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ROM-RCM of cycloalkene-yne

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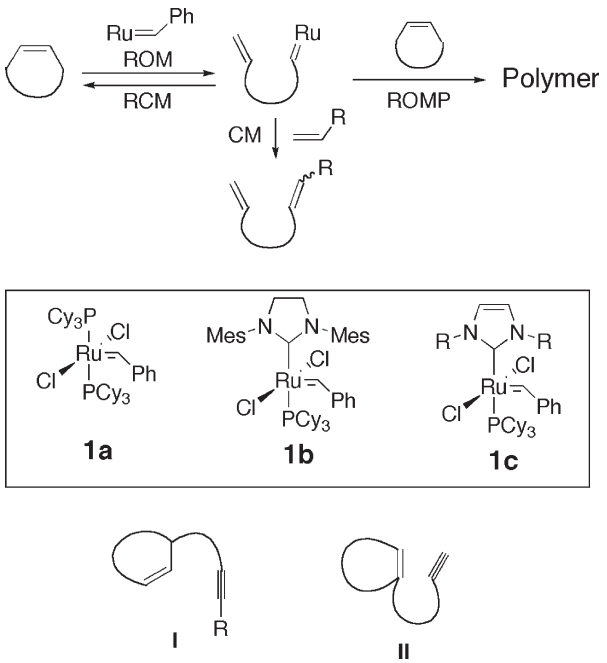
We dedicate this paper to Professor Grubbs on the occasion of his receipt of the Tetrahedron Prize

Abstract—Ring-opening metathesis and ring-closing metathesis (ROM-RCM) of cycloalkene-yne was demonstrated using a first- or second-generation ruthenium complex. When cycloalkenes bearing the alkyne part at the C-3 position were reacted with a first-generation ruthenium–carbene complex under an atmosphere of ethylene, ROM-RCM proceeded smoothly to give skeletal reorganized products in good yields. In this reaction, cycloalkene-ynes having terminal alkyne were suitable. On the other hand, when cycloalkenes bearing the alkyne part at the C-1 position were treated with a second-generation ruthenium–carbene complex, ROM-RCM proceeded smoothly to give bicyclic compounds and/or dimeric compounds in good yields.

1. Introduction

Transition metals have played an important role in recent synthetic organic chemistry, and they are now important tools for the syntheses of complex molecules, such as natural products and biologically active substances. Olefin metathesis reaction[1] using a metal carbene complex is interesting because formally the carbon–carbon double bonds are cleaved and, at the same time, new carbon–carbon double bonds are formed between the two double bonds. Intramolecular olefin metathesis is a useful methodology in synthetic organic chemistry, since carbocyclic and heterocyclic compounds having various ring sizes can be synthesized. In 1999, second-generation ruthenium–carbene complexes[2], such as **1b** and **1c**, were developed by Herrmann, Nolan and Grubbs, independently, and metathesis of olefin having substituents could be further developed. On the other hand, intramolecular enyne metathesis[3–5] is particularly attractive since the double bond of enyne is cleaved and the alkylidene part of alkene migrates to the alkyne carbon to give a cyclized compound having a diene moiety. We have already reported intramolecular enyne metathesis[3] using Grubbs' ruthenium carbene complex **1** and the syntheses of five- to nine-membered ring compounds.

The metathesis reaction of cycloalkene did not proceed under the usual reaction conditions, and cyclooctene or norbonene afforded a polymer via ring opening polymerization (ROMP). Recently, ring-opening metathesis of cycloalkene followed by cross-metathesis (ROM-CM[6]) with olefin has been developed.



Scheme 1. Metathesis reaction of alkene.

Keywords: Enyne metathesis; Ring-opening metathesis and ring-closing metathesis; ROM-RCM; Cycloalkene-yne; Pyrrole derivative; Ethylene.
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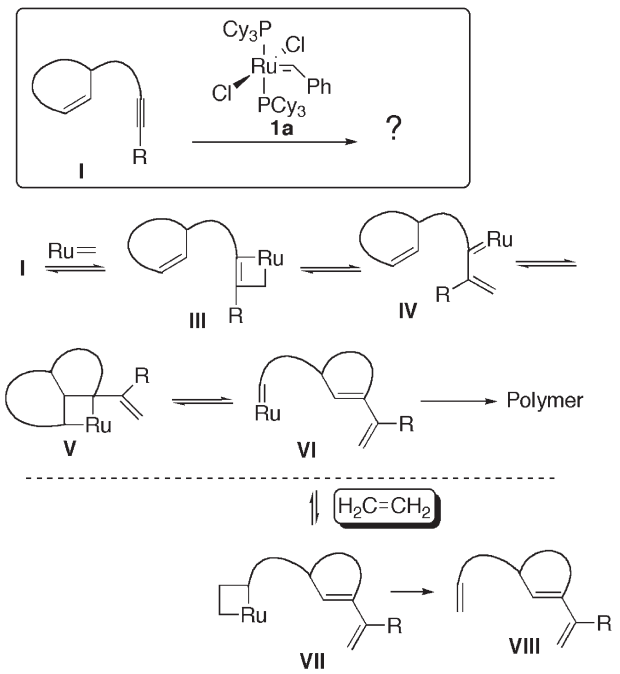
Ring-opening metathesis and ring-closing metathesis[7] (ROM-RCM) of cycloalkene-yne is also very attractive, but there have been few reports on ROM-RCM in the literature.[8] Herein, we describe in detail of ROM-RCM of cycloalkene-ynes **I** and **II** using ruthenium–carbene complex **1** (Scheme 1).[3a,b]

2. Results and discussion

2.1. Metathesis of cycloalkene having alkyne in a tether at the C-3 position

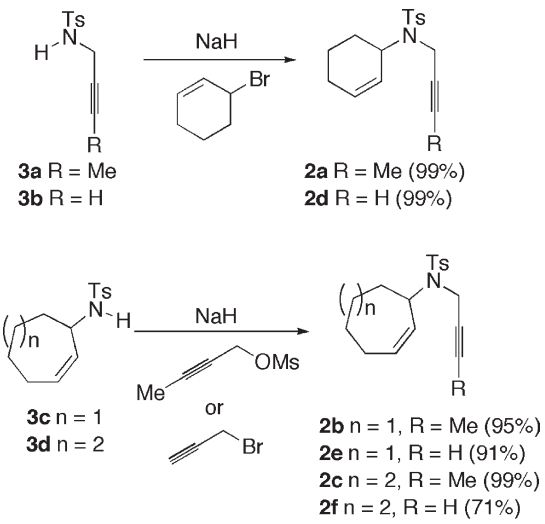
Metathesis of cycloalkene-yne, whose tether having an alkyne part is connected to the C-3 position of cycloalkene, was investigated. If the alkyne part of substrate **I** reacts with a ruthenium complex, ruthenacyclobutene **III** should be formed and it would be converted into ruthenium–carbene complex **IV** by ring-opening. Then, if this carbene complex **IV** reacts with a cycloalkene part intramolecularly, highly strained ruthenium complex **V** would be formed and it should be converted into **VI**. However, this ruthenium carbene complex **VI** cannot react with the diene moiety intramolecularly and would react with another molecule **I** to give a polymer (Scheme 2).



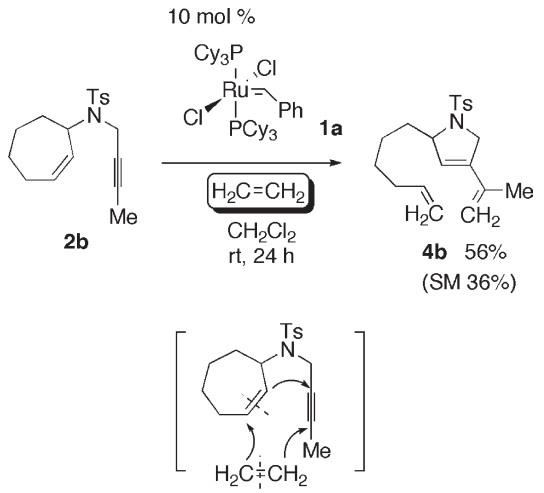
Scheme 2. Our plan for ROM-RCM of cycloalkene-yne **I**.

However, if this reaction were carried out under an atmosphere of ethylene,[3f,9] ruthenium complex **VI** would react with ethylene to give ring-opening metathesis product **VIII** via ruthenacyclobutane **VII**. The chain lengths of the tethers in the products **VIII** would be dependent on the ring-size of cycloalkene.

To examine our plan, various cycloalkene-ynes **2** were prepared as shown in Scheme 3. N-Alkylation of *N*-2-butynyl- or *N*-propargyl-*N*-tosylamide **3a** and **3b** with 3-bromocyclohexene gave cyclohexene-ynes **2a** and **2d** in quantitative yields. N-Alkylation of *N*-cycloheptenyl- or *N*-cyclooctenyl-*N*-tosylamides **3c**[10] and **3d**[7c] with but-2-ynyl methanesulfonate or propargyl bromide gave cycloalkene-ynes **2b**, **2e**, **2c** and **2f**, respectively, in good yields.



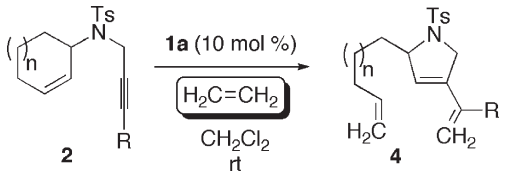
Scheme 3. Synthesis cycloalkene-yne **2**.



Scheme 4. ROM-RCM of cycloalkene-yne **2b**.

When a CH_2Cl_2 solution of cycloheptene-yne **2b** and 10 mol% of ruthenium complex **1a** was stirred at room temperature for 24 h under an atmosphere of ethylene, we were pleased to find that the desired ring-opening metathesis product **4b** was obtained in 56% yield (Scheme 4). This product **4b** should be obtained through the proposed reaction course. Thus, formally, in this reaction, the double bond of cycloalkene was cleaved, and one alkylidene carbon reacts with an alkyne carbon to form a five-membered ring, while the other alkylidene carbon and alkyne carbon react with methylene parts of ethylene. It is interesting that three new double bonds in **4b** were formed from two double bonds and one triple bond in **2b** in this process. As substrates, **2a** and **2c** were treated in a similar manner, and the desired ROM-RCM products **4a** and **4c** were obtained in 15 and 22% yields, respectively, and the starting materials **2a** and **2c** were recovered in 70 and 75% yields, respectively (Table 1, runs 1 and 3).

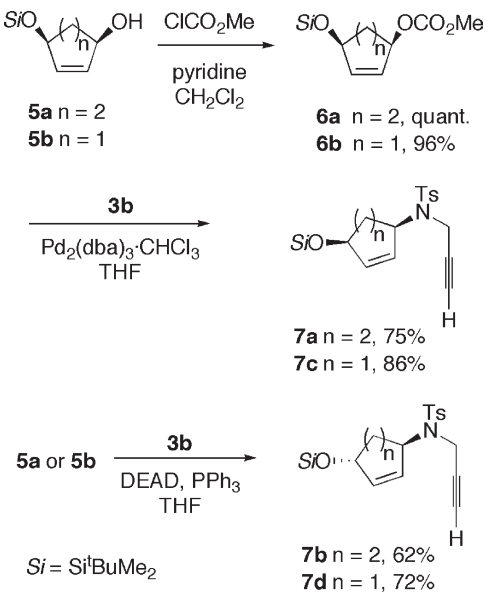
Table 1. ROM-RCM of cycloalkene-yne **2**



Run	R	*n*		Time (h)	Yield (%)
1	Me	1	**2a**	24	**4a**,15
2	Me	2	**2b**	24	**4b**,56
3	Me	3	**2c**	24	**4c**,22
4	H	1	**2d**	4	**4d**,78
5	H	2	**2e**	1	**4e**,70
6	H	3	**2f**	1	**4f**,75

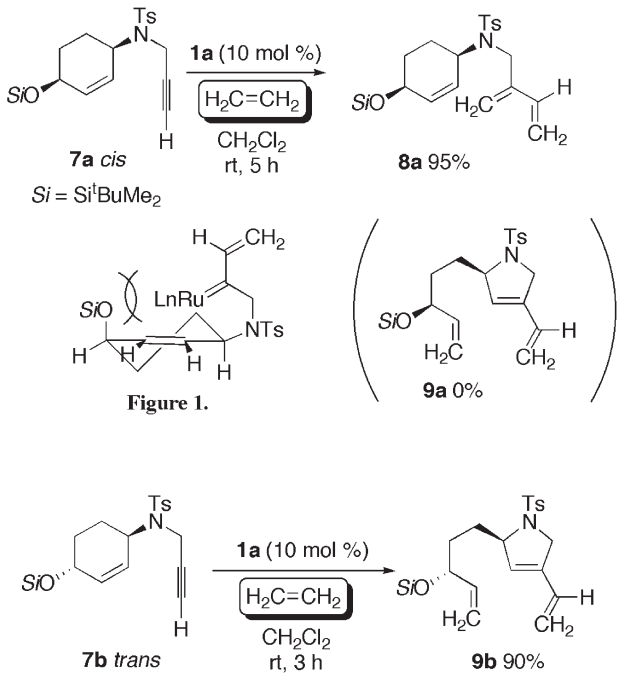
Since this reaction was carried out under ethylene gas, cycloalkene bearing terminal alkyne can be used.[3f] When a CH_2Cl_2 solution of cyclohexene-yne **2d** and 10 mol% of **1a** was stirred at room temperature under an atmosphere of ethylene, the reaction proceeded smoothly and the desired product **4d** was obtained in 78% yield (run 4). Under similar reaction conditions, metatheses of cycloalkene-ynes **2e** and **2f** were carried out and the desired products **4e** and **4f** were obtained in good yields (runs 5 and 6).

