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Nano-dispersed platinum(0) in organically modified silicate matrices as sustainable catalysts for a regioselective hydrosilylation of alkenes and alkynes

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Nano-dispersed platinum(0) particles stabilized in a range of organically modified silicate (ORMOSIL) matrices are investigated as sustainable catalysts for the hydrosilylation of alkenes and alkynes. In this study, five different siloxane matrices including triethoxysilane (HTEOS), methyltriethoxysilane (MTES), ethyltriethoxysilane (ETES), triethoxyvinylsilane (TEVS) and propyltriethoxysilane (PTES) are investigated, and the distribution of the metal particles in these materials analyzed by transition electron microscopy (TEM). The particles appeared to be generally of a small size, with a diameter of ca 2 - 5 nm in each of these catalysts, however the distribution is not equally uniform from one matrix to the other. HTEOS, MTES and ETES that respectively carry a hydrogen, a methyl and an ethyl group on the triethoxysilane moiety, displayed a more uniform distribution, while particles appeared to be more scattered in the remaining matrices. Catalysts with a uniform particles distribution produced higher and consistent yields, while those with poor particles distribution produced lower and almost random yields, suggesting that the uniformity in particle distribution, and by extension the nature of the siloxane matrix, are important for the catalytic properties of these materials. The scope of the reaction was broadened to a range of olefins, with a goal of investigating the tolerability of the reaction toward a number of reactive functional groups, resulting in the preparation of 28 compounds. This catalytic system also enabled the hydrosilylation of a limited number of alkynes under the optimized reaction conditions.

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<sup>&</sup>lt;sup>†</sup>Electronic supplementary information (ESI) available (<sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS (ESI/Q-TOF) and GC-MS)

# 1. Introduction

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Silicon is the second most abundant element in the Earth's crust (about 28% by mass) after oxygen, and as such, it is only natural for silicon-based materials to be widely used in a large number of consumer goods and commodity chemicals including polymers (adhesives, coatants, sealants, gels, foams, aerosols, encapsulants and preservatives),<sup>1-5</sup> semi-conductors,<sup>6-10</sup> agrochemical and biomedical agents.<sup>11-13</sup> In recent years, chiral organosilanes have gradually established their importance in organic synthesis,<sup>14-16</sup> material science<sup>17-21</sup> and medicinal chemistry,<sup>22, 23</sup> as a result of the involvement of silane intermediates in diverse chemical transformations including silicon-based cross-coupling reactions,<sup>24-28</sup> silanol hydrogen bond donor catalysis,<sup>29, 30</sup> and as directing groups for C–H functionalization,<sup>31-37</sup> to name just a few. Furthermore, silasubstitution of bioactive molecules, also known as "silicon switch", has become a growing practice in medicinal chemistry, especially in the preparation of silicon-based peptidomimetic analogues.<sup>22, 23, 38, 39</sup> This trend has rejuvenated hydrosilylation reactions as a strategic approach to access a large diversity of key silane intermediates.<sup>32, 40-43</sup>

Although a number of metal catalysts have been used to enable these reactions,<sup>32, 40-43</sup> the constant need for more selective, cleaner and sustainable transformations has inspired the development of alternative hydrosilylation reactions. With the emergence of the continuous flow industrial processes, which offer many advantages over traditional batch reactors, including a high surface-to-volume ratio, better heat and mass transfer, and more control over the reaction conditions,<sup>44-46</sup> there is a need for the development of a new generation of catalysts compatible with these processes. The heterogenization of homogeneous catalytic methods through the dispersion or encapsulation of metallic nanoparticles in porous matrices is one of the approaches compatible with continuous flow processes.<sup>45-50</sup> This approach, in addition to offering a unique high specific surface area and large pore volume, in conjunction with the tunability of pore size, also enables an easy separation of the product, and the reusability of the catalyst.<sup>45-52</sup> Because silica-based sol-gels are extremely porous materials with high specific area, nano-dispersed and stabilized metallic catalysts in organically modified silicates (ORMOSILs) have been investigated as potential catalysts for continuous flow processes.<sup>48, 49, 52</sup> Ciriminna et al.,<sup>45</sup> reported that Pt(0) dispersed in a methyltriethoxysilane matrix could catalyze the hydrosilylation of a number of terminal alkenes. However, in this initial study, only a very limited number of alkenes was investigated, triethoxysilane was the only silulating agent investigated, and all the yields were determined by GC-MS. This study explores and compares the catalytic properties of

nano-dispersed and stabilized Pt(0) in a series of sol-gel siloxane matrices on the hydrosilylation of a wide range of olefins, using the Speier's catalyst as a control. The scope of the reaction is expanded to include the variation of substituents on a core aromatic system, with a goal of investigating the tolerability of a number of functional groups by the reaction. Other silylating agents are investigated, and a limited number of alkynes were also hydrosilylated under the optimal reaction conditions.

#### 2. Results and discussion

The preparation of a highly dispersed metal and stabilized in the form of sol-gel using organically modified silicates is routine.<sup>45-47, 53, 54</sup> Pt@MTES was prepared by dispersing potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>) in methyltriethoxysilane, then reduced it to Pt(0) with NaBH<sub>4</sub> as previously described.<sup>45</sup> A quick optimization of the hydrosilylation reaction conditions using 1-octadecene as a substrate was undertaken, as illustrated in Table 1.

No reaction was observed with 0.01% Pt in MTES at 100 °C for 6 h in toluene (entry 1), and only traces of product were observed when 0.05% Pt in MTES was used (entry 2). Under the same conditions, the yield of the reaction improved as the catalyst load increases, however when going from 1% Pt to 2% (entries 4 and 5), the yield decreased substantially. A full conversion was achieved with 1.2 eqv of triethoxysilane and 1 mol% Pt in toluene in 18 h at 100 °C (entry 7), but the yield did not improve when the temperature was increased to 140 °C (entry 8) or lowered to 60 °C (entry 9). At 140 °C, the competitive hydrogenation of the alkene through a hydrogen-transfer reaction appeared to accelerate. Furthermore, coordinating solvents such as THF, THF/H<sub>2</sub>O (1:1), H<sub>2</sub>O, CH<sub>3</sub>CN or isopropanol failed to produced any product as indicated by GC-MS, and only dioxane was able to produce the expected product, with a very poor yield (entry 14). As a result, the conditions in entry 7 were selected for the exploration of the scope of the reaction.

With the optimal reaction conditions at hand, a comparative analysis between Pt@MTES and the Speier's catalyst (widely used for hydrosilylation in industrial settings as a homogeneous catalyst)<sup>32, 55, 56</sup> was undertaken, and the obtained results are summarized in Figure 1. The reaction with Pt@MTES was set up using the conditions in entry 7 (temperature 100 °C), while the reaction with the Speier's catalyst (H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O) was set up based on the original report by Speier *et al.*<sup>57, 58</sup> (temperature 140 °C). Due to the low boiling point of the commercially available alkenes, which makes it difficult to isolate and characterize the resulting hydrosilylated products, a number of terminal alkenes were

quickly prepared either through a Williamson etherification reaction (for ethers)<sup>59-61</sup> or by esterification of the acyl chloride (for esters).

