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Impregnated Platinum on Magnetite as an Efficient, Fast, and Recyclable Catalyst for the Hydrosilylation of Alkynes

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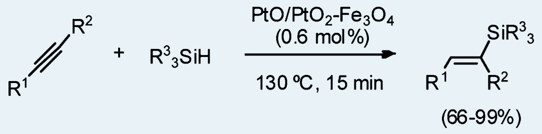
Supporting Information



ABSTRACT: New impregnated platinum on magnetite catalyst has been prepared, characterized and used for the hydrosilylation of different alkynes. The catalyst showed a wide reaction scope, allowing its use for different functionalized alkynes, localized triple bonds, and silane reagents. The reaction is selective for the case of diynes, obtaining the desired mono- or dihydrosilylation processes. The reaction with disilane reagents lead to the incorporation of two alkyne units to the final product. The catalyst is easily prepared and handled, avoiding the use of expensive and difficult to handle organic ligands, and it could be removed from the reaction medium just by sequestering by a magnet. The catalyst could be reused up to ten times with exactly the same activity.

KEYWORDS: *heterogeneous catalysis, hydrosilylation, magnetite, platinum, recycling, vinylsilane*

INTRODUCTION

Silicon derivatives are often stable, innocuous, and cheaper than related organo-metalloids and, therefore, have received great attention not only by academics but also by the industry. Alkenylsilanes[1−4] are particularly attractive scaffolds and very valuable compounds for further transformations,[5−11] since they are easy to handle and storable. The metal-catalyzed hydrosilylation of alkynes is the most straightforward, atom efficiencent[12−16] and convenient approach to achieve their synthesis. Recently, significant progress has been made in this area and a myriad of catalytic systems have been developed, with the aim of generating stereo- and regioselectively isomers. In most cases the stereo- and regioselectivity appears to be capriciously affected by various factors such as metal species, the ligand, the type of alkyne, and the silane, and the reaction parameters, such as solvent and temperature.

Among the different complexes those derived from platinum have emerged as excellent candidates for this transformation,[17−46] with the addition process being cis-mode and the thermodynamically more stable 1-vinylsilane being the major product obtained when starting from terminal alkynes. However, the general applicability is somehow limited by different factors, including the high cost and stability of platinum complexes, the difficulty of separating the catalyst from the reaction media, and the easy generation of either nanoparticles or complexes of platinum(0), which are responsible[47−49] for a number of undesired reactions (isomerizations, hydrogenations, etc). Moreover, the side products and the coloration originated from nanoplatinum species might influence their industrial application.

To avoid the aforementioned drawbacks, platinum species have been immobilized on different organic polymers,[50−52] obtaining a modest regioselectivity (about 3.5:1 isomeric ratio) with platinum loadings and reaction times from 1 to 5 mol % in from 1 to 24 h. The only catalyst which could be recovered and reused was an incarcerated platinum polymer.[51]

No better results have been achieved using platinum catalyst immobilized on carbon,[53,54] magnesium oxide,[55] γ-alumina,[56] silica,[57−60] and titania.[61] Even, the platinum(IV) oxide has been used as heterogeneous catalyst.[62] The average regioselectivity and the reaction times were similar to the organic-polymer derivatives and only in the special case of ortho-substituted arylalkynes, the regiocontrol was higher.[62] The catalyst could be reused only in the cases of the platinum supported onto silica[57,59] and titania[61] and the yield decreased notably after the fourth cycle. Moreover, all catalysts were prepared throughout sophisticated, hard-working and multistep protocols, including calcination and reduction steps, and the conditions for the hydrosilylation implied usually an inert atmosphere.

Meanwhile, we have recently developed a new, simple and robust method to immobilize different metal oxides[63−68] onto magnetite.[69−71] Along this research line, we report herein the first immobilization of platinum on magnetite[72] using the impregnation protocol and its use as a real reusable heterogeneous catalyst for the hydrosilylation of alkynes.

RESULTS AND DISCUSSION

The platinum catalyst was prepared by the classical impregnation method,[73,74] starting from commercial available microparticles of magnetite and initially characterized by XPS and XRD analyses. The XPS spectra showed, after deconvolution, four peaks placed at 72.5 and 75.9 eV, which correspond to the binding energies of PtO $4f_{7/2}$ and $4f_{5/2}$ levels, and 74.4 and 77.6 eV, which correspond to the binding energies

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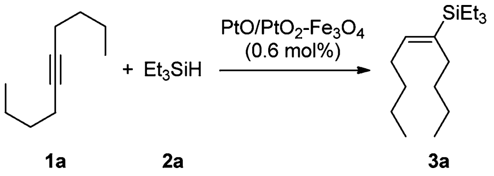
of PtO_2 $4f_{7/2}$ and $4f_{5/2}$ levels, respectively[75] (see Supporting Information), with the Pt(II)/Pt(IV) oxidation state ration being nearly 1/1 and the superficial incorporation (1 nm depth) being 32%. The XRD analysis did not provide any concluding information except that relative to the support diffraction peaks (Fe_3O_4) because of the low metal platinum loading and its high dispersion. The FXR analysis revealed that the total incorporation of platinum was 2.3%.

The BET surface area of catalyst was 8.4 m^2/g, almost the same as the initial magnetite 9.6 m^2/g, with the concordant results showing that there was not significant sinterization process under the assayed impregnation protocol. Moreover, the TEM images showed spherical particles for the catalyst with sizes in the range 0.1 ± 0.09 μm, similar to those obtained from the initial magnetite (size = 0.1 ± 0.1 μm), with a homogeneous distribution of nanoparticles of platinum (size = 1.6 ± 0.6 nm; more than 75% of particles into the range of 1−2.5 nm).

The hydrosilylation of dec-5-yne (**1a**) with triethylsilane was selected as the model reaction in order to optimize the conditions (Table 1).

Table 1. Optimization of the Reaction Conditions[a]



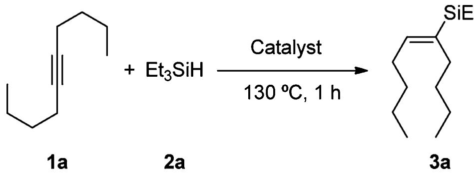
entry	T (°C)	solvent	t (h)	yield (%)[b]
1	25		24	2
2	75		24	89 (36)[c]
3	100		0.25	87
4	130		0.25	99
5	150		0.25	99
6	130	PhMe	1	94
7	130	dioxane	1	63
8	130	MeCN	1	94
9	130	H_2O	1	84
10[d]	130		1	66
11[e]	130		0.25	98
12[f]	130		24	0

[a] Reaction carried out using **1a** (1.0 mmol) and **2a** (1.0 mmol), unless otherwise stated. [b] Isolated yield after flash column chromatography. [c] Result obtained after 0.25 h. [d] Reaction performed using 0.1 mol % of the catalyst. [e] Reaction performed using 1.2 mol %. [f] Reaction performed without catalyst.

