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Note

Palladium-catalyzed Substitution Reaction of Allylic Derivatives with Tinacetylene†

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The substitution reaction of allylic derivatives (acetate, carbonate, and chloride) with tinacetylene proceeded in the presence of palladium as a catalyst to give a product having a 1-ene-4-yne system.

Key words: allylic substitution; tinacetylene; allylic derivatives; palladium catalyst

The palladium-catalyzed allylic substitution reaction by various nucleophiles has been thoroughly studied and has received wide application in organic synthesis.[1] There are many reports on the substitution reaction of allylic halides with organotin compounds such as vinyl, aryl and allyltins (so called Migita-Stille coupling).[2,3] To our knowledge, little describing the coupling reaction with tinacetylene has been reported in the literature.[4] Migita and Kosugi have reported that allyl chloride **A** (R=H) could be coupled with phenyltinacetylene to give 1-ene-4-yne compounds **B** (R=H) in a 32% yield.[5] Farina and co-workers have reported that coupling allylic chlorides **A** (R=Ph) with tinacetylene in the presence of trifurylphosphine (TFP) as a ligand did not give expected product **B** (R=Ph), but instead gave unusual product **C** in a quantitative yield.[6]

During our synthetic studies on cyclic enediyne compounds,[7] we have disclosed the Pd-catalyzed coupling reaction of allylic derivatives **1a–1c** (acetate, carbonate and chloride) with tinacetylene **2** to give normal coupling products **3** and **4** as a mixture (Scheme 2). Product **3** has been used as an intermediate for a dynemicin A model compound.[8] Attempted synthesis of the 10-membered ring by intramolecular Pd-coupling reactions failed.[9] We describe here details of an examination of the reaction conditions by using other allylic substrates which demonstrates the general usefulness of this reaction.

Tributylstannyl(trimethylsilyl)ethyne (**2**)[10] was chosen as tinacetylene because the silyl group in the product could be readily converted into a variety of substituents by acetylide or Pd coupling with suitable electrophiles. The allyl derivatives examined here are shown in Scheme 3. Substrates **5**, **8** and **10a–c** were prepared from the corresponding alcohol (R=OH)[11] by conventional methods (see the experimental section). Extensive examination of the reaction conditions, including the solvents, Pd catalyst, ligands, and the ratio of ligand to Pd, uncovered the fact that each substrate (**5**, **8** and **10**) could be converted to a 1-ene-4-yne compound under the most appropriate conditions listed in Table 1.

There have been few reports on Pd-coupling of allylic acetates with organotin compounds[3] because of their low reactivity. Stille and Hegedus have reported that coupling allylic acetates with various organotin compounds (alkyl, vinyl and aryl tins) proceeded with a Pd catalyst in the absence of a phosphine ligand ($Pd[dba]_2$, LiCl/DMF);[12] however, under such conditions, the reaction with tinacetylene **2** as the coupling partner did not proceed. As shown in Table 1, we found that a coupling reaction between allylic acetates (**5a**, **8a** and **10a**) and tin acetylene took place in a good to moderated yield when *N*-methyl pyrrolidone (NMP) was used as a solvent. In the case of **5a** and **10a**, the reaction gave a mixture of expected product **6** and **11** together with minor transposed product **7** or **12**, respectively. Although minor product **12** was obtained as a single stereoisomer, the relative stereochemistry could not be determined.

Methyl carbonates (**5b**, **8b** and **10b**)[13] have been used as the substrates for this coupling reaction under the same conditions as those for the allyl acetates, but the reaction proceeded only in the presence of LiCl (Table 1, entries 4–6).[14] In contrast to the case of allyl acetates, no solvent was essential for successful coupling of the allyl carbonates. In the case of **5b**, coupling conditions using dimethylfumarate (dmf)[15] in place of Ph_3P gave the best result (entry 4); on the contrary, in the case of the other carbonates (**8b** and **10b**), Ph_3P was found to be the better ligand.

