Novel Carbon−Carbon Bond-Forming Reactions Using Carbocations Produced from Substituted Propargyl Silyl Ethers by the Action of TMSOTf

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Highly useful carbon−carbon bond forming reactions using stable allenyl, propargyl, or allyl−propargyl hybrid cations have been developed. These carbocations could be generated from silyl 1-(π-donor)-substituted propargyl ethers by the action of trimethylsilyl trifluoromethanesulfonate in dichloromethane at −78 °C to room temperature and could be attacked nucleophilically by electron rich arenes, allylsilanes, or enol silyl ethers, giving rise to allenes, alkynes, and their derivatives. A novel method for regio- and stereoselective synthesis of conjugated enynes utilizing allyl−propargyl hybrid cations has also been established.

Introduction

Allenes, alkynes, and their derivatives have established a reputation as increasingly popular intermediates in modern organic synthesis[1] because of their unique structural characteristics and reactivities including ionic, radical, or concerted processes. The most prevailing way of carbon−carbon bond formation utilizing these compounds involves their organometallic derivatives.[2,3] On the other hand, carbon−carbon bond formation by directly employing allenyl and propargyl cationic species has not developed into a fascinating synthetic method. Indeed, structural studies on propargyl or allenyl cations generated from propargyl halides or alcohols under solvolytic conditions have been extensively conducted,[4] but only the limited methods for generating these cations under nonsolvolytic and nonnucleophilic conditions have been developed.[5] It should be mentioned, however, that the following propargylic cations or its equivalents are highly pertinent to this issue: one is carbocations α to cobalt-complexed alkynyl unit (**I**)[6] and the other is (benzene)-$Cr(CO)_3$-stabilized propargyl cation (**II**).[7] They have provided a number of synthetic applications so far. We have, therefore, developed a novel method for carbon−carbon formation using allenyl or propargyl cationic species which is more simple and direct than those so far developed including **I**[6] or **II**.[7] Also certain emphasis is placed on the development of a method for introducing enyne functionality relying on such chemistry because the enyne compounds are attracting much attention of organic chemists with regard to their versatility and high potential as a basic framework in transition metal catalyzed cyclization processes, which is one of the current topics in organic synthesis.[8]

Results and Discussion

Inter- and Intramolecular Friedel−Crafts Reactions. The expected carbocations could be generated on treating substituted propargyl silyl ethers with trimeth-

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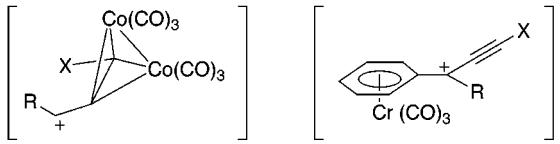
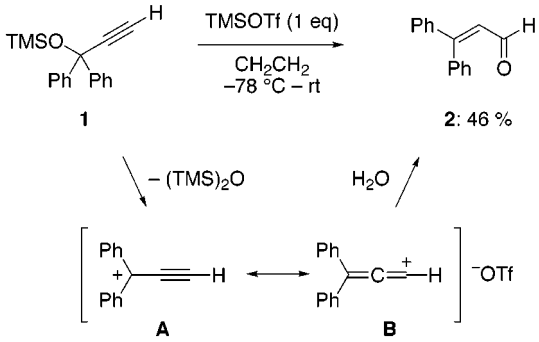
Chart 1

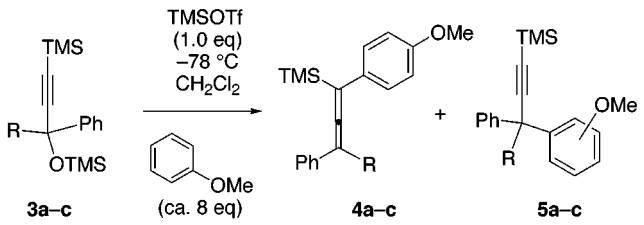


I II

Scheme 1. Propargyl or Allenyl Cation Intermediate in Nonaqueous Mayer−Schuster Rearrangement



Scheme 2. Intermolecular Friedel−Crafts Reactions



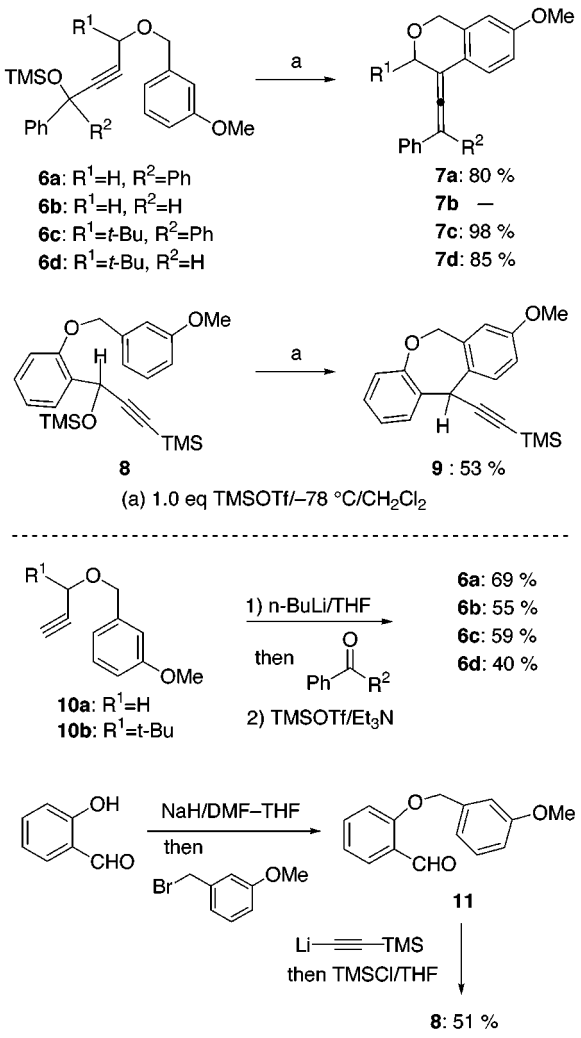
substrate	yield/% 4	5
3a: R = Ph	100	–
3b: R = Me	98	–
3c: R = H	–	88[a]

[a] a mixture of regio isomers (para : others = 7.7 : 1)

ylsilyl trifluoromethanesulfonate (TMSOTf) in dichloromethane.[9] Scheme 1 shows that propargyl (**A**) or allenyl (**B**) cationic species may be intermediates in the Mayer−Schuster rearrangement[10] before being trapped by water in the medium.

The type **A** or **B** cationic species generated under the newly developed, nonsolvolytic conditions was expected to be trapped by carbon nucleophiles. This idea was rewarded when we examined the TMSOTf-promoted Friedel−Crafts reaction[11] between propargylic silyl ethers (**3a**−**c**) and anisole as a nucleophilic partner (Scheme 2). Treatment of **3a** and **3b**, prepared from the corresponding propargylic tertiary alcohols, with TMSOTf in anisole led

Scheme 3. Intramolecular Friedel−Crafts Reactions



exclusively to allenyl arenes **4a** and **4b**, respectively, with perfect regioselectivity on the aromatic ring in quantitative yield. On the other hand, **3c** derived from secondary alcohol furnished contrasting 3-(trimethylsilyl)propargyl arene **5c** exclusively in high yield. A steric factor seems to play a role in selecting two pathways leading to **4** and **5**.

