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Electrochemical carboxylation of benzylic carbonates: alternative method for efficient synthesis of arylacetic acids

Masashi Ohkoshi, Jun-ya Michinishi, Shoji Hara, Hisanori Senboku *

Laboratory of Organic Reaction, Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

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ABSTRACT

Electrochemical carboxylation of benzylic carbonates was successfully performed as an alternative method for the synthesis of phenylacetic acids by using a one-compartment cell equipped with a Pt plate cathode and an Mg rod anode in CH_3CN to afford the corresponding phenylacetic acids in good yields.

1. Introduction

Since arylacetic acids and 2-arylpropanoic acids are well known to have biological activities, their efficient syntheses have been widely investigated. Electroorganic synthesis[1] is one effective method for the synthesis of these compounds. Electrochemical carboxylation (EC) of benzylic halides is known to proceed efficiently under mild conditions even under atmospheric pressure of carbon dioxide to afford phenylacetic acids in good yields when a reactive metal, such as magnesium or aluminum, is used as an anode in the electrolysis.[2,3] The reaction involves C–C bond formation between benzylic halides and carbon dioxide at the benzylic position under electroreductive conditions.[1b] Carbon dioxide used as a source of a carboxyl group is not only abundant and economical but also non-toxic and attractive as an environmentally benign C1 chemical reagent for organic synthesis.[4] Carbon monoxide and cyanide ion are also effective as sources of a carboxyl group for synthesis of phenylacetic acids and their esters from benzylic halides. However, they are unfortunately toxic and must be used with special caution. While various ECs of benzylic halides,[5] including benzylic fluorides[6] have been reported to synthesize phenylacetic acids, only one example of EC using benzyl carbonate, instead of benzylic halides, for the synthesis of phenylacetic acid in low yield has been reported.[7] The use of benzylic carbonates for organic synthesis, on the other hand, has been unexpectedly limited to transition metal-catalyzed coupling and related reactions[8] and only a few applications to organic synthesis have been reported.[9] During the course of our continuous studies on electroorganic synthesis,[5j,6b,c,10] we recently directed our attention to benzylic carbonate as an alternative substrate for EC yielding phenylacetic acid and found that EC of various benzylic carbonates took place efficiently under neutral and mild conditions by constant current electrolysis using a Pt cathode and an Mg anode in the presence of carbon dioxide in CH_3CN or DMF. We report herein EC of benzylic carbonates as an alternative method for the synthesis of phenylacetic acids in good yields.

2. Results and discussion

2.1. Screening of reaction conditions

The results of screening of reaction conditions, including solvent, current density, and electricity, using benzyl methyl carbonate (**1a**-**Me**) as a substrate are summarized in Table 1. When constant current electrolysis (25 mA/cm^2) of **1a**-**Me** in DMF containing 0.1 M Bu_4NBF_4 was carried out with 3 F/mol of electricity by using an undivided cell equipped with a Pt cathode and an Mg anode in the presence of CO_2 at 0 °C, phenylacetic acid (**2a**) was obtained in 38% yield and 57% of **1a**-**Me** was recovered (entry 1 in Table 1). Electrolyses at a higher current density resulted in slight increases of the yields of **2a** (entries 2 and 3). Electrolysis in CH_3CN, instead of DMF, gave a slightly better result (entries 2 and 4), while EC at a higher current density (65 mA/cm^2) in CH_3CN was not

* Corresponding author. Tel./fax: +81 11 706 6555; e-mail address: senboku@eng.hokudai.ac.jp (H. Senboku).

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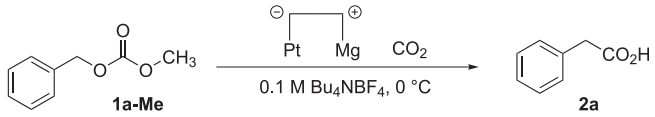
Table 1
Screening of reaction conditions in EC of **1a-Me**



1a-Me **2a**

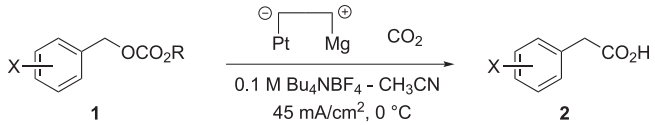
Entry	Solvent	Current Density [mA/cm^2]	Electricity [F/mol]	Yield of **2a** [%]	Recovery of **1a-Me** [%]
1	DMF	25	3	38	57
2	DMF	45	3	42	46
3	DMF	65	3	46	44
4	CH_3CN	45	3	51	40
5	CH_3CN	65	3	46	45
6	CH_3CN	45	6	72	15
7	CH_3CN	45	10	89	0

effective for improvement of the yield and conversion (entry 5). Supplying 6 F/mol of electricity resulted in an increase of the yield of **2a** and conversion of **1a-Me** (entry 6). Finally, when the electrolysis was carried out at a current density of 45 mA/cm^2 with 10 F/mol of electricity at 0 °C, phenylacetic acid (**2a**) was obtained in 89% yield with consumption of **1a-Me** (entry 7).

