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Synthesis of Pyrrolizidine, Indolizidine, and Quinolizidine Derivatives Using Ruthenium-Catalyzed Ring-Opening Metathesis and Ring-Closing Metathesis of Cycloalkene-ynes

Hideaki Wakamatsu,[a] Yoshihiro Sato,[b] Reiko Fujita,[a] and Miwako Mori[c,*]

[a] Tohoku Pharmaceutical University, Aoba-ku, Sendai 981-8558, Japan
[b] Graduate School of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan
[c] Health Sciences University of Hokkaido, Ishikari-Tobetsu, Hokkaido 061-0293, Japan
Phone/Fax: (+81)-1-1787-6045; e-mail: mori@pharm.hokudai.ac.jp

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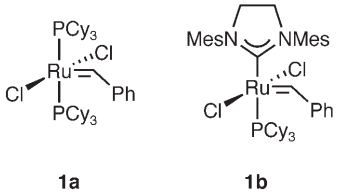
Abstract: Ring-opening metathesis and ring-closing metathesis (ROM-RCM) of a cyclopentene-yne having an ester moiety was demonstrated using first- and second-generation Grubbs' catalysts. When the reaction of cycloalkene-yne was carried out in the presence of 5 mol% of a ruthenium carbene complex under an ethylene atmosphere at room temperature, ROM-RCM proceeded smoothly to give a pyrrolidine derivative in good yield, which could be converted to a pyrrolizidine derivative. Furthermore, ROM-RCM of azabicyclo[2.2.1]heptene-ynes using the second-generation Grubbs' catalyst was investigated. When an azabicycloheptene derivative was exposed to a catalytic amount of a ruthenium carbene complex, pyrrolizidine and indolizidine derivatives were obtained in good yields. The distribution of these products depends on the substituents on the alkyne. When azabicyclo[2.2.1]heptene-ynes bearing large substituents on the alkyne were treated with ruthenium catalyst **1b**, a pyrrolizidine derivative was obtained as the major product. ROM-RCM of azabicyclo[2.2.2]octene-ynes with **1b** afforded quinolizidine derivative **20**, although the yield was moderate.

Keywords: enyne metathesis; ethylene; indolizidine; pyrrolizidine; ROM-RCM; ruthenium

Introduction

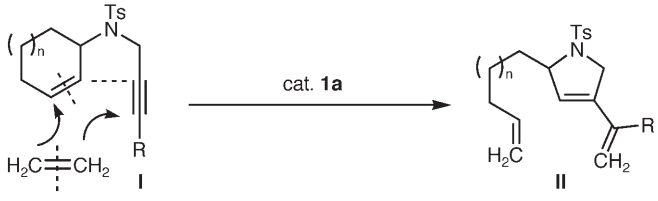
Since the development of Grubbs' ruthenium-based carbene complexes (**1a**, **1b**; Figure 1),[1] the olefin metathesis reaction plays an important role as a carbon-carbon bond forming reaction in the field of synthetic organic chemistry.[2]

It is also well known that the ruthenium-catalyzed metathesis reaction is applicable to the synthesis of natural products as a key step. Enyne metathesis, which takes place between a double bond and a triple bond to afford a diene derivative, is a synthetically useful transformation with a large number of recent applications.[3] We have already reported various enyne metathesis reactions catalyzed by ruthenium carbene complex **1a** or **1b**,[4] including the effect of ethylene for the RCM[4c] and CM (cross metathesis) of alkynes, which is an effective synthetic method for 2,3-disubstituted-1,3-dienes.[4b,d,e] Recently, the ROM-RCM[5] of cycloalkene-ynes under an ethylene atmosphere was reported by our group (Scheme 1).[4f–h] When cycloalkene **I** having substituent at the C-3 position was reacted with ruthenium carbene complex **1a** under an ethylene atmosphere, a pyrrolidine derivative was obtained in high yield. In this reaction, the double bonds of the cycloalkene and ethylene were



1a 1b

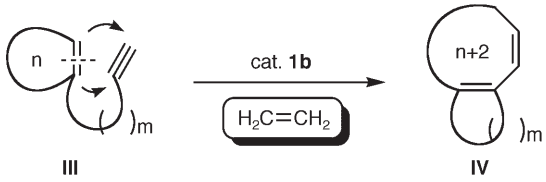
Figure 1. Ruthenium catalysts for metathesis.



Scheme 1. ROM-RCM of a cycloalkene having a substituent at the C-3 position.

cleaved, and each alkylidene part was recombined with an alkyne moiety to afford a new cyclic compound having a triene moiety.

On the other hand, when cycloalkene **III** having a substituent at the C-1 position was reacted with **1b**, a bicyclic compound was formed in high yield. In this reaction, the double bond of the cycloalkene was cleaved and carbon-carbon bonds were formed between the double bond of the cycloalkene and the triple bond to provide a bicyclic compound having a diene moiety (Scheme 2).



Scheme 2. ROM-RCM of a cycloalkene having a substituent at the C-1 position.

We have already applied this method to synthesis of isoquinoline derivatives from cyclobutene derivatives having an alkyne side chain.[4i]

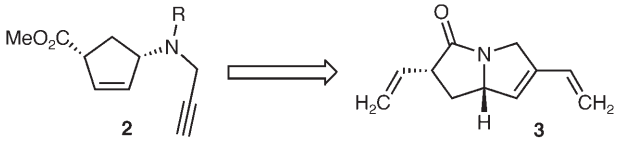
We described herein concise synthesis of pyrrolizidine derivatives using ROM-RCM as a key reaction and the syntheses of pyrrolizidine, indolizidine and quinolizidine derivatives using ROM-RCM of azabicycloalkene-ynes.

Results and Discussion

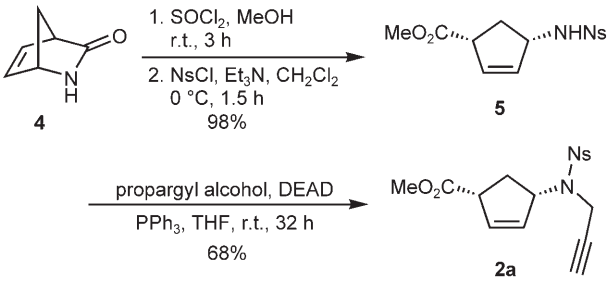
Synthesis of a Pyrrolizidine Derivative using ROM-RCM of a Cycloalkene-yne

We planned the synthesis of pyrrolizidine derivative **3** from cyclopentene derivative **2** having an alkyne moiety in the side chain using ROM-RCM (Scheme 3).

For the synthesis of the substrate **2a**, commercially available **4** was reacted with thionyl chloride in MeOH[6] followed by treatment with NsCl and Et_3N in CH_2Cl_2 at 0 °C to afford cyclopentene derivative **5** in 98% yield (Scheme 4). Introduction of an alkyne side chain to **5** was achieved by the Mitsunobu reaction[7] with propargyl alcohol to afford substrate **2a** in 68% yield.

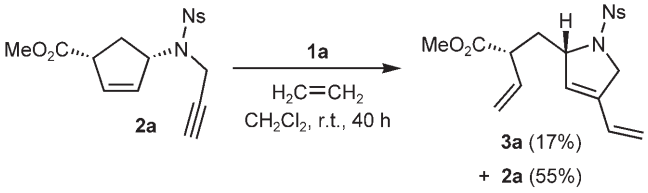


Scheme 3. Plan for the synthesis of a pyrrolizidine derivative.



Scheme 4. Synthesis of substrate **2a**. Ns = *o*-nitrobenzenesulfonyl.

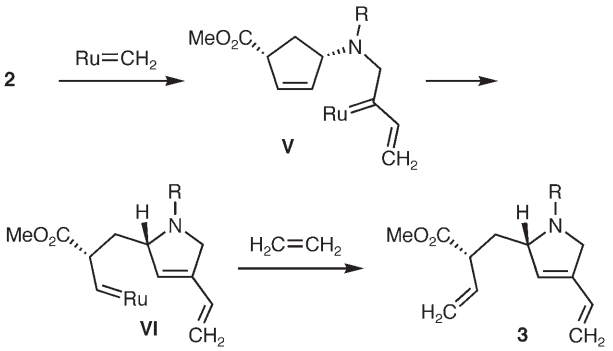
When a CH_2Cl_2 solution of **2a** and 10 mol% of **1a** was stirred under an ethylene atmosphere at room temperature for 40 h, pyrrolidine derivative **3a** was obtained in 17% yield and the starting material **2a** was recovered in 55% yield (Scheme 5).



Scheme 5. ROM-RCM of a cyclopentene-yne.

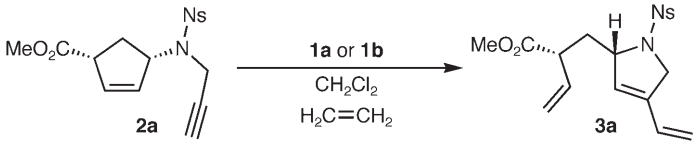
Although the yield of pyrrolidine derivative **3a** was low, the result indicated that the desired ROM-RCM of the cycloalkene-yne occurred to give **3a**. The possible reaction course for the formation of pyrrolidine derivative **3** from cyclopentene derivative **2** is shown in Scheme 6.

To improve the yield of **3a**, the reaction was carried out under the various conditions (Table 1). When a CH_2Cl_2 solution of **2a** and **1a** was refluxed, the result was unsatisfactory (entry 2). On the other hand, when the second-generation ruthenium carbene complex **1b** was used at room temperature for this reaction, the ROM-RCM proceeded smoothly to give **3a** in 75% yield (entry 3). It is generally accepted that catalyst



Scheme 6. Possible reaction course for ROM-RCM.

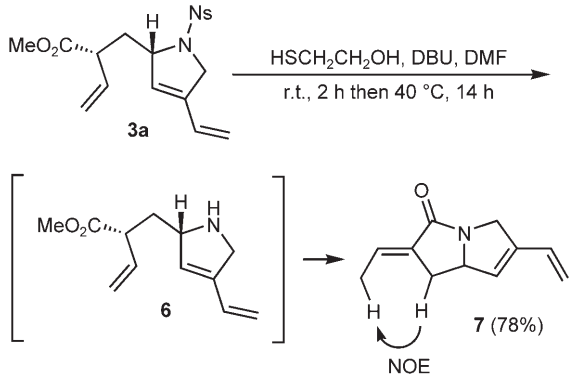
Table 1. ROM-RCM of cyclopentene-yne **2a**.



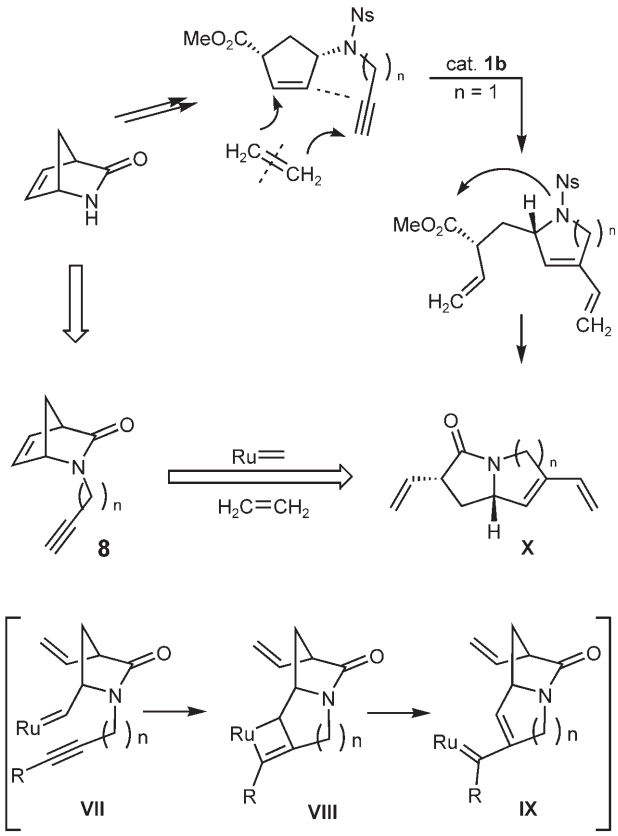
Entry	Catalyst (mol%)	Temperature	Time [h]	Yield of **3a** [%]	Recovery of **2a** [%]
1	**1a** (10)	r.t.	40	17	55
2	**1a** (10)	reflux	6	5	69
3	**1b** (10)	r.t.	2	75	0
4	**1b** (10)	reflux	2	34	25
5	**1b** (5)	r.t.	6	76	0

1b is used under a higher reaction temperature, however, poor yield and incomplete conversion were shown in this reaction (entry 4). Even upon lowering the use of **1b** to 5 mol%, **3a** was obtained in high yield (entry 5).

Subsequently, we tried to synthesize pyrrolizidine derivative **7** from triene **3a** under several sets of reaction conditions.[8] Although the nosyl group of **3a** could be removed by treatment with 2-mercaptoethanol and DBU in DMF, cyclization did not proceed at room temperature. Thus, the DMF solution was warmed at 40 °C to give pyrrolizidine derivative **7** in 78% yield (Scheme 7).[9]



Scheme 7. Synthesis of pyrrolizidine derivative **7**.



