Arene hydrogenation in *i*PrOH under $H_2$ (10 atm) at 60 °C.



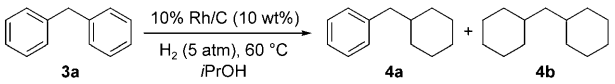

3 4

| Entry | Substrate **3** | *t* [h] | Product **4** | Yield [%][a] |
|---|---|---|---|---|
| 1 |  | 6 |  | 91[b] |
| 2 |  | 20 |  | 88[b] |
| 3 |  | 20 |  | 68[b] |
| 4 |  | 19 |  | 79[b] |

[a] Isolated yield. [b] It is hard to determine the *cis*/*trans* isomers.

**Reuse of Rh/C**: With the aim of extension to an environmentally benign and more practical method, we examined the reuse of Rh/C with diphenylmethane as a substrate. As shown in Table 10, Rh/C could be reused five times without any reactivation, although a gradual extension of the reaction time was necessary.

Table 10. Reuse of Rh/C.



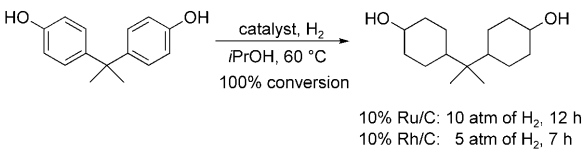

3a 4a 4b

| Entry | *t* [h] | Ratio **3a**/**4a**/**4b**[a] | Yield [%] |
|---|---|---|---|
| 1 | 4 | 0:0:100 | 90 |
| 2 | 4 | 0:0:100 | 78 |
| 3 | 5 | 0:0:100 | 87 |
| 4 | 5 | 0:0:100 | 72 |
| 5 | 7 | 0:0:100 | 74 |

[a] The ratio was determined by $^1$H NMR.

## Ru/C catalysis

**The application of Ru/C to arene hydrogenation**: During the course of our study of the Rh/C-catalyzed mild and easily applicable hydrogenation of arenes, we investigated the hydrogenation of bisphenol A, because hydrogenated bisphenol A is a useful component of functional polymers that resist yellow discoloration caused by light absorption by the aromatic rings of epoxy or polycarbonate polymers prepared from bisphenol A. In addition, bisphenol A is also suspected to be an endocrine disrupter, whereas its hydrogenated counterpart is not. The Rh/C-catalyzed hydrogenation of bisphenol A in *i*PrOH was complete after 7 h under $H_2$ (5 atm) at 60 °C. We also found that the Ru/C-catalyzed hydrogenation of bisphenol A was also complete after 12 h under $H_2$ (10 atm), giving totally hydrogenated bisphenol A (Scheme 2). Although Rh/C is highly effective as an arene hydrogenation catalyst, Rh is quite an expensive rare metal in relation to other platinum group metals such as Ru and Pd. Other platinum metals can also function as catalysts for arene hydrogenation, although their catalyst efficiencies are only applicable to certain substrates.[4] Therefore, the development of a general method for hydrogenation of aromatic nuclei based on Ru/C catalysis under medium $H_2$ pressure (< 10 atm) would provide a useful and practical procedure for the synthesis of cyclohexane derivatives, in particular for industrial application.



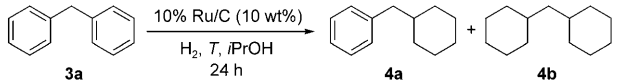

Scheme 2. Hydrogenation of bisphenol A.

Initially, we once more optimized the reaction temperature and $H_2$ pressure with diphenylmethane as a substrate. Ru/C-catalyzed hydrogenation of diphenylmethane was found to proceed efficiently under $H_2$ (5 atm) at 60 °C (Table 11, entry 7) although higher $H_2$ pressure was required than in the Rh/C-catalyzed reaction (see Table 6, entry 3).

We then studied the Ru/C-catalyzed hydrogenation of various arenes under the optimized conditions as noted above (Table 12). A variety of arenes, such as alkylbenzenes (en-

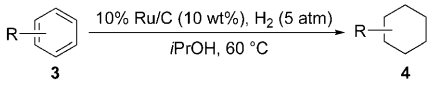
Table 11. Effect of temperature and $H_2$ pressure in the Ru/C-catalyzed hydrogenation.

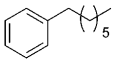
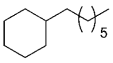
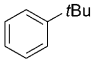
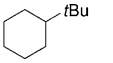
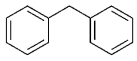
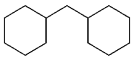
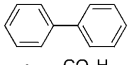
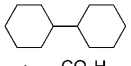
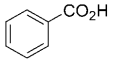
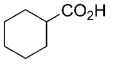
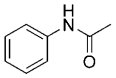
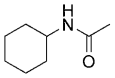



| Entry | $T$ [°C] | $H_2$ pressure [atm] | Ratio **3a**/**4a**/**4b**[a] |
|---|---|---|---|
| 1 | RT | 1 | 88:9:3 |
| 2 | RT | 1 | 48:40:12 |
| 3 | 60 | 1 | 10:65:25 |
| 4 | 80 | 1 | 92:5:3 |
| 5 | 60 | 3 | 0:28:72 |
| 6 | 80 | 3 | 0:9:91 |
| 7 | 60 | 5 | 0:0:100 |
| 8 | 80 | 5 | 0:0:100 |

[a] The ratio was determined by $^1$H NMR.

Table 12. Arene hydrogenation in $H_2O$ in the presence of Ru/C (10%) under $H_2$ (5 atm) at 80°C.

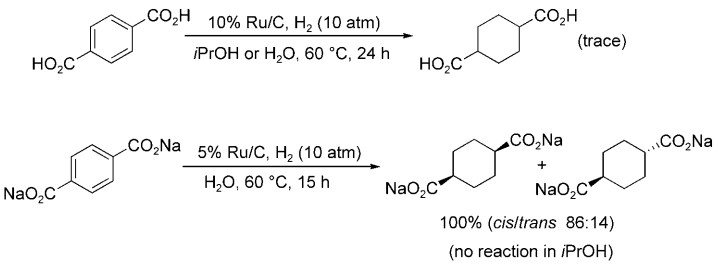



| Entry | Substrate **3** | $t$ [h] | Product **4** | Yield [%][a] |
|---|---|---|---|---|
| 1[b] |  | 24 |  | 92 |
| 2 |  | 4 |  | 60[c] |
| 3 |  | 4 |  | 92 |
| 4 |  | 4 |  | 94 |
| 5 |  | 24 |  | 87 |
| 6 |  | 24 |  | 90 |
| 7 |  | 12 |  | 89 |

[a] Isolated yield. [b] $H_2$ (1 atm). [c] The low yield is due to the volatile nature of the product.

tries 1–3), biphenyl (entry 4), and benzoic acid (entry 5), as well as acetanilide (entry 6) and an alkyl-substituted furan (entry 7), were smoothly hydrogenated in good to high yields within several hours.

