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Platinum catalysed hydrosilylation of propargylic alcohols†

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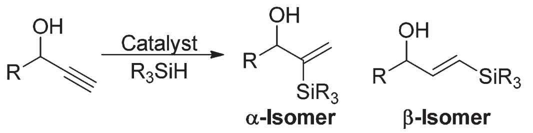
A facile and user-friendly protocol has been developed for the selective synthesis of *E*-vinyl silanes derived from propargylic alcohols using a $PtCl_2$/XPhos catalyst system. The reaction is generally high yielding and provides a single regioisomer at the β-position with *E*-alkene geometry. The reaction is extremely tolerant of functionality and has a wide scope of reactivity both in terms of alkynes and silanes used. The catalyst loading has been investigated and it is found that good reactivity is observed at extremely low catalyst loadings. This methodology has also been extended to a one-pot hydrosilylation Denmark–Hiyama coupling.

Introduction

Vinyl silanes are useful intermediates which can undergo a wide range of chemical transformations.[1] The use of silanes as a protecting group for oxygen functionalities is, of course, well documented, and much interest has focused on their use in low cost, non-toxic routes to the formation of carbon–carbon bonds. These include Sakurai allylations,[2] fluoride mediated Hiyama cross-coupling,[3] and the fluorine-free Denmark–Hiyama cross-coupling variation[4] and a number of copper mediated oxygen–carbon silicon migrations have been reported in the last decade.[5] They have also found use in the formation of carbon–oxygen bonds through Tamao–Fleming oxidation[6] and the development of an epoxidation–oxidation reaction sequence.[7,8]

There are many methods for the preparation of vinyl silanes.[9] The most widely used of these methods centre around the use of either hydrosilylation or other silylmetallation reactions. The majority of existing methods do not tolerate the incorporation of further functionality in either the substrate or the silane used, thus severely limiting their utility in synthesis. Such methods include the use of silylcuprates, developed by Fleming and later modified by Lipshutz, with each isomer of the vinyl silane being formed selectively by altering the nature of the Cu(I) species involved.[10–13] Organochromium species have proven to be of great use in the formation of vinyl silanes from aldehydes, which react selectively over ketones.[14–17] Further molecular complexity of these substrates can be achieved through Mizoroki–Heck type cross-coupling reactions[18] and Peterson olefinations.[19]

The hydrosilylation of alkynes is a powerful method of forming vinyl silanes in a stereocontrolled manner.[9,20] There are many catalysts that promote this reaction and late transition metal catalysts have been shown to be especially efficient.[21,22] There are two regioisomeric products alongside *E*/*Z* isomers available in this reaction. In the case of propargylic alcohols the two regioisomers are referred to as the α and the β-isomers where the silyl group is located α and β to the alcohol and affords 1,1 or 1,2-substituted vinyl silanes, respectively (eqn (1)).



(1)

Ruthenium complexes are especially efficient at producing the internal α-isomer with high selectivity. Trost and co-workers have investigated this reaction extensively, firstly using a cyclopentadienyl ruthenium complex to perform the desired hydrosilylation with moderate stereoselectivity.[22] Further investigation led to the development of a highly active and selective cationic catalyst, $[Cp^*Ru(MeCN)_3]PF_6$, which gives the α-vinylsilane in a >20 : 1 ratio.[23] The Lewis acid catalysed hydrosilylation of a range of alkynes with diverse functionality, as developed by Yamamoto,[24–27] also affords the α-isomer as a single product, although this method is still in its infancy.

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† Electronic supplementary information (ESI) available: Details of starting material synthesis and spectra of the compounds reported (^1H and ^{13}C NMR) are included. See DOI: 10.1039/c3ob40496j

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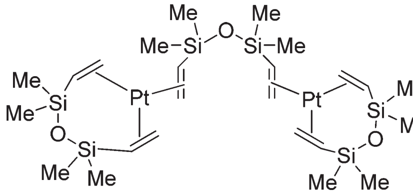
The majority of transition metal catalysed hydrosilylation reactions give the β-isomer as the major product.[28,29] Metals such as rhodium,[30–35] ruthenium[36–38] and titanium[39] have proven useful. Platinum complexes are by far the most well developed catalysts for the hydrosilylation of alkynes, affording the β-isomer, in the *E*-geometry as the major product.[21,40] Complexes such as Speier's catalyst [H_2PtCl_6] and Karstedt's catalyst [$Pt_2(dvs)_3$] (dvs = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) can produce high catalyst turnovers; however, both the regio and *E*/*Z* selectivity can be poor.[41–43]

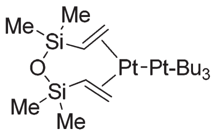
H_2PtCl_6

Speier's Catalyst

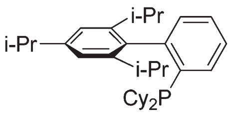


Karstedt's Catalyst

A solution to this problem was found through the use of bulky trialkylphosphine ligands[44–47] and more recently the use of platinum *N*-heterocyclic carbene complexes.[48–52] These sterically encumbered catalysts can impart high levels of selectivity on the reactions. Of note was the development of the (dvs)Pt-P*t*-Bu$_3$ catalyst which exhibits excellent catalytic activity and a high level of selectivity. The drawbacks to these methods are the cost of the Pt(0) precatalysts and the pyrophoric nature of the phosphines required.



(dvs)Pt-P*t*-Bu$_3$



XPhos

Alami reported that a combination of Pt(II) salts and bulky dialkylarylphosphines,[53] such as XPhos, catalysed the hydrosilylation of alkynes, with one example of propargyl alcohol itself reported.[54] The reaction proceeded in good yields and excellent selectivities; however, a large catalyst loading is required, typically 5 mol% Pt and 10 mol% phosphine.

We required a rapid and reliable method for the synthesis of β-silyl alyllic alcohols that was tolerant of significant steric encumbrance.[55] Panek previously disclosed the use of the highly reactive (dvs)Pt-P*t*-Bu$_3$ catalyst for the regioselective hydrosilylation of propargylic alcohols;[56,57] however, no examples of sterically congested or tertiary propargylic alcohols were reported. We speculated that we could modify the reaction reported by Alami to combine the catalytic activity of the bulky Pt(0) catalyst with the selectivity and operational ease of the air stable Pt(II) system. We discovered that the $PtCl_2$/XPhos catalyst system was very efficient for propargylic alcohols *vida infra*.[58] Under these conditions the catalyst loading could be lowered to 1 mol% and 0.5 mol% platinum(II) chloride for the secondary and tertiary propargylic alcohols, respectively.

Herein we report a full investigation into the scope and limits of these hydrosilylation reactions including the use of highly functionalised substrates.

Results and discussion

Optimisation of Pt catalysed hydrosilylation

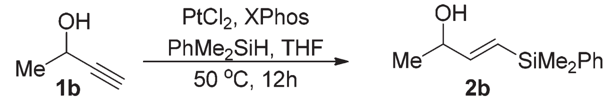
We began investigating the hydrosilylation of commercially available but-3-yn-2-ol (Table 1). Using 5 mol% $PtCl_2$ and 10 mol% XPhos the reaction afforded the vinyl silane as a single regio- and geometric isomer in excellent yield (entry 1).

When the reaction was carried out in the absence of ligand, the regioselectivity fell to 9 : 1 (entry 2). Further optimisation of the transformation led to a reduction of the amount of catalyst needed, and at 1 mol% $PtCl_2$ excellent yields were still being obtained (entry 4). If the catalyst loading is dropped further, the reaction becomes sluggish and lower yields are obtained (entry 5). The amount of silane can also be reduced, but once again a noticeable slowing of the reaction is observed (entry 6).

Hydrosilylation of secondary propargylic alcohols

With the optimised reaction conditions in hand, we began by examining the scope of the reaction using secondary propargyl alcohols (Table 2). We soon discovered that propargyl alcohol itself was a very poor substrate for this reaction with only 47% yield of the vinyl silane **2a** being produced. Contrary to this, a wide range of alkyl substituents were well tolerated, including linear **2b–c** and branched groups **2d–e** all providing good yields of the corresponding hydrosilylated product. Our attention then turned to vinyl and aryl substituents. A styrenyl derivative **2f** was well tolerated as were many aromatic groups **2g–l** even including aryl groups bearing *ortho*-substituents **2m** that are tolerated albeit in a reduced yield. We also examined heterocycles **2n–q**, especially those containing basic nitrogen atoms to test whether these would inhibit the catalyst. Gratifyingly, these were all good substrates providing the requisite

Table 1 Optimisation studies



Entry	mol% $PtCl_2$/XPhos	Equiv. R_3SiH	β : α ratio[a]	Yield[b] (%)
1	5/10	1.6	>99.1	93
2	5/10	1.6	>91.9	72
3	2/4	1.5	>99.1	93
4	**1/2**	**1.5**	**>99.1**	**91**
5	0.5/1	1.5	>99.1	74
6	1/2	1.1	>99.1	83

[a] Determined by ^1H NMR of the crude. [b] Isolated yield of the pure isomer.

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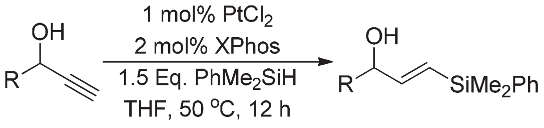
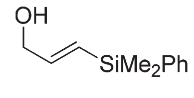
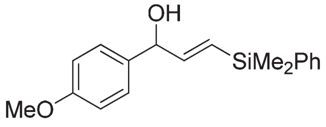
Table 2 Secondary propargylic alcohols

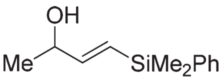




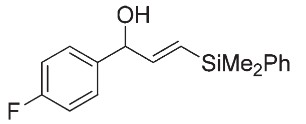
2a, 47%



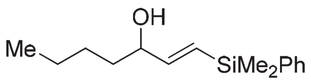
2j, 70%



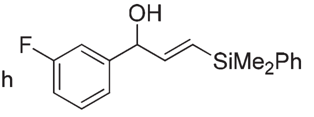
2b, 91%



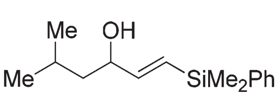
2k, 75%



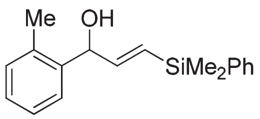
2c, 85%



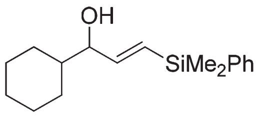
2l, 79%



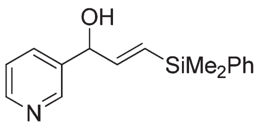
2d, 85%



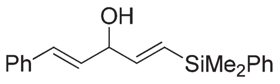
2m, 59%



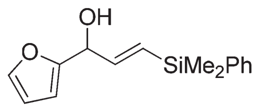
2e, 72%



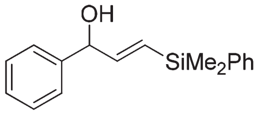
2n, 53%



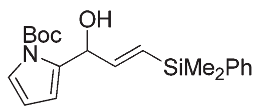
2f, 81%



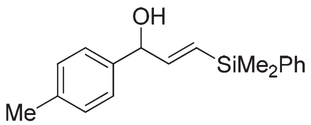
2o, 87%



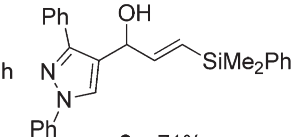
2g, 87%



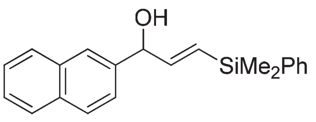
2p, 61%



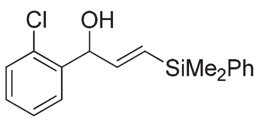
2h, 72%



2q, 71%



2i, 77%



2r, n.r.

vinyl silane in moderate to high yields in all cases. In general these heterocyclic substrates afforded slightly lower yields and required prolonged reaction times compared to their less functionalised counterparts. When the hydrosilylation was attempted using the *ortho*-chloroaryl derivative **1r**, no reaction was observed. Both increasing the reaction time and the catalyst loading did not afford any product, with starting material recovered in each case. This class of substrate is the only one we have found so far to be ineffective for this reaction.

