Synthetic and Photophysical Studies on Silicon-bridged Biaryls

Kenji Mochida

2010

Contents

Abbreviations

A	acceptor	EDG	electron-donating group
abs.	absorption	EI	electron ionization
Ac	acetyl	EWG	electron-withdrawing group
aq.	aqueous	eq.	equation
Ar	aryl	equiv	equivalent
br	broad	Et	ethyl
Bu	butyl	FAB	fast atom bombardment
ca.	about(circa)	FID	flame ionization detector
cat.	catalyst	FL	fluorescence
CIE	commission internationale de l'éclairage	GC	gas chromatography
		GPC	gel permeation chromatography
CV	cyclicvoltammetry		
Cy	cyclohexyl	h	hour(s)
Cyp	cyclopentyl	Hex	hexyl
d	doublet	HOMO	highest occupied molecular orbital
D	donor		
δ	scale (NMR)	HR MS	high-resolution mass spectra
DIBAL-H	diisobutylaluminium-hydride	Hz	hertz
		i	iso
DFT	density functional theory	IR	infrared spectroscopy
DMA	*N*,*N*-dimethylacetamide	*J*	copling constant
DMF	*N*,*N*-dimethylformamide	L	ligand
DMSO	dimethyl sulfoxide	LAH	lithium aluminum hydride
dppe	1,2-bis(diphenylphosphino)-ethane	LUMO	lowest unoccupied molecular orbital
dppm	1,1’-bis(diphenylphosphino)-methane	Me	methyl
		Mes	mesityl
dppp	1,3-bis(diphenylphosphino)-propane	min	minute(s)
		mL	milliliter

μL	microliter
mp	melting point
n	normal
NMP	*N*-methylpyrrolidone
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
PAN	polyacrylonitrile
Pent	pentyl
PEG	poly(ethylene glycol)
Ph	phenyl
pin	pinacolato
PMB	*p*-methoxybenzyl
PMMA	poly(methyl methacrylate)
Pr	propyl
PS	polystyrene
q	quartet
quant	quantative
quint	quintet
ref.	reference
rt	room temperature
s	singlet
sep	septet
SPhos	2-dicyclohexylphosphino-2’,6’-dimethoxybiphenyl
t	triplet
t	tertiary
Tf	trifluoromethanesulfonyl
TG/DTA	thermogravimetric/ differential thermal analysis
Temp.	temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
tol	tolyl
Ts	tosyl
UV	ultraviolet
vis	visible
XPhos	2-cicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl

Chapter 1
Introduction and General Summary

Introduction

Oligomers and polymers containing π-conjugated systems have emerged recently as promising materials such as organic light-emitting diodes (OLEDs), field-effect transistors (FETs), plastic lasers, photovoltaic cells, and so on.[1] These organic electronic devices are considered to be promising, because of easy processibility, flexibility, light weight, and also low cost. Such characteristic features are nicely reflected in the fabrication of high performance OLEDs, which are employed as devices for flat-panel displays of commercial products like television and cell phone.[2]

The progress in organic functional materials relies heavily on the availability of new π-conjugated molecules. Since functional materials are used as solid thin film for the practical applications, it is important to control over the properties of aggregate states of molecules.[3] Therefore, not only intrinsic opto-electronic properties of π-conjugated molecules, but also their supramolecular organizations and morphology in solid states are the critical parameters to be considered in the development of new materials. Opto-electronic properties and supramolecular organization of π-conjugated molecules are closely related to their electronic and molecular structures, which can be tuned by installation of appropriate functional groups, polycyclic structures of aromatic rings, and/or heteroatom-bridges.[4]

Modification of π-conjugated molecules

One of the major approaches for tuning electronic and solid state structures of parent chromophores is an introduction of appropriate functional groups to π-conjugated backbones. In particular, placement of an electron donor (D) at the one end of the conjugated system and an electron acceptor (A) at the other end, so called D-π-A system, is effective for attaining outstanding optical and electronic properties.[5] Donor and acceptor substituents influence not only optical and electronic properties such as colors of emission, efficiency, mobility of hole/electron transportation, and nonlinear optical properties, but also solid state structures. For example, introduction of a naphthyl(phenyl)amino group makes the chromophore amorphous and improves thermal stability.[6] Thanks to such attractive features, D-π-A type molecular design has

been applied to dyestuffs and pigments,[7] and contributed to the recent scientific and practical progress in various fields, such as nonlinear optics (NLOs),[8,9] light emitting materials,[2,10] and solar cells[11] (Chart 1).

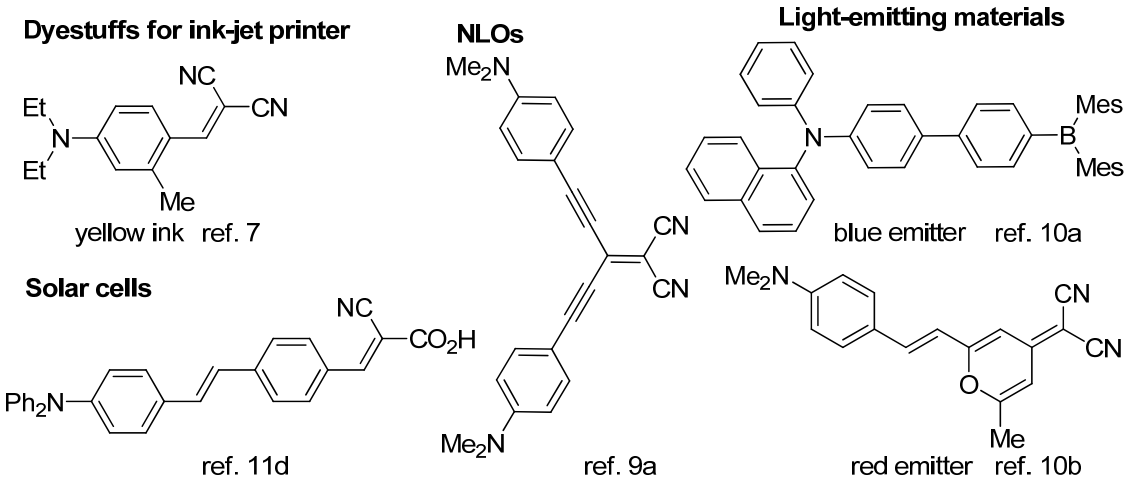
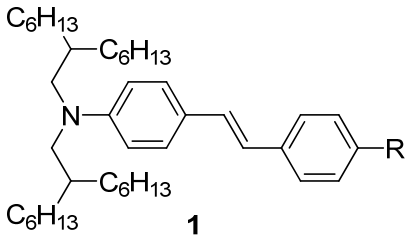


Chart 1.

It should be noted that opto-electronic properties of D-π-A type molecules can be readily tuned by proper choice of donor and/or acceptor groups. For example, D-π-A type *trans*-stilbenes **1** exhibit a bathochromic shift drastically in the absorption maxima, when electron-withdrawing nature of the acceptor R, *i.e.* σ_p value, is enhanced (Table 1).[12]

Table 1.



1

R	σ_p	$\lambda_{abs,max}$ / nm
H	0.00	366
CN	0.66	401
NO_2	0.78	461
$HC=C(CN)_2$	0.84	525
$C(CN)=C(CN)_2$	0.98	670

Fusion of aromatic ring is also effective to perturb electronic structure of the parent π-system.[1i,13] Generally, extension of conjugation length leads to a red-shift of absorption and fluorescence spectra. For example, a series of acenes, e.g. naphthalene, anthracene, tetracene, and pentacene, emit fluorescence, respectively, in the ultraviolet,

blue, green, and red regions (Chart 2).[14] In addition, larger acenes such as tetracene and pentacene exhibit excellent hole transport property due to their high-lying HOMO levels.[1j,15]

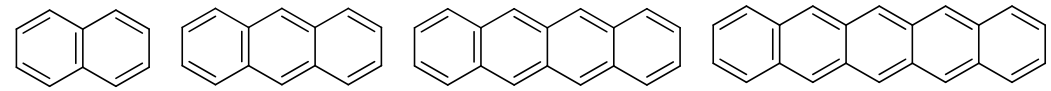


Chart 2.

Heteroacenes in which an acene skeleton is fused by heteroaromatic ring(s) are also attractive, because introduction of heteroaromatic rings such as thiophene into the arene moiety perturbs the electronic structure of the parent π-systems. In particular, terminally-fused thiophene gives an opportunity to easily functionalize the hetroacences at the 2-position of the thiophene terminal (Chart 3, R). Shown below in Chart 3 are examples of heteroacenes that exhibit superior field effect transistor properties.[16]

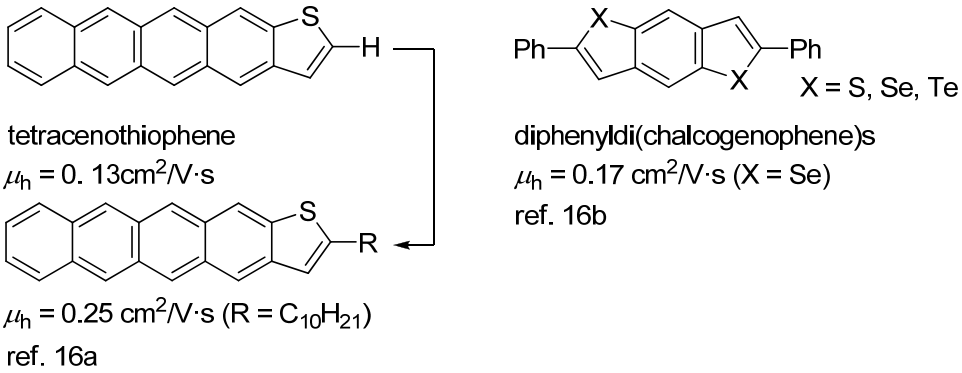


Chart 3.

Bridging between two π-modules by heteroatom(s) is the third way for controlling the electronic structure of π-conjugated system. Heteroatom bridge can perturb the electronic structures via orbital interactions such as σ–π, σ*–π*, n–π, and p–π* conjugations.[4e,17] Figure 1 shows HOMO and LUMO energies of heteroatom-bridged tetraeicosadodecaenes, which are highly dependent on the bridging elements.[18]

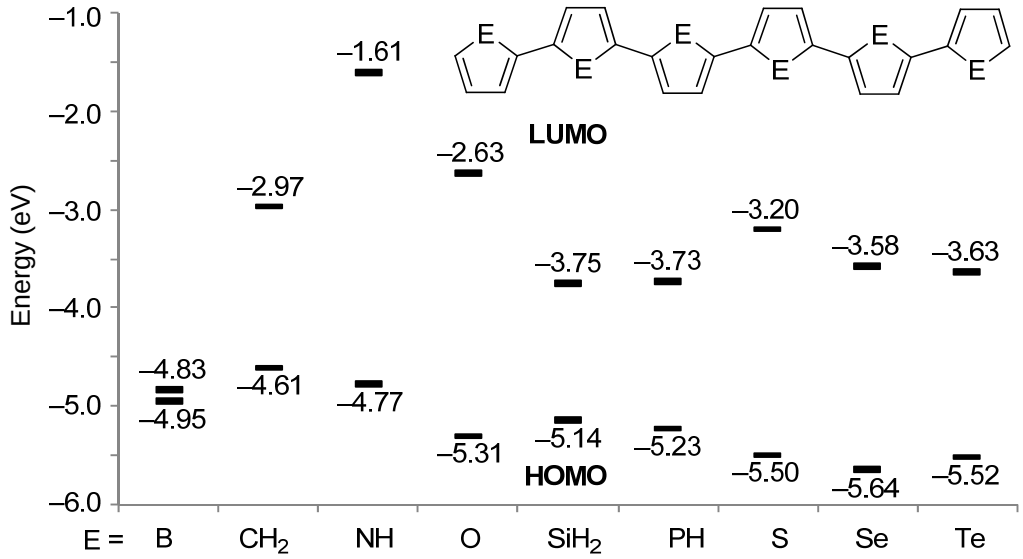


Figure 1. Calculated HOMO-LUMO energy levels of heteroatom-bridged tetraeicosadodecaenes.

Chart 4 illustrates some π-conjugated molecules that contain boron, nitrogen, phosphorus, sulfur, or selenium as a bridge of biaryl systems. These are developed for light-emitting materials,[2,4e,17a,19] host for blue emitting phosphorescent dyes,[20] and field-effect transistors.[1j,21]

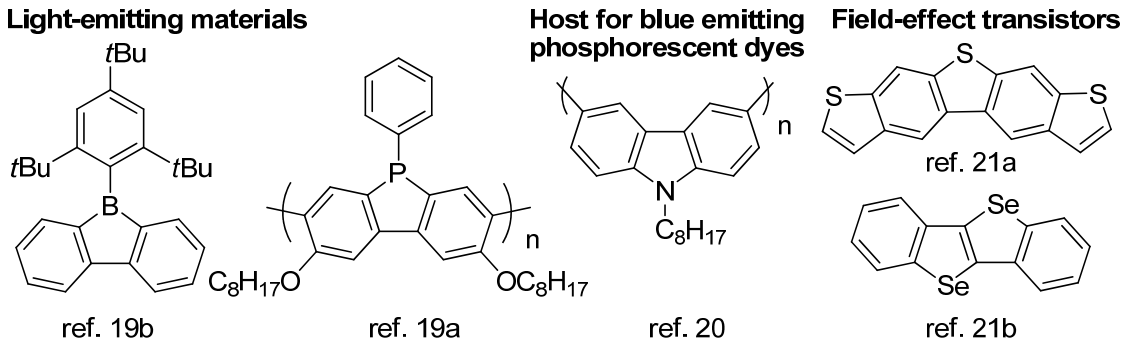


Chart 4.

Silicon bridge

Silicon bridges between such π-conjugated modules as vinylenes and phenylenes are particularly effective in modification of the electronic structure of the parent π-conjugated framework.[4e,17a,17c-17e] A representative example is silicon-bridged butadienes (siloles).[22] Silole is reported to have an electronic structure quite different from that of cyclopentadiene.[22a] *Ab initio* calculation at the HF/6-31G* level shows that HOMO of silole is about 0.4 eV lower than that of cyclopentadiene, while LUMO of silole is more than 1.2 eV lower in comparison with those of cyclopentadiene (Figure 2). The difference is interpreted as the result of unique orbital interaction between the σ* orbital of the diorganosilylene moiety and the π* orbital of the butadiene moiety, *i.e.* σ*–π* conjugation (Figure 3). It should be noted that σ* orbitals on the carbon–silicon bonds and π* orbital on the adjacent carbons are in phase, an ideal alignment for σ*–π* conjugation.

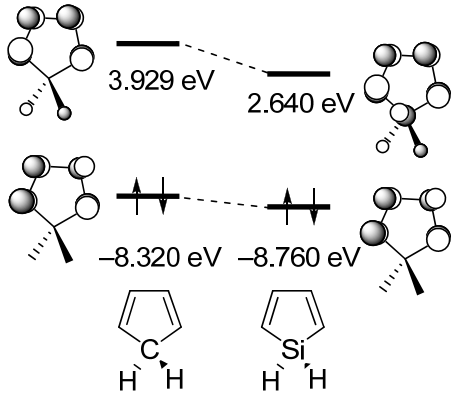


Figure 2. Relative energy levels of the HOMO and LUMO for silole and cyclopentadiene.

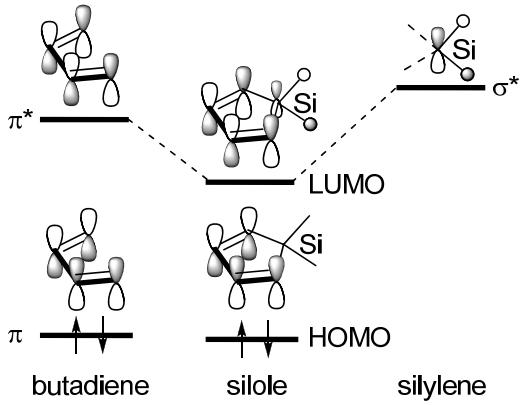


Figure 3. Orbital correlation diagram for dimethylsilole.

The low-lying LUMO level of silole is remarkable as compared with those of other heterocycles such as pyrrole, furan, and thiophene (Figure 1),[18,23] and is attributed to the narrow band gap and the high electron affinity. Accordingly, silole based-functional materials are used as electron transporting materials, light emitting materials, and sensors.[17a,22]

Silicon-bridged biaryls

Growing interest has recently been paid to silicon-bridged biphenyls (9-silafluorene) and bithiophenes as a key component of functional organic materials like light-emitting materials, electron or hole transporting materials, field-effect transistors, host materials for phosphorescent emitters, sensors, and solar cells (Chart 5).[17b,22e-f,24]

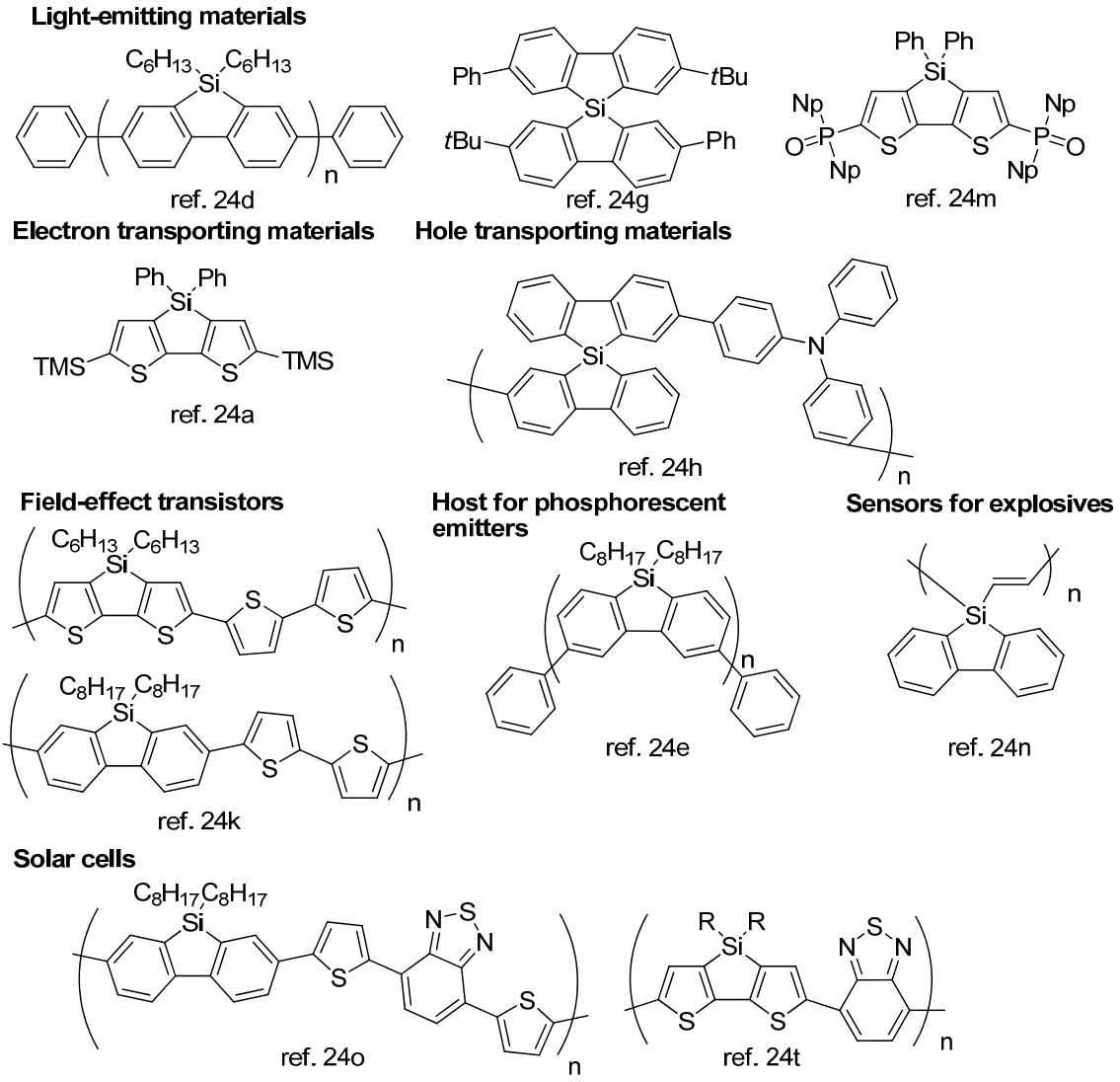


Chart 5.

Therefore, it is quite intriguing to explore novel silicon-bridged biaryls as a new module for organic functional materials that exhibit unique and superior properties.

Synthetic approaches to silicon-bridged biaryls

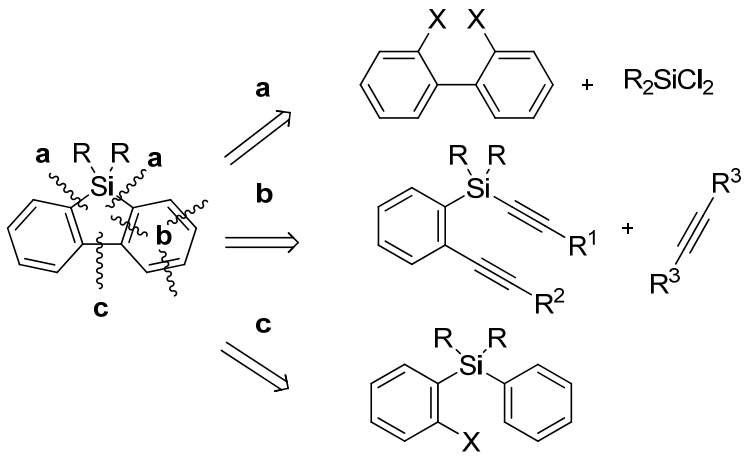
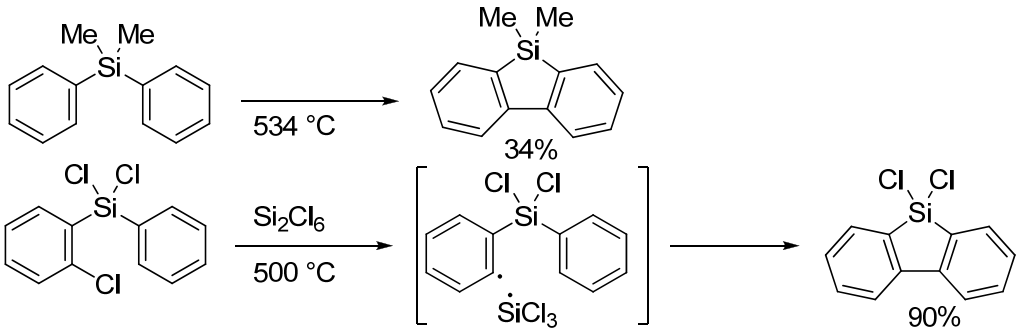


Chart 6.

A standard synthetic method for silicon-bridged biaryls involves dilithiation of the corresponding 2,2'-dihalobiaryls followed by silylation with dichlorosilanes (Chart 6, **a**).[24-25] Although the protocol is simple, structural variation of accessible silicon-bridged biaryls is highly dependent on the availability of dihalobiaryls, and thus is limited mostly to symmetrical ones.

Another notable synthetic approach is the Ir-catalyzed [2+2+2] type cycloaddition of silicon-tethered 1,6-diynes to construct one benzene ring of silafluorene (Chart 6, **b**) as reported by Murakami recently.[26] The approach allows construction of extended π-conjugate system through [2+2+2] cycloaddition. This method is versatile, but the scope of alkynes is relatively limited.

The third approach may be accessed by forming aryl-aryl bonds between two aryl groups tethered by silicon (Chart 6, **c**). Among these three strategies, type **c** looks apparently fascinating, because variation of available diarylsilanes is much broad and not only symmetrical and asymmetrical 9-silafluorenes, but also silicon-bridged heterobiaryls are accessible. There are two precedents of type **c** in the literature. However, these require harsh reaction conditions as shown in Scheme 1.[27]



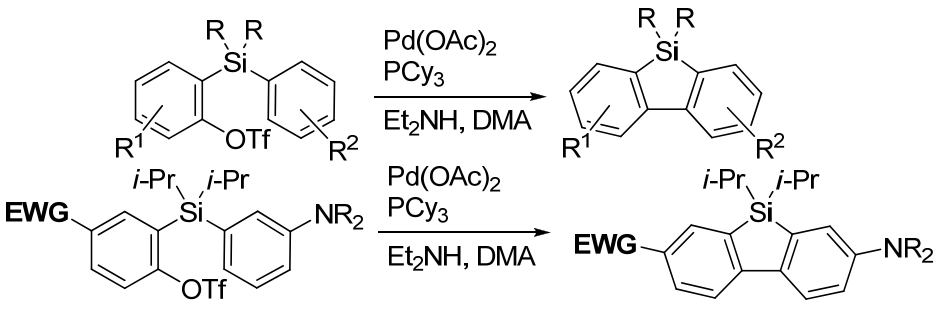
Scheme 1.

Accordingly, the author has considered synthesis of silicon-bridged biaryls under the type **c** strategy is of great importance for advanced modification and exploitation of silicon-bridged biaryls exhibiting unique properties.

Summary of this Thesis

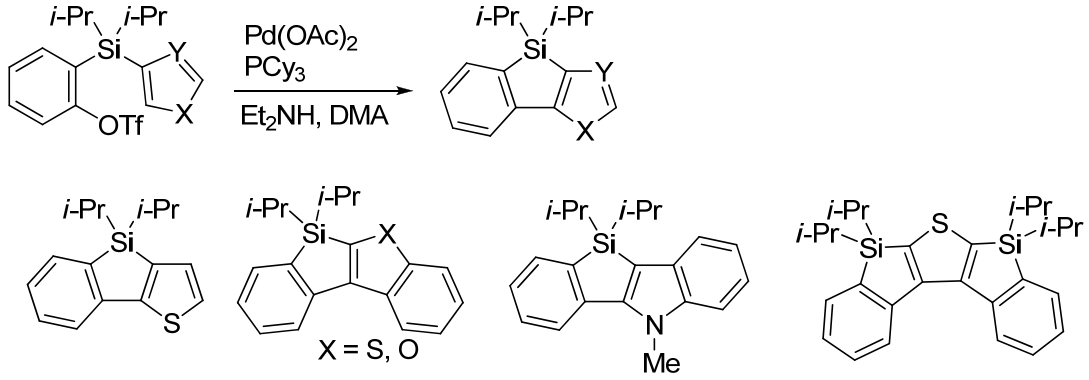
The present Thesis describes, firstly, synthesis of silicon-bridged biaryls via Pd-catalyzed intramolecular coupling of 2-(arylsilyl)aryl triflates, and, secondly, then their unique photophysical properties such as remarkable fluorescent solvatochromism and solid-state intense fluorescence. Details will be discussed in the following Chapters.

In Chapter 2, the author describes a novel annulation method for silicon-bridged biaryls, taking advantage of the Pd-catalyzed intramolecular direct arylation of 2-(arylsilyl)aryl triflates. The method allows him to synthesize a variety of symmetrical and unsymmetrical functionalized 9-silafluorenes in high yields (Scheme 2). It is noteworthy that intramolecular coupling of 2-(3-aminophenylsilyl)aryl triflates proceeds regioselectively to produce D-π-A type silafluorenes.



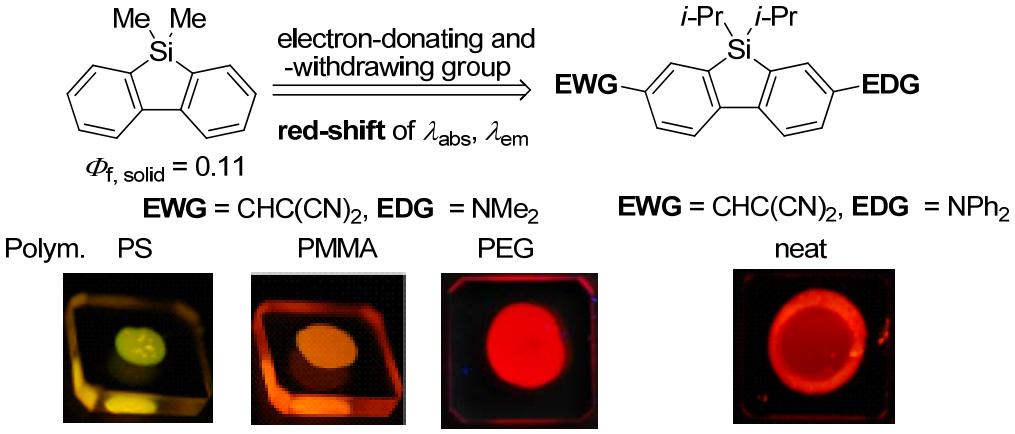
Scheme 2.

In addition, this novel transformation is applicable to the preparation of mixed biaryls like phenyl-heteroarenes starting with 2-(heteroarylsilyl)aryl triflates (Scheme 3).

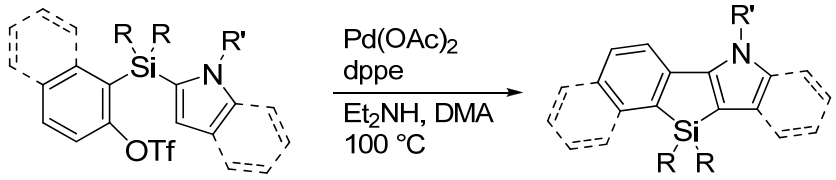


Scheme 3.

Described in Chapter 3 are photophysical properties and theoretical studies on thus prepared 2-donor-7-acceptor disubstituted 9-silafluorenes. Introduction of electron-donating and -withdrawing groups at 2,7-positions of silafluorene induces bathochromic shift of UV-absorption and fluorescence spectra. Remarkably, the emission color can be tuned from blue to red by choosing appropriate donor and acceptor substituents at 2,7-positions. Furthermore, emission color was found dependent on not only the dissolving solvent but also polymers dispersing the silafluorenes. Introduction of a bulky substituent such as diphenylamino group improves efficiency of solid state fluorescence.

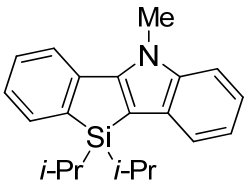


The author discussed in Chapter 4 an alternative synthesis of 3,2'-silicon-bridged 2-arylindoles through Pd-catalyzed intramolecular coupling of 2-[(2-pyrrolyl)silyl]aryl triflates. The reaction proceeds through silicon migration from 2- to 3- position of the indole ring to give 3,2'-silicon-bridged 2-arylindoles (Scheme 4). The results are the first demonstration of intramolecular direct arylation accompanied by reorganization of the bond connecting the aromatic carbon and the tethering element.

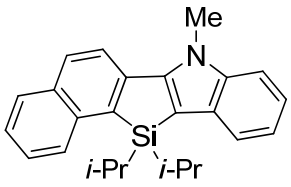


Scheme 4.

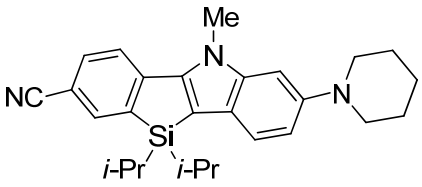
In Chapter 5, the author describes structure, photophysical properties, and theoretical studies on 3,2'-silicon-bridged 2-arylindoles. The 3,2'-silicon-bridged 2-arylindoles exhibit strong and highly efficient fluorescence not only in solution, but also in the solid state such as microcrystal and doped polymer film. The emission colors of the 3,2'-silicon-bridged 2-arylindoles can be tuned in a range from blue to yellowish green by introducing appropriate functional groups while retaining high quantum yields.



λ_{FL} = 434 nm
blue



λ_{FL} = 476 nm
greenish blue



λ_{FL} = 548 nm
yellowish green

In summary, the present Thesis demonstrates that the novel palladium-catalyzed intramolecular coupling of 2-(arylsilyl)aryl triflates produces silicon-bridged biarlys with broad structural variation. The novel structures produced by the new reactions described here led to discovery of π-conjugate molecules that exhibit photophysical properties useful for applications in opto-electronic materials.

References and Notes

(1) (a) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998. (b) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999. (c) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001. (d) *Molecular Devices and Machines*; Balzani, V., Venturi, M., Credi, A., Eds.; Wiley-VCH: Weinheim, 2003. (e) *Functional Organic Materials*; Müller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, 2007. (f) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. (g) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402. (h) Mitschke, U.; Bäuérle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (i) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (j) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (k) *Chem. Rev.* **2007**, *107*, 923–1386 (thematic issue on organic electronics and optoelectronics).

(2) (a) *Organic Light-Emitting Devices. Synthesis Properties and Applications*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006. (b) *Highly Efficient OLEDs with Phosphorescent Materials*; Yersin, H., Ed.; Wiley-VCH: Weinheim, 2008. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(3) (a) Cornil, J.; Beljonne, D.; Calbert, J. P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053. (b) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.

(4) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (b) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379. (c) Martin, R. E.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 1350. (d) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853. (e) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2. (f) Gierschner, J.; Cornil, J.; Egelhaaf, H. J. *Adv. Mater.* **2007**, *19*, 173.

(5) (a) Gompper, R.; Wagner, H.-U. *Angew. Chem. Int. Ed.* **1988**, *27*, 1437. (b) Meier, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 2482.

(6) (a) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1. (b) Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439.

(7) Kinoshita, A.; Kamiyama, M.; Abe, T.; JP Patent 2000131874: 2000.

(8) (a) Bubeck, C.; *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; p. 449-478. (b) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 1 and 2. (c) Butcher, P. N.; Cotter, D. *The Elements of Nonlinear Optics*; Cambridge University Press: Cambridge, 1990. (d) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (e) *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Solm, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington DC, 1991. (f) Boyd, R. W. *Nonlinear Optics*; Academic Press: Boston, 1992. (g) Zerbi, G. *Organic Materials for Photonics*; North-Holland: Amsterdam, 1993. (h) *Molecular Nonlinear Optics—Materials, Physics and Devices*; Zyss, J., Ed.; Academic Press: San Diego, 1994. (i) Evans, M. W. *Modern Nonlinear Optics*; Wiley: New York, 2001; Part 1-3. (j) *Chem. Rev.* **1994**, *94*, 1-278 (thematic issue on nonlinear optics)

(9) (a) May, J. C.; Lim, J. H.; Biaggio, I.; Moonen, N. N. P.; Michinobu, T.; Diederich, F. *Opt. Lett.* **2005**, *30*, 3057. (b) Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2008**, *42*, 235.
(10) (a) Jia, W. L.; Feng, X. D.; Bai, D. R.; Lu, Z. H.; Wang, S.; Vamvounis, G. *Chem. Mater.* **2004**, *17*, 164. (b) Chen, C.-T. *Chem. Mater.* **2004**, *16*, 4389. (c) Hudson, Z. M.; Wang, S. *Acc. Chem. Res.* **2009**, *42*, 1584.
(11) (a) Gratzel, M. *Nature* **2001**, *414*, 338. (b) Robertson, N. *Angew. Chem. Int. Ed.* **2006**, *45*, 2338. (c) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 2474. (d) Hwang, S.; Lee, J. H.; Park, C.; Lee, H.; Kim, C.; Park, C.; Lee, M.-H.; Lee, W.; Park, J.; Kim, K.; Park, N.-G.; Kim, C. *Chem. Commun.* **2007**, 4887.
(12) (a) Meier, H.; Gerold, J.; Kolshorn, H.; Baumann, W.; Bletz, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 292. (b) Meier, H.; Gerold, J.; Jacob, D. *Tetrahedron Lett.* **2003**, *44*, 1915. (c) Meier, H.; Gerold, J.; Kolshorn, H.; Mühling, B. *Chem. Eur. J.* **2004**, *10*, 360.
(13) (a) Watson, M. D.; Fechtenkotter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (b) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718.
(14) *Molecular Fluorescence*; Valeur, B., Ed.; Wiley-VCH: Weinheim, 2002.
(15) Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452.
(16) (a) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002. (b) Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084.
(17) (a) Hissler, M.; Dyer, P. W.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*, 1. (b) Grimsdale, A. C.; Müllen, K. *Macromol. Rapid Commun.* **2007**, *28*, 1676. (c) Ma, J.; Li, S.; Jiang, Y. *Macromolecules* **2001**, *35*, 1109. (d) Alparone, A.; Millefiori, A.; Millefiori, S. *Chem. Phys.* **2004**, *298*, 75. (e) Chen, R.-F.; Zheng, C.; Fan, Q.-L.; Huang, W. *J. Comput. Chem.* **2007**, *28*, 2091.
(18) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177.
(19) (a) Kobayashi, S.; Noguchi, M.; Tsubata, Y.; Kitano, M.; Doi, H.; Kamioka, T.; Nakazono, A.; JP Patent 2003231741: 2003. (b) Wakamiya, A.; Mishima, K.; Ekawa, K.; Yamaguchi, S. *Chem. Commun.* **2008**, 579.
(20) van Dijken, A.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stossel, P.; Brunner, K. *J. Am. Chem. Soc.* **2004**, *126*, 7718.
(21) (a) Wex, B.; Kaafarani, B. R.; Schroeder, R.; Majewski, L. A.; Burckel, P.; Grell, M.; Neckers, D. C. *J. Mater. Chem.* **2006**, *16*, 1121. (b) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044.
(22) (a) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327. (b) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (c) Tamao, K.; Yamaguchi, S. *J. Organomet. Chem.* **2000**, *611*, 5. (d) Yamaguchi, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *653*, 223. (e) Chen, J.; Cao, Y. *Macromol. Rapid Commun.* **2007**, *28*, 1714. (f) Zhan, X.; Barlow, S.; Marder, S. R. *Chem. Commun.* **2009**, 1948.
(23) (a) Tamao, K.; Ohno, S.; Yamaguchi, S. *Chem. Commun.* **1996**, 1873. (b) Tamao, K.; Yamaguchi, S.; Ito, Y.; Matsuzaki, Y.; Yamabe, T.; Fukushima, M.; Mori, S.

Macromolecules **2002**, *28*, 8668.
(24) (a) Ohshita, J.; Nodono, M.; Kai, H.; Watanabe, T.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **1999**, *18*, 1453. (b) Ohshita, J.; Kai, H.; Takata, A.; Iida, T.; Kunai, A.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K. *Organometallics* **2001**, *20*, 4800. (c) Matsushita, T.; Uchida, M. *J. Photopolym. Sci. Technol.* **2003**, *16*, 315. (d) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662. (e) Chan, K. L.; Watkins, S. E.; Mak, C. S. K.; McKiernan, M. J.; Towns, C. R.; Pascu, S. I.; Holmes, A. B. *Chem. Commun.* **2005**, 5766. (f) Lee, K.-H.; Ohshita, J.; Kimura, K.; Kunugi, Y.; Kunai, A. *J. Organomet. Chem.* **2005**, *690*, 333. (g) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071. (h) Xiao, H.; Leng, B.; Tian, H. *Polymer* **2005**, *46*, 5707. (i) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638. (j) Yamaguchi, S.; Xu, C.; Yamada, H.; Wakamiya, A. *J. Organomet. Chem.* **2005**, *690*, 5365. (k) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (l) Wang, E.; Li, C.; Mo, Y.; Zhang, Y.; Ma, G.; Shi, W.; Peng, J.; Yang, W.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 4133. (m) Ohshita, J.; Kurushima, Y.; Lee, K.-H.; Kunai, A.; Ooyama, Y.; Harima, Y. *Organometallics* **2007**, *26*, 6591. (n) Sanchez, J. C.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Chem. Mater.* **2007**, *19*, 6459. (o) Boudreault, P.-L. T.; Michaud, A.; Leclerc, M. *Macromol. Rapid Commun.* **2007**, *28*, 2176. (p) Lu, G.; Usta, H.; Risko, C.; Wang, L.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 7670. (q) Sanchez, J. C.; Urbas, S. A.; Toal, S. J.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Macromolecules* **2008**, *41*, 1237. (r) Shimizu, M.; Tatsumi, H.; Mochida, K.; Oda, K.; Hiyama, T. *Chem. Asian. J.* **2008**, *3*, 1238. (s) Wang, E.; Li, C.; Zhuang, W.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2008**, *18*, 797. (t) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144.
(25) (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1955**, *77*, 6380. (c) Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. *J. Organomet. Chem.* **1983**, *250*, 109. (d) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257. (e) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203.
(26) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2007**, *9*, 133.
(27) (a) Coutant, R. W.; Levy, A. *J. Organomet. Chem.* **1967**, *10*, 175. (b) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Shamshin, L. N.; Mosin, A. M. *Zh. Obshch. Khim.* **1985**, *55*, 2309. (c) Chernyshev, E. A.; Komalenkova, N. G.; Elagina, O. V.; Rogachevskii, V. L.; Bashkirova, S. A.; Dunaeva, L. V. *Zh. Obshch. Khim.* **1985**, *55*, 2314.

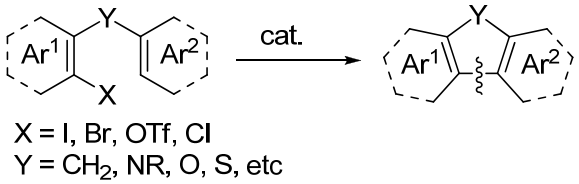
Chapter 2

Facile Synthesis of Silicon-Bridged Biaryls: Palladium Catalyzed Intramolecular Coupling of 2-(Arylsilyl)aryl Triflates

The Pd-catalyzed intramolecular coupling of 2-(arylsiyl)aryl triflates proceeded smoothly to give a variety of symmetrical and unsymmetrical functionalized 9-silafluorenes. In addition, the cyclization of 2-(3-aminophenylsilyl)aryl triflates took place at the *para*-position of the amino group regiospecifically. This method can be extended to synthesize silicon-bridged biaryls containing heteroaromatic rings.

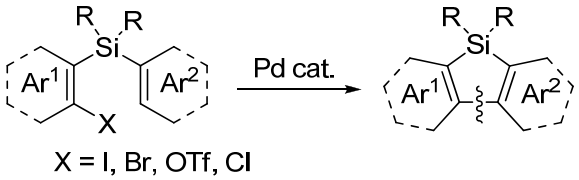
1. Introduction

Transition metal-catalyzed direct arylation has recently emerged as a versatile strategy for aryl-aryl bond formation.[1] Particularly useful is an intramolecular version that allows cyclization of tethered arenes to form fused carbo- and heterocycles such as fluorenes, carbazoles, and dibenzofurans (Scheme 1).[2] In addition, a broad range of functional groups are tolerant to intramolecular direct arylation, and both symmetrical and unsymmetrical biaryls can be readily prepared.



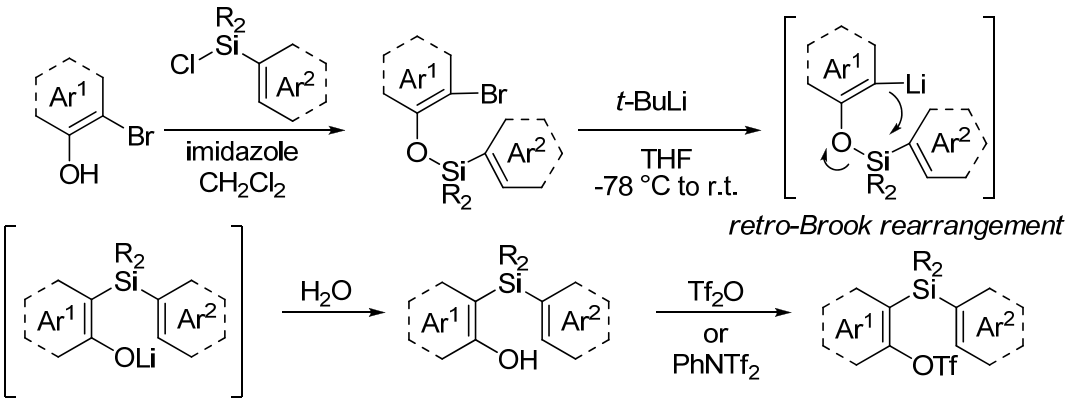
Scheme 1. Transition metal-catalyzed intramolecular coupling of tethered arenes.

From such a viewpoint, the author planned a Pd-catalyzed intramolecular coupling of two aryl groups tethered by a silylene moiety as a new synthetic route to silicon-bridged biaryls (Scheme 2). The structural variation attainable by this modular approach is potentially much broader than that by the conventional thermolytic direct coupling[3] because the catalyzed intramolecular coupling generally proceeds in milder reaction conditions and thus have high functional tolerance.



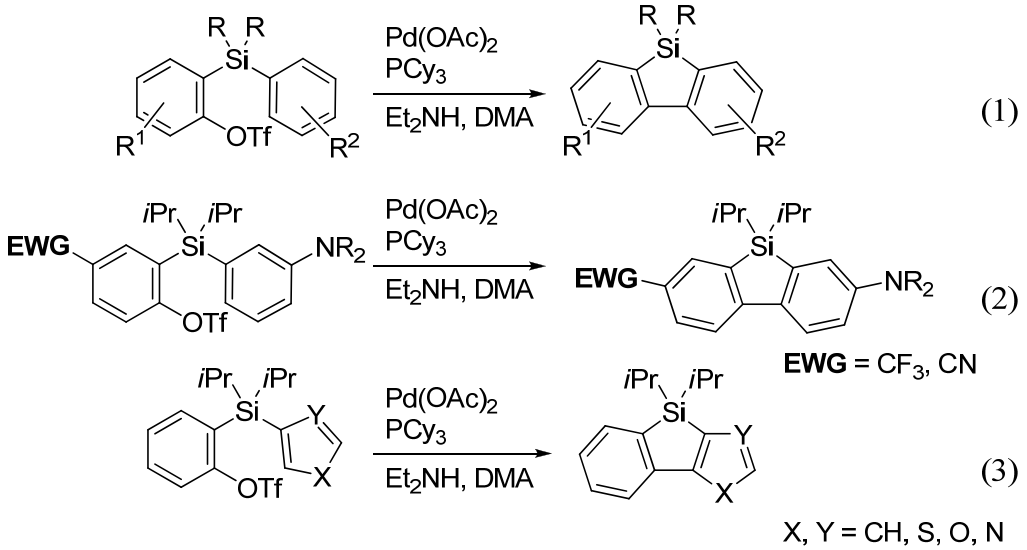
Scheme 2. Pd-catalyzed intramolecular coupling of diarylsilanes.

The author focused his attention to 2-(arylsilyl)aryl triflates as substrates for the cyclization. Such species are often used as precursors of arynes,[4] and can be readily prepared from the corresponding *o*-bromophenols and arylchlorosilanes by sequential silylation, retro-Brook rearrangement, and triflation (Scheme 3).[5]



Scheme 3. Preparation of 2-(arylsilyl)aryl triflates.

Described in this Chapter is a novel cyclization for the preparation of silicon-bridged biaryls. The reaction involves the Pd-catalyzed intramolecular direct arylation of 2-(arylsilyl)aryl triflates as summarized in Scheme 4. This approach provides a variety of symmetrical and unsymmetrical functionalized 9-silafluorenes (Eq. 1). In particular, intramolecular coupling of 2-(3-aminophenylsilyl)aryl triflates proceeds regiospecifically to produce D-π-A type silafluorenes (Eq. 2). In addition, this novel transformation is applicable to the preparation of silicon-bridged biaryls containing heteroaromatic ring (Eq. 3).



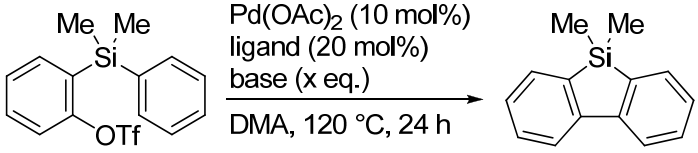
Scheme 4. Intramolecular coupling of 2-(arylsilyl)aryl trilflates.

2. Results and Discussion

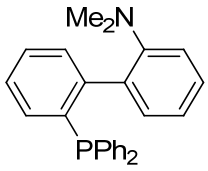
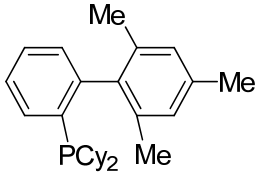
2-1. Screening of reaction conditions

Initially, 2-[dimethyl(phenyl)silyl]phenyl triflate (**1a**) was subjected to the typical conditions for Pd-catalyzed intramolecular direct arylation of 2-(phenoxymethyl)bromobenzenes ($Pd(OAc)_2$, 2-(diphenylphosphino)-2'-(*N*,*N*-dimethylamino)biphenyl, inorganic base, dimethylacetamide (DMA), 120 °C).[2b,2e] However, the use of inorganic base such as K_2CO_3, NaOAc, and Cs_2CO_3, which were effective for the reported transformations, resulted in no production of the desired 9,9-dimethyl-9-silafluorene (**2a**) (Table 1, entries 1-3). Use of Et_2NH as a base was found to be effective for this cyclization to give **2a** in only 6% yield (entry 6). He then examined the effect of ligand and found that 2-dicyclohexylphosphino- 2',4',6'-trimethylbiphenyl was the best among phosphines examined to isolate **2a** in 27% yield with complete consumption of **1a** (entry 11).

Table 1. Intramolecular coupling of 2-[dimethyl(phenyl)silyl]phenyl triflate.



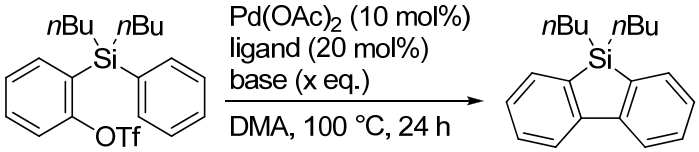
1a **2a**

entry	ligand	base (x eq.)	conv. (%)	yield (%)[a]
1		K_2CO_3 (5)	100	0
2		NaOAc (5)	100	0
3		Cs_2CO_3 (5)	100	0
4		Et_3N (10)	100	0
5		*n*Bu_2NH (10)	100	1
6		Et_2NH (15)	40	6
7	PCy_3	Et_2NH (15)	100	0
8	P(*t*Bu_3)	Et_2NH (15)	100	8
9	PPh_2*t*Bu	Et_2NH (15)	100	11
10	PPh_3	Et_2NH (15)	100	9
11		Et_2NH (15)	100	15 (27)[b]

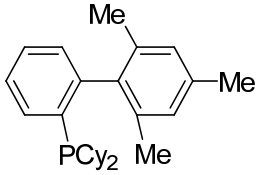
[a] Determined by GC using $C_{12}H_{26}$ as an internal standard. [b] Isolated yield.

As many unidentified products accompanied, the author 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. He exchanged the $SiMe_2$ group to Si*n*Bu_2 to induce steric protection and optimized the reaction conditions for this substrate. Pleasingly, the desired intramolecular coupling proceeded smoothly to afford the corresponding product (**2c**) in 58% yield under the optimized conditions for **1a** (Table 2, entry 1). Use of two equivalents of Et_2NH as a base with a catalyst system of $Pd(OAc)_2/2PCy_3$ in dimethyl acetamide at 100 °C was much effective to give **2c** in 70% yield (entry 7). Use of Cy_2NH as a base was also effective (entry 9). In view of easy handling and readily availability, the author selected Et_2NH as the base for further study.

Table 2. Intramolecular coupling of 2-[dibutyl(phenyl)silyl]phenyl triflate.



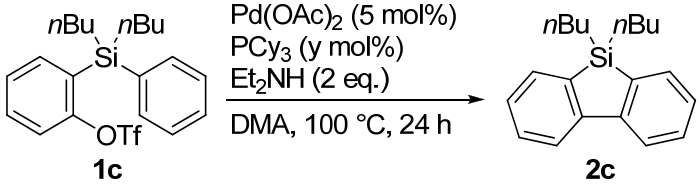
1c **2c**

entry	ligand	base (x eq.)	conv. (%)	yield (%)[a]
1		Et_2NH (15)	100	58
2	$P(tBu)_3$	Et_2NH (15)	100	57
3	PPh_3	Et_2NH (15)	100	46
4	PCy_3	Et_2NH (15)	100	63
5	PCy_3	Et_2NH (8)	100	66
6	PCy_3	Et_2NH (4)	100	70
7	PCy_3	Et_2NH (2)	100	70
8	PCy_3	Et_2NH (1)	100	68
9	PCy_3	Cy_2NH (2)	100	72
10	PCy_3	iPr_2NH (2)	100	48
11	PCy_3	$nHex_2NH$ (2)	100	48

[a] Determined by GC using $C_{12}H_{26}$ as an internal standard.

Intramolecular coupling of **1c** proceeded smoothly even in the presence of 5 mol% of $Pd(OAc)_2$ and 10 mol% of PCy_3 to give **2c** in 70 % yield (Table 3, entry 1). Use of 10 mol% of PCy_3 was found to be the most effective (entries 1-3). Polar solvents like DMSO, NMP, and dioxane were less effective (entries 4-6).

Table 3. Intramolecular coupling of 2-[dibutyl(phenyl)silyl]phenyl triflate.



1c **2c**

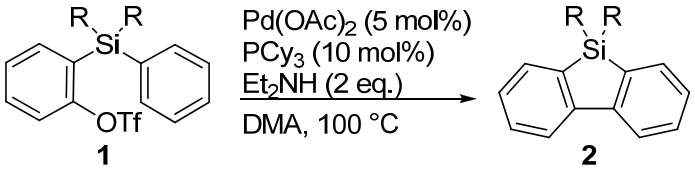
entry	x	y	solvent	conv. (%)	yield (%)[a]
1	5	10	DMA	100	70
2	5	7.5	DMA	100	65
3	5	15	DMA	100	68
4	5	10	DMSO	100	68
5	5	10	NMP	100	41
6	5	10	dioxane	100	62

[a] Determined by GC using $C_{12}H_{26}$ as an internal standard.

2-2. Effect of substituents on silicon

Under the optimized conditions, the author carried out the intramolecular coupling of various 2-(phenylsilyl)phenyl triflates **1a**-**1h** with various substituents on the silicon atom (Table 4). Bulkier substituents such as *i*Pr, *s*Bu, *t*Bu, and phenyl groups greatly increased yield of the corresponding 9-silafluorene product **2** (Table 4, entries 5-9). Such the bulkier substituent effect may be understood in terms of the Thorpe-Ingold effect (*gem*-dialkyl effect)[6] and steric protection of silicon atom.

Table 4. Palladium-catalyzed intramolecular direct arylation of **1**.[a]



1 **2**

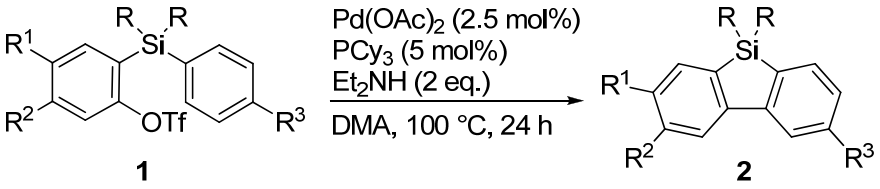
entry	**1**	R_2	time (h)	**2**	yield (%)[b]
1[c]	**1a**	Me_2	24	**2a**	27
2	**1b**	Et_2	75	**2b**	39
3	**1c**	*n*Bu_2	20	**2c**	68
4	**1d**	*n*Hex_2	24	**2d**	63
5	**1e**	*i*Pr_2	14	**2e**	92
6[d]	**1e**	*i*Pr_2	25	**2e**	91
7	**1f**	*s*Bu_2	20	**2f**	94
8	**1g**	*t*Bu, Ph	24	**2g**	88
9	**1h**	Ph_2	14	**2h**	87

[a] All the reactions of **1** (1.0 mmol) was carried out using $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), Et_2NH (2 eq.), DMA (2 mL), 100 °C, 24 h except for entry 1 and 6. [b] Isolated yield. [c] **1a** (1.0 mmol), $Pd(OAc)_2$ (10 mol%), 2-Mes-C_6H_4-PCy_2 (20 mol%), Et_2NH (15 eq.), DMA, 120 °C. [d] **1e** (1.0 mmol) and 2.5 mol% of $Pd(OAc)_2$/2PCy_3 were used.

2-3. Structural variation of 9-silafluorenes

The scope of functionalized 9-silafluorenes accessible by this method is summarized in Table 5. Symmetrical and unsymmetrical 9-silafluorenes **2i**-**2n** with electron-donating and/or -withdrawing substituents, such as NMe_2, OMe, CF_3, CN were synthesized from the corresponding triflates (**1i**-**1n**) in high to excellent yields. For a substrate incorporating CF_3 as a substituent R^3, the reaction required 120 °C to proceed smoothly (Table 5, entry 3).

Table 5. 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

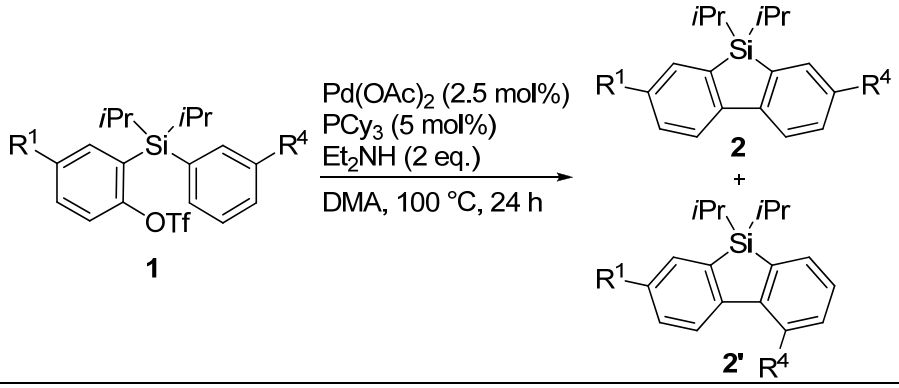
[a] All the reactions of **1** (1.0 mmol) was carried out using $Pd(OAc)_2$ (2.5 mol%), PCy_3 (5 mol%), Et_2NH (2 eq.), DMA (2 mL), 100 °C, 24 h except for entry 1 and 3. [b] Isolated yield. [c] **1i** (0.050 mmol), 5 mol% of $Pd(OAc)_2/2PCy_3$, and Et_2NH (2 eq.) were used. [d] Reaction was effected at 120 °C.

2-4. Regioselectivity in direct arylation reaction

The author next examined the regioselectivity of the direct arylation with substrates that possessed substituent R^4 at the position *meta* to the silyl moiety on the phenyl without a triflate group (Table 6). In general, arylation occurred at the *para*-position of R^4 to give regioisomer **2** preferentially. In particular, intramolecular coupling of 2-(3-aminophenylsilyl)aryl triflates **1o**-**1r** proceeds regiospecifically to produce 2-dimethylaminosilafluorene **2o** and 2-amino and 7-acceptor disubstituted silafluorene **2p**-**2r** as a sole product in high yields (entries 1-4). In case of **1s** bearing $SiMe_3$, the selectivity slightly decreased to give **2s** in 71% yield along with **2s'** in 14% yield (entry 5). The direct arylation of alkoxy-substituted silanes **1t**-**1v** resulted in moderate to low selectivity (entries 6-8). In case of **1w** bearing chlorine, the catalyst system of $Pd(OAc)_2/2PCy_3$ was ineffective, use of $Pd(OCOCF_3)_2$ with $Ph_2PCH_2CH_2NH_2$ gave corresponding silafluorene **2w** and **2w'** in 20% and 15% yields (entry 9). Conversely, the cyclization of **1x** bearing fluorine as R^4 proceeded at the position *ortho* to fluorine, giving rise to **2x'** as a major product in 47% yield. A similar regiochemical outcome was reported for the intramolecular direct arylation of methyleneoxy-tethered bromobenzenes.[2e] The product mixtures were easily separated by column chromatography on silica gel followed by GPC in all cases. The molecular

structure of **2r** was unambiguously confirmed by X-ray analysis of their single crystal (Figure 1). The structures of **2** and **2'** were characterized by ^{1}H NMR, because two signals of aromatic proton at 1- and 8-positions of silafluorene **2** show a characteristic ^4J coupling pattern.

Table 6. Regioselectivity of intramolecular coupling of **1**.[a]



entry	**1**	R^1	R^4	**2**	yield (%) of **2**[b]	**2'**	yield (%) of **2'**[b]
1	**1o**	H	NMe_2	**2o**	97	**2o'**	0
2	**1p**	CF_3	NMe_2	**2p**	95	**2p'**	0
3	**1q**	CN	NMe_2	**2q**	85	**2q'**	0
4	**1r**	CN	NPh_2	**2r**	89	**2r'**	0
5	**1s**	H	$SiMe_3$	**2s**	71	**2s'**	14
6	**1t**	H	OMe	**2t**	57	**2t'**	34
7	**1u**	H	O*i*Pr	**2u**	54	**2u'**	43
8	**1v**	H	OPMB	**2v**	47	**2v'**	47
9[c]	**1w**	H	Cl	**2w**	20	**2w'**	15
10[d]	**1x**	H	F	**2x**	10	**2x'**	47

[a] All the reactions of **1** (1.0 mmol) was carried out using $Pd(OAc)_2$ (2.5 mol%), PCy_3 (5 mol%), Et_2NH (2 eq.), DMA (2 mL), 100 °C, 24 h except for entry 9 and 10. [b] Isolated yield. [c] **1w** (1.0 mmol), 10 mol% of $Pd(OCOCF_3)_2/Ph_2PCH_2CH_2NH_2$, Et_2NH (2 eq.), DMA (2 mL), 100 °C. [d] **1x** (1.0 mmol), 10 mol% of $Pd(OAc)_2/PCy_3$, Et_2NH (2 eq.), DMA (2 mL), 120 °C.

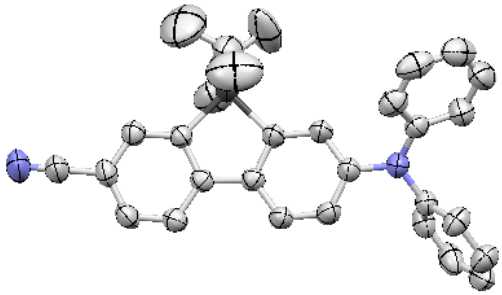
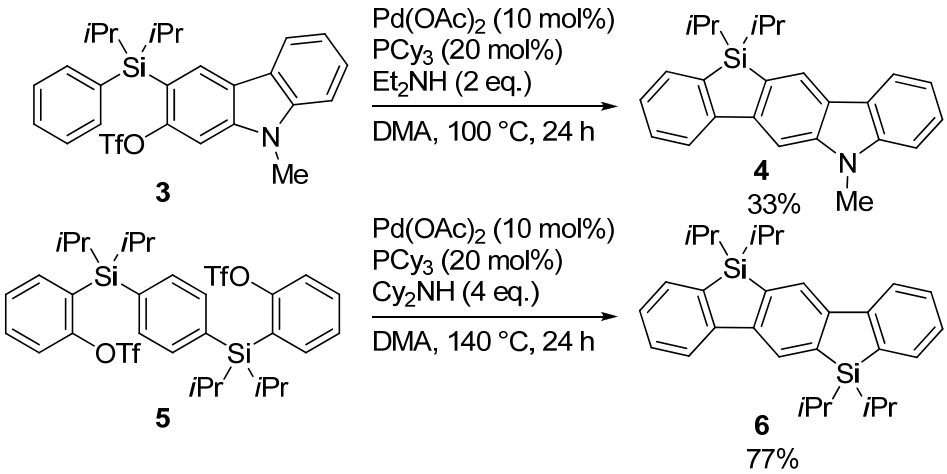


Figure 1. Molecular structure of **2r**.

2-5. Synthesis of Si-bridged terphenyl

This reaction can be applied to the synthesis of ladder type molecules. The intramolecular coupling of **3** produced Si,N-bridged terphenyl **4** in 33% (Scheme 5). While the cyclization of **5** was sluggish, replacing Et_2NH with Cy_2NH allowed for isolation of desired bissilicon-bridged terphenyl (**6**) in 77% yield after 24 h at 140 °C. The molecular structures of **4** and **6** were unambiguously confirmed by X-ray crystallographic analysis.



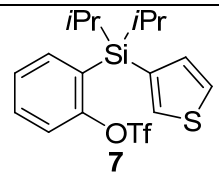
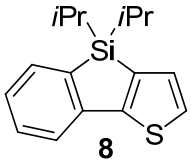
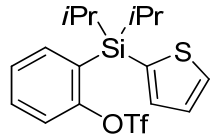
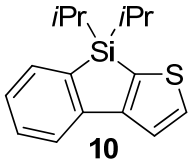
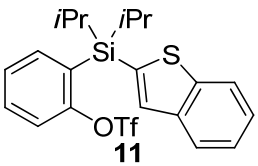
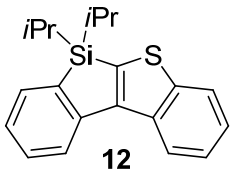
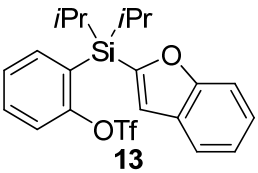
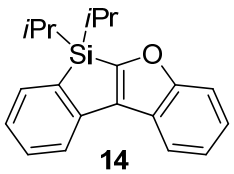
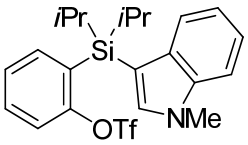
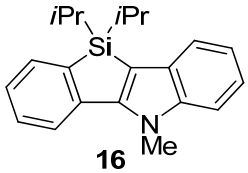
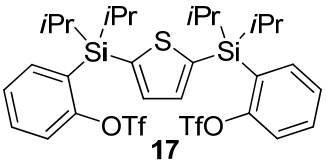
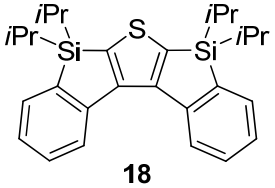
Scheme 5. Synthesis of ladder type compounds.

2-6. Synthesis of Si-bridged heterobiaryls

In addition to 9-silafluorenes, Si-bridged biaryls containing heteroaromatic ring are readily accessible by the present method (Table 7). Thiophene-containing triflates **7** and **9** cyclized smoothly at the 3- and 2-position of the thiophene ring, respectively, to give **8** and **10** in 94% and 95% yields (entries 1 and 2). Benzothiophene, benzofuran, and indole moieties also underwent direct arylation, affording tetracyclic products **12**,

14, and **16** in fair to high yields. (entry 3-6). Furthermore, twofold intramolecular coupling of 2,5-bis(silyl)thiophene **17** underwent smoothly to produce helicene-type molecule **18** in 85% yield. The molecular structures of **16** and **18** were unambiguously confirmed by X-ray analysis of their single crystals.

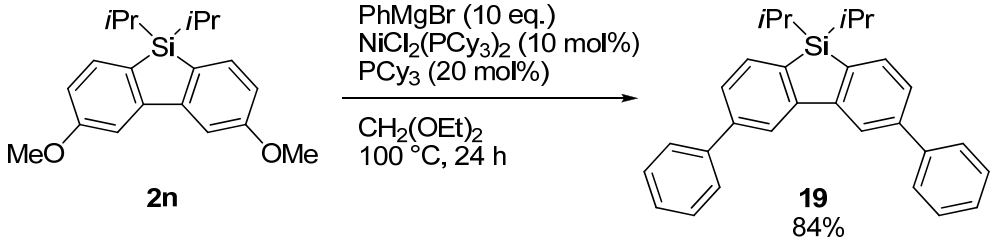
Table 7. Synthesis of silicon-bridged heterobiaryls.

entry	triflates	product	yield (%)[a]
1[b]	 **7**	 **8**	94
2[b]	 **9**	 **10**	95
3[c]	 **11**	 **12**	93
4[c]	 **13**	 **14**	85
5[d]	 **15**	 **16**	56
6[e]	 **17**	 **18**	85

[a] Isolated yield. [b] **7** or **9** (1.0 mmol), $Pd(OAc)_2$ (2.5 mol%), PCy_3 (5 mol%), Et_2NH (2 eq.), DMA (2 mL), 100 °C. [c] **11** or **13** (0.2 mmol), $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), Et_2NH (2 eq.), DMA (0.4 mL), 100 °C. [d] **15** (0.10 mmol), $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), Et_2NH (2 eq.), DMA (0.2 mL), 100 °C. [e] **17** (1.0 mmol), $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), Et_2NH (2 eq.), DMA (2 mL), 100 °C.

