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Retro-Mukaiyama aldol reaction-driven silicon catalysis†

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The use of silicon reagents as catalysts has long been an attractive yet challenging goal due to difficulties in silicon catalyst regeneration. Herein, we report a novel silicon-catalyzed formal hydroformylation of alkynes with aldehydes to access α,β-unsaturated ketones with high efficiency under mild conditions. The success of this method relies on an innovative retro-Mukaiyama aldol reaction (RMAR)-driven silyl transfer strategy, which enables efficient regeneration of silicon catalysts. Preliminary mechanistic studies reveal the evolution of key silicon catalysts during this transformation. This protocol provides valuable insights for the design of new chemical transformations based on silicon catalysis.

Silicon, the second most abundant element on Earth, makes up approximately 27.7% of the planet's crust by mass. This remarkable natural abundance drives the extensive use of silicon-based compounds in both scientific research and industrial applications.[1,2] The unique physical properties of these compounds make them indispensable in materials such as rubbers, resins, oils and other polymers, enabling the development of advanced materials with exceptional durability and thermal stability.[3] Silicon-based compounds are widely employed as essential building blocks in classical organic transformations, typically serving as leaving groups in cross-coupling reactions[4] or as linkers for synthesizing new silicon-containing compounds[5–8] (Scheme 1a). Although stoichiometric applications of silicon reagents have been extensively explored, research on silicon-catalyzed transformations,[9,10] particularly neutral silicon catalysis,[10] is still in its infancy.

Compared to transition metal catalysis, silicon catalysis has attracted considerable interest in organic transformations due to its low toxicity, environmental compatibility, ready accessibility, and versatile functionalization potential (Scheme 1b). However, the regeneration of silicon catalysts poses a significant challenge owing to the high bond energies required for Si–X bond cleavage, particularly for Si–F (135 kcal mol^{-1}) and Si–O (110 kcal mol^{-1}) bonds. Consequently, only very limited examples of silicon-catalyzed chemical transformations have been reported to date, with most relying on the use of external silicon reagents as substrates for catalyst regeneration (Scheme 1b). Thus, the development of new and efficient strategies is crucial for establishing novel silicon catalysis, which would not only significantly advance silicon chemistry but also provide substantial value to the field of synthetic chemistry. Herein, we report an unprecedented approach to overcome the inherent challenges of silicon catalyst regeneration, leading to a new silicon-catalyzed formal hydroacylation of alkynes with aldehydes[11] (Scheme 1c). This protocol provides efficient access to α,β-unsaturated ketones,[12,13] a privileged structural motif prevalent in natural products, bioactive molecules, and pharmaceuticals.

Our design for this new transformation began with the hypothesis that the reaction of an alkyne with a silicon source generates alkynylsilane **A**, which then reacts with aldehyde **2** to afford the propargyl silyl ether intermediate **B**. **B** undergoes deprotonation in the presence of a base and DMSO to form an allenyl silyl ether (Scheme 1c). This hypothesis is supported by our previous work,[14] which demonstrated that propargyl alcohol, a structural analogue of **A**, can be deprotonated to form the corresponding α-hydroxyl carbanion under similar conditions. We proposed that the allenyl silyl ether could then undergo a Mukaiyama aldol reaction with **2**, proceeding through the transition state **TS-I** to yield the allyl silyl ether **C**. We reasoned that this competitive off-cycle pathway could be suppressed by a retro-Mukaiyama aldol reaction (RMAR)-driven silyl transfer,[15] facilitated by the energetically similar cleavage and formation of Si–O bonds in the six-membered cyclic transition state. This would allow allenyl silyl ether to react with another alkyne *via* **TS-II**, producing the α,β-unsaturated ketone product **3** while regenerating the silicon catalyst **A** (Scheme 1c).

