Synthetic Methods

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Modular Approach to Silicon-Bridged Biaryls: Palladium-Catalyzed Intramolecular Coupling of 2-(Arylsilyl)aryl Triflates**

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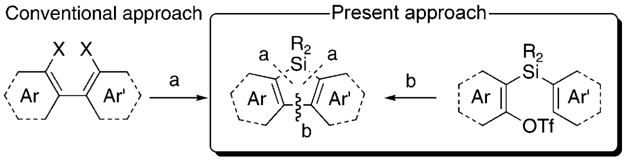
Silicon-bridged biaryls (SBArs), such as 9-silafluorenes, silicon-bridged dithienosiloles, and phenylindenes have recently been the subject of growing interest as components of light-emitting materials, thin-film transistors, host materials for electroluminescent devices, and solar cells.[1] Optical and electronic properties of π-conjugated organic materials are closely related to their electronic structures, which can be tuned by installation of appropriate functional groups, fusion of aromatic rings, and/or bridging heteroatoms.[2] For this reason, facile synthesis of SBAr compounds with broad structural variations, which satisfy such requisites for conjugation control, is of great importance for advanced modification and exploitation of functional organic materials exhibiting unique properties. Conventional synthesis of SBAr is achieved by dilithiation of the corresponding 2,2′-dihalobiaryls followed by silylation with dichlorosilanes (Scheme 1, route a).[1,3,4] Although the protocol is simple, structural variations of accessible SBAr are highly dependent on the availability of the dihalobiaryls, and thus are limited, in most cases, to symmetrical substrates. We report herein a novel and versatile approach to SBArs, which involves Pd-catalyzed intramolecular direct arylation of readily available 2-(arylsilyl)aryl triflates (Scheme 1, route b). This approach is applicable to the facile synthesis of not only symmetrical and asymmetrical functionalized 9-silafluorenes, but also SBArs containing heteroaromatic rings, such as furan, thiophene, and pyrrole. In addition, the novel silicon-bridged 2-phenylindole, readily prepared by the present approach, is disclosed to exhibit highly efficient solid-state blue fluorescence.



Scheme 1. Approaches to silicon-bridged biaryls. a) Dilithiation and subsequent silylation with Cl_2SiR_2; b) Pd catalyst, base.

Transition-metal-catalyzed direct arylation has recently emerged as a versatile strategy for aryl–aryl bond formation.[5] Intramolecular coupling reactions constitute efficient syntheses of fused carbo- and heterocycles, such as fluorenes, carbazoles, and dibenzofurans.[6] We attempted a Pd-catalyzed intramolecular direct coupling of two aryl groups, tethered by a silylene moiety, as a new synthetic route to SBArs, as the structural variation of the SBAr compounds attainable by this modular approach is potentially much broader than that by the conventional approach.[7] We focused our attention on 2-(arylsilyl)aryl triflate substrates. Such species are often used as precursors for arynes,[8] and could be readily prepared from the corresponding *o*-bromophenols and arylchlorosilanes by sequential silylation, retro-Brook rearrangement, and triflation.[9]

Initially, 2-[dimethyl(phenyl)silyl]phenyl triflate (**1a**)[10] was subjected to the typical conditions for Pd-catalyzed intramolecular direct arylation of 2-(phenoxymethyl)bromobenzenes.[11] However, the use of inorganic bases, such as NaOAc, K_2CO_3, and Cs_2CO_3, which were effective for the reported transformations, resulted in no production of the desired 9,9-dimethyl-9-silafluorene (**2a**). Use of Et_2NH as a base with $Pd(OAc)_2$/2-dicyclohexylphosphino-2′,4′,6′-trimethylbiphenyl barely afforded **2a** (27 % yield) with complete consumption of **1a**. As many unidentified compounds were produced, we suspected that the product (**2a**) might be decomposed under the conditions by nucleophilic attack of a base, an acetate ion, or a triflate ion at the $SiMe_2$ moiety. We exchanged the $SiMe_2$ group for $SiBu_2$, to induce steric protection, and screened reaction conditions for this substrate. Pleasingly, the desired intramolecular coupling proceeded smoothly to afford the corresponding product (**2c**) in 68 % yield, by using secondary amines, such as Et_2NH and Cy_2NH, as a base with a catalyst system of $Pd(OAc)_2/2PCy_3$ in dimethylacetamide (DMA) at 100 °C (Table 1, entry 2). For reasons of handling and affordability, we selected to use Et_2NH as the base for further study.

