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Inter- and Intramolecular Carbonylative Alkyne–Alkyne Coupling Reaction Mediated by Cobalt Carbonyl Complex

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Abstract—Inter- and intramolecular carbonylative coupling reactions proceed between alkynes possessing diphenylallylsilyl group mediated by dicobalt carbonyl complex under argon atmosphere. This coupling reaction directly provides various mono- and bicyclic cyclopentadienones in high yields. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

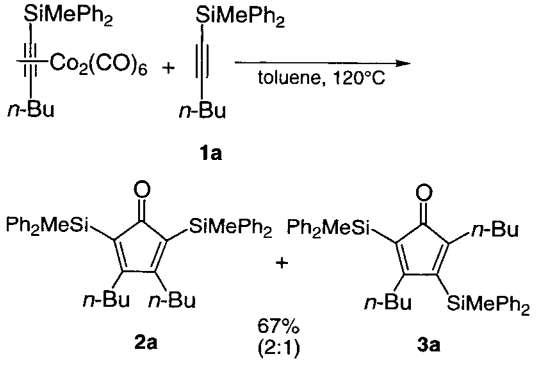
Transition metal mediated carbonylative coupling reaction is often used for the construction of ring system possessing a carbonyl group. For example, cobalt carbonyl complex-mediated carbonylative alkyne–alkene coupling (the Pauson–Khand reaction) is comprehensively examined[1] and is utilized for the synthesis of natural products. On the other hand, carbonylative alkyne–alkyne coupling reaction[2] has rarely been investigated although it gives cyclopentadienones, potentially important intermediates. All reported syntheses of cyclopentadienones by transition metal-mediated alkyne–alkyne coupling are stepwise processes: Yamazaki et al. reported a pioneering work of alkyne–alkyne coupling reaction mediated by $CpCo(PPh_3)_2$, following insertion of carbon monoxide and elimination of cobalt to give a cyclopentadienone.[3] $CpCo(CO)_2$- and $Fe(CO)_5$-mediated carbonylative alkyne–alkyne couplings were also reported[4–6] but in these reactions, products are obtained as η^4-cobalt or η^4-iron complexes of cyclopentadienones; besides, the uncomplexed cyclopentadienones, which can be given by oxidative demetallation of η^4-complexes, are generally unstable to be isolated. Thus, we examined a coupling between bulky alkynes by the use of cobalt carbonyl complex for the direct synthesis of cyclopentadienones. $Co_2(CO)_8$ was reported to mediate alkyne trimerization[7] but a bulky substituent on alkyne would interfere the insertion of the third alkyne and the insertion of carbon monoxide would preferentially proceed to give cyclopentadienone. From these assumptions, we chose silyl groups as a substituent on alkyne because sterically and electronically different groups can be introduced by the choice of three substituents on silicon and further transformation of silicon moiety in product would be conceivable.

We here disclose a direct synthesis of various cyclopentadienones by inter- and intramolecular carbonylative alkyne–alkyne coupling mediated by dicobalt carbonyl complex. Yields are dependent on the substituents on alkynes and introduction of allyldiphenylsilyl group gave the good results.[8]

Results and Discussion

Intermolecular carbonylative alkyne–alkyne coupling reaction

First, a reaction between 1-(diphenylmethylsilyl)hexan-1-yne (**1a**) and the corresponding dicobalt carbonyl complex was examined at 120°C (bath temperature) in toluene (Eq. (1)). As a result, contrarily to previous alkyne–alkyne coupling mediated by $CpCo(CO)_2$[4] and $Fe(CO)_5$,[5,6] uncomplexed cyclopentadienones were directly provided in 67% as a total yield of regioisomers **2a** and **3a**.



(1)

Keywords: alkynes; carbonylations; cobalt and compounds; coupling reactions; diynes.

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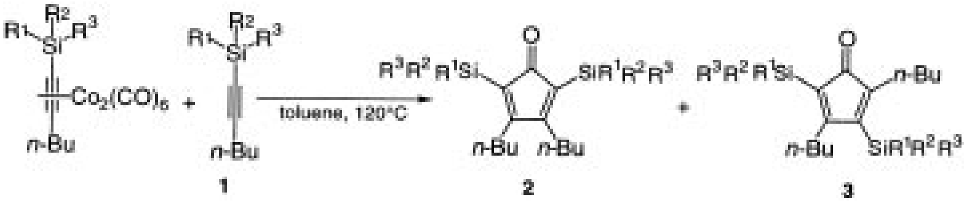
Table 1. Effect of silyl group on carbonylative alkyne–alkyne coupling reaction



Entry[a]	R^1	R^2	R^3	Alkyne	Yield/%	Ratio (**2**:**3**)	
1	*t*-Bu	Ph	Ph	**1b**	6[b]	>100:1[c]	(**2b**:**3b**)
2	Ph	Ph	Ph	**1c**	77	3.5:1	(**2c**:**3c**)
3	**Allyl**	**Ph**	**Ph**	**1d**	**99**	**7:1**	(**2d**:**3d**)
4	Allyl	Ph	Me	**1e**	48[d]		(**2e**:**3e**)
5	Allyl	Me	Me	**1f**	trace[e]		(**2f**:**3f**)
6	Vinyl	Ph	Ph	**1g**	40	2:1	(**2g**:**3g**)

[a] Molar ratio. Dicobalt carbonyl complex:alkyne=1:3. Yield is based on dicobalt carbonyl complex.

[b] Alkyne **1b** was recovered in 92% based on the total amount of submitted alkyne **1b** and **1b** derived from cobalt–alkyne complex.

[c] Regioisomer **3b** could not be detected.

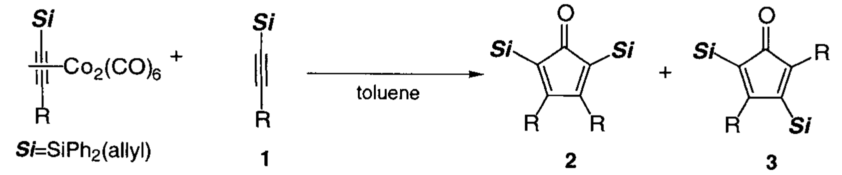
[d] Regioisomer **2e** and **3e** (28%, 8:1) and isomerized products which possess methylphenyl(1-propenyl)silyl group (ca. 20%).

[e] Trimerization of alkynes proceeded and hexasubstituted benzenes were obtained in the total yield of 67% as inseparable mixture of regioisomers and isomerized products which possess dimethyl(1-propenyl)silyl group. They are characterized by ^1H and ^{13}C NMR and high resolution mass spectra.

In order to improve yield and regioselectivity, screening of various alkynylsilanes was examined (Table 1). More bulky silyl group (*tert*-butyldiphenylsilyl group) interfered the coupling reaction. Thus demetallation exclusively proceeded prior to coupling reaction and free alkynylsilane was recovered (Entry 1). Triphenylsilyl group gave a better result (Entry 2). Moreover, introduction of allyl group instead of phenyl group dramatically improved the reaction efficiency and cyclopentadienones (**2d** and **3d**) were obtained almost quantitatively with higher regioselectivity (Entry 3). Alkynes possessing less bulky groups (methyl instead of phenyl group) were also consumed under the same reaction conditions but the yields decreased markedly (Entries 4, 5). It means that two phenyl groups on silicon probably stabilize the cyclopentadienones. The presence of carbon–carbon double bond at appropriate position is also indispensable for high yield (Entry 6). There is no direct evidence yet but coordination of allyl substituent to coordinatively unsaturated cobalt metal might facilitate the carbonylative coupling.

