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Identification of Bond-Weakening Spirosilane Catalyst for Photoredox α-C–H Alkylation of Alcohols

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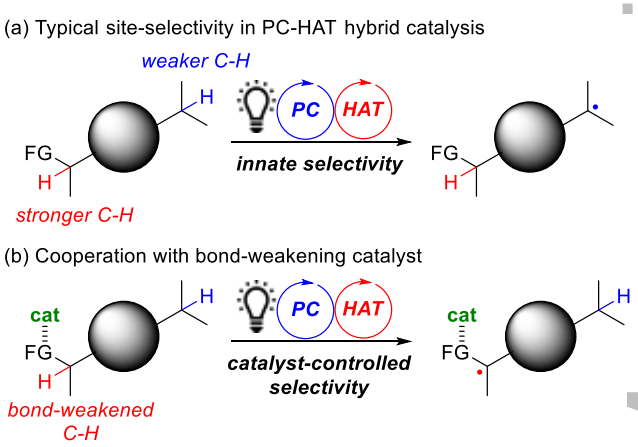
Abstract. The development of catalyst-controlled site-selective C(sp^3)–H functionalization is a current major challenge in organic synthesis. This paper describes DFT-guided identification of pentavalent silicate species as a novel bond-weakening catalyst for the α-C–H bonds of alcohols together with a photoredox catalyst and a hydrogen atom transfer catalyst. Specifically, Martin's spirosilane accelerated α-C–H alkylation of alcohols.

Keywords: alcohols; bond-weakening; C–H activation; photoredox catalysis; regioselectivity; silicates



Scheme 1. Bond-weakening Strategy toward Catalyst-controlled Site-selective C(sp^3)-H Functionalization

C–H functionalization reactions facilitate the discovery and lead optimizations of functional materials and drugs by realizing efficient production of structurally intractable compounds and late-stage diversification.[1] Particularly, C(sp^3)–H functionalizations are desired for drug discovery due to the tendency toward achieving higher success rates with C(sp^3)-rich molecules.[2,3]

Many groups, including ours, are studying C(sp^3)–H functionalizations promoted by the combination of a photoredox catalyst (PC) and hydrogen atom transfer (HAT) catalyst.[4,5] Despite the great bond dissociation energies (BDEs) of C(sp^3)–H bonds, the reactions generally proceed under mild conditions and exhibit high functional group tolerance. In most cases, however, C(sp^3)–H bonds with the smallest BDE or the most hydridic C–H bonds in a substrate are preferentially converted (Scheme 1a). Realizing catalyst-controlled site-selectivity in PC-HAT hybrid catalysis thus remains a challenge.

One potential strategy to furnish catalyst-controlled site-selectivity is the cooperative use of a bond-weakening catalyst (Scheme 1b). Coordination-induced bond-weakening of N–H and O–H bonds by low-valent metals have been studied in the field of inorganic chemistry.[6] Application of the bond-weakening phenomenon to organic synthesis, however, is limited.[7,8] Knowles and co-workers reported pioneering work on N–H bond-weakening catalysis in organic synthesis.[8] A coordination-induced bond-weakening strategy using low-valent metals, however, would be problematic in combination with the strongly oxidative PC-HAT hybrid catalysis for targeting C–H bonds. Alternatively, hydrogenphosphate[9a,b] and diphenylborinic acid[10] act as bond-weakening additives or catalysts to accelerate α-C–H alkylation of alcohols promoted by PC-HAT hybrid catalysis by increasing the electron density of the oxygen atom through hydrogen bonding or borate formation and facilitating the HAT process from the α-C–H bonds. The development of a structurally novel bond-weakening catalyst will provide great potential for exploring unprecedented reactivity, selectivity, and substrate generality in C(sp^3)–H functionalizations. Here, on the basis of DFT calculation-guided screening, we identified a structurally tunable pentavalent silicate species as a bond-weakening catalyst. This silicate species accelerated α-C–H alkylation of alcohols promoted by PC-HAT hybrid catalysis.