A regiochemical problem of this kind could be controlled in the case of an intramolecular version of Friedel−Crafts alkylation (Scheme 3). Thus, propargyl silyl ethers (**6a**−**d**), easily prepared from *m*-methoxybenzyl propargyl ethers **10**, led to the formation of allenyl isochromane derivatives (**7a**−**d**) in high yield for every case with one exception which resulted in the substrate decomposition (**7b**). No diastereoselectivity was observed for **7c**,**d** for which an sp-hybridized nature of the cationic carbon of allenyl cation intermediate should be responsible.[12] Propargyl silyl ether **8**, prepared from benzyl phenyl ether **11**, led to the formation of seven-membered dibenzooxapane derivative **9**. These reactions are highly useful for the construction of carbon frameworks containing an aromatic ring subunit.

In marked contrast to these results, silyl propargyl ethers **1**, **12**, and **13** were not amenable to the electro-

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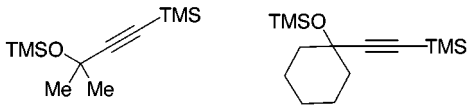
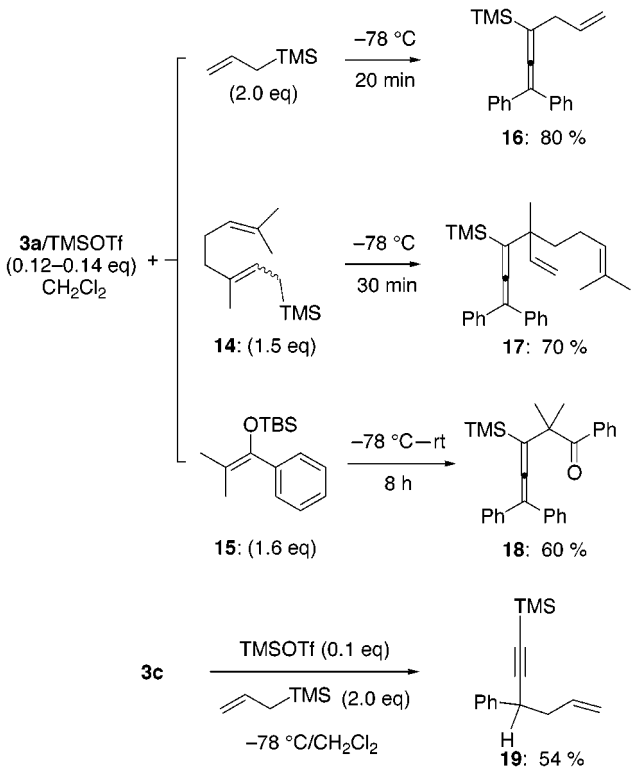
Chart 2



Scheme 4. TMSOTf-Catalyzed Allenylations and Propargylation

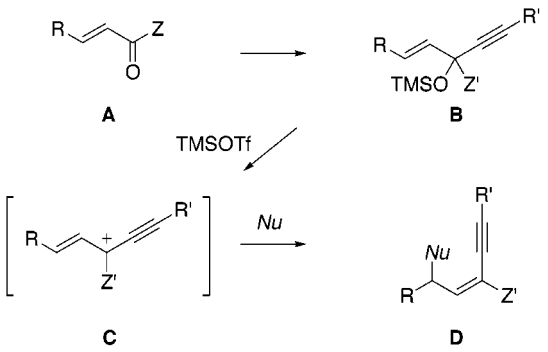


philic C−C bond formation under the conditions shown above, which resulted in the decomposition of the substrates. Thus, in order for the electrophilic C−C bond forming reaction to be successful, both σ-donor on the terminal sp-carbon and at least one π-donor on the propargylic sp^3-carbon in the substrates are necessary: **1** has the geminal phenyl groups on the propargylic sp^3-carbon but no substituent on the terminal sp-carbon, and both **12** and **13** carry the TMS group on the terminal sp-carbon but no π-donor on the propargylic sp^3-carbon.

Intermolecular Trapping with Allylsilanes and Enol Silyl Ether. When such structural demand mentioned above is satisfied, cationic species generated under nonsolvolytic conditions by the action of TMSOTf will be so stable that they could be trapped with external nucleophiles other than aromatic π-nucleophiles. The synthetic potential of the cationic intermediates along this line can be positively evaluated by the following catalytic processes.

The TMSOTf-catalyzed coupling reactions of **3a** or **3c** with other nucleophiles involving allyltrimethylsilane, geranyltrimethylsilane (**14**), or enol silyl ether (**15**) are summarized in Scheme 4. In these cases, only the catalytic amount of TMSOTf (10−14 mol %) is required because the catalytic cycle can be established by the regeneration of a silyl triflate with a silyl cation liberated from the nucleophiles. The reaction of **3a** was nicely effected under the given reaction conditions (150−200 mol % Nu) to give the corresponding allenylsilane derivatives (**16**−**18**) in acceptable yields which, otherwise, seem difficult to access. In these catalytic processes no acetylenic product was detected at all, while **3c** afforded silyl acetylene (**19**) exclusively. These regiochemical features are very much similar to the case of intermolecular Friedel−Crafts processes (see Scheme 2).

Scheme 5. Strategy of Conjugated Enyne Synthesis from Enones or Enoates



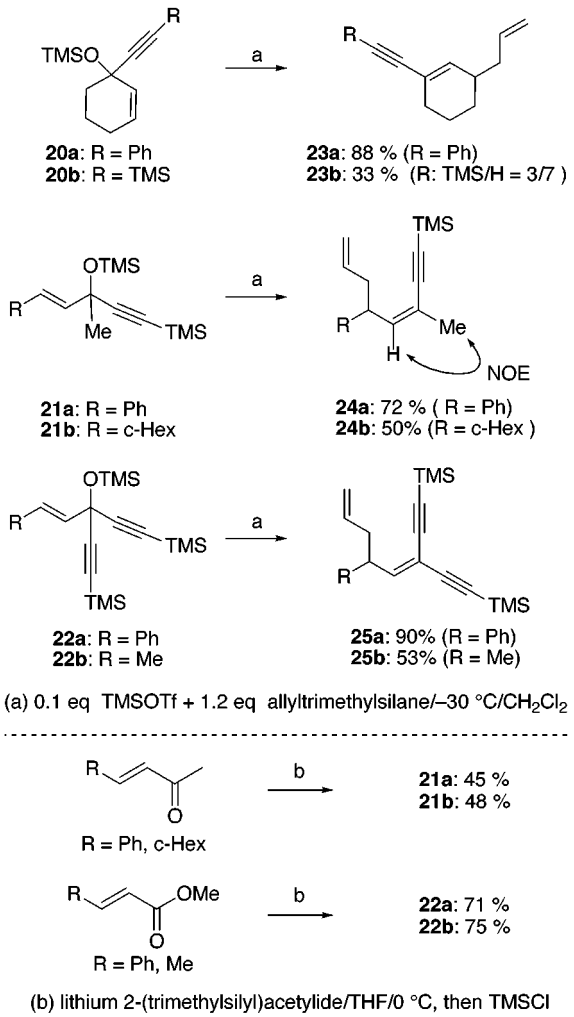
Synthesis of Conjugated Enynes. As already mentioned above, geometrically homogeneous conjugated enynes or dienynes are highly useful compounds for the short-cut construction of complex carbocyclic backbones.[8] Hence, the development of methods for synthesizing such functionality should be a fascinating goal. The concept and realization of this task are summarized in Scheme 5. Trimethylsilyl 1-(alken-1-yl)propargyl ethers (**B**) available from α,β-unsaturated carbonyl compounds (**A**) have proven promising to generate cationic species [pent-1-en-4-yn-3-yl cation systems (**C**)] capable of reacting with carbon nucleophiles regioselectively on treatment with catalytic TMSOTf in dichloromethane to afford such an important class of enynes or dienynes (**D**).[13]

