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Palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines by intramolecular Hiyama coupling†

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A palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, silicon-switched analogs of biologically relevant 4*H*-benzo[*d*][1,3]oxazines, was developed by the intramolecular Hiyama coupling of 3-amido-2-(arylsilyl)aryl triflates. The present reaction is an unusual way of utilizing the Hiyama coupling, enabling the synthesis of value-added organosilanes as the main products. The intramolecular nature of transmetalation with inversion of the stereochemistry at the silicon center was revealed by the mechanistic investigation, and an asymmetric variant of this process was also demonstrated to give silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines with relatively high enantioselectivity.

Introduction

Replacement of a carbon atom of functional organic molecules by a silicon atom (known as "silicon switch") represents one of the effective ways of improving/modifying their biological activities or physical properties by taking advantage of the difference between carbon and silicon such as in the covalent radius, lipophilicity, and electronegativity, while keeping the similarity as congeners.[1] In particular, because nitrogen- and/or oxygen-containing heterocycles often appear as structural motifs for pharmaceuticals and optoelectronic materials, introduction of a silicon atom to these heterocycles would be highly attractive. Although such a strategy had been implemented for the past decades, available synthetic methods and accessible structures of silicon-containing heterocycles are currently still limited.[2,3]

Among the nitrogen- and oxygen-containing heterocycles, 4*H*-benzo[*d*][1,3]oxazines and their derivatives constitute a useful class[4] and are often found as core structures of pharmaceuticals such as etifoxine (anxiolytic and anticonvulsant drug),[5] efavirenz (antiretroviral medicine),[6] and tanaproget (nonsteroidal progestin)[7] (Fig. 1a). However, their silicon-switched analogs, sila-4*H*-benzo[*d*][1,3]oxazines, have never been reported to date presumably due to the lack of their synthetic methods. To remedy this methodological deficiency, herein we describe a palladium-catalyzed efficient synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines (Fig. 1b) from 3-amido-2-(arylsilyl)aryl triflates by the use of intramolecular Hiyama coupling, including its asymmetric variant *via* enantioselective transmetalation.[8]

Results and discussion

Recently, we reported that the reaction of 3-amino-2-(arylsilyl) aryl triflates such as **1a** in the presence of a palladium catalyst selectively gave 5,10-dihydrophenazasilines such as **2a** *via* 1,5-palladium migration followed by an intramolecular C–N bond

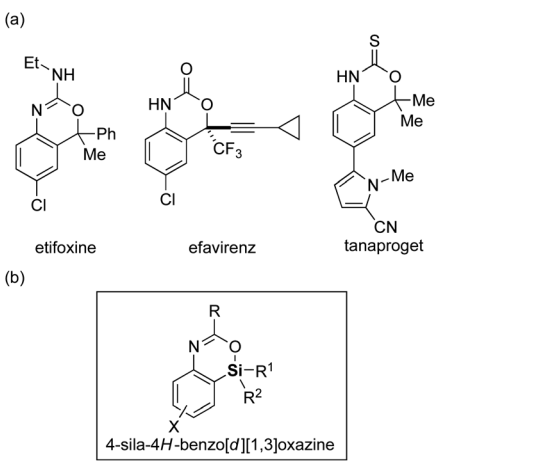

Fig. 1 (a) Examples of biologically active 4*H*-benzo[*d*][1,3]oxazine derivatives and (b) the structure of 4-sila-4*H*-benzo[*d*][1,3]oxazine.

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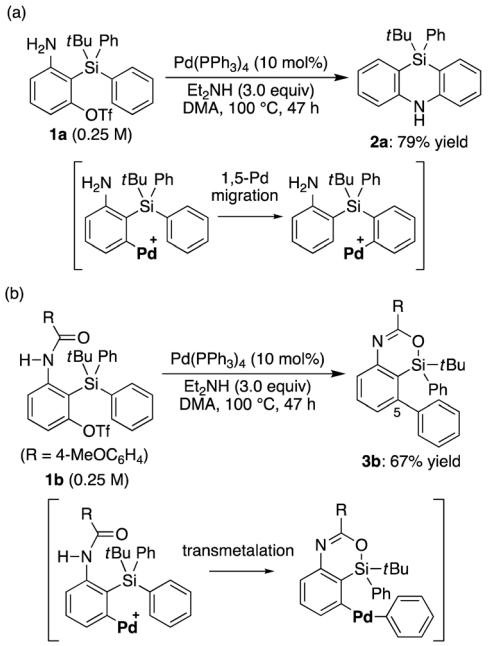
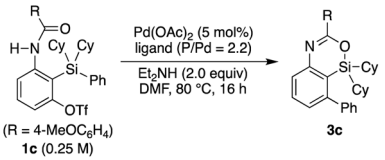