/	+	OEt   H—Si—OEt <u>Pt@</u>   OEt	②MTES ∕ent, heat	() <sub>14</sub>		t OEt t
Entry	<b>Triethoxysilane</b> <sup>a</sup>	Solvent	Pt@MTES <sup>b</sup>	Time (h)	Temp	Yield <sup>c</sup>
	(eqv)		(Pt <i>,</i> mol%)		(°C)	(%)
1	1	Toluene	0.01	6	100	N.R <sup>d</sup>
2	1	Toluene	0.05	6	100	traces
3	1	Toluene	0.5	6	100	38
4	1	Toluene	1	6	100	62
5	1	Toluene	2	6	100	53
6	1	Toluene	1	18	100	70
7	1.2	Toluene	1	18	100	73 <sup>e</sup>
8	1.2	Toluene	1	18	60	54
9	1.2	Toluene	1	18	140	66 <sup>e</sup>
10	1.2	THF	1	18	reflux	N.R
11	1.2	THF/H <sub>2</sub> O (1:1)	1	18	reflux	N.R
12	1.2	H <sub>2</sub> O	1	18	reflux	N.R
13	1.2	CH₃CN	1	18	reflux	traces
14	1.2	Dioxane	1	18	100	34
15	1.2	Isopropanol	1	18	reflux	N.R

Table 1. Hydrosilylation	of 1-octadecene with	n triethoxysilane usin	g Pt@MTES as a catalys
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Each reaction was setup under nitrogen environment, using 1 mmol of 1-octadecene. <sup>a</sup>The equivalence is related to the number of moles of 1-octadecene. <sup>b</sup>The percent mole is related to the number of moles of 1-octadecene. <sup>c</sup>The yield of the reaction was determined by GC-MS using tridecane as an internal standard. <sup>d</sup>N.R. = No Reaction. <sup>e</sup>No 1-octadecene was present in the mixture at the end of the reaction as indicated by GC-MS.

Under these conditions, the two catalysts apeared to behave amazingly in a very analogous manner, producing similar yields for a number of starting materials. Both catalytic systems selectively produced the *anti*-Markonikov product. The yields appeared to be higher for substrates with saturated carbon chains than with those bearing an aromatic ring. Ether and ester functional groups were well tolerated under these conditions, while the substrate bearing an amine functional group produced a very poor yield, although Pt@MTES generated a better yield than the Speier's catalyst in this latter case (compound **6**). Unfortunately, both catalytic systems systematically failed to produce the expected product when an alkene with an internal double bond (*trans*-stibene or cyclooctene) was used as a substrate.

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Figure 1: Comparative analysis between the Speier's and Pt@MTES (\*these are isolated yields from gram-scale reactions)

Since substrates bearing a benzene ring appeared to produce a much lower yield than their saturated counterparts, it became interesting to investigate whether substituents on the ring will have any effect on the reaction's outcome (Scheme 1). The collected results are summarized in Table 2. The reaction produced comparable and quantitative yields under both the Pt@MTES and the Speier's catalytic systems. The substituents on the aromatic ring did not appear to be affecting the outcome of the reaction in any meaningful way, which is not surprising given how far away the ring is to the site of the reaction.



**Scheme 1:** Hydrosilylation of substituted allyloxybenzenes using Pt@MTES and Speier's catalytic systems.

Compounds	R1	R <sup>2</sup>	R <sup>3</sup>	% Yield for Speier's <sup>a</sup>	% Yield for Pt@MTES <sup>a</sup>
12a	Н	Н	Н	62	55
12b	н	Н	Cl	59	62
12c	Cl	Н	Н	65	57
12d	н	Н	Br	56	58
12e	Н	Cl	Cl	46	58
12f	н	Н	Me	57	60
12g	н	Н	i-Pr	54	63
12h	Н	OMe	н	58	64
12i	н	Me	Me	54	56
12j	Н	CO <sub>2</sub> Me	н	62	61
12k	н	Н	CO <sub>2</sub> Me	39	58

Table 2: Percent yields obtained from the hydrosilylation of substituted allyloxybenzenes.

<sup>a</sup>Isolated yields from gram-scale reactions

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The collected data unambiguously showed that Pt@MTES was equally effective as the Speier's catalyst in the hydrosilylation of alkenes, making the heterogenization of homogeneous catalytic systems a viable approach for industrial application. Considering that sustainability (relationships

between manufacturing system and ecosystems, and economic viability) and process intensification (running reactions under continuous conditions that speed up conversion rates, while maintaining selectivity) are becoming more and more relevant in the chemical industry, this catalytic system might even be preferable if well integrated into a continue flow process.

In order to investigate whether the lipophilic carbon chain on the silicate matrix can impact the catalytic effect, Pt(0) was nano-dispersed in a range of matrices, including triethoxysilane (HTEOS), ethyltriethoxysilane (ETES), triethoxyvinylsilane (TEVS) and propyltriethoxysilane (PTES). The catalytic effect of the resulting materials on the hydrosilylation of alkenes was compared to that of Pt@MTES, and the obtained results are summarized in Table 3. The percent yields obtained with Pt@HTEOS and Pt@ETES were consistent and similar to those obtained with Pt@MTES, while the percent yields were more inconsistent and scattered with Pt@PTES and Pt@TEVS.

Table 3:	Comparative	analysis of	the catal	ytic effects	of Pt	t@MTES,	Pt@HTEOS,	Pt@ETES,	Pt@PTES
and Pt@	TEVS.								

O Si O H Triethoxysilane HTEOS	O Si M Methyltriethc MTE	e e oxysilane Ethyltrieth S ETH	Di Di Di Di Di Di Di Di Di Di Di Di Di D	O Si O O O O O O O O O O O O O O O O O O	O Si O Propyltriethoxysilane PTES
Compounds	Pt@MTES	Pt@HTEOS	Pt@ETES	Pt@PTES	Pt@TEVS
	(% yield)	(% yield)	(% yield)	(% yield)	(% yield)
4	61	64	42	26	40.
5	69	68	42	33	50
9	54	64	63	38	46
12a	55	48	43	38	46
12b	62	55	57	39	38
12e	58	58	51	58	44
12h	64	53	54	48	32
12i	56	44	47	40	17

\*yields are isolated from gram-scale reactions

To rationalize the observed trend, the particle distribution in Pt@MTES, Pt@HTEOS, Pt@ETES, Pt@PTES and Pt@TEVS were analyzed with a Transition Electron Microscope (TEM). The particles appeared to be generally of a small size in each of the catalysts, with a diameter mostly between 2 – 5 nm (Figure 2). However, the distribution was not equally uniform from one matrix to the other. In the catalysts that produced more consistent percent yields during the comparative analysis, namely Pt@HTEOS, Pt@MTES and Pt@ETES (Figure 2, (a), (b) and (c) respectively), the distribution was more uniform, while particles appeared to be more scattered in Pt@TEVS and Pt@PTES (Figure 2, (d) and (e), respectively), the catalysts that produced inconsistent percent yields.



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**Figure 2:** TEM pictures of (**a**) Pt@HTEOS, (**b**<sub>1</sub> and **b**<sub>2</sub>) Pt@MTES, (**c**) Pt@ETES, (**d**) Pt@TEVS and (**e**) Pt@PTES

This was not surprising since HTEOS, MTES and ETES formed a gel quite easily during the preparation of these catalysts, while PTES and TEVS slowly produced rubber-like films, resulting in the poor particles distribution observed by TEM. These observations suggest that the uniformity in particle

distribution is responsible for the catalytic trend observed. It is not sure whether (or how) the lipophilic carbon chain on the silicate matrix impact the catalytic effect of these materials, but it is obvious that the silane derivative used to generate a given catalyst and the nature of the resulting matrix has a significant impact on the particle size as well as on the uniformity of their distribution. As a result, all these parameters appeared to be interconnected, and each of them has an effect on the catalytic properties of the resulting material.

In order to determine whether other silylating agents could be used under this catalytic system, phenylsilane, diethylsilane, triethylsilane, methyldiethoxysilane and diphenylsilane were investigated, using Pt@HTEOS as the catalyst under entry 7's reaction conditions. Phenylsilane and diphenylsilane failed to produce the expected product probably because of steric hindrance generated by the benzene ring(s), and the starting materials were collected every time. However, the remaining hydrogensilanes produced the expected product in quantitative yields, as illustrated with compounds 13 - 16.



