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Regioselective Functionalization of 9,9-Dimethyl-9-silafluorenes by Borylation, Bromination, and Nitration

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KEYWORDS: *9-Silafluorene*, *Borylation, Bromination, Nitration, Regioselectivity*

ABSTRACT: Despite the utility of 9-silafluorenes as functional materials and as building blocks, methods for efficient functionalization of their backbone are rare, probably due to the presence of easily cleavable C–Si bonds. Although controlling the regioselectivity of iridium-catalyzed direct borylation of C–H bonds is difficult, we found bromination and nitration of 2-methoxy-9-silafluorene under mild conditions occurred predominantly at the electron-rich position. The resulting product having methoxy and bromo groups can be utilized as a building block for the synthesis of unsymmetrically substituted 9-silafluorene-containing π-conjugated molecules.

INTRODUCTION

Due to the low LUMO energy level of 9-silafluorene derivatives originating from conjugation between the exocyclic Si–C σ* orbital and the π* orbital of the biaryl backbone, these compounds have attracted attention as promising components of novel advanced functional materials, such as light-emitting diodes, field-effect transistors, photovoltaic cells, and fluorescent probes (Figure 1).[1,2] Thus, the development of simple and efficient chemical modification methods could provide compounds with new electro- and physical properties, and could further extend the utility of 9-silafluorene derivatives as new functional molecules. Most previous modification methods introduced functional groups before construction of 9-silafluorene framework.[2,3] A frequently employed method has been reaction of organolithium or magnesium reagents derived from functionalized 2,2'-dihalobiaryls with dichlorosilanes. These pre-installation methods have provided a number of derivatives; however, preparation of properly functionalized precursors often requires multistep transformations. This disadvantage can be circumvented with direct substitution of C–H bonds of 9-silafluorenes with functional groups. However, 9-silafluorene derivatives tend to be labile toward oxidants and acids due to the presence of easily cleavable C–Si bonds, and direct functionalization methods are limited except for stable spiro-9-silafluorenes.[4] As part of our study aimed at development of functionalized polycyclic aromatic compounds,[5] we report herein borylation, bromination, and nitration of 9-silafluorene derivatives. Focus of the study was the functionalization of 9,9-dimethyl-9-silafluorenes because the resulting derivatives can be utilized as building blocks for annulative π-extension reaction or for the synthesis of 9-dibenzoboroles (Figure 2).[6]

RESULTS AND DISCUSSION

Direct functionalization of 9-silafluorene without substituents was performed first. After many attempts, including halogenation, nitration, formylation, and silylation,[7]

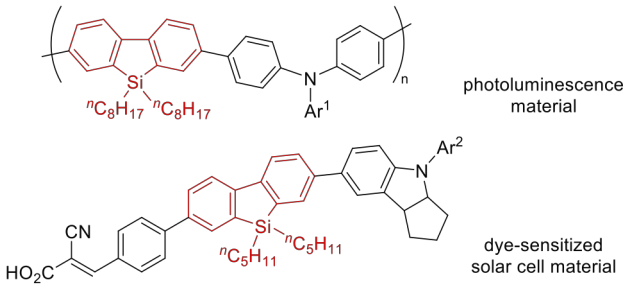


Figure 1. 9-Silafluorene Derivatives as Functional Materials (Ar^1 = 4-*sec*-butylphenyl, Ar^2 = 3,5-di(*tert*-butyl)-4-methoxyphenyl)

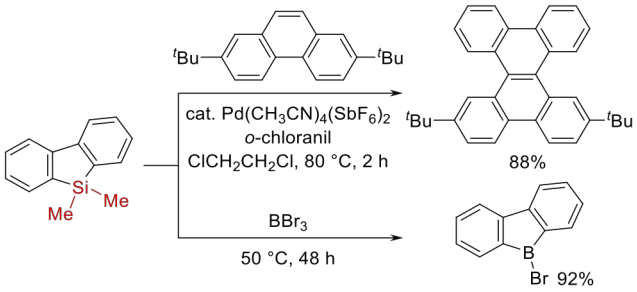
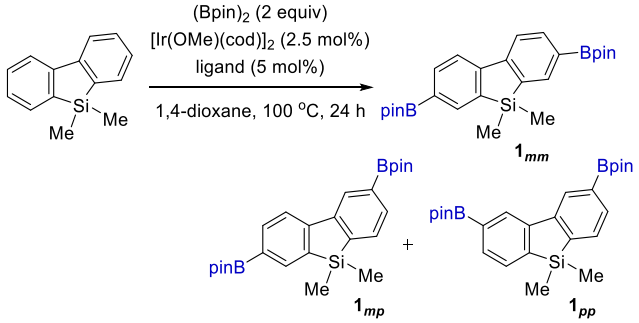


Figure 2. Utility of 9,9-Dimethyl-9-silafluorene as a Building Block for the Synthesis of Polycyclic Aromatic Compounds

iridium-catalyzed direct borylation of C–H bonds[8] gave a mixture of diborylated 9-silafluorenes $\mathbf{1}_{mm}$, $\mathbf{1}_{mp}$, and $\mathbf{1}_{pp}$ (Table 1). Borylated 9-silafluorenes are important building blocks for the preparation of several functional materials.[2] Previous synthetic methods started with dibromo-9-silafluorenes; therefore, the current catalytic borylation of C–H bonds provides a more direct and efficient approach. To control regioselectivity, effects of ligands were determined using $[Ir(OMe)(cod)]_2$ as a catalyst. 4,4'-Di-*tert*-butyl-2,2'-bipyridyl (dtbpy) and 2,2'-bipyridyl (bpy) promoted diborylation effectively to produce $\mathbf{1}_{mp}$ as a major regioisomer (entries 1 and 2). Because the proportion of $\mathbf{1}_{mm}$ was increased when using phenanthrene (phen)

as a ligand (entry 3), the effects of other phenanthrene derivatives were next examined. However, all attempts resulted in the formation of a mixture of three regioisomers (entries 4-8). A change in the iridium precursor to $[IrCl(cod)]_2$ did not improve regioselectivity (entry 9). Combining $[Ir(OMe)(cod)]_2$ or $[Ir(OH)(cod)]_2$ with phosphine ligands, such as PPh_3, dppe, BINAP, Xyl-MeOBIPHEP,[9] or DTBM-SEGPHOS, did not provide any borylated products. A mixture of mono- and diborylated 9-silafluorenes along with unreacted starting 9-silafluorene were obtained when using a decreased amount of $(Bpin)_2$, which indicates that the second borylation proceeded at nearly the same rate as the first borylation (entry 10).[10] Controlling the regioselectivity of the current borylation was difficult, but formation of $\mathbf{1}_{mm}$ was favored over that of $\mathbf{1}_{pp}$ in most cases except entry 5 with **L1** (see Table S1 in SI for the effect of solvents, temperature, and borylating reagents).[11] Because the similar preferential borylation at *meta* position of silyl group was observed in the borylation of 2-methyl-9-silafluorene using **L1** and **L3** as ligands, regioselectivity of the second borylation in Table 1 seems not to be affected by electronic factors of the boryl group incorporated in the first borylation step (Table 2). The

