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A Novel Electrosynthetic System for Anodic Substitution Reactions by Using Parallel Laminar Flow in a Microflow Reactor

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Abstract: We have developed a novel electrosynthetic system for anodic substitution reactions by using parallel laminar flow in a microflow reactor. This system enables nucleophilic reactions to overcome the restraint, such as the oxidation potential of nucleophiles and the stability of cationic intermediates, by the combined use of ionic liquids as reaction media and the parallel laminar flow in the microflow reactor. By using this novel electrosynthetic system, the anodic substitution reaction of carbamates, especially of cyclic carbamates, with allyltrimethylsilane were carried out to provide the corresponding products in moderate to good conversion yields in a single flow-through operation at ambient temperature (without the need for low-temperature conditions).

Keywords: carbamates • ionic liquids • microreactors • parallel laminar flow • substitution reactions

Introduction

Carbocations generated chemically and electrochemically are important reactive intermediates in organic synthesis.[1] Among a variety of reactions involving carbocations, especially those stabilized by neighboring heteroatoms, such as oxygen (alkoxycarbenium ion) and nitrogen (iminium ion), nucleophilic reactions between carbocations and carbon nucleophiles are one of the most important reactions because they are straightforward approaches to carbon–carbon bond formation.[2] Nevertheless, cations like alkoxycarbenium and iminium ions are still unstable intermediates at ambient temperature, and hence the oxidative generation of cations often has to be conducted in the presence of carbon nucleophiles. However, in general, the oxidation potentials of carbon nucleophiles are lower than those of organic substrates, and therefore the presence of the nucleophiles would prevent oxidation of organic substrates.[3] In this regard, two-step transformations have been used to achieve an oxidative carbon–carbon bond formation.[4] In addition, Yoshida et al. have recently developed a “cation pool” method that involves generation and accumulation of highly reactive carbocations by electrolysis.[5] Although this method enables the manipulation of cationic intermediates to achieve direct oxidative C–C bond formation, the process must be conducted with a very low temperature and its applicability strongly depends on the stability of the carbocation that is accumulated.

On the other hand, microflow reactors enable the precise control of reactive intermediates and thereby facilitate highly selective reactions that are difficult to achieve in conventional reactors,[6] because microflow reactors have several advantages, such as large specific interfacial area (liquid–liquid or liquid–solid), short molecular diffusion distance, and short residence time in reactors.[7] Such advantages would favorably affect heterogeneous processes, and therefore the application of the microflow system to heterogeneous processes, particularly electrosynthetic processes, has received much attention.[8] On the basis of the above advantages of the microflow reactor, Yoshida and co-workers have successfully demonstrated that *N*-acyliminium ions can be generated by a microflow electrochemical system with at a very low temperature. These are then immediately transferred to a vessel in which a nucleophilic reaction takes place to give the final coupling products with high selectivity.[9]

On the other hand, the channel of the microflow reactor is small enough to insure that the flow is stable and laminar. As shown in Figure 1, when two solutions are introduced through the two inlets (named as inlets 1 and 2 in Figure 1), a stable liquid–liquid interface can be formed, and mass transfer between input streams occurs only by means of diffusion. Hence substrates would be oxidized dominantly to

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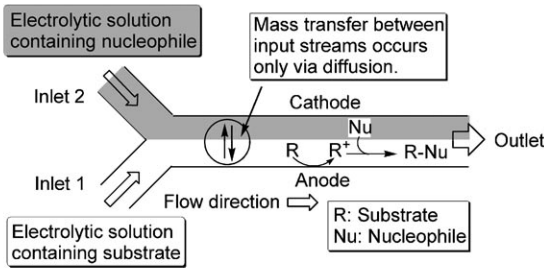
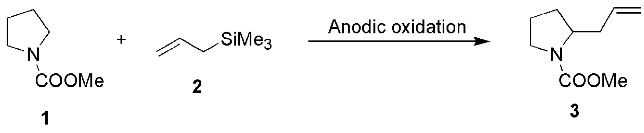


Figure 1. Schematic representation of parallel laminar flow in the microflow reactor. The illustrated model reaction is an anodic substitution reaction.

generate cationic intermediates, whereas oxidation of nucleophiles would be avoided when the opposing sidewalls of the channel are the anode and cathode, and substrate and nucleophilic solutions are introduced through inlet 1 (anode side inlet) and inlet 2 (cathode side inlet), respectively. Consequently, the cationic intermediates generated at the anode would rapidly diffuse into the bulk electrolytic solution and react with nucleophiles to afford the desired products. Thus, this system would enable nucleophilic reactions to overcome the restraints, such as the oxidation potential of the nucleophiles and the stability of cationic intermediates. Moreover, the reactions would be carried out without the need for low-temperature conditions.

