Tetrahedron 65 (2009) 3397–3403

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Novel imidazolium ion-tagged Ru-carbene complexes: synthesis and applications for olefin metathesis in ionic liquid

Shu-Wei Chen [a], Ju Hyun Kim [a], Ka Yeon Ryu [a], Won-Woong Lee [b], Jongki Hong [b], Sang-gi Lee [a,*]

[a] Department of Chemistry and Nano Science (BK21), Ewha Womans University, Seoul 120-750, Republic of Korea
[b] College of Pharmacy, Kyung Hee Univeristy, Seoul 130-701, Republic of Korea

ARTICLE INFO

Article history:
Received 15 December 2008
Received in revised form 17 February 2009
Accepted 18 February 2009
Available online 26 February 2009

ABSTRACT

Novel Hoveyda-type Ru-carbene complexes **7a**,**b** and **8a**,**b** tethering imidazolium tags at chelating isopropoxy group have been synthesized, and investigated their catalytic activities and recyclabilities in ring-closing metathesis (RCM) and cross metathesis (CM) in ionic liquids. They showed excellent catalytic activities for RCM of various dienes in [bmim][PF_6]/CH_2Cl_2 (1/1, v/v). The recyclability of these catalysts is largely dependent on the tether length and the structures of imidazolium tag and ionic liquid, as well as the composition of the ionic solvent system. A combination of the 2-methylated imidazolium ion-tagged Ru-complex **7b** with a mixture of [bdmim][PF_6]/toluene (1/3, v/v) allowed several times recycling without significant loss of catalytic activity in RCM, however low recyclabilities were observed in CMs.

1. Introduction

Olefin metathesis has become one of the simplest and effective synthetic methods for the construction of carbon–carbon double bonds, and is widely employed in a variety of fields of chemistry including natural products, pharmaceuticals, and polymer chemistry.[1] The spectacular recent success of olefin metathesis stems largely from the availability of several, well-defined Ru-catalysts such as Grubbs' Ru-benzylidenes **1** and Hoveyda's Ru-complexes **2**, which are easy to handle and tolerant toward different kinds of functional groups (Fig. 1).

Despite the widespread use of Ru-catalyzed metathesis, a major disadvantage is difficulty in the recovery and reuse of the expensive catalysts, as well as the product contamination caused by metal leaching. Hence, from an economic and environmental point of view, development of immobilization technology for recycling of the catalyst is of great importance.[2] In this context, the recently emerged room-temperature ionic liquids (RTILs) hold great potential. Given for characteristic properties of non-volatility, tunable immiscibility with organic solvents, and ability to dissolve organometallic compounds, RTILs have been utilized in many different kinds of reactions for catalyst recycling.[3] However, the recovered Ru-catalysts immobilized in ionic liquid layer rapidly lose their activity in subsequent runs, which has been ascribed largely to the leaching of the catalyst into the organic solvent used for product extraction.[4] An elegant solution to solve this leaching problem is the use of imidazolium ion-tagged catalyst, which could retain in ionic liquid layer more effectively. Numbers of different imidazolium ion-tagged Hoveyda-type Ru-complexes such as **3**–**6** have been designed and synthesized for olefin metathesis in ionic liquids (Fig. 2).[5–7] It has been observed that the catalytic activity and recyclability of the imidazolium ion-tagged Ru-complexes were largely dependent on the positions of imidazolium tag. For examples, both catalysts **3** and **4** tagging the imidazolium moiety *para*-position of chelating isopropoxy showed excellent recyclability with moderate activity.[5,6] However, much lower activity and recyclability have been observed with the catalyst **5** when the imidazolium tag anchored onto the chelating *ortho* oxygen atom. On changing the tagging position of imidazolium tag to the *meta*-position of the styrenylidene ligand, the activity was increased, but the recyclability was decreased.[7]

During our ongoing studies on the development of recyclable olefin metathesis catalysts,[8] we have interest to evaluate other possibilities of anchoring imidazolium ionic tags onto the chelating isopropoxy group. In order to investigate the effects of

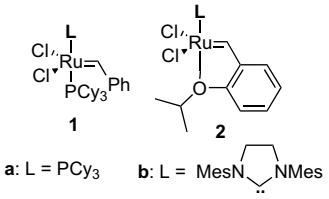


Figure 1. Grubbs and Hoveyda's Ru-complexes for olefin metathesis.

* Corresponding author. Tel.: +82 2 3277 4505; fax: +82 2 3277 3419.
E-mail address: sanggi@ewha.ac.kr (S.-gi Lee).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.02.043

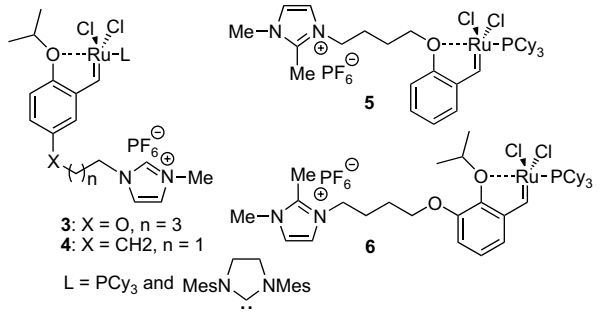


Figure 2. Imidazolium-tagged Ru-complexes.

structure and tagging position of imidazolium moiety on catalytic activity, two different types of Ru-complexes **7a**,**b** and **8a**,**b** have been designed. Herein, we report the synthesis of imidazolium ion-tagged Ru-carbene complexes **7a**,**b** and **8a**,**b** and their catalytic activities for olefin metathesis in ionic liquid-based solvent systems.