Table 1. Iridium-Catalyzed Direct C–H bond Borylation of 9-Silafluorene



entry	ligand	Total Yield of **1**[a]	Ratio of $\mathbf{1}_{mm}$ / $\mathbf{1}_{mp}$ / $\mathbf{1}_{pp}$[a]
1	dtbpy	97% (96%)	30 / 53 / 17
2	bpy	97%	36 / 54 / 10
3	phen	quant.	40 / 51 / 9
4	tmphen	quant.	33 / 53 / 14
5	**L1**	97%	24 / 50 / 26
6	**L2**	quant.	37 / 52 / 11
7	bphen	76%	33 / 57 / 10
8	**L3**	quant.	42 / 51 / 7
9[b]	dtbpy	96%	27 / 55 / 18
10[c]	dtbpy	mixture[d]	—

[a]Determined by ^{1}HNMR. The value in parentheses is the isolated yield. [b]$[IrCl(cod)]_2$ instead of $[Ir(OMe)(cod)]_2$. [c]B_2pin_2 (1 equiv). [d]Mixture of mono- and diborylated 9-silafluorenes was obtained.

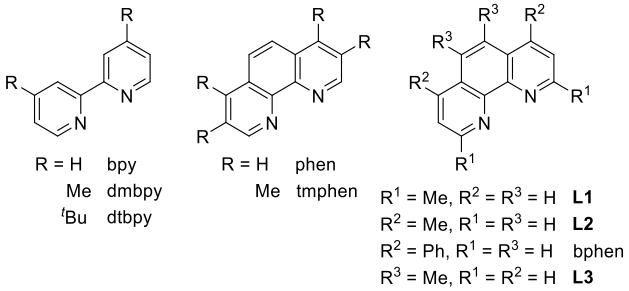
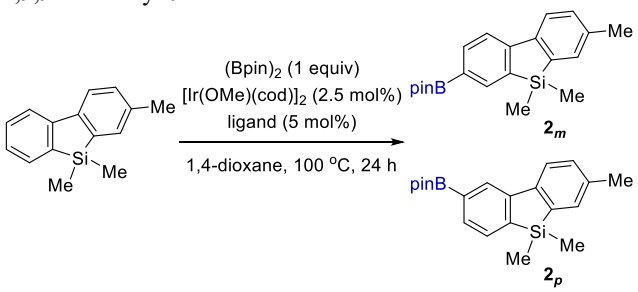


Table 2. Iridium-Catalyzed Direct C–H bond Borylation of 2,9,9-Trimethyl-9-silafluorene



Entry	Ligand	Total Yield of **2**[a]	Ratio of $\mathbf{2}_m$ / $\mathbf{2}_p$[a]
1	**L1**	84	48 / 52
2	**L3**	84 (76)	64 / 36

[a]Determined by ^{1}HNMR. The value in parentheses is the isolated yield. The structure of $\mathbf{2}_m$ was determined by X-ray crystallographic analysis.

structure of $\mathbf{2}_m$ was determined unambiguously by X-ray crystallographic analysis (see Figure S1 in SI). The exact role is unclear, but the major factor determining the regioselectivity seems to be electronic effect derived from silyl group.[12]

Although direct borylation of C–H bond of polycyclic aromatic compounds occasionally gave a mixture of regioisomers, it is still attractive as the short-cut approach to functionalized π-conjugated molecules. In fact, the resulting regioisomeric mixture of borylated compounds could be separated and used as building blocks for the construction of integrated π-systems in the previous literature.[13] However, we decided to investigate other facile methods for providing 9-silafluorene containing building blocks, especially methods for the construction of asymmetrically substituted structures. Electrophilic aromatic substitution of 2-methoxy-9-silafluorene **3a**, which can be synthesized in three steps from commercially available 2-bromophenylboronic acid,[7a] was selected as the next target reaction (Scheme 1). Note that the key step, rhodium-catalyzed dehydrogenative silylation for construction of the 9-silafluorene skeleton, proceeded

Scheme 1. Synthesis of 2-Methoxy-9-silafluorene **3a**

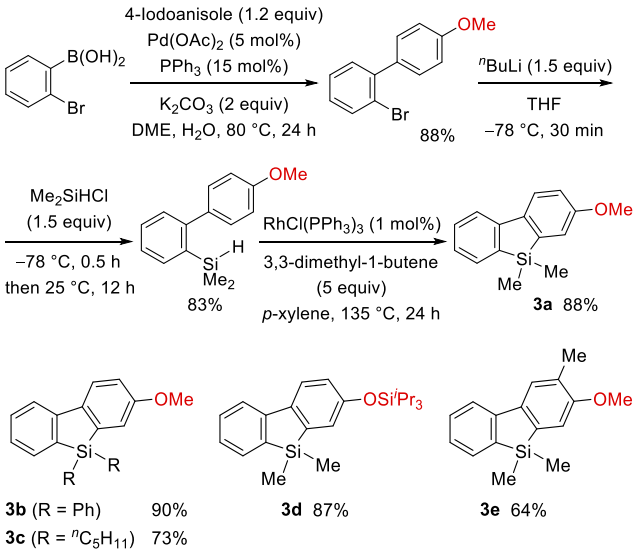
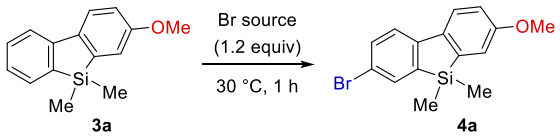


Figure 3. Yields for rhodium-catalyzed silylative cyclization leading to other 2-alkoxy-9-silafluorenes **3**

efficiently, even with 1 mol% of Wilkinson complex. Other 2-alkoxy-9-silafluorenes **3b-3e** were prepared according to the same procedure. Yields for the silylative cyclization step is summarized in Figure 3.

First, bromination with LiBr using iodobenzene diacetate as a promoter was attempted and afforded 2-bromo-7-methoxy-9-silafluorene **4** selectively in 71% yield, aided by electronic factors of the methoxy group (Table 3, entry 1).[14] Overbromination products, which are typical side products from bromination of electron-rich aromatic compounds, were not detected. The yield decreased with Me_3SiBr as a bromo source in place of LiBr (entry 3).[15] Note that typical bromination using NBS or Br_2 provided **4** in low yield, along with the formation of inseparable byproducts likely derived from the cleavage of labile C–Si bonds from acids and oxidants (entry 3). An attempt at gold-catalyzed bromination to promote reaction at lower temperatures resulted in formation of an inseparable mixture of products (entry 4).[16] These results demonstrated the importance of a mild bromination protocol with LiBr and iodobenzene diacetate. Brominated products **4c-4e** were also obtained from other 2-alkoxy-9-silafluorenes **3c-3e**. In all cases, bromination occurred selectively at 7-position without forming any other regioisomers (Figure 4).

