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Iridium-catalyzed Markovnikov hydrosilylation of terminal alkynes achieved by using a trimethylsilyl-protected trihydroxysilane

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Developing efficient strategies for Markovnikov hydrosilylation of alkynes is still an important goal. The steric and electronic properties of hydrosilanes are key factors in controlling selectivity in these reactions. Here by using a trimethylsilyl-protected trihydroxysilane, we report a mild, efficient strategy for Markovnikov hydrosilylation of terminal alkynes with the simple catalyst $[Ir(\mu\text{-}Cl)(cod)]_2$. A variety of terminal alkynes are hydrosilylated efficiently with outstanding α-regioselectivity. This protocol is successfully utilized in the late-stage hydrosilylation of derivatives of various bio-relevant molecules. The residual silyl group, $-Si(OSiMe_3)_3$, can participate in organic transformations directly, or be converted into other useful silyl groups.

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Vinyl-substituted silicon compounds, or vinylsilanes, are remarkable building blocks in organic synthesis, polymer chemistry and materials science. Hydrosilylation of alkynes is arguably the most straightforward and atom-economical route to vinylsilanes[1,2]. One main challenge in such processes is the regio- and stereoselectivity control. Compared with various well established catalytic systems for hydrosilylation of terminal alkynes towards β-(*E*)- and β-(*Z*)-vinylsilanes, the ways to geminal α-vinylsilanes are still exiguous. In recent years, this problem has been partially addressed with the developments of several efficient protocols[3–29]. For instance, Ru-based complexes have been developed as the predominant catalysts for this field since the pioneering works from Trost and Yamamoto, et al.[3–18]. Co-catalyzed α-hydrosilylation of alkynes showed superiority in modification of aryl alkynes[19–23]. Highly regioselective silylcupration of terminal alkynes reported by Loh is another efficient approach to α-vinylsilanes[24]. However, further commercial and industrial use of these methods is limited by their own properties, such as the unstability of Ru catalysts, requirement of complex ligands and low efficiency towards alkyl alkynes in Co catalysis[30], usage of expensive $PhMe_2SiBpin$ as silyl source and high catalyst loading in Cu catalysis. New strategies for Markovnikov hydrosilylation of alkynes that require simple catalysts or ligands, low-cost silanes, but have outstanding tolerance towards various functional groups and suit for large-scale operations, are still in urgent desire.

The selectivity of alkyne hydrosilylation processes is known to depend on several factors, such as the metal catalysts and ligands, steric or electronic properties of hydrosilanes and alkynes, etc. For example, studies on the Wu-Trost mechanism revealed the significance of ligands (cyclopentadiene and **L** in **a1**, Fig. 1a) in controlling the regiospecificity of the product[31–35]. Huang and Lu developed rational ligands for the cobalt-catalyzed α hydrosilylation of terminal alkynes, respectively (Fig. 1b)[19–22]. By contrast, exploitation of suitable hydrosilanes to achieve α regioselectivity under simple catalysis has been rarely studied[36]. Hydrosilanes with bulkier substituents are presumed to have lower reactivity, which might allow the coordination of the metal center with the alkyne to go first, leading the process to follow the Wu-Trost mechanism and bring α-vinylsilane adducts (Fig. 1c).

We share our findings here. By using a trimethylsilyl-protected trihydroxysilane, a mild and efficient strategy for α-hydrosilylating terminal alkynes is realized with a simple iridium catalyst, which is compatible with a variety of functional groups, and performs efficiently in modifying derivatives of bio-relevant molecules. The bulky silyl group could be easily converted into other useful silyl groups, or participate in subsequent derivatizations directly. It's noteworthy that though iridium complexes have been broadly investigated for hydrosilylation of unsaturated C–C bonds[37], *anti*-Markovnikov selectivity is usually observed in their use toward terminal alkynes[38–49]. As one example of Markovnikov hydrosilylation of internal thioalkynes has been reported by Sun and Wu[50], this is to our knowledge the first case in which α-vinylsilanes are mainly provided from terminal alkynes under iridium catalysis.

