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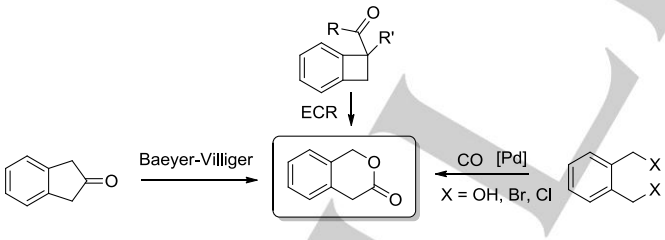
A New Synthesis of Functionalised 3-Isochromanones via Silylcarbocyclisation-Desilylation reactions

Gianluigi Albano[a], Martina Morelli[a] and Laura Antonella Aronica*[a]

Abstract: In this study, a new protocol for the synthesis of 3-isochromanone derivatives based on rhodium promoted silylcarbocyclisation reactions of ethynylbenzyl alcohol with different arylsilanes, is described. The structure of the isochromanone depends upon the experimental conditions employed: when the reaction is performed without base (*Z*)-4-((dimethyl(aryl)silyl) methylene)isochroman-3-ones are obtained as principal products. These compounds can be submitted to a desilylation/arylmigration reaction which generates 4-(methylaryl)isochroman-3-ones in high yields. On the contrary, in the presence of DBU, hydrogenation of methyleneisochroman-3-ones takes place and the corresponding β-silylmethyl-3-isochromanones are formed. Moreover, when internal alkynes are reacted with hydrosilane under silylcarbocyclisation reaction conditions, alcoholysis of hydrosilanes exclusively occurs.

Introduction

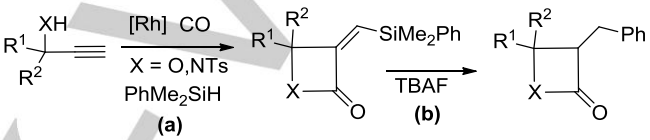
3-Isochromanone derivatives are important intermediates for the synthesis of pharmaceutical and agrochemical products, as reported in several patents[1]. Therefore many efforts have been directed toward the preparation of such compounds. The main synthetic approaches to the lactone ring are based on Baeyer-Villiger oxidation of cyclopentanone[2], tandem electrocyclic-sigmatropic reaction (ECR) of benzocyclobutanes[3], and palladium-catalysed carbonylation of benzyl haloalcohols or α,α'-dihalides[4] (Scheme 1). In the last case, deep mechanistic investigations were reported by Lindsell and coworkers[4i,j], but the method was applied only to the synthesis of 3-isochromanone itself.



Scheme 1. Main synthetic pathways to 3-isochromanones.

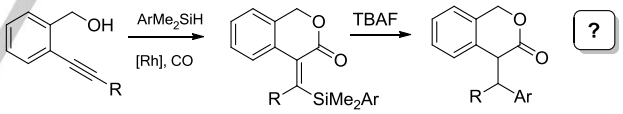
On the contrary, Takahashi and coll. described the synthesis of several functionalised 3-isochromanones through rhodium promoted cyclocarbonylation of 2-alkynylbenzylalcohol under water-gas shift reactions conditions ($CO+H_2O$); unfortunately severe experimental conditions were required (175°C and 100 atm CO)[5].

Recently we reported[6] that β-lactams and β-lactones can be easily obtained starting from propargyl amides and propargyl alcohols by means of rhodium catalysed silylcarbocyclisation reactions[7] (Scheme 2, a). Subsequently, the silylmethylene group can be submitted to further transformations such as fluoride promoted 1,2-aryl migration from the silyl moiety to the adjacent carbon atom followed by a desilylation step[6] (Scheme 2 b).



Scheme 2. Silylcarbocyclisation/desilylation of propargyl alcohols and amides.

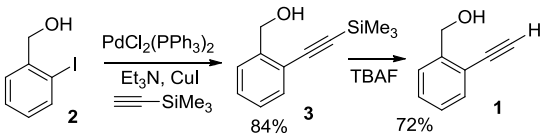
Encouraged by these results, we decided to investigate the application of this cyclisation/desilylation sequence to the synthesis of 4-methylaryl-3-isochromanones (Scheme 3) whose preparations and transformations are seldom described in the literature[8].



Scheme 3. Possible synthesis of 3-isochromanones.

Results and Discussion

At the beginning of our study, the silylcarbocyclisation reaction of 2-ethynylbenzyl alcohol **1** was investigated and the obtained results are summarized in Table 1. Requisite starting material **1** was easily prepared by Sonogashira reaction of 2-iodobenzylalcohol **2** followed by desilylation of the acetylenic moiety of **3** (Scheme 4).



Scheme 4. Synthesis of (2-ethynylphenyl)methanol **1**.

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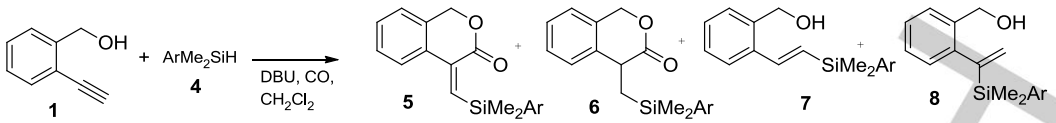
Table 1. Silylcarbocyclisation reactions of 2-ethynylbenzylalcohol **1**.