In fact, we recently reported that the anodic substitution reaction of *N*-(methoxycarbonyl)pyrrolidine (**1**) (oxidation potential $E_{ox} = 1.91$ V vs. Ag/AgCl) with allyltrimethylsilane (**2**) (oxidation potential $E_{ox} = 1.75$ V vs. Ag/AgCl) could be conducted to give the desired product **3** in good yield by using parallel laminar flow in a microflow reactor at ambient temperature (Scheme 1).[10]



Scheme 1. Anodic substitution reaction of **1** with **2**.

The successful preliminary results prompted us to perform a systematic study of the anodic substitution reaction of a variety of carbamates. Herein, we wish to report the details of our study of the anodic substitution reactions of carbamates with **2** by using parallel laminar flow in microflow reactors.

Results and Discussion

First of all, to confirm that **2** was prevented from reaching the anode by the use of parallel laminar flow, we measured linear sweep voltammograms for the oxidation of nucleophile **2** in 0.1 M *n*-tetrabutylammonium tetrafluoroborate (nBu$_4$NBF$_4$)/acetonitrile in the microflow reactor. As shown in Figure 2a, the oxidation peak of **2** could be observed clearly at 2.3 V vs. Fc/Fc$^+$ when an electrolytic stream containing **2** entered only through inlet 1. On the other hand, the peak current was decreased appreciably when an electrolytic solution with **2** was introduced through inlet 2 and a solution without **2** was introduced through inlet 1, as shown in Figure 2b. These results apparently indicate that the use of parallel laminar flow did prevent **2** from reaching the anode when it was introduced through inlet 2.

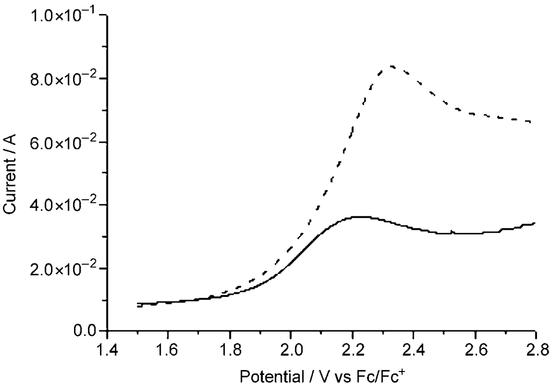


Figure 2. Linear sweep voltammograms for the oxidation of **2** in 0.1 M nBuNBF$_4$/acetonitrile in a microflow reactor at 20 °C. The Ag wire reference electrode was externally placed downstream near the outlet of the microflow reactor. Scan rate = 0.5 V s^{-1}. a) The electrolytic solution containing **2** (0.05 M) was introduced through inlet 1 at a flow rate of 0.2 mL min^{-1} (-----). b) The electrolytic solution with **2** (0.05 M) was introduced through inlet 2 and the electrolytic solution without **2** was introduced through inlet 1 at a flow rate of 0.1 mL min^{-1} each (——).

Subsequently, we carried out the anodic substitution reaction of substrate **1** (0.01 M) with nucleophile **2** (0.1 M) at the preparative scale. When an acetonitrile electrolytic solution containing both **1** and **2** was introduced through inlet 1 at a flow rate of 0.2 mL min^{-1}, both the yield and the percent conversion of **1** were low (36 % conversion, 6 % yield). In this case, **2** was probably oxidized preferentially, since substrate **1** ($E_{ox} = 1.91$ V vs. Ag/AgCl) is less easily oxidized than nucleophile **2** ($E_{ox} = 1.75$ V vs. Ag/AgCl). On the other hand, as shown in Table 1, entry 1, the use of the parallel laminar flow mode led to an improvement in the conversion of **1**. In this demonstration, because the electrolytic solutions containing **1** and **2** were introduced through inlets 1 and 2, respectively, **1** should be oxidized dominantly. However, a low yield problem still remained. This was ascribed to decomposition of the anodically generated *N*-acyliminium ion in the acetonitrile electrolytic solution before trapping by **2** at ambient temperature. To overcome this problem, the reaction was carried out in 2,2,2-trifluoroethanol (TFE), which is known as a stabilizing solvent for cationic intermediates.[11] As a result, the conversion yield of **3** was increased dramatically (entry 2). Moreover, it should be noted that the yield of **3** was improved further when ionic liquids, such as 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF$_4$],

