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Palladium-catalyzed addition of acylsilanes across alkynes *via* the activation of a C–Si bond†

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Palladium-catalyzed addition of a C–Si bond in acylsilanes across the triple bonds in an alkyne bearing a carbonyl group at one terminal is reported. The reaction proceeds with excellent regioselectivity, in which a silyl group is incorporated into the carbon α to the carbonyl group, allowing for straightforward access to a variety of functionalized alkenylsilane derivatives. Catalytic synthesis of indanones by annulation between acylsilanes and alkynes with an identical catalytic system is also reported.

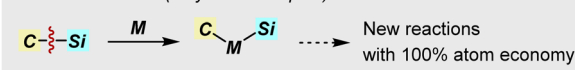
Introduction

Organosilicon compounds are indispensable molecules that find widespread use in both academia and industry that are related to synthetic organics,^{1a–c} polymers,^{1d,e} materials,^{1f,g} and bioorganic and medicinal chemistry.^{1h,i} The most widely used method for the synthesis of organosilicon compounds is the transition metal-catalyzed hydrosilylation of unsaturated hydrocarbons, in which a H–Si bond is added across alkenes or alkynes.² On the other hand, the transition metal-catalyzed carbosilylation of unsaturated hydrocarbons, in which a C–Si bond is added in a similar manner, would serve as a powerful method for the synthesis of more complex derivatives from simpler organosilicon feedstocks with an atom economy of 100%. However, the development of such carbosilylation reactions remains a challenging task because the requisite oxidative addition of a C–Si bond by a transition metal complex is an uncommon organometallic process (Fig. 1a, top).³ Although the cleavage of a C–Si bond can occur using complexes bearing an X-type ligand, the mechanism involves a transmetalation, during which the silicon group is eliminated, thus making it unsuitable for use in carbosilylation reactions (Fig. 1a, bottom).^{1b,c,4} Because of this difficulty, insertion reactions of unsaturated hydrocarbons into a C–Si bond have been limited to strained silacycles (*i.e.*, silacyclopropanes⁵ and silacyclobutanes⁶), silyl cyanides⁷ and intramolecular reactions.^{8–11}

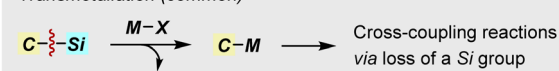
Our research program has focused on the addition reactions of a C–Si bond in acylsilanes.¹² In an early study, Narasaka and coworkers reported on the palladium-catalyzed decarbonylative bis-silylation of dimethyl acetylenedicarboxylate using a bis-silyl

(a) Cleavage of a C–Si bond by transition metal complexes

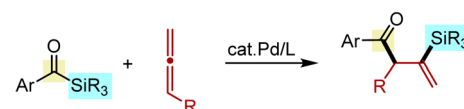
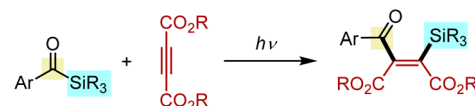
Oxidative Addition (only few examples)



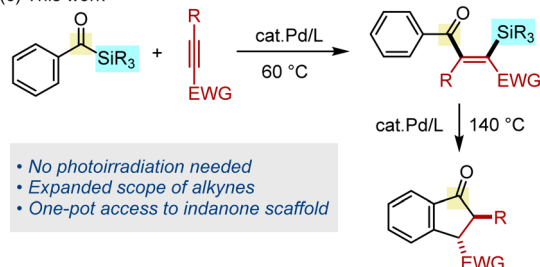
Transmetalation (common)



(b) Insertion into a C–Si bond of acylsilanes: Prior arts



(c) This work



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Fig. 1 Metal-mediated activation of a C–Si bond and its application to insertion reactions.

