Generation of Cycloalkylidene Carbenes via Exo-Type Cyclization of Alkynyllithiums Bearing Remote Leaving Group

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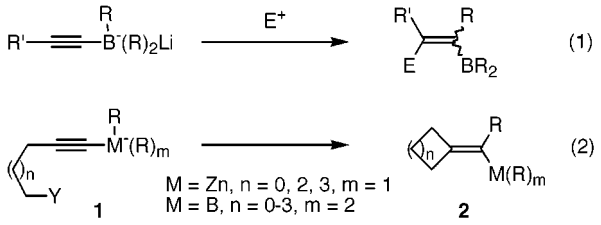
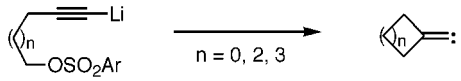
The reaction of 5-hexynyl tosylate (**3a**) with alkynyllithium (RC≡CLi; R = Ph, TMS) gives enynes **5** and **6**. The reaction proceeds through a mechanism involving a novel exo-type cyclization of 6-lithio-5-hexynyl tosylate to form cyclopentylidene carbene. Enyne **6** is produced by the addition of RC≡CLi to the carbene, whereas rearrangement of the carbene to cyclohexyne followed by carbolithiation with RC≡CLi gives enyne **5**. The formation of cyclopentylidene carbene and cyclohexyne as intermediates is clearly demonstrated by trapping experiments with cyclohexene (and triethylsilane) and with 1,3-diphenylisobenzofuran, respectively. Alkynyllithiums derived from 3-butynyl and 6-heptynyl *p*-fluorobenzenesulfonates (**19a**,**b**) undergo a similar exo-type cyclization to give cyclopropylidene and cyclohexylidene carbenes, respectively.

1-Alkynyl organometallics of main group metals have been frequently used as efficient carbon nucleophiles in organic syntheses.[1] They react with a variety of electrophilic reagents generally at the carbon α to the metal atom. Nevertheless, some alkynylmetals, specifically alkynylboronates[2,3] and -zincates,[4] are known to react at the β position.[5] It was reported that boronates react with electrophiles such as haloalkanes and aldehydes at the β position with 1,2-migration of alkyl ligands (eq 1).[2] An



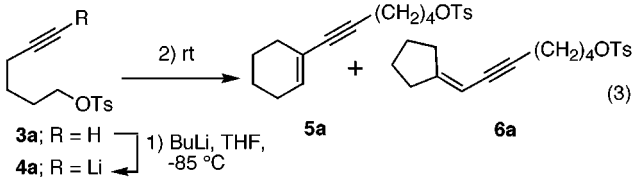
intramolecular version of such a reaction leading to exo-type cyclization products was also reported (eq 2).[3,4] We report herein that alkynyllithiums bearing a remote leaving group also undergo an exo-type cyclization to give cycloalkylidene carbenes (Scheme 1). The study demonstrates a potential reactivity of alkynylmetals other than alkynylate complexes at the β position.

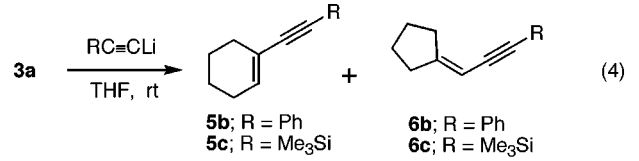
Scheme 1



Results and Discussion

6-Lithio-5-hexynyl tosylate (**4a**) was prepared by the reaction of tosylate **3a** with butyllithium (1.0 equiv) in THF at −85 °C (eq 3). Although **4a** was stable at temperatures up to ca. 0 °C, treatment at room temperature for 2 h gave a 72:28 mixture of enynyl tosylates **5a** and **6a** in 32% yield. An improved yield (63%, **5a**:**6a** = 82:18) was obtained when lithiation of **3a** was effected with 0.5 equiv of butyllithium. Reaction of tosylate **3a** with phenylethynyllithium (2.0 equiv) at room temperature for 22 h afforded enynes **5b** and **6b** (79:21) in 78% yield together with a minor formation of **5a** and **6a** (65:35, 9.1%) (eq 4). Only a small amount (2.2%) of 1-phenyl-1,7-octadiyne, an α-coupling product of the alkynyllithium, was formed in this reaction. Under similar conditions, reaction of **3a** with (trimethylsilyl)ethynyllithium gave **5c** and **6c** (83:17) in 62% yield.





The formation of enynes **6a**−**c** suggests the intermediacy of cyclopentylidene carbene **7** (Scheme 2). Thus, **6a**−**c** would be produced through addition of the alkynyllithiums to carbene **7**. Cycloalkylidene carbenes are

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(3) (a) Merril, R. E.; Allen, J. L.; Abramovitch, A.; Negishi, E. *Tetrahedron Lett.* **1977**, 1019. (b) Corey, E. J.; Seibel, W. L. *Tetrahedron Lett.* **1986**, *27*, 909. (c) Negishi, E.; Nguyen, T.; Boardman, L. D.; Sawada, H.; Morrison, J. A. *Heteroatom Chem.* **1992**, *3*, 293.

(4) (a) Harada, T.; Wada, I.; Oku, A. *J. Org. Chem.* **1995**, *60*, 5370. (b) Harada, T.; Otani, T.; Oku, A. *Tetrahedron Lett.* **1997**, *38*, 2855.

(5) Some transition metal acetylides are known to react with electrophiles at the β position to form vinylidene complexes [RC(E)=C=M]: Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

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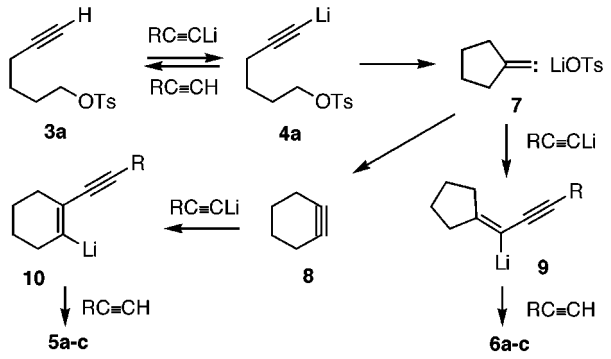
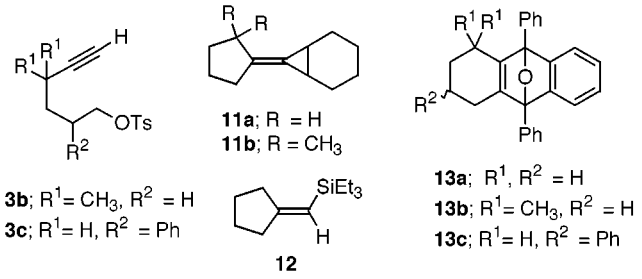
Scheme 2



known to undergo rearrangement to cycloalkynes.[6,7] Erickson and Wolinsky[7b] demonstrated the formation of reactive cyclohexyne (**8**) from cyclopentylidene carbene, generated by the reaction of bromomethylenecyclopentane with *t*-BuOK, by a trapping experiment with 1,3-diphenylisobenzofuran. The formation of enynes **5a**−**c** can be rationalized by rearrangement of carbene **7** and carbolithiation of the resulting strained alkyne **8** with the alkynyllithiums.[7a,8]