entry[a]	Ar	4	DBU	Catalyst	Mol %	T (°C)	T (h)	P_{CO} (atm)	conv. [b]	5,6,7,8	5[c]	6[c]	7+8[c]
1	Ph	**a**	10%	$Rh_4(CO)_{12}$	0.1	100	2	30	90	**a**	24	76	/
2	Ph	**a**	10%	$Rh_4(CO)_{12}$	0.1	100	4	30	100	**a**	22	78	/
3	Ph	**a**	10%	$Rh_4(CO)_{12}$	0.1	70	4	30	100	**a**	27 (10)	73 (67)	/
4	Ph	**a**	10%	$Rh_4(CO)_{12}$	1	100	2	30	100	**a**	24	76	/
5	Ph	**a**	10%	$Rh^+[(C_7H_8)(BPh_4)]^-$	0.1	100	2	30	60	**a**	33	67	/
6	Ph	**a**	/	$Rh_4(CO)_{12}$	0.1	100	2	30	100	**a**	54 (42)	12 (7)	34 (20) [d]
7	Ph	**a**	/	$Rh_4(CO)_{12}$	0.1	30	24	30	100	**a**	51	8	41[d]
8	Ph	**a**	/	$Rh_4(CO)_{12}$	0.1	30	24	50	100	**a**	56	8	36[d]
9	Ph	**a**	/	$Rh_4(CO)_{12}$	1	30	24	50	100	**a**	/	/	100[e]
10	Ph	**a**	/	$Rh^+[(C_7H_8)(BPh_4)]^-$	0.1	30	28	50	80	**a**	60	8	32[d]
11	Ph	**a**	/	$Rh^+[(C_7H_8)(BPh_4)]^-$	0.1	100	2	30	85	**a**	65	17	18[d]
12	4-MePh	**b**	/	$Rh_4(CO)_{12}$	0.2	100	2	50	100	**b**	39	7	54[f]
13	4-MePh	**b**	/	$Rh^+[(C_7H_8)(BPh_4)]^-$	0.2	100	4	50	100	**b**	65 (50)	5	30(20)[f]
14	1-Napht	**c**	/	$Rh^+[(C_7H_8)(BPh_4)]^-$	0.2	100	4	50	90	**c**	74 (60)	14 (4)	12 (8) [g]
15	4-PhPh	**d**	/	$Rh^+[(C_7H_8)(BPh_4)]^-$	0.2	100	6	50	100	**d**	67 (61)	13 (4)	20 (7) [h]

[a] Reactions were performed with 3 mmol of alcohol **1**, 3 mmol of aryldimethylsilane **4** and 3 mL of CH_2Cl_2. [b] Conversions were evaluated by GC and ^1H NMR spectroscopic analysis. [c] Selectivity was estimated by ^1H NMR spectroscopy; isolated yields of pure products are reported in parentheses. [d] Unless otherwise stated, a mixture of (*E*)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol **7a** and (2-(1-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol **8a** (ca. 65/35-75/25) was obtained. [e] A mixture of (*E*)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol7a (48%), (2-(1-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol **8a** (34%) and (*Z*)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol **9a** (18%) was exclusively formed. [f] A mixture of (*E*)-(2-(2-(dimethyl(*p*-tolyl)silyl)vinyl)phenyl)methanol **7b** and (2-(1-(dimethyl(*p*-tolyl)silyl)vinyl)phenyl)methanol **8b** (66/34) was obtained. [g] A mixture of (*E*)-(2-(2-(dimethyl(naphthalen-1-yl)silyl)vinyl)phenyl)methanol **7c** and (2-(1-(dimethyl(naphthalen-1-yl)silyl)vinyl)phenyl)methanol **8c** (85/15) was obtained.[h] Only (*E*)-(2-(2-([1,1'-biphenyl]-4-yldimethylsilyl)vinyl)phenyl)methanol **7d** was formed.

When 2-ethynylbenzyl alcohol **1** was reacted with dimethylphenylsilane **4a** under typical silylcarbocyclisation experimental conditions[6], (i.e. 100°C, for 2-4hs, 30 atm CO, DBU 10mol %, $Rh_4(CO)_{12}$), (Table 1, entries 1-2), only a small amount of desired product **5a** was obtained together with large quantities of 4-((dimethyl(phenyl)silyl)methyl)isochroman-3-one **6a.** The same trend was observed performing the reactions at lower temperature (70°C), or with a larger amount of catalyst (1mol %) (Table 1, entries 3-4). The unexpected formation of **6a** can be explained considering that a mole of hydrogen is generated during the reaction[9]: in the presence of $Rh_4(CO)_{12}$ addition of H_2 to the double bond of **5a** may occur. Thus, $Rh_4(CO)_{12}$ was replaced with $Rh^+[(C_7H_8)(BPh_4)]^-$ (Rh^{sw}), an air stable zwitterionic species usually employed in silylformylation reactions[10]. In this case a light increase in the formation of the unsaturated product **5a** was detected (Table 1, entry 5 vs. 1-4) together with a lower reagents conversion.

Surprisingly, when the silylcarbocyclization reaction was carried out in the absence of DBU (Table 1, entry 6) a significant improvement in the chemoselectivity towards (*Z*)-4-((dimethyl(phenyl)silyl)methylene)isochroman-3-one **5a** was observed, even if a considerable amount of hydrosilylation byproducts **7a** and **8a** were formed. Similar results were obtained lowering the reaction temperature and increasing the CO pressure (Table 1, entries 7-8). On the contrary, a complete selectivity towards hydrosilylated compounds was observed when the reaction was performed with 1 mol % of $Rh_4(CO)_{12}$ (Table 1, entry 9, note [e], **7a, 8a, 9a**).

Finally, the silylcarbocyclisation of ethynylbenzylalcohol **1** with dimethylphenylsilane **4a** promoted by $Rh^+[(C_7H_8)(BPh_4)]^-$ (100°C, 30atm CO), afforded isochroman-3-one **5a** with good chemoselectivity (65%, Table 1 entry 11).

The silylcarbocyclization was then applied to hydrosilanes having different stereoelectronic properties (Table 1, entries 12-

15). The reactions were performed at 100°, under 50 atm CO, for 4-6 hs with 0.2 mol% of rhodium species. As it is evident from the results, the catalysts plays an important role in the selectivity of the process (Table 1, entries 12,13), Rh^{sw} being the better choice. All methyleneisochroman-3-ones **5b-d** were obtained in good yields (not optimized) and the use of a very hindered silane such as dimethyl(naphthalen-1-yl)silane **4c** seemed to promote the cyclisation process, in agreement with our previous results on the silylcarbocyclisation of propargyl alcohols[6c].

The reactions resulted totally stereoselective since only Z isomers were formed. The configuration of the double bond of the olefinic moiety was determined by analysis of the results obtained with a NOESY (Nuclear Overhauser Effect SpectroscopY) experiment (see fig. S42 in SI). As shown in Figure 1, relevant NOE effects were detected between vinylic proton Ha and aromatic Hb and between Hc and benzyl protons Hd, thus indicating the exclusive formation of (*Z*)-isochroman-3-one **5a**.

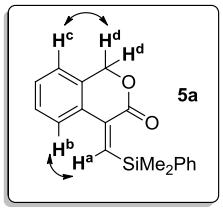
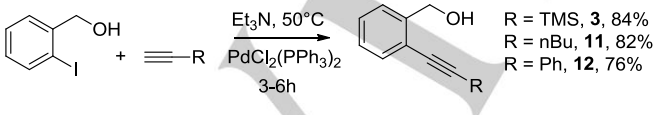


Figure 1. Structure of isochroman-3-one **5a**.