Next, the ROM-RCM reaction of cycloalkene-yne **7** having two substituents on the cycloalkene ring was investigated. These cycloalkene-ynes **7** were synthesized from cycloalkenes **5a** or **5b** as shown in Scheme 5. Cycloalkene-ynes **7a** and **7c** having *cis*-substituents were prepared using palladium-catalyzed allylic substitution of carbonates **6a** and **6b**. Cycloalkene-ynes **7b** and **7d** having *trans*-substituents were prepared from **5a** and **5b** using Mitsunobu reaction.



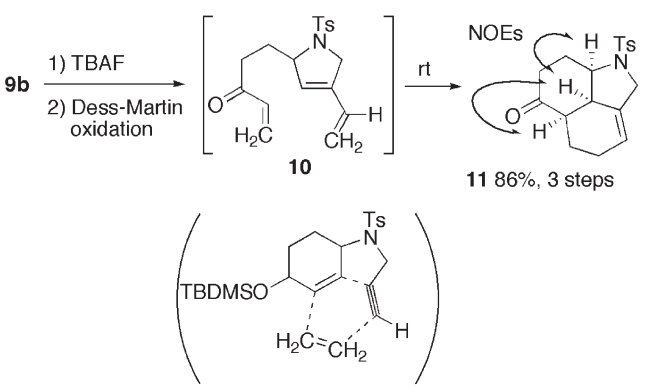
Scheme 5. Synthesis of cycloalkene-yne **7** having substituents.

When a CH_2Cl_2 solution of **7a** having *cis*-substituents and 10 mol% of **1a** was stirred at room temperature under an atmosphere of ethylene, the reaction proceeded smoothly to give a single product in high yield. However, this is a cross-metathesis product **8a** of an alkyne part of **7a** with ethylene. Presumably, the steric hindrance between the intermediate ruthenium–carbene part and the silyloxy group would prevent the intramolecular metathesis reaction (Scheme 1). As a result, the ruthenium–carbene part reacted with ethylene to yield 1,3-diene **8a**. On the other hand, when cyclohexene-yne **7b** having *trans*-substituents was treated in a similar manner, the desired ring-opening metathesis product **9b** was obtained in 90% yield as a single product (Scheme 6).



Scheme 6. ROM-RCM of cycloalkene-yne bearing substituents.

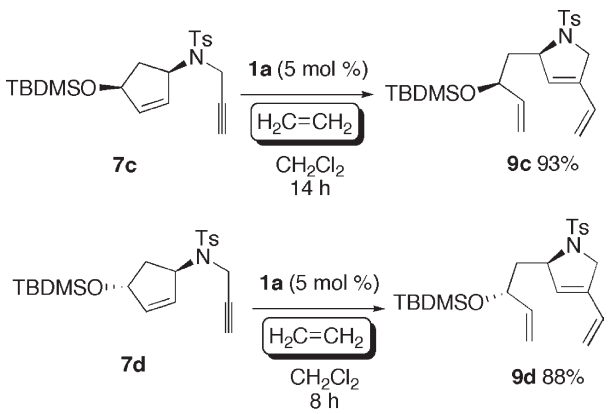
Since cyclized product **9b** has the diene moiety and an alkene part, cyclization by Diels–Alder reaction would be expected (Scheme 7). Desilylation of **9b** followed by Dess–Martin oxidation[11] at room temperature afforded a mixture of the desired ketone **10** and tricyclic compound **11**, which should be produced by Diels–Alder reaction, in 86% yield. The resultant mixture was allowed to stand at room temperature to give tricyclic compound **11** as a single product. The stereochemistry of **11** was determined by an NOESY experiment, and the cross-peaks on NOE were observed between the ring-junction protons. These results



Scheme 7. Synthesis of tricyclic compound via Diels–Alder reaction.

indicated, that formally, tricyclic compound **11** was formed via [2+2+2] cocyclization of cycloalkene, alkyne and ethylene.

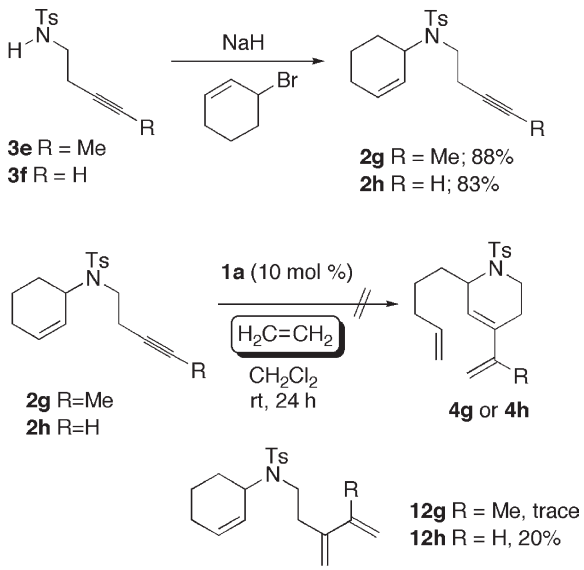
Under similar reaction conditions, metatheses of cyclopentene-ynes **7c** and **7d** were carried out. The reaction of each compound having *cis*- or *trans*-substituents proceeded smoothly to afford the desired products **9c** and **9d**, respectively in good yields (Scheme 8). Presumably, steric hindrance between the ruthenium–carbene part and the silyloxy group on the cyclopentene ring in **7c** is not affected by ring-opening metathesis and the desired product **9c** is formed.



Scheme 8. ROM-RCM of cycloalkene-ynes **7c** and **7d**.

Subsequently, the construction of a dehydropiperidine skeleton was attempted. For that purpose, one carbon in a tether of cycloalkene-yne should be elongated. Cycloalkene-ynes **2g** and **2h** having one-carbon elongated tether were synthesized from **3e** and **3f** by the usual method.

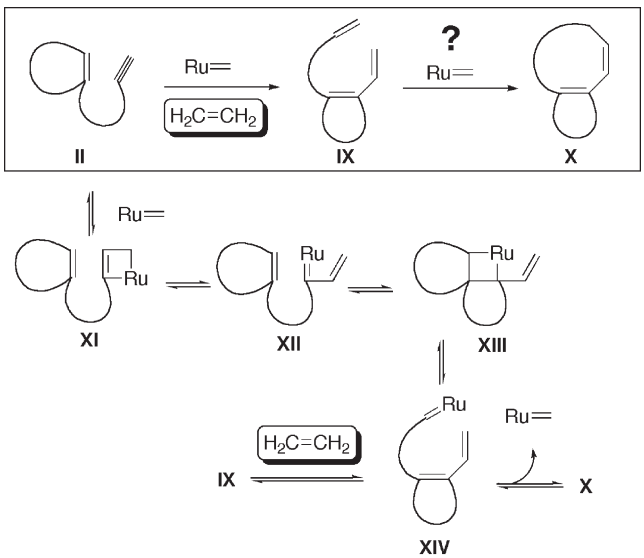
ROM-RCM of these cycloalkene-ynes **2g** and **2h** were carried out in a similar manner, but, unfortunately, no ring-opening metathesis products **4g** or **4f** were formed and the starting materials **2g** and **2h** were recovered in 96 and 66% yields, respectively, along with a small amount of cross-metathesis products **12g** and **12h** with ethylene in each case (Scheme 9). It is not clear why the starting materials were recovered without formation of ROM-RCM products.



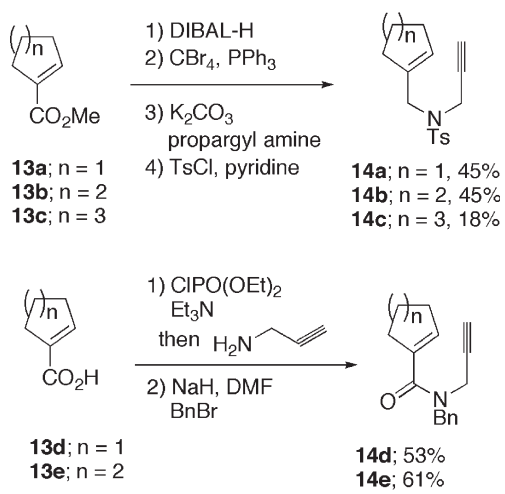
Scheme 9. Attempt to synthesize piperidine-ring.

2.2. Metathesis of cycloalkene having alkyne in a tether at the C-1 position

Subsequently, metathesis reaction of cycloalkene-yne, whose tether having an alkyne part is connected to the C-1 position of cycloalkene, was investigated (Scheme 10). If the metathesis of cycloalkene-yne **II** proceeds under ethylene gas, the alkyne part of **II** would react with the ruthenium–carbene complex to give ruthenacyclobutene **XI**, which would be converted into ruthenium–carbene complex **XII** by ring opening. Intramolecular [2+2] cycloaddition would occur to afford ruthenacyclobutane **XIII**, which would then be converted into ruthenium–carbene complex **XIV**. This would react with ethylene intermoleculary to afford triene **IX**. On the other hand, if this complex **XIV** can react with an alkene part of the diene moiety intramoleculary, bicyclic compound **X** would be obtained.



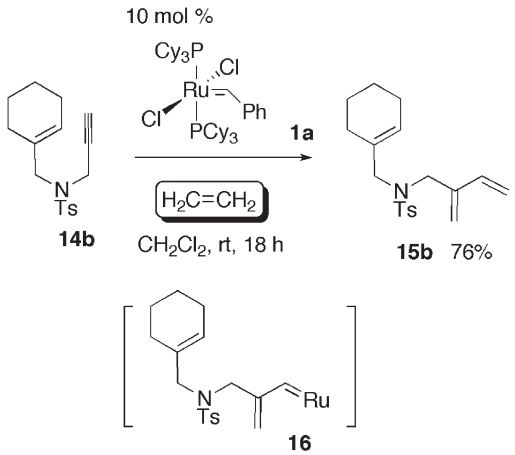
Scheme 10. Plan for ROM-RCM of cycloalkene-ynes **II**.



Scheme 11. Synthesis cycloalkene-yne **14**.

Cycloalkene-yne **14** was easily prepared from ester or carboxylic acid **13** as shown in Scheme 11. Reduction of **13a**, **13b** or **13c**[12] with DIBAL-H followed by bromination afforded a corresponding allyl bromide, which was reacted with propargyl amine followed by tosylation to afford cycloalkene-yne **14a**, **14b** or **14c** in moderate yield. Synthesis of cycloalkene-yne **14d** or **14e** was carried out by condensation of carboxylic acid **13d** or **13e** with propargylamine followed by alkylation with benzyl bromide.