The initial solvent-less process at room temperature rendered a very low yield, after a one day reaction. However, just increasing the temperature up to 130 °C permitted to obtain the expected product **3a** in practical quantitative yield after only 15 min of reaction, with a further increase of the temperature having not a significant benefit (entries 1−5). The use of different solvents has an important impact on the reaction time, being also appreciable in the chemical yields (compare entries 4, 6−9 in Table 1). Remarkably, the reaction could be performed in water. The decrease of the catalyst loading had a negative impact on the reaction time as well as the yield, whereas the increase of this amount had no benefits (entries 10 and 11). Finally, the same process was repeated under the best reaction conditions but a without catalyst, and no product was detected by GC-MS analysis after one reaction day (entry 12).

Other related metallic catalysts were also tested (Table 2). First, the magnetite was checked as possible catalyst, since this material is not an innocent oxide,[69−71,76−85] but neither the micro- nor the nanoparticle size material catalyzed the reaction (entries 1 and 2). The impregnated copper,[63,64,68] cobalt,[74] and ruthenium[66,86] on magnetite catalysts showed some activity (entries 3, 4, and 7) with other systems being totally inactive, including bimetallic species, but in all cases far inferior to that obtained with the platinum derivative.

Table 2. Optimization of the Catalyst[a]



entry	catalyst (mol %)	yield (%)[b]
1	Fe_3O_4 (65)[c]	3
2	Fe_3O_4 (65)[d]	6
3	$CuO-Fe_3O_4$ (1.3)	78
4	$CoO-Fe_3O_4$ (1.4)	51
5	$NiO-Fe_3O_4$ (1.4)	0
6	$PdO-Fe_3O_4$ (1.2)	0
7	$Ru_2O_3-Fe_3O_4$ (1.4)	24
8	$Pd(II/0)/Cu(II)-Fe_3O_4$ (1.5/0.8)	0
9	$Cu(II/0)/Ni(II)-Fe_3O_4$ (1.1/0.9)	0

[a] Reaction carried out using **1a** (1.0 mmol) and **2a** (1.0 mmol) in absence of solvent. [b] Isolated yield after flash column chromatography. [c] Result obtained using microparticles. [d] Result obtained using nanoparticles.

Once the optimal reaction conditions were established, the problem of recycling was examined. The catalyst recovered by a magnet from the reaction described in the entry 4 of Table 1 was washed with toluene and reused under the same reaction conditions, obtaining the expected product **3a** (Figure 1). The impregnated platinum on magnetite could be reused up to ten-times without losing its activity, with the lower yield obtained being 96%. In other series of examples, the reaction was quenched after 10 min, avoiding the full conversion, and the obtained results were homogeneous around 90% yield. The phenomenon of leaching was studied by ICP-MS analysis of the resulting reaction solution mixture, and only 0.01% of the initial amount of platinum was detected (0.0008% for iron), with all this data demonstrating the structural integrity of catalyst. Moreover, the TEM images of the ten-times recycled catalyst

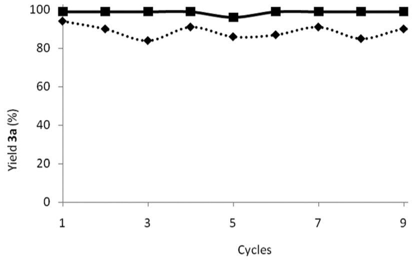


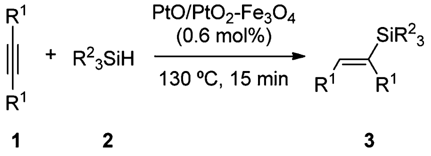
Figure 1. Recycling of $PtO/PtO_2-Fe_3O_4$ Catalyst: (■) yields after 15 min and (◆) yields after 10 min.

showed a homogeneous distribution of nanoparticles of platinum (size: 1.8 ± 0.6 nm; more than 80% of particles into the range of 1−2.5 nm), which is similar to the initial one, with the BET surface area being 7.9 m^2/g and the XPS spectra being exactly to that obtained from the fresh catalyst.

To know if the reaction took place in the organic medium by the leached platinum, we performed the standard process between compounds **1a** and **2a** (Table 1, entry 4). Then, the catalyst was removed by a magnet and washed with toluene. The solvents of the above solution, without catalyst, were removed under low pressure and hex-3-yne (**1b**) and triethylsilane (**2a**) was added to the above residue. The resulting mixture was heated again at 130 °C for 15 min. The analysis of crude mixture, after hydrolysis, revealed the formation of compound **3a** in 98% (catalyzed process) and (*E*)-triethyl(hex-3-en-3-yl)silane (**3b**) in only 25% yield. Therefore, we could exclude that the final leached platinum was the responsible for the reaction results, although a dynamic metal leach and return to the support process could not be excluded.

Then, the optimized protocol was applied to other substrates in order to study the scope of the reaction (Table 3). The reaction using triethylsilane (**2a**) gave excellent results with any type of symmetrical alkynes **3**, even for methoxy-substituted ones (entries 1−5). Only in the case of 1,2-bis(4-bromophenyl)ethyne the yield was lower (entry 6), detecting amounts of the starting alkyne in the crude mixture. The reaction with triphenylsilane needed longer reaction times and the yields were not quantitative, although they were quite satisfactory independently of the alkyne **3** used (entries 7, 10 and 11). The reaction with the poor substrate trimethoxysilane[4] was also effective (entries 8 and 12). Furthermore, the very sterically hindered 1,1,1,3,5,5,5-heptamethyltrisiloxane[31,36] afforded the initial excellent reactivity (entry 9). It should be pointed out that the reaction using the alkene (*Z*)-oct-4-ene failed after 5 h under similar conditions.

Table 3. Preparation of Vinylsilanes[a]

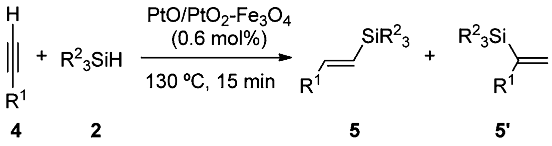


entry	R^1	R^2	product	yield (%)[b]
1	Bu^n	Et	**3a**	99
2	Et	Et	**3b**	99
3	$\mathrm{MeOCH_2}$	Et	**3c**	99
4	Ph	Et	**3d**	99
5	$4\text{-}\mathrm{Bu}^n\mathrm{C_6H_4}$	Et	**3e**	99
6	$4\text{-}\mathrm{BrC_6H_4}$	Et	**3f**	66[c]
7	Bu^n	Ph	**3g**	87[c]
8	Bu^n	MeO	**3h**	92
9	Bu^n	$\mathrm{Me_3SiO}$[d]	**3i**	99
10	$\mathrm{MeOCH_2}$	Ph	**3j**	91
11	Ph	Ph	**3k**	75[c]
12	Ph	MeO	**3l**	85[c]

[a] Reaction carried out using **1** (1.0 mmol) and **2** (1.0 mmol) in absence of solvent. [b] Isolated yield after flash column chromatography. [c] Result obtained after 3 h. [d] Reaction performed using $\mathrm{(Me_3SiO)_2MeSiH}$.

Then, we faced the regioselectivity problem (Table 4). So, the reaction with 1-alkynes **4** gave a quantitative yield, even for trimethoxysilane reagent, with in all cases an isomeric ratio around 3:1 being found (in the range for other heterogeneous catalysts). A similar distribution of compounds **5**/**5′** was found in the case of using propargyl alcohols[23,27,44] (entry 3).