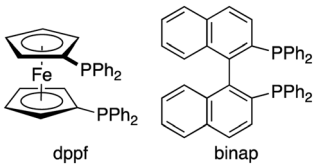
Scheme 1 (a) Synthesis of 5,10-dihydrophenazasiline from 3-amino-2-(arylsilyl)aryl triflate (previous work) and (b) initial finding for the synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazine from 3-amido-2-(arylsilyl) aryl triflate (this work).

Table 1 Palladium-catalyzed reaction of **1c** to give **3c**



Entry	Ligand	Conversion[a] (%)	Yield[b] (%)
1	None	50	46
2	PPh_3	58	47
3[c]	**PCy_3**	**100**	**94**
4[c]	$P(tBu)_3$	31	31
5	dppf	100	93
6	binap	100	86

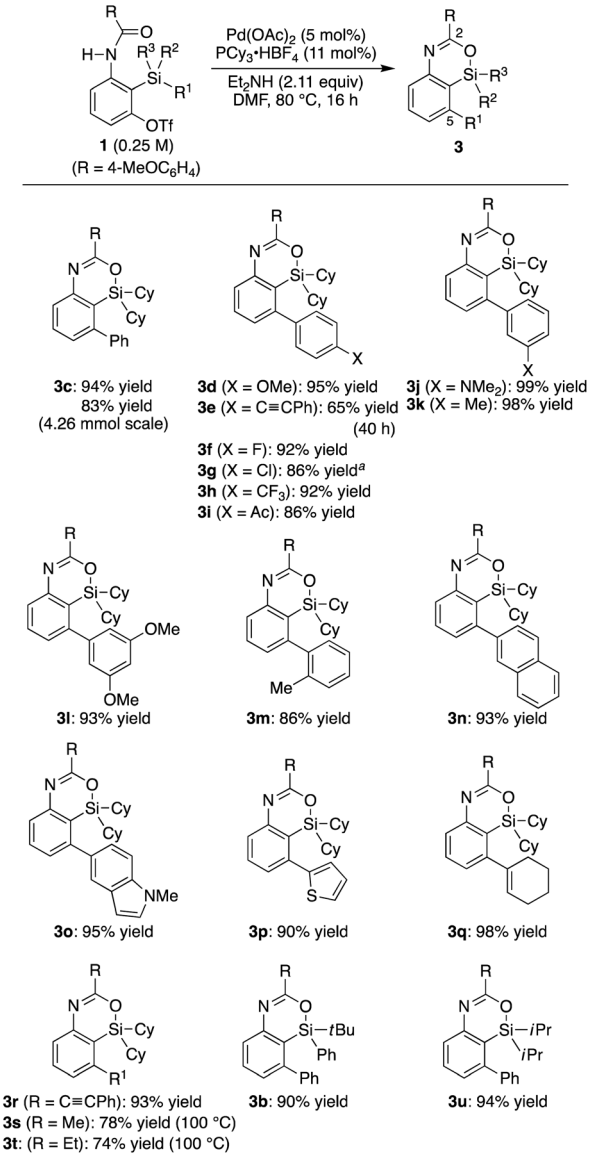
[a] Determined by ^1H NMR against internal standard ($MeNO_2$). [b] Isolated yield. [c] $PR_3 \cdot HBF_4/Et_2NH$ was used.