2-7. **Cross-coupling reaction of 3,6-dimethoxysilafluorene**

The Ni-catalyzed twofold cross-coupling reaction of 3,6-dimethoxysilafluorene **2n** with phenylmagnesium bromide under the Dankwardt's conditions[7] gave diphenylated silafluorene **19** in 84% yield with the silylene moiety intact (Eq. 4). This result demonstrates that a methoxy group that tolerates the direct arylation condition can serve as not only an electron-donating group but also as a site for functionalization to extend the π-conjugated system of silafluorenes.



(4)

3. Conclusions

The author demonstrated that intramolecular coupling of readily available 2-(arylsilyl)aryl triflates produces not only a variety of symmetrical and unsymmetrical functionalized 9-silafluorenes, but also silicon-bridged heterobialyls in high yields, which have attracted growing attention in material science. The keys to the success are the installation of bulky substituents on silicon and the use of Et_2NH as a base.

Experimental

General Remarks:

The experimental procedure described here applies to the experimental section in each Chapter. All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk technique or in a dry box under an argon atmosphere. Melting points were determined using a Yanagimoto Micro Point Apparatus or Stanford Research Systems MPA100. ^{1}H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet; brs, broad singlet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm) or chloroform-*d* (δ = 77.0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standards. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. EI-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL-HX110A spectrometer. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh) or aminopropyl-functionalized sphere silica gel (N–H silica gel) of FUJI SILYSIA CHEMICAL Ltd. NH-DM2035 (200–350 mesh). Alumina column chromatography was carried out using Merck Aluminium oxide 90 active neutral; activity grade III, 6wt% of water was added. Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC–908 chromatograph using a JAIGEL–1H and –2H GPC columns.

Materials

Dimethylacetamide (DMA) was purchased from Wako Inc. Reagent-grade dichloromethane, diethyl ether, and tetrahydrofuran were purified by passing through neutral alumina and copper oxide column under a nitrogen atmosphere before use. Dichlorodiisopropylsilane was purchased from Tokyo Chemical Industry Co., Ltd.

General Procedure for Preparation of 2-(arylsilyl)aryl triflates

Silylation of phenols with chlorosilanes:

An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-bromophenol (1.16 mL, 10 mmol), imidazole (1.02 g, 15 mmol), arylchlorosilane (10 mmol, prepared from the corresponding dichlorodiorganosilane and aryllithium), and CH_2Cl_2 (20 mL). The resulting solution was stirred at 40 °C for 12 h. The solution was then allowed to cool to room temperature before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give the corresponding aryl silyl ether as a colorless liquid.

Retro-Brook rearrangement of aryl silyl ether:

An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with aryl silyl ether (5 mmol) and THF (20 mL), and the solution was cooled to –78 °C. To the solution was added *t*-butyllithium (1.59 M in pentane, 6.3 mL, 10 mmol) dropwise via a syringe over 10 min. The resulting solution was allowed to warm to room temperature and then stirred for 10 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give 2-(arylsilyl)phenol as a colorless solid.

Triflation of 2-silylphenols:

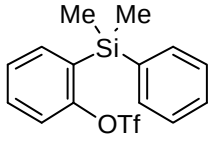
<Method A> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-(arylsilyl)phenol (3 mmol), Tf_2O (0.76 mL, 4.5 mmol), and CH_2Cl_2 (10 mL). To the solution was added pyridine (1.2 mL, 15 mmol) dropwise at room temperature. The mixture was stirred at room temperature for 12 h before quenching with saturated aq. $NaHCO_3$ (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give **1** as a colorless liquid or solid.

<Method B> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-(arylsilyl)phenol (3 mmol) and Et_2O (10 mL), and the solution was cooled to 0 °C. To the solution was added butyllithium (1.59 M in hexane, 1.9 mL, 3 mmol) dropwise via a syringe over 10 min. The solution was stirred at 0 °C for 1 h before adding Tf_2O (0.75 mL, 3 mmol). The resulting solution was allowed to warm to room temperature and then stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give **1** as a colorless liquid or solid.

<Method C> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with NaH (72 mg, 3 mmol) and DMF (5 mL). A DMF solution (5 mL) of 2-(arylsilyl)phenol (3 mmol) was added to the suspension of NaH dropwise at room temperature. The resulting solution was stirred at room temperature for 1 h and then $PhNTf_2$ (1.07 g, 3 mmol) was added to the solution. The mixture was stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to **1** as a colorless liquid or solid.

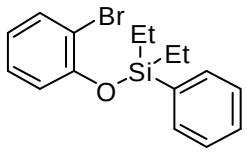
2-Bromophenyl dimethylphenylsilyl ether and 2-(dimethylphenylsilyl)phenol were prepared according to the general procedures and used for further steps without isolation.

2-(Dimethylphenylsilyl)phenyl trifluoromethanesulfonate (1a)



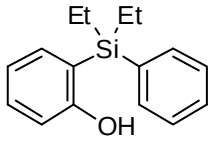
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 76%, a colorless oil. TLC: R_f 0.58 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.67 (s, 6H), 7.28 (dt, *J* = 7.2, 0.8 Hz, 1H), 7.36–7.47 (m, 6H), 7.51–7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –2.0, 118.3 (q, *J* = 317.2 Hz), 119.3, 127.2, 127.8, 129.4, 130.7, 131.4, 134.0, 136.3, 137.3, 155.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (neat): ν = 3070, 3010, 2961, 1597, 1467, 1422, 1247, 1213, 1142, 1057, 891, 816, 781, 743, 704 cm^{-1}. MS (FAB) *m/z*: 345 (26, M^+ – 15), 283 (20), 211 (10), 195 (11). Anal. Calcd for $C_{15}H_{15}F_3O_3SSi$: C, 49.99; H, 4.19. Found: C, 50.28; H, 4.23.

2-Bromophenyl diethylphenylsilyl ether



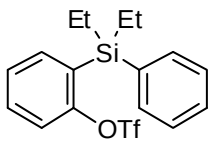
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 93%, a colorless oil. TLC: R_f 0.80 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05–1.07 (m, 10H), 6.77 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.80 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.07 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.26–7.45 (m, 3H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65–7.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.8, 6.7, 115.1, 119.9, 122.3, 127.8, 128.1, 129.8, 133.2, 133.9, 134.8, 152.2. IR (neat): ν = 2958, 2936, 2912, 1583, 1477, 1288, 1114, 916, 754, 729, 700 cm^{-1}. MS (FAB) *m/z*: 307 (100, $[M – 28]^+ + 2$), 305 (94, $[M – 28]^+$), 259 (24), 257 (25), 193 (23). Anal. Calcd for $C_{16}H_{19}BrOSi$: C, 57.31; H, 5.71. Found: C, 57.47; H, 5.81.

2-(Diethylphenylsilyl)phenol



Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 85%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99–1.03 (m, 6H), 1.09–1.23 (m, 4H), 4.76 (s, 1H), 6.72 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.95 (ddd, *J* = 7.3, 7.3, 1.1 Hz, 1H), 7.28 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.35–7.43 (m, 4H), 7.57–7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.0, 7.5, 115.1, 120.4, 120.7, 128.0, 129.4, 131.1, 134.7, 135.7, 136.3, 160.5. IR (neat): ν = 3526, 2955, 2908, 2874, 1593, 1573, 1427, 1276, 1190, 1126, 1107, 1008, 829, 758, 702 cm^{-1}. MS (FAB) *m/z*: 227 (31, $[M – 29]^+$), 199 (30), 176 (61), 154 (100), 136 (57). Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.80; H, 7.95.

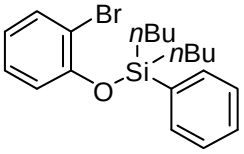
2-(Diethylphenylsilyl)phenyl trifluoromethanesulfonate (1b)



Prepared by Method A. Purification: GPC ($CHCl_3$). Yield: 84%, a colorless oil. TLC: R_f 0.54 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, *J* = 8.0 Hz, 6H), 1.16–1.27 (m, 4H), 7.31 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.33–7.40 (m, 4H), 7.43–7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.9, 7.5, 118.3 (q, *J* = 317.2 Hz), 119.2, 127.1, 127.7, 128.7, 129.3, 131.4, 134.50, 134.54, 137.9, 155.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.5. IR (neat): ν = 2958, 2912, 2878, 1595, 1467, 1421, 1248, 1213, 1142, 1057, 889, 767, 746, 729, 700, 597 cm^{-1}. MS (FAB) *m/z*: 359 (100, $[M – 29]^+$), 311 (43), 197 (35), 181 (26). Anal. Calcd for

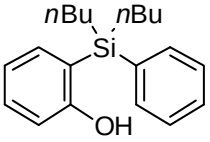
$C_{17}H_{19}F_3O_3SSi$: C, 52.56; H, 4.93. Found: C, 52.81; H, 4.91.

2-Bromophenyl di-*n*-butylphenylsilyl ether



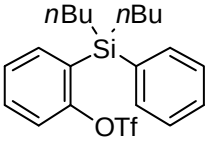
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 100%, a colorless oil. TLC: R_f 0.78 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85–0.88 (m, 6H), 1.04–1.08 (m, 4H), 1.30–1.45 (m, 8H), 6.76 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.80 (ddd, *J* = 8.1, 7.5, 1.5 Hz, 1H), 7.07 (ddd, 1H, *J* = 8.0, 7.5, 1.7 Hz), 7.37–7.44 (m, 3H), 7.51 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.65–7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.0, 25.1, 26.5, 115.1, 119.9, 122.3, 127.8, 128.0, 129.7, 133.2, 133.8, 135.4, 152.3. IR (neat): ν = 2957, 2924, 2870, 2858, 1587, 1477, 1290, 1114, 918, 752, 730, 700 cm^{-1}. MS (FAB) *m/z*: 392 (5, $M^+ + 2$), 390 (5, M^+), 335 (98), 333 (100), 315 (31), 313 (24), 279 (22), 277 (29). Anal. Calcd for $C_{20}H_{27}BrOSi$: C, 61.37; H, 6.95. Found: C, 61.60; H, 6.83.

2-(Di-*n*-butylphenylsilyl)phenol



Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 69%, a colorless solid. Mp: 34.9–40.5 °C. TLC: R_f 0.24 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 6H), 1.08–1.21 (m, 4H), 1.22–1.41 (m, 8H), 6.72 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.95 (ddd, *J* = 7.2, 7.2, 0.8 Hz, 1H), 7.28 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.35–7.42 (m, 4H), 7.56–7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 13.9, 26.0, 26.8, 115.2, 120.4, 121.2, 128.0, 129.4, 131.1, 134.6, 136.1, 136.2, 160.4. IR (KBr): ν = 3520, 3068, 3049, 3010, 2955, 2924, 2870, 2856, 1593, 1434, 1277, 1188, 883, 830, 758, 702 cm^{-1}. MS (FAB) *m/z*: 255 (60, $[M - 57]^+$), 234 (100), 181 (92), 123 (73). Anal. Calcd for $C_{20}H_{28}OSi$: C, 76.86; H, 9.03. Found: C, 76.58; H, 9.21.

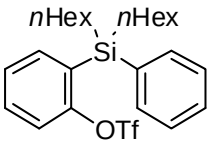
2-(Di-*n*-butylphenylsilyl)phenyl trifluoromethanesulfonate (1c)



Prepared by Method A. Purification: GPC ($CHCl_3$). Yield: 100%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 6H), 1.17–1.23 (m, 4H), 1.26–1.40 (m, 8H), 7.31 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.34–7.41 (m, 4H), 7.44–7.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 13.8, 26.0, 26.6, 118.2 (q, *J* = 316.4 Hz), 119.2, 127.1, 127.7, 129.2, 131.3, 134.5 (2C), 135.0, 137.7, 155.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6. IR (neat): ν = 2959, 2926, 2872, 2858, 1595, 1466, 1421, 1248, 1213, 1142, 891, 766, 745, 700, 598 cm^{-1}. MS (FAB) *m/z*: 387 (100, $[M - 57]^+$), 367 (38), 201 (20), 199 (12), 181 (23). Anal. Calcd for $C_{21}H_{27}F_3O_3SSi$: C, 56.73; H, 6.12. Found: C, 56.92; H, 6.09.

2-Bromophyl di-*n*-hexyl(phenyl)silyl ether and 2-(di-*n*-hexyl(phenyl)silyl)phenol were prepared according to the general procedures and used for further steps without isolation.

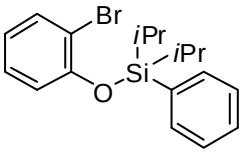
2-(Di-*n*-hexylphenylsilyl)phenyl trifluoromethanesulfonate (1d)



Prepared by Method A. Purification: GPC ($CHCl_3$). Yield: 22%, a colorless oil. TLC: R_f 0.61 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.2 Hz, 6H), 1.15–1.34 (m, 20H), 7.28–7.38 (m, 4H), 7.43–7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 14.2,

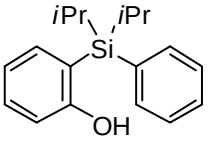
22.7, 23.8, 31.5, 33.3, 118.3 (q, J = 317.2 Hz), 119.2, 127.1, 127.7, 129.2, 129.3, 131.3, 134.5, 135.0, 137.7, 155.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6. IR (neat): ν = 2957, 2928, 2872, 1597, 1422, 1248, 1213, 1142, 1057, 889, 766, 745, 700 cm^{-1}. MS (FAB) *m/z*: 500 (1, M^+), 423 (35), 415 (100), 199 (18), 181 (37). Anal. Calcd for $C_{25}H_{35}F_3O_3SSi$: C, 59.97; H, 7.05. Found: C, 60.15; H, 7.05.

2-Bromophenyl diisopropylphenylsilyl ether



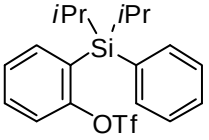
Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 87%, a colorless oil. TLC: R_f 0.51 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J = 7.6 Hz, 6H), 1.15 (d, J = 7.6 Hz, 6H), 1.51 (qq, J = 7.6, 7.6 Hz, 2H), 6.77–6.81 (m, 2H), 7.05 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.37–7.46 (m, 3H), 7.52–7.55 (m, 1H), 7.67–7.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 17.5, 17.7, 119.7, 122.0, 127.6, 127.9, 129.6, 133.2, 133.5, 134.47, 134.52, 152.5. IR (neat): ν = 2945, 2866, 1581, 1477, 1292, 1112, 922, 883, 752, 700, 667 cm^{-1}. MS (FAB) *m/z*: 365 (3, $[M + H]^+ + 2$), 363 (3, $[M + H]^+$), 321 (55), 319 (54), 287 (14), 285 (12). Anal. Calcd for $C_{16}H_{23}BrOSi$: C, 59.50; H, 6.38. Found: C, 59.74; H, 6.45.

2-(Diisopropylphenylsilyl)phenol



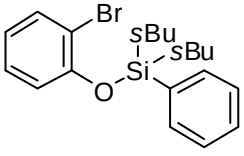
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 92%, a colorless solid. Mp: 44.3–45.4 °C. TLC: R_f 0.26 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, J = 7.2 Hz, 6H), 1.00 (d, J = 7.2 Hz, 6H), 1.66 (qq, J = 7.2, 7.2 Hz, 2H), 6.80 (d, J = 8.3 Hz, 1H), 6.97 (dd, J = 7.4, 7.3 Hz, 1H), 7.32 (dd, J = 8.3, 7.4 Hz, 1H), 7.37 (d, J = 7.3 Hz, 1H), 7.40–7.48 (m, 3H), 7.59–7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 17.5, 17.6, 115.7, 117.0, 120.1, 128.1, 129.8, 131.2, 132.0, 135.9, 137.2, 161.2. IR (KBr): ν = 3741, 3049, 2945, 2862, 1593, 1566, 1431, 1277, 1200, 1103, 995, 879, 829, 759, 700 cm^{-1}. MS (FAB) *m/z*: 241 (100, $[M – 43]^+$), 207 (36), 199 (81), 181 (25). Anal. Calcd for $C_{18}H_{24}OSi$: C, 76.00; H, 8.50. Found: C, 75.73; H, 8.52.

2-(Diisopropylphenylsilyl)phenyl trifluoromethanesulfonate (1e)



Prepared by Method A. Purification: GPC ($CHCl_3$). Yield: 84%, a colorless solid. Mp: 48.7–49.8 °C. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, J = 7.6 Hz, 6H), 1.04 (d, J = 7.6 Hz, 6H), 1.74 (qq, J = 7.6, 7.6 Hz, 2H), 7.28 (ddd, J = 7.5, 7.2, 1.1 Hz, 1H), 7.35–7.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.5, 17.8, 17.9, 118.3 (q, J = 317.2 Hz), 118.7 (d, J = 2.3 Hz), 125.8, 126.5, 127.5, 129.2, 131.3, 132.1, 135.7, 139.4, 156.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (KBr): ν = 3066, 2951, 2866, 1595, 1468, 1417, 1246, 1209, 1136, 1057, 895, 767, 745, 704, 594 cm^{-1}. MS (FAB) *m/z*: 373 (100, $[M – 43]^+$), 339 (22), 223 (6). Anal. Calcd for $C_{19}H_{23}F_3O_3SSi$: C, 54.79; H, 5.57. Found: C, 54.66; H, 5.53.

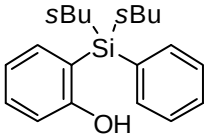
2-Bromophenyl di-*sec*-butylphenylsilyl ether



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 98%, a colorless oil. TLC: R_f 0.79 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89–0.98 (m, 6H), 1.05–1.07 (m, 3H),

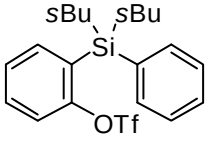
1.11–1.13 (m, 3H), 1.14–1.34 (m, 4H), 1.68–1.85 (m, 2H), 6.76–6.81 (m, 2H), 7.05 (ddd, *J* = 7.8, 7.6, 1.6 Hz, 1H), 7.35–7.44 (m, 3H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66–7.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 13.47, 13.56, 13.59, 13.7, 20.66, 20.73, 24.1, 24.3, 114.8, 119.7, 122.0, 127.6, 127.9, 129.5, 133.2, 133.9, 134.5, 152.5. IR (neat): ν = 2958, 2929, 1581, 1477, 1292, 1111, 1030, 922, 752, 700 cm^{-1}. MS (FAB) *m/z*: 335 (98, $[M - 57]^+ + 2$), 333 (100, $[M - 57]^+$), 315 (17), 313 (16), 279 (15), 277 (20). Anal. Calcd for $C_{20}H_{27}BrOSi$: C, 61.37; H, 6.95. Found: C, 61.45; H, 7.15.

2-(Di-*sec*-butylphenylsilyl)phenol



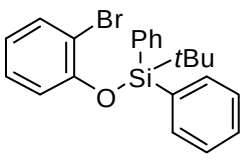
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 76%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91–1.01 (m, 14H), 1.37–1.45 (m, 2H), 1.65–1.74 (m, 2H), 4.88 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.95 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.28–7.36 (m, 2H), 7.36–7.46 (m, 3H), 7.57–7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.0, 13.10, 13.17, 13.22, 13.5, 13.6, 17.6, 24.1, 24.2, 115.6, 120.1, 128.1, 129.7, 131.1, 135.76, 135.79, 137.1, 137.2, 161.2. IR (neat): ν = 3522, 2957, 2929, 1593, 1568, 1433, 1279, 1193, 1103, 996, 758, 704, 677 cm^{-1}. MS (FAB) *m/z*: 255 (100, $[M - 57]^+$), 235 (19), 199 (80), 197 (58), 181 (56), 137 (32). Anal. Calcd for $C_{20}H_{28}OSi$: C, 76.86; H, 9.03. Found: C, 76.59; H, 9.27.

2-(Di-*sec*-butylphenylsilyl)phenyl trifluoromethanesulfonate (1f)



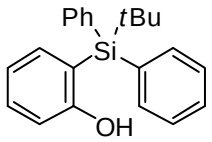
Prepared by Method A. Purification: GPC ($CHCl_3$). Yield: 63%, a colorless oil. TLC: R_f 0.58 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92–0.98 (m, 10H), 1.02–1.06 (m, 4H), 1.48–1.54 (m, 2H), 1.63–1.76 (m, 2H), 7.27 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.35–7.49 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 13.4, 13.46, 13.51, 13.53, 13.6, 17.8, 17.92, 17.94, 24.5, 24.69, 24.73, 118.3 (q, *J* = 317.2 Hz), 118.6, 126.3, 126.4, 127.51, 127.53, 129.1, 131.3, 132.6, 132.7, 132.8, 135.56, 136.63, 135.7, 139.3, 139.36, 139.39, 156.1, 156.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2961, 2932, 2872, 1595, 1421, 1247, 1213, 1142, 1055, 895, 744, 702 cm^{-1}. MS (FAB) *m/z*: 387 (100, $[M - 57]^+$), 367 (18), 201 (20), 197 (20), 181 (14). Anal. Calcd for $C_{21}H_{27}F_3O_3SSi$: C, 56.73; H, 6.12. Found: C, 56.74; H, 6.25.

2-Bromophenyl *tert*-butyldiphenylsilyl ether



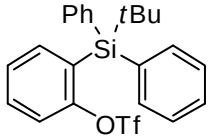
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 100%, a colorless solid. Mp: 57.4–58.5 °C. TLC: R_f 0.58 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 9H), 6.47 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.72 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 6.85 (ddd, *J* = 8.0, 7.6, 1.6, 1H), 7.36–7.40 (m, 4H), 7.42–7.46 (m, 2H), 7.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.72–7.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 26.6, 114.5, 119.8, 121.9, 127.7, 127.8, 129.9, 132.2, 133.1, 135.3, 152.1. IR (KBr): ν = 2828, 2854, 1577, 1477, 1298, 1112, 1105, 1028, 931, 752, 700, 613 cm^{-1}. MS (FAB) *m/z*: 335 (100, $[M - 57]^+$+2), 353 (100, $[M - 57]^+$). Anal. Calcd for $C_{22}H_{23}BrOSi$: C, 64.23; H, 5.63. Found: C, 64.28; H, 5.60.

2-(*tert*-Butyldiphenylsilyl)phenol



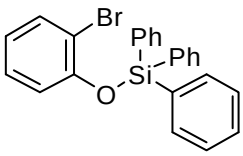
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 78%, a colorless solid. Mp: 189.0–189.6 °C. TLC: R_f 0.30 (hexane/AcOEt 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9H), 4.89 (s, 1H), 6.80 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.95 (ddd, *J* = 7.4, 7.3, 1.2 Hz, 1H), 7.32–7.50 (m, 8H), 7.50–7.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 29.1, 116.0, 120.2, 128.0, 129.6, 131.5, 134.1, 136.1, 136.3, 137.7, 160.9. IR (KBr): ν = 3239, 3047, 2924, 2859, 1591, 1483, 1433, 1423, 1315, 1278, 1170, 1105, 833, 760, 704, 603 cm^{-1}. MS (FAB) *m/z*: 275 (69, $[M - 57]^+$), 257 (37), 197 (68). Anal. Calcd for $C_{22}H_{24}OSi$: C, 79.47; H, 7.28. Found: C, 79.19; H, 7.24.

2-(*tert*-Butyldiphenylsilyl)phenyl trifluoromethanesulfonate (1g)



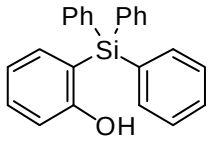
Prepared by Method A. Purification: recrystallization with hexane. Yield: quant, a colorless solid. Mp: 115.0–116.0 °C. TLC: R_f 0.62 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9H), 7.33–7.38 (m, 5H), 7.40–7.44 (m, 3H), 7.50–7.56 (m, 5H), 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 29.1, 118.0 (q, *J* = 317.9 Hz), 119.2, 126.7, 127.3, 127.7, 129.3, 131.7, 133.4, 135.9, 139.0, 155.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –75.1. IR (KBr): ν = 2936, 2861, 1595, 1466, 1427, 1247, 1209, 1138, 1055, 895, 767, 742, 704, 596 cm^{-1}. MS (FAB) *m/z*: 407 (100, $[M - 57]^+$), 387 (34), 273 (16), 257 (27). Anal. Calcd for $C_{23}H_{23}F_3O_3SSi$: C, 59.46; H, 4.99. Found: C, 59.60; H, 5.09.

2-Bromophenyl triphenylsilyl ether



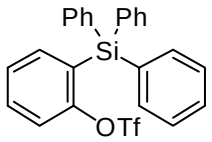
Purification: recrystallization with hexane. Yield: 89%, a colorless solid. Mp: 65.6–66.2 °C. TLC: R_f 0.61 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76–6.80 (m, 2H), 6.98 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.37–7.41 (m, 6H), 7.43–7.51 (m, 4H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71–7.74 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.1, 122.6, 127.8, 127.9, 128.0, 130.3, 133.0, 132.2, 135.2, 135.4. IR (KBr): ν = 3067, 3000, 2916, 1587, 1577, 1475, 1427, 1294, 1249, 1116, 935, 746, 711, 698 cm^{-1}. MS (FAB) *m/z*: 432 (100, $M^+ + 2$), 430 (62, M^+), 355 (86), 353 (65), 273 (65), 259 (100), 213 (24). Anal. Calcd for $C_{24}H_{19}BrOSi$: C, 66.82; H, 4.44. Found: C, 66.95; H, 4.57.

2-(Triphenylsilyl)phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 53%, a colorless solid. Mp: 224.1–224.9 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.89 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.21 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.33–7.48 (m, 10H), 7.61–7.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.9, 120.7, 128.0, 129.8, 132.1, 133.3, 136.2, 136.4, 138.0, 160.9. IR (KBr): ν = 3529, 3064, 3049, 3024, 2945, 2856, 1589, 1570, 1481, 1427, 1313, 1271, 1172, 1107, 1064, 1030, 997, 833, 759, 742, 665 cm^{-1}. MS (FAB) *m/z*: 275 (29, $[M - 77]^+$), 257 (100), 197 (42), 181 (16). Anal. Calcd for $C_{24}H_{20}OSi$: C, 81.77; H, 5.72. Found: C, 81.52; H, 5.84.

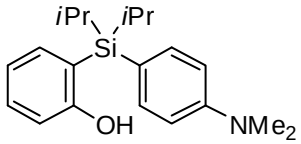
2-(Triphenylsilyl)phenyl trifluoromethanesulfonate (1h)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 51%, a colorless solid. Mp: 106.0–107.0 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.37–7.41 (m, 7H), 7.43–7.48 (m, 4H), 7.53–7.59 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.9 (q, *J* = 317.2 Hz), 118.9 (q, *J* = 1.5 Hz), 126.7, 127.0, 127.9, 129.8, 132.2, 132.5, 136.0, 139.5, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –75.1. IR (KBr): ν = 3067, 3050, 3005, 2916, 1595, 1485, 1425, 1246, 1211, 1141, 1109, 1051, 876, 773, 747, 705, 628 cm^{-1}. MS (FAB) *m/z*: 407 (100, $[M - 57]^+$), 387 (34), 273 (16), 257 (27). Anal. Calcd for $C_{23}H_{23}F_3O_3SSi$: C, 59.46; H, 4.99. Found: C, 59.60; H, 5.09.

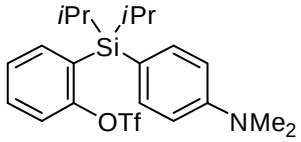
2-Bromophenyl (4-dimethylaminophenyl)diisopropylsilyl ether was prepared according to the general procedure and used for the next step without isolation.

2-{[4-(Dimethylamino)phenyl]diisopropylsilyl}phenol



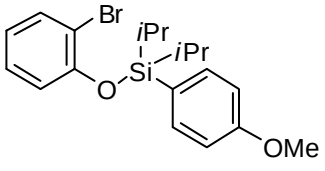
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 77%, a colorless solid. Mp: 103.0–104.0 °C. TLC: R_f 0.22 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, *J* = 7.2 Hz, 6H), 0.97 (d, *J* = 7.2 Hz, 6H), 1.58 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.01 (s, 6H), 5.37 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.81 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.96 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.31 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.38 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.1, 17.4, 17.5, 40.0, 112.1, 114.5, 115.7, 117.2, 119.8, 131.1, 136.7, 137.1, 151.4, 161.7. IR (KBr): ν = 3249, 2497, 2926, 2826, 1597, 1516, 1438, 1367, 1276, 1207, 1103, 993, 759, 665, 642 cm^{-1}. MS (FAB) *m/z*: 327 (44, M^+), 284 (100), 242 (17), 234 (13), 206 (10). Anal. Calcd for $C_{20}H_{29}NOSi$: C, 73.34; H, 8.72. Found: C, 73.26; H, 9.06.

2-{[4-(Dimethylamino)phenyl]diisopropylsilyl}phenyl trifluoromethanesulfonate (1i)



Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 91%, a colorless oil. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (d, *J* = 7.2 Hz, 6H), 1.04 (d, *J* = 7.2 Hz, 6 H), 1.69 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.00 (s, 6H), 6.74 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* =7.2, 1.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.40–7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 17.9, 18.0, 40.1, 114.4, 116.5, 118.3 (q, *J* = 318.0 Hz), 118.5 (q, *J* = 1.6 Hz), 126.3, 126.8, 131.0, 136.9, 139.9, 150.8, 156.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2947, 2928, 2893, 2866, 1599, 1514, 1417, 1209, 1141, 1107, 1053, 893, 766, 746, 665, 630 cm^{-1}. MS (FAB) *m/z*: 459 (100, M^+), 416 (91), 326 (6), 282 (18), 266 (12). Anal. Calcd for $C_{21}H_{28}F_3NO_3SSi$: C, 54.88; H, 6.14. Found: C, 54.95; H, 6.15.

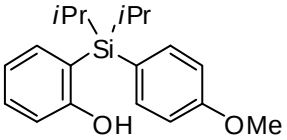
2-Bromophenyl (4-methoxyphenyl)diisopropylsilyl ether



Purification: silica gel column chromatography (hexane). Yield: 87%, a colorless oil. TLC: R_f 0.52 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.6 Hz,

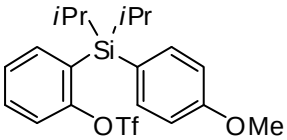
6H), 1.14 (d, *J* = 7.6 Hz, 6H), 1.47 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.84 (s, 3H), 6.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.94 (d, *J* =8.4 Hz, 2H), 7.04 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 17.5, 17.7, 55.0, 113.5, 114.8, 119.7, 121.9, 124.2, 127.9, 133.2, 136.1, 152.6, 160.7. IR (neat): ν = 2945, 2893, 2866, 1595, 1564, 1504, 1479, 1440, 1278, 1248, 1182, 1112, 1030, 995, 920, 883, 798, 752, 729, 677, 648 cm^{-1}. MS (FAB) *m/z*: 351 (100, $[M - 43]^+$+2), 349 (98, $[M - 43]^+$), 287 (48), 385 (50), 241 (22), 221 (24). Anal. Calcd for $C_{19}H_{25}BrO_2Si$: C, 58.01; H, 6.41. Found: C, 58.15; H, 6.24.

2-[(4-Methoxyphenyl)diisopropylsilyl]phenol



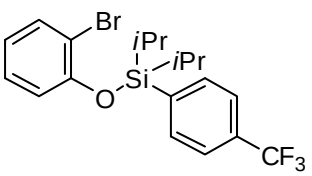
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 87%, a colorless solid. Mp: 72.4–73.4 °C. TLC: R_f 0.18 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, *J* = 7.2 Hz, 6H), 0.99 (d, *J* = 7.2 Hz, 6H), 1.61 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.85 (s, 3H), 5.02 (s, 1H), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.96 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.32 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.37 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 17.9, 18.0, 40.1, 111.4, 116.5, 118.5, 126.3, 126.8, 131.0, 136.9, 139.8, 150.8, 156.2. IR (KBr): ν = 3441, 3373, 2955, 2862, 2835, 1593, 1566, 1502, 1437, 1360, 1276, 1242, 1182, 1109, 1024, 991, 877, 819, 760, 680, 648 cm^{-1}. MS (FAB) *m/z*: 271 (62, $[M - 43]^+$), 247 (51), 229 (37), 207 (83), 179 (21), 165 (32). Anal. Calcd for $C_{19}H_{26}O_2Si$: C, 72.56; H, 8.33. Found: C, 72.26; H, 8.05.

2-[(4-Methoxyphenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (1j)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 35%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (d, *J* = 7.2 Hz, 6H), 1.03 (d, *J* = 7.2 Hz, 6 H), 1.71 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.85 (s, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* =7.2, 7.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.43–7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 17.8, 17.9, 55.0, 113.4, 118.3 (q, *J* = 317.2 Hz), 118.6, 122.7, 126.2, 126.4, 131.3, 137.1, 139.5, 156.1, 160.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 2951, 2895, 2866, 1595, 1504, 1422, 1279, 1248, 1213, 1141, 1053, 893, 825, 746, 667 cm^{-1}. MS (FAB) *m/z*: 403 (100, $[M - 43]^+$), 339 (35), 253 (8), 231 (23), 225 (12), 211 (10). Anal. Calcd for $C_{20}H_{25}F_3O_4SSi$: C, 53.79; H, 5.64. Found: C, 53.56; H, 5.75.

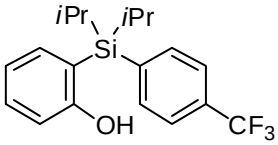
2-Bromophenyl diisopropyl[4-(trifluoromethyl)phenyl]silyl ether



Purification: silica gel column chromatography (hexane). Yield: 81%, a colorless oil. TLC: R_f 0.55 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.6 Hz, 6H), 1.14 (d, *J* = 7.6 Hz, 6H), 1.52 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.82 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 17.4, 17.5, 114.8, 119.6, 122.4, 124.1 (q, *J* = 270.6 Hz), 124.2 (q, *J* = 3.8 Hz), 128.1, 131.5 (q, *J* = 32.0 Hz), 133.4, 134.8, 138.5, 152.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.4. IR (neat): ν = 2949, 2868, 1585, 1479, 1392, 1325,

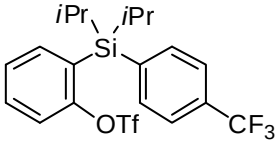
1292, 1167, 1130, 1061, 924, 829, 752, 704, 699 cm^{-1}. MS (FAB) *m/z*: 433 (100, $M^+ + 2$), 431 (3, M^+), 413 (11), 411 (9), 389 (100), 387 (100), 287 (22), 285 (22). Anal. Calcd for $C_{19}H_{22}BrF_3OSi$: C, 52.90; H, 5.14. Found: C, 53.14; H, 5.09.

2-{Diisopropyl[4-(trifluoromethyl)phenyl]silyl}phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 87%, a colorless solid. Mp: 68.0–68.7 °C. TLC: R_f 0.31 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, *J* = 7.2 Hz, 6H), 1.02 (d, *J* = 7.2 Hz, 6H), 1.70 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.67 (s, 1H), 6.77 (dd, *J* = 8.4, 0,8 Hz, 1H), 6.95 (ddd, *J* = 7.2, 7.2, 0.8 Hz, 1H), 7.30–7.34 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.5, 17.6, 17.8, 115.4, 117.0, 120.3, 124.11 (q, *J* = 269.9 Hz), 124.12 (q, *J* = 3.8 Hz), 131.1 (q, *J* = 32.0 Hz), 131.3, 136.0, 137.7, 138.5, 160.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.3. IR (KBr): ν = 3574, 2951, 2866, 1593, 1433, 1390, 1274, 1161, 1116, 1059, 881, 827, 758, 702, 663, 624 cm^{-1}. MS (FAB) *m/z*: 352 (5, M^+), 309 (100), 267 (89), 217 (14), 203 (15), 189 (35). Anal. Calcd for $C_{19}H_{23}F_3OSi$: C, 64.74; H, 6.58. Found: C, 64.49; H, 6.41.

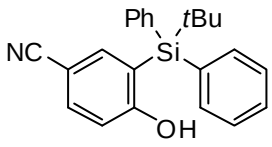
2-{Diisopropyl[4-(trifluoromethyl)phenyl]silyl}phenyl trifluoromethanesulfonate (1k)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 85%, a colorless oil. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.05 (d, *J* = 7.2 Hz, 6H), 1.76 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.32 (ddd, *J* = 7.2, 7.2, 0.9 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.45 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.52 (ddd, *J* = 7.2, 7.2, 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4, 17.68, 17.74, 118.2 (q, *J* = 317.2 Hz), 118.9 (q, *J* = 1.5 Hz), 124.0 (q, *J* = 269.9 Hz), 124.1 (q, *J* = 3.8 Hz), 124.8, 126.7, 131.2 (q, *J* = 32.0 Hz), 131.7, 135.8, 137.5, 139.1, 156.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.4, –74.9. IR (neat): ν = 2953, 2870, 1597, 1421, 1327, 1247, 1215, 1139, 1061, 893, 829, 744, 702, 603 cm^{-1}. MS (FAB) *m/z*: 441 (100, $[M - 43]^+$), 339 (19), 291 (11), 251 (10). Anal. Calcd for $C_{22}H_{25}F_6O_3SSi$: C, 49.54; H, 4.58. Found: C, 49.58; H, 4.49.

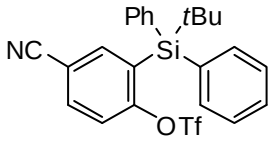
2-Bromo-4-cyanophenyl *tert*-butyldiphenylsilyl ether was prepared according to the general procedure and used for the next step without isolation.

2-(*tert*-Butyldiphenylsilyl)-4-cyanophenol



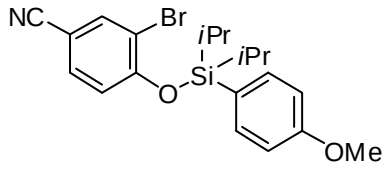
Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 37%, a colorless solid. Mp: 196.3–197.8 °C. TLC: R_f 0.21 (hexane/AcOEt 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 9H), 5.24 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 7.38–7.43 (m, 4H), 7.45–7.49 (m, 2H), 7.57–7.59 (m, 4H), 7.62 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.76 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 29.1, 103.8, 116.8, 119.4, 121.6, 128.3, 130.1, 132.6, 135.4, 135.9, 142.3, 164.4. IR (KBr): ν = 3304, 3059, 2957, 2861, 2224, 1585, 1489, 1427, 1383, 1356, 1284, 1221, 1163, 829, 704, 694, 678, 607 cm^{-1}. MS (FAB) *m/z*: 358 (46, $M^+ + 1$), 301 (7), 280 (22), 222 (21), 195 (10). Anal. Calcd for $C_{23}H_{23}NOSi$: C, 77.27; H, 6.48. Found: C, 77.12; H, 6.54.

2-(*tert*-Butyldiphenylsilyl)-4-cyanophenyl trifluoromethanesulfonate (1l)



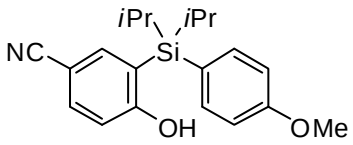
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 75%, a colorless solid. Mp: 90.7–91.8 °C. TLC: R_f 0.55 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9H), 7.37–7.40 (m, 4H), 7.44–7.46 (m, 2H), 7.48–7.51 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.99 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 29.1, 111.3, 117.5, 117.8 (q, *J* = 317.9 Hz), 119.9 (q, *J* = 2.3 Hz), 128.1, 129.9, 130.5, 131.9, 135.4, 135.7, 142.7, 157.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 3068, 2960, 2897, 2862, 2234, 1582, 1462, 1421, 1245, 1215, 1138, 1057, 891, 846, 740, 704, 619 cm^{-1}. MS (FAB) *m/z*: 490 (57, M^+ + 1), 432 (100), 412 (39), 298 (4), 240 (4), 222 (21). Anal. Calcd for $C_{24}H_{33}F_3NO_3SSi$: C, 58.88; H, 4.53. Found: C, 58.84; H, 4.61.

2-Bromo-4-cyanophenyl diisopropyl(4-methoxyphenyl)silyl ether



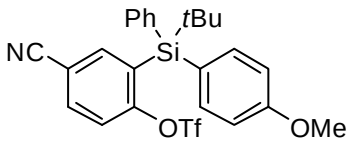
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 62%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.6 Hz, 6H), 1.15 (d, *J* = 7.6 Hz, 6H), 1.50 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.85 (s, 3H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 17.4, 17.6, 55.1, 105.4, 113.8, 115.5, 117.7, 119.9, 122.9, 132.3, 135.9, 136.9, 156.8, 161.0. IR (neat): ν = 2947, 2866, 2839, 2228, 1593, 1564, 1487, 1462, 1303, 1278, 1249, 1184, 1112, 1047, 916, 883, 823, 675, 651, 628 cm^{-1}. MS (FAB) *m/z*: 420 (65, $[M + H]^+$ + 2), 418 (62, $[M + H]^+$), 376 (88), 354 (91), 340 (25), 296 (16), 268 (6), 266(6). Anal. Calcd for $C_{20}H_{24}BrNO_2Si$: C, 57.41; H, 5.78. Found: C, 57.44; H, 5.72.

4-Cyano-2-[diisopropyl(4-methoxyphenyl)silyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 59%, a colorless solid. Mp: 178.8–180.0 °C. TLC: R_f 0.21 (hexane/AcOEt 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, *J* = 7.2 Hz, 6H), 0.98 (d, *J* = 7.2 Hz, 6H), 1.62 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.86 (s, 3H), 5.64 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.59 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0, 17.4, 55.1, 103.9, 114.5, 116.7, 119.55, 119.63, 120.1, 135.1, 137.4, 141.4, 161.5, 164.9. IR (KBr): ν = 3296, 2970, 2885, 2228, 1584, 1504, 1384, 1274, 1250, 1184, 1107, 1032, 887, 825, 813, 682, 665, 601 cm^{-1}. MS (FAB) *m/z*: 340 (40, $[M + H]^+$), 296 (100), 254 (18), 232 (70), 188 (14). HRMS Calcd for $C_{20}H_{26}NOSi$: 340.1733 (M^+). Found: 340.1723.

4-Cyano-2-[diisopropyl(4-methoxyphenyl)silyl]phenyl trifluoromethanesulfonate (1m)

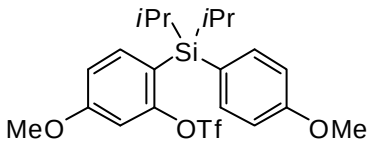


Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 99%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.71 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.86 (s, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.55 (d. *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.77 (dd, *J* = 8.6, 2.4

Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 17.8, 55.1, 111.1, 113.9, 117.5, 118.2 (q, *J* = 318.2 Hz), 119.3, 121.0, 129.6, 135.0, 136.9, 143.1, 158.0, 160.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (neat): ν = 3022, 2951, 2868, 2233, 1595, 1504, 1464, 1423, 1280, 1249, 1215, 1139, 1058, 1031, 898, 847, 798, 690, 673, 617 cm^{-1}. MS (FAB) *m/z*: 472 (3, $[M + H]^+$), 428 (100), 364 (35), 296 (3), 252 (17). Anal. Calcd for $C_{21}H_{24}F_3NO_4SSi$: C, 53.49; H, 5.13. Found: C, 53.53; H, 5.26.

2-Bromo-5-methoxyphenyl diisopropyl(4-methoxyphenyl)silyl ether and 2-[diisopropyl-(4-methoxyphenyl)silyl]phenol were prepared according to the general procedures and used for further steps without isolation.

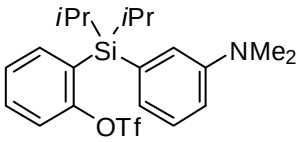
2-Diisopropyl(4-methoxyphenyl)silyl-5-methoxyphenyl trifluoromethanesulfonate (1n)



Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 15:1). Yield: 35%, a colorless oil. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, *J* = 7.2 Hz, 6H), 1.02 (d, *J* = 7.2 Hz, 6H), 1.66 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.84 (s, 3H), 3.85 (s, 3H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 17.8, 17.9, 55.0, 55.6, 105.5, 112.1, 113.3, 116.3, 118.3 (q, *J* = 317.9 Hz), 123.1, 137.1, 140.0, 156.8, 160.4, 161.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 3007, 2949, 2866, 1600, 1564, 1504, 1418, 1246, 1213, 1142, 1053, 945, 845, 667, 603 cm^{-1}. MS (FAB) *m/z*: 433 (100, $[M - 43]^+$), 369 (40), 283 (7), 261 (16), 257 (16). Anal. Calcd for $C_{21}H_{27}F_3NO_5SSi$: C, 52.92; H, 5.71. Found: C, 53.16; H, 5.67.

2-Bromophenyl diisopropyl(3-dimethylaminophenyl)silyl ether and 2-[diisopropyl-(3-dimethylaminophenyl)silyl)phenol were prepared according to the general procedures and used for further steps without isolation.

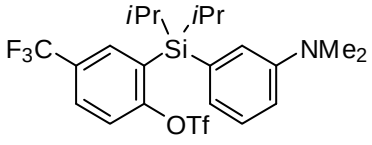
2-[(3-Dimethylaminophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (1o)



Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 21%, colorless oil. TLC: R_f 0.43 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.3 Hz, 6H), 1.07 (d, *J* = 7.5 Hz, 6H), 1.73 (qq, *J* = 7.5, 7.3 Hz, 2H), 2.93 (s, 6H), 6.79–6.90 (m, 3H), 7.25–7.29 (m, 2H), 7.42 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.47–7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 17.98, 18.00, 40.8, 113.7, 118.3 (q, *J* = 319.8 Hz), 118.5, 120.1, 124.4, 126.2, 126.3, 128.1, 131.2, 132.4, 139.7, 149.5, 156.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 2947, 2866, 1587, 1420, 1213, 1142, 1053, 991, 893, 777, 766, 745, 598, 513 cm^{-1}. MS (FAB) m/z: 459 (100, M^+), 416 (15), 348 (4). Anal. Calcd for $C_{21}H_{28}F_3NO_3SSi$: C, 54.88; H, 6.14. Found: C, 54.78; H, 6.12.

2-Bromo-4-trifluoromethylphenyl diisopropyl(3-dimethylaminophenyl)silyl ether and 2-[diisopropyl(3-dimethylaminophenyl)silyl]-4-trifluoromethylphenol were prepared according to the general procedures and used for further steps without isolation.

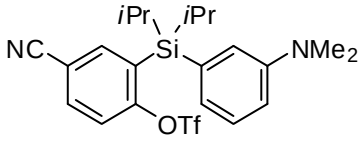
2-[(3-Dimethylaminophenyl)diisopropylsilyl]-4-trifluoromethylphenyl trifluoromethanesulfonate (1p)



Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 17%, colorless oil. TLC: R_f 0.48 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.3 Hz, 6H), 1.05 (d, *J* = 7.5 Hz, 6H), 1.75 (qq, *J* = 7.5, 7.3 Hz, 2H), 2.93 (s, 6H), 6.79–6.82 (m, 3H), 7.26–7.30 (m, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 17.7, 17.9, 40.8, 114.3, 118.3 (q, *J* = 319.5 Hz), 118.8, 119.9, 123.4 (q, *J* = 272.0 Hz), 124.3, 128.3, 128.4, 128.5 (q, *J* = 4.6 Hz), 128.7 (q, *J* = 32.7 Hz), 131.3, 136.5 (q, *J* = 3.1 Hz), 149.6, 157.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9, –74.6. IR (neat): ν = 2946, 2868, 1589, 1493, 1425, 1327, 1217, 1136, 1057, 885, 824, 725, 610 cm^{-1}. MS (FAB) *m*/*z*: 527 (100, M^+), 484 (8), 350 (13). Anal. Calcd for $C_{22}H_{27}F_6NO_3SSi$: C, 50.08; H, 5.16. Found: C, 49.92; H, 5.02.

2-Bromo-4-cyanophenyl diisopropyl(3-dimethylaminophenyl)silyl ether and 4-cyano-2-[diisopropyl(3-dimethylaminophenyl)silyl]phenol were prepared according to the general procedures and used for further steps without isolation.

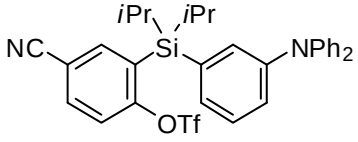
4-Cyano-2-[(3-dimethylaminophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (1q)



Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 42%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, *J* = 7.3 Hz, 6H), 1.06 (d, *J* = 7.3 Hz, 6H), 1.73 (qq, *J* = 7.3, 7.3 Hz, 2H), 2.95 (s, 6H), 6.79–6.86 (m, 3H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.76–7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 17.9, 40.6, 111.0, 114.1, 117.5, 118.2 (q, *J* = 319.8 Hz), 119.3, 119.4, 123.8, 128.6, 129.5, 130.7, 134.9, 143.3, 149.7, 158.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (neat): ν = 2949, 2868, 2234, 1587, 1566, 1495, 1408, 1348, 1284, 1211, 1138, 1057, 991, 887, 844, 777, 682, 617 cm^{-1}. MS (FAB) *m*/*z*: 484 (100, M^+), 441 (5), 351 (5). Anal. Calcd for $C_{22}H_{27}F_3N_2O_3SSi$: C, 54.53; H, 5.62. Found: C, 54.53; H, 5.50.

2-Bromo-4-cyanophenyl diisopropyl(3-diphenylaminophenyl)silyl ether and 4-cyano-2-[diisopropyl(3-diphenylaminophenyl)silyl]phenol were prepared according to the general procedures and used for further steps without isolation.

4-Cyano-2-[(3-diphenylaminophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (1r)

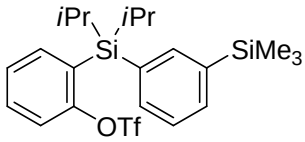


Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 19%, a colorless solid. Mp: 151.9–152.9 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, *J* = 7.6 Hz, 6H), 0.97 (d, *J* = 7.6 Hz, 6H), 1.63 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.98–7.05 (m, 3H), 7.08–7.10 (m, 4H), 7.13–7.16 (m, 2H), 7.22–7.30 (m, 5H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.76 (dd, *J* = 8.6, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4, 17.7, 17.8, 111.1, 117.6, 119.4, 119.8 (q, *J* = 317.2 Hz), 122.7, 124.0, 125.6, 128.9, 129.0,

129.1, 129.5, 130.7, 131.6, 135.0 (2C), 142.9, 147.4, 157.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 2953, 2926, 1587, 1493, 1422, 1273, 1213, 1140, 891, 844, 754, 696, 619 cm^{-1}. MS (FAB) *m/z*: 608 (37, M^+), 565 (1), 475 (1). Anal. Calcd for $C_{32}H_{31}F_3N_2O_3SSi$: C, 63.14; H, 5.13. Found: C, 62.87; H, 5.13.

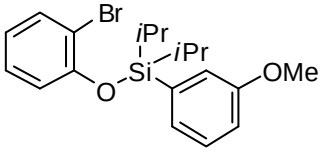
2-Bromophenyl diisopropyl(3-trimethylsilylphenyl)silyl ether and 2-[diisopropyl(3-trimethylsilylphenyl)silyl]phenol were prepared according to the general procedures and used for further steps without isolation.

2-[Diisopropyl(3-trimethylsilylphenyl)silyl]phenyl trifluoromethanesulfonate (1s)



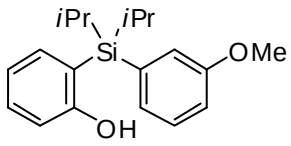
Prepared by Method A. Purification: silica gel column chromatography (hexane only). Yield: 73%, colorless oil. TLC: R_f 0.63 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H), 0.96 (d, *J* = 7.3 Hz, 6H), 1.06 (d, *J* = 7.5 Hz, 6H), 1.75 (qq, *J* = 7.5, 7.3 Hz, 2H), 7.23–7.26 (m, 1H), 7.36 (dt, *J* = 7.3, 0.5 Hz, 1H), 7.43–7.51 (m, 4H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.62 (dd, *J* = 2.0, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.0, 10.6, 17.82, 17.85, 118.3 (q, *J* = 319.0 Hz), 118.65, 118.66, 125.9, 126.5 (d, *J* = 37.6 Hz), 131.1, 131.3, 134.0, 136.0, 139.1, 139.5, 140.8, 156.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 2955, 2866, 1422, 1248, 1213, 1142, 893, 854, 839 cm^{-1}. MS (FAB) *m/z*: 488 (1, M^+), 473 (2), 445 (47). Anal. Calcd for $C_{22}H_{31}F_3OSSi_2$: C, 54.07; H, 6.39. Found: C, 54.34; H, 6.36.

2-Bromophenyl diisopropyl(3-methoxyphenyl)silyl ether



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 85%, a colorless oil. TLC: R_f 0.51 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.49 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.81 (s, 3H), 6.78 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.97 (ddd, *J* = 8.4, 8.0, 0.8 Hz, 1H), 7.06 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 7.22 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.23 (s, 1H), 7.33 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 17.5, 17.7, 55.2, 114.8, 115.1, 119.7, 119.8, 122.1, 126.7, 128.0, 128.8, 133.2, 135.0, 152.4, 158.7. IR (neat): ν = 2947, 2893, 2866, 1587, 1572, 1464, 1402, 1287, 1247, 1120, 1047, 922, 883, 753, 700, 650 cm^{-1}. MS (FAB) *m/z*: 395 (6, $M^+ + 2$), 397 (7, M^+), 351 (99), 349 (100), 287 (43), 285 (42). Anal. Calcd for $C_{19}H_{25}BrO_2Si$: C, 58.01; H, 6.41. Found: C, 58.29; H, 6.31.

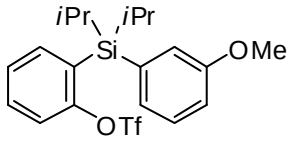
2-[Diisopropyl(3-methoxyphenyl)silyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 87%, a colorless solid. Mp: 71.4–72.5 °C. TLC: R_f 0.21 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.00 (d, *J* = 7.2 Hz, 6H), 1.64 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.81 (s, 3H), 4.91 (s, 1H), 6.81 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.95–7.01 (m, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.17 (ddd, *J* = 7.2, 1.2, 0.8 Hz, 1H), 7.30–7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 17.5, 17.6, 55.2, 115.0, 115.8, 116.9, 120.1, 121.3, 128.0, 129.4, 131.2, 135.6, 137.1, 159.0, 161.2. IR (KBr): ν = 3406, 2955, 2943, 2864, 1591, 1572, 1435, 1339, 1271, 1219, 1028, 991, 831, 762, 689, 621 cm^{-1}.

MS (FAB) *m/z*: 315 (7, $M^+ + 1$), 271 (100), 229 (32), 213 (12), 165 (16). Anal. Calcd for $C_{19}H_{26}O_2Si$: C, 72.56; H, 8.33. Found: C, 72.48; H, 8.36.

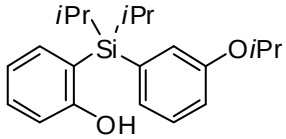
2-[Diisopropyl(3-methoxyphenyl)silyl]phenyl trifluoromethanesulfonate (1t)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 95%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, *J* = 7.2 Hz, 6H), 1.04 (d, *J* = 7.2 Hz, 6H), 1.73 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.80 (s, 3H), 6.96 (ddd, *J* = 7.6, 2.4, 1.2 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 7.06 (ddd, *J* = 7.6, 1.2, 0.8 Hz, 1H), 7.23 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.32 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.46–7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6, 17.8, 17.9, 55.1, 114.2, 118.2 (q, *J* = 317.2 Hz), 118.6, 121.4, 125.7, 126.5, 128.0, 128.7, 131.4, 133.7, 139.4, 156.1, 158.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 3001, 2949, 2937, 2868, 1584, 1465, 1425, 1246, 1219, 1134, 1040, 895, 744, 682, 661 cm^{-1}. MS (FAB) *m/z*: 403 (100, $[M - 43]^+$), 339 (41), 253 (4), 231 (13), 211 (7). Anal. Calcd for $C_{20}H_{25}F_3O_4SSi$: C, 53.79; H, 5.64. Found: C, 53.79; H, 5.49.

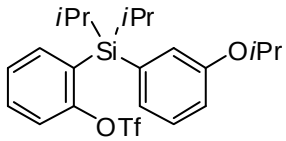
2-Bromophenyl diisopropyl(3-isopropoxylphenyl)silyl ether were prepared according to the general procedures and used for further steps without isolation.

2-[Diisopropyl(3-isopropoxyphenyl)silyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 52%, a colorless solid. Mp: 71.4–72.5 °C. TLC: R_f 0.31 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.00 (d, *J* = 7.2 Hz, 6H), 1.34 (d, *J* = 6.0 Hz, 6H), 1.64 (qq, *J* = 7.6, 7.6 Hz, 2H), 4.54 (sep, *J* = 6.0 Hz, 1H), 4.97 (s, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.94–6.98 (m, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.30–7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 17.5, 17.6, 22.1, 69.8, 115.8, 117.0, 117.5, 120.1, 123.0, 127.9, 129.4, 131.2, 133.5, 137.1, 157.4, 161.3. IR (KBr): ν = 3362, 2943, 2916, 2859, 1591, 1573, 1477, 1431, 1335, 1278, 1216, 1120, 1103, 959, 954, 881, 785, 758, 684, 659 cm^{-1}. MS (FAB) *m/z*: 343 (4, $M^+ + 1$), 302 (2), 260 (2). Anal. Calcd for $C_{21}H_{30}O_2Si$: C, 73.63; H, 8.83. Found: C, 73.59; H, 8.79.

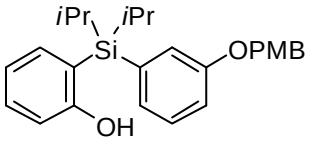
2-[Diisopropyl(3-isopropoxyphenyl)silyl]phenyl trifluoromethanesulfonate (1u)



Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 62%, a colorless oil. TLC: R_f 0.52 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, *J*= 7.6 Hz, 6H), 1.46 (d, *J* = 7.6 Hz, 6H), 1.33 (d, *J* = 6.0 Hz, 6H), 1.72 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.52 (sep, *J* = 6.0 Hz, 1H), 6.94 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.25–7.31 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.47–7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6, 17.86, 17.91, 22.2, 69.8, 116.8, 118.3 (q, *J* = 317.2 Hz), 123.2, 125.8, 126.4, 128.0, 128.7, 131.3, 133.6, 139.5, 156.1, 156.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 2976, 2947, 1583, 1566, 1479, 1421, 1402, 1278, 1246, 1141, 1055, 893, 777, 744, 702 cm^{-1}. MS (FAB) *m/z*: 474 (4, M^+), 431 (100), 389 (2). Anal. Calcd for $C_{22}H_{29}F_3O_4SSi$: C, 55.67; H, 6.16. Found: C, 55.54; H, 5.96.

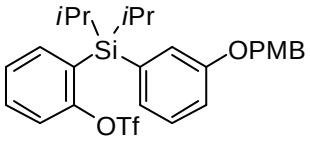
2-Bromophenyl diisopropyl[3-(4-methoxybenzyl)phenyl]silyl ether were prepared according to the general procedures and used for further steps without isolation.

2-{Diisopropyl[3-(4-methoxybenzyl)phenyl]silyl}phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 42%, a colorless solid. Mp: 95.4–96.1 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, *J* = 7.2 Hz, 6H), 0.98 (d, *J* = 7.2 Hz, 6H), 1.62 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.82 (s, 3H), 4.91 (s, 1H), 4.98 (s, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.96 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.17–7.19 (m, 2H), 7.30–7.32 (m, 1H), 7.34–7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 17.5, 17.6, 55.3, 69.8, 113.9, 115.8, 116.2, 117.0, 120.1, 122.1, 128.2, 128.8, 129.2, 129.4, 131.2, 133.6, 137.1, 158.3, 159.2, 161.2. IR (KBr): ν = 3447, 2947, 2864, 1591, 1566, 1516, 1435, 1373, 1277, 1236, 1219, 1180, 1020, 991, 829, 785 cm^{-1}. MS (FAB) *m/z*: 420 (1, M^+), 377 (11), 329 (2). Anal. Calcd for $C_{26}H_{32}O_3Si$: C, 74.24; H, 7.67. Found: C, 74.22; H, 7.76.

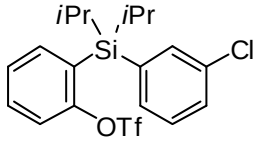
2-{Diisopropyl[3-(4-methoxybenzyl)phenyl]silyl}phenyl trifluoromethanesulfonate (1v)



Prepared by Method C. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 77%, a colorless solid. Mp: 62.0–63.0 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (d, *J* = 7.2 Hz, 6H), 1.03 (d, *J* = 7.2 Hz, 6H), 1.71 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.82 (s, 3H), 4.97 (s, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.01–7.01 (m, 3H), 7.25–7.32 (m, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.41–7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6, 17.8, 17.9, 55.3, 69.7, 113.9, 115.5, 118.3 (q, *J* = 317.2 Hz), 118.6, 122.3, 125.7, 126.5, 128.2, 128.7, 128.9, 129.1, 131.3, 133.7, 139.4, 156.1, 157.9, 159.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (KBr): ν = 2951, 2866, 1610, 1564, 1516, 1419, 1281, 1246, 1213, 1132, 1026, 900, 829, 781, 746, 692 cm^{-1}. MS (FAB) *m/z*: 552 (3, M^+), 509 (13), 445 (1). Anal. Calcd for $C_{27}H_{31}F_3O_5SSi$: C, 58.68; H, 5.65. Found: C, 58.83; H, 5.72.

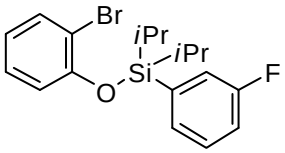
2-Bromophenyl diisopropyl(3-chlorophenyl)silyl ether and 2-[diisopropyl(3-chlorophenyl)silyl]phenol were prepared according to the general procedures and used for further steps without isolation.

2-[(3-Chlorophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (1w)



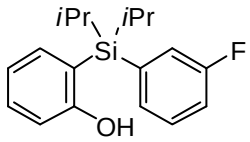
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 76%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.73 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.30–7.35 (m, 3H), 7.38–7.45 (m, 4H), 7.49–7.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4, 17.7, 17.8, 118.2 (q, *J* = 318.0 Hz), 118.8, 125.0, 126.6, 129.0, 129.3, 131.7, 133.5, 134.0, 135.0, 135.1, 139.1, 156.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 2951, 2868, 1595, 1558, 1466, 1420, 1247, 1213, 1142, 1055, 893, 777, 763, 744, 694 cm^{-1}. MS (FAB) *m/z*: 450 (100, M^+), 407 (100), 339 (31). Anal. Calcd for $C_{19}H_{22}ClF_3O_3SSi$: C, 50.60; H, 4.92. Found: C, 50.88; H, 4.86.

2-Bromophenyl (3-fluorophenyl)diisopropylsilyl ether



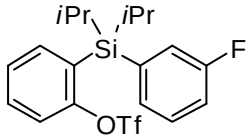
Purification: silica gel column chromatography (hexane). Yield: 66%, a colorless oil. TLC: R_f 0.64 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.49 (qq, *J* = 7.2, 7.2 Hz, 2H), 6.79–6.83 (m, 2H), 7.06–7.14 (m, 2H), 7.35–7.45 (m, 3H), 7.53 (dd, *J* = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 17.4, 17.6, 114.8, 116.9 (d, *J* = 20.6 Hz), 119.6, 120.9 (d, *J* = 19.1 Hz), 122.3, 128.0, 129.5 (d, *J* = 6.9 Hz), 130.1 (d, *J* = 3.1 Hz), 133.3, 136.6 (d, *J* = 4.0 Hz), 152.2, 162.3 (d, *J* = 246.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –113.6. IR (neat): ν = 2947, 1575, 1479, 1406, 1290, 1219, 1047, 923, 883, 752, 732, 694 cm^{-1}. MS (FAB) *m/z*: 339 (34, $[M - 43]^+ + 2$), 337 (3, $[M - 43]^+$), 287 (8), 285 (7), 261 (5), 259 (4). Anal. Calcd for $C_{18}H_{22}BrFOSi$: C, 56.69; H, 5.81. Found: C, 56.92; H, 5.77.

2-[(3-Fluorophenyl)diisopropylsilyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 66%, a colorless solid. Mp: 55.1–56.1 °C. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.01 (d, *J* = 7.2 Hz, 6H), 1.66 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.74 (s, 1H), 6.78 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.95 (ddd, *J* = 7.2, 7.2, 0.8 Hz, 1H), 7.09–7.14 (m, 1H), 7.27 (ddd, *J* = 8.0, 2.8, 0.8 Hz, 1H), 7.30–7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4, 17.6, 17.7, 115.5, 116.5 (d, *J* = 20.5 Hz), 117.0, 120.2, 122.0 (d, *J* = 18.3 Hz), 129.6 (d, *J* = 6.9 Hz), 131.28, 131.32 (d, *J* = 3.0 Hz), 136.1 (d, *J* = 3.8 Hz), 137.5, 161.0, 162.4 (d, *J* = 247.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –113.5. IR (KBr): ν = 3499, 3439, 2945, 2862, 2848, 1600, 1573, 1475, 1431, 1400, 1357, 1217, 1101, 997, 875, 759, 680, 660 cm^{-1}. MS (DI-EI) *m/z*: 259 (100, $[M - 43]^+$), 241 (22), 217 (100), 199 (46), 141 (30). Anal. Calcd for $C_{19}H_{23}F_3OSi$: C, 71.48; H, 7.66. Found: C, 71.21; H, 7.61.

2-[(3-Fluorophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (1x)

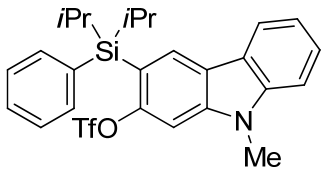


Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 77%, a colorless oil. TLC: R_f 0.55 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.05 (d, *J* = 7.2 Hz, 6H), 1.73 (qq, *J* = 7.2, 7.2 Hz, 2H), 7,08–7,17 (m, 2H), 7.24 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.30–7.38 (m, 2H), 7.42–7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.5, 17.7, 17.8, 116.2 (d, *J* = 21.3 Hz), 118.3 (q, *J* = 317.2 Hz), 118.8, 121.8 (d, *J* = 18.3 Hz), 125.2, 126.6, 129.3 (d, *J* = 6.9 Hz), 131.2 (d, *J* = 3.0 Hz), 131.6, 135.5 (d, *J* = 3.8 Hz), 139.1, 156.0, 162.2 (d, *J* =245.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9, –114.0. IR (neat): ν = 2951, 2868, 1597, 1574, 1468, 1408, 1215, 1141, 1055, 895, 777, 765, 684, 661 cm^{-1}. MS (FAB) *m/z*: 391 (100, $[M - 43]^+$), 339 (14), 241 (7), 219 (20). Anal. Calcd for $C_{19}H_{22}F_4O_3SSi$: C, 52.52; H, 5.10. Found: C, 52.71; H, 5.16.

