gem-Selective Cross-Dimerization and Trimerization of Alkynes with Silylacetylenes Promoted by a Rhodium-Pyridine-N-Heterocyclic Carbene Catalyst

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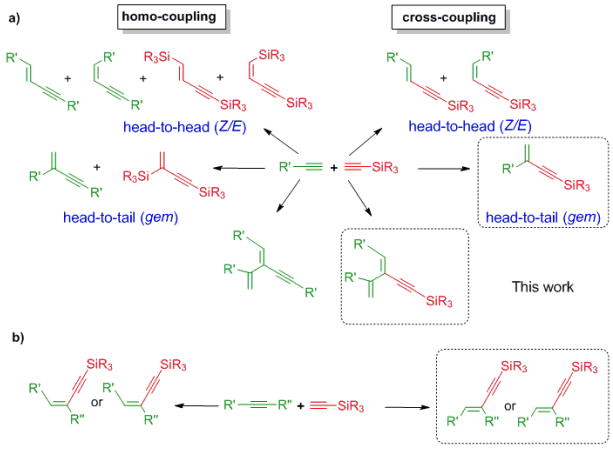
Dedication ((optional))

gem-Selective cross-dimerization and trimerization of silylacetylenes with alkynes via C-H activation using a rhodium(I)-pyridine-N-heterocyclic carbene catalyst have been developed. This protocol is applicable to variety of aliphatic or aromatic terminal alkynes, internal alkynes and *gem*-1,3-disubsituted enynes to afford the corresponding enynes and dienynes with high regio- and stereoselectivities and good isolated yields (up to 91%).

Introduction

The presence of 1,3- or 1,4-disubstituted enynes as key structural units in many biologically active molecules, polymers, or photoactive compounds has stimulated the interest in seeking for new and simple synthetic routes.[1] The metal-catalyzed homo-dimerization of terminal alkynes to selectively synthesize *E*, *Z* and geminal *(gem)* enynes has been studied in depth.[2] However, the cross-dimerization of two different alkynes is more limited because of the competitive homo- and oligo-dimerization reactions. In this context, different chemo-, regio-, and stereoselectivities have been achieved by using Ir,[3] Ni,[4] Pd,[5] Rh,[6] Ru,[7] Ti,[8] Co[9] catalysts, among others.[10] Particularly, the cross-dimerization between silylacetylenes as a donor acetylene group and unactivated internal alkynes has been disclosed.[4,5f,6b,c,7a,9c] In contrast, the addition of silylacetylenes to terminal alkynes is more challenging as a result of competitive homo-dimerization reaction, particularly for aromatic acetylenes that present comparable acidity (Scheme 1).[11] Although several Ru,[7b] Rh[6d] and Ir[3b] metal complexes selectively catalyzed the head-to-head cross-dimerization to afford both *Z* and *E*-isomers, reports on the formation of head-to-tail products are very scarce.[5f,8a] On the other hand, selective cross trimerization of three distinct alkynes by combining silylacetylene and internal alkynes leading 1,3-dien-5-ynes has been carried out using Ni[4,12] and Pd[5c] catalysts. However, the formation of selective *gem*-1,3-dien-4-ynes by combination of three terminal alkynes has not been reported up to date.



Scheme 1. Possible products from cross-coupling of silylacetylene derivatives with alkynes: a) terminal, b) internal. Compounds prepared in this work in dashed lines.

Our research group has been developing new efficient and selective catalytic systems for C-C and C-heteroatom coupling

