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Rh-catalyzed addition of boronic acids to alkynes for the synthesis of trisubstituted alkenes in a biphasic system - Mechanistic study and recycling of the Rh/*m*-TPPTC catalyst

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Abstract

The versatile preparation of trisubstituted alkenes via selective Rh-catalyzed arylation of alkynes is described in water and in a water/toluene biphasic system. For hydrophobic alkyl alkynes, the reaction afforded either alkenes or dienes depending on the temperature and the solvent conditions. Aryl, heteroaryl, silylated and alkyl substituted alkynes reacted equally well with various boronic acids, leading regioselectively to functionalized alkenyl derivatives in high yields (65–99%). The mechanism was investigated in toluene/water mixture or water and involves a vinylrhodium complex. The efficient recycling of the Rh/*m*-TPPTC system is disclosed with excellent yield (92–96%) and purity of the alkene.

Keywords: Water-soluble ligand; Boronic acids; Homogeneous biphasic catalysis; Rhodium; Arylation of alkynes

1. Introduction

The transition metal-catalyzed reactions and specifically homogeneous catalysis have given a considerable impetus to the progress of the area of organometallic, organic and industrial chemistries [1]. Among them, carbon–carbon bond formations using water-soluble organometallic catalysts are fundamentally important because they provide successful solutions to environmental, economic concerns and to the easy product/catalyst separation [2]. Recent years therefore witnessed tremendous growth in the synthesis of water-soluble ligands to solubilize easily the catalyst precursor in water [3]. The most popular sulfonated ligand TPPTS [4] has been widely utilized in a variety of transition metal-catalyzed reactions (Scheme 1) [5,6]. Some other modified triphenylphosphanes such as TPPDS, GUAPHOS have also been found to be efficient for various C–C bond formations [4,7].

We have been engaged for a long time in a program devoted to reactions in organoaqueous media using TPPTS ligand [4,8], such as palladium-catalyzed reactions [8,9], nickel-catalyzed cross-couplings [10], palladium, rhodium or nickel-catalyzed ene-reaction [11] and palladium and platinum-catalyzed carboalkoxycyclization [12]. Recently, we have reported the versatile preparation of the water-soluble ligand *m*-TPPTC (Scheme 1) [4,13]. The preparation involved a phosphorylation starting from 1,3-dibromobenzene followed by an halogen–lithium exchange and a carboxylation with CO_2 (Scheme 2). We have shown that, this ligand was particularly efficient for selected Pd-catalyzed reactions [13,14].

We also investigated Rh-catalyzed addition of boronic acids to unsaturated compounds such as α,β-unsatu-

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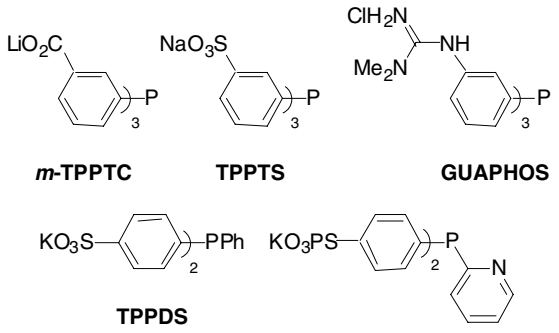
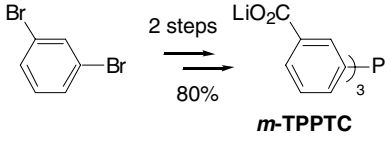
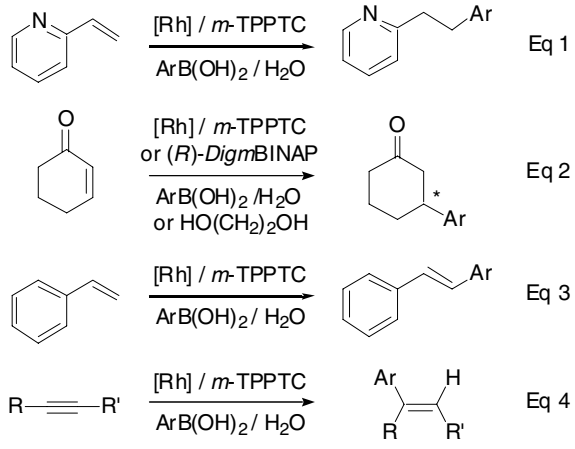


Scheme 1.



Scheme 2.

rated ketones, aromatic and heteroaromatic olefins (Scheme 3) [15]. The arylation of pyridyl-substituted alkenes and enones afforded the pyridyl derivatives and the ketones via addition-hydrolysis reaction and 1,4-addition respectively (Eqs. (1) and (2)). This latter reaction was also developed in asymmetric version using a chiral cationic BINAP-derivative ligand in ethylene glycol [16]. The styrene reacted differently and led to the Heck-compound (Eq. (3)). We sought to evaluate the reactivity of the new carboxylated ligand for other C–C bond formations and turned our attention to the Rh-catalyzed addition of boronic acids to alkynes described recently by Hayashi's group in a dioxane/water mixture (Eq. (4)) [17]. We found that the use of a Rh/*m*-TPPTC system enables the formation of alkenes [18] and wish to report a full description of our results



Scheme 3.

including the mechanism insights and the recycling of the catalyst.

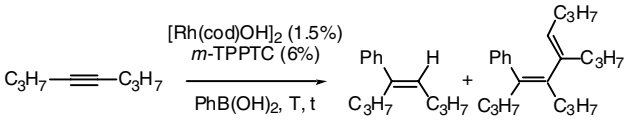
2. Results and discussion

2.1. Optimization of the catalyst system

The addition of phenylboronic acid to oct-4-yne **1** was chosen as a standard reaction for the optimization of the catalytic system (Table 1). Preliminary conditions used 3 mol% rhodium, 6 mol% of the ligand *m*-TPPTC and 5 equiv. of boronic acid at 100 °C in water. Having in hand a highly water-soluble ligand (1100 g/L), we decided to conduct the reaction directly in water without any surfactant [19]. We screened several Rh^I precursors and found that the dimer $[Rh(cod)OH]_2$ [20] was the best catalyst to enable the reaction in 99% yield (entry 1). The alkene **2a** was isolated in the presence of the diene **3a**, whose structure and stereochemistry was unambiguously determined by ^1H NMR and NOESY effect [21]. In contrast to Ni [22] or Ti [23] mediated formation of dienes, this reactivity was unprecedented in the Rh-catalyzed arylation of substituted alkynes. The formation of **3a**, in relation with the Rh-catalyzed polymerization of phenylacetylene [24], will be discussed in Section 2.3. We then studied the influence of various parameters (base, temperature, alkyne/phenylboronic acid ratio). The potential of a base was previously found to be of some importance for the Rh-catalyzed additions of boronic acids [15,11,19,25]. The use of mineral or organic bases such as Na_2CO_3 or Et_3N led to a lower selectivity (entries 2 and 3). The temperature highly influenced the outcome of the reaction (entries 4–6). The formation of **3a** was indeed favored at room temperature despite a low yield and longer reaction time (entry 4). Further improvements were attempted to completely reverse the selectivity towards the diene (entries 5–7), the highest ratio being 87% so far (entry 7).