Hydrosilylation of tertiary propargylic alcohols

We next turned our attention to tertiary propargylic alcohols as prior to our original communication the hydrosilylation of hindered propargylic alcohols was not widely reported except in the presence of non-commercial specialist ligands.[59] We found that the $PtCl_2$/XPhos system was especially efficient for the hydrosilylation of tertiary propargylic alcohols and that 0.5 mol% of $PtCl_2$ could be used to give excellent yields. We have further expanded the scope of the reaction and found that it is tolerant of a wide range of functional groups (Table 3).

We began by examining simple alkyl substituents **4a–c** and found that these underwent the hydrosilylation reaction in excellent yields. Similarly, aryl substituents, both with one and two aryl groups **4d–f**, were tolerated. Fluoroalkyl groups could be included in **4g** as could heterocycles, with thiophene **4h** substituents easily incorporated. Our attention then turned to cyclic tertiary propargylic alcohols. A wide range of cyclic alkyl substituents were addressed in this reaction, all of which proceeded in good to excellent yields **4i–n**. Substituents on these carbocycles were also tolerated with a difluoromethylene and ketal groups **4o–p**, alongside fused aromatics **4q–r** being installed with little effect on the yields of the reaction. Finally we examined heterocyclic substrates, with nitrogen containing heterocycles performing well in this reaction, including azetidines **4s**, piperidines **4t** and even tropanes **4u** to afford good yields of vinyl silanes, albeit with a substantial increase in the required reaction time. Chalcogen containing heterocycles **4v–w** were also examined, with the reaction proceeding in a similar fashion to their carbocyclic analogues providing the corresponding vinyl silanes in good to excellent yields.

Catalyst loading studies

As the reaction is highly efficient for tertiary propargylic alcohols, using just 0.5 mol% catalyst loading, we examined the effect of further reducing the amount of catalyst and whether this would have a negative effect on the reaction (Table 4). Halving the catalyst loading to 0.25 mol% proved to have very little effect on the reaction and further reductions showed that this system still gave synthetically useful yields when dropped to as low as 0.05 mol%. Further reductions, to 0.025 and 0.01 mol%, were possible; however, the reaction slows significantly. A prolonged reaction time appears to counteract this to some degree, leading to the conclusion that the catalyst is stable for extended periods of time; hence, further reductions in catalyst loading could be possible if required. A TON of 6900

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Table 3 Tertiary propargylic alcohols

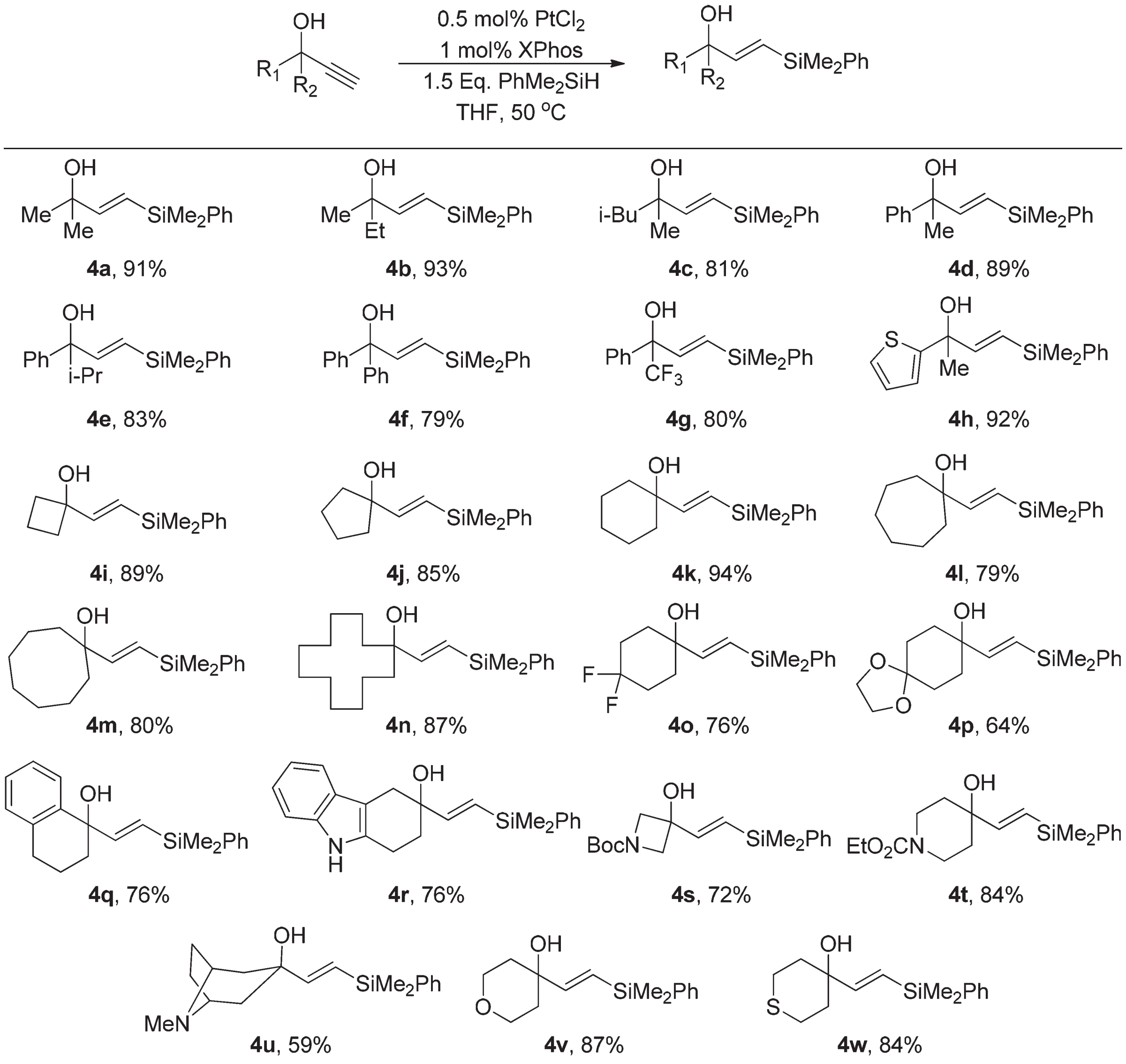
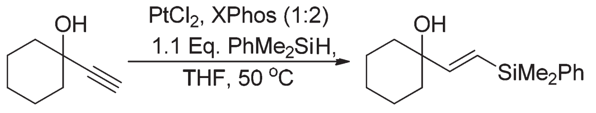


Table 4 Catalyst loading studies



3l **4l**

Entry	Pt loading	Time (h)	Yield[a]
1	0.5 mol%	16	94%
2	0.25 mol%	16	93%
3	0.1 mol%	16	83%
4	0.05 mol%	16	81%
5	0.025 mol%	40	73%
6	0.01 mol%	90	69%

[a] Isolated yield of a single isomer.

was achieved which shows the catalyst's stability and applicability. It is difficult to directly compare to other catalysts as our studies were performed using $PhMe_2SiH$ and most other hydrosilylation catalysts are tested against Et_3SiH as a standard. In general, Et_3SiH is a more reactive silane with TONs of around 70 000 being achieved in certain cases.[59] Our catalyst system does, however, benefit from excellent stability and functional group tolerance, making it a very practical method.

Use of other silanes

As all of the examples shown in Tables 1–4 utilised phenyldimethylsilane, we then began examining the use of other commercially available silanes. We found that the reaction is tolerant of a wide range of silanes, with the triethylsilyl **5a**,

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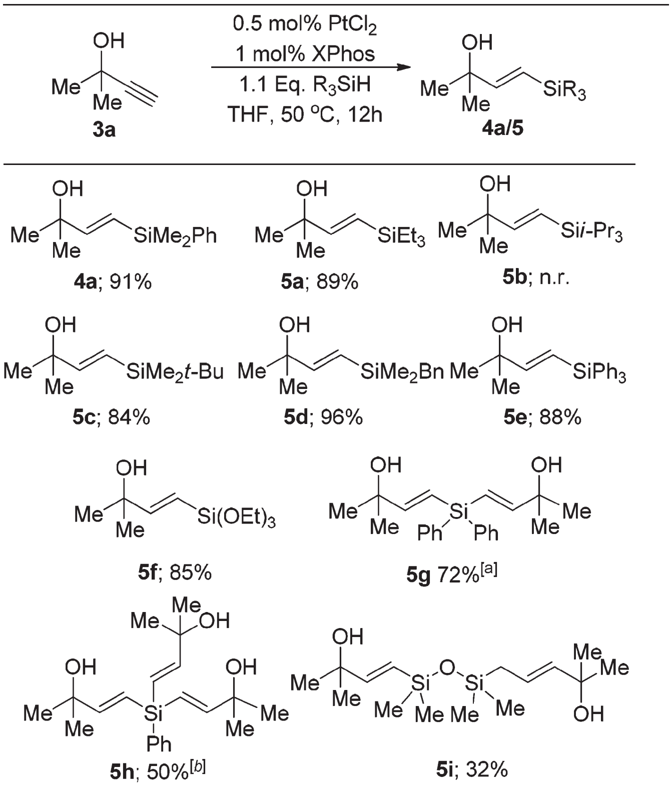
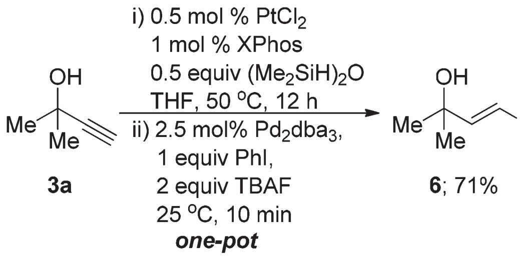
tert-butyldimethylsilyl **5c**, benzyldimethylsilyl **5d** triphenylsilyl **5e** and triethoxysilyl **5f** derivatives formed in good yields. When tri-iso-propylsilane was used no reaction was observed with quantitative recovery of starting material. Presumably the increased steric bulk of the silane prevents the reaction from occurring. Interestingly when diphenyl silane and phenylsilane were used, two or three sequential hydrosilylations could be carried out on the same silicon atom, forming dimers and trimers of the propargylic alcohols (Table 5).[60]

Table 5 Other silanes



[a] Using 0.5 equivalent of Ph_2SiH_2. [b] Using 0.3 equivalent of $PhSiH_3$.