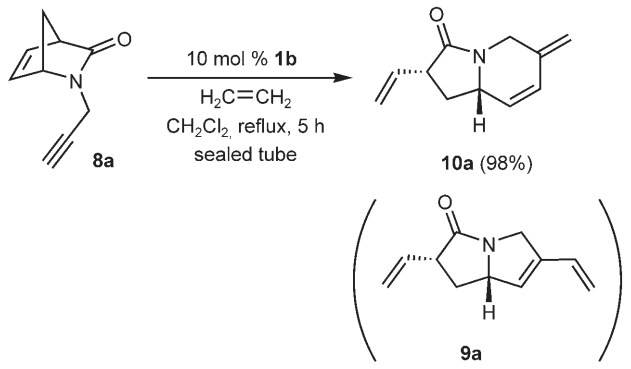
Scheme 8. Plan for one-step synthesis of bicyclic heterocycles.

Plan for One-Step Synthesis of Bicyclic Heterocycles

Next, we tried the one-step synthesis of bicyclic heterocycles from a 2-azabicyclo[2.2.1]hepten-3-one having an alkyne moiety on the nitrogen.

Our plan is shown in Scheme 8. When compound **8** is reacted with ruthenium carbene complex **1b**, bicyclic heterocycle **X** should be formed. The ruthenium methylidene carbene complex should react with an alkene moiety of the azabicycloheptene derivative **8** to afford the ruthenium carbene complex **VII**, which reacts with an alkyne moiety of **VII** to give the ruthenacyclobutene intermediate **VIII**. Ring opening of **VIII** gives ruthenium carbene complex **IX**. If the reaction is carried out under an ethylene atmosphere, the generated ruthenium carbene of **IX** should react with ethylene to provide bicyclic compound **X**.

During the course of our investigation of this project, Arjona, Plumet and co-workers reported the same ROM-RCM of an azabicycloheptene derivative **8a** (Scheme 9).[10] They obtained indolizidine derivative **10a** from **8a** in nearly quantitative yield when a CH_2Cl_2 solution of **8a** and **1b** was heated in a sealed

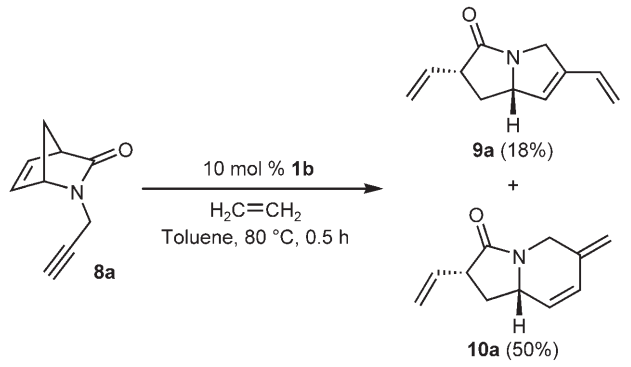


Scheme 9. ROM-RCM reported by Arjona, Plumet and coworkers.

tube. We have obtained compound **10a** along with a fair amount of pyrrolizidine derivative **9a** when the reaction was carried out in toluene upon heating. The result is interesting because the pyrrolizidine derivative is formed along with indolizidine derivatives. Thus, we decided to conduct a further investigation of this reaction, especially, the product distribution in regard to the substituent on the alkyne.

ROM-RCM of Azabicyclo[2.2.1]heptene-ynes

When a CH_2Cl_2 solution of **8a** was stirred in the presence of **1a** or **1b** under an ethylene atmosphere at room temperature, none of the product was obtained. Thus, a CH_2Cl_2 solution of **8a** and **1b** was refluxed for 5 h under ethylene gas, but the result was unsatisfactory. The solvent was changed to toluene for use of a higher reaction temperature. When a toluene solution of **8a** was stirred in the presence of 10 mol% of the second-generation ruthenium carbene complex **1b** under an ethylene atmosphere at 80 °C for 0.5 h, indolizidine derivative **10a** was obtained in 50% yield along with pyrrolizidine derivative **9a** in 18% yield (Scheme 10). It is not clear at this stage why indolizidine derivative **10a**, not pyrrolizidine derivative **9a**, is formed as a major product in the reaction of **8a**.



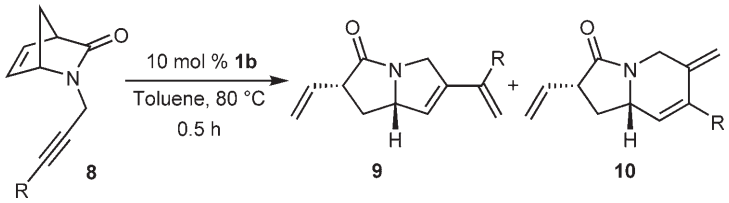
Scheme 10. ROM-RCM of azabicyclo[2.2.1]heptene-yne **8a**.

Subsequently, we examined the substituent effect on the alkyne. When the reaction of **8b** (R = Me) was carried out under our optimized reaction conditions (in toluene at 80 °C), pyrrolizidine derivative **9b** was obtained in 30% yield along with indolizidine derivative **10b** in 40% yield (Table 2, entry 1). It was interesting that ethylene is required for this reaction because compound **8b** did not provide the desired products under argon atmosphere although the starting material **8b** was consumed (entry 2).[11] The ratio of pyrrolizidine to indolizidine was changed when compound **8c** having the phenyl group on the alkyne was used for this reaction, and pyrrolizidine derivative **9c** was obtained as a major product. To examine the electronic effect of the substituent on the alkyne, compound **8d** or **8e** was subjected to the reaction. But the ratio of **9d** to **10d** is almost same as that of **9e** to **10e**, and in each case, pyrrolizidine derivative, **9d** or **9e**, was obtained as the major product (entries 3 and 4). In the case of **8d**, tetraene **11d** was obtained in 12% yield (entry 4). When **11d** was re-exposed to Grubbs' catalyst **1b** under the same reaction conditions, RCM did not proceed and **11d** was recovered in 82% yield. This means that **9d** and **10d** were not formed from **11d**. A TMS group was also effective for the formation of pyrrolizidine derivative **9f** (entry 6). To explore the steric effect on the alkyne, the bulky TIPS (triisopropylsilyl) group was introduced on the terminal alkyne. Interestingly, **8g** gave pyrrolizidine derivative **9g** in 31% yield along with ring-opening product **12g** in 36% yield.

When a toluene solution of **12g** was treated with 20 mol% of **1b** at 80 °C for 4.5 h under ethylene atmosphere, a mixture of **9g** and **9g′** (an olefin of **9g′** conjugated with the carbonyl group) was obtained in 37% yield, and the starting material **12g** and **12g′** (olefin isomer of **12g**) was recovered in 49% yield (Scheme 11). In this case, formation of indolizidine derivative **10g** was also not observed. Furthermore, the TIPS group of **12g** was removed by treatment with TBAF and the resultant **12a′** was treated in a similar manner. As a result, pyrrolizidine derivative **7** and indolizidine derivative **10a′** were obtained in 60% and 21% yields, respectively. It is noteworthy that pyrrolizidine derivative **7** was formed as a major product in this case although the reaction of **8a** gave indolizidine derivative **10a** as the major product. Furthermore, the reaction of **12c′**, which was obtained by Sonogashira coupling reaction of **12a′** and phenyl iodide, preferred the formation of pyrrolizidine derivative **9c′** other that of indolizidine derivative **10c′**. This result is similar to that of **8c**.

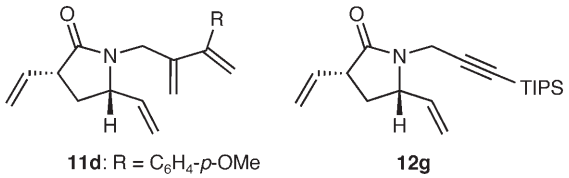
When a toluene solution of **13** having a one-carbon elongated side chain and 10 mol% of **1b** was warmed at 80 °C for 1 h, the metathesis products were not ob-

Table 2. Synthesis of bicyclic heterocycles.

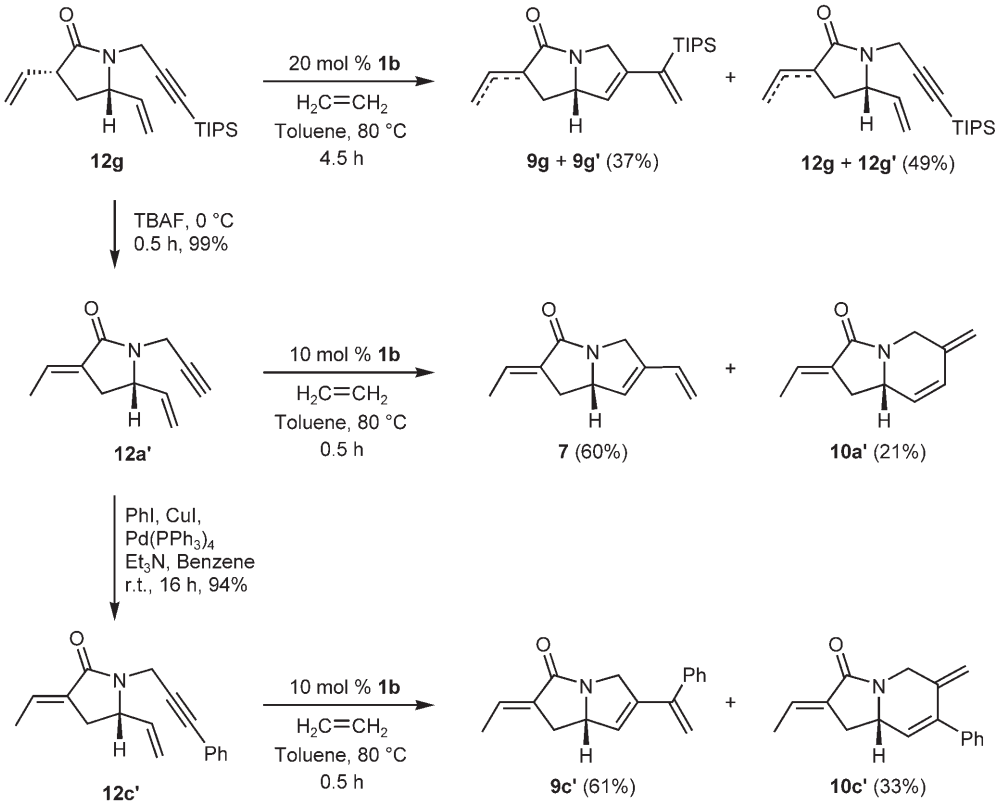


Entry	R	Atmosphere	**9** (%)[a]	**10** (%)[a]
1	Me (**8b**)	$H_2C{=}CH_2$	30	40
2	Me (**8b**)	Ar	0	0
3	Ph (**8c**)	$H_2C{=}CH_2$	56	15
4[b]	C_6H_4-*p*-OMe (**8d**)	$H_2C{=}CH_2$	40	21
5	C_6H_4-*p*-CO_2Et (**8e**)	$H_2C{=}CH_2$	34	18
6	TMS (**8f**)	$H_2C{=}CH_2$	51	23
7[c]	TIPS (**8g**)	$H_2C{=}CH_2$	31[d]	-

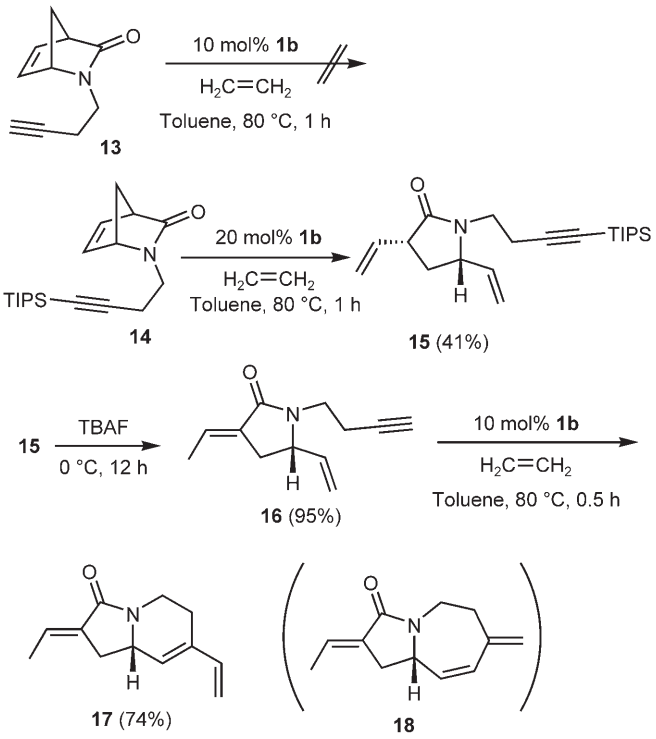
[a] Isolated yields.
[b] **11d** was obtained in 12% yield.
[c] **12g** was obtained in 36% yield.
[d] 1:1 mixture of **9g** and **9g′**.



tained although the spot of the starting material **13** disappeared on TLC (Scheme 12). However, when compound **14**, which possessed a TIPS group on the terminal alkyne, was subjected to the same reaction conditions, ROM-CM with ethylene proceeded to give **15** in 41% yield. The removal of the TIPS group



Scheme 11. Effect of alkyne TIPS-substitution on ROM-RCM product distribution.



Scheme 12. Synthesis of indolizidine derivative **17**.

of **15** gave **16**, which was subjected to the metathesis conditions to afford only indolizidine derivative **17** in 74% yield, and bicyclic compound **18**, containing a 7-membered ring was not formed.

