Experimental Section

The lanthanide oxide based catalysts were prepared by the incipient wetness impregnation technique with aqueous solutions of, for example, lanthanum acetate (Aldrich, > 99.9 %) with Al_2O_3 (Condea, surface area of 220 ṁ g^{-1}) as support. La_2O_3 (99.99 %) was purchased from Alfa Aesar. The catalyst material was dried at 100 °C for 1 h, followed by granulation. The size fraction of 0.25–0.50 mm was loaded into the catalytic reactor. Catalytic tests were performed in a fixed-bed reactor at atmospheric pressure. The reactor consisted of a quartz tube, which was loaded successively with quartz wool, quartz pearls, quartz wool, catalyst (1 g), quartz wool, quartz pearls, and quartz wool. Before the reaction started, the catalyst was calcined for 8 h in O_2 at 450 °C. During reaction, the feed consisted of a He flow, which was led through a saturator filled with CCl_4 (VEL, p.a.) and maintained at 0 °C in an icebath to preserve the same vapor pressure of CCl_4. All the tubes were made of Vitton, and the total He flow was set at 0.480 L h^{-1}. This resulted in a CCl_4 loading of 47 000 ppm (v/v). The gaseous hourly space velocity (GHSV) was 800 h^{-1} (contact time of 4.5 s). The gas flows were controlled with Bronkhorst mass flow controllers, while H_2O was added to the reactor at a rate of 1.2 mL h^{-1} by a Methrom dosimeter and evaporated at the inlet of the reactor. The reaction temperature was controlled using a K-type thermocouple placed in the reactor. The condensate was trapped after the reactor in an impinger at room temperature and analyzed by GC-MS. The remaining gases were guided to a gas chromatograph (HP 4890D with a FID detector and methanator) and analyzed on a packed Hayesep Q CP column (80–100 mesh, 3 m length). X-ray diffraction patterns of the solids were measured with a Siemens D5000 Matic instrument, while Raman spectra were recorded with a Holoprobe Kaiser Optical spectrometer equipped with a holographic notch filter and CCD camera. XPS measurements were done with a VG MT 500 spectrometer. FTIR spectra were measured using a Nicolet 730 spectrometer.

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Selective Isomerization of a Terminal Olefin Catalyzed by a Ruthenium Complex: The Synthesis of Indoles through Ring-Closing Metathesis**

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Isomerization of olefins may proceed under acidic, basic, or photochemical conditions to give a mixture of olefins that depends on their thermodynamic stability. Recent advances in transition-metal chemistry (Fe, Pd, Rh, Pt, Ni, Ir, Ru, Co, and Cr) have enabled milder conditions for olefin isomerization to be used to realize selective and synthetically useful transformations, such as the deprotection of an allyl group on nitrogen and oxygen functionalities.[1] Recently, a few reports have appeared concerning this olefin isomerization using ruthenium–carbene catalysts, such as the Grubbs catalyst.[1m–o] This isomerization reaction is limited to substrates which contain an oxygen or a nitrogen substituent in the olefinic side chain. In addition, the reaction competes with metathesis.[2]

During the course of our investigation of the synthesis of nitrogen-containing heterocycles by using ring-closing metathesis (RCM),[3] we found a novel method for synthesizing substituted quinolines by RCM, which included a metathesis reaction of a silyl-protected enol ether with an alkene.[3f] These results prompted us to investigate cross metathesis to prepare a silyl enol ether. However, unexpectedly, we found selective isomerization of the terminal olefin to the corresponding internal olefin, which made a novel indole-ring synthesis possible by RCM. Herein, we report a novel and selective isomerization of a terminal olefin by combining a ruthenium–carbene catalyst with vinyloxytrimethylsilane, and its application to the synthesis of an indole ring from 2-(*N*-allyl-*N*-tosylamino)styrene by RCM.

When **1** was heated in CH_2Cl_2 at 50 °C with 2 molar equivalents of silyl enol ether (**2a**) in the presence of the Grubbs catalyst (**A**, 5 mol %),[4] we unexpectedly found that the terminal double bond of **1** isomerized to the internal double bond to give **3** in 60 % yield, 40 % of **1** was recovered (Table 1, entry 1, full experimental details are given in the supporting information). The exclusive formation of **3** was

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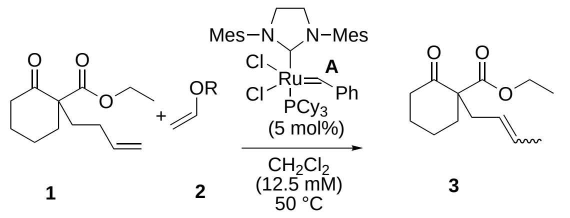
Table 1. Reaction of **1** with various silyl enol ethers and vinyl ethers in the presence of a ruthenium–carbene catalyst.



