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Review

Development of novel reactions using ruthenium carbene catalyst and its application to novel methods for preparing nitrogen-containing heterocycles ☆

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Abstract

The reaction of *N*-allyl-*ortho*-vinylaniline with ruthenium carbene catalyst at 50 °C gives substituted 1,2-dihydroquinoline through ring-closing metathesis (RCM), which is easily converted to the corresponding quinoline after deprotection. In sharp contrast, when vinyloxytrimethylsilane is added to this reaction mixture, 1,2-dihydroquinoline is not formed and selective isomerization of *N*-allyl-*ortho*-vinylaniline is observed at 50 °C to give corresponding enamide, which is successfully converted to indole derivative by RCM. The same catalyst system provide indoline derivative at 160 °C by cycloisomerization. Based on a detailed mechanistic study, it becomes clear that a ruthenium carbene catalyst, which is highly effective for RCM, reacts with an electron-rich terminal olefin selectively, and another ruthenium species, which effectively catalyzes the isomerization of terminal olefin and cycloisomerization of alpha, omega-diene, is generated.

Keywords: Ruthenium carbene; Heterocycles; Metathesis; Olefin isomerization; Cycloisomerization

Contents

☆ Short Accounts of Recent Personal Research.

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1. Introduction

Transition metal-catalyzed olefin metathesis is a remarkable topic in current chemistry. In this field, ruthenium carbene catalysts have received much attention and are frequently used in the synthesis of biologically active natural products, because of their stability, functional group tolerance, easy handling and commercial availability [1]. Over the past decades, well-defined ruthenium catalysts have been developed and Grubbs et al. [2] reported the first practical catalyst (**A**). The recent introduction of catalysts (**B** [3], **D** [4]) bearing *N*-heterocyclic carbene (NHC) ligand has led to much higher reactivity (Fig. 1). We have been exploring a synthetic methodology for nitrogen-containing heterocycles using these ruthenium carbene catalysts and application of these to the synthesis of biologically active natural products [5].

On the other hand, the non-metathetic behavior of Grubbs carbenes has recently been reported, which broadens their synthetic utility beyond olefin metathesis [6].

In this account, we present our novel reactions using ruthenium carbene catalyst and the development of a novel method for the synthesis of nitrogen-containing heterocycles, including substituted quinoline, indole and 3-methylene-2,3-dihydroindole.

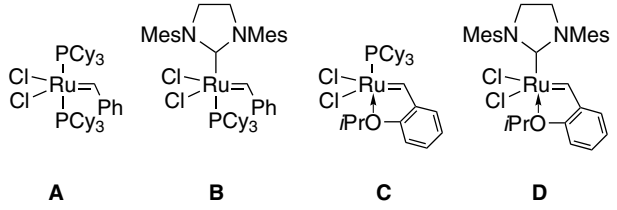


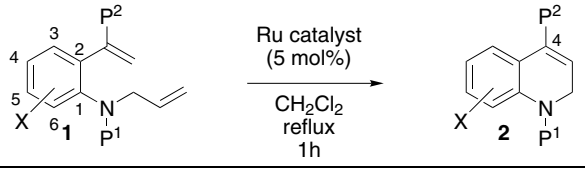
Fig. 1. Ruthenium catalysts.

2. Experimental results

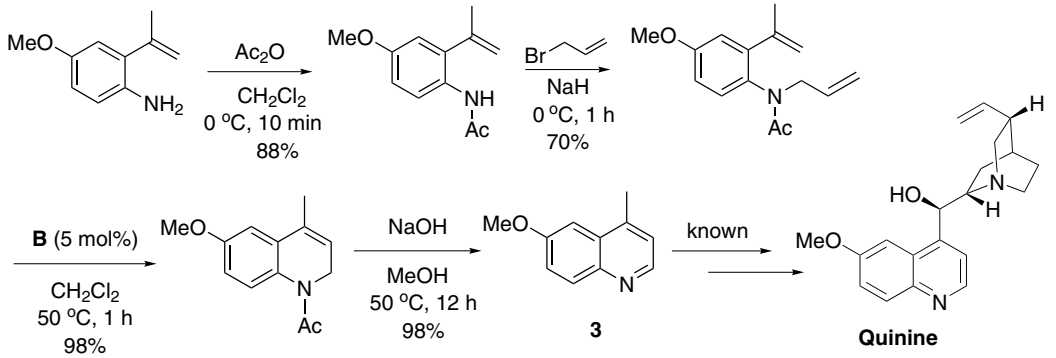
2.1. Silyl enol ether-ene metathesis and substituted quinoline synthesis