Anticipating that the formation of diene might be due to hydrophobic effects, we conducted the reaction in a biphasic 1/1 water/toluene phase and were pleased to find that the desired alkene could be isolated in 99% yield and 100% selectivity (entry 8). For economic concerns and to avoid boron residues, we then wished to find out if we could reduce the high number of equivalents of boronic acid. The arylation was still very efficient with 2.5 equiv. of phenylboronic acid (entry 9). The use of 1.2 equiv. led to still acceptable yield but the formation of the diene **3a** became competitive (entry 10). Lowering the temperature to 50 °C (entry 11) afforded a good 84% yield and a selectivity of 95% in favor of the alkene **2a**. At room temperature (entry 12), 5 equiv. of phenylboronic acid were necessary to obtain a decent yield. Thus, we further pursue our study under the following optimized conditions: 1.5 mol% of

Table 1
Rh-catalyzed arylation of oct-4-yne



1 **2a** **3a**

Entry	Conditions	$PhB(OH)_2$ (equiv.)	T (°C)	t (h)	Yield[a] (%)	**2a/3a** Ratio[b]
1	H_2O	5	100	3	99	80/20
2	H_2O, Na_2CO_3[c]	5	100	3	99	60/40
3	H_2O, Et_3N[c]	5	100	3	99	80/20[d]
4	H_2O	5	rt	69	26	40/60
5	H_2O	5	30	67	71	75/25
6	H_2O	5	50	67	99	88/12
7	H_2O, Na_2CO_3[c]	0.2	rt	69	30	13/87
8	H_2O/toluene 1/1	5	100	3	99	100/0
9	H_2O/toluene 1/1	2.5	100	3	90	98/2
10	H_2O/toluene 1/1	1.2	100	3	75	92/8
11	H_2O/toluene 1/1	2.5	50	6.3	84	95/5
12	H_2O/toluene 1/1	5	rt	66	45	97/3

[a] Isolated yield.
[b] Measured by ^1H NMR and GC.
[c] 2 equiv.
[d] Mixture of **2a** and its stereoisomer.

$[Rh(cod)OH]_2$, 6 mol% of *m*-TPPTC, 2.5 equiv. of boronic acids, 100 °C.

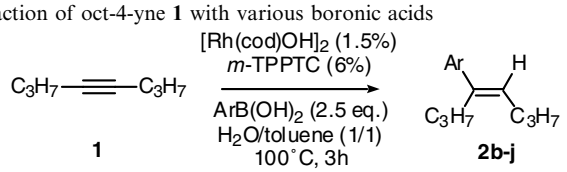
2.2. Scope and limitations

We next studied the scope of the reaction by subjecting oct-4-yne **1** to a series of substituted boronic acids. The alkyne **1** reacted very smoothly to form the corresponding alkenes **2b–j**, as shown in Table 2. No traces of dienes could be detected by ^1H NMR or gas chromatography.

The conditions were compatible with electron-donating and electron-withdrawing groups as exemplified by the addition of methylphenylboronic acids (entries 1 and 2), methoxyphenylboronic acids (entries 3 and 4), and trifluoromethylphenylboronic acid (entry 5). The corresponding alkenes **2b–f** were isolated in 80–99% yield. It has to be pointed out that in the case of the methoxyphenylboronic acids, no reduction of the boronic acid to anisole was observed, which makes these conditions very attractive compared to previously described ones [17]. The arylation was still efficient with hindered boronic acids (entries 2 and 6) and was completely chemoselective as bromophenylboronic acid could be added in 99% yield (entry 7). This latter example was particularly interesting for further organometallic coupling. Similar chemoselectivity was observed in Rh-catalyzed addition of bromo-substituted boron derivatives [15,16,25c,26]. The boronic acids bearing an aldehyde or a sulfur group were also reactive and led to the corresponding alkenes **2i–j** in 48% and 49% yields, respectively.

We then studied the reactivity of various alkynes bearing alkyl, aryl or heteroryl groups and especially unsymmetrical alkynes. On one hand, Hayashi showed that the presence of an electron withdrawing such as an ester or a phosphonate group was crucial for a high regioselectivity in organoaqueous media [17]. On the other hand, the reaction was only found to be highly regioselective in water with 2-heteroaryl substituted alkynes [19]. The presence of a chelating pyridyl group was advocated to explain this excellent stereo-outcome. The case of 1-phenylpropyne was a real challenge too, as no reaction occurred in water [19] and only a mixture of regioisomers (3:1) was obtained in the dioxane/water system [17]. All together, we therefore decided to study the hydroarylation of 1-phenylpropyne, 1-phenylhexyne, 2-(1-hexynyl)pyridine and 4-(1-hexynyl)pyridine (Table 3) [27]. We were pleased to find that 1-phenylpropyne **4** reacted smoothly: the formation of the expected alkenes **5a–c** was observed with high yields (entries 1–3). Moreover, the regioselectivity was found to be >95% as no trace of another isomer was detected by NMR or GC. The addition of the aryl groups occurs exclusively at the β position of the phenyl group. The same selectivity was observed for 1-phenylhexyne **6** as the addition of 4-methoxyphenylboronic acid led to the corresponding alkene **7** in 80% yield (entry 4). We also tested the efficiency of the system with a pyridyl substituted alkyne and an excellent regioselectivity was also observed. The alkenes **9** were isolated in high yields (entries 5–7), regardless the substitution of the aromatic ring of the boronic acid. The regioselectivity observed for these two alkynes tends to prove that no chelation-

Table 2
Reaction of oct-4-yne **1** with various boronic acids



1 **2b-j**

Entry	Ar	Product	Yield (%)[a]
1	4-MeC_6H_4	**2b**	97
2	2-MeC_6H_4	**2c**	99
3	4-$MeOC_6H_4$	**2d**	80
4	3-$MeOC_6H_4$	**2e**	93
5	4-$CF_3C_6H_4$	**2f**	99
6	1-Naphthyl	**2g**	99
7	4-BrC_6H_4	**2h**	99
8	4-$CHOC_6H_4$	**2i**	48
9	3-Thiophene	**2j**	49

[a] Isolated yield.

controlled occurs with our system. This was further confirmed in the case of the 4-substituted pyridyl alkyne **10**. Once again, the reaction occurred with a total regioselectivity an led to the 3-methoxyphenyl and napthyl derivatives **11a**,**b** in 68% and 65% yield, respectively (entries 8 and 9). The 2-(1-hexynyl)thiophene **12** had a similar behavior towards the addition of the phenylboronic acid (entry 10) as the alkene **13** was isolated in 88% yield as a single isomer. One common feature could come out from these examples. It seems that the regioselectivity is directed by the phenyl or the heteroaryl group when the alkyne is substituted by an alkyl group. An alkyl group does not therefore influence the regioselectivity of the reaction.