Under the aforementioned optimized conditions, we carried out the cyclization of various 2-(phenylsilyl)phenyl triflates **1b–h** with various substituent groups on the silicon atom (Table 1). Bulkier carbonaceous substituents, such as *i*Pr, *s*Bu, *t*Bu, and phenyl, led to a great increase in yields of the corresponding 9-silafluorene product **2** (Table 1, entries 4–8). Such effects of the bulkier substituents may be considered reasonable, as the Thorpe–Ingold effect and *gem*-dialkyl effect from these groups positions the two phenyl groups in **1** closer together, and retards the decomposition of **2**.[12]

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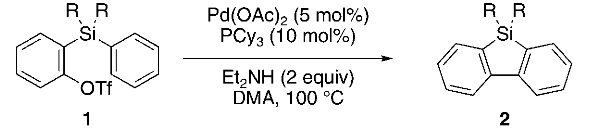
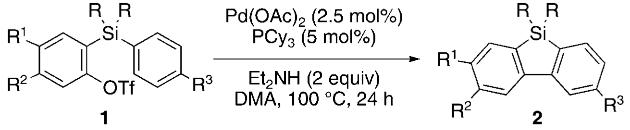
Table 1: Palladium-catalyzed intramolecular direct arylation of **1**.[a]



Entry	1	R$_2$	*t* [h]	2	Yield [%][b]
1	**1b**	Et$_2$	75	**2b**	39
2	**1c**	*n*Bu$_2$	20	**2c**	68
3	**1d**	*n*Hex$_2$	24	**2d**	63
4	**1e**	*i*Pr$_2$	14	**2e**	92
5[c]	**1e**	*i*Pr$_2$	25	**2e**	91
6	**1f**	*s*Bu$_2$	20	**2f**	94
7	**1g**	*t*Bu, Ph	24	**2g**	88
8	**1h**	Ph$_2$	14	**2h**	87

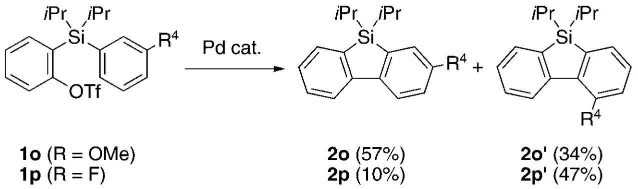
[a] Conditions, unless otherwise stated: **1** (1.0 mmol), Pd(OAc)$_2$ (11 mg, 0.050 mmol), PCy$_3$ (28 mg, 0.10 mmol), Et$_2$NH (200 μL, 2.0 mmol), dimethylacetamide (DMA, 2 mL), 100 °C. [b] Yield of isolated product. [c] **1** (1.0 mmol), Pd(OAc)$_2$ (5.5 mg, 0.025 mmol), PCy$_3$ (14 mg, 0.050 mmol), Et$_2$NH (200 μL, 2.0 mmol), DMA (2 mL), 100 °C. Cy = cyclohexyl, Tf = triflate.

Table 2: Synthesis of functionalized 9-silafluorenes **2**.[a]



Entry	1	R$_2$	R^1	R^2	R^3	2	Yield [%][b]
1[c]	**1i**	*i*Pr$_2$	H	H	NMe$_2$	**2i**	90
2	**1j**	*i*Pr$_2$	H	H	OMe	**2j**	94
3[d]	**1k**	*i*Pr$_2$	H	H	CF$_3$	**2k**	88
4	**1l**	*t*Bu, Ph	CN	H	H	**2l**	88
5	**1m**	*i*Pr$_2$	CN	H	OMe	**2m**	93
6	**1n**	*i*Pr$_2$	H	OMe	OMe	**2n**	98

[a] Conditions, unless otherwise stated: **1** (1.0 mmol), Pd(OAc)$_2$ (6 mg, 0.025 mmol), PCy$_3$ (14 mg, 0.050 mmol), Et$_2$NH (200 μL, 2.0 mmol), DMA (2 mL), 100 °C. [b] Yield of isolated product. [c] **1i** (0.050 mmol), Pd(OAc)$_2$/2PCy$_3$ (5 mol%), Et$_2$NH (0.10 mmol). [d] Reaction was effected at 120 °C.