**Effect of solubility**: The Ru/C-catalyzed hydrogenation of terephthalic acid was incomplete even under 10 atm $H_2$ pressure, so we assumed that the solubility of terephthalic acid was affecting the reaction progress. Terephthalic acid is nearly insoluble both in *i*PrOH and in $H_2O$, which might be the cause of the low reactivity of the Ru/C-catalyzed hydrogenation, although the reaction efficiency of the Rh/C-catalyzed arene hydrogenation had been only slightly affected because of the high catalyst activity. With the $H_2O$-soluble terephthalic acid disodium salt as a substrate, the hydrogenation indeed proceeded completely in $H_2O$ to give the corresponding hydrogenated product (Scheme 3), although no reaction was observed in *i*PrOH (in which terephthalic acid disodium salt does not dissolve.



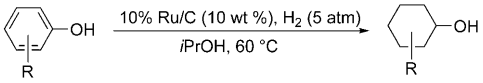

Scheme 3. Hdrogenation of terephthalic acid and its disodium salt in the presence of Ru/C.

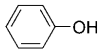
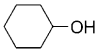
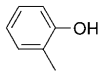
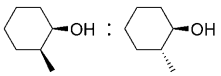
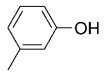
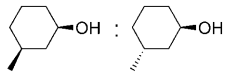
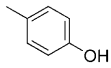
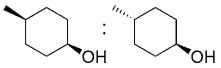
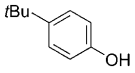
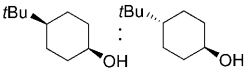
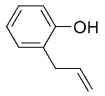
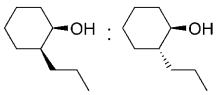
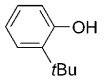
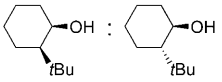
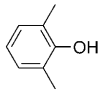
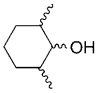
**Application to the hydrogenation of phenols**: Cyclohexanols are important and useful structural elements of many compounds, such as pharmaceuticals and functional materials. Three types of representative synthetic methods for producing the cyclohexanol moiety have been reported. Firstly, the oxidation of cyclohexane derivatives is one of the most useful methods for direct production of cyclohexanols,[13] although mixtures of cyclohexanol and cyclohexanone derivatives have been obtained due to partial over-oxidation. The second method is the reduction of cyclohexanones to cyclohexanols.[14] The utility of this method is dependent on the availabilities of the cyclohexanones, and it is rather difficult to obtain a wide variety of cyclohexanone derivatives. Thirdly, the reduction of phenols is a powerful and simple method for the syntheses of cyclohexanols, but conventional methods have problems similar to those of arene hydrogenation. In addition, it is known that the hydrogenation of phenols by the Rh catalyst may cause hydroxy group elimination.[4] We therefore decided to explore the Ru/C-catalyzed hydrogenation of phenols under optimized conditions [Ru/C (10 wt%) at 60°C under $H_2$ (5 atm) in *i*PrOH]. Phenol and alkyl-substituted phenols were completely hydrogenated to the corresponding cyclohexanol derivatives within 4–12 h in good to excellent yields (Table 13), and an olefin moiety was also hydrogenated under the same conditions (entry 6). Substituted cyclohexanols were obtained as *cis*/*trans* mixtures. The sterically hindered 2,6-dimethylphenol was also hydrogenated under the same conditions without any need for a prolonged reaction time (entry 8).

In cases of phenols possessing other oxygen functions such as ester groups or additional hydroxy groups, or possessing additional aromatic rings, the reactions did not go to completion under the same conditions, because the lone pairs of these oxygen-containing functional groups or the π electron systems of the other aromatic rings were able to coordinate strongly to the Ru metal and to decrease the catalyst activities, acting as a certain type of catalyst poison. We then examined the reaction temperature effect under 5 atm

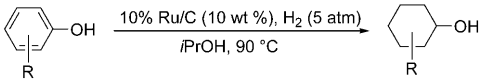
Table 13. Ru/C-catalyzed hydrogenation of phenols.

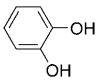
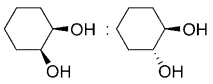
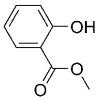
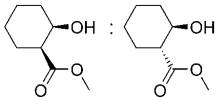
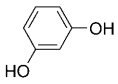
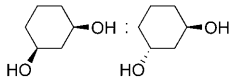
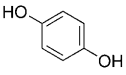
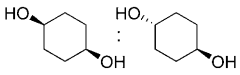
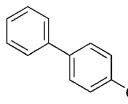
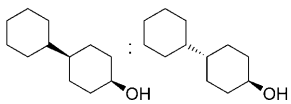
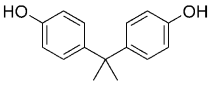
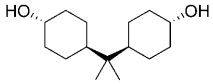



| Entry | Substrate | Product | *t* [h] | Yield [%][a] (*cis*/*trans*)[b] |
|---|---|---|---|---|
| 1 |  |  | 4 | 92 |
| 2 |  |  | 7 | 79 (62:38) |
| 3 |  |  | 7 | 75 (57:43) |
| 4 |  |  | 12 | 79 (43:57) |
| 5 |  |  | 6 | 98 (53:47) |
| 6 |  |  | 12 | 98 (65:35) |
| 7 |  |  | 7 | 100 (83:17) |
| 8 |  |  | 8 | 94[c] |

[a] Isolated yield. [b] *cis*/*trans* ratio was determined by $^1$H NMR. [c] It is hard to determine the ratio of the stereoisomers.

Table 14. Hydrogenation of phenols at 90 °C under $H_2$ (5 atm).




| Entry | Substrate | Product | *t* [h] | Yield [%][a] (*cis*/*trans*)[b] |
|---|---|---|---|---|
| 1 |  |  | 24 | 72 (17)[c] (58:23) |
| 2 |  |  | 13 | 96 (80:20) |
| 3 |  |  | 24 | 77 (61:39) |
| 4 |  |  | 24 | 75 (67:33) |
| 5 |  |  | 24 | 98 (17:83) |
| 6 |  |  | 21 | 74 |

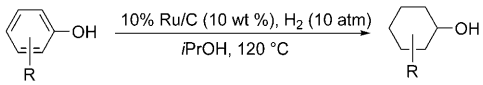
[a] Isolated yield. [b] *cis*/*trans* ratio was determined by $^1$H NMR. [c] The reaction was incomplete and the yield of the recovered starting material is indicated in parentheses.

