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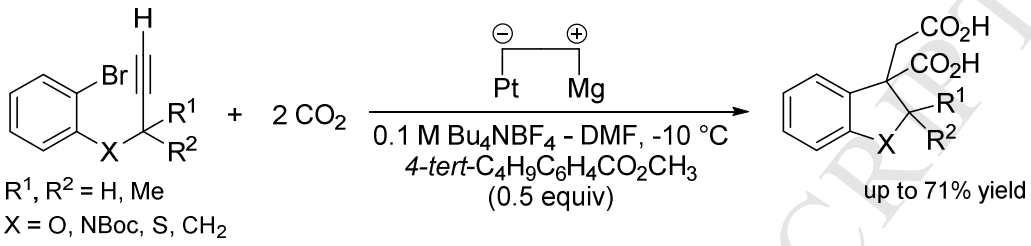

Aryl radical cyclization with alkyne followed by tandem carboxylation in methyl 4-*tert*-butylbenzoate-mediated electrochemical reduction of 2-(2-propynyloxy)bromobenzenes in the presence of carbon dioxide

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Abstract

Constant current electrolysis of 2-(2-propynyloxy)bromobenzenes in DMF using an undivided cell equipped with a Pt cathode and an Mg anode in the presence of carbon dioxide and an electron transfer mediator, methyl 4-*tert*-butylbenzoate, resulted in aryl radical cyclization with a carbon-carbon triple bond followed by fixation of two molecules of carbon dioxide to give 2,2-ring-fused succinic acid derivatives in moderate to good yields. Dihydrobenzofuran, indoline, dihydrobenzothiophene, and indane as well as tetrahydropyran skeletons were successfully constructed by aryl radical cyclization, and unique tandem carboxylation successively occurred to produce succinic acids. One of the resulting succinic acid derivatives, 3-carboxy-2,3-dihydrobenzofuran-3-ylacetic acid, was successfully applied to the synthesis of a novel spiro compound consisting of 2,3-dihydrobenzofuran and γ-butyrolactone at each C3 position in two steps in high yield.

Key Words: electrochemical carboxylation; aryl radical; radical cyclization; fixation of carbon dioxide; tandem reaction

1. Introduction

Radical cyclization is a powerful tool for synthesis of carbocycles and heterocycles.[1] The combination of organic halides and Bu_3SnH with AIBN has promoted many radical cyclizations.[2] On the other hand, one-electron reduction of organic halides or related substrates can generate carbon-centered radicals and has also been used for radical cyclization as an attractive alternative to hazardous organotin reagents from the viewpoint of green chemistry. As well as the use of organic[3] or metal[4] reductants, electrochemical reduction[5-16] can be used as a reducing method for generation of carbon-centered radicals. Direct,[6,7] metal complex-catalyzed[8-11] or mediated[12-16] electrochemical reduction of organic

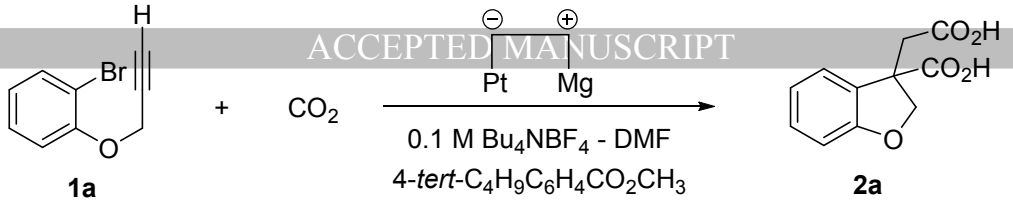
halides and diazonium salts can generate carbon-centered radicals without any tin reagents, and thus-generated carbon-centered radicals have been successfully applied to cyclization reactions yielding carbo- and heterocycles. Under reductive electron transfer conditions, a termination step involves one-electron reduction of the resulting cyclized radical, and a reaction of anion species is dominant as a termination reaction providing final products. Although anion species are known to induce various organic transformations, protonation of the resulting anion species yielding protonated cyclized products is the sole reaction in most of the termination steps in these reductive radical reactions with electron transfer. Several examples of the use of the resulting anion for further carbon-carbon bond-forming reaction under reductive electron transfer conditions have been reported.[17,18] There are, however, few reports on sequential radical cyclization-anionic carbon-carbon bond formation in electroreductive generation of carbon radicals. We recently succeeded in efficient generation of aryl radicals from 2-allyloxybromobenzenes by electrochemical reduction using methyl 4-*tert*-butylbenzoate as an electron transfer mediator. Thus-generated aryl radicals were also found to undergo radical cyclization with alkene, and after further one-electron reduction of the resulting cyclized radical, the generated anion species efficiently reacted with carbon dioxide to give 2,3-dihydrobenzofuran-3-ylacetic acids as sequential aryl radical cyclization-anionic carbon-carbon bond-forming reaction products in high selectivities and good yields.[19] In the course of our efforts to apply electrochemistry to organic synthesis,[20] we recently found a unique electrochemical reaction in aryl radical cyclization using a carbon-carbon triple bond as an aryl radical acceptor. When 2-(2-propynyloxy)bromobenzene was similarly electrolyzed using methyl 4-*tert*-butylbenzoate as an electron transfer mediator in the presence of carbon dioxide, aryl radical cyclization followed by fixation of two molecules of carbon dioxide took place efficiently to give a cyclized dicarboxylic acid, 3-carboxy-2,3-dihydrobenzofuran-3-ylacetic acid. This unique reaction involves three carbon-carbon bond-forming reactions, aryl radical cyclization and fixation of two molecules of carbon dioxide, in one step, and succinic acid derivatives could be obtained in up to 71% isolated yield. Although nickel-catalyzed electroreductive cyclization followed by carboxylation of 2-(2-propynyloxy)bromobenzene providing the same succinic acid as a mixture of three cyclized carboxylic acids was also reported by Olivero and Duñach,[21] only one example was shown and no detailed investigation has been reported. In this paper, we report the results of electrochemical aryl radical cyclization followed by tandem carboxylation involving fixation of two molecules of carbon dioxide to obtain succinic acid derivatives and one synthetic application of the resulting succinic acid to a novel spirolactone in two steps in high yields.

2. Results and discussion

2.1 Screening of reaction conditions

We first carried out reaction screening of reaction conditions using 2-(2-propynyloxy)bromobenzene (**1a**) as a substrate, and the results are shown in Table 1. Constant current electrolysis (current density of 20 mA/cm^2) of a DMF solution of **1a** containing 0.1 M Bu_4NBF_4 was carried out at 0 °C by using a one-compartment cell equipped with a platinum plate cathode (2 x 2 cm^2) and a magnesium rod anode (3 mmϕ) in the presence of 0.5 equiv. of methyl 4-*tert*-butylbenzoate as an electron transfer mediator[19] with bubbling of carbon dioxide through the solution. After supplying 4 F/mol of electricity, conversion of **1** reached 79% by ^{1}H NMR, and 3-carboxy-2,3-dihydro-3-benzofuranacetic acid (**2a**) was obtained in 45% ^{1}H NMR yield (Entry 1). In Entries 2-4, effects of temperature were examined, and electrolysis at –10 °C gave a better yield, 51% (Entry 3). Effects of current density were also investigated in Entries 3, 5 and 6. While the yield of **2a** slightly decreased to 48% with electrolysis at a current density of 15 mA/cm^2, a similar yield based on reacted **1a** was obtained and unidentified byproducts decreased in ^{1}H NMR analysis of the crude product under the conditions in Entry 5. When 6 F/mol of electricity was supplied in electrolysis at 15 mA/cm^2 and at –10 °C, the yield of **2a** increased to 55% (Entry 7). However, an efficient current could not be obtained when further electricity was supplied under these conditions. A decrease of current density to 5 mA/cm^2 in electrolysis at –10 °C solved the problem and resulted in an increase in the yield of **2a** to 62% with 6 F/mol of electricity (Entry 8). Finally, in electrolysis at 5 mA/cm^2 with 10 F/mol of electricity at –10 °C, dicarboxylic acid **2a** was obtained in 71% ^{1}H NMR yield and in 62% isolated yield after purification by silica gel column chromatography (Entry 9). Electrolysis in the absence of methyl 4-*tert*-butylbenzoate, on the other hand, gave **2a** in 32% yield along with benzoic acid derivative in 32% ^{1}H NMR yield (Entry 10). Use of acetonitrile, instead of DMF, decreased the ^{1}H NMR yield of **2a** to 40% and unidentified byproducts were detected in ^{1}H NMR (Entry 11). When a zinc plate (ca. 1.5 x 2 cm^2) was used, instead of a magnesium rod, as an anode, only 8 F/mol of electricity could be passed to provide a complex mixture (Entry 12). In the absence of carbon dioxide, similar electrolysis under the conditions in Entry 9 only gave a complex mixture (Entry 13). It was thought that **2a** was produced by the expected radical cyclization followed by fixation of two molecules of carbon dioxide. However, **2a** was also obtained as a major product even when 2 F/mol of electricity was supplied.