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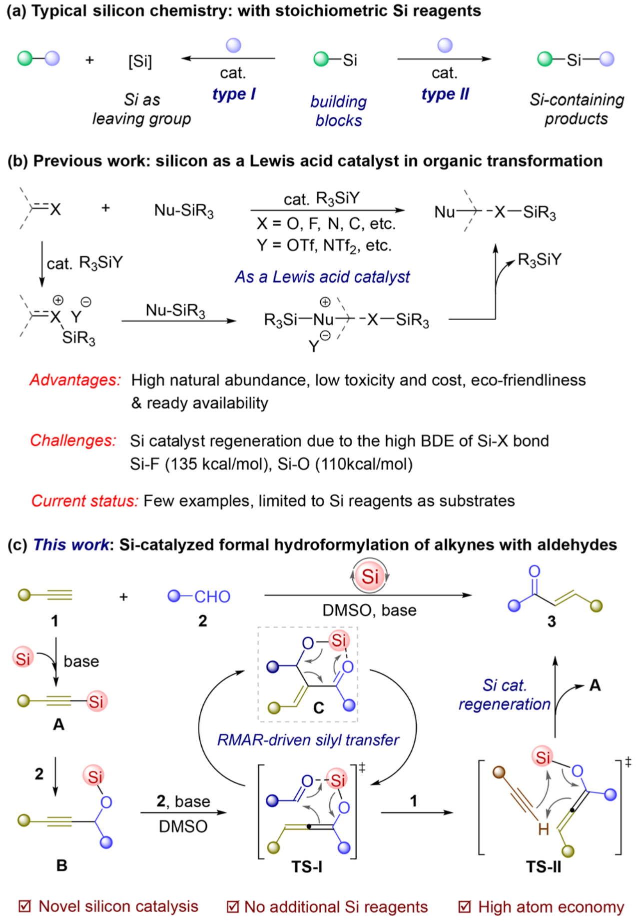
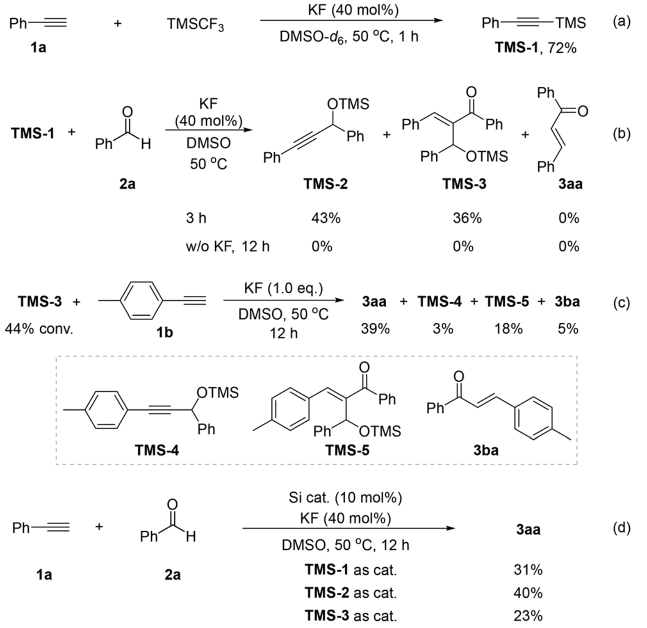


Scheme 1 New strategy for advancing silicon-based catalysis.

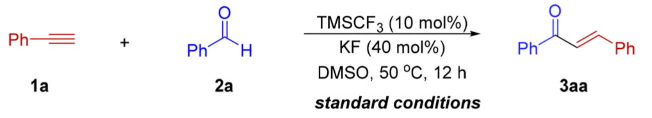
To validate our hypothesis, we initially conducted the reaction of phenylacetylene (**1a**) with (trifluoromethyl)trimethylsilane ($TMSCF_3$) in DMSO-d_6 using KF as the base. The reaction proceeded smoothly to give the desired trimethyl(phenylethynyl)silane (**TMS-1**) in 72% yield[16] (Scheme 2a). Subsequently, when **TMS-1** was reacted with benzaldehyde **2a**, the expected propargyl silyl ether product **TMS-2** and allyl silyl ether **TMS-3**[17] were indeed obtained in 43% and 36% yields, respectively, while no chalcone **3aa** was observed (Scheme 2b). Control experiments confirmed that the reaction of **TMS-1** with **2a** did not proceed in the absence of KF, indicating the essential role of the base in this transformation (Scheme 2b). These findings prompted us to investigate the possibility of a RMAR process, facilitating the formation of **3aa** and the regeneration of the Si catalyst when **TMS-3** reacts with an alkyne, as shown in Scheme 1c. Encouragingly, **TMS-3** was successfully converted to **3aa** in the presence of **1b**, and the propargyl silyl ether species **TMS-4** could also be observed (Scheme 2c). The formation of **TMS-5** and **3ba** can be rationalized through a similar transformation starting from **TMS-4**. These results prompted us to explore the reaction using **1a** and **2a** as starting materials with catalytic amounts of **TMS-1**, **TMS-2**, or **TMS-3** and KF. As expected, the reaction proceeded smoothly to deliver **3aa** in 23–40% yields (Scheme 2d), providing convincing evidence that **TMS-1**, **TMS-2**, and **TMS-3** serve as key intermediates in this transformation.



