Catalytic Synthesis of Silicon-Bridged π-Conjugated Compounds Bearing a Six- or Seven-Membered Silacycle through 1,*n*-Palladium Migration and Intramolecular Alkyne Insertion

Tomohiro Tsuda

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Tomohiro Tsuda

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Abstract

Transition-metal-catalyzed reactions involving a 1,*n*-metal migration process are of great importance in modern organic chemistry for the construction of complex molecular skeletons from relatively simple precursors by functionalizing remote C–H bonds which are difficult to activate directly. In particular, 1,4-migration reactions of palladium and rhodium have been most widely explored and a variety of reactions have been established for easy access to complicated compounds. On the other hand, catalytic reactions involving a 1,5-metal migration have been significantly less investigated so far because the greater distance between the metal center and the C–H bond makes it more difficult than the corresponding 1,4-metal migration.

Silicon-bridged π-conjugated compounds have recently been received much attention as potential candidates for organic materials because these compounds often exhibit unique optical and electronic properties. Silicon-bridged biaryls such as dibenzosiloles bearing a five-membered silacycle have particularly been investigated toward the application as organic materials, and these compounds are usually synthesized by a conventional method through reactions of dilithiobiaryls with dichlorosilanes. This synthetic approach is highly reliable, but accessible molecular structures are limited and other silicon-bridged π-conjugated compounds bearing six-membered or larger silacycles are difficult to synthesize by following this strategy.

In this context, the author developed a novel and efficient synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines bearing a six-membered silacycle under simple palladium catalysis and a synthesis of new members of 5*H*-dibenzo[*b*,*f*]silepin derivatives bearing a seven-membered silacycle, both of which are challenging to prepare by conventional synthetic methods. These developments were successfully achieved by utilizing a 1,*n*-palladium migration/alkyne insertion strategy.

Chapter 1 provides an overview of the recent development on transition-metal-catalyzed reactions involving a 1,4- and 1,5-metal migration as well as transition-metal-catalyzed syntheses of silicon-bridged π-conjugated compounds bearing a five-, six- and seven-membered silacycle.

Chapter 2 describes an efficient synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines from easily accessible 2-((2-(arylethynyl)aryl)silyl)aryl triflates under simple palladium catalysis. A series of control experiments revealed that this reaction proceeded through a new mode of 1,4-palladium migration with concomitant alkene isomerization followed by an intramolecular C–H/C–H coupling. Investigations on the optical properties of obtained benzophenanthrosilines were conducted and it was found that the properties could be tuned by introduction of substituents.

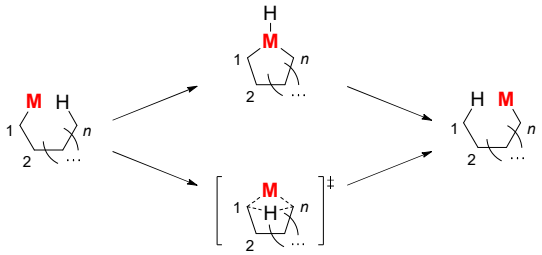
Chapter 3 describes a synthesis of new members of 5*H*-dibenzo[*b*,*f*]silepin derivatives from 2-(arylsilyl)-3-(alkynyl)aryl triflates by using a palladium/binap catalyst. The mechanistic investigation supported a catalytic cycle involving a 1,5-palladium migration and an unusual *anti*-carbopalladation of alkyne. The resulting dibenzosilepins exhibited tunable optical and electronic properties, demonstrating the power and importance of developing new synthetic methods utilizing 1,*n*-metal migration processes.

Contents

Chapter 1

General Introduction

1.1 Transition-metal catalysis involving 1,*n*-metal migration



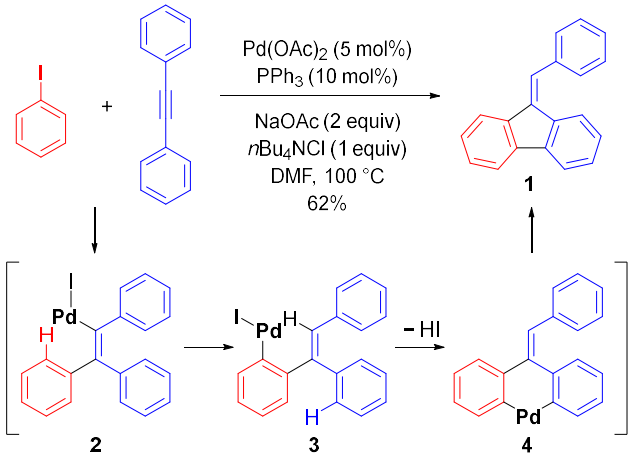
Scheme 1. Schematic drawing of 1,*n*-metal migration

Carbon–carbon bond-forming reactions catalyzed by transition-metal complexes are extremely useful and important methods in modern organic chemistry. Among them, transition-metal-catalyzed reactions involving a 1,*n*-metal migration process represent powerful ways to synthesize complicated molecules from relatively simple precursors through functionalization of inert C–H bonds at a new position, where it may not be easy or straightforward to form a carbon–metal bond (Scheme 1).[1] Since a 1,4-palladium migration reaction by Larock[2] and a 1,4-rhodium migration reaction by Miura[3a] were reported as pioneering works in 2000, a large number of reactions involving a 1,4-metal migration have been found. In particular, palladium and rhodium[3a–3m] have been most intensively explored as catalysts that undergo 1,4-metal migrations, and recently, iron,[4] cobalt,[5] iridium,[6] chromium,[7] nickel,[8] and platinum[9] complexes have also demonstrated migration behaviors in their catalytic reactions. In addition to 1,4-metal migrations, 1,5-metal migrations[3n–3r, 4c] have been increasingly developed in the last decade. In this section, some pioneering works and recent developments on 1,4- and 1,5-palladium

migration reactions are described. In addition, as a related approach, some palladium-catalyzed chain-walking processes are briefly summarized at the end of this section.

1.1.1 Reactions involving a 1,4-palladium migration

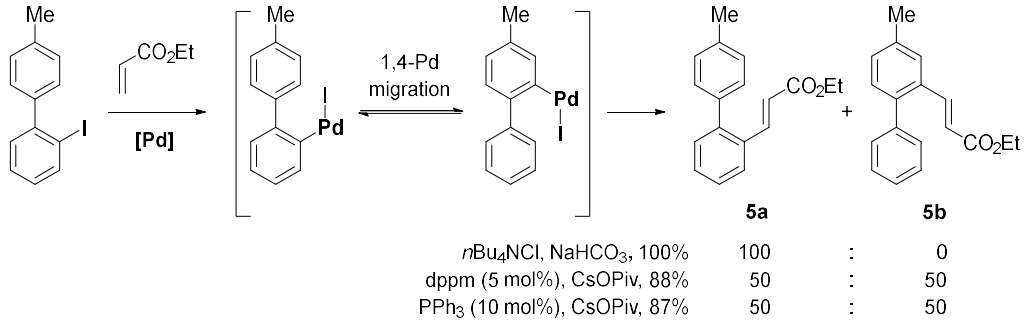
Among these 1,*n*-metal migration processes, 1,4-palladium migration has been most widely investigated in a number of catalytic reactions. In 2000, Tian and Larock reported a synthesis of 9-alkylidene-9*H*-fluorenes **1** under $Pd(OAc)_2/PPh_3$ catalysis (Scheme 2).[2] The reaction was proposed to proceed through a 1,4-migration of palladium of alkenylpalladium species **2** to form an arylpalladium species **3**. Subsequent HI elimination gave diarylpalladium **4**, which underwent reductive elimination to afford the fluorene **1** along with palladium(0) species.



Scheme 2. Palladium-catalyzed synthesis of 9*H*-fluorene **1** from iodobenzene and diphenylacetylene

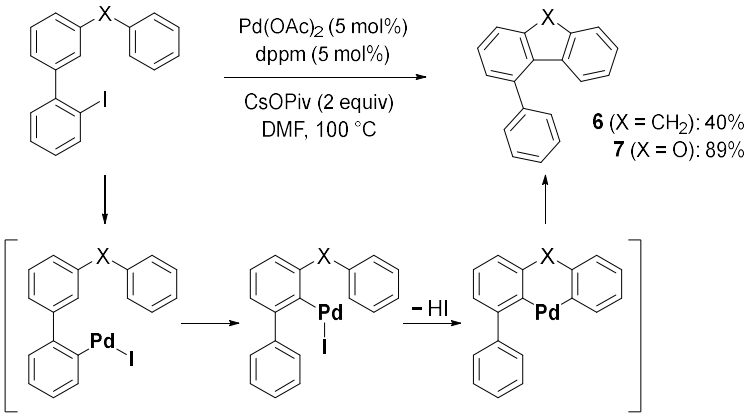
In 2002, Campo and Larock reported a palladium-catalyzed Mizoroki-Heck reaction between *ortho*-iodobiaryls and ethyl acrylate involving a 1,4-palladium migration and demonstrated that the position of palladium switched between two aryl

groups reversibly in the reaction (Scheme 3).[10] This selectivity can be tuned by modifying the reaction conditions. Indeed, product **5a** was obtained quantitatively under the conventional reaction conditions,[11] whereas a 1:1 mixture of **5a** and **5b** was afforded in the presence of PPh_3 or dppm as a ligand.

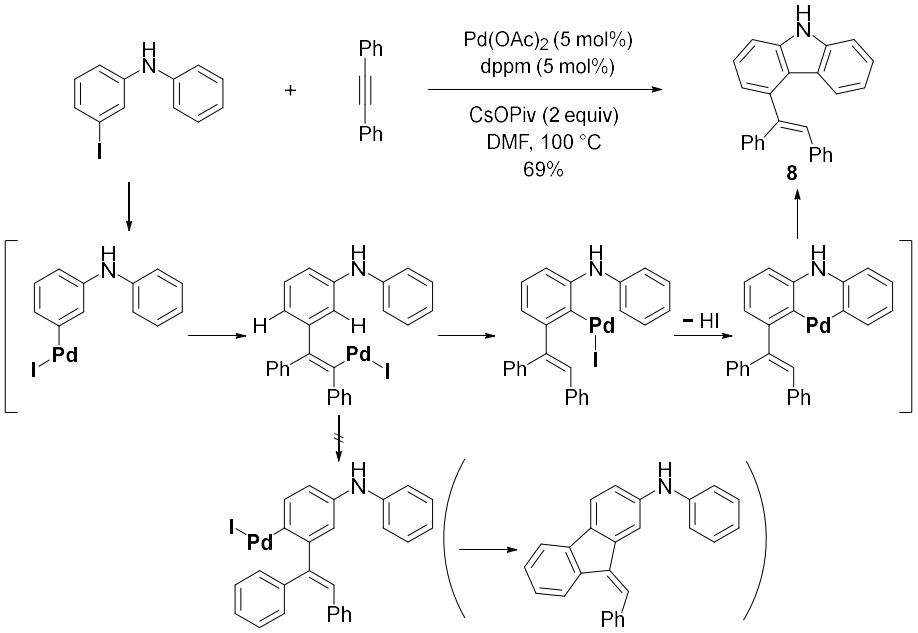


Scheme 3. Switchable regioselectivity in the 1,4-palladium migration

Larock and coworkers successfully utilized this 1,4-palladium migration for the synthesis of polycyclic compounds **6**–**8** (Schemes 4 and 5).[12] In the reaction shown in Scheme 5, palladium can migrate to either of two different *ortho* positions of the arene to generate either a carbazole or a fluorene, but the carbazole product is exclusively generated presumably due to coordination of nitrogen to palladium.

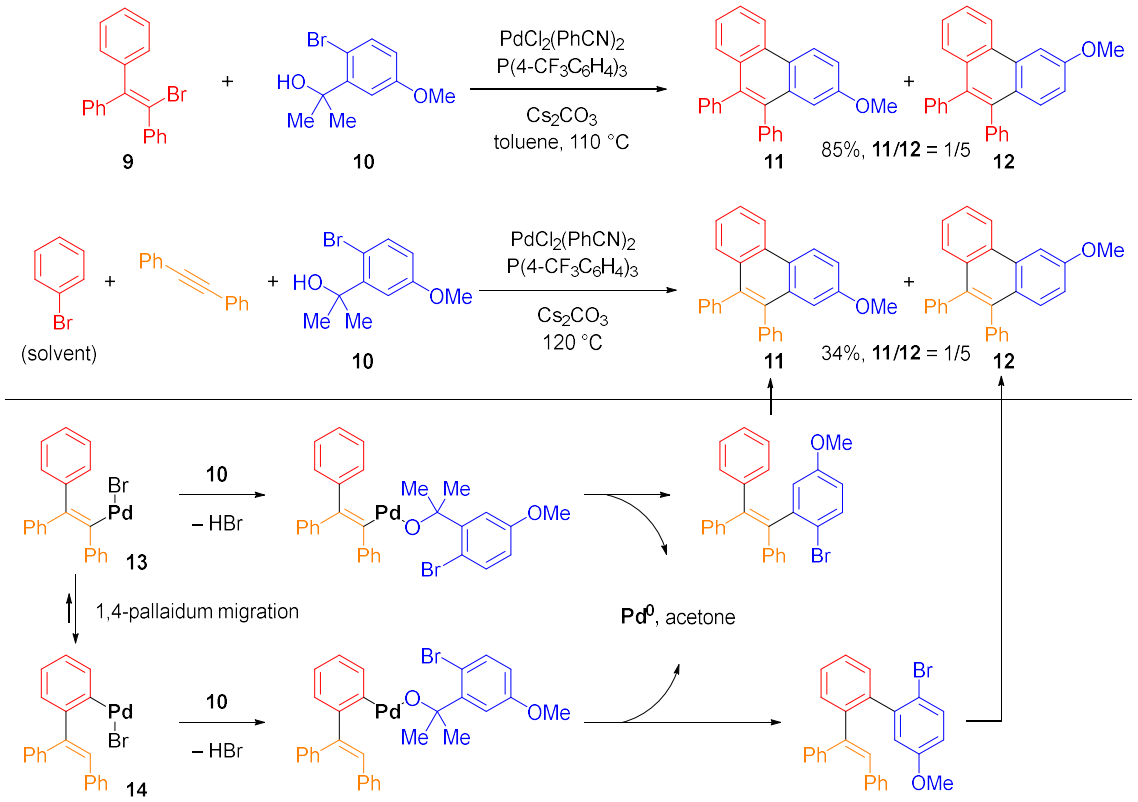


Scheme 4. Palladium-catalyzed synthesis of fluorene **6** and dibenzofuran **7**



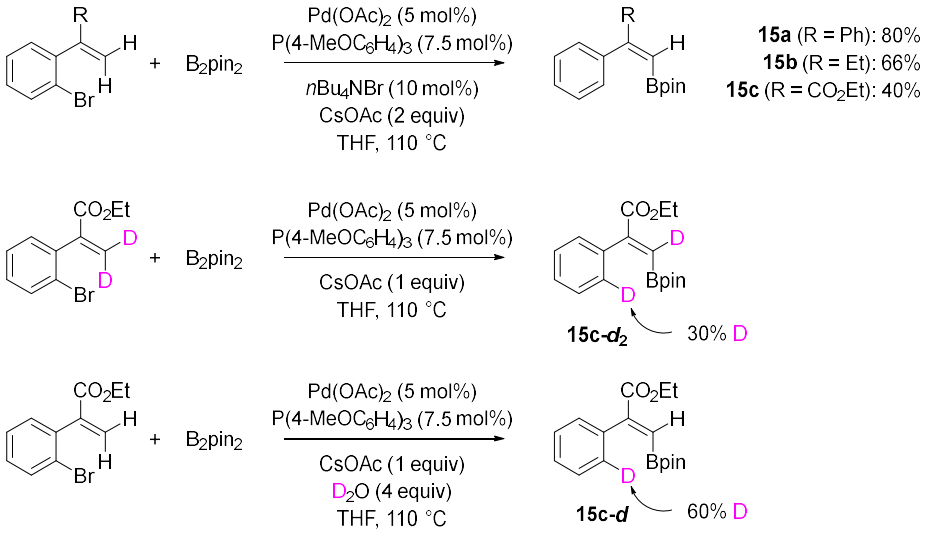
Scheme 5. Palladium-catalyzed synthesis of carbazole **8** through intermolecular alkyne insertion

Recently, Iwasaki and Nishihara developed palladium-catalyzed benzannulation of (*Z*)-β-halostyrenes with *o*-bromobenzyl alcohols as well as three-component coupling of alkynes, aryl bromides, and *o*-bromobenzyl alcohols for the novel synthesis of phenanthrenes (Scheme 6).[13] The reaction with β-bromostyrene **9** and benzyl alcohol **10** gave a mixture of **11** and **12** with a ratio of 1:5, and the use of bromobenzene and diphenylacetylene in place of **9** also gave the same mixture of **11** and **12** with the same ratio in a diminished yield. These results were explained by the isomerization of alkenylpalladium **13** to arylpalladium **14** through a 1,4-palladium migration.



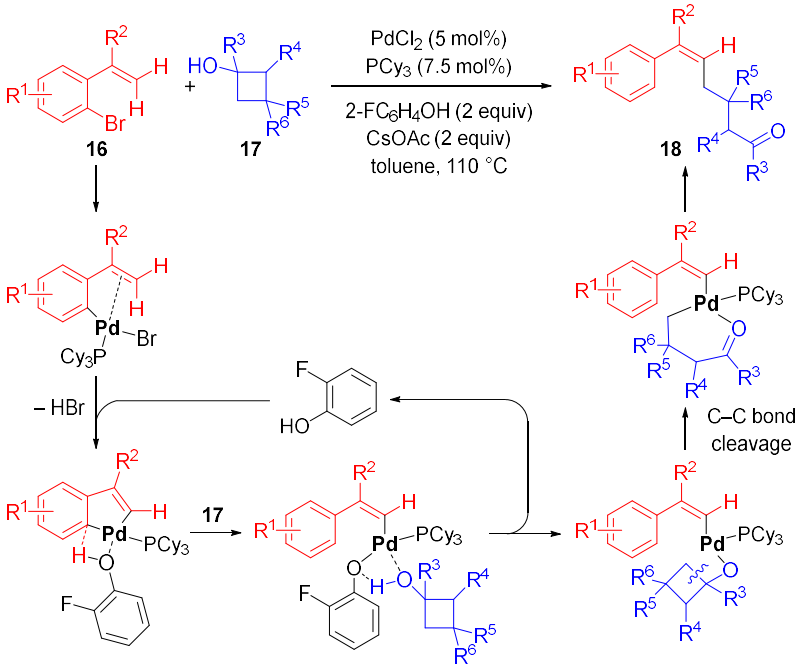
Scheme 6. Palladium-catalyzed synthesis of phenanthrenes through 1,4-palladium migration

As shown in Scheme 6, selective functionalization of vinylic position is challenging because the vinylic C–H bond has relatively weaker acidity than aryl C–H bond and palladium tends to migrate to a more acidic aryl position.[14] To overcome this shortcomings, alternative coupling reagents were investigated. In 2016, Hu and Feng achieved a selective borylation of vinylic C–H bond under Miyaura borylation reaction conditions and the selectivity of vinyl/aryl borylation was higher than 20:1 (Scheme 7).[15] In deuterium labeling experiments, H/D scrambling was observed at the *ortho*-position of phenyl ring of **15c**, indicating that the concerted metalation/deprotonation mechanism might be involved in this 1,4-migration process.



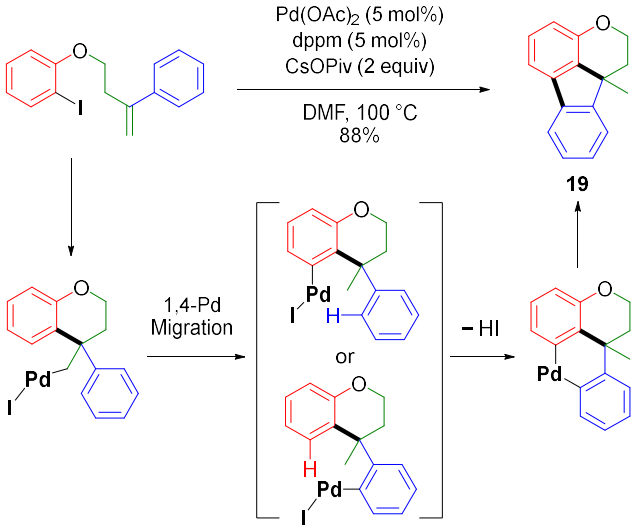
Scheme 7. Palladium-catalyzed borylation of vinylic C–H bond through aryl-to-vinyl 1,4-palladium migration

Zhou and Yu utilized this strategy to develop a palladium-catalyzed C–H alkylation of *o*-bromostyrenes **16** with cyclobutanols **17** *via* an aryl-to-vinyl 1,4-palladium migration in combination with a ring-opening C–C bond cleavage process (Scheme 8).[16] In this transformation, reactions without phenols gave only the direct cross-coupling product, whereas the reaction with phenols gave **18** as the major product, In the proposed catalytic cycle based on the mechanistic study and DFT calculations, 2-fluorophenol plays a role of a proton career.



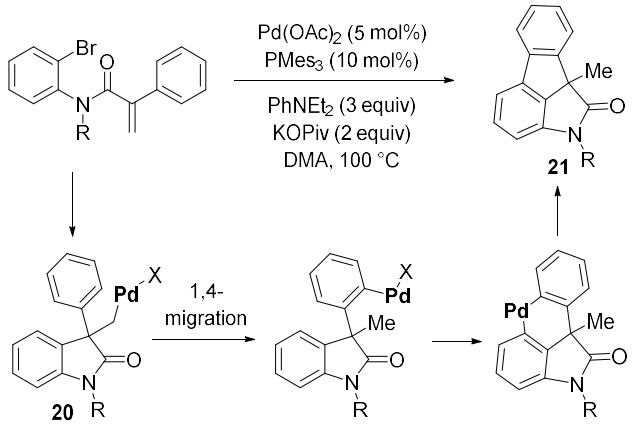
Scheme 8. Palladium-catalyzed coupling reaction *via* an aryl-to-vinyl 1,4-palladium migration/ring-opening process

In addition to C(sp^2)-to-C(sp^2) migrations of palladium, reactions involving a C(sp^3)-to-C(sp^2) migration have also been developed. Huang and Larock described a novel alkyl-to-aryl migration methodology for the synthesis of polycyclic compounds (Scheme 9).[17] The alkylpalladium species is generated by Heck-type insertion of an alkene and the palladium migrates to one of the two aryl groups followed by C–H arylation to afford **19**.



Scheme 9. Alkyl-to-aryl 1,4-palladium migration

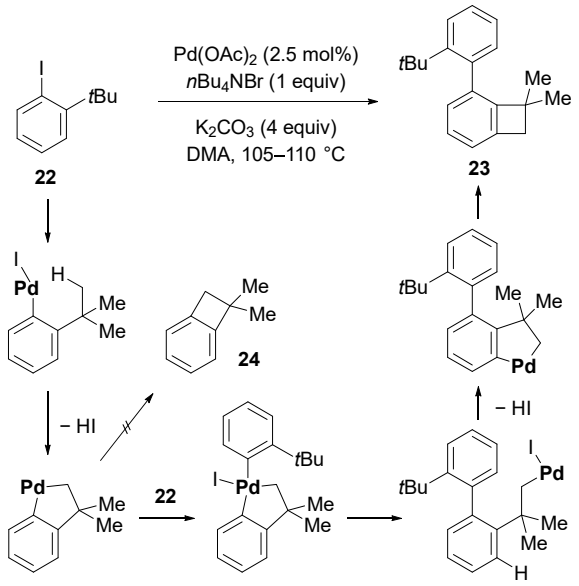
This method to generate an alkylpalladium species is often used for the reactions involving an alkyl-to-aryl 1,4-palladium migration. For example, a palladium-catalyzed synthesis of [3,4]-fused oxindoles reported by Bunescu and Zhu proceeds through an intramolecular Heck-type insertion to give alkylpalladium species **20**, which undergoes a 1,4-palladium migration followed by C–H arylation to afford **21** (Scheme 10).[18]



Scheme 10. Palladium-catalyzed synthesis of [3,4]-fused oxindoles

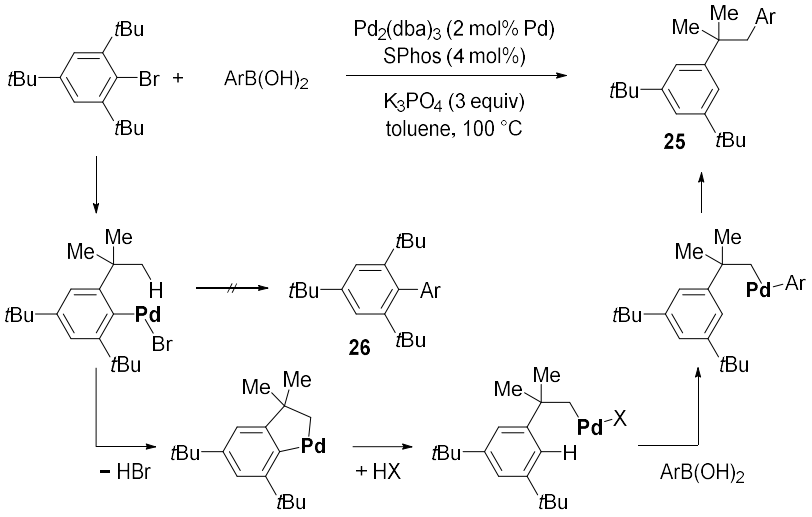
Reactions involving an aryl-to-alkyl palladium migration have also been reported,

although they are relatively limited to specific reaction conditions. Dyker described a new coupling reaction of 1-*tert*-butyl-2-iodobenzene (**22**). The reaction is proposed to proceed by oxidative addition of **22** to palladium center and subsequent C–H activation of a methyl group to form a palladacycle, which further undergoes oxidative addition of another **22** to afford palladium(IV) species. Subsequent reductive elimination of a biaryl moiety and HI elimination would lead to palladacycle intermediate. Finally, the reductive elimination leads to product **23**. The formation of **24** was not observed in this reaction (Scheme 11).[19]



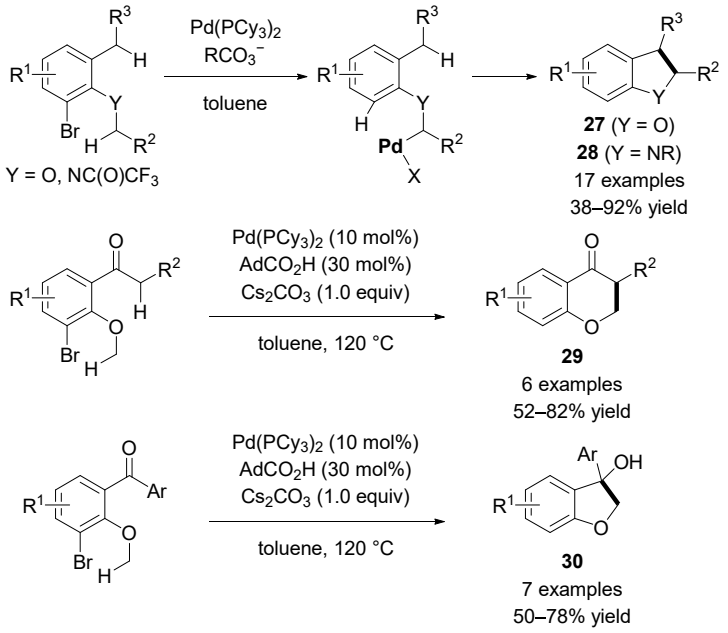
Scheme 11. Palladium-catalyzed reaction involving aryl-to-alkyl 1,4-migration

Barder and Buchwald reported a similar observation in their studies on the synthesis of sterically hindered biaryls by the Suzuki-Miyaura coupling reaction, where reactions between 2,4,6-tri-*tert*-butylbromobenzene and arylboronic acids gave α,α-dimethyl-β-arylhydrostyrenes **25** instead of expected biaryls **26** (Scheme 12).[20] The sterically congested environment may be the driving force of the migration of palladium species.



Scheme 12. Palladium-catalyzed cross-coupling reaction through an aryl-to-alkyl 1,4-palladium migration

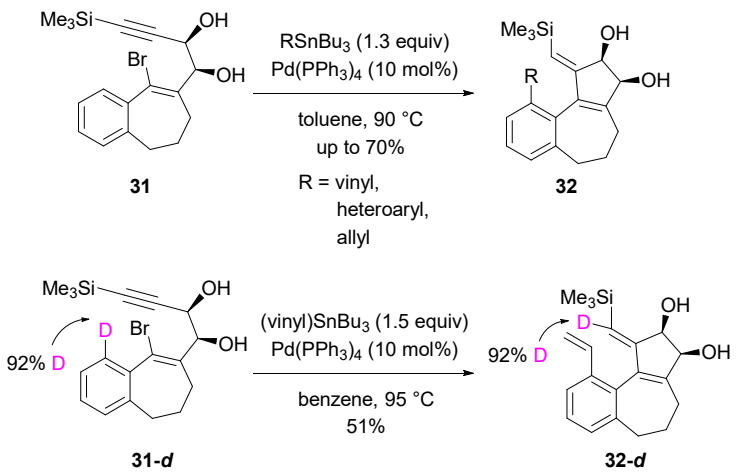
Recently, Rocaboy and Baudoin developed a redox-neutral coupling reaction between two C(sp^3)–H bonds by utilizing an aryl-to-alkyl 1,4-palladium migration. Various 2,3-dihydrobenzofurans **27** and indolines **28** could be synthesized from 1,2,3-trisubstituted aryl bromides, as well as chroman-4-ones **29** from ketones. In the absence of an enolizable position, an organopalladium intermediate arising from the 1,4-migration could attack the ketone to give tertiary alcohols **30**. However, this reaction is limited to C–H bonds activated by the adjacent oxygen or nitrogen atom on one side and benzylic C–H bonds or the ones adjacent to a carbonyl group on the other side (Scheme 13).[21]



Scheme 13. 1,4-Palladium migration-assisted C(sp^3)–H/C(sp^3)–H coupling

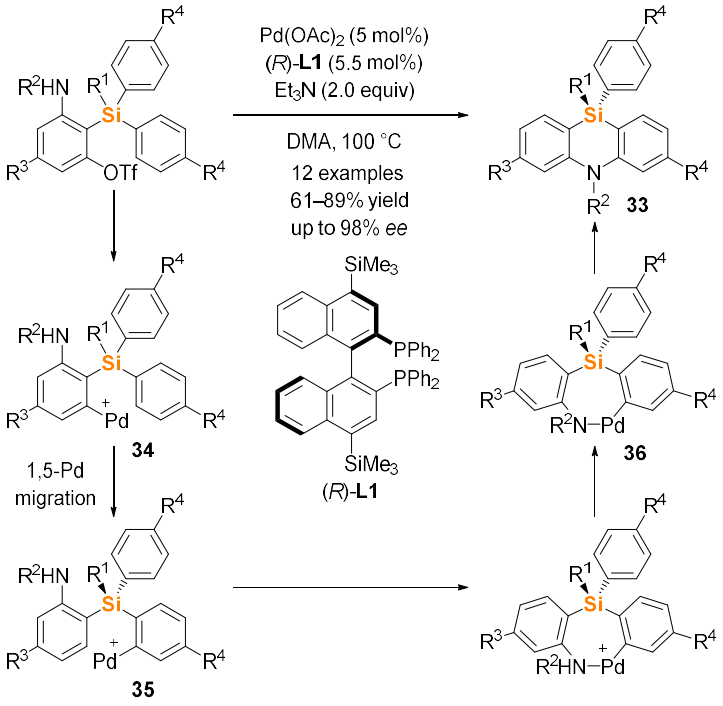
1.1.2 Reactions involving a 1,5-palladium migration

Compared to 1,4-palladium migrations, reactions involving a 1,5-palladium migration have been significantly less developed probably because the greater distance between the metal center and the C–H bond makes a 1,5-migration process more difficult than a 1,4-migration. Actually, only three catalytic reactions through a 1,5-palladium migration have been reported so far.[22] Bour and Suffert described a new cyclization reaction through intramolecular alkyne insertion and subsequent Stille coupling reaction of a benzosuberene derivative **31** (Scheme 14)[22a, 22b] Reactions of **31** with vinyl, heteroaryl and allylstannanes in the presence of palladium(0) catalyst gave corresponding products **32**, which were generated through a 1,5-palladium migration from a vinylic carbon to an aryl carbon. Deuterium labeling experiments with **31**-*d* supported that the location swap between palladium and aryl D atom occurred in the 1,5-palladium migration step.



Scheme 14. Stille coupling reaction through a 1,5-palladium migration

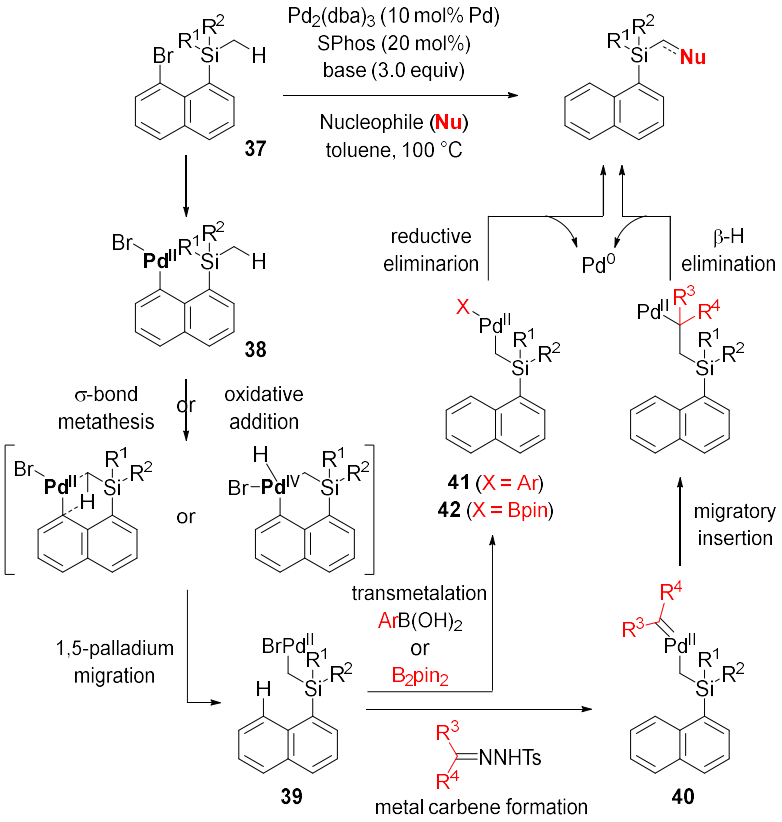
Our group developed a palladium-catalyzed asymmetric synthesis of silicon-stereogenic 5,10-dihydrophenazasilines **33** involving a 1,5-palladium migration (Scheme 15).[22c, 22d] A series of mechanistic investigation revealed that the 1,5-palladium migration is the enantio-determining step in this reaction. The catalytic cycle was proposed as shown in Scheme 15. Thus, arylpalladium species **34** was generated by oxidative addition of an aryl triflate to palladium(0) species, which undergoes a 1,5-migration to one of the two aryl groups to form **35**. Intramolecular coordination of the amino group to the palladium center and Et_3N-assisted deprotonation take place to give palladacycle **36**, and reductive elimination occurs to afford product **33**.



Scheme 15. Palladium-catalyzed asymmetric synthesis of 5,10-dihydrophenazasilines

More recently, Zhao established a C(sp^3)–H functionalization of methyl(1-naphthyl)silanes **37** with nucleophiles such as carbene precursors, aryl boronic acids and bis(pinacolato)diboron *via* an aryl-to-alkyl 1,5-palladium migration (Scheme 16).[22e] The reaction was proposed to begin with oxidative addition of a naphthyl bromide to palladium(0) species to form naphthylpalladium(II) intermediate **38**. This then undergoes a 1,5-palladium migration to give alkylpalladium species **39** through either σ-bond metathesis between the naphthyl C(sp^2)–Pd bond and the silylmethyl C(sp^3)–H bond or sequential oxidative addition of silylmethyl C(sp^3)–H bond to palladium(II) and reductive elimination to form naphthyl C(sp^2)–H *via* palladium(IV) species. In the presence of an *N*-tosylhydrazone, **39** reacts with it to give Pd^{II}–carbene complex **40**. The following migratory insertion and β-H elimination give the coupling product. The use of an arylboronic acid or bis(pinacolato)diboron in place of an *N*-tosylhydrazone leads to transmetalation with **39** to form either arylpalladium **41** or borylpalladium **42** and the

final reductive elimination affords the corresponding products with a release of palladium(0).

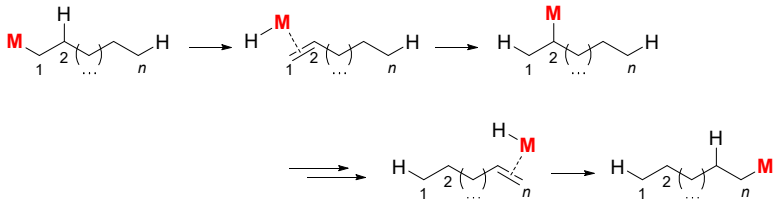


Scheme 16. Palladium-catalyzed C(sp^3)–H functionalization of a methyl group on a silicon atom

1.1.3 Reactions involving a palladium-catalyzed chain-walking process

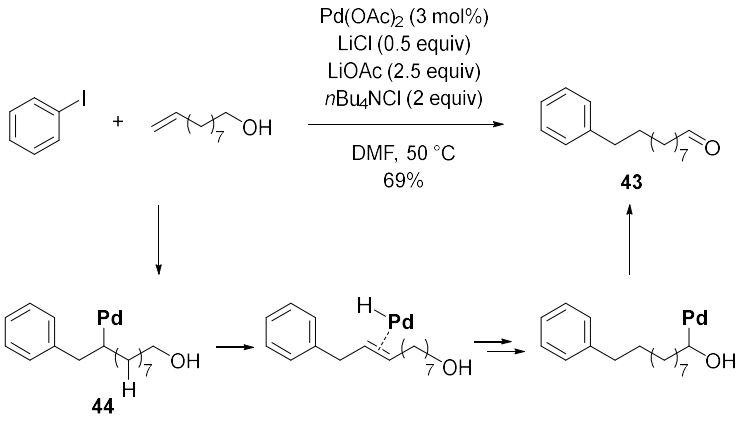
Another valuable method for related remote C–H functionalization is the transition-metal-catalyzed chain-walking process.[23] The mechanism of chain-walking is explained as a sequence of β-hydride elimination and reinsertion in the opposite direction as shown in Scheme 17, and thus, this method is highly effective for the functionalization at a distal position on the alkyl chain. Various kinds of transition catalysts such as titanium,[24] zirconium,[25] iron,[26] ruthenium,[27] cobalt,[28] rhodium,[29] iridium,[30] nickel[31] and palladium[32–35] have been demonstrated to have chain-walking activity. In particular,

palladium-based catalysts are frequently employed in this area of research because of the ready availability of easy-to-handle (pre)catalysts, mild reaction conditions and high functional group tolerance.



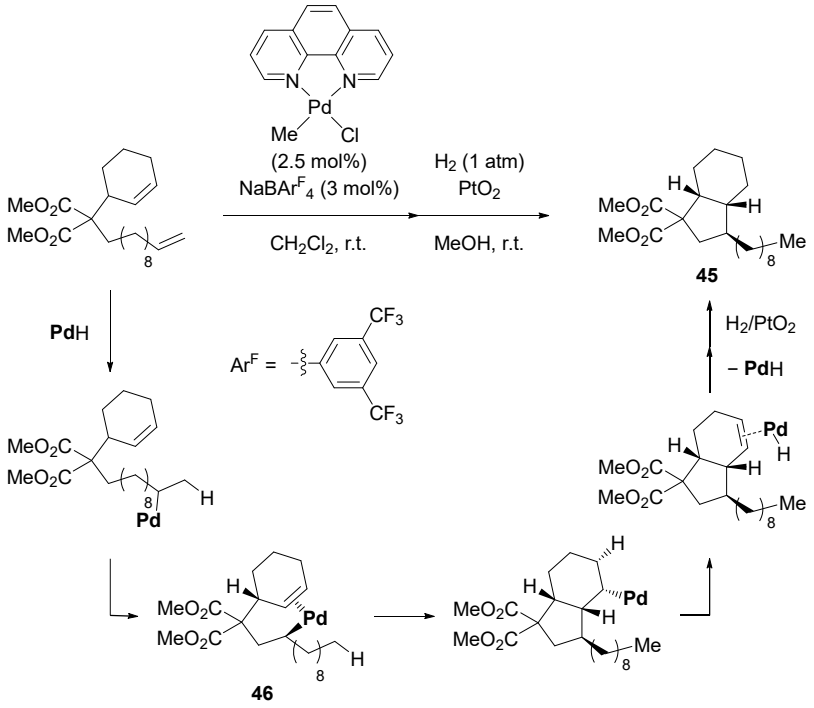
Scheme 17. Schematic drawing of transition-metal-catalyzed remote C–H functionalization through a chain-walking process (1,2-H shift)

This chain-walking process has been utilized in polymer synthesis,[32] as well as in small molecule synthesis by remote functionalization as described below. In 1989, Larock reported the remote functionalization of ω-alkenols by utilizing palladium-catalyzed Heck-type reaction combined with chain-walking (Scheme 18).[33] In this reaction, a phenylpalladium species generated from iodobenzene and the palladium catalyst reacts with alkene moiety of the ω-alkenol to give alkylpalladium **44**, which undergoes chain-walking, followed by elimination of palladium hydride to give corresponding carbonyl compound **43**.



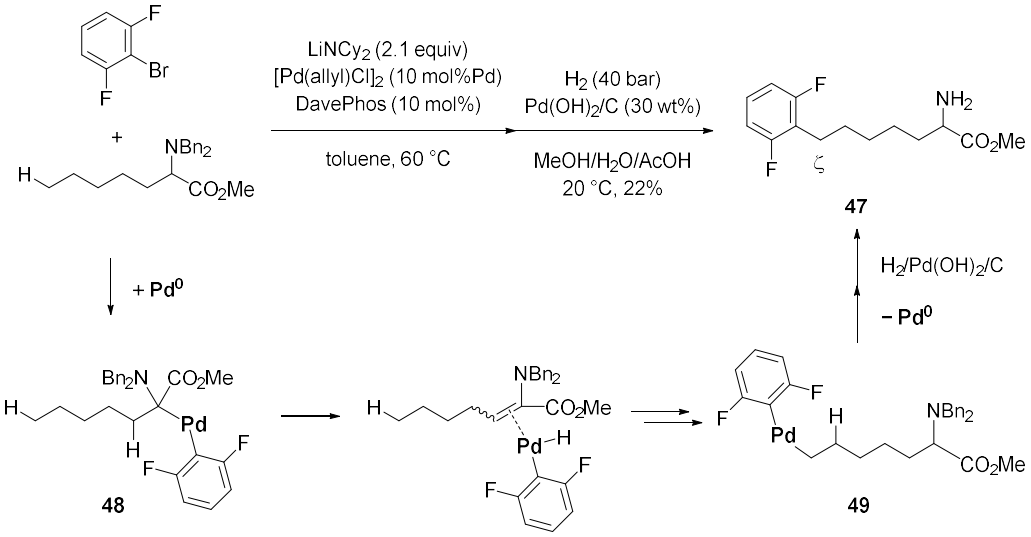
Scheme 18. Palladium-catalyzed migratory insertion reaction combined with chain-walking

When an alkene is placed at a suitable position in the substrate, cyclization through intramolecular migratory insertion can be utilized as shown in Scheme 19.[34] Kochi and Kakiuchi employed this strategy for the construction of a C–C bond and successfully achieved a sequential alkene isomerization/cyclization reaction. Hydropalladation to a terminal alkenyl group triggers the reaction and the subsequent chain-walking leads to alkene-coordinated alkylpalladium **46**. Insertion of the alkene and subsequent β-hydride elimination, followed by hydrogenolysis, gives product **45**.



Scheme 19. Palladium-catalyzed tandem isomerization/cyclization reaction

Baudoin demonstrated that a palladium(II) species generated by the reaction of an arylpalladium(II) with and ester enolate can undergo chain-walking prior to reductive elimination as shown in Scheme 20.[35] Palladium enolate **48** undergoes chain-walking to give primary alkylpalladium **49**, and reductive elimination affords a ζ-arylated product. Benzyl groups on nitrogen could be removed by hydrogenolysis to give ζ-arylated amino ester **47**.



Scheme 20. Palladium-catalyzed long-range arylation of primary C–H bonds

1.2 Silicon-bridged π-conjugated compounds

Silicon-bridged π-conjugated compounds have been intensively investigated in materials science as potentially useful functional organic molecules because these compounds often exhibit unique optical and/or electronic properties derived from the interaction between exocyclic σ*(C–Si) orbitals and a π* orbital fixed by a bridging silylene group. Actually, silicon-bridged bi(hetero)aryls bearing a 5-membered silacycle such as 5*H*-dibenzo[*b*,*d*]siloles and 4*H*-dithieno[3,2-*b*:2',3'-*d*]siloles constitute a useful class of compounds and have been widely explored for the application in organic electronics such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic cells (OPVs).[36]

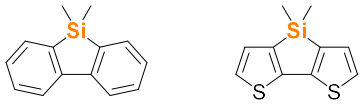
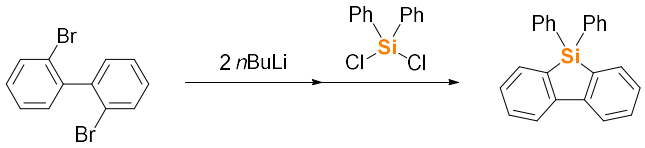


Figure 1. Molecular structures of 5*H*-dibenzo[*b*,*d*]silole (left) and 4*H*-dithieno[3,2-*b*:2',3'-*d*]silole (right) as representative silicon-bridged biaryls

The first synthesis of 5*H*-dibenzo[*b*,*d*]silole was reported by Gilman and Gorsich in 1955 by a reaction between 2,2'-dilithiobiphenyl and diphenyldichlorosilane (Scheme 21).[37] This reaction is highly reliable and a number of silicon-bridged biaryls have been synthesized by following similar procedures.[38, 39] On the other hand, this method is difficult to apply to reactions with substrates bearing functional groups sensitive to strong basic reagents. In addition, biaryl compounds possessing halogen atoms at the *o*-positions must be prepared in advance, and thus, this method cannot be employed directly for syntheses of six-membered or larger size of silacyclic compounds because the corresponding dihalogenated π-conjugated compounds are often difficult to synthesize.

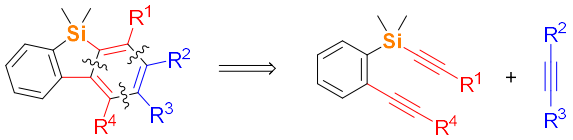
In order to overcome these drawbacks, alternative synthetic methods have been devised by employing transition-metal-catalyzed reactions. In this section, transition-metal-catalyzed synthesis of silicon-bridged π-conjugated compounds established in the past two decades are reviewed. Additionally, synthesis of silicon-bridged π-conjugated compounds bearing six- or seven-membered silacycles are also described.



Scheme 21. Conventional synthetic method of silicon-bridged biaryls

1.2.1 Transition-metal-catalyzed synthesis of silicon-bridged π-conjugated compounds bearing a silole unit

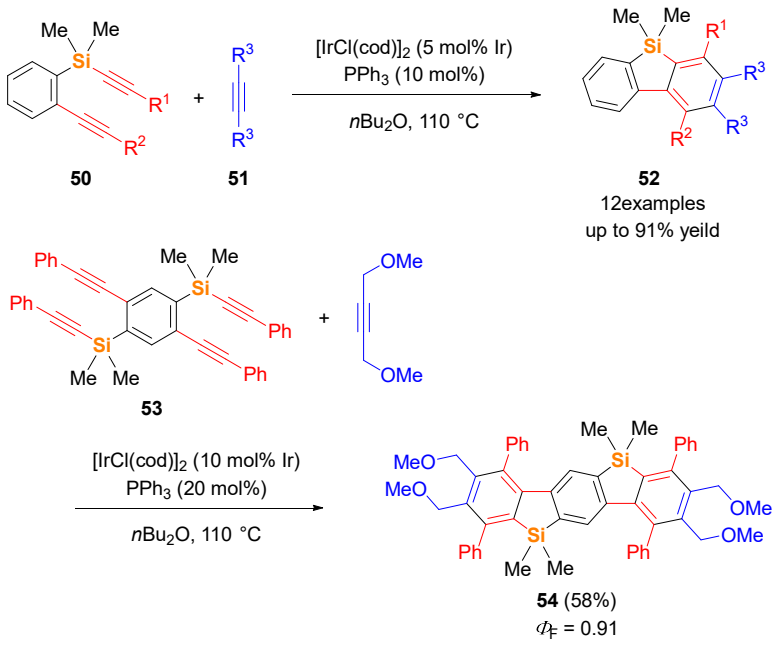
1.2.1.1 Synthesis of dibenzosiloles by [2+2+2] cycloaddition reaction



Scheme 22. Formation of dibenzosiloles *via* [2+2+2] cycloaddition reaction.

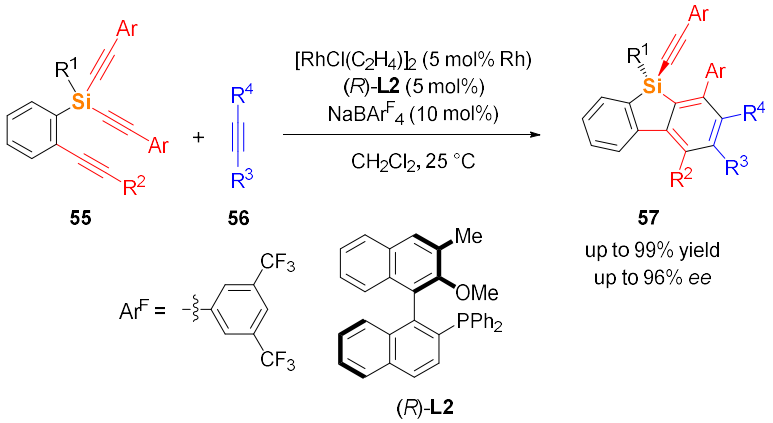
[2+2+2] Cycloaddition reaction is a useful synthetic method for the construction of highly substituted benzenoid structures such as benzene and pyridine from three unsaturated bonds.[40] This cyclotrimerization reaction has been utilized for the formation of one of the two aromatic rings that are fused to a silole unit as shown in Scheme 22. In 2007, Matsuda and Murakami reported a synthesis of dibenzosilole derivatives **52** by iridium-catalyzed [2+2+2] cycloaddition of diynes **50** with symmetric internal alkynes **51** (Scheme 23).[41] A tetrayne substrate **53** gave the corresponding ladder-type π-conjugated compound **54** bearing two silole units, and this compound was found to exhibit a higher

photoluminescence quantum yield than other obtained compounds bearing a single silole unit.



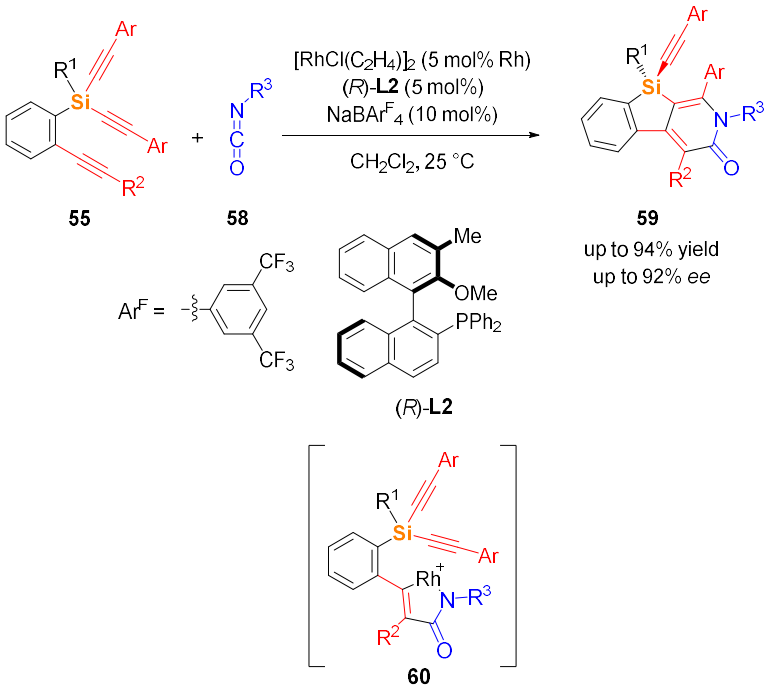
Scheme 23. Iridium-catalyzed synthesis of dibenzosiloles *via* [2+2+2] cycloaddition

Our group extended this dibenzosilole formation reaction to an asymmetric synthesis of silicon-stereogenic dibenzosiloles by rhodium-catalyzed [2+2+2] cycloaddition with triynes **55** and internal alkynes **56** (Scheme 24).[42] As a result of ligand screening, (*R*)-**L2**, a MeO-mop derivative bearing a methyl group at the 3'-position, gave the best result in this reaction, and the desired dibenzosiloles **57** were obtained in high yields (up to 99% yield) with high enantioselectivity (up to 96% *ee*).



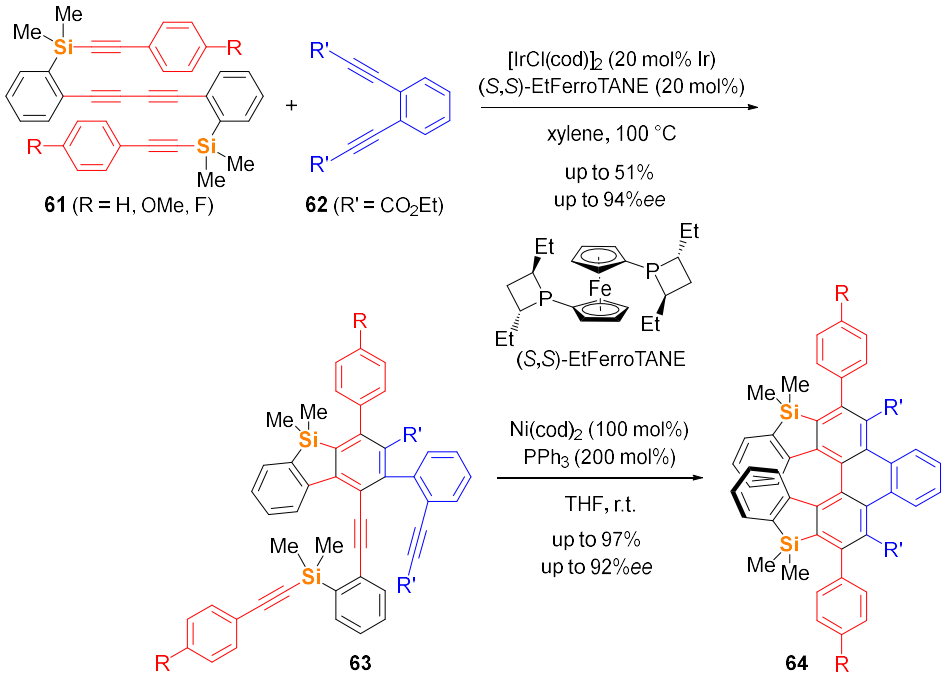
Scheme 24. Rhodium-catalyzed asymmetric synthesis of silicon-stereogenic dibenzosiloles

This asymmetric synthesis of silicon-stereogenic dibenzosiloles was also extended to a synthesis of silicon-bridged arylpyridinones **59** by using isocyanates **58** with triynes **55** under the same reaction conditions (Scheme 25).[43] High yields (up to 94%) and enantioselectivity (up to 92% *ee*) were achieved by employing axially chiral monophosphine ligand (*R*)-**L2**. The perfect regioselectivity of inserted isocyanates was confirmed by characterization of the products. Based on the mechanistic studies, this selectivity was explained by the rapid oxidative cyclization between arylalkyne and isocyanate to form intermediate **60** with coordination of nitrogen to the cationic rhodium center.