To investigate whether alkynes could be hydrosylilated under these condition, four symmetrical namely diphenylacetylene, hex-3-yne, 1,4-bis(benzyloxy)but-2-yne and 1,4-bis(4alkynes, methylbenzyloxy)but-2-yne, together with two terminal alkynes namely (prop-2-ynyloxy)benzene and 1-chloro-4-(prop-2-ynyloxy)benzene were individually reacted with triethoxysilane under the conditions shown in entry 7, Table 1. All these starting materials were efficiently hydrosilylated, with diphenylacetylene and hex-3-yne producing inseparable mixtures of (E/Z)-(1,2diphenylvinyl)triethoxysilane (17, 70%) and (E/Z)-triethoxy(hex-3-en-3-yl)silane (18, 58%) in quantitative yields, respectively (Scheme 2). The GC-MS analysis (see supplemental data) of these mixtures showed that they contain an excess of the Z isomer (the compound with a trans double bond), with roughly 70% (Z) versus 30% (E) for (1,2-diphenylvinyl)triethoxysilane, and 75% (Z) versus 25% (E) for triethoxy(hex-3-en-3-yl)silane, respectively. The low boiling point for triethoxy(hex-3-en-3-yl)silane might be responsible for the low yield obtained for this compound, as some of the product was lost during the evaporation of the solvent.



Scheme 2: Hydrosilylation of diphenylacetylene and hex-3-yne.

Interestingly, the two other symmetrical alkynes, namely, 1,4-*bis*(benzyloxy)but-2-yne and 1,4-*bis*(4-methylbenzyloxy)but-2-yne produced almost exclusively the *Z* isomer of (1,4-*bis*(benzyloxy)but-2-en-2-yl)triethoxysilane (**19**) and (1,4-*bis*(4-methylbenzyloxy)but-2-en-2-yl)triethoxysilane (**20**), respectively, in quantitative yields. Furthermore, the two terminal alkynes produced almost exclusively the *anti*-Markonikov *E* isomers (the compounds with a *trans* double bond) of the hydrosilylated product (**21** and **22**).



The reusability of the catalyst was study with Pt@MTES, using allyl glycidyl ether as a substrate in the preparation of **5**, under the optimized conditions (entry 7, Table 1). The catalyst was recovered from the reaction mixture by centrifugation followed by the removal of the supernatant by decantation at the end of each cycle. The catalyst was then sonicated for about 45 minutes in THF, washed and air-dried before the next run. It should be noted that the amount of substrate was adjusted for each run in order to make up for the catalyst loss during each recovery. The obtained results (Figure 3) show about a 10% loss in yield from one cycle to another, up to four runs before the amount of the catalyst

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recovered become too small to be used for another cycle. The decrease in yield appeared to be primarily associated with the pores blockage in the sol-gel material, rather than to the loss in catalytic activity. In fact, the reduction in yield appeared to be more dramatic when the catalyst is not sonicated between cycles. It is noteworthy to mention that a previous study with Pt@MTES under similar conditions have shown only very low levels of Pt (4-6 ppm) leaching.<sup>45</sup> The authors of that study also found that the higher level of leaching was associated with molecules bearing functional groups capable to coordinate the Pt nanoparticles.<sup>45</sup> Even so, it should be noted that this level of leaching is marginal when compared to the level observed with homogeneous Pt-catalyzed hydrosilylation applications.<sup>62, 63</sup>



**Figure 3:** Study of the reusability of Pt@MTES using allyl glycidyl ether as a substrate in the preparation of **5**.

# 3. Conclusion

Nano-dispersed platinum(0) particles stabilized in five organically modified silicate (ORMOSIL) matrices have been investigated for their catalytic effects on the hydrosilylation of alkenes and alkynes. The Transition Electron Microscopy (TEM) analysis of these material revealed that particles were mostly of a small size. However, the distribution was not equally uniform in each of the matrices. Pt@MTES, Pt@HTEOS and Pt@ETES that displayed a more uniform particle distribution, also

produced higher and consistent yields. However, catalysts with uneven particles distribution resulting from the obtained poor gel-material produced low and inconsistent results. These observations suggest that the uniformity in particle distribution, which is directly linked to the quality of the xerogel obtained, is very important for the catalytic properties of these materials. Moreover, while internal alkenes failed to produce the expected product during this study, the reaction proceeded well with internal and terminal alkynes, producing a mixture of *cis/trans* isomers for some symmetrical alkynes, and an *anti*-Markovnikov selectivity for terminal alkenes and alkynes. Considering that sustainability and process intensification are becoming more and more relevant in the chemical industry, the catalytic system investigated in this report appeared to be equally robust and could be more sustainable than the current industrial practices, if well integrated into a continue flow process.

#### 4. Experimental section

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#### 4.1. General information and chemicals

NMR data were collected on a Bruker Ascend<sup>™</sup> 400 spectrometer operating at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C. The concentration of all samples was 20 mg / 0.5 mL of CDCl<sub>3</sub>. The NMR data were recorded at 300 K, with chemical shifts ( $\delta$ ) reported in parts per million (ppm) relative to TMS ( $\delta$ H 0.00 and  $\delta$ C 0.0) used as the internal standard, or residual chloroform ( $\delta$ H 7.28 and  $\delta$ C 77.2), and coupling constants (J) in hertz. The multiplicity listed as follow: s = singlet, d = doublet, t = triplet, q =quartet,  $q^* =$  quintet, m = multiplet. Structures were confirmed based on NMR data including proton and DEPTQ135. The High Resolution Electrospray Ionization Mass Spectrometry (HR-ESIMS) for molecular weights was performed on a Q-TOF mass spectrometer, with 1 µl of each sample solution injected onto an HPLC ProtoID-Chip-43 (43mm x 75 μm; Zorbax 300SB-18). The mobile phase consisted of H<sub>2</sub>O/CH<sub>3</sub>CN mixture at 0.6 μl/min, with the initial concentration of 3% CH<sub>3</sub>CN increased to 80% CH<sub>3</sub>CN over a 15 minute period. Data were collected in MS only mode, with reference compounds (322.048121 and 1221.990637 Da) continually introduced into the system. Mass Hunter Data Analysis software (Version B 06.00) was used to analyze the data and to determine molecular weights. Reaction mixtures were monitored using a 200-MS GC/MS ion trap mass spectrometer or by TLC silica gel 60 F254 plates. Gravity and flash column chromatography were performed using type 60A silica gel (60-230 mesh). Transmission Electron Microscopy (TEM) images were recorded on a FEI

Tecnai G2 F30 Twin 300 kV / FEG Transmission Electron Microscope, equipped with Gatan cryogenic TEM system with FEI low dose capability, total solution for 3D imaging, FEI Eagle 4 k high sensitivity CCD camera, with a Point Resolution of 0.24 nm, Line Resolution of 0.144 nm, and information limit of 0.15 nm.

All chemicals and solvents were purchased from major chemical suppliers, and were used without further purification unless stated otherwise.

# 4.2. Methods

# 4.2.1 Preparation of the nano-dispersed catalysts

The general preparation procedure for the catalysts was based on a modified version of previously reported methods,<sup>45, 53</sup> and consisted in stirring vigorously a given alkoxysilane to be used as a matrix in about 10 mL of 0.05 M HCl until the solution become homogeneous. Then potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>, 0.02 equiv) dissolved in 30 mL of isopropanol: H<sub>2</sub>O (1: 4) is added, and the mixture stirred until a light-orange homogeneous solution is obtained. About 6 to 10 mL of 1 M, NaOH (0.05 eqv) was added to the mixture and stirred until gelation (which was fast for MTES, HTEOS and ETES, but took up to an hour for TEVS and PTES). The resulting light-orange homogeneous and transparent gel was allowed to air dry for 4 days. The dark-blue xerogel obtained was reduced with a solution of sodium borohydride in 50 mL THF: H<sub>2</sub>O (1:1). Pt: NaBH<sub>4</sub> = 1: 10, the resulting material was washed with 2 portions of 100 mL of distilled water, and one portion of 100 mL THF, air-dried at room temperature, and was ready to be used.<sup>45</sup>

# Preparation of the Pt@MTES catalyst

A mixture of methyltriethoxysilane (MTES: 30 g, 168.3 mmol) and 10 mL of 0.05 M HCl<sub>aq</sub> was stirred until the solution became homogeneous, and K<sub>2</sub>PtCl<sub>4</sub> (n = 3.37 mmol, m = 1.40 g) dissolved in 30 mL of isopropanol: H<sub>2</sub>O (1: 4) was added. The mixture was stirred until a complete homogeneity is achieved, 8.4 mL of 1 M NaOH was added, and the mixture was further stirred until gelation. The light-orange xerogel obtained was air-dried for 4 days, reduced with a solution of sodium borohydride, washed and air-dried at room temperature as above described.