2.2. Scope of the EC of benzyl carbonates

We next investigated the scope of the present EC using several benzylic carbonates derived from primary benzyl alcohols as substrates, and the results are summarized in Table 2. As well as benzyl methyl carbonate (**1a-Me**), benzyl ethyl carbonate (**1a-Et**) was efficiently electrocarboxylated under the same conditions (entry 2 in Table 2). When benzyl carbonates **1b-Me** and **1b-Et**, having an alkyl group at their *para* position, were used as substrates, remarkable decreases of reaction efficiency were observed, and carboxylic acid **2b** was obtained in only about 45% yield along with over 50% recovery of the substrates (entries 3 and 4). On the other hand, the EC of benzyl carbonates **1c**–**e** having an electron-withdrawing group on the phenyl group took place more efficiently than that of **1a**. Even 4.5 F/mol of electricity was sufficient for consumption of the substrate to yield carboxylic acid in high yields. The effect of another alkyl group of benzyl carbonates in the present EC was also investigated by using benzyl carbonates **1c**, having a methoxycarbonyl group at the *para* position of the phenyl group, as substrates. No remarkable influence of another alkyl group was observed, and in all cases, the EC of methyl (**1c-Me**), ethyl (**1c-Et**), isopropyl (**1c-*i*-Pr**), *tert*-butyl (**1c-*t*-Bu**), and phenyl carbonates (**1c-Ph**) gave carboxylic acid **2c** in high yields (entries 5–9). These results indicated that another alkyl group of benzyl carbonate does not affect reaction efficiency and product yield in the EC of benzyl carbonate. *p*-Cyano- and *m*-cyanobenzyl carbonates **1d-Me**, **1d-Et**, and **1e-Me** were also applicable to the present EC to give the corresponding carboxylic acids **2d** and **2e** in high yields.

Table 2
Scope of primary benzyl carbonate **1** in the present EC



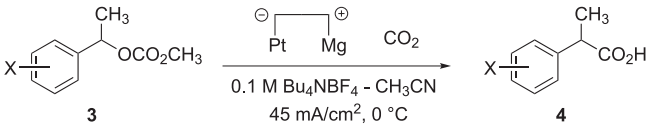
1 **2**

Entry	Substrate	X	R	Electricity [F/mol]	Product and yield [%]
1	**1a-Me**	H	CH_3	10	**2a** (89)
2	**1a-Et**	H	C_2H_5	10	**2a** (93)
3	**1b-Me**	*p*-*t*-C_4H_9	CH_3	10	**2b** (44)[a]
4	**1b-Et**	*p*-*t*-C_4H_9	C_2H_5	10	**2b** (45)[b]
5	**1c-Me**	*p*-CO_2CH_3	CH_3	4.5	**2c** (94)
6	**1c-Et**	*p*-CO_2CH_3	C_2H_5	4.5	**2c** (86)
7	**1c-*i*-Pr**	*p*-CO_2CH_3	*i*-C_3H_7	4.5	**2c** (93)
8	**1c-*t*-Bu**	*p*-CO_2CH_3	*t*-C_4H_9	4.5	**2c** (86)
9	**1c-Ph**	*p*-CO_2CH_3	C_6H_5	4.5	**2c** (90)
10	**1d-Me**	*p*-CN	CH_3	4.5	**2d** (79)
11	**1d-Et**	*p*-CN	C_2H_5	4.5	**2d** (85)
12	**1e-Me**	*m*-CN	CH_3	4.5	**2e** (81)

[a] Carbonate **1b-Me** was recovered in 55% yield.
[b] Carbonate **1b-Et** was recovered in 53% yield.

We also investigated EC of benzyl carbonates **3** derived from secondary benzyl alcohols (α-phenethyl alcohols) as substrates, and the results are summarized in Table 3. The EC of secondary benzyl carbonate **3a** took place less efficiently than that of primary benzyl carbonate **1a-Me**. While the EC of **1a-Me** gave phenylacetic acid (**2a**) in 89% yield (entry 7 in Table 1 and entry 1 in Table 2), similar EC of secondary benzyl carbonate **3a** under the same conditions gave 2-phenylpropanoic acid (**4a**) in only 56% yield along with 31% recovery of **3a** (entry 1 in Table 3). On the other hand, 2-phenylpropanoic acids **4b**–**d** were obtained in high yields by similar EC of secondary benzyl carbonates **3b**–**d** having electron-withdrawing groups on the phenyl ring (entries 2–4). When carbonate **3b** having an ester group was used as a substrate, 3.7 F/mol of electricity was sufficient for consumption of the starting carbonate **3b** to yield carboxylic acid **4b** in 95% yield (entry 2). Although the EC of carbonates **3c**–**d** having a cyano group needed 4.5 F/mol of electricity for consumption of the substrates, the yields of carboxylic acids **4c**–**d** increased up to 96%.

Table 3
Scope of secondary benzyl methyl carbonate **3** in the present EC



3 **4**

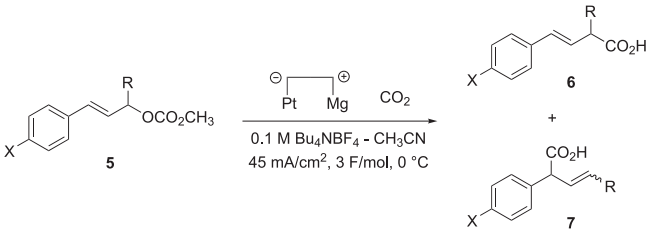
Entry	Substrate	X	Electricity [F/mol]	Product and yield [%]
1	**3a**	H	10	**4a** (56)[a]
2	**3b**	*p*-CO_2CH_3	3.7	**4b** (95)
3	**3c**	*p*-CN	4.5	**4c** (95)
4	**3d**	*m*-CN	4.5	**4d** (96)

[a] Carbonate **3a** was recovered in 31% yield.