Table 4. Hydrosilylation of 1-Alkynes[a]

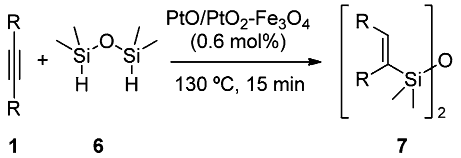


entry	R^1	R^2	product	ratio **5**/**5′**[b]
1	Ph	Et	**5**/**5′a**	3:1
2	Ph	MeO	**5**/**5′b**	2.3:1
3	$\mathrm{HOC(Me)_2}$	Et	**5**/**5′c**	3.5:1

[a] Reaction carried out using **4** (1.0 mmol) and **2** (1.0 mmol) in absence of solvent obtaining a 99% of yield for the mixture **5** and **5′**. [b] Determined by ^{1}H NMR of crude mixture.

The polyhydrosilylation of carbon−carbon multiple bonds remains the most commercially utilized process for the formation of polymeric material containing silicon units.[87] Among different strategies, the use of disilane and diynes reagents is practically unexplored, probably due to the lack on the regiocontrol of the process. To enlighten us about the use of this approach, we study first the problem of using a disilane reagent. Moreover, the high utility of vinylsilyloxy derivatives, as intermediates in cross-coupling reactions, prompted us to perform the hydrosilylation process of simple alkynes **1** with tetramethylsiloxane[24] (**6**, Table 5). So, the reaction under similar conditions but increasing the amount of alkyne gave the expected products **7** in practically quantitative yields. The process seems to be indifferent to the presence of oxygenated functions on the alkyne structure (compare entries 1 and 2). However, the presence of conjugated aromatic units decreased, in some extension, the previously found quantitative yields (entry 3 in Table 5).

Table 5. Hydrosilylation Process Using Tetramethyldisiloxane[a]



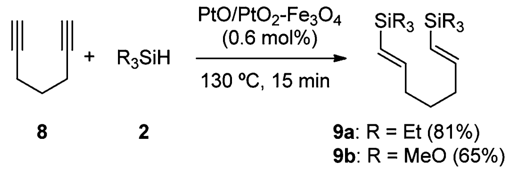
entry	R	product	yield (%)[b]
1	Bu^n	**7a**	99
2	$\mathrm{MeOCH_2}$	**7b**	99
3	Ph	**7c**	87

[a] Reaction carried out using **1** (2.0 mmol) and **6** (1.0 mmol) in absence of solvent. [b] Isolated yield after flash column chromatography.

Once we have studied the possible use of disilane reagents, we face the problem of using diynes. Initially, we studied the possible double hydrosilylation of 1,6-diyne. These starting olefinic reagents could suffer a process of cyclization,[88,89] which could be seen as an extra-problem in its use in the polymerization process. However, the reaction of triethylsilane

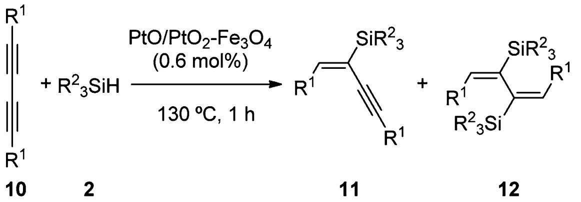
(**2a**) with diyne **8** gave the expected 1,7−divinylsilane derivative **9a** with an acceptable yield (Scheme 1). It was observed the presence of two more isomers, analyzing the crude reaction mixture, being the corresponding 1,6− and 2,6−disilane derivatives in 18% combined yield. The reaction with the less reactive trimethoxysilane did not improve the results, therefore obtaining a similar mixture distribution.

Scheme 1. Double Hydrosilylation of Hepta-1,6-diyne



After the partial success obtained in the reaction with 1,6−diynes, the hydrosilylation of 1,3−diynes[33] **10** was carried out under similar conditions (Table 6). The first trail using equimolecular amounts of both reagents, dodeca−5,7−diyne (**10a**) and triethylsilane (**2a**), gave a mixture of only two products **11a** and **12a** (entry 1). It should be pointed out that the possible isomer of **11a** with the silyl moiety at 5−position was not detected, as well as the isomers of **12a** with the silyl moieties at 5,7− or 5,8−positions, indicating a certain level of regiocontrol. Pleasantly, when the reaction was repeated with two equivalents of silylating agent only compound **12a** was obtained as the only product in quantitative yields, with the other four possible products being undetected (entry 2). In a further effort to obtain the product of monohydrosilylation **11a**, we studied the rates of formation of different products using two equivalents of triethylsilane (**2a**, Figure 2).

Table 6. Selective Hydrosilylation of 1,3-Diynes[a]



entry	R^1	R^2	product	yield **11** (%)[b]	yield **12** (%)[b]
1	Bu^n	Et[c]	**a**	38	30
2	Bu^n	Et	**a**	0	99
3[d]	Bu^n	Et	**a**	91	6
4	Bu^t	Et[c]	**b**	99	0
5	Bu^t	Et	**b**	99[e]	0
6	Bu^t	Ph	**c**	87	0
7	Bu^t	MeO	**d**	77	0
8	Ph	Me[f]	**e**	4	95
9	Ph	Me[c,f,g]	**e**	99	0

[a] Reaction carried out using **10** (1.0 mmol) and **2** (2.0 mmol), unless otherwise stated. [b] Isolated yield after flash column chromatography. [c] Result carried out using only 1 mmol of **2a**. [d] Reaction carried out in 2 mL of toluene and after 5 min of reaction time. [e] Result after 6 h. [f] Reaction performed using PhMe$_2$SiH. [g] Reaction carried out in 2 mL of toluene and after 15 min of reaction time.

The plot of the results in absence of solvent showed that there was a short period of time where the product of monohydrosilylation was the main one (up in Figure 2). With the idea of reducing the rate of the second addition, the same study was conducted in toluene as solvent (down in Figure 2) finding a broader time window where the amount of compound **11a** is higher than **12a**. In fact, the reaction in toluene using two equivalent of **3a** rendered dodec-5-en-7-yn-6-yl-triethylsilane (**11a**) with an excellent yield after only 5 min (Table 6 entry 3), showing the selectivity of the catalyst. The reaction of the more sterically crowded di-*tert*-butyl derivative **10b** gave quantitatively the product of monohydrosilylation **11b** and nothing of the double reaction product (compare entries 1 and 4 in Table 6).

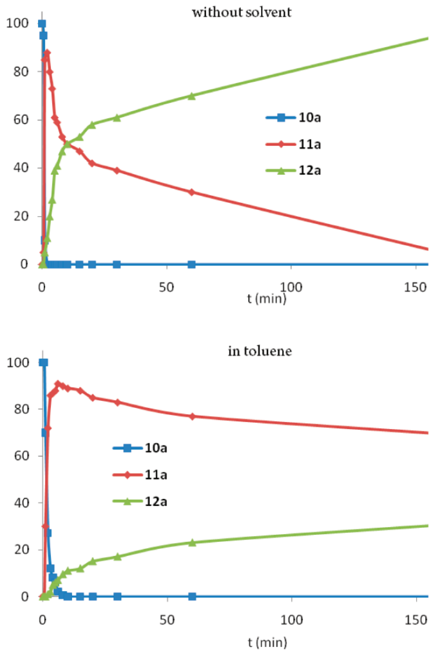


Figure 2. Plot-time yield for the double hydrosilylation of dodeca-5,7-diyne (**10a**).

