

## Electronic Supplementary Information

### Mesoporous Silica-Supported Catalysts for Metathesis: Application to a Circulating Flow Reactor

Jaehong Lim, Su Seong Lee\* and Jackie Y. Ying\*

*Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos,  
Singapore 138669*

\*E-mail: sslee@ibn.a-star.edu.sg, jyying@ibn.a-star.edu.sg; Fax: (+65) 6478-9020.

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## General

Solution NMR spectra were recorded on a Bruker spectrometer (400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ ) at ambient temperature with the solvents indicated, and referenced to the solvent peaks.  $^{13}\text{C}$  CP-MAS and  $^{29}\text{Si}$  CP-MAS NMR spectra were recorded on a 400 MHz Bruker spectrometer for compounds immobilized onto MCF. Elemental analyses were performed with CE440 CHN Analyzer (Exeter Analytical). ICP-MS data were obtained by Elan DRC II, Perkin Elmer SCIEX, USA. Mass spectra were obtained at the Elemental Analysis Laboratory, Department of Chemistry, National University of Singapore, Singapore. Conversions for RCM of dienes were determined by GC (Agilent 6890N) or LC (Agilent 1100 Series). Unless otherwise noted, reactions were performed under argon atmosphere by standard Schlenk techniques. All chemicals were purchased from Aldrich. Solvents were either purified by passage through a column of activated alumina or purchased in sealed bottles from Aldrich.

## Preparation of alkyne 1

A 100-ml one-necked flask was charged with potassium carbonate (7.00 mmol), propargyl bromide (6.00 mmol), the known phenol (5.00 mmol) and dried acetonitrile (50 ml). The resulting mixture was heated at 65 °C for 15 h, which was then roughly concentrated after cooling down to ambient temperature. Diethylether (100 ml) was introduced and the organic layer was washed with water (50 ml  $\times$  2) and brine (50 ml  $\times$  1), and then dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure, and the crude product was further purified by flash column chromatography (hexane/Et<sub>2</sub>O = 20/1  $\rightarrow$  10/1) and dried under vacuum for 24 h to produce the alkyne as colorless oil **1** (4.70 mmol, 94%).  $^1\text{H}$ -NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.33 (d, 6H,  $J$  = 6.0 Hz), 2.54 (t, 1H,  $J$  = 2.4 Hz), 4.42 (septet, 1H,  $J$  = 6.0 Hz), 5.27 (dd, 1H,  $J$  = 11.2, 1.4 Hz), 5.72 (dd, 1H,  $J$  = 17.6, 1.4 Hz), 6.85 (d, 2H,  $J$  = 1.6 Hz), 7.05 (dd, 1H,  $J$  = 17.6, 11.2 Hz), 7.14 (t, 1H,  $J$  = 1.6 Hz).  $^{13}\text{C}$ -NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  22.2, 56.5, 72.1, 75.4, 78.8, 112.7, 114.4, 115.2, 116.5, 129.2, 131.6, 150.1, 151.8.

## Preparation of azide 2

A 100-ml Schlenk flask was charged with 3-bromopropyltrimethoxysilane (10 mmol), sodium bromide (12 mmol), and tetrahydrofuran (THF, 25 ml) under argon atmosphere. The resulting mixture was heated at 65 °C with the valve closed for 15 h, and was cooled to

ambient temperature. Hexane (25 ml) was added, and the precipitate was removed by centrifugal separation. The liquid was then concentrated under reduced pressure, and dried for 24 h under vacuum to give azide **2** (*ca.* 10 mmol, quantitative) as colorless oil, which was pure enough to be used without further purification. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.68–0.72 (m, 2H), 1.68–1.75 (m, 2H), 3.27 (t, 2H, *J* = 7.2 Hz), 3.58 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 6.29, 22.44, 50.6, 53.7. MS (FAB): *m/z* (%) 206 (25) [M<sup>+</sup>+H], 174 (100), 147 (26).