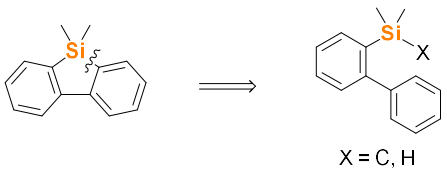
Scheme 25. Rhodium-catalyzed asymmetric synthesis of silicon-stereogenic silicon-bridged arylpyridinones

Shibata developed an enantioselective synthesis of silahelicenes by iridium-catalyzed [2+2+2] cycloaddition of tetraynes **61** and diynes **62** (Scheme 26).[44] The first cycloaddition reaction is the enantio-determining step to give axially chiral intermediates **63** in moderate yields (up to 51%) with high enantioselectivity (up to 94% *ee*) by employing (*S*,*S*)-EtFerroTANE as a chiral ligand. The second cycloaddition provided the desired product in a low yield under the iridium catalysis, however, the combination of stoichiometric $Ni(cod)_2$ and 2 equivalent of PPh_3 afforded the target silahelicenes **64** in excellent yields (up to 97%) without decrease of the enantiomeric excess (up to 92% *ee*).



Scheme 26. Synthesis of silahelicenes catalyzed by iridium and nickel complexes

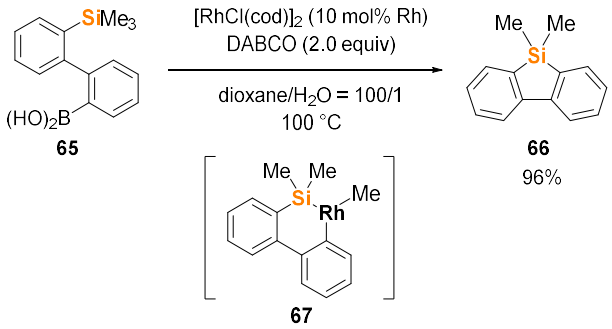
1.2.1.2 Synthesis of dibenzosiloles by C–H silylation



Scheme 27. Formation of dibenzosiloles *via* intramolecular C–H silylation

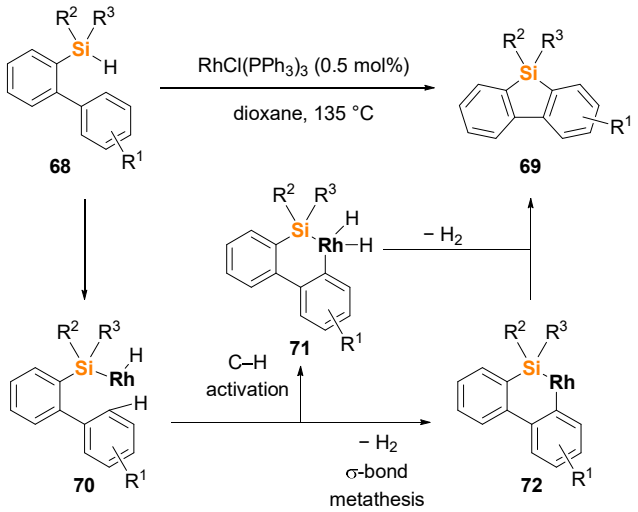
Catalytic C–H silylation reactions can provide valuable compounds in the synthetic chemistry and materials science in a single step without any prefunctionalization, which was necessary for the conventional procedures.[45] By applying this method to an intramolecular cyclization, a straightforward approach to the construction of silacycles can be achieved (Scheme 27). In 2009, Tobisu and Chatani reported that 2'-(trimethylsilyl)biphenyl-2-ylboronic acid **65** could be converted into 5,5-dimethyl-5*H*-dibenzo[*b*,*d*]silole **66** almost quantitatively under simple rhodium catalysis

(Scheme 28).[46] This transformation was proposed to proceed by a Si–Me activation to form rhodacycle **67** and subsequent reductive elimination to give **66**.



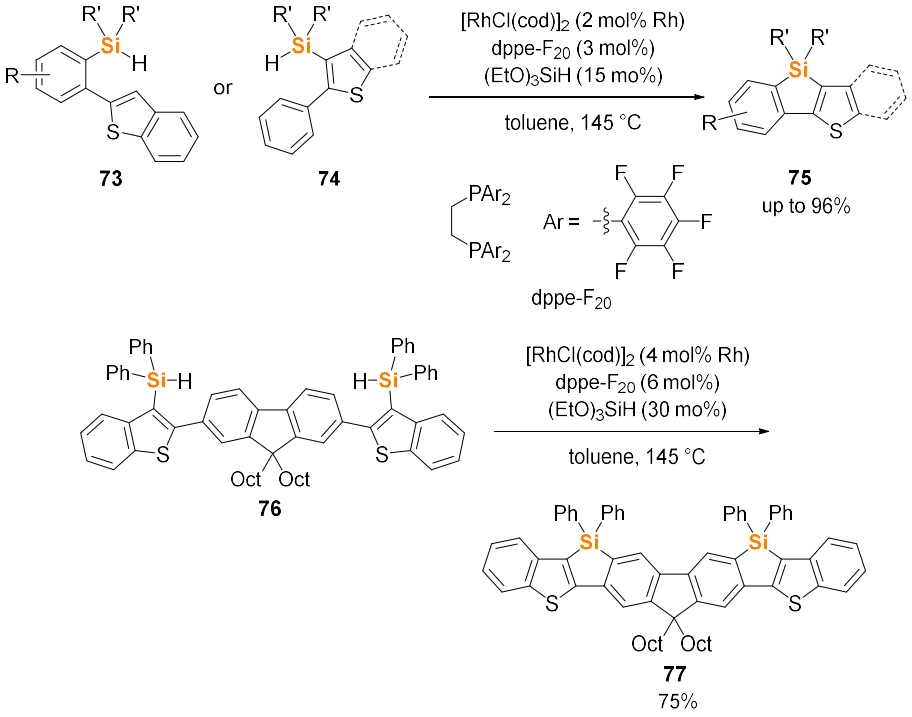
Scheme 28. Synthesis of dibenzosilole *via* intramolecular C–H silylation

Kuninobu and Takai developed an intramolecular Si–H/C–H coupling reaction catalyzed by a rhodium complex through a silylrhodium hydride intermediate (Scheme 29).[47] Various substituted 5,5-dimethyl-5*H*-dibenzo[*b*,*d*]siloles **69** were obtained from biphenyl-2-ylsilanes **68**, and the possible reaction mechanisms were proposed according to their mechanistic investigation, in which silylrhodium hydride **70** undergoes either C–H activation to form **71** or σ-bond metathesis to give **72**, followed by reductive elimination.



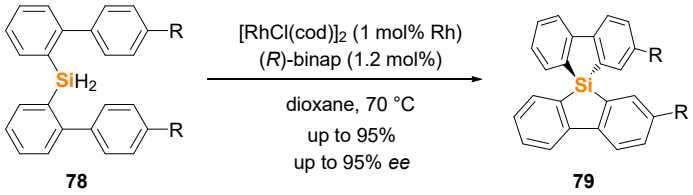
Scheme 29. Synthesis of dibenzosiloles *via* Si–H/C–H coupling reaction

This strategy was successfully applied to a synthesis of benzothienosiloles **75** from arylhydrosilanes **73** and isomeric **74** by Mitsudo and Suga, in which electron-deficient dppe-F_{20} was used as a ligand in the presence of a hydrosilane for the generation of a catalytically active rhodium hydride species (Scheme 30).[48] Fluorene derivative **76** smoothly underwent double cyclization to afford silicon-bridged ladder-type π-conjugated compound **77** in 75% yield, which exhibited high photoluminescence quantum yields in both solution and solid states (Φ= 0.81 in CH_2Cl_2 solution and 0.65 in solid state).



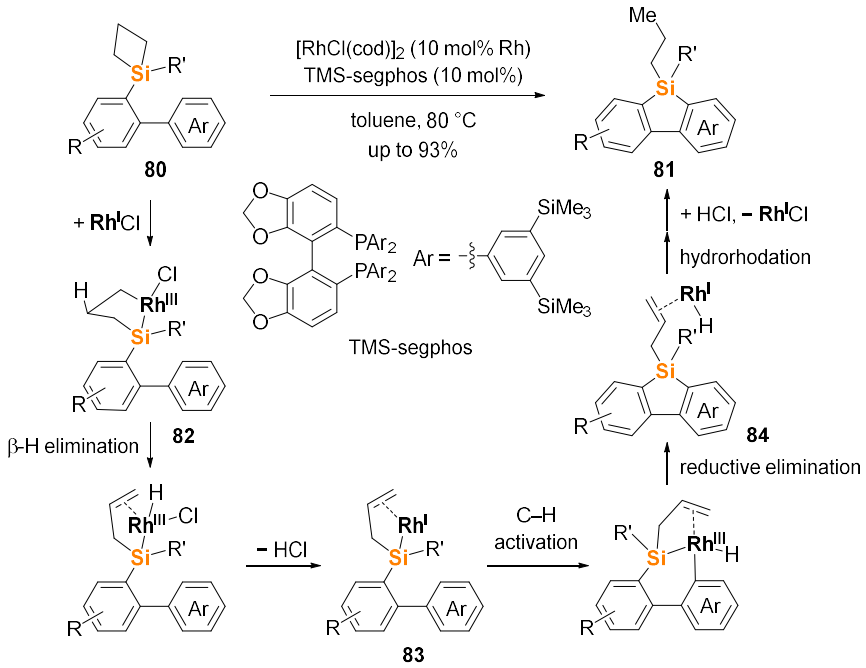
Scheme 30. Rhodium-catalyzed synthesis of π-extended thienosiloles

Intramolecular C–H silylation strategy can also be applied to a synthesis of spiro compounds from bis(biphenylyl)silanes **78** (Scheme 31).[49] Enantioselective C–H silylation was achieved by employing a rhodium/binap catalyst, affording spirobi(dibenzosilole)s **79** in excellent yields (up to 95%) and high enantioselectivity (up to 95% *ee*).



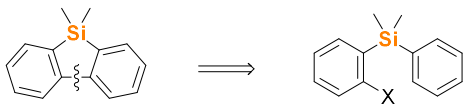
Scheme 31. Rhodium-catalyzed enantioselective C–H silylation

Silylrhodium intermediates are also accessible by insertion of rhodium center into an activated C–Si bond. Zhang and He described a rhodium-catalyzed synthesis of dibenzosilole derivatives **81** from 1-(biphenylyl)-1-methylsilacyclobutane **80** by using TMS-segphos as a ligand.[50] The reaction mechanism was proposed as shown in Scheme 32. Rhodium(I) chloride inserts into a C–Si bond to form silarhodacycle **82**, which undergoes β-H elimination and subsequent HCl elimination to afford silylrhodium(I) **83**. After C–H activation and reductive elimination to form 1-allylsilole **84** and rhodium(I) hydride, hydrorhodation to the allyl group and subsequent protonation by HCl afford product **81** along with regeneration of rhodium(I) chloride.



Scheme 32. Synthesis of silicon-bridged biaryls from silacyclobutanes

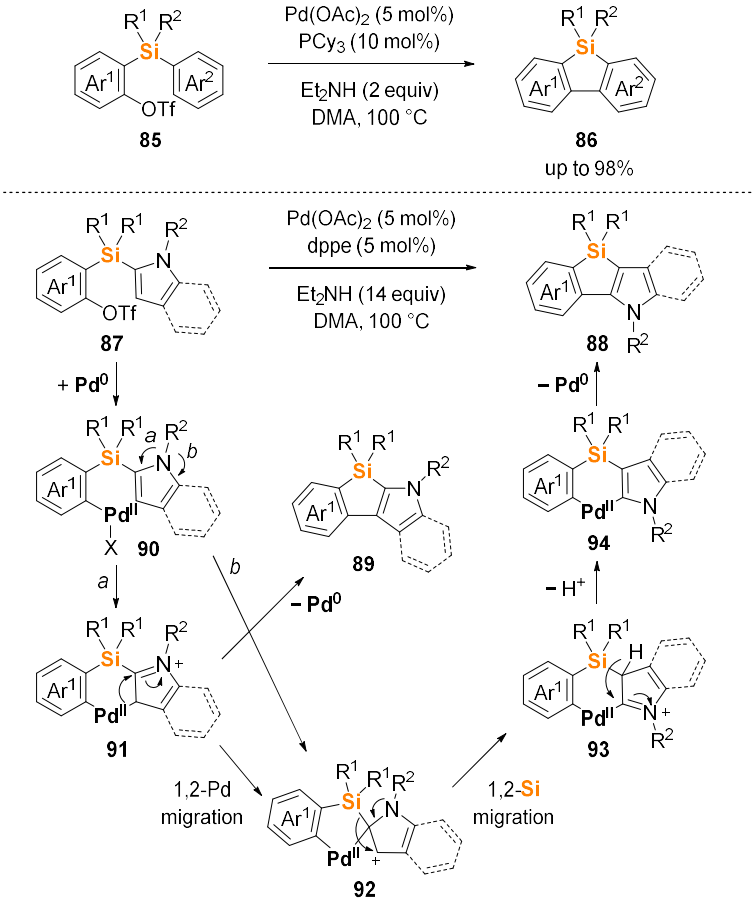
1.2.1.3 Synthesis of dibenzosiloles by intramolecular C–H arylation reaction



Scheme 33. Formation of dibenzosilole *via* C–H arylation

Transition-metal-catalyzed C–H arylation is one of the most powerful methods for the aryl–aryl bond formation in recent synthetic chemistry.[51] This approach proceeds through organometallic species, which is usually generated by oxidative addition of an aryl halide or pseudohalide to the metal center. Shimizu and Hiyama have successfully developed a palladium-catalyzed intramolecular C–H arylation of easily accessible 2-(arylsilyl)aryl triflates **85** as a new synthetic route to silicon-bridged biaryls **86** (Scheme 34).[52] Surprisingly, the use of 2-((2-pyrrolyl)silyl)aryl triflates **87** as substrates led to the generation of silicon-rearranged product **88** exclusively or preferentially over direct

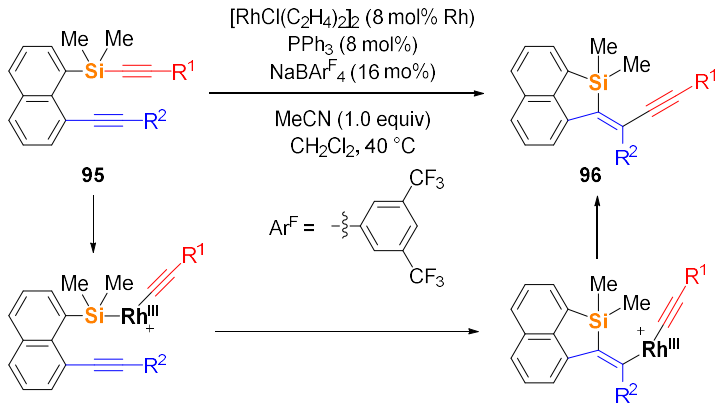
arylation product **89**.[53] The plausible mechanism for this unusual coupling products was provided as follows: Oxidative addition of **87** to palladium(0) species produces arylpalladium **90**, which undergoes intramolecular electrophilic substitution to give diarylpalladium **91**, followed by 1,2-palladium migration leading to spiro intermediate **92** (route *a*). Alternatively, direct palladation at the 2-position of pyrrole ring may lead to **92** (route *b*). 1,2-Silicon migration and subsequent deprotonation by a base followed by reductive elimination afford **88**. Isomeric **89** may be produced from **91** through deprotonation and reductive elimination.



Scheme 34. Palladium-catalyzed synthesis of silicon-bridged biaryls and Si-Pd position swap

1.2.1.4 Miscellaneous reactions

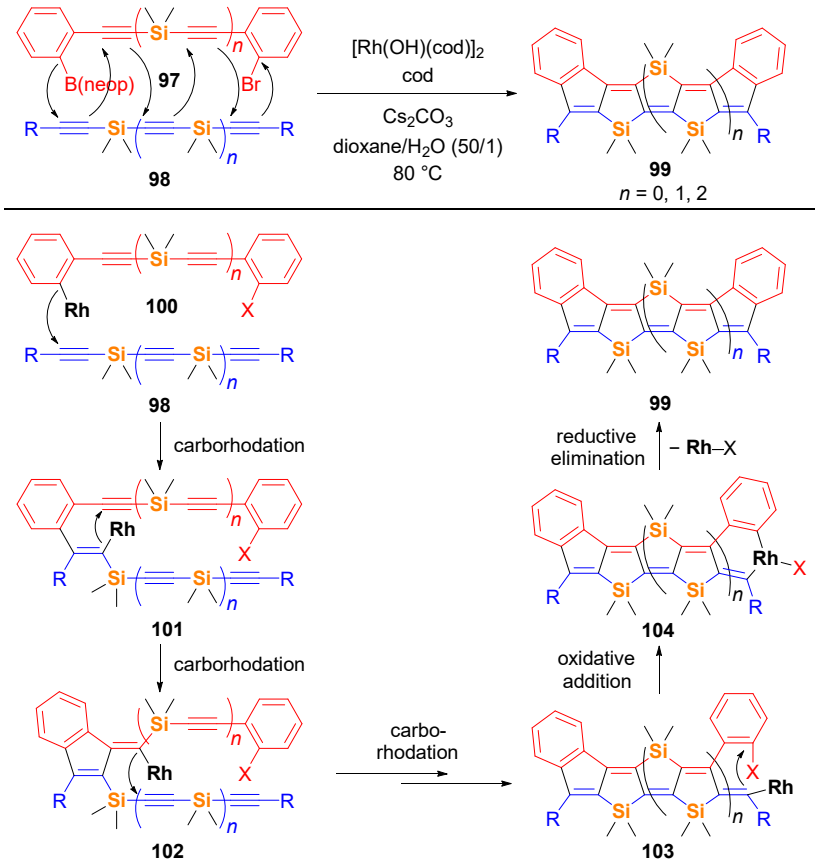
A few reports have been provided recently for the synthesis of silicon-bridged π-conjugated compounds through particular methods that are not classified in aforementioned three categories. In 2015, our group reported a rhodium-catalyzed synthesis of 2-(prop-2-yn-1-yliden)-1,2-dihydronaphtho[1,8-*bc*]siloles **96** from diynes **95** through intramolecular alkynylsilylation of alkynes (Scheme 35).[54] The product yield increased dramatically by addition of acetonitrile, which may indicate acetonitrile stabilizes the coordinatively unsaturated rhodium intermediates.



Scheme 35. Rhodium-catalyzed alkynylsilylation of alkynes

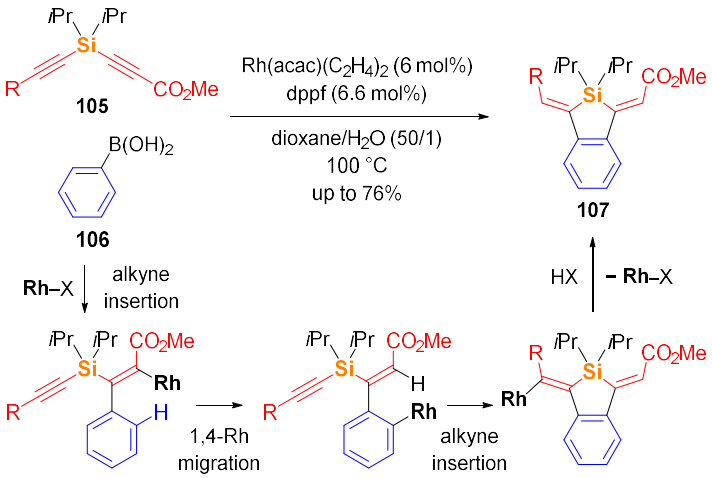
Our group also developed a rhodium-catalyzed stitching reaction for a synthesis of quinoidal fused oligosiloles **99** as a new family of silicon-bridged π-conjugated compounds.[55] This reaction proceeds between two oligo(silylene-ethynylene)s **97** and **98**, one of which (**97**) has an arylmetal moiety on one end and a haloarene moiety on the other end, under rhodium catalysis to "stitch" them together as shown in Scheme 36. Initial transmetalation of arylmetal moiety of **97** to rhodium(I) species generates arylrhodium **100**, which undergoes intermolecular carborhodation to the alkyne at the terminus of **98** to give alkenylrhodium **101**. This undergoes five-membered ring-forming intramolecular

carborhodation to give a new alkenylrhodium **102**. Repeating the ring-forming carborhodation leads to alkenylrhodium **103**, which undergoes oxidative addition of aryl–X bond and reductive elimination to afford quinoidal fused oligosilole **99** with regeneration of rhodium(I) species.



Scheme 36. Rhodium-catalyzed stitching reaction to give quinoidal fused oligosiloles

Recently, our group devised a synthesis of 1,3-dialkylidene-2,3-dihydro-1*H*-benzo[*c*]siloles **107** under rhodium catalysis. This reaction was achieved by utilizing carborhodation of arylrhodium to dialkynylsilane **105**, vinyl-to-aryl 1,4-rhodium migration and the second carborhodation (Scheme 37).[56]

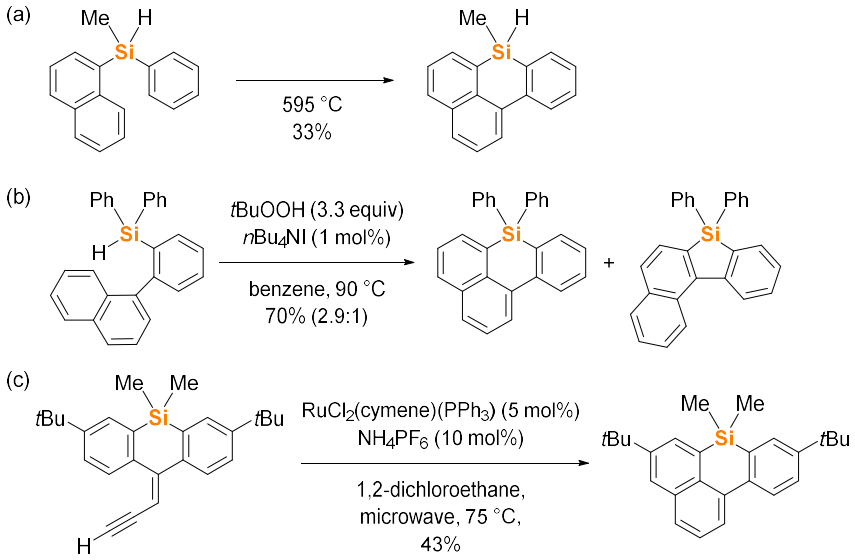


Scheme 37. Rhodium-catalyzed synthesis of 1,3-dialkylidenebenzo[*c*]siloles

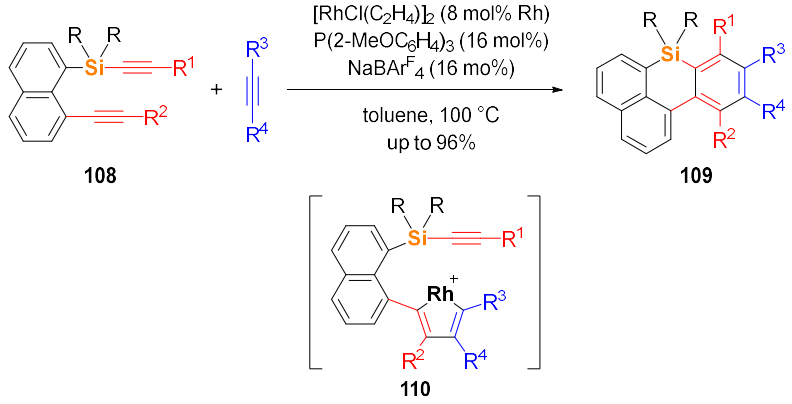
1.2.2 Synthesis of silicon-bridged π-conjugated compounds bearing a six- and seven-membered silacycle

Compared to a variety of synthetic methods for the fused siloles as described above, synthetic methods of fused silines and silepins, possessing six- and seven-membered silacycles, respectively, have been significantly less investigated, even though these compounds are also potential candidates exhibiting promising optical properties.[57] In fact, only a few reports have been made for 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines including dehydrogenetive C–C coupling of methyl(1-naphthyl)(phenyl)silane by pyrolysis (Scheme 38a),[58] oxidative Si–C coupling of 1-naphthyltriphenylsilane by a radical process (Scheme 38b),[59] and ruthenium-catalyzed cyclization of 5,5-dimethyl-10-(2-propyn-1-ylidene)-5,10-dihydrodibenzo[*b,e*]siline (Scheme 38c).[60] To expand the scope of these compounds, our group recently developed a new synthesis of 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines **109** by rhodium-catalyzed [2+2+2] cycloaddition of diynes **108** and internal alkynes, in which regioselective [2+2+2] cycloaddition would be initiated by the intermolecular formation of rhodacycle **110** (Scheme 39).[61] With regard to the synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines, there has been only one report

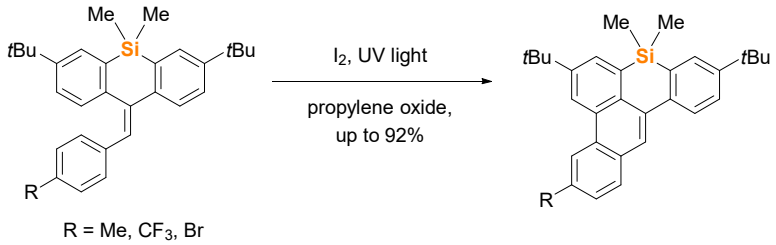
by Wagner, who utilized a photo-induced electrocyclization of 10-benzylidene-5,10-dihydrodibenzo[*b*,*e*]silines followed by oxidation (Scheme 40).[62]



Scheme 38. Reported synthesis of 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines

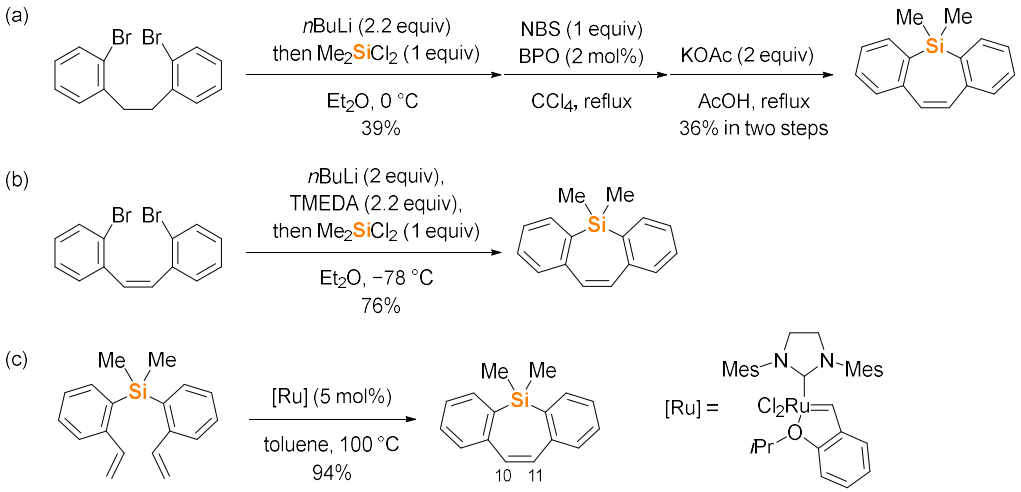


Scheme 39. Rhodium-catalyzed [2+2+2] cycloaddition reaction for the synthesis of 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines

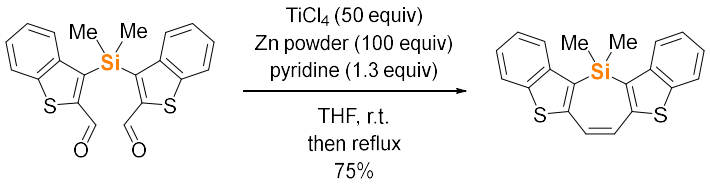


Scheme 40. Synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines

In the case of 5*H*-dibenzo[*b*,*f*]silepins, other than pioneering work for the synthesis of 5,5-dimethyl-5*H*-dibenzo[*b*,*f*]silepin (Scheme 41a),[63] their synthetic methods were mostly limited to either a reaction of (*Z*)-1,2-bis(2-lithioaryl)ethene with dichlorosilanes (Scheme 41b)[64] or a ring-closing metathesis of bis(2-vinylaryl)silanes (Scheme 41c),[64e, 65] all of which can only give products with no substituents at 10- and 11-positions. In 2008, Janosik reported a synthesis of 4,4-dimethyl-4*H*-dithieno[3,2-*b*:2',3'-*f*]silepin by intramolecular McMurry coupling from dialdehyde (Scheme 42).[66]

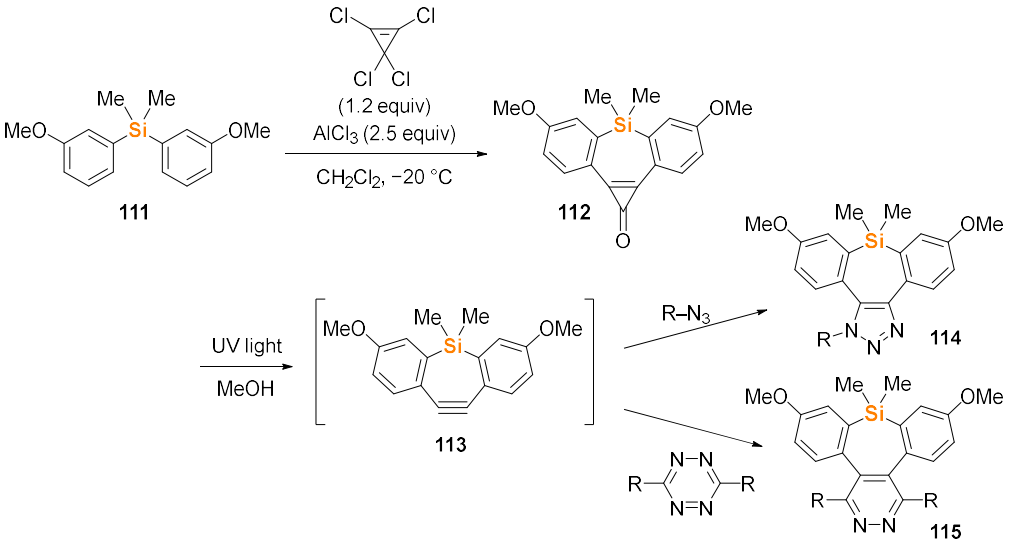


Scheme 41. Reported synthesis of 5*H*-dibenzo[*b*,*f*]silepins



Scheme 42. Synthesis of 4,4-dimethyl-4*H*-dithieno[3,2-*b*:2',3'-*f*]silepin through intramolecular McMurry coupling

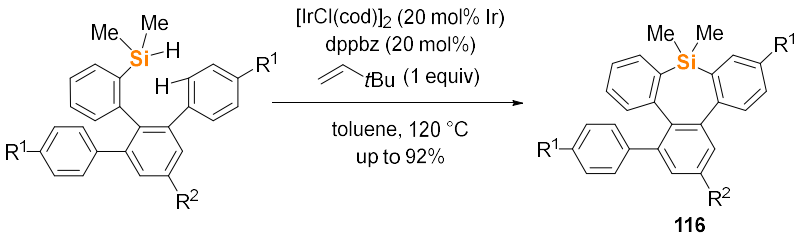
For 10,11-substituted variants, Klán reported a synthesis of triazole- and pyridazine-fused dibenzosilepins (Scheme 43).[67] The key intermediate **112** prepared from diarylsilane **111** and tetrachlorocyclopropene was irradiated by UV light to generate reactive cycloalkyne **113**, which undergoes click reactions with azides or tetrazines to afford products **114** or **115**, respectively.



Scheme 43. Synthesis of 8*H*-1,8-dihydrodibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]silepin and 9*H*-dibenzo[*b*,*f*]pyridazino[4,5-*d*]silepin by click reaction

Shibata reported a synthesis of 9*H*-tribenzo[*b*,*d*,*f*]silepins **116** by iridium-catalyzed dehydrogenative C–H/Si–H coupling (Scheme 44).[68] Dppbz ligand was the

most effective for this reaction and addition of 3,3-dimethylbut-1-ene as a hydrogen acceptor further increased the yield.

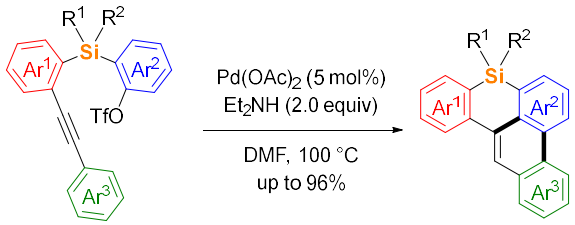


Scheme 44. Synthesis of 9*H*-tribenzo[*b*,*d*,*f*]silepins by iridium-catalyzed dehydrogenative C–H/Si–H coupling

1.3 Overview of this dissertation

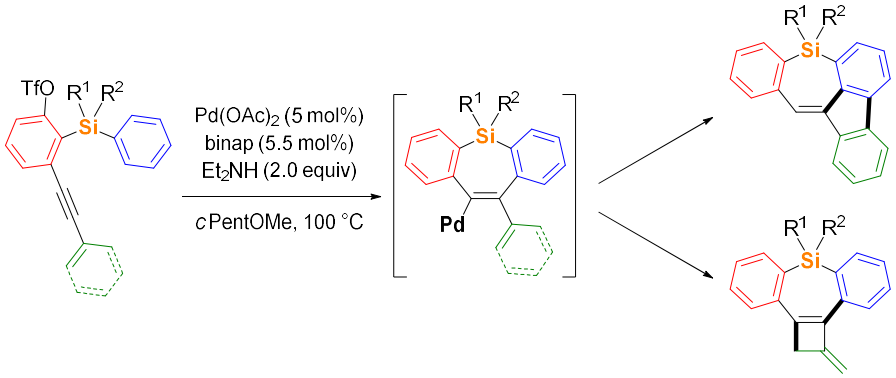
As described above, much attention has been paid to expanding diversity of accessible silacyclic structures for the application to the functional organic materials. In this context, the author considered that a 1,*n*-metal migration strategy can be highly effective to synthesize new silicon-bridged π-conjugated compounds bearing a six- or seven-membered silacycle, both of which have been difficult to synthesize by conventional synthetic methods. It is expected that an achievement of this goal can lead to an easy access to a wider variety of structural motifs bearing a silacycle, which could further enhance the utility of silicon-bridged π-conjugated compounds in the field of materials science. In this work, the author employed a combination of 1,*n*-palladium migration and intramolecular alkyne insertion, and successfully developed a new and efficient synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]siline derivatives possessing a six-membered silacycle and a synthesis of novel 5*H*-dibenzo[*b*,*f*]silepin derivatives possessing a seven-membered silacycle.

Chapter 2 describes an efficient synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]siline derivatives from easily accessible 2-((2-(arylethynyl)aryl)silyl)aryl triflates under simple palladium catalysis. Mechanistic investigation revealed that the reaction involves intramolecular C–H/C–H coupling through a new mode of 1,4-palladium migration that occurs with concomitant alkene stereoisomerization (Scheme 45).



Scheme 45. Palladium-catalyzed synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]siline derivatives described in Chapter 2

Chapter 3 describes a synthesis of novel 5*H*-dibenzo[*b*,*f*]silepin derivatives from 2-(arylsilyl)-3-(alkynyl)aryl triflates using a palladium/binap complex as the catalyst. A catalytic cycle involving 1,5-palladium migration and unusual *trans*-carbopalladation to alkyne was supported by a series of mechanistic investigation (Scheme 46).



Scheme 46. Palladium-catalyzed synthesis of 5*H*-dibenzo[*b*,*f*]silepin derivatives described in Chapter 3

1.4 References

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Chapter 2

Palladium-Catalyzed Synthesis of Benzophenanthrosilines by C−H/C−H Coupling through 1,4-Palladium Migration/Alkene Stereoisomerization

2.1 Introduction

Silicon-bridged π-conjugated compounds possessing a six-membered silacycle such as 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines and 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines constitute a potentially useful class of compounds based on the optoelectronic properties derived from their rigid and extended π-conjugation in plane (Figure 1).[1] However, in contrast to widely explored 5*H*-dibenzo[*b*,*d*]siloles and related compounds possessing a five-membered silacycle,[2] these six-membered silacycles have been significantly less investigated, which is presumably due to a lack of general and efficient synthetic methods. In fact, only a few approaches have been reported for the synthesis of 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines, such as dehydrogenative C−C coupling of methyl(1-naphthyl)(phenyl)silane by pyrolysis (Scheme 1a)[3] and oxidative Si−C coupling of 1-naphthyldiphenylsilane by a radical process (Scheme 1b).[4, 5] With regard to the synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines, only one method has been reported to date; Wagner and co-workers employed a conventional multistep π-extension process via a 5,10-dihydrodibenzo[*b*,*e*]siline as an intermediate (Scheme 1c).[6] In light of this methodological deficiency, the author developed a new and efficient synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines from easily accessible 2-((2-(arylethynyl)aryl)silyl)aryl triflates under palladium catalysis, which involves C−H/C−H coupling[7, 8] through a new mode of 1,4-palladium migration (Scheme 1d).[8, 9]

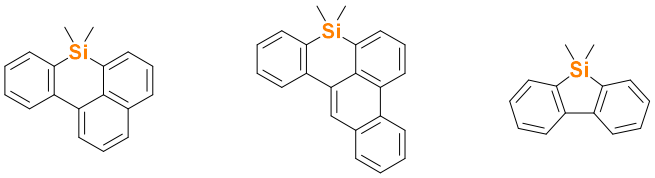
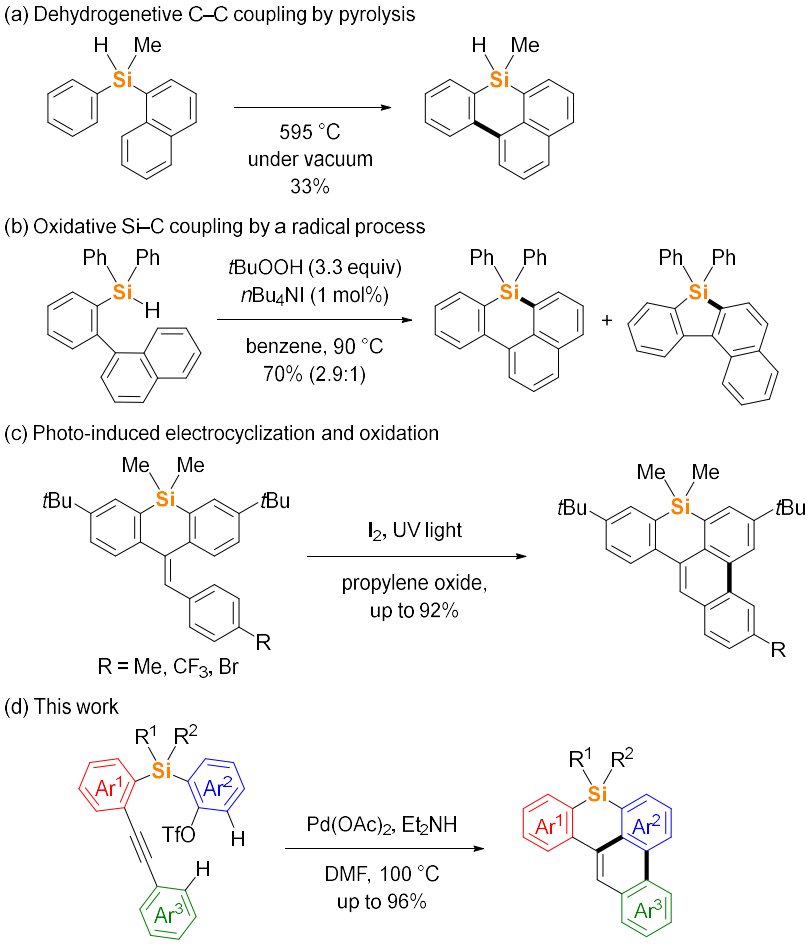


Figure 1. Structures of representative silicon-bridged π-conjugated compounds.

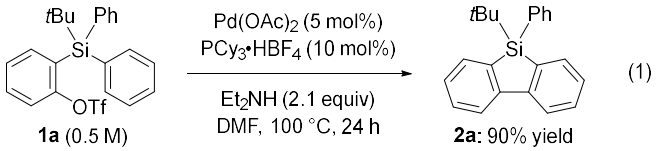


Scheme 1. Synthesis of silicon-bridged π-conjugated compounds bearing a six-membered silacycle.

2.2 Results and Discussion

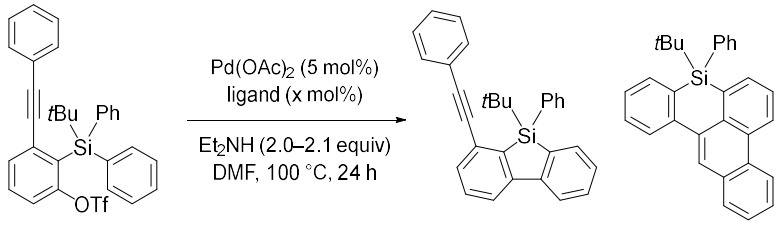
2.2.1 Reaction Development and Mechanistic Investigation

In 2008, Shimizu and co-workers reported a palladium-catalyzed synthesis of 5*H*-dibenzo[*b*,*d*]siloles from 2-(arylsilyl)aryl triflates through intramolecular C−H arylation.[10] This process is highly reliable and dibenzosilole **2a** could be obtained in 90% yield from substrate **1a** under similar reaction conditions (eq. 1). On the other hand, the author found that the use of substrate **1b**, which has a phenylethynyl group at the 3-position, resulted in no formation of dibenzosilole **2b**, and the major product obtained in 58 % yield was benzophenanthrosiline **3b** (Table 1, entry 1).[11] Reactions using other ligands such as PPh_3 and dppf also gave **3b** as the major product with no **2b** (entries 2 and 3), and the same trend was observed even in the absence of any phosphine ligands (entry 4).



(1)

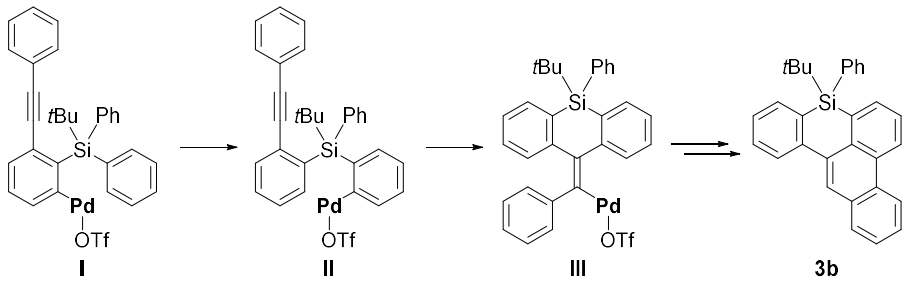
Table 1. Palladium-catalyzed reaction of **1b**



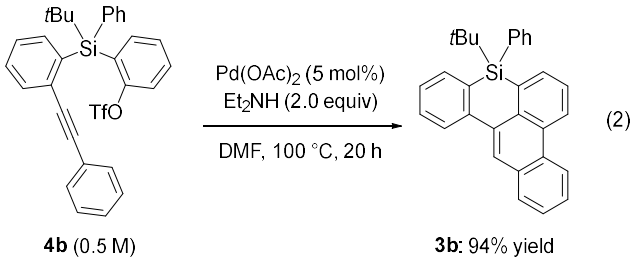
entry	ligand (x)	yield of **2b** (%)[a]	yield of **3b** (%)[a]
1	PCy_3[b](10)	0	58
2	PPh_3 (10)	0	39
3	dppf (5.5)	0	17
4	none	0	59

[a] Determined by ^1H NMR against internal standard ($MeNO_2$). [b] PCy•HBF_4 was used.

Based on these initial findings, the author decided to focus on the synthesis of benzophenanthrosilines **3**. The formation of **3b** from **1b** presumably goes through the pathway illustrated in Scheme 2. Initial oxidative adduct **I** would undergo 1,5-palladium migration[11–13] to give arylpalladium species **II**, and subsequent insertion of alkyne to the aryl–palladium bond gives alkenylpalladium intermediate **III**. If this process takes place, the same product should be obtained from compound **4b**, which can directly generate intermediate **II** without going through 1,5-palladium migration. Indeed, the reaction of compound **4b**, which is more readily accessible than **1b**, was found to give benzophenanthrosiline **3b** efficiently in a much higher yield of 94 % (eq. 2) under the same conditions as in Table 1, entry 4.

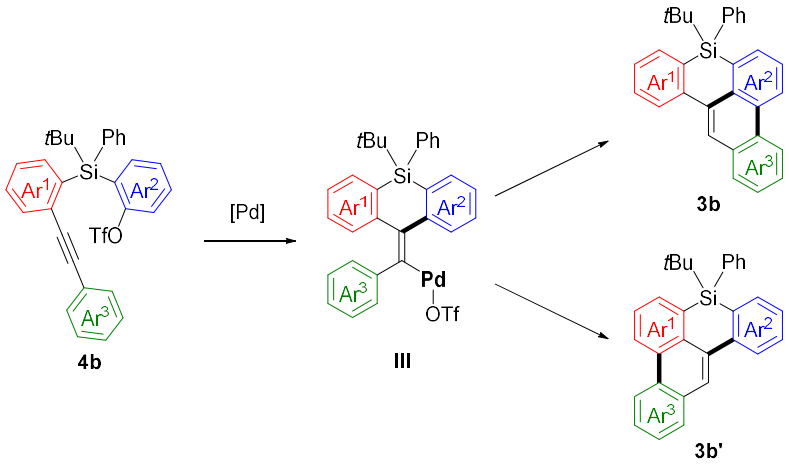


Scheme 2. Possible reaction pathway for the production of **3b**

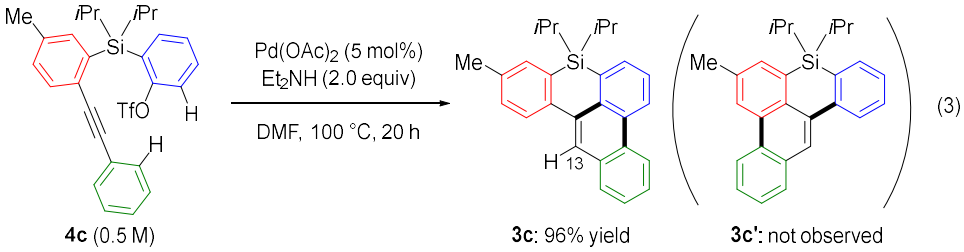


The structure of obtained benzophenanthrosiline **3b** can also be drawn as **3b'** and they cannot be distinguished (Scheme 3). If the second intramolecular C–C bond formation from intermediate **III** takes place between Ar^2 and Ar^3, the structure should be

drawn as **3b**. Alternatively, if the C–C bond formation occurs between Ar^1 and Ar^3, **3b'** represents the correct structure. To distinguish these two possibilities, a reaction of substrate **4c** bearing a methyl group on Ar^1 was conducted (eq. 3). As a result, the product **3c** was obtained in 96% yield without generation of **3c'** and its structure was unambiguously confirmed by X-ray crystallographic analysis, indicating that the C–C formation took place exclusively between Ar^2 and Ar^3.

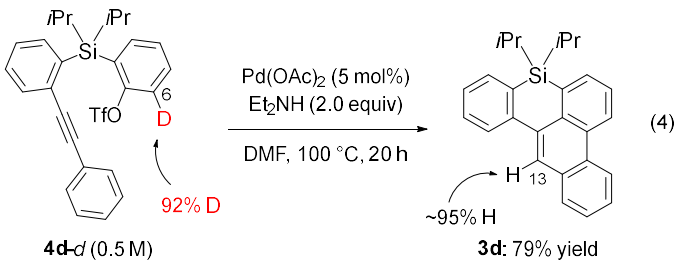


Scheme 3. Possible structures of **3b** drawn in according to two reaction pathways

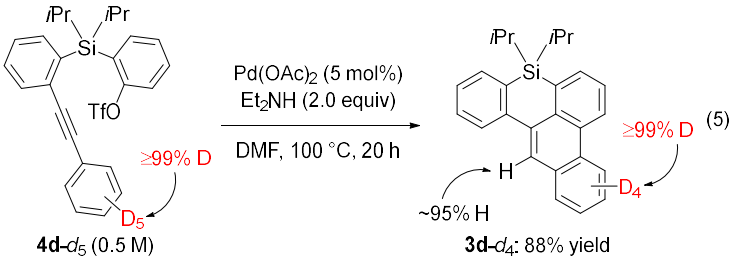


In this reaction, two C−H bonds on Ar^2 (blue) and Ar^3 (green) of substrate **4** (eq. 3) are cleaved to form a carbon–carbon bond between them, and a new C−H bond is generated at the 13-position of resulting benzophenanthrosiline **3**. To understand the fate and origin of these hydrogen atoms for elucidation of the reaction mechanism, several

deuterium-labeling experiments were carried out. The reaction of **4d-*d***, which has a deuterium at the 6-position of Ar^2, was found to give product **3d** with almost no deuterium incorporation at the 13-position (eq. 4), and the reaction of **4d-d_5**, which has a pentadeuteriophenyl group as Ar^3, gave the same result (eq. 5). These results indicate that H at the 13-position of compound **3** is not directly derived from either C−H bond that engages in the carbon–carbon bond formation. In contrast, when the reaction of **4c** is conducted in the presence of excess D_2O, the resulting product **3c** showed 78 % deuterium incorporation at the 13-position (eq. 6), indicating that the H at this position is derived from an external hydrogen donor (H derived from Et_2NH and/or residual water in solvent DMF under the standard anhydrous conditions). This reaction was carried out in the presence of non-deuterated benzophenanthrosiline **3d**, and no deuterium incorporation to **3d** was observed under these conditions, confirming that the deuterium is incorporated during the formation of compound **3** from substrate **4** and no C−H/C−D exchange occurs once compound **3** is produced. The reaction of **4d** was also carried out in the presence of 20 equiv of H_2O/D_2O and the degree of deuterium incorporation at 13-position of **3d** was compared by varying the H_2O/D_2O ratio (eq. 7). Based on these results, k_H/k_D can be roughly estimated to be >4, indicating that the protonation at this position is likely to be the turnover-limiting step for the present catalysis.

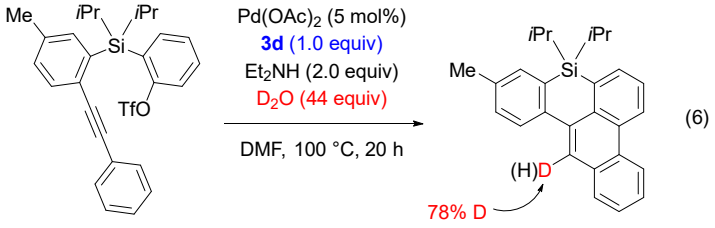


4d-*d* (0.5 M) **3d**: 79% yield



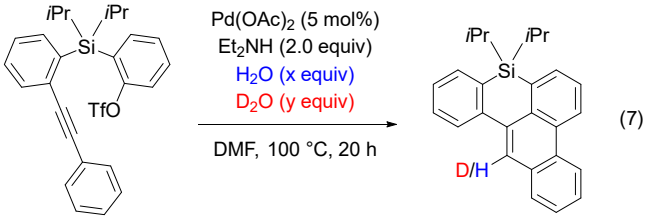
4d-d_5 (0.5 M)

3d-d_4: 88% yield (5)



4c (0.25 M)

3c-*d*: 84% yield
3d: 95% recovery
no D incorporation (6)



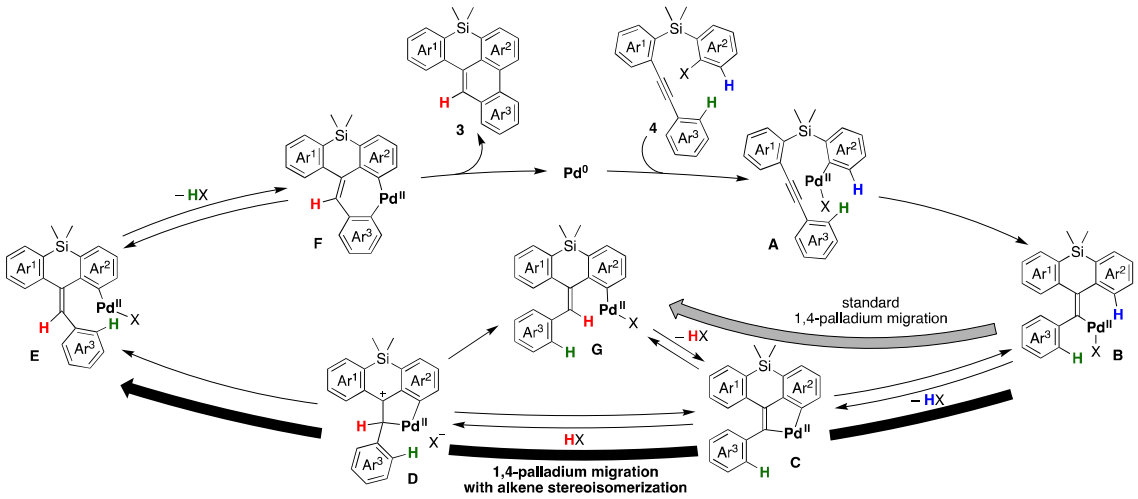
4d (0.5 M)

3d: 84–95% NMR yield (7)

x, y (equiv)	D incorporation (%)
10, 10	17
5, 15	38
0, 20	66

On the basis of these experiments and the fact that the C−H/C−H coupling takes place between Ar^2 and Ar^3, a proposed catalytic cycle for the present reaction is illustrated in Scheme 4. Thus, oxidative addition of aryl triflate **4** to palladium(0) gives arylpalladium species **A**. Intramolecular insertion of alkyne to the aryl–palladium bond takes place to give alkenylpalladium **B**. C−H bond activation on Ar^2 then leads to alkenyl(aryl)palladium intermediate **C**, which undergoes protonation by an external

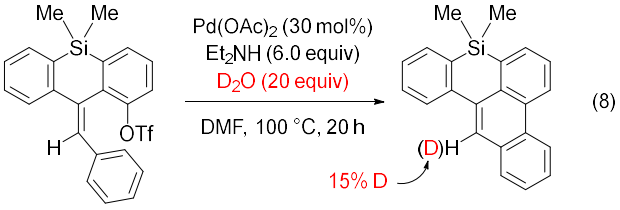
proton donor to give cationic alkyl(aryl)palladium **D**. Cleavage of alkyl–palladium bond with concomitant formation of a *Z* alkene gives arylpalladium **E**, which possesses the right stereochemistry for subsequent C−H bond activation to give diarylpalladium **F**. Finally, carbon–carbon bond-forming reductive elimination gives product **3** along with regeneration of palladium(0). The alkyl–palladium bond cleavage of intermediate **D** could also lead to arylpalladium **G** with an *E* alkene moiety, which can reenter the catalytic cycle by alkenyl C−H bond activation to give intermediate **C**. Interconversion between complexes **B** and **G** is a standard 1,4-palladium migration, which has been well explored in the literature.[8, 9] On the other hand, the presently proposed conversion from **B** to **E** can be regarded as a new mode of 1,4-palladium migration that involves concomitant alkene stereoisomerization.



Scheme 4. Proposed catalytic cycle for the reaction of **4** to **3** (X = OTf; amine base is omitted for clarity)

To probe the feasibility of the involvement of intermediate **E**, the author prepared aryl triflate **5** with *Z*-alkene geometry and conducted the palladium-catalyzed reaction

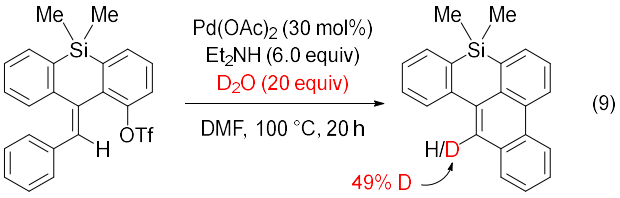
and the desired product **3e** was obtained in a high yield (eq. 8). When this reaction was conducted in the presence of excess D_2O, 15% deuterium incorporation was observed at the 13-position, thus indicating the reversible conversion from **E** to **D** (and **C**). In addition, to confirm that complex **G** can enter the catalytic cycle toward benzophenanthrosiline **3**, compound (*E*)-**5** was also prepared and subjected to this reaction, and the same product **3e** was indeed obtained as expected (eq. 9). It is worth noting that the degree of deuterium incorporation is significantly higher for the reaction of (*E*)-**5** than that of (*Z*)-**5**, which is consistent with the proposed reaction pathway where complex **G** generated from (*E*)-**5** undergoes the alkenyl C−H bond cleavage to generate intermediate **C** followed by subsequent reprotonation.



