Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 60 (2004) 1791–1801
Tetrahedron

# Regioselective synthesis of substituted 1-indanols, 2,3-dihydrobenzofurans and 2,3-dihydroindoles by electrochemical radical cyclization using an arene mediator

Nobuhito Kurono,* Eiichi Honda, Fumikazu Komatsu, Kazuhiko Orito and Masao Tokuda

*Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, kita-ku kita13 Nishi8, Sapporo 060-8628, Japan*

Received 12 November 2003; revised 13 December 2003; accepted 15 December 2003

**Abstract**—Electrochemical reduction of haloarenes carrying 2-(1-hydroxybut-3-enyl), 2-allyloxy or *N*-allyl-*N*-methylamino group in the presence of phenanthrene as a mediator generated the corresponding aryl radicals and gave the corresponding 5-*exo* cyclization products in good yields. Higher regio- and stereoselectivities than those of usual radical cyclization using AIBN-$Bu_3SnH$ were achieved.
© 2003 Elsevier Ltd. All rights reserved.

## 1. Introduction

Radical cyclization is a useful method for synthesizing cyclic compounds. Carbon radicals are usually generated by the reaction of organic halides with AIBN-organotin reagents such as tributyltin hydride ($Bu_3SnH$).[1] However, there are several drawbacks in this method, such as toxicity of tin compounds and difficulty in isolating products due to contamination of $R_3SnX$. Many methods[2] have been reported to overcome the drawbacks. On the other hand, electrochemical reaction is an environmentally benign method for organic synthesis since it can be carried out under mild conditions by using electrons as clean reagents. Therefore, electrochemical generation of carbon radicals from the corresponding organic halides and its use in cyclization reactions would be of synthetic importance. However, usual electrochemical reduction of organic halides gives the corresponding carbanions by their preferential two-electron reduction and, finally, gives simple reduction products.[3] Only a few methods for electrochemical generation of radicals to give cyclization products have been reported: i.e. direct electrochemical reduction of 2-halo-*N*-arylbenzamide derivatives[4] and arenediazonium salts carrying prop-3-enylamino groups[5] and electrochemical reduction of alkenyl and aryl halides using Ni(II) or Co(II) catalyst[6] and of *N*-(2-iodophenyl)-*N*-alkylcinnamides using an oxygen mediator.[7]

Recently, we developed an electrochemical method for the generation of aryl radicals from the corresponding aryl halides by the use of arene as a single electron transfer mediator and reported in a communication that these aryl radicals could be used to intramolecular cyclization reaction.[8] In this paper, we report the detailed results of the electrochemical generation of aryl radicals as well as its application to 5-*exo* radical cyclizations to give substituted 1-indanols, 2,3-dihydrobenzofurans and 2,3-dihydroindoles. We also report that these cyclizations undergo in more regio- and stereoselective manner than that of usual radical cyclizations using AIBN-$Bu_3SnH$. Similar electrochemical cyclization of *N*-allyl-2-chloroacetanilide using (*E*)-stilbene as an electron transfer agent was reported by Grimshaw et al.[9]

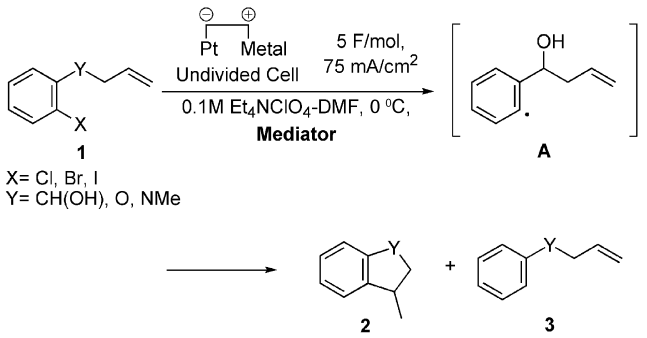
## 2. Results and discussion

### 2.1. Generation of aryl radicals

Electrochemical reduction of 1-(2-iodophenyl)-3-buten-1-ol (**1a**: X=I, Y=CH(OH)) in the presence of arene mediator generated the corresponding aryl radical (A) and gave the corresponding 5-*exo* cyclization product **2a** and simple reduction product (**3a**) (Scheme 1). This radical cyclization reaction was first examined under various conditions to optimize the reaction conditions. These results are summarized in Tables 1 and 2. Electrolysis was carried out at a constant current in an undivided cell equipped with a platinum cathode and a sacrificial anode. An anode material used as a sacrificial anode was very effective for the reactions. It was found that the use of Mg or Zn metal as an anode gave an *exo*-cyclized product **2a**, although electrolysis using a Pt anode gave **2a** only in 12% yield (Table 1). Therefore, a platinum cathode and a magnesium anode were

*Keywords*: Electrolysis; Radical cyclization; 5-*exo* Cyclization; Arene mediator; Regioselectivity.
* Corresponding author. Tel.: +81-11-706-6601; fax: +81-11-706-6598; e-mail address: chlono@org-mc.eng.hokudai.ac.jp

0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2003.12.038




**Scheme 1.**

**Table 1**. Effect of anode materials on electrochemical cyclization of **1a**[a]

| Entry | Anode (metal) | Yields (%)[b] | |
|---|---|---|---|
| | | **2a** (*syn*:*anti*)[c] | **3a** |
| 1 | Pt | 12 (2.2:1) | 18 |
| 2 | Zn | 60 (1.7:1) | 28 |
| 3 | Mg | 76 (2.5:1) | 14 |

[a] Electrolysis of **1a** in 0.1 M $Et_4NClO_4$-DMF was carried out at 0 °C in the presence of 6 equiv. of naphthalene using a Pt cathode (75 mA/cm$^2$, 5 F/mol).
[b] Isolated yields.
[c] Isomer ratios of *syn* and *anti* were determined by $^1$H NMR analysis.

used in the following electrolyses. The effect of current density was also examined, and the electrolysis of **1a** at current densities of 45, 60, 75 and 90 mA/cm$^2$ gave **2a** in yields of 67, 69, 76 and 58%, respectively. Electricity of 5 F/mol was needed for complete consumption of **1a**.

Effects of various mediators and their amounts on the cyclization of **1a** were also examined, and the results are summarized in Table 2. Electrolysis of **1a** in the absence of any mediator gave the cyclization product **2a** only in 11% yield (entry 1). Use of 6 equiv. of naphthalene gave **2a** in 76% yield (entry 2). When phenanthrene was used as a mediator, **2a** was obtained in 73% yield even when 2 equiv. of phenanthrene was used (entry 5). When 9,10-diphenylanthracene, 9-phenylanthracene or 9-cyanophenanthrene was used, the cyclized product was obtained in low to moderate yields (entries 8–10). Finally, all of the following electrolyses were carried out in a one-compartment cell equipped with a Pt cathode and an Mg anode in 0.1 M $Et_4NClO_4$-DMF solution containing a substrate and phenanthrene as a mediator at a current density of 75 mA/cm$^2$. Electricity of 5 F/mol was passed (Scheme 1).

## 2.2. Synthesis of substituted 1-indanols

The present radical cyclization by electrolysis was applied to a synthesis of substituted 1-indanols (**2**). Electrolysis of aryl iodide (**1a**), bromide (**1b**), or chloride (**1c**) in 0.1 M $Et_4NClO_4$-DMF containing 2.0 or 4.0 equiv. of phenanthrene at 75 mA/cm$^2$ using a Pt cathode and Mg anode gave the 5-*exo* cyclization product **2a** having *syn* and *anti*-isomers in yields of 62–80% (Table 3). Conventional radical cyclization of **1c** using AIBN-$Bu_3SnH$ gave no **2a** and the starting **1c** was recovered unreacted (Table 3, entry 8). Substituted indanols **2b** and **2c**, tricyclic indanol (**2d**) were also obtained in good yields. Cyclization of **1g** having α,β-unsaturated ester group proceeded smoothly without the reduction of carbon–carbon double bond in the ester moiety. It has also been found that a higher diastereomeric ratio of *syn*- and *anti*-**2a**[10] (2.3:1) was obtained in the electrochemical cyclization of **1a** (Table 3, entries 1 and 2), although a similar cyclization using AIBN-$Bu_3SnH$ gave *syn*- and *anti*-**2a** in a ratio of 1.4:1 (entry 3). It is not clear about the reason why the difference of diastereoselectivity appeared in the present stage. However, various reaction conditions, such as mediator compounds or equivalents of mediator, affected on the diastereomeric ratio (Table 2). Particularly, remarkable effect of anode materials on the diastereomeric ratio of the electrochemical cyclization was observed. Electrolysis of **1a** using an Mg anode gave the higher diastereomeric ratio of *syn*- and *anti*-**2a** (2.5:1) than that using a Zn anode (1.7:1) (Table 1, entries 1 and 2).

## 2.3. Synthesis of substituted 2,3-dihydrobenzofurans

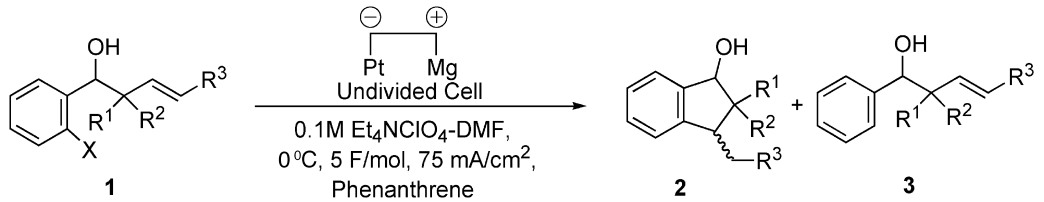
5-*exo* Cyclization of aryl radical proceeded efficiently by