Table 3. Bromination of 2-Methoxy-9-silafluorene **3a**



Entry	Br source and additive	Solvent	Yield of **4a**[a]	Recov. of **3a**
1	LiBr $PhI(OAc)_2$ (0.6 equiv)	THF	71%	9%
2	Me_3SiBr $PhI(OAc)_2$ (0.6 equiv)	THF	33%	38%
3[b]	NBS	CH_2ClCH_2Cl	42%[c]	40%
4	NBS, $AuCl_3$ (1 mol%)	CH_2ClCH_2Cl	mixture	

[a]Isolated yields. [b]For 16 h. [c]Containing inseparable side products.

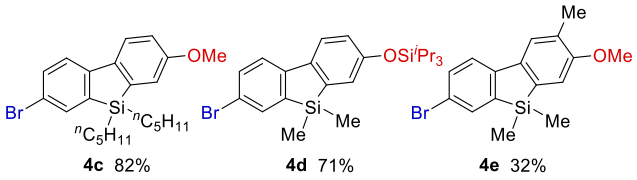
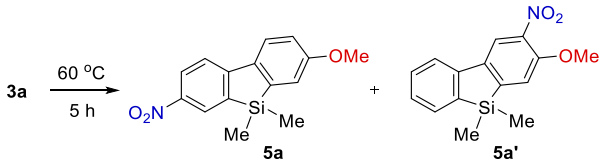


Figure 4. Bromination of other 2-alkoxy-9-silafluorenes

Nitration of 2-methoxy-9-silafluorene **3a** was also conducted. Partial decomposition of the 9-silafluorene backbone was observed from classical nitration using HNO_3 (Table 4, entry 1).[4c] 2-Methoxy-7-nitro-9-silafluorene **5a** and its regioisomer 2-methoxy-3-nitro-9-silafluorene **5a'** were obtained in better yields using $Fe(NO_3)_3{\cdot}9H_2O$ as a nitrating reagent in acetonitrile (entry 2).[17] The structures of **5a** and **5a'** were determined unambiguously by X-ray crystallographic analysis (see Figures S2 and S3 in SI). This is a rare example of nitration *under mild conditions* without using acidic promoters, supported metal nitrates, pyridine based- directing groups, or ionic liquids.[18] The regioselectivity depended on the solvent used, and the ratio and yield of **5a** were improved using 1,2-dichloroethane as a solvent (entry 3).[19] $Fe(NO_3)_3{\cdot}9H_2O$ is known to generate a free radical species, nitrogen dioxide

Table 4. Nitration of 2-Methoxy-9-silafluorene **3a**

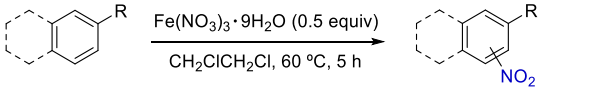


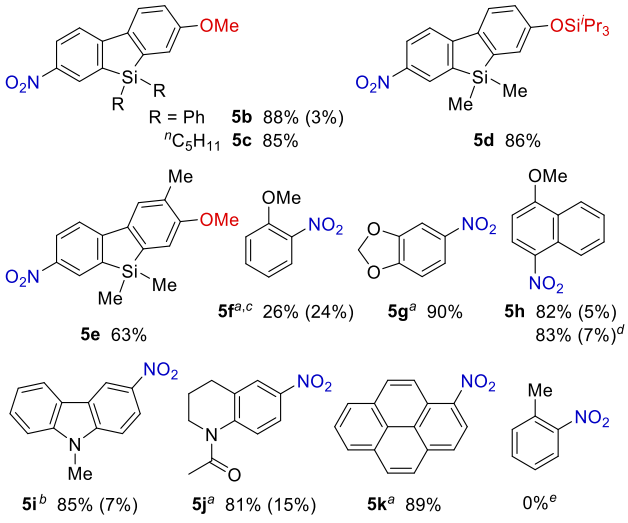
Entry	Conditions	Yield of **5a** / %[a]	Yield of **5a'** / %[a]
1[b]	HNO_3 (1.2 equiv), CH_2Cl_2	58	5
2	$Fe(NO_3)_3{\cdot}9\,H_2O$ (0.5 equiv) CH_3CN	73 (70)	27 (20)
3	$Fe(NO_3)_3{\cdot}9\,H_2O$ (0.5 equiv) CH_2ClCH_2Cl	95 (92)	5 (trace)
4[c]	$Bi(NO_3)_3{\cdot}5\,H_2O$ (0.5 equiv) CH_2ClCH_2Cl	67	5
5	$Cu(NO_3)_2{\cdot}3\,H_2O$ (0.75 equiv) Ac_2O / CH_2ClCH_2Cl	53	18

[a]Determined by ^{1}HNMR. Values in parentheses are the isolated yields. [b]At 25 °C for 5 h. [c]28% of **3** was recovered.

($\cdot NO_2$), by thermal decomposition.[17] Thus, the regioselectivity of the current nitration might be different from that of ionic electrophilic bromination shown in Table 3.[20] Although $Bi(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ can be also used as nitro sources, yields from them were less than that with $Fe(NO_3)_3{\cdot}9H_2O$ (entry 4).[19] In contrast, use of $Cu(NO_3)_2{\cdot}3H_2O$ and acetic anhydride, a common combined nitration reagent, was also effective for 2-methoxy-9-germafluorene, and gave a mixture of **5a**, **5a'**, and dinitrated 9-silafluorenes in lower yields (entry 5).[21] For a preliminary study, the current mild protocol was confirmed to be applicable to nitration of other

Table 5. Preliminary Study for Nitration of Other Aromatic Compounds with $Fe(NO_3)_3{\cdot}9H_2O$



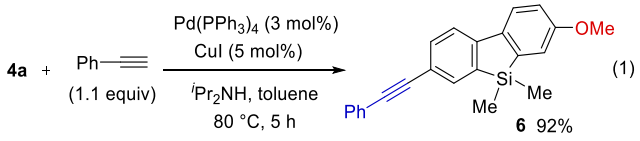


Values in parentheses are isolated yields of regioisomers (see SI for details). Reactions were conducted under Ar. [a]CH_3CN was used as a solvent. [b]3,6-Dinitrocarbazole was also obtained in 7% yield. [c]120 °C, 24 h. 38% of anisole was recovered. [d]25 °C under air. [e]130 °C, 24 h.

