

Electronic Supplementary Information for

Anodic aromatic C,C cross-coupling reaction using parallel laminar flow mode in a flow microreactor

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1. Instrumentation

Nuclear magnetic resonance (^1H NMR) spectra were measured on BRUKER DRX 300 spectrometer operating at 300 MHz (^1H NMR) in CDCl_3 . All ^1H NMR chemical shifts were reported in ppm relative to internal references of TMS at 0.00. Preparative electrolyses were carried out with a HOKUTO DENKO HABF-501A Potentiostat/Galvanostat. GCMS analyses were performed with a Shimadzu gas chromatograph mass spectrometer GCMS-QP2010.

2. Materials

Acetonitrile, acetic acid, and naphthalene (**1**) were purchased from Kanto Chemical and used as received. Pentamethylbenzene (**2**), isodurene (**5**), mesitylene (**6**), 2-bromonaphthalene (**8**), and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were purchased from Tokyo Chemical Industry and used as received.

3. Flow Microreactor

Figure S1 shows construction procedure for the electrochemical two-inlet flow microreactor. The reactor was constructed from glass plates and two platinum (Pt) plates (3 cm width, 3 cm length each) (Step 1 of Figure S1). A spacer (20 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: $1 \times 3 \text{ cm}^2$). A slit was provided on cathode side for introducing nucleophile solution into the reactor (Step 2). After connecting Teflon tubing to inlets and outlet, the reactor was sealed with epoxy resin (Steps 3 and 4).

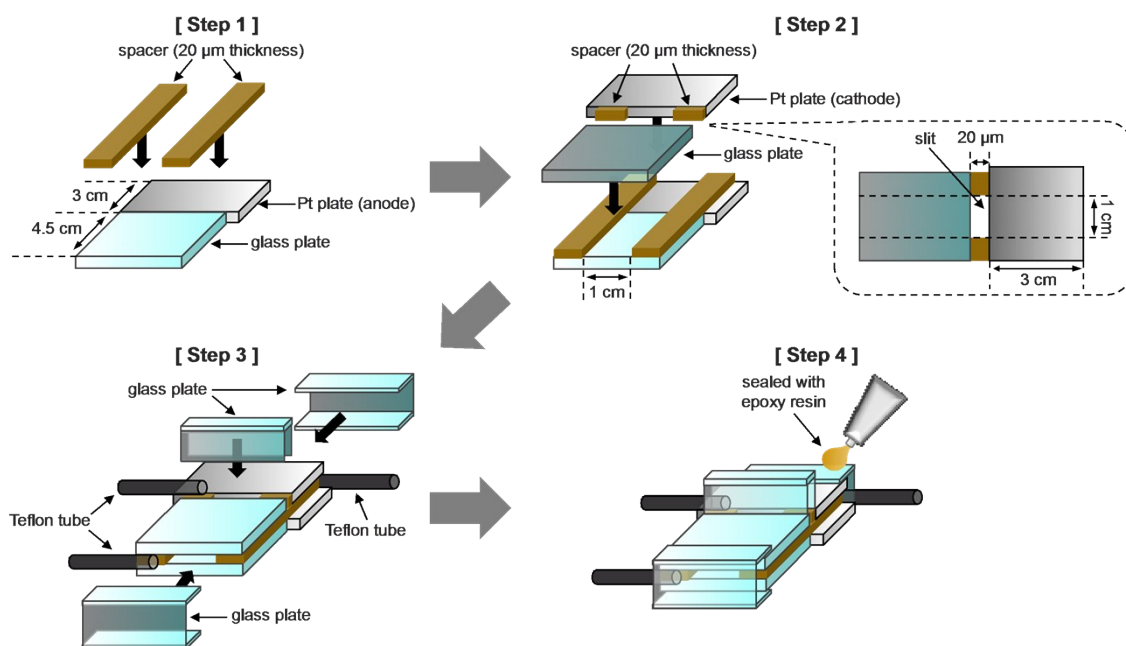


Figure S1. Construction procedure for the electrochemical two-inlet flow microreactor.

As shown in Figure S2, the inlets 1 and 2 were provided for introducing substrate and nucleophile electrolytic solutions, respectively.

