Regio- and Chemoselective Coupling of Polyalkynes: A Convenient Access to Polyarylacetylenes and Polyenynes

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Mono- or disilylated α,ω-diynes and disilylated triynes can be regioselectively homologated at each acetylenic end, silylated or not, by two and three, respectively, successive Pd/Ag-catalyzed coupling reactions. Each coupling being selective either for terminal alkyne, trimethylsilylalkyne or for trialkylsilylalkyne, the combination of these coupling methods offers a unique and rapid access to polyunsaturated compounds.

Introduction

The rapid construction of polyunsaturated systems is of prime importance for material science[1] and to a less extend for natural products chemistry.[2] The elaboration of regular arrays of triple and double bonds is indeed often required as core or building blocks for organic materials, especially for molecular electronics,[1,3] nonlinear optic applications[1,4] and organic crystals assemblies.[5] Such building blocks are often obtained through cross-coupling reactions. However, nonsymmetrical structures cannot easily be obtained through classical methods, and their constructions usually require multi-step sequences involving protection–deprotection steps.[1–5] Avoiding such tedious steps would be interesting. Moreover, building up molecules over di- or tritopic compounds from either side in a controlled manner would be an interesting and efficient way towards organic crystals or organic-based materials, especially electronic devices.

Based on mechanistic considerations and on solving synthetic problems related to enediyne antibiotics,[6,7] we developed several new methods for the synthesis of conjugated enynes. These methods rely on the coupling of vinyl triflates with either free alkynes,[7] 1-(trimethylsilyl)alkynes[8] or 1-(trialkylsilyl)alkynes.[9] Here we demonstrated that these coupling methods are in fact *orthogonal*, each one being selective for one kind of alkynes. Thus, each kind of acetylenic end could be selectively elongated by one of our specifically designed cross-coupling reactions, enabling for the oriented construction of polytopic enyne or arylyne systems (Figure 1). Applied to polyacetylenic compounds protected or not by trimethylsilyl and/or trialkylsilyl groups, we were indeed able to successively and selectively couple each acetylenic end.

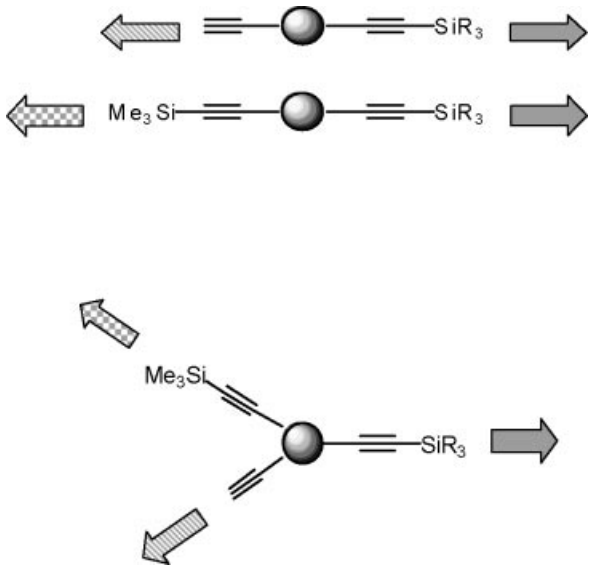

Figure 1. The different arrows indicate that each kind of acetylenic end could be independently elongated through a specific cross-coupling reaction.

Results and Discussion

The oriented synthesis of ditopic arylynes or enynes can be achieved through two routes including each two steps. The first approach is based on two successive coupling reactions onto 1-silylated 1,ω-diynes. The latter can easily be coupled at their free acetylenic end with different aryl or vinyl triflates or halides using various Sonogashira coupling conditions,[10] including ours (Scheme 1).[7–9]

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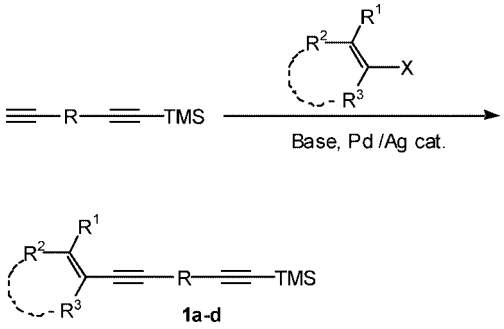
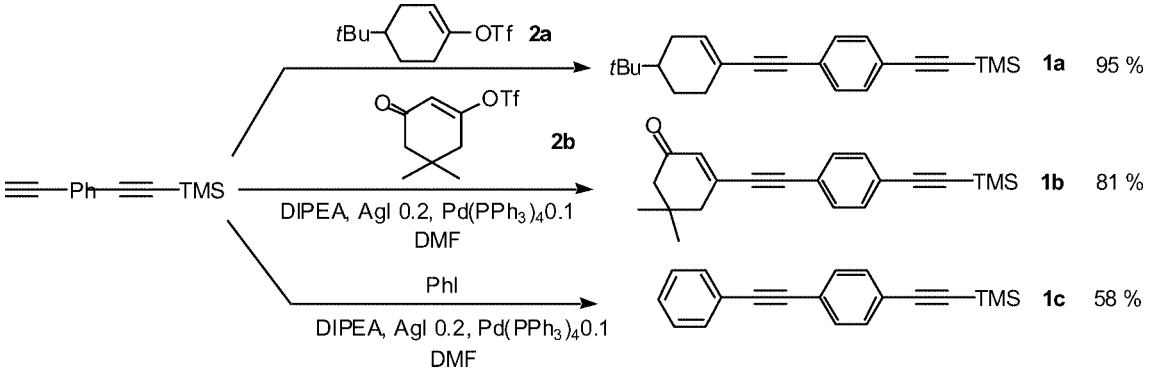


Scheme 1.