9-Methyl-3-(diisopropylphenylsilyl)carbazo-2-yl trifluoromethanesulfonate (3)

3-Bromo-2-hydroxy-9-methylcarbazole was prepared by demethylation of 3-bromo-2-methoxy-9-methylcarbazole[8] as described below. An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with

3-bromo-2-methoxy-9-methylcarbazole[8] (4.81 g, 16.6 mmol), sodium ethanethiolate (3.93 g, 46.6 mmol), and DMF (30 mL). The resulting mixture was stirred at 130 °C for 12 h before quenching with saturated aq. $NaHCO_3$ (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 3:2) to give 3-bromo-2-hydroxy-9-methylcarbazole (3.33 g, 73%) as a colorless solid. 3-Bromo-2-hydroxy-9-methylcarbazole was subjected to the general procedure for synthesis of **1**.

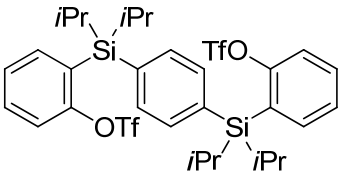


Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 78 %, a colorless solid. Mp: 122.0–122.8 °C. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.3 Hz, 6H), 1.09 (d, *J* = 7.3 Hz, 6H), 1.82 (qq, *J* = 7.3, 7.3 Hz, 2H)), 3.87 (s, 3H), 7.25 (dd, *J* = 7.7, 7.1 Hz, 1H), 7.38–7.45 (m, 4H), 7.47 (s, 1H), 7.49–7.53 (m, 1H), 7.56–7.58 (m, 2H), 7.99 (dd, *J* = 7.8, 0.6 Hz, 1H) 8.14 (d, *J* = 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 18.0, 18.1, 29.4, 99.2, 108.6, 113.9, 118.4 (q, *J* = 319.7 Hz), 119.8, 120.4, 121.5, 121.7, 126.3, 127.5, 129.0, 130.5, 133.1, 135.7, 141.8, 142.0, 154.6 ; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 2949, 2864, 1630, 1597, 1474, 1456, 1422, 1242, 1215, 1206, 1142, 1111, 961, 864, 748, 704, 667, 604, 515 cm^{-1}. MS (FAB) m/z: 520 (34, M + H^+), 476 (100), 442 (7). HRMS Calcd for $C_{26}H_{28}F_3N_2O_3SSi$: 519.1511 (M^+). Found: 519.1505.

1,4-Bis[diisopropyl(2-trifluoromethanesulfonyloxyphenyl)silyl]benzene (5)

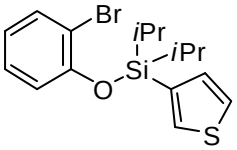
An oven-dried 250-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 1,4-dibromobenzene (2.36 g, 10 mmol) and THF (80 mL). To the solution cooled to –78 °C was added *t*-butyllithium (1.59 M in pentane, 25.2 mL, 40 mmol) dropwise via syringe over 20 min. The resulting solution was stirred at –78 °C for 1 h before addition of dichlorodiisopropylsilane (3.61 mL, 20 mmol). The resulting solution was allowed to warm to room temperature, then stirred for 12 h and then diluted with hexane (50 mL). The mixture was passed through a Celite pad to remove precipitates. The filtrate was concentrated by rotary evaporation to give 1,4-bis(chlorodiisopropylsilyl)benzene (3.85 g, quant.) as a colorless liquid. An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-bromophenol (2.32 mL, 20 mmol), imidazole (2.04 g, 30 mmol), 1,4-bis(chlorodiisopropylsilyl)benzene (3.85 g, 10 mmol), and CH_2Cl_2 (50 mL). The resulting solution was stirred at 40 °C for 12 h. The solution was then cooled to room temperature before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 30:1) to give 1,4-bis[(2-bromophenoxy)diisopropylsilyl]benzene (4.62 g, 67%) as a colorless liquid. An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 1,4-bis[(2-bromophenoxy)diisopropylsilyl]benzene (4.62 g, 6.7 mmol) and THF (30 mL). To the solution cooled to –78 °C was added *t*-butyllithium (1.59 M in pentane, 17.0 mL, 28 mmol) dropwise via syringe over 10 min. The resulting solution was allowed to warm to

room temperature and then stirred for 10 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 3:2) to give 1,4-bis[(2-hydroxyphenyl)diisopropylsilyl]benzene (1.68 g, 51%) as a colorless solid. An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 1,4-bis[(2-hydroxyphenyl)diisopropylsilyl]benzene (1.68 g, 3.4 mmol) and Et_2O (10 mL). To the solution cooled to 0 °C was added *n*-butyllithium (1.59 M in hexane, 4.3 mL, 6.9 mmol) dropwise via syringe over 10 min. The solution was stirred at 0 °C for 1 h before adding Tf_2O (1.7 mL, 6.9 mmol). The resulting solution was allowed to warm to room temperature and then stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography (hexane/ethyl acetate 10:1) on silica gel to give **5** (1.82 g, 71%) as a colorless solid.



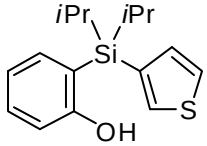
Mp: 164.8–165.7 °C. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.3 Hz, 12H), 1.06 (d, *J* = 7.3 Hz, 12H), 1.73 (qq, *J* = 7.3, 7.3 Hz, 4H), 7.31 (dt, *J* = 7.3, 1.1 Hz, 2H), 7.41–7.43 (m, 2H), 7.46 (s, 4H), 7.47–7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6, 17.8, 17.9, 118.2 (q, *J* = 319.0 Hz), 118.62, 118.65, 125.8, 126.5, 131.3, 133.4, 134.6, 139.3, 156.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (KBr): ν = 2953, 2870, 1418, 1246, 1206, 1146, 1057, 912, 745, 635, 599, 538 cm^{-1}. MS (FAB) *m/z*: 754 (2, M^+), 711 (100), 685 (7). HRMS Calcd for $C_{32}H_{40}F_6O_6S_2Si_2$: 754.1709 ($M^+$). Found: 754.1682.

2-Bromophenyl diisopropyl(3-thienyl)silyl ether



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 86%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.45 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.79 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.29 (dd, *J* = 4.4, 0.4 Hz, 1H), 7.43 (dd, *J* = 4.4, 2.8 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.72 (dd, *J* = 2.8, 0.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 17.5, 17.6, 114.9, 119.6, 122.1, 125.4, 128.0, 131.2, 133.2, 133.4, 134.2, 152.4. IR (neat): ν = 2945, 2891, 1581, 1477, 1440, 1290, 1246, 1105, 1047, 1030, 924, 883, 752, 688, 650 cm^{-1}. MS (FAB) *m/z*: 327 (100, $[M - 43]^+ + 2$), 325 (93, $[M - 43]^+$), 287 (52), 285 (51), 229 (10), 227 (9). Anal. Calcd for $C_{16}H_{21}BrOSSi$: C, 52.02; H, 5.73. Found: C, 51.81; H, 5.57.

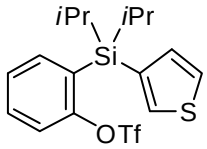
2-[Diisopropyl(3-thienyl)silyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 65%, a colorless solid. Mp: 57.6–59.0 °C. TLC: R_f 0.22 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.2 Hz, 6H), 1.02 (d, *J* = 7.2 Hz, 6H), 1.60 (qq, *J* = 7.2, 7.2 Hz, 2H), 5.01 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.27–7.35 (m, 3H), 7.51 (dd, *J* = 4.8, 2.4 Hz, 1H), 7.67 (dd, *J*= 2.4, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 17.6, 17.7, 115.7, 117.4, 120.1, 126.4, 131.3, 132.7, 132.9, 135.0, 136.8, 161.3. IR (KBr): ν =

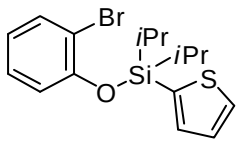
3495, 3464, 2943, 2926, 2864, 1599, 1562, 1469, 1438, 1278, 1199, 1099, 995, 854, 777, 756, 667, 619 cm^{-1}. MS (FAB) *m/z*: 247 (32, $[M - 43]^+$), 205 (10), 165 (7), 151 (5). Anal. Calcd for $C_{16}H_{22}OSSi$: C, 66.15; H, 7.63. Found: C, 66.02; H, 7.54.

2-[Diisopropyl(3-thienyl)silyl]phenyl trifluoromethanesulfonate (7)



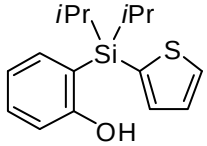
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 80%, a colorless oil. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.06 (d, *J* = 7.2 Hz, 6H), 1.69 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.15 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.27 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.40–7.50 (m, 4H), 7.54 (dd, *J* = 2.4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 18.1, 118.3 (q, *J* = 318.0 Hz), 118.6 (q, *J* = 2.0 Hz), 125.3, 126.4, 126.6, 131.4, 132.3, 132.9, 134.2, 139.2, 155.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2949, 2893, 1595, 1465, 1421, 1213, 1141, 1053, 997, 893, 777, 744, 667, 615 cm^{-1}. MS (FAB) *m/z*: 379 (100, $[M - 43]^+$), 339 (71), 273 (8), 231 (12), 203 (39). Anal. Calcd for $C_{17}H_{21}F_3O_3S_2Si$: C, 48.32; H, 5.01. Found: C, 48.05; H, 4.95.

2-Bromophenyl diisopropyl(2-thienyl)silyl ether



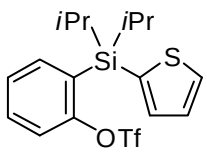
Purification: silica gel column chromatography (hexane/AcOEt 0:1). Yield: 96%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, *J* = 7.2 Hz, 6H), 1.18 (d, *J* = 7.2 Hz, 6H), 1.49 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.78–6.83 (m, 2H), 7.06 (ddd, *J* = 8.0, 7,6, 1.6 Hz, 1H), 7.25 (dd, *J* = 4.4, 1.2 Hz, 1H), 7.49–7.53 (m, 2H), 7.69 (dd, *J* = 4.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 17.49, 17.52, 115.0, 119.8, 122.3, 127.95, 127.97, 131.5, 131.8, 133.2, 136.6, 152.2. IR (neat): ν = 2945, 2866, 1581, 1477, 1440, 1290, 1213, 1047, 1003, 924, 883, 709, 690, 677 cm^{-1}. MS (FAB) *m/z*: 371 (6, $M^+ + 2$), 369 (6, M^+), 327 (94), 325 (100), 287 (44), 285 (44). Anal. Calcd for $C_{16}H_{21}BrOSSi$: C, 52.02; H, 5.73. Found: C, 52.15; H, 5.50.

2-[Diisopropyl(2-thienyl)silyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 94%, a colorless solid. Mp: 45.8–47.0 °C. TLC: R_f 0.21 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.06 (d, *J* = 7.2 Hz, 6H), 1.62 (qq, *J* = 7.2, 7.2 Hz, 2H), 5.14 (s, 1H), 6.79 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.94 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.29–7.36 (m, 3H), 7.46 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.77 (dd, *J* = 4.8, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 17.7, 17.8, 115.6, 117.4, 120.0, 128.5, 131.1, 131.3, 132.4, 136.8, 137.6, 161.3. IR (KBr): ν = 3457, 2955, 2864, 1599, 1564, 1472, 1440, 1277, 1211, 1200, 991, 879, 829, 756, 707, 669 cm^{-1}. MS (FAB) *m/z*: 247 (7, $[M - 43]^+$), 205 (64), 165 (19), 151 (21). Anal. Calcd for $C_{16}H_{22}OSSi$: C, 66.15; H, 7.63. Found: C, 66.12; H, 7.61.

2-[Diisopropyl(2-thienyl)silyl]phenyl trifluoromethanesulfonate (9)

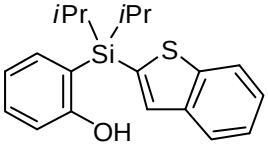


Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 49%, a colorless oil. TLC: R_f 0.51 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.71 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.25–7.29 (m, 2H), 7.36 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.41 (d, *J* = 7.6 Hz,

1H), 7.44–7.55 (m, 2H), 7.71 (dd, J = 4.4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 18.1, 18.2, 118.3 (q, J = 317.2 Hz), 118.5 (q, J = 1.5 Hz,), 126.3, 126.6, 127.9, 130.6, 131.3, 131.5, 137.2, 139.3, 155.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (neat): ν = 2949, 2868, 1595, 1467, 1421, 1247, 1213, 1141, 1053, 1001, 891, 763, 745, 709, 667, 628 cm^{-1}. MS (FAB) *m/z*: 379 (100, $[M - 43]^+$), 339 (58), 273 (7), 231 (10), 203 (33). Anal. Calcd for $C_{17}H_{21}F_3O_3S_2Si$: C, 48.32; H, 5.01. Found: C, 48.09; H, 4.96.

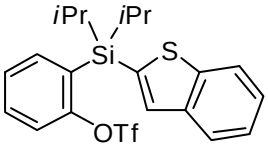
2-Bromophenyl (2-benzothienyl)diisopropylsilyl ether were prepared according to the general procedures and used for further steps without isolation.

2-[(2-Benzothienyl)diisopropylsilyl]phenol



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 62%, a colorless oil. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, J = 7.2 Hz, 6H), 1.12 (d, J = 7.2 Hz, 6H), 1.70 (qq, J = 7.2, 7.2 Hz, 2H), 5.11 (s, 1H), 6.80 (dd, J = 8.0, 1.2 Hz, 1H), 6.95 (ddd, J = 7.6, 7.2, 1.2 Hz, 1H), 7.30–7.40 (m, 4H), 7.66 (s, 1H), 7.84–7.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 17.9, 18.0, 115.5, 117.4, 120.1, 122.0, 123.6, 124.0, 124.5, 132.0, 134.4, 134.5, 137.2, 140.7, 144.0, 161.1. IR (neat): ν = 3721, 2943, 2862, 1645, 1593, 1573, 1435, 1278, 1242, 1122, 1072, 997,958, 881, 833, 756, 686, 626 cm^{-1}. MS (FAB) *m/z*: 340 (6, M^+), 297 (47), 253 (15), 207 (15). HRMS Calcd for $C_{20}H_{24}OSSi$: 340.1317 (M^+). Found: 340.1314.

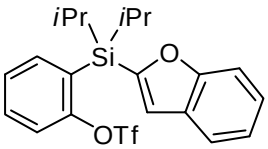
2-[(2-Benzothienyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (11)



Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 53%, a colorless oil. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 7.2 Hz, 6H), 1.16 (d, J = 7.2 Hz, 6H), 1.78 (qq, J = 7.2, 7.2 Hz, 2H), 7.27 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.34–7.41 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.47–7.52 (m, 2H), 7.59 (s, 1H), 7.85–7.88 (m, 1H), 7.90–7.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 18.1, 18.2, 118.3 (q, J = 317.2 Hz), 118.6, 121.9, 123.5, 124.0, 124.5, 125.7, 126.7, 131.7, 133.4, 134.3, 139.4, 140.5, 143.7, 155.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (neat): ν = 2949, 2893, 2868, 1595, 1492, 1464, 1421, 1290, 1246, 1215, 1140, 1055, 891, 744, 671, 629 cm^{-1}. MS (FAB) *m/z*: 472 (3, M^+), 429 (100), 339 (45), 253 (24), 221 (5). Anal. Calcd for $C_{21}H_{23}F_3O_3S_2Si$: C, 53.37; H, 4.91. Found: C, 53.51; H, 4.93.

2-Bromophenyl (2-benzofuranyl)diisopropylsilyl ether and 2-[(2-benzofuranyl)diisopropyl]silylphenol were prepared according to the general procedures and used for further steps without isolation.

2-[(2-Benzofuranyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (13)

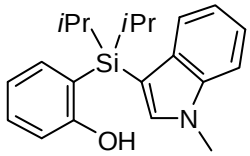


Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 9% (3 step yield), a colorless oil. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J = 7.2 Hz, 6H), 1.16 (d, J = 7.2 Hz, 6H), 1.73 (qq, J = 7.2, 7.2 Hz, 2H), 7.19 (d, J = 0.9 Hz, 1H), 7.23–7.29

(m, 2H), 7.32 (ddd, *J* = 7.6, 7.2, 1.6 Hz, 1H), 7.41–7.45 (m, 2H), 7.49 (ddd, *J* = 7.6, 7.2, 1.6 Hz, 1H), 7.53 (dd, *J*= 8.0, 0.8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.1, 18.2, 111.4, 118.3 (q, *J* = 318.0 Hz), 118.6, 120.0, 121.0, 122.4, 124.6, 125.3, 126.9, 127.5, 131.7, 138.9, 155.5, 156.8, 158.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (neat): ν = 2951, 2893, 1597, 1523, 1470, 1422, 1247, 1215, 1142, 1055, 891, 790, 744, 669, 628 cm^{-1}. MS (FAB) *m/z*: 456 (2, M^+), 413 (100), 339 (29), 237 (14). Anal. Calcd for $C_{21}H_{23}F_3O_4SSi$: C, 55.25; H, 5.08. Found: C, 55.30; H, 5.09.

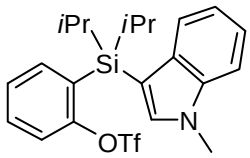
2-Bromophenyl (1-methylindol-3-yl)diisopropylsilyl ether was prepared according to the general procedure and used for the next step without isolation.

2-[(Diisopropyl(1-methylindol-3-yl)silyl)phenol



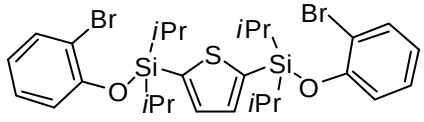
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 20%, a colorless solid. Mp: 126.5–126.7 °C. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (d, *J* = 7.2 Hz, 12H), 1.66 (sep, *J* = 7.2 Hz, 12H), 3.87 (s, 3H), 5.87 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.07 (dd, *J* = 8.4, 8.0 Hz, 1H), 7.26 (dd, *J* = 8.4, 8.0 Hz, 1H), 7.28 (s, 1H), 7.33 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.45(dd, *J* = 7.2, 1.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 17.7, 17.8, 33.3, 99.1, 109.4, 115.8, 117.4, 119.7, 120.1, 122.1, 122.5, 131.2, 133.3, 136.3, 138.2, 138.6, 162.1. IR (KBr): ν = 3427, 2947, 2928, 2682, 1601, 1566, 1498, 1460, 1440, 1279, 1203, 995, 879, 827, 761, 663, 630 cm^{-1}. MS (FAB) *m/z*: 337 (7, M^+), 294 (62), 250 (19), 236 (6), 206 (8). Anal. Calcd for $C_{21}H_{27}NOSi$: C, 74.73; H, 8.06. Found: C, 74.43; H, 8.16.

2-[Diisopropyl(1-methylindol-3-yl)silyl]phenyl trifluoromethanesulfonate (15)



Prepared by Method B. Purification: recrystallization with hexane. Yield: 58%, a colorless solid. Mp: 120.2–120.6 °C. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.2 Hz, 6H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.74 (qq, *J* = 7.2, 7.2 Hz, 2H), 6.99 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.17 (s, 1H), 7.20–7.24 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.41–7.48 (m, 2H), 7.55 (dd, *J* = 7.6, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.4, 33.1, 100.4, 109.2, 118.3 (q, *J* = 317.9 Hz), 118.5, 119.2, 121.3, 123.1, 126.4, 126.7, 131.1, 133.2, 137.6, 138.3, 139.9, 155.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (neat): ν = 2949, 2866, 1654, 1504, 1462, 1419, 1246, 1211, 1143, 1049, 881, 746, 734, 667, 632 cm^{-1}. MS (FAB) *m/z*: 469 (29, M^+), 426 (100), 276 (9), 250 (24). Anal. Calcd for $C_{21}H_{23}F_3O_4SSi$: C, 56.27; H, 5.58. Found: C, 56.06; H, 5.58.

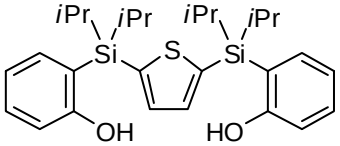
2,5-Bis[(2-bromophenoxy)diisopropylsilyl]thiophene



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 84%, a colorless oil. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, *J* = 7.2 Hz, 12H), 1.19 (d, *J* = 7.2 Hz, 12H), 1.50 (qq, *J* = 7.2, 7.2 Hz, 4H), 6.77–6.81 (m, 4H), 7.04 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 2H), 7.50 (d, *J* = 8.0, 1.2 Hz, 2H), 7.58 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 17.52, 17.54, 115.0, 119.8, 122.3, 127.9, 133.2, 137.3, 139.0, 152.2. IR (neat): ν = 2945,

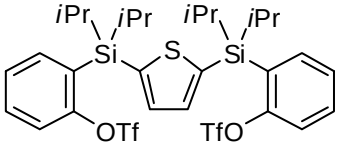
2866, 1581, 1477, 1290, 1246, 1047, 1010, 922, 753, 732, 690, 621 cm^{-1}. MS (FAB) *m/z*: 613 (60, $[M - 43]^+ + 4$), 611 (96, $[M - 43]^+ + 2$), 609 (47, $[M - 43]^+$), 483 (12), 481 (11), 287 (100), 285 (98). Anal. Calcd for $C_{28}H_{38}Br_2O_2SSi_2$: C, 51.37; H, 5.85. Found: C, 51.36; H, 5.63.

2,5-Bis[(2-hydroxyphenyl)diisopropylsilyl]thiophene



Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 60%, a colorless solid. Mp: 118.3–118.8 °C. TLC: R_f 0.25 (hexane/AcOEt 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 12H), 1.07 (d, *J* = 7.2 Hz, 12H), 1.65 (qq, *J* = 7.2, 7.2 Hz, 4H), 5.11 (s, 2H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.94 (ddd, *J* = 7.6, 7.4, 0.8 Hz, 2H), 7.29–7.34 (m, 4H), 7.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 17.8, 17.9, 115.5, 117.5, 120.1, 131.4, 136.9, 138.7, 139.5, 161.1. IR (KBr): ν = 3427, 2955, 2862, 1593, 1568, 1475, 1464, 1433, 1346, 1278, 1202, 1122, 1077, 1003, 881, 831, 765, 682, 665, 628 cm^{-1}. MS (FAB) *m/z*: 453 (6, $[M - 43]^+$), 413 (15), 369 (16), 247 (23), 207 (100). Anal. Calcd for $C_{28}H_{40}O_2SSi_2$: C, 67.69; H, 8.11. Found: C, 67.43; H, 8.16.

2,5-Bis[(2-trifluoromethanesulfonyloxyphenyl)diisopropylsilyl]thiophene (17)

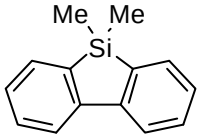


Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 92%, a colorless solid. Mp: 42.1–43.1 °C. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 12H), 1.11 (d, *J* = 7.2 Hz, 12H), 1.72 (qq, *J* = 7.2, 7.2 Hz, 4H), 7.29 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 2H), 7.41 (dd, *J* = 8.8, 0.8 Hz, 2H), 7.46 (s, 2H), 7.47–7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 18.1, 18.2, 118.3 (q, *J* = 318.0 Hz), 118.6, 126.3, 126.7, 131.6, 137.7, 137.8, 139.2, 155.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 2951, 2866, 1597, 1564, 1465, 1415, 1246, 1205, 1141, 1053, 1006, 887, 746, 667, 628, 601 cm^{-1}. MS (FAB) *m/z*: 717 (100, $[M - 43]^+$), 541 (5), 339 (75). Anal. Calcd for $C_{30}H_{38}F_6O_6S_3Si_2$: C, 47.35; H, 5.03. Found: C, 47.10; H, 5.08.

General Procedure for Pd-catalyzed Intramolecular Coupling Reaction

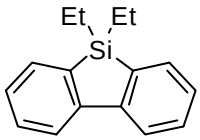
An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with 2-(arylsilyl)aryl triflate (1.0 mmol) and DMA (1.0 mL). To the solution was added a solution of $Pd(OAc)_2$ (11 mg, 0.05 mmol) and PCy_3 (28 mg, 0.1 mmol) in DMA (1.0 mL), and then Et_2NH (200 μL, 2.0 mmol). The reaction mixture was stirred at 100 °C until Pd-black precipitated. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution, and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give silicon-bridged biaryl.

9,9-Dimethyl-9-silafluorene (2a, CAS No. 13688-68-1)



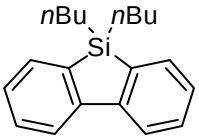
Purification: silica gel column chromatography (hexane only). Yield: 27%, a colorless solid.

9,9-Diethyl-9-silafluorene (2b, CAS No. 5372-63-4)



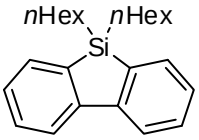
Purification: silica gel column chromatography (hexane only). Yield: 39%, a colorless solid.

9,9-Di-*n*-butyl-9-silafluorene (2c)



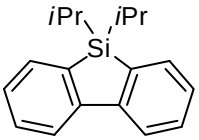
Purification: silica gel column chromatography (hexane only). Yield: 68 %, a colorless oil. TLC: R_f 0.31 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, *J* = 7.2 Hz, 6H), 0.93–0.97 (m, 4H), 1.27–1.40 (m, 8H), 7.26 (ddd, *J* = 7.4, 7.1, 0.9 Hz, 2H), 7.43 (ddd, *J* = 7.9, 7.4, 1.2 Hz, 2H), 7.62 (dd, *J* = 7.1, 1.2 Hz, 2H), 7.82 (dd, *J* = 8.0 Hz, 0.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.2, 13.8, 26.2, 26.5, 120.7, 127.0, 129.8, 133.1, 137.7, 148.1. IR (neat): ν = 2957, 2922, 2870, 2856, 1593, 1458, 1431, 743, 704, 505 cm^{-1}. MS (FAB) *m/z*: 294 (96, M^+), 237 (44), 197 (21), 181 (100), 154 (22), 136 (13). Anal. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 9.11. Found: C, 81.69; H, 9.11.

9,9-Di-*n*-hexyl-9-silafluorene (2d)



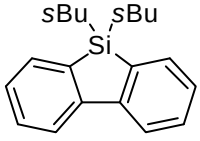
Purification: silica gel column chromatography (hexane only) followed by GPC ($CHCl_3$). Yield: 63%, a colorless oil. TLC: R_f 0.34 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, *J* = 6.8 Hz, 6H), 0.92–0.96 (m, 4H), 1.20–1.30 (m, 12H), 1.33–1.39 (m, 4H), 7.25 (dd, *J* = 7.3, 7.1 Hz, 2H), 7.42 (ddd, *J* = 7.7, 7.3, 1.3 Hz, 2H), 7.61 (dd, *J* = 7.1, 1.3 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 14.2, 22.7, 24.0, 31.5, 33.2, 120.7, 127.0, 129.8, 133.1, 137.7, 148.2. IR (neat): ν = 2957, 2930, 2909, 1593, 1460, 1431, 1377, 1258, 1126, 1062, 997, 846, 729, 711, 621 cm^{-1}. MS (FAB) *m/z*: 350 (20, M^+), 265 (31), 207 (4), 197 (11), 181 (100), 165 (7). Anal. Calcd for $C_{24}H_{34}Si$: C, 82.22; H, 9.77. Found: C, 82.24; H, 9.87.

9,9-Diisopropyl-9-silafluorene (2e)



Purification: silica gel column chromatography (hexane only). Yield: 91 %, a colorless solid. Mp: 53.8–54.9 °C. TLC: R_f 0.31 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 12H), 1.39 (sep, *J* = 7.6 Hz, 2H), 7.25 (ddd, *J* = 7.4, 7.2, 0.9 Hz, 2H), 7.42 (ddd, *J* = 7.9, 7.4, 1.3 Hz, 2H), 7.61 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.82 (dd, *J* = 7.9, 0.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.3, 120.6, 126.9, 129.8, 133.5, 136.0, 148.7. IR (KBr): ν = 3037, 2956, 2860, 1589, 1458, 1425, 1255, 1126, 1061, 879, 748, 729, 671, 606 cm^{-1}. MS (FAB) *m/z*: 266 (52, M^+), 223 (84), 195 (100), 181 (52), 165 (25). Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 80.91; H, 8.49.

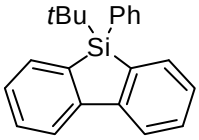
9,9-Di-*sec*-butyl-9-silafluorene (2f)



Purification: silica gel column chromatography (hexane only). Yield: 94%, a colorless oil. TLC: R_f 0.32 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (q, *J* = 6.8 Hz, 6H), 1.02 (t, *J* = 6.8 Hz, 3H), 1.05 (t, *J* = 6.8 Hz, 3H), 1.16–1.27 (m, 4H), 1.53–1.63 (m, 4H), 7.24 (ddd, *J* = 8.9,

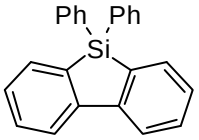
7.2, 0.9 Hz, 2H), 7.42 (ddd, *J* = 7.9, 7.7, 1.3 Hz, 2H), 7.61 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.82 (dd, *J* = 7.7, 0.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.51, 13.54, 14.19, 14.25, 18.7, 25.1, 25.2, 120.6, 126.8, 129.7, 133.52, 133.56, 133.60, 136.3, 136.5, 136.7, 148.6, 148.7, 148.8. IR (neat): ν = 2955, 2922, 2870, 1593, 1458, 1431, 1257, 1128, 1062, 765, 744, 704 cm^{-1}. MS (FAB) *m/z*: 294 (46, M^+), 237 (57), 195 (53), 181 (100), 165 (13), 154 (8). Anal. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 9.11. Found: C, 81.67; H, 8.90.

9-*tert*-Butyl-9-phenyl-9-silafluorene (2g)



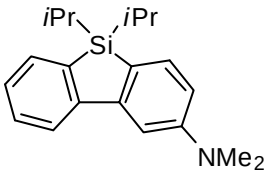
Purification: silica gel column chromatography (hexane only). Yield: 88%, a colorless solid. Mp: 98.3–99.4 °C. TLC: R_f 0.31 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 9H), 7.31–7.38 (m, 5H), 7.45 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H), 7.78–7.80 (m, 2H), 7.87 (dd, *J* = 7.2, 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 26.8, 109.7, 121.0, 127.3, 127.6, 129.3, 130.2, 133.7, 135.0, 135.6, 148.5. IR (KBr): ν = 3066, 3038, 2949, 2926, 2850, 1591, 1460, 1427, 1257, 1111, 1060, 819, 744, 727, 698, 613 cm^{-1}. MS (FAB) *m/z*: 314 (20, M^+), 273 (10), 257 (100), 237 (14), 165 (10). Anal. Calcd for $C_{22}H_{22}Si$: C, 84.02; H, 7.05. Found: C, 83.81; H, 7.35.

9,9-Diphenyl-9-silafluorene (2h, CAS No. 5550-08-3)



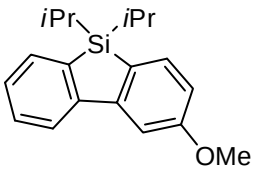
Purification: silica gel column chromatography (hexane/CH_2Cl_2 10:1). Yield: 88%, a colorless solid.

3-Dimethylamino-9,9-diisopropyl-9-silafluorene (2i)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 90%, a colorless oil. TLC: R_f 0.55 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.35 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.06 (s, 6H), 6.67 (d, *J* = 8.0, 2.4 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.23 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.40 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.3, 18.4, 40.5, 104.7, 111.5, 120.3, 126.6, 129.4, 133.2, 134.3, 136.1, 137.5, 149.2, 150.1, 151.9. IR (neat): ν = 2939, 2888, 2860, 1597, 1493, 1435, 1356, 1261, 1226, 1126, 1062, 882, 772, 712, 615 cm^{-1}. MS (FAB) *m/z*: 309 (100, M^+), 266 (54), 238 (11), 224 (11), 208 (13). HRMS Calcd for $C_{20}H_{27}ONSi$: 309.1913 (M^+). Found: 309.1905.

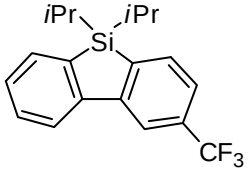
9,9-Diisopropyl-3-methoxy-9-silafluorene (2j)



Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 94%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.37 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.90 (s, 3 H), 6.83 (dd, *J* = 8.0, 2.2 Hz, 2H), 7.25 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.37 (d, *J* = 2.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* =7.2 Hz, 1H), 7.78 (d, *J* =8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.3, 55.2, 106.8, 112.7, 120.6, 126.8, 127.0, 130.0, 133.4, 134.4, 137.1, 148.4, 150.8, 161.5. IR (neat): ν = 3063, 2940, 2862, 1597, 1558, 1462, 1431, 1307, 1286, 1211, 1174, 1080, 1037, 880, 773, 721, 669 cm^{-1}. MS (FAB) *m/z*: 296 (80, M^+), 253 (100), 225 (40), 211 (25), 195

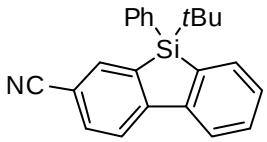
(15). Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 77.05; H, 8.11.

9,9-diisopropyl-3-trifluoromethyl-9-silafluorene (2k)



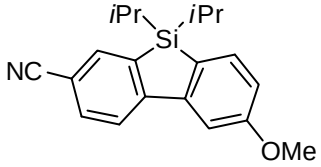
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 88%, a colorless oil. TLC: R_f 0.42 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.04 (d, *J* = 7.2 Hz, 6H), 1.42 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.31 (ddd, *J* = 7.2, 7.2, 0.8 Hz, 1H), 7.45–7.50 (m, 2H), 7.63 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.16, 18.19, 117.1 (q, *J* = 3.8 Hz), 121.1, 123.2, 123.3, 126.8 (q, *J* = 228.0 Hz), 127.8, 130.2, 132.0 (q, *J* = 31.3 Hz), 133.6, 136.0, 140.8, 147.4, 149.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.2. IR (neat): ν = 2943, 2864, 1604, 1591, 1462, 1402, 1333, 1265, 1167, 1126, 1057, 881, 833, 775, 711, 700, 665 cm^{-1}. MS (FAB) *m/z*: 334 (77, M^+), 315 (33), 291 (100), 263 (57), 249 (27). Anal. Calcd for $C_{19}H_{21}F_3Si$: C, 68.23; H, 6.33. Found: C, 68.49; H, 6.31.

9-*tert*-Butyl-2-cyano-9-phenyl-9-silafluorene (2l)



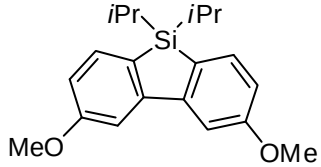
Purification: silica gel column chromatography (hexane only). Yield: 95% a colorless solid. Mp: 159.5–160.0 °C. TLC: R_f 0.34 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 9H), 7.34–7.43 (m, 3H), 7.43 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.52 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.72–7.75 (m, 3H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.90–7.92 (m, 2H), 8.11 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 26.7, 110.6, 119.5, 121.3, 122.1, 127.9, 128.9, 129.9, 130.6, 131.1, 133.9, 134.0, 134.9, 136.4, 136.9, 137.2, 146.6, 152.5. IR (neat): ν = 2928, 2857, 2222, 1586, 1466, 1429, 1390, 1362, 1193, 1008, 912, 841, 820, 777, 735, 700, 620 cm^{-1}. MS (FAB) *m/z*: 340 (68, $[M + H]^+$), 282 (55), 220 (8), 166 (5). Anal. Calcd for $C_{23}H_{21}NSi$: C, 81.37; H, 6.23. Found: C, 81.47; H, 6.21.

2-Cyano-9,9-diisopropyl-6-methoxy-9-silafluorene (2m)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 93%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.03 (d, *J* = 7.2 Hz, 6H), 1.38 (qq, *J* = 7.6, 7.2 Hz, 2H), 3.91 (s, 3H), 6.92 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.55 (d, *J* = 8.0, 2.4 Hz, 1H), 7.70 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.83 (d, *J* =2.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.1, 18.2, 55.3, 107.9, 110.4, 114.4, 119.5, 120.9, 127.5, 133.6, 134.8, 136.6, 138.6, 148.8, 152.5, 161.8. IR (neat): ν = 2941, 2889, 2862, 2224, 1599, 1562, 1470, 1305, 1215, 1176, 1080, 1060, 1031, 991, 723, 671, 658, 621 cm^{-1}. MS (FAB) *m/z*: 322 (100, M^++1), 307 (18), 278 (59), 250 (26), 236 (11), 220 (5). Anal. Calcd for $C_{20}H_{23}NSi$: C, 74.72; H, 7.21. Found: C, 74.48; H, 7.27.

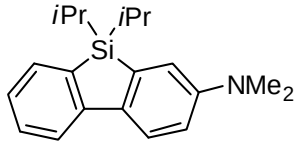
9,9-Diisopropyl-3,6-dimethoxy-9-silafluorene (2n)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 98%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 12H), 1.34 (sep, *J* = 7.2 Hz, 2H), 3.90 (s, 6

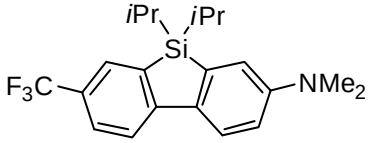
H), 6.83 (dd, *J* = 7.6, 2.4 Hz, 2H), 7.30 (d, *J* = 2.4 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.3, 55.2, 106.9, 112.7, 127.9, 134.3, 150.4, 161.5. IR (neat): ν = 2999, 2939, 2862, 1597, 1556, 1483, 1462, 1303, 1288, 1222, 1203, 1070, 1033, 880, 808, 723, 673 cm^{-1}. MS (FAB) *m/z*: 326 (47, M^+), 283 (100), 255 (29), 241 (21), 225 (14), 211 (7). Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03. Found: C, 73.32; H, 8.00.

2-Dimethylamino-9,9-diisopropyl-9-silafluorene (2o)



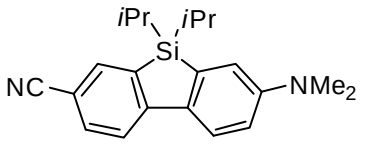
Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 97%, colorless solid. Mp: 89.5–90.2 °C. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.5 Hz, 6H), 1.06 (d, *J* = 7.5 Hz, 6H), 1.37 (qq, *J* = 7.5, 7.5 Hz, 2H), 3.02 (s, 6H), 6.83 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 7.16 (dd, *J* = 7.3, 7.1 Hz, 1H), 7.40 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.3, 40.9, 113.9, 117.2, 119.3, 121.4, 125.1, 129.7, 133.4, 134.3, 134.7, 137.4, 137.8, 149.5. IR (KBr): ν = 3000, 2850, 1749, 1734, 1717, 1699, 1684, 1559, 1541, 1506, 1489, 1456, 1417, 1339, 1223, 1175, 1057, 883, 770, 725, 673, 609 cm^{-1}. MS (FAB) m/z: 309 (100, M^+), 266 (11), 224 (7). Anal. Calcd for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79. Found: C, 77.55; H, 8.67.

2-Dimethylamino-7-tifluoromethyl-9,9-diisopropyl-9-silafluorene (2p)



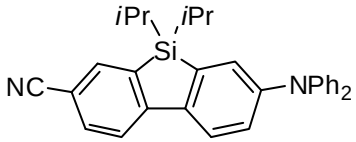
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 95%, colorless solid. Mp: 124.9–125.8 °C. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.3 Hz, 6H), 1.06 (d, *J* = 7.3 Hz, 6H), 1.40 (qq, *J* = 7.3, 7.3 Hz, 2H), 3.05 (s, 6H), 6.76–6.84 (brs, 1H), 6.94–7.00 (brs, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.71–7.73 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.18, 18.21, 40.7, 113.8, 116.8, 119.1, 122.3, 124.8 (q, *J* = 271.2 Hz), 126.7 (q, *J* = 30.7 Hz), 127.0 (q, *J* = 3.8 Hz), 129.6 (q, *J* = 3.8 Hz), 135.4, 136.1, 138.0, 150.0,153.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.3. IR (KBr): ν = 2942, 2862, 1587, 1557, 1489, 1460, 1354, 1327, 1287, 1263, 1136, 1111, 1074, 880, 812, 725, 635 cm^{-1}. MS (FAB) *m/z*: 377 (100, M^+), 334 (12), 292 (6). Anal. Calcd for $C_{21}H_{26}F_3NSi$: C, 66.81; H, 6.94. Found: C, 66.53; H, 6.77.

2-Cyano-7-dimethylamino-9,9-diisopropyl-9-silafluorene (2q)



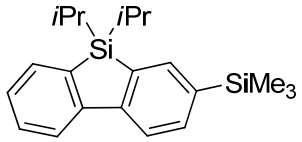
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 85%, a colorless solid. Mp: 113.6–114.4 °C. TLC: R_f 0.18 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.5 Hz, 6H), 1.05 (d, *J* = 7.3 Hz, 6H), 1.39 (qq, *J* = 7.5, 7.3 Hz, 2H), 3.06 (s, 6H), 6.78–6.84 (brs, 1H), 6.93–6.97 (brs, 1H), 7.62 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.10, 18.15, 40.6, 107.8, 113.7, 116.5, 119.4, 120.1, 122.8, 133.8, 135.8, 136.6, 138.4, 150.3, 153.8, 154.6. IR (KBr): ν = 2938, 2861, 2216, 1582, 1560, 1491, 1456, 1356, 1177, 882, 808, 721, 665, 638, 494 cm^{-1}. MS (FAB) *m/z*: 334 (100, M^+), 291 (10), 248 (3). Anal. Calcd for $C_{21}H_{26}N_2Si$: C, 75.40; H, 7.83. Found: C, 75.20; H, 7.99.

2-Cyano-7-diphenylamino-9,9-diisopropyl-9-silafluorene (2r)



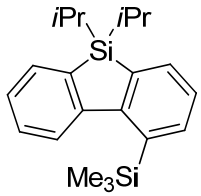
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 81%, a colorless solid. Mp: 178.8–179.8 °C. TLC: R_f 0.24 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 7.6 Hz, 6H), 1.01 (d, *J* = 7.6 Hz, 6H), 1.34 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.03–7.08 (m, 2H), 7.09–7.15 (m, 5H), 7.25–7.30 (m, 4H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.64–7.69 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.80 (dd, *J* = 2.6, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 18.1, 18.2, 109.1, 119.8, 120.2, 122.7, 123.2, 124.4, 124.8, 127.8, 129.2, 133.8, 136.7, 136.9, 138.2, 140.7, 147.2, 148.1, 152.8. IR (KBr): ν = 2937, 2862, 2218, 1581, 1492, 1282, 1267, 881, 825, 748, 729, 694 cm^{-1}. MS (FAB) *m*/*z*: 458 (49, M^+), 415 (2), 373 (2). Anal. Calcd for $C_{31}H_{20}N_2Si$: C, 81.18; H, 6.59. Found: C, 81.32; H, 6.50.

2-Trimethylsilyl-9,9-diisopropyl-9-silafluorene (2s)



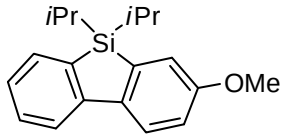
Purification: silica gel column chromatography (hexane only) followed by HPLC (hexane only). Yield: 51 %, colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H), 1.10 (d, *J* = 7.5 Hz, 12H), 1.44 (sep, *J* = 7.5, 2H), 7.28 (t, *J* = 7.2, 1H), 7.45 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.61–7.66 (m, 2H), 7.79 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.8, 11.3, 18.37, 18.39, 119.9, 120.8, 127.0, 129.8, 133.5, 135.0, 135.2, 136.2, 138.4, 138.6, 148.8, 149.3. IR (neat): ν = 2953, 2862, 1591, 1582, 1462, 1364, 1248, 1113, 856, 839, 829, 752 cm^{-1}. MS (FAB) *m*/*z*: 338 (16, M^+), 323 (76), 295 (68). Anal. Calcd for $C_{21}H_{30}Si_2$: C, 74.48; H, 8.93. Found: C, 74.31; H, 9.09.

4-Trimethylsilyl-9,9-diisopropyl-9-silafluorene (2s')



Purification: silica gel column chromatography (hexane only) followed by HPLC (hexane only). Yield: 8 %, colorless solid. Mp: 71.4–72.6 °C. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.34 (s, 9H), 1.05 (d, *J* = 7.5 Hz, 6H), 1.06 (d, *J* = 7.5 Hz, 6H), 1.38 (qq, *J* = 7.5, 7.5 Hz, 2H), 7.25 (dt, *J* = 7.2, 0.9 Hz, 1H), 7.40 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.43 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.59–7.62 (m, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.9, 11.3, 18.3, 120.5, 125.2, 126.8, 129.7, 131.9, 132.8, 133.5, 136.1, 136.7, 141.8, 147.7, 149.0. IR (KBr): ν = 2953, 2862, 1458, 1248, 1103, 858, 839, 822, 775, 729, 673, 631 cm^{-1}. MS (FAB) *m*/*z*: 338 (17, M^+), 323 (78), 295 (82). HRMS Calcd for $C_{20}H_{30}Si_2$: 338.1886 (M^+). Found: 338.1895.

9,9-Diisopropyl-2-methoxy-9-silafluorene (2t)



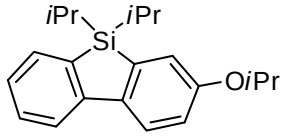
Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 57%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.05 (d, *J* = 7.2 Hz, 6H), 1.38 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.87 (s, 3H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.18 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.39 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.56 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.2, 55.4, 114.6,

119.0, 119.9, 121.6, 125.9, 129.8, 133.4, 135.2, 138.0, 141.6, 148.7, 158.6. IR (neat): ν = 2889, 2862, 1587, 1536, 1454, 1427, 1269, 1213, 1182, 1128, 1043, 989, 877, 821, 771, 715, 677, 628 cm^{-1}. MS (FAB) *m/z*: 296 (100, M^+), 253 (40), 225 (24), 211 (17), 195 (5). Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.72; H, 8.05.

9,9-Diisopropyl-4-methoxy-9-silafluorene (2t′)

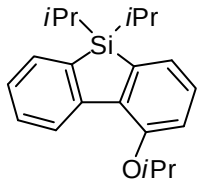
Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 34%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.38 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.99 (s, 3H), 7.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.20–7.27 (m, 3H), 7.41 (ddd, *J* = 8.0, 7.6, 1.2 Hz, 1H), 7.58 (dd, *J* = 7.6, 0.8 Hz, 1H), 8.55 (dd, *J* = 8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.2, 55.1, 113.0, 125.4, 125.9, 126.5, 127.9, 129.7, 132.8, 136.0, 136.3, 138.9, 148.8, 157.0. IR (neat): ν = 3051, 2937, 2889, 2862, 1568, 1462, 1446, 1267, 1180, 1047, 882, 791, 752, 675, 623 cm^{-1}. MS (FAB) *m/z*: 296 (100, M^+), 253 (57), 225 (21), 211 (26), 195 (7). Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.80; H, 8.12.

2-Isopropoxy-9,9-diisopropyl-9-silafluorene (2u)



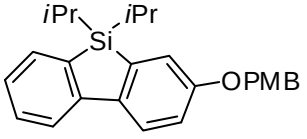
Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 54%, a colorless solid. Mp: 33.2–33.6 °C. TLC: R_f 0.15 (hexane/AcOEt 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 12H), 1.37 (sep, *J* = 7.6 Hz, 2H), 1.38 (d, *J* = 6.0 Hz, 6H), 4.60 (sep, *J* = 6.0 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 7.18 (dd, *J* = 7.3, 7.1 Hz, 1H), 7.38 (dd, *J* = 7.9,7.3 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.3, 22.3, 69.9, 116.8, 119.9, 121.1, 121.6, 125.8, 129.8, 133.4, 15.2, 137.9, 141.5, 148.8, 156.9. IR (KBr): ν = 2974, 2862, 1587, 1557, 1466, 1431, 1267, 1209, 1138, 1114, 964, 881, 773, 725, 673 cm^{-1}. MS (FAB) *m/z*: 324 (100, M^+), 281 (21), 239 (31). Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.64; H, 8.73.

4-Isopropoxy-9,9-diisopropyl-9-silafluorene (2u′)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 43%, a colorless oil. TLC: R_f 0.20 (hexane/AcOEt 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.37 (qq, *J* = 7.6, 7.6 Hz, 2H), 1.49 (d, *J* = 6.0 Hz, 6H), 5.83 (sep, *J* = 6.0 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 7.17–7.23 (m, 3H), 7.40 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 8.67 (d, *J*= 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.2, 22.5, 70.3, 115.3, 125.2, 125.8, 126.6, 127.7, 129.6, 132.7, 136.1, 137.0, 139.1, 149.1, 155.3. IR (neat): ν = 3051, 2974, 2939, 1566, 1464, 144, 1383, 1251, 1159, 1114, 974, 881, 789, 739, 727 cm^{-1}. MS (FAB) *m/z*: 324 (65, M^+), 281 (35), 239 (20). Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.95; H, 8.84.

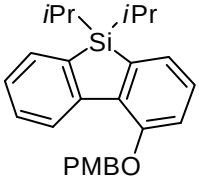
9,9-Diisopropyl-2-(4-methoxybenzyloxy)-9-silafluorene (2v)



Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 47%, a colorless solid.

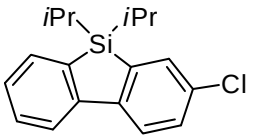
Mp: 100.3–101.3 °C. TLC: R_f 0.40 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 6H), 1.05 (d, *J* = 7.6 Hz, 6H), 1.38 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.84 (s, 3H), 5.04 (s, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 7.03 (dd, *J* = 8.4, 2.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 2.7 Hz, 1H), 7.28–7.42 (m, 3H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.2, 55.3, 70.0, 113.9, 115.7, 120.0, 120.1, 121.6, 125.9, 128.9, 129.3, 129.8, 133.4, 135.3, 138.0, 141.8, 148.7, 157.9, 159.3. IR (KBr): ν = 2937, 2861, 1614, 1558, 1516, 1458, 1429, 1271, 1251, 1205, 1174, 1031, 1018, 993, 879, 823, 673 cm^{-1}. MS (FAB) *m/z*: 402 (11, M^+), 359 (1), 329 (2). Anal. Calcd for $C_{26}H_{30}O_2Si$: C, 77.57; H, 7.51. Found: C, 77.39; H, 7.44.

9,9-Diisopropyl-4-(4-methoxybenzyloxy)-9-silafluorene (2v′)



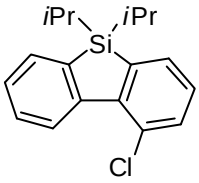
Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 47%, a colorless solid. Mp: 72.0–73.0 °C. TLC: R_f 0.40 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.05 (d, *J* = 7.2 Hz, 6H), 1.39 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.86 (s, 3 H), 5.16 (s, 2H), 7.06–7.08 (m, 1H), 7.18–7.24 (m, 3H), 7.33 (dd, *J* = 7.8, 7.5 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.2, 55.3, 70.1, 113.9, 114.4, 125.7, 125.9, 126.7, 127.8, 129.0, 129.3, 129.8, 132.7, 136.0, 136.5, 139.1, 148.7, 156.2, 159.2. IR (KBr): ν = 2939, 2862, 1612, 1564, 1514, 1458, 1435, 1375, 1242, 1175, 1012, 995, 882, 827, 791, 703, 727, 680 cm^{-1}. MS (FAB) *m/z*: 402 (3, M^+), 359 (1), 329 (2). Anal. Calcd for $C_{26}H_{30}O_2Si$: C, 77.57; H, 7.51. Found: C, 77.73; H, 7.54.

2-Chloro-9,9-diisopropyl-9-silafluorene (2w)



Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 20%, a colorless solid. Mp: 71.6–73.0 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 6H), 1.05 (d, *J* = 7.6 Hz, 6H), 1.40 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.24–7.28 (m, 1H), 7.39 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.43 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.17, 18.19, 120.7, 121.9, 123.4, 127.1, 129.8, 130.0, 133.0, 133.5, 135.7, 138.6, 147.1, 147.7. IR (KBr): ν = 2943, 2862, 1581, 1458, 1423, 1384, 1246, 1138, 1096, 1058, 1003, 881, 831, 774, 723, 673 cm^{-1}. MS (FAB) *m/z*: 300 (100, M^+), 257 (93), 215 (24). Anal. Calcd for $C_{18}H_{21}ClSi$: C, 71.85; H, 7.03. Found: C, 71.58; H, 6.97.

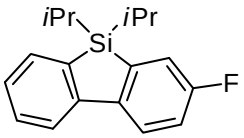
4-Chloro-9,9-diisopropyl-9-silafluorene (2w′)



Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC ($CHCl_3$). Yield: 15%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.03 (d, *J* = 7.6 Hz, 6H), 1.40 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.16 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.30 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.40–7.50 (m, 3H), 7.63 (d, *J* = 7.1 Hz, 1H), 8.91 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.1, 18.2, 126.1, 127.1, 127.5, 129.7, 130.9, 131.5, 133.16, 133.19, 137.1, 140.6, 144.4, 148.2. IR (neat): ν = 2941, 2889, 1587, 1462, 1445, 1424, 1398, 1130, 1097, 1080, 881, 783, 723, 646 cm^{-1}. MS (FAB) *m/z*: 300 (69, M^+), 257 (100), 215 (33).

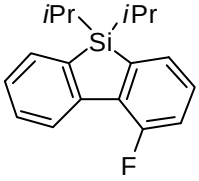
Anal. Calcd for $C_{18}H_{21}ClSi$: C, 71.85; H, 7.03. Found: C, 72.06; H, 7.01.

2-Fluoro-9,9-diisopropyl-9-silafluorene (2x)



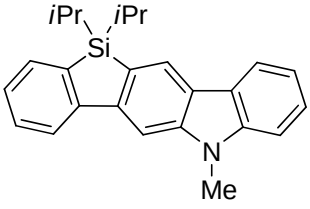
Purification: preparative TLC (hexane/AcOEt 10:1) followed by HPLC (hexane/AcOEt 10:1). Yield: 10%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.40 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.09 (ddd, *J* = 8.4, 8.4, 2.5 Hz, 1H), 7.23 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.42 (ddd, *J* = 7.6, 7.2, 1.6 Hz, 1H), 7.60 (dm *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6, 0.8 Hz, 1H), 7.77 (dd, *J* = 8.4, 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.2, 18.3, 116.6 (d, *J* = 22.1 Hz), 119.7 (d, *J* = 19.9 Hz), 120.4, 122.0 (d, *J* = 7.6 Hz), 126.6, 130.0, 133.5, 135.5, 139.0 (d, *J* = 5.4 Hz), 144.7 (d, *J* = 3.0 Hz), 147.9, 162.1 (d, *J* = 246.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –116.6. IR (neat): ν = 2943, 2889, 1574, 1465, 1433, 1255, 1194, 1128, 879, 773, 675, 628 cm^{-1}. MS (FAB) *m/z*: 284 (74, M^+), 241 (63), 213 (29), 199 (21), 165 (16). Anal. Calcd for $C_{18}H_{21}FSi$: C, 76.01; H, 7.44. Found: C, 76.03; H, 7.70.

4-Fluoro-9,9-diisopropyl-9-silafluorene (2x′)



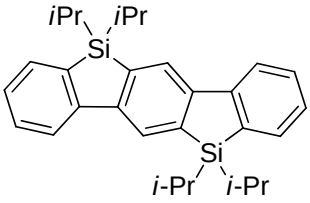
Purification: preparative TLC (hexane/AcOEt 10:1) followed by HPLC (hexane/AcOEt 10:1). Yield: 47%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.04 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.10 (dd, *J* = 12.3, 8.0 Hz, 1H), 7.20–7.25 (m, 1H), 7.27 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.44 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.1, 117.8 (d, *J* = 22.9 Hz), 125. 9 (d, *J* = 15.2 Hz), 126.9, 128.4 (d, *J* = 6.8 Hz), 128.8 (d, *J* = 3.1 Hz), 130.2, 133.1, 135.1 (d, *J* = 6.8 Hz), 136.0, 140.0, 146.4 (d, *J* = 4.6 Hz), 160.1 (d, *J* = 252.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –115.9 (d, *J* = 12.3 Hz). IR (neat): ν = 2942, 2864, 1585, 1566, 1462, 1435, 1222, 1190, 1130, 881, 721 cm^{-1}. MS (FAB) *m/z*: 284 (73, M^+), 241 (100), 213 (62), 199 (53), 165 (31). Anal. Calcd for $C_{18}H_{21}FSi$: C, 76.01; H, 7.44. Found: C, 76.13; H, 7.59.

6-Methyl-12,12-diisopropyl-*12H*-indololo[3,2-b][1]silafluorene (4)



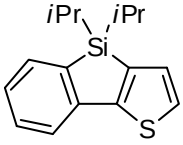
Purification: silica gel column chromatography (hexane/AcOEt 50:1). Yield: 33 %, a colorless solid. Mp: 148.4–149.6 °C. TLC: R_f 0.48 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.5 Hz, 6H), 1.10 (d, *J* = 7.3 Hz, 6H), 1.47 (qq, *J* = 7.5, 7.3 Hz, 2H) , 3.92 (s, 3H), 7.23–7.29 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.44–7.49 (m, 2H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.86 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.29 (d, *J* = 0.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.4, 29.1, 101.1, 108.3, 119.0, 119.9, 120.5, 122.6, 125.2, 125.36, 125.43, 126.7, 129.7, 133.5, 137.2, 141.3, 142.9, 146.8, 149.4. IR (KBr): ν = 2951, 2938, 2861, 1595, 1476, 1458, 1327, 1246, 1123, 1074, 882, 766, 752, 706, 675, 656, 486, 421 cm^{-1}. MS (FAB) *m/z*: 369 (100, M^+), 326 (71), 284 (25). HRMS Calcd for $C_{25}H_{27}NSi$: 369.1913 (M^+). Found: 369.1904.

5,5,11,11-tetraisopropyl-*5,11H*-benzosilolo[3,2-*c*]silafluorene(6)



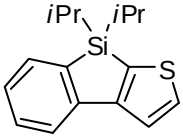
Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by HPLC (hexane/AcOEt 100:1). Yield: 77 %, a colorless solid. Mp: 203.0–203.8 °C. TLC: R_f 0.58 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, *J* = 7.3 Hz, 12H), 1.10 (d, *J* = 7.5 Hz, 12H), 1.44 (qq, *J* = 7.5, 7.3 Hz, 4H), 7.25 (dt, *J* = 7.1, 0.7 Hz, 2H) , 7.44 (dt, *J* = 7.5, 1.3 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 2H), 8.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.3, 18.4, 120.5, 125.4, 126.6, 129.8, 133.5, 136.2, 138.3, 147.4, 148.9. IR (KBr): ν = 2938, 2861, 1559, 1506, 1506, 1458, 1362, 1128, 1082, 990, 882, 767, 662, 642 cm^{-1}. MS (FAB) *m/z*: 454 (100, M^+), 411 (27), 369 (13). HRMS Calcd for $C_{30}H_{38}Si_2$: 454.2512 (M^+). Found: 454.2501.

4,4-Diisopropylthieno-*4H*-[3,2-*b*][1]benzosilole (8)



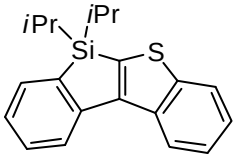
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 94%, a colorless solid. Mp: 34.5–35.2 °C. TLC: R_f 0.50 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.06 (d, *J* = 7.2 Hz, 6H), 1.36 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.11 (d, *J* = 4.8 Hz, 1H), 7.16 (d, *J*= 7.6, 7.6, 1.2 Hz, 1H), 7.30 (d, *J* = 4.8 Hz, 1H), 7.34 (ddd, *J* = 8.0, 7.6, 1.2 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.3, 18.4, 120.5, 125.9, 126.1, 129.5, 129.8, 133.2 (2C), 137.6, 144.6, 157.0. IR (KBr): ν = 3061, 2939, 2862, 1587, 1462, 1384, 1184, 1122, 1062, 991, 879, 796, 761, 717, 669, 644 cm^{-1}. MS (FAB) *m/z*: 272 (47, M^+), 229 (73), 201 (100), 187 (47), 171 (7). Anal. Calcd for $C_{16}H_{20}SSi$: C, 70.53; H, 7.40. Found: C, 70.24; H, 7.51.

8,8-Diisopropylthieno-*8H*-[2,3-*b*][1]benzosilole (10)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 95%, a colorless solid. Mp: 43.5–44.3 °C. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.06 (d, *J* = 7.2 Hz, 6H), 1.37 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.16 (ddd, *J* = 7.2, 7.2, 0.8 Hz, 1H), 7.36 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.48 (d, *J* = 4.6 Hz, 1H), 7.52–7.54 (m, 2H), 7.68 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.15, 18.18, 120.8, 121.5, 125.6, 129.8, 132.0, 133.5, 135.1, 138.2, 145.5, 157.8. IR (KBr): ν = 2942, 2862, 1587, 1460, 1439, 1379, 1128, 1093, 1001, 987, 879, 775, 715, 677, 644, 601 cm^{-1}. MS (FAB) *m/z*: 272 (100, M^+), 229 (73), 201 (51), 187 (19), 171 (3). Anal. Calcd for $C_{16}H_{20}SSi$: C, 70.53; H, 7.40. Found: C, 70.36; H, 7.38.

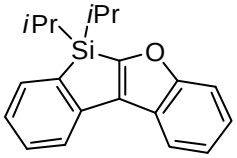
9,9-Diisopropyl-9*H*-[1]benzosilolo[2,3-*b*][1]benzothiophene (12)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 93%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.09 (d, *J* = 7.2 Hz, 6H), 1.43 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.23 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.37 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.44–7.49 (m, 2H), 7.58 (dm, *J* = 7.2 Hz, 1H), 7.94 (dm, *J* = 7.2 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 18.11, 18.14, 121.2, 122.7, 123.2, 123.9, 124.3, 125.5, 129.8, 133.4, 135.7, 137.0, 138.4, 146.6, 148.6, 150.0. IR (KBr): ν = 3051, 2941, 2926,

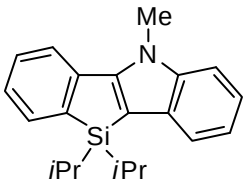
2862, 1583, 1460, 1346, 1082, 989, 879, 775, 732, 667 cm^{-1}. MS (FAB) *m/z*: 322 (100, M^+), 307 (13), 279 (30), 251 (23), 237 (13). Anal. Calcd for $C_{20}H_{22}SSi$: C, 74.48; H, 6.88. Found: C, 74.31; H, 7.12.

10,10-Diisopropyl-10*H*-[1]benzosilolo[2,3-*b*][1]benzofuran (14)



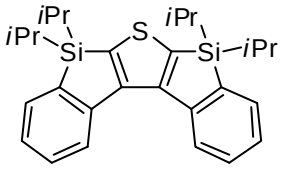
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 85%, a colorless oil. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.11 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.47 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.19 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.30–7.35 (m, 2H), 7.44 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.49 (dm, *J* = 7.6 Hz, 1H), 7.56–7.58 (m, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.92–7.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 18.2, 18.3, 112.1, 120.1, 121.1, 122.7, 123.9, 124.3, 125.7, 129.9, 133.6, 135.5, 139.8, 142.9, 162.4, 164.4. IR (KBr): ν = 2943, 2864, 1593, 1501, 1460, 1371, 1222, 1192, 1010, 964, 878, 808, 771, 750, 675 cm^{-1}. MS (FAB) *m/z*: 306 (100, M^+), 263 (31), 235 (18), 221 (13). Anal. Calcd for $C_{20}H_{22}OSi$: C, 78.38; H, 7.24. Found: C, 78.52; H, 7.48.

10,10-Diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-*b*][1]indole (16)



Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 56%, a colorless solid. Mp: 122.6–123.7 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.13 (s, 3H), 7.13 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.18–7.24 (m, 2H), 7.35–7.39 (m, 2H), 7.56–7.60 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.8, 32.3, 108.4, 109.4, 120.0, 120.1, 121.3, 122.1, 126.0, 129.1, 130.5, 133.7, 142.1, 142.28, 142.32, 153.3. IR (KBr): ν = 2937, 2887, 2860, 1583, 1462, 1398, 1329, 1282, 1130, 1068, 974, 879, 821, 773, 680, 634 cm^{-1}. MS (FAB) *m/z*: 319 (100, M^+), 276 (13), 248 (11), 234 (10), 218 (6). Anal. Calcd for $C_{21}H_{25}NSi$: C, 78.94; H, 7.89. Found: C, 78.89; H, 8.16. CCDC–697662 contains the crystallographic data for **16**.

5,5,7,7-Tetraisopropylbisbenzosilolo[2,3-*b*:2',3'-*d*]thiophene (18)



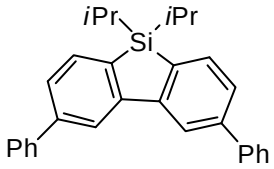
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 85%, a colorless solid. Mp: 119.8–121.0 °C. TLC: R_f 0.50 (hexane/AcOEt 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 12H), 1.08 (d, *J* = 7.2 Hz, 12H), 1.38 (qq, *J* = 7.2, 7.2 Hz, 4H), 7.19 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.40 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H), 7.56 (dd, *J* = 7.2, 1.2 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.2, 123.2, 125.2, 129.3, 133.7, 139.8, 146.5, 147.1, 153.3. IR (KBr): ν = 2939, 2885, 2860, 1583, 1456, 1435, 1363, 1278, 1132, 1076, 1047, 986, 881, 763, 684, 673, 623 cm^{-1}. MS (FAB) *m/z*: 461 (100, M^++1), 417 (66), 389 (15), 375 (14). Anal. Calcd for $C_{28}H_{36}SSi_2$: C, 72.98; H, 7.87. Found: C, 73.05; H, 7.82. CCDC–698962 contains the crystallographic data for **18**.

Nickel-catalyzed cross coupling reaction of 2n with PhMgBr

An oven-dried 3-mL vial equipped with a magnetic stir bar and a rubber septum was

charged with **2n** (65 mg, 0.2 mmol) and PhMgBr (3.00 M in THF, 0.70 mL, 2.0 mmol). After THF was removed in vacuo, diethoxymethane (2 mL) was added to the vial. The tube was moved into a glove box and was added $NiCl_2(PCy_3)_2$ (14 mg, 0.020 mmol) and PCy_3 (11 mg, 0.040 mmol). The mixture was heated at 100 °C on a hot plate for 24 h. The resulting mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give **19**.

9,9-Diisopropyl-3,6-diphenyl-9-silafluorene (19)



Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 84%, a colorless solid. Mp: 51.1–52.0 °C. TLC: R_f 0.45 (hexane/AcOEt 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (d, *J* = 7.2 Hz, 12H), 1.45 (sep, *J* = 7.2 Hz, 2H), 7.38 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.46–7.52 (m, 6H), 7.68–7.71 (m, 6H), 8.10 (d, *J* = 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.4, 119.6, 126.1, 127.2, 127.3, 128.6, 133.9, 135.2, 141.4, 142.8, 149.3. IR (KBr): ν = 3057, 3026, 2937, 2860, 1597, 1541, 1460, 1383, 1244, 1074, 882, 760, 696, 677 cm^{-1}. MS (FAB) *m/z*: 418 (66, M^+), 375 (100), 347 (46), 333 (23), 317 (19), 259 (17). Anal. Calcd for $C_{30}H_{30}Si$: C, 86.07; H, 7.22. Found: C, 85.97; H, 7.32.