Table 1. Anodic substitution reaction of **1** with **2** by using the parallel laminar flow mode.[a]

Entry	Electrolytic solution	Conversion of **1** [%][b]	Yield of **3** [%][b,c]
1	0.1 M nBuN_4BF_4/acetonitrile	73	0.6
2	0.1 M nBuN_4BF_4/TFE	58	59
3	[emim][BF_4]	61	62
4	[emim][TFSI]	66	73
5	[deme][TFSI]	54	91 (71)[d]
6	[deme][TFSI][e]	51	87

[a] The flow rates of two electrolytic solutions containing **1** and **2**, respectively, were fixed at 0.1 mL min^{-1} each. Current density = 3 mA cm^{-2}. The reaction temperature was kept at 20 °C. [b] Determined by GC. [c] Yields based on the amount of consumed starting material. [d] Isolated yield in parenthesis. [e] The recovered [deme][TFSI] was reused for the reaction.

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [emim][TFSI], and *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide [deme][TFSI] were used as reaction media (entries 3–5). These results apparently suggest that ionic liquids have an excellent stabilizing ability for the cationic intermediate, and hence the *N*-acyliminium ion generated oxidatively from **1** could react with **2** before its decomposition. In addition, an ionic liquid, such as [deme][TFSI], was easily recovered after the electrolysis simply by extracting the remaining substrate and product with diethyl ether, and the recovered [deme][TFSI] could be reused without significant loss of reactivity for the anodic substitution reaction (see entry 6).

To evaluate the stability of the cationic intermediate generated anodically from **1** in the electrolytic media used, we measured the in situ FTIRA (Fourier transform infrared reflection absorption) spectra of the cation in 0.1 M $n\mathrm{Bu_4NBF_4}$/acetonitrile and [deme][TFSI], respectively.[12] After 20 s of an applied potential (2.4 V vs. Fc/Fc$^+$), a new IR signal appeared at 1815 cm^{-1} (see Figure 3). The band at 1815 cm^{-1} is consistent with the band reported in the literature (1814 cm^{-1}).[9] Figures 4 and 5 show the continual observation of the IR shift of anodically generated cationic intermediates and the change of normalized absorbance of the IR signal at 1815 cm^{-1}, respectively, after stopping the potential application. In 0.1 M $n\mathrm{Bu_4NBF_4}$/acetonitrile electrolytic solution, absorbance of the cationic intermediate decreased dramatically. In contrast, in [deme][TFSI], absorbance of the cation decayed very slowly even at ambient temperature (24 °C). From these results, it is confirmed that ionic liquids have an excellent ability to stabilize the cationic intermediate.

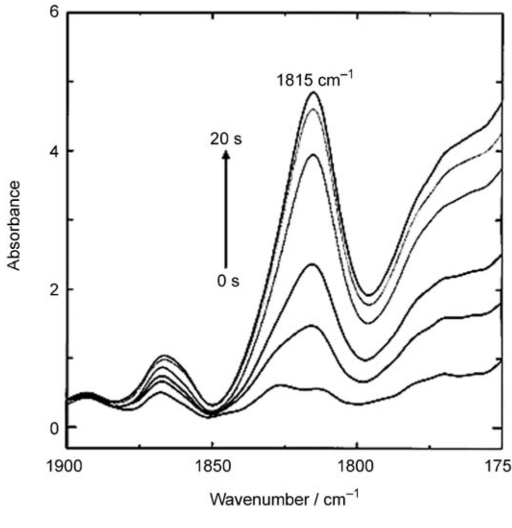


Figure 3. Continuous observation of **1** (0.1 M) at the Pt disk electrode in [deme][TSFI] by using a FTS-6000 FTIR spectrometer under an applied electrolytic potential at ambient temperature (24 °C).