For example, compounds **1a**–**c** have been obtained by coupling 1-ethynyl-4-(trimethylsilylethynyl)benzene with the vinyl triflates derived from 4-*tert*-butylcyclohexene (**2a**)[11] or dimedone (**2b**)[12] or with phenyl iodide (Scheme 2).

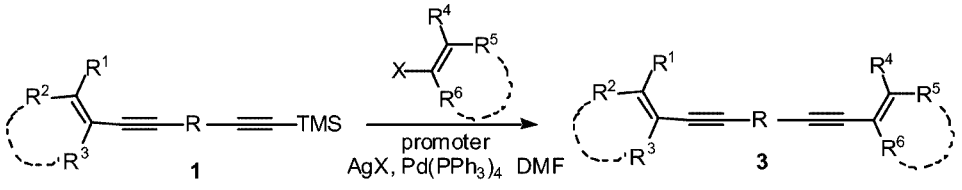
Instead of deprotecting the untouched silylated acetylenic end and performing another coupling reaction, we found that the so obtained (trimethylsilyl)acetylenes **1** can then be directly homologated with either aryl iodides or vinyl triflates (Table 1).

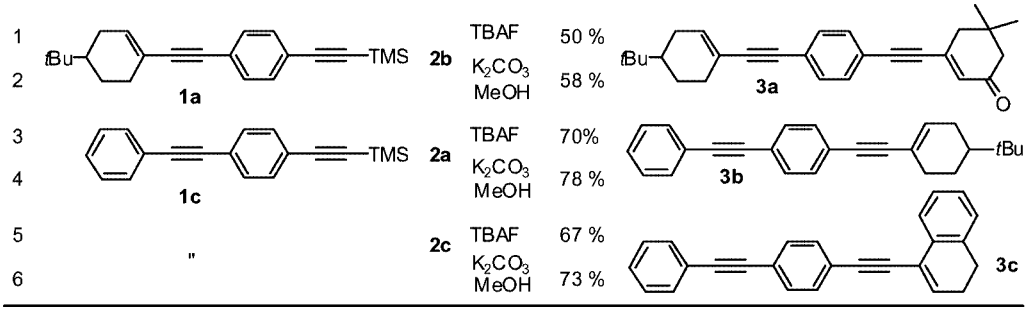
Two set of conditions could be used for converting **1** to the corresponding bis(enynes) **3**: The promoter required to initiate the Pd/Ag-catalyzed coupling reaction could be either the commercially available salt tetrabutylammonium fluoride trihydrate[9] or a combination of carbonate salt and methanol.[8] Typical examples are provided by the coupling of **1a** and **1c**. Compound **1a** smoothly reacted with the vinyl triflate **2b**, yielding the expected 1,4-bis(enynyl)benzene derivative **3a** whatever the conditions used (Table 1, Entries 1–2). However, the product was quite sensitive and decomposed under both conditions, but nevertheless, it could be isolated in reasonable yields. Compound **1c** was conveniently converted into the highly conjugated aryl enediynes **3b**–**c** in good yields through coupling with the vinyl triflate **2a** or the triflate derived from tetralone (**2c**)[13] (Table 1, Entries 3, 4 and 5, 6, respectively).



Scheme 2.

Table 1. Yields given for pure isolated products; a) TBAF = nBu$_4$NF·3H$_2$O; b) conditions: nBu$_4$NF·3H$_2$O 1.5 equiv., AgI 0.2 equiv., [Pd(PPh$_3$)$_4$] 0.1 equiv., DMF, room temp.; c) conditions: K$_2$CO$_3$ 4 equiv., MeOH 4 equiv., AgCl 0.2 equiv., [Pd(PPh$_3$)$_4$] 0.1 equiv., DMF, room temp.





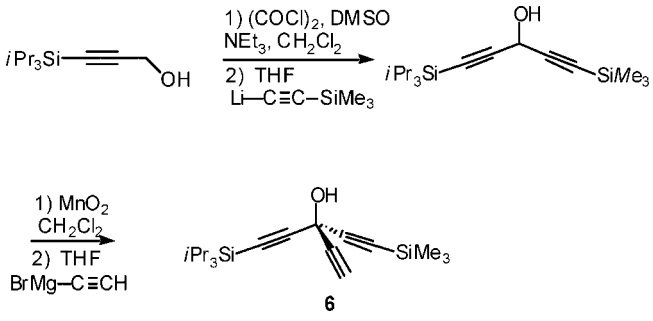
In the second and more innovative approach, bis(acetylenic) compounds bearing two different kinds of silyl groups at their acetylenic ends, e.g. **4**, could be specifically coupled at one end using the appropriate coupling method. Indeed, the 1-(triisopropylsilyl)ethynyl-4-[(trimethylsilyl)ethynyl]-benzene (**4a**)[14] or its aliphatic analog **4b** can thus be directly coupled at their TMS ends using the potassium carbonate–methanol method[8] (Table 2). With different vinyl triflates, the expected enynes **5a**–**b**, **5d**–**e** were always obtained very cleanly and in excellent yields (Entries 1–2, 5,6). However, with aryl iodides, these coupling conditions proved to be less efficient and for example, **5c** was obtained in around 50% (Entry 3). A screening of bases showed that the coupling efficiency could be restored by replacing potassium carbonate by cesium carbonate (Entry 4 vs. 3), yielding **5c** with 83%.