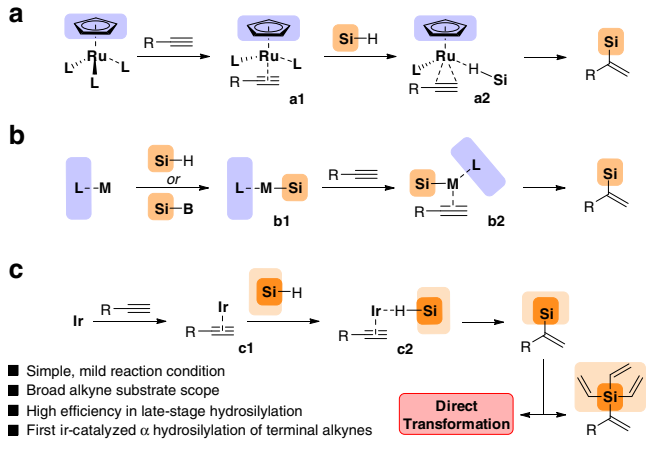


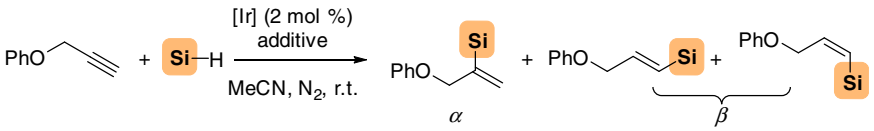
Fig. 1 Markovnikov hydrosilylation of terminal alkynes. **a** Ruthenium-based catalytic system for α hydrosilylation of terminal alkynes. **b** Copper- and cobalt-based catalytic systems for α hydrosilylation of terminal alkynes. **c** This work: iridium-based catalytic system for α hydrosilylation of terminal alkynes

Results

Reaction condition optimization. Heteroatoms and functional groups are commonly encountered in natural and pharmaceutical molecules. Developing hydrosilylation systems showing excellent tolerance toward them would be of great value. Meanwhile, the pre-existing heteroatoms or functional groups could usually provide inductive effect[51,52], or coordinate with the metal center[53–57], both of which might contribute to enhancing the selectivity in hydrofunctionalization reactions. With above considerations, phenyl propargyl ether was selected as the model alkyne substrate to initiate our study (Table 1). The bulky $(TMSO)_3SiH$, which is easily prepared from $HSiCl_3$ and $(TMS)_2O$, was chosen as the silane partner to verify our anticipation. It is noteworthy that though in contrast with the wide utilization of Et_3SiH, $(EtO)_3SiH$ and other common hydrosilanes in hydrosilylation of unsaturated molecules, examples that use $(TMSO)_3SiH$ as hydrosilane source are still limited[58–64], it showed its unique function in promoting the reaction selectivity[63] or inducing different selectivities[64]. Several simple iridium catalysts were tested firstly under a mild condition (entry 1–4). The desired α-vinylsilane product was obtained in 72% yield with excellent α regioselectivity under the catalysis by $[Ir(\mu\text{-}Cl)(cod)]_2$ (entry 1). Decreased yield and selectivity was observed with the utilization of $(EtO)_3SiH$ (entry 5). Using Et_3SiH as the silyl source provided β-addition products as the majority in poor yield (entry 6). The yield was promoted to 88% with the addition of a catalytic amount of 1,5-cyclooctadiene (entry 7). Decreased yield and regioselectivity were observed when this process was performed under air and moisture (entry 8 and 9). In addition, other kinds of metal catalysts, including $[Rh(\mu\text{-}Cl)(cod)]_2$, $Ni(cod)_2$, $[Pd(allyl)Cl]_2$, were tested instead of $[Ir(\mu\text{-}Cl)(cod)]_2$ under the optimized condition, but giving no desired product.

Substrate scope. With this simple and mild optimum condition in hand, we then evaluated its generality towards alkynes (Fig. 2). Both of propargyl alcohol and a variety of its derivatives were highly regioselectively hydrosilylated under this catalytic system, affording related products in good to excellent yields (**1**–**11**). Hydrosilylation of electron-deficient propargylic acid and methyl propiolate proceeded with high efficiency and regioselectivity (**12** and **13**). Non-protected and protected homopropargyl alcohols could likewise participate in this hydrosilylation process smoothly (**14**–**16**). The regioselectivity deteriorated slightly in the hydrosilylation of alkynyl alcohol or acid substrates with extended main chains (**17**–**19**). Replacement of hydroxyl group with aryl group led to decreased regioselectivity as well (**20**). Various nitrogen-containing terminal alkynes were then tested, all of which could be transformed into corresponding vinylsilanes with high α regioselectivity (**21**–**26**). To further probe the efficiency of this protocol, reactions involving internal alkynes were carried out. Unsymmetrical 2-hexyn-1-ol was converted to a 2.2:1 mixture of α- and β-(*E*)-vinylsilanes in a total yield of 85% (**27** and **28**).