Our attention next turned to the hydrosilylation using bis-(dimethylsiloxane) to allow subsequent Hiyama couplings. Unfortunately this afforded poor isolated yields, although there was complete conversion to the vinylsilane from analysis of the crude reaction mixture suggesting that the product **5h** was unstable for silica gel chromatography. To circumvent this issue, a one-pot Denmark–Hiyama coupling was attempted.[61] The hydrosilylation occurred in good conversion using the standard conditions and then simply cooling the reaction, adding TBAF followed by Pd_2dba_3 and iodobenzene afforded a very facile cross-coupling which gave 72% yield after just 10 minutes (eqn (2)).



(2)

Internal alkynes

We also examined internal alkynes to investigate whether the Lewis basic oxygen atom was co-ordinating to the metal and directing the addition[62] or whether the regioselectivity was based purely on steric factors. The first substrate attempted was but-2-yn-1-ol **7**, which gave a 1 : 1 mixture of regioisomers (eqn (3)). This clearly suggests that the oxygen is not directing the addition and that pure sterics govern the regioselectivity. This also demonstrates that primary propargylic alcohols can participate well in this reaction when extra substitution is present at the β-position as an overall yield of 84% was obtained. When steric bulk is increased in the propargylic position the ratio increases to give moderate β selectivity. Alkyl groups give around 3 : 1 selectivity with methyl **9** affording 2.7 : 1 β : α, butyl **11** 3.2 : 1 and when a cyclohexyl group **13** is introduced a β-selectivity of 3.2 : 1 was observed (eqn (4)–(6)). This is in line with what one would expect based on the steric environment of the alkyne.

When the terminal alkyne position of propargyl alcohol was substituted with a phenyl group **15**, modest selectivity was observed with the β-isomer **16a** prevailing in a 4.1 : 1 ratio (eqn (7)). This is contrary to the steric environment around the alkyne and is clearly showing preference for hydride attack at the more electrophilic terminus of the alkyne.[23,47,63,64] Indeed, Alami observed this effect when applied to the palladium catalyzed hydrostannylation of **13**, with 4 : 1 regioselectivity for β-substitution being observed.[65] They also showed that the regioselectivity in these systems directly correlated to the Hammett σ-value for substituted benzene rings. When strong electron withdrawing groups were present in the *para*-position of the benzene ring a single β-regioisomer was obtained whereas electron releasing groups produce selectivities of the order of a 3 : 1 β : α ratio.

Similarly when a trimethylsilyl group is installed at the β-position **17**, the product ratio is contrary to the steric environment (eqn (8)). The mild polarisation of the alkyne group caused by the silane is enough to override the significant steric bias to afford the β-regioisomer **18a** as the major product. If the steric environment at the β-position is increased greatly by installing a *tert*-butyl group **19**, the regioselectivity of the reaction can be switched to give solely the α-isomer. No traces of the β-isomer **20a** were observed with only the α-isomer **20b** being formed in good yield (eqn (9)). A single regioisomer could again be obtained when the propargylic position was highly substituted compared to the β-position **21**. In this instance only the β-isomer **20a** was observed again in good yield (eqn (10)). The results in eqn (9) and (10) demonstrate that the steric environment around the alkyne plays a pivotal role in determining the selectivity of the products. However, when the alkyne is polarised and an

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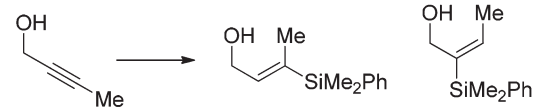
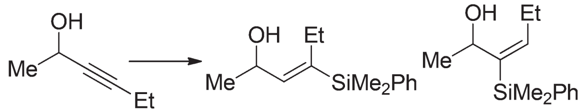
electronic bias is present, such as eqn (7) and (8), the regiochemistry will be dictated by the attack of the hydridic hydrogen at the more electron deficient terminus.



7 **8a**; 43% **8b**; 41%

1:1 Regioselectivity

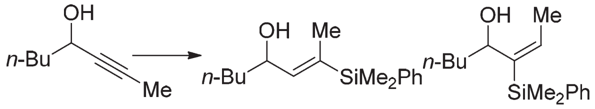
(3)



9 **10a**; 58% **10b**; 21%

2.7:1 Regioselectivity

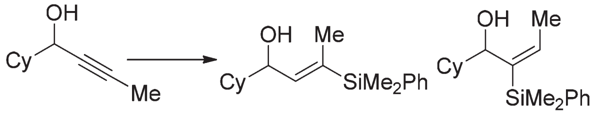
(4)



11 **12a**; 64% **12b**; 21%

3:1 Regioselectivity

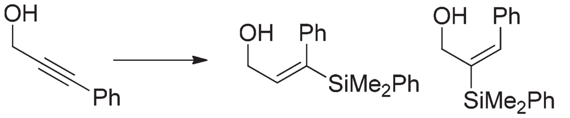
(5)



13 **14a**; 65% **14b**; 20%

3.2:1 Regioselectivity

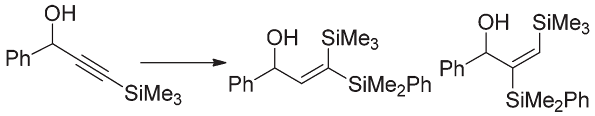
(6)



15 **16a**; 66% **16b**; 16%

4.1:1 Regioselectivity

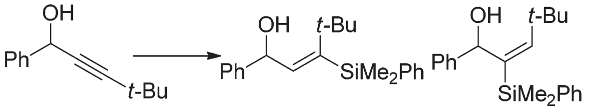
(7)



17 **18a**; 46% **18b**; 21%

2.2:1 Regioselectivity

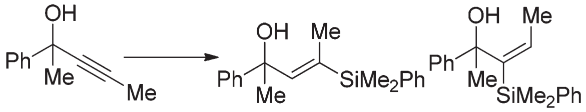
(8)



19 **20a**; 0% **20b**; 76%

Single Regioisomer

(9)



21 **22a**; 73% **22b**; 0%

Single Regioisomer

Conditions: 0.5 mol% PtCl$_2$, 1 mol% XPhos, 1.1 Equiv. HSiMe$_2$Ph, THF 50 ^{o}C, 12h

(10)

Similarly, when a trimethylsilyl substituted alkyne was used the hydrosilylation gave a 2.2 : 1 mixture of β : α isomers. The reaction proceeds to give a differentially substituted 1,1-vinyldisilane. Again the polarising effect of the silane can rationalise the regiochemical outcome as the β position is more electrophilic than the α.

Mechanistic insights

Fig. 1 highlights our model for regioselectivity. In the cases where there is a steric bias, the large group orientates itself away from the bulky XPhos ligand. The result of this is the selective formation of a product with the hydrogen adjacent to the large group and the silyl group next to the smaller group. In the case of the electronically biased substrates, the phenyl or silyl group creates a polarised alkyne and the hydridic hydrogen on the platinum adds at the more electrophilic terminus thus resulting in the hydrogen adjacent to the less electron withdrawing group and the silyl group next to the electron withdrawing substituent. This polarisation appears to be significant enough to override the inherent steric bias for one product over the other.

We conducted a competition experiment between propargyl alcohol **1a**, but-3-yn-2-ol **1b**, and 2-methyl but-3-yn-2-ol **3a** where the reaction was conducted with one equivalent of each of the substrates and one equivalent of PhMe$_2$SiH to ascertain the relative rate of reactions. As expected the tertiary alcohol reacted faster than the secondary which in turn was faster than the primary in a k_{rel} of 2.7 : 1.7 : 1. This proves that the enhanced reactivity observed for tertiary propargylic alcohols is due to an inherently faster reaction rate rather than factors such as product inhibition or catalyst decomposition (Scheme 1).

We next examined whether the incorporation of deuterium at the terminal position of the alkyne led to an observable kinetic isotope effect. Alkyne **23** was readily prepared and was subjected to competition experiment with its non-deuterated analogue. Following conversion to 49%, the product **4k**/**24** was protioenriched alongside the recovered starting material being deuteroenriched in the same ratio. Both recovered starting material and product conversion gave a k_H/k_D value of 1.44. This suggests a large secondary kinetic isotope effect consistent with a change in geometry from sp to sp^2 during the rate limiting step (Scheme 2).[66]

We observed significant evolution of gas, presumably hydrogen, upon addition of the silane to the reaction mixture. This led us to examine the origin of this gas. There are several