Entry		R	Equiv	t [h]	Product [%]	E/Z Ratio of **3**[a]
1	**2a**	TMS	2	20	60	3.2/1
2	**2a**	TMS	10	3	quantitative	3.5/1
3	**2b**	Ac	10	23	no reaction	
4	**2c**	Et	10	3	12	–[b]
5	**2c**	Et	10	24	quantitative	3.2/1

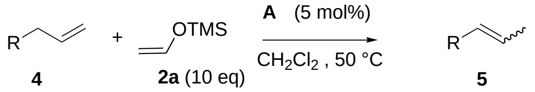
[a] The ratios were determined by ^{1}H NMR spectroscopy. [b] Not determined.

observed in the reaction with 10 equivalents of **2a**, again as a mixture of E and Z isomers (entry 2). However, neither isomerization nor dimerization of **1** occurred when vinyl acetate **2b** was subjected to similar reaction conditions (entry 3). On the other hand, the combination of ethylvinyl ether **2c** with catalyst **A** under optimized conditions promoted the quantative isomerization of **1** (entry 5).[5] Clearly, **2a** is the most favorable enol ether for isomerization.

Several terminal olefins were subjected to the same reaction conditions (Table 2). All of the monosubstituted olefins (**4a**–**4g**) were isomerized in moderate to excellent yields, even when the substrate did not have an oxygen substituent. Therefore, this reaction is quite general and selective for terminal olefins.

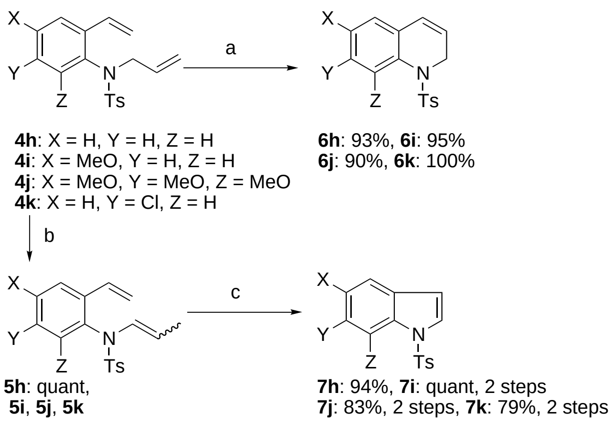
We carried out the isomerization of **4h** (Scheme 1) in competition with RCM. While the reaction of **4h** with ruthenium-catalyst **A** gave 1,2-dihydroquinoline (**6h**) in excellent yield,[3f] the reaction of **4h** with catalyst **A** in the presence of vinyloxytrimethylsilane (1 equiv is sufficient for this substrate) gave enamine (**5h**; Scheme 1) in quantitative yield, which is inaccessible by conventional methods. Although the use of a ruthenium–carbene catalyst in the isomerization of olefin has been reported,[1m–o], to our knowledge, this is the first example of a highly selective isomerization using a ruthenium–carbene complex that proceeds faster than RCM.

Table 2. Novel isomerization of various terminal olefins.



Entry	Substrate	t [h]	Product	Yield [%][a]	E/Z[b]
1	PhCH$_2$CH=CH$_2$ (**4a**)	1.5	PhCH=CHCH$_3$ (**5a**)	34 (quantitative)	12.8/1
2	Ph(CH$_2$)$_2$CH=CH$_2$ (**4b**)	3.0	PhCH$_2$CH=CHCH$_3$ (**5b**)	58	2.8/1
3	pMeOC$_6$H$_4$CH$_2$CH=CH$_2$ (**4c**)	3.0	pMeOC$_6$H$_4$CH=CHCH$_3$ (**5c**)	78	8.5/1
4	HO(CH$_2$)$_4$CH=CH$_2$ (**4d**)	3.0	HO(CH$_2$)$_3$CH=CHCH$_3$ (**5d**)	34 (quantitative)	6.1/1
5	BnO(CH$_2$)$_4$CH=CH$_2$ (**4e**)	3.0	BnO(CH$_2$)$_3$CH=CHCH$_3$ (**5e**)	96 (quantitative)	8.2/1
6	BnOCH$_2$CH=CH$_2$ (**4f**)	3.0	BnOCH=CHCH$_3$ (**5f**)	73	1/1.25
7	BnO(CH$_2$)$_2$C(Me)=CH$_2$ (**4g**)	3.0	BnOCH$_2$CH=CMe$_2$ (**5g**)	no reaction	–

[a] Isolated yield. Yields in parenthesis were estimated by ^{1}H NMR spectroscopy. [b] Determined by ^{1}H NMR spectroscopy.