The so obtained 1-triisopropylsilyl acetylenic derivatives **5** could then be directly homologated at their triisopropylsilyl end using the TBAF coupling method[9] (Table 3). In these conditions, the 1-(triisopropylsilyl)ethynyl-4-(phenylethynyl)benzene (**5c**) reacted quantitatively with the *para*-nitrophenyl iodide yielding the highly conjugated polyarylacetylenic derivative **3d**[15] (Entry 1). **5c** also reacted very efficiently with various vinyl triflates such as **2a** and **2c** giving the corresponding arylenynes **3b**–**c,** respectively, in excellent yields (Entry 2 and 3 respectively).

To illustrate the versatility of the methods, **3c** was also prepared from **5a** by coupling with phenyl iodide (Entry 4). It is worth to note that **3a**–**c** have also been prepared starting from the corresponding 1-trimethylsilyl-1,ω-diyne (see Table 1, Table 2). The same compound can thus be obtained through different sequences of coupling *using the appropriate method at each step.* Whatever the route, only two steps suffice to get compounds, which can be used as molecular wired, organic diodes or NLO devices.[1–4]

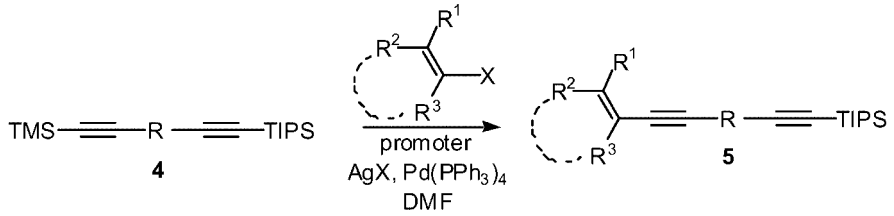
To demonstrate further the usefulness of our methods, and as a step toward organic transistors, we prepared a tritopic triyne, and we selectively elongated it at each acetylenic end by coupling reactions.

The disilylated triyne **6** was obtained by successive oxidation and alkynylation starting from the readily available 3-(triisopropylsilyl)propynol (Scheme 3).[16]



Scheme 3.

Table 2. Yields given for pure isolated products; conditions: K_2CO_3 4 equiv., MeOH 4 equiv., AgCl 0.2 equiv., $Pd(PPh_3)_4$ 0.1 equiv., DMF, room temp., except for Entry 4 where K_2CO_3 was replaced by Cs_2CO_3.



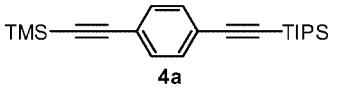
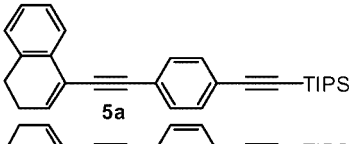
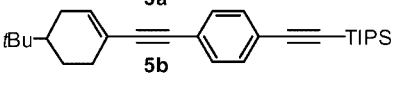
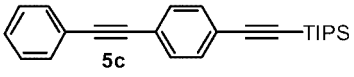
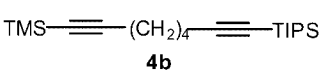
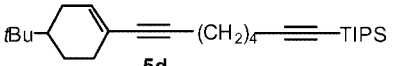
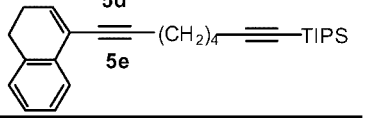
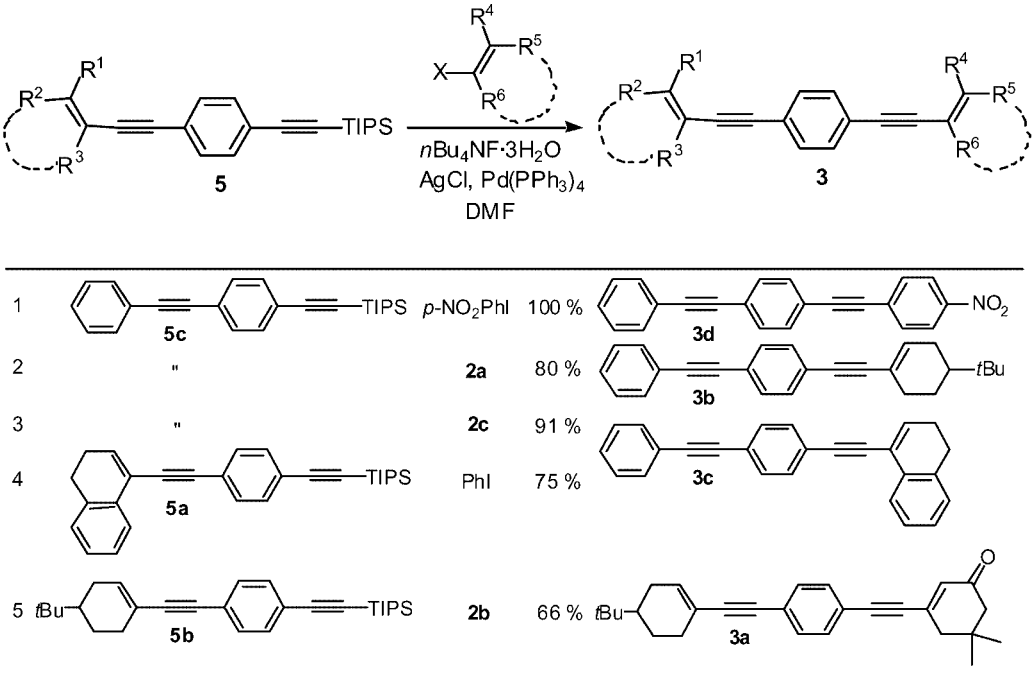
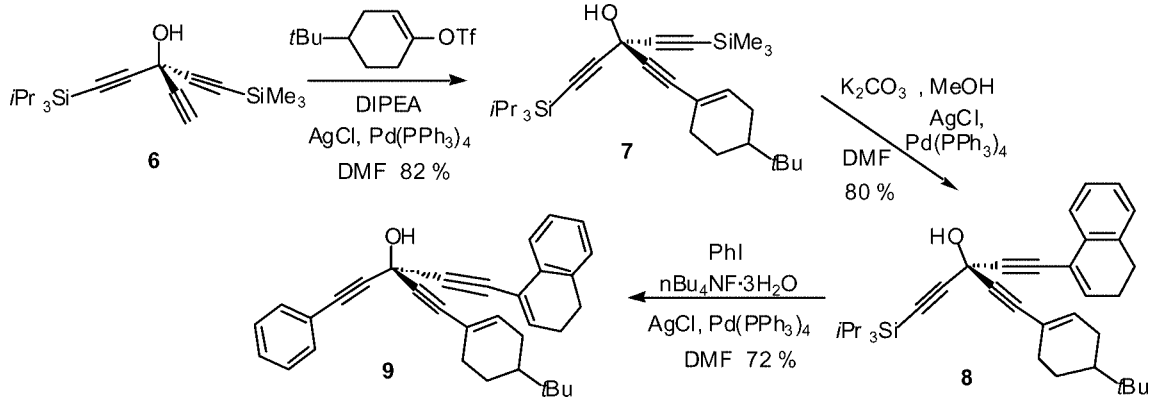
1		**4a**	**2c**	K_2CO_3 MeOH	87 %	 **5a**
2	"		**2a**	K_2CO_3 MeOH	86 %	 **5b**
3	"		PhI	K_2CO_3 MeOH	47%	 **5c**
4	"		PhI	Cs_2CO_3 MeOH	83 %	
5		**4b**	**2a**	K_2CO_3 MeOH	87 %	 **5d**
6	"		**2c**	K_2CO_3 MeOH	95 %	 **5e**

