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# Oxidative radical divergent Si-incorporation: facile access to Si-containing heterocycles<sup>†</sup>

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A copper-catalyzed oxidative radical strategy to avoid the use of the highly expensive noble metal/ligand catalytic systems is described, which allows selective activation of dual chemical bonds around the Si-atom center relying on the nature of alkylsilanes. While for tertiary silanes selective functionalization of Si-H/silyl  $C(sp^3)$ -H bonds in intermolecular oxidative annulation cascades with N-(2-(ethynyl)aryl)acrylamides toward silino[3,4-c]quinolin-5(3H)-ones, when using secondary silanes and HSi(TMS)<sub>3</sub>, dual Si-H bonds or Si-H/Si-Si bonds are selectively cleaved leading to 4H-silolo[3,4-c]quinolin-4-ones.

Silicon-containing heterocycles are a class of valuable compounds with unique chemical, physical, physiological and biological properties, and are essential in many domains of chemistry, such as synthesis, agrochemicals, pharmaceuticals, polymers and functional materials.<sup>1</sup> Accordingly, substantial efforts have been made to the development of practical and effective methods for the construction of Si-heterocyclic rings from simple silicon-based synthons.<sup>2</sup> In particular, approaches *via* intermolecular annulation with silicon atoms<sup>3</sup> are exceptionally promising, as they have board applicability for the easy incorporation of different functional groups into the Si-heterocyclic frameworks from the readily available starting materials compared to the common intramolecular annulation methodologies.<sup>4</sup> However, the vast majority of which are achieved by the cleavage of the highly active Si–X (X = C, H, Si, B) bonds.<sup>2–4</sup>

Around the Si-atom center in an alkylsilane core Si-H,  $Si-C(sp^3)$  and silyl  $C(sp^3)$ -H bonds are present which can be

cleaved and functionalized, and the usual reactivity decreased from Si-H to Si-C(sp<sup>3</sup>) to silyl C(sp<sup>3</sup>)-H bonds.<sup>5</sup> Examples for silvl C(sp<sup>3</sup>)-H bond transformation are therefore scarce and remain a great challenge.<sup>6</sup> The available methods include deprotonation/lithiation with n-BuLi,6a radical chlorination with Cl<sub>2</sub>,<sup>6b</sup> iridium-catalyzed borylation,<sup>6c-g</sup> iridium-catalyzed dimerization/silylation<sup>6h</sup> and palladium-catalyzed coupling with aryl bromides.<sup>6i-k</sup> In this context, few papers reported on transformations of the silyl C(sp<sup>3</sup>)-H bonds toward Si-heterocycles, but all require the use of the highly expensive noble metals (e.g. Pd, Ir) and ligand catalytic systems which limit their extensive applications in synthesis. Xi's group<sup>6i</sup> has developed the first Pd-catalyzed intramolecular coupling between silyl C(sp<sup>3</sup>)-H bonds and aryl C-Br bonds leading to six-membered silacycles (Scheme 1a). Very recently, Murai/Takai's group<sup>6h</sup> reported Ir-catalyzed dehydrogenative dimerization of benzylmethylsilanes to access benzo[d][1,3]disilines via the cleavage of dual Si-H, silyl  $C(sp^3)$ -H and aryl  $C(sp^2)$ -H bonds (Scheme 1b). Undoubtedly, new efficient strategies enabling functionalization of Si-H, Si-C(sp<sup>3</sup>) and silyl C(sp<sup>3</sup>)-H bonds in an alkylsilane core, especially for preparing Si-heterocycles, are in high demand.

Among the transformations of Si–H bonds, radical-mediated versions<sup>7</sup> have attracted much attention as they represent a unique tool for constructing diverse Si-based chemical bonds



Scheme 1 Silyl C(sp<sup>3</sup>)-H functionalization approaches.