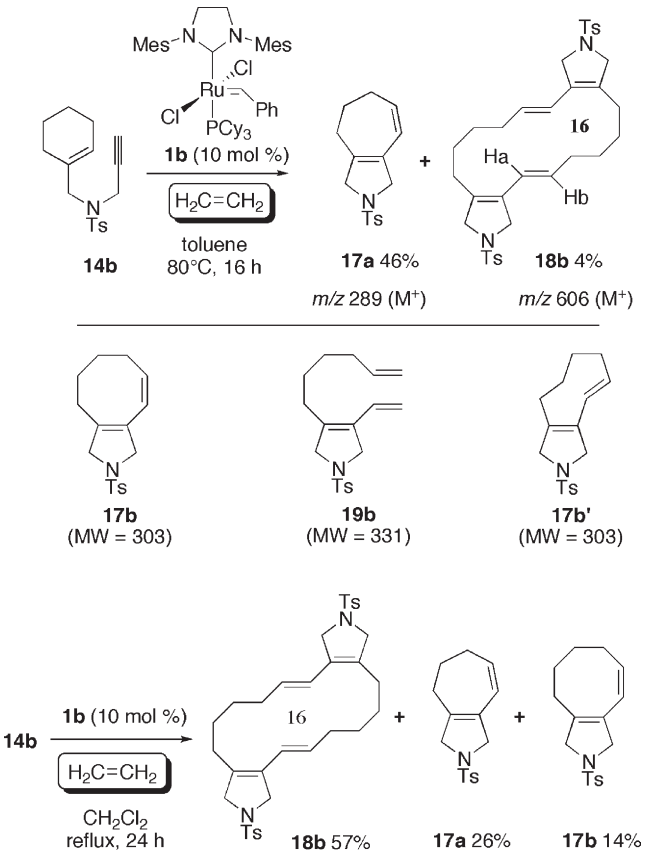
When a CH_2Cl_2 solution of cyclohexene-yne **14b** and 10 mol% of a first-generation ruthenium carbene complex **1a** was stirred at room temperature for 18 h under an atmosphere of ethylene, cross-enyne metathesis product **15b** was obtained in 76% yield instead of the ROM-RCM product (Scheme 12). Presumably, carbene complex **16** cannot react with trisubstituted alkene moiety. A second-generation ruthenium carbene complex was therefore used for ROM-RCM of **14b**.



Scheme 12. Reaction of **14b** with **1a**.

When a toluene solution of **14b** and 10 mol% of a second-generation ruthenium carbene complex **1b** was stirred at 80 °C for 16 h under an atmosphere of ethylene, two products were obtained (Scheme 13). Surprisingly, the expected products **17b** and **19b** were not obtained, and ^{1}H NMR and mass spectra revealed that one is compound **17a** having a 5,7-fused ring system, which was obtained in 46% yield. The structure was confirmed by X-ray crystallographic analysis.[13] The other is 16-membered ring compound **18b**, which was obtained in 4% yield. The structure of **18b** was confirmed as follows. From the coupling constant of Ha and Hb on a ^{1}H NMR spectrum (J_{Ha-Hb}=16.0 Hz), this compound was first thought to be **17b′** having *trans*-olefin because one set of peaks corresponding to **17b′** were seen on ^{1}H NMR and ^{13}C NMR spectra. However, a mass spectrum of **18b** (*m*/*z* 606 [M$^+$]) indicated that it is a dimeric compound, formed from intermolecular metathesis of two molecules.

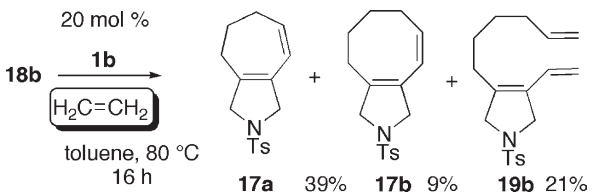
When a solution of **14b** and 10 mol% of **1b** in CH_2Cl_2 was refluxed under an atmosphere of ethylene for 24 h, the yields were improved. Although the expected product **17b** was obtained in 14% yield under these reaction conditions, the main product was dimeric compound **18b** (57% yield)



Scheme 13. ROM-RCM of **14b** using **1b**.

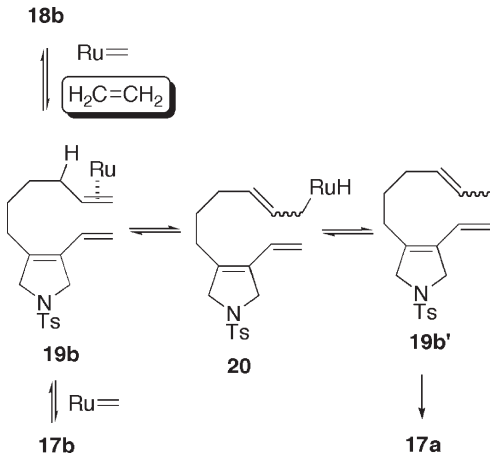
and the yield of 5,7-fused ring compound **17a** was greater than that of 5,8-fused ring compound **17b**.

Next, to examine whether dimeric compound **18b** is converted into a 5,7 or 5,8-fused ring compounds under the metathesis reaction conditions, a solution of **18b** and 20 mol% of **1b** in toluene was stirred at 80 °C for 16 h under an atmosphere of ethylene. Interestingly, **17a**, **17b** and **19b** were obtained in 39, 9 and 21% yields, respectively (Scheme 14). In this case, the yield of **17a** was also higher than that of **17b**. These results suggest that **18b** reacted with ethylene in the presence of ruthenium complex **1b** to afford **19b** and that **17a** and **17b** were then formed.



Scheme 14. ROM of dimeric compound **18b**.

Since ring-closure of **19b** into an eight-membered ring is difficult, olefin migration[14] followed by olefin metathesis would occur to give 5,7-fused ring compound **17a**. Isomerization of the double bond of **19b** should be caused by a ruthenium complex. Coordination of the terminal olefin of **19b** into a ruthenium complex followed by hydrogen elimination and then reductive elimination gives **19b′** via **20**. Olefin metathesis of **19b′** affords 5,7-fused ring compound **17a**. At a higher reaction temperature, **17b** was

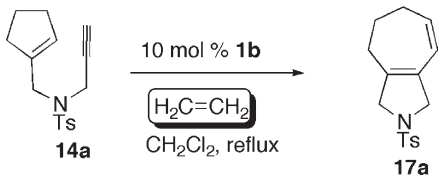


Scheme 15. Possible reaction course for formation of **17a**.

not formed because **19b** was easily converted into **19b′** and **17a** should be stable under these reaction conditions (Scheme 15).

Subsequently, ROM-RCM of cyclopentene-yne **14a** was investigated (Table 2). When a CH_2Cl_2 solution of **14a** and 10 mol% of **1b** was refluxed under an atmosphere of ethylene for 2 h, the desired ROM-RCM product **17a** was obtained in 95% yield (run 1). Even in the case of longer reaction time (26 h), **17a** was obtained in a quantitative yield (run 2). The results indicated that ring-closure into a seven-membered ring is easier and that **17a** is stable under these reaction conditions. The use of 5 mol% of **1b** gave similar results (run 3). In this reaction, ethylene was not introduced into the product. Thus, the reaction was carried out in the absence of ethylene to give **17a** in 81% yield, although the yield was slightly decreased (run 4).

Table 2. ROM-RCM of cycloalkene-yne **14a**

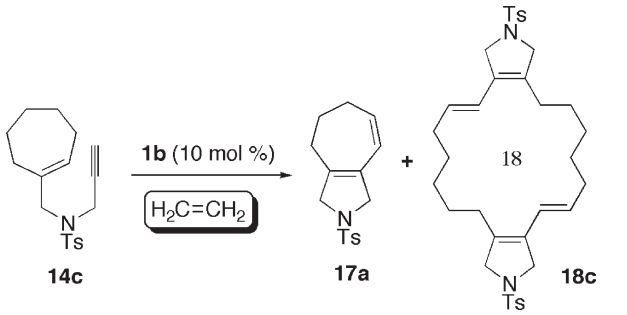


Run	Time (h)	Yield (%)
1	2	96
2	26	Quant.
3[a]	4	90
4[b]	1	81

[a] 5 mol % of **1b** was used.
[b] Reactions were carried out under an atmosphere of Ar.

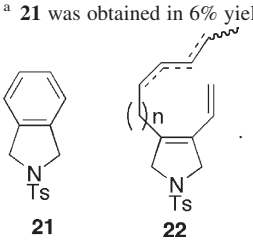
Furthermore, ROM-RCM of cycloheptene-yne **14c** was investigated (Table 3). When the reaction of **14c** was carried out in toluene at 80 °C for 21 h, 5,7-fused ring compound **17a**, dimeric compound **18c** and isoindoline derivative **21**[15] were obtained in 36, 8 and 6% yields, respectively, along with an inseparable mixture of **22** (run 1). GC–MS analysis of **22** showed that it is a mixture of dihydropyrrole derivatives having different carbon lengths and/or having olefin at various positions in a tether. On the other hand, when the reaction was carried out in CH_2Cl_2 upon heating

Table 3. ROM-RCM of cycloalkene-yne **14c**



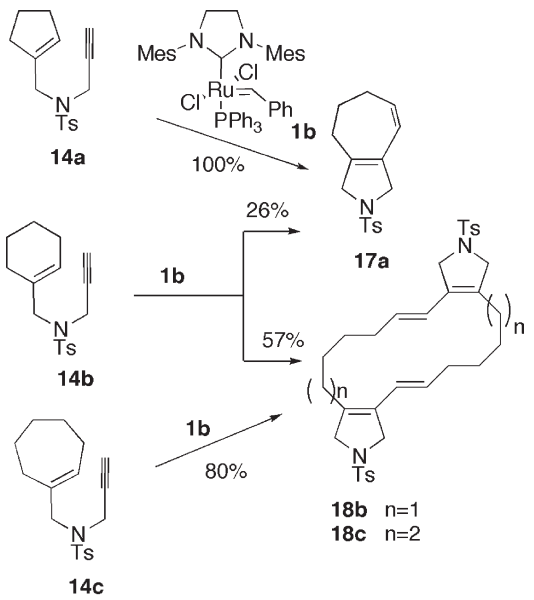
Run	Conditions	Yields (%)	
		17a	**18c**
1[a]	Toluene, 80 °C, 21 h	36	8
2	CH_2Cl_2, reflux, 15 h	Trace	58
3	CH_2Cl_2, reflux, 1 h	0	80

[a] **21** was obtained in 6% yield.



for 15 h, dimerization product **18c** was obtained in 58% yield along with a considerable amount of **22** (run 2). However, when the reaction was quenched after the spot of the starting material **14c** had disappeared on TLC, only **18c** was obtained in 80% yield (run 3).

ROM-RCM of 5-, 6-, and 7-membered cycloalkene-ynes **14** are summarized in Scheme 16. When the reaction was carried out in CH_2Cl_2, cyclopentene-yne **14a** gave 5,7-fused

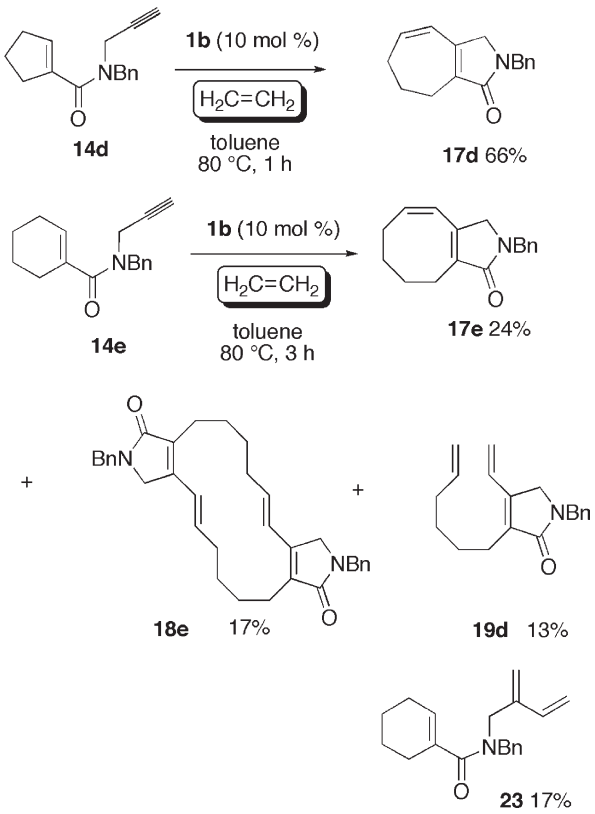


All reactions were carried out in CH_2Cl_2 with 10 mol % of **1b** under an atmosphere of ethylene.

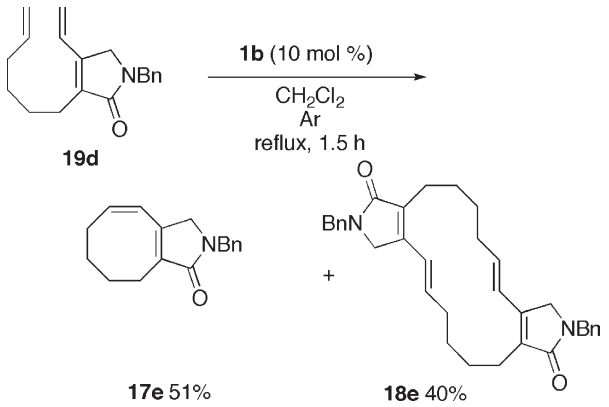
Scheme 16. Summary of ROM-RCM of cycloalkene-yne **14a–14c**.

ring compound **17a** in high yield, but cycloheptene-yne **14c** afforded dimeric compound **18c** in high yield. However, under similar reaction conditions, cyclohexene-yne **14b** gave **17a** and dimeric compound **18b** in 26 and 57% yields, respectively. Since the reaction of **14c** in toluene at 80 °C gave **17a** in good yield, **17a** was obtained in all cases due to the easy isomerization of the terminal olefin in a tether and the easy formation of a seven-membered ring.