$Co_2(CO)_8$ is known to promote alkyne trimerization to

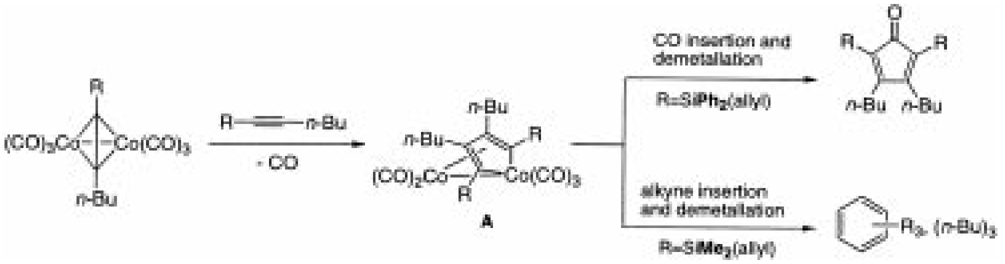
Table 2. The intermolecular carbonylative coupling of various alkynylsilanes



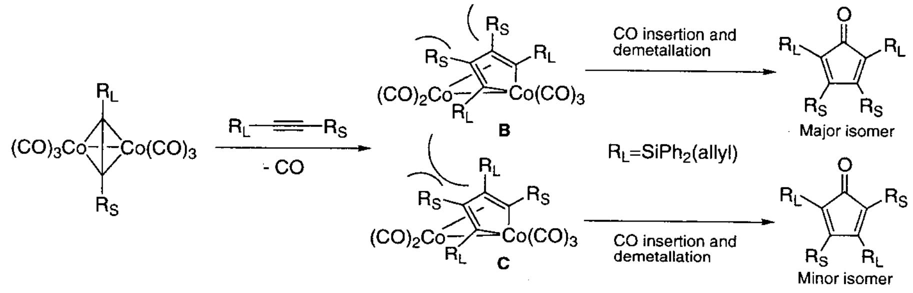
Entry[a]	R	Alkyne	Bath temp./°C	Yield/%	Ratio (**2**:**3**)	
1	*n*-Bu	**1d**	120	99	7:1	(**2d**:**3d**)
2	Ph	**1h**	120	85	4:1	(**2h**:**3h**)
3	Me	**1i**	100	91	10:1	(**2i**:**3i**)
4	H	**1j**	100	70	>100:1[b]	(**2j**:**3j**)

[a] Molar ratio. Dicobalt carbonyl complex:alkyne=1:3. Yield is based on dicobalt carbonyl complex.

[b] Regio isomer **3j** could not be detected.



Scheme 1.



Scheme 2.

provide benzene derivatives predominantly.[7] In the dicobalt carbonyl-mediated reaction of alkyne possessing allyldiphenylsilyl group, however, carbonylative coupling exclusively proceeded to give cyclopentadienones. These results mean that insertion of carbon monoxide to cobaltacyclopentadiene intermediate[9] **A** proceeds prior to the insertion of the third alkyne due to the steric bulkiness on alkyne (Scheme 1). In fact, in the reaction of alkynylsilane possessing smaller substituent (allyldimethylsilyl group, Entry 5 in Table 1), trimerization predominates over carbonylative coupling and benzene derivatives are major products.

Various alkynes possessing an allyldiphenylsilyl group on its terminal position were submitted to this carbonylative coupling mediated by dicobalt carbonyl complex (Table 2). The corresponding cyclopentadienones were isolated in good to high yield. The regioselectivity (**2**:**3**) is dependent on substituent on alkynes and only symmetrical cyclopentadienone **2j** could be detected in the reaction of alkynylsilane **1j** which has no substituent on its terminal position (Entry 4). These results can be explained by steric repulsion of substituents in cobaltacyclopentadienes (**B** and **C**): an allyldiphenylsilyl group operates as a large substituent (R_L) and hydrogen does as a small one (R_S) and less sterically congested intermediate **B** is converted into major product (Scheme 2). Besides steric factor, electronic factor might be also considered: in the formation of metallacycle, silyl and phenyl groups tend to be allocated at the position next metal.[10]

Intramolecular carbonylative alkyne–alkyne coupling reaction

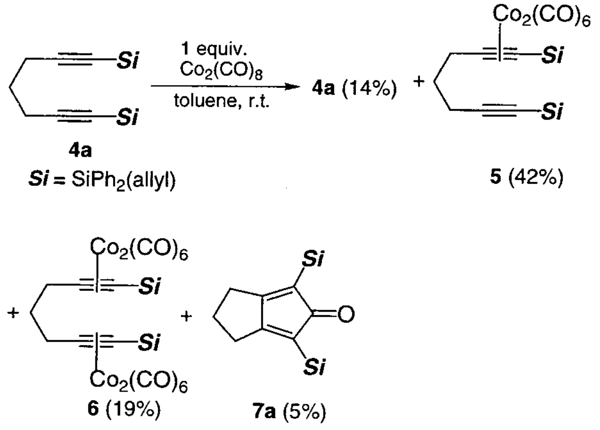
We next applied the present carbonylative coupling for intramolecular reaction. As a preliminary experiment, a reaction of 1,6-diyne **4a** possessing allyldiphenylsilyl groups on its terminal positions with an equivalent amount of dicobalt octacarbonyl was examined at room temperature (Eq. (2)). Complexes **5** and **6** were obtained in 42%, 19% yield, respectively. Coupling product **7a** was not detected in situ, therefore, **7a** was probably formed in purified process using TLC on silica gel.

Table 3. Effect of concentration of toluene solution of diyne **4a** and $Co_2(CO)_8$

$$\underset{\text{in hot toluene}}{\mathbf{4a}} \xrightarrow[\text{dropwise addition then 1 h}]{Co_2(CO)_8 \text{ in toluene}} \mathbf{7a}$$

Entry[a]	**4a**/M	$Co_2(CO)_8$/M	Bath temp./°C	Yield/%
1	0.05	0.05	100 then 120	69
2	0.01	0.05	100 then 120	72
3	0.01	0.01	90	95

[a] Molar ratio. Dicobalt octacarbonyl:diyne=1:1.5. Yield is based on dicobalt octacarbonyl.



(2)

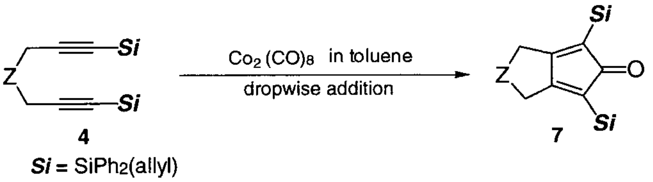
Isolated complexes **5** and **6** were submitted to the thermal reaction condition. **5** was smoothly transformed into **7a** in high yield along with the formation of a small amount of **6** at 90°C in toluene (Eq. (3)). On the contrary, it took higher reaction temperature and longer reaction time to consume **6** (Eq. (4)). These results are reasonable because decomplexation of one of two cobalt carbonyl complexes from **6** must be occurred prior to coupling reaction. Therefore dominant formation of **5** and suppression of formation of **6** might realize highly efficient intramolecular coupling.

$$\mathbf{5} \xrightarrow[\text{toluene, 90 °C, 1h}]{} \mathbf{7a}\ (71\%) + \mathbf{6}\ (5\%) \qquad (3)$$

$$\mathbf{6} \xrightarrow[\text{toluene, 120 °C, 6h}]{} \mathbf{7a}\ (55\%) \qquad (4)$$

A prompt coupling of in situ generated complex **5** could suppress the second complexation to **5**, which provides undesired complex **6**. In fact, dropwise addition of a toluene solution of $Co_2(CO)_8$ into a hot toluene solution of diyne **4a** gave **7a** in good yield, but the formation of **6** was observed and higher temperature (120°C) was need to consume **6** completely (Table 3, Entry 1). Dilution of diyne solution gave almost the same result (Entry 2), but when both of diyne **4a** and $Co_2(CO)_8$ solution were diluted, the reaction smoothly proceeded at 90°C to give **7a** in dramatically

Table 4. The intramolecular carbonylative coupling of various diynes



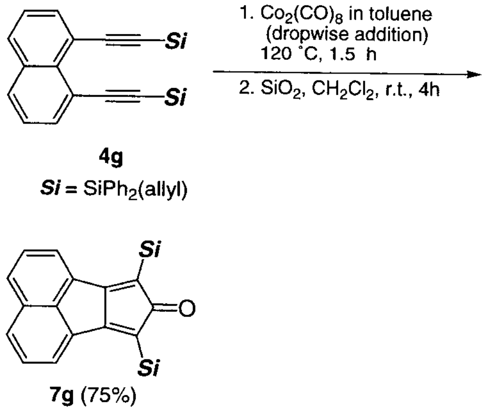
Entry[a]	Z	Diyne	Bath temp. /°C	Time/h	Yield/%
1	CH_2	**4a**	90	1.5	95 (**7a**)
2	$(CH_2)_2$	**4b**	120	2.0	58 (**7b**)
3	$(CH_2)_3$	**4c**	120	2.7	34 (**7c**)
4	O	**4d**	100	1.5	98 (**7d**)
5	S	**4e**	100	1.5	60 (**7e**)
6	$C(CO_2Me)_2$	**4f**	100	2.0	85 (**7f**)

[a] Molar ratio. Dicobalt octacarbonyl:diyne=1:1.5. Yield is based on dicobalt octacarbonyl.

