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Visible-light-promoted cross-coupling reaction of hypervalent bis-catecholato silicon compounds with selenosulfonates or thiosulfonates†

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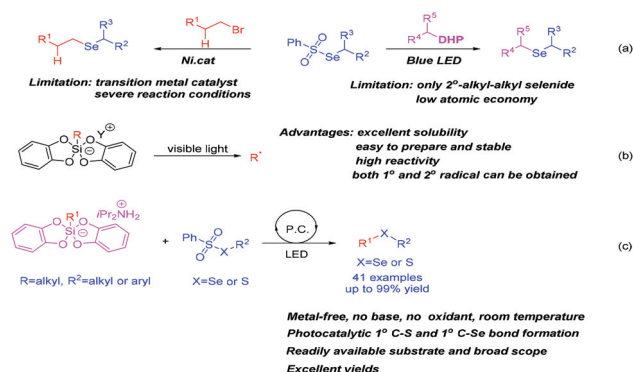
Under mild metal-free conditions, we successfully developed a visible-light-promoted free radical cross coupling of hypervalent bis-catecholato silicon compounds with selenosulfonates or thiosulfonates and efficiently constructed unsymmetrical 1°-alkyl-alkyl selenide compounds which are difficult to prepare. This protocol uses mild reaction conditions and easily available substrates, has a wide range substrate scope, high yields, and simple operation and no need of expensive photosensitive catalysts. It provides a green and simple method for the preparation of unsymmetrical alkyl-alkyl selenide compounds. At the same time, this strategy is also applicable for the efficient construction of aryl-alkyl selenides, heteroaryl-alkyl selenides and aryl-alkyl sulfides.

Introduction

Selenium is an essential trace element for the human body, and it mainly exists in internal organs and blood in the form of selenoamino acids and peptides in organisms.¹ Selenium is the basic component of some enzyme active parts, and affects the activity and function of enzymes. In the human body, it participates in the formation of thyroxine deiodinase, glutathione peroxidase and other proteins in the form of selenocysteine.² In recent years, many commercial selenium supplement products have appeared on the market. Relevant studies have shown that adequate selenium supplementation is beneficial to health. In addition, organic selenium compounds are widely used in organic chemistry,³ selenium-containing biologically active molecules,⁴ pesticides⁵ and materials.⁶ It can be seen that the synthesis of organic selenium compounds has important practical significance. In the past few years, selenosulfonates have been widely used in the construction of organoselenide compounds as an important class of reagents and intermediates. Common strategies include transition metal-catalyzed C–Se bond construction⁷ (Scheme 1a, left), C–Se bond construction under metal-free catalysis⁸ and C–Se bond construction under photocatalysis⁹ (Scheme 1a, right). However, these strategies need to use expensive transition metal catalysts or additives. On the other

hand, low atom economy and confined secondary alkyl-alkyl selenides scope limit their further applications. Therefore, it is of great significance to develop a simple, mild and efficient method to prepare organoselenide compounds with wide substrate scope.

In recent years, visible light-mediated photoredox catalysis has received more and more attention. Due to its special reaction mode, many transformations that could not be achieved through the transition metal catalytic process before are possible. However, finding free radical precursors with sufficient stability and functional group compatibility is a big challenge. For instance, organoborates (especially alkyl trifluoroborate),¹⁰ 4-alkyl-1,4-dihydropyridines (DHPs)¹¹ have been widely applied



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Scheme 1 (a) Ni-catalyzed C–Se bond construction and C–Se bond construction under photocatalysis. (b) Hypervalent silicon compounds as a source of C-radicals. (c) Visible-light-promoted free radical cross coupling of hypervalent bis-catecholato silicon compounds with selenosulfonates or thiosulfonates.

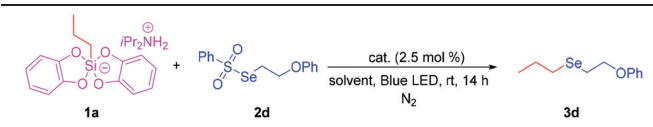
in the synthesis of various compounds. However, the main drawbacks are the formation of polluting boron fluoride side products and the continuing difficulty in generating primary radicals under photocatalytic conditions. Therefore, it is particularly important to find a free radical precursor that is more environmentally friendly and has high substrate universality. In recent years, hypervalent silicon compounds¹² have been widely used in various free radical reaction strategies as a kind of highly active free radical precursor. Kumada *et al.*¹³ first reported the free radical reaction of organic pentafluorosilicate under copper catalysis conditions, however its poor solubility severely limited its application in organic synthesis. The hypervalent silicon derivative of bis-catechol reported by Frye's group has received widespread attention due to its more soluble properties (Scheme 1b).¹⁴ These ideal radical precursors can generate various functionalized alkyl radicals especially the primary alkyl radicals smoothly under low-energy visible light using ready-made photocatalysts, which has attracted wide attention from chemists. Prof. Molander's group¹⁵ and other groups¹⁶ have done a lot of excellent work in this area. Herein, we developed a free radical cross-coupling reaction between bis-catechol hypervalent silicon derivatives and alkylselenosulfonates under visible light mediation, and successfully constructed primary unsymmetrical alkyl-alkyl selenide compounds. This strategy is also applicable to the construction of aryl-alkyl selenides, heteroaryl-alkyl selenides and aryl-alkyl sulfides (Scheme 1c). More importantly, we used this strategy to successfully construct the selenocarbamate compound **3r**. This shows that the strategy has broad application prospects in the biological field.

