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Communication

Catalytic Enantioselective Dehydrogenative Si−O Coupling to Access Chiroptical Silicon-Stereogenic Siloxanes and Alkoxysilanes

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ABSTRACT: A rhodium-catalyzed enantioselective construction of triorgano-substituted silicon-stereogenic siloxanes and alkoxysilanes is developed. This process undergoes a direct intermolecular dehydrogenative Si−O coupling between dihydrosilanes with silanols or alocohols, giving access to a variety of highly functionalized chiral siloxanes and alkoxysilanes in decent yields with excellent *stereo*control, that significantly expand the chemical space of the silicon-centered chiral molecules. Further utility of this process was illustrated by the construction of CPL-active (circularly polarized luminescence) silicon-stereogenic alkoxysilane small organic molecules. Optically pure bis-alkoxysilane containing two silicon-stereogenic centers and three pyrene groups displayed a remarkable g_{lum} value with a high fluorescence quantum efficiency (g_{lum} = 0.011, Φ_F = 0.55), which could have great potential application prospects in chiral organic optoelectronic materials.

Silicon-containing molecules are of great academic and industrial importance with widespread applications in many areas. In the past few decades, the development of new methods for the preparation of novel types of organosilicon compounds has been intensively studied, which has led to their broad use in a diverse range of organic, organometallic, and polymeric chemistry.[1−3] In particular, siloxanes and alkoxysilanes (silyl ethers) are fundamentally important skeletons, which are widely used as privileged monomers in silicon-based materials, and valuable protecting groups, reagents, intermediates in organic synthesis.[4−10] Despite vast methods for the synthesis of siloxanes and alkoxysilanes,[1−10] the access of these organosilicon compounds bearing silicon-stereogenic centers in enantioenriched forms has been significantly less explored, which severely hampers their applications in the design and development of new chiral silicon-based materials.

Historically, the synthesis of silicon-stereogenic alkoxysilanes relied on the optical resolution and kinetic resolution with chiral alcohol auxiliaries.[11−15] Despite the success of these resolution methods, they are limited in substrate scope along with low efficiency and poor atom-economy. Thus, the development of novel synthetic methods toward silicon-stereogenic alkoxysilanes based on asymmetric synthesis is more attractive but was proved to be very challenging. In the 1970s, the Corriu group developed a seminal work for the asymmetric alcoholysis of dihydrosilanes in the presence of rhodium catalyst.[16,17] When a chiral alcohol, such as (−)-menthol, was used in the Si−O coupling reaction, a moderate enantioselectivity of the silicon-stereogenic center was achieved (48% *ee*, determined after stereospecific nucleophilic displacement, Scheme 1a). Later, Leighton and co-workers realized a chiral alcohol substrate- and chiral copper catalyst-induced variant, which produced the desired silicon-stereogenic alkoxysilanes with high diastereoselectivity (90:10 *dr*, Scheme 1a).[18] In addition, a number of asymmetric substitutions of one of two amino or alkoxy groups or chlorine atoms at the silicon atom has also been demonstrated for the generation of silicon-stereogenic alkoxysilanes via the control of stoichiometric chiral reagents or chiral auxiliaries.[19−25] Apart from the stoichiometric chiral substrates-induced approach, asymmetric catalysis for the construction of silicon-stereogenic silanes is undoubtably more fascinating.[26−34] To the best of our knowledge, the first example for the catalytic enantioselective alcoholysis of dihydrosilanes with achiral alcohols was also reported by Corriu and co-workers in the 1970s using a chiral Rh/(*S*,*S*)-DIOP catalyst (19% *ee* obtained).[16,17] Later, the Xu group made several efforts to access silicon-stereogenic alkoxysilanes via enantioselective alcoholysis of dihydrosilanes[35,36] (Scheme 1b). Besides the alcoholysis of dihydrosilanes, a few examples of transition-metal-catalyzed enantioselective hydrosilylation of ketones[37−39] and desymmetrization of tetraorganosilanes via cleavage of a Si−C bond along with formation of a Si−O bond[40,41] could also produce the silicon-stereogenic alkoxysilanes. It is noteworthy that the catalytic asymmetric synthesis of enantioenriched silicon-stereogenic siloxanes has remained unknown up to date. Given the increasing demand for the synthesis of novel functional-materials-oriented chiral organosilicon compounds, the exploration and development of new general strategies for the facile access of silicon-stereogenic siloxanes and alkoxysilanes with high efficiency and enantioselectivity are highly desirable.

Recently, we have reported an enantioselective intramolecular C−H silylation strategy for the synthesis of enantioenriched silicon-stereogenic silanes.[42−45] With the

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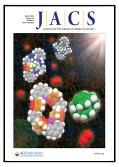
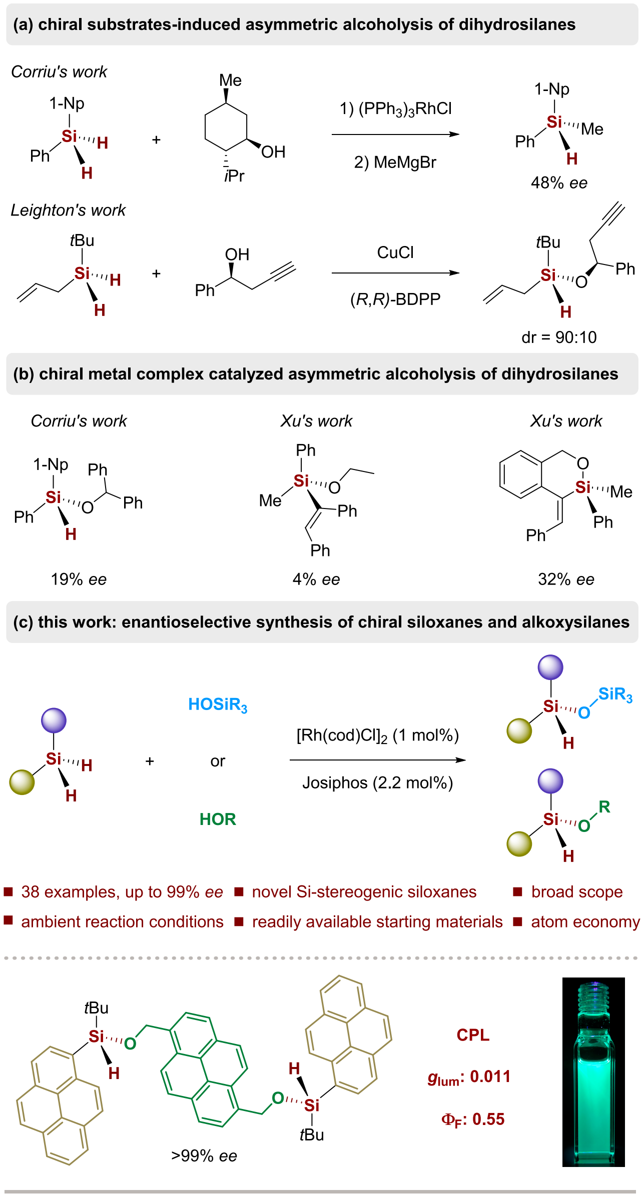