### Preparation of triazole **3**

A 50-ml flask was charged with alkyne **1** (1.00 mmol), azide **2** (1.00 mmol), copper (I) iodide (0.01 mmol), N,N-diisopropylethylamine (DIPEA, 2.00 mmol), and THF (15 ml). The resulting mixture was stirred for 15 h at ambient temperature, concentrated and further dried under vacuum for 24 h. The resulting triazole **3** (1.00 mmol, quantitative), a colorless oil, was pure enough to be used without further purification. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.61–0.65 (m, 2H), 1.32 (d, 6H, *J* = 6.0 Hz), 2.00–2.08 (m, 2H), 3.57 (s, 9H), 4.37 (t, 2H, *J* = 7.2 Hz), 4.40 (septet, 1H, *J* = 6.0 Hz), 5.20 (s, 2H), 5.25 (dd, 1H, *J* = 11.2, 1.4 Hz), 5.72 (dd, 1H, *J* = 17.6, 1.4 Hz), 6.85 (dd, 2H, *J* = 4.0, 1.4 Hz), 7.04 (dd, 1H, *J* = 17.6, 11.2 Hz), 7.14 (d, 1H, *J* = 2.8 Hz), 7.62 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 6.16, 22.2, 24.0, 50.7, 52.5, 62.7, 72.1, 112.5, 114.4, 114.9, 116.7, 122.6, 129.3, 131.6, 144.3, 149.8, 152.5. MS (FAB): *m/z* (%) 422 (16) [M<sup>+</sup>+H], 371 (9), 155 (100).

### Preparation of immobilized ligand **5**

A 100-ml Schlenk flask, charged with the precapped MCF **4** (3.00 g, 0.60 mmol of TMS/g), was placed under vacuum for 24 h at 120 °C. The flask was purged with argon at ambient temperature and charged with triethylamine (0.44 ml), dried toluene (40 ml), and trimethoxysilane **3** (1.05 mmol). The resulting mixture was stirred for 15 h at 80 °C. The white solid was thoroughly rinsed by toluene, DCM, methanol, and DCM (50 ml each), and then transferred to a 100-ml Schlenk flask and dried under vacuum for 12 h at 80 °C. After cooling down to ambient temperature, the flask was placed in a liquid nitrogen bath for 10 min, and hexamethyldisilazane (HMDS) (1 ml) was added under vacuum. The flask was sealed and kept at 80 °C for 5 h. The resulting solid was cooled to ambient temperature, washed thoroughly with DCM (100 ml), and then dried under vacuum for 24 h to give the corresponding immobilized ligand **5** as a white powder. <sup>13</sup>C CP-MAS NMR (100 MHz): δ (ppm) = 1.8, 11.2, 21.9, 25.3, 52.7, 64.0, 72.7, 113.3, 117.5, 123.2, 131.1, 133.5, 145.9, 151.4,

154.6.  $^{29}\text{Si}$  CP-MAS NMR (75 MHz):  $\delta$  (ppm) = -105.1, -96.9, -62.3, 17.4. Elemental analysis, found: C, 9.16; H, 1.90; N, 0.87. Loading of ligand: 0.19 mmol/g.

### **Preparation of catalyst 6**

A 50-ml two-necked flask equipped with a reflux condenser was charged with ligand **5** (0.18 mmol), second-generation Grubbs' catalyst (0.18 mmol), copper(I) chloride (0.18 mmol) and dried DCM (20 ml) under argon. The reaction mixture was heated for 5 h under reflux in argon. It gradually changed from dark brown to deep green. After cooling to ambient temperature, the fine powder was washed thoroughly with DCM (100 ml), and dried under vacuum for 24 h to give the immobilized catalyst **6** as a green powder.  $^{13}\text{C}$  CP-MAS NMR (100 MHz):  $\delta$  (ppm) = 1.6, 10.8, 19.3, 39.4, 52.1, 63.8, 74.8, 112.6, 122.4, 129.3, 138.9, 146.8, 154.9, 238.1.  $^{29}\text{Si}$  CP-MAS NMR (75 MHz):  $\delta$  (ppm) = -105.0, -96.6, -63.0, -54.0, 17.3. Elemental analysis, found: C, 12.65; H, 2.15; N, 1.28. Loading of ruthenium: 0.16 mmol/g.

### **General procedure for testing catalytic activity**

Reactions were run under argon in a vial containing a magnetic stir bar. The vial was charged with catalysts **6** (5  $\mu\text{mol}$ ) and DCM (2 ml). A substrate (0.10 mmol) was injected, and the conversion was monitored by GC or LC after fresh filtration through a short pad of silica gel by elution with DCM.

### **General procedure for testing catalyst recyclability in a batch reaction**

Reactions were run at 50 °C in a similar manner as described above. On completion of each run, the reaction vial was centrifuged at 4000 rpm for 3 min, and the supernatant was characterized by GC for conversion. The vial was charged with a fresh aliquot of DCM, stirred for 1 min, and centrifuged again. Two more rinses were performed before the next run was conducted with fresh substrate.

