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Iron-Catalysed Chemo-, Regio-, and Stereoselective Hydrosilylation of Alkenes and Alkynes using a Bench-Stable Iron(II) Pre-Catalyst

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Abstract: The chemo-, regio-, and stereoselective iron-catalysed hydrosilylation of alkenes and alkynes with excellent functional group tolerance is reported (34 examples, 41–96% yield). The catalyst and reagents are commercially available and easy to handle, with the active iron catalyst being generated *in situ*, thus providing a simple and practical methodology for iron-catalysed hydrosilylation. The silane products can be oxidised to the anti-Markovnikov product of olefin hydration, and the one-pot iron-catalysed hydrosilylation–oxidation of olefins to give silane(di)ols directly is also reported. The iron pre-catalyst was used at loadings as low as 0.07 mol%, and displayed catalyst turnover frequencies (TOF) approaching 60,000 mol h^{-1}. Initial mechanistic studies indicate an iron(I) active catalyst.

Keywords: catalysis; hydrosilylation; iron; olefins; synthetic methods

Iron offers significant advantages as a catalyst over precious metals due to its low toxicity, low cost, natural abundance and sustainable long-term commercial availability.[1] Although iron catalysis is well established for cross-coupling[2] and redox reactions,[3] the hydrofunctionalisation of olefins has been less developed. In part, this can be attributed to the procedurally challenging reaction conditions and catalyst syntheses required, in comparison to the simplicity of iron-catalysed cross-coupling reactions. Building upon our work,[4] and previous work of others,[5] in which low-valent iron catalysts were generated *in situ*, we sought to develop an operationally simple iron-catalysed hydrosilylation of olefins, in which all reagents were inexpensive, widely available and bench-stable. Furthermore, we sought to use this method for the introduction of silyl groups which could undergo further synthetic transformations (Figure 1).

The hydrosilylation of alkenes and alkynes can produce alkyl-, allyl-, and vinylsilanes,[6] which are used in fine chemical synthesis for stereospecific oxidation[7] and cross-coupling reactions,[8] amongst other applications (Figure 1).[9] The cross-linking of silicone polymers by hydrosilylation represents one of the largest applications of homogeneous catalysis on an industrial scale.[6] To date, hydrosilylation has been dominated by precious metal catalysts such as platinum, palladium, ruthenium and rhodium, however these catalysts can suffer from competitive alkene isomerisation, dehydrosilylation reactions, and incompatibility with amino-substituted olefins.[10]

Chirik has reported that bis(imino)pyridine iron(0) bis(dinitrogen) complexes,[11] and terpyridine and bis(imino)pyridine iron(II) dialkyl complexes,[12] are pre-catalysts for the hydrosilylation of alkenes and alkynes under mild conditions. Despite the high activity, only limited functional group tolerance has been disclosed, and the pre-catalysts are air- and moisture-sensitive.[5e] Ritter reported an iminopyridine iron(0) complex as a (pre-)catalyst for the regio- and stereo-

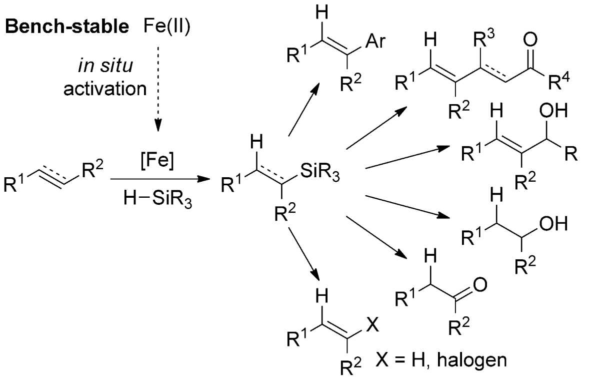
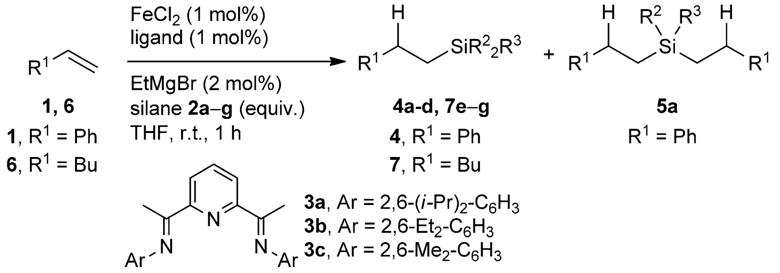


Figure 1. Selected synthetic transformations of alkyl- and vinylsilanes.