2-alkoxy-9-silafluorenes **3b-3e**, anisole, 1,3-benzodioxole, 1-methoxynaphthalene, 1-methylcarbazole, 1-acetyl-1,2,3,4-

tetrahydroquinoline, and pyrene to yield **5b**-**5k** (Table 5). The reaction could be conducted even at 25 °C under air, which confirmed the practicality and robustness of the current nitration protocol. Unfortunately, nitrated products were not obtained from toluene, *N*,*N*-dimethylaniline, thioanisole, and chlorobenzene even at 130 °C. Nitroarenes are useful building blocks in organic synthesis, and are also constituents for dyes, rubber, plastics, and pharmaceuticals.[22] Their synthetic potential as coupling partners in Suzuki-Miyaura cross-coupling and Buchwald-Hartwig amination was also recently reported.[23] The current mild procedure with inexpensive $Fe(NO_3)_3{\cdot}9H_2O$ can be used for nitration methods of acid- and oxidant-sensitive aromatic compounds.

The bromo group of resulting 9-silafluorene **4a** was converted into a phenylethynyl group by palladium-catalyzed Sonogashira coupling reaction to give **6** in 92% yield without affecting other functional groups (Eq 1).[24] Cross-coupling reactions with aryl Grignard regents *via* cleavage of a methoxy group[25] in 9-silafluorene frameworks has been demonstrated previously by Shimizu[3b] and us.[7g] Thus, 9-silafluorene **4a** with methoxy and bromo functionalities can be utilized as a useful building block for the synthesis of unsymmetrically substituted 9-silafluorene-containing π-conjugated molecules.



CONCLUSION

A novel method for borylation, bromination, and nitration of 9-silafluorene derivatives was developed. Despite the utility of 9-silafluorenes, the number of functionalization methods for them is limited compared to other dibenzoheterocycles, including carbazoles, dibenzofurans, and dibenzothiophenes. Although controlling the regioselectivity of iridium-catalyzed direct borylation of C–H bonds was difficult, bromination and nitration of 2-methoxy-9-silafluorene occurred selectively due to electronic factors of the methoxy group. The orthogonal reactivity of bromide and methoxy groups in cross-coupling reactions will enable rapid access to 9-silfluorenes containing π-conjugated functional molecules through two sequential cross-coupling reactions.

EXPERIMENTAL SECTION

General. All reactions were conducted in dry solvent under an argon atmosphere, and heated with an oil bath. *p*-Xylene, toluene, THF, and 1,4-dioxane were purchased from Wako Pure Chemical Industries, and degassed with argon for 20 min before use. Di-*tert*-butyl-2,2'-bipyridine (dtbpy) and LiBr were purchased from Tokyo Chemical Industry. $PhI(OAc)_2$ was purchased from Oakwood Chemical. $[Ir(OMe)(cod)]_2$ and $Fe(NO_3)_3{\cdot}9H_2O$ were purchased from Wako Pure Chemical Industries. Unless otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. 9,9-Dimethyl-9-silafluorene[7a] 2,9,9-trimethyl-9-silafluorene,[7a] and 2-methoxy-9,9-diphenyl-9-silafluorene (**3b**)[3i] were prepared according to a previously reported method. Column chromatography was performed with silica gel 60N (neutral, 40-50 μm) purchased from Kanto Chemical. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL ECS-400 spectrometer. Proton chemical shifts are reported in ppm based on the solvent resonance resulting from incomplete deuteration ($CDCl_3$ at 7.26 ppm) as the internal standard. ^{13}C NMR spectra were recorded with complete proton decoupling, and the chemical shifts reported relative to $CDCl_3$ at 77.00 ppm. The following abbreviations are used; s: singlet, d: doublet, t: triplet, sept: septet, m: multiplet. IR spectra were recorded using a SHIMADZU IRAFFINITY-1 100V J. High-resolution mass spectra (HRMS) were measured by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer (JEOL JMS-700 MStation FAB-MS). Melting points were measured on a Yanaco micromelting point apparatus and are uncorrected.

Typical Procedure for Preparation of 9,9-Dimethyl-9-silafluorene Derivatives 3 (Scheme 1). A flame-dried Schlenk flask was charged with $Pd(OAc)_2$ (112 mg, 0.50 mmol), PPh_3 (393 mg, 1.5 mmol), K_2CO_3 (2.76 g, 20 mmol), DME (30 mL), H_2O (10 mL), 2-bromophenylboronic acid (2.01 g, 10 mmol), and 4-iodoanisole (2.81 g, 12 mmol), and the resulting mixture was stirred at 80 °C for 24 h. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent afforded 2-bromo-4'-methoxy-1,1'-biphenyl (2.32 g, 8.8 mmol, 88% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.97 (dt, J = 2.4, 8.8 Hz, 2H), 7.14-7.20 (m, 1H), 7.30-7.37 (m, 4H), 7.65 (d, J = 8.0 Hz, 1H). The analytical data matched those reported in the literature.[3i,26] A solution of 2-bromo-4'-methoxy-1,1'-biphenyl (2.10 g, 8.0 mmol) in THF (15 mL) was added to ^{n}BuLi (1.6 M in hexane, 7.5 mL, 12 mmol) at -78 °C, and the mixture was stirred for 30 min. Chlorodimethylsilane (1.14 g, 12 mmol) was added dropwise, and the resultant mixture was gradually warmed to 25 °C. After stirring for 12 h, the reaction mixture was quenched with *sat.* NH_4Cl *aq*. (10 mL), and extracted with EtOAc (30 mL×3). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent afforded 2-(dimethylsilyl)-4'-methoxy-1,1'-biphenyl (1.60 g, 6.6 mmol, 83% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 0.08 (d, J = 3.6 Hz, 6H), 3.86 (s, 3H), 4.38 (sept, J = 3.6 Hz, 1H), 6.94 (dt, J = 2.8, 8.8 Hz, 2H), 7.24-7.29 (m, 3H), 7.33 (dt, J = 1.2, 7.2 Hz, 1H), 7.41 (dt, J = 1.2, 7.6 Hz, 1H), 7.62 (dd, J = 1.2, 7.6 Hz, 1H). The analytical data matched those reported in the literature.[7a] A flame-dried 7 mL sealed tube was charged with $RhCl(PPh_3)_3$ (13.9 mg, 0.015 mmol), *p*-xylene (3.0 mL), 2-(dimethylsilyl)-4'-methoxy-1,1'-biphenyl (362 mg, 1.5 mmol), and 3,3-dimethyl-1-butene (0.97 mL, 7.5 mmol), and the resulting mixture was stirred at 135 °C for 24 h. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexane as the eluent to afford 2-methoxy-9,9-dimethyl-9-silafluorene (**3a**) (317 mg, 1.3 mmol, 88% yield) as a colorless solid. ^1H NMR (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 3.87 (s, 3H), 6.96 (dd, J = 2.0, 8.0 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 1.6, 8.0 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.73 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -3.2, 55.4, 115.5, 117.8, 120.1, 121.9, 126.3, 130.2, 132.7, 138.1, 140.6, 140.9, 147.8, 159.2. The analytical data matched those reported in the literature.[7a]