Results and discussion

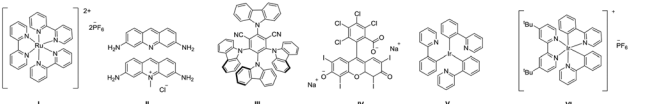
Initially, we tried the reaction of propylsilicate **1a**, Se-(2-phenoxyethyl) benzenesulfonoselenoate **2d**, and organometallic photocatalyst Ru(bpy)₃(PF₆)₂ in (dry) DMF at room temperature for 14 h under a N₂ atmosphere. Gratifyingly, the reaction proceeded smoothly to give the target product (2-phenoxyethyl) (propyl)selane **3d**. With this promising result in hand, we tried to optimize the reaction conditions. First we investigated the ratio effects of **1a** and **2a**. It was found that when the ratio of **1a** to **2a** is 1.67 : 1.0, **3d** could be obtained in 64% GC-yield (Table 1, entries 1–4). Then, we tried the reactions in several different dry solvents such as DMA, MeCN, and DMSO. It was found that when anhydrous DMSO was used, the target product **3d** could be obtained in 73% GC-yield (Table 1, entries 5–7). We also investigated other different photosensitive catalysts. To our delight, **3d** was obtained in 85% GC-yield when the reaction was carried out utilizing acriflavin **II** as the catalyst (Table 1, entries 8–12). It should be noted that the reaction could not proceed under an air atmosphere. (Table 1, entry 13). **3d** was obtained in 99% isolated yield when the reaction time was prolonged to 24 h (Table 1, entry 14).

With the optimized reaction conditions in hand, we set about assessing the generality of this protocol. First, we exam-

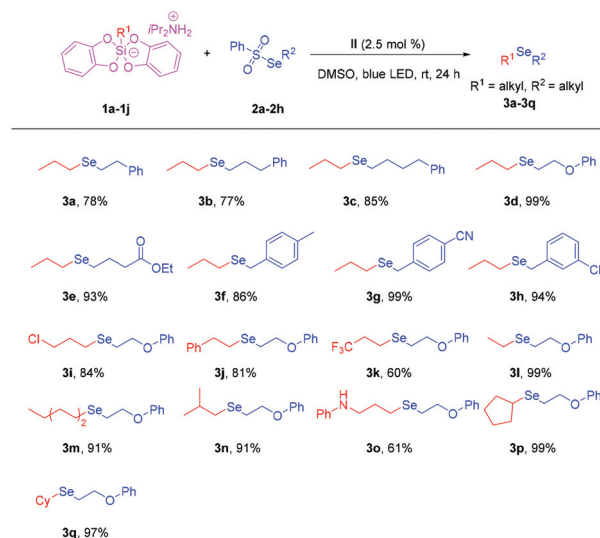
Table 1 Optimization of the reaction conditions for the preparation of unsymmetrical alkyl-alkyl selenide compounds^{a,b}



Entry	1a (equiv.)	2a (equiv.)	Cat	Solvent	GC-yield ^b
1	1.00	2.0	1	DMF	45%
2	1.50	1.0	1	DMF	56%
3	1.67	1.0	1	DMF	64%
4	2.50	1.0	1	DMF	58%
5	2.00	1.0	1	DMA	29%
6	2.00	1.0	1	DMSO	73%
7	2.00	1.0	1	MeCN	48%
8	2.00	1.0	2	DMSO	85%
9	2.00	1.0	3	DMSO	75%
10	2.00	1.0	4	DMSO	56%
11	2.00	1.0	5	DMSO	69%
12	2.00	1.0	6	DMSO	81%
13 ^c	2.00	1.0	2	DMSO	N.R
14 ^d	2.00	1.0	2	DMSO	99% ^e



^a Reaction conditions: propylsilicate **1a**, Se-(2-phenoxyethyl) benzenesulfonoselenoate **2d**; photosensitive catalyst (2.5 mol%), solvent(dry) (1 ml), room temperature, 14 h. ^b Yields were determined by GC-MS analysis using biphenyl as an internal standard, GC-yield. ^c Under an air atmosphere. ^d 24 h. ^e Isolated yield.