Table 3. Yields given for pure isolated products; conditions: nBu$_4$NF·3H$_2$O 1.5 equiv., AgI 0.2 equiv., Pd(PPh$_3$)$_4$ 0.1 equiv., DMF, room temp.



Compound **6** was engaged in a coupling reaction with **2a** using DIPEA as a base and [Pd(PPh$_3$)$_4$] and AgCl as catalysts.[7] The expected enetriyne **7** was cleanly obtained in good isolated yield. The TMS and TIPS ethynyl groups remained unaffected as shown by their typical signals in the ^{1}H and ^{13}C NMR spectra of **7** (δ = 0.18 and –0.48 ppm for TMS; 1.08, 11.2 and 18.5 ppm for TIPS). Using the potassium carbonate–methanol coupling method,[8] **7** was then specifically coupled at its trimethylsilyl acetylenic end, furnishing **8** in good yield. This compound exhibited in its ^{1}H NMR spectrum the characteristic signal of the enyne moieties (δ = 6.05 and 6.52 ppm) and the set of signals typical of the triisopropylsilyl acetylenic unit (δ = 11.2 and 18.5 ppm, 84.5 and 104.6 ppm). This remaining acetylenic unit was then directly substituted by a phenyl group through coupling using our TBAF method,[9] providing the differentiated trienyne **9** in good overall yield (Scheme 4).

In conclusion, we have demonstrated that mono- or disilylated diynes and disilylated triynes can be regioselectively homologated at each acetylenic end by respectively two and three successive Pd/Ag-catalyzed coupling reactions using the appropriate conditions. The combination of these coupling methods offers thus a unique and rapid access to polyunsaturated compounds, which could be used as molecular electronic devices. Further works toward such devices are now in progress.



Scheme 4.

Experimental Section

General: All experiments have been carried out under inert gas. Common reagents and materials were purchased from commercial sources. Thin layer chromatography has been performed on silica gel from Merck, Art. 7748 Kieselgel 60 PF_{254}. The column chromatography has been carried out with Merck Art. 9385 Kieselgel 60 (0.04–0.06). The solvents used for the column chromatography have been distilled before use. The NMR spectra were recorded with a Bruker Avance 300 spectrometer, with working frequencies of 300 MHz for ^1H and 75.43 MHz for ^{13}C NMR spectroscopy. Chemical shifts δ are expressed relative to internal TMS for ^1H NMR spectra, ^{13}C NMR spectra are referenced to $CDCl_3$ (δ = 77.0 ppm). The coupling constants J are given in Hz. The multiplets have been indicated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), m (multiplet). The infrared spectra were recorded with Fourier Transform Spectrafile IR™ Plus as film on NaCl slides or as KBr pellets, $\tilde{\nu}$ is given in cm^{-1}. Mass spectra have been recorded with a Fisons Autospec apparatus using positive FAB ionisation. Elementary analysis were realised by the elementary analysis service at the Université Louis Pasteur, Strasbourg I.

