JOC Article

Rh(I)-Catalyzed Pauson−Khand Reaction and Cycloisomerization of Allenynes: Selective Preparation of Monocyclic, Bicyclo[*m*.3.0], and Bicyclo[5.2.0] Ring Systems

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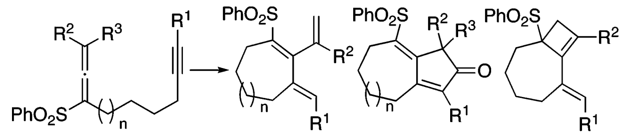

Rhodium(I)-catalyzed PKR of allenynes was found to be applicable for constructing azabicyclo-[5.3.0]decadienone as well as oxabicyclo[5.3.0]decadienone frameworks. In addition, a reliable procedure for constructing a 10-monosubstituted bicyclo[5.3.0]deca-1,7-dien-9-one ring system by the rhodium(I)-catalyzed PKR of allenynes was developed under the condition of 10 atm of CO. Investigation of the rhodium(I)-catalyzed cycloisomerization of 4-phenylsulfonylnona-2,3-dien-8-ynes under nitrogen atmosphere gave the corresponding cyclohexene derivatives, whereas the C_1-homologated allenynes produced cycloheptene derivatives and/or bicyclo[5.2.0]nonene skeletons depending on the substitution pattern at the allenic terminus. Thus, proper choice of the starting allenynes and reaction conditions led to the selective formation of 2-phenylsulfonylbicyclo[5.3.0]-deca-1,7-dien-9-ones (Pauson−Khand-type product), 3-alkylidene-1-phenylsulfonyl-2-vinylcyclo-heptene derivatives, and bicyclo[5.2.0]nonene frameworks.

Introduction

The $Co_2(CO)_8$-mediated Pauson−Khand reaction (PKR)[1] is well recognized as a formal [2 + 2 + 1] cyclization of three components, an alkyne, an alkene, and carbon monoxide, on the two cobalt atoms of the cluster complex to produce cyclopentenone derivatives. The intramolecular version of this intriguing [2 + 2 + 1] cyclization procedure has emerged as one of the most convenient and straightforward methods for the construction of the bicyclo[*m*.3.0] skeletons (m = 3, 4) in one operation. However, this attractive ring-closing method generally is not effective for the synthesis of bicyclo[5.3.0]decenones[2,3] in large part due to entropic as well as enthalpic factors which could impede the formation of larger rings.[4] In the previous papers,[5] we developed a new and efficient procedure for the construction of the bicyclo[5.3.0]-decadienone framework **2** ($R^3 = R^4$ = H) based on the Rh(I)-catalyzed intramolecular PKR of 1,1-disubstituted

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(1) For leading reviews, see: (a) Pauson, P. L. In *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field*; de Meijere, A., tom Dieck, H., Eds.; Springer: Berlin, 1988; pp 233−246. (b) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (c) Schore, N. E. *Org. React.* **1991**, *40*, 1−90. (d) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, pp 1037−1064. (e) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: New York, 1995; Vol. 12, pp 703−739. (f) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523−596. (g) Jeong, N. In *Transition Metals in Organic Synthesis*; Beller, H., Bolm, C., Eds; Wiley-VCH: Weinheim, 1998; Vol. 1, pp 560−577. (h) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911−914. (i) Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297−341. (j) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263−3283. (k) Bonaga, L. V. R.; Krafft, M. E. *Tetrahedron* **2004**, *60*, 9795−9833.

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(4) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95−102.

(5) (a) Mukai, C.; Nomura, I.; Yamanishi, K.; Hanaoka, M. *Org. Lett.* **2002**, *4*, 1755−1758. (b) Mukai, C.; Nomura, I.; Kitagaki, S. *J. Org. Chem.* **2003**, *68*, 1376−1385.

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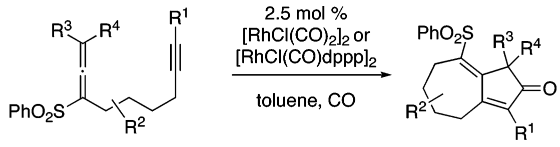
SCHEME 1



1 2

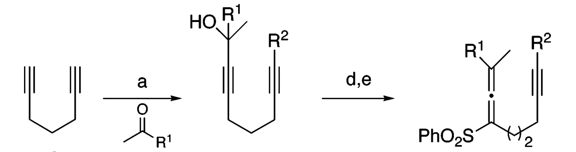
allenynes **1** ($R^3 = R^4 = H$) possessing a phenylsulfonyl group at the C_1-position. In fact, allenynes **1** were refluxed in toluene in the presence of a catalytic amount of commercially available $[RhCl(CO)_2]_2$[6] or $[RhCl(CO)dppp]_2$,[7] prepared from commercially available $[RhCl(cod)]_2$ and 1,3-bis(diphenylphosphino)propane (dppp), under a carbon monoxide atmosphere to afford **2** as the sole product in a moderate to high yield. This ring-closing reaction was shown to occur selectively between the distal double bond of the allenic moiety and the alkyne counterpart of **1** ($R^3 = R^4 = H$), resulting in the exclusive formation of the bicyclo[5.3.0]decadienone framework **2** ($R^3 = R^4 = H$) (Scheme 1).[8]

Our next endeavors focused on (i) the PKR of allenynes **1** having substituents at the allenic terminus (R^3 and/or R^4 = carbon appendage) to confirm the scope and limitations of this rhodium(I)-catalyzed intramolecular ring-closing reaction, (ii) the cycloisomerization reaction of allenynes **1** (R^3 and/or R^4 = carbon appendage) for construction of other carbon frameworks, and (iii) the application of these reactions to the construction of heterocycles. This paper describes the results of the above three topics in detail. [9]

Results and Discussion

Pauson–Khand Reaction of 4-Phenylsulfonylnona-2,3-dien-8-yne Derivatives. At the beginning of this program before considering the ring-closing reaction of allenynes leading to construction of the 10-substituted bicyclo[5.3.0]deca-1,7-dien-9-one frameworks, our first efforts were preliminarily directed toward the PKR of the 4-phenylsulfonylnona-2,3-dien-8-yne derivatives, which would hopefully give the 9-substituted bicyclo[4.3.0]nona-1,6-dien-8-ones. Thus, the required allenynes **5** were easily prepared from commercially available 1,6-heptadiyne (**3**) in a straightforward manner as shown in Scheme 2. According to the literature precedents,[10] compound **3** was treated with EtMgBr in THF, and the resulting acetylide was quenched by addition of acetaldehyde and acetone to afford the propargyl alcohol derivatives **4a** and **4d** in the respective yields of 60% and 52%. Introduction of a silyl group at the triple bond terminus of **4a** and **4d** was realized under conventional conditions to furnish **4b** and **4e** in the respective yields of 76% and 70%. On the other hand, the Sonogashira coupling reaction[11] of **4a** and **4d** with iodobenzene in the presence of $Pd(PPh_3)_2Cl_2$ provided **4c** and **4f** in 85 and 83% yields, respectively. Exposure of **4** to benzenesulfenyl chloride (PhSCl)[12] in THF at −78 °C in the presence of Et_3N effected successive sulfenic ester formation and the [2,3]-sigmatropic rearrangement resulting in the formation of the sulfinyl allenynes, which were subsequently oxidized with *m*-CPBA to produce **5** (Scheme 2).

SCHEME 2[a]



3

b (**4a**: $R^1 = R^2 = H$; **4b**: $R^1 = H$, $R^2 = TMS$) c
4c: $R^1 = H$, $R^2 = Ph$
b (**4d**: $R^1 = Me$, $R^2 = H$; **4e**: $R^1 = Me$, $R^2 = TMS$) c
4f: $R^1 = Me$, $R^2 = Ph$

5a: $R^1 = R^2 = H$
5b: $R^1 = H$, $R^2 = TMS$
5c: $R^1 = H$, $R^2 = Ph$
5d: $R^1 = Me$, $R^2 = H$
5e: $R^1 = Me$, $R^2 = TMS$
5f: $R^1 = Me$, $R^2 = Ph$

[a] Reaction conditions: (a) EtMgBr, THF, 0 °C, **4a** (60%), **4d** (52%); (b) nBuLi, TMSCl, THF, −78 °C, then 10% HCl, rt, **4b** (76%), **4e** (70%); (c) PhI, $Pd(PPh_3)_2Cl_2$, CuI, iPr_2NH, THF, rt, **4c** (85%), **4f** (83%); (d) PhSCl, Et_3N, THF, −78 °C; (e) *m*-CPBA, CH_2Cl_2, 0 °C, **5a** (71%); **5b** (70%), **5c** (93%), **5d** (76%), **5e** (72%), **5f** (78%).

With the required allenynes **5** for the ring-closing reaction in hand, these compounds were submitted to the rhodium(I)-catalyzed ring-closing conditions that had been established for the preparation of bicyclo[5.3.0]deca-1,7-dien-9-ones **1** ($R^3 = R^4 = H$).[5] For the initial evaluation of the rhodium(I)-catalyzed PKR of the allenynes **5** with substitutents at the allenic terminus, a solution of **5a** in toluene in the presence of 2.5 mol % of $[RhCl(CO)dppp]_2$[13] was refluxed under an atmosphere of CO to give the cyclohexene derivative **7a** with a crossed-triene moiety in 95% yield together with a small amount of the bicyclo[4.3.0]nonadienone derivative **6a** (4%) (Table 1, entry 1). The formation of **7a** could be rationalized in terms of the intermediacy of the rhodacyclo intermediate **I**, which would collapse to **7a** via the β-hydride elimination of the methyl group at the allenic terminus,[14−18] whereas **6a** must be produced through a CO-insertion step from the common intermediate **I**. This was not the case for the rhodacyclo intermediate, derived from 1,1-disubstituted allenynes (e.g., **1**, $R^3 = R^4 = H$),[5,6] where no β-hydrogens existed. Trisubstituted allene **5c** with a

(6) Brummond and co-workers have reported the $[RhCl(CO)_2]_2$-catalyzed PKR of allenynes, which involves three successful examples of the formation of the bicyclo[5.3.0]decadienone skeleton: Brummond, K. M.; Chen, H.; Fisher, K. D.; Kerekes, A. D.; Rickards, B.; Sill, P. C.; Geib, S. J. *Org. Lett.* **2002**, *4*, 1931−1934.

(7) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120−129.

(8) For other examples of the formation of the bicyclo[5.3.0]decane skeleton via transition metal-catalyzed PKR of allenynes, see: (a) Shibata, T.; Koga, Y.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 911−919. (b) Ahmar, M.; Locatelli, C.; Colombier, D.; Cazes, B. *Tetrahedron Lett.* **1997**, *38*, 5281−5284.

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(11) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467−4470.

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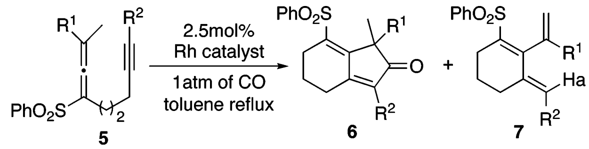
(13) $[RhCl(CO)dppp]_2$ was first used in PKR by Jenog and co-workers, see: (a) Jeong, N.; Lee, S.; Sung, B. K. *Organometallics* **1998**, *17*, 3642−3644. (b) Jeong, N.; Sung, B. K.; Choi, Y. K. *J. Am. Chem. Soc.* **2000**, *122*, 6771−6772.

(14) For reviews on cycloisomerization of enynes, see: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34−42. (b) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813−834.

(15) For Rh(I)-catalyzed enyne cycloisomerization, see: Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490−6491.

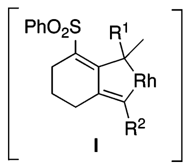
(16) For Rh(I)-catalyzed allenene cycloisomerization, see: (a) Makino, T.; Itoh, K. *Tetrahedron Lett.* **2003**, *44*, 6335−6338. (b) Makino, T.; Itoh, K. *J. Org. Chem.* **2004**, *69*, 395−405.