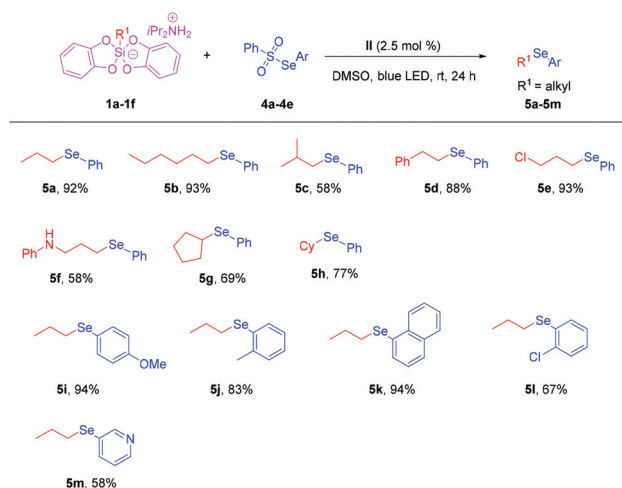
Scheme 2 Substrate scope for unsymmetrical alkyl-alkyl selenide compounds. Reaction conditions: substituted silicate **1** (0.34 mmol), substituted selenosulfonates **2** (0.2 mmol), **II** (2.5 mol%), (dry) DMSO (1 mL), room temperature, blue LED, N₂, 24 h. Isolated yields.

ined the reactivity of different substituted selenosulfonates (Scheme 2). The reaction of propylsilicate **1a** with Se-phenethyl benzenesulfonoselenoate **2a** gave the target product **3a** in 78% yield. The reaction of propylsilicate **1a** with Se-(3-phenylpropyl)

benzenesulfonoselenoate **2b** afforded the desired product **3b** in 77% yield. The reaction of propylsilicate **1a** with Se-(4-phenylbutyl) benzenesulfonoselenoate **2c** furnished **3c** in 85% yield. To our delight, when ethyl 4-((phenylsulfonyl)selenyl) butanoate **2e** was applied to the reaction, the target product **3e** was obtained in 93% yield successfully, which demonstrates excellent functional group tolerance. Next, we investigated the universality of different substituted benzylselenosulfonates. It should be noted that whether it is a methyl-substituted benzylselenosulfonate **2f** or an electron-withdrawing group functionalized benzylselenosulfonate **2g**, or a halogen-substituted benzylselenosulfonate **2h** were applied to the reactions with **1a**, the desired products **3f–h** could be obtained in good to excellent yields, respectively.

Then, we further investigated the universality of different substituted alkylsilicates (Scheme 2). The reaction showed a broad functional group compatibility, in which both halogen substituted alkylsilicate, phenyl substituted alkylsilicate and trifluoromethyl substituted alkylsilicate were well tolerated. The target products **3i–k** were uniformly obtained in excellent yields. It was found that the length of the chain has no effect on the yields. The target products **3l–n** were uniformly obtained in excellent yields too. Surprisingly, the secondary amine substituted alkylsilicate substrate was also well tolerated. The product **3o** could be obtained in 61% yield. When cyclopentylsilicate and cyclohexylsilicate were applied to the reaction, the target products **3p** and **3q** were isolated in excellent yields, respectively.

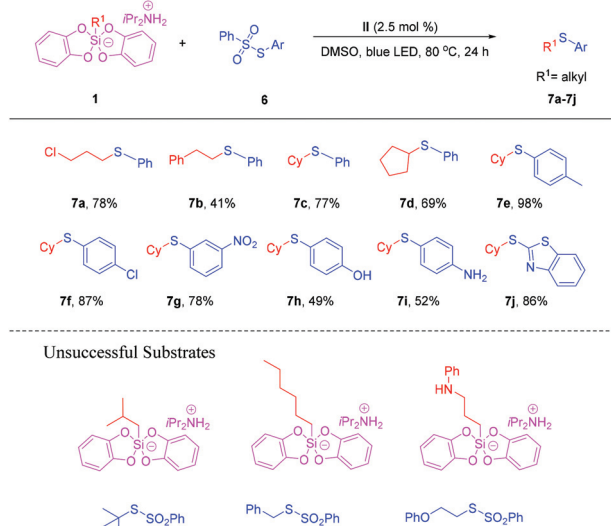
Encouraged by the above achievements, we turned attention to extending the method to arylselenosulfonates. However, under the previous conditions, the reaction of propylsilicate **1a** with Se-phenyl benzenesulfonoselenoate **4a** failed to afford product **5a**. To our satisfaction, when the reaction temperature was increased to 80 °C, it smoothly led to the target product **5a** in 92% yield. With the optimal modified reaction conditions in hand, we explored the scope of different substituted alkylsilicates (Scheme 3). Similarly, the reaction showed a broad functional group compatibility. When hexylsilicate was applied to the reaction, the target product **5b** could be obtained in 93% yield. When isobutylsilicate was applied to the reaction, the target product **5c** could also be isolated in 58% yield. When phenethylsilicate and chloropropylsilicate were applied to the reaction. The target products **5d** and **5e** could be obtained in 88% and 93% yields, respectively. The secondary amine substituted alkylsilicate substrate was well tolerated and the target product **5f** could be obtained in 58% yield. Subsequently, we examined the substrate scope of arylselenosulfonates (Scheme 3). It was found that when Se-phenyl arylsulfonates bore electron donating groups (4-OMe, 3-Me), the target products **5i** and **5j** could be obtained in 94% and 83% yields, respectively. The reaction of **1a** with Se-(naphthalen-1-yl) benzenesulfonoselenoate **4c** led to the desired product **5k** in 94% yield. When Se-(2-chlorophenyl) benzenesulfonoselenoate **4c** and Se-(pyridin-3-yl) benzenesulfonoselenoate **4d** were applied to the reaction, the target products **5l** and **5m** could also be obtained in 67% and 58% yields, respectively. This study pro-



Scheme 3 Substrate scope for aryl-alkyl selenides compounds. Reaction conditions: substituted silicate **1** (0.34 mmol), substituted selenosulfonates **4** (0.2 mmol), **II** (2.5 mol%), (dry)DMSO (1 mL), 80 °C, Blue LED, N₂, 24 h. Isolated yields.

vides a new method for the construction of heteroaryl alkyl selenide compounds.

