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Synthesis of Silacycles via Intramolecular Si–C Bond Activation Under Palladium or Nickel Catalysis

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March 2025

Synthesis of Silacycles via Intramolecular Si–C Bond Activation Under Palladium or Nickel Catalysis

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by

Donghyeon Lee

March 2025

Abstract

Silacycles, silicon-containing cyclic compounds, have gained significant interest due to their unique chemical properties and broad applications in pharmaceuticals, agrochemicals, and advanced materials. Compared to their carbon counterparts, silacycles exhibit distinct reactivity and structural characteristics, such as silicon's ability to achieve higher coordination numbers, stabilize α-carbanions, and form longer and more polarized bonds. These features make silacycles invaluable as isosteres of carbocycles, offering unique advantages in the design of functional molecules with optimized properties. However, challenges remain in the synthesis of silacycles, particularly those containing multiple heteroatoms or involving ring-contraction strategies through the activation of stable Si–C bonds, potentially limiting their broader application.

In this context, this dissertation addresses these challenges by exploring transition-metal-catalyzed synthesis of silacycles, focusing on intramolecular processes that enable precise Si–C bond activation coupled with Si–X bond formation. The author developed a palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, a novel class of *N*,*O*-containing silacycles, and a nickel-catalyzed synthesis of 3,3-disubstituted 1-silaindanes via a six-to-five ring contraction.

Chapter 1 provides a comprehensive overview of Si–C bond activating silacycle synthesis, highlighting the unique properties of Si–C bonds and the advantages of transition-metal-catalyzed methods over conventional approaches. This chapter explores the transition-metal-catalyzed activation of strained and unstrained Si–C bonds for constructing silacycles of various sizes.

Chapter 2 describes a palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, a novel class of *N*,*O*-containing six-membered silacycles. This transformation proceeds via intramolecular Si–C bond activation and transmetalation, leading to the formation of a Si–O bond. Mechanistic investigations revealed that the reaction involves inversion of stereochemistry at the silicon center. The reaction was further extended to an asymmetric variant by employing a chiral ligand, enabling the synthesis of silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines.

Chapter 3 describes a nickel-catalyzed synthesis of 3,3-disubstituted 1-silaindanes via a six-to-five ring contraction. This transformation proceeds through novel 1,5-nickel migration via C–H bond activation and 1,4-nickel migration via Si–C bond activation. Deuterium labeling experiments and DFT calculations provided insights into each migration step.

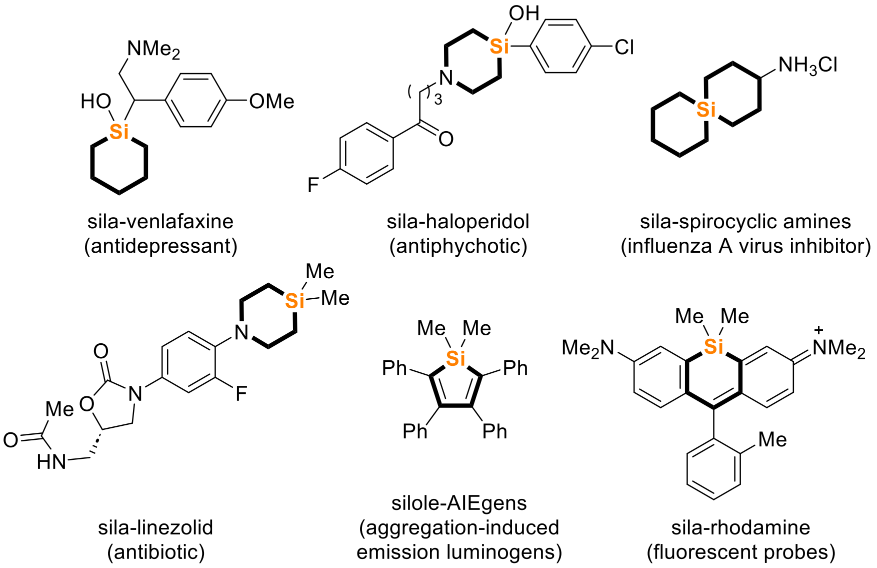
The work presented in this dissertation expands the synthetic toolbox for silacycles, providing innovative methodologies that deepen the understanding of Si–C bond reactivity and broaden the scope of silacycles in functional molecules and materials.

Contents

Chapter 1

General Introduction

1.1 Organosilicon compounds and synthesis of silacycles



sila-venlafaxine
(antidepressant)

sila-haloperidol
(antiphychotic)

sila-spirocyclic amines
(influenza A virus inhibitor)

sila-linezolid
(antibiotic)

silole-AIEgens
(aggregation-induced
emission luminogens)

sila-rhodamine
(fluorescent probes)

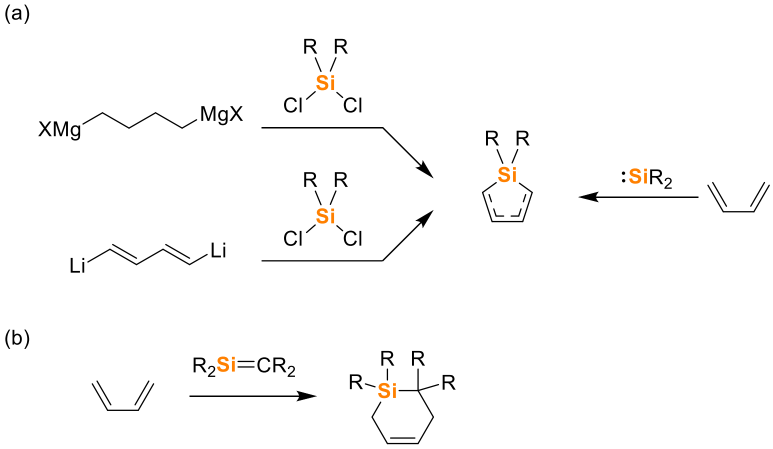
Scheme 1. Silacycle-containing bioactive compounds and functional molecules