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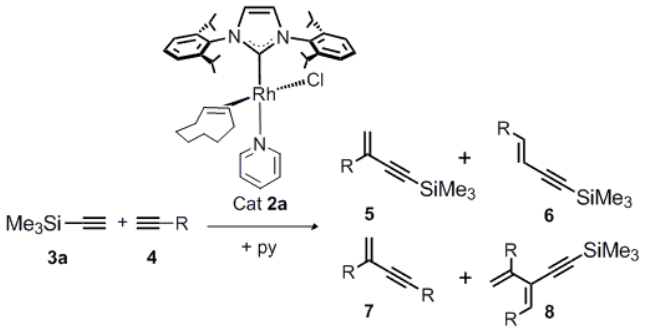
reactions based on rhodium-N-heterocyclic carbene (NHC) metal complexes.[13] Particularly, dinuclear compounds of type [Rh(μ-Cl)(NHC)(η^2-olefin)]$_2$, (**1**) have been revealed as valuable starting materials for the preparation of mononuclear complexes of type RhCl(NHC)(η^2-olefin)(L) (**2**), by simple bridge-cleavage with a nuchleophilic ligand.[13d-h] These derivatives exhibited excellent performance in catalytic alkyne hydrothiolation,[13d,h] and in the preparation of 4*H*-quinolizines via C-H activation.[13e] Indeed, it has also been found that complex RhCl(IPr)(η^2-coe)(py) (**2a**) [IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene, coe = cyclooctene, py = pyridine] promotes the selective homo-dimerization of alkynes to head-to-tail enynes, in which the chemo- and regioselectivity is controlled by the addition of pyridine.[13f] Now, we report an efficient chemo-, regio-, and stereoselective Markonikov-type cross-dimerization and trimerization involving trimethylsilylacetylene and aliphatic and aromatic terminal alkynes, internal alkynes and *gem*-1,3-disubstituted enynes.

Results and Discussion

Cross-dimerization of trimethylsilylacetylene with terminal alkynes. The catalytic system **2a** + 10 equiv of pyridine[14] was tested for the cross-dimerization of trimethylsilylacetylene (**3a**) with phenylacetylene (**4a**) (Table 1, Scheme 2). At 40 ºC, the reaction is fully selective to head-to-tail (*gem*) dimerization products being prevalent the phenylacetylene homo-dimerization enyne **7a** (entry 1). However, we observed that selectivity changes dramatically with the temperature. At 60 ºC, a 37% of cross- phenylacetyle-trimethylsilylacetylene dimerization product **5a** and 50% of phenylacetylene homo-dimerization derivative **7a** was obtained (entry 2). Interestingly at 80 ºC, the cross-coupled compound **5a** was the major product (81%) with a 5% of homo-dimerization product **7a** (entry 3). In both cases, the formation of the trimer **8a** (~14 %), resulting from the coupling of two molecules of phenylacetylene with trimethylsilylacetylene, was also observed as a by-product. The observed temperature effect over the selectivity is probably due to a modification of the overall kinetic parameters, indicating that at high temperature the C-H activation plays a preeminent role, thereby favouring cross dimerization. Moreover, an excess amount of pyridine accelerates the cross-dimerization to form **5a** with good chemo- and regioselectivity. Noteworthy, when dinuclear complexes **1**, lacking of a pyridine ligand, were used as catalysts, no dimerization products were formed, but the presence of cyclotrimers was observed instead, as described in our previous work.[13f]



Scheme 2. Catalytic transformation of alkynes with **2a** + 10 equiv py.

Table 1. Temperature screening for the cross-dimerization between trimethylsilylacetylene (**3a**) and phenylacetylene (**4a**) catalysed by **2a** + 10 equiv py.[a]

Entry 1	t(h)	T(ºC)	Conv %	**5a**	**6a**	**7a**	**8a**
1	3	40	65	18	--	82	--
2	3	60	99	37	--	50	13
3	2	80	99	81	--	5	14

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.2 mmol of **3a**, 0.2 mmol of **4a**, 0.01 of catalysts **2a** + 0.1 mmol of pyridine..

The unequivocal characterization of the head-to-tail cross-dimerization product **5a**, was achieved by comparison with the reported ^{1}H and ^{13}C{^{1}H} NMR data[15] and the heteronuclear correlation ^{1}H-^{13}C HMBC experiment. The more significant part of the 2D-NMR spectrum is shown in Figure 1. The terminal olefinic protons (δ 5.80 and 5.77 ppm) display correlation peak with one C_{sp} carbon atom (δ 104.8 ppm), whereas, more significantly, the other alkynyl carbon atom (δ 95.9 ppm) interacts with the protons of the trimethylsilyl group (δ 0.31 ppm) and not with the aromatic protons, discarding the phenyl-alkynyl connectivity. Indeed, correlation between the *gem*-protons and the ipso-phenyl quaternary carbon (δ 137.3 ppm) was also observed (See Supporting Information).