Consideration of the Reaction Mechanism of Azabicyclo[2.2.1]heptene-ynes

The possible reaction course for the formation of indolizidine and quinolizidine derivatives is shown in Scheme 13 on the basis of the preceding results. The cycloaddition and subsequent cycloreversion of the ruthenium methylidene complex to the double bond of cycloalkene **8** provide **XI** and **VII**, which would be converted to **12** under an ethylene atmosphere. If the ruthenium carbene of **VII** reacts with the alkyne part intramolecularly, **IX** would be formed *via* ruthenacyclobutene **VIII**, and **IX** reacts with ethylene to afford pyrrolizidine derivative **9**. The ruthenium carbene of **XI** would not react with the alkyne moiety due to the ring strain of formed ruthenacyclobutene. On the other hand, if the ruthenium methylidene complex reacts with the alkyne moiety in **12**, complexes **XIII** and **XII** would be formed, giving pyrrolizidine derivative **9** and indolizidine derivative **10** by intramolecular reaction. It is also possible that these complexes (**XII** and **XIII**) can react with ethylene to provide tetraene **XIV**.[10] However, RCM of complex **XII** or **XIII** should be faster than CM with ethylene in our case because of the higher reaction temperature. Ethylene is required for the formation of **9** and **10** from ruthenium carbene complexes **XI**, **VII** and **IX**. If the reaction proceeds through this reaction mechanism, an indolizidine derivative would be formed from complex **XII**. Since the bulky substituents on the alkyne would disturb the formation of **XII** from **12**, the formation of pyrrolizidine derivative **9** *via* **IX** or **XIII** would be taken precedence.

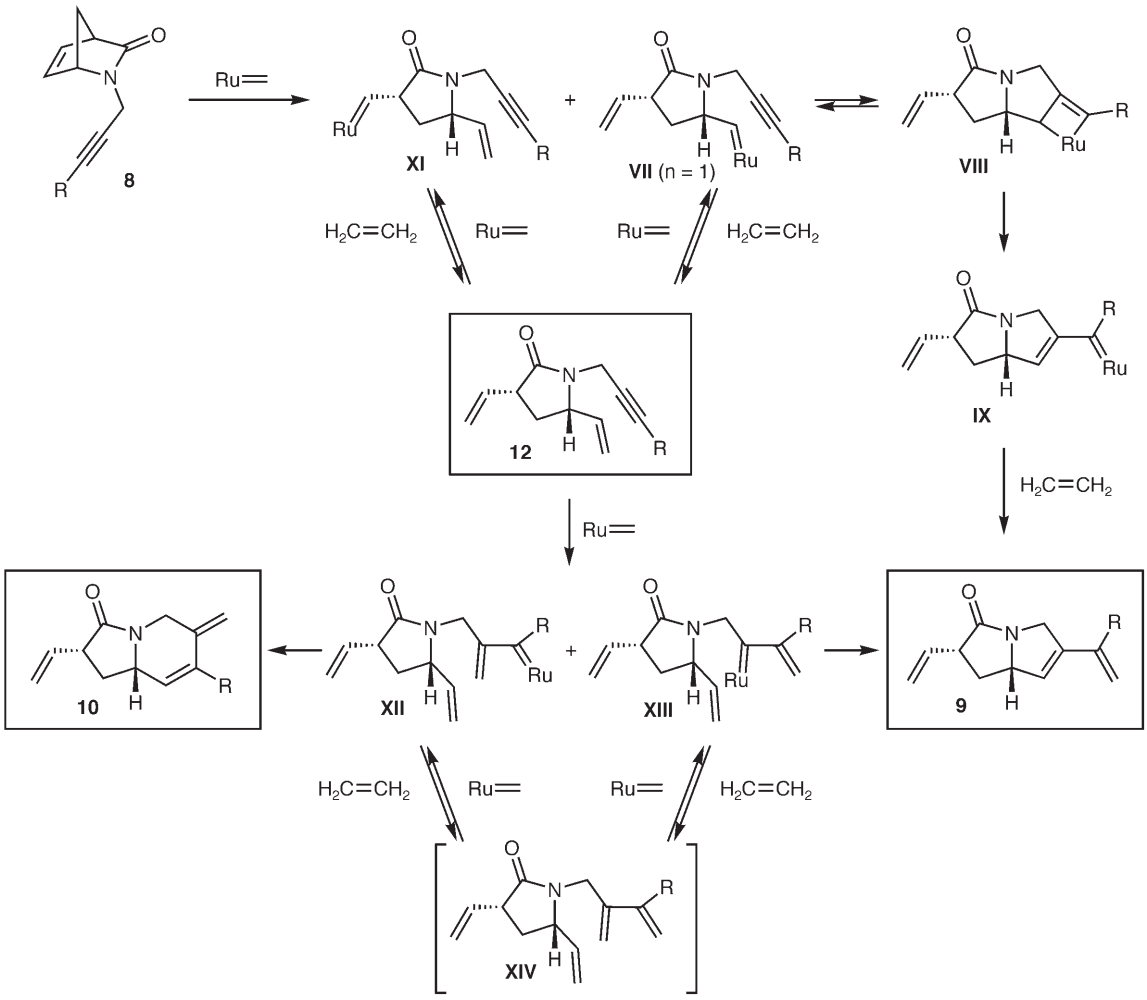
ROM-RCM of Azabicyclo[2.2.2]octene-ynes

ROM-RCM of azabicyclo[2.2.2]octene-yne was carried out. When a CH_2Cl_2 solution of **19a** was refluxed in the presence of 10 mol% of **1b** under an ethylene atmosphere, **19a** was recovered in 73% yield (Table 3, entry 1). Ethylene gas was important for this reaction and starting material **19a** was recovered in only 39% yield when the reaction was carried out under argon atmosphere (entry 2). When a toluene solution of **19a** and 10 mol% of **1b** was stirred at 80 °C for 0.5 h, quinolizidine derivative **20a** was obtained in 27% yield along with triene **21a**, which was provided by cross enyne metathesis of **19a** and ethylene, in 42% yield (entry 3). The higher reaction temperature led to a slight change of the products ratio (entry 4). In the case of **19b**, cross metathesis product **21b** was obtained in 78% yield (entry 5). This means that the bulky substituent of TMS group on the alkyne disturbs the formation of quinolizidine derivative **20b**, and only CM of the alkyne part with ethylene proceeded.

These results are summarized as follows: (1) initial reaction would proceed *via* CM of the alkyne part and ethylene; (2) because of the slow reaction rate of a cyclohexene part with ruthenium carbene of **XV** or **XVI** generated on the side chain, the yield of quinolizidine derivative **20** is low; (3) due to the bulky substituent on the alkyne, the formation of **XVI** is suppressed; (4) indolizidine derivative **22** could not be obtained in this reaction, because of the low reactivity of the cyclohexene part to ROM. From these results, the reaction mechanism of azabicyclo[2.2.2]octene-ynes should be different from that of azabicyclo-[2.2.1]heptene-ynes (Scheme 14).

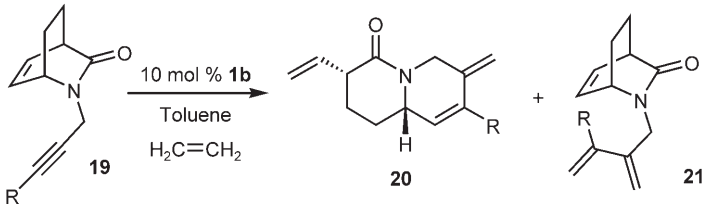
Conclusions

A simple construction method for a pyrrolizidine skeleton *via* ROM-RCM of cyclopentene-yne catalyzed by the ruthenium carbene complex **1b**, and one-step synthesis of bicyclic heterocycles by ROM-RCM of azabicycloalkene-ynes were investigated. In the



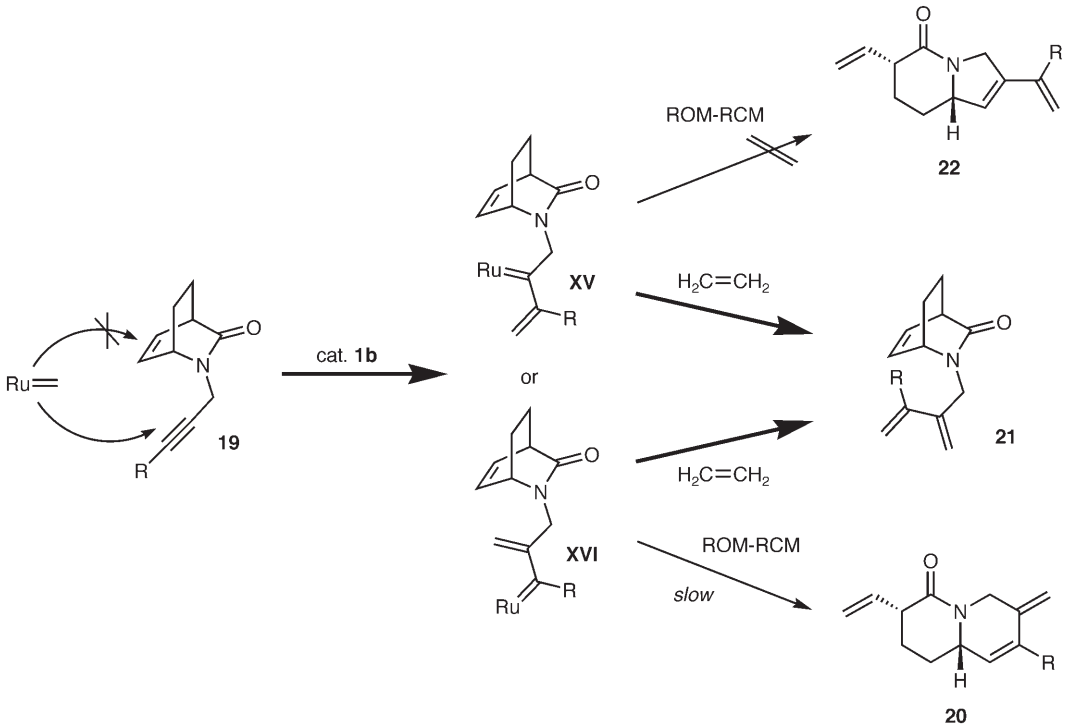
Scheme 13. Possible reaction course for the formation of pyrrolizidine and indolizidine derivatives.

Table 3. ROM-RCM of azabicyclo[2.2.2]octene-ynes **19**.



Entry	R	Temperature [°C]	Time [h]	**20** [%][a]	**21** [%][a]	Recovery of **19** [%][b]
1[c]	H (**19a**)	reflux	21	-	-	73
2[d]	H (**19a**)	80	3	-	-	39
3	H (**19a**)	80	0.5	27	42	-
4	H (**19a**)	reflux	0.5	22	50	-
5	TMS (**19b**)	80	0.5	-	78[b]	-

[a] Yield was determined by ^{1}H NMR using (*E*)-stilbene as an internal standard.
[b] Isolated yield.
[c] In CH_2Cl_2.
[d] Under an argon atmosphere.



Scheme 14. Plausible reaction course for the reaction of **19**.

former case, ROM-RCM of cyclopentene-ynes proceeded smoothly at room temperature to give pyrrolidines derivative having a triene moiety in good yield, which were converted into pyrrolizidine derivatives by simple treatment. In the latter case, pyrrolizidine and indolizidine derivatives were obtained in only one step from azabicyclo[2.2.1]heptene-ynes, and the ratio of the pyrrolizidine and the indolizidine derivatives was affected by the substituent on the alkyne. When azabicyclo[2.2.1]heptene-ynes bearing large substituents on the alkyne were treated with ruthenium catalyst **1b**, a pyrrolizidine derivative was obtained as the major product. From azabicyclo-[2.2.2]octene-yne, a quinolizidine derivative was obtained although the yield was moderate.

Experimental Section

General Remarks

The metathesis reactions were carried out under an atmosphere of ethylene (1 atm) unless otherwise mentioned. All other manipulations were carried out under an atmosphere of argon unless otherwise mentioned. Ruthenium complexes were purchased from Aldrich Chemical Company. All other solvents and reagents were purified when necessary using standard procedure. Column chromatography was performed on silica gel 60 N (spherical, neutral, 40–60 μm, Kanto Chemical Co.).

Methyl 4-(2-Nitrobenzenesulfonylamino)-cyclopent-2-enecarboxylate (5)

To a solution of **4** (504.5 mg, 4.62 mmol) in MeOH (24 mL) was added $SOCl_2$ (0.6 mL, 8.23 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. The volatiles were removed under reduce pressure, and the residue was dissolved in CH_2Cl_2 (23 mL). To this solution were added Et_3N (1.9 mL, 13.87 mmol) and NsCl (1.54 g, 6.93 mmol) at 0 °C, and the solution was stirred for 1.5 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to afford **5**; yield: 1.47 g (98%). IR (neat): $\nu = 1714$ (s), 1545 (s), 1364 (s), 1167 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.89$ (ddd, $J = 3.0$, 3.5, 14.1 Hz, 1H), 2.33 (ddd, $J = 7.9$, 8.6, 14.1 Hz, 1H), 3.44 (dddd, $J = 2.0$, 2.5, 3.5, 8.6 Hz, 1H), 3.71 (s, 3H), 4.67 (ddddd, $J = 1.4$, 2.3, 3.0, 7.9, 8.5 Hz, 1H), 5.72 (ddd, $J = 2.0$, 2.3, 5.6 Hz, 1H), 5.85 (br, 1H), 5.90 (ddd, $J = 1.4$, 2.5, 5.6 Hz, 1H), 7.71–7.78 (m, 2H), 7.84–7.89 (m, 1H), 8.16–8.20 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 34.3$, 49.3, 52.5, 59.6, 125.2, 130.4, 132.7, 132.8, 133.1, 133.4, 135.1, 147.8, 173.8; EI-LR-MS: $m/z = 326$ (M^+), 295, 267, 186, 140, 108, 80.