The substrate trimethylsilyl ethers involve nonconjugated trimethylsilyl 1-ethynyl-2-cyclohexen-1-yl ethers (**20**), trimethylsilyl [1-(alken-1-yl)-1-methyl]propargyl ethers (**21**), and trimethylsilyl [1-(alken-1-yl)-1-ethynyl]-propargyl ethers (**22**) to which we can uneventfully gain access through 1,2-addition of acetylide anions to enones or enoates which is outlined in Scheme 6. The reaction of these trimethylsilyl ethers **21** and **22** with allyltrimethylsilane (1.2 equiv) are summarized again in Scheme 6. Catalytic amount of TMSOTf (0.1 equiv) effected the desired reaction (CH_2Cl_2/−30 °C) to give conjugated (*E*)-dienynes containing cyclohexene unit (**23**), acyclic (*Z*)-dienynes (**24**), and diendiynes (**25**), respectively, with excellent regio- and stereoselectivity (only *Z* for **24**). The geometry of **24** was confirmed to be *Z* on the basis of NOE experiments.

Such a stereochemical consequence can be explained by invoking sterically less demanding nature of an ethynyl group than a methyl group. The plausible mechanism for the formation of *Z*-**24** is shown in Scheme 7. Two routes can explain the exclusive formation of such

(13) For the synthesis of conjugated enynes, see: (a) Trost, B. M.; Sorum, T. S.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698−708. (b) Trost, B. M.; Frontier, J. *J. Am. Chem. Soc.* **2000**, *122*, 11727−11728.

Scheme 6. TMSOTf-Catalyzed Conjugated Enyne Synthesis Using Trimethylsilyl 1-(Alken-1-yl)propargyl Ethers and Allyltrimethylsilane



a *Z*-enyne product.[14] The reaction probably commences with the formation of an oxonium ion-like intermediate $\mathbf{I_1}$, which can dissociate to form cationic intermediate $\mathbf{I_2}$ rather than $\mathbf{I_3}$ for steric reason to be trapped by allyltrimethylsilane, giving rise to *Z*-**24** (S_N1-like mechanism). On the other hand S_N2'-like pathway can also lead to *Z*-**24** via transition state TS_1 rather than TS_2 again for steric reason to lead to $\mathbf{I_4}$, direct precursor for *Z*-**24**.

Nucleophiles other than allyltrimethylsilane such as enol silyl ether **15** or anisole can also be amenable to this class of reaction with **20a** and **21a** to give the corresponding conjugated enynes **26** and **27** or **28** in very high yields and in a highly stereoselective manner again under the given reaction conditions (Scheme 8).

It should be pointed out that the S_N2'-like nucleophilic attack uniformly took place at C(1) of the present cation system **C** (Scheme 7) with profoundly high regioselectivity to furnish the conjugated enynes **23**−**28**. The regiochemical feature of the reaction of this class was, though fragmentary, observed 45 years ago by Braude[15,16] for the solvolytic reactions of [1-(alken-1-yl)-1-ethynyl]propargyl alcohols in 60% aqueous dioxane containing hydrogen chloride. Although water could be an ultimate nucleophile in this instance, such a preliminary finding should have led to an approach of synthesizing carbon chains that contain a conjugated enyne functionality. However, no effort was made to realize the carbon−carbon bond formation using the cation system **C** until Nicholas[17] disclosed that such was the case when the alkyne moiety of **B** was converted to an alkyne−$Co_2(CO)_6$ complex: this resulted not only in extraordinary stabilization of a cation α to this cobalt complex but also in successful reaction with various carbon nucleophiles to selectively afford conjugated enynes with not *Z* but *E* geometry because of the increasing steric bulkiness of this complex group. The present approach to the conjugated (*Z*)-enynes, therefore, may be irreplaceable.

It should be noted that the conjugated *Z*-enynes are potent intermediates which possess suitable functionality locations for various intramolecular reactions. For example, Pauson−Khand reaction[18] of the dienyne **24a** proceeded to afford substituted bicyclo[4,3,0]nonadienones **29** and **30** as a separable mixture of diastereomers (Scheme 9).[19]

Conclusion

We have developed the highly useful C−C bond-forming protocol through the reactions of allenyl, propargyl, or propargyl−allyl hybrid cations with soft carbon nucleophiles which features not only operational simplicity but also versatility in terms of reaction types. The allenes and enyne compounds available through this process can serve as interesting intermediates for various synthetic purposes. The newly developed conditions for the regio- and stereoselective synthesis of the conjugated enynes in this work may enable organic chemists to design multifarious intramolecular cyclization reactions directed to complex molecules. Further synthetic explorations using the cations adjacent to the π framework of multiple bonds including the development of a new enyne cyclization process for natural products synthesis are under active investigations.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR at 75 MHz using $CDCl_3$ as a solvent unless otherwise specified. The chemical shifts (δ) are given in parts per million relative to internal C*H*Cl_3 (7.26 ppm for ^{1}H) or *C*DCl_3 (77 ppm for ^{13}C). The ^{1}H NMR spectral data were indicated in the form: δ-value of signal (peak multiplicity, integrated number of protons, and coupling constant (if any)). Splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. All the chemical shift assignments were consistent with COSY spectra, and confor-

(14) At present stage of our research on this project we are thinking that the S_N2'-like route seems more plausible because the product-determining transition states come earlier and more demanding than the S_N1-like route in which the product determining step comes after the formation of $\mathbf{I_2}$ or $\mathbf{I_3}$, and their reactions with allyltrimethylsilane seem less demanding. The final decision on this point, however, must await future studies.

(15) Braude, E. A.; Coles, J. A.; Evans, E. A.; Timmons, C. J. *Nature* **1956**, *177*, 1167−1169.