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by avoiding the use of an expensive noble metal catalytic system. On this basis and in connection with our ongoing interest in the development of oxidative radical chemistry for the efficient transformations of unsaturated carbon-carbon bonds into valuable cyclic compounds, we thought of developing an oxidative radical strategy as a potentially useful new method to achieve selective transformations of Si-H, Si-C(sp<sup>3</sup>) and silyl C(sp<sup>3</sup>)-H bonds. We envisioned that the success of this strategy hinges on the oxidative cleavage of a Si-H bond to form a silvl radical, which would sequentially trigger annulation with the unsaturated carbon-carbon bonds and 1,6-HAT from a silyl C(sp<sup>3</sup>)-H bond to access Si-heterocyclic skeletons. Herein, we report new radicalmediated intermolecular annulation cascades of N-(2-(ethynyl)aryl)-acrylamides with tertiary silanes for producing silino[3,4-c]quinolin-5(3H)-ones by means of a Cu(MeCN)<sub>4</sub>PF<sub>6</sub> catalyst and a tert-butyl peroxybenzoate (TBPB) oxidant (Scheme 1c). This method proceeds via an oxidative radical strategy, which allows the formation of three new chemical bonds, including one C-Si bond and two C-C bonds, through simultaneous functionalization of both Si-H and silyl C(sp<sup>3</sup>)-H bonds. Furthermore, this oxidative radical strategy can be extended to secondary silanes or HSi(TMS)<sub>3</sub> leading to 4H-silolo[3,4-c]quinolin-4-ones via selective cleavage of the corresponding dual Si-H bonds or Si-H/Si-Si bonds.

We first investigated the reaction between *N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide **1a** and triisopropylsilane **2a** under various oxidative conditions (Table 1). By employing 10 mol % of Cu(MeCN)<sub>4</sub>PF<sub>6</sub> and 4 equiv. of TBPB, the reaction of substrate **1a** with silane **2a** was smoothly performed in C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> for 48 h to afford the desired silino[3,4-*c*]quinolin-5(3*H*)-one **3aa** in 67% yield (entry 1). Control experiments showed that both the Cu-catalyst and peroxide-oxidant are crucial for this reaction: the reaction could not occur in the absence of either Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (entry 2) or TBPB (entry 7). Both CuCl and CuBr proved to be less

Table 1 Optimization of the reaction conditions<sup>a</sup> Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mol %) TBPB (4 equiv) PhCF<sub>2</sub>, 120 °C, Ar, 48 h 3aa Entry Variation from the standard conditions Isolated yield (%) 1 None 67 Without Cu(MeCN)<sub>4</sub>PF<sub>6</sub> Trace 2 Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (5 mol%) 3 45 4  $Cu(MeCN)_4PF_6$  (15 mol%) 68 5 CuCl instead of Cu(MeCN)<sub>4</sub>PF<sub>6</sub> 49 6 CuBr instead of Cu(MeCN)<sub>4</sub>PF<sub>6</sub> 51 7 Without TBPB 0 8 TBHP instead of TBPB 6 9 DTBP instead of TBPB 33 10 PhCl instead of PhCF<sub>3</sub> 37 11 tBuOH instead of PhCF<sub>3</sub> 48  $12^{b}$ None 65

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (3 equiv.), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mol%), TBPB (4 equiv.), PhCF<sub>3</sub> (2 mL), 120  $^{\circ}$ C, argon and 48 h. <sup>*b*</sup> **1a** (1 mmol).

efficient than  $Cu(MeCN)_4PF_6$  (entries 5 and 6). Notably, performing the reaction with other oxidant, including TBHP and DTBP, resulted in lower efficiency (entries 8 and 9). Screening the effect of solvents revealed that the reaction in  $C_6H_5CF_3$  was preferential (entries 1, 10 and 11). Delightfully, a scale-up experiment with 1 mmol of **1a** proceeded efficiently, giving **3aa** in 65% yield (entry 12).