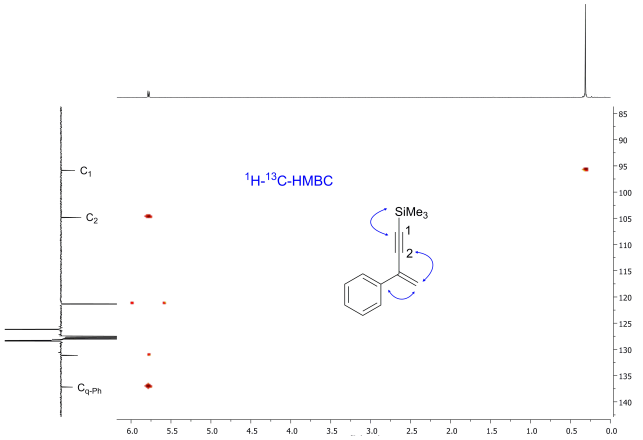


Figure 1. ^{1}H-^{13}C HMBC spectrum of compound **5a** in C_6D_6.

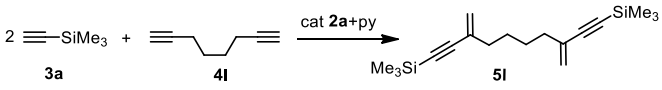
Then, we have studied the scope of the cross-dimerization reaction between terminal alkynes and trimethylsilylacetylene (Table 2). In general, full alkyne conversion was attained in 1-4 hours to give the corresponding *gem*-1,3-disubstituted enynes (**5**) which were isolated in good yields (up to 80%). Cross *E*-enynes (**6**), homo-dimerization derivatives (**7**), and *gem*-dienyne trimers (**8**) were also formed in variable amounts. As general trend, aromatic alkynes react faster than aliphatic alkynes (entries 1-4 *vs* 6-12). Phenylacetylene was almost completely consumed after 2 hours to afford *gem*-**5a** with 81% selectivity (entry 1). Substituted phenylacetylenes bearing an electron-donating group such as –OMe, either at the *para* or *meta* position, or *tert*-butyl, display good regioselectivities and yields (entries 2-4). However, *para* CF_3-substituted substrate **4e** gave exclusively the homo-dimerization product **7e**. In the case of aliphatic alkynes, head-to-tail products were obtained as the major product (>75%). In contrast with aromatic alkynes, *E*-

enynes (**6**) were also formed in some cases (<15%). Thereby, 1-benzylacetylene was transformed in 2 hours leading to 82% *gem*-**5f** (entry 6). 1-hexyne reacted in 3 hours to give 75% *gem*-**5g** and 12% of *E*-**6g** as main products (entry 7). Terminal alkynes bearing -NMe_2 and -OMe groups were also cross-dimerized with **3a** to form **5h** and **5i** with good yields and regioselectivities (entries 8 and 9). The reaction worked equally well with functionalized enynes as 2-methyl-1-buten-3-yne and 1-cyclohexenylacetylene to give *gem*-dienynes **5j** and **5k**, respectively, in good yields and high regioselectivities (entries 10 and 11). Interestingly, 1,7-octadiyne reacted with two equivalents of **3a** to afford the *gem*-bis-enyne **5l** in good yield, as a result of a double cross-dimerization process (entry 12 and Scheme 3).

Table 2. Catalytic cross-dimerization of alkynes with trimethylsilylacetylene (**3a**) mediated by **2a** +10 equiv of pyridine.[a]