The reaction of **7** and **8** with an alkynyllithium would initially produce the corresponding alkenyllithium species **9** and **10**, respectively. The low yield of **5a** and **6a** in the reaction of **3a** using 1.0 equiv of butyllithium can be explained by the instability of the resulting alkenyllithiums with a reactive TsO group [**9** and **10**; R = $(CH_2)_4$-OTs]. On the other hand, the use of 0.5 equiv of butyllithium may improve the products yield because of a rapid protonation of the alkenyllithiums by alkyne **3a**, leading to stable products **5a** and **6a** as well as formation of alkynyllithium **4a**. In the reaction with external alkynyllithium (RC≡CLi; R = Ph, TMS), both **3a** and RC≡CH may serve as a proton donor for **9** and **10**.

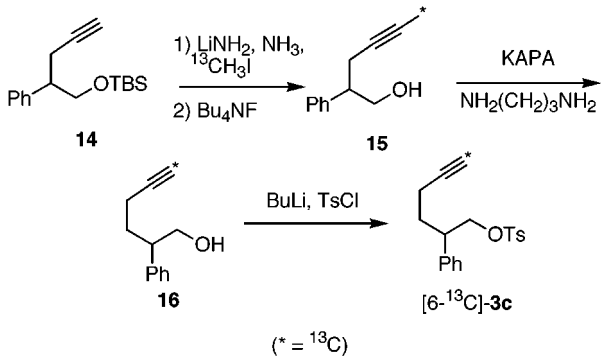
The intermediacy of cyclopentylidene carbene and cyclohexyne was confirmed by the following trapping experiments. Slow addition of butyllithium (1.0 equiv) to a mixture of **3a** and cyclohexene (10 equiv) in THF during 7 h at room temperature afforded carbene adduct **11a** in 18% yield together with **5a** and **6a** (88:12, 25%).[9] Under similar conditions, alkynyl tosylate **3b** afforded adduct **11b** in 20% yield. A trapping experiment with triethylsilane (3.0 equiv) gave the Si−H insertion product **12** in 13% yield together with **5a** and **6a** (89:11, 59%). On the other hand, treatment of alkynyllithium **4a** in the presence of 1,3-diphenylisobenzofuran (3.0 equiv) at room temperature for 3 h afforded [4+2] cycloadduct **13a** in 33% yield. Substituted cyclohexynes were also gener-



ated from tosylates **3b** and **3c**; under similar conditions, reactions of the corresponding alkynyllithiums gave cycloadducts **13b** and **13c**[10] in 54% and 30% yield, respectively.

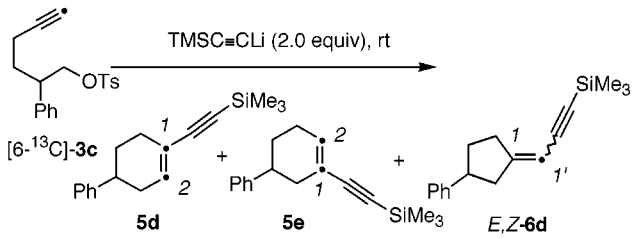
To verify that cyclohexyne **8** was formed through the rearrangement of carbene **7**, alkynyl tosylate [6-^{13}C]-**3c** in which the terminal acetylenic carbon is labeled with ^{13}C was prepared (Scheme 3) and subjected to the

Scheme 3



reaction with (trimethylsilyl)ethynyllithium. The reaction of [6-^{13}C]-**3c** (20% ^{13}C content) gave a 32:31:37 mixture of enynes **5d**, **5e**, and **6d** in 37% combined yield (Scheme 4). Nonselective formation of **5d** and **5e** is an

Scheme 4



products	**5d**	**5e**	*E,Z*-**6d** [a]
relative yield (%)	32	31	37
	-C(2)H=	-C(2)H=	-C(1')H=
^{13}C content (%)	15	6.9	20

[a] A 19:18 mixture of stereoisomers. (• ; ^{13}C)

additional support for their formation via carbolithiation of cyclohexyne intermediate **8′** (Scheme 5). ^{13}C NMR analyses of **5d** and **5e** showed the scrambling of the label between olefinic carbons. For each product, the ^{13}C content of the olefinic methyne carbon (−*C*H=) was determined by ^{1}H NMR integration of the attached proton. Observation of ^{13}C scrambling at −*C*(2)H= of **5e** as well as the loss of ^{13}C label at −*C*(2)H= of **5d** is

(6) (a) Hartzler, H. D. *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, chapter 2, p 43. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (c) Stang, P. J. In *Methoden der Organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19b. p 84. (d) Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1164.

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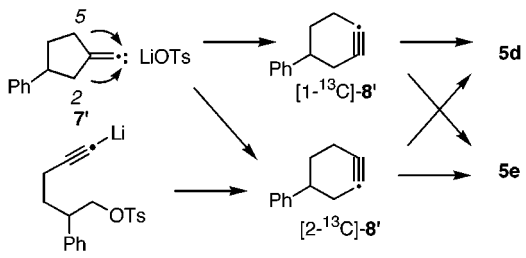
(8) (a) Nakagawa, M. *Cyclic Acetylenes.* In *The Chemistry of Carbon−Carbon Triple Bond*; Patai, S., Ed.; J. Wiley & Sons: New York, 1978, 635. (b) Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 4750. (c) Wittig, G.; Pohlke, R. *Chem. Ber.* **1961**, *94*, 3276. (d) Gassman, P. G.; Valcho, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4768.

(9) Formation of the [2+2] cycloadduct derived from cyclohexyne was not detected.

(10) Adduct **13c** was obtained as a 1:1 mixture of diastereomers.

Scheme 5

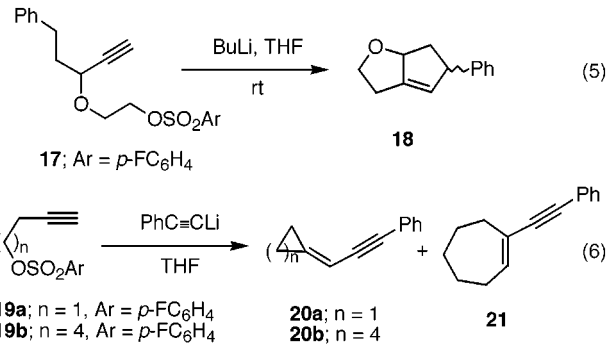


consistent with the formation of cyclohexyne **8′** through rearrangement of carbene **7′**.