With the optimized reaction conditions in hand, the scope of this protocol with respect to N-(2-(ethynyl)aryl)acrylamides and tertiary silanes was exploited (Table 2). Initially, substitution on the nitrogen atom was investigated. Substrates 1b-e, possessing a N-Bn group, a N-allyl group, a N-Ts group or a free *N*-H group, smoothly reacted with silane 2a,  $Cu(MeCN)_4PF_6$  and TBPB to afford silino[3,4-c]quinolin-5(3H)-ones 3ba-ea in moderate to good yields.<sup>[8]</sup> Gratifyingly, a wide range of substituents, namely, MeC<sub>6</sub>H<sub>4</sub>, MeOC<sub>6</sub>H<sub>4</sub>, PhC<sub>6</sub>H<sub>4</sub>, ClC<sub>6</sub>H<sub>4</sub>, FC<sub>6</sub>H<sub>4</sub>, thiophen-2-yl and n-pentyl, at the terminal alkyne were well tolerated, and their electronic properties and steric hindrance slightly affected the reactivity (3fa-na). While substrates 1f and 1k, having a Me group at the para or meta position on the aryl ring at the terminal alkyne, afforded 3fa and 3ka in 71% and 64% yields,<sup>9</sup> respectively, substrate 1j with a weak electron-withdrawing  $FC_6H_4$ group was a suitable substrate as well to provide 3ja in 57% yield. It is noted that terminal alkyne 10 was competent for producing 30a. Substrate 1p bearing a CF<sub>3</sub> group at the 5 position of the N-aryl moiety provided 3pa in 71% yield. Likewise, substrates 1q-r having a Me or a Cl group at the 4 position of the N-aryl moiety succeed to assemble 3qa-ra efficiently. Notably,



Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mol%) TBPB (4 equiv) PhCF<sub>3</sub>, 120 °C, Ar, 48 h R 3 = Me, **3fa**, 71% R<sup>3</sup> = Bn, **3ba**, 70% R<sup>5</sup> = MeO, **3ga**, 61% R<sup>5</sup> = Ph, **3ha**, 51% R<sup>5</sup> = Cl, **3ia**, 72% = allyl, 3ca, 68%  $R^3 = Ts 3da 60\%$ R<sup>5</sup> = F, 3ja, 57% R<sup>2</sup> = Me, 3qa, 47% 3ab. 61% (dr = 1:1) R<sup>2</sup> = CL 3ra, 63% C<sub>6</sub>H<sub>13</sub> SiEt 0 3ac. 43% (dr > 20:1) 3ad. 50% (dr > 20:1)

 $^a$  Reaction conditions: 1 (0.2 mmol), 2 (3 equiv.), Cu(MeCN)\_4PF\_4 (10 mol%), TBPB (4 equiv.), PhCF\_3 (2 mL), 120 °C, argon and 48 h.  $^b$  *t*BuOH (2 mL) instead of PhCF\_3.

selectivity toward functionalization of the aryl  $C(sp^2)$ -H bond, not the silyl  $C(sp^3)$ -H bond, occurs when a phenyl group or a benzyl group was presented at the 2 position of the acrylamide moiety (**4sd-td**).

Next, the compatibility of this protocol with different types of silanes **2** was tested. Three other tertiary silanes, diisopropyl-(*p*-tolyl)silane **2b**, trihexylsilane **2c** and triethylsilane **2d**, were also viable for producing the desired silino[3,4-c]quinolin-5(3H)-ones **3ab–ad** in reasonable yields (Table 2). For diethylsilane **2e** as outlined in Table 3, a secondary silane, dual Si–H bond functionalization takes precedence over the Si–H/silyl C(sp<sup>3</sup>)–H bond functionalization, thus giving 4*H*-silolo[3,4-c]quinolin-4-one **5ae** in 73% yield. Notably, the reaction can proceed efficiently without Cu catalysts at a lower loading of TBPB.

