Synthesis and Properties of Sila[*n*]helicenes via Dehydrogenative Silylation of C–H Bonds under Rhodium Catalysis

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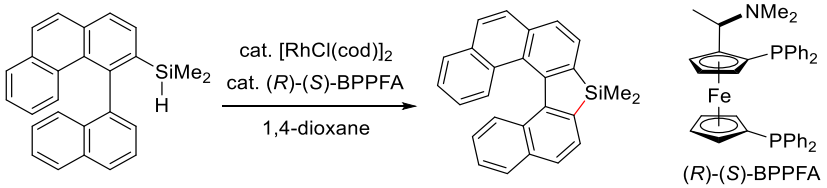
Supporting Information



ABSTRACT: Use of a rhodium catalyst with (*R*)-(*S*)-BPPFA ligand allows efficient synthesis of sila[*n*]helicenes *via* dehydrogenative silylation of C–H bonds. By selecting the proper ligands, the current method provides the ability to prepare unsymmetrical sila[*n*]helicene derivatives without any oxidants. The resulting sila[*6*]helicene is a rare example of a five-membered ring-fused [*6*]helicene, which was isolated as a single pure enantiomer without substituents on the terminal benzene rings.

Silicon-containing π-conjugated molecules show promise as materials useful in the areas of electro- and photoluminescence.[1] The incorporated silicon atom has a significant impact on the energy levels of the frontier orbital, and that of the LUMO is effectively stabilized by the interaction between the low lying σ* orbital of two exocyclic σ-bonds of the silicon atom and the π* orbital of the conjugated π-system of the backbone. Catalytic dehydrogenative silylation of C–H bonds is a straightforward, atom-efficient, and sustainable route toward these silicon-containing π-conjugated molecules.[2-5] Since our first report in 2010 on the synthesis of silafluorenes,[3a] rhodium-catalyzed dehydrogenative silylation has been developed for the synthesis of various silicon-containing π-conjugated molecules, such as silicon-bridged *p*-terphenyl,[3a] spirosilabifluorenes,[3b,3j] benzosilolometallocenes,[3e-g] dihydrobenzosilole,[3i] and phenazasilines[3d] (Figure 1). To further demonstrate the utility of this silylative cyclization, development of a robust catalyst system with improved reaction efficiency is highly desirable for the synthesis of more challenging silicon-containing π-systems. The present paper describes the synthesis of sila[*n*]helicenes (n = 4, 5 and 6) with uniquely merged π-conjugated systems of helicene and silole. This study also demonstrates that the amino group-substituted (*R*)-(*S*)-BPPFA ((*R*)-*N*,*N*-dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine) ligand is highly effective for the rhodium-catalyzed dehydrogenative silylation of C–H bonds.

Helicene possesses a unique screw-shaped π-system consisting of all *ortho*-annelated aromatic rings.[6] In addition to a unique function as an optoelectronic material, these compounds can be utilized as ligands and organocatalysts.[6c] Despite their promising potential for functional materials, few

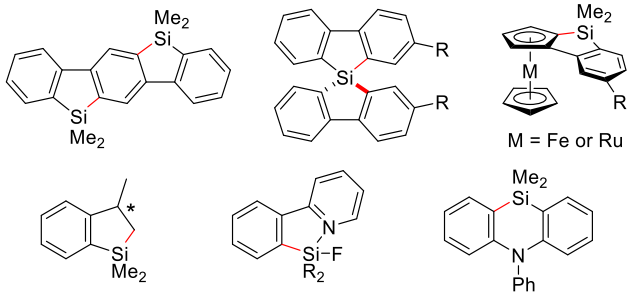


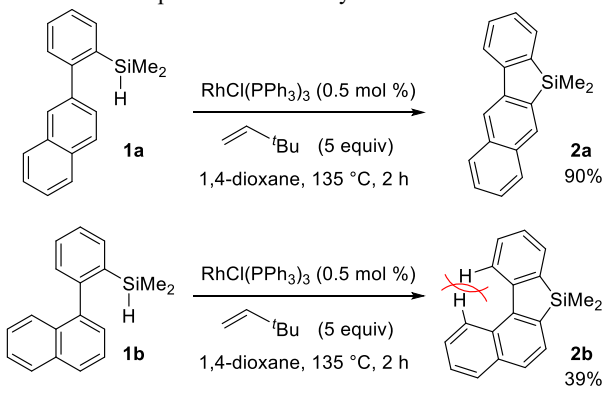
Figure 1. Silicon-containing π-conjugated molecules synthesized by dehydrogenative silylation of C–H bonds