The above result pointed out the dramatic effect of the hindrance of the reagents on the selectivity. The only product detected was, again, compound **11a** when the reaction was performed using even two equivalents of the reagent **2a** after 6 h of the reaction (entry 5). The reaction with two equivalents of a more crowded silyl derivative decreased the yield (entry 6), indicating that the hindrance of all reagents has a capital importance for the selectivity of the reaction. As expected, the reaction with less reactive trimethoxysilane reagent gave lower yield (entry 7). Finally, the reaction with the phenyl substituted alkyne could be performed in a highly selectivity manner. So, in absence of solvent, the reaction with two equivalents of dimethylphenylsilane gave compound **12** (entry 8). However, a similar reaction by using toluene, as solvent, and with only one equivalent of silane reagent, gave quantitatively the expected enyne **11c** in only 15 min (entry 9).

■ CONCLUSIONS

In conclusion, impregnated platinum on magnetite is the first real heterogeneous and recyclable catalyst for the hydrosilylation of alkynes. The reaction-catalyst fulfils the principle of green chemistry, avoiding the use of solvent and any type of wastes. The catalyst is very robust, easy to prepare, handle and store. In the reaction with 1,3-diynes the control of the reaction is absolute, with in all cases the only product being the one produced by cis-mode addition, the first silyl unit always is placed at the 2-position of the diyne system and the second silyl moiety is placed at the 3-position. All these facts, together with the simple recovering of catalyst by sequestering with a simple magnet, without losing its activity, permits us to anticipate a good future for the process shown in this study not only in the laboratory but also in industry.

EXPERIMENTAL SECTION

General Information. Melting points were obtained with a Reichert Thermovar apparatus. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as a solvent and TMS as internal standard for ^{1}H and ^{13}C; chemical shifts are given in δ (parts per million) and coupling constants (J) in Hertz. FT−IR spectra were obtained on Jasco 4100 LE (Pike Miracle ATR) spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Himazdu QP-5000 spectrometer, giving fragment ions in m/z with relative intensities (%) in parentheses. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light, staining with phosphomolybdic acid [25 g phosphomolybdic acid, 10 g $Ce(SO_4)_2{\cdot}4H_2O$, 60 mL of concentrated H_2SO_4 and 940 mL of H_2O]. Column chromatography was performed using silica gel 60 of 35−70 mesh. All reagents were commercially available (Acros, Aldrich, Fluorochem) and were used as received. The ICP−MS analyses were carried out on a Thermo Elemental VGPQ−ExCell spectrometer. The X−ray Fluorescence analyses were carried out on a PHILIPS MAGIX PRO (PW2400) X−ray spectrometer equipped with a rhodium X−ray tube and a beryllium window. The BET analyses were carried out on a automatic volumetric AUTOSORB-6 from Quantachrome and its degasser unit. N_2 at 77K was used as gas. X−ray photoelectron spectroscopy analyses were carried out on a VG−Microtech Multilab 3000 equipped with a hemispheric electron analyzer with 9 channeltrons (pass energy between 2 and 200 eV) and a X-ray tube with Mg and Al anodes. TEM analyses were carried out on a JEOL JEM−2010 microscope, equipped with a X−Ray detector Oxford Inca Energy TEM 100 for microanalysis (EDS). XRD analyses were obtained on a Bruker D−8 advance diffractometer with Göebel mirror with high temperature chamber and X−ray generator Kristalloflex K 760−80F (3 kW, 20−60 kW and 5−80 mA).

General Procedure for the Preparation of Catalyst. To a stirred solution of the metal salt $PtCl_2$ (1 mmol, 266 mg) in deionized water (120 mL) was added commercially available Fe_3O_4 (4 g, 17 mmol, powder <5 μm, BET area: 9.86 m^2g^{-1}). After 10 min at room temperature, the mixture was slowly basified with NaOH (1M) until pH around 13. The mixture was stirred during one day at room temperature in air. After that, the catalyst was filtered and washed several times with deionized water (3 × 10 mL). The solid was dried at 100 °C during 24 h in a standard glassware oven, obtaining the expected catalyst.

Representative Procedure for the Hydrosililation of Alkynes. To a vessel containing $PtO/PtO_2{-}Fe_3O_4$ (50 mg) was added alkyne (**1**, **4**, **8**, or **10**, 1 or 2 mmol) and silane (**2** or **6**, 1 or 2 mmol). The resulting mixture was stirred at 130 °C until the end of reaction (see Tables 3, 5, and 6, and Scheme 1). Then, ethyl acetate (5 mL) was added and the catalyst was removed by a magnet. To the resulting organic phase, water (5 mL) was added. The resulting mixture was extracted with EtOAc (2 × 5 mL). The organic phase was dried over $MgSO_4$, followed by evaporation of solvents under reduced pressure. The product was purified by flash chromatography on silica gel (hexane/ethyl acetate), if necessary, to give the corresponding products **3**, **5**, **7**, **9**, **11**, or **12**. Physical and spectroscopic data, as well as literature for known compounds, follow.

(E)-Dec-5-en-5-yltriethylsilane (**3a**):[61] R_f = 0.8 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1608, 1459, 1236, 1006, 714 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (q, J = 8 Hz, 6H, $SiCH_2$ × 3), 0.85−0.95, 1.2−1.4, 2−2.15 (3 m, 15, 8 and 4H, respectively, CH_3 × 5 and CH_2 × 6), 5.66 (t, J = 6.8 Hz,1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.2 (3C), 7.5 (3C), 14, 14.4, 22.5, 23.2, 28.1, 29.7, 32, 32.4, 137.2, 141.9; EI-MS m/z 254 (M^+, 2%), 226 (21), 225 (100), 197 (23), 113 (13), 87 (37), 59 (30).

(E)-Triethyl(hex-3-en-3-yl)silane (**3b**):[53] R_f = 0.77 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1609, 1457, 1416, 1236, 1006, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (q, J = 7.7 Hz, 6H, $SiCH_2$ × 3), 0.91 (t, J = 7.7 Hz, 12H, $SiCH_2CH_3$ × 3 and CH_2CH_3), 0.98 (t, J = 7.5 Hz, 3H, CH_2CH_3), 2−2.2 (m, 4H, CH_2CH_3), 5.65 (t, J = 6.8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.1 (3C), 7.4 (3C), 14.3, 14.7, 21.5, 22.6, 138.2, 143.3; EI-MS m/z 198 (M^+, 8%), 170 (15), 169 (100), 142 (11), 141 (85), 115 (16), 113 (24), 87 (29), 59 (27).