2.3. EC of cinnamyl carbonates

Similar EC of cinnamyl carbonate **5** was also investigated, and the results are summarized in Table 4. In all cases, a reductive C–O

Table 4
EC of cinnamyl carbonates **5**



5 **6** **7**

Entry	Substrate	X	R	Product and yield [%]	Isomer ratio[a] (**6**/**7**)
1	**5a**	H	H	**6a**+**7a** (81)	31/69
2	**5b**	F	H	**6b**+**7b** (84)	38/62
3	**5c**	CH_3O	H	**6c**+**7c** (81)	51/49
4	**5d**	C_6H_5	H	**6d**+**7d** (92)	18/82
5	**5e**	H	CH_3	**6e**+**7e** (87)	9/91[b]

[a] Isomer ratio was determined by ^{1}H NMR.
[b] Compound **7e** consists of a 82/18 mixture of *E* and *Z* isomers.

bond cleavage of cinnamyl carbonate **5** at the cinnamylic position followed by a fixation of CO_2 took place smoothly and efficiently even supply of 3 F/mol of electricity and without any electron-withdrawing group on their phenyl ring to yield 4-phenyl-3-butenoic acid **6** and 2-phenyl-3-butenoic acid **7** as an inseparable mixture in high combined yields.[11,12] EC of secondary cinnamyl carbonate **5e** with 3 F/mol of electricity afforded **6e** and **7e** in 87% combined yield (entry 5 in Table 4), while similar EC of secondary benzyl carbonate **3a** with 10 F/mol of electricity gave **4a** in only 69% conversion and 56% yield (entry 1 in Table 3). Regioselectivity of CO_2 fixation yielding α-adduct **6** and γ-adduct **7** can be rationalized by considering the relative stability of two anion forms for cinnamyl anion as shown in Figure 1, which are generated by a two-electron reduction of cinnamyl carbonate **5**, as well as EC of allyl bromides.[13] Thus, the anion ***B*** generated from **5a** is more stable than the anion ***A*** under the present reaction conditions. The addition of more stable anion ***B*** to carbon dioxide gives the corresponding carboxylate anion of **7a** as a major product (entry 1). A fluorine atom at the *para* position on the phenyl ring has almost no effect on the stability of anions ***A*** and ***B***, resulting in products in a similar ratio (entry 2). In the case of **5c**, the generated anion ***B*** is destabilized by an electron-donating methoxy group at the *para* position and the stability of anions ***A*** and ***B*** becomes approximately equal to give the same amount of **7c** and **6c** (entry 3). On the other hand, in the case of **5d**, the generated anion ***B*** is stabilized by a phenyl group at the *para* position to yield **7d** with a higher ratio than that of **7a** (entry 4). In the reaction using **5e** as a substrate, the generated anion ***A*** is a secondary anion and is more unstable than the anion ***B***, resulting in the formation of **7e** with a much higher ratio than that of **7a** (entry 5).

Figure 1.

2.4. Reaction mechanism

A probable reaction mechanism in the present EC of benzyl and cinnamyl carbonates is shown in Scheme 1. At the cathode, two-electron reduction of the carbonate results in C–O bond cleavage at the benzylic position to generate benzylic anion **C** as an intermediate. Although cyclic voltammetry of **1a**-**Me** in CH_3CN showed no obvious reduction peak at >-3.5 V versus Ag/Ag^+, cyclic voltammetry of **1c**-**Me** in CH_3CN showed two irreversible reduction peaks at -2.8 V versus Ag/Ag^+ and -2.4 V versus Ag/Ag^+, respectively. Cinnamyl carbonate **5a** also showed an irreversible reduction peak at -2.7 V versus Ag/Ag^+ in its cyclic voltammetry in CH_3CN. On the other hand, a reduction peak potential of carbon dioxide in CH_3CN containing 0.1 M Bu_4NBF_4 appeared at -3.3 V versus Ag/Ag^+. These results indicate that electrochemical reduction of benzyl and cinnamyl carbonates would take place more easily than that of carbon dioxide. It also seems likely that electrochemical reduction of carbon dioxide would competitively proceed in the EC of **1a**-**Me**, resulting in an excess amount of electricity (10 F/mol) for a high yield. The generated anion **C** attacks carbon dioxide to give carboxylate ion **D**. On the other hand, at the anode, dissolution of magnesium takes place to produce magnesium cation, which captures carboxylate ion **D** to give magnesium carboxylate **E** and/or **F**. Acid treatment in workup gives carboxylic acid.

