Catalytic Membrane-Installed Microchannel Reactors for One-Second Allylic Arylation

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General

A microchannel reactor having a channel pattern of 100 μm width, 40 μm depth, 40 mm length, and a Y-junction (purchased from the Institute of Microchemical Technology, Co., Ltd., (Kangawa, Japan; URL: http://www.i-mt.co.jp) was used, the ends of which were connected via a Teflon tubing to a flow-controlled syringe on a syringe pump.

Experimental Section

Preparation of a $PdCl_2$/PA-TAP Membrane inside a Microchannel (μ-device 1). An ethyl acetate solution of PA-TAP (5.0 mM phosphorus residue; solution A) and an aqueous solution of $(NH_4)_2PdCl_4$ (1.7 mM) (solution B) were charged oppositely into the microchannel (100 μm width, 40 μm depth, 40 mm length) at 50 °C for 10 min with a flow rate of 20 μl/min. Two-phase parallel laminar flow was formed under the flowing conditions and a yellowish polymer membrane **1** was precipitated out at the interface between the two parallel flows (thickness of membrane **1** = 1 μm).

Preparation of a $PdCl_2$/polyPy Membrane inside a Microchannel (μ-device 2). An ethyl acetate solution of poly(4-vinylpyridine) (5.0 mM; solution A) and an aqueous solution of $PdCl_2$ (1.7 mM) and NaCl (17 mM) (solution B) were charged oppositely into the microchannel (100 μm width, 40 μm depth, 40 mm length) at 25 °C for 10 min with a flow rate of 20 μl/min. Two-phase parallel laminar flow was formed under the flowing conditions and a yellowish polymer membrane **2** was precipitated out at the interface between the two parallel flows (thickness of membrane **2** = 10 μm). IR(ATR) ν 3476, 1612, 1427, 1221, 1068, 829 cm^{-1}; Anal. Calcd for $[(PdCl_2)_3(C_7H_7N)_6 \bullet CH_3CO_2Et]_n$: C 44.17%, H 4.03%, N 6.72%. Found: C 44.11%, H 4.15%, N 7.18%.

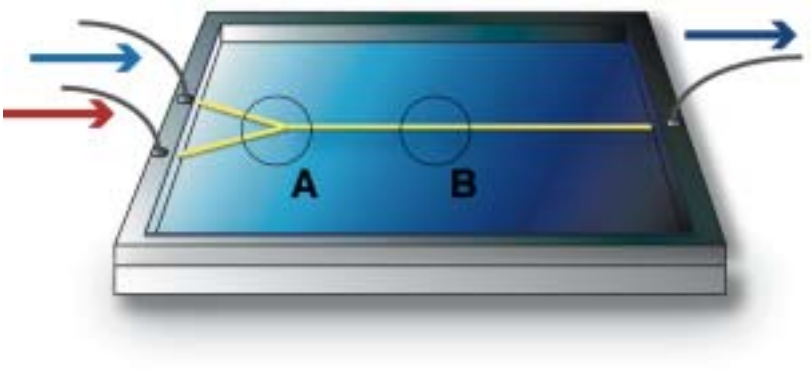
Preparation of a $PdCl_2$/polyviologen Membrane inside a Microchannel (μ-device 3). An *i*-PrOH-EtOAc-H_2O (2:1:1) solution of poly(4,4'-bipyridyl-*co*-1,4-bis(bromomethyl)benzene) (1.7 mM; solution A) and an aqueous solution of $PdCl_2$ (1.7 mM) and NaCl (17 mM) (solution B) were charged oppositely into the microchannel at 25 °C for 10 min with a flow rate of 20 μl/min. Two-phase parallel laminar flow was formed under the flowing conditions, and a yellowish polymer membrane **3** was precipitated out at the interface between the two parallel flows (thickness of membrane **3** = 10 μm).

General procedure for the Allylic Arylation Reaction Using a Microchannel Having a Pd Membrane (μ-device 1-3)

An *i*-PrOH solution of cinnamyl acetate (5.8 mM; solution A) and an aqueous solution of sodium

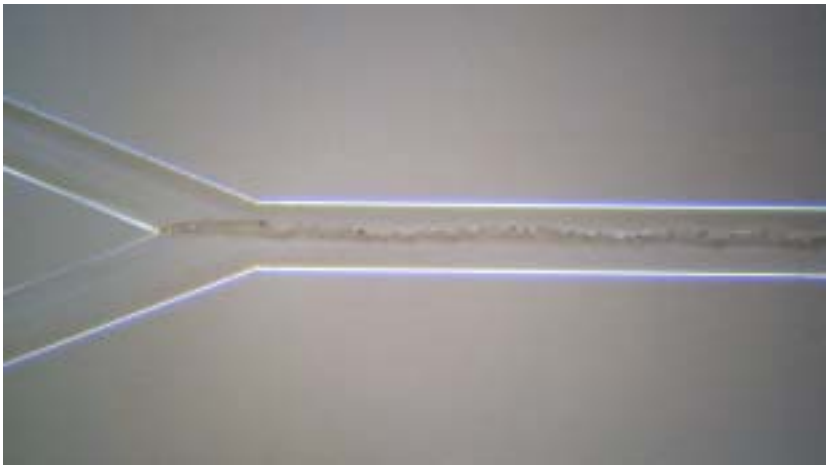
tetraphenylborate (58 mM; solution B) were oppositely introduced into the membrane-divided channels at 50 °C with a flow rate of 3.0 μl/min, and two parallel laminar layers flowed through the channel in 1 second. The resulting organic/aqueous micro stream was collected from the outlet of the channel to afford a quantitative yield of 1,3-diphenyl-1-propene.

