Lewis acid-mediated intramolecular addition of silyl enol ethers to internal unactivated alkynes

Ken-ichiro Imamura, Eiji Yoshikawa, Vladimir Gevorgyan, Tomoko Sudo, Naoki Asao, and Yoshinori Yamamoto

Abstract: The $EtAlCl_2$-mediated intramolecular addition of silyl enol ethers to both terminal and internal unactivated alkynes, bearing alkyl and phenyl susbstituents at the alkyne moiety, gave mono- and bicyclic β,γ-unsaturated ketones in good to excellent yields. On the other hand, the silyloxy-substituted cyclic vinylsilanes were obtained in moderate to high yields when the reactions were catalyzed by $B(C_6F_5)_3$ in the presence of triethylsilane. All the reactions proceeded via *endo*-fashion exclusively. The mechanisms of these regiospecific Lewis acid-assisted carbocyclizations are proposed.

Key words: Lewis acid, silyl enol ethers, carbocyclization, alkynes.

Résumé : La réaction, catalysée par le $EtAlCl_2$, d'addition intramoléculaire d'éthers énoliques silylés sur des alcynes internes ou en position terminale portant des substituants alkyles et phényles au niveau de l'alcyne conduit à la formation de cétones β,γ-insaturées mono- et bicycliques, avec des rendements allant de bons à excellents. Par ailleurs, les réactions catalysées par du $B(C_6F_5)_3$ en présence de triéthylsilane conduisent à la formation de vinylsilanes cycliques, substitués par des groupes silyloxy, avec des rendements allant de modérés à élevés. Toutes les réactions se produisent exclusivement de façon *endo*. On propose des mécanismes pour ces carbocyclisations régiospécifiques assistées par des acides de Lewis.

Mots clés : acide de Lewis, éthers énoliques, carbocyclisation, alcynes.

[Traduit par la Rédaction]

Introduction

The development of new selective carbocyclization methodologies is an important task for synthetic organic chemists (for reviews see ref. 1). Carbocyclization of alkynes is of particular interest since it provides an access to unsaturated carbo- and heterocycles (for a review, see for example ref. 2). Among several known methods of carbocyclization of alkynes (1, 2), the intramolecular addition of silyl enol ethers to acetylenes has proven to become one of the effective complementary tools towards medium-sized carbocycles. Two approaches are known to date to encourage a weak nucleophile, such as a silyl enol ether, to add intramolecularly across a carbon—carbon triple bond (3).[2] First is a well explored $HgCl_2$-mediated *exo*-carbocyclization (eq. [1]) (4, 5),[3] in which mercury activates an enolate moiety of **1** by forming a transient α-keto mercurial species **2**. Either the product **4** or the isomeric *trans*-addition product **6** is obtained through *syn*-addition of enolate to the η^2 neutral **3** (pathway **A**) or *anti*-addition to the η^2 cationic **5** (pathway **B**) species, respectively.

The second is a very recent approach where a W complex catalytically activates an alkyne moiety (toward nucleophilic addition of enolate) via formation of the alkyne–vinilydene intermediate **7**, which, after concomitant *anti*-addition of silyl enol ether to its electrophilic central carbon, forms an *endo*-carbocyclization product **8** (eq. [2]) (6).[4]

Despite the obvious synthetic importance of the mentioned methodologies (7),[5] the scope of their application is limited to use of terminal (4–6)[3,4] and masked terminal (silyl-protected) (4*c*-4*d*, 7)[5] alkynes. Recently, we reported the first examples of the third alternative approach: Lewis acid-mediated intramolecular addition of silyl enol ethers to both terminal and internal unactivated alkynes (8). Now we report the $B(C_6F_5)_3$-catalyzed cyclization reactions of the carbon-tethered alkynyl silyl enol ether in the presence of

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This paper is dedicated to Professor Victor Snieckus in recognition of his contributions to organic chemistry.

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[2]There are reports on the intermolecular addition of silyl enol ethers to terminal alkynes mediated by the $SnCl_4$–Bu_3N system and by $GaCl_3$, proceeding via *syn*-addition of metal enolates to metalacetylides. See ref. 3.

[3]There are reports in which the authors state an exclusive *anti*-selective addition of α-keto carbons to the terminal alkynes mediated by mercuric chloride. See ref. 5.

[4]When this project was undergoing in our labs, a paper describing a W-catalyzed *endo*-selective carbocyclization of silyl enol ethers with terminal alkynes had appeared. See ref. 6.

[5]Mercury-mediated carbocylization approach was recently successfully used for the natural products syntheses. See ref. 7.

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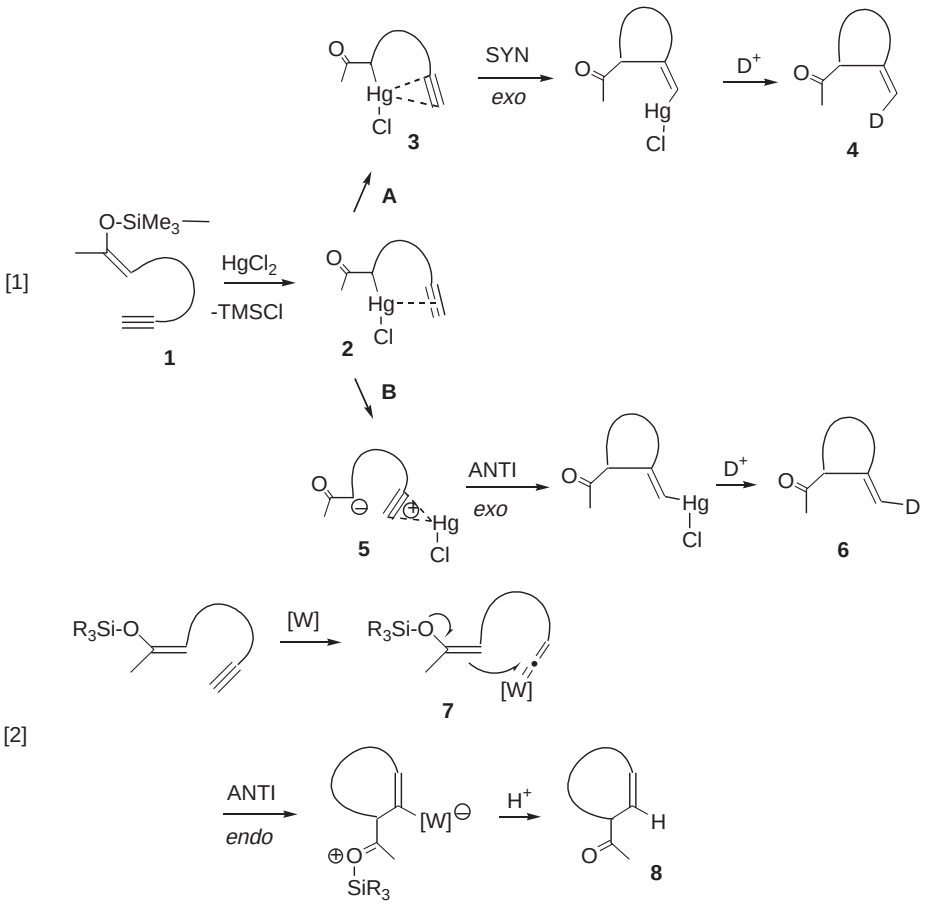
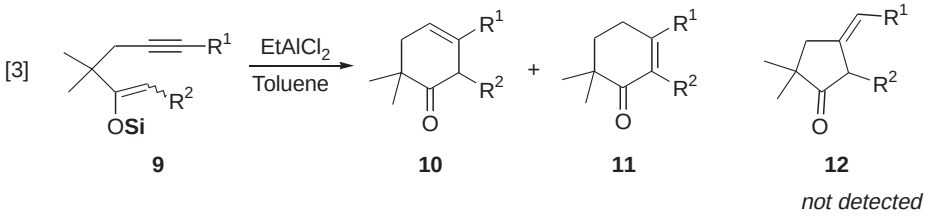


