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Stepwise on-demand functionalization of multihydrosilanes enabled by a hydrogen-atom-transfer photocatalyst based on eosin Y

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Organosilanes are of vital importance for modern human society, having found widespread applications in functional materials, organic synthesis, drug discovery and life sciences. However, their preparation remains far from trivial, and on-demand synthesis of heteroleptic substituted silicon reagents is a formidable challenge. The generation of silyl radicals from hydrosilanes via direct hydrogen-atom-transfer (HAT) photocatalysis represents the most atom-, step-, redox- and catalyst-economic pathway for the activation of hydrosilanes. Here, in view of the green characteristics of neutral eosin Y (such as its abundance, low cost, metal-free nature, absorption of visible light and excellent selectivity), we show that using it as a direct HAT photocatalyst enables the stepwise custom functionalization of multihydrosilanes, giving access to fully substituted silicon compounds. By exploiting this strategy, we realize preferable hydrogen abstraction of Si–H bonds in the presence of active C–H bonds, diverse functionalization of hydrosilanes (for example, alkylation, vinylation, allylation, arylation, deuteration, oxidation and halogenation), and remarkably selective monofunctionalization of di- and trihydrosilanes.

Modular assembly of chemical feedstocks into complex molecules through a systematic and generalized building-block-based strategy enables a broadly accessible solution for on-demand synthesis of organic molecules with great chemical complexity. Tremendous progress has been achieved in this field through the iterative assembly of building blocks[1], such as iterative cross-coupling with *N*-methyliminodiacetic acid boronates[2] and iterative homologations of boronic esters by using chiral lithiated benzoate esters and chloromethyl-lithiums[3]. On the other hand, stepwise functionalization of synthons with multiple reactive sites represents another powerful strategy for custom synthesis of functional molecules, which normally relies on the usage of polyhalo- or polymetallic reagents[4,5]. Even though

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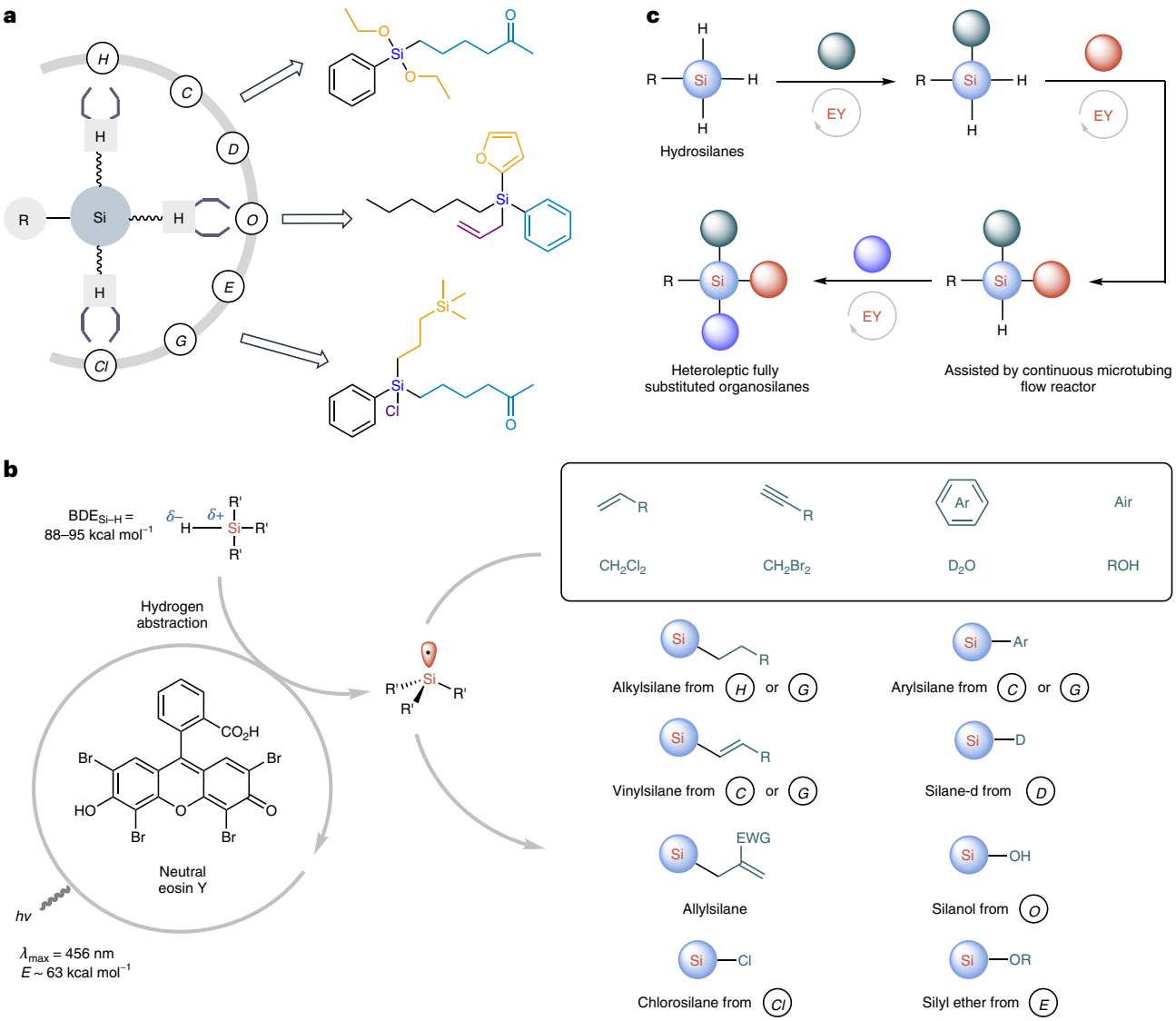

Fig. 1 | Neutral eosin Y-catalysed functionalization of hydrosilanes. a, Targeted stepwise on-demand functionalization of multihydrosilanes. To achieve this goal, three requirements have to be fulfilled: (1) selective Si–H activation versus C–H activation; (2) compatibility with a wide array of building blocks; (3) controllable stepwise functionalization. *H*, hydrosilylation; *C*, acceptorless CDC; *D*, H/D exchange; *O*, aerobic oxidation; *E*, bromination followed by adding alcohols; *G*, bromination followed by adding Grignard reagents; *Cl*, chlorination. **b**, Diverse functionalizations of hydrosilanes through Si–H activation. This strategy features versatile reactivities, novel reaction patterns, overcoming redox limitations, the metal-free character, broad substrate scopes and atom- and step-economic synthesis. EWG, electron-withdrawing group. **c**, Stepwise and modular Si–H functionalization. EY, neutral eosin Y.

functionalization of ubiquitous C–H bonds can be achieved in a site- and stereoselective fashion[6], stepwise functionalizations of the multiple C–H bonds of a methylene or a methyl group, in principle, is an extremely challenging task due to the interference of C–H bonds from the newly installed functional moieties[7]. In stark contrast, Si–H bonds, usually with a bond dissociation energy of ~90 kcal mol^{-1}, are more hydridic than C–H bonds due to silicon's electropositive character (electronegativity of 1.90 versus 2.55 on the Pauling scale). This offers opportunities for preferable Si–H functionalization in the presence of various C–H bonds, a prerequisite to the realization of selective decoration of the silicon atom.