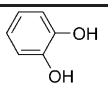
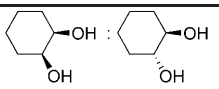
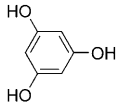
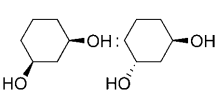
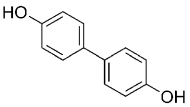
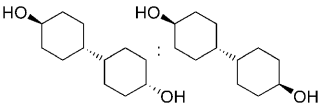
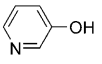
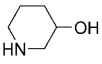
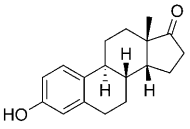
$H_2$ pressure. The hydrogenation of such substrates proceeded at 90 °C to give the corresponding cyclohexanols (Table 14, entries 2–6) except in the case of catechol (entry 1).

The hydrogenation of catechol was not complete even after 24 h at 90 °C, because of the strong coordination between the 1,2-diol functionality and Ru metal (entry 1). It is noteworthy that the 4-phenylphenol, which has stronger resonance stabilization, underwent hydrogenation in high yield to give the *trans* cyclohexanol derivative as the major product (entry 5).

To develop the applicability of this synthetic method for cyclohexanol derivatives, we conducted reactions under 10 atm of $H_2$ at 120 °C for those phenolic substrates, such as catechol, that had been resistant to the milder conditions. Fortunately, catechol was completely hydrogenated within 8 h (Table 15, entry 1). The hydrogenation of benzene-1,3,5-triol proceeded with accompanying dehydroxylation to give cyclohexene-1,3-diol in 77% yield as a *cis*/*trans* mixture (entry 2). 4,4′-Dihydroxybiphenyl and 3-hydroxypyridine, which can act as relatively strong catalyst poisons, were hydrogenated to give the corresponding 4,4′-bicyclohexyl and piperidin-3-ol in 97% and 94% yields, respectively (entries 3 and 4). Furthermore, the hydrogenation of estrone, with its rigid structure, also proceeded smoothly both at the aromatic ring and at the ketone functionality (entry 5).

Table 15. Hydrogenation of phenols at 120 °C under $H_2$ (10 atm).



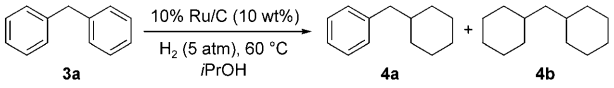

| Entry | Substrate | Product | *t* [h] | Yield [%][a] (*cis*/*trans*)[b] |
|---|---|---|---|---|
| 1 |  |  | 8 | 89 (59:41) |
| 2 |  |  | 24 | 77 (65:35) |
| 3 |  |  | 12 | 97 (67:33) |
| 4 |  |  | 4 | 94 |
| 5 |  |  | 24 | 100[c] |

[a] Isolated yield. [b] *cis*/*trans* ratio was determined by $^1$H NMR. [c] It is hard to determine the ratio of the stereoisomers.

**Reuse of Ru/C**: Finally, we examined the reuse of the Ru/C catalyst for the hydrogenation of diphenylmethane (Table 16). The reaction proceeded in high yield each time, although the reaction time had to be extended for each reuse.

Table 16. Reuse of Ru/C.




| Entry | $t$ [h] | Ratio **3a**/**4a**/**4b**[a] | Yield [%] |
|---|---|---|---|
| 1 | 1 | 0:0:100 | 93 |
| 2 | 2 | 0:0:100 | 92 |
| 3 | 3 | 0:0:100 | 95 |
| 4 | 3 | 0:0:100 | 94 |
| 5 | 4.5 | 0:0:100 | 92 |

[a] Confirmed by $^1$H NMR.

## Conclusions

In conclusion, we have developed an efficient and practical hydrogenation method under mild conditions, both with the heterogeneous Rh/C catalyst and also with Ru/C as a cheaper and in some cases more practical heterogeneous catalyst. The method is effective and applicable for the hydrogenation of a wide variety of arenes, including phenols. The use of recoverable catalysts and *i*PrOH and the employment of mild reaction conditions should lead to a practical and environmentally friendly strategy for the synthesis of cyclohexane derivatives.

## Experimental Section

**Arene hydrogenation in $H_2O$ (Tables 1–4)**: A mixture of substrate (1.0 mmol) and Rh/C (10%; Rh on activated carbon, N.E. Chemcat; 10 wt% of substrate) in $H_2O$ (1 mL) in a sealed tube was stirred at 80°C under $H_2$ pressure (5 atm) for the given time. Reaction completion was generally indicated by a constant $H_2$ pressure after a gradual decrease. After cooling to room temperature, the reaction mixture was diluted with ether (20 mL) and then filtered through a membrane filter (Millipore, Millex-LH, 0.45 μm). The filtrate was partitioned between ether (20 mL) and water (20 mL) and the aqueous layer was extracted with ether. The combined ethereal organic layers were washed with brine and dried over anhydrous $MgSO_4$. After removal of the drying agent by simple filtration, the filtrate was concentrated in vacuo to give the corresponding hydrogenated product.

**Arene hydrogenation in *i*PrOH (Tables 6–16)**: A mixture of substrate (1.0 mmol) and catalyst (Rh or Ru on activated carbon, N.E. Chemcat; 10 wt% of substrate) in *i*PrOH (1 mL) in a sealed tube was stirred at the given temperature and pressure. Reaction completion was indicated by a constant $H_2$ pressure after a gradual decrease. After cooling to room temperature, the reaction mixture was diluted with $CH_3OH$ (20 mL) and the catalyst was removed by filtration through a membrane filter (Millipore, Millex-LH, 0.45 μm). The filtrate was concentrated in vacuo to give the corresponding hydrogenated product.