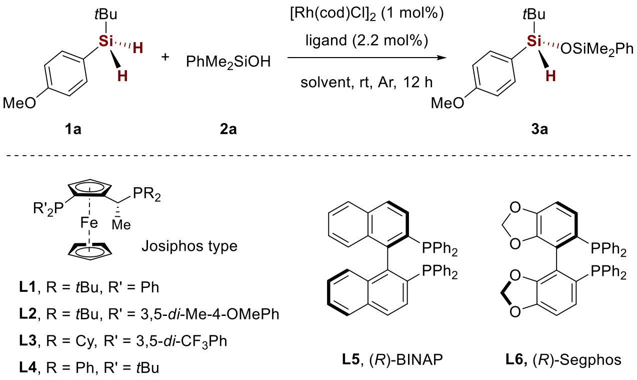
Scheme 1. Asymmetric Synthesis of Si-Stereogenic Alkoxysilanes



continued interest in the construction of novel silicon-stereogenic organosilicon compounds, we questioned whether we could expand the toolbox to achieve a general intermolecular dehydrogenative Si−H/O−H coupling, enabling the streamlined synthesis of silicon-stereogenic siloxanes and alkoxysilanes. Herein, we report the development of a rhodium-catalyzed enantioselective intermolecular dehydrogenative Si−O coupling reaction between dihydrosilanes with silanols or alocohols, which gives access to a wide range of highly functionalized chiral siloxanes and alkoxysilanes in good to excellent yields and enatioselectivities (Scheme 1c). Further utility of this enantioselective dehydrogenative Si−O coupling was illustrated by the construction of CPL-active (circularly polarized luminescence) silicon-stereogenic alkoxysilane small organic molecules. Optically pure bis-alkoxysilane containing two silicon-stereogenic centers and three pyrene groups displayed a remarkable g_{lum} value with a high fluorescence quantum efficiency ($g_{\mathrm{lum}} = 0.011$, $\Phi_F = 0.55$), which could have great potential applications in chiral organic optoelectronic materials.

At the outset of our research, we mainly focused on the catalytic asymmetric synthesis of enantioenriched silicon-stereogenic siloxanes. We commenced our studies by examining the intermolecular dehydrogenative Si−O coupling reaction of *tert*-butyl(4-methoxyphenyl)silane **1a** with dimethyl(phenyl)silanol **2a** in the presence of Rh catalyst. At room temperature in the solvent of toluene, several chiral diphosphine ligands were tested. Treatment of **1a** with **2a** by using $[Rh(cod)Cl]_2$ (1 mol %) as the catalyst and Josiphos **L1** (2.2 mol %) as the chiral ligand successfully delivered the desired Si−O coupling silicon-stereogenic siloxane product **3a** in 36% yield with good enantiocontrol (74% *ee*) (Table 1, entry 1). Other Josiphos type ligands with different electronic properties (**L2** and **L3**) did not increase the yields and enantioselectivities (Table 1, entries 2 and 3). Interestingly, when exchanging the *t*Bu-substituent and the Ph-substituent on the two phosphine atoms of the Josiphos ligand (**L4**), both the yield and enantioselectivity were sharply increased affording 68% yield with 97% *ee* (Table 1, entry 4). Further examination of the chiral ligands found that BINAP **L5** and Segphos **L6** were also effective for this reaction, albeit in a relatively lower yields and *ee* (Table 1, entries 5−6). Investigation of other common solvents in the presence of **L4** disclosed that DCE (1,2-dichloroethane) and 1,4-dioxane could also afford moderate yields of the desired siloxane **3a** with good enantioselectivities, while MeCN failed to produce the corresponding product (Table 1, entries 7−9).

Table 1. Development of Reaction Conditions[a]