(*Z*)-**5** (0.17 M)

3e: 85% yield
(w/o D_2O: 89% yield)

(8)



(*E*)-**5** (0.17 M)

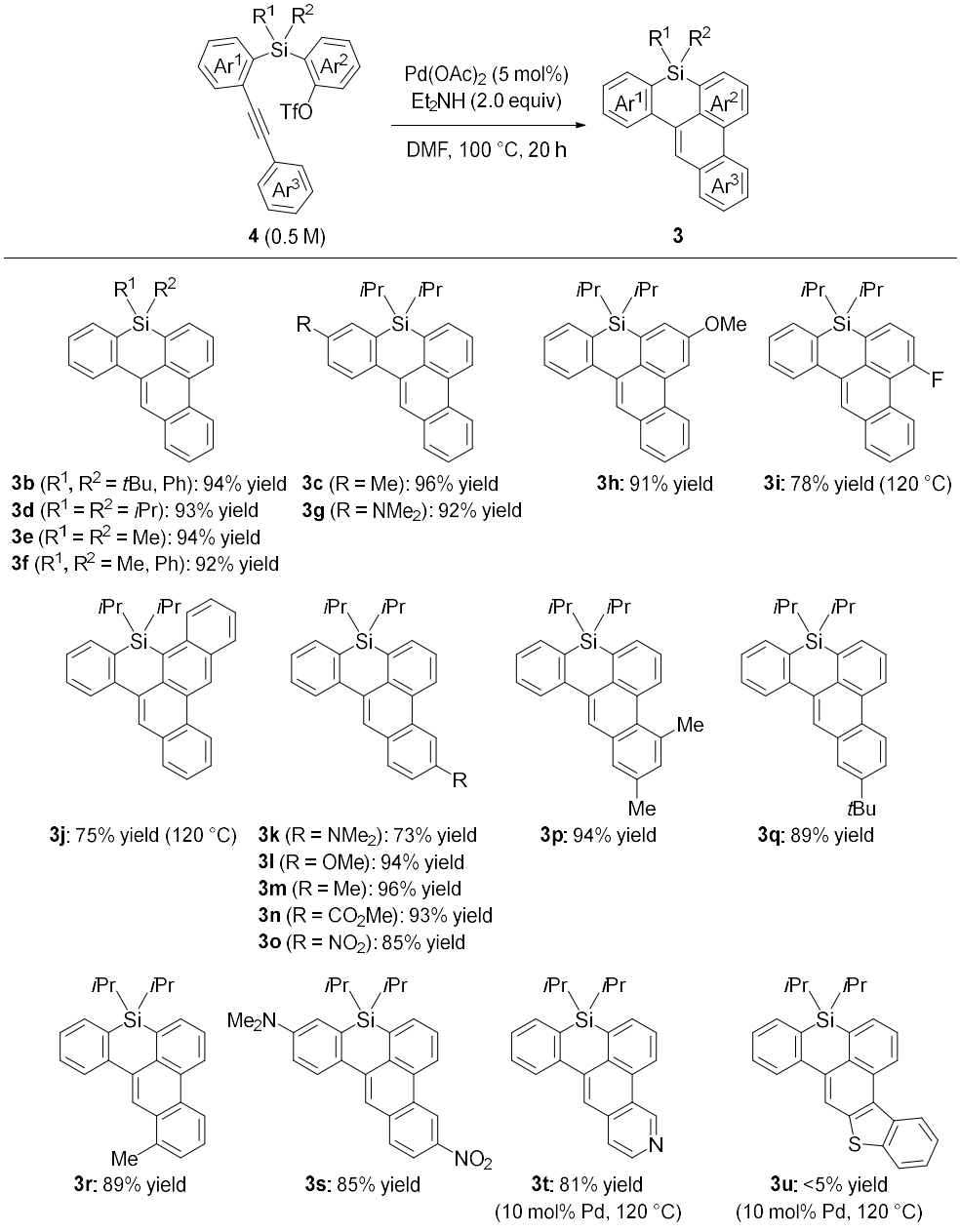
3e: 84% yield
(w/o D_2O: 92% yield)

(9)

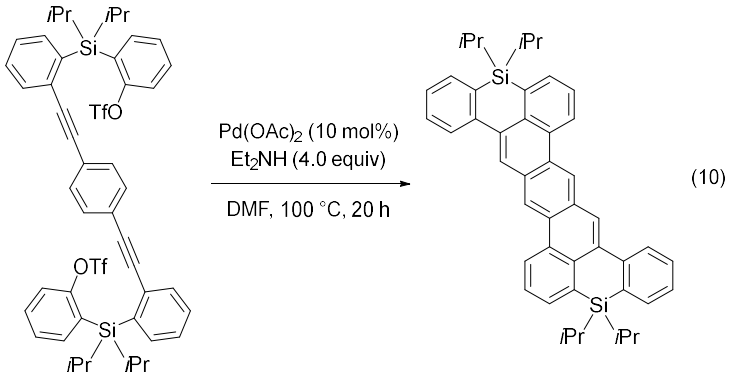
2.2.2 Reaction Scope for the Synthesis of Benzophenanthrosilines

The scope of this reaction was found to be reasonably broad, as summarized in Scheme 5. For example, in addition to compound **3b**, which has a (*tert*-butyl)phenylsilylene bridging unit, benzophenanthrosilines **3d**–**3f** with other silylene units can be obtained in similarly high yields (92–94 % yield). With regard to the substituents on the aromatic rings, various groups can be installed at any of them (Ar^1, Ar^2, and Ar^3) while retaining high yields. For example, electron-donating groups such as dimethylamino (**3g**, **3k**, **3s**) and methoxy (**3h**) group can be utilized in the reaction. Electron-withdrawing methoxycarbonyl (**3n**) and nitro (**3o**) groups can also be used without decrease of the yields. Both of these substituents can be installed at the same time and a donor-acceptor-type benzophenanthrosiline **3s** can be synthesized as well. Synthesis of 5-substituted benzophenanthrosiline required the higher reaction temperature as shown for **3i** bearing a fluoro group at 5-position. The reaction for tetraphene-fused **3j** also needed a harsh condition, presumably because the steric repulsion between naphthyl and isopropyl groups slowed down the reaction rate. The structures of products **3g**–**3j** also establish that the C−H/C−H couplings take place exclusively between Ar^2 and Ar^3 rather than between Ar^1 and Ar^3. It is worth mentioning that substrate **4p**, which has a 3,5-dimethylphenyl group as Ar^3, can also undergo the C−H/C−H coupling to give **3p** despite its steric hindrance. On the other hand, the reaction of **4q**, which has a 3-*tert*-butylphenyl group as Ar^3, selectively provides **3q** through the formation of a carbon–carbon bond at the less hindered position. This catalytic method also accommodates a pyridine ring, as shown for **3s**, whereas benzothiophene-fused **3u** was not obtained even under the larger amount of catalyst loading at 120 °C. Furthermore, the reaction of ditriflate **6** gives a new type of π-extended silicon-bridged compound (**7**), which possesses a benzo[*k*]tetraphene moiety, through this two-fold reaction sequence (eq. 10). In the preliminary experiments,

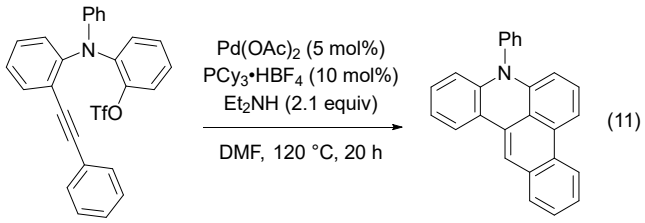
the author also found that this method can be extended to the synthesis of a nitrogen-bridged analogue, 8*H*-naphtho[1,2,3-*kl*]acridine (**9**), under slightly modified conditions (eq. 11). An aryl bromide **4e'** was also examined as a substrate bearing a bromo group in place of OTf, however, only 10% of the product **3e** was observed under the standard conditions (eq. 12).



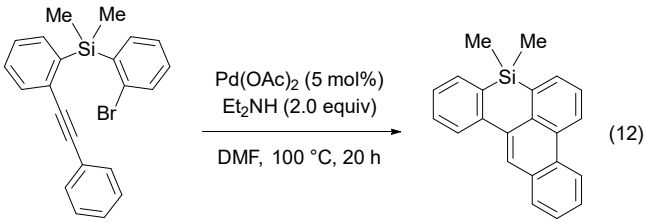
Scheme 5. Scope of the palladium-catalyzed synthesis of benzophenanthrosilines



6 (0.25 M) **7**: 72% yield (10)



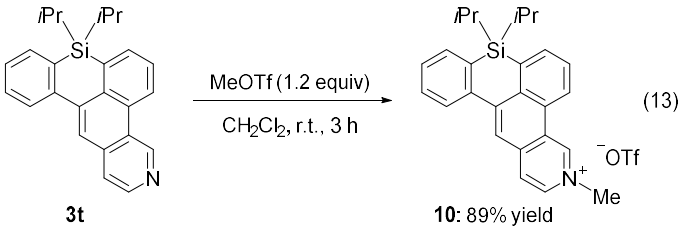
8 (0.5 M) **9**: 47% yield (11)



4e' (0.5 M) **3e**: 10% NMR yield (12)

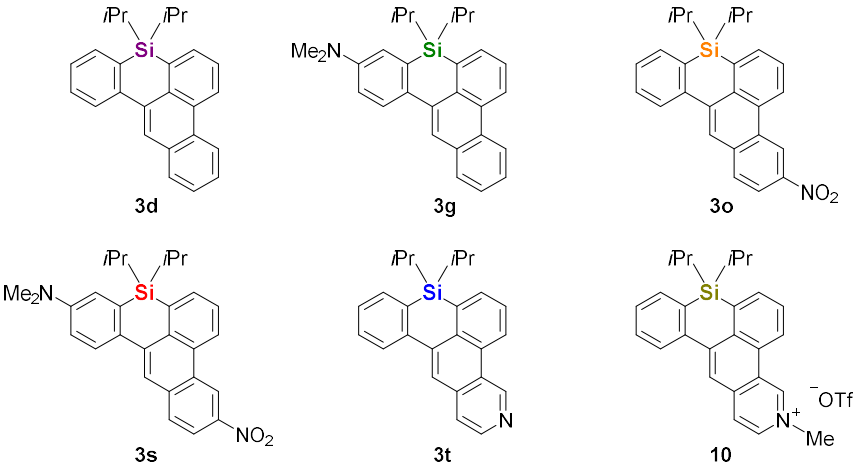
2.2.3 Optical Properties of the Obtained Benzophenanthrosilines

The author also examined the optical properties of benzophenanthrosilines **3** obtained in this study. Some of the compounds were chosen for comparison as summarized in Table 2 (**3d**: parent, **3g**: 10-NMe_2, **3o**: 3-NO_2, **3s**: 10-NMe_2-3-NO_2). Based on UV-vis absorption (Figure 2) and fluorescence spectra (Figure 3), introduction of an electron-donating group at the 10-position (**3g**) or an electron-withdrawing group at 3-position (**3o**) led to a red-shift in their UV-vis absorption and emission band maxima compared to the parent compound (**3d**), and a significantly higher quantum yield was obtained for **3g** (Φ_F = 0.66 vs. Φ_F = 0.10 for **3d** and **3o**). Even more significant red-shifts of the UV-vis absorption and emission band maxima were observed for donor–acceptor compound **3s**. Furthermore, while pyridine-containing compound **3t** had very similar absorption and emission spectra compared with the parent compound (**3d**), *N*-methylated derivative **10**, which can be readily synthesized from **3t** (eq. 13), showed red-shifts for both UV-vis absorption and emission band maxima with a high quantum yield (Φ_F = 0.83).[14] These results demonstrate that the optical properties can be effectively tuned by changing the substituents or derivatization of these benzophenanthrosilines.



(13)

Table 2. Optical Properties of Compounds **3d**, **3g**, **3o**, **3s**, **3t**, and **10** in CH_2Cl_2 at 25 °C



compound	UV-vis absorption λ_{max} (nm) (ε (10^4 M^{-1} cm^{-1}))	Fluorescence λ_{max} (nm) (λ_{ex} (nm))	Φ_F (λ_{ex} (nm))
3d[a]	254 (3.4), 266 (3.7), 324 (2.3), 335 (2.0)	393 (334)	0.10 (334)
3g[b]	263 (3.7), 366 (1.9)	451 (365)	0.66 (365)
3o[c]	260 (3.8), 301 (1.0), 314 (0.8), 384 (2.1)	527 (384)	0.10 (384)
3s[d]	255 (4.3), 316 (1.0), 448 (2.6)	585 (448)	– (448)[g]
3t[e]	252 (3.7), 326 (2.3), 363 (0.1)	370, 387 (326)	0.12 (326)
10[f]	256 (2.8), 311 (1.6), 394 (2.2)	437 (380)	0.83 (380)

[a] At 3.3×10^{-5} M. [b] At 5.9×10^{-5} M. [c] At 3.4×10^{-5} M. [d] At 2.4×10^{-5} M. [e] At 3.5×10^{-5} M. [f] At 2.5×10^{-5} M. [g] Not determined.

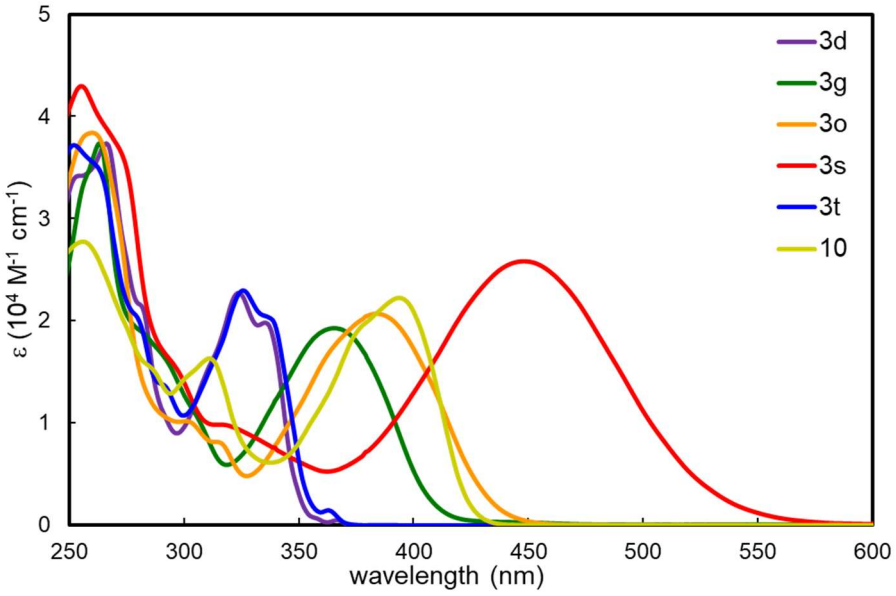


Figure 2. UV-vis absorption spectra of compounds **3d** (purple), **3g** (green), **3o** (orange), **3s** (red), **3t** (blue), and **10** (dark yellow) in CH_2Cl_2 (2.4–5.9 x 10^{-5} M) at 25 °C.

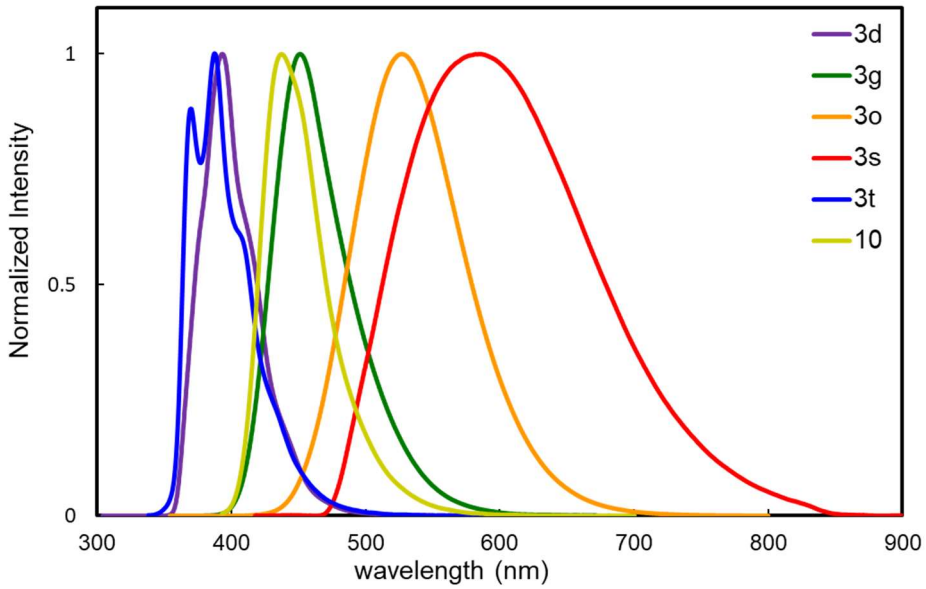


Figure 3. Fluorescence spectra of compounds **3d** (purple), **3g** (green), **3o** (orange), **3s** (red), **3t** (blue), and **10** (dark yellow) in CH_2Cl_2 (2.4–5.9 x 10^{-5} M) at 25 °C.

2.3 Conclusion

The author has developed a new and efficient synthesis of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines, silicon-bridged π-conjugated compounds with a six-membered silacycle, from 2-((2-(arylethynyl)aryl)silyl)aryl triflates under simple palladium catalysis. The reaction involves C−H/C−H coupling through 1,4-palladium migration with concomitant alkene stereoisomerization, which has been supported by a series of experimental mechanistic investigations. Optical properties of obtained benzophenanthrosilines were investigated and introduction of substituents and derivatization were proved to be effective for tuning their properties.

2.4 Experimental Section

General

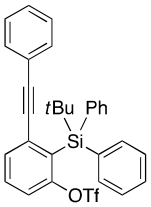
All reactions were carried out with standard Schlenk techniques under nitrogen unless otherwise noted. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 or Bruker micrOTOF II spectrometer. UV-vis spectra were recorded on HITACHI U-2900 spectrophotometer. Fluorescence spectra were recorded on JASCO FP6500 Spectrofluorometer. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200. Preparative GPC was performed with JAI LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent.

DMF (Wako Chemicals; dehydrated) was degassed by purging nitrogen prior to use. Et_2NH (Wako Chemicals), iPr$_2$NH (Wako Chemicals), and Et_3N (Wako Chemicals) were distilled over KOH under vacuum. Pyridine (Wako Chemicals) was dried over MS4A and degassed by purging nitrogen prior to use. D_2O (ISOTEC) was degassed by purging nitrogen prior to use. THF (Kanto Chemical; dehydrated), Et_2O (Wako Chemicals; dehydrated), CH_2Cl_2 (Wako Chemicals or Kanto Chemical; dehydrated), toluene (Wako Chemicals; dehydrated), acetone (Wako Chemicals), 1,2-dichloroethane (Wako Chemicals), phenylacetylene (Kanto Chemical), tert-butylchlorodiphenylsilane (TCI), *tert*-butyldichloro(phenyl)silane (TCI), dichloromethylphenylsilane (TCI), dichlorodimethylsilane (TCI), dichlorodiisopropylsilane (TCI), imidazole (Nacalai Tesque), trifluoromethanesulfonic anhydride (TCI), methyl trifluoromethanesulfonate (Wako Chemicals), 1-bromo-2-iodobenzene (TCI or Oakwood Chemical), 4-iodoanisole (TCI), 1,2-dibromobenzene (TCI), 1,4-diiodobenzene (Kanto Chemical), iodobenzene (Wako Chemicals), 2-methoxyaniline (Wako Chemicals), chloromethyl methyl ether (Nacalai Tesque), benzyl bromide (TCI), 2-bromophenol (TCI), 2,6-dibromophenol

(TCI), [bis(trifluoroacetoxy)iodo]benzene (Aldrich), PPh_3 (Wako Chemicals), dppf (TCI), PCy_3•HBF_4 (Wako Chemicals), P*t*Bu_3•HBF_4 (Wako Chemicals), toluenesulfonic acid (Kishida Chemical; monohydrate), *n*BuLi (Kanto Chemical; 1.55–1.57 M solution in hexane), *t*BuLi (Kanto Chemical; 1.53–1.64 M solution in pentane), NaO*t*Bu (TCI), NaH (Kishida Chemical; 60 wt% in mineral oil), BBr_3 (Wako Chemicals; 1.0 M solution in CH_2Cl_2), $ZnCl_2$ (Kishida Chemical), Mg turnings (Kishida Chemical), $AgNO_3$ (Kishida Chemical), $Pd(OAc)_2$ (Wako Chemicals), and CuI (Wako Chemicals) were used as received. **1a**,[10a] 2-bromo-3-iodophenol,[15] ((2-bromophenyl)ethynyl)trimethylsilane,[16] 5,5-dimethyldibenzo[*b*,*e*]silin-10(5*H*)-one,[17] $PdCl_2(PPh_3)_2$,[18] $Pd(PPh_3)_4$,[19] and $Pd_2(dba)_3$•$CHCl_3$[20] were synthesized following the literature procedures.

Representative Procedures for Substrates:

2-(*tert*-Butyldiphenylsilyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1b)



A mixture of phenylacetylene (923 μL, 8.40 mmol), 2-bromo-3-iodophenol (2.09 g, 6.99 mmol), $PdCl_2(PPh_3)_2$ (156 mg, 0.210 mmol), CuI (84.6 mg, 0.420 mmol), and Et_3N (2.93 mL, 21.0 mmol) in THF (7.0 mL) was stirred for 2 h at 60 °C. The mixture was diluted with Et_2O, and this was passed through a pad of Celite and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/4 → 1/3 to afford 2-bromo-3-(phenylethynyl)phenol as a brown solid (1.91 g, 6.99 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 7.64-7.53 (m, 2H), 7.44-7.31 (m, 3H), 7.24-7.12 (m, 2H),

7.01 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 5.68 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 152.9, 131.9, 128.9, 128.57, 128.55, 126.0, 125.5, 122.9, 116.1, 113.6, 94.1, 87.9.

tert-Butylchlorodiphenylsilane (2.72 mL, 10.5 mmol) was added to a solution of 2-bromo-3-(phenylethynyl)phenol (1.91 g, 6.99 mmol) and imidazole (1.43 g, 21.0 mmol) in DMF (10 mL) and the mixture was stirred for 20 h at 35 °C. The reaction was quenched with H_2O and extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford (2-bromo-3-(phenylethynyl)phenoxy)(*tert*-butyl)diphenylsilane as a yellow viscous oil (3.39 g, 6.63 mmol; 95% yield).

^{1}H NMR ($CDCl_3$): δ 7.82-7.70 (m, 4H), 7.65-7.56 (m, 2H), 7.50-7.31 (m, 9H), 7.09 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.81 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 6.44 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 1.17 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 153.0, 135.6, 132.3, 131.9, 130.3, 128.7, 128.5, 128.1, 127.4, 127.0, 125.8, 123.3, 119.8, 118.2, 93.8, 88.6, 26.6, 19.9.

*n*BuLi (4.44 mL, 6.97 mmol; 1.57 M solution in hexane) was added slowly over 10 min to a solution of (2-bromo-3-(phenylethynyl)phenoxy)(*tert*-butyl)diphenylsilane (3.39 g, 6.63 mmol) in THF (20 mL) at −78 °C, and the mixture was stirred for 30 min at −78 °C and for 1.5 h at room temperature. The reaction was quenched with H_2O and extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/15 → 1/8 to afford 2-(*tert*-butyldiphenylsilyl)-3-(phenylethynyl)phenol as a white solid (2.50 g, 5.78 mmol; 87% yield).

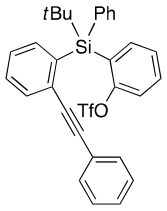
^{1}H NMR ($CDCl_3$): δ 7.81-7.74 (m, 4H), 7.37-7.30 (m, 6H), 7.28 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.23 (dd, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.21-7.15 (m, 1H), 7.15-7.09 (m, 2H), 6.75 (dd, $^{3}J_{HH}$ = 8.0 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.73-6.68 (m, 2H), 5.50 (s, 1H), 1.40

(s, 9H). ^{13}C NMR ($CDCl_3$): δ 162.8, 136.4, 135.8, 131.3, 129.7, 128.4, 128.0, 127.9, 127.8, 123.4, 120.2, 117.1, 95.4, 93.2, 29.8, 20.6.

*n*BuLi (4.04 mL, 6.35 mmol; 1.57 M solution in hexane) was added slowly over 10 min to a solution of 2-(*tert*-butyldiphenylsilyl)-3-(phenylethynyl)phenol (2.50 g, 5.78 mmol) in Et_2O (20 mL) at −78 °C and the mixture was stirred for 30 min at −78 °C. Trifluoromethanesulfonic anhydride (1.04 mL, 6.35 mmol) was added to it, and the mixture was stirred for 30 min at −78 °C and for 1 h at room temperature. The reaction was quenched with H_2O and extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/30 → 1/20 and the solid thus obtained was washed with hexane to afford compound **1b** as a white solid (2.72 g, 4.82 mmol; 83% yield).

^{1}H NMR ($CDCl_3$): δ 7.69-7.62 (m, 4H), 7.59 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.46 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.40 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.32-7.20 (m, 7H), 7.19-7.13 (m, 2H), 6.84-6.78 (m, 2H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.9, 135.8, 134.1, 133.8, 131.5, 131.0, 129.5, 129.0, 128.5, 128.0, 127.8, 122.8, 118.9 (q, $^5J_{CF}$ = 1.9 Hz), 118.5 (q, $^1J_{CF}$ = 321 Hz), 97.8, 91.4, 29.8, 20.6. HRMS (FAB) calcd for $C_{31}H_{27}F_3O_3SSi$ (M^+) 564.1397, found 564.1398.

2-(*tert*-Butyl(phenyl)(2-(phenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4b)



1-Bromo-2-iodobenzene (1.25 mL, 9.99 mmol), phenylacetylene (1.15 mL, 10.5 mmol), and THF (5 mL) were successively added to a mixture of $Pd(PPh_3)_4$ (347 mg, 0.300 mmol), CuI (116 mg, 0.609 mmol), and Et_3N (4.18 mL, 30.0 mmol) in THF (10 mL), and the mixture was stirred for 14 h at room temperature. The precipitates were filtered off with Et_2O and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane only → EtOAc/hexane = 1/100 → 1/50 to afford 1-bromo-2-(phenylethynyl)benzene (CAS 21375-88-2) as a colorless oil (2.54 g, 9.87 mmol; 99% yield).

^{1}H NMR ($CDCl_3$): δ 7.65-7.52 (m, 4H), 7.41-7.33 (m, 3H), 7.29 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.18 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H).

*t*BuLi (4.39 mL, 7.20 mmol; 1.64 M solution in pentane) was added slowly over 11 min to a solution of 1-bromo-2-(phenylethynyl)benzene (927 mg, 3.61 mmol) in THF (7 mL) at –70 °C, and the mixture was stirred for 25 min. *tert*-Butyldichloro(phenyl)silane (756 µL, 3.60 mmol) was added to it, and this was stirred for 30 min at –70 °C and for 17 h at room temperature. Imidazole (309 mg, 4.54 mmol) and 2-bromophenol (316 µL, 3.00 mmol) were then added to the mixture with THF (2 mL), and this was stirred for 48 h at 35 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford (2-bromophenoxy)(*tert*-butyl)(phenyl)(2-(phenylethynyl)phenyl)silane as an orange viscous oil (1.24 g, 2.43 mmol; 81% yield).

^{1}H NMR ($CDCl_3$): δ 7.96 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.84 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 2H), 7.63 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.50-7.28 (m, 6H), 7.25-7.14 (m, 3H), 6.95 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 2H), 6.88-6.81 (m, 1H), 6.68 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.52 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz,

1H), 1.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 152.5, 136.9, 136.0, 135.5, 133.6, 133.3, 132.8, 131.4, 130.12, 130.06, 129.5, 128.2, 128.04, 128.01, 127.9, 127.5, 123.2, 122.0, 119.9, 114.8, 93.5, 91.7, 28.0, 21.2.

*n*BuLi (1.72 mL, 2.67 mmol; 1.55 M solution in hexane) was added slowly over 7 min to a solution of (2-bromophenoxy)(*tert*-butyl)(phenyl)(2-(phenylethynyl)phenyl)silane (1.24 g, 2.43 mmol) in THF (11 mL) at –78 °C. The mixture was stirred for 30 min at –78 °C and for 45 min at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/10 → 1/5 to afford 2-(*tert*-butyl(phenyl)(2-(phenylethynyl)phenyl)silyl)phenol as a yellow viscous oil (846 mg, 1.96 mmol; 80% yield).

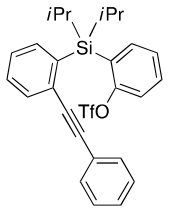
^{1}H NMR ($CDCl_3$): δ 7.72 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.71-7.66 (m, 2H), 7.64 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.54 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.45-7.31 (m, 5H), 7.29 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.23-7.17 (m, 1H), 7.13 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 6.89 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.82-6.75 (m, 3H), 4.98 (s, 1H), 1.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 161.0, 137.9, 137.4, 137.0, 136.8, 134.5, 134.1, 131.4, 131.3, 130.3, 129.6, 129.4, 128.1, 127.92, 127.86, 127.7, 123.2, 120.4, 120.2, 115.8, 94.3, 92.1, 30.0, 19.5.

*n*BuLi (1.39 mL, 2.15 mmol; 1.55 M solution in hexane) was added slowly over 4 min to a solution of 2-(*tert*-butyl(phenyl)(2-(phenylethynyl)phenyl)silyl)phenol (846 mg, 1.96 mmol) in Et_2O (7 mL) at –75 °C and the mixture was stirred for 30 min. Trifluoromethanesulfonic anhydride (363 μL, 2.16 mmol) was added to it and this was stirred for 30 min at –70 °C and for 45 min at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The

residue was chromatographed on silica gel with EtOAc/hexane = 1/20 and further purified by GPC with $CHCl_3$ to afford compound **4b** as a pale yellow viscous oil (849 mg, 1.50 mmol; 77% yield).

^{1}H NMR ($CDCl_3$): δ 7.83 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.77 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.67-7.62 (m, 2H), 7.61 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.46-7.32 (m, 7H), 7.23-7.08 (m, 4H), 6.79-6.73 (m, 2H), 1.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.0, 138.8, 136.84, 136.78, 136.1, 133.9, 133.4, 131.3, 129.9, 129.6, 129.5, 128.1, 127.9, 127.8, 127.6, 126.7, 123.2, 118.9 (q, $^5J_{CF}$ = 1.9 Hz), 118.4 (q, $^1J_{CF}$ = 320 Hz), 93.8, 92.1, 29.8, 19.7. HRMS (FAB) calcd for $C_{31}H_{28}F_3O_3SSi$ ($M+H^+$) 565.1475, found 565.1477.

2-(Diisopropyl(2-(phenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4d)



*t*BuLi (13.5 mL, 21.1 mmol; 1.56 M solution in pentane) was added slowly over 15 min to a solution of 1-bromo-2-(phenylethynyl)benzene (2.70 g, 10.5 mmol) in THF (18 mL) at –78 °C, and the mixture was stirred for 30 min. Dichlorodiisopropylsilane (1.89 mL, 10.5 mmol) was added to it, and this was stirred for 10 min at –75 °C and for 2.5 h at room temperature. A solution of 2-bromophenol (740 μL, 7.01 mmol) and imidazole (715 mg, 10.5 mmol) in THF (9 mL) was then added to the mixture, and this was stirred for 18 h at 35 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel

with hexane to afford (2-bromophenoxy)diisopropyl(2-(phenylethynyl)phenyl)silane as a yellow oil (2.22 g, 4.79 mmol; 68% yield).

^{1}H NMR ($CDCl_3$): δ 7.77 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.62 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.52 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.48-7.39 (m, 3H), 7.39-7.30 (m, 4H), 7.05 (td, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.85 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.78 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 1.73 (sept, $^{3}J_{HH}$ = 7.6 Hz, 2H), 1.15 (d, $^{3}J_{HH}$ = 7.8 Hz, 6H), 1.13 (d, $^{3}J_{HH}$ = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 153.1, 137.4, 136.1, 133.5, 133.2, 131.4, 129.7, 128.54, 128.47, 128.4, 128.2, 127.6, 123.4, 122.2, 120.1, 115.0, 91.5, 91.3, 18.3, 17.6, 14.2.

*n*BuLi (3.36 mL, 5.28 mmol; 1.57 M solution in hexane) was added slowly over 6 min to a solution of (2-bromophenoxy)diisopropyl(2-(phenylethynyl)phenyl)silane (2.22 g, 4.79 mmol) in THF (21 mL) at –78 °C. The mixture was stirred for 30 min at –78 °C and for 1 h at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/2 to afford 2-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol as a white solid (1.73 g, 4.50 mmol; 94% yield).

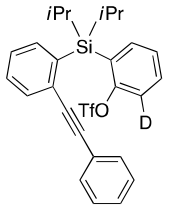
^{1}H NMR ($CDCl_3$): δ 7.67-7.60 (m, 2H), 7.48-7.39 (m, 2H), 7.36 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.32-7.17 (m, 4H), 7.05-6.94 (m, 3H), 6.79 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 4.84 (s, 1H), 1.82 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.04 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 161.4, 137.0, 136.9, 134.9, 134.0, 131.4, 131.1, 130.5, 129.7, 128.2, 128.1, 127.6, 123.3, 120.4, 118.6, 115.9, 92.1, 91.4, 18.1, 17.9, 11.3.

*n*BuLi (3.05 mL, 4.79 mmol; 1.57 M solution in hexane) was added slowly over 5 min to a solution of 2-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol (1.67 g, 4.34 mmol) in Et_2O (13 mL) at –78 °C and the mixture was stirred for 5 min.

Trifluoromethanesulfonic anhydride (803 μL, 4.77 mmol) and Et_2O (7 mL) were added to it and this was stirred for 40 min at –78 °C and for 4 h at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/10 to afford compound **4d** as a white solid (2.04 g, 3.95 mmol; 91% yield).

^{1}H NMR ($CDCl_3$): δ 7.63-7.57 (m, 2H), 7.55 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.44-7.32 (m, 4H), 7.27-7.14 (m, 4H), 7.01-6.93 (m, 2H), 1.86 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.07 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.7, 136.4, 134.7, 133.7, 131.2, 131.1, 130.1, 129.3, 128.12, 128.09, 127.3, 126.5, 126.3, 123.3, 118.50 (q, $^1J_{CF}$ = 320 Hz), 118.46 (q, $^5J_{CF}$ = 1.9 Hz), 92.3, 92.0, 18.2, 18.0, 11.4. HRMS (FAB) calcd for $C_{27}H_{28}F_3O_3SSi$ ($M+H^+$) 517.1475, found 517.1480.

2-Deuterio-6-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (**4d-*d***)



*t*BuLi (16.4 mL, 25.6 mmol; 1.56 M solution in pentane) was added slowly over 25 min to a solution of 1-bromo-2-(phenylethynyl)benzene (3.29 g, 12.8 mmol) in THF (24 mL) at –78 °C, and the mixture was stirred for 30 min. Dichlorodiisopropylsilane (2.30 mL, 12.8 mmol) was added to it, and this was stirred for 30 min at –75 °C and for 4.5 h at room temperature. A solution of 2,6-dibromophenol (2.14 g, 8.51 mmol) and imidazole (871 mg, 12.8 mmol) in THF (15 mL) was then added to the mixture, and this

was stirred for 15 h at 35 °C and for 2 h at 40 °C. After cooled to room temperature, the reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residual solid was washed with cold hexane to afford (2,6-dibromophenoxy)diisopropyl(2-(phenylethynyl)phenyl)silane as a white solid (3.60 g, 6.64 mmol; 78% yield).

^{1}H NMR ($CDCl_3$): δ 7.89 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.59 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.46-7.28 (m, 9H), 6.67 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 1.95 (sept, $^3J_{HH}$ = 7.6 Hz, 2H), 1.12 (d, $^3J_{HH}$ = 7.4 Hz, 6H), 1.11 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 151.1, 137.0, 136.4, 133.1, 132.8, 131.3, 129.3, 128.5, 128.34, 128.26, 126.8, 123.7, 123.3, 116.2, 92.1, 90.9, 17.8, 17.3, 14.2.

*n*BuLi (5.48 mL, 8.60 mmol; 1.57 M solution in hexane) was added slowly over 12 min to a solution of (2,6-dibromophenoxy)diisopropyl(2-(phenylethynyl)phenyl)silane (3.59 g, 6.62 mmol) in THF (40 mL) at –78 °C. The mixture was stirred for 20 min at –78 °C and for 2.5 h at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford 2-bromo-6-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol as a white solid (2.93 g, 6.32 mmol; 95% yield).

^{1}H NMR ($CDCl_3$): δ 7.59 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.55 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.45-7.30 (m, 4H), 7.28-7.19 (m, 3H), 7.08-7.01 (m, 2H), 6.75 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 5.66 (s, 1H), 1.85 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.04 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.7, 137.3, 136.6, 136.2, 133.5, 133.3, 131.3, 130.1, 129.0, 128.2, 128.1, 127.1, 123.5, 121.5, 121.4, 110.9,

92.1, 91.8, 18.4, 18.2, 11.8.

*t*BuLi (5.77 mL, 9.00 mmol; 1.56 M solution in pentane) was added slowly over 12 min to a solution of 2-bromo-6-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol (1.39 g, 3.00 mmol) in THF (21 mL) at –75 °C. The mixture was stirred for 3 h while gradually raising the temperature to –5 °C. D_2O (11 mL) was then added to it and the mixture was stirred for 30 min at room temperature. This was extracted with Et_2O, and the organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/3 to afford 2-deuterio-6-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol as a white solid (887 mg, 2.30 mmol; 77% yield, 92% D).

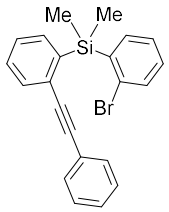
^{1}H NMR ($CDCl_3$): δ 7.68-7.59 (m, 2H), 7.48-7.40 (m, 2H), 7.36 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.32-7.17 (m, 4H), 7.05-6.95 (m, 3H), 6.79 (d, $^3J_{HH}$ = 7.4 Hz, 0.08H), 4.83 (s, 1H), 1.82 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.05 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 161.4, 137.0, 136.9, 134.9, 134.0, 131.4, 131.0, 130.5, 129.7, 128.2, 128.1, 127.6, 123.3, 120.3, 118.6, 115.6 (t, $^1J_{CD}$ = 25.9 Hz), 92.1, 91.4, 18.1, 17.9, 11.3.

*n*BuLi (1.40 mL, 2.20 mmol; 1.57 M solution in hexane) was added slowly over 6 min to a solution of 2-deuterio-6-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol (770 mg, 2.00 mmol; 92% D) in Et_2O (8 mL) at –75 °C and the mixture was stirred for 5 min. Trifluoromethanesulfonic anhydride (368 μL, 2.19 mmol) was added to it and this was stirred for 40 min at –75 °C and for 1 h at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/10 to afford

compound **4d-*d*** as a white solid (804 mg, 1.55 mmol; 78% yield). The deuterium content was estimated to be 92% based on that of starting 2-deuterio-6-(diisopropyl(2-(phenylethynyl)phenyl)silyl)phenol.

^{1}H NMR ($CDCl_3$): δ 7.62-7.57 (m, 2H), 7.55 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.43-7.32 (m, 3.08H), 7.28-7.15 (m, 4H), 7.00-6.94 (m, 2H), 1.86 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.7, 136.4, 134.7, 133.7, 131.2, 131.0, 130.1, 129.3, 128.13, 128.09, 127.3, 126.5, 126.3, 123.3, 118.5 (q, $^{1}J_{CF}$ = 320 Hz), 118.2 (tq, $^{1}J_{CD}$ = 25.9 Hz and $^{5}J_{CF}$ = 2.9 Hz), 92.3, 92.0, 18.2, 18.0, 11.4. HRMS (FAB) calcd for $C_{27}H_{27}DF_3O_3SSi$ ($M+H^+$) 518.1538, found 518.1547.

(2-Bromophenyl)dimethyl(2-phenylethynylphenyl)silane (4d')



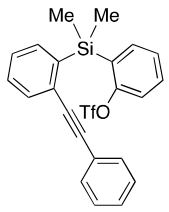
*n*BuLi (2.52 mL, 4.00 mmol; 1.59 M solution in hexane) was added slowly over 30 min to a solution of 1,2-dibromobenzene (474 μL, 4.00 mmol) in THF-Et_2O (8 mL / 8 mL) at –116 °C (EtOH + liquid nitrogen), and the mixture was stirred for 35 min. Dichlorodimethylsilane (965 μL, 8.00 mmol) was added to it slowly over 6 min, and this was stirred for 2 h at –116 °C and then slowly warmed up to room temperature. The volatiles were removed under vacuum to afford crude (2-bromophenyl)chlorodimethylsilane.

*t*BuLi (4.97 mL, 8.00 mmol; 1.61 M solution in pentane) was added slowly over 11 min to a solution of 1-bromo-2-phenylethynylbenzene (1.03 g, 4.00 mmol) in THE (4

mL) at −78 °C, and the mixture was stirred for 30 min at −78 °C and for 10 min at room temperature. This was added to a solution of (2-bromophenyl)chlorodimethylsilane in THF (4 mL) slowly over 11 min at −78 °C, and this was stirred for 4 h at −78 °C to room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/50 → 1/40 to afford **4d'** as a pale yellow oil (1.10 g, 2.81 mmol; 70% yield).

^{1}H NMR ($CDCl_3$): δ 7.58-7.50 (m, 3H), 7.47-7.42 (m, 1H), 7.38 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 7.32 (td, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.30-7.24 (m, 3H), 7.24-7.16 (m, 4H), 0.78 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 140.1, 139.4, 137.6, 135.4, 132.9, 132.7, 131.4, 131.0, 130.7, 129.3, 128.8, 128.32, 128.27, 127.7, 126.5, 123.4, 92.8, 91.1, −1.3. HRMS (APCI) calcd for $C_{22}H_{20}BrSi$ ($M+H^+$) 391.0513, found 391.0512.

2-(Dimethyl(2-(phenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4e)



*n*BuLi (1.94 mL, 3.01 mmol; 1.55 M solution in hexane) was added slowly over 9 min to a solution of 1-bromo-2-(phenylethynyl)benzene (771 mg, 3.00 mmol) in THF (6 mL) at –75 °C, and the mixture was stirred for 25 min. Dichlorodimethylsilane (724 μL, 6.00 mmol) was added to it, and this was stirred for 20 min at –75 °C and for 30 min at room temperature. The volatiles were removed under vacuum, and imidazole (287 mg, 4.22 mmol) and THF (6 mL) were added to it. The mixture was cooled to –70 °C and 2-

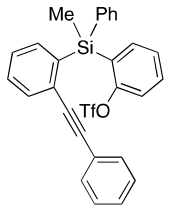
bromophenol (295 μL, 2.80 mmol) was added to it with THF (1 mL). After stirring for 1 h 45 min at room temperature, the reaction mixture was diluted with Et_2O (10 mL), filtered through Celite with Et_2O, and concentrated under vacuum. The residue was dissolved in THF (8 mL) and cooled to –75 °C. *n*BuLi (3.61 mL, 5.60 mmol; 1.55 M solution in hexane) was then added slowly over 8 min, and the mixture was stirred for 25 min at –75 °C and for 1 h at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/10 → 1/5 to afford 2-(dimethyl(2-(phenylethynyl)phenyl)silyl)phenol as a white solid (429 mg, 1.31 mmol; 47% yield).

^{1}H NMR ($CDCl_3$): δ 7.61-7.52 (m, 2H), 7.43-7.35 (m, 2H), 7.32 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.29-7.20 (m, 6H), 6.91 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.71 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.75 (s, 1H), 0.71 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 160.6, 140.2, 136.4, 135.2, 132.8, 131.4, 131.2, 129.5, 129.1, 128.33, 128.29, 127.8, 123.4, 123.1, 120.7, 115.1, 92.9, 90.9, –1.8.

*n*BuLi (900 μL, 1.40 mmol; 1.55 M solution in hexane) was added slowly over 4 min to a solution of 2-(dimethyl(2-(phenylethynyl)phenyl)silyl)phenol (429 mg, 1.31 mmol) in Et_2O (4 mL) at –75 °C and the mixture was stirred for 30 min. Trifluoromethanesulfonic anhydride (235 μL, 1.40 mmol) and Et_2O (1 mL) were added to it and this was stirred for 35 min at –75 → –50 °C and for 40 min at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/40 and further purified by GPC with $CHCl_3$ to afford compound **4e** as a colorless viscous oil (448 mg, 0.972 mmol; 74% yield).

^{1}H NMR ($CDCl_3$): δ 7.59 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.8 Hz, 2H), 7.51 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.46-7.32 (m, 4H), 7.32-7.21 (m, 4H), 7.19-7.12 (m, 2H), 0.78 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 155.3, 138.8, 137.8, 135.2, 132,7, 131.4, 131.3, 130.9, 129.7, 129.0, 128.4, 128.3, 127.8, 127.4, 123.2, 119.5 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.6 (q, $^{1}J_{CF}$ = 321 Hz), 93.1, 90.8, –1.6. HRMS (FAB) calcd for $C_{23}H_{19}F_3O_3SSi$ (M^+) 460.0771, found 460.0774.

2-(Methyl(phenyl)(2-(phenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4f)



*t*BuLi (4.62 mL, 7.21 mmol; 1.56 M solution in pentane) was added slowly over 10 min to a solution of 1-bromo-2-(phenylethynyl)benzene (926 mg, 3.60 mmol) in THF (7 mL) at –70 °C, and the mixture was stirred for 25 min. Dichloro(methyl)phenylsilane (585 μL, 3.60 mmol) was added to it, and this was stirred for 35 min at –70 °C and for 7 h at room temperature. Imidazole (307 mg, 4.51 mmol) and 2-bromophenol (316 μL, 3.00 mmol) was then added to the mixture at 0 °C with THF (2 mL), and this was stirred for 15 min at 0 °C and for 14 h at room temperature. The reaction mixture was diluted with Et_2O and the precipitates were filtered off. The solvent was removed under vacuum, and the residue was chromatographed on silica gel with EtOAc/hexane = 1/50 to afford (2-bromophenoxy)(methyl)(phenyl)(2-(phenylethynyl)phenyl)silane as a pale yellow viscous oil (1.41 g, 3.00 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 8.09-8.05 (m, 1H), 7.72-7.68 (m, 2H), 7.60-7.57 (m, 1H),

7.51 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.46 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.7 Hz, 1H), 7.43 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.41-7.37 (m, 1H), 7.36-7.31 (m, 2H), 7.29-7.22 (m, 3H), 7.16-7.13 (m, 2H), 7.02 (ddd, $^{3}J_{HH}$ = 8.0 and 7.5 Hz and $^{4}J_{HH}$ = 1.7 Hz, 1H), 6.79 (ddd, $^{3}J_{HH}$ = 8.0 and 7.5 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.74 (dd, $^{3}J_{HH}$ = 8.0 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 0.92 (s, 3H).

*n*BuLi (2.01 mL, 3.16 mmol; 1.57 M solution in hexane) was added slowly over 6 min to a solution of (2-bromophenoxy)(methyl)(phenyl)(2-(phenylethynyl)phenyl)silane (1.41 g, 3.00 mmol) in THF (11 mL) at –70 °C. The mixture was stirred for 30 min at –70 → –60 °C and for 30 min at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/5 to afford 2-(methyl(phenyl)(2-(phenylethynyl)phenyl)silyl)phenol as a yellow viscous oil (1.00 g, 2.56 mmol; 85% yield).

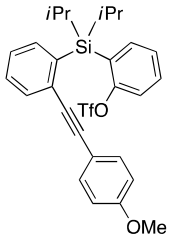
^{1}H NMR ($CDCl_3$): δ 7.63-7.58 (m, 3H), 7.44-7.35 (m, 4H), 7.35-7.26 (m, 4H), 7.25-7.17 (m, 3H), 6.98-6.94 (m, 2H), 6.92 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.80-6.76 (m, 1H), 4.87 (s, 1H), 1.02 (s, 3H).

*n*BuLi (1.79 mL, 2.81 mmol; 1.57 M solution in hexane) was added slowly over 3 min to a solution of 2-(methyl(phenyl)(2-(phenylethynyl)phenyl)silyl)phenol (1.00 g, 2.56 mmol) in Et_2O (10 mL) at –75 °C and the mixture was stirred for 30 min. Trifluoromethanesulfonic anhydride (462 μL, 2.82 mmol) was added to it and this was stirred for 5 h while gradually raising the temperature to 15 °C. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/10 to afford

compound **4f** as a white solid (1.16 g, 2.22 mmol; 87% yield).

^{1}H NMR ($CDCl_3$): δ 7.63-7.58 (m, 1H), 7.57-7.51 (m, 2H), 7.47-7.35 (m, 7H), 7.31-7.16 (m, 6H), 6.97-6.92 (m, 2H), 1.07 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 155.6, 139.0, 137.3, 136.6, 135.5, 134.5, 132.7, 131.8, 131.2, 129.94, 129.86, 129.4, 129.0, 128.3, 128.2, 128.1, 127.8, 127.3, 123.1, 119.4, 118.4 (q, $^1J_{CF}$ = 320 Hz), 93.7, 91.0, –2.6. HRMS (FAB) calcd for $C_{28}H_{21}F_3O_3SSi$ (M^+) 522.0927, found 522.0931.

2-(Diisopropyl(2-((4-methoxyphenyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (**4l**)



*t*BuLi (54.6 mL, 83.5 mmol; 1.53 M solution in pentane) was added slowly over 40 min to a solution of ((2-bromophenyl)ethynyl)trimethylsilane (10.6 g, 41.9 mmol) in THF (70 mL) at –75 °C, and the mixture was stirred for 30 min. Dichlorodiisopropylsilane (7.50 mL, 41.7 mmol) was added to it, and this was stirred for 30 min at –75 °C and for 3.5 h at room temperature. A solution of 2-bromophenol (6.60 mL, 62.6 mmol) and imidazole (4.84 g, 71.1 mmol) in THF (70 mL) was then added to the mixture, and this was stirred for 17 h at 35 °C and for 8 h at 40 °C. After cooled to room temperature, the reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford (2-bromophenoxy)diisopropyl(2-((trimethylsilyl)ethynyl)phenyl)silane as a yellow oil (14.0 g, 30.5 mmol; 73% yield).

^{1}H NMR ($CDCl_3$): δ 7.76-7.70 (m, 1H), 7.58-7.50 (m, 2H), 7.36 (td, $^3J_{HH}$ = 7.8

Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.33 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.09-7.02 (m, 1H), 6.82 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.79 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 1.71 (sept, $^3J_{HH}$ = 7.6 Hz, 2H), 1.12 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.09 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 0.18 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 153.1, 137.8, 136.1, 133.54, 133.48, 129.5, 128.3, 128.2, 127.8, 122.2, 120.2, 115.0, 106.8, 96.8, 18.3, 17.5, 14.2, –0.3.

*n*BuLi (21.5 mL, 33.8 mmol; 1.57 M solution in hexane) was added slowly over 25 min to a solution of (2-bromophenoxy)diisopropyl(2-((trimethylsilyl)ethynyl)phenyl)silane (14.0 g, 30.5 mmol) in THF (100 mL) at –75 °C. The mixture was stirred for 30 min at –75 °C and for 75 min at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford 2-(diisopropyl(2-((trimethylsilyl)ethynyl)phenyl)silyl)phenol as a yellow oil (9.93 g, 26.1 mmol; 86% yield).

^{1}H NMR ($CDCl_3$): δ 7.58 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.53 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.39 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.36 (td, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.33-7.27 (m, 2H), 6.96 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.79 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 4.72 (s, 1H), 1.86 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.04 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^3J_{HH}$ = 7.4 Hz, 6H), 0.08 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 161.3, 137.2, 137.0, 135.3, 134.6, 131.1, 130.2, 129.5, 127.8, 120.3, 118.6, 115.8, 106.7, 96.9, 18.1, 11.6, –0.3.

*n*BuLi (18.1 mL, 28.4 mmol; 1.57 M solution in hexane) was added slowly over 10 min to a solution of 2-(diisopropyl(2-((trimethylsilyl)ethynyl)phenyl)silyl)phenol (9.93 g, 26.1 mmol) in Et_2O (80 mL) at –75 °C and the mixture was stirred for 5 min. Trifluoromethanesulfonic anhydride (4.77 mL, 28.4 mmol) was added to it and this was

stirred for 40 min at –75 °C and for 2.5 h at room temperature. The reaction was quenched with H_2O, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/50 to afford 2-(diisopropyl(2-((trimethylsilyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate as a yellow oil (12.4 g, 24.2 mmol; 93% yield).

^{1}H NMR ($CDCl_3$): δ 7.58-7.51 (m, 2H), 7.50-7.43 (m, 2H), 7.41 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.37-7.27 (m, 3H), 1.88 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.03 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.00 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.00 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.4, 138.9, 136.5, 134.8, 134.5, 131.2, 130.0, 129.1, 127.5, 126.5, 126.4, 118.6 (q, $^5J_{CF}$ = 1.9 Hz), 118.5 (q, $^1J_{CF}$ = 320 Hz), 107.1, 97.0, 18.3, 18.0, 11.5, –0.4.

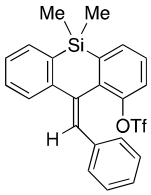
$AgNO_3$ (3.16 g, 18.6 g) and H_2O (33 mL) were added to a solution of 2-(diisopropyl(2-((trimethylsilyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (9.52 g, 18.6 mmol) in acetone (140 mL) and the mixture was stirred for 18 h at room temperature. The reaction was quenched with saturated NaClaq, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/10 to afford 2-((2-ethynylphenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate as a white solid (7.45 g, 16.9 mmol; 91% yield).

^{1}H NMR ($CDCl_3$): δ 7.57 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.56-7.48 (m, 2H), 7.46 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.38-7.33 (m, 2H), 7.31 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 2.72 (s, 1H), 1.88 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.04 (d, $^3J_{HH}$ = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.6, 136.4, 135.7, 134.3, 131.3, 129.2, 128.8, 127.8, 126.6, 126.5, 118.5 (q, $^1J_{CF}$ = 320 Hz), 118.4 (q, $^5J_{CF}$ = 1.9 Hz), 85.4, 80.2, 18.3, 18.1, 11.5.

A solution of 2-((2-ethynylphenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (749 mg, 1.70 mmol) in THF (1.7 mL) was added to a mixture of 4-iodoanisole (477 mg, 2.04 mmol), $Pd(PPh_3)_4$ (58.9 mg, 51.0 μmol), CuI (19.4 mg, 0.102 mmol), and Et_3N (710 μL, 5.09 mmol) in THF (0.5 mL), and the mixture was stirred for 17 h at 45 °C. The reaction mixture was directly passed through a pad of Celite with Et_2O. After removal of the solvent under vacuum, the residue was chromatographed on silica gel with CH_2Cl_2/hexane = 3/10 to afford compound **4l** as a white solid (847 mg, 1.55 mmol; 91% yield).

^{1}H NMR ($CDCl_3$): δ 7.62-7.51 (m, 3H), 7.43-7.30 (m, 4H), 7.29-7.22 (m, 1H), 6.90 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.72 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.79 (s, 3H), 1.86 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.06 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.01 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 159.6, 156.3, 138.8, 136.3, 134.5, 133.5, 132.6, 131.1, 130.5, 129.2, 127.0, 126.5, 126.4, 118.5 (q, $^1J_{CF}$ = 320 Hz), 118.4, 115.5, 113.8, 92.3, 90.7, 55.4, 18.2, 18.0, 11.4. HRMS (FAB) calcd for $C_{28}H_{29}F_3O_4SSi$ (M^+) 546.1502, found 546.1513.

(*Z*)-10-benzylidene-5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]silin-1-yl trifluoromethanesulfonate ((*Z*)-5)



A mixture of 5,5-dimethyldibenzo[*b*,*e*]silin-10(5*H*)-one (1.50 g, 6.29 mmol), [bis(trifluoroacetoxy)iodo]benzene (3.33 g, 7.74 mmol), and $Pd(OAc)_2$ (70.7 mg, 0.315 mmol) in 1,2-dichloroethane (25 mL) was stirred for 3.5 h at 80 °C under air. The mixture was cooled to room temperature and poured into H_2O with EtOAc. This was extracted with EtOAc, and the organic layer was washed with saturated NaClaq, dried over $MgSO_4$,

filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/40 to afford 1-hydroxy-5,5-dimethyldibenzo[*b*,*e*]silin-10(5*H*)-one as a yellow solid (1.48 g, 5.80 mmol; 92% yield).