# Preparation of the Pt@HTEOS catalyst

A mixture of triethoxysilane (HTEOS: 30 g, 182.6 mmol) and 10 mL of 0.05 M HCl<sub>aq</sub> was stirred until the solution became homogeneous, and  $K_2PtCl_4$  (n = 3.65 mmol, m = 1.52 g) dissolved in 30 mL of isopropanol:  $H_2O$  (1: 4) was added. The mixture was stirred until a complete homogeneity is achieved, 9.1 mL of 1 M NaOH was added, and the mixture was further stirred until gelation. The light-orange xerogel obtained was air-dried for 4 days, reduced with a solution of sodium borohydride, washed and air-dried at room temperature as above described.

# Preparation of the Pt@ETES catalyst

A mixture of ethyltriethoxysilane (ETES: 30 g, 156.0 mmol) and 10 mL of 0.05 M HCl<sub>aq</sub> was stirred until the solution became homogeneous, and  $K_2PtCl_4$  (n = 3.12 mmol, m = 1.29 g) dissolved in 30 mL of isopropanol:  $H_2O$  (1: 4) was added. The mixture was stirred until a complete homogeneity is achieved, 7.8 mL of 1 M NaOH was added, and the mixture was further stirred until gelation. The light-orange xerogel obtained was air-dried for 4 days, reduced with a solution of sodium borohydride, washed and air-dried at room temperature as above described.

# Preparation of the Pt@TEVS catalyst

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A mixture of triethoxyvinylsilane (TEVS: 30 g, 157.6 mmol) and 10 mL of 0.05 M HCl<sub>aq</sub> was stirred until the solution became homogeneous, and K<sub>2</sub>PtCl<sub>4</sub> (n = 3.15 mmol, m = 1.31 g) dissolved in 30 mL of isopropanol: H<sub>2</sub>O (1: 4) added. The mixture was stirred until a complete homogeneity is achieved, 7.9 mL of 1 M NaOH was added, and the mixture was further stirred until gelation. The light-orange xerogel obtained was air-dried for 4 days, reduced with a solution of sodium borohydride, washed and air-dried at room temperature as above described.

# Preparation of the Pt@PTES catalyst

A mixture of propyltriethoxysilane (PTES: 30 g, 145.4 mmol) and 10 mL of 0.05 M HCl<sub>aq</sub> was stirred until the solution became homogeneous, and  $K_2PtCl_4$  (n = 2.91 mmol, m = 1.21 g) dissolved in 30 mL of isopropanol:  $H_2O$  (1: 4) was added. The mixture was stirred until a complete homogeneity is achieved, 7.3 mL of 1 M NaOH was added, and the mixture was further stirred until gelation. The light-orange xerogel obtained was air-dried for 4 days, reduced with a solution of sodium borohydride, washed and air-dried at room temperature as above described.

# 4.2.2 Preparation and characterization of compounds

Most reactions were setup in a gram-scale, using 1 g of the olefins, 1.2 eqv. of triethoxysilane and either 1 mol% of the nano-dispersed catalyst or 10<sup>-4</sup> eqv of the Speier's catalyst, under a nitrogen saturated environment. The reaction with the Speier's catalyst was run under neat condition, and heated at 140 °C for 18 h, while toluene was used as a solvent for the reaction with the nano-dispersed catalyst, and heated at 100 °C for 18 h. Each reaction mixture was analyzed by GC-MS and TLC, and purified on a CombiFlash apparatus using a gradient elution of hexane and ethyl acetate, or by column chromatography.

# **4.2.2.1.** *Triethoxy(octadecyl)silane* (1)

Octadecene (1g, 3.96 mmol) and triethoxysilane (0.78 g, 4.75 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (87.6 mg, 3.96  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (7.33  $\mu$ L, 3.96  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a silica gel column using a mixture of hexanes – ethyl acetate (95: 5), to produce the expected compound as a clear oil. Pt@MTES (1.05 g, 64%), Speier's catalyst (1.12 g, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.63 (2H, t, *J* = 8.0 Hz), 0.88 (3H, t, *J* = 6.8 Hz), 1.22 (9H, t, *J* = 6.8 Hz), 1.26 (30H, m), 1.41 (2H, m), 3.81 (6H, q, *J* = 6.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 10.5, 14.2, 18.3, 22.8, 22.9, 29.4, 29.5, 29.7, 29.8, 29.9, 32.0, 33.3, 58.3. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>53</sub>O<sub>3</sub>Si, 417.3758; Found 417.3757.

# 4.2.2.2. Triethoxy[3-(octadecyloxy)propyl]silane (2)

1-Allyloxyoctadecane (1 g, 3.22 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 1bromooctadecane and allyl alcohol) and triethoxysilane (0.63 g, 3.86 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (71.2 mg, 3.21 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (5.96  $\mu$ L, 3.22 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a silica gel column using a mixture of hexanes – ethyl acetate (97.5: 2.5), to produce the expected compound as a clear oil. Pt@MTES (1.04 g, 68%), Speier's catalyst (1.07 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 0.67 (2H, t, *J* = 8.0 Hz), 0.88 (3H, t, *J* = 7.2 Hz), 1.22 (9H, t, *J* = 7.2 Hz), 1.26 (30H, m), 1.56 (2H, m), 1.70 (2H, m), 3.38 (4H, q, *J* = 6.4 Hz), 3.82 (6H, q, *J* = 6.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 6.5, 14.2, 18.4, 22.7, 23.0, 26.2, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 58.3, 70.9, 73.1. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>58</sub>NaO<sub>4</sub>Si 497.3997; Found 497.3999.

#### 4.2.2.3. [10-(Decyloxy)decyl]triethoxysilane (3)

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10-Decyloxydec-1-ene (1 g, 3.37 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 1bromodecane and dec-9-en-1-ol) and triethoxysilane (0.66 g, 4.05 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (74.6 mg, 3.37 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (6.24  $\mu$ L, 3.37 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a silica gel column using a mixture of hexanes – ethyl acetate (97: 3), to produce the expected compound as a clear oil. Pt@MTES (1.02 g, 65%), Speier's catalyst (0.99 g, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.62 (2H, t, *J* = 8.0 Hz), 0.88 (3H, t, *J* = 7.2 Hz), 1.23 (9H, t, *J* = 7.2 Hz), 1.27 (28H, m), 1.56 (4H, m), 3.86 (4H, t, *J* = 6.8 Hz), 3.81 (6H, q, *J* = 6.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 10.4, 14.2, 18.4, 22.7, 22.8, 26.3, 29.3, 29.5, 29.6, 29.7, 29.9, 32.0, 33.2, 58.3, 71.0. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>57</sub>O<sub>4</sub>Si 461.4021; Found 461.4019.

### 4.2.2.4. [3-(cyclohexyloxy)propyl]triethoxysilane (4)

Allyloxycyclohexane (1 g, 7.13 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between cyclohexanol and allylbromide) and triethoxysilane (1.41 g, 8.56 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (156 mg, 7.13  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (13.2  $\mu$ L, 7.13  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a silica gel column using a mixture of hexanes – ethyl acetate (97.5: 2.5), to produce the expected compound as a clear oil. Pt@MTES (1.33 g, 61%), Speier's catalyst (1.46 g, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.64 (2H, t, *J* = 8.4 Hz), 1.22 (9H, t, *J* = 7.2 Hz), 1.24 (5H, m), 1.54 (1H, m), 1.70 (4H, m), 1.89 (2H, m), 3.21 (1H, m), 3.41 (2H, t, *J* = 7.2 Hz), 3.82 (6H, q, *J* = 7.2 Hz). <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>): δ (ppm) 6.6, 18.4, 23.5, 24.3, 25.9, 32.4, 58.3, 70.2, 77.4. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>32</sub>NaO<sub>4</sub>Si 327.1962; Found 327.1973.