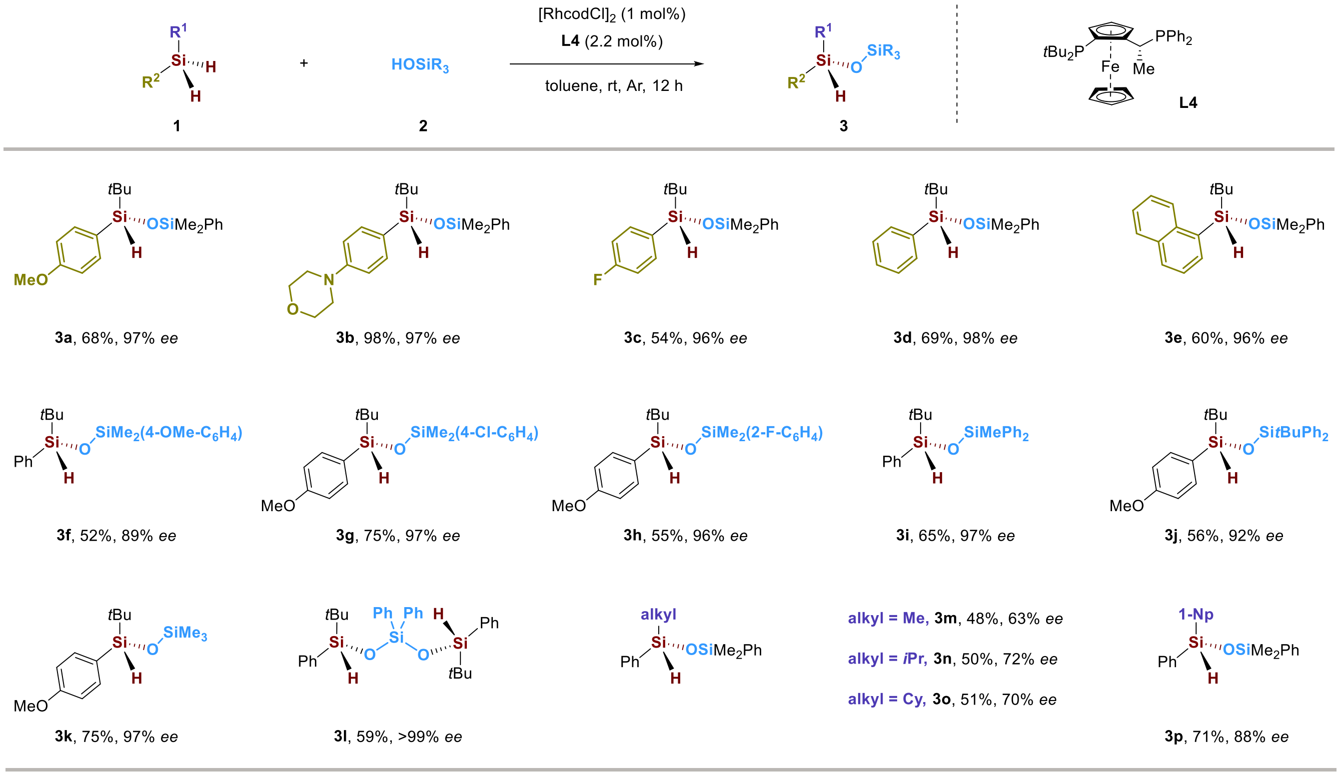


Entry	Ligand	Solvent	Yield (%)	*ee* (%)
1	**L1**	toluene	36	74
2	**L2**	toluene	23	10
3	**L3**	toluene	33	70
4	**L4**	toluene	68	97
5	**L5**	toluene	42	70
6	**L6**	toluene	43	89
7	**L4**	CH_3CN	0	
8	**L4**	DCE	47	86
9	**L4**	dioxane	45	97

[a] Conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), $[Rh(cod)Cl]_2$ (1 mol %), ligand (2.2 mol %), in 2.0 mL solvent, under argon atmosphere, 12 h. The yield was determined by ^1H NMR using CH_2Br_2 as internal standard. The *ee* values were determined by chiral HPLC.

Having identified the optimized conditions for the enantioselective dehydrogenative Si−O coupling reaction, we

Table 2. Substrate Scope of Si-Stereogenic Siloxanes[a]

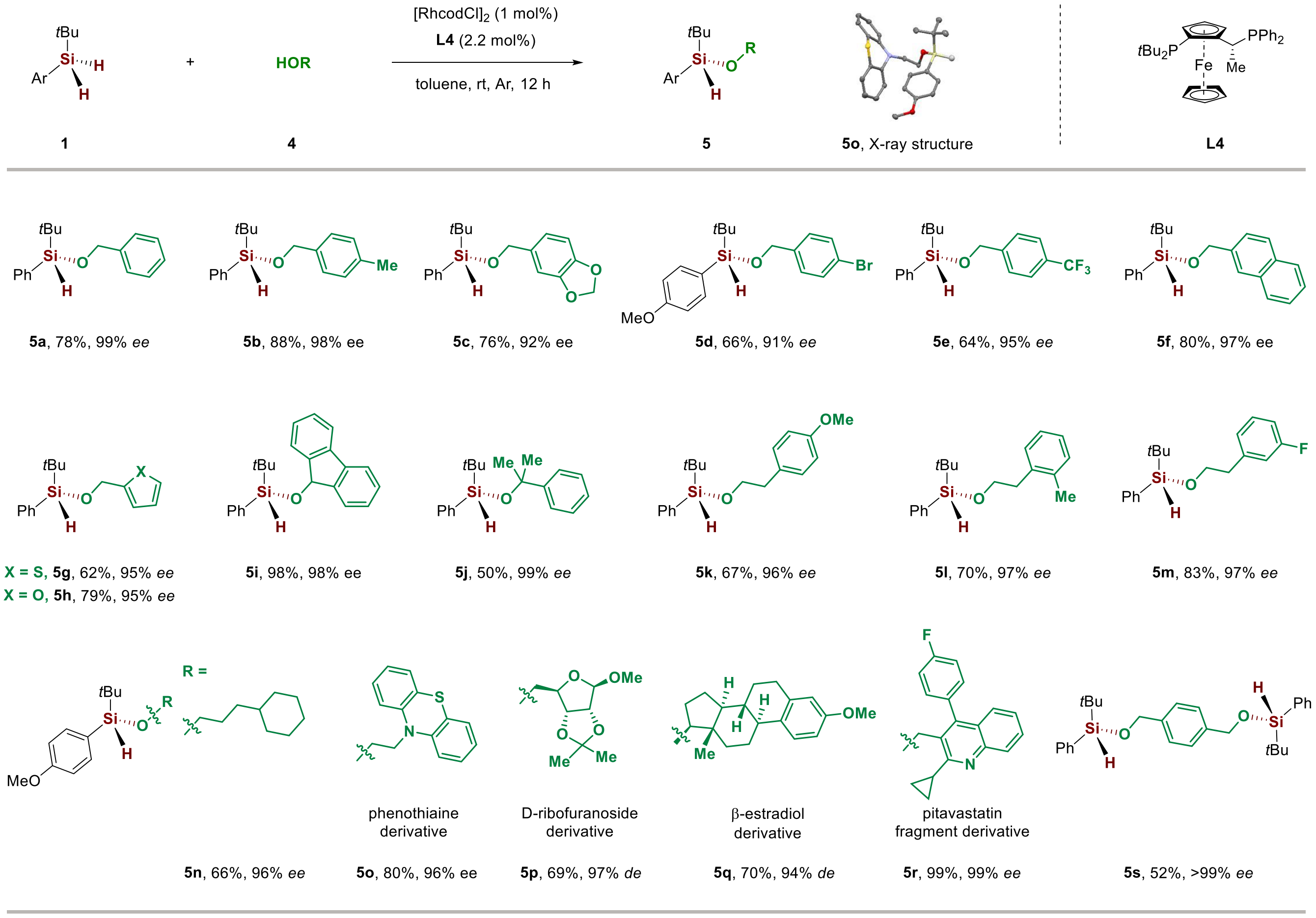


[a] Conditions: **1** (0.24 mmol), **2** (0.2 mmol), $[Rh(cod)Cl]_2$ (1 mol %), **L4** (2.2 mol %), in 2.0 mL toluene, under argon atmosphere, 12 h. Isolated yields. The *ee* values were determined by chiral HPLC.