examples of helicenes with fused-silacycles have been reported.[7] Sila[*n*]helicenes (n = 5 or 7) have been synthesized by reaction of dilithiobiaryls with dichlorosilane,[7a-d] rhodium- or iridium-catalyzed [2+2+2] cycloaddition of silicon-tethered polyynes,[7e,g] and platinum-catalyzed arylative cyclization of 2-alkynylbiaryls with a dibenzosilole backbone.[7f] While these methods provide a route to sila[*n*]helicenes, their utility can be limited by requiring complicated precursors containing the proper reactive functional groups. Thus far, no syntheses of sila[*n*]helicenes with an unsymmetrical structure have been reported. Development of flexible and convenient synthetic methods for sila[*n*]helicenes could allow customization of their properties, and dehydrogenative silylation with the activation of ubiquitous C–H bonds is thought to allow a more straightforward approach.

We previously reported that Wilkinson's catalyst, $RhCl(PPh_3)_3$, is effective for the silylative cyclization of 2-(2-

hydrosilylphenyl)naphthalene **1a** to benzosilafluorene **2a** in the presence of 3,3-dimethyl-1-butene as a hydrogen acceptor (Scheme 1(a)).[3a] However, the corresponding cyclization of its isomer **1b** under the same reaction conditions resulted in formation of the expected sila[*4*]helicene **2b** in low yield (Scheme 1(b)).[8] This reactivity difference was rationalized by the steric repulsion between the two hydrogen atoms in the terminal benzene ring of helicene structures (see Figure S4 in Supporting Information (SI)). Considering our previous study on the promotion of dehydrogenative silylation with the proper choice of ligand,[3e,3i,3j] the effect of ligands was investigated in the reaction of **1b** with $[RhCl(cod)]_2$ as the precatalyst.

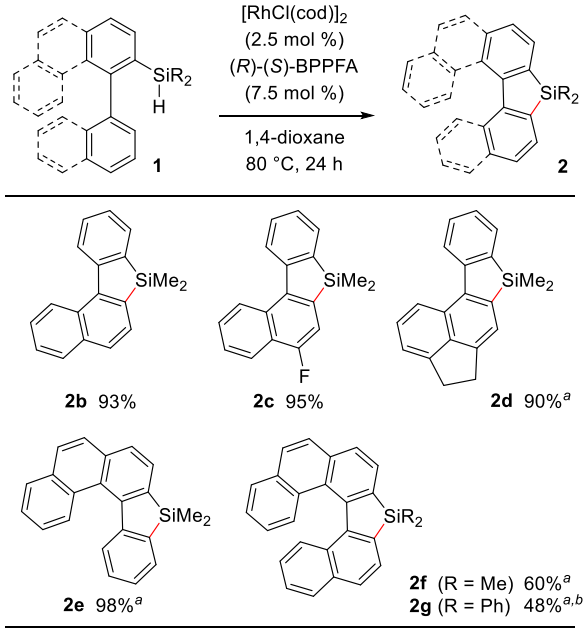
Scheme 1. Comparison of reactivity



The study revealed that the use of electron-rich monodentate phosphine ligands, such as PCy_3 and $P(4\text{-}MeOC_6H_4)_3$, furnished the expected **2b** in low yield, whereas the electron-deficient phosphine and phosphite ligands failed to promote the reaction efficiently (Table S1 in SI, entries 1-8). The use of bidentate phosphine ligands resulted in formation of **2b** in moderate to good yield (entries 9-12). Although the typical C_2-symmetric diphosphines, including BINAP[3b,3j] and SEGPHOS, were less effective, the yield increased to 96% when (*R*)-(*S*)-BPPFA was used as a ligand even in the absence of a hydrogen acceptor (entries 13-17).[9] Bulky and electron-rich (*R*)-DTBM-SEGPHOS, which was the best ligand for the enantioselective dehydrogenative silylation in our previous study,[3e,3i] produced **2b** in lower yield (entry 15). In contrast, nitrogen-based bidentate ligands, which were useful for a previous intermolecular dehydrogenative silylation of C–H bonds,[10] were less reactive and resulted in recovery of most of precursor **1b**. The combination of other rhodium and iridium precursors, $[Rh(OMe)(cod)]_2$, $[IrCl(cod)]_2$, and $[Ir(OMe)(cod)]_2$, with (*R*)-(*S*)-BPPFA was also tested, but none of them were superior to $[RhCl(cod)]_2$.[11,12]