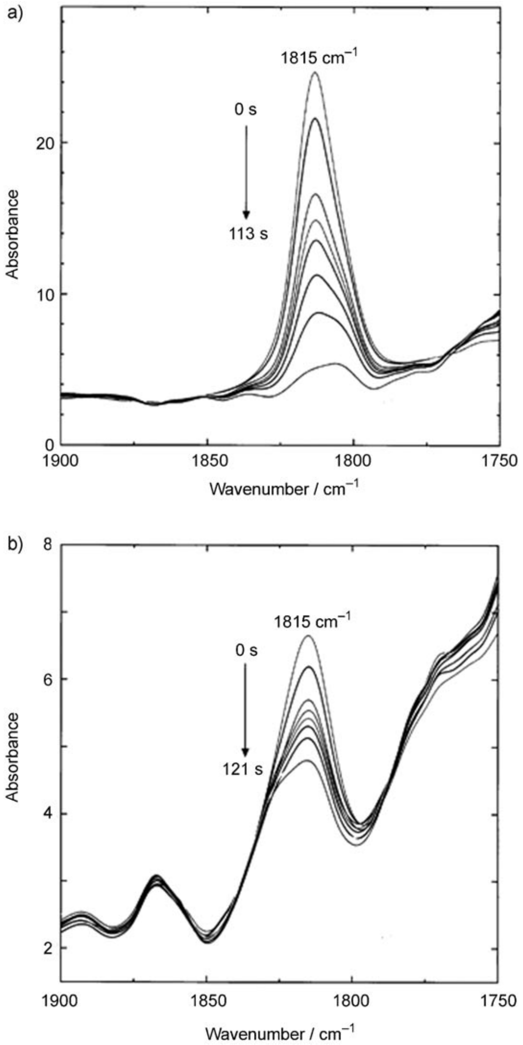


Figure 4. Continuous observation of **1** (0.1 M) at a Pt disk electrode by using an FTS-6000 FTIR spectrometer after stopping the potential application at ambient temperature (24 °C). Electrolytic solution: a) 0.1 M $n\mathrm{Bu_4NBF_4}$/acetonitrile, b) [deme][TFSI].

Next, we investigated the utility of the parallel laminar flow mode illustrated in Figure 6 a for the effective production of **3** in the anodic substitution reaction of substrate **1** with nucleophile **2**. In the previous section, we confirmed that the cationic intermediate generated from **1** could be

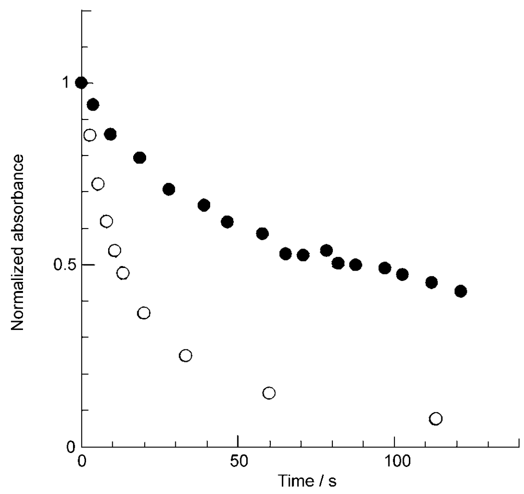


Figure 5. Time changes in the absorbance of the cationic intermediate at 1815 cm^{-1} observed after electrolysis of substrate **1** (0.1 M) in 0.1 M nBu_4NBF_4/acetonitrile (○) and [deme][TFSI] (●), respectively, at 24 °C.