ketone, although its application to acylsilanes was not mentioned.¹³ The photochemical addition of acylsilanes to activated alkynes was also reported, although the applicable alkynes are limited to acetylene dicarboxylates or intramolecular reactions (Fig. 1b, top).¹⁴ Although this photocatalytic process involves a formal insertion into a C–Si bond, the reaction proceeds through the generation of a siloxycarbene, cyclopropanation, followed by ring opening. We previously reported on the palladium-catalyzed addition of a C–Si bond in acylsilanes across allenes, in which a C–C double bond can be functionalized with both acyl and silyl groups (Fig. 1b, bottom).¹⁵ These studies led us to hypothesize that it might be possible to capture the postulated oxidative addition intermediate (acyl–Pd–SiR₃) by alkynes, instead of allenes.¹⁶ We report herein on the palladium-catalyzed addition of acylsilanes across alkynes, allowing a C–C triple bond to be functionalized with both acyl and silyl groups (Fig. 1c). Moreover, we also found that the silylacylation products obtained in this insertion process could be directly transformed into indanone derivatives at higher temperature.

Results and discussion

Palladium-catalyzed silylacylation of alkynes

On the basis of our previous studies on the palladium-catalyzed silylacylation of allenes,¹⁵ we investigated the possibility of expanding the scope to the reaction with alkynes. After screening a series of alkynes (see the ESI for details[†]), internal alkynes bearing an ester group at one terminal were found to participate in the silylacylation reaction. Thus, the reaction of acylsilane **1a** with alkyne **2a** in the presence of Pd₂(dba)₃ (10 mol% [Pd]) and IPr (10 mol%) at 60 °C afforded the silylacylation product **3aa** in 83% yield (Fig. 2). The reaction proceeded with excellent regio- and stereo-selectivity; a silyl group is incorporated into the carbon α to the ester group in **2a**, while an acyl group is attached to the β -position with a high *syn* selectivity. Alkynes without an ester group, such as dec-5-yne (**2b**) and oct-1-yne (**2c**), failed to afford the corresponding silylacylation products under these conditions, indicating that an ester group is required for this reaction to proceed.

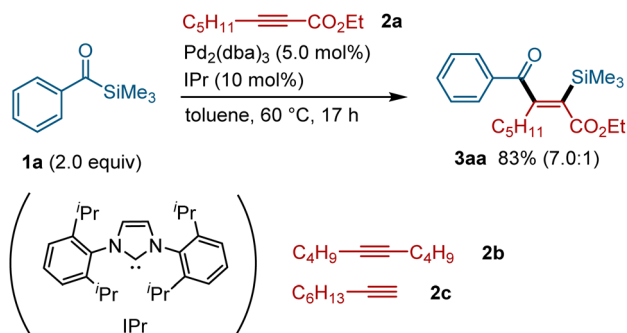


Fig. 2 Palladium-catalyzed silylacylation of alkynes using acylsilane **1a**.^a ^aIsolated yield with a ratio of **3aa** and its isomers in the parentheses.

The palladium-catalyzed silylacylation reaction is applicable to a range of alkynes and acylsilanes (Fig. 3). Alkynes bearing alkyl groups, such as phenethyl (*i.e.*, **2d**), cyclohexyl (*i.e.*, **2e**) and methyl groups (*i.e.*, **2f**), successfully participated in this silylacylation reaction, providing the corresponding addition products in a regioselective manner. Alkynes bearing more elaborate substructures, such as terpenes (*i.e.*, **2h**) and sugars (*i.e.*, **2i**), also underwent this silylacylation reaction. Moreover, alkynoates bearing aryl (*i.e.*, **2j–2l**) and heteroaryl groups such as thiophene (*i.e.*, **2m**) were also applicable to this reaction with the corresponding silylacylated products being formed in a regioselective manner.¹⁷ In addition to an ester group, alkynes with a ketone group (*i.e.*, **2n**) could also be silylacylated under these palladium-catalyzed conditions. With respect to the acylsilane component, various benzoylsilane derivatives, including those bearing ether (**1b**), ester (**1c**), fluoride (**1d**), cyano (**1e**), and 2-naphthyl groups (**1g**), smoothly participated in the silylacylation reaction with a high regio- and stereo-selectivity. Acylsilanes bearing a PhMe₂Si group (*i.e.*, **1h**) can also be used successfully to form the corresponding silylacylated products.