Scheme 2 Validation of the reaction proposal.

Following the initial experimental results shown in Scheme 2, we further explore the reaction using 10 mol% $TMSCF_3$ and 40 mol% KF in DMSO at 50 °C for 12 h. To our delight, the reaction successfully afforded **3aa** in 73% yield (Table 1, entry 1). Encouraged by this result, we then investi-

Table 1 Optimization of reaction conditions[a]



Entry	Variation from standard conditions	Yield[b] (%)
1	None	73
2	TMSCl or TMSBr instead of $TMSCF_3$	0
3	$Me_2PhSiCl$ instead of $TMSCF_3$	0
4	Et_3SiH instead of $TMSCF_3$	47
5	$PhSiH_3$ instead of $TMSCF_3$	69
6	K_2CO_3 instead of KF	61
7	K_3PO_4 instead of KF	65
8	CsF instead of KF	53
9	^{t}BuOK, ^{t}BuONa or MeOK instead of KF	6–20
10	DBU, DMAP or Et_3N instead of KF	0
11	**$TMSCF_3$ (20 mol%)**	**83 (80)**[b]
12	No $TMSCF_3$ or KF	0
13[c]	DMAc or DMF instead of DMSO	13 or 26
14[c]	CH_3CN, dioxane, toluene or THF instead of DMSO	0
15[c]	80 °C instead of 50 °C	72
16[c]	**1a** (10 mmol, 1 eq.), **2a** (2 eq.)	74

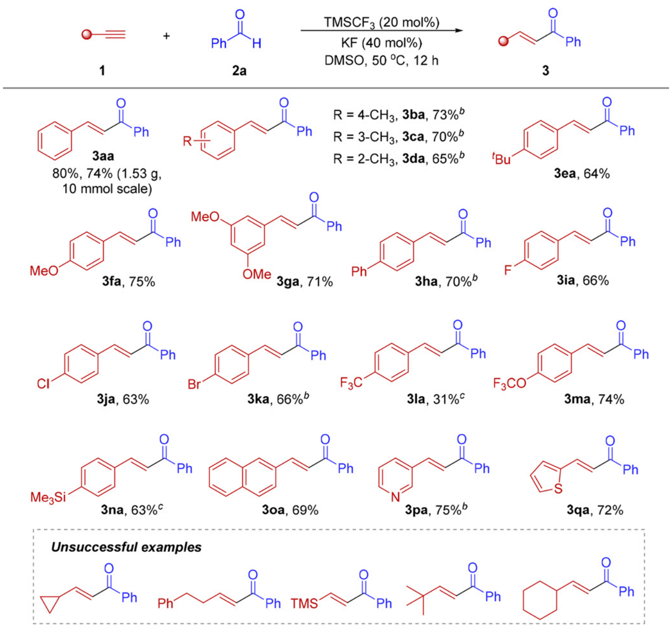
[a] Reaction conditions: **1a** (0.2 mmol, 1 eq.), **2a** (0.4 mmol, 2 eq.), $TMSCF_3$ (20 mol%), KF (40 mol%), DMSO (1.5 mL), 50 °C, 12 h, under N_2. [b] Isolated yield. [c] $TMSCF_3$ (20 mol%).