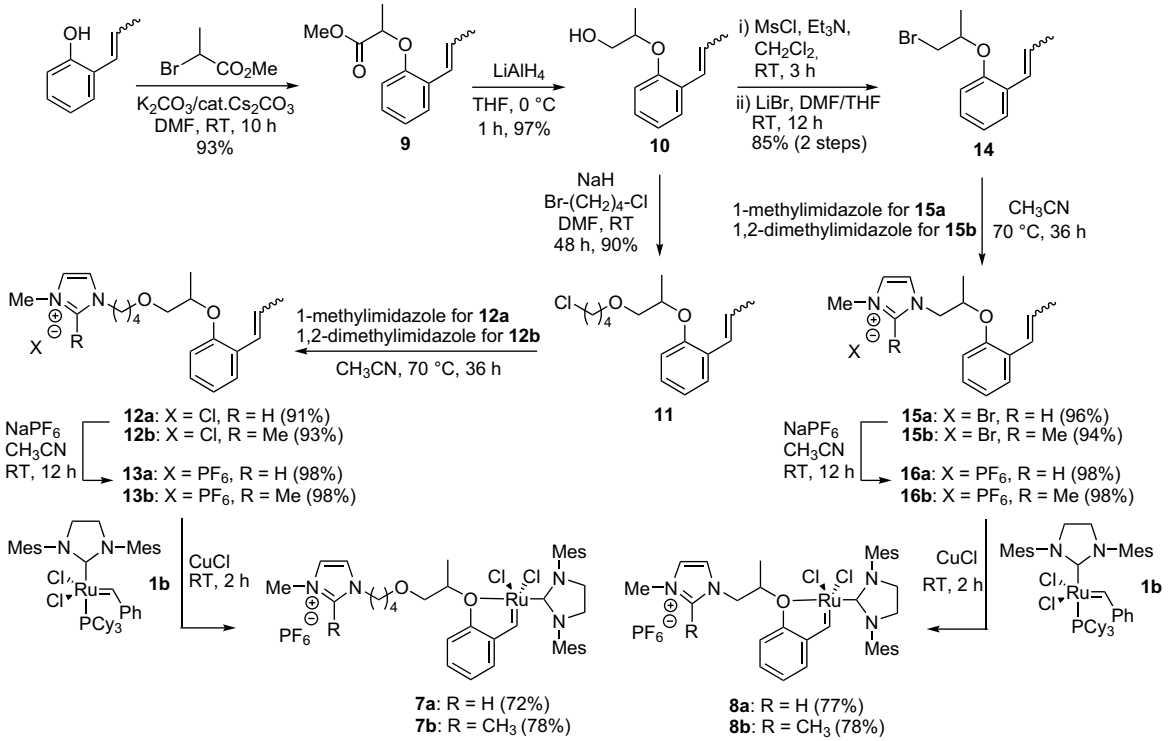
2. Results and discussion

2.1. Synthesis of imidazolium ion-tagged Ru-complexes 7a,b and 8a,b

The Ru-complexes **7a**,**b** and **8a**,**b** could be synthesized efficiently in seven steps starting from the commercially available (*E*/*Z*)-2-propenylphenol and methyl 2-bromopropionate (Scheme 1). The Ru-complexes **7a** and **7b** were synthesized first. Reaction of (*E*/*Z*)-2-propenylphenol with methyl 2-bromopropionate afforded the ester-functionalized olefin **9** in 93% yield.[9] The ester was reduced with LAH to give alcohol **10** in 98%, which has been used as key intermediate for the synthesis of both **7** and **8**. The alcohol **10** was reacted with 1-bromo-4-chlorobutane to afford the chlorinated ether **11** in 90% yield. To introduce the imidazolium moiety, the chloride **11** was reacted with an excess amount (2 equiv) of 1-methylimidazole for **12a** and 1,2-dimethylimidazole for **12b** in CH_3CN for 36 h at 70 °C to afford the corresponding imidazolium chlorides **12a** and **12b** in 91% and 93%, respectively. The chloride anion was exchanged with $NaPF_6$ to give the 1-methylimidazolium and 1,2-dimethylimidazolium hexafluorophosphate-tagged styrenyl **13a** and **13b** in almost quantitative yield. Compounds **13a** and **13b** were then reacted with Grubbs 2nd-generation catalyst **1b** in the presence of CuCl, and purified by silica column chromatography followed by solidifying with a mixture of CH_2Cl_2/pentane (1/1, v/v) to provide the pure imidazolium ion-tagged Ru-complexes **7a** (72%) and **7b** (78%) as air-stable, greenish powder. In order to investigate the effects of tether length on the activity and recyclability, the Ru-complexes **8a**,**b** tethering imidazolium tag onto chelating isopropoxy group directly were synthesized. For the synthesis of **8a** and **8b**, the hydroxy group of **10** was converted to the bromide **14** through the mesylation followed by nucleophilic substitution with LiBr in two steps 85% yield. The remaining synthetic steps are the same as those followed for the synthesis of **7a**,**b**. Thus, starting from the bromide **14**, both the ionic complex **8a** and **8b** were prepared in three steps with overall yields of 77% and 78%. In NMR analyses, the characteristic Ru=CH resonance signals were observed at 16.62 ppm for **7a**, 16.57 ppm for **7b**, 16.64 ppm for **8a**, 16.57 ppm for **8b** in ^{1}H NMR and 296.4 ppm for **7a**, 296.6 ppm for **7b**, 297.4 ppm for **8a**, 296.6 ppm for **8b** in ^{13}C NMR spectra. In HRMS analyses, the parent peaks, m/z=924.2074 for **7a** and m/z=938.2231 for **7b**, were also detected indicating clearly formation of the desired Ru-complexes.

2.2. Olefin metathesis in ionic liquids using imidazolium ion-tagged Ru-complexes 7a,b and 8a,b

First, we investigated the effects of counter anion of ionic liquid on the catalytic activity using **7a**. Thus, the RCM reactions of the benchmark substrate, *N*,*N*-bisallyl-*p*-toluenesulfonamide **17a** were



Scheme 1. Synthesis of imidazolium ion-tagged Ru-complexes **7a**,**b** and **8a**,**b**.

carried out in monophasic ionic solvent systems composed of [bmim][NTf_2]/CH_2Cl_2, [bmim][SbF_6]/CH_2Cl_2, and [bmim][PF_6]/CH_2Cl_2 (1/1, v/v) (bmim=1-butyl-3-methylimidazolium) at room temperature in the presence of 1.0 mol % of **7a**.

The reactions were monitored by TLC and the final conversion was determined by GC and NMR analyses. As observed by Dixneuf et al. in RCM with ruthenium allenylidene salts in ionic liquids,[4b] the catalytic activity was significantly dependent on the nature of counter anion of ionic liquid. The reactions in [bmim][NTf_2]/CH_2Cl_2 (entry 1, Table 1) and [bmim][SbF_6]/CH_2Cl_2 (entry 2, Table 1) showed 74% and 51% conversions, respectively, for 2 h, whereas the reaction in [bmim][PF_6]/CH_2Cl_2 (entry 3, Table 1) was completed within 10 min to provide ring-closed product **18a** in over 98% conversion. Based on these results, we investigated the catalytic activity of **7b**, **8a**, and **8b** in [bmim][PF_6]/CH_2Cl_2 solvent. It has been found that all of the imidazolium ion-tagged Ru-complexes showed extremely high catalytic activities, and complete conversions achieved within 10–15 min at room temperature (entries 4–6, Table 1). For comparison, the RCM reaction with original Hoveyda catalyst **2b** was conducted under the same condition completing in 45 min (entry 7, Table 1) indicating that anchoring imidazolium tag onto chelating isopropoxy group increased the catalytic activity.