Furthermore, ROM-RCM of cycloalkenecarboxamide having an alkyne moiety on nitrogen was carried out. When a toluene solution of **14d** and 10 mol% of **1b** was stirred in toluene at 80 °C for 1 h under an atmosphere of ethylene, the desired 5,7-fused ring compound **17d** was obtained in 66% yield as a single product. On the other hand, when ROM-RCM of cyclohexene-yne **14e** was carried out in a similar manner, 5,8-fused ring compound **17e**, dimeric compound **18e**, pyrrolidine derivative **19d** and cross-metathesis product **23** with ethylene were obtained in 24, 17, 13 and 17% yields, respectively. In this case, it was interesting that 5,7-fused ring compound **17d** was not formed. Presumably, before isomerization of the double bond of **19d**, olefin metathesis should occur to give **17e**, which is stable under the reaction conditions. Although it is not clear why a dimeric compound is formed, a relatively large amount of dimeric compound **18e** was also obtained in this case. Since compound **19d** was thought to be a product of ring-opening metathesis followed by cross-metathesis with ethylene, further treatment of compound **19d** with **1b** was carried out. When a CH_2Cl_2 solution of **19d** and 10 mol% of **1b** was refluxed for 1.5 h under argon gas upon heating, 5,8-fused ring compound **17e** and dimeric compound **18e** were obtained in 51 and 40% yields, respectively (Scheme 17 and 18).



Scheme 17. ROM-RCM of cycloalkene-yne **14d** and **14e**.



Scheme 18. Reaction of **19d** with **1b**.

3. Conclusions

ROM-RCM of cycloalkene-yne was realized. In the first ROM-RCM of cycloalkene having alkyne in a tether at the C-3 position, the reaction proceeded smoothly and the expected products were obtained in high yields. Ethylene gas is essential for these reactions. Formally, in this reaction, the double bond of cycloalkene was cleaved, and one alkylidene carbon reacts with an alkyne carbon to form a five-membered ring, while the other alkylidene carbon and alkyne carbon react with methylene parts of ethylene to form two terminal olefins, respectively. However, in the second ROM-RCM of cycloalkene having alkyne in a tether at the C-1 position, unexpected 5,7-fused ring compound **17a** was formed from all cycloalkene-ynes. Moreover, dimeric compounds **18** were obtained from cyclohexene and cycloheptene derivatives. Presumably, the reaction rate of ROM-RCM of cyclopentene is fast and the expected stable product **17a** would be produced predominantly. However, since ROM-RCM products of cyclohexene and cycloheptene derivatives were unstable under these reaction conditions, further reactions would proceed to give a dimeric compound and the cross-metathesis product with ethylene.

4. Experimental

4.1. General

The metathesis reactions were carried out under an atmosphere of ethylene (1 atm). All other manipulations were carried out under an atmosphere of argon unless otherwise mentioned. Solvents were distilled under an atmosphere of argon from sodium–benzophenone (toluene), or CaH_2 (CH_2Cl_2). Ethylene gas was purified by passage through the aqueous CuCl solution (2 g of CuCl in 180 mL of saturated NH_4Cl aqueous) and concentrated H_2SO_4 and then KOH tubes. Ruthenium complexes were purchased from Strem Chemicals. All other solvents and reagents were purified when necessary using standard procedure.

4.2. Typical procedure for the metathesis reaction

To a solution of enyne **2d** (98.2 mg, 0.34 mmol) in a CH_2Cl_2 solution (11.3 mL) was added **1a** (26.1 mg, 34 μmol), and the solution was degassed through freeze–pump–thaw cycle, and stirred at room temperature under an atmosphere of ethylene for 4 h. To this solution was added an excess of ethyl vinyl ether. After the solvent was removed, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate 9:1) to yield **4d** (83.6 mg, 78%) as a colorless solid.

4.3. Spectral data for metathesis products

4.3.1. 4-Isopropenyl-2-pent-4-enyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (4a). A colorless oil; IR (neat) ν 1640, 1600, 1346, 1164 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.31–1.52 (m, 2H), 1.77–1.86 (m, 2H), 1.83 (s, 3H), 2.07 (dt, J=6.7, 7.3 Hz, 2H), 2.41 (s, 3H), 4.19–4.27 (m, 2H), 4.52 (br, 1H), 4.76 (s, 1H), 4.93–5.04 (m, 3H), 5.50 (s, 1H), 5.79 (ddt, J=17.0, 10.1, 6.7 Hz, 1H), 7.29 (d, J=8.3 Hz, 2H), 7.71 (d, J=8.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.0 (CH_3), 21.5 (CH_3), 24.0 (CH_2), 33.7 (CH_2), 35.6 (CH_2), 55.2 (CH_2), 67.8 (CH), 114.5 (CH_2), 114.7 (CH_2), 125.0 (CH), 127.4 (CH×2), 129.7 (CH×2), 134.9 (C), 136.6 (C), 138.4 (C), 138.6 (CH), 143.3 (C); LRMS m/z 331 (M^+), 262, 176, 155, 107, 91; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1613.

4.3.2. 2-Hex-5-enyl-4-isopropenyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (4b). A colorless oil; IR (neat) ν1640, 1600, 1346, 1164 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.26–1.43 (m, 4H), 1.75–1.87 (m, 2H), 1.83 (s, 3H), 2.04 (dt, J=6.5, 6.5 Hz, 2H), 2.41 (s, 3H), 4.19–4.31 (m, 2H), 4.51 (br, 1H), 4.76 (s, 1H), 4.92 (m, 1H), 4.96 (m, 1H), 5.02 (m, 1H), 5.50 (s, 1H), 5.80 (ddt, J=17.0, 10.1, 6.7 Hz, 1H), 7.29 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.0 (CH_3), 21.5 (CH_3), 24.1 (CH_2), 28.9 (CH_2), 33.6 (CH_2), 35.9 (CH_2), 55.2 (CH_2), 67.8 (CH), 114.3 (CH_2), 114.5 (CH_2), 125.1 (CH), 127.4 (CH×2), 129.7 (CH×2), 134.9 (C), 136.6 (C), 138.3 (C), 138.8 (CH), 143.3 (C); LRMS m/z 345 (M^+), 262, 155, 107, 91; HRMS calcd for $C_{20}H_{27}NO_2S$ (M^+) 345.1762, found 345.1752.

4.3.3. 2-Hept-6-enyl-4-isopropenyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (4c). A colorless oil; IR (neat) ν 1640, 1598, 1346, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24–1.86 (m, 8H), 1.82 (s, 3H), 2.03 (dt, J=6.7, 6.4 Hz, 2H), 2.41 (s, 3H), 4.20–4.30 (m, 2H), 4.50 (br, 1H), 4.76 (s, 1H), 4.92–5.01 (m, 2H), 4.96 (s, 1H), 5.50 (s, 1H), 5.80 (ddt, J=16.7, 10.0, 6.7 Hz, 1H), 7.29 (d, J=8.3 Hz, 2H), 7.71 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1 (CH_3), 21.6 (CH_3), 24.5 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 33.8 (CH_2), 36.1 (CH_2), 55.2 (CH_2), 67.9 (CH), 114.2 (CH_2), 114.4 (CH_2), 125.1 (CH), 127.3 (CH×2), 129.6 (CH×2), 134.8 (C), 136.5 (C), 138.1 (C), 138.9 (CH), 143.2 (C); LRMS m/z 359 (M^+), 262, 155, 107, 91; HRMS calcd for $C_{21}H_{29}NO_2S$ (M^+) 359.1919, found 359.1919.

4.3.4. 2-Pent-4-enyl-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (4d). A colorless solid; IR (nujol) ν 1642, 1598, 1344, 1166 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.24–1.49 (m, 2H), 1.76–1.85 (m, 2H), 2.06 (dt, J=6.8, 7.3 Hz, 2H), 2.41 (s, 3H), 4.16–4.28 (m, 2H), 4.50 (br, 1H), 4.92–5.03 (m, 2H), 5.01 (d, J=17.8 Hz, 1H), 5.14 (d, J=10.5 Hz, 1H), 5.51 (br, 1H), 5.78 (ddt, J=17.0, 10.3, 6.8 Hz, 1H), 6.32 (dd, J=17.8, 10.5 Hz, 1H), 7.29 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 23.9 (CH_2), 33.7 (CH_2), 35.5 (CH_2), 54.3 (CH_2), 67.3 (CH), 114.6 (CH_2), 116.7 (CH_2), 127.3 (CH×2), 127.8 (CH), 129.7 (CH×2), 129.9 (CH), 134.8 (C), 136.6 (C), 138.5 (CH), 143.3 (C); LRMS m/z 317 (M^+), 248, 155, 91; HRMS calcd for $C_{18}H_{23}NO_2S$ (M^+) 317.1449, found 317.1455.

4.3.5. 2-Hex-5-enyl-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (4e). A colorless oil; IR (neat) ν 1640, 1598, 1346, 1162 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.23–1.46 (m, 4H), 1.71–1.86 (m, 2H), 2.04 (dt, J=6.7, 6.5 Hz, 2H), 2.41 (s, 3H), 4.16–4.28 (m, 2H), 4.49 (br, 1H), 4.91–5.03 (m, 2H), 5.01 (d, J=17.8 Hz, 1H), 5.14 (d, J=11.1 Hz, 1H), 5.52 (m, 1H), 5.79 (ddt, J=17.0, 10.1, 6.7 Hz, 1H), 6.33 (dd, J=17.8, 11.1 Hz, 1H), 7.29 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.4 (CH_3), 24.1 (CH_2), 28.8 (CH_2), 33.6 (CH_2), 35.9 (CH_2), 54.2 (CH_2), 67.4 (CH), 114.3 (CH_2), 116.6 (CH_2), 127.3 (CH×2), 127.9 (CH), 129.7 (CH×2), 129.9 (CH), 134.5 (C), 136.6 (C), 138.8 (CH), 143.3 (C); LRMS m/z 331 (M^+), 248, 155, 91; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1604.

4.3.6. 2-Hept-6-enyl-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (4f). A colorless oil; IR (neat) ν 1640, 1598, 1346, 1164 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21–1.39 (m, 6H), 1.73–1.82 (m, 2H), 1.99–2.06 (m, 2H), 2.41 (s, 3H), 4.16–4.29 (m, 2H), 4.49 (br, 1H), 4.90–5.03 (m, 2H), 5.01 (d, J=17.6 Hz, 1H), 5.14 (d, J=10.8 Hz, 1H), 5.52 (m, 1H), 5.80 (ddt, J=17.0, 10.3, 6.8 Hz, 1H), 6.33 (dd, J=17.6, 10.8 Hz, 1H), 7.29 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 24.4 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 33.7 (CH_2), 36.0 (CH_2), 54.3 (CH_2), 67.5 (CH), 114.2 (CH_2), 116.6 (CH_2), 127.3 (CH×2), 127.9 (CH), 129.7 (CH×2), 123.0 (CH), 134.9 (C), 136.6 (C), 139.0 (CH), 143.3 (C); LRMS m/z 345 (M^+), 248, 155, 106, 91; HRMS calcd for $C_{20}H_{27}NO_2S$ (M^+) 345.1762, found 345.1760.

4.3.7. *N*-{(1*R,4*S**)-4-(*tert*-Butyl-dimethylsilanyloxy)-cyclohex-2-enyl}-4-methyl-*N*-(2-methylene-but-3-enyl)-benzenesulfonamide (8a).** A colorless oil; IR (neat) ν 1638, 1598, 1342, 1253, 1163, 1093 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ −0.02 (s, 3H), −0.01 (s, 3H), 0.81 (s, 9H), 1.54–1.66 (m, 3H), 1.79–1.87 (m, 1H), 2.43 (s, 3H), 3.76 (d, J=17.6 Hz, 1H), 4.00 (br, 1H), 4.04 (d, J=17.6 Hz, 1H), 4.44–4.48 (m, 1H), 5.03–5.09 (m, 2H), 5.17–5.24 (m, 2H), 5.42 (br, 1H), 5.69–5.75 (m, 1H), 6.40 (dd, J=18.1, 11.3 Hz, 1H), 7.30 (d, J=8.4 Hz, 2H), 7.74 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −4.9 (CH_3), −4.6 (CH_3), 17.9 (C), 21.5 (CH_3), 22.9 (CH_2), 25.7 (CH_3×3), 30.4 (CH_2), 45.1 (CH_2), 55.6 (CH), 62.6 (CH), 113.3 (CH_2), 117.4 (CH_2), 127.2 (CH×2), 129.0 (CH), 129.7 (CH×2), 134.1 (CH), 136.9 (CH), 137.9 (C), 142.5 (C), 143.2 (C); LRMS m/z 447 (M^+), 390, 248, 132, 91; HRMS calcd for $C_{24}H_{37}NO_3SSi$ (M^+) 447.2263, found 447.2244.