Data of X-ray crystallographic analysis

Crystallographic data for **2r**, **4**, and **6** are listed in Table 8.

Table 8. Crystallographic data for **2r**, **4**, and **6**.

Compound	**2r**	**4**	**6**
Empirical formula	$C_{31}H_{30}N_2Si$	$C_{25}H_{27}NSi$	$C_{30}H_{38}Si_2$
Formula weight	458.66	369.57	454.78
Temperature (K)	300(2)	300(2)	300(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$
a (Å)	8.4497(7)	7.7183(6)	12.018(3)
b (Å)	13.2197(10)	14.9962(12)	7.7566(17)
c (Å)	23.800(2)	36.785(3)	15.289(4)
α (°)	90	90	90
β (°)	95.9840(10)	90	108.540(4)
γ (°)	90	90	90
Volume ($Å^3$)	2644.0(4)	4257.7(6)	1351.3(5)
Z	4	8	2
Density (calculated) (Mg/m^3)	1.152	1.153	1.118
Absorption coefficient (mm^{-1})	0.110	0.119	0.146
F(000)	976	1584	492
Reflection collected	14091	21208	7111
Independent reflections	4890	3963	2521
Goodness-of-fit on F^2	1.100	1.096	1.084
Data/restraints/parameters	4890/24/311	3963/12/249	2521/0/149
Final R indices [$I>2\sigma(I)$]			
R_1	0.0724	0.0577	0.0549
wR_2	0.2307	0.1541	0.1623
R indices (all data)			
R_1	0.0845	0.0662	0.0605
wR_2	0.2492	0.1593	0.1685

Reference

(1) (a) Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1698. (b) Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211. (c) Echavarren, A. M.; Gómez-Lor, B.; González, J. J.; de Frutos, Ó. *Synlett* **2003**, 0585. (d) Kakiuchi, F.; Chatani, N. *Advanced Synthesis & Catalysis* **2003**, *345*, 1077. (e) Campeau, L.-C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (f) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (g) Pascual, S.; Mendoza, P. d.; Echavarren, A. M. *Organic & Biomolecular Chemistry* **2007**, *5*, 2727. (h) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200. (i) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094. (j) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (k) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447.

(2) (a) Liu, Z.; Larock, R. C. *Org. Lett.* **2004**, *6*, 3739. (b) Campeau, L.-C.; Parisien, M.; Leblanc, M.; Fagnou, K. *J. Am. Chem. Soc.* **2004**, *126*, 9186. (c) Campeau, L.-C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857. (d) Bedford, R. B.; Betham, M. *J. Org. Chem.* **2006**, *71*, 9403. (e) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581. (f) Garcia-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066.

(3) (a) Coutant, R. W.; Levy, A. *J. Organomet. Chem.* **1967**, *10*, 175. (b) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Shamshin, L. N.; Mosin, A. M. *Zh. Obshch. Khim.* **1985**, *55*, 2309. (c) Chernyshev, E. A.; Komalenkova, N. G.; Elagina, O. V.; Rogachevskii, V. L.; Bashkirova, S. A.; Dunaeva, L. V. *Zh. Obshch. Khim.* **1985**, *55*, 2314.

(4) (a) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701. (b) Dyke, A. M.; Hester, A. J.; Lloyd-Jones, G. C. *Synthesis* **2006**, *2006*, 4093. (c) Yoshida, H.; Honda, Y.; Hiyama, T.; Shirakawa, E. *Chem. Commun.* **2001**, 1880. (d) Yoshida, H.; Shirakawa, E.; Honda, Y.; Hiyama, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 3247.

(5) (a) Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975. (b) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis* **2002**, 1454.

(6) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.

(7) Dankwardt, J. W. *Angew. Chem. Int. Ed.* **2004**, *43*, 2428.

(8) Ponce, B.; Cabrerizo, F.; Bonesi, S.; Erra-Balsells, R. *Helv. Chim. Acta* **2006**, *89*, 1123.

Chapter 3

Photophysical Properties of D-π-A type Silafluorenes

Introduction of electron-donating and -withdrawing groups at 2,7-positions of silafluorene induces bathochromic shift of UV-absorption and fluorescence spectra drastically. Remarkably, the emission color can be tuned from blue to red by choosing appropriate donor and acceptor substituents at 2,7-positions. Furthermore, emission color was found dependent on not only the dissolving solvent but also polymers dispersing the silafluorenes. Introduction of bulky substituent such as diphenylamino group improves efficiency of solid state fluorescence.

1. Introduction

Silicon-bridged biaryls represented by 9-silafluorenes have recently been the subject of growing interest as components of light emitting materials, field effect transistors, host materials for electroluminescent devices, and solar cells.[1] The examples are shown in Chart 1.

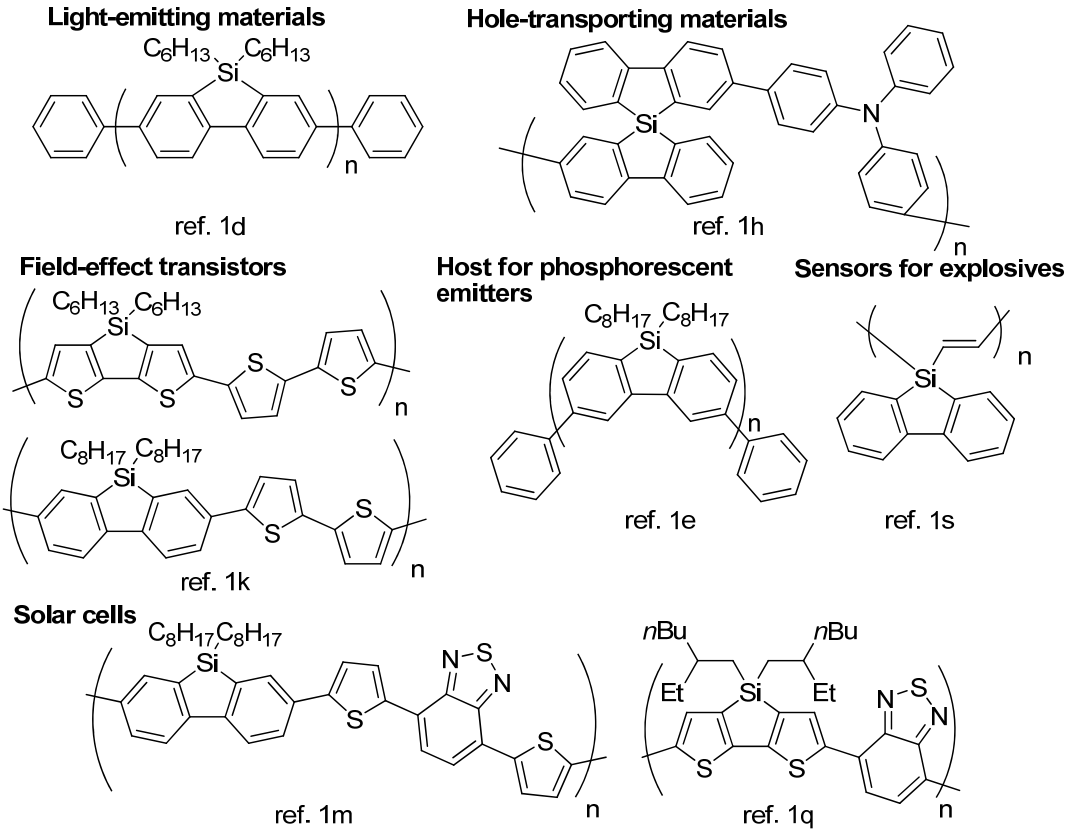
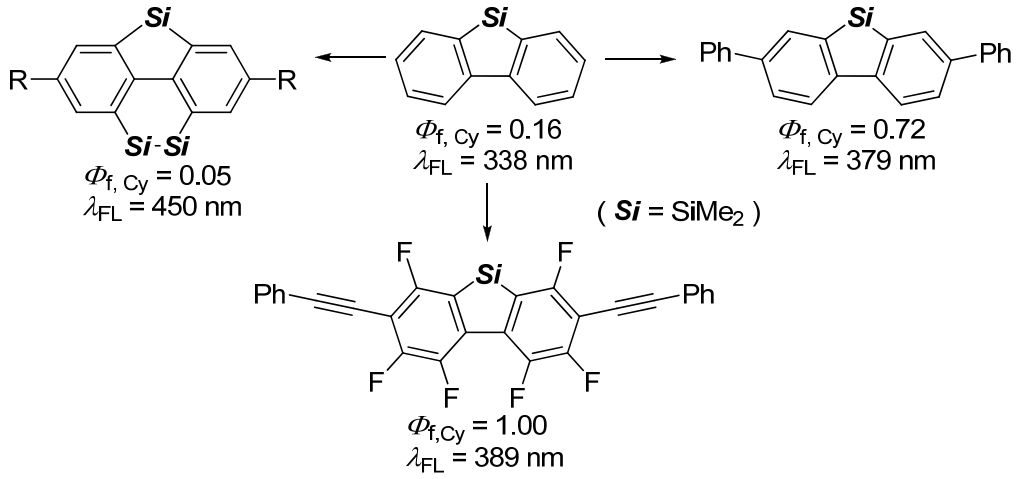


Chart 1. Organic functional materials consisting of silicon-bridged biaryl modules.

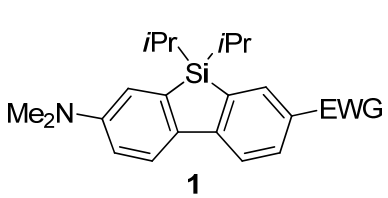
As readily seen in Chart 1, the present research for applications to opto-electronic devices focuses on silafluorene polymers and oligomers. However basic research on properties of 9-silafluorenes remains yet to be studied except for those of 9,9-dialkyl and 9,9-diphenylsilafluorenes with no substituent on the aromatic moieties.[2] Recently, Shimizu and Hiyama revealed that introduction of a disilylene-bridge at 4,5-position to 9-silafluorene induced bathochromic shift of absorption and fluorescence, giving rise to blue emission.[1t] In addition, 2,7-diphenyl-9,9-dimethyl-9-silafluorene was found to exhibit purple emission with quantum yield of 0.72, which was higher than that of 9-silafluorene.[1t] Tilley reported that 2,7-bis(phenylethynyl)hexafluorosilafluorene

exhibits purple emission with excellent quantum yield.[3] In view that unsubstituted 9,9-dimethyl-9-silafluorene did not emit in visible region, it is noteworthy that these substituted silafluorenes emit purple to blue light as a single molecular component of emitting materials.



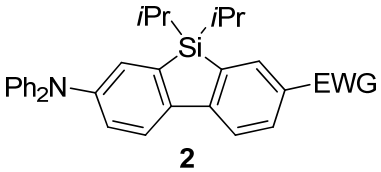
Meanwhile, introduction of an electron donor (D) at the one end of the conjugated system and an electron acceptor (A) at the other end, so called D-π-A system, is effective for attaining outstanding optical and electronic properties[4] and hence the D-π-A type molecular design has been applied to nonlinear optics (NLOs),[5] light emitting materials,[6] and solar cells.[7] However, D-π-A type silafluorene has not attracted much attention as a component of organic opto-electronic materials to date probably because difficulty in preparing D-π-A type silafluorenes.

Discussed in this Chapter are the synthesis, photophysical properties, and theoretical calculations on 2-donor-7-acceptor disubstituted 9-silafluorenes **1**-**2**.



1

EWG
1a: H
1b: CF_3
1c: CN
1d: CHO
1e: $CHC(CN)_2$

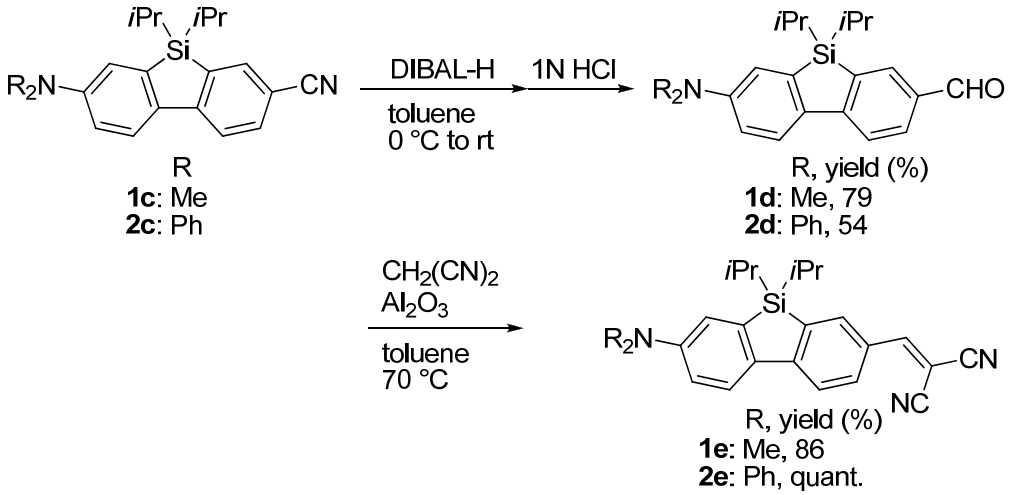


2

EWG
2c: CN
2d: CHO
2e: $CHC(CN)_2$

2. Synthesis

Silafluorenes **1a**-**1c** and **2c** were prepared by the intramolecular direct arylation of 2-(3-aminophenylsilyl)aryl triflates discussed in Chapter 2. Reduction of cyano group of **1c** and **2c** with DIBAL-H gave 2-amino-7-formyl-silafluorenes **1d** and **2d**, respectively. Furthermore, Knoevenagel condensation reaction of formyl products **1d** and **2d** with malononitrile proceeded smoothly to give dicyanoethenyl products **1e** and **2e** in high yields, respectively (Scheme 1).



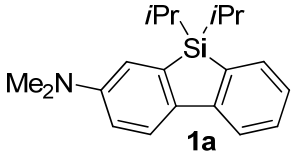
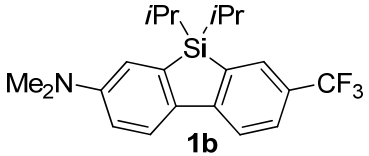
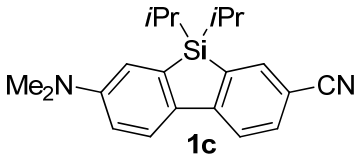
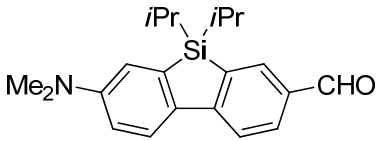
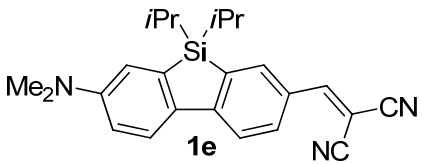
Scheme 1. Synthesis of **1d**, **1e**, **2d**, and **2e**.

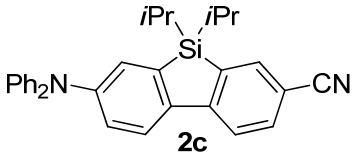
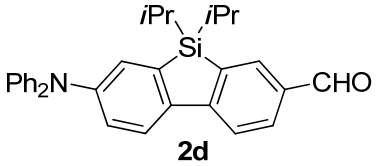
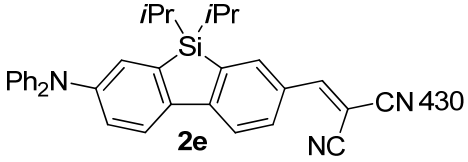
3. Results and Discussions

3-1. Photophysical properties of D-π-A type silafluorenes in solution

The structure and photophysical properties of **1** and **2** measured in various solvents are summarized in Table 1.

Table 1. Photophysical properties of **1** and **2**.[a,b]

Compd	Ex. (nm)[c]		cyclohexane	benzene	Et_2O	dioxane	CH_2Cl_2	EtOH	CH_3CN	DMSO
		ε_r[d]	2.0	2.3	4.3	2.2	9.1	24	37	47
 **1a**	290	$\lambda_{abs,max}$ / nm	323	323	318	320	323	319	321	324
		ε / $M^{-1}cm^{-1}$	17100	23800	32100	25900	17100	23900	23400	22700
		$\lambda_{FL,max}$ / nm	397	404	406	406	410	405	418	424
		Φ_f	0.26	0.22	0.22	0.37	0.13	0.11	0.28	0.12
 **1b**	290	$\lambda_{abs,max}$ / nm	331	338	334	336	338	335	337	344
		ε / $M^{-1}cm^{-1}$	24600	23400	26700	31200	24300	22500	23100	22400
		$\lambda_{FL,max}$ / nm	402	410	410	417	423	422	440	451
		Φ_f	0.37	0.29	0.35	0.25	0.33	0.28	0.40	0.17
 **1c**	320	$\lambda_{abs,max}$ / nm	357	360	358	357	368	360	360	375
		ε / $M^{-1}cm^{-1}$	28700	16100	28900	21400	28200	26300	26500	19600
		$\lambda_{FL,max}$ / nm	410	422	423	425	442	456	464	473
		Φ_f	0.60	0.62	0.66	0.67	0.79	0.74	0.65	0.51
 **1d**	320	$\lambda_{abs,max}$ / nm	390	392	384	384	397	395	391	400
		ε / $M^{-1}cm^{-1}$	32900	32300	35200	35200	27100	25400	28200	25900
		$\lambda_{FL,max}$ / nm	414	450	449	449	501	565	528	541
		Φ_f	0.08	0.75	0.79	0.79	0.71	0.40	0.81	0.60
 **1e**	390	$\lambda_{abs,max}$ / nm	480	480	469	466	489	489	475	488
		ε / $M^{-1}cm^{-1}$	54800	50000	40700	32400	38300	38300	33700	28200
		$\lambda_{FL,max}$ / nm	509	566	584	585	644	644	694	714
		Φ_f	0.08	0.36	0.56	0.47	0.56	0.56	0.32	0.23

 **2c**	390	$\lambda_{abs,max}$ / nm	391	389	383	385	388	385	381	387
		ε / $M^{-1}cm^{-1}$	29300	27900	28900	25200	28600	26200	29500	26500
		$\lambda_{FL,max}$ / nm	413	432	436	441	470	482	500	500
		Φ_f	0.64	0.75	0.74	0.81	0.80	0.72	0.67	0.81
 **2d**	390	$\lambda_{abs,max}$ / nm	403	398	393	394	401	396	392	398
		ε / $M^{-1}cm^{-1}$	35800	31700	30546	30000	27800	25400	28000	27300
		$\lambda_{FL,max}$ / nm	425	456	459	464	524	482	555	557
		Φ_f	0.50	0.77	0.76	0.81	0.80	0.11	0.48	0.58
 **2e**	430	$\lambda_{abs,max}$ / nm	484	477	467	465	481	467	461	466
		ε / $M^{-1}cm^{-1}$	44600	36800	35300	37000	30500	36800	31300	30800
		$\lambda_{FL,max}$ / nm	515	564	586	567	674	-[e]	-[e]	-[e]
		Φ_f	0.46	0.69	0.80	0.76	0.43	-[e]	-[e]	-[e]

[a] Measured at 1×10^{-5} M. [b] Absolute quantum yield determined by a calibrated integrating sphere system. [c] Excitation wavelength [d] Dielectric constant. [e] No fluorescence was observed.

UV absorption spectra of **1a**-**1e** measured in cyclohexane are shown in Figure 1. These D-π-A type silafluorenes exhibited a bathochromic shift drastically in the absorption maxima when electron-withdrawing nature of the acceptor (A) increased.

Normalized fluorescence spectra of **1** measured in cyclohexane are shown in Figure 2. As well as the absorption spectra, the emission maxima of **1a**-**1e** red-shifted in the order of electron-withdrawing nature of the acceptor: **1a** (397 nm) < **1b** (402 nm) < **1c** (410 nm) < **1d** (414 nm) < **1e** (509 nm). Quantum yields of fluorescence are also dependent on the acceptor group. In particular, quantum yield of cyano-substituted silafluorene **1c** reaches 0.60, while those of **1d** and **1e** are low.

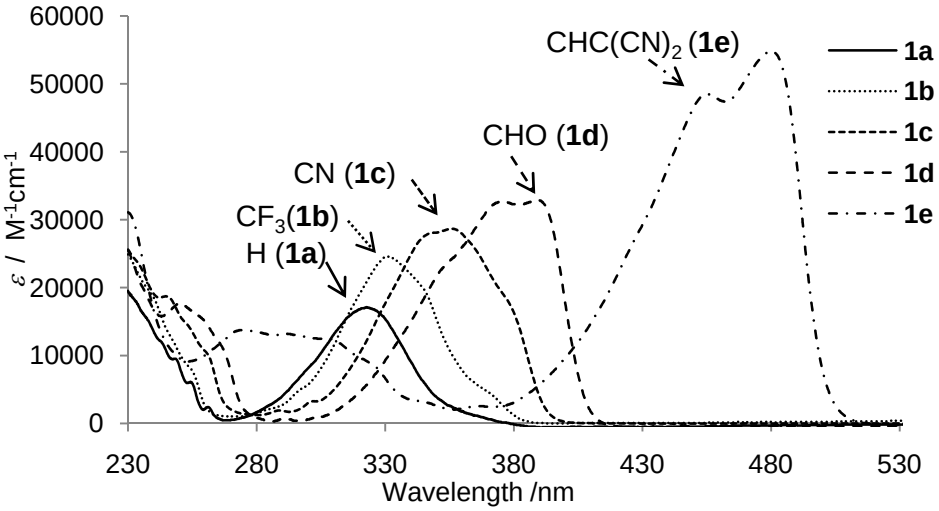


Figure 1. UV absorption spectra of **1** in cyclohexane.

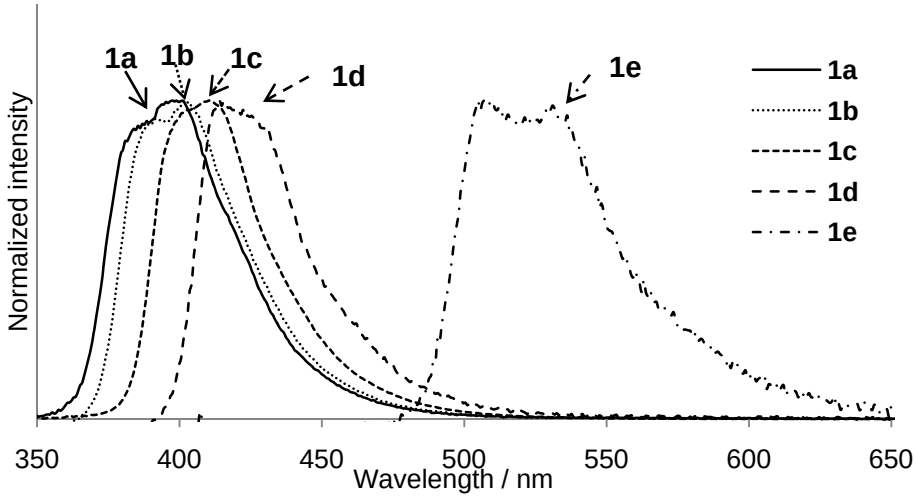


Figure 2. Normalized fluorescence spectra of **1** in cyclohexane (excited at 290 nm for **1a** and **1b**, 320 nm for **1c** and **1d**, and 390 nm for **1e**).

Furthermore, emission maxima and fluorescence quantum yield of **1d** were found highly dependent on solvents. Thus, use of benzene, Et_2O, dioxane, CH_2Cl_2, EtOH, CH_3CN, and DMSO in place of cyclohexane induced red-shift of the emission maxima (Figure 3). The red-shift of the emission maxima becomes larger as the polarity of the solvent increased. In addition, quantum yields measured in Et_2O and dioxane reach 0.79. These phenomena can be understood in terms that polar solvents stabilize charge-transfer exited states of D-π-A type silafluorenes.

As opposed to remarkable fluorescence solvatochromism of **1d**, solvent effect in UV absorption spectra is quite small. In fact, absorption maxima measured in DMSO red-shifted by only 10 nm compared with that measured in cyclohexane (Figure 4).

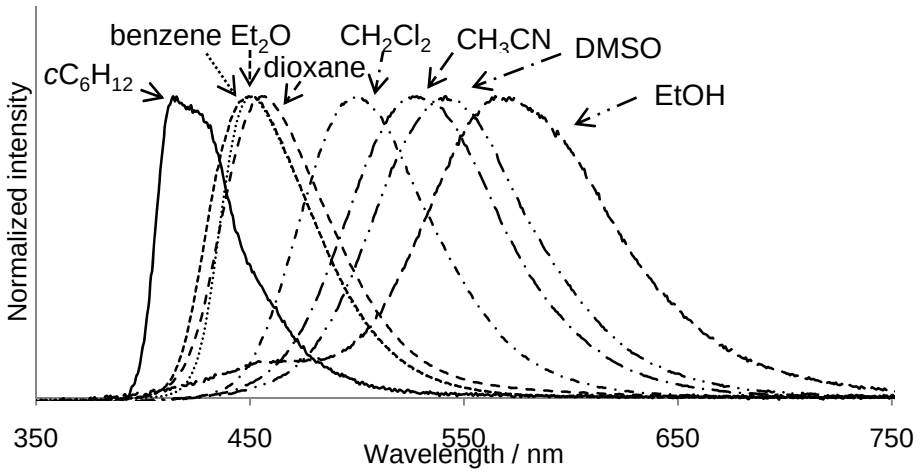


Figure 3. Solvatochromism of fluorescence spectra of **1d** (excited at 320 nm).

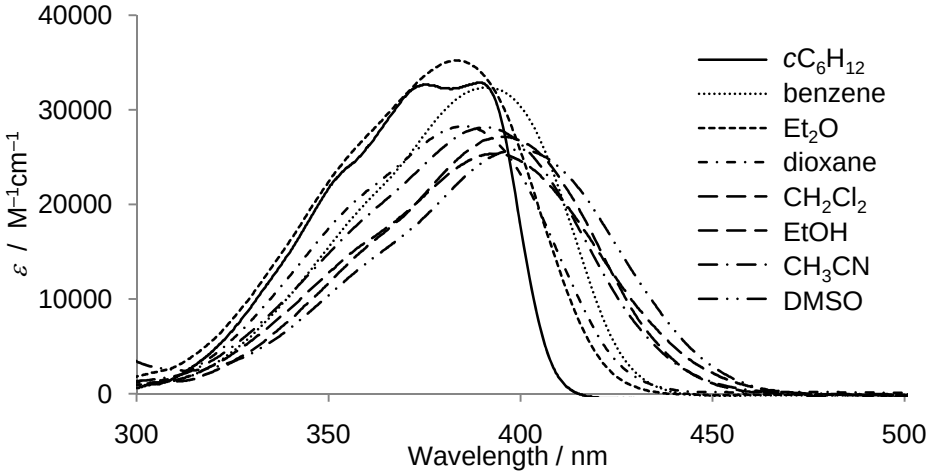


Figure 4. UV absorption spectra of **1d** in various solvents.

Fluorescence maxima of **1**-**2** measured in cyclohexane and CH_2Cl_2 are plotted in Figure 5. Difference of fluorescence maxima between those measured in cyclohexane and CH_2Cl_2 apparently increased as electron-withdrawing nature of acceptor become stronger. As well as **1d**, formyl-substituted silafluorene **2d** and dicyanoethenyl-substituted silafluorenes **1e** and **2e** exhibited the remarkable fluorescence solvatochromism. In addition, quantum yields of **1e**, **2d** and **2e** increased when measured in polar solvents such as dioxane and CH_2Cl_2 and solvent effects in UV absorption spectra of **1e**, **2d**, and **2e** are quite small.

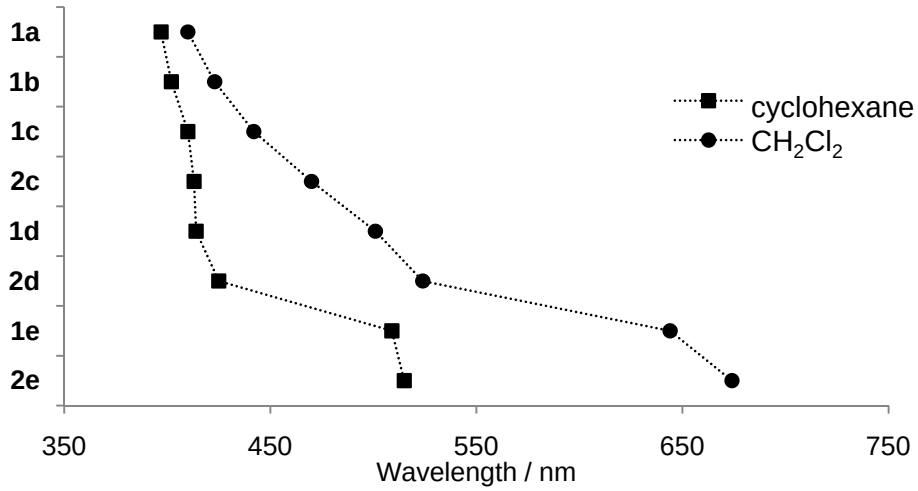


Figure 5. Fluorescence maxima of **1** and **2** in cyclohexane and CH_2Cl_2.

3-2. Fluorescence lifetime study

In addition, fluorescence lifetimes (τ_s) of **1**-**2** were measured and the results are summarized in Table 2. On the basis of fluorescence quantum yield Φ_f and fluorescence lifetime τ_s, the author calculated radiative and non-radiative decay rate constants from the singlet excited states, based on Eqs. (1) and (2). Radiative rate constant k_f for all compounds in cyclohexane and CH_2Cl_2 were similar value. On the other hand, non-radiative rate constants k_n are highly solvent dependent. In particular, non-radiative rate constants of **1d** ($k_n = 2.7 \times 10^9\ s^{-1}$) and **1e** ($k_n = 2.9 \times 10^9\ s^{-1}$) in cyclohexane was about 28-fold and 21-fold as compared with those in CH_2Cl_2, respectively. These phenomena suggest an additional radiationless channel is

operating only in a nonpolar solvent. Similar conclusion is drawn with that of 2-cyano-7-(dimethylamino)fluorene.[9]

$$k_f = \Phi_f / \tau, \quad (1)$$

$$k_n = (1 - \Phi_f) / \tau, \quad (2)$$

Table 2. Fluorescence lifetimes (τ_s), radiative rate constants (k_f), and non-radiative rate constants for **1** and **2**.

Compd	Solvent	Φ_f	τ_s (ns)	k_f ($10^7 s^{-1}$)	k_n ($10^7 s^{-1}$)
1a[a]	cyclohexane	0.26	6.5	4.0	11
	CH_2Cl_2	0.13	4.0	3.3	22
1b[a]	cyclohexane	0.37	3.3	11	19
	CH_2Cl_2	0.33	2.5	13	27
1c[b]	cyclohexane	0.60	2.6	23	16
	CH_2Cl_2	0.79	2.6	31	8.1
1d[b]	cyclohexane	0.08	0.3	24	270
	CH_2Cl_2	0.71	3.0	24	9.7
1e[c]	cyclohexane	0.08	0.3	25	290
	CH_2Cl_2	0.56	3.2	18	14

[a] Excited at 340 nm. [b] Excited at 388 nm. [c] Excited at 474 nm.

3-3. Solid states fluorescence of D-π-A type silafluorenes.

Silafluorenes **1** and **2** emitted fluorescence in a doped polymer film and in such solid states as neat thin film and microcrystal as summarized in Table 3.

Fluorescence spectra of **1** and **2** in microcrystals are shown in Figure 6. As observed in fluorescence spectra measured in solution, the emission maxima of them red-shifted in the order of **1a** (406 nm) < **1b** (432 nm) < **1c** (464 nm) < **2c** (473 nm) < **1d** (414 nm) < **2d** (500 nm) < **2e** (617 nm). Quantum yields of these compounds were generally low; fluorescence of **1e** was not observed. However, replacement of the dimethylamino group in **1e** by a diphenylamino group (**2e**) improves efficiency of solid state fluorescence, resulting red emission in a higher quantum yield (Φ_f = 0.36). It may be attributed to the bulky diphenyl amino group which prevents intermolecular interaction such as π–π stacking that leads to quenching of emission.

Table 3. Photophysical properties of **1** and **2** in solid states.[a]

Compd	Ex. (nm)[b]		PS[c]	PMMA[d]	PAN[e]	PEG[f]	thin-film	microcrystal
1a	290	$\lambda_{FL,max}$ / nm	402	404	404	418	403	406
		Φ_f	0.47	0.45	0.10	0.27	0.30	0.26
1b	290	$\lambda_{FL,max}$ / nm	409	416	417	417	417	432
		Φ_f	0.26	0.37	0.39	0.39	0.39	0.33
1c	320	$\lambda_{FL,max}$ / nm	422	434	446	460	457	464
		Φ_f	0.65	0.66	0.34	0.28	0.25	0.22
1d	320	$\lambda_{FL,max}$ / nm	455	472	501	512	515	485
		Φ_f	0.76	0.76	0.31	0.21	0.06	0.12
1e	390	$\lambda_{FL,max}$ / nm	573	607	644	671	-[g]	-[g]
		Φ_f	0.48	0.61	0.14	0.08	-[g]	-[g]
2c	390	$\lambda_{FL,max}$ / nm	447	446	465	467	461	473
		Φ_f	0.83	0.82	0.48	0.71	0.39	0.26
2d	390	$\lambda_{FL,max}$ / nm	454	469	501	523	503	500
		Φ_f	0.82	0.80	0.31	0.57	0.31	0.14
2e	430	$\lambda_{FL,max}$ / nm	573	594	627	656	665	617
		Φ_f	0.78	0.80	0.08	0.22	0.33	0.36

[a] Absolute quatum yield determined by a calibrated integrating sphere system. [b] Excited wavelength. [c] Dispersed in polystyrene (PS). [d] Dispersed in poly(methyl methacrylate) (PMMA). [e] Dispersed in polyacrylonitrile (PAN). [f] Disperesed in poly(ethylene glycol) (PEG). [g] No fluorescence was observed.

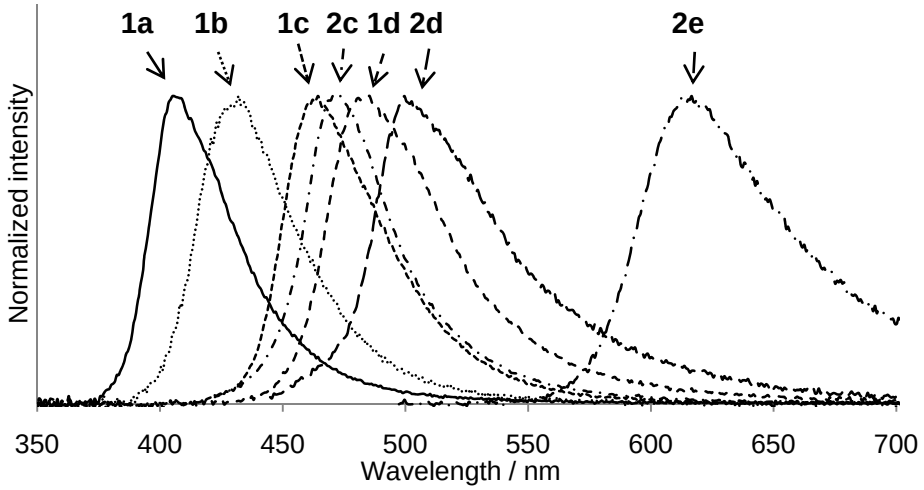


Figure 6. Fluorescence spectra of **1** and **2** in the microcrystal (excited at 290 nm for **1a** and **1b**, 320 nm for **1c** and **1d**, 390 nm for **2c** and **2d**, and 430 nm for **2e**).

It is noteworthy that emission maxima of **1d** is highly dependent on polarity of polymer (Figure 7). In proportion to polarity of polymer, emission maxima drastically red-shifted in the order of PS (455 nm) < PMMA (472 nm) < PAN (501 nm) < PEG (512 nm).

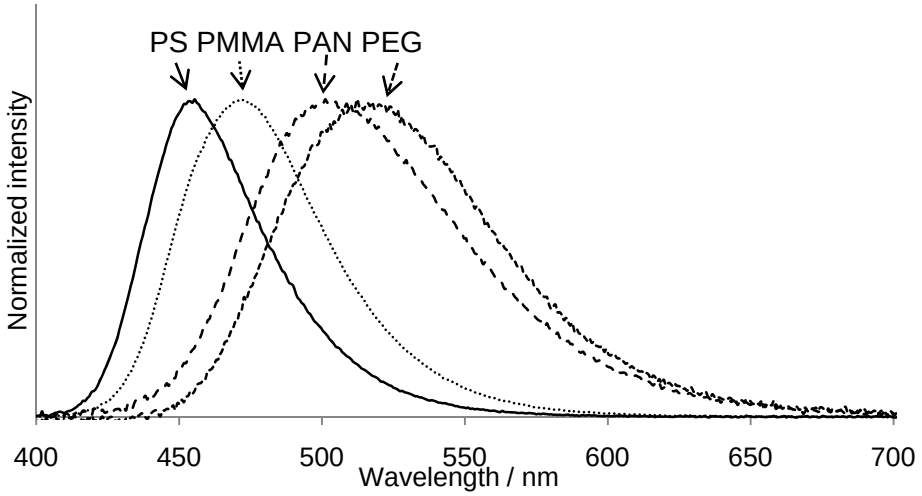


Figure 7. Fluorescence spectra of **1d** in doped polymer film (excited at 320 nm).

In addition, **1e**, **2d**, and **2e** exhibit similar polymer effects (Figure 8). The red-shift of fluorescence maxima apparently increased as an electron-withdrawing nature of an acceptor becomes stronger, suggesting that charge-transfer excited states can be stabilized by polar polymer. Mostly, use of PMMA resulted in more efficient emission than use of PS, PAN, and PEG. In particular, quantum yields of diphenylamino-substituted silafluorenes **2c**, **2d**, and **2e** in doped PMMA film was 0.82, 0.80, and 0.80, respectively.

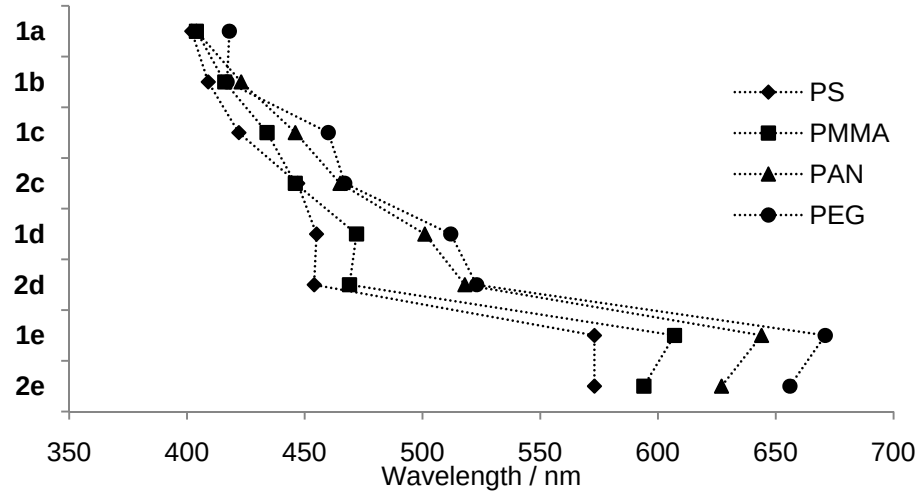


Figure 8. Comparison of fluorescence maxima of **1** and **2** in doped polymer film.

Furthermore, spin-coated film was prepared from a mixture of **1c**, **1d**, and **1e** in a ratio **1c** : **1d** : **1e** = 66 : 83 : 1 in saturated benzene solution of PMMA. This film showed a white emission with CIE coordinates of (0.33, 0.33) (Figure 9), which corresponds to pure white light. Worth noting is the fact that this film exhibited the high quantum yield of 0.60.

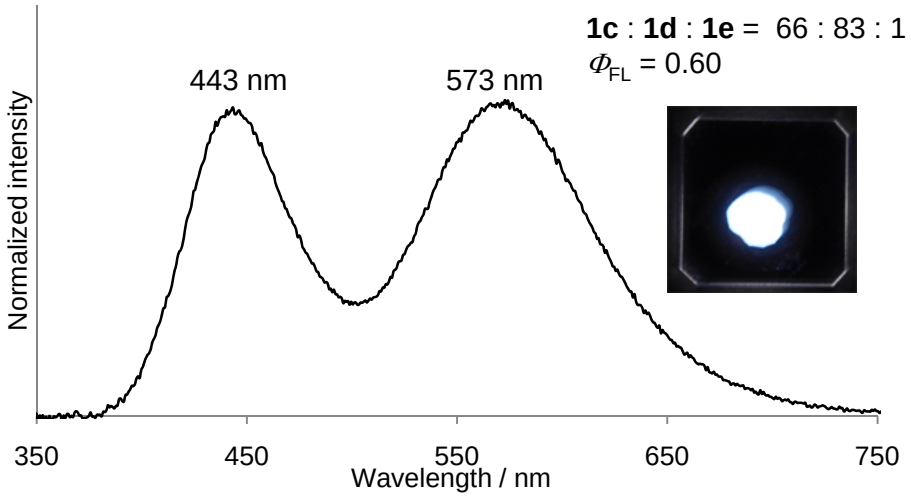


Figure 9. Fluorescence spectra of **1c**-**1e** in doped PMMA film (excited at 320 nm).

3-4. Photophysical properties of carbon analogue

To study the effect of a silicon-bridge in silafluorene, the author prepared the corresponding D-π-A type fluorenes **3**. Photophysical properties of **3b**, **3d**, and **3e** are summarized in Tables 4 and 5.

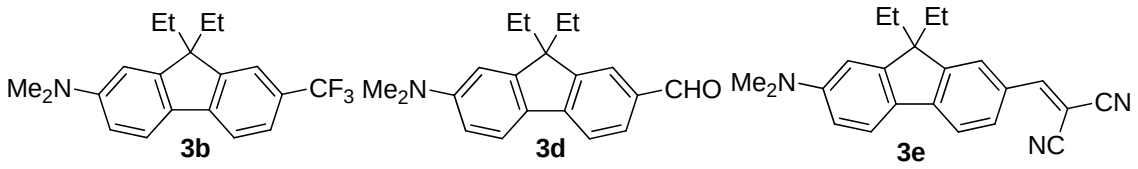


Table 4. Photophysical properties of **3** in various solvents.[a,b]

Compd	Ex. (nm)		cyclohexane	benzene	Et_2O	dioxane	CH_2Cl_2	EtOH	CH_3CN	DMSO
		ε_r[c]	2.0	2.3	4.3	2.2	9.1	24	37	47
3b	300	$\lambda_{abs,max}$ / nm	341	346	342	303	344	342	302	350
		ε / $M^{-1}cm^{-1}$	27600	25700	30218	18300	25200	25400	13200	27700
		$\lambda_{FL,max}$ / nm	360	374	373	376	387	388	337	414
		Φ_f	0.67	0.59	0.63	0.07	0.44	0.58	0.04	0.53
3d	360	$\lambda_{abs,max}$ / nm	385	388	379	382	392	388	385	395
		ε / $M^{-1}cm^{-1}$	40700	31600	35300	35300	33000	20400	33700	30600
		$\lambda_{FL,max}$ / nm	416	437	436	446	491	562	521	532
		Φ_f	0.02	0.82	0.71	0.87	0.91	0.64	0.81	0.92
3e	390	$\lambda_{abs,max}$ / nm	480	480	470	468	490	478	474	490
		ε / $M^{-1}cm^{-1}$	58800	39300	39300	33200	39300	37900	37500	17600
		$\lambda_{FL,max}$ / nm	528	560	579	581	631	677	688	711
		Φ_f	0.04	0.22	0.39	0.33	0.62	0.18	0.26	0.24

[a] Measured at 1×10^{-5} M. [b] Absolute quantum yield determined by a calibrated integrating sphere system. [c] Dielectric constant.

Table 5. Photophysical properties of **3** in doped polymer film and solid states.[a]

Compd	Ex. (nm)[b]		PS[c]	PMMA[d]	PAN[e]	PEG[f]	thin-film	microcrystal
3b	300	$\lambda_{FL,max}$ / nm	384	388	400	403	408	425
		Φ_f	0.74	0.60	0.20	0.50	0.19	0.14
3d	360	$\lambda_{FL,max}$ / nm	446	459	497	512	515	558
		Φ_f	0.64	0.76	0.54	0.34	0.07	0.08
3e	390	$\lambda_{FL,max}$ / nm	580	598	632	657	–[g]	–[g]
		Φ_f	0.47	0.64	0.17	0.05	–[g]	–[g]

[a] Absolute quantum yield determined by a calibrated integrating sphere system. [b] Excited wavelength. [c] Dispersed in polystyrene (PS). [d] Dispersed in poly(methyl methacrylate) (PMMA). [e] Dispersed in polyacrylonitrile (PAN). [f] Dispersed in (polyethylene glycol) (PEG). [g] No fluorescence was observed.

UV absorption and fluorescence spectra of **3b**, **3d**, and **3e** measured in Et_2O are shown in Figures 10 and 11 along with those of **1b**, **1d**, and **1e**. Compared with silafluorenes **1**, absorption edges of **3b** and **3d** blue-shifted by 32 nm from **1b** (358 nm) to **3b** (390 nm), by 14 nm from **1d** (415 nm) to **3d** (429 nm). In case of **3e** (531 nm) bearing a dicyanoethenyl group, such blue shift was not observed. In this way, the stronger the electron-withdrawing nature of an acceptor became, the smaller the absorption edge blue-shifted. As well as absorption spectra, the difference in

fluorescence maxima between **1** and **3** are highly dependent on the electron-withdrawing nature of the acceptor group. This trend suggests that an introduction of a strong acceptor group such as CHO and $CHC(CN)_2$ weaken σ*–π* conjugation of silafluorene, which lowers the energy level of LUMO and contribute to bathochromic shift of absorption and fluorescence spectra (for molecular orbital calculations, see below). While fluorescence quantum yields of **1** in various solution and doped polymer film are generally lower than those of **3**, microcrystals and thin-films of **1** exhibited more efficient emission than those of **3**, suggesting that a bulky silicon-bridge prevents intermolecular interaction such as π–π stacking, which leads to quenching of emission, resulting in higher fluorescence quantum yield.

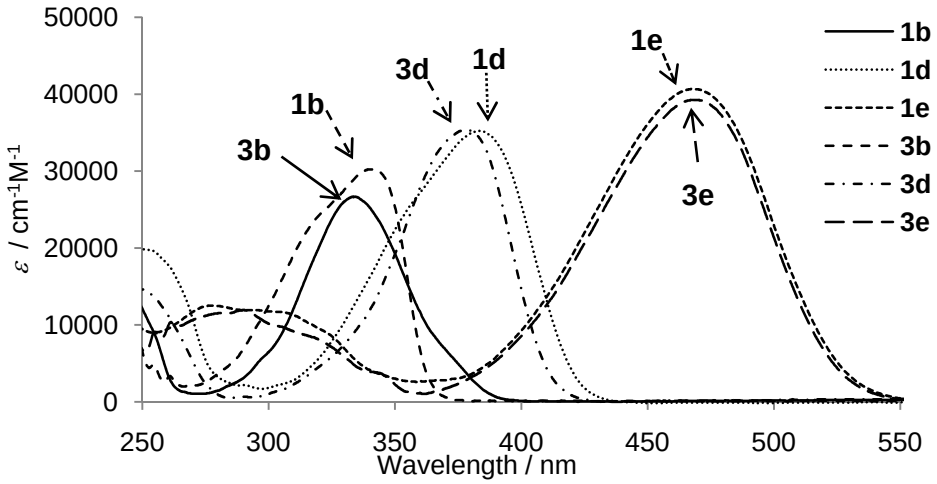


Figure 10. UV absorption spectra of **1** and **3** in Et_2O.

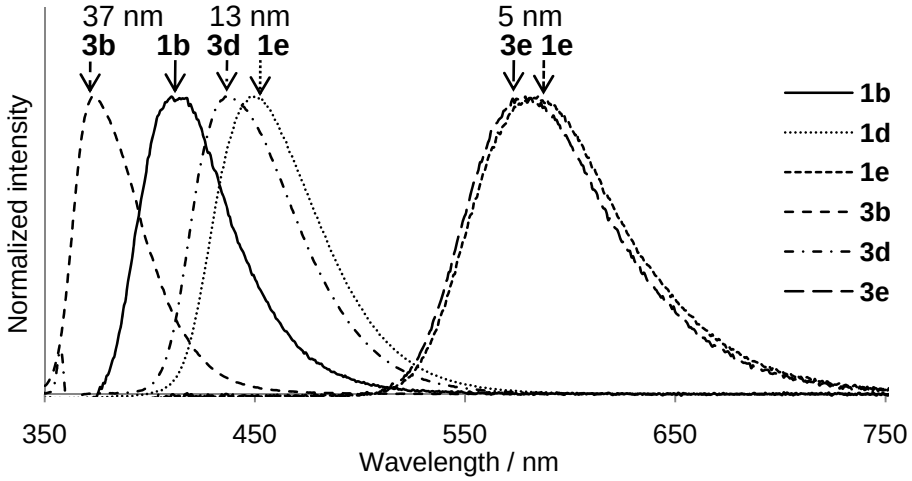


Figure 11. Fluorescence spectra of **1** and **3** measured in Et_2O (excited at 290 nm for **1b**, 300 nm for **3b**, 320 nm for **1d**, 360 nm for **3d**, and 390 nm for **1e** and **3e**).

3-5. **Electrochemical properties.**

In order to obtain insights into the electrochemical properties of D-π-A type silafluorenes, the cyclic voltammograms of **1-3** were measured in CH_2Cl_2. All compounds exhibited reversible oxidation waves (Figure 12), whereas reduction waves were structureless and hence reduction potential could not be detected.

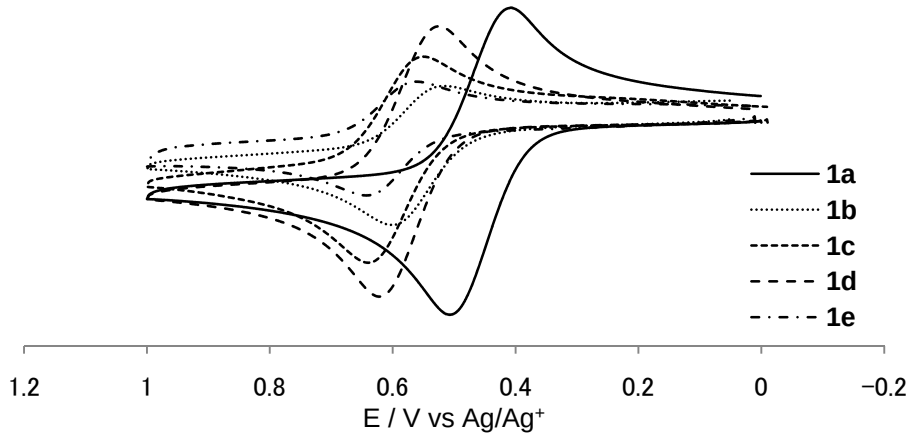


Figure 12. Cyclic voltammograms of **1**.

Their oxidation potentials are summarized in Table 6. Although spirosilabifluorene only showed an irreversible one-electron oxidation wave,[1g] **1-3** exhibited reversible one-electron oxidation waves, suggesting that the radical cation produced thereby can be stabilized in D-π-A type silafluorene structure. The first oxidation peak potential (E_{ox}) of dimethylamino-substituted silafluorenes gradually shifts to less positive potential in the order of **1e** (+0.60 V vs Ag/Ag^+) = **1c** (+0.60 V) > **1d** (+0.57 V) > **1b** (+0.56 V) > **1a** (+0.46 V). In case of diphenylamino-substituted silafluorenes **2**, similar trend was observed. As an acceptor group becomes more electron-withdrawing, E_{ox} becomes higher, indicating that electronic structures can be tuned by choosing a substituent on the arene moiety of silafluorene.

Table 6. Oxidation potential of **1-3**.[a]

Compd	E_{ox} (V)[b]	Compd	E_{ox} (V)[b]	Compd	E_{ox} (V)[b]
1a	0.46	**1e**	0.60	**3b**	0.55
1b	0.56	**2c**	0.73	**3d**	0.55
1c	0.60	**2d**	0.72	**3e**	0.59
1d	0.57	**2e**	0.74		

[a] Measured in CH_2Cl_2 at room temperature in the presence of nBu$_4$ClO$_4$ (0.1 M) as an electrode with scan rate of 100 mV/s using Pt as a working electrode and as a working electrode and Ag/AgCl as a reference electrode. [b] Versus Ag/Ag^+.

3-6. Molecular orbital calculation

Molecular orbital calculations of **1-3** were carried out by the DFT method at the B3LYP/6-31G*//B3LYP/6-31G* level using the Gaussian 03 package.[8] The results are summarized in Table 7.

Table 7. HOMO and LUMO energies of **1-3**.

Compd	LUMO (ev)[a]	HOMO (ev)[a]	ΔE (ev)[a]	ΔE (ev) (abs. edge)[b]
1a	–0.57	–4.80	4.23	3.20 (388 nm)
1b	–1.00	–5.05	4.05	3.08 (403 nm)
1c	–1.38	–5.17	3.79	3.00 (413 nm)
1d	–1.55	–5.09	3.54	2.80 (443 nm)
1e	–2.51	–5.30	2.79	2.26 (549 nm)
2c	–1.67	–5.12	3.45	2.86 (434 nm)
2d	–1.81	–5.07	3.26	2.72 (456 nm)
2e	–2.68	–5.26	2.58	2.23 (556 nm)
3b	–0.83	–5.01	4.18	3.35 (370 nm)
3d	–1.48	–5.06	3.58	2.89 (429 nm)
3e	–2.49	–5.29	2.80	2.26 (549 nm)

[a] Calculated at the B3LYP/6-31G*//B3LYP/6-31G* level. [b] Estimated from absorption edge.

Compared with the corresponding diphenylamino products **2c**-**2e**, dimethylamino derivatives **1c**-**1e** have higher LUMO levels but similar HOMO levels. Accordingly, HOMO-LUMO gap in **1c**-**1e** are larger than those of **2c**-**2e**. This is consistent with the absorption edges in the UV/visible spectra. Shapes of HOMO and LUMO in **1** are

visualized in Figure 13. HOMO of them are delocalized over the biphenyl and the amino moiety. Although LUMO of **1a**, **1b**, and **1c** are delocalized over the biphenyl moiety, an electron-withdrawing group, and the silicon bridge, orbital lobes on the silicon become smaller as electron-withdrawing nature of the acceptor become stronger. In particular, no lobes on silicon were observed in case of **1d** and **1e**, *i.e.* no σ*–π* conjugation was operating. Both HOMO and LUMO orbitals of **1d** and **1e** are quite similar to those of **3d** and **3e** (Figure 14), respectively, thus resulting in similar HOMO and LUMO levels. Accordingly, HOMO-LUMO gaps of **1d** and **1e** are almost the same as those of **3d** and **3e**, whereas HOMO-LUMO gap of **1b** is smaller than that of **3b** due to σ*–π* conjugation. For such a reason, difference in UV absorption and fluorescence spectra between **1** and **3** (Figures 10 and 11) decreased as electron-withdrawing nature of the acceptor become stronger.

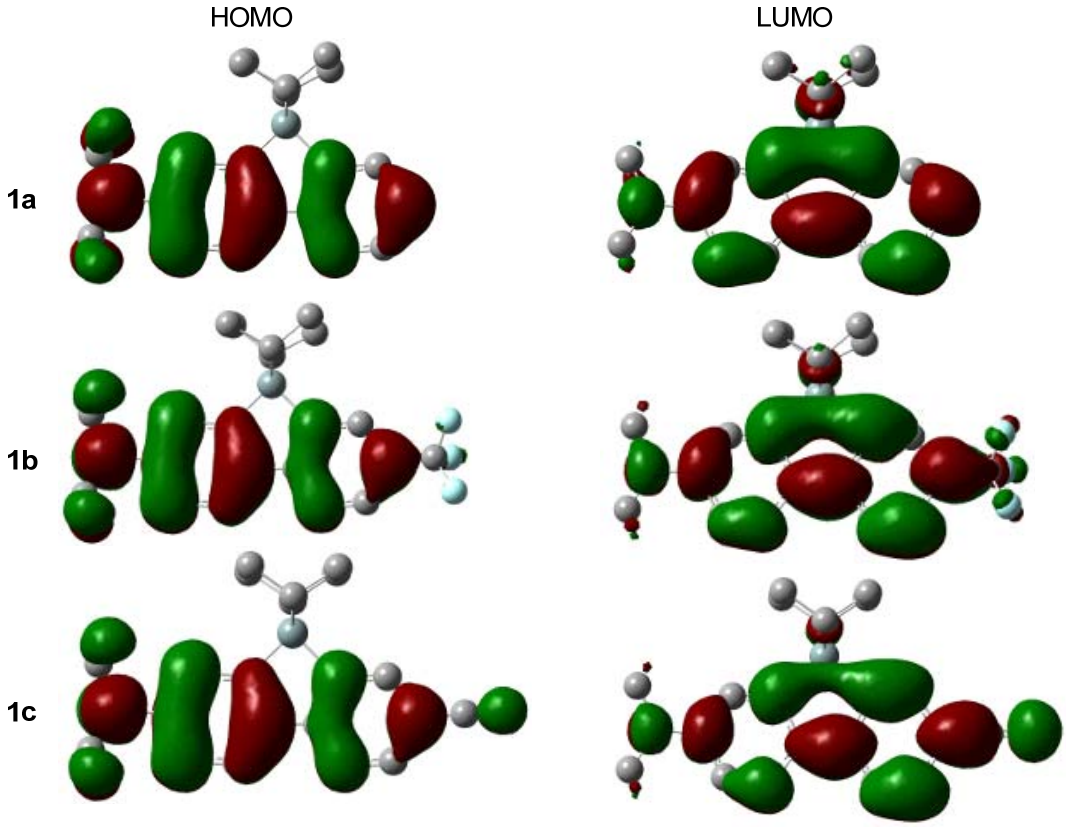


Figure 13. Molecular orbital drawings of HOMO and LUMO of **1**.

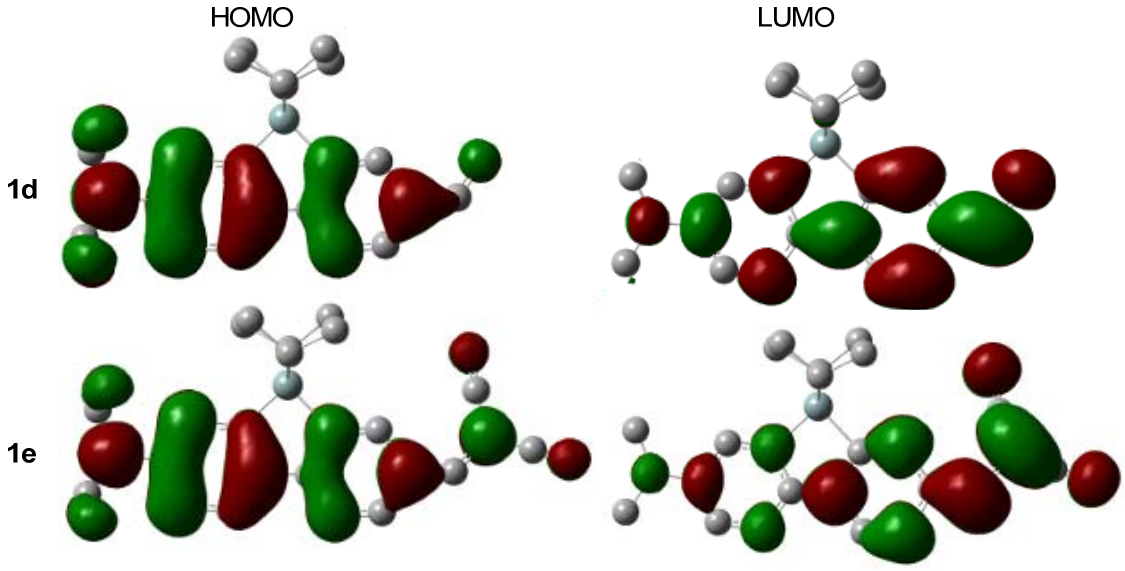


Figure 13. *Continued.*

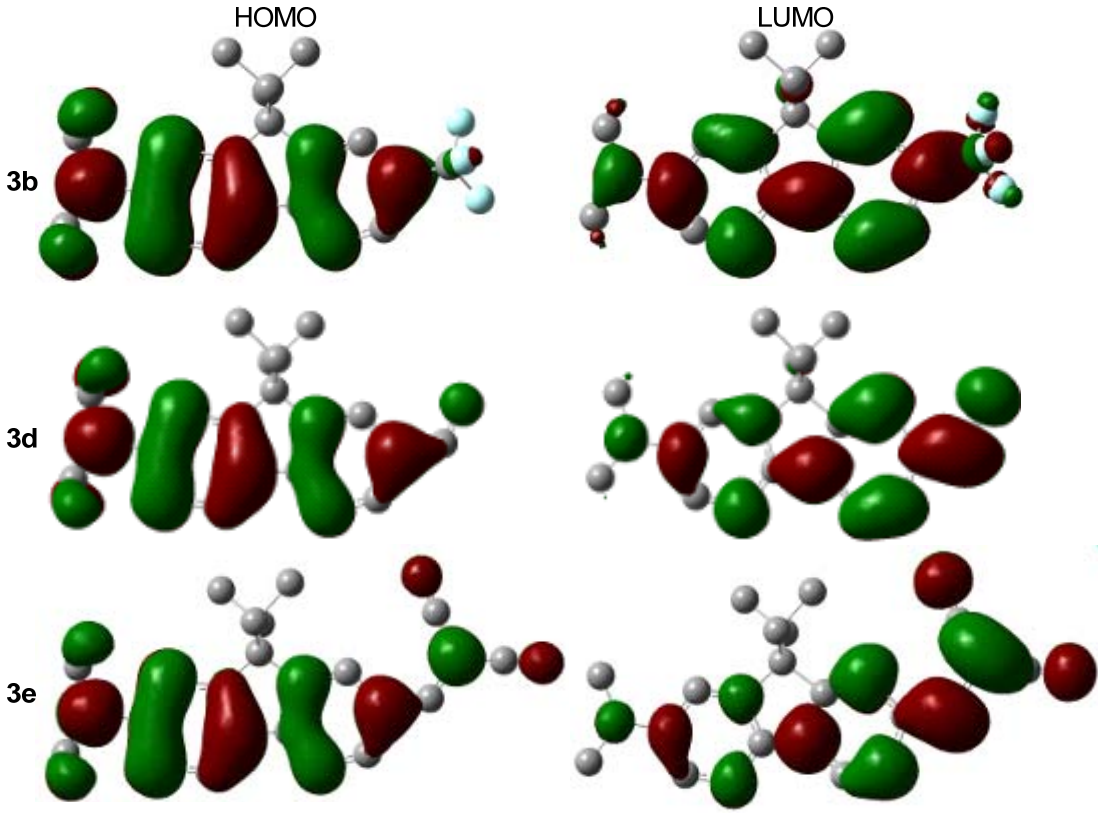


Figure 14. Molecular orbital drawing of HOMO and LUMO of **3**.

4. Conclusions

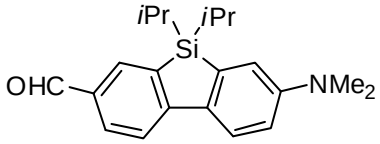
In summary, the author has demonstrated that introduction of donor and acceptor substituent at 2,7-posotion of silafluorene induced considerably large red-shift in their absorption and fluorescence maxima compared with those of the parent 9,9-dimethyl-9-silafluorene. Furthermore, silafluorenes having a strong electron-withdrawing group such as CN, CHO, and $CHC(CN)_2$ show significant solvatochromism of fluorescence not only in solution but also in doped polymer films.

Experimental

Preparation of 2-amino-7-formylsilafluorene

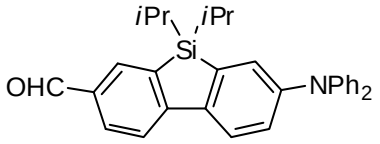
An oven-dried 20 mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-amino-7-cyanosilafluorene (0.9 mmol) and toluene (5 mL). To the solution was added DIBAL-H (1.5 M toluene solution, 0.9 mL, 1.35 mmol) dropwise at 0 °C. The resulting solution was warmed to room temperature and then stirred for 12 h before addition of $CHCl_3$ (5 mL) and 1N HCl aq. (5 mL). The mixture was stirred for 1 h, and then the aqueous layer was extracted with $CHCl_3$ (20 mL × 3). The combined organic layer was washed with H_2O (15 mL), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give 2-amino-7-formyl-silafluorene.

2-Dimethylamino-7-formyl-9,9-diisopropyl-*9H*-silafluorene (**1d**)



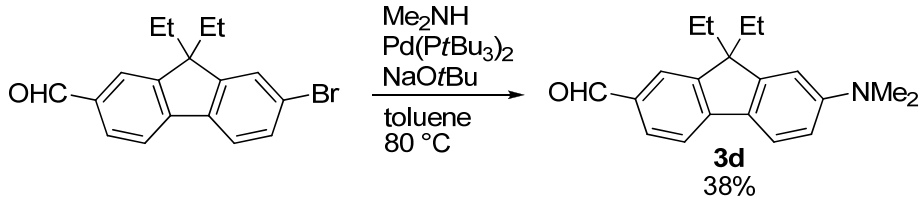
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 79%, a yellowgreen solid. Mp: 85.6–86.0 °C. TLC: R_f 0.33 (hexane/AcOEt 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.3 Hz, 12H), 1.42 (sep, *J* = 7.3 Hz, 2H), 3.07 (s, 6H), 6.76–6.90 (brs, 1H), 6.98–7.00 (brs, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.03 (d, *J* = 1.5 Hz, 1H), 9.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.2, 18.3, 40.5, 113.6, 116.6, 119.4, 123.1, 132.7, 133.1, 134.4, 135.3, 135.6, 139.2, 150.2, 156.0, 191.9. IR (KBr): ν = 2943, 2862, 1684, 1576, 1560, 1493, 1445, 1356, 1288, 1180, 1051, 899, 816, 725, 679 cm^{-1}. MS *m*/*z*: 337 (100, M^+), 294 (14), 266 (6), 252 (6). Anal. Calcd for $C_{21}H_{27}NOSi$: C, 74.73; H, 8.06. Found: C, 74.46; H, 8.02.

2-Diphenylamino-7-formyl-9,9-diisopropyl-*9H*-silafluorene (**2d**)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 54%, a yellow solid. Mp: 143.6–144.5 °C. TLC: R_f 0.22 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.6 Hz, 2H), 1.02 (d, *J* = 7.6 Hz, 2H), 1.36 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.04–7.10 (m, 2H), 7.10–7.15 (m, 6H), 7.25–7.28 (m, 3H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.06 (d, *J* = 1.6 Hz, 1H), 10.00 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.21, 18.24, 120.3, 122.9, 123.1, 124.4, 124.8, 127.9, 129.2, 132.6, 133.9, 134.5, 136.4, 139.0, 141.2, 147.2, 148.0, 154.8, 192.0. IR (KBr): ν = 2955, 2937, 2862, 1688, 1582, 1491, 1277, 1195, 875, 826, 754, 696, 629 cm^{-1}. MS *m*/*z:* 461 (100, M^+), 418 (14), 376 (3). Anal. Calcd for $C_{31}H_{31}NOSi$: C, 80.65; H, 6.77. Found: C, 80.93; H, 6.96.