***n*-Heptylcyclohexane (2; Table 2, entry 1; Table 4, entry 1; Table 12, entry 1)**: $^1$H NMR ($CDCl_3$): $\delta$ = 1.70–1.32 (m, 5H), 1.26–1.09 (m, 16H), 0.90–0.81 ppm (m, 5H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 37.8, 37.7, 32.1, 30.1, 29.5, 27.0, 26.9, 26.6, 22.8, 14.1 ppm; MS (EI): $m/z$ (%): 182 $[M]^+$ (34), 83 (100), 67 (18), 55 (68); HRMS (EI): $m/z$ calcd for $C_{13}H_{26}$: 182.20345 $[M]^+$; found: 182.20444. The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

***tert*-Butylcyclohexane (Table 2, entry 2; Table 4, entry 2; Table 12, entry 2)**: $^1$H NMR ($CDCl_3$): $\delta$ = 1.76–1.63 (m, 5H), 1.21–0.83 ppm (m, 15H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 48.4, 32.6, 27.8, 27.7, 27.5, 27.3, 26.8 ppm; MS (EI): $m/z$ (%): 140 $[M]^+$ (8), 125 (13), 83 (25), 69 (25), 56 (100). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**Cyclohexylmethylbenzene (5; Table 2, entry 3; Table 3, entries 1–5)**:[15] This compound was obtained together with dicyclohexylmethane by the hydrogenation of diphenylmethane (**3a**). The $^1$H NMR spectrum of the product was identical with that in the literature.[15]

**Dicyclohexylmethane (6; Table 2, entry 3; Table 4, entry 3; Table 7, entry 1; Table 12, entry 3)**:[16] $^1$H NMR ($CDCl_3$): $\delta$ = 1.68–1.60 (m, 10H), 1.34–1.12 (m, 8H), 1.02 (t, $J$ = 7.0 Hz, 2H), 0.87–0.77 ppm (m, 4H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 45.7, 34.4, 33.8, 26.8, 26.6 ppm; MS (EI): $m/z$ (%): 180 $[M]^+$ (53), 97 (37), 83 (100), 67 (34), 55 (71); HRMS (EI): $m/z$ calcd for $C_{13}H_{24}$: 180.18780 $[M]^+$; found: 180.18865. The $^1$H NMR spectrum of the product was identical with that in the literature.[16]

**Cyclohexanecarboxylic acid (Table 2, entry 4; Table 7, entry 3; Table 12, entry 5)**: $^1$H NMR ($CDCl_3$): $\delta$ = 2.32 (m, 1H), 1.91–1.14 ppm (m, 10H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 43.0, 28.8, 25.8, 25.4 ppm; MS (EI): $m/z$ (%): 128 $[M]^+$ (51), 99 (21), 83 (69), 73 (64), 55 (100); HRMS (EI): $m/z$ calcd for $C_7H_{12}O_2$ $[M]^+$: 128.08373; found: 128.08336. The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Nacalai Tesque Co., Ltd.

**Piperidin-3-ol (Table 2, entry 5; Table 4, entry 9; Table 8, entry 9; Table 15, entry 4)**: $^1$H NMR ($CD_3OD$): $\delta$ = 3.56 (m, 1H), 2.99 (dd, $J$ = 12.1, 3.4 Hz, 1H), 2.80 (dt, $J$ = 12.6, 4.1 Hz, 1H), 2.49 (m, 1H), 2.39 (dd, $J$ = 12.3, 8.5 Hz, 1H), 1.93 (m, 1H), 1.74 (m, 1H), 1.51–1.33 ppm (m, 2H); $^{13}$C NMR ($CD_3OD$): $\delta$ = 67.7, 53.9, 46.4, 34.2, 25.2 ppm; MS (EI): $m/z$ (%): 101 $[M]^+$ (30), 57 (42), 44 (100); HRMS (EI): $m/z$ calcd for $C_5H_{11}NO$: 101.08407 $[M]^+$; found: 101.08329. The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**Bicyclohexyl (Table 4, entry 4; Table 7, entry 2; Table 12, entry 4)**: $^1$H NMR ($CDCl_3$): $\delta$ = 1.73–1.60 (m, 10H), 1.20–0.90 ppm (m, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 43.5, 30.2, 26.9 ppm; MS (EI): $m/z$ (%): 166 $[M]^+$ (36), 82 (100), 67 (40), 55 (45); HRMS (EI): $m/z$ calcd for $C_{12}H_{12}$: 166.17215 $[M]^+$; found: 166.17129. The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**Cyclohexane-1,3-dicarboxylic acid (*cis* and *trans* mixture; Table 4, entry 6; Table 7, entry 6; Table 12, entry 6)**: $^1$H NMR ($CD_3OD$): $\delta$ = 5.44 (br s, 2H), 2.67–1.25 ppm (m, 10H); $^{13}$C NMR ($CD_3OD$): $\delta$ = 179.4, 179.3, 43.7, 40.4, 32.6, 30.7, 29.9, 29.1, 26.1, 23.4 ppm; MS (FAB$^+$, Gly): $m/z$ (%): 173 $[M+H]^+$ (5), 155 (6); HRMS (FAB$^+$, Gly): $m/z$ calcd for $C_8H_{13}O_4$: 173.0814 $[M+H]^+$; found: 173.0806. The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

***N*-Cyclohexylacetamide (Table 4, entry 7; Table 7, entry 8; Table 12, entry 6)**:[17] $^1$H NMR ($CDCl_3$): $\delta$ = 6.06 (br s,1H), 3.73 (m, 1H), 1.97 (s, 3H), 1.90 (m, 2H), 1.73 (m, 2H), 1.62 (m, 1H), 1.33 (m, 2H), 1.22–1.14 ppm (m, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 169.1, 47.9, 32.7, 25.2, 24.9, 22.9. ppm; MS (EI): $m/z$ (%): 100 $[M]^+$ (7), 141 (50), 98 (24), 70 (11), 60 (100); HRMS (FAB$^+$, Gly): $m/z$ calcd for $C_8H_{15}NO$: 141.11537 $[M+H]^+$; found: 141.11555. The $^1$H NMR spectrum of the product was identical with that in the literature.[17]

**2-Pentyltetrahydrofuran (Table 4, entry 8; Table 7, entry 10; Table 12, entry 7)**: $^1$H NMR ($CDCl_3$): $\delta$ = 3.74 (m, 1H), 3.66 (m, 1H), 3.58 (m, 1H), 1.84 (m, 1H), 1.74 (m, 2H), 1.45 (m, 1H), 1.36–1.18 (m, 8H), 0.78 ppm (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 80.0, 68.1, 36.3, 32.6, 32.0, 26.7, 26.3, 23.2, 14.5 ppm; MS (FAB$^+$, Gly): $m/z$: 143 $[M+H]^+$ (4%); HRMS (FAB$^+$, Gly): $m/z$ calcd for $C_9H_{19}O$: 143.1436 $[M+H]^+$; found: 143.1441.