TABLE 1. Rh(I)-Catalyzed Ring-Closing Reaction of Compounds 5 under an Atmosphere of CO



a: R^1 = H, R^2 = H, **b**: R^1 = H, R^2 = TMS, **c**: R^1 = H, R^2 = Ph,
d: R^1 = Me, R^2 = H, **e**: R^1 = Me, R^2 = TMS, **f**: R^1 = Me, R^2 = Ph

entry	substrate	R^1	R^2	catalyst	time (h)	product and yield (%)	
1	**5a**	H	H	$[RhCl(CO)dppp]_2$	0.5	**6a** (4)	**7a** (95)
2	**5b**	H	TMS	$[RhCl(CO)dppp]_2$	7	**6b** (62)	**7b** (29)
3	**5c**	H	Ph	$[RhCl(CO)dppp]_2$	12	**6c** (8)	**7c** (63)
4	**5a**	H	H	$[RhCl(CO)_2]_2$	0.2	**6a** (59)	**7a** (30)
5	**5b**	H	TMS	$[RhCl(CO)_2]_2$	0.2	**6b** (55)	**7b** (43)
6	**5c**	H	Ph	$[RhCl(CO)_2]_2$	0.2	**6c** (2)	**7c** (61)
7	**5d**	Me	H	$[RhCl(CO)dppp]_2$	6		**7d** (21)
8	**5e**	Me	TMS	$[RhCl(CO)dppp]_2$	12	**6e** (48)	**7e** (29)
9	**5f**	Me	Ph	$[RhCl(CO)dppp]_2$	12		**7f** (83)
10	**5d**	Me	H	$[RhCl(CO)_2]_2$	2		**7d** (66)
11	**5e**	Me	TMS	$[RhCl(CO)_2]_2$	2	**6e** (26)	**7e** (71)
12	**5f**	Me	Ph	$[RhCl(CO)_2]_2$	5		**7f** (60)



phenyl group at the triple bond terminus behaved similarly to **5a** (entry 3). In contrast to these compounds, **5b** provided the Pauson–Khand-type product **6b** as a major product (62%) along with **7b** (29%) (entry 2). Changing a rhodium(I) catalyst from $[RhCl(CO)dppp]_2$ to $[RhCl(CO)_2]_2$[19] brought about some improvement in the PKR of **5a**, resulting in the formation of the bicyclo[4.3.0] derivative **6a** in 59% yield as a major product (entry 4). However, no significant improvement in the chemical yield of **6b** and **6c** was realized when $[RhCl(CO)_2]_2$ was used in the PKR of **5b** and **5c** (entries 5 and 6).[20] The tetrasubstituted allenes **5d–f** were found not to be suitable substrates for rhodium(I)-catalyzed PKR. Thus, allenes **5d** and **5f** exclusively produced the corresponding cyclohexene deriviatives **7d** and **7f** irrespective of the rhodium(I) catalyst (entries 7, 9, 10, and 12). The behavior of allene **5e** with a terminal TMS group was different from those of **5d** and **5f**. Compound **5e** provided the Pauson–Khand-type product **6e** in 48% yield as a major product upon exposure to $[RhCl(CO)dppp]_2$ (entry 8).[21] The ring-closing reaction of **5e** in the presence of $[RhCl(CO)_2]_2$ also gave **6e** in 26% yield, although the predominant production of cyclohexene derivative **7e** was observed in 71% yield (entry 11). The stereochemistry of the *exo*-methylene moiety of cyclohexene derivatives **7** was unambiguously determined to be (*E*) on the basis of ^1H NMR spectral considerations. For example, 13 and 15% enhancement of vinyl protons was recorded when Ha in **7b** was irradiated in an NOE experiment. An NOE experiment with **7f** revealed a 7% enhancement between Ha and R^1 (Me).

We envisaged that increasing the CO pressure in the ring-closing reaction of **5** would facilitate the CO insertion process resulting in the preferential production of the bicyclo[4.3.0]nonadienone skeleton **6** over the *β*-hydride elimination product **7**. To search for what atm of CO pressure was efficient for acceleration of the CO insertion process, the ring-closing reaction of **5e** under several CO pressures was investigated because **5e** was the only tetrasubstituted allene which produced the Pauson–Khand-type product **6e** (Table 1, entries 8 and 11). Thus, a solution of compound **5e** in toluene was heated at 120 °C in the presence of 2.5 mol % of $[RhCl(CO)_2]_2$ under 5 atm of CO for 4 h to furnish predominantly the desired **6e** in 84% yield along with **7e** in 10% yield (Table 2, entry 2). The selective formation of **6e** was realized by increasing the CO pressure. Further increasing the CO pressure from 5 to 10 atm produced **6e** in the highest chemical yield (93%) (entry 3). A pressure higher than 10 atm of CO was found to be ineffective in comparison with 10 atm of CO. In fact, a slightly lowered chemical yield of

(17) During this ongoing study, a similar Rh(I)-catalyzed allenyne cycloisomerization has been reported independently by two groups. Brummond and co-workers have reported the $[RhCl(CO)_2]_2$-catalyzed construction of six-membered triene derivatives: (a) Brummond, K. M.; Chen, H.; Sill, P.; You, L. *J. Am. Chem. Soc.* **2002**, *124*, 15186–15187. (b) Brummond, K. M.; Mitasev, B. *Org. Lett.* **2004**, *6*, 2245–2248. An example of the preparation of seven-membered oxacycle with triene moiety using a $RhCl(PPh_3)_3$-catalyzed reaction, developed by Shibata and co-workers, has also been reported. Shibata, T.; Takesue, Y.; Kadowaki, S.; Takagi, K. *Synlett* **2003**, 268–270.

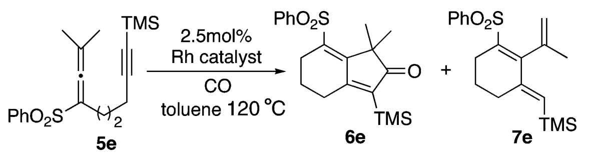
(18) For other examples of transition-metal-catalyzed allenyne cycloisomerizations, see: (a) Pagenkopf, B. L.; Belanger, D. B.; O'Mahony, D. J. R.; Livinghouse, T. *Synthesis* **2000**, 1009–1019. (b) Oh, C. H.; Jung, S. H.; Rhim, C. Y. *Tetrahedron Lett.* **2001**, *42*, 8669–8671.

(19) $[RhCl(CO)_2]_2$ was first used in PKR by Narasaka and co-workers, see: (a) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249–250. (b) Kobayashi, T.; Koga, Y.; Narasaka, K. *J. Organomet. Chem.* **2001**, *624*, 73–87.

(20) $[RhCl(COD)]_2$ was examined for PKR of compounds **5a–c** under an atmosphere of CO gave **6a–c** (21–65%) and **7a–c** (25–58%). No significant difference from $[RhCl(CO)dppp]_2$ and $[RhCl(CO)_2]_2$ could be observed.

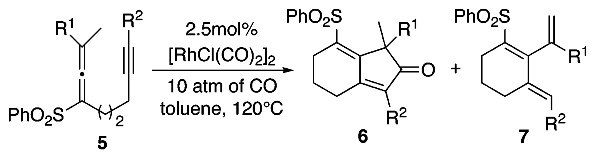
(21) Compound **6e** (81%) was predominantly formed along with **7e** (18%) when treated with 2.5 mol % of $[RhCl(COD)]_2$.

TABLE 2. Rh(I)-Catalyzed Ring-Closing Reaction of Compounds 5e under CO Pressure



entry	CO pressure (atm)	catalyst	time (h)	product and yield (%) 6e	7e
1	1	$[RhCl(CO)_2]_2$	2	26	73
2	5	$[RhCl(CO)_2]_2$	4	84	10
3	10	$[RhCl(CO)_2]_2$	5	93	5
4	20	$[RhCl(CO)_2]_2$	9	87	6
5	20	$[RhCl(CO)dppp]_2$	20	2	21

TABLE 3. Rh(I)-Catalyzed Ring-Closing Reaction of Compounds 5a−d in the Presence of $[RhCl(CO)_2]_2$ under 10 atm of CO Pressure



a: R^1 = H, R^2 = H, **b**: R^1 = H, R^2 = TMS, **c**: R^1 = H, R^2 = Ph,
d: R^1 = Me, R^2 = H

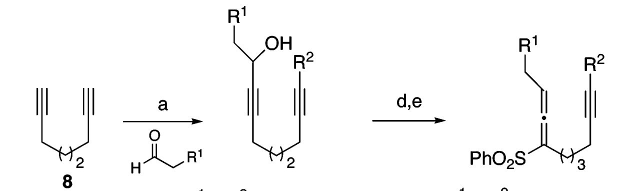
entry	substrate	R^1	R^2	time (h)	product and yield (%)	
1	**5a**	H	H	0.3	**6a** (65)	**7a** (23)
2	**5b**	H	TMS	0.5	**6b** (72)	**7b** (25)
3	**5c**	H	Ph	0.3	**6c** (26)	**7c** (56)
4	**5d**	Me	H	6		**7d** (57)

6e (87%) was observed when the ring-closing reaction was performed under 20 atm CO with otherwise identical conditions (entry 4).[22] $[RhCl(CO)dppp]_2$ gave a trace amount of **6e** (2%) (entry 5).

The Pauson−Khand-type compound, [4.3.0]nonadienone derivative **6e**, was obtained in 93% yield upon exposure of tetrasubstituted allenyne **5e** to 2.5mol % of $[RhCl(CO)_2]_2$ under 10 atm of CO. Therefore, we next examined application of the optimized conditions to other 4-phenylsulfonylnona-2,3-dien-8-yne derivatives. The results are presented in Table 3. As can be seen in Table 3, preferential formation of the Pauson−Khand-type products **6a** and **6b** could be attained (entries 1 and 2), although the selectivity was much lower than that of **5e** where the Pauson−Khand-type compound **6e** was formed in an almost exclusive manner. In the case of **5c**, the bicyclic derivative **6c** was no longer a major product (entry 3). In addition, **6d** could not be isolated from the reaction mixture (entry 4). Thus, it turned out that increasing the CO pressure (10 atm) in the ring-closing reaction of trisubstituted allenynes **5** favored Pauson−Khand-type products **6** over β-elimination compounds **7**, compared with those under an atmosphere of CO. In the cases of tetrasubstituted allenynes **5**, however, the formation of Pauson−Khand-type products **6** seemed to be unfavorable even under 10 atm of CO except for the case of **5e**.

(22) 2.5 mol % of $[RhCl(COD)]_2$ catalyzed PKR of **5e** under 10 atm of CO to give **6e** in 87% yield along with a small amount of **7e** (5%). When **5e** was treated with 2.5 mol % of $[RhCl(COD)]_2$ under 20 atm of CO, **6e** was obtained in 81% yield along with **7e** in 15% yield.

SCHEME 3[a]



b (**9a**: R^1 = R^2 = H; **9b**: R^1 = H, R^2 = TMS) c
9c: R^1 = H, R^2 = Ph
9d: R^1 = ^{n}Pr, R^2 = TMS
9e: R^1 = Ph, R^2 = TMS
9f: R^1 = BnO, R^2 = TMS

10a: R^1 = R^2 = H
10b: R^1 = H, R^2 = TMS
10c: R^1 = H, R^2 = Ph
10d: R^1 = ^{n}Pr, R^2 = TMS
10e: R^1 = Ph, R^2 = TMS
10f: R^1 = BnO, R^2 = TMS

[a] Reaction conditions: (a) EtMgBr, THF, 0 °C, **9a** (58%); (b) nBuLi, TMSCl, THF, −78 °C, then 10% HCl, rt, **9b** (85% from **9a**), **9d** (41% from **8**), **9e** (47% from **8**), **9f** (40% from **8**); (c) PhI, $Pd(PPh_3)_2Cl_2$, CuI, iPr_2NH, THF, rt, **9c** (95%); (d) PhSCl, Et_3N, THF, −78 °C; (e) *m*-CPBA, CH_2Cl_2, 0 °C, **10a** (65%), **10b** (77%), **10c** (67%), **10d** (88%), **10e** (87%), **10f** (88%).

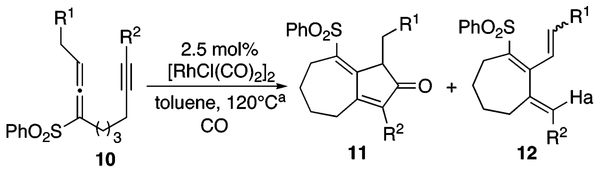
Preparation of 10-Substituted 2-Phenylsulfonylbicyclo[5.3.0]deca-1,7-dien-9-ones by Pauson−Khand Reaction. By taking advantage of the optimized conditions for the PKR of 4-phenylsulfonylnona-2,3-dien-8-ynes **5**, the formation of 10-substituted bicyclo[5.3.0]-decadienone frameworks from trisubstituted allenes **10** was investigated. According to the procedure[10] described for the preparation of **5** from **3**, commercially available 1,7-octadiyne (**8**) was converted into the corresponding propargyl alcohol derivatives **9**, which were then submitted to [2,3]-sigmatropic rearrangement and oxidation to provide six trisubstituted allenes **10** as depicted in Scheme 3.

Upon exposure to the optimized conditions (2.5 mol % of $[RhCl(CO)_2]_2$ under 10 atm of CO in toluene at 120°C), **10a** predominantly produced 10-methylbicyclo[5.3.0]deca-1,7-dien-9-one **11a**, but the yield was fairly low (17%) (Table 4, entry 1). Similar congeners possessing TMS or a phenyl group at the triple bond terminus, **10b** and **10c**, gave the corresponding bicyclic compounds **11b** and **11c** in high yield in a highly selective manner (entries 2 and 3). Furthermore, exclusive construction of 10-butyl-, 10-benzyl-, and 10-benzyloxymethylbicyclo[5.3.0]decadienone skeletons **11d**−**f** was realized in acceptable yield (entries 4−6). In these cases, the formation of cycloheptene derivatives **12d**−**f** could be completely suppressed. Compounds **10a** without a substituent at the triple bond terminus furnished **11a** in a low yield (entry 1). However, **11a** might be prepared in an acceptable yield via the TMS-congener **11b** because the TMS group can be regarded as a surrogate for H.[23] The ring-closing reaction of **10** under an atmosphere of CO was examined as a control experiment (entries 7−13), where the predominant formation of cycloheptene derivatives **12** was consistently observed except for the benzyl congener **10e**.

1-Methyl-4-phenylsulfonyldeca-2,3-dien-9-ynes **14** (tetrasubstituted allenes) were prepared from **8** via diynes **13** (Scheme 4) and subsequently exposed to the best conditions so far ($[RhCl(CO)_2]_2$ under 10 atm of CO in toluene at 120 °C). However, Pauson−Khand-type prod-

(23) (a) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825−2828. (b) Büchi, G.; Wüest, H. *Tetrahedron Lett.* **1977**, 4305−4306. (c) Miller, R. B.; Al-Hassan, M. I. *J. Org. Chem.* **1983**, *48*, 4113−4116.