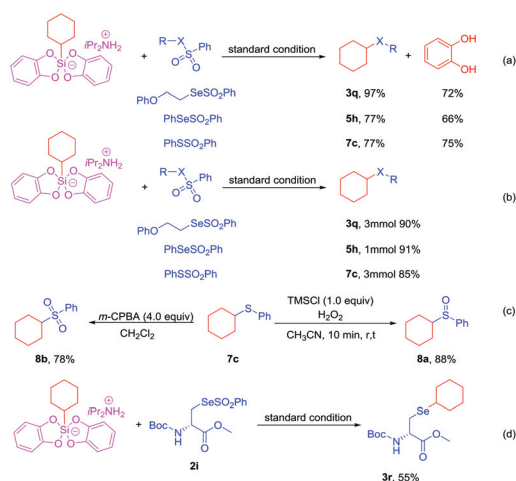
In order to investigate the applicability of this free radical cross-coupling strategy, we tried the reaction of alkylsilicates with thiosulfonates under similar reaction conditions (Scheme 4). It was found that the reactivity of thiosulfonates is lower than that of selenosulfonates. There are limited four substituted alkylsilicates, which were successfully applied to the reaction to afford the desired products. The target products **7a–d** were obtained in 41%–78% yields, respectively. Next, we examined the reactivity of different substituted thiosulfonates.



Scheme 4 Substrate scope for aryl-alkyl sulfides compounds. Reaction conditions: substituted silicate **1** (0.34 mmol), substituted thiosulfonates **6** (0.2 mmol), **II** (2.5 mol%), (dry)DMSO (1 mL), 80 °C, blue LED, N₂, 24 h. Isolated yields.

It is worth pointing out that the reaction showed a broad functional group compatibility, in which both electron-donating group Me and electron-donating withdrawing groups such as Cl and NO₂, were well tolerated. The target products **7e–7f** could be observed in excellent yields. To our delight, when *S*-(4-hydroxyphenyl) benzenesulfonothioate and *S*-(4-aminophenyl) benzenesulfonothioate were applied to the reaction, the target products **7h** and **7i** were obtained in moderate yields, respectively. The reaction of *S*-(benzo[*d*]thiazol-2-yl) benzenesulfonothioate with cyclohexylsilicate led to **7j** in 86% yield. Unfortunately, alkyl thiosulfonates failed to afford the desired products under the identical reaction conditions.

In order to improve the atom economy of the reaction and explore the further application of this reaction, we successfully recovered catechol with good yield (Scheme 5a). The successful recovery and reuse of catechol shows that this protocol has high atom economy. In order to explore the further application of this reaction, we tried the scale-up reaction of products **3q**, **5h** and **7c**. To our delight, the target products **3q**, **5h** and **7c** could be obtained in excellent yields, respectively (Scheme 5b). In addition, according to the relevant literature,¹⁶ the treatment of compound **7c** with different oxidizing agents successfully led to sulfoxide **8a** and sulfone **8b** in 88% and 78% yields, respectively (Scheme 5c). The above experiments show that this strategy has huge advantages in the potential industrial applications. What is exciting is that the reaction of cyclohexylsilicate with methyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(phenoxyselemonothioyl)propanoate **2i** under the optimized conditions successfully constructed the target product methyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(cyclohexylselanyl)propanoate **3r** in 55% yields

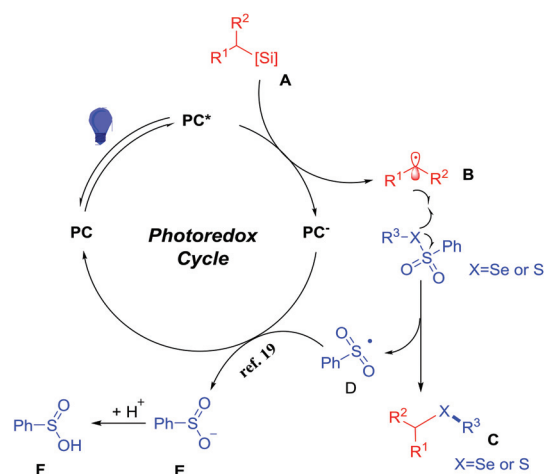


Scheme 5 Related derivative reactions. (a) Recovery and reuse of catechol. (b) The scale-up reaction of products **3q**, **5h** and **7c**. (c) Under suitable oxidation conditions, the sulfide could be selectively oxidized to sulfoxide or sulfone. (d) Successfully constructed the target product methyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(cyclohexylselanyl)propanoate.