# 4.2.2.5. Triethoxy[3-(oxiran-2-ylmethoxy)propyl]silane (5)

Allyl glycidyl ether (1 g, 8.76 mmol) and triethoxysilane (1.73 g, 10.5 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (194 mg, 8.76  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (16.2 µL, 8.76  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a silica gel column using a mixture of hexanes – ethyl acetate (97.5: 2.5), to produce the expected compound as a clear oil. Pt@MTES (1.68 g, 69%), Speier's catalyst (1.61 g, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.65 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 7.2 Hz), 1.71 (2H, m), 2.61 (1H, dd, *J* = 5.2 and 6.3 Hz), 2.79 (1H, dd, *J* = 5.2 and 6.3 Hz), 3.14 (1H, m), 3.40 (1H, dd, *J* = 5.6 and 6.0 Hz), 3.48 (2H, m), 3.71 (1H, dd, *J* = 11.6 and 3.2 Hz), 3.84 (6H, q, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.3, 23.0, 44.4, 50.9, 58.4, 71.4, 73.8. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>26</sub>NaO<sub>5</sub>Si 301.1442; Found 301.1457.

# 4.2.2.6. 4-[2-(triethoxysilyl)ethyl]aniline (6)

4-Vinylaniline (1 g, 8.39 mmol) and triethoxysilane (1.65 g, 10.07 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (185.6 mg, 8.39 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (15.5 μL, 8.39 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (9: 1). The compound came out in 12 minutes as a clear oily material. Pt@MTES (944 mg, 40%), Speier's catalyst (438 mg, 18%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 0.95 (2H, t, *J* = 8.8 Hz), 1.23 (9H, t, *J* = 6.8 Hz), 2.63 (2H, t, *J* = 8.8 Hz), 3.54 (2H, brs), 3.81 (6H, q, *J* = 7.2 Hz), 6.61 (2H, d, *J* = 8.0 Hz), 7.00 (2H, d, *J* = 8.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 12.7, 18.3, 27.9, 58.2, 115.3, 128.5, 134.8, 144.1. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>26</sub>NO<sub>3</sub>Si 284.1676; Found 284.1676.

4.2.2.7. Phenethyl 4-(triethoxysilyl)butanoate (7)

Phenethyl but-3-enoate (1 g, 5.26 mmol) (obtained through the esterification of but-3-enoyl chloride with Phenethyl alcohol) and triethoxysilane (1.04 g, 6.31 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (116 mg, 5.27  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (9.73 µL, 5.27  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (9: 1). The compound came out in 6.1 minutes as a clear oily material. Pt@MTES (1.04 g, 56%), Speier's catalyst (990 mg, 53%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.64 (2H, t, *J* = 8.1 Hz), 1.22 (9H, t, *J* = 6.8 Hz), 1.74 (2H, m), 2.34 (2H, t, *J* = 7.2 Hz), 2.92 (2H, t, *J* = 7.2 Hz), 3.81 (6H, q, *J* = 6.8 Hz), 4.28 (2H, t, *J* = 7.2Hz), 7.22 (2H, m), 7.29 (3H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 10.1, 18.3, 18.6, 35.2, 37.2, 58.2, 64.7, 126.5, 128.5, 128.9, 137.9, 173.4. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>31</sub>O<sub>5</sub>Si 355.1935; Found 355.1952.

#### 4.2.2.8. Phenethyl 11-(triethoxysilyl)undecanoate (8)

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Phenethyl undec-10-enoate (1 g, 3.47 mmol) (obtained through the esterification of undec-10-enoyl chloride with Phenethyl alcohol) and triethoxysilane (0.68 g, 4.16 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (76.7 mg, 3.47  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (6.42 µL, 3.47  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (9: 1). The compound came out in 6.0 minutes as a clear oily material. Pt@MTES (859 mg, 55%), Speier's catalyst (866 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.63 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 6.8 Hz), 1.26 (12H, m), 1.40 (2H, m), 1.58 (2H, m), 2.27 (2H, t, *J* = 7.6 Hz), 2.93 (2H, t, *J* = 6.8 Hz), 3.81 (6H, t, *J* = 7.2 Hz), 4.28 (2H, t, *J* = 7.2 Hz), 7.21 (2H, m), 7.29 (3H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 10.4, 18.5, 22.8, 25.0, 29.1, 29.3, 29.4, 29.5, 33.2, 34.1, 34.3, 35.2, 58.3, 64.7, 126.5, 128.5, 128.9, 137.9, 173.8. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>45</sub>O<sub>5</sub>Si 453.3031; Found 453.3021.

4.2.2.9. Triethoxy(3-phenethoxypropyl)silane (9)

[2-(Allyloxy)ethyl]benzene (1 g, 6.16 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 2-phenylethanol and allyl bromide), and triethoxysilane (1.22 g, 7.40 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (136 mg, 6.16  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (11.4 µL, 6.16  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.3 minutes as a clear oily material. Pt@MTES (1.09 g, 54%), Speier's catalyst (1.16 g, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.63 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 7.2 Hz), 1.69 (2H, m), 2.88 (2H, t, *J* = 7.2 Hz), 3.42 (2H, t, *J* = 6.8 Hz), 3.63 (2H, t, *J* = 7.2 Hz), 3.80 (6H, q, *J* = 6.8 Hz), 7.26 (5H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.4, 18.3, 23.1, 36.6, 58.4, 71.7, 73.2, 124.3, 126.1, 128.9, 139.3. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>30</sub>NaO<sub>4</sub>Si 349.1806; Found 349.1811.

# 4.2.2.10. [3-(benzyloxy)propyl]triethoxysilane (10)

(Allyloxymethyl)benzene (1 g, 6.75 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between benzyl chloride and allyl alcohol) and triethoxysilane (1.33 g, 8.10 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (149 mg, 6.75  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (12.50 µL, 6.75  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.2 minutes as a clear oily material. Pt@MTES (1.11 g, 53%), Speier's catalyst (1.16 g, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.67 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 6.8 Hz), 1.74 (2H, m), 3.50 (2H, t, *J* = 6.8 Hz), 3.81 (6H, q, *J* = 7.2 Hz), 4.50 (2H, s), 7.26 (5H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.6, 18.3, 23.0, 58.4, 72.6, 127.0, 127.5, 128.3, 138.8. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>27</sub>O<sub>4</sub>Si 313.1830; Found 313.1843.

4.2.2.11. Triethoxy[3-(naphthalen-2-yloxy)propyl]silane (11)

2-(Allyloxy)naphthalene (1 g, 5.43 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 2naphthol and allyl bromide) and triethoxysilane (1.07 g, 6.51 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (120 mg, 5.43  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (10.1 µL, 5.43  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 5.5 minutes as a clear oily material. Pt@MTES (1.01 g, 53%), Speier's catalyst (1.02 g, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.81 (2H, t, *J* = 8.4 Hz), 1.23 (9H, t, *J* = 6.8 Hz), 1.98 (2H, m), 3.84 (6H, q, *J* = 6.8 Hz), 4.06 (2H, t, *J* = 6.8 Hz), 7.14 (2H, m), 7.32 (1H, m), 7.41 (1H, m), 7.72 (3H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.9, 18.3, 22.9, 58.6, 70.0, 106.7, 119.0, 123.5, 126.3, 126.7, 127.7, 129.3, 134.8, 157.2. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>28</sub>NaO<sub>4</sub>Si 371.1649; Found 371.1660.