TABLE 4. Rh(I)-Catalyzed PKR of Compounds 10 under 10 atm of CO

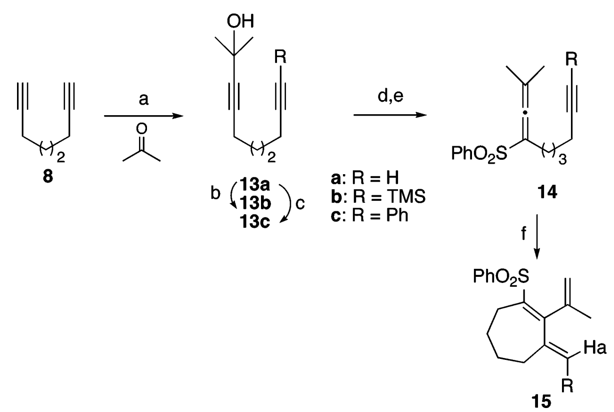


a: $R^1 = R^2$ = H; **b**: R^1 = H, R^2 = TMS, **c**: R^1 = H, R^2 = Ph; **d**: R^1 = ^{n}Pr, R^2 = TMS; **e**: R^1 = Ph, R^2 = TMS; **f**: R^1 = BnO, R^2 = Ph

entry	substrate	R^1	R^2	CO (atm)	time (h)	product and yield (%)	
1	**10a**	H	H	10	3	**11a** (17)	**12a** (2)
2	**10b**	H	TMS	10	13	**11b** (79)	**12b** (8)
3	**10c**	H	Ph	10	6	**11c** (80)	**12c** (8)
4	**10d**	nPr	TMS	10[b]	13	**11d** (67)	
5	**10e**	Ph	TMS	10[b]	12	**11e** (86)	
6	**10f**	BnO	TMS	10	6	**11f** (91)	
7	**10a**	H	H	1[c]	1	**11a** (4)	**12a** (77)
8	**10a**	H	H	1[c,d]	15	**11b** (7)	**12a** (43)
9	**10b**	H	TMS	1[c]	3	**11b** (19)	**12b** (68)
10	**10b**	H	TMS	1[c,d]	6	**11b** (37)	**12b** (47)
11	**10c**	H	Ph	1[c]	4	**11c** (14)	**12c** (62)
12	**10d**	nPr	TMS	1[c]	5	**11d** (24)	**12d** (70)[e]
13	**10e**	Ph	TMS	1[c]	6	**11e** (79)	**12e** (7)[f]

[a] Bath temperature. [b] 10 mol% of $[RhCl(CO)_2]_2$ was used. [c] Refluxed in toluene. [d] $[RhCl(CO)dppp]_2$ was used instead of $[RhCl(CO)_2]_2$. [e] A mixture of (*E*)- and (*Z*)-isomers was obtained in a ratio of 4 to 1. [f] A mixture of (*E*)- and (*Z*)-isomers was obtained in a ratio of 3 to 1.

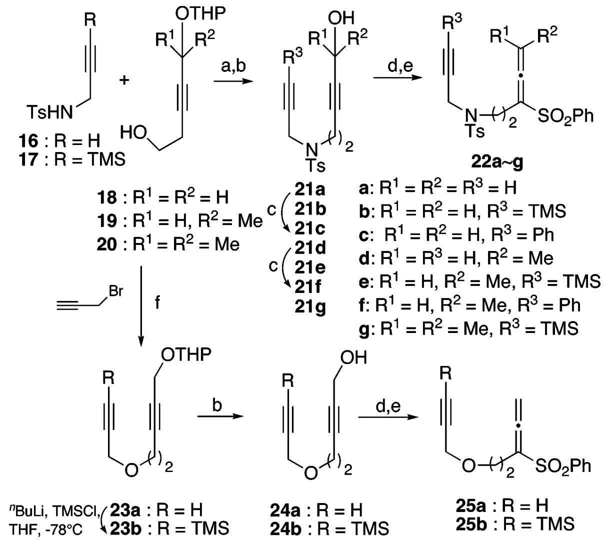
SCHEME 4[a]



[a] Reaction conditions: (a) EtMgBr, THF, 0 °C, **13a** (54%); (b) nBuLi, TMSCl,THF, −78 °C, then 10% HCl, rt, **13b** (68%); (c) PhI, $Pd(PPh_3)_2Cl_2$, CuI, iPr_2NH, THF, rt, **13c** (92%); (d) PhSCl, Et_3N, THF, −78 °C; (e) *m*-CPBA, CH_2Cl_2, 0 °C, **14a** (73%), **14b** (81%), **14c** (77%); (f) 2.5 mol % $[RhCl(CO)_2]_2$, toluene, CO (10 atm), 120 °C, **15a** (6%), **15b** (14%) [recovery of **14b** (20%)], **15c** (69%)

ucts could not be detected in the reaction mixture. Production of cycloheptene frameworks **15a**,**b**[24] in low yield was observed instead. In the case of the phenyl congener **14c**, the triene derivative **15c** was formed in good yield (69%). The formation of the triene skeleton **15** was consistent with that observed in the ring-closing reaction of 1-methylnona-2,3-dien-8-yne derivative **5d** under 10 atm of CO pressure, where cyclohexene derivative **7d** was exclusively produced (see Table 3). On the

SCHEME 5[a]



[a] Reaction conditions: (a) DEAD, PPh_3, THF, 0 °C to rt; (b) PPTS, EtOH, 55 °C, **21a** (53%), **21b** (37%), **21d** (63%), **21e** (47%), **21g** (52%), **24a** (92% from **18**), **24b** (36% from **18** via **23a**); (c) PhI, $Pd(PPh_3)_2Cl_2$, CuI, iPr_2NH, THF, rt, **21c** (88%), **21f** (85%); (d) PhSCl, Et_3N, THF, −78 °C; (e) *m*-CPBA, CH_2Cl_2, 0 °C, **22a** (72%), **22b** (91%), **22c** (86%), **22d** (81%), **22e** (95%), **22f** (88%), **22g** (94%), **25a** (82%), **25b** (89%); (f) tBuOK, THF, 0 °C

basis of these results obtained in Table 4 and Scheme 4 in combination with those in Table 3, it might be concluded that $[RhCl(CO)_2]_2$-catalyzed the intramolecular PKR of trisubstituted allenes under 10 atm of CO proceeded selectively to afford the corresponding 10-monosubstituted 2-phenylsulfonylbicyclo[5.3.0]deca-1,7-dien-9-ones **11** in reasonable yield. However, tetrasubstituted allenes were shown to be generally not suitable substrates for rhodium(I)-catalyzed PKR.

Application of rhodium(I)-catalyzed PKR to the construction of azabicyclo as well as oxabicyclo[5.3.0] ring systems was the next subject in this investigation. To this end, the starting allenynes were synthesized by conventional means as depicted in Scheme 5. Condensation of *N*-tosylpropargylamides **16**[17a] and **17**[25] with homopropargyl alcohols **18**–**20**[26] under the Mitsunobu conditions[18a] gave the corresponding condensed products, which were treated with PPTS in EtOH to afford **21**. On the other hand, the oxygen congeners **24** were prepared from homopropargyl alcohol **18** via the Williamson ether synthesis. The diyne derivatives **21a**–**g** and **24a**,**b** were then exposed to the two-step conditions for transformation of the propargyl alcohol moiety into a phenylsulfonylallene group to provide the corresponding aza-allenynes **22a**–**g** and oxa-allenynes **25a**,**b**, respectively.

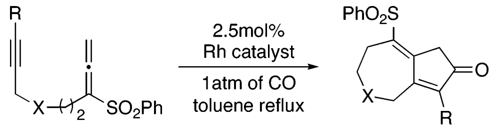
According to the previously reported procedure for the PKR of 1,1-disubstituted allenes,[5] the *N*-tosylamide derivatives **22a**–**c** were exposed to a rhodium(I) catalyst in refluxing toluene under an atmosphere of CO to afford the desired azabicyclo[5.3.0]decadienone derivatives **26a**–**c** in high yield (Table 5, entries 1–6). Similarly, the oxygen

(24) (*E*)-Stereochemistry of **15** was determined on the basis of NOE experiments. For instance, 3.4% enhancement of vinyl protons and 1.5% enhancement of methyl group were recorded when Ha of **15c** was irradiated.

(25) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, *124*, 5025–5036.

(26) (a) Landor, P. D.; Landor, S. R.; Pepper, E. S. *J. Chem. Soc. C* **1967**, 185–189. (b) Claesson, A.; Tämnefors, I.; Olsson, L. I. *Tetrahedron Lett.* **1975**, *16*, 1509–1512. (c) Kim, H. J.; Jang, J. Y.; Chung, K. H.; Lee, J. H. *Biosci. Biotechnol. Biochem.* **1999**, *63*, 494–499.

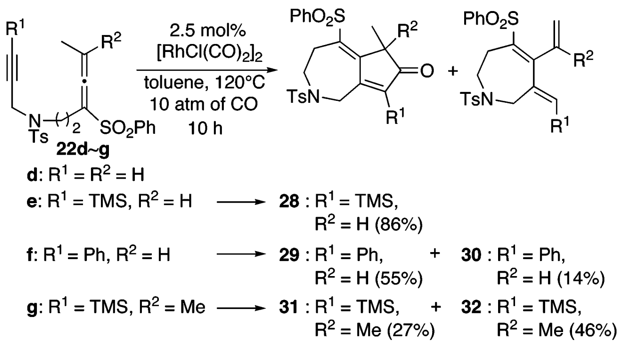
TABLE 5. Rh(I)-Catalyzed Ring-Closing Reaction of Compounds 22a−c and 25a,b under an Atmosphere of CO



22 : X = NTs **a**: R = H, **b**: R = TMS, **26** : X = NTs
25 : X = O **c**: R = Ph **27** : X = O

entry	substrate	X	R	catalyst	time (h)	product and yield (%)
1	**22a**	NTs	H	$[RhCl(CO)dppp]_2$	1	**26a** (89)
2	**22b**	NTs	TMS	$[RhCl(CO)dppp]_2$	1	**26b** (99)
3	**22c**	NTs	Ph	$[RhCl(CO)dppp]_2$	1	**26c** (94)
4	**22a**	NTs	H	$[RhCl(CO)_2]_2$	1	**26a** (67)
5	**22b**	NTs	TMS	$[RhCl(CO)_2]_2$	1	**26b** (84)
6	**22c**	NTs	Ph	$[RhCl(CO)_2]_2$	1	**26c** (94)
7	**25a**	O	H	$[RhCl(CO)dppp]_2$	1	**27a** (66)
8	**25b**	O	TMS	$[RhCl(CO)dppp]_2$	4	**27b** (81)
9	**25a**	O	H	$[RhCl(CO)_2]_2$	2	**27a** (59)
10	**25b**	O	TMS	$[RhCl(CO)_2]_2$	1	**27b** (69)

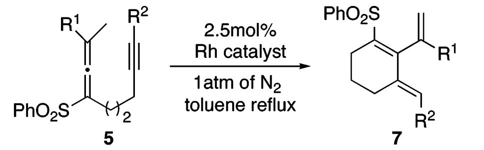
SCHEME 6



congeners **25a**,**b** produced the corresponding oxabicyclo-[5.3.0]decadienone compounds **27a**,**b** in good yield (entries 7−10). The chemical yields in the preparation of the azabicyclic frameworks seemed to be generally higher than those of oxabicyclic ones. Both $[RhCl(CO)dppp]_2$ and $[RhCl(CO)_2]_2$ catalysts served as superior catalysts for this ring-closing reaction under an atmosphere of CO. In particular, the former was consistently more effective than the latter. This result is in good accordance with the previously observed tendency[5] in the PKR of allenynes **1** ($R^3 = R^4 = H$).

$[RhCl(CO)dppp]_2$-catalyzed PKR of the tosylamide derivative **22e** with a trisubstituted-allenyl moiety was carried out under the aforementioned conditions (10 atm of CO in toluene at 120 °C), described for the selective preparation of the bicyclo[5.3.0]decadienone skeleton, to produce the desired product **28** in 86% yield (Scheme 6). The corresponding triene compound could not be found in more than trace quantities in the reaction mixture. The phenyl congener **22f** afforded the azabicyclic product **29** in rather lower yield (55%) along with the triene derivative **30** in 14% yield. However, compound **22d** without a substituent at the triple bond terminus gave an intractable mixture in which neither the azabicyclic product nor the triene derivative could be detected. The PKR of tetrasubstituted allenyne **22g** under 10 atm of CO was fruitless, as can be predicted based on the results of **14** in Scheme 4. Interestingly, a similar PKR of **22g** under an atmosphere of CO provided **31** in 27% yield as

TABLE 6. Rh(I)-Catalyzed Cycloisermerization of Compounds 5 under an Atmosphere of N_2



a: R^1 = H, R^2 = H, **b**: R^1 = H, R^2 = TMS, **c**: R^1 = H, R^2 = Ph,
d: R^1 = Me, R^2 = H, **e**: R^1 = Me, R^2 = TMS, **f**: R^1 = Me, R^2 = Ph

entry	substrate	R^1	R^2	catalyst	time (h)	product and yield (%)
1	**5a**	H	H	$[RhCl(CO)dppp]_2$	2	**7a** (95)
2	**5b**	H	TMS	$[RhCl(CO)dppp]_2$	12	**7b** (74)
3	**5c**	H	Ph	$[RhCl(CO)dppp]_2$	0.2	**7c** (89)
4	**5a**	H	H	$[RhCl(CO)_2]_2$	0.2	**7a** (70)
5	**5b**	H	TMS	$[RhCl(CO)_2]_2$	2	**7b** (73)[a]
6	**5c**	H	Ph	$[RhCl(CO)_2]_2$	0.2	**7c** (59)
7	**5d**	Me	H	$[RhCl(CO)dppp]_2$	3	**7d** (58)[b]
8	**5e**	Me	TMS	$[RhCl(CO)dppp]_2$	5	**7e** (92)
9	**5f**	Me	Ph	$[RhCl(CO)_2]_2$	7	**7f** (78)[c]
10	**5d**	Me	H	$[RhCl(CO)_2]_2$	3	**7d** (93)
11	**5e**	Me	TMS	$[RhCl(CO)_2]_2$	5	**7e** (57)[d,e]
12	**5f**	Me	Ph	$[RhCl(CO)_2]_2$	7	**7f** (79)[f]

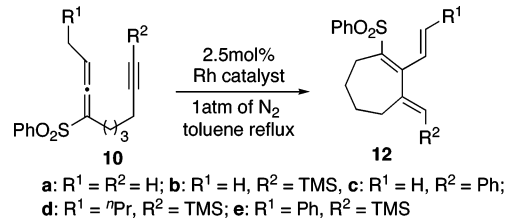
[a] Compound **6b** was obtained in 10% yield. [b] Compound **5d** was recovered in 4% yield. [c] Compound **5f** was recovered in 5% yield. [d] Compound **6e** was obtained in 5% yield. [e] Compound **5e** was recovered in 17% yield. [f] Compound **5f** was recovered in 11% yield.

a minor product along with the triene derivative **32** (46%). This behavior might be the same as that of **5e** (Table 1, entry 11). Thus, the rhodium(I)-catalyzed PKR of not only 1,1-disubstituted but also 1,1,3-trisubstituted allenynes can be applicable to the construction of the corresponding azabicyclo- as well as oxabicyclo[5.3.0]-deca-1,7-diene-9-one frameworks in reasonable yield.