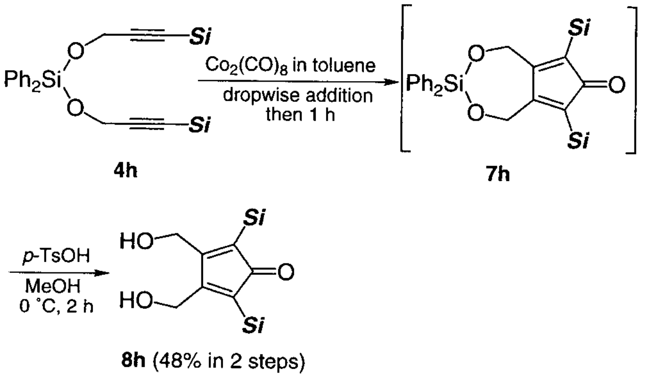
improved yield and formation of complex **6** was not detected (Entry 3).

Various diynes were submitted under the above best reaction conditions (Table 4). 1,7-Diyne **4b** and 1,8-diyne **4c** were directly converted into bicyclic cyclopentadienones **7b**, **c** (Entries 2,3). Dipropargyl ether **4d** was the best substrate and coupling product **7d** was obtained in almost quantitative yield (Entry 4). Dipropargyl sulfide **4e** also reacted but gave relatively complex mixtures and **7e** was isolated in moderate yield (Entry 5). Dipropargylmalonate **4f** was also a good substrate (Entry 6).

In the reaction of 1,8-dialkynylnaphthalene **4g**, unidentified complexes were provided. After a dichloromethane solution of the reaction mixture with silica gel was stirred, multicyclic product **7g** was isolated as a crystal (Eq. (5)). The structure of **7g** was ascertained by X-ray measurement (Fig. 1). This is one of the rare examples where the structures of cyclopentadienones were established by X-ray crystallography.[11,12] Siloxy tethered[13] diyne **4h** was transformed into bicyclic cyclopentadienone **7h**, which was protonated to diol **8h** by following acidic treatment (Eq. (6)).



(5)



(6)

In summary, we developed inter- and intramolecular carbonylative couplings of alkynes possessing allyldiphenylsilyl group. The present reactions are mediated by dicobalt carbonyl complex under argon atmosphere and directly afford various cyclopentadienones in good to high isolated yields. These results extend the utility of carbonylative alkyne–alkyne coupling reaction, which provides a facile method for preparing cyclopentadienones, promising synthetic intermediates in organic synthesis.

Color	red
Crystal shape	prismatic
Molecular formula	$C_{45}H_{36}OSi_2$
Formula weight	648.95
Crystal size/mm	0.50x0.40x0.10
Crystal system	monoclinic
Space group	$P2_1/A$
a / Å	18.285(1)
b / Å	8.721(1)
c / Å	22.510(2)
β / °	100.28(6)
V / Å^3	3532.1(6)
Z value	4
D_c /gcm^{-3}	1.220
(MoKα) / cm^{-1}	1.35
No. of reflections	
Total, Unique	32783, 8084
Residuals: R, R_w	0.043, 0.069

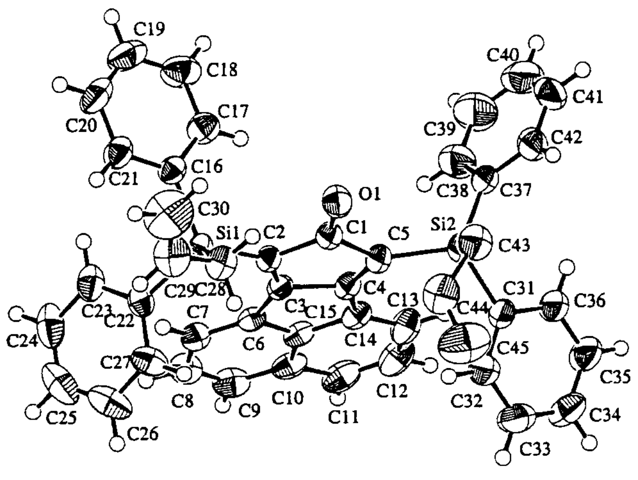


Figure 1. Molecular structure of compound **7g**. Selected bond lengths [Å] and angles [°] C(1)–O(1) 1.224(2), C(1)–C(2) 1.516(2), C(2)–C(3) 1.350(2), C(3)–C(4) 1.526(2), C(4)–C(5) 1.348(3), C(1)–C(5) 1.515(2), C(3)–C(6) 1.468(2), C(4)–C(14) 1.462(3), O(1)–C(1)–C(2) 124.5(2), O(1)–C(1)–C(5) 125.2(2), C(1)–C(2)–C(3) 104.1(1), C(2)–C(3)–C(4) 110.4(2), C(3)–C(4)–C(5) 111.3(1), C(1)–C(5)–C(4) 103.5(1), C(4)–C(3)–C(6) 106.9(1), C(3)–C(4)–C(14) 107.1(1).

Experimental

General

IR spectra were recorded on a Hitachi 260-30 spectrometer. UV/vis spectra were recorded on a Shimadzu UV-365 spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX300 spectrometer with tetramethylsilane as an internal standard. $CDCl_3$ was used as a solvent. High resolution mass spectra (HRMS) were obtained with JEOL JMS-SX102A mass spectrometer. X-Ray diffraction intensities were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation (Fig. 1). Toluene was distilled from calcium hydride, and THF was distilled from $LiAlH_4$ before use. All reactions were carried out under an argon atmosphere.

Intermolecular carbonylative coupling

Alkynylsilanes **1a**–**1g** were prepared by the reaction between lithium salt of hex-1-yne and chlorodiphenylmethylsilane, *tert*-butylchlorodiphenylsilane, chlorotriphenylsilane, allyldiphenylmethoxysilane, allylmethoxymethylphenylsilane, allylchlorodimethylsilane, chlorodiphenylvinylsilane, respectively. Alkynylsilane **1h** was prepared by the reaction between lithium salt of ethynylbenzene and allyldiphenylmethoxysilane. Alkynylsilanes **1i** and **1j** were prepared by the reaction between allyldiphenylmethoxysilane and 1-propynylmagnesium bromide ethynylmagnesium chloride, respectively.

Typical procedure for the preparation of alkynylsilanes (1a as an example)

To a stirred THF solution (10 ml) of hex-1-yne (437 mg, 5.3 mmol) was added *n*-BuLi (3.0 ml, 1.54 M hexane solution, 4.6 mmol) at −78°C. The reaction mixture was stirred for 10 min at −78°C and for 1 h at 0°C. Then it is cooled to −78°C again and a THF solution (5 ml) of chlorodiphenylmethylsilane (716 mg, 3.1 mmol) was added. The resulting solution was warmed to 0°C over 2 h and quenched by addition of 1 M HCl (10 ml). Organic materials were extracted with ethyl acetate and the combined extracts were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purification of the residue by column chromatography using silica gel afforded alkynylsilane **1a** (843 mg, 3.0 mmol).

1-(Diphenylmethylsilyl)hex-1-yne (1a). Yield 98%. Colorless oil. IR (neat) 2173, 1429, 1115 cm^{-1}; ^{1}H NMR δ=0.66 (s, 3H), 0.93 (t, *J*=7.2 Hz, 3H), 1.42–1.63 (m, 4H), 2.34 (t, *J*=6.9 Hz, 2H), 7.33–7.42 (m, 6H), 7.63–7.66 (m, 4H); ^{13}C NMR δ=−1.8, 13.6, 19.8, 22.0, 30.6, 80.4, 111.3, 127.8, 129.4, 134.4, 135.9; HRMS found *m/z* 278.1491, calcd for $C_{19}H_{22}Si$: 278.1491.

