Development of an Anodic Substitution Reaction System Using Acoustic Emulsification

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SUPPLEMENTARY INFORMATION

General remarks.

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM EX-270 (^{1}H 270 MHz, ^{13}C 68 MHz) spectrometer in $CDCl_3$. The chemical shifts for ^{1}H and ^{13}C NMR spectra were given in δ (ppm) from internal trimethylsilane (TMS) and chloroform respectively. LR mass spectra were measured with Shimadzu GCMS-QP5050A mass spectrometer and HR mass spectra were measured with JEOL JMS-700 mass spectrometer. IR spectra were measured with Shimadzu FTIR-1800A spectrometer. Linear sweep voltammetry and preparative electrolysis were performed by using a potentio-galvanostat (HABF501, Hokuto Denko, Japan).

Materials.

1-Ethyl-3-methylimidazorium tetrafluoroborate (EMIM BF_4) was purchased from Kanto Chem. Co. and used after drying under vacuum for 24 h. Acetonitrile and diethyl ether were purchased from Kanto Chem. Co. and used as received. Allyltrimethylsilane (**2**), *N*-(acetyl) pyrrolidine (**4**) and tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) were purchased from Tokyo Kasei Kogyo Co. and used as received. *N*-(methoxycarbonyl) pyrrolidine (**1**), methyl 2-(2-propenyl) pyrrolidinecarboxylate (**3**), 1-(2-Allyl-pyrrolidine-1-yl) ethanone (**5**), *N*-(methoxycarbonyl) piperidine (**6**), methyl 2-(2-propenyl) piperidinecarboxylate (**7**) and *N*-(methoxycarbonyl) dimethylamine (**8**) were prepared according to a literature procedure, respectively.[1-3] The ^{1}H NMR and mass spectral data of all of the prepared compounds were consistent with the expected structure.[4,5]

Investigation of suitable electrolytic medium for our electrosynthetic system.

In this system, the electrolytic medium needs to possess the solubilizing ability for a substrate, but should not exhibit solubilizing ability for a nucleophile such as allyltrimethylsilane. From the above point of view, we explored suitable electrolytic medium by the following procedures. From the next sentence, acetonitrile and EMIM BF_4 take as example media. The 0.2 ml of allyltrimethylsilane was added to the 0.8 ml of acetonitrile and EMIM BF_4 including a piece of methylene blue (methylene blue was used as an indicator for the phase separation). Allyltrimethylsilane was soon dissolved in acetonitrile as shown in Figure S1(a). In the contrast, allyltrimethylsilane could hardly dissolve in EMIM BF_4, and consequently the mixture was separated into an upper phase (allyltrimethylsilane) and a lower phase (EMIM BF_4) as shown in Figure S1(b). These results indicated that EMIM BF_4 is better electrolytic medium for our system.

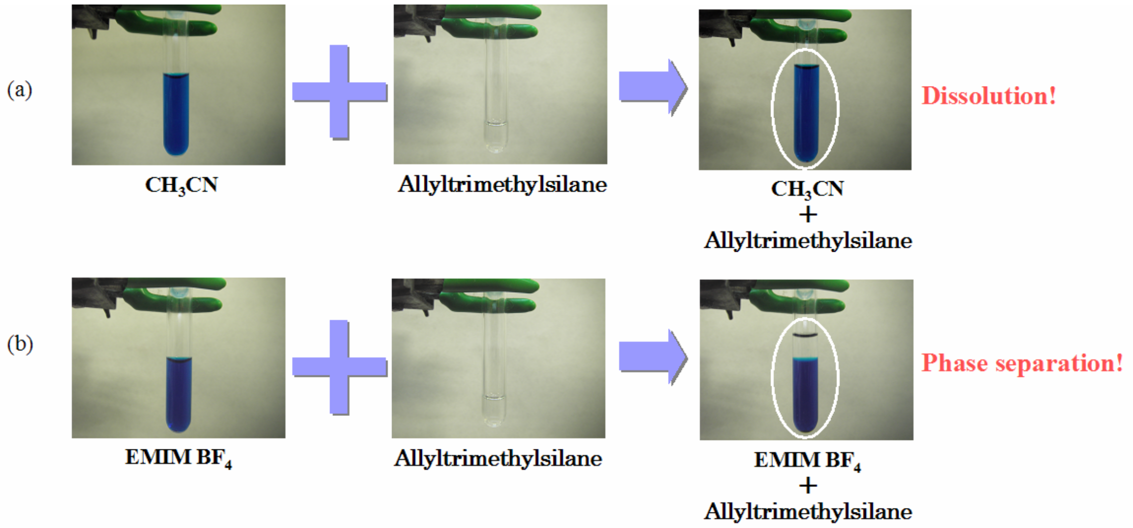

Figure S1. Dissolution and phase separation of allyltrimethylsilane in (a) acetonitrile and (b) EMIM BF_4 (acetonitrile and EMIM BF_4 layers were colored by methylene blue).