^{1}H NMR ($CDCl_3$): δ 13.63 (s, 1H), 8.55-8.47 (m, 1H), 7.73-7.55 (m, 3H), 7.52 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.18-7.12 (m, 1H), 7.09 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 0.48 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 193.3, 164.9, 141.2, 140.5, 139.8, 135.8, 135.3, 133.4, 132.5, 130.3, 129.9, 124.6, 120.3, –1.1.

NaH (282 mg, 7.05 mmol; 60 wt% in mineral oil) was added to a solution of 1-hydroxy-5,5-dimethyldibenzo[*b*,*e*]silin-10(5*H*)-one (1.48 g, 5.80 mmol) in THF (16 mL) at 0 °C and the mixture was stirred for 10 min at 0 °C. Chloromethyl methyl ether (567 μL, 7.54 mmol) was then added to it with THF (1 mL) and the mixture was stirred for 12 h at room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/5 to afford 1-(methoxymethoxy)-5,5-dimethyldibenzo[*b*,*e*]silin-10(5*H*)-one as a yellow oil (1.53 g, 5.12 mmol; 88% yield).

^{1}H NMR ($CDCl_3$): δ 8.15-8.07 (m, 1H), 7.66-7.58 (m, 1H), 7.57-7.45 (m, 3H), 7.35-7.27 (m, 2H), 5.30 (s, 2H), 3.55 (s, 3H), 0.49 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 190.4, 157.3, 145.1, 140.7, 136.9, 132.7, 132.5, 132.3, 130.8, 130.1, 128.6, 126.6, 119.1, 95.8, 56.5, –1.6.

Mg turnings (460 mg, 18.9 mmol) was stirred for 34 h at room temperature under nitrogen. Et_2O (3 mL) was added to it and this was cooled to 0 °C. A solution of benzyl bromide (1.48 mL, 12.5 mmol) in Et_2O (22 mL) was added to it slowly over 70 min, and the mixture was stirred for 15 min at 0 °C and for 2.5 h at room temperature. The resulting solution was added slowly over 24 min with Et_2O (2 mL) to a solution of 1-

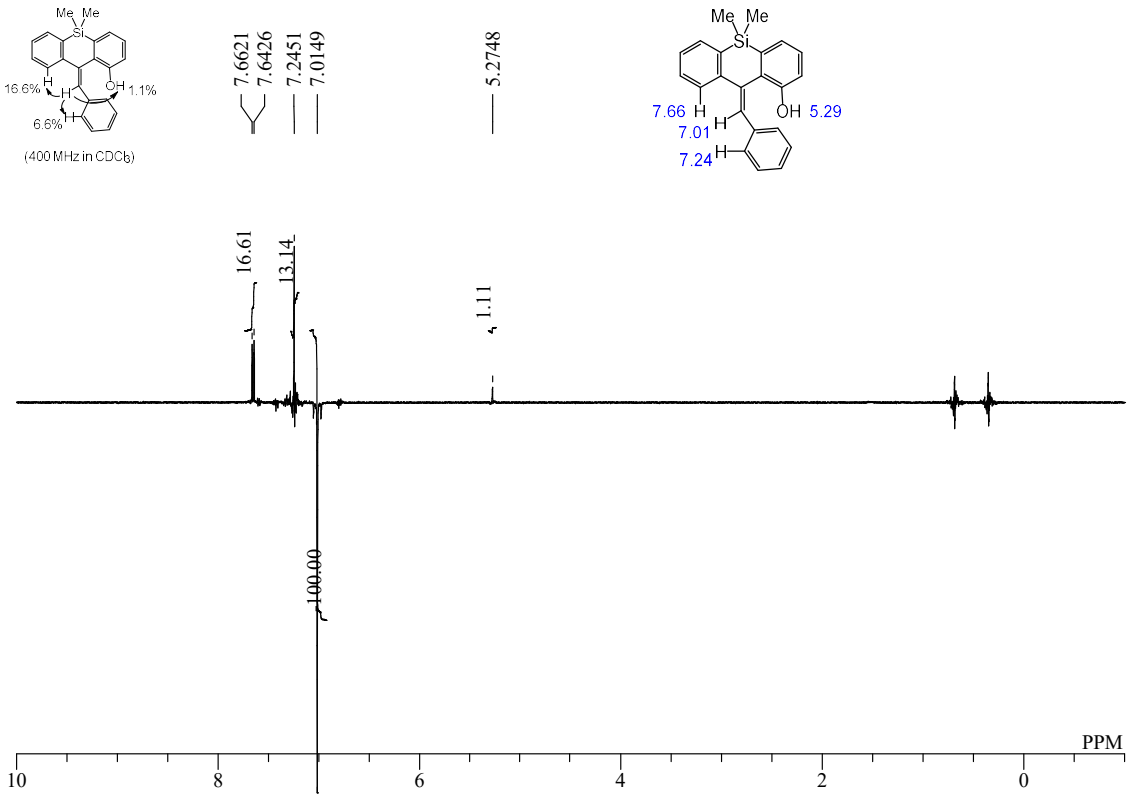
(methoxymethoxy)-5,5-dimethyldibenzo[*b*,*e*]silin-10(5*H*)-one (2.47 g, 8.28 mmol) in THF (9 mL) at 0 °C, and the mixture was stirred for 3 h at 0 °C. The reaction was quenched with saturated NH_4Claq and diluted with H_2O. This was extracted with Et_2O, and the organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. Toluenesulfonic acid (169 mg, 0.888 mmol; monohydrate) and toluene (45 mL) were added to the residue, and the mixture was stirred for 38 h at room temperature. This was washed with saturated NaClaq, and the aqueous layer was extracted with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/24 to afford (*Z*)-10-benzylidene-5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]silin-1-ol as a yellow amorphous (1.65 g, 5.03 mmol; 61% yield) and (*E*)-10-benzylidene-5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]silin-1-ol as a pale yellow amorphous (208 mg, 0.632 mmol; 8% yield). The stereochemistry was determined by the NOE experiment.

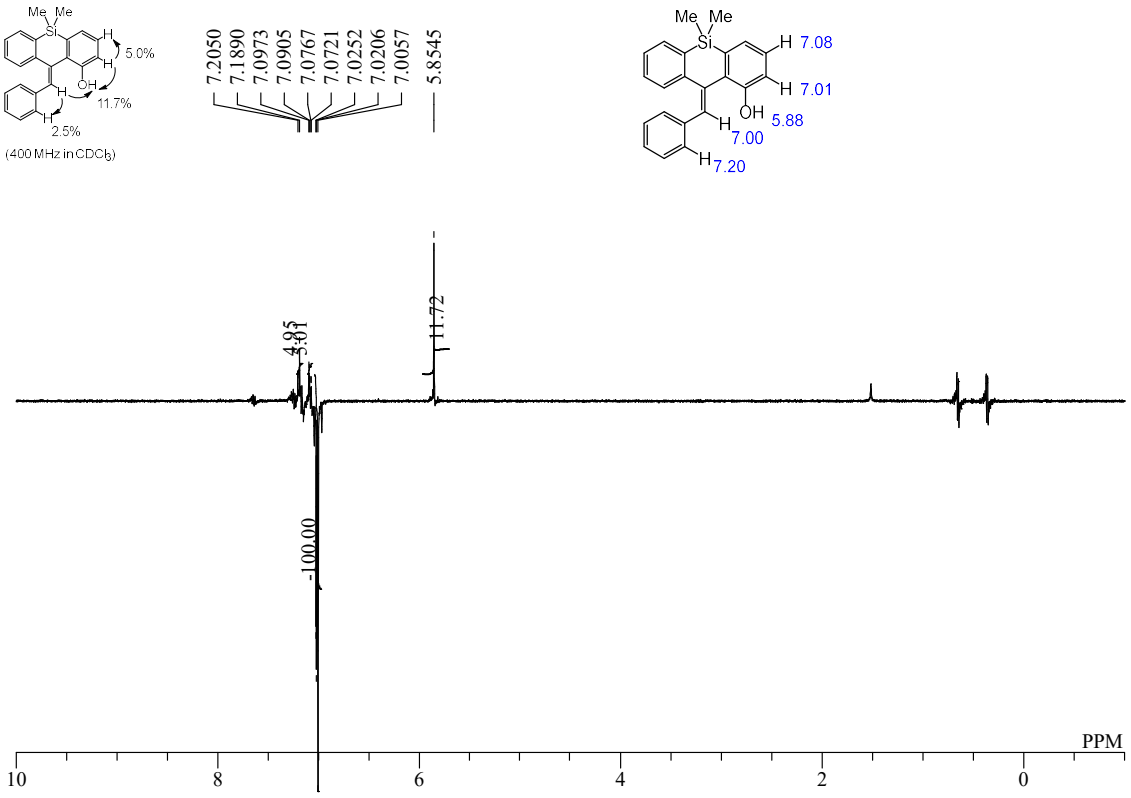
(*Z*)-isomer: ^{1}H NMR ($CDCl_3$): δ 7.66 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.61 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.43 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.32 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.28-7.20 (m, 7H), 7.02 (s, 1H), 6.83-6.77 (m, 1H), 5.29 (bs, 1H), 0.70 (s, 3H), 0.36 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 150.9, 149.5, 138.4, 137.0, 136.1, 135.4, 132.2, 131.3, 129.7, 129.6, 129.0, 128.8, 128.4, 128.3, 126.4, 125.4, 125.1, 117.1, –1.5, –5.5. (*E*)-isomer: ^{1}H NMR ($CDCl_3$): δ 7.68-7.62 (m, 1H), 7.29-7.23 (m, 2H), 7.22-7.06 (m, 8H), 7.04-6.98 (m, 2H), 5.88 (bs, 1H), 0.66 (s, 3H), 0.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 150.9, 144.7, 138.1, 137.4, 137.1, 136.4, 133.7, 133.0, 130.4, 129.8, 128.9, 128.7, 128.3, 128.1, 127.5, 127.0, 124.7, 117.1, –1.6, –5.4.

NaH (102 mg, 2.56 mmol; 60 wt% in mineral oil) was added to a solution of (*Z*)-10-benzylidene-5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]silin-1-ol (560 mg, 1.70 mmol) in

Et_2O (4 mL) at 0 °C and the mixture was stirred for 45 min at 0 °C. Trifluoromethanesulfonic anhydride (336 μL, 2.05 mmol) was then added to it and the mixture was stirred for 4.5 h while gradually raising the temperature to room temperature. This was poured into H_2O and extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/30 to afford compound (*Z*)-**5** as a white solid (670 mg, 1.45 mmol; 86% yield).

^{1}H NMR ($CDCl_3$): δ 7.73 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.66 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.61-7.56 (m, 1H), 7.48 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.38-7.30 (m, 2H), 7.23-7.15 (m, 3H), 7.07-6.97 (m, 4H), 0.72 (s, 3H), 0.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 148.6, 145.6, 141.8, 138.0, 137.6, 135.1, 134.6, 134.3, 132.7, 132.1, 130.0, 128.6, 128.5, 128.3, 127.6, 126.6, 126.2, 122.6, 118.7 (q, $^1J_{CF}$ = 321 Hz), –1.8, –5.5. HRMS (FAB) calcd for $C_{23}H_{19}F_3O_3SSi$ (M^+) 460.0771, found 460.0770.

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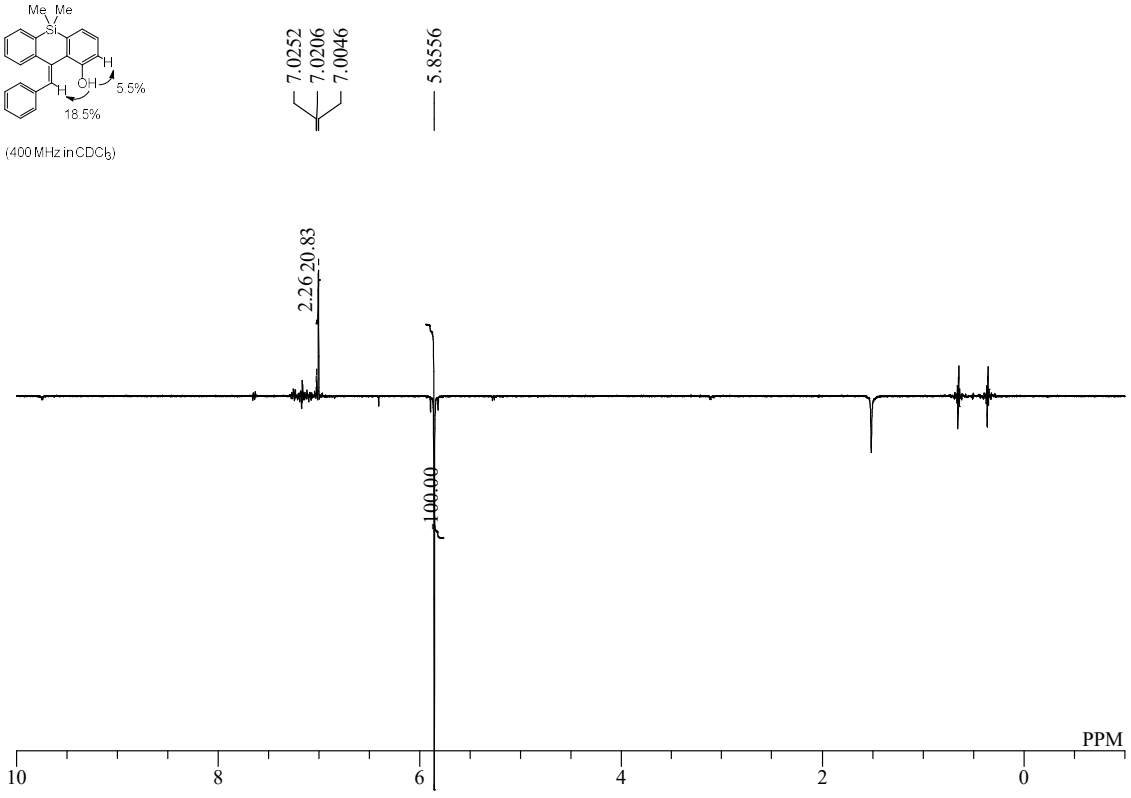
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PPM
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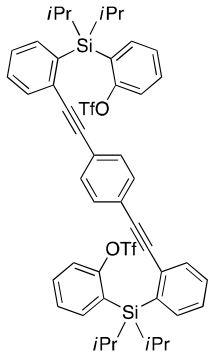
2
0

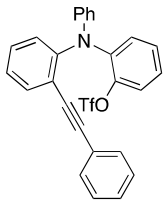
(((1,4-Phenylenebis(ethyne-2,1-diyl))bis(2,1-phenylene))bis(diisopropylsilanediyl))bis(2,1-phenylene) bis(trifluoromethanesulfonate) (6)



A mixture of 2-((2-ethynylphenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (555 mg, 1.26 mmol), 1,4-diiodobenzene (198 mg, 0.600 mmol), $Pd(PPh_3)_4$ (69.3 mg, 60.0 μmol), CuI (22.9 mg, 0.120 mmol), and Et_3N (500 μL, 3.59 mmol) in THF (2.5 mL) was stirred for 19 h at 45 °C. The mixture was diluted with Et_2O and passed through a pad of Celite with Et_2O. This was concentrated under vacuum and the residue was chromatographed on silica gel with hexane to afford compound **6** as a white solid (539 mg, 0.564 mmol; 94% yield).

^{1}H NMR ($CDCl_3$): δ 7.63-7.52 (m, 6H), 7.45-7.32 (m, 8H), 7.29-7.22 (m, 2H), 6.75 (s, 4H), 1.84 (sept, $^3J_{HH}$ = 7.3 Hz, 4H), 1.06 (d, $^3J_{HH}$ = 7.8 Hz, 12H), 1.01 (d, $^3J_{HH}$ = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.7, 136.4, 134.7, 133.7, 131.2, 130.7, 129.9, 129.3, 127.5, 126.5, 126.2, 122.8, 118.49 (q, $^1J_{CF}$ = 320 Hz), 118.46 (q, $^5J_{CF}$ = 1.9 Hz), 93.8, 92.0, 18.2, 17.9, 11.3. HRMS (FAB) calcd for $C_{48}H_{49}F_6O_6S_2Si_2$ ($M+H^+$) 955.2408, found 955.2415.

2-(Phenyl(2-(phenylethynyl)phenyl)amino)phenyl trifluoromethanesulfonate (8)



A mixture of 2-methoxyaniline (3.37 mL, 30.0 mmol), iodobenzene (1.11 mL, 10.0 mmol), $Pd(OAc)_2$ (67.0 mg, 0.298 mmol), P*t*Bu_3•HBF_4 (348 mg, 1.20 mmol), and NaO*t*Bu (1.35 g, 14.0 mmol) in toluene (15 mL) was stirred for 24 h at 100 °C. The mixture was cooled to room temperature and the reaction was quenched with 2 M NH_4Claq. This was extracted with EtOAc, and the organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/10 to afford 2-methoxy-*N*-phenylaniline (CAS 1207-92-7) as a purple oil (1.99 g, 9.99 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 7.34-7.26 (m, 3H), 7.19-7.13 (m, 2H), 6.95 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.92-6.83 (m, 3H), 6.18 (bs, 1H), 3.90 (s, 3H).

A mixture of 2-methoxy-*N*-phenylaniline (996 mg, 5.00 mmol), 1-bromo-2-iodobenzene (663 μL, 5.25 mmol), $Pd(OAc)_2$ (56.0 mg, 0.249 mmol), P*t*Bu_3•HBF_4 (290 mg, 1.00 mmol), and NaO*t*Bu (673 mg, 7.00 mmol) in toluene (8 mL) was stirred for 25 h at 100 °C. The mixture was cooled to room temperature and the reaction was quenched with 2 M NH_4Claq. This was extracted with EtOAc, and the organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford 2-bromo-*N*-(2-methoxyphenyl)-*N*-phenylaniline as a white solid (1.42 g, 4.02 mmol; 80% yield).

^{1}H NMR ($CDCl_3$): δ 7.61 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.25 (d, J_{HH} = 3.7 Hz, 2H), 7.21-

7.13 (m, 4H), 7.03 (dt, J_{HH} = 7.8 and 4.6 Hz, 1H), 6.95 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.91 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.86 (tt, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.1 Hz. 1H), 6.72-6.63 (m, 2H), 3.66 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 155.4, 147.9, 145.9, 135.5, 134.3, 130.3, 128.7, 128.4, 126.5, 126.3, 122.8, 121.4, 120.2, 118.7, 113.2, 55.9.

BBr_3 (6.03 mL, 6.03 mmol; 1.0 M solution in CH_2Cl_2) was added slowly over 10 min to a solution of 2-bromo-*N*-(2-methoxyphenyl)-*N*-phenylaniline (1.42 g, 4.02 mmol) in CH_2Cl_2 (20 mL) at −78 °C, and the mixture was stirred for 1 h at −78 °C and for 15 h at room temperature. The reaction was quenched with saturated $NaHCO_3$aq and extracted with CH_2Cl_2. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/10 to afford 2-((2-bromophenyl)(phenyl)amino)phenol as a white solid (1.12 g, 3.30 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.64 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.36-7.28 (m, 2H), 7.23-7.15 (m, 3H), 7.11 (ddd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz and $^{4}J_{HH}$ = 2.3 Hz, 1H), 7.06 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.03 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.97-6.87 (m, 2H), 6.71-6.63 (m, 2H), 5.79 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 152.8, 147.2, 145.0, 134.3, 132.6, 130.1, 129.3, 129.0, 128.3, 127.8, 127.5, 122.9, 121.6, 121.2, 118.7, 116.6.

Trifluoromethanesulfonic anhydride (650 μL, 3.96 mmol) was added slowly over 4 min to a solution of 2-((2-bromophenyl)(phenyl)amino)phenol (1.12 g, 3.30 mmol) and pyridine (1.06 mL, 13.2 mmol) in CH_2Cl_2 at 0 °C, and the mixture was stirred for 2 h at 0 °C. The reaction was quenched with H_2O and this was extracted with CH_2Cl_2. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford 2-((2-bromophenyl)(phenyl)amino)phenyl

trifluoromethanesulfonate as a white solid (1.54 g, 3.28 mmol; 99% yield).

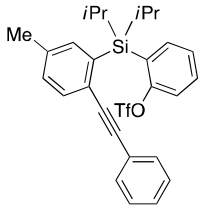
^{1}H NMR ($CDCl_3$): δ 7.62 (dd, $^{3}J_{HH}$ = 8.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.34-7.20 (m, 6H), 7.15 (td, $^{3}J_{HH}$ = 8.0 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.13-7.06 (m, 2H), 7.02 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.89-6.82 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 146.9, 145.0, 143.5, 139.8, 134.9, 130.3, 129.2, 129.1, 128.8, 128.4, 127.3, 124.9, 123.0, 122.9, 122.0, 121.9, 118.6 (q, $^{1}J_{CF}$ = 320 Hz).

Phenylacetylene (205 μL, 1.87 mmol) was added to a mixture of 2-((2-bromophenyl)(phenyl)amino)phenyl trifluoromethanesulfonate (800 mg, 1.70 mmol), $Pd_2(dba)_3$•$CHCl_3$ (17.6 mg, 34.0 μmol Pd), P*t*Bu_3•HBF_4 (10.2 mg, 35.2 μmol), $ZnCl_2$ (23.2 mg, 0.170 mmol) and *i*Pr_2NH (834 μL, 5.95 mmol) in THF (2 mL), and this was stirred for 44 h at 50 °C. $Pd_2(dba)_3$•$CHCl_3$ (8.8 mg, 17 μmol Pd), P*t*Bu_3•HBF_4 (5.2 mg, 18 μmol), $ZnCl_2$ (11.6 mg, 85.1 μmol), and phenylacetylene (102 μL, 0.929 mmol) were added to the reaction mixture and further stirred for 7 h at 50 °C. After cooled to room temperature, the mixture was diluted with EtOAc, and this was passed through a pad of silica gel with EtOAc and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/15 and further purified by GPC with $CHCl_3$ to afford compound **8** as a brown viscous oil (493 mg, 1.00 mmol; 59% yield).

^{1}H NMR ($CDCl_3$): δ 7.54 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.31-7.09 (m, 12H), 7.08-6.95 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 147.4, 143.9, 140.7, 134.5, 131.6, 129.6, 129.3, 129.2, 128.1, 128.0, 127.2, 124.9, 124.8, 123.3, 122.99, 122.97, 122.6, 120.3, 118.6 (q, $^{1}J_{CF}$ = 321 Hz), 95.9, 87.1. HRMS (FAB) calcd for $C_{27}H_{18}F_3NO_3S$ (M^+) 493.0954, found 493.0962.

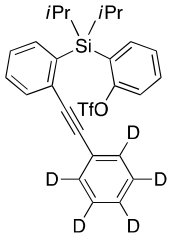
Analytical Data for Other Substrates:

2-(Diisopropyl(5-methyl-2-(phenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4c)



^{1}H NMR ($CDCl_3$): δ 7.58 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.48 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.39-7.34 (m, 2H), 7.32 (s, 1H), 7.28-7.15 (m, 5H), 7.02-6.95 (m, 2H), 2.38 (s, 3H), 1.87 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.06 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.03 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.8, 137.17, 137.15, 134.5, 133.6, 131.2, 131.1, 130.1, 128.1, 128.0, 127.0, 126.48, 126.46, 123.5, 118.5122 (q, $^5J_{CF}$ = 1.9 Hz), 118.5121 (q, $^1J_{CF}$ = 320 Hz), 92.2, 91.5, 21.8, 18.3, 18.0, 11.4. HRMS (FAB) calcd for $C_{28}H_{29}F_3O_3SSi$ (M^+) 530.1553, found 530.1561.

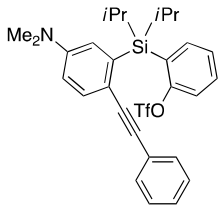
2-(Diisopropyl(2-(pentadeuteriophenylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4d-*d*$_5$)



^{1}H NMR ($CDCl_3$): δ 7.62–7.57 (m, 2H), 7.55 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.43-7.33 (m, 4H), 7.34-7.22 (m, 1H), 1.86 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.07 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.7, 136.4, 134.7, 133.7, 131.1, 130.8 (t, $^1J_{CD}$ = 24.9 Hz), 130.1, 129.3, 127.6 (t, $^1J_{CD}$ = 24.0 Hz), 127.3, 126.5, 126.3, 123.1, 118.49 (q, $^1J_{CF}$ = 320 Hz), 118.45 (q, $^5J_{CF}$ = 1.9 Hz), 92.2,

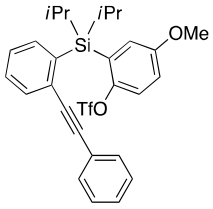
92.0, 18.2, 18.0, 11.4. HRMS (FAB) calcd for $C_{27}H_{23}D_5F_3O_3SSi$ ($M+H^+$) 522.1789, found 522.1785.

2-((5-(Dimethylamino)-2-(phenylethynyl)phenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (4g)



^{1}H NMR ($CDCl_3$): δ 7.61 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.46 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.38-7.33 (m, 2H), 7.26-7.21 (m, 1H), 7.20-7.14 (m, 3H), 7.01-6.93 (m, 2H), 6.86 (d, $^4J_{HH}$ = 2.8 Hz, 1H), 6.74 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 2.7 Hz, 1H), 2.98 (s, 6H), 1.88 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.09 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.05 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 149.1, 139.1, 135.3, 134.8, 131.0, 130.9, 128.0, 127.3, 126.7, 126.4, 124.2, 120.1, 118.6 (q, $^1J_{CF}$ = 320 Hz), 118.4 (q, $^5J_{CF}$ = 1.9 Hz), 116.9, 113.1, 93.2, 90.2, 40.3, 18.4, 18.2, 11.6. HRMS (FAB) calcd for $C_{29}H_{32}F_3NO_3SSi$ (M^+) 559.1819, found 559.1822.

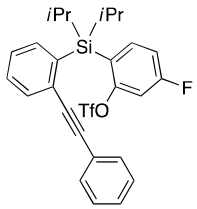
2-(Diisopropyl(2-(phenylethynyl)phenyl)silyl)-4-methoxyphenyl trifluoromethanesulfonate (4h)



^{1}H NMR ($CDCl_3$): δ 7.58 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.55 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.40 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.35 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.26-7.18 (m, 4H), 7.07 (d, $^4J_{HH}$ = 2.9 Hz, 1H), 7.05 (d, $^3J_{HH}$ = 7.1 Hz, 2H), 6.79 (dd, $^3J_{HH}$ = 9.0 Hz and $^4J_{HH}$

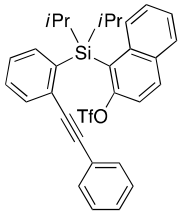
= 2.9 Hz, 1H), 3.68 (s, 3H), 1.86 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.08 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.04 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 157.4, 149.7, 136.3, 134.7, 133.6, 131.2, 130.0, 129.3, 128.12, 128.09, 128.0, 127.4, 123.7, 123.3, 119.6 (q, $^5J_{CF}$ = 1.9 Hz), 118.5 (q, $^1J_{CF}$ = 320 Hz), 115.1, 92.1, 91.9, 55.7, 18.3, 18.0, 11.3. HRMS (FAB) calcd for $C_{28}H_{29}F_3O_4SSi$ (M^+) 546.1502, found 546.1508.

2-(Diisopropyl(2-(phenylethynyl)phenyl)silyl)-5-fluorophenyl trifluoromethanesulfonate (4i)



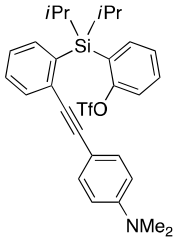
^{1}H NMR ($CDCl_3$): δ 7.62-7.52 (m, 3H), 7.41 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.36 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.28-7.19 (m, 3H), 7.12 (dd, $^3J_{HF}$ = 9.6 Hz and $^4J_{HH}$ = 2.3 Hz), 7.05-7.00 (m, 2H), 6.97 (td, ^3J = 8.0 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 1.84 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.06 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.01 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 163.7 (d, $^1J_{CF}$ = 252 Hz), 156.0 (d, $^3J_{CF}$ = 10.5 Hz), 139.5 (d, $^3J_{CF}$ = 8.6 Hz), 136.3, 134.4, 133.7, 131.1, 130.0, 129.4, 128.3, 128.2, 127.4, 123.1, 121.8 (d, $^4J_{CF}$ = 3.8 Hz), 118.4 (q, $^1J_{CF}$ = 320 Hz), 113.9 (d, $^2J_{CF}$ = 19.2 Hz), 107.1 (dq, $^2J_{CF}$ = 25.9 Hz and $^5J_{CF}$ = 1.9 Hz), 92.3, 91.9, 18.2, 17.9, 11.3. HRMS (FAB) calcd for $C_{27}H_{27}F_4O_3SSi$ ($M+H^+$) 535.1381, found 535.1386.

1-(Diisopropyl(2-(phenylethynyl)phenyl)silyl)-2-naphthyl trifluoromethanesulfonate (4j)



^{1}H NMR ($CDCl_3$): δ 7.92 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.76-7.68 (m, 2H), 7.61-7.55 (m, 1H), 7.52-7.46 (m, 1H), 7.43-7.33 (m, 4H), 7.22-7.13 (m, 2H), 7.10 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 6.71 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 2.09 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.15 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.03 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 155.2, 139.0, 137.4, 135.4, 133.6, 132.8, 132.0, 131.1, 130.5, 129.5, 129.0, 128.5, 128.0, 127.9, 127.4, 126.1, 126.0, 123.2, 122.9, 118.8 (q, $^{1}J_{CF}$ = 321 Hz), 117.3 (q, $^{5}J_{CF}$ = 2.9 Hz), 91.9, 91.8, 19.0, 18.7, 13.2. HRMS (FAB) calcd for $C_{31}H_{30}F_3O_3SSi$ ($M+H^+$) 567.1632, found 567.1637.

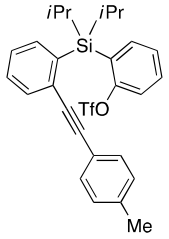
2-((2-((4-(Dimethylamino)phenyl)ethynyl)phenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (4k)



^{1}H NMR ($CDCl_3$): δ 7.60 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.55 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.51 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.43-7.33 (m, 3H), 7.32-7.23 (m, 2H), 6.87 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.52 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 2.95 (s, 6H), 1.88 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.07 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H), 1.02 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 150.1, 138.9, 136.4, 134.1, 133.3, 132.3, 131.1, 131.0, 129.2, 126.51, 126.46, 126.4, 118.5 (q, $^{1}J_{CF}$ = 320 Hz), 118.4 (q, $^{5}J_{CF}$ = 1.9 Hz), 111.7, 110.4, 93.6, 90.1, 40.3, 18.3,

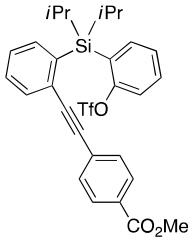
18.0, 11.4. HRMS (FAB) calcd for $C_{29}H_{32}F_3NO_3SSi$ (M^+) 559.1819, found 559.1826.

2-(Diisopropyl(2-((4-methylphenyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4m)



^{1}H NMR ($CDCl_3$): δ 7.62-7.56 (m, 2H), 7.54 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.43-7.31 (m, 4H), 7.30-7.23 (m, 1H), 7.00 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.86 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 2.31 (s, 3H), 1.86 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.06 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 138.8, 138.2, 136.4, 134.6, 133.6, 131.14, 131.10, 130.3, 129.3, 128.9, 127.2, 126.5, 126.3, 120.3, 118.50 (q, $^1J_{CF}$ = 320 Hz), 118.47 (q, $^5J_{CF}$ = 1.9 Hz), 92.5, 91.4, 21.6, 18.2, 18.0, 11.4. HRMS (FAB) calcd for $C_{28}H_{29}F_3O_3SSi$ (M^+) 530.1553, found 530.1555.

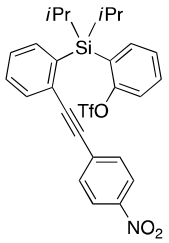
2-(Diisopropyl(2-((4-methoxycarbonylphenyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4n)



^{1}H NMR ($CDCl_3$): δ 7.85 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.63-7.56 (m, 3H), 7.46-7.33 (m, 4H), 7.30-7.23 (m, 1H), 6.97 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 3.91 (s, 3H), 1.83 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.06 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.01 (d, $^3J_{HH}$ = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 166.6, 156.3, 138.5, 136.3, 134.9, 133.8, 131.3, 131.0, 129.5, 129.4, 129.3, 129.2, 127.9,

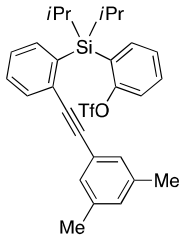
127.8, 126.5, 126.1, 118.48 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.45 (q, $^{1}J_{CF}$ = 320 Hz), 95.0, 91.4, 52.2, 18.1, 17.8, 11.2. HRMS (FAB) calcd for $C_{29}H_{30}F_3O_5SSi$ ($M+H^+$) 575.1530, found 575.1534.

2-(Diisopropyl(2-((4-nitrophenyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4o)



^{1}H NMR ($CDCl_3$): δ 8.04 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.68-7.56 (m, 3H), 7.48-7.41 (m, 2H), 7.41-7.35 (m, 2H), 7.33-7.26 (m, 1H), 7.00 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 1.82 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.05 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.00 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 146.9, 138.5, 136.3, 135.1, 134.0, 131.8, 131.4, 130.0, 129.4, 128.9, 128.3, 126.6, 126.1, 123.3, 118.6 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.4 (q, $^{1}J_{CF}$ = 320 Hz), 97.3, 90.3, 18.1, 17.7, 11.1. HRMS (FAB) calcd for $C_{27}H_{27}F_3NO_5SSi$ ($M+H^+$) 562.1326, found 562.1337.

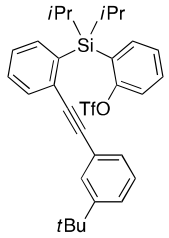
2-((2-((3,5-Dimethylphenyl)ethynyl)phenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (4p)



^{1}H NMR ($CDCl_3$): δ 7.61 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.59-7.52 (m, 2H), 7.44-7.37 (m, 3H), 7.35 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.31-7.26 (m, 1H), 6.86 (s, 1H), 6.52 (s, 2H), 2.22 (s, 6H), 1.85 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.00 (d,

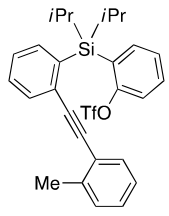
$^{3}J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.4, 139.0, 137.6, 136.4, 134.5, 133.7, 131.1, 130.4, 130.1, 129.3, 128.8, 127.2, 126.5, 126.3, 122.9, 118.52 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.51 (q, $^{1}J_{CF}$ = 320 Hz), 92.9, 91.4, 21.2, 18.3, 18.0, 11.4. HRMS (FAB) calcd for $C_{29}H_{32}F_3O_3SSi$ ($M+H^+$) 545.1788, found 545.1789.

2-((2-((3-(*tert*-Butyl)phenyl)ethynyl)phenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (4q)



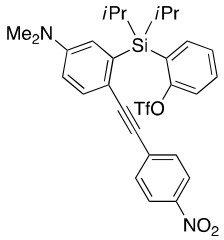
^{1}H NMR ($CDCl_3$): δ 7.63-7.57 (m, 2H), 7.54 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.40 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.37-7.30 (m, 3H), 7.30-7.21 (m, 2H), 7.16-7.10 (m, 2H), 6.80 (dt, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 1.89 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.29 (s, 9H), 1.07 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H), 1.04 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 151.1, 138.7, 136.4, 134.7, 133.7, 131.1, 130.2, 129.3, 128.4, 128.2, 127.9, 127.2, 126.5, 126.4, 125.4, 122.9, 118.49 (q, $^{1}J_{CF}$ = 320 Hz), 118.47 (q, $^{5}J_{CF}$ = 1.9 Hz), 92.7, 91.4, 34.7, 31.3, 18.3, 18.0, 11.4. HRMS (FAB) calcd for $C_{31}H_{35}F_3O_3SSi$ (M^+) 572.2023, found 572.2030.

2-(Diisopropyl(2-((2-methylphenyl)ethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4r)



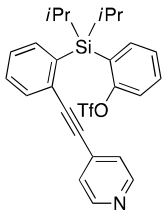
^{1}H NMR ($CDCl_3$): δ 7.63-7.53 (m, 3H), 7.43-7.32 (m, 4H), 7.29-7.23 (m, 1H), 7.18-7.10 (m, 2H), 7.02-6.96 (m, 1H), 6.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 2.33 (s, 3H), 1.89 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.03 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 140.1, 138.7, 136.4, 134.5, 133.8, 131.3, 131.2, 130.3, 129.4, 129.3, 128.2, 127.3, 126.5, 126.3, 125.3, 123.1, 118.49 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.48 (q, $^{1}J_{CF}$ = 320 Hz), 95.8, 91.3, 20.6, 18.3, 18.0, 11.4. HRMS (FAB) calcd for $C_{28}H_{30}F_3O_3SSi$ ($M+H^+$) 531.1632, found 531.1636.

2-((5-(Dimethylamino)-2-((4-nitrophenyl)ethynyl)phenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (**4s**)



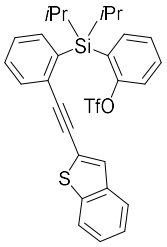
^{1}H NMR ($CDCl_3$): δ 8.03-7.99 (m, 2H), 7.66-7.60 (m, 1H), 7.49 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H), 7.42-7.35 (m, 2H), 7.28 (ddd, $^{3}J_{HH}$ = 7.6 and 6.1 Hz and $^{4}J_{HH}$ = 2.4 Hz, 1H), 6.98-6.92 (m, 2H), 6.89 (d, $^{4}J_{HH}$ = 2.6 Hz. 1H), 6.75 (dd, $^{3}J_{HH}$ = 8.5 Hz and $^{4}J_{HH}$ = 2.6 Hz, 1H), 3.03 (s, 6H), 1.83 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.08 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 1.03 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 149.6, 146.1, 138.9, 135.7, 135.5, 131.3, 131.1, 126.5, 126.4, 123.3, 119.7, 118.54 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.47 (q, $^{1}J_{CF}$ = 320 Hz), 115.1, 112.8, 99.7, 89.2, 40.1, 18.2, 17.9, 11.3. HRMS (FAB) calcd for $C_{29}H_{31}F_3N_2O_5SSi$ (M^+) 604.1670, found 604.1670.

2-(Diisopropyl(2-(4-pyridylethynyl)phenyl)silyl)phenyl trifluoromethanesulfonate (4t)



^{1}H NMR (acetone-d_6): δ 8.45 (d, $^{3}J_{HH}$ = 5.0 Hz, 2H), 7.79-7.63 (m, 3H), 7.58 (ddd, $^{3}J_{HH}$ = 8.2 and 7.3 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.55-7.42 (m, 4H), 6.84 (dd, $^{3}J_{HH}$ = 4.6 Hz and $^{4}J_{HH}$ = 1.8 Hz, 2H), 1.92 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). 1.02 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR (acetone-d_6): δ 157.1, 150.5, 139.4, 137.1, 135.7, 134.8, 132.8, 131.4, 130.4, 129.6, 129.2, 127.9, 126.4, 125.6, 119.3 (q, $^{5}J_{CF}$ = 1.9 Hz), 119.2 (q, $^{1}J_{CF}$ = 319 Hz), 96.7, 90.1, 18.4, 18.1, 11.7. HRMS (FAB) calcd for $C_{26}H_{27}F_3NO_3SSi$ ($M+H^+$) 518.1428, found 518.1434.

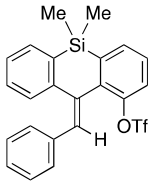
2-((2-(benzo[*b*]thiophen-2-ylethynyl)phenyl)diisopropylsilyl)phenyl trifluoromethanesulfonate (4u)



^{1}H NMR ($CDCl_3$): δ 7.74-7.70 (m, 1H), 7.69-7.65 (m, 1H), 7.61 (d, $^{3}J_{HH}$ = 7.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.45-7.36 (m, 4H), 7.35-7.31 (m, 2H), 7.31-7.26 (m, 1H), 6.97 (s, 1H), 1.89 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.08 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). 1.04 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.3, 140.3, 139.1, 138.7, 136.5, 135.1, 133.5, 131.3, 129.3, 129.2, 128.4, 127.8, 126.6, 126.0, 125.4, 124.7, 126.8, 123.2, 122.0, 118.6 (q, $^{5}J_{CF}$

= 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 320 Hz), 97.4, 85.9, 18.2, 18.0, 11.4. HRMS (FAB) calcd for $C_{29}H_{27}F_3O_3S_2Si$ (M^+) 572.1117, found 572.1129.

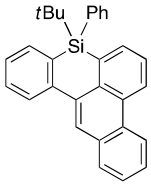
(*E*)-10-benzylidene-5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]silin-1-yl trifluoromethanesulfonate ((*E*)-5)



^{1}H NMR ($CDCl_3$): δ 7.65-7.61 (m, 1H), 7.59 (dd, $^{3}J_{HH}$ = 6.4 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.37-7.29 (m, 2H), 7.28-7.22 (m, 2H), 7.21-7.06 (m, 6H), 7.04 (s, 1H), 0.70 (s, 3H), 0.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.8, 144.0, 141.4, 141.3, 136.7, 136.1, 134.7, 134.2, 132.7, 132.3, 130.1, 129.7, 129.0, 128.2, 127.9, 127.4, 126.9, 122.9, 118.9 (q, $^{1}J_{CF}$ = 321 Hz), –1.8, –5.5. HRMS (FAB) calcd for $C_{23}H_{19}F_3O_3SSi$ (M^+) 460.0771, found 460.0779. The stereochemistry was further confirmed by X-ray crystallographic analysis.

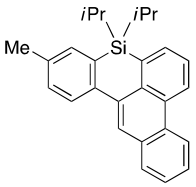
General Procedure for Scheme 5 and Equations 2–5.

Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 9.8 μmol) and compound **4** (0.200 mmol) in DMF (0.40 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and this was washed with H_2O for three times. The aqueous layer was extracted with EtOAc, and the combined organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC to afford compound **3**.



Compound 3b. EtOAc/hexane = 1/50 was used for preparative TLC. White solid. 94% yield (78.2 mg).

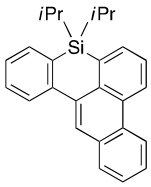
^{1}H NMR ($CDCl_3$): δ 8.85 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 8.70 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 8.54 (s, 1H), 8.23 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.01 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.86 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 2H), 7.77 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.71-7.52 (m, 5H), 7.48-7.36 (m, 3H), 7.32 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 0.94 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 144.5, 137.0, 136.2, 135.4, 135.3, 134.7, 133.9, 132.3, 132.1, 131.3, 130.6, 130.3, 130.1, 129.6, 129.3, 128.0, 127.2, 127.03, 126.95, 126.6, 126.5, 125.4, 124.7, 122.6, 27.2, 19.9. HRMS (FAB) calcd for $C_{30}H_{26}Si$ (M^+) 414.1798, found 414.1799.



Compound 3c. EtOAc/hexane = 1/55 was used for preparative TLC. Pale yellow solid. 96% yield (73.2 mg).

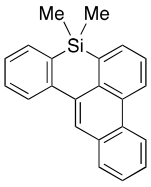
^{1}H NMR ($CDCl_3$): δ 8.85 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 8.67 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 8.46 (s, 1H), 8.16 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.96 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.92 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.70 (dd, $^{3}J_{HH}$ = 8.2 and 6.4 Hz, 1H), 7.67-7.57 (m, 2H), 7.55 (d, $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 2.3 Hz, 1H), 2.45 (s, 3H), 1.49 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^{3}J_{HH}$ = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 141.9, 136.0, 135.6, 134.7, 133.7,

133.4, 132.2, 131.6, 131.1, 131.0, 130.7, 130.5, 129.1, 127.1, 126.9, 126.7, 125.9, 125.3, 124.6, 122.5, 21.3, 18.3, 18.1, 13.1. HRMS (FAB) calcd for $C_{27}H_{29}Si$ ($M+H^+$) 381.2033, found 381.2041.



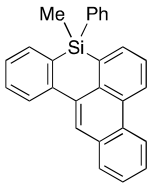
Compound 3d. EtOAc/hexane = 1/50 was used for preparative TLC. White solid. 93% yield (68.2 mg).

^{1}H NMR ($CDCl_3$): δ 8.85 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.68 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.49 (s, 1H), 8.25 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.97 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.93 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.78 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.71 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.68-7.58 (m, 2H), 7.56 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.39 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 1.50 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 144.7, 135.5, 134.2, 133.7, 133.5, 132.1, 131.8, 131.2, 130.6, 130.5, 130.0, 129.2, 127.2, 126.93, 126.89, 126.6, 126.5, 125.4, 124.6, 122.5, 18.2, 18.1, 13.0. HRMS (FAB) calcd for $C_{26}H_{27}Si$ ($M+H^+$) 367.1877, found 367.1880.



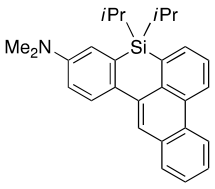
Compound 3e (CAS 2050036-72-9)**.** The reaction was conducted on 0.300 mmol scale. EtOAc/hexane = 1/50 and then hexane were used for preparative TLC. White solid. 94% yield (87.6 mg).

^{1}H NMR ($CDCl_3$): δ 8.90-8.84 (m, 1H), 8.71 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.57 (s, 1H), 8.26 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.05-7.99 (m, 1H), 7.98 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.80 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.76 (dd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.72-7.55 (m, 3H), 7.46 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 0.55 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 143.2, 134.8, 134.1, 133.8, 133.6, 133.1, 133.0, 132.1, 131.2, 130.6, 130.1, 129.3, 127.1, 127.03, 126.96, 126.9, 126.6, 125.8, 124.7, 122.6, –0.4.



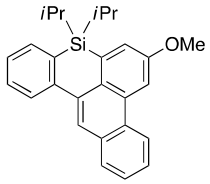
Compound 3f. CH_2Cl_2/hexane = 1/8 was used for preparative TLC. White amorphous. 92% yield (68.6 mg).

^{1}H NMR ($CDCl_3$): δ 8.86 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 8.69 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.57 (s, 1H), 8.26 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.01 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.91 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.75-7.54 (m, 5H), 7.52-7.43 (m, 2H), 7.39 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.34-7.23 (m, 3H), 0.86 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.7, 137.4, 134.8, 134.7, 134.4, 134.0, 133.10, 133.05, 132.1, 131.7, 131.2, 130.6, 130.4, 129.5, 129.3, 128.0, 127.13, 127.11, 127.0, 126.8, 125.9, 125.0, 122.6, –2.7. HRMS (FAB) calcd for $C_{27}H_{20}Si$ (M^+) 372.1329, found 372.1333.



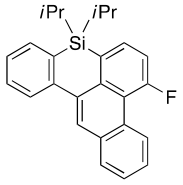
Compound 3g. EtOAc/hexane = 1/20 was used for preparative TLC and the product was further purified by GPC with $CHCl_3$. Yellow oil. 92% yield (75.2 mg).

^{1}H NMR ($CDCl_3$): δ 8.84 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.69-8.62 (m, 1H), 8.37 (s, 1H), 8.17 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 7.95-7.88 (m, 2H), 7.68 (dd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.62-7.53 (m, 2H), 7.05 (d, $^{4}J_{HH}$ = 3.2 Hz, 1H), 6.97 (dd, $^{3}J_{HH}$ = 9.2 Hz and $^{4}J_{HH}$ = 2.8 Hz, 1H), 3.07 (s, 6H), 1.50 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.04 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.99 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 148.6, 135.5, 134.1, 133.3, 132.8, 132.5, 132.3, 130.8, 130.5, 130.4, 128.7, 128.1, 126.7, 126.0, 125.1, 124.5, 124.1, 122.5, 116.8, 114.7, 40.4, 18.4, 18.1, 13.1. HRMS (FAB) calcd for $C_{28}H_{32}NSi$ ($M+H^+$) 410.2299, found 410.2298.



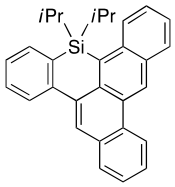
Compound 3h. EtOAc/hexane = 1/25 was used for preparative TLC and the product was further purified by GPC with $CHCl_3$. Pale yellow oil. 91% yield (72.1 mg).

^{1}H NMR ($CDCl_3$): δ 8.64-8.58 (m, 1H), 8.38 (s, 1H), 8.26 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.21 (d, $^{4}J_{HH}$ = 2.7 Hz, 1H), 7.99-7.92 (m, 1H), 7.75 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.66-7.51 (m, 4H), 7.38 (td, $^{3}J_{HH}$ = 7.1 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 4.08 (s, 3H), 1.49 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.9, 144.7, 134.1, 133.6, 132.8, 132.6, 132.5, 131.4, 130.6, 130.02, 130.00, 129.2, 127.1, 127.0, 126.52, 126.48, 124.4, 122.8, 122.6, 105.9, 55.4, 18.1, 18.0, 13.0. HRMS (FAB) calcd for $C_{27}H_{29}OSi$ ($M+H^+$) 397.1982, found 397.1989.



Compound 3i. The reaction was conducted at 120 °C. EtOAc/hexane = 1/40 was used for preparative TLC and the product was further purified by recrystallization from MeOH/CH_2Cl_2. Pale yellow solid. 78% yield (59.8 mg).

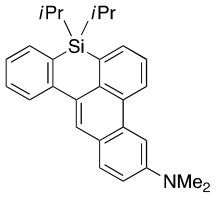
^{1}H NMR ($CDCl_3$): δ 9.16-9.09 (m, 1H), 8.47 (s, 1H), 8.17 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.03-7.96 (m, 1H), 7.86 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HF}$ = 6.0 Hz, 1H), 7.76 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.71-7.61 (m, 2H), 7.56 (ddd, $^3J_{HH}$ = 8.2 and 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.45 (dd, $^3J_{HF}$ = 14.2 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 7.40 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 1.49 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.01 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.96 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 163.3 (d, $^1J_{CF}$ = 255 Hz), 144.6, 138.6 (d, J_{CF} = 3.8 Hz), 134.0, 133.6 (d, J_{CF} = 2.9 Hz), 133.5 (d, $^3J_{CF}$ = 10.5 Hz), 132.6, 131.6, 130.1, 129.1, 129.0 (d, J_{CF} = 4.8 Hz), 128.4 (d, J_{CF} = 1.9 Hz), 127.8 (d, $^2J_{CF}$ = 27.8 Hz), 127.6, 127.5 (d, J_{CF} = 2.9 Hz), 127.2 (d, J_{CF} = 1.9 Hz), 126.7, 125.9 (d, J_{CF} = 4.8 Hz), 120.5 (d, $^3J_{CF}$ = 7.7 Hz), 112.8 (d, $^2J_{CF}$ = 24.0 Hz), 18.1, 18.0, 12.9. HRMS (FAB) calcd for $C_{26}H_{26}FSi$ ($M+H^+$) 385.1782, found 385.1789.



Compound 3j. The reaction was conducted at 120 °C. EtOAc/hexane = 1/20 was used for preparative TLC and the product was further purified by GPC with $CHCl_3$ followed by recrystallization from MeOH/$CHCl_3$. Yellow solid. 75% yield (62.5 mg).

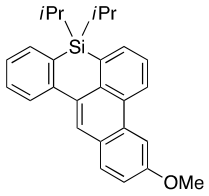
^{1}H NMR ($CDCl_3$): δ 9.37 (s, 1H), 8.82 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.47-8.40 (m, 2H),

8.30 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.20-8.14 (m, 1H), 7.94-7.86 (m, 2H), 7.70-7.54 (m, 5H), 7.43 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 1.90 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.18 (d, $^3J_{HH}$ = 7.4 Hz, 6H), 0.85 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 144.6, 136.7, 136.0, 135.0, 133.8, 131.7, 131.59, 131.55, 130.8, 129.9, 129.6, 129.2, 129.0, 128.0, 127.4, 127.3, 126.5, 126.3, 125.64, 125.60, 125.3, 122.9, 19.5, 19.1, 15.2. HRMS (FAB) calcd for $C_{30}H_{28}Si$ (M^+) 416.1955, found 416.1955.



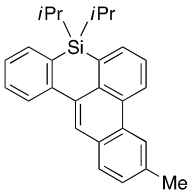
Compound 3k. The reaction was conducted on 0.400 mmol scale. EtOAc/hexane = 1/20 was used for preparative TLC. Orange solid. 73% yield (119 mg).

^{1}H NMR ($CDCl_3$): δ 8.77 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.38 (s, 1H), 8.21 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.89 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.84 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.80 (s, 1H), 7.73 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.65 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.52 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 7.20 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 3.18 (s, 6H), 1.48 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.97 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 149.7, 145.2, 136.2, 134.1, 133.3, 132.5, 130.9, 130.23, 130.17, 129.84, 129.79, 129.5, 126.6, 126.5, 125.7, 124.6, 124.5, 124.1, 115.2, 103.0, 40.9, 18.2, 18.1, 13.1. HRMS (FAB) calcd for $C_{28}H_{31}NSi$ (M^+) 409.2220, found 409.2228.



Compound 3l. The reaction was conducted on 0.400 mmol scale. CH_2Cl_2/hexane = 1/4 was used for preparative TLC. Orange solid. 94% yield (149 mg).

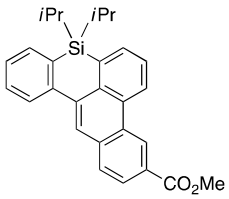
^{1}H NMR ($CDCl_3$): δ 8.76 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 8.44 (s, 1H), 8.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.05 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 7.93 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.75 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.69 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.58-7.50 (m, 1H), 7.36 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.26 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 4.05 (s, 3H), 1.49 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.02 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 0.98 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 159.0, 144.8, 135.8, 134.1, 133.6, 132.5, 131.4, 131.3, 130.7, 130.5, 130.0, 129.9, 126.84, 126.82, 126.3, 126.1, 125.0, 124.6, 117.1, 104.0, 55.6, 18.2, 18.1, 13.0. HRMS (FAB) calcd for $C_{27}H_{28}OSi$ (M^+) 396.1904, found 396.1908.



Compound 3m. The reaction was conducted on 0.400 mmol scale. EtOAc/hexane = 1/55 was used for preparative TLC. Pale yellow solid. 96% yield (146 mg).

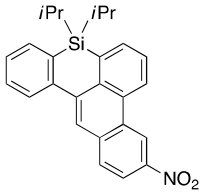
^{1}H NMR ($CDCl_3$): δ 8.84 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 8.46 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.45 (s, 1H), 8.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.91 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.75 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.69 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.59-7.51 (m, 1H), 7.44 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.37 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 2.64 (s, 3H), 1.49

(sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.97 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 144.8, 136.7, 135.7, 134.1, 133.3, 132.8, 131.6, 131.2, 130.4, 130.2, 130.0, 129.9, 129.1, 128.6, 127.0, 126.4, 126.3, 125.2, 124.6, 122.3, 22.4, 18.2, 18.1, 13.0. HRMS (FAB) calcd for $C_{27}H_{29}Si$ ($M+H^+$) 381.2033, found 381.2039.



Compound 3n. The reaction was conducted on 0.400 mmol scale. EtOAc/hexane = 1/12 was used for preparative TLC. Pale yellow solid. 93% yield (158 mg).

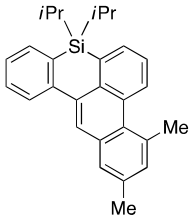
^{1}H NMR ($CDCl_3$): δ 9.43 (s, 1H), 8.95 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 8.50 (s, 1H), 8.26 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 8.22 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 8.00 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.97 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.82-7.73 (m, 2H), 7.62-7.54 (m, 1H), 7.42 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 4.04 (s, 3H), 1.51 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 167.4, 144.1, 136.1, 135.5, 134.8, 134.2, 133.9, 132.2, 130.9, 130.8, 130.4, 130.0, 129.1, 127.9, 127.4, 127.0, 126.7, 125.9, 125.7, 125.0, 124.8, 52.3, 18.1, 18.0, 12.9. HRMS (FAB) calcd for $C_{28}H_{29}O_2Si$ ($M+H^+$) 425.1931, found 425.1941.



Compound 3o. The reaction was conducted on 0.400 mmol scale. EtOAc/hexane = 1/50 was used for preparative TLC. Yellow solid. 85% yield (141 mg).