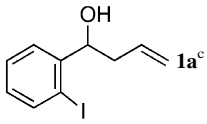
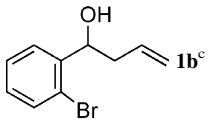
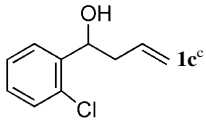
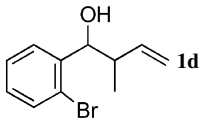
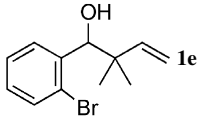
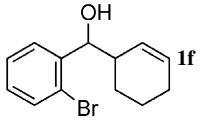
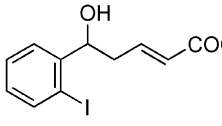
**Table 2**. Effects of various polyaromatic compounds on electrochemical radical cyclization of **1a**[a]

| Entry | Mediator | Reduction potential[b] (V vs. Ag/Ag$^+$) | Equivalent[c] | Yield (%)[d] | | |
|---|---|---|---|---|---|---|
| | | | | **2a** (*syn*:*anti*)[e] | **3a** | Recov. **1a** |
| 1 | None | — | — | 11 (1.7:1) | 78 | 0 |
| 2 | Naphthalene | −2.94 | 6.0 | 76 (2.5:1) | 14 | 0 |
| 3 | Naphthalene | | 2.0 | 59 (2.4:1) | 8 | 18 |
| 4 | Phenanthrene | −2.87 | 4.0 | 80 (2.3:1) | 14 | 0 |
| 5 | Phenanthrene | | 2.0 | 73 (2.3:1) | 12 | 0 |
| 6 | Phenanthrene | | 1.0 | 58 (2.2:1) | 4 | 22 |
| 7 | Phenanthrene | | 0.5 | 36 (2.5:1) | 3 | 44 |
| 8 | 9,10-Diphenylanthracene | −2.27 | 2.0 | 48 (1.1:1) | 8 | 23 |
| 9 | 9-Phenylanthracene | −2.31 | 2.0 | 30 (4.4:1) | 15 | 21 |
| 10 | 9-Cyanophenanthrene | −2.22 | 2.0 | 47 (2.2:1) | 4 | 22 |

[a] Electrolysis of **1a** in 0.1 M $Et_4NClO_4$-DMF was carried out at 0 °C with a constant current of 75 mA/cm$^2$ (5 F/mol) in a one-compartment cell equipped with a Pt cathode and Mg anode.
[b] Reduction potentials of **1a** and arene compounds were measured by cyclic voltammetry in 0.1 M $Et_4NClO_4$-DMF using Ag/Ag$^+$ reference electrode. Reduction potential of **1a** was −2.50 V vs. Ag/Ag$^+$.
[c] Equivalents of mediator to **1a**.
[d] Isolated yields.
[e] Determined by $^1$H NMR analysis.

**Table 3**. Synthesis of substituted 1-indanols by electrochemical radical cyclizations




| Entry | Substrate | Equiv.[a] | Yield (%)[b] | |
|---|---|---|---|---|
| | | | **2** (*syn*:*anti*) | **3** |
| 1 |  **1a**[c] | 2.0 | 64 (2.3:1) | 11 |
| 2 | | 4.0 | 80 (2.3:1) **2a** | 14 **3a** |
| 3 | | AIBN-TBTH[d] | 86 (1.4:1) | |
| 4 |  **1b**[c] | 2.0 | 64 (2.4:1) **2a** | 11 **3a** |
| 5 | | 4.0 | 73 (2.4:1) | 10 |
| 6 |  **1c**[c] | 2.0 | 62 (2.1:1) | 10 |
| 7 | | 4.0 | 69 (2.5:1) **2a** | 8 **3a** |
| 8 | | AIBN-TBTH[d] | No reaction | |
| 9 |  **1d** | 2.0 | 64 (nd[e]) **2b** | 11 **3b** |
| 10 | | 4.0 | 72 (nd[e]) | 10 |
| 11 |  **1e** | 2.0 | 61 (1.6:1) **2c** | 15 **3c** |
| 12 | | 4.0 | 69 (1.5:1) | 14 |
| 13 |  **1f** | 2.0 | 63 (nd[f]) **2d** | 20 **3d** |
| 14 | | 4.0 | 65 (nd[f]) | 14 |
| 15 |  **1g** | 2.0 | 72 (1.7:1) **2e** | |
| 16 | | 4.0 | 82 (1.7:1) | |

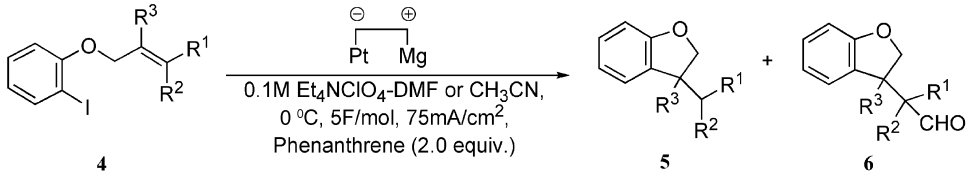
[a] Equivalents of mediator to substrate.
[b] Isolated yields. Diastereomer ratios were determined by $^1$H NMR.
[c] Reduction peak potentials of **1a**, **1b** and **1c** were −2.50, −2.96 and −3.18 V vs. Ag/Ag$^+$, respectively.
[d] Reaction of **1a** or **1c** (0.5 mmol) was carried out in toluene (25 ml) under reflux by using 0.2 equiv. of AIBN and 1.1 equiv. of tributyltin hydride.
[e] Four diastereomers were obtained. The ratios were not determined.
[f] Two diastereomers were obtained. The ratios were estimated to be of 5.8:1 (entry 13) and 5.0:1 (entry 14), respectively, by $^1$H NMR spectra.

using the electrochemical method and, therefore, this reaction was applied to a synthesis of benzofuran. Similar electrochemical reduction of allyl *o*-iodophenyl ethers using phenanthrene mediator gave the corresponding 2,3-dihydrobenzofurans **5a**–**d** and **6a**–**c**. The results are summarized in Table 4. The products carrying formyl group (**6a**–**c**) were also obtained in 20–27%, when DMF was used as a solvent. The use of acetonitrile as a solvent in the electrochemical cyclization of **4c** prevented the introduction of a formyl group and a cyclized product **5c** was obtained as a sole product in 72% yield (Table 4, entry 4). Similarly, electrolysis of **4d** and **4e** in acetonitrile solvent gave the cyclized products **5d** and **5e** in 64 and 69% yield, respectively, without a formation of the corresponding formylated products.

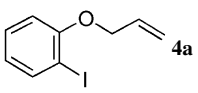
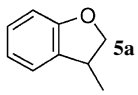
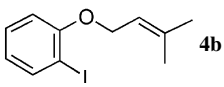
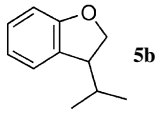
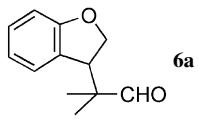
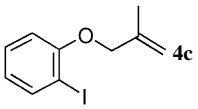
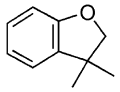
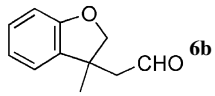
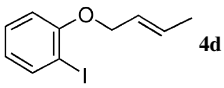
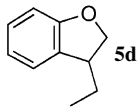
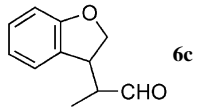
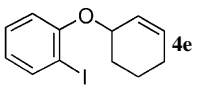
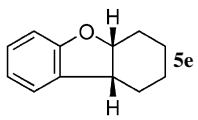
## 2.4. Synthesis of substituted 2,3-dihydroindoles

The results described above suggested that the electrolysis in acetonitrile gave the desired cyclization products in higher yields than those in DMF. Therefore, the following electrolyses were carried out in acetonitrile. Electrolysis of *N*-methyl-2-iodoanilines carrying various *N*-allyl substituents (**7a**–**e**) gave the corresponding substituted

**Table 4**. Synthesis of substituted 2,3-dihydrobenzofurans




**4** **5** **6**

| Entry | Solvent | Substrate | Product and yield (%)[a] | | |
|---|---|---|---|---|---|
| 1 | DMF |  **4a** |  **5a** | 41 | |
| 2 | DMF |  **4b** |  **5b** | 53 |  **6a** 27 |
| 3 | DMF |  **4c** |  **5c** | 59 |  **6b** 20 |
| 4 | AN | | | 72 | 0 |
| 5 | DMF |  **4d** |  **5d** | 54 |  **6c** 25 |
| 6 | AN | | | 64 | 0 |
| 7 | AN |  **4e** |  **5e** | 69 | |

[a] Isolated yields.

2,3-dihydroindoles (**8a**–**8e**) in 48–73% yields (Table 5). It is noteworthy that the electrolysis of **7e** provided the cyclized product **8e** in 73% yield, although the electrolysis of similar substrate, *N*-cinnamyl-2-chloroacetanilide, using (*E*)-stilbene as a mediator was reported to give a low yield of the cyclization product along with a larger amount of decomposed product, 2-chloroacetanilide.[7]

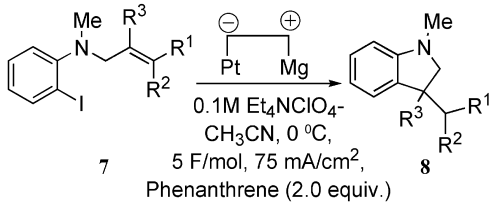
## 2.5. Regioselective radical cyclization

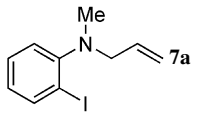
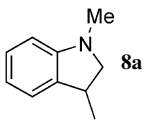
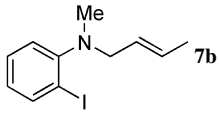
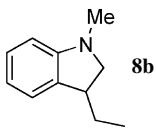
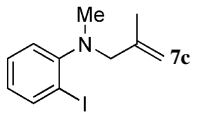
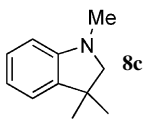
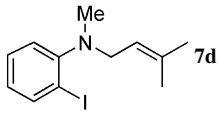
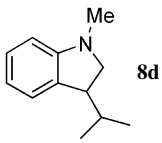
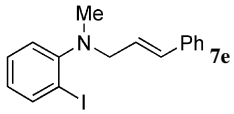
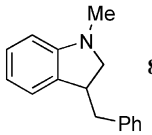
Regioselectivity of the present electrochemical cyclization is interesting from a synthetic viewpoint. In carbon radical cyclizations, 6-*endo* cyclization preferentially occurs to give a six-membered ring when there are any substituents at the C-5 position of 5-hexenyl radical.[11] Conventional radical cyclization of **1h** using AIBN-$Bu_3SnH$ in refluxing toluene gave 5-*exo* (**2f**) and 6-*endo* cyclization products (**9a**) in a ratio of 45:55 (Table 6, entry 3). It has been reported that the ratio in the 5-*exo*/6-*endo* cyclization varied depending on the reaction conditions.[12] Effect of the reaction temperature was examined by the use of benzene as a solvent, **2f** and **9a** were obtained in the ratio of 48:52 (Table 6, entry 4). Effect of the concentration of $Bu_3SnH$ was also examined (Table 6, entries 3, 5 and 6). These results show that the ratio of 5-*exo*/6-*endo* was slightly affected by the reaction temperature and the concentration of $Bu_3SnH$. When the radical cyclizaions of **4c** or **7c** using AIBN-$Bu_3SnH$ was carried out, the corresponding 6-*endo* cyclization products (**9b** or **9c**) was also obtained (entries 5 and 7). However, the electrochemical cyclization of **1h** preferentially gave 5-*exo* cyclization product **2f** (entry 1). Similar electrochemical cyclization of 2-methallyloxyphenyl iodide (**4c**) and 2-iodo-*N*-methallyl-*N*-methylaniline (**7c**) gave exclusively 5-*exo* cyclization product **5c** and **8c**, respectively (entries 4 and 6). 5-*exo* Cyclized product **5c** was also obtained in the Ni-catalyzed electrochemical cyclization that was carried out at 20 °C.[6e,f] These higher regioselectivity are probably due to a lower reaction temperature in the present electrochemical radical cyclizations. Effect of the reaction temperature on a ratio of 5-*exo*/6-*endo* in the radical cyclization reaction has been reported by Walling et al.[13] In the present electrochemical radical cyclization, the electrolysis at higher temperature resulted in an increase of 6-*endo* cyclization although a total yield of two products was decreased (Table 6, entry 2).