Linear sweep voltammetry of *N*-(methoxycarbonyl) pyrrolidine (1) and allyltrimethylsilane (2).

Linear sweep voltammograms for oxidation of **1** (1 mmol), **2** (1 mmol) and mixture of them were measured with a three-electrode system using a platinum plate (1×1 cm^2) working electrode, a platinum plate (2×2 cm^2) counter electrode, and a saturated calomel electrode (SCE) as a reference electrode in 10 ml of 0.1 M *n*-Bu_4NBF_4/acetonitrile solution or EMIM BF_4 under ultrasonication at a solution temperature of 25 ± 1 °C.

Measurement of supporting electrolyte concentration in nucleophile (allyltrimethylsilane) phase.

1 ml of allyltrimethylsilane was added to 5 ml of EMIM BF_4. Next, the solution was left to stand for 12 h at 25°C, and then 0.5 ml of allyltrimethylsilane phase was pipetted into the 25 ml plastic graduated flask and diluted with acetonitrile. Subsequently, the concentration of boron in the sample solution was measured by inductively coupled plasma spectrometry (ICPS-8100, Shimadzu Co.).

Measurement of partition ratio.

The 0.3 mmol of **1** or **3** was added to the mixture of 3 ml of EMIM BF_4 and 0.5 ml (ca. 3 mmol) of allyltrimethylsilane. Next, the solutions were left to stand for 12 h at 25°C, and then 0.1 ml of allyltrimethylsilane phase was pipetted into 5 ml glass graduated flask and diluted with acetonitrile. Subsequently, the partition ratio of substrate **1** or product **3** between electrolytic medium (EMIM BF_4) and nucleophile phase (allyltrimethylsilane) were determined by gas chromatography (GC-2014 with Tween 80, 3 m column, Shimadzu, Japan).

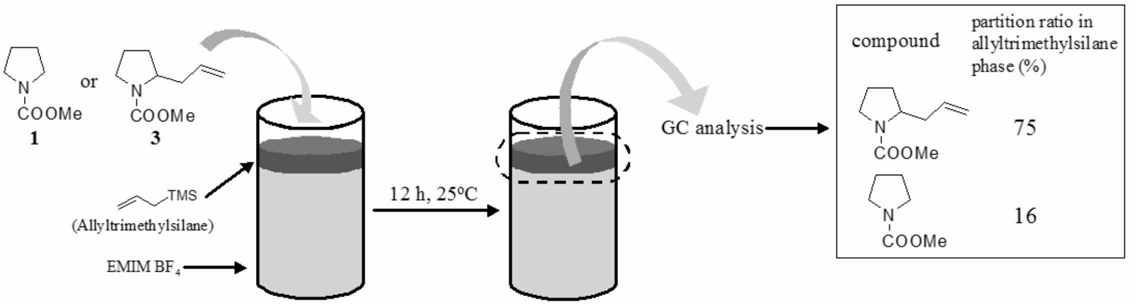

Figure S2. Schematic illustration of the experimental procedures for the measurement of partition ratio.

Linear sweep voltammetry of methyl 2-(2-propenyl) pyrrolidinecarboxylate (3) in the absence and presence of nucleophile droplets.

Linear sweep voltammograms of **3** were recorded with same system used for measurement of the starting substrate **1**. As shown in Figure S3(i), the anodic oxidation of **3** was proceeded smoothly in the absence of allyltrimethylsilane. On the other hand, the oxidation current was decreased appreciably in the presence of the nucleophile droplet (Figure S3(ii)). This result also indicates that allylated product **3** was extracted from EMIM BF_4 electrolytic medium into the nucleophile phase, and consequently the overoxidation of **3** was suppressed effectively.

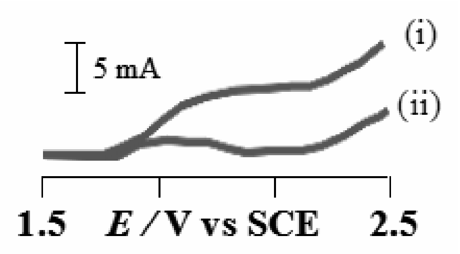

Figure S3. Linear sweep voltammograms of (i) 0.1 M methyl 2-(2-propenyl) pyrrolidinecarboxylate and (ii) 0.1 M methyl 2-(2-propenyl) pyrrolidinecarboxylate with 0.1 M allyltrimethylsilane in EMIM BF_4 under ultrasonication. Scan rate was 0.1 V s^{-1}.