Recently, we reported that related alkynylzincates **1** (M = Zn, $n = 2$, $m = 1$, eq 2) undergo direct endo-type cyclization to form cyclohexyne in competition with exo-type cyclization to form (cyclopentylidene)alkylzinc **2** (M = Zn, $n = 2$, $m = 1$).[4b] If we assume that carbene **7′** undergoes C(2) and C(5) migration in a 1:1 ratio, the ^{13}C contents of **5d** and **5e** will be 10.5% each. Deviation of the observed ^{13}C contents from the value may imply preferential migration of C(2), rather than C(5), or participation of a direct endo-type cyclization pathway leading to cyclohexyne [2-^{13}C]-**8′**.

Cyclopentylidene carbene can be generated by bromine/lithium exchange reaction of dibromomethylenecyclopentane. It was demonstrated that the resulting reactive species is an encumbered carbene (or a carbenoid) in which LiBr are associated with the carbene.[6b,11,12] When we examined the reaction of dibromomethylenecyclopentane with BuLi in the presence of 1,3-diphenylisobenzofuran (3 equiv) (THF, −85 °C, room temperature), only a small amount (4.4% yield) of cyclohexyne adduct **13a** was formed. Brinker and colleagues[13] reported that cyclopentylidene and cyclohexylidene carbenes, generated by the ultrasonicated reaction of the corresponding dibromomethylenecycloalkanes with lithium, were efficiently trapped with alkenes. Specifically, 67% yield of **12a** was reported when cyclohexene (4 equiv) was used as an alkene.[13] These results imply that carbene **7** generated from alkynyllithium **4a** is more feasible to rearrangement to cyclohexyne. The difference in reactivity might be due to the less encumbered nature[6b] of carbene **7** in which lithium tosylate is less tightly associated.

Results for related alkynyllithiums bearing a remote leaving group suggest the generality of carbene formation via exo-type cyclization. Thus, the reaction of *p*-fluorobenzenesulfonate **17** afforded intramolecular C−H insertion product **18** in 55% yield as a 93:7 mixture of diastereomers (eq 5).[14] 4-Butynyl sulfonate **19a** reacted with phenylethynyllithium at room temperature to give methylenecyclopropane **20a** (56%) without byproduct formation of cyclobutene derivative (eq 6).[14] The result is in accord with a recent theoretical prediction that conversion of cyclopropylidene carbene into cyclobutyne is an endothermic process.[15] At room temperature, the reaction of 6-heptynyl derivative **19b** was sluggish. The reaction at 65 °C, however, afforded exo-cyclization product **20b** selectively (**20b**:**21** = 75:25, 69%).



We have shown that alkynyllithiums bearing a remote leaving group undergo a novel exo-type cyclization to give cycloalkylidene carbenes. The study not only discloses a novel reactivity of alkynylmetals at their β position but also provides a new method for generating alkylidene carbenes that can be subsequently utilized in construction of a variety of carbon frameworks.

Experimental Section

General Information. Unless otherwise noted, ^1H and ^{13}C NMR spectra were recorded at 300 and 75.6 MHz, respectively, in $CDCl_3$. All commercially available reagents were used without further purification unless otherwise noted. Diisopropylamine, 1,3-diaminopropane, triethylamine, and DMF were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. All reactions were performed under argon. Unless otherwise noted, organic extracts were dried over Na_2SO_4. Flash chromatography was conducted on silica gel (Wakogel C-300).

6-Heptyn-1-ol was prepared according to the literature procedure.[16] Preparation of 4,4-dimethyl-5-hexyn-1-ol, 5-(*tert*-butyldimethylsilyloxy)-4-phenyl-1-pentyne (**14**), 2-phenyl-4-hexyn-1-ol (**16**), and 4-(2-phenylethyl)-3-oxa-5-hexyn-1-ol is described in *Supporting Information*.

Preparation of Alkynyl Arenesulfonates. To a solution of the corresponding alcohol in THF (1 M) at −78 °C was added an equimolar amount of BuLi (1.6 M in hexane). After being stirred for 1 h, a THF solution (1 M) of an arenesulfonyl chloride (1.2 equiv) was added to the mixture at −78 °C. The reaction mixture was allowed to warm to room temperature over ca. 2 h, stirred further for 15 h, and then poured into water. The mixture was extracted twice with ether. The combined extracts were washed with aqueous $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (10% ethyl acetate in hexane) gave the corresponding arenesulfonates in 77−93% yield. For the spectral data of alkynyl arenesulfonates **3a**,**b**,**c**, **17**, and **19a**,**b**, see Supporting Information.

6-(Cyclohexenyl)-5-hexynyl *p*-Toluenesulfonate (5a) and 7-(Cyclopentylidene)-5-heptynyl *p*-Toluenesulfonate (6a). To a solution of 5-hexynyl tosylate (**3a**) (252 mg, 1.0 mmol) in THF (4.5 mL) at −85 °C was added butyllithium (1.6 M in hexane) (0.31 mL, 0.5 mmol). The resulting solution of alkynyllithium **4a** was allowed to warm to room temperature over 3 h and was stirred for 3.5 h at room temperature. The mixture was poured into brine and extracted twice with ethyl acetate. The organic layers were dried and concentrated in vacuo. Purification of the residue by flash chromatography (6−10% ethyl acetate in hexane) gave, in the order of elution, a 82:18 mixture of enynyl tosylates **5a** and **6a** (106 mg, 63% combined yield) and the starting tosylate **3a** (50.4 mg, 20%). Separation of the mixture of **5a** and **6a** by a recycling preparative HPLC, equipped with a GPC column (JAIGEL-1H column, Japan Analytical Industry) using $CHCl_3$ as an eluent, afforded a pure **5a** and a 1:1 mixture of **5a** and **6a**. **5a**: ^1H NMR δ 1.57 (6H, m), 1.77 (2H, m), 2.05 (4H, m), 2.26 (2H,

(11) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.
(12) (a) Patrick, T. B.; Haynie, E. C.; Probst, W. J.; *J. Org. Chem.* **1972**, *37*, 1553. (b) Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 6748.
(13) Xu, L.; Lin, G.; Tao, F., Brinker, U. H. *Acta Chem. Scand.* **1992**, *46*, 650.
(14) The reactions shown in eqs 5 and 6 proceeded for tosylate derivatives as well, albeit with lower efficiency.
(15) Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362.
(16) Reference 1b, p 104.