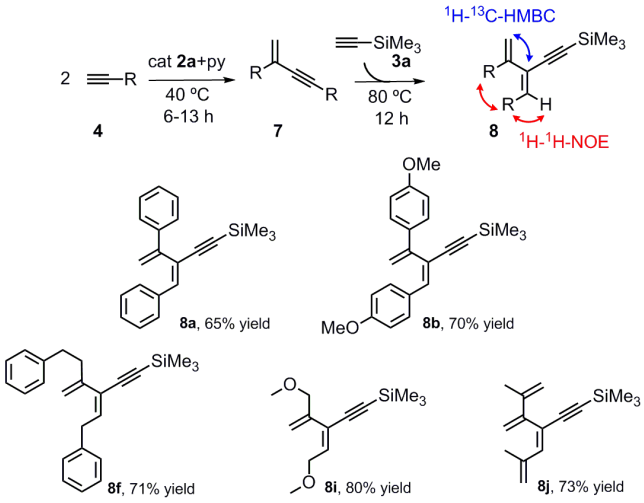
Entry	Alkyne		t(h)	Conv %	**5**	**6**	**7**	**8**	Yield %[b]
1		**4a**	2	99	81	--	5	14	71 (**5a**)
2		**4b**	1	99	91	--	4	5	83 (**5b**)
3		**4c**	2	99	85	--	--	15	78 (**5c**)
4		**4d**	2	99	86	--	10	4	76 (**5d**)
5		**4e**	1	92	--	--	98[c]	--	0 (**5e**)
6		**4f**	2	99	82	--	3	15	70 (**5f**)
7		**4g**	3	99	75	12	8	5	68 (**5g**)
8		**4h**	4	90	81	11	6	2	74 (**5h**)
9		**4i**	4	95	80	12	--	8	70 (**5i**)
10		**4j**	5	98	83	--	4	13	71 (**5j**)
11		**4k**	3	99	78	--	22	--	60 (**5k**)
12		**4l**	4	99	86	14	--	--	80 (**5l**)

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.2 mmol of **3a**, 0.2 mmol of **4**, 0.01 mol of catalyst **2a** + 0.1 mmol of pyridine at 80 ºC. [b] Isolated yield of **5**. [c] 2% of *E*-homo-dimer was also observed.



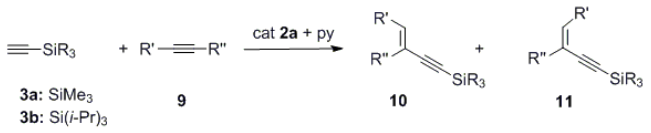
Scheme 3. Double cross-dimerization between 2 equiv of trimethylsilylacetylene and 1 equiv of 1,7 dioctyne.

Cross-trimerization of terminal alkynes with trimethylsilylacetylene. As can be seen in Table 2, aromatic and aliphatic trimers **8** were also formed as secondary products in some cases. Most probably these derivatives result from the homocoupling reaction of the corresponding terminal alkyne and a subsequent cross-trimerization with trimethylsilylacetylene. Thus, this process could be a straightforward way to construct π-conjugated systems. In order to promote the formation of (*E*)-(2-alkynyl)-(1,3-disubstituted)-1,3-butadiene derivatives, **8**, as major product, we decided to perform the reaction in two steps. First, the homo-dimerization reaction of the corresponding terminal alkyne was carried out under reaction conditions of our previous reported work using 5 mol % of catalyst **2a** and 10 equiv of pyridine at 40 ºC in C_6D_6.[13f] In the second step, trimethylsilylacetylene was added and the crude mixture heated at 80 ºC for 12 h to form *gem*-1,3-dienynes with high regioselectivity and good isolated yields (Scheme 4). The structure of the dienynes was confirmed by ^1H-^{13}C HMBC and ^1H-^1H NOE NMR experiments (See Supporting Information). Reactions of aromatic-substituted *gem*-1,3-enynes **7** gave good yields of the expected *gem*-dienyne products, eg. **8a** and **8b**. Unfortunately, compound **8e** could not be obtained due to the decomposition of dienyne **7e**, bearing a *para*-C_6H_4-CF_3 substituent, under reaction conditions. Aliphatic-substituted *gem*-1,3-enyne arising from benzylacetylene gave **8f** which was isolated in 71% yield. Heteroatom-substituted and olefin functionalized alkynes also undergoes coupling reaction toward the head-to-tail trimers **8i** and **8j**, respectively.



Scheme 4. Rhodium-catalyzed cross-trimerization of terminal alkynes with trimethylsilylacetylene via formation of 1,3-*gem* enynes.

Cross-dimerization of trialkylsilylacetylenes with internal alkynes. The efficiency of catalyst **2a** was demonstrated for cross-dimerization of internal alkynes (**9**) with trimethylsilylacetylene (**3a**) and triisopropylsilylacetylene (**3b**) (Scheme 5, Table 3). Both silylacetylenes reacted with 3-hexyne (**9a**) and diphenylacetylene (**9b**) to give preferentially the syn-addition *E*-enynes **10,** which were isolated with moderate to high yields. Formation of thermodinamically more stable *Z*-enynes **11** resulted from isomerization of **10**, as observed in prolonged reaction times. Alkyne **3a** was slightly more reactive and selective than **3b** (entries 1-2 *vs* 4-5). Unsymmetrical internal alkyne such as 1-phenyl-1-propyne (**9c**) reacted with **3a** to lead preferentially *E*-1-trimethylsilyl-3-phenylpent-3-en-1-yne with high yield (entry 3). In contrast, with **3b** afforded a mixture of *E*-regioisomers in 40/60 (3-phenyl/4-phenyl) ratio (entry 6).