next assessed the scope of this transformation to establish the general methodology for the construction of enantioenriched silicon-stereogenic siloxanes (Table 2). First, the aromatic rings (yellow part) of dihydrosilane substrates bearing different functional groups, including an electron-donating methoxy group (**1a**), amino group (**1b**), electron-withdrawing fluoro group (**1c**), and phenyl, naphthyl groups (**1d**, **1e**), all reacted smoothly with dimethyl(phenyl)silanol **2a** to afford the desired silicon-stereogenic siloxane products **3a**−**3e** in moderate to good yields (54−98%) with excellent enantioselectivities (96−98% *ee*). Second, the scope of silanols (blue part) was investigated under the standard conditions. Methoxy, chloro, and fluoro groups (**2f**−**2h**) on the aromatic ring of the dimethylphenylsilanols were well tolerated in the reaction, producing the corresponding siloxanes **3f**−**3h** in good yields with 89−97% *ee*. Moreover, methyldiphenylsilanol (**1i**), *tert*-butyldiphenylsilanol (**1j**), and trimethylsilanol (**1k**) were also found to be competent substrates in the reaction, giving the desired product **3i**−**3k** in 56−75% yields without the loss of enantioselectivities (92−97% *ee*). It is noteworthy that the enantiopure bis-silicon-stereogenic siloxane **3l** (>99% *ee*) could easily be constructed via this strategy by the double coupling of silanediol with dihydrosilane, which could be highly attractive to organic material chemists due to their wide applications as privileged monomers in silicon-based materials.[46−48] Third, replacing the bulky *t*Bu group into a methyl (**1m**), isopropyl (**1n**), cyclohexyl (**1o**), or 1-naphthyl (**1p**) group on the dihydrosilane gave the corresponding siloxane products **3m**−**3p** in moderate to good yields with 63−88% *ee* (purple part).

Since this intermolecular dehydrogenative Si−O coupling reaction enables the facile access to silicon-stereogenic siloxane derivatives with high enantioselectivity, we questioned whether we could expand this process to the coupling of dihydrosilane with alcohol, challenging the historic problem of the catalytic enantioselective alcoholysis of dihydrosilane for the construction of architecturally complex and functionally diverse enantioenriched silicon-stereogenic alkoxysilanes with high efficiency and enantioselectivity. On the basis of the established reaction conditions (for a detailed account of the optimization study, see Supporting Information Table S1), a wide range of alcohols displaying a variety of substituents were found to be suitable substrates in the Rh-catalyzed enantioselective dehydrogenative Si−O coupling reaction (Table 3). Benzylic alcohol substrates bearing various electron-donating or withdrawing substituents, such as methyl, methoxy, bromo, and trifluoromethyl, were all well accommodated in this transformation to deliver the corresponding silicon-stereogenic alkoxysilanes in 64−88% yields with 91−99% *ee* (**5a**−**5e**). This process was also effective with naphthalene (**5f**) and heterocycles such as furan (**5g**) and thiophene (**5h**). Sterically hindered secondary and tertiary alcohols **5i** and **5j** also proceeded smoothly in the reaction without any difficulty affording the desired products with excellent enantioselectivities (98−99% *ee*). Besides benzylic alcohol, aliphatic alcohols with a number of different substituents were also suitable substrates undergoing this dehydrogenative Si−O coupling giving the corresponding products **5k**−**5n** in 66−83% yields with 96−97% *ee*. To further illustrate the utility of this methodology, we then examined the reaction employing the core structures of several bioactive molecules, pharmaceuticals, or materials building blocks, such as phenothiaine (**4o**), D-ribofuranoside (**4p**), *β*-estradiol (**4q**),

Table 3. Substrate Scope of Si-Stereogenic Alkoxysilanes[a]



5a, 78%, 99% *ee*

5b, 88%, 98% ee

5c, 76%, 92% ee

5d, 66%, 91% *ee*

5e, 64%, 95% *ee*

5f, 80%, 97% ee

X = S, 5g, 62%, 95% *ee*

X = O, 5h, 79%, 95% *ee*

5i, 98%, 98% ee

5j, 50%, 99% *ee*

5k, 67%, 96% *ee*

5l, 70%, 97% *ee*

5m, 83%, 97% *ee*

5n, 66%, 96% *ee*

5o, 80%, 96% ee

5p, 69%, 97% *de*

5q, 70%, 94% *de*

5r, 99%, 99% *ee*

5s, 52%, >99% *ee*

[a]Conditions: **1** (0.24 mmol), **4** (0.2 mmol), [Rh(cod)Cl]$_2$ (1 mol %), **L4** (2.2 mol %), in 2.0 mL toluene, under argon atmosphere, 12 h. Isolated yields. The *ee* values were determined by chiral HPLC. X-ray crystallographic analysis of **5o** allowed determination of the absolute configuration; and configurations of the products **5** were assigned by analogy.

and pitavastatin fragment (**4r**). We were delighted to find that the corresponding silicon-stereogenic alkoxysilane products **5o**−**5r** could be obtained in good yields with excellent stereoselectivities, irrespective of existing diverse functional groups and complex molecular structures. Finally, the interesting bis-silicon-stereogenic alkoxysilane **5s** was also obtained by the double coupling between 1,4-phenylenedimethanol with dihydrosilane in 52% yield with excellent enantioselectivity (>99% *ee*).

