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Rh(I)-catalyzed Pauson–Khand reaction of 1-phenylsulfonyl-1,2-octadien-7-yne derivatives

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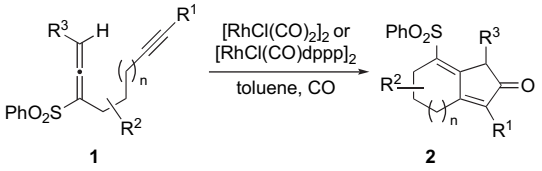
Abstract—The Rh(I)-catalyzed PKR of 1-phenylsulfonyl-1,2-octadien-7-ynes and their aza derivatives exclusively produced the corresponding 9-phenylsulfonylbicyclo[4.3.0]nona-1,6-dien-8-ones and no 4-(phenylsulfonylmethylidene)bicyclo[3.3.0]oct-1-en-3-ones could be detected. Thus, the ring-closing pattern was found to be the same as those of the previously reported 3-phenylsulfonyl-1,2-octadien-7-yne derivatives. However, the formation of 4-(phenylsulfonylmethylidene)-7-oxabicyclo[3.3.0]oct-1-en-3-ones was observed as a minor product when the 5-oxa congeners were used. In addition, a larger ring-sized product, 10-phenylsulfonyl-5-azabicyclo[5.3.0]deca-1,7-dien-9-one derivative, was obtained from the 6-aza derivative of 1-phenylsulfonyl-1,2-nonadien-8-yne.

1. Introduction

In our previous studies,[1] we developed an effective method for the construction of the bicyclo[*m*.3.0] ring system (*m*=4, 5, 6) based on the Rh(I)-catalyzed Pauson–Khand reaction (PKR)[2] of allenynes in which the distal double bond of the allenyl moiety consistently took part in the ring-closing process.[1,3] Thus, a solution of 3-phenylsulfonyl-1,2-octadien-7-yne derivatives **1** (*n*=1) was heated in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ or $[RhCl(CO)dppp]_2$ in toluene under CO pressure to produce the corresponding 2-phenylsulfonylbicyclo[4.3.0]nona-1,6-dien-8-ones **2** (*n*=1) in high to reasonable yields (Scheme 1). This ring-closing reaction could be applied to the construction of 2-phenylsulfonylbicyclo[5.3.0]deca-1,7-dien-9-ones as well as 2-phenylsulfonylbicyclo[6.3.0]undeca-1,8-dien-10-ones. In this study, we investigated the Rh(I)-catalyzed PKR of 1-phenylsulfonyl-1,2-octadien-7-yne derivatives, regioisomers of **1** regarding the position of the phenylsulfonyl group on the allenyl moiety, in order to obtain information on the effect of the phenylsulfonyl group on the regioselectivity.

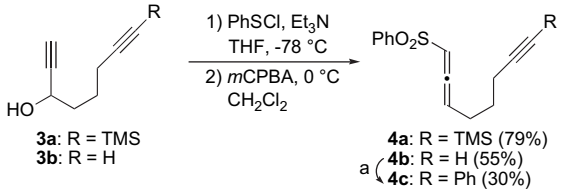


1 **2**

Scheme 1.

2. Results and discussion

The allenynes **4** were chosen as the first starting materials for the Rh(I)-catalyzed PKR and were prepared as follows (Scheme 2). Successive exposure of the known **3a**,[1b]**b**[4] to benzenesulfenyl chloride (PhSCl) and *m*-chloroperbenzoic acid (*m*CPBA) produced the 1-phenylsulfonyl derivatives **4a**,**b** in 79 and 55% yields, respectively. The Sonogashira reaction of **4b** with iodobenzene furnished the phenylacetylene derivative **4c** in a rather low yield (30%).



Scheme 2. Reagents and conditions: (a) PhI, $Pd(PPh_3)_2Cl_2$, CuI, $^iPr_2NH$, THF, rt.

With the required allenynes **4** in hand, compound **4a** was first used for the ring-closing reaction in the presence of a catalytic amount of $[RhCl(CO)dppp]_2$ (2.5 mol %) in refluxing toluene for 3 h under an atmosphere of CO, that had been employed for the preparation of 2-

Keywords: Rh(I)-catalyzed Pauson–Khand reaction; 1-Phenylsulfonylallenyne; Bicyclo[4.3.0]; Distal double bond; Proximal double bond; $[RhCl(CO)_2]_2$.
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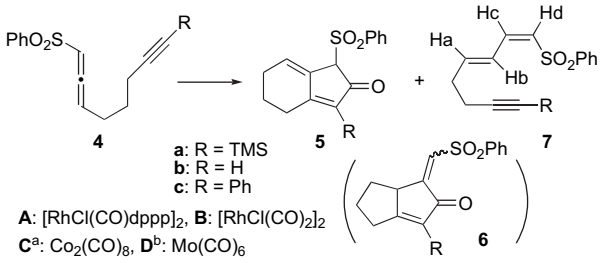
Table 1. Rh(I)-catalyzed ring-closing reaction of compounds **4**

