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Efficient Construction of the Bicyclo[5.3.0]decenone Skeleton Based on the Rh(I)-Catalyzed Allenic Pauson−Khand Reaction

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A reliable procedure for constructing a bicyclo[5.3.0]deca-1,7-dien-9-one ring system by rhodium-catalyzed Pauson−Khand reaction (PKR) of allenynes with a sulfonyl group has been developed. Investigation of the rhodium-catalyzed PKR on 19 examples of 1,2-nonadien-8-yne derivatives demonstrated that (i) acceptable yields could be consistently achieved through the proper choice of the rhodium catalyst ($[RhCl(CO)_2]_2$ or $[RhCl(CO)dppp]_2$) depending on the starting allenyne and that (ii) an ester functionality as well as hydroxy and siloxy groups could be tolerated in this rhodium-catalyzed PKR.

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. Recent efforts from this laboratory have established an efficient procedure for the highly stereoselective construction of the optically active bicyclo[3.3.0]octenone **2** (n = 1)[2a,b] and bicyclo[4.3.0]nonenone **2** (n = 2)[2c,d] frameworks having a bis(*tert*-butyldimethylsiloxy) functionality (R = TBDMS) at both the allyl and homoallyl positions based on an intramolecular PKR of the optically active enyne **1** (n = 1, 2), which was easily derived from L-tartrate. This scheme would allow us to prepare the enantiomer of **2** when the commercially available D-tartrate is employed as a starting material.

When the enyne **1** (n = 3) was submitted to similar ring closure conditions, however, none of target bicyclo[5.3.0]decenone derivative **2** (n = 3)[3] could be detected in the reaction mixture. Contrary to our expectations, the unexpected bicyclo[4.3.0]nonenone compound **3** with a methyl group α to the carbonyl moiety was produced in a stereoselective manner. The formation of **3** could tentatively be rationalized in terms of the intermediacy of the cobalt complex **4**[3] with the isomerized internal double bond, which should give rise to the formation of **3**. In fact, the application of the $Co_2(CO)_8$-mediated intramolecular PKR of the enynes to the synthesis of the bicyclo[5.3.0] ring system[3,4] has not yet been realized, except for the preparation of the azabicyclo[5.3.0]-decenone derivatives[5] and medium-sized oxacyclic compounds[6,7] from enynes with an aromatic ring as a template.

On the other hand, the alkyne derivatives **5** with an allenyl functionality[8−11] instead of an olefin group were found to produce the corresponding bicyclo[5.3.0]deca-1,7-dien-9-one **6** under $Co_2(CO)_8$-mediated PKR conditions,[8c] although the chemical yields were far from satisfactory. In addition, Narasaka[9] has developed a new procedure for the synthesis of bicyclo[5.3.0]deca-1,7-dien-9-one **8** in low yield (15%) from allenyne **7** through an $Fe(CO)_4(NMe_3)$-mediated PKR-type reaction. If a straight-

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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, Germany, 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.

(2) (a) Mukai, C.; Uchiyama, M.; Sakamoto, S.; Hanaoka, M. *Tetrahedron Lett.* **1995**, *36*, 5761−5764. (b) Mukai, C.; Kim, J. S.; Uchiyama, M.; Sakamoto, S.; Hanaoka, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2903−2915. (c) Mukai, C.; Kim. J. S.; Uchiyama, M.; Hanaoka, M. *Tetrahedron Lett.* **1998**, *39*, 7909−7912. (d) Mukai, C.; Kim, J. S.; Sonobe, H.; Hanaoka, M. *J. Org. Chem.* **1999**, *64*, 6822−6832.

(3) Mukai, C.; Sonobe, H.; Kim, J. S.; Hanaoka, M. *J. Org. Chem.* **2000**, *65*, 6654−6659.

(4) A bicyclo[5.3.0]decenone framework with an oxygen-bridged structure was synthesized in 29% yield by the zirconocene-mediated PKR. See: Wender, P. A.; McDonald, F. E. *Tetrahedron Lett.* **1990**, *31*, 3691−3694. However, this structure can be regarded as an oxabicyclo[4.3.0]nonenone skeleton. In addition, attempted $Co_2(CO)_8$-mediated PKR was unsuccessful.

(5) Pérez-Serrano, L.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Chem. Commun.* **2001**, 2602−2603.

(6) (a) Krafft, M. E.; Fu, Z.; Boñaga, L. V. R. *Tetrahedron Lett.* **2001**, *42*, 1427−1431. (b) Lovely, C. J.; Seshadri, H.; Wayland, B. R.; Cordes, A. W. *Org. Lett.* **2001**, *3*, 2607−2610.

(7) Zr-Mediated PKR for the preparation of medium-sized rings with an aromatic ring was also reported. Barluenga, J.; Sanz, R.; Fañanás, F. J. *Chem. Eur. J.* **1997**, *3*, 1324−1336.

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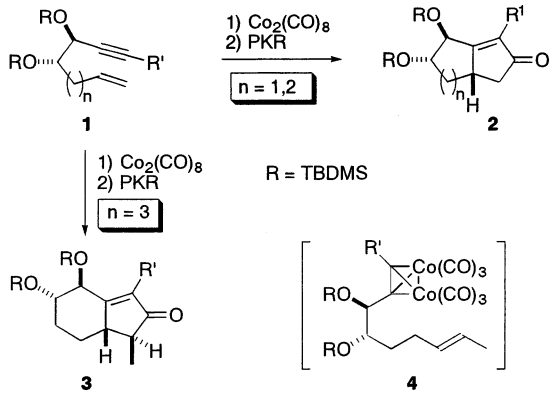
forward efficient procedure for the preparation of bicyclo-[5.3.0]decane ring systems under PKR conditions in an acceptable yield could be developed, it would become a useful alternative method for the synthesis of many bioactive natural products possessing a bicyclo[5.3.0]-decane skeleton[12] as the basic carbon core framework.

In this paper, we describe the efficient rhodium-catalyzed PKR of allenynes for the construction of 2-phenylsulfonylbicyclo[5.3.0]deca-1,7-dien-9-one derivatives.[13,14]

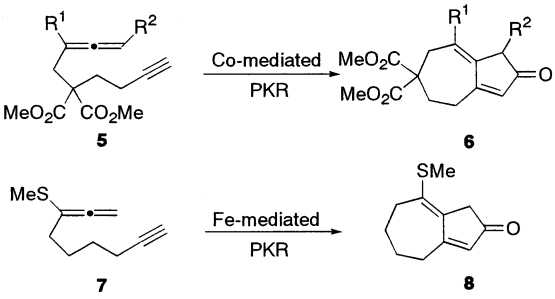
Results and Discussion

Pauson−Khand Reaction of 3-Phenylsulfonylocta-1,2-dien-7-yne Derivatives. We have devoted considerable attention to allenynes with a sulfinyl or sulfonyl group as starting materials for this investigation, because (i) various allenynes could be prepared from the corresponding propargyl alcohols through a [2,3]-sigmatropic rearrangement by using arenesulfenyl halide[15] and (ii) chemical transformation of the sulfur-containing groups into other functionalities would be easily achieved. At the beginning of this program, our first efforts were focused on the PKR of the octa-1,2-dien-7-yne species **11** and **12** to find efficient and practical conditions for constructing the bicyclo[4.3.0]nonane and/or bicyclo[3.3.0]octane ring systems. Thus, the required allenynes **11** and **12** were easily prepared from 4-pentyn-1-ol (**9**) via the [2,3]-sigmatropic rearrangement of the propargyl alcohol **10** as shown in Scheme 3. Introduction of a silyl group at the triple-bond terminus of **9** was followed by iodination to give the corresponding iodo derivative, which was subsequently exposed to the coupling reaction with 3-(*tert*-butyldiphenylsiloxy)prop-1-yne producing the diyne

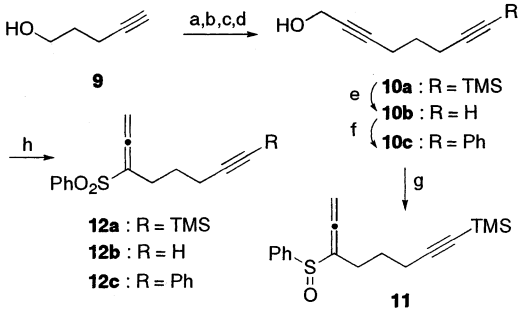
SCHEME 1



SCHEME 2



SCHEME 3[a]



[a] Reaction conditions: (a) ^{n}BuLi, TMSCl, THF, −78 °C, then 10% HCl, rt; (b) I_2, PPh_3, imidazole, CH_2Cl_2, rt; (c) $TBDPSOCH_2C{\equiv}CH$, ^{n}BuLi, THF−DMPU, −78 °C; (d) 10% HCl, MeOH, rt, (59%); (e) TBAF, THF, rt, (72%); (f) PhI, CuI, $Pd(PPh_3)_2Cl_2$, $^i Pr_2NH$, THF, rt, (82%); (g) PhSCl, Et_3N, THF, −78 °C, (96%); (h) (i) PhSCl, Et_3N, THF, −78 °C, (ii) *m*CPBA, CH_2Cl_2, 0 °C, **12a** (85%), **12b** (74%), **12c** (84%).

derivative. Subsequent removal of the silyl group on the primary hydroxyl group furnished **10a** in 59% overall yield. The other diynes **10b** and **10c**[16] were obtained from **10a** under conventional conditions. Exposure of **10a** to benzenesulfenyl chloride[15] in THF at −78 °C in the presence of Et_3N brought about the following transformation: (i) sulfenic ester formation, and (ii) the [2,3]-sigmatropic rearrangement resulting in the formation of the sulfinyl allenyne **11** in 96% yield. However, the Pauson−Khand reaction of **11** under several conditions was unsuccessful, presumably due to the sulfinyl moiety that might act as a weak oxidant leading to the deactivation of the catalysts employed. Therefore, we next examined the PKR of the sulfonyl derivatives **12**, which

(8) For Co-mediated PKR of allenynes, see: (a) Ahmar, M.; Antras, F.; Cazes, B. *Tetrahedron Lett.* **1995**, *36*, 4417−4420. (b) Ahmar, M.; Chabanis, O.; Gauthier, J.; Cazes, B. *Tetrahedron Lett.* **1997**, *38*, 5277−5280. (c) Ahmar, M.; Locatelli, C.; Colombier, D.; Cazes, B. *Tetrahedron Lett.* **1997**, *38*, 5281−5284. (d) Pagenkopf, B. L.; Belanger, D. B.; O'Mahony, D. J. R.; Livinghouse, T. *Synthesis* **2000**, 1009−1019. (e) Antras, F.; Ahmar, M.; Cazes, B. *Tetrahedron Lett.* **2001**, *42*, 8153−8156. (f) Antras, F.; Ahmar, M.; Cazes, B. *Tetrahedron Lett.* **2001**, *42*, 8157−8160.