br t, J = ca. 7 Hz), 2.44 (3H, s), 4.05 (2H, t, J = 6.3 Hz), 5.97 (1H, br s), 7.33 (2H, m), 7.78 (2H, m); ^{13}C NMR (125.8 MHz) δ 18.58, 21.52, 21.63, 22.33, 24.63, 25.51, 27.89, 29.50, 70.09, 83.07, 85.96, 120.77, 127.87, 129.81, 133.10, 133.55, 144.69; IR (liquid film) 2360, 1595 cm^{-1}; MS (CI), *m/z* (relative intensity) 333 (MH^+, 100), 161 (38); HRMS calcd for $C_{19}H_{24}O_3S$ 332.1446, found 332.1457. **6a**: ^{1}H NMR (a 1:1 mixture of **6a** and **5a**) δ 1.57 (8H for **6a** and **5a**, m), 1.66 (2H for **6a**, m), 1.77 (2H, for **5a**, m), 2.05 (4H for **5a**, m), 2.2−2.40 (6H for **6a** and 2H for **5a**, m), 2.44 (3H for **6a** and **5a**, s), 4.05 (2H for **6a** and **5a**, t, J = 6.3 Hz), 5.31 (1H for **6a**, br s), 5.97 (1H for **5a**, br s), 7.33 (2H for **6a** and **5a**, m), 7.78 (2H for **6a** and **5a**, m); ^{13}C NMR (125.8 MHz) (a 1:1 mixture of **6a** and **5a**) δ 18.58 (**5a**), 18.83 (**6a**), 21.52 (**5a**), 21.63 (**6a** and **5a**), 22.33 (**5a**), 24.63 (**5a**), 24.77 (**6a**), 25.51 (**5a**), 25.98 (**6a**), 26.59 (**6a**), 27.85 (**6a**), 27.89 (**5a**), 29.50 (**5a**), 31.89 (**6a**), 33.54 (**6a**), 70.09 (**6a** and **5a**), 79.56 (**6a**), 83.07 (**5a**), 85.96 (**5a**), 91.09 (**6a**), 100.12 (**6a**), 120.77 (**5a**), 127.87 (**6a** and **5a**), 129.81 (**6a** and **5a**), 133.10 (**6a** and **5a**), 133.55 (**5a**), 144.69 (**6a** and **5a**), 159.61 (**6a**); MS (CI) (a 1:1 mixture of **6a** and **5a**), *m/z* (relative intensity) 333 (MH^+, 100), 187 (64), 161 (38); HRMS (a 1:1 mixture of **6a** and **5a**) calcd for $C_{19}H_{24}O_3S$ 332.1446, found 332.1455.

The reaction using 1.0 equiv of butyllithium was performed by a procedure similar to that described above except that the reaction mixture was stirred for 2 h after being allowed to warm from −85 °C to room temperature. Purification by flash chromatography gave a 72:28 mixture of **5a** and **6a**, and tosylate **3a** (10%).

(Phenylethynyl)cyclohexene (5b)[17] **and (3-Phenyl-2-propynylidene)cyclopentane (6b).** To a solution of phenylacetylene (204 mg, 2.0 mmol) in THF (32 mL) at −85 °C was added butyllithium (1.6 M in hexane) (1.25 mL, 2.0 mmol). The mixture was stirred for 15 min at this temperature. To the resulting solution of phenylethynyllithium at −85 °C was added a THF (8 mL) solution of tosylate **3a** (252 mg, 1.0 mmol). The mixture was allowed to warm to room temperature over 2 h and stirred further for 22 h. The mixture was poured into brine and extracted twice with ether. The organic layers were dried and concentrated in vacuo. Purification of the residue by flash chromatography (0−20% ethyl acetate in hexane) gave, in the order of elution, a 79:21 mixture of **5b**[17] and **6b** (142 mg, 78% combined yield), 1-phenyl-1,7-octadiyne[18] (4.1 mg, 2.2%), and a 65:35 mixture of **5a** and **6a** (15.1 mg, 9.1% combined yield). Pure **6b** was obtained by separation of the mixture with a recycling preparative HPLC equipped with a GPC column (JAIGEL-1H column, Japan Analytical Industry) using $CHCl_3$ as an eluent. **6b**: ^{1}H NMR δ 1.70−1.78 (4H, m), 2.41 (2H, m), 2.54 (2H, m), 5.60 (1H, quintet, J = 2.3 Hz), 7.28 (3H, m), 7.41 (2H, m); ^{13}C NMR δ 26.02, 26.62, 32.20, 33.90, 88.05, 91.91, 100.16, 124.15, 127.54, 128.20, 131.20, 161.43; IR (liquid film) 2200, 1595 cm^{-1}; MS, *m/z* (relative intensity) 182 (M^+, 100); 167 (40), 154 (37); HRMS calcd for $C_{14}H_{14}$ 182.1095, found 182.1095. Anal. calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.88; H, 7.79.

Reaction of tosylate **3a** with trimethylethynyllithium by a procedure similar to that described above gave a 83:17 mixture of (cyclohexenylethynyl)trimethylsilane (**5c**)[17] and (3-cyclopentylidene-1-propynyl)trimethylsilane (**6c**)[19] in 62% combined yield.

7-Cyclopentylidenebicyclo[4.1.0]heptane (11a).[13] To a solution of tosylate **3a** (252 mg, 1.0 mmol) and cyclohexene (1.01 mL, 10.0 mmol) in THF (4.5 mL) at room temperature was slowly added butyllithium (1.6 M in hexane) (0.63 mL, 1.0 mmol) during 7 h by using a syringe pump. After being stirred further for 1.5 h at room temperature, the mixture was poured into 1N HCl and extracted twice with ether. The organic layers were washed with brine, dried, and concentrated in vacuo. Kugelrohr distillation (80−110 °C/10 mmHg) of the residue gave 29.6 mg (18%) of **11a**.[13] Flash chromatography (20% ethyl acetate in hexane) of the residue gave a 88:12 mixture of **5a** and **6a** (41.6 mg, 25% combined yield).

7-(2,2-Dimethylcyclopentylidene)bicyclo[4.1.0]heptane (11b). The compound was obtained from tosylate **3b** in 20% yield by a procedure similar to that described above. **11b**: ^{1}H NMR δ 1.05−1.35 [11H, m, including two singlets (3H each) at 1.07 and 1.11], 1.5−1.85 (9H, m), 2.34 (1H, m), 2.49 (1H, m); ^{13}C NMR (125.8 MHz) δ 10.18, 13.36, 21.05, 21.89, 22.25, 23.21, 24.02, 27.70, 28.23, 31.24, 42.28, 42.55, 119.29, 139.47. Anal. calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.37; H, 11.91.