Silicon is an oxophilic element. Nevertheless, alkoxy-ligands on a silicon atom are exchangeable

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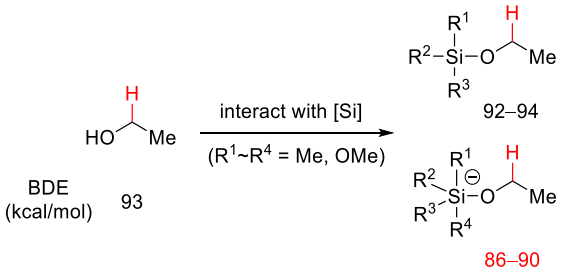
through the formation of hypervalent silicate species.[11] We conducted DFT calculations to estimate the BDEs of α-C–H bonds in various silyl ethyl ethers as model compounds. When a pentavalent anionic silicate was formed, the BDE of the α-C–H bond was weakened by 3–7 kcal/mol, whereas neutral silyl ethers never underwent such bond-weakening (Scheme 2).[12] From these results, we hypothesized that silicon compounds, which easily form pentavalent silicates, could potentially be utilized as an alcohol-selective bond-weakening catalyst by accelerating the HAT process at the α-C–H bond of alcohols.

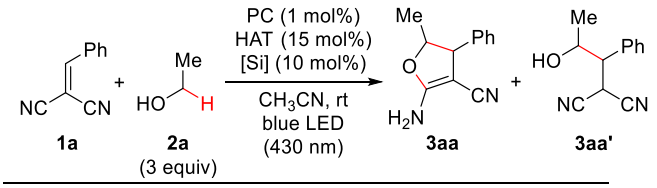


Scheme 2. Bond-weakening Effects by Silicate Formation Supported by DFT Calculation

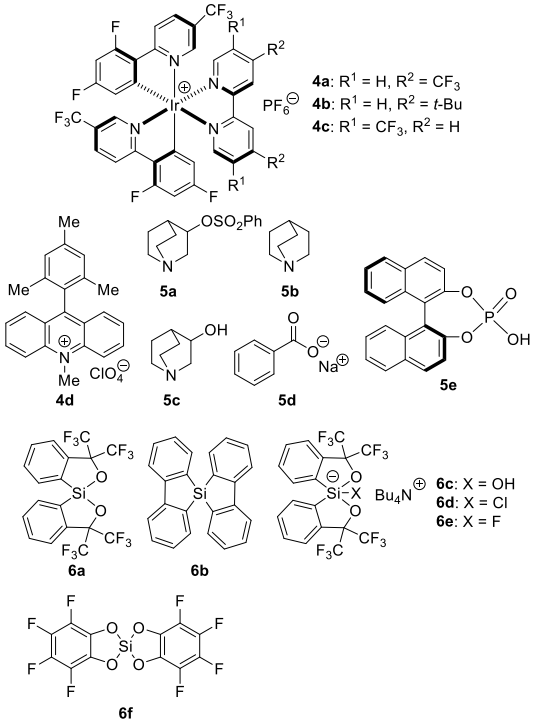
According to this hypothesis, we screened silicon compounds that would accelerate α-C–H alkylation of alcohols catalyzed by PC-HAT hybrid systems (Table 1). Benzalmalononitrile (**1a**), ethanol (**2a**), photoredox catalyst **4a**,[13] and HAT catalyst **5a**[14] were selected as the initial components. In the absence of any silicon source under visible-light irradiation, the desired C–H alkylation products were obtained as a mixture of **3aa** and **3aa'** in only 24% yield (Table 1, Entry 1).[15] Next, a catalytic amount of various silanes was added to this reaction system (Entries 2–11). Only the addition of Martin's spirosilane (**6a**)[16] drastically improved the yield to 81% (Entry 2). When the reaction concentration was changed to 0.05 M, the yield further improved to 94%. Simple silanes did not improved the yield (Entries 3–5), probably due to the inefficient formation of hypervalent silicate species with **2a**. Spirosilane **6b**, which forms pentavalent silicate species,[17] improved the yield by only 15% (Entry 6) compared with the absence of any silicone source. Stable and isolatable pentavalent silicates (**6c**, **6d**, **6e**)[17] prepared from **6a** improved the yield to only a limited extent (Entries 7–9). Lewis acidic bis(perfluorocatecholato)silane[18] (**6f**) inhibited this reaction (Entry 10).

We next tried other PCs (Entries 11–13). When using a PC with either a lower oxidation potential (**4b**) or a much higher oxidation potential (**4d**), the desired products **3aa** and **3aa'** were not obtained (Entries 11 and 13). When **4c**[13] was used, the product was obtained in 63% yield (Entry 12). The oxidation potential of PC **4c** was almost identical to that of **4a** ($E(Ir^{III*}/Ir^{II})$ = +1.68 V for **4c** and +1.65 V for **4a** *vs* SCE in CH_3CN), but the slightly weaker

Table 1. Optimization of Reaction Conditions[a]



