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Silver-Mediated Oxidative Functionalization of Alkylsilanes

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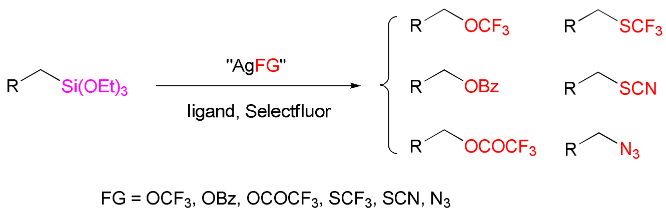
A general approach to the functionalization of aliphatic C-Si bonds in the presence of silver salt and oxidant has been reported. This strategy encompasses a range of valuable C-Si transformations, including the direct conversions of a C-Si bond to C-OCF_3, C-OBz, C-$OCOCF_3$, C-SCF_3, C-SCN, C-N_3 bonds. Among them, trifluoromethoxylation of alkylsilanes is reported in the first time. In addition, mechanistic studies indicate that the reaction may proceed through a radical mechanism.

Organosilicon compounds have a multitude of applications in basic science, medicine, and industry due to their stability, non-toxicity, and natural abundance of silicon.[1] For example, organosilicon compounds have been received much attention to the cross-coupling reaction.[2] However, the strategic functionalization of aliphatic carbon-silicon bonds is limited.[3] For example, trifluoromethoxy (OCF_3) group and trifluoromethylthio (SCF_3) group are becoming increasingly important in medicinal, agrochemical and materials science due to their strong electron-withdrawing effect and high lipophilicity.[4] Thus, the development of efficient methods for the synthesis of OCF_3 and SCF_3 compounds is of great importance.[5,6] However, the trifluoromethoxylation and trifluoromethylthiolation of organosilanes are extremely underdeveloped.[7] To the best of our knowledge, no trifluoromethoxylation of alkylsilanes has been reported to date. Herein, we sought a strategy that would facilitate the direct conversion of aliphatic C-Si bonds into a variety of functional groups, including the trifluoromethoxylation and trifluoromethylthiolation of alkylsilanes (Scheme 1).

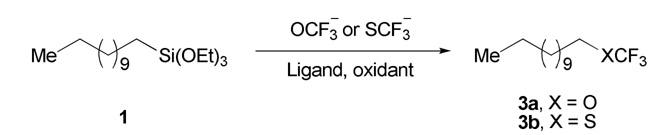


Scheme 1. Silver-mediated oxidative functionalization of alkylsilanes.

Methods for aliphatic C−Si oxidation,[8] halogenation,[9] and azidation[10] have been reported, but new reaction systems are typically required to promote each transformation. In addition, methods for trifluoromethoxylation of organosilanes are rare, and only two examples were reported. In 2008, using trifluoromethyl triflate as the trifluoromethoxylation reagent, Kolomeitsev group reported the trifluoromethoxylation of arynes from o-trimethylsilylphenyl-triflate.[7a] In 2018, trifluoromethyl benzoate (TFBz) was reported as a new trifluoromethoxylation reagent by Hu group, and was used to prepare trifluoromethyl ether from trifluoromethoxylation-halogenation of arynes, which was generated in situ from o-trimethylsilylphenyl triflate.[7g] Despite the advances of these methods, trifluoromethoxylation of alkylsilanes was not reported to date, so the development of a general approach for functionalization including trifluoromethoxylation of alkylsilanes is highly desirable.

Inspired by our previous work of a hypervalent iodine-mediated fluorination of alkylsilanes using fluoride ions as the fluorinating agent,[9e] we became interested in the possibility of functionalization

Table 1. Optimizing reaction conditions.[a]