In recent years, there has been growing interest in the chiroptical molecules that display circularly polarized luminescence (CPL), which has great potential applications in 3D displays, communication of spin information, information storage and processing, CPL lasers, and biological probes.[49−53] Among various chiral luminescent systems, chromophores with silicon-stereogenic centers exhibited potential intense CPL emission properties due to their $\sigma^*-\pi^*$ conjugation.[54−59] To demonstrate the utility of these interesting chiral organosilicon compounds, we finally synthesized three enantioenriched silicon-stereogenic alkoxysilanes **6a**−**6c** containing pyrene groups[60] under the standard conditions (Figure 1a) and examined their photophysical properties. Under UV light irradiation (365 nm), the solution of **6a** and **6b** in CH_2Cl_2 exhibited blue luminescence, while **6c** displays bright green luminescence (Figure 1b). These compounds show similar UV−vis spectra; the absorption maxima are at around 317, 332, and 349 nm, respectively (Figure 1c). The emission maxima vary from 396 to 508 nm. Both the monomer (around 400 nm) and excimer (around 500 nm) emission peaks were observed for **6a** and **6b**. However, only a red-shifted, broadened excimer emission peak (around 500 nm) was seen for **6c**, which may originate from the multiple pyrene units within the molecule in proximity (Figure 1d).[61] It is worthy of mention that **6c** has a larger Stokes shifts (159 nm) and a higher absolute fluorescence quantum yield (0.55) compared with **6a** and **6b** (see Supporting Information Table S2 for details), which is suitable for the potential applications in chiroptical materials. Then, we further investigated the chiroptical properties of these π-conjugated silicon-stereogenic alkoxysilanes via circular dichroism (CD) and circular polarized luminescence (CPL) spectra. The CD spectra are mirror images of each other, in which **6a**, **6b**, and their enantiomers display clear Cotton effects at about 330 and 348 nm, while (*R*, *R*)-**6c** and (*S*, *S*)-**6c** exhibit stronger opposite signals at around 330 and 355 nm, respectively (Figure 1e). Finally, the CPL experiment which reflected the chirality of emitting excited states was conducted. To our delight, **6a**−**6c** are all CPL-active, displaying clear mirror images of each pair of the enantiomers (Figure 1f). It is noteworthy that (*R*, *R*)-**6c** and (*S*, *S*)-**6c** containing two silicon-stereogenic centers and

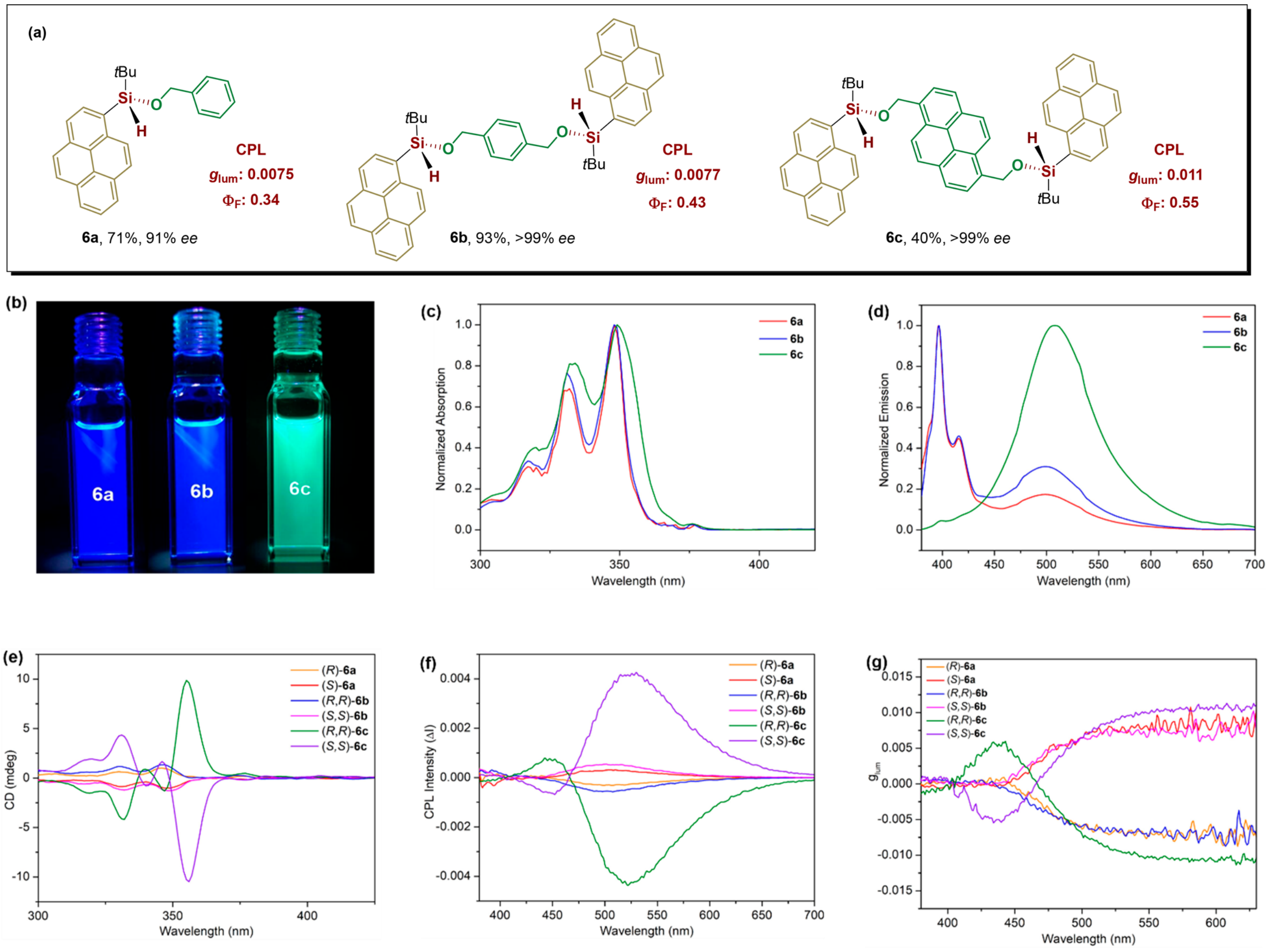


Figure 1. Photophysical properties investigations. (a) Enantioselective synthesis of effective CPL-active silicon-stereogenic alkoxysilanes. (b) Fluorescence images of π-conjugated silicon-stereogenic alkoxysilanes (λ_{ex} = 365 nm). (c) Absorption spectra of π-conjugated silicon-stereogenic alkoxysilanes in CH_2Cl_2 (10^{-5} M). (d) Emission spectra of π-conjugated silicon-stereogenic alkoxysilanes in CH_2Cl_2 (10^{-3} M). (e) CD spectra of **6a**–**6c** and their enantiomers in CH_2Cl_2 (2.0×10^{-5} M) at room temperature. (f) CPL spectra of **6a**–**6c** and their enantiomers in CH_2Cl_2 (1.0×10^{-3} M) at room temperature, excited at 349 nm. (g) g_{lum} values—wavelength curve for **6a**–**6c** and their enantiomers.