Table 1 Screening of reaction conditions



Entry	Current density [mA/cm^{2}]	Temperature [°C]	Electricity [F/mol]	Conversion of **1a** [%][a]	Yield of **2a** [%][b]
1	20	0	4	79	45 (57)
2	20	20	4	82	42 (51)
3	20	-10	4	80	51 (64)
4	20	-20	4	70	42 (60)
5	15	-10	4	75	48 (65)
6	10	-10	4	73	46 (63)
7	15	-10	6	80	55 (69)
8	5	-10	6	81	62 (77)
9	5	-10	10	91	71 (78) [62]
10[c]	5	-10	6	89	32 (36)[d]
11[e]	5	-10	10	96	40 (42)
12[f]	5	-10	8	---	---
13[g]	5	-10	10	---	---

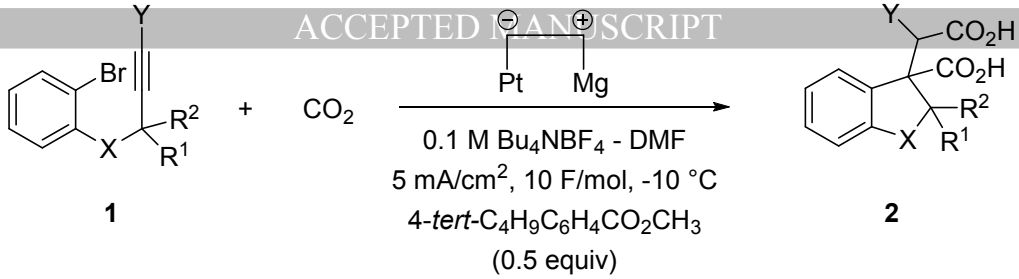
a) Conversion of **1a** was determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard.
b) Yield of **2a** was determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard.
The yield based on reacted **1a** and isolated yield are shown in parenthesis and bracket, respectively.
c) Electrolysis was carried out in the absence of 4-*tert*-$C_4H_9C_6H_4CO_2CH_3$.
d) Direct carboxylation product, 2-(2-propynyloxy)benzoic acid, was obtained in 32% ^{1}H NMR yield.
e) Instead of DMF, acetonitrile was used as a solvent.
f) A zinc plate (ca. 1.5 x 2 cm^{2}), instead of a magnesium rod, was used as an anode.
g) Electrolysis was carried out in the absence of carbon dioxide under nitrogen atmosphere.

2.2 Substrate scope for aryl radical cyclization followed by fixation of two molecules of carbon dioxide

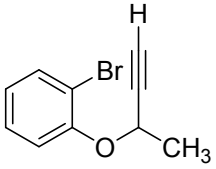
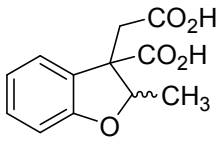
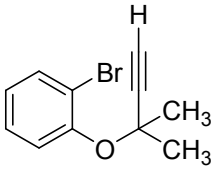
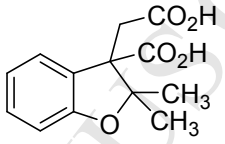
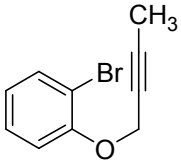
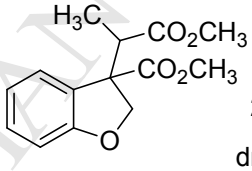
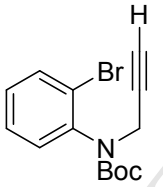
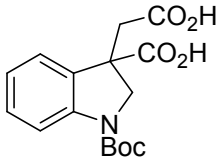
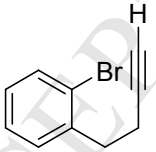
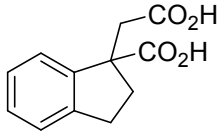
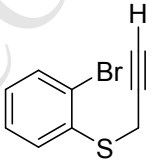
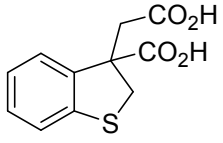
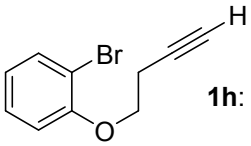
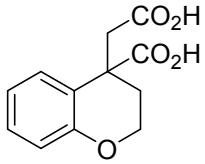
Substrate scope was investigated under the optimized conditions shown in Entry 9 in Table 1, and the results are shown in Table 2. When substrates **1b** and **1c**, having methyl groups at the α-position of the oxygen atom, were subjected to the present reaction, the corresponding cyclized dicarboxylic acids **2b** and **2c** were obtained in 62% and 55% isolated yields, respectively (Entries 1 and 2). Dicarboxylic acid **2b** was obtained as a 63:37 mixture of diastereoisomers, while the stereochemistry of them could not be determined (Entry 1). Electrolysis of 2-(2-butynyloxy)bromobenzene (**1d**) having an internal alkyne under the same conditions provided the expected dicarboxylic acid in lower yield, and the product was isolated as its dimethyl ester by treatment of the crude product with trimethylsilyldiazomethane-CH_3OH in benzene. After column chromatography on silica gel, the corresponding dimethyl ester **2d** was obtained in 39% isolated yield as a 56:44 mixture of diastereoisomers (Entry 3). Indoline, indane and dihydrobenzothiophene skeletons could also be constructed by

the present radical cyclization-dicarboxylation sequence. Constant current electrolysis of *N*-Boc-*N*-(2-propynyl)-2-bromoaniline (**1e**) at 5 mA/cm^2 in the presence of 0.5 equiv. of methyl 4-*tert*-butylbenzoate with bubbling of carbon dioxide through the solution at –10 °C provided indoline dicarboxylic acid **2e** in 71% isolated yield after 10 F/mol of electricity was supplied (Entry 4). Similar electrolysis of 2-(3-butynyl)bromobenzene (**1f**) gave 1-carboxy-2,3-dihydro-1*H*-inden-1-acetic acid (**2f**) in 30% isolated yield (Entry 5). 3-Carboxy-2,3-dihydrobenzo[*b*]thiophen-3-ylacetic acid (**2g**) was also obtained by electrolysis of **1g** in 38% yield (Entry 6). Construction of a 6-membered ring followed by fixation of two molecules of carbon dioxide was also achieved when 2-(3-butynyloxy)bromobenzene (**1h**) was used as a substrate. 4-Carboxy-3,4-dihydro-2*H*-1-benzopyran-4-acetic acid (**2h**) was afforded in 51% isolated yield (Entry 7).

Table 2 Scope of aryl bromides in the radical cyclization followed by tandem carboxylation



1 **2**

Entry	Substrate and conversion	Product and isolated yield
1	 **1b**: 87%	 **2b**: 62% dr[a] = 63 : 37
2	 **1c**: 87%	 **2c**: 55%
3[b]	 **1d**: 93%	 **2d**: 39% dr[a] = 56 : 44
4	 **1e**: 87%	 **2e**: 71%
5	 **1f**: 84%	 **2f**: 30%
6	 **1g**: 78%	 **2g**: 38%
7	 **1h**: 91%	 **2h**: 51%

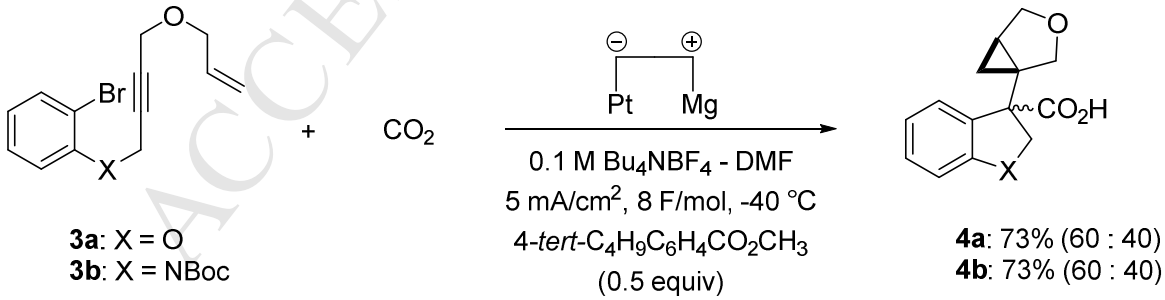
a) Diastereomeric ratio is shown as dr, which was determined by ^{1}H NMR.

b) Diester was isolated after treatment of the crude diacid with $TMSCHN_2$-CH_3OH in benzene.

2.3 Aryl radical cyclization with internal alkyne

In relation to the results of electrolysis of **1d** having internal alkyne as a radical acceptor (Entry 3 in Table 2), we tried electrolysis of **3** having an ene-yne unit to obtain some information about reaction pathways. When electrolysis of **3a** was carried out under the optimized conditions shown in Table 2, monocarboxylic acid **4a** was obtained in 55% isolated yield as a 59/41 mixture of diastereoisomers. After several attempts to improve the yield, **4a** could be obtained from **3a** in 73% isolated yield as a 60/40 mixture of diastereoisomers under the conditions shown in Scheme 1. Although diastereoisomers, **4a-major** and **4a-minor**, could fortunately be separated by recrystallization, stereochemistry of the isomers could unfortunately not be determined by spectroscopic analyses using the NOESY technique. Indoline derivative **4b** was also obtained in 73% isolated yield as a 60/40 mixture of diastereoisomers by similar electrolysis of **3b** (Scheme 1). Monocarboxylic acid **4** would be produced through 5-*exo* cyclization of the electrochemically-generated aryl radical with alkyne and sequential 5-*exo* and 3-*exo* tandem cyclization followed by one-electron reduction of the radical to the corresponding anion and fixation of carbon dioxide at the benzylic position. It is noteworthy that a four carbon-carbon bond-forming reaction took place in one step, and the high yield of the product **4**, 73%, indicates that all of these processes proceeded efficiently, especially aryl radical cyclization with internal alkyne as the first step. These results indicate that the aryl radical cyclization process for internal alkyne also proceeded efficiently even in the case of **1d** (Entry 3 in Table 2), and low yield of **2d** would result from processes following aryl radical cyclization.