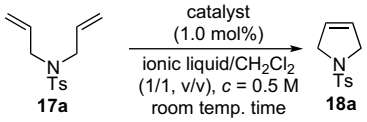
To evaluate the substrate scope of imidazolium-tagged Ru-complexes, RCM reactions of various dienes **17b**–**17h** with **7a** and **8a** were conducted in [bmim][PF_6]/CH_2Cl_2 at room temperature, and the results are summarized in Table 2.

Both **7a** and **8a** showed excellent catalytic activity for all sterically less demanding dienes **17b**–**17f**, and thus, the reactions were completed within 10 min to give the corresponding ring-closed products **18b**–**18f** in almost quantitative conversions (entries 1–5, Table 2). The RCM of olefin **17g** affording trisubstituted cyclic olefin **18g** was also completed at room temperature with prolonged reaction time (entry 6, Table 2). Moreover, the sterically more demanding diene **17h**, known to be a difficult substrate for RCM, can be cyclized smoothly, but required high temperature (40 °C) (entry 7, Table 2).

We next investigated the recyclability of the imidazolium ion-tagged catalysts. To recover the catalyst immobilized in ionic liquid, volatile CH_2Cl_2 was evaporated and the product was extracted with diethyl ether (2.0 mL×5). The recovered catalyst/ionic liquid was reused for next run. Disappointingly, the catalytic activity of the recovered **7a**, immobilized in [bmim][PF_6], was dramatically decreased in the 2nd cycle (entry 1, Table 3).

A recent report by Maudit and Guillemin indicated that a biphasic [bmim][PF_6]/toluene is to be effective recyclable solvent system in RCM reactions by using the imidazolium ion-tagged Ru-complex **4**.[6b] Thus, the ionic solvent system was changed to a biphasic [bmim][PF_6]/toluene (1/3, v/v) resulted in improved recyclability, allowing two iterations of recycling with diminished reactivity (entry 2, Table 3). Compared to reaction in [bmim][PF_6]/CH_2Cl_2, the reaction rate was relatively decreased in [bmim][PF_6]/toluene solvent system, which could be ascribed to its biphasic nature. The level of recyclability of **7a** was improved further as the ionic liquid was changed from [bmim][PF_6] to [bdmim][PF_6] (bdmim=1-butyl-2,3-dimethylimidazolium) (entry 3, Table 3). To our delight, in contrast to **7a**, the use of 1,2-dimethylimidazolium ion-tagged **7b** dramatically increased recyclability, thus, the recovered **7b**/[bdmim][PF_6] could be reused for several times without any loss of catalytic activity (entry 4, Table 3). These results clearly indicated that the structures of imidazolium tag and ionic liquid used have a pronounced effect on recyclability. Comparisons of the levels of Ru residue in toluene layer from 1st run with **7a** in [bmim][PF_6]/toluene (entry 2, Table 3), **7a** in [bdmim][PF_6]/[toluene] (entry 3, Table 3), and **7b** in [bdmim][PF_6]/toluene (entry 4, Table 3) also supported the structural effects of imidazolium moiety on catalyst stability. Combination of 2-methylated imidazolium-tagged **7b** with [bdmim][PF_6]/toluene minimized Ru leaching. Interestingly, the Ru-complexes **8a** and **8b**, in which the imidazolium moieties are in the proximity of reaction metal center, showed higher conversion rate compared with the **7a** and **7b** in a biphasic

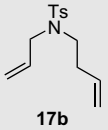
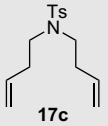
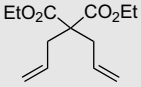
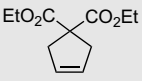
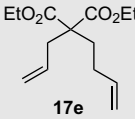
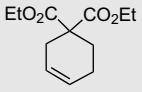
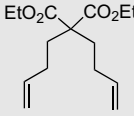
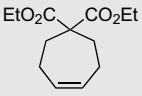
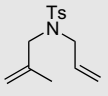
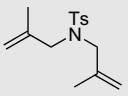
Table 1
RCM of **17a** with catalysts **7a**,**b** and **8a**,**b** in ionic liquids[a]



Entry	Catalyst	Ionic liquid	Time[b]	Conv[c] (%)
1	**7a**	[bmim][NTf_2]	2 h	74
2	**7a**	[bmim][SbF_6]	2 h	51
3	**7a**	[bmim][PF_6]	10 min	>98
4	**7b**	[bmim][PF_6]	10 min	>98
5	**8a**	[bmim][PF_6]	10 min	>98
6	**8b**	[bmim][PF_6]	15 min	>98
7	**2b**	[bmim][PF_6]	45 min	>98

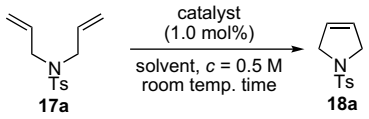
[a] Reactions were carried out at room temperature using 1.0 mol % of catalyst in ionic liquid/CH_2Cl_2 (1/1, v/v, *c*=0.5 M).
[b] Time for completion.
[c] Determined by GC and ^{1}H NMR analyses.

Table 2
RCMs of various dienes with **7a** and **8a** in [bmim][PF_6]/CH_2Cl_2[a]

Entry	17	18	7a		8a	
			Time[b]	Conv[c] (%)	Time[b]	Conv[c] (%)
1	 **17b**	 **18b**	10 min	>98	10 min	>98
2	 **17c**	 **18c**	10 min	>98	10 min	>98
3	 **17d**	 **18d**	10 min	>98	10 min	>98
4	 **17e**	 **18e**	10 min	>98	10 min	>98
5	 **17f**	 **18f**	10 min	>98	10 min	>98
6	 **17g**	 **18g**	2.5 h	>98	2 h	>98
7[d]	 **17h**	 **18h**	36 h	72	36 h	86

[a] Reactions were carried out at room temperature using 1.0 mol % of catalyst in [bmim][PF_6]/CH_2Cl_2 (1/1, v/v, *c*=0.5 M).
[b] Time for completion.
[c] Determined by ^{1}H NMR analysis.
[d] Reaction was conducted at 40 °C.