Quinolines are very important building blocks for quinoline alkaloids and also have interesting biological activities. Although methods for the preparation of quinolines have been studied since the 1800s, a novel method for the preparation of quinolines using transition metal catalysts has recently been developed. We found that RCM of *N*-allyl-*ortho*-vinylaniline (**1**) in the presence of 5 mol% of catalyst **A** or **B** in CH_2Cl_2 at refluxing temperature for 1 h gave the corresponding 1,2-dihydroquinoline (**2**) in quantitative yield (Table 1, entries 1–9). Although there are many quinoline alkaloids with a substituent at the 4 position in the quinoline ring, it is quite difficult to directly introduce a substituent at the 4 position in quinoline. To overcome this problem, we developed RCM of enol ether with olefin to give 4-methoxy-quinoline or 4-silyloxy-quinoline, as an application of our quinoline synthesis (Table 1, entries 10 and 11). This is the first example of silyl enol ether-ene metathesis [7], and it proceeds effectively under mild conditions. Using this novel method, we have successfully synthesized key intermediates (**3**, **4**, **5**) of anti-malarial agents, quinine, chloroquine and PPMP (1-phenyl-2-palmitoylamino-3-morpholino-1-propanol) hybrid, respectively (Schemes 1–3) [8]. We also synthesized (+)-(*S*)-angustureine and determined the absolute configuration of an anti-malarial compound, natural angustureine, which turned out to be a (−)-(*R*)-enantiomer (Scheme 4) [9].

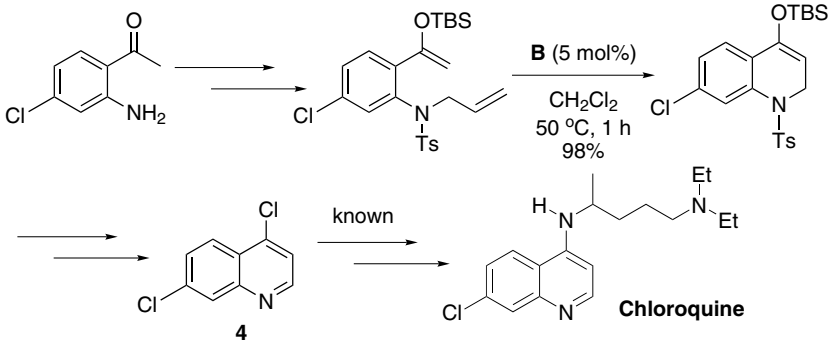
Table 1
RCM of 1 to give 1,2-dihydroquinolines (**2**)



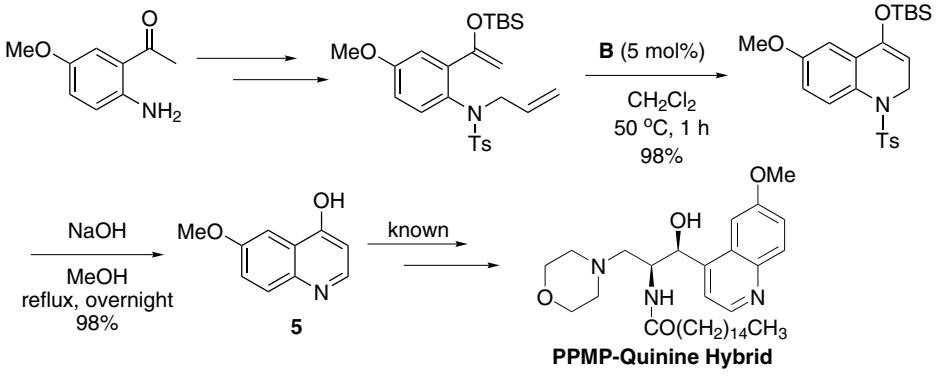
Entry	Substrate				Ru catalyst	Yield (%)
		X	P^1	P^2		
1	**1a**	H	Ts	Me	**A**	92
2	**1b**	H	Ts	H	**A**	93
3	**1c**	4,5,6-triMeO	Ts	H	**A**	90
4	**1d**	4-MeO	Ts	H	**A**	95
5	**1e**	4-CI	Ts	H	**A**	90
6	**1f**	5-CI	Ts	H	**B**	100
7	**1g**	H	Bn	Me	**A**	99
8	**1h**	H	Ac	Me	**B**	98
9	**1i**	H	Boc	Me	**B**	92
10	**1j**	H	Ts	OMe	**B**	95
11	**1k**	H	Ts	OTBS	**B**	96