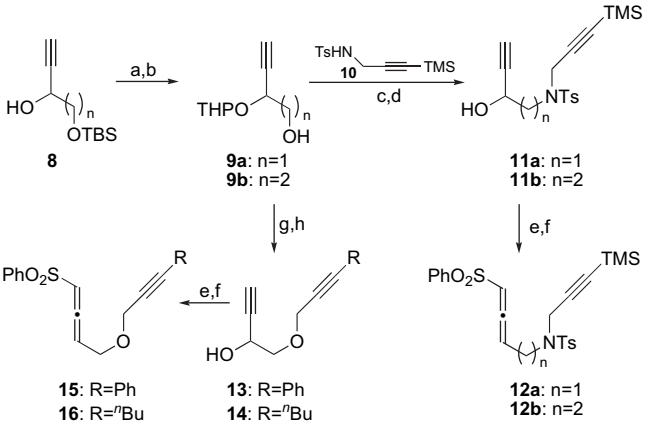


Entry	s.m.	R	Rh (mol %)	CO (atm)	Solv.	Temp.	Time (h)	Product (%)
1	**4a**	TMS	**A** (2.5)	1	Toluene	Reflux	3	**5a** (11)+**7a** (78)
2	**4a**	TMS	**B** (2.5)	1	Toluene	Reflux	18	**5a** (45)
3	**4a**	TMS	**B** (2.5)	1	Xylene	Reflux	2	**5a** (73)
4	**4a**	TMS	**B** (5)	1	Xylene	Reflux	1	**5a** (72)
5	**4a**	TMS	**B** (2.5)	5	Xylene	150 °C	2	**5a** (73)
6	**4a**	TMS	**B** (2.5)	1	Mesitylene	Reflux	1	**5a** (63)
7	**4a**	TMS	**C** (30)	1	Xylene	Reflux	1	**5a** (35)
8	**4a**	TMS	**D** (120)	1	Xylene	Reflux	2	**5a** (18)
9	**4b**	H	**B** (2.5)	1	Xylene	Reflux	2	**5b** (23)
10	**4c**	Ph	**B** (2.5)	1	Xylene	Reflux	2	**5c** (30)
11	**4b**	H	**B** (2.5)	1	Toluene	Reflux	2	**5b** (30)
12	**4c**	Ph	**B** (2.5)	1	Toluene	Reflux	1	**5c** (40)

[a] Tetramethylthiourea (TMTU) of 30 mol % was used together.
[b] DMSO (10 equiv) was used together.

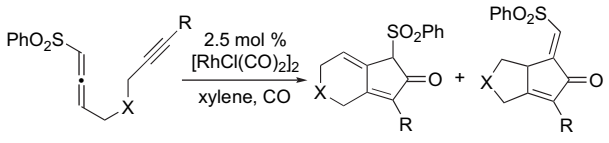
phenylsulfonylbicyclo[4.3.0]nona-1,6-dien-8-ones **2** (n=1), to afford the bicyclo[4.3.0] derivative **5a** in 11% yield (Table 1, entry 1). The [RhCl(CO)dppp]$_2$-catalyzed isomerization of the allenyl moiety to the 1,3-diene functionality became the major pathway giving rise to the formation of compound **7**.[5] No formation of the corresponding bicyclo[3.3.0] derivative **6a** could be detected. Changing the Rh(I) catalyst from [RhCl(CO)dppp]$_2$ to [RhCl(CO)$_2$]$_2$ brought about a significant improvement in the chemical yield of **5a** (45%, entry 2). Again, compound **6a** could not be detected. Under otherwise identical conditions, but in refluxing xylene, the yield of **5a** was markedly increased to 73% (entry 3). When the ring-closing reaction was carried out in the presence of 5 mol % of [RhCl(CO)$_2$]$_2$ in refluxing xylene, compound **5a** was obtained in a similar yield (72%, entry 4). Neither increasing the CO pressure (5 atm, heated at 150 °C) nor a higher reaction temperature (1 atm of CO in refluxing mesitylene) produced a further improvement in the chemical yield (entries 5 and 6). Two other catalysts, $Co_2(CO)_8$[6] and $Mo(CO)_6$,[7] were examined resulting in chemical yields much lower than 73% (entries 7 and 8). The best conditions for the preparation of **5a** (entry 3) were then applied to other allenynes **4b**,**c**, but lower yields (23 and 30%) were recorded (entries 9 and 10). Interestingly, higher yields (30 and 42%) were obtained when **4b**,**c** were refluxed in toluene (entries 11 and 12), which are in sharp contrast to the case of **4a** (entries 2 and 3). We had tentatively anticipated the preferential formation of the bicyclo[3.3.0] frameworks **6** over the bicyclo[4.3.0]ones because the phenylsulfonyl group at the C_1-position of **4** would decrease the electron density of the distal double bond of the allenyl moiety, thereby the proximal double bond might participate in the ring-closing process. In contrast to our prediction, the PKR of **4** exclusively produced the 9-phenylsulfonylbicyclo[4.3.0] products **5**, although the chemical yields were significantly lower than those of 2-phenylsulfonylbicyclo[4.3.0] derivatives **2** (n=1).[1]

Our endeavors then turned to the application of this Rh(I)-catalyzed PKR for the allenynes **12**, **15**, and **16** possessing a hetero atom on the carbon appendage. Thus, protection of the propargyl alcohol of **8**[8] with dihydropyran (DHP) was followed by treatment with tetrabutylammonium fluoride (TBAF) to afford **9a**, which was subsequently reacted with the tosylamide derivative **10**[9] under the Mitsunobu conditions to give **11a** in 41% overall yield after removal of THP group. According to a similar procedure, the one-carbon homologated compound **11b** was prepared in a 50% overall yield starting from the known **9b**.[10] Transformation of **11a**,**b** into the 1-phenylsulfonylallenynes **12a**,**b** was realized by the standard method (PhSCl and mCPBA).[1] In addition, the oxygen congeners **15** and **16** were synthesized from **9a** by the conventional means as shown in Scheme 3.[11,12]



Scheme 3. Reagents and conditions: (a) DHP, PPTS, CH_2Cl_2, 0 °C; (b) TBAF, THF, rt; (c) **10**, DIAD, PPh_3, THF, rt; (d) p-TsOH, MeOH, rt, **11a** (41% from **8**), **11b** (50% from **9b**); (e) PhSCl, Et_3N, THF, −78 °C: (f) mCPBA, CH_2Cl_2, 0 °C, **12a** (80%), **12b** (56%), **15** (75%), **16** (77%); (g) 3-iodo-1-phenylprop-1-yne, NaH, DMF, 0 °C, then p-TsOH, MeOH, rt, **13** (70%); (h) 1-iodohept-2-yne, NaH, DMF, 0 °C, then p-TsOH, MeOH, rt, **14** (80%).