Several sila[*n*]helicenes (n = 4, 5 and 6) were obtained under the current optimized reaction conditions (Figure 2). With (*R*)-(*S*)-BPPFA as a ligand, the reaction temperature could be decreased to 80 °C while still affording sila[*4*]helicene **2b** in 93% yield. Similarly, 1-(2-hydrosilylphenyl)naphthalene derivatives were converted to the corresponding sila[*4*]helicenes **2c** and **2d** in 95% and 90% yields, respectively. Sila[*5*]- and sila[*6*]helicenes **2e** and **2f** were also obtained, although a slightly higher temperature (135 °C) was required for the transformations due to the higher steric repulsion compared with that of sila[*4*]helicenes. The substituents on the silicon center were also variable, and diphenylsilane afforded the corresponding sila[*6*]helicene **2g** in slightly lower yield compared with the reaction of dimethylsilane **2f**.

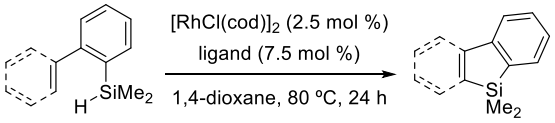
Figure 2 Rhodium-catalyzed dehydrogenative silylation of **1** leading to sila[*n*]helicene derivative **2**

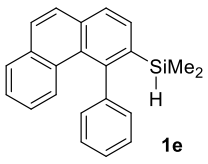
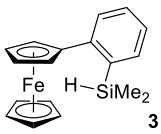


[a] At 135 °C. [b] 29% of the cyclization precursor was recovered.

As shown in Table S1 in SI, the current silylative cyclization was greatly facilitated when using (*R*)-(*S*)-BPPFA as a ligand. To investigate this result, a control experiment using 3-hydrosilyl-4-phenylphenanthrene **1e** as a precursor was performed (Table 1). Comparison of reactions using dppf and (*R*)-(*S*)-BPPFA as ligands indicated that the presence of an alkylamino group in the ligand structure promoted the reaction efficiently (entries 1 and 3). This is consistent with the increase of yield in the reaction using dppf as a ligand with triethylamine as an additive (entry 2). A similar trend in reactivity was observed for silylative cyclization of hydrosilyl-2-ferrocenylbenzene **3** (entries 4-6).[3e-g] These results can be explained by the facilitation of cleavage and oxidative addition

Table 1. Control experiment to clarify the effect of (*R*)-(*S*)-BPPFA



Entry	Substrate	ligand	Yield[a] / %
1[b]		dppf	87
2[b]		dppf + Et_3N (20 mol%)	93
3[b]		(*R*)-(*S*)-BPPFA	99 (98)
4		dppf	72
5		dppf + Et_3N (20 mol%)	77
6		(*R*)-(*S*)-BPPFA	80 (75[c])

[a]Determined by ^1H NMR. Isolated yields are in parentheses. [b]At 135 °C. [c](*R*)-8,8-Dimethylbenzosilolo[2,3-*a*]ferrocene was obtained in 26% *ee*.

of C–H bonds to the rhodium center by the amino group on (*R*)-(*S*)-BPPFA.

The optical properties of the resulting sila[*n*]helicenes **2b**, **2e**, and **2f** were investigated by UV-Vis absorption and fluorescence spectroscopy (Figure 3). The compounds showed a maximum peak around 290-300 nm along with a broad shoulder peak in the region of 330-360 nm in dichloromethane. The absorption maximum was red-shifted in the order of silafluorene (286 nm), **2b**, **2e**, and **2f**, which clearly indicates a decreased HOMO-LUMO energy gap due to effective expansion of π-conjugation (see Figure 4 for calculated molecular orbitals). Blue luminescence was observed for dichloromethane solutions of these sila[*n*]helicenes upon excitation at 290 nm. These values are summarized in Table 2 along with the fluorescence quantum yield (Φ), and torsion angles (θ) estimated from the optimized structure calculated using a DFT (density functional theory) method (Figures 4(c) and S2 in SI). The relatively high fluorescence quantum yield for the silole derivatives was reflected by the rigidity of the helicene backbone.