### **General procedure for testing catalyst recyclability in a continuous flow reactor**

A stainless steel column (4.6 mm  $\times$  50 mm, Alltech) was filled with **6** (225 mg, 36  $\mu\text{mol}$ ) eluting with DCM as a slurry. After drying, the column was heated at 50 °C with a column heater, and fitted into a solvent delivery system (4-channel model with a degasser, Waters). The starting material **7** (0.15 M solution in DCM) was eluted at a flow rate of 0.5

ml/min. An aliquot was taken from the outlet of the column, and the conversion at each time point was measured by GC.

**General procedure for testing catalyst recyclability in a circulating flow reactor**

A stainless steel column (4.6 mm × 50 mm, Alltech) was filled with **6** (225 mg, 36 μmol) eluting with DCM as a slurry. After drying, the column was heated at 50 °C with a column heater, and fitted into a circulating flow reactor (as depicted in Figure 2), which involved a solvent delivery system (4-channel model with a degasser, Waters). The starting material **7** (0.15 M solution in DCM) was injected into a system whereby DCM was circulating at a flow rate of 0.5 ml/min. An aliquot was taken from the reservoir at the end of each run to determine the conversion by GC.

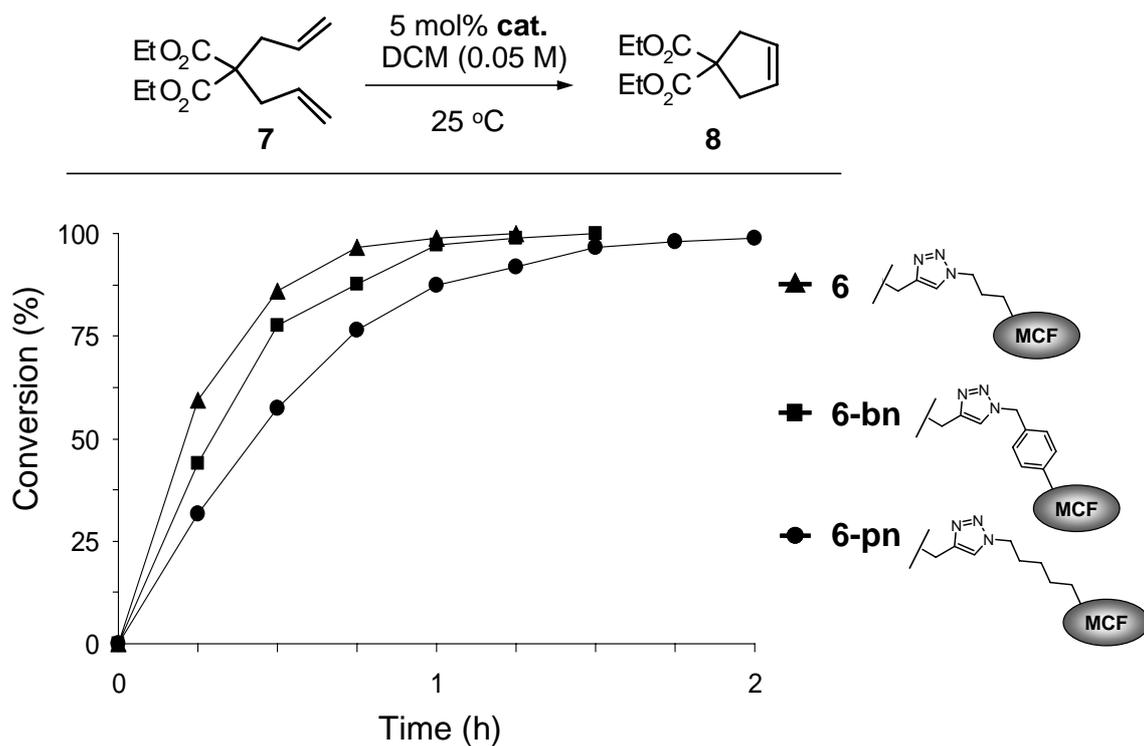


Figure S1 Catalytic activities of **6** and its derivatives for the RCM of **7**.

