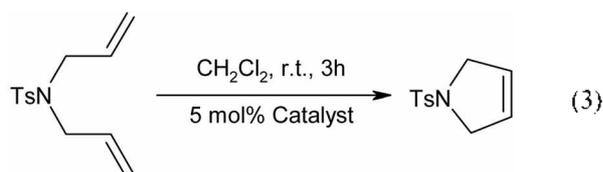


Figure 2. Catalysts used in this work.

The synthesized monosubstituted imidazoles were reacted with (3-bromopropyl) trimethoxysilane to make precursor **1a-5a**. Compounds **1a-5a** were linked to MCF under the condition of refluxing dichloromethane. Reaction of **1a-5a** with Grubbs' catalyst yielded catalysts 1-5. The synthesized catalysts were analyzed by combustion analysis and ICS-AES (Eq. 2).¹⁷

Using *N,N*-diallyl-4-methylbenzenesulfonamide as a model substrate, we studied the performance of catalysts in the RCM reaction (Eq. 3 and Table 1).



As shown in the Table 1, the best result (93%) was obtained with catalyst **1**, and this catalyst was reused at least seven times without any significant loss of catalytic activity. An inductively coupled plasma-mass spectrometry (ICP-MS) study showed that the ruthenium bled from the catalyst was negligible, ranging from 0.00074% to 0.00519%. These results confirm that the catalytic system presented here satisfies the conditions for heterogeneous catalysts of easy separation, recyclability, and persistence.

Next, we investigated the versatility of dienes (Table 2). High yields were observed for all dienes except entries 3 and 11. In particular, the use of a diene with a substituted double bond (entry 11) diminished the yield to 30%. However, no reaction was observed for an intermolecular RCM (entry 12). We could get one with satisfactory yield not influenced by the functional group of various dienes. However, in case there is a hydroxyl group, the yield went down to 53%, which seems to have resulted from that substrate is absorbed by hydrophilic silica.

As shown in Table 1, the catalyst had no problem with its activity when it was re-used (no. 7). However, our catalyst system uses silica as a supporting body, but silica disintegrates after recycling, a problem that is more serious than

Table 1. Ring closing metathesis of *N,N*-diallyl-4-methylbenzenesulfonamide by the supported catalysts^a

Entry	Catalyst	Yield (%)	Ru Residue (ppm) ^b
1	1	93	1.2
2	recovered from # 1	91	1.3
3	recovered from # 2	89	2.1
4	recovered from # 3	88	0.3
5	recovered from # 4	88	0.3
6	recovered from # 5	89	0.4
7	recovered from # 6	90	0.4
8	2	90	
9	3	79	
10	4	73	
11	5	85	

^aIsolated yield. ^bDetermined by ICP-Mass spectroscopic analysis

ruthenium metal leaching. Generally, this problem became serious when the catalytic system was used more than three times. Separation of the catalysts from the reaction mixture became tough and annoying. To overcome this problem, we introduced a flow micro reactor (Figure 2) and used it for the RCM reaction. However, when the reaction was carried out in the flow micro reactor, the reaction gave 50% yield in

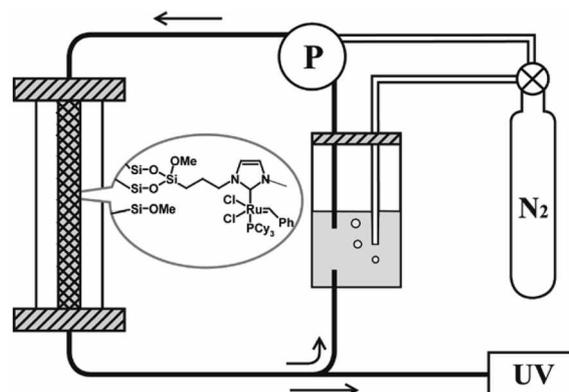


Figure 3. Flow microreactor used for RCM.

Table 2. Olefin metathesis using 1

entry	substrate	product	yield (%) ^a	entry	substrate	product	yield (%) ^a
1			93	7			88
2			90	8			73
3			53	9			91
4			75	10			79
5			92	11			30
6			87	12		—	—

^aIsolated yield.

case of *N,N*-diallyl-4-methylbenzenesulfonamide for 1 hour. We expected that lengthening a reaction time would increase a yield. However, because of the restriction in the flow micro reactor system, it was impossible to get a result for a longer reaction time. This problem will be overcome by developing a more reactive catalyst.

In summary, we developed heterogeneous Ru-NHC catalysts by immobilization of Grubbs catalysts on the MCF-type mesoporous silica through a modification of the NHC ligand. Starting from NHC ligand, a facile three-step reaction gave the supported catalyst which is a robust, stable, and easy to reuse. In addition to the advantages discussed above, the developed catalyst was highly effective for the intramolecular RCM reaction and could be reused at least seven times without any loss of its catalytic activities. Moreover, research is being conducted to further develop our RCM catalysts system for application to enantioselective catalysis.

Experimental Section

Representative procedure of the catalytic ring-closing metathesis (RCM) reaction. To a flame-dried 25 mL Schlenk flask capped with a rubber septum, a diene substrate (0.40 mmol) and NHC-bounded mesoporous silica catalyst (0.2 g, 0.02 mmol Ru) were dissolved in 10 mL of CH₂Cl₂. After the resulting solution was stirred for 3 h, the solution

was filtered, concentrated, and chromatographed on a silica gel column eluting with hexane/diethyl ether (10:1) to give the product. When the catalyst was recycled, the catalyst was filtered, dried in vacuum, and reused for the further catalytic reaction.