Table 3
Recycling of catalysts **7a**,**b** and **8a**,**b** for RCM of **17a** in ionic liquid

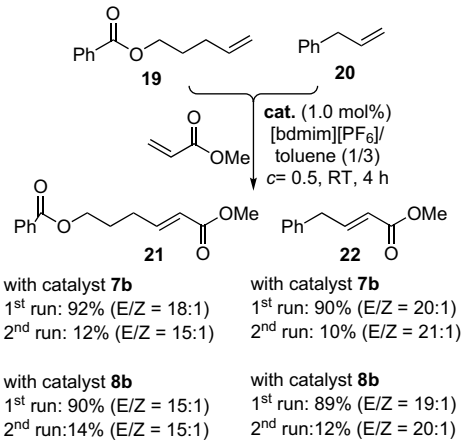


Entry	Cat.	Solvent	Cycle	Time	Conv[a] (%)
1	**7a**	[bmim][PF_6]/MC	1	10 min	>98
			2	1 h	20
2	**7a**	[bmim][PF_6]/toluene	1	1.5 h	>98
		Ru residue: 89 ppm[b]	2	4 h	>98
			3	12 h	46
3	**7a**	[bdmim][PF_6]/toluene	1	1 h	>98
		Ru residue: 87 ppm[b]	2	3 h	>98
			3	12 h	80
4	**7b**	[bdmim][PF_6]/toluene	1	1 h	>98
		Ru residue: 21 ppm[b]	2	1 h	>98
			3	1 h	>98
			4	1 h	>98
			5	1 h	>98
			6	2 h	>98
			7	6 h	>98
			8	6 h	77
5	**8a**	[bdmim][PF_6]/toluene	1	30 min	>98
			2	30 min	97
			3	30 min	11
6	**8b**	[bdmim][PF_6]/toluene	1	30 min	>98
			2	30 min	93
			3	30 min	27

[a] Determined by GC and ^{1}H NMR analyses.
[b] Ru contents in toluene layer after 1st run and determined by ICP-AES.

solvent system. Thus, the RCM reactions with **8a** (entry 5, Table 3) and **8b** (entry 6, Table 3) in [bdmim][PF_6]/toluene were completed within 30 min. However, the catalytic activities of the recovered catalysts were dramatically decreased in 3rd runs. Taken all together, it can be concluded that the structure of the imidazolium tag and ionic liquid, as well as the choice of the anchoring position of the imidazolium tag, and composition of ionic solvent system are important for the development of highly reactive and recyclable Ru-catalysts for RCMs in ionic liquids.

Finally, we investigated catalytic activity and recyclability of the imidazolium ion-tagged Ru-complexes for cross metathesis (CM) in ionic liquids (Scheme 2).



Scheme 2. Cross metatheses with **7b** and **8b** in [bdmim][PF_6]/toluene.

Based on the results from ring-closing metathesis described above, the Ru-complexes **7b** and **8b** anchoring 2-methylated imidazolium ion tag and [bdmim][PF_6]/toluene solvent system were selected for CMs of 5-pentenylbenzoate **19** and 3-phenyl-1-propene **20** with a standard electron demanding substrate, methyl acrylate. Both **7b** and **8b** showed excellent catalytic activities in the first runs, and thus the cross metathesis products **21** and **22** were formed in over 90% with *E*-isomer selectivity. However, the catalytic activities of the recovered catalysts immobilized in ionic liquid layer were dramatically decreased in 2nd runs, which could be ascribed to the remained methyl acrylate. To avoid the self-cross metathesis, at least 2 equiv methyl acrylate was used, and the remained methyl acrylate provokes a competitive metathesis reaction against the styrenyl ether inhibiting the return process of the catalytically active Ru-catalyst.

3. Conclusion

A new-type of Hoveyda-type Ru-complexes **7a**,**b** and **8a**,**b** anchoring imidazolium ion onto the chelating isopropoxy group has been designed and synthesized to perform olefin metathesis in ionic liquid. These catalysts exhibited excellent catalytic activities for ring-closing metathesis and cross metathesis. The present work highlights the fact that changing the location of the tagging and the structures of imidazolium tag and ionic liquid as well as the composition of ionic solvent can dramatically improve the catalyst/ionic liquid and minimized residual Ru levels in the RCM products. Thus, combination of 2-methylated imidazolium ion-tagged Ru-complex **7b** with a biphasic [bdmim][PF_6]/toluene medium increased dramatically the recycling of the catalyst and low residual Ru levels were detected by ICP-AES in the product. Excellent activities were also observed in first runs of cross metathesis, however, the recyclability was very low. Further studies on the development of a more effective recyclable catalytic system for cross metathesis in ionic liquids are currently underway.

4. Experimental

4.1. General

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury VX250 NMR spectrometer (250 MHz) in given solvent. Chemical shifts were expressed in parts per million with TMS as an internal standard (δ=0 ppm) for ^{1}H NMR, coupling constants (*J*) are in hertz. The anhydrous toluene was distilled from sodium benzophenone ketyl. The DMF and methylene chloride were freshly distilled from calcium hydride. The purchased reagents are used as-received without further purification. All manipulations involving air and moisture-sensitive compounds and reactions were carried out using standard Schlenk technique under nitrogen atmosphere.

4.2. Synthesis

*4.2.1. 2-(2-Propenylphenoxy)propionic acid methyl ester (**9**)*

To a solution of *E*/*Z* mixture of 2-propenylphenol (3.03 g, 22.58 mmol) and methyl 2-bromopropionate (5.63 g, 33.70 mmol) in anhydrous DMF (30 mL) were added Cs_2CO_3 (1.47 g, 4.52 mmol) and K_2CO_3 (4.66 g, 33.70 mmol). After stirring for 10 h at room temperature, the reaction mixture was poured into water (100 mL) and extracted with EtOAc (3×50 mL). The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated under vacuum. Purification by silica gel chromatography (EtOAc/hexane=1/9 v/v) afforded the desired product **9** as a colorless oil (4.65 g, 93.6%). Spectral data for major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.41 (dd, *J*=7.7, 1.7 Hz, 1H), 7.18–7.06 (m, 1H), 6.94–6.88 (m, 1H), 6.78 (dq, *J*=15.9, 1.8 Hz, 1H), 6.69 (dq, *J*=8.2, 1.0 Hz, 1H), 6.23 (dq, *J*=15.9, 6.6 Hz, 1H), 4.73 (q, *J*=6.8 Hz, 1H), 3.72 (s, 3H), 1.90 (dd, *J*=6.6, 1.8 Hz, 3H), 1.63 (d, *J*=6.8 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 172.7, 154.2, 130.5, 127.9, 127.6, 126.6, 125.4, 121.7, 113.0, 73.3, 52.2, 18.9, 18.6 ppm.

4.2.2. 2-(2-Propenylphenoxy)propan-1-ol (**10**)

To a stirred solution of **9** (6.0 g, 27.24 mmol) in anhydrous THF (100 mL) was added $LiAlH_4$ (32.7 mL, 1 M in THF) dropwise at 0 °C. After stirring for 1 h at 0 °C, the excess of $LiAlH_4$ was destroyed by addition of saturated aqueous Na_2SO_4 dropwise. The appeared white precipitate was filtered and the residue was washed with THF several times. The THF filtrate was dried with anhydrous Na_2SO_4, and the THF was evaporated to afford **10** (5.12 g, 97.7%) as a slightly yellow oil, which was used for next reaction without further purification. The spectral data of major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39 (dd, J=8.0, 1.6 Hz, 1H), 7.16–7.09 (m, 1H), 6.93–6.86 (m, 2H), 6.71 (dq, J=15.9, 1.6 Hz, 1H), 6.19 (dq, J=15.9, 6.6 Hz, 1H), 4.47–4.40 (m, 1H), 3.74–3.68 (m, 2H), 2.52 (br s, 1H), 1.88 (dd, J=6.6, 1.6 Hz, 3H), 1.22 (d, J=6.2 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 154.8, 130.7, 128.7, 128.3, 127.2, 125.9, 121.6, 114.9, 76.3, 66.5, 19.0, 16.2 ppm. IR: 3591, 3374, 3038, 2985, 2940, 2090, 1594, 1484, 1447, 1241, 1148, 1041, 914, 742 cm^{-1}.