(Cyclopentylidenemethyl)triethylsilane (12). To a solution of tosylate **3a** (252 mg, 1.0 mmol) and triethylsilane (0.48 mL, 3.0 mmol) in THF (4.5 mL) at room temperature was slowly added butyllithium (1.6 M in hexane) (0.63 mL, 1.0 mmol) during 7 h by using a syringe pump. After being stirred further for 1 h at room temperature, the mixture was poured into brine and extracted twice with ether. The yield of **12** was determined to be 13% by GC analysis of the dried organic layers using tetradecane (30.1 mg) as an internal standard. The mixture was concentrated in vacuo. Flash chromatography (20% ethyl acetate in hexane) of the residue gave a 89:11 mixture of **5a** and **6a** (98.4 mg, 59% combined yield).

An authentic sample of **12** was prepared as follows. Dibromomethylenecyclopentane was prepared according to the literature.[20] To a solution of the dibromo compound (1.91 g, 7.96 mmol) in THF (60 mL) at −95 °C was added BuLi (1.6 M in hexane) (5.0 mL, 8.0 mmol). After being stirred for 20 min at the same temperature, the reaction was quenched by the addition of AcOH−THF (1:1). The mixture was poured into brine and extracted three times with pentane. The combined extracts were washed with aqueous $NaHCO_3$, dried over K_2CO_3, and concentrated in vacuo. Purification of residue by Kugelrohr distillation (90 °C/8 mmHg) afforded 1.02 g (80% yield) of (bromomethylene)cyclopentane: ^{1}H NMR δ 1.73 (4H, m), 2.28 (4H, m), 5.92 (1H, m).

To a solution of (bromomethylene)cyclopentane (551 mg, 3.43 mmol) in THF (17 mL) at −95 °C was added *t*-BuLi (1.5 M in pentane) (8 mL, 12 mmol). After being stirred at −95 °C over a period of 6 h, triethylchlorosilane (1.44 mL, 8.6 mmol) was added to the mixture at the same temperature. After being stirred further at −95 °C for 2 h, the reaction was quenched by the addition of MeOH at this temperature. The mixture was poured into aqueous NH_4Cl and extracted three times with ether. The combined extracts were washed with aqueous $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by Kugelrohr distillation (140−150 °C/0.8 mmHg) afforded 245 mg (36% yield) of **12**: ^{1}H NMR δ 0.58 (6H, q, J = 7.8 Hz), 0.93 (9H, t, J = 7.8 Hz), 1.50−1.75 (4H, m), 2.24 (2H, br t, J = ca. 7 Hz), 2.33 (2H, br t, J = ca. 7 Hz), 5.30 (1H, quint, J = 2.1 Hz); ^{13}C NMR δ 4.27, 7.59, 25.97, 27.28, 32.85, 37.51, 114.36, 164.01; IR (liquid film) 1620, 1015, 735 cm^{-1}; MS, *m/z* (relative intensity) 196 (M^+, 14), 167 (100), 139 (95); HRMS calcd for $C_{12}H_{24}Si$ 196.1647, found 196.1656.

[4+2] Cycloadduct 13b (Representative Procedure for Trapping Experiment with 1,3-Diphenylisobenzofuran). To a solution of tosylate **3b** (140 mg, 0.50 mmol) in THF (2.0 mL) at −85 °C was added butyllithium (1.6 M in hexane) (0.31 mL, 0.5 mmol). A solution of 1,3-diphenylisobenzofuran (405 mg, 1.5 mmol) in THF (2.5 mL) was slowly added to the cooled solution of the resulting alkynyllithium. The mixture was allowed to warm to room temperature over 2.5 h and stirred further for 62 h. The mixture was poured into 1N HCl and extracted twice with ether. The organic layers were washed with aqueous $NaHCO_3$, dried, and concentrated in vacuo. Flash chromatography (50% benzene in hexane) of the residue gave 103 mg (54% yield) of **13b**: mp 183−184 °C (recrystallized from chloroform and hexane); ^{1}H NMR δ 0.82 (3H, s), 0.96 (3H, s), 1.13 (1H, m), 1.39 (1H, m), 1.58 (2H, m), 2.00 (1H, td, J =

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7.0 and 17.8 Hz), 2.32 (1H, t, d, J = 5.3 and 17.8 Hz), 7.02 (1H, t, J = 7.0 Hz), 7.09 (1H, t, J = 7.0 Hz), 7.27 (1H, d, J = 6.8 Hz), 7.4−7.6 (6H, m), 7.78 (3H, m), 8.12 (2H, br d, J = ca. 7 Hz); ^{13}C NMR (125.8 MHz) δ 19.64, 24.38, 25.44, 28.09, 33.49, 40.90, 90.96, 92.64, 119.06, 120.56, 124.36, 124.61, 126.46, 127.61, 127.98, 128.03, 128.27, 135.58, 138.15, 149.43, 151.57, 152.56, 156.30; IR (liquid film) 1600, 740, 700 cm^{-1}; MS, *m*/*z* (relative intensity) 378 (M^+, 5), 360 (16), 105 (100); HRMS calcd for $C_{28}H_{26}O$ 378.1984, found 378.1980. Anal. calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.90; H, 7.07.

[4+2] Cycloadduct 13c. The compound was obtained as a mixture of stereoisomers (69:31) in 30% yield by a procedure similar to that described above. The isomers were separated by a recycling preparative HPLC, equipped with a GPC column (JAIGEL-1H column) using $CHCl_3$ as an eluent. Major isomer: ^{1}H NMR δ 1.56 (1H, m), 1.91 (1H, m), 2.10−2.25 (2H, m), 2.40 (1H, m), 2.61 (1H, br d, J = ca. 16 Hz), 2.85 (1H, m), 6.95−7.05 (4H, m), 7.15−7.30 (5H, m), 7.35−7.55 (6H, m), 7.71 (2H, m), 7.79 (2H, m); ^{13}C NMR (125.8 MHz) δ 22.93, 29.68, 31.40, 39.59, 92.22, 92.28, 119.06, 119.38, 124.74, 124.80, 125.96, 126.14, 126.47, 126.83, 127.66, 127.90, 128.34, 128.41, 128.44, 135.12, 135.32, 146.01, 149.69, 150.79, 151.24, 142.02. Minor isomer: ^{1}H NMR δ 1.79 (1H, br dt, J = ca. 5 and 11 Hz), 1.85 (1H, br d, J = ca. 11 Hz), 2.17 (1H, m), 2.35−2.55 (4H, m), 7.01 (2H, m), 7.10−7.30 (7H, m), 7.35−7.55 (6H, m), 7.70−7.80 (4H, m); ^{13}C NMR (125.8 MHz) δ 24.53, 29.61, 31.53, 41.05, 92.17, 92.22, 118.94, 119.34, 124.74, 124.79, 125.86, 126.28, 126.56, 126.91, 127.65, 127.95, 128.41, 128.42, 128.46, 135.20, 135.24, 146.25, 149.44, 151.14 (2C), 152.20. IR (a mixture of the stereoisomers) (KBr disk) 995, 965, 740, 700 cm^{-1}; MS (a mixture of the stereoisomers), *m*/*z* (relative intensity) 426 (M^+, 12), 408 (8), 105 (100); HRMS (a mixture of the stereoisomers) calcd for $C_{32}H_{26}O$ 426.1984, found 426.1973.