Table 2. Rh(I)-catalyzed ring-closing reaction of compounds **12a**, **15**, and **16**



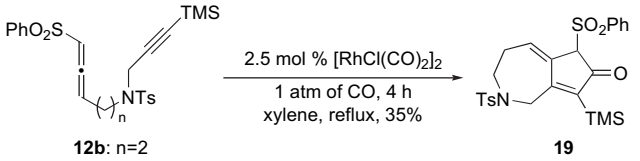
12a: R = TMS, X=NTs **17a**: R = TMS, X=NTs **18a**: R = TMS, X=NTs
15: R = Ph, X=O **17b**: R = Ph, X=O **18b**: R = Ph, X=O
16: R = ^{n}Bu, X=O **17c**: R = ^{n}Bu, X=O **18c**: R = ^{n}Bu, X=O

Entry	s.m.	R	X	CO (atm)	Temp.	Time (h)	Product (%)
1	**12a**	TMS	NTs	1	Reflux	2	**17a** (61)
2	**15**	Ph	O	1	Reflux	3	**17b** (45)
3	**15**	Ph	O	10	150 °C	2	**17b** (44)+**18b** (17)
4	**16**	^{n}Bu	O	1	Reflux	2	**17c** (26)+**18c** (19)
5	**16**	^{n}Bu	O	10	150 °C	2	**17c** (42)+**18c** (7)

A solution of the aza derivative **12a** and 2.5 mol % of $[RhCl(CO)_2]_2$ in xylene was refluxed for 2 h to produce the cyclized product **17a** in 61% yield (Table 2, entry 1). The oxa compound **15** having a terminal phenyl group afforded the corresponding bicyclo[4.3.0] derivative **17b** in 45% yield (entry 2). These two results are in good agreement with those of Table 1. However, upon exposure to the conditions with 10 atm of CO at 150 °C for 2 h, **15** produced **17b** in 44% yield accompanied by the production of a new product, the bicyclo[3.3.0]octenone derivative **18b**[13] in 17% yield (entry 3). The butyl congener **16** also provided the bicyclo[3.3.0] skeleton **18c** in a low yield (19%) under the standard conditions (entry 4). Contrary to the prediction based on entries 2 and 3, increasing the CO pressure for compound **16** did not improve the ratio of the bicyclo[3.3.0] compound **18c** to the bicyclo[4.3.0] one **17c** (entry 5).

It has been reported that the PKR of 1,2-octadien-7-yne derivatives mediated by $Mo(CO)_6$ consistently affords α-alkylidenebicyclo[3.3.0]oct-1-en-3-ones (e.g., **18**),[7] in which the proximal double bond of the allenyl moiety is incorporated into the cyclopentenone frameworks. On the other hand, the distal double bond of the allenyl moiety of 1,2-octadien-7-yne derivatives exclusively takes part in the ring-closing process under the Rh(I)-catalyzed conditions[14] to provide the bicyclo [4.3.0]nona-1,6-dien-7-ones like **17a**.[1,3] This propensity was recently rationalized by calculations[15] in terms of the difference in the transition state structure of the product-determining step (the oxidative addition of the metal to the alkyne–allene functionalities), in which the molybdenacycles would have a distorted trigonal bipyramidal geometry, whereas the rhodacycles would have the distorted square planar one. In line with the conclusion based on the calculations,[15] our results in Tables 1 and 2 strongly indicate that the $[RhCl(CO)_2]_2$-catalyzed PKR of allenynes exclusively or predominantly occurs between the distal double bond and the triple bond irrespective of the position of the phenylsulfonyl group.

The final subject in this investigation was the Rh(I)-catalyzed PKR of the 1-phenylsulfonyl derivative **12b**. Treatment of **12b** under the standard conditions (1 atm of CO in refluxing xylene) for 4 h afforded the seven-membered compound **19** in 35% yield, which resulted from the reaction between the distal double bond of the allenyl moiety and a triple bond (Scheme 4). The proximal double bond was again inactive under the Rh(I)-catalyzed PKR conditions.



12b: n=2 **19**

Scheme 4.

3. Conclusions

In summary, we have studied the Rh(I)-catalyzed PKR of the 1-phenylsulfonylallenynes. 1-Phenylsulfonyl-1,2-octadien-7-yne and its analogs possessing a substituent at the alkyne terminus exclusively afforded the corresponding 9-phenylsulfonylbicyclo[4.3.0]nona-1,6-dien-8-ones. The ring-closing pattern was found to be the same as that of the previously reported 3-phenylsulfonyl-1,2-octadien-7-yne derivatives. Similarly, the 5-aza derivative of 1-phenylsulfonyl-1,2-octadien-7-yne provided the corresponding bicyclo[4.3.0] compound. However, the 5-oxa congeners produced the α-alkylidene-7-oxabicyclo[3.3.0]oct-1-en-3-one derivatives as a minor product. In addition, 10-phenylsulfonylbicyclo[5.3.0] framework could also be prepared.

4. Experimental

4.1. General

Melting points are uncorrected. Infrared spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in chloroform-*d* ($CDCl_3$). $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.0 ppm) as an internal standard. All reactions were carried out under N_2 atmosphere unless otherwise stated. Silica gel (Silica gel 60, 40–50 μm) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

4.2. General procedure for preparation of allenyl sulfones

To a solution of propargyl alcohol in THF (0.1 M) were added successively Et_3N (3.0 equiv) and PhSCl (1.5 equiv) at −78 °C. The reaction mixture was stirred until complete disappearance of the starting material (monitored by TLC). The reaction mixture was quenched by addition of water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was passed through a short pad of silica gel with hexane–AcOEt to afford the crude sulfoxide. *m*CPBA (1.5 equiv) was added to a solution of the crude sulfoxide in CH_2Cl_2 (0.1 M) at 0 °C. The reaction mixture was stirred until complete disappearance of the starting material (monitored by TLC). The reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with

water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with hexane–AcOEt to afford allenyl sulfones. Chemical yields are summarized in tables.