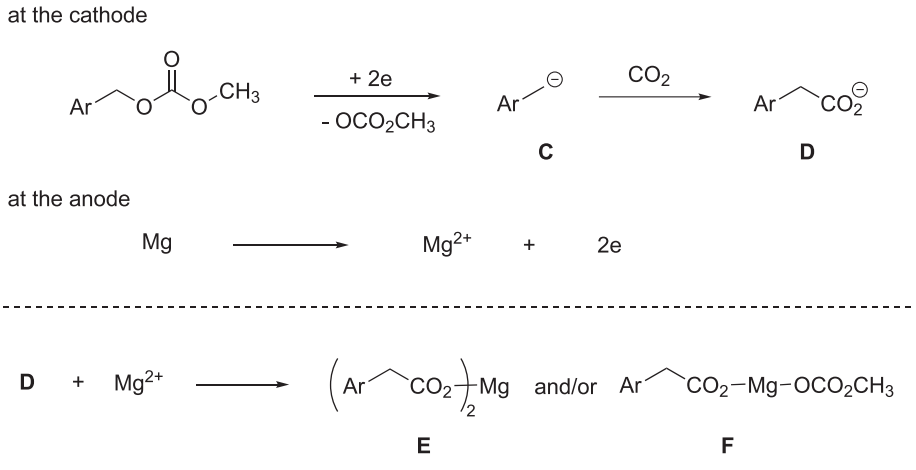
3. Conclusion

In conclusion, we have successfully carried out electrochemical carboxylation of benzyl carbonates by using a Pt cathode and an Mg anode to afford phenylacetic acids in high yields. We have also shown that the present method is applicable to cinnamyl carbonates. The results indicate that the present EC should be useful and attractive as an alternative method for synthesis of phenylacetic acids and β,γ-unsaturated carboxylic acids.

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. ^1H (270 MHz or 400 MHz) and ^{13}C (67.5 MHz or 100 MHz) NMR spectra were recorded in $CDCl_3$ with a JEOL EX-270, JEOL ECX-400P or JEOL A400II FT NMR spectrometer. Unless otherwise stated, NMR spectra were performed at 400 MHz (^1H) and 100 MHz (^{13}C), respectively. The chemical shifts, δ, are given in parts per million with tetramethylsilane as a reference. *J* values are in hertz. Peak multiplicities were given as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. MS spectra were determined using a JEOL JMS-FABmate, JEOL JMS-T100GC or Thermo Scientific Exactive. Elemental analyses were performed at Instrumental Analysis Division, Equipment Management Center, Creative Research Institution Sousei in Hokkaido University. Electrochemical reactions were carried out using a Constant Current Power Supply (model 5944), Metronix Corp. Tokyo. Cyclic voltammetry was performed by a Hokuto Denko HSV-100 in CH_3CN containing 0.1 M Bu_4NBF_4 using a Pt disk electrode (φ 1.6 mm) as a working electrode,



Scheme 1.

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 0.1 V/s. Column chromatography was carried out using Kanto Kagaku Silica gel 60 N with hexane/EtOAc as an eluant. All reagents and solvents were commercially available and were used as received without further purification.

4.2. Preparation of benzyl carbonates 1, 3, and 5; general procedure except for 1c-*t*-Bu

To a solution of an alcohol (10 mmol) and pyridine (11 mmol) in 60 mL of CH_2Cl_2 was added dropwise an appropriate chloroformate ($ClCO_2R$; R=CH_3, C_2H_5, *i*-C_3H_7, or C_6H_5, 18 mmol) at 0 °C. After stirring at room temperature for 2 h, 1 M HCl (30 mL) was added to the solution. Then the resulting mixture was extracted with CH_2Cl_2 (30 mL×3) and the combined organic layer was washed with 1 M HCl (50 mL). After drying over $MgSO_4$, evaporation of the solvent gave a crude product, which was purified by recrystallization with hexane/EtOAc or by column chromatography on silica gel to obtain a pure carbonate.

*4.2.1. Benzyl methyl carbonate (**1a**-**Me**)*[14]. Yield: 97%. ^{1}H NMR (270 MHz): δ 3.79 (3H, s), 5.16 (2H, s), 7.34–7.37 (5H, m).

*4.2.2. Benzyl ethyl carbonate (**1a**-**Et**)*[14]. Yield: 96%. ^{1}H NMR (270 MHz): δ 1.31 (3H, t, *J*=7.0 Hz), 4.21 (2H, d, *J*=7.0 Hz), 5.16 (2H, s), 7.34–7.39 (5H, m).

*4.2.3. p-tert-Butylbenzyl methyl carbonate (**1b**-**Me**).* Yield: 86%. ^{1}H NMR: δ 1.32 (9H, s), 3.79 (3H, s), 5.14 (2H, s), 7.33 (2H, d, *J*=8.3 Hz), 7.39 (2H, d, *J*=8.3 Hz). ^{13}C NMR: δ 31.2, 34.6, 54.8, 69.5, 125.5, 128.2, 132.2, 151.6, 155.7. IR: 3041, 2790, 2361, 2341, 1750, 1270 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{18}O_3$ 222.1256. Found 222.1260.

*4.2.4. p-tert-Butylbenzyl ethyl carbonate (**1b**-**Et**).* Yield: 92%. ^{1}H NMR: δ 1.30 (3H, t, *J*=7.3 Hz), 1.31 (9H, s), 4.20 (2H, q, *J*=7.3 Hz), 5.13 (2H, s), 7.33 (2H, d, *J*=8.3 Hz), 7.39 (2H, d, *J*=8.3 Hz). ^{13}C NMR: δ 14.0, 31.1, 34.3, 63.7, 69.0, 125.2, 128.0, 132.3, 151.2, 154.9. IR: 2963, 1746, 1379, 1364, 1261, 1010 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{20}O_3$ 236.1412. Found 236.1416.