Reaction of Dibromomethylenecyclopentane with BuLi in the Presence of 1,3-Diphenylisobenzofuran. To a solution of dibromomethylenecyclopentane (120 mg, 0.50 mmol) and 1,3-diphenylisobenzofuran (406 mg, 1.5 mmol) in THF (20 mL) at −85 °C was added butyllithium (1.6 M in hexane) (0.31 mL, 0.5 mmol). The cooling bath was removed and the mixture was stirred for 5 h at room temperature. The mixture was poured into water and extracted twice with ether. The organic layers were dried and concentrated in vacuo. Flash chromatography (50% benzene in hexane) of the residue gave 7.7 mg (4.4% yield) of **13a**: mp 169−171 °C (recrystallized from petroleum ether and EtOH) (lit.[7b] mp 170−171.5 °C); ^{1}H NMR δ 1.46 (m, 2H), 1.58 (m, 2H), 2.06 (m, 2H), 2.27 (m, 2H), 6.98 (m, 2H), 7.22 (m, 2H), 7.42 (m, 2H), 7.52 (m, 4H), 7.74 (m, 4H); ^{13}C NMR δ 22.44, 23.47, 92.32, 119.01, 124.61, 126.40, 127.72, 128.36, 135.53, 150.22, 151.91.

[6-^{13}C]-2-Phenyl-4-hexyn-1-ol (15). To a stirred suspension of lithium amide (22 mmol) in liquid ammonia[21] (80 mL) was slowly added a solution of silyl ether **14** (5.06 g, 18.6 mmol) in THF (40 mL) at −55 °C. The resulting suspension was stirred for 1 h and then a THF (2.5 mL) solution of [^{13}C]-iodomethane (3.12 g, 22 mmol, ca. 40% ^{13}C content) was added. The mixture was stirred for 1 h. The cooling bath was removed and ammonia was allowed to evaporate. The mixture was poured into ice water and extracted three times with a mixed solvent of ethyl acetate and hexane. The combined organic layers were dried and concentrated in vacuo. The crude product was then treated with tetrabutylammonium fluoride (1M in THF) (18.6 mL, 18.6 mmol) in THF (100 mL) at room temperature for 2 h. The reaction mixture was poured into water and extracted twice with ether. The combined organic layers were dried and concentrated in vacuo. Purification of the residue by flash chromatography (20% ethyl acetate in hexane) gave 2.78 g (86% yield) of **15**. The ^{13}C content of the product was determined to be 39% on the basis of ^{1}H NMR integration of the 6-$^{13}CH_3$ (td, J = 2.4 and 131.0 Hz) and 6-$^{12}CH_3$ protons (t, J = 2.4 Hz). **15**: ^{1}H NMR δ 1.60 (1H, br), 1.76 (1.83H, t, J = 2.4 Hz and 1.27H, td, J = 2.4 and 131.0 Hz), 2.52 (2H, m), 3.00 (1H, quint, J = 6.9 Hz), 3.8−4.0 (2H, m), 7.25 (3H, m), 7.33 (2H, m); IR (liquid film) 3360 (br), 755, 700 cm^{-1}.

[6-^{13}C]-2-Phenyl-5-hexyn-1-ol (16). To a brown suspension of potassium 3-aminopropylamide (KAPA)[16,22] (23.1 mmol) in 1,3-diaminopropane (25 mL) at room temperature was added alcohol **15** (1.34 g, 7.70 mmol). After being stirred for 20 h, the reaction mixture was poured into aqueous NH_4Cl under argon at 0 °C and extracted twice with ether. The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (5−15% ethyl acetate in hexane) gave 0.230 g (17% yield) of **16**: ^{1}H NMR δ 1.40 (1H, br), 1.74−2.20 [5H, m, including t (J = 2.4 Hz) and td (J = 2.4 and 247.0 Hz) at 1.96], 2.97 (1H, ddt, J = 4.5, 6.6, and 11.1 Hz), 3.77 (2H, d, J = 6.9 Hz), 7.21−7.28 (3H, m), 7.31−7.37 (2H, m); IR (liquid film) 3400 (br), 3280, 2110, 760, 700 cm^{-1}.

[6-^{13}C]-2-Phenyl-5-hexynyl *p*-Toluenesulfonate ([6-^{13}C]-3c). The tosylate was prepared from alcohol **16** in 81% yield by a method similar to that described before. The terminal acetylenic carbon of the ^{13}C labeled tosylate resonated at 1.93 ppm (td, J = 2.4 and 247.0 Hz).

^{13}C Labeling Experiment. The labeled tosylate (128 mg, 0.39 mmol), whose ^{13}C content was estimated to be 39% as described above, was mixed with nonlabeled tosylate **3c** (122 mg, 0.37 mmol) and the resulting tosylate of 20% ^{13}C content was used in the reaction with ethynyltrimethylsilane. To a solution of ethynyltrimethylsilane (147 mg, 1.5 mmol) in THF (6 mL) at −85 °C was added butyllithium (1.6 M in hexane) (0.94 mL, 1.5 mmol). The mixture was stirred 10 min at this temperature. To the resulting solution of (trimethylsilyl)-ethynyllithium at room temperature was added a THF (2 mL) solution of the labeled tosylate [6-^{13}C]-**3c** (249 mg, 0.75 mmol). After being stirred at room temperature for 24 h, the mixture was poured into water and extracted twice with ether. The combined organic layers were dried and concentrated in vacuo. Purification of the residue by flash chromatography (0−20% ethyl acetate in hexane) gave, in the order of elution, a 32:31:37 mixture of enynes **5d**, **5e**, and **6d** (a 19:18 mixture of geometrical isomers **6d-1** and **6d-2**) (71.9 mg, 38% combined yield), and the starting tosylate [6-^{13}C]-**3c** (69.7 mg, 28%). Separation of the mixture of enynes by a recycling preparative HPLC, equipped with a GPC column (JAIGEL-1H column) using $CHCl_3$ as an eluent, gave, in the order of elution, **6d-2**, a mixture of **5d** and **6d-1**, and **5e**.