4.2.1. 1-(Phenylsulfonyl)-8-(trimethylsilyl)octa-1,2-dien-7-yne (4a). A colorless oil; IR: 2172, 1958, 1321, 1148 cm^{-1}; ^1H NMR δ: 7.85–7.83 (m, 2H), 7.58–7.54 (m, 1H), 7.49–7.46 (m, 2H), 6.16 (dt, 1H, J=6.1, 2.9 Hz), 5.80 (q, 1H, J=6.1 Hz), 2.20–2.14 (m, 4H), 1.53 (quin, 2H, J=7.1 Hz), 0.08 (s, 9H); ^{13}C NMR δ: 205.4, 141.0, 133.2, 129.0, 127.3, 105.9, 101.2, 100.2, 85.1, 26.9, 26.4, 18.9, −0.1; MS m/z: 318 (M^+, 1.6); HRMS calcd for $C_{17}H_{22}O_2SSi$: 318.1110, found: 318.1100.

4.2.2. 1-(Phenylsulfonyl)octa-1,2-dien-7-yne (4b). A colorless oil; IR: 3308, 2866, 1958, 1321, 1150 cm^{-1}; ^1H NMR δ: 7.93–7.91 (m, 2H), 7.64–7.61 (m, 1H), 7.56–7.53 (m, 2H), 6.21 (dt, 1H, J=5.8, 2.9 Hz), 5.86 (q, 1H, J=7.0 Hz), 2.29–2.22 (m, 4H), 1.96 (t, 1H, J=2.5 Hz), 1.66–1.60 (m, 2H); ^{13}C NMR δ: 205.4, 141.0, 133.3, 129.0, 127.3, 101.2, 100.1, 83.2, 69.0, 26.7, 26.2, 17.4; MS m/z: 246 (M^+, 2.2); HRMS calcd for $C_{14}H_{14}O_2S$: 246.0715, found: 246.0720.

4.2.3. 8-Phenyl-1-(phenylsulfonyl)-octa-1,2-dien-7-yne (4c). To a solution of **4b** (250 mg, 1.0 mmol) in THF (10 mL) were successively added CuI (3.8 mg, 2.0×10^{-2} mmol), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 1.0×10^{-2} mmol), and iodobenzene (0.22 mL, 2.0 mmol). After being stirred for 5 min at room temperature, $^iPr_2NH$ (1.4 mL, 10 mmol) was added, and the mixture was further stirred for 10 h. The precipitates were filtered off and the filtrate was concentrated to leave a residual oil, which was chromatographed with hexane–AcOEt (2:1) to afford **4c** (97 mg, 30%) as a yellow oil. IR: 2864, 1958, 1321, 1148 cm^{-1}; ^1H NMR δ: 7.93–7.90 (m, 2H), 7.62–7.46 (m, 3H), 7.41–7.36 (m, 2H), 7.29–7.26 (m, 3H), 6.23 (dt, 1H, J=6.0, 3.0 Hz), 5.89 (dt, 1H, J=6.0, 6.9 Hz), 2.46 (t, 2H, J=6.9 Hz), 2.33 (dq, 2H, J=3.0, 6.9 Hz), 1.70 (quin, 2H, J=6.9 Hz); ^{13}C NMR δ: 205.7, 141.2, 133.4, 131.5, 129.1, 128.7, 128.2, 127.6, 123.7, 101.4, 100.4, 88.9, 81.4, 27.2, 26.7, 18.6; MS m/z: 322 (M^+, 10.9); HRMS calcd for $C_{20}H_{18}O_2S$: 322.1028, found: 322.1023.

4.2.4. *N*-[4-(Phenylsulfonyl)buta-2,3-dienyl]-*N*-[3-(trimethylsilyl)propyn-2-yl]-(4-methylbenzene)sulfonamide (12a). Colorless needles; mp 110.5–111 °C (AcOEt); IR: 2177, 1961, 1308, 1151 cm^{-1}; ^1H NMR δ: 7.93–7.91 (m, 2H), 7.73–7.55 (m, 5H), 7.30 (d, 2H, J=7.9 Hz), 6.27 (dt, 1H, J=6.1, 2.4 Hz), 5.83 (q, 1H, J=6.1 Hz), 4.17 (AB-q, 2H, J=18.3 Hz), 3.98 (AB-qdd, 2H, J=14.9, 6.1, 2.4 Hz), 2.42 (s, 3H), 0.00 (s, 9H); ^{13}C NMR δ: 206.0, 143.8, 140.8, 135.8, 133.7, 129.7, 129.3, 127.7, 102.6, 97.4, 96.6, 91.6, 44.1, 37.4, 21.5, −0.47; MS m/z: 473 (M^+, 20); HRMS calcd for $C_{23}H_{27}O_4NSiS_2$: 473.1151, found: 473.1165; Anal. Calcd for $C_{23}H_{27}NO_4S_2Si$: C, 58.32; H, 5.75; N, 2.96. Found: C, 58.07; H, 5.73; N, 2.96.

4.2.5. *N*-[5-(Phenylsulfonyl)penta-3,4-dienyl]-*N*-[3-(trimethylsilyl)propyn-2-yl]-(4-methylbenzene)sulfonamide (12b). Colorless plates; mp 91.5–92.5 °C (AcOEt); IR: 2177, 1950, 1308, 1150 cm^{-1}; ^1H NMR δ: 7.93–7.91 (m, 2H), 7.72–7.54 (m, 5H), 7.30–7.28 (m, 2H), 6.23 (dt, 1H, J=6.1, 2.7 Hz), 5.87 (q, 1H, J=6.1 Hz), 4.13 (s, 2H), 3.28 (t, 2H, J=7.3 Hz), 2.48–2.44 (m, 2H), 2.42 (s, 3H), 0.00 (s, 9H); ^{13}C NMR δ: 205.8, 143.6, 141.2, 135.6, 133.5, 129.6, 129.2, 127.7, 127.6, 101.7, 97.6, 97.5, 91.3, 45.3, 37.8, 26.6, 21.5, −0.49; MS m/z: 487 (M^+, 5.7); HRMS calcd for $C_{24}H_{29}O_4NSiS_2$: 487.1307, found: 487.1327; Anal. Calcd for $C_{24}H_{29}NO_4S_2Si$: C, 59.10; H, 5.99; N, 2.87. Found: C, 58.79; H, 5.99; N, 2.76.