As far as the hydrogenated by-products **6** are concerned, it is worth noting that this compounds can be useful building blocks for the synthesis of polyfunctionalised molecules by means of transformations involving the silyl group in the β position to the carbonyl moiety[11].

Once obtained, silylmethyleneisochroman-3-ones **5a-d** were submitted to desilylation by means of excess tetrabutyl ammonium fluoride (1M in THF). According to our previous data[6], in the presence of TBAF, anionotropic migration of aryl group from silicon to adjacent carbon atom occurred yielding exclusively 4-(methylaryl)isochroman-3-ones **10a-d**, (Table 2).

Prompted by these results, we decided to investigate the extension of our silylcarbocyclisation/desilylation/aryl migration sequence to internal 2-ethynylbenzyl alcohols, generated by a simple Sonogashira reaction as depicted in Scheme 5.

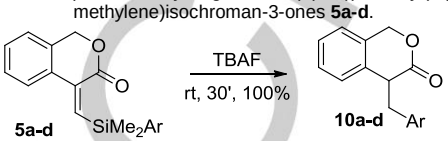


Scheme 5. Synthesis of 2-alkynylbenzyl alcohols **3**, **11**, **12**.

First of all, 2-((trimethylsilyl)ethynylbenzyl alcohol **3** was tested in the silylcarbocyclisation reaction operating under the same experimental conditions optimised for terminal acetylene **1** (50 atm CO, 100°C, 0.2 mol %, Rh^{sw}). After 18 h we observed a partial conversion of the reagents (40%, Table 3, entry 1) and the formation of silylether **13a** as sole product.

The same chemoselectivity was detected when the reaction was carried out with an increased amount of catalyst (Table 3, entry 2). In order to clarify if the observed results could be ascribed to the steric hindrance of TMS group on alkyne **3**, 2-(hex-1-yn-1-yl)benzylalcohol **11** was reacted with dimethylphenylsilane **4a** under CO atmosphere. One more time the exclusive formation of silylether **13b** occurred (Table 3, entries 3, 4).

Table 2. TBAF-promoted aryl migration of (*Z*)-4-((dimethyl(aryl)silyl) methylene)isochroman-3-ones **5a-d**.

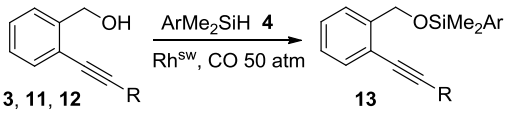


Entry[a]	5	Ar	10	Yield[b]
1	**a**	Ph	**a**	76
2	**b**	4-MePh	**b**	82
3	**c**	1-Naptht	**c**	68
4	**d**	4-PhPh	**d**	81

[a] Reactions were performed at rt with 1mmol of methyleneisochroman-3-ones and 5mmol of TBAF. [b] Yield of pure products.

Finally, the reaction between alkyne **12** and [1,1'-biphenyl]-4-yldimethylsilane **4d** afforded **13c** (Table 3, entries 5,6), thus indicating that the cyclization process is clearly disfavored by the presence of an internal triple bond, regardless of the structure of the hydrosilane employed.

Table 3. Reactions of internal 2-ethynylbenzylalcohols **3**, **11**, **12** under silylcarbocyclization reaction conditions.



Entry[a]	R		4	Ar	13	Cat (%)	t(h)	Conv.[b] (%)
1	**3**	TMS	**a**	Ph	**a**	0.2	18	40
2	**3**	TMS	**a**	Ph	**a**	1	4	72 (52)
3	**11**	nBu	**a**	Ph	**b**	1	4	61
4	**11**	nBu	**a**	Ph	**b**	1	24	81 (68)
5	**12**	Ph	**d**	4-PhPh	**c**	1	24	89
6	**12**	Ph	**d**	4-PhPh	**c**	2	24	91 (76)

[a] Reactions were performed with 3 mmol of alcohol, 3 mmol of silane **4**, 3 mL of CH_2Cl_2 , at 100°C. [b] Conversions were determined by GC and ^1H NMR analysis.

A further proof of the synthesis of silylethers was obtained by reacting **13b** with TBAF. Indeed a quantitative desilylation to the corresponding alcohol **11** was observed.

However, the unexpected formation of silylethers under our experimental conditions represents a quite interesting result since transformation of alcohols into silylethers can be considered one of the best methods for the protection of O-H functional group. This reaction is generally performed in the presence of hydrosilanes and alcohols but a transition metal derived catalyst (Pt[12], Pd[13], Au[14], Ru[15], Cu[16], Mn[17]; Ir[18], Fe[19], Rh[20]) is necessary for silane alcoholysis to proceed at a synthetically useful rate. In particular, with regard to the case of rhodium promoted synthesis of silylethers, to our knowledge, only a few examples are described in the literature[20]. On the base of the obtained results, Rh^{sw} can be considered a promising catalyst for this reaction.

Conclusions

In conclusion, we have successfully employed the silylcarbocyclisation reaction in the preparation of functionalised isochroman-3-ones. The reaction proceeds with good chemoselectivity towards the synthesis of methyleneisochroman-3-ones **5** only if 2-ethynylbenzyl alcohol **1** is employed and if the reaction is performed without a base. In the presence of DBU the cyclisation is still favoured, but the unsaturated isochroman-3-ones are readily hydrogenated, generating the corresponding silylmethyl derivatives **6**.
TBAF promoted aryl migration from silicon to the adjacent carbon atom has been applied to silylmethyleneisochroman-3-ones which yielded quantitatively the methylaryl derivatives **10**. On the contrary, when internal alkynes were tested under the silylcarbocyclisation reaction conditions, no cyclisation occurred, and silane alcoholysis selectively took place.

Keywords: Isochromanone, cyclisation, carbon monoxide, hydrosilane, silylether

Experimental Section

General remarks. Solvents were purified by conventional methods, distilled and stored under argon. Noncommercial silanes **4b-d** were prepared from the corresponding Grignard reagents according to the method described by Hiyama and Fujita.[21] $Rh_4(CO)_{12}$[22] and $Rh^+[(C_7H_8)(BPh_4)]^-$[23] were prepared according to literature. All the other chemicals were purchased from commercial sources and used as received. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded in $CDCl_3$ solution with a Varian XL 300 spectrometer, with $CHCl_3$ as internal standard; δ values are given in parts per million (ppm) and coupling constants (J) in hertz. Mass spectra were obtained with a Varian Saturn® Ion Trap 2000 mass spectrometer connected to a Varian 3800 gas chromatograph. FT-IR spectra were recorded with a Fourier Transform Infrared Perkin-Elmer 1710 spectrophotometer, operating in the range 4000-400 cm^{-1}. Column chromatography was performed on silica gel 60 (70-230 mesh). All products were identified and characterized by spectroscopic and spectrometric data.