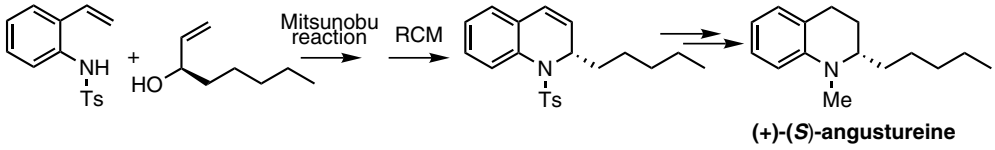
Scheme 1. Preparation of 4-methyl-6-methoxyquinoline (**3**).



Scheme 2. Preparation of 4,7-dichloroquinoline (**4**).



Scheme 3. Preparation of 4-hydroxy-6-methoxyquinoline (**5**).

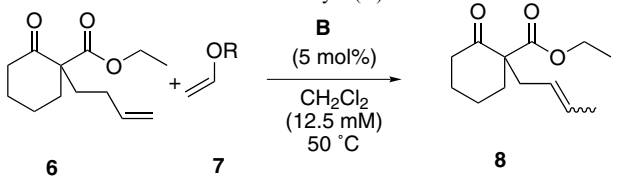


Scheme 4. Asymmetric total synthesis of (+)-(*S*)-angustureine.

2.2. Selective isomerization of terminal olefin and synthesis of substituted indole [10]

According to our findings regarding silyl enol ether-ene metathesis, we attempted the cross-metathesis of silyl enol ether with terminal olefin. Although this cross-metathesis did not succeed, we found that selective isomerization of terminal olefin ($R–CH_2–CH{=}CH_2$) to internal alkene ($R–CH{=}CH–CH_3$) took place, when 5 mol% of catalyst **B** was used together with 10 eq. of vinyloxytrimethylsilane

Table 2
Reaction of **6** with various silyl enol ethers and vinyl ethers in the presence of ruthenium carbene catalyst (**B**)



6 **7** **8**

Entry	Enol ethers			Time (h)	**8** (%)	*E*/*Z* ratio of **8**[a]
		R	eq.			
1	**7a**	TMS	2	20	60	2.6/1
2	**7a**	TMS	10	3	Quant.	3.5/1
3	**7b**	Ac	10	23	NR	
4	**7c**	Et	10	3	12	–[b]
5	**7c**	Et	10	24	Quant.	3.2/1

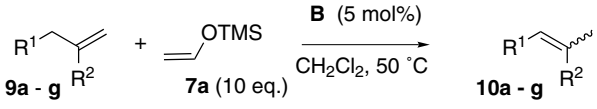
[a] The ratio were determined by ^{1}H NMR.
[b] Not determined.

(**7a**) (Table 2). This novel isomerization is effective for monosubstituted terminal olefins (Table 3). Applying these conditions to *N*-allyl-*ortho*-vinylaniline (**1**), the corresponding enamide (**11**) was selectively obtained, which was readily converted to indole (**12**) by normal RCM in high yield (Scheme 5). This is the first example of indole synthesis using RCM. Although indoles are also very important molecules in medicinal and organic chemistry, therefore, a variety of synthetic method for indole ring have developed since the 1800s, a practical preparation of substituted indoles is still a challenging subject in chemistry. The complete isomerization of olefins has been reported in metathesis using Grubbs catalyst **B** [11]. However, under our conditions, with the combination of **B** and **7a**, isomerization of terminal olefin proceeded selectively even using alpha, omega-diene, such as **1**, that can easily give an RCM product [12].