Allyl chlorides (**5c**, **8c** and **10c**) were found to be the most reactive among the other allylic substrates tested here under conditions using dimethylfumarate (dmf) in place of Ph_3P as the ligand and benzene as the solvent[14] (entries 8, 10 and 11). In particular, these new conditions reduced the reaction period. Even functionalized a substrate such as **1c** or **10c** gave the best results under these conditions (entry 11). Although we examined the corresponding allyl phosphates ($X=OPO(OEt)_2$) as an alternative leaving group for this coupling reaction under various conditions, all attempts gave only low yields.

From the mechanistic point of view, the intermediate of this reaction seemed to be a π-allyl palladium complex. The proposed catalytic mechanism is depicted in

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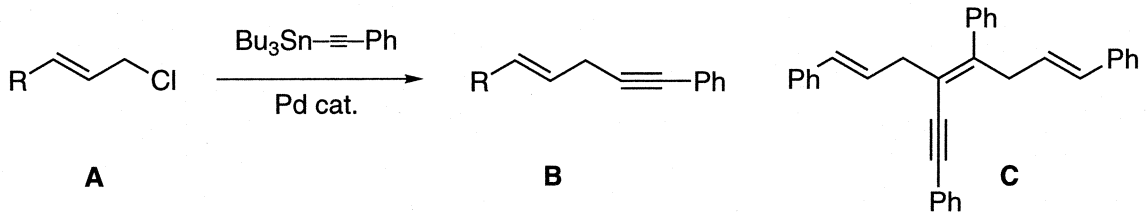
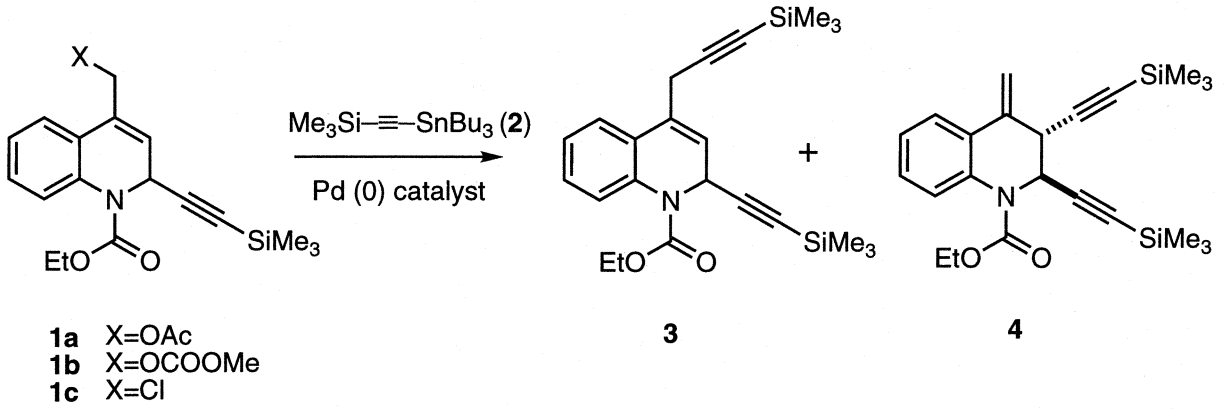
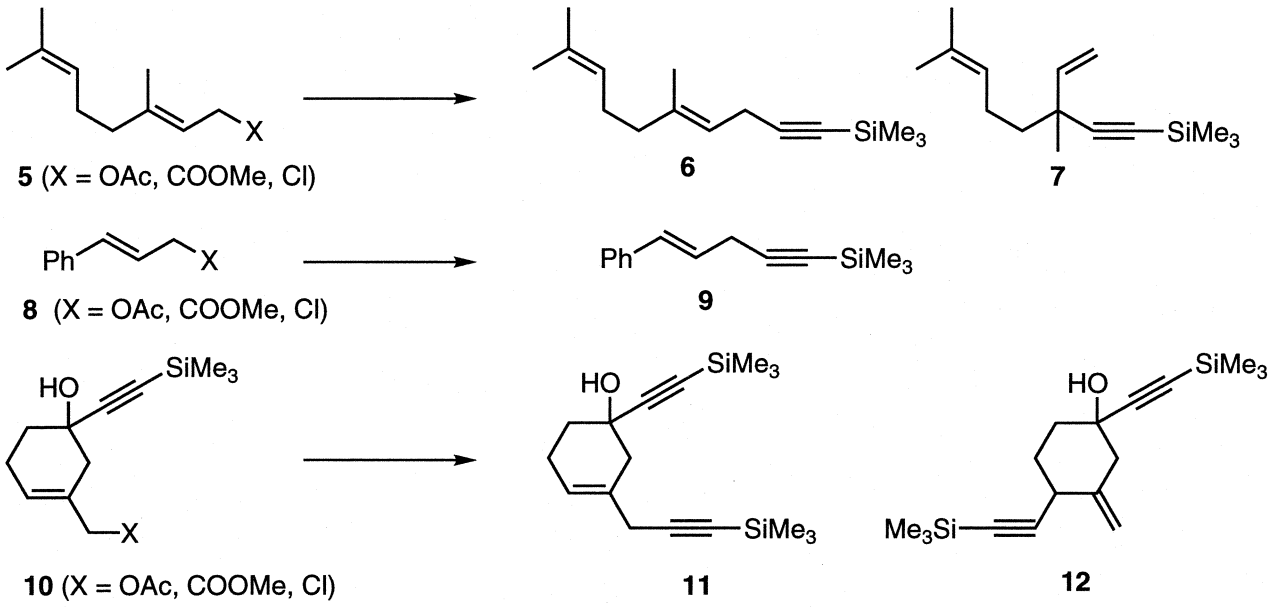