*4.2.5. p-Methoxycarbonylbenzyl methyl carbonate (**1c**-**Me**).* Yield: 93%. Mp: 100–103 °C. ^{1}H NMR: δ 3.82 (3H, s), 3.92 (3H, s), 5.22 (2H, s), 7.45 (2H, d, *J*=8.3 Hz), 8.04 (2H, d, *J*=8.3 Hz). ^{13}C NMR: δ 52.1, 55.0, 68.7, 127.6, 129.8, 130.1, 140.2, 155.5, 166.6. IR (KBr): 2959, 2360, 2341, 1748, 1716, 1269 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{12}O_5$ 224.0685. Found 224.0681. Anal. Calcd for $C_{11}H_{12}O_5$: C, 58.93; H, 5.39. Found: C, 58.83; H, 5.36.

*4.2.6. Ethyl p-methoxycarbonylbenzyl carbonate (**1c**-**Et**).* Yield: 96%. ^{1}H NMR: δ 1.32 (3H, t, *J*=7.2 Hz), 3.92 (3H, s), 4.23 (2H, q, *J*=7.2 Hz), 5.21 (2H, s), 7.45 (2H, d, *J*=8.2 Hz), 8.04 (2H, d, *J*=8.2 Hz). ^{13}C NMR: δ 14.2, 52.1, 64.3, 68.5, 127.6, 129.8, 130.0, 140.3, 154.9, 166.6. IR: 2989, 2959, 1745, 1719, 1256 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{14}O_5$ 238.0841. Found 238.0840.

*4.2.7. Isopropyl p-methoxycarbonylbenzyl caebonate (**1c**-**i**-**Pr**).* Yield: 85%. Mp: 30–33 °C. ^{1}H NMR: δ 1.31 (6H, d, *J*=6.2 Hz), 3.92 (3H, s), 4.90 (1H, sept, *J*=6.2 Hz), 5.19 (2H, s), 7.45 (2H, d, *J*=8.3 Hz), 8.04 (2H, d, *J*=8.2 Hz). ^{13}C NMR: δ 21.7, 52.1, 68.4, 72.4, 127.7, 129.8, 130.0, 140.4, 154.4, 166.7. IR (KBr): 2973, 1744, 1726, 1276, 1110 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{15}O_5$ 252.0998. Found 252.1004.

*4.2.8. p-Methoxycarbonylbenzyl phenyl carbonate (**1c**–**Ph**).* Yield: 93%. Mp: 80–83 °C. ^{1}H NMR: δ 3.93 (3H, s), 5.32 (2H, s), 7.17–7.19 (2H, m), 7.23–7.27 (1H, m), 7.37–7.41 (2H, m), 7.50 (2H, d, *J*=8.2 Hz), 8.07 (2H, d, *J*=8.2 Hz). ^{13}C NMR: δ 52.2, 69.3, 120.9, 126.1, 127.9, 129.5, 129.9, 130.3, 139.6, 151.0, 153.5, 166.6. IR (KBr): 1764, 1714, 1247 cm^{-1}. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{16}H_{14}O_5Na$ 309.0733. Found 309.0733.

*4.2.9. p-Cyanobenzyl methyl carbonate (**1d**-**Me**).* Yield: 89%. Mp: 91–93 °C. ^{1}H NMR: δ 3.82 (3H, s), 5.21 (2H, s), 7.49 (2H, d, *J*=8.2 Hz), 7.67 (2H, d, *J*=8.2 Hz). ^{13}C NMR: δ 55.1, 68.1, 112.2, 118.4, 128.2, 132.3, 140.4, 155.4. IR (KBr): 2965, 2225, 1746, 1383, 1293 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{10}H_9NO_3$ 191.0582. Found 191.0581. Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.87; H, 4.74; N, 7.33.

*4.2.10. p-Cyanobenzyl ethyl carbonate (**1d**-**Et**).* Yield: 87%. Mp: 56–58 °C. ^{1}H NMR: δ 1.33 (3H, t, *J*=7.3 Hz), 4.24 (2H, q, *J*=7.3 Hz), 5.20 (2H, s), 7.49 (2H, d, *J*=8.2 Hz), 7.67 (2H, d, *J*=8.2 Hz). ^{13}C NMR: δ 14.2, 64.5, 68.0, 112.2, 118.5, 128.2, 132.4, 140.6, 155.8. IR (KBr): 2225, 1738, 1264, 1020 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}NO_3$ 205.0739. Found 205.0739. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.42; H, 5.38; N, 6.83.

*4.2.11. m-Cyanobenzyl methyl carbonate (**1e**-**Me**).* Yield: 86%. Mp: 43–44 °C. ^{1}H NMR: δ 3.83 (3H, s), 5.19 (2H, s), 7.50 (1H, t, *J*=7.8 Hz), 7.65–7.61 (2H, m), 7.69 (1H, s). ^{13}C NMR: δ 55.1, 68.0, 112.8, 118.3, 129.5, 131.5, 132.0, 132.3, 136.8, 155.4. IR (KBr): 2970, 2233, 1746, 1441, 1282 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{10}H_9NO_3$ 191.0582. Found 191.0582. Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.80; H, 4.68; N, 7.33.

*4.2.12. Methyl (1-phenyl)ethyl carbonate (**3a**)*[15]. Yield: 93%. ^{1}H NMR: δ 1.59 (3H, d, *J*=6.6 Hz), 3.75 (3H, s), 5.73 (1H, q, *J*=6.6 Hz), 7.29–7.39 (5H, m).