Table 1 Optimization of the reaction conditions[a]



Entry	Si-H	Cat.	Yield[b]	α/β[b]
1	$(TMSO)_3SiH$	$[Ir(\mu\text{-}Cl)(cod)]_2$	72%	>20:1
2	$(TMSO)_3SiH$	$[Ir(\mu\text{-}OMe)(cod)]_2$	<5%	n.d.
3	$(TMSO)_3SiH$	$[Ir(\mu\text{-}Cl)\ (coe)_2]_2$	trace	n.d.
4	$(TMSO)_3SiH$	$[Cp^*IrCl_2]_2$	trace	n.d.
5	$(EtO)_3SiH$	$[Ir(\mu\text{-}Cl)(cod)]_2$	53%	4:1
6	Et_3SiH	$[Ir(\mu\text{-}Cl)(cod)]_2$	16%	<1:20
7[c]	$(TMSO)_3SiH$	$[Ir(\mu\text{-}Cl)(cod)]_2$	88%	>20:1
8[c, d]	$(TMSO)_3SiH$	$[Ir(\mu\text{-}Cl)(cod)]_2$	72%	15:1
9[c–e]	$(TMSO)_3SiH$	$[Ir(\mu\text{-}Cl)(cod)]_2$	60%	11:1

TMS trimethylsilyl
[a]Reaction conditions: The mixture of alkyne (0.20 mmol, 1.0 equiv.), silane (0.30 mmol, 1.5 equiv.) and catalyst (0.004 mmol, 2 mol %) in solvent (1.00 mL) was stirred for 6 h under room temperature
[b]Yield and ratio were determined by ^1H NMR spectroscopy of the crude product using dimethyl sulfone as internal standard
[c]4 mol % of cyclooctadiene (cod) was added
[d]The reaction was carried out under air
[e]H_2O (10.00 mmol, 50.0 eq.) was added