Methyl 4-[(2-Nitrobenzenesulfonyl)-prop-2-ynyl-amino]-cyclopent-2-enecarboxylate (2a)

To a solution of **5** (315.1 mg, 0.97 mmol), PPh_3 (303.9 mg, 1.16 mmol), and propargyl alcohol (0.07 mL, 1.16 mmol) in THF (10 mL) was added DEAD (0.53 mL, 1.16 mmol, 40% toluene solution) at 0 °C. The solution was stirred at room

temperature for 32 h, and the volatiles were removed under reduce pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to afford **2a**; yield: 237.5 mg (68%). IR (neat): $\nu = 2124$ (w), 1734 (s), 1546 (s), 1372 (s), 1166 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 2.07$ (t, $J = 2.5$ Hz, 1H), 2.20 (ddd, $J = 5.6$, 6.3, 15.3 Hz, 1H), 2.61 (ddd, $J = 8.4$, 9.2, 15.3 Hz, 1H), 3.51 (ddddd, $J = 1.5$, 2.1, 2.1, 6.3, 9.2 Hz, 1H), 3.72 (s, 3H), 4.10 (d, $J = 2.5$ Hz, 2H), 5.21 (ddddd, $J = 1.5$, 2.1, 2.1, 5.6, 8.4 Hz, 1H), 5.87 (ddd, $J = 2.1$, 2.1, 5.6 Hz, 1H), 6.00 (ddd, $J = 2.1$, 2.1, 5.6 Hz, 1H), 7.65–7.73 (m, 3H), 8.17–8.20 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 30.8$, 32.8, 48.9, 52.2, 64.2, 72.6, 79.5, 124.1, 131.4, 131.6, 132.2, 133.4, 133.5, 133.6, 147.8, 173.6.

Typical Procedure for the Metathesis Reaction of 2a (Table 1, entry 3)

To a solution of ruthenium carbene complex **1b** (9.3 mg, 11.01 μmol, 10 mol%) in CH_2Cl_2 (2 mL) was added **2a** (40.1 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) at 0 °C, and the solution was stirred at room temperature for 2 h. A few drops of ethyl vinyl ether were added to the mixture, and the volatiles were removed under reduce pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford methyl 2-[1-(2-nitrobenzenesulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrol-2-ylmethyl]-but-3-enoate (**3a**); yield: 32.3 mg (75%). IR (neat): $\nu = 1735$ (s), 1640 (w), 1546 (s), 1372 (s), 1170 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 2.04 (ddd, $J = 4.7$, 6.0, 13.7 Hz, 1H), 2.33 (ddd, $J = 2.5$, 8.7, 13.7 Hz, 1H), 3.20 (ddd, $J = 4.7$, 8.0, 8.7 Hz, 1H), 3.62 (s, 3H), 4.28 (ddd, $J = 1.2$, 4.5, 13.8 Hz, 1H), 4.32 (ddd, $J = 1.1$, 2.0, 13.8 Hz, 1H), 4.88 (m, 1H), 5.05–5.25 (m, 4H), 5.56 (ddd, $J = 1.1$, 1.2, 1.8 Hz, 1H), 5.75 (ddd, $J = 8.0$, 9.9, 17.3 Hz, 1H), 6.37 (dd, $J = 10.2$, 15.0 Hz, 1H), 7.61–7.73 (m, 3H), 7.92–7.96 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta =$ 37.4, 45.6, 52.0, 54.5, 66.1, 117.1, 117.6, 124.2, 126.7, 129.3, 130.1, 131.5, 131.8, 133.6, 135.4, 137.0, 148.4, 173.9; EI-LR-MS: $m/z = 392$ (M^+), 361, 279, 206, 186, 106, 93; EI-HR-MS: $m/z = 392.1051$, calcd. for $C_{18}H_{20}O_6N_2S$ (M^+): 392.1042.

2-Ethylidene-6-vinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (7)

To a solution of **3a** (10.1 mg, 0.03 mmol) in DMF (0.5 mL) was added DBU (38 μL, 0.26 mmol) and $HSCH_2CH_2OH$ (18 μL, 0.26 mmol) at 0 °C. The resultant solution was stirred at room temperature for 2 h, and then at 40 °C for 14 h. Saturated $NaHCO_3$ solution was added at 0 °C, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NH_4Cl solution and saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 1:1) to afford **7**; yield: 3.5 mg (78%). IR (neat): $\nu = 1747$ (s), 1706 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.77$ (ddd, $J = 1.3$, 2.3, 7.1 Hz, 3H), 2.49 (dddq, $J = 3.3$, 5.6, 16.1, 2.3 Hz, 1H), 3.04 (dddq, $J = 2.1$, 7.9, 16.1, 1.3 Hz, 1H), 3.90 (ddd, $J = 2.0$, 3.8, 14.5 Hz, 1H), 4.63 (ddd, $J = 1.5$, 3.0, 14.5 Hz, 1H), 4.70 (m, 1H), 5.17 (d, $J = 17.5$ Hz, 1H), 5.21 (d, $J = 10.6$ Hz, 1H), 5.84 (m, 1H), 6.49 (dd, $J =$ 10.6, 17.5 Hz, 1H), 6.53 (ddq, $J = 2.1$, 3.3, 7.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 14.9$, 30.4, 50.1, 64.1, 117.3, 128.6, 129.0, 130.3, 134.0, 141.9, 172.0; EI-LR-MS: $m/z = 175$ (M^+), 160, 148, 132, 118, 106, 93; EI-HR-MS: $m/z = 175.0979$, calcd. for $C_{11}H_{13}ON$ (M^+): 175.09970.

2-Prop-2-ynyl-2-azabicyclo[2.2.1]hept-5-en-3-one (8a)

To a suspension of NaH (98.3 mg, 2.46 mmol) in DMF (5.5 mL) was added 2-azabicyclo[2.2.1]hept-5-en-3-one (223.4 mg, 2.05 mmol) in DMF (4.5 mL) at 0 °C, and the mixture stirred at room temperature for 1 h. To this suspension was added propargyl bromide (0.23 mL, 3.07 mmol) at 0 °C, and stirred at room temperature for 1 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with H_2O and saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **8a**; yield: 245.3 mg (81%). IR (neat): $\nu = 2118$ (w), 1707 (s), 1560 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 2.15$ (ddd, $J = 1.5$, 1.6, 7.7 Hz, 1H), 2.23 (t, $J = 2.6$ Hz, 1H), 2.31 (ddd, $J = 1.5$, 1.6, 7.7 Hz, 1H), 3.37 (ddt, $J = 0.5$, 3.3, 1.5 Hz, 1H), 3.74 (dd, $J =$ 2.6, 17.6 Hz, 1H), 4.00 (dd, $J = 2.6$, 17.6 Hz, 1H), 4.33 (ddt, $J = 1.5$, 2.0, 1.6 Hz, 1H), 6.58 (ddd, $J = 1.5$, 3.3, 5.3 Hz, 1H), 6.92 (ddd, $J = 0.5$, 2.0, 5.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 33.0$, 53.2, 57.4, 62.6, 72.7, 76.5, 136.0, 139.1, 178.9; EI-LR-MS: $m/z = 147$ (M^+), 88, 66; EI-HR-MS: $m/z = 147.0672$, calcd. for C_9H_9ON (M^+): 147.0684.

Typical Procedure for the Metathesis Reaction of 8 (Scheme 10)

To a solution of ruthenium carbene complex **1b** (9.9 mg, 11.62 μmol, 10 mol%) in toluene (3 mL) was added **8a** (17.1 mg, 0.12 mmol) in toluene (3 mL) at 0 °C, and the solution was stirred at 80 °C for 0.5 h. A few drops of ethyl vinyl ether were added to the mixture, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **9a** and **10a**.

2,6-Divinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (9a): yield: 3.7 mg (18%); IR (neat): $\nu = 1704$ (s), 1641 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.76$ (ddd, $J = 9.7$, 9.7, 12.2 Hz, 1H), 2.60 (ddd, $J = 6.1$, 7.3, 12.2 Hz, 1H), 3.48 (ddd, $J = 6.1$, 6.8, 9.7 Hz, 1H), 3.81 (m, 1H), 4.56 (m, 1H), 4.66 (m, 1H), 5.12–5.25 (m, 4H), 5.80 (m, 1H), 5.94 (ddd, $J = 6.8$, 10.4, 17.1 Hz, 1H), 6.48 (dd, $J = 10.9$, 17.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 36.4$, 48.4, 48.8, 65.2, 117.1, 117.4, 127.8, 130.2, 134.6, 140.5, 176.7; EI-LR-MS: $m/z = 175$ (M^+), 160, 146, 132, 117, 106, 93; EI-HR-MS: $m/z = 175.0979$, calcd. for $C_{11}H_{13}ON$ (M^+): 175.09970.

6-Methylene-2-vinyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10a): yield: 10.1 mg (50%); IR (neat): $\nu = 1689$ (s), 1642 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.56$ (m, 1H), 2.52 (m, 1H), 3.23 (ddd, $J = 6.8$, 6.9, 7.1 Hz, 1H), 3.60 (d, $J = 15.6$ Hz, 1H), 4.19 (m, 1H), 4.73 (d, $J = 15.6$ Hz, 1H), 4.98 (s, 2H), 5.18 (d, $J = 17.1$ Hz, 1H), 5.21 (d, $J = 9.6$ Hz, 1H), 5.78 (d, $J = 9.8$ Hz, 1H), 5.92 (ddd, $J = 6.8$, 9.6, 17.1 Hz, 1H), 6.22 (d, $J = 9.8$ Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 32.9$, 42.0, 46.7, 52.7, 113.2, 117.5, 127.2, 128.9, 134.8, 136.7, 172.1; EI-LR-MS: $m/z = 175$ (M^+), 160, 146, 132, 117, 106, 93; EI-HR-MS: $m/z = 175.0985$, calcd. for $C_{11}H_{13}ON$ (M^+): 175.09970.

2-But-2-ynyl-2-azabicyclo[2.2.1]hept-5-en-3-one (8b)

To a suspension of NaH (160.0 mg, 4.00 mmol) in DMF (8 mL) was added 2-aza-bicyclo[2.2.1]hept-5-en-3-one (363.7 mg, 3.33 mmol) in DMF (10 mL) at 0 °C, and stirred at room temperature for 1 h. To this suspension was added 1-bromo-2-butyne (0.44 mL, 5.00 mmol) at 0 °C, and stirred at room temperature for 1 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with H_2O and saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 1:1) to afford **8b**; yield: 418.1 mg (78 %). IR (neat): $\nu = 2228$ (w), 1712 (s), 1559 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.81$ (t, $J = 2.5$ Hz, 3H), 2.12 (dt, $J = 7.7$, 1.5 Hz, 1H), 2.31 (dt, $J = 7.7$, 1.5 Hz, 1H), 3.36 (m, 1H), 3.68 (dq, $J = 17.2$, 2.5 Hz, 1H), 3.94 (dq, $J = 17.2$, 2.5 Hz, 1H), 4.31 (ddd, $J = 1.5$, 1.6, 1.8 Hz, 1H), 6.56 (ddd, $J = 1.5$, 3.1, 5.3 Hz, 1H), 6.92 (dd, $J = 2.1$, 5.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 3.5$ (CH_3), 33.8 (CH_2), 53.7 (CH), 57.7(CH_2), 62.8 (CH), 72.8 (C), 80.7 (C), 136.5 (CH), 139.7 (CH), 179.6 (C); EI-LR-MS: $m/z = 161$ (M^+), 88, 66; EI-HR-MS: $m/z = 161.0810$, calcd. for $C_{10}H_{11}ON$ (M^+): 161.0841.

6-Isopropenyl-2-vinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (9b) and 7-Methyl-6-methylene-2-vinyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10b)

According to the typical procedure for the metathesis reaction of **8**, a solution of **8b** (48.5 mg, 0.30 mmol) and **1b** (25.5 mg, 0.03 mmol) in toluene (15 mL) was stirred at 80 °C for 0.5 h to afford **9b** and **10b**.

9b: yield: 16.9 mg (30 %); IR (neat): $\nu = 1701$ (s), 1644 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.77$ (ddd, $J =$ 9.7, 9.7, 12.2 Hz, 1H), 1.93 (s, 3H), 2.61 (ddd, $J = 5.6$, 6.2, 12.2 Hz, 1H), 3.48 (m, 1H), 3.85 (ddd, $J = 2.0$, 2.6, 14.5 Hz, 1H), 4.58 (ddd, $J = 1.5$, 3.5, 14.5 Hz, 1H), 4.69 (m, 1H), 4.91 (s, 1H), 5.04 (s, 1H), 5.15 (ddd, $J = 1.3$, 1.3, 17.3 Hz, 1H), 5.21 (ddd, $J = 1.3$, 1.3, 10.6 Hz, 1H), 5.81 (d, $J = 1.6$ Hz, 1H), 5.95 (ddd, $J = 6.8$, 10.6, 17.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 20.2$ (CH_3), 36.4 (CH_2), 48.4 (CH), 49.7 (CH_2), 65.6 (CH), 115.0 (CH_2), 117.4 (CH_2), 125.1 (CH), 134.8 (CH), 136.9 (C), 142.4 (C), 176.8 (C); EI-LR-MS: $m/z = 189$ (M^+), 174, 148, 107, 88; EI-HR-MS: $m/z = 189.1179$, calcd. for $C_{12}H_{15}ON$ (M^+): 189.1154.