triethylsilane along with a detailed study on the $EtAlCl_2$-mediated reactions (Lewis acid-catalyzed intramolecular carbosilylation of alkynes are reported; see ref. 9).

Results and discussion

$EtAlCl_2$-mediated intramolecular addition of silyl enol ether to alkynes

As we have previously shown, the intramolecular addition of silyl enol ethers of **9** to internal alkynes is mediated by $EtAlCl_2$ to give cyclic products **10** in good to high yields (eq. [3], Table 1). The reaction of **9a** in the presence of stoichiometric amounts of $EtAlCl_2$[6] afforded the cyclization product **10a** in 70% isolated yield (entry 1). The reaction of **9b** bearing *t*-Bu-Me_2Si group instead of Me_3Si group also proceeded smoothly to give **10a** in 63% (entry 2). Optimization experiments revealed that the reaction under 0.1 mol L^{-1} concentration gave the best result (entries 1, 3–5). The carbocyclizations of methyl- (**9c**) and butyl-substituted (**9d**) alkynyl silyl enol ethers gave β,γ-unsaturated ketones **10b–c** in 57 and 80%, respectively. The reaction of the silyl enol ether containing trisubstituted alkene **9e** also proceeded smoothly to give **10d** in 76% yield. In all above cases, the β,γ-unsaturated ketones **10a–d** were accompanied with detectable amounts of isomeric α,β-unsaturated cyclohexenones **11a–d**, which are obviously the thermodynamic products.[7] It should be pointed out that in all cases the carbocyclizations proceeded in exclusive *endo*-fashion and no traces of *exo*-cyclization product **12** were detected by GC–MS and NMR analyses of the crude reaction mixtures.



9 **10** **11** **12**

not detected

[6] Other Lewis acids such as $HfCl_4$, $ZrCl_4$, and $InCl_3$ did not mediate this carbocyclization, whereas the use of $AlBr_3$, $MeAlCl_2$, Et_2AlCl, and $GaCl_3$ in some cases gave the carbocyclization products although the chemical yields with these Lewis acids were low (≤40%).

[7] The control experiments have confirmed that β,γ-enone **10** is the kinetic product, which isomerized into the thermodynamic product (α,β-enone **11**) under the reaction conditions. Thus, normally the carbocyclization of **9c** gives about a 95:5 ratio of **10c**:**11c** (eq. [3]); after being stirred for an additional 3 h at room temperature, the mentioned ratio changed to 44:56, whereas after 12 h, the isomeric **11c** became the major reaction product accompanied by traces of **10c**.

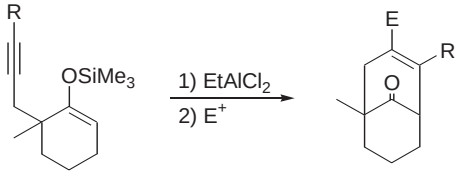
Table 1. $EtAlCl_2$-mediated cyclization reaction of **9**.[a]

Entry	Si	R^1	R^2	9	Lewis acid (equiv)		(mol L^{-1})	Yield (%) 10		11	
1	Me_3Si	Ph	H	**9a**	$EtAlCl_2$	(1.2)	0.4	**10a**	70	**11a**	6
2	*t*-Bu-Me_2Si	Ph	H	**9b**	$EtAlCl_2$	(1.2)	0.4	**10a**	63	**11a**	11
3	Me_3Si	Ph	H	**9a**	$EtAlCl_2$	(1.2)	0.1	**10a**	75	**11a**	4
4	Me_3Si	Ph	H	**9a**	$EtAlCl_2$	(1.5)	0.08	**10a**	77	**11a**	5
5	Me_3Si	Ph	H	**9a**	$EtAlCl_2$	(1.2)	0.01	**10a**	60	**11a**	4
6	Me_3Si	Me	H	**9c**	$EtAlCl_2$	(1.2)	0.1	**10b**	57	**11b**	11
7	Me_3Si	Bu	H	**9d**	$EtAlCl_2$	(1.2)	0.1	**10c**	80	**11c**	6
8	Me_3Si	Ph	Me	**9e**	$EtAlCl_2$	(1.2)	0.1	**10d**	76	**11d**	8

[a]Reactions were conducted in toluene at 0°C for 3 h.

$EtAlCl_2$-mediated carbocyclization of cyclic substrates **13**, as well as that of their acyclic analogues **9**, proceeded in exclusive *endo*-fashion to give bicylic β,γ-cyclohexenones **14** in good yields (eq. [4]). Substrates possessing both terminal (**13a**) and internal (**13b**) alkynyl moieties effectively cyclized to give the bicylic **14a** and **14c** in 78 and 84% isolated yields, respectively. Furthermore, quenching the reaction mixtures with electrophiles, such as D_2O and I_2, afforded the corresponding D- (**14b**) and I-containing (**14d**) products in good yields.