Entry	PC	HAT	[Si]	Yield/%[b]
1	**4a**	**5a**	none	24
2	**4a**	**5a**	**6a**	81 (94)[c]
3	**4a**	**5a**	$Si(OEt)_4$	20
4	**4a**	**5a**	$Si(OEt)_3F$	30
5	**4a**	**5a**	$Me_3SiC_6F_5$	27
6	**4a**	**5a**	**6b**	39
7	**4a**	**5a**	**6c**	37
8	**4a**	**5a**	**6d**	38
9	**4a**	**5a**	**6e**	31
10	**4a**	**5a**	**6f**	5
11	**4b**	**5a**	**6a**	<1
12	**4c**	**5a**	**6a**	63
13	**4d**	**5a**	**6a**	0
14	**4a**	**5b**	**6a**	5
15	**4a**	**5c**	**6a**	<1
16	**4a**	**5d**	**6a**	0
17	**4a**	**5e**	**6a**	0
18	none	**5a**	**6a**	0
19	**4a**	None	**6a**	0
20[d]	**4a**	**5a**	**6a**	0



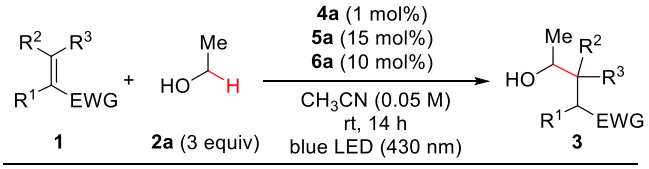
[a] General conditions: **1a** (1 equiv, 0.10 mmol), **2a** (3 equiv), PC (1 mol%), HAT (15 mol%), Si source ([Si]: 10 mol%), CH_3CN (0.1 M to **1a**), blue LED was irradiated at room temperature for 14 h. [b] Combined yield (**3aa** + **3aa'**) was determined by ^1H NMR analysis in the presence of 1,1,2,2-tetrachloroethane as an internal standard. [c] CH_3CN (0.05 M to **1a**). [d] No light irradiation.

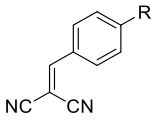
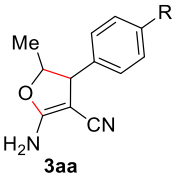
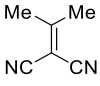
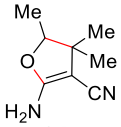
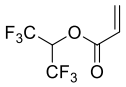
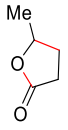
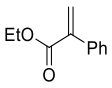
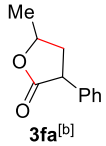
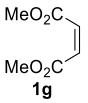
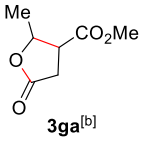
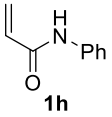
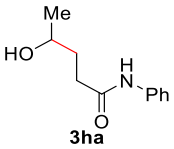
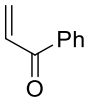
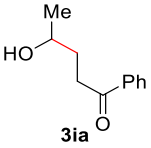
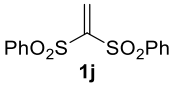
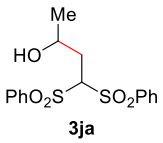
reduction potential ($E_{1/2}(Ir^{II}/Ir^{III})$ = –0.69 V for **4b** and –0.79 V for **4a** *vs* SCE in CH_3CN) perhaps rendered the catalyst regeneration step more difficult. When other HAT catalysts (**5d**[19] and **5e**[5b]) and quinuclidine derivatives (**5b**[9a, 9b, 20] and **5c**) were used instead of **5a**, the C–H alkylation product was obtained in only low yield (Entries 14–17). **5a** might function as not only a HAT catalyst but also a base to form a silicate.[21] When we applied previously reported reaction conditions of α-C–H alkylation of alcohols[9a, 9b, 10] to **1a** and **2a**, products **3aa** + **3aa'** were not obtained.[12] In the absence of any elemental factors, PC, HAT, or blue LED irradiation, the products were not obtained (Entries 18–20).

Having determined the optimal conditions (Table 1, Entry 2), we next investigated the substrate scope (Tables 2 and 3). In many cases, C–H alkylated products were isolated after cyclization (Table 2, Entries 1–6 and Table 3). Using ethanol (**2a**) as an alcohol substrate, arylidene malononitriles **1a**–**1c** led to products **3aa**–**3ca** in excellent yield regardless of the presence of an electron-donating or -withdrawing group (Table 2, Entries 1–3). The reaction with sterically hindered dialkylidene malononitrile **1d** also proceeded in good yield (**3da**, Entry 4). A range of acrylates was applicable as acceptors (Entries 5–7). *N*-Phenylacrylamide (**1h**), phenylvinylketone (**1i**) and 1,1-bis(phenylsulfonyl)ethylene (**1j**) were also competent (Entries 8-10).