4.2.6. 1-(Phenylsulfonyl)-4-(3-phenyl-2-propynyloxy)-buta-1,2-diene (15). A brown oil; IR: 1961, 1310, 1150 cm^{-1}; ^1H NMR δ: 7.95–7.93 (m, 2H), 7.61–7.57 (m, 1H), 7.51–7.48 (m, 2H), 7.45–7.43 (m, 2H), 7.34–7.31 (m, 3H), 6.32 (dt, 1H, J=6.1, 2.7 Hz), 5.96 (q, 1H, J=6.1 Hz), 4.42 (s, 2H), 4.29 (dd, 2H, J=6.1, 2.7 Hz); ^{13}C NMR δ: 205.7, 141.1, 133.5, 131.8, 129.2, 128.6, 128.3, 127.7, 122.3, 102.3, 98.0, 86.9, 84.2, 65.1, 58.1; MS m/z: 324 (M^+, 15); HRMS calcd for $C_{19}H_{16}O_3S$: 324.0820, found: 324.0827.

4.2.7. 1-[4-(Phenylsulfonyl)-2,3-butadienyloxy]-2-heptyne (16). A colorless oil; IR: 1961, 1310, 1150 cm^{-1}; ^1H NMR δ: 7.92–7.91 (m, 2H), 7.63–7.60 (m, 1H), 7.55–7.52 (m, 2H), 6.28 (dt, 1H, J=6.1, 3.1 Hz), 5.91 (q, 1H, J=6.1 Hz), 4.17 (dd, 2H, J=6.1, 3.1 Hz), 4.13 (t, 2H, J=2.4 Hz), 2.20 (tt, 2H, J=7.3, 2.4 Hz), 1.50–1.45 (m, 2H), 1.42–1.35 (m, 2H), 0.89 (t, 3H, J=7.3 Hz); ^{13}C NMR δ: 205.6, 141.0, 133.5, 129.1, 127.6, 102.1, 98.1, 87.8, 75.0, 64.7, 57.9, 30.5, 21.8, 18.3, 13.5; MS m/z: 304 (M^+, 0.1); HRMS calcd for $C_{17}H_{20}O_3S$: 304.1133, found: 304.1120.

4.3. Preparation of propargyl alcohol derivatives

4.3.1. *N*-(2-Hydroxy-3-butynyl)-*N*-[3-(trimethylsilyl)-2-propynyl]-(4-methylbenzene)sulfonamide (11a). To a solution of **8**[8] (1.15 g, 5.76 mmol) in CH_2Cl_2 (14 mL) were added PPTS (150 mg, 0.60 mmol) and DHP (1.6 mL, 17 mmol) at room temperature. After being stirred for 10 h, the mixture was concentrated to leave the residual oil, which was passed through a short pad of silica gel with hexane–AcOEt (9:1) to afford the crude acetal. TBAF (1.0 M in THF, 6 mL, 6 mmol) was added to a solution of the crude acetal in THF (6 mL) at room temperature. After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with hexane–AcOEt (3:1) to afford **9a** (970 mg) as a pale yellow oil. DIAD (0.30 mL, 1.4 mmol) was gradually added to a solution of **9a** (220 mg, 1.3 mmol), PPh_3 (370 mg), and **10**[9] (280 mg, 1.0 mmol) in THF (7 mL) at 0 °C. After being stirred for 24 h at room temperature, the reaction mixture was concentrated to leave the residual oil, which was passed through a short pad of silica gel with hexane–AcOEt (5:1) to afford the crude diyne. *p*-TsOH (20 mg, 0.10 mmol) was added to a solution of the crude diyne in MeOH (10 mL) at room temperature. After being stirred for 12 h, the reaction mixture was concentrated to leave the residual oil, which was chromatographed with hexane–AcOEt (3:1) to afford **11a** (146 mg, 41% for four steps) as a colorless oil. IR: 3503, 3306, 2177 cm^{-1}; ^1H NMR δ: 7.76–7.73 (m, 2H), 7.31–7.25 (m, 2H), 4.67–4.60 (m, 1H), 4.29 (s, 2H), 3.42–3.40 (m, 2H), 2.81 (d, 1H, J=5.4 Hz), 2.50 (d, 1H, J=2.1 Hz), 2.41 (s, 3H), 0.00 (s, 9H); ^{13}C NMR δ: 144.3,

136.0, 130.1, 128.3, 98.6, 91.7, 82.6, 74.8, 61.9, 52.6, 40.3, 22.0, 0.00; MS *m/z*: 349 (M^+, 8.1); HRMS calcd for $C_{17}H_{23}O_3NSSi$: 349.1168, found: 349.1159.

4.3.2. *N*-(3-Hydroxy-4-pentynyl)-*N*-[3-(trimethylsilyl)-2-propynyl]-(4-methylbenzene)sulfonamide (11b). According to the procedure for the conversion of **9a** into **11a**, **9b**[10] (156 mg, 0.85 mmol) was treated with DIAD (0.20 mL, 1.1 mmol), PPh_3 (290 mg, 1.1 mmol), and **10**[9] (200 mg, 0.7 mmol) to give the crude diyne, which was exposed to *p*-TsOH (70 mg, 0.36 mmol) to afford **11b** (127 mg, 50% for two steps) as a colorless oil. IR: 3524, 3308, 2177 cm^{-1}; ^1H NMR δ: 7.69 (d, 2H, J=8.3 Hz), 7.25 (d, 2H, J=8.3 Hz), 4.55 (br s, 1H), 4.18 (d, 1H, J=18.8 Hz), 4.03 (d, 1H, J=18.8 Hz), 3.44 (ddd, 1H, J=14.3, 8.2, 6.3 Hz), 3.22 (ddd, 1H, J=13.7, 6.3, 5.1 Hz), 2.92 (s, 1H), 2.45 (d, 1H, J=2.2 Hz), 2.38 (s, 3H), 2.02–1.87 (m, 2H), −0.04 (s, 9H); ^{13}C NMR δ: 143.5, 135.4, 129.5, 127.7, 97.8, 91.1, 84.1, 73.0, 59.0, 42.5, 37.7, 35.4, 21.4, −0.5; MS *m/z*: 363 (M^+, 1.2); HRMS calcd for $C_{18}H_{25}O_3NSSi$: 363.1325, found: 363.1320.