gated the reaction parameters. Other silicon sources such as TMSCl, TMSBr, or $Me_2PhSiCl$ completely inhibited the reaction (Table 1, entries 2 and 3), while Si–H sources promoted the process (Table 1, entries 4 and 5). The Si–H species would generate the catalytically active propargyl silyl ether intermediate to initiate the catalytic cycle analogous to $TMSCF_3$ (see the ESI†). Subsequently, the effect of bases was also screened. The use of K_2CO_3, K_3PO_4 or CsF provided **3aa** in 53–65% yields (Table 1, entries 6–8), whereas ^{t}BuOK, ^{t}BuONa or MeOK gave only poor results (Table 1, entry 9). Further evaluation confirmed that KF was the optimal base (see Table 1, entries 6–10 and the ESI†). Increasing $TMSCF_3$ loading to 20 mol% slightly improved the yield of **3aa** (Table 1, entry 11). Control experiments confirmed that both $TMSCF_3$ and KF are essential, as no reaction occurred in their absence (Table 1, entry 12). The solvent used also played an important role in this reaction, with other solvents resulting in no or low conversions (see Table 1, entries 13 and 14 and the ESI†). Furthermore, increasing the temperature to 80 °C did not significantly affect the yield of **3aa** (Table 1, entry 15). It should be mentioned that the reaction could be easily scaled up to 10 mmol without any loss of reactivity and 1.53 g (74%) of **3aa** was isolated.

With the optimized reaction conditions established, we next investigated the generality of this protocol (Table 2). A wide range of alkynes bearing diverse substituents, including methyl, *tert*-butyl, methoxy, phenyl, fluoro, chloro, bromo, trifluoromethoxy, and trimethylsilyl groups, smoothly participated in the desired reaction, affording the corresponding α,β-unsaturated ketones (**3aa–3na**) in good to excellent yields, regardless of electronic properties or steric hinderances on the aromatic rings. Apart from phenyl rings, a naphthyl-derived substrate was also compatible with this process and afforded the expected product **3oa** in 69% yield. It is worth mentioning that pyridyl- and thienyl-substituted alkynes were successfully converted to the heterocyclic products **3pa** and **3qa** in 75% and 72% yields, respectively. Unfortunately, aliphatic alkynes were not compatible with the current conditions to give the desired products.

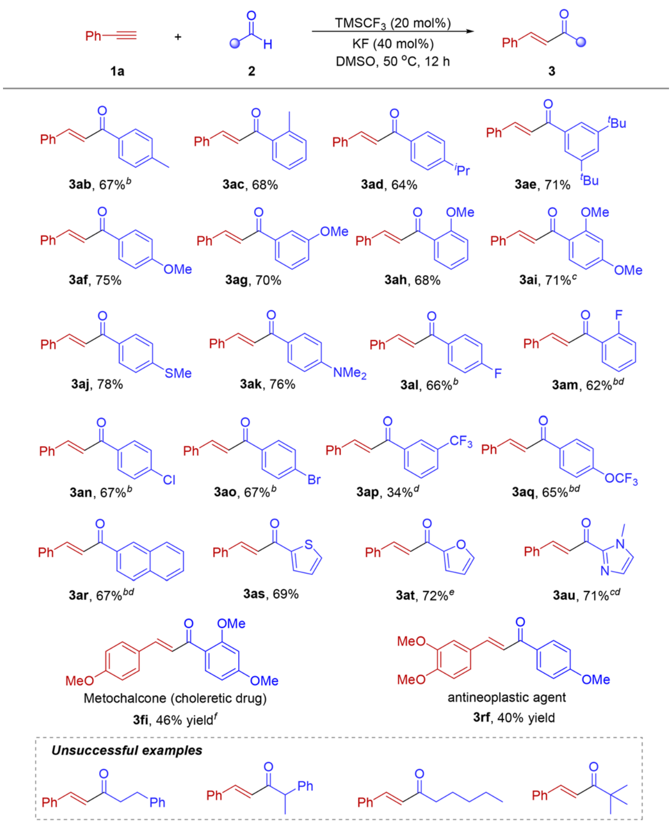
We next turned our attention to evaluate the scope of aldehydes (Table 3). A diverse range of aryl-substituted aldehydes, including both electron-rich and electron-deficient groups, reacted smoothly to deliver the expected α,β-unsaturated ketones in 34–78% yields (**3ab–3aq**). The compatibility of free halogen atoms and trifluoromethyl groups on the aromatic ring offers significant potential for further elaboration of the products. In addition, naphthyl-substituted aldehyde was also compatible with the current conditions (**3ar**). Notably, thienyl-, furyl-, and imidazolyl-substituted aldehydes were also suitable candidates, affording the corresponding products (**3as–3au**) in acceptable yields. To demonstrate the utility of this method, drug-like molecules **3fi** and **3rf** were readily prepared from their corresponding alkynes and aldehydes, further highlight-