A: Vinyl Triflates: 4-*tert*-Butylcyclo-1-hexenyl Trifluoromethanesulfonate (**2a**), 4,4-dimethyl-3-oxocyclohex-1-enyl trifluoromethanesulfonate (**2b**) and 3,4-dihydronaphtalen-1-yl trifluromethanesulfonate (**2c**) have been prepared according to ref.[11–13].

B: Starting Diynes: 1-(Triisopropylethynyl)-4-(trimethylsilylethynyl)benzene (**4a**) has been obtained according to ref.[11].

1-(Triisopropylsilyl)-8-(trimethylsilyl)octa-1,7-diyne (4b): 1-Trimethylsilyl-1,7-octadiyne[17] (1.78 g, 10 mmol) was dissolved in THF and cooled to –78 °C. Butyllithium (1.25 M soln. in hexane, 0.76 mL, 0.95 equiv.) was slowly added via syringe. The solution was stirred for ten minutes and then TIPSCl (1.92 g, 1 equiv.) was added. The mixture was warmed to room temperature. An aqueous solution of NH_4Cl was added and the phases were separated. The aqueous layer was extracted three times with diethyl ether and the combined organic phases are dried with $MgSO_4$. After evaporation of the solvents, the crude product purified via column chromatography (pentane 100%). ^1H NMR ($CDCl_3$): δ = 0.07 (s, 9 H, TMS), 1.00 (s, 21 H, TIPS), 1.54 (m, 4 H, H4,5), 2.19 (t, J = 3.7 Hz, 4 H, H3,6) ppm. ^{13}C NMR ($CDCl_3$): δ = 0.06 (TMS), 15.2 (TIPS), 18.6 (TIPS), 19.3 (C3, 6), 27.5 (C4), 27.6 (C5), 80.4 (C1), 84.6 (C8), 107.0 (C7), 108.5 (C2) ppm.$C_{20}H_{38}Si_2$ (343.68): calcd. C 71.77, H 11.44; found C 71.79, H 11.50.

C: General Procedure for the Successive Pd/Ag-Catalyzed Coupling Reactions. Pd/Ag-Catalyzed Coupling of Terminal Alkynes: The vinyl triflate (0.5 mmol) was dissolved in 10 mL anhydrous and degassed DMF under argon. [$Pd(PPh_3)_4$] (0.1 equiv.) and AgCl (0.2 equiv.) were added, followed by DIPEA (1.2 equiv.). The mixture was stirred for five minutes and the alkyne, dissolved in 2 mL of DMF (1.1 equiv.) was added through a syringe. Once the starting material had disappeared as judged by TLC, of diethyl ether (10 mL) was added, followed by 10 mL of water. The mixture was filtered through Celite. The aqueous layer was extracted three times with ether, the combined organic layers were washed three times with water to remove DMF. The organic phase was then dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified over a silica gel column to give the pure product.

Pd/Ag-Catalyzed Coupling of 1-(Trimethylsilyl)alkynes: The vinyl triflate (0.5 mmol) was dissolved in 10 mL anhydrous and degassed DMF under argon. [$Pd(PPh_3)_4$] (0.1 equiv.) was added and then AgCl (0.2 equiv.). K_2CO_3 (4 equiv.) was added as a solid and methanol was added through a microsyringe. The mixture was stirred for five minutes in the dark and the alkyne (1.1 equiv.), dissolved in 2 mL of DMF was added through a syringe. Once the starting material had disappeared as judged by TLC, diethyl ether (10 mL) was added, followed by 10 mL of water. The mixture was filtered through Celite and the phases were separated. The aqueous layer was extracted three times with diethylether, the combined organic layers were washed three times with water to remove DMF. The organic phase was dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was passed over a silica gel column to give the pure product.

Pd/Ag-Catalyzed Coupling of 1-(Trialkylsilyl)alkynes: The vinyl triflate (0.5 mmol) was dissolved in 10 mL anhydrous and degassed DMF under argon. [$Pd(PPh_3)_4$] (0.1 equiv.) and AgCl (0.2 equiv.) were added. The trialkylsilyl alkyne (1.1 equiv.) was dissolved in 2 mL of DMF and added through a syringe. Then, TBAF was dissolved in 5 mL DMF and added to the reaction mixture. The mixture was stirred in the dark until the starting material had disappeared according to TLC. Diethyl ether (10 mL) was added, followed by 10 mL of water. The mixture was filtered through Celite and the phases were separated. The aqueous layer was extracted three times with diethyl ether, the combined organic layers were washed three times with water to remove the DMF. The organic phase was dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified over a silica gel column to give the pure product.

1-(4-*tert*-Butylcyclohexenyl)ethynyl-4-(trimethylsilylethynyl)benzene (1a): M.p. 118–120 °C. ^1H NMR ($CDCl_3$): δ = 0.25 (s, 9 H, TMS), 0.87 (s, 9 H, *t*Bu), 1.05–1.32 (m, 2 H, H3,5), 1.76–1.91 (m, 2 H, H3,6), 2.04–2.15 (m, 3 H, H4,6), 5.98 (m, 1 H, H2), 7,31–7,35 (m, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = 0.0 (TMS), 22.4 (C5), 27.2 (*t*Bu), 27.6 (C3), 30.9 (C6), 32.2 (*t*Bu), 43.3 (C4), 86.3 (C≡*C*–Si), 89.1 (C≡C–Ar), 92.3 (C≡C), 104.6 (*C*≡C–Si), 120.45 (C1), 123.1, 123.9, 131.3, 131.9 (C_{ar}), 136.2 (C2) ppm. MS: m/z = 334 [M^+], 270, 255, 225, 120, 73, 57. HRMS ($C_{23}H_{30}Si$): found 334.2071, calcd. 334.2116.