(E)-(1,4-Dimethoxybut-2-en-2-yl)triethylsilane (**3c**):[90] R_f = 0.73 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1718, 1457, 1373, 1237, 1197, 1100, 1004, 718 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.63 (q, J = 7.8 Hz, 6H, $SiCH_2$ × 3), 0.93 (t, J = 7.8 Hz, 9H, $SiCH_2CH_3$ × 3), 3.28, 3.35 (2s, 3H each one, OCH_3 × 2), 4 (s, 2H, $SiCCH_2$), 4.09 (d, J = 5.2 Hz, 2H, $CHCH_2$), 5.95 (t, J = 5.2 Hz,1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3 (3C), 7.3 (3C), 58, 58.1, 69.6, 71.1, 138.4, 140.3; EI-MS m/z 169 (24%), 149 (61), 118 (15), 117 (100), 89 (77), 87 (16), 61 (25), 59 (23).

(E)-(1,2-Diphenylvinyl)triethylsilane (**3d**):[61] R_f = 0.87 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1599, 1491, 1457, 1006, 764, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64 (q, J = 7.9 Hz, 6H, $SiCH_2$ × 3), 0.96 (t, J = 7.9 Hz, 9H, CH_3 × 3), 6.77 (s,1H, CH), 6.9−7, 7.05−7.1, 7.15−7.2, 7.25−7.3 (4 m, 4, 3, 1 and 2H, respectively, Ph × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.8 (3C), 7.3 (3C),125.5, 126.9, 127.3 (2C), 127.8 (2C), 128.6 (2C), 129.5 (2C), 137.4, 138.7, 143.1, 144.1; EI-MS m/z 294 (M^+, 31%), 266 (26), 265 (100), 237 (33), 209 (13), 207 (19), 163 (15), 135 (24), 107 (21), 87 (13), 59 (23).

(E)-[1,2-bis(4-Butylphenyl)vinyl]triethylsilane (**3e**). R_f = 0.9 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1602, 1507, 1457, 1237, 1006, 728, 715 cm^{-1}; ^{1}H−NMR (300 MHz, $CDCl_3$): δ 0.65 (q, J = 7.5 Hz, 6H, $SiCH_2$ × 3), 0.88 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.97 (t, J = 7.5 Hz, 12H,$SiCH_2CH_3$ × 3 and CH_2CH_3), 1.2−1.4 (m, 4H, CH_2CH_3 × 2), 1.45−1.55, 1.55−1.65 (2 m, 2H each one, $CH_2CH_2CH_3$ × 2), 2.48 (t, J = 7.6 Hz, 2H, CCH_2), 2.61 (t, J = 7.6 Hz, 2H, CCH_2), 6.74 (s, 1H, CH), 6.85−6.95, 7.05−7.15 (2 m, 6 and 2H, respectively, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.8 (3C), 7.3 (3C), 13.9, 14, 22.3, 22.3, 33.4, 33.6, 35.3, 35.3, 127 (2C), 127.9 (2C), 128.7 (2C), 129.5 (2C), 134.9, 138.7, 139.8, 140.5, 141.7, 142.8; EI-MS m/z 406 (M^+, 39%), 378 (33), 377 (100), 191 (13), 163 (22). HRMS calcd. (%) for $C_{28}H_{42}Si$: 406.3056; found: 406.3060.

(E)-[1,2-Bis(4-bromophenyl)vinyl]triethylsilane (**3f**). R_f = 0.87 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1482, 1457, 1413, 1389, 1237, 1075, 1002, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.62 (q, J = 7.9 Hz, 6H, $SiCH_2$ × 3), 0.94 (t, J = 7.9 Hz, 9H, $SiCH_2CH_3$ × 3), 6.71 (s,1H, SiCCH), 6.8, 6.83, 7.23, 7.41 (4d, J = 8.4 Hz, 2H each one, ArH × 8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.7 (3C), 6.8 (3C), 119.7, 121.2, 129 (2C),

130.9 (2C), 131.1 (2C), 131.9 (2C), 135.9, 138.1, 141.7, 144; EI−MS *m/z* 452 (M^++2, 43%), 450 (M^+, 22), 426 (12), 425 (51), 424 (24), 423 (100), 422 (13), 421 (51), 396 (14), 394 (27), 392 (15), 364 (14), 345 (17), 344 (69), 343 (17), 342 (69), 316 (25), 315 (24), 314 (26), 313 (18), 286 (41), 285 (14), 284 (42), 257 (19), 255 (19), 242 (22), 240 (21), 214 (28), 212 (29), 186 (29), 184 (37), 178 (18), 177 (16), 176 (49), 151 (13), 115 (30), 103 (11), 88 (10), 87 (88), 87 (89). HRMS Calcd. (%) for $C_{20}H_{24}Br^{(79)}Br^{(81)}Si$: 452.0014; found 452.0015. HRMS Calcd. (%) for $C_{20}H_{24}Br_2^{(79)}Si$: 450.0014; found 450.0041.

*(E)-Dec-5-en-5-yltriphenylsilane (**3g**):*[61] R_f = 0.87 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1483, 1463, 1427, 1239, 1106, 739, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.67 (t, *J* = 6.7 Hz, 3H, CH_3), 0.9 (t, *J* = 6.9 Hz, 3H, CH_3), 1−1.15, 1.3−1.4 (2 m, 4H each one, CH_2CH_3 × 2 and $CH_2CH_2CH_3$ × 2), 2.15−2.3 (m, 4H, $CH_2CH_2CH_2CH_3$ × 2), 5.96 (t, *J* = 6.9 Hz, 1H, CH), 7.3−7.45, 7.5−7.6 (2 m, 9 and 6H, respectively, Ph × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 14, 22.6, 22.9, 28.7, 29.9, 31.7, 32.2, 127.6 (6C), 129.2 (3C), 135 (3C), 136.1, 136.3 (6C), 147.4; EI-MS *m/z* 398 (M^+, 11%), 320 (29), 263 (13), 260 (37), 259 (100), 183 (53), 182 (10), 181 (33), 104 (17).

*(E)-Dec-5-en-5-yltrimethoxysilane (**3h**):*[91] R_f = 0.77 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1458, 1378, 1189, 1074, 807, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.9 (t, *J* = 6.4 Hz, 6H, CH_2CH_3 × 2), 1.25−1.45, 2.05−2.2 (2 m, 8 and 4H, respectively, CH_2 × 6), 3.55 (s, 9H, $=CH_3$), 6.07 (t, *J* = 6.9 Hz,1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14 (2C), 22.5, 22.9, 28, 28.8, 31.5, 32, 50.5 (3C), 131.4, 146.6; EI-MS *m/z* 260 (M^+, 3%), 228 (10), 218 (15), 138 (50), 123 (10), 122 (17), 121 (100), 91 (60).

*(E)-3-(Dec-5-en-5-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**3i**).* R_f = 0.8 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1457, 1252, 1040, 837, 782, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 3H, $CSiCH_3$), 0.2 (s, 18H, $Si(CH_3)_3$ × 2), 1.01 (t, *J* = 6.8 Hz, 6H, CH_2CH_3 × 2), 1.35−1.5, 2.15−2.25 (2 m, 8 and 4H, respectively, CH_2 × 6), 5.93 (t, *J* = 6.9 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 1.8 (6C), 14, 14.1, 22.5, 23.2, 27.9, 28.8, 31.7, 32.4, 139.7, 141.6; EI-MS *m/z* 345 (19%), 223 (18), 222 (32), 221 (100), 209 (12), 208 (22), 207 (100), 205 (11), 191 (11), 133 (11), 73 (53). HRMS Calcd (%) for $C_{17}H_{40}O_2Si_3CH_3$: 345.2101; found 345.2071.

