Electronic Supplementary Information for

Continuous *In Situ* Electrogenaration of 2-Pyrrolidone Anion in Microreactor: Application to Highly Efficient Monoalkylation of Methyl Phenylacetate

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1. Instrumentations

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). Reverse phase high performance liquid chromatography (RP-HPLC) analyses were performed by using a Shimadzu LC-20AS liquid chromatograph equipped with a UV detector (SPD-10AVi, Shimadzu) and a column (Mightysil RP-18GP 5μm, 4 mm ϕ x 25 cm). Linear sweep voltammetry measurements were performed by using a computer-controlled electrochemical analyzer (ALS/CH Instruments 630C).

2. Materials

Anhydrous N,N-Dimethylformamide (DMF), acetonitrile were obtained from Kanto Chemical Co., Inc. and used as received. 2-Pyrrolidone (**1**), methyl phenylacetate (**3**), methyl iodide, isopropyl iodide, hexyl iodide, *tert*-butyl iodide, ethylbenzene, and tetrabutylammonium perchlorate were obtained from Tokyo Chemical Industry and used as received. Toluene was obtained from Wako Pure Chemical Industries, Ltd. and used as received. Distilled water was prepared by automatic water distillation apparatus (SA-2100E1, Tokyo Rikakikai Co., LTD.). As authentic samples for RP-HPLC analysis, methyl 2-phenylpropanoate (**5a**), methyl 2-methyl-2-phenylpropionate (**6a**), and methyl 3-methyl-2-phenylbutanoate (**5b**) were synthesized according to the literatures.[1,2]

3. Linear Sweep Voltammetry Measurements

Linear sweep voltammetry measurements were performed by using an undivided cell equipped with a working electrode (3 mm ϕ, platinum disk electrode, ALS Co., Ltd), an auxiliary electrode (3 x 3 cm^2, Pt plate), and a saturated calomel reference electrode (SCE). Liner sweep voltammograms of 2-pyrrolidon and methyl phenylacetate were shown in Fig. S1.

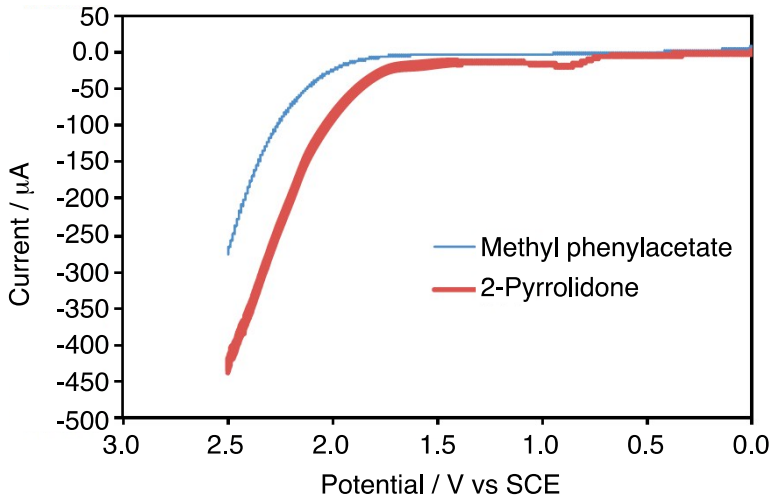

Fig. S1 Liner sweep voltammograms of 2-pyrrolidon (10 mM) and methyl phenylacetate (10 mM) in DMF solution of Bu_4NClO_4 (100 mM) at scan rate of 100 mV s^{-1}.

4. General Procedure for Preparative Electrolysis Using Batch Type Cell

Bulk electrolyses were carried out using a divided cell equipped with an anode (Pt mesh, 90 cm^2), and a cathode (Pt mesh, 40 cm^2) in DMF solution (20 mL) containing 2-pyrrolidone (**1**: 500 mM), and Bu_4NClO_4 (750 mM) at 0 ºC. Constant current (5.0 mA cm^{-2}) was applied for the electrolysis. After the charge was passed (1.5 F mol^{-1} of **1**), 10 mL cathode side reaction mixture was dropped slowly to DFM solution of methyl phenylacetate (**3**: 125 mM) at –70 ºC under nitrogen. Then, 5.0 mL DMF solution of alkyl iodide (500 mM) was added to the reaction mixture and stirred for 15 min under nitrogen at –70 ºC or ambient temperature. After the reaction, it was subjected to RP-HPLC to determine the yield of the alkylated products. Ethylbenzene was used as internal standard material for the RP-HPLC analysis.