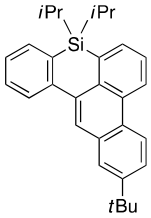
^{1}H NMR ($CDCl_3$): δ 9.61 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H), 8.91 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 8.52

(s, 1H), 8.40 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.9 Hz, 1H), 8.26 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 8.07 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 8.03 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H), 7.85-7.77 (m, 2H), 7.60 (td, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.46 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 1.52 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.97 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 146.0, 143.6, 137.9, 135.69, 135.67, 134.7, 134.3, 132.5, 131.5, 130.7, 130.5, 130.2, 130.1, 127.7, 127.5, 126.5, 125.0, 124.8, 120.7, 119.0, 18.1, 18.0, 12.9. HRMS (FAB) calcd for $C_{26}H_{26}NO_2Si$ ($M+H^+$) 412.1727, found 412.1730.



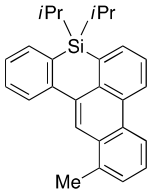
Compound 3p. The reaction was conducted on 0.400 mmol scale. EtOAc/hexane = 1/55 was used for preparative TLC. Pale yellow solid. 94% yield (148 mg).

^{1}H NMR ($CDCl_3$): δ 8.91 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.33 (s, 1H), 8.15 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.88 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.75 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.634 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.631 (s, 1H), 7.57-7.50 (m, 1H), 7.37 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.34 (s, 1H), 3.10 (s, 3H), 2.54 (s, 3H), 1.50 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.97 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 144.9, 136.4, 135.7, 134.6, 134.0, 133.9, 133.39, 133.37, 132.3, 131.9, 131.7, 129.9, 129.6, 129.3, 128.9, 127.7, 127.5, 127.4, 126.4, 124.0, 26.9, 21.2, 18.2, 18.1, 13.1. HRMS (FAB) calcd for $C_{28}H_{31}Si$ ($M+H^+$) 395.2190, found 395.2196.



Compound 3q. EtOAc/hexane = 1/50 was used for preparative TLC and the product was further purified by GPC with $CHCl_3$. Pale yellow solid. 89% yield (75.2mg).

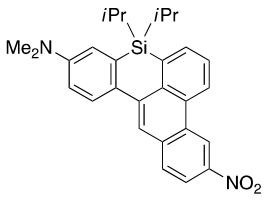
^{1}H NMR ($CDCl_3$): δ 8.82 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 8.61 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 8.49 (s, 1H), 8.27 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.93 (d, $^4J_{HH}$ = 1.8 Hz, 1H), 7.90 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.76 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.73 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 7.69 (dd, $^3J_{HH}$ = 8.2 and 6.4 Hz, 1H), 7.55 (ddd, $^3J_{HH}$ = 8.2 and 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.38 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 1.494 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.488 (s, 9H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.97 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 149.8, 144.9, 135.4, 134.1, 133.7, 133.1, 131.9, 131.8, 130.5, 130.4, 130.0, 129.1, 127.2, 127.0, 126.4, 125.4, 125.3, 124.8, 124.5, 122.4, 34.9, 31.5, 18.2, 18.1, 13.0. HRMS (FAB) calcd for $C_{30}H_{35}Si$ ($M+H^+$) 423.2503, found 423.2510.



Compound 3r. The reaction was conducted on 0.400 mmol scale. EtOAc/hexane = 1/55 was used for preparative TLC. Pale yellow solid. 89% yield (136 mg).

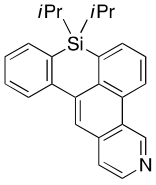
^{1}H NMR ($CDCl_3$): δ 8.86 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.69 (s, 1H), 8.58 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 8.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.93 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.77 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.71 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.62-7.50 (m, 2H), 7.46 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.40 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 2.87 (s, 3H), 1.50

(sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 145.2, 135.4, 135.1, 134.2, 133.4, 133.3, 131.9, 131.3, 130.9, 130.8, 130.3, 130.0, 128.1, 127.4, 126.6, 126.4, 125.4, 124.9, 122.6, 120.8, 20.0, 18.2, 18.1, 13.0. HRMS (FAB) calcd for $C_{27}H_{29}Si$ ($M+H^+$) 381.2033, found 381.2031.



Compound 3s. The reaction was conducted on 0.150 mmol scale. The extraction was carried out using CH_2Cl_2 instead of EtOAc, and the product was purified by passing through a pad of silica gel with CH_2Cl_2 followed by GPC with $CHCl_3$. Red solid. 85% yield (57.8 mg).

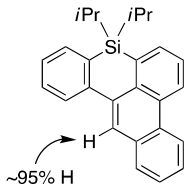
^{1}H NMR ($CDCl_3$): δ 9.57 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 8.88 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 8.38 (s, 1H), 8.35 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 8.18 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 8.02-7.95 (m, 2H), 7.78 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.04 (d, $^4J_{HH}$ = 2.8 Hz, 1H), 6.96 (dd, $^3J_{HH}$ = 9.2 Hz and $^4J_{HH}$ = 3.2 Hz, 1H), 3.10 (s, 6H), 1.52 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.04 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.99 (d, $^3J_{HH}$ = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 149.2, 145.5, 138.6, 136.4, 135.8, 134.5, 133.3, 132.0, 131.4, 130.9, 129.7, 129.5, 128.9, 126.2, 124.8, 122.4, 120.7, 119.2, 116.7, 114.6, 40.3, 18.3, 18.1, 13.1. HRMS (FAB) calcd for $C_{28}H_{31}N_2O_2Si$ ($M+H^+$) 455.2149, found 455.2169.



Compound 3t. The reaction was conducted using 10 mol% Pd at 120 °C. EtOAc/hexane

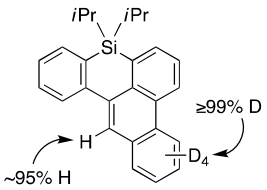
= 1/4 was used for preparative TLC and the product was further purified by washing with pentane. Pale brown solid. 81% yield (59.2 mg).

^{1}H NMR ($CDCl_3$): δ 10.04 (s, 1H), 8.96 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 8.71 (d, $^{3}J_{HH}$ = 5.5 Hz, 1H), 8.40 (s, 1H), 8.24 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.99 (d, $^{3}J_{HH}$ = 6.4 Hz, 1H), 7.82-7.74 (m, 3H), 7.58 (td, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.44 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 1.51 (sept, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.8 Hz, 6H), 0.97 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 146.6, 145.3, 143.7, 138.5, 135.8, 135.7, 134.3, 134.1, 132.5, 131.3, 130.2, 129.8, 127.7, 127.4, 126.4, 125.7, 124.1, 123.8, 121.4, 18.1, 17.9, 12.9. HRMS (FAB) calcd for $C_{25}H_{26}NSi$ ($M+H^{+}$) 368.1829, found 368.1836.



Compound 3d (Eq 4). EtOAc/hexane = 1/50 was used for preparative TLC. White solid. 79% yield (58.0 mg).

^{1}H NMR ($CDCl_3$): δ 8.86 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 8.68 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 8.49 (s, 0.95H), 8.25 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 8.01-7.95 (m, 1H), 7.94 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.77 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.71 (dd, $^{3}J_{HH}$ = 8.2 and 6.8 Hz, 1H), 7.68-7.53 (m, 3H), 7.39 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H), 1.50 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H), 0.98 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H).

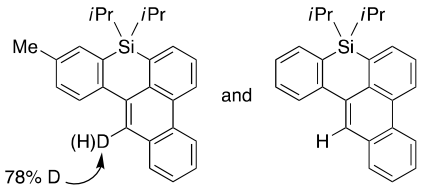


Compound 3d-*d*$_4$ (Eq 5). EtOAc/hexane = 1/50 was used for preparative TLC. White

solid. 88% yield (64.9 mg).

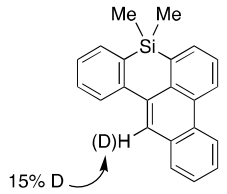
^{1}H NMR ($CDCl_3$): δ 8.85 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 8.49 (s, 0.95H), 8.25 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.94 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.77 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.71 (dd, $^3J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.56 (ddd, $^3J_{HH}$ = 8.7 and 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.39 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 1.50 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^3J_{HH}$ = 7.4 Hz, 6H), 0.98 (d, $^3J_{HH}$ = 7.8 Hz, 6H).

Procedure for Equation 6.



Et_2NH (61.8 μL, 0.600 mmol) and D_2O (120 μL, 6.63 mmol) were added to a mixture of $Pd(OAc)_2$ (3.4 mg, 15 μmol), compound **4c** (79.6 mg, 0.150 mmol), and compound **3d** (56.7 mg, 0.150 mmol) in DMF (0.60 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was passed through a pad of silica gel with EtOAc and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/100 to afford a 47/53 mixture of compound **3c-*d*** (78% D) and compound **3d** (0% D) as a white solid (100 mg, 0.126 mmol of **3c-*d*** and 0.142 mmol of **3d**; 84% yield and 95% recovery, respectively).

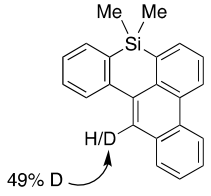
Procedure for Equation 8.



Et_2NH (92.7 μL, 0.900 mmol) and D_2O (54.1 μL, 3.00 mmol) were added to a mixture of $Pd(OAc)_2$ (10.1 mg, 45.0 μmol) and compound (*Z*)-**5** (69.1 mg, 0.150 mmol) in DMF (0.90 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and this was washed with H_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/50 to afford compound **3e** (15% D) as a white solid (39.8 mg, 0.128 mmol; 85% yield). 89% yield of **3e** was obtained in the absence of D_2O under otherwise the same conditions.

^1H NMR ($CDCl_3$): δ 8.87 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 8.71 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.57 (s, 0.85H), 8.26 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.05-7.99 (m, 1H), 7.98 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.80 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.76 (dd, $^3J_{HH}$ = 8.2 and 6.4 Hz, 1H), 7.72-7.56 (m, 3H), 7.46 (td, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 0.55 (s, 6H).

Procedure for Equation 9.

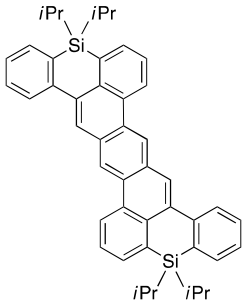


Et_2NH (74.2 μL, 0.720 mmol) and D_2O (43.3 μL, 2.40 mmol) were added to a mixture of $Pd(OAc)_2$ (8.1 mg, 36 μmol) and compound (*E*)-**5** (55.3 mg, 0.120 mmol) in DMF (0.72 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to

room temperature, the reaction mixture was diluted with EtOAc and this was washed with H_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/50 to afford compound **3e** (49% D) as a white solid (31.3 mg, 0.101 mmol; 84% yield). 92% yield of **3e** was obtained in the absence of D_2O under otherwise the same conditions.

^{1}H NMR ($CDCl_3$): δ 8.87 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 8.70 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.56 (s, 0.51H), 8.26 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.05-7.99 (m, 1H), 7.96 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.79 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.75 (dd, $^3J_{HH}$ = 8.2 and 6.8 Hz, 1H), 7.71-7.55 (m, 3H), 7.45 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 0.54 (s, 6H).

Procedure for Equation 10.

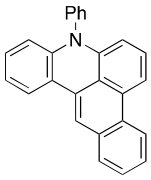


Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.3 mg, 10 μmol) and compound **6** (95.5 mg, 0.100 mmol) in DMF (0.40 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with $CHCl_3$ and this was washed with H_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was washed with hexane/CH_2Cl_2 to afford compound **7** as a yellow solid (46.9 mg, 71.6 μmol; 72% yield).

^{1}H NMR ($CDCl_3$): δ 9.21 (s, 2H), 9.06 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 8.72 (s, 2H), 8.35

(d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.98 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 0.9 Hz, 2H), 7.84-7.74 (m, 4H), 7.61 (td, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 2H), 7.43 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.54 (sept, $^{3}J_{HH}$ = 7.4 Hz, 4H), 1.06 (d, $^{3}J_{HH}$ = 7.3 Hz, 12H), 1.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 144.8, 136.1, 134.3, 134.1, 133.7, 132.1, 131.4, 130.9, 130.7, 130.4, 130.1, 127.3, 126.7, 125.7, 124.9, 122.6, 18.3, 18.2, 13.2. HRMS (FAB) calcd for $C_{46}H_{47}Si_2$ ($M+H^+$) 655.3211, found 655.3214.

Procedure for Equation 11.

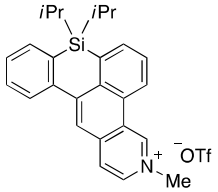


Et_2NH (32.4 μL, 0.315 mmol) was added to a mixture of $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), PCy_3•HBF_4 (5.5 mg, 15 μmol), and compound **8** (74.0 mg, 0.150 mmol) in DMF (0.30 mL), and the resulting solution was stirred for 20 h at 120 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and this was washed with H_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by preparative TLC with EtOAc/hexane = 1/30 and the solid thus obtained was washed with MeOH and hexane to afford compound **9** as a yellow solid (24.2 mg, 70.5 μmol; 47% yield).

^{1}H NMR ($CDCl_3$): δ 8.47 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 8.09 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.99 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.89 (s, 1H), 7.83 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.75-7.65 (m, 2H), 7.61-7.46 (m, 3H), 7.43-7.34 (m, 2H), 7.26 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.06 (ddd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.00 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.28 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.12 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 141.9, 141.3, 140.7, 133.2, 132.5, 131.7, 131.0, 129.2,

128.9, 128.8, 128.5, 128.3, 127.5, 127.2, 125.4, 123.3, 123.2, 121.20, 121.17, 120.7, 115.7, 113.3, 112.8, 108.9. HRMS (FAB) calcd for $C_{26}H_{17}N$ (M^+) 343.1356, found 343.1361.

Procedure for Equation 13.

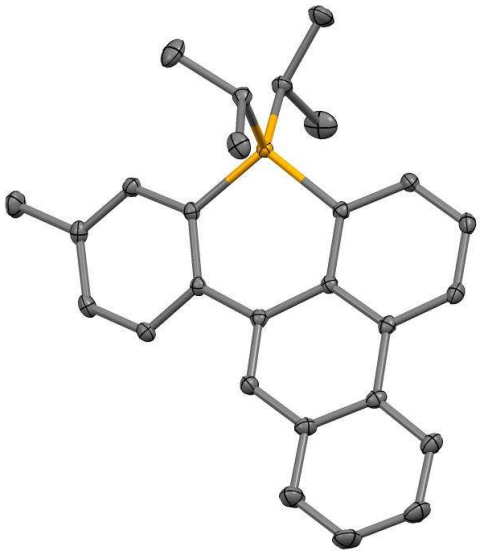


Methyl trifluoromethanesulfonate (13.6 μL, 0.120 mmol) was added to a solution of compound **3t** (36.8 mg, 0.100 mmol) in CH_2Cl_2 (1.0 mL), and the mixture was stirred for 3 h at room temperature. The volatiles were removed under vacuum and the residue was washed with hexane/CH_2Cl_2 to afford compound **10** as a pale yellow solid (47.6 mg, 89.5 μmol; 89% yield).

^{1}H NMR (DMSO-d_6): δ 10.59 (s, 1H), 9.20 (dd, $^3J_{HH}$ = 8.5 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 9.04 (s, 1H), 8.89 (dd, $^3J_{HH}$ = 6.6 Hz and $^4J_{HH}$ = 0.7 Hz, 1H), 8.64, (d, $^3J_{HH}$ = 6.6 Hz, 1H), 8.52 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 8.26 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 8.09 (dd, $^3J_{HH}$ = 8.3 and 7.0 Hz, 1H), 7.90 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.74 (ddd, $^3J_{HH}$ = 8.3 and 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.63 (td, $^3J_{HH}$ = 7.2 Hz and $^4J_{HH}$ = 0.7 Hz, 1H), 4.55 (s, 3H), 1.58 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 0.95 (d, $^3J_{HH}$ = 7.5 Hz, 6H), 0.90 (d, $^3J_{HH}$ = 7.5 Hz, 6H). ^{13}C NMR (DMSO-d_6): δ 144.3, 143.0, 141.7, 138.40, 138.38, 136.3, 135.1, 134.3, 132.5, 131.5, 130.7, 129.0, 128.9, 128.8, 128.0, 125.8, 125.5, 125.4, 125.3, 122.9, 120.7 (q, $^1J_{CF}$ = 323 Hz), 47.9, 17.7, 17.5, 11.8. HRMS (FAB) calcd for $C_{26}H_{28}NSi$ (M^-OTf) 382.1986, found 382.1989.

X-ray Crystal Structures

Compound 3c



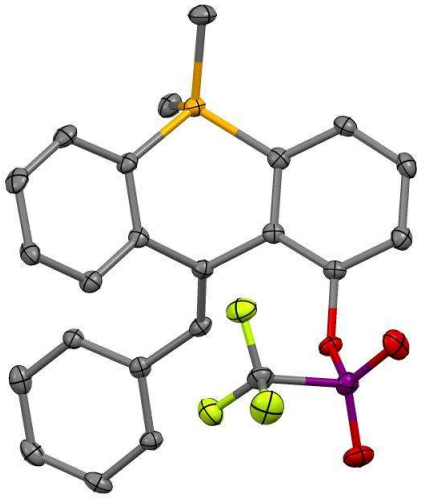
A pale yellow CH_2Cl_2 solution of compound **3f** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{27}H_{28}Si$	
Formula Weight	380.58	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit Cell Dimensions	a = 15.8820(17) Å	α = 90°
	b = 7.3591(7) Å	β = 111.371(2)°
	c = 19.280(2) Å	γ = 90°
Volume	2098.4(4) $Å^3$	

Z Value	4
Calculated Density	1.205 g/cm^3
Absorption Coefficient	0.122 mm^{-1}
F(000)	816
Crystal Size	0.300 x 0.300 x 0.200 mm
Theta Range for Data Collection	3.092–27.470°
Index Ranges	$-20 \leq h \leq 20$, $-9 \leq k \leq 9$, $-25 \leq l \leq 24$
Reflections Collected	20019
Independent Reflections	4792 [R(int) = 0.0284]
Completeness to Theta = 25.242°	99.8%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.946
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	4792 / 0 / 258
Goodness-of-Fit on F^2	1.070
Final R Indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0996
R Indices (All Data)	R1 = 0.0402, wR2 = 0.1019
Largest Diff. Peak and Hole	0.374 and –0.309 e$^-$/Å^3

Compound (*E*)-5



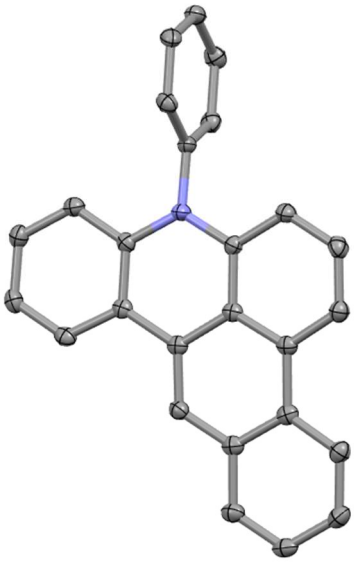
A colorless hexane solution of compound (*E*)-**5** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{23}H_{19}F_3O_3SSi$	
Formula Weight	460.53	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit Cell Dimensions	a = 13.0008(15) Å	α = 90°
	b = 17.7824(19) Å	β = 108.414(2)°
	c = 19.987(2) Å	γ = 90°
Volume	4384.1(8) $Å^3$	
Z Value	8	
Calculated Density	1.395 g/cm^3	

Absorption Coefficient	0.250 mm^{-1}
F(000)	1904
Crystal Size	0.200 x 0.200 x 0.200 mm
Theta Range for Data Collection	3.096–27.515°
Index Ranges	$-16 \leq h \leq 15$, $-23 \leq k \leq 18$, $-25 \leq l \leq 25$
Reflections Collected	39977
Independent Reflections	10028 [R(int) = 0.0434]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.889
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	10028 / 0 / 563
Goodness-of-Fit on F^2	1.246
Final R Indices [I>2sigma(I)]	R1 = 0.0882, wR2 = 0.2009
R Indices (All Data)	R1 = 0.1006, wR2 = 0.2045
Largest Diff. Peak and Hole	0.521 and −0.480 $e^-/Å^3$

Compound 9



A pale yellow CH_2Cl_2 solution of compound **9** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{26}H_{17}N$	
Formula Weight	343.40	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Triclinic	
Space Group	P −1	
Unit Cell Dimensions	a = 8.587 (2) Å	α = 111.245(4)°
	b = 10.418(3) Å	β = 98.933(2)°
	c = 10.740(3) Å	γ = 106.165(3)°
Volume	824.1(4) $Å^3$	

Z Value	2
Calculated Density	1.384 g/cm^3
Absorption Coefficient	0.080 mm^{-1}
F(000)	360
Crystal Size	0.200 x 0.200 x 0.020 mm
Theta Range for Data Collection	3.325–27.549°
Index Ranges	$-11 \leq h \leq 10$, $-10 \leq k \leq 13$, $-13 \leq l \leq 13$
Reflections Collected	15062
Independent Reflections	3777 [R(int) = 0.0244]
Completeness to Theta = 25.242°	99.4%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.885
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	3777 / 0 / 244
Goodness-of-Fit on F^2	1.235
Final R Indices [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1861
R Indices (All Data)	R1 = 0.0762, wR2 = 0.1918
Largest Diff. Peak and Hole	0.401 and −0.280 e$^-$/Å^3

2.5 References

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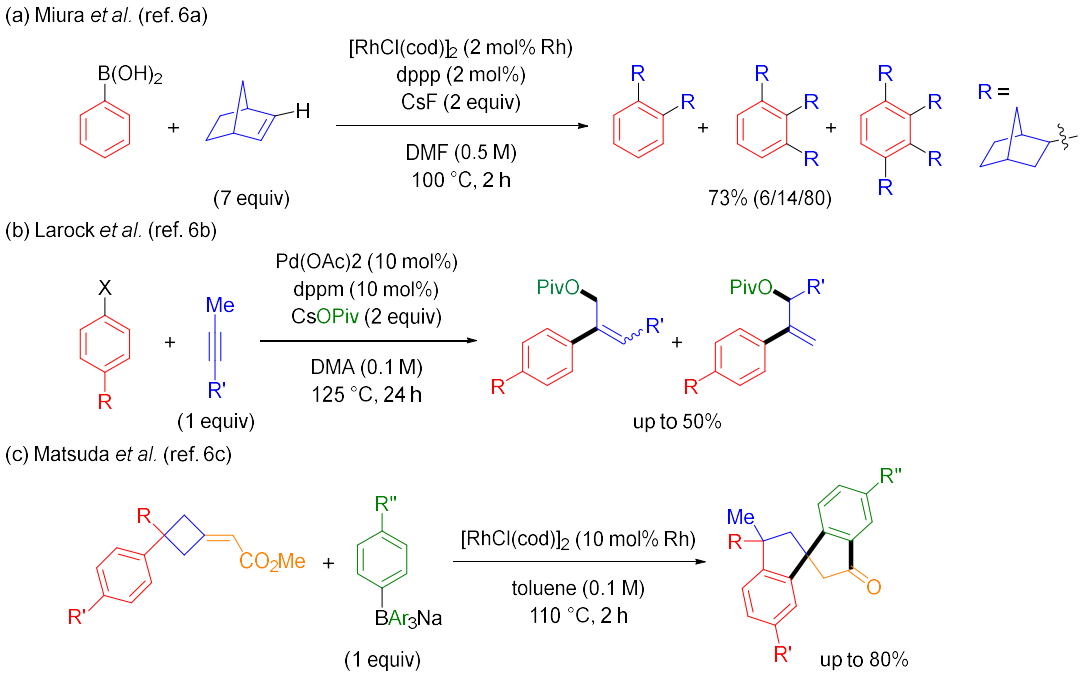
Chapter 3

Palladium-Catalyzed Synthesis of Dibenzosilepin Derivatives via 1,*n*-Palladium Migration Coupled with *anti*-Carbopalladation of Alkyne

3.1 Introduction

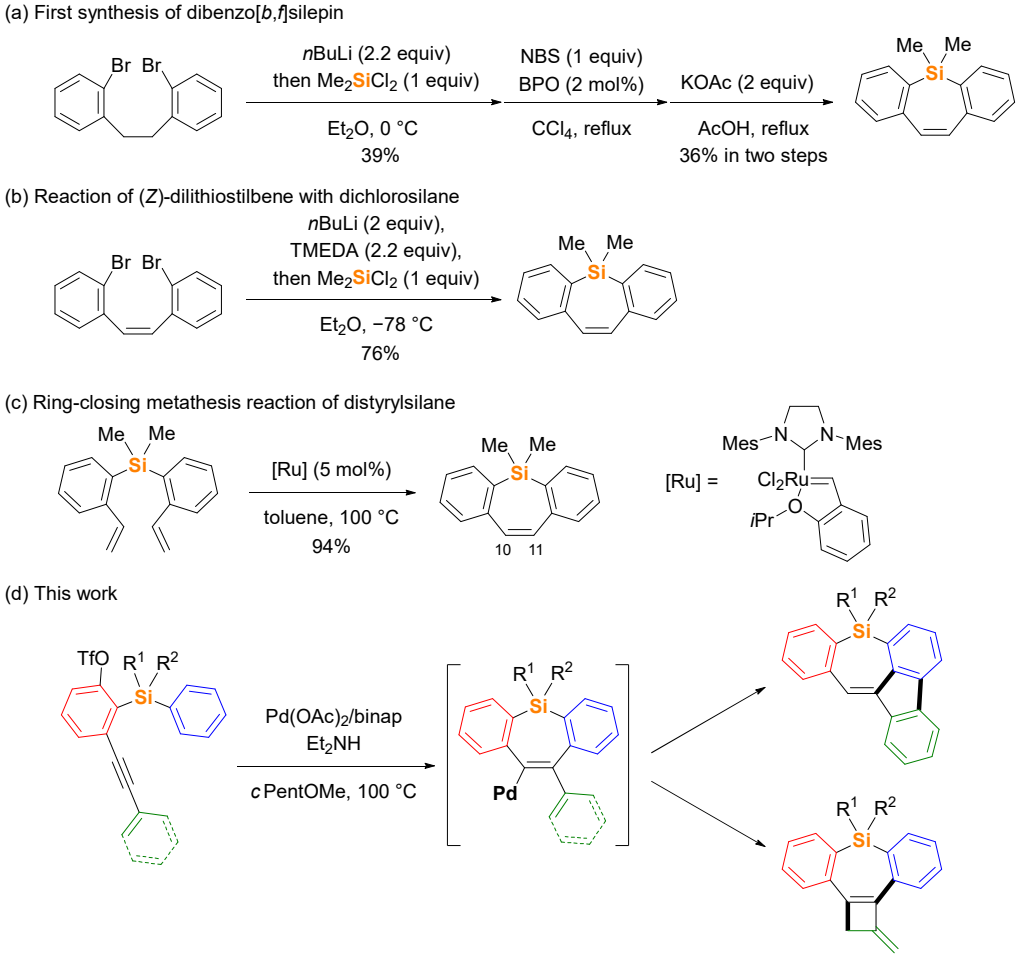
Transition-metal-catalyzed reactions involving metal migration from carbon to carbon within organic substrates in a 1,*n*-fashion represent a powerful way of synthesizing complex molecules from relatively simple precursors through activation of C–H bonds that are difficult to functionalize directly.[1] Among the known such processes, reactions involving 1,4-migration of palladium[2] or rhodium[3] have been most widely explored and several effective examples of the corresponding 1,5-migrations have also been developed.[4,5] Despite the synthetic utility of these 1,*n*-metal migration processes, the transformations reported to date usually include only one such migration during a catalytic cycle, although a reaction involving multiple 1,*n*-metal migrations in a cascade manner would be highly attractive toward rapid construction of a complex molecular skeleton through remote functionalization in a single operation (Scheme 1).[6]



Scheme 1. Catalytic reactions involving multiple 1,*n*-metal migration

Recently, our group has been focusing on the development of new synthetic methods of underexplored silicon-bridged functional organic compounds such as 5,10-dihydrophenazasilines,[7] 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines,[8] and others[9] through the use of 1,*n*-palladium or rhodium migrations to realize an easy access to these potentially useful molecules. In this regard, 5*H*-dibenzo[*b*,*f*]silepins belong to a class of silicon-bridged π-conjugated compounds and half a century has passed since the first synthesis of 5,5-dimethyl-5*H*-dibenzo[*b*,*f*]silepin by the reaction of 1,2-bis(2-lithiophenyl)ethane with dichlorodimethylsilane followed by conversion of the carbon–carbon single bond to a double bond (Scheme 2a).[10] However, very little progress has been made on the detailed study of this class of compounds, and some scattered reports on their promising features started to appear only recently.[11] This slowness of the research progress on the chemistry of 5*H*-dibenzo[*b*,*f*]silepins is most likely due to the lack of efficient synthetic methods, which results in insufficient diversity of accessible structures. In fact, other than

pioneering synthesis of 5,5-dimethyl-5*H*-dibenzo[*b*,*f*]silepin,[10] synthetic methods of 5*H*-dibenzo[*b*,*f*]silepins are essentially limited to either a reaction of (*Z*)-1,2-bis(2-lithioaryl)ethene with dichlorosilanes (Scheme 2b)[11a–c] or a ring-closing metathesis reaction of bis(2-vinylaryl)silanes (Scheme 2c),[11e, 12] all of which can only be used for the synthesis of 10,11-unsubstituted compounds.[13] In this chapter, the author describes a palladium-catalyzed synthesis of novel 5*H*-dibenzo[*b*,*f*]silepin derivatives, 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepins and 1-alkylidene-2,7-dihydro-1*H*-dibenzo[*b*,*f*]cyclobuta[*d*]silepins, through a reaction sequence triggered by 1,5-palladium migration followed by unusual *anti*-carbopalladation of alkyne (Scheme 2d).[14, 15] Mechanistic insights of the present catalysis as well as properties of the obtained products are also provided.



Scheme 2. Synthesis of dibenzosilepins bearing a seven-membered silacycle

3.2 Results and Discussion

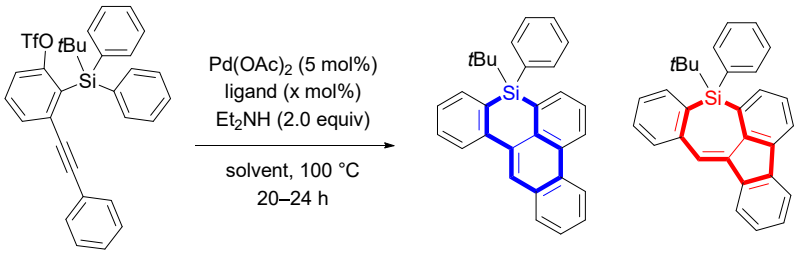
3.2.1 Synthesis of 13*H*-Benzo[*e*]fluoreno[1,9-*bc*]silepins

3.2.1.1 Reaction Development

As exemplified by the relationship between naphthalene and azulene, replacing a 6,6-fused bicyclic π-conjugated system by its 5,7-fused isomer can change the overall properties, and this phenomenon is also incorporated into the field of graphene nanoribbons in recent years.[16] In a synthetic point of view, it is highly attractive and convenient if the same precursor can be used to selectively provide either 6,6-fused system or 5,7-fused system depending on the reaction conditions. In this regard, the author recently found that 8*H*-benzo[*e*]phenanthro[1,10-*bc*]silines **2**, rarely explored silicon-bridged π-conjugated compounds possessing a 6,6-fused 2-siladihydronaphthalene structure,[17] can be synthesized from 2-(arylsilyl)-3-(arylethynyl)aryl triflates **1** under simple palladium catalysis (Chapter 2).[8] For example, as shown in Table 1, the reaction of **1a** proceeded smoothly in the presence of $Pd(OAc)_2$ (5 mol%) and Et_2NH (2.0 equiv) in DMF at 100 °C without using any additional ligands to give benzophenanthrosiline **2a** in 59% yield (entry 1). The use of monophosphine ligands such as PPh_3, PCy_3, and $P(tBu)_3$ led to selective formation of **2a** in 39–58% yield as well (entries 2–4). In the present study, the author examined several bisphosphine ligands such as dppe, dppb, dppf, and xantphos, and found that **2a** was still the major product with somewhat lower efficiency (14–32% yield; entries 5–8). In stark contrast, as shown in entries 9–12, reactions using bisphosphine ligands possessing a biaryl backbone were found to provide 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepin **3a**, a novel silicon-bridged π-conjugated compound possessing a 5,7-fused 5-siladihydroazulene structure, with no formation of compound **2a**. Among them, binap (61% yield; entry 11) and H_8-binap (63% yield; entry 12) were particularly effective, and through a brief examination

of the reaction solvent using binap as the ligand (entries 11 and 13–15), cyclopentyl methyl ether (*c*PentOMe) was found to be more suitable for the production of compound **3a** (77% yield (67% isolated yield); entry 15).

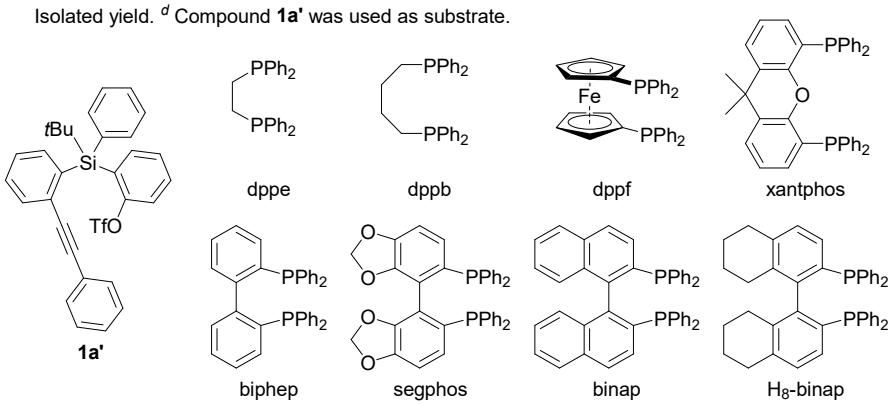
Table 1. Ligand and solvent effects for the reaction of **1a** to **2a** or **3a**



1a (0.5 M) **2a** **3a**

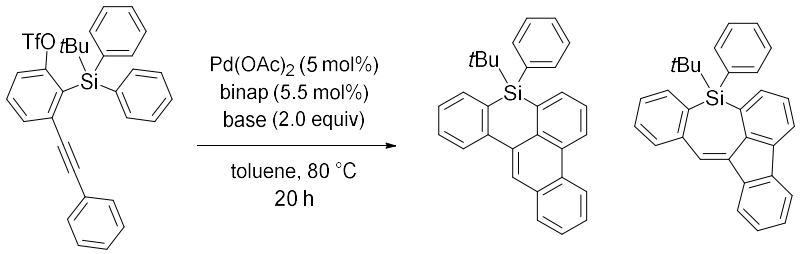
entry	ligand (x)	solvent	conversion of **1a** (%)[a]	yield of **2a** (%)[a]	yield of **3a** (%)[a]
1	none	DMF	100	59	0
2	PPh_3 (10)	DMF	100	39	0
3	PCy_3[b](10)	DMF	100	58	0
4	$P(tBu)_3$[b](10)	DMF	100	55	0
5	dppe (5.5)	DMF	33	14	0
6	dppb (5.5)	DMF	68	32	0
7	dppf (5.5)	DMF	100	17	0
8	xantphos (5.5)	DMF	46	17	0
9	biphep (5.5)	DMF	100	0	52
10	segphos (5.5)	DMF	100	0	55
11	binap (5.5)	DMF	100	0	61
12	H_8-binap (5.5)	DMF	100	0	63
13	binap (5.5)	toluene	100	0	73
14	binap (5.5)	1,4-dioxane	100	<1	74
15	binap (5.5)	*c*PentOMe	100	0	77 (67[c])

[a] Determined by ^1H NMR against internal standard ($MeNO_2$). [b] PR_3•HBF_4/Et_2NH was used. [c] Isolated yield. [d] Compound **1a'** was used as substrate.



The author also examined the effect of bases for this reaction as shown in Table 2. *n*Bu$_2$NH was found to give **3a** in the comparable yield to Et$_2$NH (entries 1 and 2), whereas bulky *i*Pr$_2$NH slowed down the reaction rate (entry 3). Tertiary amines such as Et$_3$N and dabco were not effective and the yields of **3a** were low (entries 4 and 5). In the case of primary amines such as *n*BuNH$_2$ and *t*BuNH$_2$, almost no reaction was observed (entries 6 and 7). The use of inorganic bases such as K_2CO_3 and NaOAc resulted in the decomposition of **1a** to give a protodetriflated compound or a desilylated compound as major products (entries 8 and 9).

Table 2. Base effects for the reaction of **1a**.

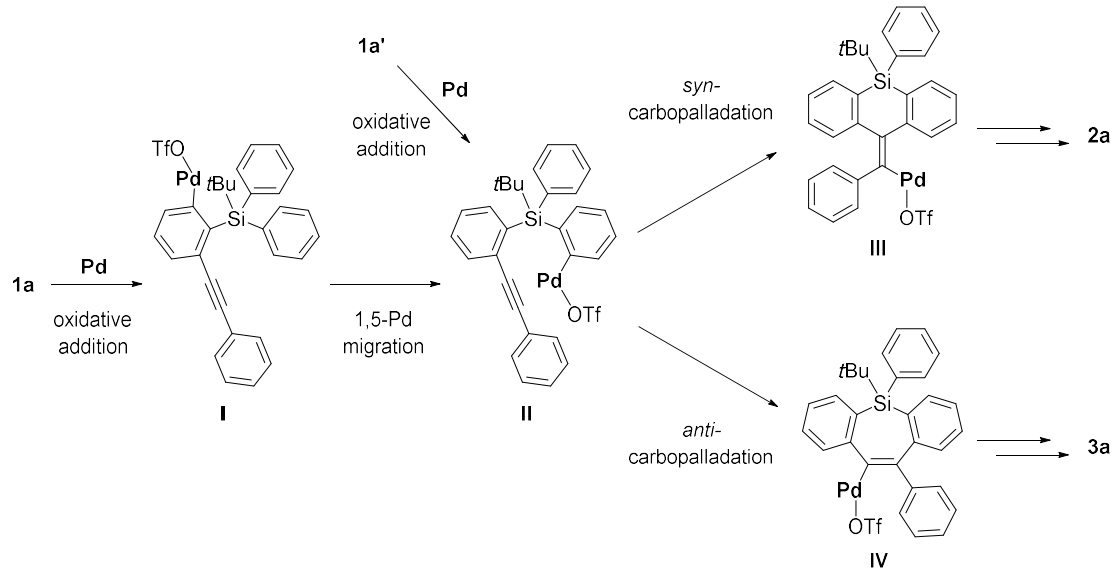


1a (0.5 M) **2a** **3a**

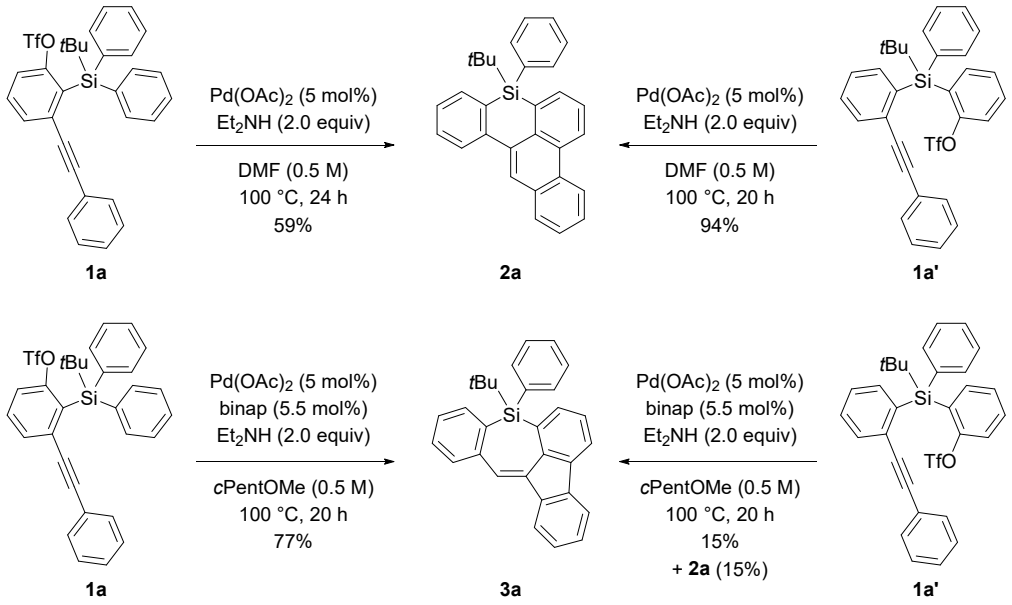
entry	base	conversion of **1a** (%)[a]	yield of **2a** (%)[a]	yield of **3a** (%)[a]
1	Et$_2$NH	100	0	68
2	*n*Bu$_2$NH[c]	100	0	72 (65[b])
3	*i*Pr$_2$NH	23	0	23
4	Et$_3$N	59	<1	35
5	dabco	10	<1	10
6	*n*BuNH$_2$	<1	0	0
7	*t*BuNH$_2$	3	0	3
8	K_2CO_3[d]	100	0	0
9	NaOAc[d]	85	17	0

[a] Determined by ^{1}H NMR against internal standard ($MeNO_2$). [b] Isolated yield. [c] In *c*PentOMe at 100 °C. [d] In DMF at 100 °C.

The present reaction presumably takes place via 1,5-palladium migration (**I** → **II**; Scheme 3), which either gives **2a** through **III** or **3a** through **IV**, indicating that the use of isomeric substrate **1a'** should provide the same products by direct formation of **II** without 1,5-palladium migration. Indeed, as described in Chapter 2,[8] the reaction of **1a'** in the absence of phosphine ligands led to compound **2a** in a much higher yield of 94% compared to the reaction of **1a** via 1,5-palladium migration (Scheme 4, top). On the other hand, the reaction of **1a'** in the presence of binap unexpectedly showed much lower reactivity and product selectivity compared to the reaction of **1a** (Scheme 4, bottom).

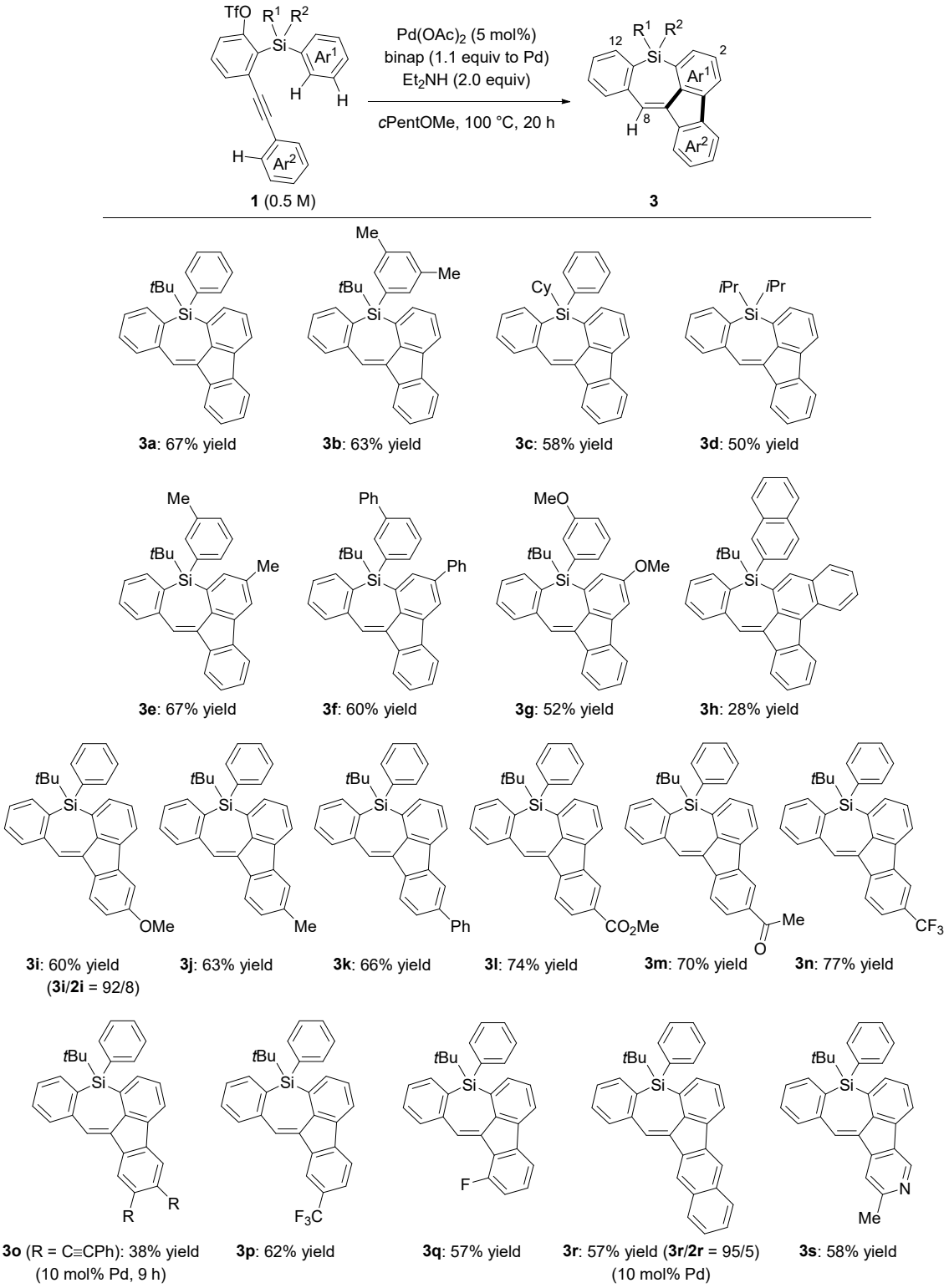


Scheme 3. Possible reaction pathway for the production of **2a** and **3a**



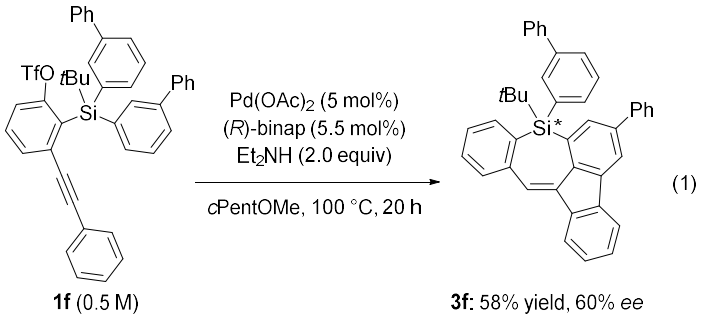
Scheme 4. Comparison of the reactivity between **1a** and **1a'**

Under the conditions in Table 1, entry 15, the scope of the reaction toward benzofluorenosilepins **3** was found to be reasonably broad as summarized in Scheme 5. For example, in addition to compound **3a** having a (*tert*-butyl)phenylsilylene bridging unit, benzofluorenosilepins **3b–3d** with other silylene units could also be synthesized in 50–63% yield. With regard to the substituents on the aromatic rings, introduction of a *meta*-substituent to Ar^1 led to 2-substituted benzofluorenosilepins **3e–3g**, and the substrate having 2-naphthyl group as Ar^1 gave π-extended 10*H*-benzo[*f*]benzo[3,4]fluoreno[1,9-*bc*]silepin **3h**. For substituents on Ar^2, various functional groups such as methoxy (**3i**), methoxycarbonyl (**3l**), acetyl (**3m**), and trifluoromethyl (**3n**, **3p**) groups were tolerated to give products **3** in up to 77% yield, and naphthyl and heteroaryl groups could also be used as Ar^2 to give corresponding products **3r** and **3s**. The carbon–carbon bond formation between Ar^1 and Ar^2 took place selectively at the less hindered position for the synthesis of **3o**, **3p**, **3r**, and **3s**.



Scheme 5. Scope of palladium-catalyzed synthesis of 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepins

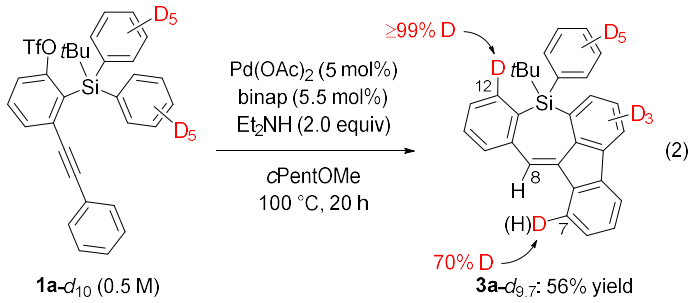
Most of the substrates employed here are prochiral and the corresponding products possess a silicon stereocenter.[18] Although satisfactory results have not been achieved yet, somewhat promising enantioselectivity can be induced by simply employing enantiopure (*R*)-binap as the ligand as exemplified in the reaction of **1f** to give **3f** (eq. 1).

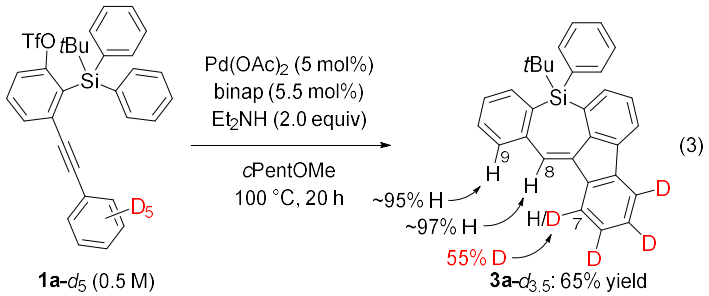


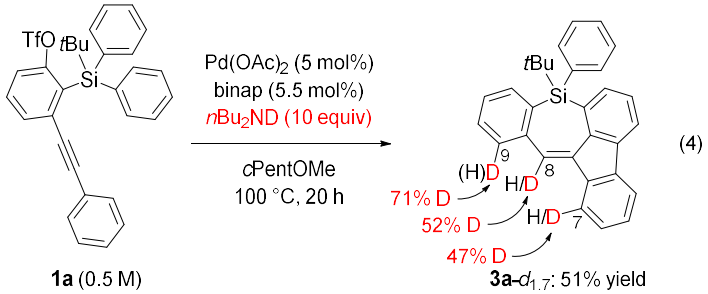
3.2.1.2 Mechanistic Investigation

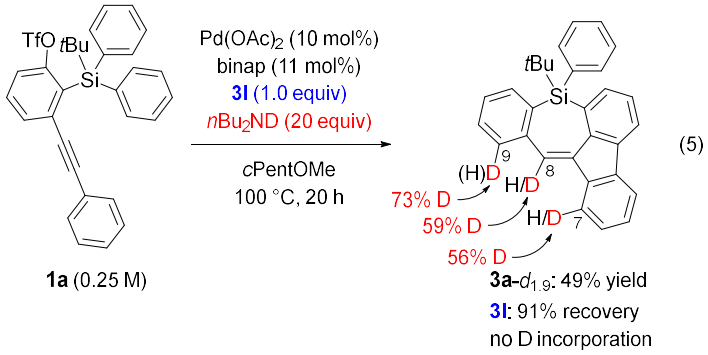
To understand how the reaction proceeds for the synthesis of 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepins **3**, the author decided to carry out some control experiments. In this transformation, two C–H bonds of Ar^1 and one C–H bond of Ar^2 in substrate **1** (see equation in Scheme 5) are cleaved to form two new carbon–carbon bonds, and two C–H bonds are newly generated at 8- and 12-positions of resulting benzofluorenosilepin **3**. At first, substrate **1a**-d_{10} having (*tert*-butyl)bis(pentadeuteriophenyl)silyl group was prepared and was subjected to the present reaction (eq. 2). Compound **3a** thus obtained showed quantitative deuterium incorporation at 12-position along with significant deuterium incorporation (70% D) at 7-position, but no deuterium incorporation was observed at 8-position. On the other hand, the reaction of substrate **1a**-d_5 having pentadeuteriophenylethynyl group gave product **3a** with significant decrease of deuterium content at 7-position (55% D) and only negligible amount of deuterium incorporation at 8-position (eq. 3). These results indicate that C–

H/C–D exchange seems to occur at 7-position of compound **3** and that H at 8-position is not directly derived from C–H bonds that engage in the carbon–carbon bond formation, whereas H at 12-position quantitatively comes from the H at *ortho*-position of the phenyl group on silicon of **1**. In contrast, when the reaction of **1a** is conducted in the presence of nBu$_2$ND (10 equiv) in place of Et$_2$NH, significant deuterium incorporation was observed at 7-, 8-, and 9-positions (eq. 4), indicating that the hydrogens at these positions are scrambled with an external hydrogen donor. In addition, the same reaction was carried out in the presence of non-deuterated benzofluorenosilepin **3l** to find that no deuterium incorporation to **3l** was observed under these conditions (eq. 5). This result establishes that the deuterium is incorporated only during the formation of compound **3** from substrate **1** and no C–H/C–D exchange occurs once compound **3** is produced.



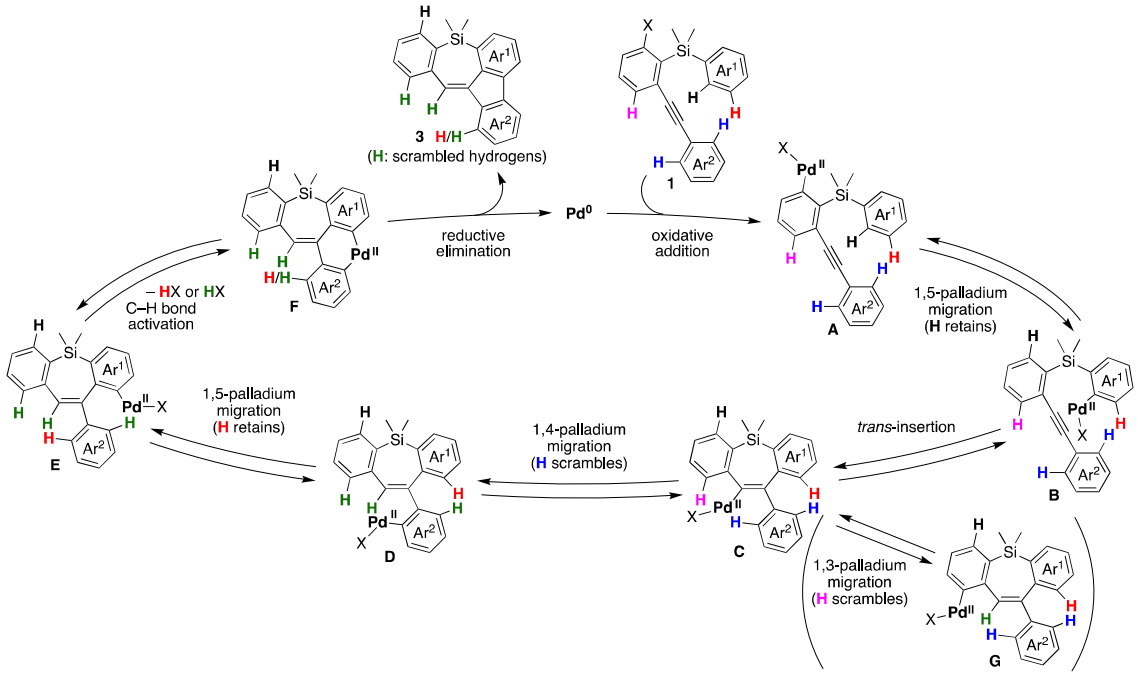






On the basis of these experiments, a proposed catalytic cycle for the present reaction is illustrated in Scheme 6. Thus, oxidative addition of aryl triflate **1** to palladium(0) gives arylpalladium species **A**, which undergoes 1,5-palladium migration[4] with retentive migration of H to give another arylpalladium species **B**. Intramolecular *anti*-arylpalladation of alkyne[14, 15] then takes place to give alkenylpalladium **C**. Successive 1,4-palladium migration[2] with scrambling of H leads to arylpalladium species **D**, which further undergoes 1,5-palladium migration with retentive migration of H to give another arylpalladium species **E**. C–H bond activation[19] then takes place and reductive elimination of product **3** from resulting diarylpalladium species **F** closes the catalytic cycle to regenerate palladium(0) species. Considering the deuterium incorporation at 7-position of **3a** in eq. 2, it is plausible to propose occurrence of 1,5-palladium migration from **D** to **E** prior to the formation of **F**. In addition, based on the deuterium incorporation at 9-position of **3a** in eqs 4 and 5, it is possible that alkenylpalladium **C** reversibly (and

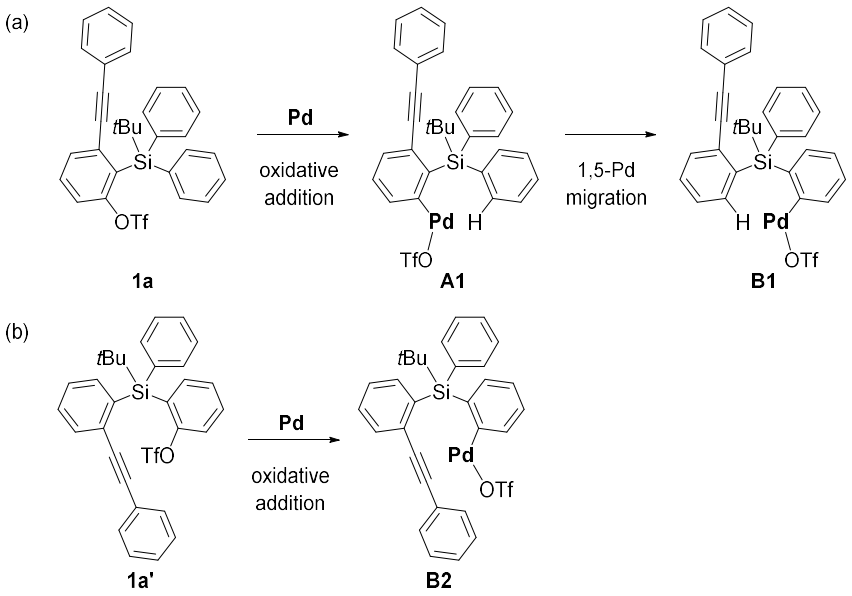
non-productively) undergoes 1,3-palladium migration to and from arylpalladium **G** with scrambling of H, although no example of 1,3-palladium migration between sp^2-hybridized carbons has been reported to date in the literature.[20]



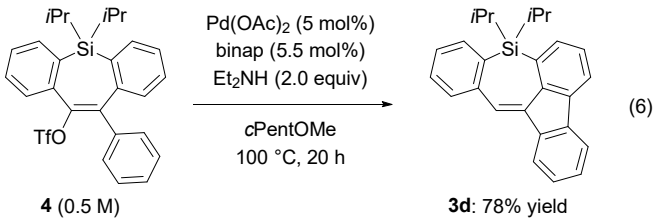
Scheme 6. Proposed catalytic cycle for the reaction of **1** to **3** (**Pd** = Pd(binap), X = OTf; amine base is omitted for clarity)

In Scheme 4, it was found that, while the reaction of **1a** proceeded smoothly to give benzofluorenosilepin **3a** selectively, isomeric compound **1a'** behaved quite differently. Oxidative addition of aryl triflate **1a'** should directly form intermediate **B**, and one might think that it should lead to the same outcome. A possible explanation for these seemingly inconsistent results would be the difference of alkyne orientation toward successive insertion. Thus, in the case of **1a**, alkyne moiety needs to flip away when 1,5-palladium migration takes place (**A1** → **B1**; Scheme 7a),[21] but alkyne moiety of **1a'** can face toward palladium during the formation of oxidative adduct (**B2**; Scheme 7b), which

could change the reactivity and selectivity of the subsequent steps. Regarding the conversion from **C** to product **3**, model compound **4** was prepared, which could enter the catalytic cycle from **C** via oxidative addition. Indeed, the reaction of **4** proceeded smoothly to give corresponding benzofluorenosilepin **3d** in 78% yield (eq. 6).