We decided to investigate the influence of a silyl group compared to an alkyl and a phenyl group (Table 4). Organosilanes have indeed recently been recognized to be practical for various couplings [28]. The additions of various boronic acids to 4-(trimethylsilylethynyl) bromobenzene **14** proceed efficiently with high chemoselectivity (entries 1–3), leading to corresponding alkenes **15** in 98% yield. Nevertheless, these alkenyl compounds were respectively isolated as a 1/1 mixture of inseparable isomers **15a**–**b**, **15c**–**d** and **15e**–**f**.

The structures of **15a**,**b** were demonstrated by the desilylation reaction under standard conditions (*n*-Bu_4NF in THF at 60 °C) to give the 1/1 mixture of *gem*-disubstituted ($J = 1.1$ Hz) and *trans*-disubstituted ($J = 16.5$ Hz) alkenes **16** in 99% yield (Scheme 4).

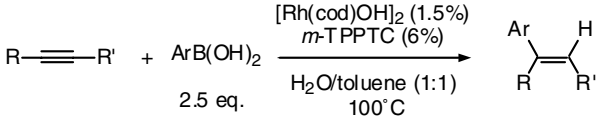
It seems therefore that the trimethylsilyl group has the same effect as the phenyl group and promotes the addition of the aryl group at the β position, which may be explained by the electronic effects of silicium. This trend was further confirmed by testing the reactivity of a substrate bearing an alkyl group such as **17**. The addition of phenylboronic acid to the alkyne **17** indeed gave exclusively a unique isomer **18a** in 94% yield (entry 4). The structure of this latter was confirmed by ^1H and NOESY analyses. Other boronic acids bearing electron-donating and electron-withdrawing groups also afforded the corresponding alkenes **18b**,**c** in 73% and 77% isolated yields (entries 5 and 6).

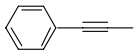
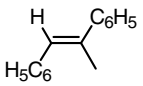
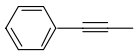
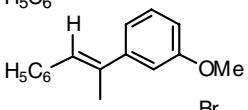
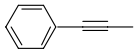
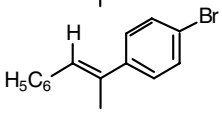
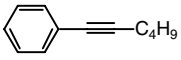
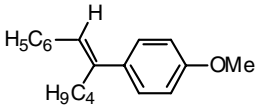
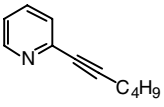
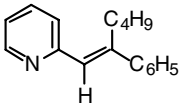
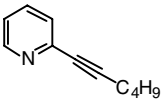
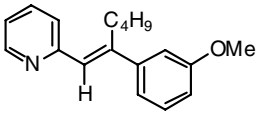
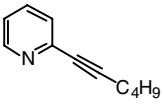
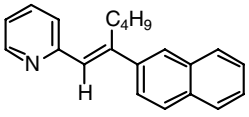
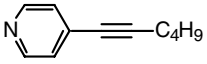
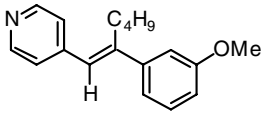
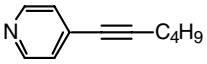
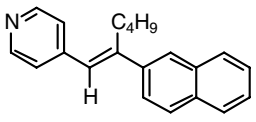
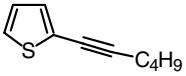
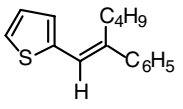
2.3. Mechanistic investigation

The mechanistic study of the addition of boronic acids to alkynes was studied in biphasic system and in water. Considering the previous apparently similar reports [17,19], one may either envisage a vinylrhodium intermediate or an arylrhodium species. Hayashi reported that the vinylrhodium intermediate **A** rearranges to an arylrhodium one **B** [17]. Lautens proposed a chelated alkenylrhodium intermediate, based on deuteration on the alkene position and due to the fact that only 2-pyridyl substituted substrates are reactive [19]. The rhodium-catalyzed chelation-controlled was excluded in our case, as we have shown that the hydroarylations of either 1-phenylpropyne **4**, 1-phenylhexyne **6**, 2-(1-hexynyl)pyridine **8**, 4-(1-hexynyl)pyridine **10** and 2-(1-hexynyl)thiophene **12** were regioselective (Table 3). We therefore, conducted the reactions in a 1/1 D_2O/toluene mixture and in D_2O. The reaction of **1** with $PhB(OH)_2$ in the biphasic D_2O/toluene mixture led to alkene **d-2a**, which showed 90% deuterium incorporation at the vinylic position by ^1H NMR analysis (Scheme 5) [29]. The addition of phenylboronic acid to oct-4-yne in D_2O afforded a 8/2 mixture of **2a**/**3a** with a 70% deuterium incorporation for **d-2a**.