entry	$^-OCF_3$ or $^-SCF_3$	Ligand	Oxidant	Yield (%)[c]
1	Et_3N•3HF, TFMS (**2**)	3,4,7,8-Me_4-Phen	Selectfluor	**3a**, 0
2	CsF, TFMS (**2**)	3,4,7,8-Me_4-Phen	Selectfluor	**3a**, 0
3	TBAF, TFMS (**2**)	3,4,7,8-Me_4-Phen	Selectfluor	**3a**, 0
4	FeF_3, TFMS (**2**)	3,4,7,8-Me_4-Phen	Selectfluor	**3a**, 0
5	AgF, TFMS (**2**)	3,4,7,8-Me_4-Phen	Selectfluor	**3a**, 61
6	AgF, TFMS (**2**)	Phen	Selectfluor	**3a**, 45
7	AgF, TFMS (**2**)	neocuproine	Selectfluor	**3a**, 8
8	AgF, TFMS (**2**)	4,7-Ph_2-Phen	Selectfluor	**3a**, 52
9	AgF, TFMS (**2**)	5,6-dione-Phen	Selectfluor	**3a**, 2
10	AgF, TFMS (**2**)	dtbpy	Selectfluor	**3a**, 56
11	AgF, TFMS (**2**)	3,4,7,8-Me_4-Phen	NFSI	**3a**, 0
12	AgF, TFMS (**2**)	3,4,7,8-Me_4-Phen	PhIO	**3a**, 0
13	AgF, TFMS (**2**)	3,4,7,8-Me_4-Phen	$PhI(OAc)_2$	**3a**, 0
14	AgF, TFMS (**2**)	3,4,7,8-Me_4-Phen	$K_2S_2O_8$	**3a**, 0
15[b]	$AgSCF_3$	dtbpy	Selectfluor	**3b**, 80

[a] General conditions: **1** (1.0 equiv), silver salt (4.0 equiv), TFMS (**2**) (5.0 equiv), ligand (0.3 equiv), oxidant (3.0 equiv), MeCN/DCM (v/v 7:2), 25 °C, N_2. [b] $AgSCF_3$ (4.0 equiv), CsF (4.0 equiv), dtbpy (0.4 equiv), Selectfluor (3.0 equiv), MeCN/dioxane (v/v 1:1), 50 °C, N_2. [c] Yields were determined by ^{19}F NMR with benzotrifluoride as a standard.

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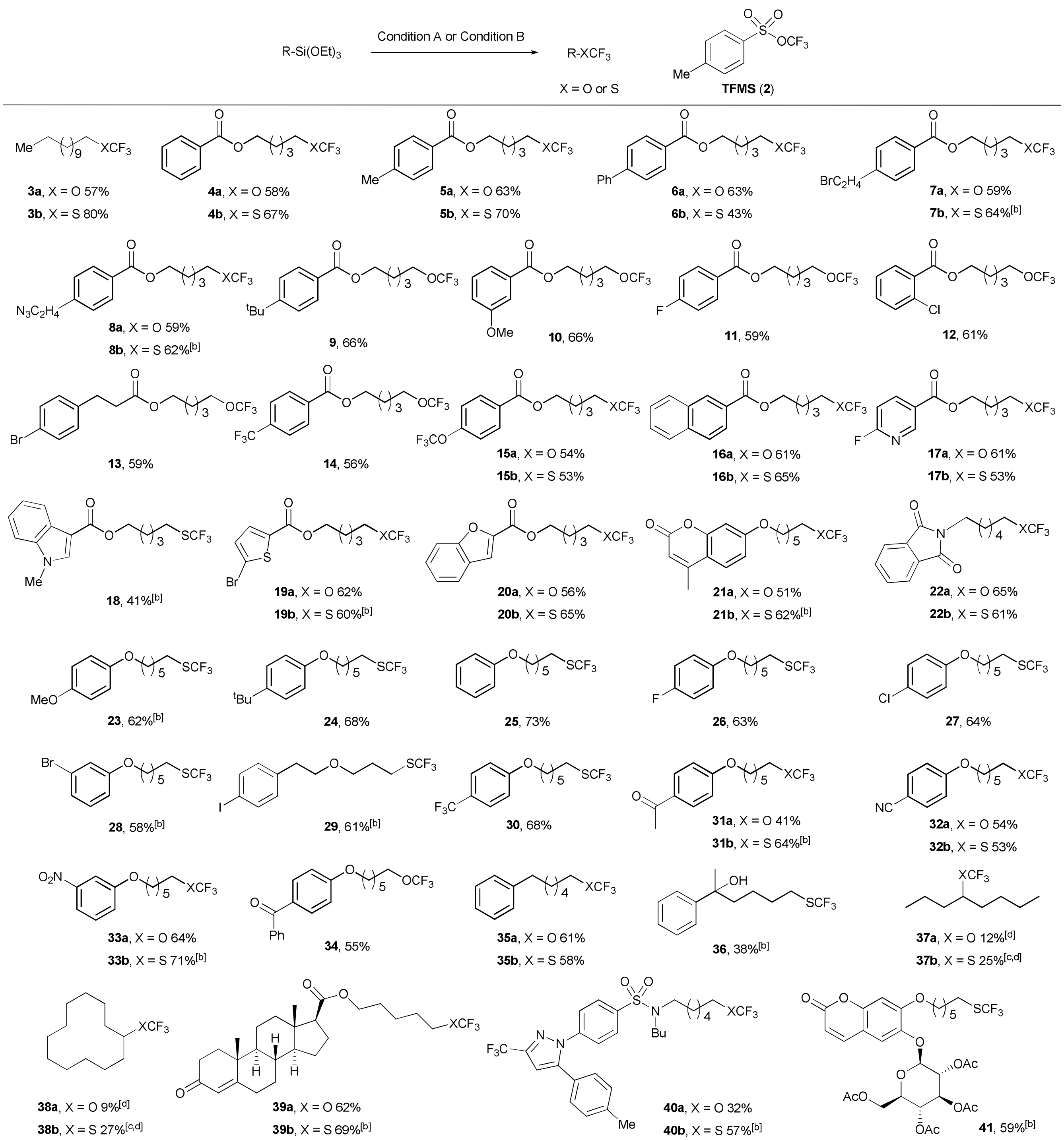
Table 2. Substrate scope for silver-mediated oxidative trifluoromethoxylation and trifluoromethylthiolation of alkylsilanes