Silicon, the second most abundant element in the earth's crust after oxygen, has long been a subject of significant interest to both organic and inorganic chemists. In organic synthesis, organosilicon functional groups are widely utilized as synthetic intermediates such as in anion relay chemistry, cross-coupling reactions, and as protective groups. An important feature of silicon is its position in the periodic table, directly below carbon. Although silicon shares similarities with carbon such as its tetravalency and tetrahedral geometry, it also exhibits distinct differences.[1] Silicon does not form stable π-bonds, is more electropositive than carbon, has longer bond lengths, can have higher coordination number up to 6, and stabilizes α-carbanions, whereas carbon stabilizes αcarbocations.

This “the same and not the same” feature makes silicon an attractive (bio)isostere of carbon, leading to its increasing use in the design of functional organic molecules. However, since organosilicon compounds are not readily available in nature, the development of comprehensive synthetic methods for these compounds is essential for their broader utilization in functional organic molecules and pharmaceuticals (Scheme 1).

Cyclic organosilanes hold a distinct position in this context. Cyclic compounds are particularly important due to their ubiquitous presence in natural products, pharmaceuticals, agrochemicals, and advanced materials. Silacycles, as isosteres of carbocycles, offer unique advantages over their carbon counterparts, making them invaluable for the development of functional molecules and the optimization of their properties. For example, silacycles such as sila-haloperidol and sila-linezolids, exhibit distinct pharmacological profiles due to their enhanced lipophilicity, altered metabolic pathways, and conformational changes that modulate receptor interactions.[2] Additionally, silicon-bridged π-conjugated cyclic compounds, such as silole-AIEgens and sila-rhodamine, represent a valuable class of materials and have been widely explored for applications in organic electronics including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and molecular wires.[3] The various applications of silacycles underscore the growing demand for innovative synthetic methods to access a diverse and broad range of silacycles.

Conventionally, silacycles have been synthesized through reactions between bis-nucleophiles and dichlorosilanes or via cycloadditions of highly reactive silenes or silylenes with olefins (Scheme 2).[4] While these approaches are reliable and have produced a variety of silicon-containing cyclic compounds, they have notable limitations. For example, substrates with functional groups sensitive to strong basic reagents often show low yields in reactions involving bis-nucleophiles. Similarly, cycloadditions with silenes or silylens often require harsh conditions or depend on unstable precursors, restricting their practical application.

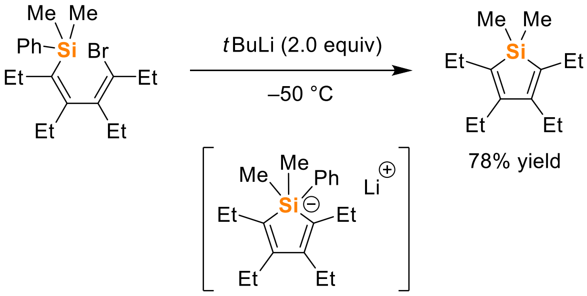


Scheme 2. Synthesis of (a) five-membered and (b) six-membered silacycles.

To address these challenges, transition-metal-catalyzed cross-coupling techniques have emerged as a promising alternative. Widely explored for carbon–carbon and carbon–heteroatom bond formation, these techniques have also been adapted for the silacycle synthesis through Si–H, Si–Si, or Si–C bond activation.[5] Among these, Si–C bond activation is particularly attractive due to its prevalence and robustness in organosilicon compounds and its utility in view of efficiency of the overall synthetic process. In this chapter, the characteristics of the Si–C bond and representative works on transition-metal-catalyzed silacycle synthesis via Si–C bond activation and related reactions are discussed.

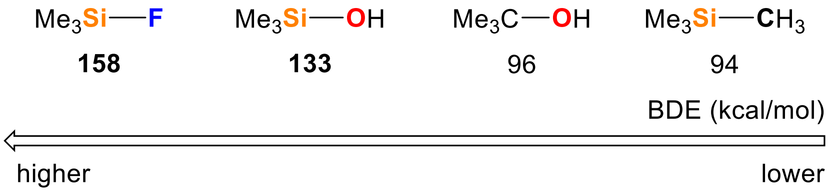
1.1.1 Characteristics of the Si–C bond and its activation.

The Si–C bond is more polar than the C–C bond due to the lower Pauling's electronegativity of silicon (1.90) compared to that of carbon (2.55), which enhances its reactivity in polar processes.[6] While the Si–C bond is generally stable, it can undergo cleavage by strong nucleophiles such as organomagnesium or organolithium reagents, which is generally not observed with C–C bonds (Scheme 3).[7] Additionally, the Si–C bond length (~1.86 Å) is approximately 20% longer than the C–C bond (~1.51 Å),[8] allowing the accommodation of bulky substituents as in triisopropylsilyl, *tert*-butyldiphenylsilyl, and *tert*-butyldimethylsilyl groups which are widely utilized as protecting groups for alcohols.[9] Furthermore, 3p orbitals of silicon are more diffuse and have higher energy compared to 2p orbitals of carbon, resulting in less stable Si=C and Si=O double bonds compared to C=C and C=O double bonds.