Preparation of 2-dimethylamino-7-formyl-9,9-diethylfluorene (**3d**)

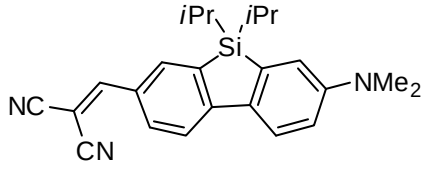


An oven-dried 3 ml vial equipped with a magnetic stir bar was charged with 2-bromo-7-formyl-9,9-diethylfluorene[10] (82 mg, 0.25 mmol), dimethylamine (50 wt% in H_2O, 0.1 mL, 2.0 mmol), $Pd(PtBu_3)_2$ (13 mg, 0.025 mmol), NaO*t*Bu (96 mg, 1.0 mmol), and toluene (2 mL). The mixture was heated at 80 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt 10:1) to give 2-dimethylamino-7-formyl-9,9-diethylfluorene (28 mg, 0.1 mmol, 38 %) as a yellow solid. Mp: 126.7–127.4 °C. R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.31–0.34 (m, 6H), 1.93–2.13 (m, 4H), 6.63 (brs, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 7.61–7.66 (m, 2H), 7.77–7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.6, 33.0, 40.8, 56.1, 106.1, 111.4, 117.9, 121.7 (2C), 122.5, 131.1, 133.3, 149.0, 149.4, 151.4, 153.2, 192.0. IR (KBr): ν = 2959, 2816, 1678, 1589, 1506, 1361, 1296, 1166, 1076, 800, 743, 680 cm^{-1}. MS *m*/*z*: 293 (54, M^+), 264 (2), 248 (3). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90. Found: C, 81.83; H, 7.98.

Preparation of dicyanoethenyl-substituted silafluorene and fluorene

An oven-dried 3 mL vial equipped with a magnetic stir bar was charged with formyl product (0.1 mmol), malononitrile (13.2 mg, 0.2 mmol), basic Al_2O_3 (47.3 mg) and toluene (0.5 mL). The reaction mixture was stirred at 70 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel or recrystallization to give dicyanoethenyl compounds.

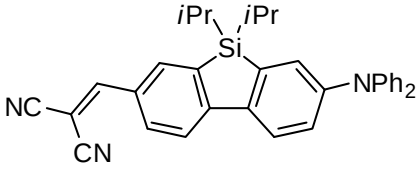
2-(2,2-Dicyanoethenyl)-7-dimethylamino-9,9-diisopropyl-*9H*-silafluorene (**1e**)



Purification: silica gel column chromatography (hexane/AcOEt 1:1). Yield: 86%, a red solid. Mp: 169.4–170.8 °C. TLC: R_f 0.39 (hexane/AcOEt 2.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.3 Hz, 6H), 1.07 (d, *J* = 7.3 Hz, 6H), 1.42 (qq, *J* = 7.3, 7.3 Hz, 2H), 3.09 (s, 6H), 6.79–6.85 (brs, 1H), 6.93–6.99 (brs, 1H), 7.68 (s, 1H), 7.74 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.92 (dd, *J* = 8.3, 1.9 Hz, 1H), 8.06 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.13, 18.18,

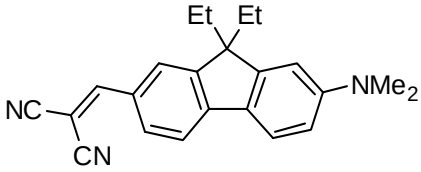
40.6, 78.0, 113.6, 113.7, 114.8, 116.6, 119.9, 123.7, 127.8, 133.4, 136.0, 140.0, 150.5, 150.6, 156.6, 159.2. IR (KBr): ν = 2938, 2861, 2220, 1566, 1545, 1462, 1402, 1354, 1217, 1167, 1055, 810, 725, 677, 611 cm^{-1}. MS *m/z*: 385 (100, M^+), 342 (6), 300 (6). Anal. Calcd for $C_{24}H_{27}N_3Si$: C, 74.76; H, 7.06. Found: C, 74.73; H, 7.00.

2-(2,2-Dicyanoethenyl)-7-diphenylamino-9,9-diisopropyl-*9H*-silafluorene (**2e**)



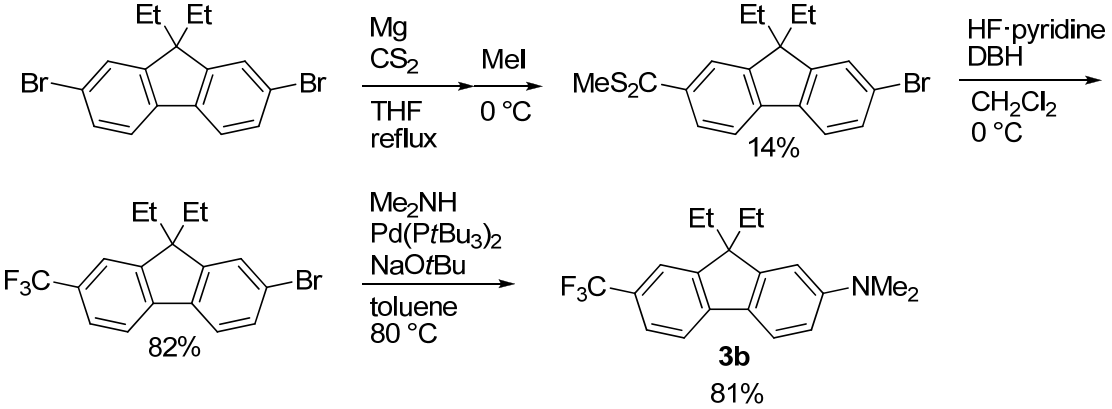
Purification: recrystallization (hexane/CH_2Cl_2). Yield: quant., a red solid. Mp: 144.9–145.9 °C. TLC: R_f 0.28 (hexane/AcOEt 2.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.6 Hz, 6H), 1.02 (d, *J* = 7.6 Hz, 6H), 1.36 (qq, *J* = 7.6, 7.6 Hz, 2H), 7.06–7.14 (m, 3H), 7.14–7.16 (m, 4H), 7.27–7.33 (m, 5H), 7.70–7.72 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.95 (dd, *J* = 8.3, 1.9 Hz, 1H), 8.09 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.18, 18.21, 79.4, 113.3, 114.4, 120.7, 123.3, 123.5, 124.3, 124.7, 127.3, 128.6, 129.3, 133.2, 136.0, 137.3, 139.2, 140.4, 147.0, 148.7, 155.3, 159.2. IR (KBr): ν = 2940, 2861, 2360, 2224, 1568, 1489, 1273, 1220, 883, 754, 696 cm^{-1}. MS *m/z*: 509 (25, M^+), 460 (4), 438 (1). Anal. Calcd for $C_{34}H_{31}N_3Si$: C, 80.12; H, 6.13. Found: C, 80.01; H, 6.20.

2-(2,2-Dicyanoethenyl)-7-dimethylamino-9,9-diethylfluorene (**3e**)



Purification: recrystallization (hexane/CH_2Cl_2). Yield: quant., a red solid. Mp: 160.4–161.4 °C. TLC: R_f 0.28 (hexane/AcOEt 2.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.33–0.37 (m, 6H), 1.93–2.11(m, 4H), 6.60 (d, *J* = 2.1 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.72 (s, 1H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.88 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.6, 32.9, 40.7, 56.2, 77.4, 105.7, 111.5, 113.9, 114.9, 118.4, 122.2, 124.1, 127.5, 128.1, 131.9, 149.8, 149.9, 151.8, 153.9, 159.6. IR (KBr): ν = 2959, 2850, 2222, 1566, 1541, 1431, 1357, 1301, 1219, 1182, 1082, 808, 744 cm^{-1}. MS *m/z*: 341 (6, M^+), 242 (1), 176 (4). Anal. Calcd for $C_{23}H_{23}N_3$: C, 80.90; H, 6.79. Found: C, 80.60; H, 6.82.

Preparation of 2-dimethylamino-7-trifluoromethyl-9,9-diethylfluorene (**3b**)



An oven-dried 20 mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with magnesium turnings (160 mg, 6.5 mmol) and THF (2 mL). To the vigorously stirred suspension was added 1,2-dibromoethane (43 μL, 0.5 mmol) dropwise. A small portion of 2,7-dibromo-9,9-diethylfluorene was added to initiate the reaction. After color of the reaction mixture turned pale orange, the remaining solution of 2,7-dibromo-9,9-diethylfluorene (totally, 1.9 g, 5.0 mmol) in THF (3 mL) was added. The reaction mixture was stirred at room temperature for 6 h before quenching carbon disulfide (0.93 ml, 15.5 mmol). The mixture was further stirred at room temperature for 12 h before methyl iodide (0.47 mL, 7.5 mmol) was added dropwise to the reaction mixture at 0 °C. The resulting mixture was stirred at room temperature for 5 h, then diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to give methyl 7-(dimethylamino)-9,9-dithylfluorene-2-carbodithioate (260 mg, 0.69 mmol, 14%) as a red oil. A 5 mL PE vial equipped with a magnetic stir bar was charged with 7-(dimethylamino)-9,9-dithylfluorene-2-carbodithioate (260 mg, 0.69 mmol), 1,3-dibromo-5,5-dimethylhydantoin (789 mg, 2.8 mmol), and CH_2Cl_2 (2 mL). To a solution was added HF/Py (70/30 wt%, 0.3 mL, F^-: 20.0 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1 h, then poured into an aqueous solution of sodium hydrogencarbonate and sodium hydrogensulfite, and extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to give 2-bromo-7-trifluoromethyl-9,9-diethylfluorene (210 mg, 0.57 mmol, 82%) as a colorless solid. An oven-dried 3 ml vial equipped with a magnetic stir bar was charged with 2-bromo-7-trifluoromethyl-9,9-diethylfluorene (210 mg, 0.57 mmol), dimethylamine (50 wt% in H_2O, 0.23 mL, 4.6 mmol), $Pd(PtBu_3)_2$ (31 mg, 0.06 mmol), NaO*t*Bu (219 mg, 2.3 mmol), and toluene (2 mL). The mixture was heated at 80 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt 50:1) to give 2-dimethylamino-7-trifluoromethyl-9,9-diethylfluorene (154 mg, 0.46 mmol, 81 %) as a colorless solid.

Mp: 80.1–81.0 °C. R_f 0.05 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.32–0.35 (m, 6H), 1.93–2.09 (m, 4H), 3.05 (s, 6H), 6.64 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.46–7.47 (m, 1H), 7.52 (dm, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.6, 33.0, 40.9, 56.3, 106.36, 111.3, 117.8, 119.1 (q, *J* = 3.1 Hz), 120.9, 124.0 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 271.9 Hz), 125.0 (q, *J* = 31.2 Hz), 128.9, 145.6, 149.1, 151.0, 152.1. IR (KBr): ν = 2965, 2911, 2359, 1608, 1506, 1361, 1325, 1314, 1161, 1109, 1062, 842, 810, 739 cm^{-1}. MS *m*/*z*: 333 (100, M^+), 308 (3), 288 (6). Anal. Calcd for $C_{20}H_{22}F_3N$: C, 72.05; H, 6.65. Found: C,

72.04; H, 6.65.

UV-vis absorption and fluorescent measurement

The spectroscopic-grade solvents for UV–vis absorption and fluorescence measurements were purchased from Kanto Chemical Co., Inc. and degassed with argon before use. Thin films and polymer bounded films were prepared by spin-coating method with a MIKASA MS-A-100 spincoater. UV–vis absorption spectra were measured with a Shimadzu UV-2550 spectrometer. Fluorescence spectra and absolute quantum yields were recorded by Hamamatsu Photonics C9920-02 Absolute PL Quantum Yield Measurement System. Fluorescent life times were measured with a HORIBA TemPro.

Preparation of neat thin film

In a tube glass, each sample (EXSTAR 6000 TG/DTA, Seiko Instruments Inc., was used for weighing sample) was dissolved in toluene with concentration of 0.1 mg/mL. The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated (MIKASA MS-A-100 was used) at 100 rpm for 20 sec followed by further spin-coat at 1000 rpm over a period of 100 sec. The deposited film was dried under reduced pressure at 50 °C for 1 h.

Preparation of dispersed polymer film

In a tube glass, each sample was dissolved in a saturated solution of polymer with concentration of 0.1 mg/mL. The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated at 100 rpm for 20 sec followed by further spin-coat at 1000 rpm over a period of 100 sec. The deposited film was dried under reduced pressure at 50 °C for 1 h.

Solvents for dissolving polymer are as follows: benzene for polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(ethylene glycol) and DMF for poly(acrylonitrile).

Preparation of the white emission film

In a glass tube, silafluorene **1c** (0.347 mg, 10.4 μmol), **1d** (0.437 mg, 12.9 μmol), and **1e** (0.062 mg, 0.15 μmol) was dissolved in a saturated benzene solution of PMMA (1 ml). The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated at 100 rpm for 20 sec followed by further spin-coat at 1000 rpm over a period of 100 sec. The deposited film was dried under reduced pressure at 50 °C for 1 h.

CV measurement

Cyclic voltammetry (CV) was performed on BAS ALS610c electrochemical analyzer. The CV cell consisted of a Pt disk electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The measurement was carried out under argon atmosphere using a CH_2Cl_2 solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) as a supporting electrolyte at a scan rate of 100 mV/s.

Reference

(1) (a) Ohshita, J.; Nodono, M.; Kai, H.; Watanabe, T.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **1999**, *18*, 1453. (b) Ohshita, J.; Kai, H.; Takata, A.; Iida, T.; Kunai, A.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K. *Organometallics* **2001**, *20*, 4800. (c) Matsushita, T.; Uchida, M. *J. Photopolym. Sci. Technol.* **2003**, *16*, 315. (d) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662. (e) Chan, K. L.; Watkins, S. E.; Mak, C. S. K.; McKiernan, M. J.; Towns, C. R.; Pascu, S. I.; Holmes, A. B. *Chem. Commun.* **2005**, 5766. (f) Lee, K.-H.; Ohshita, J.; Kimura, K.; Kunugi, Y.; Kunai, A. *J. Organomet. Chem.* **2005**, *690*, 333. (g) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071. (h) Xiao, H.; Leng, B.; Tian, H. *Polymer* **2005**, *46*, 5707. (i) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638. (j) Yamaguchi, S.; Xu, C.; Yamada, H.; Wakamiya, A. *J. Organomet. Chem.* **2005**, *690*, 5365. (k) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (l) Wang, E.; Li, C.; Mo, Y.; Zhang, Y.; Ma, G.; Shi, W.; Peng, J.; Yang, W.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 4133. (m) Boudreault, P.-L. T.; Michaud, A.; Leclerc, M. *Macromol. Rapid Commun.* **2007**, *28*, 2176. (n) Li, L.; Xiang, J.; Xu, C. *Org. Lett.* **2007**, *9*, 4877. (o) Ohshita, J.; Kurushima, Y.; Lee, K.-H.; Kunai, A.; Ooyama, Y.; Harima, Y. *Organometallics* **2007**, *26*, 6591. (p) Sanchez, J. C.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Chem. Mater.* **2007**, *19*, 6459. (q) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144. (r) Lu, G.; Usta, H.; Risko, C.; Wang, L.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 7670. (s) Sanchez, J. C.; Urbas, S. A.; Toal, S. J.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Macromolecules* **2008**, *41*, 1237. (t) Shimizu, M.; Tatsumi, H.; Mochida, K.; Oda, K.; Hiyama, T. *Chem. Asian. J.* **2008**, *3*, 1238. (u) Wang, E.; Li, C.; Zhuang, W.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2008**, *18*, 797.

(2) (a) Eliseeva, N. V.; Krasnova, T. L.; Chernyshev, E. A.; Pravednikov, A. N.; Rogachevskii, V. L. *J. Struct. Chem.* **1972**, *13*, 484. (b) Davydov, S. N.; Rodionov, A. N.; Shigorin, D. N.; Syutkina, O. P.; Krasnova, T. L. *Russ. J. Phys. Chem.* **1981**, *55*, 444. (c) Terunuma, D.; Nakamura, M.; Miyazawa, E.; Nohira, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2263. (d) Fajarí, L.; Juliá, L.; Riera, J.; Molins, E.; Miravitlles, C. *J. Organomet. Chem.* **1990**, *381*, 321. (e) Hoshi, T.; Nakamura, T.; Suzuki, T.; Ando, M.; Hagiwara, H. *Organometallics* **2000**, *19*, 4483. (f) Kai, H.; Ohshita, J.; Ohara, S.; Nakayama, N.; Kunai, A.; Lee, I.-S.; Kwak, Y.-W. *J. Organomet. Chem.* **2008**, *693*, 3490.

(3) Geramita, K.; McBee, J.; Tilley, T. D. *J. Org. Chem.* **2008**, *74*, 820.

(4) (a) Gompper, R.; Wagner, H.-U. *Angew. Chem. Int. Ed.* **1988**, *27*, 1437. (b) Meier, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 2482.

(5) (a) Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2008**, *42*, 235. (b) May, J. C.; Lim, J. H.; Biaggio, I.; Moonen, N. N. P.; Michinobu, T.; Diederich, F. *Opt. Lett.* **2005**, *30*, 3057.

(6) (a) *Organic Light-Emitting Devices. Synthesis Properties and Applications*; Wiley-VCH: Weinheim, 2006. (b) *Highly Efficient OLEDs with Phosphorescent*

Materials; Wiley-VCH: Weinheim, 2008. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(7) (a) Gratzel, M. *Nature* **2001**, *414*, 338. (b) Robertson, N. *Angew. Chem. Int. Ed.* **2006**, *45*, 2338. (c) Hwang, S.; Lee, J. H.; Park, C.; Lee, H.; Kim, C.; Park, C.; Lee, M.-H.; Lee, W.; Park, J.; Kim, K.; Park, N.-G.; Kim, C. *Chem. Commun.* **2007**, 4887. (d) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 2474. (e) Peter, L. *Acc. Chem. Res.* **2009**, *42*, 1839.

(8) *Gaussian 03*, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Laham, A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

(9) Maus, M.; Rettig, W.; Bonafoux, D.; Lapouyade, R. *J. Phys. Chem. A* **1999**, *103*, 3388.

(10) Reinhardt, B. A.; Reinhardt, E. D.; Reinhardt, J. A.; Kannan, R. Benzothiazole-containing two-photon chromophores exhibitting strong frequency upconversion. U.S. Pat. 6,100,405, Aug 08, 2000.

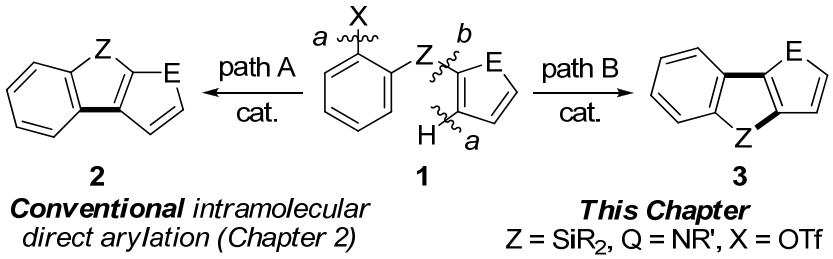
Chapter 4

Palladium-Catalyzed Intramolecular Coupling of 2-[(2-Pyrrolyl)silyl]aryl Triflates through 1,2-Silicon Migration

Conformationally fixed π-conjugate system such as 3,2'-silicon-bridged 2-arylindoles and -pyrroles are prepared by intramolecular arylation of 2-[(2-indolyl and -pyrrolyl)silyl]aryl triflates with the aid of a palladium catalyst. The reaction proceeds through cleavage of C−OTf, C−Si, and C−H bonds to result in the formation of C−C and C−Si bonds. Various kinds of functional groups such as OMe, CN, Cl, F, and $SiMe_3$ tolerated the conditions to allow synthesis of new type of π-conjugate organic materials.

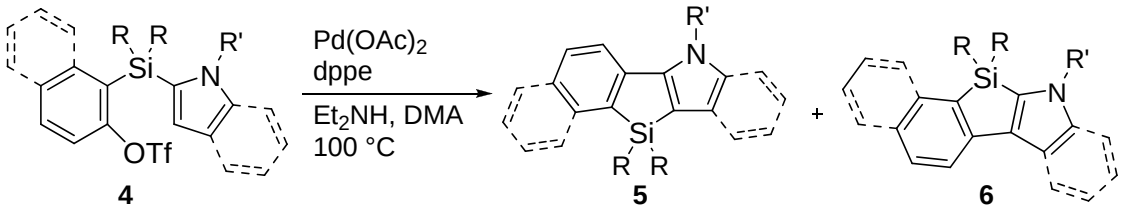
1. Introduction

Transition metal-catalyzed direct arylation of arenes with aryl halides or their equivalents via C–H bond activation has recently emerged as a straightforward and useful tool for aryl-aryl bond formations.[1] In particular, intramolecular direct arylation using heteroatom-tethered heterocycles **1** (X = halogen or leaving group; Z and/or E = heteroatom) constitutes a straightforward approach to highly fused polycyclic (hetero)aromatics **2**, which can serve as platforms of various biologically active molecules and functional organic materials (Scheme 1, path A).[2] The intramolecular coupling involves the activation of C–X and C–H bonds (indicated by waved line *a*), leading to direct C–C bond connection. In Chapter 2, the author described palladium-catalyzed intramolecular coupling of 2-(arylsilyl)aryl triflates (**1**, Z = SiR_2, X = OTf, E = –CH=CH–, S, or O), a reaction that proceeded via path A. This reaction was shown to be a versatile method for silicon-bridged biaryls **2**, which exhibit superior photophysical properties useful for applications in opto-electronic materials. In contrast, intramolecular cyclization has no precedents that involve direct arylation accompanied by reorganization of a C–Z bond leading to a cyclized product of type **3** (path B).



Scheme 1. Intramolecular coupling of tethered bi(aryl)s.

This Chapter deals with the first example of a path B type transformation with silicon-tethered indoles and pyrroles **1** (Z = SiR_2, E = NR′, X = OTf). Namely, palladium-catalyzed intramolecular coupling of 2-[(2-pyrrolyl)silyl]aryl triflates **4** proceeds through silicon migration from 2- to 3- position of the indole ring to give 3,2'-silicon-bridged 2-arylindoles **5** exclusively or preferentially over the conventional type of products **6** in good to high yields (Scheme 2).



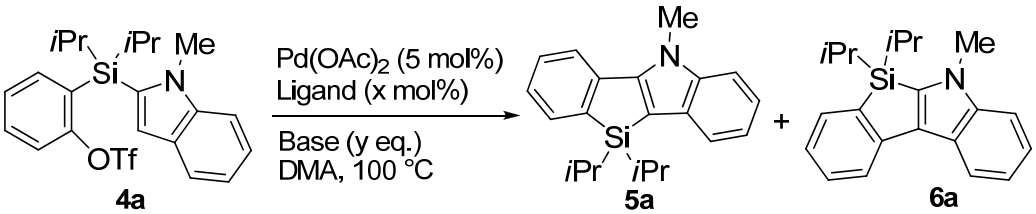
Scheme 2. Intramolecular coupling of 2-[(2-pyrrolyl)silyl]aryl triflates.

2. Results and Discussion

2-1. Screening of reaction conditions

Initially, 2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (**4a**) was subjected to the original conditions for the cyclization of 2-(arylsilyl)aryl triflates using $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), and Et_2NH (2.0 eq.) in dimethylacetamide (DMA) at 100 °C. The author was pleased to observe that **5a** was isolated as a major product (62% yield) along with expected product **6a** (8%) (Table 1, entry 1). Thus, the path B transformation was found to take place as a major reaction with **4a**. Then, he screened the conditions for the novel intramolecular coupling using **4a** and found that the use of 1,2-bis(diphenylphosphino)ethane (dppe) and Et_2NH in excess (14 eq.) in the presence of $Pd(OAc)_2$ was extremely effective in suppressing the formation of **6a**, so that **5a** was isolated in 89% yield and **6a** (3%) (entry 5). Use of Et_3N (14 eq.) as a base was also effective to suppress the formation of **6a** (entry 7), while use of inorganic base such as K_2CO_3 and Cs_2CO_3 resulted only in decomposition of **4a** (entries 8 and 9). He then examined the effect of ligand and found that the silicon-migrative intramolecular coupling proceeded even without a phosphine ligand (entry 15). However, palladium black rapidly precipitated under this reaction conditions and hence **4a** was not fully converted, suggesting that the phosphine ligand is responsible for stabilization of Pd(0) species rather than promotion of the silicon-migration under the reaction conditions. In the absence of the palladium catalyst, the reaction did not proceed at all (entry 16).

Table 1. Optimization of Pd-catalyzed cyclization of **4a**.[a]



4a **5a** **6a**

entry	ligand (x mol%)	base (y eq.)	conv.	**5a** (yield)[b]	**6a** (yield)[b]
1	PCy_3 (10)	Et_2NH (2.0)	100	67 (62)[c]	8 (8)[c]
2	dppe (5)	Et_2NH (2.0)	100	49	45
3	dppe (5)	Et_2NH (5.0)	100	63	33
4	dppe (5)	Et_2NH (10.0)	100	67	12
5	dppe (5)	Et_2NH (14.0)	100	91 (89)[c]	7 (3)[c]
6	dppe (5)	Et_2NH (19.0)	100	36	6
7	dppe (5)	Et_3N (14.0)	100	76	4
8	dppe (5)	K_2CO_3 (2.0)	100	0	0
9	dppe (5)	Cs_2CO_3 (2.0)	100	0	0
10	PCy_3 (10)	Et_2NH (14.0)	100	74	12
11	$P(Cyp)_3$ (10)	Et_2NH (14.0)	100	78	14
12	PPh_3 (10)	Et_2NH (14.0)	100	50	6
13	dppm (5)	Et_2NH (14.0)	100	54	27
14	dppp (5)	Et_2NH (14.0)	100	82	7
15	none	Et_2NH (14.0)	65	52	3
16[d]	dppe (5)	Et_2NH (14.0)	0	0	0

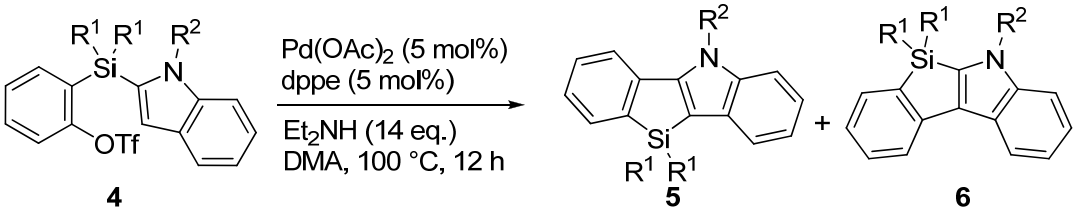
[a] All the reaction of **4a** (0.1 mmol) was carried out using $Pd(OAc)_2$ (5 mol%), ligand (x mol%), and base (y eq.) in DMA (0.5 mL) at 100 °C for 12 h.
[b] Determined by GC using $C_{12}H_{26}$ as an internal standard. [c] Isolated yield.
[d] Reaction was conducted without $Pd(OAc)_2$.

2-2. Effect of substituent on silicon and nitrogen

Under the optimized conditions, the author carried out the intramolecular coupling of various 2-(*indolylsilyl*)phenyl triflates **4a**-**4g** with various substituents on the silicon and nitrogen atom (Table 2). Whereas 2-(diphenylsilyl)indole **4b** produced **5b** in a moderated yield (59%) along with **6b** in a fair amount (17%) (entry 2), *N*-arylated and -tosylated indoles **4c**-**4f** gave **5c**-**5f** in good yields, respectively (entries 3-6). In case of *N*-H indole **4g**, isolated yield of **5g** was only 10% along with silanol **6g*** in 75% yield (entry 7). The author suspected that the product (**5g**) might be decomposed under the conditions by nucleophilic attack of a base, an acetate ion, or a

triflate ion at the Si*i*Pr$_2$ moiety. Thereupon, **5g** and **4f** were subjected to the reaction conditions (Eq. 1) to give rise to **5f** in 83% (GC) yield as expected along with silanol **6g*** in 99% (GC) yield with complete consumption of **5g**.

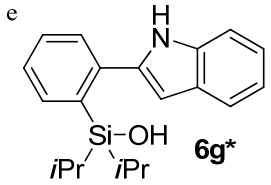
Table 2. Pd-catalyzed intramolecular coupling of 2-(indolylsilyl)phenyl triflates.[a]



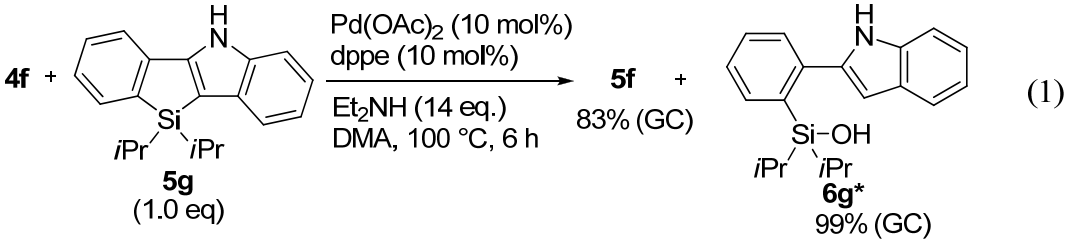
4 **5** **6**

entry	**4**	R^1	R^2	**5** (yield)[b]	**6** (yield)[b]
1[c]	**4a**	*i*Pr	Me	**5a** (89)[d]	**6a** (3)
2	**4b**	Ph	Me	**5b** (59)	**6b** (17)
3	**4c**	*i*Pr	*p*-MeC_6H_4	**5c** (74)	**6c** (nd)
4	**4d**	*i*Pr	*p*-$MeOC_6H_4$	**5d** (73)	**6d** (nd)
5	**4e**	*i*Pr	*p*-$CF_3C_6H_4$	**5e** (80)[d]	**6e** (nd)
6	**4f**	*i*Pr	Ts	**5f** (83)[d]	**6f** (nd)
7	**4g**	*i*Pr	H	**5g** (10)[d]	**6g*** (75)[e]

[a] All the reactions of **4** (0.3 mmol) was carried out using $Pd(OAc)_2$ (5 mol%), dppe (5 mol%), and Et_2NH (14 eq.) in DMA (1.5 mL) at 100 °C for 12 h except for entry 1. [b] Isolated yields. nd: not detected. [c] Reaction was conducted with 1 mmol of **4a**. [d] Molecular structure was unambiguously determined by X-ray diffraction analysis of the single crystal.

[e] 

was obtained.



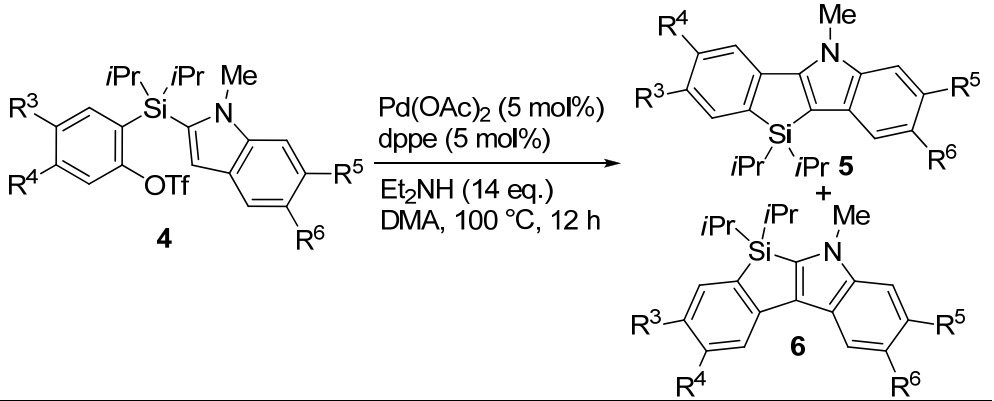
(1)

2-3. Substituent effect on arene moiety

The author next examined substituent effect on arene moiety with substrates **4h-4s**. The presence of functional groups such as OMe, CN, Cl, F, $SiMe_3$, and piperidyl on TfO-substituted and/or pyrrole-fused benzene rings generally did not affect

the preference for the path B transformation over path A, and functionalized Si-bridged 2-phenylindoles **5h-5s** were isolated in good to high yields (Table 3). Byproducts **6** formed to some extent in the case of **4** bearing such an electron-withdrawing group as CN, Cl, or F. In particular, the intramolecular coupling of CN and Cl substituted silylindole **4r** resulted in no selection, giving rise to **5r** and **6r** in 40 and 40% yields, respectively (entry 11). It is noteworthy that chlorine tolerated the conditions to give chlorinated products in high yields; further extension of the π-conjugated system is possible by use of the chlorine functionality (*vide infra*).

Table. 3. Substituent effect of arene moiety.[a]



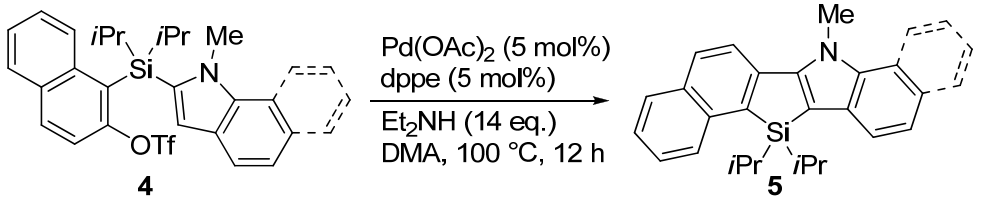
entry	**4**	R^3	R^4	R^5	R^6	**5** (yield)[b]	**6** (yield)[b]
1	**4h**	OMe	H	H	H	**5h** (77)	**6h** (nd)
2	**4i**	CN	H	H	H	**5i** (75)[d]	**6i** (15)
3[c]	**4j**	Cl	H	H	H	**5j** (81)	**6j**(nd)
4	**4k**	H	F	H	H	**5k** (74)	**6k** (6)
5	**4l**	H	H	Cl	H	**5l** (70)[d]	**6l** (10)
6	**4m**	H	H	$SiMe_3$	H	**5m** (82)	**6m** (5)
7	**4n**	H	H	H	OMe	**5n**(88)	**6n** (nd)
8[c]	**4o**[d]	H	H	H	Cl	**5o** (63)[d]	**6o** (22)
9	**4p**	Cl	H	Cl	H	**5p** (84)	**6p** (nd)
10[c]	**4q**	OMe	H	Cl	H	**5q** (78)	**6q** (nd)
11	**4r**	CN	H	Cl	H	**5r** (40)	**6r** (40)
12	**4s**	CN	H	—N⟨ ⟩	H	**5s** (86)[d]	**6s** (9)

[a] All the reactions of **4** (0.3 mmol) was carried out using $Pd(OAc)_2$ (5 mol%), dppe (5 mol%), and Et_2NH (14 eq.) in DMA (1.5 mL) at 100 °C for 12 h except for entries 3, 8, and 10. [b] Isolated yields. nd: not detected. [c] Reaction was conducted with 1 mmol of **4**. [d] Molecular structure was unambiguously determined by X-ray diffraction analysis of the single crystal.

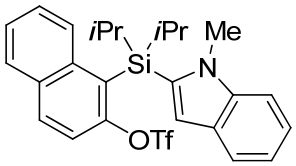
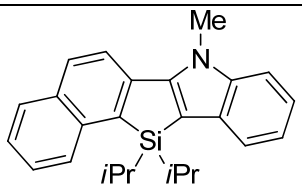
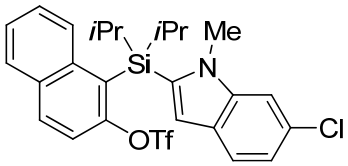
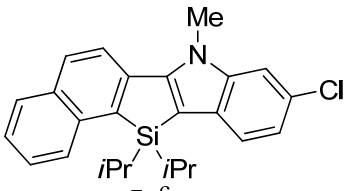
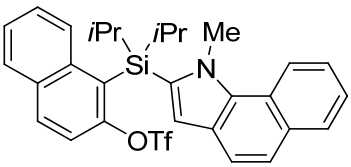
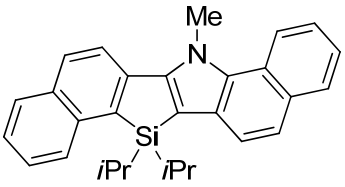
2-4. Synthesis of silicon-bridged polycyclic aromatics

Naphthylsilyl derivatives **4t-4v** were also applicable to the present cyclization, giving rise to pentacyclic products **5t** and **5u** in 91 and 91% yields, respectively, and hexacyclic product **5v** in 93% yield as a sole product (Table 4).

Table 4. Intramolecular cyclization of naphthylsilyl derivatives.[a]



4 **5**

entry	**4**	**5**	yield (%)[b]
1	 **4t**	 **5t**	91
2	 **4u**	 **5u**[c]	91
3	 **4v**	 **5v**	93

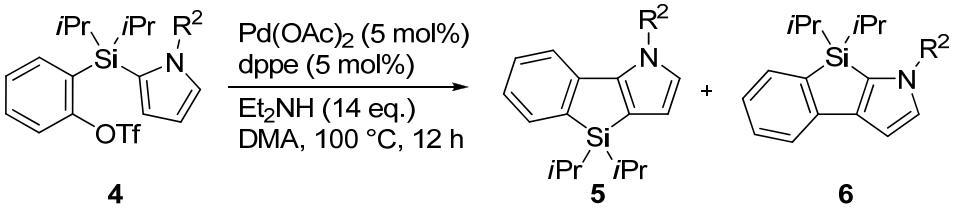
[a] All the reactions of **4** (0.3 mmol) was carried out using $Pd(OAc)_2$ (5 mol%), dppe (5 mol%), and Et_2NH (14 eq.) in DMA (1.5 mL) at 100 °C for 12 h.
[b] Isolated yield. [c] Molecular structure was unambiguously determined by X-ray diffraction analysis of the single crystal.

2-5. Pyrrole derivatives

Intramolecular cyclization of 2-silylpyrroles **4w** and **4x** proceeded similarly to give **5w** and **5x** in 78 and 73% yields, respectively (Table 5, entries 1 and 2), whereas *N*-tosylated pyrroles **4y** afforded **6y** as a major product (entry 3). The fact that the corresponding 2-silylbenzofuran and -benzothiophene did not undergo silicon migration (Eq. 2) suggests that the remarkable electron-donating nature of nitrogen in the

indole/pyrrole moiety should be the key factor for realization of the novel intramolecular coupling.

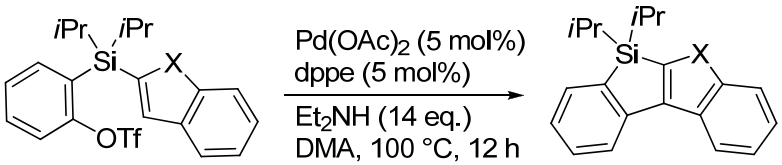
Table 5. Intramolecular cyclization of 2-silylpyrroles.[a]



4 **5** **6**

entry	**4**	R^2	**5** (yield)[b]	**6** (yield)[b]
1[c]	**4w**	Me	**5w** (78)	**6w** (nd)
2	**4x**	Ph	**5x** (73)	**6x** (23)
3	**4y**	Ts	**5y** (31)	**6y** (42)

[a] All the reactions of **4** (0.3 mmol) was carried out using $Pd(OAc)_2$ (5 mol%), dppe (5 mol%), and Et_2NH (14 eq.) in DMA (1.5 mL) at 100 °C for 12 h except for entry 1. [b] Isolated yield. nd: not detected. [c] Reaction was conducted with 1 mmol of **4w**.



7a: X = O
7b: X = S

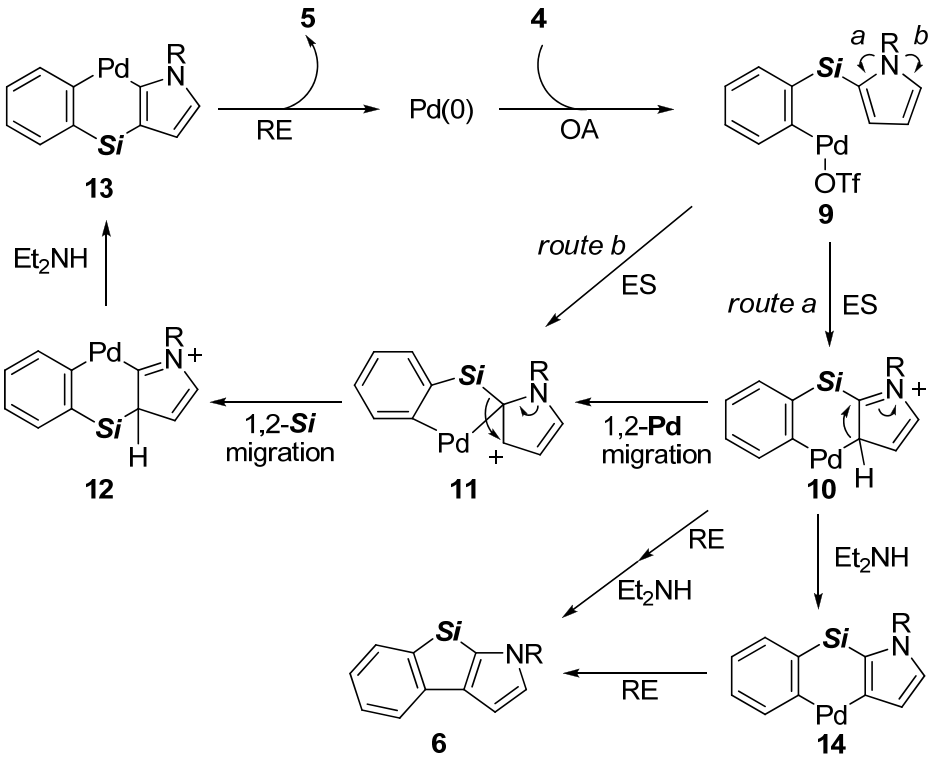
8a: X = O, 80%
8b: X = S, 96%

(2)

2-6. Mechanism

The author proposes a plausible catalytic cycle shown in Scheme 3. Arylpalladium **9** generated by oxidative addition (OA) of **4** to a Pd(0) complex would undergo intramolecular electrophilic substitution (ES) at the 3-position of the pyrrole/indole ring to give **10** (*route a*), followed by migration of the Pd atom to the 2-position, giving rise to cationic intermediate **11**. The silicon β-cation stabilizing effect may assist the migration to overcome the steric hindrance caused by the spirocyclic structure in **11**. Alternatively, direct palladation at the 2-position in **9** leading to **11** may be operative (*route b*).[3] Subsequent 1,2-Si migration followed by deprotonation by a base and reductive elimination (RE) completes the catalytic cycle to produce **5**. The *route a* mechanism looks more likely according to the paper by Sames

and his co-workers who observed a Pd-catalyzed intermolecular direct C2-arylation of indole with iodobenzene and proposed a mechanism involving an electrophilic palladation of indole at the 3-position first, followed by 1,2-migration to give a C2-palladated indole.[4] Byproduct **6** may be produced from **10** via deprotonation followed by RE or RE followed by deprotonation. The dependency of product ratio **5**/**6** on substrates **4** may be explained by assuming that the presence of an electron-withdrawing group destabilizes **11** and thus retards the palladium migration.

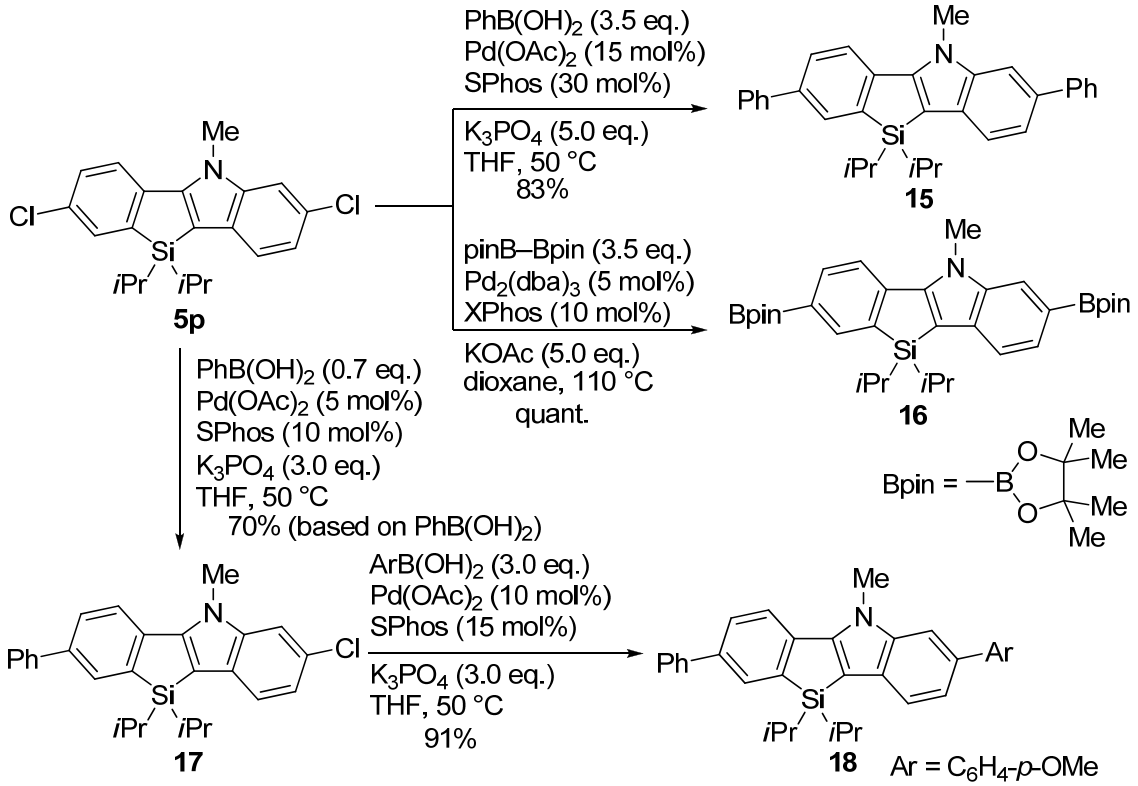


Scheme 3. Plausible mechanism.

3. Transformation of silicon-bridged phenylindole

Finally, demonstrated in Scheme 4 are examples of synthetic transformations of dichlorinated **5p** using Pd-catalyzed cross-coupling reactions. Thus, the 2-fold cross-coupling with $PhB(OH)_2$ and bis(pinacolate)diboron (pinB–Bpin) under the slightly modified Buchwald's conditions for aryl chlorides gave **15** and **16** in high yields, respectively.[5] Meanwhile, the reaction of $PhB(OH)_2$ with **5p** in slight excess achieved monocoupling selectively at the chlorine *meta* to the silylene bridge to give **17** only in

70% yield. The molecular structure of **17** was unambiguously confirmed by X-ray analysis of its single crystal (Figure 1). Such a selectivity for mono-coupling may be attributed the fact that chlorine atom *meta* to the silicon-bridge is more electron deficient (cf. Figure 2) and thus shows higher reactivity.[6] Further cross-coupling of **17** with *p*-OMeC$_6$H$_4$B(OH)$_2$ gave **18** in an excellent yield. Thus, introduction of any two different aryl groups into **5p** is possible, allowing beneficial modification of 3,2'-silicon-bridged 2-phenylindoles.



Scheme 4. Transformation of **5p**.

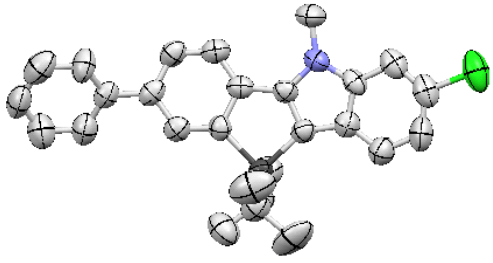


Figure 1. Molecular structure of **17**.

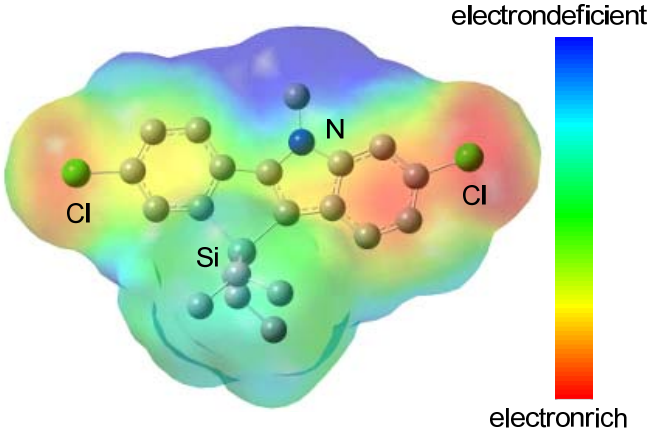


Figure 2. Electron density map of **5p**.

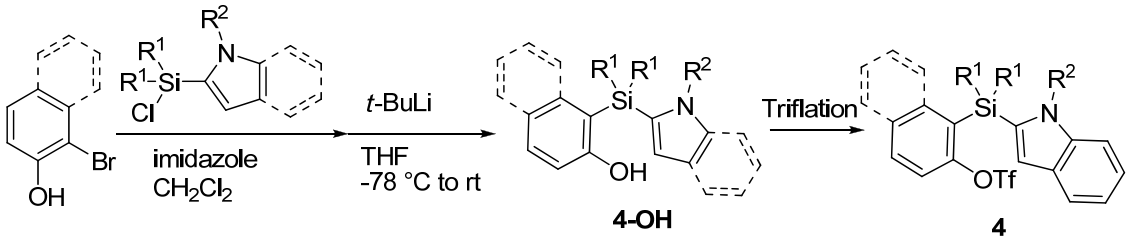
4. Conclusions

Demonstrated in this Chapter is that in the presence of a Pd catalyst and diethylamine in excess 2-(2-pyrrolylsilyl)aryl triflates undergo a new type of intramolecular coupling that involves direct arylation accompanied by reorganization of the C–Si bond. This novel transformation can be applied to synthesis of variously functionalized 3,2'-silicon-bridged 2-heteroaromatics, which may show characteristic electrophysical properties like organic semiconductors and light-emitting materials as will be discussed in the following Chapter.

Experimental

General Procedure for Preparation of 2-Silylindoles and –pyrroles

Silylindoles and -pyrroles **4** were prepared according to the following scheme.



Synthesis of 2-silylphenols:

2-Silylphenols **4-OH** were prepared by silylation of the corresponding 2-bromophenols with chloro(2-indolyl)silane (prepared from the corresponding dichlorodiorganosilane and 2-lithiatedindole), followed by retro-Brook rearrangement of the silyl ethers in a manner similar to those described in Chapter 2.

Synthesis of 2-silylindoles and -pyrroles 4:

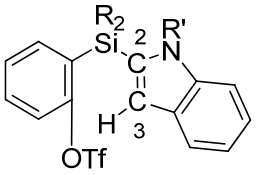
Triflation of **4–OH** was effected by either Method A or B.

<**Method A**> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-(2-pyrrolylsilyl)phenol **4-OH** (3.0 mmol) and Et_2O (10 mL). To the solution cooled to 0 °C was added butyllithium (1.59 M in hexane, 1.9 mL, 3.0 mmol) dropwise via a syringe over 10 min. The solution was stirred at 0 °C for 1 h before addition of Tf_2O (0.75 mL, 3 mmol). The resulting solution was warmed to room temperature and then stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **4** as a colorless solid or oil.

<**Method B**> An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with NaH (72 mg, 3.0 mmol) and DMF (5 mL). A DMF solution (5 mL) of 2-(2-pyrrolylsilyl)phenol **4-OH** (3.0 mmol) was added to the suspension dropwise at room temperature. The resulting solution was stirred at room temperature for 1 h and then $PhNTf_2$ (1.07 g, 3.0 mmol) was added to the solution. The mixture was stirred for 12 h at room temperature before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **4** as a colorless solid or oil.

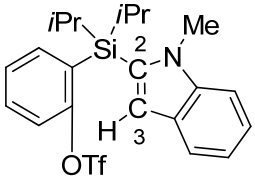
The structure of **4o** was confirmed unambiguously by X-ray crystallographic analysis. The structures of other **4** were confirmed by characteristic ^1H and ^{13}C NMR data regarding 2- and 3-positions of the indole moieties in **4** on the basis of comparison of **4a** and the reported regioisomeric congener as shown in the following figure.

Characteristic NMR data of **4**



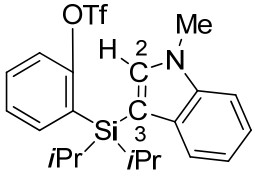
^{1}H NMR H(3) δ 6.81~6.90 ppm
^{13}C NMR C(2) δ 131.5~135.9 ppm
C(3) δ 112.7~117.3 ppm

NMR data of **4**



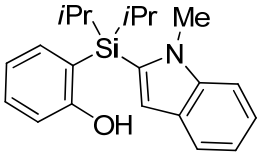
^{1}H NMR H(3) δ 6.90 ppm
^{13}C NMR C(2) δ 133.4 ppm
C(3) δ 115.0 ppm

Previously reported data (Chapter 2)



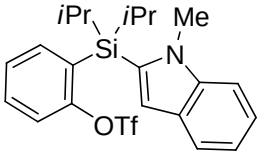
^{1}H NMR H(2) δ 7.17 ppm
^{13}C NMR C(2) δ 137.6 ppm
C(3) δ 100.4 ppm

2-[Diisopropyl(1-methylindol-2-yl)silyl]phenol (4a-OH)



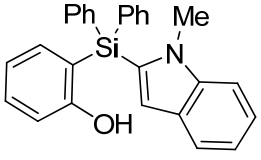
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 57%, a colorless solid. Mp: 109.0–110.0 °C. TLC: R_f 0.15 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, J = 7.2 Hz, 6H), 1.08 (d, J = 7.2 Hz, 6H), 1.72 (qq, J = 7.2, 7.2 Hz, 2H), 3.69 (s, 3H), 5.20 (s, 1H), 6.82 (d, J = 8.3 Hz, 1H), 6.96–7.00 (m, 2H), 7.14 (dd, J = 7.9, 7.8 Hz, 1H), 7.25–7.29 (m, 1H), 7.33–7.36 (m, 2H), 7.41 (dd, J = 7.4, 1.7 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 33.7, 109.5, 115.3, 115.8, 117.3, 119.4, 120.2, 120.8, 122.5, 128.4, 131.5, 133.4, 136.2, 140.8, 161.3. IR (KBr): ν = 3158, 2949, 2832, 2943, 1591, 1574, 1485, 1462, 1435, 1277, 1174, 1072, 993, 879, 781, 752, 659, 630 cm^{-1}. MS (FAB) *m/z*: 337 (28, M^+), 294 (28), 250 (5), 236 (6), 206 (4). Anal. Calcd for $C_{21}H_{27}NOSi$: C, 74.73; H, 8.06. Found: C, 74.84; H, 7.99. CCDC–722329 contains the crystallographic data for **4a-OH**.

2-[Diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4a)



Prepared by Method A. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 85%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, J = 7.2 Hz, 6H), 1.12 (d, J = 7.2 Hz, 6H), 1.80 (qq, J = 7.2, 7.2 Hz, 2H), 3.54 (s, 3H), 6.90 (s, 1H), 7.13 (dd, J = 7.7, 7.6 Hz, 1H), 7.24–7.33 (m, 3H), 7.45–7.53 (m, 3H), 7.68 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.3, 34.5, 109.2, 115.0, 118.2 (q, J = 318.0 Hz), 118.9, 119.2, 120.6, 122.2, 125.8, 126.8, 128.4, 131.7, 133.4, 138.9, 140.4, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2949, 2985, 1595, 1464, 1417, 1356, 1248, 1213, 1142, 1055, 897, 797, 746, 737, 661, 631 cm^{-1}. MS (FAB) *m/z*: 469 (100, M^+), 426 (21), 250 (13), 154 (19). Anal. Calcd for $C_{21}H_{23}F_3O_4SSi$: C, 56.27; H, 5.58. Found: C, 56.02; H, 5.60.

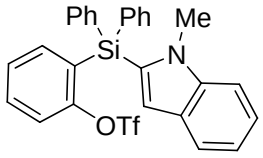
2-[(1-Methylindol-2-yl)diphenylsilyl]phenol (4b-OH)



Purification: silica gel column chromatography (hexane/AcOEt 5:1). Yield: 51%, a colorless solid. Mp: 170.5–171.4 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (s, 3H), 5.08 (s, 1H), 6.69 (d, J = 0.7 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 6.94 (ddd, J = 7.3, 7.3, 0.9 Hz, 1H), 7.11 (ddd, J = 7.4, 7.4, 0.9 Hz, 1H), 7.25–7.30 (m, 1H), 7.29–7.42 (m, 7H), 7.45–7.49 (m, 2H), 7.59 (d, J = 7.9 Hz, 1H), 7.67–7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.9, 109.3, 116.1, 116.8, 118.5, 119.4,

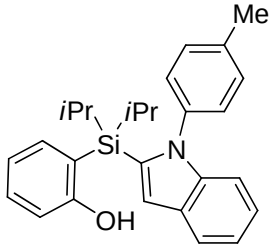
120.8, 121.1, 122.7, 128.1, 128.3, 130.0, 132.3, 132.9, 134.8, 135.9, 137.4, 140.9, 160.8. IR (KBr): ν = 3545, 3061, 3045, 2935, 1591, 1570, 1483, 1435, 1354, 1278, 1234, 1167, 1103, 1068, 831, 798, 744, 704, 630 cm^{-1}. MS (FAB) *m/z*: 405 (6, M^+), 330 (1), 274 (3). Anal. Calcd for $C_{27}H_{23}NOSi$: C, 79.96; H, 5.72. Found: C, 79.73; H, 5.66.

2-[(1-Methylindol-2-yl)diphenylsilyl]phenyl trifluoromethanesulfonate (4b)



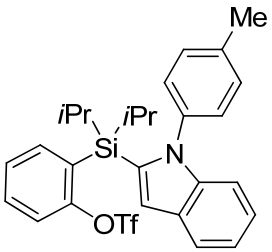
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 52%, a colorless solid. Mp: 166.8–167.6 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.49 (s, 3H), 6.65 (d, *J* = 0.8 Hz, 1H), 7.10 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 7.25–7.29 (m, 1H), 7.32–7.35 (m, 2H), 7.38–7.42 (m, 4H), 7.45–7.52 (m, 4H), 7.56–7.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.9, 109.2, 117.1, 117.9 (q, *J* = 318.0 Hz), 119.1, 119.3, 121.1, 122.6, 126.4, 127.3, 128.0, 128.3, 130.1, 131.9, 132.5, 134.0, 135.8, 139.1, 140.8, 155.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (KBr): ν = 3061, 2934, 2854, 1595, 1562, 1492, 1465, 1415, 1354, 1228, 1139, 1057, 997, 900, 798, 744, 700, 626 cm^{-1}. MS (FAB) *m/z*: 597 (100, M^+), 460 (3), 404 (6), 386 (2). Anal. Calcd for Calcd for $C_{28}H_{22}F_3NO_3SSi$: C, 62.55; H, 4.12. Found: C, 62.57; H, 4.26.

2-[Diisopropyl[1-(4-methylphenyl)indol-2-yl]silyl]phenol (4c-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 51%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.03 (d, *J* = 7.6 Hz, 6H), 1.33 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.39 (s, 3H), 5.46 (s, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.87 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.00–7.08 (m, 5H), 7.11–7.17 (m, 4H), 7.26–7.30 (m, 1H), 7.67–7.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 18.6, 18.8, 21.3, 110.7, 116.0, 116.2, 119.9, 120.0, 120.6, 122.9, 128.1, 128.4, 129.2 (2C), 131.1, 135.6, 136.1, 136.7, 137.9, 142.1, 160.8. IR (neat): ν = 3445, 2947, 2926, 2866, 1593, 1514, 1464, 1435, 1361, 1276, 1211, 1120, 1012, 906, 837, 752, 678 cm^{-1}. MS (FAB) *m/z*: 413 (35, M^+), 370 (50), 326 (10), 312 (2). Anal. Calcd for $C_{27}H_{31}NOSi$: C, 78.40; H, 7.55. Found: C, 78.29; H, 7.83.

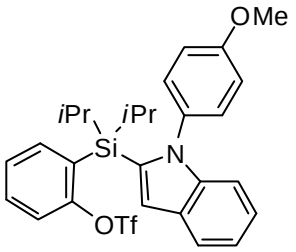
2-[Diisopropyl[1-(4-methylphenyl)indol-2-yl]silyl]phenyl trifluoromethanesulfonate (4c)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 40:1). Yield: 77%, a colorless solid. Mp: 122.1–122.8 °C. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.6 Hz, 6H), 1.13 (d, *J* = 7.6 Hz, 6H), 1.56 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.38 (s, 3H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.93–6.96 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 7.07–7.11 (m, 3H), 7.17 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.21 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.41 (ddd, *J* = 7.6, 7.4, 2.0 Hz, 1H), 7.67–7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 18.9, 19.0, 21.3, 110.3, 116.1, 118.2 (q, *J* = 317.9 Hz), 118.5, 119.5, 120.5, 122.4, 126.5, 128.06, 128.12, 128.3, 129.2, 131.0, 135.8, 137.0, 137.66, 137.68, 141.4, 155.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6. IR (KBr): ν = 2949, 2924, 2862, 1597, 1514, 1466, 1417, 1247, 1203, 1140, 1122, 1053, 902, 840, 743, 660cm^{-1}. MS (FAB) *m/z*: 545 (100, M^+), 502 (35), 412

(18), 368 (8). Anal. Calcd for $C_{28}H_{30}F_3NO_3SSi$: C, 61.63; H, 5.54. Found: C, 61.43; H, 5.55.

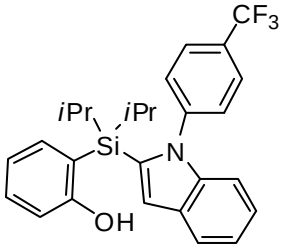
2-[Diisopropyl[1-(4-methoxylphenyl)indol-2-yl)silyl]phenol was prepared according to the general procedures and used for further steps without isolation.



2-[Diisopropyl[1-(4-methoxylphenyl)indol-2-yl]silyl]phenyl trifluoromethanesulfonate (4d)

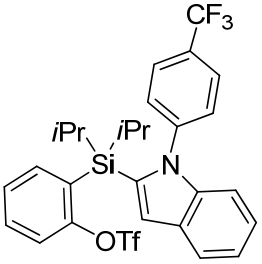
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 13%, a colorless solid. Mp: 111.2–112.2 °C. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 7.6 Hz, 6H), 1.14 (d, J = 7.6 Hz, 6H), 1.56 (qq, J = 7.6, 7.6 Hz, 2H), 3.84 (s, 3H), 6.71 (d, J = 8.7 Hz, 2H), 6.89–8.93 (m, 3H), 7.07 (s, 1H), 7.10–7.12 (m, 2H), 7.18 (dd, J = 7.4, 7.9 Hz, 1H), 7.22 (dd, J = 7.4, 1.8 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.41 (ddd, J = 8.8, 8.2, 2.0 Hz, 1H), 7.67–7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 18.9, 19.0, 55.5, 110.3, 113.7, 116.0, 118.2 (q, J = 317.9 Hz), 118.6, 119.5, 120.5, 122.4, 126.6, 128.06, 128.13, 129.7, 131.1, 1324, 136.0, 137.7, 141.7, 155.4, 158.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6. IR (KBr): ν = 3064, 2949, 2906, 2868, 1593, 1514, 1466, 1410, 1300, 1246, 1219, 1138, 1120, 1051, 889, 842, 767, 682, 826 cm^{-1}. MS (FAB) *m/z*: 561 (100, M^+), 518 (29), 428 (6), 384 (6). Anal. Calcd for $C_{28}H_{30}F_3NO_4SSi$: C, 59.87; H, 5.38. Found: C, 59.93; H, 5.40.

2-[Diisopropyl[1-(4-trifluoromethylphenyl)indol-2-yl]silyl]phenol (4e-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 21%, a colorless solid. Mp: 126.9–127.6 °C. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, J = 7.6 Hz, 6H), 1.09 (d, J = 7.6 Hz, 6H), 1.43 (qq, J = 7.6, 7.6 Hz, 2H), 5.12 (s, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.83 (ddd, J = 7.8, 7.0, 0.8 Hz, 1H), 7.00–7.02 (m, 1H), 7.07 (dd, J = 7.3, 1.7 Hz, 1H), 7.16–7.18 (m, 2H), 7.21–7.27 (m, 4H), 7.47 (d, J = 7.4 Hz, 2H), 7.67–7.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 18.82, 18.85, 110.3, 115.7, 116.85, 116.89, 119.9, 120.4, 120.8, 123.3, 123.7 (q, J = 269.9 Hz), 125.7, 128.4, 128.9, 130.0 (q, J = 32.8 Hz), 131.3, 135.5, 136.6, 141.4, 142.6, 160.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9. IR (KBr): ν = 3500, 2967, 2947, 2866, 1614, 1595, 1520, 1466, 1438, 1323, 1165, 1124, 1066, 852, 800, 746, 688 cm^{-1}. MS (FAB) *m/z*: 467 (28, M^+), 424 (57), 380 (13), 330 (14). Anal. Calcd for $C_{27}H_{28}F_3NOSi$: C, 69.35; H, 6.04. Found: C, 69.36; H, 6.12. CCDC–722330 contains the crystallographic data for **4e-OH**.

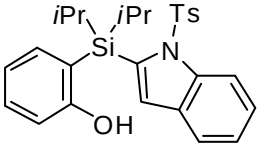
2-[Diisopropyl[1-(4-trifluoromethylphenyl)indol-2-yl]silyl]phenyl trifluoromethanesulfonate (4e)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 20:1). Yield: 47%, a colorless solid. Mp: 115.3–116.3 °C. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J = 7.6 Hz, 6H), 1.19 (d, J = 7.6 Hz, 6H), 1.61 (qq, J = 7.6, 7.6 Hz, 2H), 6.91–6.95 (m, 1H), 7.08–7.17 (m 7H), 7.26–7.28 (m, 1H), 7.39–7.43 (m, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.70–7.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.7, 18.8, 19.1, 109.9,

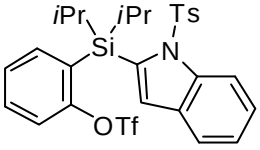
117.3, 118.2 (q, J = 318.0 Hz), 118.9, 120.1, 120.8, 123.0, 123.7 (q, J = 269.9 Hz), 125.8 (q, J = 3.9 Hz),126.9, 127.8, 128.4, 128.9, 129.8 (q, J = 32.0 Hz), 131.4, 135.5, 137.0, 141.1, 143.0, 155.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9, –74.6. IR (KBr): ν = 3063, 2957, 2935, 2858, 1616, 1597, 1521, 1467, 1413, 1327, 1246, 1165, 1068, 999, 898, 744, 678 cm^{-1}. MS (FAB) *m/z*: 599 (100, M^+), 556 (67), 466 (8), 422 (9). Anal. Calcd for $C_{28}H_{27}F_6NO_3SSi$: C, 56.08; H, 4.54. Found: C, 55.93; H, 4.61.