2-Methoxy-9,9-dipentyl-9-silafluorene (**3c**). Following the aforementioned procedure for rhodium-catalyzed silylative cyclization with dehydrogenation using 2-(dipentylsilyl)-4'-methoxy-1,1'-biphenyl (354 mg, 1.0 mmol) provided 257 mg (0.73 mmol, 73% yield) of **3c** as a colorless oil after purification by flash chromatography on silica gel with hexane as the eluent. ^1H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, J = 7.2 Hz, 6H), 0.89-0.95 (m, 4H), 1.20-1.28 (m, 8H), 1.32-1.49 (m, 4H), 3.86 (s, 3H), 6.95 (dd, J = 2.8, 7.6 Hz, 1H), 7.14 (d, J = 2.8 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.39 (dt, J = 2.8, 7.2 Hz, 1H), 7.57 (d,

J = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 12.2, 13.9, 22.1, 23.5, 35.6, 55.3, 115.1, 118.5, 120.1, 121.8, 126.1, 130.0, 133.2, 137.1, 139.9, 141.2, 148.3, 159.0. HRMS (FAB^+): calcd for $C_{23}H_{33}OSi$ ($[M+H]^+$) 353.2301; found. 353.2300.

9,9-Dimethyl-2-triisopropylsiloxy-9-silafluorene (**3d**). Following the general procedure for rhodium-catalyzed silylative cyclization with dehydrogenation using 2-(dimethylsilyl)-4'-triisopropylsiloxy-1,1'-biphenyl (692 mg, 1.8 mmol) provided 599 mg (1.6 mmol, 87% yield) of **3d** as a colorless solid after purification by flash chromatography on silica gel with hexane as the eluent. mp 36.9-37.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.40 (s, 6H), 1.12 (d, *J* = 7.6 Hz, 18H), 1.22-1.32 (m, 3H), 6.92 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.20 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.39 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ –3.3, 12.7, 18.0, 120.1, 121.4, 121.8, 123.9, 126.2, 130.1, 132.6, 138.3, 140.7, 140.8, 147.9, 155.8. HRMS (FAB^+): calcd for $C_{23}H_{34}OSi_2$ ($[M]^+$) 382.2148; found. 382.2164.

2-Methoxy-3,9,9-trimethyl-9-silafluorene (**3e**). Following the general procedure for rhodium-catalyzed silylative cyclization with dehydrogenation using 2-(dimethylsilyl)-4'-methoxy-3'-methyl-1,1'-biphenyl (462 mg, 1.8 mmol) provided 293 mg (1.2 mmol, 64% yield) of **3e** as a colorless solid after purification by flash chromatography on silica gel with hexane as the eluent. mp 111.7-112.2 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 2.29 (s, 3H), 3.91 (s, 3H), 7.07 (s, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.39 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.61 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -3.1, 16.8, 55.5, 113.4, 120.0, 123.5, 126.1, 128.8, 130.1, 132.5, 137.5, 138.3, 140.4, 148.0, 157.7. HRMS (FAB^+): calcd for $C_{16}H_{18}OSi$ ($[M]^+$) 254.1127; found. 254.1134.

General Procedure of Iridium-Catalyzed Borylation of 9-Silafluorene (Table 1). A flame-dried sealed tube was charged with $[Ir(OMe)(cod)]_2$ (3.3 mg, 5.0 μmol), ligand (10 μmol), 9,9-dimethyl-9-silafluorenes (0.20 mmol), bis(pinacolato)diboron (101.5 mg, 0.40 mmol), 1,4-dioxane (0.20 mL), and stirred at 100 °C for 24 h. The residue was directly subjected to flash column chromatography on silica gel with hexane / EtOAc as the eluent to afford borylated 9,9-dimethyl-9-silafluorenes **1** or **2** as mixture of regioisomers.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dimethylsilyl-9-silafluorene (**1_{mm}**) *and 2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dimethylsilyl-9-silafluorene* (**1_{mp}**) *and 3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dimethylsilyl-9-silafluorene* (**1_{pp}**) *(Table 1, entry 1).* Following the general procedure using 9,9-dimethyl-9-silafluorene (42.0 mg, 0.20 mmol) and dtbpy (2.7 mg, 10 μmol) provided 86.1 mg (0.19 mmol, 96% yield) of the mixture of diborylated 9-silafluorenes **1_{mm}**, **1_{mp}**, and **1_{pp}** as a colorless solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. ^1H NMR for **1_{mm}** (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 1.39 (s, 24H), 7.88 (d, *J* = 7.8, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 8.10 (s, 2H). ^1H NMR for **1_{mp}** (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 1.39 (s, 24H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 8.09 (s, 1H), 8.29 (s, 1H). ^1H NMR for **1_{pp}** (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 1.39 (s, 24H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 8.37 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -3.4, -3.3, -3.2, 24.9, 83.75, 83.78, 83.9, 120.5, 120.6, 127.0, 127.2, 132.0, 132.1, 133.7, 134.1, 136.90, 136.94, 137.6, 138.6, 139.25, 139.29, 142.5, 143.5, 146.9, 147.2, 150.4, 150.7 (The boron-bound carbon was not detected due to quadrupolar relaxation). HRMS (FAB^+): calcd for $C_{26}H_{36}O_4SiB_2$ ($[M]^+$) 462.2569; found. 462.2556.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-7,9,9-trimethylsilyl-9-silafluorene (**2_m**) *and 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-7,9,9-trimethylsilyl-9-sila- fluorene* (**2_p**) *(Table 2, entry 2).* Following the general procedure using 2,9,9-trimethyl-9-silafluorene (44.8 mg, 0.20 mmol) and **L3** (2.1 mg, 10 μmol) provided 54.2 mg (0.15 mmol, 76% yield) of borylated 9-silafluorenes **2_m** and **2_p** as a colorless solid after purification by flash chromatography on silica gel with hexane / EtOAc = 50 / 1 as the eluent. The regioselectivity was determined to be **2_m** / **2_p** = 64 / 36 by ^1H NMR analysis of the crude product. The major isomer **2_m** was partially separable by purification using GPC with toluene as the eluent, and the structure of which was unambiguously determined by X-ray crystallographic analysis (see Figures S1 and Tables S2). ^1H NMR for **2_m** (400 MHz, $CDCl_3$): δ 0.41 (s, 6H), 1.37 (s, 12H), 2.39 (s, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.87 (dd, *J* = 0.8, 7.6 Hz, 1H), 8.07 (s, 1H). ^1H NMR for **2_p** (400 MHz, $CDCl_3$): δ 0.41 (s, 6H), 1.37 (s, 12H), 2.38 (s, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H). $^{13}C\{^1H\}$ NMR for **2_m** (100 MHz, $CDCl_3$): δ -3.2, 21.3, 24.9, 83.7, 119.8, 121.2, 130.9, 133.4, 137.0, 137.5, 137.6, 139.3, 139.8, 145.0, 150.8 (The boron-bound carbon was not detected due to quadrupolar relaxation). $^{13}C\{^1H\}$ NMR for **2_p** (100 MHz, $CDCl_3$): δ -3.3, 21.3, 24.9, 83.8, 121.1, 126.4, 130.9, 132.0, 133.2, 133.4, 136.8, 138.7, 142.5, 145.2, 147.2 (The boron-bound carbon was not detected due to quadrupolar relaxation). HRMS (FAB^+): calcd for $C_{21}H_{28}O_2SiB$ ($[M+H]^+$) 351.1952; found. 351.1953.