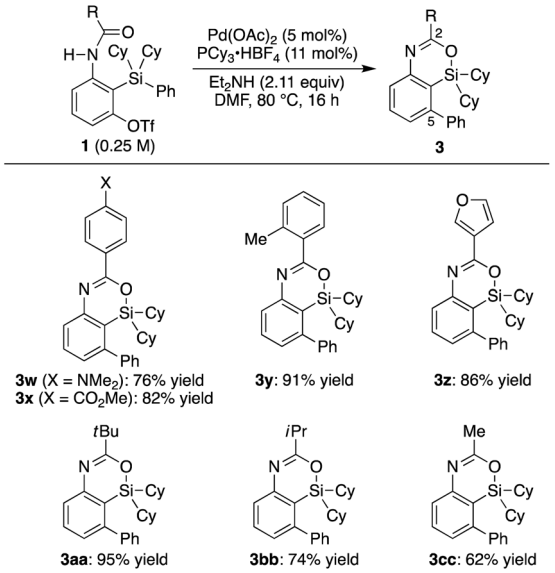
formation (Scheme 1a).[9] In stark contrast, we newly found that, when we employed *N*-acylated variant **1b** as the substrate under the same reaction conditions, 5-phenylated 4-sila-4*H*-benzo[*d*][1,3]oxazine **3b** was selectively obtained without forming the corresponding 5,10-dihydrophenazasiline (Scheme 1b). This reaction presumably took place through intramolecular transmetalation of a phenyl group from silicon to palladium with the aid of the acyl group on nitrogen instead of 1,5-palladium migration.[10] The overall process here can therefore be described as an intramolecular Hiyama coupling reaction, but it is quite different from the typical Hiyama coupling, where a carbon–carbon bond formation between organic (pseudo)halides and organosilanes is the primary process, and the resulting silicon moiety after the reaction is considered as a low-value byproduct and usually treated as waste.[11] On the other hand, the present reaction of **1b** to give **3b** is a rare example in that the Hiyama coupling provides a silicon-containing heterocycle as the value-added main product.[12]

Based on this finding, we initiated our studies for the palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines by the intramolecular Hiyama coupling of 3-amido-2-(arylsilyl)aryl triflates. As a starting point, we employed **1c** as the model substrate and examined the reaction conditions toward 4-sila-4*H*-benzo[*d*][1,3]oxazine **3c** (Table 1). When the reaction was conducted in the presence of $Pd(OAc)_2$ (5 mol%) and Et_2NH (2.0 equiv.) in DMF at 80 °C for 16 h, product **3c** was obtained in a moderate yield of 46% (entry 1). The use of PPh_3 (11 mol%) as the ligand for palladium did not change the reaction outcome (47% yield; entry 2). In contrast, a significantly higher yield of **3c** was achieved by using PCy_3 as the ligand (94% yield; entry 3), although the use of bulkier $P(tBu)_3$ resulted in the decrease of the yield (31% yield; entry 4). It was also found that the use of bisphosphine ligands such as dppf and binap could promote this reaction effectively as well (86–93% yield; entries 5 and 6).

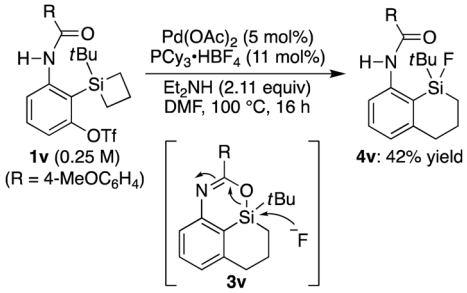
Under the conditions in Table 1, entry 3, various substituted aryl groups on the silicon atom could be transferred to the 5-position to give corresponding 4-sila-4*H*-benzo[*d*][1,3]oxazines **3d–m** in good to high yields irrespective of the electronic and steric nature of the aryl groups as summarized in Scheme 2 (65–99% yield). 2-Naphthyl, 5-indolyl, 2-thienyl, 1-cyclohexenyl, and phenylethynyl groups were also applicable as the migrating group from silicon to carbon, giving products **3n–r** in similarly high yields (90–98% yield). In addition to these (hetero)aryl, alkenyl, and alkynyl groups, methyl and ethyl groups were successfully transferred as well to give compounds **3s–t** in 74–78% yield by conducting the reaction at an elevated temperature (100 °C).[13,14] Regarding the 'spectator' substituents on the silicon atom, relatively bulky groups were found to be suitable such as *tert*-butyl and phenyl (**3b**) as well as diisopropyl (**3u**) other than dicyclohexyl, but sterically less hindered ones such as dimethyl were not applicable to the present catalysis.[15] On the other hand, substrate **1v** having a silacyclobutane as the silicon moiety underwent a ring-expansion reaction with concomitant cleavage of the initially formed silicon–oxygen bond by the fluoride, which is most likely derived from BF_4^- of the phosphine ligand salt, to give compound **4v** as the major product in 42% yield (eqn (1)).[12a,16,17] With regard to the substituent of the carbonyl group on nitrogen, various electronically and