Scheme 1 Tandem radical cyclization followed by carboxylation of ene-yne **3**

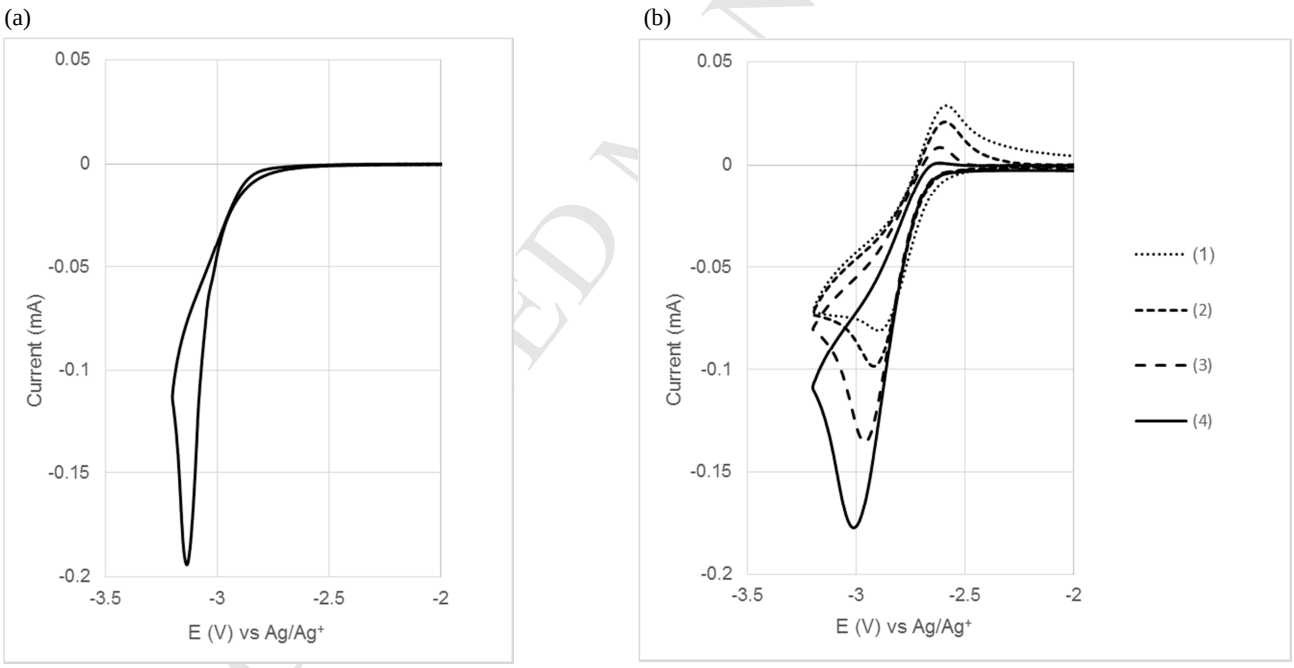


2.4 Reaction mechanism

In order to obtain several information about reaction mechanism in the present reaction, cyclic voltammetry (CV) of aryl bromide **1a** and methyl 4-*tert*-butylbenzoate was carried out and the results are shown in Figure 1. In CV of **1a** in

DMF, one irreversible reduction peak appeared at –3.2 V *vs.* Ag/Ag^+ (Figure 1(a)). On the other hand, a reversible reduction peak at –2.9 V *vs.* Ag/Ag^+ was appeared in CV of methyl 4-*tert*-butylbenzoate (Figure 1(b), (1)). When CV of methyl 4-*tert*-butylbenzoate was performed under the conditions of (1) in the presence of 0.01 mmol of **1a**, an increase in reduction peak current and a decrease in oxidation peak current of methyl 4-*tert*-butylbenzoate was observed (Figure 1(b), (2)). Further additions of **1a** resulted in further increases in reduction peak current and further decreases in oxidation peak current (Figure 1(b), (3) and (4)). Finally, the oxidation peak in methyl 4-*tert*-butylbenzoate disappeared when CV of methyl 4-*tert*-butylbenzoate was carried out in the presence of 0.04 mmol (0.8 equivalents for the benzoate) of **1a** (Figure 1(b), (4)). Similar results were obtained in the study on electroreductive generation of aryl radicals from 2-allyloxybromoarenes using the same mediator system.[19] These results clearly indicate that methyl 4-*tert*-butylbenzoate works as an electron transfer mediator in the present electroreductive generation of aryl radicals from aryl bromides.

Figure 1 CV of aryl bromide **1a** (a) and methyl 4-*tert*-butylbenzoate (b) in the absence and presence of aryl bromide **1a**.



1a (0.075 mmol) in DMF (5 mL)

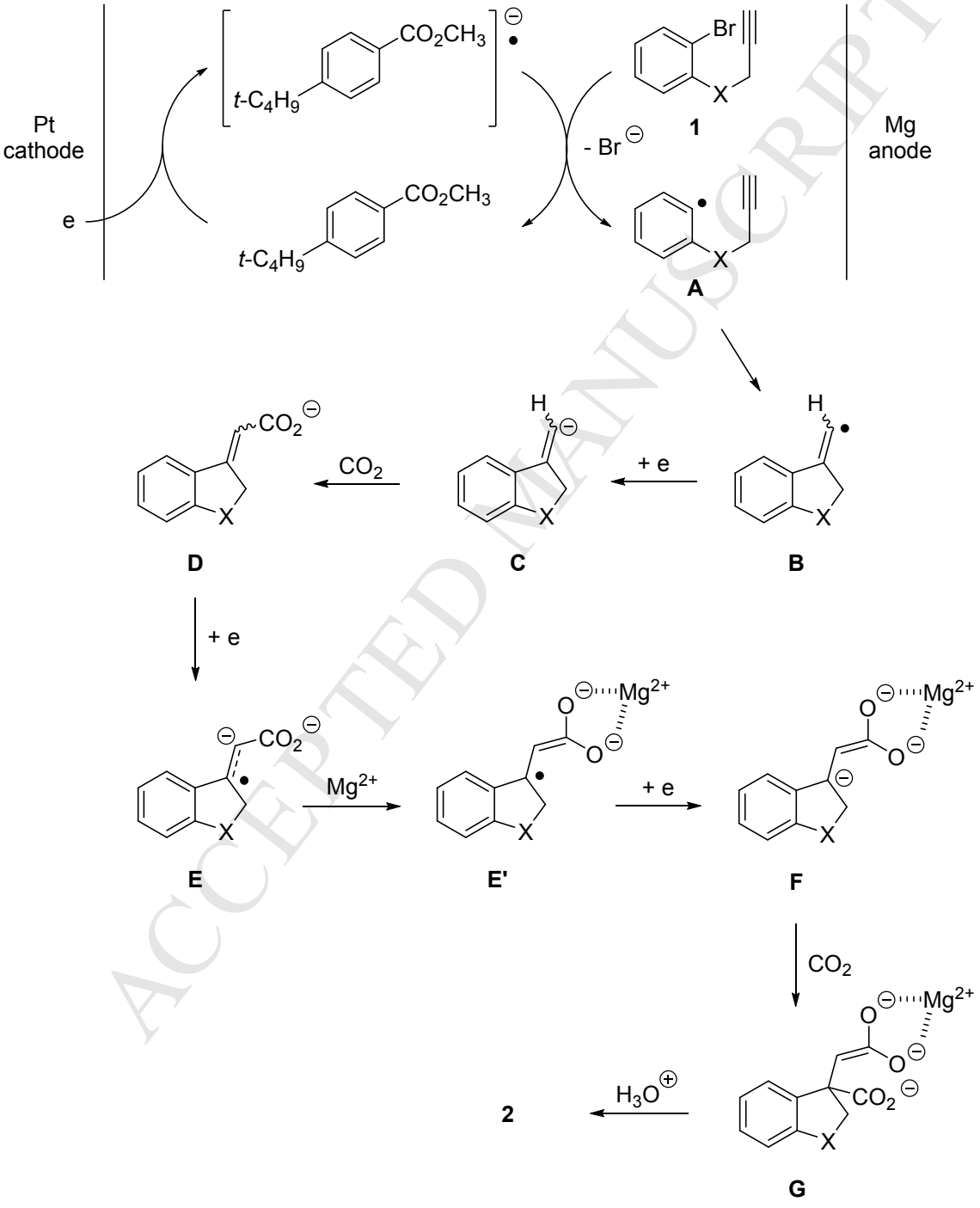
(1): methyl 4-*tert*-butylbenzoate (0.05 mmol) in DMF (5 mL)
(2): (1) + 0.01 mmol of **1a**
(3): (2) + 0.01 mmol of **1a**
(4): (3) + 0.02 mmol of **1a**

Based on these results, a probable reaction mechanism in the present aryl radical cyclization followed by tandem carboxylation is shown in Scheme 2. At the cathode, one-electron reduction of methyl 4-*tert*-butylbenzoate, used as an electron transfer mediator, generates the corresponding radical anion. One-electron reduction of aryl bromide **1** by the