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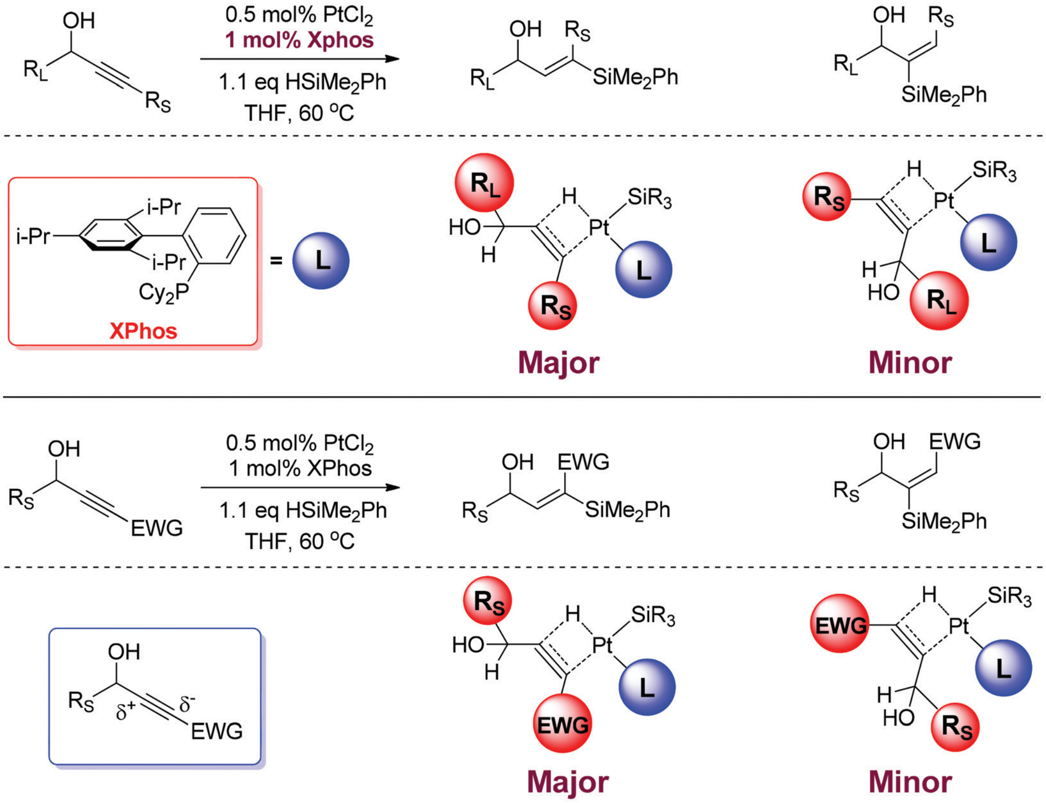
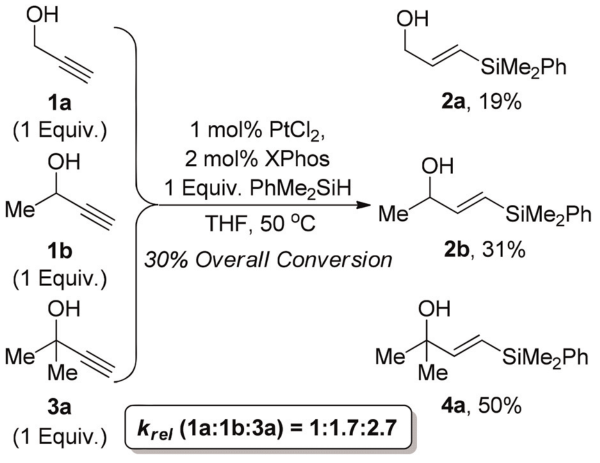
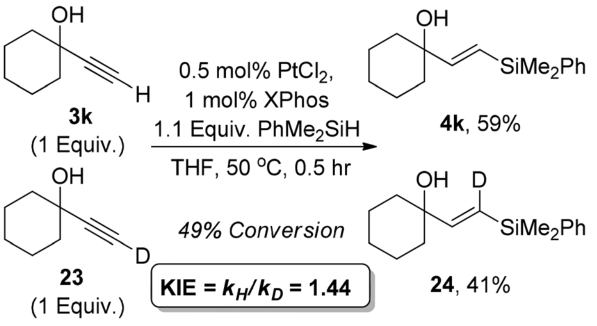


Fig. 1 Origin of regioselectivity.

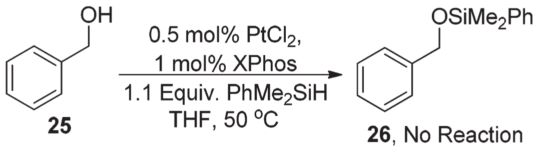


Scheme 1 Primary/secondary/tertiary competition experiment.

possible explanations including: the simple reduction of the Pt(II) salt to Pt(0) producing H$_2$ and a disilane or the OH bond reacting directly with the catalyst producing a Pt(OR) type complex. To probe the effect the O–H bond may have on the reactivity of this reaction a series of experiments were conducted. Firstly we performed a control experiment with benzyl alcohol to determine whether any *O*-silylation was observed during the reaction (eqn (11)). No reaction or *O*-silylation was observed with quantitative recovery of the starting material being achieved.

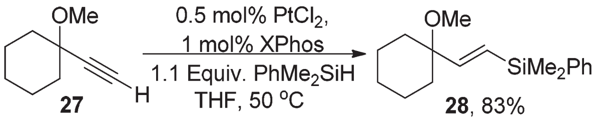


Scheme 2 Alkyne kinetic isotope effect.



(11)

We next investigated the use of the methyl ether **27** and found that the hydrosilylation occurred in a similar overall yield to the hydroxyl analogue **28** (eqn (12)). This suggests that the OH is not required for reactivity and to obtain high yields.



(12)

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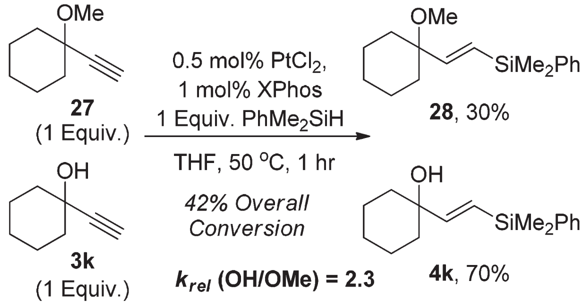
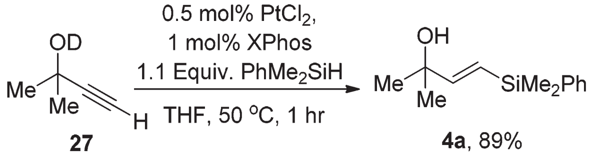


Scheme 3 Role of the OH bond.

A competition experiment was conducted between the OH and OMe compounds to elucidate the relative rates of the reactions. The OH compound **3k** reacted much faster than the OMe analogue **27** with a k_{rel} of 2.3 being observed, suggesting that the OH does accelerate the reaction (Scheme 3).

To further probe this effect, we prepared the *O*-deuterated analogue and subjected this to the reaction conditions. Again the reaction proceeded with a similar overall yield and with no deuterium incorporated into the resultant alkene (eqn (13)). This suggests that the formation of Pt(OR) complexes is unlikely as deuterium would also be delivered to the platinum catalyst which in turn be observed in the vinyl silane product.



(13)

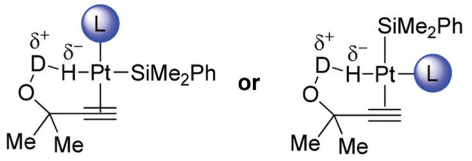
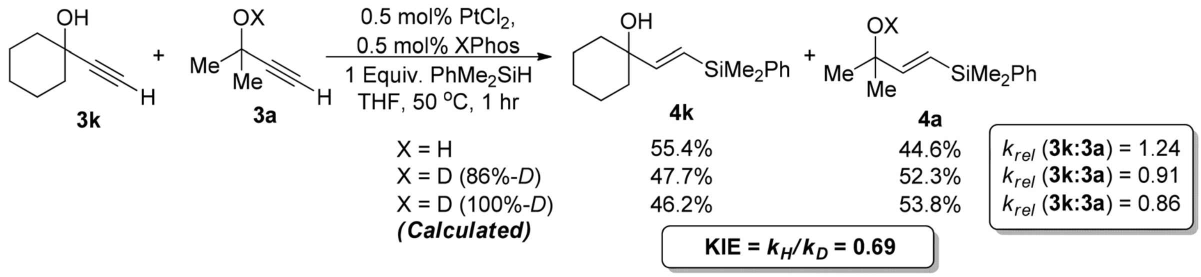


Fig. 2 Possible H-bond acceleration of hydrometallation.

Finally, we examined whether there was a OH/OD kinetic isotope effect which would elucidate the true role of the alcohol moiety. As this is an exchangeable deuterium measuring the product or recovered starting material, deuterium enrichment would be difficult. We therefore took two alkynes, the dimethyl substrate **3a** and the cyclohexyl derivative **3k**. We first of all performed a control experiment where we measured the relative rate of reactions between the two compounds. The cyclohexyl analogue was found to have a faster rate of reaction with a k_{rel} (**3k** : **3a**) of 1.24 and this was used as a correction factor in the kinetic isotope effect calculations. When the reaction was performed using equimolar amounts of **3k** and d_1-**3a**, which was formed in 86% isotopic purity,[67] the order of reactivity was reversed with the dimethyl compound reacting at a faster rate. As the alcohol was only deuterated to 86% we had to adjust this value to 100% isotopic purity assuming a linear relationship and found a k_{rel} (**3k** : d_1-**3a**) of 0.86. This was then used to measure the kinetic isotope effect which equated to 0.69 (Scheme 4).

An inverse kinetic isotope effect could be due to several factors, including a pre-equilibrium; however, the absence of deuterium in the vinyl silane and the rapid evolution of hydrogen gas make this unlikely. A more likely scenario is the OH moiety hydrogen bonding to the hydridic hydrogen bound to the platinum centre and accelerating the hydrometallation step through mild acid catalysis. Indeed, this is consistent with the hydrometallation step being rate limiting. This can be seen in Fig. 2 where the OD/OH group can H-bond to the hydridic hydrogen, thus weakening the Pt–H bond and accelerating the reaction. This interaction does explain the rate acceleration; however, one would predict some regioselectivity based on this, which is not seen in the case of internal alkynes. Either this chelate is not possible in the internal cases or this occurs in an intermolecular fashion.

More sterically hindered substrates react much faster in this reaction and we sought to rationalise this mechanistically. In the standard Chalk–Harrod mechanism[28] for hydrosilylation of alkynes, there are two events that can occur to lead to product (Fig. 3): either oxidative addition of the silane followed by alkyne coordination (Pathway 1) or alkyne coordination followed by oxidative addition (Pathway 2). Pathway 1 would favour relatively small alkynes as the coordination event occurs on a sterically congested Pt(II) species **C**. These types of substrates are excellent with Speier's catalyst and Karstedt's catalyst.



Scheme 4 OH kinetic isotope effects.