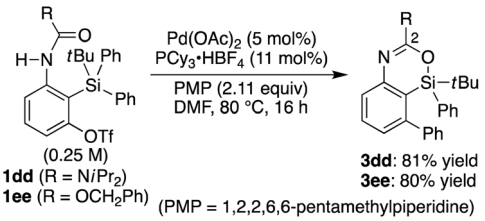
Scheme 2 Palladium-catalyzed synthesis of **3**: scope of R^1–R^3 on silicon. 0.15 mmol of **1** was used unless otherwise noted. [a]5.5 mol% of binap was used as the ligand instead of $PCy_3 \cdot HBF_4/Et_2NH$.



Scheme 3 Palladium-catalyzed synthesis of **3**: scope of R on carbonyl.



(1)



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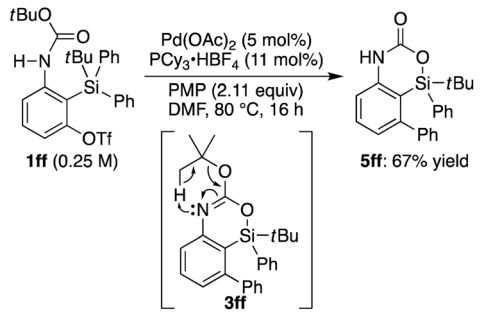


(3)

sterically different (hetero)aryl groups and alkyl groups could be tolerated, and corresponding 2-substituted 4-sila-4*H*-benzo[*d*][1,3]oxazines **3w–cc** were obtained in 62–95% yield (Scheme 3). In addition, diisopropyl urea **1dd** and benzyl carbamate **1ee** could also be employed in the present catalysis to give 2-heteroatom-substituted 4-sila-4*H*-benzo[*d*][1,3]oxazines **3dd** and **3ee** under the slightly modified reaction conditions (eqn (2)). It is worth noting that *tert*-butyl carbamate **1ff** gave 4-sila-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **5ff** as the major product, presumably through intramolecular elimination of the *tert*-butyl group of initially formed 4-sila-4*H*-benzo[*d*][1,3]oxazine **3ff** under the reaction conditions (eqn (3)).

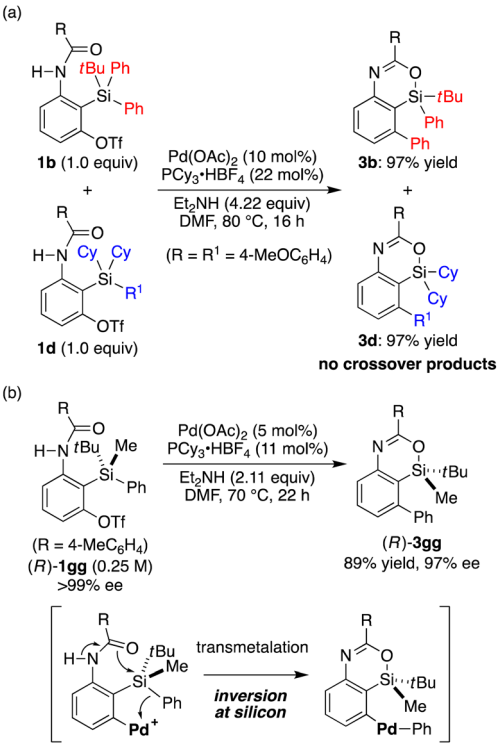
The obtained 4-sila-4*H*-benzo[*d*][1,3]oxazines **3** were found to be reasonably stable against H_2O under neutral conditions, and complete hydrolytic ring-opening of **3c** required a prolonged

heating in H_2O at 110 °C for 40 h, giving corresponding silanol **6** in 90% yield (Scheme 4a). In addition, in analogy to the derivatization of 4*H*-benzo[*d*][1,3]oxazines,[18] the C–N double bond of **3c** could be dialkylated by sequential treatment with methyl triflate and *n*-butyllithium to give compound **7** in 62% yield with retaining the silacyclic structure (Scheme 4b). Furthermore, selective C–H borylation at the least hindered 7-position of **3l** was achieved under iridium catalysis to give compound **8** in 87% yield (Scheme 4c).[19]