[4]

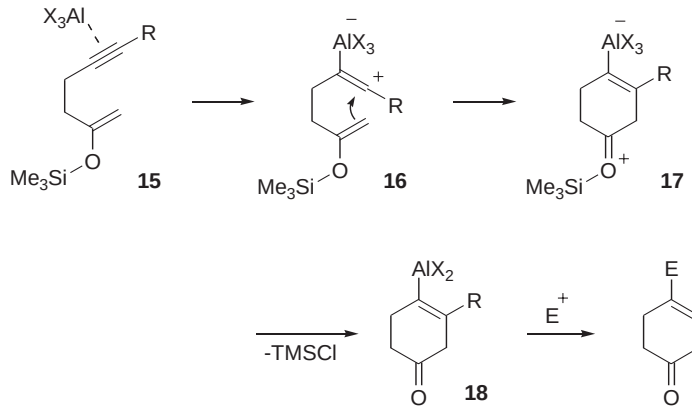


13 a: R=H
b: R=Me

14 a: R=E=H, 78%
b: R=H, E=D, 71%
c: R=Me, E=H, 84%
d: R=Me, E=I, 75%

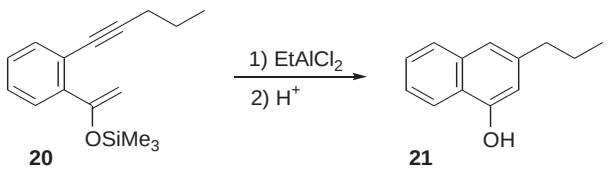
We propose the following plausible mechanism for the observed Lewis acid-mediated exclusive *endo*-carbocyclization of carbon-tethered alkynyl silyl enol ethers. As we previously proposed for the Lewis acid-catalyzed hydro- and allylmetalation of alkynes (9), the coordination of the triple bond of **15** to Lewis acid would form zwitterionic intermediate **16** (eq. [5]). The double bond of silyl enol ether moiety would attack the vinyl cation of **16** at the most nucleophilic terminal position in an *anti*-fashion affording the *endo*-mode cyclization intermediate **17**. The elimination of the TMSCl from **17** would form the vinyl metal **18**, which after trapping with an electrophile would produce **19**.

[5]



An application of the above methodology is shown in eq. [6]. Naphthol **21** could be synthesized from the unsaturated analogue **20**, although in modest unoptimized yield (40% by ^1H NMR, eq. [6]).

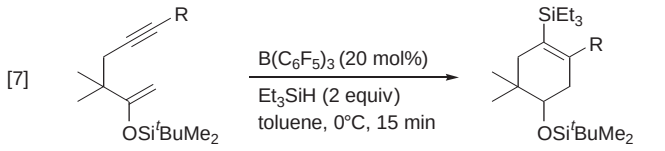
[6]



20 **21**

$B(C_6F_5)_3$-catalyzed intramolecular addition of silyl enol ether to alkynes

Although the above mentioned carbocyclization reaction demonstrated the first example of the Lewis acid-mediated addition of silyl enol ethers to internal unactivated alkynes, the synthetic utility of this methodology is limited by the fact that a stoichiometric amount of $EtAlCl_2$ is needed. This prompted us to search for a more synthetically useful catalyst for this reaction. Attempted reaction of **9b** in the presence of a catalytic amount of $B(C_6F_5)_3$ did not proceed at all. However, the $B(C_6F_5)_3$-catalyzed reaction proceeded dramatically by addition of triethylsilane and the silyloxy-substituted cyclic vinylsilane **22a** was obtained in 49% yield (eq. [7]) (10).[8] The compound **10a**, which was produced in the $EtAlCl_2$-mediated reaction, was not formed at all. The $B(C_6F_5)_3$-catalyzed cyclization reaction using other substituted substrates **9f** and **9g** also proceeded smoothly under the same conditions as those in the case of **9b** to afford **22b** and **22c** in 61 and 63% yield, respectively.



9b: R=Ph
9f : R=Me
9g: R=Bu

22a: R=Ph 49%
22b: R=Me 61%
22c: R=Bu 63%

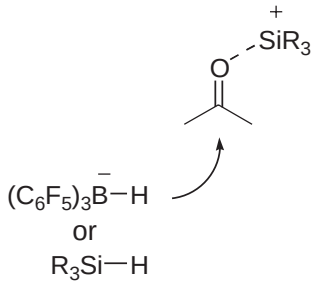
Piers and co-workers (10)[8] proposed the interesting silane activation mechanism in the $B(C_6F_5)_3$-catalyzed hydrosilylation of aldehydes and ketones; the ordinary mechanism, in which the carbonyl oxygen of the electrophiles coordinates to $B(C_6F_5)_3$ and thus carbonyl substrates are activated, is not operative in the $B(C_6F_5)_3$-catalyzed reduction. Their extensive mechanistic studies clarify that $B(C_6F_5)_3$ activates the silane via hydride abstraction to form the incipient silylium species which enhances the electrophilicity of carbonyl group, facilitating the reduction by $[HB(C_6F_5)_3]^-$ or R_3SiH (Fig. 1).

Most probably, silylium species **23** is generated here also and a plausible mechanism for the $B(C_6F_5)_3$-catalyzed cyclization reaction of **9** is shown in Scheme 1. The π-coordination of acetylenic bond of **9** to the silylium species would form the cationic intermediate **24**. The silyl enol ether moiety would attack the electron deficient triple bond from the side opposite to the silylium species to produce an oxonium cation **25**. The reduction of an intermediate **25** by $[HB(C_6F_5)_3]^-$ would form cyclization products **22** and regenerate $B(C_6F_5)_3$.

Experimental

^1H and ^{13}C NMR spectra were recorded on a JEOL LA-300 (300 MHz) and JEOL α–500 (500 MHz) spectrometers. IR spectra were recorded on a Shimadzu FT IR-8200A spectrometer. High-resolution mass spectra were recorded on a JEOL HX-110 spectrometer. Elemental analyses were carried out at the Analytical Center of Tohoku University. GC–MS analysis was performed on a Hewlett-Packard Model 6890 GC interfaced to a Hewlett-Packard Model 5973 mass selective detector (30 m × 0.25 mm capillary column). Column chromatography was carried out employing Merck silica gel (Kieselgel 230–400 mesh), and analytical thin layer chromatography (TLC) was performed on 0.2-mm precoated silica gel plates (Kieselgel 60 F_{254}). All manipulations were conducted under an argon atmosphere using standard Schlenk techniques. Anhydrous solvents were purchased from Kanto Chemicals. Alkyl-tethered alkynyl silyl enol ethers **9** were obtained by consecutive ester propargylation (for a review see ref. 13), conversion to ketone, and silyl enolization (for a review see ref. 14). All other compounds used were commercially available and purchased from Aldrich.