2-[Diisopropyl(1-tosylindol-2-yl)silyl]phenol (4f-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 46%, a colorless solid. Mp: 165.0–165.9 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (d, J = 7.6 Hz, 6H), 1.26 (d, J = 7.6 Hz, 6H), 2.17–2.27 (m, 5H), 4.99 (s, 1H), 6.71 (dd, J = 8.2, 0.7 Hz, 1H), 6.88 (d, J = 8.1 Hz, 2H), 7.00–7.05 (m, 3H), 7.22 (ddd, J = 7.4, 7.4, 0.9 Hz, 1H), 7.24 (d, J = 0.7 Hz, 1H), 7.27–7.34 (m, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.63 (dd, J = 7.4, 1.7 Hz, 1H), 8.01 (dd, J = 8.4, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 19.15, 19.17, 21.5, 114.4, 115.4, 120.6, 121.0, 121.1, 123.1, 123.8, 125.0, 126.7, 129.1, 130.7, 130.9, 135.1, 136.7, 138.3, 138.6, 144.0, 160.4. IR (KBr): ν = 3487, 3059, 2948, 2946, 2868, 1595, 1435, 1359, 1220, 1168, 1128, 1090, 1022, 810, 750, 687, 648 cm^{-1}. MS (FAB) *m/z*: 477 (1, M^+), 434 (100), 384 (23), 342 (1). HR MS Calcd for $C_{24}H_{24}NO_3SSi$ (– *i*Pr): 434.1246 (M^+–43). Found: 434.1264.

2-[Diisopropyl(1-tosylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4f)

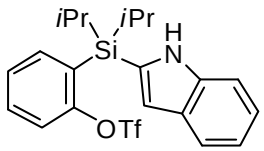


Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 79%, a colorless solid. Mp: 152.0–152.7 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, J = 7.6 Hz, 6H), 1.25 (d, J = 7.6 Hz, 6H), 2.22 (s, 3H), 2.29 (qq, J = 7.6, 7.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 7.24 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 7.26–7.31 (m, 3H), 7.40 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 7.48 (ddd, J = 8.4, 7.5, 1.8 Hz, 1H), 7.58 (m, 1H), 7.86 (dd, J = 7.5, 1.8 Hz, 1H), 7.97 (dd, J = 8.4, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 19.00, 19.01, 21.5, 114.3, 118.0, 118.1 (q, J = 318.0 Hz), 121.2, 123.2, 125.1, 129.1, 129.8, 130.8, 131.0, 135.3, 136.3, 138.3, 138.8, 143.9, 155.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ –75.0. IR (KBr): ν = 3068, 2970, 2943, 2866, 1593, 1467, 1413, 1363, 1230, 1197, 1105, 1031, 922, 882, 810, 760, 680, 648 cm^{-1}. MS (FAB) *m/z*: 609 (1, M^+), 566 (100), 434 (2), 384 (28). HR MS Calcd for $C_{28}H_{30}F_3NO_5S_2Si$: 609.1287 (M^+). Found: 609.1313.

Preparation of 2-[(2-indolyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (4g)

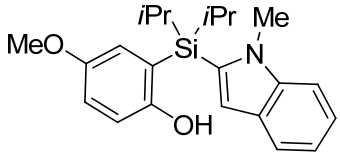
An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with **4f-OH** (954 mg, 2.0 mmol), magnesium turning (480 mg, 20 mmol), and MeOH (30 mL). The resulting solution was sonicated for 30 min at room temperature before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give 2-[diisopropyl(2-indolyl)silyl]phenol (**4g-OH**) (570 mg, 88%) as a colorless solid. An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with NaH (36 mg, 1.5 mmol) and DMF (5 mL). A DMF solution (5 mL) of **4g-OH** (480 mg, 1.5 mmol) was added to the suspension dropwise at room temperature.

The resulting solution was stirred at room temperature for 1 h and then $PhNTf_2$ (0.48 g, 1.5 mmol) was added to the solution. The mixture was stirred for 12 h at room temperature before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL x 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) to give 2-[diisopropyl(2-indolyl)silyl]phenyl trifluoromethanesulfonate (**4g**) (600 mg, 89%) as a colorless solid .



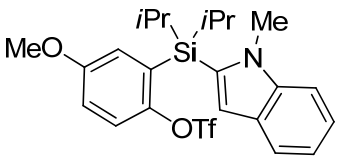
Mp: 89.2–90.6 °C. TLC: R_f 0.29 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.76 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.92 (d, *J* = 2.0 Hz, 1H), 7.14 (dd, *J* = 7.9, 7.1 Hz, 1H), 7.23 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.26–7.29 (m, 1H), 7.40–7.46 (m, 3H), 7.51 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 8.08 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.2, 110.8, 115.2, 118.3 (q, *J* = 317.2 Hz), 118.9, 119.7, 120.6, 122.6, 125.6, 127.0, 128.2, 130.3, 131.8, 138.7, 139.3, 155.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 3475, 3412, 2951, 2866, 1593, 1465, 1421, 1392, 1246, 1211, 1139, 1055, 895, 754, 669, 636 cm^{-1}. MS (FAB) *m/z*: 455 (100, M^+), 412 (82), 339 (70). Anal. Calcd for $C_{21}H_{24}F_3NO_3SSi$: C, 55.37; H, 5.31. Found: C, 55.47; H, 5.51.

2-[Diisopropyl(1-methylindol-2-yl)silyl]-4-methoxyphenol (4h-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 35%, a colorless solid. Mp: 95.4–96.2 °C. TLC: R_f 0.12 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.70 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.70 (s, 3H), 3.79 (s, 3H), 4.87 (s, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.90 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.96 (d, *J* = 3.1 Hz, 1H), 6.97 (s, 1H), 7.13 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.27 (dd, *J* = 8.2, 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.01, 18.03, 33.7, 55.8, 109.5, 115.3, 116.5, 116.6, 118.5, 119.4, 120.8, 121.1, 122.6, 128.4, 133.3, 140.8, 153.0, 155.3. IR (KBr): ν = 3460, 2957, 2938, 2899, 2860, 1583, 1489, 1462, 1400, 1269, 1201, 1138, 1069, 1034, 995, 879, 808, 796, 752, 723, 692, 659, 638 cm^{-1}. MS (FAB) *m/z*: 366 (14, M^+), 323 (4), 281 (2), 253 (4). Anal. Calcd for $C_{22}H_{29}NO_2Si$: C, 71.89; H, 7.95. Found: C, 71.59; H, 8.13.

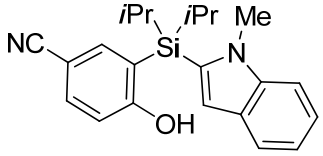
2-[Diisopropyl(1-methylindol-2-yl)silyl]-4-methoxyphenyl trifluoromethanesulfonate (4h)



Prepared by Method A. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 10:1). Yield: 73%, a colorless solid. Mp: 92.5–93.5 °C. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.78 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.57 (s, 3H), 3.72 (s, 3H), 6.89 (s, 1H), 6.95–6.99 (m, 2H), 7.13 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.24–7.27 (m, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.3, 34.5, 55.7, 109.2, 115.1, 115.8, 118.3 (q, *J* = 317.2 Hz), 119.1, 120.2, 120.7, 122.2, 123.7, 127.6, 128.4, 133.3, 140.4, 148.9, 157.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (KBr): ν = 2949, 2935, 2870, 1585, 1483, 1464, 1393, 1377, 1304, 1229, 1207, 1139, 1125,

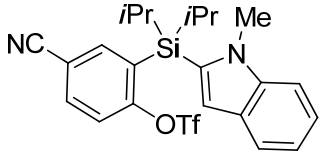
1031, 898, 866, 796, 756, 740, 678, 665 cm^{-1}. MS (FAB) *m/z*: 499 (100, M^+), 456 (11), 366 (11), 350 (13), 322 (47). Anal. Calcd for $C_{23}H_{28}F_3NO_4SSi$: C, 55.29; H, 5.65. Found: C, 55.51; H, 5.65.

4-Cyano-2-[diisopropyl(1-methylindol-2-yl)silyl]phenol (4i-OH)



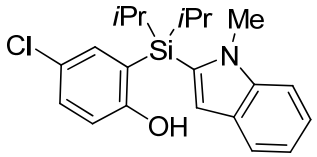
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 50%, a colorless solid. Mp: 167.6–168.5 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.73 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.69 (s, 3H), 5.95 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 0.7 Hz, 1H), 7.16 (dd, *J* = 8.2, 7.8 Hz, 1H), 7.31 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.36 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 17.87, 17.89, 33.8, 104.1, 109.6, 116.1, 116.9, 119.3, 119.8, 119.9, 121.0, 123.2, 128.3, 131.6, 135.5, 140.5, 141.0, 164.8. IR (KBr): ν = 3289, 2945, 2928, 2864, 2228, 1583, 1491, 1464, 1385, 1356, 1329, 1286, 1211, 1070, 997, 883, 833, 796, 748, 731, 636 cm^{-1}. MS (FAB) *m/z*: 362 (42, M^+), 319 (21), 277 (4), 261 (2). HR MS Calcd for $C_{22}H_{26}N_2OSi$: 362.1814 (M^+). Found: 362.1815.

4-Cyano-2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4i)



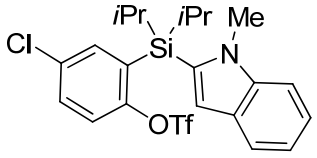
Prepared by Method B. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 10:1). Yield: 70%, a colorless solid. Mp: 59.2–60.2 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.81 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.57 (s, 3H), 6.89 (s, 1H), 7.15 (dd, *J* = 7.6, 6.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.83–7.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.0, 18.2, 34.4, 109.3, 115.5, 115.7, 117.2, 118.1(q, *J* = 318.0 Hz), 119.5, 119.7, 120.8, 122.7, 128.3, 129.1, 131.5, 135.4, 140.5, 142.2, 157.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 3061, 2951, 2895, 2808, 2233, 1583, 1446, 1408, 1357, 1249, 1215, 1139, 1058, 996, 896, 844, 796, 752, 736, 690, 632, 617 cm^{-1}. MS (FAB) *m/z*: 494 (100, M^+), 451 (15), 318 (18), 275 (12), 231 (4). Anal. Calcd for $C_{23}H_{25}F_3N_2O_3SSi$: C, 55.85; H, 5.09. Found: C, 55.62; H, 5.04.

4-Chloro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenol (4j-OH)



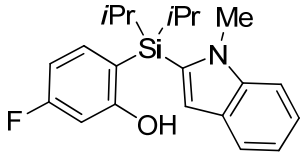
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 36%, a colorless solid. Mp: 107.0–108.0 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 12H), 1.71 (sep, *J* = 7.2Hz, 2H), 3.69 (s, 3H), 5.26 (s, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.99 (s, 1H), 7.14 (dd, *J* = 7.9, 7.5 Hz, 1H), 7.27–7.31 (m, 2H), 7.34 (d, *J* = 2.8 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.9, 18.0, 33.8, 109.5, 115.7, 117.5, 119.6, 119.9, 120.9, 122.8, 125.5, 128.4, 131.4, 132.4, 135.0, 140.9, 159.8. IR (KBr): ν = 3549, 2943, 2902, 2864, 1589, 1460, 1375, 1267, 1234, 1134, 1109, 1064, 997, 878, 815, 750, 734, 651, 638 cm^{-1}. MS (FAB) *m/z*: 372 (30, M^+ + H), 328 (19), 240 (11), 198 (3). Anal. Calcd for $C_{21}H_{26}ClNOSi$: C, 67.81; H, 7.05. Found: C, 67.66; H, 7.05.

4-Chloro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4j)



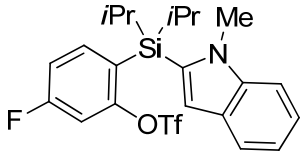
Prepared by Method A. Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 30:1). Yield: 76%, a colorless oil. TLC: R_f 0.51 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.79 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.58 (s, 3H), 6.90 (s, 1H), 7.15 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.26–7.30 (m, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.7 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.2, 34.5, 109.3, 115.3, 118.2 (q, *J* = 317.2 Hz), 119.3, 120.4, 120.7, 122.4, 128.3, 131.5, 132.4, 133.0, 137.9, 140.4, 153.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 3061, 2951, 2931, 2868, 1585, 1492, 1446, 1402, 1359, 1329, 1247, 1207, 1138, 1105, 1072, 1055, 995, 883, 798, 752, 665, 613 cm^{-1}. MS (FAB) *m/z*: 503 (100, M^+), 460 (51), 370 (9), 354 (4), 328 (10). Anal. Calcd for $C_{22}H_{25}ClF_3NO_3SSi$: C, 52.42; H, 5.00. Found: C, 52.52; H, 5.12.

5-Fluoro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenol (4k-OH)



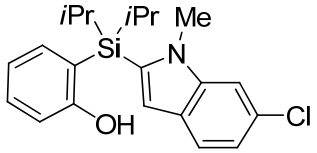
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 43%, a colorless solid. Mp: 119.4–120.4 °C. TLC: R_f 0.19 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.69 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.70 (s, 3H), 5.41 (s, 1H), 6.56 (dd, *J* = 10.6, 2.5 Hz, 1H), 6.73 (ddd, *J* = 8.4, 8.4, 2.5 Hz, 1H), 6.99 (d, *J* = 0.7 Hz, 1H), 7.15 (ddd, *J* = 7.5, 7.3, 1.1 Hz, 1H), 7.29 (ddd, *J* = 7.8, 7.5, 1.1 Hz, 1H), 7.34–7.38 (m, 2H), 7.68 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.91, 17.92, 33.7, 103.6 (d, *J* = 22.9 Hz), 197.8 (d, *J* = 19.8 Hz), 109.5, 112.8 (d, *J* = 3.0 Hz), 115.7, 119.5, 120.9, 122.8, 128.4, 132.7, 137.3 (d, *J* = 9.9 Hz), 141.0, 163.0 (d, *J* = 11.4 Hz), 165.2 (d, *J* = 266.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –109.7. IR (KBr): ν = 3466, 2945, 2862, 1585, 1464, 1402, 1282, 1190, 1147, 1070, 976, 881, 835, 783, 740, 655 cm^{-1}. MS (FAB) *m/z*: 355 (100, M^+), 312 (74), 270 (8). Anal. Calcd for $C_{21}H_{26}FNOSi$: C, 70.95; H, 7.37. Found: C, 70.87; H, 7.30.

5-Fluoro-2-[diisopropyl(1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4k)



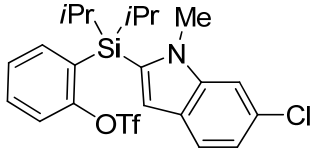
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 83%, a colorless oil. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.78 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.56 (s, 3H), 6.89 (s, 1H), 7.05 (ddd, *J* = 8.5, 7.9, 2.2 Hz, 1H), 7.14 (dd, *J* = 7.6, 7.0 Hz, 1H), 7.23–7.28 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 7.2, 7.0 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.1, 18.3, 34.5 107.6 (d, *J* = 25.9 Hz), 109.2, 114.4 (d, *J* = 19.1 Hz), 115.2, 118.2 (q, *J* = 318.0 Hz), 119.3, 120.7, 121.4 (d, *J* = 3.8 Hz), 122.3, 128.4, 133.0, 139.9 (d, *J* = 7.6 Hz), 140.4, 155.4 (d, *J* = 9.9 Hz), 163.8 (d, *J* = 251.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.6, –106.2. IR (neat): ν = 2951, 2906, 2868, 1599, 1487, 1386, 1356, 1246, 1141, 1070, 968, 854, 796, 752, 736, 657 cm^{-1}. MS (FAB) *m/z*: 487 (100, M^+), 444 (33), 354 (8), 266 (10). Anal. Calcd for $C_{22}H_{25}NO_3SSi$: C, 54.19; H, 5.17. Found: C, 54.39; H, 5.11.

2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl]phenol (4l-OH)



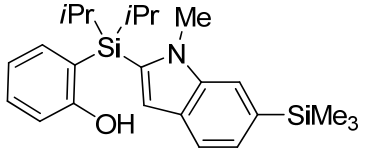
Purification: silica gel column chromatography (hexane/AcOEt: 10:1). Yield: 46%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.6 Hz, 6H), 1.07 (d, *J* = 7.6 Hz, 6H), 1.70 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.63 (s, 3H), 5.04 (s, 1H), 6.81 (dd, *J* = 8.0, 0.7 Hz, 1H), 6.92 (d, *J* = 0.7 Hz, 1H), 6.98 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1H), 7.09 (d, *J* = 8.4, 1.8 Hz, 1H), 7.33–7.36 (m, 2H), 7.39 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 33.9, 109.5, 115.0, 115.7, 117.2, 120.1, 120.4, 121.5, 126.9, 128.7, 131.6, 135.0, 136.3, 141.1, 161.1. IR (neat): ν = 3445, 3068, 2945, 2867, 1593, 1566, 1435, 1383, 1359, 1329, 1278, 1192, 1120, 1053, 997, 916, 884, 829, 760, 682, 667 cm^{-1}. MS (FAB) *m/z*: 371 (70, M^+), 328 (62), 300 (6), 284 (11), 250 (10). Anal. Calcd for $C_{21}H_{26}ClNOSi$: C, 67.81; H, 7.05. Found: C, 67.52; H, 6.90.

2-[Diisopropyl(6-chloro-1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4l)



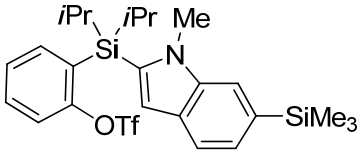
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt: 40:1). Yield: 78%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.11 (d, *J* = 7.6 Hz, 6H), 1.78 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.50 (s, 3H), 6.85 (s, 1H), 7.09 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.30–7.34 (m, 2H), 7.45–7.49 (m, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.3, 34.5, 109.2, 114.9, 118.2 (q, *J* = 317.2 Hz), 119.0, 119.9, 121.4, 125.6, 126.9 (2C), 128.3, 131.9, 134.6, 138.6, 140.8, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2951, 2895, 2868, 1607, 1595, 1444, 1402, 1360, 1329, 1287, 1240, 1138, 1053, 997, 918, 816, 766, 667, 651 cm^{-1}. MS (FAB) *m/z*: 503 (100, M^+), 460 (29), 370 (5), 268 (5). HR MS Calcd for $C_{22}H_{25}ClF_3NO_3SSi$: 503.0965 (M^+). Found: 503.0942.

2-[Diisopropyl(1-methyl-6-trimethylsilylindol-2-yl)silyl]phenol (4m-OH)



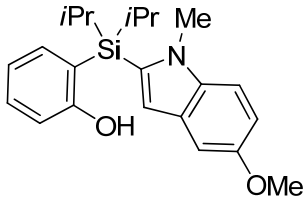
Purification: silica gel column chromatography (hexane/AcOEt 13:1). Yield: 41%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.34 (s, 9H), 1.06 (d, *J* = 7.2 Hz, 12H), 1.71 (sep, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 5.14 (s, 1H), 6.82 (dd, *J* = 8.0, 0.7 Hz, 1H), 6.96–7.00 (m, 2H), 7.29 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.34 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.49 (d, *J* = 0.7 Hz, 1H), 7.68 (dd, *J* = 7.9, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.4, 18.0, 33.7, 114.3, 115.1, 115.8, 117.2, 120.2, 120.3, 123.9, 129.0, 131.6, 133.6, 133.8, 136.2, 140.6, 161.3. IR (neat): ν = 3443, 3050, 3014, 2965, 2891, 1599, 1568, 1469, 1435, 1314, 1360, 1277, 1192, 1148, 1121, 1076, 997, 881, 835, 810, 756, 692 cm^{-1}. MS (FAB) *m/z*: 409 (89, M^+), 394 (20), 366 (24), 350 (9), 338 (4). HR MS Calcd for $C_{24}H_{25}NOSi_2$: 409.2257 (M^+). Found: 409.2257.

2-[Diisopropyl(1-methyl-6-trimethysilylindol-2-yl)silyl] phenyl trifluoromethanesulfonate (4m)



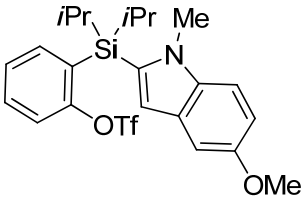
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 26%, a colorless solid. Mp: 88.9–89.7 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H), 1.01 (d, *J* = 7.6 Hz, 6H), 1.12 (d, *J* = 7.6 Hz, 6H), 1.80 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.57 (s, 3H), 6.88 (s, 1H), 7.25–7.30 (m, 2H), 7.41 (m, 4H), 7.68 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.6, 18.2, 18.3, 34.6, 114.0, 115.0, 118.3 (q, *J* = 318.0 Hz), 119.0, 120.2, 123.8, 125.8, 126.8, 128.9, 131.7, 133.2, 133.8, 139.1, 140.1, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 2953, 2935, 2866, 1468, 1423, 1357, 1247, 1219, 1142, 1122, 1055, 995, 897, 841, 813, 766, 744, 628 cm^{-1}. MS (FAB) *m/z*: 541 (100, M^+), 498 (11), 430 (3), 350 (13). Anal. Calcd for $C_{25}H_{34}F_3NO_3SSi_2$: C, 55.42; H, 6.33. Found: C, 55.33; H, 6.38.

2-[Diisopropyl(5-methoxy-1-methylindol-2-yl)silyl]phenol (4n-OH)



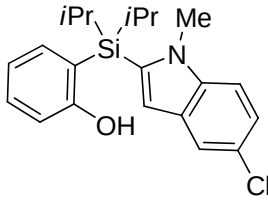
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 46%, a colorless solid. Mp: 122.0–123.0 °C. TLC: R_f 0.15 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.70 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.66 (s, 3H), 3.87 (s, 3H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.89 (s, 1H), 6.94 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.98 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 7.34 (ddd, *J* = 8.1, 8.1, 1.7 Hz, 1H), 7.41 (dd, *J* = 7.3, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.0, 33.9, 55.9, 101.8, 110.2, 113.5, 114.6, 115.8, 117.3, 120.2, 128.6, 131.5, 133.8, 136.1, 136.5, 153.9, 161.3. IR (KBr): ν = 3377, 2949, 2928, 1616, 1587, 1570, 1500, 1456, 1433, 1344, 1276, 1209, 1177, 1074, 1033, 995, 883, 835, 787, 758, 689, 658, 646, 605 cm^{-1}. MS (FAB) *m/z*: 367 (100, M^+), 324 (44), 266 (14), 176 (13). Anal. Calcd for $C_{22}H_{29}NO_2Si$: C, 71.89; H, 7.95. Found: C, 71.64; H, 7.91. CCDC–722331 contains the crystallographic data for **4n-OH**.

2-[Diisopropyl(5-methoxy-1-methylindol-2-yl)silyl]phenyl trifluoromethanesulfonate (4n)



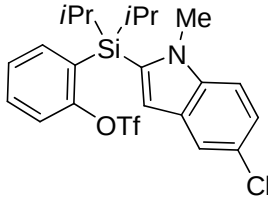
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 81%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.79 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.52 (s, 3H), 3.88 (s, 3H), 6.81 (s, 1H), 6.94 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.45–7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.2, 18.3, 34.6, 55.9, 101.8, 109.9, 112.9, 114.3, 118.2 (q, *J* = 317.2 Hz), 118.9, 125.9, 126.8, 128.6, 131.7, 133.9, 135.9, 138.9, 153.8, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2949, 2868, 2539, 1620, 1595, 1504, 1454, 1415, 1336, 1288, 1246, 1207, 1139, 1122, 1055, 997, 885, 835, 777, 765, 745, 655, 597 cm^{-1}. MS (FAB) *m/z*: 499 (100, M^+), 456 (9), 366 (7), 350 (3), 308 (5). Anal. Calcd for $C_{23}H_{28}F_3NO_4SSi$: C, 55.29; H, 5.65. Found: C, 55.29; H, 5.71.

2-[(5-Chloro-1-methylindol-2-yl)diisopropylsilyl]phenol (4o-OH)



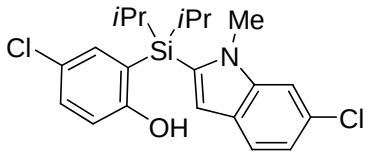
Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 46%, a colorless solid. Mp: 100.0–100.5 °C. TLC: R_f 0.17 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.71 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.65 (s, 3H), 5.05 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 1H), 6.98 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.34 (ddd, *J* = 8.8, 7.5, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.0, 34.0, 110.4, 114.2, 115.7, 117.2, 120.0, 120.4, 122.6, 125.2, 129.3, 131.6, 135.8, 136.3, 139.1, 161.1. IR (KBr): ν = 3507, 2949, 2926, 2862, 1591, 1572, 1481, 1435, 1360, 1317, 1274, 1057, 993, 880, 794, 760, 684, 653 cm^{-1}. MS (FAB) *m/z*: 371 (48, M^+), 328 (61), 284 (12), 270 (7), 250 (11). Anal. Calcd for $C_{21}H_{26}ClNOSi$: C, 67.81; H, 7.05. Found: C, 67.73; H, 7.08. CCDC–722332 contains the crystallographic data for **4o-OH**.

2-[(5-Chloro-1-methylindol-2-yl)diisopropylsilyl]phenyl trifluoromethanesulfonate (4o)



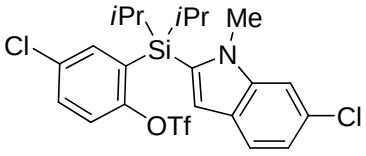
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 81%, a colorless solid. Mp: 77.5–78.5 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.17 (d, *J* = 7.2 Hz, 6H), 1.78 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.52 (s, 3H), 6.81 (s, 1H), 7.18 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.33 (ddd, *J* = 7.4, 7.3, 0.8 Hz, 1H), 7.45–7.49 (m, 2H), 7.53 (ddd, *J* = 7.9, 7.4, 1.9 Hz, 1H), 7.62 (dd, *J* = 1.8, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.2, 34.6, 110.1, 114.2, 118.2 (q, *J* = 317.2 Hz), 119.1, 119.9, 122.4, 125.0, 125.5, 126.9, 129.3, 131.9, 135.3, 138.5, 138.6, 155.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (KBr): ν = 2965, 2951, 2868, 1485, 1467, 1417, 1244, 1217, 1203, 1140, 1053, 891, 814, 748, 667, 640 cm^{-1}. MS (FAB) *m/z*: 503 (100, M^+), 460 (21), 370 (9), 328 (11), 312 (4). Anal. Calcd for $C_{22}H_{25}ClF_3NO_3SSi$: C, 52.42; H, 5.00. Found: C, 52.14; H, 4.92. CCDC–722333 contains the crystallographic data for **4o**.

4-Chloro-2-[(6-chloro-1-methylindol-2-yl)diisopropylsilyl]phenol (4p-OH)



Purification: silica gel column chromatography (hexane/AcOEt: 10:1). Yield: 59%, a colorless oil. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.6 Hz, 6H), 1.76 (sep, *J* = 7.6 Hz, 2H), 3.64 (s, 3H), 5.10 (s, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 0.7 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 7.33 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.95, 17.98, 33.9, 109.5, 115.4, 117.4, 119.9, 120.3, 121.6, 125.6, 126.8, 129.0, 131.4, 134.0, 135.1, 141.2, 159.6. IR (neat): ν = 3548, 3063, 2960, 2889, 1874, 1606, 1444, 1384, 1327, 1286, 1224, 1182, 1134, 1107, 1053, 997, 918, 882, 825, 752, 740, 665, 632 cm^{-1}. MS (FAB) *m/z*: 405 (22, M^+), 362 (18), 318 (4), 318 (4), 290 (3). Anal. Calcd for $C_{21}H_{25}Cl_2NOSi$: C, 62.06; H, 6.20. Found: C, 62.20; H, 6.39.

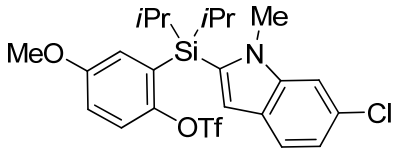
4-Chloro-2-[(6-chloro-1-methylindol-2-yl)diisopropylsilyl] phenyl trifluoromethanesulfonate (4p)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt: 20:1). Yield: 84%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.6 Hz, 6H), 1.11 (d, *J* = 7.6 Hz, 6H), 1.78 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.53 (s, 1H), 6.85 (d, *J* = 0.7 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.32 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.48 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.1, 18.2, 34.5, 115.2, 109.3, 118.1 (q, *J* = 317.2 Hz), 120.1, 120.5, 121.4, 126.9, 128.59, 128.64, 131.7, 133.1, 133.7, 137.6, 140.8, 153.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.7. IR (neat): ν = 2953, 2930, 2868, 1608, 1447, 1427, 1417, 1368, 1248, 1138, 1056, 996, 919, 816, 767, 667, 613 cm^{-1}. MS (FAB) *m/z*: 537 (100, M^+), 494 (20), 404 (7), 362 (13), 318 (12). Anal. Calcd for $C_{22}H_{24}Cl_2F_3NO_3SSi$: C, 49.07; H, 4.49. Found: C, 49.00; H, 4.68.

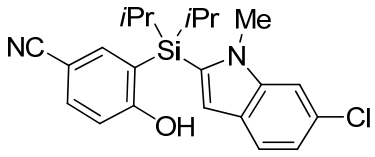
2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl]-4-methoxyphenol was prepared according to the general procedures and used for further steps without isolation.

2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl] -4-methoxylphenyl trifluoromethanesulfonate (4q)



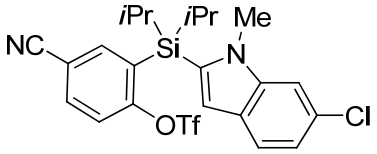
Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt: 10:1). Yield: 31%, a colorless solid. Mp: 105.1–106.1 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.77 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.53 (s, 3H), 3.75 (s, 3H), 6.86 (s, 1H), 6.97–7.00 (m, 2H), 7.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.30 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.2, 18.3, 34.4, 55.7, 109.2, 114.9, 115.7, 118.2 (q, *J* = 317.2 Hz), 119.9, 120.3, 121.4, 123.6, 126.9, 127.3, 128.3, 134.5, 140.8, 148.8, 157.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.9. IR (KBr): ν = 2949, 2868, 1578, 1477, 1464, 1416, 1248, 1221, 1207, 1142, 1132, 1028, 916, 904, 813, 678 cm^{-1}. MS (FAB) *m/z*: 533 (100, M^+), 490 (8), 400 (9). Anal. Calcd for $C_{23}H_{27}ClF_3NO_4SSi$: C, 51.73; H, 5.10. Found: C, 51.61; H, 5.13.

2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl]-4-cyanophenol (4r-OH)



Purification: silica gel column chromatography (hexane/AcOEt: 5:1). Yield: 47%, a colorless solid. Mp: 188.8–189.2 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.07 (d, *J* = 7.2 Hz, 6H), 1.72 (qq, *J* = 7.2, 7.2 Hz, 2H), 5.92 (s, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.94 (s, 1H), 7.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.34 (d, *J* = 1.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.70 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 17.89, 17.92, 33.9, 104.2, 109.6, 115.8, 116.8, 119.2, 119.9, 120.5, 121.7, 126.8, 129.3, 133.2, 135.5, 140.6, 141.3, 164.6. IR (KBr): ν = 3298, 2953, 2862, 2228, 1587, 1458, 1387, 1286, 1224, 1074, 1055, 997, 918, 833, 817, 669 cm^{-1}. MS (FAB) *m/z*: 396 (5, M^+), 353 (3), 329 (2). Anal. Calcd for $C_{22}H_{25}ClN_2OSi$: C, 66.56; H, 6.35. Found: C, 66.75; H, 6.46.

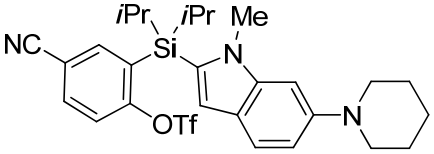
2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl] -4-cyanophenyl trifluoromethanesulfonate (4r)



Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt: 10:1). Yield: 80%, a colorless solid. Mp: 113.1–114.1 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.79 (qq, *J*= 7.2, 7.2 Hz, 2H), 3.52 (s, 3H), 6.85 (s, 1H), 7.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.83 (dd, *J* = 8.6, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.0, 18.2, 64.4, 109.3, 111.6, 115.6, 117.2, 118.1 (q, *J* = 318.0 Hz), 119.8, 120.3, 121.5, 126.8, 128.8, 128.9, 132.8, 135.5, 140.1, 141.9, 157.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 2926, 2868, 2223, 1465, 1288, 1249, 1217, 1141, 1062, 916, 848, 814, 669 cm^{-1}. MS (FAB) *m/z*: 528 (100, M^+), 485 (9), 395 (4). Anal. Calcd for $C_{23}H_{24}ClF_3N_2O_3SSi$: C, 52.22; H, 4.57. Found: C, 52.26; H, 4.56.

6-Piperidylindole was prepared by the procedure of ref 7 and then subjected to general procedure for synthesis of 2-silylphenols followed by triflation under Method B.

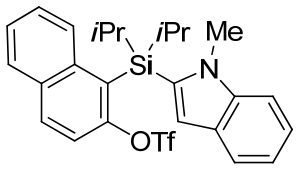
4-Cyano-2-[(1-methyl-6-piperidylindol-2-yl)diisopropylsilyl]phenyl trifluoromethanesulfonate (4s)



Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 18%, a colorless solid. Mp: 138.5–139.6 °C. TLC: R_f 0.50 (hexane/AcOEt 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6H), 1.10 (d, *J* = 7.6 Hz, 6H), 1.61 (qq, *J* = 7.6, 7.6 Hz, 2H), 1.77–1.83 (m, 6H), 3.22 (t, *J* = 5.4 Hz, 4H), 3.50 (s, 3H), 6.78–6.82 (m, 2H), 6.95 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.80–7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.1, 18.3, 24.4, 26.2, 34.4, 52.6, 96.5, 111.4, 113.4, 115.8, 117.3, 118.1 (q, *J* = 317.2 Hz), 119.6, 119.7, 120.9, 129.4, 135.3, 141.5, 142.5, 157.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 2943, 2866, 2232, 1618, 1466, 1422, 1140, 1097, 1061, 961, 901, 887, 847, 822, 644 cm^{-1}. MS (FAB) *m/z*: 577 (100, M^+), 444 (11), 364 (5). Anal. Calcd for $C_{28}H_{34}F_3N_3O_3SSi$: C, 58.21; H, 5.93. Found: C, 57.94; H, 5.84.

2-[Diisopropyl(1-methylindol-2-yl)silyl]naphtalen-2-ol was prepared according to the general procedures and used for further steps without isolation.

2-[Diisopropyl(1-methylindol-2-yl)silyl]naphtalen-1-yl trifluoromethanesulfonate (4t)

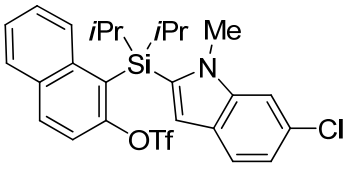


Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 30:1). Yield: 36%, a colorless solid. Mp: 66.8–67.7 °C. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.15 (d, *J* = 7.2 Hz, 6H), 2.03 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.09 (s, 3H), 6.99 (d, *J* = 0.8 Hz, 1H), 7.08 (ddd, *J* = 7.9, 7.7, 1.4 Hz, 1H), 7.14–7.23 (m, 3H), 7.40 (ddd, *J* = 7.8, 7.4, 1.1 Hz, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.73 (dm, *J* = 7.8 Hz, 1H), 7.84 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.89 (dd, *J* = 8.8, 0.7 Hz, 1H), 8.02 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9, 18.5, 18.9, 33.8, 109.3, 112.7, 117.4, 118.5 (q, *J* = 317.2 Hz), 119.2, 120.6, 121.9, 122.0, 126.2, 127.0, 128.5, 128.6, 129.0, 131.9, 133.5, 136.0, 138.6,

140.1, 154.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 3057, 2949, 2868, 1620, 1587, 1566, 1508, 1464, 1421, 1354, 1327, 1300, 1246, 1215, 1159, 1070, 1003, 984, 925, 883, 829, 810, 797, 750, 699, 615 cm^{-1}. MS (FAB) *m/z*: 519 (100, M^+), 476 (34), 386 (64), 370 (27), 342 (23). HR MS Calcd for $C_{26}H_{28}F_3NO_3SSi$: 519.1511 (M^+). Found: 519.1487.

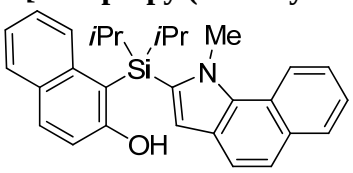
2-[(6-Chloro-1-methylindol-2-yl)diisopropylsilyl]naphtalen-2-ol was prepared according to the general procedures and used for further steps without isolation.

2-[Diisopropyl(1-methylindol-2-yl)silyl]naphtalen-1-yl trifluoromethanesulfonate (4u)



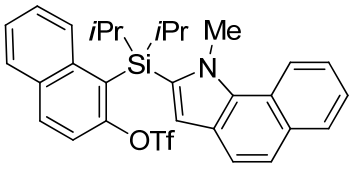
Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 24%, a colorless solid. Mp: 137.9–138.9 °C. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.15 (d, *J* = 7.2 Hz, 6H), 2.02 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.04 (s, 3H), 6.96 (s, 1H), 7.07–7.13 (m, 2H), 7.17 (d, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.0, 7.9 Hz, 1H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9, 18.5, 18.9, 33.9, 109.3, 112.7, 117.40, 117.42, 118.4 (q, *J* = 318.0 Hz), 120.0, 121.4, 121.7, 126.3, 127.0, 127.1, 128.1, 128.6, 128.7, 131.9, 133.7, 137.2, 138.4, 140.5, 154.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.4. IR (KBr): ν = 2961, 2868, 1566, 1460, 1425, 1249, 1227, 1138, 932, 918, 827, 810, 777, 671 cm^{-1}. MS (FAB) *m/z*: 553 (100, M^+), 510 (23), 420 (26). Anal. Calcd for $C_{26}H_{27}F_3NO_3SSi$: C, 56.36; H, 4.91. Found: C, 56.21; H, 4.84.

1-[Diisopropyl(1-methyl-benzo[*g*]indol-2-yl)silyl]naphtalen-2-ol (4v-OH)



1-Methyl-benzo[g]indol was prepared by the procedure of ref 8 and then subjected to general procedure for synthesis of 2-silylphenols. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 64%, a colorless solid. Mp: 147.1–148.1 °C. TLC: R_f 0.08 (hexane/AcOEt 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 2.02 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.08 (s, 3H), 5.98 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 7.19 (s, 1H), 7.27–7.30 (m, 2H), 7.43–7.50 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.77–7.79 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.97–8.00 (m, 2H), 7.46 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 18.76, 18.79, 39.9, 109.9, 115.9, 118.4, 120.9, 121.2, 121.3, 122.9, 123.3, 123.7, 125.1, 126.0, 126.3, 127.2, 128.6, 129.1, 129.2, 130.0, 132.8, 134.2, 134.8, 139.1, 161.3. IR (KBr): ν = 3528, 2939, 2860, 1614, 1595, 1506, 1425, 1393, 1325, 1238, 1182, 1068, 991, 881, 812, 744, 688 cm^{-1}. MS (FAB) *m/z*: 437 (1, M^+), 394 (2), 256 (5). Anal. Calcd for $C_{29}H_{31}NOSi$: C, 79.59; H, 7.14. Found: C, 79.44; H, 7.19.

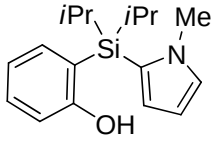
1-[Diisopropyl(1-methyl-benzo[*g*]indol-2-yl)silyl]naphtalen-2-yl trifluoromethanesulfonate (4v)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 89%, a colorless solid. Mp: 147.1–148.1 °C. TLC: R_f 0.27 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, *J* = 7.6 Hz, 6H), 1.22 (d, *J* = 7.6 Hz, 6H), 2.09 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.69 (s, 3H), 7.05 (dd, *J* = 7.7, 7.0 Hz, 1H), 7.15 (s, 1H), 7.38 (dd, *J* = 8.9,

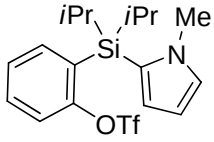
8.4 Hz, 1H), 7.43–7.45 (m, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.96–8.00 (m, 2H), 8.04 (d, *J* = 9.3 Hz, 1H), 8.30 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 18.6, 18.9, 40.0, 114.2, 117.3, 118.5 (q, *J* = 317.2 Hz), 120.9, 121.1, 122.1, 122.3, 123.4, 125.0, 126.0, 126.2, 127.1, 128.5, 128.8, 129.1, 131.8, 131.9, 133.5, 133.8, 135.5, 138.6, 154.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.3. IR (KBr): ν = 2959, 2866, 1560, 1508, 1420, 1246, 1215, 1138, 1126, 984, 928, 829, 812, 775, 688 cm^{-1}. MS (FAB) *m/z*: 569 (100, M^+), 526 (16), 436 (17). HR MS Calcd for $C_{30}H_{30}F_3NO_3SSi$: 569.1668 (M^+). Found: 569.1679.

2-[Diisopropyl(1-methylpyrrol-2-yl)silyl]phenol (4w-OH)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 23%, a colorless solid. Mp: 46.4–47.4 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.04 (d, *J* = 7.2 Hz, 6H), 1.59 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.59 (s, 1H), 5.56 (s, 1H), 6.28 (dd, *J* = 3.3 1.3 Hz, 1H), 6.67 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.93–6.98 (m, 2H), 7.32 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.38 (dd, *J* = 7.3, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 17.9, 18.0, 37.3, 109.3, 115.8, 117.4, 119.9, 123.5 (2C), 129.3, 131.4, 135.7, 161.7. IR (KBr): ν = 3418, 2943, 2862, 1599, 1564, 1512, 1471, 1438, 1278, 1203, 1118, 997, 882, 829, 760, 731, 677, 628 cm^{-1}. MS (FAB) *m/z*: 288 (13, M^++H), 244 (28), 202 (7), 164 (6). Anal. Calcd for $C_{17}H_{25}NOSi$: C, 71.03; H, 8.77. Found: C, 70.80; H, 8.56.

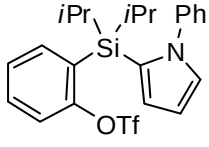
2-[Diisopropyl(1-methylpyrrol-2-yl)silyl]phenyl trifluoromethanesulfonate (4w)



Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 40:1). Yield: 73%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.6 Hz, 6H), 1.04 (d, *J* = 7.6 Hz, 6H), 1.58 (qq, *J* = 7.6, 7.6 Hz, 2H), 3.72 (s, 3H), 6.21 (dd, *J* = 3.9, 1.8 Hz, 1H), 6.70 (dd, *J* = 1.8, 1.7 Hz, 1H), 6.75 (dd, *J* = 2.2, 2.2 Hz, 1H), 7.22–7.26 (m, 1H), 7.36–7.44 (m, 2H), 7.56 (dd, *J* = 7.3, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 18.3, 18.4, 36.0, 108.2, 115.5, 118.3, 118.4 (q, *J* = 318.0 Hz), 122.7, 126.3, 128.2, 129.7, 130.8, 139.7, 155.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2947, 2866, 2359, 2341, 1595, 1514, 1468, 1417, 1246, 1211, 1130, 1051, 891, 779, 765, 746, 684 cm^{-1}. MS (FAB) *m/z*: 420 (6, M^++H), 376 (100), 340 (9), 242 (6). Anal. Calcd for $C_{18}H_{24}F_3NO_3SSi$: C, 51.53; H, 5.77. Found: C, 51.62; H, 5.67.

2-[Diisopropyl(1-phenylpyrrol-2-yl)silyl]phenol was prepared according to the general procedures and used for further steps without isolation.

2-[Diisopropyl(1-phenylpyrrol-2-yl)silyl]phenyl trifluoromethanesulfonate (4x)

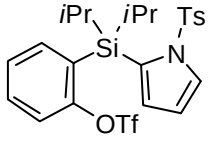


Prepared by Method A. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 25%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.6 Hz, 6H), 1.08 (d, *J* = 7.6 Hz, 6H), 1.64 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.40 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.17 (dd, *J* = 1.7, 1.4 Hz, 1H), 7.22 (dd, *J* = 2.6, 2.2 Hz, 1H), 7.25–7.30 (m, 2H), 7.39–7.46 (m, 6H), 7.62 (dd, *J* = 7.5, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.3, 18.4, 110.9, 117.3, 118.4 (q, *J* = 317.1 Hz), 118.5, 120.4, 120.5, 125.6, 126.6,

126.8, 127.7, 129.4, 131.0, 139.5, 140.3, 155.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ –74.8. IR (neat): ν = 2947, 2866, 2359, 1600, 1508, 1417, 1246, 1216, 1142, 1053, 893, 758, 688 cm^{-1}. MS (FAB) *m/z*: 482 (7, M^++H), 438 (100), 288 (7), 262 (20). Anal. Calcd for $C_{23}H_{26}F_3NO_3SSi$: C, 57.36; H, 5.44. Found: C, 57.34; H, 5.42.

2-[Diisopropyl(1-tosylpyrrol-2-yl)silyl]phenol was prepared according to the general procedures and used for further steps without isolation.

2-[Diisopropyl(1-tosylpyrrol-2-yl)silyl]phenyl trifluoromethanesulfonate (4y)

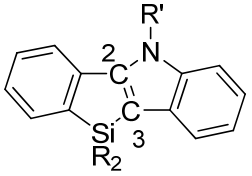


Prepared by Method B. Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 11%, a colorless solid. Mp: 91.8–92.8 °C. TLC: R_f 0.27 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, *J* = 7.6 Hz, 6H), 1.19 (d, *J* = 7.6 Hz, 6H), 2.11 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.23 (s, 3H), 6.45 (dd, *J* = 3.3, 3.1 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.86 (dd, *J* = 3.3, 1.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.44 (ddd, *J* = 8.1, 7.3, 2.0 Hz, 1H), 7.50 (dd, *J* = 3.1, 1.4 Hz, 1H), 7.78 (dd, *J* = 7.3, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 19.3, 19.4, 21.8, 113.9, 118.37, 118.40 (q, *J* = 318.0 Hz), 125.9, 127.0, 128.0, 128.1, 128.8, 129.6, 129.9, 131.2, 136.4, 138.4, 144.0, 155.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ –75.2. IR (KBr): ν = 2963, 2951, 2872, 1595, 1421, 1362, 1244, 1213, 1175, 1146, 1088, 1049, 891, 806, 781, 745, 675 cm^{-1}. MS (FAB) *m/z*: 560 (8, M^++H), 516 (100), 384 (2), 334 (30). Anal. Calcd for $C_{24}H_{28}FNO_5S_2Si$: C, 51.50; H, 5.04. Found: C, 51.71; H, 5.08.

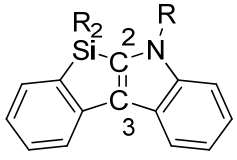
General procedure for Pd-catalyzed intramolecular coupling reaction of 4

An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with 2-(arylsilyl)aryl triflate **4** (0.3 mmol), dppe (3.4 mg, 0.015 mmol), Et_2NH (0.45 ml, 4.2 mmol), and DMA (1.0 mL). Then, the mixture was stirred for 3 min at rt. To the resulting solution was added a solution of $Pd(OAc)_2$ (11 mg, 0.015 mmol) in DMA (0.5 mL). The reaction mixture was stirred at 100 °C for 12 h, cooled down to room temperature, and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with H_2O (15 mL × 3), saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on N-H silica gel to give **5** solely or **5** and **6**.

The structures of **5a**, **5e**, **5f**, **5g**, **5i**, **5l**, **5o**, **5s**, and **5u** were unambiguously determined by X-ray analysis. The structures of other **5**/**6** were assigned by the similarity of the characteristic ^{13}C NMR data of the indole moieties as shown in the Figure below.

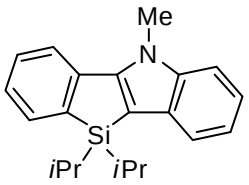


^{13}C NMR C(2) δ 151.2~154.4 ppm
C(3) δ 106.5~110.4 ppm



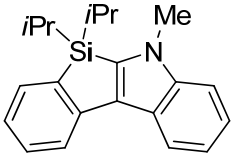
^{13}C NMR C(2) δ 146.3~150.9 ppm
C(3) δ 124.1~124.9 ppm

10,10-Diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5a)



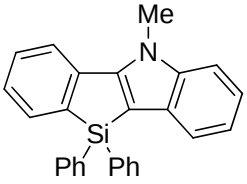
Purification: N-H silica gel column chromatography (hexane/AcOEt 40:1). Yield: 89%, a colorless solid. CCDC–697662 contains the crystallographic data for **5a**.

6,6-Diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6a)



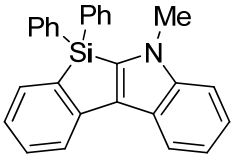
Purification: N-H silica gel column chromatography (hexane/AcOEt 40:1). Yield: 3%, a colorless oil. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6 H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.89 (s, 3H), 7.06 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.19 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.23–7.26 (m, 1H), 7.34–7.40 (m, 2H), 7.44 (d, *J* = 7.0, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.8, 34.8, 109.9, 119.6, 119.9, 120.1, 121.8, 123.7, 124.2, 129.9, 132.6, 133.3, 134.9, 142.8, 143.1, 146.6. IR (neat): ν = 2942, 2862, 1587, 1479, 1456, 1373, 1337, 1182, 1090, 991, 882, 814, 772, 750, 673 cm^{-1}. MS (FAB) *m/z*: 319 (100, M^+), 276 (13), 234 (9) 218 (4). HR MS Calcd for $C_{21}H_{25}NSi$: 319.1756 (M^+). Found: 319.1763.

5-Methyl-10,10-diphenyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5b)



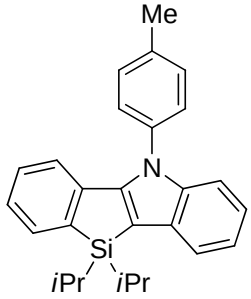
Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 59%, a colorless solid. Mp: 205.5–206.5 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (s, 3H), 7.16 (dd, *J* = 7.6, 7.1 Hz, 1H), 7.23–7.28 (m, 2H), 7.31–7.35 (m, 4H), 7.37–7.44 (m, 4H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.72–7.75 (m, 4H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.3, 108.2, 109.7, 120.5, 120.6, 121.7, 121.8, 126.8, 127.9, 129.8, 129.9, 130.1, 133.3, 134.2, 135.3, 141.8, 141.9, 142.5. 153.6. IR (KBr): ν = 3064, 3050, 2995, 2359, 2341, 1471, 1427, 1392, 1352, 1111, 1014, 977, 819, 773, 742, 692 cm^{-1}. MS (FAB) *m/z*: 387 (100, M^+), 310 (21), 240 (2). Anal. Calcd for $C_{27}H_{21}Si$: C, 83.68; H, 5.46. Found: C, 83.52; H, 5.61.

5-Methyl-6,6-diphenyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6b)



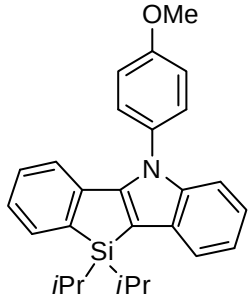
Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 17%, a colorless solid. Mp: 192.0–193.0 °C. TLC: R_f 0.15 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 7.10 (dd, *J* = 7.3, 7.0 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.26–7.34 (m, 1H), 7.34–7.41 (m, 5H), 7.43–7.47 (m, 3H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.70–7.72 (m, 4H), 7.81 (d, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.3, 110.1, 119.9, 120.1, 120.6, 122.4, 124.2, 124.5, 128.2, 130.3, 130.7, 131.3, 132.8, 133.7, 135.46, 135.50, 142.4, 143.0, 146.3. IR (KBr): ν = 3063, 3016, 2359, 2341, 1585, 1479, 1427, 1375, 1338, 1255, 1112, 943, 815, 767, 750, 698, 660 cm^{-1}. MS (FAB) *m/z*: 387 (27, M^+), 310 (7), 232 (1). HR MS Calcd for $C_{27}H_{21}Si$: 387.1443 (M^+). Found: 387.1453.

10,10-Diisopropyl-5-(4-methylphenyl)-10*H*-[1]benzosilolo[3,2-b][1]indole (5c)



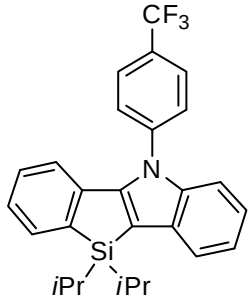
Purification: N-H silica gel column chromatography (hexane/AcOEt 30:1), followed by recrystalization from hexane. Yield: 74%, a colorless solid. Mp: 111.5–112.5 °C. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.44 (qq, *J* = 7.2, 7.2 Hz, 2H), 2.53 (s, 3H), 6.61 (d, *J* = 7.5 Hz, 1H), 7.00–7.06 (m, 2H), 7.08–7.18 (m, 3H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 19.0, 19.2, 21.9, 109.6, 111.1, 120.8 (2C), 121.0, 120.0, 122.2, 126.3, 128.6, 129.1, 130.5, 130.9, 133.7, 136.1, 138.7, 142.0, 144.1, 153.3. IR (KBr): ν = 2940, 2861, 1585, 1514, 1458,1388, 1334, 1008, 881, 854, 736, 686, 665 cm^{-1}. MS (FAB) *m/z*: 395 (100, M^+), 352 (41), 324 (13), 310 (13). Anal. Calcd for $C_{27}H_{29}NSi$: C, 81.97; H, 7.39. Found: C, 82.03; H, 7.55.

10,10-Diisopropyl-5-(4-methoxylphenyl)-10*H*-[1]benzosilolo[3,2-b][1]indole (5d)



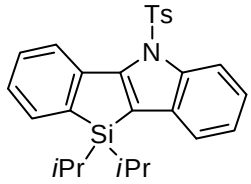
Purification: N-H silica gel column chromatography (hexane only), followed by recrystalization from hexane. Yield: 73%, a colorless solid. Mp: 159.4–160.4 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.44 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.95 (s, 3H), 6.61 (d, *J* = 8.0 Hz, 1H), 7.02–7.16 (m, 7H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.7, 18.9, 55.6, 109.1, 110.7, 114.6, 120.4, 120.6, 121.7, 121.9, 126.0, 128.8, 129.6, 130.5, 131.2, 133.4, 141.6, 141.7, 143.9, 153.2, 159.4. IR (KBr): ν = 3005, 2939, 2860, 2835, 1583, 1512, 1460, 1393, 1246, 1166, 1031, 989, 854, 745, 713, 689 cm^{-1}. MS (FAB) *m/z*: 411 (100, M^+), 368 (24), 326 (8). Anal. Calcd for $C_{27}H_{29}NOSi$: C, 78.79; H, 7.10. Found: C, 78.50; H, 7.32.

10,10-Diisopropyl-5-(4-trifluoromethylphenyl)-10*H*-[1]benzosilolo[3,2-b][1]indole (5e)



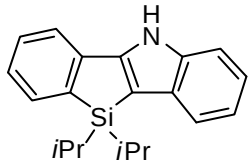
Purification: N-H silica gel column chromatography (hexane only), followed by recrystalization from hexane. Yield: 80%, a colorless solid. Mp: 176.0–177.0 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.47 (qq, *J* = 7.2, 7.2 Hz, 2H), 6.56 (d, *J* = 7.5 Hz, 1H), 7.04–7.09 (m, 2H), 7.11–7.17 (m 2H), 7.20 (ddd, *J* = 7.6, 7.1, 1.3 Hz, 1H), 7.55 (d, *J* = 6.2 Hz, 1H), 7.62–7.66 (m, 3H), 7.87 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.7, 18.9, 110.4, 111.1, 120.4, 121.3, 122.2, 122.3, 123.8 (q, *J* = 270.7 Hz), 126.6, 126.7 (q, *J* = 3.8 Hz), 128.89, 128.91, 130.5 (q, *J* = 32.8 Hz), 130.8, 133.6, 141.1, 141.5, 141.9, 142.3, 152.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.7. IR (KBr): ν = 3072, 2938, 2860, 1616, 1518, 1458, 1388, 1323, 1132, 1067, 1014, 868, 744, 684 cm^{-1}. MS (FAB) *m/z*: 449 (100, M^+), 406 (25), 378 (11), 364 (10). Anal. Calcd for $C_{27}H_{26}F_3NSi$: C, 72.13; H, 5.83. Found: C, 71.86; H, 5.96. CCDC–722334 contains the crystallographic data for **5e**.

10,10-Diisopropyl-5-tosyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5f)



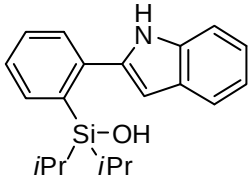
Purification: N-H silica gel column chromatography (hexane/AcOEt 100:1). Yield: 83%, a colorless solid. Mp: 98.0–99.0 °C. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, *J* = 7.6 Hz, 6H), 0.94 (d, *J* = 7.6 Hz, 6H), 1.35 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.22 (s, 3H), 6.94 (d, *J* = 8.2 Hz, 2H), 7.21–7.31 (m, 5H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.43 (ddd, *J* = 8.0, 8.0, 1.4 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 18.1, 18.3, 21.5, 117.8, 122.0, 124.5, 124.6, 124.7, 125.1, 126.4, 126.6, 129.0, 129.6, 132.9, 133.0, 133.9, 139.2, 141.6, 142.6, 144.2, 154.7. IR (KBr): ν = 3047, 2936, 2860, 1597, 1464, 1450, 1423, 1373, 1178, 1091, 1076, 947, 748, 721, 692, 658 cm^{-1}. MS (FAB) *m/z*: 459 (100, M^+), 352 (9), 262 (12). Anal. Calcd for $C_{27}H_{29}NO_2SSi$: C, 70.55; H, 6.36. Found: C, 70.46; H, 6.37. CCDC–731564 contains the crystallographic data for **5f**.

10,10-Diisopropyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5g)



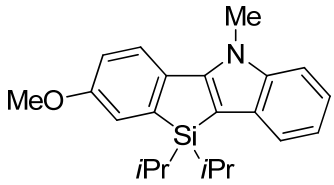
Purification: GPC ($CHCl_3$). Yield: 10%, a colorless solid. Mp: 108.9–109.9 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (d, *J* = 7.6 Hz, 6H), 1.03 (d, *J* = 7.6 Hz, 6H), 1.61 (qq, *J* = 7.6, 7.6 Hz, 2H), 6.83 (d, *J* = 0.7 Hz, 1H), 7.09 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.16 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.24–7.28 (m, 1H), 7.34 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.45 (dd, *J* = 7.8, 7.4 Hz, 1H)), 7.60 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 17.4, 17.6, 97.6, 112.4, 120.0, 121.0, 121.7, 122.0, 127.0, 130.4, 133.0, 133.2, 134.0, 139.5, 141.2, 148.2. IR (KBr): ν = 3446, 2947, 2862, 1593, 1456, 1433, 1300, 1276, 1128, 1057, 1005, 750, 682, 611 cm^{-1}. MS (FAB) *m/z*: 305 (100, M^+), 262 (31), 234 (29). HR MS Calcd for $C_{20}H_{23}NSi$: 305.1600 (M^+). Found: 305.1597.

[2-(Indol-2-yl)phenyl]diisopropylsilanol (6g*)



Purification: GPC ($CHCl_3$). Yield: 75%, a colorless solid. Mp: 61.4–62.4 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 7.6 Hz, 6H), 0.99 (d, *J*= 7.6 Hz, 6H), 1.61 (qq, *J* = 7.6, 7.6 Hz, 2H), 2.10 (s, 1H), 6.60 (dd, *J*= 2.2, 0.9 Hz, 1H), 7.14 (ddd, *J* = 8.1, 7.8, 1.2 Hz, 1H), 7.20 (ddd, *J* = 8.1, 8.0, 1.2 Hz, 1H), 7.37–7.41 (m, 2H), 7.46 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H), 7.58–7.62 (dm, *J* = 7.5 Hz, 1H), 7.62–7.65 (m, 2H), 9.24 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 17.4, 17.7, 101.9, 111.0, 120.0, 122.0, 127.0, 128.4, 129.2, 130.5, 134.2, 134.9, 136.1, 139.5, 140.1. IR (KBr): ν = 3857, 3502, 3292, 3254, 2943, 2864, 1454, 1427, 1348, 1298, 1125, 1004, 882, 840, 810, 767, 744, 717, 659, 609 cm^{-1}. MS (FAB) *m/z*: 323 (70, M^+), 306 (66), 280 (100). Anal Calcd for $C_{20}H_{25}NOSi$: C, 74.25; H, 7.79. Found: C, 74.30; H, 7.55.

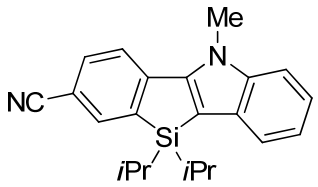
10,10-Diisopropyl-2-methoxy-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5h)



Purification: N-H silica gel column chromatography (hexane/AcOEt 50:1). Yield: 77%, a colorless solid. Mp: 151.6–152.0 °C. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.39 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.87 (s, 3H), 4.09 (s, 3H), 6.86 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.11 (dd, *J* = 7.9, 7.1 Hz,

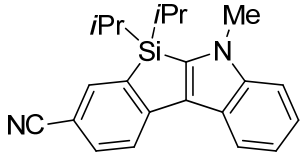
1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.18 (dd, *J* = 8.2, 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.8, 32.1, 55.4, 106.5, 109.3, 112.5, 120.0, 120.80, 120.83, 120.9, 121.7, 130.7, 135.1, 142.0, 144.7, 152.3, 157.9. IR (KBr): ν = 2935, 2859, 1573, 1458, 1398, 1281, 1234, 1045, 880, 740, 707, 680, 638 cm^{-1}. MS (FAB) *m/z*: 349 (100, M^+), 306 (25), 280 (3), 264 (79), 248 (4). Anal. Calcd for $C_{22}H_{27}NOSi$: C, 75.59; H, 7.79. Found: C, 75.33; H, 7.69.

2-Cyano-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5i)



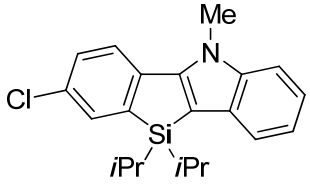
Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 75%, a colorless solid. Mp: 167.7–168.2 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.44 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.13 (s, 3H), 7.17 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.29 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.75 (d, *J* = 1.5 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.5, 18.6, 32.4, 108.9, 109.8, 112.1, 119.6, 119.8, 120.7, 122.7, 122.9, 130.1, 133.8, 136.1, 142.8, 143.3, 146.2, 151.2. IR (KBr): ν = 2941, 2887, 2860, 2220, 1587, 1479, 1458, 1398, 1332, 1188, 1066, 1028, 991, 877, 764, 738, 680, 646 cm^{-1}. MS (FAB) *m/z*: 344 (67, M^+), 301 (25), 273 (10), 259 (9), 243 (4). Anal. Calcd for $C_{22}H_{24}N_2Si$: C, 76.70; H, 7.02. Found: C, 76.53; H, 6.98. CCDC–722335 contains the crystallographic data for **5i**.

8-Cyano-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6i)



Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 15%, a colorless oil. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.52 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.91 (s, 3H), 7.22–7.26 (m, 1H), 7.31 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.4, 18.7, 35.0, 106.3, 110.3, 119.7, 119.8, 120.2, 120.6, 122.7, 124.1, 131.4, 134.6, 136.0, 136.2, 143.1, 145.4, 150.9. IR (neat): ν = 2943, 2864, 2216, 1587, 1556, 1454, 1381, 1336, 1193, 1089, 908, 881, 815, 738, 677 cm^{-1}. MS (FAB) *m/z*: 344 (100, M^+), 301 (12) 259 (10). HR MS Calcd for $C_{22}H_{24}N_2Si$: 344.1709 (M^+). Found: 344.1717.

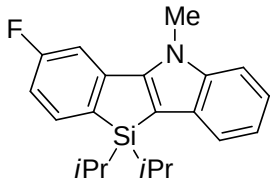
2-Chloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5j)



Purification: N-H silica gel column chromatography (hexane/AcOEt 50:1). Yield: 81%, a colorless solid. Mp: 163.1–164.0 °C. TLC: R_f 0.48 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.41 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.10 (s, 3H), 7.14 (dd, *J* = 8.2, 7.4 Hz, 1H), 7.23 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.2, 108.6, 109.5, 120.3, 120.9, 121.7, 122.1, 128.9, 130.4, 132.0, 133.4, 140.6, 142.3, 144.9, 152.2. IR (KBr): ν = 2935, 2922, 2860, 1554, 1458, 1396, 1379, 1097, 879, 815, 775, 736, 680, 638 cm^{-1}. MS (FAB) *m/z*:

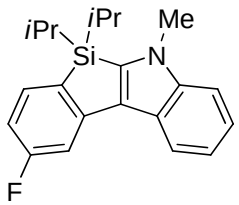
354 (67, M^+ + H), 312 (9), 282 (9), 268 (8), 254 (3). Anal. Calcd for $C_{21}H_{24}ClNSi$: C, 71.26; H, 6.83. Found: C, 71.01; H, 6.88.

3-Fluoro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5k)



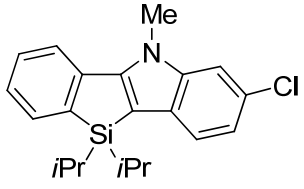
Purification: N-H silica gel column chromatography (hexane/AcOEt 40:1), followed by reverse phase HPCL (CH_3CN). Yield: 74%, a colorless solid. Mp: 111.1–112.1 °C. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.10 (s, 3H), 6.87–6.91 (m, 1H), 7.14 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H), 7.22–7.26 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.45–7.50 (m, 2H), 7.58 (dm, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.1, 108.3 (d, *J* = 23.6 Hz), 109.6, 110.3, 112.2 (d, *J* = 20.6 Hz), 120.3, 121.9, 122.3, 130.3, 134.6 (d, *J* = 8.4 Hz), 136.8 (d, *J* = 3.8 Hz), 142,3, 144.4 (d, *J* = 8.4 Hz), 151.8 (d, *J* = 3.1 Hz), 164.6 (d, *J* = 243.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –122.4. IR (KBr): ν = 2935, 2859, 1589, 1479, 1402, 1330, 1283, 1219, 1170, 1016, 910, 852, 808, 735, 665 cm^{-1}. MS (FAB) *m/z*: 337 (100, M^+), 294 (35), 266 (9), 252 (7). Anal. Calcd for $C_{21}H_{24}FNSi$: C, 74.13; H, 7.17. Found: C, 74.41; H, 7.13.

9-Fluoro-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6k)



Purification: N-H silica gel column chromatography (hexane/AcOEt 40:1), followed by reverse phase HPCL (CH_3CN). Yield: 6%, a colorless oil. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.47 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.89 (s, 3H), 6.74 (ddd, *J* = 10.5, 7.4, 2.2 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.7, 1.1 Hz, 1H), 7.27 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.35–7.38 (m, 2H), 7.42 (dd, *J* = 10.5, 2.2 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.4, 18.7, 34.8, 108.0 (d, *J* = 11.0 Hz), 109.8, 110.0, 119.6, 120.0, 122.1, 124.0, 129.7 (d, *J* = 3.6 Hz), 131.5 (d, *J* = 3.1 Hz), 134.3 (d, *J* = 8.4 Hz), 142.8, 144.3, 149.0 (d, *J* = 9.2 Hz), 165.0 (d, *J* = 243.3); ^{19}F NMR (282 MHz, $CDCl_3$): δ –112.1. IR (neat): ν = 3050, 2942, 2864, 1595, 1576, 1485, 1454, 1394, 1356, 1269, 1134, 1085, 979, 881, 866, 814, 742, 680 cm^{-1}. MS (FAB) *m/z*: 337 (100, M^+), 294 (33), 266 (6), 252 (7). HR MS Calcd for $C_{21}H_{24}FNSi$: 337.1662 (M^+). Found: 337.1654.