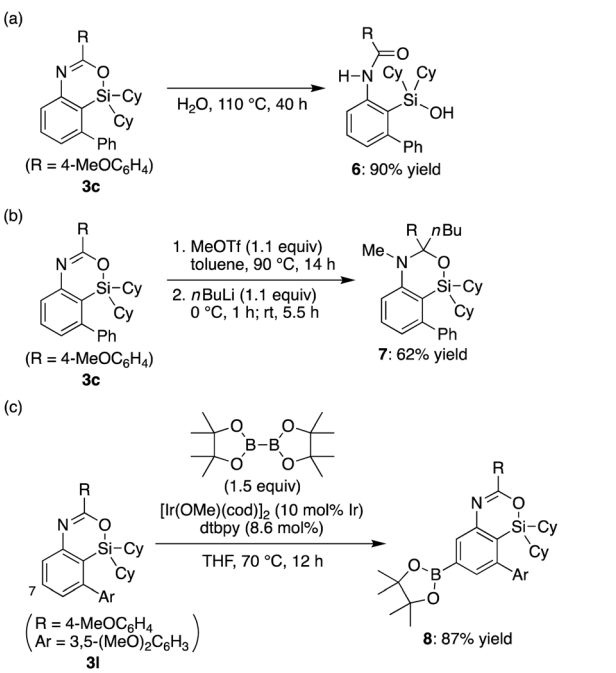
To gain insights into the reaction mechanism of the present catalysis, we conducted a control experiment. When the 1 : 1 mixture of substrates **1b** and **1d** was subjected to the present reaction conditions, products **3b** and **3d** were obtained in nearly quantitative yields without forming any crossover products (Scheme 5a). This result indicates that the transmetalation of an aryl group from silicon to palladium takes place intramolecularly once the arylpalladium species is generated by oxidative addition of an aryl triflate to the palladium catalyst.[20] We also prepared silicon-stereogenic enantiopure substrate (*R*)-**1gg**[17,21] and conducted the present reaction to probe the stereochemical outcome at the silicon atom (Scheme 5b). As a result, 4-sila-4*H*-benzo[*d*][1,3]oxazine **3gg** was obtained in 89% yield with 97% ee (*R*),[17,22] confirming that the transmetalation of the phenyl group from silicon to palladium takes place with inversion of configuration at the silicon stereocenter in a stereospecific manner. This represents the first example of the stereochemical investigation at silicon during transmetalation in the Hiyama coupling reaction as far as we are aware,[23,24] although the present result may not be directly generalized due to its intramolecular nature.

Based on the above consideration, a proposed catalytic cycle for the synthesis of **3c** from **1c** in the present catalysis is shown in Scheme 6. Oxidative addition of aryl triflate of **1c** to palladium(0) gives arylpalladium(II) species **A**. This then undergoes intramolecular transmetalation *via* inversion at silicon to give diarylpalladium(II) species **B**. Subsequent carbon–carbon bond-forming reductive elimination gives 4-sila-4*H*-benzo[*d*][1,3]oxazine **3c** along with regeneration of palladium(0).

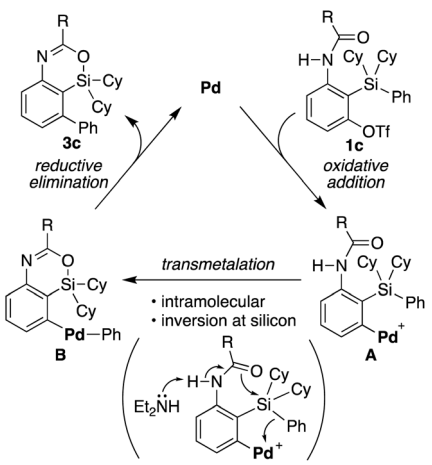
In our preliminary study, we found that the present catalysis could also be applied to enantioselective synthesis of silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines by using prochiral substrates in the presence of an appropriate chiral ligand.[25] According to our survey, Josiphos-type ligand **L*** was found to be