Based on these experiments, a plausible mechanism could be described on Scheme 5. The reaction first involves a classic transmetallation leading to a [RhL_n]–Ph intermediate, then a complexation of the catalyst to the alkyne, and the *syn* addition [30] to the alkyne leading to the vinylrhodium specie **A**. At this stage, the equilibrium between the intermediate **A** and an arylrhodium specie **B** is a minor phenomena implying a low rate constant in our case as the vinylic intermediate is either trapped by another molecule of alkyne leading to **3a** (path b) or/and hydrolyzed to give **2a** (path a). Subsequent hydrolysis with water results in the formation of the desired alkene and regeneration of the catalyst. The kinetics of the hydrolysis step (path a) and the second addition of the alkyne (path b) are presumably influenced by the nature of the phosphane. Moreover, the formation of the diene **3a** in water may be due to the unique structure and properties of water compared to organic solvents. It is now well-known that water has the highest cohesive energy density, a very large surface tension and a high heat capacity [1–3]. The principal consequence of these effects is the entropy-driven

Table 3
Reaction of unsymmetrical alkynes with various boronic acids



Entry	Alkyne		Ar	Product		*t* (h)	yield[a] (%)
1		**4**	C_6H_5		**5a**	2.5	95
2		**4**	3-$MeOC_6H_4$		**5b**	2.5	96
3		**4**	4-BrC_6H_4		**5c**	2.5	73
4		**6**	4-$MeOC_6H_4$		**7**	3	80
5		**8**	C_6H_5		**9a**	3	98
6		**8**	3-$MeOC_6H_4$		**9b**	3	98
7		**8**	2-Naphtyl		**9c**	3	80
8		**10**	3-$MeOC_6H_4$		**11a**	3	68
9		**10**	2-Naphtyl		**11b**	3	65
10		**12**	C_6H_5		**13**	3	88

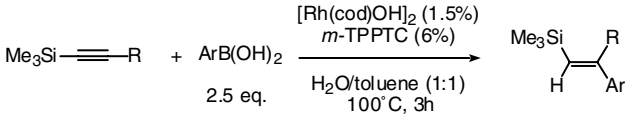
[a] Isolated yield.

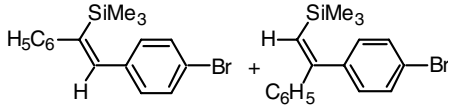
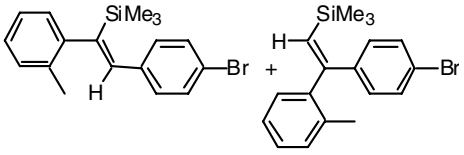
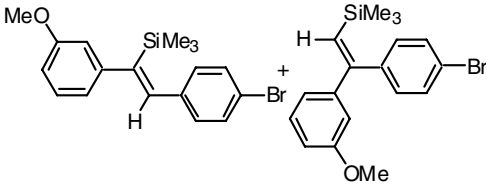
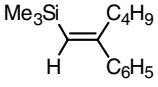
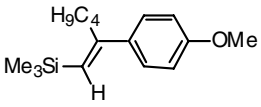
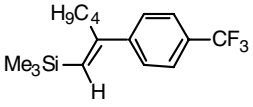
association of apolar solutes in water. The hydrophobic effect in our case, due to the low water-solubility of the alkyl alkyne, may therefore promote a second addition of alkyne, as several alkynes are close to each other (Fig. 1). The use of a biphasic system may control the concentration [31] of the alkyne in the water phase and therefore influences the selectivity of the reaction in favor of the monoaddition of the alkyne.

2.4. Recycling

A major advantage of water-soluble phosphane lies in the recycling possibility of the catalyst, that is therefore preserved in water. For that reason we envisaged improving our catalyst system Rh(I)/*m*-TPPTC by recycle experiments. We performed the hydroarylation of oct-4-yne **1** with phenylboronic acid using 1.5 mol%

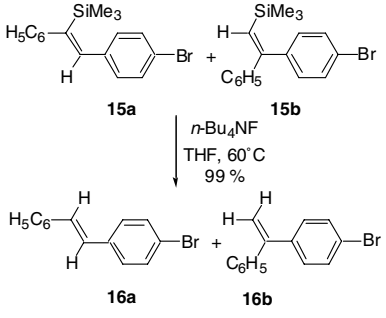
Table 4
Reaction of unsymmetrical silylated alkynes with various boronic acids



Entry	R		Ar	Product		Yield (%)[a]
1	4-BrC_6H_4	**14**	C_6H_5		**15a,b**	99[b]
2	4-BrC_6H_4	**14**	2-MeC_6H_4		**15c,d**	98[b]
3	4-BrC_6H_4	**14**	3-$MeOC_6H_4$		**15e,f**	98[b]
4	C_4H_9	**17**	C_6H_5		**18a**	94
5	C_4H_9	**17**	4-$MeOC_6H_4$		**18b**	73
6	C_4H_9	**17**	4-$CF_3C_6H_4$		**18c**	77

[a] Isolated yield.
[b] 1/1 Mixture measured by ^{1} NMR and gas chromatography.

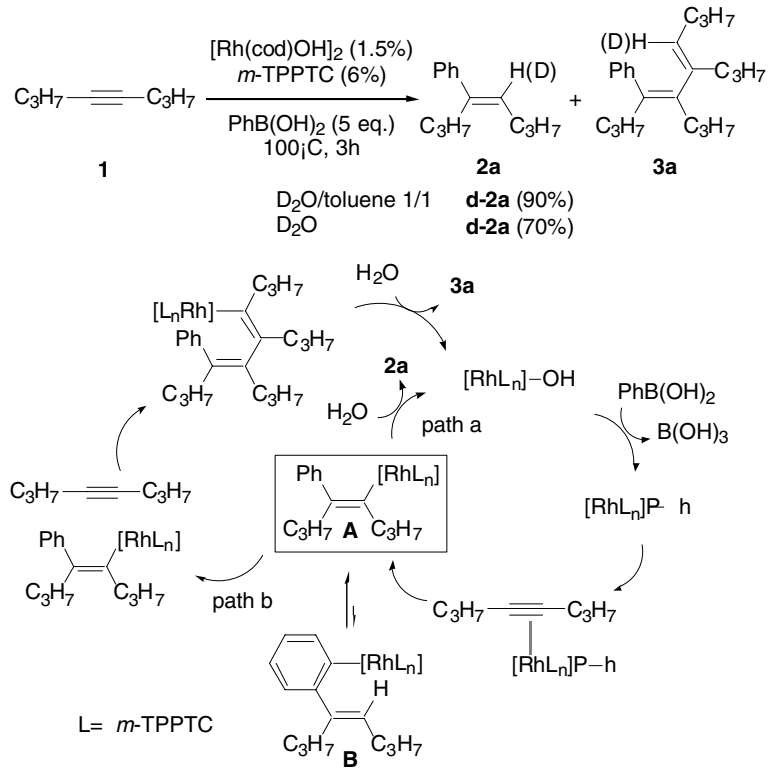
$[Rh(cod)OH]_2$, 6 mol% *m*-TPPTC under our standard conditions. As shown in Fig. 2, we were pleased to find that the benefits of the water-soluble ligand lied in the successful recycling of the expensive rhodium. Indeed, after completion of the reaction, the organic phase (containing the product) was separated, the water phase was then extracted two times with toluene and reloaded with substrates. The reaction time was still very short for each of the 4 cycles (1.5 h). The alkene **2a** was isolated with 93–98% yield and with excellent purity (98%).