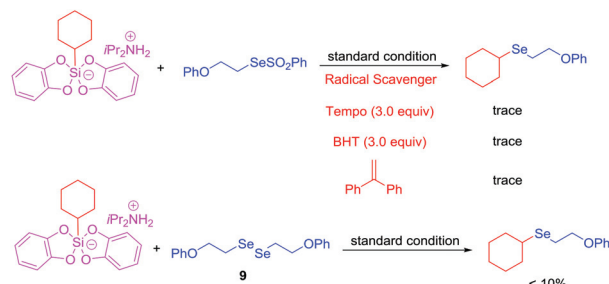
(Scheme 5d). This shows that the strategy has broad application prospects in the biological field.

Further mechanistic studies were conducted to gain deeper insight into the reaction pathway. Adding stoichiometric amounts of radical scavenger TEMPO or BHT and 1,1-diphenylethylene to the reaction significantly suppressed the conversion, which revealed that a radical mechanism might be involved in this transformation. The reaction of cyclohexylsilicate with diselenide compound **9** instead of selenosulfonate gave **3q** in only <10% yield. This result indicates that diselenide compound **9** was not the main reaction intermediate of this reaction (Scheme 6).

Based on the above experimental results and previous reports,^{17,18} we proposed a plausible mechanism in Scheme 7. The photocatalyst assists the single electron transfer of the alkylsilicate to generate an alkyl radical B. Subsequently, alkyl radical reacts B with selenosulfonates or sulfonothioates to afford the desired products and a sulfone radical intermediate.¹⁹ Then the sulfone radical is reduced to a sulfone anionic intermediate E. Subsequently, protonation of intermediate E affords the benzosulfonic acid.²⁰



Scheme 6 Mechanistic studies. (a) Radical scavengers are added under standard conditions, the target product could only be obtained in trace yields. (b) Treatment of cyclohexyl silicon and diselenide **9** under standard reaction conditions could not lead the target product.



Scheme 7 A plausible mechanism.

Conclusion

In summary, we have successfully developed a light-mediated two-component free radical cross-coupling reaction between alkylsilicate compounds and selenosulfonates under metal-free catalysis conditions. At the same time, this strategy is also applicable to the efficient construction of aryl-alkyl selenides, heteroaryl-alkyl selenides and aryl-alkyl sulfides. A new method for efficiently constructing C_{sp^3} -Se and C_{sp^3} -S bonds without any additives was developed. Successful construction of the unsymmetrical primary alkyl-alkyl selenide compounds, which are difficult to prepare, is the highlight of this work. It provides a green and simple method for the preparation of alkyl-alkyl selenide and aryl-alkyl selenide compounds. The recovery and reuse of catechol and the scale-up experiments show the broad prospects of this strategy in industrial applications. Successful construction of the selenocarbamate compound **3r** shows that the strategy has broad application prospects in the biological field.

Experimental section

General procedure

Synthesis of 3d. In a glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with diisopropylammonium bis(catecholato)propylsilicate **1a** (129.6 mg, 0.34 mmol) and Se-(2-phenoxyethyl) benzenesulfonate **2d** (68.4 mg 0.2 mmol), cat (1.4 mg, 2.5 mol%), and DMSO (1.0 mL) were added *via* a syringe. The reaction mixture was stirred at r.t for 24 h under a 40 W LED lamp (40 W; λ = 450–460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass). After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL \times 3). The organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography to afford the pure product **3d**.

Synthesis of 5a. In a glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with diisopropylammonium bis(catecholato)propylsilicate **1a** (129.6 mg, 0.34 mmol) and Se-phenyl benzenesulfonate **4a** (59.6 mg 0.2 mmol), cat (1.4 mg, 2.5 mol%), and DMSO (1.0 mL) were added *via* a syringe. The reaction mixture was stirred at 80 °C for 24 h under a 40 W LED lamp (40 W; λ = 450–460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass). After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL \times 3). The organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography to afford the pure product **5a**.

Synthesis of 7c. In a glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with bis(catechol)diisopropyl ammonium cyclohexyl silicate **1f** (129.6 mg, 0.34 mmol) and *S*-phenyl benzenesulfonothioate **6a** (50.0 mg 0.2 mmol), cat (1.4 mg, 2.5 mol%), and DMSO (1.0 mL) were added *via* a syringe. The reaction mixture was