The mechanism for the palladium-catalyzed silylacylation of alkynes was investigated by DFT calculations (Fig. 4). The oxidative addition of acylsilane **1a** to Pd–IPr proceeds *via* a three-centered transition state **TS1** with a reasonable activation barrier of 9.1 kcal mol^{–1} to generate **INT2**. The subsequent insertion of alkyne **2j** could proceed *via* eight different transition states, depending on which of the Pd–Si and Pd–acyl bonds are added, on the orientation of alkyne **2j**, and on whether the silyl and benzoyl ligands are located in a *cis* or *trans* configuration. A comparison of all the possible transition states revealed that **TS2-1**, which leads to alkenylpalladium **INT4**, was the most stable (see Fig. S3 and S5[†] for details). Finally, C–C bond-forming reductive elimination *via* **TS3** from **INT4** provides the silylacylated product, which is in agreement with the experimentally observed regio- and stereo-selectivity. We previously reported that the Pd/IPr system catalyzes siloxycyclopropanation reactions through the generation of a siloxycarbene–Pd intermediate when acylsilanes are reacted with terminal alkenes.¹⁶ In the case of the reaction with alkynes, the generation of the carbene complex *via* **TS4** is energetically less favorable by 18.1 kcal mol^{–1} compared to **TS2-1**.

Palladium-catalyzed indanone synthesis from acylsilanes and alkynes

During the course of our investigations of silylacylation reactions of **2j**, we discovered that indanone derivative **4aj** was formed when the reaction was carried out at higher temperature (see the ESI for the details of optimization[†]). Since indanone derivatives are compounds of great value as pharmaceuticals and agrochemicals,¹⁸ we decided to optimize the reaction conditions that allow for the selective formation of indanone derivatives. Thus, the reaction of acylsilane **1a** with alkyne **2j** (1.2 equiv.) in the presence of Pd₂(dba)₃ (10 mol% [Pd]) and IPr (10 mol%) at 140 °C was found to afford the indanone derivative **4aj** in 87% yield (Fig. 5a). The analysis of the crude reaction