Scheme 4.

3. Conclusion

The rhodium/*m*-TPPTC system therefore provides a convenient catalyst for the hydroarylation of substituted alkynes. The addition of various arylboronic acids to alkynes afforded very efficiently trisubstituted alkenes in excellent yields and purity. The reaction was found to be highly chemo-, stereo- and regioselective in a water/toluene biphasic system. The conditions were compatible either with alkyl, aryl, heteroaryl and silyl-substituted alkynes. The regioselectivity follows a general trend showing that aromatic and silyl groups promote the addition of the aryl group at the β position.



Scheme 5.

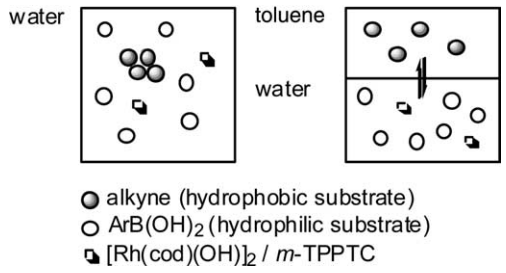


Fig. 1.

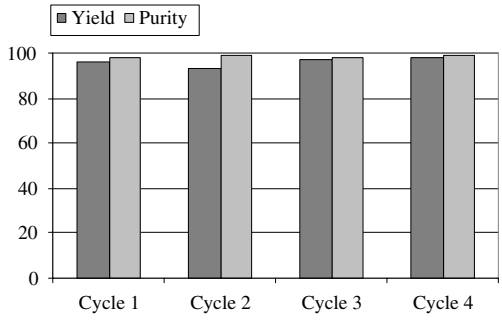


Fig. 2.

The mechanism was investigated in water and in toluene/water biphasic system and involves a vinylrhodium complex. The recycling of the catalyst was performed efficiently too. Further applications of the rhodium/*m*-TPPTC system are currently under high investigation in our laboratory and will be reported in due course.

4. Experimental

Reagents were commercially available from Acros, Aldrich or Avocado and used without further purification. $[Rh(cod)OH]_2$ was prepared according to the reported procedure [20a]. All manipulations involving air-sensitive reagents were carried out under argon and Schlenk techniques for catalytic tests. Water and toluene were degassed by sparging with argon and/or exposure to vacuum. Column chromatography was performed with E. Merck 0.040–0.063 mm Art. 11567 silica gel. ^{1}H NMR, ^{13}C NMR and $^{19}FNMR$ were recorded on a Bruker AV 300 instrument. All signals for ^{1}H, ^{13}C and $^{19}FNMR$ were expressed as ppm down field from, respectively, Me_4Si and $CFCl_3$ used as an internal standard (δ) Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. GC analyses were performed with a Hewlett–Packard 5890 instrument equipped with a *J&W* Scientific DB-1701 capillary column (15 m, $d = 0.254$ μm), using flame ionization detector. Elemental analyses were performed at the University of Pierre et Marie Curie (UPMC Paris VI). Mass spectrometry analyses were performed at the Ecole Nationale Supérieure de Chimie de Paris with a Hewl-

ett–Packard HP 5989 A. Direct introduction experiments were done by electronic impact. High resolution mass spectra were performed on a Varian MAT311 instrument at the Ecole Normale Supérieure (Paris). The spectral characterizations of alkenes **2a–b** [17], **2d** [17], **2f** [17], **2g** [32], **2i** [33], **5a** [17], **5c** [34], **9a** [19b], **13** [35], **18a** [36] are identical to those published in the literature.

4.1. Typical procedure for rhodium-catalyzed hydroarylation of alkyne with arylboronic acids

To a degassed mixture of $[Rh(cod)OH]_2$ (1.5 mol%), *m*-TPPTC (6 mol%) and arylboronic acid (2.5 equiv.) at room temperature was successively added the alkyne (1 equiv.) and solvents (water/toluene 1/1, 2.5 M). The mixture was stirred at 100 °C for 3 h, cooled to room temperature and then filtered on a short pad of silica gel with 25 mL of ethyl acetate and evaporate under reduce pressure to give the product. No further purification by silica gel chromatography was necessary.

4.1.1. (4Z,6E)-4-phenyl-5,6-dipropyl-4,6-decadiene (**3a**)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.57 (t, J = 7.1 Hz, 3H, CH_3), 0.73 (t, J = 7.0 Hz, 3H, CH_3), 0.78 (t, J = 7.1 Hz, 3H, CH_3), 0.86 (t, J = 7.1 Hz, 3H, CH_3), 0.91–0.98 (m, 2H, CH_2), 1.17–1.37 (m, 6H, 3 CH_2), 1.67 (q, J = 7.2 Hz, 2H, CH_2), 1.75 (t, J = 7.9 Hz, 2H, CH_2), 2.13 (t, J = 7.9 Hz, 2H, CH_2), 2.28 (t, J = 7.5 Hz, 2H, CH_2), 4.83 (t, J = 7.2 Hz, 1H, CH), 6.95–7.04 (m, 3H, CH ar), 7.08–7.13 (m, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 14.7 (CH_3), 15.0 (CH_3), 15.1 (CH_3), 15.6 (CH_3), 22.4 (CH_2), 22.7 (CH_2), 22.9 (CH_2), 23.5 (CH_2), 30.7 (CH_2), 33.4 (CH_2), 34.4 (CH_2), 37.4 (CH_2), 126.1 (CH), 128.1 (2 CH ar), 130.4 (2 CH ar), 132.1 (CH ar), 137.1 (C_q), 140.1 (C_q), 141.9 (C_q), 145.5 (C_q); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 8.9 min; MS (EI, *m*/*z*): 298 $(M)^{+\cdot}$, 255 $(M-C_3H_7)^+$.

4.1.2. (E)-4-(2-methylphenyl)oct-4-ene (**2c**)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.94 (t, J = 7.3 Hz, 3H, CH_3), 1.03 (t, J = 7.3 Hz, 3H, CH_3), 1.36 (sext, J = 7.3 Hz, 2H, CH_2), 1.52 (sext, J = 7.3 Hz, 2H, CH_2), 2.22 (q, J = 7.3 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.38 (t, J = 7.3 Hz, 2H, CH_2), 5.31 (t, J = 7.3 Hz, 1H, CH), 7.1–7.2 (m, 4H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 14.2 (CH_3), 19.9 (CH_3), 21.4 (CH_2), 23.1 (CH_2), 30.1 (CH_2), 33.9 (CH_2), 125.2 (CH), 126.3 (CH ar), 129.0 (CH ar), 129.8 (CH ar), 129.9 (CH ar), 135.2 (C_q ar), 140.6 (C_q ar), 144.7 (C_q); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 6.7 min; MS (EI, *m*/*z*): 202 $(M)^{+\cdot}$, 187 $(M-CH_3)^+$, 173 $(M-C_2H_5)^+$, 159 $(M-C_3H_7)^+$.