stirred at 80 °C for 24 h under a 40 W LED lamp (40 W; λ = 450–460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass). After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL \times 3). The organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography to afford the pure product **7c**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 T. Maseko, D. L. Callahan, F. R. Dunshea, A. Doronila, S. D. Kolev and K. Ng, Chemical characterisation and speciation of organic selenium in cultivated selenium-enriched *Agaricus bisporus*, *Food Chem.*, 2013, **141**, 3681.
- 2 E. Dumont, F. Vanhaecke and R. Cornelis, Selenium speciation from food source to metabolites: a critical review, *Anal. Bioanal. Chem.*, 2006, **385**, 1304.
- 3 (a) J. Luo, Z.-C. Zhu, Y.-N. Liu and X.-D. Zhao, Diaryl Selenide Catalyzed Vicinal Trifluoromethylthioamination of Alkenes, *Org. Lett.*, 2015, **17**, 3620; (b) L.-H. Liao, R.-Z. Guo and X.-D. Zhao, Organoselenium-Catalyzed Regioselective C-H Pyridination of 1,3-Dienes and Alkenes, *Angew. Chem., Int. Ed.*, 2017, **56**, 3201.
- 4 P. C. Srivastava and R. K. Robins, Synthesis and antitumor activity of 2- β -D-ribofuranosylselenazole-4-carboxamide and related derivatives, *J. Med. Chem.*, 1983, **26**, 445.
- 5 L. L. Miller, J. B. Rasmussen, V. P. Palace and A. Hontela, Physiological stress response in white suckers from agricultural drain waters containing pesticides and selenium, *Ecotoxicol. Environ. Saf.*, 2009, **72**, 1249.
- 6 E. C. Mägi, L. B. Fu, H. C. Nguyen, M. R. E. Lamont, D. I. Yeom and B. J. Eggleton, Enhanced Kerr nonlinearity in sub-wavelength diameter As_2Se_3 chalcogenide fiber tapers, *Opt. Express*, 2007, **15**, 10324.
- 7 Y. Fang, T. Rogge, L. Ackermann, S.-Y. Wang and S.-J. Ji, Nickel-catalyzed reductive thiolation and selenylation of unactivated alkyl bromides, *Nat. Commun.*, 2018, **9**, 2240.
- 8 (a) S.-L. Huang, Z.-L. Chen, H. Mao, F.-L. Hu, D.-M. Li, Y. Tan, F.-Q. Yang and W.-L. Qin, Metal-free difunctionalization of alkynes to access tetrasubstituted olefins through spontaneous selenosulfonylation of vinylidene orthoquinone methide (VQM), *Org. Biomol. Chem.*, 2019, **17**, 1121; (b) Z.-L. Chen, F.-L. Hu, S.-L. Huang, Z.-G. Zhao,