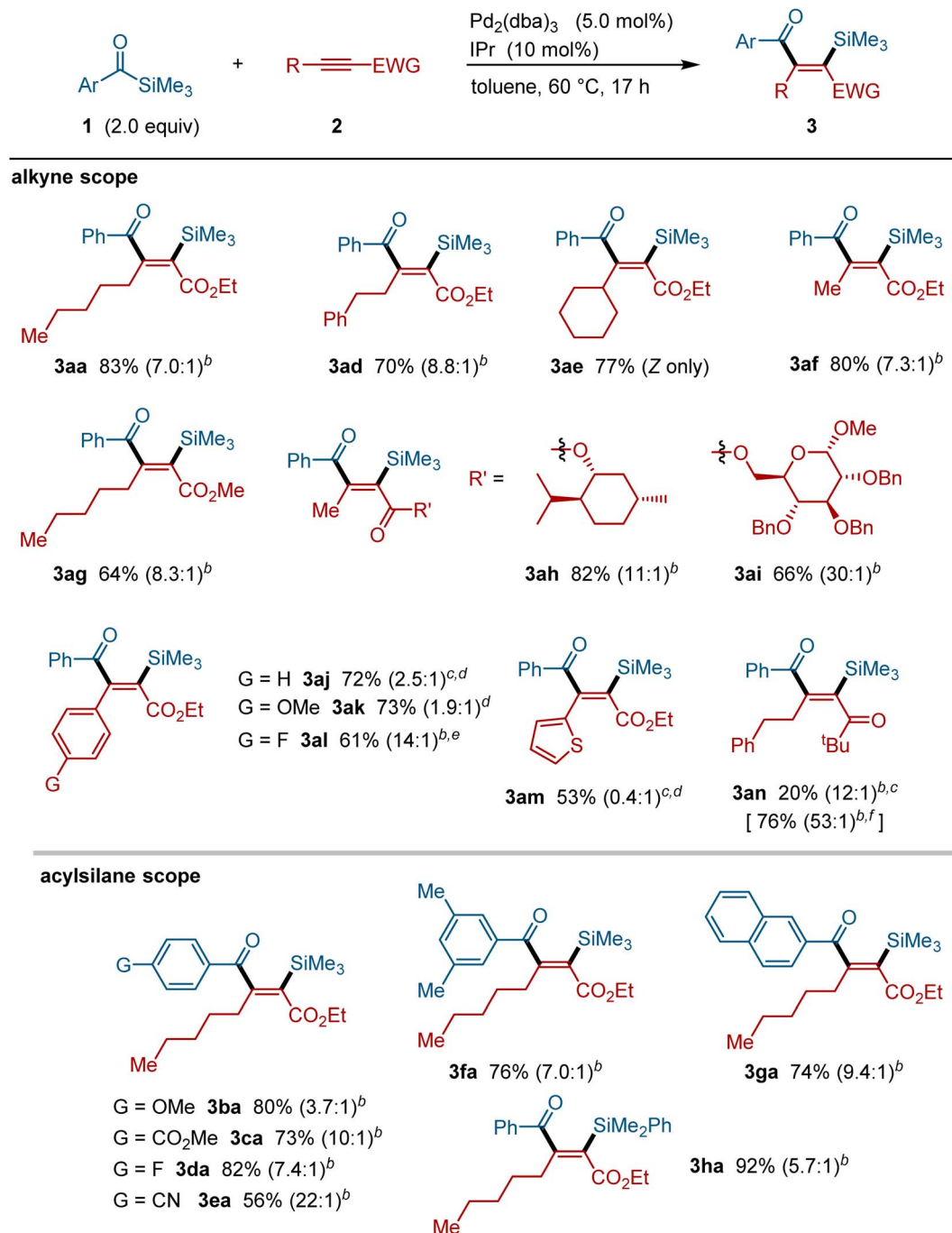


Fig. 3 Scope of the palladium-catalyzed silylacylation of alkynes.^a Acylsilane (0.40 mmol), alkyne (0.20 mmol), Pd₂(dba)₃ (0.010 mmol), IPr (0.020 mmol) and toluene (0.60 mL) in a sealed tube at 60 °C for 17 h. ^bRatios in parentheses refer to the ratios to their minor isomer(s). ^cPd₂(dba)₃ (0.0075 mmol) and IPr (0.015 mmol) were used. ^dRatios in parentheses refer to the ratios of Z/E isomers. ^ePd₂(dba)₃ (0.0050 mmol) and IPr (0.010 mmol) were used. ^fThe isolated yield of desilylated product 3an'.

mixture by ¹H and ¹³C NMR as well as GC/MS revealed that silyl enol ether 4aj' was formed as the primary product, which was converted into 4aj during chromatographic isolation (see the ESI for details[†]). To examine the relevance of silylacylation product 3aj in the formation of indanone 4aj, 3aj was treated with Pd₂(dba)₃/IPr at 140 °C, which resulted in the formation of 4aj (Fig. 5b). It is important to note that 3aj was not converted

into 4aj in the absence of a Pd(0) catalyst or in the presence of a Pd(II) catalyst, indicating that 4aj was formed from 3aj via the action of a Pd(0) catalyst (see the ESI for details[†]).