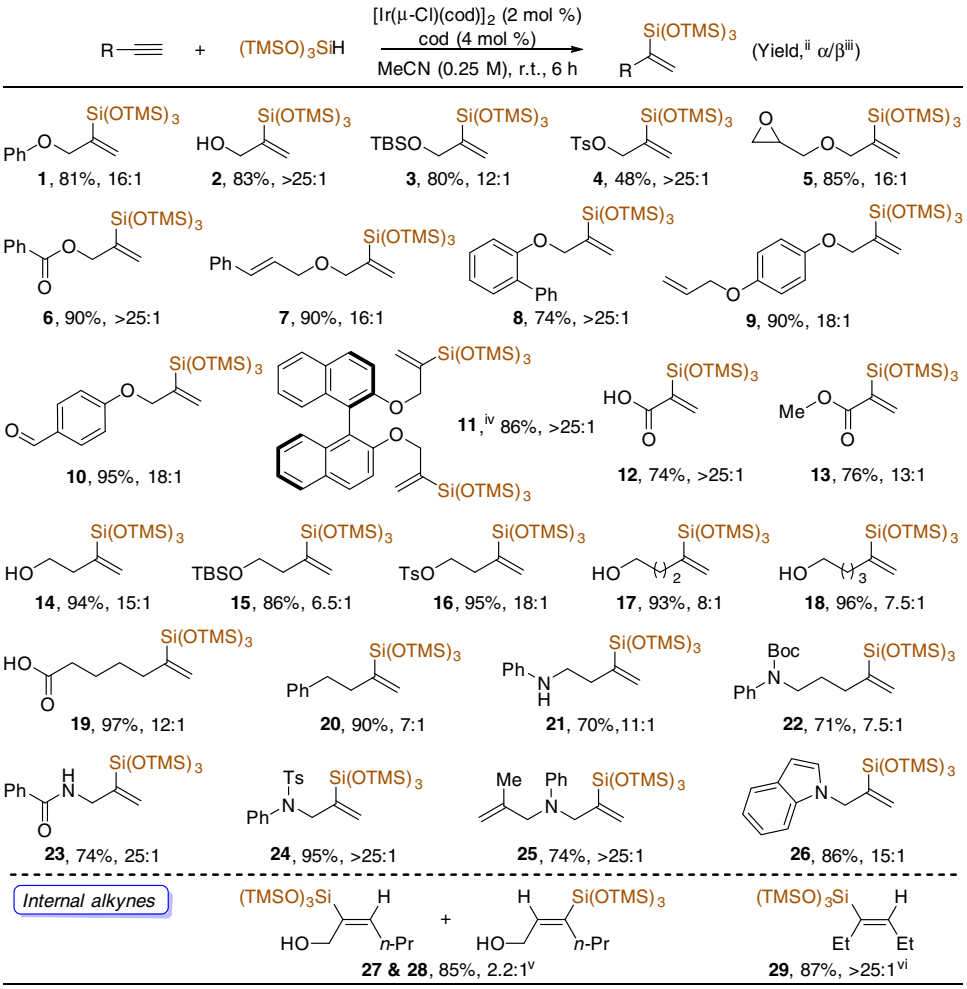


Fig. 2 Scope of alkyne. i. Reaction conditions: The mixture of alkyne (0.50 mmol, 1.0 equiv), $(TMSO)_3SiH$ (0.75 mmol, 1.5 equiv), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.01 mmol, 2 mol %) and cod (0.02 mmol, 4 mol %) in MeCN (2.0 mL) was stirred for 6 h under room temperature; ii. Isolated total yield; iii. Determined by ^1H NMR result of crude product; iv. 3.0 Equiv of silane was used; v. β-(*E*)/β-(*Z*) ratio is over 25/1; vi. Ratio of β-(*E*)/β-(*Z*)