- H. Mao and W.-L. Qin, Organocatalytic Enantioselective Selenosulfonylation of a C–C Double Bond To Form Two Stereogenic Centers in an Aqueous Medium, *J. Org. Chem.*, 2019, **84**, 8100; (c) M. J. Davies and C. H. Schiesser, 1,4-Anhydro-4-seleno-D-talitol (SeTal): a remarkable selenium-containing therapeutic molecule, *New J. Chem.*, 2019, **43**, 9759; (d) N. Al-Maharik, L. Engman, J. Malmstrom and C. H. Schiesser, Intramolecular Homolytic Substitution at Selenium: Synthesis of Novel Selenium-Containing Vitamin E Analogues, *J. Org. Chem.*, 2001, **66**, 6286; (e) M. W. Carland, R. L. Martin and C. H. Schiesser, Preparation of novel selenapenam and selenacephem by nucleophilic and radical chemistry involving benzyl selenides, *Org. Biomol. Chem.*, 2004, **2**, 2612; (f) K. M. Aumann, P. J. Scammells, J. M. White and C. H. Schiesser, On the stability of 2-aminoselenophene-3-carboxylates: potential dual-acting selenium-containing allosteric enhancers of A1 adenosine receptor binding, *Org. Biomol. Chem.*, 2007, **5**, 1276.
- 9 (a) C. Ghiazza, L. Khrouz, C. Monnereau, T. Billard and A. Tlili, A. Visible-light promoted fluoroalkylselenolation: toward the reactivity of unsaturated compounds, *Chem. Commun.*, 2018, **54**, 9909; (b) M. R. Mutra, V. S. Kudale, J. Li, W.-H. Tsaia and J.-J. Wang, Alkene versus alkyne reactivity in unactivated 1,6-enynes: regio- and chemoselective radical cyclization with chalcogens under metal- and oxidant-free conditions, *Green Chem.*, 2020, **22**, 2288; (c) R. Zhang, P. Xu, S.-Y. Wang and S.-J. Ji, Visible Light-Induced Co- or Cu-Catalyzed Selenosulfonylation of Alkynes: Synthesis of β -(Seleno)vinyl Sulfones, *J. Org. Chem.*, 2019, **84**, 12324; (d) J. Li, X.-E. Yang, S.-L. Wang, L.-L. Zhang, X.-Z. Zhou, S.-Y. Wang and S.-J. Ji, Visible-Light-Promoted Cross-Coupling Reactions of 4-Alkyl-1,4-dihydropyridines with Thiosulfonate or Selenium Sulfonate: A Unified Approach to Sulfides, Selenides, and Sulfoxides, *Org. Lett.*, 2020, **22**, 4908.
- 10 For representative works, see: (a) Y. Nishigaichi, T. Orimi and A. Takuwa, Photo-allylation and photo-benzylation of carbonyl compounds using organotrifluoroborate reagents, *J. Organomet. Chem.*, 2009, **694**, 3837; (b) G. Sorin, R. M. Mallorquin, Y. Contie, A. Baralle, M. Malacria, J.-P. Goddard and L. Fensterbank, Oxidation of Alkyl Trifluoroborates: An Opportunity for Tin-Free Radical Chemistry, *Angew. Chem., Int. Ed.*, 2010, **49**, 8721; (c) G. A. Molander, V. Colombel and V. A. Braz, Direct Alkylation of Heteroaryls Using Potassium Alkyl- and Alkoxyethyltrifluoroborates, *Org. Lett.*, 2011, **13**, 1852; (d) J. W. Lockner, D. D. Dixon, R. Risgaard and P. S. Baran, Practical Radical Cyclizations with Arylboronic Acids and Trifluoroborates, *Org. Lett.*, 2011, **13**, 5628; (e) S. R. Neufeldt, C. K. Seigerman and M. S. Sanford, Mild Palladium-Catalyzed C–H Alkylation Using Potassium Alkyltrifluoroborates in Combination with MnF_3 , *Org. Lett.*, 2013, **15**, 2302.
- 11 For representative works, see: (a) K. Nakajima, X.-F. Guo and Y. Nishibayashi, Cross-Coupling Reactions of Alkenyl Halides with 4-Benzyl-1,4-Dihydropyridines Associated with E to Z Isomerization under Nickel and Photoredox Catalysis, *Chem. – Asian J.*, 2018, **13**, 3653; (b) W.-W. Chen, Z. Liu, J.-Q. Tian, J. Li, J. Ma, X. Cheng and G.-G. Li, Building Congested Ketone: Substituted Hantzsch Ester and Nitrile as Alkylation Reagents in Photoredox Catalysis, *J. Am. Chem. Soc.*, 2016, **138**, 12312; (c) X. Liu, R.-Y. Liu, J. Dai, X. Cheng and G.-G. Li, Application of Hantzsch Ester and Meyer Nitrile in Radical Alkynylation Reactions, *Org. Lett.*, 2018, **20**, 6906; (d) K. Nakajima, Y.-L. Zhang and Y. Nishibayashi, Alkylation Reactions of Azodicarboxylate Esters with 4-Alkyl-1,4-Dihydropyridines under Catalyst-Free Conditions, *Org. Lett.*, 2019, **21**, 4642; (e) S.-Z. Liang, T. Kumon, R. A. Angnes, M. Sanchez, B. Xu and G. B. Hammond, Synthesis of Alkyl Halides from Aldehydes via Deformylative Halogenation, *Org. Lett.*, 2019, **21**, 3848.
- 12 (a) R. R. Holmes, The stereochemistry of nucleophilic substitution of tetracoordinate silicon, *Chem. Rev.*, 1990, **90**, 17; (b) C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, Reactivity of penta- and hexacoordinate silicon compounds and their role as reaction intermediates, *Chem. Rev.*, 1993, **93**, 1371.
- 13 J. Yoshida, K. Tamao, T. Kakui, A. Kurita, M. Murata, K. Yamada and M. Kumada, Organofluorosilicates in organic synthesis. 13. Copper(II) oxidation of organopentafluorosilicates, *Organometallics*, 1982, **1**, 369.
- 14 C. L. Frye, Pentacoordinate Silicon Derivatives. II.1 Salts of Bis(o-arylenedioxy) organosiliconic Acids, *J. Am. Chem. Soc.*, 1964, **86**, 3170.
- 15 For representative works, see: (a) N. R. Patel, C. B. Kelly, M. Jouffroy and G. A. Molander, Engaging Alkenyl Halides with Alkylsilicates via Photoredox Dual Catalysis, *Org. Lett.*, 2016, **18**, 764; (b) M. Jouffroy, D. N. Primer and G. A. Molander, Base-Free Photoredox/Nickel Dual-Catalytic Cross-Coupling of Ammonium Alkylsilicates, *J. Am. Chem. Soc.*, 2016, **138**, 475; (c) S. Zheng, D. N. Primer and G. A. Molander, Nickel/Photoredox-Catalyzed Amidation via Alkylsilicates and Isocyanates, *ACS Catal.*, 2017, **7**, 7957; (d) A. G. Domínguez, R. Mondal and C. Nevado, Dual Photoredox/Nickel-Catalyzed Three-Component Carbonylfunctionalization of Alkenes, *Angew. Chem.*, 2019, **131**, 12414; (e) J. K. Matsui, S. B. Lang, D. R. Heitz and G. A. Molander, Photoredox-Mediated Routes to Radicals: The Value of Catalytic Radical Generation in Synthetic Methods Development, *ACS Catal.*, 2017, **7**, 2563 For representative works, see: (f) N. R. Patel, C. B. Kelly, A. P. Siegenfeld and G. A. Molander, Mild, Redox-Neutral Alkylation of Imines Enabled by an Organic Photocatalyst, *ACS Catal.*, 2017, **7**, 1766; (g) S. B. Lang, R. J. Wiles, C. B. Kelly and G. A. Molander, Photoredox Generation of Carbon-Centered Radicals Enables the Construction of 1,1-Difluoroalkene Carbonyl Mimics, *Angew. Chem., Int. Ed.*, 2017, **56**, 15073; (h) S. T. J. Cullen and G. K. Friestad, Alkyl Radical Addition to Aliphatic and Aromatic