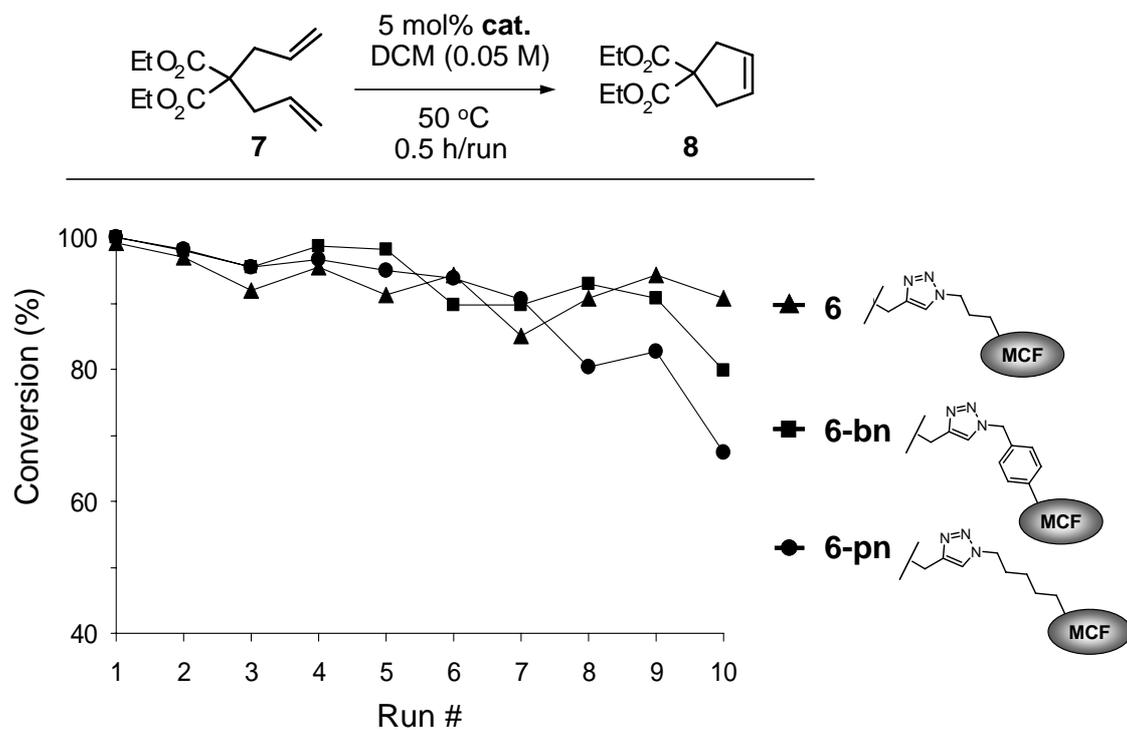
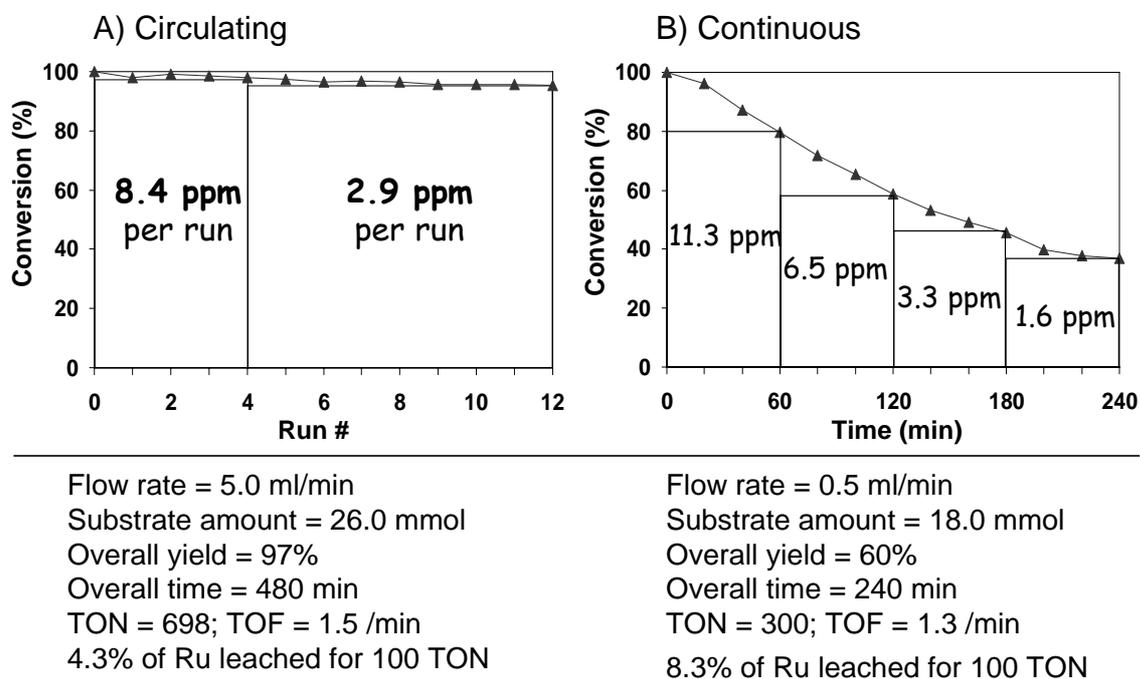
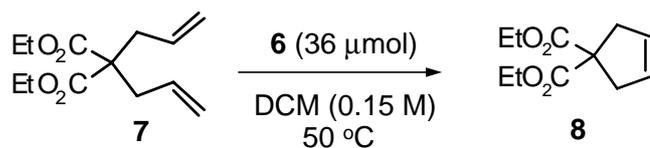
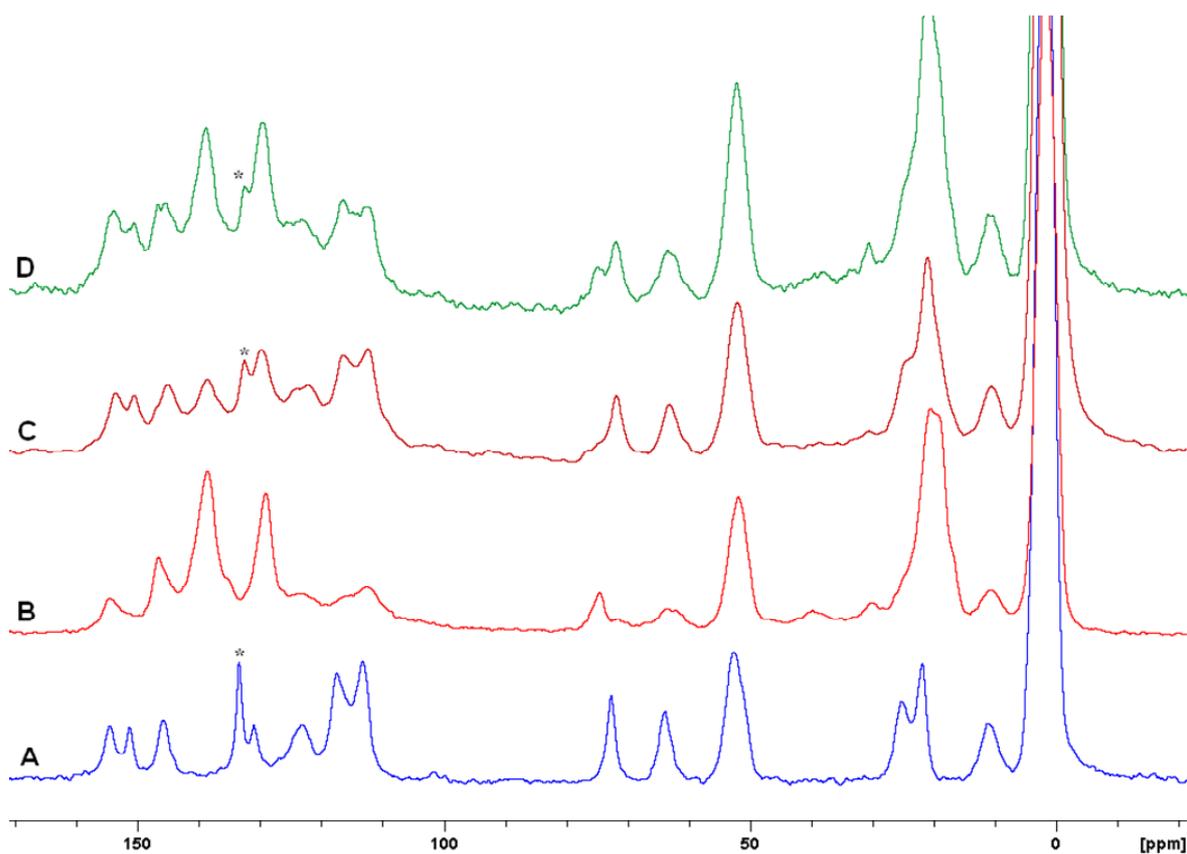


Figure S2 RCM of **7** catalyzed by **6** and its derivatives.



**Figure S3** The conversion and leaching in the recycling RCM of **7** catalyzed by **6** in (A) a circulating flow reactor and (B) a continuous flow reactor.



**Figure S4**  $^{13}\text{C}$  CP-MAS NMR spectra of (A) the immobilized ligand **5**, (B) the immobilized catalyst **6**, (C) the used catalyst **6** after 240 min of RCM of **7** in a continuous flow reactor using DCM (Figure 1), and (D) the used catalyst **6** after 12 runs of RCM of **7** in a circulating flow reactor using DCM (Figure 3). A series of peaks marked with asterisk (\*), associated with the mesityl group, clearly indicated that more ruthenium species leached out in a continuous flow reaction than in a circulating flow reaction, even though the turnover number (TON) was higher in the latter.