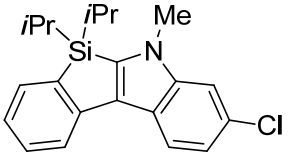
7-Chloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5l)



Purification: N-H silica gel column chromatography (hexane only). Yield: 70%, a colorless solid. Mp: 144.6–145.2 °C. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.09 (s, 3H), 7.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.37 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.5, 108.6, 109.6, 120.2, 120.7, 122.7, 126.2, 127.2, 129.0, 129.3, 133.8, 141.8, 141.9, 142.7, 154.0. IR (KBr): ν = 2940, 2888, 1587, 1473, 1460, 1417, 1389, 1325, 1281, 1205, 1136, 1063, 987, 974, 880, 842, 797,

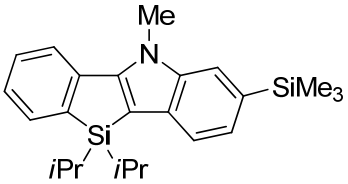
765, 682 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (37), 282 (11), 268 (9). Anal. Calcd for $C_{21}H_{24}ClNSi$: C, 71.26; H, 6.83. Found: C, 71.20; H, 6.83. CCDC–722337 contains the crystallographic data for **5l**.

3-Chloro-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6l)



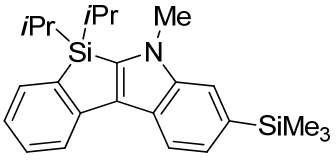
Purification: N-H silica gel column chromatography (hexane only). Yield: 10%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6H), 1.11 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.85 (s, 3H), 7.08 (dd, *J* = 7.4, 6.9 Hz, 1H), 7.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.45 (d, *J* = 6.9 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.4, 18.8, 34.9, 109.9, 120.1, 120.2, 120.5, 122.7, 124.1, 128.0, 130.0, 132.7, 133.4, 134.9, 142.8, 143.2, 146.0. IR (neat): ν = 2942, 2887, 1589, 1483, 1456, 1375, 1364, 1332, 1062, 947, 881, 850, 800, 742, 709, 675 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (14), 238 (8), 248 (2). HR MS Calcd for $C_{21}H_{24}ClNSi$: 353.1367 (M^+). Found: 353.1379.

10,10-Diisopropyl-5-methyl-7-trimethylsilyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5m)



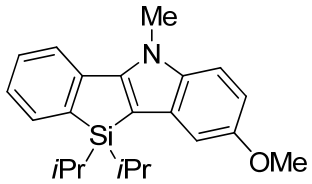
Purification: N-H silica gel column chromatography (hexane only). Yield: 82%, a colorless oil. TLC: R_f 0.50 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H), 1.03 (d, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.39 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.15 (s, 3H), 7.20 (dd, *J* = 7.7, 6.9 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.51 (s, 1H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.4, 18.6, 18.8, 32.2, 108.3, 114.2, 120.2 (2C), 121.6, 124.7, 126.1, 129.1, 131.2, 132.0, 133.7, 142.1, 142.3, 153.6. IR (neat): ν = 3048, 2951, 2864, 1599, 1454, 1415, 1325, 1281, 1122, 1080, 881, 748, 731, 682 cm^{-1}. MS (FAB) *m/z*: 391 (100, M^+), 348 (44), 332 (6), 320 (11). Anal. Calcd for $C_{24}H_{33}NSi_2$: C, 73.59; H, 8.49. Found: C, 73.40; H, 8.49.

6,6-Diisopropyl-5-methyl-3-trimethylsilyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6m)



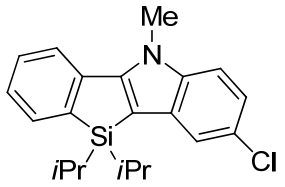
Purification: N-H silica gel column chromatography (hexane only). Yield: 5%, a colorless oil. TLC: R_f 0.52 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.36 (s, 9H), 1.08 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.92 (s, 3H), 7.05 (dd, *J* = 7.3, 7.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.49 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.5, 11.3, 18.5, 18.8, 34.8, 114.6, 119.4, 120.1, 123.7, 124.2, 124.6, 129.9, 132.6, 132.7, 133.3, 134.9, 142.6, 143.6, 146.6. IR (neat): ν = 3046, 2951, 2862, 1589, 1454, 1375, 1335, 1246, 1150, 1112, 866, 829, 748, 675 cm^{-1}. MS (FAB) *m/z*: 391 (100, M^+), 348 (7), 306 (4), 248 (6). HR MS Calcd for $C_{24}H_{33}NSi_2$: 391.2152 (M^+). Found: 391.2158.

10,10-diisopropyl-8-methoxy-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5n)



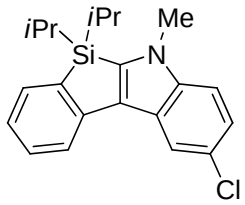
Purification: N-H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 88%, a colorless solid. Mp: 151.5–151.9 °C. TLC: R_f 0.37 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6 H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.40 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.88 (s, 3H), 4.09 (s, 3H), 6.87 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 7.4, 7.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.36 (dd, *J* = 8.8, 7.4 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.9, 32.4, 56.0, 104.6, 109.7, 109.9, 110.7, 120.0, 125.9, 129.1, 131.0, 133.7, 137.7, 142.0, 142.3, 153.7, 154.4. IR (KBr): ν = 2953, 2935, 2860, 1614, 1568, 1485, 1460, 1415, 1342, 1221, 1198, 1170, 1036, 984, 883, 870, 832, 769, 690, 661 cm^{-1}. MS (FAB) *m/z*: 349 (100, M^+), 306 (35), 264 (8), 248 (4). Anal. Calcd for $C_{22}H_{27}NOSi$: C, 75.59; H, 7.79. Found: C, 75.59; H, 7.58.

8-Chloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5o)



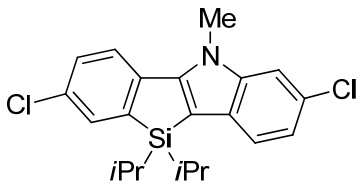
Purification: N-H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 63%, a colorless solid. Mp: 162.7–163.5 °C. TLC: R_f 0.38 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6 H), 1.12 (d, *J* = 7.6 Hz, 6H), 1.40 (qq, *J* = 7.6, 7.6 Hz, 2H), 4.10 (s, 3H), 7.15 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.20–7.26 (m, 2H), 7.38 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.8, 32.5, 108.0, 110.4, 120.3, 121.2, 121.5, 125.8, 126.4, 129.2, 131.5, 133.8, 140.7, 141.8, 142.0, 154.4. IR (KBr): ν = 2922, 2888, 2860, 2359, 1606, 1585, 1471, 1462, 1417, 1398, 1329, 1296, 1063, 989, 980, 880, 837, 790, 769, 713, 685, 655 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (45), 282 (13), 268 (11), 252 (5). Anal. Calcd for $C_{21}H_{24}ClNSi$: C, 71.26; H, 6.83. Found: C, 71.22; H, 6.75. CCDC–722336 contains the crystallographic data for **5o**.

2-Chloro-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6o)



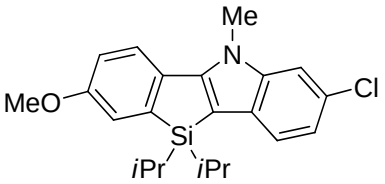
Purification: N-H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 22%, a colorless oil. TLC: R_f 0.42 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6 H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.48 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.87 (s, 3H), 7.08 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.39 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.4, 18.8, 35.0, 110.7, 119.2, 120.1, 122.0, 124.0, 124.9, 125.5, 130.0, 132.0, 133.4, 134.7, 141.2, 144.8, 145.9. IR (neat): ν = 3068, 2941, 2862, 2360, 2341, 1589, 1479, 1406, 1385, 1307, 1143, 1091, 991, 881, 835, 795, 768, 677 cm^{-1}. MS (FAB) *m/z*: 353 (100, M^+), 310 (15), 268 (7), 234 (2). HR MS Calcd for $C_{21}H_{24}ClNSi$: 353.1367 (M^+). Found: 353.1379.

2,7-Dichloro-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5p)



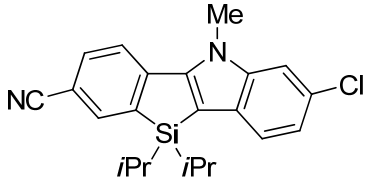
Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 84%, a colorless solid. Mp: 148.3–149.3 °C. TLC: R_f 0.32 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.6 Hz, 6 H), 1.13 (d, *J* = 7.6 Hz, 6H), 1.41 (qq, *J* = 7.6, 7.6 Hz, 2H), 4.05 (s, 3H), 7.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.32–735 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H) 7.66 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.5, 18.6, 32.4, 108.7, 109.7, 121.0 (2c), 122.7, 127.6, 128.8, 129.1, 132.3, 133.5, 140.2, 142.7, 144.6, 152.9. IR (KBr): ν = 2953, 2940, 2862, 1553, 1460, 1419, 1391, 1327, 1263, 1099, 1060, 974, 882, 845, 808, 797, 680 cm^{-1}. MS (FAB) *m/z*: 387 (100, M^+), 344 (24), 302 (6), 266 (2). Anal. Calcd for $C_{21}H_{23}Cl_2NSi$: C, 64.94; H, 5.97. Found: C, 65.00; H, 6.08.

7-Chloro-10,10-diisopropyl-5-methyl-2-methoxy-10*H*-[1]benzosilolo[3,2-b][1]indole (5q)



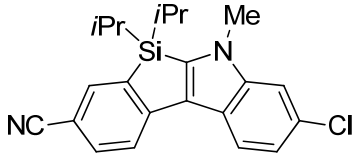
Purification: N-H silica gel column chromatography (hexane/AcOEt 20:1). Yield: 78%, a colorless solid. Mp: 157.8–158.6 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.39 (qq, *J* = 7.2 ,7.2 Hz, 2H), 3.87 (s, 3H), 4.04 (s, 3H), 6.86 (dd, *J* = 8.4, 2.6 Hz ,1H), 7.08 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 18.7, 32.3, 55.4, 106.6, 109.5, 112.6, 120.6, 120.93, 120.94, 122.2, 126.6, 129.2, 134.7, 142.5, 144.5, 154.2, 158.1. IR (KBr): ν = 2943, 2862, 1572, 1456, 1408, 1292, 1215, 1182, 1045, 879, 835, 800, 682 cm^{-1}. MS (FAB) *m/z*: 383 (100, M^+), 340 (19), 298 (5). Anal. Calcd for $C_{22}H_{26}ClNOSi$: C, 68.81; H, 6.82. Found: C, 68.54; H, 6.84.

7-Chloro-2-cyano-10,10-diisopropyl-5-methyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5r)



Purification: N-H silica gel column chromatography (hexane/AcOEt 25:1). Yield: 40%, a colorless solid. Mp: 158.7–159.7 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.43 (qq, *J* = 7.2 ,7.2 Hz, 2H), 4.09 (s, 3H), 7.12 (dd, *J* = 8.4, 1.8 Hz ,1H), 7.37 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 18.4, 18.6, 32.5, 109.2, 109.9, 112.2, 119.4, 119.8, 121.4, 123.3, 128.6, 128.7, 133.9, 136.2, 143.11, 143.14, 145.8, 151.9. IR (KBr): ν = 2945, 2862, 1572, 1458, 1408, 1327, 1292, 1216, 1182, 1045, 879, 853, 800, 683 cm^{-1}. MS (FAB) *m/z*: 378 (18, M^+), 335 (1), 291 (4). Anal. Calcd for $C_{22}H_{23}ClN_2Si$: C, 69.72; H, 6.12. Found: C, 69.71; H, 5.99.

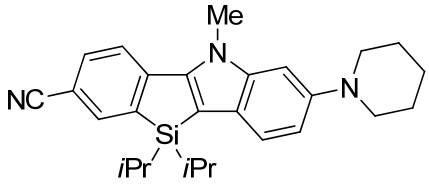
3-Chloro-8-cyano-6,6-diisopropyl-5-methyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6r)



Purification: N-H silica gel column chromatography (hexane/AcOEt 25:1). Yield: 40%, a colorless solid. Mp: 73.4–74.4 °C. TLC: R_f 0.20 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.2 Hz, 6H), 1.10 (d,

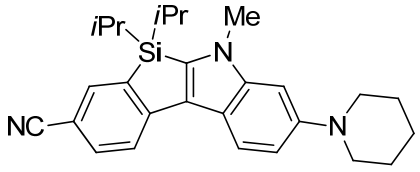
J = 7.2 Hz, 6H), 1.51 (qq, *J* = 7.2 ,7.2 Hz, 2H), 3.87 (s, 3H), 7.20 (dd, *J* = 8.4, 1.7 Hz ,1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.64–7.68 (m, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 18.3, 18.6, 35.1, 106.8, 110.4, 119.8, 120.0, 120.4, 121.2, 122.6, 128.9, 131.4, 134.6, 136.1, 136.2, 143.5, 146.3, 150.2. IR (KBr): ν = 2945, 2864, 2218, 1587, 1464, 1446, 1381, 1332, 1248, 1060, 947, 858, 824, 702, 675 cm^{-1}. MS (FAB) *m/z*: 378 (18, M^+), 335 (2), 291 (2). Anal. Calcd for $C_{22}H_{23}ClN_2Si$: C, 69.72; H, 6.12. Found: C, 69.78; H, 6.08.

2-Cyano-10,10-diisopropyl-5-methyl-7-piperidyl-10*H*-[1]benzosilolo[3,2-b][1]indole (5s)



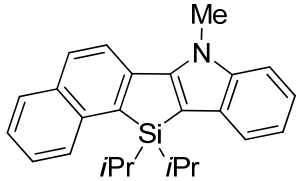
Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 86%, a colorless solid. Mp: 208.3–209.3 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.41 (qq, *J* = 7.2, 7.2 Hz, 2H), 1.61–1.65 (m, 2H), 1.76–1.82 (m, 4H), 3.22 (t, *J* = 5.5 Hz, 4H), 4.05 (s, 3H), 6.82 (brs, 1H), 6.93 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.62 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.70 (d, *J* = 1.3 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.5, 18.6, 24.4, 26.2, 32.2, 52.2, 96.9, 107.9, 112.4, 114.0, 118.9, 119.8, 122.9, 124.0, 133.8, 135.9, 142.7, 143.9, 146.5, 149.8. IR (KBr): ν = 2887, 2860, 2218, 1614, 1583, 1558, 1489, 1454, 1433, 1396, 1381, 1222, 1207, 1186, 1134, 947, 815, 678 cm^{-1}. MS (FAB) *m/z*: 427 (100, M^+), 384 (5), 356 (2). Anal. Calcd for $C_{27}H_{33}CN_3Si$: C, 75.83; H, 7.78. Found: C, 76.09; H, 7.62.

8-Cyano-6,6-diisopropyl-5-methyl-3-piperidyl-6*H*-[1]benzosilolo[2,3-b][1]indole (6s)



Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 9%, a colorless solid. Mp: 146.9–147.9 °C. TLC: R_f 0.10 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J* = 7.6 Hz, 6H), 1.09 (d, *J* = 7.6 Hz, 6H), 1.48 (qq, *J* = 7.6, 7.6 Hz, 2H), 1.58–1.65 (m, 2H), 1.76–1.82 (m, 4H), 3.22 (t, *J* = 5.3 Hz, 4H), 3.83 (s, 3H), 6.80 (brs, 1H), 7.00 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.60–7.64 (m, 2H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.4, 18.7, 24.4, 26.2, 34.9, 52.3, 97.3, 106.0, 109.7, 113.8, 119.5, 119.9, 120.4, 131.6, 134.5, 135.9, 136.5, 143.6, 144.3, 149.6, 151.0. IR (KBr): ν = 2938, 28692, 2214, 1616, 1587, 1552, 1450, 1390, 1217, 1084, 962, 880, 837, 819, 709, 673 cm^{-1}. MS (FAB) *m/z*: 427 (100, M^+), 384 (8), 342 (3). Anal. Calcd for $C_{27}H_{33}CN_3Si$: C, 75.83; H, 7.78. Found: C, 75.76; H, 7.83.

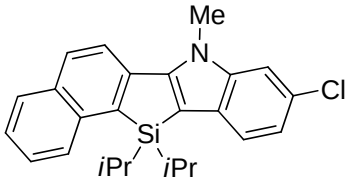
12,12-Diisopropyl-7-methyl-12*H*-indololo[3,2-d]-naphtho[1,2-b][1]silole (5t)



Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 91%, an yellow solid. Mp: 173.8–174.6 °C. TLC: R_f 0.35 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, *J* = 7.2 Hz, 6H), 1.28 (d, *J* = 7.2 Hz, 6H), 1.61 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.23 (s, 3H), 7.15 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.21–7.26 (m, 1H), 7.38–7.43 (m, 2H), 7.49 (dd, *J* = 7.5, 7.3 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H),

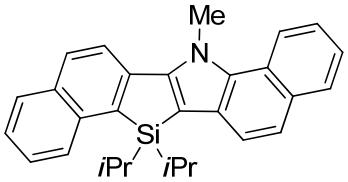
8.04 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 18.6,.19.3, 32.4, 107.1, 109.5, 119.2, 120.2, 121.2, 122.1, 125.1, 126.4, 128.6, 128.7, 129.9, 130.8, 131.9, 137.1, 141.1, 141.3, 142.4, 153.5. IR (KBr): ν = 2939, 2924, 2860, 2831, 1581, 1512, 1462, 1398, 1311, 1213, 1136, 1066, 1014, 974, 881, 814, 746, 699, 623 cm^{-1}. MS (FAB) *m/z*: 369 (100, M^+), 326 (21), 284 (9), 270 (3). Anal. Calcd for $C_{25}H_{27}NSi$: C, 81.25; H, 7.36. Found: C, 81.05; H, 7.29.

9-Chloro-12,12-diisopropyl-7-methyl-12*H*-indololo[3,2-d]-naphtho[1,2-b][1]silole (5u)



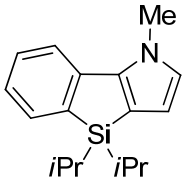
Purification: N-H silica gel column chromatography (hexane/AcOEt 10:1). Yield: 91%, an yellow solid. Mp: 211.6–212.4 °C. TLC: R_f 0.31 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, J = 7.2 Hz, 6H), 1.25 (d, J = 7.2 Hz, 6H), 1.61 (qq, J = 7.2, 7.2 Hz, 2H), 4.19 (s, 3H), 7.11 (dd, J = 7.6, 1.7 Hz, 1H), 7.37 (d, J = 1.7 Hz, 1H), 7.43 (dd, J = 7.6, 7.4 Hz, 1H), 7.48–7.52 (m, 2H), 7.78 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 18.6, 19.2, 32.6, 107.2, 109.7, 119.2, 120.9, 125.3, 126.5, 127.0, 128.58, 128.64, 129.3, 130.1, 132.0, 137.1, 140.9, 141.1, 142.8, 154.3. IR (KBr): ν = 2953, 2935, 2858, 1510, 1460, 1396, 1294, 1062, 987, 881, 802, 739, 667, 644 cm^{-1}. MS (FAB) *m/z*: 403 (24, M^+), 360 (4), 318 (2). Anal. Calcd for $C_{25}H_{27}NSi$: C, 74.32; H, 6.49. Found: C, 74.12; H, 6.38.

7,7-Diisopropyl-14-methyl-14*H*-dibenzo[g][6,7]benzosilolo[1,2-b]indole (5v)



Purification: N-H silica gel column chromatography (hexane/CH_2Cl_2 5:1). Yield: 93%, an yellow solid. Mp: 218.6–219.7 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, J = 7.2 Hz, 6H), 1.32 (d, J = 7.2 Hz, 6H), 1.67 (qq, J = 7.2, 7.2 Hz, 2H), 4.66 (s, 3H), 7.40–7.45 (m, 2H), 7.50–7.60 (m, 3H), 7.74 (dd, J = 8.1, 7.7 Hz, 1H), 7.84 (dd, J = 8.1, 7.7 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 18.6, 19.3, 37.7, 109.5, 119.4, 120.7, 122.1, 122.4, 123.0, 123.3, 125.01, 125.04, 126.4, 128.2, 128.56, 128.61, 129.3, 130.0, 131.4, 131.8, 136.6, 137.2, 140.5, 141.4, 153.9. IR (KBr): ν = 2935, 2858, 1579, 1508, 1460, 1369, 1197, 1163, 1076, 983, 877, 802, 739, 667 cm^{-1}. MS (FAB) *m/z*: 419 (100, M^+), 376 (15), 334 (6). Anal. Calcd for $C_{29}H_{29}NSi$: C, 83.00; H, 6.97. Found: C, 82.92; H, 7.04.

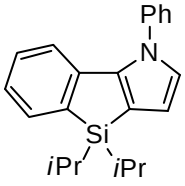
4,4-Diisopropyl-1-methyl-4*H*-[1]benzosilolo[3,2-b][1]pyrrole (5w)



Purification: neutral alumina column chromatography (activated level III, hexane/AcOEt 50:1). Yield: 78%, a colorless solid. Mp: 57.1–58.0 °C. TLC: R_f 0.60 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, J = 7.2 Hz, 6 H), 1.07 (d, J = 7.2 Hz, 6H), 1.28 (qq, J = 7.2, 7.2 Hz, 2H), 3.94 (s, 3H), 6.19 (d, J = 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 7.06 (dd, J = 7.5, 7.2 Hz, 1H), 7.26–7.30 (m, 1H), 7.46–7.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.50, 18.54, 36.2, 110.9, 116.1, 117.9, 124.1, 127.7, 129.0, 133.7, 140.2, 142.7, 146.4. IR (KBr): ν = 2940, 2924, 2860, 1583, 1498, 1475, 1448, 1357, 1280, 1198, 1124, 999, 985, 880, 765, 688 cm^{-1}. MS (FAB) *m/z*: 269 (100, M^+), 226 (42),

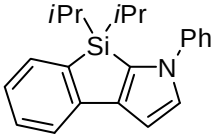
198 (17), 184 (11), 154.8 (8). Anal. Calcd for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60. Found: C, 75.56; H, 8.42.

4,4-Diisopropyl-1-phenyl-4*H*-[1]benzosilolo[3,2-b][1]pyrrole (5x)



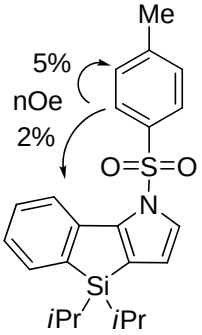
Purification: N-H silica gel column chromatography (hexane only). Yield: 73%, a colorless oil. TLC: R_f 0.45 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 7.2 Hz, 6H), 1.12 (d, *J* = 7.2 Hz, 6H), 1.33 (qq, *J* = 7.2, 7.2 Hz, 2H), 6.35 (d, *J* = 2.7 Hz, 1H), 6.54–6.58 (m, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.96–7.00 (m, 2H), 7.44–7.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 18.57, 18.61, 112.2, 117.0, 118.5, 124.3, 126.7, 127.8, 128.1, 128.6, 129.0, 133.4, 140.1, 140.5, 142.1, 146.2. IR (neat): ν = 2939, 2889, 2862, 1597, 1587, 1503, 1464, 1423, 1354, 1188, 1070, 991, 881, 766, 687 cm^{-1}. MS (FAB) *m/z*: 331 (100, M^+), 288 (43), 260 (18), 246 (11). Anal. Calcd for $C_{22}H_{25}NSi$: C, 79.70; H, 7.60. Found: C, 79.49; H, 7.56.

8,8-Diisopropyl-1-phenyl-8*H*-[1]benzosilolo[2,3-b][1]pyrrole (6x)



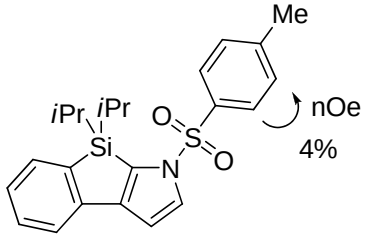
Purification: N-H silica gel column chromatography (hexane only). Yield: 23%, a colorless oil. TLC: R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.32 (qq, *J* = 7.2, 7.2 Hz, 2H), 7.09–7.13 (m, 2H), 7.22–7.28 (m, 1H), 7.32 (ddd, *J* = 7.5, 7.4, 1.6 Hz, 1H), 7.40 (d, *J* = 1.6 Hz, 1H), 7.41–7.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.4, 18.5, 112.3, 116.9, 120.2, 120.5, 122.8, 124.9, 125.4, 129.36, 129.39, 133.6, 138.9, 139.8, 140.5, 144.7. IR (neat): ν = 2939, 2887, 1707, 1591, 1506, 1460, 1386, 1251, 1124, 1045, 881, 758, 733, 705, 690, 678 cm^{-1}. 0 HR MS Calcd for $C_{22}H_{25}NSi$: 331.1756 (M^+). Found: 331.1757.

4,4-Diisopropyl-1-tosyl-4*H*-[1]benzosilolo[3,2-b][1]pyrrole (5y)



Purification: N-H silica gel column chromatography (hexane only). Yield: 31%, a colorless oil. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (d, *J* = 7.2 Hz, 6H), 0.96 (d, *J* = 7.2 Hz, 6H), 1.14 (qq, *J* = 7.2, 7.2 Hz, 2H), 2.32 (s, 3H), 6.38 (d, *J* = 3.1 Hz, 1H), 7.07 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.26 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 3.1 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6, 18.1, 18.2, 21.6, 114.6, 121.8, 125.0, 125.3, 126.3, 128.9, 129.5, 129.6, 133.1, 135.8, 138.8, 140.7, 144.5, 147.2. ^{1}H NMR (400 MHz, C_6D_6): δ 0.92 (d, *J* = 7.2 Hz, 6H), 0.94 (d, *J* = 7.2 Hz, 6H), 1.14 (qq, *J* = 7.2, 7.2 Hz, 2H), 1.60 (s, 3H), 6.20 (d, *J* = 3.1 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 2H), 6.92 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.21 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 3.1 Hz, 1H), 8.73 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 11.4, 18.7, 18.8, 21.5, 115.2, 123.0, 125.5, 126.4, 127.0, 127.9, 129.9, 130.0, 130.4, 133.9, 139.5, 141.9, 144.6, 148.3. IR (neat): ν = 2941, 2890, 1587, 1460, 1361, 1180, 1167, 1117, 1072, 767, 690, 667, 642 cm^{-1}. MS (FAB) *m/z*: 409 (100, M^+), 366 (14), 256 (4), 212 (8). Anal. Calcd for $C_{23}H_{27}NO_2SSi$: C, 67.44; H, 6.64. Found: C, 67.50; H, 6.58.

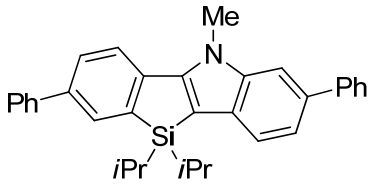
8,8-Diisopropyl-1-tosyl-8*H*-[1]benzosilolo[2,3-b][1]pyrrole (6y)



Purification: N-H silica gel column chromatography (hexane only). Yield: 42%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, C_6D_6): δ 0.81 (d, *J* = 7.2 Hz, 6H), 1.13 (d, *J* = 7.2 Hz, 6H), 1.52 (qq, *J* = 7.2, 7.2 Hz, 2H), 2.40 (s, 3H), 6.62 (d, *J* = 3.0 Hz, 1H), 7.12 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 7.6, 7.0 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 3.0 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.0, 18.1, 21.7, 108.4, 120.1, 125.6, 126.7, 128.1, 129.5, 129.7, 133.3, 133.8, 136.2, 136.3, 143.5, 144.7, 146.9. ^{1}H NMR (400 MHz, C_6D_6): δ 0.97 (d, *J* = 7.2 Hz, 6H), 1.17 (d, *J* = 7.2 Hz, 6H), 1.63 (qq, *J* = 7.2, 7.2 Hz, 2H), 1.78 (s, 3H), 6.42 (d, *J* = 3.0 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.19 (dd, *J* = 7.6, 7.0 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 3.0 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6): δ 12.5, 18.6, 18.9, 21.7, 109.2, 121.2, 126.6, 127.3, 129.1, 130.2, 130.4, 134.2, 134.6, 137.2, 137.7, 144.6, 144.8, 148.1. IR (neat): ν = 2943, 2864, 1595, 1462, 1368, 1173, 1140, 1092, 812, 717, 675, 636 cm^{-1}. MS (FAB) *m/z*: 409 (100, M^+), 366 (16), 324 (3), 212 (5). Anal. Calcd for $C_{23}H_{27}NO_2SSi$: C, 67.44; H, 6.64. Found: C, 67.47; H, 6.61.

Palladium-catalyzed twofold cross coupling reaction of 5p with PhB(OH)$_2$

An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with **5p** (39 mg, 0.1 mmol), $PhB(OH)_2$ (43 mg, 0.35 mmol), $Pd(OAc)_2$ (3.4 mg, 15 μmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 12.3 mg, 30μmol), K_3PO_4 (106 mg, 0.5 mmol), and THF (1 ml). The mixture was heated at 60 °C for 16 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography on N-H silica gel (hexane) to give 10,10-diisopropyl-5-methyl-2,7-diphenyl-10H-[1]benzosilolo[3,2-b][1]indole (**15**) (39 mg, 83%) as a colorless solid.

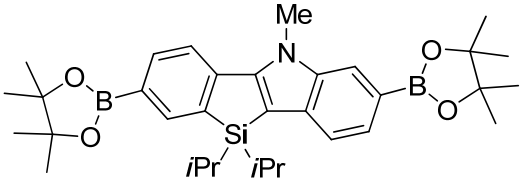


Mp: 143.6–144.8 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.46 (qq, *J* = 7.2, 7.2 Hz, 2H), 4.20 (s, 3H), 7.32–7.45 (m, 3H), 7.45–7.49 (m, 4H), 7.56 (d, *J* = 1.1 Hz, 1H), 7.61 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.64–7.67 (m, 3H), 7.71–7.80 (m, 2H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.7, 18.9, 32.3, 108.1, 108.7, 120.1, 120.3, 122.2, 126.4, 126.8, 127.1, 127.3, 128.0, 128.6, 128.7, 129.9, 132.4, 135.1, 138.6, 140.9, 141.3, 142.4, 142.9, 150.9, 153.7. IR (KBr): ν = 2934, 2858, 1595, 1468, 1396, 1352, 1261, 1203, 1097, 1074, 1030, 879, 810, 760, 694, 682, 640 cm^{-1}. MS (FAB) *m/z*: 471 (100, M^+), 428 (21), 386 (7), 370 (4). Anal. Calcd for $C_{27}H_{28}ClNSi$: C, 84.03; H, 7.05. Found: C, 83.79; H, 7.05.

Palladium-catalyzed twofold cross coupling reaction of 5p with bis(pinacolate)diboron

An oven-dried 80-mL Schlenk tube equipped with a magnetic stir bar was charged

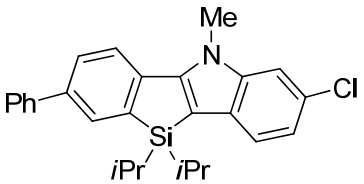
with **5p** (0.34 g, 1.0 mmol), bis(pinacolate)diboron (0.89 mg, 3.5 mmol), $Pd_2(dba)_3$ (46 mg, 50 μmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 47 mg, 0.1 mmol), KOAc (0.49 g, 5.0 mmol), and dioxane (20 mL). The mixture was heated at 60 °C on a hot plate for 16 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by GPC ($CHCl_3$) to give 10,10-diisopropyl-5-methyl-2,7-bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-[1]benzosilolo[3,2-b][1]indole (**16**) (0.61 g, quant.) as a colorless solid.



Mp: 132.4–133.3 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, J = 7.6 Hz, 6H), 1.15 (d, J = 7.6 Hz, 6H), 1.38 (s, 12H), 1.39 (s, 12H), 1.42 (qq, J = 7.6, 7.6 Hz, 2H), 4.17 (s, 3H), 7.58–7.59 (m, 2H), 7.79 (dd, J = 7.8, 0.7 Hz, 1H), 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.87 (s, 1H), 7.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ11.3, 18.6, 18.8, 25.00, 25.03, 32.5, 109.8, 116.4, 119.6, 121.6, 126.1, 133.1, 136.4, 139.6, 141.1, 142.2, 144.7, 154.2. IR (KBr): ν = 2976, 2939, 2862, 1604, 1593, 1462, 1348, 1263, 1146, 1096, 962, 879, 841, 686 cm^{-1}. MS (FAB) *m/z*: 571 (100, M^+), 528 (21), 472 (10). Anal. Calcd for $C_{33}H_{47}B_2NO_4Si$: C, 69.36; H, 8.29. Found: C, 69.15; H, 8.49.

Palladium-catalyzed cross coupling reaction of 5p with $PhB(OH)_2$

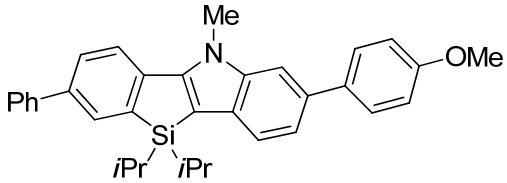
An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with **5p** (39 mg, 0.1 mmol), $PhB(OH)_2$ (8.2 mg, 0.07 mmol), $Pd(OAc)_2$ (0.5 mg, 2 μmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 1.6 mg, 4μmol), K_3PO_4 (43 mg, 0.2 mmol), and THF (0.5 mL). The mixture was heated at 50 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on N-H silica gel (hexane) to give 7-chloro-10,10-diisopropyl-5-methyl-2-phenyl-10H-[1]benzosilolo[3,2-b][1]indole (**17**) (20 mg, 70%) as a colorless solid..



Mp: 157.4–158.2 °C. TLC: R_f 0.30 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 7.3 Hz, 6 H), 1.15 (d, J = 7.2 Hz, 6H), 1.43 (qq, J = 7.2, 7.2 Hz, 2H), 4.11 (s, 3H), 7.10 (dd, J = 8.2, 1.8 Hz, 1H), 7.35–7.39 (m, 2H), 7.45–7.49(m, 3H), 7.61 (dd, J = 8.0, 2.0 Hz, 1H), 7.63–7.65 (m, 2H), 7.78 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.6, 18.8, 32.4, 108.9, 109.6, 120.3, 120.8, 122.7, 126.8, 127.1, 127.3, 128.1, 128.7, 129.0, 132.4, 138.8, 140.8, 141.0, 142.7, 142.8, 153.7. IR (KBr): ν = 2942, 2888, 2860, 1597, 1460, 1442, 1397, 1323, 1296, 1153, 1074, 974, 882, 829, 802, 766, 694 cm^{-1}. MS (FAB) *m/z*: 429 (100, M^+), 386 (27), 344 (8), 252 (2). Anal. Calcd for $C_{27}H_{28}ClNSi$: C, 75.41; H, 6.56. Found: C, 75.54; H, 6.60. CCDC–722338 contains the crystallographic data for **17**.

Palladium-catalyzed cross coupling reaction of 17 with 4-OMeC$_6$H$_4$B$_2$

An oven-dried 3-mL vial equipped with a magnetic stir bar was charged with **17** (50 mg, 0.1 mmol), 4-OMeC$_6$H$_4$B$_2$ (50 mg, 0.3 mmol), Pd(OAc)$_2$ (2.5 mg, 10 μmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 9.0 mg, 20μmol), K_3PO_4 (70 mg, 0.3 mmol), and THF (1.0 mL). The mixture was heated at 50 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (15 mL) was added to the solution and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on N-H silica gel (hexane/AcOEt 10:1) to give 10,10-diisopropyl-7-(4-methoxyphenyl)-5-methyl-2-phenyl-10H-[1]benzosilolo[3,2-b] [1] indole (**18**) (50 mg, 91%).



Mp: 170.6–171.6 °C. TLC: R_f 0.05 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 6H), 1.19 (d, *J* = 7.2 Hz, 6H), 1.46 (qq, *J* = 7.2, 7.2 Hz, 2H), 3.88 (s, 3H), 4.19 (s, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.35–7.39 (m, 2H), 7.45–7.52 (m, 3H), 7.60–7.67 (m, 6H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 18.7, 18.9, 32.3, 55.4, 107.7, 108.7, 114.1, 119.9, 120.2, 122.2, 126.8, 127.1, 128.0, 128.2, 128.7, 129.5, 132.4, 134.8, 135.0, 138.5, 140.9, 141.3, 142.9, 143.0, 153.5, 158.5. IR (KBr): ν = 2939, 2922, 2860, 1608, 1518, 1470, 1460, 1394, 1279, 1242, 1180, 1043, 814, 766, 690 cm^{-1}. MS (FAB) *m/z*: 501 (100, M^+), 458 (17), 416 (4). Anal Calcd for $C_{34}H_{35}NOSi$: C, 81.39; H, 7.03. Found: C, 81.30; H, 6.94.

Computation method

DFT calculation of **5p** was carried out with the Gaussian 03 program.[9] All of the calculations was performed at the B3LYP/6-31G* level. For initial geometries, X-ray structures of **5j** were used as a reference.

Reference

(1) (a) Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1698. (b) Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211. (c) Echavarren, A. M.; Gómez-Lor, B.; González, J. J.; de Frutos, Ó. *Synlett* **2003**, 0585. (d) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (e) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (f) Campeau, L.-C.; Stuart, D. R.; Fagnou, K. *Aldrichimica Acta* **2007**, *40*, 35. (g) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200. (h) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094. (i) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (j) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447.

(2) (a) Campeau, L.-C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (b) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644. (c) Pascual, S.; Mendoza, P. d.; Echavarren, A. M. *Org. Biomol. Chem.* **2007**, *5*, 2727. (d) Campeau, L.-C.; Parisien, M.; Leblanc, M.; Fagnou, K. *J. Am. Chem. Soc.* **2004**, *126*, 9186. (e) Liu, Z.; Larock, R. C. *Org. Lett.* **2004**, *6*, 3739. (f) Campeau, L.-C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857. (g) Bedford, R. B.; Betham, M. *J. Org. Chem.* **2006**, *71*, 9403. (h) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581. (i) Garcia-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066.

(3) Verma, A. K.; Kesharwani, T.; Singh, J.; Tandon, V.; Larock, R. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 1138.

(4) (a) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050. (b) Grimster, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 3125.

(5) (a) Billingsley, K. L.; Barder, T. E.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 5359. (b) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 1871.

(6) Ahlquist, M.; Norrby, P.-O. *Organometallics* **2007**, *26*, 550.

(7) Charles, M. D.; Schultz, P.; Buchwald, S. L. *Org. Lett.* **2005**, *7*, 3965.

(8) Bartoli, G.; Palmieri, G.; Bosco, M.; Dalpozzo, R. *Tetrahedron Lett.* **1989**, *30*, 2129.

(9) *Gaussian 03*, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Laham, A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

Chapter 5

Photophysical Properties of 3,2'-Silicon-bridged 2-Arylindoles

Strong and highly efficient fluorescence from 3,2'-silicon-bridged 2-arylindoles was observed not only in solution but also in the solid state such as microcrystal and doped polymer film. UV absorption and fluorescence maxima, thermal stability, and radical ion stability of these indoles were found to be tunable by introduction of an appropriate functional group.

1. Introduction

Efficient solid-state emission of organic materials is essential for opto-electronic devices such as organic light-emitting diodes, light-emitting thin film transistors, semiconductor lasers, and solid luminescent sensors. Thus, invention of π-conjugated molecules exhibiting efficient solid-state emission is an extremely challenging task. However most organic chromophores are weakly emissive or non-emissive in the solid state due to concentration quenching attributed by intermolecular electronic interactions such as excimer formation and energy migration in the condensed phase. Accordingly, organic solids that exhibit intense emission with high absolute quantum yield are quite limited.[1] Representative examples are illustrated in Chart 1. Therefore, exploration of new emissive organic solid and understanding of their characteristics regarding molecular and electronic structures as well as three-dimensional alignment in the solid state are very important for the invention of emitting materials employed in such opto-electronic devices.

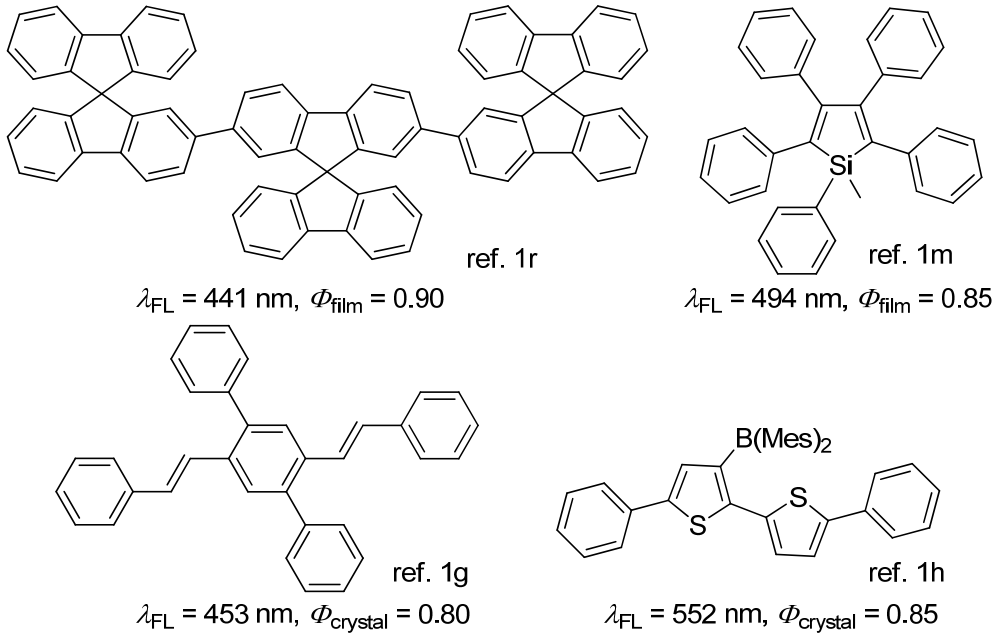
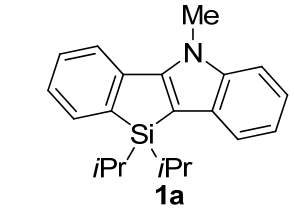


Chart 1. Examples of organic solids that emit visible light with high quantum yield.

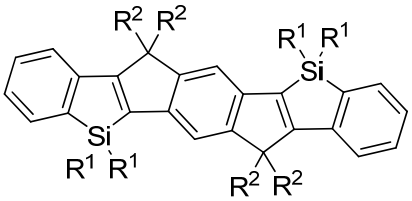
In the course of the research on the palladium-catalyzed intramolecular coupling of 2-(arylsilyl)aryl triflates described in Chapters 2-4, the author observed that 3,2'-diisopropylsilylene-bridged 2-phenylindole **1a** was blue-fluorescent in solid states

with excellent quantum yields. The striking fact may be attribute to the diisopropylsilylene-bridge that prevents intermolecular electronic interactions in the solid states. Very recently, Yamaguchi and co-workers reported that introduction of bulky substituents such as *n*Pr group in place of Me into silicon and carbon bridges of distyrylbenzene improved efficiency of solid state fluorescence.[2]



1a

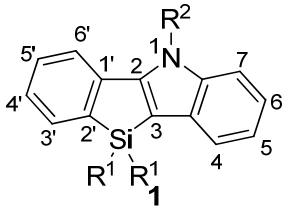
λ_{FL} = 434 nm, $\Phi_{crystal}$ = 0.91



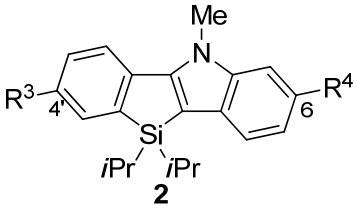
R^1 = Me, R^2 = Ph: λ_{FL} = 481 nm $\Phi_{crystal}$ = 0.22

$R^1 = R^2$ = *n*Pr; λ_{FL} = 475 nm $\Phi_{crystal}$ = 0.63

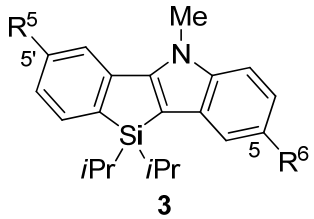
Accordingly, the author has focused his attention to 3,2'-silicon-bridged 2-arylindoles **1**-**4** as a new class of emissive fluorophore. Described in this Chapter are structures, photophysical properties, and theoretical calculations of **1**-**4**, which were prepared by the silicon-migrative intramolecular coupling of 2-(indolylsilyl)aryl triflates as discussed in Chapter 4.



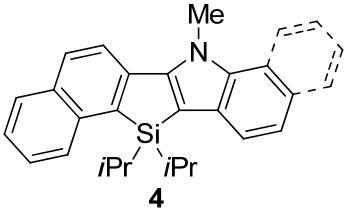
1



2



3



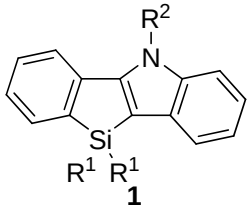
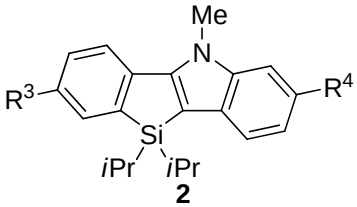
4

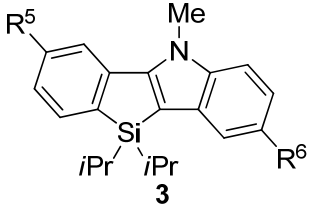
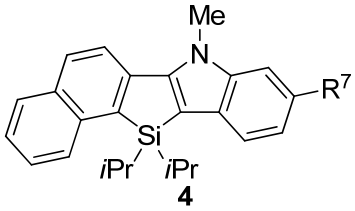
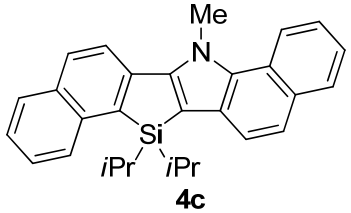
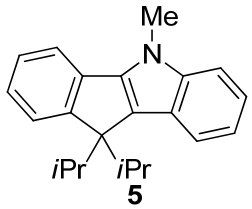
2. Results and Discussion

2-1. Photophysical properties of 3,2'-silicon-bridged 2-arylindoles

The structures and photophysical properties of 3,2'-silicon-bridged 2-arylindoles **1**-**4** along with those of carbon analogue **5** are summarized in Table 1.

Table 1. Structures and photophysical properties of **1**-**5**.

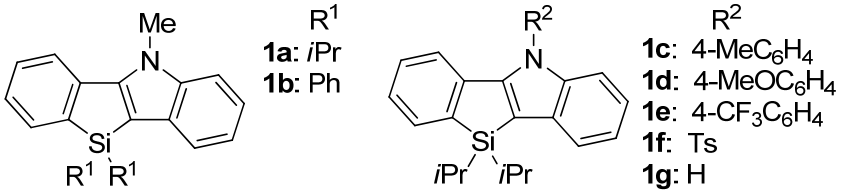
Compd		UV absorption cyclohexane[a]		Fluorescence[b,c] cyclohexane[a]		PMMA[d]		microcrystal	
		$\lambda_{abs,\,max}$ / nm	ε / $M^{-1}cm^{-1}$	$\lambda_{FL,\,max}$ / nm	Φ_f	$\lambda_{FL,\,max}$ / nm	Φ_f	$\lambda_{FL,\,max}$ / nm	Φ_f
	R^1, R^2								
 **1**	**1a**: *i*Pr, Me	309	17300	402	0.70	408	1.00	434	0.91
	1b: Ph, Me	309	16100	410	0.76	415	0.86	435	0.90
	1c: *i*Pr, 4-MeC_6H_4	334	5900	394	0.79	401	0.81	408	0.70
	1d: *i*Pr, 4-$MeOC_6H_4$	307	7700	394	0.70	401	0.77	409	0.61
	1e: *i*Pr, 4-$CF_3C_6H_4$	308	17200	394	0.71	395	0.76	413	0.82
	1f: *i*Pr, Ts	334	14100	391	0.06	403	0.04	-[e]	-[e]
	1g: *i*Pr, H	322	23100	364	0.74	370	0.62	393	0.21
	R^3, R^4								
 **2**	**2a**: OMe, H	315	21100	417	0.65	416	0.77	424	0.74
	2b: CN, H	372	16400	426	0.85	439	0.92	450	0.57
	2c: Cl, H	317	17600	412	0.72	418	0.86	445	0.79
	2d: H, Cl	318	22100	410	0.68	414	0.83	436	0.68
	2e: H, $SiMe_3$	320	16600	403	0.79	407	0.82	433	0.38
	2f: Cl, Cl	319	22100	409	0.71	402	0.80	437	0.64
	2g: OMe, Cl	331	22900	417	0.65	415	0.74	432	0.74
	2h: CN, Cl	372	18500	425	0.84	435	0.84	465	0.84
	2i: CN, piperidyl	404	25500	468	0.73	510	0.86	548	0.21
	2j: Ph, Ph	371	33000	438	0.83	441	0.86	458	0.65
	2k: Ph, 4-$MeOC_6H_4$	374	32000	443	0.80	446	0.87	483	0.71

 **3**	R^5, R^6								
	3a: F, H	319	14700	394	0.74	403	0.87	422	0.76
	3b: H, OMe	320	20100	403	0.58	407	0.61	422	0.61
	3c: H, Cl	318	18500	394	0.44	400	0.14	421	0.17
 **4**	R^7								
	4a: H	353	14800	453	0.46	459	0.69	476	0.70
	4b: Cl	354	17600	453	0.39	454	0.60	488	0.43
 **4c**	**4c**	354	27700	449	0.55	458	0.73	479	0.31
 **5**	**5**	332	27700	374	0.80	379	0.62	435	0.34

[a] Measured at 1×10^{-5} M in cyclohexane. [b] Irradiation was performed with a UV light (λ = 320 nm). [c] Absolute quantum yield determined by a calibrated integrating sphere system. [d] Dispersed in poly(methyl methacrylate) (PMMA) [e] No fluorescence was observed.

2-1-1. Photophysical properties of 3,2'-silicon-bridged 2-phenylindoles 1

Described in this section is photophysical properties of 3,2'-silicon-bridged 2-phenylindoles **1a**-**1g**.



UV absorption spectra of **1** measured in cyclohexane are collected in Figure 1. The absorption edge of **1b** (390 nm) slightly red-shifted as compared with those of **1a** (382 nm), indicating that phenyl groups on silicon could influence the electronic structures to extend the parent π-conjugate system. Meanwhile, absorption edges of *N*-arylated indole derivatives **1c**-**1e** (ca. 377 nm) blue-shifted by 5 nm compared with that of **1a**, possibly because an aryl group on nitrogen is oriented perpendicular to the aromatic plane and hence π-conjugation is not well extended (for molecular structure of the single crystal, see below). Absorption edges of *N*-tosylated **1f** and *N*-H **1g** also blue-shifted by 8 nm from **1a** to **1f** (374 nm) and 30 nm from **1a** to **1g** (352 nm). This fact may be understood in terms of lowered HOMO levels due to an electron-withdrawing Ts substituent as compared with Me, thus making HOMO-LUMO gap larger (for molecular orbital calculations, see below).

Normalized fluorescence spectra of **1** in cyclohexane are shown in Figure 2. Compared with **1a** (λ_{FL}: 402 nm), emission maxima of **1b** red-shifted by 8 nm, which was consistent with bathochromic shifts of the absorption spectra shown in Figure 1. Meanwhile, *N*-arylated and -tosylated derivatives **1c**-**1f** showed almost the same emission maxima (ca. 394 nm). Fluorescence quantum yields (Φ_f) of **1a**-**1e** and **1g** (Φ_f = 0.70~0.79) were excellent, whereas quantum yield of **1f** was only 0.06 due probably to the heavy atom effect of sulfur. Namely, intersystem crossing from the singlet excited state to the triplet excited state should be promoted.

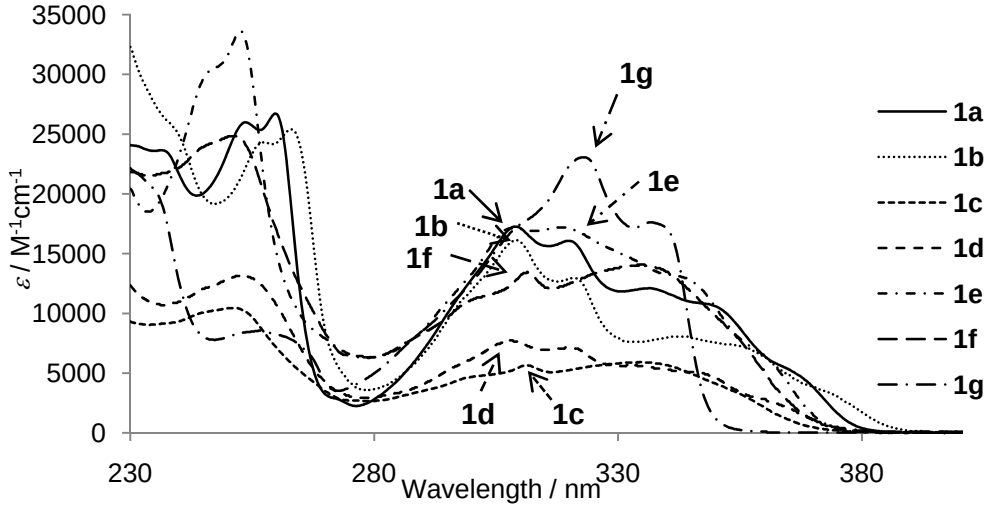


Figure 1. UV absorption spectra of **1** in cyclohexane.

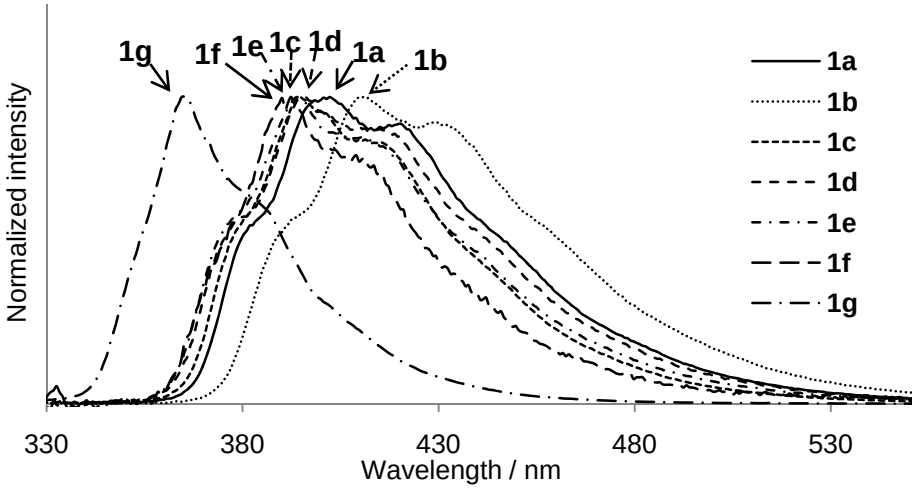


Figure 2. Fluorescence spectra of **1** in cyclohexane (excited at 320 nm).

Fluorescence spectra of **1** in doped PMMA film are shown in Figure 3. The spectra red-shifted by 5~10 nm compared with those measured in cyclohexane. Except for **1f** and **1g**, doped PMMA film of **1** showed excellent fluorescence quantum yield. In particular, quantum yield of **1a** reaches 1.00. The high quantum yield may be ascribed to suppressed conformational change of **1a** in doped PMMA film particularly in the excited states.

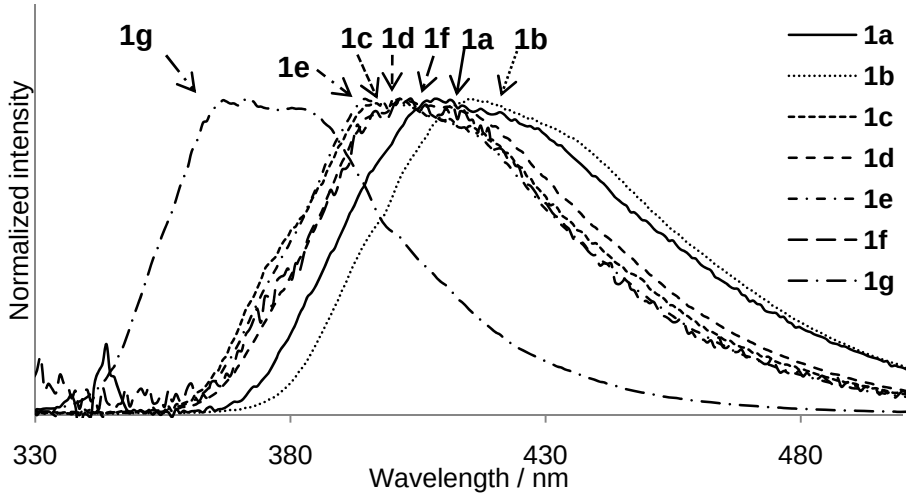


Figure 3. Fluorescence spectra of **1** in doped PMMA film (excited at 320 nm)

Fluorescence spectra of **1** in microcrystals are shown in Figure 4. As observed in the fluorescence spectra in cyclohexane, the emission maxima red-shifted in the order of **1g** (393 nm) < **1c** (408 nm) ≃ **1d** (409 nm) ≃ **1e** (413 nm) < **1a** (434 nm) ≃ **1b** (435 nm). *N*-Tosylated derivative **1f** was non-emissive in the microcrystal and hence any fluorescence were not observed. It is noteworthy that fluorescence quantum yields of **1a** and **1b** were extremely high (Φ_f = 0.91 and 0.90, respectively). Such high quantum yields in the solid states indicate that the molecular and electronic structures of **1a** and **1b** in the condensed phases efficiently retard the intermolecular electronic interaction that leads to concentration quenching (for molecular structure of the single crystal see below). In fact, overlap of absorption and fluorescence spectra in **1a** and **1b** measured in cyclohexane, respectively, were quite small (Figure 5). Thus, the electronic structures of **1a** and **1b** are appropriate for suppressing the intermolecular energy transfer of the excited molecules via Förster mechanism.

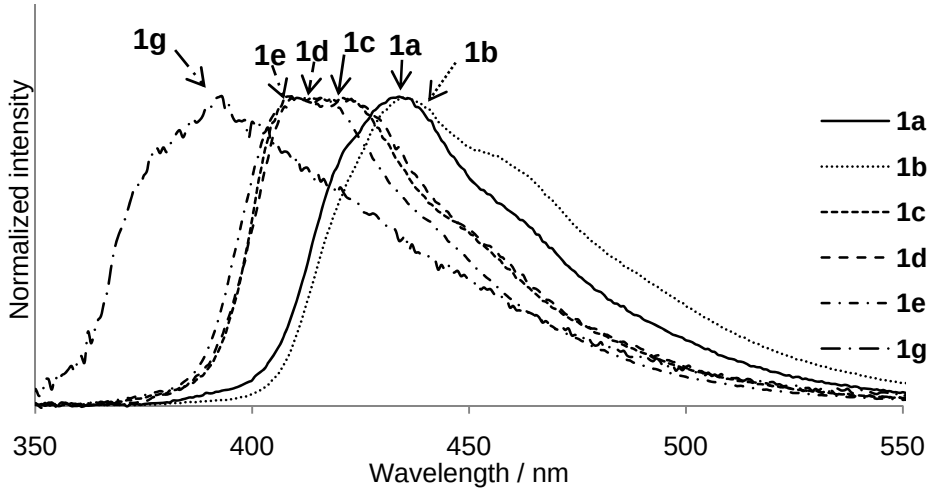


Figure 4. Fluorescence spectra of **1** in the microcrystal (excited at 320 nm).

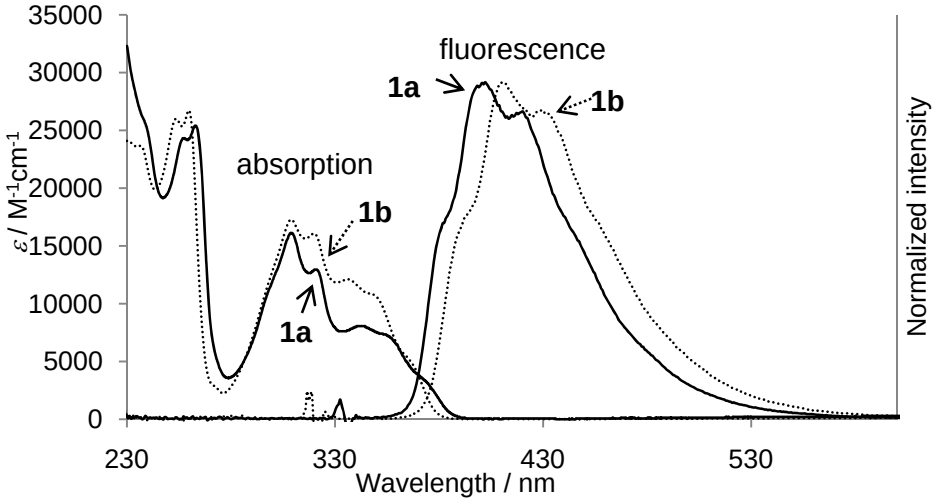


Figure 5. Absorption and fluorescence spectra of **1a** and **1b** in cyclohexane (excited at 320 nm).

To gain further insight into the electronic structure of **1a**, the author measured UV absorption and fluorescence spectra of **1a** in various solvents (Table 2). Absorption maxima in DMSO red-shifted by only 1 nm compared with that in cyclohexane. In contrast, fluorescence maxima in CH_3CN red-shifted by 15 nm compared with that in cyclohexane. Although solvent effect was small, red-shift of absorption and fluorescence maxima in polar solvents was observed, suggesting that **1a** in the excited states has π-π^* transition rather than CT transition.

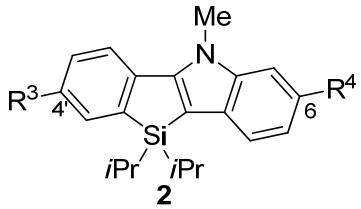
Table 2. Solvent effects of UV absorption and fluorescence spectra of **1a**.[a,b,c]

	cyclohexane	benzene	Et_2O	CH_2Cl_2	CH_3CN	DMSO
$\lambda_{abs,max}$ / nm	309	309	309	309	309	310
ε / $M^{-1}{}_{cm}{}^{-1}$	17300	16200	16300	15200	14500	13800
$\lambda_{FL,max}$ / nm	402	407	404	410	417	414
Φ_f	0.70	0.71	0.62	0.74	0.56	0.72

[a] Measured at 1×10^{-5} M. [b] Absolute quantum yield determined by a calibrated integrating sphere system. [c] Irradiation was performed with a UV light (λ = 320 nm)

2-1-2. Photophysical properties of 3,2'-silicon-bridged 2-arylindoles 2

Discussed in this section are photophysical properties of 6- and/or 4'-substituted 3,2'-silicon-bridged 2-phenylindoles **2** shown below.



2

R^3, R^4	R^3, R^4
2a: OMe, H	**2f**: Cl, Cl
2b: CN, H	**2g**: OMe, Cl
2c: Cl, H	**2h**: CN, Cl
2d: H, Cl	**2i**: CN, piperidyl
2e: H, $SiMe_3$	**2j**: Ph, Ph
	2k: Ph, 4-$MeOC_6H_4$

UV absorption spectra of mono-substituted 3,2'-silicon-bridged 2-arylindoles **2a**-**2e** are shown in Figure 6. Absorption maxima of **2a** (315 nm) bearing OMe group at 4'-position red-shifted by 6 nm compared with that of **1a** (309 nm). Introduction of a cyano group at 4'-position induced bathochromic shift of absorption maxima by 63 nm: **2b** (372 nm). Chlorine substitution in 3,2'-silicon-bridged 2-arylindoles (**2c** and **2d**) induced red-shift of absorption maxima (ca. 317 nm). Absorption maxima of **2e** (320 nm) red-shifted by 11 nm compared with that of **1a**. Thus, installation of a functional group at 6- and/or 4'-position is highly effective to expand π-conjugation because such a substituent dramatically perturbs the electronic structure of the 3,2'-silicon-bridged 2-phenylindole core structure and thus makes HOMO-LUMO gap smaller (for molecular orbital calculations, see below).

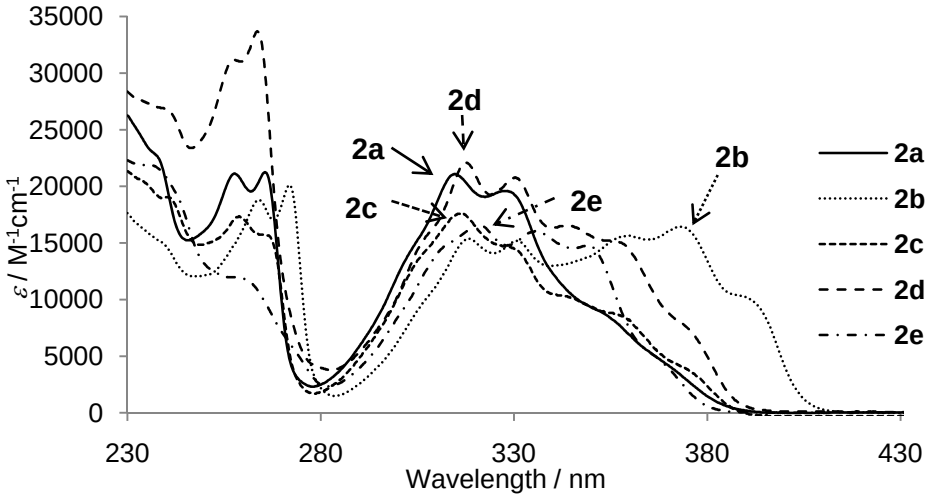


Figure 6. UV absorption spectra of **2a**-**2e** in cyclohexane.

Fluorescence spectra of **2a**-**2e** in cyclohexane are shown in Figure 7. Fluorescence maxima red-shifted in the order of **2e** (403 nm) < **2d** (410 nm) ≃ **2c** (412 nm) < **2a** (417 nm) < **2b** (426 nm) with generally high quantum yields. Introduction of cyano group at *meta*-position to silicon-bridge was found to improve efficiency of fluorescence: quantum yield of **2b** reached 0.85.