# 4.2.2.12.Triethoxy(3-phenoxypropyl)silane (12a)

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Allyloxybenzene (1 g, 7.45 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between phenol and allyl bromide) and triethoxysilane (1.47 g, 8.94 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (165 mg, 7.45  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (13.8 µL, 7.45  $10^{-5}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 5.3 minutes as a clear oily material. Pt@MTES (1.22 g, 55%), Speier's catalyst (1.37 g, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.77 (2H, t, *J* = 8.0 Hz), 1.23 (9H, t, *J* = 7.2 Hz), 1.90 (2H, m), 3.83 (6H, q, *J* = 7.2 Hz), 3.94 (2H, t, *J* = 6.8 Hz), 6.91 (3H, m), 7.25 (2H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.8, 18.3, 22.9, 58.6, 69.8, 114.5, 120.5, 129.4, 159.1. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>27</sub>O<sub>4</sub>Si 299.1673; Found 299.1675.

# 4.2.2.13. [3-(4-chlorophenoxy)propyl]triethoxysilane (12b)

1-(Allyloxy)-4-chlorobenzene (1 g, 5.93 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 4-chlorophenol and allyl bromide) and triethoxysilane (1.17 g, 7.12 mmol) were stirred and heated in

the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (131 mg, 5.93  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (11.0 µL, 5.93  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.1 minutes as a clear oily material. Pt@MTES (1.23 g, 62%), Speier's catalyst (1.17 g, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.75 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 7.2 Hz), 1.87 (2H, m), 3.82 (6H, q, *J* = 6.8 Hz), 3.90 (2H, t, *J* = 6.8 Hz), 6.81 (2H, d, *J* = 9.2 Hz), 7.20 (2H, d, *J* = 8.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.2, 22.7, 58.4, 70.2, 115.9, 125.3, 129.5, 157.7. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>26</sub>ClO<sub>4</sub>Si 333.1283; Found 333.1280.

#### 4.2.2.14. [3-(2-chlorophenoxy)propyl]triethoxysilane (12c)

1-(Allyloxy)-2-chlorobenzene (1 g, 5.93 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 4-chlorophenol and allyl bromide) and triethoxysilane (1.17 g, 7.12 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (131 mg, 5.93  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (11.0 µL, 5.93  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.4 minutes as a clear oily material. Pt@MTES (1.12 g, 57%), Speier's catalyst (1.29 g, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.75 (2H, t, *J* = 8.0 Hz), 1.21 (9H, t, *J* = 7.2 Hz), 3.83 (6H, q, *J* = 6.8 Hz), 3.92 (2H, t, *J* = 6.8 Hz), 6.78 (1H, d, *J* = 7.2 Hz), 6.90 (2H, m), 7.14 (1H, t, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.3, 22.7, 58.4, 70.1, 113.0, 114.9, 120.6, 130.2, 134.8, 159.9. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>25</sub>ClO<sub>4</sub>Si 333.1283; Found 333.1271.

#### 4.2.2.15. [3-(4-bromophenoxy)propyl]triethoxysilane (12d)

1-(Allyloxy)-4-bromobenzene (1 g, 4.69 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 4-bromphenol and allyl bromide) and triethoxysilane (0.93 g, 5.63 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (104 mg,

4.69 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (8.69 µL, 4.69 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.5 minutes as a clear oily material. Pt@MTES (1.03 g, 58%), Speier's catalyst (0.983 g, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.76 (2H, t, *J* = 8.0 Hz), 1.23 (9H, t, *J* = 7.2 Hz), 1.88 (2H, m), 3.85 (6H, q, *J* = 6.8 Hz), 3.91 (2H, t, *J* = 6.8 Hz), 6.77 (2H, d, *J* = 8.8 Hz), 7.35 (2H, d, *J* = 8.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.2, 22.7, 58.4, 70.1, 112.6, 116.4, 132.2, 158.2. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>25</sub>BrNaO<sub>4</sub>Si 399.0598; Found 399.0595.

#### 4.2.2.16. [3-(3,4-dichlorophenoxy)propyl]triethoxysilane (12e)

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4-(Allyloxy)-1,2-dichlorobenzene (1 g, 4.92 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 3,4-dichlorophenol and allyl bromide) and triethoxysilane (0.97 g, 5.91 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (109 mg, 4.92  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (9.12 µL, 4.92  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 7.4 minutes as a clear oily material. Pt@MTES (1.05 g, 58%), Speier's catalyst (836 mg, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.75 (2H, t, *J* = 8.0 Hz), 1.23 (9H, t, *J* = 7.2 Hz), 1.89 (2H, m), 3.83 (6H, q, *J* = 7.2 Hz), 3.86 (2H, t, *J* = 6.8 Hz), 6.74 (1H, dd, *J* = 9.2 and 2.8 Hz), 6.98 (1H, d, *J* = 2.8Hz), 7.29 (1H, d, *J* = 9.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.6, 18.3, 22.9, 58.6, 70.5, 114.6, 116.3, 123.8, 130.6, 132.9, 158.3. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>24</sub>Cl<sub>2</sub>NaO<sub>4</sub>Si 389.0713; Found 389.0714.

#### 4.2.2.17. Triethoxy[3-(p-tolyloxy)propyl]silane (12f)

1-(Allyloxy)-4-methylbenzene (1 g, 6.75 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 1-bromooctadecane and allyl alcohol) and triethoxysilane (1.33 g, 8.10 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (149

mg, 6.75 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (12.5  $\mu$ L, 6.75 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.0 minutes as a clear oily material. Pt@MTES (1.27 g, 60%), Speier's catalyst (1.21 g, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.77 (2H, t, *J* = 8.0 Hz), 1.23 (9H, t, *J* = 7.2 Hz), 1.88 (2H, m), 2.28 (3H, s), 3.83 (6H, q, J = 7.2 Hz), 3.91 (2H, t, *J* = 6.4 Hz), 6.79 (2H, d, *J* = 8.8 Hz), 7.06 (2H, d, *J* = 8.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.5, 20.6, 22.8, 58.4, 70.0, 114.6, 129.8, 130.0, 157.0. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>28</sub>NaO<sub>4</sub>Si 335.1649; Found 335.1645.

#### 4.2.2.18. Triethoxy[3-(4-isopropylphenoxy)propyl]silane (12g)

1-(Allyloxy)-4-isopropylbenzene (1 g, 5.67 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 1-bromooctadecane and allyl alcohol) and triethoxysilane (1.12 g, 6.81 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (125 mg, 5.67  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (10.5 µL, 5.68  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.3 minutes as a clear oily material. Pt@MTES (1.21 g, 63%), Speier's catalyst (1.04 g, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.76 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 6.8 Hz), 1.23 (6H, d, *J* = 7.2 Hz), 1.89 (2H, m), 2.85 (1H, m), 3.84 (6H, q, *J* = 7.2 Hz), 3.92 (2H, t, *J* = 6.4 Hz), 6.82 (2H, d, *J* = 8.4 Hz), 7.12 (2H, d, *J* = 8.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.6, 18.3, 23.1, 24.2, 33.3, 58.6, 70.2, 114.4, 127.2, 141.0, 157.3. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>33</sub>O<sub>4</sub>Si 341.2143; Found 341.2149.

#### 4.2.2.19. Triethoxy[3-(3-methoxyphenoxy)propyl]silane (12h)

1-(Allyloxy)-3-methoxybenzene (1 g, 6.09 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 3-methoxyphenol and allyl bromide) and triethoxysilane (1.20 g, 7.31 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum

content (135 mg, 6.09 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (11.3  $\mu$ L, 6.09 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.3 minutes as a clear oily material. Pt@MTES (1.27 g, 64%), Speier's catalyst (1.16 g, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.76 (2H, t, *J* = 8.0 Hz),1.23 (9H, t, *J* = 6.8 Hz), 1.90 (2H, m), 3.78 (3H, s), 3.83 (6H, q, *J* = 6.8 Hz), 3.92 (2H, t, *J* = 7.2 Hz), 6.47 (3H, m), 7.16 (1H, dd, *J* = 8.0 and 8.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.4, 22.8, 55.2, 58.4, 69.9, 101.0, 106.2, 106.7, 129.9, 160.4, 160.8. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>28</sub>NaO<sub>5</sub>Si 351.1598; Found 351.1597.