Table 1. Development and optimisation of iron-catalysed hydrosilylation of alkenes.[a]



Entry	R^1	Ligand	Silane (equiv.)	Yield [%][b]	
				4/7	**5**[c]
1	Ph	**3a**	$PhSiH_3$ **2a** (1)	>95	–
2[d]	Ph	**3a**	$PhSiH_3$ **2a** (1)	–	–
3[e]	Ph	**3a**	$PhSiH_3$ **2a** (1)	5	–
4[f]	Ph	**3b**	$PhSiH_3$ **2a** (1.1)	>95	–
5[g]	Ph	**3b**	$PhSiH_3$ **2a** (1.1)	42	12
6	Ph	**3b**	$PhSiH_3$ **2a** (1)	60	40
7	Ph	**3b**	$PhSiH_3$ **2a** (1.1)	>95	–
8	Ph	**3b**	$PhSiH_3$ **2a** (0.5)	–	>95
9	Ph	**3c**	$PhSiH_3$ **2a** (1.2)	10	90
10	Ph	**3b**	Ph_2SiH_2 **2b** (1)	>95	–
11	Ph	**3b**	Et_2SiH_2 **2c** (1)	>95	–
12	Ph	**3b**	Me_2PhSiH **2d** (1)	14	N/A
13	Bu	**3b**	$BnMe_2SiH$ **2e** (1)	78	N/A
14	Bu	**3b**	$(Me_3SiO)_2MeSiH$ **2f** (1)	85	N/A
15	Bu	**3b**	$Me_3SiOSiMe_2H$ **2g** (1)	86	N/A

[a] *Conditions:* 0.7 mmol of **1**/**6**, $FeCl_2$ (1 mol%), ligand (1 mol%), EtMgBr (2 mol%), silane (0.5–1.2 equiv.), THF (0.25 M), 1 h, room temperature.

[b] Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard.

[c] Based on silane.

[d] EtMgBr (1 mol%).

[e] EtMgBr (5 mol%).

[f] PhMgBr (3 mol%) in place of EtMgBr.

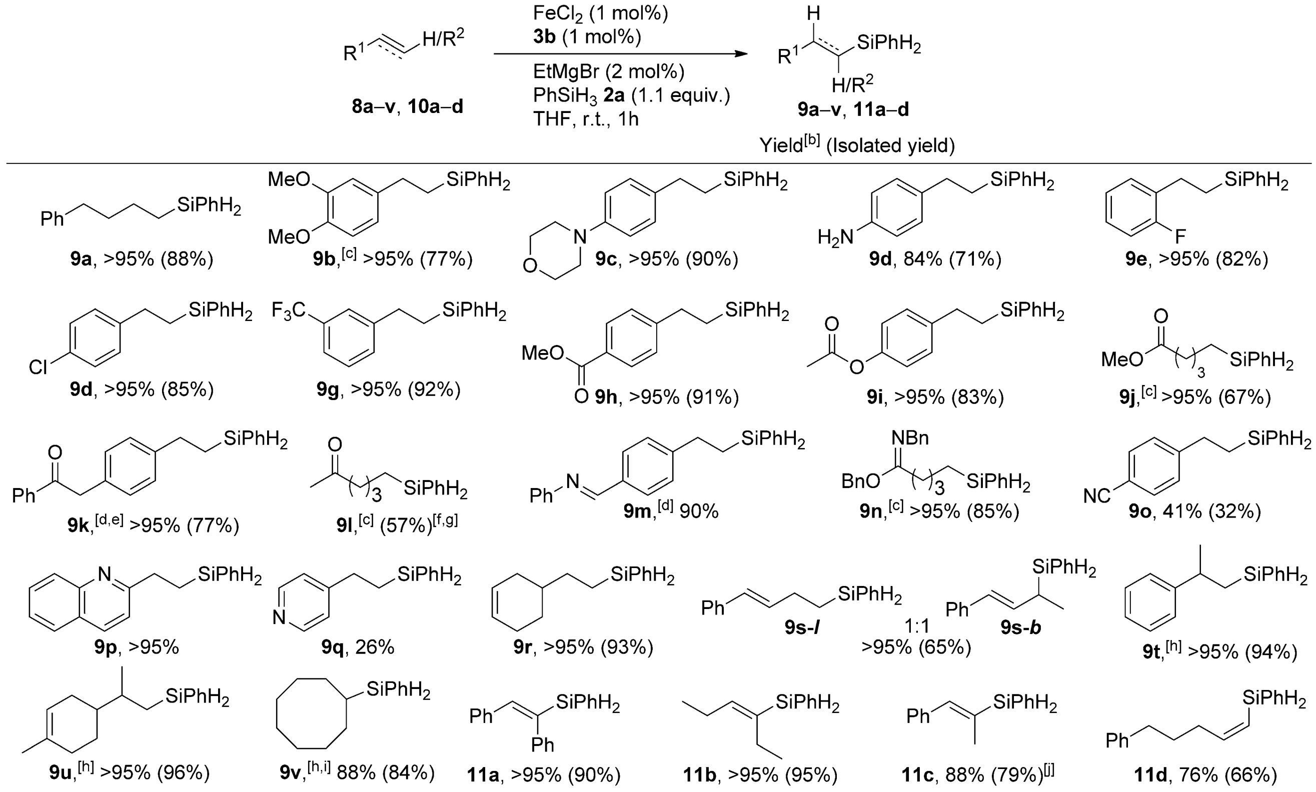
[g] $NaBEt_3H$ (3 mol%) in place of EtMgBr.