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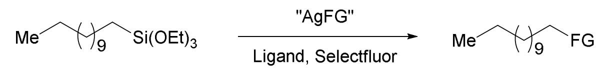
[a] Condition A: alkylsilanes (1.0 equiv), AgF (4.0 equiv), 3,4,7,8-tetramethyl-1,10-phenanthroline (0.3 equiv), Selectfluor (3.0 equiv), TFMS (**2**) (5.0 equiv), MeCN/DCM (v/v 7:2), N_2 atmosphere, 25°C. Condition B: alkylsilanes (1.0 equiv), $AgSCF_3$ (4.0 equiv), 4,4'-di-tert-butyl-2,2'-bipyridine (0.4 equiv), Selectfluor (3.0 equiv), CsF (4.0 equiv), MeCN/dioxane (v/v 1:1), N_2 atmosphere, 50°C. Yields of isolated products are given. [b] 25 °C was used. [c] MeCN/DCM (v/v 1:1) was used. [d] Yield was determined by ^{19}F NMR with benzotrifluoride as a standard.

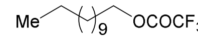
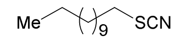
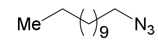
of alkylsilanes using other nucleophiles such as $^{-}OCF_3$. Recently, trifluoromethyl arylsulfonate (TFMS) as a new trifluoromethoxylation reagent was disclosed by our group, which was used to generate $AgOCF_3$ in situ in the presence of silver salts and fluoride ions.[11] Thus, we envisioned whether the oxidative trifluoromethoxylation of alkylsilanes could be achieved with $^{-}OCF_3$ which was generated in situ in the presence of fluoride ions and TFMS. Initial investigations focused on the reaction of alkylsilane **1** with various fluorine sources in the presence of trifluoromethyl 4-methylbenzenesulfonate (TFMS, **2**) (Table 1, see more details in the Supporting Information). No desired product **3a** was observed when Et_3N•3HF, CsF, TBAF or FeF_3 was used as the fluoride ion sources (Table 1, entries 1-4). We were delighted to find that 61% yield of the desired product **3a** was observed in the presence of AgF (Table 1, entry 5). Different ligands were evaluated and 3,4,7,8-tetramethyl-1,10-phenanthroline gave the highest yield (Table 1, entries 5-10). Switching to the other oxidants such as N-fluorobenzenesulfonimide (NFSI), PhIO, $PhI(OAc)_2$, $K_2S_2O_8$ could not generate **3a** (Table 1, entries 11-14). No desired products were detected in control experiments with AgF or oxidant omitted. After extensive screening of various solvents, different substitution on TFMS, and temperatures (see more details in the Supporting Information), the ideal conditions of 4.0 equiv of AgF, 0.3 equiv of 3,4,7,8-tetramethyl-1,10-phenanthroline, 3.0 equiv of Selectfluor, 5.0 equiv of TFMS (**2**) in 7:2 (v:v) MeCN/DCM under N_2 atmosphere at 25°C were found to produce the highest yields. Encouraged by these results, we successfully extended the present system to a trifluoromethylthiolation of alkylsilanes by changing the ligand and silver salt. After optimization of the reaction conditions, the desired trifluoromethylthiolated product (**3b**) was observed in 80% yield under 4.0 equiv of $AgSCF_3$, 0.4 equiv of 4,4'-di-tert-butyl-2,2'-bipyridine, 3.0 equiv of Selectfluor, 4.0 equiv of CsF in 1:1 (v:v) MeCN/dioxane under N_2 atmosphere at 50 °C (Table 1, entry 15, see more details in the Supporting Information).