10b: yield: 22.8 mg (40 %); IR (neat): $\nu = 1691$ (s), 1643 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.55$ (ddd, $J =$ 9.7, 9.7, 12.2 Hz, 1H), 1.87 (s, 3H), 2.49 (ddd, $J = 6.4$, 7.9, 12.2 Hz, 1H), 3.21 (m, 1H), 3.59 (dd, $J = 1.8$, 15.3 Hz, 1H), 4.18 (m, 1H), 4.70 (d, $J = 15.3$ Hz, 1H), 4.99 (s, 1H), 5.09 (d, $J = 1.5$ Hz, 1H), 5.17 (ddd, $J = 1.3$, 1.5, 17.1 Hz, 1H), 5.21 (ddd, $J = 1.3$, 1.5, 10.6 Hz, 1H), 5.63 (s, 1H), 5.92 (ddd, $J =$ 6.8, 10.6, 17.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta =$ 19.1 (CH_3), 33.2 (CH_2), 42.9 (CH_2), 46.5 (CH), 53.3 (CH), 110.6 (CH_2), 117.5 (CH_2), 126.8 (CH), 131.4 (C), 135.1 (CH), 138.4 (C), 172.2 (C); EI-LR-MS: $m/z = 189$ (M^+), 174, 149, 88; EI-HR-MS: $m/z = 189.1149$, calcd. for $C_{12}H_{15}ON$ (M^+): 189.1154.

2-(3-Phenyl-prop-2-ynyl)-2-azabicyclo[2.2.1]hept-5-en-3-one (8c)

To the solution of **8a** (145.4 mg, 0.99 mmol), CuI (9.4 mg, 49.40 μmol), $Pd(PPh_3)_4$ (57.1 mg, 49.40 μmol) and Et_3N (2.5 mL) in benzene (1 mL) was added PhI (0.12 mL, 1.04 mmol) at room temperature, and stirred for 14 h. The volatiles were removed under reduce pressure, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **8c**; yield: 181.3 mg (82 %). IR (neat): $\nu = 2243$ (w), 1710 (s), 1599 (w), 1560 (w), 757 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 2.15$ (ddd, $J = 1.5$, 1.6, 7.7 Hz, 1H), 2.34 (ddd, $J = 1.6$, 1.8, 7.7 Hz, 1H), 3.39 (m, 1H), 4.02 (d, $J = 17.6$ Hz, 1H), 4.18 (d, $J = 17.6$ Hz, 1H), 4.37 (m, 1H), 6.59 (ddd, $J = 1.5$, 3.3, 5.2 Hz, 1H), 6.96 (ddd, $J = 0.5$, 2.0, 5.2 Hz, 1H), 7.28–7.44 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 33.5$, 53.0, 57.0, 62.4, 82.4, 84.2, 121.9, 127.7, 127.8, 131.0, 135.7, 139.1, 178.9; EI-LR-MS: $m/z = 223$ (M^+), 194, 167, 129, 115, 66; EI-HR-MS: $m/z =$ 223.0990, calcd. for $C_{15}H_{13}ON$ (M^+): 223.0997.

6-(1-Phenylvinyl)-2-vinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (9c) and 6-Methylene-7-phenyl-2-vinyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10c)

According to the typical procedure for the metathesis reaction of **8**, a solution of **8c** (30.8 mg, 0.14 mmol) and **1b** (11.7 mg, 13.79 μmol) in toluene (7 mL) was stirred at 80 °C for 0.5 h to afford **9c** and **10c**.

9c: yield: 19.3 mg (56 %); IR (neat): $\nu = 1737$ (m), 1699 (s), 1644 (m), 756 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 1.75 (ddd, $J = 9.6$, 11.7, 12.4 Hz, 1H), 2.57 (ddd, $J = 5.9$, 7.3, 11.7 Hz, 1H), 3.48 (m, 1H), 3.97 (m, 1H), 4.64–4.74 (m, 2H), 5.15 (dt, $J = 17.3$, 1.5 Hz, 1H), 5.18–5.25 (m, 3H), 5.69 (d, $J = 1.2$ Hz, 1H), 5.96 (ddd, $J = 6.8$, 10.6, 17.3 Hz, 1H), 7.25–7.39 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 36.4$, 48.3, 50.0, 65.7, 116.5, 117.5, 127.7, 128.2, 128.3, 128.5, 134.7, 140.5, 141.5, 143.4, 176.9; EI-LR-MS: $m/z = 251$ (M^+), 169, 148; EI-HR-MS: $m/z = 251.1331$, calcd. for $C_{17}H_{17}ON$ (M^+): 251.1310.

10c: yield: 5.1 mg (15 %); IR (neat): $\nu = 1674$ (s), 1644 (m), 776 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.67$ (ddd, $J = 10.0$, 11.7, 12.2 Hz, 1H), 2.58 (ddd, $J = 6.5$, 7.9, 12.2 Hz, 1H), 3.28 (m, 1H), 3.74 (m, 1H), 4.36 (m, 1H), 4.82 (d, $J = 15.0$ Hz, 1H), 4.94 (m, 1H), 5.14 (m, 1H), 5.21 (ddd, $J = 1.3$, 1.5, 17.1 Hz, 1H), 5.25 (ddd, $J = 1.3$, 1.5, 10.5 Hz, 1H), 5.74 (br, 1H), 5.98 (ddd, $J = 6.8$, 10.5, 17.1 Hz, 1H), 7.23–7.39 (m, 5H); EI-LR-MS: $m/z = 251$ (M^+), 222, 174, 128, 115; EI-HR-MS: $m/z = 251.1333$, calcd. for $C_{17}H_{17}ON$ (M^+): 251.1310.

2-[3-(*p*-Methoxyphenyl)-prop-2-ynyl]-2-azabicyclo-[2.2.1]hept-5-en-3-one (8d)

To the solution of **8a** (203.9 mg, 1.39 mmol), CuI (13.2 mg, 69.27 μmol), $Pd(PPh_3)_4$ (80.0 mg, 69.27 μmol) and Et_3N (4 mL) in benzene (3 mL) was added 1-iodo-4-methoxy-benzene (340.5 mg, 1.45 mmol) at room temperature, and stirred for 36 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **8d**; yield: 123.3 mg (35 %); IR (neat): $\nu = 2241$ (w), 1710 (s), 1607 (m), 1568 (w), 1249 (s), 1033 (m), 756 (s) cm^{-1}; ^1H NMR

(270 MHz, $CDCl_3$): $\delta = 2.14$ (ddd, $J = 1.5$, 1.5, 7.7 Hz, 1H), 2.33 (ddd, $J = 1.5$, 1.8, 7.7 Hz, 1H), 3.39 (m, 1H), 3.81 (s, 3H), 4.01 (d, $J = 17.6$ Hz, 1H), 4.17 (d, $J = 17.6$ Hz, 1H), 4.37 (m, 1H), 6.58 (ddd, $J = 1.5$, 3.3, 5.3 Hz, 1H), 6.84 (d, $J = 8.9$ Hz, 2H), 6.94 (ddd, $J = 0.5$, 2.0, 5.3 Hz, 1H), 7.35 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 34.0$ (CH_2), 53.4 (CH), 55.0 (CH_3), 57.4 (CH_2), 62.7 (CH), 81.3 (C), 84.5 (C), 113.7 (CH), 114.4 (C), 132.8 (CH), 136.0 (CH), 139.6 (CH), 159.5 (C), 179.3 (C); EI-LR-MS: $m/z = 253$ (M^+), 187, 159, 145, 132, 102, 66; EI-HR-MS: $m/z = 253.1100$, calcd. for $C_{16}H_{15}O_2N$ (M^+): 253.1103.

6-[1-(*p*-Methoxyphenyl)-vinyl]-2-vinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (9d), 7-(*p*-Methoxyphenyl)-6-methylene-2-vinyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10d) and 1-[3-(*p*-Methoxyphenyl)-2-methylene-but-3-enyl]-3,5-divinylpyrrolidin-2-one (11d)

According to the typical procedure for the metathesis reaction of **8**, a solution of **8d** (42.5 mg, 0.17 mmol) and **1b** (14.2 mg, 16.78 μmol) in toluene (8.5 mL) was stirred at 80 °C for 0.5 h to afford **9d**, **10d** and **11d**.

9d: yield: 18.9 mg (40 %); IR (neat): $\nu = 1693$ (s), 1608 (s), 1249 (s), 1033 (m), 755 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.76$ (ddd, $J = 9.6$, 11.9, 12.2 Hz, 1H), 2.57 (ddd, $J = 5.8$, 7.3, 11.9 Hz, 1H), 3.48 (m, 1H), 3.83 (s, 3H), 3.96 (m, 1H), 4.63–4.74 (m, 2H), 5.11–5.25 (m, 4H), 5.71 (br, 1H), 5.96 (ddd, $J = 6.8$, 10.4, 17.1 Hz, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 7.23 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 36.4$ (CH_2), 48.3 (CH), 50.1 (CH_2), 55.3 (CH_3), 65.6 (CH), 113.6 (CH), 115.8 (CH_2), 117.5 (CH_2), 128.3 (CH), 129.4 (CH), 132.9 (C), 134.7 (CH), 141.7 (C), 142.8 (C), 159.2 (C), 176.9 (C); EI-LR-MS: $m/z = 281$ (M^+), 199, 184, 148, 133; EI-HR-MS: $m/z = 281.1445$, calcd. for $C_{18}H_{19}O_2N$ (M^+): 281.1416.

10d: yield: 9.8 mg (21 %); IR (neat): $\nu = 1690$ (s), 1609 (s), 1247 (s), 1032 (m), 755 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.66$ (ddd, $J = 10.1$, 11.4, 12.0 Hz, 1H), 2.57 (ddd, $J = 6.4$, 7.7, 12.0 Hz, 1H), 3.27 (m, 1H), 3.72 (dd, $J = 1.8$, 15.0 Hz, 1H), 3.83 (s, 3H), 4.35 (m, 1H), 4.80 (d, $J = 15.0$ Hz, 1H), 4.96 (d, $J = 0.8$ Hz, 1H), 5.13 (d, $J = 0.8$ Hz, 1H), 5.21 (ddd, $J = 1.5$, 1.5, 17.1 Hz, 1H), 5.24 (ddd, $J = 1.3$, 1.5, 10.6 Hz, 1H), 5.71 (br, 1H), 5.98 (ddd, $J = 6.8$, 10.6, 17.1 Hz, 1H), 6.88 (d, $J = 8.8$ Hz, 2H), 7.18 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 33.4$ (CH_2), 43.4 (CH_2), 46.6 (CH), 53.7 (CH), 55.3 (CH_3), 113.6 (CH), 114.7 (CH_2), 117.6 (CH_2), 127.5 (CH), 130.0 (CH), 131.6 (C), 135.0 (CH), 137.8 (C), 138.3 (C), 159.1 (C), 172.2 (C); EI-LR-MS: $m/z = 281$ (M^+), 266, 250, 198, 174, 115; EI-HR-MS: $m/z = 281.1446$, calcd. for $C_{18}H_{19}O_2N$ (M^+): 281.1416.

11d: yield: 6.0 mg (12 %); IR (neat): $\nu = 1693$ (s), 1642 (w), 1608 (s), 1248 (s), 1033 (m), 755 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.69$ (ddd, $J = 7.6$, 9.4, 13.0 Hz, 1H), 2.44 (ddd, $J = 7.3$, 8.9, 13.0 Hz, 1H), 3.10 (m, 1H), 3.65 (d, $J = 15.7$ Hz, 1H), 3.82 (s, 3H), 4.01 (m, 1H), 4.50 (d, $J = 15.7$ Hz, 1H), 5.09 (br, 1H), 5.11 (br, 1H), 5.16–5.28 (m, 6H), 5.63 (ddd, $J = 8.7$, 9.7, 17.3 Hz, 1H), 5.96 (ddd, $J = 6.6$, 9.9, 17.8 Hz, 1H), 6.86 (d, $J = 8.9$ Hz, 2H), 7.24 (d, $J = 8.9$ Hz, 2H); EI-LR-MS: $m/z = 309$ (M^+), 294, 281, 266, 226, 186, 173, 159; EI-HR-MS: $m/z = 309.1713$, calcd. for $C_{20}H_{23}O_2N$ (M^+): 309.1729.

Ethyl 4-[3-(3-Oxo-2-azabicyclo[2.2.1]hept-5-en-2-yl)-prop-1-ynyl]-benzoate (8e)

To the solution of **8a** (225.1 mg, 1.53 mmol), CuI (14.6 mg, 76.48 μmol), $Pd(PPh_3)_4$ (88.4 mg, 76.48 μmol) and Et_3N (4 mL) in benzene (3 mL) was added ethyl 4-iodobenzoate (0.27 mL, 1.61 mmol) at room temperature, and stirred for 14 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **8e**; yield: 418.7 mg (93 %). IR (neat): $\nu = 2245$ (w), 1715 (s), 1606 (m), 1560 (w), 756 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.40$ (t, $J = 7.1$ Hz, 3H), 2.17 (ddd, $J = 1.5$, 1.5, 7.7 Hz, 1H), 2.35 (ddd, $J = 1.6$, 1.6, 7.7 Hz, 1H), 3.41 (m, 1H), 4.05 (d, $J = 17.8$ Hz, 1H), 4.20 (d, $J = 17.8$ Hz, 1H), 4.38 (m, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 6.60 (ddd, $J = 1.5$, 3.1, 4.9 Hz, 1H), 6.95 (ddd, $J = 0.5$, 1.6, 4.9 Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 33.7 (CH_2), 53.1 (CH), 57.1 (CH_2), 60.6 (CH_2), 62.6 (CH), 83.6 (C), 85.8 (C), 126.6 (C), 129.0 (CH), 129.6 (C), 131.0 (CH), 135.9 (CH), 139.2 (CH), 165.3 (C), 179.0 (C); EI-LR-MS: $m/z = 295$ (M^+), 266, 250, 230, 222, 202, 184, 159, 114, 101, 66; EI-HR-MS: $m/z = 295.1193$, calcd. for $C_{18}H_{17}O_3N$ (M^+): 295.1208.