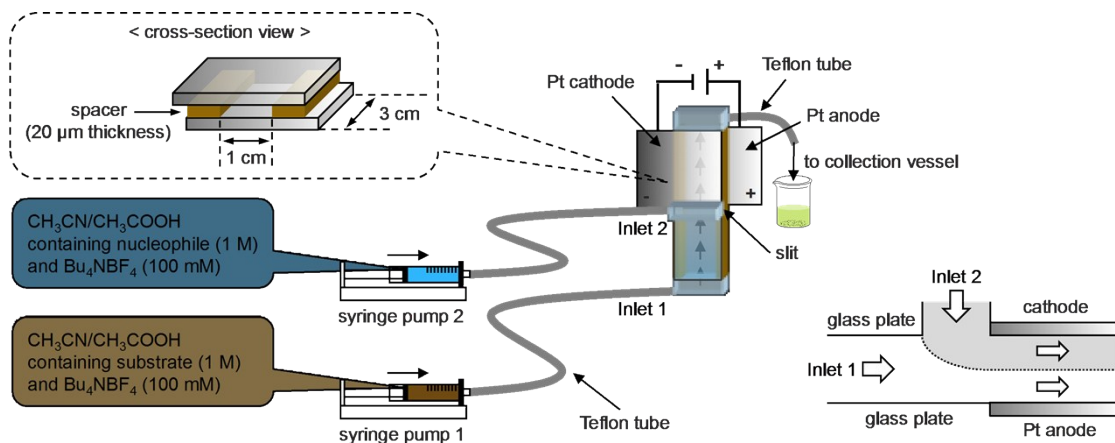


Figure S2. Schematic illustration of the electrochemical two-inlet flow microreactor.

Also another type of electrochemical two-inlet flow microreactor was constructed for the electrolysis using flow mode (c) of Table 1 in the main text. As shown in Figure S3, Teflon tubing was connected to the outlet of the flow microreactor and nucleophile electrolytic solution was introduced through the inlet 2.

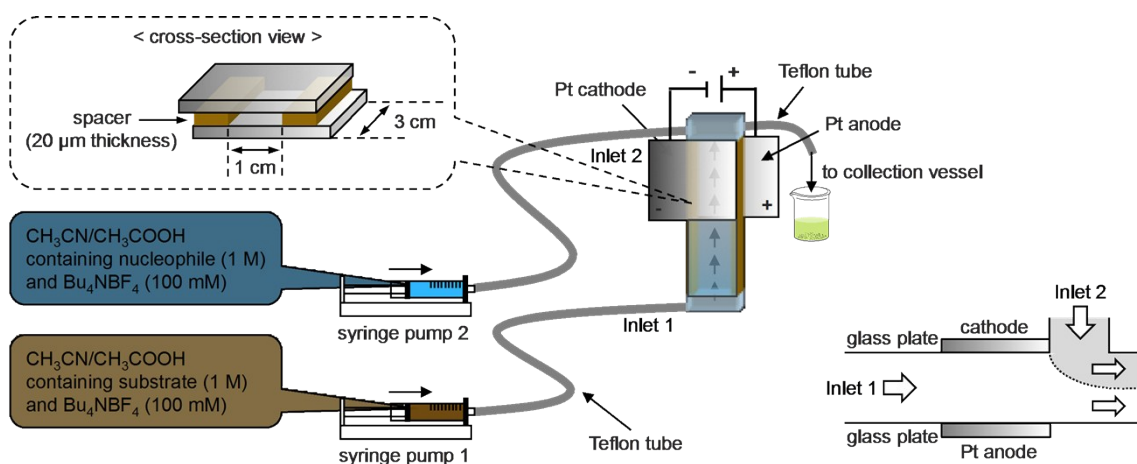


Figure S3. Schematic illustration of the electrochemical flow microreactor for flow mode (c) of Table 1 in the main text.

4. Linear Sweep Voltammetry for the Oxidation of **1**, **2**, and the Cross-Coupling Product **3**

Linear sweep voltammograms for the oxidation of substrate **1**, nucleophile **2**, and the cross-coupling product **3** were measured by using a computer-controlled electrochemical analyzer (ALS/CH Instruments 630C). Linear sweep voltammograms were recorded at a temperature of $25 \pm 2^\circ\text{C}$ using an undivided cell equipped with a working electrode (Pt disk electrode, 3 mm of diameter), a counter electrode (Pt plate, $2 \times 2\text{ cm}^2$), and a saturated calomel reference electrode (SCE).