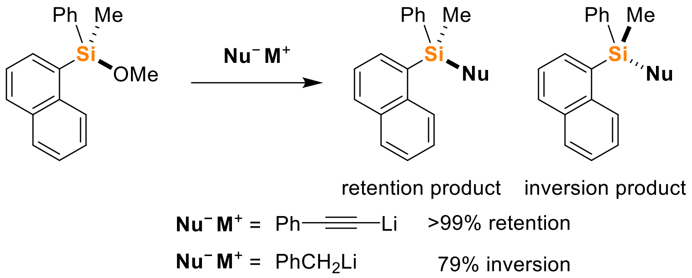
Scheme 3. Cleavage of Si–C bond by intramolecular nucleophilic attack.

The activation of Si–C bonds can be facilitated by the formation of thermodynamically more stable bonds, such as Si–F (158 kcal/mol) and Si–O bonds (133 kcal/mol), which are significantly stronger than Si–C (94 kcal/mol) and C–O (96 kcal/mol) bonds (Scheme 4).[10] Similarly, Si–C bonds in strained organosilanes such as silacyclobutanes are more prone to cleavage than Si–C bonds in unstrained organosilanes, providing a practical strategy for synthesizing (cyclic) organosilicon compounds.



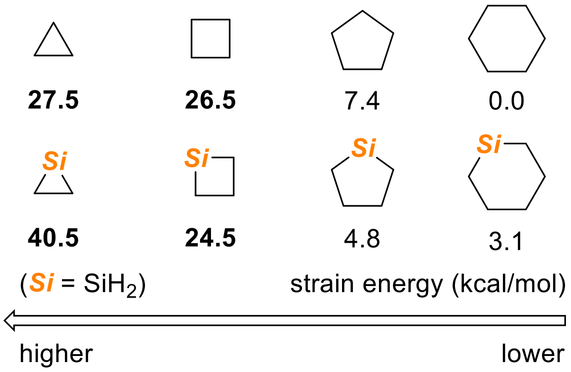
Scheme 4. Bond dissociation energies (BDEs) of Si–F, Si–O, C–O, and Si–C bonds.

Unlike carbon, silicon can achieve coordination numbers up to six using its low lying vacant 3d orbitals. This property not only expands the possible conformational space but also influences reaction selectivity.[11] For example, during the nucleophilic addition in Scheme 3, a pentacoordinate silicate is generated with the phenyl group serving as the leaving group over the methyl group, owing to the greater thermodynamic stability of the phenyl anion. Additionally, while nucleophilic substitution at carbon stereocenters typically results in inversion of configuration via Walden inversion (S_N2) or a 1:1 mixture of inversion and retention products through a carbocation intermediate (S_N1), the configuration of silicon stereocenters varies depending on nucleophiles, substituents on silicon, and other reaction conditions (Scheme 5).[12] These differences in bond stability and orbital properties give distinct reactivities and structural characteristics that are not accessible with carbon analogs.



Scheme 5. Stereochemistry of silicon stereocenter during nucleophilic substitution.

1.1.2 Synthesis of silacycles by transition-metal-catalyzed cleavage of strained Si–C bonds



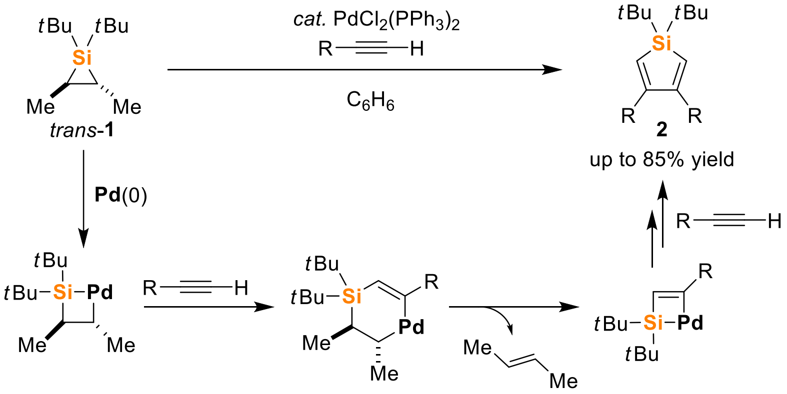
Scheme 6. Strain energies of cycloalkanes and silacycloalkanes.

Ring strain, a term that was used to justify the synthetic difficulties of small ring systems, has now been used as a powerful tool in modern chemistry. In recent decades, chemists have harnessed this strain energy to drive reactions including those for the synthesis of larger cyclic compounds via ring-expansion reactions. Strained carbocycles, such as cyclopropanes, cyclobutanes, propellanes, and bicyclobutanes, have been widely employed in this context, often in the presence of Lewis acids, transition-metal catalysts, or photocatalysts.[13]

Similarly, strained silacycles such as silacyclopropanes and silacyclobutanes have demonstrated their utility in the synthesis of larger silacycles using their high strain energies of 40.5 kcal/mol and 24.5 kcal/mol, respectively (Scheme 6).[14] Strained silanes can readily undergo oxidative addition or transmetalation with transition metals such as palladium, nickel, platinum, rhodium, and cobalt. The following ring-expansion reactions by transition-metal catalysts have also been well developed, providing access to structurally diverse silacycles.[15]