## 2.6. Reaction pathways

One of the speculated reaction pathways are shown in Scheme 2. It has already been reported that the radical anion generated by electrochemical reduction of arene mediator can reduce aryl halides to give the corresponding aryl radicals or aryl anion.[14] In the present electrochemical reaction, aryl radicals **A** are also generated by a one-electron reduction of aryl halides with phenanthrene radical anions. This is supported by the result that a dark-blue color of the phenanthrene radical anion appeared on the surface of the platinum cathode. Two-electron reduction of aryl halides occurs preferentially in the absence of arene mediator to give the corresponding aryl anions which are protonated to

**Table 5**. Synthesis of substituted 2,3-dihydroindoles




| Entry | Substrate | Product and yield (%)[a] |
|---|---|---|
| 1 |  |  60 |
| 2 |  |  62 |
| 3 |  |  51 |
| 4 |  |  48 |
| 5 |  |  73 |

[a] Isolated yields.

afford simple reduction products **3** (Table 2, entry 1). Dissolution of an Mg anode prevents a reoxidation of the radical anion. 5-*exo* Cyclization of **A** to give cyclized radical **B** proceeds faster than a further reduction of the aryl radicals. Carbon radicals **B** resulted from the radical cyclization are reduced to give anionic intermediates **C** that finally afford 1-indanol, 2,3-dihydrobenzofuran or 2,3-dihydroindole derivatives. Formylated products **6a–c** are obtained by an attack of the anionic intermediates **C** to DMF molecules (Table 2, entries 2, 3, 5). No formylated product was obtained in the electrolysis of **1a–h** even when DMF was used as a solvent (Table 3 and Table 6, entry 1). This is probably due to a ready protonation of anionic intermediates **C** with a hydroxy group in the starting substrates **1a–h**.

## 3. Conclusion

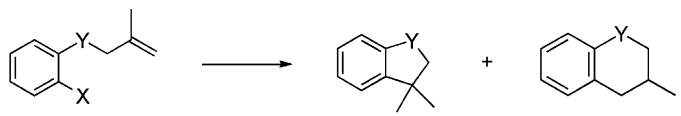
In conclusion, electrochemical reduction of halobenzenes carrying *o*-(1-hydroxy-3-butenyl), *o*-allyloxy or *o*-allylamino group in the presence of phenanthrene mediator generated the corresponding aryl radicals efficiently and gave various 5-*exo* cyclized products, substituted 1-indanols, 2,3-dihydrobenzofurans or 2,3-dihydroindoles, in moderate to good yields. Higher regio- and stereoselectivities than those of usual radical cyclizations using AIBN-$Bu_3SnH$ were observed in the present electrochemical radical cyclization. Exclusive 5-*exo* cyclization proceeded to give substituted 1-indanols, 2,3-dihydrobenzofurans and 2,3-dihydroindoles.

## 4. Experimental

### 4.1. General procedures

The NMR spectra were recorded on a JEOL JNM-EX270 ($^1$H, 270 MHz; $^{13}$C, 67.8 MHz) FT NMR spectrometer. $^1$H and $^{13}$C Chemical shifts were represented as $\delta$-values relative to the internal standard, tetramethylsilane. IR spectra were recorded on a JASCO IR-810 infrared spectrometer. High and low resolution mass spectra were determined with a JEOL JMS-AX500 or JEOL JMS-SX102A spectrometer. Cyclic voltammetry was carried out with BAS-50W using Pt disc electrode (1 mm ∅ as a

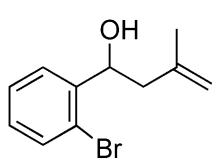
**Table 6**. Regioselectivity in the electrochemical and the conventional radical cyclizations



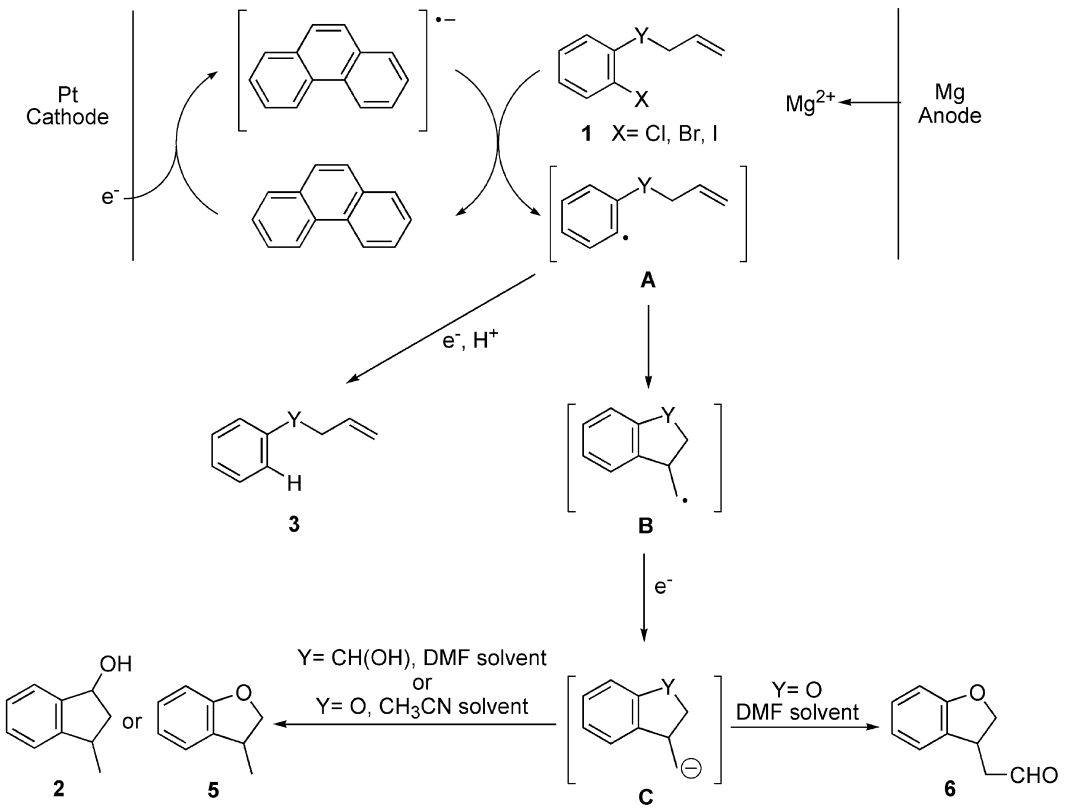

**1h** X=Br,Y=CH(OH)
**4c** X=I,Y=O
**7c** X=I, Y=$NCH_3$

**2f, 5c, 8c**
5-*exo* cyclized product

**9a-c**
6-*endo* cyclized product

| Entry | Substrate | Conditions | Yield (%)[a] | Product | Ratio (5-*exo*/6-*endo*)[b] |
|---|---|---|---|---|---|
| 1 |  | Electrolysis at 0 °C | 68 | | 78/22 |
| 2 | | Electrolysis at 100 °C | 27 | | 64/36 |
| 3 | | AIBN-TBTH (0.022 M), toluene, reflux | 71 | **2f/9a** | 45/55 |
| 4 | | AIBN-TBTH (0.022 M), benzene, reflux | 76 | | 48/52 |
| 5 | | AIBN-TBTN (0.05 M), toluene, reflux | 63 | | 52/48 |
| 6 | | AIBN-TBTH (0.5 M), toluene, reflux | 33 | | 55/45 |
| 7 | **4c** | Electrolysis at 0 °C | 79 | **5c/9b** | 100/0 |
| 8 | | AIBN-TBTH (0.022 M), toluene, reflux | 56 | | 82/18 |
| 9 | **7c** | Electrolysis at 0 °C | 51 | **8c/9c** | 100/0 |
| 10 | | AIBN-TBTH (0.022 M), toluene, reflux | 68 | | 51/49 |

[a] Isolated yields.
[b] Ratios of regioisomers were determined by $^1$H NMR.




**Scheme 2.**

working electrode and Pt wire as a counter electrode in 0.1 M $Et_4NClO_4$-DMF solution ($Ag/Ag^+$ reference electrode). Thin-layer chromatography and column chromatography were carried out on a Merck Silica gel 60 $PF_{254}$. Anhydrous *N*,*N*-dimethylformamide (DMF) and tetraethylammonium perchlorate (TEAP) were commercially available and were used without further purification. Acetonitrile was freshly distilled under nitrogen from $P_2O_5$. Metal plates for electrodes are commercially available in more than 99.9% purities, and they were washed with 2 N HCl, methanol, and acetone and dried before electrolysis.

### 4.2. Preparation of 1-(2-halophenyl)-3-buten-1-ols

1-(2-Halophenyl)-3-buten-1-ol derivatives (**1a**–**h**) were prepared by allylation of 2-halobenzaldehydes with the corresponding substituted allyl bromides using electrochemically generated reactive zinc (EGZn).[15]

**4.2.1. 2-Iodobenzaldehyde.** To a solution of pyridinium chlorochromate (9.7 g, 45.0 mmol), silica gel (20 g) and $CH_2Cl_2$ (120 ml) were added 2-iodobenzyl alcohol (7.03 g, 30.0 mmol). The solution was stirred at room temperature for 4 h. The reaction mixture was filtrated and evaporated. The residue was extracted with $Et_2O$. The combined organic layers were washed with water and brine, dried over $MgSO_4$. Concentration gave 6.80 g of the crude product, which was purified by recrystallization from hexane to give 5.91 g (85%) of 2-iodobenzaldehyde.