Cycloisomerization of 4-Phenylsulfonylnona-2,3-dien-8-yne and 4-Phenylsulfonyldeca-2,3-dien-9-yne Derivatives under Nitrogen Atmosphere. In the rhodium(I)-catalyzed PKR of 4-phenylsulfonylnona-2,3-dien-8-yne derivatives **5** under an atmosphere of CO (previously reported conditions),[5] undesirable cyclohexene compounds **7** with a crossed-triene moiety were isolated as a major product. On the other hand, preferential formation of bicyclo[4.3.0]nonadienones **6** as well as bicyclo[5.3.0]decadienones **11** under the Pauson−Khand conditions was realized by increasing the CO pressure (1−10 atm). Thus, the next phase of this program involved development of a reliable procedure for the selective construction of 3-alkylidene-1-phenylsulfonyl-2-vinylcyclohex-1-ene derivatives **7**. A solution of trisubstituted allene **5a** in toluene was refluxed in the presence of 2.5 mol % of $[RhCl(CO)dppp]_2$ under an atmosphere of nitrogen to give **7a** in 95% yield as a sole product (Table 6, entry 1). A similar treatment of compounds **5b** and **5c** afforded **7b** and **7c** in respective yields of 74% and 89% (entries 2 and 3). $[RhCl(CO)_2]_2$ also worked well to furnish the corresponding triene derivatives **7a**−**c** (entries 4−6).[27] In the case of **5b** with $[RhCl(CO)_2]_2$, unexpected formation of bicyclo[4.3.0] derivative **6b** (10%) was recorded (entry 5). Presumably, one of two carbon monoxide ligands on the rhodium catalyst would, in part,

(27) $[RhCl(COD)_2]_2$ could be used for transformation of **5a**−**c** into **7a**−**c** in slightly lower yield [**7a** (69%), **7b** (66%), and **7c** (44%)].

TABLE 7. Rh(I)-Catalyzed Cycloisomerization of Compounds 10 under an Atmosphere of N_2



entry	substrate	R^1	R^2	catalyst	time (h)	product and yield (%)
1	**10a**	H	H	$[RhCl(CO)dppp]_2$	2	**12a** (82)
2	**10b**	H	TMS	$[RhCl(CO)dppp]_2$	6	**12b** (83)
3	**10c**	H	Ph	$[RhCl(CO)dppp]_2$[a]	5	**12c** (29)
4	**10a**	H	H	$[RhCl(CO)_2]_2$	6	**12a** (78)
5	**10b**	H	TMS	$[RhCl(CO)_2]_2$	6	**12b** (69)[b]
6	**10c**	H	Ph	$[RhCl(CO)_2]_2$	9	**12c** (65)
7	**10d**	nPr	TMS	$[RhCl(CO)_2]_2$[a]	5	**12d** (65)[c]
8	**10e**	Ph	TMS	$[RhCl(CO)_2]_2$[d]	5	**12e** (65)[a]

[a] 5 mol% of catalyst was used. [b] The reported yield (59%) in a preliminary communication[9] was improved. [c] A mixture of (*E*)- and (*Z*)-pentenyl isomers, in a ratio of 4 to 1, was obtained. The ratio was determined by ^{1}H NMR. [d] 10 mol% of catalyst was used. [f] A mixture of (*E*)- and (*Z*)-trimethylsilylmethylidene isomers, in a ratio of 3 to 5, was obtained. The ratio was determined by ^{1}H NMR.

participate in the ring-closing reaction. Tetrasubstituted allenes **5d–f** were exposed to both catalysts under an atmosphere of nitrogen to afford the corresponding cyclohexene derivatives **7d–f** in acceptable yields as shown in Table 6. $[RhCl(COD)]_2$ was found to be a less effective catalyst, in comparison with the above two catalysts.[28] Compound **5e** provided a small amount of the bicyclic derivative **6e** (5%) when treated with $[RhCl(CO)_2]_2$ (entry 11), which is in accordance with the result of entry 5.

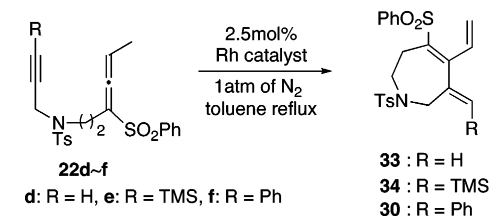
By analogy to the selective transformation of allenes **5** into the cyclohexene derivatives **7** under an atmosphere of nitrogen, the C_1-homologated trisubstituted allenes **10a**,**b** were exposed to 2.5 mol % of $[RhCl(CO)dppp]_2$ in refluxing toluene under an atmosphere of nitrogen to afford the cychoheptene derivatives **12a**,**b** in high yield as expected (Table 7, entries 1 and 2). When **10c** was submitted to the ring-closing conditions with $[RhCl(CO)dppp]_2$, the reaction rate was rather slow and **12c** was formed in 29% yield along with the recovery of the starting material **10c** (51%) (entry 3). $[RhCl(CO)_2]_2$ consistently produced the corresponding cycoheptene derivatives **12a–c** in reasonable yields (entries 4–6). The other two substrates **10d**,**e** also afforded the corresponding cycloheptene derivatives **12d**,**e** in good yields when treated with $[RhCl(CO)_2]_2$ (entries 7 and 8).[29] The nitrogen congeners **22d–f** with a trisubstituted allenyl moiety underwent similar Rh(I)-catalyzed cycloisomerization reaction under the standard conditions to give the corresponding tetrahydroazepines **33**, **34**, and **30**[30] as a sole product (Table 8).

(28) Compounds **7d** (6%), **7e** (31%), and **7f** (48%) were obtained with recovery of the starting materials **5d** (72%), **5e** (51%), and **5f** (36%), respectively.

(29) $[RhCl(COD)_2]_2$ was found not to be a suitable catalyst for transformation of **10** into **12** [**12a** (30%), **12b** (13%), and **12c** (16%)].

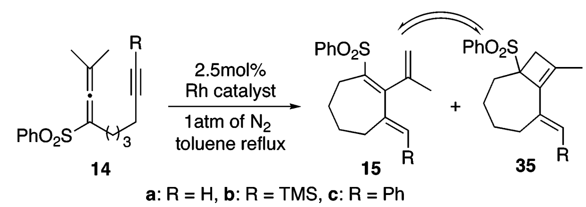
(30) The stereochemistry of tetrahydroazepine derivatives was determined by comparison of ^{1}H NMR spectra with those of carbon congeners.

TABLE 8. Rh(I)-Catalyzed Cycloisomerization of Compounds 22d–f under an Atmosphere of N_2



entry	substrate	R^1	R^2	catalyst	time (h)	product and yield (%)
1	**22d**	H	H	$[RhCl(CO)dppp]_2$	1	**33** (97)
2	**22e**	H	TMS	$[RhCl(CO)dppp]_2$	4	**34** (67)
3	**22f**	H	Ph	$[RhCl(CO)dppp]_2$	4	**30** (48)
4	**22d**	H	H	$[RhCl(CO)dppp]_2$	2	**33** (72)
5	**22e**	H	TMS	$[RhCl(CO)dppp]_2$	2	**34** (91)
6	**22f**	H	Ph	$[RhCl(CO)dppp]_2$	4	**30** (74)

TABLE 9. Rh(I)-Catalyzed Cycloisomerization of Compounds 14 under an Atmosphere of N_2



entry	substrate	R	catalyst	time (h)	product and yield (%)
1	**14a**	H	$[RhCl(CO)dppp]_2$	12	**35a** (22)[a]
2	**14b**	TMS	$[RhCl(CO)dppp]_2$	48	**35b** (19)[b]
3	**14c**	Ph	$[RhCl(CO)dppp]_2$	120	**35c** (49)
4	**14a**	H	$[RhCl(CO)_2]_2$	6	**35a** (58)
5	**14b**	TMS	$[RhCl(CO)_2]_2$	6	**15b** (14) + **35b** (34)[c]
6	**14c**	Ph	$[RhCl(CO)_2]_2$	12	**15c** (12) + **35c** (60)[d]
7	**14c**	Ph	$[RhCl(CO)_2]_2$	120	**35c** (77)
8	**14c**	Ph	$[RhCl(CO)_2]_2$[e]	20	**15c** (62)
9	**14c**	Ph	$[RhCl(CO)_2]_2$[f]	12	**15c** (10) + **35c** (80)

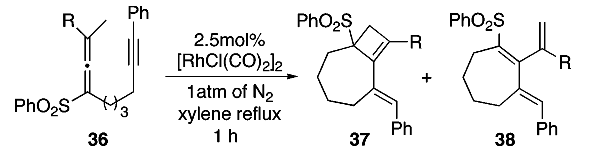
[a] Compound **14a** was recovered in 2% yield. [b] Compound **14b** was recovered in 49% yield. [c] Compound **14b** was recovered in 16% yield. [d] Compound **14c** was recovered in 24% yield. [e] Heated at 80 °C. [f] Refluxed in xylene.

We next investigated rhodium(I)-catalyzed cycloisomerization of 2-methyl-4-phenylsulfonyldeca-2,3-dien-9-yne derivatives (tetrasubstituted allenes), which would afford the cycloheptene skeleton possessing a 2-propenyl moiety at the C_2-position. Thus, allenyne **14a** was refluxed in toluene for 12 h in the presence of 2.5 mol % of $[RhCl(CO)dppp]_2$ to give unexpectedly the bicyclo[5.2.0]nonene compound **35a** in 22% yield instead of the triene derivative **15a** along with the recovery of a small amount of the starting material **14a** (2%) (Table 9, entry 1). Bicyclo[5.2.0] frameworks **35b**,**c** were also formed under similar conditions, but the corresponding triene derivatives **15b**,**c** could not be isolated from the reaction mixture (entries 2 and 3). $[RhCl(CO)_2]_2$ catalyzed the formation of the bicyclo[5.2.0] skeleton to afford **35a–c** more effectively (entries 4–6). The structure of **35** was elucidated by spectral evidence.[31] Furthermore, X-ray crystallographic analysis[32] of **35c** unambiguously established its structure as depicted. To obtain more information on the transformation of alleynes **14** into **35**, several experiments were performed using phenyl derivative **14c**. As mentioned earlier, **14c** produced **35c** (60%) and the triene derivative **15c** (12%) along with the starting **14c** (24%) upon exposure to $[RhCl(CO)_2]_2$ in refluxing toluene for 12 h (entry 6). When the reaction time was prolonged to 120 h under the same conditions, exclusive formation of **35c** in 77% was observed (entry 7). On the other hand, the cycloisomerization reaction of **14c** at lower reaction temperature (80 °C in toluene) for 20 h furnished the triene compound **15c** in 62% yield as a sole product (entry 8). Refluxing in xylene fairly shortened the reaction time (12 h) leading to the formation of **35c** in 80% yield along with **15c** in 10% yield (entry 9).

The formation of **35** can be attributable to a thermal 4π-electrocyclic reaction[33] of the primarily formed triene derivatives **15**, and transformation of the latter to the former seemed to require refluxing temperature in xylene. Thus, compound **15c** was refluxed in xylene for 9 h in the absence of a rhodium catalyst to give a mixture of **15c** and **35c** in a ratio of 30:70.[34] A similar mixture (**15c**/**35c** = 30:70) was obtained when **35c** was exposed to xylene refluxing conditions for 9 h. These transformation reactions suggested that the bicyclo[5.2.0]nonene framework is thermodynamically more stable than the corresponding triene derivative.[35] Rhodium catalyst was found to accelerate the conversion of **15** into **35**. As a matter of fact, a solution of **15c** in xylene was refluxed for 9 h in the presence of 2.5 mol % of $[RhCl(CO)_2]_2$ to furnish **35c** in 60% yield along with the recovery of **15c** in 11% yield.