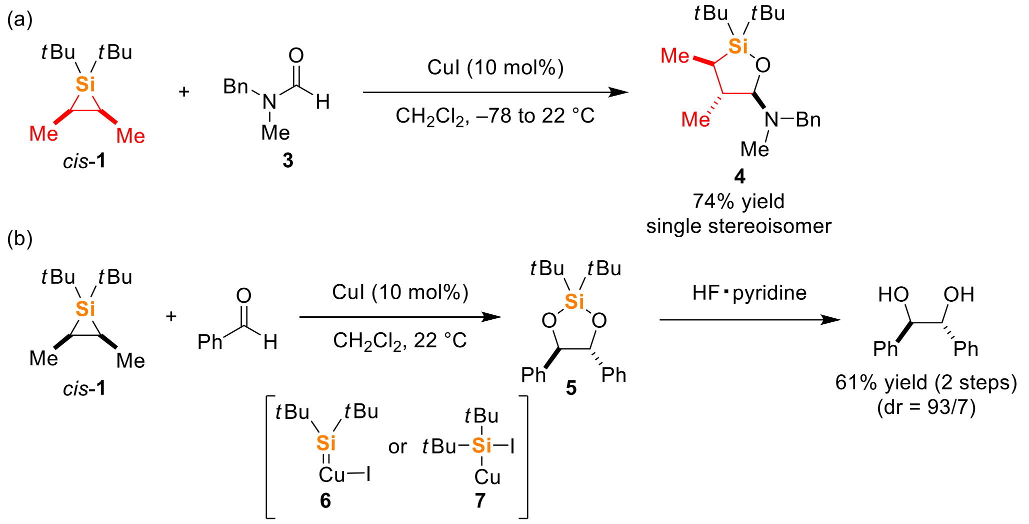
Reactions using silacyclopropanes

Because of their low thermal stability, reactions using silacyclopropanes are rarely reported in the literature and are limited to stable and isolable ones with bulky substituents.[16] One of the seminal works was reported by Woerpel and coworkers, who demonstrated palladium-catalyzed reactions of 1,1-di-*tert*-butyl-2,3-dimethylsilirane (*trans*-**1**) with alkynes to form siloles **2** via silylene extrusion (Scheme 7).[17] The proposed reaction mechanism involves the oxidative addition of the strained Si–C bond in *trans*-**1** to Pd(0), followed by migratory insertion of the alkyne, β-silicon elimination to release *trans*-2-butene, and subsequent second migratory insertion, followed by reductive elimination to give siloles **2**.



Scheme 7. Palladium-catalyzed reactions of silacyclopropane **1** with alkynes.

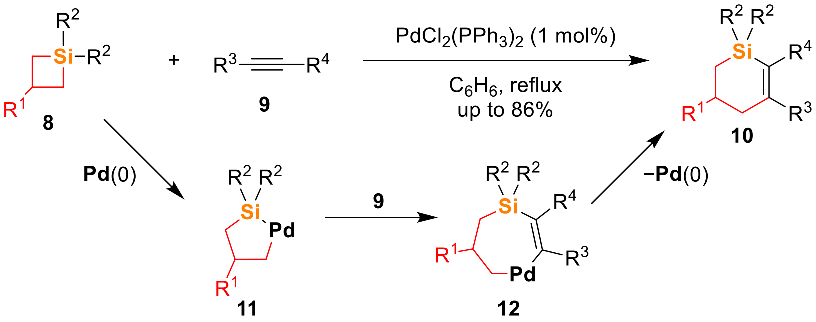
They also reported the reaction of *cis*-**1** with *N*-benzyl-*N*-methylformamide **3** in the presence of CuI as a catalyst, which afforded the *N*,*O*-acetal **4** as a single isomer in 72% yield, whereas the reaction of *cis*-**1** with amide **3** without a copper catalyst produced only a trace amount of the insertion product even at the elevated temperatures (Scheme 8a).[18] Additionally, the reaction of *cis*-**1** with benzaldehyde yielded dioxasilolane **5** along with the liberation of 2-butene (Scheme 8b). The formation of compound **5** is proposed to occur via the trapping of *in-situ* generated silylene **6** or silylenoid **7**, which induced reductive dimerization of benzaldehydes. Subsequent treatment of **5** with HF gave *trans*-hydrobenzoin as a 93:7 mixture of diastereomers.



Scheme 8. (a) Copper-catalyzed ring-expansion of silacyclopropane **1** with formamide **3**. (b) Copper-catalyzed reaction of silacyclopropane **1** with benzaldehyde.

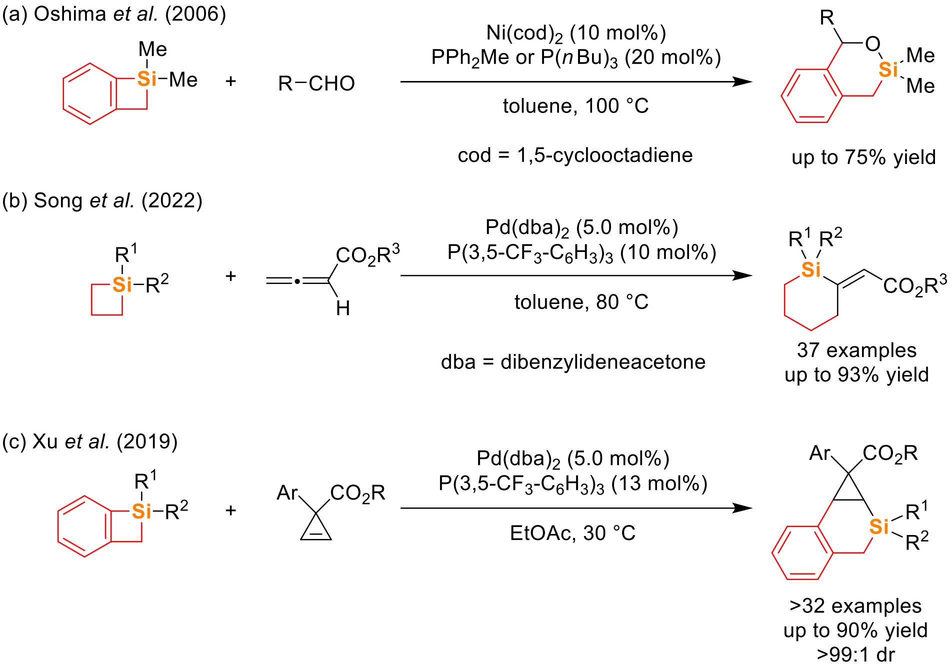
Reactions using silacyclobutanes and silacyclobutenes