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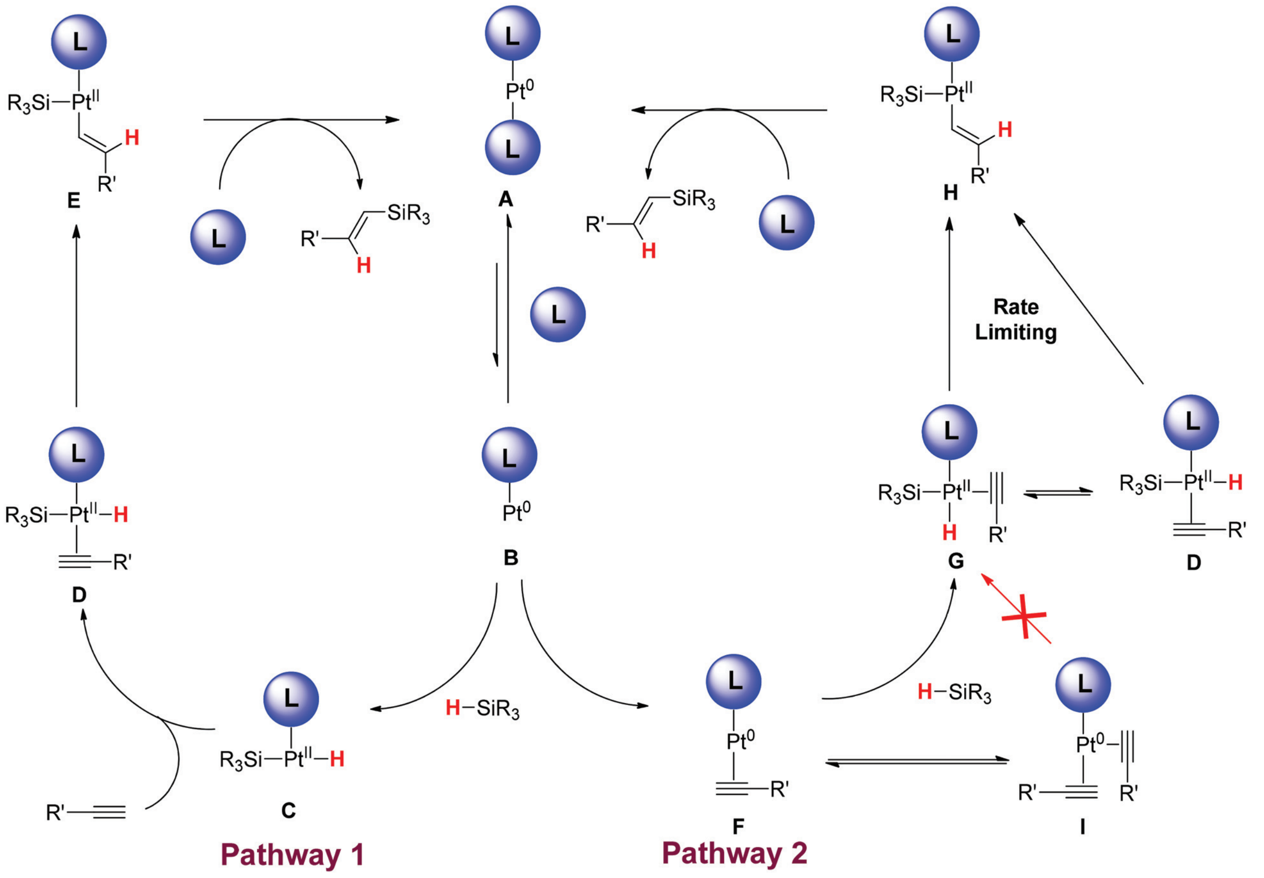

Fig. 3 Proposed catalytic cycle.

Our results suggest that Pathway 2 is operating as the major pathway as more hindered substrates are superior. A large alkyne can bind to the coordinatively unsaturated Pt(0) species **B** thus stabilising this prior to oxidative addition. Alternatively, if a small alkyne is bound to the coordinately unsaturated platinum–ligand complex **F**, a second alkyne can then bind, thus removing the coordination sites needed for the oxidative addition reaction. The result is that the catalyst is removed from the productive cycle **I** and the rate of reaction is based on the decomplexation of the second alkyne. When a bulky alkyne is used the complexation of two substrates is disfavoured, thus leaving the catalytically active species available for subsequent oxidative addition to form **G**, migratory insertion **H** and reductive elimination. This is very clearly demonstrated in the case of propargyl alcohol **1a**.

Our experiments suggest that the migratory insertion event is rate limiting with a large sp–sp^2 secondary kinetic isotope effect being observed. This could occur from **G** or an isomerisation event to **D** could occur due to the large *trans*-effect of both silanes and hydrides. Both complexes would give a similar result in terms of kinetic isotope effects and therefore cannot be distinguished.

It is also possible that the silane can react directly with **F** in a concerted manner to proceed directly to **H** with the same factors that would govern reactivity as in the two-step complexation migratory insertion process.

Conclusions

We have shown the effectiveness and robustness of $PtCl_2$/XPhos catalysed hydrosilylation. Both secondary and tertiary propargyl alcohols perform well as do internal alkynes. Furthermore, the catalyst system is tolerant of various silanes which improves the usefulness of this protocol. A one-pot Hiyama–Denmark cross-coupling reaction was also performed using the catalyst system which allows access to a range of functionalities. We have examined the use of internal alkynes and have found that this is governed by both steric and electronic factors.

Experimental section

Compounds **2a–2g**, **2o**, **4a–4d**, **4e**, **4j–4k** and **4v** were fully characterised and reported previously.[58] For the synthesis of the starting alkynes see the ESI.†

General methods

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. All reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualised with ultraviolet

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light and then developed with iodine and basic potassium permanganate solution. Flash chromatography was performed on Sigma-Aldrich silica gel 60 as the stationary phase and the solvents employed were of analytical grade. ^{1}H NMR spectra were recorded on a Bruker AVX400 (400 MHz) spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from deuterated chloroform ($CDCl_3$) taken as 7.26 ppm, integration, multiplicity (s = singlet; d = doublet; t = triplet; dd = double doublets; m = multiplet), and coupling constant (Hz). ^{13}C NMR spectra were recorded on a Bruker AVX400 (100 MHz) spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ taken as 77.0 ppm. Infrared spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer as liquid films or as dilute solutions between two KBr discs. Mass spectra were recorded on either a Micromass GCT Premier or a Waters Micromass LCT Premier spectrometer using electron ionisation (EI) at 70 eV or electrospray (ES) techniques, respectively. Unless stated otherwise, all commercially available reagents were used as received. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.

General procedure A: hydrosilylation secondary propargyl alcohols

To an oven dried 5 mL round bottom flask equipped with a reflux condenser and magnetic stirrer was added $PtCl_2$ (1 mol%) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (2 mol%) (XPhos). The flask was then flushed quickly with argon and dry THF was added. The mixture was then stirred at 50 °C for 20 minutes until a yellow homogeneous mixture was obtained. The corresponding propargyl alcohol (1 eq.) was added followed by the silane (1.1 equivalents) *via* syringe (CAUTION: Rapid evolution of hydrogen gas) and the solution was stirred at 50 °C overnight. The solvent was evaporated and the crude mixture was applied to the top of a column and chromatographed to afford the requisite (*E*)-vinyl silane.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(*p*-tolyl)prop-2-en-1-ol (2h). The title compound was prepared according to general procedure A from 1-(*p*-tolyl)prop-2-yn-1-ol[68] **1h** (990 mg, 6.77 mmol) and dimethylphenylsilane (1.38 g, 10.2 mmol) using $PtCl_2$ (18.0 mg, 0.0677 mmol) and XPhos (64.3 mg, 0.135 mmol) in THF (2 mL), which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2h** (1.38 g, 72%) as a colourless oil.

R_f (9 : 1 hexane–EtOAc) = 0.29; ν_{max} (thin film)/cm^{-1}; 3001, 3068, 2956, 1619, 1427, 248, 1114, 842, 822, 730, 699; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.53–7.48 (2H, m), 7.37–7.32 (3H, m), 7.25–7.21 (2H, m), 7.18–7.13 (2H, m), 6.28 (1H, m), 6.12 (1H, dt, J = 18.8, 1.28 Hz), 5.17 (1H, t, J = 4.3 Hz), 2.43 (3H, s), 1.96 (1H, m), 0.35 (3H, d, J = 2.0 Hz), 0.34 (3H, d, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 139.5, 138.4, 137.5, 133.7, 129.3, 129.0, 127.8, 127.2, 126.5, 76.5, 21.1, −2.65; HRMS (ES+) calcd for $C_{18}H_{22}OSiNa$ $[M + Na]^+$ 305.1330. Found 305.1338.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(naphthalen-2-yl)prop-2-en-1-ol (2i). The title compound was prepared according to general procedure A, from 1-(naphthalen-2-yl)prop-2-yn-1-ol[68] **1i** (500 mg, 2.71 mmol) and dimethylphenylsilane (552 mg, 4.07 mmol) using $PtCl_2$ (7.0 mg, 0.0263 mmol) and XPhos (25.6 mg, 0.0537 mmol) in THF (1 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2i** (660.6 mg, 77%) as a colourless solid.

R_f (9 : 1 hexane–EtOAc) = 0.41; ν_{max} (thin film)/cm^{-1}; 3434, 1634, 1247, 1114, 730.8, 699.4; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.88–7.83 (4H, m), 7.58–7.47 (5H, m), 7.40–7.36 (3H, m), 6.39 (1H, dd, J = 18.6, 5.0 Hz), 6.22 (1H, dd, J = 18.8, 1.5 Hz), 5.41 (1H, t, J = 4.0 Hz), 2.18 (1H, s), 0.39 (3H, s), 0.39 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 139.8, 138.4, 133.9, 133.4, 133.1, 129.1, 128.5, 128.1, 128.0, 127.9, 127.7, 126.2, 126.0, 125.2, 124.5, 76.9, −2.6; HRMS (EI) calcd for $C_{21}H_{23}OSi$ $[M + H]^+$ 319.1518. Found 319.1513.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)prop-2-en-1-ol (2j). The title compound was prepared according to general procedure A, from 1-(4-methoxyphenyl)prop-2-yn-1-ol[68] **1j** (500 mg, 3.08 mmol) and dimethylphenylsilane (631 mg, 4.64 mmol) using $PtCl_2$ (8.2 mg, 0.0308 mmol) and XPhos (29.4 mg, 0.0616 mmol) in THF (1 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2j** (643 mg, 70%) as a clear oil.

R_f (9 : 1 hexane–EtOAc) = 0.29; ν_{max} (thin film)/cm^{-1}; 3412, 2955, 1612, 1512, 1247, 828; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55–7.50 (2H, m), 7.38–7.35 (3H, m), 7.31–7.27 (2H, m) 6.92–6.89 (2H, m), 6.30 (1H, dd, J = 18.6, 4.8 Hz), 6.14 (1H, dd, J = 18.8, 1.5 Hz), 5.19 (1H, t, J = 3.52 Hz), 3.82, (3H, s), 1.95 (1H, d, J = 4.0 Hz), 0.37 (3H, s) 0.37 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 149.1, 138.4, 134.7, 133.8, 129.0, 127.9, 127.8, 114.0, 76.3, 55.3, −2.6; HRMS (EI) calcd for $C_{18}H_{21}O_2Si$ $[M - H]^+$ 297.1311. Found 297.1321.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(4-fluorophenyl)prop-2-en-1-ol (2k). The title compound was prepared according to general procedure A, from 1-(4-fluorophenyl)prop-2-yn-1-ol[69] **1k** (350 mg, 2.33 mmol) and dimethylphenylsilane (473 mg, 3.50 mmol) using $PtCl_2$ (6.2 mg, 0.0233 mmol) and XPhos (22.2 mg, 0.0466 mmol) in THF (1 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2k** (501 mg, 75%) as a clear oil.