Organosilanes have widespread applications in organic synthesis, polymer synthesis, advanced materials, medicinal chemistry and agricultural science, benefiting human lives in many ways[8–10], and their market reached US$1.1 billion in 2019 (https://www.grandviewresearch.com/industry-analysis/silane-market). Conventionally, organosilanes can be accessed from various silicon electrophiles (for example, silyl chlorides and alkoxysilanes) or nucleophiles (for example, silyl boranes and silyl cuprates)[11]. However, controllable functionalization of multialkoxysilanes and multichlorosilanes is often problematic, as the reaction does not stop at monosubstitution[12]. In this context, Oestreich and coworkers have employed easy-to-handle surrogates for SiH_4, with cyclohexa-1,4-diene units serving as placeholders for hydrogen atoms, which undergo Si–H bond release and hydrosilylation with $B(C_6F_5)_3$ Lewis-acid catalysis for the preparation of various hydrosilanes in a one-pot fashion[13]. Later, this strategy was integrated with palladium-catalysed arylation and a $B(C_6F_5)_3$-catalysed sila-Friedel–Crafts reaction to enable custom synthesis of a diverse set of tri-, di- and monohydrosilanes[12]. However, the development of a more unified catalytic platform for stepwise and programmable functionalization of multihydrosilanes is still greatly in demand, as this will facilitate the rational design of organosilanes with predictable functions, where bespoke silane molecules are required. To realize such a catalytic platform, three

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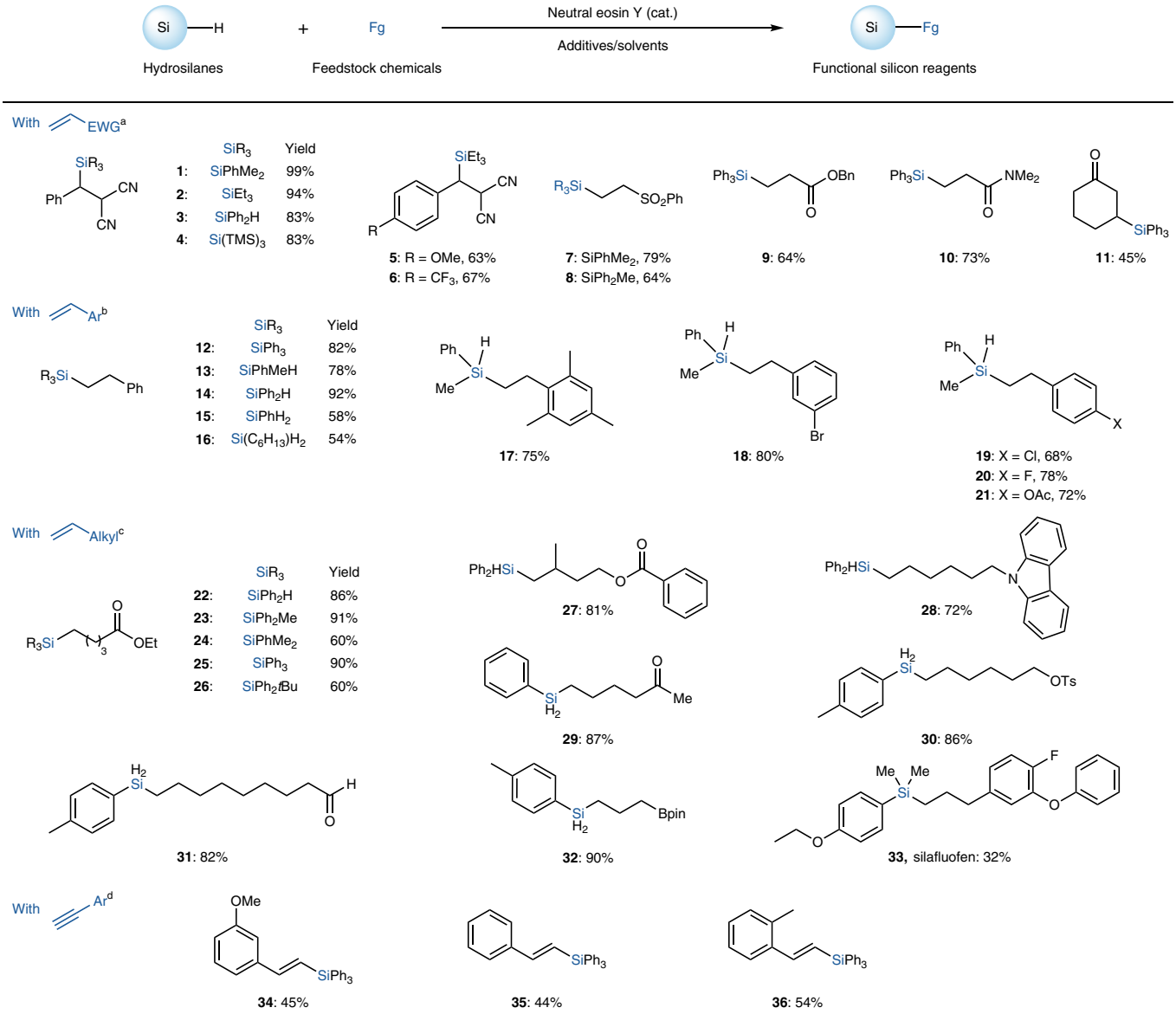
Table 1 | Hydrosilylation through neutral eosin Y-promoted HAT photocatalysis



[a]Eosin Y (2 mol%), DCE (0.2 M) or EtOAc (0.1 M), 60 or 80 °C, 40-W 456-nm LEDs, 48 h; [b]eosin Y (5 mol%), EtOAc (0.1 M), 80 °C, 40-W 456-nm LEDs, 36 h; [c]eosin Y (5 mol%), $^{i}Pr_3SiSH$ (10 mol%), dioxane/H_2O (40:1), 40–50 °C, 40-W 456-nm LEDs, 48 h; [d]eosin Y (5 mol%), $^{i}Pr_3SiSH$ (10 mol%), dioxane/H_2O (40:1), 80 °C, 40-W 456-nm LEDs, 48 h. DCE, 1,1-dichloroethene; LED, light-emitting diode.

requirements have to be fulfilled at the same time (Fig. 1a): (1) a selective and preferable hydrogen-atom abstraction of Si–H bonds in the presence of various activated C–H bonds; (2) amenability to a wide range of building block patterns to access a diverse array of functionalities; (3) selective and controllable monofunctionalization or difunctionalization of multihydrosilanes.

Besides the aforementioned silicon electrophiles and nucleophiles, silyl radicals are another type of versatile intermediate for the synthesis of organosilicon compounds[14]. The inherent nucleophilic character of silyl radicals offers complementary reactivity compared to that of silylium ions generated by Lewis-acid catalysis[15]. Although hydrosilanes are the predominant and usually the most convenient precursors to access silyl radicals though hydrogen-atom-transfer (HAT) processes, conventional HAT protocols involve the use of excess hazardous hydrogen acceptor precursors, such as peroxides, and often require high temperatures or transition-metal initiators, usually resulting in a mixture of Si–H and C–H activation products[16]. The advent of photoinduced HAT catalysis has offered enormous opportunities for direct Si–H functionalizations, where a photoredox catalyst has normally been employed to activate a HAT agent by photoinduced single-electron oxidation, generating an active open-shell species for subsequent HAT with hydrosilanes[17–21].