*4.2.13. 1-(p-Methoxycarbonylphenyl)ethyl methyl carbonate (**3b**).* Yield: 60% (67% conversion). ^{1}H NMR: δ 1.59 (3H, d, *J*=6.6 Hz), 3.77 (3H, s), 3.91 (3H, s), 5.76 (1H, q, *J*=6.6 Hz), 7.44 (2H, d, *J*=8.3 Hz), 8.03 (2H, d, *J*=8.3 Hz). ^{13}C NMR: δ 22.1, 51.9, 54.5, 75.5, 125.6, 129.6, 129.7, 145.9, 154.8, 166.4. IR: 2988, 2952, 1749, 1719, 1267 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{14}O_5$ 238.0841. Found 238.0849.

*4.2.14. 1-(p-Cyanophenyl)ethyl methyl carbonate (**3c**).* Yield: 45% (52% conversion). Mp: 40–43 °C. ^{1}H NMR: δ 1.59 (3H, d, *J*=6.6 Hz), 3.78 (3H, s), 5.74 (1H, q, *J*=6.6 Hz), 7.47 (2H, d, *J*=8.2 Hz), 7.66 (2H, d, *J*=8.2 Hz). ^{13}C NMR: δ 22.2, 54.9, 75.31, 111.9, 118.5, 126.5, 132.5, 146.3, 154.9. IR (KBr): 2985, 2227, 1753, 1442, 1267, 1056, 1010, 940, 892, 836, 790 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}NO_3$ 205.0739. Found 205.0737. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.44; H, 5.38; N, 6.84.

*4.2.15. 1-(m-Cyanophenyl)ethyl methyl carbonate (**3d**).* Yield: 71% (76% conversion). ^{1}H NMR: δ 1.60 (3H, d, *J*=6.6 Hz), 3.78 (3H, s), 5.73 (1H, q, *J*=6.6 Hz), 7.48 (1H, t, *J*=7.7 Hz), 7.62–7.60 (2H, m), 7.67 (1H, s). ^{13}C NMR: δ 21.8, 54.5, 74.7, 112.3, 118.1, 129.1, 129.2, 130.1, 131.3, 142.3, 154.5. IR: 2986, 2959, 2230, 1746, 1264 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}NO_3$ 205.0739. Found 205.0739.

*4.2.16. Methyl 3-phenyl-2-propenyl carbonate (**5a**)*[16]. Yield: 96%. ^{1}H NMR (270 MHz): δ 3.81 (3H, s), 4.79 (2H, dd, *J*=1.2 and 6.4 Hz), 6.30 (1H, dt, *J*=6.4 and 16.0 Hz), 6.69 (1H, d, *J*=16.0 Hz), 7.23–7.42 (5H, m).

*4.2.17. 3-(p-Fluorophenyl)-2-propenyl methyl carbonate (**5b**).* Yield: 90%. ^{1}H NMR (270 MHz): δ 3.82 (3H, s), 4.78 (2H, d, *J*=4.4 Hz), 6.22 (1H, dt, *J*=4.4 and 10.8 Hz), 6.66 (1H, d, *J*=10.8 Hz), 7.02 (2H, t, *J*=5.9 Hz), 7.36 (2H, dd, *J*=3.7 and 5.9 Hz). ^{13}C NMR: δ 54.8, 68.2, 82.2, 115.5 (2C, d, *J*=21.5 Hz), 122.1 (d, *J*=2.1 Hz), 128.2 (2C, d, *J*=8.2 Hz), 133.5, 155.6, 162.6 (d, *J*=246.3 Hz). IR: 1751, 1509, 1442,

1281, 954, 852, 795 cm^{-1}. HRMS (GC): m/z $[M]^+$ calcd for $C_{11}H_{11}O_3F$ 210.0692. Found 210.0688.

*4.2.18. 3-(p-Methoxyphenyl)-2-propenyl methyl carbonate (**5c**).* Yield: 93%. Mp: 81–83 °C. ^1H NMR: δ 3.80 (3H, s), 3.81 (3H, s), 4.77 (2H, dd, J=1.2 and 6.7 Hz), 6.17 (1H, dt, J=6.6 and 15.9 Hz), 6.64 (1H, d, J=15.9 Hz), 6.86 (2H, d, J=8.7 Hz), 7.33 (2H, d, J=8.7 Hz). ^{13}C NMR: δ 54.8, 55.3, 68.7, 114.0, 120.0, 127.9, 128.7, 134.7, 155.7, 159.7. IR: 1751, 1607, 1515, 1441, 1386, 1274, 1177, 1032, 953, 795 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.71; H, 6.33.

*4.2.19. Biphenyl-4-yl methyl carbonate (**5d**)[16a].* Yield: 90%. ^1H NMR: δ 3.82 (3H, s), 4.81 (2H, dd, J=1.0 and 6.3 Hz), 6.34 (1H, dt, J=6.3 and 16.0 Hz), 6.73 (1H, d, J=16.0 Hz), 7.34–7.61 (9H, m).

*4.2.20. Methyl 1-methyl-4-phenyl-2-propenyl carbonate (**5e**)[17].* Yield: 85%. ^1H NMR: δ 1.47 (3H, d, J=6.6 Hz), 3.78 (3H, s), 5.37 (dquint, J=0.9 and 6.6 Hz), 6.20 (1H, dd, J=7.0 and 15.9 Hz), 6.65 (1H, d, J=15.9 Hz), 7.21–7.41 (5H, m).