References (Electronic Supplementary Information)

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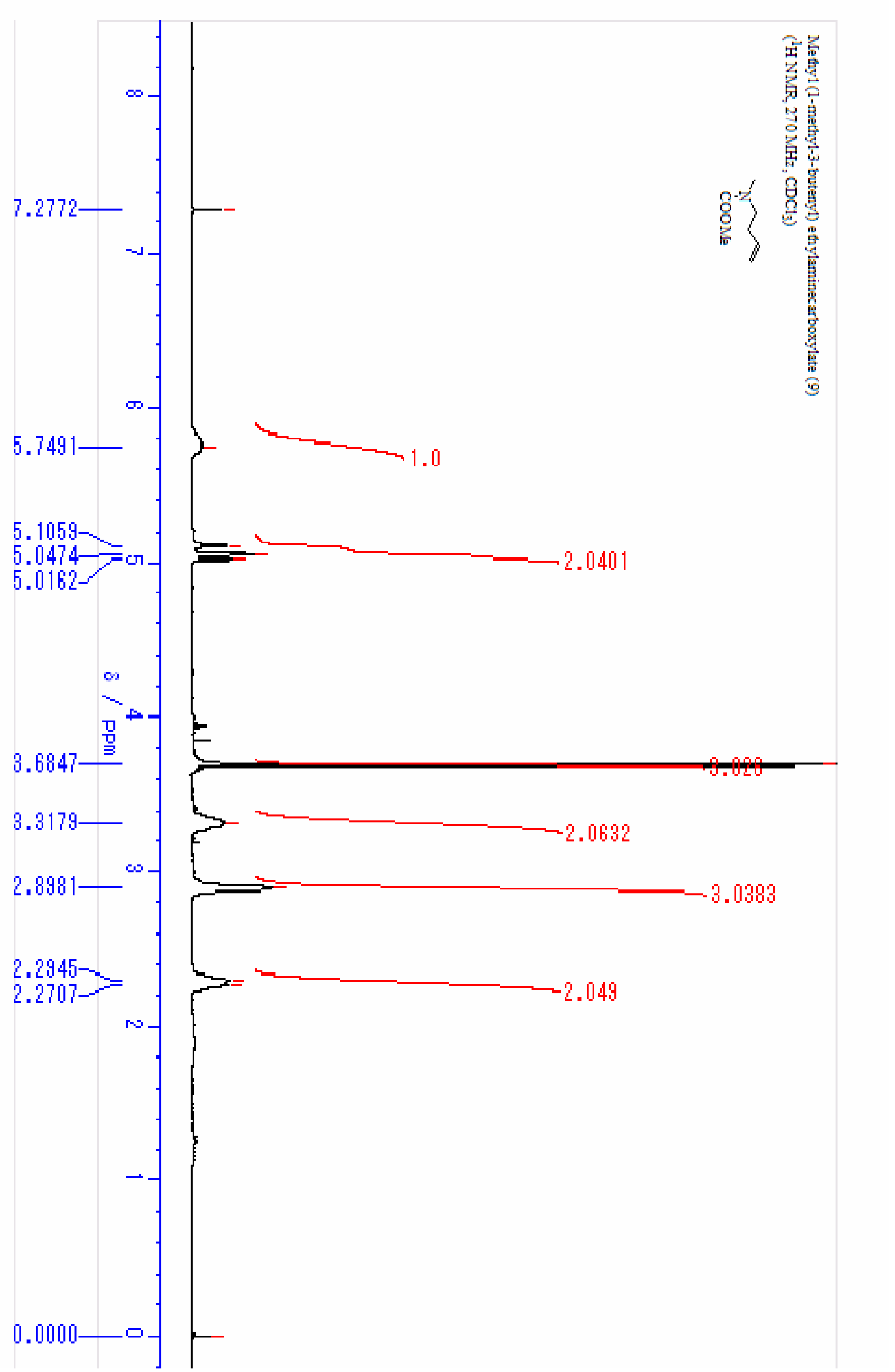
Methyl (1-methyl-3-butenyl) ethylaminecarboxylate (9)
(1H NMR, 270 MHz, CDCl3)
N
COOMe
7.2772
5.7491
5.1059
5.0474
5.0162
3.6847
3.3179
2.8981
2.2945
2.2707
0.0000
8
7
6
5
4
3
2
1
0
δ / ppm
1.0
2.0401
3.020
2.0632
3.0383
2.049