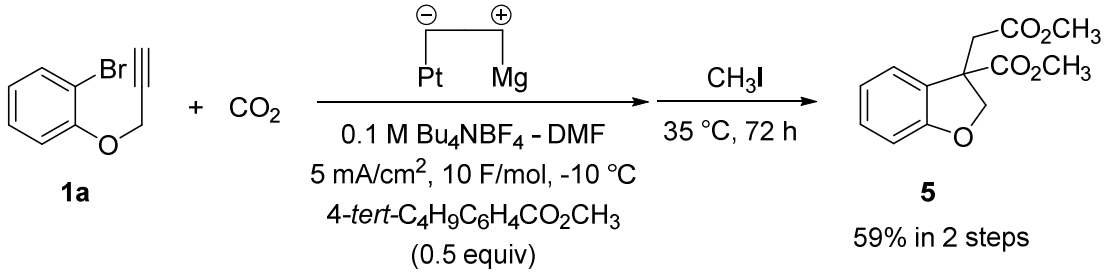
radical anion of methyl 4-*tert*-butylbenzoate generates the anion radical of **1**, resulting in carbon-bromine bond cleavage to generate aryl radical **A**.[19] In the absence of an electron transfer mediator, methyl 4-*tert*-butylbenzoate, two-electron reduction of aryl bromide **1** competitively occurs at the cathode to generate the corresponding aryl anion species, directly producing carboxylated benzoic acid (Entry 10 in Table 1). Intramolecular 5-*exo* cyclization of aryl radical **A** with a carbon-carbon triple bond takes place efficiently to generate the corresponding cyclized vinyl radical **B**. Further one-electron reduction generates the corresponding vinyl anion **C**, which reacts with carbon dioxide to produce the corresponding α,β-unsaturated carboxylate ion **D**, which has a cinnamic acid moiety. It is known that cinnamic acid derivatives can readily be reduced and carboxylated under reductive electron transfer conditions.[22-27] Therefore, further one-electron reduction of α,β-unsaturated carboxylate ion **D** is likely to take place easily to generate the corresponding radical anion **E**. Resonance of the radical anion **E** to stable enol form **E'** followed by further one-electron reduction of **E'** would generate benzylic anion **F**. Selective fixation of carbon dioxide at the benzylic position gives dicarboxylate ion **G**. Acid treatment in workup gives dicarboxylic acid **2**. On the other hand, at the anode, dissolution of an Mg anode as magnesium ion proceeds to result in prevention of any species from oxidizing at the anode.[28,29] Direct treatment of the electrolysis mixture with iodomethane was carried out to obtain some information about any anionic intermediates in the medium at the end of the reaction. After electrolysis of **1a** under the optimized reaction conditions shown in Entry 9 in Table 1, additional DMF (10 mL) and an excess amount of iodomethane (50 mmol) were added to the reaction mixture and the mixture was stirred at 35 °C for 72 h. Usual workup followed by column chromatography on silica gel gave dimethyl ester **5**, probably derived from the dicarboxylate ion of **2a**, in 59% isolated yield as a major product along with 18% of recovered **1a** (Scheme 3). These results indicate that carboxylation of α,β-unsaturated carboxylate ion **D** predominantly and selectively occurred only at the benzylic position (β-position) and no carboxylation occurred at the α-position of the carboxyl group. Although electrochemical carboxylation of cinnamic acid derivatives and β-phenyl-α,β-unsaturated carbonyl compounds often gave a mixture of α- and/or β-carboxylated and α,β-dicarboxylated products along with a hydrogenated product,[22-27] β-selective acylation[30-34] and silylation[35] as well as mono-carboxylation[36] have also been reported under electroreductive[30-33,35-36] or Mg-promoted[34] reaction conditions. β-Selective electrochemical mono-carboxylation of α,β-unsaturated carbonyl compounds, flavones, has been successfully performed under similar electrolysis conditions using an undivided cell equipped with a Pt cathode and an Mg anode in DMF containing 0.1 M Bu_4NBF_4.[36] In the case of the reaction of **1d** having an internal alkyne as a radical acceptor, on the other hand, electron

transfer steps following aryl radical cyclization might be problematic considering the results of tandem cyclization as shown in Scheme 1, though it is still unclear.

Scheme 2 Probable reaction mechanism of the present radical cyclization followed by tandem carboxylation



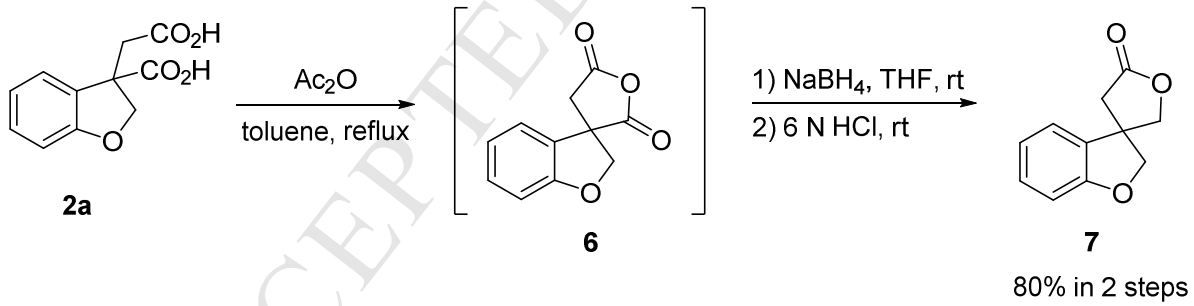
Scheme 3 Direct treatment of the electrolysis mixture of **1a** with iodomethane



2.5 Synthetic application of the resulting succinic acid

One synthetic application of the obtained succinic acids was successfully performed and the result is shown in Scheme 4. Treatment of succinic acid **2a** with acetic anhydride in toluene under reflux gave the corresponding spiro succinic anhydride **6**. Sequential treatment of **6** with $NaBH_4$ in THF followed by 6 M HCl gave a novel spirolactone, spiro[benzofuran-3(2*H*),3'(2'*H*)-furan]-5'(4'*H*)-one (**7**), in 2 steps in 80% yield (Scheme 4). These results indicate that succinic acid derivatives **2** can be good precursors and that the present process is promising as an efficient and easy way to access a novel spirolactone skeleton such as **7**.

Scheme 4 Synthesis of novel spirolactone **7** from aryl radical cyclization-tandem carboxylation product **2a**



3 Conclusion

In conclusion, we found a unique tandem carboxylation following aryl radical cyclization with alkyne by electrolysis of 2-(2-propargyloxy)bromobenzene derivatives **1** in the presence of carbon dioxide using methyl 4-*tert*-butylbenzoate as an electron transfer mediator. By aryl radical cyclization, dihydrobenzofuran, indoline, dihydrobenzothiophene, and indane as well as tetrahydropyran skeletons could be constructed efficiently, and subsequent tandem carboxylation afforded the corresponding 2,2-ring-fused succinic acid derivatives **2** in moderate to good yields. As

one synthetic application, transformation of the resulting succinic acid derivative **2a** into a novel spirolactone skeleton was successfully performed in high yield.

4 Experimental section

4.1 General

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were determined with a JASCO FT/IR-410 spectrometer in neat form unless otherwise stated. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in indicated solvents with a JEOL ECX400P or ECS400 FT NMR spectrometer. The chemical shifts, δ, are given in ppm with tetramethylsilane for ^{1}H and solvents for ^{13}C as references. *J* values are in Hz. Peak multiplicities were given as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. MS spectra and elemental analyses were carried out using a JEOL JMS-T100GCv or Thermo Scientific Exactive and Exacter Analytical CE440 or J-Science Lab JM10, respectively, at Instrumental Analysis Division, Equipment Management Center Creative Research Institution, Hokkaido University. Electrochemical reactions were carried out using a Constant Current Power Supply (model 5944), Metronix Corp., Tokyo. Cyclic voltammetry was carried out by a Hokuto Denko HSV-100 in DMF containing 0.1 M Bu_4NBF_4 using a Pt disk electrode (ϕ 1.6 mm) as a working electrode, a Pt wire (ϕ 0.5 mm) as a counter electrode, and $Ag/Ag^{+}/CH_3CN/Bu_4NClO_4$ (0.01 M $AgNO_3$ in 0.1 M Bu_4NClO_4 in CH_3CN), purchased from BAS (product code; RE-7), as a reference electrode, respectively, with a scan rate 100 mV/sec (for **1a**) or 200 mV/sec (for methyl 4-*tert*-butylbenzoate in the absence and presence of **1a**). Column chromatography was carried out using Kanto Kagaku Silica gel 60N. Reagents and solvents were commercially available and were used as received without further purification.

*4.1.1 2-(2-Propynyloxy)bromobenzene (**1a**).*[19, 37] To a solution of 2-bromophenol (3.46 g, 20 mmol) in DMF (10 mL) were added K_2CO_3 (8.29 g, 60 mmol) and propargyl bromide (8.29 g, 24 mmol) at 0 °C, and then the mixture was stirred at rt overnight. After addition of H_2O (20 mL), the reaction mixture was extracted with ether (30 mL×3). The combined ethereal solution was washed with H_2O (30 mL×3) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a crude product, which was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give 2-(2-propynyloxy)bromobenzene (**1a**, 4.11 g, 97%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.56 (1H, dd, *J* = 7.9 and 1.6 Hz), 7.31–7.26 (1H, m), 7.07 (1H, dd, *J* = 8.3 and 1.5 Hz), 6.89 (1H, dt, *J* = 7.9 and 1.5 Hz), 4.78 (2H, d, *J* = 2.4 Hz), 2.54 (1H, t, *J* = 2.4 Hz). ^{13}C NMR ($CDCl_3$): δ 153.7, 133.3, 128.2, 122.6, 113.9, 112.1, 77.8, 76.1, 56.6.

*4.1.2 2-(1-Methyl-2-propynyloxy)bromobenzene (**1b**).* To a solution of DMAP (37 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) were successively added aqueous 3-butyn-2-ol (7.5 M, 1.5 mL, 11.3 mmol), aqueous NaOH (25%, 2 mL) and tosyl chloride (1.90 g, 10 mmol) at 0 °C, and then the mixture was stirred at rt for 2 h. After addition of H_2O (30 mL), the reaction mixture was extracted with CH_2Cl_2 (30 mL×3). Combined organic layer was washed with H_2O (50 mL×3) and then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the corresponding 3-butyn-2-yl tosylate (1.97 g, 88%), which was used for next step without further purification. In a similar manner to preparation of **1a**, reaction of 2-bromophenol (1.21 g, 7 mmol) with K_2CO_3 (1.16 g, 8.4 mmol) and the prepared 3-butyn-2-yl tosylate (1.88 g, 8.4 mmol) in DMF (15 mL) gave 2-(1-Methyl-2-propynyloxy)bromobenzene (**1b**, 1.30 g, 82%) after a similar work-up followed by column chromatography on silica gel (hexane/ethyl acetate = 20/1). Oil. ^{1}H NMR ($CDCl_3$): δ 7.55 (1H, dd, *J* = 7.8 and 1.8 Hz), 7.29–7.25 (1H, m), 7.14 (1H, dd, *J* = 8.2 and 1.4 Hz), 6.89 (1H, dt, *J* = 7.8 and 1.4 Hz), 4.78 (2H, dq, *J* = 6.8 and 1.8 Hz), 2.50 (1H, d, *J* = 1.8 Hz), 1.74 (3H, d, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 153.8, 133.3, 128.2, 122.8, 116.0, 113.0, 82.3, 74.4, 65.0, 22.0. IR: 3294, 2116, 1588, 1476, 1278, 1242, 1090, 1032, 942, 748 cm^{-1}. HRMS (EI): *m/z* 223.9834 (M^+). Calcd for $C_{10}H_9{}^{79}BrO$ 223.9837.