Given the fact that catalytic synthesis of indanones by annulation between acylsilanes and alkynes is unprecedented, the scope of this indanone synthesis was explored (Fig. 6). Aromatic alkynoates bearing electronically diverse substituents,



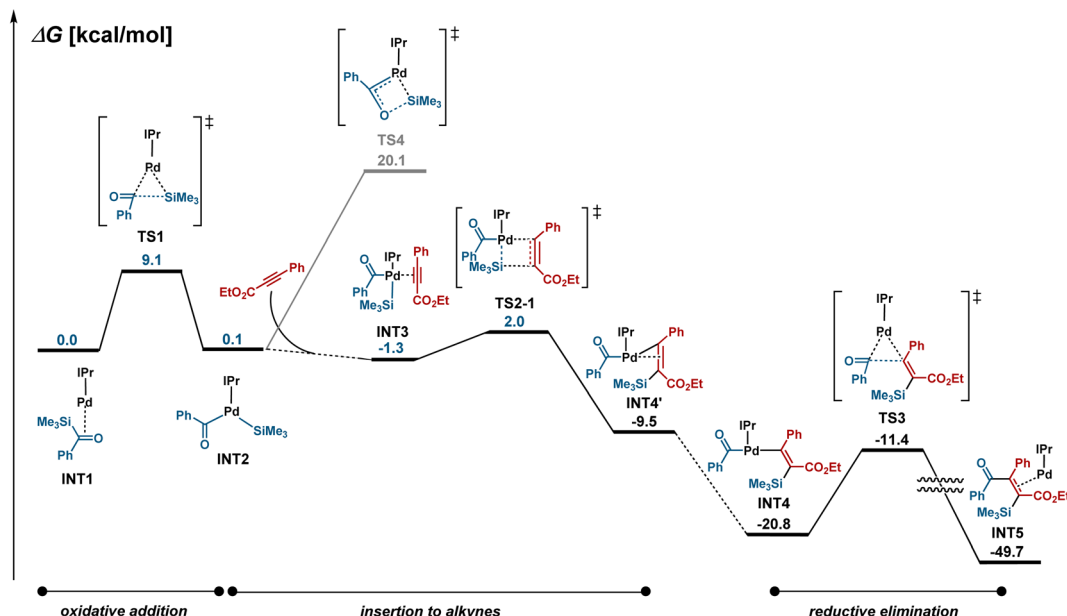
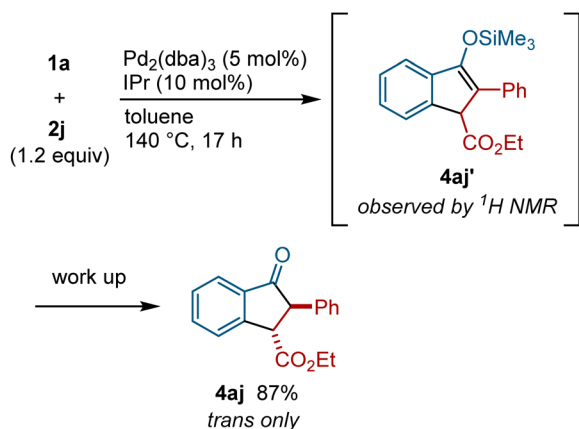


Fig. 4 DFT calculations.^{a, b} Computed energy profiles of the Pd-catalyzed silylacetylation pathways of acylsilane **1a** with alkyne **2j** at the ω B97XD/SDD-6-311+G**// ω B97XD/LANL2DZ-6-31G* level of theory.