General procedure for silylcarbocyclizations of 2-ethynylbenzyl alcohol 1. Silylcarbocyclization reactions were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a magnetic stirring bar. In a typical run, ethynylbenzyl alcohol **1**, dimethyl(aryl)silane (1.0 eq.) and CH_2Cl_2 (and eventually 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) were put, under CO atmosphere, in a 10 mL Pyrex Schlenk tube. This solution was introduced in the autoclave, previously carried with Rh catalyst and placed under vacuum (0.1 Torr), by a steel siphon. The reactor was pressurized with carbon monoxide and the mixture was stirred for a selected time at a selected temperature. After removal of excess CO (fume hood), the reaction mixture was diluted with CH_2Cl_2, filtered on celite and the solvent was removed under vacuum. The reagent conversion and the product composition were determined by ^{1}H-NMR spectroscopic analysis. All the crude products were purified through column chromatography on silica gel and characterized with ^{1}H-NMR, ^{13}C-NMR, FT-IR and GC-MS techniques.

Silylcarbocyclization with dimethyl(phenyl)silane (4a) catalysed by $Rh_4(CO)_{12}$ (0.1 mol%) with DBU (Table 1, entry 3). Following the general procedure, 2.2 mg (0.003 mmol) of $Rh_4(CO)_{12}$, 396 mg (3.0 mmol) of (2-ethynylphenyl)methanol (**1**), 0.41 mL (3.0 mmol) of dimethyl(phenyl)silane (**4a**), 45 µL (0.3 mmol) of DBU and 3 mL of CH_2Cl_2 were put in the autoclave charged with 30 atm of CO. The resulting mixture was stirred for 4 h at 70°C. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 90 mg (yield 10%) of (*Z*)-4-((dimethyl(phenyl)silyl) methylene)isochroman-3-one (**5a**) and 600 mg (yield 67%) of 4-((dimethyl(phenyl)silyl)methyl)isochroman-3-one (**6a**).
5a: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.66-7.64 (2H, m); 7.61-7.58 (1H, m); 7.39-7.32 (5H, m); 7.19-7.17 (1H, m); 7.03 (1H, s); 5.33 (2H, s); 0.58 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 160.82; 144.13; 139.58; 138.59; 133.79 (2C); 133.32; 130.17; 128.85; 128.73 (2C); 127.74 (2C); 124.25; 124.13; 69.20; - 2.18 (2C). FT-IR, ν_{max} (cm^{-1}): 3068; 2953; 1728; 1572; 1422; 1383; 1244; 1166. GC-MS, m/z (%): 294 (M^+, 32); 281 (26); 279 (100); 217 (70); 173 (10); 137 (18); 115 (27); 75 (19).
6a: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.58-7.53 (2H, m); 7.41-7.38 (3H, m); 7.31-7.10 (4H, m); 5.42 (1H, d, J = 14.1 Hz); 5.23 (1H, d, J = 14.1 Hz); 3.69 (1H, t, J = 7.5 Hz); 1.61 (1H, dd, J = 14.8, 7.5 Hz); 1,39 (1H, dd, J = 14.8, 7.5 Hz); 0.39 (3H, s); 0.35 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 173.64; 138.05; 136.37; 133.52 (2C); 131.42; 129.08; 128.48; 127.81 (2C); 126.94; 125.81; 124.66; 69.21; 41.97; 15.94; - 2.39; - 2.55. FT-IR, ν_{max} (cm^{-1}): 2953; 1744; 1425; 1383; 1247; 1113. GC-MS, m/z (%): 281 (M^+ - CH_3, 13); 209 (8); 147 (22); 129 (100); 128 (38); 111 (97); 110 (28); 84 (20); 71 (41); 55 (69).

Silylcarbocyclization with dimethyl(phenyl)silane (4a) catalysed by $Rh_4(CO)_{12}$ (0.1 mol%) without DBU (Table 1, entry 6). Following the general procedure, 2.2 mg (0.003 mmol) of $Rh_4(CO)_{12}$, 396 mg (3.0 mmol) of (2-ethynylphenyl)methanol (**1**), 0.41 mL (3.0 mmol) of dimethyl(phenyl)silane (**4a**) and 3 mL of CH_2Cl_2 were put in the autoclave charged with 30 atm of CO. The resulting mixture was stirred for 2 h at 100°C. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 371 mg (yield 42%) of (*Z*)-4-((dimethyl(phenyl)silyl)methylene) isochroman-3-one (**5a**), 62 mg (yield 7%) of 4-((dimethyl(phenyl)silyl)methyl)isochroman-3-one (**6a**) and 161 mg (yield 20%) of a mixture of (*E*)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol (**7a**) and (2-(1-(dimethyl(phenyl)silyl)vinyl)phenyl)metha-nol (**8a**) in the molar ratio 65/35.
7a + 8a: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.63-7.18 (9.65H, m); 6.57 (0.65H, d, J = 19.0 Hz); 5.85 (0.35H, d, J = 3.2 Hz); 5.78 (0.35H, d, J = 3.2 Hz); 4.73 (1.3H, s); 4.34 (0.7H, s); 2.15 (1H, bs); 0.49 (3.9H, s); 0.42 (2.1H, s). GC-MS **7a**, m/z (%): 253 (M^+ - CH_3, 3); 231 (2); 209 (2); 192 (53); 194 (15); 191 (8); 165 (2); 143 (1); 138 (7); 135 (100); 115 (13); 105

(6); 76 (14); 75 (22); 74 (4). GC-MS **8a**, m/z (%): 253 (M^+ - CH_3, 21); 190 (43); 136 (32); 135 (100); 115 (50); 107 (11); 75 (46).

Silylcarbocyclization with dimethyl(phenyl)silane (4a) catalysed by $Rh_4(CO)_{12}$ (1 mol%) without DBU (Table 1, entry 9).