2.3. Cycloisomerization of alpha, omega-diene and substituted indole synthesis [13]

Considering the reaction mechanism of isomerization of terminal olefin in the presence of ruthenium carbene catalyst and electron-rich olefin such as **7a**, ruthenium hydride might be an actual active catalyst for isomerization. If alkyl ruthenium species are generated as an intermediate, it could react with another olefin in the molecule to give a cycloisomerization product [14]. Since cycloisomerization proceeds without a loss of carbon units, selective and catalytic cycloisomerization can be considered highly atom-economical. Hence, diallyltosylamide (**13**), which is widely used in cycloisomerization and RCM studies, was subjected to the above conditions. As expected, cycloisomerized products (**14** and **15**) were obtained in excellent yields (Table 4). As the reaction temperature is increased, the yield of thermodynamically stable compound increases (entries 1–4). Ruthenium catalysts without *N*-heterocyclic carbene

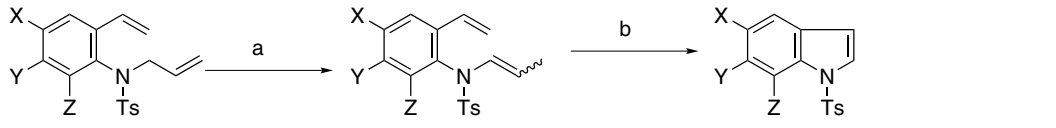
Table 3
Novel isomerization of various terminal olefins (**9**)



9a - g **7a** (10 eq.) **10a - g**

Entry	Substrate	R^1	R^2	Time (h)	Yield (%)[a]	*E*/*Z*[b]
1	**9a**	Ph	H	1.5	Quant. (34)	12.8/1
2	**9b**	$PhCH_2$	H	3.0	58	2.8/1
3	**9c**	*p*-$MeOC_6H_4CH_2$	H	3.0	78	8.5/1
4	**9d**	$HO(CH_2)_3$	H	3.0	Quant. (34)	6.1/1
5	**9e**	$BnO(CH_2)_3$	H	3.0	Quant. (96)	8.2/1
6	**9f**	BnO	H	3.0	73	1/1.25
7	**9g**	$BnOCH_2$	CH_3	3.0	NR	–

[a] Yields in parenthesis indicate the isolated yields.
[b] Determined by ^{1}H NMR.



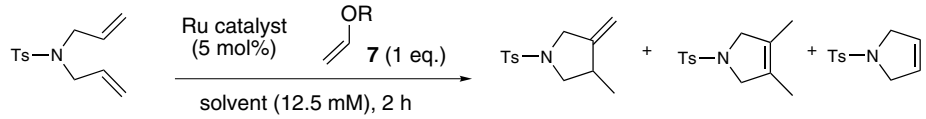
1b: X = H, Y = H, Z = H
1c: X = MeO, Y = MeO, Z = MeO
1d: X = MeO, Y = H, Z = H
1f: X = H, Y = Cl, Z = H

11b: quant.,
11c, **11d**, **11f**

12b: 94%, **12c**: 80%, 2 steps,
12d: quant, 2 steps, **12f**: 79%, 2 steps

Scheme 5. Novel indole synthesis via olefin isomerization followed by RCM. (a) **B** (5 mol%), vinyloxytrimethylsilane (**7a**, 1 eq.) CH_2Cl_2, 50 °C, 1.5 h; (b) for **11a**: **B** (5 mol%), benzene, 80 °C, 1 h, for **11c**: **B** (5 mol%), toluene, 110 °C, 17 h, for **11d**: **B** (5 mol%), benzene, 80 °C, 3 h, for **11f**: **B** (5 mol%), toluene, 110 °C, 13 h.

Table 4
Cycloisomerization of *N*,*N*-diallyl-*p*-toluenesulfonamide (**13**)



13 **14** **15** **16**

Entry	Ru catalyst		R	Solvent	Temperature (°C)	Yield (%)[a]		
						14	**15**	**16**
1	**B**	**7a**	TMS	CH_2CI_2	rt	65	0	21
2	**B**	**7a**	TMS	CH_2CI_2	40	86	14	0
3	**B**	**7a**	TMS	Benzene	80	43	56	0
4	**B**	**7a**	TMS	Toluene	110	22	78	0
5	**A**	**7a**	TMS	CH_2CI_2	40	10[b]	0	59
6	**B**	**7c**	Et	CH_2CI_2	40	37[c]	0	5
7	**B**	**7c**	Et	Toluene	110	52	46	0
8	**C**	**7a**	TMS	CH_2CI_2	40	29	0	64
9	**D**	**7a**	TMS	CH_2Cl_2	40	71	24	0