General Procedure for Hypervalent Iodine-Promoted Bromination of 2-Alkoxy-9-silafluorene Derivatives (Table 3 and Figure 3): A flame-dried sealed tube was charged with LiBr (31.3 mg, 0.36 mmol), 2-alkoxy-9-silafluorenes **3** (0.30 mmol), (diacetoxyiodo)benzene (58.0 mg, 0.18 mmol) and THF (1.0 mL), and stirred at 0 °C for 30 min. Additional iodobenzene diacetate (58.0 mg, 0.18 mmol) was added at 0 °C, and stirred for 30 min. After stirring at 25 °C for further 1 h, the solvent was removed under the reduced pressure. The residue was subjected to flash column chromatography on silica gel with hexane / EtOAc as the eluent to afford brominated 9,9-dimethyl-9-silafluorenes **4**.

2-Bromo-7-methoxy-9,9-dimethyl-9-silafluorene (**4a**). Following the general procedure using **3a** (71.8 mg, 0.30 mmol) provided 67.0 mg (0.21 mmol, 71% yield) of **4a** as a colorless solid after purification by flash chromatography on silica gel with hexane / EtOAc = 20 / 1 as the eluent. mp 64.5-70.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.44 (s, 6H), 3.87 (s, 3H), 6.96 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -3.3, 55.4, 115.7, 117.8, 120.8, 121.7, 122.0, 133.0, 135.3, 139.5, 140.4, 141.1, 146.5, 159.4. IR (KBr / cm^{-1}): 2963, 2938, 2837, 1599, 1566, 1458, 1410, 1217, 1070, 1059, 1038, 868. HRMS (FAB^+): calcd for $C_{15}H_{15}BrOSi$ ($[M]^+$) 318.0076; found. 318.0066.

2-Bromo-7-methoxy-9,9-dipentyl-9-silafluorene (**4c**). Following the general procedure using **3c** (106 mg, 0.30 mmol) provided 106 mg (0.21 mmol, 82% yield) of **4c** as a colorless oil after purification by flash chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1) and HPLC (eluent: hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 0.82 (t, *J* = 7.2 Hz, 6H), 0.89-0.94 (m, 4H), 1.21-1.28 (m, 8H), 1.30-1.36 (m, 4H), 3.86 (s, 3H), 6.95 (dd, *J* = 2.4, 8.0 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.49 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 12.1, 13.9, 22.1, 23.4, 35.5, 55.4, 115.3, 118.6, 120.7, 121.7, 122.0, 132.8, 135.6, 139.4, 140.1, 147.0,

159.3. HRMS (FAB$^+$): calcd for $C_{23}H_{31}BrOSi$ ([M]$^+$) 430.1328; found. 430.1322.

2-Bromo-9,9-dimethyl-7-triisopropylsiloxy-9-silafluorene (**4d**). Following the general procedure using **3d** (115 mg, 0.30 mmol) provided 98.3 mg (0.21 mmol, 71% yield) of **4d** as a colorless oil after purification by flash chromatography on silica gel with hexane / EtOAc = 30 / 1 as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 1.13 (d, J = 7.2 Hz, 18 H), 1.23-1.34 (m, 3H), 6.93 (dd, J = 2.0, 8.0 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 7.49 (dd, J = 2.0, 8.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ -3.4, 12.7, 17.9, 120.7, 121.5, 121.7, 121.9, 124.0, 132.9, 135.3, 139.7, 140.4, 141.3, 146.6, 156.1. HRMS (FAB$^+$): calcd for $C_{23}H_{34}BrSi_2$ ([M+H]$^+$) 445.1382; found. 445.1385.

7-Bromo-3,9,9-trimethyl-2-methoxy-9-silafluorene (**4e**). Following the general procedure using **3e** (76.3 mg, 0.30 mmol) provided 31.8 mg (0.096 mmol, 32% yield) of **4e** as a colorless solid after purification by flash chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1) and HPLC (eluent: hexane). mp 131.1-131.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.42 (s, 6H), 2.29 (s, 3 H), 3.90 (s, 3H), 7.05 (s, 1H), 7.49 (dd, J = 2.0, 8.4 Hz, 1H), 7.56 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ -3.2, 16.8, 55.5, 113.4, 120.6, 121.6, 123.5, 129.1, 132.9, 135.2, 137.1, 139.3, 141.3, 146.7, 157.9. HRMS (FAB$^+$): calcd for $C_{16}H_{18}BrOSi$ ([M+H]$^+$) 333.0310; found. 333.0319.

General Procedure for Nitration of Aromatic Compounds with Iron Nitrate Nonahydrate (Tables 4 and 5): A flame-dried sealed tube was charged with $Fe(NO_3)_3{\cdot}9H_2O$ (60.6 mg, 0.15 mmol), aromatic compound (0.30 mmol), CH_2ClCH_2Cl or CH_3CN (1.5 mL), and stirred at 60 °C for 5 h. The residue was directly subjected to flash column chromatography on silica gel with hexane / EtOAc as the eluent to afford the corresponding nitroarenes **5**.