Modification of MCF surface with NHC ligands. MCF (2 g) was dispersed in dry CH₂Cl₂ (25 mL) at room temperature under N₂, after which ligand (**1a-5a**) (0.3 mmol) was added. The mixture was filtered after being stirred for 12 h. After drying in a vacuum for 1 day, NHC-bounded mesoporous silica was obtained.

Representative procedure of the Ruthenium-NHC complexes-immobilized on MCF. To a flame-dried 25 mL Schlenk flask capped with a rubber septum, NHC-bounded mesoporous silica (silica were combined with 0.3 mmol of NHC ligand) were dissolved in 10 mL of THF and K^tOBu (0.4 mmol) was added. After the mixture was stirred for 1 h, Grubbs' catalyst (0.3 mmol) was added. The mixture was filtered after being stirred for 12 h and the brown product was washed with 50 mL of pentane. After drying in a vacuum for 1 day, the Ruthenium-NHC complexes-immobilized on MCF was obtained.

1-Methyl-3-(3-trimethoxysilanopropyl)-imidazolium (1a): ¹H NMR (CDCl₃, 300 MHz): δ 0.67 (d, *J* = 8.0 Hz, 2H), 2.04 (m, 2H), 3.58 (s, 9H), 4.13 (s, 3H), 4.35 (t, *J* = 7.8 Hz, 2H), 7.47 (s, 1H), 7.59 (s, 1H), 9.84 (s, 1H); ¹³C NMR

(CDCl₃, 75 MHz): δ 6.1, 24.3, 37.3, 51.0, 52.0, 122.3, 123.8, 137.14; exact mass for (C₁₀H₂₀SiO₃N₂): [M+1] calcd 244.1243, obsd 245.1322.

1-Phenyl-3-(3-trimethoxysilanopropyl)-imidazolium (2a): ¹H NMR (CDCl₃, 300 MHz): δ 0.73 (t, *J* = 7.7 Hz, 2H), 2.12 (m, 2H), 3.59 (s, 9H), 4.61 (t, *J* = 7.2 Hz, 2H), 7.58 (m, 5H), 7.81 (d, *J* = 6.8 Hz, 2H), 10.56 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 0.2, 6.1, 24.4, 50.8, 51.0, 52.5, 120.8, 122.2, 123.3, 130.7, 130.9, 134.5, 135.6; exact mass for (C₁₅H₂₂SiO₃N₂): [M+1] calcd 306.1400, obsd 307.1480.

1-(4-*t*-Butyl-phenyl)-3-(3-trimethoxysilanopropyl)-imidazolium (3a): ¹H NMR (CDCl₃, 300 MHz): δ 0.73 (t, *J* = 7.9 Hz, 1H), 1.34 (s, 9H), 2.12 (m, 2H), 3.58 (s, 9H), 4.60 (t, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 6.7 Hz, 2H), 7.72 (d, *J* = 6.5 Hz, 4H), 10.46 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 6.0, 24.3, 31.3, 35.1, 50.7, 51.0, 52.3, 121.0, 121.7, 123.4, 126.0, 127.7, 132.0, 135.1, 154.1; exact mass for (C₁₉H₃₀SiO₃N₂): [M+1] calcd 362.2026, obsd 363.2106.

1-Methyl-3-(3-trimethoxysilanopropyl)-4,5-diphenyl-imidazolium (4a): ¹H NMR (CDCl₃, 300 MHz): δ 0.63 (t, *J* = 6.8 Hz, 2H), 1.91 (m, 2H), 3.50 (s, 9H), 4.23 (t, *J* = 8.1 Hz, 2H), 5.31 (s, 3H), 7.41 (m, 10H), 10.32 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 6.2, 10.6, 24.0, 27.4, 35.0, 35.5, 49.9, 50.7, 50.9, 124.8, 125.1, 126.1, 127.6, 129.3, 129.4, 129.9, 130.5, 130.6, 130.7, 130.8, 131.0, 131.9, 132.7, 136.9; exact mass for (C₁₈H₂₈SiO₃N₂): [M+1] calcd 396.1869, obsd 397.1945.

1-(2,4,6-Trimethyl-phenyl)-3-(3-trimethoxysilanopropyl)-imidazolium (5a): ¹H NMR (CDCl₃, 300 MHz): δ 0.71 (t, *J* = 8.0 Hz, 2H), 2.10 (m, 8H), 2.32 (s, 3H), 3.59 (s, 9H), 4.71 (t, *J* = 7.1 Hz, 2H), 7.02 (s, 2H), 7.25 (s, 1H), 7.79 (s, 1H), 9.91 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 10.7, 18.0, 21.3, 27.4, 50.8, 51.0, 126.0, 130.1, 134.4, 141.6; exact mass for (C₁₈H₂₈SiO₃N₂): [M+1] calcd 348.1869, obsd 349.1941.

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- Through the element analysis, nitrogen was checked, through which the existence of NHC ring could be confirmed indirectly. Amount of Nitrogen in Catalyst **1**: 2.7277%, **2**: 0.8561%, **3**: 1.0663%, **4**: 1.3447%, **5**: 0.9415%. Showing loading of catalyst (0.11-0.175 mmol Ru/g; ICP-AES analysis).