4.1.3. (E)-4-(3-methoxyphenyl)oct-4-ene (**2e**)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (t, J = 7.3 Hz, 3H, CH_3), 0.98 (t, J = 7.3 Hz, 3H, CH_3), 1.39 (sext, J = 7.3 Hz, 2H, CH_2), 1.49 (sext, J = 7.3 Hz, 2H, CH_2), 2.19 (q, J = 7.3 Hz, 2H, CH_2), 2.48 (t, J = 7.3 Hz, 2H, CH_2), 3.83 (s, 3H, OCH_3), 5.69 (t, J = 7.3 Hz, 1H, CH), 6.78 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H, CH ar), 6.91 (appt, J = 2.6 Hz, 1H, CH ar), 6.97 (ddd, J = 7.6, 1.5, 0.9 Hz, 1H, CH ar), 7.23 (appt, J = 7.9 Hz, 1H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 14.0 (CH_3), 21.8 (CH_2), 23.1 (CH_2), 30.6 (CH_2), 31.8 (CH_2), 55.1 (CH_3), 111.5 (CH ar), 112.5 (CH ar), 119.0 (CH), 129.0 (CH ar), 129.3 (CH ar), 140.0 (C_q ar), 145.2 (C_q), 159.5 (C_q ar); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 8.2 min; MS (EI, *m*/*z*): 218 $(M)^{+\cdot}$, 189 $(M-C_2H_5)^+$, 175 $(M-C_3H_7)^+$. Anal. Calc. for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.91; H, 10.58%.

4.1.4. (E)-4-(4-bromophenyl)oct-4-ene (**2h**)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, J = 7.3 Hz, 3H, CH_3), 0.98 (t, J = 7.3 Hz, 3H, CH_3), 1.36 (sext, J = 7.3 Hz, 2H, CH_2), 1.49 (sext, J = 7.3 Hz, 2H, CH_2), 2.18 (q, J = 7.3 Hz, 2H, CH_2), 2.46 (t, J = 7.3 Hz, 2H, CH_2), 5.67 (t, J = 7.3 Hz, 1H, CH), 7.21 (d, J = 8.6 Hz, 2H, CH ar), 7.42 (d, J = 8.6 Hz, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (2 CH_3), 21.7 (CH_2), 23.0 (CH_2), 30.7 (CH_2), 31.6 (CH_2), 120.1 (C_q ar), 128.0 (2 CH ar), 129.8 (CH), 131.2 (2 CH ar), 139.1 (C_q ar), 142.4 (C_q); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 8.5 min; MS (EI, *m*/*z*): 266 $(M)^{+\cdot}$, 239 $(M-C_2H_5)^+$, 223 $(M-C_3H_7)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{14}H_{19}Br$: 266.0670, 268.0651. Found 266.0673, 268.0653.

4.1.5. (E)-3-(1-propyl-pent-1-enyl)-thiophene (**2j**)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85 (t, J = 7.5 Hz, 3H, CH_3), 0.89 (t, J = 7.2 Hz, 3H, CH_3), 1.35 (sext, J = 7.2 Hz, 4H, 2 CH_2), 2.08 (q, J = 7.5 Hz, 2H, CH_2), 2.34 (t, J = 7.2 Hz, 2H, CH_2), 5.75 (t, J = 7.2 Hz, 1H, CH), 7.08 (dd, J = 2.8, 1.4 Hz, 1H, CH ar), 7.19–7.26 (m, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 14.2 (CH_3), 22.2 (CH_2), 23.0 (CH_2), 30.4 (CH_2), 32.0 (CH_2), 118.6 (CH ar), 125.0 (CH), 125.8 (CH ar), 127.9 (CH ar), 134.6 (C_q ar), 144.3 (C_q); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 6.8 min; MS (EI, *m*/*z*): 194 $(M)^{+\cdot}$, 179 $(M-CH_3)^+$, 165 $(M-C_2H_5)^+$, 151 $(M-C_3H_7)^+$.

4.1.6. (E)-1-phenyl-2-(3-methoxyphenyl)propene (**5b**)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.90 (s, 1H, CH), 7.13–7.44 (m, 9H, H_{ar}); ^{13}C ($CDCl_3$, 75 MHz): δ 17.6 (CH_3), 55.3 (OCH_3), 112.1 (CH ar), 112.5 (CH ar), 118.7 (CH), 126.6 (CH ar), 127.9 (CH ar), 128.3 (2 CH ar), 129.2 (2 CH ar), 129.3 (CH ar), 137.4 (C_q), 138.3 (C_q ar),

145.6 (C_q ar), 159.7 (C_q ar); GC (150 °C, 1 min, 20 °C/min, 250 °C): t_R = 6.4 min; MS (EI, *m/z*): 224 $(M)^{+\cdot}$, 209 $(M-CH_3)^+$, 194 $(M-CH_2OH)^+$. Anal. Calc. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.33; H, 7.21%.

*4.1.7. (E)-1-phenyl-2-(4-methoxyphenyl)hexene (**7**)*

^1H NMR ($CDCl_3$, 300 MHz): δ 0.76 (t, J = 7.2 Hz, 3H, CH_3), 1.17–1.36 (m, 4H, 2 CH_2), 2.59 (t, J = 7.2 Hz, 2H, CH_2), 3.73 (s, 3H, CH_3), 6.56 (s, 1H, CH), 6.81 (d, J = 8.8 Hz, 2H, CH ar), 7.13–7.26 (m, 5H, CH ar), 7.31 (d, J = 8.8 Hz, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 22.8 (CH_2), 29.9 (CH_2), 31.0 (CH_2), 55.3 (OCH_3), 113.7 (2 CH ar), 126.3 (CH), 126.8 (CH ar), 127.6 (2 CH ar), 128.1 (2 CH ar), 128.8 (2 CH ar), 135.5 (C_q), 138.6 (C_q ar), 142.7 (C_q ar), 158.9 (C_q ar); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 11.2 min; MS (EI, *m/z*): 266 $(M)^{+\cdot}$, 209 $(M-CH_3)^+$, 194 $(M-OCH_3)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{19}H_{22}O$: 266.1671. Found 266.1672.