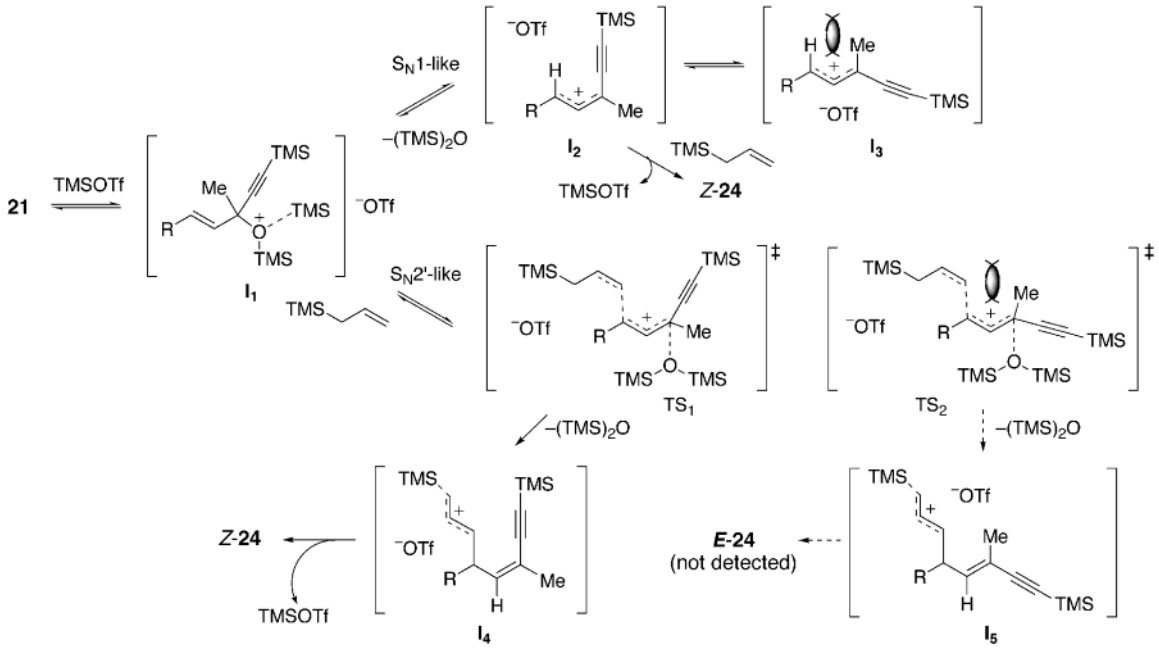
(16) For related synthesis of enyne compounds under solvolytic conditions, see: Descoins, C.; Samain, D. *Tetrahedron Lett.* **1976**, 745−748.

(17) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1982**, *23*, 2555−2558.

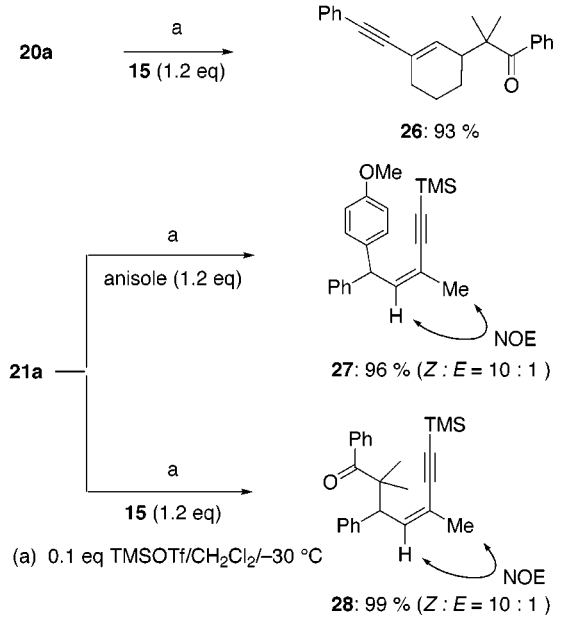
(18) For reviews, see: (a) Schore, N. E. *Org. React.* **1991**, *40*, 1−90. (b) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I. Eds.; Pergamon: Oxford, 1991; Vol. 5, Chapter 9.1.

(19) The relative configurations of these cycloadducts were determined by careful analyses of ^{1}H NMR spectra (*J*-value, NOE).

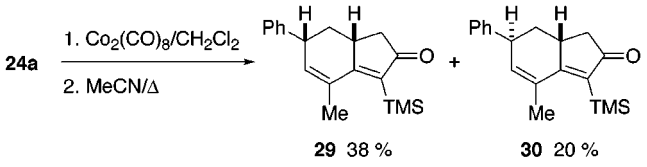
Scheme 7. Mechanism of Conjugated Enyne Formations for the TMSOTf-Catalyzed Reaction between Trimethylsilyl 1-(Alken-1-yl)propargyl Ethers and Allyltrimethylsilane



Scheme 8. TMSOTf-Catalyzed Conjugated Enyne Synthesis Using Trimethylsilyl 1-(Alken-1-yl)propargyl Ethers and Various Carbon Nucleophiles



Scheme 9. Pauson−Khand Reaction of Representative Conjugated Enyne



mational analyses and determination of configurations were carried out on the basis of a combination of *J* values, NOE data, and NOESY correlations. FT-IR spectra were recorded using NaCl plates. Analytical thin-layer chromatography was performed on Merck precoated silica gel 60 F-254 (0.25 mm thickness). Column chromatography was performed on a Merck silica gel 60 7734 using an appropriate ratio of ethyl acetate−hexane mixed solvent and abbreviated as CC. Elemental analyses were carried out by Dr. Miyoko Izawa of this laboratory. All reactions, unless otherwise noted, were conducted under a nitrogen or an argon atmosphere. Liquid reagents are transferred via a dry hypodermic syringe and added through a rubber septum wired onto a reaction flask from which a steady stream of inert gas was flowing. Organic extracts were concentrated by evaporation with a rotary evaporator evacuated at around 60 mmHg. Unless otherwise noted, materials were obtained from commercial suppliers and reagent grade materials were used without further purification. Triethylamine (Et_3N), dichloromethane (CH_2Cl_2), and dimethylformamide (DMF) were freshly distilled from CaH_2 prior to use. Tetrahydrofuran purchased from Kanto Chemical Co., Inc., is dehydrated and stabilizer-free grade and was used as received.

***O*-(Trimethylsilyl)-1,1-diphenyl-2-propyn-1-ol (1).** To a solution of 1,1-diphenyl-2-propyn-1-ol (1.411 g, 6.8 mmol) and triethylamine (2.8 mL) in CH_2Cl_2 (15 mL) was added TMSOTf (2.8 mL, 13.8 mmol, 2.0 equiv) at 0 °C. The reaction was stirred at 0 °C for 25 min followed by the addition of water. The mixture was extracted with several portions of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (70:1 hexane/EtOAc) provided **1** (1.890 g, 99%); IR (film) 2950, 2100 cm^{-1}; ^1H NMR δ 0.10 (S, 9H), 2.90 (s, 1H), 7.19−7.32 (m, 6H), 7.54−7.58 (m, 4H); ^{13}C NMR δ 1.54, 75.4, 76.7, 86.5, 125.9, 127.3, 128.0, 146.1.