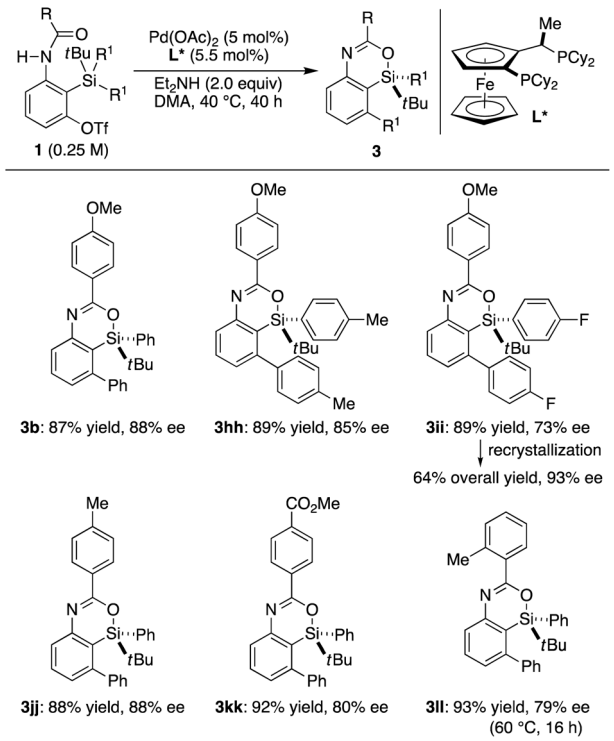
Scheme 5 Mechanistic insights of the present catalysis.



Scheme 4 Transformation of 4-sila-4*H*-benzo[*d*][1,3]oxazines **3**. dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl.



Scheme 6 A proposed catalytic cycle for the palladium-catalyzed synthesis of **3c** from **1c**.



Scheme 7 Palladium-catalyzed asymmetric synthesis of silicon-stereogenic 3 *via* enantioselective transmetalation.

promising in inducing relatively high enantioselectivity. Thus, the reaction of **1b** having two phenyl groups on the silicon atom led to the formation of compound **3b** in 87% yield with 88% ee (*R*) by selective transmetalation of one phenyl group over the other in the presence of a Pd/**L*** catalyst (Scheme 7).[17] Other aryl groups could also be accommodated on the silicon atom for this desymmetrization with moderate to good efficiency (**3hh** and **3ii**). Electronically or sterically different benzoyl groups on nitrogen were tolerated as well to give corresponding silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines **3jj–ll** with up to 88% ee. Although further improvement on the enantioselectivity is desirable, the ee of **3ii** could be upgraded from 73% to 93% by recrystallization from hexane, and the result obtained here is a rare example of asymmetric catalysis involving an enantioselective transmetalation to give silicon-stereogenic compounds.[8]

Conclusions

We developed a palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, silicon-switched analogs of biologically relevant 4*H*-benzo[*d*][1,3]oxazines, by the intramolecular Hiyama coupling of 3-amido-2-(arylsilyl)aryl triflates. The present reaction represents an unusual way of utilizing the Hiyama coupling toward the synthesis of functional organosilanes as the main products and it proceeds through intramolecular transmetalation with inversion of the stereochemistry at the silicon center. An asymmetric variant of this process was also demonstrated by employing prochiral substrates in the presence of a Josiphos-type chiral ligand to give silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines with relatively high enantioselectivity. Future studies will be directed toward further expansion of this process for the synthesis of various functional organosilicon compounds.

Data availability

Experimental procedures, characterization data, X-ray crystallographic data, and NMR spectra are available in the ESI.†

Author contributions

R. S. conceptualized the project. D. L. conducted all the experiments and compound characterizations. D. L. and R. S. wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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14 Primary alkyl groups are known to undergo transmetalation preferentially over secondary alkyl groups. The same trend would be expected for methyl group *vs.* secondary alkyl groups. See ref. 13*b*.

15 2-(4-Methoxyphenyl)benzo[*d*]oxazole was obtained as the major product presumably through the aryne formation from 2-(dimethyl(phenyl)silyl)aryl triflate. See the ESI for details.†

16 See the ESI for details.†

17 Deposition numbers 2194996 (for **S2**), 2194997 (for **3gg**·HOTf), 2194998 (for **3b**), and 2247904 (for **4v**) contain the supplementary crystallographic data for this paper.†

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