Scheme 1.



Scheme 2.



Scheme 3.

Scheme 4. It is proposed that the palladium(0) catalyst may oxidatively add to an allylic derivative to form a π-allyl palladium complex (**D**), which would be transmetallated with tinacetylene to give intermediate **E**. Finally, reductive elimination could generate a new C–C bond to give the desired product. This mechanism explains allylic transposition products **7** and **12**.

In summary, we identified the mild and neutral conditions for the coupling reaction between allylic derivatives and tinacetylene in the presence of a palladium catalyst. This reaction provides important synthetic intermediates not only for the synthesis of enediyne compounds, but also for other natural products having wide functionality.

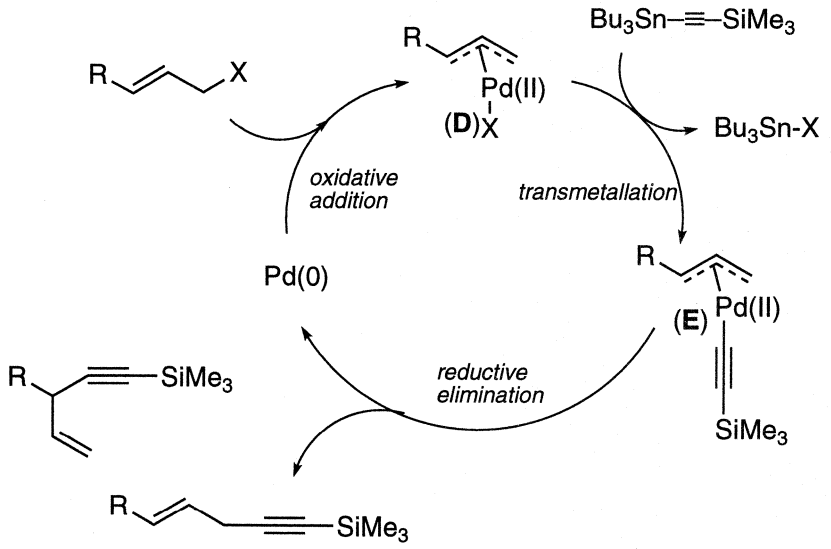
Experimental

Melting point (mp) data were recorded on a Yanaco MP-S3 melting point apparatus and are uncorrected. Infrared spectra were recorded with a JASCO FT/IR-8300 spectrophotometer and are reported in wave num-