Fig. 1. Mechanism of the $B(C_6F_5)_3$-catalyzed hydrosilylation of the carbonyl group.

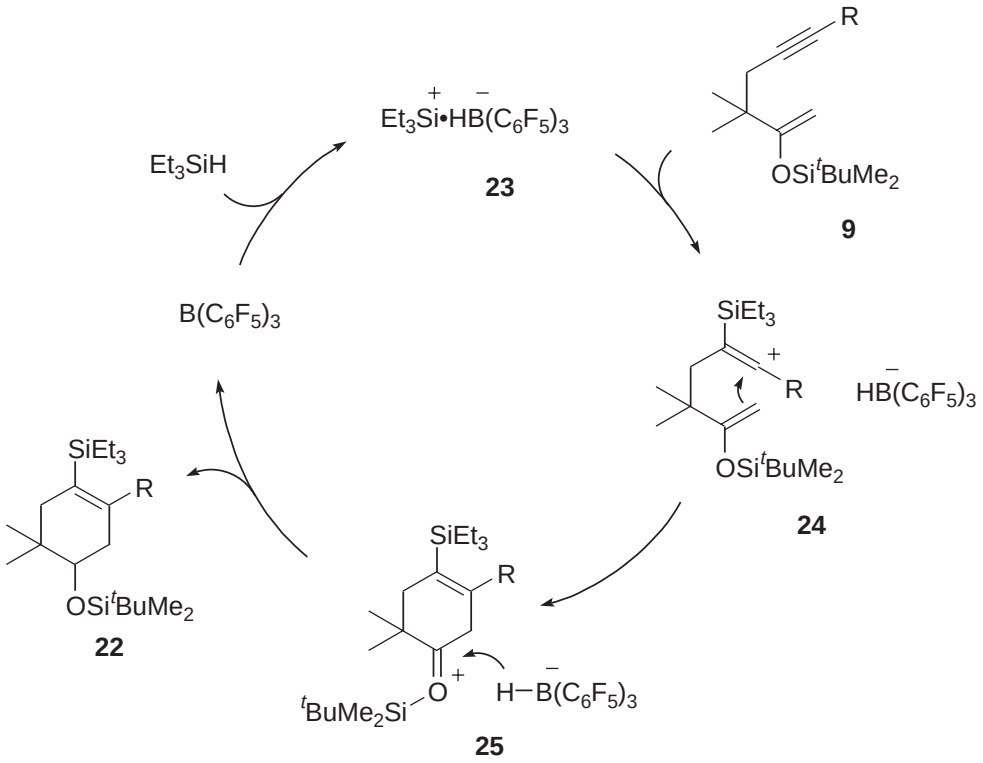


Preparation of alkynyl silyl enol ethers 9

The preparation of **9e** is representative. (*i*) To a solution of diisopropylamine (6.73 mL, 48 mmol) in THF (40 mL) was added *n*-BuLi (1.61 M in hexane, 28.6 mL) at 0°C. After being stirred for 30 min, the mixture was cooled to –78°C. To the solution was added methyl isobutyrate (4.58 mL, 40 mmol), and the reaction mixture was stirred for 1 h. To the resulting mixture, phenylpropargyl *p*-toluenesulfonate (11.4 g, 40 mmol) in THF (20 mL) – 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (5.0 mL) was added. The mixture was stirred for 15 min, and then allowed to warm to 0°C. After being stirred for additional 10 min at this temperature, the mixture was quenched with ice-cold saturated, aq NH_4Cl solution and three times extracted with ether. The combined organic phase was washed with H_2O, brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, eluent: hexane – ethyl acetate, 15:1) to give methyl 2,2-dimethyl-5-phenyl-4-pentylate (6.96 g, 80% yield). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.41–7.35 (m, 2H), 7.30–7.24 (m, 3H), 3.71 (s, 3H), 2.66 (s, 2H), 1.34 (s, 6H). (*ii*) To a solution of methyl 2,2-dimethyl-5-phenyl-4-pentylate (1.92 g, 8.9 mmol) in THF (18 mL) were added sequentially $TMSCH_2Li$ (1.0 M in pentane, 19.5 mL) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (2.15 mL, 18 mmol) at –78°C. After being stirred for 30 min, the mixture was quenched with ice-cold saturated, aq NH_4Cl solution and three times extracted with ether. The combined organic phase was washed with H_2O, brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, eluent: hexane – ethyl acetate, 30:1) to give 1-(trimethylsilyl)-3,3-dimethyl-6-phenyl-5-hexyn-2-one (1.85 g, 76% yield). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.40–7.34 (m, 2H), 7.30–7.24 (m, 3H), 2.59 (s,

[8] Piers and his co-workers found that $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl functions, such as aldehydes, ketones, and esters, proceeded very smoothly to give the corresponding reduced compounds in high yields.

Scheme 1.