1-(*t*-Butyldiphenylsilyl)hex-1-yne (1b). Yield 89%. Colorless oil. IR (neat) 2173, 1429, 1109 cm^{-1}; ^{1}H NMR δ=0.93 (t, *J*=7.2 Hz, 3H), 1.07 (s, 9H), 1.45–1.67 (m, 4H), 2.39 (t, *J*=6.9 Hz, 2H), 7.32–7.40 (m, 6H), 7.77–7.83 (m, 4H); ^{13}C NMR δ=13.6, 18.5, 19.8, 22.0, 27.1, 30.8, 79.2, 111.9, 127.6, 129.3, 133.9, 135.6; HRMS found *m/z* 320.1946, calcd for $C_{22}H_{28}Si$: 320.1960.

1-(Triphenylsilyl)hex-1-yne (1c). Yield 93%. Colorless oil. IR (neat) 2173, 1429, 1111 cm^{-1}; ^{1}H NMR δ=0.96 (t, *J*=7.2 Hz, 3H), 1.45–1.69 (m, 4H), 2.41 (t, *J*=6.9 Hz, 2H), 7.35–7.46(m, 9H), 7.65–7.69 (m, 6H); ^{13}C NMR δ=13.6, 19.9, 22.0, 30.6, 79.2, 112.8, 127.9, 129.7, 134.2, 135.5; HRMS found *m/z* 340.1662, calcd for $C_{24}H_{24}Si$: 340.1647.

1-(Allyldiphenylsilyl)hex-1-yne (1d). Yield 76%. Colorless oil. IR (neat) 2175, 1631, 1427, 1111 cm^{-1}; ^{1}H NMR δ=0.93 (t, *J*=7.2 Hz, 3H), 1.41–1.63 (m, 4H), 2.12 (d, *J*=7.9 Hz 2H), 2.35 (t, *J*=6.9 Hz, 2H), 4.87–4.97 (m, 2H), 5.85 (ddt, J_d=10.0, 17.0 Hz, J_t=7.9 Hz, 1H), 7.32–7.41(m, 6H), 7.63–7.66 (m, 4H); ^{13}C NMR δ=13.6, 19.8, 21.9, 22.3, 30.6, 79.0, 112.3, 114.9, 127.8, 129.6, 133.3, 134.3, 134.8; HRMS found *m/z* 304.1649, calcd for $C_{21}H_{24}Si$: 304.1647.

1-(Allylmethylphenylsilyl)hex-1-yne (1e). Yield 76%. Colorless oil. IR (neat) 2175, 1631, 1427, 1115 cm^{-1}; ^{1}H NMR δ=0.39 (s, 3H), 0.92 (t, *J*=7.2 Hz, 3H), 1.40–1.60 (m, 4H),1.81–1.84 (m, 2H), 2.29 (t, *J*=6.9 Hz, 2H), 4.87–4.93 (m, 2H), 5.74–5.88 (m, 1H), 7.34–7.39 (m, 3H), 7.61–7.64 (m, 2H); ^{13}C NMR δ=−3.2, 13.6, 19.7, 21.9, 23.7, 30.6, 80.6, 110.6, 114.1, 127.7, 129.4, 133.8, 134.0, 136.0; HRMS found *m/z* 242.1491, calcd for $C_{16}H_{22}Si$: 242.1491.

1-(Allyldimethylsilyl)hex-1-yne (1f). Yield 79%. Colorless oil. IR (neat) 2173, 1631 cm^{-1}; ^{1}H NMR δ=0.13 (s, 6H), 0.91 (t, *J*=7.2 Hz, 3H), 1.37–1.56 (m, 4H), 1.61 (d, *J*=8.0 Hz, 2H), 2.23 (t, *J*=6.9 Hz, 2H), 4.86–4.92 (m, 2H), 5.82 (ddt, J_d=10.3, 16.8 Hz, J_t=8.0 Hz, 1H); ^{13}C NMR δ=−2.0, 13.6, 19.5, 21.9, 24.3, 30.7, 82.6, 108.6, 113.5, 134.3; HRMS found *m/z* 180.1355, calcd for $C_{11}H_{20}Si$: 180.1334.

1-(Diphenylvinylsilyl)hex-1-yne (1g). Yield 92%. Colorless oil. IR (neat) 2175, 1589, 1427, 1115 cm^{-1}; ^{1}H NMR δ=0.93 (t, *J*=7.2 Hz, 3H), 1.42–1.63 (m, 4H), 2.36 (t, *J*=6.9 Hz, 2H), 5.96 (dd, *J*=3.9, 19.8 Hz, 1H), 6.23 (dd, *J*=3.9, 14.4 Hz, 1H), 6.43 (dd, *J*=14.4, 19.8 Hz, 1H), 7.33–7.42 (m, 6H), 7.63–7.67 (m,4H); ^{13}C NMR δ=13.6, 19.8, 22.0, 30.6, 78.6, 112.5, 127.9, 129.7, 133.5, 134.1, 135.1, 136.3; HRMS found *m/z* 290.1485, calcd for $C_{20}H_{22}Si$: 290.1491.

1-(Allyldiphenylsilyl)-2-phenylethyne (1h). Yield 85%. Colorless oil. IR (neat) 2160, 1631, 1427, 1111 cm^{-1}; ^{1}H NMR δ=2.24 (d, *J*=7.9 Hz, 2H), 4.92–5.04 (m, 2H), 5.91 (ddt, J_d=10.1, 17.0 Hz, J_t=7.9 Hz, 1H), 7.29–7.44 (m, 9H), 7.54–7.58 (m, 2H), 7.69–7.74 (m, 4H); ^{13}C NMR δ=22.2, 88.8, 109.2, 115.2, 122.7, 127.9, 128.3, 129.0, 129.8, 132.2, 133.0, 133.7, 134.9; HRMS found *m/z* 324.1336, calcd for $C_{23}H_{20}Si$: 324.1334.

1-(Allyldiphenylsilyl)prop-1-yne (1i). Yield 76%. Colorless oil. IR (neat) 2183, 1631, 1427, 1115 cm^{-1}; ^{1}H NMR δ=2.01 (s, 3H), 2.12–2.15 (m, 2H), 4.87–4.98 (m, 2H), 5.78–5.92 (m, 1H), 7.32–7.42 (m, 6H), 7.61–7.67 (m, 4H); ^{13}C NMR δ=5.2, 22.2, 78.6, 107.5, 114.9, 127.8, 129.7, 133.2, 134.1, 134.8; HRMS found *m/z* 262.1180, calcd for $C_{18}H_{18}Si$: 262.1178.

Allyldiphenylethynylsilane (1j). Yield 70%. Colorless oil. IR (neat) 2036, 1631, 1427, 1115 cm^{-1}; ^{1}H NMR δ=2.18

(d, J=7.8 Hz, 2H), 2.69 (s, 1H), 4.91–5.01 (m, 2H), 5.85 (ddt, J_d=10.0, 17.4 Hz, J_t=7.8 Hz, 1H), 7.34–7.44 (m, 6H), 7.64–7.67 (m, 4H); ^{13}C NMR δ=21.7, 85.0, 97.3, 115.5, 128.0, 130.0, 132.6, 132.9, 134.8; HRMS found *m*/*z* 248.1015, calcd for $C_{17}H_{16}Si$: 248.1021.

Typical experimental procedure for intermolecular carbonylative coupling (Table 2, Entry 1)

A toluene solution (2 ml) of **1d** (107.0 mg, 0.35 mmol) and the corresponding dicobalt carbonyl complex of **1d** (68.2 mg, 0.12 mmol) in a 30 ml round-bottomed flask with reflux condenser was immersed in a hot oil bath (120°C). The reaction mixture was stirred for 2 h, then the resulting precipitates were removed by filtration through a small pad of silica gel using a mixed eluent of hexane and ethyl acetate (5/1,*v*/*v*). After the solvent was removed under reduced pressure, purification of the residue by thin-layer chromatography (TLC) of silica gel afforded products in 99% yield (**2d**: 63.4 mg, 0.10 mmol, 86%, **3d**: 9.4 mg, 0.015 mmol, 13%).