*4.1.3 2-(1,1-Dimethyl-2-propynyloxy)bromobenzene (**1c**).* 2-(1,1-Dimethyl-2-propynyloxy)bromobenzene (**1c**) was prepared according to the reported procedure.[38] 2-Methyl-3-butyn-2-ol (1.00 g, 12 mmol) was dissolved in anhydrous CH_3CN (6 mL) and to this solution were successively added DBU (2.44 g, 16 mmol) and trifluoroacetic anhydride (2.52 g, 12 mmol) at 0 °C, and then the mixture was stirred at the same temperature for 30 min. To a solution of 2-bromophenol (1.73 g, 10 mmol) in anhydrous CH_3CN (6 mL) were successively added DBU (1.83 g, 12 mmol) and $CuCl_2 \cdot H_2O$ (1.7 mg, 0.01 mmol) at 0 °C. To this solution was dropwise added the prepared solution of 2-methyl-3-butyn-2-ol in CH_3CN for 30 min, and then the mixture was stirred at the same temperature for 5 h. After addition of 1 M hydrochloric acid (50 mL), the mixture was extracted with ethyl acetate (50 mL×3). Combined organic layer was washed with 1 M hydrochloric acid (50 mL×2) and H_2O (100 mL) successively and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (hexane/ethyl acetate = 10/1) gave 2-(1,1-Dimethyl-2-propynyloxy)bromobenzene (**1c**, 1.66 g, 69%) and recovered 2-bromophenol (301 mg, 17%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.62 (1H, dd, *J* = 8.2 and 1.4 Hz), 7.54 (1H, dd, *J* = 7.8 and 1.8 Hz), 7.26–7.21 (1H, m), 6.92 (1H, dt, *J* = 7.8 and 1.4 Hz), 2.60 (1H, s), 1.71 (6H, s). ^{13}C NMR ($CDCl_3$): δ 153.0, 133.4, 127.9, 124.1, 121.5, 117.1, 86.1, 74.2, 74.1, 29.6. IR: 3293, 2113, 1584, 1472, 1239, 1138, 1047, 1029, 951,

901, 753 cm^{-1}. MS (EI): *m/z* 240 [$(M+2)^+$, 3], 238 (M^+, 3), 174 (94), 172 (100). HRMS (EI): *m/z* 237.9992 (M^+). Calcd for $C_{11}H_{11}{}^{79}BrO$ 237.9993.

*4.1.4 2-(2-Butynyloxy)bromobenzene (**1d**).*[39] To a solution of 2-(2-propynyloxy)bromobenzene (**1a**, 2.11 g, 10 mmol) in anhydrous THF (20 mL) was added dropwise 1 M solution of NaHMDS in THF (12 mL, 12 mmol) under nitrogen atmosphere at 0 °C. After stirring for 30 min at the same temperature, iodomethane (7.10 g, 50 mmol) was added to the solution and the reaction mixture was stirred at rt overnight. Saturated aqueous NH_4Cl solution (50 mL) was added to the reaction mixture and the mixture was then extracted with ether (30 mL×3). The combined ethereal solution was washed with 100 mL of 1 M hydrochloric acid and H_2O (100 mL×3) successively and then dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (hexane/ethyl acetate = 20/1) gave 2-(2-butynyloxy)bromobenzene (**1d**, 2.13 g, 97%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.55 (1H, dd, *J* = 7.8 and 1.4 Hz), 7.30–7.26 (1H, m), 7.06 (1H, dd, *J* = 8.3 and 1.4 Hz), 6.87 (1H, dt, *J* = 7.8 and 1.4 Hz), 4.74 (2H, q, *J* = 2.3 Hz), 1.86 (3H, t, *J* = 2.3 Hz). ^{13}C NMR ($CDCl_3$): δ 154.0, 133.2, 128.2, 122.2, 113.8, 112.0, 84.2, 73.4, 57.2, 3.6.

*4.1.5 tert-Butyl N-(2-bromophenyl)-N-(2-propynyl)carbamate (**1e**).*[40] To a solution of 2-bromoaniline (3.43 g, 20 mmol) in THF (40 mL) was added di-*tert*-butyl dicarbonate (10.90 g, 50 mmol) and then the mixture was stirred under reflux for 3 days. To the reaction mixture was added ether (50 mL) and the organic layer was washed with saturated brine (50 mL×3) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a crude product, which was subjected to column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give *tert*-butyl *N*-(2-bromophenyl)carbamate (4.73 g, 87%). Spectral data were in good accordance with reported data.[40,41] To a suspension of NaH (722 mg, 60% oil dispersion, 18 mmol, washed with hexane before use) in anhydrous THF (60 ml) was added dropwise *tert*-butyl *N*-(2-bromophenyl)carbamate (4.08 g, 15 mmol) at 0 °C. After stirring for 30 min at rt, propargyl bromide (2.14 g, 1.2 equiv) was added and the mixture was stirred at 30 °C overnight. 60 mL of H_2O was added to the reaction mixture, which was then extracted with ethyl acetate (50 mL×3). The combined organic layer was washed with H_2O (50 mL×3) and dried over anhydrous $MgSO_4$. After evaporation of the solvent, column chromatography on silica gel (hexane/ethyl acetate = 10/1) gave *tert*-butyl *N*-(2-bromophenyl)-*N*-(2-propynyl)carbamate (**1e**, 3.88 g, 83%). Solid, mp: 55–58°C. ^{1}H NMR ($CDCl_3$): δ 7.62 (1H, d, *J* = 7.8 Hz), 7.47–7.31 (2H, m), 7.20–7.16 (1H, m), 4.78 (0.7H, dd, *J* = 17.6 and 2.4 Hz), 4.64 (0.3H,

br d, *J* = 17.8 Hz), 4.04–3.86 (1H, m), 2.23 (0.3H, br s), 2.20 (0.7H, br t, *J* = 2.4 Hz) 1.55 (2.7H, s), 1.35 (6.3H, s). ^{13}C NMR ($CDCl_3$): δ 153.5 (153.3), (140.2), 139.9, (133.1), 132.8, (130.9), 130.6, (129.1), 128.9, (128.1), 127.8, 123.4, (81.3), 80.7, (79.2), 79.1, 72.3, (72.0), (39.3), 37.9, (28.2), 27.9. Chemical shifts of observed signals of a minor rotamer are shown in parentheses.

*4.1.6 2-(3-Butynyl)bromobenzene (**1f**).*[42] In a round-bottom flask flushed with N_2 was placed Mg turning (1.22 g, 50 mmol) and then anhydrous ether (10 mL), a tip of iodine and a drop of 1,2-dibromoethane was successively added. After leaving the mixture at 0 °C for 30 min, a solution of allyl bromide (2.43 g, 20 mmol) in dry ether (20 mL) was added dropwise to the mixture to prepare a solution of a Grignard reagent. To a solution of 2-bromobenzyl bromide (2.49 g, 10 mmol) in anhydrous THF (20 mL) was added dropwise a prepared solution of a Grignard reagent at rt and the reaction mixture was stirred at rt overnight. 100 mL of H_2O was added to the mixture, which was then extracted with ether (50 mL×3). The combined ethereal solution was washed with H_2O (100 mL×3) and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (hexane) gave 2-(3-butenyl)bromobenzene (1.82 g, 87%). Spectral data were in good accordance with reported data.[19,37] To a solution of 2-(3-butenyl)bromobenzene (633 mg, 3 mmol) in CH_2Cl_2 (10 mL) was added dropwise bromine (480 mg, 3 mmol) at 0 °C and then the mixture was stirred at rt for 1 h. The solvent was evaporated to give a crude 2-(3,4-dibromobutyl)bromobenzene, which was dissolve in DMSO (5 mL). To this solution was slowly added a solution of *t*-BuOK (740 mg, 6.6 mmol) in DMSO (15 mL) at rt for 1h. After stirring at rt for 3 h followed by addition of 1 M hydrochloric acid (30 mL), the mixture was extracted with ether (50 mL×3). The combined ethereal solution was washed with H_2O (50 mL×3) and then dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (hexane) gave 2-(3-butynyl)bromobenzene (**1f**, 438 mg, 70%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.54 (1H, dd, *J* = 7.6 and 1.1 Hz), 7.29 (1H, dd, *J* = 7.6 and 2.0 Hz), 7.25 (1H, dt, *J* = 7.6 and 1.1 Hz), 7.09 (1H, dt, *J* = 7.6 and 2.0 Hz), 2.98 (2H, t, *J* = 7.5 Hz), 2.52 (2H, dt, *J* = 7.5 and 2.6 Hz), 1.99 (1H, t, *J* = 2.6 Hz). ^{13}C NMR ($CDCl_3$): δ 139.3, 132.7, 130.6, 128.0, 127.3, 124.2, 83.2, 69.2, 35.0, 18.7.

*4.1.7 2-(2-Propynylthio)bromobenzene (**1g**)*. In a similar manner to preparation of **1a**, reaction of 2-bromothiophenol (3.78 g, 20 mmol) with K_2CO_3 (3.32 g, 24 mmol) and propargyl bromide (2.86 g, 24 mmol) in DMF (20 mL) gave 2-(2-propynylthio)bromobenzene (**1g**, 4.01 g, 88%) after a similar work-up followed by column chromatography on silica

gel (hexane/ethyl acetate = 20/1). Oil. ^{1}H NMR ($CDCl_3$): δ 7.57 (1H, dd, *J* = 7.8 and 1.4 Hz), 7.44 (1H, dd, *J* = 7.8 and 1.4 Hz), 7.32 (1H, dt, *J* = 7.8 and 1.4 Hz), 7.09 (1H, dt, *J* = 7.8 and 1.4 Hz), 3.67 (2H, d, *J* = 2.8 Hz), 2.24 (1H, t, *J* = 2.8 Hz). ^{13}C NMR ($CDCl_3$): δ 136.2, 132.8, 128.6, 127.7, 127.2, 123.4, 78.8, 71.8, 21.2. IR: 3296, 2244, 1576, 1450, 1428, 1233, 1109, 1020, 908, 742 cm^{-1}. HRMS (EI): *m/z* 225.9448 (M^+). Calcd for $C_9H_7{}^{79}Br{}^{32}S$ 225.9452.