2H), 2.27 (s, 2H), 1.27 (s, 6H), 0.13 (s, 9H). (*iii*) To a mixture of 1-(trimethylsilyl)-3,3-dimethyl-6-phenyl-5-hexyn-2-one (1.85 g, 6.8 mmol) and NaI (1.22 g, 8.1 mmol) in CH_3CN (14 mL) were added sequentially Et_3N (4.54 mL, 33 mmol) and TMSCl (2.58 mL, 20 mmol) at room temperature. After being stirred for 30 min, the mixture was quenched with saturated, aq $NaHCO_3$ solution and three times extracted with pentane. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, eluent: hexane – ethyl acetate – pyridine, 20:1:0.1) to give **9a** (1.81 g, 98% yield). (*iv*) To a solution of **9a** (1.33 g, 4.9 mmol) in THF (9.8 mL) was added *n*-BuLi (1.54 M in hexane, 3.32 mL) at 0°C, and the mixture was stirred for 20 min. To the resulting mixture was added MeI (455 μL, 7.3 mmol), and the mixture was allowed to warm to room temperature. After being stirred for 25 min, the reaction mixture was quenched with ice-cold saturated, aq NH_4Cl solution and three times extracted with ether. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, eluent: hexane – ethyl acetate, 30:1) to give 4,4-dimethyl-7-phenyl-6-heptyn-3-one (327 mg, 31% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40–7.33 (m, 2H), 7.30–7.24 (m, 3H), 2.61 (s, 2H), 2.59 (q, *J* = 7.2 Hz, 2H), 1.28 (s, 6H), 1.06 (t, *J* = 7.2 Hz, 3H). (*v*) To a solution of 4,4-dimethyl-7-phenyl-6-heptyn-3-one (281 mg, 1.3 mmol) in CH_2Cl_2 (2.8 mL) were added sequentially Et_3N (274 μL, 2.0 mmol) and TMSOTf (304 μL, 1.6 mmol) at 0°C. The mixture was stirred for 30 min, and then allowed to warm to room temperature. After being stirred for an additional 1 h at this temperature, the mixture was quenched with saturated, aq $NaHCO_3$ solution and three times extracted with pentane. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, eluent: hexane – ethyl acetate – pyridine, 20:1:0.1) to give **9e** (302 mg, 81% yield).

*2-(Trimethylsilyloxy)-3,3-dimethyl-6-phenyl-1-hexen-5-yne (**9a**):* colorless oil. HRMS calcd. for $C_{17}H_{24}OSi$ 272.1597; found 272.1600. IR (neat) (cm^{-1}): 3125, 1654, 1624, 1599, 1254, 1021, 847, 755, 691. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41–7.36 (m, 2H), 7.30–7.24 (m, 3H), 4.18 (d, *J* = 1.7 Hz, 1H), 4.04 (d, *J* = 1.7 Hz, 1H), 2.48 (s, 2H), 1.19 (s, 6H), 0.23 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 164.4, 131.5, 128.1, 127.4, 124.2, 88.4, 87.4, 82.2, 40.0, 30.8, 25.4, 0.2. Anal. calcd. for $C_{17}H_{24}OSi$: C 74.94, H 8.88; found: C 74.72, H 8.68.

*2-(*tert*-Butyldimethylsilyloxy)-3,3-dimethyl-6-phenyl-1-hexen-5-yne (**9b**):* colorless oil. HRMS calcd. for $C_{20}H_{30}OSi$: 314.2066; found: 314.2067. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41–7.37 (m, 2H), 7.28–7.26 (m, 2H), 4.15 (d, *J* = 1.8 Hz, 1H), 4.03 (d, *J* = 1.8 Hz, 1H), 2.50 (s, 2H), 1.20 (s, 6H), 0.96 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 164.4, 134.5, 128.1, 127.4, 124.2, 88.4, 86.2, 82.2, 40.4, 30.9, 25.8, 25.5, 18.2, –4.8. Anal. calcd. for $C_{20}H_{30}OSi$: C 76.37, H 9.61; found: C 76.22, H 9.56.

*2-(Trimethylsilyloxy)-3,3-dimethyl-1-hepten-5-yne (**9c**):* colorless oil. HRMS calcd. for $C_{12}H_{22}OSi$: 210.1440; found: 210.1422. IR (neat) (cm^{-1}): 3125, 1655, 1622, 1254, 1021, 848. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.12 (d, *J* = 1.6 Hz, 1H), 3.99 (d, *J* = 1.6 Hz, 1H), 2.20 (q, *J* = 2.6 Hz, 2H), 1.78

(t, J = 2.6 Hz, 3H), 1.10 (s, 6H), 0.21 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 164.9, 87.2, 39.7, 30.2, 25.2, 3.5, 0.1. Anal. calcd. for $C_{12}H_{22}OSi$: C 68.51, H 10.54; found: C 68.50, H 10.21.

*2-(Trimethylsilyloxy)-3,3-dimethyl-1-decen-5-yne (**9d**):* colorless oil. HRMS calcd. for $C_{15}H_{28}OSi$: 252.1909; found: 252.1911. IR (neat) (cm^{-1}): 3125, 1658, 1622, 1254, 1021, 846. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.11 (d, J = 1.7 Hz, 1H), 3.99 (d, J = 1.7 Hz, 1H), 2.22 (t, J = 2.3 Hz, 2H), 2.15 (tt, J = 6.8, 2.3 Hz, 2H), 1.51–1.34 (m, 4H), 1.10 (s, 6H), 0.90 (t, J = 7.2 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 164.8, 87.2, 81.9, 77.9, 39.8, 31.3, 30.2, 25.2, 21.9, 18.4, 13.6, 0.1. Anal. calcd. for $C_{15}H_{28}OSi$: C 71.36, H 11.18; found: C 71.22, H 10.92.

*3-(Trimethylsilyloxy)-4,4-dimethyl-7-phenyl-2-hepten-6-yne (**9e**):* colorless oil. HRMS calcd. for $C_{18}H_{26}OSi$: 286.1752; found: 286.1758. IR (neat) (cm^{-1}): 1664, 1598, 1253, 1074, 842, 755, 691. ^{1}H NMR (300 MHz, $CDCl_3$, a major isomer) δ: 7.41–7.36 (m, 2H), 7.30–7.24 (m, 3H), 4.70 (q, J = 6.8 Hz, 1H), 2.47 (s, 2H), 1.55 (d, J = 6.8 Hz, 3H), 1.18 (s, 6H), 0.26 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 156.8, 131.5, 128.1, 127.4, 124.2, 99.3, 88.6, 82.4, 39.9, 31.1, 25.8, 11.8, 1.2.

*2-(*tert*-Butyldimethylsilyloxy)-3,3-dimethyl-1-hepten-5-yne (**9f**):* colorless oil. HRMS calcd. for $C_{15}H_{28}OSi$: 252.1910; found: 252.1908. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.08 (d, J = 1.7 Hz, 1H), 3.97 (d, J = 1.7 Hz, 1H), 2.22 (q, J = 2.6 Hz, 2H), 1.78 (t, J = 2.6 Hz, 3H), 1.11 (s, 6H), 0.93 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 164.9, 86.5, 77.2, 76.9, 40.0, 30.3, 25.8, 25.3, 18.2, 3.5, –4.8. Anal. calcd. for $C_{15}H_{28}OSi$: C 71.36, H 11.18; found: C 71.34, H 10.92.