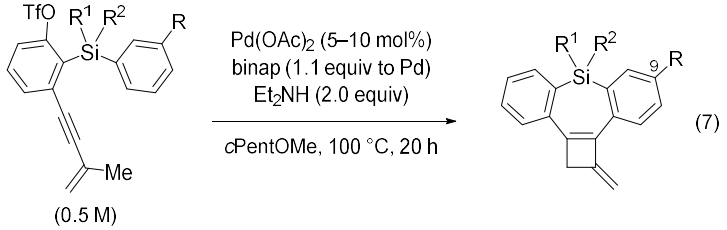
Scheme 7. Schematic comparison of initial step between (a) **1a** and (b) **1a'**



3.2.2 Synthesis of 1-Alkylidene-2,7-dihydro-1*H*-dibenzo[*b*,*f*]cyclobuta[*c*]silepins

In the above mentioned catalysis, the author further examined the effect of substituents and found that the reaction of **5a** having 2-propenyl group instead of an aryl group on the alkyne of **1** led to selective formation of methylenecyclobutene-fused dibenzosilepin, 1-methylene-2,7-dihydro-1*H*-dibenzo[*b*,*f*]cyclobuta[*d*]silepin **6a** in 70%

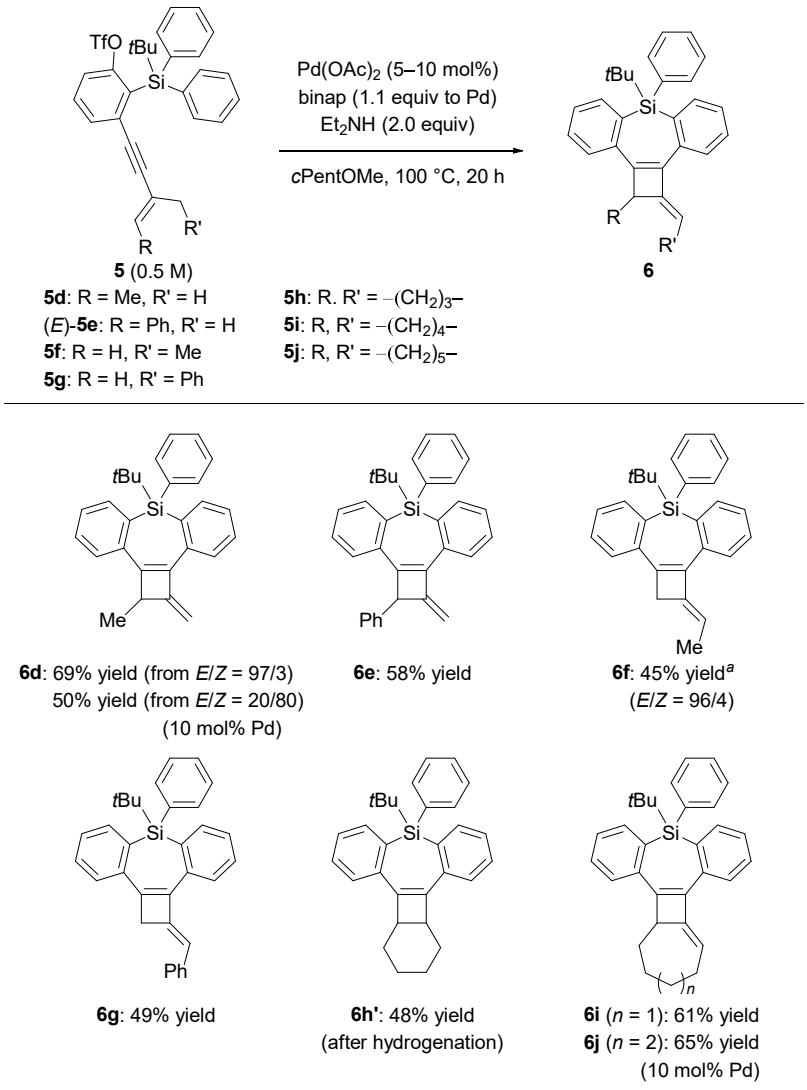
yield under the same reaction conditions (eq. 7). Similarly, diisopropylsilylene-bridged product **6b** as well as 9-phenylated compound **6c** were also obtained in 59–63% yield, and these results represent rare examples of methylenecyclobutene formation under palladium catalysis.[22] The scope of this new transformation was briefly investigated as shown in Scheme 8. For example, substrate (*E*)-**5d** (*E*/*Z* = 97/3) having 2-butenyl group gave product **6d** where methyl group was installed exclusively on the cyclobutene ring rather than on the exomethylene, indicating that C1', not C3', was selectively engaged in the four-membered ring-formation. The same product was obtained from (*Z*)-**5d** (*E*/*Z* = 20/80), although the reactivity was somewhat lower. This position selectivity was also observed for the reaction of (*E*)-**5e** to give **6e** having a phenyl group on the four-membered ring. C1'-selective ring-formation was further confirmed by the reaction of **5f** having 1-buten-2-yl group and **5g** having 3-phenyl-1-propen-2-yl group, giving products **6f** having methyl group and **6g** having phenyl group on the exomethylene without forming isomeric **6d** and **6e**, respectively. It is worth noting that substrates **5h–5j** having a cycloalkenyl group also followed the same reaction pathway toward the formation of cyclobutene rings to give **6h–6j** in up to 65% yield. Unlike **6i** and **6j**, **6h** was obtained as a mixture of isomers having a carbon–carbon double bond at different positions within the six-membered ring presumably due to the ring-strain of initially formed 4,6-fused product, and this was isolated as **6h'** in 48% overall yield after hydrogenation of the double bond.



(0.5 M) (7)

5a :R = H, R^1,R^2 = *t*Bu, Ph
5b :R = H, R^1 = R^2 = *i*Pr
5c :R = Ph, R^1,R^2 = *t*Bu, 3-PhC_6H_4

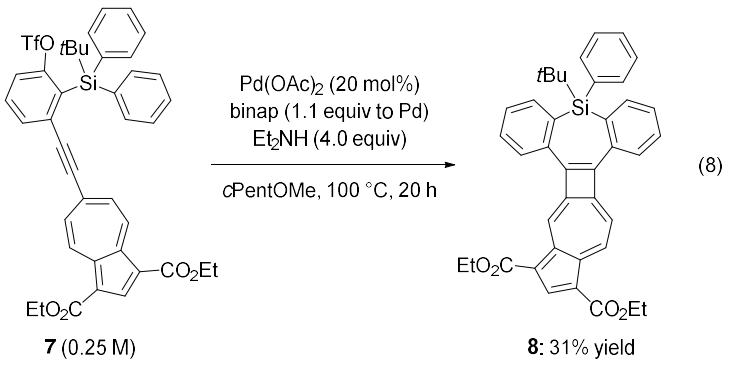
6a :70% yield (5 mol%)
6b :59% yield (10 mol%)
6c :63% yield (5 mol%)



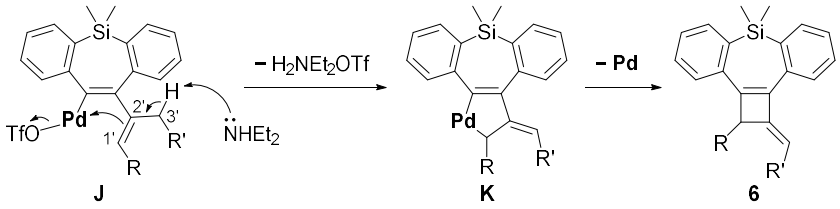
[a] Determined by ^{1}H NMR against internal standard after chromatographic purification.

Scheme 8. Palladium-catalyzed synthesis of 1-alkylidene-2,7-dihydro-1*H*-dibenzo[*b*,*f*]cyclobuta[*c*]silepins

A similar four-membered ring formation was observed for the reaction of substrate **7** having an electron-deficient azulenyl group to give compound **8** as the major product in a moderate yield (eq. 8), although the reaction of a related azulenyl substrate having no ester groups resulted in a complex mixture. This outcome is in stark contrast to the reaction of substrates **1** having a benzenoid substituent on the alkyne, which selectively gave benzofluorenosilepins **3** (Section 3.2.1).



With regard to the reaction pathway from **5** to 1-alkylidene-2,7-dihydro-1*H*-dibenzo[*b*,*f*]cyclobuta[*d*]silepins **6**, after the same oxidative addition–1,5-palladium migration–alkyne insertion steps toward compounds **3** from compounds **1** (Scheme 4 in Section 3.2.1), alkenylpalladium species **J** would be generated (Scheme 9). Considering the position-specific carbon–carbon bond-formation (at C1' over C3') as observed in Scheme 8, concerted deprotonation–allylation may be operative to give alkenyl(σ-allyl)palladium species **K**, and reductive elimination would lead to compound **6**.[23]



Scheme 9. Proposed reaction pathway toward **6**

3.2.3 Physical Properties of Newly Synthesized Dibenzosilepin Derivatives

With new members of dibenzosilepins in hand, the author first compared optical properties of 8*H*-benzo[*e*]phenanthro[1,10-*bc*]siline **2a** and isomeric 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepin **3a** (Table 3 and Figure 1). While compound **2a** showed

absorption maximum at 336 nm in its UV-vis absorption spectrum in CH_2Cl_2, a significant red-shift was observed for compound **3a** (λ_{max} = 376 nm), and these absorption peaks mainly consist of the HOMO–LUMO transition on the basis of time-dependent density functional theory (TD-DFT) calculations, indicating the narrower HOMO–LUMO energy gap for compound **3a** (Section 3.5, Figure 7 and Table 5). In addition, both of these compounds were found to be somewhat emissive in a solution state, and while compound **2a** showed emission maximum in the UV range, compound **3a** emitted a green light (λ_{max} = 523 nm) albeit in a low quantum yield. The narrower HOMO–LUMO energy gap of compound **3a** was also confirmed by the electrochemical analysis using cyclic voltammetry and it was found that the lower LUMO level is mostly responsible for this outcome (Table 4 and Figure 5). Thus, compound **3a** showed a reversible reduction potential at –2.05 V, which is 0.20 V higher than the irreversible reduction potential of compound **2a**. It is also worth noting that, through extension of the π-conjugation, a larger absorption coefficient and a longer absorption wavelength (λ_{max} = 398 nm) can be observed as shown for compound **3o** possessing two phenylethynyl substituents (Table 3 and Figure 1). The nature of extended π-conjugation of compound **3o** was confirmed by the electrochemical analysis, which showed a higher HOMO and a lower LUMO compared to unsubstituted compound **3a** (Table 4 and Figure 5). In addition, selective increase of the HOMO energy level can be achieved by introduction of an electron-donating group at 5-position of compound **3** as shown by the electrochemical analysis of compound **3i**, whereas selective decrease of the LUMO energy level can be realized by introduction of an electron-withdrawing group as shown in compound **3l**. The red-shift observed in UV-vis absorption spectra agree with these narrow energy gaps (Table 3 and Figure 2).

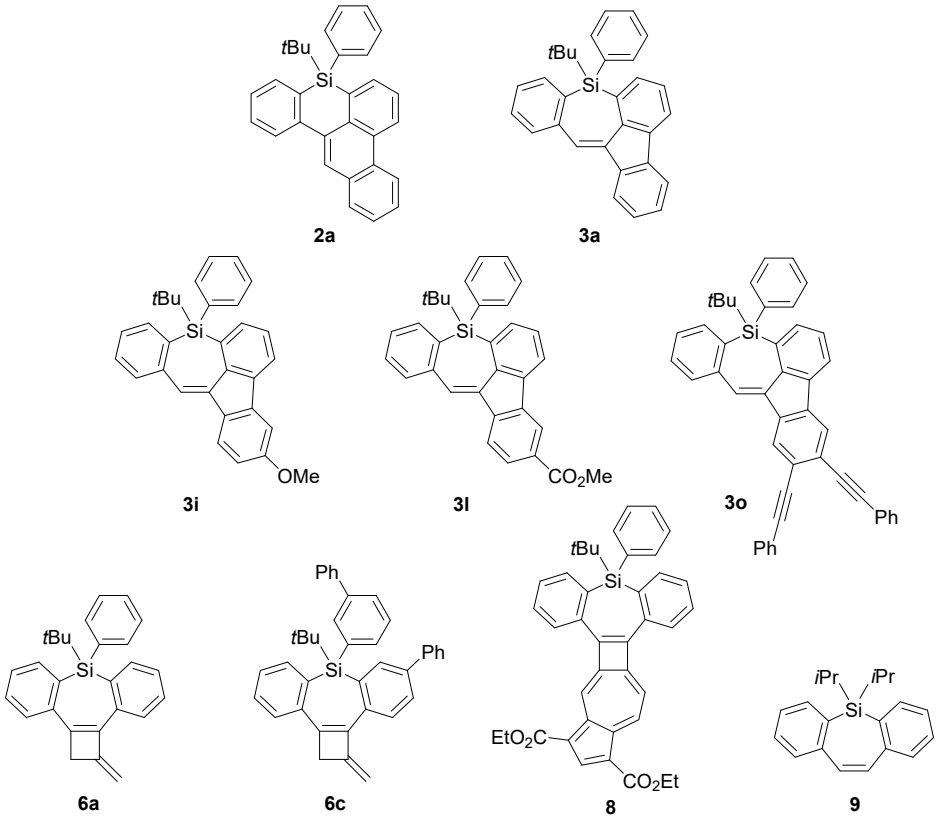
With regard to the optical properties of 1-alkylidene-2,7-dihydro-1*H*-

dibenzo[*b*,*f*]cyclobuta[*d*]silepin **6a**, the author compared it with unsubstituted 5*H*-dibenzo[*b*,*f*]silepin **9** (Table 3 and Figure 3). Although their structural difference is relatively subtle, a significant red-shift was observed in the UV-vis absorption spectrum of compound **6a**, and it showed a much higher quantum yield in the photoluminescence (Φ_F = 0.52 vs. Φ_F = 0.08 for **9**). Introduction of a phenyl group at 9-position led to an even higher quantum yield as observed in the emission of compound **6c** (Φ_F = 0.67).[11a]

It is also worth noting that azulene-fused compound **8** showed absorption peaks at much longer wavelength (Table 3 and Figure 4) with a broad shoulder at 600–820 nm, which mostly consists of the HOMO–LUMO transition (Section 3.5, Figure 13 and Table 11). The HOMO–LUMO energy gap of this compound was estimated to be as narrow as 1.76 eV by the electrochemical analysis (Table 4 and Figure 5).

These results clearly demonstrate that the optical and electronic properties of 5*H*-dibenzo[*b*,*f*]silepins can be effectively modified by devising a synthetic method of structurally new members with various functional groups.

Table 3. Optical properties of compounds **2a**, **3a**, **3o**, **6a**, **6c**, **8** and **9** in CH_2Cl_2 at 25 °C.



compound	UV-vis absorption λ_{max} (nm) (ε (10^4 M^{-1} cm^{-1}))	Fluorescence λ_{max} (nm) (λ_{ex} (nm))	Φ_F (λ_{ex} (nm))
2a[a]	254 (3.9), 268 (4.3), 325 (2.6), 336 (2.3)	371, 391, 411 (336)	0.19 (336)
3a[b]	250 (4.0), 278 (2.4), 298 (0.6), 309 (0.6), 359 (2.2), 376 (1.9)	523 (376)	0.01 (376)
3i[c]	262 (4.9, 282 (3.3.), 318 (1.2), 358 (2.7), 376 (2.8)	508 (376)	0.04 (376)
3l[d]	259 (6.1), 368 (3.0), 384 (2.6)	523 (384)	0.01 (384)
3o[e]	273 (3.8), 303 (7.3), 339 (3.7), 353 (3.8), 379 (3.9), 398 (4.3)	529 (398)	0.05 (398)
6a[f]	252 (3.6), 342 (1.8)	383, 403, 425 (342)	0.52 (342)
6c[g]	262 (4.4), 355 (2.2)	399, 421 (355)	0.67 (355)
8[h]	250 (2.9), 282 (2.5), 345 (5.9), 485 (0.6), 513 (0.7), 553 (0.6)	–	–
9[i]	256 (2.8), 311 (1.6), 394 (2.2)	349, 366, 383 (394)	0.08 (394)

[a] At 4.8×10^{-5} M. [b] At 3.4×10^{-5} M. [c] At 2.7×10^{-5} M. [d] At 2.5×10^{-5} M. [e] At 3.3×10^{-5} M. [f] At 4.0×10^{-5} M. [g] At 2.6×10^{-5} M. [h] At 2.6×10^{-5} M, not emissive. [i] At 5.8×10^{-5} M.

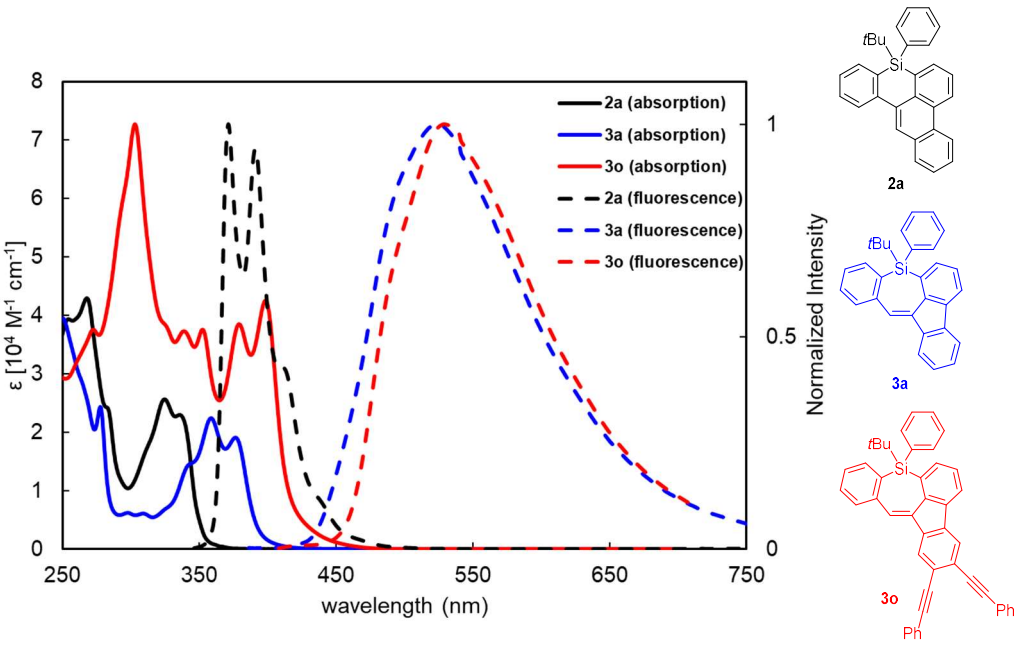


Figure 1. UV-vis absorption (solid lines) and fluorescence (broken lines) spectra of **2a** (black), **3a** (blue) and **3o** (red) in CH_2Cl_2 ($3.3–4.8 \times 10^{-5}$ M) at 25 °C

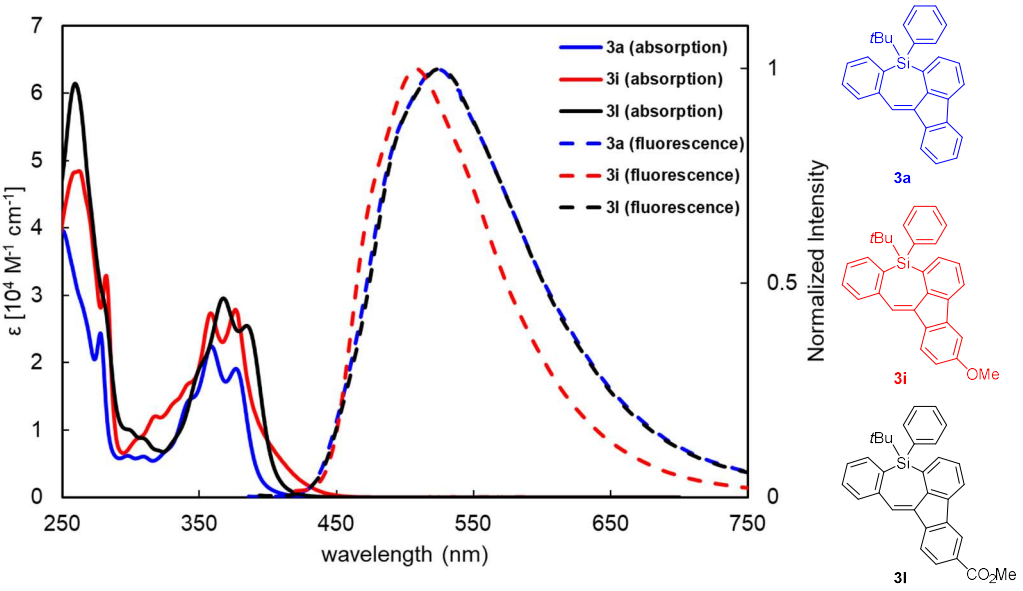


Figure 2 UV-vis absorption (solid lines) and fluorescence (broken lines) spectra of **3a** (blue), **3i** (red) and **3l** (black) in CH_2Cl_2 ($2.5–3.4 \times 10^{-5}$ M) at 25 °C

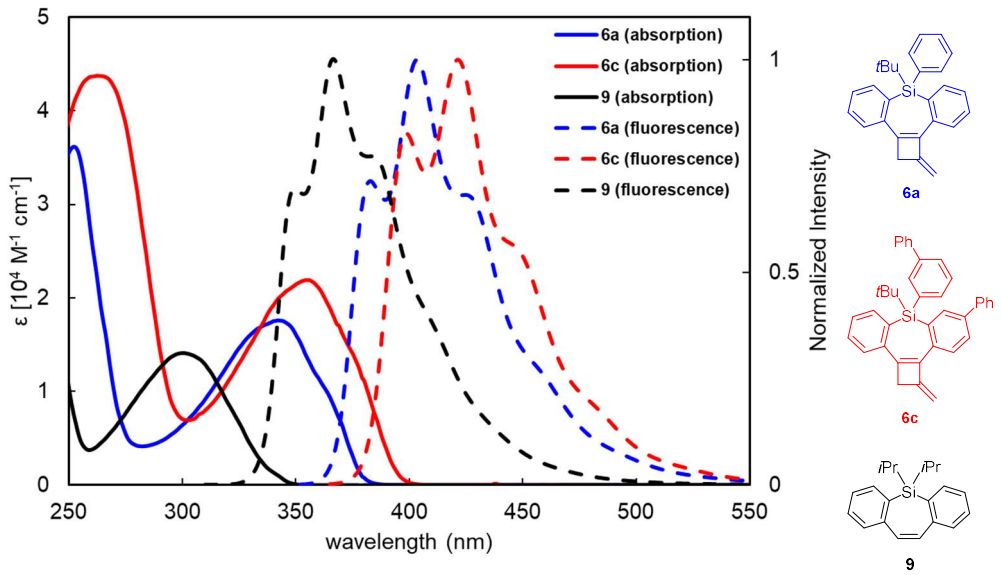


Figure 3. UV-vis absorption (solid lines) and fluorescence (broken lines) spectra of **6a** (blue), **6c** (red) and **9** (black) in CH_2Cl_2 ($2.6–5.8 \times 10^{-5}$ M) at 25 °C

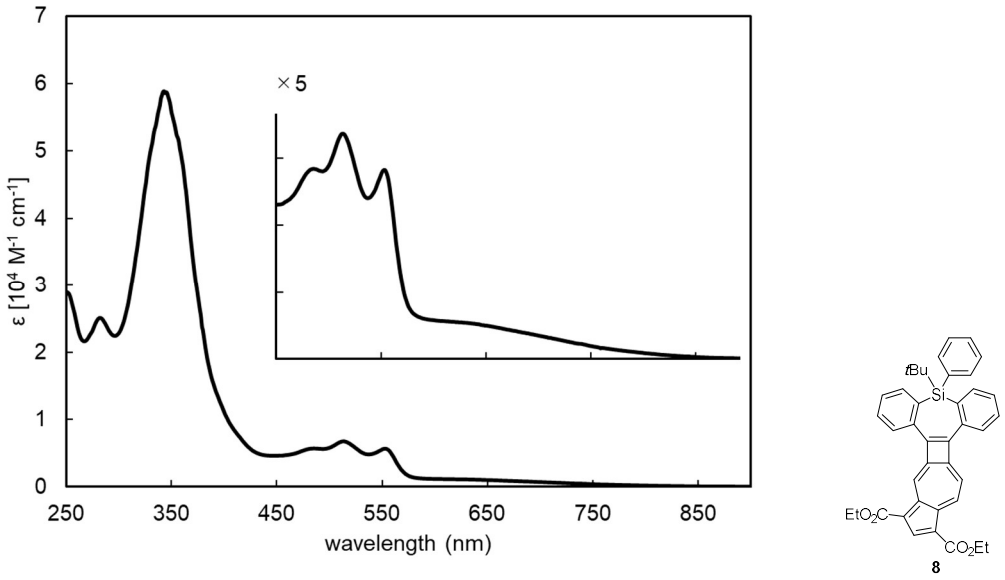
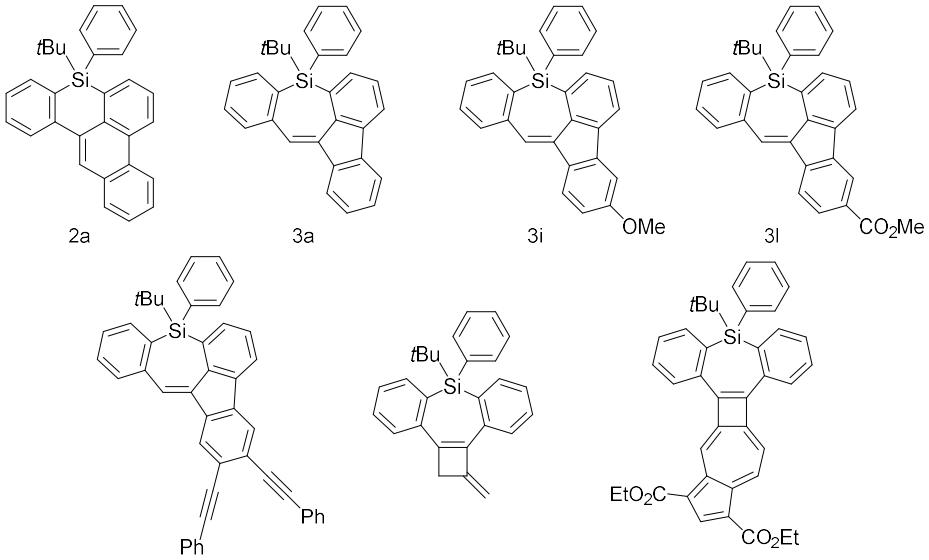


Figure 4. UV-vis absorption spectrum of **8** in CH_2Cl_2 (2.6×10^{-5} M) at 25 °C

Table 4. Electrochemical data for compounds **2a**, **3a**, **3i**, **3l**, **3o**, **6a** and **8**



2a 3a 3i 3l

3o **6a** **8**

compound	E_{ox}^{onset} (V)[a,b]	E_{red}^{onset} (V)[a,c]	E_{HOMO}^{onset} (V)[d,e]	E_{LUMO}^{onset} (V)[e,f]	E_{g}^{onset} (V)[e]
2a	0.96	−2.25	−5.76 [−5.50]	−2.55 [−1.41]	3.21 [4.09]
3a	1.02	−2.05	−5.82 [−5.54]	−2.75 [−1.87]	3.07 [3.67]
3i	0.72	−2.04	−5.52 [−5.26]	−2.76 [−1.78]	2.76 [3.48]
3l	1.06	−1.90	−5.86 [−5.72]	−2.90 [−2.13]	2.96 [3.59]
3o	1.91	−1.91	−5.71 [−5.26]	−2.89 [−2.14]	2.82 [3.12]
6a	0.71	−2.35	−5.51 [−5.37]	−2.45 [−1.53]	3.06 [3.84]
8	0.61	−1.15	−5.41 [−5.12]	−3.65 [−2.73]	1.76 [2.39]

[a] Measured with 0.1 M $(n\text{Bu})_4\text{NBF}_4$ as the supporting electrolyte, Ag/Ag^+ as the reference electrode, glassy carbon as the working electrode, Pt plate as the counter electrode at room temperature under nitrogen with a scan rate of 100 mV/s. The potential was externally calibrated against Fc/Fc^+. [b] In CH_2Cl_2. [c] In THF. [d] $E_{HOMO}^{onset} = -(4.8 + E_{ox}^{onset})$. [e] Values in brackets are calculated at the B3LYP/6-31G(d) level of theory. [f] $E_{LUMO}^{onset} = -(4.8 + E_{red}^{onset})$.

3.3 Conclusion

The author developed a palladium-catalyzed synthetic method of new members of 5*H*-dibenzo[*b*,*f*]silepins, a class of underexplored silicon-bridged π-conjugated compounds. The reaction sequence is composed of (multiple) 1,*n*-palladium migrations and unusual *anti*-carbopalladation of alkynes, which was realized by the proper choice of ligand for palladium. The mechanistic investigation was performed through a series of deuterium-labeling experiments and plausible catalytic cycles were proposed. The resulting 5*H*-dibenzo[*b*,*f*]silepins exhibited tunable optical and electronic properties, demonstrating the power and importance of development of a new synthetic method utilizing 1,*n*-metal migration processes.

3.4 Experimental Section

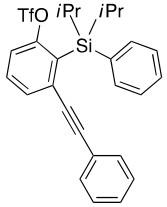
General

All reactions were carried out with standard Schlenk techniques under nitrogen unless otherwise noted. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 or Bruker micrOTOF II spectrometer. UV-VIS spectra were recorded on JASCO V-770 spectrophotometer. Fluorescence spectra were recorded on JASCO FP-8500 Spectrofluorometer. Optical rotations were recorded on JASCO P-2200 polarimeter. Cyclic voltammograms were recorded on BAS ALS electrochemical analyzer model 600C. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200. Preparative GPC was performed with JAI LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent. Computations were performed using workstation at Research Center for Computational Science, National Institutes of Natural Sciences, Okazaki, Japan.

CCl_4 (Wako Chemicals) was dried over $MgSO_4$ and degassed by purging nitrogen prior to use. DMF (Wako Chemicals; dehydrated) and D_2O (ISOTEC) were degassed by purging nitrogen prior to use. *n*$BuNH_2$ (TCI), *t*$BuNH_2$ (TCI), Et_2NH (Wako Chemicals), *i*Pr_2NH (Wako Chemicals) *n*Bu_2NH (Wako Chemicals), and Et_3N (Wako Chemicals) were distilled over KOH under vacuum. THF (Kanto Chemical; dehydrated), Et_2O (Wako Chemicals; dehydrated), CH_2Cl_2 (Wako Chemicals or Kanto Chemical; dehydrated), toluene (Wako Chemicals; dehydrated), 1,4-dioxane (Wako Chemicals; dehydrated), cyclopentyl methyl ether (Wako Chemicals; dehydrated), acetone (Wako Chemicals), MeOH (Wako Chemicals), 3-bromotoluene (Aldrich), 4-iodotoluene (TCI), bromobenzene (Wako Chemicals), trimethylsilylacetylene (Kanto Chemical), *tert*-butyltrichlorosilane (Aldrich), *tert*-butylchlorodiphenylsilane (TCI), dichlorodiisopropylsilane (TCI), imidazole (Nacalai Tesque), trifluoromethanesulfonic anhydride (TCI), *N*-Phenylbis(trifluoromethanesulfonimide) (Wako Chemicals), *m*-chloroperbenzoic acid (Wako Chemicals; 69 wt%), dabco (Wako Chemcals) PPh_3 (Wako Chemicals), PCy_3•HBF_4 (Wako Chemicals), P(*t*Bu)$_3$•HBF_4 (Wako Chemicals), dppe (TCI), dppb (TCI), dppf (TCI), xantphos (Wako Chemicals), biphep (TCI), binap (Wako Chemicals), (*R*)-binap (TCI), K_2CO_3 (Wako Chemicals), NaOAc (Wako Chemicals), *n*BuLi (Kanto Chemical; 1.56–1.57 M solution in hexane), *t*BuLi (Kanto Chemical; 1.52–1.53 M solution in pentane), pyridinium chlorochromate (TCI), NaH (Kishida Chemical; 60 wt% in mineral oil), Mg turnings (Kishida Chemical), Pd on C (Aldrich; 10 wt% Pd), $PdCl_2$ (Tanaka Kikinzoku), $Pd(OAc)_2$ (Wako Chemicals), CuI (Wako Chemicals), and $AgNO_3$ (Kishida Chemical) were used as received. **1a**,[8] **1a'**,[8] diisopropyl(phenyl)silane,[24] 2-bromo-3-(phenylethynyl)phenol,[8] 2-bromo-3-iodophenol,[25] 1,2-bis(2-bromophenyl)ethene,[26] segphos,[27] H_8-binap,[28] $PdCl_2(PPh_3)_2$,[29] and $Pd(PPh_3)_4$[30] were synthesized following the literature procedures.

Representative Procedures for Substrates:

2-(Diisopropyl(phenyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1d)



A solution of diisopropyl(phenyl)silane (670 mg, 3.48 mmol) in CCl_4 (2 mL) was added slowly over 20 min to a suspension of $PdCl_2$ (30.9 mg, 174 μmol) in CCl_4 (1 mL) at room temperature (water bath). The mixture was stirred for 2 h at room temperature and the precipitates were filtered off through Celite with THF. The solvent was removed under reduced pressure and the residue was dissolved in THF (2 mL). A solution of 2-bromo-3-(phenylethynyl)phenol (714 mg, 2.50 mmol) and imidazole (340 mg, 5.00 mmol) in THF (4 mL) was added to it, and the mixture was stirred for 3 h at 60 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/40 to afford (2-bromo-3-(phenylethynyl)phenoxy)diisopropyl(phenyl)silane as a yellow oil (1.02 g, 2.19 mmol, 88% yield).

^{1}H NMR ($CDCl_3$): δ 7.68 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.8 Hz, 2H), 7.62-7.57 (m, 2H), 7.48-7.33 (m, 6H), 7.15 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.02 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 6.76 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 1.51 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.17 (d, $^3J_{HH}$ = 7.4 Hz, 6H), 1.09 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 153.4, 134.8, 133.7, 131.9, 129.9, 128.7, 128.5, 128.0, 127.6, 127.1, 125.9, 123.3, 119.7, 118.5, 93.7, 88.7, 17.7, 17.5, 13.2.

*n*BuLi (1.51 mL, 2.38 mmol; 1.57 M solution in hexane) was added slowly over 10 min to a solution of (2-bromo-3-(phenylethynyl)phenoxy)diisopropyl(phenyl)silane (1.00 g, 2.16 mmol) in THF (4 mL) at −78 °C, and the mixture was stirred for 1 h at −78 °C and for 2.5 h at room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/15 → 1/10 to afford 2-(diisopropyl(phenyl)silyl)-3-(phenylethynyl)phenol as a pale yellow solid (794 mg, 2.06 mmol; 96% yield).

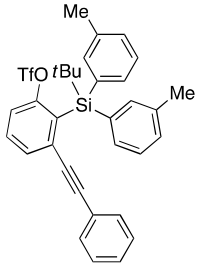
^{1}H NMR ($CDCl_3$): δ 7.69-7.63 (m, 2H), 7.48-7.42 (m, 3H), 7.42-7.36 (m, 2H), 7.36-7.30 (m, 3H), 7.30-7.24 (m, 2H), 6.76 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 2.8 Hz, 1H), 5.29 (s, 1H), 2.04 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.16 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.93 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 162.4, 136.0, 132.5, 131.3, 131.2, 131.1, 130.4, 128.6, 128.5, 128.3, 127.5, 123.7, 119.1, 116.9, 92.5, 91.1, 18.0, 17.9, 11.7.

*n*BuLi (1.44 mL, 2.27 mmol; 1.57 M solution in hexane) was added slowly over 10 min to a solution of 2-(*tert*-butyldiphenylsilyl)-3-(phenylethynyl)phenol (2.50 g, 5.78 mmol) in Et_2O (20 mL) at −78 °C, and the mixture was stirred for 1 h while gradually raising the temperature from −60 °C to −20 °C. Trifluoromethanesulfonic anhydride (372 μL, 2.27 mmol) was then added to it, and the mixture was stirred for 1.5 h while gradually raising the temperature from −20 °C to room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/30 and further purified by GPC with $CHCl_3$ to afford compound **1d** as a white solid (929 g, 1.80 mmol; 88% yield).

^{1}H NMR ($CDCl_3$): δ 7.58 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.50-7.43 (m, 3H), 7.40 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.33-7.18 (m, 6H), 7.01-6.96 (m,

2H), 1.93 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.07 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.00 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.9, 135.1, 133.9, 133.83, 133.77, 131.4, 130.9, 128.9, 128.6, 128.13, 128.10, 127.5, 122.8, 118.7 (q, $^5J_{CF}$ = 2.2 Hz), 118.6 (q, $^1J_{CF}$ = 320 Hz), 95.9, 91.1, 18.4, 18.2, 11.8. HRMS (FAB) calcd for $C_{27}H_{27}F_3O_3SSi$ (M^+) 516.1397, found 516.1403.

2-(*tert*-Butyldi(3-methylphenyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1e)



*t*BuLi (12.4 mL, 18.8 mmol; 1.52 M solution in pentane) was added slowly over 30 min to a solution of 3-bromotoluene (1.15 mL, 9.45 mmol) in THF (8 mL) at −78 °C, and the mixture was stirred for 15 min at −78 °C and for 10 min at room temperature. This was added slowly over 10 min to a solution of *tert*-butyltrichlorosilane (862 mg, 4.50 mmol) in THF (4 mL) at −78 °C, and this was stirred for 15 min at −78 °C and for 3 h at room temperature. The volatiles were removed under vacuum and THF (1.5 mL) was added to the residue. A solution of 2-bromo-3-(phenylethynyl)phenol (820 mg, 3.00 mmol) and imidazole (612 mg, 9.00 mmol) in THF (3.5 mL) was added to it, and the mixture was stirred for 5 h at 60 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/50 → 1/40 to afford (2-bromo-3-(phenylethynyl)phenoxy)(*tert*-butyl)di(3-methylphenyl)silane as a yellow oil (1.35 g,

2.51 mmol, 84% yield).

^{1}H NMR ($CDCl_3$): δ 7.62-7.57 (m, 2H), 7.55 (s, 2H), 7.52 (d, $^{3}J_{HH}$ = 6.4 Hz, 2H), 7.40-7.32 (m, 3H), 7.31-7.23 (m, 4H), 7.07 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.81 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 6.44 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 2.34 (s, 6H), 1.15 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 153.1, 137.4, 136.2, 132.8, 132.2, 131.9, 131.1, 128.7, 128.5, 127.9, 127.3, 126.9, 125.7, 123.3, 119.9, 118.2, 93.7, 88.7, 26.7, 21.8, 19.9.

*n*BuLi (1.77 mL, 2.76 mmol; 1.56 M solution in hexane) was added slowly over 5 min to a solution of (2-bromo-3-(phenylethynyl)phenoxy)(*tert*-butyl)di(3-methylphenyl)silane (1.35 g, 2.51 mmol) in THF (4 mL) at −78 °C, and the mixture was stirred for 20 min at −78 °C and for 14 h at room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/15 → 1/10 to afford 2-(*tert*-butyldi(3-methylphenyl)silyl)-3-(phenylethynyl)phenol as a brown solid (880 mg, 1.91 mmol; 76% yield).

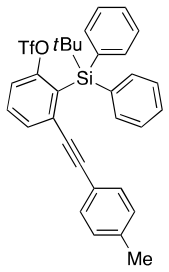
^{1}H NMR ($CDCl_3$): δ 7.61 (s, 2H), 7.57 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H), 7.29 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.26-7.20 (m, 3H), 7.20-7.10 (m, 5H), 6.78-6.70 (m, 3H), 5.59 (s, 1H), 2.27 (s, 6H), 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 162.9, 137.6, 136.8, 135.5, 133.5, 131.3, 131.2, 130.5, 128.3, 127.9, 127.8, 127.7, 123.5, 120.4, 117.1, 95.1, 93.3, 29.9, 21.8, 20.7.

A solution of 2-(*tert*-butyldi(3-methylphenyl)silyl)-3-(phenylethynyl)phenol (852 mg, 1.85 mmol) in Et_2O (5 mL) was added slowly over 10 min to a suspension of NaH (81.4 mg, 2.04 mmol; 60wt% in mineral oil) in Et_2O (1 mL) at 0 °C and this was stirred for 40 min at 0 °C. Trifluoromethanesulfonic anhydride (335 μL, 2.04 mmol) was added to it, and the mixture was stirred for 14 h while gradually raising the temperature from 0 °C to room temperature. The reaction was quenched with H_2O and this was extracted

with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/40 → 1/30, and further purified by GPC with $CHCl_3$ to afford compound **1e** as a pale yellow oil (920 mg, 1.55 mmol; 84% yield).

^{1}H NMR ($CDCl_3$): δ 7.57 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.50 (s, 2H), 7.48-7.37 (m, 4H), 7.24-7.11 (m, 5H), 7.07 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 6.85-6.80 (m, 2H), 2.23 (s, 6H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 136.9, 136.4, 135.7, 134.0, 133.9, 133.0, 131.4, 130.9, 129.8, 129.7, 128.4, 127.9, 127.6, 122.9, 118.7 (q, $^5J_{CF}$ = 1.9 Hz), 118.5 (q, $^1J_{CF}$ = 321 Hz), 97.5, 91.3, 29.8, 21.7, 20.6. HRMS (FAB) calcd for $C_{33}H_{32}F_3O_3SSi$ ($M+H^+$) 593.1788, found 593.1794.

2-(*tert*-Butyldiphenylsilyl)-3-((4-methylphenyl)ethynyl)phenyl trifluoromethanesulfonate (**1j**)



A mixture of trimethylsilylacetylene (4.57 mL, 33.0 mmol), 2-bromo-3-iodophenol (8.97 g, 30.0 mmol), $PdCl_2(PPh_3)_2$ (632 mg, 0.900 mmol), CuI (343 mg, 1.80 mmol), and Et_3N (12.5 mL, 90.0 mmol) in THF (30 mL) was stirred for 2.5 h at room temperature. The mixture was diluted with Et_2O and this was passed through a pad of Celite with Et_2O. After removal of the volatiles under vacuum, the residue was chromatographed on silica gel with EtOAc/hexane = 1/5 → 1/3.5 to afford 2-bromo-3-((trimethylsilyl)ethynyl)phenol as a brown solid (7.82 g, 29.0 mmol; 97% yield).

^{1}H NMR ($CDCl_3$): δ 7.15 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.08 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$

= 1.8 Hz, 1H), 6.98 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 5.63 (s, 1H), 0.28 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 152.8, 128.4, 125.82, 125.80, 116.3, 113.8, 102.8, 99.9, 0.0.

tert-Butylchlorodiphenylsilane (9.78 mL, 37.7 mmol) was added to a solution of 2-bromo-3-((trimethylsilyl)ethynyl)phenol (7.82 g, 29.0 mmol) and imidazole (5.92 g, 87.0 mmol) in THF (38 mL) and the mixture was stirred for 19 h at 40 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/35 to afford (2-bromo-3-(*tert*-butyldiphenylsilyloxy)phenyl)ethynyltrimethylsilane as a yellow viscous oil (14.7 g, 29.0 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 7.73 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H), 7.45 (t, $^{3}J_{HH}$ = 6.9 Hz, 2H), 7.39 (t, $^{3}J_{HH}$ = 6.9 Hz, 4H), 7.02 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.76 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 6.41 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 1.15 (s, 9H), 0.30 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 152.9, 135.6, 132.3, 130.3, 128.1, 127.2, 126.8, 126.1, 120.0, 118.4, 103.6, 99.4, 26.6, 19.9, 0.0.

*n*BuLi (20.3 mL, 31.9 mmol; 1.57 M solution in hexane) was added slowly over 15 min to a solution of (2-bromo-3-(*tert*-butyldiphenylsilyloxy)phenyl)ethynyltrimethylsilane (14.7 g, 29.0 mmol) in THF (30 mL) at −78 °C, and the mixture was stirred for 15 min at −78 °C and for 2 h at room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/15 → 1/10 to afford 2-(*tert*-butyldiphenylsilyl)-3-((trimethylsilyl)ethynyl)phenol as a white solid (11.0 g, 25.6 mmol; 88% yield).

^{1}H NMR ($CDCl_3$): δ 7.76-7.70 (m, 4H), 7.40-7.30 (m, 6H), 7.23 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.19 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.72 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ =

1.4 Hz, 1H), 5.44 (s, 1H), 1.40 (s, 9H), –0.15 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 162.6, 136.4, 136.0, 131.4, 131.1, 129.6, 129.0, 128.3, 120.2, 117.2, 107.7, 100.6, 30.0, 20.7, –0.4.

*n*BuLi (17.9 mL, 28.2 mmol; 1.57 M solution in hexane) was added slowly over 30 min to a solution of 2-(*tert*-butyldiphenylsilyl)-3-((trimethylsilyl)ethynyl)phenol (11.0 g, 25.6 mmol) in Et_2O (50 mL) at −78 °C and the mixture was stirred for 1 h while gradually raising the temperature from −78 °C to −20 °C. Trifluoromethanesulfonic anhydride (4.62 mL, 28.2 mmol) was added to it, and the mixture was stirred for 1.5 h while gradually raising the temperature from −20 °C to room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/35 to afford 2-(*tert*-butyldiphenylsilyl)-3-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate as a white solid (14.4 g, 25.6 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 7.64-7.59 (m, 4H), 7.55 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.41 (dd, $^3J_{HH}$ = 8.3 and 7.3 Hz, 1H), 7.36 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.35-7.25 (m, 6H), 1.36 (s, 9H), –0.10 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.9, 136.0, 135.8, 135.2, 133.8, 130.8, 129.6, 129.0, 127.7, 119.1 (q, $^5J_{CF}$ = 1.9 Hz), 118.5 (q, $^1J_{CF}$ = 321 Hz), 105.7, 103.7, 29.9, 20.7, –0.5.

$AgNO_3$ (878 mg, 5.17 mmol) in H_2O (18.6 mL) was added to a solution of 2-(*tert*-butyldiphenylsilyl)-3-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate (5.80 g, 10.3 mmol) in acetone (80 mL) and the mixture was stirred for 30 h at room temperature in the dark. The reaction was quenched with saturated NaClaq, and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/30 and the solid thus obtained was washed with hexane to afford

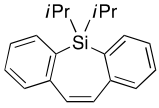
2-(*tert*-butyldiphenylsilyl)-3-ethynylphenyl trifluoromethanesulfonate as a white solid (4.31 g, 8.79 mmol; 85% yield).

^{1}H NMR ($CDCl_3$): δ 7.73-7.68 (m, 4H), 7.54 (dd, $^3J_{HH}$ = 6.4 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 7.48-7.41 (m, 2H), 7.40-7.29 (m, 6H), 2.67 (s, 1H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.8, 135.90, 135.88, 134.7, 132.8, 131.1, 130.2, 129.1, 127.8, 119.3 (q, $^5J_{CF}$ = 2.2 Hz), 118.4 (q, $^1J_{CF}$ = 321 Hz), 84.4, 83.7, 29.8, 20.4.

A mixture of 2-(*tert*-butyldiphenylsilyl)-3-ethynylphenyl trifluoromethanesulfonate (489 mg, 1.0 mmol), 4-iodotoluene (240 mg, 1.1 mmol), $Pd(PPh_3)_4$ (57.8 mg, 50.0 μmol), CuI (19.0 mg, 0.10 mmol), and Et_3N (420 μL, 5.09 mmol) in THF (2.0 mL) was stirred for 15 h at 45 °C. The reaction mixture was diluted with Et_2O and this was passed through a pad of Celite with Et_2O. After removal of the volatiles under vacuum, the residue was chromatographed on silica gel with EtOAc/hexane = 1/40 to afford compound **1j** as a white solid (578 mg, 1.0 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 7.68-7.63 (m, 4H), 7.58 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.45 (dd, $^3J_{HH}$ = 8.5 and 7.5 Hz, 1H), 7.38 (dd, $^3J_{HH}$ = 8.5 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 7.32-7.22 (m, 6H), 6.98 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 2.30 (s, 3H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 138.7, 135.9, 135.8, 134.0, 131.4, 131.0, 129.3, 129.0, 128.8, 127.7, 119.7, 118.7 (q, $^5J_{CF}$ = 1.9 Hz), 118.5 (q, $^1J_{CF}$ = 321 Hz), 98.1, 90.9, 29.8, 21.6, 20.6. HRMS (FAB) calcd for $C_{32}H_{29}F_3O_3SSi$ (M^+) 578.1553, found 578.1557.

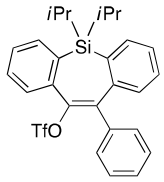
5,5-Diisopropyl-5*H*-dibenzo[*b*,*f*]silepin (9)



*t*BuLi (10.46 mL, 16.0 mmol; 1.53 M solution in pentane) was added slowly over 15 min to a solution of 1,2-bis(2-bromophenyl)ethene (1.35 g, 4.0 mmol; *E*/*Z* = 1/10) in THF (30 mL) at −78 °C and the mixture was stirred for 1 h at −78 °C. Dichlorodiisopropylsilane (0.862 mL, 4.80 mmol) was added to it, and the mixture was stirred for 30 min at −78 °C and for 1.5 h at room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with $CHCl_3$ to afford compound **9** as a white solid (828 mg, 2.83 mmol; 78% yield).

^{1}H NMR ($CDCl_3$): δ 7.72 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 7.40-7.35 (m, 4H), 7.35-7.30 (m, 2H), 6.83 (s, 2H), 1.67 (sept, $^3J_{HH}$ = 7.6 Hz, 2H), 1.19 (d, $^3J_{HH}$ = 7.8 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 142.6, 134.5, 134.4, 133.4, 130.8, 129.0, 127.0, 18.5, 10.6.tt-07-081 HRMS (FAB) calcd for $C_{20}H_{24}Si$ (M^+) 292.1642, found 292.1654.

5,5-Diisopropyl-11-phenyl-5*H*-dibenzo[*b*,*f*]silepin-10-yl trifluoromethanesulfonate (4)



A solution of compound **9** (783 mg, 2.68 mmol) in CH_2Cl_2 (10 mL) was added to a solution of *m*-chloroperbenzoic acid (1.67 g, 6.69 mmol; 69 wt%) in CH_2Cl_2 (20 mL) at 0 °C and the mixture was stirred for 48 h while gradually raising the temperature from 0 °C to room temperature. The reaction was quenched with saturated $NaHCO_3$aq and this was extracted with CH_2Cl_2. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed

on silica gel with EtOAc/hexane = 1/20 to afford 6,6-diisopropyl-1a,10b-dihydro-6*H*-dibenzo[2,3:6,7]silepino[4,5-*b*]oxirene as a white solid (661 mg, 2.13 mmol, 79% yield).

^{1}H NMR ($CDCl_3$): δ 7.68 (dd, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 7.49 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 7.36 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 1.4 Hz, 2H), 7.28 (td, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 4.30 (s, 2H), 1.82 (sept, $^3J_{HH}$ = 7.5 Hz, 1H), 1.77 (sept, $^3J_{HH}$ = 7.6 Hz, 1H), 1.32 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.10 (d, $^3J_{HH}$ = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 141.5, 135.6, 133.2, 130.8, 129.2, 127.3, 63.8, 19.1, 18.3, 16.3, 11.8.

Bromobenzene (455 μL, 4.32 mmol) was slowly added over 20 min to a suspension of Mg turnings (115 mg, 4.75 mmol) in THF (5 mL) and the mixture was stirred for 30 min at room temperature. This was added slowly over 20 min to a suspension of CuI (144 mg, 0.756 mmol) in THF (1 mL) at −78 °C and stirred for 10 min at −78 °C. A solution of 6,6-diisopropyl-1a,10b-dihydro-6*H*-dibenzo[2,3:6,7]silepino[4,5-*b*]oxirene (334 mg, 1.08 mmol) in THF (2 mL) was added slowly over 5 min to it at −78 °C and stirred for 26 h while gradually raising the temperature from −78 °C to room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 → 1/7 to afford 5,5-diisopropyl-11-phenyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin-10-ol as a white solid (198 mg, 0.469 mmol, 43% yield).

^{1}H NMR ($CDCl_3$): δ 7.74 (dd, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.63 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.34-7.25 (m, 2H), 7.25-7.02 (m, 7H), 6.98 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 5.46 (dd, $^3J_{HH}$ = 7.1 and 5.3 Hz, 1H), 4.97 (bs, 1H), 1.98 (bs, 1H), 1.67 (sept, $^3J_{HH}$ = 7.4 Hz, 1H), 1.60 (sept, $^3J_{HH}$ = 7.4 Hz, 1H), 1.17 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 1.05

(d, $^{3}J_{HH}$ = 7.5 Hz, 3H), 0.99 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H), 0.93 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 141.2, 135.8, 135.7, 134.7, 133.0, 132.4, 129.9, 129.5, 129.1, 128.1, 126.4, 126.2, 125.2, 79.5, 60.1, 19.0, 18.8, 18.7, 18.6, 13.9, 13.3.