1-(4,4-Dimethyl-3-oxocyclohex-1-enylethynyl)-4-(trimethylsilylethynyl)benzene (1b): ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 9 H, TMS), 1.08 (s, 6 H, Me), 2.28 (s, 2 H, H6), 2.41 (d, J = 1.4 Hz, 2 H, H4), 6.28 (t, J = 1.4 Hz, 1 H, H2), 7.40–7.47 (m, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = 0.03 (TMS), 28.1 (Me), 32.2 (C5), 43.2 (C6), 51.1 (C4), 89.6 (C≡*C*–Si), 90.1 (C≡*C*–C1), 99.1 (*C*≡C–C1), 104.6 (*C*≡C–Si), 121.0, 125.0 (C_{ar}), 131.4 (C2), 131.4, 131.8 (C_{ar}), 141.0 (C1), 198.9 (C3) ppm. MS: m/z = 320 (85) [M^+], 305 (100), 264, (14), 249 (22). HRMS ($C_{21}H_{24}OSi$): calcd. 320.5002, found 320.4987.

1-[(4-*tert*-Butylcyclohexenyl)ethynyl]-4-(4,4-dimethyl-3-oxohex-1-enylethynyl)benzene (3a): M.p. 132–134 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 9 H, *t*Bu), 1.08 (s, 6 H, Me), 1.15–1.29 (m, 2 H, H4,6), 1.83–1.95 (m, 2 H, H3,6), 2.15–2.27 (m, 3 H, H3,5), 2.28 (s, 2 H, H6′), 2.41 (d, J = 1.4 Hz, 2 H, H4′), 6.23 (m, J = 2.3 Hz, 1 H, H2), 6.28 (t, J = 1.4 Hz, 1 H, H2′), 7.39 (s, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.3 (C5), 27.6 (*t*Bu), 28.0 (C3), 28.1 (Me), 30.6 (C6), 32.2 (C5′), 33.8 (*t*Bu), 43.2 (C6′), 44.3 (C4), 51.1 (C4′), 86.6 (C≡*C*–C1), 90.1 (C≡*C*–C1′), 93.8 (*C*≡C–C1), 99.1 (*C*≡C–C1′), 120.3 (C1), 121.0, 125.0, 131.4 (C2′), 131.4, 131.8, 136.5 (C2), 141.0 (C1′), 198.9 (C3′) ppm. MS: m/z = 384.245 [M^+]. $C_{28}H_{32}O$ (384.55): calcd. C 87.45, H 8.39, O 4.16; found C 87.99, H 8.25, O 3.95.

1-[(4-*tert*-Butylcyclohexenyl)ethynyl]-4-(phenylethynyl)benzene (3b): M.p. 128–130.5 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 9 H, *t*Bu), 1.14–1.30 (m, 2 H, H3,5), 1.83–1.95 (m, 2 H, H3,6), 2.14–

2.28 (m, 3 H, H4,6), 6.22 (m, J = 2.4 Hz, 1 H, H2), 7.32–7.35 (m, 3 H, H_{ar}), 7.38 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.4 Hz, 2 H, H_{ar}), 7.49–7.53 (m, 2 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.79(C5), 27.12 (*t*Bu), 27.58 (C3), 30.67 (C6), 32.20 (*t*Bu), 43.20 (C4), 86.81(C≡C–C), 89.22 (C≡C–C), 90.92 (C≡C–Ar), 92.97 (C≡C–Ar), 120.41 (C1), 122.46, 123.11, 123.68, 128.36, 131.34, 131.42, 131.59 (C_{ar}), 136.04 (C2) ppm. MS: m/z = 338 (100) [M^+], 295 (7), 281 (14), 254 (44), 215 (6), 189 (3). $C_{26}H_{26}$ (338.48): calcd. C 92.0, H 7.85; found C 92.26, H 7.74.

1-(3,4-Dihydronaphthylethynyl)-4-(phenylethynyl)benzene (3c): ^{1}H NMR ($CDCl_3$): δ = 2.36 (dt, J = 4.8, J = 8.1, 2 H, H3), 2.77 (t, J = 8.1, 2 H, H4), 6.50 (d, J = 4.8, 1 H, H2), 7.00–7.64 (m, 9 H, H_{ar}), 7.28 (d, J = 9.3, 2 H, H_{ar}), 7.45 (d, J = 9.3, 2 H, H_{ar}) ppm. ^{13}C ($CDCl_3$): δ = 22.8 (C3), 27.1 (C4), 89.0, 89.2, 90.0, 91.1(*C*≡*C*), 122.3 (C_{ar}), 122.9 (C3′), 125.0 (C1′), 125.6, 126.1, 126.7, 127.5, 127.8, 128.1, 128.4, 131.51, 132.4, 134.2 (C_{ar}), 136.0 (C2), 137.46 (C_{ar}) ppm. $C_{30}H_{30}$ (390.56): calcd. C 94.51, H 5.49; found C 94.77, H 5.55.