*2-(*tert*-Butyldimethylsilyloxy)-3,3-dimethyl-1-decen-5-yne (**9g**):* colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.08 (d, J = 1.7 Hz, 1H), 3.97 (d, J = 1.7 Hz, 1H), 2.24 (t, J = 2.4 Hz, 2H), 2.15 (tt, J = 6.8 and 2.4 Hz, 2H), 1.51–1.34 (m, 4H), 1.11 (s, 6H), 0.94 (s, 9H), 0.90 (t, J = 7.2 Hz, 3H), 0.38 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 164.8, 86.5, 81.8, 77.9, 40.1, 31.3, 30.3, 25.8, 25.3, 21.9, 18.4, 18.2, 13.6, –4.8. Anal. calcd. for $C_{18}H_{34}OSi$: C 73.40, H 11.63; found: C 73.32, H 11.57.

*2-(Trimethylsilyloxy)-3-methyl-3-(2-propynyl)-1-cyclohexene (**13a**):* colorless oil. HRMS calcd. for $C_{13}H_{22}OSi$: 222.1439; found: 222.1446. IR (neat) (cm^{-1}): 2962, 2933, 2118, 1713, 1659, 1458, 1252, 1178. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.72 (t, J = 4.0 Hz, 1H), 2.35 (dd, J = 16.2, 2.7 Hz, 1H), 2.27 (dd, J = 16.2, 2.7 Hz, 1H), 2.03–1.95 (m, 2H), 1.95 (t, J = 2.7 Hz, 1H), 1.87–1.74 (m, 1H), 1.60–1.48 (m, 3H), 1.10 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 154.7, 102.6, 82.6, 69.8, 37.9, 35.0, 28.8, 24.5, 24.2, 19.2, 0.4.

*2-(Trimethylsilyloxy)-3-(2-butynyl)-3-methyl-1-cyclohexene (**13b**):* colorless oil. HRMS calcd. for $C_{14}H_{24}OSi$: 236.1596; found: 236.1600. IR (neat) (cm^{-1}): 2962, 2932, 2126, 1656, 1252, 1178, 842. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.70 (t, J = 4.0 Hz, 1H), 2.28 (dq, J = 16.5, 2.5 Hz, 1H), 2.19 (dq, J = 16.5, 2.5 Hz, 1H), 1.98 (dt, J = 6.0, 4.0 Hz, 2H), 1.85–1.76 (m, 1H), 1.78 (t, J = 2.5 Hz, 3H), 1.58–1.46 (m, 2H), 1.50–1.42 (m, 1H), 1.06 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 155.3, 102.4, 77.04, 76.95, 38.1, 35.1, 29.1, 24.6, 24.2, 19.3, 0.4. Anal. calcd. for $C_{14}H_{24}OSi$: C 71.12, H 10.23; found: C 70.93, H 10.06.

α*-(Trimethylsilyloxy)-*o*-(1-pentynyl)styrene (**20**):* colorless oil. HRMS calcd. for $C_{16}H_{22}OSi$: 258.1439; found: 258.1465. IR (neat) (cm^{-1}): 2963, 2933, 2235, 1621, 1480, 1307, 1253, 1014, 848. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54–7.45 (m, 2H), 7.28–7.23 (m, 2H), 5.13 (d, J = 1.2 Hz, 1H), 4.07 (d, J = 1.2 Hz, 1H), 2.46 (t, J = 7.0 Hz, 2H), 1.68 (tq, J = 7.0, 7.0 Hz, 2H), 1.10 (t, J = 7.0 Hz, 3H), 0.27 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 154.8, 139.9, 133.5, 127.7, 127.4, 127.2, 121.4, 95.9, 94.3, 80.4, 22.1, 21.7, 13.6, 0.0.

$EtAlCl_2$-mediated carbocyclization of 9 (general procedure)

$EtAlCl_2$ (1.2 equiv) was added to a stirred solution of **9** (0.5 mmol) in toluene (5.0 mL) at 0°C. After being stirred for 3 h, the reaction mixture was quenched with Et_2NH, diluted with saturated, aq $NaHCO_3$ solution, and extracted with ether three times. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The products (**10** and **11**) were purified by column chromatography (silica gel, eluent: hexane – ethyl acetate).

*6,6-Dimethyl-3-phenyl-3-cyclohexenone (**10a**):* colorless oil. HRMS calcd. for $C_{14}H_{16}O$: 200.1201; found: 200.1211. IR (neat) (cm^{-1}): 1714, 1672, 1599, 751, 694. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41–7.25 (m, 5H), 6.22 (tt, J = 4.2, 1.8 Hz, 1H), 3.31 (dt, J = 1.8, 1.8 Hz, 2H), 2.46 (dt, J = 4.2, 1.8 Hz, 2H), 1.20 (s, 6H). ^{13}C NMR (75.5 MHz, CDCl3) δ: 213.4, 139.4, 134.2, 128.5, 127.5, 124.9, 122.1, 43.3, 40.8, 40.1, 24.3. Anal. calcd. for $C_{14}H_{16}O$: C 83.96, H 8.05; found: C 83.91, H 8.01.

*6,6-Dimethyl-3-phenyl-2-cyclohexenone (**11a**):* colorless oil. HRMS calcd. for $C_{14}H_{16}O$: 200.1201; found: 200.1201. IR (CCl_4) (cm^{-1}): 1667, 1611, 1573, 725, 693. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.52 (m, 2H), 7.44–7.38 (m, 3H), 6.35 (t, J = 1.5 Hz, 1H), 2.79 (td, J = 6.1, 1.5 Hz, 2H), 1.98 (t, J = 6.1 Hz, 2H), 1.18 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 204.7, 157.3, 138.5, 129.8, 128.7, 126.0, 123.8, 40.4, 36.4, 25.2, 24.1.

*3,6,6-Trimethyl-3-cyclohexenone (**10b**):* colorless oil. HRMS calcd. for $C_9H_{14}O$: 138.1045; found: 138.1067. IR (neat) (cm^{-1}): 3041, 1715. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.44 (ttq, J = 3.9, 1.8, 1.4 Hz, 1H), 2.80 (dtq, J = 1.8, 1.8, 0.9 Hz, 2H), 2.21 (dtq, J = 3.9, 1.8, 1.8 Hz, 2H), 1.70 (tdt, J = 1.8, 1.4, 0.9 Hz, 3H), 1.11 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 214.1, 131.5, 119.7, 43.3, 42.7, 40.6, 24.3, 22.4. Anal. calcd. for $C_9H_{14}O$: C 78.21, H 10.21; found: C 77.92, H 10.67.