**Piperidine-3-carboxamide (Table 4, entry 10; Table 7, entry 9)**: $^1$H NMR ($CD_3OD$): $\delta = 2.95$ (dd, $J = 12.2$ Hz, 4.4 Hz, 1H), 2.84 (m, 1H), 2.59 (m, 1H), 2.47 (m, 1H), 2.27 (m, 1H), 1.82 (m, 1H), 1.64–1.36 ppm (m, 3H); $^{13}$C NMR ($CD_3OD$): $\delta = 180.6$, 47.6, 45.2, 29.8, 26.9 ppm; MS (FAB$^+$, Gly): $m/z$: 129 $[M+H]^+$ (4%); HRMS (FAB$^+$, Gly): $m/z$ calcd for $C_6H_{13}N_2O$: 129.10280 $[M+H]^+$; found: 129.10331. The $^1$H NMR spectrum of the product was identical to that of an authentic sample from Aldrich Co., Ltd.

**4-Isopropylcyclohexanecarboxylic acid (*cis* and *trans* mixture; Table 7, entry 4)**: $^1$H NMR ($CDCl_3$): $\delta = 2.62$ (m, 0.66H, *cis*-CH–$CO_2$H), 2.23 (m, 0.33H, *trans*-C*H*–$CO_2$H), 2.18–1.97 (m, 2H), 1.40–1.19 ppm (m, 4H); $^{13}$C NMR ($CDCl_3$): $\delta = 176.76$, 175.52, 45.00, 42., 28, 29.20, 26.57, 25.57, 24.07 ppm; MS (EI): $m/z$ (%): 170 $[M]^+$ (31), 152 (10), 127 (38), 109 (38), 98 (8), 81(100), 59 (23), 41 (16). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**Cyclohexane-1,4-dicarboxylic acid (*cis* and *trans* mixture; Table 7, entry 7)**: $^1$H NMR ([$D_6$]DMSO): $\delta = 12.09$ (brs, 2H), 2.35–2.12 (m, 2H), 1.88 (m, 1H), 1.69–1.55 (m, 6H), 1.30 ppm (m, 1H); $^{13}$C NMR ([$D_6$]DMSO): $\delta = 176.6$, 176.3, 41.8, 41.8, 27.8, 25.7 ppm; MS (EI): $m/z$ (%): 154 $[M-18]^+$ (16), 126 (68), 108 (52), 81 (100), 67 (28), 54 (23). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**2-Amino-3-cyclohexylpropanoic acid (not isolated; Table 7, entry 11)**:[18] $^1$H NMR ($D_2O$): $\delta = 3.64$ (dd, $J = 8.5$, 5.4 Hz, 1H), 1.69–0.79 ppm (m, 13H). The $^1$H NMR spectrum of the product was identical with that in the literature.[18]

**2-Acetylamino-3-cyclohexylpropanoic acid (Table 7, entry 12; Table 8, entry 1)**: $^1$H NMR ($CD_3OD$): $\delta = 4.39$ (dd, $J = 10.2$, 5.0 Hz, 1H), 1.93 (s, 3H), 1.75 (m, 1H), 1.68–1.58 (m, 5H), 1.52 (m, 1H), 1.33 (m, 1H), 1.25–1.12 (m, 3H), 0.95 (m, 1H), 0.84 ppm (m, 1H); $^{13}$C NMR ($CD_3OD$): $\delta =$ 176.7, 173.9, 173.8, 52.0, 40.7, 35.9, 35.3, 33.7, 28.0, 27.8, 27.6, 22.9, 22.8 ppm; MS (FAB$^+$, NBA): $m/z$: 214 $[M+H]^+$ (17%); HRMS (FAB$^+$, NBA): $m/z$ calcd for $C_{11}H_{20}NO_3$: 214.1443 $[M+H]^+$; found: 214.1447.

**Ethyl 2-acetamido-3-cyclohexylpropanoate (Table 8, entry 2)**: $^1$H NMR ($CD_3OD$): $\delta = 4.43$ (dd, $J = 9.8$, 5.5 Hz, 1H), 4.14 (qd, $J = 7.1$, 1.5 Hz, 2H), 1.97 (s, 3H), 1.78–1.51 (m, 7H), 1.37 (m, 1H), 1.26–1.12 (m, 3H), 1.25 (t, $J = 7.1$ Hz, 3H), 0.98 (m, 1H), 0.90 ppm (m, 1H); $^{13}$C NMR ($CD_3OD$): $\delta = 174.2$, 173.1, 173.0, 62.0, 51.6, 51.5, 40.1, 40.0, 35.3, 34.6, 33.3, 27.5, 27.3, 27.1, 22.4, 22.3, 14.5 ppm; MS (FAB$^+$, NBA): $m/z$ (%): 242 $[M+H]^+$ (92), 168 (26), 126 (15); HRMS (FAB$^+$, NBA): $m/z$ calcd for $C_{13}H_{24}NO_3$: 242.1756 $[M+H]^+$; found: 242.1751.

**Cyclohexane-1,2-dicarboxylic acid (*cis* and *trans* mixture; Table 8, entry 3)**: $^1$H NMR ([$D_6$]DMSO): $\delta = 12.08$ (brs, 2H), 2.71 (m, 1.69H, *cis*-C*H*–$CO_2$H), 2.40 (m, 0.31H, *trans*-C*H*–$CO_2$H), 1.92–1.91 (m, 2H), 1.73–1.70 (m, 2H), 1.24–0.90 ppm (m, 4H); $^{13}$C NMR ([$D_6$]DMSO): $\delta = 182.9$, 182.3, 43.3, 42.9, 39.9, 32.7, 31.4, 28.9, 28.7, 26.6, 26.4, 20.0, 19.7 ppm; MS (EI): $m/z$ (%): 154 $[M-18]^+$ (20), 126 (72), 108 (36), 81 (100), 66 (55), 41 (46). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Wako Pure Chemical Product.

**1,2,4,5-Tetramethylcyclohexane (mixture of isomers; Table 8, entry 4)**: $^1$H NMR ($CDCl_3$): $\delta = 1.75$–1.64 (m, 4H), 1.43–1.26 (m, 4H), 0.86 ppm (d, $J = 7.1$ Hz, 12H); $^{13}$C NMR ($CDCl_3$): $\delta = 43.3$, 39.6, 38.0, 36.6, 36.1, 35.2, 34.1, 33.6, 32.3, 20.2, 19.9, 17.8, 12.2 ppm; MS (EI): $m/z$ (%): 140 $[M]^+$ (32), 125 (57), 98 (21), 83 (31), 69 (100), 55 (54); HRMS (EI): $m/z$ calcd for $C_{10}H_{20}$ $[M]^+$ 140.1565; found: 140.1560.