1-(3,4-Dihydronaphthyl)ethynyl-4-(triisopropylsilylethynyl)benzene (5a): ^{1}H ($CDCl_3$): δ = 1.05 (s, 21 H, TIPS), 2.76 (t, J = 8.11 Hz, 2 H, H4), 2.36 (dt, J = 4.8, J = 8.1 Hz, 2 H, H3), 6.50 (t, J = 4.8 Hz, 1 H, H2), 7.28 (d, J = 9.3 Hz, 2 H, H3,5), 7.45 (d, J = 9.3 Hz, 2 H, H2,6), 7.00–7.25 (m, 4 H, H6, 7, 8, 9). ^{13}C NMR ($CDCl_3$): δ = 11.3 (TIPS), 18.7 (TIPS), 27.1 (C3), 40.8 (C4), 88.8 (C≡*C*–Si), 89.7 (C≡*C*–C), 92.3 (*C*≡C–C), 106.3 (*C*≡C–Si), 122.0 (C_{ar}), 125.0 (C1), 126.6, 126.7, 127.4, 127.6(C_{ar}), 131.3 (C2), 131.7, 134.3, 136.0, 137.9, 150.3 (C_{ar}) ppm. $C_{29}H_{34}Si$ (410.67): calcd. C 84.82, H 8.34; found C 84.55, H: 8.40.

1-(4-*tert*-Butylcyclohexenylethynyl)-4-(triisopropylethynyl)benzene (5b): M.p. 118–120 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (s, 9 H, *t*Bu), 1.11 (s, 21 H, TIPS), 1.05–1.32 (m, 2 H, H3,5), 1.76–1.91 (m, 2 H, H3,6), 2.04–2.15 (m, 3 H, H4,6), 5.98 (m, 1 H, H2) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.3 (TIPS), 18.5 (TIPS), 22.4 (C5), 27.2 (*t*Bu), 27.6 (C3), 30.9 (C6), 32.2 (*t*Bu), 43.3 (C4), 88.3 (C≡*C*–Si), 89.1 (C≡C–Ar), 92.3 (C≡C), 106.2 (*C*≡C–Si), 120.45 (*C*1), 123.1, 123.9, 131.3, 131.9 (C_{ar}), 136.2 (*C*2) ppm. MS: m/z = 418.311 [M^+], $C_{29}H_{42}Si$ (418.31): calcd. C 83.18, H 10.11; found C 82.85, H 10.15.

4-(Phenylethynyl)1-(triisopropylsilylethynyl)benzene (5c): ^{1}H NMR ($CDCl_3$): δ = 1.11 (s, 21 H, TIPS), 7.16–7.37 (m, 9 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.3 (TIPS), 18.7 (TIPS), 88.1 (*C*≡C–Ar), 88.9 (*C*≡C–Si), 92.5 (C≡*C*–Ar), 105.6 (C≡*C*–Si), 123.9, 125.5, 126.3, 130.2, 130.8, 133.9, 134.7 (C_{ar}) ppm. $C_{25}H_{30}Si$ (358.59), MS: 358 [M^+], 269, 255, 241, 225, 183, 120.

1-(4-*tert*-Butylcyclohex-1-enyl)-8-(triisopropylsilyl)-1,7-octadiyne (5d): ^{1}H NMR ($CDCl_3$): δ = 0.81 (s, 9 H, *t*Bu),1.00 (s, 21 H, TIPS), 1.05–1.24 (m, 3 H, H3′,5′), 1.54 (m, 4 H, H4,5), 1.68–1.87 (m, 2 H, H3′,6′), 1.93–2.09 (m, 2 H, H4′,6′), 2.19 (t, J = 3.7 Hz, 2 H, H6), 2.44 (t, J = 6.7 Hz, 2 H, H3), 5.97 (t, 1 H, J = 1.5, H2) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.2 (TIPS), 18.6 (TIPS), 18.9 (C3), 19.3 (C6), 23.9 (C5), 27.2 (*t*Bu), 27.3 (C3), 27.5 (C6), 31.0 (C_4), 31.2 (C5), 32.2 (*t*Bu), 43.4 (C4), 80.4 (C≡*C*–Si), 84.7 (C≡*C*–C), 86.9 (*C*≡C–C), 108.5 (*C*≡C–Si), 120.9 (C1), 133.4 (C2′) ppm. IR: $\tilde{\nu}$ 3052, 2959, 2253, 2171, 1422, 1265, 1047 cm^{-1}. MS: 398 [M^+], 355, 334, 291, 249, 207, 175, 129. HRMS $C_{27}H_{46}Si$: calcd. 398.3368, found 398.3357.

1-(3,4-Dihydronaphtyl)-8-(triisopropylsilyl)-1,7-octadiyne (5e): ^{1}H NMR ($CDCl_3$): δ = 1.00 (s, 21 H, TIPS), 1.54 (m, 4 H, H4,5), 2.19 (t, J = 3.7 Hz, 2 H, H6), 2.37 (dt, J = 7.9, J = 4.8 Hz, 2 H, H3′), 2.44 (t, J = 6.7 Hz, 2 H, H3), 2.79 (t, J = 7.9 Hz, 2 H, H4′), 6.38 (t, J = 4.8 Hz, 1 H, H2′), 7.08–7.28 (m, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.2 (TIPS), 18.6 (TIPS), 19.1 (C3), 19.5 (C6), 22 (C5), 23.5 (C4), 27.2 (C3′), 31.0 (C4′), 78.3 (C≡*C*–C), 84.1 (C≡*C*–Si), 91.1 (*C*≡C–C), 108.7 (*C*≡C–Si), 125.0 (C_{ar}), 126.4 (C1′), 127.2, 127.3 (C_{ar}), 133.2 (*C*2′), 133.8 (C_{ar}), 135.1 (C_{ar}) ppm. $C_{27}H_{38}Si$ (390.67): calcd. C 83.01, H 9.80; found C 82.90 H 9.81.