(9) For Fe-mediated PKR of allenynes, see: Shibata, T.; Koga, Y.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 911−919.

(10) For Mo-mediated PKR of allenynes, see: (a) Kent, J. L.; Wan, H.; Brummond, K. M. *Tetrahedron Lett.* **1995**, *36*, 2407−2410. (b) Brummond, K. M.; Wan, H. *Tetrahedron Lett.* **1998**, *39*, 931−934. (c) Brummond, K. M.; Wan, H.; Kent, J. L. *J. Org. Chem.* **1998**, *63*, 6535−6545. (d) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087−5088. (e) Brummond, K. M.; Lu, J.; Petersen, J. *J. Am. Chem. Soc.* **2000**, *122*, 4915−4920. (f) Xiong, H.; Hsung, R. P.; Wei, L.-L.; Berry, C. R.; Mulder, J. A.; Stockwell, B. *Org. Lett.* **2000**, *2*, 2869−2871. (g) Brummond, K. M.; Kerekes, A. D.; Wan, H. *J. Org. Chem.* **2002**, *67*, 5156−5163.

(11) For Zr-mediated PKR of allenynes, see refs 10b, 10c and 10g.

(12) For example, see: (a) Herz, W.; Santhanam, P. S. *J. Org. Chem.* **1965**, *30*, 4340−4342. (b) Lansbury, P. T.; Hangauer, D. G., Jr.; Vacca, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3964−3965. (c) Heathcock, C. H.; DelMar, E. G.; Graham, S. L. *J. Am. Chem. Soc.* **1982**, *104*, 1907−1917. (d) Grieco, P. A.; Majetich, G. F.; Ohfune, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4226−4233. (e) Heathcock, C. H.; Tice, C. M.; Germroth, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6081−6091.

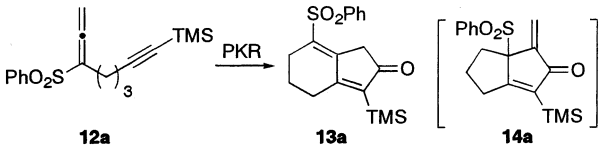
(13) Part of this work was published as a preliminary communication: Mukai, C.; Nomura, I.; Yamanishi, K.; Hanaoka, M. *Org. Lett.* **2002**, *4*, 1755−1758.

(14) Brummond and co-workers very recently reported the $[RhCl(CO)_2]_2$-catalyzed PKR of allenynes, which includes three examples of the formation of bicyclo[5.3.0]deca-1,7-dien-9-one derivatives: 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.

(15) Horner, L.; Binder, V. *Ann. Chem.* **1972**, *757*, 33−68.

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

TABLE 1. Pauson−Khand Reaction of 12a



12a **13a** **14a**

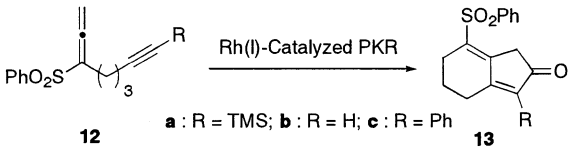
entry	condition	product	yield (%)
1	$Co_2(CO)_8$, TMANO, 4 Å MS, toluene, −10 °C	**13a**	52
2	$Co_2(CO)_8$, MeCN, 75 °C	**13a**	46
3	$Mo(CO)_6$, DMSO, toluene, 100 °C	**13a**	trace
4	$Fe(CO)_4(NMe_3)$, THF, *hν*, −30 °C	**13a**	18
5	$Fe_2(CO)_9$, DMSO, toluene, 100 °C	**13a**	18
6	$Ru_3(CO)_{12}$, DMF, 5 atm of CO, 130 °C		0

was easily prepared from **10** by consecutive sulfinylation and *m*CPBA oxidation (Scheme 3).

With the required allenynes **12** for the ring closure reaction in hand, these enynes were then submitted to the $Co_2(CO)_8$-mediated, as well as other metal-catalyzed, PKR conditions (Table 1). According to the general procedure for the formation of the alkyne−$Co_2(CO)_6$ complex,[1] allenyne **12a** was treated with $Co_2(CO)_8$ in Et_2O at room temperature to give an intractable mixture, from which the desired cobalt-complexed **12a** could not be isolated. Upon direct exposure to $Co_2(CO)_8$ and trimethylamine *N*-oxide (TMANO) in toluene at −10 °C in the presence of 4 Å molecular sieves,[17] **12a** underwent a ring closure reaction to provide the bicyclo[4.3.0]nonadienone derivative **13a** in 52% yield (entry 1). When directly treated with $Co_2(CO)_8$ in acetonitrile at 70−75 °C,[18] **12a** afforded **13a** in 46% yield (entry 2). Other typical $Co_2(CO)_8$-mediated PKR conditions were unsuccessful. It should be noted that the $Co_2(CO)_8$-mediated PKR of **12a** gave the bicyclo[4.3.0]nonadienone **13a** chemoselectively but not the corresponding bicyclo[3.3.0]-octenone derivative **14a**. We next examined the other metal-catalyzed PKR of **12a**. $Mo(CO)_6$ has recently been shown by Brummond[10] to be effective for the intramolecular PKR of allenynes. However, the desired ring-closed product **13a** was obtained only in trace amounts (entry 3). Narasaka's procedures with Fe catalysts[9] provided **13a** in rather lower yields (entries 4 and 5). $Ru_3(CO)_{12}$[19] was also ineffective in this PKR, resulting in a mixture of decomposed products (entry 6).

In the case of the $Co_2(CO)_8$-mediated PKR of **12a**, the bicyclo[4.3.0]nonadienone framework was chemoselectively formed in moderate yields (entries 1 and 2). However, these chemical yields are lower compared to those generally observed in the intramolecular PKR of alkyne-olefin species (nonenyne derivatives).[1] Therefore, we needed more reliable conditions with higher yield for the preparation of the bicyclo[4.3.0]nonadienone skeleton, which would ensure the construction of the bicyclo[5.3.0]decadienone framework. Recent reports from

TABLE 2. Pauson−Khand Reaction of 12 with Rh(I) Catalyst



a : R = TMS; **b** : R = H; **c** : R = Ph

12 **13**

entry	R	condition[a]	product	yield (%)
1	TMS	A	**13a**	63
2	H	A	**13b**	56
3	Ph	A	**13c**	58
4	TMS	B	**13a**	97
5	H	B	**13b**	85
6	Ph	B	**13c**	65

[a] Condition A: 2.5 mol % $[RhCl(CO)_2]_2$, toluene, 1 atm CO. Condition B: 2.5 mol % $[RhCl(CO)dppp]_2$, toluene, 1 atm CO.

Jeong[20] and Narasaka[21] independently disclosed that rhodium(I) catalysts are effective in the PKR of enynes. To develop a high-yielding reliable procedure for preparing bicyclo[4.3.0]nonadienone as well as bicyclo[5.3.0]-decadienone derivatives from allenynes by PKR,[22] we applied these rhodium-catalyzed conditions to the ring closure reaction of **12a**. The results are summarized in Table 2. According to Narasaka's procedure,[21] **12a** was treated with a catalytic amount of commercially available $[RhCl(CO)_2]_2$ (2.5 mol %) in refluxing toluene under a carbon monoxide atmosphere (conditions A)[23] for 6 h to afford **13a** in 63% yield as the sole product (entry 1). The hydrogen and phenyl congeners **12b** and **12c** also produced the corresponding bicyclic derivatives **13b** and **13c** in 56 and 58% yields, respectively (entries 2 and 3). $[RhCl(CO)dppp]_2$,[24] prepared from $[RhCl(cod)]_2$ and 1,3-bis(diphenylphosphino)propane (dppp), was found to be a more powerful catalyst in the transformation of **12** into **13**. Thus, on the basis of Jeong's procedure,[20] a mixture of **12a** in toluene was refluxed in the presence of 2.5 mol % $[RhCl(CO)dppp]_2$ for 8 h under an atmosphere of carbon monoxide (conditions B)[23] to give **13a** in 97% yield (entry 4). Similar treatment of **12b** and **12c** under conditions B furnished **13b** and **13c** in 85 and 65% yields, respectively (entries 5 and 6). The formation of **14** could not be detected in the reaction mixture in any case. These observations are in accordance with those reported in Table 1. Both rhodium(I) catalysts are regarded as superior catalysts for the construction of bicyclo[4.3.0]-nona-1,6-dien-8-ones **13** from allenynes **12** in comparison with other metal catalysts. In particular, $[RhCl(CO)-dppp]_2$ provided very satisfactory results. Thus, hoping to develop an efficient method for the synthesis of the corresponding bicyclo[5.3.0]deca-1,7-dien-9-one derivatives, we turned our attention to the intramolecular PKR

(17) Pérez-Serrano, L.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Org. Lett.* **1999**, *1*, 1187−1188.

(18) (a) Hoye, T. R.; Suriano, J. A. *J. Org. Chem.* **1993**, *58*, 1659−1660. (b) Chung, Y. K.; Lee, B. Y.; Jeong, N.; Hudecek, M.; Pauson, P. L. *Organometallics* **1993**, *12*, 220−223.

(19) (a) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762−3765. (b) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187−6188.

(20) (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.

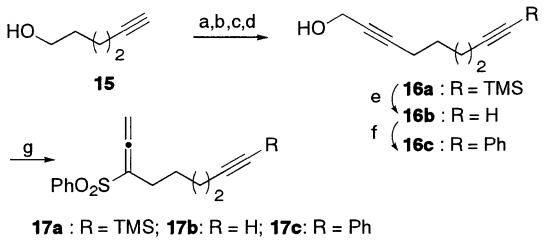
(21) (a) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249−250. (b) Kobayashi, T.; Koga, Y.; Narasaka, K. *J. Organomet. Chem.* **2001**, *624*, 73−87.

(22) During this investigation, the $[RhCl(CO)_2]_2$-catalyzed PKR of an allenyne leading to formation of the bicyclo[4.3.0]nona-1,6-dien-8-one derivative in 61% yield was reported. See ref 21b.

(23) Rh(I)-catalyzed PKR of the sulfoxide **11** was examined under conditions A and B; however, no reaction took place and the starting sulfoxide was completely recovered intact.