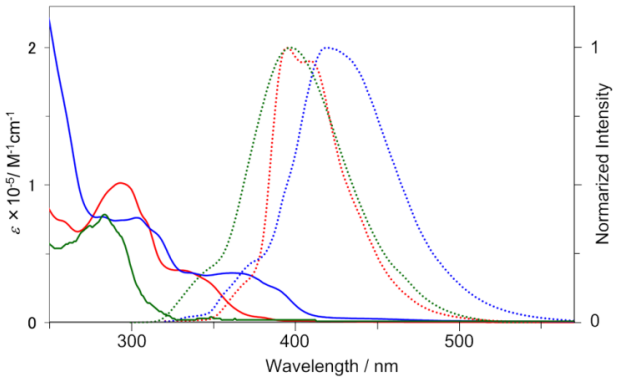


Figure 3. UV-Vis absorption (solid line) and fluorescence (dashed line) spectra of sila[*n*]helicenes **2b** (green), **2e** (red), and **2f** (blue) in CH_2Cl_2 (1×10^{-5} M) at 25 °C.

Table 2. Optical data and torsion angles for sila[*n*]helicenes

Compound	λ_{abs} / nm (ε x10^{-4} / M^{-1}cm^{-1})[a]	λ_{max}^{em} / nm[b]	Φ[c]	θ / °[d]
2b	288 (6.0), 349 (0.31)	397	0.12	16.6
2e	294 (10.2), 333 (3.8)	395, 409	0.15	17.6
2f	304 (7.6), 362 (3.6)	420	0.16	32.4

[a] Absorption in CH_2Cl_2 (1×10^{-5} M). [b] Maximum fluorescence emission in CH_2Cl_2 (5×10^{-6} M). [c] Absolute quantum yield determined by using a calibrated integrating sphere system. [d] Torsion angles estimated for the structure optimized by DFT method at the B3LYP/6-31G(d) level of theory.

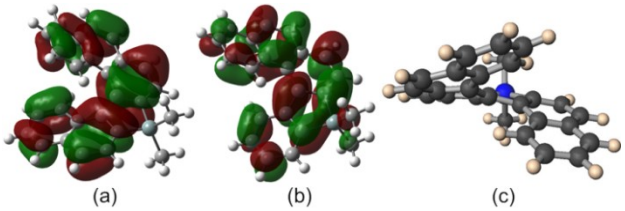


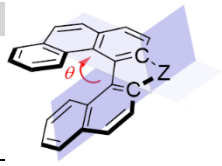
Figure 4. (a) HOMO, (b) LUMO orbitals, and (c) front view of the optimized structure of **2f** calculated by DFT

The optimized structure calculated by DFT clearly indicated that sila[*6*]helicenes **2f** and **2g** had large overlapping terminal benzene rings (Figure 4(c)). As expected, a single enantiomer of sila[*6*]helicene **2f** was obtained by optical resolution using HPLC with a chiral stationary phase at 25 °C. The optical rotation ($[\alpha]_D^{25}$) of enantio-enriched (*M*)-**2f** was −1625 (c = 0.09, $CHCl_3$).[13] The racemization rate constant k, which obeyed first-order kinetics, was determined at different temperatures (Table S3 and Figure S5 in SI). The activation energy for racemization ΔE was estimated from the k values to be 28.2 kcal/mol, which was lower than that reported for all benzene-[*6*]helicene by 5-10 kcal/mol (Figure S6).[14] Note that **2f** is a rare example of a five-membered ring-fused [*6*]helicene without any substitutions, which was isolated as a single pure enantiomer. Syntheses and optical resolutions of pyrrole or thiophene-fused [*6*]helicenes have been previously reported, but the molecules contained substituents on the terminal benzene rings that prevented rapid racemization.[15] The results of the DFT study indicate that the choice of bridging atom significantly affects the torsion angles, and a silicon atom induces a larger overlap of the two terminal benzene rings, which increases the resistance to racemization (Table 3). Due to the high fluorescence quantum yield compared with that of all benzene-[*6*]helicene,[16] **2f** can be expected as a novel chiral host molecule applicable to luminescent materials.[6]