Table 1. Palladium-catalyzed Coupling of Allylic Derivatives with Tinacetylene **2**

Entry	Substrate		Reagent[a]	Solvent	Temp., time	Products	Yield (ratio[b])
1	**5a**	X=OAc	Ph_3P (12 mol%)	NMP	80°C, 42 h	**6**, **7**	57 (15:1)
2	**8a**	X=OAc	Ph_3P (12 mol%)	NMP	50°C, 48 h	**9**	87
3	**10a**	X=OAc	Ph_3P (12 mol%)	NMP	85°C, 40 h	**11**, **12**	47 c
4	**5b**	X=OCOOMe	dmf (20 mol%), LiCl (2 eq)	PhH	60°C, 7 h	**6**, **7**	66 c
5	**8b**	X=OCOOMe	Ph_3P (12 mol%), LiCl (2 eq)	NMP	50°C, 44 h	**9**	43
6	**10b**	X=OCOOMe	Ph_3P (15 mol%), LiCl (2 eq)	THF	65°C, 8 h	**11**, **12**	24 c
7	**5c**	X=Cl	Ph_3P (12 mol%)	NMP	80°C, 12 h	**6**, **7**	61 (8:1)
8	**5c**	X=Cl	dmf (20 mol%)	PhH	60°C, 11 h	**6**, **7**	70 (17:1)
9	**8c**	X=Cl	Ph_3P (12 mol%)	NMP	60°C, 44 h	**9**	92
10	**8c**	X=Cl	dmf (20 mol%)	PhH	60°C, 4.5 h	**9**	60
11	**10c**	X=Cl	dmf (20 mol%)	PhH	50°C, 35 h	**11**, **12**	83 (22:1)

[a] Me_3Si-≡-$SnBu_3$ (1.1 eq), $Pd_2[dba]_3 \cdot CHCl_3$ (3–4 mol%).
[b] Determined by ^{1}H-NMR.
[c] Not determined.



Scheme 4. Proposed Catalytic Mechanism.

ber (cm^{-1}). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded with a JEOL EX-270 (270 MHz) spectrometer, and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded with a JEOL EX-270 (67.9 MHz) spectrometer. Optical rotation was measured by a JASCO DIP-370 digital polarimeter, and mass spectra (EI) were recorded by a JEOL JMS-D 100 spectrometer.

[3-(Trimethylsilylethynyl)-3-hydroxycyclohex-1(6)-enyl]methyl acetate (**10a**). A solution of 1-(trimethylsilylethynyl)-3-(hydroxymethyl)cyclohex-3-en-1-ol (575 mg, 2.56 mmol) in Ac_2O (5 ml) and pyridine (5 ml) was stirred at r.t. for 30 min. After diluting with toluene, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica (30 g), ether/hexane=1:2) to give acetate **10a** (679 mg, 99.5%). IR ν_{max} (KBr) cm^{-1}: 3420, 2961, 2166, 1741, 1251. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.15 (9H, s, $Si(CH_3)_3$), 1.86 (2H, t, J=6.5 Hz, C=CH-CH_2CH_2), 2.07 (3H, s, $OCOCH_3$), 2.18–2.30 (2H, m, C=C-CH_2-CH_2), 2.31 (1H, br d, J=17 Hz, C=C-CH_AH_B-C-OH), 2.47 (1H, br d, J=17 Hz, C=C-CH_AH_B-C-OH), 4.43 (1H, d, J=12 Hz, CH_AH_B-OAc), 4.49 (1H, d, J=12 Hz, CH_AH_B-OAc), 5.77 (1H, br s, olefinic). ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: −0.1, 20.8, 34.6, 40.2, 66.1, 68.1, 87.2, 108.9, 125.4, 129.3, 170.9. MS (EI) m/z: 266 (M^+), 248 (M-18), 206, 191. *Anal.* Found: C, 63.10; H, 8.43%. Calcd. for $C_{14}H_{22}O_3Si$: C, 63.12; H, 8.32%.