4.2.3. 1-[2-(4-Chlorobutoxy)-1-methylethoxy]-2-propenylbenzene (**11**)

To a solution of **10** (4.6 g, 23.93 mmol) in anhydrous DMF (50 mL) was added NaH (1.44 g, 35.89 mmol) at 0 °C. After stirring for 10 min at 0 °C, 1-bromo-4-chlorobutane (8.21 g, 47.86 mmol) was added. The resulting mixture was stirred for 48 h at room temperature and the reaction mixture was quenched with water (50 mL), and extracted with ethyl acetate (3×25 mL). The combined organic layer was dried with Na_2SO_4 and concentrated by vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc/hexane 1/5) to give the product **11** (6.1 g, 90.0%) as a colorless oil. The spectral data of major isomer: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.40 (dd, J=8.2, 1.7 Hz, 1H), 7.22–7.09 (m, 1H), 6.95–6.89 (m, 2H), 6.72 (dq, J=15.9, 1.6 Hz, 1H), 6.20 (dq, J=15.9, 6.6 Hz, 1H), 4.49–4.47 (m, 1H), 3.62–3.47 (m, 6H), 1.88 (dd, J=6.6, 1.6 Hz, 3H), 1.73–1.70 (m, 4H), 1.32 (d, J=6.2 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 154.6, 130.3, 128.4, 127.8, 126.4, 125.9, 121.1, 114.8, 74.2, 74.1, 70.6, 44.9, 29.4, 27.0, 18.9, 17.3 ppm. IR: 3049, 2982, 2875, 1597, 1447, 1261, 1114, 747, 705 cm^{-1}.

4.2.4. 3-Methyl-1-{4-[2-(2-propenylphenoxy)-propoxy]-butyl}-3H-imidazolium chloride (**12a**)

A 50 mL round bottomed flask equipped with a condenser was charged with **11** (1.0 g, 3.53 mmol), 1-methylimidazole (0.72 g, 8.84 mmol), and anhydrous acetonitrile (15 mL). The mixture was refluxed for 36 h. After cooling to room temperature, the solvent was evaporated, and the residue was washed with diethyl ether (3×25 mL) to remove unreacted 1-methylimidazole to give **12a** as pale yellowish oil (1.18 g, 91.2%). The spectral data of major isomer: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.40–7.14 (m, 4H), 6.96–6.88 (m, 2H), 6.69 (dq, J=15.9, 1.6 Hz, 1H), 6.23 (dq, J=15.9, 6.6 Hz, 1H), 4.60–4.50 (m, 1H), 4.31 (t, J=7.2 Hz, 2H), 3.98 (s, 3H), 3.62–3.51 (m, 4H), 3.02 (br s, 1H), 1.99–1.93 (m, 2H), 1.86 (dd, J=6.6, 1.6 Hz, 3H), 1.62–1.56 (m, 2H), 1.27 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 154.9, 138.2, 130.6, 128.1, 126.7, 125.9, 123.6, 122.3, 121.4, 120.7, 114.7, 74.7, 74.6, 71.1, 49.9, 36.7, 27.9, 26.3, 19.1, 17.1 ppm. IR: 3382, 3058, 2970, 1594, 1458, 1385, 1278, 1168, 1114, 970, 733, 606 cm^{-1}.

4.2.5. 2,3-Dimethyl-1-{4-[2-(2-propenylphenoxy)-propoxy]-butyl}-3H-imidazolium chloride (**12b**)

Prepared by the same method for **12a** using 1,2-dimethylimidazole. Yield: 93%. The spectral data of major isomer: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.82 (d, J=1.8 Hz, 1H), 7.58 (d, J=1.9 Hz, 1H), 7.31 (dd, J=1.1, 7.6 Hz, 1H), 7.16–7.04 (m, 1H), 6.87–6.77 (m, 2H), 6.64 (dq, J=16.0, 1.5 Hz, 1H), 6.17 (dq, J=15.8, 6.6 Hz, 1H), 4.52–4.40 (m, 1H), 4.16 (t, J=7.3 Hz, 2H), 3.88 (s, 3H), 3.55–3.42 (m, 4H), 2.60 (s, 3H), 1.81–1.72 (m, 5H), 1.56–1.51 (m, 2H), 1.20 (d, J=6.2 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 155.0, 144.0, 130.5, 128.1, 126.5, 125.7, 123.3, 121.6, 120.6, 114.8, 114.5, 74.6, 74.4, 71.0, 48.6, 35.9, 27.4, 26.5, 19.1, 17.2, 10.7 ppm. IR: 3343, 3050, 2957, 2316, 1594, 1458, 1258, 1123, 970, 905, 753 cm^{-1}.

4.2.6. 3-Methyl-1-{4-[2-(2-propenylphenoxy)-propoxy]-butyl}-3H-imidazolium hexafluorophosphate (**13a**)

To a stirred solution of **12a** (1.0 g, 2.74 mmol) in anhydrous CH_3CN (15 mL) was added $NaPF_6$ (1.15 g, 6.85 mmol). The resulting mixture was stirred for 12 h at room temperature, and then filtered. After evaporation of the solvent, the resulting residue was distributed in water and methylene chloride, and the water layer was washed with methylene chloride. The combined methylene chloride layer was evaporated, and dried under vacuum to give **13a** (1.27 g, 98.2%) as colorless oil. The spectral data of major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.36 (dd, J=1.4, 7.6 Hz, 1H), 7.26–7.14 (m, 3H), 6.95–6.85 (m, 2H), 6.65 (dq, J=15.9, 1.5 Hz, 1H), 6.20 (dq, J=15.8, 6.5 Hz, 1H), 4.48–4.60 (m, 1H), 4.11 (t, J=7.2 Hz, 2H), 3.74 (s, 3H), 3.66–3.41 (m, 4H), 2.00–1.75 (m, 5H), 1.57–1.51 (m, 2H), 1.27 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 154.5, 135.8, 130.3, 128.1, 126.4, 125.5, 123.4, 122.2, 121.2, 120.5, 114.4, 74.4, 74.1, 70.8, 49.5, 35.9, 27.5, 25.5, 18.9, 16.8 ppm. IR: 3055, 2993, 2308, 1594, 1430, 1266, 1106, 849, 731, 553 cm^{-1}.