4.3.3. 1-(3-Phenyl-2-propynyloxy)-3-butyn-2-ol (13). NaH (160 mg, 4.0 mmol, 60% in oil) was added to a solution of **9a** (340 mg, 2.0 mmol) in DMF (10 mL) at 0 °C. After being stirred for 30 min, 3-iodo-1-phenylprop-1-yne (1.4 g, 5.7 mmol) was added to the mixture at 0 °C. The mixture was stirred for 2 h, quenched by addition of water and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was passed through a short pad of silica gel with hexane–AcOEt (5:1) to afford the crude ether. *p*-TsOH (16 mg, 0.10 mmol) was added to a solution of the crude ether in MeOH (10 mL). After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and MeOH was evaporated off. The residual oil was extracted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with hexane–AcOEt (5:1) to afford **13** (280 mg, 70%) as a colorless oil. IR: 3578, 3306 cm^{-1}; ^1H NMR δ: 7.45–7.44 (m, 2H), 7.32–7.31 (m, 3H), 4.62–4.61 (m, 1H), 4.48 (AB-q, 2H, J=15.9 Hz), 3.76 (AB-qd, 2H, J=9.7, 3.6 Hz), 2.62 (d, 1H, J=5.5 Hz), 2.48 (d, 1H, J=2.4 Hz); ^{13}C NMR δ: 131.7, 128.5, 128.2, 122.2, 86.8, 84.3, 81.5, 73.8, 73.1, 61.3, 59.3; MS *m/z*: 200 (M^+, 1.3); HRMS calcd for $C_{13}H_{12}O_2$: 200.0837, found: 200.0845.

4.3.4. 1-(2-Heptynyloxy)-3-butyn-2-ol (14). According to the procedure for the preparation of **13** from **9a**, **14** (140 mg, 80%) was obtained from **9b** (170 mg, 1.0 mmol) as a colorless oil. IR: 3566, 3308 cm^{-1}; ^1H NMR δ: 4.59–4.54 (m, 1H), 4.23 (AB-qt, 2H, J=13.2, 2.3 Hz), 3.68 (AB-qd, 2H, J=9.6, 3.6 Hz), 2.47 (d, 1H, J=2.1 Hz), 2.25–2.19 (m, 3H), 1.55–1.36 (m, 4H), 0.93–0.88 (m, 3H); ^{13}C NMR δ: 87.7, 81.6, 75.1, 73.6, 72.8, 61.1, 59.1, 30.5, 21.8, 18.2, 13.4; MS *m/z*: 180 (M^+, 0.1); HRMS calcd for $C_{11}H_{16}O_2$: 180.1150, found: 180.1149.

4.4. Pauson–Khand reaction of allenynes

4.4.1. Pauson–Khand reaction of allenyne 4a with [RhCl(CO)dppp]$_2$. $[RhCl(CO)dppp]_2$ (2.7 mg, 2.4×10^{-3} mmol) was added to a solution of allenyne **4a** (30 mg, 9.4×10^{-2} mmol) in toluene (1.0 mL). The reaction mixture was refluxed under a CO atmosphere for 3 h. Toluene was evaporated off, and the residual oil was chromatographed with CH_2Cl_2 to afford **5a** (3.5 mg, 11%) and **7a** (24 mg, 78%). 9-(Phenylsulfonyl)-7-(trimethylsilyl)bicyclo[4.3.0]nona-1,6-dien-8-one (**5a**); yellow plates; mp 122–123 °C (AcOEt); IR: 1695, 1321, 1144 cm^{-1}; ^1H NMR δ: 7.76–7.74 (m, 2H), 7.64–7.60 (m, 1H), 7.50–7.47 (m, 2H), 6.71 (t, 1H, J=3.7 Hz), 4.22 (s, 1H), 2.66–2.60 (m, 1H), 2.55–2.52 (m, 1H), 2.50–2.33 (m, 2H), 1.83–1.72 (m, 2H), 0.10 (s, 9H); ^{13}C NMR δ: 197.3, 177.3, 137.6, 136.7, 133.8, 133.7, 132.0, 129.4, 128.4, 69.0, 27.1, 25.3, 21.5, −1.0; MS *m/z*: 346 (M^+, 8.8); HRMS calcd for $C_{18}H_{22}O_3SSi$: 346.1059, found 346.1068; Anal. Calcd for $C_{18}H_{22}O_3SSi$: C, 62.39; H, 6.40. Found: C, 62.04; H, 6.41. (1*Z*,3*E*)-1-(Phenylsulfonyl)-8-(trimethylsilyl)octa-1,3-dien-7-yne (**7a**); a colorless oil; IR: 2174, 1637, 1321, 1147 cm^{-1}; ^1H NMR δ: 7.90 (d, 2H, J=7.9 Hz), 7.60 (t, 1H, J=7.9 Hz), 7.53 (t, 2H, J=7.9 Hz), 7.36 (dd, 1H, J=14.6, 11.6 Hz), 6.58 (dd, 1H, J=11.6, 11.0 Hz), 6.15 (dt, 1H, J=14.6, 7.3 Hz), 6.03 (d, 1H, J=11.0 Hz), 2.46–2.43 (m, 2H), 2.36 (t, 2H, J=7.3 Hz), 0.14 (s, 9H); ^{13}C NMR δ: 145.6, 141.8, 141.6, 133.1, 129.1, 127.1, 125.7, 124.8, 105.5, 85.7, 32.0, 19.3, 0.0; MS *m/z*: 318 (M^+, 1.6); HRMS calcd for $C_{17}H_{22}O_2SSi$: 318.1110, found: 318.1118.