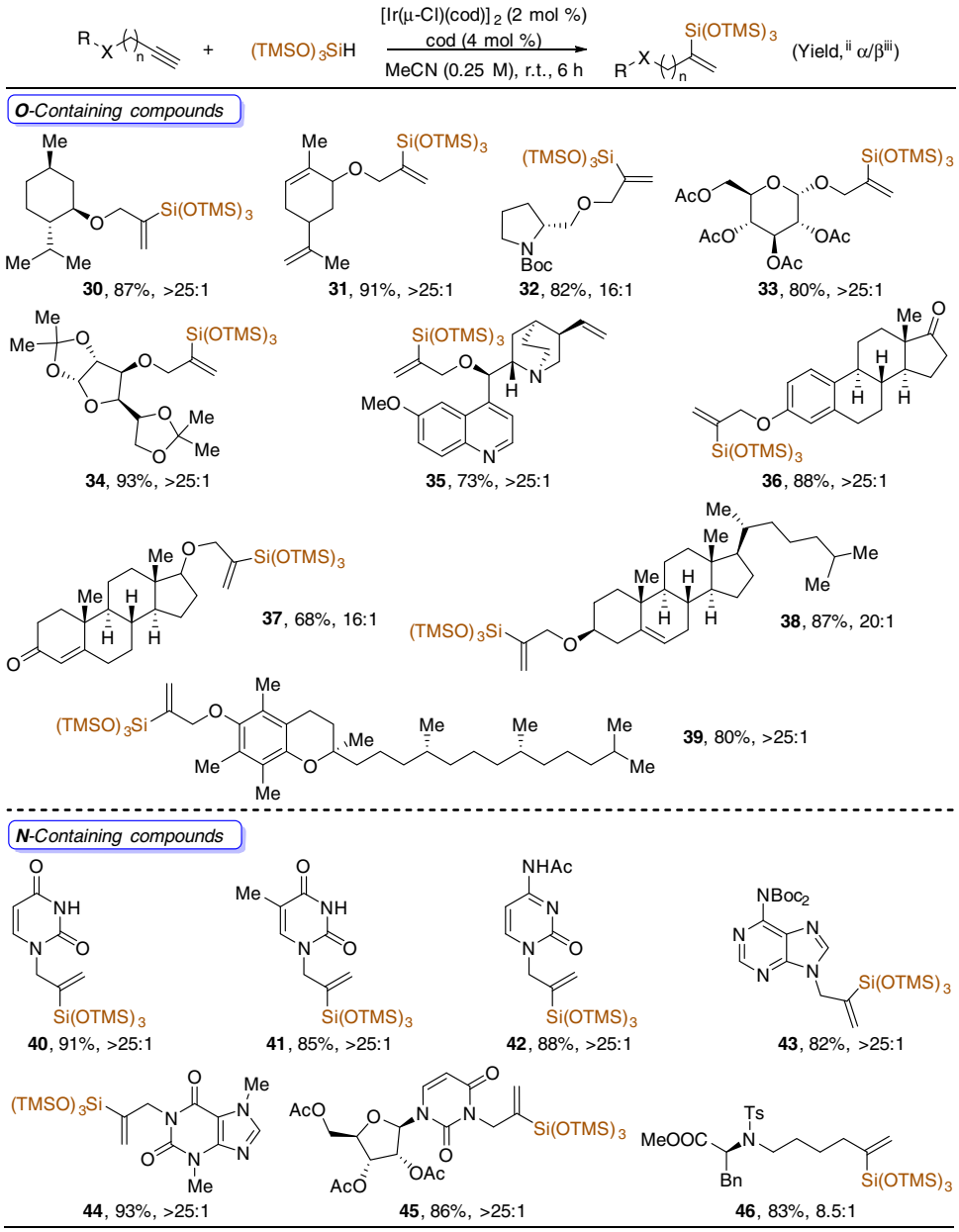


Fig. 3 Late-stage hydrosilylation of bio-relevant compounds. i. Reaction conditions: The mixture of alkyne (0.50 mmol, 1.0 equiv.), $(TMSO)_3SiH$ (0.75 mmol, 1.5 equiv), $[Ir(\mu\text{-Cl})(cod)]_2$ (0.01 mmol, 2 mol %) and cod (0.02 mmol, 4 mol %) in MeCN (2.0 mL) was stirred for 6 h under room temperature; ii. Isolated total yield; iii. Determined by ^1H NMR result of crude product

Hydrosilylation of symmetric dialkyl alkyne provided *syn* adduct **29** in 87% yield with excellent stereoselectivity.

Late-state hydrosilylation. Inspired by the excellent tolerance of this efficient strategy towards various functional groups, such as hydroxyl group, carboxyl group, alkenyl group, oxirane, ether, ester, amine and amide, etc., we were eager to learn about its performance in late-stage hydrosilylation of bio-relevant molecules (Fig. 3). Considering the widespread hydroxyl and amino groups in biomolecules, propargyl derivatives from them were selected as representatives in most cases (**30**–**45**). Propargyl ether analogues of menthol, carveol, prolinol, glucose and glucofuranose were successfully transformed into corresponding α-vinylsilanes in good to excellent yields (**30**–**34**). Other propargyl ethers derived from quinine, estrone, testosterone, cholesterol, and vitamin E could be effectively hydrosilylated as well, providing desired products with outstanding α regioselectivity (**35**–**39**). It is worthwhile to note that though terminal alkynyl derivatives from nitrogenous bases, theobromine, uridine, and phenylalanine showed poor solubility in acetonitrile, this protocol is well applicable in Markovnikov hydrosilylation of them as well (**40**–**46**).

Product derivatizations. The bulky hindrance of -$Si(TMSO)_3$ group has little influence on its further transformations, such as desilylation and Tamao oxidation (Fig. 4a). To simplify purification, compound **48** was easily obtained from Markovnikov hydrosilylation of homopropargyl alcohol under this newly-established mild condition and subsequent Hiyama cross-coupling[65] with 4-iodotoluene in one pot (Fig. 4b). In addition, –$Si(OTMS)_3$ is useful in silicone materials because of the easy