*(E)-(1,4-Dimethoxybut-2-en-2-yl)triphenylsilane (**3j**).* R_f = 0.63 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1617, 1588, 1484, 1449, 1428, 1189, 1105, 768, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.17 (s, 3H, $SiCCH_2OCH_3$), 3.41 (s, 3H, $CHCH_2OCH_3$), 4.2 (s, 2H, CCH_2), 4.3 (d, *J* = 5.3 Hz, 2H, $CHCH_2$), 6.3 (t, *J* = 5. Hz,1H, CH), 7.4−7.55, 7.65−7.75 (2 m, 15H, Ph × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58, 58.2, 70.1, 70.6, 127.7 (6C), 129.3 (3C), 134 (3C), 135.6, 136.1 (6C), 145.6; EI−MS *m/* 260 (24%), 259 (100), 215 (10), 214 (38), 213 (100), 183 (44), 181 (40), 180 (14), 167 (65), 155 (11), 128 (13), 104 (22), 84 (16). HRMS Calcd (%) for $C_{24}H_{26}O_2Si-C_6H_{11}O_2$: 259.0943; found 259.0941.

*(E)-(1,2-Diphenylvinyl)triphenylsilane (**3k**):*[33] R_f 0.83 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1597, 1589, 1568, 1486, 1444, 1427, 1106, 757, 741, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.85−7, 7−7.15, 7.25−7.4, 7.45−7.6 (4 m, 4, 6, 10 and 6H, respectively, Ph × 5 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.9, 127.4, 127.7 (6C), 127.9 (2C), 128.3 (2C), 128.4 (2C), 129.5 (3C), 129.7 (2C), 133.7 (3C), 136.5 (6C), 137, 141, 141.8, 143.3; E-MS *m/z* 438 (M^+, 24%), 360 (17), 260 (24), 259 (100), 181 (19), 178 (10).

*(E)-(1,2-Diphenylvinyl)trimethoxysilane (**3l**):*[92] R_f = 0.8 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1599, 1572, 1492, 1446, 1189, 1073, 968, 802, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 9H, OCH_3 × 3), 7−7.05, 7.1−7.2, 7.2−7.25, 7.25−7.3 (4 m, 2, 6, 1 and 2H, respectively, Ph × 2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.9 (3C), 126.3, 127.6, 127.9 (2C), 128.1 (2C), 128.6 (2C), 129.9 (2C), 135.6, 136.6, 140.4, 142.8; EI MS *m/z* 301 (M^+ + 1, 39%), 300 (M^+, 100), 270 (14), 268 (10), 267 (13), 238 (33), 237 (10), 180 (37), 179 (40), 178 (100), 177 (10), 176 (16), 167 (21), 152 (12), 122 (12), 121 (100), 91 (91).

*(E)-Triethyl(styryl)silane (**5a**) and Triethyl(1-phenylvinyl)silane (**5a′**):*[61] R_f = 0.9 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1602, 1494, 1458, 1447, 1415, 1236, 1008, 827, 784, 735, 720, 688 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.65 (q, *J* = 7.9 Hz, 12H, (5a)-$SiCH_2$ × 3 and (5a′)−$SiCH_2$ × 3), 0.92 (t, *J* = 8.1 Hz, 9H, (5a′)−$SiCH_2CH_3$ × 3), 0.99 (t, *J* = 8.1 Hz, 9H, (5a)−$SiCH_2CH_3$ × 3), 5.56, 5.86 (2d, *J* = 3.1 Hz, 1H each one, (5a′)−CCH_2), 6.42 (d, *J* = 19.3 Hz, 1H, (5a)−SiCH), 6.89 (d, *J* = 19.3 Hz, 1H, (5a)−SiCHC*H*), 7.1−7.45 (m, 10H, (5a′)−Ph and (5a)−Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ (5a) 3.5 (3C), 7.4 (3C), 125.8, 126.3 (2C), 127.8, 128.5 (2C), 138.5, 144.9; (5a′) 3.3 (3C), 7.3 (3C), 126.1, 126.6 (2C), 128.1 (2C), 128.7, 132, 150.5; EI-MS *m/z* (5a) 218 (M^+, 13%), 190 (21), 189 (100), 162 (11), 161 (68), 159 (27), 133 (35), 131 (47), 107 (12), 105 (21); (5a′) 218 (M^+, 4), 191 (15), 190 (74), 189 (71), 162 (17), 161 (100), 159 (11), 135 (18), 133 (50), 131 (22), 107 (41), 105 (21), 103 (12), 87 (17).

*(E)-Trimethoxy(styryl)silane (**5b**) and Trimethoxy(1-phenylvin-yl)silane (**5b′**):*[61] R_f = 0.7 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1604, 1574, 1494, 1447, 1219, 1189, 1029, 996, 946, 847, 800, 733, 713, 690, 671, 636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 9H, (5b′)−OCH_3 × 3), 3.68 (s, 9H, (5b)−OCH_3 × 3), 6, 6.22 (2d, *J* = 2.8 Hz, 1H each one, (5b′)−CCH_2), 6.2 (d, *J* = 19.3 Hz, 1H, (5b)−SiCH), 7.28 (d, *J* = 19.3 Hz, 1H, (5b)−SiCHC*H*), 7.25−7.55 (m, 10H, (5b′)−Ph and (5b)−Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ (5b) 50.5 (3C), 115.7, 126.6, 126.7 (2C), 128.4 (2C), 141.4, 149.7; (5b′) 50.6 (3C), 127, 128.3 (2C), 128.8 (2C), 131.8, 137.2, 142; EI-MS *m/z* (5b) 225 (M^+ + 1, 11%), 224 (M^+, 58), 223 (49), 196 (11), 195 (14), 194 (41), 193 (12), 192 (15), 163 (21), 162 (100), 161 (31), 132 (11), 131 (20), 121 (37), 120 (11), 107 (35), 105 (12), 104 (39), 103 (10), 102 (15), 91 (68), 90 (39), 77 (22); (5b′) 224 (M^+, 22), 209 (25), 195 (14), 194 (82), 192 (25), 167 (17), 162 (19), 121 (100), 118 (35), 107 (30), 103 (17), 102 (17), 91 (87), 90 (11), 77 (27).