*4.1.8. (E)-2-[2-(3-methoxyphenyl)-1-hexenyl]pyridine (**9b**)*

^1H NMR ($CDCl_3$, 300 MHz): δ 0.85 (t, J = 7.1 Hz, 3H, CH_3), 1.32–1.45 (m, 4H, 2 CH_2), 3.03 (app t, J = 8.0 Hz, 2H, CH_2), 3.84 (s, 3H, CH_3), 6.72 (s, 1H, CH), 6.86 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H, CH ar), 7.05 (appt, J = 7.7 Hz, 1H, CH ar), 7.09–7.13 (m, 2H, CH ar), 7.26–7.32 (m, 2H, CH ar), 7.65 (apptd, J = 7.7, 1.9 Hz, 1H, CH ar), 8.64 (ddd, J = 4.8, 1.7, 0.8 Hz, 1H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 22.8 (CH_2), 30.2 (CH_2), 30.8 (CH_2), 55.2 (OCH_3), 112.6 (CH ar), 112.8 (CH ar), 119.2 (CH ar), 121.0 (CH), 124.3 (CH ar), 127.1 (CH ar), 129.2 (CH ar), 136.0 (CH ar), 144.8 (C_q ar), 147.5 (C_q), 149.2 (CH ar), 157.0 (C_q ar), 159.6 (C_q ar); GC (130 °C, 1 min, 20 °C/min, 250 °C): t_R = 8.6 min; MS (EI, *m/z*): 267 $(M)^{+\cdot}$, 252 $(M-CH_3)^+$, 238 $(M-C_2H_5)^+$, 224 $(M-C_3H_7)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{18}H_{21}NO$: 267.1623. Found 267.1626.

*4.1.9. (E)-2-[2-(2-naphthyl)-1-hexenyl]pyridine (**9c**)*

^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 7.2 Hz, 3H, CH_3), 1.34–1.52 (m, 4H, 2 CH_2), 3.19 (appt, J = 7.4 Hz, 2H, CH_2), 6.89 (s, 1H, CH), 7.13 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H, CH ar), 7.34 (dd, J = 7.8, 0.8 Hz, 1H, CH ar), 7.46–7.53 (m, 2H, CH ar), 7.65–7.70 (m, 2H, CH ar), 7.84–7.90 (m, 3H, CH ar), 7.98 (dd, J = 1.1, 0.6 Hz, 1H, CH ar), 8.68 (ddd, J = 4.7, 1.7, 0.8 Hz, 1H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 22.8 (CH_2), 30.0 (CH_2), 30.9 (CH_2), 121.0 (CH), 124.3 (CH ar), 125.1 (CH ar), 125.5 (CH ar), 125.9 (CH ar), 126.1 (CH ar), 127.5 (CH ar), 127.7 (CH ar), 127.9 (CH ar), 128.2 (CH ar), 132.9 (C_q ar), 133.5 (C_q ar), 136.0 (CH ar), 140.7 (C_q ar), 147.5 (C_q), 149.3 (CH ar), 157.1 (C_q ar); GC (130 °C, 1 min, 20 °C/min, 250 °C): t_R = 13.1 min; MS (EI, *m/z*): 287 $(M)^{+\cdot}$, 272 $(M-CH_3)^+$, 258 $(M-C_2H_5)^+$, 244 $(M-C_3H_7)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{21}H_{21}N$: 287.1674. Found 287.1669.

*4.1.10. (E)-4-[2-(3-methoxyphenyl)-1-hexenyl]pyridine (**11a**)*

^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J = 7.2 Hz, 3H, CH_3), 1.26–1.45 (m, 4H, 2 CH_2), 2.68 (appt, J = 7.2 Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 6.58 (s, 1H, CH), 6.88 (ddd, J = 8.4, 2.5, 0.9 Hz, 1H, CH ar), 6.98 (appt, J = 1.6 Hz, 1H, CH ar), 7.03 (ddd, J = 7.8, 1.5, 0.9 Hz, 1H, CH ar), 7.20 (d, J = 5.8 Hz, 2H, CH ar), 7.29 (t, J = 7.9 Hz, 1H, CH ar), 8.58 (d, J = 5.8 Hz, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.8 (CH_3), 22.7 (CH_2), 30.3 (CH_2), 30.8 (CH_2), 55.3 (OCH_3), 112.7 (CH ar), 112.9 (CH ar), 119.1 (CH), 123.5 (2 CH ar), 125.4 (CH ar), 129.4 (CH ar), 143.9 (C_q ar), 145.8 (C_q ar), 147.2 (C_q), 149.8 (2 CH ar), 159.7 (C_q ar); GC (130 °C, 1 min, 20 °C/min, 250 °C): t_R = 9.1 min; MS (EI, *m/z*): 267 $(M)^{+\cdot}$, 224 $(M-C_3H_7)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{18}H_{21}ON$: 267.1623. Found 267.1625.

*4.1.11. (E)-4-[2-(2-naphthyl)-1-hexenyl]pyridine (**11b**)*

^1H NMR ($CDCl_3$, 300 MHz): δ 0.86 (t, J = 7.2 Hz, 3H, CH_3), 1.35–1.47 (m, 4H, 2 CH_2), 2.82 (t, J = 7.2 Hz, 2H, CH_2), 6.72 (s, 1H, CH), 7.25 (d, J = 6.0 Hz, 2H, CH ar), 7.48–7.51 (m, 2H, CH ar), 7.6 (dd, J = 8.7, 1.9 Hz, 1H, CH ar), 7.84–7.91 (m, 4H, CH ar), 8.62 (d, J = 6.0 Hz, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 13.8 (CH_3), 22.7 (CH_2), 30.2 (CH_2), 30.9 (CH_2), 123.5 (2 CH ar), 124.8 (CH), 125.5 (CH ar), 125.9 (CH ar), 126.1 (CH ar), 126.3 (CH ar), 127.6 (CH ar), 128.1 (CH ar), 128.2 (CH ar), 133.0 (C_q ar), 133.4 (C_q ar), 139.7 (C_q ar), 145.8 (C_q ar), 147.2 (C_q), 149.9 (2 CH ar); GC (130 °C, 1 min, 20 °C/min, 250 °C): t_R = 13.8 min.