Mp 34 °C; IR (nujol) 2922, 1689, 1460, 1202, 1016 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 10.07 (1H, S), 7.96 (1H, d, $J$=7.9 Hz), 7.88 (1H, dd, $J$=1.7, 7.9 Hz), 7.47 (1H, t, $J$=7.9 Hz), 7.29 (1H, t, $J$=7.9 Hz); EIMS *m*/*z* (relative intensity) 248 (100), 231 (62), 203 (18), 76 (29), 65 (25). Anal. calcd for $C_7H_5IO$: C, 36.24; H, 2.17. Found: C, 36.12; H, 2.20.

**4.2.2. 1-(2-Iodophenyl)-3-buten-1-ol (1a).** Mp 42 °C; IR (nujol) 3368, 1640, 1462, 1436, 1011 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.80 (1H, dd, $J$=1.3, 7.6 Hz), 7.52 (1H, dd, $J$=1.3, 7.6 Hz), 7.37 (1H, dt, $J$=1.3, 7.6 Hz), 6.97 (1H, dt, $J$=1.3, 7.6 Hz), 5.90 (1H, m), 5.21 (2H, m), 4.93 (1H, dt, $J$=3.3, 8.9 Hz), 2.62 (1H, m), 2.27 (2H, m). Anal. calcd for $C_{10}H_{11}OI$: C, 43.82; H, 4.04; I, 46.30. Found: C, 43.90; H, 4.05; I, 46.57.

**4.2.3. 1-(2-Bromophenyl)-3-buten-1-ol (1b).** Bp 68 °C/0.5 mm Hg; IR (neat) 3372, 1640, 1568, 1467, 1439, 1023 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.55 (2H, m), 7.34 (1H, dt, $J$=1.7, 6.9 Hz), 7.13 (1H, dt, $J$=1.7, 6.9 Hz), 5.89 (1H, m), 5.16 (3H, m), 2.65 (1H, m), 2.36 (1H, m), 2.13 (1H, d, $J$=3.3 Hz); HRMS calcd for $C_{10}H_{10}BrO$ ($M^+-1$). *m*/*z* 224.9915. Found *m*/*z* 224.9924. Anal. calcd for $C_{10}H_{11}BrO$: C, 52.99; H, 4.88; Br, 35.18. Found: C, 52.74; H, 4.88; Br, 35.25.

**4.2.4. 1-(2-Chlorophenyl)-3-buten-1-ol (1c).** Bp 68 °C/0.27 mm Hg; IR (neat) 3376, 1641, 1474, 1439, 1033 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.57 (1H, dd, $J$=1.7, 7.6 Hz), 7.30 (2H, m), 7.20 (1H, dt, $J$=1.7, 7.6 Hz), 5.86 (1H, m), 5.18 (3H, m), 2.64 (1H, m), 2.38 (1H, m), 2.13 (1H, d, $J$=3.6 Hz). Anal. calcd for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07; Cl, 19.41. Found: C, 65.69; H, 6.19; Cl, 19.29.

**4.2.5. 1-(2-Bromophenyl)-2-methyl-3-buten-1-ol (1d).** Bp 80 °C/0.2 mm Hg; IR (neat) 3410, 1641, 1568, 1468, 1440, 1012 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.45 (2H, m), 7.33 (1H, dt, $J$=1.3, 7.6 Hz), 7.13 (1H, m), 5.90 (1H, m), 5.20–4.91 (3H, m), 2.78–2.59 (1H, m), 2.14 (*syn*, 1H, d, $J$=3.6 Hz), 1.94 (*anti*, 1H, d, $J$=3.6 Hz), 1.05 (*syn*, 3H, d, $J$=6.9 Hz), 0.98 (*anti*, 3H, d, $J$=6.9 Hz); EIMS *m/z* (relative intensity) 242 ([M+2], 3), 187 (90), 185 (100), 159 (17), 157 (21), 105 (10), 77 (53). Anal. calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 54.67; H, 5.46; Br, 33.17.

**4.2.6. 1-(2-Bromophenyl)-2,2-dimethyl-3-buten-1-ol (1e).** IR (neat) 3432, 1638, 1468, 1434, 1017 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.52 (1H, dd, $J$=1.3, 7.9 Hz), 7.48 (1H, dd, $J$=1.3, 7.9 Hz), 7.30 (1H, dt, $J$=1.3, 7.9 Hz), 7.12 (1H, dt, $J$=1.3, 7.9 Hz), 6.03 (1H, dd, $J$=10.9, 17.5 Hz), 5.15–5.05 (3H, m), 2.01 (1H, d, $J$=3.3 Hz), 1.27 (3H, s), 1.04 (3H, s); HRMS calcd for $C_{12}H_{15}BrO$ *m/z* 254.0306. Found *m/z* 254.0321. Anal. calcd for $C_{12}H_{15}BrO$: C, 56.49; H, 5.93; Br, 31.32. Found: C, 56.56; H, 6.00; Br, 31.15.

**4.2.7. 2-Bromo-α-(2-cyclohexenyl)benzyl alcohol (1f).** Mixture of diastereomers. IR (neat) 3404, 1650, 1469, 1437, 1017 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.54 (2H, m), 7.33 (1H, dt, $J$=1.3, 7.3 Hz), 7.13 (1H, dt, $J$=1.3, 7.3 Hz), 5.94 (1H, m), 5.67 (0.15H, dd, $J$=1.7, 9.9 Hz), 5.52 (0.85H, dd, $J$=1.7, 9.9 Hz), 5.06 (0.85H, m), 4.92 (0.15H, m), 2.68 (1H, m), 2.03 (1H, m), 1.92 (1H, d, $J$=2.3 Hz), 1.78 (1H, m), 1.60–1.44 (3H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 142.4, 141.4, 132.8, 132.6, 131.2, 130.4, 128.7 (two signals), 128.5, 128.1, 128.0, 127.4, 127.3, 125.4, 122.4, 122.3, 75.8, 75.3, 41.3, 40.8, 26.5, 25.2 (two signals), 22.7, 21.8, 21.3; HRMS calcd for $C_{13}H_{15}BrO$ *m/z* 266.0306. Found *m/z* 266.0306. Anal. calcd for $C_{13}H_{15}BrO$: C, 58.44; H, 5.66; Br, 29.91. Found: C, 58.61; H, 5.76; Br, 29.82.

**4.2.8. Ethyl 5-(2-iodophenyl)-5-hydroxy-2-pentenoate (1g).** IR (neat) 3450, 1700, 1655, 1269, 1043 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.81 (1H, dd, $J$=1.7, 7.9 Hz), 7.54 (1H, dd, $J$=1.7, 7.9 Hz), 7.39 (1H, dt, $J$=1.7, 7.9 Hz), 7.05 (1H, d, $J$=15.8 Hz), 6.99 (1H, td, $J$=1.7, 7.9 Hz), 5.97 (1H, d, $J$=15.8 Hz), 5.03 (1H, dt, $J$=3.6, 8.6 Hz), 4.29 (2H, q, $J$=7.3 Hz), 2.70 (1H, m), 2.49 (1H, m), 2.13 (1H, d, $J$=3.6 Hz), 1.30 (3H, t, $J$=7.3 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 166.3, 145.1, 144.5, 139.4, 129.5, 128.7, 126.8, 124.2, 97.2, 76.1, 60.3, 40.3, 14.2; HRMS calcd for $C_{13}H_{15}IO$ *m/z* 346.0066. Found *m/z* 346.0062. Anal. calcd for $C_{13}H_{15}IO$: C, 45.11; H, 4.37; I, 36.66. Found: C, 45.16; H, 4.27; I, 36.88.

**4.2.9. 1-(2-Bromophenyl)-3-methyl-3-buten-1-ol (1h).** IR (neat) 3388, 1648, 1441, 1024 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.62 (1H, dd, $J$=1.7, 7.9 Hz), 7.52 (1H, dd, $J$=1.7, 7.9 Hz), 7.34 (1H, td, $J$=1.7, 7.9 Hz), 7.13 (1H, td, $J$=1.7, 7.9 Hz), 5.16 (1H, dt, $J$=2.6, 9.9 Hz), 4.96 (1H, m), 4.91 (1H, s), 2.60 (1H, dd, $J$=1.3, 13.9 Hz), 2.22 (1H, d, $J$=1.32 Hz), 2.20 (1H, dd, $J$=9.9, 13.9 Hz), 1.88 (3H, s); HRMS calcd for $C_{11}H_{13}BrO$ *m/z* 240.0149. Found *m/z* 240.0150. Anal. calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 54.82; H, 5.43; Br, 33.29.

### 4.3. Typical procedure for preparation of allyl aryl ethers

Alk-2-enyl *o*-iodophenyl ethers (**4a–e**) were prepared according to literature.[16] To a solution of 2-iodophenol (4 mmol), anhydrous potassium carbonate (8 mmol) and DMF (10 ml) was added allyl bromide (6 mmol) at room temperature. The solution was stirred for 4 h at 70 °C. The reaction mixture was filtrated and extracted with $Et_2O$. The combined ether extracts were washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column or distillation.

**4.3.1. Allyl *o*-iodophenyl ether (4a).** IR (neat) 1582, 1472, 1276, 1248, 1018, 996 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.78 (1H, dd, $J$=1.3, 7.9 Hz), 7.28 (1H, dt, $J$=1.3, 7.9 Hz), 6.81 (1H, dd, $J$=1.3, 7.9 Hz), 6.71 (1H, dt, $J$=1.3, 7.9 Hz), 6.10 (1H, m), 5.52 (1H, d, $J$=1.7 Hz), 5.31 (1H, d, $J$=1.7 Hz), 4.60 (2H, dt, $J$=1.7, 4.6 Hz); EIMS *m/z* (relative intensity) 260 (6), 133 (15), 105 (18), 92 (13), 77 (7), 63 (21), 50 (8), 41 (100), 39 (36); HRMS calcd for $C_9H_9IO$ *m/z* 259.9698. Found *m/z* 259.9678.