4.4.2. General procedure for Pauson–Khand reaction of allenynes with [RhCl(CO)$_2$]$_2$ under a CO atmosphere. $[RhCl(CO)_2]_2$ (1.0 mg, 2.5×10^{-3} mmol or 2.0 mg, 5.0×10^{-3} mmol) was added to a solution of allenyne (0.10 mmol) in toluene, xylene, or mesitylene (1.0 mL). The reaction mixture was refluxed under a CO atmosphere until the starting material completely disappeared (monitored 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.

4.4.3. General procedure for Pauson–Khand reaction of allenynes with [RhCl(CO)$_2$]$_2$ under 5 or 10 atm of CO. $[RhCl(CO)_2]_2$ (1.0 mg, 2.5×10^{-3} mmol) was added to a solution of allenyne (0.10 mmol) in xylene (1.0 mL). The reaction mixture was stirred at 150 °C under 5 or 10 atm of CO until the starting material completely disappeared (monitored by TLC). Xylene was evaporated off and the residual oil was chromatographed with hexane–AcOEt to afford cyclized products. Chemical yields are summarized in tables.

4.4.4. Pauson–Khand reaction of allenyne 4a with Co$_2$(CO)$_8$ and TMTU. $Co_2(CO)_8$ (10 mg, 3.0×10^{-2} mmol) was added to a solution of allenyne **4a** (32 mg, 0.10 mmol) and TMTU (4.0 mg, 3.0×10^{-2} mmol) in xylene (1.0 mL). The reaction mixture was refluxed under a CO atmosphere for 1 h. Xylene was evaporated off and the residual oil was chromatographed with hexane–AcOEt (3:1) to afford **5a** (12 mg, 35%).

4.4.5. Pauson–Khand reaction of allenyne 4a with Mo(CO)$_6$ and DMSO. $Mo(CO)_6$ (32 mg, 0.12 mmol) was added to a solution of allenyne **4a** (32 mg, 0.10 mmol) and DMSO (8.0×10^{-2} mL, 1.0 mmol) in xylene (1 mL). The reaction mixture was refluxed under a CO atmosphere for 2 h. Xylene was evaporated off and the residual oil was

chromatographed with hexane–AcOEt (3:1) to afford **5a** (6.2 mg, 18%).

4.4.6. 9-(Phenylsulfonyl)bicyclo[4.3.0]nona-1,6-dien-8-one (5b). A yellow oil; IR: 1701, 1310, 1144 cm^{-1}; ^1H NMR δ: 7.80–7.78 (m, 2H), 7.66–7.62 (m, 1H), 7.52–7.49 (m, 2H), 6.71 (t, 1H, J=4.2 Hz), 5.74 (d, 1H, J=0.7 Hz), 4.29 (s, 1H), 2.64–2.51 (m, 2H), 2.47–2.36 (m, 2H), 1.79 (quin, 2H, J=6.3 Hz); ^{13}C NMR δ: 193.5, 171.8, 136.9, 134.7, 134.1, 130.6, 129.5, 128.7, 126.3, 68.6, 26.2, 25.6, 21.3; MS m/z: 274 (M^+, 2.0); HRMS calcd for $C_{15}H_{14}O_3S$: 274.0664, found: 274.0654.

4.4.7. 7-Phenyl-9-(phenylsulfonyl)bicyclo[4.3.0]nona-1,6-dien-8-one (5c). A yellow oil; IR: 1703, 1323, 1175 cm^{-1}; ^1H NMR δ: 7.75–7.72 (m, 2H), 7.58–7.53 (m, 1H), 7.45–7.39 (m, 2H), 7.31–7.16 (m, 3H), 7.12–7.09 (m, 2H), 6.73 (t, 1H, J=4.3 Hz), 4.36 (s, 1H), 2.72–2.49 (m, 2H), 2.41–2.39 (m, 2H), 1.71 (quin, 2H, J=6.4 Hz); ^{13}C NMR δ: 192.0, 165.6, 136.9, 136.3, 134.2, 134.1, 130.1, 129.7, 129.5, 128.8, 128.7, 128.22, 128.17, 68.7, 25.74, 25.67, 21.4; MS m/z: 350 (M^+, 3.8); HRMS calcd for $C_{21}H_{18}O_3S$: 350.0977, found: 350.0975.

4.4.8. *N*-[4-(Methylbenzene)sulfonyl]-9-(phenylsulfonyl)-7-(trimethylsilyl)-4-azabicyclo[4.3.0]nona-1,6-dien-8-one (17a). A pale yellow oil; IR: 1699, 1310, 1165 cm^{-1}; ^1H NMR δ: 7.72 (d, 2H, J=8.3 Hz), 7.65–7.62 (m, 3H), 7.52–7.49 (m, 2H), 7.31 (d, 2H, J=8.3 Hz), 6.53–6.52 (m, 1H), 4.45 (d, 1H, J=16.8 Hz), 4.15 (dd, 1H, J=18.8, 4.4 Hz), 4.11 (s, 1H), 4.00–3.92 (m, 2H), 2.42 (s, 3H), 0.15 (s, 9H); ^{13}C NMR δ: 196.6, 168.6, 144.4, 139.5, 136.7, 134.3, 133.5, 130.8, 129.9, 129.4, 128.9, 127.6, 126.7, 68.2, 44.9, 44.6, 21.5, −1.3; MS m/z: 501 (M^+, 17); HRMS calcd for $C_{24}H_{27}O_5NS_2Si$: 501.1100, found: 501.1099.

4.4.9. 7-Phenyl-9-(phenylsulfonyl)-4-oxabicyclo[4.3.0]-nona-1,6-dien-8-one (17b). A pale yellow oil; IR: 1711, 1325, 1155 cm^{-1}; ^1H NMR δ: 7.85–7.33 (m, 8H), 7.16–7.12 (m, 2H), 6.81 (t, 1H, J=3.3 Hz), 4.72 (AB-q, 2H, J=16.3 Hz), 4.51–4.48 (m, 3H); ^{13}C NMR δ: 191.4, 159.7, 136.7, 134.4, 134.3, 130.6, 129.5, 129.2, 128.8, 128.5, 127.2, 68.1, 65.1, 63.8; MS m/z: 352 (M^+, 2.4); HRMS calcd for $C_{20}H_{16}O_4S$: 352.0769, found: 352.0766.