*4.1.8 2-(3-Butynyloxy)bromobenzene (**1h**)*. To a solution of 3-butyn-1-ol (351 mg, 5 mmol) in anhydrous THF (20 mL) was successively added 2-bromophenol (1.04 g, 6 mmol), PPh_3 (1.57 g, 6 mmol) and diisopropyl azodicarboxylate (1.21 g, 6 mmol) at 0 °C. After stirring at rt overnight, the solvent was evaporated to give a residue, to which was added a 4/1 mixture of hexane/ether (50 mL) and the mixture was stirred at rt for 30 min. Precipitated solid, triphenylphosphine oxide, was removed by filtration and the resulting solution was evaporated to give a crude product, which was subjected to column chromatography on silica gel (hexane/ethyl acetate = 10/1 to 5/1) to give 2-(3-butynyloxy)bromobenzene (**1h**, 769 mg, 68%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.54 (1H, dd, *J* = 7.8 and 2.0 Hz), 7.28–7.24 (1H, m), 6.91 (1H, dd, *J* = 8.3 and 1.4 Hz), 6.86 (1H, dt, *J* = 7.8 and 1.4 Hz), 4.16 (2H, t, *J* = 7.3 Hz), 2.75 (2H, dt, *J* = 7.3 and 2.8 Hz), 2.06 (1H, t, *J* = 2.8 Hz). ^{13}C NMR ($CDCl_3$): δ 154.7, 133.4, 128.4, 122.3, 113.6, 112.3, 79.9, 70.1, 67.1, 19.4. IR: 3297, 2123, 1587, 1480, 1279, 1248, 1054, 1031, 900, 748 cm^{-1}. MS (EI): *m/z* 226 [$(M+2)^+$, 31], 224 (M^+, 33), 187 (7), 185 (8), 174 (98), 172 (100), 145 (37), 117 (28), 53 (29). HRMS (EI): *m/z* 223.9832 (M^+). Calcd for $C_{10}H_9{}^{79}BrO$ 223.9837.

*4.1.9 2-[(4-Allyloxy-2-butynyl)oxy]bromobenzene (**3a**)*. To a suspension of NaH (480 mg, 60% oil dispersion, 12 mmol, washed with hexane before use) in anhydrous DMF (10 mL) was dropwise added a solution of 2-butyn-1,4-diol (1.73 g, 20 mmol) in DMF (10 mL) at 0 °C and then the mixture was stirred at 80 °C for 1 h. To this solution was dropwise added a solution of allyl bromide (1.20 g, 10 mmol) in DMF (10 mL) and then the mixture was stirred at the same temperature for 4 h. After cooling to rt, 50 mL of 1 M hydrochloric acid was added and the resulting aqueous solution was extracted with ether (50 mL×3). The combined ethereal solution was washed with saturated brine (100 mL×2) and then dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (hexane/ethyl acetate = 2/1) gave 4-allyloxy-2-butyn-1-ol (705 mg, 56%). Spectral data were in good accordance with reported data.[43] To a solution of 4-allyloxy-2-butyn-1-ol (630 mg, 5 mmol) in anhydrous THF (20 mL) was successively added 2-bromophenol (1.04 g, 6 mmol), PPh_3 (1.57 g, 6 mmol) and diisopropyl azodicarboxylate (1.21 g, 6 mmol) at 0 °C. After stirring at rt overnight, the

solvent was evaporated to give a residue, to which was added a 4/1 mixture of hexane/ether (50 mL) and the mixture was stirred for 30 min. Precipitated solid was removed by filtration and the resulting solution was evaporated to give a crude product, which was subjected to column chromatography on silica gel (hexane/ethyl acetate = 10/1 to 5/1) to give 2-[(4-allyloxy-2-butynyl)oxy)]bromobenzene (**3a**, 1.16 g, 83%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.55 (1H, dd, *J* = 7.9 and 1.6 Hz), 7.28 (1H, ddd, *J* = 8.2, 7.4 and 1.6 Hz), 7.06 (1H, dd, *J* = 8.2 and 1.4 Hz), 6.88 (1H, ddd, *J* = 7.9, 7.4 and 1.4 Hz), 5.88 (1H, ddt, *J* = 17.2, 10.4 and 5.8 Hz), 5.27 (1H, dq, *J* = 17.2 and 1.6 Hz), 5.20 (1H, ddt, *J* = 10.4, 1.6 and 1.4 Hz), 4.83 (2H, t, *J* = 1.8 Hz), 4.19 (2H, t, *J* = 1.8 Hz), 4.02 (2H, dt, *J* = 5.8 and 1.4 Hz). ^{13}C NMR ($CDCl_3$): δ 153.6, 133.5, 133.1, 128.0, 122.3, 117.5, 113.7, 111.9, 83.8, 80.4, 70.2, 56.9, 56.6. IR: 2853, 1586, 1575, 1477, 1444, 1354, 1279, 1229, 1126, 1082, 1052, 1032, 1005, 930, 749, 660 cm^{-1}. HRMS (ESI): *m/z* 302.9992 [$(M+Na)^+$]. Calcd for $C_{13}H_{13}{}^{79}BrNaO_2$ 302.9991.

*4.1.10 tert-Butyl N-(2-bromophenyl)-N-(4-allyloxy-2-butynyl)carbamate (**3b**)*. To a solution of 4-(allyloxy)-2-butyn-1-ol (1.88 g, 15 mmol) and Et_3N (1.88 g, 18 mmol) in CH_2Cl_2 (30 mL) was added methanesulfonyl chloride (2.06 g, 18 mmol) at 0 °C. After stirring for 2 h at the same temperature, 50 mL of H_2O was added and organic layer was separated. The resulting aqueous solution was extracted with CH_2Cl_2 (30 mL×2) and the combined organic layer was washed with H_2O (100 mL×3). After drying over anhydrous $MgSO_4$ and evaporation of the solvent, column chromatography on silica gel (hexane/ether = 1/1) gave 4-allyloxy-2-butyn-1-ly methanesulfonate (2.45 g, 12 mmol, 83%). Spectral data were in good accordance with reported data.[44] To a suspension of NaH (480 mg, 60% oil dispersion, 12 mmol, washed with hexane before use) in anhydrous THF (20 mL) was dropwise added *tert*-butyl *N*-(2-bromophenyl)carbamate (2.72 g, 10 mmol) at 0 °C under nitrogen atmosphere and then the reaction mixture was stirred at rt for 30 min. To this solution was dropwise added 4-allyloxy-2-butynyl methanesulfonate (2.45 g, 12 mmol) and the resulting mixture was stirred at rt overnight. After addition of H_2O (100 mL), the reaction mixture was extracted with ethyl acetate (50 mL×3). The combined organic layer was washed with H_2O (100 mL×3) and then dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (hexane/ethyl acetate = 4/1) gave *tert*-butyl *N*-(2-bromophenyl)-*N*-(4-allyloxy-2-butynyl)carbamate (**3b**, 3.38 g, 9 mmol, 89%). Oil. ^{1}H NMR ($CDCl_3$): δ 7.64–7.60 (1H, m), 7.46–7.30 (2H, m), 7.19–7.15 (1H, m), 5.91–5.81 (1H, m), 5.28–5.18 (2H, m), 4.78 (0.8H, br.d, *J* = 17.4 Hz), 4.66 (0.2H, br.d, *J* = 17.1 Hz), 4.16–3.92 (5H, m), 1.55 (1.8H, s), 1.35 (7.2H, s). ^{13}C NMR ($CDCl_3$): δ 153.3, (153.2), (140.1), 139.8, 133.7, (133.0), 132.7, (130.8), 130.5, (128.9), 128.7, (127.9), 127.6, 123.4, 117.3, (81.6), 81.5, (81.0), 80.4, 79.9,

(79.7), 70.0, 57.0, (39.4), 38.0, (28.0), 27.8. Chemical shifts of the observed signals of a minor rotamer are shown in parentheses. IR: 1708, 1477, 1382, 1304, 1253, 1167, 1116, 1067, 1017, 935, 862, 758 cm^{-1}. MS (ESI): *m/z* 402.0675 [$(M+Na)^+$]. Calcd for $C_{18}H_{22}O_3{}^{79}BrNNa$ 402.0675.

*4.2 General procedure for electrochemical reaction of **1** or **3***

A solution of aryl bromide **1** or **3** (1 mmol) in anhydrous DMF (10 mL) containing Bu_4NBF_4 (0.1 M) was electrolyzed at –10 °C for **1** (at –40 °C for **3**) with a constant current (5 mA/cm^2) in the presence of methyl 4-*tert*-butylbenzoate (96 mg, 0.5 mmol) under atmospheric pressure of bubbling carbon dioxide. A test tube-like (ca. 25 mmϕ) undivided cell equipped with a Pt plate cathode (2×2 cm^2), an Mg rod anode (3 mmϕ, ca. 25 mm) and a Teflon® tube (ϕ 1 mm) for supplying carbon dioxide was used for the electrolysis. After an appropriate amount of electricity had been passed (shown in the tables and schemes), 1 M hydrochloric acid (100 mL) was added to the electrolyzed solution and then the mixture was extracted with ethyl acetate (30 mL×5). The combined organic layer was washed with saturated $NaHCO_3$ (40 mL×3) and the resulting aqueous solution was acidified with 3 M hydrochloric acid and then extracted with ethyl acetate (30 mL×5). The combined ethyl acetate solution was washed with H_2O (100 mL×3) and dried over $MgSO_4$. Evaporation of the solvent gave a crude product. i) In the reaction of **1** and **3** except **1d**; a crude product was purified by column chromatography on silica gel (hexane/ethyl acetate/acetic acid = 20/10/3 for the reaction of **1**, hexane/ethyl acetate/acetic acid = 8/2/1 for the reaction of **3**) to give pure dicarboxylic acid **2** or tandem-cyclized carboxylic acid **4**. ii) In the reaction of **1d**; a crude product was dissolved in benzene (7 mL) and CH_3OH (3 mL). To this solution was added trimethylsilyldiazomethane (0.6 M solution in hexane, 3.5 mL) at rt and the mixture was stirred at rt for 2h. Evaporation of the solvent followed by column chromatography on silica gel (hexane/ethyl acetate = 4/1) gave diester **2d** (101 mg, 39%).