[3-(Trimethylsilylethynyl)-3-hydroxycyclohex-1(6)-enyl]methyl methoxyformate (**10b**). To a solution of 1-(trimethylsilylethynyl)-3-(hydroxymethyl)cyclohex-3-en-1-ol (560 mg, 2.49 mmol) in CH_2Cl_2 were added pyridine (0.72 ml, 8.92 mmol) and methyl chloroformate (0.34 ml, 4.46 mmol). After stirring at r.t. for 30 min, the reaction was quenched with 1N HCl, and the resulting mixture was extracted with CH_2Cl_2 (×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica (35 g), ether hexane=1:2) to give carbonate **10b** (705 mg, 100%). IR ν_{max} (KBr) cm^{-1}: 3462, 2960, 2164, 1752, 1445, 1280. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.15 (9H, s,

$Si(CH_3)_3$), 1.86 (2H, t, J=6 Hz, C=CH-CH_2), 2.25 (3H, m, C=CH-CH_2-CH_2-CH-OH), 2.32 (1H, br d, J=17 Hz, CH=C-$CH_A$$H_B$-CH-OH), 2.51 (1H, br d, J=17 Hz, CH=C-$CH_A$$H_B$-CH-OH), 3.78 (3H, s, OCH_3), 4.50 (1H, br d, J=12 Hz, $CH_A$$H_B$-OCOOMe), 4.55 (1H, br d, J=12 Hz, $CH_A$$H_B$-OCOOMe), 5.81 (1H, br s, olefinic). ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: −0.1, 22.8, 24.6, 40.2, 54.7, 66.0, 71.6, 87.3, 108.8, 126.2, 128.8, 155.6. MS (EI) m/z: 282 (M^+), 267 (M-15), 206, 191. *Anal.* Found: C, 59.61; H, 7.80%. Calcd. for $C_{14}H_{22}O_4Si$: C, 59.54; H, 7.85%.

1-(Trimethylsilylethynyl)-3-(chloromethyl)cyclohex-3-en-1-ol (**10c**). To a solution of 1-(trimethylsilylethynyl)-3-(hydroxymethyl)cyclohex-3-en-1-ol (1.12 g, 50 mmol) in CH_2Cl_2 (28 ml) were successively added DMAP (336 mg, 3.00 mmol), TsCl (1.14 g, 6.00 mmol) and Et_3N (0.69 ml, 5.00 mmol). After stirring at r.t. for 6.3 h, the mixture was concentrated to about 5 ml, and purified by column chromatography (silica (80 g), CH_2Cl_2) to give allyl chloride **10c** (1.06 g, 85%). IR ν_{max} (KBr) cm^{-1}: 3371, 2962, 2166, 1670, 1250. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.16 (9H, s, $Si(CH_3)_3$), 1.86 (2H, t, J=6 Hz, C=CH-CH_2-CH_2-), 2.26 (2H, m, C=CH-CH_2-), 2.39 (1H, br d, J=17 Hz, C(OH)-$CH_A$$H_B$-C=C), 2.59 (1H, br d, J=17 Hz, C(OH)-$CH_A$$H_B$-C=C), 4.01 (2H, br s, CH_2-Cl), 5.83 (1H, m, C=CH-). ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: −0.1, 23.6, 34.6, 40.5, 49.6, 66.3, 67.7, 108.7, 126.3, 130.8. MS (EI) m/z: 244 (M^+, ^{37}Cl), 242 (M^+, ^{35}Cl), 207 (M-Cl). *Anal.* Found: C, 59.28; H, 7.89%. Calcd. for $C_{12}H_{19}OSiCl$: C, 59.36; H, 7.89%.