4.2.7. 2,3-Methyl-1-{4-[2-(2-propenylphenoxy)-propoxy]-butyl}-3H-imidazol-1-ium hexafluorophosphate (**13b**)

Prepared by the same method for **13a** using **12b**. Yield: 98%. The spectral data of major isomer: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.40 (dd, J=1.4, 7.6 Hz, 1H), 7.21–7.13 (m, 3H), 6.95–6.89 (m, 2H), 6.72 (dq, J=16.0, 1.4 Hz, 1H), 6.24 (dq, J=15.9, 6.6 Hz, 1H), 4.62–4.53 (m, 1H), 4.05 (t, J=7.5 Hz, 2H), 3.75 (s, 3H), 3.64–3.54 (m, 4H), 2.51 (s, 3H), 1.90–1.81 (m, 5H), 1.64–1.59 (m, 2H), 1.30 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 155.1, 144.1, 130.6, 128.3, 126.6, 125.9, 122.7, 121.4, 120.7, 114.8, 114.7, 74.8, 74.4, 71.1, 48.9, 35.5, 27.5, 26.3, 19.1, 17.0, 9.5 ppm. IR: 3050, 2985, 2299, 1585, 1444, 1267, 1117, 979, 835, 756, 556 cm^{-1}.

4.2.8. 1-(2-Bromo-1-methylethoxy)-2-propenylbenzene (**14**)

To a solution of **10** (3.0 g, 15.60 mmol) and triethylamine (3.26 mL, 23.41 mmol, 1.5 equiv) in dry dichloromethane (90 mL) was added methanesulfonyl chloride (1.82 mL, 23.41 mmol, 1.5 equiv) at 0 °C. The reaction mixture was stirred for 3.5 h at room temperature. After filtration of the precipitates, the organic phase was washed four times with a 5% citric acid solution, dried over sodium sulfate, and concentrated to give the mesylated compound, which was used without further purification in the following reaction. The spectral data of major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40 (dd, J=8.0, 1.8 Hz, 1H), 7.18–7.10 (m, 1H), 6.95–6.85 (m, 2H), 6.71 (dq, J=15.9, 1.7 Hz, 1H), 6.19 (dq, J=15.8, 6.6 Hz, 1H), 4.62–4.56 (m, 1H), 4.37–4.26 (m, 2H), 2.94 (s, 3H), 1.87 (dd, J=6.6, 1.6 Hz, 3H), 1.30 (d, J=6.2 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 153.7, 128.5, 127.9, 126.6, 125.5, 121.9, 121.2, 114.7, 72.5, 72.0, 37.4, 18.9, 16.3 ppm. To a solution of mesylate (2.97 g, 11 mmol) obtained from above procedure in tetrahydrofuran (40 mL) and dimethylformamide (16 mL) was added lithium bromide (1.92 g, 22 mmol, 2 equiv) in one portion. The mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was diluted in ethyl acetate. The organic layer was washed three times successively with a saturated $NaHCO_3$ solution and brine, dried over magnesium sulfate, filtrated, and concentrated. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (20/1) as the eluent to afford **14** as colorless oil (2.33 g, 9.12 mmol, 85% (two steps)). The spectral data of major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.42 (dd, J=7.6, 1.5 Hz, 1H), 7.18–7.12 (m, 1H), 6.94–6.85 (m, 2H), 6.73 (dq, J=15.9, 1.5 Hz, 1H), 6.23 (dq,

J=15.8, 6.6 Hz, 1H), 4.55–4.50 (m, 1H), 3.60–3.42 (m, 2H), 1.90 (dd, J=6.6, 1.8 Hz, 3H), 1.28 (d, J=6.2 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 153.8, 128.7, 127.7, 126.6, 125.5, 121.8, 121.2, 114.8, 74.4, 35.6, 18.9, 14.7 ppm. IR: 3041, 2976, 2398, 2071, 1602, 1453, 1278, 1230, 1140, 1026, 950, 742 cm^{-1}.

4.2.9. 3-Methyl-1-[2-(2-propenylphenoxy)]propyl-3H-imidazolium bromide (**15a**)

A 100 mL round bottomed flask equipped with a condenser was charged with compound **14** (2.5 g, 9.80 mmol), 1-methyl-1*H*-imidazole (1.61 g, 19.60 mmol), and anhydrous acetonitrile (50 mL). The mixture was refluxed for 36 h and cooled to room temperature. After evaporation of the solvent, the residue was washed with diethyl ether (3×30 mL) to afford imidazolium bromide **15a** as slightly yellow oil (3.17 g, 95.6%). The spectral data of major isomer: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 9.95 (s, 1H), 7.62 (d, J=1.4 Hz, 1H), 7.50 (d, J=1.5 Hz, 1H), 7.37 (dd, J=7.6, 1.4 Hz, 1H), 7.14–7.07 (m, 1H), 6.92–6.83 (m, 2H), 6.64 (dq, J=15.9, 1.5 Hz, 1H), 6.20 (dq, J=15.9, 6.6 Hz, 1H), 4.89–4.84 (m, 2H), 4.56–4.41 (m, 1H), 3.98 (s, 3H), 1.90 (dd, J=6.6, 1.5 Hz, 3H), 1.33 (d, J=6.1 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 151.2, 135.9, 128.6, 126.4, 126.0, 125.1, 124.6, 123.3, 121.4, 121.3, 119.9, 112.4, 71.3, 34.7, 16.9, 14.8 ppm. IR: 3374, 3049, 2956, 2434, 2090, 1594, 1453, 1238, 970, 888, 761, 618, 536 cm^{-1}.

4.2.10. 2,3-Methyl-1-[2-(2-propenylphenoxy)]propyl-3H-imidazolium bromide (**15b**)

Prepared by the same method for **15a** using 1,2-dimethylimidazole. Yield: 94%. The spectral data of major isomer: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.88 (d, J=2.1 Hz, 1H), 7.58 (d, J=2.1 Hz, 1H), 7.28 (dd, J=7.6, 1.5 Hz, 1H), 7.04–6.98 (m, 1H), 6.82–6.70 (m, 2H), 6.48 (dq, J=15.9, 1.5 Hz, 1H), 6.09 (dq, J=15.9, 6.6 Hz, 1H), 4.84–4.70 (m, 2H), 4.40–4.34 (m, 1H), 3.78 (s, 3H), 2.67 (s, 3H), 1.79 (dd, J=7.0, 1.8 Hz, 3H), 1.30 (d, J=6.1 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 151.1, 142.9, 128.5, 126.3, 126.0, 124.9, 124.5, 123.3, 120.8, 120.3, 119.8, 112.3, 71.6, 33.9, 16.8, 14.9, 9.1 ppm. IR: 3366, 3067, 2957, 1594, 1492, 1456, 1266, 1241, 1131, 1041, 976, 894, 742 cm^{-1}.