4.3. Preparation of *p*-methoxycarbonylbenzyl *tert*-butyl carbonate (1c-*t*-Bu)

A solution of methyl 4-(hydroxymethyl)benzoate (10 mmol), Boc_2O (11 mmol), and $Zn(OAc)_2\cdot 2H_2O$ (1 mmol, 10 mol %) in CH_2Cl_2 (10 mL) was heated under reflux for 16 h. After the solution has been poured into ice-water, the resulting mixture was extracted with CH_2Cl_2 (30 mL×3). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated to give a crude product, which was subjected to column chromatography on silica gel to give *t*-butyl carbonate **1c-*t*-Bu** (2.23 g, 84%).

^1H NMR: δ 1.50 (9H, s), 3.92 (3H, s), 5.14 (2H, s), 7.44 (2H, d, J=8.2 Hz), 8.03 (2H, d, J=8.2 Hz). ^{13}C NMR: δ 27.6, 52.0, 67.7, 82.4, 127.5, 129.7, 129.8, 140.6, 153.1, 166.5. IR: 2981, 1744, 1727, 1277 cm^{-1}. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{18}O_5Na$ 289.1046. Found 289.1048.

4.4. Electrochemical carboxylation of benzyl carbonates 1, 3 and cinnamyl carbonates 5; general procedure

A solution of benzyl carbonate **1** (1.0 mmol) in anhyd CH_3CN (10 mL for **1** and **3**; 12 mL for **5**) containing Bu_4NBF_4 (0.1 M) was electrolyzed at 0 °C with a constant current (45 mA/cm^2) under atmospheric pressure of bubbling carbon dioxide. An undivided cell equipped with a Pt plate cathode (2×2 cm^2) and an Mg rod anode (ϕ 3 mm) was used for the electrolysis. After an appropriate amount of electricity was passed (shown in tables), the electrolyzed solution was poured into 1 M HCl (50 mL) and then extracted with Et_2O (3×30 mL). The combined ethereal solution was washed with satd $NaHCO_3$ (3×40 mL). The resulting aqueous solution was acidified with 3 M HCl and then extracted with Et_2O (3×30 mL). The combined ethereal solution was washed with satd brine and dried over $MgSO_4$. Evaporation of the solvent gave an almost pure carboxylic acid **2**.

*4.4.1. Phenylacetic acid (**2a**).* ^1H NMR (270 MHz): δ 3.65 (2H, s), 7.27–7.37 (5H, m).

*4.4.2. p-tert-Butylphenyl acetic acid (**2b**)[18].* ^1H NMR: δ 1.31 (9H, s), 3.62 (2H, s), 7.22 (2H, d, J=8.4 Hz), 7.35 (2H, d, J=8.4 Hz).

*4.4.3. p-Methoxycarbonylphenyl acetic acid (**2c**).* Mp: 112–115 °C. ^1H NMR: δ 3.72 (2H, s), 3.91 (3H, s), 7.36 (2H, d, J=8.2 Hz), 8.01 (2H, d, J=8.2 Hz). ^{13}C NMR: δ 40.8, 52.2, 129.3, 129.5, 129.9, 138.2, 166.8, 176.8. IR (KBr): 3500–2500, 1718, 1426, 1409, 1285, 1238, 1107, 763, 714 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_{10}H_{10}O_4$ 194.0579. Found 194.0570. Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.69; H, 5.01.

*4.4.4. p-Cyanophenyl acetic acid (**2d**).* Mp: 152–154 °C. ^1H NMR: δ 3.73 (2H, s), 7.41 (2H, d, J=8.2 Hz), 7.64 (2H, d, J=8.2 Hz). ^{13}C NMR: δ 41.1, 111.0, 118.7, 130.3, 132.3, 139.4, 173.7. IR (KBr): 3600–2400, 2229, 1696, 1251 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_9H_7NO_2$ 161.0477. Found 161.0477. Anal. Calcd for $C_9H_7NO_2$: C, 67.07; H, 4.38; N, 8.69. Found: C, 66.90; H, 4.38; N, 8.59.

*4.4.5. m-Cyanophenyl acetic acid (**2e**).* Mp: 116–118 °C. ^1H NMR: δ 3.71 (2H, s), 7.46 (1H, t, J=7.8 Hz), 7.52–7.56 (1H, m), 7.59–7.61 (2H, m). ^{13}C NMR: δ 40.3, 112.7, 118.4, 129.4, 131.1, 133.0, 134.0, 134.5, 176.7. IR (KBr): 3700–2400, 2228, 1697, 1412, 1223 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_9H_7NO_2$ 161.0477. Found 161.0476. Anal. Calcd for $C_9H_7NO_2$: C, 67.07; H, 4.38; N, 8.69. Found: C, 66.89; H, 4.41; N, 8.62.

*4.4.6. 2-Phenylpropanoic acid (**4a**).* ^1H NMR: δ 1.51 (3H, d, J=7.2 Hz), 3.74 (1H, q, J=7.2 Hz), 7.24–7.35 (5H, m).