An authentic sample of **5d** was prepared from 4-phenylcyclohexanone in two steps. Treatment of the ketone with LDA (1.1 equiv) in THF at −78 °C for 1 h followed by the reaction of the resulting enolate with *N*-phenyltrifluoromethanesulfonamide (1.1 equiv)[19] gave 4-phenylcyclohexenyl trifluoromethanesulfonate (91% yield): ^{1}H NMR δ 1.9−2.15 (2H, m), 2.3−2.65 (4H, m), 2.86 (1H, m), 3.86 (1H, t, J = 2.7 Hz), 7.24 (3H, m), 7.33 (2H, m); ^{13}C NMR δ 27.81, 29.64, 31.51, 38.70, 118.04, 118.39 (q, J_{C-F} = 320 Hz), 126.60, 126.71, 128.59, 144.52, 148.96; 1690, 1210, 1145, 860 660, 700 cm^{-1}; MS, *m*/*z* (relative intensity) 306 (M^+, 24), 104 (100); HRMS calcd for $C_{13}H_{13}O_3F_3S$ 306.0537, found 306.0545.

A mixture of $Pd(PPh_3)_2Cl_2$ (34.9 mg, 0.05 mmol), 4-phenylcyclohexenyl trifluoromethanesulfonate (613 mg, 2.0 mmol), trimethylsilylacetylene (0.42 mL, 3.0 mmol), and triethylamine (0.96 mL, 6.9 mmol) in DMF (8 mL) was heated at 75 °C for 1.5 h. The mixture was poured into water and extracted with a mixed solvent of ether and hexane (1:1). The organic layer was washed with brine, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (0−5% ethyl acetate in hexane) afforded 375 mg (74% yield) of **5d**: ^{1}H NMR δ 0.24 (9H, s), 1.80 (1H, m), 1.99 (1H, br d, J = ca. 12 Hz), 2.18−2.50 (4H, m), 2.79 (1H, m), 6.30 (1H, br s), 7.24 (3H, m), 7.33 (2H, m); ^{13}C NMR δ 0.07, 29.41, 29.73, 33.73, 39.03, 91.54, 106.73, 120.68, 126.16, 126.74, 128.40, 128.42, 135.43, 146.23; IR (liquid film) 2140, 1605 cm^{-1}; MS, *m*/*z*

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(relative intensity) 254 (M^+, 83), 239 (55), 104 (100); HRMS calcd for $C_{17}H_{22}Si$ 254.1499, found 254.1493. Anal. calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.71. Found: C, 80.03; H, 8.69.

Trimethyl[2-(5-phenylcyclohexenyl)ethynyl]silane (**5e**): ^{1}H NMR (500 MHz) δ 0.21 (9H, s), 1.73 (1H, tt, J = 8.4 and 12.3 Hz), 1.96 (1H, br d, J = ca. 12 Hz), 2.26−2.40 (3H, m), 2.46 (1H, br d, J = ca. 18 Hz), 2.82 (1H, m), 6.28 (1H, br s), 7.26 (3H, m), 7.34 (2H, m); ^{13}C NMR (125.8 MHz) δ 0.04, 26.38, 28.55, 37.03, 39.77, 91.50, 106.59, 120.57, 126.20, 126.79, 128.43, 135.55, 146.12; IR (liquid film) 2140, 1600 cm^{-1}; MS, *m*/*z* (relative intensity) 254 (M^+, 62), 239 (100), 226 (18); HRMS calcd for $C_{17}H_{22}Si$ 254.1499, found 254.1495. Trimethyl-[3-(3-phenylcyclopentylidene)-1-propynyl]silane (**6d**): Minor isomer **6d-2**; ^{1}H NMR (500 MHz) δ 0.24 (9H, s), 1.83 (1H, m), 2.26 (1H, m), 2.49−2.64 (2H, m), 2.74−2.92 (2H, m), 3.20 (1H, tt, J = 6.9 and 10.5 Hz), 5.52 (1H, quint, J = 2.1 Hz), 7.24 (3H, m), 7.30 (2H, m); ^{13}C NMR (125.8 MHz) δ 0.16, 31.91, 33.69, 41.44, 45.38, 97.18, 101.09, 103.42, 126.22, 126.90, 128.38, 144.13, 161.36; IR (liquid film) 2130, 1600 cm^{-1}; MS, *m*/*z* (relative intensity) 254 (M^+, 57), 239 (100), 180 (40); HRMS calcd for $C_{17}H_{22}Si$ 254.1499, found 254.1491. Major isomer **6d-1**; ^{1}H NMR (500 MHz) (a mixture of **6d-1** and **5d**) δ 0.21 (9H of **6d-1**, s), 0.24 (9H for **5d**, s), 1.74−1.83 (1H for **5d** and **6d-1**, m), 2.00 (1H for **5d**, br d, J = ca. 12 Hz), 2.17−2.58 (4H for **5d** and 3H for **6d-1**, m), 2.66 (1H for **6d-1**, br dd, J = ca. 5 and 18 Hz), 2.80 (1H for **5d**, m), 3.07 (1H for **6d-1**, br dd, J = ca. 7 and 16 Hz), 3.20 (1H for **6d-1**, m), 5.50 (1H for **6d-1**, quint, J = 2.1 Hz), 6.30 (1H for **5d**, br s), 7.11−7.37 (5H for **5d** and **6d-1**, m); ^{13}C NMR (125.8 MHz) (a mixture of **6d-1** and **5d**) δ 0.07 (**5d**), 0.14 (**6d-1**), 29.43 (**5d**), 29.74 (**5d**), 33.30 (**6d-1**), 33.74 (**5d**), 34.43 (**6d-1**), 39.05 (**5d**), 40.26 (**6d-1**), 45.17 (**6d-1**), 91.59 (**5d**), 96.97 (**6d-1**), 101.11 (**6d-1**), 103.34 (**6d-1**), 106.73 (**5d**), 120.67 (**5d**), 126.19 (**5d**), 126.24 (**6d-1**), 126.79 (**5d**), 127.03 (**6d-1**), 128.40 (**6d-1**), 128.42 (**5d**), 135.53 (**5d**), 144.36 (**6d-1**), 146.29 (**5d**), 161.21 (**6d-1**); IR (liquid film) (a mixture of **6d-1** and **5d**) 2140, 1605 cm^{-1}; MS (a mixture of **6d-1** and **5d**), *m*/*z* (relative intensity) 254 (M^+, 33), 239 (30), 163 (100); HRMS (a mixture of **6d-1** and **5d**) calcd for $C_{17}H_{22}Si$ 254.1499, found 254.1496.

In the ^{1}H NMR analysis of **5d**, the olefinic proton H(2) appeared at 6.30 ppm as a br s along with ^{13}C satellites (J_{C-H} = 160 Hz). The ^{13}C content of **5d** at C(2) was estimated to be 15% on the basis of the integration of the signals. Similarly, the olefinic proton H(2) of **5e** appeared at 6.28 ppm as a br s with ^{13}C satellites (J_{C-H} = 160 Hz) and the ^{13}C content of **5e** was estimated to be 7%. The olefinic protons H(1′) of **6d-1** and **6d-2** appeared at 5.50 and 5.52 ppm with ^{13}C satellites (J_{C-H} = 162 and 163 Hz), respectively, and the ^{13}C contents of **6d-1** and **6d-2** were estimated to be 20% and 21%, respectively. In ^{13}C NMR analyses, enhancement of the following resonances were observed: **5d**, 120.67 (C-2) and 135.53 ppm (C-1); **5e**, 120.57 (C-2) and 135.55 ppm (C-1); **6d-1**, 101.11 ppm (C-1′); **6d-2**, 101.09 ppm (C-1′).