5. Schematic illustrations of Flow microreactors

The flow microreactors were prepared according to the literature.[3] Illustrations of various types of flow microreactors used in this work were given in Figs. S2 ~ S4.

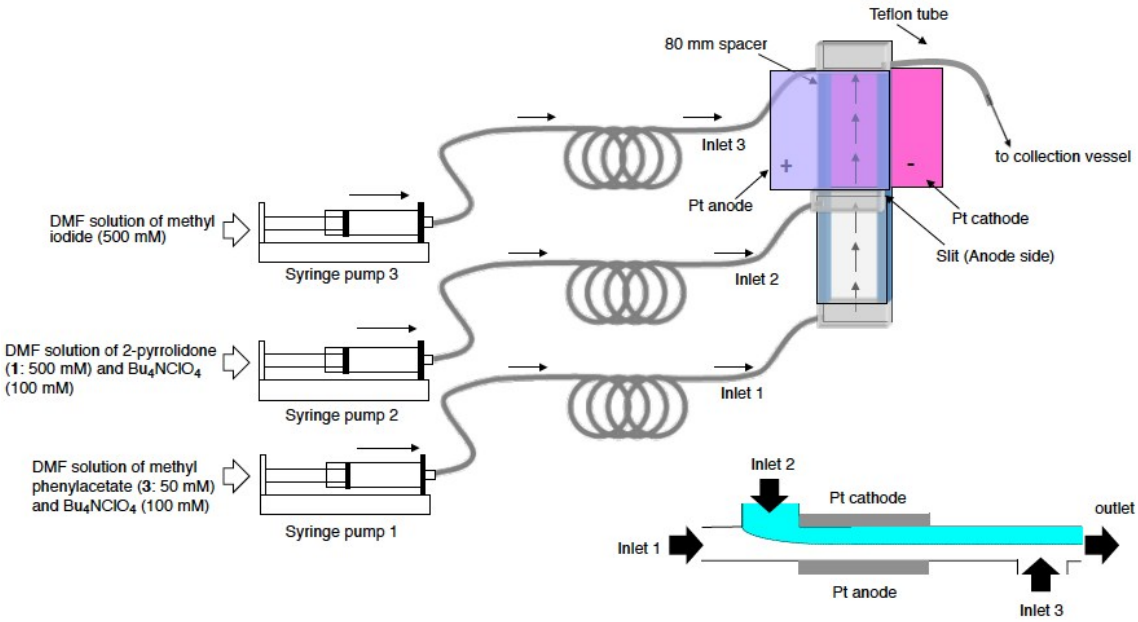

Fig. S2 Schematic illustration of the three-inlet type microflow system (Flow mode A).