2-Methoxy-7-nitro-9,9-dimethyl-9-silafluorene (**5a**). Following the general procedure using **3a** (71.8 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 78.8 mg (0.28 mmol, 92% yield) of 2-methoxy-7-nitro-9,9-dimethyl-9-silafluorene (**5a**) as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. On the other hand, 1.7 mg (0.060 mmol, 20% yield) of minor isomer, 2-methoxy-3-nitro-9,9-dimethyl-9-silafluorene (**5a'**), was obtained as a yellow solid by using CH_3CN as a solvent. Structures of **5a** and **5a'** were unambiguously determined by X-ray crystallographic analysis (see Figures S2-3 and Tables S3-4). mp 146.0-146.9 °C. ^{1}H NMR for **5a** (400 MHz, $CDCl_3$): δ 0.48 (s, 6H), 3.89 (s, 3H), 7.02 (dd, J = 2.8, 8.8 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 8.26 (dd, J = 2.0, 8.8 Hz, 1H), 8.42 (d, J = 2.0 Hz, 1H). ^{1}H NMR for **5a'** (400 MHz, $CDCl_3$): δ 0.47 (s, 6H), 4.03 (s, 3H), 7.30 (dt, J = 1.2, 7.2 Hz, 1H), 7.32 (s, 1H), 7.46 (dt, J = 1.2, 7.2 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 8.20 (s, 1H). ^{13}C{^{1}H} NMR for **5a** (100 MHz, $CDCl_3$): δ -3.5, 55.5, 116.2, 118.1, 120.2, 123.8, 126.1, 127.8, 138.2, 139.8, 142.8, 146.3, 154.0, 160.6. ^{13}C{^{1}H} NMR for **5a'** (100 MHz, $CDCl_3$): δ -3.4, 56.7, 117.2, 117.4, 120.8, 127.6, 130.8, 132.9, 137.8, 140.4, 141.2, 145.7, 147.3, 152.0. IR for **5a** (KBr / cm^{-1}): 3067, 3013, 2936, 2837, 1591, 1562, 1518, 1416, 1353, 1219, 1057, 862, 787. HRMS for **5a** (FAB$^+$): calcd for $C_{15}H_{16}NO_3Si$ ([M+H]$^+$) 286.0899; found. 286.0898.

2-Methoxy-7-nitro-9,9-diphenyl-9-silafluorene (**5b**). Following the general procedure using **3b** (109 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 108 mg (0.26 mmol, 88% yield) of **5b** as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. mp 208.5-210.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.08 (dd, J = 2.8, 8.8 Hz, 1H), 7.33 (d, J = 2.8 Hz, 1H), 7.39 (t, J = 7.2 Hz, 4H), 7.46 (t, J = 7.2 Hz, 2H), 7.64 (d, J = 7.2 Hz, 4H), 7.87 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 8.32 (dd, J = 2.4, 8.8 Hz, 1H), 8.53 (d, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.5, 116.8, 119.4, 120.7, 124.2, 126.6, 128.4, 128.8, 130.7, 130.8, 135.5, 137.3, 139.1, 139.7, 146.6, 154.9, 160.9. HRMS (FAB$^+$): calcd for $C_{25}H_{20}NO_3Si$ ([M+H]$^+$) 410.1213; found. 410.1192.

2-Methoxy-7-nitro-9,9-dipentyl-9-silafluorene (**5c**). Following the general procedure using **3c** (106 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 101 mg (0.26 mmol, 85% yield) of **5c** as a yellow oil after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, J = 7.2 Hz, 6H), 0.91-1.00 (m, 4H), 1.22-1.26 (m, 8H), 1.32-1.40 (m, 4H), 3.89 (s, 3H), 7.01 (dd, J = 2.8, 8.4 Hz, 1H),7.18 (d, J = 2.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 8.26 (dd, J = 2.8, 8.8 Hz, 1H), 8.39 (d, J = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.9, 13.9, 22.1, 23.4, 35.4, 55.4, 115.8, 118.9, 120.2, 123.7, 126.0, 128.0, 138.8, 141.7, 146.2, 154.6, 160.4. HRMS (FAB$^+$): calcd for $C_{23}H_{32}NO_3Si$ ([M+H]$^+$) 398.2151; found. 398.2155.

9,9-Dimethyl-7-nitro-2-triisopropylsiloxy-9-silafluorene (**5d**). Following the general procedure using **3d** (115 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 110 mg (0.26 mmol, 86% yield) of **5d** as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. mp 86.1-87.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.46 (s, 6H), 1.13 (d, J = 7.6 Hz, 18H), 1.24-1.34 (m, 3H), 6.98 (dd, J = 2.4, 8.4 Hz, 1H),7.16 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 8.25 (dd, J = 2.0, 8.4 Hz, 1H), 8.41 (d, J = 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ -3.6, 12.7, 17.8, 120.3, 121.9, 123.7, 124.3, 126.1, 127.7, 138.4, 139.9, 142.7, 146.2, 154.1, 157.5. HRMS (FAB$^+$): calcd for $C_{23}H_{34}NO_3Si_2$ ([M+H]$^+$) 428.2077; found. 428.2080.

2-Methoxy-3,9,9-trimethyl-7-nitro-9-silafluorene (**5e**). Following the general procedure using **3e** (76.3 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 56.6 mg (0.19 mmol, 63% yield) of **5e** as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. mp 151.9-152.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (s, 6H), 2.31 (s, 3H), 3.93 (s, 3H), 7.11 (s, 1H), 7.67 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 8.25 (dd, J = 2.4, 8.4 Hz, 1H), 8.41 (t, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ -3.4, 16.8, 55.5, 113.5, 120.1, 125.0, 126.1, 127.6, 129.7, 138.0, 139.7, 139.9, 146.1, 154.3, 159.1. HRMS (FAB$^+$): calcd for $C_{16}H_{18}NO_3Si$ ([M+H]$^+$)300.1056; found. 300.1061.

2-Nitroanisole (**5f**). Following the general procedure using anisole (32.4 mg, 0.30 mmol) in CH_3CN at 100 °C for 24 h provided 11.9 mg (0.078 mmol, 26% yield) of 2-nitroanisole (**5f**) as a yellow oil and 11.0 mg (0.072 mmol, 24% yield) of 4-nitroanisole (**5f'**) as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. ^{1}H NMR for **5f** (400 MHz, $CDCl_3$): δ 3.96 (s, 3H), 7.03 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.54 (dt, J = 1.2, 7.6 Hz, 1H), 7.84 (dd, J = 1.2, 7.6 Hz, 1H). ^{1}H NMR for **5f'** (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 6.96 (d, J = 9.2 Hz, 2H), 8.21 (d, J = 9.2 Hz, 2H). The analytical data matched those reported in the literature.[27]

5-Nitro-2H-1,3-benzodioxole (**5g**). Following the general procedure using 2*H*-1,3-benzodioxole (36.6 mg, 0.30 mmol) in CH_3CN provided 45.1 mg (0.27 mmol, 90% yield) of 5-nitro-2*H*-1,3-benzodioxole (**5g**) as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (s, 2H), 6.87 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.90 (dd, J = 2.4, 8.8 Hz, 1H). The analytical data matched those reported in the literature.[28]

1-Methoxy-4-nitronaphthalene (**5h**). Following the general procedure using 1-methoxynaphthalene (47.4 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 49.9 mg (0.25 mmol, 82% yield) of 1-methoxy-4-nitronaphthalene (**5h**) as a yellow solid and 3.0 mg (0.015 mmol, 5% yield) of 1-methoxy-2-nitronaphthalene (**5h'**) as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. ^{1}H NMR for **5h** (400 MHz, $CDCl_3$): δ 4.11 (s, 3H), 6.83 (d, J = 8.8 Hz, 1H), 7.58-7.62 (m, 1H), 7.72-7.77 (m, 1H), 8.38 (d, J = 7.6 Hz, 1H), 8.42 (d, J = 8.8 Hz, 1H), 8.79 (d, J = 8.8 Hz, 1H). ^{1}H NMR for **5h'** (400 MHz, $CDCl_3$): δ 4.15 (s, 3H), 7.61-7.70 (m, 3H), 7.89-7.93 (m, 2H), 8.30-8.33 (m, 1H). The analytical data matched those reported in the literature.[29]