three pyrene groups show intense CPL signals that range from 470 to 675 nm. The luminescence dissymmetry factors (g_{lum}) were measured as -1.1×10^{-2} for (*R*, *R*)-**6c** and $+1.1 \times 10^{-2}$ for (*S*, *S*)-**6c** at 573 nm (Figure 1g). To the best of our knowledge, it is fairly rare that small organic compounds with a stereogenic center exhibit such a high g_{lum} value with a high fluorescence quantum efficiency (g_{lum} = 0.011, Φ_F = 0.55).[62] To further demonstrate the importance of silicon-stereogenic centers in these chiroptical alkoxysilanes, the chiral-at-carbon linked pyrene analogue of **6a** was synthesized and numbered as **6a′**. The photophysical properties showed that the absorption and CD spectra of **6a′** were similar to **6a**. However, the excimer emission peak of **6a′** became structureless. In addition, both the CPL intensity and Φ_F of **6a′** (g_{lum} = 0.0030, Φ_F = 0.07) were lower than **6a** (see Supporting Information Table S2 and Figure S1 for details). This comparison indicates that chromophores linked with silicon-stereogenic centers could be quite attractive. We believe that these easily accessed silicon-stereogenic alkoxysilanes with intense CPL properties could have great potential application in the development of interesting chiroptical devices in the near future.

In summary, we have developed a rhodium-catalyzed enantioselective intermolecular dehydrogenative Si–O coupling reaction between dihydrosilanes with silanols or alocohols, which gives access to a wide range of highly functionalized chiral siloxanes and alkoxysilanes in good to excellent yields and enatioselectivities. Further utility of this process was illustrated by the construction of CPL-active silicon-stereogenic alkoxysilane small organic molecules displaying large g_{lum} values with high emission efficiency, which could have great potential applications in chiral organic optoelectronic materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01106.

Materials and methods, experimental procedures, optimization studies, characterization data, photophysical properties studies, ^1H, ^{13}C, and ^{19}F NMR spectra, HPLC spectra and mass spectrometry data of new compounds (PDF)

Accession Codes

CCDC 2053379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Brook, M., Eds. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley, New York, 2000.

(2) Rappoport, Z., Apeloig, Y., Eds. *The Chemistry of Organic Silicon Compounds*; Wiley, Chichester, 2003.

(3) Hiyama, T., Oestreich, M., Eds. *Organosilicon Chemistry: Novel Approaches and Reactions*; Wiley: Weinheim, Germany, 2019.

(4) Lalonde, M.; Chan, T. H. Use of Organosilicon Reagents as Protective Groups in Organic Synthesis. *Synthesis* **1985**, *1985*, 817−845.

(5) Chan, T. H.; Wang, D. Chiral Organosilicon Compounds in Asymmetric Synthesis. *Chem. Rev.* **1992**, *92*, 995−1006.

(6) Kamino, B. A.; Bender, T. P. The Use of Siloxanes, Silsesquioxanes, and Silicones in Organic Semiconducting Materials. *Chem. Soc. Rev.* **2013**, *42*, 5119−5130.

(7) Kuroda, K.; Shimojima, A.; Kawahara, K.; Wakabayashi, R.; Tamura, Y.; Asakura, Y.; Kitahara, M. Utilization of Alkoxysilyl Groups for the Creation of Structurally Controlled Siloxane-Based Nanomaterials. *Chem. Mater.* **2014**, *26*, 211−220.

(8) Xu, L.-W.; Chen, Y.; Lu, Y. Catalytic Silylations of Alcohols: Turning Simple Protecting-Group Strategies into Powerful Enantioselective Synthetic Methods. *Angew. Chem., Int. Ed.* **2015**, *54*, 9456−9466.

(9) Issa, A. A.; Luyt, A. S. Kinetics of Alkoxysilanes and Organoalkoxysilanes Polymerization: A Review. *Polymers* **2019**, *11*, 537.

(10) Reyes-Rodriguez, G. J.; Rezayee, N. M.; Vidal-Albalat, A.; Joergensen, K. A. The Prevalence of Diarylprolinol Silyl Ethers as Catalysts in Total Synthesis and Patents. *Chem. Rev.* **2019**, *119*, 4221−4260.

(11) Oestreich, M. Silicon-Stereogenic Silanes in Asymmetric Catalysis. *Synlett* **2007**, *2007*, 1629−1643.

(12) Weickgenannt, A.; Mewald, M.; Oestreich, M. Asymmetric Si-O Coupling of Alcohols. *Org. Biomol. Chem.* **2010**, *8*, 1497−1504.

(13) Xu, L.-W.; Li, L.; Lai, G.-Q.; Jiang, J.-X. The Recent Synthesis and Application of Silicon-Stereogenic Silanes: A Renewed and Significant Challenge in Asymmetric Synthesis. *Chem. Soc. Rev.* **2011**, *40*, 1777−1790.

(14) Sommer, L. H.; Frye, C. L. Optically Active Organosilicon Compounds Having Reactive Groups Bonded to Asymmetric Silicon. Displacement Reactions at Silicon with Pure Retention and Pure Inversion of Configuration. *J. Am. Chem. Soc.* **1959**, *81*, 1013.

(15) Rendler, S.; Auer, G.; Keller, M.; Oestreich, M. Preparation of a Privileged Silicon-Stereogenic Silane: Classical versus Kinetic Resolution. *Adv. Synth. Catal.* **2006**, *348*, 1171−1182.

(16) Corriu, R. J. P.; Moreau, J. J. E. Asymmetric Synthesis of Alkoxysilanes Catalyzed by Rhodium Complexes. *Tetrahedron Lett.* **1973**, 4469−4472.

(17) Corriu, R. J. P.; Moreau, J. J. E. Asymmetric Synthesis at Silicon. II. Alcoholysis of Prochiral Organosilicon Compounds Catalyzed by Rhodium Complexes. *J. Organomet. Chem.* **1976**, *120*, 337−346.

(18) Schmidt, D. R.; O'Malley, S. J.; Leighton, J. L. Catalytic Asymmetric Silane Alcoholysis: Practical Access to Chiral Silanes. *J. Am. Chem. Soc.* **2003**, *125*, 1190−1191.

(19) Bauer, J. O.; Strohmann, C. Recent Progress in Asymmetric Synthesis and Application of Difunctionalized Silicon-Stereogenic Silanes. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2868−2881.

(20) Klebe, J. F.; Finkbeiner, H. L. Asymmetric Synthesis of an Optically Active Difunctional Silane. *J. Am. Chem. Soc.* **1966**, *88*, 4740−4741.