A more catalyst-economical strategy is direct HAT photocatalysis, in which the photoactivated catalyst can directly abstract a hydrogen atom from hydrosilanes to omit the redox activation step. In 2015, Fagnoni, Ravelli and coworkers first disclosed the hydrosilylation of electron-poor alkenes by using tetrabutylammonium decatungstate as a direct HAT catalyst under UV light irradiation[22]. However, a mixture of Si–H and C–H activation products was obtained with trialkylsilanes. We recently discovered the unique property of neutral eosin Y, which can function as an effective direct HAT photocatalyst for an extremely broad scope of C–H bonds[23]. Excited eosin Y is generated upon absorption of a blue photon (~63 kcal mol^{-1}), which can break C–H bonds with bond dissociation

energies (BDEs) of ~90 kcal mol^{-1}, to generate an active open-shell species beyond its redox capacity. Neutral eosin Y is an excellent photocatalyst because of its visible-light absorption, metal-free character, ready availability and low cost. Furthermore, we have proven that this strategy can be extended to selective functionalization of more hydridic Si–H bonds in the presence of C–H bonds[24]. Density functional theory (DFT) calculations indicated that the HAT between photoexcited eosin Y and silane is kinetically favoured, and the transition state possesses a notable charge-transfer character (δ^{TS} = 0.78; Fig. 1b and Supplementary Section 2).

Learning from our experience with eosin Y-catalysed C–H functionalization[23,25,26], we set out to expand the scope of Si–H activation for diverse functionalizations (for example, alkylation, vinylation, arylation, allylation, oxidation, deuteration and cross-coupling) of hydrosilanes by intercepting the generated silyl radicals with a range of feedstock chemicals to synthesize various functional silicon reagents. In these transformations, the eosin Y catalyst fulfils multifaceted roles, not only supplying the key silyl radical intermediates, but also orchestrating reversed HAT or photoredox-mediated dehydrogenation processes to deliver the desired products. Furthermore, we envisioned that controllable stepwise functionalization of di- and trihydrosilanes could be realized with the assistance of continuous-flow microtubing reactors[27] (Fig. 1c), eventually accomplishing on-demand successive decoration of silicon atoms from multihydrosilanes.

Hydrosilylation

Hydrosilylation occurs with 100% atom efficiency and is one of the most important reactions in the silicone industry[28]. Industrial manufacturing is mainly based on the use of the platinum catalysts developed by Speier and Karstedt[29]. Intensive efforts have been devoted to developing alternative low-cost and environmentally benign catalytic systems, especially in a metal-free manner[30]. However, such a catalytic protocol that is both effective and with a broad scope of alkenes remains rare. We envisioned that the silyl radicals generated by eosin Y HAT photocatalysis could be trapped by an electron-deficient alkene[23]. The radical adduct formed could undergo a reverse HAT process with eosin Y–H to deliver the hydrosilylation product and regenerate the eosin Y catalyst. A diverse range of silanes and Michael acceptors bearing various functional groups afforded the corresponding hydrosilylation products under blue-light irradiation in good to excellent yields (**1** to **11**, Table 1). Michael acceptors, including methylene-malononitriles, unsaturated sulfones, ketones, esters and amides, were all feasible substrates. Hydrosilylation of styrene-type substrates could also be achieved effectively with excellent functional group tolerance (**12** to **21**) by eosin Y photocatalysis in EtOAc at 80 °C in the absence of any additive. It is important to note that trihydroalkylsilanes could also participate in the eosin Y photocatalysis, smoothly and selectively (**16**). When unactivated alkenes were employed as silyl radical scavengers, the reactions, unsurprisingly, became sluggish, as the in situ-formed alkyl radical adduct could not convert eosin Y–H back to eosin Y. This hurdle was addressed by including a catalytic amount of a thiol hydrogen-atom donor (tri-iso-propylsilanethiol) to quench the radical adduct and turn over the catalytic cycle (Supplementary Section 5.5). Various organosilanes and a range of functionalities (for example, ester, aldehyde, ketone, amine, borate, ether, **22** to **33**) were compatible, reflecting the mildness of the reaction conditions. Importantly, benzylic, α-oxy, α-amino and aldehydic C–H bonds that are labile towards eosin Y-catalysed HAT[23] were unperturbed, highlighting the excellent selectivity for Si–H activation. Moreover, silafluofen (**33**), an organosilicon pyrethroid insecticide[31], was synthesized by eosin Y-photocatalysed hydrosilylation in a useful yield.

We were also able to extend this mild protocol to aryl alkynes for direct access to synthetically useful vinylsilanes (**34**–**36**). Notably, the *E* conformation of the vinyl alkenes was exclusively obtained, which differs from the results of a study by Yao regarding redox eosin Y-catalysed hydrosilylation of phenylacetylenes, in which mixtures of *E* and *Z* conformations were obtained[32,33]. This is possibly due to the less bulky silanes enabled by HAT catalysis in our study favouring the more thermodynamically stable product (Supplementary Section 6.3) compared to the sterically hindered supersilane required in Yao's photoredox catalysis, which favoured the kinetic products.

Acceptorless cross-dehydrogenative coupling (CDC) with hydrogen evolution

Direct silylation of alkenes and arenes using hydrosilanes is an ideal pathway for the synthesis of vinylsilanes and arylsilanes, avoiding the use of prefunctionalized pyrophoric organometallic reagents and halide species. Elegant seminal works on acceptorless dehydrosilylation by transition-metal catalysis[34,35], sila-Friedel–Crafts reaction[36] and Lewis-base activation[37] have recently been reported. However, a metal-free protocol under mild conditions (for example, without the use of a strong acid or base) remains a considerable challenge and is highly attractive. During the optimization of eosin Y-catalysed hydrosilylation of styrenes, we found that simply changing the reaction solvent to ^{t}BuOH allowed the formation of vinylsilane products without the formation of any hydrosilylation products. Hydrogen gas was detected as the by-product. A variety of monohydrosilanes (**35**, **37**, **38**) and styrenes (both electron-poor and electron-rich, **41**–**44**) could be employed to afford vinylsilanes in moderate to good yields under eosin Y photocatalysis in the absence of any additives, offering an operationally simple and environmentally benign protocol for vinylsilane synthesis (Table 2). However, di- and trihydrosilanes displayed inferior efficiency in this dehydrosilylation (**39**, **40**).

