Electronic Supplementary Information for

Development of a novel electrochemical carboxylation system using a flow microreactor

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This PDF file includes:

- Instrumentation
- Materials
- Experimental procedure

1. Instrumentation

Preparative electrolyses were carried out with a Galvanostat (HOKUTO DENKO HABF-501A).

2. Materials

All reagents were purchased from commercial supplier and used without further purification. (1-Chloroethyl)benzene (**1**), (1-bromoehtyl)benzene (**1'**), benzyl chloride (**3**), 4-methoxybenzyl chloride (**5**), 4-cyanobenzyl chloride (**7**) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were purchased from Tokyo Chemical Industry. *N*,*N*-Dimethylmethanamide (DMF) was purchased from Kanto Chemical Co. CO_2 gas cylinder (>99.999%) was purchased from Toho Sanso Kogyo Co., Ltd.

3. Flow Microreactor

Figure S1 shows schematic illustration of the electrosynthetic flow microreactor. The reactor was constructed from platinum (Pt) plate anode (3 cm width, 3 cm length) and Pt, glassy carbon (GC), Stainless, Silver (Ag) or Graphite plate cathodes (3 cm width, 3 cm length). A spacer (20 ~ 80 μm thickness double faced adhesive tape) was used to leave a rectangular channel exposed, and the two electrodes were simply sandwiched together (area of the two electrodes: 1×3 cm^2). After connecting Teflon tubing to inlets and outlet, the reactor was sealed with epoxy resin (Figure S2).

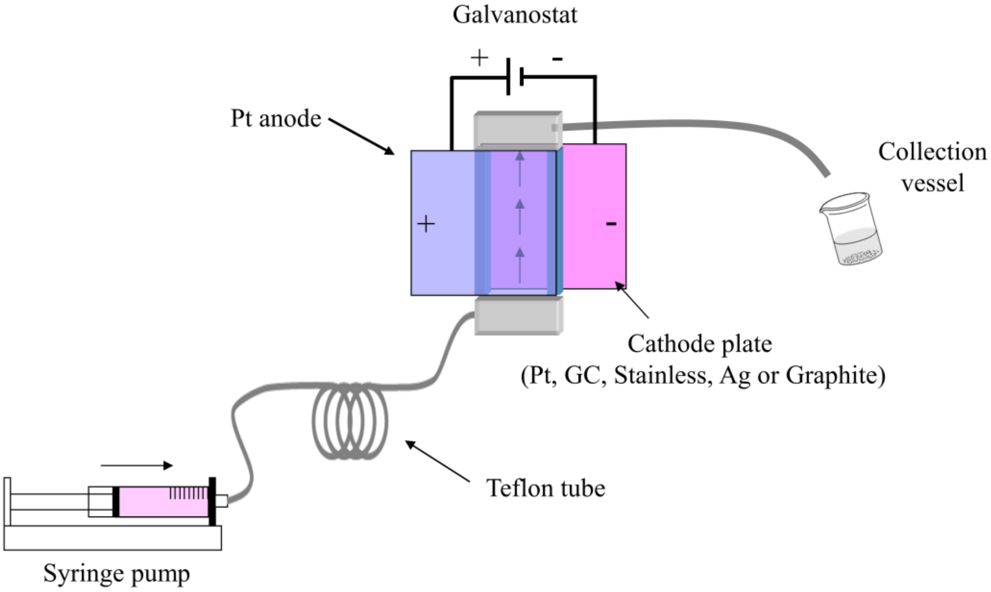

Figure S1. Schematic illustration of the electrosynthetic flow microreactor.