Typical experimental procedure for entries 1–3, 7 and 9 in Table 1. In a two-necked flask equipped with an argon inlet, rubber septum and a magnetic stirring bar, $Pd_2[dba]_3 \cdot HCl_3$ (31 mg, 0.03 mmol) and Ph_3P (31 mg, 0.12 mmol) were dissolved in NMP (2 ml). The whole mixture was degassed three times and covered with argon. After stirring until the mixture became yellow, geranyl acetate **5a** (196 mg, 1.00 mmol) and tinacetylene **2** (425 mg, 1.10 mmol) in degassed NMP (3 ml) were added. The mixture was heated at 50–60°C for 20 h. After cooling to r.t., the mixture was poured into an ice-cold $NaHCO_3$ solution, and the resulting solution was extracted with ether (×3). The combined organic layers were successively washed with water (×2) and brine (×2), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (alumina (20 g), ether/hexane=1:10; and then silica (10 g), hexane→ether/hexane=1:40) to give **6** (102 mg, 44%) and **7** (8.2 mg, 3.5%).

Typical experimental procedure for coupling reactions in the presence of LiCl (entries 4–6 in Table 1). Carbonate **5b** (212 mg, 1.00 mmol), $Pd_2[dba]_3 \cdot HCl_3$ (31 mg, 0.030 mmol), dimethyl fumarate (21 mg, 0.15 mmol) and LiCl (84 mg, 2.0 mmol) were dissolved in THF (5 ml), and the mixture was stirred at r.t. for 15 min under an argon atmosphere. To this solution was added tinacetylene **2** (425 mg, 1.10 mmol). After stirring at 55°C for 7 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (alumina (25 g), hexane; and then silica (12 g), hexane) to give **6** and **7** (155 mg, 66%).

Typical experimental procedure for entries 8, 10 and 11 in Table 1. In a two-necked flask equipped with an argon inlet, a rubber septum, and a magnetic stirring bar were placed allyl chloride **10c** (1.06 g, 4.36 mmol), $Pd_2[dba]_3 \cdot CHCl_3$ (112 mg, 0.109 mmol), dimethyl fumarate (125 mg, 0.87 mmol) and benzene (20 ml). The whole mixture was degassed by three freeze-thaw cycles and then covered with argon. After stirring at r.t. for 1.5 h, tinacetylene **2** (1.85 g, 4.79 mmol) was added. The mixture was heated at 55°C for 17 h, and then concentrated under reduced pressure. The residue was purified by column chromatography (silica (150 g), ether/hexane=1:10) to give **11** (1.05 g, 80%) and **12** (48 mg, 3.6%).

(2E, 6E)-2,6-Dimethyldeca-2,6-dien-10-trimethylsilyl-9-yne (**6**). IR ν_{max} (KBr) cm^{-1}: 2962, 2175, 1459, 1376, 1250. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.15 (9H, s, $Si(CH_3)_3$), 1.60 (6H, br s, CH=C-CH_3 ×2), 1.68 (3H, br s, CH=C-CH_3), 1.96–2.14 (4H, m, C=CH-$CH_2$$CH_2$-C=C), 2.94 (2H, d, J=7 Hz, propargylic), 5.09 (1H, br t, J=7 Hz, olefinic), 5.18 (1H, br t, J=7 Hz, olefinic). ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: 0.1, 16.1, 17.7, 19.0, 25.7, 26.4, 39.4, 83.7, 106.0, 118.6, 124.0, 131.5, 137.3. *Anal.* Found: C, 76.81; H, 11.40%. Calcd. for $C_{15}H_{26}Si$: C, 76.84; H, 11.17%.