This photomediated hydrogen-evolution CDC strategy can be smoothly extended to arylation. A phenyl substituent could be incorporated to replace the hydrogen atom in various hydrosilanes when using benzene as the solvent (**45**–**48**). Notably, di- and trihydrosilanes afforded monoarylation products **49**–**52** in good yields and with excellent selectivity. Moreover, arylation of hydrosilanes with functionalized arenes and heteroarenes was feasible with eosin Y photocatalysis when using three equivalents of (hetero)arenes in acetonitrile under blue-light irradiation. As shown in Table 2, both electron-rich and electron-deficient arenes underwent silylation effectively, but poor regioselectivity was obtained with electron-rich arenes (for example, **53**). For electron-deficient arenes, the silyl group could be selectively installed at the electron-deficient site of the arene due to the nucleophilic nature of the silyl radicals (**54**–**59**). Steric factors also played an important role in favouring *para* over *ortho* substitutions in the cases of ester and sulfone mono-substituted arenes (**54**, **55**). Notably, cyano-substituted benzenes that were labile in radical substitution reactions[38] were well tolerated under our reaction conditions and displayed excellent regioselective control (**57**–**59**). Excellent regioselectivity for the mono-silylation product at the C1 position was observed for thiophene with various hydrosilanes, including mono-, di-, and trihydrosilanes (**60**–**64**). Useful regioselectivity could still be achieved with substituted thiophenes (**65**, **66**), with silylation occurring at the most electron-deficient site. Good regioselectivity could be maintained with furan substrates, albeit with lower efficiency (for example, **67**). N-containing heteroarenes were, however, not compatible (not shown).

The eosin Y-based photomediated hydrogen-evolution CDC strategy represents an alternative mode of catalysis for sustainable synthesis. To shed light on the reaction mechanism, a series of control experiments were performed, including radical trapping experiments, cyclic voltammetry measurements, determination of the hydrogen source by gas chromatography mass spectrometry (GC-MS) analysis, kinetic isotope effect studies, and transient absorption spectroscopy measurements (Supplementary Sections 7.4 and 8.5). The mechanistic pathways are proposed in accordance with all the experimental results, where eosin Y not only acts as a HAT catalyst for radical generation,

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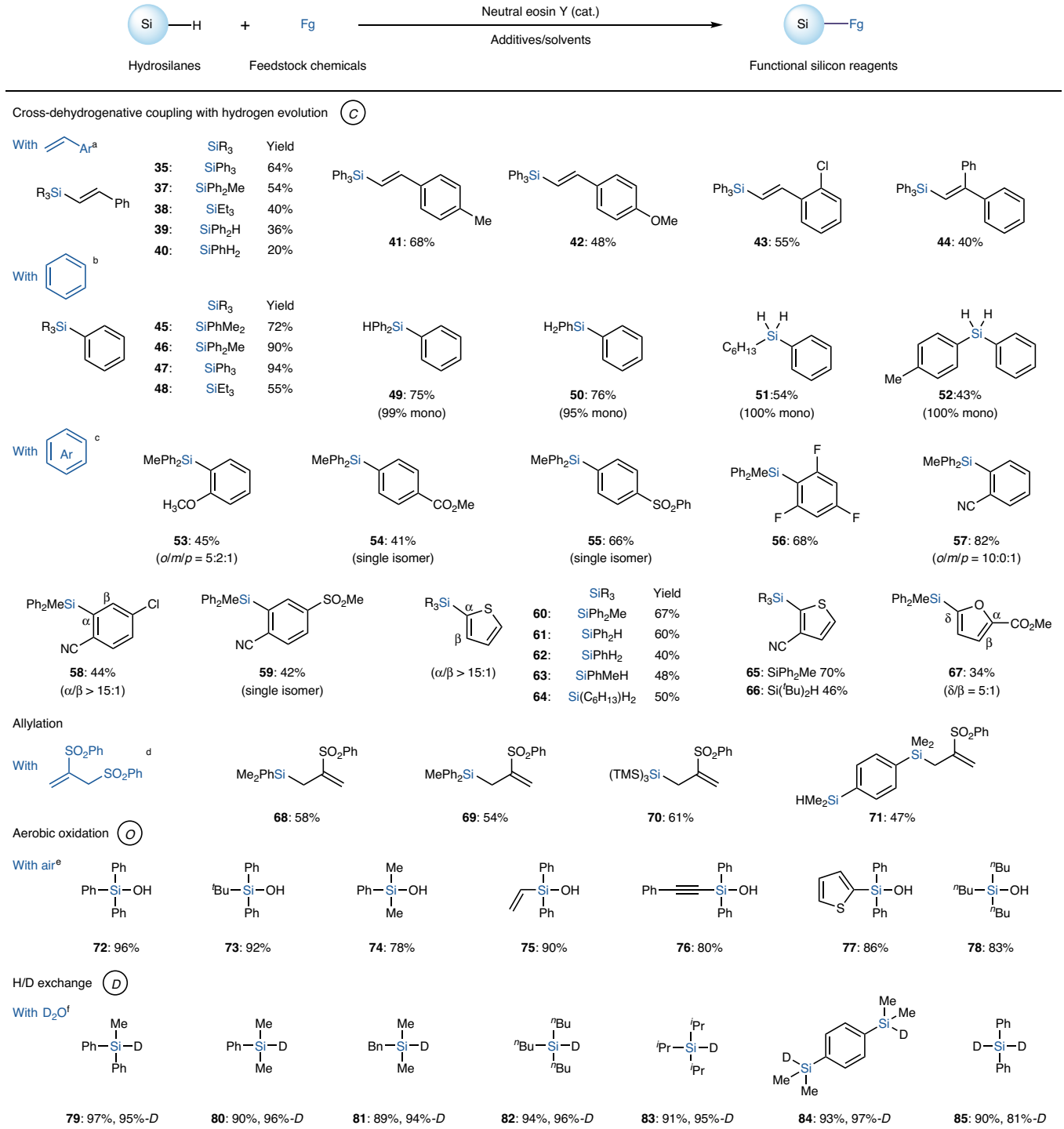
Table 2 | Diverse functionalizations of hydrosilanes through neutral eosin Y-promoted HAT photocatalysis



[a]Eosin Y (5 mol%), ^{t}BuOH (0.1 M), 60 °C, 40-W 456-nm LEDs, 48 h; [b]eosin Y (5 mol%), benzene (0.04 M), 60 °C, 40-W 456-nm LEDs, 48 h; [c]eosin Y (5 mol%), CH_3CN (for **60**–**64** in thiophene), room temperature (r.t.), 40-W 456-nm LEDs, 48 h; [d]eosin Y (2 mol%), benzene (0.2 M), 50 °C, 40-W 456-nm LEDs, 48 h; [e]eosin Y (2 mol%), CH_3CN/H_2O (vol/vol=50:1), air, 40-W 456-nm LEDs, r.t., 24 h; [f]eosin Y (2 mol%), ^{i}Pr$_3$SiSH (10 mol%), EtOAc/D_2O (vol/vol=3:1), 40-W 456-nm LEDs, r.t., 36–48 h. *o*, ortho; *m*, meta; *p*, para.

but also triggers the photoredox catalytic cycle to reduce proton for H_2 generation (Supplementary Figs. 35 and 43)[39].

Silyl radical trapping by other quenchers and synthesis of allylsilanes, silanols and deuterated silanes

We posited that the silyl radicals generated by eosin Y HAT photocatalysis could be trapped by other radical quenchers to access different types of functional silicon reagent. We were able to extend this strategy to allylsilane formation (**68**–**71**) using allyl phenyl sulfones as radical scavengers (Table 2).