Following the general procedure, 22 mg (0.03 mmol) of $Rh_4(CO)_{12}$, 396 mg (3.0 mmol) of (2-ethynylphenyl)methanol (**1**), 0.41 mL (3.0 mmol) of dimethyl(phenyl)silane (**4a**) and 3 mL of CH_2Cl_2 were put in the autoclave charged with 50 atm of CO. The mixture was stirred for 24 h at 30°C. The composition of crude product was determined by ^{1}H-NMR and GC-MS analysis, resulting in a mixture of (*E*)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol (**7a**), (2-(1-(dimethyl(phenyl)silyl)vinyl)phenyl)metha-nol (**8a**) and (*Z*)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)methanol (**9a**) in the molar ratio 48/34/18.

7a + 8a + 9a: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.63-7.13 (9.66H, m); 6.60 (0.48H, d, J = 19.0 Hz); 6.18 (0.18H, d, J = 14.6 Hz); 5.85 (0.34H, d, J = 3.2 Hz); 5.78 (0.34H, d, J = 3.2 Hz); 4.80 (0.96H, s); 4.62 (0.36H, s); 4.38 (0.68H, s); 1.82 (0.82H, bs); 1.30 (0.18H, bs); 0.49 (2.88H, s); 0.42 (2.04H, s); 0.37 (1.08H, s). GC-MS **9a**, m/z (%): 268 (M^+, 41); 239 (16); 223 (27); 192 (26); 177 (73); 149 (88); 115 (100); 91 (47); 75 (53).

Silylcarbocyclization with dimethyl(*p*-tolyl)silane (4b) (Table 1, entry 13). Following the general procedure, 3.4 mg (0.006 mmol) of $Rh^+[(C_7H_8)(BPh_4)]^-$, 396 mg (3.0 mmol) of (2-ethynylphenyl) methanol (**1**), 451 mg (3.0 mmol) of dimethyl(*p*-tolyl)silane (**4b**) and 3 mL of CH_2Cl_2 were put in the autoclave charged with 50 atm of CO. The resulting mixture was stirred for 4 h at 100°C. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 463 mg (yield 50%) of (*Z*)-4-((dimethyl(*p*-tolyl)silyl)methylene)isochroman-3-one (**5b**) and 170 mg (yield 20%) of a mixture of (*E*)-(2-(2-(dimethyl(*p*-tolyl)silyl)vinyl)phenyl) methanol (**7b**) and (2-(1-(dimethyl(*p*-tolyl)silyl)vinyl)phenyl)methanol (**8b**) in the molar ratio 66/34.

5b: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.48-7.43 (3H, m); 7.25-7.21 (2H, m); 7.13-7.03 (3H, m); 6.92 (1H, s); 5.19 (2H, s); 2.25 (3H, s); 0.46 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 165.86; 144.39; 138.66; 138.45; 135.78; 133.83 (2C); 133.36; 130.14; 128.68; 128.63; 128.56 (2C); 124.19; 124.08; 69.14; 21.42; **-** 2.09 (2C). FT-IR, ν_{max} (cm^{-1}): 3010; 2953; 1730; 1602; 1460; 1245; 1169. GC-MS, m/z (%): 308 (M^+, 6); 294 (16); 293 (68); 249 (9); 218 (19); 217 (100); 151 (11); 115 (20); 75 (10).

7b + 8b: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.56-7.09 (8.66H, m); 6.52 (0.66H, d, J = 19.0 Hz); 5.75 (0.34H, d, J = 3.3 Hz); 5.67 (0.34H, d, J = 3.3 Hz); 4.66 (1.32H, bs); 4.29 (0.68H, bs); 2.32 (1.98H, s); 2.30 (1.02H, s); 2.17 (0.66H, bs); 1.50 (0.34H, bs); 0.42 (3.96H, s); 0.35 (2.04H, s). GC-MS **7b**, m/z (%): 282 (M^+, 0.2); 267 (M^+ - CH_3, 0.6); 253 (0.8); 206 (50); 149 (100); 115 (10); 75 (19). GC-MS **8b**, m/z (%): 267 (M^+ - CH_3, 14); 190 (28); 151 (45); 149 (100); 115 (29); 75 (56).

Silylcarbocyclization with dimethyl(naphthalen-1-yl)silane (4c) (Table 1, entry 14). Following the general procedure, 3.4 mg (0.006 mmol) of $Rh^+[(C_7H_8)(BPh_4)]^-$, 396 mg (3.0 mmol) of (2-ethynylphenyl) methanol (**1**), 560 mg (3.0 mmol) of dimethyl(naphthalen-1-yl)silane (**4c**) and 3 mL of CH_2Cl_2 were put in the autoclave charged with 50 atm of CO. The resulting mixture was stirred for 4 h at 100°C. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 620 mg (yield 60%) of (*Z*)-4-((dimethyl(naphthalen-1-yl) silyl)methylene)isochroman-3-one (**5c**), 42 mg (yield 4%) of 4-((dimethyl(naphthalen-1-yl)silyl)methyl)isochroman-3-one (**6c**) and 76 mg (yield 8%) of a mixture of of (*E*)-(2-(2-(dimethyl(naphthalen-1-yl)silyl)vinyl) phenyl)methanol (**7c**) and (2-(1-(dimethyl(naphthalen-1-yl)silyl)vinyl)phenyl)methanol (**8c**) in the molar ratio 85/15.

5c: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.97-7.83 (4H, m); 7.56-7.44 (4H, m); 7.35-7.29 (2H, m); 7.19 (1H, s); 7.17-7.14 (1H, m); 5.28 (2H, s); 0.74 (6H, s).^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 165.84; 144.66; 138.17; 137.52; 136.31; 133.69; 133.52; 133.34; 130.23; 129.75; 129.25; 128.73; 128.70; 128.19; 125.57; 125.20; 125.17; 124.38; 124.14; 69.25; - 1.25 (2C). GC-MS, m/z (%): 344 (M^+, 33); 329 (100); 285 (16); 217 (75); 173 (10); 145 (6); 115 (25); 75 (12).

6c: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.06-8.03 (1H, m); 7.89-7.86 (2H, m); 7.69-7.66 (1H, m); 7.51-7.43 (3H, m); 7.18-7.10 (3H, m); 6.94-6.92 (1H, m); 5.37 (1H, d, J = 14.0 Hz); 5.16 (1H, d, J = 14.0 Hz); 3.68 (1H, t, J = 7.5 Hz); 1.79 (1H, dd, J = 15.0, 7.5 Hz); 1.62 (1H, dd, J = 15.0, 7.5 Hz); 0.57 (3H, s); 0.49 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 173.68; 136.73; 136.20; 135.98; 133.96; 133.38; 131.47; 130.13; 129.24; 128.37; 127.56; 126.94; 125.92; 125.89; 125.38; 125.10; 124.59; 69.30; 42.25; 16.57; - 0.59; - 1.15. FT-IR, ν_{max} (cm^{-1}): 2953; 1741; 1457; 1249; 1142. GC-MS, m/z (%): 316 (M^+ - CH_2O, 17); 283 (51); 241 (72) ; 185 (21); 149 (65); 127 (18); 115 (100); 103 (13); 75 (42).