Silacyclobutanes and silacyclobutenes exhibit better thermal stability compared to silacyclopropanes while still possessing sufficient strain energy to drive ring-expansion reactions, which makes them valuable starting materials for the synthesis of silacycles. In 1975, Sakurai and Imai first reported a palladium-catalyzed strain-releasing cycloaddition of silacyclobutanes.[19] Later in 1991, Oshima, Utimoto, and coworkers revisited the same reaction and demonstrated silacyclobutanes **8** react with alkynes **9** in the presence of a palladium catalyst to give 1-sila-2-cyclohexenes **10** (Scheme 9).[20] The proposed reaction mechanism involves the oxidative addition of the silacyclobutane to palladium to form palladacycle species **11**. This is followed by the 1,2-alkyne insertion, producing seven-membered-ring intermediate **12**, and the reductive elimination to afford silacyclohexene **10**.



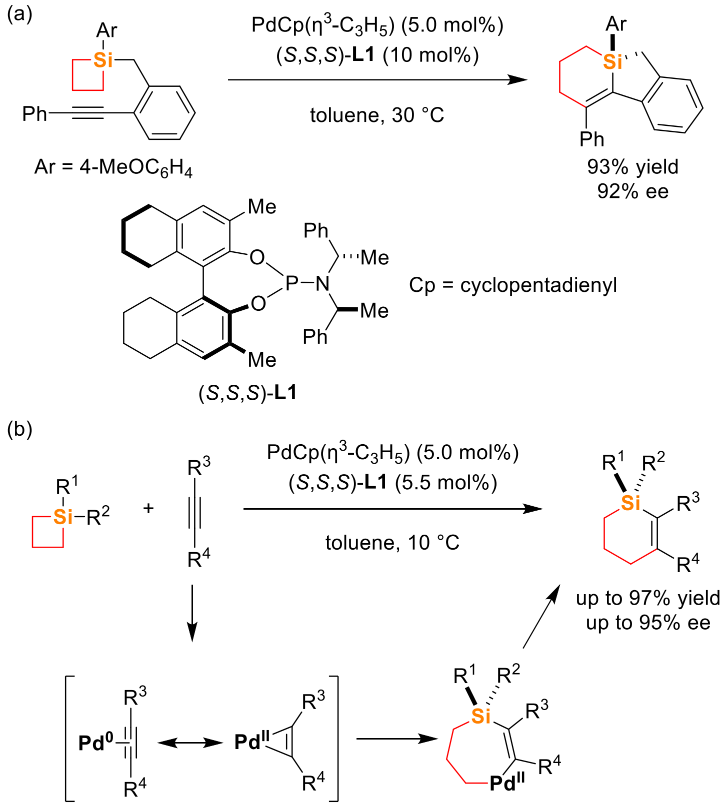
Scheme 9. Palladium-catalyzed reaction of silacyclobutanes **8** with alkynes **9**.

Based on these findings, several transition-metal-catalyzed reactions using silacyclobutanes and silacyclobutenes have been developed such as palladium-catalyzed reactions with alkenes, allenoates,[21] and cyclopropenes,[22] as well as nickel-catalyzed reactions with aldehydes,[23] carbon dioxide[24] to construct six-membered silacycles (Scheme 10).



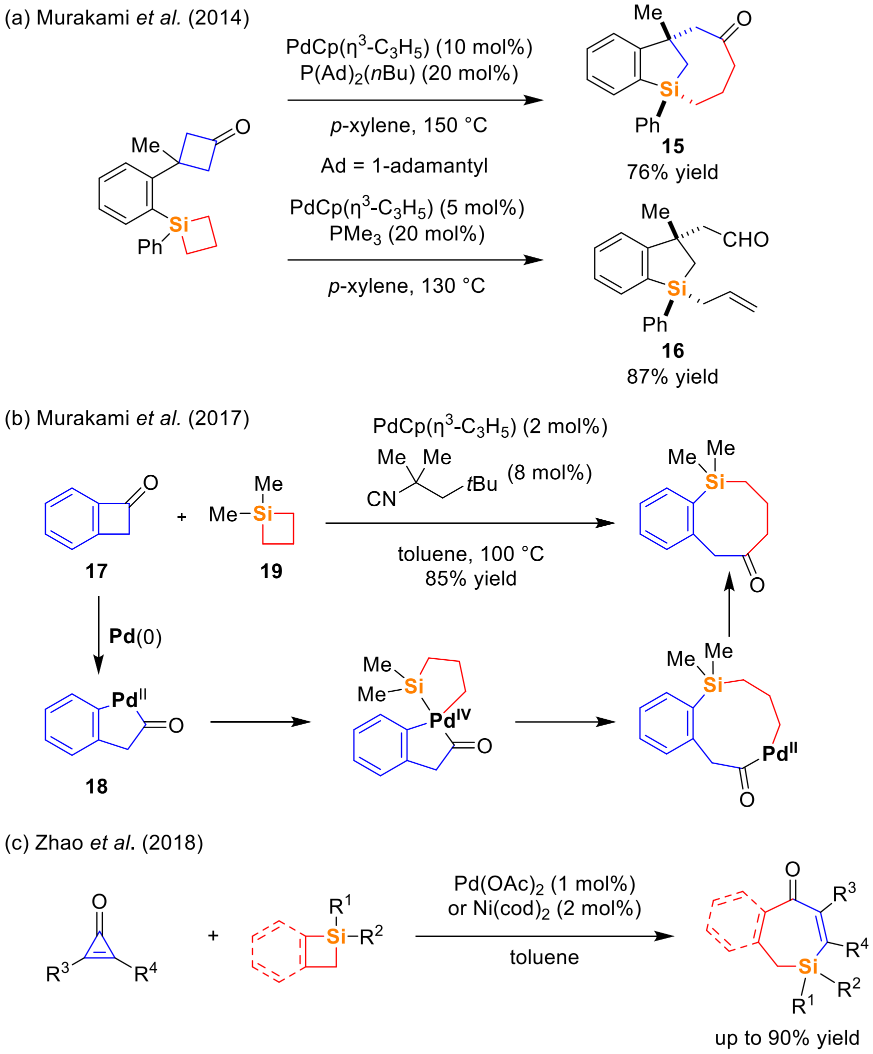
Scheme 10. Four-to-six ring-expansion reactions of four-membered silacycles with (a) aldehydes, (b) allenes, and (c) cyclopropenes.