Ethyl 4-[1-(5-Oxo-6-vinyl-5,6,7,7a-tetrahydro-3*H*-pyrrolizin-2-yl)-vinyl]-benzoate (9e) and Ethyl 4-(6-Methylene-3-oxo-2-vinyl-1,2,3,5,6,8a-hexahydro-indolizin-7-yl)-benzoate (10e)

According to the typical procedure for the metathesis reaction of **8**, a solution of **8e** (89.1 mg, 0.30 mmol) and **1b** (25.6 mg, 30.17 μmol) in toluene (15 mL) was stirred at 80 °C for 0.5 h to afford **9e** and **10e**.

9e: yield: 32.8 mg (34 %); IR (neat): $\nu = 1713$ (s), 1609 (m), 756 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.41$ (t, $J = 7.1$ Hz, 3H), 1.76 (ddd, $J = 9.6$, 11.9, 12.2 Hz, 1H), 2.58 (ddd, $J = 5.9$, 7.3, 11.9 Hz, 1H), 3.49 (m, 1H), 3.98 (m, 1H), 4.40 (q, $J = 7.1$ Hz, 2H), 4.65–4.76 (m, 2H), 5.16 (ddd, $J = 1.2$, 1.3, 17.3 Hz, 1H), 5.22 (ddd, $J = 1.0$, 1.3, 10.4 Hz, 1H), 5.27 (s, 1H), 5.28 (s, 1H), 5.66 (br, 1H), 5.97 (ddd, $J = 6.8$, 10.4, 17.3 Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 2H), 8.04 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 36.2 (CH_2), 48.2 (CH), 49.9 (CH_2), 61.0 (CH_2), 65.6 (CH), 117.2 (CH_2), 117.5 (CH_2), 128.3 (CH), 128.8 (CH), 129.5 (CH), 129.8 (C), 134.6 (CH), 140.9 (C), 142.6 (C), 144.9 (C), 166.2 (C), 176.9 (C); EI-LR-MS: $m/z = 323$ (M^+), 294, 278, 250, 241, 167, 148; EI-HR-MS: $m/z = 323.1507$, calcd. for $C_{20}H_{21}O_3N$ (M^+): 323.1522.

10e: yield: 17.5 mg (18 %); IR (neat): $\nu = 1713$ (s), 1695 (s), 1608 (m), 753 (m) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.41$ (t, $J = 7.1$ Hz, 3H), 1.69 (ddd, $J = 10.1$, 11.7, 12.2 Hz, 1H), 2.60 (ddd, $J = 6.6$, 7.9, 12.2 Hz, 1H), 3.29 (m, 1H), 3.74 (dd, $J = 1.7$, 15.1 Hz, 1H), 4.37 (m, 1H), 4.39 (q, $J = 7.1$ Hz, 1H), 4.83 (d, $J = 15.1$ Hz, 1H), 4.89 (br, 1H), 5.16 (br, 1H), 5.22 (ddd, $J = 1.5$, 1.5, 17.1 Hz, 1H), 5.25 (ddd, $J = 1.3$, 1.5, 10.4 Hz, 1H), 5.79 (br, 1H), 5.98 (ddd, $J = 6.6$, 10.4, 17.1 Hz, 1H), 7.33 (d, $J = 8.6$ Hz, 2H), 8.03 (d, $J = 8.6$ Hz, 2H); EI-LR-MS: $m/z = 323$ (M^+), 294, 278, 250, 174; EI-HR-MS: $m/z = 323.1505$, calcd. for $C_{20}H_{21}O_3N$ (M^+): 323.1522.

2-[3-(Trimethylsilyl)-prop-2-ynyl]-2-azabicyclo[2.2.1]-hept-5-en-3-one (8f)

To a solution of **8a** (83.9 mg, 0.57 mmol) in THF (6 mL) was added BuLi (0.44 mL, 0.68 mmol, 1.57 M hexane solution) at −78 °C, and stirred for 1 h. To the resultant solution was added TMSCl (0.14 mL, 1.14 mmol), and stirred for 1 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **8f**; yield: 97.3 mg (78 %). IR (neat): $\nu = 2178$ (w), 1716 (s), 1560 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.14$ (s, 9H), 2.11 (d, $J =$ 7.6 Hz, 1H), 2.27 (d, $J = 7.6$ Hz, 1H), 3.33 (br, 1H), 3.77 (d, $J = 17.6$ Hz, 1H), 3.94 (d, $J = 17.6$ Hz, 1H), 4.29 (dd, $J = 1.8$, 3.6 Hz, 1H), 6.52 (ddd, $J = 1.8$, 3.6, 5.1 Hz, 1H), 6.88 (dd, $J = 1.8$, 5.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = -0.3$, 34.2, 53.5, 57.5, 62.7, 89.7, 99.3, 136.1, 139.5, 179.2; EI-LRMS: $m/z = 219$ (M^+), 204, 176, 161, 88; EI-HR-MS: $m/z = 219.1092$, calcd. for $C_{12}H_{17}ONSi$ (M^+): 219.1079.

6-[1-(Trimethylsilyl)-vinyl]-2-vinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (9f) and 6-Methylene-7-(trimethylsilyl)-2-vinyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10f)

According to the typical procedure for the metathesis reaction of **8**, a solution of **8f** (35.2 mg, 0.16 mmol) and **1b** (13.6 mg, 16.05 μmol) in toluene (8 mL) was stirred at 80 °C for 0.5 h to afford **9f** and **10f**.

9f: yield: 21.0 mg (53 %); IR (neat): $\nu = 1705$ (s), 1644 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.18$ (s, 9H), 1.75 (ddd, $J = 9.6$, 12.2, 12.2 Hz, 1H), 2.61 (ddd, $J = 5.6$, 6.1, 12.2 Hz, 1H), 3.47 (m, 1H), 3.83 (m, 1H), 4.57 (ddd, $J = 1.6$, 1.6, 14.6 Hz, 1H), 4.68 (m, 1H), 5.15 (ddd, $J = 1.3$, 1.4, 17.1 Hz, 1H), 5.21 (ddd, $J = 1.3$, 1.4, 10.4 Hz, 1H), 5.53 (d, $J = 2.1$ Hz, 1H), 5.67 (d, $J = 2.1$ Hz, 1H), 5.82 (d, $J = 1.6$ Hz, 1H), 5.96 (ddd, $J = 6.7$, 10.4, 17.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = -0.8$, 36.6, 48.4, 50.2, 65.7, 117.4, 126.5, 127.4, 134.8, 142.9, 143.8, 176.8; EI-LR-MS: $m/z = 247$ (M^+), 232, 148, 106; EI-HR-MS: $m/z = 247.1394$, calcd. for $C_{14}H_{21}ONSi$ (M^+): 247.1392.

10f: yield: 9.2 mg (23 %); IR (neat): $\nu = 1695$ (s), 1621 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.19$ (s, 9H), 1.54 (ddd, $J = 10.1$, 10.2, 12.0 Hz, 1H), 2.51 (ddd, $J = 6.4$, 7.9, 12.0 Hz, 1H), 3.22 (m, 1H), 3.53 (dd, $J = 1.6$, 15.0 Hz, 1H), 4.15 (m, 1H), 4.60 (d, $J = 15.0$ Hz, 1H), 5.05 (br, 1H), 5.09 (br, 1H), 5.18 (ddd, $J = 1.2$, 1.5, 17.1 Hz, 1H), 5.21 (ddd, $J =$ 1.3, 1.5, 10.4 Hz, 1H), 5.94 (ddd, $J = 6.6$, 10.4, 17.1 Hz, 1H), 6.02 (br, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = -0.7$, 33.0, 43.7, 46.7, 53.8, 114.1, 117.5, 135.0, 137.2, 138.2, 138.8, 171.1; EI-LR-MS: $m/z = 247$ (M^+), 232, 219, 174, 73; EI-HR-MS: $m/z = 247.1366$, calcd. for $C_{14}H_{21}ONSi$ (M^+): 247.1392.

2-[3-(Triisopropylsilyl)-prop-2-ynyl]-2-azabicyclo-[2.2.1]hept-5-en-3-one (8g)

To a solution of **8a** (563.8 mg, 3.83 mmol) in THF (38 mL) was added BuLi (2.8 mL, 4.41 mmol, 1.56 M hexane solution) at −78 °C, and stirred for 1 h. To the resultant solution was added TIPSOTf (2.1 mL, 7.66 mmol), and stirred for 0.5 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:1) to afford **8g**; yield: 185.0 mg (16 %). IR (neat): $\nu = 2175$ (w), 1714 (s), 1561 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.01$–1.07 (m, 21H), 2.13 (ddd, $J = 1.5$, 1.6, 7.7 Hz, 1H), 2.30 (ddd, $J = 1.5$, 1.8, 7.7 Hz, 1H), 3.35 (m, 1H), 3.83 (d, $J = 17.8$ Hz, 1H), 4.03 (d, $J = 17.8$ Hz, 1H), 4.34 (m, 1H), 6.56 (ddd, $J = 1.5$, 3.3, 5.3 Hz, 1H), 6.92 (ddd, $J = 0.5$, 2.0, 5.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 11.0$ (CH), 18.4 (CH_3), 34.1 (CH_2), 53.5 (CH), 57.8 (CH_2), 62.7 (CH), 85.7 (C), 100.8 (C), 136.4 (CH), 139.6 (CH), 179.1 (C); EI-LR-MS: $m/z = 303$ (M^+), 260, 237, 194, 166, 138, 100; EI-HR-MS: $m/z = 303.2035$, calcd. for $C_{18}H_{29}ONSi$ (M^+): 303.2018.

6-[1-(Triisopropylsilyl)-vinyl]-2-vinyl-1,2,5,7a-tetrahydropyrrolizin-3-one (9g), 1-[3-(Triisopropylsilyl)-prop-2-ynyl]-3,5-divinylpyrrolidin-2-one (12g) and 2-Ethylidene-6-[1-(triisopropylsilyl)-vinyl]-1,2,5,7a-tetrahydropyrrolizin-3-one (9g′)

According to the typical procedure for the metathesis reaction of **8**, a solution of **8g** (26.9 mg, 0.09 mmol) and **1b** (7.5 mg, 8.86 μmol) in toluene (4.4 mL) was stirred at 80 °C for 0.5 h to afford the mixture of **9g** and **9g′** (yield: 9.0 mg, 31 %, 1:1) and **12g**. After the ratio of **9g** and **9g′** had been determined by ^1H NMR, the CH_2Cl_2 solution of **9g** and **9g′** was stirred with silica gel at room temperature for 3 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford **9g′** as a sole product.

12g: yield: 10.7 mg (36 %); IR (neat): $\nu = 2176$ (w), 1704 (s), 1644 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.98$–1.12 (m, 21H), 1.68 (ddd, $J = 8.2$, 9.9, 12.9 Hz, 1H), 2.48 (ddd, $J = 6.9$, 8.7, 12.9 Hz, 1H), 3.10 (dddt, $J = 6.6$, 6.9, 8.2, 1.5 Hz, 1H), 3.60 (d, $J = 17.5$ Hz, 1H), 4.17 (ddd, $J = 8.7$, 8.7, 9.9 Hz, 1H), 4.61 (d, $J = 17.5$ Hz, 1H), 5.20 (ddd, $J = 1.3$, 1.5, 17.8 Hz, 1H), 5.21 (ddd, $J = 1.3$, 1.5, 9.9 Hz, 1H), 5.29 (dd, $J = 1.3$, 9.9 Hz, 1H), 5.39 (dd, $J = 1.3$, 17.0 Hz, 1H), 5.63 (ddd, $J = 8.7$, 9.9, 17.0 Hz, 1H), 5.93 (ddd, $J = 6.6$, 9.9, 17.8 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 11.1$ (CH), 18.5 (CH_3), 31.3 (CH_2), 31.9 (CH_2), 45.8 (CH), 58.8 (CH), 84.8 (C), 101.1 (C), 117.3 (CH_2), 119.7 (CH_2), 135.2 (CH), 137.2 (CH), 174.0 (C); EI-LR-MS: $m/z = 331$ (M^+), 288, 260, 138, 109; EI-HR-MS: $m/z = 331.2320$, calcd. for $C_{20}H_{33}ONSi$ (M^+): 331.2332.

9g′: IR (neat): $\nu = 1699$ (s), 1674 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.80$–1.05 (m, 21H), 1.77 (ddd, $J =$ 1.3, 2.3, 7.1 Hz, 3H), 2.46 (m, 1H), 3.03 (m, 1H), 3.96 (m, 1H), 4.59–4.73 (m, 2H), 5.58 (d, $J = 2.1$ Hz, 1H), 5.78 (m, 1H), 5.89 (d, $J = 2.1$ Hz, 1H), 6.52 (m, 1H); EI-LR-MS: $m/z = 331$ (M^+), 288, 274, 244, 218, 202, 149, 109; EI-HR-MS: $m/z = 331.2321$, calcd. for $C_{20}H_{33}ONSi$ (M^+): 331.2332.