**4.3.2. Prenyl *o*-iodophenyl ether (4b).**[16] IR (neat) 1677, 1471, 1241, 1017 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.77 (1H, dd, $J$=1.3, 7.9 Hz), 7.27 (1H, m), 6.81 (1H, dd, $J$=1.3, 7.9 Hz), 6.69 (1H, td, $J$=1.3, 7.9 Hz), 5.50 (1H, m), 4.58 (2H, d, $J$=6.6 Hz), 1.79 (3H, s), 1.74 (3H, s).

**4.3.3. Methallyl *o*-iodophenyl ether (4c).**[17] IR (neat) 1660, 1583, 1245, 1018 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.92 (1H, dd, $J$=1.7, 7.9 Hz), 7.27 (1H, m), 6.80 (1H, dd, $J$=1.3, 8.3 Hz), 6.70 (1H, dt, $J$=1.3, 7.9 Hz), 5.19 (1H, d, $J$=0.7 Hz), 5.02 (1H, t, $J$=1.3 Hz), 4.48 (2H, s), 1.87 (3H, d, $J$=0.7 Hz).

**4.3.4. Crotyl *o*-iodophenyl ether (4d).** *E* and *Z* mixture.[16] IR (neat) 1676, 1582, 1471, 1244, 1017 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.77 (1H, dd, $J$=1.7, 7.9 Hz, *E* and *Z*), 7.31–7.24 (1H, m, *E* and *Z*), 6.81 (1H, dd, $J$=1.7, 7.9 Hz, *E* and *Z*), 6.69 (1H, dt, $J$=1.7, 7.9 Hz, *E* and *Z*), 5.98–5.68 (1H, m, *E* and *Z*), 4.66 (1H, d, $J$=4.3 Hz, *Z*), 4.52 (1H, d, $J$=5.6 Hz, *E*), 1.87 (3H, d, $J$=1.7 Hz, *Z*), 1.32 (3H, d, $J$=1.7 Hz, *E*).

**4.3.5. Cyclohex-2-enyl *o*-iodophenyl ether (4e).** IR (neat) 1649, 1580, 1468, 1241 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.77 (1H, dd, $J$=1.7, 7.9 Hz), 7.25 (1H, m), 6.88 (1H, dd, $J$=1.0, 8.3 Hz), 6.69 (1H, dt, $J$=1.7, 7.9 Hz), 6.02–5.95 (1H, m), 5.93–5.87 (1H, m), 4.78 (1H, m), 2.24–2.03 (2H, m), 2.02–1.85 (3H, m), 1.74–1.60 (1H, m); EIMS *m/z* (relative intensity) 300 (5), 220 (11), 81 (58) 80 (100); HRMS calcd for $C_{12}H_{13}IO$ *m/z* 300.0011. Found *m/z* 300.0009. Anal. calcd for $C_{12}H_{13}IO$: C, 48.02; H, 4.37; I, 42.28. Found: C, 48.19; H, 4.39; I, 42.32.

### 4.4. Preparation of *N*-alk-2-enyl-*N*-methyl-2-iodoanilines (7a–7e)

*N*-Alk-2-enyl-*N*-methyl-2-iodoanilines (**7a–e**) were prepared by *N*-allylation of *N*-methyl-2-iodoaniline or *N*-methylation of *N*-allyl-2-iodoaniline.[18,19]

**4.4.1. *N*-Methyl-2-iodoaniline.**[18] Bp 68–72 °C/0.6 mm Hg; IR (neat) 3400, 1515, 1316 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.65

(1H, dd, *J*=1.3, 7.6 Hz), 7.23 (1H, dt, *J*=1.3, 7.6 Hz), 6.55 (1H, dd, *J*=1.3, 7.6 Hz), 6.44 (1H, dt, *J*=1.3, 7.6 Hz), 4.19 (1H, br), 2.88 (3H, d, *J*=5.0 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 148.14, 138.85, 129.45, 118.46, 109.97, 85.10, 30.96; EIMS *m/z* (relative intensity) 233 (100), 232 (37), 105 (23), 77 (22); HRMS calcd for $C_7H_8NI$ *m/z* 232.9702. Found *m/z* 232.9704.

**4.4.2. *N*-Allyl-*N*-methyl-2-iodoaniline (7a).**[20] Bp 90 °C/1.0 mm Hg; IR (neat) 1643, 1580, 1470, 1348 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.85 (1H, dd, *J*=1.3, 7.6 Hz), 7.30 (1H, dt, *J*=1.3, 7.6 Hz), 7.06 (1H, dd, *J*=1.3, 7.6 Hz), 6.77 (1H, dt, *J*=1.3, 7.6 Hz), 5.88–6.03 (1H, m), 5.15–5.29 (2H, m), 3.55 (2H, d, *J*=6.3 Hz), 2.69 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 153.94, 140.07, 135.27, 128.84, 125.14, 121.82, 117.75, 98.26, 60.22, 41.03; EIMS *m/z* (relative intensity) 273 (49), 252 (37), 246 (33), 146 (100), 144 (36), 132 (34), 131 (32), 91 (32), 77 (34), 44 (38); HRMS calcd for $C_{10}H_{12}NI$ *m/z* 273.0015. Found *m/z* 273.0026.

**4.4.3. *N*-Crotyl-*N*-methyl-2-iodoaniline (7b).** Mixture of *E* and *Z* isomers (4.3:1). IR (neat) 1672, 1357 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.85 (1H, dd, *J*=1.3, 7.6 Hz), 7.30 (1H, dt, *J*=1.3, 7.6 Hz), 7.06 (1H, dd, *J*=1.3, 7.6 Hz), 6.77 (1H., dt, *J*=1.3, 7.6, Hz), 5.72–5.54 (m, 2H), 3.60 (minor, 1H, dd, *J*=0.7, 5.6 Hz), 3.46 (major, 1H, dd, *J*=0.7, 5.4 Hz), 2.70 (minor, 3H, s), 2.67 (major, 3H, s), 1.72 (major, 3H, dd, *J*=0.7, 5.4 Hz), 1.64 (minor, 3H, dd, *J*=0.7, 5.6 Hz); $^{13}$C NMR ($CDCl_3$) (major isomer) $\delta$ 154.16, 140.04, 128.81, 127.92, 127.08, 124.96, 121.74, 98.24, 59.60, 40.68, 17.79 (minor isomer) $\delta$ 153.94, 140.04, 128.97, 127.92, 127.19, 125.07, 121.82, 98.24, 53.41, 41.10, 13.12; EIMS *m/z* (relative intensity) 287 (42), 273 (32), 160 (100), 144 (71), 132 (67), 104 (20), 77 (22); HRMS calcd for $C_{11}H_{14}NI$ *m/z* 287.0171. Found *m/z* 287.0164. Anal. calcd for $C_{11}H_{14}NI$: C, 46.01; H, 4.91; N, 4.88; I, 44.20. Found: C, 46.19; H, 4.87; N, 4.89, I, 44.37.

**4.4.4. *N*-Methallyl-*N*-methyl-2-iodoaniline (7c).** IR (neat) 1655, 1579, 1470, 1372 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.85 (1H, dd, *J*=1.6, 7.6 Hz), 7.30 (1H, dt, *J*=1.6, 7.6 Hz), 7.09 (1H, dd, *J*=1.6, 7.6 Hz), 6.78 (1H, dt, *J*=1.6, 7.6 Hz), 5.00 (1H, d, *J*=0.7 Hz), 4.9 (1H, d, *J*=0.7 Hz), 3.48 (2H, s), 2.61 (3H, s), 1.82 (3H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 154.50, 142.75, 140.00, 128.95, 125.32, 122.10, 113.30, 98.65, 63.02, 42.18, 20.74; EIMS *m/z* (relative intensity) 287 (48), 246 (100), 160 (88), 144 (26), 118 (25); HRMS calcd for $C_{12}H_{16}NI$ *m/z* 287.0171. Found *m/z* 287.0170.

**4.4.5. *N*-Methyl-*N*-prenyl-2-iodoaniline (7d).** IR (neat) 1671, 1580, 1469, 1359 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.85 (1H, dd, *J*=1.3, 7.6 Hz), 7.30 (1H, dt, *J*=1.3, 7.6 Hz), 7.06 (1H, dd, *J*=1.3, 7.6 Hz), 6.76 (1H, dt, *J*=1.3, 7.6 Hz), 5.34 (1H, m), 3.52 (1H, d, *J*=6.9 Hz), 2.68 (3H, s), 1.74 (3H, d, *J*=1.3 Hz), 1.64 (3H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 154.16, 140.03, 135.34, 128.77, 124.94, 121.74, 121.27, 98.33, 54.88, 40.86, 25.86, 18.02; EIMS *m/z* (relative intensity) 301 (32), 286 (22), 233 (15), 175 (14), 174 (100), 132 (49); HRMS calcd for $C_{12}H_{16}NI$ *m/z* 301.0327. Found *m/z* 301.0323.

**4.4.6. *N*-Cinnamyl-*N*-methyl-2-iodoaniline (7e).** IR (neat) 1650, 1598, 1580, 1469, 1360, 1337 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.87 (1H, dd, *J*=1.3, 7.6 Hz), 7.42–7.20 (6H, m), 7.10 (1H, dd, *J*=1.3, 7.6 Hz), 6.78 (1H, dt, *J*=1.3, 7.6 Hz), 6.60 (1H, d, *J*=15.8 Hz), 6.35 (1H, dt, *J*=6.3, 15.8 Hz), 3.70 (2H, d, *J*=6.3 Hz), 2.74 (3H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 153.96, 140.13, 137.00, 132.78, 128.91, 128.52 (two signals), 127.44, 126.97, 126.36 (two signals), 125.19, 121.82, 98.22, 59.79, 41.03; EIMS *m/z* (relative intensity) 349 (10), 233 (13), 222 (100), 144 (28), 132 (56), 117 (65), 115 (29), 91 (50), 77 (16); HRMS calcd for $C_{16}H_{16}NI$ *m/z* 349.0328. Found *m/z* 349.0326.

## 4.5. Typical procedure for electrochemical radical cyclization. Cyclization of 1a

A mixture of **1a** (0.5 mmol) and phenanthrene (1 mmol) in 0.1 M $Et_4NClO_4$-DMF (10 ml) was electrolyzed at 0 °C with a Pt cathode and an Mg anode under nitrogen atmosphere. Electrolysis was carried out at 75 mA/cm$^2$, and an electricity of 5 F/mol of substrate was passed. The reaction mixture was quenched with 2 N HCl and diluted with water, and extracted with $Et_2O$. The combined ether extracts were washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by TLC.