Silanols are important monomers for silicon-based polymer synthesis[40] and serve as important reagents in organic synthesis[9] and medicinal chemistry[10]. The direct transformation of hydrosilanes into silanols has conventionally been achieved by using stoichiometric strong oxidants, which often encounter unwanted disiloxane

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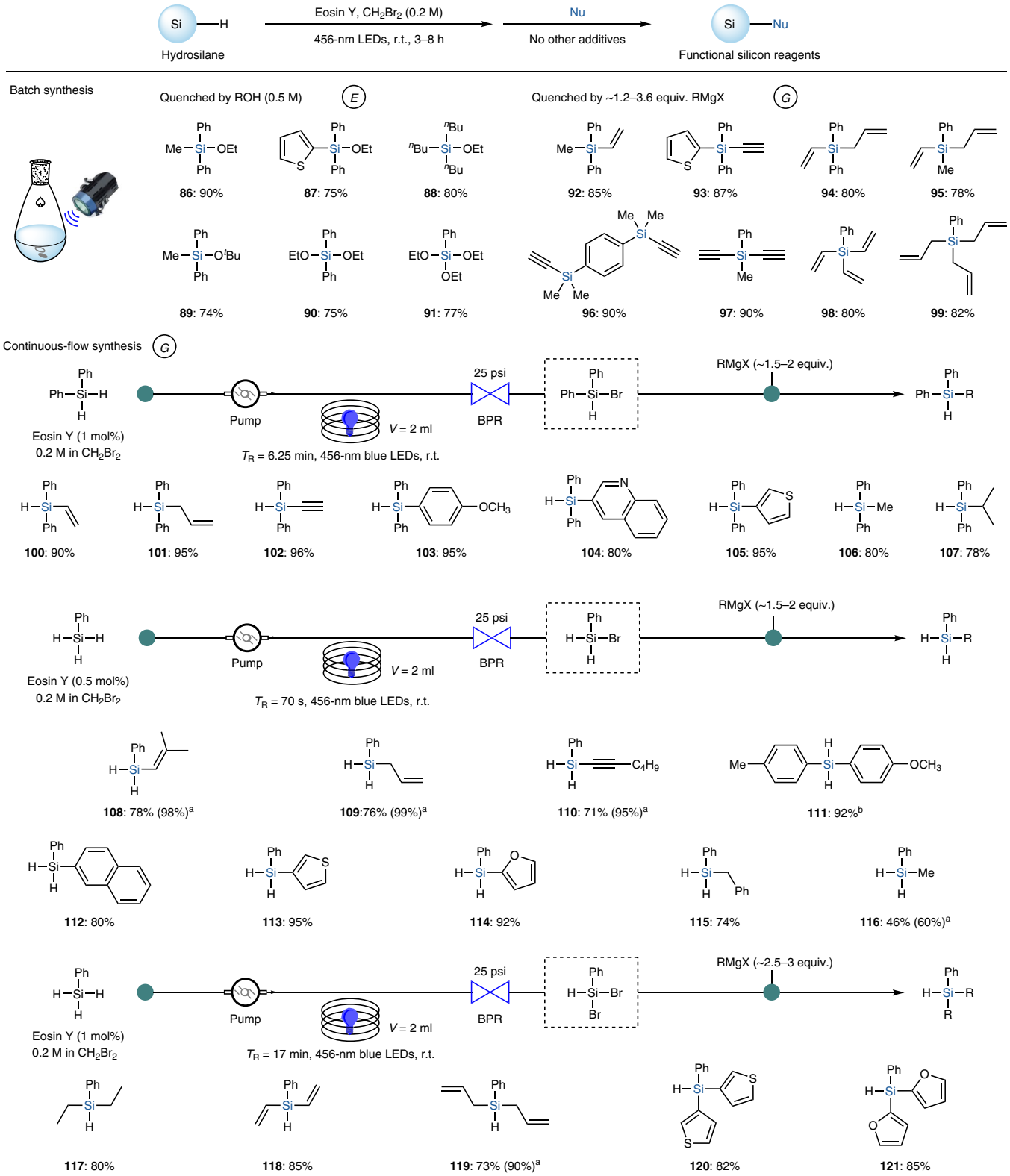
Table 3 | Additive-free cascade bromination/nucleophilic substitution



[a]Reaction yields in parentheses were based on GC analysis due to the volatility of the products. [b]T_R=78 s. Nu, nucleophiles; psi, pounds per square inch; BPR, back-pressure regulator; T_R, residence time; *V*, volume.

formation. The selective synthesis of silanols employing metal-free and environmentally friendly conditions remains rare[41,42]. We disclosed that a variety of monohydrosilanes could be smoothly converted into the corresponding silanols (**72**–**78**) with excellent yields by neutral eosin Y photocatalysis under air at ambient temperature. Functional groups such as alkenes, alkynes and electron-rich heteroarenes, which

are labile under strong oxidation conditions, were well tolerated. In all cases, the formation of disiloxane byproducts was not observed (Supplementary Section 10.4.7).

The effectiveness of eosin Y-catalysed hydrosilylation of unactivated alkenes assisted by thiol as the hydrogen donor prompted investigation of the deuteration of hydrosilanes using D_2O as the deuterium source. After optimization, a variety of monohydrosilanes with different steric and electronic properties underwent efficient deuteration (**79**–**85**) when a catalytic amount of tri-iso-propylsilanethiol was used in EtOAc/D_2O (vol/vol = 3:1).

Cascade silane bromination and nucleophilic substitution

The reactions described thus far ultimately rely on the silyl radical generated by eosin Y HAT photocatalysis. However, the nucleophilic nature of silyl radicals still limits the reaction patterns and the scope of silicon products that can be accessed. In an effort to establish the generality of the eosin Y photocatalysis strategy, we envisioned that the in situ formation of a silyl electrophile could realize polarity inversion, which would subsequently be quenched by a nucleophilic reagent to allow the synthesis of silicon reagents that cannot be directly accessed by silyl radical chemistry. We accomplished silane chlorination by eosin Y photocatalysis in dichloromethane[24]. Even though silyl chlorides are versatile silicon electrophiles, promoters (for example, bases, transition metals) are normally required for nucleophilic substitutions[43]. To realize an operationally simple and reagent-saving process, we aimed to generate more reactive silyl bromides in situ, which can react with a wide range of nucleophilic reagents without the requirement of promoters or additives. We expected that by changing the solvent from dichloromethane to dibromomethane, silyl bromides would be generated rapidly by eosin Y HAT photocatalysis due to rapid bromine atom abstraction (Supplementary Section 12.7). Treatment of hydrosilanes in dibromomethane in the presence of 2 mol% neutral eosin Y under blue-light irradiation indeed efficiently generated silyl bromides, which were unstable during isolation processes because of their hydroscopic properties. By simply quenching the reaction mixtures with alcohols, silylethers (**86**–**89**) were generated in good yields (Table 3). More importantly, dialkoxy- and trialkoxysilanes, which are important feedstocks in polymer and materials science, could be directly accessed from dihydro- and trihydrosilanes by this simple protocol (**90**, **91**). Incorporation of a slight excess of Grignard reagents as part of the workup procedure allowed the formation of Si–C coupling products. Vinyl, alkynyl and allyl Grignard reagents afforded vinylsilanes, alkynylsilanes and allylsilanes (**92**–**99**), respectively, in the absence of any other additive[43].