We then investigated C–H alkylation between various alcohols and **1e** or **1f** (Table 3). The reaction with methanol (**2b**) produced corresponding lactone **3fb** in moderate yield due to instability of the primary carbon radical (Table 3, Entry 1). Despite increased steric hindrance at the β-position, **3fc** was produced in excellent yield (Entry 2). Long-chain alcohol **2d** could be used to produce lactone **3ed** in high yield (Entry 3). The reaction proceeded efficiently even when using alcohol **2e** having an electron-withdrawing group, although the isolated yield of lactone **3ee** was low due to its volatility (Entry 4). The presence of a *p*-toluenesulfonylamide functional group acting as a hydrogen-bonding donor was not problematic for the reaction, and product **3ef** was obtained in good yield (Entry 5). For mono-protected diol **2g**, C–H alkylation occurred selectively at the α-position of the unprotected hydroxy group to produce **3eg** in excellent yield (Entry 5). Alcohols containing benzylic C–H bonds (**2h**), α-C–H bonds of a cyclic ether (**2i**), and α-C–H bonds of an *N*-heterocycle (**2j**) afforded the corresponding products. Although these C–H bonds are generally more reactive than the α-C–H bonds of alcohols in the HAT process, the desired lactones **3eh**–**3ej** were selectively obtained in good yield (Entries 7–9).

Table 2. Substrate Scope of Acceptors



Entry	Acceptor	Product	Yield/%[a]
1	 **1a** (R = H)	 **3aa**	94[c]
2	**1b** (R = OMe)	**3ba**	81[c]
3	**1c** (R = CF_3)	**3ca**	75[c]
4	 **1d**	 **3da**	61
5	 **1e**	 **3ea**	52 (80)[d]
6	 **1f**	 **3fa**[b]	92[e]
7	 **1g**	 **3ga**[b]	94[f]
8	 **1h**	 **3ha**	45
9	 **1i**	 **3ia**	42
10	 **1j**	 **3ja**	44

[a] Isolated yields. ^{1}H NMR yields (1,1,2,2-tetrachloroethane was used as an internal standard) are described in the parenthesis. [b] After blue LED irradiation, acidic work-up (with Amberlyst-15 (100 mg) for 3 h at 50 degrees) was conducted. [c] d.r. = 1:1.0 ~ 1:1.5. See SI for details. [d] Low isolated yield was due to volatility of the product. [e] *cis/trans* = 2/1. [f] *cis/trans* = 1.5/1.

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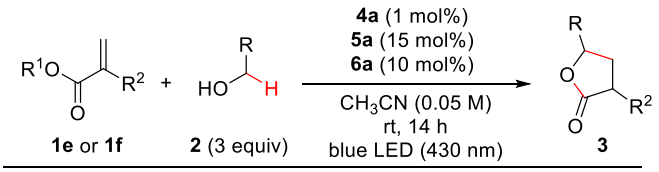
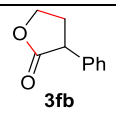
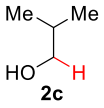
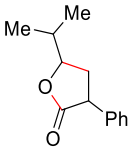
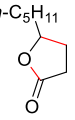
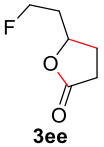
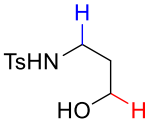
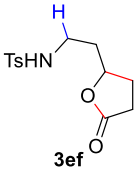
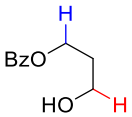
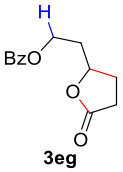
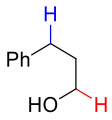
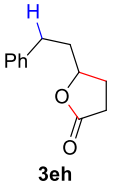
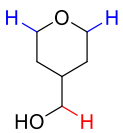
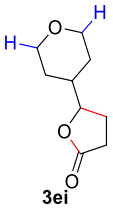
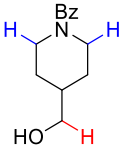
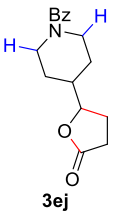
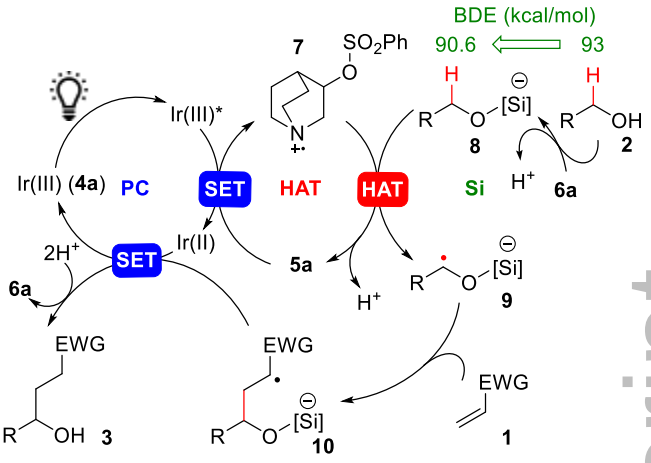
Table 3. Substrate Scope of Alcohols