Opical Microscopic Images of μ-Devices 1-3



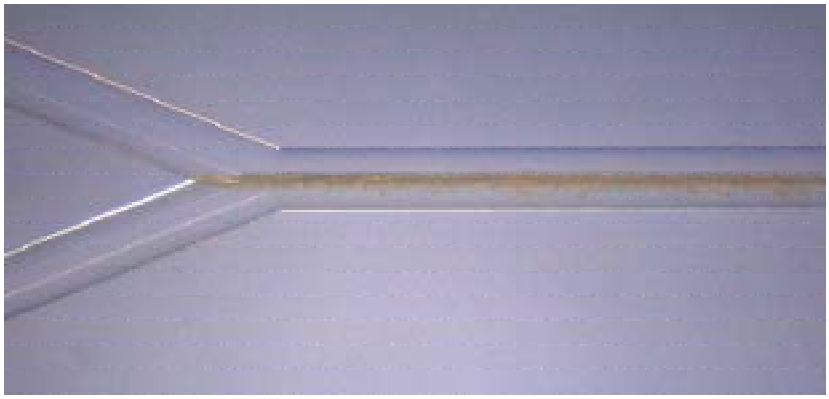
μ-device 1: [Palladium loading: (ICP-AES analysis) 0.50 mmol/g (1.2 nmol/channel)]

Position A

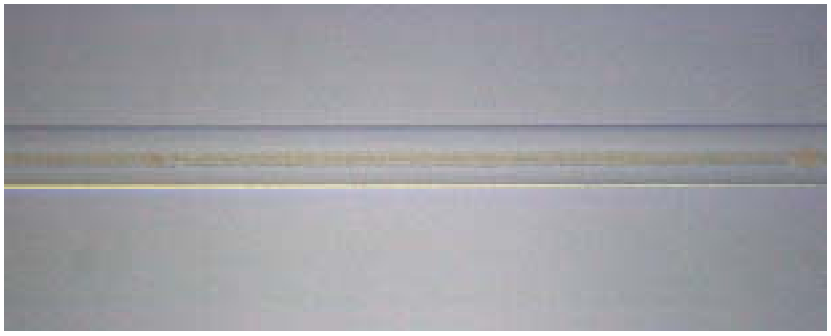


Position B

μ-device 2
Position A



Position B



μ-device 3
Position A

Position B

GC #1

Snapshot at 1 h

GC #2

Snapshot at 2 h

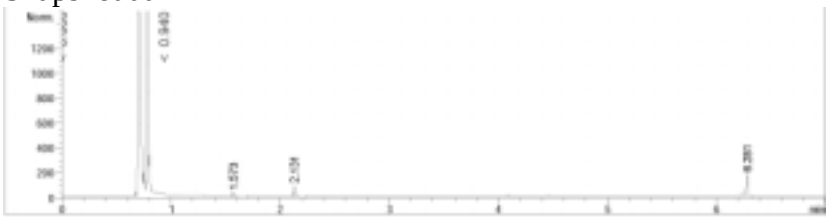
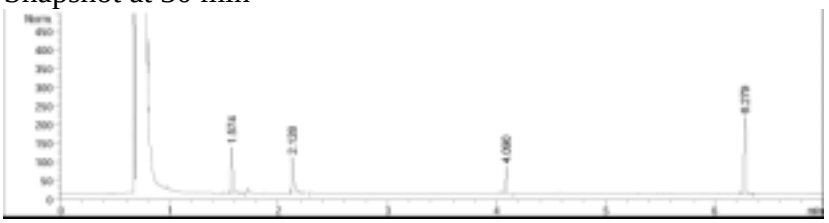


Figure S-1. 6a from **4a** (Entry 1, Table 1): The reaction was monitored by GC in a snapshot manner at 1 h and 2 h (GC #1- #2: 2.1 min: internal standard; 6.3 min: **6a**).

GC #3

Snapshot at 30 min



GC #4

Snapshot at 50 min

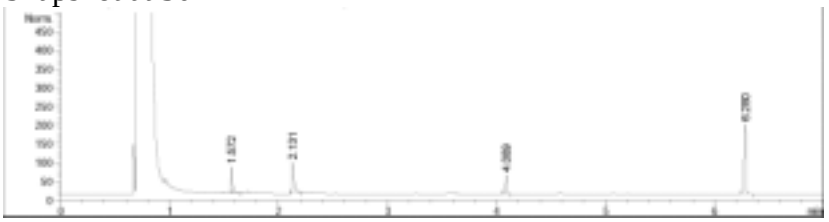


Figure S-2. 6a from **4b** (Entry 5, Table 1): The reaction was monitored by GC in a snapshot manner at 30 min and 50 min (GC #3- #4: 2.1 min: internal standard; 6.3 min: **6a (**4.1 min: a peak derived from $NaBPh_4$)).