7c + 8c: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.24-8.20 (0.85H, m); 8.16-8.04 (0.30H, m); 7.93-7.80 (3.70H, m); 7.73-7.70 (0.30H, m); 7.63-7.60 (0.85H, m); 7.53-7.50 (3H, m); 7.39-7.26 (2.55H, m); 7.19-7.11 (0.30H, m); 6.75 (0.85H, d, J = 19.0 Hz); 5.91 (0.15H, d, J = 3.3 Hz); 5.83 (0.15H, d, J = 3.3 Hz); 4.70 (1.70H, s); 4.46 (0.30H, s); 1.68 (0.85H, s); 1.30 (0.15H, s); 0.66 (5.1H, s); 0.58 (0.9H, s). GC-MS **7c**, m/z (%): 318 (M^+, 7); 301 (M^+ - OH, 12); 243 (54); 188 (14); 185 (100); 141 (16); 115 (27); 75 (63); 47 (6). GC-MS **8c**, m/z (%): 303 (M^+ - CH_3, 47); 283 (8); 187 (42); 185 (81); 141 (12); 115 (46); 75 (100); 43 (8).

Silylcarbocyclization with [1,1'-biphenyl]-4-yldimethylsilane (4d) (Table 1, entry 15). Following the general procedure, 3.4 mg (0.006 mmol) of $Rh^+[(C_7H_8)(BPh_4)]^-$, 396 mg (3.0 mmol) of (2-ethynylphenyl) methanol (**1**), 638 mg (3.0 mmol) of [1,1'-biphenyl]-4-yldimethylsilane (**4d**) and 3 mL of CH_2Cl_2 were put in the autoclave charged with 50 atm of CO. The resulting mixture was stirred for 6 h at 100°C. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 678 mg (yield 61%) of (*Z*)-4-(([1,1'-biphenyl]-4-yldimethyl silyl)methylene)isochroman-3-one (**5d**), 45 mg (yield 4%) of 4-(([1,1'-biphenyl]-4-yldimethylsilyl)methyl)isochroman-3-one (**6d**) and 72 mg (yield 7%) of (*E*)-(2-(2-([1,1'-biphenyl]-4-yldimethylsilyl)vinyl)phenyl) methanol (**7d**).

5d: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (2H, d, J = 7.8 Hz); 7.72-7.64 (5H, m); 7.54-7.49 (2H, m); 7.44-7.37 (3H, m); 7.20-7.17 (1H, m); 7.15 (1H, s); 5.35 (2H, s); 0.72 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 165.91; 143.92; 141.56; 141.05; 138.58; 138.22; 134.32 (2C); 133.19; 130.13; 128.73 (2C); 128.68 (2C); 127.27; 127.09 (2C); 126.46 (2C); 124.23; 124.12; 69.19; -2.04 (2C). GC-MS, m/z (%): 370 (M^+, 47); 355 (100); 217 (47); 173 (11); 143 (11); 115 (31); 75 (12).

6d: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.63-7.60 (6H, m); 7.49-7.44 (2H, m); 7.39-7.33 (1H, m); 7.30-7.24 (2H, m); 7.21-7.18 (1H, m); 7.14-7.11 (1H, m); 5.41 (1H, d, J = 13.9 Hz); 5.23 (1H, d, J = 13.9 Hz); 3.70 (1H, t, J = 7.5Hz); 1.62 (1H, dd, J = 15.0, 7.5 Hz); 1.41 (1H, dd, J = 15.0, 7.5 Hz); 0.40 (3H, s); 0.36 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 173.68; 141.86; 140.88; 136.86; 136.43; 134.11 (2C); 131.49; 128.74 (2C); 128.57; 127.40; 127.08 (2C); 127.02; 126.57 (2C); 125.90; 124.74; 69.30; 42.06; 16.04; - 2.22; - 2.43. FT-IR, ν_{max} (cm^{-1}): 2951; 1742; 1459; 1247; 1165. GC-MS, m/z (%): 357 (M^+ - CH_3, 100); 219 (35); 167 (6); 115 (7).

7d: ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.71-7.62 (8H, m); 7.50-7.45 (2H, m); 7.41-7.29 (4H, m); 6.61 (1H, d, J = 18.9 Hz); 4.80 (2H, d, J = 5.4 Hz); 1.72 (1H, t, J = 5.4 Hz); 0.51 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 142.00; 141.84; 141.01; 137.46; 137.21; 137.17; 134.37 (2C); 130.49; 128.74 (2C); 128.19; 128.15; 128.10; 127.36; 127.13 (2C);

126.57 (2C); 125.96; 63.18; - 2.45 (2C). FT-IR, ν_{max} (cm^{-1}): 3351; 3059; 1596; 1482; 1250; 1112. GC-MS, m/z (%): 268 (M^+ - C_6H_5, 69); 211 (100); 165 (12); 115 (15); 75 (35).

General procedure for TBAF-promoted aryl migration of (*Z*)-4-((dimethyl(aryl)silyl)methylene)isoch-roman-3-ones 5a-d. In a typical run, 1.0 M in THF tetrabutylammonium fluoride and distilled THF were mixed together in a a 50 mL two-necked round bottom flask, equipped with dropping funnel and magnetic stirring bar, then a solution of 4-((dimethyl-arylsilyl)methylene)isochroman-3-one **5** in distilled THF was dropped. The mixture was left under stirring for 30 minutes at room temperature, then it was hydrolyzed with water and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. All the crude products were purified through column chromatography on silica gel and characterized with ^{1}H-NMR, ^{13}C-NMR, FT-IR and GC-MS techniques.