2,5-Bis(diphenylmethylsilyl)-3,4-dibutylcyclopenta-2,4-dien-1-one (2a). Yellow oil. IR (neat) 1682, 1550, 1427, 1111 cm^{-1}; λ_{max} (MeOH) 408 nm (ϵ 907); ^{1}H NMR δ=0.65 (t, J=7.0 Hz, 6H), 0.77 (s, 6H), 0.78–0.94 (m, 4H), 1.01–1.11 (m, 4H), 1.90–1.95 (m, 4H), 7.30–7.40 (m, 12H), 7.48–7.51 (m, 8H); ^{13}C NMR δ=−2.4, 13.6, 23.0, 27.9, 32.4, 125.2, 127.7, 129.2, 135.0, 136.6, 176.3, 210.1; HRMS found *m*/*z* 584.2938, calcd for $C_{39}H_{44}OSi_2$: 584.2931.

2,4-Bis(diphenylmethylsilyl)-3,5-dibutylcyclopenta-2,4-dien-1-one (3a). Orange oil. IR (neat) 1693, 1589, 1427, 1107 cm^{-1}; ^{1}H NMR δ=0.36–0.39 (m, 5H), 0.64–0.80 (m, 11H), 0.82–1.11 (m, 4H), 1.83–1.90 (m, 4H), 7.29–7.40 (m, 12H), 7.48–7.55 (m, 8H); ^{13}C NMR δ=−2.3, −1.0, 13.5, 13.7, 22.6, 23.1, 25.4, 31.6, 32.5, 32.8, 118.3, 127.7, 128.0, 129.1, 129.6, 134.9, 135.0, 135.9, 136.7, 146.0, 151.2, 184.7, 207.7; HRMS found *m*/*z* 584.2927, calcd for $C_{39}H_{44}OSi_2$: 584.2931.

2,5-Bis(*t*-butyldiphenylsilyl)-3,4-dibutylcyclopenta-2,4-dien-1-one (2b). Yellow oil. IR (neat) 1685, 1538, 1427, 1105 cm^{-1}; λ_{max} (MeOH) 410 nm (ϵ 893) ^{1}H NMR δ=0.55 (t, J=6.6 Hz, 6H), 0.64–0.76 (m, 4H), 0.85–0.96 (m, 4H), 1.18 (s, 18H), 1.62–1.67 (m, 4H), 7.30–7.42 (m, 12H), 7.57–7.60 (m, 8H); HRMS found *m*/*z* 668.3885, calcd for $C_{45}H_{56}OSi_2$: 668.3870.

2,5-Bis(triphenylsilyl)-3,4-dibutylcyclopenta-2,4-dien-1-one (2c). Yellow solid. Mp. 201°C. IR (neat) 1685, 1550, 1427, 1107 cm^{-1}; λ_{max} (MeOH) 406 nm (ϵ 765) ^{1}H NMR δ=0.64 (t, J=6.8 Hz, 6H), 0.75–0.87 (m, 4H), 1.06–1.17 (m, 4H), 1.85–1.90 (m, 4H), 7.30–7.42 (m, 18H), 7.54–7.57 (m, 12H); ^{13}C NMR δ=13.6, 23.0, 27.6, 32.9, 124.4, 127.7, 129.3, 134.6, 136.3, 178.2, 210.4; HRMS found *m*/*z* 708.3234, calcd for $C_{49}H_{48}OSi_2$: 708.3244.

2,4-Bis(triphenylsilyl)-3,5-dibutylcyclopenta-2,4-dien-1-one (3c). Orange solid. Mp. 172°C. IR (neat) 1693, 1585, 1427, 1107 cm^{-1}; λ_{max} (MeOH) 426 nm (ϵ 437) ^{1}H NMR δ=−0.21−0.11 (m, 2H), 0.12 (t, J=7.1 Hz, 3H), 0.47–0.58 (m, 5H), 0.66–0.86 (m, 2H), 0.90–1.01 (m, 2H),1.64–1.77 (m, 4H), 7.30–7.46 (m, 18H), 7.56–7.66(m, 12H); ^{13}C NMR δ=13.3, 13.6, 22.3, 23.0, 25.6, 32.2, 32.3, 33.1, 117.5, 127.6, 128.0, 129.3, 129.8, 133.9, 134.7, 136.1, 136.2, 145.3, 152.6, 186.8, 207.2; HRMS found *m*/*z* 708.3237, calcd for $C_{49}H_{48}OSi_2$: 708.3244.

2,5-Bis(allyldiphenylsilyl)-3,4-dibutylcyclopenta-2,4-dien-1-one (2d). Yellow oil. IR (neat) 1682, 1627, 1546, 1427, 1107 cm^{-1}; λ_{max} (MeOH) 406 nm (ϵ 307) ^{1}H NMR δ=0.54 (t, J=7.0 Hz, 6H), 0.68–0.80 (m, 4H), 0.90–1.00 (m, 4H), 1.74–1.79 (m, 4H), 2.32 (d, J=8.0 Hz, 4H), 4.77–4.86 (m, 4H), 5.79 (ddt, J_d=10.1, 17.0 Hz, J_t=8.0 Hz, 2H), 7.24–7.35 (m, 12H), 7.44–7.47 (m, 8H); ^{13}C NMR δ=13.5, 21.7, 22.9, 27.9, 32.3, 114.6, 124.3, 127.7, 129.4, 134.5, 134.9, 135.6, 177.3, 210.2; HRMS found *m*/*z* 636.3244, calcd for $C_{43}H_{48}OSi_2$: 636.3244.

2,4-Bis(allyldiphenylsilyl)-3,5-dibutylcyclopenta-2,4-dien-1-one (3d). Orange oil. IR (neat) 1693, 1627, 1589, 1427, 1107 cm^{-1}; ^{1}H NMR δ=0.20–0.26 (m, 5H), 0.57–0.73 (m, 5H), 0.92–1.20 (m, 4H), 1.73–1.79 (m, 2H),1.93–1.98 (m, 2H), 2.32–2.40 (m, 4H), 4.82–5.00 (m, 4H), 5.75–5.91 (m, 2H), 7.29–7.58 (m, 20H); HRMS found *m*/*z* 636.3248, calcd for $C_{43}H_{48}OSi_2$: 636.3244.

2,5-Bis(allylmethylphenylsilyl)-3,4-dibutylcyclopenta-2,4-dien-1-one (2e). Yellow oil. IR (neat) 1682, 1631, 1550, 1427, 1111 cm^{-1}; ^{1}H NMR δ=0.50 (s, 6H), 0.75 (t, J=6.9 Hz, 6H), 1.04–1.25 (m, 8H), 1.98–2.18 (m, 8H), 4.81–4.94 (m, 4H), 5.66–5.82 (m, 2H), 7.27–7.39 (m, 6H), 7.48–7.56(m, 4H); HRMS found *m*/*z* 512.2927, calcd for $C_{33}H_{44}OSi_2$: 512.2932.

2-(Allylmethylphenylsilyl)-3,4-dibutyl-5-{methylphenyl-(1-propenyl)silyl}cyclopenta-2,4-dien-1-one. It can not be completely purified. Yellow oil. IR (neat) 1682, 1620, 1550, 1427, 1111 cm^{-1}; ^{1}H NMR δ=0.49 (s, 3H), 0.55 (s, 3H), 0.734–0.81 (m, 6H), 1.02–1.25 (m, 8H), 1.87 (dd, J=1.3, 5.9 Hz, 3H), 2.00–2.17 (m, 6H), 4.79–4.89 (m, 2H), 5.66–5.81 (m, 1H), 5.97 (dd, J=1.3, 18.4 Hz, 1H), 6.07–6.19 (m, 1H),7.31–7.40 (m, 6H), 7.49–7.61 (m, 4H); HRMS found *m*/*z* 512.2930, calcd for $C_{33}H_{44}OSi_2$: 512.2932.