A mixture of 5,5-diisopropyl-11-phenyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin-10-ol (561 mg, 1.45 mmol), pyridinium chlorochromate (625 mg, 2.90 mmol), and Celite (1.5 g) in CH_2Cl_2 (8 mL) was stirred for 3 h at room temperature. The mixture was diluted with Et_2O and passed through a pad of Celite with Et_2O. After removal of the solvents under vacuum, the residue was chromatographed on silica gel with EtOAc/hexane = 1/10 to afford 5,5-diisopropyl-11-phenyl-5,11-dihydro-10*H*-dibenzo[*b*,*f*]silepin-10-one as a pale yellow oil (515 mg, 1.34 mmol, 92 % yield).

^{1}H NMR ($CDCl_3$): δ 7.76 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.63 (dd, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.62-7.57 (m, 3H), 7.49 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.44 (td, $^{3}J_{HH}$ = 7.5 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.38-7.27 (m, 4H), 7.24 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.09 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.14 (s, 1H), 1.68 (sept, $^{3}J_{HH}$ = 7.4 Hz, 1H), 1.67 (sept, $^{3}J_{HH}$ = 7.4 Hz, 1H), 1.17 (d, $^{3}J_{HH}$ = 7.5 Hz, 3H), 1.15 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H), 1.13 (d, $^{3}J_{HH}$ = 7.6 Hz, 3H), 0.75 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 202.6, 149.4, 147.0, 137.1, 135.5, 134.7, 134.4, 133.5, 130.6, 130.0, 129.6, 129.5, 128.5, 127.5, 127.4, 127.3, 126.1, 62.6, 18.8, 18.0, 17.89, 17.86, 13.4, 12.4.

A solution of 5,5-diisopropyl-11-phenyl-5,11-dihydro-10*H*-dibenzo[*b*,*f*]silepin-10-one (515 mg, 1.34 mmol) in DMF (3 mL) was added slowly over 10 min to a suspension of NaH (70.0 mg, 1.74 mmol; 60 wt% in mineral oil) in DMF (1 mL) at 0 °C, and the mixture was stirred for 3 h at room temperature. *N*-Phenylbis(trifluoromethanesulfonimide) (550 mg, 1.54 mmol) was then added to it and the mixture was stirred for 22 h at room temperature. NaH (15.0 mg, 0.38 mmol; 60 wt% in mineral oil) and *N*-phenylbis(trifluoromethanesulfonimide) (100 mg, 0.28 mmol) were

further added to it and the mixture was stirred for additional 30 h at room temperature. The mixture was diluted with Et_2O, and this was washed with H_2O and then saturated NaClaq, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/30 and further purified by GPC with $CHCl_3$ to afford compound **4** as a white solid (288 mg, 0.557 mmol, 42% yield).

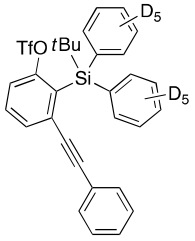
^{1}H NMR ($CDCl_3$): δ 7.88-7.83 (m, 1H), 7.78-7.73 (m, 1H), 7.71 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.51-7.32 (m, 7H), 7.30 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.18 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.01 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 2.07 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.60 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 1.59 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 1.21 (d, $^3J_{HH}$ = 7.8 Hz, 3H), 1.11 (d, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 145.2, 142.1, 140.2, 138.7, 138.2, 137.5, 137.2, 134.0, 133.8, 132.4, 130.4, 129.2, 129.0, 128.5, 128.3, 128.1, 127.6, 118.0 (q, $^1J_{CF}$ = 320 Hz), 19.4, 18.0, 17.7, 10.2, 9.3. HRMS (FAB) calcd for $C_{27}H_{27}F_3O_3SSi$ (M^+) 516.1397, found 516.1395.

nBu$_2$ND

A mixture of nBu$_2$NH (3.0 mL) and D_2O (16 mL) was vigorously stirred for 17 h at room temperature. The amine layer was taken up and dried over Na_2SO_4 under nitrogen to afford nBu$_2$ND as a colorless oil. The deuterium content was determined as >95% by ^{1}H NMR.

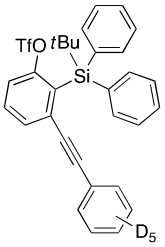
Analytical Data for Other Substrates:

2-(*tert*-Butylbis(pentadeuteriophenyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1a-*d*$_{10}$)



^{1}H NMR ($CDCl_3$): δ 7.59 (dd, $^{3}J_{HH}$ = 7.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.46 (dd, $^{3}J_{HH}$ = 8.7 and 7.3 Hz, 1H), 7.40 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.26-7.20 (m, 1H), 7.20-7.13 (m, 2H), 6.85-6.77 (m, 2H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.6, 135.4 (t, $^{1}J_{CD}$ = 23.0 Hz), 134.1, 133.8, 131.5, 131.0, 129.5, 128.49, 128.46 (t, $^{1}J_{CD}$ = 24.0 Hz), 128.0, 127.2 (t, $^{1}J_{CD}$ = 23.5 Hz), 122.8, 118.9, 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 97.8, 91.5, 29.8, 20.6. HRMS (FAB) calcd for $C_{31}H_{17}D_{10}F_3O_3SSi$ (M^+) 574.2025, found 574.2033.

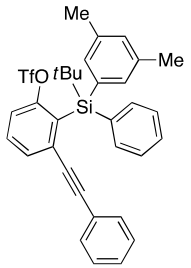
2-(*tert*-Butyldiphenylsilyl)-3-(pentadeuteriophenylethynyl)phenyl trifluoromethanesulfonate (1a-*d*$_5$)



^{1}H NMR ($CDCl_3$): δ 7.69-7.62 (m, 4H), 7.59 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.46 (dd, $^{3}J_{HH}$ = 8.7 and 7.3 Hz, 1H), 7.40 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.32-7.22 (m, 6H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.9, 135.7, 134.1, 133.8, 131.1 (t, $^{1}J_{CD}$ = 24.9 Hz), 131.0, 129.5, 129.0, 128.0 (t, $^{1}J_{CD}$ = 28.7 Hz), 127.8, 127.5 (t,

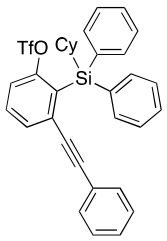
$^{1}J_{CD}$ = 24.4 Hz), 122.6, 118.9 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 97.7, 91.5, 29.8, 20.6. HRMS (FAB) calcd for $C_{31}H_{22}D_5F_3O_3SSi$ (M^+) 569.1711, found 569.1725.

2-(*tert*-Butyl(3,5-dimethylphenyl)(phenyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1b)



^{1}H NMR ($CDCl_3$): δ 7.70-7.64 (m, 4H), 7.57 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.45 (dd, $^{3}J_{HH}$ = 8.7 and 7.4 Hz, 1H), 7.41 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.30-7.14 (m, 8H), 6.89 (s, 1H), 6.85-6.80 (m, 2H), 2.19 (s, 6H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 136.8, 136.1, 135.9, 135.4, 134.0, 133.9, 133.5, 131.4, 130.9, 130.7, 129.8, 128.9, 128.4, 127.9, 127.7, 122.9, 118.7 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 97.5, 91.3, 29.8, 21.6, 20.6. HRMS (FAB) calcd for $C_{33}H_{31}F_3O_3SSi$ (M^+) 592.1710, found 592.1728.

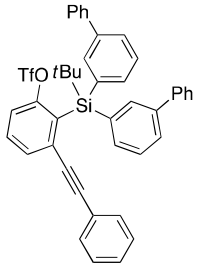
2-(Cyclohexyldiphenylsilyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1c)



^{1}H NMR ($CDCl_3$): δ 7.68-7.62 (m, 4H), 7.55 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.43 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.40-7.26 (m, 8H), 7.25-7.18 (m, 2H), 6.95-6.90 (m,

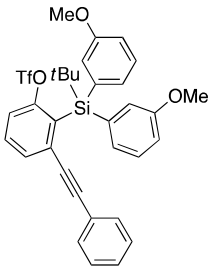
2H), 2.15 (tt, $^{3}J_{HH}$ = 12.4 and 2.3 Hz, 1H), 1.82 (d, $^{3}J_{HH}$ = 13.3 Hz, 2H), 1.69-1.58 (m, 3H), 1.39-1.25 (m, 2H), 1.11-0.90 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 155.8, 135.8, 133.9, 133.6, 133.3, 131.5, 131.0, 130.1, 129.4, 128.7, 128.1, 127.8, 122.7, 119.8, 118.6 (q, $^{1}J_{CF}$ = 321 Hz), 96.8, 90.4, 28.2, 28.1, 26.9, 24.5. HRMS (FAB) calcd for $C_{33}H_{29}F_3O_3SSi$ (M^+) 590.1553, found 590.1562.

2-(*tert*-Butylbis(3-phenylphenyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1f)



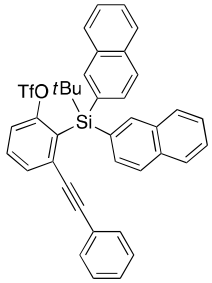
^{1}H NMR ($CDCl_3$): δ 7.95 (s, 2H), 7.67 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 7.61 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.52-7.27 (m, 16H), 7.17 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.07 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H), 6.82-6.76 (m, 2H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 141.9, 140.5, 136.5, 134.7, 134.6, 134.0, 133.8, 131.3, 131.2, 129.2, 128.8, 128.4, 128.2, 128.01, 127.97, 127.3, 127.1, 122.6, 118.9 (q, $^{5}J_{CF}$ = 2.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 97.9, 91.4, 29.9, 20.7. HRMS (FAB) calcd for $C_{43}H_{35}F_3O_3SSi$ (M^+) 716.2023, found 716.2034.

2-(*tert*-Butylbis(3-methoxyphenyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1g)



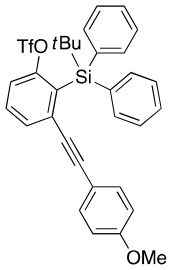
^{1}H NMR ($CDCl_3$): δ 7.58 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.46 (dd, $^{3}J_{HH}$ = 8.2 and 7.3 Hz, 1H), 7.41 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.28-7.15 (m, 9H), 6.91-6.86 (m, 2H), 6.81 (ddd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 2.8 and 1.4 Hz, 2H), 3.67 (s, 6H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 158.8, 157.0, 137.2, 134.0, 133.9, 131.4, 131.1, 129.3, 128.9, 128.4, 128.2, 128.0, 122.8, 121.5, 118.8 (q, $^{5}J_{CF}$ = 2.2 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 114.3, 97.5, 91.2, 55.1, 29.8, 20.6. HRMS (FAB) calcd for $C_{33}H_{32}F_3O_5SSi$ ($M+H^+$) 625.1686, found 625.1693.

2-*(tert*-Butylbis(2-naphthyl)silyl)-3-(phenylethynyl)phenyl trifluoromethanesulfonate (1h)



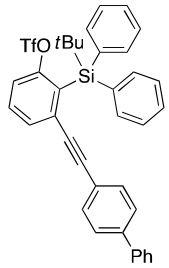
^{1}H NMR ($CDCl_3$): δ 8.20 (s, 2H), 7.82-7.67 (m, 8H), 7.61 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.50 (dd, $^{3}J_{HH}$ = 8.7 and 7.3 Hz, 1H), 7.47-7.36 (m, 5H), 7.03 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 6.84 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 6.39 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 136.7, 134.1, 133.9, 133.8, 133.4, 133.1, 132.1, 131.2, 131.0, 129.3, 128.5, 128.2, 127.7, 127.6, 126.9, 126.6, 125.8, 122.3, 119.0 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.4 (q, $^{1}J_{CF}$ = 321 Hz), 97.6, 91.2, 30.1, 21.0. HRMS (FAB) calcd for $C_{39}H_{31}F_3O_3SSi$ (M^+) 664.1710, found 664.1709.

2-(*tert*-Butyldiphenylsilyl)-3-((4-methoxyphenyl)ethynyl)phenyl trifluoromethanesulfonate (1i)



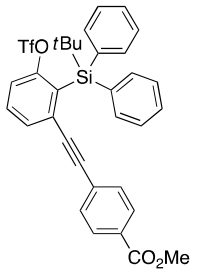
^{1}H NMR ($CDCl_3$): δ 7.68-7.63 (m, 4H), 7.57 (dd, $^{3}J_{HH}$ = 7.5 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.44 (dd, $^{3}J_{HH}$ = 8.5 and 7.5 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 8.3 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.31-7.23 (m, 6H), 6.76-6.72 (m, 2H), 6.72-6.67 (m, 2H), 3.78 (s, 3H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 159.9, 157.0, 136.0, 135.8, 134.1, 133.9, 133.0, 130.9, 129.1, 128.9, 127.7, 118.6 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 114.9, 113.6, 98.0, 90.4, 55.3, 29.8, 20.6. HRMS (FAB) calcd for $C_{32}H_{29}F_3O_4SSi$ (M^+) 594.1502, found 594.1517.

2-(*tert*-Butyldiphenylsilyl)-3-((4-phenylphenyl)ethynyl)phenyl trifluoromethanesulfonate (1k)



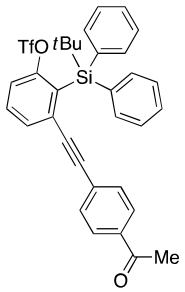
^{1}H NMR ($CDCl_3$): δ 7.72-7.65 (m, 4H), 7.61 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.55 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.51-7.38 (m, 6H), 7.38-7.26 (m, 7H), 6.87 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 141.2, 140.4, 135.9, 135.8, 134.1, 133.8, 131.9, 131.0, 129.4, 129.02, 128.96, 127.8, 127.1, 126.6, 121.6, 118.9 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 97.8, 92.2, 29.8, 20.6. HRMS (FAB) calcd for $C_{37}H_{31}F_3O_3SSi$ (M^+) 640.1710, found 640.1724.

2-(*tert*-Butyldiphenylsilyl)-3-((4-methoxycarbonylphenyl)ethynyl)phenyl trifluoromethanesulfonate (1l)



^{1}H NMR ($CDCl_3$): δ 7.83 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.67-7.63 (m, 4H), 7.60 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.49 (dd, $^{3}J_{HH}$ = 8.5 and 7.5 Hz, 1H), 7.44 (dd, $^{3}J_{HH}$ = 8.5 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.31-7.23 (m, 6H), 6.83 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 3.90 (s, 3H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 166.6, 157.0, 135.8, 135.7, 134.1, 133.2, 131.3, 131.1, 129.8, 129.7, 129.12, 129.08, 127.8, 127.4, 119.3 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 96.7, 94.1, 52.3, 29.7, 20.6. HRMS (FAB) calcd for $C_{33}H_{30}F_3O_5SSi$ ($M+H^+$) 623.1530, found 623.1539.

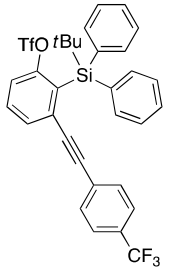
2-(*tert*-Butyldiphenylsilyl)-3-((4-acetylphenyl)ethynyl)phenyl trifluoromethanesulfonate (1m)



^{1}H NMR ($CDCl_3$): δ 7.75 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.68-7.63 (m, 4H), 7.60 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.49 (dd, $^{3}J_{HH}$ = 8.2 and 7.3 Hz, 1H), 7.45 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.32-7.23 (m, 6H), 6.86 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 2.57 (s, 3H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 197.3, 157.0, 136.4, 135.8, 135.7, 134.1, 133.1,

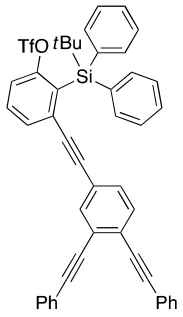
131.5, 131.1, 129.8, 129.1, 127.9, 127.8, 127.5, 119.4 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.4 (q, $^{1}J_{CF}$ = 321 Hz), 96.7, 94.4, 29.7, 26.6, 20.6. HRMS (FAB) calcd for $C_{33}H_{30}F_3O_4SSi$ ($M+H^+$) 607.1581, found 607.1589.

2-(*tert*-Butyldiphenylsilyl)-3-((4-(trifluoromethyl)phenyl)ethynyl)phenyl trifluoromethanesulfonate (1n)



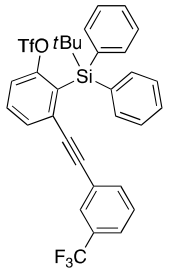
^{1}H NMR ($CDCl_3$): δ 7.68-7.63 (m, 4H), 7.60 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.49 (dd, $^{3}J_{HH}$ = 8.5 and 7.5 Hz, 1H), 7.45 (dd, $^{3}J_{HH}$ = 8.3 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.42 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.32-7.24 (m, 6H), 6.86 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.8, 135.7, 134.1, 133.0, 131.7, 131.2, 130.1 (q, $^{2}J_{CF}$ = 32.6 Hz), 129.8, 129.1, 127.8, 126.5 (q, $^{4}J_{CF}$ = 1.9 Hz), 124.9 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.0 (q, $^{1}J_{CF}$ = 272 Hz), 119.5 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 96.0, 93.5, 29.8, 20.6. HRMS (FAB) calcd for $C_{32}H_{26}F_6O_3SSi$ (M^+) 632.1271, found 632.1269.

2-(*tert*-Butyldiphenylsilyl)-3-((3,4-di(phenylethynyl)phenyl)ethynyl)phenyl trifluoromethanesulfonate (1o)



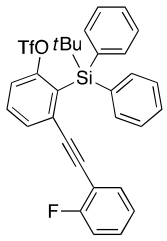
^{1}H NMR ($CDCl_3$): δ 7.72-7.64 (m, 4H), 7.63-7.58 (m, 3H), 7.58-7.53 (m, 2H), 7.49 (dd, $^{3}J_{HH}$ = 8.7 and 7.3 Hz, 1H), 7.44 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.42-7.26 (m, 13H), 6.86 (d, $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.73 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.84, 135.76, 134.7, 134.0, 133.3, 131.81, 131.79, 131.4, 131.1, 130.6, 129.7, 129.1, 128.8, 128.61, 128.55, 127.9, 125.74, 125.66, 123.3, 123.2, 122.5, 119.2 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 96.7, 95.6, 94.1, 93.5, 88.3, 87.7, 29.8, 20.6. HRMS (FAB) calcd for $C_{47}H_{35}F_3O_3SSi$ (M^+) 764.2023, found 764.2028.

2-(*tert*-Butyldiphenylsilyl)-3-((3-(trifluoromethyl)phenyl)ethynyl)phenyl trifluoromethanesulfonate (1p)



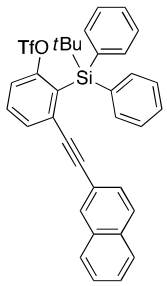
^{1}H NMR ($CDCl_3$): δ 7.69-7.62 (m, 4H), 7.60 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.52-7.43 (m, 3H), 7.33-7.22 (m, 7H), 7.02 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.92 (s, 1H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 135.81, 135.75, 134.5, 134.1, 133.1, 131.2, 130.7 (q, $^{2}J_{CF}$ = 32.6 Hz), 129.8, 129.1, 128.5, 128.4 (q, $^{3}J_{CF}$ = 3.8 Hz), 127.9, 125.0 (q, $^{3}J_{CF}$ = 3.8 Hz), 123.8 (q, $^{1}J_{CF}$ = 272 Hz), 123.6, 119.4 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 96.0, 92.7, 29.8, 20.6. HRMS (FAB) calcd for $C_{32}H_{26}F_6O_3SSi$ (M^+) 632.1271, found 632.1278.

2-(*tert*-Butyldiphenylsilyl)-3-((2-fluorophenyl)ethynyl)phenyl trifluoromethanesulfonate (1q)



^{1}H NMR ($CDCl_3$): δ 7.70-7.64 (m, 4H), 7.63 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.47 (dd, $^{3}J_{HH}$ = 8.7 and 7.3 Hz, 1H), 7.42 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.29-7.18 (m, 7H), 6.98-6.88 (m, 2H), 6.54 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 162.5 (d, $^{1}J_{CF}$ = 252 Hz), 157.0, 135.8, 134.4, 133.4 (d, $^{3}J_{CF}$ = 9.6 Hz), 131.1, 130.2 (d, $^{3}J_{CF}$ = 7.7 Hz), 129.5, 129.0, 127.8, 123.5 (d, $^{4}J_{CF}$ = 3.8 Hz), 119.2 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 115.3 (d, $^{2}J_{CF}$ = 20.1 Hz), 111.5 (d, $^{2}J_{CF}$ = 15.3 Hz), 95.9 (d, $^{3}J_{CF}$ = 3.8 Hz), 91.0, 29.8, 20.5. HRMS (FAB) calcd for $C_{31}H_{27}F_4O_3SSi$ ($M+H^+$) 583.1381, found 583.1387.

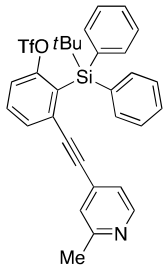
2-(*tert*-Butyldiphenylsilyl)-3-(2-naphthylethynyl)phenyl trifluoromethanesulfonate (1r)



^{1}H NMR ($CDCl_3$): δ 7.79-7.73 (m, 1H), 7.72-7.60 (m, 7H), 7.52-7.40 (m, 4H), 7.34-7.25 (m, 6H), 7.17 (s, 1H), 6.90 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.1, 136.0, 135.9, 134.1, 133.8, 132.9, 132.8, 131.7, 131.1, 129.5, 129.0, 128.0, 127.9, 127.8, 127.6, 126.9, 126.5, 120.0, 119.0 (q, $^{5}J_{CF}$ = 1.9 Hz),

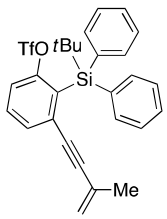
118.5 (q, $^{1}J_{CF}$ = 321 Hz), 98.3, 91.8, 29.9, 20.7. HRMS (FAB) calcd for $C_{35}H_{29}F_3O_3SSi$ (M^+) 614.1553, found 614.1561.

2-(*tert*-Butyldiphenylsilyl)-3-((2-methyl-4-pyridyl)ethynyl)phenyl trifluoromethanesulfonate (1s)



^{1}H NMR (acetone-d_6): δ 8.30 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H), 7.77-7.67 (m, 6H), 7.63-7.57 (m, 1H), 7.37-7.27 (m, 6H), 6.62 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H), 6.53 (s, 1H), 2.40 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (acetone-d_6): δ 159.1, 157.8, 149.7, 136.6, 136.5, 135.3, 133.6, 132.8, 131.2, 130.4, 129.9, 128.6, 125.1, 122.7, 120.7 (q, $^{5}J_{CF}$ = 1.9 Hz), 119.3 (q, $^{1}J_{CF}$ = 320 Hz), 95.8, 95.2, 30.0, 24.3, 21.0. HRMS (FAB) calcd for $C_{31}H_{29}F_3NO_3SSi$ ($M+H^+$) 580.1584, found 580.1596.

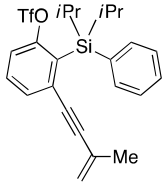
2-(*tert*-Butyldiphenylsilyl)-3-(3-methyl-3-buten-1-ynyl)phenyl trifluoromethanesulfonate (5a)



^{1}H NMR ($CDCl_3$): δ 7.69-7.63 (m, 4H), 7.52 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.43 (dd, $^{3}J_{HH}$ = 8.7 and 6.9 Hz, 1H), 7.39 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.36-7.27 (m, 6H), 5.06-5.01 (m, 1H), 4.80-4.76 (m, 1H), 1.50 (s, 3H), 1.39 (s, 9H).

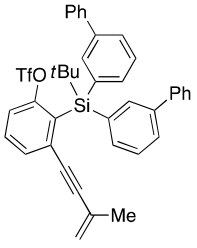
^{13}C NMR ($CDCl_3$): δ 157.0, 135.9, 135.8, 134.1, 133.8, 130.9, 129.3, 128.9, 127.7, 126.5, 122.6, 118.7 (q, $^5J_{CF}$ = 1.9 Hz), 118.4 (q, $^1J_{CF}$ = 321 Hz), 98.8, 90.3, 29.8, 22.5, 20.6. HRMS (FAB) calcd for $C_{28}H_{28}F_3O_3SSi$ ($M+H^+$) 529.1475, found 529.1477.

2-(Diisopropyl(phenyl)silyl)-3-(3-methyl-3-buten-1-ynyl)phenyl trifluoromethanesulfonate (5b)



^{1}H NMR ($CDCl_3$): δ 7.48 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.45-7.27 (m, 7H), 5.12-5.07 (m, 1H), 4.95-4.90 (m, 1H), 1.90 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.61 (s, 3H), 1.05 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.99 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.9, 135.1, 133.9, 133.7, 130.9, 128.8, 128.1, 127.4, 126.5, 122.5, 118.58 (q, $^1J_{CF}$ = 320 Hz), 118.57 (q, $^5J_{CF}$ = 1.9 Hz), 96.9, 90.0, 22.6, 18.3, 18.2, 11.8. HRMS (FAB) calcd for $C_{24}H_{28}F_3O_3SSi$ ($M+H^+$) 481.1475, found 481.1479.

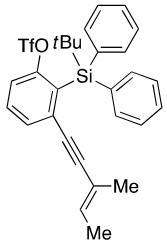
2-(*tert*-Butylbis(3-phenylphenyl)silyl)-3-(3-methyl-3-buten-1-ynyl)phenyl trifluoromethanesulfonate (5c)



^{1}H NMR ($CDCl_3$): δ 7.99 (s, 2H), 7.73 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 2H), 7.62-7.53 (m, 7H), 7.51-7.40 (m, 8H), 7.39-7.33 (m, 2H), 5.05-5.00 (m, 1H), 4.84-4.79 (m, 1H), 1.52 (s, 9H), 1.50 (d, $^4J_{HH}$ = 0.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 157.0, 141.9,

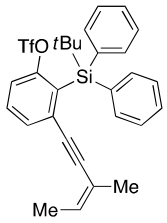
140.4, 136.5, 134.6, 134.0, 133.8, 131.1, 129.0, 128.9, 128.8, 128.2, 127.9, 127.3, 127.2, 126.4, 122.6, 118.8 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.4 (q, $^{1}J_{CF}$ = 321 Hz), 98.9, 90.3, 29.9, 22.4, 20.7. HRMS (FAB) calcd for $C_{40}H_{36}F_3O_3SSi$ ($M+H^+$) 681.2101, found 681.2116.

(*E*)-2-(*tert*-Butyldiphenylsilyl)-3-(3-methyl-3-penten-1-ynyl)phenyl trifluoromethanesulfonate ((*E*)-5d (*E*/*Z* = 97/3))



(*E*)-5d: ^{1}H NMR ($CDCl_3$): δ 7.70-7.64 (m, 4H), 7.50 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.41 (dd, $^{3}J_{HH}$ = 8.2 and 7.4 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.36-7.27 (m, 6H), 5.36 (qq, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 1.58 (dq, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 3H), 1.39 (s, 9H), 1.39-1.37 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 157.0, 136.0, 135.8, 134.5, 133.9, 133.5, 130.8, 128.9, 128.8, 127.6, 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 118.31, 118.30 (q, $^{5}J_{CF}$ = 2.2 Hz), 101.1, 88.1, 29.8, 20.6, 15.8, 14.0. HRMS (FAB) calcd for $C_{29}H_{30}F_3O_3SSi$ ($M+H^+$) 543.1632, found 543.1638.

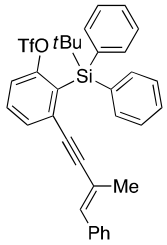
(*Z*)-2-(*tert*-Butyldiphenylsilyl)-3-(3-methyl-3-penten-1-ynyl)phenyl trifluoromethanesulfonate ((*Z*)-5d (*E*/*Z* = 20/80))



(*Z*)-5d: ^{1}H NMR ($CDCl_3$): δ 7.70-7.64 (m, 4H), 7.55 (dd, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$

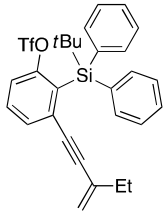
= 1.8 Hz, 1H), 7.47-7.38 (m, 2H), 7.36-7.28 (m, 6H), 5.57 (qq, $^{3}J_{HH}$ = 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 1.62 (dq, $^{3}J_{HH}$ = 6.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 3H), 1.41 (s, 9H), 1.37-1.33 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.9, 135.8, 134.6, 134.2, 133.9, 133.2, 130.9, 128.9, 127.7, 118.8, 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 118.4 (q, $^{5}J_{CF}$ = 2.2 Hz), 97.4, 94.9, 29.9, 21.8, 20.5, 16.3. HRMS (FAB) calcd for $C_{29}H_{30}F_3O_3SSi$ ($M+H^+$) 543.1632, found 543.1638.

(*E*)-2-(*tert*-Butyldiphenylsilyl)-3-(3-methyl-4-phenyl-3-buten-1-ynyl)phenyl trifluoromethanesulfonate (5e)



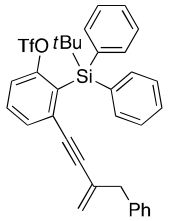
^{1}H NMR ($CDCl_3$): δ 7.80-7.73 (m, 4H), 7.64-7.57 (m, 1H), 7.51-7.45 (m, 2H), 7.43-7.35 (m, 8H), 7.33-7.22 (m, 3H), 6.19 (s, 1H), 1.76 (d, $^{4}J_{HH}$ = 1.8 Hz, 3H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 136.8, 136.5, 135.9, 135.8, 134.1, 134.0, 131.0, 129.1, 129.0, 128.9, 128.4, 127.7, 127.4, 119.4, 118.6 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 101.6, 90.5, 29.8, 20.6, 18.2. HRMS (FAB) calcd for $C_{34}H_{32}F_3O_3SSi$ ($M+H^+$) 605.1788, found 605.1789.

2-(*tert*-Butyldiphenylsilyl)-3-(3-methylene-1-pentynyl)phenyl trifluoromethanesulfonate (5f)



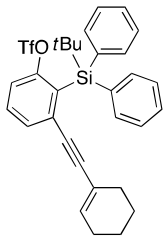
^{1}H NMR ($CDCl_3$): δ 7.65-7.60 (m, 4H), 7.49 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.42 (dd, $^{3}J_{HH}$ = 8.3 and 7.3 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.33-7.24 (m, 6H), 5.02-4.98 (m, 1H), 4.67-4.63 (m, 1H), 1.81 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.35 (s, 9H), 0.88 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 157.0, 135.9, 135.8, 134.1, 134.0, 132.8, 130.9, 129.3, 128.9, 127.7, 120.6, 118.7 (q, $^{5}J_{CF}$ = 2.2 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 98.5, 91.0, 29.8, 29.5, 20.5, 12.8. HRMS (FAB) calcd for $C_{29}H_{30}F_3O_3SSi$ ($M+H^+$) 543.1632, found 543.1634.

2-(*tert*-Butyldiphenylsilyl)-3-(3-benzyl-3-buten-1-ynyl)phenyl trifluoromethanesulfonate (5g)



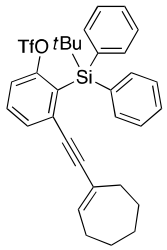
^{1}H NMR ($CDCl_3$): δ 7.65-7.60 (m, 4H), 7.42-7.24 (m, 11H), 7.23-7.18 (m, 1H), 7.09-7.04, (m, 2H), 4.94-4.91 (m, 1H), 4.76-4.73 (m, 1H), 3.08 (s, 2H), 1.32 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.9, 138.3, 135.9, 135.8, 134.1, 133.8, 130.9, 130.5, 129.23, 129.21, 129.0, 128.4, 127.7, 126.5, 122.8, 118.7 (q, $^{5}J_{CF}$ = 2.2 Hz), 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 98.3, 91.5, 42.5, 29.7, 20.5. HRMS (FAB) calcd for $C_{34}H_{32}F_3O_3SSi$ ($M+H^+$) 605.1788, found 605.1793.

2-(*tert*-Butyldiphenylsilyl)-3-(1-cyclohexenylethynyl)phenyl trifluoromethanesulfonate (5h)



^{1}H NMR ($CDCl_3$): δ 7.65-7.60 (m, 4H), 7.46 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.39 (dd, $^3J_{HH}$ = 8.7 and 7.3 Hz, 1H), 7.33 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.32-7.24 (m, 6H), 5.57-5.52 (m, 1H), 2.01-1.93 (m, 2H), 1.67-1.59 (m, 2H), 1.52-1.44 (m, 4H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 136.0, 135.8, 135.7, 134.4, 133.9, 130.8, 129.0, 128.8, 127.6, 120.5, 118.5 (q, $^1J_{CF}$ = 321 Hz), 118.3 (q, $^5J_{CF}$ = 1.9 Hz), 99.8, 89.0, 29.8, 28.0, 25.7, 22.2, 21.5, 20.6. HRMS (FAB) calcd for $C_{31}H_{32}F_3O_3SSi$ ($M+H^+$) 569.1788, found 569.1798.

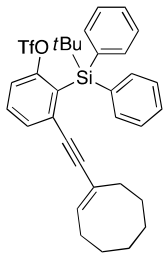
2-(*tert*-Butyldiphenylsilyl)-3-(1-cycloheptenylethynyl)phenyl trifluoromethanesulfonate (5i)



^{1}H NMR ($CDCl_3$): δ 7.73-7.63 (m, 4H), 7.49 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.41 (dd, $^3J_{HH}$ = 8.2 and 7.4 Hz, 1H), 7.38-7.27 (m, 7H), 5.77 (t, $^3J_{HH}$ = 6.9 Hz, 1H), 2.09 (dd, $^3J_{HH}$ = 11.0 and 6.4 Hz, 2H), 1.89-1.82 (m, 2H), 1.74-1.64 (m, 2H), 1.50-1.31 (m, 4H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 141.0, 136.0, 135.8, 134.6, 133.8, 130.8, 128.8, 127.6, 126.6, 118.5 (q, $^1J_{CF}$ = 321 Hz), 118.2 (q, $^5J_{CF}$ = 1.9 Hz), 101.5, 89.2,

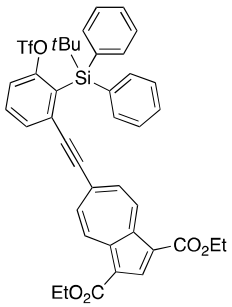
32.9, 32.2, 29.9, 29.3, 26.6, 26.5, 20.6. HRMS (FAB) calcd for $C_{32}H_{34}F_3O_3SSi$ ($M+H^+$) 583.1945, found 583.1947.

2-(*tert*-Butyldiphenylsilyl)-3-(1-cyclooctenylethynyl)phenyl trifluoromethanesulfonate (5j)



^{1}H NMR ($CDCl_3$): δ 7.73-7.63 (m, 4H), 7.51 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.41 (dd, $^3J_{HH}$ = 8.2 and 7.4 Hz, 1H), 7.39-7.27 (m, 7H), 5.44 (t, $^3J_{HH}$ = 8.5 Hz, 1H), 2.11-2.02 (m, 2H), 2.00-1.92 (m, 2H), 1.54-1.30 (m, 8H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.0, 138.9, 136.0, 135.8, 134.6, 134.2, 130.8, 128.9, 127.7, 123.5, 118.5 (q, $^1J_{CF}$ = 321 Hz), 118.3 (q, $^5J_{CF}$ = 1.9 Hz), 101.0, 88.8, 29.9, 29.5, 29.2, 28.7, 26.9, 26.3, 25.9, 20.6. HRMS (FAB) calcd for $C_{33}H_{36}F_3O_3SSi$ ($M+H^+$) 597.2101, found 597.2113.

2-(*tert*-Butyldiphenylsilyl)-3-((1,3-bis(ethoxycarbonyl)-6-azulenyl)ethynyl)phenyl trifluoromethanesulfonate (7)

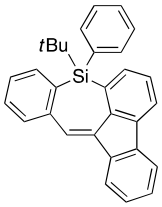


^{1}H NMR ($CDCl_3$): δ 9.48 (d, $^3J_{HH}$ = 11.0 Hz, 2H), 8.78 (s, 1H), 7.77-7.63 (m, 5H), 7.56-7.49 (m, 2H), 7.38-7.27 (m, 6H), 7.05 (d, $^3J_{HH}$ = 11.4 Hz, 2H), 4.44 (q, $^3J_{HH}$ = 7.2

Hz, 4H), 1.46 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.9, 157.0, 143.8, 143.4, 137.1, 135.8, 135.48, 135.46, 134.4, 132.9, 132.4, 131.3, 130.2, 129.3, 127.9, 120.0 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.4 (q, $^{1}J_{CF}$ = 321 Hz), 116.9, 100.2, 96.6, 60.2, 29.6, 20.5, 14.6. HRMS (FAB) calcd for $C_{41}H_{38}F_3O_7SSi$ ($M+H^+$) 759.2054, found 759.2057.

General Procedure for Schemes 5 and 8, and Equations 2, 3, and 7

Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.3 mg, 10 μmol), binap (6.9 mg, 11.1 μmol), and compound **1** or **5** (0.200 mmol) in cyclopentyl methyl ether (0.40 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc. After removal of the volatiles under vacuum, the residue was purified by preparative TLC on silica gel with EtOAc/hexane = 1/50 and by GPC with $CHCl_3$ to afford compound **3** or **6**.



Scheme 5, Compound 3a. Yellow solid. 67% yield (55.2 mg). Each ^{1}H NMR signal was assigned by the ^{1}H-^{1}H COSY experiment (Figure 5).

^{1}H NMR ($CDCl_3$): δ 7.91-7.85 (m, 3H), 7.79 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.77-7.72 (m, 1H), 7.68 (s, 1H), 7.65 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.51-7.40 (m, 4H), 7.40-7.33 (m, 3H), 7.30 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.24 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.13 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 143.1, 142.2, 141.3, 139.6, 139.1, 139.0, 137.5, 137.4, 136.0, 135.9, 134.3, 133.6, 131.2,

131.1, 129.8, 129.4, 128.0, 127.9, 127.8, 127.1, 120.8, 120.0, 119.9, 27.0, 20.8. HRMS (FAB) calcd for $C_{30}H_{27}Si$ ($M+H^+$) 415.1877, found 415.1888.

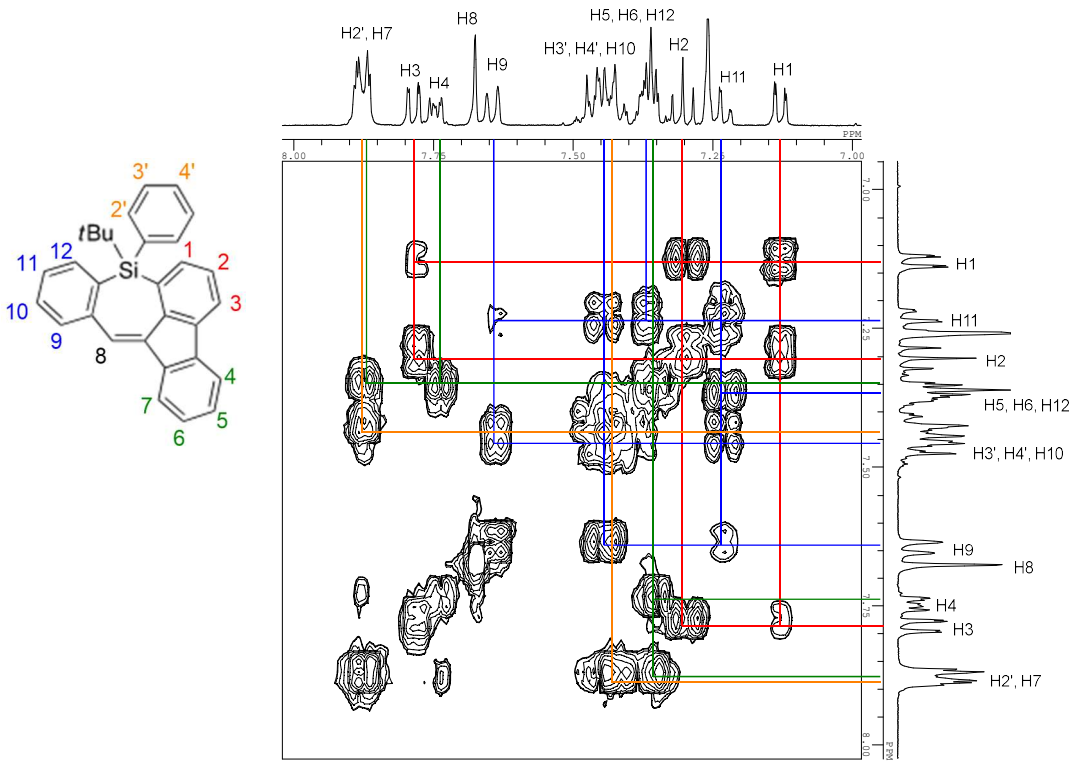
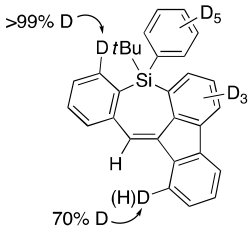
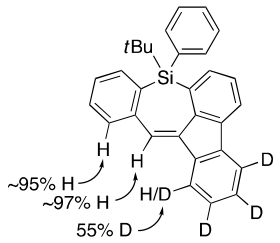


Figure 5. ^{1}H-^{1}H COSY spectrum (aromatic region) of **3a** in $CDCl_3$



Equation 2, Compound 3a-*d*$_{9.7}$. Yellow solid. 56% yield (47.6 mg).

^{1}H NMR ($CDCl_3$): δ 7.92-7.85 (m, 0.3H), 7.78-7.72 (m, 1H), 7.67 (s, 1H), 7.65 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.46 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.40-7.33 (m, 2H), 7.24 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 0.94 (s, 9H).



Equation 3, Compound 3a-$d_{3.5}$. Yellow solid. 65% yield (54.5 mg).

^{1}H NMR ($CDCl_3$): δ 7.91-7.84 (m, 2.45H), 7.79 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.68 (s, 0.97H), 7.65 (d, $^{3}J_{HH}$ = 7.8 Hz, 0.95H), 7.51-7.40 (m, 4H), 7.37 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.31 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 7.24 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.13 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 0.94 (s, 9H).

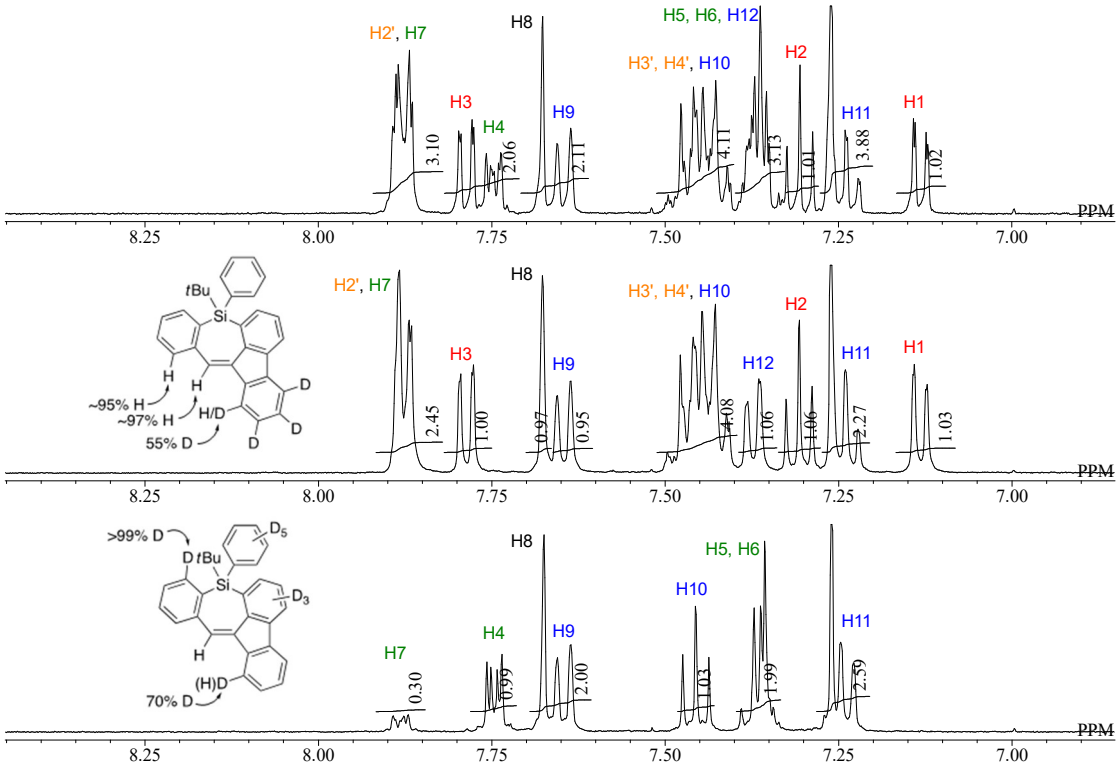
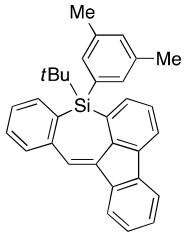
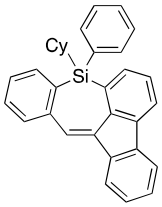


Figure 6. ^{1}H NMR spectra (aromatic region) of **3a**, **3a**-$d_{3.5}$, and **3a**-$d_{9.7}$ in $CDCl_3$



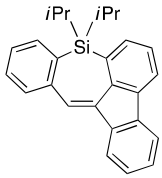
Scheme 5, Compound 3b. Yellow solid. 63% yield (55.8 mg).

^{1}H NMR ($CDCl_3$): δ 7.95-7.89 (m, 1H), 7.82 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.80-7.75 (m, 1H), 7.72 (s, 1H), 7.68 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.53 (s, 2H), 7.51-7.43 (m, 2H), 7.42-7.37 (m, 2H), 7.35 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.28 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.22 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.15 (s, 1H), 2.38 (s, 6H), 0.98 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 143.0, 142.2, 141.3, 139.5, 139.12, 139.06, 137.4, 137.0, 136.2, 135.5, 135.1, 134.2, 133.9, 131.5, 131.2, 131.1, 129.7, 127.9, 127.8, 127.0, 120.8, 120.0, 119.8, 27.1, 21.7, 20.8. HRMS (FAB) calcd for $C_{32}H_{31}Si$ ($M+H^+$) 443.2190, found 443.2187.



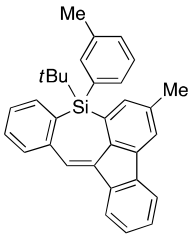
Scheme 5, Compound 3c. Yellow solid. 58% yield (51.5 mg).

^{1}H NMR ($CDCl_3$): δ 7.93-7.86 (m, 1H), 7.82-7.73 (m, 4H), 7.68 (s, 1H), 7.64 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.53-7.42 (m, 4H), 7.41-7.35 (m, 3H), 7.33 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.25 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.16 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 1.63-1.51 (m, 5H), 1.35-1.25 (m, 1H), 1.19-0.92 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 142.9, 142.0, 141.4, 139.6, 139.2, 137.8, 137.4, 136.8, 135.0, 134.8, 134.0, 133.5, 131.0, 130.9, 129.8, 129.7, 128.24, 128.20, 128.1, 127.9, 127.1, 120.9, 120.1, 119.9, 28.11, 28.09, 27.40, 27.36, 26.7, 26.3. HRMS (FAB) calcd for $C_{32}H_{28}Si$ (M^+) 440.1955, found 440.1956.



Scheme 5, Compound 3d. The reaction was conducted on a 1.30 mmol scale. Yellow solid. 50% yield (238 mg).

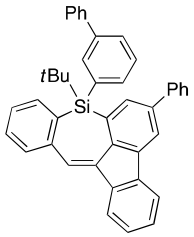
^{1}H NMR ($CDCl_3$): δ 7.88-7.83 (m, 1H), 7.82-7.78 (m, 2H), 7.76-7.71 (m, 1H), 7.623 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.617 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.60 (s, 1H), 7.48 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.44 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.39 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.38-7.31 (m, 2H), 1.53 (sept, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.07 (d, $^{3}J_{HH}$ = 7.8 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 143.0, 142.2, 141.2, 139.9, 139.0, 137.1, 135.7, 134.7, 133.9, 133.2, 131.2, 131.1, 129.6, 128.1, 128.0, 127.8, 127.0, 120.7, 119.9, 119.7, 18.3, 18.2, 13.0. HRMS (FAB) calcd for $C_{26}H_{27}Si$ ($M+H^+$) 367.1877, found 367.1870.



Scheme 5, Compound 3e. Yellow solid. 67% yield (59.4 mg).

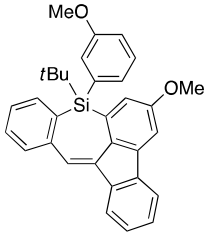
^{1}H NMR ($CDCl_3$): δ 7.90-7.83 (m, 1H), 7.75-7.63 (m, 4H), 7.61 (s, 1H), 7.60 (d, $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.44 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.38-7.27 (m, 5H), 7.22 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^{4}J_{HH}$ = 0.9 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 0.92 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 142.3, 141.7, 140.8, 139.9, 139.1, 139.0, 138.0, 137.8, 137.3, 137.2, 136.6, 135.8, 134.4, 134.1, 133.7, 131.1, 130.2, 130.1, 129.7, 127.8, 127.7, 127.6, 126.9, 121.8, 120.0, 119.7, 27.1, 22.0, 21.8, 20.8. HRMS (FAB) calcd

for $C_{32}H_{31}Si$ ($M+H^+$) 443.2190, found 443.2193.



Scheme 5, Compound 3f. Yellow amorphous. 60% yield (67.6 mg).

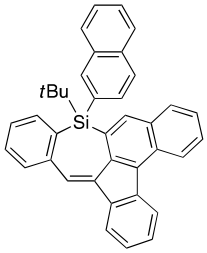
^{1}H NMR ($CDCl_3$): δ 8.15 (s, 1H), 8.01 (d, $^4J_{HH}$ = 1.4 Hz, 1H), 7.94-7.86 (m, 2H), 7.85-7.78 (m, 1H), 7.73-7.68 (m, 2H), 7.67 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.62-7.56 (m, 2H), 7.54-7.23 (m, 15H), 1.01 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 142.33, 142.27, 141.7, 141.5, 141.4, 140.8, 140.6, 140.4, 139.0, 138.9, 137.1, 136.32, 136.27, 136.0, 134.8, 134.4, 133.3, 131.5, 131.0, 129.9, 128.93, 128.89, 128.44, 128.40, 128.0, 127.9, 127.5, 127.40, 127.36, 127.3, 120.1, 119.9, 119.8, 27.2, 20.8. HRMS (FAB) calcd for $C_{42}H_{35}Si$ ($M+H^+$) 567.2503, found 567.2508.



Scheme 5, Compound 3g. EtOAc/hexane = 1/20 was used for preparative TLC. Yellow solid. 52% yield (49.2 mg).

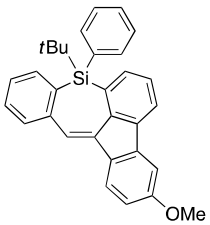
^{1}H NMR ($CDCl_3$): δ 7.91-7.85 (m, 1H), 7.76-7.70 (m, 1H), 7.63 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.58 (s, 1H), 7.50-7.30 (m, 8H), 7.24 (td, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.02 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 2.8 Hz, 1H), 6.73 (d, $^4J_{HH}$ = 2.7 Hz, 1H), 3.81 (s, 6H), 0.98 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 159.9, 158.9, 142.5, 142.3, 141.8, 138.9, 137.1, 136.8, 136.4, 133.9, 132.74, 132.69, 129.8, 129.7, 129.1, 128.9, 127.8, 127.5, 127.2, 122.8, 121.6,

120.0, 119.8, 114.8, 106.1, 55.5, 55.3, 27.2, 20.8. HRMS (FAB) calcd for $C_{32}H_{30}O_2Si$ (M^+) 474.2010, found 474.2014.



Scheme 5, Compound 3h. Yellow solid. 28% yield (29.6 mg).

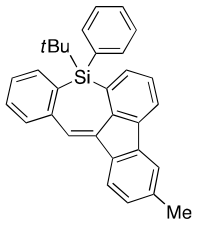
^{1}H NMR ($CDCl_3$): δ 8.82 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 8.60 (s, 1H), 8.40 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 8.03 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.01-7.85 (m, 5H), 7.77-7.68 (m, 3H), 7.68-7.55 (m, 3H), 7.54-7.37 (m, 5H), 7.22 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 1.06 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 142.2, 141.9, 140.1, 139.9, 139.1, 138.5, 138.3, 137.6, 134.8, 134.7, 134.3, 134.0, 133.8, 133.5, 133.3, 132.9, 131.9, 129.97, 129.95, 129.6, 128.9, 128.6, 128.1, 128.03, 127.98, 127.6, 127.3, 127.1, 126.3, 126.2, 125.8, 124.4, 123.1, 119.8, 27.3, 20.9. HRMS (FAB) calcd for $C_{38}H_{30}Si$ (M^+) 514.2111, found 514.2116.



Scheme 5, Compound 3i. EtOAc/hexane = 1/30 was used for preparative TLC. Yellow solid. 63% yield (53.7 mg; **3i**/**2i** = 92/8). Pure compound **3i** was obtained by recrystallization from CH_2Cl_2/MeOH for investigation of optical and electronic properties.

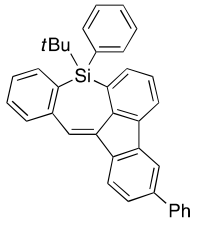
^{1}H NMR ($CDCl_3$): δ 7.94-7.88 (m, 2H), 7.80 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.77 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.63 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.56 (s, 1H), 7.53-7.42 (m,

4H), 7.39 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.32 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.30 (d, $^{4}J_{HH}$ = 2.3 Hz, 1H), 7.23 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.17 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.94 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 2.3 Hz, 1H), 3.94 (s, 3H), 0.98 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 160.4, 143.8, 142.4, 140.4, 139.2, 138.9, 137.3, 137.1, 136.1, 136.0, 134.1, 133.9, 133.1, 131.2, 129.7, 129.5, 129.4, 127.9, 127.8, 127.4, 121.1, 120.7, 113.6, 104.8, 55.8, 27.0, 20.8. HRMS (FAB) calcd for $C_{31}H_{28}OSi$ (M^+) 444.1904, found 444.1909.



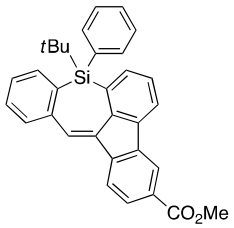
Scheme 5, Compound 3j. Yellow solid. 63% yield (54.3 mg).

^{1}H NMR ($CDCl_3$): δ 7.92-7.85 (m, 2H), 7.79-7.73 (m, 2H), 7.66-7.60 (m, 2H), 7.56 (s, 1H), 7.51-7.39 (m, 4H), 7.36 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.29 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.22 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.17 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.11 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 2.48 (s, 3H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 143.5, 142.4, 139.6, 139.3, 138.9, 138.7, 137.9, 137.5, 137.4, 136.0, 135.9, 134.1, 133.4, 131.2, 130.3, 129.8, 129.4, 128.0, 127.9, 127.6, 120.7, 120.5, 119.9, 27.0, 21.8, 20.8. HRMS (FAB) calcd for $C_{31}H_{28}Si$ (M^+) 428.1955, found 428.1963.



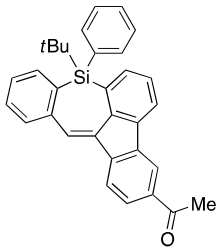
Scheme 5, Compound 3k. Yellow solid. 66% yield (65.1 mg).

^{1}H NMR ($CDCl_3$): δ 7.96 (d, $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.94 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.92-7.87 (m, 2H), 7.85 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.73-7.68 (m, 3H), 7.66 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.60 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.52-7.35 (m, 8H), 7.33 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.25 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.16 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 0.94 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 143.5, 142.2, 141.6, 141.2, 140.4, 139.6, 139.4, 139.0, 137.3, 137.2, 136.2, 135.9, 134.3, 133.6, 131.3, 131.2, 129.8, 129.5, 128.9, 128.0, 127.92, 127.86, 127.4, 127.3, 126.2, 120.9, 120.4, 118.6, 27.0, 20.8. HRMS (FAB) calcd for $C_{36}H_{31}Si$ ($M+H^+$) 491.2190, found 491.2196.