Some additional tetrasubstituted allenes **36**[36] with a terminal methyl group were exposed to 2.5 mol % of $[RhCl(CO)_2]_2$ in refluxing xylene. The results were summarized in Table 10. Tetrasubstituted allene **36a** possessing a phenyl group at the allenic terminus gave the bicyclo[5.2.0] compound **37a** in 88% yield (Table 10, entry 1). The electronic property on the aromatic ring of an allenic terminus did not affect this transformation. Thus, *p*-methoxy and *p*-nitro derivatives **36b**,**c** provided the corresponding bicyclic compounds **37b**,**c** in high yield (entries 2 and 3). Compound **36d** having an ethoxycarbonyl group instead of a phenyl group also produced the bicyclo[5.2.0] derivative **37d** in rather lower yield (19%). The triene derivative **38d** was obtained as a major product even for a prolonged reaction time (12 h) (entry 4). A terminal hydroxyl group tolerates this transformation to give **37e** in 21% yield along with a small amount of **38e** (entry 5).

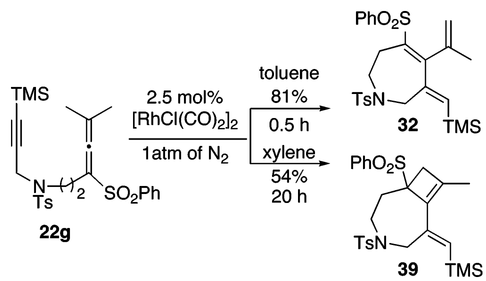
TABLE 10. Rh(I)-Catalyzed Cycloisomerization of Compounds 36 under an Atmosphere of N_2



entry	substrate	R	time (h)	product and yield (%)
1	**36a**	Ph	1	**37a** (88)
2	**36b**	*p*-$MeOC_6H_4$	1	**37b** (87)
3	**36c**	*p*-$NO_2C_6H_4$	1	**37c** (84)
4	**36d**	CO_2Et^a	12	**37d** (19) + **38d** (43)^b
5	**36e**	CH_2OH	6	**37e** (21) + **38e** (3)

^{a} Refluxed in xylene for 12 h. ^{b} Compounds **37d** (12%) and **38d** (56%) were obtained when refluxed in xylene for 1 h.[9]

SCHEME 7



The tetrasubstituted allene **22g** having an *N*-tosylamide functionality behaved similarly to the carbon congeners **14** and **36**. The exclusive construction of the tetrahydroazepine derivative **32** in 81% yield was observed when **22g** was refluxed in toluene in the presence of 2.5 mol % of $[RhCl(CO)_2]_2$, whereas the bicyclo[5.2.0]-nonene framework **39** (54%) was formed in a highly selective manner under xylene refluxing conditions (Scheme 7).

Interestingly, exclusive formation of triene derivatives **41** having a trisubstituted olefin functionality at the C_2-position was observed when the allene **40** with a diethyl group at the allenic terminus was submitted to xylene refluxing conditions (Scheme 8). The corresponding bicyclo[5.2.0] derivative **42** could not be detected in the reaction mixture. The cyclohexyl derivative **43** also produced **44** in a high yield instead of **45**. These observations were in sharp contrast to those observed in the cycloisomerization of compounds **14**, **22g**, and **36** under refluxing xylene conditions, where the formation of bicyclo[5.2.0] derivatives via the intermediacy of the triene derivatives commonly having a 1,1-disubstituted olefin functionality at the C_2-position was observed. On the other hand, no formation of bicyclo[4.2.0]nonene skeleton **46** could be detected in the cycloisomerization reaction of 4-phenylsulfonylnona-2,3-dien-8-yne derivatives **5** under toluene refluxing conditions (see Table 6). The cyclohexene derivatives **7** with a vinyl or a propenyl group at the C_2-position, which are regarded as presumable intermediates for the construction of bicyclo[4.2.0]-nonene derivatives **46**, were refluxed in xylene to afford only an intractable mixture or the recovery of **7**. In addition, conversion of the cycloheptene derivatives **12** into the bicyclo[5.2.0] derivatives **37** could not be realized (Scheme 8).[37]

(31) For example, an NOE experiment of **35b** showed 6.1% enhancement of methyl group upon irradiation of vinyl proton, while 5.6% enhancement between methyl group and vinyl proton of **35c** was observed.

(32) Data for crystallographic analysis of **35c** was described in the Supporting Information.

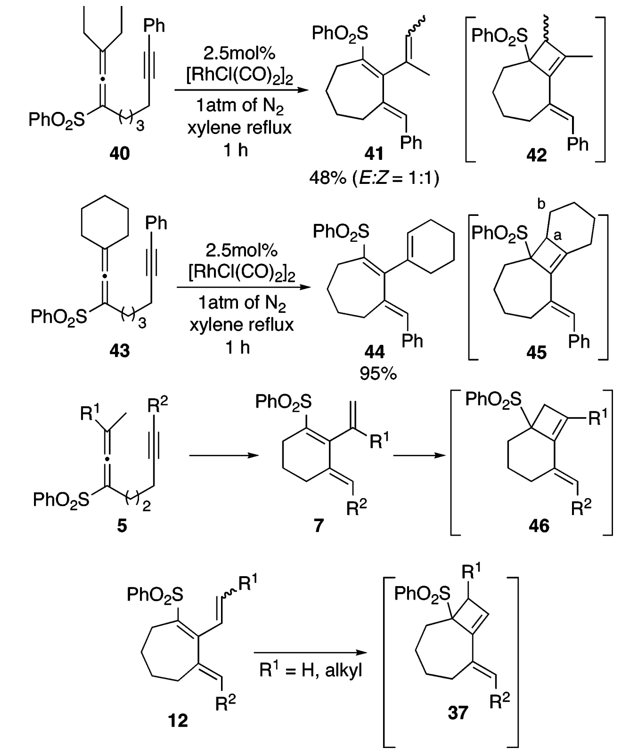
(33) (a) Doorakian, G. A.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 3582−3584. (b) Doorakian, G. A.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 5310−5311. (c) Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471−477 and references therein.

(34) Determined by ^{1}H NMR.

(35) Compounds **15c** (10%) and **35c** (42%) were isolated after refluxing a solution of **15c** in xylene for 9 h.

(36) Compounds **36** were prepared by the standard procedure described in this paper; see the Supporting Information.

SCHEME 8



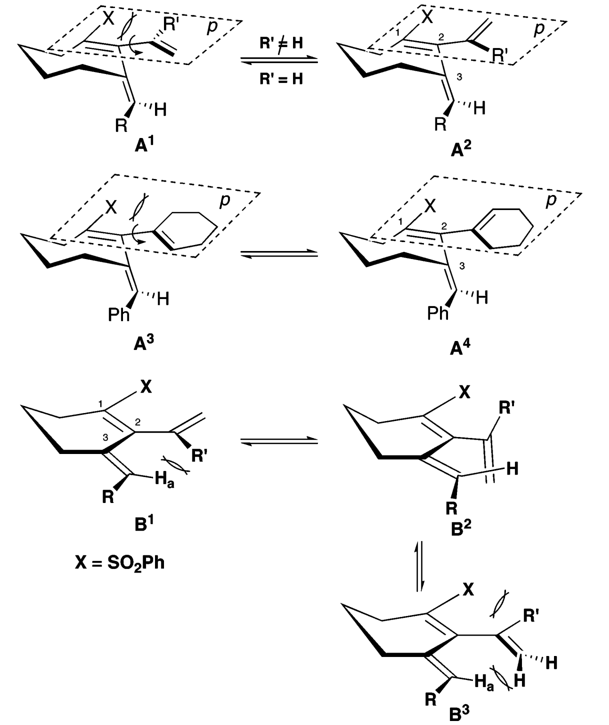


FIGURE 1. Conformational analysis of cyclohexene and cycloheptene derivatives.

To summarize the results so far obtained, there are several comments concerning the formation of the cyclobutene-fused bicyclic frameworks such as bicyclo[5.2.0]-nonenes via thermal 4π-electrocyclic reaction, which should deserve mention. (i) The thermal 4π-electrocyclic reaction leading to cyclobutene-fused bicyclic frameworks proceeds whenever the substrates not only have a seven-membered basic skeleton but also a 1,1-disubstituted olefin moiety at the C$_2$-position such as **15**, **32**, and **38**. In other words, one of two substituents at the allenic terminus of the starting tetrasubstituted allenes has to be a methyl group. (ii) Irrespective of the substitutent at the triple bond terminus, cyclobutene formation can be attained if the substrates meet the requirement (i). (iii) Cycloheptene derivatives **12**, **30**, **33**, **34**, **41**, and **44**, possessing a vinyl group, a 1,2-disubstituted olefin, or a trisubstituted olefin moiety at the C$_2$-position, were unable to convert into the corresponding cyclobutene-fused bicyclic compounds. (iv) Cyclohexene derivatives **7** never produced bicyclo[4.2.0] derivatives **46**, even if compounds **7** had a 1,1-disubstituted olefin moiety at the C$_2$-position.

Molecular model considerations of 3-alkylidene-2-vinyl-1-phenylsulfonylcyclohex-1-ene as well as 3-alkylidene-2-vinyl-1-phenylsulfonylcyclohept-1-ene skeletons provided clues to better understand the production of the 6-alkylidene-1-phenylsulfonylbicyclo[5.2.0]non-7-ene framework (Figure 1). A molecular model of 3-alkylidene-2-vinyl-1-phenylsulfonylcyclohept-1-ene skeletons indicates that the alkylidene moiety at the C$_3$-position must be out of the plane p, on which a double bond between C$_1$ and C$_2$, and an olefin moiety at the C$_2$-position both exist. There are two significant conformers, which should be considered for cycloheptene derivatives with a vinyl group or a 1,1-di-substituted olefin part at the C$_2$-position; one is **A**^{1} and the other **A**^{2}. Conformer **A**^{1} (R′ = alkyl) would suffer from a serious nonbonding interaction with a phenylsulfonyl group. This would not be the case with conformer **A**^{2} where unfavorable interaction could not be predicted. By that means, conformer **A**^{2} (R′ = alkyl) must be thermodynamically preferred over conformer **A**^{1}, the former of which would therefore readily undergo a thermal 4π-electrocyclic reaction resulting in the formation of the bicyclo[5.2.0]nonene framework. In the case of cycloheptene derivatives (R′ = H), however, both conformers **A**^{1} and **A**^{2} no longer have such a significantly unfavorable interaction with a phenylsulfonyl group. Therefore, conformational bias due to the rotational barrier of a vinyl group at the C$_2$-position is not expected, and this would make its reactivity toward 4π-electrocyclic reaction very poor. A similar analysis would be applied to cycoheptene derivatives having a trisubstituted olefin functionality at the C$_2$-position. Figure 1 shows two possible conformers **A**^{3} and **A**^{4} for compound **44** as a typical example. Conformer **A**^{3} has a nonbonding interaction with a phenylsulfonyl group like conformer **A**^{1} does. This unfavorable interaction would shift the equilibrium to a more stable conformer **A**^{4}, which might be expected to produce the corresponding cyclobutene derivative **45** (see Scheme 8). Because the thermal 4π-electrocylic reaction proceeds reversibly in a conrotatory ring-closing mode,[33] conformer **A**^{4} must produce **45** with a *cis*-stereochemical relationship between a phenylsulfonyl group and the C$_a$–C$_b$ bond of the cyclohexyl ring, and this steric congestion would exclusively lead to **44** from **45**.[38] The conformation of 3-alkylidene-2-vinylcyclohex-1-ene is quite different from that of 3-alkylidene-2-vinylcyclohept-1-ene. As can be seen in Figure 1, exami-

(37) Compounds **12d**,**e** were exposed to xylene refluxing conditions leading to an intractable mixture.

nation of the molecular model indicates that six sp^2-hybridized carbon centers involving C_1, C_2, C_3, and the C_2-vinyl group can exist on the same plane. There are three possible conformers, $\mathbf{B}^1$, $\mathbf{B}^2$, and $\mathbf{B}^3$, which must be considered for understanding the most preferred conformer. Conformer $\mathbf{B}^1$, leading to the cyclobutene derivative, would suffer from an unfavorable nonbonding interaction between Ha and R′ on the vinyl group at the C_2-position, whereas a more serious interaction of a phenylsulfonyl group with R′ as well as other interactions between two vinyl hydrogens are predicted in conformer $\mathbf{B}^3$. However, the C_2-vinyl group of conformer $\mathbf{B}^2$ can orient perpendicular to the plane, which consists of a double bond between C_1 and C_2, and a C_3-alkylidene moiety, to avoid a nonbonding interaction with not only a phenylsulfonyl group but also the C_3-alkylidene moiety. Therefore, conformer $\mathbf{B}^2$ seems to be the most stable conformer among them. The fact that the bicyclo[4.2.0]-octene framework could not be formed might reflect the stability of conformer $\mathbf{B}^2$.

In summary, we have disclosed that the rhodium(I)-catalyzed PKR of allenynes can be applicable for constructing azabicyclo[5.3.0]decadienone as well as oxabicyclo[5.3.0]decadienone frameworks. A reliable procedure for constructing a 10-monosubstituted-bicyclo[5.3.0]deca-1,7-dien-9-one ring system by the rhodium(I)-catalyzed PKR of allenynes was also developed under the condition of 10 atm of CO. Investigation of the rhodium(I)-catalyzed cycloisomerization of 4-phenylsulfonylnona-2,3-dien-8-ynes under nitrogen atmosphere gave the corresponding cyclohexene derivatives, whereas the C_1-homologated allenynes produced cycloheptene derivatives and/or bicyclo-[5.2.0]nonene skeletons depending on the substitution pattern at the allenic terminus. Thus, proper choice of the starting allenynes and reaction conditions led to the selective formation of 2-phenylsulfonylbicyclo[5.3.0]deca-1,7-dien-9-ones (Pauson−Khand-type product), 3-alkylidene-1-phenylsulfonyl-2-vinylcycloheptene derivatives, and bicyclo[5.2.0]nonene frameworks. The application of this rhodium(I)-catalyzed PKR as well as the cycloisomerization reaction of allenynes to the synthesis of bioactive compounds is now in progress.