R_f (9 : 1 hexane–EtOAc) = 0.30 ν_{max} (thin film)/cm^{-1}; 3350, 2956, 1604, 1508, 1223, 838; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55–7.50 (2H, m), 7.40–7.30 (5H, m), 7.09–7.03 (2H, m), 6.28 (1H, dd, J = 18.6, 4.8 Hz), 6.14 (1H, dd, J = 18.6, 1.3 Hz), 5.22 (1H, d, J = 4.5 Hz), 2.07 (1H, s), 0.39 (3H, s), 0.38 (3H, s) ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{C-F}$ = 244.3 Hz), 158.7, 138.2, 138.1 (d, $^4J_{C-F}$ = 3.3 Hz), 133.8, 129.1, 128.1 (d, $^3J_{C-F}$ = 8.3 Hz), 127.9, 127.8, 115.4 (d, $^2J_{C-F}$ = 21.1 Hz), 76.1, −2.7; HRMS (EI) calcd for $C_{17}H_{17}SiF$ $[M - H_2O]^+$ 268.1084. Found 268.1103.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(3-fluorophenyl)prop-2-en-1-ol (2l). The title compound was prepared according to general procedure A, from 1-(3-fluorophenyl)prop-2-yn-1-ol **1l** (930 mg, 6.18 mmol) and dimethylphenylsilane (1.22 g, 9.27 mmol) using $PtCl_2$ (16.4 mg, 0.0618 mmol) and XPhos (63.3 mg,

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0.133 mmol) in THF (5 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2l** (1.31 g, 79%) as a colourless oil.

R_f (9 : 1 hexane–EtOAc) = 0.33; ν_{max} (thin film)/cm^{-1}; 3391, 3069, 2957, 1613, 1591, 1486, 1449, 1428, 1249, 1115, 844, 699; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55–7.49 (2H, m), 7.43–7.30 (4H, m), 7.16–7.08 (2H, m) 7.02–6.96 (1H, m), 6.26 (1H, dd, J = 18.8, 5.0 Hz), 6.15 (1H, dd, J = 18.8, 1.2 Hz), 5.23 (1H, t, J = 5.08 Hz), 2.09 (1H, d, J = 4.0 Hz), 0.38 (3H, s), 0.38 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^1J_{C-F}$ = 245.6 Hz), 148.2, 145.0 (d, $^3J_{C-F}$ = 6.6 Hz), 138.1, 133.8, 133.0, 130.0, (d, $^3J_{C-F}$ = 8.4 Hz), 129.1, 128.5, 127.8, 122.0, 121.9, 114.5 (d, $^2J_{C-F}$ = 21.1 Hz), 113.2 (d, $^2J_{C-F}$ = 21.9 Hz), 76.2 (d, $^4J_{C-F}$ = 1.8 Hz), −2.7; HRMS (ES+) calcd for $C_{17}H_{19}OFNaSi$ $[M + Na]^+$ 309.1087. Found 309.1085.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(*o*-tolyl)prop-2-en-1-ol (2m). The title compound was prepared according to general procedure A, from 1-(*o*-tolyl)prop-2-yn-1-ol[68,70] **1m** (102 mg, 0.721 mmol) and dimethylphenylsilane (108 mg, 0.793 mmol) using $PtCl_2$ (1.9 mg, 7.21 μmol) and XPhos (6.9 mg, 14.4 μmol) in THF (0.75 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2m** (109 mg, 56%) as a colourless oil.

R_f (9 : 1 hexane–EtOAc) = 0.32; ν_{max} (thin film)/cm^{-1}; 3069, 3001, 2954, 1628, 1427, 1114, 842, 830, 738, 699; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.53–7.46 (2H, m), 7.41–7.32 (3H, m), 7.23–7.18 (2H, m), 7.17–7.13 (2H, m), 6.27 (1H, dd, J = 18.6, 4.8 Hz), 6.11 (1H, dd, J = 18.6, 4.8 Hz), 5.42 (1H, dt, J = 18.8, 1.28 Hz), 2.35 (3H, s), 0.35 (3H, s), 0.34 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 134.7, 133.8, 133.0, 130.6, 130.3, 129.7, 128.9, 127.8, 126.6, 73.6, 72.9, 32.1, 19.2, 11.7, −2.6; HRMS (ES+) calcd for $C_{18}H_{22}OSi$ $[M]^+$ 282.1493. Found 282.1440.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(pyridin-3-yl)prop-2-en-1-ol (2n). The title compound was prepared according to general procedure A, from 1-(pyridin-3-yl)prop-2-yn-1-ol **1n**[71] (257 mg, 1.9 mmol) and dimethylphenylsilane (284 mg, 2.09 mmol) using $PtCl_2$ (5.1 mg, 19.2 μmol) and XPhos (18.4 mg, 38.7 μmol) in THF (0.75 mL) which following the conversion to the vinyl silane and column chromatography (3 : 2 hexane–EtOAc) afforded **2n** (271 mg, 53%) as a yellow oil.

R_f (9 : 1 hexane–EtOAc) = 0.35; ν_{max} (thin film)/cm^{-1}; 3290, 2853, 2114, 1581, 1427, 1248, 1041, 1028, 947, 823, 710, 634; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.94–7.90 (2H, m), 7.72–7.69 (1H, m), 7.51–7.47 (2H, m), 7.37–7.30 (4H, m), 6.25 (1H, dd, J = 18.6, 4.8 Hz), 6.17 (1H, dd, J = 18.6, 1.1 Hz), 5.27 (1H, d, J = 4.8 Hz), 1.43 (1H, s), 0.35 (3H, s), 0.35 (3H, s) ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 149.2, 148.1, 134.7, 133.8, 129.2, 127.9, 123.6, 75.3, 75.4, 62.1, 61.9, −2.7, −2.7; HRMS (ES+) calcd for $C_{16}H_{19}NOSi$ 269.1236. Found 269.1293.

(*E*)-*tert*-Butyl 2-(3-(dimethyl(phenyl)silyl)-1-hydroxyallyl)-1*H*-pyrrole-1-carboxylate (2p). The title compound was prepared according to general procedure A, from *tert*-butyl 2-(1-hydroxyprop-2-yn-1-yl)-1*H*-pyrrole-1-carboxylate[72] **1p** (302 mg, 1.34 mmol) and dimethylphenylsilane (200 mg, 1.47 mmol) using $PtCl_2$ (3.6 mg, 13.4 μmol) and XPhos (18.4 mg, 0.027 mmol) in THF (1.5 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **2r** (297 mg, 61%) as a yellow oil.

R_f (9 : 1 hexane–EtOAc) = 0.49; ν_{max} (thin film)/cm^{-1}; 3466, 3068, 2979, 2900, 1724, 1617, 1478, 1427, 1408, 1371, 1342, 1248, 1229, 1162, 1124, 1064, 998, 884, 821, 728, 700; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.53 (2H, m), 7.47–7.44 (2H, m), 7.35–7.30 (2H, m), 7.17 (1H, m), 6.40–6.34 (1H, dd, J = 18.6, 4.3 Hz), 6.13 (1H, d, J = 7.8 Hz), 6.10 (1H, d, J = 3 Hz), 6.03–5.99 (1H, m), 1.57 (9H, d, J = 11.5 Hz), 0.36 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 136.2, 134.1, 128.9, 127.9, 127.6, 122.3, 114.7, 113.4, 110.3, 110.1, 84.8, 69.8, 69.0, 27.9, −2.3; HRMS (EI+) calcd for $C_{16}H_{16}Si$ 236.1021. Found 236.1025.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(1,3-diphenyl-1*H*-pyrazol-4-yl)prop-2-en-1-ol (2q). The title compound was prepared according to general procedure A, from 1-(1,3-diphenyl-1*H*-pyrazol-4-yl)prop-2-yn-1-ol **1q** (275 mg, 1.01 mmol) and dimethylphenylsilane (150 mg, 1.11 mmol) using $PtCl_2$ (2.7 mg, 0.011 mmol) and XPhos (9.6 mg, 0.020 mmol) in THF (2 mL) which following conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **2q** (290 mg, 71%) as a colourless oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.26; IR: ν_{max} (thin film)/cm^{-1}; 3402, 2953, 1600, 1503, 1426, 1355, 1248, 1113, 1060, 820, 773, 756, 698; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.87 (2H, d, J = 5.0 Hz), 7.83–7.80 (1H, m), 7.77–7.69 (2H, m), 7.61–7.57 (1H, m), 7.83–7.80 (1H, m), 7.50–7.27 (7H, m), 7.20 (2H, m), 6.37 (1H, dd, J = 18.5, 4.8 Hz), 6.18 (1H, dd, J = 18.5, 1.25 Hz), 5.42 (1H, s), 0.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 148.1, 140.0, 139.9, 138.8, 133.8, 133.2, 133.0, 129.4, 129.2, 128.9, 128.6, 128.3, 127.8, 126.4, 125.7, 124.6, 119.0, 68.6, −2.5, −2.7; HRMS (ES) calcd for $C_{26}H_{27}N_2OSi$ $[M + H]^+$ 256.1647. Found 411.1873.

General procedure B: hydrosilylation of disubstituted propargyl alcohols

To an oven dried 5 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer was added $PtCl_2$ (0.5 mol%) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (1 mol%) (XPhos). The flask was then flushed quickly with argon and dry THF was added. The mixture was then stirred at 50 °C for 20 minutes until a yellow homogeneous mixture was obtained. The corresponding propargyl alcohol (1 eq.) was added followed by the silane (1.1 eq.) *via* syringe (CAUTION: Rapid evolution of hydrogen gas) and the solution was stirred at 50 °C overnight. The solvent was evaporated and the crude mixture was applied to the top of a column and chromatographed to afford the requisite (*E*)-vinyl silane.

(*E*)-1-(Dimethyl(phenyl)silyl)-4-methyl-3-phenylpent-1-en-3-ol (4e). The title compound was prepared according to general procedure B, from 4-methyl-3-phenylpent-1-yn-3-ol[73] **3e** (104 mg, 0.601 mmol) and dimethylphenylsilane (89.9 mg, 0.661 mmol) using $PtCl_2$ (1.8 mg, 6.61 μmol) and XPhos (5.8 mg, 12.2 μmol) in THF (2 mL) which following the conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **4e** (154 mg, 83%) as a colourless oil.

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R_f (9 : 1 hexane–EtOAc) = 0.39; ν_{max} (thin film)/cm^{-1}; 3479, 3068, 3023, 2960, 1685, 1446, 1427, 1254, 1118, 1048, 998, 832, 795, 729, 699, 469; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.98 (1H, d, J = 7.0), 7.55–7.51 (2H, m), 7.50–7.46 (1H, m), 7.44 (2H, d, J = 7.8), 7.39–7.29 (4H, m), 6.53 (1H, dd, J = 18.6 Hz), 6.10 (1H, d, J = 18.8 Hz), 2.24–2.17 (1H, dq, J = 13, 6.8 Hz), 0.90 (6H, d, J = 6.8 Hz), 0.35 (3H, s) ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.5, 144.7, 133.0, 132.7, 132.2, 128.4, 128.2, 127.2, 126.7, 125.2, 124.6, 79.2, 78.9, 16.3, 15.9, −3.2; HRMS (ES+) calcd for $C_{20}H_{26}ONaSi$ $[M + Na]^+$ 333.1651. Found 333.1573.