*4.4.7. 2-(4-Methoxycarbonylphenyl)propanoic acid (**4b**).* Mp: 85–87 °C. ^1H NMR: δ 1.54 (3H, d, J=7.2 Hz), 3.81 (1H, q, J=7.2 Hz), 3.91 (3H, s), 7.39 (2H, d, J=8.3 Hz), 8.01 (2H, d, J=8.3 Hz). ^{13}C NMR: δ 18.0, 45.3, 52.1, 127.7, 129.3, 130.0, 144.7, 166.8, 179.8. IR (KBr): 3700–2400, 1722, 1703, 1287 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_{11}H_{12}O_4$ 208.0736. Found 208.0738. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.33; H, 5.82.

*4.4.8. 2-(4-Cyanophenyl)propanoic acid (**4c**).* Mp: 103–105 °C. ^1H NMR: δ 1.54 (3H, d, J=7.2 Hz), 3.81 (1H, q, J=7.2 Hz), 7.44 (2H, d, J=8.3 Hz), 7.63 (2H, d, J=8.3 Hz). ^{13}C NMR: δ 17.9, 45.3, 111.4, 118.5, 128.5, 132.5, 144.8, 179.4. IR (KBr): 3500–2400, 2228, 1700, 1228 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_{10}H_9NO_2$ 175.0633. Found 175.0633. Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.27; H, 5.05; N, 7.89.

*4.4.9. 2-(3-Cyanophenyl)propanoic acid (**4d**).* Mp: 85–87 °C. ^1H NMR: δ 1.55 (3H, d, J=7.2 Hz), 3.79 (1H, q, J=7.2 Hz), 7.46 (1H, t, J=7.8 Hz), 7.56–7.59 (2H, m), 7.63 (1H, s). ^{13}C NMR: δ 18.0, 44.9, 112.8, 118.5, 129.5, 131.2, 131.3, 132.2, 140.9, 179.5. IR (KBr): 3600–2400, 2229, 1697 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_{10}H_9NO_2$ 175.0633. Found 175.0633. Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.64; H, 5.17; N, 7.97.

*4.4.10. 4-Phenyl-3-butenoic acid (**6a**)[19] and 2-phenyl-3-butenoic acid (**7a**)[20].* Yield: 81%. ^1H NMR (270 MHz): δ 3.29 (0.6H, dd, J=1.1 and 7.2 Hz), 4.33 (0.7H, d, J=7.8 Hz), 5.16–5.27 (1.4H, m), 6.15–6.33 (1H, m), 5.52 (0.3H, d, J=15.9 Hz), 7.16–7.39 (5H, m).

*4.4.11. 4-(p-Fluorophenyl)-3-butenoic acid (**6b**)[19] and 2-(p-fluorophenyl)-3-butenoic acid (**7b**).* Yield: 84%. ^1H NMR (270 MHz): δ 3.28 (0.8H, dd, J=1.3 and 7.1 Hz), 4.31 (0.6H, d, J=7.8 Hz), 5.17 (0.6H, dt, J=1.1 and 17.1 Hz), 5.26 (0.6H, dt, J=1.1 and 10.2 Hz), 6.11–6.24 (1H, m), 6.48 (0.4H, d, J=16.0 Hz), 6.96–7.36 (5H, m).

*4.4.12. 4-(p-Methoxyphenyl)-3-butenoic acid (**6c**)[19] and 2-(p-methoxyphenyl)-3-butenoic acid (**7c**).* Yield: 81%. ^1H NMR (270 MHz): δ 3.27 (1H, dd, J=1.4 and 7.1 Hz), 3.79 (1.5H, s), 3.80 (1.5H, s), 4.28 (0.5H, d, J=7.9 Hz), 5.17 (0.5H, dt, J=1.1 and 17.1 Hz), 5.23 (0.5H, dt, J=1.1 and 10.2 Hz), 6.12 (0.5H, dt, J=7.1 and 15.9 Hz), 6.19 (0.5H, ddd, J=7.9, 10.2 and 17.1 Hz), 6.46 (0.5H, d, J=15.9 Hz), 6.85 (1H, d, J=8.9 Hz), 6.88 (1H, d, J=8.9 Hz), 7.24 (1H, d, J=8.9 Hz), 7.31 (1H, d, J=8.9 Hz).

*4.4.13. 4-(Biphenyl-4-yl)-3-butenoic acid (**6d**) and 2-(biphenyl-4-yl)-3-butenoic acid (**7d**).* Yield: 92%. ^1H NMR (270 MHz): δ 3.30 (0.4H, dd, J=0.9 and 7.0 Hz), 4.37 (0.8H, d, J=8.0 Hz), 5.19–5.29

(1.6H, m), 6.24 (0.8H, ddd, *J*=8.0, 10.1 and 17.1 Hz), 6.30 (0.2H, dt, *J*=7.0 and 15.9 Hz), 6.54 (0.2H, d, *J*=15.9 Hz), 7.22–7.60 (9H, m).

*4.4.14. 4-Phenyl-2-methyl-3-butenoic acid (**6e**)[21] and (E)- and (Z)-2-phenyl-3-pentenoic acid (**7e**)[22].* Yield: 87%. ^{1}H NMR (270 MHz): δ 1.38 (0.3H, d, *J*=7.1 Hz), 1.67–1.73 (2.7H, m), 3.33 (0.1H, m), 4.27 (0.73H, d, *J*=8.3 Hz), 4.62 (0.17H, d, *J*=9.4 Hz), 5.55–5.94 (1.8H, m), 6.26 (0.1H, *J*=7.9 and 16.0 Hz), 6.51 (0.1H, d, *J*=16 Hz), 7.23–7.39 (5H, m).

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