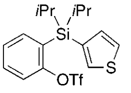
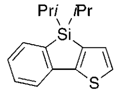
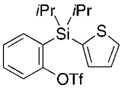
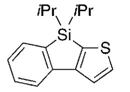
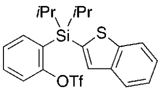
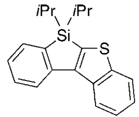
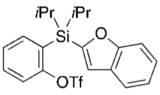
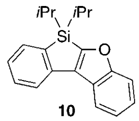
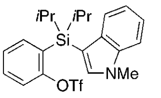
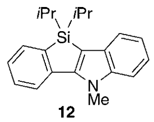
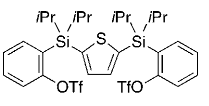
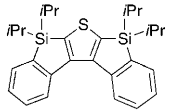
Scheme 2. Regioselectivity of intramolecular coupling of **1o** and **1p**. Conditions for **1o**: Pd(OAc)$_2$ (2.5 mol%), PCy$_3$(5 mol%), Et$_2$NH (2 equiv), DMA, 24 h, 100 °C; for **1p**: Pd(OAc)$_2$ (10 mol%), PCy$_3$ (20 mol%), Et$_2$NH (2 equiv), DMA, 24 h, 120 °C.

The scope of variety in functionalized 9-silafluorenes, accessible by using this method, is summarized in Table 2. Symmetrical and asymmetrical 9-silafluorenes **2i–n**, substituted with electron-donating and/or -withdrawing groups, such as NMe$_2$, OMe, CF$_3$, and CN, were synthesized from the corresponding triflates in high to excellent yields. For a substrate incorporating CF$_3$ as substituent R^3, the reaction required 120 °C to proceed smoothly (Table 2, entry 3).

We next examined the regioselectivity of the direct arylation with substrates that possessed a substituent R^4, *meta* to the silyl moiety on the phenyl ring without the triflate group (Scheme 2). When substituent R^4 was a methoxy group, the arylation occurred preferentially at the carbon center *para* to the methoxy group, giving **2o** as a major product along with **2o′**. Conversely, in the case of **1p**, bearing fluorine as R^4, the carbon center *ortho* to the fluorine substituent was the more reactive position, giving rise to **2p′** as a major product. Compound **1p** required a higher reaction temperature (120 °C) and catalyst loading (10 mol% of Pd(OAc)$_2$, 20 mol% of PCy$_3$) than **1o** for the cyclization to proceed smoothly. A similar regiochemical outcome was reported for the intramolecular direct arylation of methyleneoxy-tethered bromobenzenes.[6b] Although these systems gave mixtures of regioisomers, the mixtures were easily separated by column chromatography on silica gel followed by gel-permeation chromatography to give each isomer as an isomeric pure form, in both cases.

In addition to 9-silafluorenes, the present method can be extended to the preparation of silicon-bridged benzene-heteroarenes (Table 3). Thiophene-containing triflates **3** and

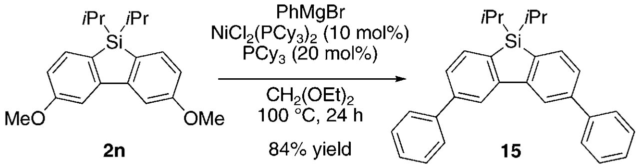
Table 3: Synthesis of silicon-bridged biaryls.