4.4.10. 7-Butyl-9-(phenylsulfonyl)-4-oxabicyclo[4.3.0]-nona-1,6-dien-8-one (17c). Colorless plates; 156–157.5 °C (AcOEt); IR: 1709, 1622, 1310, 1150 cm^{-1}; ^1H NMR δ: 7.82–7.80 (m, 2H), 7.67–7.64 (m, 1H), 7.54–7.51 (m, 2H), 6.64 (t, 1H, J=3.1 Hz), 4.62 (d, 1H, J=16.5 Hz), 4.49 (d, 1H, J=16.5 Hz), 4.42–4.41 (m, 2H), 4.35 (s, 1H), 2.17–2.11 (m, 1H), 2.03–1.98 (m, 1H), 1.26–1.05 (m, 4H), 0.82 (t, 3H, J=6.7 Hz); ^{13}C NMR δ: 193.0, 159.8, 137.2, 136.8, 134.2, 129.4, 128.8, 128.5, 127.3, 67.5, 64.9, 63.1, 29.8, 22.7, 22.3, 13.7; MS m/z: 332 (M^+, 0.2); HRMS calcd for $C_{18}H_{20}O_4S$: 332.1082, found: 332.1093.

4.4.11. 2-Phenyl-4-[(*E*)-(phenylsulfonyl)methylene]-7-oxabicyclo[3.3.0]oct-1-en-3-one (18b). A pale yellow oil; IR: 1719, 1325, 1153 cm^{-1}; ^1H NMR δ: 7.96–7.94 (m, 2H), 7.72–7.69 (m, 1H), 7.62–7.59 (m, 2H), 7.56–7.54 (m, 2H), 7.46–7.40 (m, 3H), 7.14 (d, 1H, J=2.0 Hz), 5.05 (dd, 1H, J=16.6, 1.5 Hz), 4.95 (t, 1H, J=8.3 Hz), 4.66 (dd, 1H, J=16.6, 1.0 Hz), 4.35–4.32 (m, 1H), 3.49 (dd, 1H, J=10.5, 8.3 Hz); ^{13}C NMR δ: 193.1, 175.0, 142.6, 139.6, 136.0, 134.4, 131.2, 129.8, 129.7, 129.5, 128.8, 128.1, 127.9, 69.4, 66.3, 46.9; MS m/z: 352 (M^+, 4.1); HRMS calcd for $C_{20}H_{16}O_4S$: 352.0769, found: 352.0776.

4.4.12. 2-Butyl-4-[(*E*)-(phenylsulfonyl)methylene]-7-oxabicyclo[3.3.0]oct-1-en-3-one (18c). A pale yellow oil; IR: 1708, 1637, 1310, 1153 cm^{-1}; ^1H NMR δ: 7.92–7.90 (m, 2H), 7.68–7.66 (m, 1H), 7.60–7.57 (m, 2H), 7.01 (d, 1H, J=1.8 Hz), 4.85 (t, 1H, J=7.9 Hz), 4.64 (AB-q, 2H, J=15.9 Hz), 4.16–4.12 (m, 1H), 3.43 (dd, 1H, J=10.3, 7.9 Hz), 2.40–2.34 (m, 1H), 2.24–2.18 (m, 1H), 1.48–1.26 (m, 4H), 0.87 (t, 3H, J=7.3 Hz); ^{13}C NMR δ: 195.1, 173.6, 142.2, 139.7, 138.6, 134.3, 130.3, 129.6, 127.9, 70.0, 64.7, 46.8, 29.8, 24.3, 22.5, 13.7; MS m/z: 332 (M^+, 0.1); HRMS calcd for $C_{18}H_{20}O_4S$: 332.1082, found: 332.1084.

4.4.13. *N*-[4-(Methylbenzene)sulfonyl]-10-(phenylsulfonyl)-8-(trimethylsilyl)-5-azabicyclo[5.3.0]deca-1,7-dien-9-one (19). A brown oil; IR: 1697, 1308, 1161 cm^{-1}; ^1H NMR δ: 7.74–7.72 (m, 2H), 7.66–7.52 (m, 5H), 7.32–7.30 (m, 2H), 6.51 (t, 1H, J=5.1 Hz), 4.42 (d, 1H, J=17.8 Hz), 4.16–4.01 (m, 2H), 3.56–3.46 (m, 2H), 2.80–2.74 (m, 2H), 2.43 (s, 3H), 0.16 (s, 9H); ^{13}C NMR δ: 196.9, 174.4, 143.9, 143.4, 136.4, 135.8, 134.2, 133.8, 131.6, 129.9, 129.4, 128.9, 126.9, 72.5, 50.7, 48.4, 32.2, 21.5, −0.8; MS m/z: 515 (M^+, 74.6); HRMS calcd for $C_{25}H_{29}O_5NS_2Si$: 515.1257, found: 515.1265.

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11. Both 3-iodo-1-phenylprop-1-yne (Richard, C. L.; Chow, M.-S. *Tetrahedron Lett.* **1984**, *25*, 2727–2728) and 1-iodohept-2-yne (Homsi, F.; Rousseau, G. *Tetrahedron Lett.* **1999**, *40*, 1495–1498) are known compounds.
12. We have tried to prepare the 5-oxa congener of **4a** in order to compare its reactivity with those of the allenynes **4a** and **12a**, both of which have a trimethylsilyl group at the triple bond terminus. However, the Williamson ether synthesis of **9a** with 3-iodo-1-trimethylsilylprop-1-yne did not produce the corresponding ether derivative except for the formation of the desilylated product.
13. The stereochemistry of compound **18** was determined to be (*E*) by comparison of the NMR spectral data with those of the compounds obtained by the $Mo(CO)_6$-mediated PKR, see Ref. 7.
14. Two examples for the low-yield formation of the α-alkylidenebicyclo[3.3.0]oct-1-en-3-one skeleton by the Rh(I)-catalyzed PKR were reported, see Refs. 3c,e.
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