selective 1,4-hydrosilylation of terminal 1,3-dienes to give allylsilanes.[13] The iron(0) (pre-)catalyst was elegantly synthesised *in situ* by a ligand-initiated reductive elimination of an iron(II) complex, however the iron(II) precursor itself was still relatively unstable. Only limited substrate scope was disclosed and reaction times of up to 24 h and catalyst loadings of 5 mol% were required. Other notable recent examples of iron-catalysed hydrosilylation of olefins have been reported by Enthaler,[14] Plietker,[15] and Nakazawa,[16] however high temperatures and/or long reaction times were required in each case.

The addition of a Grignard reagent to a bench-stable iron(II) salt gives a low-valent, active iron species,[17] which we speculated might operate as a hydrofunctionalisation catalyst.[4d] This would overcome the practical constraints of using an unstable iron (pre-)catalyst and only require a catalytic amount of Grignard reagent for activation.

Initial studies focussed on the hydrosilylation of styrene **1** with phenylsilane **2a** (1 equiv.), using nitrogen- and phosphine-based ligands in combination with $FeCl_2$ (1 mol%) and ethylmagnesium bromide (2 mol%) as *in situ* activator.[18] The bis(imino)pyridine class of ligands **3a–c**, gave silylation products in quantitative yield within 1 hour at room temperature (Table 1). Minimal activity was observed for all other ligand/salt combinations.[18] No activity was observed in the absence of ligand, and high purity $FeCl_2$ (99.99%) in combination with **3b** showed equal catalytic activity.[18] The hydrosilylation of styrene with phenylsilane using $FeCl_2$ (1 mol%) and the 2,6-diisopropylaryl-substituted bis(imino)pyridine ligand **3a** (1 mol%) gave the linear hydrosilylation product **4a** in quantitative yield and with perfect regioselectivity (Table 1, entry 1). Significantly reduced activity was observed when either 1 mol% or more than 3 mol% EtMgBr were used (entries 2 and 3). Phenylmagnesium bromide (3 mol%) was also an effective activating agent, however sodium triethylborohydride[16b] (3 mol%) gave only a moderate yield and a mixture of both mono- and bis-silylation products

Table 2. Iron-catalysed hydrosilylation of olefins: Scope, and functional group tolerance.[a]



[a] *Conditions:* olefin (0.7 mmol), FeCl$_2$ (1 mol%), **3b** (1 mol%), EtMgBr (2 mol%), PhSiH$_3$ (1.1 equiv.), THF (0.25 M), 1 h, room temperature.

[b] Yield determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard, isolated yield given in parentheses.

[c] FeCl$_2$ (3 mol%), **3b** (3 mol%), EtMgBr (6 mol%) used.

[d] FeCl$_2$ (5 mol%), **3b** (5 mol%), EtMgBr (10 mol%) used.

[e] Olefin added after addition of EtMgBr and PhSiH$_3$.

[f] 14% alcohol product isolated.

[g] NMR yield not determined.

[h] *Conditions:* olefin (0.7 mmol), [**3b**FeCl$_2$] (1 mol%), *n*-BuLi (2 mol%), PhSiH$_3$ (1.1 equiv.), toluene (0.25 M), 1 h, room temperature.