Diphenylsilane 2f was also subjected to dual Si-H bond functionalization (5af). Gratifyingly, HSi(TMS)3 2g was a competent substrate which undergoes Si-H/Si-Si bond cleavage and annulation with various N-(2-(ethynyl)aryl)acrylamides to afford 4H-silolo-[3,4-c]quinolin-4-ones 5 (Table 3). In the presence of TBPB and HSi(TMS)<sub>3</sub> 2g, substitution in the nitrogen atom with Me, Bn, N-Ts and free N-H groups was well tolerated as demonstrated by the construction of 5ag-bg and 5dg-eg in high yields. The use of thiophen-2-yl-substituted internal alkyne 1m or terminal alkyne 10 both smoothly afforded 5mg and 5og in synthetically useful yields.<sup>9</sup> Substrate **1p** having an electron-withdrawing CF<sub>3</sub> group was transformed into 5pg in 83% yield. Substitution factors in the 2 position of the acrylamide moiety seem to have an impact on the chemoselectivity of the reaction, as the 2-phenyl-substituted substrate 1s afforded 4H-silolo[3,4-c]quinolin-4-one 5sg via Si-H/Si-Si bonds cleavage,9 but the 2-benzyl-substituted substrate 1t yielded benzo *j* phenanthridin-6(5*H*)-one 4tg by Si-H/aryl C(sp<sup>2</sup>)-H bond cleavage. The reason may be that the formation of the stable sixmembered ring is prior to the five-membered ring. Delightfully, aliphatic alkyne 1u proceeded well, giving 5ug in 59% yield.

The reaction might include a free-radical process, as the control experiment between substrate **1a** and silane **2a** was



<sup>*a*</sup> Reaction conditions: **1** (0.2 mmol), **2** (2 equiv.), TBPB (2 equiv.), PhCF<sub>3</sub> (2 mL), 120 °C, argon and 15 h. <sup>*b*</sup> Cu(MeCN)<sub>4</sub>PF<sub>4</sub> (10 mol%), TBPB (2 equiv.), argon and 15 h.



Scheme 2 Control experiments and possible reaction mechanisms.

completely inhibited by a stoichiometric amount of radical inhibitor, such as TEMPO, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and hydroquinone (Scheme 2a).

The possible mechanisms for the reaction with different types of silanes were proposed (Scheme 2b).<sup>5-8</sup> With the aid of the active Cu<sup>I</sup> species, TBPB readily splits upon heating to give the *tert*-butoxyl radical and the Cu<sup>II</sup>(PhCO<sub>2</sub>) species.<sup>7</sup> Subsequently, the *tert*-butoxyl radical cleaved the Si–H bond in tertiary silane 2a, delivering the silicon-centered radical **A**, followed by addition across the C=C bond of substrate 1a produces the alkyl radical intermediate **B**. Annulation of intermediate **B** occurs to form vinyl radical intermediate **C**, which sequentially undergoes 1,6-HAT with the silyl C(sp<sup>3</sup>)–H bond<sup>8a</sup> to afford silyl alkyl radical intermediate **E**. Finally, the oxidation of intermediate **E** through single electron oxidation by the Cu<sup>II</sup>(PhCO<sub>2</sub>) species and subsequent deprotonation afford **3aa**.

When silanes are changed to secondary silanes, intermediate C' sequentially undergoes 1,5-HAT with the Si-H bond,<sup>8b</sup> further annulation, and oxidation, affording 4*H*-silolo[3,4-*c*]quinolin-4-ones 5. When silanes are changed to HSi(TMS)<sub>3</sub>, intermediate C' is potentially reactive for attacking the silyl group in an S<sub>H</sub>i manner<sup>8*c*-*f*</sup> to give a Me<sub>3</sub>Si radical and 5.

In summary, we have developed the first example of an intermolecular annulation cascades of N-(2-(ethynyl)aryl)-acrylamides with tertiary silanes *via* Cu-catalyzed oxidative radical functionalization of Si–H and silyl C(sp<sup>3</sup>)–H bonds. This oxidative radical strategy avoids the use of the highly expensive noble metal/ligand catalytic systems, and represents an important methodology that is expected to be capable of being substantially expanded to other system in highly selective transformations of the chemical bonds around the Si-atom center. Notably, this strategy enables an efficient and selective conversion of We thank the Natural Science Foundation of China (No. 21472039, 21625203 and 21762030), the Jiangxi Province Science and Technology Project (No. 20171BCB23055, 20171ACB21032, 20171ACB20015 and 20165BCB18007), and the Technology Project of Jiangxi Provincial Department of Education (GJJ160725) for financial support. Dr Y. Yang also thank the Hunan Provincial Innovation Foundation for Postgraduate (CX2017B144).

### Conflicts of interest

There are no conflicts to declare.

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- 9 CCDC 1569980 (3fa), 1569934 (5mg) and 1570015 (5sg).†.