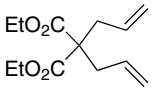
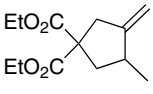
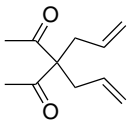
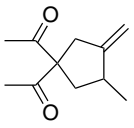
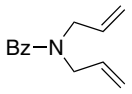
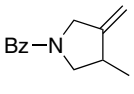
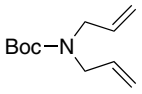
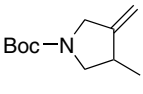
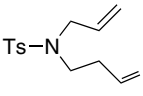
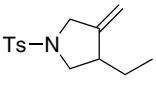
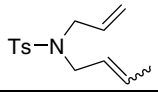
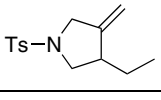
[a] Yields in parenthesis were estimated by ^{1}H NMR spectroscopy.
[b] **13** was recovered in 28% yield.
[c] **13** was recovered in 58% yield.

(NHC) ligand such as **A** and **C** are ineffective for cycloisomerization (entries 5 and 8). Other alpha, omega-dienes gave the corresponding cycloisomerized products in yields of 13–87% (Table 5).

According to these results, we envisioned that enamide (**11b**), obtained by the reaction of *N*-allyl-*ortho*-vinylaniline (**1b**) with 1 eq. of **7a** in CH_2Cl_2 at 50 °C, would readily be cycloisomerized to give **17b** at higher temperature. When a solution of **1b** in toluene was stirred in the presence of 5 mol% of **B** and 1 eq. of **7a** at 110 °C for 2 h, the expected 3-methylene-2,3-dihydroindole (**17b**) was obtained in 35% yield along with enamide (**11b**) (Table 6, entry 3). Finally, we found that the reaction of **1b** in the presence of **B** (10 mol%) and **7a** (1 eq.) in xylene at refluxing temperature for 2 h gave **17b** in 81% yield (entry 5). This procedure could be applied to other substituted *N*-allyl-*ortho*-vinylaniline (**1**) and the corresponding 3-methylene-2,3-dihydroindoles (**17**) were obtained in yields of 24–84% (Table 7). Although a few articles described the synthesis of 3-methylene-2,3-dihydroindoles, substituted 3-methylene-2,3-dihydroindoles can be good synthons for indole alkaloids as well as other biologically active natural products [15].

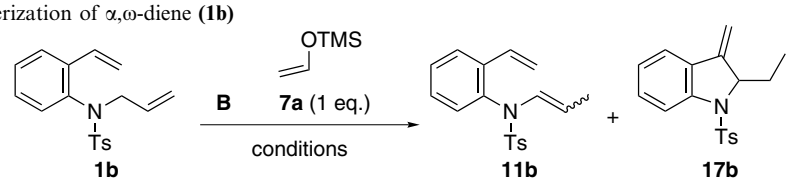
To obtain more detailed information on cycloisomerization, the reaction of **13** with **B** and **7a** in toluene-d_8 was monitored using ^{1}H and ^{31}P NMR. The relative amounts of **13** and the cyclized products **14** and **15**, were analyzed by ^{1}H NMR. The relative amounts of ruthenium complexes, including **B** and **E** [16], were also analyzed by ^{1}H and ^{31}P NMR. First, we periodically monitored the reaction of **13** with **B** in the presence of **7a** in toluene-d_8 (0.17 M) at 50 °C. The reaction was complete within 10 min, and **13** and **B** were completely

Table 5
Cycloisomerization of dienes[a]

Entry	Substrate	Product	Yield (%)[b]
1			83
2			87
3			75
4			47
5			18
6			13

[a] Conditions: **B** (5 mol%), **7a** (1 eq.), CH_2CI_2 (12.5 mM), reflux, 2 h.
[b] Isolated yield.