(6E)-3-(Trimethylsilylethynyl)-3,7-dimethylocta-1,6-diene (**7**). IR ν_{max} (KBr) cm^{-1}: 2960, 2111, 1458, 1376, 1249. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.17 (9H, s, $Si(CH_3)_3$), 1.26 (3H, s, CH_3-C-C≡C), 1.44 (2H, m, CH_2-C-CH_3), 1.55 (3H, s, CH_3-C=C), 1.68 (3H, s, CH_3-C=C), 2.04 (2H, m, C=CH-CH_2), 5.04 (1H, dd, J=10, 2 Hz, CH=$CH_A$$H_B$), 5.12 (1H, m, Me_2C=CH), 5.35 (1H, dd, J=17, 2 Hz, CH=$CH_A$$H_B$), 5.65 (1H, dd, J=17, 10 Hz, CH=CH_2).

(1E)-5-Trimethylsilyl-1-phenylpent-1-en-4-yne (**9**). IR ν_{max} (KBr) cm^{-1}: 2959, 2175, 1495, 1448, 1415, 1250. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.19 (9H, s, $Si(CH_3)_3$), 3.17 (2H, dd, J=5.5, 1.5 Hz, allylic), 6.15 (1H, dt, J=16, 5.5 Hz, Ph-CH=CH), 6.63 (1H, dt, J=16, 1.5 Hz, Ph-CH=CH), 7.17–7.39 (5H, m, aromatic). ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: 0.1, 23.4, 87.1, 103.6, 124.0, 126.3, 127.3, 128.5, 131.4, 137.8. MS (EI) m/z: 214 (M^+), 199 (M-15). HR-MS (EI) for $C_{14}H_{18}Si$ (M^+): calcd., 214.1177; found, 214.1179.

1-Trimethylsilylethynyl-3-[3-trimethylsilyl-prop-2'-ynyl]cyclohex-3-en-1-ol (**11**). IR ν_{max} (KBr) cm^{-1}: 3422, 2956, 2176, 1250. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.16 (9H, s, $Si(CH_3)_3$), 0.17 (9H, s, $Si(CH_3)_3$), 1.84 (2H, t, J=6 Hz, C(OH)-CH_2-CH_2-), 2.18–2.32 (3H, m, C(OH)-CH_2-CH_2- & CH=C-$CH_A$$H_B$), 2.47 (1H, br d, J=16 Hz, CH=C-$CH_A$$H_B$), 2.90 (2H, br s, C≡C-

CH_2–), 5.71 (1H, m, olefinic). ^{13}C-NMR (67.9 MHz, $CDCl_3$) δ: −0.1, 0.1, 23.0, 27.9, 35.0, 42.4, 66.7, 87.1, 87.2, 103.5, 109.0, 121.6, 128.8. MS (EI) *m/z*: 304 (M^+), 289 (M-15). HR-MS (EI) for $C_{17}H_{28}OSi_2$ (M^+): calcd., 304.1678; found, 304.1670.

1,4-Bis[trimethylsilylethynyl]-3-methylenecyclohexan-1-ol (**12**). IR ν_{max} (KBr) cm^{-1}: 3419, 2961, 2170, 1250. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.15 (9H, s, $Si(CH_3)_3$), 0.16 (9H, s, $Si(CH_3)_3$), 1.70–2.10 (4H, m, $CH_2 \times 2$), 2.44 (1H, br d, J=13.5 Hz, CH_AH_B), 2.67 (1H, br d, J=13.5 Hz, CH_AH_B), 3.07 (1H, m, C≡C-C*H*), 4.91 (1H, br s, olefinic), 5.22 (1H, br s, olefinic). MS (EI) *m/z*: 304 (M^+), 289 (M-15). HR-MS (EI) for $C_{17}H_{28}OSi_2$ (M^+): calcd., 304.1678; found, 304.1672.

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