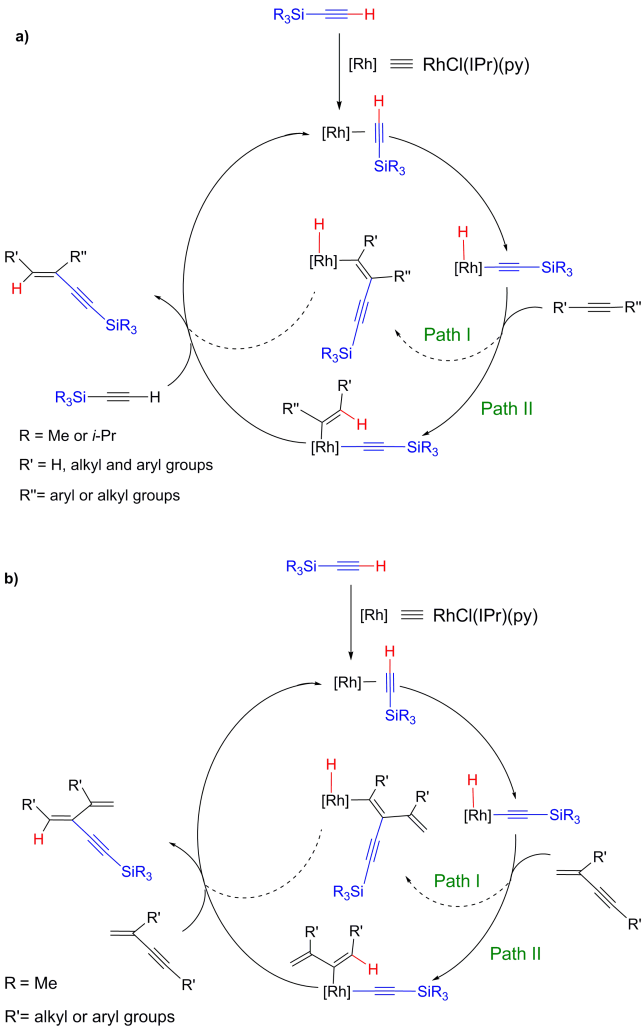
Scheme 5. Cross-dimerization of trialkylsilylacetylenes and internal alkynes.

Table 3. Cross-dimerization of silylacetylenes with internal alkynes.[a]

Entry	Alkyne		3	t(h)	Conv %	10/11	Yield[b] %
1		9a	3a	12	71	90/10	64 (**10a**)
2		9b	3a	1	99	100/--	91 (**10b**)
3		9c	3a	3	92	(100/--)[c]/--	83 (**10c**)
4		9a	3b	32	93	80/20	76 (**10d**)
5		9b	3b	24	92	82/18	75 (**10e**)
6		9c	3b	44	90	(40/60)[d]/--	81 (**10f**)[d]

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.2 mmol of **3a** or **3b**, 0.2 mmol of **9** 0.01 mmol of catalysts **2a** + 0.1 mmol of pyridine at 80 ºC [b] Isolated yield. [c] (*E*)-1-trimethylsilyl-3-phenylpent-3-en-1-yne derivative as the mayor regioisomer. [d] Isolated as a mixture of regioisomers.