*4.2.1 3-Carboxy-2,3-dihydrobenzo[b]furan-3-ylacetic acid (**2a**).*[19] Yield: 62%. Solid, mp: 186–187 °C. ^{1}H NMR ($CDCl_3$+DMSO-d_6): δ 7.27 (1H, dd, *J* = 7.5 and 0.8 Hz), 7.19–7.15 (1H, m), 6.89–6.83 (1H, dd, *J* = 7.5 and 0.9 Hz), 6.79 (1H, br.d, *J* = 8.1 Hz), 5.31 (1H, dd, *J* = 9.7 and 0.8 Hz), 4.46 (1H, d, *J* = 9.7 Hz), 3.39 (1H, dd, *J* = 17.4 and 0.8 Hz), 2.69 (1H, d, *J* = 17.4 Hz). ^{13}C NMR (DMSO-d_6): δ 173.8, 172.7, 159.4, 129.8, 128.7, 124.1, 120.6, 109.9, 79.2, 53.3, 42.3.

*4.2.2 3-Carboxy-2,3-dihydro-2-methylbenzo[b]furan-3-ylacetic acid (**2b**).* Yield: 62% (a 60/40 mixture of isomers). Solid,

mp: 176–178 °C. ^{1}H NMR (DMSO-d_6): δ 7.36 (0.6H, br.d, J = 7.6 Hz), 7.28 (0.4H, br.d, J = 7.6 Hz), 7.18–7.11 (1H, m), 6.86–6.81 (1H, m), 6.764 (0.4H, d, J = 7.6 Hz), 6.755 (0.6H, d, J = 7.6 Hz), 5.35 (0.4H, q, J = 6.4 Hz), 4.73 (0.6H, q, J = 6.4 Hz), 3.16 (0.4H, d, J = 18.0 Hz), 2.99 (0.6H, d, J = 17.2 Hz), 2.78 (0.4H, d, J = 18.0 Hz), 2.75 (0.6H, d, J = 17.2 Hz), 1.36 (1.8H, d, J = 6.4 Hz), 1.23 (1.2H, d, J = 6.4 Hz). ^{13}C NMR (DMSO-d_6): δ (173.6), (172.6), 172.4, 172.0, 159.1, (157.9), 130.3, (129.6), 128.9, (128.5), 126.1, (124.9), 120.3 (may be overlapped), (109.6), 109.4, 85.7, (83.7), 56.7, (55.3), 41.8, (37.4), 16.4, (16.3). Chemical shifts of the signals probably derived from a minor isomer are shown in parentheses. IR (KBr): 3500–2300, 1704, 1596, 1481, 1436, 1280, 1241, 1071, 751 cm^{-1}. Anal: Calcd for $C_{12}H_{12}O_5$: C, 61.02; H, 5.12. Found: C, 60.93; H, 5.04.

*4.2.3 3-Carboxy-2,3-dihydro-2,2-dimethylbenzo[b]furan-3-ylacetic acid (**2c**)*. Yield: 55%. Solid, mp: 173–175 °C. ^{1}H NMR (DMSO-d_6): δ 7.33 (1H, dd, J = 7.6 and 1.2 Hz), 7.09 (1H, dt, J = 7.6 and 1.2 Hz), 6.79 (1H, dt, J = 7.6 and 1.2 Hz), 6.71 (1H, d, J = 7.6 Hz), 3.04 (1H, d, J = 17.2 Hz), 2.38 (1H, d, J = 17.2 Hz), 1.42 (3H, s), 1.19 (3H, s). ^{13}C NMR (DMSO-d_6): δ 172.5, 171.8, 157.6, 130.0, 128.8, 127.8, 120.1, 109.7, 89.5, 58.7, 40.0, 24.1, 22.2. IR (KBr): 3500–2500, 1701, 1475, 1460, 1248, 940, 849, 749 cm^{-1}. Anal: Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.02; H, 5.36.

*4.2.4 Methyl 2-(3-methoxycarbonyl-2,3-dihydrobenzo[b]furan-3-yl)propanoate (**2d**)*. Yield: 39% (a 55/45 mixture of isomers). Oil. ^{1}H NMR ($CDCl_3$): δ 7.39 (0.55H, dd, J = 7.6 and 1.2 Hz), 7.22‑7.15 (1.45H, m), 6.90‑6.86 (2H, m), 6.82 (0.45H, d, J = 7.8 Hz), 6.79 (0.55H, d, J = 8.2 Hz), 5.28 (0.45H, d, J = 10.5 Hz), 4.97 (0.55H, d, J = 9.6 Hz), 4.74 (0.55H, d, J = 9.6 Hz), 4.64 (0.45H, d, J = 10.5 Hz), 3.76 (1.65H, s), 3.73, (1.35H, s), 3.71, (1.35H, s), 3.55 (0.45H, q, J = 7.3 Hz), 3.53 (1.65H, s), 3.35 (0.55H, q, J = 7.3 Hz), 1.18 (1.65H, d, J = 7.3 Hz), 1.02 (1.35H, d, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 175.0, 173.6, 173.0, 172.3, 160.2, 160.1, 130.0, 129.9, 126.3, 126.0, 125.5, 123.6, 120.7, 120.5, 110.1, 110.0, 75.9, 74.9, 58.7, 58.2, 52.94, 52.85, 52.1, 51.8, 45.4, 44.8, 13.0, 12.0. IR: 2953, 1734, 1597, 1483, 1460, 1435, 1226, 1119, 1077, 981, 838, 753 cm^{-1}. HRMS (EI): *m/z* 264.0994 $(M)^+$. Calcd for $C_{14}H_{16}O_5$ 264.0998.

*4.2.5 1-tert-Butoxycarbonyl-3-carboxy-2,3-dihydro-1H-indol-3-ylacetic acid (**2e**)*. Yield: 71%. Solid, mp: 188–189 °C. ^{1}H NMR (DMSO-d_6): δ 7.72 (0.7H, br. s), 7.39 (0.3H, br. s), 7.32–7.22 (2H, m), 6.95 (1H, m), 4.60 (1H, d, J = 11.5 Hz), 3.82 (1H, d, J = 11.5 Hz), 3.23 (1H, d, J = 17.4 Hz), 2.80 (1H, d, J = 7.4 Hz), 1.52 (9H, s). ^{13}C NMR (DMSO-d_6): δ 173.9, 172.6,

151.5, 142.3, (141.3), (132.7), 131.8, 129.2, 123.9, 122.4, 114.4, (81.31), 80.4, 56.7, 50.9, (50.1), 42.6, 28.1. Chemical shifts of the observed signals of a minor rotamer are shown in parentheses. IR (KBr): 3600–2400, 1710, 1489, 1402, 1351, 1247, 1146, 1049, 753 cm^{-1}. Anal: Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.36. Found: C, 59.55; H, 5.87; N, 4.31.

*4.2.6 1-Carboxy-2,3-dihydro-1H-indene-1-ylacetic acid (**2f**)*. Yield: 30%. Solid, mp: 175–177 °C. ^{1}H NMR (DMSO-d_6): δ 12.3 (2H, br.s), 7.28–7.14 (4H, m), 3.15 (1H, d, *J* = 17.6 Hz), 3.04–2.96 (1H, m), 2.92–2.84 (1H, m), 2.81–2.74 (1H, m), 2.50 (1H, d, *J* = 17.6 Hz), 2.13–1.95 (1H, m). ^{13}C NMR (DMSO-d_6): δ 175.5, 172.6, 144.3, 143.8, 127.8, 126.5, 124.8, 123.7, 55.5, 42.6, 34.8, 30.7. IR (KBr): 3500–2300, 1710, 1419, 1297, 1249, 1210, 928, 768 cm^{-1}. Anal: Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.35; H, 5.28.

*4.2.7 3-Carboxy-2,3-dihydro-1H-benzo[b]thiophen-3-ylacetic acid (**2g**)*. Yield: 30%. Solid, mp: 174–176 °C. ^{1}H NMR (CD_3OD): δ 7.30 (1H, d, *J* = 7.8 Hz), 7.15–7.18 (2H, m), 7.03–7.08 (1H, m), 4.15 (1H, d, *J* = 11.9 Hz), 3.47 (1H, d, *J* = 11.9 Hz), 3.03 (1H, d, *J* = 17.4 Hz), 2.87 (1H, d, *J* = 17.4 Hz). ^{13}C NMR (CD_3OD): δ 175.6, 174.4, 142.7, 141.7, 130.0, 125.7, 125.4, 123.4, 60.2, 41.4, 40.4. IR (KBr): 3500–2500, 1721, 1460, 1426, 1355, 1300, 1250, 1228, 1200, 1070, 941, 853, 795, 744 cm^{-1}. Anal: Calcd for $C_{11}H_{10}O_4S$: C, 55.45; H, 4.23; S, 13.46. Found: C, 55.31; H, 4.23, S, 13.46.