Experimental Section

3,8-Nonadiyn-2-ol (4a).[10a] EtMgBr in THF (1.0 M, 5.2 mL, 5.2 mmol) was added to a 0 °C solution of 1,6-heptadiyne (**3**) (400 mg, 19.7 mmol) in THF (8 mL). After the mixture was heated at 50 °C for 1 h and then cooled to 0 °C, acetaldehyde (0.30 mL, 5.2 mmol) was rapidly added. The reaction mixture was further stirred for 15 min at 0 °C and then poured into water. The resulting mixture was extracted with Et_2O, and the extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane−AcOEt (5:1) to afford **4a** (355 mg, 60%) as a colorless oil: IR 3308 cm^{-1}; ^{1}H NMR δ 4.51 (tq, 1H, J = 7.0, 2.0 Hz), 2.37−2.27 (m, 4H), 1.97 (t, 1H, J = 2.0 Hz), 1.73 (tt, 2H, J = 7.0, 7.0 Hz), 1.43 (d, 3H, J = 7.0 Hz); ^{13}C NMR δ 83.5, 83.2, 83.0, 68.9, 58.5, 27.4, 24.6, 17.6, 17.5.

(38) We tried to convert **44** into **45** with a *trans*-relationship between a phenylsulfonyl group and the C_a-C_b bond by a disrotatory ring-closing mode. Thus, a solution of **44** in CH_2Cl_2 was irradiated with a high-pressure mercury lamp through a Pyrex filter to afford a mixture of **44** and its isomer with (*Z*)-benzylidene group at the C_3-position. The formation of **45** with a *trans*-relationship between a phenylsulfonyl group and the C_a-C_b bond could not be detected.

9-(Trimethylsilyl)-3,8-nonadiyn-2-ol (4b). To a solution of **4a** (102 mg, 0.750 mmol) in THF (4 mL) was added nBuLi in hexane (1.4 M, 1.6 mL, 2.3 mmol) at −78 °C. After the mixture was stirred for 1 h, TMSCl (0.60 mL, 4.5 mmol) was added at −78 °C, and the reaction mixture was stirred for 15 min at room temperature. Then, 10% aqueous HCl was added to the reaction mixture, which was stirred for 30 min and then extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with hexane−AcOEt (6:1) to afford **4b** (161 mg, 76%) as a colorless oil: IR 3605, 2172 cm^{-1}; ^{1}H NMR δ 4.50−4.46 (m, 1H), 2.29 (t, 2H, J = 6.9 Hz), 2.28 (dt, 2H, J = 6.9, 2.0 Hz), 1.68 (quin, 2H, J = 6.9 Hz), 1.40 (d, 3H, J = 6.6 Hz); ^{13}C NMR δ 106.2, 85.1, 83.4, 82.8, 58.4, 27.6, 24.6, 19.0, 17.7, 0.1; MS m/z 208 (M^+, 3.8); HRMS calcd for $C_{12}H_{20}OSi$ 208.1283, found 208.1280.

9-Phenyl-3,8-nonadiyn-2-ol (4c).[10b] To a solution of **4a** (134 mg, 0.990 mmol) in THF (5 mL) were successively added CuI (3.8 mg, 2.0×10^{-2} mmol), $Pd(PPh_3)_2Cl_2$ (6.9 mg, 1.0×10^{-2} mmol), and iodobenzene (0.20 mL, 2.0 mmol). After the mixture was stirred for 5 min at room temperature, iPr_2NH (1.4 mL, 10 mmol) was added, and the mixture was further stirred for 15 h. The precipitates were filtered off, and the filtrate was concentrated to leave a residual oil, which was chromatographed with hexane−AcOEt (3:1) to afford **4c** (177 mg, 85%) as a pale yellow oil: IR 3601, 2239 cm^{-1}; ^{1}H NMR δ 7.56−7.41 (m, 2H), 7.30−7.25 (m, 3H), 4.53−4.47 (m, 1H), 2.52 (t, 2H, J = 7.0 Hz), 2.37 (t, 2H, J = 7.0 Hz), 1.98−1.96 (m, 1H), 1.80−1.76 (m, 2H), 1.41 (d, 3H, J = 7.2 Hz); ^{13}C NMR δ 131.5, 128.2, 127.6, 123.7, 89.0, 83.5, 82.9, 81.2, 58.5, 27.8, 24.7, 18.5.

4-(Phenylsulfonyl)-2,3-nonadien-8-yne (5a). To a solution of **4a** (186 mg, 1.37 mmol) and Et_3N (0.60 mL, 4.1 mmol) in THF (14 mL) was gradually added PhSCl (590 mg, 4.10 mmol) at −78 °C. After being stirred for 1.5 h at the same temperature, the reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane−AcOEt (6:1) to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH_2Cl_2 (12 mL) was added m-CPBA (300 mg, 1.70 mmol) at 0 °C. After being stirred for 30 min, the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ and $NaHCO_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with brine, dried, and concentrated to dryness. The residue was chromatographed with hexane−AcOEt (5:1) to afford **5a** (232 mg, 71% for two steps) as a colorless oil: IR 3308, 1960, 1306, 1150 cm^{-1}; ^{1}H NMR δ 7.91−7.87 (m, 2H), 7.65−7.50 (m, 3H), 5.74 (tq, 1H, J = 7.3, 3.1 Hz), 2.41−2.34 (m, 2H), 2.17 (dt, 2H, J = 6.9, 2.6 Hz), 1.90 (t, 1H, J = 2.6 Hz), 1.73 (d, 6H, J = 7.3 Hz); ^{13}C NMR δ 204.3, 140.2, 133.3, 129.0, 128.0, 112.1, 96.4, 83.2, 68.9, 26.4, 25.8, 17.5, 13.4; MS m/z 260 (M^+, 0.6); HRMS calcd for $C_{15}H_{16}O_2S$ 260.0871, found 260.0881.

***N*-(5-Hydroxy-3-pentynyl)-*N*-2-propynyl-(4-methylbenzene)sulfonamide (21a).** To a solution of **16**[17a] (790 mg, 3.80 mmol), PPh_3 (1.1 g, 4.1 mmol), and **18**[26a] (597 mg, 3.24 mmol) in THF (10 mL) was added dropwise DEAD (0.74 mL, 4.1 mmol) at 0 °C. After the mixture was stirred for 2 h at room temperature, THF was evaporated off. The residue was passed through a short pad of silica gel with hexane−AcOEt (7:1) to afford the crude sulfonamide. To a solution of the crude sulfonamide in EtOH (15 mL) was added PPTS (63 mg, 0.25 mmol) at room temperature. Afrer the mixture was stirred for 3 h at 55 °C, EtOH was evaporated off. Chromatography of the residue with hexane−AcOEt (2:1) afforded **21a** (505 mg, 53%) as a colorless oil: IR 3607, 3520, 3306, 1348, 1306, 1163 cm^{-1}; ^{1}H NMR δ 7.74 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.3 Hz), 4.24−4.22 (m, 2H), 4.19 (d, 2H, J = 2.3 Hz), 3.38 (t, 2H, J = 7.3 Hz), 2.56 (tt, 2H, J = 7.3, 2.2 Hz), 2.43 (s, 3H), 2.08 (t, 1H, J = 2.3 Hz), 1.74 (br s, 1H); ^{13}C NMR δ 143.7, 135.6, 129.5, 127.5, 82.1, 80.5, 73.9, 50.9, 45.3, 37.0, 21.4, 18.9; MS m/z 291

(M$^+$, 0.1); HRMS calcd for $C_{15}H_{17}NO_3S$ 291.0929, found 291.0923.

***N*-[3-(Phenylsulfonyl)-3,4-pentadienyl]-*N*-2-propynyl-(4-methylbenzene)sulfonamide (22a).** According to the same procedure described for preparation of **5a**, **22a** (304 mg, 72%) was obtained from **21a** (297 mg, 1.02 mmol) as colorless needles: mp 111.5−113 °C (hexane−AcOEt); IR 3308, 1969, 1936, 1350, 1308, 1161 cm^{-1}; ^{1}H NMR δ 7.94−7.90 (m, 2H), 7.69−7.53 (m, 5H), 7.30−7.26 (m, 2H), 5.43 (t, 2H, J = 2.8 Hz), 4.03 (d, 2H, J = 2.3 Hz), 3.33 (t, 2H, J = 6.8 Hz), 2.60−2.52 (m, 2H), 2.42 (s, 3H), 2.01 (t, 1H, J = 2.3 Hz); ^{13}C NMR δ 208.1, 143.7, 139.6, 135.5, 133.6, 129.5, 129.1, 128.1, 127.5, 109.6, 85.0, 76.3, 74.0, 44.9, 36.7, 25.6, 21.5; MS *m/z* 415 (M$^+$, 0.6). Anal. Calcd for $C_{21}H_{21}NO_4S_2$: C, 60.70; H, 5.10; N, 3.32. Found: C, 60.61; H, 5.10; N, 3.32.

5-(2-Propynyloxy)-2-pentyn-1-ol (24a). tBuOK (300 mg, 2.70 mmol) was added to a solution of **18** (103 mg, 0.559 mmol) in THF (6 mL) at 0 °C. After the mixture was stirred for 30 min, propargyl bromide (0.60 mL, 6.7 mmol) was added at 0 °C. The mixture was further stirred overnight at room temperature, and the reaction mixture was quenched by addition of water, extracted with Et_2O, washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (7:1) gave **23a** (120 mg). To a solution of **23a** (457 mg, 2.05 mmol) in EtOH (16 mL) was added PPTS (52 mg, 0.21 mmol) at room temperature. The mixture was stirred for 1.5 h at 55 °C and then cooled to room temperature. The reaction mixture was concentrated to dryness, and the residue was chromatographed with hexane−AcOEt (2:1) to give **24a** (273 mg, 92% for two steps) as a pale yellow oil: IR 3609, 3308 cm^{-1}; ^{1}H NMR δ 4.24−4.18 (m, 4H), 3.64 (t, 2H, J = 6.8 Hz), 2.52 (tt, 2H, J = 6.8, 2.3 Hz), 2.44 (t, 1H, J = 2.3 Hz), 1.97 (m, 1H); ^{13}C NMR δ 82.2, 79.6, 79.1, 74.7, 67.8, 57.9, 50.7, 19.7; MS *m/z* 138 (M$^+$, 0.1); HRMS calcd for $C_8H_{10}O_2$ 138.0681, found 138.0683.

5-(3-Trimethylsilyl-2-propynyloxy)-2-pentyn-1-ol (24b). nBuLi (4.8 mL, 6.4 mmol, 1.4 M in hexane) was added to a solution of **23a** (954 mg, 4.28 mmol) in THF (9.0 mL) at −78 °C. After the mixture was stirred for 1 h, TMSCl (1.6 mL, 13 mmol) was added at same temperature. The mixture was stirred for 1 h at room temperature, and the reaction mixture was quenched by addition of water, extracted with AcOEt, washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (8:1) gave **23b** (670 mg). To a solution of **23b** in EtOH (18 mL) was added PPTS (57 mg, 0.23 mmol) at room temperature. Then the mixture was stirred for 3 h at 55 °C, and the reaction mixture was concentrated to dryness. Chromatography of the residue with hexane−AcOEt (3:1) gave **24b** (336 mg, 36% for three steps) as a pale yellow oil: IR 3609, 3433, 2174 cm^{-1}; ^{1}H NMR δ 4.25−4.18 (m, 4H), 3.63 (t, 2H, J = 6.9 Hz), 2.53 (tt, 2H, J = 6.9, 2.0 Hz), 1.72 (s, 1H), 0.18 (s, 9H); ^{13}C NMR δ 101.0, 91.6, 82.7, 79.5, 67.9, 58.9, 51.2, 19.9, −0.3; MS *m/z* 210 (M$^+$, 0.1); HRMS calcd for $C_{11}H_{18}O_2Si$ 210.1076, found 210.1062.

3-(Phenylsulfonyl)-5-(2-propynyloxy)-1,2-pentadiene (25a). According to the same procedure described for preparation of **5a**, **25a** (463 mg, 82%) was obtained from **24a** (301 mg, 2.18 mmol) as a colorless oil: IR 3308, 1971, 1938, 1308, 1151 cm^{-1}; ^{1}H NMR δ 7.92−7.89 (m, 2H), 7.67−7.51 (m, 3H), 5.40 (t, 2H, J = 3.3 Hz), 4.06 (d, 2H, J = 2.3 Hz), 3.61 (t, 2H, J = 6.6 Hz), 2.55 (tt, 2H, J = 6.6, 3.3 Hz), 2.39 (t, 1H, J = 2.3 Hz); ^{13}C NMR δ 208.1, 140.0, 133.5, 129.1, 128.1, 109.9, 84.4, 79.3, 74.6, 67.1, 58.0, 27.2; MS *m/z* 262 (M$^+$, 0.4); HRMS calcd for $C_{14}H_{14}O_3S$ 262.0664, found 262.0673.

General Procedure for Ring-Closing Reaction with Rh(I) Catalyst under an Atmosphere of CO. To a solution of allenyne (0.10 mmol) in toluene (1.0 mL) was added 2.5 mol % of Rh(I) catalyst. The reaction mixture was refluxed under a CO atmosphere until the complete disappearance of the starting material as indicated by TLC. Toluene was evaporated off, and the residual oil was chromatographed with hexane−AcOEt to afford cyclized products. Chemical yields are summarized in Tables 1, 2, 4, and 5.