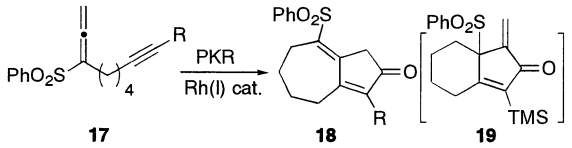
(24) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120−129.

SCHEME 4[a]



[a] Reaction conditions: (a) ^{n}BuLi, TMSCl, THF, −78 °C, then 10% HCl, rt; (b) I_2, PPh_3, imidazole, CH_2Cl_2, rt; (c) $TBDMSOCH_2C{\equiv}CH$, ^{n}BuLi, THF−DMPU, −78 °C; (d) 10% HCl, MeOH, rt, (54%); (e) TBAF, THF, rt, (96%); (f) PhI, CuI, $Pd(PPh_3)_2Cl_2$, $^i Pr_2NH$, THF, rt, (68%); (g) (i) PhSCl, Et_3N, THF, −78 °C, (ii) *m*CPBA, CH_2Cl_2, 0 °C, **17a** (78%), **17b** (69%), **17c** (69%).

TABLE 3. Pauson−Khand Reaction of 17 with Rh(I) Catalyst



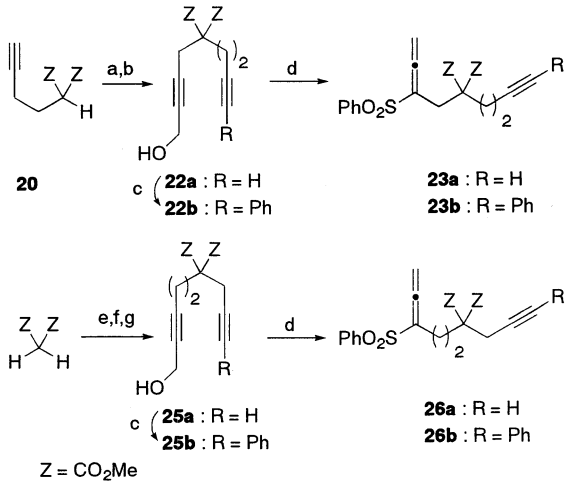
entry	R	condition[a]	mol % catalyst	product	yield (%)
1	TMS	A	5.0	**18a**	45
2	H	A	2.5	**18b**	61
3	H	A	5.0	**18b**	58
4	Ph	A	2.5	**18c**	55
5	TMS	B	5.0	**18a**	74
6	H	B	2.5	**18b**	69
7	H	B	5.0	**18b**	75
8	Ph	B	2.5	**18c**	84

[a] Condition A: 2.5 or 5.0 mol % $[RhCl(CO)_2]_2$, toluene, 1 atm CO. Condition B: 2.5 or 5.0 mol % [RhCl(CO)dppp]$_2$, toluene, 1 atm CO.

of the one-carbon-homologated allenynes **17** under the two rhodium-catalyzed conditions A and B.

Rhodium-Catalyzed Pauson−Khand Reaction of 3-Phenylsulfonylnona-1,2-dien-8-yne Derivatives. By analogy to the preparation of the octa-1,2-dien-7-yne derivatives **12**, the one-carbon-homologated starting allenynes **17** for rhodium-catalyzed PKR were prepared in a straightforward manner from 5-hexyn-1-ol (**15**), as shown in Scheme 4. For the initial evaluation of the rhodium-catalyzed PKR of the allenynes **17**, we first attempted the cyclization of compound **17b** under conditions A with 2.5 mol % catalyst to afford the bicyclo[5.3.0]-deca-1,7-dien-9-one derivative **18b** in 61% yield as the sole isolable product (Table 3, entry 2).[25] The other possible isomer **19b**, which would arise from the reaction of the alkyne moiety with the internal double bond of the 1,2-diene functionality, could never be detected in the reaction mixture.[26] Increasing the amount of the catalyst to 5.0 mol % in the same reaction did not improve the chemical yield (entry 3). The TMS and phenyl congeners **17a** and **17c** also underwent the [2 + 2 + 1]-type ring closure reaction to give the corresponding bicyclo[5.3.0]-deca-1,7-dien-9-ones **18a** and **18c** in yields of 58 and 55%, respectively (entries 1 and 4). We could then reproducibly obtain the bicyclo[5.3.0]deca-1,7-dien-9-one skeleton by PKR reaction, although the chemical yields were moderate. Furthermore, the transformation of the allenynes **17** into the desired **18** in higher chemical yields was realized when **17** was exposed to conditions B (entries 5−8). Thus, we revealed the efficiency for intramolecular rhodium-catalyzed PKR of the allenynes leading to the construction of not only the bicyclo[4.3.0]nona-1,6-dien-8-one but also the bicyclo[5.3.0]deca-1,7-dien-9-one frameworks in reasonable chemical yields.

SCHEME 5[a]



[a] Reaction conditions: (a) NaH, THF, $ICH_2C{\equiv}CCH_2OTBDPS$ (**21**), from 0 °C to rt; (b) TBAF, THF, rt, (80%); (c) PhI, $PdCl_2(PPh_3)_2$, CuI, $^i Pr_2NH$, THF, rt, **22b** (82%), **25b** (95%); (d) (i) PhSCl, Et_3N, THF, −78 °C, (ii) *m*CPBA, CH_2Cl_2, 0 °C, **23a** (78%), **23b** (80%), **26a** (77%), **26b** (80%); (e) NaH, DMF, $ICH_2CH_2C{\equiv}CCH_2OTHP$ (**24**), from 0 °C to rt; (f) NaH, THF, $BrCH_2C{\equiv}CH$, from 0 °C to rt; (g) *p*-TsOH, MeOH, rt, (56%).

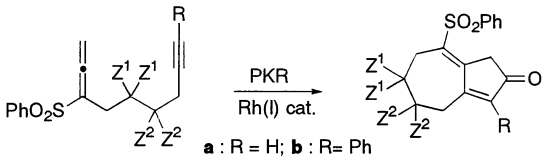
The next phase of this program involved the application of this newly developed rhodium-catalyzed procedure to the construction of other bicyclo[5.3.0]deca-1,7-dien-9-ones. To this end, two types of 1,2-nonadien-8-yne derivatives **23** and **26** were prepared under conventional means, as depicted in Scheme 5. Upon exposure to both conditions A and B, **23a** and **23b** produced the corresponding bicyclo[5.3.0]deca-1,7-dien-9-one derivatives **27a** and **27b** in high yields (Table 4, entries 1−4).[27] In one series of compounds **26**, an efficient production of the cyclized compounds **28a** and **28b** in high yields was observed under conditions B (entries 7 and 8). In contrast to the results in entries 7 and 8, conditions A produced **28a** and **28b** in lower yields (entries 5 and 6). Table 4 indicates that the rhodium-catalyzed intramolecular PKR of the 1,2-nonadien-8-yne derivatives with the methoxycarbonyl functionality proceeded as anticipated. In particular, conditions B ([RhCl(CO)dppp]$_2$ catalyst) were consistently effective for the [2 + 2 + 1] ring closure reaction of both compounds **23** and **26**.

(25) Examination of each experiment was carried out several times to confirm its reproducibility. In some cases, the chemical yields we reported in the previous paper[13] were improved. In particular, we reported that cyclization of **17a** under conditions B gave **18a** in 7% yield along with recovered starting material (45%). It was ultimately found that the low reactivity of **17a**, observed under conditions B, was due to contamination by impurities. Thus, the purified **17a** produced **18a** under conditions B in 74% yield (entry 5).

(26) A similar behavior was observed by Brummond.[14]

(27) Examination of each experiment was carried out several times to confirm its reproducibility. In some cases, the chemical yields reported in our previous paper[13] were improved.

TABLE 4. Pauson−Khand Reaction of 23 and 26 with Rh(I) Catalyst

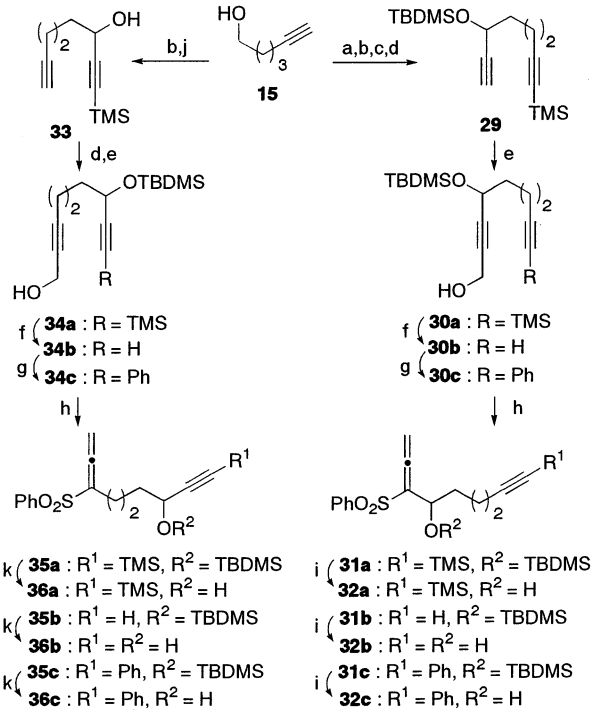


23: Z^1 = CO_2Me, Z^2 = H
26: Z^1 = H, Z^2 = CO_2Me
27: Z^1 = CO_2Me, Z^2 = H
28: Z^1 = H, Z^2 = CO_2Me

entry	SM	R	condition[a]	product	yield (%)
1	**23a**	H	A	**27a**	84
2	**23b**	Ph	A	**27b**	70
3	**23a**	H	B	**27a**	80
4	**23b**	Ph	B	**27b**	89
5	**26a**	H	A	**28a**	58
6	**26b**	Ph	A	**28b**	40
7	**26a**	H	B	**28a**	83
8	**26b**	Ph	B	**28b**	96

[a] Condition A: 2.5 mol % $[RhCl(CO)_2]_2$, toluene, 1 atm CO. Condition B: 2.5 mol % $[RhCl(CO)dppp]_2$, toluene, 1 atm CO.