Table 6
Isomerization and cycloisomerization of α,ω-diene **(1b)**



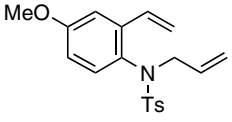
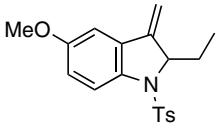
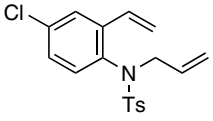
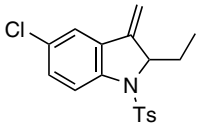
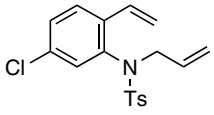
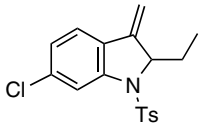
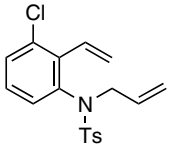
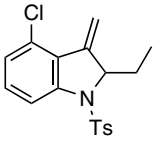
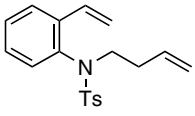
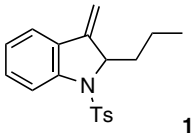
1b **11b** **17b**

Entry	**B** (mol%)	Conditions	Yield (%)[a]	
			11b	**17b**
1	5	CH_2CI_2, reflux, 1.5 h	Quant.	0
2	5	Toluene, 40 °C, 2 h	97	3
3	5	Toluene, reflux, 2 h	65	35
4	5	Xylene, reflux, 2 h	30	68
5	10	Xylene, reflux, 2 h	12	81

[a] Yields were estimated by ^{1}H NMR spectroscopy.

consumed. Next, **7c** was used instead of **7a** to slow the reaction, and the results are summarized in Fig. 2. After 15 min of heating, ^{31}P NMR showed the disappearance of a peak at 29.8 ppm due to **B**, accompanied by the emergence of a new peak at 30.6 ppm. Similarly, ^{1}H NMR showed the disappearance of a peak at

Table 7
Synthesis of 3-methylene-2,3-dihydroindoles[a]

Entry	Substrate	Product	Yield (%)[b]
1	 **1d**	 **17d**	24[c]
2	 **1e**	 **17e**	84
3	 **1f**	 **17f**	78
4	 **1l**	 **17l**	78
5	 **1m**	 **17m**	58

[a] Conditions: **B** (10 mol%), **7a** (1 eq.), xylene (12.5 mM), reflux, 2 h.
[b] Isolated yield unless otherwise noted.
[c] Determined by ^{1}H NMR.

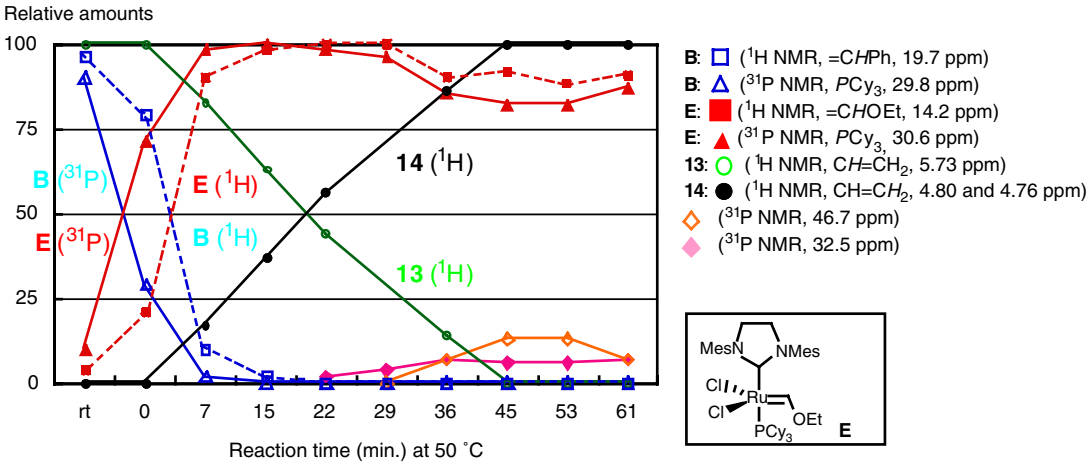
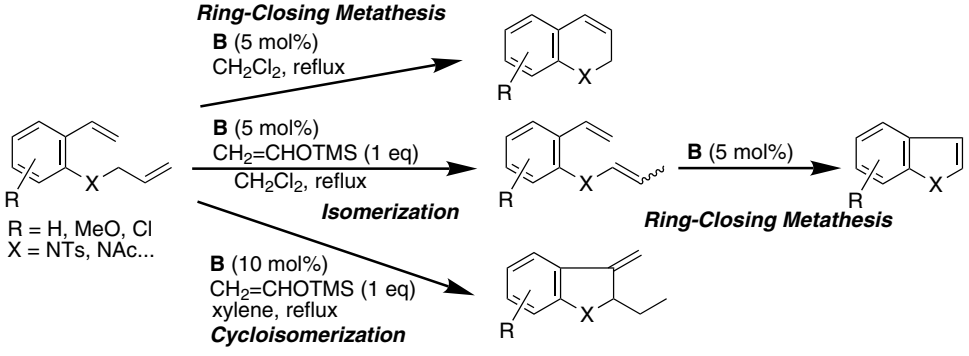