4.3.8. (2*S* *)-2-{(3*S* *)-3-(*tert*-Butyl-dimethylsilanyloxy)-pent-4-enyl}-1-(toluene-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (9b). A colorless oil; IR (neat) ν 1646, 1598, 1348, 1252, 1163, 1096 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 3H), 0.06 (s, 3H), 0.89 (s, 9H), 1.41–1.57 (m, 2H), 1.76–1.91 (m, 2H), 2.41 (s, 3H), 4.07 (dt, *J*=6.4, 6.0 Hz, 1H), 4.17–4.26 (m, 2H), 4.54 (br, 1H), 4.98 (d, *J*=17.6 Hz, 1H), 5.01 (d, *J*=10.4 Hz, 1H), 5.13 (d, *J*=17.2 Hz, 1H), 5.14 (d, *J*=10.8 Hz, 1H), 5.47 (br, 1H), 5.76 (ddd, *J*=17.2, 10.4, 6.4 Hz, 1H), 6.32 (dd, *J*=17.6, 10.8 Hz, 1H), 7.29 (d, *J*=8.4 Hz, 2H), 7.71 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.7 (CH_3), −4.2 (CH_3), 18.3 (C), 21.6 (CH_3), 25.9 (CH_3×3), 31.7 (CH_2), 32.7 (CH_2), 54.4 (CH_2), 67.3 (CH), 73.7 (CH), 113.7 (CH_2), 116.6 (CH_2), 127.3 (CH×2), 127.7 (CH), 129.6 (CH×2), 129.8 (CH), 134.7 (C), 136.6 (C), 141.5 (CH), 143.3 (C); LRMS *m*/*z* 432 (M^+-CH_3), 390, 292, 262, 248, 236, 155, 91; HRMS calcd for $C_{23}H_{34}NO_3SSi$ (M^+-CH_3) 432.2067, found 432.2048. Anal. calcd for $C_{24}H_{37}NO_3SSi$: C, 64.39; H, 8.33; N, 3.13; S, 7.16. Found: C, 64.48; H, 8.48; N, 2.91; S, 7.21.

4.3.9. (2*S* *)-2-[(2*R* *)-2-(*tert*-Butyl-dimethyl-silanyloxy)-but-3-enyl]-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (9c). A colorless oil; IR (neat) ν 2954, 2928, 2856, 1646, 1599, 1348, 1163 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.02 (s, 3H), 0.88 (s, 9H), 1.75 (ddd, *J*=13.8, 9.7, 4.3 Hz, 1H), 2.37 (m, 1H), 2.39 (s, 3H), 4.12 (m, 1H), 4.22 (m, 1H), 4.28 (m, 1H), 4.48 (br, 1H), 4.98 (d, *J*=17.6 Hz, 1H), 5.09 (dt, *J*=10.8 1.6 Hz, 1H), 5.11 (d, *J*=10.3 Hz, 1H), 5.20 (dt, *J*=17.8, 1.6 Hz,1H), 5.68 (br, 1H), 5.88 (ddd, *J*=17.6, 10.3, 5.7 Hz, 1H), 6.29 (dd, *J*=17.8, 10.8 Hz, 1H), 7.26 (d, *J*=9.7 Hz, 2H), 7.68 (d, *J*=9.7 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −5.0 (CH_3), −4.3 (CH_3), 18.1 (C), 21.5 (CH_3), 25.8 (CH_3×3), 44.5 (CH_2), 53.9 (CH_2), 64.4 (CH), 71.2 (CH), 114.3 (CH_2), 116.5 (CH_2), 127.5 (CH×2), 128.8 (CH), 129.7 (CH×2), 130.1 (CH), 134.2 (C), 135.6 (C), 140.8 (CH), 143.4 (C); LRMS *m*/*z* 432 (M^+-1), 418, 403, 376, 278, 220, 155, 91. Anal. calcd for $C_{23}H_{35}NO_3SSi$: C, 63.70; H, 8.13; N, 3.23; S, 7.39. Found: C, 63.47; H, 8.07; N, 3.20; S, 7.23.

4.3.10. (2*S* *)-2-[(2*S* *)-2-(*tert*-Butyl-dimethyl-silanyloxy)-but-3-enyl]-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (9d). A colorless solid. Mp 91 °C (ether/hexane); IR (nujol) ν 3088, 1829, 1597, 1343, 1165 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.08 (s, 3H), 0.89 (s, 9H), 1.77–1.85 (m, 1H), 2.25–2.31 (m, 1H), 2.39 (s, 3H), 4.02 (m, 1H), 4.10 (m, 1H), 4.30–4.35 (m, 1H), 4.46 (br, 1H), 4.97 (d, *J*=17.8 Hz, 1H), 5.05 (dt, *J*=10.4, 1.6 Hz, 1H), 5.10 (d, *J*=10.4 Hz, 1H), 5.16 (dt, *J*=17.8, 1.6 Hz,1H), 5.63 (br, 1H), 5.79 (ddd, *J*=17.8, 10.4, 6.2 Hz, 1H), 6.28 (dd, *J*=17.8, 10.4 Hz, 1H), 7.27 (d, *J*=8.2 Hz, 2H), 7.68 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −4.7 (CH_3), −4.3 (CH_3), 18.2 (C), 21.5 (CH_3), 25.9 (CH_3×3), 45.0 (CH_2), 53.7 (CH_2), 65.2 (CH), 72.0 (CH), 114.3 (CH_2), 116.5 (CH_2), 127.5 (CH×2), 128.8 (CH), 129.7 (CH×2), 130.1 (CH), 134.2 (C), 135.6 (C), 147.4 (CH), 143.4 (C); LRMS *m*/*z* 433 (M^+), 418, 376, 278, 248, 220, 155, 91; HRMS calcd for $C_{22}H_{32}NO_3SSi$ (M^+-Me) 418.1892, found 418.1872. Anal. calcd for $C_{23}H_{35}NO_3SSi$: C, 63.70; H, 8.13; N, 3.23; S, 7.39. Found: C, 63.68; H, 8.12; N, 3.20; S, 7.29.

4.3.11. *N*-Cyclohex-2-enyl-4-methyl-*N*-(3-methylene-pent-4-enyl)-benzenesulfonamide (12h). A colorless oil; IR (neat) ν 2934, 1648, 1595, 1494, 1450, 1392, 1340, 1224, 1160, 1126, 1097, 1019 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.48–1.96 (m, 6H), 2.42 (s, 3H), 2.46–2.82 (m, 2H), 2.99–3.28 (m, 2H), 4.48 (m, 1H), 5.01 (s, 1H), 5.05 (s, 1H), 5.07–5.12 (m, 1H), 5.11 (d, *J*=10.8 Hz, 1H), 5.40 (d, *J*=17.3 Hz, 1H), 5.75–5.80 (m, 1H), 6.33 (dd, *J*=10.8, 17.3 Hz, 1H), 7.28 (d, *J*=8.1 Hz, 2H), 7.72 (d, *J*=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 21.8 (CH_2), 24.4 (CH_2), 29.0 (CH_2), 34.6 (CH_2), 44.0 (CH_2), 55.4 (CH), 114.2 (CH_2), 117.3 (CH_2), 127.1 (CH), 127.7 (CH×2), 129.7 (CH×2), 132.3 (CH), 138.1 (C), 138.2 (CH), 143.0 (C), 145.9 (C); LRMS *m*/*z* 331 (M^+), 316, 288, 364, 351, 184, 176, 155, 91; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1605.

4.3.12. *N*-Cyclohex-1-enylmethyl-4-methyl-*N*-(2-methyl-ene-but-3-enyl)-benzenesulfonamide (15b). A colorless oil; IR (neat) ν 1597, 1338, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ δ 1.46–1.51 (m, 4H), 1.81 (br, 2H), 1.90 (br, 2H), 2.42 (s, 3H), 3.64 (s, 2H), 3.91 (s, 2H), 5.05 (s, 1H), 5.06 (d, *J*=10.8 Hz, 1H), 5.13 (s, 1H), 5.29 (d, *J*=18.0 Hz, 1H), 5.46 (br, 1H), 6.30 (dd, *J*=18.0, 10.8 Hz, 1H), 7.29 (d, *J*=8.4 Hz, 2H), 7.70 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (CH_3), 22.1 (CH_2), 22.5 (CH_2), 25.2 (CH_2), 26.2 (CH_2), 48.6 (CH_2), 54.6 (CH_2), 114.3 (CH_2), 117.6 (CH_2), 126.8 (CH), 127.2 (CH×2), 129.4 (CH×2), 132.3 (C), 136.6 (CH), 137.0 (C), 140.3 (C), 142.9 (C); LRMS *m*/*z* 331 (M^+), 316, 302, 290, 276, 264, 249, 236, 198, 184, 176, 155, 148, 133, 119, 106; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1606. Anal. calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23; S, 9.67. Found: C, 68.73; H, 7.61; N, 4.29; S, 9.77.

4.3.13. 2-(Toluene-4-sulfonyl)-1,2,3,4,5,6-hexahydro-cyclohepta[*c*]pyrrole (17a). A colorless crystals. Mp 111–113 °C (ether); IR (nujol) ν 2924, 2854, 1654, 1344, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.78 (m, 2H), 2.20 (br, 2H), 2.31 (m, 2H), 2.43 (s, 3H), 4.10 (br, 4H), 5.52 (d, *J*=11.6 Hz, 1H), 5.83 (dt, *J*=11.6, 5.6 Hz, 1H), 7.32 (d, *J*=8.0 Hz, 2H), 7.72 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (CH_3), 23.4 (CH_2), 29.5 (CH_2), 30.6 (CH_2), 58.4 (CH_2), 59.5 (CH_2), 120.3 (CH), 127.2 (C), 127.4 (CH×2), 129.6 (CH×2), 133.9 (C), 134.1 (C), 134.7 (CH), 143.2 (C); LRMS *m*/*z* 289 (M^+), 155, 134, 91; HRMS calcd for $C_{16}H_{19}NO_2S$ (M^+) 289.1136, found 289.1124.

4.3.14. Dimeric compound 18b. A colorless solid; IR (nujol) ν 2924, 2854, 1598, 1348, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29–1.39 (m, 8H), 2.05–2.09 (m, 4H), 2.12–2.16 (m, 4H), 2.41 (s, 6H), 4.06 (s, 4H), 4.16 (s, 4H), 5.34 (m, 2H), 6.10 (d, *J*=16.0 Hz, 2H), 7.30 (d, *J*=8.0 Hz, 4H), 7.70 (d, *J*=8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (CH_3×2), 24.4 (CH_2×2), 25.6 (CH_2×2), 26.8 (CH_2×2), 30.9 (CH_2×2), 55.1 (CH_2×2), 57.5 (CH_2×2), 121.8 (CH×2), 127.4 (CH×4), 129.0 (C×2), 129.7 (CH×4), 131.6 (CH×2), 133.2 (C×2), 134.3 (C×2), 143.4 (C×2); LRMS *m*/*z* 606 (M^+), 518, 451, 295, 155, 91; HRMS calcd for $C_{34}H_{42}N_2O_4S_2$ (M^+) 606.2586, found 606.2581.

4.3.15. 2-(Toluene-4-sulfonyl)-2,3,4,5,6,7-hexahydro-1*H*-cycloocta[*c*]pyrrole (17b). A colorless solid; IR (nujol) ν

2924, 2854, 1654, 1344, 1162 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.45–1.52 (m, 2H), 1.59–1.67 (m, 2H), 2.03–2.07 (m, 2H), 2.13–2.17 (m, 2H), 2.43 (s, 3H), 4.03 (s, 4H), 5.62–5.66 (m, 2H), 7.32 (d, J=8.1 Hz, 2H), 7.72 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.6 (CH_3), 21.6 (CH_2), 25.4 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 58.2 (CH_2), 59.2 (CH_2), 122.3 (CH), 127.1 (C), 127.5 (CH×2), 129.7 (CH×2), 132.7 (CH), 132.9 (C), 134.3 (C), 143.3 (C); LRMS m/z 303 (M^+), 155, 148, 91; HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1299.