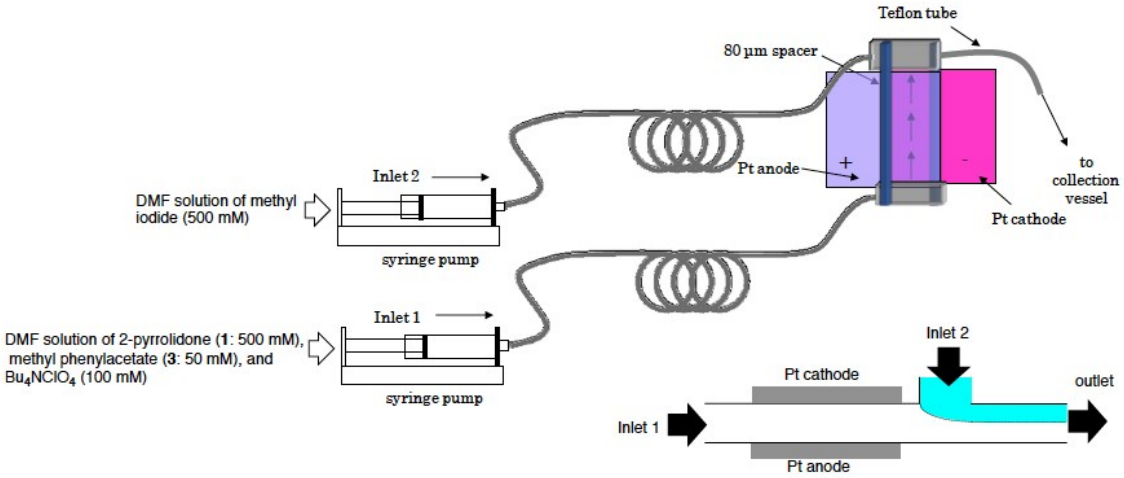

Fig. S3 Schematic illustration of the two-inlet type microflow system (Flow mode B).

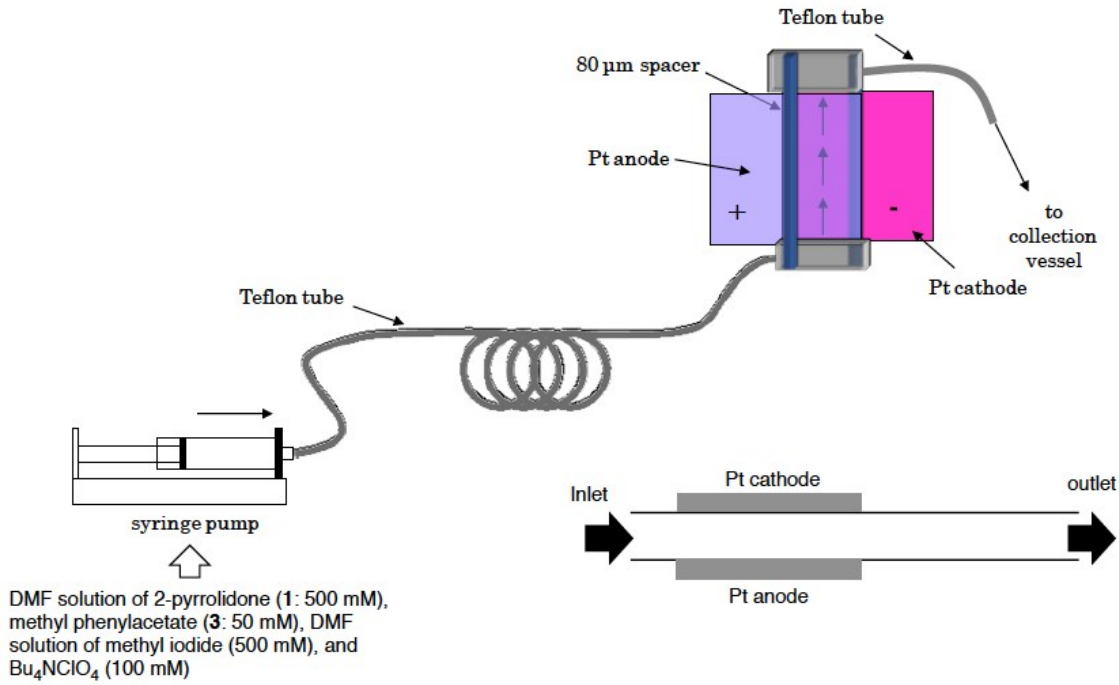

Fig. S4 Schematic illustration of the two-inlet type microflow system (Flow mode C).

References

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2 W. Adam, S.-G. Bosio, N.-J. Turro, and B.-T. Wolff, *J. Org. Chem.* 2004, **69**, 1704.

3 T. Arai, H. Tateno, K. Nakabayashi, T. Kashiwagi, and M. Atobe, *Chem. Commun.*, 2015, **51**, 4891.