(21) Kobayashi, K.; Kato, T.; Unno, M.; Masuda, S. Asymmetric Synthesis of Organosilicon Compounds using a C2 Chiral Auxiliary. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1393−1401.

(22) Oestreich, M.; Schmid, U. K.; Auer, G.; Keller, M. A Convergent Method for the Synthesis of Highly Enantiomerically Enriched Cyclic Silanes with Silicon-Centered Chirality. *Synthesis* **2003**, 2725−2739.

(23) Igawa, K.; Takada, J.; Shimono, T.; Tomooka, K. Enantioselective Synthesis of Silanol. *J. Am. Chem. Soc.* **2008**, *130*, 16132−16133.

(24) Bauer, J. O.; Strohmann, C. Stereoselective Synthesis of Silicon-Stereogenic Aminomethoxysilanes: Easy Access to Highly Enantiomerically Enriched Siloxanes. *Angew. Chem., Int. Ed.* **2014**, *53*, 720−724.

(25) Bai, X.-F.; Zou, J.-F.; Chen, M.-Y.; Xu, Z.; Li, L.; Cui, Y.-M.; Zheng, Z.-J.; Xu, L.-W. Lewis-Base-Mediated Diastereoselective Silylations of Alcohols: Synthesis of Silicon-Stereogenic Dialkoxysilanes Controlled by Chiral Aryl BINMOLs. *Chem. - Asian J.* **2017**, *12*, 1730−1735.

(26) Xu, L.-W. Desymmetrization Catalyzed by Transition-Metal Complexes: Enantioselective Formation of Silicon-Stereogenic Silanes. *Angew. Chem., Int. Ed.* **2012**, *51*, 12932−12934.

(27) Shintani, R. Recent Advances in the Transition-Metal-Catalyzed Enantioselective Synthesis of Silicon-Stereogenic Organosilanes. *Asian J. Org. Chem.* **2015**, *4*, 510−514.

(28) Cui, Y.-M.; Lin, Y.; Xu, L.-W. Catalytic Synthesis of Chiral Organoheteroatom Compounds of Silicon, Phosphorus, and Sulfur via Asymmetric Transition Metal-Catalyzed C-H Functionalization. *Coord. Chem. Rev.* **2017**, *330*, 37−52.

(29) Shintani, R. Recent Progress in Catalytic Enantioselective Desymmetrization of Prochiral Organosilanes for the Synthesis of Silicon-Stereogenic Compounds. *Synlett* **2018**, *29*, 388−396.

(30) Igawa, K.; Yoshihiro, D.; Ichikawa, N.; Kokan, N.; Tomooka, K. Catalytic Enantioselective Synthesis of Alkenylhydrosilane. *Angew. Chem., Int. Ed.* **2012**, *51*, 12745−12748.

(31) Kurihara, Y.; Nishikawa, M.; Yamanoi, Y.; Nishihara, H. Synthesis of Optically Active Tertiary Silanes via Pd-Catalyzed Enantioselective Arylation of Secondary Silanes. *Chem. Commun.* **2012**, *48*, 11564−11566.

(32) Kuninobu, Y.; Yamauchi, K.; Tamura, N.; Seiki, T.; Takai, K. Rhodium-Catalyzed Asymmetric Synthesis of Spirosilabifluorene Derivatives. *Angew. Chem., Int. Ed.* **2013**, *52*, 1520−1522.

(33) Zhang, Q.-W.; An, K.; Liu, L.-C.; Zhang, Q.; Guo, H.; He, W. Construction of Chiral Tetraorganosilicons by Tandem Desymmetrization of Silacyclobutanes/Intermolecular Dehydrogenative Silylation. *Angew. Chem., Int. Ed.* **2017**, *56*, 1125−1129.

(34) Ma, W.; Liu, L.-C.; An, K.; He, T.; He, W. Rhodium-Catalyzed Synthesis of Chiral Monohydrosilanes by Intramolecular C-H Functionalization of Dihydrosilanes. *Angew. Chem., Int. Ed.* **2021**, *60*, 4245−4251.

(35) Xu, J.-X.; Chen, M.-Y.; Zheng, Z.-J.; Cao, J.; Xu, Z.; Cui, Y.-M.; Xu, L.-W. Platinum-Catalyzed Multicomponent Alcoholysis/Hydrosilylation and Bis-hydrosilylation of Alkynes with Dihydrosilanes. *ChemCatChem* **2017**, *9*, 3111−3116.

(36) Long, P.-W.; Bai, X.-F.; Ye, F.; Li, L.; Xu, Z.; Yang, K.-F.; Cui, Y.-M.; Zheng, Z.-J.; Xu, L.-W. Construction of Six-Membered Silacyclic Skeletons via Platinum-Catalyzed Tandem Hydrosilylation/Cyclization with Dihydrosilanes. *Adv. Synth. Catal.* **2018**, *360*, 2825−2830.

(37) Hayashi, T.; Yamamoto, K.; Kumada, M. Asymmetric Synthesis of Bifunctional Organosilicon Compounds by Hydrosilylation. *Tetrahedron Lett.* **1974**, *15*, 331−334.

(38) Corriu, R. J. P.; Moreau, J. J. E. Asymmetric Hydrosilylation of Ketones Catalyzed by a Chiral Rhodium Complex. *J. Organomet. Chem.* **1974**, *64*, C51−C54.

(39) Ohta, T.; Ito, M.; Tsuneto, A.; Takaya, H. Asymmetric Synthesis of Silanes with a Stereogenic Center at Silicon via Hydrosilylation of Symmetric Ketones with Prochiral Diaryl Silanes Catalyzed by Binap-RhI Complexes. *J. Chem. Soc., Chem. Commun.* **1994**, 2525−2526.

(40) Shintani, R.; Maciver, E. E.; Tamakuni, F.; Hayashi, T. Rhodium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzooxasilines via Enantioselective Transmetalation. *J. Am. Chem. Soc.* **2012**, *134*, 16955−16958.

(41) Kumar, R.; Hoshimoto, Y.; Yabuki, H.; Ohashi, M.; Ogoshi, S. Nickel(0)-Catalyzed Enantio- and Diastereoselective Synthesis of Benzoxasiloles: Ligand-Controlled Switching from Inter- to Intramolecular Aryl-Transfer Process. *J. Am. Chem. Soc.* **2015**, *137*, 11838−11845.