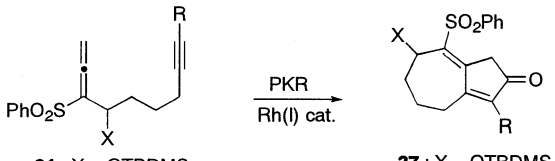
SCHEME 6[a]



[a] Reaction conditions: (a) ^{n}BuLi, TMSCl, THF, −78 °C, then 10% HCl, rt; (b) Py·SO_3, DMSO, Et_3N, rt; (c) HC≡CMgBr, THF, −20 °C; (d) TBDMSCl, imidazole, DMF, rt, (45%); (e) ^{n}BuLi, $(HCHO)_n$, THF, −78 °C, **30a** (73%), **34a** (86%) from **33**; (f) K_2CO_3, MeOH, rt, **30b** (95%), **34b** (91%); (g) PhI, $PdCl_2(PPh_3)_2$, CuI, $^i Pr_2NH$, THF, rt, **30c** (93%), **34c** (89%); (h) PhSCl, Et_3N, THF, −78 °C, then *m*CPBA, CH_2Cl_2, 0 °C, **31a** (94%), **31b** (94%), **31c** (85%), **35a** (35%), **35b** (81%), **35c** (70%); (i) 10% HCl, MeOH, rt, **32a** (77%), **32b** (98%), **32c** (85%); (j) ^{n}BuLi, TMS−C≡CH, THF, −78°C, **33** (51%) from **15**; (k) 10% HCl, THF, rt, **36a** (94%), **36b** (98%), **36c** (quantitative).

We next investigated some additional examples of the rhodium-catalyzed PKR of the 1,2-nonadien-8-yne derivatives possessing a hydroxyl or a siloxy group, both of which might be considered as latent functionalities for further elaboration. According to the aforementioned procedure in Scheme 4, the common starting material, 5-hexyn-1-ol (**15**), was easily converted into four types of 1,2-nonadien-8-yne derivatives **31**, **32**, **35**, and **36** as depicted in Scheme 6. The rhodium-catalyzed PKR of **31** and **32** was carried out under the standard conditions A and B. The results are summarized in Table 5. The bicyclo[5.3.0]deca-1,7-dien-9-one skeletons **37** and **38** were formed reproducibly, although the chemical yields vary ranging from 41 to 91%. It should be mentioned that a significant difference between conditions A and B in the PKR of **31** and **32** could not be found. This observation is in contrast to the PKR of the 1,2-nonadien-8-yne derivatives **17** and **26** (Tables 3 and 4), in which conditions B consistently provided the ring-closed products in higher yields than conditions A, i.e., conditions B seemed to be superior to conditions A as long as **17** and **26** were used as the starting allenyne. A similar tendency (chemical yields and behavior toward conditions A and B) was observed when the 1,2-nonadien-8-yne derivative **35** with a siloxy group at the propargyl position was submitted to the rhodium-catalyzed PKR resulting in the formation of **39** in a range of 47−94% yield. The results obtained are summarized as entries 1−6 in Table 6. In the case of **36** with a free hydroxyl group at the propargyl position, the corresponding bicyclo[5.3.0]deca-1,7-dien-9-one **40** was produced in moderate to high yield under conditions B (entries 10−12). When **36b** was exposed to conditions A, however, the desired product **40b** was obtained in only 15% yield as the sole isolable product (entry 8). In addition, the ring closure reaction of **36c** proceeded under conditions A, but the product isolated from the reaction mixture was the dehydrated compound 8-phenyl-2-phenylsulfonylbicyclo[5.3.0]deca-1,5,7-trien-9-one (**41**) in 13% yield, presumably formed from the desired **40c** in the reaction mixture (entry 9). The instability of **41** might explain the low chemical yield. The behavior of compound **36** toward the rhodium-catalyzed conditions was similar to that of compounds **17** and **26**.

TABLE 5. Pauson−Khand Reaction of 31 and 32 with Rh(I) Catalyst



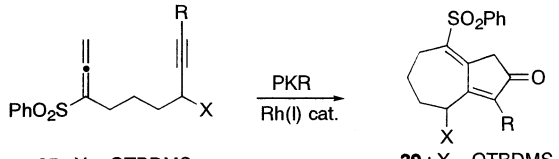
31 : X = OTBDMS
32 : X = OH
37 : X = OTBDMS
38 : X = OH

a : R = TMS; **b** : R = H; **c** : R = Ph

entry	SM	R	condition[a]	product	yield (%)
1	**31a**	TMS	A	**37a**	89
2	**31b**	H	A	**37b**	49
3	**31c**	Ph	A	**37c**	51
4	**31a**	TMS	B	**37a**	91
5	**31b**	H	B	**37b**	66
6	**31c**	Ph	B	**37c**	45
7	**32a**	TMS	A	**38a**	68
8	**32b**	H	A	**38b**	46
9	**32c**	Ph	A	**38c**	41
10	**32a**	TMS	B	**38a**	66
11	**32b**	H	B	**38b**	83
12	**32c**	Ph	B	**38c**	42

[a] Condition A: 2.5 mol % $[RhCl(CO)_2]_2$, toluene, 1 atm CO. Condition B: 2.5 mol % $[RhCl(CO)dppp]_2$, toluene, 1 atm CO.

TABLE 6. Pauson−Khand Reaction of 35 and 36 with Rh(I) Catalyst



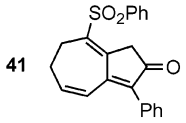
35 : X = OTBDMS
36 : X = OH

39 : X = OTBDMS
40 : X = OH

a : R = TMS; **b** : R = H; **c** : R = Ph

entry	SM	R	condition[a]	product	yield (%)
1	**35a**	TMS	A	**39a**	87
2	**35b**	H	A	**39b**	47
3	**35c**	Ph	A	**39c**	66
4	**35a**	TMS	B	**39a**	65
5	**35b**	H	B	**39b**	53
6	**35c**	Ph	B	**39c**	94
7	**36a**	TMS	A	**40a**	53
8	**36b**	H	A	**40b**	15
9	**36c**	Ph	A	**40c**	trace[b]
10	**36a**	TMS	B	**40a**	93
11	**36b**	H	B	**40b**	45
12	**36c**	Ph	B	**40c**	84

[a] Condition A: 2.5 mol % $[RhCl(CO)_2]_2$, toluene, 1 atm CO. Condition B: 2.5 mol % $[RhCl(CO)dppp]_2$, toluene, 1 atm CO. [b] 8-Phenyl-2-phenylsulfonylbicyclo[5.3.0]deca-1,5,7-trien-9-one (**41**) was obtained in 13% yield.



In summary, we have developed a reliable procedure for constructing a bicyclo[5.3.0]deca-1,7-dien-9-one ring system by the rhodium-catalyzed PKR of allenynes with a sulfonyl group, in which commercially available $[RhCl(CO)_2]_2$ as well as $[RhCl(CO)dppp]_2$, derived from $[RhCl(cod)]_2$, were employed as catalysts. Investigation of the rhodium-catalyzed PKR on the 19 examples of the 1,2-nonadien-8-yne derivatives demonstrated (i) that acceptable yields could be consistently achieved through the proper choice of the rhodium catalyst depending on the starting allenyne and (ii) that not only an ester functionality but also hydroxyl and siloxy groups can be tolerated in this rhodium-catalyzed PKR. The application of this rhodium-catalyzed PKR of allenynes to the construction of other ring systems as well as to the synthesis of bioactive compounds is now in progress.

Experimental Section

Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in $CDCl_3$. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CHCl_3$ (77.00 ppm) as an internal standard. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Silica gel (silica gel 60, 230−400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

1-(Trimethylsilyl)-1,6-octadiyn-8-ol (10a). To a solution of 4-pentyn-1-ol (155 mg, 1.85 mmol) in dry THF (18 mL) was added *n*-BuLi in hexane (1.53 M, 3.60 mL, 5.54 mmol) at −78 °C. After the mixture was stirred for 30 min, TMSCl (1.40 mL, 11.1 mmol) was added, and the reaction mixture was gradually warmed to room temperature and stirred for 3 h. Then, 10% aqueous HCl (6.0 mL) was added to the reaction mixture. After being stirred for 4 h, the reaction mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. To the crude alcohol in dry CH_2Cl_2 (18 mL) were added PPh_3 (1.74 g, 6.64 mmol) and imidazole (452 mg, 6.64 mmol). Then, I_2 (1.69 g, 6.64 mmol) was added to the reaction mixture. After the mixture was stirred for 2 h, CH_2Cl_2 was evaporated off, and the residue was passed through a short pad of silica gel with 10:1 hexane−AcOEt to afford the crude iodide. To a solution of 1-(*tert*-butyldiphenylsiloxy)-2-propyne (815 mg, 2.77 mmol) in dry THF (16 mL) was added *n*-BuLi in hexane (1.41 M, 1.70 mL, 2.40 mmol) at −78 °C. After the mixture was stirred for 30 min, a THF solution of the crude iodide (2.0 mL) was added, and the reaction mixture was gradually warmed to 50 °C. After being stirred for 3.5 h, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in MeOH (18 mL) was added 10% aqueous HCl (6.0 mL), and the solution was stirred at room temperature for 12 h. MeOH was evaporated off, and the residue was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 7:1 hexane−AcOEt to afford **10a** (211 mg, 59%) as a colorless oil: IR 3422, 2172 cm^{-1}; ^1H NMR δ 4.23 (t, 2H, J = 2.4 Hz), 2.32 (tt, 4H, J = 7.3, 2.4 Hz), 1.75−1.67 (m, 3H), 0.13 (s, 9H); ^{13}C NMR δ 106.15, 85.39, 85.20, 78.90, 51.29, 27.60, 18.98, 17.80, 0.08; MS *m*/*z* 194 (M^+, 2.6); HRMS calcd for $C_{11}H_{18}OSi$ 194.1127, found 194.1113.

1,6-Octadiyn-8-ol (10b).[28] To a solution of **10a** (57.0 mg, 0.29 mmol) in dry THF (2.9 mL) was added TBAF in THF (1.0 M, 0.44 mL, 0.44 mmol) at room temperature. After the mixture was stirred for 4 h, the reaction was quenched by addition of water, and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 5:1 hexane−AcOEt to afford **10b** (25.7 mg, 72%) as a colorless oil: IR 3609, 3308 cm^{-1}; ^1H NMR δ 4.22 (t, 2H, J = 2.0 Hz), 2.33 (tt, 2H, J = 6.8, 2.5 Hz), 2.29 (dt, 2H, J = 6.8, 2.5 Hz), 1.98 (br s, 1H), 1.95 (t, 1H, J = 2.5 Hz), 1.75−1.67 (m, 2H); ^{13}C NMR δ 85.05, 83.37, 79.02, 68.95, 51.16, 27.30, 17.67, 17.44.