Continuous-flow microtubing reactors provide an excellent platform for photochemical reactions owing to enhanced and uniform light irradiation and improved mass and heat transfer[27]. The bromination of dimethylphenyl silane could achieve full conversion within a residence time of 70 min assisted by an operationally simple microflow reactor, in stark contrast to the 4 h required in the batch reactor (Supplementary Section 12.4). Intriguingly, selective mono- or di-bromination of di- and trihydrosilanes was successfully achieved by taking advantage of the excellent mixing efficiency and precise residence time control associated with microflow reactors. A wide range of functionalized mono- and dihydrosilanes (**100**–**121**) were obtained in excellent yields and selectivity; these were not accessible under conventional batch conditions. The flow reaction could easily achieve 10-g-scale production within several hours of continuous collection (Supplementary Section 12.5). Notably, silicon products such as dialkoxysilanes, trialkoxysilanes, methyl-substituted silanes and arylsilanes with silyl substitution at the electron-rich site, which are difficult or impossible to access directly by silyl radical chemistry, were accessible with this additive-free cascade bromination/nucleophilic substitution protocol, thereby significantly expanding the scope of silicon reagents that can be prepared by eosin Y HAT photocatalysis.

On-demand stepwise decoration of silicon atoms

The diverse functionalization and observed highly selective monofunctionalization of di- and trihydrosilanes with eosin Y HAT photocatalysis offer opportunities for stepwise on-demand decoration of silicon atoms to access silanes with four different substituents. Treatment of trihydroarylsilanes under eosin Y-catalysed photohydrosilylation conditions followed by additive-free cascade bromination and nucleophilic substitution or chlorination, silyldiether (**122**), dichlorosilane (**123**), dialkynyl- (**124**), divinyl- (**125**) and diallylsilanes (**126**) with two identical functional groups were obtained smoothly (Table 4). Difuryl alkynylsilane **127** could be easily prepared by selective di-bromination/Grignard reagent quenching in a microtubing flow reactor followed by another bromination/Grignard reagent quenching in a batch reactor.

More diverse functional silanes were accomplished by three-step decorations of trihydrosilanes. Through the proper selection and sequencing of eosin Y-catalysed photochemical Si–H functionalization, fully substituted deuterated silanes (**128**, **129**), chlorosilanes (**130**, **131**), silylethers (**132**, **133**), silanols (**134**–**136**) and all-carbon-substituted alkyl-, allyl- and arylsilanes (**137**, **138** and **139**, respectively) were generated with excellent selectivity and good yields. A broad range of functionalities could be incorporated, including ketones, esters, nitriles, aryl fluoride/bromides, heterocycles, borates and silanes. This enables a straightforward and versatile strategy for the synthesis of heteroleptic substituted functional silicon compounds in a programmable manner.

Further synthetic applications

To further demonstrate functional group compatibility and synthetic utilization, various complex natural products and pharmaceutical molecules were incorporated into the silane products, such as ibuprofen, citronellic acid, menthol, vitamin E, indomethacin and oestrone (**140**–**146**). Another functional group, for example, silane (**140**), ketone (**142**, **144**), borate (**143**), ester (**145**, **146**) or a galactose derivative (**141**), could be easily integrated close to the bioactive molecule though the silicon tether (Fig. 2a). This indicated the rich potential to apply the present strategy in antibody–drug conjugates[44] and biomolecule labelling.

Moreover, vinylsilanol **147** could be prepared from dihydrodiphenylsilane via a dehydrosilylation/aerobic oxidation cascade, which underwent Hiyama–Denmark cross-coupling[9] to deliver sp^2–sp^2 coupling products (**148**) with aryliodides (Fig. 2b). The capacity of the present strategy was further illustrated by the preparation of diallylsilane **126** and dialkynylsilane **150** from phenyltrihydrosilane, which can be directly converted to silacyclopentene **149** through Grubbs ring-closing metathesis, and silole **151** through intramolecular reductive cyclization[45] followed by Sonogashira cross-coupling, respectively. The ability to control the electronic and steric nature of these silacycles by varying the functional groups allows fine-tuning of their physical properties.

The unique functions of organosilicon polymers ensure their wide application in almost every aspect of human activity[46]. By exploiting eosin Y HAT photocatalysis, functionality on silicon monomers could be easily introduced and fine-tuned to synthesize well-defined functionalized polymer/oligomer architectures (Fig. 2c). A dialkynylsilane possessing a terminal pentafluorobenzene moiety (**152**) was generated by two-step eosin Y catalysis, and this compound condensed with a diazide through click chemistry to afford a silyl triazole oligomer **153**. The two-step synthesis of allylhydrosilane **154** allowed access to hydrosilylation polymer **155** bearing terminal acetate as a handle for post-functionalization. A siloxane polymer **157** could be prepared by polycondensation between dimethoxysilane **156** and a commercial disilyl hydride through Piers–Rubinsztajn reaction[47].

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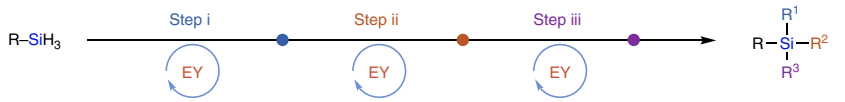
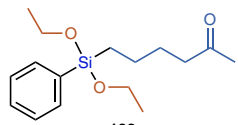
Table 4 | On-demand stepwise decoration of the silicon atom from trihydrosilanes

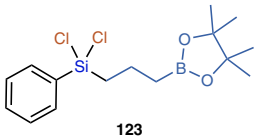


Two-step decoration



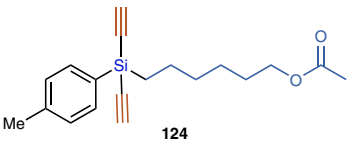
122

H → E
i) 87% yield
ii) 80% yield



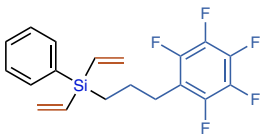
123

H → Cl
i) 90% yield
ii) 97% yield



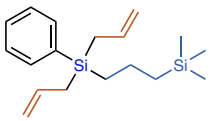
124

H → G
i) 78% yield
ii) 84% yield



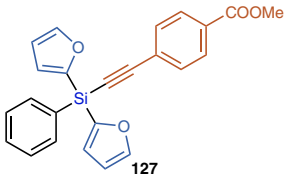
125

H → G
i) 79% yield
ii) 81% yield



126

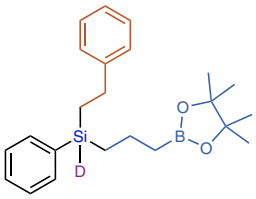
H → G
i) 80% yield
ii) 76% yield



127

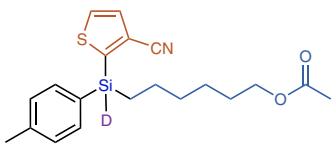
G → G
i) 85% yield
ii) 79% yield

Three-step decoration



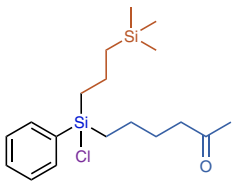
128

H → H → D
i) 90% yield
ii) 70% yield
iii) 95% yield, 96% D incorp.