*3,6,6-Trimethyl-2-cyclohexenone (**11b**):* colorless oil. HRMS calcd. for $C_9H_{14}O$: 138.1045; found: 138.1045. IR (neat) (cm^{-1}): 3031, 1670, 1638. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.77 (tq, J = 1.5, 1.3 Hz, 1H), 2.29 (tdq, J = 6.1, 1.5, 0.7 Hz, 2H), 1.92 (dt, J = 1.3, 0.7 Hz, 3H), 1.80 (t, J = 6.1 Hz, 2H), 1.08 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 204.5, 160.3, 125.1, 40.1, 36.3, 28.4, 24.2, 24.0.

*3-Butyl-6,6-dimethyl-3-cyclohexenone (**10c**):* colorless oil. HRMS calcd. for $C_{12}H_{20}O$: 180.1514; found: 180.1510. IR (neat) (cm^{-1}): 3043, 1717, 1676. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.45 (ttt, *J* = 3.9, 1.8, 1.3 Hz, 1H), 2.81 (dtt, *J* = 1.8, 1.7, 0.7 Hz, 2H), 2.23 (dtt, *J* = 3.9, 1.7, 1.6 Hz, 2H), 2.00 (ttdt, *J* = 6.8, 1.6, 1.3, 0.7 Hz, 2H), 1.44–1.24 (m, 4H), 1.12 (s, 6H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 214.5, 135.6, 119.1, 43.5, 41.1, 40.6, 36.1, 29.5, 24.4, 22.3, 13.9. Anal. calcd. for $C_{12}H_{20}O$: C 79.94, H 11.18; found: C 79.77, H 10.96.

*3-Butyl-6,6-dimethyl-2-cyclohexenone (**11c**):* colorless oil. HRMS calcd. for $C_{12}H_{20}O$: 180.1514; found: 180.1515. IR (neat) (cm^{-1}): 3028, 1668, 1632. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.76 (tt, *J* = 1.3, 0.9 Hz, 1H), 2.29 (tdt, *J* = 6.1, 1.3, 0.7 Hz, 2H), 2.18 (tdt, *J* = 7.4, 0.9, 0.7 Hz, 2H), 1.80 (t, *J* = 6.1 Hz, 2H), 1.53–1.43 (m, 2H), 1.38–1.25 (m, 2H), 1.09 (s, 6H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 204.8, 164.3, 124.1, 40.4, 37.4, 36.4, 29.2, 27.0, 24.2, 22.3, 13.8.

*2,6,6-Trimethyl-3-phenyl-3-cyclohexenone (**10d**):* colorless oil. HRMS calcd. for $C_{15}H_{18}O$: 214.1357; found: 214.1322. IR (neat) (cm^{-1}): 1710, 1599, 756, 698. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.38–7.24 (m, 5H), 5.98 (ddd, *J* = 5.4, 3.3, 1.5 Hz, 1H), 3.48 (qddd, *J* = 7.3, 1.8, 1.5, 0.9 Hz, 1H), 2.43 (ddd, *J* = 17.6, 3.3, 1.8 Hz, 1H), 2.37 (ddd, *J* = 17.6, 5.4, 0.9 Hz, 1H), 1.24 (s, 3H), 1.19 (s, 3H), 1.15 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 216.0, 141.2, 140.3, 128.4, 127.2, 126.1, 122.7, 43.0, 39.8, 25.2, 24.6, 15.4.

*2,6,6-Trimethyl-3-phenyl-2-cyclohexenone (**11d**):* colorless oil. HRMS calcd. for $C_{15}H_{18}O$: 214.1357; found: 214.1361. IR (neat) (cm^{-1}): 1665, 1625, 1599, 751, 701. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.42–7.28 (m, 3H), 7.21–7.17 (m, 2H), 2.62 (tq, *J* = 6.0, 2.0 Hz, 2H), 1.93 (t, *J* = 6.0 Hz, 2H), 1.70 (t, *J* = 2.0 Hz, 3H), 1.18 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 204.7, 154.4, 141.4, 129.9, 128.3, 127.7, 127.1, 40.3, 36.1, 29.6, 24.6, 13.4.

*5-Methyl-9-oxobicyclo[3,3,1]non-2-ene (**14a**):* colorless oil. HRMS calcd. for $C_{10}H_{14}O$: 150.1044; found: 150.1044. IR (neat) (cm^{-1}): 2929, 1718, 1445. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.86 (dt, *J* = 9.5, 3.5 Hz, 1H), 5.55 (dddd, *J* = 9.5, 5.5, 2.0, 1.5 Hz, 1H), 2.91 (dt, *J* = 5.5, 3.0 Hz, 1H), 2.54 (ddd, *J* = 18.5, 3.5, 1.5 Hz, 1H), 2.37 (d, *J* = 18.5 Hz, 1H), 2.15–1.98 (m, 1H), 1.88–1.80 (m, 3H), 1.63–1.47 (m, 2H), 1.03 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 217.1, 129.4, 127.1, 48.2, 46.3, 44.8, 44.5, 33.2, 23.7, 18.1.

*3-Deuterio-5-methyl-9-oxobicyclo[3,3,1]non-2-ene (**14b**):* colorless oil. HRMS calcd. for $C_{10}H_{13}DO$: 151.1106; found: 151.1096. IR (neat) (cm^{-1}): 2929, 1720, 1445. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.58–5.53 (m, 1H), 2.91 (dt, *J* = 5.5, 3.0 Hz, 1H), 2.54 (dd, *J* = 18.5, 1.5 Hz, 1H), 2.37 (d, *J* = 18.5 Hz, 1H), 2.15–1.98 (m, 1H), 1.88–1.80 (m, 3H), 1.63–1.47 (m, 2H), 1.03 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 217.1, 129.4 (*C*—D), 129.1 (*C*—D), 128.8 (*C*—D), 126.9, 48.1, 46.3, 44.8, 44.4, 33.2, 23.7, 18.0.