1-Phenyl-1,6-octadiyn-8-ol (10c). To a solution of **10b** (305 mg, 2.49 mmol), $PdCl_2(PPh_3)_2$ (17.5 mg, 2.49×10^{-2} mmol), and CuI (9.50 mg, 4.99×10^{-2} mmol) in dry THF (12 mL) was added iodobenzene (0.56 mL, 4.99 mmol) at room temperature. $^iPr_2NH$ (3.50 mL, 24.9 mmol) was added to the reaction mixture, which was stirred for 18 h. THF was evaporated off, and the residue was chromatographed with 6:1 hexane−AcOEt to afford **10c** (402 mg, 82%) as a yellow oil: IR 3609, 3435, 2226 cm^{-1}; ^1H NMR δ 7.42−7.36 (m, 2H), 7.30−7.25 (m, 3H), 4.29−4.21 (m, 2H), 2.53 (t, 2H, J = 6.8 Hz), 2.41 (tt, 2H, J = 6.8, 2.0 Hz), 1.85−1.77 (m, 2H); ^{13}C NMR δ 131.51, 128.16, 127.62, 123.70, 88.97, 85.39, 81.24, 79.00, 51.31, 27.68, 18.53, 17.92; MS *m*/*z* 198 (M^+, 13); HRMS calcd for $C_{14}H_{14}O$ 198.1044, found 198.1034.

3-(Phenylsulfinyl)-8-(trimethylsilyl)-1,2-octadien-7-yne (11). To a solution of **10a** (792 mg, 4.00 mmol) in THF (35 mL) was added Et_3N (1.70 mL, 12.2 mmol) at −78 °C. After the mixture was stirred for 15 min, a solution of PhSCl (1.77 g, 12.2 mmol) in THF (5.0 mL) was added. The reaction mixture was stirred for 1 h at −78 °C and then gradually warmed to 0 °C over a period of 1 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residual

(28) Carruthers, W.; Pellatt, M. G. *J. Chem. Soc. C* **1971**, 1485−1488.

oil was chromatographed with 5:1 hexane−AcOEt to afford **11** (1.19 g, 96%) as a colorless oil: IR 2172, 1969, 1944 cm^{-1}; ^1H NMR δ 7.67−7.42 (m, 5H), 5.29 (qt, 2H, J = 11.9, 3.3 Hz), 2.35−2.20 (m, 1H), 2.16 (t, 2H, J = 6.9 Hz), 2.04−1.87 (m, 1H), 1.69−1.45 (m, 2H), 0.10 (s, 9H); ^{13}C NMR δ 205.28, 143.38, 130.87, 129.00, 124.42, 112.49, 106.06, 85.10, 82.50, 26.35, 21.98, 19.18, 0.06; MS m/z 302 (M^+, 0.78); HRMS calcd for $C_{17}H_{22}OSSi$ 302.1160, found 302.1153.

3-(Phenylsulfonyl)-8-(trimethylsilyl)-1,2-octadien-7-yne (12a). To a solution of **10a** (157 mg, 0.81 mmol) in THF (6.0 mL), was added Et_3N (0.34 mL, 2.43 mmol) at −78 °C. After the mixture was stirred for 15 min, a solution of PhSCl (351 mg, 2.43 mmol) in THF (2.0 mL) was added, and the reaction mixture was stirred for 1.5 h at −78 °C. The reaction was quenched by addition of water, and the mixture was 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 6:1 hexane−AcOEt to afford the crude sulfoxide. A solution of *m*CPBA (209 mg, 1.21 mmol) in CH_2Cl_2 (2.0 mL) was added to a solution of the crude sulfoxide in CH_2Cl_2 (6.0 mL) at 0 °C. After the reaction mixture was stirred for 1 h, the reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with aqueous $Na_2S_2O_3$ and brine, dried, and concentrated to dryness. The residual oil was chromatographed with 6:1 hexane−AcOEt to afford **12a** (218 mg, 85%) as colorless needles: mp 74.5−75.5 °C (hexane); IR 2172, 1971, 1938 cm^{-1}; ^1H NMR δ 7.93−7.86 (m, 2H), 7.65−7.50 (m, 3H), 5.38 (t, 2H, J = 3.4 Hz), 2.38−2.29 (m, 2H), 2.21 (t, 2H, J = 6.8 Hz), 1.69−1.60 (m, 2H), 0.11 (s, 9H); ^{13}C NMR δ 207.69, 140.14, 133.45, 129.05, 128.06, 112.69, 105.78, 85.44, 84.48, 26.36, 25.85, 19.04, 0.06; MS m/z 318 (M^+, 10); HRMS calcd for $C_{17}H_{22}O_2SSi$ 318.1109, found 318.1112. Anal. Calcd for $C_{17}H_{22}O_2SSi$: C, 64.11; H, 6.96. Found: C, 64.00; H, 7.05.

1-(Trimethylsilyl)-1,7-nonadiyn-9-ol (16a). To a solution of **15** (2.60 g, 26.5 mmol) in dry THF (130 mL) was added *n*-BuLi in hexane (1.43 M, 55.6 mL, 79.5 mmol) at −78 °C. After the mixture was stirred for 45 min, TMSCl (20.2 mL, 159 mmol) was added, and the reaction mixture was gradually warmed to room temperature. Then, 10% aqueous HCl (20 mL) was added to the reaction mixture. After being stirred for 3 h, the reaction mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. To the crude alcohol in dry CH_2Cl_2 (90 mL) were added PPh_3 (20.9 g, 79.5 mmol) and imidazole (5.42 g, 79.5 mmol) at 0 °C. Then I_2 (20.2 g, 79.5 mmol) was added to the reaction mixture, which was gradually warmed to room temperature. After the mixture was stirred for 12 h, CH_2Cl_2 was evaporated off, and the residue was passed through a short pad of silica gel with 10:1 hexane−AcOEt to afford the crude iodide. To a solution of 1-(*tert*-butyldimethylsiloxy)-2-propyne (5.87 g, 34.5 mmol) in dry THF (48 mL) was added *n*-BuLi in hexane (1.43 M, 20.4 mL, 29.2 mmol) at −78 °C. After the mixture was stirred for 30 min, a THF−DMPU solution of the crude iodide (THF 20 mL, DMPU 13 mL) was added, and the reaction mixture was stirred at the same temperature for 1 h and then gradually warmed to room temperature. After the reaction mixture was stirred for 5 h, the reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in MeOH (60 mL) was added 10% aqueous HCl (10 mL), and the mixture was stirred at room temperature for 12 h. MeOH was evaporated off, and the residue was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 5:1 hexane−AcOEt to afford **16a** (2.98 g, 54%) as a colorless oil: IR 3609, 3449, 2172 cm^{-1}; ^1H NMR δ 4.25 (t, 2H, J = 2.4 Hz), 2.30−2.19 (m, 4H), 1.68−1.58 (m, 4H), 0.14 (s, 9H); ^{13}C NMR δ 106.94, 86.04, 84.76, 78.62, 51.38, 27.66, 27.58, 19.38, 18.28, 0.13; MS m/z 208 (M^+, 4.0); HRMS calcd for $C_{12}H_{20}OSi$ 208.1284, found 208.1282.

3-(Phenylsulfonyl)-9-(trimethylsilyl)-1,2-nonadien-8-yne (17a). According to the procedure described for preparation of **12a**, **17a** (259 mg, 78%) was obtained from **16a** (207 mg, 0.99 mmol) as a colorless oil: IR 2170, 1969, 1942 cm^{-1}; ^1H NMR δ 7.92−7.87 (m, 2H), 7.65−7.50 (m, 3H), 5.36 (dt, 2H, J = 8.8, 3.4 Hz), 2.28−2.19 (m, 2H), 2.16 (t, 2H, J = 6.8 Hz), 1.58−1.36 (m, 4H), 0.12 (s, 9H); ^{13}C NMR δ 207.60, 140.05, 133.42, 129.02, 128.05, 113.08, 106.67, 84.82, 84.51, 27.55, 26.36, 26.02, 19.41, 0.07; MS m/z 332 (M^+, 2.0); HRMS calcd for $C_{18}H_{24}O_2SSi$ 332.1266, found 332.1264. Anal. Calcd for $C_{18}H_{24}O_2SSi$: C, 65.01; H, 7.27. Found: C, 64.70; H, 7.33.

4-(*tert*-Butyldiphenylsiloxy)-1-iodo-2-butyne (21). To a solution of 4-(*tert*-butyldiphenylsiloxy)-2-butyn-1-ol[29] (815 mg, 2.5 mmol) in dry CH_2Cl_2 (25 mL) were added PPh_3 (983 mg, 3.8 mmol) and imidazole (255 mg, 3.8 mmol) at room temperature. Then, I_2 (953 mg, 3.8 mmol) was added to the reaction mixture, which was stirred for 30 min. CH_2Cl_2 was evaporated off, and the residue was chromatographed with 30:1 hexane−AcOEt to afford **21** (963 mg, 89%) as a colorless oil; ^1H NMR δ 7.75−7.66 (m, 4H), 7.49−7.35 (m, 6H), 4.33 (t, 2H, J = 2.3 Hz), 3.66 (t, 2H, J = 2.3 Hz), 1.07 (s, 9H); ^{13}C NMR δ 135.60, 132.97, 129.81, 127.73, 83.67, 81.89, 52.89, 26.70, 19.16, −18.51; MS m/z 434 (M^+, 0.2); HRMS calcd for $C_{20}H_{23}IOSi$ 434.0563, found 434.0549. Anal. Calcd for $C_{20}H_{23}IOSi$: C, 55.30; H, 5.34. Found: C, 54.93; H, 5.41.

5,5-Bis(methoxycarbonyl)-1,7-nonadiyn-9-ol (22a). To a solution of **20**[30] (378 mg, 2.05 mmol) in THF (20 mL) was added NaH (60% in mineral oil, 90.4 mg, 2.26 mmol) at 0 °C. After the mixture was stirred for 30 min, a solution of **21** (985 mg, 2.27 mmol) in THF (5.0 mL) was added, and stirring was continued for an additional 1 h at 0 °C. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in THF (20 mL) was added TBAF in THF (1.0 M, 2.10 mL, 2.10 mmol) at room temperature. The reaction mixture was stirred at room temperature for 30 min and concentrated to dryness. The residue was passed through a short pad of silica gel with 2:1 hexane−AcOEt to afford **22a** (414 mg, 80%) as a colorless oil: IR 3524, 3308, 2122, 1732 cm^{-1}; ^1H NMR δ 4.21 (t, 2H, J = 2.0 Hz), 3.74 (s, 6H), 2.88 (t, 2H, J = 2.0 Hz), 2.37−2.15 (m, 4H), 1.97 (t, 1H, J = 2.6 Hz); ^{13}C NMR δ 170.22, 82.79, 81.94, 79.91, 69.00, 56.28, 52.85, 51.00, 31.11, 23.34, 13.86; MS m/z 252 (M^+, 1.3); HRMS calcd for $C_{13}H_{16}O_5$ 252.0998, found 252.1008.