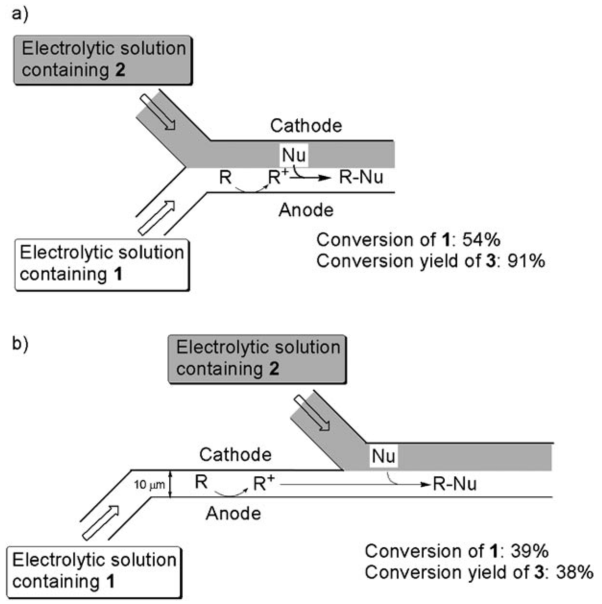


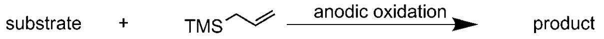
Figure 6. Schematic illustration of two kinds of flow modes for the microflow reactor and their application to the anodic substitution reaction of **1** with **2**. a) Parallel laminar flow mode in an electric field, b) single laminar flow mode in an electric field. The flow rates of two electrolytic solutions containing **1** and **2**, respectively, were fixed at 0.1 mL min^{-1} each. Current density = 3 mA cm^{-2}. The reaction temperature was kept at 20 °C. Electrode areas of reactor a) and b) were 1 × 3 cm^2 each. The concentrations of **1** and **2** were 0.01 M and 0.1 M, respectively.

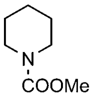
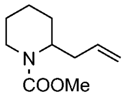
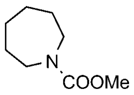
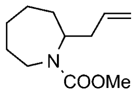
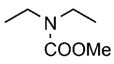
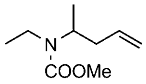
stabilized appreciably in the ionic liquids. Therefore, if the intermediate can be transferred to the outlet of the electrochemical reactor without its decomposition by using ionic liquids, a flow mode (Figure 6b), in which an electrolytic solution with **2** is introduced at the outlet of the electrochemical reactor, would be useful for the effective production of **3**. In practice, however, the conversion yield of **3** (38 %) was significantly low compared with the result obtained by the use of the parallel laminar flow mode illustrated in Figure 6a. This is ascribed to the fact that the stability of the *N*-acyliminium ion generated from **1** was insufficient to transfer it to the outlet of the reactor without decomposition, even by using the ionic liquid as the reaction medium. In contrast, in the parallel laminar flow, nucleophile **2** can be provided in situ with the unstable intermediate, and thereby the cationic intermediate is effectively trapped before its decomposition. Hence, it can be stated that the parallel laminar flow mode is essentially required for an efficient anodic substitution reaction.

Finally, to demonstrate the generality of this new methodology, we also investigated the anodic substitution reactions of other carbamates with **2**. As shown in Table 2, entry 1, when the anodic substitution reaction of **4** was carried out by using the parallel laminar flow mode, the conversion yield of **5** was low compared to the case with substrate **1**. This result suggests that the stability of the anodically generated cationic intermediate from **4** is lower than that from **1** and consequently the cation from **4** might be decomposed before trapping by **2** even in [deme][TFSI]. This was actually supported by observations from in situ FTIRA, that is, the IR shift signal assigned to the cation from **4** (ca. 1832 cm^{-1})[13] could not be observed in the spectra during the electrooxidation of **4** in [deme][TFSI] (Figure 7).

Meanwhile, Chiba et al. reported that the use of moderately acidic conditions, by the addition of acetic acid, assists nucleophilic attack of nucleophiles by further stabilization of the cationic intermediates.[14] Hence, we then carried out the anodic substitution reaction of **4** with **2** in [deme][TFSI] containing 0.08 M acetic acid. As a result, the conversion yield of **5** was increased dramatically (Table 2, entry 2). Sub-

Table 2. Anodic substitution reaction of carbamates with **2** by using the parallel laminar flow mode.[a]



Entry	Substrate	Product	Conversion [%][b]	Yield [%][c]
1	 **4**	 **5**	45	37
2[d]			42	52
3[d]	 **6**	 **7**	42	62
4[d]	 **8**	 **9**	42	12

[a] The flow rates of two [deme][TFSI] solutions containing substrate and **2**, respectively, were fixed at 0.05 mL min^{-1} each. Current density = 3 mA cm^{-2}. The reaction temperature was kept at 20 °C. [b] Determined by GC. [c] Yields based on the amount of consumed starting material. [d] Acetic acid (0.08 M) was added.