[i] Reaction in neat cyclooctene.

[j] 10% α-isomer [$C_6H_5C(SiPhH_2)=CHCH_3$] produced.

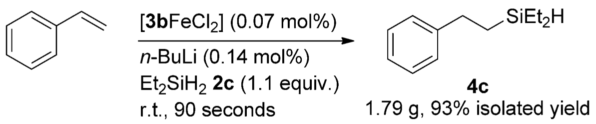
4a and **5a** (entries 4 and 5). Thus, 2 mol% EtMgBr was used for all further experiments. Variation of the 2,6-aryl substituents of the bis(imino)pyridine ligand from isopropyl **3a** to ethyl **3b** gave a more active catalyst, however some further reaction of the secondary silane product **4a**, to give the tertiary silane (bis-silylation product) **5a**, was observed (entry 6). The monosilylation product **4a** was produced exclusively when 1.1 equiv. of phenylsilane was used, whilst the bis-silylation product **5a** was quantitatively prepared using 0.5 equiv. of phenylsilane (entries 7 and 8). The 2,6-dimethyl ligand **3c** showed decreased selectivity with respect to multiple silylations, even with excess silane (entry 9). Secondary silanes (Ph$_2$SiH$_2$ **2b** and Et$_2$SiH$_2$ **2c**) gave the linear silane products **4b** and **4c** in quantitative yield with complete regioselectivity; however tertiary silane **2d** gave only small quantities of quaternary silane **4d** (entries 10–12). The hydrosilylation of 1-hexene **6** with tertiary silanes, benzyldimethylsilane **2e** and the industrially representative silicone polymer cross-linkers, heptamethyltrisiloxane **2f** and pentamethyldisiloxane **2g**, gave quaternary silanes **7e, 7f** and **7g** in excellent yield and with perfect regioselectivity (entries 13–15).

The applicability of the developed iron-catalysed hydrosilylation was investigated using a range of functionalised alkenes and alkynes under the optimised conditions of FeCl$_2$ (1 mol%), **3b** (1 mol%), EtMgBr (2 mol%) and phenylsilane (1.1 equiv.) (Table 2). 4-Phenylbutene **8a** was hydrosilylated to give linear silane product **9a** in quantitative yield as a single regioisomer, demonstrating equal catalytic activity and regioselectivity for aliphatic alkenes. Styrene derivatives **8b–i** bearing electron-donating and electronwithdrawing groups gave linear silane products **9b–i** in excellent yield with perfect regioselectivity. The differing electronic nature of each substrate had no influence on activity or regioselectivity. Significantly, a primary amine **8d** was tolerated,[19] and aryl fluoride **8e** and chloride **8f** functionalities were conserved, with no addition into the aryl-halide bond.[17b,20] The ester functionalised styrene derivatives **8h** and **8i** gave linear silane products **9h** and **9i**, respectively, with no C–O bond cleavage,[21] ester hydrosilylation,[22] or Grignard addition observed. An aliphatic ester **8j** was also tolerated. Iron-catalysed hydrosilylation of ketones[3a,b,23] and imines[24] has been well documented; however ketone **8k** underwent chemoselective hydrosilylation at the alkene, with no ketone reduction. Aliphatic ketone **8l** underwent chemoselective hydrosilylation at the alkene, albeit with lower selectivity – 4:1 in favour of alkene hydrosilylation. This result is complementary to that using bis(imino)pyridine iron(II) dialkyl complexes, which have been shown to be chemoselective for the hydrosilylation of ketones at room temperature.[23e] Imine and imino ester functionalities were also tolerated and gave silanes **9m** and **9n** in excellent yield and regioselectivity, however cyanostyrene **8o** gave only a moderate yield of silane **9o**.

A heteroaromatic substrate, 2-vinylquinoline **8p**, gave the linear silylation product **9p** in quantitative yield and with complete regioselectivity, however 4-vinylpyridine **8q** reacted in only 26% yield due to competing polymerisation. 4-Vinylcyclohexene **8r**, was hydrosilylated selectively at the terminal alkene, leaving the internal alkene intact. The conjugated diene 1-phenyl-*trans*-butadiene **8s** reacted selectively at the terminal alkene to give a 1:1 regioisomeric mixture of the linear and branched silane products **9s**-*l* and **9s**-*b*.