2,5-Bis(diphenylvinylsilyl)-3,4-dibutylcyclopenta-2,4-dien-1-one (2g). Yellow oil. IR (neat) 1685, 1589, 1547, 1427, 1111 cm^{-1}; ^{1}H NMR δ=0.69 (t, J=7.1 Hz, 6H), 0.89–1.20 (m, 8H), 2.00–2.05 (m, 4H), 5.71 (dd, J=3.6, 20.3 Hz, 2H), 6.21 (dd, J=3.6, 14.5 Hz, 2H), 6.43 (dd, J=14.5, 20.3 Hz, 2H), 7.31–7.53 (m, 20H); HRMS found *m*/*z* 608.2919, calcd for $C_{41}H_{44}OSi_2$: 608.2931.

2,4-Bis(diphenylvinylsilyl)-3,5-dibutylcyclopenta-2,4-dien-1-one (3g). Yellow oil. IR (neat) 1693, 1589, 1543, 1427, 1107 cm^{-1}; ^{1}H NMR δ=0.25–0.41 (m, 5H), 0.63 (t, J=7.1 Hz, 3H), 0.69–0.79 (m, 2H), 0.83–0.95 (m, 2H), 0.98–1.08 (m, 2H), 1.89–1.94 (m, 4H), 5.67 (dd, J=3.5, 20.1 Hz, 1H), 5.78 (dd, J=3.5, 20.1 Hz, 1H), 6.18 (dd, J=3.5, 14.5 Hz, 1H), 6.23 (dd, J=3.5, 14.5 Hz, 1H), 6.58 (dd, J=14.5, 20.1 Hz, 2H), 6.72 (dd, J=14.5, 20.1 Hz, 2H), 7.28–7.64 (m, 20H); HRMS found *m*/*z* 608.2932, calcd for $C_{41}H_{44}OSi_2$: 608.2931.

2,5-Bis(allyldiphenylsilyl)-3,4-diphenylcyclopenta-2,4-dien-1-one (2h). Yellow solid. Mp. 120°C (dec). IR (neat) 1685, 1627, 1542, 1427, 1111 cm^{-1}; λ_{max} (MeOH) 420 nm (ϵ 663) 324 nm (ϵ 590) ^{1}H NMR δ=2.17 (d, J=7.9 Hz, 4H), 4.66–4.77 (m, 4H), 5.54–5.69 (m, 2H), 6.62 (d, J=7.4 Hz, 4H), 6.77 (t, J=7.4 Hz, 4H), 6.94 (t, J=7.4 Hz, 2H), 7.17–7.41 (m, 20H); ^{13}C NMR δ=22.2, 115.1, 127.1, 127.3, 127.9, 128.7, 128.8, 129.5, 134.2, 134.5, 134.7, 135.8, 174.2, 209.0; HRMS found m/z 676.2621, calcd for $C_{47}H_{40}OSi_2$: 676.2618.

2,4-Bis(allyldiphenylsilyl)-3,5-diphenylcyclopenta-2,4-dien-1-one (3h). Orange solid. Mp. 120°C (dec). IR (neat) 1693, 1628, 1547, 1427, 1111 cm^{-1}; λ_{max} (MeOH) 453 nm (ϵ 968) ^{1}H NMR δ=1.23 (d, J=7.8 Hz, 2H), 1.89 (d, J=7.9 Hz, 2H), 4.41 (dd, J=1.9, 16.9 Hz, 1H), 4.54–4.67 (m, 3H), 5.22–5.36 (m, 1H), 5.42– 5.56 (m, 1H), 6.54–6.64 (m, 4H), 6.82–7.37 (m, 26H); ^{13}C NMR δ=21.1, 21.6, 114.6, 115.1, 121.4, 127.2, 127.3, 127.3, 127.4, 127.5, 127.6, 128.2, 129.0, 129.2, 130.1, 131.7, 133.5, 133.6, 134.0, 134.2, 135.3, 135.4, 136.9, 147.8, 149.0, 180.3, 205.6; HRMS found m/z 676.2621, calcd for $C_{47}H_{40}OSi_2$: 676.2618.

2,5-Bis(allyldiphenylsilyl)-3,4-dimethylcyclopenta-2,4-dien-1-one (2i). Yellow oil. IR (neat) 1682, 1627, 1558, 1427, 1111 cm^{-1}; ^{1}H NMR δ=1.65 (s, 6H), 2.40 (d, J=7.9 Hz, 4H), 4.82–4.88 (m, 4H), 5.73–5.88 (m, 2H), 7.32–7.49 (m, 12H), 7.51–7.55 (m, 8H); ^{13}C NMR δ=15.2, 21.4, 114.7, 124.5, 127.8, 129.4, 134.2, 134.6, 135.4, 172.9, 209.2; HRMS found m/z 552.2316, calcd for $C_{37}H_{36}OSi_2$: 552.2305.

2,5-Bis(allyldiphenylsilyl)cyclopenta-2,4-dien-1-one (2j). Yellow oil. IR (neat) 1739, 1697,1631, 1581, 1427, 1111 cm^{-1}; ^{1}H NMR δ=2.33 (d, J=7.9 Hz, 4H), 4.87–4.95 (m, 4H), 5.83 (ddt, J_d=10.0, 17.1 Hz, J_t=7.9 Hz, 2H), 7.20–7.62 (m, 22H); ^{13}C NMR δ=20.7, 115.0, 127.8, 129.6, 132.9, 133.6, 133.6, 135.3, 159.6, 208.5; HRMS found m/z 524.1981, calcd for $C_{35}H_{32}OSi_2$: 524.1992.

Intramolecular carbonylative coupling

1,ω-Diynes **4a**–**4d** were prepared by the reaction between allyldiphenylmethoxysilane and dilithium salt of hepta-1,6-diyne, octa-1,7-diyne, nona-1,8-diyne, dipropargyl ether, respectively.

Typical procedure for the preparation of 1,ω-diynes (4a as an example)

To a stirred THF solution (3 ml) of hepta-1,6-diyne (92 mg, 1.0 mmol) was added n-BuLi (1.6 ml, 1.54 M hexane solution, 2.5 mmol) at −78°C. The reaction mixture was stirred for 10 min at −78°C and for 30 min at 0°C. To the resulting mixture, HMPA (0.3 ml) and a THF solution (3 ml) of allyldiphenylmethoxysilane (702 mg, 2.8 mmol) was added at 0°C. The resulting solution was warmed to room temperature and stirred for 2 h and quenched by addition of 1 M HCl (5 ml) at 0°C. Organic materials were extracted with diethyl ether and the combined extracts were washed by H_2O three times then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purification of the residue by thin-layer chromatography (TLC) of silica gel afforded diyne **4a** (260 mg, 0.49 mmol).

1,7-Bis(allyldiphenylsilyl)hepta-1,6-diyne (4a). Yield 49%. Colorless oil. IR (neat) 2175, 1630, 1427, 1113 cm^{-1}; ^{1}H NMR δ(ppm)=1.88 (quintet, J=7.0 Hz, 2H), 2.13–2.15 (m, 4H), 2.54 (t, J=7.0 Hz, 4H), 4.88–4.98 (m, 4H), 5.85 (ddt, J_d=10.0, 17.0 Hz, J_t=7.8 Hz, 2H), 7.32–7.42 (m, 12H), 7.62–7.67 (m, 8H); ^{13}C NMR δ=19.2, 22.2, 27.4, 80.1, 110.6, 115.0, 127.9, 129.7, 133.2, 134.0, 134.8; HRMS found m/z 536.2361, calcd for $C_{37}H_{36}Si_2$: 536.2356.

1,8-Bis(allyldiphenylsilyl)octa-1,7-diyne (4b). Yield 54%. Colorless oil. IR (neat) 2173, 1630, 1427, 1113 cm^{-1}; ^{1}H NMR δ=1.76–1.80 (m, 4H), 2.14 (d, J=7.9 Hz, 4H), 2.40–2.44 (m, 4H), 4.88–4.98 (m, 4H), 5.85 (ddt, J_d=10.1, 17.0 Hz, J_t=7.9 Hz, 2H), 7.32–7.42(m, 12H), 7.61–7.67 (m, 8H); ^{13}C NMR δ=19.6, 22.2, 27.5, 79.6, 114.4, 115.0, 127.8, 129.7, 133.2, 134.1, 134.8; HRMS found m/z 550.2520, calcd for $C_{38}H_{38}Si_2$: 550.2512.