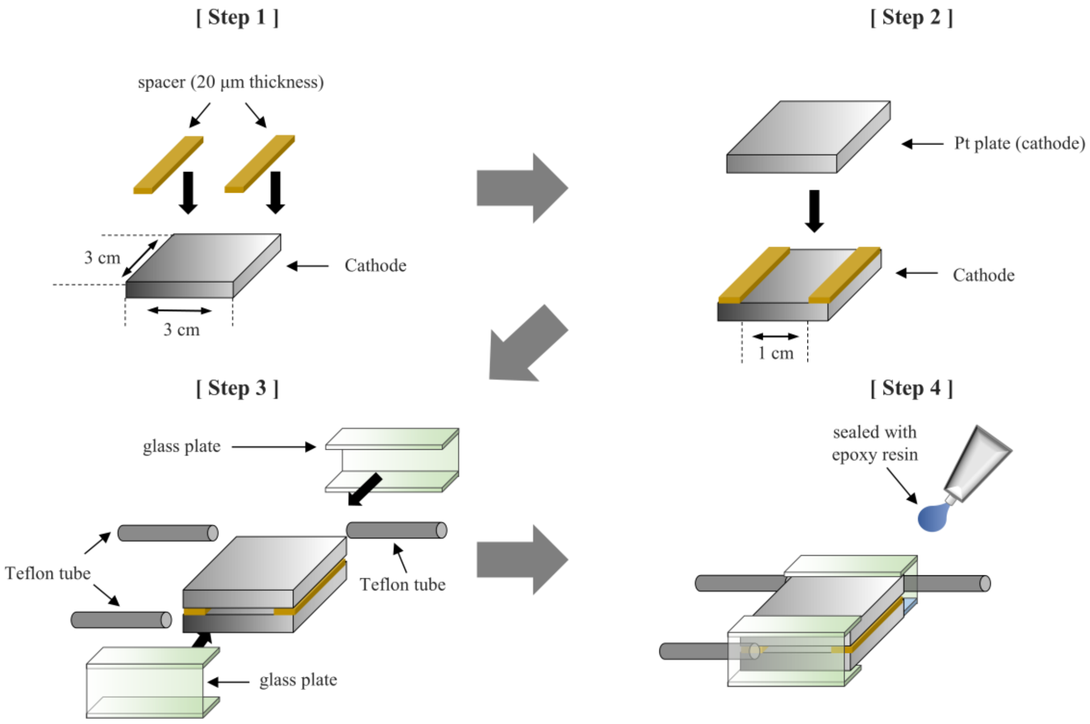

Figure S2. Schematic illustration of construction procedure for the electrochemical flow microreactor.

4. General Procedure for Electrochemical Carboxylation of (1-Chloroethyl)benzene Using Bath Type Reactor

Constant current electrolyses were conducted using a galvanostat (Hokuto Denko HABF-501). Electrochemical fixation of CO_2 to (1-chloroethyl)benzene **1** (0.1 mmol, 10 mM) was performed using Pt plate cathode (working electrode, 1.5×2 cm^2) and Mg ribbon sacrificial anode or Pt plate anode (counter electrode, 1.5×2 cm^2) in 0.1 M Bu_4NBF_4/DMF (10 mL). Electrolysis was conducted in constant current mode (18 mA cm^{-2}) under mechanical stirring with a rotating magnet bar under CO_2 bubbling. After the electrolysis, the reaction mixture was evaporated under reduced pressure. 1.0 M aqueous HCl solution was poured into residues and then extracted with diethyl ether three times. The organic phase was evaporated under reduced pressure and the crude product was diluted with MeCN, and then analyzed using high-performance liquid chromatography (HPLC; Shimadzu LC-20AD and SPD-20A) to determine the yield of carboxylated product.

5. General Procedure for Electrochemical Carboxylation of Various Benzyl Halides Using Flow Microreactors

KdScientific model 100 syringe pumps were used to pump the reaction solutions. Benzyl halides **1**, **1'**, **3**, **5**, **7** were used as substrates for the electrochemical carboxylation. The solution containing of substrate (0.2 mmol, 10 mM) and saturated CO_2 in 0.1 M Bu_4NBF_4/DMF (20 mL) was introduced into the reactor. Constant current electrolyses (18 mA cm^{-2}) were performed using the electrosynthetic flow microreactors composed of Pt plate anode (1×3 cm^2) and various cathodes (1×3 cm^2). The electrolytic solution ejected from the reactor was poured into 1.0 M aqueous HCl solution for acidification of the carboxylate ion, as shown in Figure S1. Then, the resulting solution was extracted with diethyl ether. The organic phase was analyzed using HPLC to determine the yield of carboxylated product.