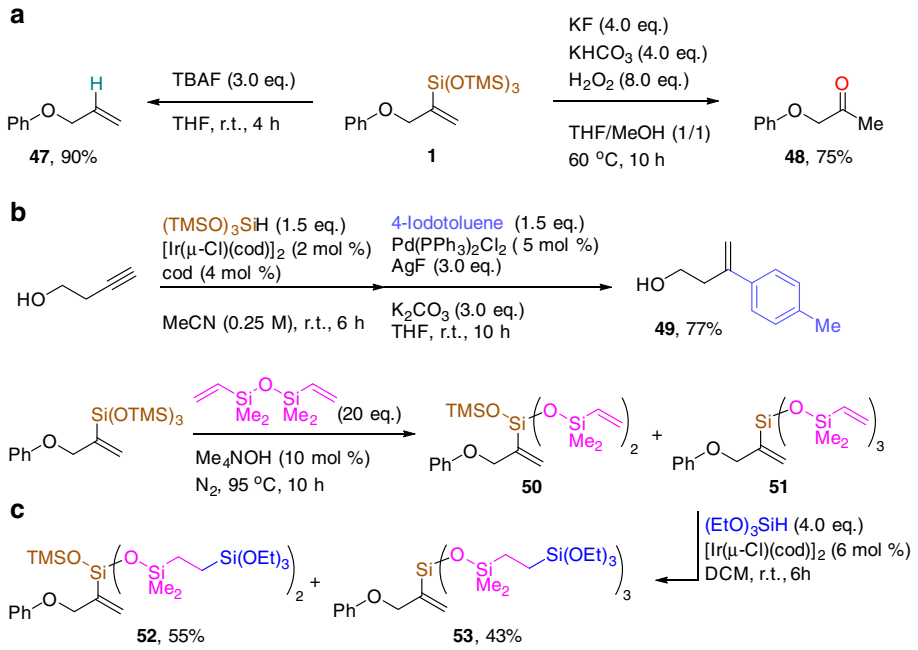


Fig. 4 Product derivatizations. **a** Desilylation and Tamao oxidation. **b** One-pot hydrosilylation/Hiyama coupling reaction. **c** Replacement of silyl group and subsequent modification. TBAF: tetra-*n*-butylammonium fluoride. THF: tetrahydrofuran. DCM: dichloromethane

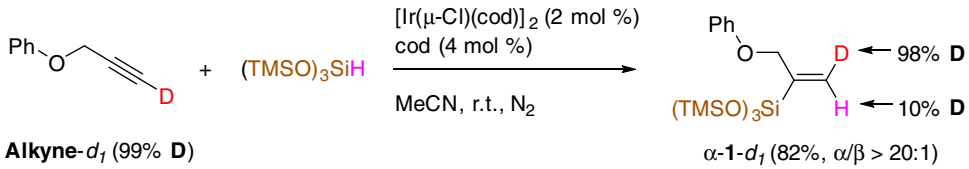


Fig. 5 Deuterium labeling experiment. The ^{1}H NMR result of the product revealed the *syn* addition of $(TMSO)_3SiH$ to the terminal alkyne in this process

conversion of it into other kinds of silyl groups[66,67]. For instance, –$OSiMe_2$(vinyl) was successfully anchored to replace the –OTMS group, which could be further decorated by other means (Fig. 4c)[68].

Stereochemistry study. As mentioned above, under this iridium catalytic system, excellent *syn* addition stereoselectivity was observed in the trisubstituted vinylsilanes derived from internal alkynes (**27**–**29** in Fig. 2). The result of deuterium labeling experiment toward terminal alkynes showed the same stereochemistry (Fig. 5).

Mechanistic considerations. A plausible catalytic cycle is accordingly proposed as shown in Fig. 6. Instead of oxidation with $(TMSO)_3SiH$, the iridium center will probably coordinate with alkyne to afford intermediate **A** in the initial step. Due to the steric repulsion between the bulky silyl group and the substituent on the alkyne, intermediate **B** is supposed to form and could be further stabilized through the chelation of the pre-existing heteroatoms or functional groups with iridium center. The following oxidative hydrometallation step via transition state **C** generates intermediate **D**, which finally affords α addition product and active catalytic species **A** for the next cycle through reductive silyl migration.

Some experiments were carried out to probe the mechanistic details (Fig. 7). $(TMSO)_3SiH$ was found to be stable when mixing with $[Ir(\mu\text{-Cl})(cod)]_2$ at a ratio of 2:1 in CD_3CN (Fig. 7a). Subsequent addition of alkyne to this mixture provided α-vinylsilane **1** in quantitative yield. By contrast, consumption of $(EtO)_3SiH$ was observed after the addition of iridium complex to its solution in CD_3CN, and no signal of desired hydrosilylation product showed up in the ^{1}H NMR spectra with further alkyne addition (Fig. 7b). The proposal for formation of intermediate **A** could be in some degree support by these findings and further mechanistic studies (see Supplementary Figs. 7–14 and Supplementary Discussions). More detailed studies are currently ongoing in our lab.

Gram-scale reaction. The stability of the mixture involving $[Ir(\mu\text{-Cl})(cod)]_2$ and $(TMSO)_3SiH$ promoted us to investigate the efficiency of this protocol towards large-scale reactions. With lower loading of catalyst and silane, α-hydrosilylation products **1** and **2** were respectively afforded on gram scale (Fig. 8).