9-Methyl-3-nitro-9H-carbazole (**5i**). Following the general procedure using 1-methylcarbazole (54.4 mg, 0.30 mmol) in CH_2ClCH_2Cl provided 57.7 mg (0.26 mmol, 85% yield) of 9-methyl-3-nitro-9*H*-carbazole **5i** as a yellow solid, 4.7 mg (0.021 mmol, 7% yield) of 9-methyl-1-nitro-9*H*-carbazole **5i'** as a yellow solid, and 5.7 mg (0.021 mmol, 7% yield) of 9-methyl-3,6-dinitro-9*H*-carbazole **5i''** as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent. ^{1}H NMR for **5i** (400 MHz, $CDCl_3$): δ 3.94 (s, 3H), 7.35-7.39 (m, 1H), 7.42 (d, J = 9.2 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.57-7.62 (m, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.41 (dd, J = 2.0, 9.2 Hz, 1H), 9.03 (d, J = 2.0 Hz, 1H). ^{1}H NMR for **5i'** (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 7.26-7.29 (m, 1H), 7.33-7.37 (m, 1H), 7.51-7.53 (m, 1H), 7.57-7.61 (m, 1H), 8.02 (dd, J = 1.2, 8.0 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 8.32 (dd, J = 1.2, 8.0 Hz, 1H). ^{1}H NMR for **5i''** (400 MHz, $CDCl_3$): δ 4.02 (s, 3H), 7.55 (d, J = 9.2 Hz, 2H), 8.51 (dd, J = 2.0, 9.2 Hz, 2H), 9.10 (d, J = 2.0 Hz, 2H). The analytical data matched those reported in the literature.[30]

1-Acetyl-6-nitro-1,2,3,4-tetrahydroquinoline (**5j**). Following the general procedure using 1-acetyl-1,2,3,4-tetrahydroquinoline (52.6 mg, 0.30 mmol) in CH_3CN provided 63.4 mg (0.29 mmol, 96% yield) of mixture of 1-acetyl-8-nitro-1,2,3,4-tetrahydroquinoline (**5j**) and 1-acetyl-6-nitro-1,2,3,4-tetrahydroquinoline (**5j'**) as a brown oil after purification by flash chromatography on silica gel with hexane / EtOAc = 1 / 1 as the eluent. The regioselectivity was determined to be **5j** / **5j'** = 81 / 15 by ^{1}H NMR analysis of the crude product. ^{1}H NMR for **5j** (400 MHz, $CDCl_3$): δ 2.03 (quint, J = 6.4 Hz, 2H), 2.31 (s, 3H), 2.86 (t, J = 6.4 Hz, 2H), 3.81 (t, J = 6.4 Hz, 2H), 7.64 (d, J = 6.8 Hz, 1H), 8.04 (s, 1H). 8.04-8.07 (m, 1H). ^{1}H NMR for **5j'** (400 MHz, $CDCl_3$): δ 2.03 (quint, J = 6.4 Hz, 2H), 2.26 (s, 3H), 2.86 (t, J = 6.4 Hz, 2H), 3.81 (t, J = 6.4 Hz, 2H), 7.19 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H). The analytical data matched those reported in the literature.[31]

1-Nitropyrenene (**5k**). Following the general procedure using pyrene (60.7 mg, 0.30 mmol) in CH_3CN provided 66.0 mg (0.26 mmol, 89% yield) of 1-nitropyrenene (**5k**) as a yellow solid after purification by flash chromatography on silica gel with hexane / EtOAc = 5 / 1 as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.17 (m, 2H), 8.21 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.34-8.38 (m, 3H), 8.70 (d, J = 8.4 Hz, 1H), 8.94 (d, J = 8.4 Hz, 1H). The analytical data matched those reported in the literature.[32]

Sonogashira Coupling Reaction of 6 (eq 1): A flame-dried Schlenk flask was charged with $Pd(PPh_3)_4$ (6.9 mg, 0.0060 mmol), CuI (1.9 mg, 0.010 mmol), 2-bromo-7-methoxy-9,9-dimethyl-9-silafluorene (**4**) (63.6 mg, 0.20 mmol), phenylacetylene (24 μL, 0.22 mmol), *N*,*N*-diisopropylamine (1.0 mL), and toluene (1.0 mL), and the resulting mixture was stirred at 80 °C for 5 h. The reaction mixture was quenched with *sat.* NH_4Cl *aq*. (5 mL), and extracted with EtOAc (10 mL×3). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent afforded 2-methoxy-9,9-dimethyl-7-(phenylethynyl)-9-silafluorene (**6**) (62.7 mg, 0.19 mmol, 92% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.44 (s, 6H), 3.87 (s, 3H), 6.97 (dd, J = 2.8, 8.0 Hz, 1H), 7.17 (d, J = 2.4 Hz, 1H), 7.32-7.38 (m, 3H), 7.53-7.56 (m, 2H), 7.57 (dd, J = 2.0, 8.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ -3.3, 55.4, 89.6, 90.1, 115.7, 117.9, 120.0, 120.9, 122.4, 123.5, 128.1, 128.3, 131.5, 133.5, 135.9, 138.3, 140.0, 141.3, 147.6, 159.5. IR (KBr / cm^{-1}): 3050, 3005, 2959, 2937, 2833, 1601, 1566, 1456, 1439, 1412, 1389, 1290, 1256, 1217, 1186, 1061, 1040, 893, 866. HRMS (FAB$^+$): calcd for $C_{23}H_{20}OSi$ ([M]$^+$) 340.1283; found. 340.1277.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX. X-ray crystallography data, CIF files, and copies of ^{1}H and ^{13}C NMR spectra.

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(11) Assuming that regioselectivity of the second borylation was not affected by electronic factors of the boryl group incorporated in the first borylation step, formation of a mixture of $\mathbf{1}_{mm}$: $\mathbf{1}_{mp}$: $\mathbf{1}_{pp}$ = 32 : 49 : 19 = (1.3×1.3) : (1.3×1+1×1.3) : (1×1) indicates that regioselectivity of the current borylation is *meta* : *para* = 1.3 : 1 relative to the position of silicon atom. Preferencial borylation at *meta* position of silyl group was also observed in the other system, *i.e.* borylation at *meta* position of 8-silylquinoline took place much efficiently compared with that of 8-methylquinoline. See ref. 7k.

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