**1,3,5-Tri-*tert*-butylcyclohexane (mixture of isomers; Table 8, entry 5)**: $^1$H NMR ($CDCl_3$): $\delta = 2.08$–0.52 ppm (m, 36H); $^{13}$C NMR ($CDCl_3$): $\delta =$ 48.5, 32.8, 28.1, 27.8 ppm; MS (EI): $m/z$ (%): 252 $[M]^+$ (14), 196 (23), 139 (29), 125 (19), 111 (12), 83 (20), 69 (18), 57 (100); HRMS (EI): $m/z$ calcd for $C_{18}H_{36}$: 252.2817 $[M]^+$; found: 252.2803.

**Dodecahydro-1*H*-fluorene (Table 8, entry 6)**: $^1$H NMR ($CDCl_3$): $\delta = 2.08$–1.05 ppm (m, 22H); $^{13}$C NMR ($CDCl_3$): $\delta = 43.0$, 37.3, 35.3, 29.2, 24.4, 24.2, 22.1 ppm; MS (EI): $m/z$: 178 $[M]^+$ (44), 135 (7), 121 (18), 97 (100), 67 (60), 55(24); HRMS (EI): $m/z$ calcd for $C_{18}H_{36}$: 178.17215 $[M]^+$; found: 178.17115.

**Decahydronaphthalen-2-ol (mixture of isomers; Table 8, entry 7)**:[19] $^1$H NMR ($CDCl_3$): $\delta = 4.14$ (m, 0.01H), 3.81 (brs, 0.33H), 3.58 (m, 0.65H), 2.12 (brs, 1H), 1.87–0.86 ppm (m, 16H); $^{13}$C NMR ($CDCl_3$): $\delta =$ 66.6, 50.0, 35.2, 34.8, 34.5, 31.6, 30.2, 26.6, 25.7, 24.7, 20.9 ppm; MS (EI): $m/z$ (%): 136 $[M-18]^+$ (100), 121 (38), 107 (26), 94 (58), 67 (30), 55 (26). The $^1$H NMR spectrum of the product was identical with that in the literature.[19]

**Pyrrole-2-carboxylic acid (Table 8, entry 8)**:[20] $^1$H NMR ($D_2O$): $\delta = 4.10$ (m, 1H), 3.25 (m, 2H), 2.21 (m, 1H), 1.92 ppm (m, 3H); $^{13}$C NMR ($D_2O$): $\delta = 174.7$, 61.4, 46.2, 29.1, 23.9 ppm; MS (EI): $m/z$ (%): 71 $[M-CO_2]^+$ (91), 70 (100), 44 (15), 41 (21). The $^1$H NMR spectrum of the product was identical with that in the literature.[20]

**4-(4-Hydroxycyclohexyl)cyclohexanecarboxylic acid (mixture of isomers; Table 8, entry 10)**: $^1$H NMR ($CDCl_3$): $\delta = 4.00$ (m, 0.74H), 3.53 (m, 0.26H), 2.61 (m, 0.71H), 2.23 (m, 0.29H, C*H*$CO_2$H), 1.86–0.88 ppm (m, 2H); $^{13}$C NMR ($CDCl_3$): $\delta = 24.1$, 25.4, 35.5, 70.3 ppm; MS (EI): $m/z$ (%): 162 $[M-18]^+$ (18), 149 (12), 127 (32), 109 (22), 81 (100), 67 (26), 55 (22); elemental analysis (%) calcd for $C_{13}H_{22}O_3$: C 68.99, H 9.80; found: C 68.63, H 9.98.

**1-(2-Hydroxy-5,6,7,8-tetrahydronaphthalen-1-yl)-5,6,7,8-tetrahydronaphthalen-2-ol (mixture of isomers; Table 8, entry 11)**: $^1$H NMR ($CDCl_3$): $\delta = 7.04$ (d, $J = 6.0$ Hz, 2H), 6.81 (d, $J = 6.0$ Hz, 2H), 4.61 (brs, 2H), 2.73 (t, $J = 5.6$ Hz, 4H), 2.31–2.25 (m, 2H), 2.18–2.12 (m, 2H), 1.74–1.65 ppm (m, 8H); $^{13}$C NMR ($CDCl_3$): $\delta = 151.3$, 137.1, 130.9, 130.2, 118.9, 112.9, 29.2, 27.0, 22.9 ppm; MS (EI): $m/z$ (%): 294 $[M]^+$ (100), 276 (8), 248 (13), 237 (8), 147 (12), 126 (8), 84 (85), 47(11); HRMS (EI): $m/z$ calcd for $C_{20}H_{22}O_2$: 294.16138 $[M]^+$; found: 252.2803.

**(8*R*,9*R*,13*S*,14*R*)-13-Methyl-hexadecahydro-1*H*-cyclopenta[α]phenanthrene-3, 17-diol (hydrogenated estrone, mixture of isomers; Table 8, entry 12; Table 9, entry 1; Table 15, entry 5)**: $^1$H NMR ($CDCl_3$): $\delta = 3.76$–3.61 (m, 2H), 2.33–0.63 ppm (m, 26H); $^{13}$C NMR ($CDCl_3$): $\delta = 81.5$, 79.7, 66.8, 50.7, 48.4, 46.9, 45.6, 43.3, 41.5, 40.1, 38.5, 38.4, 36.7, 36.0, 34.5, 32.4, 32.1, 31.6, 31.5, 30.2, 26.6, 26.0, 25.9, 24.3, 23.1, 20.1, 16.8, 11.0 ppm; MS (EI): $m/z$ (%): 278 $[M]^+$ (18), 260 (98), 242 (86), 216 (55), 201 (100); elemental analysis (%) calcd for $C_{18}H_{30}O_2$: C 77.65, H 10.86; found: C 76.82, H 10.77.