Table 3. Optimized torsion angles (θ) for [*6*]helicene derivatives[a]

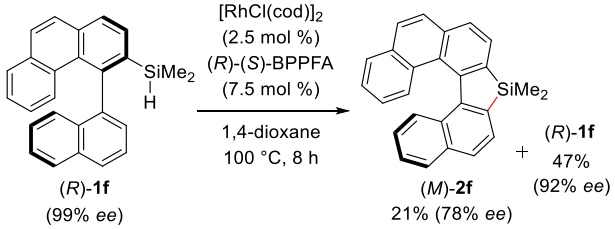
Z	CH_2	NH	O	SiH_2	P(=O)H
∠C–Z–C / °	102.6	109.4	105.9	91.9	91.4
θ / °	21.5	18.7	17.0	32.3	29.1

[a]Estimated for the structure optimized by DFT at the B3LYP/6-31G(d) level of theory.



Since optically active **1f** was obtained using HPLC with a chiral stationary phase at 25 °C, stereospecific cyclization of **1f** was attempted.[17,18] Treatment of axially chiral atropisomer (*R*)-**1f** (99% *ee*) with a catalytic amount of $[RhCl(cod)]_2$ and (*R*)-(*S*)-BPPFA at 100 °C for 8 h gave (*M*)-**2f** in 21% yield (78% *ee*) with 47% recovery of **1f** (92% *ee*) (Scheme 2).[13,19] This result implies that transfer from axial to helical chirality leading to **2f** was achieved during the silylative cyclization of **1f**, and that the loss of *ee* occurred after the catalytic reaction due to the competitive racemization of both **1f** and **2f**.[20,21]

Scheme 2. Transfer from axial to helical chirality by stereospecific cyclization of **1f**



In conclusion, a novel catalytic synthesis of sila[*n*]helicene derivatives with an unsymmetical structure was developed *via* activation of both Si–H and C–H bonds. Due to promotion of the reaction by (*R*)-(*S*)-BPPFA, the current dehydrogenative silylation proceeded under neutral conditions without any oxidants. The resulting sila[*6*]helicene was a rare example of the five-membered ring-fused [*6*]helicene, which was isolated as a pure single enantiomer without substituents on the terminal benzene rings. The stereochemical information relay from axial to helical was also attempted.

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REFERENCES

(1) (a) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley: New York, 2000. (b) *The Chemistry of Organic Silicon Compounds*, Vol. 1; Patai, S.; Rappoport, Z. Eds., Wiley: Chichester, U.K., 1989. (c) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2. (d) Fukazawa, A.; Yamaguchi, S. *Chem. Asian J.* **2009**, *4*, 1386. (e) Mortensen, M.; Husmann, R.; Veri, E.; Bolm, C. *Chem. Soc. Rev.* **2009**, *38*, 1002. (f) Franz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388.

(2) For reviews, see: (a) Cheng, C.; Hartwig, J. F. *Chem. Rev.* **2015**, *115*, 8946. (b) Yang, Y.; Wang, C. *Sci. China: Chem.* **2015**, *58*, 1266. (c) Sharma, R.; Kumar, R.; Kumar, I.; Singh, B.; Sharma, U. *Synthesis* **2015**, *47*, 2347. (d) Xu, Z.; Huang, W.-S.; Zhang, J.; Xu, L.-W. *Synthesis* **2015**, *47*, 3645.

(3) (a) Ureshino, T.; Yoshida, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324. (b) Kuninobu, Y.; Yamauchi, K.; Tamura, N.; Seiki, T.; Takai, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 1520. (c) Xiao, Q.; Meng, X.; Kanai, M.; Kuninobu, Y. *Angew. Chem. Int. Ed.* **2014**, *53*, 3168. (d) Li, H.; Wang, Y.; Yuan, K.; Tao, Y. Chen, R.; Zheng, C.; Zhou, X.; Li, J.; Huang, W. *Chem. Commun.* **2014**, *50*, 15760. (e) Murai, M.; Matsumoto, K.; Takeuchi, Y.; Takai, K. *Org. Lett.* **2015**, *17*, 3102. (f) Zhang, Q.-W.; An, K.; Liu, L.-C.; Yue, Y.; He, W. *Angew. Chem. Int. Ed.* **2015**, *54*, 6918. (g) Shibata, T.; Shizuno, T.; Sasaki, T. *Chem. Commun.* **2015**, *51*, 7802. (h) Lee, T.; Wilson, T. W.; Berg, R.; Ryberg, P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 6742. (i) Murai, M.; Takeshima, H.; Morita, H.; Kuninobu, Y.; Takai, K. *J. Org. Chem.* **2015**, *80*, 5407. (j) Murai, M.; Takeuchi, Y.; Yamauchi, K.; Kuninobu, Y.; Takai, K. *Chem.–A Eur. J.* **2016**, *22*, 6048.