Entry	Triflate	Product	Yield [%][a]
1[b]	 **3**	 **4**	94
2[b]	 **5**	 **6**	95
3[c]	 **7**	 **8**	93
4[c]	 **9**	 **10**	85
5[d]	 **11**	 **12**	56
6[e]	 **13**	 **14**	85

[a] Yield of isolated product. [b] Triflate (1.0 mmol), Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), PCy$_3$ (14 mg, 0.050 mmol), Et$_2$NH (200 μL, 2.0 mmol), DMA (2 mL), 100 °C. [c] Triflate (0.20 mmol), Pd(OAc)$_2$ (2.2 mg, 0.010 mmol), PCy$_3$ (5.6 mg, 0.020 mmol), Et$_2$NH (40 μL, 0.40 mmol), DMA (0.4 mL), 100 °C. [d] **11** (0.10 mmol), Pd(OAc)$_2$ (1.1 mg, 0.005 mmol), PCy$_3$ (2.8 mg, 0.010 mmol), Et$_2$NH (20 μL, 0.20 mmol), DMA (0.2 mL), 100 °C. [e] **13** (1.0 mmol), Pd(OAc)$_2$ (11 mg, 0.050 mmol), PCy$_3$ (28 mg, 0.10 mmol), Et$_2$NH (400 μL, 4.0 mmol), DMA (2 mL), 100 °C.

5 cyclized smoothly at the 3- and 2-positions of the thiophene ring, respectively, to give **4** and **6** in 94% and 95% yield (Table 3, entries 1 and 2). Benzothiophene, benzofuran, and indole moieties also underwent direct arylation, affording tetracyclic products **8**, **10**, and **12** in fair to high yields (Table 3, entries 3–5). Furthermore, helicene-type molecule **14** was efficiently synthesized in 85% yield by twofold intramolecular coupling of 2,5-bis(silyl)thiophene **13** (Table 3, entry 6). The molecular structures of **12** and **14** were unambiguously confirmed by X-ray analysis of their single crystals (for **12**, see Figure 3).[13]

The Ni-catalyzed twofold cross-coupling reaction of 3,6-dimethoxy-9-silafluorene **2n** with phenylmagnesium bromide under the Dankwardt's conditions,[14] led to the isolation of diphenylated silafluorene **15** in 84% yield with the silylene moiety intact (Scheme 3). This result demonstrates that a methoxy group that is tolerated in the direct arylation can serve as not only an electron-donating group but also as a site for substitution to extend the π-conjugated system of silafluorenes.



Scheme 3. Ni-catalyzed cross-coupling reaction of **2n** with PhMgBr.

Among the silicon-bridged biaryls presented here, silicon-bridged 2-phenylindole **12** was found to exhibit noteworthy solid-state fluorescence. The photoluminescent properties, spectra, and images are shown in Table 4, Figures 1 and 2. A solution of **12** in cyclohexane was, upon irradiation with UV light ($\lambda_{ex} = 320$ nm), strongly fluorescent with an emission maximum at 402 nm and a high quantum yield (Φ_f) of 0.70 (Table 4, entry 1), whereas the microcrystal, powder, and spin-coated thin-film of **12** showed slightly red-shifted emission maxima of 414–434 nm (Figure 1) and excellent quantum yields of 0.90–0.91 (Table 4, entries 2–4). Remarkably, the quantum yield of **12** dispersed in a poly(methyl methacrylate) (PMMA) film was 1.0, with intense blue emission (Figure 2e; Table 4, entry 5). High solid-state luminescent efficiency is essential for the development of optoelectronic devices, such as organic light-emitting diodes (OLEDs) and solid-state organic lasers,[15] and, in addition, the development of efficient blue-emitters for OLEDs is currently the subject of intense research efforts in materials science.[16] Silicon-bridged 2-phenylindoles are a new and attractive class of high performance blue-emitters, although further studies of their chemical, physical, optical, and electrical properties are required for practical application.

Table 4: Photoluminescent properties of **12**.[a]

Entry		λ_{max} [nm][b]	Φ_f[c]
1	solution[d]	402	0.70
2	microcrystal	434	0.91
3	powder	433	0.91
4	thin-film[e]	414	0.90
5	in PMMA[f]	408	1.00

[a] Excited under UV light ($\lambda_{ex} = 320$ nm). [b] Emission maxima. [c] Absolute quantum yield determined by a calibrated integrating sphere system. [d] 1.9×10^{-5} M in cyclohexane. [e] Prepared by spin-coating from a toluene solution. [f] Dispersed in poly(methyl methacrylate) (PMMA) film.