Mechanism of Cross-Dimerization and -Trimerization of Terminal Alkynes. A plausible mechanism for head-to-tail cross-dimerization (a) and head-to-tail cross-trimerization (b) is shown in Scheme 6. This reaction probably proceeds by a similar mechanism to that proposed for the Rh-catalyzed dimerization of terminal alkynes.[13f] The first step involves the substitution of the cyclooctene ligand by the alkyne and subsequent oxidative addition generates Rh^{III}-alkynyl-hydride intermediates. Then, alkyne or *gem*-1,3-enyne insertion can proceed by two pathways: carbometalation via 1,2 insertion (Path I) or hydrometalation via 2,1 insertion (Path II). Finally, reductive elimination affords the corresponding enynes or dienynes and the coordination of a second alkyne or *gem*-1,3-enynes into the metal regenerates the Rh^{I} active species. The selectivity outcome seems to be governed by two key facts. *i*) C-H activation of trimethylsilylacetylene in the first step should be favoured versus that of aromatic or aliphatic alkynes due to its higher acidity,[11] and *ii*) the bulkier trimethylsilyl group hampers the insertion step for this substrate, thus, aliphatic and aromatic alkynes react faster. The acidity increase of the alkyne by incorporation of a $-CF_3$ group in 1-ethynyl-4-(trifluoromethyl)benzene (**4e**) could explain the observed preferential homo-dimerization of this alkyne. Finally, it is worth mentioning the beneficial effect of using an excess of pyridine which should play a crucial role in the catalytic cycle for stabilization of rhodium-alkynyl-hydride intermediates.[13f]



Scheme 6. A plausible mechanism for cross-dimerization and trimerization of alkynes.

Conclusion

In summary, we have described an efficient protocol for the selective head-to-tail cross-dimerization, and trimerization of silylacetylenes with alkynes promoted by a rhodium-N-heterocyclic-carbene catalyst. This catalytic system is an alternative for the synthesis of elaborated enynes and dienynes, which are difficult to prepare by other available procedures. The reaction could be applied to a variety of terminal alkynes, symmetrical and unsymmetrical internal alkynes, and *gem*-1,3-disubstituted enynes with substituents of different electronic character.

Experimental Section

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. All reagents are commercially available and were used as received, except for phenylacetylene that was distilled under argon and stored over molecular sieves. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The starting complexes [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ **1**,[16] and RhCl(IPr)(η^2-coe)(py), **2**,[13d] were prepared as previously described in the literature. ^{1}H, and ^{13}C{^{1}H} NMR were

recorder either a Bruker ARX 300 MHz or a Bruker 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}). Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C APT and ^{1}H-^{13}C HSQC/HMBC experiments. GC-MS analysis were recorder on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system, using a HP-5MS 5% phenyl methyl siloxane column (30m x 250mm with a 0.25 mm film thickness).

Catalytic cross-dimerization of silylacetylenes with terminal or internal alkynes. A NMR tube containing a solution of 0.01 mmol of catalyst **2a** (5 mol %) in 0.5 ml of C_6D_6 was treated with 0.2 mmol of silylacetylene (**3a** or **3b**), 0.2 mmol of terminal alkyne (**4**) or internal alkyne (**9**) and 0.1 mmol of pyridine and heated at 80 ºC. The conversion was monitored in a NMR apparatus and quantified by the integration of the ^{1}H NMR signals of the aliphatic or aromatic alkyne and the products formed.

General procedure for isolation of *gem*-1,3-disubstituted-enynes. In a Schlenk tube containing 0.02 mmol of catalyst **2a**, 0.2 mmol of pyridine, 0.4 mmol of silylacetylene (**3a** or **3b**) and 0.4 mmol of the terminal alkyne (**4**) or internal alkyne (**9**) in 10 mL of toluene was stirred at 80 ºC for the time indicated in Table 1. The solution was analysed by GC-MS to quantify the remaining substrate, and was later concentrated under reduced pressure, affording a crude residue, which was purified by column chromatography over silica gel (70-230 mesh), and eluted with hexane-diethyl ether (99:1) to isolate the corresponding products.

General procedure for isolation of *gem*-1,3-disubstituted-dienyne derivatives. In a Schlenk tube containing 0.02 mmol of catalyst **2a**, 0.4 mmol of terminal alkyne (**4**) and 0.2 mmol of pyridine in 10 mL of toluene was stirred at 40 ºC. When the corresponding alkyne was converted into *gem*-1,3-enyne (**7**), trimethylsilylacetylene (**3a**, 0.2 mmol) was added and heated at 80 ºC for 12 h. The solution was concentrated under reduced pressure, affording a crude residue, which was purified by column chromatography over silica gel (70-230 mesh), and eluted with hexane- diethyl ether (90:10) to isolate the corresponding dienynes (**8**).