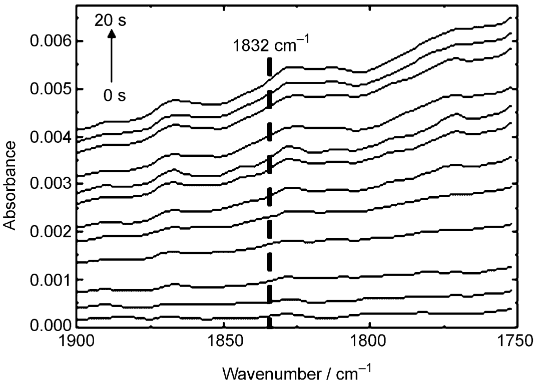


Figure 7. Continuous observation of an anodically generated cationic intermediate from **4** at the Pt disk electrode in [deme][TSFI] by using an FTS-6000 FTIR spectrometer under an applied electrolytic potential at ambient temperature (24 °C).

sequently, the anodic substitution reaction of **6** was carried out to provide **7** in good yield (entry 3). On the other hand, the anodic substitution reaction of **8** took place to provide **9** in low yield, even in the ionic liquid containing acetic acid (entry 4). From these results, the efficiency of the anodic substitution reaction of carbamates by using our system seems to depend greatly on the stability of the anodically generated cationic intermediate, and therefore application of our system to reactions that involve highly unstable cationic intermediates is still limited, even by the use of ionic liquids as reaction media.

Conclusions

We have developed a novel electrosynthetic system for the anodic substitution reaction of cyclic carbamates by using parallel laminar flow in a microflow reactor. This new methodology has many practical advantages and characteristics: 1) efficient nucleophilic reactions in a single flow-through operation, 2) selective oxidation of substrates without affecting the oxidation of nucleophile, 3) stabilization of the cationic intermediates, even at ambient temperatures, by the use of ionic liquids as reaction media, and 4) effective trapping of unstable cationic intermediates with a nucleophile. It is hoped that this facile and novel electrolytic system will open a new aspect not only of synthetic electrochemistry but also of general synthetic chemistry.

Experimental Section

Materials: Dehydrated acetonitrile was purchased from Wako Pure Chemical Industries and used as received. [deme][TFSI], [emim][BF], and [emim][TFSI] were purchased from Kanto Chemical and used as received. Allyltrimethylsilane (**2**), TFE, and $n\mathrm{Bu_4NBF_4}$ were purchased from Tokyo Kasei Kogyo and used as received. *N*-(Methoxycarbonyl)pyrrolidine (**1**), *N*-(methoxycarbonyl)piperidine (**4**), *N*-(methoxycarbonyl)-hexamethylimine (**6**), *N*-(methoxycarbonyl)diethylamine (**8**), methyl 2-(2-propenyl)pyrrolidinecarboxylate (**3**), methyl 2-(2-propenyl)piperidinecarboxylate (**5**), methyl 2-(2-propenyl)hexamethyliminecarboxylate (**7**), and methyl 2-(2-propenyl)diethylaminecarboxylate (**9**) were synthesized according to the literature.[15–18]

Microflow reactor: The microflow reactor consisted of both a platinum (Pt) (3 cm width, 3 cm length) and a glass plate (2.6 cm width, 3 cm length) that were glued together. A slit was provided on the cathode side for introducing the nucleophilic solutions into the reactor, as shown in Figure 8. A spacer (both sides adhesive tape, 20 μm thickness, Nitto Denko) was used to leave a rectangular channel exposed, and the two plates were simply sandwiched together. After connecting Teflon tubing to the inlets and the outlet, the reactor was sealed with epoxy resin. The dimensions of the channel were 1 cm wide, 20 μm high, and 6 cm long and the area of the two electrodes was 3 cm^2.