Entry	Alcohol	Product	Yield/%[a]
1	 **2b**	 **3fb**	38[b]
2	 **2c**	 **3fc**	84[b][c]
3	 **2d**	 **3ed**	82
4	 **2e**	 **3ee**	25 (89)[d]
5	 **2f**	 **3ef**	75
6	 **2g**	 **3eg**	85
7	 **2h**	 **3eh**	75
8	 **2i**	 **3ei**	62
9	 **2j**	 **3ej**	69

[a] Isolated yields. ^{1}H NMR yields (1,1,2,2-tetrachloroethane was used as an internal standard) are described in the parenthesis. [b] After blue LED irradiation, acidic work-up (with Amberlyst®-15 (100 mg) for 3 h at 50 °C) was conducted. [c] *cis/trans* = 2/1. [d] Low isolated yield was due to volatility of the product.



Scheme 3. Proposed Catalytic Cycle

Our working hypothesis for the catalytic cycle of this reaction is shown in Scheme 3. First, PC **4a** is excited by visible light irradiation. The excited PC ($E(Ir^{III}*/Ir^{II})$ = +1.65 V *vs* SCE)[13] oxidizes the HAT catalyst **5a** ($E_{1/2}$ = +1.41 V *vs* SCE)[14] to generate radical cation **7** and Ir(Ⅱ) species. Silane catalyst **6a** forms an anionic pentavalent silicate **8** through a reaction with alcohol **2**, leading to the lowered BDE of the α-C–H bond by 2–3 kcal/mol (supported by DFT calculations[12]). Quinuclidinium radical **7** abstracts the α-C–H bond of silicate **8** to produce carbon radical **9** and regenerate **5a** after releasing a proton. Improvement of the yield might also partially originated from electrostatic interation between the anionic silicates and the quinulidiunm radical cation during this HAT process.[22] The thus-generated carbon radical **9** reacts with acceptors **1**, forming stabilized radical **10**. After reducing **10** by the Ir(Ⅱ) species ($E_{1/2}$ (Ir^{II}/Ir^{III}) = –0.79 V *vs* SCE)[13], protonation, and alcohol exchange at the silane center, product **3** is generated.

In conclusion, we demonstrated that Martin's spirosilane **6a** functioned as a novel bond-weakening catalyst for the α-C–H bond of alcohols by forming silicate species. In cooperation with a PC-HAT hybrid system, α-C–H alkylation of alcohols was realized using a range of substrates. Further applications of this bond-weakening catalyst to other reactions are ongoing in our laboratory.

Experimental Section

Typical Procedure for Photocatalytic α-C–H Alkylation of Alcohols Catalyzed by Silicon-Photoredox-HAT Hybrid System (represented by the synthesis of 3aa)

$Ir[dF(CF_3)ppy]_2[4,4'\text{-}d(CF_3)bpy]PF_6$ (**4a**, 1.2 mg, 0.001 mmol, 1 mol%), HAT catalyst **5a** (4.0 mg, 0.015 mmol, 15 mol%), Martin's spirosilane (**6a**, 5.1 mg, 0.01 mmol, 10 mol%), and benzalmalononitrile (**1a**, 15.4 mg, 0.1 mmol, 1 eq) were added to a dried screw-cap vial. Ethanol (**2a**, 17.5 µL, 0.3 mmol, 3 equiv) and degassed CH_3CN (2 mL) were added to the vial under argon atmosphere in a glovebox. The vial was sealed with the screw cap. The resulting mixture was then placed near a light source[23] and irradiated with blue LED lights while stirring at ambient temperature for 14 h. After evaporation, the residue was purified by flash column chromatography to afford **3aa** (18.8 mg, 94 % yield, white solid).

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COMMUNICATION

Identification of Bond-Weakening Spirosilane Catalyst for Photoredox α-C–H Alkylation of Alcohols

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