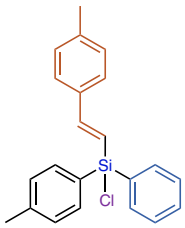
129

H → C → D
i) 78% yield
ii) 71% yield
iii) 89% yield, 91% D incorp.



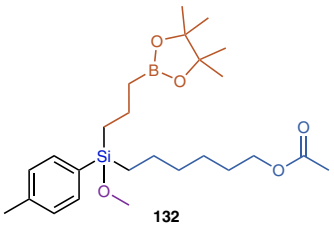
130

H → H → Cl
i) 87% yield
ii) 64% yield
iii) 99% yield



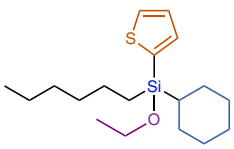
131

C → C → Cl
i) 43% yield
ii) 46% yield
iii) 99% yield



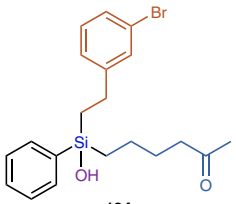
132

H → H → E
i) 78% yield
ii) 81% yield
iii) 80% yield



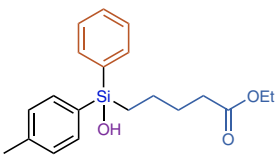
133

G → C → E
i) 90% yield
ii) 54% yield
iii) 82% yield



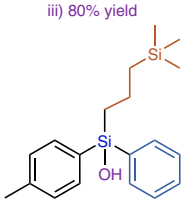
134

H → H → O
i) 87% yield
ii) 74% yield
iii) 68% yield



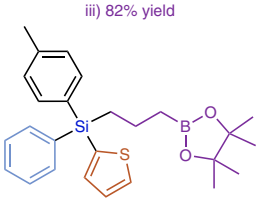
135

H → C → O
i 82% yield
ii) 64% yield
iii) 63% yield



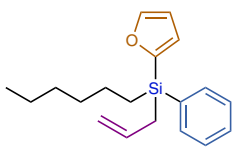
136

C → H → O
i) 43% yield
ii) 86% yield
iii) 73% yield



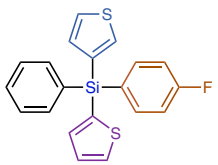
137

C → C → H
i) 43% yield
ii) 54% yield
iii) 71% yield



138

C → G → G
i) 54% yield
ii) 86% yield
iii) 90% yield



139

G → G → C
i) 95% yield
ii) 88% yield
iii) 36% yield

EY, neutral eosin Y; *H*, hydrosilylation; *C*, acceptorless CDC; *D*, H/D exchange; *O*, aerobic oxidation; *E*, bromination/alcohol substitution; *G*, bromination/Grignard; *Cl*, chlorination.

Conclusion

In summary, we have demonstrated that neutral eosin Y-based HAT photocatalysis represents an ideal strategy to enable stepwise functionalizations of multihydrosilanes to access fully substituted silicon reagents in a programmable and on-demand fashion[48]. The success of this strategy relies on (1) the selective and preferable hydrogen-atom

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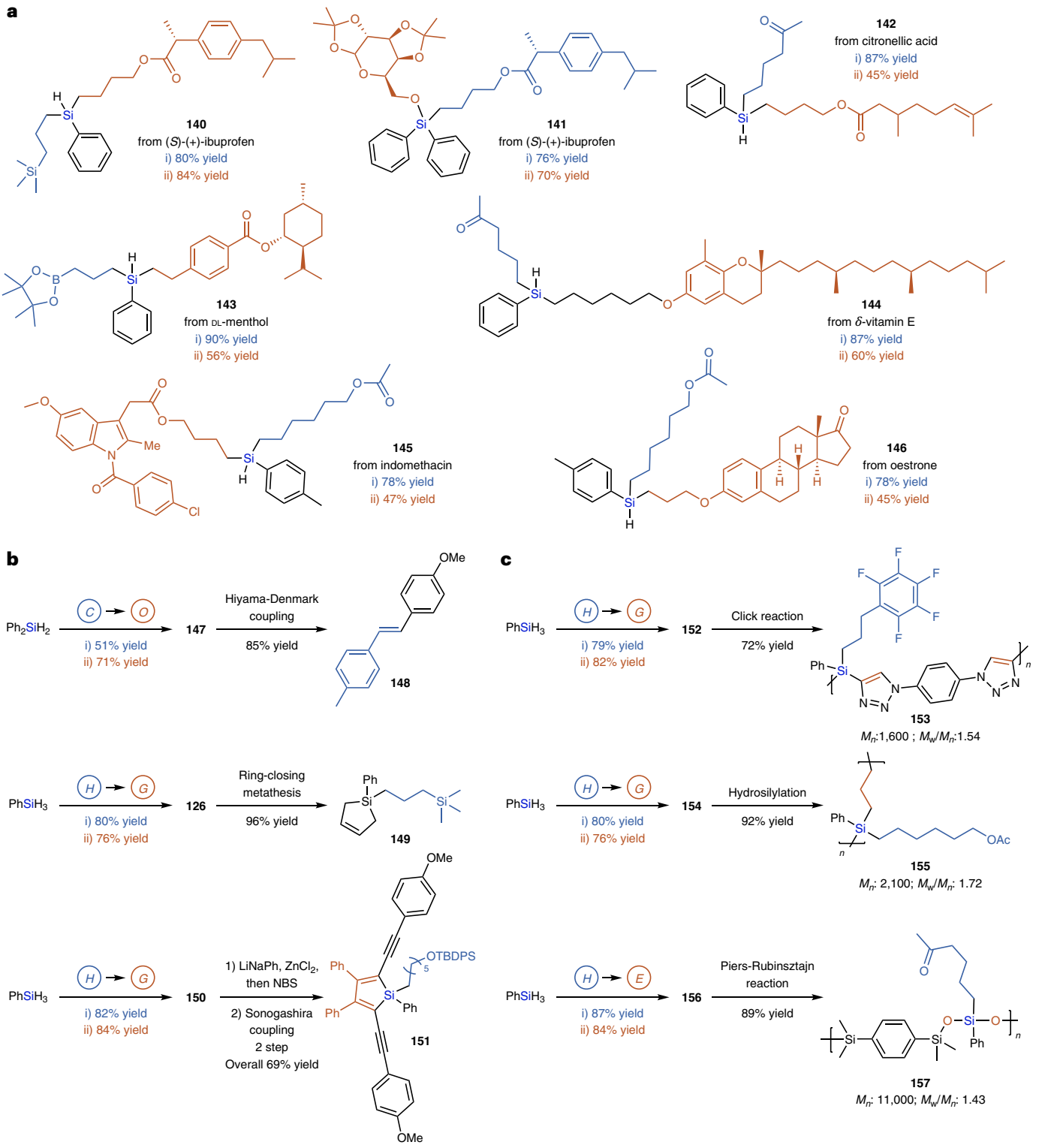