**Decahydronaphthalen-1-ol (mixture of isomers; Table 9, entry 2)**:[20] $^1$H NMR ($CDCl_3$): $\delta = 3.76$ (m, 0.26H), 3.65 (m, 0.67H), 3.18 (m, 0.07H), 2.13–0.87 ppm (m, 17H); $^{13}$C NMR ($CDCl_3$): $\delta = 73.3$, 42.9, 41.0, 35.6, 31.7, 29.2, 26.3, 24.4, 24.2, 21.4, 18.8 ppm; MS (EI): $m/z$ (%): 100 $[M-18]^+$ (7), 136 (100), 121 (23), 107(22), 94(33), 81 (28), 67 (26), 55 (16). The $^1$H NMR spectrum of the product was identical with that in the literature.[20]

**1-Cyclohexyl-4-(4-cyclohexylcyclohexyl)cyclohexane (mixture of isomers; Table 9, entry 3)**: $^1$H NMR ($CDCl_3$): $\delta = 1.89$–0.80 ppm (m, 42H); $^{13}$C NMR ($CDCl_3$): $\delta = 43.4$, 41.4, 41.1, 39.8, 39.3, 35.7, 30.9, 30.7, 30.6, 30.4, 30.2, 30.2, 26.9, 26.8, 26.7, 26.5, 26.0 ppm; MS (EI): $m/z$: 100 $[M-18]^+$ (7%); elemental analysis (%) calcd for $C_{24}H_{42}$: C 87.19, H 12.81; found: C 86.93, H 13.06.

**4-Aminocyclohexanecarboxylic acid (*cis* and *trans* mixture; Table 9, entry 4)**: $^1$H NMR ($D_2O$): $\delta = 3.03$ (m, 1H), 2.28–1.10 ppm (m, 13H); $^{13}$C NMR ($CDCl_3$): $\delta = 199.2$, 198.0, 64.5, 63.7, 61.3, 59.7, 56.0, 44.4, 44.3, 42.3, 42.0, 40.3, 40.1, 39.5 ppm; MS (EI): $m/z$ (%): 100 $[M]^+$ (7), 145 (16), 129 (12), 83 (15), 58 (100), 45 (38). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Aldrich Co., Ltd.

**Cyclohexanol (Table 13, entry 1)**:[21] $^1$H NMR ($CDCl_3$): $\delta = 3.62$ (m, 1H), 1.99–1.82 (m, 2H), 1.80–1.62 (m, 2H), 1.53 (m, 1H), 1.32–1.18 ppm (m, 5H); $^{13}$C NMR ($CDCl_3$): $\delta = 70.3$, 35.5, 25.4, 24.1 ppm; MS (EI): $m/z$ (%): 100 $[M]^+$ (7), 82 (89), 57 (100). The $^1$H NMR spectrum of the product was identical with that in the literature.[21]

**2-Methylcyclohexanol (*cis* and *trans* mixture; Table 13, entry 2)**: $^1$H NMR ($CDCl_3$): $\delta = 3.78$ (m, 0.62H, *cis*-C*H*OH), 3.12 (m, 1H), 1.94 (m, 1H), 1.75–1.24 (m, 8H), 1.91–0.93 ppm (m, 3H); $^{13}$C NMR ($CDCl_3$): $\delta = 76.4$, 71.1, 40.2, 35.8, 35.4, 33.6, 32.4, 28.7, 25.4, 25.2, 24.4, 20.6, 18.5, 16.9 ppm; MS (EI): $m/z$ (%): 114 $[M]^+$ (9), 96 (52), 81 (55), 57 (100). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**3-Methylcyclohexanol (*cis* and *trans* mixture; Table 13, entry 3)**:[22] $^1$H NMR ($CDCl_3$): $\delta=4.05$ (m, 0.43H, *trans*-C*H*OH,), 3.55 (m, 0.57H, *cis*-C*H*OH), 1.96–0.74 ppm (m, 12H); $^{13}$C NMR ($CDCl_3$): $\delta=70.7$, 66.8, 44.6, 41.5, 35.4, 31.4, 26.5, 24.1, 22.3, 21.9, 20.0 ppm; MS (EI): *m*/*z* (%): 96 (9), 81 (76), 71 (100), 57 (35). The $^1$H NMR spectrum of the product was identical with that in the literature.[22]

**4-Methylcyclohexanol (*cis* and *trans* mixture; Table 13, entry 4)**:[23] $^1$H NMR ($CDCl_3$): $\delta=3.94$ (m, 0.47H, *cis*-C*H*OH), 3.53 (m, 0.53H, *trans*-C*H*OH), 1.93 (m, 1H), 1.71–1.68 (m, 2H), 1.34–1.20 (m, 2.5H), 1.01–0.87 ppm (m, 4.5H); $^{13}$C NMR ($CDCl_3$): $\delta=70.8$, 66.8, 35.5, 33.3, 32.1, 31.7, 31.0, 28.9, 21.9, 21.5 ppm; MS (EI): *m*/*z* (%): 114 $[M]^+$ (26), 96 (100), 81 (85), 57 (78). The $^1$H NMR spectrum of the product was identical with that in the literature.[23]

**4-*tert*-Butylcyclohexanol (*cis* and *trans* mixture; Table 13, entry 5)**: $^1$H NMR ($CDCl_3$): $\delta=4.03$ (m, 0.53H, *cis*-C*H*OH), 3.51 (m, 0.47H, *trans*-C*H*OH), 2.02–0.85 ppm (m, 18H); $^{13}$C NMR ($CDCl_3$): $\delta=71.1$, 65.8, 48.0, 47.1, 36.0, 33.3, 32.5, 27.6, 27.4, 25.6, 20.9 ppm; MS (EI): *m*/*z* (%): 156 $[M]^+$ (2), 138 (19), 123 (23), 99 (28), 81 (51), 57 (100). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**2-Propylcyclohexanol (*cis* and *trans* mixture; Table 13, entry 6)**: $^1$H NMR ($CDCl_3$): $\delta=3.86$ (m, 0.65H, *cis*-C*H*OH), 3.20 (m, 0.35H, *trans*-C*H*OH), 1.96–1.08 (m, 13H), 1.00–0.89 ppm (m, 3H); $^{13}$C NMR ($CDCl_3$): $\delta=75.7$, 70.4, 45.8, 41.9, 36.6, 35.4, 35.1, 34.0, 31.1, 27.5, 26.5, 26.2, 25.8, 21.5, 21.1, 20.6, 15.4, 15.3 ppm; MS (EI): *m*/*z* (%): 124 (27), 95 (46), 82 (100), 57 (69). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**2-*tert*-Butylcyclohexanol (*cis* and *trans* mixture; Table 13, entry 7)**:[24] $^1$H NMR ($CDCl_3$): $\delta=4.25$ (m, 0.83H, *cis*-C*H*OH), 3.47 (m, 0.17H, *trans*-C*H*OH), 1.94–0.79 ppm (m, 18H); $^{13}$C NMR ($CDCl_3$): $\delta=73.4$, 67.8, 53.6, 50.9, 37.8, 35.0, 32.5, 29.2, 28.5, 26.7, 26.1, 25.1, 21.1, 19.9 ppm; MS (FAB$^+$, NPOE): *m*/*z* (%): 156 $[M]^+$ (7), 123 (55), 71 (79), 57 (100). The $^1$H NMR spectrum of the product was identical with that in the literature.[24]