## **4.2.2.20.** [3-(3,4-dimethylphenoxy)propyl]triethoxysilane (**12i**)

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4-(Allyloxy)-1,2-dimethylbenzene (1 g, 6.16 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 3,4-dimethylphenol and allyl bromide) and triethoxysilane (1.22 g, 7.40 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (136 mg, 6.16 10<sup>-5</sup> mol) in toluene at 100 °C, or 10<sup>-4</sup> eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (11.4 µL, 6.16 10<sup>-7</sup> mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 5.7 minutes as a clear oily material. Pt@MTES (1.12 g, 56%), Speier's catalyst (1.09 g, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 0.77 (2H, t, *J* = 8.0 Hz), 1.22 (9H, t, *J* = 6.8 Hz), 1.88 (2H, m), 2.18 (3H, s), 2.22 (3H, s), 3.82 (6H, q, *J* = 7.2 Hz), 3.90 (2H, t, *J* = 6.8 Hz), 6.63 (1H, dd, *J* = 8.0 and 2.8 Hz), 6.70 (1H, d, *J* = 2.8 Hz), 7.00 (1H, d, *J* = 8.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 6.6, 18.8, 20.0, 22.7, 58.4, 59.3, 69.9, 111.5, 116.2, 128.5, 130.2, 137.5, 157.5. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>30</sub>NaO<sub>4</sub>Si 349.1806; Found 349.1809.

#### 4.2.2.21. Methyl 3-[3-(triethoxysilyl)propoxy]benzoate (12j)

Methyl 3-(allyloxy)benzoate (1 g, 5.20 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between methyl 3-hydroxybenzoate and allyl bromide) and triethoxysilane (1.03 g, 6.24 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum

content (115 mg, 5.20  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (9.63 µL, 5.20  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (9: 1). The compound came out in 6 minutes as a clear oily material. Pt@MTES (1.13 g, 61%), Speier's catalyst (1.15 g, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.78 (2H, t, *J* = 8.4 Hz), 1.23 (9H, t, *J* = 7.2 Hz), 1.92 (2H, m), 3.85 (6H, q, *J* = 6.8 Hz), 3.91 (3H, s), 3.99 (2H, t, *J* = 6.8 Hz), 7.10 (1H, dd, *J* = 8.4 and 1.6 Hz), 7.32 (1H, t, *J* = 8.0 Hz), 7.55 (1H, d, J = 1.6 Hz), 7.62 (1H, d, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.6, 22.7, 52.3, 58.4, 70.1, 115.0, 129.0, 121.9, 129.4, 131.4, 159.1, 167.0. HRMS (ESI/Q-TOF): [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>28</sub>NaO<sub>6</sub>Si 379.1547; Found 379.1543.

# 4.2.2.22. Methyl 4-[3-(triethoxysilyl)propoxy]benzoate (12k)

Methyl 4-(allyloxy)benzoate (1 g, 5.20 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between methyl 4-hydroxybenzoate and allyl bromide) and triethoxysilane (1.03 g, 6.24 mmol) were stirred and heated in the presence of either 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (115 mg, 5.20  $10^{-5}$  mol) in toluene at 100 °C, or  $10^{-4}$  eqv of a 0.054 M solution of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in isopropanol (9.63 µL, 5.20  $10^{-7}$  mol) under neat conditions at 140 °C, both under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap (if applicable) was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 8 minutes as a clear oily material. Pt@MTES (1.07 g, 58%), Speier's catalyst (720 mg, 39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.77 (2H, t, *J* = 8.4 Hz), 1.23 (9H, t, *J* = 6.8 Hz), 1.93 (2H, m), 3.85 (6H, q, *J* = 7.2 Hz), 3.88 (3H, s), 4.00 (2H, t, *J* = 6.8 Hz), 6.90 (2H, d, *J* = 8.8 Hz), 7.96 (2H, d, *J* = 8.4Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.5, 18.3, 22.7, 52.0, 58.5, 70.0, 114.2, 122.3, 131,8, 162.9, 166.9. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>28</sub>NaO<sub>6</sub>Si 379.1547; Found 379.1548.

# 4.2.2.23. Diethoxy(methyl)(3-phenoxypropyl)silane (13)

Allyloxybenzene (0.5 g, 3.73 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between phenol and allyl bromide) and diethoxymethyllsilane (600 mg, 4.47 mmol) were stirred and heated in the presence of 1 mol% of the Pt@HTEOS catalyst having *c.a.* 6.5% platinum content (112 mg, 3.73  $10^{-5}$ 

mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 7.0 minutes as a clear oily material (547 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm). 0.15 (3H, s), 0.75 (2H, t, *J* = 8.4Hz), 1.22 (6H, t, *J* = 6.8 Hz), 1.86 (2H, m), 3.78 (4H, q, *J* = 6.8 Hz), 3.94 (2H, t, *J* = 6.8 Hz), 6.92 (3H, m), 7.25 (2H, t, *J* = 8.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 5.6, 10.1, 18.4, 23.0, 58.1, 70.0, 114.5, 120.5, 129.4, 159.1. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>24</sub>NaO<sub>3</sub>Si 291.1387; Found 291.1391.

## 4.2.2.24. Diethyl(3-phenethoxypropyl)silane (14)

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[2-(Allyloxy)ethyl]benzene (0.5 g, 3.08 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 2-phenylethanol and allyl bromide) and diethylsilane (326 mg, 3.70 mmol) were stirred and heated in the presence of 1 mol% of the Pt@HTEOS catalyst having *c.a.* 6.5% platinum content (92.5 mg, 3.08  $10^{-5}$  mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.3 minutes as a clear oily material (515 g, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm). 0.59 (6H, m), 0.97 (6H, t, *J* = 8.0 Hz), 1.60 (2H, m), 2.91 (2H, t, *J* = 7.2 Hz), 3.41 (2H, t, *J* = 6.8 Hz), 3.63 (2H, t, *J* = 7.2 Hz), 7.21 – 7.28 (5H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 2.8, 6.7, 8.4, 24.8, 36.4, 71.8, 73.6, 126.3, 128.2, 129.0, 139.1. HRMS (ESI/Q-TOF): [M-H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>25</sub>Osi 249.1675; Found 249.1674.

# 4.2.2.25. [3-(cyclohexyloxy)propyl]diethylsilane (15)

Allyloxycyclohexane (0.5 g, 3.57 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between phenol and allyl bromide) and diethylsilane (377 mg, 4.28 mmol) were stirred and heated in the presence of 1 mol% of the Pt@HTEOS catalyst having *c.a.* 6.5% platinum content (107 mg, 3.57 10<sup>-5</sup> mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 5.5 minutes as a clear oily material (327 mg, 33%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.60 (6H, m), 0.98 (6H, t, *J* = 8.0 Hz), 1.26 (5H, m), 1.61 (1H, m), 1.67 (2H, m), 1.73 2H, q, *J* =

6.9 Hz), 1.90 (2H, q, *J* = 7.0 Hz), 3.21 (1H, m), 3.41 (2H, t, *J* = 6.8 Hz), 3.66 (1H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 2.8, 6.7, 8.2, 24.3, 25.3, 25.9, 32.4, 70.6, 77.6. HRMS (ESI/Q-TOF): [M - H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>27</sub>OSi 227.1831; Found 227.1835.