*(E)-2-Methyl-4-(triethylsilyl)but-3-en-2-ol (**5c**) and 2-Methyl-3-(triethylsilyl)but-3-en-2-ol (**5c′**):*[44] R_f = 0.73 (hexane/ethyl acetate: 4/1); IR (ATR) ν 3369, 1619, 1459, 1416, 1360, 1235, 1146, 1004, 960, 795, 714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.57 (q, *J* = 7.9 Hz, 6H, (5c)−$SiCH_2$ × 3), 0.69 (q, *J* = 7.9 Hz, 6H, (5c′)−$SiCH_2$ × 3), 0.92 (t, *J* = 7.8 Hz, 9H, (5c) −$SiCH_2CH_3$ × 3), 0.98 (t, *J* = 7.8 Hz, 9H, (5c′)−$SiCH_2CH_3$ × 3), 1.3 (s, 6H, (5c)−CCH_3 × 2), 1.34 (s, 6H, (5c′)−CCH_3 × 2), 1.52 (s, 1H, (5c′)−OH), 1.83 (s, 1H, (5c)−OH), 5.31, 5.76 (2d, *J* = 1.8 Hz, 1H each one, (5c′)−$SiCCH_2$), 5.73 (d, *J* = 19 Hz, 1H, (5c)−SiCH), 6.18 (d, *J* = 19.1 Hz, 1H, (5c) −SiCHC*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (5c) 3.3 (3C), 7.2 (3C), 29.3 (2C), 72.1, 120.3, 154.7; (5c′) 4.1 (3C), 7.4 (3C), 31.3 (2C), 75.5, 123.7, 154.7; EI-MS *m/z* (5c) 200 (M^+, 0.02%), 172 (23), 171 (100), 129 (11), 115 (17), 103 (51), 101 (12), 97 (10), 89 (26), 87 (24), 75 (84); (5c′) 143 (68), 129 (16), 104 (18), 103 (100), 75 (100).

*1,3-Di-((E)-dec-5-en-5-yl)-1,1,3,3-tetramethyldisiloxane (**7a**):* R_f = 0.9 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1465, 1252, 1036, 922, 831, 780 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.11 (s, 12H, Si(CH$_3$)$_2$ × 2), 0.9 (t, J = 6.6 Hz, 12H, CH$_2$CH_3 × 4), 1.2–1.4, 2–2.15 (2 m, 16 and 8H, respectively, CH$_2$ × 12), 5.78 (t, J = 6.9 Hz, 2H, SiCCH × 2); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.8 (4C), 14.1 (4C), 22.6 (2C), 23.2 (2C), 28 (2C), 28.9 (2C), 31.8 (2C), 32.5 (2C), 140.7 (2C), 141 (2C); EI-MS m/z 271 (18%), 270 (39), 257 (10), 255 (17), 201 (11), 187 (14), 173 (14), 157 (10), 134 (26), 133 (100), 119 (54), 117 (13). HRMS Calcd (%) for $C_{24}H_{50}OSi_2$: 410.3400; found 410.3411.

*1,3-Bis((E)-1,4-dimethoxybut-2-en-2-yl)-1,1,3,3-tetramethyldisiloxane (**7b**):* R_f = 0.4 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1451, 1373, 1252, 1197, 1088, 1050, 834, 782 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.15 (s, 12H, SiCH$_3$ × 4), 3.25, 3.31 (2s, 6H each one, OCH$_3$ × 4), 4.03 (s, 8H, OCH$_2$ × 4), 6.03 (m, 2H, CH × 2); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.7 (4C), 57.9 (2C), 58.1 (2C), 69.4 (2C), 70.4 (2C), 139 (2C), 141 (2C); EI-MS m/z 179 (54%), 165 (17), 164 (30), 163 (100), 149 (42), 135 (10), 134 (10), 133 (70), 119 (22), 84 (15), 75 (12). HRMS Calcd (%) for $C_{16}H_{34}O_5Si_2-C_8H_{23}O_4$: 179.0348; found 179.0348.

*1,3-Bis((E)-1,2-diphenylvinyl)-1,1,3,3-tetramethyldisiloxane (**7c**):* mp 68–71 °C (hexane), R_f = 0.8 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1597, 1493, 1447, 1252, 1069, 1028, 921, 792, 782, 694 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.23 (s, 12H, SiCH$_3$ × 4), 6.97 (s, 2H, CH), 7–7.05, 7.05–7.15, 7.2–7.25, 7.3–7.35 (4 m, 4, 10, 3, and 3H, respectively, Ph × 4); ^{13}C NMR (75 MHz, CDCl$_3$): δ 0.1 (4C), 125.7 (2C), 127.1 (2C), 127.7 (4C), 127.9 (4C), 128.6 (4C), 129.6 (4C), 137.1 (2C), 137.9 (2C), 141.9 (2C), 146.1 (2C); EI-MS m/z 490 (M$^+$, 18%), 313 (11), 312 (29), 311 (100), 295 (30), 209 (13), 193 (33), 179 (14), 178 (14), 135 (14), 133 (50). HRMS Calcd (%) for $C_{32}H_{34}OSi_2$: 490.2148; found 490.2158.

*(1E,6E)-1,7-Bis(triethylsilyl)hepta-1,6-diene (**9a**):* R_f = 0.97 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1616, 1458, 1415, 1236, 1011, 988, 780, 716 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.54 (q, J = 8 Hz, 12H, SiCH$_2$ × 6), 0.93 (t, J = 8 Hz, 18H, SiCH$_2$CH_3 × 6), 1.45–1.55, 2.05–2.2 (2m, 2, and 4H, respectively, CH$_2$ × 3), 5.54 (d, J = 18.7 Hz, 2H, SiCH × 2), 6.02 (dt, ^1J = 18.6 Hz, ^2J = 6.3 Hz, 2H, SiCHCH × 2); ^{13}C NMR (75 MHz, CDCl$_3$) δ 3.5 (6C), 7.4 (6C), 27.9, 36.4 (2C), 126 (2C), 148.3 (2C); EI-MS m/z 208 (15%), 180 (21), 179 (68), 152 (14), 151 (85), 123 (13), 119 (12), 116 (14), 115 (100), 105 (21), 91 (14), 87 (82). HRMS Calcd (%) for $C_{19}H_{40}Si_2$: 324.2669; found 324.2661.

*(4E,9E)-3,3,11,11-Tetramethoxy-2,12-dioxa-3,11-disilatrideca-4,9-diene (**9b**):* R_f = 0.7 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1461, 1190, 1073, 799, 745 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.5–1.65 (m, 2H, CH$_2$CH_2CH$_2$), 2.1–2.25 (m, 4H, CH_2CH$_2$CH_2), 3.57 (s, 18H, Si(OMe)$_3$ × 2), 5.4 (d, J = 18.7 Hz, 2H, SiCH$_2$ × 2), 6.43 (dt, ^1J = 19.1 Hz, ^2J = 5.6 Hz 2H, SiCHCH × 2); ^{13}C NMR (75 MHz, CDCl$_3$) δ 26.7, 35.9 (2C), 50.6 (6C), 117.7 (2C), 154.1 (2C); EI-MS m/z 304 (18%), 257 (16), 227 (10), 143 (12), 122 (12), 121 (100), 91 (48). HRMS Calcd (%) for $C_{13}H_{28}O_6Si_2$: 336.1424; found 336.1415.