4.2.11. 3-Methyl-1-[2-(2-propenylphenoxy)]propyl-3H-imidazolium hexafluorophosphate (**16a**)

To a stirred solution of **15a** (0.8 g, 2.37 mmol) in anhydrous CH_3CN (15 mL) was added $NaPF_6$ (0.48 g, 2.85 mmol). The resulting mixture was stirred for 12 h, and then filtered through Celite. After evaporation of solvent, the residue was dissolved in methylene chloride, and washed with water, and evaporated to give **16a** as dark yellow oil (0.95 g, 97.6%). The spectral data of major isomer: ^{1}H NMR (250 MHz, acetone) δ 8.93 (s, 1H), 7.72 (d, J=1.4 Hz, 1H), 7.62 (d, J=1.3 Hz, 1H), 7.44 (dd, J=7.6, 1.6 Hz, 1H), 7.21–7.12 (m, 1H), 6.99–6.89 (m, 2H), 6.71 (dd, J=15.9, 1.5 Hz, 1H), 6.23 (dq, J=15.9, 6.6 Hz, 1H), 4.96–4.92 (m, 1H), 4.67–4.57 (m, 2H), 3.99 (s, 3H), 1.88 (dd, J=6.6, 1.5 Hz, 3H), 1.33 (d, J=6.1 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, acetone) δ 154.2, 138.1, 131.3, 129.1, 128.9, 127.3, 126.2, 124.6, 124.2, 122.7, 115.3, 73.8, 54.8, 36.7, 19.0, 17.0 ppm. IR: 3165, 3058, 2990, 1594, 1447, 1258, 1176, 852, 739, 553 cm^{-1}.

4.2.12. 2,3-Methyl-1-[2-(2-propenylphenoxy)]propyl-3H-imidazolium hexafluorophosphate (**16b**)

Prepared by the same method for **16a** using **15b**. Yield: 98%. The spectral data of major isomer: ^{1}H NMR (250 MHz, acetone) δ 7.70 (d, J=2.1 Hz, 1H), 7.60 (d, J=2.1 Hz, 1H), 7.44 (dd, J=7.7, 1.5 Hz, 1H), 7.15–7.12 (m, 1H), 6.97–6.88 (m, 2H), 6.65 (dq, J=15.9, 1.5 Hz, 1H), 6.24 (dq, J=15.9, 6.6 Hz, 1H), 4.99–4.97 (m, 1H), 4.70–4.64 (m, 2H), 3.94 (s, 3H), 2.85 (s, 3H), 1.87 (dd, J=6.6, 1.5 Hz, 3H), 1.40 (d, J=6.1 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 153.1, 145.3, 128.9, 128.3, 127.6, 127.0, 125.5, 122.8, 122.5, 122.2, 114.5, 73.4, 35.6, 19.0, 17.0, 14.7, 10.2 ppm. IR: 3061, 2993, 2310, 1421, 1258, 846, 756, 710, 553 cm^{-1}.

4.2.13. Imidazolium ion-tagged Ru-carbene complexes **7a**,**b** and **8a**,**b**

A degassed solution of **13a** (14.9 mg, 0.031 mmol), Grubbs 2nd-generation catalyst, $RuCl_2$(=CHPh)(PCy_3)(NHC), (40.0 mg, 0.047 mmol), and CuCl (3.88 mg, 0.039 mmol) in dry dichloromethane (5 mL) was stirred at room temperature for 1 h. After short column silica chromatography (MC/MeOH=9/1, v/v), the resulting material was treated with a mixture of CH_2Cl_2/pentane (1/1, v/v) to provide the pure imidazolium-tagged Ru-carbene complexes **7a** as air-stable, greenish powder (56.6 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 16.62 (s, 1H), 8.30 (s, 1H), 7.51–7.47 (m, 1H), 7.08–6.97 (m, 8H), 6.84–6.83 (m, 2H), 4.98–4.96 (m, 1H), 4.15 (s, 4H), 4.10–3.84 (m, 2H), 3.68–3.60 (m, 2H), 3.55 (s, 3H), 3.32–3.26 (m, 2H), 3.15–3.12 (m, 1H), 2.43–2.29 (m, 18H), 1.74–1.70 (m, 2H), 1.45–1.42 (m, 2H), 1.20 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 296.4, 209.8, 152.3, 144.6, 139.0, 130.1, 129.8, 129.4, 123.6, 123.4, 123.1, 122.8, 122.3, 122.2, 113.5, 73.6, 70.2, 51.6, 49.4, 36.0, 27.6, 25.1, 21.1, 18.8, 17.4, 17.1 ppm; HRMS (m/z) Calcd for $[M]^+$: $C_{39}H_{51}Cl_2F_6N_4O_2PRu^+$: 924.2069. Found: 924.2074. Compound **7b** was prepared from **13b**. Yield: 78%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 16.57 (s, 1H), 7.56–7.52 (m, 2H), 7.10–7.04 (m, 5H), 6.96 (d, J=8.2 Hz, 1H), 6.84–6.82 (m, 2H), 4.99–4.93 (m, 1H), 4.14 (s, 4H), 3.70–3.62 (m, 5H), 3.30–3.25 (m, 4H), 2.44–2.30 (m, 18H), 1.63–1.58 (m, 2H), 1.47–1.44 (m, 2H), 1.19 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 296.6, 210.1, 152.4, 144.6, 143.5, 139.0, 129.8, 128.7, 127.5, 126.4, 123.6, 122.6, 122.1, 120.7, 113.5, 73.5, 70.0, 51.5, 48.1, 34.9, 26.8, 25.8, 21.1, 19.3, 17.4, 16.9, 9.1 ppm; HRMS (m/z) Calcd for $[M]^+$: $C_{40}H_{53}Cl_2F_6N_4O_2PRu^+$: 938.2225. Found: 938.2231. Compound **8a** was prepared from **16a**. Yield: 77%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 16.64 (s, 1H), 8.25 (s, 1H), 7.53–7.26 (m, 4H), 6.96–6.84 (m, 5H), 6.50–6.48 (m, 1H), 5.37–5.34 (m, 1H), 4.45–4.18 (m, 4H), 3.53 (s, 3H), 2.47–2.31 (m, 18H), 1.26 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 297.4, 208.9, 151.8, 143.7, 140.9, 139.2, 134.9, 130.1, 129.5, 129.0, 126.5, 124.1, 123.5, 122.6, 111.2, 53.8, 51.6, 36.5, 21.1, 19.4, 17.8, 17.5 ppm. IR: 3058, 2990, 2308, 1430, 1267, 897, 843, 742, 561 cm^{-1}; HRMS (m/z) Calcd for $[M-HPF_6]^+$: $C_{35}H_{43}Cl_2N_4ORu^+$: 707.1861. Found: 707.1892. Compound **8b** was prepared from **16b**. Yield: 78%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 16.57 (s, 1H), 7.56–7.52 (m, 1H), 7.37–7.26 (m, 4H), 6.96–6.87 (m, 4H), 6.50–6.43 (m, 1H), 4.99–4.93 (m, 1H), 4.30–4.17 (m, 5H), 3.62–3.48 (m, 4H), 2.53–2.30 (m, 21H), 1.30 (d, J=6.3 Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 296.6, 209.0, 151.4, 144.8, 144.3, 139.2, 130.0, 129.4, 128.9, 126.4, 123.6, 122.6, 122.0, 114.0, 111.2, 75.3, 51.7, 35.0, 21.0, 19.5, 17.4, 16.8, 9.6 ppm. IR: 3066, 2197, 2082, 1972, 1258, 843, 733, 552 cm^{-1}; HRMS (m/z) Calcd for $[M-HPF_6]^+$: $C_{36}H_{45}Cl_2N_4ORu^+$: 721.2018. Found: 721.2026.