To demonstrate increased industrial applicability, the methodology was developed to operate in toluene, or 'solvent-free' conditions.[25,26] A suspension of preformed bis(imino)pyridine iron(II) complex [**3b**FeCl$_2$][27] (1 mol%) in either toluene or neat alkene, was activated by addition of n-BuLi (2 mol%) to give an active catalyst which was used for the hydrosilylation of 1,1- and 1,2-disubstituted alkenes **8t–v**. Silanes **9t–v** were obtained in excellent yield within 1 hour, and in the case of **9t** and **9u** with complete regioselective control for the linear silane product. Using 'solvent-free' reaction conditions, the gram-scale hydrosilylation of styrene using diethylsilane was complete within just 90 seconds using only 0.07 mol% iron catalyst, corresponding to a catalyst turnover frequency (TOF) approaching 60,000 mol h^{-1} (Scheme 1).

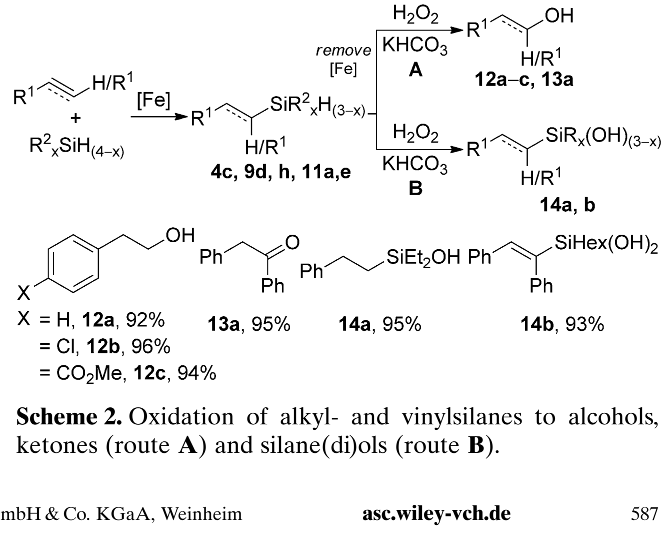
Alkynes were also suitable substrates, giving vinylsilanes with high stereoselectivity, and without multiple hydrosilylation. Interestingly, whilst internal alkynes **10a–c** gave (*E*)-vinylsilanes **11a–c** stereoselectively in excellent yield (*syn*-addition of Si–H) (Table 2), the terminal alkyne **10d** gave (*Z*)-vinylsilane **11d** arising from a formal *trans*-addition of the Si–H bond. The formation of the thermodynamically unfavoured (*Z*)-vinylsilane product has been observed with other transition metal catalysts,[6] and may be explained using the mechanisms proposed by Crabtree[28] and Ojima[29] in which silylmetallation is followed by *E*/*Z* isomerisation of the intermediate silylvinylene complex through either a zwitterionic carbene[29] or a metallocyclopropene[28] intermediate.



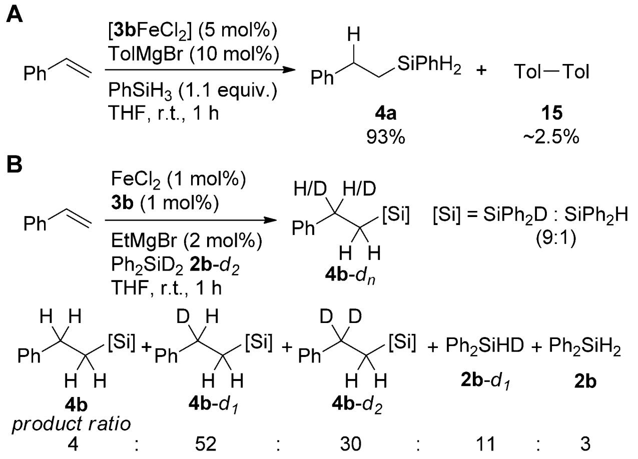
Scheme 1. Gram-scale, 'solvent-free' hydrosilylation of styrene.