3,3-Diphenyl-2-propen-1-al (2). To a solution of **1** (0.283 g, 1.0 mmol) in THF (5.0 mL) was added TMSOTf (0.18 mL, 1.0 mmol) at −78 °C. The mixture was stirred at −78 °C to room temperature for 3 h followed by the addition of saturated aqueous solution of sodium chloride at 0 °C. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (30:1 hexane/EtOAc) provided **2** (0.131 g, 46%). IR (film) 3056, 1667 cm^{-1}; ^1H NMR δ 6.61 (d, 1H, J = 8.3 Hz), 7.20−7.55 (m, 10H), 9.35 (d, 1H, J = 8.3 Hz); ^{13}C NMR δ 127.2, 128.3, 128.5, 128.6, 129.4, 130.4, 130.7, 136.6, 139.7, 162.2, 193.5.

***O*-(Trimethylsilyl)-3-trimethylsilyl-1,1-diphenyl-2-propyn-1-ol (3a).** To a solution of 1,1-diphenyl-2-propyn-1-ol (10.66 g, 58 mmol) in THF (50 mL) was added butyllithium (1.54 M in hexane, 114 mL, 176 mmol, 3.0 equiv) during 17

min at 0 °C. To the solution was added chlorotrimethylsilane (30 mL, 236 mmol, 4.0 equiv). The reaction was stirred at room temperature for 10 min followed by the addition of saturated aqueous solution of sodium chloride at 0 °C. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (100: 1 hexane/EtOAc) provided **3a** (16.68 g, 81%); bp 110−119 °C (0.02 mmHg); IR (film) 2950, 2110 cm^{-1}; ^1H NMR δ 0.17 (s, 9H), 0.29 (s, 9H), 7.21−7.36 (m, 5H), 7.59−7.64 (m, 5H); ^{13}C NMR δ −0.3, 1.6, 75.7, 92.9, 108.0, 125.9, 127.0, 127.9, 146.51.

1-Trimethylsilyl-1-(4-methoxyphenyl)-3,3-diphenylallene (4a). To a solution of **3a** (0.080 g, 0.23 mmol) and anisole (0.2 mL, 1.84 mmol, 8 equiv) in CH_2Cl_2 (3 mL) was added TMSOTf (0.04 mL, 0.22 mmol) at −78 °C. The solution was stirred at −78 °C for 3 h followed by the addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (100:1 hexane/EtOAc) provided **4a** (0.084 g, 100%); IR (film) 2950, 1920 cm^{-1}; ^1H NMR δ 0.36 (s, 9H), 3.83 (s, 3H), 6.90−7.00 (m, 2H), 7.21−7.50 (m, 12H); ^{13}C NMR δ −0.04, 55.2, 102.8, 106.6, 114.1, 126.7, 128.0, 128.4, 128.9, 136.9, 158.5, 209.1; exact mass, *m/z* 370.1741 (calcd for $C_{25}H_{26}OSi$ *m/z* 370.1753). Anal. Calcd for $C_{25}H_{26}OSi$: C, 81.03; H, 7.07. Found: C, 81.14; H, 10.87.

4-*O*-(3-Methoxybenzyl)-1-*O*-(trimethylsilyl)-1,1-diphenyl-2-butyne-1,4-diol (6a). To a solution of **10a** (0.89 g, 5.1 mmol) in THF (8 mL) was added butyllithium (1.53 M in hexane, 4.3 mL, 6.6 mmol, 1.3 equiv) at 0 °C. After stirring at 0 °C for 15 min, benzophenone (0.98 g, 5.4 mmol, 1.1 equiv) was added to the mixture. The resulting solution was stirred at 0 °C to room temperature for 1.5 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (7:1 hexane/EtOAc) provided 4-*O*-(3-methoxybenzyl)-1,1-diphenyl-2-butyne-1,4-diol (1.37 g, 76%). To a solution of this diol (0.51 g, 1.4 mmol) and triethylamine (2 mL) in CH_2Cl_2 (4 mL) was added TMSOTf (0.46 mL, 2.5 mmol). The resulting solution was stirred at 0 °C to room temperature for 4 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (50:1 hexane/EtOAc) provided **6a** (0.56 g, 91%); IR (film) 2960, 2110 cm^{-1}; ^1H NMR δ 0.12 (s, 9H), 3.79 (s, 3H), 4.35 (s, 2H), 4.61 (s, 2H), 6.82−6.93 (m, 2H), 7.19−7.33 (m, 8H), 7.55−7.58 (m, 4H); ^{13}C NMR δ 1.6, 55.1, 57.5, 71.5, 75.6, 84.3, 89.4, 113.1, 113.7, 120.3, 126.0, 127.2, 129.4, 138.9, 146.4, 159.7. Anal. Calcd for $C_{27}H_{30}O_3Si$: C, 75.31; H, 7.02. Found: C, 75.17; H, 7.23.

5-*O*-(3-Methoxybenzyl)-2-*O*-(trimethylsilyl)-6,6-dimethyl-2-phenyl-3-heptyne-2,5-diol (6c). To a solution of **10b** (0.39 g, 1.7 mmol) in THF (6 mL) was added butyllithium (1.53 M in hexane, 1.3 mL, 2.0 mmol, 1.2 equiv) at 0 °C. After stirring at 0 °C for 15 min, acetophenone (0.21 mL, 1.8 mmol, 1.05 equiv) was added to the mixture at 0 °C. The resulting solution was stirred at 0 °C to room temperature for 2.5 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (10:1 hexane/EtOAc) provided 5-*O*-(3-methoxybenzyl)-6,6-dimethyl-2-phenyl-3-heptyne-2,5-diol (0.38 g, 64%). To a solution of this diol (0.279 g, 0.79 mmol) and triethylamine (2 mL) in CH_2Cl_2 (4 mL) was added TMSOTf (0.21 mL, 1.16 mmol, 1.5 equiv) at 0 °C. The solution was stirred at 0 °C for 1 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (70:1 hexane/EtOAc) provided **6c** (0.309 g, 92%) as a 1:1 mixture of diastereomers; IR (film) 2970, 2100 cm^{-1};^1H NMR (as a 1:1 diastereomeric pair) δ 0.15 (s, 9H), (1.04, 1.05)(s, 9/2H for each), (1.75, 1.76) (s, 3/2H for each), 3.79 (s, 1H), 3.80 (s, 3H), (4.46 and 4.50, 4.81 and 4.85) (ABq, 1H for each, J = 4.9, 3.6 Hz), 6.80−7.00 (m, 3H), 7.20−7.38 (m, 4H), 7.58−7.66 (m, 2H); ^{13}C NMR (as a 1:1 diastereomeric pair) δ 1.73, 26.0, (35.7, 35.8), (36.4, 36.5), 55.1, (70.7, 70.8), 71.4, 77.7, (83.8, 84.0), (90.2, 90.3), 113.0, 113.1, 120.0, 125.0, 127.1, 127.9, 129.2, 139.9, (147.0, 147.1), 159.8.