(*E*)-4-(Dimethyl(phenyl)silyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-ol (4g). The title compound was prepared according to general procedure B, from 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol **3g** (273 mg, 1.37 mmol) and dimethylphenylsilane (205 mg, 1.51 mmol) using PtCl$_2$ (3.6 mg, 13.7 μmol) and XPhos (13.3 mg, 0.028 mmol) in THF (2 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4g** (369 mg, 80%) as a yellow oil.

R_f (9 : 1 hexane–EtOAc) = 0.41; ν_{max} (thin film)/cm^{-1}; 3546, 3070, 2958, 1958, 18883, 1602, 1497, 1450, 1428, 1214, 11163, 1115, 997, 938, 844, 825, 761, 734, 699, 647; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.56 (2H, d, J = 8.0 Hz), 7.50–7.46 (2H, m), 7.42–7.33 (6H, m), 6.63 (1H, d, J = 18.8 Hz), 6.42 (1H, d, J = 18.8 Hz), 0.38 (6H, s) ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.3, 137.1, 133.8, 133.5, 131.6, 129.4, 128.7, 128.3, 128.0, 127.9, 126.7 (t, $^2J_{C-F}$ = 223 Hz), 7.4, −2.8, −2.8; HRMS (ES+) calcd for $C_{18}H_{18}OF_3Si$ $[M - H^+]^+$ 335.1079. Found 335.1081.

(*E*)-4-(Dimethyl(phenyl)silyl)-2-(thiophen-3-yl)but-3-en-2-ol (4h). The title compound was prepared according to general procedure B, from 2-(thiophen-3-yl)but-3-yn-2-ol **3h** (176 mg, 0.761 mmol) and dimethylphenylsilane (89.9 mg, 0.662 mmol) using PtCl$_2$ (2.0 mg, 7.61 μmol) and XPhos (7.2 mg, 0.0152 mmol) in THF (2 mL) which following the conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **4h** (202 mg, 92%) as a yellow oil.

R_f (9 : 1 hexane–EtOAc) = 0.39; ν_{max} (thin film)/cm^{-1}; 3399, 3068, 2956, 1617, 1427, 1248, 1114, 991, 844, 827, 730. 698, 644; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.52 (2H, dd, J = 5.5, 2.0 Hz), 7.40–7.32 (4H, m), 6.96–6.93 (2H, m), 6.42 (1H, d, J = 18.2 Hz), 6.13 (1H, d, J = 18.2 Hz), 1.72 (3H, s), 0.35 (6H, s) ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.4, 138.3, 133.8, 133.6, 128.9, 127.8, 126.7, 124.7, 124.4, 123.3, 74.2, 30.1, 9.7, −2.6; HRMS (ES+) calcd for $C_{16}H_{21}OSSi$ $[M + H^+]^+$ 289.1082. Found 289.1112.

(*E*)-1-(2-(Dimethyl(phenyl)silyl)vinyl)cyclobutanol (4i). The title compound was prepared according to general procedure B, from 1-ethynylcyclobutan-1-ol **3i**[74] (133 mg, 1.38 mmol) and dimethylphenylsilane (207 mg, 1.52 mmol) using PtCl$_2$ (1.9 mg, 6.95 μmol) and XPhos (6.7 mg, 0.014 mmol) in THF (1.5 mL) which following conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **4i** (287 mg, 88%) as a colourless oil.

R_f (9 : 1 hexane–EtOAc) = 0.40; ν_{max} (thin film)/cm^{-1}; 3329, 3068, 3049, 2984, 2956, 1616, 1427, 1248, 1169, 1114, 991, 844, 826, 729, 698; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.54–7.47 (2H, m), 7.40–7.31 (3H, m), 6.38 (1H, d, J = 18.2 Hz), 5.98 (1H, d, J = 18.2 Hz), 1.72 (2H, s), 2.24–2.10 (1H, m), 2.00–1.92 (1H, m), 1.83–1.76 (1H, m), 1.65–1.52 (2H, m), 0.37 (6H, s) ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.6, 138.7, 133.8, 133.0, 129.0, 127.9, 122.7, 36.1, −2.4, −3.2; HRMS (ES+) calcd for $C_{14}H_{20}NaOSi$ $[M + Na^+]^+$ 255.3833. Found 255.3819.

(*E*)-1-(2-(Dimethyl(phenyl)silyl)vinyl)cycloheptanol (4j). The title compound was prepared according to general procedure B, from 1-ethynylcycloheptan-1-ol **3l**[75] (360 mg, 2.62 mmol) and dimethylphenylsilane (389 mg, 2.86 mmol) using PtCl$_2$ (3.5 mg, 0.013 mmol) and XPhos (12.4 mg, 0.026 mmol) in THF (2 mL) which following conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **4l** (562 mg, 79%) as a colourless oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.48; IR: ν_{max} (thin film)/cm^{-1}; 3372, 3068, 2925, 1616, 1459, 1427, 1246, 1113, 1027, 993, 822, 731, 698; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.53–7.50 (2H, m), 7.38–7.34 (3H, m), 6.28 (1H, d, J = 20 Hz), 5.96 (1H, d, J = 20 Hz), 1.79–1.40 (12H, m), 0.36 (6H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.3, 136.3, 131.4, 130.2, 123.9, 43.5, 33.4, 32.3, 31.9, 24.9, 24.7, −2.5; HRMS (ES) calcd for $C_{17}H_{26}OSiNa$ $[M + Na]^+$ 297.1651. Found 297.1620.

(*E*)-1-(2-(Dimethyl(phenyl)silyl)vinyl)cyclooctanol (4m). The title compound was prepared according to general procedure B, from 1-ethynylcyclooctan-1-ol **3m**[75] (201 mg, 1.32 mmol) and dimethylphenylsilane (0.22 mL, 1.45 mmol) using PtCl$_2$ (1.8 mg, 6.60 μmol) and XPhos (6.2 mg, 0.0130 mmol) in THF (2 mL) which following conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4m** (303 mg, 80%) as a colourless oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.41; IR: ν_{max} (thin film)/cm^{-1}; 3362, 3068, 2922, 2854, 1613, 1470, 1446, 1427, 1264, 1246, 1113, 1064, 994, 843, 828, 733, 698, 642; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.52–7.49 (2H, m), 7.36–7.33 (3H, m), 6.27 (1H, d, J = 18.8 Hz), 5.97 (1H, d, J = 18.8 Hz), 1.80–1.60 (9H, m), 1.57–1.41 (5H, m), 0.34 (6H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.6, 141.4, 136.2, 135.4, 131.3, 130.2, 125.4, 78.5, 38.7, 30.7, 27.1, 24.5, 2.4, −0.27, −0.71; HRMS (ES) calcd for $C_8H_{28}OSiNa$ $[M + Na]^+$ 311.1807. Found 311.1787.

(*E*)-1-(2-(Dimethyl(phenyl)silyl)vinyl)cyclododecanol (4n). The title compound was prepared according to general procedure B, from 1-ethynylcyclododecan-1-ol **3n**[76] (188 mg, 0.901 mmol) and dimethylphenylsilane (135 mg, 0.099 mmol) using PtCl$_2$ (1.2 mg, 4.52 μmol) and XPhos (4.3 mg, 9.04 μmol) in THF (2 mL) which following conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4n** (285 mg, 91%) as a yellow oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.46; IR: ν_{max} (thin film)/cm^{-1}; 3364, 3070, 2940, 2848, 1615, 1469, 1427, 1246, 1114, 994, 844, 823, 730, 698; ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.53–7.49 (2H, m), 7.36–7.34 (3H, m), 6.24 (1H, d, J = 18.8 Hz), 5.97 (1H, d, J = 18.8 Hz), 1.66–1.58 (2H, m), 1.53–1.42 (5H, m), 1.40–1.32 (18H, m), 0.34 (6H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.0, 141.3, 136.3, 131.3, 130.1, 125.4, 78.7, 37.1, 28.9, 28.4, 25.0, 24.6, 22.1, 2.5, 0.3, −0.3; HRMS (ES) calcd for $C_{22}H_{35}OSi$ $[M - H^+]^+$ 343.2457. Found 343.2454.

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(*E*)-1-(2-(Dimethyl(phenyl)silyl)vinyl)-4,4-difluorocyclohexanol (4o). The title compound was prepared according to general procedure B, from 1-ethynyl-4,4,-difluorocyclohexan-1-ol **3o** (98 mg, 0.605 mmol) and dimethylphenylsilane (90.4 mg, 0.665 mmol) using $PtCl_2$ (0.9 mg, 3.2 μmol) and XPhos (3.1 mg, 6.4 μmol) in THF (1 mL) which following conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4o** (136 mg, 76%) as a colourless oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.43; IR: ν_{max} (thin film)/cm^{-1}; 3419, 3069, 2953, 1700, 1618, 1443, 1427, 1377, 1358, 1250, 1117, 1113, 991, 844, 825, 721, 700, 667; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.51–7.48 (2H, m), 7.40–7.33 (3H, m), 6.28 (1H, d, J = 18.8 Hz), 5.96 (1H, d, J = 18.8 Hz), 2.16–2.07 (4H, m), 1.86–1.76 (2H, m), 1.70–1.61 (2H, m) 0.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 133.9, 133.5, 129.1, 129.0, 127.9 (t, $^1J_{C-F}$ = 241.6 Hz), 127.8, 33.8, 33.7, −2.4, −3.6; HRMS (ES) calcd for $C_{16}H_{21}F_2OSi$ $[M - H^+]^+$ 295.1337. Found 295.1330.

(*E*)-8-(2-(Dimethyl(phenyl)silyl)vinyl)-1,4-dioxaspiro[4.5]decan-8-ol (4p). The title compound was prepared according to general procedure B, from 8-ethynyl-1,4-dioxaspiro[4.5]decan-8-ol **3p**[77] (195 mg, 1.07 mmol) and dimethylphenylsilane (160 mg, 1.18 mmol) using $PtCl_2$ (1.2 mg, 5.4 μmol) and XPhos (5.2 mg, 0.011 mmol) in THF (1.5 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4p** (240 mg, 64%) as a yellow oil.

R_f (4 : 1 hexane–ethyl acetate) = 0.41; IR: ν_{max} (thin film)/cm^{-1}; 3444, 2922, 2854, 1640, 1397, 1268, 1248, 1102, 845, 749; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.51–7.48 (2H, m), 7.36–7.32 (3H, m), 6.21 (1H, dd, J = 18.8, 5.8 Hz), 6.03 (1H, d, J = 18.8 Hz), 4.03, (1H, s), 3.95 (4H, ddd, J = 5.5, 3.5, 1.7 Hz), 2.03–1.79 (4H, m), 1.65–1.57 (4H, m), 0.34 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 138.5, 133.8, 129.1, 127.8, 123.7, 108.5, 71.9, 64.3, 64.2, 34.9, 30.4, −2.5; HRMS (ES) calcd for $C_{18}H_{30}NO_3Si$ $[M + NH_4]^+$ 336.1995. Found 336.1996.