Table 2 Substrate scope of alkynes[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv.), $TMSCF_3$ (20 mol%), KF (40 mol%), DMSO (1.5 mL), 50 °C, 12 h, under N_2. Isolated yields. [b] 24 h. [c] $PhSiH_3$ as catalyst.

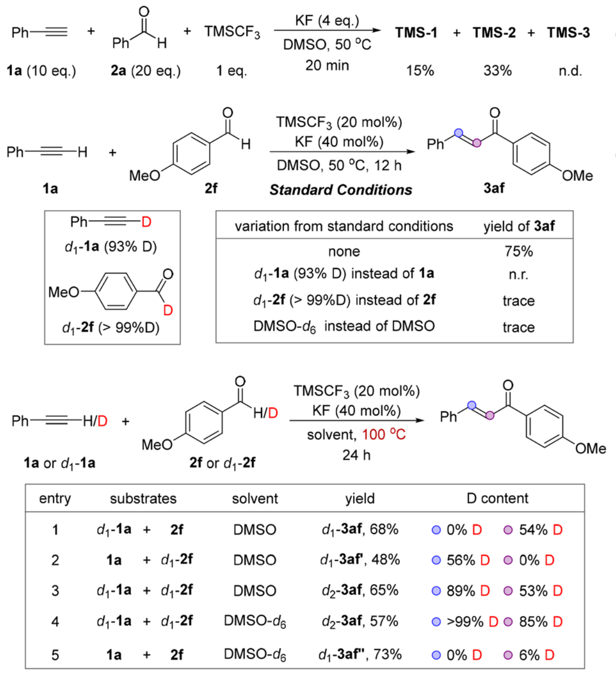
Table 3 Substrate scope of aldehydes[a]



[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol, 2 equiv.), $TMSCF_3$ (20 mol%), KF (40 mol%) and DMSO (1.5 mL), 50 °C, 12 h, under N_2. Isolated yields. [b] 24 h. [c] 100 °C. [d] $PhSiH_3$ as catalyst. [e] 80 °C. [f] 150 °C.

ing the application potential of this approach. However, aliphatic aldehydes failed to afford the desired α,β-unsaturated ketones.