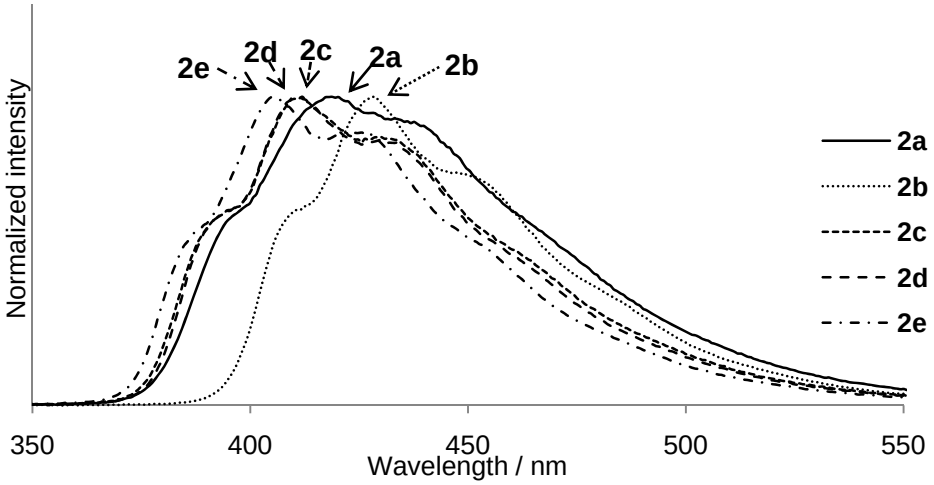


Figure 7. Fluorescence spectra of **2a**-**2e** in cyclohexane (excited at 320 nm).

Fluorescence spectra of **2a**-**2e** in doped PMMA film are shown in Figures 8. Generally, fluorescence spectra of **2a**-**2e** in doped PMMA film red-shifted as compared

with those measured in cyclohexane with excellent fluorescence quantum yields (Φ_f = 0.77~0.92). In the microcrystal, quantum yields of **2a**-**2e** (Φ_f = 0.38~0.79) were lower than those in doped PMMA.

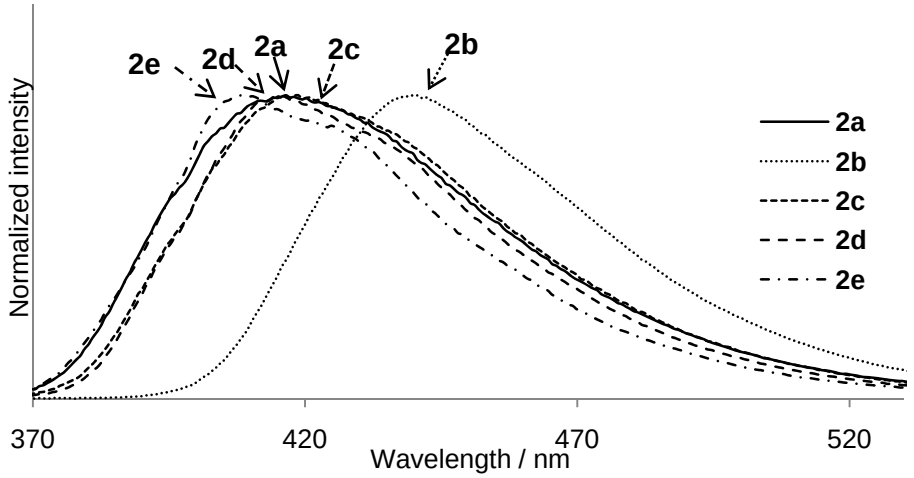


Figure 8. Fluorescence spectra of **2a**-**2e** in doped PMMA film (excited at 320 nm)

UV absorption spectra of 6,4'-disubstituted 3,2'-silicon-bridged 2-arylindoles **2f**-**2k** are collected in Figure 9. For **2j** and **2k**, the shape of absorption spectra are similar. Absorption maxima appeared in the order of **2f** (319 nm) < **2g** (331 nm) < **2j** (371 nm) ≃ **2h** (372 nm) ≃ **2k** (374 nm). Introduction of an electron donor at the 6-position and an electron acceptor at 4'-position, so called D-π-A system, was effective to extend π-conjugated length in the parent molecule. In fact, the absorption maxima of **2i** bearing a CN group at 4'-position and a piperidyl group at 6-position reached 402 nm.

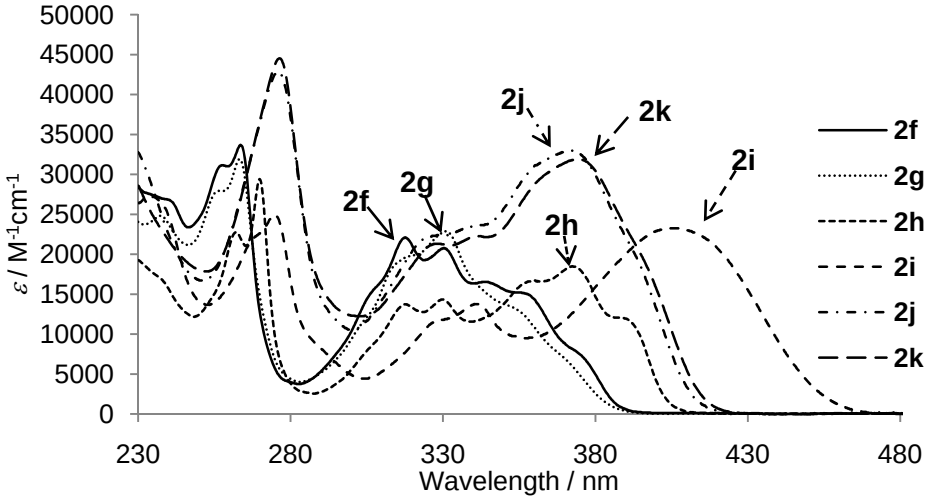


Figure 9. Fluorescence spectra of **2f**-**2k** in cyclohexane.

Fluorescence spectra of **2f**-**2k** in cyclohexane and doped PMMA film are shown in Figures 10 and 11, respectively. Fluorescence maxima in cyclohexane were observed in the order of **2f** (409 nm) < **2g** (417 nm) < **2h** (425 nm) < **2j** (438 nm) < **2k** (443 nm) < **2i** (468 nm). Fluorescence quantum yields (Φ_f) of **2a**-**2e** (Φ_f = 0.65~0.83) were almost the same as that of **1a** (Φ_f = 0.70). Fluorescence spectra of **2f**-**2k** in doped PMMA film were structureless and red-shifted in the order of **2f** (402 nm) < **2g** (415 nm) < **2h** (435 nm) < **2j** (441 nm) < **2k** (446 nm) < **2i** (510 nm). Like mono-substituted product **2a**-**2e**, quantum yield of **2f**-**2k** (Φ_f = 0.74~0.87) in doped PMMA film are higher than those measured in cyclohexane. Possibly, intramolecular rotation which results in consumption of photon energies and deactivation of all the excited states are suppressed in doped PMMA film.

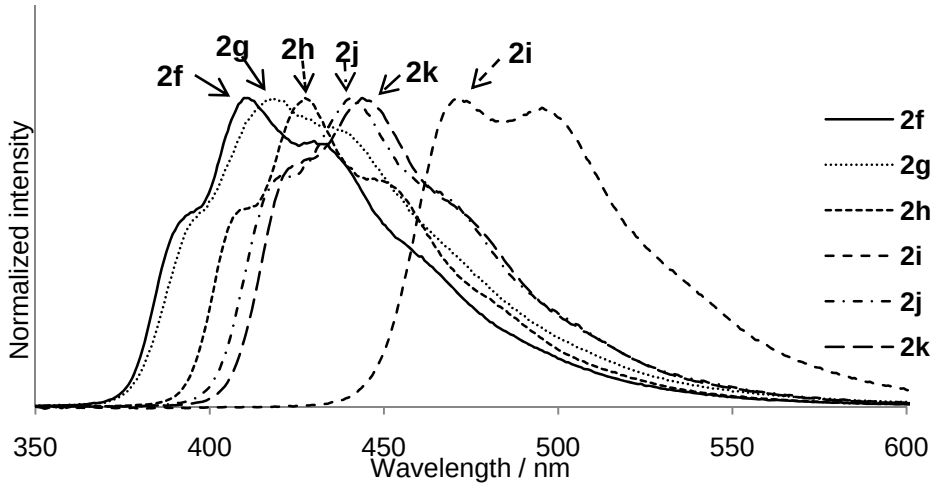


Figure 10. Fluorescence spectra of **2f**-**2k** in cyclohexane (excited at 320 nm).

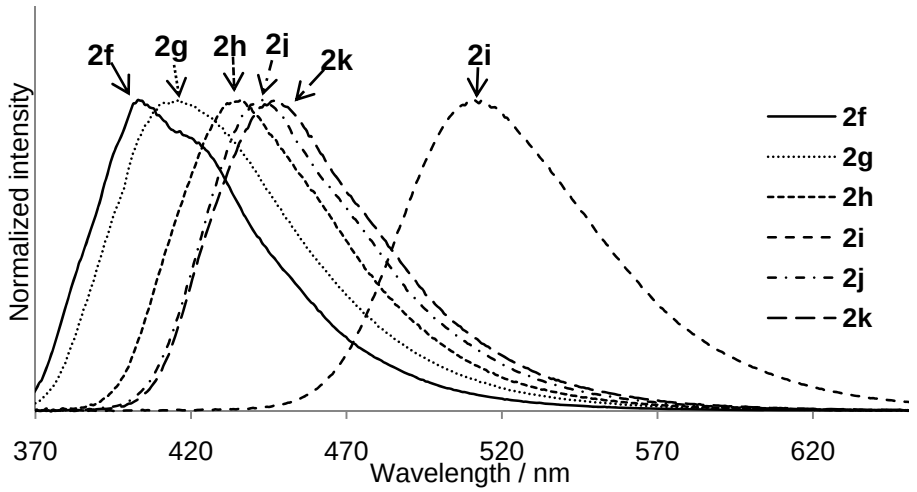


Figure 11. Fluorescence spectra of **2f**-**2k** in doped PMMA film (excited at 320 nm).

Fluorescence spectra of **2f**-**2k** in microcrystals are shown in Figures 12. Emission maxima of **2f**-**2h** and **2j**-**k** red-shifted by ca. 30 nm from those measured in cyclohexane with good to excellent quantum yields (Φ_f = 0.64~0.84). On the other hand, emission maxima of **2i** (548 nm) in the microcrystal red-shifted by 80 nm from that in cyclohexane (468 nm). Quantum yield of **2i** was only 0.21, indicating that the intermolecular electronic interaction occurred (for molecular packing of single crystal, see below) in the microcrystal and led to quenching of fluorescence.

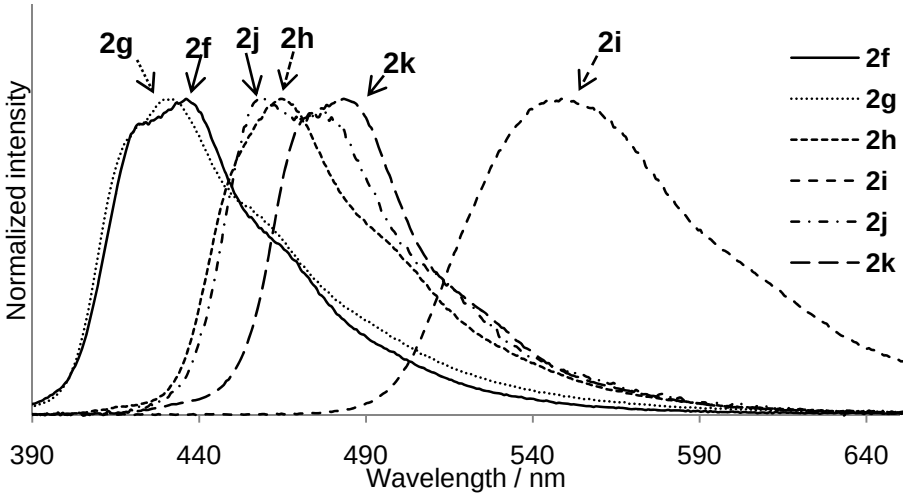
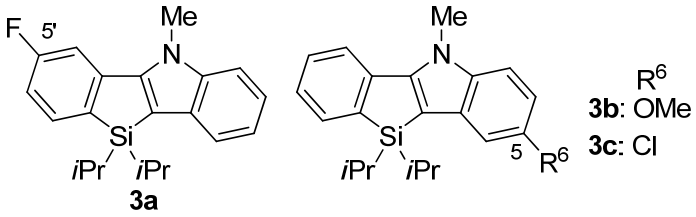


Figure 12. Fluorescence spectra of **2f**-**2k** in the microcrystal (excited at 320 nm).

2-1-3. Photophysical properties of 3,2'-silicon-bridged 2-arylindoles 3

Discussed in this section are UV absorption and fluorescence studies on 5- or 5'-substituted 3,2'-silicon-bridged 2-phenylindoles **3**.



UV absorption and fluorescence spectra of **3** measured in cyclohexane are shown in Figures 13 and 14, respectively. For **3b** and **3c**, absorption spectra showed similar vibrational structures. Absorption maxima of **3a** (319 nm), **3b** (320 nm) and **3c** (318 nm) red-shifted by ca. 10 nm as compared with that of **1a** (309 nm). Fluorescence spectra of **3** also showed quite similar vibrational structures, indicating that installation of a functional group at 5- and 5'-position did not perturb the electronic structure of the parent π-system. Fluorescence maxima of **3c** (394 nm) blue-shifted by 8 nm from **3c** compared with that of **1a** (402 nm). While fluorescence quantum yield of **3a** (Φ_f = 0.74) is almost the same level with that of **1a** (Φ_f = 0.70), substitution at 5-position led to low efficiency of fluorescence.

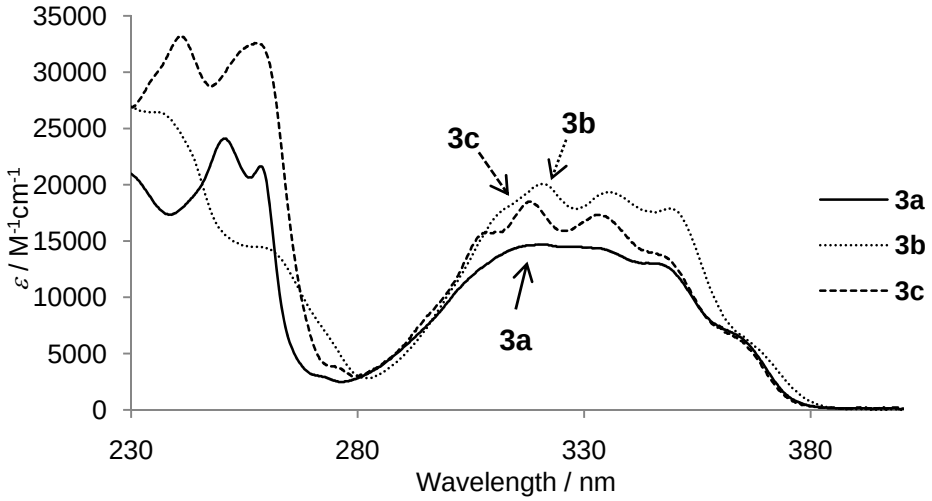


Figure 13. UV absorption spectra of **3** in cyclohexane.

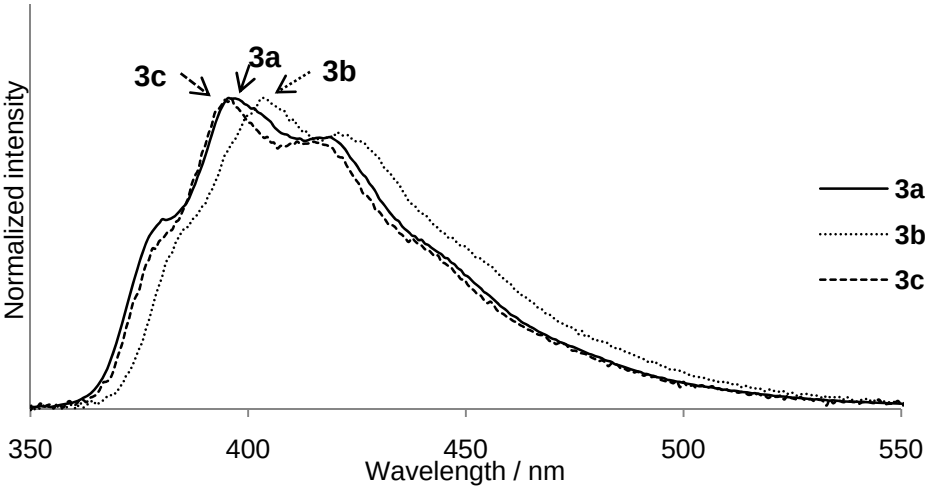


Figure 14. Fluorescence spectra of **3** in cyclohexane (excited at 320 nm).

Fluorescence spectra of **3** in doped PMMA film are shown respectively in Figure 15. Emission maxima of **3** in doped PMMA film red-shifted in the order **3c** (400 nm) < **3a** (403 nm) < **3b** (407 nm) with low quantum yield particularly for **3b** and **3c**. In addition, fluorescence quantum yield of **3c** in the microcrystal was only 0.17.

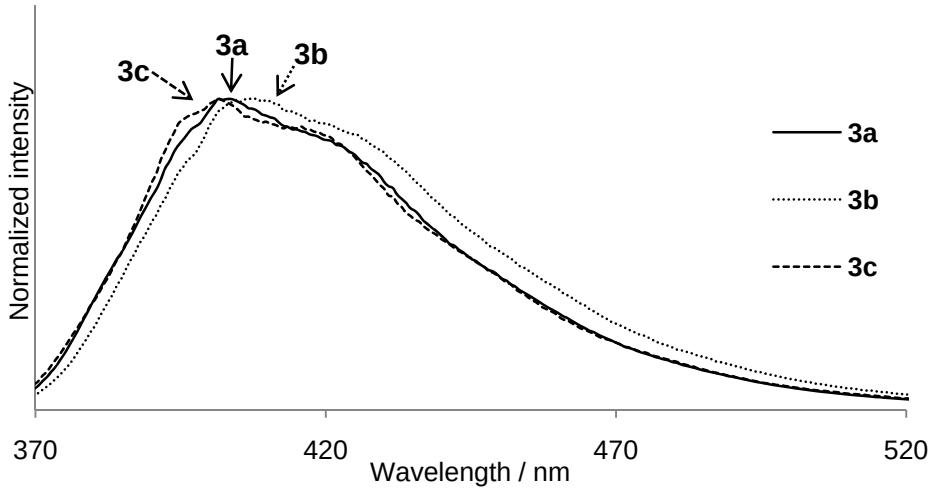
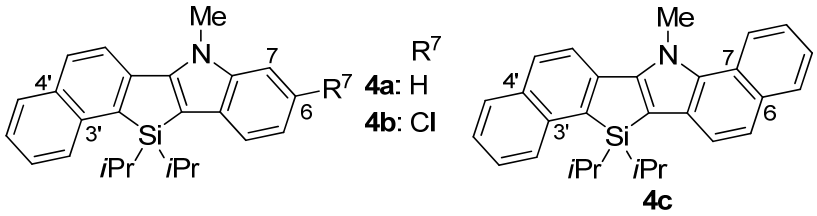


Figure 15. Fluorescence spectra of **3** in doped PMMA film (excited at 320 nm).

2-1-4. Photophysical properties of benzo 3,2'-silicon-bridged 2-phenylindoles 4

Discussed in this section are photophysical properties of benzo[3',4'] 3,2'-silicon-bridged 2-phenylindoles **4a-4b** and dibenzo[6,7][3',4'] 3,2'-silicon-bridged 2-phenylindoles **4c**.



UV absorption spectra of **4** measured in cyclohexane are shown in Figure 16. Absorption maxima of **4a** (353 nm), **4b** (354 nm), and **4c** (354 nm) red-shifted as compared with that of **1a** (307 nm). The fact that **4a** and **4c** have similar absorption maxima suggested that fused benzene ring at 3'- to 4'-position did not contribute to extension of effective conjugation (for molecular orbital calculations, see below).

Quantum yields of **4** were lower than those of **1a** in all state. Difference in emission maxima among **4** was quite small. For example, emission maxima of **4** in doped PMMA film are 454 nm for **4b**, 458 nm for **4c**, and 459 nm for **4a** (Figure 17).

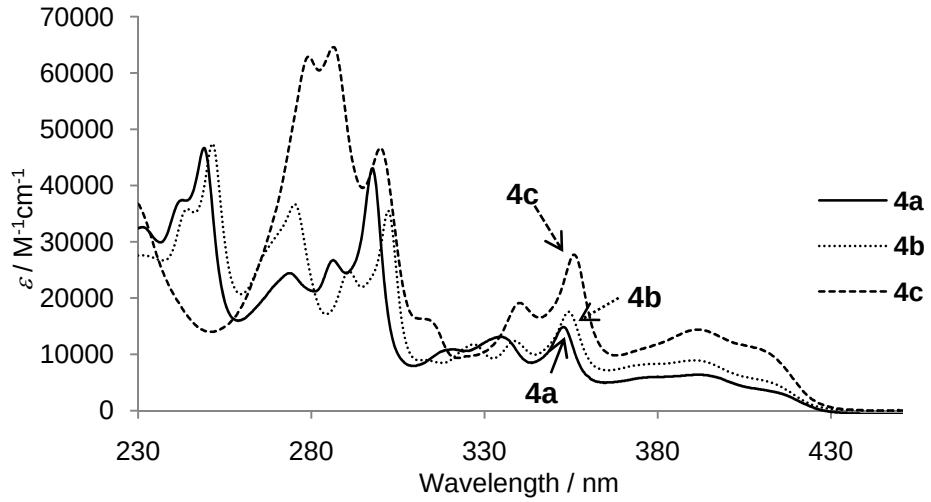


Figure 16. UV absorption spectra of **4** in cyclohexane.

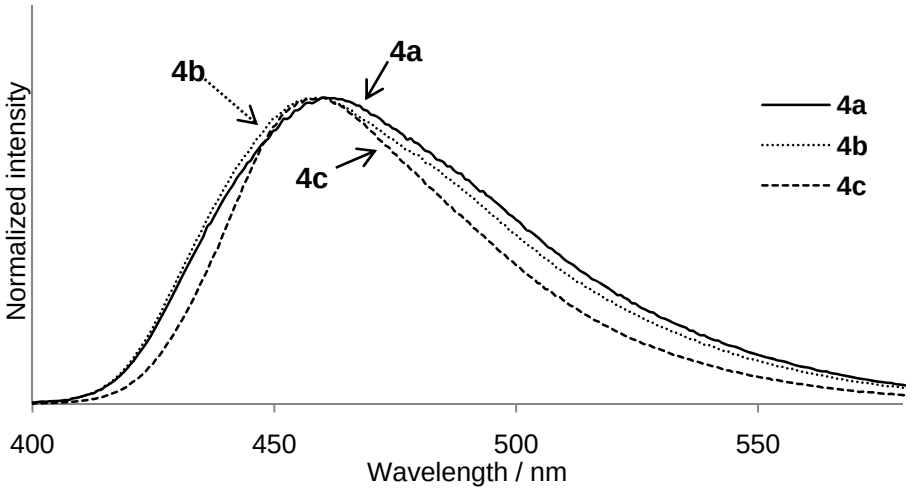


Figure 17. Fluorescence spectra of **4** in doped PMMA film (excited at 320 nm).

2-1-4. Fluorescence lifetimes of 3,2'-silicon-bridged 2-arylindoles

The fluorescence lifetimes (τ_s) of **1-4** were measured in the microcrystal and the results are summarized in Table 3. On the basis of the fluorescence quantum yield Φ_f and fluorescence lifetime τ_s, the author calculated the radiative (k_f) and non-radiative (k_n) decay rate constants from the singlet excited states, based on Eqs. (1) and (2). The installation of a functional group and/or a benzene ring fused at the arene moiety in **1a** was found to significantly increase the k_n value except for **4a**, whereas k_f values were not affected by a substituent compared with k_n. These results mean that decrease in Φ_f

is mainly attributed to accelerated non-radiative decay pathways including internal energy conversion and intersystem crossing.

$k_f = \Phi_f / \tau$, (1)

$k_n = (1 - \Phi_f) / \tau$, (2)

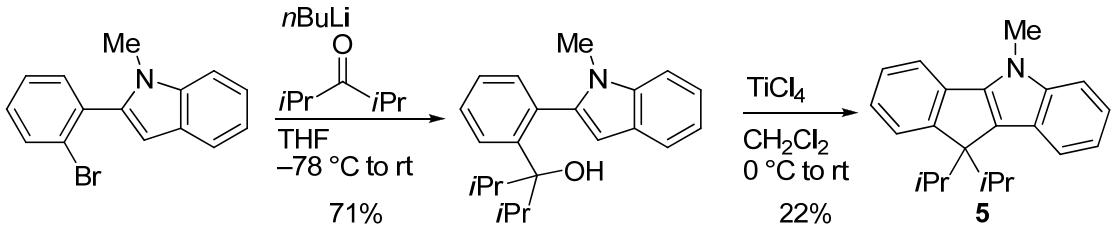
Table 3. Fluorescence lifetimes (τ_s), radiative rate constants (k_f), and non-radiative rate constants (k_n) for **1**-**4**.[a]

Compd	$\Phi_{f,solid}$	τ_s (ns)	k_f ($10^7 s^{-1}$)	k_n ($10^7 s^{-1}$)
1a	0.91	6.4	14.3	1.4
2f	0.64	2.5	25.3	14.2
2h	0.84	5.1	16.6	3.2
2i	0.21	4.8	4.4	16.6
2j	0.65	2.4	27.2	14.6
2k	0.71	3.2	22.4	9.1
3b	0.61	4.6	13.2	8.4
4a	0.70	15.5	4.5	1.9
4b	0.43	5.3	8.1	10.8
4c	0.31	5.2	6.0	13.4

[a] Excited at 388 nm.

2-1-5. Photophysical properties of carbon analogue

To examine the effect of silicon-bridge, the author prepared the corresponding carbon analogue **5** according to Scheme 1.



Scheme 1. Preparation of the corresponding carbon analogue **5**.

UV absorption and fluorescence spectra of **5** in cyclohexane are shown in Figure 18 along with those of **1a**. Compared to **1a** (382 nm), absorption edge of **5** (366 nm) blue-shifted by 16 nm. Fluorescence maxima of **5** (374 nm) also blue-shifted by 28 nm. These blue-shifts clearly show that σ*–π* conjugation in **1a** contributed to reduction in HOMO-LUMO gap (for molecular orbital calculations, see below).

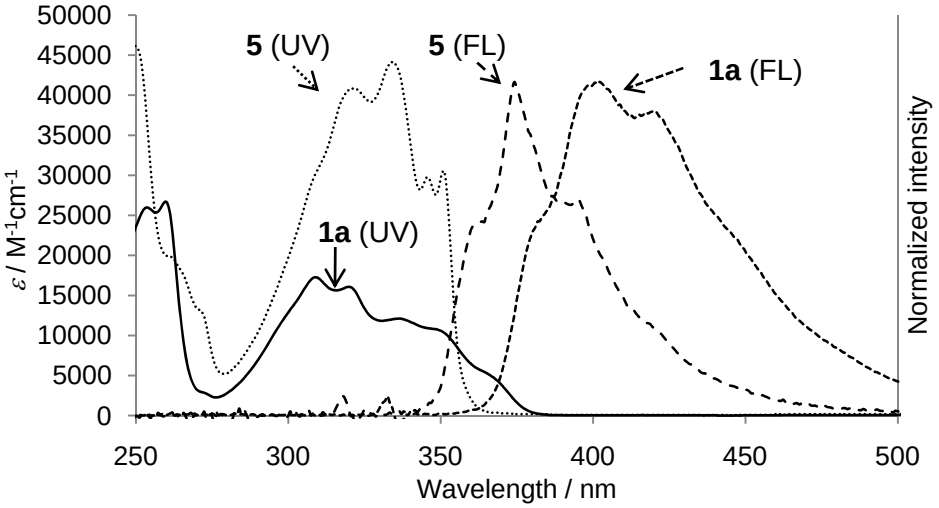


Figure 18. UV absorption spectra of **1a** and **5** in cyclohexane.

Fluorescence spectra of **5** in doped PMMA film and the microcrystal are shown in Figure 19. While fluorescence maxima (379 nm) of **5** in doped PMMA film blue-shifted by 29 nm as compared with that **1a** (408 nm), fluorescence maxima in the microcrystal were almost same (ca. 434 nm). Whereas quantum yield of **5** (Φ_f = 0.80) in cyclohexane is comparable to that of **1a** (Φ_f = 0.70), **5** (Φ_f = 0.34) in the microcrystal exhibited significantly lower Φ_f than **1a** (Φ_f = 0.91) due probably to the larger overlap between absorption and fluorescence spectra of **5** in cyclohexane than that of **1a** (Figure 22), suggesting an intermolecular energy transfer from the excited molecules via Förster mechanism occurring the microcrystal.

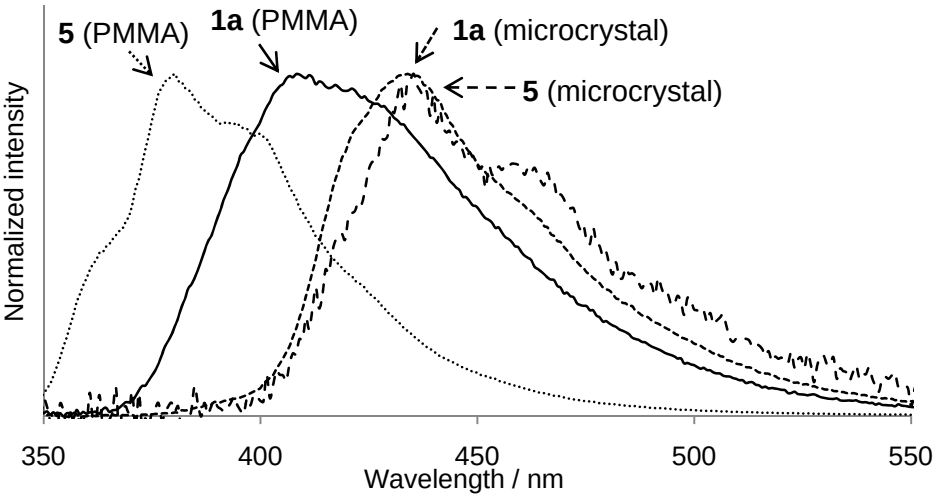


Figure 19. Fluorescence spectra of **1a** and **5** (excited at 320 nm).

2-2. Molecular Structures

To gain more insight into the excellent solid-state luminescent efficiency of 3,2'-silicon-bridged 2-arylindoles, the crystal structures of **1a**, **1e**, **1f**, and **2i** were analyzed by single crystal X-ray diffraction. Each of **1a**, **1e**, **1f**, and **2i** was recrystallized from a hexane/CH_2Cl_2 solution. The molecular structure of **1a**, shown in Figure 20, demonstrates that the phenylindole moiety and the silylene bridge is co-planar and the isopropyl groups on silicon are orienting perpendicular to the plane, an ideal conformation for efficient σ*–π* conjugation. The geometry of silicon atom is significantly deformed from tetrahedral: bond angles of C5–Si1–C1, C6–Si1–C1, C5–Si1–C4, C6–Si1–C4, and C5–Si1–C6 are expanded to 111.9°, 113.2°, 114.6°, 114.3°, and 110.6°, respectively, while that of C2–Si1–C2' in five-membered ring was 91.0°, smaller than the standard sp^3-hybridized silicon (109.5°). However this is typical value for the silafluorenes.[3] The bond lengths of Si1–C1, Si1–C4, Si1–C5, and Si1–C6 are 1.890 Å, 1.832 Å, 1.878 Å, and 1.876 Å, similar to the standard Si–C length of 1.88 Å in neutral tetrahedral silanes and the previously reported silafluorenes.[3] Configuration of nitrogen (N1) is trigonal planar, the dihedral angle of C4–C3–N1–C7 being 176.4°. Conversely, in case of **1f** (Figure 21), configuration of nitrogen atom deformed to trigonal pyramidal with a dihedral angle C1–C2–N1–S1 of 136.9°. Considering the fact that **1f** did not emit fluorescence, a trigonal planar structure of nitrogen may be one of the key factors for the realization of the efficient solid-state emission of **1**.

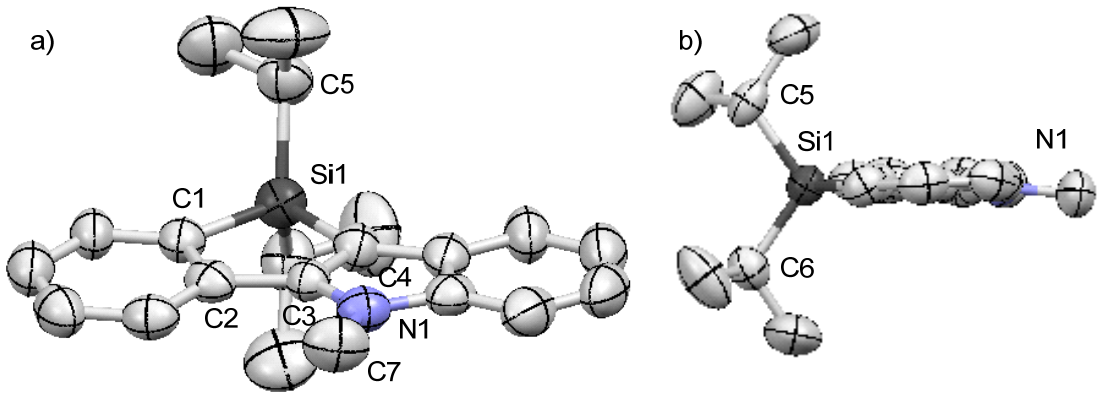


Figure 20. Molecular structure of **1a** (a) front view, (b) side view.

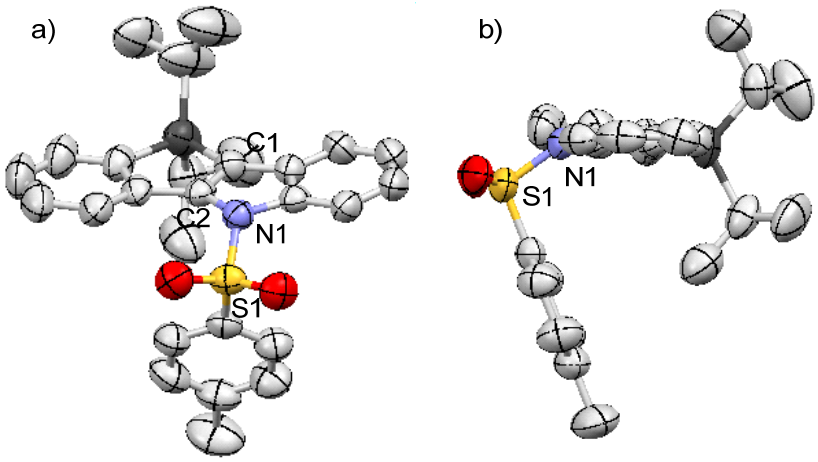


Figure 21. Molecular structure of **1f** (a) front view, (b) side view.

In case of **1e**, the molecular framework consisting of the phenylindole moiety and the silylene bridge is planar, and not only the isopropyl groups on silicon but also a 4-trifluoromethylphenyl group on nitrogen are oriented perpendicular to the aromatic plane (Figure 22). Therefore, effective conjugation is not extended to the aryl group on nitrogen and hence absorption edge blue-shifted compared with that of **1a** (Figure 1).

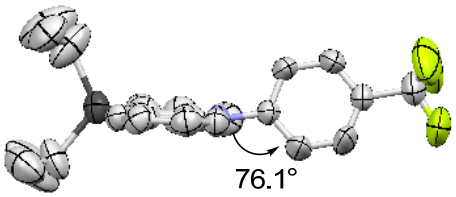


Figure 22. Molecular structure of **1e**.

The packing diagram of **1a**, and **2i** are shown in Figure 23. In case of **1a**, two adjacent molecules are well separated probably due to the steric repulsion between isopropyl groups. The distance between centroids of two adjacent molecules is 6.977 Å, long enough to suppress intermolecular electronic interactions, such as π– π stacking that lead to luminescence quenching. Conversely, in the packing diagram of **2i**, cyano and piperidyl groups align alternately and hence their dipole moments are cancelled. In addition, the distance between centroids of two adjacent molecules is short (5.707 Å). Such a packing form is called *H*-aggregation that results in quenching of fluorescence.[4]

In fact, quantum yield of **2i** (Φ_f = 0.21) in the microcrystal is significantly lower than those in cyclohexane (Φ_f = 0.73) and doped PMMA film (Φ_f = 0.86).

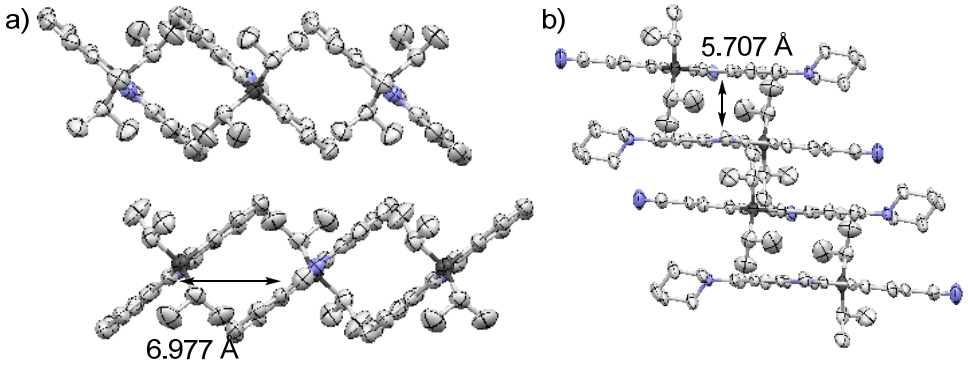


Figure 23. Packing diagram of **1a** (a), **2i** (b).

2-3. Thermal stability

Thermal stabilities of 3,2'-silicon-bridged 2-arylindoles **1**-**4** along with carbon analogue **5** were evaluated using TG/DTA and the results are summarized in Table 4. All compounds did not exhibit mesophase or glass transition. Introduction of an aryl group (**1b**, **2j**, and **2k**) or a fused benzene ring (**4**) was particularly effective to improve thermal stability. Increasing the size of a nitrogen substituent also enhanced thermal stability. In fact, *N*-arylated and *N*-tosylated products exhibited higher T_d than that of **1a** (208 °C). Conversely, *N*-H derivative **1f** exhibited a T_d = 170 °C and was found to slowly decompose even at ambient temperature over time. Decomposition temperature of **5** (T_d = 194 °C) is lower than that of **1a**, indicating that silicon-bridge is beneficial for the improvement of thermal stability in addition to fluorescence efficiency in the microcrystal as mentioned above.

Table 4. Thermal stability.

Compd	Mp (°C)[a]	T_d (°C)[b]	Compd	Mp (°C)[a]	T_d (°C)[b]
1a	128	208	**2g**	156	231
1b	206	>260	**2h**	218	237
1c	111	233	**2i**	207	>260
1d	156	240	**2j**	147	>260
1e	172	210	**2k**	162	>260
1f	97	253	**3a**	112	186
1g	110	170	**3b**	148	209
2a	148	211	**3c**	160	221
2b	163	234	**4a**	174	244
2c	146	209	**4b**	209	254
2d	144	206	**4c**	204	>260
2e	89	179	**5**	151	194
2f	141	234			

[a] Melting points determined using TG/DTA analysis. [b] Decomposition temperature (T_d) determined using TG/DTA analysis under an atmosphere of nitrogen and defined as the temperature at which 5% mass loss occurred.

2-4. Electrochemical properties

In order to obtain insights into the electrochemical properties of 3,2'-silicon-bridged 2-arylindoles, CV of **1-4** along with carbon analogue **5** were measured in CH_2Cl_2. Their oxidation potentials are summarized in Table 5. Only **2i** bearing a piperidyl group showed reversible oxidation wave and the other compounds exhibited irreversible oxidation waves. For all compounds reduction waves were structureless and hence reduction potential could not be detected. This fact means lifetime of the corresponding radical anion is extremely short.[1n,5] For **1a** and **1c**-**1g**, the oxidation peak potential (E_{ox}) gradually shifted to less positive potential in the order of **1f** (+1.22 V vs Ag/Ag^+) > **1e** (+0.91 V) > **1g** (+0.90 V) > **1d** (+0.83 V) > **1c** (+0.81 V) > **1a** (+0.74 V) in proportion to the electron-withdrawing nature of the substituent on nitrogen. In the case of **2** and **3** which have a substituted arene moiety, similar trend was observed. These results clearly suggest that the electrochemical properties can be tuned by tuning a substituent on 3,2'-silicon-bridged 2-arylindoles.

Table 5. Oxidation potential of **1-5**.[a]

Compd	E_{ox} (V)[b]	Compd	E_{ox} (V)[b]	Compd	E_{ox} (V)[b]
1a	0.74	**2c**	0.80	**3a**	0.80
1b	0.76	**2d**	0.84	**3b**	0.72
1c	0.81	**2e**	0.79	**3c**	0.87
1d	0.83	**2f**	0.89	**4a**	0.69
1e	0.91	**2g**	0.68	**4b**	0.79
1f	1.22	**2h**	1.07	**4c**	0.69
1g	0.90	**2i**	0.27	**5**	0.71
2a	0.59	**2j**	0.72		
2b	1.02	**2k**	0.66		

[a] Measured in CH_2Cl_2 at room temperature in the presence of nBu$_4$ClO$_4$ (0.1 M) as an electrode with scan rate of 100 mV/s using Pt as a working electrode and as a working electrode and Ag/AgCl as a reference electrode. [b] Versus Ag/Ag^+.

2-5. Molecular orbital calculation

Molecular orbital calculations of **1-5** were carried out by the DFT method at the B3LYP/6-31G*//B3LYP/6-31G* level using the Gaussian 03 package.[6] The results are summarized in Table 6.

Table 6. HOMO and LUMO energies of **1-5**.

Compd	HOMO (eV)[a]	LUMO (eV)[a]	ΔE (eV)[a]	ΔE (eV) (abs. edge)[b]
1a	–5.07	–0.99	4.08	3.25 (382 nm)
1d	–5.00	–0.86	4.14	3.29 (377 nm)
1f	–5.43	–1.50	3.93	3.32 (374 nm)
1g	–5.13	–0.99	4.14	3.52 (352 nm)
2a	–4.85	–0.75	4.11	3.16 (393 nm)
2b	–5.46	–1.79	3.67	3.01 (412 nm)
2c	–5.20	–1.20	3.99	3.20 (388 nm)
2d	–5.23	–1.18	4.05	3.12 (397 nm)
2f	–5.36	–1.38	3.97	3.12 (398 nm)
2i	–4.93	–1.65	3.28	2.66 (466 nm)
2j	–4.96	–1.29	3.67	2.95 (420 nm)
3c	–5.32	–1.19	4.13	3.23 (384 nm)
4a	–4.97	–1.39	3.58	2.90 (427 nm)
4c	–4.95	–1.39	3.56	2.86 (434 nm)
5	–4.95	–0.80	4.15	3.39 (366 nm)

[a] Calculated at the B3LYP/6-31G*//B3LYP/6-31G* level. [b] Estimated from absorption edge.

Compared with the corresponding carbon analogue (**5**), **1a** has a lower-lying HOMO by only 0.12 eV and a much lower-lying LUMO by 0.18 eV due probably to σ*–π* conjugation (Figure 24). Thus, the HOMO-LUMO energy gap in **1a** is reduced by 0.07 eV as compared with **5**. This is consistent with the bathochromic shift of the absorption edge shown in Table 6.

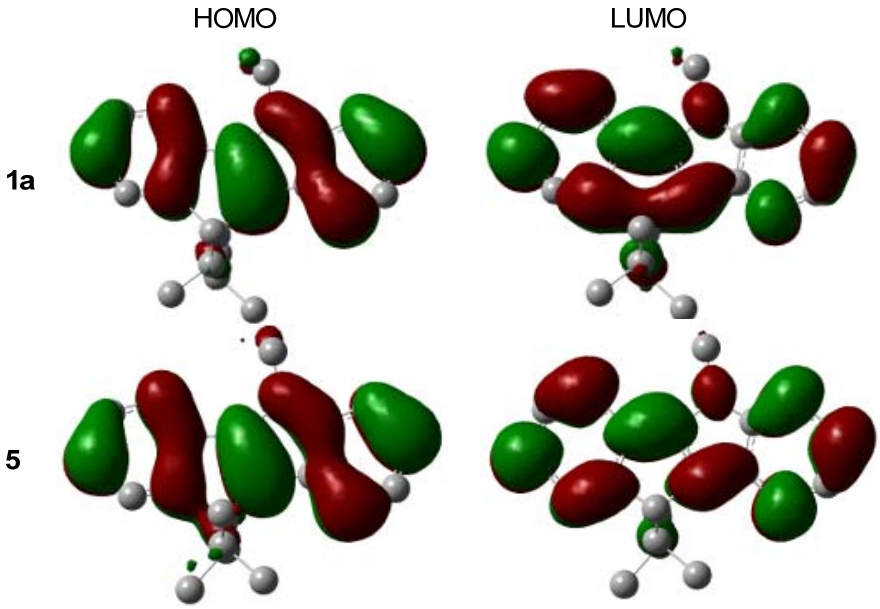


Figure 24. Molecular orbital drawings of HOMO and LUMO of **1a** and **5**.

Introduction of an electron-withdrawing group such as CN and/or Cl at the arene moiety and Ts on nitrogen resulted in lowering of HOMO, which is consistent with their oxidation peak potential. Substitution with Cl at the 6-position (**2d**) resulted in a delocalization of LUMO not only over the arene moiety but also to the chlorine atom (Figure 25), giving rise to a lower-lying LUMO level compared with that of **1a**. However, substitution at the 5-position (**3c**) did not extend LUMO to chlorine atom and .resulted in higher-lying LOMO as compared with **2d**. This is consistent with a bathochromic shift of the absorption edge shown in Table 6. Meanwhile, HOMO and LUMO of 6,4'-diphenyl compound **2j** were delocalized over the arene moiety and the phenyl substituents, resulting in narrow HOMO-LUMO gap compared with **1a**. These results clearly suggest that functionalization at 6- and/or 4'-position(s) is the best

approach to tune photophysical properties such as UV absorption and fluorescence of **1a**.

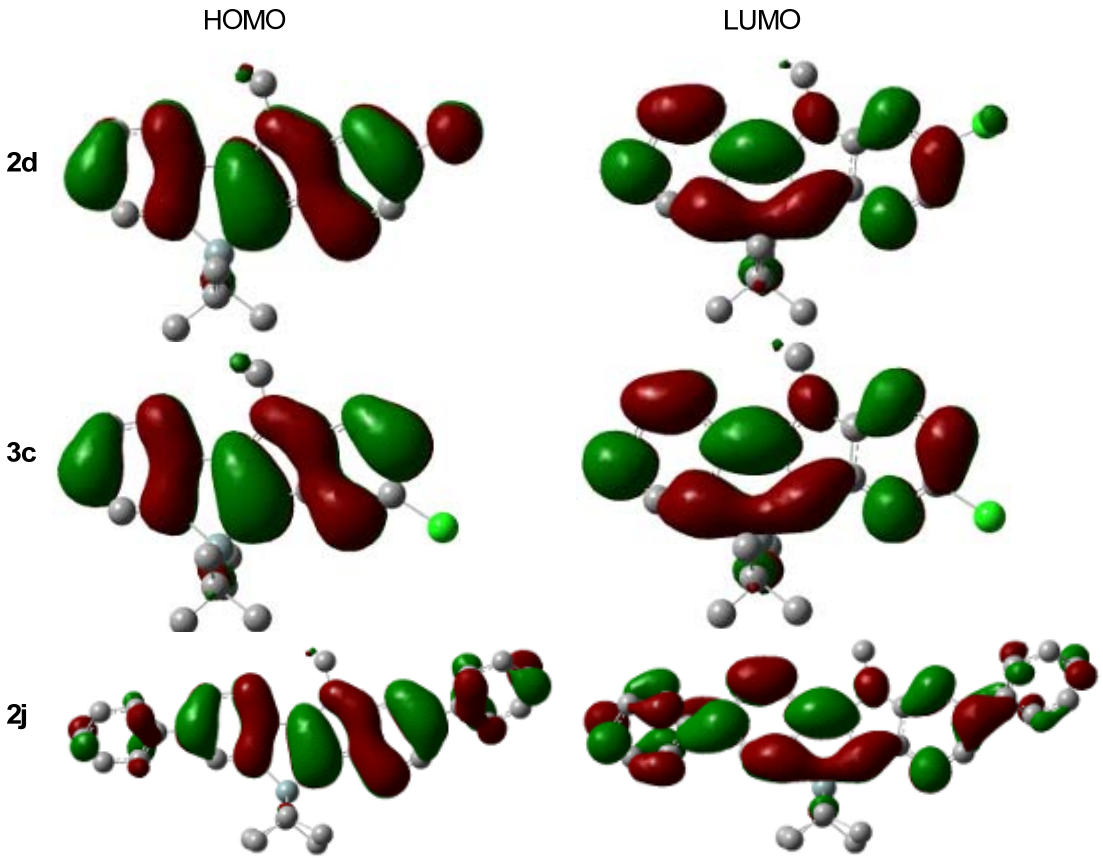


Figure 25. Molecular orbital drawings of HOMO and LUMO of **2d**, **2j** and **3c**.

Shapes of HOMO and LUMO in **4a** and **4c** are visualized in Figure 26. Although HOMO of **4c** delocalized over the arene moiety, LUMO of **4c** localized to the silole side rather than the pyrrole side. LUMO of **4a** also localized to the silole side. Accordingly, compared to pentacyclic compound **4a**, hexacyclic compound **4c** has a slightly higher-lying HOMO by only 0.02 eV with the same LUMO level, resulting in similar HOMO-LUMO gap, which is consistent with their UV absorption (Figure 20) and fluorescence spectra (Figure 21).

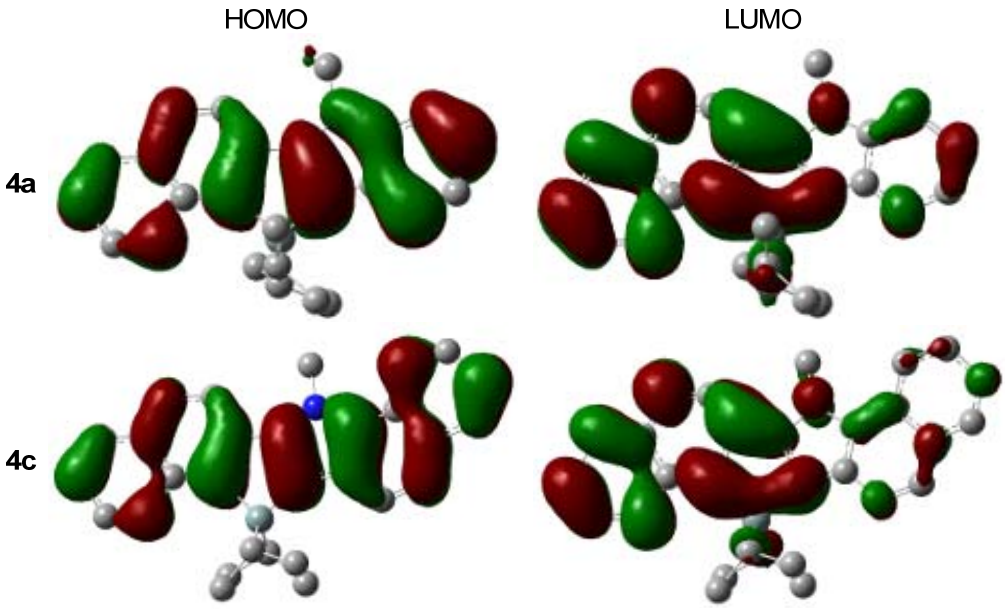


Figure 26. Molecular orbital drawings of HOMO and LUMO of **4a** and **4c**.

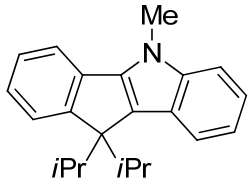
3. Conclusions

In summary, the author has demonstrated that 3,2'-silicon-bridged 2-arylindoles exhibit highly efficient fluorescence not only in solution, but also in the solid state such as microcrystal and in doped polymer film. In particular, introduction of various functional groups at the 6,4'-position(s) of 3,2'-silicon-bridged 2-phenylindoles induces bathochromic shift of absorption and fluorescence maxima while retaining high quantum yields. These results imply that 3,2'-silicon-bridged 2-arylindoles are superior materials as a new class of emissive conjugated modules.

Experimental

Preparation of 10,10-diisopropyl-5-methyl-*10H*-indeno[3,2-*b*]indole (5)

2-(2-Bromophenyl)-1-methylindole was prepared by the procedure reported in the reference 7. An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with 2-(2-bromophenyl)-1-methylindole (0.86 g, 3.0 mmol) and THF (10 mL). To the solution cooled to –78 °C was added butyllithium (1.59 M in hexane, 1.9 mL, 3.0 mmol) dropwise via syringe over 10 min. The solution was stirred at –78 °C for 1 h before addition of diisopropylketone (0.42 mL, 3 mmol). The resulting solution was warmed to room temperature and then stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The organic layer was separated and the aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/AcOEt 10:1) on silica gel to give 2,4-dimethyl-3-[2-(1-methylindol-2-yl)phenyl]pentan-3-ol (0.68 g, 71%) as a colorless solid. An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with the alcohol obtained above (64 mg, 0.2 mmol) and CH_2Cl_2 (5 mL). To the solution cooled to 0 °C was added titanium tetrachloride (26 μL, 0.24 mmol) dropwise via a syringe over 1 min. The resulting solution was warmed to room temperature and then stirred for 12 h before quenching with saturated aq. NH_4Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/AcOEt 10:1) on silica gel followed by GPC ($CHCl_3$) to give 10,10-diisopropyl-5-methyl-10*H*-indeno[3,2-b]indole (**5**) (14 mg, 22%) as a colorless solid.



Mp: 150.9–151.9 °C. TLC: R_f 0.28 (hexane/AcOEt 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77 (d, *J* = 6.8 Hz, 6H), 0.79 (d, *J* = 6.8 Hz, 6H), 2.69 (qq, *J* = 6.8, 6.8 Hz, 2H), 4.06 (s, 3H), 7.12 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.15–7.20 (m, 2H), 7.28 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 18.7, 31.3, 32.0, 59.7, 109.5, 117.4, 119.1, 120.3, 120.7, 124.2, 124.4, 124.5, 125.4, 126.2, 135.8, 142.1, 143.9, 154.0. IR (KBr): ν = 2960, 2949, 2887, 1602, 1532, 1460, 1359, 1300, 1211, 1157, 1020, 738, 696 cm^{-1}. MS *m/z*: 303 (51, M^+), 260 (57), 217 (4). Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30. Found: C, 86.80; H, 8.47.

UV-vis absorption and fluorescent measurement

The spectroscopic-grade cyclohexane for UV–vis absorption and fluorescence measurements were purchased from Kanto Chemical Co., Inc. and degassed with argon before use. Polymer films were prepared by spin-coating method with a MIKASA MS-A-100 spincoater. UV–vis absorption spectra were measured with a Shimadzu UV-2550 spectrometer. Fluorescence spectra and absolute quantum yields were recorded by a Hamamatsu Photonics C9920-02 Absolute PL Quantum Yield Measurement System. Fluorescent life times were measured with a HORIBA TemPro.

Preparation of dispersed PMMA film

In a tube glass, each sample was dissolved in a saturated benzene solution of poly(methyl methacrylate) (PMMA) with concentration of 0.1 mg/mL. The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated at 100 rpm for 20 sec followed by further spin-coat at 1000 rpm over a period of 100 sec. The deposited film was dried under reduced pressure at 50 °C for 1 h.

TG/DTA measurement

TG/DTA was performed on EXSTAR 6000 TG/DTA, Seiko Instruments Inc. The measurement was carried out under an atmosphere of nitrogen at a heating rate of 5 °C/min.

CV measurement

CV was performed on BAS ALS610c electrochemical analyzer. The CV cell consisted of a Pt disk electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The measurement was carried out under argon atmosphere using a CH_2Cl_2 solution of sample with a concentration of 1 mM and 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) as a supporting electrolyte at a scan rate of 100 mV/s.

Computation method

All calculations were conducted using the Gaussian 03 program. For initial geometries, X-ray structures were used as a reference. The geometries were optimized at the B3LYP/6-31G* level. Energy levels of molecular orbitals were calculated by the gauge-including atomic orbital (GIAO) method at the B3LYP/6-31G*//B3LYP/6-31G* level. Absolute energies (in a.u.) of calculated compound are listed in Table 7.

Table 7. Absolute energies of calculated compounds.

compd	Total Energy (a.u.)
1a	-1159.584033
1d	-1465.843599
1f	-1939.196388
1g	-1120.274047
2a	-1274.104089
2b	-1251.827396
2c	-1619.178851
2d	-1619.180658
2f	-2078.775787
2i	-1502.535893
2j	-1621.696819
3c	-1619.180609
4a	-1313.224636
4c	-1466.860022
5	-908.1637585

Data of X-ray crystallographic analysis

Crystallographic data for **1a**, **1e**, **1f**, and **2i** are listed in Table 8.

Table 8. Crystallographic data for **1a**, **1f**, and **2i**.

compound	**1a**	**1e**	**1f**	**2i**
Empirical formula	$C_{21}H_{25}NSi$	$C_{27}H_{26}F_3NSi$	$C_{27}H_{29}NO_2SSi$	$C_{27}H_{33}N_3Si$
Formula weight	319.51	449.58	459.66	427.65
Temperature (K)	300(2)	300(2)	300(2)	300(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	*P*1	$P2_12_12_1$	$P2_1/c$	*P*1
a (Å)	10.7935(9)	8.0586(13)	17.8271(14)	8.245(3)
b (Å)	11.3034(9)	14.782(2)	14.2864(11)	12.675(7)
c (Å)	16.2004(13)	20.240(3)	20.0246(16)	13.527(7)
α (°)	107.8020(10)	90	90	115.683(8)
β (°)	93.422(2)	90	96.7790(10)	90.067(10)
γ (°)	95.478(2)	90	90	102.600
Volume ($Å^3$)	1865.0(3)	2411.0(7)	5064.3(7)	1235.9(12)
Z	4	4	8	2
Density (calculated) (Mg/m^3)	1.138	1.239	1.206	1.149
Absorption coefficient (mm^{-1})	0.126	0.135	0.198	0.113
F(000)	688	944	1952	460
Reflection collected	10230	13193	26817	6354
Independent reflections	6814	4494	9424	4463
Goodness-of-fit on F^2	1.086	1.057	1.061	0.939
Data/restraints/parameters	6814/0/425	4494/0/293	9424/0/587	4463/0/285
Final R indices [$I>2\sigma(I)$]				
R_1	0.0685	0.0746	0.0684	0.0736
wR_2	0.1855	0.2021	0.1787	0.1811
R indices (all data)				
R_1	0.0940	0.0870	0.1135	0.1251
wR_2	0.1995	0.2140	0.1960	0.2036

Reference

(1) (a) Lai, W.-Y.; Xia, R.; He, Q.-Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. *Adv. Mater.* **2009**, *21*, 355. (b) Lai, M.-Y.; Chen, C.-H.; Huang, W.-S.; Lin, Jiann T.; Ke, T.-H.; Chen, L.-Y.; Tsai, M.-H.; Wu, C.-C. *Angew. Chem. Int. Ed.* **2008**, *47*, 581. (c) Kitamura, C.; Matsumoto, C.; Kawatsuki, N.; Yoneda, A.; Asada, K.; Kobayashi, T.; Naito, H. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 754. (d) Ishow, E. n.; Brosseau, A.; Clavier, G.; Nakatani, K.; Tauc, P.; Fiorini-Debuisschert, C. l.; Neveu, S.; Sandre, O.; Léaustic, A. *Chem. Mater.* **2008**, *20*, 6597. (e) Huang, J.; Qiao, X.; Xia, Y.; Zhu, X.; Ma, D.; Cao, Y.; Roncali, J. *Adv. Mater.* **2008**, *20*, 4172. (f) Chen, Z.; Bouffard, J.; Kooi, S. E.; Swager, T. M. *Macromolecules* **2008**, *41*, 6672. (g) Xie, Z.; Wang, H.; Li, F.; Xie, W.; Liu, L.; Yang, B.; Ye, L.; Ma, Y. *Cryst. Growth Des.* **2007**, *7*, 2512. (h) Wakamiya, A.; Mori, K.; Yamaguchi, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 4273. (i) Luo, J.; Zhou, Y.; Niu, Z.-Q.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 11314. (j) Li, Y.; Li, F.; Zhang, H.; Xie, Z.; Xie, W.; Xu, H.; Li, B.; Shen, F.; Ye, L.; Hanif, M.; Ma, D.; Ma, Y. *Chem. Commun.* **2007**, 231. (k) Zhao, C.-H.; Wakamiya, A.; Inukai, Y.; Yamaguchi, S. *J. Am. Chem. Soc.* **2006**, *128*, 15934. (l) Hayer, A.; de Halleux, V.; Kohler, A.; El-Garoughy, A.; Meijer, E. W.; Barbera, J.; Tant, J.; Levin, J.; Lehmann, M.; Gierschner, J.; Cornil, J.; Geerts, Y. H. *The Journal of Physical Chemistry B* **2006**, *110*, 7653. (m) Yu, G.; Yin, S.; Liu, Y.; Chen, J.; Xu, X.; Sun, X.; Ma, D.; Zhan, X.; Peng, Q.; Shuai, Z.; Tang, B.; Zhu, D.; Fang, W.; Luo, Y. *J. Am. Chem. Soc.* **2005**, *127*, 6335. (n) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071. (o) Kim, Y.; Bouffard, J.; Kooi, S. E.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 13726. (p) Chao, T.-C.; Lin, Y.-T.; Yang, C.-Y.; Hung, T. S.; Chou, H.-C.; Wu, C.-C.; Wong, K.-T. *Adv. Mater.* **2005**, *17*, 992. (q) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662. (r) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576. (s) Ariu, M.; Lidzey, D. G.; Sims, M.; Cadby, A. J.; Lane, P. A.; Bradley, D. D. C. *J. Phys. Condens. Matter* **2002**, *14*, 9975.

(2) Yamada, H.; Xu, C.; Fukazawa, A.; Wakamiya, A.; Yamaguchi, S. *Macromol. Chem. Phys.* **2009**, *210*, 904.

(3) (a) Fajarí, L.; Juliá, L.; Riera, J.; Molins, E.; Miravitlles, C. *J. Organomet. Chem.* **1990**, *381*, 321. (b) Ghosh, P.; Shabat, D.; Kumar, S.; Sinha, S. C.; Grynszpan, F.; Li, J.; Noodleman, L.; Keinan, E. *Nature* **1996**, *382*, 339. (c) Hoshi, T.; Nakamura, T.; Suzuki, T.; Ando, M.; Hagiwara, H. *Organometallics* **2000**, *19*, 4483. (d) Liu, Y.; Stringfellow, T. C.; Ballweg, D.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2001**, *124*, 49. (e) Yasuike, S.; Iida, T.; Okajima, S.; Yamaguchi, K.; Seki, H.; Kurita, J. *Tetrahedron* **2001**, *57*, 10047. (f) Ballweg, D.; Liu, Y.; Guzei, I. A.; West, R. *Silicon Chem.* **2002**, *1*, 55. (g) Russell, A. G.; Spencer, N. S.; Philp, D.; Kariuki, B. M.; Snaith, J. S. *Organometallics* **2003**, *22*, 5589.

(4) (a) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Brédas, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 1289. (b) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053.

(5) Moiseeva, A. A.; Rakhimov, R. D.; Beloglazkina, E. K.; Butin, K. P.; Nosov, K. S.; Lee, V. Y.; Egorov, M. P. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 2071.

(6) *Gaussian 03*, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.;

Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Laham, A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

(7) So, C. M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 8059.

List of Publications

I. Parts of the present Thesis have been or are to be published in the following journals.

Chapter 2

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

Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem. Int. Ed*. **2008**, *47*, 9760-9764.

Chapter 3

Synthesis, Structure, and Photophysical Properties of D-π-A type Silafluorenes

Shimizu, M.; Mochida, K.; Katoh, M.; Hiyama, T. manuscript in preparation.

Chapter 4

Palladium-Catalyzed Intramolecular Coupling of 2-[(2-Pyrrolyl)silyl]aryl Triflates through 1,2-Silicon Migration

Mochida, K.; Shimizu, M.; Hiyama, T. *J. Am. Chem. Soc*. **2009**, *131*, 8350–8351.

Chapter 5

Synthesis, Structure, and Photophysical Properties of 3,2'-Silicon-bridged 2-Arylindoles

Shimizu, M.; Mochida, K.; Hiyama, T. manuscript in preparation.

II. Following publications are not included in this Thesis.

1-Alkyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes: Unconventional Class of Mesomorphic Columnar Compounds

Shimizu, M.; Nata, M.; Mochida, K.; Hiyama, T.; Ujiie, S.; Yoshio, M.; Kato, T. *Angew. Chem. Int. Ed*. **2007**, *46*, 3055-3058.

A Novel Strategy for Two-photon Holographic Recording: Stepwise Two-photon Absorption of α-Quinquethiophene Followed by Energy Transfer to an Aryl Azide
Shimizu, M.; Schelper, M.; Mochida, K.; Hiyama, T.; Adachi, M.; Sasaki, Y.; Akiyama, S.; Maeda, S.; Kanbara, H.; Mori, Y.; Kurihara, T. *Adv*. *Mater*. **2007**, *19*, 1826-1829.

Solid State Structures and Photophysical Properties of (Trimethylsilyl) methyl-substituted Anthracenes and Pyrenes
Shmizu, M.; Tatsumi, H.; Mochida, K.; Hiyama, T. *Chem. Commun.* **2008**, 2134-2136.

Silicon-bridge Effects on Photophysical Properties of Silafluorenes
Shimizu, M.; Tatsumi, H.; Mochida, K.; Oda, K.; Hiyama, T. *Chem. Asian J.* **2008**, *3*, 1238-1247.

Synthesis, Crystal Structure, and Photophysical Properties of (1E,3E,5E)-1,3,4,6-Tetraarylhexa-1,3,5-trienes: A New Class of Fluorophores Exhibiting Aggregation-Induced Emission
Shimizu, M.; Tatsumi, H.; Mochida, K.; Shimono, K.; Hiyama, T. *Chem. Asian J.* **2009**, *4*, 1289-1297.

Acknowledgment

The study described in this Thesis has been carried out under the direction of Professor Tamejiro Hiyama at Kyoto University during the period of 5 years from April 2005 to March, 2010. The author sincerely thanks him for his constant support, guidance, and encouragement with warm enthusiasm during the course of this study.

The author is deeply indebted to Professor Masaki Shimizu at Kyoto University for his practical every day guidance, continuous advice, helpful discussions, and suggestions throughout this study.

The author wishes to express his gratitude to Professors Koichiro Oshima, Seijiro Matsubara, Hideki Yorimitsu, Yoshiaki Nakao, and Takuya Kurahashi for helpful discussions and suggestions.

The author owes to Mmes. Suzan Goto, Hanako Yorimitsu and Ms. Mona Shapiro for kind assistance, Mrs. Hiromi Yoshida and Dr. Keiko Kuwata for mass spectroscopy measurements, and Dr. Suguru Inoue in HORIBA Ltd. for fluorescence lifetime measurements discussed in Chapters 3 and 5. It is his great pleasure to express thanks to Messrs. Hironori Tatsumi and Masaki Katoh. He wishes to thank all members of the Hiyama group in the past 5 years for their warm friendship.

Finally, the author would like to express his sincere acknowledgment to his parents, Kosaku and Naoko, for their constant understanding, assistance and encouragement.

Kenji Mochida
Department of Material Chemistry
Graduate School of Engineering

Kyoto University