5,5-Bis(methoxycarbonyl)-3-(phenylsulfonyl)-1,2-nonadien-8-yne (23a). According to the procedure described for preparation of **12a**, **23a** (76.8 mg, 78%) was obtained from **22a** (66.0 mg, 0.26 mmol) as colorless needles: mp 69.5−70.5 °C (hexane−AcOEt); IR 3308, 1967, 1936, 1734 cm^{-1}; ^1H NMR δ 7.93−7.84 (m, 2H), 7.69−7.50 (m, 3H), 5.37 (t, 2H, J = 3.3 Hz), 3.67 (s, 6H), 2.92 (t, 2H, J = 3.3 Hz), 2.24−2.02 (m, 4H), 1.91 (t, 1H, J = 2.6 Hz); ^{13}C NMR δ 208.16, 169.99, 139.68, 133.73, 129.20, 128.21, 108.75, 85.61, 82.71, 68.91, 56.10, 52.69, 30.77, 28.63, 13.84; MS m/z 376 (M^+, 1.4); HRMS calcd for $C_{19}H_{20}O_6S$ 376.0981, found 376.0985. Anal. Calcd for $C_{19}H_{20}O_6S$: C, 60.62; H, 5.36. Found: C, 60.63; H, 5.40.

1-Iodo-5-[(tetrahydro-2*H*-pyran-2-yl)oxy]-3-pentyne (24). To a solution of 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]-3-pentyn-1-ol[31] (800 mg, 4.4 mmol) in dry CH_2Cl_2 (40 mL) were added PPh_3 (1.4 g, 5.3 mmol) and imidazole (360 mg, 5.3 mmol) at room temperature. Then, I_2 was added to the reaction mixture, which was stirred for 30 min. CH_2Cl_2 was evaporated off, and the residue was chromatographed with 10:1 hexane−AcOEt to afford **24** (1.0 g, 81%) as a colorless oil: ^1H NMR δ 4.82 (t, 1H, J = 3.4 Hz), 4.23 (qt, 2H, J = 15.6, 2.0 Hz), 3.87−3.79 (m,

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1H), 3.57−3.48 (m, 1H), 3.21 (t, 2H, J = 7.3 Hz), 2.81 (tt, 2H, J = 7.3, 2.0 Hz), 1.88−1.46 (m, 6H); ^{13}C NMR δ 96.55, 84.73, 77.83, 61.89, 54.25, 30.12, 25.23, 23.97, 18.98, 1.24; MS m/z 294 (M^+, 5.8); HRMS calcd for $C_{10}H_{15}IO_2$ 294.0117, found 294.0111. Anal. Calcd for $C_{10}H_{15}IO_2$: C, 40.83; H, 5.14. Found: C, 40.76; H, 5.25.

4,4-Bis(methoxycarbonyl)-1,7-nonadiyn-9-ol (25a). To a solution of dimethyl malonate (0.20 mL, 1.80 mmol) in dry DMF (10 mL) was added NaH (60% in mineral oil, 81.0 mg, 2.03 mmol) at 0 °C. After the mixture was stirred for 30 min, a DMF solution (2.0 mL) of **24** (541 mg, 1.84 mmol) was added, and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in dry THF (10 mL) was added NaH (60% in mineral oil, 81.0 mg, 2.03 mmol) at 0 °C. After the mixture was stirred for 30 min, propargyl bromide (0.14 mL, 1.90 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in MeOH (10 mL) was added *p*-TsOH (34.2 mg, 0.18 mmol) at room temperature. After the mixture was stirred for 12 h, MeOH was evaporated off, and the residue was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 3:1 hexane−AcOEt to afford **25a** (249 mg, 56%) as a colorless oil: IR 3528, 3308, 1734 cm^{-1}; ^{1}H NMR δ 4.24−4.17 (m, 2H), 3.77 (s, 6H), 2.85 (d, 2H, J = 2.6 Hz), 2.37−2.18 (m, 4H), 2.02 (t, 1H, J = 2.6 Hz), 1.94 (br s, 1H); ^{13}C NMR δ 170.21, 84.33, 79.28, 78.31, 71.75, 56.14, 52.87, 51.09, 30.82, 22.82, 14.09; MS m/z 252 (M^+, 1.0); HRMS calcd for $C_{13}H_{16}O_5$ 252.0998, found 252.0998. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.52; H, 6.48.

6,6-Bis(methoxycarbonyl)-3-(phenylsulfonyl)-1,2-nonadien-8-yne (26a). According to the procedure described for preparation of **12a**, **26a** (289 mg, 77%) was obtained from **25a** (252 mg, 1.00 mmol) as colorless needles: mp 94−95 °C (hexane−AcOEt); IR 3308, 1971, 1936, 1734 cm^{-1}; ^{1}H NMR δ 7.91−7.82 (m, 2H), 7.66−7.47 (m, 3H), 5.41 (t, 2H, J = 3.0 Hz), 3.69 (s, 6H), 2.77 (d, 2H, J = 3.0 Hz), 2.26−2.08 (m, 4H), 1.95 (t, 1H, J = 2.6 Hz); ^{13}C NMR δ 207.51, 169.97, 139.95, 133.50, 129.04, 128.03, 112.53, 85.27, 78.10, 71.72, 56.25, 52.87, 30.30, 23.09, 21.75; MS m/z 376 (M^+, 8.6); HRMS calcd for $C_{19}H_{20}O_6S$ 376.0981, found 376.0985. Anal. Calcd for $C_{19}H_{20}O_6S$: C, 60.62; H, 5.36. Found: C, 60.44; H, 5.54.

6-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)-1,7-octadiyne (29). To a solution of 5-hexyn-1-ol (**15**) (2.15 g, 21.9 mmol) in dry THF (65 mL) was added *n*-BuLi in hexane (1.46 M, 36.0 mL, 52.6 mmol) at −78 °C. After the mixture was stirred for 1 h, TMSCl (14.0 mL, 110 mmol) was added, and the reaction mixture was stirred at the same temperature for 30 min and then at room temperature for 12 h. Then, 10% aqueous HCl (18 mL) was added to the reaction mixture, which was stirred for 1 h, neutralized with saturated aqueous $NaHCO_3$, and 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 3:1 hexane−AcOEt to afford the C-silylated hexynol. To a solution of the hexynol, DMSO (5.00 mL, 70.4 mmol), and Et_3N (10.0 mL, 71.7 mmol) in dry CH_2Cl_2 (100 mL) was added SO_3·pyridine (10.5 g, 66.0 mmol) at 0 °C. After the mixture was stirred for 6 h at room temperature, the reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with CH_2Cl_2. 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 8:1 hexane−AcOEt to afford the crude aldehyde. To a solution of the crude aldehyde in dry THF (100 mL) was added ethynylmagnesium bromide in THF (0.50 M, 57.0 mL, 28.5 mmol) at −20 °C. The reaction mixture was stirred at the same temperature for 2.5 h; the reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. 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 6:1 hexane−AcOEt to afford the crude alcohol. The alcohol was taken up in DMF (20 mL), to which imidazole (3.42 g, 50.3 mmol) and TBDMSCl (3.81 g, 25.2 mmol) were added at room temperature. The reaction mixture was stirred at room temperature for 12 h; the reaction was quenched by addition of water, and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with 40:1 hexane−AcOEt to afford **29** (3.04 g, 45%) as a colorless oil: IR 3306, 2172 cm^{-1}; ^{1}H NMR δ 4.39 (td, 1H, J = 6.3, 2.0 Hz), 2.38 (d, 1H, J = 2.0 Hz), 2.27 (t, 2H, J = 6.9 Hz) 1.89−1.60 (m, 4H), 0.91 (s, 9H), 0.14 (s, 9H), 0.12 (s, 6H); ^{13}C NMR δ 106.90, 85.19, 84.73, 72.20, 62.32, 37.36, 25.75, 24.08, 19.46, 18.17, 0.13, −4.60, −5.08; MS m/z 308 (M^+, 0.7); HRMS calcd for $C_{17}H_{32}OSi_2$ 308.1992, found 308.1979.

6-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)-1,7-nonadiyn-9-ol (30a). To a solution of **29** (871 mg, 2.82 mmol) in dry THF (28 mL) was added *n*-BuLi in hexane (1.36 M, 2.49 mL, 3.39 mmol) at −78 °C. After the mixture was stirred for 40 min, $(HCHO)_n$ (425 mg, 14.1 mmol) was added, and the reaction mixture was stirred at room temperature for 6 h. The reaction was quenched by addition of aqueous saturated NH_4Cl, and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with 6:1 hexane−AcOEt to afford **30a** (699 mg, 73%) as a colorless oil: IR 3609, 3422, 2170 cm^{-1}; ^{1}H NMR δ 4.43 (tt, 1H, J = 6.3, 2.0 Hz), 4.29 (dd, 2H, J = 6.4, 2.0 Hz), 2.26 (t, 2H, J = 6.8 Hz), 1.81−1.62 (m, 4H), 1.50−1.45 (m, 1H), 0.91 (s, 9H), 0.15 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR δ 107.00, 87.26, 84.70, 82.29, 62.53, 51.18, 37.42, 25.79, 24.20, 19.51, 18.22, 0.14, −4.49; MS m/z 338 (M^+, 0.3); HRMS calcd for $C_{18}H_{34}O_2Si_2$ 338.2097, found 338.2086.

4-(*tert*-Butyldimethylsiloxy)-3-(phenylsulfonyl)-9-(trimethylsilyl)-1,2-nonadien-8-yne (31a). According to the procedure described for preparation of **12a**, **31a** (237 mg, 94%) was obtained from **30a** (184 mg, 0.54 mmol) as a colorless oil: IR 2172, 1971, 1931 cm^{-1}; ^{1}H NMR δ 7.93−7.87 (m, 2H), 7.65−7.50 (m, 3H), 5.43−5.33 (m, 2H), 4.49−4.44 (m, 1H), 2.20−2.15 (m, 2H), 1.91−1.68 (m, 2H), 1.56−1.48 (m, 2H), 0.79 (s, 9H), 0.14 (s, 9H), −0.06 (s, 3H), −0.18 (s, 3H); ^{13}C NMR δ 208.80, 140.88, 133.50, 129.02, 128.10, 117.34, 106.96, 85.21, 84.71, 68.45, 37.07, 25.63, 23.96, 19.55, 18.01, 0.13, −5.17, −5.34; FABMS m/z 463 (M^+ + 1, 2.8); FABHRMS calcd for $C_{24}H_{39}O_3SSi_2$ 463.2158, found 463.2160.