7-Phenyl-2-oxabicyclo[3.3.0]oct-6-ene (**18**): To a solution of *p*-fluorobenzenesulfonate **17** (462 mg, 1.0 mmol) in THF (4.5 mL) at room temperature was slowly added butyllithium (1.6 M in hexane) (0.63 mL, 1.0 mmol) during 7 h by using a syringe pump. After being stirred further for 0.5 h at room temperature, the mixture was poured into brine and extracted twice with ether. The organic layers were dried and concentrated in vacuo. Flash chromatography of the residue (5−20% ethyl acetate in hexane) gave, in the order of elution, **18** (a 93:7 mixture of stereoisomers) (102 mg, 55% yield) and the recovery of **17** (17%). **18**: ^{1}H NMR (500 MHz) δ 1.72 (1H, ddd, J = 7.8, 9.6, and 12.2 Hz), 2.45−2.65 (2H, m), 2.72 (1H, td, J = 6.0 and 12.2 Hz), 4.13−4.30 (3H, m), 4.80 (1H, br t, J = ca. 6.5 Hz), 5.54 (1H, br s), 7.20−7.27 (3H, m), 7.32 (2H, m) [minor stereoisomer resonated at 5.00 (1H, br t, J = ca. 6 Hz) and 5.67 (1H, br s)]; ^{13}C NMR δ 25.74, 44.19, 54.87, 71.26, 88.14, 124.88, 126.38, 127.21, 128.41, 144.98, 148.67 (minor stereoisomer resonated at 25.52, 41.01, 36.56, 71.67, 87.68, 124.56, 126.08, 126.95, 128.41, 144.81, 148.67); IR (liquid film) 1600, 970, 760, 700 cm^{-1}; MS, *m*/*z* (relative intensity) 186 (M^+, 100); 155 (19), 129 (28); HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1043. Anal. calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 83.43; H, 7.60.

(3-Phenyl-2-propynylidene)cyclopropane (20a). To a solution of phenylacetylene (204 mg, 2.0 mmol) in THF (32 mL) at −85 °C was added butyllithium (1.6 M in hexane) (1.25 mL, 2.0 mmol). The mixture was stirred for 15 min at this temperature. To the resulting solution of phenylethynyllithium at −85 °C was a THF (8 mL) solution of *p*-fluorobenzenesulfonate **19a** (228 mg, 1.0 mmol). The mixture was allowed to warm to room temperature over 2 h and stirred further for 3.5 h at 30 °C. The mixture was poured into brine and extracted twice with ether. The organic layers were dried and concentrated in vacuo. Purification of the residue by flash chromatography (hexane) gave 85.9 mg (56% yield) of **20a**: ^{1}H NMR δ 1.29 (4H, m), 6.15 (1H, br s), 7.30 (3H, m), 7.46 (2H, m); ^{13}C NMR δ 3.43, 4.14, 87.51, 88.76, 99.69, 123.68, 127.88, 128.22, 131.50, 138.60; IR (liquid film), 1600, 915, 755, 690 cm^{-1}; MS, *m*/*z* (relative intensity) 154 (M^+, 100); 153 (92), 152 (58); HRMS calcd for $C_{12}H_{10}$ 154.0783, found 154.0789.

(3-Phenyl-2-propynylidene)cyclohexane (20b) and 2-(Phenylethynyl)cycloheptene (21). To a solution of phenylacetylene (102 mg, 1.0 mmol) in THF (16 mL) at −85 °C was added butyllithium (1.6 M in hexane) (0.63 mL, 1.0 mmol). The mixture was stirred for 15 min at this temperature. To the resulting solution of phenylethynyllithium at −80 °C was a THF (8 mL) solution of *p*-fluorobenzenesulfonate **19b** (135 mg, 0.5 mmol). The mixture was allowed to warm to room temperature over 2.5 h and stirred further at 65 °C for 19 h. The mixture was poured into brine and extracted twice with ether. The organic layers were dried and concentrated in vacuo. Purification of the residue by flash chromatography (hexane) gave a 75:25 mixture of **20b** and **21** (67.8 mg, 69% combined yield). Pure **20b** was isolated by a recycling preparative HPLC equipped with a GPC column (JAIGEL-1H column) using $CHCl_3$ as an eluent. **20b**: ^{1}H NMR δ 1.60 (6H, m), 2.22 (2H, m), 2.50 (2H, m), 5.44 (1H, br s), 7.28 (3H, m), 7.43 (2H, m); ^{13}C NMR δ 26.30, 27.55, 28.27, 31.72, 36.05, 87.33, 91.26, 101.62, 124.07, 127.56, 128.19, 131.25, 156.32; IR (liquid film) 2200, 1595, 830, 755, 690 cm^{-1}; MS, *m*/*z* (relative intensity) 196 (M^+, 100); 167 (40), 128 (30); HRMS calcd for $C_{15}H_{16}$ 196.1252, found 196.1260. Anal. calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.41; H, 8.26.

An authentic sample of **21** was prepared by a palladium(0)-catalyzed cross-coupling reaction of cycloheptenyl trifluoromethanesulfonate and phenylacetylene in 49% yield.[23] **21**: ^{1}H NMR δ 1.50−1.67 (4H, m), 1. 78 (2H, m), 2.25 (2H, m), 2.45 (2H, m), 6.42 (1H, br t, J = ca. 6.5 Hz), 7.28 (3H, m), 7.41 (2H, m); ^{13}C NMR δ 26.53, 26.60, 29.26, 32.14, 34.28, 86.77, 92.93, 123.86, 126.89, 127.57, 128.15, 131.30, 140.20; IR (liquid film) 2200, 1595, 850, 755, 690 cm^{-1}; MS, *m*/*z* (relative intensity) 196 (M^+, 100); 168 (40), 167 (52); HRMS calcd for $C_{15}H_{16}$ 196.1252, found 196.1254. Anal. calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.46; H, 8.21.

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Supporting Information Available: Preparation of **14**, **16**, 4,4-dimethyl-5-hexyn-1-ol, and 4-(2-phenylethyl)-3-oxa-5-hexyn-1-ol as well as spectral data of **3a**,**b**,**c**, **17**, and **19a**,**b** and ^{1}H or ^{13}C NMR spectra of new compounds not accompanied by elemental analyses (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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