Discussion

To sum up, we reported here a mild and efficient strategy for Markovnikov hydrosilylation of terminal alkynes with excellent regio- and stereoselectivity. With a silane with bulky substituents and a simple iridium catalyst, a variety of terminal alkynes, especially those with heteroatoms or functional groups, were α-hydrosilylated smoothly in up to nearly quantitative yield. It's noteworthy that this is, to our knowledge, the first iridium-catalyzed hydrosilylation of terminal alkynes with outstanding α regioselectivity. Furthermore, this strategy showed high efficiency in late-stage hydrosilylation of bio-relevant derivatives. The steric hindrance of the silyl group not only has little influence on

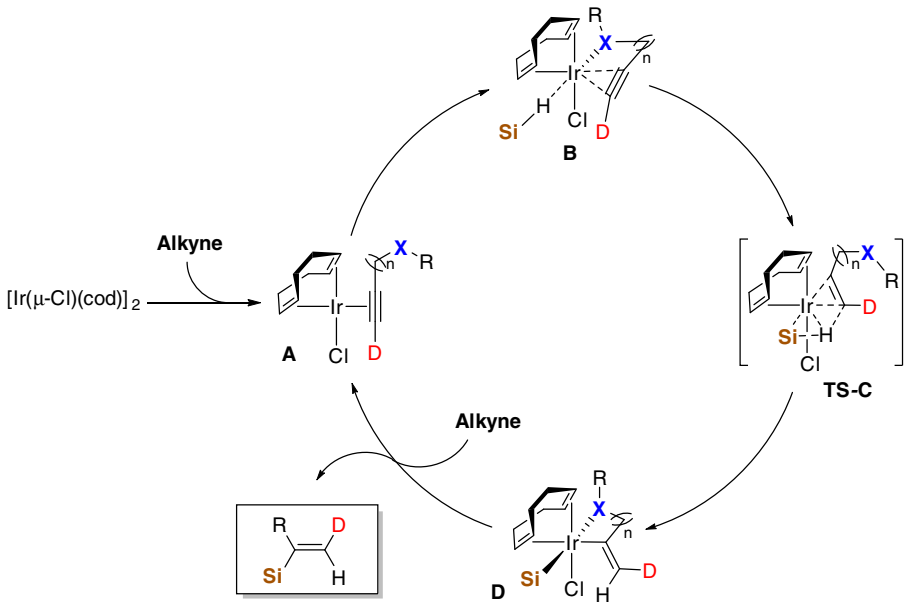


Fig. 6 Mechanistic proposal. A plausible mechanism for this iridium catalysis process