4.3.16. 3-Hex-5-enyl-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (19b). A colorless solid; IR (film) ν 2926, 2855, 1654, 1598, 1347, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26–1.40 (m, 4H), 1.98–2.05 (m, 2H), 2.12–2.15 (m, 2H), 2.43 (s, 3H), 4.11 (s, 2H), 4.22 (s, 2H), 4.93–4.99 (m, 3H), 5.12 (d, J=10.8 Hz, 1H), 5.74 (m, 1H), 6.43 (dd, J=17.2, 10.8 Hz, 1H), 7.32 (d, J=8.1 Hz, 2H), 7.73 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (CH_3), 26.0 (CH_2), 27.3 (CH_2), 28.5 (CH_2), 33.4 (CH_2), 54.9 (CH_2), 57.6 (CH_2), 114.7 (CH_2), 115.3 (CH_2), 127.4 (CH×2), 129.4 (CH), 129.7 (CH×2), 130.8 (C), 133.9 (C), 135.8 (C), 138.3 (CH), 143.4 (C); LRMS m/z 331 (M^+), 248, 176, 155, 91; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1592.

4.3.17. Dimeric compound 18c. A colorless solid; IR (nujol) ν 2923, 2854, 1598, 1348, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99–1.38 (m, 12H), 2.01–2.14 (m, 8H), 2.42 (s, 6H), 4.05 (s, 4H), 4.19 (s, 4H), 5.33 (m, 2H), 6.02 (d, J=15.6 Hz, 2H), 7.32 (d, J=8.0 Hz, 4H), 7.73 (d, J=8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (CH_3×2), 25.3 (CH_2×2), 26.9 (CH_2×2), 27.0 (CH_2×2), 27.9 (CH_2×2), 33.1 (CH_2×2), 55.2 (CH_2×2), 57.0 (CH_2×2), 121.6 (CH×2), 127.4 (CH×4), 129.5 (C×2), 129.6 (CH×4), 132.1 (CH×2), 132.4 (C×2), 134.1 (CH×2), 143.3 (C×2); LRMS m/z 634 (M^+), 479. 451, 323, 155, 91; HRMS calcd for $C_{36}H_{46}N_2O_4S_2$ (M^+) 634.2899, found 634.2902.

4.3.18. *N*-Benzyl-3,6,7,8-tetrahydro-cyclohepta[*c*]-pyrrol-1(2*H*)-one (17d). A colorless liquid; IR (neat) ν 1674 (s), 1495 (m), 1452 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.84–1.92 (m, 2H), 2.47 (dt, J=5.6, 5.4 Hz, 2H), 2.63 (br, 2H), 3.71 (t, J=2.2 Hz, 2H), 4.63 (s, 2H), 5.78 (dt, J=11.3, 2.0 Hz, 1H), 6.10 (dt, J=11.3, 5.6 Hz, 1H), 7.23–7.35 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 22.8, 27.3, 31.9, 46.2, 52.4, 121.0, 127.3, 127.9, 128.6, 133.9, 137.4, 139.1, 143.8, 172.0; EI-LRMS m/z 239 (M^+), 162, 148, 105, 91, 77; EI-HRMS m/z calcd for $C_{16}H_{17}ON$ (M^+) 239.1310, found 239.1320.

4.3.19. *N*-Benzyl-2,3,6,7,8,9-hexahydro-1*H*-cycloocta[*c*]-pyrrol-1-one (17e). A colorless liquid; IR (neat) ν 1683 (s), 1636 (m), 1604 (w), 1495 (m), 1453 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.55–1.64 (m, 2H), 1.78–1.87 (m, 2H), 2.27–2.34 (m, 2H), 2.48–2.52 (m, 2H), 3.64 (t, J=2.1 Hz, 2H), 4.62 (s, 2H), 5.78–5.95 (m, 2H), 7.22–7.36 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.4, 25.0, 25.4, 27.1, 46.3, 52.6, 123.0, 127.3, 128.0, 128.6, 133.0, 135.2, 137.4, 143.5, 172.1; EI-LRMS m/z 253 (M^+), 224, 162, 91; EI-HRMS m/z calcd for $C_{17}H_{19}ON$ (M^+) 253.1467, found 253.1463.

4.3.20. Dimeric compound 18e. A colorless liquid; IR (neat) ν 1678 (s), 1480 (m), 1453 (m), 1410 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.46–1.64 (m, 8H), 2.20–2.29 (m, 4H), 2.36–2.43 (m, 4H), 3.83 (br, 4H), 4.61 (br, 4H), 5.80 (dt, J=6.6, 16.0 Hz, 2H), 6.42 (d, J=16.0 Hz, 2H), 7.21–7.34 (m, 10H); EI-LRMS m/z 506 (M^+), 415, 368, 304, 227, 91; EI-HRMS m/z calcd for $C_{34}H_{38}O_2N_2$ (M^+) 506.2933, found 506.2916.

4.3.21. *N*-Benzyl-3-(hex-5-enyl)-4-vinyl-5-hydro-1*H*-pyrrol-1-one (19d). A colorless liquid; IR (neat) ν 1681 (s), 1640 (m), 1624 (m), 1452 (m), 1408 (m) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.40–1.64 (m, 4H), 2.03–2.13 (m, 2H), 2.40 (t, J=7.4 Hz, 2H), 3.87 (s, 2H), 4.64 (s, 2H), 4.90–5.04 (m, 2H), 5.28 (d, J=10.9 Hz, 1H), 5.31 (d, J=17.6 Hz, 1H), 5.81 (ddt, J=10.2, 17.0, 6.6 Hz, 1H), 6.70 (dd, J=10.9, 17.6 Hz, 1H), 7.21–7.38 (m, 5H); EI-LRMS m/z 281 (M^+), 252, 240, 226, 213, 190, 149, 122, 109, 91; EI-HRMS m/z calcd for $C_{19}H_{23}ON$ (M^+) 281.1779, found 281.1755.

4.3.22. *N*-Benzyl-*N*-(2-methylene-but-3-enyl)-1-cyclohexene-1-carboxamide (23). A colorless liquid; IR (neat) ν 1658 (m), 1621 (s), 1495 (m), 1453 (s), 1418 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.55–1.72 (m, 4H), 2.02–2.10 (m, 2H), 2.21–2.27 (m, 2H), 4.02–4.22 (m, 2H), 4.58 (s, 2H), 4.88–5.36 (m, 4H), 5.87 (m, 1H), 6.38 (dd, J=11.0, 17.7 Hz, 1H), 7.15–7.38 (m, 5H); EI-LRMS m/z 281 (M^+), 240, 214, 190, 172, 109; EI-HRMS m/z calcd for $C_{19}H_{23}ON$ (M^+) 281.1779, found 281.1754.

4.4. Procedure for the Diels–Alder reaction

4.4.1. (2*S)-2-{(3*S**)-3-Hydroxy-pent-4-enyl}-1-(toluene-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole.** A solution of **9b** (55 mg, 0.12 mmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 0.2 mL, 0.2 mmol) at 0 °C, and the solution was stirred at room temperature for 3 h. To this solution was added saturated NH_4Cl aq., and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 4:1–1:1) to yield title alcohol (40 mg, 98%) as a colorless oil. IR (neat) ν 3518, 1647, 1598, 1342, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45–1.53 (m, 1H), 1.59–1.68 (m, 1H), 1.86 (br, 1H), 1.87–1.92 (m, 2H), 2.41 (s, 3H), 4.13 (dt, J=6.4, 6.4 Hz, 1H), 4.17–4.28 (m, 2H), 4.57 (m, 1H), 5.01 (d, J=17.6 Hz, 1H), 5.11 (d, J=10.0 Hz, 1H), 5.11 (d, J=10.8 Hz, 1H), 5.23 (d, J=17.6 Hz, 1H), 5.48 (m, 1H), 5.85 (ddd, J=17.6, 10.0, 6.4 Hz, 1H), 6.32 (dd, J=17.6, 10.8 Hz, 1H), 7.30 (d, J=8.0 Hz, 2H), 7.71 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (CH_3), 31.5 (CH_2), 31.5 (CH_2), 54.4 (CH_2), 67.0 (CH), 72.9 (CH), 114.7 (CH_2), 116.8 (CH_2), 127.3 (CH×2), 127.5 (CH), 129.6 (CH×2), 129.7 (CH), 134.3 (C), 136.6 (C), 140.8 (CH), 143.4 (C); LRMS m/z 315 (M^+-H_2O), 248, 178, 155, 91; HRMS calcd for $C_{18}H_{21}NO_2S$ (M^+-H_2O) 315.1293, found 315.1301.

4.4.2. (5a*S,8a*S**,8b*R**)-1-(Toluene-4-sulfonyl)-2,4,5,5a,7,8,8a,8b-octahydro-1*H*-benzo[*cd*]indol-6-one (11).** To a suspension of Dess–Martin periodinane (77 mg, 0.18 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of

alcohol (40 mg, 0.12 mmol) in CH_2Cl_2 (0.7 mL) at 0 °C, and the solution was stirred at room temperature for 1 h. To this solution was added saturated $NaHCO_3$ aq. and saturated $Na_2S_2O_3$ aq., and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 3:1) to yield **10** and **11** as an inseparable mixture. This mixture was allowed at room temperature to give **11** (35 mg, 88%) as colorless needles. Mp 136.5–139 °C. (Ethyl acetate/hexane); IR (film) ν 1713, 1598, 1341, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24–1.33 (m, 1H), 1.86–1.98 (m, 2H), 2.08–2.16 (m, 2H), 2.24–2.37 (m, 3H), 2.43 (s, 3H), 2.60 (m, 1H), 2.79 (br, 1H), 3.79–3.83 (m, 1H), 3.91 (d, J=13.2 Hz, 1H), 4.24 (ddd, J=13.2, 8.0, 5.2 Hz, 1H), 5.61 (br, 1H), 7.33 (d, J=8.0 Hz, 2H), 7.75 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9 (CH_2), 21.0 (CH_2), 21.6 (CH_3), 28.5 (CH_2), 36.6 (CH_2), 41.9 (CH), 42.3 (CH), 51.1 (CH_2), 58.2 (CH), 121.6 (CH), 127.4 (CH×2), 129.7 (CH×2), 134.0 (C), 134.7 (C), 143.6 (C), 209.9 (C); LRMS m/z 331 (M^+), 274, 176, 155, 120, 91; HRMS calcd for $C_{18}H_{21}NO_3S$ (M^+) 331.1242, found 331.1233. Anal. calcd for $C_{18}H_{21}NO_3S$: C, 65.23; H, 6.39; N, 4.23; S, 9.68. Found: C, 65.03; H, 6.40; N, 4.22; S, 9.52.

4.5. Typical procedure for the preparation of cycloalkene-yne 2

To a suspension of NaH (60% oil suspension, 147 mg, 3.6 mmol) in THF/DMF (5 mL each) was added a solution of **3a** (673 mg, 3.0 mmol) in THF/DMF (5 mL each) at 0 °C, and the solution was stirred at room temperature for 60 min. To this solution was added 3-bromocyclohexene (0.4 mL, 3.6 mmol). The whole solution was warmed at 40 °C for 4.5 h. To this solution was added saturated NH_4Cl aq., and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ether 5:1) to yield **2a** (900 mg, quant.) as a colorless solid.

4.6. Spectral data for cycloalkene-yne 2

4.6.1. *N*-But-2-ynyl-*N*-cyclohex-2-enyl-4-methyl-benzenesulfonamide (2a). A colorless solid. Mp 84–86 °C. (Ether/hexane); IR (film) ν 2225, 1647, 1334, 1160 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.68 (t, J=2.4 Hz, 3H), 1.74–1.81 (m, 4H), 1.95 (br, 2H), 2.42 (s, 3H), 3.83–4.09 (m, 2H), 4.49 (br, 1H), 5.30–5.33 (m, 1H), 5.83–5.87 (m, 1H), 7.27 (d, J=8.3 Hz, 2H), 7.81 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.4 (CH_3), 21.4 (CH_3), 21.4 (CH_2), 24.3 (CH_2), 27.9 (CH_2), 33.1 (CH_2), 54.9 (CH), 75.5 (C), 79.6 (C), 127.1 (CH), 127.2 (CH×2), 129.0 (CH×2), 132.5 (CH), 138.1 (C), 142.7 (C); LRMS m/z 303 (M^+), 155, 148, 91; HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1287. Anal. calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62; S, 10.57. Found: C, 67.22; H, 6.82; N, 4.54; S, 10.56.