(4) For the dehydrogenative silylation of C–H bonds leading to 9-silafluorenes via the generation of silylcation or silylradical species, see: (a) Furukawa, S.; Kobayashi, J.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 14192. (b) Furukawa, S.; Kobayashi, J.; Kawashima, T. *Dalton Trans.* **2010**, *39*, 9329. (c) Curless, L. D.; Ingleson, M. J. *Organometallics* **2014**, *33*, 7241. (d) Leifert, D.; Studer, A. *Org. Lett.* **2015**, *17*, 386. (e) Xu, L.; Zhang, S.; Li, P. *Org. Chem. Front.* **2015**, *2*, 459.

(5) For recent works on dehydrogenative functionalization, including phosphination, borylation, and germylation of C–H bonds, see: (a) Kuninobu, Y.; Yoshida, T.; Takai, K. *J. Org. Chem.* **2011**, *76*, 7370. (b) Kuninobu, Y.; Iwanaga, T.; Omura, T.; Takai, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 4431. (c) Murai, M.; Matsumoto, K.; Okada, R.; Takai, K. *Org. Lett.* **2014**, *16*, 6492. (d) Murai, M.; Omura, T.; Kuninobu, Y.; Takai, K. *Chem. Commun.* **2015**, *51*, 4583. For our recent contributions on the synthesis of functionalized π-systems, see: (e) Murai, M.; Maekawa, H.; Hamao, S.; Kubozono, Y.; Roy, D.; Takai, K. *Org. Lett.* **2015**, *17*, 708. (f) Murai, M.; Yanagawa, M.; Nakamura, M.; Takai, K. *Asian J. Org. Chem.* **2016**, *5*, 629.

(6) For reviews, see: (a) Shen, Y.; Chen, C.-F. *Chem. Rev.* **2011**, *112*, 1463. (b) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 1051. (c) Saleh, N.; Shen, C.; Crassous, J. *Chem. Sci.* **2014**, *5*, 3680. (d) Tanaka, K.; Kimura, Y.; Murayama, K. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 375.

(7) (a) Hoshi, T.; Nakamura, T.; Suzuki, T.; Ando, M.; Hagiwara, H. *Organometallics* **2000**, *19*, 3170. (b) Hoshi, T.; Nakamura, T.; Suzuki, T.; Ando, M.; Hagiwara, H. *Organometallics* **2000**, *19*, 4483. (c) Yasuike, S.; Iida, T.; Okajima, S.; Yamaguchi, K.; Seki, H.; Kurita, J. *Tetrahedron* **2001**, *57*, 10047. (d) Schafer, A. G.; Wieting, J. M.; Mattson, A. E. *Org. Lett.* **2011**, *13*, 5228. (e) Shibata, T.; Uchiyama, T.; Yoshinami, Y.; Takayasu, S.; Tsuchikama, K.; Endo, K. *Chem. Commun.* **2012**, *48*, 1311. (f) Oyama, H.; Nakano, K.; Harada, T.; Kuroda, R.; Naito, M.; Nobusawa, K.; Nozaki, K. *Org. Lett.* **2013**, *15*, 2104. (g) Murayama, K.; Oike, Y.; Furumi, S.; Takeuchi, M.; Noguchi, K.; Tanaka, K. *Eur. J. Org. Chem.* **2015**, 1409.

(8) 1,1,3,3-Tetramethyl-1,3-di(2-(1-naphthyl)phenyl)disiloxane (**4**) was obtained as a side product probably due to the competitive oxidation by the dissolved oxygen in dioxane. The structure of this product corresponded to that synthesized by reaction of 1-(2-lithiophenyl)naphthalene with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane.