1,9-Bis(allyldiphenylsilyl)nona-1,8-diyne (4c). Yield 57%. Colorless oil. IR (neat) 2173, 1630, 1425, 1113 cm^{-1}; ^{1}H NMR δ=1.57–1.69 (m, 6H), 2.13 (d, J=7.9 Hz, 4H), 2.35 (t, J=6.7 Hz, 4H), 4.87–4.97 (m, 4H), 5.84 (ddt, J_d=10.0, 17.0 Hz, J_t=7.9 Hz, 2H), 7.32–7.41 (m, 12H), 7.61–7.67 (m, 8H); ^{13}C NMR δ=20.0, 22.2, 28.0, 28.1, 79.3, 111.9, 114.9, 127.8, 129.6, 133.2, 134.2, 134.8; HRMS found m/z 564.2646, calcd for $C_{39}H_{40}Si_2$: 564.2669.

Bis(3-allyldiphenylsilyl-2-propynyl) ether (4d). Yield 78%. Colorless oil. IR (neat) 2177, 1630, 1429, 1113 cm^{-1}; ^{1}H NMR δ=2.17 (d, J=7.8 Hz, 4H), 4.47 (s, 4H), 4.47–4.99 (m, 4H), 5.84 (ddt, J_d=10.0, 17.0 Hz, J_t=7.8 Hz, 2H), 7.33–7.44 (m, 12H), 7.63–7.66 (m, 8H); ^{13}C NMR δ=21.9, 57.2, 87.3, 104.7, 115.4, 128.0, 129.9, 132.7, 133.1, 134.9; HRMS found m/z 538.2153, calcd for $C_{36}H_{34}OSi_2$: 538.2148.

3-(Allyldiphenylsilyl)prop-2-yn-1-ol. 3-(Allyldiphenylsilyl)-prop-2-yn-1-ol was prepared by the reaction between allyldiphenylmethoxysilane and lithium salt of propargyl tetrahydropyranyl (THP) ether following deprotection of THP moiety under acidic condition. Yield 72% in 2 steps. Pale yellow oil. IR (neat) 3320, 2177, 1630, 1427, 1113 cm^{-1}; ^{1}H NMR δ=1.93 (t, J=3.6 Hz, 1H), 2.17, (d, J=7.8 Hz, 2H), 4.34 (d, J=3.6 Hz, 2H), 4.90–4.99 (m, 2H), 5.84 (ddt, J_d=10.1, 15.7 Hz, J_t=8.0 Hz, 1H), 7.33–7.45 (m, 6H), 7.59–7.66 (m, 4H); ^{13}C NMR δ=21.8, 51.7, 85.6, 108.0, 115.3, 127.9, 129.9, 132.8, 133.1, 134.8; HRMS found m/z 278.1110, calcd for $C_{18}H_{18}OSi$: 278.1127.

1-(Allyldiphenylsilyl)-3-bromoprop-1-yne. 1-(Allyldiphenylsilyl)-3-bromoprop-1-yne was prepared by the bromination of 3-(allyldiphenylsilyl)prop-2-yn-1-ol using PBr_3. Yield 77%. Pale yellow oil. IR (neat), 2179, 1630, 1425, 1113 cm^{-1}; ^{1}H NMR δ=2.17, (d, J=7.8 Hz, 2H), 3.99 (s, 2H), 4.91–5.00 (m, 2H), 5.83 (ddt, J_d=9.8, 17.4 Hz, J_t=8.0 Hz, 1H), 7.30–7.46 (m, 6H), 7.57–7.71 (m, 4H); ^{13}C NMR δ=14.3, 21.7, 87.3, 104.0, 115.5, 128.0, 130.0, 132.5, 132.9, 134.9; HRMS found m/z 340.0283, calcd for $C_{18}H_{17}BrSi$: 340.0283.

Bis(3-allyldiphenylsilyl-2-propynyl) sulfide (4e). 4e was prepared by the reaction between $Na_2S \cdot 9H_2O$ and 2 equiv.of 1-(allyldiphenylsilyl)-3-bromoprop-1-yne in ether in the presence of phase transfer catalyst. Yield 45%. Colorless oil. IR (neat) 2175, 1630, 1429, 1113 cm^{-1}; ^1H NMR δ=2.15 (dd, *J*=1.0, 7.8 Hz, 4H), 3.59 (s, 4H), 4.88–4.99 (m, 4H), 5.77–5.91 (m, 2H), 7.21–7.42 (m, 12H), 7.63–7.66 (m, 8H); ^{13}C NMR δ=20.0, 22.0, 83.4, 105.0, 115.3, 127.9, 129.8, 132.8, 133.4, 134.8; HRMS found *m/z* 554.1931, calcd for $C_{36}H_{34}SSi_2$: 554.1920.

1,7-Bis(allyldiphenylsilyl)-4,4-bis(methoxycarbonyl)hepta-1,6-diyne (4f). 4f was prepared by the stepwise dialkylation of dimethyl malonate using 1-(allyldiphenylsilyl)-3-bromoprop-1-yne under basic condition (NaH). Yield 56% in 2 steps. Colorless oil. IR (neat) 1743, 2181, 1630, 1433, 1113 cm^{-1}; ^1H NMR δ=2.12 (d, *J*=7.9 Hz, 4H), 3.22 (s, 4H), 3.70 (s, 6H), 4.87–4.97 (m, 4H), 5.81 (ddt, J_d=10.0, 17.0 Hz, J_t=7.9 Hz, 2H), 7.31–7.42 (m, 12H), 7.60–7.63 (m, 8H); ^{13}C NMR δ=22.0, 24.5, 53.1, 56.8, 83.5, 105.1, 115.2, 127.9, 129.8, 132.8, 133.5, 134.8, 168.9; HRMS found *m/z*, 652.2466 calcd for $C_{41}H_{40}O_4Si_2$: 652.2465.

1,8-Bis(allyldiphenylsilylethynyl)naphthalene (4g). 4g was prepared by Sonogashira coupling reaction between 1,8-diiodonaphthlene and 2 equiv. of alkynylsilane **1j** using a catalytic amount of $Pd(PPh_3)_4$ and CuI. Yield 60%. Pale yellow solid. Mp. 107°C. IR (KBr disk) 2144, 1631, 1429, 1115 cm^{-1}; ^1H NMR δ=1.85 (d, *J*=7.9 Hz, 4H), 4.73–4.79 (m, 4H), 5.64–5.79 (m, 2H), 7.21–7.26 (m, 8H), 7.30–7.36 (m, 4H), 7.45 (dd, *J*=7.3, 8.2 Hz, 2H) 7.64 (dd, *J*=1.4, 8.0 Hz, 8H), 7.86 (dd, *J*=1.2, 8.2 Hz, 2H), 7.94 (dd, *J*=1.2, 7.3 Hz, 2H); ^{13}C NMR δ=22.0, 98.5, 109.5, 114.9, 120.3, 125.6, 127.8, 129.6, 130.2, 130.3, 133.3, 133.8, 133.9, 135.1, 137.6; HRMS found *m/z* 620.2355, calcd for $C_{44}H_{36}Si_2$: 620.2356.

Bis(3-allyldiphenylsilyl-2-propynyloxy)diphenylsilane (4h). 4h was prepared by the reaction between dichlorodiphenylsilane and 2 equiv. of 3-(allyldiphenylsilyl)prop-2-yn-1-ol using triethylamine as a base. Yield 91%. Colorless oil. IR (neat) 2179, 1630, 1423, 1115 cm^{-1}; ^1H NMR δ=2.12 (d, *J*=7.8 Hz, 4H), 4.56 (s, 4H), 4.86–4.99 (m, 4H), 5.73–5.87 (m, 2H), 7.28–7.47 (m, 18H), 7.60 (dd, *J*=1.7, 7.6 Hz, 8H), 7.72 (dd, *J*=1.3, 7.9 Hz, 4H); ^{13}C NMR δ=21.8, 52.5, 85.1, 107.5, 115.3, 127.9, 127.9, 129.8, 130.7, 131.3, 132.8, 133.3, 134.9, 135.1; HRMS found *m/z* 736.2664, calcd for $C_{48}H_{44}O_2Si_3$: 736.2649.