General Procedure for Ring-Closing Reaction with Rh(I) Catalyst under 5−20 atm of CO. To a solution of allenyne (0.10 mmol) in toluene (1.0 mL) was added 2.5 mol % of $[RhCl(CO)_2]_2$. The reaction mixture was heated at 120 °C (the oil bath temperature) under CO pressure shown in the tables until the complete disappearance of the starting material as indicated by TLC. Toluene was evaporated off, and the residual oil was chromatographed with hexane−AcOEt to afford cyclized products. Chemical yields are summarized in Tables 2−4 and Schemes 4 and 6.

General Procedure for Ring-Closing Reaction with Rh(I) Catalyst under N_2. To a solution of allenyne (0.10 mmol) in toluene or xylene (1.0 mL) was added 2.5 mol % of Rh(I) catalyst. The reaction mixture was refluxed under a N_2 atmosphere until the complete disappearance of the starting material as indicated by TLC. Solvent was evaporated off, and the residual oil was chromatographed with hexane−AcOEt to afford cyclized products. Chemical yields are summarized in Tables 6−10 and Schemes 7 and 8.

9-Methyl-2-(phenylsulfonyl)bicyclo[4.3.0]nona-1,6-dien-8-one (6a): colorless plates; mp 88−88.5 °C (Et_2O); IR 1705, 1308, 1151 cm^{-1}; ^{1}H NMR δ 7.90−7.87 (m, 2H), 7.68−7.53 (m, 3H), 6.12 (s, 1H), 3.58 (q, 1H, J = 7.3 Hz), 2.77−2.57 (m, 2H), 2.48 (dt, 2H, J = 17.5, 5.6 Hz), 2.27−2.16 (m, 1H), 1.85−1.74 (m, 2H), 1.54 (d, 3H, J = 7.3 Hz); ^{13}C NMR δ 207.0, 167.2, 148.9, 139.5, 134.3, 133.8, 130.4, 129.3, 128.0, 43.5, 25.82, 25.79, 21.7, 18.4; MS *m/z* 288 (M$^+$, 26.3). Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.57; H, 5.61.

9,9-Dimethyl-2-(phenylsulfonyl)-7-(trimethylsilyl)bicyclo[4.3.0]nona-1,6-dien-8-one (6e): pale yellow plates; mp 122 °C (Et_2O); IR 1692, 1308, 1155 cm^{-1}; ^{1}H NMR δ 7.92−7.88 (m, 2H), 7.67−7.52 (m, 3H), 2.68 (t, 2H, J = 6.3 Hz), 2.31 (t, 2H, J = 6.3 Hz), 1.74 (tt, 2H, J = 6.3, 6.3 Hz), 1.54 (s, 6H), 0.26 (s, 9H); ^{13}C NMR δ 212.9, 172.1, 153.3, 141.6, 140.0, 134.6, 133.4, 129.2, 127.8, 47.2, 27.6, 27.4, 22.6, 22.0, −0.7; MS *m/z* 374 (M$^+$, 26). Anal. Calcd for $C_{19}H_{20}O_3SSi$: C, 64.13; H, 7.00. Found: C, 64.06; H, 7.13.

2-Ethenyl-3-methylene-1-(phenylsulfonyl)cyclohexene (7a): colorless oil; IR 1306, 1148 cm^{-1}; ^{1}H NMR δ 7.86−7.84 (m, 2H), 7.59−7.55 (m, 1H), 7.51−7.48 (m, 2H), 6.79 (ddt, 1H, J = 17.7, 11.7, 1.7 Hz), 5.44−5.42 (m, 2H), 5.21−5.20 (m, 1H), 5.10 (dd, 1H, J = 17.7, 1.7 Hz), 2.58−2.55 (m, 2H), 2.36−2.33 (m, 2H), 1.78−1.73 (m, 2H); ^{13}C NMR δ144.8, 142.5, 141.5, 136.1, 133.0, 131.8, 128.8, 127.6, 121.5, 119.9, 31.5, 27.3, 22.6; MS *m/z* 260 (M$^+$, 0.5); HRMS calcd for $C_{15}H_{16}O_2S$ 260.0871, found 260.0867.

2-(1-Methylethenyl)-1-(phenylsulfonyl)-3-[(*E*)-(trimethylsilyl)methylene]cyclohexene (7e): colorless oil; IR 1304, 1150 cm^{-1}; ^{1}H NMR δ 7.90−7.84 (m, 2H), 7.60−7.45 (m, 3H), 5.98 (s, 1H), 5.17−5.16 (m, 1H), 4.57−4.56 (m, 1H), 2.55−2.53 (m, 4H), 1.84 (s, 3H), 1.80−1.58 (m, 2H), 0.11 (s, 9H); ^{13}C NMR δ 150.7, 148.5, 141.7, 141.1, 135.7, 134.5, 132.9, 128.7, 128.0, 117.0, 30.3, 27.2, 24.1, 22.6, −0.3; MS *m/z* 346 (M$^+$, 0.2); HRMS calcd for $C_{19}H_{26}O_2SSi$ 346.1423, found 346.1430.

10-Methyl-2-(phenylsulfonyl)bicyclo[5.3.0]deca-1,7-dien-9-one (11a): colorless oil; IR 1705, 1308, 1148 cm^{-1}; ^{1}H NMR δ 7.90−7.88 (m, 2H), 7.67−7.55 (m, 3H), 6.12 (s, 1H), 3.59 (q, 1H, J = 7.3 Hz), 2.74−2.54 (m, 2H), 2.25−2.19 (m, 1H), 1.84−1.75 (m, 4H), 1.53 (d, 3H, J = 7.3 Hz); ^{13}C NMR δ 207.3, 172.8, 152.6, 139.9, 136.6, 133.64, 133.59, 129.3, 127.8, 46.4, 28.8, 26.5, 25.8, 22.8, 19.6; MS *m/z* 302 (M$^+$, 1.7); HRMS calcd for $C_{17}H_{18}O_3S$ 302.0977, found 302.0976.

2-Ethenyl-3-methylene-1-(phenylsulfonyl)cycloheptene (12a): colorless oil; IR 1308, 1148 cm^{-1}; ^{1}H NMR δ 7.97 (dd, 1H, J = 17.0, 11.0 Hz), 7.90−7.48 (m, 5H), 5.56 (dd, 1H, J = 17.0, 1.7 Hz), 5.48 (dd, 1H, J = 11.0, 1.7 Hz), 5.35 (d, 1H, J = 1.0 Hz), 4.80 (d, 1H, J = 1.0 Hz), 2.55−2.50 (m, 2H), 2.15−2.11 (m, 2H), 1.71−1.62 (m, 2H), 1.37−1.29 (m, 2H); ^{13}C NMR δ 152.2, 145.9, 141.6, 134.7, 133.0, 131.8, 129.0, 127.2, 124.0, 116.8, 33.9, 30.8, 30.1, 24.7; MS *m/z* 274 (M^+, 5.0); HRMS calcd for $C_{16}H_{18}O_2S$ 274.1028, found 274.1019.

3-Methylene-2-(1-methylethenyl)-1-(phenylsulfonyl)-cycloheptene (15a): colorless oil; IR 1304, 1146 cm^{-1}; ^{1}H NMR δ 7.88−7.86 (m, 2H), 7.58−7.48 (m, 3H), 5.24 (s, 1H), 5.20 (d, 1H, J = 1.5 Hz), 5.01 (t, 1H, J = 1.5 Hz), 4.76 (d, 1H, J = 1.0 Hz), 2.57−2.55 (m, 2H), 2.33 (t, 2H, J = 6.4 Hz), 1.74−1.69 (m, 5H), 1.60−1.57 (m, 2H); ^{13}C NMR δ 155.7, 146.1, 143.6, 141.7, 138.1, 132.7, 128.7, 128.3, 118.9, 115.9, 34.5, 29.4, 29.1, 24.7, 21.6; MS *m/z* 288 (M^+, 81); HRMS calcd for $C_{17}H_{20}O_2S$ 288.1184, found 288.1187.

***N*-(4-Methylbenzenesulfonyl)-6-(phenylsulfonyl)-3-azabicyclo[5.3.0]deca-1(10),6-dien-9-one (26a):** colorless plates; mp 172−173 °C (hexane−AcOEt); IR 1701, 1350, 1308, 1159 cm^{-1}; ^{1}H NMR δ 7.82−7.77 (m, 2H), 7.72−7.51 (m, 5H), 7.28−7.22 (m, 2H), 6.28 (s, 1H), 4.48 (s, 2H), 3.58 (t, 2H, J = 6.3 Hz), 3.24 (s, 2H), 2.85 (t, 2H, J = 6.3 Hz), 2.42 (s, 3H); ^{13}C NMR δ 201.7, 166.2, 145.9, 144.2, 139.5, 136.9, 135.8, 134.1, 133.9, 129.8, 129.6, 127.6, 127.2, 47.4, 44.6, 41.0, 27.1, 21.5; MS *m/z* 443 (M^+, 17.4). Anal. Calcd for $C_{22}H_{21}NO_5S_2$: C, 59.57; H, 4.77; N, 3.16. Found: C, 59.66; H, 4.94; N, 3.15.

6-(Phenylsulfonyl)-3-oxabicyclo[5.3.0]deca-1(10),6-dien-9-one (27a): colorless oil; IR 1705, 1308, 1151 cm^{-1}; ^{1}H NMR δ 7.90−7.87 (m, 2H), 7.67−7.55 (m, 3H), 6.30 (s, 1H), 4.67 (s, 2H), 3.91 (t, 2H, J = 5.6 Hz), 3.61 (s, 2H), 2.99 (t, 2H, J = 5.6 Hz); ^{13}C NMR δ 201.9, 170.0, 145.1, 139.9, 135.9, 135.0, 133.9, 129.5, 127.6, 69.1, 66.6, 41.5, 31.1; MS *m/z* 290 (M^+, 2.5); HRMS calcd for $C_{15}H_{14}O_4S$ 290.0613, found 290.0614.

***N*-(4-Methylbenzenesulfonyl)-8-methyl-6-(phenylsulfonyl)-10-(trimethylsilyl)-3-azabicyclo[5.3.0]deca-1(10),6-dien-9-one (28):** colorless plates; mp 131−132 °C (hexane−AcOEt); IR 1701, 1350, 1308, 1159, 1150 cm^{-1}; ^{1}H NMR δ 7.83−7.80 (m, 2H), 7.70−7.64 (m, 1H), 7.60−7.54 (m, 4H), 7.29−7.26 (m, 2H), 4.76 (d, 1H J = 17.5 Hz), 4.25 (d, 1H, J = 17.5 Hz), 3.64 (q, 1H J = 7.3 Hz), 3.41−3.20 (m, 2H), 2.78−2.57 (m, 2H), 2.42 (s, 3H), 1.26 (d, 3H, J = 7.3 Hz), 0.35 (s, 9H); ^{13}C NMR δ 209.9, 172.1, 153.6, 147.9, 143.9, 139.5, 136.1, 133.9, 130.2, 129.7, 129.4, 127.7, 127.0, 46.6, 44.4, 27.1, 21.4, 18.9, −0.8; MS *m/z* 529 (M^+, 0.7); HRMS calcd for $C_{26}H_{31}NO_5S_2Si$ 529.1413, found 529.1420.

4-Ethenyl-1-(4-methylbenzenesulfonyl)-3-[(*Z*)-phenylmethylene]-5-(phenylsulfonyl)-2,3,6,7-tetrahydro-1*H*-azepine (30): colorless plates; mp 126−127 °C (hexane−AcOEt); IR 1340, 1306, 1163, 1151 cm^{-1}; ^{1}H NMR δ 7.80−7.78 (m, 2H), 7.68 (dd, 2H, J = 17.0, 10.5 Hz), 7.53−7.43 (m, 5H), 7.32−7.29 (m, 4H), 7.25−7.16 (m, 3H), 6.45 (s, 1H), 5.43 (dd, 1H, J = 10.7, 1.5 Hz), 5.42 (dd, 1H, J = 17.0, 1.5 Hz), 3.82 (s, 2H), 3.01 (t, 2H, J = 6.1 Hz), 2.65 (t, 2H, J = 6.1 Hz), 2.33 (s, 3H); ^{13}C NMR δ 151.1, 143.8, 141.1, 136.5, 134.6, 133.6, 133.3, 132.8, 132.6, 132.2, 129.8, 129.4, 129.3, 128.6, 128.5, 127.6, 127.3, 125.3, 47.5, 45.6, 29.3, 21.5; MS *m/z* 505 (M^+, 4.5). Anal. Calcd for $C_{28}H_{27}NO_4S_2$: C, 66.51; H, 5.38; N, 2.77. Found: C, 66.38; H, 5.55; N, 2.72.

***N*-(4-Methylbenzenesulfonyl)-8,8-dimethyl-6-(phenylsulfonyl)-10-(trimethylsilyl)-3-azabicyclo[5.3.0]deca-1(10),6-dien-9-one (31):** colorless needles; mp 181−181.5 °C (hexane−AcOEt); IR 1699, 1350, 1308, 1157 cm^{-1}; ^{1}H NMR δ 7.86−7.81 (m, 2H), 7.73−7.50 (m, 5H), 7.30−7.24 (m, 2H), 4.48 (s, 2H), 2.99 (t, 2H, J = 6.3 Hz), 2.64 (t, 2H, J = 6.3 Hz), 2.41 (s, 3H), 1.43 (s, 6H), 0.35 (s, 9H);^{13}C NMR δ 212.0, 171.8, 157.7, 147.2, 144.0, 139.5, 136.0, 133.9, 131.9, 129.8, 129.4, 128.1, 127.0, 50.2, 46.2, 45.1, 28.9, 22.3, 21.5, −0.7; MS *m/z* 543 (M^+, 8.3); HRMS calcd for $C_{27}H_{33}NO_5S_2Si$ 543.1569, found 543.1569.