In 2011 and 2012, Shintani, Hayashi, and coworkers reported the first asymmetric variant of this type of reaction, describing a palladium-catalyzed intra- and intermolecular enantioselective desymmetrization of silacyclobutanes to give silicon-stereogenic tetraorganosilacycles (Scheme 11).[25] Instead of the mechanism proposed by Oshima and Utimoto, where oxidative addition of silacyclobutane occurs first, they suggested an alternative reaction mechanism in which oxidative cycloaddition of an alkyne occurs first to form 1-pallada-2-cyclopropene **13**, followed by σ-bond metathesis with a silacyclobutane to generate intermediate **14**. The formation of palladacycle **13** was confirmed by the stoichiometric reaction and X-ray crystal structure analysis. Additionally, DFT calculations on this system conducted by Xu and coworkers also supported this mechanism.[26]



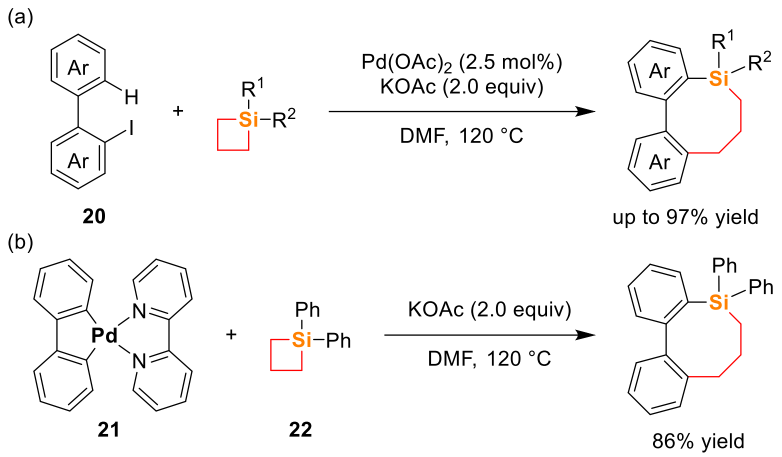
Scheme 11. Palladium-catalyzed (a) intra- and (b) intermolecular enantioselective desymmetrization of silacyclobutanes with alkynes.

Reactions to construct larger silacycles have also been achieved. Especially, the reactions combining with other strained molecules provided efficient strategies to construct larger silacycles. In 2014 and 2017 Murakami and coworkers reported intra- and intermolecular C–C and Si–C bond exchanges to synthesize eight-membered silacycles in the presence of a palladium catalyst (Scheme 12).[27] These reactions showed remarkable product selectivity shifts depending on the choice of ligands. When sterically bulky $P(Ad)_2(nBu)$ was employed, silabicyclo[5.2.1]decane **15** was formed (Scheme 12a). In contrast, the use of less bulky PMe_3 selectively yielded ring-opened aldehydes **16**. In the intermolecular reaction, *tert*-octyl isocyanide was proved to be an effective ligand to furnish the product (Scheme 12b). A stoichiometric reaction of a palladium-isocyanide complex with benzocyclobutenone **17** produced palladacycle **18** coordinated with two *tert*-ocyl isocyanide ligands in a quantitative yield. In contrast, no reaction occurred with silacyclobutane **19**, suggesting that benzocyclobutenone **17**, not silacyclobutane **19**, undergoes oxidative addition to the palladium complex. Presumably inspired by these findings, Zhao and coworkers later reported the reaction of silacyclobutanes and benzosilacyclobutenes with cyclopropenones to yield silacycloheptenones as seven-membered silacycles (Scheme 12c).[28,29]