*4.2.8 4-Carboxy-3,4-dihydro-2H-benzo[b]pyran-4-ylacetic acid (**2h**)*. Yield: 51%. Solid, mp: 197–199 °C. ^{1}H NMR (DMSO-d_6): δ 7.50 (1H, dd, *J* = 8.4 and 1.6 Hz), 7.14–7.10 (1H, m), 6.88–6.84 (1H, m), 6.76 (1H, dd, *J* = 8.4 and 1.6 Hz), 4.26–4.20 (1H, m), 4.19–4.13 (1H, m), 3.13 (1H, d, *J* = 16.8 Hz), 2.63 (1H, d, *J* = 16.8 Hz), 2.60–2.54 (1H, m), 2.12–2.06 (1H, m). ^{13}C NMR (DMSO-d_6): δ 175.2, 172.2, 154.4, 128.5, 128.2, 123.1, 120.5, 117.3, 63.0, 43.9, 42.7, 29.7. IR (KBr): 3500–2300, 1700, 1490, 1450, 1431, 1299, 1227, 1059, 939, 753 cm^{-1}. Anal: Calcd for $C_{12}H_{12}O_5$: C, 61.02; H, 5.12. Found: C, 60.73; H, 5.01.

*4.2.9 (±)-3-(3-oxabicyclo[3.1.0]hexan-1-yl)-2,3-dihydrobenzofuran-3-carboxylic acid (**4a-major**).* Solid, mp: 108–109 °C. ^{1}H NMR ($CDCl_3$): δ 7.39 (1H, d, *J* = 7.6 Hz), 7.25–7.21 (1H, m), 6.92 (1H, br. t, *J* = 7.6 Hz), 6.83 (1H, br. d, *J* = 8.1 Hz), 4.99 (1H, d, *J* = 9.5 Hz), 4.59 (1H, d, *J* = 9.5 Hz), 3.86 (1H, d, *J* = 8.4 Hz), 3.78 (2H, s), 3.57 (1H, d, *J* = 8.4 Hz), 1.44–1.37 (1H, m), 0.94–0.87 (1H, m), 0.70 (1H, d, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$): δ 177.3, 159.9, 130.1, 126.2, 125.0, 120.7, 110.3,

77.2, 70.6, 70.0, 56.4, 33.7, 20.8, 11.0. IR (KBr): 3500–2500, 1713, 1476, 1457, 1297, 1259, 1234, 1021, 835, 750 cm^{-1}. Anal.: Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.31; H, 5.81.

*4.2.10 (±)-3-(3-oxabicyclo[3.1.0]hexan-1-yl)-2,3-dihydrobenzofuran-3-carboxylic acid (**4a-minor**)*. Solid, mp: 166–168 °C. ^{1}H NMR ($CDCl_3$): δ 7.35 (1H, dd, *J* = 7.6 and 1.0 Hz), 7.26–7.21 (1H, m), 6.89 (1H, dt, *J* = 7.6 and 1.0 Hz), 6.84 (1H, br. d, *J* = 8.1 Hz), 5.04 (1H, d, *J* = 9.2 Hz), 4.50 (1H, d, *J* = 9.2 Hz), 3.84–3.80 (3H, m), 3.69 (1H, dd, *J* = 8.1 and 1.2 Hz), 1.80–1.76 (1H, m), 0.55 (1H, t, *J* = 4.9 Hz), 0.40–0.35 (1H, m). ^{13}C NMR ($CDCl_3$): δ 177.4, 159.9, 130.3, 125.2, 124.8, 120.7, 110.4, 77.2, 70.4, 69.9, 56.2, 33.8, 21.9, 9.2. IR (KBr): 3500–2400, 1724, 1481, 1459, 1234, 894, 761 cm^{-1}. Anal.: Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.14; H, 5.83.

*4.2.11 (±)-3-(3-oxabicyclo[3.1.0]hexan-1-yl)-1-(tert-butoxycarbonyl)indoline-3-carboxylic acid (**4b**) (a 60/40 mixture of diastereoisomers)*. Yield: 73 %. Solid, mp: 86–87 °C. ^{1}H-NMR ($CDCl_3$): δ 7.88 (0.6H, br. s), 7.48 (0.4H, br. s), 7.41–7.39 (0.6H, m), 7.36 (0.4H, d, *J* = 7.8 Hz), 7.29–7.25 (1H, m), 7.02–6.93 (1H, m), 4.57 (0.4H, d, *J* = 11.9 Hz), 4.52 (0.6H, d, *J* = 11.9 Hz), 4.02 (1H, br. s), 3.89–3.74 (3H, m), 3.68 (1H, d, *J* = 8.0 Hz), 1.79–1.74 (0.4H, m), 1.57 (9H, br. s), 1.49–1.46 (0.6H, m), 0.87–0.83 (0.6H, m), 0.67 (0.6H, t, *J* = 5.0 Hz), 0.50 (0.4H, t, *J* = 4.8 Hz), 0.29 (0.4H, dd, *J* = 8.0 and 5.0 Hz). ^{13}C-NMR ($CDCl_3$): 174.6, 174.5, 151.7, 142.2, 141.2, 129.3, 129.1, 128.4, 127.9, 125.7, 124.5, 122.0, 121.9, 114.6, 82.1, 80.9, 70.2, 69.5, 55.2, 53.5, 53.3, 34.2, 33.8, 27.9, 21.3, 20.4, 10.6, 8.6. IR (KBr): 3415, 1737, 1707, 1487, 1393, 1148, 754 cm^{-1}. Anal.: Calcd for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.89; H, 6.86; N, 3.94.

*4.3 Direct treatment of the electrolysis mixture of **1a** with iodomethane*

Electrolysis of **1a** (1 mmol) was carried out as described in *4.2 General procedure for electrochemical reaction of **1** or **3***. After electrolysis, anode metal, magnesium rod, was removed from the electrolyzed mixture, and then to the electrolyzed mixture was added anhydrous DMF (10 mL) and iodomethane (7.1 g, 50 mmol), and then the mixture was stirred at 35 °C for 72 h. To the mixture was added 1 M HCl (100 mL) and the mixture was extracted with ethyl acetate (30 mL×5). Combined organic layer was washed with saturated $NaHCO_3$ (40 mL×3) and H_2O (100 mL×3) successively and then was dried over $MgSO_4$. Evaporation followed by column chromatography on silica gel (hexane/ethyl acetate = 10/1) gave methyl 3-methoxycarbonyl-2,3-dihydrobenzo[b]furan-3-ylaceate (**5**, 149 mg, 59%) and recovered **1a** (38 mg, 18%).

*4.3.1 Methyl 3-methoxycarbonyl-2,3-dihydrobenzo[b]furan-3-ylaceate (**5**).* Yield: 59%. Solid, mp: 103–104 °C. ^{1}H NMR ($CDCl_3$): δ 7.23–7.15 (2H, m), 6.88 (1H, t, *J* = 7.5 Hz), 6.84 (1H, d, *J* = 8.2 Hz), 5.31 (1H, dd, *J* = 10.1 Hz), 4.44 (1H, d, *J* = 10.1 Hz), 3.74 (3H, s), 3.71 (3H, s), 3.44 (1H, d, *J* = 17.4 Hz), 2.75 (1H, d, *J* = 17.4 Hz). ^{13}C NMR ($CDCl_3$): δ 172.4.8, 171.3, 159.6, 130.1, 127.4, 123.8, 120.8, 110.3, 78.9, 53.7, 53.0, 52.0, 42.3. IR (KBr): 1731, 1596, 1484, 1364, 1297, 1258, 1230, 1213, 1168, 962, 756 cm^{-1}. Anal.: Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.35; H, 5.54.

*4.4 Transformation of diacid **2a** into spirolactone **7**.*

A mixture of **2a** (111.1 mg, 0.5 mmol) and acetic anhydride (61 mg, 0.6 mmol) in toluene (5 mL) was heated under reflux for 4 h. Evaporation gave a crude anhydride **6**, which was used for a next reaction without further purification. To a solution of anhydride **6** in THF (5 mL) was added $NaBH_4$ (37.8 mg, 1.0 mmol) at rt. After stirring at rt for 2 h, 6 M HCl (10 mL) was added to the mixture and stirring was continued at rt for 12 h. The mixture was extracted with ethyl acetate (30 mL×3) and combined organic layer was washed with H_2O (30 mL×3). Dryness over $MgSO_4$ and evaporation of the solvent gave a crude product, which was purified by column chromatography on silica gel (hexane/ethyl acetate = 2/1) to give spirolactone **7** (76 mg, 80%).

*4.4.1 Spiro[benzofuran-3(2H),3'(4'H)-furan]-2',5'-dione (**6**)(not isolated).* ^{1}H NMR ($CDCl_3$): δ 7.29 (1H, dt, *J* = 7.5 and 1.4 Hz), 7.15 (1H, dd, *J* = 7.5 and 0.9 Hz), 6.99 (1H, dt, *J* = 7.5 and 0.9 Hz), 6.93 (1H, d, *J* = 8.2 Hz), 5.07 (1H, d, *J* = 9.6 Hz), 4.58 (1H, d, *J* = 9.6 Hz), 3.32 (1H, d, *J* = 19.2 Hz), 3.27 (1H, d, *J* = 19.2 Hz). ^{13}C NMR ($CDCl_3$): δ 172.8, 168.0, 159.5, 131.1, 126.7, 122.1, 122.0, 110.9, 78.6, 54.8, 42.3.

*4.4.2 Spiro[benzofuran-3(2H),3'(2'H)-furan]-5'(4'H)-one (**7**).* Solid, mp: 68–70 °C. ^{1}H NMR ($CDCl_3$): δ 7.22–7.27 (2H, m), 6.98 (1H, dt, *J* = 7.6 and 0.8 Hz), 6.87 (1H, d, *J* = 7.6 Hz), 4.60 (1H, d, *J* = 9.2 Hz), 4.48 (1H, d, *J* = 9.2 Hz), 4.44 (1H, d, *J* = 9.2 Hz), 4.40 (1H, d, *J* = 9.2 Hz), 2.96 (1H, d, *J* = 17.6 Hz), 2.76 (1H, d, *J* = 17.6 Hz). ^{13}C NMR ($CDCl_3$): δ 174.8, 159.6, 129.9, 128.2, 122.4, 121.5, 110.3, 81.2, 77.5, 49.8, 40.5. IR (KBr): 1774, 1601, 1482, 1459, 1409, 1242, 1182, 1039, 1010, 977, 840, 753 cm^{-1}. Anal.: Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.54; H, 5.31.

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