*2,5-Dimethyl-9-oxobicyclo[3,3,1]non-2-ene (**14c**):* colorless oil. HRMS calcd. for $C_{11}H_{16}O$: 164.1200; found: 164.1205. IR (neat) (cm^{-1}): 2966, 2927, 1716, 1446, 1379. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.54 (tq, *J* = 4.0, 1.5 Hz, 1H), 2.70 (t, *J* = 3.0 Hz, 1H), 2.43 (ddq, *J* = 18.0, 4.0, 2.0 Hz, 1H), 2.27 (d, *J* = 18.0 Hz, 1H), 2.00–1.87 (m, 2H), 1.84–1.75 (m, 2H), 1.66 (dt, *J* = 2.0, 1.5 Hz, 3H), 1.62–1.46 (m, 2H), 1.01 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 217.2, 133.8, 122.8, 52.8, 45.1, 44.7, 43.3, 31.5, 23.5, 21.3, 18.5. Anal. calcd. for $C_{11}H_{16}O$: C 80.44, H 9.82; found: C 80.42, H 9.93.

*2,5-Dimethyl-3-iodo-9-oxobicyclo[3,3,1]non-2-ene (**14d**):* colorless oil. HRMS calcd. for $C_{11}H_{15}IO$: 290.0167; found: 290.0177. IR (neat) (cm^{-1}): 2932, 2864, 1720, 1446. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.95 (t, *J* = 3.0 Hz, 1H), 2.95 (dd, *J* = 18.0, 2.0 Hz, 1H), 2.76 (d, *J* = 18.0 Hz, 1H), 2.05–1.70 (m, 7H), 1.63–1.53 (m, 2H), 1.00 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 213.5, 138.3, 95.3, 57.0, 54.8, 49.0, 44.4, 31.9, 27.5, 22.6, 18.8. Anal. calcd. for $C_{11}H_{15}IO$: C 45.54, H, 5.21, I 43.74; found: C 45.63, H 5.24, I 43.84.

*3-Propyl-1-naphthol (**21**):* colorless oil. HRMS calcd. for $C_{13}H_{14}O$: 186.1044; found: 186.1045. IR (neat) (cm^{-1}): 3393, 2958, 2929, 1638, 1599, 1578. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.13–8.08 (m, 1H), 7.75–7.71 (m, 1H), 7.48–7.38 (m, 2H), 7.22 (s, 1H), 6.67 (s, 1H), 5.39 (s, 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.70 (tq, *J* = 7.5, 7.5 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 151.2, 140.6, 134.8, 127.2, 126.4, 124.4, 122.8, 121.3, 119.2, 110.1, 38.2, 24.2, 13.8.

$B(C_6F_5)_3$-mediated carbocyclization of 9 (general procedure)

To a solution of $B(C_6F_5)_3$ (0.1 mmol, 20 mol%) in toluene (1.0 mL) were added triethylsilane (0.16 mL, 1.0 mmol) and substrate **9** (0.5 mmol) at 0°C, successively. After being stirred for 15 min, the reaction mixture was diluted with pentane, quenched with Et_2NH, filtered through Al_2O_3, and concentrated. The product was purified by column chromatography (silica gel, eluent: hexane).

*[5-(*tert*-Butyldimethylsilyloxy)-4,4-dimethyl-2-(triethylsilyl)-cyclohex-1-enyl]-benzene (**22a**):* colorless oil. HRMS calcd. for $C_{26}H_{46}OSi$: 430.3087; found: 430.3081. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.27–7.23 (m, 3H), 7.10–7.07 (m, 2H), 3.57 (dd, *J* = 6.8 and 4.9 Hz, 1H), 2.45 (ddt, *J* = 18.3, 5.1, and 2.0 Hz, 1H), 2.18 (ddt, *J* = 18.3, 5.1, and 2.0 Hz, 1H), 2.12 (dt, *J* = 17.4 and 1.7 Hz, 1H), 1.89 (dt, *J* = 17.4 and 1.7 Hz, 1H), 0.96 (s, 3H), 0.92 (s, 3H), 0.89 (s, 9H), 0.79 (t, *J* = 6.4 Hz, 9H), 0.21 (q, *J* = 6.4 Hz, 6H), 0.04 (d, *J* = 5.3 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 147.0, 145.8, 130.0, 128.3, 127.7, 126.5, 74.1, 42.3, 35.9, 33.9, 26.7, 25.8, 21.6, 18.0, 15.3, 7.5, 3.4, –4.1, –4.9. Anal. calcd. for $C_{26}H_{46}OSi$: C 72.49, H 10.76; found: C 72.36, H 10.77.

*5-(*tert*-Butyldimethylsilyloxy)-1,4,4-trimethyl-2-(triethylsilyl)-cyclohexene (**22b**):* colorless oil. HRMS calcd. for $C_{21}H_{44}OSi_2$: 368.2931; found: 368.2938. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.46 (dd, *J* = 7.7 and 5.6 Hz, 1H), 2.17–1.76 (m, 4H), 1.70 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.89 (s, 9H), 0.85 (s, 3H), 0.77 (s, 3H), 0.64 (q, *J* = 7.9 Hz, 6H), 0.03 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 141.2, 125.2, 74.3, 43.2, 40.8, 34.0, 27.2, 25.8, 23.1, 20.5, 18.3, 7.6, 4.2, –4.1, –4.9. Anal. calcd. for $C_{21}H_{44}OSi_2$: C 68.40, H 12.03; found: C 68.27, H 12.17.

*1-Butyl-5-(*tert*-butyldimethylsilyloxy)-4,4-dimethyl-2-(triethylsilyl)-cyclohexene (**22c**):* colorless oil. HRMS calcd. for $C_{24}H_{50}OSi_2$: 410.3401; found: 410.3400. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.46 (dd, *J* = 7.5 and 5.5 Hz, 1H), 2.12–1.73 (m, 6H), 1.39–1.26 (m, 4H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.88 (s, 3H), 0.77 (s, 3H), 0.62 (q, *J* = 8.0 Hz, 6H), 0.03 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 145.9, 125.1, 74.4, 43.1, 37.7, 37.4, 34.1, 31.6, 31.3, 27.1, 25.9, 23.1, 22.7, 20.7, 18.0, 14.2, 7.6, 4.3, −4.0, − 4.9.

Conclusion

We demonstrated for the first time an intramolecular addition of silyl enol ethers to both terminal and internal unactivated alkynes by using Lewis acid. While the $EtAlCl_2$-mediated reaction gave cyclohexenone derivatives, the silyloxy-substituted cyclic vinylsilanes were produced in the $B(C_6F_5)_3$-catalyzed reaction in the presence of Et_3SiH. The presented *endo*-selective method could be used for the construction of mono- and bicyclic compounds possessing a cyclohexenone framework.

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