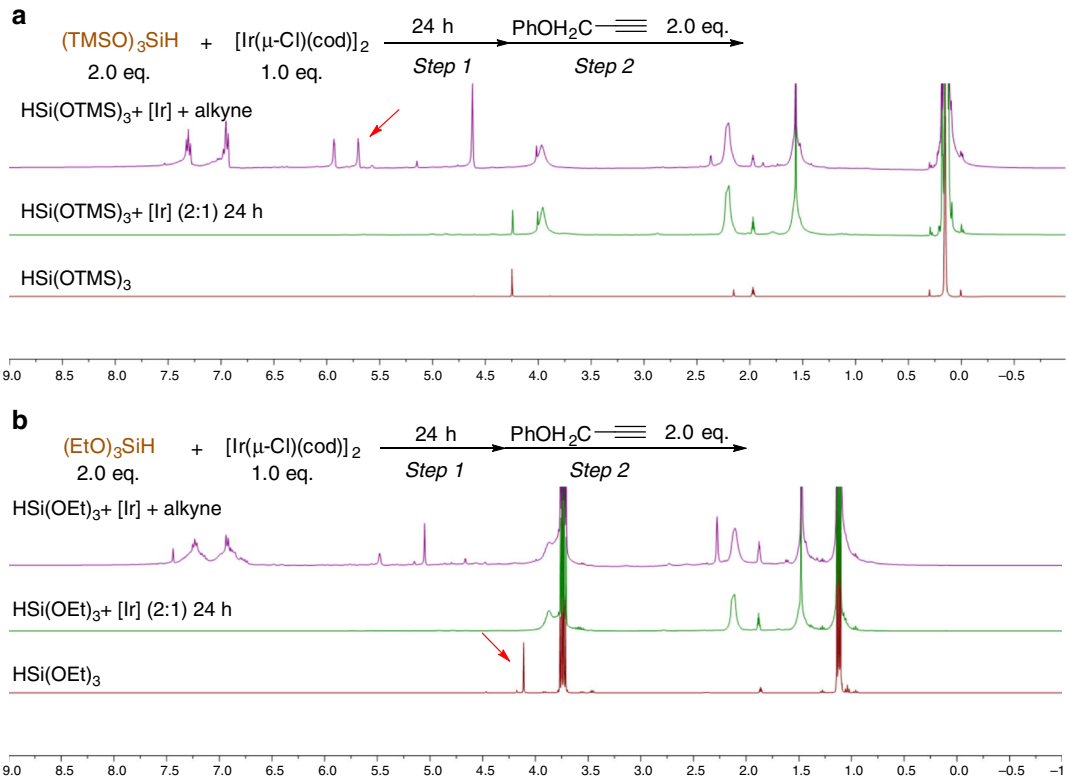


Fig. 7 Mechanistic studies. **a** Comparison of ^{1}H NMR spectra of $(TMSO)_3SiH$, mixture of $(TMSO)_3SiH$ with $[Ir(\mu\text{-}Cl)(cod)]_2$ (2:1), and mixture with further alkyne addition (2.0 eq.). **b** Comparison of ^{1}H NMR spectra of $(EtO)_3SiH$, mixture of $(EtO)_3SiH$ with $[Ir(\mu\text{-}Cl)(cod)]_2$ (2:1), and mixture with further alkyne addition (2.0 eq.)

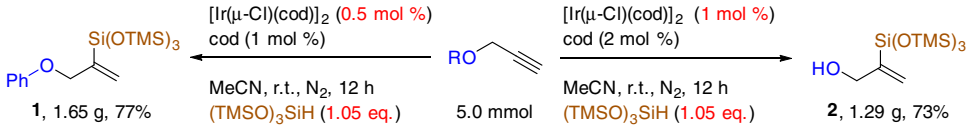


Fig. 8 Gram-scale reactions. Two examples with lower loading of catalyst and silane were carried out in 5.0 mmol scale, both of which provided their related product over one gram

subsequent manipulations of the α-vinylsilane products, but also permits increased stability of the silane towards the iridium catalyst, which allows this protocol to be used in larger-scale reactions with lower loading of both catalyst and silane. A catalytic cycle that is similar to the Wu-Trost mechanism was proposed for this new method. Further mechanistic investigations and exploration of other metal-based catalytic systems that could use the intrinsic properties of silanes to achieve selectivity control are on the way.

Methods

General procedure for iridium-catalyzed Markovnikov hydrosilylation of terminal alkynes. In a glove box, to an oven-dried 5-mL vial was added the alkyne (0.50 mmol), the silane (0.75 mmol), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.01 mmol, 2 mol %), cod (0.02 mmol, 4 mol %) and MeCN (2.0 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 6 h, and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 0–50% EtOAc in petroleum ether or 0–20% MeOH in DCM) to give the desired product.

Product derivatizations. Full procedures for synthetic transformations of compounds **47**–**53** are available in the Supplementary Methods and Supplementary Figures. 1–3.

Deuterium labeling experiment. Please see Supplementary Methods and Supplementary Figs. 4–6.

Mechanistic study experiments. Please see Supplementary Methods, Supplementary Figs. 7–14, and Supplementary Discussion.

NMR spectra. ^1H and ^{13}C NMR Spectra of all hydrosilylation products and unknown substrate were provided. ^{13}C DEPT135 NMR Spectra of products **3, 4, 5, 6, 7, 9, 10, 12, 13, 15, 19, 20, 21, 26, 30, 31, 32, 36, 37, 38, 39, 40, 41, 42, 44, 45** were afford. 2D NOESY Results of products **1** and **27** are also provided. Please see Supplementary Figs. 15–145.

Data availability

The authors declare that all the data supporting the findings of this study are available within the paper and its supplementary information files, and also are available from the corresponding author upon reasonable request.

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Author contributions

X.X., X.Z., W.G., C.M. and X.W. performed the experiments and prepared the Supplementary Information. S.D. conceived and directed the project. S.D. wrote the manuscript.

Additional information

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