3-Ethylidene-1-[3-(triisopropylsilyl)-prop-2-ynyl]-5-vinyl-pyrrolidin-2-one (12g′)

According to the typical procedure for the metathesis reaction of **8**, a solution of **12g** (8.6 mg, 0.03 mmol) and **1b** (4.4 mg, 5.18 μmol,) in toluene (2.0 mL) was stirred at 80 °C for 4.5 h to afford the mixture of **9g** and **9g′** (yield: 3.2 mg,

37%, 1:1) and the mixture of **12g** and **12g′** (yield: 4.2 mg, 49%, 9:1).

12g′: IR (neat): ν = 2176 (w), 1701 (s), 1679 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 0.95–1.13 (m, 21H), 1.71 (ddd, J = 1.8, 1.8, 7.1 Hz, 3H), 2.32 (m, 1H), 2.87 (m, 1H), 3.60 (d, J = 17.5 Hz, 1H), 4.22 (ddd, J = 4.3, 8.4, 8.7 Hz, 1H), 4.66 (d, J = 17.5 Hz, 1H), 5.19 (dd, J = 1.3, 9.7 Hz, 1H), 5.28 (dd, J = 1.3, 17.0 Hz, 1H), 5.54 (ddd, J = 8.7, 9.7, 17.0 Hz, 1H), 6.48 (m, 1H); EI-LR-MS: m/z = 331 (M^+), 288, 274, 250, 202, 149, 123, 109; EI-HR-MS: m/z = 331.2320, calcd. for $C_{20}H_{33}ONSi$ (M^+): 331.2332.

3-Ethylidene-1-prop-2-ynyl-5-vinylpyrrolidin-2-one (12a′)

To a solution of **12g** (16.5 mg, 0.05 mmol) in THF (0.5 mL) was added TBAF (0.15 mL, 0.15 mmol, 1 M THF solution) at 0 °C, and stirred for 0.5 h. NH_4Cl was added and the volatiles were concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to afford **12a′**; yield: 8.7 mg (99%). IR (neat): ν = 2117 (w), 1696 (s), 1676 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.78 (ddd, J = 1.8, 1.8, 7.1 Hz, 3H), 2.18 (t, J = 2.5 Hz, 1H), 2.40 (m, 1H), 2.95 (m, 1H), 3.61 (dd, J = 2.5, 17.3 Hz, 1H), 4.25 (ddd, J = 4.5, 4.5, 8.6 Hz, 1H), 4.64 (dd, J = 2.5, 17.3 Hz, 1H), 5.28 (dd, J = 1.0, 9.9 Hz, 1H), 5.36 (dd, J = 1.0, 17.0 Hz, 1H), 5.62 (ddd, J = 8.6, 9.9, 17.0 Hz, 1H), 6.57 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 14.6 (CH_3), 29.2 (CH_2), 30.0 (CH_2), 57.6 (CH), 71.7 (CH), 77.8 (C), 119.1 (CH_2), 128.9 (CH), 130.8 (C), 137.1 (CH), 167.7 (C); EI-LR-MS: m/z = 175 (M^+), 88, 73, 70; EI-HR-MS: m/z = 175.0967, calcd. for $C_{11}H_{13}ON$ (M^+): 175.0997.

2-Ethylidene-6-methylene-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10a′)

According to the typical procedure for the metathesis reaction of **8**, a solution of **12g′** (8.7 mg, 0.05 mmol) and **1b** (4.2 mg, 4.96 μmol,) in toluene (2.5 mL) was stirred at 80 °C for 0.5 h to afford **7** (yield: 5.2 mg, 60%) and **10a′**.

10a′: 1.8 mg (21%); IR (neat): ν = 1694 (s), 1668 (s), 1599 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.78 (ddd, J = 1.5, 1.8, 6.9 Hz, 3H), 2.31 (m, 1H), 2.98 (m, 1H), 3.68 (d, J = 15.4 Hz, 1H), 4.29 (m, 1H), 4.85 (d, J = 15.4 Hz, 1H), 4.98 (s, 1H), 5.00 (s, 1H), 5.79 (d, J = 9.9 Hz, 1H), 6.23 (dd, J = 1.9, 9.9 Hz, 1H), 6.52 (m, 1H); EI-LR-MS: m/z = 175 (M^+), 160, 146, 131, 117; EI-HR-MS: m/z = 175.0995, calcd. for $C_{11}H_{13}ON$ (M^+): 175.0997.

3-Ethylidene-1-(3-phenylprop-2-ynyl)-5-vinylpyrrolidin-2-one (12c′)

To the solution of **12a′** (25.5 mg, 0.15 mmol), CuI (1.4 mg, 7.28 μmol), $Pd(PPh_3)_4$ (8.4 mg, 7.28 μmol) and Et_3N (2 mL) in benzene (1 mL) was added PhI (0.02 mL, 0.15 mmol) at rt, and stirred for 16 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **12c′**; yield: 34.3 mg (94%). IR (neat): ν = 2235 (w), 1697 (s), 1677 (s), 757 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.78 (ddd, J = 1.6, 1.7, 7.1 Hz, 3H), 2.41 (m, 1H), 2.96 (m, 1H), 3.85 (d, J = 17.5 Hz, 1H), 4.32 (ddd, J = 4.5, 8.2, 8.9 Hz, 1H), 4.86 (d, J = 17.5 Hz, 1H), 5.30 (dd, J = 0.8, 9.8 Hz, 1H), 5.39 (dd, J = 0.8, 17.0 Hz, 1H), 5.67 (ddd, J = 8.9, 9.8, 17.0 Hz, 1H), 6.58 (m, 1H), 7.27–7.44 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 14.6 (CH_3), 29.3 (CH_2), 30.9 (CH_2), 57.7 (CH), 83.3 (C), 83.6 (C), 118.9 (CH_2), 122.7 (C), 128.2 (CH), 128.3 (CH), 128.8 (CH), 131.0 (C), 131.7 (CH), 137.3 (CH), 167.7 (C); EI-LR-MS: m/z = 251 (M^+), 236, 146, 115, 105; EI-HR-MS: m/z = 251.1323, calcd. for $C_{17}H_{17}ON$ (M^+): 251.1310.

2-Ethylidene-6-(1-phenylvinyl)-1,2,5,7a-tetrahydropyrrolizin-3-one (9c′) and 2-Ethylidene-6-methylene-7-phenyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (10c′)

According to the typical procedure for the metathesis reaction of **8**, a solution of **12c′** (13.9 mg, 0.06 mmol) and **1b** (4.7 mg, 5.53 μmol,) in toluene (2.8 mL) was stirred at 80 °C for 0.5 h to afford **9c′** and **10c′**.

9c′: yield: 8.5 mg (61%); IR (neat): ν = 1736 (m), 1698 (s), 1669 (s), 758 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.76 (ddd, J = 1.3, 2.3, 7.1 Hz, 3H), 2.48 (m, 1H), 3.00 (m, 1H), 4.05 (m, 1H), 4.69–4.80 (m, 2H), 5.23 (br, 2H), 5.71 (br, 1H), 6.55 (ddq, J = 2.3, 3.3, 7.1 Hz, 1H), 7.25–7.40 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 14.9, 30.3, 51.3, 64.6, 116.5, 127.7, 128.2, 128.3, 129.1, 129.3, 133.9, 140.5, 142.8, 143.4, 172.1; EI-LR-MS: m/z = 251 (M^+), 148, 83; EI-HR-MS: m/z = 251.1299, calcd. for $C_{17}H_{17}ON$ (M^+): 251.1310.

10c′: yield: 4.6 mg (33%); IR (neat): ν = 1694 (s), 1673 (s), 755 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.79 (ddd, J = 1.6, 1.9, 7.1 Hz, 3H), 2.42 (m, 1H), 3.04 (m, 1H), 3.82 (ddd, J = 1.8, 2.0, 15.2 Hz, 1H), 4.47 (m, 1H), 4.93 (d, J = 15.2 Hz, 1H), 4.93 (m, 1H), 5.16 (br, 1H), 5.74 (br, 1H), 6.56 (m, 1H), 7.21–7.36 (m, 5H); EI-LR-MS: m/z = 251 (M^+), 236, 222, 174; EI-HR-MS: m/z = 251.1336, calcd. for $C_{17}H_{17}ON$ (M^+): 251.1310.

2-[4-(Triisopropylsilyl)-but-3-ynyl]-2-azabicyclo-[2.2.1]hept-5-en-3-one (14)

To a solution of **4** (3.07 g, 28.13 mmol) in CH_3CN (150 mL) was added K_2CO_3 (4.67 g, 33.76 mmol), KOH (4.74 g, 84.39 mmol) and $BnNEt_3Br$ (100 mg, 0.37 mmol) at room temperature, and stirred for 5 min. To this solution was added 2-(2-bromoethyl)-1,3-dioxolane (4.0 mL, 33.76 mmol), and stirred at reflux for 1 h. The reaction mixture was filtered, and undissolved material was washed with Et_2O. The filtrate was evapolated, and the residue was purified by column chromatography on silica gel (AcOEt) to afford *2-(2-[1,3]doxolan-2-yl-ethyl)-2-aza-bicyclo[2.2.1]hept-5-en-3-one*; yield: 5.44 g (92%). IR (neat): ν = 1699 (s), 1559 (w), 1140 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 1.76–1.85 (m, 2H), 2.13 (ddd, J = 1.5, 1.5, 7.6 Hz, 1H), 2.31 (ddd, J = 1.6, 1.6, 7.6 Hz, 1H), 3.01 (ddd, J = 6.8, 7.9, 14.3 Hz, 1H), 3.31–3.43 (m, 2H), 3.82–4.00 (m, 4H), 4.21 (m, 1H), 4.86 (t, J = 4.7 Hz, 1H), 6.64 (ddd, J = 1.5, 3.3, 5.3 Hz, 1H), 6.84 (ddd, J = 0.7, 2.0, 5.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 31.6 (CH_2), 38.6 (CH_2), 53.3 (CH), 58.2 (CH_2), 62.9 (CH), 64.3 (CH_2), 64.4 (CH_2), 102.0 (CH), 137.4 (CH), 139.2 (CH), 179.8 (C); EI-LR-MS: m/z = 209 (M^+), 142, 66; EI-HR-MS: m/z = 209.1078, calcd. for $C_{11}H_{15}O_3N$ (M^+): 209.1052.

To a solution of 2-(2-[1,3]doxolan-2-yl-ethyl)-2-azabicyclo[2.2.1]hept-5-en-3-one (290.6 mg, 1.39 mmol) in acetone (28 mL) was added H_2O (4 mL) and $TsOH \cdot H_2O$

(132.1 mg, 0.70 mmol) at room temperature, and stirred at reflux for 26 h. After cooling to room temperature, saturated $NaHCO_3$ solution was added, and the aqueous solution was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was used next reaction without further purification.

To a solution of the crude product in CH_2Cl_2 (7 mL) was added CBr_4 (690.9 mg, 2.08 mmol) and PPh_3 (1.09 g, 4.17 mmol) at 0 °C, and stirred for 1 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (AcOEt) to afford *2-(4,4-dbromo-but-3-enyl)-2-aza-bicyclo[2.2.1]hept-5-en-3-one*; yield: 135.7 mg (30%, 2 steps). IR (neat): $\nu = 1698$ (s), 1560 (w) cm^{-1}, ^1H NMR (270 MHz, $CDCl_3$): $\delta = 2.14$–2.35 (m, 4H), 2.96 (dt, $J = 13.8$, 6.8 Hz, 1H), 3.33 (dt, $J = 13.8$, 6.6 Hz, 1H), 3.35 (m, 1H), 4.20 (m, 1H), 6.35 (t, $J = 7.1$ Hz, 1H), 6.66 (ddd, $J = 1.5$, 3.3, 5.3 Hz, 1H), 6.85 (ddd, $J = 0.7$, 2.0, 5.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 31.6$ (CH_2), 41.4 (CH_2), 53.5 (CH), 58.7 (CH_2), 63.1 (CH), 90.4 (C), 135.1 (CH), 138.0 (CH), 139.3 (CH), 180.3 (C); EI-LR-MS: $m/z = 323$ (M^+), 321, 199, 122, 94, 88; EI-HR-MS: $m/z = 322.9181$, calcd. for $C_{10}H_{11}ON^{81}Br_2$ (M^+): 322.9167.

To a solution of 2-(4,4-dibromo-but-3-enyl)-2-aza-bicyclo-[2.2.1]hept-5-en-3-one (128.8 mg, 0.40 mmol) in THF (4 mL) was added BuLi (0.56 mL, 0.88 mmol, 1.58 M in hexane solution) at −78 °C, and stirred for 1 h. To this solution was added TIPSOTf (0.17 mL, 0.64 mmol), and stirred at 0 °C for 1 h and at room tempertaure for 0.5 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to afford **14**; yield: 21.2 mg (17%). IR (neat): $\nu = 2173$ (m), 1714 (s), 1560 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.98$–1.16 (m, 21H), 2.14 (d, $J = 7.6$ Hz, 1H), 2.28–2.49 (m, 3H), 3.08 (dt, $J = 13.7$, 6.9 Hz, 1H), 3.33 (m, 1H), 3.39 (dt, $J = 13.7$, 6.8 Hz, 1H), 4.40 (m, 1H), 6.64 (ddd, $J = 1.5$, 3.3, 5.1 Hz, 1H), 6.87 (dd, $J = 2.1$, 5.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 11.2$ (CH), 18.5 (CH_3), 19.8 (CH_2), 43.0 (CH_2), 53.7 (CH), 58.9 (CH_2), 63.9 (CH), 82.2 (C), 105.8 (C), 138.2 (CH), 139.8 (CH), 180.5 (C); EI-LR-MS: $m/z = 317$ (M^+), 274, 208, 180, 166, 138, 100, 86, 66; EI-HR-MS: $m/z = 317.2171$, calcd. for $C_{19}H_{31}ONSi$ (M^+): 317.2175.