4.6.2. *N*-But-2-ynyl-*N*-cyclohept-2-enyl-4-methyl-benzenesulfonamide (2b). A colorless solid. Mp 93–96 °C. (Ether/hexane); IR (nujol) ν 2213, 1647, 1596, 1336, 1162 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.26–2.23 (m, 8H), 1.68 (t, J=2.4 Hz, 3H), 2.42 (s, 3H), 3.93–4.10 (m, 2H), 4.56 (br, 1H), 5.52 (m, 1H), 5.70–5.79 (m, 1H), 7.27 (d, J=8.3 Hz, 2H), 7.77 (d, J=8.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 3.5 (CH_3), 21.5 (CH_3), 26.3 (CH_2), 27.6 (CH_2), 28.2 (CH_2), 33.2 (CH_2), 33.7 (CH_2), 59.6 (CH), 75.2 (C), 80.1 (C), 127.5 (CH×2), 129.2 (CH×2), 132.3 (CH), 133.4 (CH), 138.2 (C), 142.9 (C); LRMS m/z 317 (M^+), 249, 234, 162, 155, 94, 91; HRMS calcd for $C_{18}H_{23}NO_2S$ (M^+) 317.1449, found 317.1442. Anal. calcd for $C_{18}H_{23}NO_2S$: C, 68.10; H, 7.30; N, 4.41; S, 10.10. Found: C, 68.08; H, 7.18; N, 4.37; S, 10.15.

4.6.3. *N*-But-2-ynyl-*N*-cyclooct-2-enyl-4-methyl-benzenesulfonamide (2c). A colorless solid. Mp 85–87 °C. (Ethyl acetate/hexane); IR (nujol) ν 2214, 1648, 1597, 1333, 1162 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.32–1.77 (m, 8H), 1.67 (t, J=2.4 Hz, 3H), 2.11–2.21 (m, 2H), 2.40 (s, 3H), 3.96–4.16 (m, 2H), 4.79–4.88 (m, 1H), 5.54–5.62 (m, 2H), 7.24 (d, J=8.3 Hz, 2H), 7.75 (d, J=8.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 3.4 (CH_3), 21.5 (CH_3), 24.6 (CH_2), 26.1 (CH_2), 26.2 (CH_2), 29.0 (CH_2), 33.5 (CH_2), 34.5 (CH_2), 55.6 (CH), 75.1 (C), 80.2 (C), 127.6 (CH×2), 128.4 (CH), 129.0 (CH×2), 130.1 (CH), 138.0 (C), 142.8 (C); LRMS m/z 331 (M^+), 249, 234, 176, 155, 94, 91; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1631. Anal. calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23; S, 9.67. Found: C, 68.87; H, 7.56; N, 4.24; S, 9.66.

4.6.4. *N*-Cyclohex-2-enyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (2d). A colorless solid; IR (nujol) ν 2116, 1653, 1596, 1332, 1157 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.52–1.98 (m, 6H), 2.16 (t, J=2.4 Hz, 1H), 2.42 (s, 3H), 3.91 (dd, J=18.4, 2.4 Hz, 1H), 4.13 (dd, J=18.4, 2.4 Hz, 1H), 4.46–4.51 (m, 1H), 5.29–5.33 (m, 1H), 5.86–5.91 (m, 1H), 7.28 (d, J=8.4 Hz, 2H), 7.81 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.4 (CH_2), 21.5 (CH_3), 24.3 (CH_2), 28.0 (CH_2), 32.6 (CH_2), 55.1 (CH), 72.0 (CH), 80.6 (C), 127.0 (CH), 127.4 (CH×2), 129.4 (CH×2), 133.2 (CH), 137.9 (C), 143.2 (C); LRMS m/z 289 (M^+), 155, 134, 91; HRMS calcd for $C_{16}H_{19}NO_2S$ (M^+) 289.1136, found 289.1126. Anal. calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84; S, 11.08. Found: C, 66.46; H, 6.58; N, 4.89; S, 11.04.

4.6.5. *N*-Cyclohept-2-enyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (2e). A colorless oil; IR (neat) ν 2120, 1654, 1598, 1336, 1160 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30–2.24 (m, 8H), 2.17 (t, J=2.4 Hz, 1H), 2.42 (s, 3H), 4.01 (d, J=2.4 Hz, 1H), 4.14 (d, J=2.4 Hz, 1H), 4.56 (br, 1H), 5.49 (m, 1H), 5.71–5.81 (m, 1H), 7.27 (d, J=8.1 Hz, 2H), 7.78 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 26.2 (CH_2), 27.3 (CH_2), 28.1 (CH_2), 33.1 (CH_2), 33.2 (CH_2), 59.7 (CH), 72.2 (CH), 80.1 (C), 127.4 (CH×2), 129.4 (CH×2), 132.7 (CH), 132.9 (CH), 137.8 (C), 143.2 (C); LRMS m/z 303 (M^+), 155, 148, 91; HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1282. Anal. calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62; S, 10.57. Found: C, 67.10; H, 6.93; N, 4.60; S, 10.58.

4.6.6. *N*-Cyclooct-2-enyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (2f). The title compound was prepared in quantitative yield according to the literature procedure.[7c]

4.6.7. *N*-Cyclohex-2-enyl-4-methyl-*N*-pent-3-ynyl-benzenesulfonamide (2g). A colorless oil; IR (neat) ν 2934, 1598, 1494, 1448, 1393, 1340, 1233, 1161, 1097, 1044 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.47–1.96 (m, 6H), 1.77 (t, J=2.4 Hz, 3H), 2.42 (s, 3H), 2.36–2.70 (m, 2H), 3.01–3.29 (m, 2H), 4.45 (m, 1H), 5.01–5.05 (m, 1H), 5.75–5.80 (m, 1H), 7.29 (d, J=8.4 Hz, 2H), 7.73 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 3.4 (CH_3), 21.5 (CH_3), 21.7 (CH_2), 22.3 (CH_2), 24.4 (CH_2), 28.9 (CH_2), 43.6 (CH_2), 55.4 (CH), 76.12 (C), 77.4 (C), 127.1 (CH), 127.4 (CH×2), 129.7 (CH×2), 132.5 (CH), 137.8 (C), 143.1 (C); LRMS m/z 317 (M^+), 302, 288, 264, 250, 236, 184, 182, 155, 91; HRMS calcd for $C_{18}H_{23}NO_2S$ (M^+) 317.1449, found 317.1455.

4.6.8. *N*-But-3-ynyl-*N*-cyclohex-2-enyl-4-methyl-benzenesulfonamide (2h). A colorless crystals. Mp 66–67 °C; IR (nujol) ν 3277, 2968, 2867, 1697, 1648, 1597, 1493, 1450, 1336, 1238, 1198, 1162, 1097 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.46–1.62 (m, 2H), 1.75–1.96 (m, 4H), 2.02 (t, J=2.7 Hz, 1H), 2.42 (s, 3H), 2.46–2.78 (m, 2H), 3.07–3.34 (m, 2H), 4.45 (m, 1H), 5.03 (m, 1H), 5.76–5.82 (m, 1H), 7.30 (d, J=8.1 Hz, 2H), 7.73 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.4 (CH_3), 21.6 (CH_2), 21.9 (CH_2), 24.3 (CH_2), 28.8 (CH_2), 43.0 (CH_2), 55.3 (CH), 70.0 (C), 81.3 (CH), 127.0 (CH), 127.1 (CH×2), 129.7 (CH×2), 132.7 (CH), 137.6 (C), 143.2 (C); LRMS m/z 303 (M^+), 264, 249, 184, 155, 148, 108, 91. Anal. calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62. Found: C, 67.15; H, 7.08; N, 4.73.

4.7. Synthesis of cycloalkene-yne 7

4.7.1. Carbonic acid (1*R* *, 4*S* *)-4-(*tert*-butyl-dimethyl-silanyloxy)-cyclohex-2-enyl ester methyl ester (6a). A solution of **5a** (789 mg, 3.45 mmol) in CH_2Cl_2 (17 mL) was added pyridine (0.84 mL, 10.4 mmol), methyl chloroformate (0.53 mL, 6.9 mmol) at 0 °C, and the solution was stirred at 0 °C for 1 h. To this solution was added water, and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 9:1) to yield **6a** (988 mg, quant.) as a colorless oil. IR (neat) ν 1747, 1472, 1462, 1442, 1395, 1360, 1344, 1321, 1309, 1270, 1224, 1205, 1149, 1094, 1046, 1025, 1005 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.89 (s, 9H), 1.72–2.00 (m, 4H), 3.77 (s, 3H), 4.16 (br, 1H), 5.01 (br, 1H), 5.78 (dd, J=3.8, 10.3 Hz, 1H), 5.89 (dd, J=2.7, 10.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −4.7 (CH_3), −4.6 (CH_3), 18.0 (C), 25.3 (CH_2), 25.8 (CH_3×3), 28.2 (CH_2), 54.5 (CH_3), 66.2 (CH), 70.9 (CH), 125.4 (CH), 136.9 (CH), 155.4 (C); LRMS m/z 229 (M^+−Bu), 211, 185, 151, 133; HRMS calcd for $C_{10}H_{17}O_4Si$ (M^+−Bu) 229.0896, found 229.0880. Anal. calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.73; H, 9.20.

4.7.2. Carbonic acid (1*R* *,4*S* *)-4-(*tert*-butyl-dimethyl-silanyloxy)-cyclopent-2-enyl ester methyl ester (6b). A colorless oil; IR (neat) ν 1748, 1472, 1462, 1443, 1375, 1361, 1335, 1268, 1193, 1132, 1098, 1048, 1007 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.06 (s, 6H), 0.86 (s, 9H), 1.65 (dt, J=13.9, 7.3 Hz, 1H), 2.80 (dt, J=13.9, 7.3 Hz, 1H), 3.74 (s, 3H), 4.68 (t, J=5.7 Hz, 1H), 5.35 (t, J=5.7 Hz, 1H), 5.89 (d, J=5.4 Hz, 1H), 5.97 (d, J=5.4 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −4.8 (CH_3), −4.7 (CH_3), 18.0 (C), 25.8 (CH_3×3), 40.9 (CH_2), 54.5 (CH_3), 74.6 (CH), 80.4 (CH), 130.5 (CH), 139.4 (CH), 155.4 (C); LRMS m/z 271 (M^+−H), 215, 197, 171, 151, 133, 125, 111; HRMS calcd for $C_{13}H_{23}O_4Si$ (M^+−H) 271.1365, found 271.1363.

4.7.3. *N*-{(1*R* *,4*S* *)-4-(*tert*-Butyl-dimethylsilanyloxy)-cyclohex-2-enyl}-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (7a). To a solution of **6a** (430 mg, 1.5 mmol), **3b** (337 mg, 1.6 mmol), and PPh_3 (37 mg, 0.15 mmol) in THF (15 mL) was added $Pd_2dba_3{\cdot}CHCl_3$ (37 mg, 0.04 mmol), and the solution was degassed through freeze–pump–thaw cycle. The whole solution was stirred at room temperature for 48 h. The solvent was removed, and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate 20:1–10:1) to yield **7a** (471 mg, 75%) as colorless needles. IR (film) ν 2121, 1654, 1598, 1338, 1255, 1163, 1093 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.87 (s, 9H), 1.56–1.72 (m, 3H), 2.01–2.08 (m, 1H), 2.14 (t, J=2.4 Hz, 1H), 2.42 (s, 3H), 3.95 (dd, J=18.4, 2.7 Hz, 1H), 4.06 (m, 1H), 4.11 (dd, J=18.4, 2.7 Hz, 1H), 4.35–4.40 (m, 1H), 5.41 (dd, J=10.0, 2.4 Hz, 1H), 5.83–5.89 (m, 1H), 7.28 (d, J=8.4 Hz, 2H), 7.81 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −4.8 (CH_3), −4.5 (CH_3), 18.0 (C), 21.5 (CH_3), 22.5 (CH_2), 25.8 (CH_3×3), 30.4 (CH_2), 32.9 (CH_2), 54.7 (CH), 63.0 (CH), 72.1 (CH), 80.3 (C), 127.5 (CH×2), 129.1 (CH), 129.5 (CH×2), 135.0 (CH), 137.9 (C), 143.3 (C); LRMS m/z 404 (M^+−CH_3), 362, 266, 155, 132, 117, 91; HRMS calcd for $C_{18}H_{24}NO_3SSi$ (M^+−Bu) 362.1246, found 362.1233. Anal. calcd for $C_{22}H_{33}NO_3SSi$: C, 62.97; H, 7.93; N, 3.34; S, 7.64. Found: C, 63.05; H, 7.80; N, 3.22; S, 7.59.