**2,6-Dimethylcyclohexanol (mixture of isomers; Table 13, entry 8)**: $^1$H NMR ($CDCl_3$): $\delta=3.55$ (m, 0.37H), 3.34 (m, 0.09H), 2.68 (t, $J=9.4$ Hz, 0.23H), 1.67–1.22 (m, 8H), 0.98 ppm (m, 6H); $^{13}$C NMR ($CDCl_3$): $\delta=82.1$, 75.6, 39.8, 37.2, 34.2, 33.6, 33.1, 30.5, 27.3, 25.8, 25.5, 19.9, 18.7, 18.6, 18.0 ppm; MS (EI): *m*/*z* (%): 128 $[M]^+$ (65), 110 (35), 95 (51), 81 (27), 71 (100). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**Cyclohexane-1,2-diol (*cis* and *trans* mixture; Table 14, entry 1; Table 15 entry 1)**: $^1$H NMR ($CDCl_3$): $\delta=3.75$ (m, 0.59H, *cis*-C*H*OH), 3.32 (m, 0.41H, *trans*-C*H*OH), 1.92 (m, 1H), 1.74–1.53 (m, 4H), 1.30–1.24 ppm (m, 3H); $^{13}$C NMR ($CDCl_3$): $\delta=75.2$, 70.3, 32.56, 29.5, 24.0, 21.1, 24.0 ppm; MS (EI): *m*/*z* (%): 116 $[M]^+$ (21), 98 (40), 70 (100), 57 (58).

**Methyl 2-hydroxycyclohexanecarboxylate (*cis* and *trans* mixture; Table 14, entry 2)**:[22] $^1$H NMR ($CDCl_3$): $\delta=4.14$ (m, 0.65H, *cis*-C*H*OH), 3.76 (m, 0.35H, *trans*-C*H*OH), 3.71 (s, 3H), 3.15 (brs, 0.65H), 2.95 (brs, 0.35H), 2.48 (m, 0.65H, *trans*-C*H*CO$_2$-), 2.25 (m, 0.35H, *cis*-C*H*CO$_2$-), 2.01–1.76 (m, 5H), 1.48–1.26 ppm (m, 4H); $^{13}$C NMR ($CDCl_3$): $\delta=176.1$, 175.6, 70.8, 66.7, 51.7, 51.2, 46.6, 33.7, 31.7, 28.0, 24.9, 24.7, 24.3, 23.8, 20.0 ppm; MS (EI): *m*/*z* (%): 140 $[M]^+$ (8), 130 (41), 108 (15), 87 (100), 81 (34). The $^1$H NMR spectrum of the product was identical with that in the literature.[22]

**Cyclohexane-1,3-diol (*cis* and *trans* mixture; Table 14, entry 3; Table 15, entry 2)**: $^1$H NMR ($CDCl_3$): $\delta=4.08$ (m, 0.39H, *trans*-C*H*OH), 3.75 (m, 0.61H, *cis*-C*H*OH), 3.13 (brs, 1H), 2.05 (m, 1H), 1.87–1.27 ppm (m, 7H); $^{13}$C NMR ($CDCl_3$): $\delta=68.4$, 66.7, 41.9, 33.8, 33.6, 18.8, 18.5 ppm; MS (EI): *m*/*z* (%): 116 $[M]^+$ (3), 98 (100), 80 (57), 70 (51). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**Cyclohexane-1,4-diol (*cis* and *trans* mixture; Table 14, entry 4)**: $^1$H NMR ([D$_6$]DMSO): $\delta=4.42$ (m, 1.34H, *cis*-C*H*OH), 4.29 (m, 0.66H, *trans*-C*H*OH), 3.52 (m, 0.33H), 3.35 (m, 0.67H), 1.79–1.68 (m, 2.5H), 1.61–1.50 (m, 1.5H), 1.40 (m, 1H), 1.21–1.11 ppm (m, 2.5H); $^{13}$C NMR ([D$_6$]DMSO): $\delta=68.2$, 65.9, 33.0, 30.3 ppm; MS (EI): *m*/*z* (%): 116 $[M]^+$ (2), 98 (57), 83 (42), 80 (27), 70 (37), 54 (100). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**4-Cyclohexylcyclohexanol (*cis* and *trans* mixture; Table 14, entry 5)**: $^1$H NMR ($CDCl_3$): $\delta=3.96$ (m, 0.17H, *cis*-C*H*–OH), 3.49 (m, 0.83H, *trans*-C*H*–OH), 2.00–0.93 ppm (m, 20H); $^{13}$C NMR ($CDCl_3$): $\delta=71.4$, 67.1, 42.9, 42.5, 36.0, 32.9, 30.5, 30.4, 28.2, 26.9, 23.9 ppm; MS (EI): *m*/*z* (%): 182 $[M]^+$ (2), 164 (100), 82 (82). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

**2, 2-Bis(4′-hydroxycyclohexyl)propane (mixture of isomers; Table 14, entry 6)**: $^1$H NMR ($CD_3OD$): $\delta=3.50$ (m, 0.83H), 2.05–1.90 (m, 4H), 1.62–1.79 (m, 4H), 1.29–1.02 (m, 10H), 0.74 ppm (s, 6H); $^{13}$C NMR ($CD_3OD$): $\delta=71.8$, 44.7, 37.5, 36.9, 26.2, 21.1 ppm; elemental analysis (%) calcd for $C_{15}H_{28}O_2$: C 74.95, H 11.74; found: C 74.40, H 11.75.

**4,4′-Bicyclohexanol (*cis* and *trans* mixture; Table 15, entry 3)**: $^1$H NMR ($CD_3OD$): $\delta=3.90$–3.82 (m, 0.66H, *cis*-C*H*–OH), 3.49–3.31 (m, 1.34H, *trans*-C*H*–OH), 2.00–1.90 (m, 2H), 1.85–1.60 (m, 4H), 1.55–1.35 (m, 4H), 1.21–1.04 ppm (m, 8H); $^{13}$C NMR ($CD_3OD$): $\delta=71.9$, 71.8, 67.6, 43.5, 43.4, 42.9, 36.7, 33.7, 31.7, 29.7, 29.6, 28.1, 25.4, 25.3 ppm; MS (EI): *m*/*z* (%): 180 $[M]^+$ (8), 162 (69), 81 (100). The $^1$H NMR spectrum of the product was identical with that of an authentic sample from Tokyo Chemical Industry Co., Ltd.

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