Fig. 2 | Synthetic applications of functional silanes generated from eosin Y-promoted HAT photocatalysis. a, Incorporation of pharmaceutical molecules. **b**, Cross-coupling and silacycle formations. **c**, Synthesis of oligomers and polymers bearing functional handles. (i) and (ii) refer to steps 1 and 2, respectively.

abstraction of Si–H bonds in the presence of various activated C–H bonds; (2) a diverse range of Si–H functionalizations; and (3) highly selective monofunctionalization of di- and trihydrosilanes in batch or flow reactors enabled by eosin Y photocatalysis. This approach is distinguished by its versatility (>150 examples), modularity, excellent selectivity and scalability. Due to the green nature of eosin Y photocatalysis[23] and the wide utility of silicon compounds, this approach promises to find broad applications in both academic and industrial settings.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions

and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41557-023-01155-8.

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Methods

General procedure for the hydrosilylation of styrenes

To a 10-ml seal tube equipped with a magnetic stir bar was added neutral eosin Y (6.5 mg, 0.01 mmol, 5 mol%) and ethyl acetate (2 ml), followed by bubbling with an argon balloon for 20 min. Alkene (0.2 mmol, 1.0 equiv.) and silane (0.4 mmol, 2.0 equiv.) were then added sequentially into the reaction mixture. The resulting mixture was sealed with an aluminium crimp cap and stirred under irradiation with a 40-W blue LED at a distance of 5 cm at 80 °C. Upon completion (monitored by thin layer chromatography (TLC)), the solution was concentrated under vacuum. The residue was further purified by column chromatography over silica gel to afford the desired product.

General procedure for the CDC of hydrosilanes with alkenes

In a glove box, to a 10-ml seal tube equipped with a magnetic stir bar was added neutral eosin Y (6.5 mg, 0.01 mmol, 5 mol%) and distilled and degassed *tert*-butanol (2 ml). An alkene (0.2 mmol, 1.0 equiv.) and silane (0.6 mmol, 3.0 equiv.) were then sequentially added into the reaction mixture. The resulting mixture was sealed with an aluminium crimp cap and taken out of the glove box. The reaction mixture was protected with an argon balloon and was stirred under the irradiation of a 40-W 456-nm Kessil light at a distance of 5 cm at 60 °C. Upon completion (monitored by TLC), the solution was concentrated under vacuum. The residue was further purified by column chromatography over silica gel to afford the desired vinylsilanes.

General procedure for the CDC of hydrosilanes with (hetero) arenes

In a glove box, to a 10-ml seal tube equipped with a magnetic stir bar was added neutral eosin Y (6.5 mg, 0.01 mmol, 5 mol%) and distilled and degassed acetonitrile (2 ml). An arene (0.6 mmol, 3.0 equiv.) and silane (0.2 mmol, 1.0 equiv.) were then sequentially added into the reaction mixture. The resulting mixture was sealed with an aluminium crimp cap and taken out of the glove box. The reaction mixture was protected with an argon balloon and was stirred under the irradiation of a 40-W 456-nm Kessil light at a distance of 5 cm at 60 °C. Upon completion (monitored by TLC), the solution was concentrated under vacuum. The residue was further purified by column chromatography over silica gel to afford the coupling product.

General procedure for deuteration of hydrosilanes

In a glove box, to a 10-ml seal tube equipped with a magnetic stir bar was added the corresponding silane (0.2 mmol, 1.0 equiv.), neutral eosin Y (2.6 mg, 0.004 mmol, 2 mol%), $^{i}Pr_3SiSH$ (3.8 mg, 0.02 mmol, 10 mol%), dry and degassed ethyl acetate (1.5 ml) and D_2O (0.5 ml). The resulting mixture was sealed with an aluminium crimp cap with a septum and taken out of the glove box. After that, the reaction was stirred under the irradiation of a 40-W blue LED at a distance of 5 cm at room temperature for 36–60 h. The solvent was removed under vacuum, and the crude product was purified by column chromatography with hexane as an eluent to give deuterated silane.

General procedure for aerobic oxidation of hydrosilanes to silanols

To a 10-ml seal tube equipped with a magnetic stir bar was added neutral eosin Y (2.6 mg, 0.004 mmol, 2 mol%), silane (0.2 mmol, 1 equiv.) and CH_3CN:H_2O (2 ml:40 µl). The reaction mixture was open to the air (with a syringe needle inserted into the rubber cover to introduce air into the system and avoid heavy solvent evaporation) and stirred under the irradiation of a 40-W blue LED at a distance of 5 cm at room temperature for 24 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum, and the crude product was purified by column chromatography with hexane/ethyl acetate (10:1) as an eluent to give the desired silanol.

General procedure for eosin Y-catalysed monobromination/nucleophilic quenching in continuous-flow reactors

In a glove box, a 500-ml round-bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with phenylsilane (8.64 ml, 70 mmol), neutral eosin Y (455 mg, 0.35 mmol, 0.5 mol%) and distilled dibromomethane (350 ml). The resulting mixture was sealed and taken out from the glove box. The flow apparatus was purged with argon. As shown in Supplementary Fig. 56, an Asia Syrris pump was filled with the reaction reagents and then attached to the flow apparatus with a 25-psi back-pressure regulator. The tubing (polytetrafluoroethylene; outer diameter, 1/16 inch; inner diameter, 0.03 inch; 15.24 m; volume, 2.0 ml) was placed into the centre of a 18-W blue LED strip at ~23 °C (the temperature was controlled by a fan; the distance between the tubing and the light source was ~2 cm). The flow apparatus itself was set up with $T_R = 70$ s and a flow rate of 1,714 µl min^{-1}. After ~5 min of equilibration, the product solution was collected and added into the corresponding quenching reagents (Grignard reagent solution) under an argon atmosphere. After a desired collecting time, the mixture was quenched by water. The organic phase was collected and the organic solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography with hexane as an eluent to afford the desired product.

Data availability

The authors declare that all data supporting the findings of this study are available within the Article and its Supplementary Information. Computational raw data are available at https://doi.org/10.6084/m9.figshare.20154056.

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Author contributions

J.W. conceived the project and directed the research. X.F. and M.Z. designed and performed the experiments. Y.G. and G.C. performed the DFT calculations. Y.L. performed the GC-MS analysis for H_2 source investigation. X.F., M.Z., Q.Z., Y.Z., J. Yu, H.L., W.X., Y.C.T., J. Yan and S.C. conducted experiments to demonstrate the substrate scope. J.W., X.F., M.Z., Z.L., Y.G. and G.C. wrote the paper. All authors commented on the final paper and contributed to the analysis and interpretation of the results.

Competing interests

J.W., F.X. and M.Z. are inventors on an International Patent Application (PCT/SG2022/050462) submitted by the National University of Singapore that covers the synthesis of functional silanes from multihydrosilanes by neutral eosin Y HAT photocatalysis. The other authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41557-023-01155-8.

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