(42) Mu, D.; Yuan, W.; Chen, S.; Wang, N.; Yang, B.; You, L.; Zu, B.; Yu, P.; He, C. Streamlined Construction of Silicon-Stereogenic Silanes by Tandem Enantioselective C-H Silylation/Alkene Hydrosilylation. *J. Am. Chem. Soc.* **2020**, *142*, 13459−13468.

(43) Yang, B.; Yang, W.; Guo, Y.; You, L.; He, C. Enantioselective Silylation of Aliphatic C-H Bonds for the Synthesis of Silicon-Stereogenic Dihydrobenzosiloles. *Angew. Chem., Int. Ed.* **2020**, *59*, 22217−22222.

(44) Yuan, W.; You, L.; Lin, W.; Ke, J.; Li, Y.; He, C. Asymmetric Synthesis of Silicon-Stereogenic Monohydrosilanes by Dehydrogenative C-H Silylation. *Org. Lett.* **2021**, *23*, 1367−1372.

(45) Chen, S.; Mu, D.; Mai, P.-L.; Ke, J.; Li, Y.; He, C. Enantioselective Construction of Six- and Seven-Membered Triorgano-Substituted Silicon-Stereogenic Heterocycles. *Nat. Commun.* **2021**, *12*, 1249.

(46) Kawakami, Y.; Kakihana, Y.; Ooi, O.; Oishi, M.; Suzuki, K.; Shinke, S.; Uenishi, K. Control of Stereochemical Structures of Silicon-Containing Polymeric Systems. *Polym. Int.* **2009**, *58*, 279−284.

(47) Xue, L.; Kawakami, Y. Precise Synthesis of Poly(Silphenylenesiloxane)s with Epoxy Side Functional Groups by Tris(pentafluorophenyl)borane as a Catalyst. *Polym. J.* **2007**, *39*, 379−388.

(48) Wang, X.-Q.; Zhai, X.-Y.; Wu, B.; Bai, Y.-Q.; Zhou, Y.-G. Synthesis of Chiral Poly(silylether)s via CuH-Catalyzed Asymmetric Hydrosilylation Polymerization of Diketones with Silanes. *ACS Macro Lett.* **2020**, *9*, 969−973.

(49) Riehl, J. P.; Richardson, F. S. Circularly polarized luminescence spectroscopy. *Chem. Rev.* **1986**, *86*, 1−16.

(50) Kumar, J.; Nakashima, T.; Kawai, T. Circularly Polarized Luminescence in Chiral Molecules and Supramolecular Assemblies. *J. Phys. Chem. Lett.* **2015**, *6*, 3445−3452.

(51) Han, J.; Guo, S.; Lu, H.; Liu, S.; Zhao, Q.; Huang, W. Recent Progress on Circularly Polarized Luminescent Materials for Organic Optoelectronic Devices. *Adv. Opt. Mater.* **2018**, *6*, 1800538.

(52) Sang, Y.; Han, J.; Zhao, T.; Duan, P.; Liu, M. Circularly Polarized Luminescence in Nanoassemblies: Generation, Amplification, and Application. *Adv. Mater.* **2020**, *32*, 1900110.

(53) Zhao, T.; Han, J.; Duan, P.; Liu, M. New Perspectives to Trigger and Modulate Circularly Polarized Luminescence of Complex and Aggregated Systems: Energy Transfer, Photon Upconversion, Charge Transfer, and Organic Radical. *Acc. Chem. Res.* **2020**, *53*, 1279−1292.

(54) Yamaguchi, S.; Tamao, K. Silole-Containing π-Conjugated Polymers. 5. Theoretical Study of the Electronic Structure of 2,2′-Bisilole in Comparison with 1,1′-Bi-1,3-cyclopentadiene: σ^*-π^* Conjugation and a Low-Lying LUMO as the Origin of the Unusual Optical Properties of 3,3′,4,4′-Tetraphenyl-2,2′-bisilole. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327−2334.

(55) Yamaguchi, S.; Tamao, K. Silole-Containing σ- and π-Conjugated Compounds. *J. Chem. Soc., Dalton Trans.* **1998**, 3693−3702.

(56) Shimizu, M.; Hiyama, T. Silicon-Bridged Biaryls: Molecular Design, New Synthesis, and Luminescence Control. *Synlett* **2012**, *23*, 973−989.

(57) Zhao, Z.; He, B.; Tang, B. Z. Aggregation-Induced Emission of Siloles. *Chem. Sci.* **2015**, *6*, 5347−5365.

(58) Koga, S.; Ueki, S.; Shimada, M.; Ishii, R.; Kurihara, Y.; Yamanoi, Y.; Yuasa, J.; Kawai, T.; Uchida, T. A.; Iwamura, M.; Nozaki, K.; Nishihara, H. Access to Chiral Silicon Centers for Application to Circularly Polarized Luminescence Materials. *J. Org. Chem.* **2017**, *82*, 6108−6117.

(59) Tang, R.-H.; Xu, Z.; Nie, Y.-X.; Xiao, X.-Q.; Yang, K.-F.; Xie, J.-L.; Guo, B.; Yin, G.-W.; Yang, X.-M.; Xu, L.-W. Catalytic Asymmetric *trans*-Selective Hydrosilylation of Bisalkynes to Access AIE and CPL-Active Silicon-Stereogenic Benzosiloles. *iScience* **2020**, *23*, 101268.

(60) Niko, Y.; Kawauchi, S.; Otsu, S.; Tokumaru, K.; Konishi, G.-I. Fluorescence Enhancement of Pyrene Chromophores Induced by Alkyl Groups through σ-π Conjugation: Systematic Synthesis of Primary, Secondary, and Tertiary Alkylated Pyrenes at the 1, 3, 6, and 8 Positions and Their Photophysical Properties. *J. Org. Chem.* **2013**, *78*, 3196−3207.

(61) Ohishi, Y.; Inouye, M. Circularly polarized luminescence from pyrene excimers. *Tetrahedron Lett.* **2019**, *60*, 151232.

(62) Sanchez-Carnerero, E. M.; Agarrabeitia, A. R.; Moreno, F.; Maroto, B. L.; Muller, G.; Ortiz, M. J.; de la Moya, S. Circularly Polarized Luminescence from Simple Organic Molecules. *Chem. - Eur. J.* **2015**, *21*, 13488−13500.