4-benzylisochroman-3-one (10a)[5] (Table 2, entry 1). Following the general procedure, a solution of 490 mg (1.7 mmol) of (*Z*)-4-((dimethyl(phenyl)silyl)methylene) isochroman-3-one (**5a**) in 7 mL of THF was dropped in a mixture of 5.0 mL (5.0 mmol) of 1.0 M in THF tetrabutylammonium fluoride and 10 mL of THF. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 308 mg (yield 76%) of 4-benzylisochroman-3-one (**10a**) as colourless oil, with spectroscopic constants in agreement with those reported in the literature[5]. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.31-7.18 (5H, m); 7.14-7.10 (1H, m); 7.01-6.96 (3H, m); 5.09 (1H, d, J = 14.2 Hz); 4.75 (1H, d, J = 14.2 Hz); 4.01 (1H, t, J = 6.0 Hz); 3.30 (2H, d, J = 6.0 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 172.36; 136.95; 133.44; 131.19; 129.19 (2C); 128.34 (3C); 127.26; 127.23; 126.90; 124.15; 69.56; 47.27; 38.35. FT-IR, ν_{max} (cm^{-1}): 2933; 1741; 1425; 1388; 1244; 1193; 1048.

4-(4-methylbenzyl)isochroman-3-one (10b) (Table 2, entry 2). Following the general procedure, a solution of 463 mg (1.50 mmol) of (*Z*)-4-((dimethyl(*p*-tolyl)silyl)methylene)isochro-man-3-one (**5b**) in 5 mL of THF was dropped in a mixture of 5.0 mL (5.0 mmol) of 1.0 M in THF tetrabutylammonium fluoride and 10 mL of THF. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 310 mg (yield 82%) of 4-(4-methylbenzyl)isochroman-3-one (**10b**) as colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.30-7.24 (2H, m); 7.12-7.07 (1H, m); 7.03-6.97 (3H, m); 6.85 (2H, d, J = 7.9 Hz); 5.07 (1H, d, J = 14.4 Hz); 4.74 (1H, d, J = 14.4 Hz); 3.97 (1H, t, J = 6.3 Hz); 3.24 (2H, d, J = 6.3 Hz); 2.30 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 172.48; 136.45; 133.73; 133.52; 131.14; 129.01 (2C); 128.99 (2C); 128.29; 127.22; 127.17; 124.11; 69.56; 47.35; 38.00; 20.99. FT-IR, ν_{max} (cm^{-1}): 2920; 1742; 1390; 1189. GC-MS, m/z (%): 252 (M^+, 7); 207 (10); 160 (12); 105 (100); 77 (9).

4-(naphthalen-1-ylmethyl)isochroman-3-one (10c) (Table 2, entry 3). Following the general procedure, a solution of 620 mg (1.8 mmol) of (*Z*)-4-((dimethyl(naphthalen-1-yl)silyl)methylene) isochroman-3-one (**5c**) in 8 mL of THF was dropped in a mixture of 5.0 mL (5.0 mmol) of 1.0 M in THF tetrabutylammonium fluoride and 10 mL of THF. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 353 mg (yield 68%) of 4-(naphthalen-1-ylmethyl)isochroman-3-one (**10c**) as colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.05-7.99 (1H, m); 7.89-7.86 (1H, m); 7.76 (1H, d, J = 8.4 Hz); 7.54-7.46 (2H, m); 7.31-7.22 (2H, m); 7.13 (2H, t, J = 7.1 Hz); 7.00 (1H, d, J = 7.1 Hz); 6.68 (1H, d, J = 7.1 Hz); 5.16 (2H, s); 4.13 (1H, dd, J = 8.8, 4.8 Hz); 3.89 (1H, dd, J = 14.1, 4.8 Hz); 3.53 (1H, dd, J = 14.1, 8.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 172.47; 133.63; 133.57; 132.88; 131.46; 130.79; 128.72; 128.11; 127.62; 127.56; 127.17 (2C); 126.18; 125.56; 124.97; 124.29; 123.08; 69.49; 46.54; 34.10. FT-IR, ν_{max} (cm^{-1}): 2923; 1737; 1385; 1191. GC-MS, m/z (%): 288 (M^+, 18); 243 (9); 141 (100); 115 (22); 50 (5).

4-([1,1'-biphenyl]-4-ylmethyl)isochroman-3-one (10d) (Table 2, entry 4). Following the general procedure, a solution of 678 mg (1.8 mmol) of (*Z*)-4-(([1,1'-biphenyl]-4-yldimethylsilyl) methylene)isochroman-3-one (**5d**) in 8 mL of THF was dropped in a mixture of 5.0 mL (5.0 mmol) of 1.0 M in THF tetrabutylammonium fluoride and 10 mL of THF. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 458 mg (yield 81%) of 4-([1,1'-biphenyl]-4-ylmethyl)isochroman-3-one (**10d**) as colourless oil**.** ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.61-7.58 (2H, m); 7.50-7.42 (4H, m); 7.38-7.26 (3H, m); 7.15-7.03 (4H, m); 5.12 (1H, d, J = 14.0 Hz); 4.84 (1H, d, J = 14.0 Hz); 4.04 (1H, t, J =6.6 Hz); 3.35 (2H, d, J = 6.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 172.32; 140.37; 139.60; 136.02; 133.36; 131.14; 129.56 (2C); 128.66 (2C); 128.35; 127.24; 127.20; 127.13; 126.89 (2C); 126.79 (2C); 124.18; 69.55; 47.11; 37.75. FT-IR, ν_{max} (cm^{-1}): 2923; 1741; 1385; 1194. GC-MS, m/z (%): 314 (M^+, 6); 269 (3); 253 (1); 167 (100); 152 (3); 115 (2); 91 (2); 63 (1).

General procedure for silylcarbocyclization attempts of 2-alkynylbenzyl alcohols 3, 11, 12. Reactions were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a magnetic stirring bar. In a typical run, alkynylbenzyl alcohol, dimethyl(aryl)silane (1.0 eq.) and CH_2Cl_2 were put, under CO atmosphere, in a 10 mL Schlenk tube. This solution was introduced in the autoclave, previously carried with $Rh^+[(C_7H_8)(BPh_4)]^-$ and placed under vacuum (0.1 Torr), by a steel siphon. The reactor was pressurized with carbon monoxide (50 atm) and the mixture was stirred for a selected time at 100 °C. After removal of excess CO (fume hood), the reaction mixture was diluted with CH_2Cl_2, filtered on celite and the solvent was removed under vacuum. The reagent conversion and the product composition were deter-mined by ^{1}H-NMR spectroscopic analysis. All crude products were purified through column chromatography on silica gel and characterized with ^{1}H-NMR, ^{13}C-NMR, FT-IR and GC-MS techniques.