3-(Phenylsulfonyl)-9-(trimethylsilyl)-1,2-nonadien-8-yn-4-ol (32a). To a solution of **31a** (160 mg, 0.35 mmol) in MeOH (3.4 mL) was added 10% aqueous HCl (0.6 mL) at room temperature. After the mixture was stirred for 14 h, MeOH was evaporated off, and the residue was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with 7:3 hexane−AcOEt to afford **32a** (92.8 mg, 77%) as a colorless oil: IR 3551, 2172, 1967, 1929 cm^{-1}; ^{1}H NMR δ 7.94−7.89 (m, 2H), 7.66−7.52 (m, 3H), 5.45 (d, 2H, J = 1.5 Hz), 4.49−4.43 (m, 1H), 2.93 (d, 1H, J = 4.4 Hz), 2.18 (td, 2H, J = 6.8, 3.4 Hz), 1.80−1.41 (m, 4H), 0.12 (s, 9H); ^{13}C NMR δ 207.44, 140.35, 133.76, 129.09, 128.06, 115.86, 106.59, 85.46, 85.04, 67.88, 34.16, 24.48, 19.40, 0.10; MS m/z 348 (M^+, 0.4); HRMS calcd for $C_{18}H_{24}O_3SSi$ 348.1216, found 348.1219. Anal. Calcd for $C_{18}H_{24}O_3SSi$: C, 62.03; H, 6.94. Found: C, 61.78; H, 7.02.

1-(Trimethylsilyl)-1,7-octadiyn-3-ol (33). To a solution of 5-hexyn-1-ol (**15**) (1.96 g, 20.0 mmol), DMSO (6.40 mL, 90.0 mmol), and Et_3N (12.5 mL, 90.0 mmol) in dry CH_2Cl_2 (100 mL) was added SO_3·pyridine (14.3 g, 90.0 mmol) at 0 °C. After the mixture was stirred for 1 h, the reaction was quenched by

addition of water, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness to afford the crude aldehyde. To a solution of trimethylsilylacetylene (4.80 mL, 34.0 mmol) in dry THF (100 mL) was added *n*-BuLi in hexane (1.43 M, 21.0 mL, 30.0 mmol) at −78 °C. After the mixture was stirred for 1 h, a THF solution (20 mL) of the crude aldehyde was added, and the reaction mixture was stirred for 3 h. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 5:1 hexane−AcOEt to afford **33** (1.99 g, 51%) as a pale yellow oil: IR 3601, 3435, 3308, 2172, 2118 cm^{-1}; ^1H NMR δ 4.38 (t, 1H, J = 6.8 Hz), 2.24 (td, 2H, J = 6.8, 2.4 Hz), 2.01 (br s, 1H), 1.95 (t, 1H, J = 2.4 Hz), 1.87−1.61 (m, 4H), 0.15 (s, 9H); ^{13}C NMR δ 106.38, 89.60, 83.95, 68.68, 62.27, 36.46, 24.01, 18.04, −0.20; FABMS m/z 195 (M^+ + 1, 3.0); FABHRMS calcd for $C_{11}H_{19}OSi$ 195.1205, found 195.1213. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.68; H, 9.53.

3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)-1,7-nonadiyn-9-ol (34a). To a solution of **33** (800 mg, 4.12 mmol) in dry DMF (2.0 mL) were added TBDMSCl (747 mg, 4.94 mmol) and imidazole (421 mg, 6.19 mmol) at room temperature. After being stirred at 60 °C for 1 h, the reaction mixture was cooled to room temperature; the reaction was quenched by addition of water, 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 20:1 hexane−AcOEt. To a solution of the crude product in dry THF (40 mL) was added *n*-BuLi in hexane (1.43 M, 4.30 mL, 6.14 mmol) at −78 °C. After the mixture was stirred for 1 h, $(HCHO)_n$ (615 mg, 20.5 mmol) was added, and the reaction mixture was gradually warmed to room temperature over a period of 2 h. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 5:1 hexane−AcOEt to afford **34a** (1.19 g, 86%) as a colorless oil: IR 3609, 3435, 2170 cm^{-1}; ^1H NMR δ 4.35 (t, 1H, J = 6.3 Hz), 4.24 (t, 2H, J = 2.5 Hz), 2.25 (tt, 2H, J = 6.8, 2.5 Hz), 1.80−1.54 (m, 5H), 0.90 (s, 9H), 0.15 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR δ 107.37, 88.70, 86.02, 78.60, 62.89, 51.30, 37.45, 25.77, 24.35, 18.42, 18.22, −0.21, −4.51, −4.99; FABMS m/z 339 (M^+ + 1, 0.4); FABHRMS calcd for $C_{18}H_{35}O_2Si_2$ 339.2176, found 339.2166. Anal. Calcd for $C_{18}H_{34}O_2Si_2$: C, 63.84; H, 10.12. Found: C, 63.48; H, 10.21.

7-(*tert*-Butyldimethylsiloxy)-3-(phenylsulfonyl)-9-(trimethylsilyl)-1,2-nonadien-8-yne (35a). According to the procedure described for preparation of **12a**, **35a** (415 mg, 35%) was obtained from **34a** (870 mg, 2.57 mmol) as a colorless oil: IR 2170, 1971, 1940 cm^{-1}; ^1H NMR δ 7.91−7.86 (m, 2H), 7.64−7.59 (m, 1H), 7.56−7.50 (m, 2H), 5.37 (t, 2H, J = 3.4 Hz), 4.29−4.22 (m, 1H), 2.31−2.18 (m, 2H), 1.66−1.48 (m, 4H), 0.86 (s, 9H), 0.13 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR δ 207.64, 140.11, 133.42, 129.02, 128.07, 113.23, 107.21, 88.75, 84.57, 62.80, 37.32, 26.11, 25.75, 23.08, 18.19, −0.23, −4.53, −5.03; FABMS m/z 463 (M^+ + 1, 1.0); FABHRMS calcd for $C_{24}H_{39}O_3SSi_2$ 463.2158, found 463.2151.

3-(Phenylsulfonyl)-9-(trimethylsilyl)-1,2-nonadien-8-yn-7-ol (36a). To a solution of **35a** (185 mg, 0.40 mmol) in THF (6.0 mL) was added 10% aqueous HCl (2.0 mL) at room temperature. After being stirred for 8 h, the reaction mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 3:1 hexane−AcOEt to afford **36a** (131 mg, 94%) as a colorless oil: IR 3601, 3510, 2170, 1971, 1940 cm^{-1}; ^1H NMR δ 7.91−7.86 (m, 2H), 7.65−7.59 (m, 1H), 7.57−7.50 (m, 2H), 5.37 (t, 2H, J = 3.4 Hz), 4.33−4.25 (m, 1H), 2.31−2.22 (m, 2H), 1.90 (d, 1H, J = 5.4 Hz), 1.70−1.54 (m, 4H), 0.14 (s, 9H); ^{13}C NMR δ 207.60, 140.00, 133.48, 129.04, 128.05, 113.01, 106.20, 89.70, 84.66, 62.23, 36.48, 26.15, 22.93, −0.20; MS m/z 348 (M^+, 0.8). FABHRMS calcd for $C_{18}H_{25}O_3SSi$ 349.1294, found 349.1272.

Ring Closure of 12a with $Co_2(CO)_8$ and TMANO. To a solution of **12a** (42.1 mg, 0.132 mmol), TMANO (99.3 mg, 1.32 mmol), and 4 Å MS (336 mg) in dry toluene (1.32 mL) was added $Co_2(CO)_8$ (49.7 mg, 0.145 mmol) under an Ar atmosphere at −10 °C. After being stirred for 17 h, the reaction mixture was passed through a short pad of Celite with AcOEt and concentrated to dryness. The residue was chromatographed with 7:1 hexane−AcOEt to afford 2-(phenylsulfonyl)-7-trimethylsilylbicyclo[4.3.0]nona-1,6-dien-8-one (**13a**) (23.9 mg, 52%) as a yellow oil: IR 1690 cm^{-1}; ^1H NMR δ 7.92−7.86 (m, 2H), 7.68−7.61 (m, 1H), 7.59−7.53 (m, 2H), 3.40 (s, 2H), 2.68 (t, 2H, J = 6.4 Hz), 2.47 (t, 2H, J = 5.9 Hz), 1.88−1.80 (m, 2H), 0.23 (s, 9H); ^{13}C NMR δ 207.32, 173.76, 145.71, 144.44, 140.07, 134.07, 133.64, 129.35, 127.66, 39.45, 26.72, 25.09, 22.04, −0.80; MS m/z 346 (M^+, 47); HRMS calcd for $C_{18}H_{22}O_3SSi$ 346.1059, found 346.1058. **Ring Closure of 12a with $Co_2(CO)_8$ in CH_3CN.** To a solution of **12a** (10 mg, 3.1×10^{-2} mmol) in dry CH_3CN (0.3 mL) was added $Co_2(CO)_8$ (13 mg, 3.8×10^{-2} mmol) under an Ar atmosphere, and the reaction mixture was stirred for 20 min at 75 °C. Workup and chromatography as described above gave **13a** (5.0 mg, 46%). **Ring Closure of 12a with $Fe(CO)_4(NMe_3)$.** To a THF solution (1.0 mL) of TMANO (61 mg, 0.81 mmol) in a Pyrex test tube was added $Fe(CO)_5$ (50 μL, 0.37 mmol) under an Ar atmosphere at −30 °C. After the mixture was stirred for 1 h, a THF solution of **12a** (43 mg, 0.14 mmol, 0.35 mL) was added, and the reaction mixture was stirred under external photoirradiation by a 100 W high-pressure mercury lamp at room temperature for 18 h. Workup and chromatography as described above gave **13a** (8.3 mg, 18%). **Ring Closure of 12a with $Fe_2(CO)_9$.** To a solution of **12a** (30 mg, 0.094 mmol) and DMSO (70 μL, 0.94 mmol) in dry toluene (1.0 mL) was added $Fe_2(CO)_9$ (51 mg, 0.14 mmol). The reaction mixture was stirred for 1 h under an Ar atmosphere at 100 °C. Workup and chromatography as described above gave **13a** (5.7 mg, 18%).

General Procedure for Ring Closure Reaction with $[RhCl(CO)_2]_2$: Condition A. To a solution of allenyne (0.10 mmol) in dry toluene (1.0 mL) was added 2.5 or 5.0 mol % $[RhCl(CO)_2]_2$. 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 residue was chromatographed with hexane−AcOEt to afford cyclized products. Chemical yields are summarized in Tables 2−6.