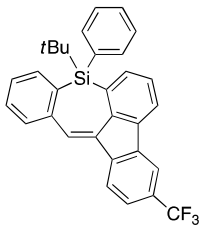
Scheme 5, Compound 3l. EtOAc/hexane = 1/15 was used for preparative TLC. Yellow solid. 74% yield (69.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.42 (d, $^{4}J_{HH}$ = 1.4 Hz, 1H), 8.06 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.93 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.90-7.84 (m, 3H), 7.76 (s, 1H), 7.68 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.52-7.37 (m, 5H), 7.35 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.27 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.18 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 3.99 (s, 3H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 167.4, 145.5, 143.1, 141.8, 139.1, 139.0, 138.7, 137.3, 136.7, 136.6, 135.6, 134.7, 134.0, 133.3, 131.3, 129.9, 129.53, 129.46, 128.5, 128.4, 128.2, 128.0, 121.24, 121.19, 119.8, 52.3, 27.0, 20.7. HRMS (FAB) calcd for $C_{32}H_{29}O_2Si$ ($M+H^+$) 473.1931, found 473.1936.



Scheme 5, Compound 3m. EtOAc/hexane = 1/10 was used for preparative TLC. Yellow solid. 70% yield (64.4 mg).

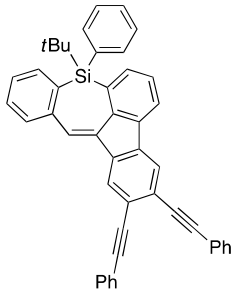
^{1}H NMR ($CDCl_3$): δ 8.34 (s, 1H), 8.01-7.93 (m, 2H), 7.91-7.84 (m, 3H), 7.77 (s, 1H), 7.68 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.52-7.37 (m, 5H), 7.36 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.28 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.19 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 2.71 (s, 3H), 0.94 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 198.0, 145.6, 143.2, 141.7, 139.2, 139.0, 138.6, 137.3, 136.7, 136.63, 136.57, 135.6, 134.8, 134.1, 133.5, 131.3, 129.9, 129.5, 128.5, 128.2, 128.0, 127.5, 121.2, 119.9, 119.7, 27.0, 26.9, 20.7. HRMS (FAB) calcd for $C_{32}H_{29}OSi$ ($M+H^+$) 457.1982, found 457.1985



Scheme 5, Compound 3n. EtOAc/hexane = 1/20 was used for preparative TLC. Yellow solid. 74% yield (74.1 mg).

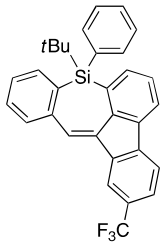
^{1}H NMR ($CDCl_3$): δ 7.98 (s, 1H), 7.97 (d, $^{3}J_{HH}$ = 8.0 Hz,1H), 7.89-7.85 (m, 1H), 7.84 (dd, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.75 (s, 1H), 7.68 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.61 (d, $^{3}J_{HH}$ = 8.3 Hz,1H), 7.52-7.41 (m, 4H), 7.39 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H), 7.36 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.28 (td, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.20 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 144.3, 143.1, 141.7, 139.3,

139.1, 138.2, 137.3, 136.9, 136.3, 135.6, 134.8, 134.1, 133.2, 131.5, 129.9, 129.8 (q, $^{2}J_{CF}$ = 32.0 Hz), 129.6, 128.5, 128.3, 128.0, 124.8 (q, $^{1}J_{CF}$ = 273 Hz), 123.8 (q, $^{3}J_{CF}$ = 3.8 Hz), 121.3, 120.2, 116.8 (q, $^{3}J_{CF}$ = 3.8 Hz), 27.0, 20.8. HRMS (FAB) calcd for $C_{31}H_{26}F_3Si$ ($M+H^+$) 483.1750, found 483.1754.



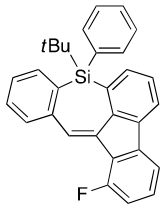
Scheme 5, Compound 3o. The reaction was conducted for 9 h at 0.25 M using 10 mol% of $Pd(OAc)_2$ and 11 mol% of binap in the presence of 4.0 equiv of Et_2NH. Yellow solid. 38% yield (34.6 mg).

^{1}H NMR ($CDCl_3$): δ 8.11 (s, 1H), 7.97 (s, 1H), 7.93-7.87 (m, 2H), 7.82 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.73 (s, 1H), 7.71-7.62 (m, 5H), 7.53-7.32 (m, 12H), 7.28 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.20 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 0.97 (s, 9H). ^{13}C NMR ($CDCl_3$): δ .143.6, 141.9, 140.9, 139.0, 138.7, 138.4, 137.3, 136.8, 136.4, 135.7, 134.6, 133.8, 132.5, 131.84, 131.82, 131.4, 129.9, 129.5, 128.6, 128.54, 128.51, 128.48, 128.3, 128.2, 128.0, 125.1, 124.3, 123.72, 123.67, 123.5, 123.2, 121.3, 94.1, 93.7, 89.5, 89.4, 27.0, 20.8. HRMS (FAB) calcd for $C_{46}H_{34}Si$ (M^+) 614.2424, found 614.2432.



Scheme 5, Compound 3p. Yellow solid. 62% yield (59.5 mg).

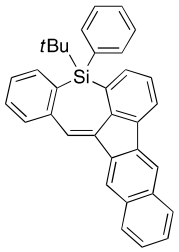
^{1}H NMR ($CDCl_3$): δ 8.12 (s, 1H), 7.91-7.81 (m, 4H), 7.74 (s, 1H), 7.71 (d, $^{3}J_{HH}$ = 7.5 Hz,1H), 7.63 (d, $^{3}J_{HH}$ = 7.8 Hz,1H), 7.52-7.46 (m, 2H), 7.46-7.41 (m, 2H), 7.39 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.36 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.28 (td, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.22 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 143.5, 142.0, 141.7, 141.4, 139.0, 138.1, 137.3, 137.2, 136.2, 135.6, 134.7, 133.9, 132.5, 131.7, 130.0, 129.6, 129.0 (q, $^{2}J_{CF}$ = 32.0 Hz), 128.4, 128.2, 128.0, 124.9 (q, $^{1}J_{CF}$ = 272 Hz), 124.7 (q, $^{3}J_{CF}$ = 3.8 Hz), 121.6, 120.0, 117.0 (q, $^{3}J_{CF}$ = 3.8 Hz), 27.0, 20.8. HRMS (FAB) calcd for $C_{31}H_{25}F_3Si$ (M^+) 482.1672, found 482.1676.



Scheme 5, Compound 3q. Yellow solid. 57% yield (49.2 mg).

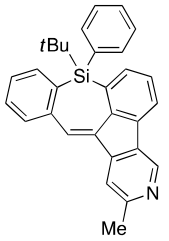
^{1}H NMR ($CDCl_3$): δ 8.23 (d, $^{5}J_{HF}$ = 5.5 Hz, 1H), 7.92-7.84 (m, 2H), 7.78 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.65 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.54 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.51-7.40 (m, 4H), 7.37 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.34-7.21 (m, 3H), 7.18 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.03 (dd, $^{3}J_{HF}$ = 11.9 Hz and $^{3}J_{HH}$ = 8.2 Hz, 1H), 0.97 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 159.8 (d, $^{1}J_{CF}$ = 251 Hz), 143.0, 142.6, 142.0 (d, J_{CF} = 5.8 Hz), 138.93 (d, J_{CF} = 1.9 Hz), 138.86, 137.4, 136.8 (d, $^{2}J_{CF}$ = 15.3 Hz), 136.7, 136.2 (d, J_{CF} =

5.8 Hz), 135.8, 135.0, 133.8, 131.3, 129.8, 129.5, 128.7 (d, $^3J_{CF}$ = 8.6 Hz), 128.1, 127.9, 127.8, 127.0 (d, $^3J_{CF}$ = 9.6 Hz), 121.1, 115.8 (d, J_{CF} = 2.9 Hz), 114.8 (d, $^2J_{CF}$ = 22.0 Hz), 27.0, 20.8. HRMS (FAB) calcd for $C_{30}H_{25}FSi$ (M^+) 431.1704, found 432.1701.



Scheme 5, Compound 3r. The reaction was conducted using 10 mol% of $Pd(OAc)_2$ and 11 mol% of binap. Yellow solid. 57% yield (53.3 mg; **3r**/**2r** = 95/5).

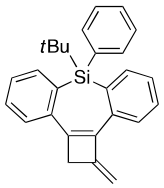
^{1}H NMR ($CDCl_3$): δ 8.32 (s, 1H), 8.16 (s, 1H), 8.00-7.89 (m, 5H), 7.85 (s, 1H), 7.72 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.55-7.44 (m, 6H), 7.42 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 7.38 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.32-7.18 (m, 2H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 144.7, 142.4, 140.0, 139.3, 138.9, 137.5, 137.4, 137.1, 136.8, 135.9, 134.1, 133.9, 133.4, 133.3, 131.4, 129.8, 129.5, 128.8, 128.4, 128.3, 128.0, 127.6, 126.0, 125.8, 121.6, 118.6, 118.0, 27.1, 20.8. HRMS (FAB) calcd for $C_{34}H_{28}Si$ (M^+) 464.1955, found 464.1954.



Scheme 5, Compound 3s. EtOAc/hexane = 1/4 was used for preparative TLC and GPC purification was not performed. Yellow solid. 62% yield (53.4 mg).

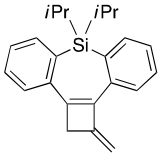
^{1}H NMR ($CDCl_3$): δ 8.91 (s, 1H), 7.88-7.83 (m, 3H), 7.82 (s, 1H), 7.73-7.67 (m, 2H), 7.54-7.47 (m, 2H), 7.47-7.39 (m, 3H), 7.37 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.21 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.80 (s, 3H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): δ

156.2, 149.7, 142.6, 141.3, 140.3, 139.1, 137.3, 137.2, 136.5, 135.7, 135.3, 134.9, 134.4, 131.9, 131.5, 129.9, 129.6, 128.9, 128.3, 128.0, 121.2, 114.2, 26.9, 24.7, 20.7. HRMS (FAB) calcd for $C_{30}H_{28}NSi$ ($M+H^+$) 430.1986, found 430.1986.



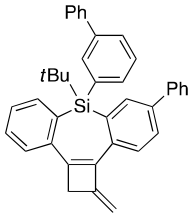
Equation 7, Compound 6a. Recrystallization from CH_2Cl_2/MeOH was performed instead of GPC purification. Yellow solid. 70% yield (53.1 mg).

^{1}H NMR ($CDCl_3$): δ 7.86-7.76 (m, 3H), 7.51-7.38 (m, 6H), 7.25-7.16 (m, 4H), 5.34 (s, 1H), 4.88 (s, 1H), 3.56 (d, $^2J_{HH}$ = 14.2 Hz, 1H), 3.19 (d, $^2J_{HH}$ = 14.2 Hz, 1H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.7, 143.7, 142.4, 140.9, 139.7, 138.5, 138.3, 137.4, 136.1, 135.2, 134.6, 129.5, 129.4, 129.3, 128.0, 127.8, 127.2, 127.1, 127.0, 99.8, 36.6, 27.2, 20.3. HRMS (FAB) calcd for $C_{27}H_{26}Si$ (M^+) 378.1798, found 378.1805.



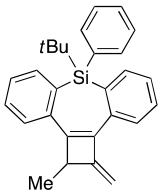
Equation 7, Compound 6b. The reaction was conducted using 10 mol% of $Pd(OAc)_2$ and 11 mol% of binap. White solid. 59% yield (39.1 mg).

^{1}H NMR ($CDCl_3$): δ 7.79-7.70 (m, 3H), 7.48-7.32 (m, 5H), 5.27 (s, 1H), 4.85 (s, 1H), 3.34 (s, 2H), 1.54 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.12 (d, $^3J_{HH}$ = 7.8 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 147.8, 143.7, 142.7, 140.8, 139.4, 135.2, 135.1, 135.0, 134.4, 129.3, 129.2, 128.3, 127.6, 127.4, 127.3, 99.6, 36.7, 18.4, 18.3, 11.5. HRMS (FAB) calcd for $C_{23}H_{26}Si$ (M^+) 330.1798, found 330.1804.



Equation 7, Compound 6c. Pale yellow amorphous. 63% yield (67.0 mg).

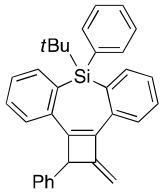
^{1}H NMR ($CDCl_3$): δ 8.06 (s, 1H), 7.87 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.81 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.66 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.56 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.53-7.47 (m, 2H), 7.47-7.37 (m, 4H), 7.37-7.20 (m, 8H), 5.36 (s, 1H), 4.90 (s, 1H), 3.57 (d, $^{2}J_{HH}$ = 14.2 Hz, 1H), 3.21 (d, $^{2}J_{HH}$ = 14.2 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.8, 143.6, 142.0, 141.5, 140.87, 140.85, 140.5, 139.6, 138.8, 138.3, 137.2, 136.5, 136.3, 136.1, 135.1, 134.8, 129.7, 128.93, 128.88, 128.3, 128.2, 128.1, 127.5, 127.4, 127.2, 127.0, 99.9, 36.7, 27.4, 20.4. HRMS (FAB) calcd for $C_{39}H_{34}Si$ (M^+) 530.2424, found 530.2438.



Scheme 8, Compound 6d (from (*E*)-5d). Yellow oil. 69% yield (53.9 mg; dr = 60/40).

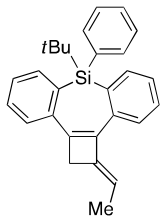
^{1}H NMR ($CDCl_3$): δ 7.86-7.73 (m, 1.8H), 7.68-7.53 (m, 1.8H), 7.51-7.31 (m, 6.6H), 7.30-7.16 (m, 2.8H), 5.30 (s, 0.4H), 5.20 (s, 0.6H), 4.92 (s, 0.4H), 4.82 (s, 0.6H), 3.83 (q, $^{3}J_{HH}$ = 6.7 Hz, 0.4H), 3.61 (q, $^{3}J_{HH}$ = 6.7 Hz, 0.6H), 1.46 (d, $^{3}J_{HH}$ = 6.4 Hz, 1.8H), 1.39 (d, $^{3}J_{HH}$ = 6.9 Hz, 1.2H), 1.10 (s, 5.4H), 1.04 (s, 3.6H). ^{13}C NMR ($CDCl_3$): δ 152.5, 152.4, 150.9, 150.8, 142.1, 141.3, 141.2, 139.72, 139.69, 139.6, 138.7, 138.6, 137.9, 137.8, 137.4, 136.9, 136.3, 136.2, 135.9, 135.5, 134.74, 134.65, 129.42, 129.40, 129.36, 129.3, 129.2, 129.1, 127.81, 127.75, 127.64, 127.58, 127.5, 127.4, 127.33, 127.26, 126.9, 97.9, 97.1, 44.3, 42.8, 27.5, 27.4, 20.5, 19.7, 17.8, 14.9. HRMS (FAB) calcd for $C_{28}H_{28}Si$

(M^+) 392.1955, found 392.1960.



Scheme 8, Compound 6e. Yellow oil. 58% yield (50.2 mg; dr = 59/41).

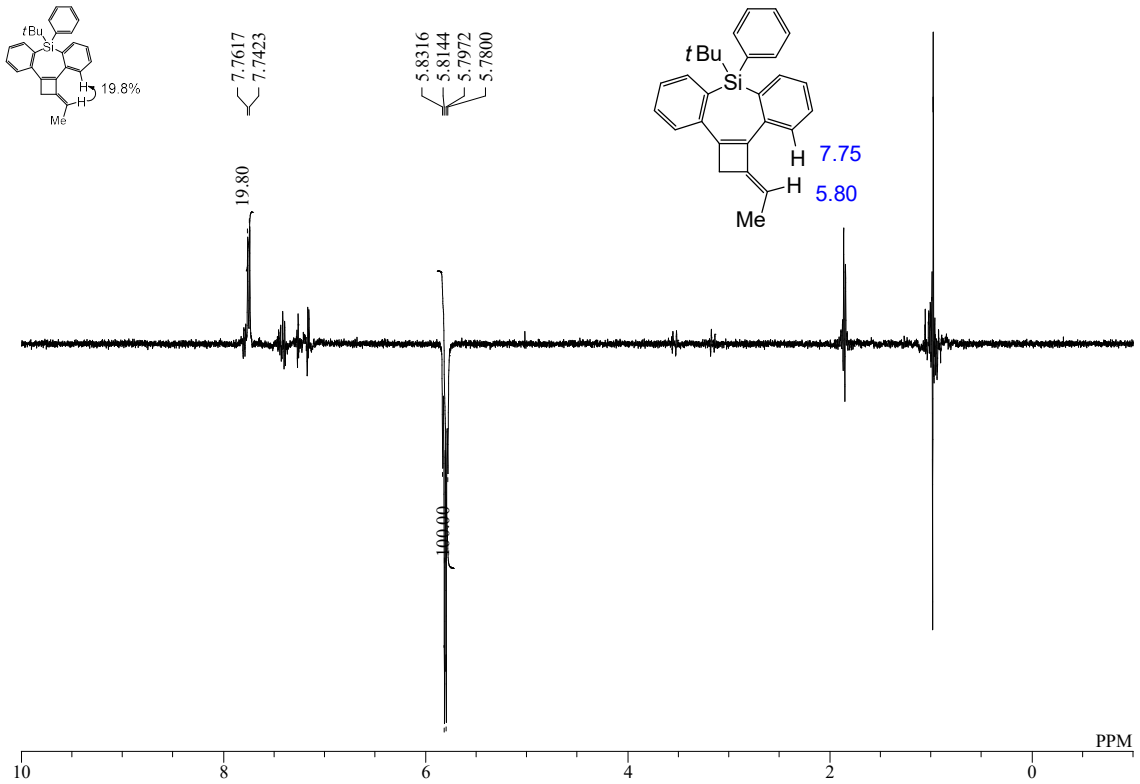
^{1}H NMR ($CDCl_3$): δ 7.94 (d, $^3J_{HH}$ = 7.8 Hz, 0.41H), 7.88 (d, $^3J_{HH}$ = 7.8 Hz, 0.59H), 7.85-7.78 (m, 2H), 7.53-7.13 (m, 15H), 5.42 (s, 0.41H), 5.30 (s, 0.59H), 4.86 (s, 0.41H), 4.82 (s, 0.41H), 4.72 (s, 0.59H), 4.63 (s, 0.59H), 1.12 (s, 3.69H), 1.09 (s, 5.31H). ^{13}C NMR ($CDCl_3$): δ 150.6, 149.9, 149.7, 149.4, 144.9, 143.5, 141.6, 140.5, 139.8, 139.5, 139.4, 139.3, 138.9, 138.7, 138.3, 138.2, 137.3, 136.8, 135.9, 135.7, 135.2, 134.9, 134.5, 129.44, 129.43, 129.38, 129.30, 129.26, 128.8, 128.6, 128.5, 128.1, 127.83, 127.81, 127.74, 127.67, 127.61, 127.55, 127.5, 126.9, 126.8, 100.1, 98.9, 55.2, 53.7, 27.5, 27.4, 20.6, 20.1. HRMS (APCI) calcd for $C_{33}H_{31}Si$ ($M+H^+$) 455.2190, found 455.2216.

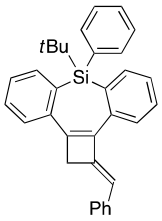


Scheme 8, Compound 6f. White solid. 45% yield against internal standard (28.0 mg; *E*/*Z* = 96/4). The stereochemistry was determined by the NOE experiment.

^{1}H NMR ($CDCl_3$): δ 7.81-7.76 (m, 2H), 7.74 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.47-7.37 (m, 6H), 7.18-7.14 (m, 4H), 5.80 (q, $^3J_{HH}$ = 6.8 Hz, 1H), 3.53 (d, $^2J_{HH}$ = 14.6 Hz, 1H), 3.15 (d, $^2J_{HH}$ = 14.1 Hz, 1H), 1.85 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.97 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 143.8, 142.4, 141.3, 139.9, 138.5, 138.2, 137.4, 137.0, 136.3, 134.74, 134.65, 129.5, 129.24, 129.20, 127.8, 127.44, 127.41, 127.1, 126.7, 110.1, 34.4, 27.3, 20.3, 13.7. HRMS

(FAB) calcd for $C_{28}H_{28}Si$ (M^+) 392.1955, found 392.1963.

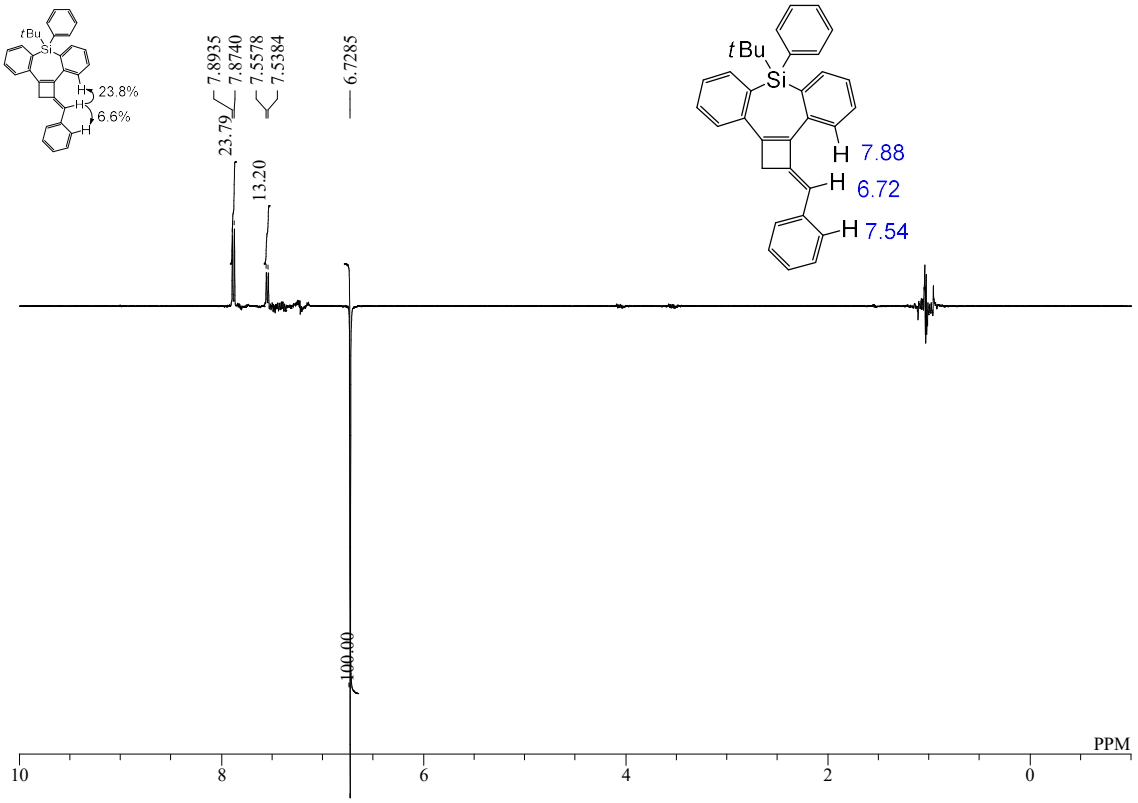


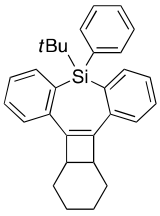


Scheme 8, Compound 6g. Pale yellow solid. 49% yield (33.2 mg). The stereochemistry was determined by the NOE experiment.

^{1}H NMR ($CDCl_3$): δ 7.88 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.84-7.78 (m, 2H), 7.54 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 7.52-7.34 (m, 8H), 7.26-7.18 (m, 5H), 6.72 (s, 1H), 4.05 (d, $^2J_{HH}$ = 14.2 Hz, 1H), 3.54 (d, $^2J_{HH}$ = 14.2 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.5, 143.8, 140.8, 139.2, 138.9, 138.7, 138.4, 138.3, 137.4, 136.0, 135.3, 135.2, 129.6, 129.4, 129.3, 128.8, 127.9, 127.8, 127.6, 127.5, 127.4, 126.9, 126.5, 115.1, 37.6, 27.3, 20.3. HRMS

(FAB) calcd for $C_{33}H_{30}Si$ (M^+) 454.2111, found 454.2117.

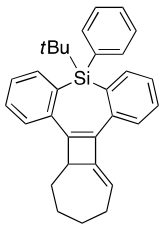




Scheme 8, Compound 6h'. Hexane was used for preparative TLC. The product was isolated and characterized after hydrogenation: Pd on C (10 mg, 9.4 μmol Pd; 10 wt% Pd) was added to a solution of compound **6h** (51 mg, ca. 0.12 mmol; mixture of isomers) in MeOH (3 mL). The reaction vessel was evacuated and backfilled with H_2 gas quickly for three times, and the mixture was stirred under H_2 for 9 h at room temperature. The catalyst was filtered off with hexane and the solvents were removed under vacuum. The residue was purified by preparative TLC on silica gel with hexane to afford compound **6h'** as a

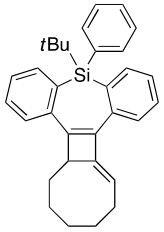
white solid (40.3 mg, 95.8 μmol; 48% overall yield, dr = 72/28).

^{1}H NMR ($CDCl_3$): δ 7.78 (d, $^{3}J_{HH}$ = 6.8 Hz, 0.56H), 7.57 (d, $^{3}J_{HH}$ = 6.9 Hz, 1.44H), 7.52-7.27 (m, 8.44H), 7.24-7.09 (m, 2.56H), 3.42-3.35 (m, 0.56H), 3.26-3.15 (m, 1.44H), 2.10-1.93 (m, 2H), 1.87-1.37 (m, 6H), 1.05 (s, 6.48H), 1.02 (s, 2.52H). ^{13}C NMR ($CDCl_3$): δ 146.1, 145.5, 142.2, 140.9, 138.7, 137.5, 137.3, 137.2, 136.8, 136.7, 133.5, 133.4, 129.34, 129.32, 129.1, 129.0, 127.7, 127.5, 126.72, 126.66, 126.4, 126.2, 38.7, 36.3, 27.6, 27.3, 25.0, 24.2, 20.5, 20.4, 19.7. HRMS (FAB) calcd for $C_{30}H_{32}Si$ (M^+) 420.2268, found 420.2273.



Scheme 8, Compound 6i. Pale yellow amorphous. 61% yield (52.4 mg; dr = 71/29).

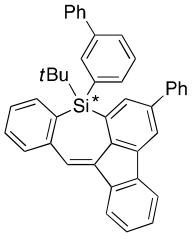
^{1}H NMR ($CDCl_3$): δ 7.79 (d, $^{3}J_{HH}$ = 6.9 Hz, 0.58H), 7.73 (d, $^{3}J_{HH}$ = 7.8 Hz, 0.71H), 7.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 0.29H), 7.58-7.48 (m, 2H), 7.47-7.32 (m, 5.42H), 7.32-7.11 (m, 4H), 6.06 (dd, $^{3}J_{HH}$ = 6.4 and 5.0 Hz, 0.29H), 5.97 (dd, $^{3}J_{HH}$ = 7.3 and 5.0 Hz, 0.71H), 3.64 (dd, $^{3}J_{HH}$ = 12.4 and 2.8 Hz, 0.29H), 3.43 (dd, $^{3}J_{HH}$ = 12.4 and 3.2 Hz, 0.71H), 2.52-2.17 (m, 3H), 2.11-1.83 (m, 2H), 1.56-1.02 (m, 3H), 1.10 (s, 6.39H), 0.99 (s, 2.61H). ^{13}C NMR ($CDCl_3$): δ 149.3, 148.2, 145.5, 145.4, 141.90, 141.86, 141.0, 140.4, 140.1, 139.8, 138.6, 138.5, 137.6, 137.5, 137.4, 136.8, 136.5, 136.4, 135.1, 135.0, 134.7, 134.5, 129.4, 129.31, 129.27, 129.24, 129.17, 129.0, 127.8, 127.4, 127.3, 127.2, 127.12, 127.08, 127.0, 126.6, 115.4, 115.2, 50.4, 48.7, 33.0, 31.8, 30.9, 30.4, 29.8, 29.5, 29.3, 29.2, 27.7, 27.4, 20.4, 19.6. HRMS (APCI) calcd for $C_{31}H_{33}Si$ ($M+H^+$) 433.2346, found 433.2333.



Scheme 8, Compound 6j. The reaction was conducted using 10 mol% of $Pd(OAc)_2$ and 11 mol% of binap. Pale yellow amorphous. 65% yield (43.5 mg; dr = 76/24).

^{1}H NMR ($CDCl_3$): δ 7.86-7.73 (m, 1.52H), 7.69-7.12 (m, 11.48H), 5.93 (t, $^3J_{HH}$ = 6.2 Hz, 0.24H), 5.74 (t, $^3J_{HH}$ = 6.2 Hz, 0.76H), 3.94 (dd, $^3J_{HH}$ = 10.5 and 5.0 Hz, 0.24H), 3.74 (dd, $^3J_{HH}$ = 11.0 and 5.0 Hz, 0.76H), 2.68-2.10 (m, 3H), 2.03-1.61 (m, 4H), 1.51-1.05 (m, 3H), 1.33 (s, 6.84H), 1.06 (s, 2.16H). ^{13}C NMR ($CDCl_3$): δ 150.2, 149.9, 142.8, 141.8, 141.7, 141.4, 141.1, 140.1, 139.9, 139.8, 138.7, 138.6, 137.7, 137.6, 137.4, 136.8, 136.7, 136.4, 135.04, 135.01, 134.6, 129.31, 129.29, 129.2, 129.1, 129.0, 127.8, 127.7, 127.5, 127.3, 127.2, 127.1, 127.0, 126.91, 126.89, 113.9, 112.6, 48.7, 47.3, 34.8, 33.0, 28.4, 28.1, 27.64, 27.59, 27.5, 27.1, 26.4, 26.0, 25.8, 25.7, 20.4, 19.6. HRMS (FAB) calcd for $C_{32}H_{34}Si$ (M^+) 446.2424, found 446.2429.

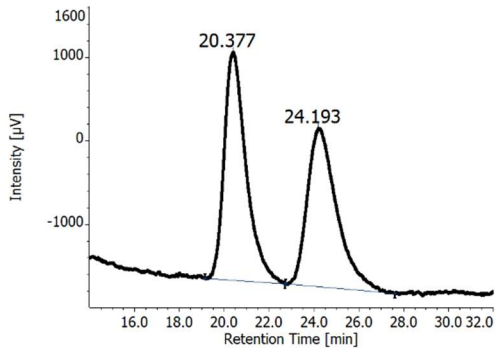
Procedure for Equation 1.



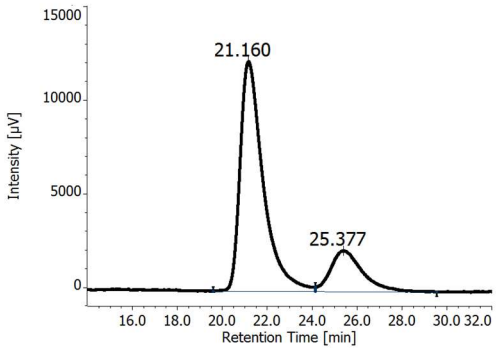
Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.3 mg, 10 μmol), (*R*)-binap (6.9 mg, 11.1 μmol), and compound **1f** (143 mg, 0.200 mmol) in DMF (0.40 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc. After removal of the volatiles under vacuum, the residue was

purified by preparative TLC on silica gel with EtOAc/hexane = 1/50 and by GPC with $CHCl_3$ to afford compound **3f** as a yellow amorphous (65.8 mg, 0.116 mmol; 58% yield). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 200/1, flow 0.7 mL/min. Retention times: 21.2 min [major enantiomer], 25.4 min [minor enantiomer]. 60% ee. $[\alpha]^{24}_{D}$ +9.1 (*c* 0.64, $CHCl_3$). The absolute configuration has not been determined.

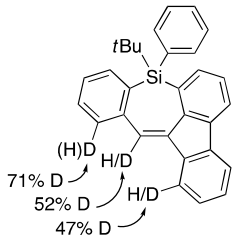
racemate



59.9% ee



Procedure for Equation 4.



nBu_2ND (255 μL, 1.50 mmol) was added to a mixture of $Pd(OAc)_2$ (1.7 mg, 7.6 μmol), binap (5.1 mg, 8.2 μmol), and compound **1a** (84.7 mg, 0.150 mmol) in cyclopentyl methyl ether (0.30 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc. After removal of the volatiles under vacuum, the residue was purified by preparative TLC on silica gel with EtOAc/hexane = 1/50 and by GPC with $CHCl_3$ to afford compound **3a**-$d_{1.7}$ as a yellow solid (31.6 mg, 75.9 μmol; 51%

yield).

^{1}H NMR ($CDCl_3$): δ 7.91-7.84 (m, 2.53H), 7.79 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.77-7.73 (m, 1H), 7.68 (s, 0.48H), 7.64 (d, $^3J_{HH}$ = 7.8 Hz, 0.29H), 7.51-7.40 (m, 4H), 7.39-7.33 (m, 3H), 7.31 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.24 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.13 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 0.94 (s, 9H).

Procedure for Equation 5

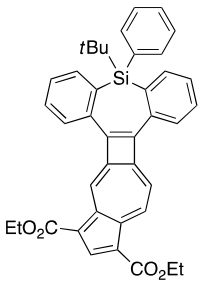
nBu_2ND (340 μL, 2.00 mmol) was added to a mixture of $Pd(OAc)_2$ (2.3 mg, 10 μmol), binap (6.9 mg, 11.1 μmol), compound **1a** (56.5 mg, 0.100 mmol) and compound **3l** (47.3 mg, 0.100 mmol) in cyclopentyl methyl ether (0.40 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc. After removal of the volatiles under vacuum, the residue was purified by preparative TLC on silica gel with EtOAc/hexane = 1/15 to afford compound **3l** (0% D) as a yellow solid (43.0 mg, 91% recovery). The fraction containing compound **3a** was further purified by GPC with $CHCl_3$ to afford compound **3a**-$d_{1.9}$ as a yellow solid (31.6 mg, 75.9 μmol; 51% yield).

Procedure for Equation 6.

Et_2NH (31.0 μL, 0.300 mmol) was added to a mixture of $Pd(OAc)_2$ (1.7 mg, 7.6 μmol), binap (5.1 mg, 8.2 μmol), and compound **4** (77.5 mg, 0.150 mmol) in cyclopentyl methyl ether (0.30 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc. After removal of the volatiles under vacuum, the residue was purified by preparative TLC on silica gel with EtOAc/hexane = 1/50 and by

GPC with $CHCl_3$ to afford compound **3d** as a yellow solid (43.0 mg, 0.117 mmol; 78% yield).

Procedure for Equation 8.

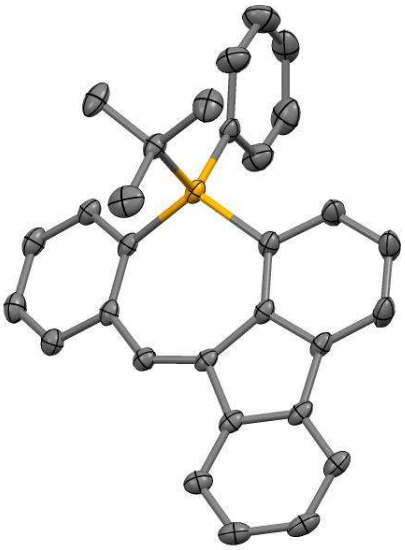


Et_2NH (62.1 μL, 0.600 mmol) was added to a mixture of $Pd(OAc)_2$ (6.7 mg, 30 μmol), binap (20.5 mg, 32.9 μmol), and compound **7** (113.7 mg, 0.150 mmol) in cyclopentyl methyl ether (0.60 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc. After removal of the volatiles under vacuum, the residue was purified by preparative TLC on silica gel with EtOAc/hexane = 1/9 and by GPC with $CHCl_3$, and the solid thus obtained was further purified by recrystallization from $MeOH/CH_2Cl_2$ to afford compound **8** as a dark purple solid (28.4mg, 46.6 μmol; 31% yield).

^1H NMR ($CDCl_3$): δ 8.75 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 8.26 (s, 1H), 7.90 (s, 1H), 7.88 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.76-7.68 (m, 2H), 7.66 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.55-7.36 (m, 5H), 7.35-7.24 (m, 2H), 7.21 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 6.61 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 4.43-4.26 (m, 4H), 1.43 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 1.39 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 1.08 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.1, 164.6, 164.5, 156.7, 152.6, 151.7, 145.8, 144.9, 141.14, 141.06, 138.7, 138.6, 137.33, 137.26, 135.5, 135.0, 134.8, 130.0, 129.8, 129.6, 129.3, 128.0, 126.4, 125.7, 122.4, 120.8, 115.4, 113.4, 60.2, 59.9, 27.3, 20.5, 14.6. HRMS (FAB) calcd for $C_{40}H_{37}O_4Si$ ($M+H^+$) 609.2456, found 609.2451.

X-ray Crystal Structures

Compound 3a



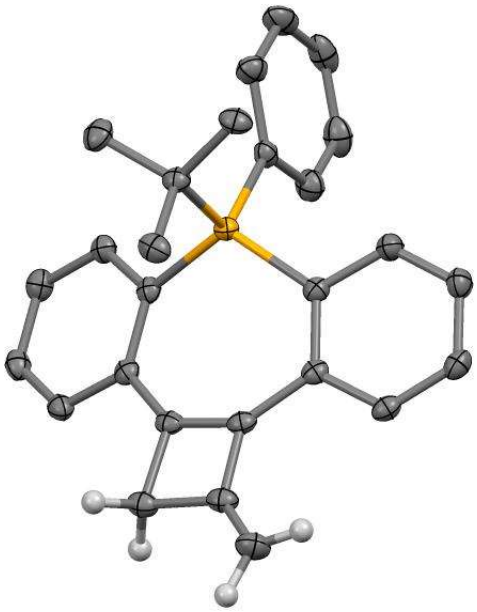
A yellow CH_2Cl_2 solution of compound **3a** was prepared. Crystals suitable for X-ray analysis were obtained by layering hexane and slow diffusion of the solvents at room temperature.

Crystal Data and Structure Refinement

Empirical Formula	$C_{30}H_{26}Si$
Formula Weight	414.60
Temperature	113 ± 2 K
Wavelength	0.71075 Å
Crystal System	Triclinic
Space Group	P−1
Unit Cell Dimensions	a = 10.3171(18) Å α = 75.678(7)°
	b = 12.986(2) Å β = 85.033(9)°
	c = 17.529(3) Å γ = 86.4309(10)°
Volume	2264.9(7) $Å^3$

Z Value	4
Calculated Density	1.216 g/cm^3
Absorption coefficient	0.119 mm^{-1}
F(000)	880
Crystal size	0.300 x 0.300 x 0.300 mm
Theta Range for Data Collection	3.078–27.499°
Index Ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 16$, $-22 \leq l \leq 22$
Reflections Collected	19611
Independent Reflections	9740 [R(int) = 0.0413]
Completeness to Theta = 25.242°	96.2%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.801
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	9740 / 0 / 565
Goodness-of-Fit on F^2	0.972
Final R Indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1249
R Indices (All Data)	R1 = 0.0643, wR2 = 0.1311
Largest Diff. Peak and Hole	0.416 and –0.271 e$^-$/Å^3

Compound 6a



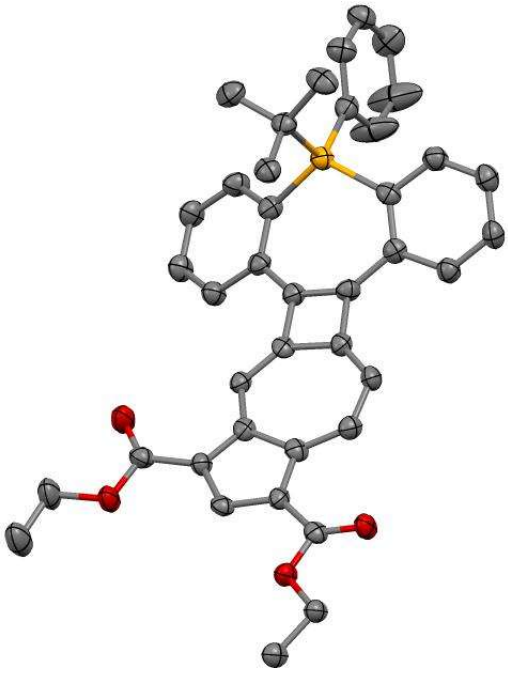
A colorless CH_2Cl_2 solution of compound **6a** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature.

Crystal Data and Structure Refinement

Empirical Formula	$C_{27}H_{26}Si$
Formula Weight	378.57
Temperature	113 ± 2 K
Wavelength	0.71075 Å
Crystal System	Monoclinic
Space Group	$P2_1/a$
Unit Cell Dimensions	a = 10.5521(8) Å α = 90°
	b = 24.7884(16) Å β = 107.7290(15)°
	c = 16.8422(13) Å γ = 90°
Volume	4196.2(5) $Å^3$

Z Value	8
Calculated Density	1.198 g/cm^3
Absorption coefficient	0.121 mm^{-1}
F(000)	1616
Crystal size	0.300 x 0.300 x 0.200 mm
Theta Range for Data Collection	3.025–27.652°
Index Ranges	$-13 \leq h \leq 11$, $-32 \leq k \leq 32$, $-21 \leq l \leq 21$
Reflections Collected	28896
Independent Reflections	9049 [R(int) = 0.0253]
Completeness to Theta = 25.242°	95.2%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.918
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	9049 / 0 / 511
Goodness-of-Fit on F^2	1.044
Final R Indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0974
R Indices (All Data)	R1 = 0.0500, wR2 = 0.1025
Largest Diff. Peak and Hole	0.491 and −0.255 e$^-$/Å^3

Compound 8



A colorless CH_2Cl_2 solution of compound **8** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature.

Crystal Data and Structure Refinement

Empirical Formula	$C_{40}H_{36}O_4Si$	
Formula Weight	608.78	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Triclinic	
Space Group	P−1	
Unit Cell Dimensions	a = 8.035(3) Å	α = 107.477(8)°
	b = 19.954(7) Å	β = 90.378(6)°
	c = 20.955(8) Å	γ = 98.013(8)°

Volume	3169(2) $Å^3$
Z Value	4
Calculated Density	1.276 g/cm^3
Absorption coefficient	0.116 mm^{-1}
F(000)	1288
Crystal size	0.200 x 0.050 x 0.050 mm
Theta Range for Data Collection	3.062–27.481°
Index Ranges	$-10 \leq h \leq 10$, $-25 \leq k \leq 25$, $-27 \leq l \leq 27$
Reflections Collected	60482
Independent Reflections	14436 [R(int) = 0.2227]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.654
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	14436 / 0 / 821
Goodness-of-Fit on F^2	0.954
Final R Indices [I>2sigma(I)]	R1 = 0.0877, wR2 = 0.1836
R Indices (All Data)	R1 = 0.2454, wR2 = 0.2418
Largest Diff. Peak and Hole	0.440 and −0.318 $e^-/Å^3$

3.5 Theoretical Calculations

All the density functional theory (DFT) calculations were performed by using Gaussian 09 (revision E.01) program.[31] The geometry optimizations of ground-state structures were performed using DFT with B3LYP method[32] with 6-31G(d) basis sets,[33] and the orbital energies were obtained at the same level.

TD-DFT calculations

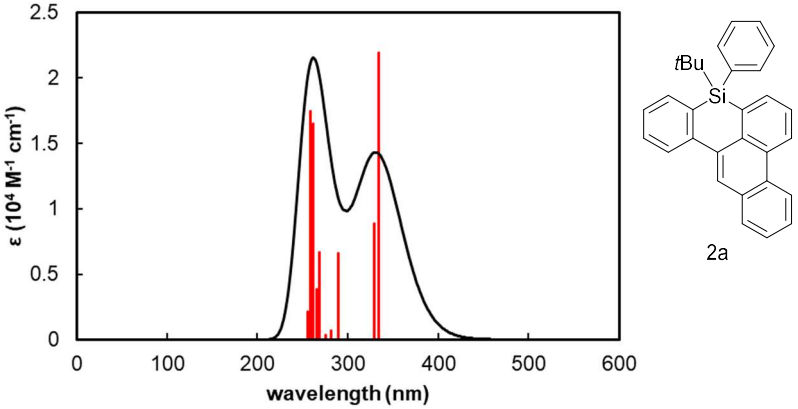


Figure 7. Absorption spectrum of **2a** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 5. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **2a** calculated at the B3LYP/6-31G(d) level of theory.

2a		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
334.2	0.2438	HOMO→LUMO (0.58763) HOMO→LUMO+1 (–0.30493)
261.0	0.1836	HOMO–5→LUMO (0.46442) HOMO–1→LUMO+1 (0.43206)
257.1	0.1942	HOMO–3→LUMO (0.25416) HOMO–1→LUMO+1 (0.23383) HOMO→LUMO+4 (0.44684)

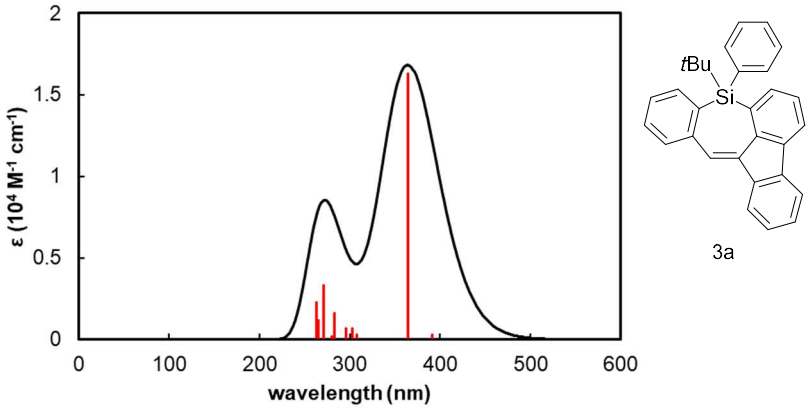


Figure 8. Absorption spectrum of 3**a** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 6. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound 3**a** calculated at the B3LYP/6-31G(d) level of theory.

3a		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
364.5	0.4081	HOMO→LUMO (0.66745)
271.2	0.0831	HOMO–3→LUMO (–0.23027)
		HOMO–1→LUMO+1 (0.43707)
		HOMO→LUMO+2 (–0.33350)
		HOMO→LUMO+3 (0.22989)
263.2	0.0567	HOMO–6→LUMO (0.56290)
		HOMO→LUMO+3 (–0.29989)

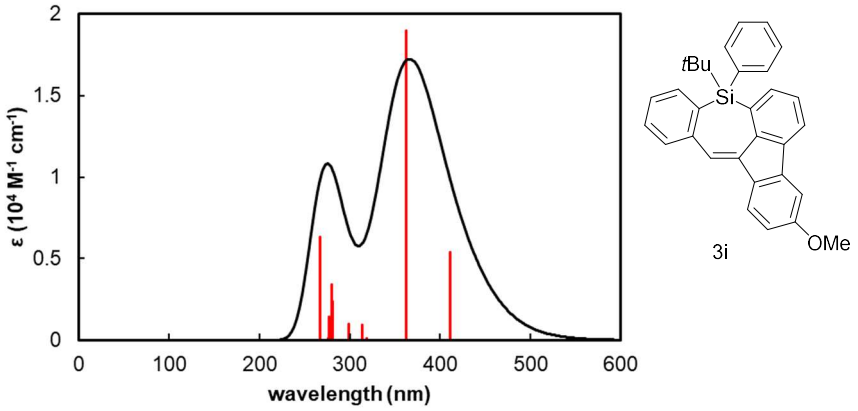


Figure 9. Absorption spectrum of **3i** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 7. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3i** calculated at the B3LYP/6-31G(d) level of theory.

3i		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
411.5	0.1081	HOMO–1→LUMO (–0.35789) HOMO→LUMO (0.60565)
362.2	0.3795	HOMO–1→LUMO (0.60067) HOMO→LUMO (–0.35110)
267.0	0.1266	HOMO–6→LUMO (0.44504) HOMO–5→LUMO (–0.32177) HOMO→LUMO+3 (0.30429)

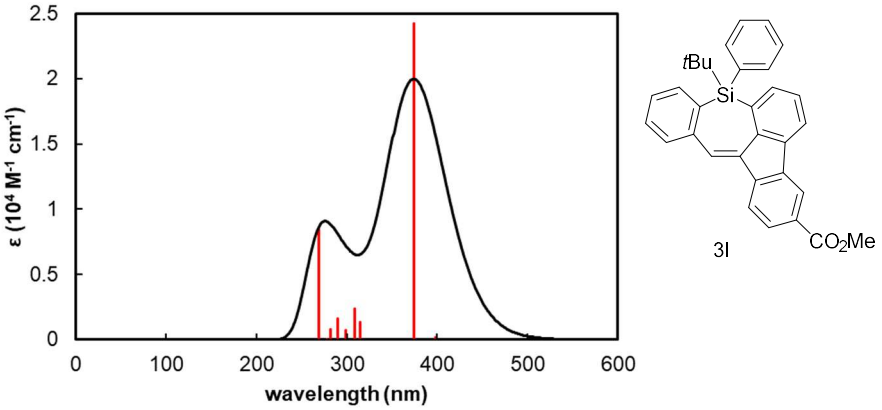


Figure 10. Absorption spectrum of **3l** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 8. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3l** calculated at the B3LYP/6-31G(d) level of theory.

3l		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
374.3	0.4851	HOMO→LUMO (0.69067)
269.0	0.1694	HOMO–7→LUMO (0.48519)
		HOMO–1→LUMO+1 (0.22751)

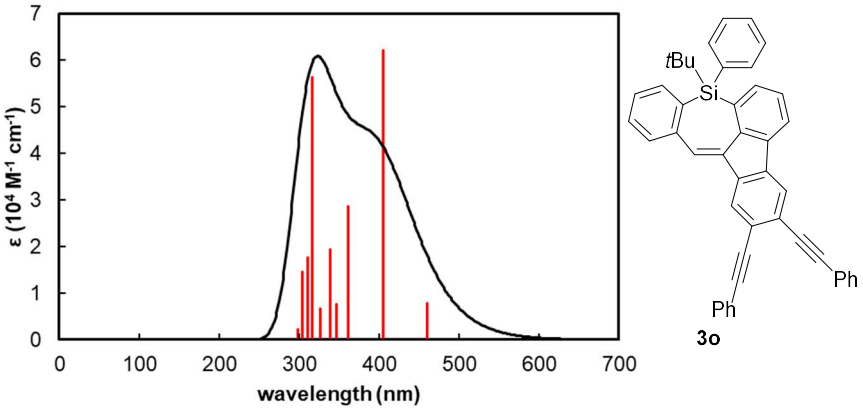


Figure 11. Absorption spectrum of **3o** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 9. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3o** calculated at the B3LYP/6-31G(d) level of theory.

3o		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
460.4	0.0993	HOMO→LUMO (0.66209)
404.8	0.7768	HOMO–1→LUMO (0.64631)
		HOMO→LUMO (–0.22582)
361.2	0.3585	HOMO–2→LUMO (–0.33390)
		HOMO→LUMO+1 (0.58676)
316.5	0.7048	HOMO–3→LUMO (–0.23854)
		HOMO–1→LUMO+1 (0.30313)
		HOMO→LUMO+2 (0.40073)

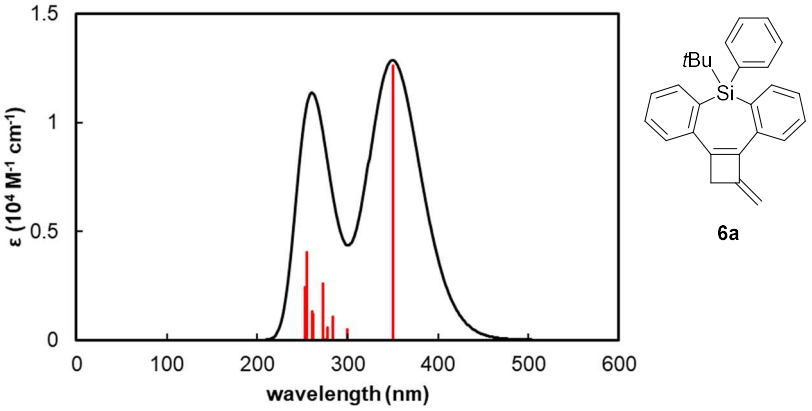


Figure 12. Absorption spectrum of **6a** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 10. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **6a** calculated at the B3LYP/6-31G(d) level of theory.

6a		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
349.9	0.3158	HOMO→LUMO (0.69392)
254.8	0.1013	HOMO–5→LUMO (0.44063)
		HOMO–3→LUMO (–0.22375)
		HOMO→LUMO+3 (–0.40362)

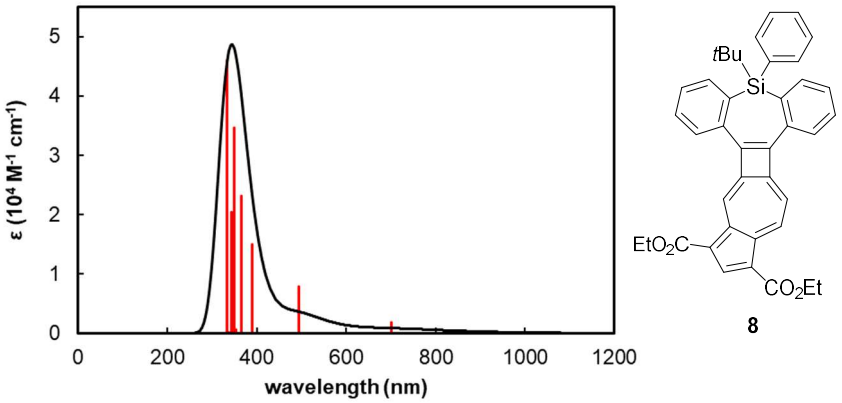


Figure 13. Absorption spectrum of **8** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table 11. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **8** calculated at the B3LYP/6-31G(d) level of theory.

8		
wavelength (nm)	oscillator strength (*f*)	Major Contributions (Coefficients)
700.6	0.0191	HOMO→LUMO (0.70355)
493.4	0.0793	HOMO–1→LUMO (0.64973)
347.1	0.3471	HOMO–4→LUMO (0.50345)
		HOMO–2→LUMO (–0.26995)
		HOMO→LUMO+2 (0.24135)
331.4	0.4610	HOMO–4→LUMO (0.22598)
		HOMO–2→LUMO (0.25407)
		HOMO–1→LUMO+1 (0.47391)
		HOMO→LUMO+1 (–0.26208)

3.6 References

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List of Publications

Publications

1. “Palladium-Catalyzed Synthesis of Benzophenanthrosilines by C–H/C–H Coupling through 1,4-Palladium Migration/Alkene Stereoisomerization”

   Tomohiro Tsuda, Yuka Kawakami, Seung-Min Choi and Ryo Shintani; *Angew. Chem., Int. Ed.* **2020**, *59*, 8057–8061.

2. “Palladium-Catalyzed Synthesis of Dibenzosilepin Derivatives via 1,*n*-Palladium Migration Coupled with *anti*-Carbopalladation of Alkyne”

   Tomohiro Tsuda, Seung-Min Choi and Ryo Shintani; *J. Am. Chem. Soc.* **2021**, *143*, 1641–1650.

Related Publications

3. “Synthesis of Quinoidal Fused Oligosiloles by Rhodium-Catalyzed Stitching Reaction and Theoretical Investigation of Their Properties”

   Ryo Shintani, Nana Misawa, Tomohiro Tsuda, Ryo Iino, Mikiya Fujii, Koichi Yamashita and Kyoko Nozaki; *J. Am. Chem. Soc.* **2017**, *139*, 3861–3867.

4. “Palladium-Catalyzed Intramolecular C–H Arylation versus 1,5-Palladium Migration: A Theoretical Investigation”

   Nana Misawa, Tomohiro Tsuda, Ryo Shintani, Koichi Yamashita and Kyoko Nozaki; *Chem. Asian J.* **2018**, *13*, 2566–2572.

5. “Synthesis of carbonyl-bridged dibenzofulvalenes and related compounds by rhodium-catalyzed stitching reaction”

   Ryo Shintani, Shinnosuke Kishikawa, Kimihiro Nakamura, Tomohiro Tsuda and Kyoko Nozaki; *Chem. Commun.* **2019**, *55*, 1072–1075.

6. “Single-Molecule Single-Electron Transistor (SM-SET) Based on π-Conjugated Quinoidal-Fused Oligosilole and Heteroepitaxial Spherical Au/Pt Nanogap Electrodes”

   Seung Joo Lee, Jaeyeon Kim, Tomohiro Tsuda, Ryo Takano, Ryo Shintani, Kyoko Nozaki and Yutaka Majima; *Appl. Phys. Express* **2019**, *12*, 125007.

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