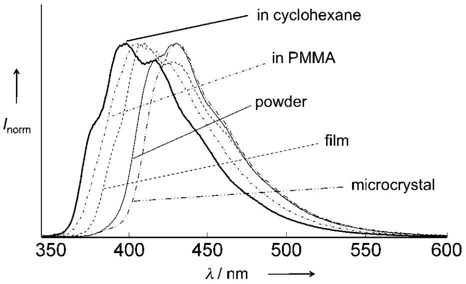


Figure 1. Photoluminescence spectra of **12**.

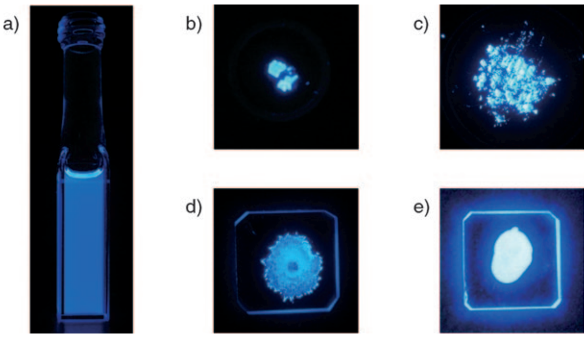


Figure 2. Fluorescence images of **12** ($\lambda_{ex} = 365$ nm): a) 1.9×10^{-5} M solution in cyclohexane; b) microcrystal; c) powder; d) thin-film prepared by spin-coating from a toluene solution; e) dispersed in PMMA film.

To gain insight into the excellent solid-state luminescent efficiency of **12**, we inspected the crystal structure by single-crystal X-ray diffraction. The molecule crystallizes in triclinic space group $P\bar{1}$ from a hexane/CH_2Cl_2 solution. The silicon-bridged tetracyclic framework is almost planar and two isopropyl groups are oriented perpendicular to the plane, respectively, to induce efficient σ*–π* conjugation (Figure 3a).[17] The asymmetric unit contains two molecules that are well separated with an almost orthogonal arrangement of the chromophores. The crystal packing is thus suitable to prevent intermolecular electronic interactions, such as π–π stacking, that lead to luminescence quenching (Figure 3b).

In summary, we have described the Pd-catalyzed intramolecular direct arylation of readily available 2-(arylsilyl)aryl triflates as a novel and versatile synthetic route to silicon-bridged biaryls, which have attracted growing attention in materials science. Key to this success is the installation of bulky substituents on silicon and the use of Et_2NH as a base. In addition, the development of this new approach has led to the discovery of the highly blue-emissive organic solid **12**.

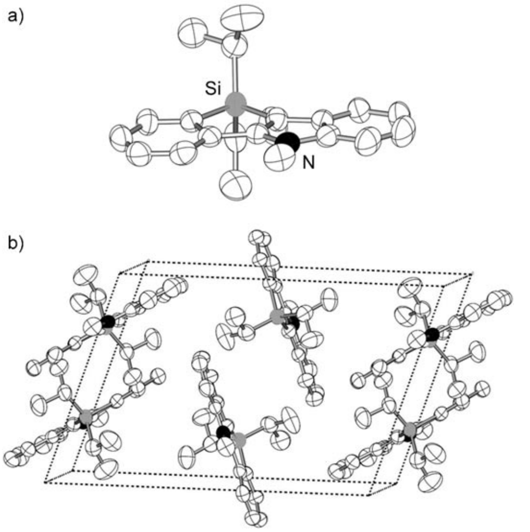


Figure 3. a) Molecular structure of **12** determine by single-crystal X-ray diffraction. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity; b) packing of **12** within the crystal. C white, N black, Si gray.

Efforts toward expansion of the reaction scope, as well as detailed analysis of properties of the obtained silicon-bridged biaryls are currently underway.

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Keywords: biaryls · C–H activation · luminescence · palladium · silicon

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