(9) Dehydrogenative functionalization without any hydrogen acceptors (oxidants) is rare. For reviews, see: (a) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10236. (b) Mo, J.; Wang, L.; Liu, Y.; Cui, X. *Synthesis* **2015**, *47*, 439. The efficiency of the current silylative cyclization was not improved by addition of hydrogen acceptors, such as 3,3-dimethyl-1-butene, norbornene, cyclohexene, and methyl acrylate, in contrast to the results of our previous study (ref. 3a).

(10) (a) Simmons, E. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 17092. (b) Kuznetsov, A.; Gevorgyan, V. *Org. Lett.* **2012**, *14*, 914. (c) Li, B.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 6586. (d) Murai, M.; Takami, K.; Takai, K. *Chem.-Eur. J.* **2015**, *21*, 4566. (e) Murai, M.; Takami, K.; Takeshima, H.; Takai, K. *Org. Lett.* **2015**, *17*, 1798. (f) Cheng, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 592.

(11) Effect of precatalysts with a catalytic amount of (*R*)-(*S*)-BPPFA at 135 °C in 1,4-dioxane for 24 h: $[Rh(OMe)(cod)]_2$ 89%, $[IrCl(cod)]_2$ 24%, and $[Ir(OMe)(cod)]_2$ 19% of **2b** was obtained, respectively.

(12) Effect of solvents (0.50 M) with a catalytic amount of $[RhCl(cod)]_2$ and (*R*)-(*S*)-BPPFA at 80 °C for 24 h: toluene 84%, 1,2-dichloroethane 82%, MeCN 4%, THF 79%, and DMF 0% of **2b** was obtained, respectively.

(13) The absolute stereochemistry of **2f** was assigned by comparison of experimentally obtained optical rotation with that reported for sila[7]helicene in ref 7f.

(14) Martin, R. H.; Marchant, M.-J. *Tetrahedron Lett.* **1972**, *13*, 3707.

(15) (a) Moussa, S.; Aloui, F.; Hassine, B. B. *Tetrahedron Lett.* **2012**, *53*, 5824. (b) Pischel, I.; Grimme, S.; Kotila, S.; Nieger, M.; Vögtle, F. *Tetrahedron: Asymmetry* **1996**, *7*, 109. (c) Kötzner, L.; Webber, M. J.; Martínez, A.; De Fusco, C.; List, B. *Angew. Chem. Int. Ed.* **2014**, *53*, 5202.

(16) Vander Donckt, E.; Nasielski, J.; Greenleaf, J. R.; Birks, J. B. *Chem. Phys. Lett.* **1968**, *2*, 409.

(17) The structure and absolute configuration of **1f** were unambiguously determined by single crystal X-ray crystallography. See Figure S3 and Table S2 in SI for details.

(18) Stereospecific transformation from axial to helical chirality for the synthesis of chiral helicenes is rare. See: (a) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806. (b) Nakano, K.; Hidehira, Y.; Takahashi, K.; Hiyama, T.; Nozaki, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 7136.

(19) The same reaction at 100 °C for 24 h gave **2f** in 30% yield (56% *ee*) with the recovery of **1f** in 20% yield (74% *ee*), and at 135 °C for 12 h gave **2f** in 31% yield (0% *ee*) with the recovery of **1f** in 13% yield (64% *ee*).

(20) Treatment of optically active sila[*6*]helicene **2f** (99% *ee*) in dioxane at 135 °C for 12 h resulted in complete racemization (0% *ee*). Racemization of the precursor **1f** (99% *ee*) was much slower under the same reaction conditions (**1f** was recovered with 64% *ee*).

(21) The *ee* of the sila[*6*]helicenes **2f** obtained from silylative cyclization of *rac*-**1f** with (*R*)-(*S*)-BPPFA, (*R*)-BINAP, and (*R*)-DTBM-SEGPHOS at 100 °C for 24 h was less than 5%. The cyclization of **1e** and *rac*-**1g** also gave a similar result due to the rapid racemization of the resulting sila[*n*]helicenes at high temperature. An attempted kinetic resolution of *rac*-**1f** with (*R*)-(*S*)-BPPFA at 100 °C for 8 h gave **2f** in 16% yield (2% *ee*) together with recovery of **1f** in 42% yield (5% *ee*).