4.7.4. *N*-[(1*R* *,4*S* *)-4-(*tert*-Butyl-dimethyl-silanyloxy)-cyclopent-2-enyl]-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (7c). A colorless crystal. Mp 97.5 °C (EtOAc/hexane); IR (nujol) ν 3261, 2925, 2855, 2120, 1594, 1330, 1154 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.84 (s, 9H), 1.57 (m, 1H), 2.08 (t, J=2.4 Hz, 1H), 2.41 (s, 3H), 2.46 (m, 1H), 4.02 (brs, 2H), 4.58 (br, 1H), 4.80 (br, 1H), 5.63 (m, 1H), 5.87 (m, 1H), 7.27 (d, J=8.6 Hz, 2H), 7.79 (d, J=8.6 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −4.8 (CH_3), −4.7 (CH_3), 18.0 (C), 21.5 (CH_3), 25.8 (CH_3×3), 32.4 (CH_2), 38.7 (CH_2), 61.8 (CH), 71.9 (C), 74.6 (CH), 80.7 (CH), 127.5 (CH×2), 129.4 (CH×2), 131.6 (CH), 137.5 (C), 138.2 (CH), 143.3 (C); LRMS m/z 405 (M^+), 390, 348, 308, 250, 155, 139, 118, 91. Anal. calcd for $C_{21}H_{31}NO_3SSi$: C, 62.18; H, 7.70; N, 3.45. Found: C, 61.97; H, 7.69; N, 3.47.

4.7.5. *N*-{(1*S* *,4*S* *)-4-(*tert*-Butyl-dimethylsilanyloxy)-cyclohex-2-enyl}-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (7b). To a solution of **5a** (437 mg, 1.92 mmol), **3b** (570 mg, 2.88 mmol), and PPh_3 (1.03 g, 3.83 mmol) in THF (10 mL) was added DEAD (0.6 mL, 3.83 mmol) at 0 °C, and the solution was stirred at room temperature for 10 h. The solvent was removed, and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate 9:1) to yield **7b** (500 mg, 62%) as a colorless oil. IR (neat) ν 2120, 1654, 1598, 1338, 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.87 (s, 9H), 1.47–1.56

(m, 1H), 1.73–1.83 (m, 1H), 1.87–1.91 (m, 1H), 1.97–2.01 (m, 1H), 2.17 (t, J=2.4 Hz, 1H), 2.42 (s, 3H), 3.88 (dd, J=18.4, 2.4 Hz, 1H), 4.07 (dd, J=18.4, 2.4 Hz, 1H), 4.24 (m, 1H), 4.50 (m, 1H), 5.29 (dd, J=10.4, 1.6 Hz, 1H), 5.74 (dd, J=10.4, 2.0 Hz, 1H), 7.27 (d, J=8.0 Hz, 2H), 7.78 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.7 (CH_3), −4.5 (CH_3), 18.2 (C), 21.6 (CH_3), 25.9 (CH_3×3), 27.0 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 55.3 (CH), 66.9 (CH), 72.3 (CH), 80.3 (C), 127.3 (CH×2), 127.8 (CH), 129.4 (CH×2), 137.5 (C), 137.6 (CH), 143.3 (C); LRMS m/z 404 (M^+-CH_3), 362, 288, 264, 155, 132, 91; HRMS calcd for $C_{18}H_{24}NO_3SSi$ (M^+-Bu) 362.1246, found 362.1230. Anal. calcd for $C_{22}H_{33}NO_3SSi$: C, 62.97; H, 7.93; N, 3.34; S, 7.64. Found: C, 62.83; H, 7.72; N, 3.16; S, 7.67.

4.7.6. *N*-[(1*S,4*S**)-4-(*tert*-Butyl-dimethyl-silanyloxy)-cyclopent-2-enyl]-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (7d).** A colorless oil; IR (neat) ν 3277, 2954, 2930, 2856, 2361, 2344, 1598, 1339, 1162 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.84 (s, 9H), 1.84 (m, 1H), 2.07 (t, J=2.4 Hz, 1H), 2.13 (m, 1H), 2.41 (s, 3H), 3.78 (dd, J=18.9, 2.4 Hz, 1H), 3.97 (dd, J=18.9, 2.4 Hz, 1H), 4.98 (m, 1H), 5.20 (m, 1H), 5.55–5.59 (m, 1H), 5.89–5.93 (m, 1H), 7.27 (d, J=8.4 Hz, 2H), 7.77 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ−4.7 (CH_3×2), 18.1 (C), 21.5 (CH_3), 25.8 (CH_3×3), 32.5 (CH_2), 38.4 (CH_2), 63.3 (CH), 72.2 (C), 76.3 (CH), 79.9 (CH), 127.5 (CH×2), 129.5 (CH×2), 131.8 (CH), 137.3 (C), 139.6 (CH), 143.4 (C); LRMS m/z 405 (M^+), 390, 348, 250, 155, 139, 118, 91; HRMS calcd for $C_{20}H_{28}NO_3SSi$ (M^+-Me) 390.1559, found 390.1547. Anal. calcd for $C_{21}H_{31}NO_3SSi$: C, 62.18; H, 7.70; N, 3.45; S, 7.91. Found: C, 61.99; H, 7.68; N, 3.42; S, 8.08.

4.8. Typical procedure for the preparation of cycloalkene-yne 14

To a solution of **13a** (2.2 mL, 17.3 μmol) in CH_2Cl_2 (49 mL) was added DIBAL-H (42 mL, 39 mmol, 0.93 M in hexane), and the solution was stirred at −78 °C for 1 h. To this solution was added MeOH and 3 N NaOH aq. at −78 °C and the aqueous layer was extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated. To a solution of the crude alcohol in CH_2Cl_2 (32 mL) were added CBr_4 (6.5 g, 19.5 mmol) and PPh_3 (5.9 g, 22.5 mmol), and the solution was stirred at room temperature for 2 h. To a solution of propargyl bromide (5.9 mL, 86 mmol) and K_2CO_3 (9.6 g, 69 mmol) in CH_3CN (115 mL) was added the above solution, and the whole solution was stirred at room temperature for 16 h. Then the solution was filtered through Celite. To this mother liquid was added pyridine (15.5 mL, 193 mmol) and *p*-toluenesulfonyl chloride (24.5 g, 130 mmol), and the solution was stirred at room temperature for 25 h. To this solution was added MeOH and the solution was diluted with ethyl acetate. The organic layer was washed with 10% HCl aq., 10% NaOH aq., and brine, dried over Na_2SO_4 and evaporated. After the solvent was removed, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate 5:1) to yield **14a** (2.3 g, 45%) as a colorless crystal.

Typical procedure for the preparation of cycloalkene-yne **14d–e**. Et_3N (0.30 mL, 2.13 mmol) and $ClPO(OEt)_2$ (0.17 mL, 1.16 mmol) was added to a solution of **13d** (108.5 mg, 0.97 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After stirring for 1 h at the same temperature, propargylamine (0.10 mL, 1.45 mmol) was added. The resulting solution was stirred for 22 h at room temperature. Saturated $NaHCO_3$ solution was added, and the aqueous phase was extracted with AcOEt. The organic phase was washed with saturated NH_4Cl solution and brine, and dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt 3:2) to afford crude amide (89.7 mg, 62%). A solution of crude amide (260 mg, 1.74 mmol) in DMF (6 mL) was added to a suspension of NaH (85 mg, 2.09 mmol) in DMF (3 mL) at 0 °C. After stirring for 1 h at room temperature, BnBr (0.33 mL, 2.79 mmol) was added at 0 °C. The resulting solution was stirred for 30 min at room temperature. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with AcOEt. The organic phase was washed with H_2O and brine, and dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt 3:1) to afford **14d** (353 mg, 85%) as a pale yellow oil.

4.9. Spectral data for 14

4.9.1. *N*-Cyclopent-1-enylmethyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (14a). A colorless crystal. Mp 55.5 °C. (Ether/hexane); IR (nujol) ν 3259, 2923, 2114, 1654, 1596, 1343, 1160 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.89 (dt, J=7.3 Hz, 2H), 1.97 (t, J=2.4 Hz, 1H), 2.24–2.36 (m, 4H), 2.42 (s, 3H), 3.86 (s, 2H), 4.04 (d, J=2.4 Hz, 2H), 5.69 (brs, 1H), 7.28 (d, J=8.1 Hz, 2H), 7.74 (d, J=8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 23.4 (CH_2), 32.5 (CH_2), 33.0 (CH_2), 35.6 (CH_2), 46.5 (CH_2), 73.5 (CH), 76.7 (C), 127.8 (CH×2), 129.4 (CH×2), 130.6 (CH), 136.1 (C), 138.2 (C), 143.4 (C); LRMS m/z 289 (M^+), 155, 134, 91. Anal. calcd for $C_{16}H_{19}NO_2S$: C, 66.41; H, 6.62; N, 4.84; S, 11.08. Found: C, 66.42; H, 6.73; N, 4.79; S, 11.14.

4.9.2. *N*-Cyclohex-1-enylmethyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (14b). A colorless crystal. Mp 54–54.5 °C. (Ether/hexane); IR (nujol) ν 3292, 2926, 2853, 1596, 1346, 1158 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.57 (m, 4H), 1.94 (t, J=2.4 Hz, 1H), 1.99 (m, 4H), 2.42 (s, 3H), 3.67 (s, 2H), 4.02 (d, J=2.4 Hz, 2H), 5.68 (s, 1H), 7.28 (J=8.4 Hz, 2H), 7.73 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 22.2 (CH_2), 22.5 (CH_2), 25.2 (CH_2), 25.8 (CH_2), 35.2 (CH_2), 52.8 (CH_2), 73.4 (CH), 76.6 (C), 127.6 (CH), 127.8 (CH×2), 129.3 (CH×2), 131.6 (C), 136.2 (C), 143.3 (C); LRMS m/z 303 (M^+), 288, 222, 155, 148, 91; HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1303. Anal. calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62; S, 10.57. Found: C, 67.11; H, 7.13; N, 4.47; S, 10.71.

4.9.3. *N*-Cyclohept-1-enylmethyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (14c). A colorless crystal. Mp 72–73 °C. (Ether/hexane); IR (nujol) ν 3304, 2922, 2852, 1654, 1597, 1348, 1163 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.48–1.54 (m, 4H), 1.69 (m, 2H), 1.92 (t, J=2.4 Hz, 1H), 2.08–2.21 (m, 4H), 2.42 (s, 3H), 3.65 (s, 2H), 4.04 (d,

J=2.4 Hz, 2H), 5.79 (m, 1H), 7.28 (d, J=8.4 Hz, 2H), 7.74 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (CH_3), 26.7 (CH_2), 27.0 (CH_2), 28.5 (CH_2), 30.0 (CH_2), 32.2 (CH_2), 35.1 (CH_2), 54.4 (CH_2), 73.6 (CH), 77.2 (C), 127.9 (CH×2), 129.3 (CH×2), 132.9 (CH), 136.2 (C), 137.7 (C), 143.3 (C); LRMS m/z 317 (M^+), 162, 155, 91. Anal. calcd for $C_{16}H_{19}NO_2S$: C, 68.10; H, 7.30; N, 4.41; S, 10.10. Found: C, 68.00; H, 7.28; N, 4.46; S, 10.16.

4.9.4. *N*-Benzyl-*N*-(prop-2-ynyl)-1-cyclopentene-1-carboxamide (14d). A pale yellow oil; IR (neat) ν 2120 (w), 1714 (s), 1644 (s), 1606 (s), 1454 (s), 1244 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.93 (tt, J=7.5, 7.5 Hz, 2H), 2.25 (br, 1H), 2.43–2.52 (br, 2H), 2.63–2.72 (m, 2H), 4.06–4.14 (br, 2H), 4.75 (s, 2H), 6.08 (br, 1H), 7.24–7.37 (m, 5H); ^{13}C NMR (67.8 MHz, DMSO) δ 21.9, 32.4, 33.6, 35.4, 48.6, 73.7, 78.9, 126.5, 126.7, 127.7, 131.6, 136.4, 137.3, 167.7; EI-LRMS m/z 239 (M^+), 211, 200, 95, 91; EI-HRMS m/z calcd for $C_{16}H_{17}ON$ (M^+) 239.1310, found 239.1297.

4.9.5. *N*-Benzyl-*N*-(prop-2-ynyl)-1-cyclohexene-1-carboxamide (14e). A colorless liquid; IR (neat) ν 2118 (w), 1621 (s), 1495 (m), 1451 (s), 1239 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.58–1.75 (m, 4H), 2.07–2.15 (m, 2H), 2.23–2.30 (m, 3H), 4.04–4.10 (br, 2H), 4.73 (s, 2H), 5.99 (br, 1H), 7.23–7.37 (m, 5H); ^{13}C NMR (67.8 MHz, DMSO) δ 20.7, 21.1, 23.6, 24.9, 35.6, 48.5, 73.7, 78.9, 126.6, 126.9, 126.9, 127.9, 133.4, 136.6, 171.3; EI-LRMS m/z 253 (M^+), 214, 109, 91; EI-HRMS m/z calcd for $C_{17}H_{19}ON$ (M^+) 253.1467, found 253.1467.

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