- N-Acylhydrazones Using an Organic Photoredox Catalyst, *Org. Lett.*, 2019, **21**, 8290.
- 16 For representative works, see: (a) V. Corcé, L. M. Chamoreau, E. Derat, J. P. Goddard, C. Ollivier and L. Fensterbank, Silicates as Latent Alkyl Radical Precursors: Visible-Light Photocatalytic Oxidation of Hypervalent Bis-Catecholato Silicon Compounds, *Angew. Chem., Int. Ed.*, 2015, **54**, 11414; (b) L. Chenneberg, C. Lévêque, V. Corcé, A. Baralle, J. P. Goddard, C. Ollivier and L. Fensterbank, Single-Electron-Transfer Oxidation of Trifluoroborates and Silicates with Organic Reagents: A Comparative Study, *Synlett*, 2016, 731; (c) C. Lévêque, L. Chenneberg, J. P. Goddard, C. Ollivier and L. Fensterbank, Primary alkyl bis-catecholato silicates in dual photoredox/nickel catalysis: aryl- and heteroarylalkyl cross coupling reactions, *Org. Chem. Front.*, 2016, **3**, 462; (d) C. Lévêque, L. Chenneberg, J. P. Goddard, C. Ollivier and L. Fensterbank, Organic photoredox catalysis for the oxidation of silicates: applications in radical synthesis and dual catalysis, *Chem. Commun.*, 2016, **52**, 9877; (e) A. Cartier, E. Levernier, A. L. Dhimane, T. Fukuyama, C. Ollivier, I. Ryu and L. Fensterbank, Synthesis of Aliphatic Amides through a Photoredox Catalyzed Radical Carbonylation Involving Organosilicates as Alkyl Radical Precursors, *Adv. Synth. Catal.*, 2020, **362**, 2254; (f) T. Guo, L. Zhang, X.-B. Liu, Y.-W. Fang, X.-P. Jin, Y. Yang, Y. Li, B. Chen and M.-H. Ouyang, Visible-Light-Promoted Redox-Neutral Cyclopropanation Reactions of α -Substituted Vinylphosphonates and Other Michael Acceptors with Chloromethyl Silicate as Methylene Transfer Reagent, *Adv. Synth. Catal.*, 2018, **360**, 4459; (g) Y.-J. Liu, W.-P. Luo, J.-L. Wu, Y.-W. Fang, Y. Li, X.-P. Jin, L. Zhang, Z.-Y. Zhang, F.-F. Xu and C. Du, Radical addition-polar termination cascade: efficient strategy for photoredox-neutralcatalysed cyclopropanation and Giese-type reactions of alkenyl N-methyliminodiacetyl boronates, *Org. Chem. Front.*, 2020, **7**, 1588; (h) K. D. Raynor, G. D. May, U. K. Bandarage and M. J. Boyd, Generation of Diversity Sets with High sp^3 Fraction Using the Photoredox Coupling of Organotrifluoroborates and Organosilicates with Heteroaryl/Aryl Bromides in Continuous Flow, *J. Org. Chem.*, 2018, **83**, 1551; (i) A. Cartier, E. Levernier, V. Corcé, T. Fukuyama, A. L. Dhimane, C. Ollivier, I. Ryu and L. Fensterbank, Carbonylation of Alkyl Radicals Derived from Organosilicates through Visible-Light Photoredox Catalysis, *Angew. Chem., Int. Ed.*, 2019, **58**, 1789.
 - 17 (a) K. Bahrami, M. M. Khodaei, B. H. Yousefi and M. S. Arabi, TMSCl-promoted selective oxidation of sulfides to sulfoxides with hydrogen peroxide, *Tetrahedron Lett.*, 2010, **51**, 6939; (b) Y. Fang, T. Rogge, L. Ackermann, S.-Y. Wang and S.-J. Ji, Nickel-catalyzed reductive thiolation and selenylation of unactivated alkyl bromides, *Nat. Commun.*, 2018, **9**, 2240.
 - 18 (a) N. R. Patel, C. B. Kelly, A. P. Siegenfeld and G. A. Molander, Mild, Redox-Neutral Alkylation of Imines Enabled by an Organic Photocatalyst, *ACS Catal.*, 2017, **7**, 1766; (b) J. Li, X.-E. Yang, S.-L. Wang, L.-L. Zhang, X.-Z. Zhou, S.-Y. Wang and S.-J. Ji, Visible-Light-Promoted Cross-Coupling Reactions of 4-Alkyl-1,4-dihydropyridines with Thiosulfonate or Selenium Sulfonate: A Unified Approach to Sulfides, Selenides, and Sulfoxides, *Org. Lett.*, 2020, **22**, 4908.
 - 19 P. Carta, N. Puljic, C. Robert, A. L. Dhimane, C. Ollivier, L. Fensterbank, E. Lacôte and M. Malacria, Intramolecular homolytic substitution at the sulfur atom: an alternative way to generate phosphorus- and sulfur-centered radicals, *Tetrahedron*, 2008, **64**, 11865.
 - 20 (a) P.-Z. Xie, J.-Y. Wang, Y.-N. Liu, J. Fan, X.-Y. Wo, W.-S. Fu, Z.-L. Sun and T. P. Loh, Water-promoted C-S bond formation reactions, *Nat. Commun.*, 2018, **9**, 1321; (b) J. Li, X.-E. Yang, S.-L. Wang, L.-L. Zhang, X.-Z. Zhou, S.-Y. Wang and S.-J. Ji, Visible-Light-Promoted Cross-Coupling Reactions of 4-Alkyl-1,4-dihydropyridines with Thiosulfonate or Selenium Sulfonate: A Unified Approach to Sulfides, Selenides, and Sulfoxides, *Org. Lett.*, 2020, **22**, 4908.