Having established optimized reaction conditions, we then explored the scope of trifluoromethoxylation and trifluoromethylthiolation with structurally diverse alkylsilanes. As displayed in Table 2, a wide range of primary alkylsilanes bearing electron-donating and electron-withdrawing substituents on aryl rings were successfully converted into the desired trifluoromethoxylated and trifluoromethylthiolated products with good isolated yields (**4** to **16**). Notably, heteroaromatic substrates, such as pyridine, indole, and thiophene were also successfully employed to provide the corresponding trifluoromethoxylated and trifluoromethylthiolated products (**17** to **21**). A good range of functional groups including ester, ether, ketone, nitrile, nitro, amide, chloride, bromide, and even iodide were well tolerated under the mild reaction conditions. Moreover, the trifluoromethylthiolation of alkylsilane with tertiary alcohol also proceeded smoothly (**36**). These results encouraged the application of this method to more complex small molecules, which gave the corresponding trifluoromethoxylated and trifluoromethylthiolated products in moderate yields (**39**, **40**, **41**). For example, the alkylsilane derived from celecoxib, which is a nonsteroidal anti-inflammatory drug, were converted to the trifluoromethoxylated product (**40a**) in 31% yield, or trifluorome thylthiolated product (**40b**) in 57% yield. In addition, we prepared compound **5a**, **5b** in gram scale under the standard reaction conditions in 44%, 69% isolated yield, respectively, which demonstrates the scalability of this method. However, trifluoromethoxylation and trifluoromethylthiolation of secondary alkylsilanes were observed with low yields (**37**, **38**), and alkenes were the major byproducts.

Table 3. Substrate scope for silver-mediated oxidative functionalization of alkylsilanes.



1

Entry	AgFG	Ligand	Yield(%)
1[a]	AgOBz	3,4,7,8-Me_4-Phen	 **42**, 61%
2[b]	$AgOCOCF_3$	4,7-MeO_2-Phen	 **43**, 61%
3[c]	AgSCN	4,4'-MeO_2-bpy	 **44**, 43%
4[d]	AgF + TsN_3	4,7-MeO_2-Phen	 **45**, 63%

[a] **1** (1.0 equiv), AgOBz (4.0 equiv), CsF (4.0 equiv), ligand (0.4 equiv), Selectfluor (3.0 equiv), MeCN/DCE (v/v 1:1), 50 °C, N_2. [b] **1** (1.0 equiv), $AgOCOCF_3$ (4.0 equiv), CsF (4.0 equiv), ligand (0.4 equiv), Selectfluor (3.0 equiv), DMC, 50 °C, N_2. [c] **1** (1.0 equiv), AgSCN (4.0 equiv), CsF (4.0 equiv), ligand (0.4 equiv), Selectfluor (3.0 equiv), MeCN/DCE (v/v 1:1), 50 °C, N_2. [d] **1** (1.0 equiv), AgF (4.0 equiv), TsN_3 (4.0 equiv), ligand (0.4 equiv), Selectfluor(II) (3.0 equiv), MeCN/DCE/EtOH (v/v/v 5:5:1), 25 °C, N_2.

Encouraged by our success with trifluoromethoxylation and trifluoromethylthiolation of alkylsilanes, we investigated the use of other silver salt to develop the functionalization of alkylsilanes (Table 3). When AgOBz, $AgOCOCF_3$, or AgSCN was used, the corresponding products (**42**, **43**, **44**) were obtained in moderate yields. Installation of an azide group have proven to be useful in chemical biology, medicinal chemistry, and materials science.[12] The use of AgF and TsN_3 enabled azidation of alkylsilanes **1** to prepare the desired product **45** in 63% isolated yield. We note that in each system, both the silver salt and oxidant were necessary for productive reactivity. Although these reactions are not fully optimized, they provide a general strategy for the functionalization of alkylsilanes.