**4.5.1. 3-Methylindan-1-ol (2a).** Mixture of *syn* and *anti* diastereomers.[10] IR (neat) 3316, 1609, 1477, 1459, 1330, 1088, 1057 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.31 (4H, m), 5.24 (*anti*, 1H, m), 5.18 (*syn*, 1H, m), 3.45 (*syn*, 1H, sextet, *J*=6.9 Hz), 3.05 (*syn*, 1H, sextet, *J*=6.9 Hz), 2.77 (*syn*, 1H, dt, *J*=6.9, 12.9 Hz), 2.26 (*anti*, 1H, m), 1.97 (*anti*, 1H, dt, *J*=6.9, 12.9 Hz), 1.82 (*syn*, 1H, br), 1.63 (*anti*, 1H, br), 1.44 (*anti*, 1H, m), 1.36 (*anti*, 3H, d, *J*=6.9 Hz), 1.27 (*syn*, 3H, d, *J*=6.9 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 148.63, 147.33, 145.00, 144.28, 128.72, 128.10, 126.83, 126.74, 124.40, 123.76, 123.61, 123.31, 75.13, 45.70, 44.71, 36.66, 36.25, 20.25, 20.15; EIMS *m/z* (relative intensity) 148 (81), 147 (100), 133 (50), 131 (27), 130 (87), 129 (84), 128 (36), 127 (16), 116 (11), 115 (64), 105 (34), 103 (12), 91 (28), 79 (12), 77 (22), 64 (10), 51 (14); HRMS calcd for $C_{10}H_{12}O$ *m/z* 148.0888. Found *m/z* 148.0880.

**4.5.2. 2,3-Dimethylindan-1-ol (2b).** Mixture of diastereoisomers. IR (neat) 3350, 1477, 1459, 1050 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.30 (4H, m), 5.05 (1H, d, *J*=6.6 Hz), 4.94 (1H, d, *J*=5.6 Hz), 4.79 (1H, d, *J*=6.3 Hz), 4.68 (1H, d, *J*=6.3 Hz), 3.32–2.54 (1H, m), 2.34–1.80 (2H, m), 1.34–0.92 (6H, m); EIMS *m/z* (relative intensity) 162 (39), 161 (28), 147 (21), 144 (65), 143 (28), 133 (12), 129 (100), 128 (41), 127 (13), 119 (10), 115 (16), 105 (18), 91 (18), 77 (14); HRMS calcd for $C_{11}H_{14}O$ *m/z* 162.1045. Found *m/z* 162.1048.

**4.5.3. 2,2,3-Trimethylindan-1-ol (*syn*-2c).** Configuration of **2c** was determined by comparison of $^1$H NMR and DIFNOE spectra of two isomers. IR (neat) 3258, 1058 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.36–7.13 (4H, m), 4.72 (1H, s), 2.72 (1H, q, *J*=6.9 Hz), 1.7 (1H, s), 1.22 (3H, s), 1.21 (3H, d, *J*=6.9 Hz), 1.11 (3H, s), 0.68 (3H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 145.3, 143.7, 127.7, 126.6, 123.0, 129.9, 83.4, 49.6, 45.8, 24.6, 14.6, 12.4; EIMS *m/z* (relative intensity) 176 (29), 158 (51), 143 (100), 133 (69), 128 (38), 115 (25),

105 (31) 91 (27), 77 (20); HRMS calcd for $C_{12}H_{16}O$ *m/z* 176.1201. Found *m/z* 176.1210.

**4.5.4. 2,2,3-Trimethylindan-1-ol (*anti*-2c).** IR (neat) 3268, 1056 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.39–7.15 (4H, m), 4.60 (1H, s), 3.02 (1H, q, *J*=7.3 Hz), 1.51 (1H, s), 1.16 (3H, d, *J*=7.3 Hz), 1.12 (3H, s), 0.87 (3H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 147.7, 143.5, 128.5, 126.6, 124.7, 123.9, 82.9, 46.4, 46.0, 21.6, 21.2, 13.3; EIMS *m/z* (relative intensity) 176 (28), 158 (48), 143 (100), 133 (60), 128 (38), 115 (23), 105 (25) 91 (23), 77 (16); HRMS calcd for $C_{12}H_{16}O$ *m/z* 176.1201. Found *m/z* 176.1209.

**4.5.5. 1,2,3,4,4a,9a-Hexahydrofluoren-9-ol (2d).** Mixture of two diasteromers. Analytical data of one isomer; IR (neat) 3336, 1450, 1052 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.41 (1H, dd, *J*=2.3, 5.9 Hz), 7.42–7.18 (4H, m), 5.15 (1H, d, *J*=5.6 Hz), 3.10 (1H, m), 2.61 (1H, m), 2.20 (1H, m), 1.83–1.48 (5H, m), 1.20 (2H, m), 0.94 (1H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 145.2, 142.8, 127.6, 126.4, 123.8, 122.7, 77.9, 46.1, 40.3, 25.6, 24.3, 21.9, 21.3; EIMS *m/z* (relative intensity) 188 (100), 170 (62), 145 (22), 142 (52), 141 (42), 129 (33), 120 (21), 115 (20), 105 (20), 91 (25); HRMS calcd for $C_{13}H_{16}O$ *m/z* 188.1201. Found *m/z* 188.1214.

Analytical data of another isomer; IR (neat) 3336, 1450, 1052 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.40 (1H, dd, *J*=2.3, 5.9 Hz), 7.27–7.16 (3H, m), 4.89 (1H, d, *J*=6.3 Hz), 3.19 (1H, q, *J*=6.3 Hz), 2.23 (1H, quint, *J*=6.3 Hz), 1.86 (2H, m), 1.60 (2H, m), 1.51–1.36 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 147.2, 144.3, 128.1, 126.5, 124.7, 123.4, 77.7, 49.2, 41.4, 29.5, 24.9, 23.6, 22.8; EIMS *m/z* (relative intensity) 188 (100), 187 (68), 170 (80), 145 (27), 142 (61), 141 (49), 129 (33), 120 (22), 115 (21), 91 (22); HRMS calcd for $C_{13}H_{16}O$ *m/z* 188.1201. Found *m/z* 188.1206.

**4.5.6. Ethyl (3-hydroxyindan-1-yl)acetate (*syn*-2e).** Configurations of **2e** was determined by the comparison of $^1H$ NMR and DIFNOE spectra of two isomers. IR (neat) 3362, 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.43 (1H, m), 7.30–7.19 (3H, m), 5.20 (1H, d, *J*=5.0 Hz), 4.16 (2H, q, *J*=7.3 Hz), 3.48 (1H, dt, *J*=7.6, 13.5 Hz), 2.92–2.77 (2H, m), 2.58 (1H, dd, *J*=8.6, 15.8 Hz), 2.15 (1H, br, s), 1.69 (1H, ddd, *J*=5.9, 7.3, 13.5 Hz), 1.26 (3H, t, *J*=7.3 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 172.6, 145.1, 144.6, 128.5, 127.5, 124.3, 123.6, 75.0, 60.6, 42.8, 40.3, 38.4, 14.3; EIMS *m/z* (relative intensity) 202 ($M-H_2O$, 29), 131 (27), 129 (49), 128 (100), 115 (20). Anal. calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.18; H, 7.26.

**4.5.7. Ethyl (3-hydroxyindan-1-yl)acetate (*anti*-2e).** IR (neat) 3424, 1736 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.42 (1H, m), 7.33–7.21 (3H, m), 5.28 (1H, dd, *J*=4.0, 6.3 Hz), 4.18 (2H, q, *J*=7.3 Hz), 3.83 (1H, quint, *J*=5.9 Hz), 2.73 (1H, dd, *J*=5.9, 15.2 Hz), 2.41 (1H, dd, *J*=8.9, 15.2 Hz), 2.31 (1H, ddd, *J*=4.0, 7.9, 13.9 Hz), 2.16 (1H, dt, *J*=6.3, 13.9 Hz) 1.73 (1H, br,s), 1.27 (3H, t, *J*=7.3 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 172.4, 145.4, 144.6, 128.8, 127.5, 124.6, 124.0, 74.9, 60.5, 42.6, 40.2, 38.8, 14.2; EIMS *m/z* (relative intensity) 220 (8), 202 (72), 146 (33), 132 (96), 128 (100), 115 (18); HRMS calcd for $C_{13}H_{16}O_3$ *m/z* 220.1099. Found *m/z* 220.1107.

**4.5.8. 3,3-Dimethylindan-1-ol (2f).** IR (neat) 3332, 1455, 1056 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.38 (1H, dd, *J*=1.3, 5.9 Hz), 7.35–7.18 (3H, m), 5.26 (1H, t, *J*=6.3 Hz), 2.38 (1H, dd, *J*=6.9, 12.9 Hz), 1.83 (1H, dd, *J*=6.3, 12.9 Hz), 1.80 (1H, br, s), 1.39 (3H, s), 1.22 (3H, s); EIMS *m/z* (relative intensity) 162 (38), 147 (100), 129 (56); HRMS calcd for $C_{11}H_{14}O$ *m/z* 162.1045. Found *m/z* 162.1062.

**4.5.9. 1-Phenyl-3-buten-1-ol (3a).**[21] IR (neat) 3398, 1642, 1494, 1455 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.37–7.23 (5H, m), 5.81 (1H, m), 5.19 (2H, m), 4.76 (1H, m), 2.51 (1H, m), 2.07 (1H, t, *J*=2.6 Hz).

**4.5.10. 2-Methyl-1-phenyl-3-buten-1-ol (3b).**[21] IR (neat) 3404, 1640, 1604, 1495, 1455, 1020, 914 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.37–7.22 (5H, m), 5.78 (1H, m), 5.19 (1H, m), 5.05 (1H, m), 4.60 (*anti*, 1H, m), 4.35 (*syn*, 1H, m), 2.54 (1H, m), 2.16 (*syn*, 1H, m), 1.96 (*anti*, 1H, m), 0.99 (*anti*, 3H, d, *J*=6.9 Hz), 0.87 (*syn*, 3H, d, *J*=6.9 Hz); EIMS *m/z* (relative intensity) 162 (1), 145 (9), 129 (17), 107 (100), 79 (83), 51 (10).