## 4.2.2.26. Triethyl(3-phenoxypropyl)silane (16)

Allyloxybenzene (0.5 g, 3.73 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between phenol and allyl bromide) and triethylsilane (520 mg, 4.47 mmol) were stirred and heated in the presence of 1 mol% of the Pt@HTEOS catalyst having *c.a.* 6.5% platinum content (112 mg, 3.73 10<sup>-5</sup> mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.5 minutes as a clear oily material (421 mg, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.53 (6H, q, *J* = 8.0 Hz), 0.62 (2H, t, *J* = 6.9 Hz), 0.94 (9H, t, *J* = 8.0 Hz), 1.74 – 1.80 (2H, m), 3.90 (2H, t, *J* = 6.8 Hz), 6.92 (3H, m), 7.25 (2H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.3, 7.3, 7.9, 23.8, 70.8, 114.6, 116.5, 120.5, 129.6, 159.1. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>27</sub>OSi 251.1826; Found 251.1832.

# 4.2.2.27. (E/Z)-(1,2-diphenylvinyl)triethoxysilane (17)

Diphenylacetylene (500 mg, 2.81 mmol) and triethoxysilane (553 mg, 3.37 mmol) were stirred and heated in the presence of 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (62 mg, 2.81  $10^{-5}$  mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (97.5: 2.5). The compound came out in 5.7 minutes as a yellowish oily material (669 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.03 (6H, t, *J* = 7.2 Hz), 1.19 (3H, t, *J* = 7.2 Hz), 3.65 (4H, q, *J* = 7.2 Hz), 3.83 (2H, q, *J* = 7.2 Hz), 7.02 – 7.20 (9H, m), 7.57 (2H, d, *J* = 8.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 17.9, 18.2, 58.5, 58.8, 126.1, 127.7, 127.9, 128.0, 128.3, 128.5, 129.0, 129.9, 137.3, 138.4, 142.5, 145.5, 149.2. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>27</sub>O<sub>3</sub>Si 343.1724; Found 343.1723.

Hex-3-yne (500 mg, 6.09 mmol) and triethoxysilane (1.20 g, 7.30 mmol) were stirred and heated in the presence of 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (135 mg, 6.09  $10^{-5}$  mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (97.5: 2.5). The compound came out in 3.7 minutes as a yellowish oily material (1.73 g, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.92 (6H, m), 1.16 (9H, t, *J* = 6.8 Hz), 2.07 (4H, m), 3.74 (6H, m), 6.01 (1H, t, *J* = 6.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 12.9, 13.4, 17.2, 20.5, 21.1, 57.1, 57.4, 132.6, 146.2. GC-MS: *m/z* 246 (5%), 217 (3%), 200 (67%) and 163 (100%).

#### **4.2.2.28.** (*Z*)-(1,4-bis(benzyloxy)but-2-en-2-yl)triethoxysilane (19)

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1,4-Bis(benzyloxy)but-2-yne (500 mg, 1.88 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between but-2-yne-1,4-diol and benzyl bromide) and triethoxysilane (370 mg, 2.25 mmol) were stirred and heated in the presence of 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (41.5 mg, 1.88  $10^{-5}$  mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 7.4 minutes as a clear oily material (612 mg, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.98 (9H, t, *J* = 7.2 Hz), 3.83 (6H, q, *J* = 6.8 Hz), 4.09 (2H, s), 4.18 (2H, s), 4.49 (4H, d, *J* = 6.8 Hz), 6.46 (1H, m), 7.2 – 7.23 (10H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 18.3, 58.7, 67.6, 67.7, 72.6, 72.7, 127.5, 127.7, 127.8, 127.9, 128.3, 128.4, 132.9, 138.2, 138.5, 145.1. HRMS (ESI/Q-TOF): [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>35</sub>O<sub>5</sub>Si 431.2248; Found 431.2239.

#### **4.2.2.29.** (Z)-(1,4-bis(4-methylbenzyloxy)but-2-en-2-yl)triethoxysilane (20)

1,4-Bis(4-methylbenzyloxy)but-2-yne (500 mg, 1.70 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between but-2-yne-1,4-diol and 4-methylbenzyl bromide) and triethoxysilane (335 mg, 2.04 mmol) were stirred and heated in the presence of 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (37.6 mg, 1.70 10<sup>-5</sup> mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.4 minutes as

a clear oily material (548 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 1.21 (9H, t, *J* = 6.8 Hz), 2.33 (6H, s), 3.83 (6H, q, *J* = 6.8 Hz), 4.06 (2H, s), 4.15 (2H, d, *J* = 5.2 Hz), 4.44 (4H, d, *J* = 5.2 Hz), 6.44 (1H, m), 7.13 (4H, d, *J* = 7.6 Hz), 7.20 (4H, d, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 18.2, 21.2, 58.6, 67.4, 67.5, 72.4, 72.5, 127.8, 128.0, 128.9, 129.1, 132.8, 135.1, 135.4, 137.1, 137.3, 145.2. GC-MS: m/z 458 (1%), 336 (1.5%), 290 (5.6%), 163 (100%).

#### 4.2.2.30. (E)-triethoxy(3-phenoxyprop-1-enyl)silane (21)

(Prop-2-ynyloxy)benzene (500 mg, 3.78 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between phenol and propargyl bromide) and triethoxysilane (370 mg, 4.54 mmol) were stirred and heated in the presence of 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (83.7 mg, 3.78  $10^{-5}$  mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 5.6 minutes as a clear oily material (811 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.23 (9H, t, *J* = 7.2 Hz), 3.86 (6H, q, *J* = 7.2 Hz), 4.61 (2H, m), 5.86 (1H, m), 6.01 (1H, s), 6.57 (3H, m), 7.25 (2H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 17.4, 57.7, 69.2, 113.9, 119.8, 128.5, 128.7, 138.1, 157.7. GC-MS: *m/z* 295 (25%), 267 (46%), 252 (100%), 163 (63%)

# 4.2.2.30. (E)-(3-(4-chlorophenoxy)prop-1-enyl)triethoxysilane (22)

1-chloro-4-(prop-2-ynyloxy)benzene (500 mg, 3.00 mmol) (obtained through a Williamson reaction<sup>59-61</sup> between 4-chlorophenol and propargyl bromide) and triethoxysilane (370 mg, 3.60 mmol) were stirred and heated in the presence of 1 mol% of the Pt@MTES catalyst having *c.a.* 8.82% platinum content (66.4 mg, 3.00  $10^{-5}$  mol) in toluene at 100 °C, under a nitrogen environment. The reaction mixture, after the removal of the solvent under a reduced pressure on a rotavap, was then purified on a CombiFlash using a gradient of hexane – ethyl acetate, with the polarity ranging from pure hexane to a mixture of hexane-ethyl acetate (95: 5). The compound came out in 6.3 minutes as a clear oily material (1.42 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.23 (9H, t, *J* = 7.2 Hz), 3.86 (6H, q, 7.2 Hz), 4.58 (2H, m), 5.84 (1H, m), 6.52 (1H, m), 6.82 (2H, d, *J* = 8.8 Hz), 7.22 (2H, d, 8.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 18.4, 58.6, 70.0, 116.0, 121.5, 128.5, 129.7, 129.8, 146.4, 157.1. GC-MS: *m/z* 330 (5%), 301 (20%), 163 (100%).

The authors declare no competing financial interest or conflicts of interest of any kind.

# Acknowledgements

J.F. acknowledges the financial support from the Louisiana Board of Regents' Research and Development Program, Industrial Ties Research Subprogram (ITRS) LEQSF(2015-18)-RD-B-04. The S.V.B. and S.V.B (twin sisters) acknowledge the financial support from the Louisiana Board of Regents' NSF EPSCoR Supervised Undergraduate Research Experiences (SURE) program LEQSF-EPS(2017)-SURE-188 and LEQSF-EPS(2017)-SURE-189.

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Nano-dispersed platinum(0) in organically modified silicate matrices as sustainable catalysts for a regioselective hydrosilylation of alkenes and alkynes

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Comparative analysis of the catalytic effect of Pt(0) nano-dispersed in siloxane matrices on the hydrosilylation of alkenes and alkynes