

Supplementary Information

**Catalytic Ring-Opening Allylation of Cyclic Acetals with Allylsilanes Using
Silica-Alumina**

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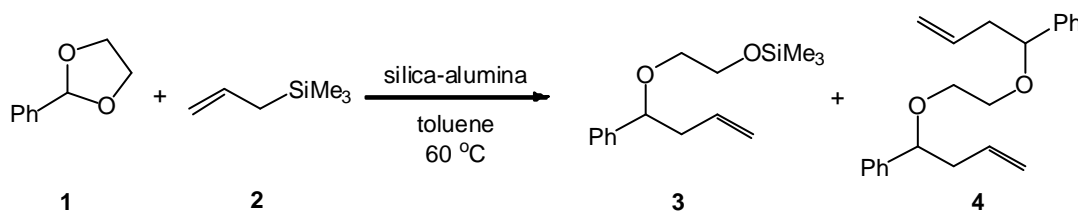
Experimental Procedures

General

Proton nuclear magnetic resonance (^1H NMR), carbon nuclear magnetic resonance (^{13}C NMR), were recorded in CDCl_3 with a JNM-AL300 spectrometer operating at 300 and 75 MHz, respectively. Analytical GLC was measured using a Shimadzu GC-8A equipped with a Silicon SE-30 and OV-17 column and a thermal conductivity detector. Shimadzu QP5000 was used as GC-MS equipped with DB-1 column. The products were confirmed by comparison with reported NMR, MS, and IR data.

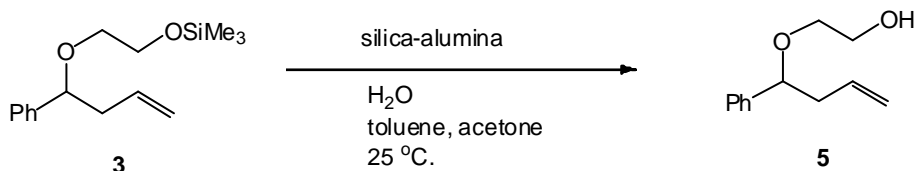
Silica-alumina was available from Nikki Chemical Co. as N633L (SiO_2 , 80.6, Al_2O_3 , 12.8 wt%, 408 m^2/g). H^+ -montmorillonite was prepared from Na^+ -montmorillonite using ion exchange procedure with aqueous hydrogen chloride, see: K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Angew. Chem. Int. Ed.* **2006**, *45*, 2605. H^+ -Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3=25$), H^+ -Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=18.0$), H^+ -L ($\text{SiO}_2/\text{Al}_2\text{O}_3=6.3$), H^+ -USY ($\text{SiO}_2/\text{Al}_2\text{O}_3=5.9$) were purchased from Nikki Chemical Co.. H^+ -ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=23.8$) was obtained from Toso Co.. Aerosil 300 was used as SiO_2 .. These inorganic solid acids, except for H^+ -montmorillonite, were treated at 500 °C under air and 120 °C under vacuum before use. Amberlyst was purchased from Organo Co. as Amberlyst® 15DRY. Nafion was purchased from Aldrich Inc. as Nafion® NR50. Unless otherwise noted, other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto kagaku Co. and Aldrich Inc.

Typical reaction procedures for ring-opening allylation of **1** with **2** using silica-alumina