(*E*)-2-(2-(Dimethyl(phenyl)silyl)vinyl)-1,2,3,4-tetrahydronaphthalen-2-ol (4q). The title compound was prepared according to general procedure B, from 2-ethynyl-1,2,3,4-tetrahydronaphthalen-2-ol **3q** (35.2 mg, 0.204 mmol) and dimethylphenylsilane (30.6 mg, 0.225 mmol) using $PtCl_2$ (0.3 mg, 1.02 μmol) and XPhos (1.0 mg, 2.02 μmol) in THF (1 mL) which following the conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **4q** (47 mg, 77%) as a yellow oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.26; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.53–7.47 (2H, m), 7.40–7.35 (3H, m), 7.17 (3H, m), 7.10 (1H, m), 6.31 (1H, dd, J = 18.8 Hz), 6.12 (1H, d, J = 18.8 Hz), 2.84–2.78 (2H, m), 2.21 (2H, m), 2.07–1.88 (2H, ddddd, J = 18.1, 12.3, 7.8, 6.0, 5.8 Hz), 0.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 136.3, 131.5, 131.4, 130.6, 130.2, 130.0, 128.8, 127.1, 76.7, 40.1, 32.4, 32.2, 21.7, 12.2, 0.1, −0.6, −0.9; HRMS (ES) calcd for $C_{20}H_{25}OSi$ $[M + H]^+$ 309.1675. Found 309.1678.

(*E*)-3-(2-(Dimethyl(phenyl)silyl)vinyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-ol (4r). The title compound was prepared according to general procedure B, from 3-ethynyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-ol **3r**[78] (43.7 mg, 0.208 mmol) and dimethylphenylsilane (31.1 mg, 0.228 mmol) using $PtCl_2$ (0.6 mg, 2.08 μmol) and XPhos (2.0 mg, 4.16 μmol) in THF (1 mL) which following the conversion to the vinyl silane and column chromatography (4 : 1 hexane–EtOAc) afforded **4r** (55 mg, 76%) as a colourless solid.

R_f (4 : 1 hexane–ethyl acetate) = 0.35; IR: ν_{max} (thin film)/cm^{-1}; 3402, 3284, 2340, 2275, 1704, 1667, 1604, 1468, 1329, 1052, 962, 748, 667; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.76 (1H, s), 7.55–7.49 (2H, d, J = 6.0, 3.6 Hz), 7.44–7.33 (3H, m), 7.25 (1H, m), 7.15–7.14 (2Hm), 6.37 (1H, d, J = 18.7 Hz), 6.17 (1H, d, J = 18.7 Hz), 2.95 (2H, d, J = 15.6 Hz), 2.88–2.70 (2H, dd, J = 14.4, 3.9 Hz), 2.04–1.87 (2H, m), 0.34 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ153.0, 138.3, 136.0, 133.4, 132.2, 128.6, 127.5, 127.5, 124.3, 121.1, 118.9, 117.4, 110.0, 106.9, 76.9, 72.2, 34.1, 33.7, 19.7, −3.0; HRMS (ES) calcd for $C_{22}H_{26}NOSi$ $[M + H]^+$ 348.1784. Found 348.1778.

(*E*)-*tert*-Butyl-3-(2-(dimethyl(phenyl)silyl)vinyl)-3-hydroxyazetidine-1-carboxylate (4s). The title compound was prepared according to general procedure B, from *tert*-butyl 3-ethynyl-3-hydroxyazetidine-1-carboxylate **3s**[79] (135 mg, 0.685 mmol) and dimethylphenylsilane (102 mg, 0.753 mmol) using $PtCl_2$ (0.9 mg, 3.43 μmol) and XPhos (3.3 mg, 6.85 μmol) in THF (1.5 mL) which following the conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4s** (163 mg, 72%) as a yellow oil.

R_f (4 : 1 hexane–ethyl acetate) = 0.21; IR: ν_{max} (thin film)/cm^{-1}; 2977, 2881, 1679, 1427, 1367, 1248, 1158, 1114, 825, 764, 699, 667; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.53–7.47 (2H, m), 7.40–7.35 (3H, m), 6.36 (1H, dd, J = 18.8 Hz), 6.12 (1H, d, J = 18.8 Hz), 3.98 (1H, d, J = 9.3 Hz), 3.92 (1H, d, J = 9.3 Hz), 1.44 (9H, s), 0.38 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.5, 137.7, 128.9, 127.9, 127.8, 126.5, 79.8, 70.6, 62.3, 28.4, −2.8; HRMS (ES) calcd for $C_{18}H_{27}NO_3SiNa$ $[M + NH_4]^+$ 356.1658. Found 356.1661.

(*E*)-3-(2-(Dimethyl(phenyl)silyl)vinyl)-8-methyl-8-azabicyclo-[3.2.1]octan-3-ol (4u). The title compound was prepared according to general procedure B, from 3-ethynyl-8-methyl-8-azabicyclo[3.2.1]octan-3-ol **3u** (78 mg, 0.472 mmol) and dimethylphenylsilane (70.2 mg, 0.520 mmol) using $PtCl_2$ (0.6 mg, 2.36 μmol) and XPhos (2.2 mg, 4.7 μmol) in THF (1.5 mL) which following conversion to the vinyl silane and column chromatography (SCX-2 ion exchange resin) afforded **4u** (82.7 mg, 59%) as a yellow oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.35; IR: ν_{max} (thin film)/cm^{-1}; 3435, 3069, 2957, 1656, 1639, 1427, 1253, 1119, 1054, 1027, 998, 830, 789, 725, 698, 649; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.54–7.44 (2H, m), 7.38–7.31 (3H, m), 6.06 (1H, d, J = 18.8 Hz), 5.90 (1H, d, J = 18.8 Hz), 2.51 (1H, s), 2.30–2.27 (3H, d, J = 7.4 Hz), 2.20–2.11 (3H, m), 2.07–1.90 (6 H, m), 0.33 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 141.2, 136.3, 132.1, 130.1, 125.3, 37.2, 28.9, 25.0, 24.4, 22.0, −0.69; HRMS (ES) calcd for $C_{16}H_{24}NOSi$ $[M - CH_3]^+$ 286.1627. Found 286.1661.

(*E*)-4-(2-(Dimethyl(phenyl)silyl)vinyl)tetrahydro-2*H*-thiopyran-4-ol (4w). The title compound was prepared according to general procedure B, from 4-ethynyl-tetrahydro-2*H*-thiopyran-4-ol **3w** (107 mg, 0.760 mmol) and dimethylphenylsilane (113 mg, 0.836 mmol) using $PtCl_2$ (1.0 mg, 3.80 μmol) and

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XPhos (3.6 mg, 7.60 μmol) in THF (2 mL) which following conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **4w** (173 mg, 82%) as a yellow oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.43; IR: ν_{max} (thin film)/cm^{-1}; 3426, 2922, 2854, 1640, 1397, 1268, 1247, 1113, 849, 825, 748, 699; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49 (2H, m), 7.41–7.33 (3H, m), 6.15 (1H, d, J = 18.8 Hz), 6.00 (1H, d, J = 18.8 Hz), 3.06–2.97 (4H, ddd, J = 10.3, 4.0, 3.8 Hz), 1.86–1.80 (4H, ddd, J = 13.5, 3.5, 1.8 Hz), 0.39 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 138.4, 133.8, 132.9. 129.7, 129.1, 127.8, 115.3, 71.3, 38.0, 24.0, −2.6; HRMS (ES) calcd for $C_{15}H_{2721}OSSi$ $[M - H]^+$ 277.1082. Found 277.1062.

(*E*)-4-(*tert*-Butyldimethylsilyl)-2-methylbut-3-en-2-ol (5c). The title compound was prepared according to general procedure B, from 2-methyl-3-butyn-2-ol **3a** (97.0 μL, 1.00 mmol) and *tert*-butyldimethyl silane (0.18 mL, 1.1 mmol) using $PtCl_2$ (1.3 mg, 5.00 μmol) and XPhos (4.8 mg, 10.00 μmol) in THF (1 mL) which following conversion to the vinyl silane and column chromatography (19 : 1 hexane–EtOAc) afforded **5c** (173 mg, 84%) as a yellow oil.

R_f (9 : 1 hexane–ethyl acetate) = 0.76; IR: ν_{max} (thin film)/cm^{-1}; 3362, 2953, 2928, 2856, 1616, 1470, 1361, 1390, 1247, 1147, 963, 908, 830; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.18 (1H, d, J = 18.8 Hz), 5.84 (1H, d, J = 18.8 Hz), 1.31 (6H, s), 0.88 (9H, s), 0.04 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 121.8, 72.1, 29.5, 26.4, 16.6, −6.14; HRMS (ES) calcd for $C_{11}H_{24}NaOSi$ $[M + Na]^+$ 223.1494. Found 223.1397.

(*E*)-4-(Benzyldimethylsilyl)-2-methylbut-3-en-2-ol (5f). The title compound was prepared according to general procedure B, from 2-methyl-3-butyn-2-ol **3a** (300 mg, 3.57 mmol) and dimethylbenzylsilane (803 mg, 3.93 mmol) using $PtCl_2$ (4.8 mg, 0.018 mmol) and XPhos (17.1 mg, 0.036 mmol) in THF (1.5 mL) which following conversion to the vinyl silane and column chromatography (9 : 1 hexane–EtOAc) afforded **5f** (808 mg, 97%) as a colourless oil.

R_f (9 : 1 hexane–EtOAc) = 0.45; IR: ν_{max} (thin film)/cm^{-1}; 3496, 2900, 2655, 1644, 1066, 978; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.24–7.17 (2H, m), 7.10–7.04 (1H, m), 7.01–6.97 (2H, m), 6.09 (1H, d, J = 19.1 Hz), 5.77 (1H, d, J = 19.1 Hz), 2.15 (2H, s), 1.42 (1H, s), 1.29 (6H, s), 0.06 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.9, 128.3, 128.0, 124.0, 122.6, 74.0, 30.9, 29.3, 26.1, −3.4; HRMS (ES) calcd for $C_{14}H_{23}OSi$ $[M + H]^+$ 235.1518. Found 235.1528.

1-(^{2}*H*)-Ethynyl-1-cyclohexanol (23). 1-Ethynyl-1-cyclohexanol (270 mg, 2.18 mmol) was added to an oven dried round bottom flask and placed under argon. Dry THF (4.5 mL) was added to this and the temperature was lowered to −78 °C. *n*-Butyl lithium (2.5 M) (1.04 mL, 2.61 mmol) was added slowly and the reaction mixture was allowed to stir at this temperature for 1.5 hours. The reaction mixture was quenched with D_2O, extracted with dry Et_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the deuterated product was used without any further purification. Product was obtained (200 mg, 74%, 86% deuterium incorporation as determined by ^{1}H NMR) as a colourless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 2.48 (0.15H, s), 1.99, (1H, s), 1.96–1.83 (2 H, m), 1.77–1.48 (6H, m), 1.33–1.66 (1H, m).

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