3-Ethynyl-1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ol (6): ^{1}H NMR: δ = 0.19 (s, 9 H, TMS), 1.07 (s, 21 H, TIPS), 2.16 (s, 1 H, H7), 2.63 (s, 1 H, OH). ^{13}C NMR: δ = –0.57 (TMS), 11.2 (TIPS), 18.5 (TIPS), 54.2 (C3), 71.0 (C7), 81.2 (C6), 85.5 (C1), 88.1 (C5), 101.3 (C4), 103.6 (C2) ppm. FAB-MS: m/z (%) = 395.2 (100) [M + Na^+], 355,2 (15), 315 (15). $C_{19}H_{32}OSi_2$ (332.63) calcd. C 68.01, H 9.70, O 4.81; found: C 68.25, H 9.81, O 4.90.

3-[(*tert*-Butylcyclohex-1-enyl)ethynyl]-1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ol (7): ^{1}H NMR: δ = 0.18 (s, 9 H, TMS), 0.85 (s, 9 H, H8′), 1.08 (s, 21 H, TIPS), 1.18–1.23 (m, 3 H, H4′, 6′), 1.72–1.92 (m, 2 H, H3′,6′), 2.15–2.26 (m, 3 H, H3′,5′), 2.80 (s, 1 H, OH), 6.05 (t, 1 H, H2′) ppm. ^{13}C NMR: δ = –0.48 (TMS), 11.2 (TIPS), 18.5 (TIPS), 23.6 (C6′), 27.0 (C8′), 27.4 (C3′), 30.3 (C5′), 32.1 (C7′), 43.1 (C4′), 55.0 (C3), 65.8, 84.2 (C1), 84.3, 87.4 (C5), 102.1 (C4), 104.6 (C2), 119.3 (C1′), 137.4 (C2′) ppm. FAB-MS: m/z (%) = 470.2 (20) [M^+], 442 (85), 355 (100).

3-[(*tert*-Butylcyclohex-1-enyl)ethynyl]-5-(3,4-dihydronaphthyl)-1-(triisopropylsilyl)penta-1,4-diyn-3-ol (8): ^{1}H NMR: δ = 0.86 (s, 9 H, H8′), 1.08 (s, 21 H, TIPS), 1.18–1.23 (m, 3 H, H4′,6′), 1.25 (s, 1 H, OH), 1.72–1.92 (m, 2 H, H3′,6′), 2.15–2.26 (m, 3 H, H3′,5′), 2.37 (m, 2 H, H3′′), 2.79 (t, J = 7.9 Hz, 2 H, H4′′), 6.05 (m, 1 H, H2′), 6.52 (t, 1 H, J = 4.8 Hz, H2′′), 7.08–7.28 (m, 3 H, H_{ar}), 7.58 (d, J = 7.2 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR: δ = 11.2 (TIPS), 18.6 (TIPS), 23.6 (C6′), 26.9 (C8′), 27.1 (C3′′), 27.4 (C8′), 29.7 (C3′), 30.1 (C5′), 30.3 (C4′′), 32.2 (C7′), 43.1 (C4′), 55.0 (C3), 72.3 (C5), 84.5 (C1), 88.0 (C4), 104.6 (C2), 119.3 (C1′), 125.1 (C1′′), 125.5, 126.6, 127.3, 127.7, 132.3(C_{ar}), 134.8 (C2′′), 137.1(C_{ar}), 137.4 (C2′) ppm. FAB-MS: m/z (%) = 547 (45) [M + Na^+], 507 (100) [M^+ – OH], 165 (100).

3-[(*tert*-Butylcyclohex-1-enyl)ethynyl]-5-(3,4-dihydronaphthyl)-1-phenylpenta-1,4-diyn-3-ol (9): ^{1}H NMR: δ = 0.86 (s, 9 H, H8′), 1.08 (s, 21 H, TIPS), 1.18–1.23 (m, 3 H, H4′,6′), 1.25 (s, 1 H, OH), 1.72–1.92 (m, 2 H, H3′,6′), 2.15–2.26 (m, 3 H, H3′, 5′), 2.37 (m, 2 H, H3′′), 2.79 (t, J = 7.9 Hz, 2 H, H4′′), 6.05 (m, 1 H, H2′), 6.52 (t, J = 4.8 Hz, 1 H, H2′′), 7.08–7.28 (m, 3 H, H_{ar}), 7.58 (d, J = 7.2 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR: δ = 23.6 (C6′), 26.9 (C8′), 27.1 (C3′′), 27.4 (C8′), 29.7 (C3′), 30.1 (C5′), 30.3 (C4′′), 32.2 (C7′), 43.1 (C4′), 55.0 (C3), 72.3 (C5), 84.5 (C1), 88.0 (C4), 104.6 (C2), 119.3 (C1′), 125.1 (C1′′), 125.5 (C_{ar}), 126.6(C_{ar}), 127.3(C_{ar}), 127.6 (C_{ar}), 127.7 (C_{ar}), 128.2 (C_{ar}), 128.7 (C_{ar}), 128.9 (C_{ar}), 130.2 (C_{ar}), 132.3(C_{ar}), 134.8 (C2′′), 135.2 (C_{ar}), 137.1 (C_{ar}), 137.6 (C2′) ppm. FAB-MS: m/z (%) = 467 (20) [M + Na^+], 427 (40) [M – OH] , 104 (100).

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