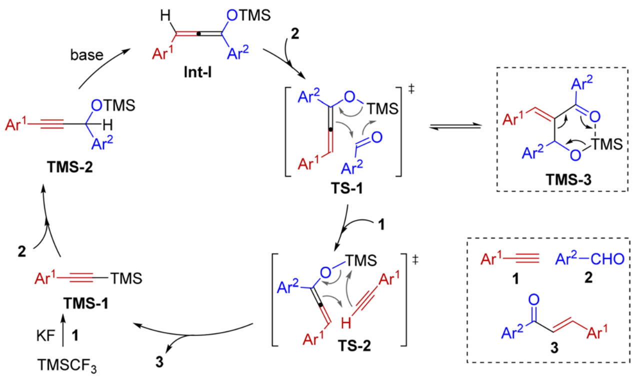
To elucidate the reaction mechanism, we conducted several mechanistic investigations. When the reaction between **1a** and **2a** was quenched after 20 minutes, **TMS-1** and **TMS-2** were obtained in 15% and 33% yields, respectively (Scheme 3a), providing further evidence for their involvement as intermediates in this transformation. Furthermore, several deuterium labelling experiments were conducted. Notably, almost no reaction was observed when deuterium-labelled d_1-**1a**, d_1-**2f** or DMSO-d_6 was used (Scheme 3b), suggesting a significant kinetic isotopic effect in this transformation. Consequently, the reaction temperature was increased to 100 °C and under these conditions, 54% D and 56% D incorporation was observed at the α-position of d_1-**3af** and the β-position of d_1-**3af′**, when either d_1-**1a** or d_1-**2f** was used (Scheme 3c, entries 1 and 2). Moreover, the combined use of d_1-**1a** and d_1-**2f** significantly increased the deuterium content at the β-position of d_2-**3af** to 89%, while that at the α-position remained unchanged (Scheme 3c, entry 3). In contrast, replacing DMSO with DMSO-d_6 provided d_2-**3af** with 85% D incorporation at the α-position and nearly complete deuteration at the β-position (Scheme 3c, entry 4). In addition, almost no deuterium scrambling was observed in d_1-**3af″** during the reaction of **1a** and **2f** in DMSO-d_6 (Scheme 3c, entry 5). These results clearly revealed that the hydrogen at the α-position of the α,β-unsaturated ketone products originates from the alkyne and DMSO, while the hydrogen at the β-position is derived from the alkyne, aldehyde and DMSO.



variation from standard conditions	yield of **3af**
none	75%
d_1-**1a** (93% D) instead of **1a**	n.r.
d_1-**2f** (> 99%D) instead of **2f**	trace
DMSO-d_6 instead of DMSO	trace

entry	substrates	solvent	yield	D content
1	d_1-**1a** + **2f**	DMSO	d_1-**3af**, 68%	● 0% D ● 54% D
2	**1a** + d_1-**2f**	DMSO	d_1-**3af′**, 48%	● 56% D ● 0% D
3	d_1-**1a** + d_1-**2f**	DMSO	d_2-**3af**, 65%	● 89% D ● 53% D
4	d_1-**1a** + d_1-**2f**	DMSO-d_6	d_2-**3af**, 57%	● >99% D ● 85% D
5	**1a** + **2f**	DMSO-d_6	d_1-**3af″**, 73%	● 0% D ● 6% D

Scheme 3 Mechanistic studies.



Scheme 4 Proposed mechanism.

Based on the experimental results, a plausible reaction mechanism is proposed (Scheme 4). The reaction begins with the silylation of alkyne **1** in the presence of TMSCF$_3$ and KF to provide **TMS-1**, which undergoes nucleophilic addition with aldehyde **2** to form the propargyl silyl ether **TMS-2**. Deprotonation of **TMS-2** in the presence of DMSO and the base, followed by propargyl-allenyl isomerization,[18] affords the allenyl silyl ether **Int-I**. This intermediate reacts with another aldehyde through the Mukaiyama aldol-type transition state **TS-1** to produce **TMS-3**. The RMAR-facilitated silyl transfer then promoted the deconstruction of **TMS-3** back to **Int-I** and aldehyde. Then the reaction of **Int-I** with another alkyne *via* **TS-2** gives the final product **3** and regenerates **TMS-1** for the next catalytic cycle.

Conclusions

In summary, we have developed a novel RMAR-driven silyl transfer strategy that enables the challenging regeneration of silicon catalysts under mild conditions. This approach facilitates an unprecedented silicon-catalyzed formal hydroformylation of alkynes with aldehydes, providing access to a diverse range of valuable α,β-unsaturated ketones. Control experiments and mechanistic studies elucidated the transformation of the silicon catalyst during the reaction, and the true active catalyst was identified and validated in the catalytic cycle. We believe this study will open new avenues in silicon chemistry and inspire further exploration of new chemical transformations based on silicon catalysis.

Author contributions

Y. Hu and Y. Xie designed the project and supervised the investigation. Y. Hu wrote the manuscript. Y. Dong performed most of the experiments. Y. Hu and Y. Xie analysed the data. L. Jin and Y. Wang helped discuss the results and commented on the manuscript.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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