**4.5.11. 2,2-Dimethyl-1-phenyl-3-buten-1-ol (3c).**[21] IR (neat) 3452, 1730, 1639, 1495, 1026 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.34–7.28 (5H, m), 5.91 (1H, d, *J*=10.6 Hz), 5.13 (2H, m), 4.43 (1H, d, *J*=2.0 Hz), 2.00 (1H, d, *J*=2.0 Hz), 1.02 (3H, s), 0.96 (3H, s).

**4.5.12. α-(2-Cyclohexenyl)benzyl alcohol (3d).** IR (neat) 3384, 1690, 1465, 1018 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.35–7.23 (5H, m), 5.81 (1H, m), 5.38 (1H, dd, *J*=2.3, 9.9 Hz), 4.58 (1H, d, *J*=6.3 Hz), 2.49 (1H, m), 1.99 (2H, m), 1.85–1.66 (2H, m), 1.58–1.47 (2H, m); EIMS *m/z* (relative intensity) 107 (100) 79 (33); HRMS calcd for $C_{13}H_{16}O$ *m/z* 188.1201. Found *m/z* 188.1201.

**4.5.13. 2,3-Dihydro-3-methylbenzofuran (5a).** Bp 60 °C/5 mm Hg; IR (neat) 1598, 1482, 1463, 1450, 1228, 967 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.11 (2H, m), 6.85 (1H, dt, *J*=1.0, 7.9 Hz), 6.77 (1H, d, *J*=7.9 Hz), 4.66 (1H, dd, *J*=6.9, 15.8 Hz), 4.06 (1H, dd, *J*=6.9, 15.8 Hz), 3.54 (1H, sixt, *J*=6.9 Hz), 1.32 (3H, d, *J*=6.9 Hz); EIMS *m/z* (relative intensity) 134 (85), 119 (100), 91 (64); HRMS calcd for $C_9H_{10}O$ *m/z* 134.0732. Found *m/z* 134.0726. Anal. calcd for $C_9H_{10}O$: C, 80.56; H; 7.51. Found: C, 80.31; H, 7.54.

**4.5.14. 2,3-Dihydro-3-isopropylbenzofuran (5b).**[16] IR (neat) 1596, 1484, 1233 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.19–7.09 (2H, m), 6.84 (1H, dt, *J*=1.0, 7.3 Hz), 6.77 (1H, d, *J*=7.3 Hz), 4.51 (1H, t, *J*=8.9 Hz), 4.37 (1H, dd, *J*=5.3, 8.9 Hz), 3.34 (1H, dt, *J*=5.3, 8.9 Hz), 2.02–1.90 (1H, m), 0.95 (3H, d, *J*=6.93 Hz), 0.87 (3H, d, *J*=6.60 Hz).

**4.5.15. 2,3-Dihydro-3,3-dimethylbenzofuran (5c).**[22] IR (neat) 1600, 1480, 1191 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 7.15–7.09 (2H, m), 6.88 (1H, td, *J*=1.0, 7.6 Hz), 6.79 (1H, d, *J*=7.6 Hz), 4.23 (2H, s), 1.34 (6H, s).

**4.5.16. 3-Ethyl-2,3-dihydrobenzofuran (5d).**[23] IR (neat) 1597, 1482, 1229 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.19–7.09 (2H, m), 6.85 (1H, dt, *J*=1.0, 7.9 Hz), 6.79 (1H, d, *J*=7.9 Hz), 4.63 (1H, t, *J*=8.9 Hz), 4.21 (1H, dd, *J*=6.6, 8.9 Hz), 3.37 (1H, m), 1.86–1.73 (1H, m), 1.68–1.52 (1H, m), 0.97 (3H, t, *J*=7.6 Hz).

**4.5.17. 1,2,3,4,4a,9b-Hexahydrodibenzofuran (5e).** Configurations of **5e** was determined by DIFNOE spectrum. IR (neat) 1596, 1474, 1226 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.16–7.08 (2H, m), 6.87 (1H, dd, $J$=1.0, 7.6 Hz), 6.80 (1H, d, $J$=7.6 Hz), 4.67 (1H, dt, $J$=5.0, 7.3 Hz), 3.19 (1H, q, $J$=7.3 Hz), 2.04–1.75 (3H, m), 1.62–1.44 (4H, m), 1.42–1.26 (1H, m); EIMS $m/z$ (relative intensity) 174 (100), 159 (33), 145 (56), 131 (84), 120 (36), 91 (21); HRMS calcd for $C_{12}H_{14}O$ $m/z$ 174.1045. Found $m/z$ 174.1048. Anal. calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.50; H, 8.01.

**4.5.18. 2,3-Dihydro-3-(1-formyl-1-methylethyl)benzofuran (6a).** IR (neat) 1723, 1594, 1484, 1460, 1232 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.56 (1H, s), 7.15 (2H, m), 6.86 (1H, dd, $J$=1.0, 7.6 Hz), 6.80 (1H, m), 4.56 (1H, dd, $J$=4.0, 9.2 Hz), 4.38 (1H, dd, $J$=4.0, 9.2 Hz), 3.66 (1H, dd, $J$=4.0, 9.2 Hz), 1.12 (3H, s), 1.03 (3H, s); EIMS $m/z$ (relative intensity) 190 (17), 119 (100), 91 (78); HRMS calcd for $C_{12}H_{14}O_2$ $m/z$ 190.0994. Found $m/z$ 190.0986. Anal. calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.54; H, 7.42.

**4.5.19. 2,3-Dihydro-3-formylmethyl-3-methylbenzofuran (6b).**[24] IR (neat) 1722, 1598, 1481, 1460, 1243 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.70 (1H, dd, 1.7, 2.3 Hz), 7.16 (2H, m), 6.91 (1H, dt, $J$=1.0, 8.3 Hz), 6.81 (1H, d, $J$=8.3 Hz), 4.44 (1H, d, $J$=9.2 Hz), 4.35 (1H, d, $J$=9.2 Hz), 4.34 (1H, d, $J$=9.2 Hz), 2.85 (1H, dd, $J$=2.3, 16.8 Hz), 2.72 (1H, dd, $J$=1.7, 16.8 Hz), 1.46 (3H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 200.8, 159.0, 133.8, 128.7, 122.8, 120.9, 120.7, 110.1, 82.2, 53.5, 25.3; EIMS $m/z$ (relative intensity) 176 (66), 133 (100), 105 (53), 77 (26); HRMS calcd for $C_{11}H_{12}O_2$ $m/z$ 176.0837. Found $m/z$ 176.0835.

**4.5.20. 3-(1-Formylethyl)-2,3-dihydrobenzofuran (6c).** IR (neat) 1723, 1596, 1483, 1461, 1230, 1017 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.76 (0.4H, s), 9.72 (0.6H, s), 7.15 (2H, m), 6.93–6.79 (2H, m), 4.62 (1H, m), 4.30 (1H, m), 3.94 (0.4H, m), 3.83 (0.6H, m), 2.84 (0.4H, m), 2.70 (0.6H, quint, $J$=7.3 Hz), 1.14 (1.8H, d, $J$=7.3 Hz), 1.06 (1.2H, d, $J$=7.6 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 203.4, 160.4, 128.8, 126.9, 125.4, 120.5, 109.7, 75.0, 50.4, 41.9, 10.4; EIMS $m/z$ (relative intensity) 176 (35), 119 (100), 91 (98); HRMS calcd for $C_{11}H_{12}O_2$ $m/z$ 176.0837. Found $m/z$ 176.0843.

**4.5.21. 2,3-Dihydro-1,3-dimethylindole (8a).** IR (neat) 3048, 1610, 1492, 1462 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.08 (2H, m), 6.70 (1H, dt, $J$=0.7, 7.6 Hz), 6.49 (1H, dd, $J$=0.7, 7.6 Hz), 3.52 (1H, t, $J$=8.3 Hz), 3.27 (1H, m), 2.79 (1H, t, $J$=8.3 Hz), 2.74 (3H, s), 1.31 (3H, d, $J$=6.9 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 152.88, 135.31, 127.42, 122.91, 117.93, 107.35, 64.13, 36.23, 35.31, 18.22; EIMS $m/z$ (relative intensity) 147 (62), 146 (16), 143 (15), 132 (100), 131 (16), 117 (34); HRMS calcd for $C_{10}H_{13}N$ $m/z$ 147.1048. Found $m/z$ 147.1041.

**4.5.22. 3-Ethyl-2,3-dihydro-1-methylindole (8b).** IR (neat) 3046, 1609, 1492, 1461 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.07 (2H, m), 6.58 (1H, dt, $J$=0.7, 7.6 Hz), 6.48 (1H, dd, $J$=0.7, 7.6 Hz), 3.38 (1H, t, $J$=8.3 Hz), 3.11 (1H, m), 2.92 (1H, t, $J$=8.3 Hz), 2.74 (3H, s), 1.88 (1H, m), 1.55 (1H, m) 1.00 (3H, t, $J$=7.6 Hz); $^{13}C$ NMR ($CDCl_3$)$\delta$ 153.19, 134.05, 127.48, 123.43, 117.61, 107.21, 61.89, 42.37, 36.17, 26.65, 11.93; EIMS $m/z$ (relative intensity) 161 (32), 133 (11), 132 (100), 131 (10), 130 (11), 117 (37), 40, (21); HRMS calcd for $C_{11}H_{15}N$ $m/z$ 161.1204. Found $m/z$ 161.1221.

**4.5.23. 2,3-Dihydro-1,3,3-trimethylindole (8c).**[25] IR (neat) 3022, 1608, 1491, 1462 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 7.09 (1H, dt, $J$=1.3, 7.6 Hz), 7.01 (1H, dd, $J$=1.3, 7.6 Hz), 6.70 (1H, dt, $J$=1.3, 7.6 Hz), 6.49 (1H, dd, $J$=1.3, 7.6 Hz), 3.06 (2H, s), 2.75 (3H, s), 1.30 (6H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 151.97, 139.21, 127.42, 121.49, 117.82, 107.29, 70.30, 40.23, 35.97, 27.37 (two signals).

**4.5.24. 3-Isopropyl-2,3-dihydro-1-methylindole (8d).** IR (neat) 3046, 1609, 1491, 1458 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.09 (2H, m), 6.66 (1H, dt, $J$=0.7, 7.3 Hz), 6.46 (1H, dd, $J$=0.7, 7.3 Hz), 3.30 (1H, t, $J$=8.2 Hz), 3.12 (2H, m), 2.73 (3H, s), 2.02 (1H, m), 0.99 (3H, d, $J$=6.9 Hz), 0.88 (3H, d, $J$=6.9 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 153.91, 132.85, 127.71, 124.60, 117.50, 107.21, 58.55, 47.35, 36.35, 30.73, 20.83, 19.10; EIMS $m/z$ (relative intensity) 175 (23), 158 (19), 133 (11), 132 (100), 117 (30); HRMS calcd for $C_{12}H_{17}N$ $m/z$ 175.1361. Found $m/z$ 1751355.