(a) Pd-catalyzed synthesis of indanone derivatives



(b) Pd-catalyzed conversion of **3aj** to **4aj**

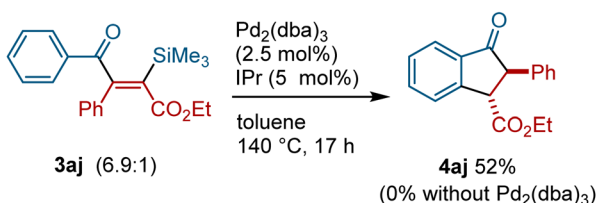


Fig. 5 The palladium-catalyzed synthesis of indanone derivatives.

including methoxy (*i.e.*, **2k**), fluoro (*i.e.*, **2l**) and acetyl groups (*i.e.*, **2o**), as well as heteroaryl alkynoate **2m**, served as suitable coupling partners to provide the corresponding indanone

derivatives. An alkyne bearing a sterically hindered *o*-tolyl group (*i.e.*, **2p**) was also tolerated. Alkyl-substituted alkyne **2g** was also applicable to this reaction. Interestingly, an alkyne with an amide group (*i.e.*, **2q**) was efficiently converted into indanone **4aq** even at 60 °C. Regarding the scope of acylsilanes, a range of derivatives including both electron-rich (**1b**) and electron-deficient (**1d** and **1e**) acylsilanes successfully reacted with alkyne **2j** to provide the corresponding indanone products. With respect to the acylsilane bearing a cyano group (*i.e.*, **1e**), indenone **4ej** was obtained selectively, rather than an indanone derivative.¹⁹ An acylsilane with a 2-naphthyl group (*i.e.*, **1g**) was selectively cyclized at a more sterically hindered position of the naphthalene ring to afford the corresponding indanone derivative **4gj**.

This transformation can be classified as a Nazarov-type cyclization, in which dialkenyl ketones are cyclized to form cyclopentenone derivatives *via* a pentadienyl cation intermediate.²⁰ Although most Nazarov-type cyclization reactions are promoted by (Lewis) acid catalysts, Tius reported that the non-Lewis acidic Pd(0) can serve as a catalyst for the Nazarov-type cyclization of alkenyl diketoesters.²¹ Based on the study reported by Tius, a possible mechanism for our indanone synthesis is proposed in Fig. 7. The nucleophilic attack of Pd(0) on the β -carbon of the α,β -unsaturated ketone backbone of **3** generates π -allylpalladium intermediate **A**. A cationic π -allylpalladium moiety in **A** is susceptible to an intramolecular nucleophilic attack by a neighboring aromatic ring to form cyclized intermediate **B**. The subsequent migration of the silyl group and proton in **B** affords silyl enol ether **C**, which would then be transformed into indanone derivative **4** by hydrolysis.