*4.1.12. (E)-[2-(4-bromophenyl)-1-phenyl-vinyl]trimethylsilane, (E)-[2-(4-bromophenyl)-2-phenyl-vinyl]trimethylsilane (**15a,b**)*

^1H NMR ($CDCl_3$, 300 MHz): δ −0.08 (s, 9H, $Si(CH_3)_3$), −0.03 (s, 9H, $Si(CH_3)_3$), 6.31 (s, 1H, CH), 7.11–7.53 (m, 19H, CH and CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ −0.7 ($Si(CH_3)_3$), 0.0 ($Si(CH_3)_3$), 120.4 (C_q), 120.7 (C_q), 125.1 (CH ar), 126.3 (2 CH ar), 126.4 (2 CH ar), 127.0 (CH ar), 127.2 (2 CH ar), 127.3 (2 CH ar), 129.5 (2 CH ar), 129.7 (CH ar), 130.3 (2 CH ar), 130.6 (2 CH ar), 138.1 (C_q), 140.8 (C_q), 142.0 (C_q), 142.7 (CH ar), 146.1 (C_q), 147.5 (C_q), 155.0 (C_q); GC (150 °C, 1 min, 20 °C/min, 250 °C): t_R = 6.4 min, 6.7 min; MS (EI, *m/z*): 332, 330 $(M)^{+\cdot}$, 317, 315 $(M-CH_3)^+$.

*4.1.13. (E)-[2-(4-bromophenyl)-1-(2-methylphenyl)-vinyl]trimethylsilane, (E)-[2-(4-bromophenyl)-2-(2-methylpheny)-vinyl]trimethylsilane (**15c,d**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.09 (s, 9H, $Si(CH_3)_3$), 0.00 (s, 9H, $Si(CH_3)_3$), 2.09 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 5.82 (s, 1H, CH), 6.95–7.14 (m, 17H, CH and CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 0.0 ($Si(CH_3)_3$), 0.2 ($Si(CH_3)_3$), 20.1 (CH_3), 20.2 (CH_3), 120.9 (C_q), 121.1 (C_q), 125.0 (CH ar), 125.2 (CH ar), 125.5 (CH ar), 127.0 (CH ar), 127.2 (CH ar), 129.1 (CH ar), 129.6 (CH ar), 129.8 (2 CH ar), 130.0 (CH ar), 130.2 (2 CH ar), 130.6 (2 CH ar), 130.7 (2 CH ar),133.6 (CH ar), 133.8 (C_q), 134.7 (C_q), 138.4 (C_q), 141.7 (C_q), 142.9 (CH ar), 144.8 (C_q), 145.7 (C_q), 147.9 (C_q), 156.9 (C_q); GC (150 °C, 1 min, 20 °C/min, 250 °C): t_R = 6.6 min, 7.0 min; MS (EI, *m/z*): 346, 344 $(M)^{+\cdot}$, 331, 329 $(M-CH_3)^+$.

*4.1.14. (E)-[2-(4-bromophenyl)-1-(3-methoxyphenyl)-vinyl]trimethylsilane, (E)-[2-(4-bromophenyl)-2-(3-methoxyphenyl)-vinyl]trimethylsilane (**15e,f**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.05 (s, 9H, $Si(CH_3)_3$), 0.00 (s, 9H, $Si(CH_3)_3$), 3.79 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 6.35 (s, 1H, CH), 6.79–7.53 (m, 17H, CH and CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 0.0 ($Si(CH_3)_3$), 0.7 ($Si(CH_3)_3$), 55.1 (OCH_3), 55.2 (OCH_3), 111.1 (CH ar), 112.9 (CH ar), 113.0 (CH ar), 113.1 (CH ar), 119.6 (CH ar), 119.8 (CH ar), 121.2 (C_q), 121 5 (C_q), 128.9 (CH ar), 129.0 (CH ar), 130.2 (2 CH ar), 130.6 (CH ar), 131.0 (4 CH ar), 131.3 (2 CH ar), 138.7 (C_q), 141.4 (C_q), 143.3 (CH ar), 144.3 (CH ar), 148.0 (C_q), 148.1 (C_q), 155.6 (C_q), 159.3 (C_q), 159.4 (C_q); GC (150 °C, 1 min, 20 °C/min, 250 °C): t_R = 8.0, 8.5 min.

*4.1.15. (E)-2-(4-methoxyphenyl)-1-(trimethylsilyl)-1-hexene (**18b**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.20 (s, 9H, $Si(CH_3)_3$), 1.32 (t, J = 7.0 Hz, 3H, CH_3), 1.33–1.36 (m, 4H, 2 CH_2), 2.57–2.62 (m, 2H, CH_2), 3.82 (s, 3H, OCH_3), 5.68 (s, 1H, CH), 6.85 (d, J = 8.9 Hz, 2H, CH ar), 7.35 (d, J = 8.9 Hz, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 0.0 ($Si(CH_3)_3$), 13.7 (CH_3), 22.6 (CH_2), 31.4 (CH_2), 34.4 (CH_2), 54.9 (OCH_3), 113.1 (2 CH ar), 125.6 (CH), 126.9 (2 CH ar), 135.8 (C_q), 156.7 (C_q ar), 158.5 (C_q ar); GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 14.0 min; MS (EI, *m/z*): 262 $(M)^{+\cdot}$, 247 $(M-CH_3)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{16}H_{26}O$: 262.1753. Found 262.1748.

*4.1.16. (E)-2-(4-trifluorophenyl)-1-(trimethylsilyl)-1-hexene (**18c**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.20 (s, 9H, $Si(CH_3)_3$), 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.28–1.33 (m, 4H, 2 CH_2), 2.60–2.65 (m, 2H, CH_2), 5.79 (s, 1H, CH), 7.47 (d, J = 8.1 Hz, 2H, CH ar), 7.56 (d, J = 8.1 Hz, 2H, CH ar); ^{13}C ($CDCl_3$, 75 MHz): δ 0.0 ($Si(CH_3)_3$), 13.8 (CH_3), 22.6 (CH_2), 31.2 (CH_2), 34.4 (CH_2), 124.9 (2 CH ar), 125.3 (q, J = 164 Hz, CF_3), 126.3 (2 CH ar), 129.0 (q, J = 32 Hz, CH ar), 130.2 (CH ar), 147.4 (C_q ar), 156.4 (C_q); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.4; GC (70 °C, 1 min, 20 °C/min, 250 °C): t_R = 7.0 min; MS (EI, *m/z*): 300 $(M)^{+\cdot}$, 285 $(M-CH_3)^+$, 281 $(M-F)^+$; HRMS-EI: $(M)^{+\cdot}$. Calculated for $C_{16}H_{23}F_3Si$: 300.1521. Found 300.1527.

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