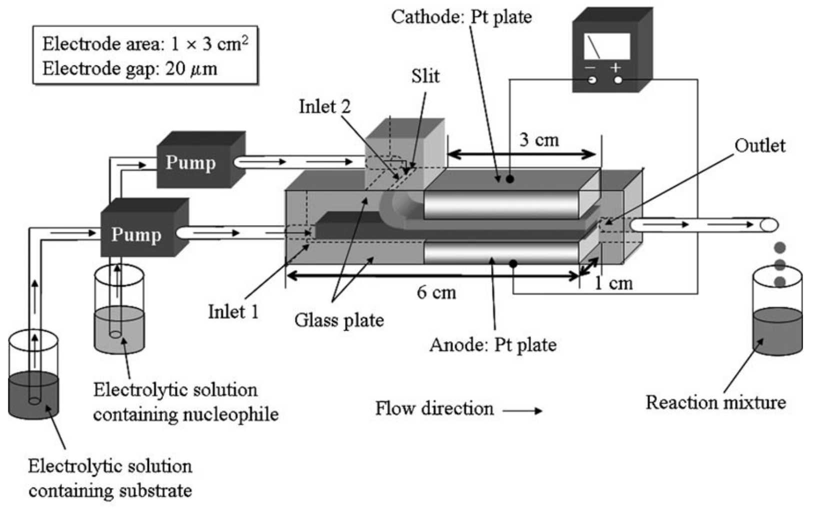


Figure 8. Schematic representation of the microflow reactor for the anodic substitution reaction with parallel laminar flow.

Linear sweep voltammetry: The linear sweep voltammetry in the microflow reactor was performed by a computer-controlled electrochemical system (ALS/CH Instruments 630C). Linear sweep voltammograms were recorded at (20 ± 2) °C in a Pt working electrode/Pt counter electrode flow reactor. The area of the electrode was 1 × 3 cm^2. An Ag wire (0.2 mm ϕ) was used as the reference electrode and was externally placed downstream near the outlet of the microflow reactor. Potentials are referenced to that of the reversible oxidation of ferrocene (Fc). The steady pressure-driven flow was created by a syringe pump (kdScientific model 100) from inlets 1 and 2.

Preparative electrolysis experiments: Preparative electrolysis experiments were carried out with a Potentiostat/Galvanostat (HA 501, Hokuto Denko, Japan). Anodic substitution reactions of the substrate (0.01 M) with **2** (0.1 M) were conducted with a constant current (3 mA cm^{-2}) and with solution flowing through the electrolysis cell. The flow rates of two electrolytic solutions containing substrate and **2**, respectively, were fixed at 0.1 mL min^{-1} each. The reaction temperature was 20 °C. Electrolyzed solutions (1.0 mL) were collected and then analyzed by GC to determine substrate conversions and product yields. The GC analysis was performed by an external standard method with a Shimadzu GC-8A gas chromatograph equipped with an FID detector and a Tween 80 column (2 m). In the case of the reaction by using [deme][TFSI] as an electrolytic medium, electrolyzed solution (100 mL) was collected and then the reaction mixture was extracted with diethyl ether. After the removal of diethyl ether under reduced pressure, the residue was purified by a preparative HPLC (LC-6AD, Shimadzu) equipped with a UV detector (SPD-10A, Shimadzu) and an ODS column (20 mm $\phi \times 500$ mm, Superiorex ODS, Shiseido) to give product **3** in a 71 % yield (based on the amount of consumed starting material). ^{1}H NMR (270 MHz, $CDCl_3$) of **3**: $\delta = 1.61$–1.95 (m, 4H), 2.03–2.20 (m, 1H), 2.36–2.63 (m, 1H), 3.27–3.52 (m, 2H), 3.69 (s, 3H), 3.76–3.99 (m, 1H), 4.95–5.13 (m, 2H), 5.62–5.85 ppm (m, 1H); NMR data of **3** was actually consistent with that in the literature, see reference [9]. After the extraction, the [deme][TFSI] phase was treated under reduced pressure for one day to remove the remaining diethyl ether and moisture, and was then reused for the anodic substitution reaction of **1** with **2** to demonstrate its recyclability.

In situ FTIRA measurements: Cationic intermediates generated anodically were observed by using an FTS-6000 FTIR spectrometer (Bio-Rad Laboratories) equipped with a liquid N_2 cooled wide-band MCT detector. The spectroelectrochemical cell was equipped with Pt disc working electrode (10 mm in diameter), a Pt wire auxiliary electrode, and an Ag wire reference electrode. Potentials are referenced to that of the reversible oxidation of Fc. IR shift data were recorded at ambient temperature (24 °C). The substrate (0.1 M) was dissolved in an electrolytic solution, and an electrolytic potential (2.4 V vs. Fc/Fc^+) was applied.

DFT calculations: DFT calculations were carried out at the B3LYP/6-31G(d) level with full geometry optimization by using the G98W program.[19] Frequencies are scaled by the factor of 0.9668.

Acknowledgements

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