General Procedure for Ring Closure Reaction with $[RhCl(CO)dppp]_2$: Condition B. To a solution of allenyne (0.10 mmol) in dry toluene (1.0 mL) was added 2.5 or 5.0 mol % $[RhCl(CO)dppp]_2$. The reaction mixture was refluxed under a CO atmosphere until the complete disappearance of the starting material as indicated by TLC. Workup and chromatography as described for condition A afforded cyclized products. Chemical yields are summarized in Tables 2−6.

2-(Phenylsulfonyl)-8-(trimethylsilyl)bicyclo[5.3.0]deca-1,7-dien-9-one (18a): colorless needles, mp 106−106.5 °C (hexane−AcOEt); IR 1695 cm^{-1}; ^1H NMR δ 7.89−7.85 (m, 2H), 7.65−7.52 (m, 3H), 3.49 (s, 2H), 2.79 (t, 2H, J = 6.8 Hz), 2.72 (t, 2H, J = 6.4 Hz), 1.81−1.71 (m, 4H), 0.26 (s, 9H); ^{13}C NMR δ 207.46, 179.13, 148.48, 148.43, 140.50, 137.38, 133.50, 129.33, 127.54, 42.47, 29.02, 26.45, 26.15, 23.44, −0.43; MS m/z 360 (M^+, 78); HRMS calcd for $C_{19}H_{24}O_3SSi$ 360.1215, found 360.1218. Anal. Calcd for $C_{19}H_{24}O_3SSi$: C, 63.29; H, 6.71. Found: C, 63.19; H, 6.82.

4,4-Bis(methoxycarbonyl)-2-(phenylsulfonyl)bicyclo[5.3.0]deca-1,7-dien-9-one (27a): pale yellow needles, mp 164.5−165.5 °C (hexane−AcOEt); IR 1732, 1701 cm^{-1}; ^1H NMR δ 7.91−7.80 (m, 2H), 7.70−7.50 (m, 3H), 6.23 (s, 1H), 3.73 (s, 6H), 3.39 (s, 2H), 3.34 (s, 2H), 2.81−2.67 (m, 2H), 2.49−2.35 (m, 2H); ^{13}C NMR δ 202.10, 171.64, 170.82, 147.91, 140.18, 136.23, 133.80, 133.53, 129.47, 127.75, 57.22, 53.21, 41.44,

30.82, 29.27, 26.49; MS *m*/*z* 404 (M^+, 100); HRMS calcd for $C_{20}H_{20}O_7S$ 404.0929, found 404.0931. Anal. Calcd for $C_{20}H_{20}O_7S$: C, 59.40; H, 4.98. Found: C, 59.34; H, 5.02.

5,5-Bis(methoxycarbonyl)-2-(phenylsulfonyl)bicyclo-[5.3.0]deca-1,7-dien-9-one (28a): colorless plates, mp 128.5−129 °C (hexane−AcOEt); IR 1732, 1711 (sh) cm^{-1}; ^1H NMR δ 7.91−7.81 (m, 2H), 7.71−7.50 (m, 3H), 6.37 (s, 1H), 3.71 (s, 6H), 3.55 (s, 2H), 3.27 (s, 2H), 2.84−2.71 (m, 2H), 2.32−2.19 (m, 2H); ^{13}C NMR δ 202.41, 170.82, 166.94, 146.18, 139.68, 139.16, 138.96, 133.91, 129.51, 127.66, 55.49, 53.17, 41.62, 34.49, 33.86, 24.96; MS *m*/*z* 404 (M^+, 100); HRMS calcd for $C_{20}H_{20}O_7S$ 404.0930, found 404.0926. Anal. Calcd for $C_{20}H_{20}O_7S$: C, 59.40; H, 4.98. Found: C, 59.31; H, 5.07.

3-(*tert*-Butyldimethylsiloxy)-2-(phenylsulfonyl)-8-(trimethylsilyl)bicyclo[5.3.0]deca-1,7-dien-9-one (37a): colorless oil; IR 1697 cm^{-1}; ^1H NMR δ 7.88−7.84 (m, 2H), 7.62−7.49 (m, 3H), 5.16 (dd, 1H, J = 4.4, 2.4 Hz), 3.34 (AB-q, 2H, J = 21.5 Hz), 3.36−3.28 (m, 1H), 2.88 (dt, 1H, J = 15.1, 3.9 Hz), 2.10−1.95 (m, 2H), 1.69−1.54 (m, 2H), 0.84 (s, 9H), 0.24 (s, 9H), 0.14 (s, 3H), 0.01 (s, 3H); ^{13}C NMR δ 206.24, 179.49, 151.63, 149.75, 141.18, 138.83, 133.40, 129.19, 127.40, 67.99, 42.84, 33.10, 29.59, 25.65, 21.33, 18.00, −0.57, −4.90; MS *m*/*z* 490 (M^+, 0.1); HRMS calcd for $C_{25}H_{38}O_4SSi_2$ 490.2029, found 490.2015. Anal. Calcd for $C_{25}H_{38}O_4SSi_2$: C, 61.18; H, 7.80. Found: C, 61.55; H, 8.17.

3-Hydroxy-2-(phenylsulfonyl)-8-(trimethylsilyl)bicyclo-[5.3.0]deca-1,7-dien-9-one (38a): pale yellow plates, mp 147−148 °C (hexane−CH_2Cl_2); IR 3566, 1699 cm^{-1}; ^1H NMR δ 7.91−7.87 (m, 2H), 7.65−7.52 (m, 3H), 5.02−4.97 (m, 1H), 3.46 (AB-q, 2H, J = 21.5 Hz), 3.16 (ddd, 1H, J = 14.7, 10.7, 5.9 Hz), 2.94−2.87 (m, 2H), 2.22−2.03 (m, 2H), 1.69−1.57 (m, 2H), 0.25 (s, 9H); ^{13}C NMR δ 206.50, 178.06, 152.49, 150.55, 140.18, 138.41, 133.69, 129.46, 127.46, 67.21, 43.21, 31.59, 29.99, 20.76, −0.54; MS *m*/*z* 376 (M^+, 12); HRMS calcd for $C_{19}H_{24}O_4SSi$ 376.1164, found 376.1164. Anal. Calcd for $C_{19}H_{24}O_4SSi$: C, 60.60; H, 6.42. Found: C, 60.38; H, 6.43.

6-(*tert*-Butyldimethylsiloxy)-2-(phenylsulfonyl)-8-(trimethylsilyl)bicyclo[5.3.0]deca-1,7-dien-9-one (39a): colorless needles, mp 140−141 °C (hexane−AcOEt); IR 1697 cm^{-1}; ^1H NMR δ 7.89−7.81 (m, 2H), 7.63−7.47 (m, 3H), 5.13−5.07 (m, 1H), 3.66 (d, 1H, J = 21.5 Hz), 3.41 (dd, 1H, J = 21.5, 2.0 Hz), 2.93 (dd, 1H, J = 16.6, 11.7 Hz), 2.76 (dd, 1H, J = 17.6, 6.8 Hz), 2.03−1.85 (m, 3H), 1.64−1.52 (m, 1H), 0.76 (s, 9H), 0.26 (s, 9H), 0.02 (s, 3H), −0.14 (s, 3H); ^{13}C NMR δ 207.74, 177.30, 147.28, 144.47, 140.50, 140.09, 133.33, 129.18, 127.66, 70.82, 42.97, 33.78, 28.39, 26.06, 25.54, 17.76, −0.41, −4.69, −4.81; FABMS *m*/*z* 491 (M^+ + 1, 1.7); FABHRMS calcd for $C_{25}H_{39}O_4SSi_2$ 491.2108, found 491.2105. Anal. Calcd for $C_{25}H_{38}O_4SSi_2$: C, 61.18; H, 7.80. Found: C, 61.12; H, 8.01.

6-Hydroxy-2-(phenylsulfonyl)-8-(trimethylsilyl)bicyclo-[5.3.0]deca-1,7-dien-9-one (40a): colorless plates, mp 113−114 °C (hexane−AcOEt); IR 3601, 3503, 1699 cm^{-1}; ^1H NMR δ 7.87−7.81 (m, 2H), 7.65−7.58 (m, 1H), 7.57−7.50 (m, 2H), 5.08 (t, 1H, J = 4.9 Hz), 3.54 (AB-q, 2H, J = 21.5 Hz), 2.97 (ddd, 1H, J = 17.1, 10.3, 2.4 Hz), 2.66 (ddd, 1H, J = 17.1, 7.3, 2.4 Hz), 2.09−1.96 (m, 2H), 1.94−1.78 (m, 2H), 1.71−1.59 (m, 1H), 0.27 (s, 9H); ^{13}C NMR δ 207.20, 177.93, 150.31, 145.27, 140.27, 138.08, 133.53, 129.33, 127.44, 69.29, 42.98, 31.66, 27.91, 24.03, 0.04; MS *m*/*z* 376 (M^+, 1.8); HRMS calcd for $C_{19}H_{24}O_4SSi$ 376.1164, found 376.1167. Anal. Calcd for $C_{19}H_{24}O_4SSi$: C, 60.60; H, 6.42. Found: C, 60.53; H, 6.48.

8-Phenyl-2-(phenylsulfonyl)bicyclo[5.3.0]deca-1,5,7-trien-9-one (41): colorless oil; IR 1701 cm^{-1}; ^1H NMR δ 7.95−7.88 (m, 2H), 7.69−7.55 (m, 3H), 7.47−7.30 (m, 5H), 6.59 (d, 1H, J = 11.7 Hz), 6.34 (dt, 1H, J = 11.7, 5.9 Hz), 3.81 (s, 2H), 2.92−2.82 (m, 2H), 2.54−2.42 (m, 2H); ^{13}C NMR δ 201.15, 156.73, 145.68, 143.81, 141.28, 140.50, 136.95, 133.64, 130.08, 129.43, 129.16, 128.39, 127.49, 124.42, 41.62, 28.48, 28.41; FABMS *m*/*z* 363 (M^+ + 1, 31); FABHRMS calcd for $C_{22}H_{19}O_3S$ 363.1055, found 363.1048.

Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **10a**,**c**, **11**, **12b**,**c**, **13a**, **16a**, **17b**,**c**, **22a**,**b**, **29**, **30a**−**c**, **31a**−**c**, **32b**, **35a**−**c**, and **41** and characterization data for compounds **12b**,**c**, **13b**,**c**, **16b**,**c**, **17b**,**c**, **18b**,**c**, **22b**, **23b**, **25b**, **26b**, **27b**, **28b**, **30b**,**c**, **31b**,**c**, **32b**,**c**, **34b**,**c**, **35b**,**c**, **36b**,**c**, **37b**,**c**, **38b**,**c**, **39b**,**c**, and **40b**,**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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