*(E)-Dodec-5-en-7-yn-6-yltriethylsilane (**11a**):* R_f = 0.9 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1581, 1458, 1430, 1415, 1378, 1237, 1005, 718 cm^{-1}; ^{1}H–NMR (300 MHz, CDCl$_3$): δ 0.66 (q, J = 7.9 Hz, 6H, SiCH$_2$ × 3), 0.9–1 (m, 15H, CH$_3$ × 5), 1.3–1.6, 2.35–2.45 (2 m, 8 and 4H, respectively, CH$_2$ × 6), 6.02 (t, J = 6.9 Hz, 1H, CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 2.9 (3C), 7.2 (3C), 13.5, 13.9, 19.5, 22, 22.4, 31.2, 31.3, 31.9, 79.9, 97.3, 121.5, 151; EI-MS m/z 278 (M$^+$, 33%), 250 (17), 249 (52), 207 (11), 179 (12), 168 (16), 167 (100), 165 (14), 151 (10), 137 (10), 109 (12), 97 (11), 87 (51). HRMS Calcd (%) for $C_{18}H_{34}Si$: 278.2430; found 278.2415.

*(E)-Triethyl(2,2,7,7-tetramethyloct-3-en-5-yn-3-yl)silane (**11b**):* R_f = 0.97 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1475, 1459, 1415, 1246, 1203, 1081, 1005, 730, 719, 696 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.62 (q, J = 7.8 Hz, 6H, SiCH$_2$ × 3), 0.94 (t, J = 7.8 Hz, 9H, SiCH$_2$CH_3), 1.19, 1.23 (2s, 9H each one, ^{t}Bu × 2), 5.85 (s, 1H, CCHC); ^{13}C NMR (75 MHz, CDCl$_3$) δ 2.92 (3C), 7.36 (3C), 28.5, 29.7 (3C), 30.9 (3C), 35.6, 78.9, 108.3, 118.8, 158.8; EI-MS m/z 279 (M$^+$+1, 12%), 278 (M$^+$, 50), 263 (29), 250 (18), 249 (61), 221 (12), 193 (13), 168 (18), 167 (100), 162 (13), 141 (15), 140 (10), 139 (79), 127 (16), 115 (77), 111 (27), 109 (11), 99 (13), 87 (88), 83 (17), 73 (13). HRMS Calcd (%) for $C_{18}H_{34}Si$: 278.2430; found 278.2455.

*(E)-Triphenyl(2,2,7,7-tetramethyloct-3-en-5-yn-4-yl)silane (**11c**):* mp 81–86 °C (hexane); R_f = 0.83 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1428, 1360, 1109, 738, 697 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.05, 1.22 (2s, 9H each one, C(CH$_3$)$_3$ × 2), 6.08 (s, 1H, CCHC), 7.25–7.4, 7.55–7.65 (2 m, 9 and 6H, respectively, Ph × 3); ^{13}C NMR (75 MHz, CDCl$_3$) δ 28.4, 29.6 (3C), 30.4 (3C), 36, 79.5, 110.6, 117, 127.5 (6C), 129.4 (3C), 134.1 (3C), 136.4 (6C), 164; EI-MS m/z 422 (M$^+$, 8%), 260 (28), 259 (100), 181 (17). HRMS Calcd (%) for $C_{30}H_{34}Si$: 422.2430; found 422.2480.

*(E)-Trimethoxy(2,2,7,7-tetramethyloct-3-en-5-yn-4-yl)silane (**11d**):* R_f = 0.77 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1457, 1362, 1242, 1200, 1085, 825, 810, 753, 688 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.22, 1.23 (2s, 9H each one, C(CH$_3$)$_3$ × 2), 3.61 (s, 9H, OCH$_3$ × 3), 6.29 (s, 1H, CCHC); ^{13}C NMR (75 MHz, CDCl$_3$) δ 27.9, 29.4 (3C), 30.7 (3C), 35.7, 51.7 (3C), 86.1, 108.1, 111.8, 163.8; EI-MS m/z 269 (11), 257 (15%), 187 (10), 173 (17), 159 (10), 135 (14), 134 (26), 133 (100), 117 (15), 73 (23). HRMS calcd. (%) for $C_{15}H_{28}O_3Si-CH_3$: 269.1573; found 269.1582.

*(E)-(1,4-Diphenylbut-1-en-3-yl)dimethyl(phenyl)silane (**11e**):*[33] R_f = 0.63 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1596, 1584, 1489, 1427, 1248, 1112, 822, 753, 688 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.59 (2, 6H, SiCH$_3$ × 2), 6.84 (s, 1H, SiCCHPh), 7.25–7.45, 7.65–7.7, 7.95–8 (3 m, 11, 2 and 2H, respectively, Ph × 3); ^{13}C NMR (75 MHz, CDCl$_3$) δ −3.1 (2C), 90.4, 101.4, 121.2, 124.2, 127.8 (2C), 128, 128.2 (2C), 128.3 (2C), 128.6, 128.8 (2C), 129.4, 131.3 (2C), 134.2 (2C), 136.9, 137.6, 145.6; EI-MS m/z 339 (M$^+$+1, 13%), 338 (M$^+$, 45), 323 (15), 279 (14), 245 (36), 221 (15), 202 (12), 136 (13), 135 (100), 105 (10).

*(5E, 7E)-Dodeca-5,7-diene-6,7-diylbis(triethylsilane) (**12a**):* R_f = 0.93 (hexane/ethyl acetate: 4/1); IR (ATR) ν 1458, 1414, 1378, 1237, 1006, 717 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.58 (q, J = 7.9 Hz, 12H, SiCH$_2$ × 6), 0.8–1 (m, 24H, CH$_3$ × 8), 1.25–1.35, 1.9–2 (2 m, 8 and 4H, respectively, CH$_2$ × 6), 5.61 (t, J = 6.6 Hz, 2H, CH × 2); ^{13}C NMR (75 MHz, CDCl$_3$) δ 3.9 (6C), 7.5 (6C), 14 (2C), 22.8 (2C), 30.6 (2C), 31.7 (2C), 139.6 (2C), 140.3 (2C); EI-MS m/z 394 (M$^+$, 13%), 365 (13), 337 (14), 251 (10), 250 (39), 249 (100), 222 (10), 221 (43), 180 (12), 179 (14), 162 (12), 116 (25), 115 (100), 88 (15), 87 (100). HRMS Calcd (%) for $C_{24}H_{50}Si_2$: 394.3451; found 394.3459.

((1E,3E)-1,4-Diphenylbuta-1,3-diene-2,3-diyl)bis(dimethyl-(phenyl)silane) ***(12e)***:[33] $R_f = 0.8$ (hexane/ethyl acetate: 4/1); IR (ATR) ν 1595, 1491, 1427, 1248, 1109, 1040, 1026, 806, 732, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.41, 0.42 (2s, 6H each one, $SiCH_3 \times 4$), 7.1 (s, 2H, SiCCHPh), 7.45−7.7, 7.8−7.9 (2 m, 16 and 4H, respectively, Ph × 4); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.2 (2C), −1.4 (2C), 127.4 (2C), 127.5 (4C), 127.8 (2C), 128.2 (4C), 128.8 (4C), 134.2 (2C), 138.1 (2C), 138.4 (2C), 139.5 (2C), 146 (2C); EI-MS *m/z* 474 (M^+, 5%), 136 (15), 135 (100).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Catalyst characterization data, XPS data, TEM images of starting micromagnetite and catalyst (after and before reactions), particle distribution (after and before reactions) and copies of ^{1}H and ^{13}C for compounds **3**, **5**, **7**, **9**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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