Typical experimental procedure for intramolecular carbonylative coupling (Table 4, Entry 1)

To a hot toluene solution (15 ml, 120°C bath temperature) of **4a** (80.4 mg, 0.15 mmol) was dropwisely added a toluene solution (13 ml) of dicobalt octacarbonyl (34.2 mg, 0.10 mmol) over 30 min. The resulting mixture was stirred for additional 1 h then the resulting precipitates were removed by filtration through a small pad of silica gel using a mixed eluent of hexane and ethyl acetate (5/1,*v*/*v*). After the solvent was removed under reduced pressure, purification of the residue by thin-layer chromatography (TLC) of silica gel afforded **7a** (53.6 mg, 0.095 mmol, 95%).

2,4-Bis(allyldiphenylsilyl)bicyclo[3.3.0]octa-1,4-dien-3-one (7a). Yellow oil. IR 1689, 1630, 1583, 1425, 1111 cm^{-1}; λ_{max} (MeOH) 401 nm (ϵ 1100) ^1H NMR δ=1.69 (quintet, *J*=7.3 Hz, 2H), 1.88 (t, *J*=7.3 Hz, 4H), 2.37 (d, *J*=7.9 Hz, 4H), 4.84–4.94 (m, 4H), 5.86 (ddt, J_d=10.0, 17.0 Hz, J_t=7.9 Hz, 2H), 7.31–7.42 (m, 12H), 7.52–7.55 (m, 8H); ^{13}C NMR δ=21.0, 26.4, 27.4, 114.7, 119.4, 127.7, 129.5, 134.1, 134.4, 135.5, 182.7, 212.0; HRMS found *m/z* 564.2321, calcd for $C_{38}H_{36}OSi_2$: 564.2305.

7,9-Bis(allyldiphenylsilyl)bicyclo[4.3.0]nona-6,9-dien-8-one (7b). Yellow oil. IR 1684, 1620, 1547, 1425, 1109 cm^{-1}; λ_{max} (MeOH) 417 nm (ϵ 450) ^1H NMR δ=1.29–1.39 (m, 4H), 2.06–2.16 (m, 4H), 2.39 (d, *J*=7.9 Hz, 4H), 4.82–4.88 (m, 4H), 5.81 (ddt, J_d=10.1, 16.9 Hz, J_t=7.9 Hz, 2H), 7.32–7.43 (m, 12H), 7.51–7.54 (m, 8H); ^{13}C NMR δ=21.4, 22.4, 28.3, 114.7, 122.8, 127.8, 129.4, 134.3, 134.5, 135.5, 173.1, 209.0; HRMS found *m/z* 578.2460, calcd for $C_{39}H_{38}OSi_2$: 578.2461.

8,10-Bis(allyldiphenylsilyl)bicyclo[5.3.0]deca-7,10-dien-9-one (7c). Yellow oil. IR 1682, 1627, 1550, 1427, 1111 cm^{-1}; ^1H NMR δ=1.28–1.41 (m, 6H), 2.13–2.16 (m, 4H), 2.41 (d, *J*=7.9 Hz, 4H), 4.81–4.86 (m, 4H), 5.80 (ddt, J_d=10.9, 16.2 Hz, J_t=7.9 Hz, 2H), 7.31–7.42 (m, 12H), 7.51–7.54 (m, 8H); ^{13}C NMR δ=21.4, 29.3, 30.3, 30.9, 114.6, 123.2, 127.7, 129.4, 134.3, 134.9, 135.4, 178.1, 210.6; HRMS found *m/z* 592.2612, calcd for $C_{40}H_{40}OSi_2$: 592.2618.

2,4-Bis(allyldiphenylsilyl)-7-oxabicyclo[3.3.0]octa-1,4-dien-3-one (7d). Yellow oil. IR 1699, 1630, 1593, 1427, 1111 cm^{-1}; ^1H NMR δ=2.37 (d, *J*=7.9 Hz, 4H), 3.37 (s, 4H), 4.88–4.97 (m, 4H), 5.86 (ddt, J_d=10.0, 17.0 Hz, J_t=7.9 Hz, 2H), 7.33–7.53 (m, 20H); ^{13}C NMR δ=20.7, 66.0, 115.2, 119.3, 128.0, 129.9, 133.5, 133.6, 135.4, 177.8, 209.9; HRMS found *m/z* 566.2083, calcd for $C_{37}H_{34}O_2Si_2$: 566.2097.

2,4-Bis(allyldiphenylsilyl)-7-thiabicyclo[3.3.0]octa-1,4-dien-3-one (7e). IR (neat) 1689, 1630, 1592, 1429, 1111 cm^{-1}; Yellow oil. ^1H NMR δ=2.32 (d, *J*=7.9 Hz, 4H), 2.85 (s, 4H), 4.80–4.89 (m, 4H), 5.72–5.86 (m, 2H), 7.18–7.38 (m, 12H), 7.43–7.46 (m, 8H); ^{13}C NMR δ=20.8, 30.3, 115.1, 121.5, 128.0, 129.9, 133.6, 133.7, 135.5, 177.8, 211.0; HRMS found *m/z* 582.1880, calcd for $C_{37}H_{34}OSSi_2$: 582.1869.

2,4-Bis(allyldiphenylsilyl)-7,7-di(methoxycarbonyl)bicyclo[3.3.0]octa-1,4-dien-3-one (7f). Yellow oil. IR 1695, 1736, 1631, 1589, 1431, 1111 cm^{-1}; λ_{max} (MeOH) 397 nm (ϵ 1120) ^1H NMR δ=2.37 (d, *J*=7.9 Hz, 4H), 2.54 (s, 4H), 3.63 (s, 6H), 4.84–4.92 (m, 4H), 5.82 (m, 2H), 7.32–7.43 (m, 12H), 7.50–7.53 (m, 8H); ^{13}C NMR δ=20.7, 35.8, 53.0, 61.2, 114.9, 121.2, 127.9, 129.7, 133.8, 133.8, 135.4, 170.7, 177.7, 210.0; HRMS found *m/z* 680.2399, calcd for $C_{40}H_{40}O_5Si_2$: 680.2414.

1-Oxo-2,5-bis(allyldiphenylsilyl)cyclopenta-1,4-dieno-[3,4-a]acenaphthene (7g). Red solid Mp. 196°C. IR (KBr disk) 1672, 1556, 1427 cm^{-1}; λ_{max} (MeOH) 493 nm (ϵ 560) ^1H NMR δ=2.50 (d, *J*=7.9 Hz, 4H), 4.77–4.88 (m, 4H), 5.75–5.90 (m, 2H), 6.04 (d, J=7.5 Hz, 2H), 7.00 (dd, J_d=7.5, 7.5 Hz, 2H), 7.26–7.39 (m, 12H), 7.55–7.58 (m, 10H); ^{13}C NMR δ=21.1, 114.9, 121.2, 123.9, 127.6, 128.1, 129.7, 131.3, 131.3, 134.1, 134.3, 134.3, 135.5, 145.0, 172.5, 211.6; HRMS found *m/z* 648.2318, calcd for $C_{45}H_{36}OSi_2$: 648.2305.

2,5-Bis(allyldiphenylsilyl)-3,4-bis(hydroxymethyl)cyclopenta-2,4-dien-1-one (8h). Yellow oil. IR (neat) 3292, 1691, 1624, 1427, 1111 cm^{-1}; ^{1}H NMR δ=2.41 (d, J=7.9 Hz, 4H), 2.63 (bs, 2H), 4.08 (s, 4H), 4.17–4.88 (m, 4H), 5.70–5.85 (m, 2H), 7.24–7.44 (m, 12H), 7.53 (dd, J=1.6, 7.6 Hz, 8H); ^{13}C NMR δ=21.2, 58.1, 115.2, 128.1, 128.3, 129.9, 133.7, 134.0, 135.2, 171.3, 208.9; HRMS found *m/z* 584.2198, calcd for $C_{37}H_{36}O_3Si_2$: 584.2203.

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