1-[4-(Triisopropylsilyl)-but-3-ynyl]-3,5-divinyl-pyrrolidin-2-one (15)

According to the typical procedure for the metathesis reaction of **8**, a solution of **14** (30.5 mg, 0.10 mmol) and **1b** (16.3 mg, 19.21 μmol,) in toluene (4.8 mL) was stirred at 80 °C for 1 h to afford **15**; yield: 13.5 mg (41%). IR (neat): $\nu = 2173$ (m), 1695 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.98$–1.10 (m, 21H), 1.67 (ddd, $J = 7.9$, 9.7, 13.0 Hz, 1H), 2.36–2.65 (m, 3H), 3.05–3.19 (m, 2H), 3.68 (ddd, $J = 6.4$, 6.6, 7.1 Hz, 1H), 4.17 (dt, $J = 8.1$, 7.7 Hz, 1H), 5.19 (ddd, $J = 1.3$, 1.5, 17.1 Hz, 1H), 5.20 (ddd, $J = 1.3$, 1.5, 10.7 Hz, 1H), 5.27 (dd, $J = 1.3$, 9.9 Hz, 1H), 5.34 (dd, $J = 1.3$, 17.0 Hz, 1H), 5.65 (ddd, $J = 8.7$, 9.9, 17.0 Hz, 1H), 5.94 (ddd, $J = 6.6$, 10.7, 17.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 11.2$ (CH), 18.6 (CH_2), 18.6 (CH_3), 32.4 (CH_2), 39.8 (CH_2), 45.6 (CH), 60.3 (CH), 81.9 (C), 105.5 (C), 117.1 (CH_2), 119.1 (CH_2), 135.5 (CH), 138.3 (CH), 174.5 (C); EI-LR-MS: $m/z = 345$ (M^+), 302, 150, 109; EI-HR-MS: $m/z = 345.2497$, calcd. for $C_{21}H_{35}ONSi$ (M^+): 345.2488.

1-But-3-ynyl-3-ethylidene-5-vinylpyrrolidin-2-one (16)

To a solution of **15** (11.5 mg, 0.03 mmol) in THF (0.5 mL) was added TBAF (0.17 mL, 0.17 mmol, 1 M THF solution) at 0 °C, and stirred for 12 h. NH_4Cl was added and the volatiles were concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:2) to afford **16**; yield: 6.0 mg (95%). IR (neat): $\nu = 2120$ (w), 1694 (s), 1673 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.76$ (ddd, $J = 1.8$, 1.8, 7.1 Hz, 3H), 1.97 (t, $J = 2.6$ Hz, 1H), 2.33–2.57 (m, 3H), 2.93 (m, 1H), 3.19 (ddd, $J = 6.7$, 7.1, 13.7 Hz, 1H), 3.77 (ddd, $J = 6.1$, 7.6, 13.7 Hz, 1H), 4.22 (ddd, $J = 4.1$, 8.4, 8.4 Hz, 1H), 5.25 (dd, $J = 1.2$, 9.8 Hz, 1H), 5.30 (dd, $J = 1.2$, 17.0 Hz, 1H), 5.63 (ddd, $J = 8.9$, 9.8, 17.0 Hz, 1H), 6.55 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 14.6$ (CH_3), 17.5 (CH_2), 29.6 (CH_2), 39.6 (CH_2), 59.2 (CH), 69.7 (CH), 81.7 (C), 118.5 (CH_2), 128.1 (CH), 131.1 (C), 138.1 (CH), 168.4 (C); EI-LR-MS: $m/z = 189$ (M^+), 150, 88; EI-HR-MS: $m/z = 189.1138$, calcd. for $C_{12}H_{15}ON$ (M^+): 189.1154.

2-Ethylidene-7-vinyl-1,5,6,8a-tetrahydro-2*H*-indolizin-3-one (17)

According to the typical procedure for the metathesis reaction of **8**, a solution of **16** (9.2 mg, 0.05 mmol) and **1b** (4.1 mg, 4.86 μmol,) in toluene (2.4 mL) was stirred at 80 °C for 0.5 h to afford **17**; yield: 6.8 mg (74%). IR (KBr): $\nu = 1687$ (s), 1664 (s), 1638 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.76$ (ddd, $J = 1.6$, 2.0, 7.1 Hz, 3H), 2.24–2.35 (m, 3H), 2.89–3.03 (m, 2H), 4.28 (m, 1H), 4.41 (dd, $J = 2.6$, 5.2, 13.1 Hz, 1H), 5.06 (d, $J = 10.7$ Hz, 1H), 5.18 (d, $J = 17.6$ Hz, 1H), 5.71 (br, 1H), 6.34 (dd, $J = 10.7$, 17.6 Hz, 1H), 6.51 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 14.6$, 23.4, 29.3, 36.5, 52.4, 113.0, 127.6, 128.8, 132.2, 134.7, 138.1, 166.9; EI-LR-MS: $m/z = 189$ (M^+), 174, 162, 146, 132, 117, 106, 91; EI-HR-MS: $m/z = 189.1169$, calcd. for $C_{12}H_{15}ON$ (M^+): 189.1154.

2-Prop-2-ynyl-2-azabicyclo[2.2.2]oct-5-en-3-one (19a)

To a suspension of NaH (75 mg, 1.87 mmol) in DMF (5 mL) was added 2-azabicyclo[2.2.2]oct-5-en-3-one (192.4 mg, 1.56 mmol), which was prepared by a literature procedure,[12] in DMF (5 mL) at 0 °C, and stirred at room temperature for 1 h. To this suspension was added propargyl bromide (0.18 mL, 2.34 mmol) at 0 °C, and stirred at room temperature for 2 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:3) to afford **19a**; yield: 250 mg (99%). IR (neat): $\nu = 2117$ (w), 1670 (s), 1614 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.41$–1.55 (m, 2H), 1.84 (m, 1H), 2.02 (m, 1H), 2.22 (t, $J = 2.6$ Hz, 1H), 3.48 (m, 1H), 4.03 (dd, $J = 2.6$, 7.6 Hz, 1H), 4.17 (dd, $J = 2.6$, 7.6 Hz, 1H), 4.43 (m, 1H), 6.36 (ddd, $J = 1.8$, 6.1, 7.6 Hz, 1H), 6.46 (ddd, $J = 1.5$, 5.4, 7.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 21.0$, 25.9, 32.6, 43.8, 53.2, 71.7, 77.8,

131.3, 132.3, 172.5; EI-LR-MS: $m/z = 161$ (M^+), 133, 104, 88, 80; EI-HR-MS: $m/z = 161.0825$, calcd. for $C_{10}H_{11}ON$ (M^+): 161.0841.

7-Methylene-3-vinyl-1,2,3,6,7,9a-hexahydroquinolizin-4-one (20a) and 5-(3-Oxo-2-azabicyclo[2.2.2]oct-5-en-2-ylmethyl)-2-phenyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione (23a)

According to the typical procedure for the metathesis reaction of **8**, a solution of **19a** (37.2 mg, 0.23 mmol) and **1b** (19.6 mg, 23.08 μmol,) in toluene (12 mL) was stirred at 80 °C for 0.5 h to afford **20a** and **21a** as an inseparable mixture by column chromatography on silica gel. The yields of **20a** (11.7 mg, 27 %) and **21a** (18.4 mg, 42 %) were determined by ^{1}H NMR using (*E*)-stilbene as an internal standard.

The mixture of **20a** (27.5 mg) and **21a** (47.3 mg, 0.25 mmol) with *N*-phenylmaleimide (43.3 mg, 0.25 mmol, 1.0 equiv. for **21a**) in toluene (1.2 mL) was stirred at 60 °C for 18 h. The volatiles were removed in reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 1:2) to afford **23a** as a diastereomeric mixture (ratio of diastereomers was 2:3), and recovered **20a**.

20a: IR (neat): $\nu = 1716$ (m), 1643 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.60$–2.00 (m, 4H), 3.22 (m, 1H), 3.34 (d, $J = 14.9$ Hz, 1H), 4.09 (m, 1H), 4.93 (s, 1H), 5.00 (s, 1H), 5.12 (d, $J = 16.8$ Hz, 1H), 5.15 (d, $J = 10.6$ Hz, 1H), 5.30 (d, $J = 14.9$ Hz, 1H), 5.62 (d, $J = 9.9$ Hz, 1H), 5.90 (ddd, $J = 6.1$, 10.6, 16.8 Hz, 1H), 6.25 (dd, $J = 2.5$, 9.9 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 24.5$, 25.9, 44.1, 45.1, 55.0, 112.5, 116.4, 127.7, 130.4, 136.8, 138.0, 169.6; EI-LR-MS: $m/z = 189$ (M^+), 160, 136, 121, 107, 81; EI-HR-MS: $m/z = 189.1124$, calcd. for $C_{12}H_{15}ON$ (M^+): 189.1154.

23a: yield: 90.3 mg (99 %); IR (neat): $\nu = 1710$ (s), 1667 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.38$–1.49 (m, 2H), 1.77–1.88 (m, 2H), 2.21–2.42 (m, 2H), 2.47 (m, 0.6H), 2.53 (m, 0.4H), 2.64 (m, 0.6H), 2.70 (m, 0.4H), 3.18–3.30 (m, 2H), 3.43–3.52 (m, 1.6H), 3.66 (d, $J = 15.8$ Hz, 0.6H), 3.93–4.28 (m, 1.8H), 5.65 (m, 0.4H), 5.73 (m, 0.6H), 6.24–6.40 (m, 2H), 7.20–7.50 (m, 5H); EI-LR-MS: $m/z = 362$ (M^+), 334, 283, 255, 240, 200, 160, 142, 80; EI-HR-MS: $m/z = 362.1619$, calcd. for $C_{22}H_{22}O_3N_2$ (M^+): 362.1630.

2-[3-(Trimethylsilyl)-prop-2-ynyl]-2-azabicyclo-[2.2.2]oct-5-en-3-one (19b)

To a solution of **19a** (307.1 mg, 1.91 mmol) in THF (19 mL) was added BuLi (1.46 mL, 2.29 mmol, 1.57 M hexane solution) at −78 °C, and stirred for 1 h. To the resultant solution was added TMSCl (0.48 mL, 3.81 mmol), and stirred for 1 h. Saturated NH_4Cl solution was added, and the mixture was extracted with AcOEt. The organic phase was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 1:1) to afford **19b**; yield: 258.9 mg (58 %). IR (neat): $\nu = 2178$ (w), 1682 (s), 1614 (m) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.16$ (s, 9H), 1.40–1.53 (m, 2H), 1.85 (m, 1H), 2.00 (m, 1H), 3.47 (m, 1H), 3.98 (d, $J =$ 17.6 Hz, 1H), 4.21 (d, $J = 17.6$ Hz, 1H), 4.44 (m, 1H), 6.35 (ddd, $J = 1.9$, 6.1, 7.4 Hz, 1H), 6.44 (ddd, $J = 1.8$, 5.5, 7.4 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = -0.6$, 21.0, 25.9, 33.6, 43.9, 53.0, 88.3, 99.8, 131.5, 132.4, 172.6; EI-LR-MS: $m/z = 233$ (M^+), 205, 190, 106; EI-HR-MS: $m/z = 233.1249$, calcd. for $C_{13}H_{19}ONSi$ (M^+): 233.1236.

2-[2-Methylene-3-(trimethylsilyl)-but-3-enyl]-2-azabicyclo[2.2.2]oct-5-en-3-one (21b)

According to the typical procedure for the metathesis reaction of **8**, a solution of **19b** (38.4 mg, 0.16 mmol) and **1b** (14.0 mg, 16.45 μmol,) in toluene (8.2 mL) was stirred at 80 °C for 0.5 h to afford **21b**; yield: 33.4 mg (78 %). IR (neat): $\nu = 1673$ (s), 1616 (m) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.16$ (s, 9H), 1.39–1.45 (m, 2H), 1.75–1.83 (m, 2H), 3.45 (m, 1H), 3.86 (d, $J = 15.7$ Hz, 1H), 4.11 (m, 1H), 4.17 (d, $J = 15.7$ Hz, 1H), 4.96 (s, 1H), 5.05 (s, 1H), 5.44 (d, $J = 2.1$ Hz, 1H), 5.77 (d, $J = 2.1$ Hz, 1H), 6.30–6.40 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = -0.7$, 21.5, 26.0, 44.3, 47.6, 53.1, 115.1, 126.9, 132.1, 132.8, 145.6, 149.3, 173.3; EI-LR-MS: $m/z = 261$ (M^+), 246, 233, 218, 188, 160, 80; EI-HR-MS: $m/z = 261.1523$, calcd for $C_{15}H_{23}ONSi$ (M^+): 261.1549.

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