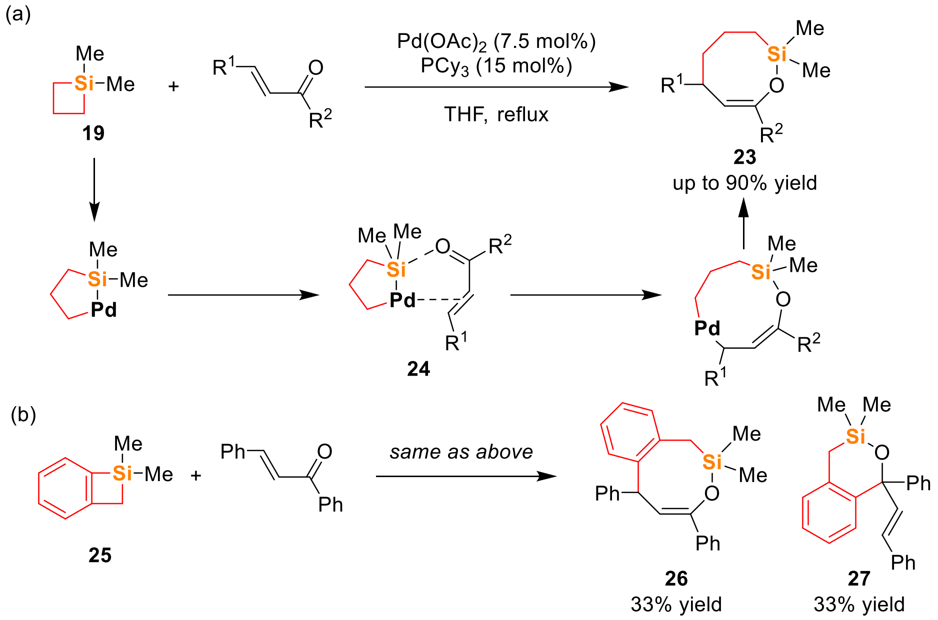
Scheme 12. (a) and (b) Palladium-catalyzed synthesis of 8-membered silacycles via C–C/Si–C bond exchange. (c) Synthesis of silacycloheptenones via C–C/Si–C bond exchange.

In addition to ring-expansion via C–C bond activation, Liu and coworkers reported a palladium-catalyzed [4+4] annulation of silacyclobutanes with 2-iodobiaryls to form eight-membered silacycles through C–H and C–Si bond activation (Scheme 13a).[30] Mechanistic investigations, including stoichiometric experiments, revealed that the oxidative addition of 2-iodobiaryl **20** to Pd(0) occurs first, rather than the oxidative addition of silacyclobutane to Pd(0). Furthermore, separately prepared palladacycle **21** successfully reacted with silacyclobutane **22** to yield the corresponding product (Scheme 13b).



Scheme 13. (a) Palladium-catalyzed [4+4] annulation of silacyclobutanes and 2-iodobiaryls. (b) Stoichiometric experiment with palladacycle **21** and silacyclobutane **22**.

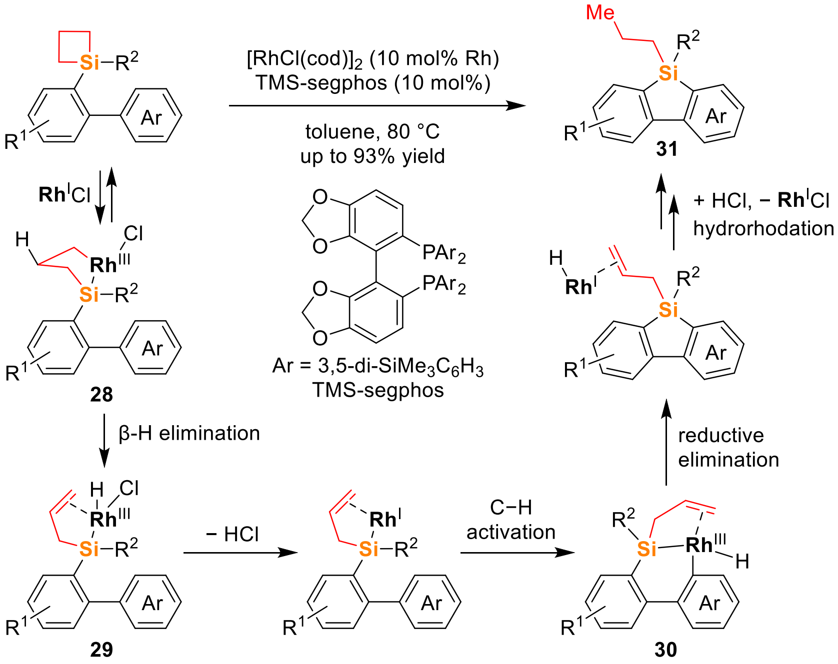
In 2008, Oshima and coworkers reported a palladium-catalyzed formal cycloaddition of silacyclobutane **19** with enones, yielding eight-membered cyclic silyl enol ethers **23** (Scheme 14a).[31] The use of strongly σ-donating PCy_3 ligand was essential to enable the formation of complex **24** by π-back donation from the palladium center to the olefin which increases the electron density of the carbonyl oxygen, facilitating Si–O bond formation. This reaction is also applicable to benzosilacyclobutene **25** to give the corresponding cyclic silyl enol ethers **26** in a moderate yield, along with the formation of silyl ether **27** (Scheme 14b).



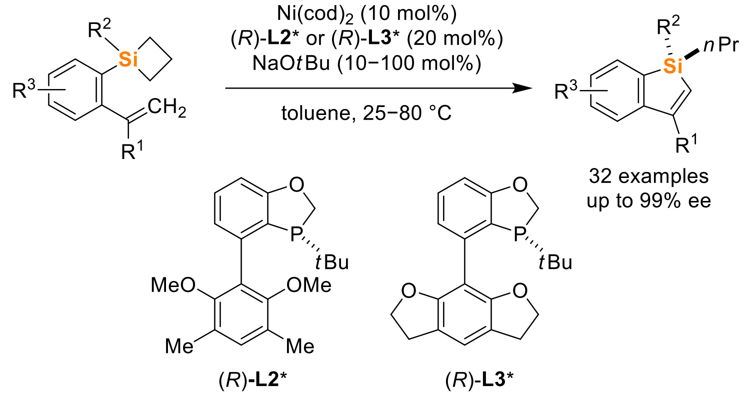
Scheme 14. Palladium-catalyzed formal cycloaddition of (a) silacyclobutanes and (b) benzosilacyclobutenes with enones.