NMR data for selected compounds (See Supporting Information for full NMR data of all compounds)**: *1-trimethylsilyl-3-phenylbut-3-en-1-yne*,** (**5a**): Isolted as a colourless oil. Yield (71%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.81 (d, $J_{H\text{-}H}$ = 8.3, 2H, $H_{o\text{-}Ph}$), 7.23 (dd, $J_{H\text{-}H}$ = 8.3, 7.4, 2H, $H_{m\text{-}Ph}$), 7.18 (t, $J_{H\text{-}H}$ = 7.4, 1H, $H_{p\text{-}Ph}$), 5.80 and 5.77 (both d, $J_{H\text{-}H}$ = 1.0, 2H, H_4), 0.31 (s, 9H, SiMe). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (100 MHz, C_6D_6, 298 K): δ 137.3 (s, $C_{q\text{-}Ph}$), 131.1 (s, C_3), 128.5 and 128.4 (both s, $C_{m,p\text{-}Ph}$), 126.2 (s, $C_{o\text{-}Ph}$), 121.5 (s, C_4), 104.7 (s, C_2), 88.8 (s, C_1), -0.3 (s, SiMe). GC/MS: *m/z* 200 (M^+), 185 (M^+-Me), 170, 145, 129, 105. ***(E)-1-trimethylsilyl-3-benzylidene-4-phenylpent-4-en-1-yne*, (8a)**: Isolated as a colorless oil. Yield (65%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.42 (d, $J_{H\text{-}H}$ = 8.2, 2H, $H_{o\text{-}Ph\beta}$), 7.15 (d, $J_{H\text{-}H}$ = 8.0, 2H, $H_{o\text{-}Ph\alpha}$), 7.09 (s, 1H, H_6), 6.93 (dd, $J_{H\text{-}H}$ = 8.2, 7.6, 2H, $H_{m\text{-}Ph\beta}$), 6.89 (t, $J_{H\text{-}H}$ = 7.6, 1H, $H_{p\text{-}Ph\beta}$), 6.75 (dd, $J_{H\text{-}H}$ = 8.0, 7.6, 2H, $H_{m\text{-}Ph\alpha}$), 6.72 (t, $J_{H\text{-}H}$ = 7.6, 1H, $H_{p\text{-}Ph\alpha}$), 5.40 and 5.25 (both d, $J_{H\text{-}H}$ = 1.0, 2H, H_5), 0.00 (s, 9H, SiMe). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (100 MHz, C_6D_6, 298 K): δ 145.6 (s, C_4), 139.4 (s, C_6), 138.0 (s, $C_{q\text{-}Ph\beta}$), 136.0 (s, $C_{q\text{-}Ph\alpha}$), 129.4 (s, $C_{o\text{-}Ph\alpha}$), 128.7 and 128.6 (both s, $C_{m,p\text{-}Ph\beta}$), 128.3 and 128.2 (both s, $C_{m,p\text{-}Ph\alpha}$), 126.8 (s, $C_{o\text{-}Ph\beta}$), 124.6 (s, C_3), 116.2 (s, C_5), 107.8 (s, C_2), 92.0 (s, C_1), 0.0 (s, SiMe). HRMS (ESI) *m/z* calcd for $C_{21}H_{22}Si$ (M^+ +1), 303.1564, found 303.1544. ***(E)-1-trimethylsilyl-3,4-diphenylbut-3-en-1-yne*, (10b)**: Isolated as a colourless oil. Yield (91%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.55 (d, $J_{H\text{-}H}$ = 8.1, 2H, $H_{o\text{-}Ph}$), 7.30 (s, 1H, H_4), 7.15-7.07 (m, 6H, H_{Ph}), 6.98 (d, $J_{H\text{-}H}$ = 8.1, 2H, $H_{o\text{-}Ph}$), 0.32 (s, 9H, SiMe). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (100 MHz, C_6D_6, 298 K): δ 137.8 and 136.2 (both s, $C_{q\text{-}Ph}$), 137.6 (s, C_4), 129.5, 129.2, 128.6, 128.2, 127.8, and 127.7 (all s, C_{Ph}), 124.7 (s, C_3), 108.4 (s, C_2), 94.5 (s, C_1), -0.1 (s, SiMe). HRMS (ESI) *m/z* calcd for $C_{19}H_{20}Si$ (M^+ +1), 277.1407, found 277.1426.

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