((2-(((dimethyl(phenyl)silyl)oxy)methyl)phenyl)ethynyl)trimethylsilane (13a) (Table 3, entry 2). Following the general procedure, 17 mg (0.03 mmol) of $Rh^+[(C_7H_8)(BPh_4)]^-$, 614 mg (3.0 mmol) of (2-((trimethylsilyl) ethynyl)phenyl)methanol (**3**), 0.41 mL (3.0 mmol) of dimethyl(phenyl)silane (**4a**) and 3 mL of CH_2Cl_2 were put in the autoclave The resulting mixture was stirred for 4 h. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 528 mg (yield 52%) of ((2-(((dimethyl(phenyl)silyl)oxy)methyl)phenyl)ethynyl)trimethylsilane (**13a**). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.66-**7**.63 (2H, m); 7.60-7.55 (1H, m); 7.44-7.33 (5H, m); 7.20 (1H, td, J = 7.5, 0.7 Hz); 4.90 (2H, s); 0.46 (6H, s); 0.24 (9H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 143.02; 137.56; 133.44 (2C); 131.74; 129.62; 128.68; 127.86 (2C); 126.49; 126.06; 120.09; 102.41; 99.37; 63.10; - 0.05 (3C); - 1.78 (2C). GC-MS, m/z (%): 338 (M^+, 6); 323 (M^+ - CH_3, 15); 265 (100); 233 (53); 193 (15); 149 (19); 135 (45); 128 (8); 105 (10); 73 (32); 45 (23).

((2-(hex-1-yn-1-yl)benzyl)oxy)dimethyl(phenyl)silane (13b) (Table 3, entry 4). Following the general procedure, 23 mg (0.04 mmol) of $Rh^+[(C_7H_8)(BPh_4)]^-$, 754 mg (4.0 mmol) of (2-(hex-1-yn-1-yl) phenyl)methanol (**11**), 0.55 mL (4.0 mmol) of dimethyl(phenyl)silane (**4a**) and 3 mL of CH_2Cl_2 were put in the autoclave. The resulting mixture was

stirred for 24 h. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 877 mg (yield 68%) of ((2-(hex-1-yn-1-yl)benzyl)oxy)dimethyl(phenyl)silane (**13b**). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.66-7.63 (2H, m); 7.57-7.54 (2H, m); 7.42-7.28 (4H, m); 7.21-7.16 (1H, m); 4.88 (2H, s); 2.41 (2H, t, J = 6.9 Hz); 1.61-1.41 (4H, m); 0.94 (3H, t, J = 6.0 Hz); 0.45 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 142.45; 137.88; 133.64 (2C); 131.73; 129.77; 128.01 (2C); 127.83; 126.66; 126.15; 121.25; 95.53; 78.13; 63.44; 30.96; 22.12; 19.37; 13.81; - 1.54 (2C). FT-IR, ν_{max} (cm^{-1}): 1422; 1251; 1072; 1115. GC-MS, m/z (%): 322 (M^+, 7); 307 (M^+ - CH_3, 16); 280 (31); 235 (17); 205 (49); 169 (24); 135 (100); 115 (28); 91 (18); 75 (32).

[1,1'-biphenyl]-4-yldimethyl((2-(phenylethynyl)benzyl)oxy)silane (13c) (Table 3, entry 6). Following the general procedure, 21 mg (0.036 mmol) of $Rh^+[(C_7H_8)(BPh_4)]^-$, 375 mg (1.8 mmol) of (2-(phenylethynyl) phenyl)methanol (**12**), 383 mg (1.8 mmol) of [1,1'-biphenyl]-4-yldimethylsilane (**4d**) and 3 mL of CH_2Cl_2 were put in the autoclave. The resulting mixture was stirred for 24 h. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2), obtaining 573 mg (yield 76%) of [1,1'-biphenyl]-4-yldimethyl((2-(phenylethynyl)benzyl)oxy)si-lane (**13c**). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.77-7.75 (1H, m); 7.68-7.62 (7H, m); 7.52-7.44 (5H, m); 7.43-7.28 (5H, m); 5.05 (2H, s); 0.53 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 142.41; 142.31; 140.90; 136.17; 134.00; 133.48; 131.65; 131.40 (2C); 128.83; 128.71 (2C); 128.50; 128.28; 128.23; 127.40; 127.10 (2C); 126.73; 126.57 (2C); 126.42; 123.15; 120.34; 94.14; 86.81; 63.28; - 1.62 (2C). FT-IR, ν_{max} (cm^{-1}): 1440; 1253; 1069; 1116. GC-MS, m/z (%): 418 (M^+, 49); 344 (100); 264 (13); 191 (10); 75 (10).

Desilylation of ((2-(hex-1-yn-1-yl)benzyl)oxy)dimethyl(phenyl)silane (13b). In a 50 mL two-necked round bottom flask, equipped with dropping funnel and magnetic stirring bar, 5 mL (5.0 mmol) of 1.0 M in THF tetrabutylammonium fluoride and 10 mL of distilled THF were mixed together, then a solution of 645 mg (2.0 mmol) of ((2-(hex-1-yn-1-yl)benzyl)oxy)dimethyl(phenyl)silane (**13b**) in 7 mL of distilled THF was dropped. The mixture was left under stirring for 30 minutes at room temperature, then it was hydrolyzed with water and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum, giving 336 mg (yield 89%) of **11** as brownish oil.

Supporting Information (see footnote on the first page of this article): Synthesis of precursors (**1**, **3**, **11**, **12**) and copies of the ^{1}H-NMR and ^{13}C-NMR spectra of all product synthesized.

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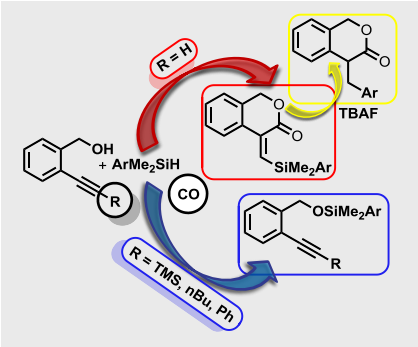
FULL PAPER

A rhodium promoted silylcarbocyclization reaction between 2-alkynylbenzyl alcohols and hydrosilanes under CO atmosphere is reported. Different products can be obtained depending on the experimental conditions and on the nature of the alkynes. When terminal acetylenes are reacted under CO pressure and without base, (dimethylarylsilyl)methylene isochroman-3-ones are obtained in good yields.



Silylcarbocyclisation, Isochromanone

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Page No. – Page No.

A New Synthesis of Functionalised 3-Isochromanones via Silylcarbocyclisation-Desilylation reactions