4-*O*-(3-Methoxybenzyl)-1-*O*-(trimethylsilyl)-5,5-dimethyl-1-phenyl-2-hexyne-1,4-diol (6d). To a solution of **10b** (0.304 g, 1.3 mmol) in THF (5 mL) was added butyllithium (1.53 M in hexane, 1.2 mL, 1.8 mmol, 1.4 equiv) at 0 °C. After stirring at 0 °C for 20 min, benzaldehyde (0.15 mL, 1.5 mmol, 1.2 equiv) was added to the mixture. The resulting solution was stirred at 0 °C to room temperature for 2 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (15:1 hexane/EtOAc) provided 4-*O*-(3-methoxybenzyl)-5,5-dimethyl-1-phenyl-2-hexyne-1,4-diol (0.267 g, 60%). To a solution of this diol (0.204 g, 0.60 mmol) and triethylamine (3 mL) in CH_2Cl_2 (5 mL) was added TMSOTf (0.16 mL, 0.88 mmol, 1.5 equiv). The solution was stirred at 0 °C to room temperature for 4 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (100:1 hexane/EtOAc) provided **6d** (0.166 g, 67%) as a 1:1 mixture of diastereomers; IR (film) 2970, 2100 cm^{-1}; ^1H NMR (as a 1:1 diastereomeric pair) δ (0.237, 0.244)-(s, 9/2H for each), (1.01, 1.03) (s, 9/2H for each), (3.77, 3.78) (s, 1/2H for each), (3.79, 3.80) (s, 3/2H for each), (4.44 and 4.48, 4.79 and 4.83) (ABq, 1H for each, J = 4.7, 6.0 Hz), 5.59 (s, 1H), 6.80−6.94 (m, 3H), 7.22−7.40 (m, 4H), 7.50−7.56 (m, 2H); ^{13}C NMR (as a 1:1 diastereomeric pair) δ 0.28, 26.0, (35.6, 35.7), 55.1, 64.6, 70.7, (77.5, 77.6), (83.8, 83,9), (87.1, 87.2), (113.0, 113.1), 120.0, 126.3, 126.4, (127.7, 127.8), 128.3, 129.2, 140.0, (141.5, 141.6), 159.6.

7-Methoxy-4-(2,2-diphenylvinylidene)isochroman (7a). To a solution of **6a** (0.087 g, 0.2 mmol) in CH_2Cl_2 (5 mL) was added TMSOTf (0.035 mL, 0.2 mmol). The solution was stirred at −78 °C for 3.5 h followed by the addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (30:1 hexane/EtOAc) provided **7a** (0.054 g, 80%); IR (film) 2970, 1910 cm^{-1};^1H NMR δ 3.81 (s, 3H), 4.72 (s, 2H), 4.83 (s, 2H), 6.62 (d, 1H,J = 2.8 Hz), 6.82 (dd, 1H, J = 2.8, 8.5 Hz), 7.28−7.46 (m, 10H), 7.54 (d, 1H, J = 8.5 Hz); ^{13}C NMR δ 55.3, 67.7, 68.9, 101.0, 109.3, 114.0, 115.4, 120.4, 127.5, 127.8, 128.42, 128.45, 135.2, 136.5, 159.0, 201.6; exact mass, *m/z* 342.1627 (calcd for $C_{24}H_{22}O_2$ *m/z* 342.1619). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.31; H, 6.22.

3-[2-(3-Methoxybenzyloxy)phenyl]-3-*O*-(trimethylsilyl)-1-trimethylsilyl-1-butyn-3-ol (8). To a solution of salicylaldehyde (0.85 mL, 8.0 mmol) in THF (5 mL) and DMF (5 mL) was added sodium hydride (60% in oil, 360 mg, 8.9 mmol) at 0 °C. After stirring at 0 °C for 30 min, 3-methoxybenzyl bromide (1.2 mL, 8.6 mmol) was introduced to the mixture at 0 °C. The resulting mixture was stirred at room temperature for 24 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (15:1 hexane/EtOAc) provided *O*-(3-methoxybenzyl)salicylaldehyde **11** (1.92 g, 99%). To a solution of trimethylsilylacetylene (0.25 mL, 1.77 mmol) in THF (5 mL) was added butyllithium (1.53 M in hexane, 1.1 mL, 1.7 mmol) at 0 °C. After stirring at 0 °C for 20 min, a solution of **11** (362 mg, 1.50 mmol) in THF (3 mL) was added to the mixture. The resulting solution was stirred at 0 °C to room temperature for 2 h followed by the addition of chlorotrimethylsilane (0.28 mL, 2.24 mmol). The reaction was stirred at room temperature for 2 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (70:1 hexane/EtOAc) provided **8** (0.322 g, 52%). IR (film) 2950, 2100 cm^{-1}; ^1H NMR δ 0.152 (s, 9H), 0.153 (s, 9H), 3.81 (s, 3H), 5.10 (s, 2H), 5.90 (s, 1H), 6.80−7.75 (m, 7H); ^{13}C NMR δ −0.21, −0.27, 55.2, 59.5, 69.9, 89.3,

106.3, 111.8, 112.6, 113.1, 119.3, 120.9, 127.9, 129.0, 129.5, 129.8, 138.7, 155.1, 159.7.

3-*O*-(3-Methoxybenzyl)-1-propyn-3-ol (10a). To a solution of 3-methoxybenzyl alcohol (3.51 g, 25.4 mmol) in THF (15 mL) and DMF (15 mL) was added sodium hydride (60% in oil, 1.24 g, 31.0 mmol, 1.2 equiv) at 0 °C. The solution was stirred at 0 °C for 25 min followed by the addition of propargyl bromide (2.5 mL, 28.1 mmol, 1.1 equiv). The solution was stirred at 0 °C to room temperature for 2 h followed by the addition of water, and extracted with several portions of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (30:1 hexane/EtOAc) provided **10a** (4.16 g, 93%); IR (film) 2970, 2100 cm^{-1}; ^1H NMR δ 2.47 (t, 1H, J = 2.5 Hz), 3.82 (s, 3H), 4.18 (d, 2H, J = 2.5 Hz), 4.59 (s, 2H), 6.81−6.96 (m, 3H), 7.24−7.30 (m, 1H); ^{13}C NMR δ 54.9, 56.9, 71.2, 74.6, 79.5, 113.1, 113.4, 120.0, 129.2, 138.7, 159.5.

3-(3-Methoxybenzyloxy)-4,4-dimethylpentyne (10b). To a solution of 3-hydroxy-4,4-dimethylpentyne (0.452 g, 4.0 mmol) in THF (7 mL) and DMF (2.5 mL) was added sodium hydride (60% in oil, 0.208 g, 5.2 mmol, 1.3 equiv) at 0 °C. After stirring at 0 °C for 20 min, 3-methoxybenzyl bromide (0.60 mL, 4.3 mmol, 1.1 equiv) was added to the mixture. The reaction was stirred at 0 °C to room temperature for 1 h followed by the addition of water. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (50:1 hexane/EtOAc) provided **10b** (0.928 g, 99%); IR (film) 2960, 1610 cm^{-1}; ^1H NMR δ 1.02 (s, 9H), 2.44 (d, 1H, J = 2.0 Hz), 3.68 (d, 1H, J = 2.0 Hz), 3.81 (s, 3H), 4.47 and 4.83 (ABq, 2H, J = 12.1 Hz), 6.80−6.86 (m, 1H), 6.91−6.96 (m, 2H), 7.22−7.30 (m, 1H); ^{13}C NMR δ 25.8, 35.3, 55.1, 70.7, 74.5, 76.6, 77.3, 81.6, 113.1, 120.0, 129.2, 139.8, 159.6.