The synthetic utility of the silane products was then investigated. Selected alkyl- and vinylsilane products were directly oxidised using hydrogen peroxide[30] to give alcohols **12a–c** and ketone **13a** in excellent yield and with no over-oxidation observed (Scheme 2, route **A**). A one-pot hydrosilylation–oxidation protocol was also developed (Scheme 2, route **B**), where in the presence of the iron catalyst selective Si–H bond (over Si–C bond) oxidation occurred, to give silane(di)ol products **14a** and **14b** in excellent yield. Alkylsilanols have numerous applications in materials chemistry,[6,31] and vinylsilanol products, such as **14b**, can be used as substrates in cross-coupling,[32] Mizoroki–Heck,[33] and carbonyl addition reactions.[34]

A large body of work has focussed on the development and mechanistic understanding of polymerisation reactions catalysed by iron bis(imino)pyridine complexes.[35] Chirik has also identified and characterised iron(II) dialkyl[5d,12] and iron(0) bis(dinitrogen) and bis(silane) complexes[11] which are effective precatalysts for hydrosilylation, however the *in situ* observation of the true catalytic species has proved chal-



Scheme 2. Oxidation of alkyl- and vinylsilanes to alcohols, ketones (route **A**) and silane(di)ols (route **B**).



Scheme 3. Mechanistic investigations on the iron-catalysed hydrosilylation of alkenes

lenging.[36] We sought to provide some insight by calculating the average oxidation state of iron attained under catalytic conditions by activation of the iron(II) pre-catalyst using tolylmagnesium bromide (TolMgBr).[4d,17a,37a–e] Using the formation of bitolyl **15** as a measure of the reduction of iron, maximum catalytic activity was calculated to correspond to an average oxidation state of iron(I) (Scheme 3, **A**).[18,37] This is in keeping with our previously reported mechanistic studies on iron-catalysed hydroboration.[4d]

The mechanism was further probed using diphenyl(silane-d_2) **2b**-d_2 for the deuterosilylation of styrene (Scheme 3, **B**).[18] The expected addition product **4b**-d_1, with a single deuterium at the benzylic position was formed as the major product, however double deuterium incorporation in the benzylic position **4b**-d_2, along with the non-deuterated product **4b** were also formed. H-transfer from the benzylic methylene to silicon was observed in both hydrosilylation products (**4b**-d_n) and recovered diphenylsilane (**2b**-d_1 and **2b**). No deuterium incorporation in the homobenzylic position (alpha to silicon) was observed. Although reversible hydrometallation cannot be ruled out, previous work[4b] would not support a hydrometallation step with the regioselectivity observed in this process. The H/D-scrambling between the benzylic position and silicon may be explained by the formation of iron carbenoid intermediates (on- or off-cycle); however more in-depth mechanistic studies are required, and are currently underway.

In summary, we have developed an operationally simple, chemo-, regio- and stereoselective iron-catalysed hydrosilylation of alkenes and alkynes, which uses just 1 mol% iron catalyst [$FeCl_2$ (1 mol%), ligand **3b** (1 mol%)] and 1.1 equivalents of silane at room temperature. All reagents used were commercially available and easily handled, and the active iron catalyst was generated *in situ*. A broad range of functional groups were tolerated, without deleterious side-reactions. Primary, secondary and tertiary silanes were used for the hydrosilylation of terminal, 1,1- and 1,2-disubstituted alkenes, and internal and terminal alkyl- and arylalkynes. The methodology was extended to operate under 'solvent-free' conditions, improving industrial applicability and ease of product isolation. The silane products were oxidised selectively to give alcohol, ketone or silane(di)ol products. Preliminary mechanistic studies indicate the formation of an iron(I) catalyst. The use of an *in situ* generated iron catalyst simplifies the operational requirements of these hydrosilylation reactions, compared to those using highly active but unstable iron (pre-)catalysts, and should allow the non-expert to fully utilise this synthetic methodology.

Experimental Section

General Iron-Catalysed Hydrosilylation Procedure

An olefin (0.7 mmol) was added to a solution of iron(II) chloride (0.9 mg, 0.007 mmol) and 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **3b** (3.0 mg, 0.007 mmol) in anhydrous tetrahydrofuran (3 mL) at room temperature under an atmosphere of nitrogen. Ethylmagnesium bromide (1.5 M in Et_2O, 10 μL, 2 drops, 0.015 mmol) was added, followed by a silane (0.77 mmol) and the reaction mixture was stirred at room temperature for 1 hour. Aqueous sulfate buffer (10 mL) was added and the aqueous phase extracted with diethyl ether (3×20 mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated under vacuum. 1,3,5-Trimethoxybenzene (23.5 mg, 0.14 mmol) was added as an internal standard, and a yield for the reaction determined by ^1H NMR. Isolated yields were determined after purification by silica chromatography.

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