Fig. 2. Cycloisomerization of *N*,*N*-diallyl-*p*-toluenesulfonamide **(13)** in toluene-d_8 (0.17 M) at 50 °C in the presence of **B** (5 mol%) and **7c** (1 eq.). The relative amounts of **B**, **E** and its decomposition products were estimated by ^{31}P NMR using H_3PO_4 (85%) as an external standard, and ^1H NMR using 1,2;5,6-dibenzanthracene (5 mol%) as an internal standard. The relative amounts of **13** and **14** were estimated by ^1H NMR.

19.7 ppm, an olefinic proton of **B**, while a new peak appeared at 14.2 ppm. These observations show the rapid formation of Fischer-type carbene **E** by the reaction between **B** and **7c**. After 29 min, ^{31}P NMR showed that **E** had partially decomposed to other unidentified ruthenium species (46.7, 32.5 ppm). In contrast to the reaction of **B**, the conversion of **13** to **14** proceeded gradually under these conditions, and was complete after 45 min. The formation of **15** was not observed.

As demonstrated in the ^1H and ^{31}P NMR analyses, catalyst **E** appears to play an important role in cycloisomerization. According to the report by Grubbs and Louie, **E** shows catalytic reactivity in metathesis, such as ROMP and RCM [16]. Therefore, we synthesized **E** and confirmed that it efficiently catalyzes the RCM reaction of **13** in toluene at 50 °C to give **16** in 79% yield, along with unreacted **13** (21%). However, in the presence of both **E** (5 mol%) and **7c** (1 eq.), the reaction of **13** gave **14** in 98% yield. Although the structure of the ruthenium species that play a role in this cycloisomerization is unclear, a ruthenium-hydride species might participate in this reaction, according to the mechanism proposed by Itoh and co-workers [17]. Moreover, it has been reported that ruthenium-hydride species [18] are generated from Grubbs carbene complex via the formation of ruthenium Fischer carbene [19]. However, the following findings may lead to a new perspective on ruthenium catalysts. (1) $RuClH(CO)(PPh_3)_3$ [20] was ineffective, (2) ruthenium carbene catalysts without the *N*-heterocyclic carbene (NHC) ligand (**A** and **C**) were less effective for cycloisomerization, (3) ruthenium catalysts (**B** and **D**) gave cycloisomerized product in good to excellent yields, indicating that NHC ligand in ruthenium carbene catalyst is essential for cycloisomerization, and (4) our cycloisomerization of **1** can give 3-methylene-2,3-dihydroindoles, *N*-benzo-fused heterocycles, the synthesis of which has not been reported with the most successful Ru catalyst $[Ru(cod)Cl_2]_n$. These novel methods are applicable to the synthesis of oxygen-containing heterocycles. Further studies on the ruthenium species involved and an investigation of the reaction mechanism are currently in progress.



Scheme 6. Summary of our novel discoveries.

3. Conclusion

In conclusion, a new methodology for silyl enol ether-ene metathesis, the selective isomerization of terminal olefins and the cycloisomerization of dienes using a Grubbs carbene complex without/with vinyloxytrimethylsilane was established. The utility of these reactions was demonstrated in the synthesis of nitrogen-containing heterocyclic compounds, 1,2-dihydroquinoline, indole, and 3-methylene-2,3-dihydroindole, which might be key intermediates for pharmacologically important compounds (Scheme 6). We believe that these results may offer further insight into the chemistry of ruthenium carbene complexes.

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