***O*-(*tert*-Butyldimethylsilyl)-2-methyl-1-phenylpropen-1-ol (15).** To a solution of isobutyrophenone (0.745 g, 5.0 mmol) in triethylamine (3 mL) and CH_2Cl_2 (4 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.7 mL, 7.4 mmol, 1.5 equiv). The solution was stirred at 0 °C to room temperature for 2.5 h followed by the addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (100: 1 hexane/EtOAc) provided **15** (1.19 g, 90%); IR (film) 2970, 1610 cm^{-1}; ^1H NMR δ −0.20 (s, 6H), 0.89 (s, 9H), 1.65 (s, 3H), 1.80 (s, 3H), 7.20−7.32 (m, 5H); ^{13}C NMR δ −4.3, 18.2 (2C), 19.9, 25.8, 112.5, 127.1, 127.6, 129.3, 139.2, 143.6.

1-Allyl-1-trimethylsilyl-3,3-diphenylallene (16). To a solution of **3a** (0.080 g, 0.23 mmol) and allyltrimethylsilane (0.075 mL, 0.47 mmol, 2.0 equiv) in CH_2Cl_2 (3 mL) was added TMSOTf (0.005 mL, 0.028 mmol, 0.12 equiv) at −78 °C. The solution was stirred at −78 °C for 20 min followed by the addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (300:1 hexane/EtOAc) provided **16** (0.055 g, 80%); IR (film) 2960, 1910 cm^{-1}; ^1H NMR δ 0.21 (s, 9H), 2.97 (dt, 2H, J = 1.4, 6.6 Hz), 5.00−5.20 (m, 2H), 5.90−6.05 (m, 1H), 7.20−7.35 (m, 10H); ^{13}C NMR δ 1.1, 34.4, 98.8, 105.3, 115.6, 126.4, 128.0, 128.3, 136.9, 137.6, 206.2; exact mass, m/z 304.1635 (calcd for $C_{21}H_{24}Si$ m/z 304.1647). Anal. Calcd for $C_{21}H_{24}Si$: C, 82.83; H, 7.94. Found: C, 82.75; H, 8.07.

3-Trimethylsilyl-4,8-dimethyl-1,1-diphenyl-4-vinyl-1,2,7-nonatriene (17). To a solution of **3a** (0.072 g, 0.20 mmol) and geranyltrimethylsilane (0.066 g, 0.31 mmol, 1.5 equiv) in CH_2Cl_2 (3 mL) was added TMSOTf (0.005 mL, 0.028 mmol, 0.14 equiv) at −78 °C. The solution was stirred at −78 °C for 30 min followed by the addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (hexane) provided **17** (0.057 g, 70%); IR (film) 2960, 1910 cm^{-1}; ^1H NMR δ 0.17 (s, 9H), 1.28 (s, 3H), 1.48 (s, 3H), 1.60−1.70 (m, 2H), 1.64 (s, 3H), 1.82−1.94 (m, 2H), 4.98−5.02 (m, 2H), 5.04 (dd, 1H, J = 14.3, 17.6 Hz), 5.05 (dd, 1H, J = 10.4, 14.3 Hz), 5.96 (dd, 1H, J = 10.4, 17.6 Hz), 7.20−7.35 (m, 10 H); ^{13}C NMR δ 1.4, 17.6, 23.5, 24.5, 25.7, 41.0, 45.4, 105.9, 108.4, 111.9, 126.27, 126.3, 127.7, 127.9, 128.3, 131.2, 137.5, 206.1; exact mass, m/z 400.2571 (calcd for $C_{28}H_{36}Si$ m/z 400.2586). Anal. Calcd for $C_{28}H_{36}Si$: C, 83.93; H, 9.06. Found: C, 84.15; H, 8.88.

4-Benzoyl-4-methyl-3-trimethylsilyl-1,3-diphenyl-1,2-pentadiene (18). To a solution of **3a** (0.143 g, 0.41 mmol) and **15** (0.169 g, 0.64 mmol, 1.6 equiv) in dichloromethane (4 mL) was added TMSOTf (0.01 mL, 0.055 mmol, 0.13 equiv) at −78 °C. The solution was stirred at −78 °C to room temperature for 8 h followed by the addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with several portions of ethyl acetate, and the combined organic layers were dried over Na_2SO_4 concentrated. Purification by CC (70:1 hexane/EtOAc) provided **18** (0.100 g, 60%); IR (film) 1910, 1670 cm^{-1};^1H NMR δ 0.06 (s, 9H), 1.59 (s, 6H), 7.10−7.16 (m, 2H), 7.26−7.42 (m, 11H), 7.86−7.94 (m, 2H); ^{13}C NMR δ 0.6, 28.16, 28.18, 51.2, 108.0, 108.3, 126.9, 127.8, 127.9, 128.0, 128.4, 128.5, 129.77, 129.79, 132.0 (2C), 136.2, 136.5, 203.5, 205.3; exact mass, m/z 410.2073 (calcd for $C_{28}H_{30}OSi$ m/z 410.2066). Anal. Calcd for $C_{28}H_{30}OSi$: C, 81.90; H, 7.36. Found: C, 81.81; H, 7.21.

1-(*O*-Trimethylsilyl)-1-phenylethynyl-2-cyclohexen-1-ol (20a). To a solution of phenylacetylene (0.69 mL, 6.24 mmol) in THF (12 mL) was added butyllithium in hexane (1.56 M, 3.7 mL, 5.7 mmol) at 0 °C. The mixture was stirred at 0 °C for 5 min. To the mixture was added 2-cyclohexenone (0.50 mL, 5.2 mmol), and the stirring was continued at 0 °C for 20 min. Chlorotrimethylsilane (1.3 mL, 10 mmol) was added to the mixture, and the stirring was continued at 0 °C for 30 min. The reaction was quenched by the addition of water, and the resulting mixture was extracted with several portions of ethyl acetate−hexane mixed solvent. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (50:1 hexane/EtOAc) provided **20a** (0.535 g, 38%) as a colorless oil. IR (film) 2953, 2112 cm^{-1}; ^1H NMR δ 0.25 (s, 9H), 1.75−1.87 (m, 2H), 1.92−2.15 (m, 4H), 5.79−5.82 (m, 2H), 7.28−7.35 (m, 3H), 7.38−7.44 (m, 2H); ^{13}C NMR δ 2.1, 19.3, 24.7, 39.2, 67.1, 84.6, 93.3, 123.0, 128.1, 128.2, 131.4 (2C), 131.9.