1-(4-Methylbenzenesulfonyl)-4-(1-methylethenyl)-5-(phenylsulfonyl)-3-[(*Z*)-(trimethylsilyl)methylene]-2,3,6,7-tetrahydro-1*H*-azepine (32): colorless needles; mp 52−53 °C (hexane−AcOEt); IR 1350, 1306, 1161, 1142 cm^{-1}; ^{1}H NMR δ 7.91−7.90 (m, 2H), 7.65−7.63 (m, 3H), 7.58−7.48 (m, 2H), 7.33−7.32 (m, 2H), 5.92 (s, 1H), 5.09 (s, 1H), 5.04 (s, 1H), 3.93 (s, 2H), 3.37−3.36 (m, 2H), 2.74−2.72 (m, 2H), 2.43 (s, 3H), 1.14 (s, 3H), 0.13 (s, 9H); ^{13}C NMR δ 154.4, 149.4, 143.6, 141.1, 140.6, 136.3, 135.4, 134.2, 132.8, 129.9, 129.2, 128.5, 127.0, 120.8, 49.0, 45.4, 27.1, 21.5, 20.5, −0.6; MS *m/z* 512 (M^+, 1.2). Anal. Calcd for $C_{26}H_{33}NO_4S_2Si$: C, 60.55; H, 6.45; N, 2.72. Found: C, 60.46; H, 6.73; N, 2.64.

4-Ethenyl-1-(4-methylbenzenesulfonyl)-3-methylene-5-(phenylsulfonyl)-2,3,6,7-tetrahydro-1*H*-azepine (33): colorless plates; mp 73−74 °C (hexane−AcOEt); IR 1340, 1306, 1163, 1148 cm^{-1}; ^{1}H NMR δ 7.89−7.85 (m, 2H), 7.77−7.51 (m, 6H), 7.30−7.27 (m, 2H), 5.63−5.61 (m, 1H), 5.52−5.49 (m, 1H), 5.46−5.44 (m, 1H), 5.16−5.13 (m, 1H), 3.76 (s, 2H), 3.12 (t, 2H, J = 6.0 Hz), 2.73 (t, 2H, J = 6.0 Hz), 2.42 (s, 3H); ^{13}C NMR δ 149.8, 143.6, 141.0, 140.7, 133.3, 132.9, 131.5, 129.8, 129.28, 129.27, 127.3, 127.2, 124.9, 121.9, 50.6, 44.8, 29.8, 21.5; MS *m/z* 429 (M^+, 2.4); HRMS calcd for $C_{22}H_{23}NO_4S$ 429.1068, found 429.1068**.** Anal. Calcd for $C_{22}H_{23}NO_4S_2$: C, 61.51; H, 5.40; N, 3.26. Found: C, 61.40; H, 5.57; N, 3.21.

4-Ethenyl-1-(4-methylbenzenesulfonyl)-5-(phenylsulfonyl)-3-[(*Z*)-(trimethylsilyl)methylene]-2,3,6,7-tetrahydro-1*H*-azepine (34): colorless needles; mp 49−50 °C (hexane−AcOEt); IR 1352, 1306, 1165 cm^{-1}; ^{1}H NMR δ 8.01−7.94 (m, 2H), 7.83−7.61 (m, 6H), 7.50−7.26 (m, 2H), 5.77 (s, 1H), 5.57−5.45 (m, 2H), 3.90 (s, 2H), 3.16 (t, 2H, J = 6.1 Hz), 2.79 (t, 2H, J = 6.1 Hz), 2.54 (s, 3H), 0.28 (s, 9H); ^{13}C NMR δ? 151.5, 148.1, 143.7, 141.2, 137.2, 134.0, 133.2, 131.6, 130.5, 129.8, 129.2, 127.4, 127.2, 124.9, 49.4, 44.9, 29.0, 21.5, −0.4; MS *m/z* 501 (M^+, 0.7). Anal. Calcd for $C_{25}H_{31}NO_4S_2Si$: C, 59.85; H, 6.23; N, 2.79. Found: C, 59.53; H, 6.47; N, 2.75.

9-Methyl-2-methylene-7-(phenylsulfonyl)bicyclo[5.2.0]-non-1(9)-ene (35a): colorless oil; IR 1296, 1138 cm^{-1}; ^{1}H NMR δ 7.89−7.82 (m, 2H), 7.63−7.45 (m, 3H), 5.02 (s, 1H), 4.93 (s, 1H), 2.95−2.84 (m, 1H), 2.75−2.67 (m, 1H), 2.56−2.51 (m, 1H), 2.39 (dd, 1H, J = 15.5, 6.6 Hz), 2.25−2.05 (m, 2H), 1.99−1.89 (m, 1H), 1.84−1.73 (m, 1H), 1.71−1.53 (m, 1H), 1.63 (s, 3H), 1.38−1.23 (m, 1H); ^{13}C NMR δ 143.7, 142.4, 139.9, 136.8, 133.2, 129.6, 128.2, 112.3, 69.9, 42.6, 36.0, 33.6, 28.0, 27.3, 15.2; FABMS *m/z* 289 (M^++1, 6.2); FABHRMS calcd for $C_{17}H_{20}O_2S$ 289.1262, found 289.1266.

9-Phenyl-2-[(*E*)-6-phenylmethylene]-7-(phenylsulfonyl)-bicyclo[5.2.0]non-1(9)-ene (37a): colorless needles; mp 195−195.5 °C (hexane); IR 1298, 1140 cm^{-1}; ^{1}H NMR δ 7.98 (d, 2H, J = 7.6 Hz), 7.61−7.26 (m, 13H), 6.89 (s, 1H), 3.12 (d, 1H, J = 14.0 Hz), 3.07−3.02 (m, 1H), 2.92−2.73 (m, 2H), 2.39 (d, 1H, J = 14.0 Hz), 2.23−2.11 (m, 1H), 2.10−1.73 (m, 3H), 1.54−1.38 (m, 1H); ^{13}C NMR δ 141.5, 138.8, 137.11, 137.07, 136.9, 133.7, 133.6, 129.7, 129.0, 128.6, 128.41, 128.36, 128.3, 127.0, 126.4, 69.3, 39.5, 34.2, 30.7, 27.6, 27.4; MS *m/z* 426 (M^+, 0.1); HRMS calcd for $C_{28}H_{26}O_2S$ 426.1653, found 426.1651.

2-[1-(Ethoxycarbonyl)ethenyl]-3-[(*E*)-phenylmethylene]-1-(phenylsulfonyl)cycloheptene (38d): colorless oil; IR 1717, 1304, 1144 cm^{-1}; ^{1}H NMR δ 7.89−7.85 (m, 2H), 7.62−7.47 (m, 3H), 7.36−7.21 (m, 5H), 6.52 (d, 1H, J = 1.2 Hz), 6.51 (s, 1H), 5.74 (d, 1H, J = 1.2 Hz), 4.09 (q, 2H, J = 7.2 Hz), 2.65 (t, 2H, J = 6.1 Hz), 2.59 (t, 2H, J = 6.1 Hz), 1.83 (quin, 2H, J = 6.1 Hz), 1.55 (quin, 2H, J = 6.1 Hz), 1.23 (t, 3H, J = 7.2 Hz); ^{13}C NMR δ 164.8, 149.3, 140.9, 140.3, 139.8, 138.5, 136.4, 133.3, 132.9, 129.3, 129.0, 128.7, 128.34, 128.28, 127.5, 60.9, 29.6, 28.7, 26.2, 24.3, 14.0; MS *m/z* 422 (M^+, 1.8); HRMS calcd for $C_{25}H_{26}O_4S$ 422.1552, found 422.1551.

***N*-(4-Methylbenzenesulfonyl)-9-methyl-7-(phenylsulfonyl)-2-[(*Z*)-(trimethylsilyl)methylene]-4-azabicyclo-[5.2.0]non-1(9)-ene (39):** colorless oil; IR 1333, 1157, 1146 cm^{-1}; ^{1}H NMR δ 7.81−7.79 (m, 2H), 7.76−7.61 (m, 2H), 7.48−7.45 (m, 2H), 7.27−7.25 (m, 3H), 5.47 (s, 1H), 4.65 (d, 1H, J = 6.6 Hz), 4.09−4.05 (m, 2H), 3.68−3.63 (m, 1H), 2.68−2.65 (m, 1H), 2.47−2.43 (m, 3H), 2.40 (s, 3H), 2.07−2.00 (m, 2H), 1.50 (s, 3H), 0.26 (s, 9H); ^{13}C NMR δ 148.1, 145.0, 144.0, 139.9, 137.8, 135.8, 133.7, 129.6, 129.5, 128.2, 126.8, 68.8, 53.4, 49.9, 42.3, 33.9, 21.4, 15.0, 0.1; MS *m/z* 515 (M^+, 0.9); HRMS calcd for $C_{26}H_{33}NO_4S_2Si$ 289.1262, found 289.1266.

2-[(*E*)- and (*Z*)-1-Methyl-1-propenyl]-3-[(*E*)-phenylmethylene]-1-(phenylsulfonyl)cycloheptene (41). A 50:50 mixture of (*E*)- and (*Z*)-**41** was obtained as colorless plates: mp 73−74 °C (hexane−AcOEt); IR 1304, 1146 cm^{-1};

^{1}H NMR δ 7.89−7.83 (m, 2H), 7.59−7.50 (m, 3H), 7.36−7.24 (m, 5H), 6.60 (s, 50/100 × 1H), 6.56 (s, 50/100 × 1H), 5.54−5.50 (m, 50/100 × 1H), 5.43 (q, 50/100 × 1H, *J* = 6.6 Hz), 2.78−2.73 (m, 50/100 × 1H), 2.69−2.46 (m, 50/100 × 6H), 2.34−2.28 (m, 50/100 × 1H), 2.17−2.01 (m, 50/100 × 2H), 1.94 (q, 50/100 × 2H, *J* = 7.6 Hz), 1.84−1.71 (m, 50/100 × 6H), 1.66−1.51 (m, 50/100 × 5H), 1.47−1.42 (m, 50/100 × 1H), 1.07 (t, 50/100 × 3H, *J* = 7.6 Hz), 0.92 (t, 50/100 × 3H, *J* = 7.6 Hz); ^{13}C NMR δ 158.0, 154.0, 142.4, 141.3, 140.9, 139.9, 139.5, 138.9, 137.9, 137.4, 137.3, 137.0, 136.8, 133.6, 132.7, 132.5, 129.0, 128.9, 128.8, 128.6, 128.33, 128.30, 128.29, 128.1, 127.5, 127.4, 127.3, 121.8, 29.9, 29.8, 29.5, 29.3, 28.8, 27.2, 26.9, 24.8, 24.7, 22.9, 15.4, 13.7, 13.0, 12.3; MS *m/z* 392 (M^+, 0.3). Anal. Calcd for $C_{23}H_{28}O_2S$: C, 76.49; H, 7.19. Found: C, 76.35; H, 7.38.

2-(1-Cyclohexenyl)-3-[(*E*)-phenylmethylene]-1-(phenylsulfonyl)cycloheptene (44): pale yellow oil; IR 1288, 1140 cm^{-1}; ^{1}H NMR δ 7.85−7.84 (m, 2H), 7.57−7.49 (m, 3H), 7.36−7.23 (m, 5H), 6.59 (s, 1H), 5.59−5.58 (m, 1H), 2.73 (t, 2H, *J* = 5.6 Hz), 2.51−2.50 (m, 2H), 2.09−2.07 (m, 2H), 1.84 (quin, 2H, *J* = 6.2 Hz), 1.72 (quin, 2H, *J* = 6.2 Hz), 1.67−1.66 (m, 2H), 1.52−1.47 (m, 2H), 1.44−1.39 (m, 2H); ^{13}C NMR δ 157.0, 142.6, 139.6, 137.6, 136.8, 136.4, 132.6, 132.4, 130.0, 128.9, 128.6, 128.3, 127.8, 127.3, 29.9, 28.8, 27.2, 27.0, 25.3, 24.8, 22.2, 21.4; MS *m/z* 404 (M^+, 52.0); HRMS calcd for $C_{26}H_{28}O_2S$ 404.1810, found 404.1800.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **4b**,**d**−**f**, **5a**,**c**,**d**,**f**, **6c**, **7a**−**f**, **9b**−**d**,**f**, **10a**−**d**,**f**, **11a**,**f**, **12a**−**e**, **13b**,**c**, **14a**, **15a**−**c**, **21a**,**d**, **24a**,**b**, **25a**,**b**, **27a**, **28**, **29**, **31**, **35a**,**c**, **36a**−**e**, **37a**−**c**,**e**, **38d**,**e**, **39**, and **44**; characterization data for compounds **4d**−**f**, **5b**−**f**, **6b**,**c**, **7b**−**d**, **f**, **9a**−**f**, **10a**−**f**, **11b**−**f**, **12b**−**e**, **13a**−**c**, **14a**−**c**, **15b**,**c**, **21b**−**g**, **22b**−**g**, **25b**, **26b**,**c**, **27b**, **29**, **35b**,**c**, **36a**−**e**, **37b**−**e**, **38e**, **40**, and **43**; and X-ray crystallographic data for **35c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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