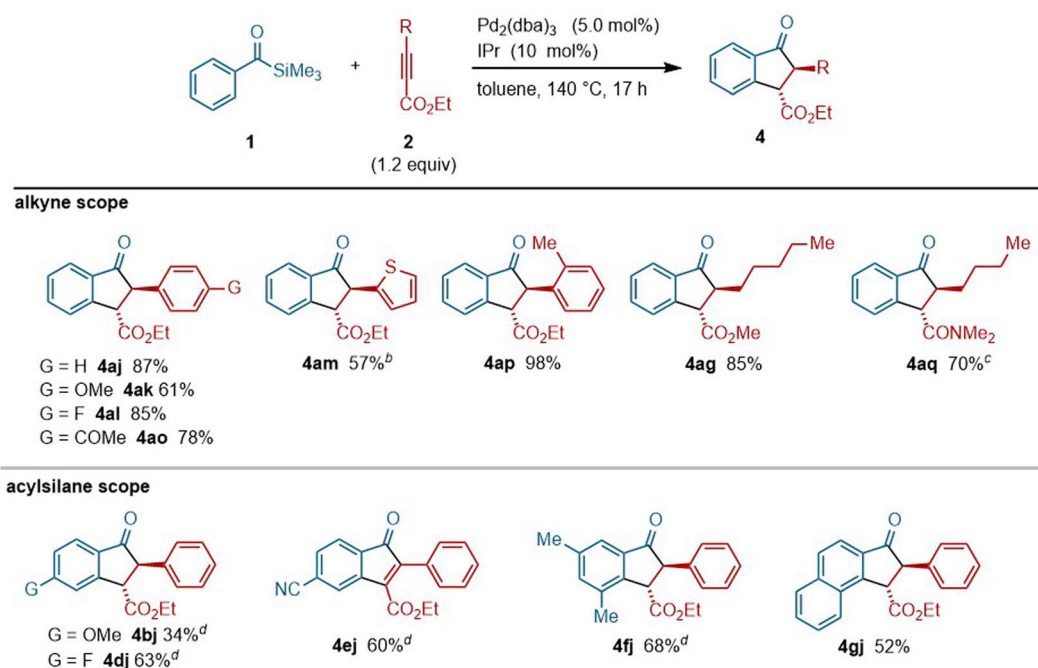


Fig. 6 Scope of the palladium-catalyzed synthesis of indanone derivatives using acylsilanes and alkynes.^a Acylsilane (0.20 mmol), alkyne (0.24 mmol), Pd₂(dba)₃ (0.010 mmol), IPr (0.020 mmol) and toluene (0.60 mL) in a sealed tube at 140 °C for 17 h. ^bIndenone **4am'** was also obtained in 27% yield. ^cAcylsilane (0.40 mmol), alkyne (0.20 mmol), Pd₂(dba)₃ (0.0075 mmol), IPr (0.015 mmol) and toluene (0.60 mL) in a sealed tube at 60 °C. A silylacylated Product **3aq** was also obtained in 26% yield. ^dRun at 160 °C.

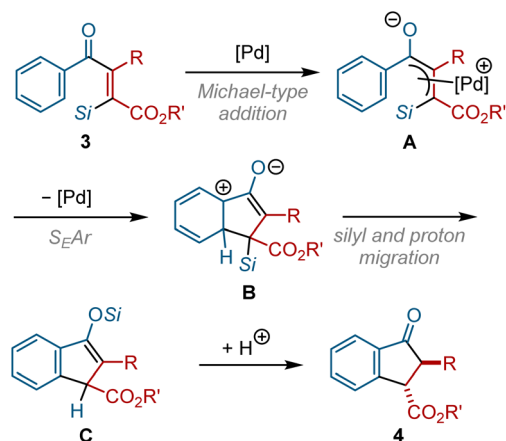


Fig. 7 Proposed mechanism for indanone synthesis.

Conclusions

In summary, we report on the palladium-catalyzed addition of a C–Si bond in acylsilanes across alkynes bearing a carbonyl group at one terminal, leading to the atom economical formation of functionalized alkenylsilanes. The elaborate organosilane derivatives synthesized by this silylacylation reaction can serve as versatile building blocks for use in the construction of more elaborate molecular architectures *via* silicon-based organic synthesis. Computational studies indicate that the reaction proceeds through the oxidative addition of a C–Si bond to Pd(0). We also report on the palladium-catalytic synthesis of

indanones by annulation between acylsilanes and alkynes. Mechanistic studies revealed that Pd(0) can serve as a catalyst for converting the silylacylated products to indanone derivatives. These studies pave the way for the further development of catalytic transformations that proceed *via* the oxidative addition of a C–Si bond, which is the subject of our ongoing research.

Data availability

Additional data and spectra, NMR spectra, details on the DFT calculations and Cartesian coordinates of the DFT optimized structures can be found in the ESI.†

Author contributions

T. I., T. A., S. S., M. Y. and M. T. conceived the project. T. I., T. A., and S. S. performed the experiments. T. I. performed the quantum chemical calculations and M. Y. supervised it. T. I. and M. T. wrote the manuscript. All authors discussed the results and reviewed the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Instrumental Analysis Center, Graduate School of Engineering, Osaka University, for their assistance with HRMS.

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E ratio of 31/1, when the reaction was terminated at 4 h. See the ESI† for details.

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