3-(*O*-Trimethylsilyl)-1-phenyl-3-methyl-5-trimethylsilyl-1-penten-4-yn-3-ol (21a). To a solution of trimethylsilylacetylene (1.0 mL, 7.2 mmol) in THF (15 mL) was added butyllithium in hexane (1.50 M, 4.4 mL, 6.5 mmol) at 0 °C. Benzalacetone (1.27 g, 8.68 mmol) was added to the mixture, and the stirring was continued at 0 °C for 1 h. Chlorotrimethylsilane was introduced to the mixture at 0 °C, and the stirring was continued at 0 °C to room temperature for 1 h. The reaction was quenched by the addition of water, and the resulting mixture was extracted with several portions of ethyl acetate−hexane mixed solvent. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude residue was purified by CC (50:1 hexane/EtOAc) to give **21a** (1.03 g, 45%) as a colorless oil. IR (film) 2950, 2110 cm^{-1}; ^1H NMR δ 0.258 (s, 9H), 0.264 (s, 9H), 1.65 (s, 3H), 6.26 (d, 1H, J = 15.7 Hz), 6.82 (d, 1H, J = 15.7 Hz), 7.24−7.47 (m, 5H); ^{13}C NMR δ −0.2, 2.0, 32.7, 69.6, 90.3, 108.0, 126.7, 127.6, 128.0, 128.5, 134.5, 136.6.

3-Methyl-5-phenyl-1-trimethylsilyl-3(*Z*),7-octadien-1-yne (24a). To a solution of **21a** (0.220 g, 0.695 mmol) and allyltrimethylsilane (0.13 mL, 0.83 mmol) in CH_2Cl_2 (5 mL) was added TMSOTf (0.013 mL, 0.070 mmol) at −30 °C. The solution was stirred at −30 °C for 20 min. The reaction was quenched by the addition of saturated aqueous solution of $NaHCO_3$, and the resulting mixture was extracted with several portions of ethyl acetate−hexane mixed solvent. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude residue was purified by CC (hexane) to give **24a** (0.135 g, 72%) as a colorless oil. IR (film) 2950, 2120 cm^{-1}; ^1H NMR δ 0.22 (s, 9H), 1.82 (d, 3H, J = 1.5 Hz), 2.38−2.54 (m, 2H), 3.95 (dt, 1H, J = 7.5, 9.6 Hz), 4.92−5.07 (m, 2H), 5.64−5.82 (m, 2H), 7.15−7.35 (m, 5H); ^{13}C NMR δ 0.1, 22.8, 40.0, 46.6, 98.0, 104.7, 116.0, 118.0, 126.2, 127.4, 128.4, 136.4, 142.0, 144.0; exact mass, m/z 268.16475 (calcd for $C_{18}H_{24}Si$ m/z 268.16472). Anal. Calcd for $C_{18}H_{24}Si$: C, 80.53; H, 9.01. Found: C, 80.81; H, 8.87.

3-Methyl-5-(4-methoxyphenyl)-5-phenyl-1-trimethylsilyl-3(*Z*)-penten-1-yne (27). To a solution of **20a** (0.068 g, 0.22 mmol) in CH_2Cl_2 (2 mL) was added anisole (0.035 g, 0.32 mmol) at −30 °C. TMSOTf (0.004 mL, 0.02 mmol) was added to the mixture, and the stirring was continued at −30 °C for 10 min. The reaction was quenched by the addition of saturated aqueous solution of $NaHCO_3$, and the resulting mixture was extracted with several portions of ethyl acetate−hexane mixed solvent. The organic layers were dried over Na_2SO_4 and concentrated. Purification by CC (30:1 hexane/EtOAc) provided **27** (0.069 g, 96%, *Z*:*E* = 10:1) as a yellow oil; data for *Z*-isomer: IR (film) 3050, 2950, 2110 cm^{-1}; ^1H NMR δ 0.24 (s, 9H), 1.93 (d, 3H, J = 1.4 Hz), 3.81 (s, 3H), 5.25 (d, 1H, J = 10.2), 6.17 (dq, 1H, J = 1.4, 10.2 Hz), 6.83−7.38 (m, 9H); ^{13}C NMR δ 0.06, 22.9, 50.9, 55.2, 98.2, 104.4, 113.8, 118.5, 126.2, 128.2, 128.4, 129.2, 135.9, 140.5, 144.0, 158.0. Anal. Calcd for $C_{25}H_{30}OSi$: C, 78.99; H, 7.83. Found: C, 78.82; H, 7.71.

4-Phenyl-2-methyl-9-(trimethylsilyl)bicyclo[4.3.0]nona-2,9-dien-8-one (29 and **30).** To a solution of **24a** (0.124 g, 0.462 mmol) in CH_2Cl_2 (4 mL) was added cobalt octacarbonyl (0.189 g, 0.554 mmol), and the mixture was stirred at room temperature for 1.5 h. The mixture was filtered through a Celite pad and concentrated to give an acetylene−cobalt complex (0.256 g) in quantitative yield as a dark brown oil. A solution of the acetylene−cobalt complex (0.133 g) in acetonitrile (4 mL) was stirred at 62 to 70 °C for 6 h. The mixture was filtered through silica gel and florisil pads and concentrated. Purification by CC (20:1 hexane/EtOAc) provided **29** (0.027 g, 38%) and **30** (0.014 g, 20%) as a colorless oil. Data for **29**: IR (film) 2954, 1689, 1540 cm^{-1}; ^1H NMR (500 MHz) δ 0.32 (s, 9H), 1.58 (dt, 1H, J = 11.0, 13.1 Hz), 1.98 (dd, 1H, J = 4.3, 18.0 Hz), 2.11 (q, 3H, J = 1.2 Hz), 2.39−2.45 (m, 1H), 2.59 (dd, 1H, J = 6.9, 18.2 Hz), 2.94−3.01 (m, 1H), 3.69−3.76 (m, 1H), 5.97−6.00 (m, 1H), 7.15−7.35 (m, 5H); ^{13}C NMR δ 1.3, 22.9, 40.3, 41.9, 42.2, 44.7, 126.7, 127.4, 128.7, 132.9, 136.4, 139.1, 144.8, 181.9, 212.6; Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.83; H, 8.11; Data for **30**: IR (film) 2955, 1690, 1540 cm^{-1}; ^1H NMR δ 0.31 (s, 9H), 1.87−2.10 (m, 6H), 2.44 (dd, 1H, J = 7.0, 18.0 Hz), 2.80−2.92 (m, 1H), 3.70−3.79 (b, 1H), 6.01−6.06 (m, 1H), 7.20−7.40 (m, 5H); ^{13}C NMR δ 1.4, 23.0, 35.3, 37.6, 41.3, 42.0, 126.6, 128.1, 128.5, 133.5, 136.9 (2C), 143.5, 181.3, 212.6. Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.81; H, 8.33.

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Supporting Information Available: The copies of ^1H NMR and ^{13}C NMR spectra of **4**, **5**, **7**, **9**, **16**−**19**, **23**−**30** and spectral data for compounds **3b**,**c**, **4b**, **5c**, **7c**,**d**, **9**, **19**, **20b**, **21b**, **22**, **23**, **24b**, **25**, **26**, and **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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