To gain some insight into the reaction mechanism, we performed some preliminary studies (Scheme 2a). Less than 10% trifluoromethoxylated or trifluoromethylthiolated product was formed when a radical inhibitor 2,6-di-tert-butyl-4-methylphenol (BHT) (8 equiv) was added. In addition, When 4 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added, the TEMPO adduct **46** or **47** was obtained in 25% and 38% isolated yield, respectively. Furthermore, the reaction of alkene silanes under the standard reaction conditions (condition B) gave the trifluoromethylthiolated product **48** (37%) accompanied with the 5-exo-cyclization trifluoromethylthiolated product **48'** in 12% yield. Together, these observations strongly suggested that a radical-chain mechanism or single-electron transfer (SET) was involved in the reactions. In addition, 28% trifluoromethoxylated products was observed when AgF_2 was used in the absence of AgF and Selectfluor, which indicated that Ag(II) species could be involved in the reaction (see

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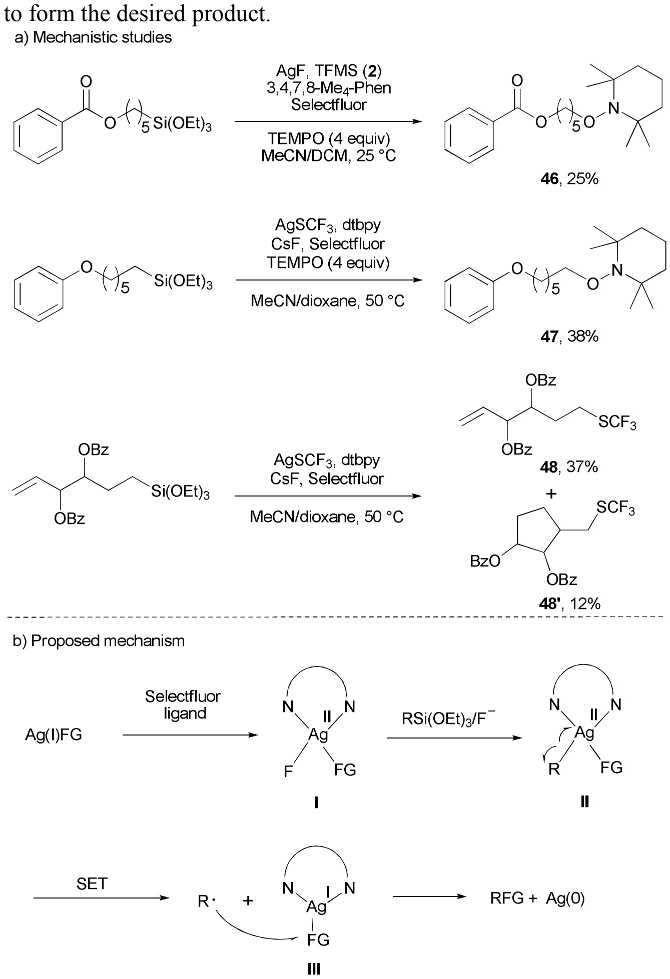
more details in the Supporting Information). Finally, silver mirror was observed in the reaction, which suggested that Ag(0) was generated.

On the basis of these mechanistic investigations, we proposed the mechanism depicted in Scheme 2b. In the presence of ligand and Selectfluor, AgFG (FG = OCF_3, OBz, $OCOCF_3$, SCF_3, SCN, N_3) is oxidized to produce Ag(II) intermediate **I**,[11d] then R group transmetalation from silicon to Ag(II) intermediate **I** can afford alkylsilver species **II**. The subsequent single-electron transfer between Ag(II) and R group in intermediate **II** leads to the generation of R radical and Ag(I) species **III**. Finally, the FG group transfer from the intermediated **III** to R radical generates RFG and Ag(0). At present, we cannot rule out the possibility of an alternative mechanism that R radical intermediate is further oxidized to generate R carbocation intermediate, which is trapped by FG anion to form the desired product.



Scheme 2. Mechanistic studies and proposed mechanism

Conclusions

In conclusion, we have developed a silver-mediated oxidative functionalization of alkylsilanes. This strategy enables to access a range of functionalized products directly, thus obviating the need to develop new methodology for each specific C−Si transformation. Furthermore, a first example of silver-mediated trifluoromethoxylation of alkylsilanes was developed using trifluoromethyl arylsulfonate (TFMS) as the trifluoromethoxylation reagent. Additionally, preliminary mechanistic studies suggested that the reaction may proceed through a radical mechanism.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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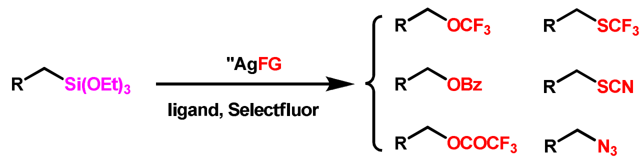

FG = OCF_3, OBz, $OCOCF_3$, SCF_3, SCN, N_3

A general approach to the functionalization of aliphatic C-Si bonds in the presence of silver salt and oxidant has been reported.