4.3. Olefin metathesis in ionic liquid

4.3.1. A typical procedure for ring-closing metathesis in ionic liquid using imidazolium ion-tagged catalysts

A solution of **7b** (3.68 mg, 4.0×10^{-3} mmol) in a mixture of [bmim][PF_6]/CH_2Cl_2 (1.0 mL/1.0 mL) (or [bdmim][PF_6]/toluene, 0.5 mL/1.5 mL) was stirred at room temperature for 1 h, at which point diene **17a** (100 mg, 0.4 mmol) was added. The reaction mixture was stirred until completion of the conversion (by TLC). After evaporation of CH_2Cl_2, the ionic liquid layer was extracted with dry diethyl ether (2 mL×5), and then the diethyl ether was evaporated. For the [bmim][PF_6]/toluene solvent system: the toluene layer was separated and then the ionic liquid layer was extracted with toluene (2 mL×5). After evaporation of the diethyl ether (or toluene), the crude residue was subjected to GC and ^{1}H NMR analyses to reveal complete conversion. The ionic liquid phase containing **7b** was reused for subsequent runs.

4.3.2. A typical procedure for cross metathesis in [bdmim][PF_6]/toluene

A solution of **7b** (4.9 mg, 5.2×10^{-3} mmol) in a mixture of [bdmim][PF_6]/toluene (0.3 mL/0.9 mL) was stirred at room temperature for 30 min, at which point olefin **19** (100 mg, 0.52 mmol) and methyl acrylate (90.5 mg, 1.05 mmol) were added all at once. The reaction mixture was stirred at room temperature for 4 h. After separation of toluene, the ionic liquid layer was extracted with toluene (1 mL×3), and the combined toluene was evaporated. The residue was subjected to GC and ^{1}H NMR analyses to determine the conversion and *E*/*Z* ratio of the cross-coupled product. The ionic liquid layer containing **7b** was reused for 2nd run.

Acknowledgements

This work was supported by the Korean Research Foundation (KRF-2006-312-C00587).

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.043.

References and notes

1. Selected reviews on olefin metathesis: (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18; (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592; (c) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003; (d) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900; (e) Astruc, A. *New J. Chem.* **2005**, *29*, 42.
2. Review on supported Ru-catalysts, see: Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6786.
3. Recent reviews on ionic liquids: (a) Lee, S.-g. *Chem. Commun.* **2006**, 1049; (b) Song, C. E. *Chem. Commun.* **2004**, 1033; (c) Antonietti, M.; Kuang, D.; Smarsly, B.; Xhou, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 4988; (d) Davis, J. H., Jr.; Fox, P. A. *Chem. Commun.* **2003**, 1209; (e) Dupont, J.; de Souza, R. F.; Saurez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667; (f) Olivier-Bourbiou, H.; Magna, L. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 419; (g) Sheldon, R. *Chem. Commun.* **2001**, 2399; (h) Wasserchеid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772; (i) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
4. (a) Buijsman, R. C.; van Vuuren, E.; Sterrenburg, J. G. *Org. Lett.* **2001**, *3*, 3785; (b) Semeril, D.; Olivier-Bourgbigou, H.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **2002**, 146; (c) Mayo, K. G.; Nearhoof, E. H.; Kiddle, J. J. *Org. Lett.* **2002**, *4*, 1567; (d) Csihony, S.; Fischmeister, C.; Bruneau, C.; Horváth, I. T.; Dixneuf, P. H. *New J. Chem.* **2002**, *26*, 1667; (e) Ding, X.; Lv, X.; Hui, B.; Chen, Z.; Xiao, M.; Guo, B.; Tang, W. *Tetrahedron Lett.* **2006**, *47*, 2921.
5. (a) Yao, Q.; Zhang, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3395; (b) Yao, Q.; Sheets, M. *J. Organomet. Chem.* **2005**, *690*, 3577.
6. (a) Audic, N.; Clavier, H.; Mauduit, M.; Guillemin, J.-C. *J. Am. Chem. Soc.* **2003**, *125*, 9248; (b) Clavier, H.; Audic, N.; Mauduit, M.; Guillemin, J.-C. *Chem. Commun.* **2004**, 2282; (c) Clavier, H.; Audic, N.; Mauduit, M.; Guillemin, J.-C. *J. Organomet. Chem.* **2005**, *690*, 3585; (d) Rix, D.; Cïjo, F.; Laurent, I.; Gułajski, Ł.; Grela, K.; Mauduit, M. *Chem. Commun.* **2007**, 3771.
7. (a) Thurier, C.; Fischmeister, C.; Bruneau, C.; Olivier-Bourbigou, H.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **2007**, *268*, 127; (b) Thurier, C.; Fischemister, C.; Bruneau, C.; Olivier-Bourbiou, H.; Dixneuf, P. H. *ChemSusChem* **2008**, *1*, 118.
8. (a) Lee, B. S.; Namgoong, S. K.; Lee, S.-g. *Tetrahedron Lett.* **2005**, *46*, 4501; (b) Chen, S.-W.; Kim, J. H.; Song, C. E.; Lee, S.-g. *Org. Lett.* **2007**, *9*, 3845; (c) Chen, S.-W.; Kim, J. H.; Shin, H.; Lee, S.-g. *Org. Biomol. Chem.* **2008**, *6*, 2676.
9. Bieniek, M.; Bujok, R.; Cabaj, M.; Lugan, N.; Lavigne, G.; Arit, D.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128*, 13652.