5. General Procedure for Preparative Electrolysis Using Bath Type Cell

Bulk electrolysis was carried out using an undivided cell equipped with a working electrode (Pt plate, $2 \times 2\text{ cm}^2$) and a counter electrode (Pt plate, $2 \times 2\text{ cm}^2$) in $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$ (volume ratio = 9:1) solution (25 mL) containing naphthalene **1** (500 mM), pentamethylbenzene **2** (500 mM), and Bu_4NBF_4 (100 mM). Constant current (25 mA cm^{-2}) was applied for the electrolysis. After the charge was passed (0.2 F mol^{-1} of **1**), reaction mixture was subjected to HPLC to determine the current yield of the cross-coupling product **3**. HPLC analysis was performed by an internal standard method with a Shimadzu 880-PU equipped with UV detector (875-UV, Shimadzu) and a Mightysil column (RP-18 GP Aqua 250-4.6 ($5\text{ }\mu\text{m}$), Kanto Chemical). 1,3,5-Trimethylbenzene was used as internal standard material.

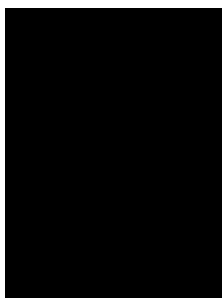
6. General Procedure for Preparative Electrolysis Using Flow Microreactors

KdScientific model 100 syringe pumps were used to pump the reaction solutions. All reactions were conducted with a constant current (25 mA cm^{-2}) and solution flowing through the electrolysis cell. Conditions of the anodic C,C cross-coupling reaction between **1** and **2** in the two-inlet flow microreactor were described in footnotes *a* of Table 1 in the main text. It is well known that the use of a capillary gap type microreactor allows to conduct electrosynthetic processes without intentionally added supporting electrolyte.¹⁻³ In this system, the electrode distance is sufficiently small enough to ensure that the electrogenerated ions derived from substrate and solvent can play the role of electrolyte, and consequently, the process becomes to be self-supported. However, the reaction media of the system are limited to protic solvents such as methanol and ethanol in all cases. Other solvents such as acetonitrile cannot be used for the self-supported systems due to the extremely high cell voltage. Hence, Bu_4NBF_4 was used as a supporting electrolyte for the present microreactor system. Reaction mixture was subjected to HPLC to determine the current yield of **3**. HPLC analysis was performed as described above. Conditions of the anodic C,C cross-coupling reaction between naphthalene derivatives and alkylbenzenes (Table 2, entry 2-4 in the main text) were described in footnotes *a* of Table 2 in the main text. Cross-coupling products **5**, **7**, and **9** were identified by literatures (**5**⁴, **7**⁵, and **9**⁵) using ^1H NMR and mass spectroscopy. ^1H NMR current yields of the crude mixture was determined with an internal standard (CH_3NO_2).

7. Synthesis and Characterization of Authentic Sample for HPLC Analysis

1-Pentamethylphenyl-naphthalene

1-Pentamethylphenyl-naphthalene was synthesized according to the literature.⁴ Bulk electrolysis was carried out using an undivided cell equipped with two working electrodes (Pt plate, $2 \times 2 \text{ cm}^2$) and two counter electrodes (Pt plate, $2 \times 2 \text{ cm}^2$) in $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$ (volume ratio = 9:1) solution (50 mL) containing naphthalene **1** (6.41 g, 50 mmol), pentamethylbenzene **2** (7.41 g, 50 mmol) and Bu_4NBF_4 (1.65 g, 5 mmol). Constant current (25 mA cm^{-2}) was applied for the electrolysis. After the charge was passed (1 F mol^{-1} of **1**), the solvent was removed by rotary evaporation and diethylether was added to the residue. Then the salt was filtered off and diethylether was removed by rotary evaporation. Crude product was purified by silica gel column chromatography (Hexane) to give white solid (9.1 % yield).



$^1\text{H-NMR}$ (300 MHz; CDCl_3): δ 1.80 (s, 6H), 2.29 (s, 6H), 2.36 (s, 3H), 7.22-7.91 (m, 7H).

MS: m/e 274 (100 % abundance), 259 (51 %), 244 (33 %), 229 (32 %).

8. References

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