Into a glass reactor were placed silica-alumina (0.05 g), toluene (3.0 mL), **1** (3.7 mmol), **2** (4.4 mmol) in a dry Ar atmosphere. The resulting mixture was vigorously stirred at 60 °C. After 27 h, the catalyst was separated by filtration and GC analysis of the filtrate showed an 81% yield of the allylated product **3**. The filtrate was evaporated and the crude product was purified by column chromatography using silica (*n*-hexane/ether = 9/1) to afford a pure product **3**: ^1H NMR (300 MHz, CDCl_3): δ 0.10 (s, 9H), 2.36-2.64 (m, 2H), 3.32-3.44 (m, 2H), 3.70 (t, $J = 5.3$ Hz, 2H), 4.31 (t, $J = 6.5$ Hz, 1H), 4.98-5.06 (m, 2H), 5.70-5.84 (m, 1H), 7.23-7.43 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3): -0.44, 42.6, 62.0, 70.0, 82.4, 116.7, 126.8, 127.5, 128.2, 134.9, 142.1; MS (EI) m/z (%): 45, 73(100), 82, 91, 117, 131, 179, 223(M^+ -allyl). The spectra of by-product **4** is as follows: ^1H NMR (300 MHz, CDCl_3): δ 2.35-2.63 (m, 4H), 3.36-3.51 (m, 4H), 4.32 (t, $J = 8.8$ Hz, 2H), 4.98-5.06 (m, 4H), 5.69-5.86 (m, 2H), 7.23-7.35 (m, 10H); ^{13}C $\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3): 42.6, 68.0, 82.1, 116.7, 126.8, 127.5, 128.2, 135.0, 142.0; MS (EI) m/z (%): 41, 51, 77, 91, 105, 120, 131(100), 151, 191, 281(M^+ -allyl).

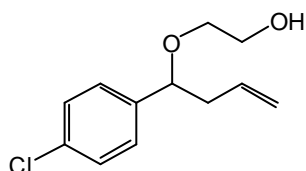
Typical reaction procedure for hydrolysis of **3**



After the ring-opening allylation using silica-alumina, water (0.2 mL, 11 mmol) and acetone (3.0 mL) were added to the same flask. The resulting mixture was vigorously stirred at 25 °C for 3 h. Then, the catalyst was separated by filtration and GC analysis of the filtrate showed a 77% yield of homoallyloxyalcohol **5**. The filtrate was evaporated and the crude product was purified by column chromatography using silica (*n*-hexane/ether = 9/1 to 1/1) to afford a pure product **5**: ¹H NMR (300 MHz, CDCl₃): δ 2.14 (br, 1H), 2.40-2.64 (m, 2H), 3.36-3.50 (m, 2H), 3.70 (t, *J* = 5.9 Hz, 2H), 4.31 (t, *J* = 8.8 Hz, 1H), 5.03-5.10 (m, 2H), 5.72-5.86 (m, 1H), 7.26-7.37 (m, 5H); ¹³C {¹H} NMR (75.45 MHz, CDCl₃): 42.5, 61.9, 69.9, 82.2, 117.2, 126.6, 127.7, 128.4, 134.7, 141.7; MS (EI) *m/z* (%): 45, 51, 65, 77, 79, 91, 107(100), 131, 151(M⁺-allyl).

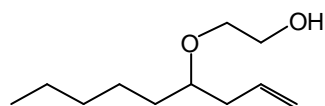
Product Identification

2-(1-(4-chlorophenyl)but-3-enyloxy)ethanol



^1H NMR (300 MHz, CDCl_3): δ 2.25 (br, 1H), 2.26-2.54 (m, 2H), 3.26-3.38 (m, 2H), 3.61 (br, 2H), 4.21 (t, $J = 6.6$ Hz, 1H), 4.95-5.00 (m, 2H), 5.60-5.74 (m, 1H), 7.20 (dd, $J = 26.7, 8.3$ Hz, 4H); ^{13}C $\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3): 42.3, 61.8, 70.0, 81.5, 117.5, 127.9, 128.6, 133.3, 134.2, 140.1; MS (EI) m/z (%): 45(100), 51, 77, 113, 129, 141, 143, 185(M^+ -allyl), 187.

2-(non-1-en-4-yloxy)ethanol



^1H NMR (300 MHz, CDCl_3): 0.89 (t, $J = 6.6$ Hz, 3H), 1.21-1.52 (m, 8H), 2.27 (br, 3H), 3.36 (quint, $J = 5.9$ Hz, 1H), 3.53-3.60 (m, 2H), 3.70 (br, 2H), 5.05-5.12 (m, 2H), 5.76-5.90 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3): 14.0, 22.6, 25.0, 31.9, 33.8, 38.3, 62.0, 69.9, 79.4, 117.0, 135.0; MS (EI) m/z (%): 45, 55(100), 73, 83, 101, 145(M^+ -allyl).