**4.5.25. 3-Benzyl-2,3-dihydro-1-methylindole (8e).** IR (neat) 3026, 1607, 1492, 1460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.34–7.21 (5H, m), 7.11 (1H, dt, $J$=0.7, 7.6 Hz), 6.93 (1H, dd, $J$=0.7, 7.3 Hz), 6.66 (1H, dt, $J$=0.7, 7.3 Hz), 6.51 (1H, dd, $J$=0.7, 7.3 Hz), 3.49 (1H, m), 3.28 (1H, t, $J$=8.6 Hz), 3.11 (1H, dd, $J$=6.0, 13.5 Hz), 3.02 (1H, dd, $J$=6.6, 8.6 Hz), 2.78 (1H, dd, $J$=9.6, 13.5 Hz), 2.73 (3H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 153.14, 140.20, 133.30, 128.97 (two signals), 128.39 (two signals), 127.78, 126.15, 123.65, 117.68, 107.37, 61.69, 42.37, 60.06, 36.08; EIMS $m/z$ (relative intensity) 223 (12), 132 (100), 117 (25), 91 (10); HRMS calcd for $C_{16}H_{17}N$ $m/z$ 223.1361. Found $m/z$ 223.1361.

**4.5.26. 3-Methy-1,2,3,4-tetrahydro-1-naphthol (9a).**[26] IR (neat) 3332, 1455, 1056 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.35–7.18 (4H, m), 2.80 (1H, m), 2.41 (1H, m), 2.19 (1H, m), 1.88 (2H, m), 1.08 (1H, d, $J$=6.3 Hz).

**4.5.27. 3-Methychroman (9b).**[27] IR (neat) 2922, 1734, 1456, 1261 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 6.7–7.2 (4H, m), 4.17 (1H, ddd, $J$=2.0, 5.6, 10.6 Hz), 3.68 (1H, t, $J$=9.6 Hz), 2.83 (1H, ddd, $J$=2.0, 5.6, 16.2 Hz), 2.44 (1H, dd, $J$=9.6, 16.2 Hz), 2.15 (1H, m), 1.04 (3H, d, $J$=6.6 Hz).

**4.5.28. 1,3-Dimethy-1,2,3,4-tetrahydroquinoline (9c).**[28] IR (neat) 3024, 1605, 1492, 1459 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.07 (1H, t, $J$=9.8 Hz), 6.95 (1H, d, $J$=6.8 Hz), 6.59 (2H, m), 3.15 (1H, ddd, $J$=2.0, 4.2, 11.0 Hz), 2.88 (3H, s), 2.72–2.79 (2H, m), 2.41 (1H, dd, $J$=10.7, 15.8 Hz), 2.12 (1H, m), 1.03 (3H, d $J$=6.5 Hz).

### 4.6. Typical procedure for radical cyclization using $Bu_3SnH$ and AIBN

To a solution of substrate (0.5 mmol) and toluene (25 ml) was added $n$-$Bu_3SnH$ (0.55 mmol) and AIBN (0.1 mmol) at room temperature. The solution was heated under reflux for 4 h. The solvent was evaporated and diluted with hexane. The solution was extracted with $CH_3CN$. The combined $CH_3CN$ extracts were washed with hexane, dried over

$Na_2SO_4$ and concentrated in vacuo. The crude product was purified by TLC.

## Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 11450342) from The Ministry of Education, Culture, Sports, Science and Technology of Japan.

## References and notes

1. Neumann, W. P. *Synthesis* **1987**, 665–683.
2. (a) Baguley, P. A.; Walton, J. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3072–3082. (b) Studer, A.; Amrein, S.; Schleth, F.; Schulte, T.; Walton, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 5726–5733. (c) Studer, A.; Amrein, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3080–3082. (d) Takami, K.; Mikami, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2003**, *59*, 6627–6635. (e) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *J. Org. Chem.* **1993**, *58*, 6838–6842. (f) Graham, S. R.; Murphy, J. A.; Coates, D. *Tetrahedron Lett.* **1999**, *40*, 2415–2416. (g) Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn* **2001**, *74*, 225–235. (h) Nakao, J.; Inoue, R.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1997**, *62*, 1910–1911. (i) Inoue, R.; Nakao, J.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn* **1997**, *70*, 2039–2049. (j) Clark, A. J.; Davies, D. I.; Jones, K.; Millbanks, C. *J. Chem. Soc., Chem. Commun.* **1994**, 41–42.
3. Fry, A. J. Synthetic organic electrochemistry; Wiley: New York, 1989; pp 136–156.
4. Generation of aryl radicals by the direct electrochemically reduction of aryl halides has been reported. Yields of the corresponding simple reduction products and cyclized products were dependent on the structure of the substrates and the electrochemical conditions. (a) Grimshaw, J.; Trocha-Grimshaw, J. *Tetrahedron Lett.* **1974**, *12*, 993–996. (b) Grimshaw, J.; Haslett, R. J.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2448–2455. (c) Grimshaw, J.; Mannus, D. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2456. (d) Donnelly, S.; Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2171–2172.
5. LeStrat, F.; Murphy, J. A.; Hughes, M. *Org. Lett.* **2002**, *4*, 2735–2738.
6. (a) Ozaki, S.; Matsushita, H.; Ohmori, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1120–1122. (b) Ozaki, S.; Matsushita, H.; Ohmori, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2339–2344. (c) Ozaki, S.; Horiguchi, J.; Matsushita, H.; Ohmori, H. *Tetrahedron Lett.* **1994**, *35*, 725–728. (d) Ihara, M.; Katsumata, A.; Setsu, F.; Tokunaga, Y.; Fukumoto, K. *J. Org. Chem.* **1996**, *61*, 677–684. (e) Sandra, O.; Clinet, J. C.; Duñach, E. *Tetrahedron Lett.* **1995**, *36*, 4429–4432. (f) Clinet, J. C.; Duñach, E. *J. Organomet. Chem.* **1995**, *503*, C48–C50. (g) Gómez, M.; Muller, G.; Penyella, D.; Rocamora, M. *Organometallics* **1997**, *16*, 5900–5908. (h) Sandra, O.; Rolland, J-P.; Duñach, E. *Organometallics* **1998**, *17*, 3747–3753. (i) Torii, S.; Inokuchi, T.; Yukawa, T. *J. Org. Chem.* **1985**, *50*, 5875–5877.
7. Munusamy, R.; Dhathathreyan, K. S.; Balasubramanian, K. K.; Venkatachalam, C. H. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1154–1166.
8. Kurono, N.; Honda, E.; Komatsu, F.; Orito, K.; Tokuda, M. *Chem. Lett.* **2003**, *32*, 720–721.
9. Dias, M.; Gibson, M.; Grimshaw, J.; Hill, I.; Trocha-Grimshaw, J.; Hammerich, O. *Acta Chem. Scand.* **1998**, *52*, 549–554.
10. Clerici, A.; Pastori, N.; Porta, O. *Eur. J. Org. Chem.* **2001**, 2235–2243.
11. (a) Rigollier, P.; Young, J. R.; Fowley, L. A.; Still, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 9441–9442. (b) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn* **1989**, *62*, 143–147.
12. Abeywickrema, A. N.; Beckwith, A. L. J.; Gerba, S. *J. Org. Chem.* **1987**, *52*, 4072–4078.
13. Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059–6064.
14. Peters, D. G. Halogenated organic compounds. In *Organic electrochemistry*; Lund, H., Baizer, M. M., Eds.; Marcel Dekker: New York, 1991; pp 390–392.
15. (a) Tokuda, M.; Kurono, N.; Mimura, N. *Chem. Lett.* **1996**, 1091–1092. (b) Kurono, N.; Sugita, K.; Takasugi, S.; Tokuda, M. *Tetrahedron* **1999**, *55*(19), 6097–6108. (c) Jalil, A. A.; Kurono, N.; Tokuda, M. *Synlett* **2001**(12), 1944–1946. (d) Jalil, A. A.; Kurono, N.; Tokuda, M. *Tetrahedron* **2002**, *58*, 7477–7484. (e) Jalil, A. A.; Kurono, N.; Tokuda, M. *Synthesis* **2002**(18), 2681–2686.
16. Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050–6058.
17. Casaschi, A.; Grigg, R.; Sansano, J. M. *Tetrahedron* **2000**, *56*, 7553–7560.
18. Larock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem.* **1998**, *63*, 7652–7662.
19. Stevens, R. V.; Bisacchi, G. S.; Goldsmith, L.; Strouse, C. E. *J. Org. Chem.* **1980**, *45*, 2709–2710.
20. Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 795–802.
21. Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415–2420.
22. Janusz, J. M.; Young, P. A.; Scherz, M. W.; Enzweiler, K.; Wu, L. I.; Gan, L.; Pikul, S.; McDow-Dunham, K. L.; Johnson, C. R.; Senanayake, C. B.; Kellstein, D. E.; Green, S. A.; Tulich, J. L.; Rosario-Jansen, T.; Magrisso, I. J.; Wehmeyer, K. R.; Kuhlenbeck, D. L.; Eichhold, T. H.; Dobson, R. L. M. *J. Med. Chem.* **1998**, *41*, 1124–1137.
23. Rajesh, C. S.; Thanulingam, T. L.; Das, S. *Tetrahedron* **1997**, *53*, 16817–16834.
24. Brown, S.; Clarkson, S.; Grigg, R.; Thomas, W. A.; Sridharam, V.; Wilson, D. M. *Tetrahedron* **2001**, *57*, 1347–1359.
25. Nishio, T.; Okuda, N.; Kashima, C. *Helv. Chim. Acta* **1990**, *73*, 1719–1723.
26. Mitsui, S.; Kasahara, A.; Hanaya, K. *Bull. Chem. Soc. Jpn* **1968**, *41*, 2526–2527.
27. Wipf, P.; Ribe, S. *Org. Lett.* **2001**, *3*, 1503–1505.
28. Katritzky, A. R.; Rachwal, B.; Rachwal, S. *J. Org. Chem.* **1995**, *60*, 7631–7640.