Scheme 1. Selective isomerization of terminal olefins, a) **A** (5 mol%), CH$_2$Cl$_2$, 50 °C, 1 h; b) **A** (5 mol%), vinyloxytrimethylsilane (1 eq.), CH$_2$Cl$_2$, 50 °C, 1.5 h; c) for **5h**: **A** (5 mol%), benzene, 80 °C, 1 h, for **5i**: **A** (5 mol%), benzene, 80 °C, 3 h, for **5j**: **A** (5 mol%), toluene, 110 °C, 17 h for **5k**: **A** (5 mol%), toluene, 110 °C, 13 h.

Since this method is quite effective for generating enamines, we applied this reaction to the synthesis of indoles.[6] Enamine **5h** was obtained by the evaporation of volatile material after the isomerization of **4h** and was subjected to normal RCM conditions using catalyst **A** at 80 °C in benzene. The expected indole (**7h**) was isolated in 94 % yield. Similarly, **4i**, **4j**, and **4k** gave **7i**, **7j**, and **7k** via isomerized enamines **5i**, **5j**, and **5k**, respectively.

The protective group on a nitrogen atom is not limited to the p-toluenesulfonyl group. 2-(N-Acetyl-N-allylamino)styrene gave N-acetylindole in 96 % yield under the same conditions.

While a detailed mechanism of this isomerization is not clear, we considered that the new catalyst was formed by the reaction of **A** and vinyloxytrimethylsilane. The results of monitoring the reaction of the Grubbs catalyst **A** with **2a** in CDCl$_3$ at 50 °C by ^{1}H and ^{31}P NMR spectroscopy showed that: 1) in the ^{1}H NMR spectrum, the signal arising from the methyne proton of the Grubbs catalyst (19.1 ppm) disappeared and signals associated with styrene appeared; and 2) in the ^{31}P NMR spectrum, the signal arising from the tricyclohexylphosphane group of the Grubbs catalyst (29.6 ppm) completely disappeared and a new signal appeared at 33.1 ppm. Furthermore, the IR spectrum of the crude product showed a new signal at 1935 cm^{-1}.

These results offer an extremely facile and selective isomerization of terminal olefins by combining a ruthenium–carbene catalyst and vinyloxytrimethylsilane. The utility of this reaction was demonstrated in a novel and efficient synthesis of an indole ring from 2-(N-allylamino)-styrene using RCM. As a consequence of its simplicity, chemo-selectivity, and the mild reaction conditions, this procedure should lead to new aspects of olefin metathesis.

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[5] Grubbs and co-workers found that vinylic ethers were not reactive in cross-metathesis. He also reported the formation of a new Fischer carbene species prepared by the reaction of a ruthenium–alkylidene complex with ethyl vinyl ether. (a) A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783–3784; b) J. Louie, R. H. Grubbs, Organometallics **2002**, *21*, 2153–2164).

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The Structure of the Peroxo Species in the TS-1 Catalyst as Investigated by Resonant Raman Spectroscopy**

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Ti-silicalite-1 (TS-1)[1] has exhibited a remarkably high efficiency and molecular selectivity in oxidation reactions with H_2O_2 under mild conditions, such as for olefin epoxidation, phenol hydroxylation, cyclohexanone ammoximation, and conversions of ammonia to hydroxylamine, secondary alcohols to ketones, and secondary amines to dialkylhydroxylamines[2] (Figure 1). Because of its relevance in industrial applications, it has been one of the most studied materials in heterogeneous catalysis in recent years.[3–13]

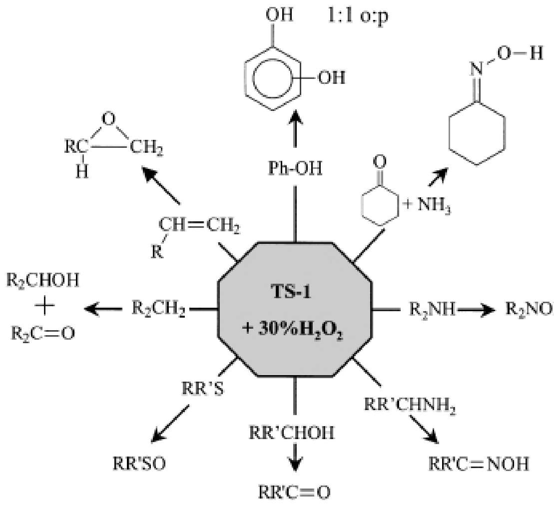

Figure 1. Schematic representation of the most relevant oxidation reactions catalyzed by TS-1.

It has been shown that the active species is a Ti^{IV} atom isomorphically inserted into the MFI-type framework.[1] TS-1 is characterized by an increase of the unit cell volume proportional to the Ti content[1,5,7,14] and by the presence of a "fingerprint" IR absorption component[1,6b,8–10,13] centered at $960\ cm^{-1}$, the intensity of which grows proportionally with increased Ti content. This band is clearly visible in IR spectra appearing on the low-energy tail of the very strong absorption resulting from the ν_{asym}(Si-O-Si) modes that appear in the broad 1250–1030 cm^{-1} region. In addition to the component at

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