In addition to the palladium- and nickel-catalyzed ring-expansion of silacyclobutanes described above, rhodium and cobalt[32] complexes have also been identified as effective catalysts for activating Si–C bonds in silacyclobutanes. In 2016, He and coworkers developed a C–H silylation of silacyclobutanes using a Rh/TMS-segphos catalyst to yield dibenzosiloles (Scheme 15).[33] The proposed reaction mechanism involves reversible oxidative addition of a silacyclobutane to a Rh(I) complex, forming rhodacycle **28**. This is followed by β-hydride elimination, generating key intermediate **29** that activates the C–H bond. The resulting aryl(silyl)rhodium species **30** undergoes reductive elimination to construct the dibenzosilole moiety, forming a five-membered silacycle. Finally, hydrorhodation of the allyl group and subsequent protodemetalation by

HCl regenerate the Rh(I) chloride catalyst and yield dibenzosilole **31**. An enantioselective variant of this transformation producing silicon-stereogenic dibenzosiloles was also reported by the same group.[34] More recently, Zhao and coworkers developed a relevant nickel-catalyzed asymmetric intramolecular coupling of silacyclobutanes with alkenes, synthesizing silicon-stereogenic benzosiloles (Scheme 16).[35]

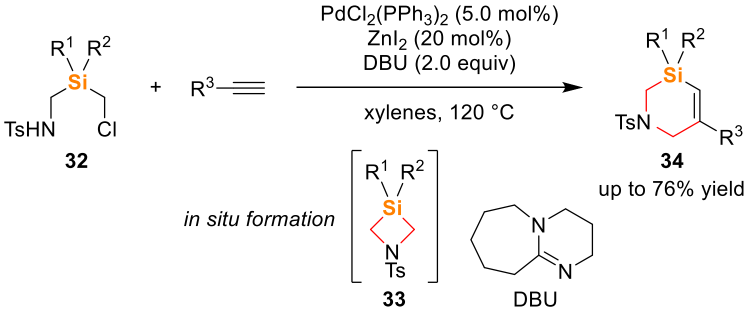


Scheme 15. Rhodium-catalyzed C−H silylation of silacyclobutanes.



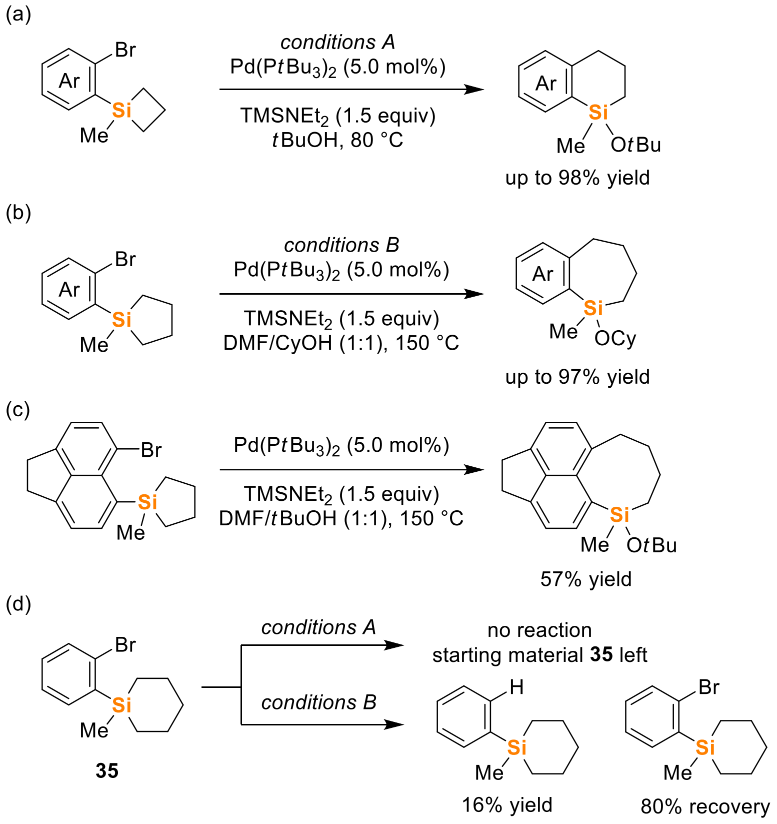
Scheme 16. Nickel-catalyzed asymmetric ring-expansion of silacyclobutanes toward benzosiloles.

In addition to silacyclobutanes and silacyclobutenes, Song and coworkers demonstrated that *in-situ* generated 3-silaazetidines could serve as versatile organosilane species for ring-expansion toward silaazacycles (Scheme 17).[36] They designed and prepared air-stable 3-silaazetidine precursors **32**, which reacted with DBU and underwent an intramolecular *N*-substitution to give 3-silaazetidine derivatives **33**. Although silaazetidine derivatives **33** could not be isolated, they were stable *in-situ* and subsequently reacted with terminal alkynes in the presence of a palladium catalyst, which resulted in the formation of 3-silatetrahydropyridines **34** via formal ring-opening cycloaddition.



Scheme 17. Palladium-catalyzed ring-expansion of *in-situ* generated 3-silaazetidines.

Limited reports describe the ring-expansion of silacyclopentanes. Zhao and coworkers reported intramolecular Hiyama coupling reactions via ring-expansion of four-, and five-membered silacycles, yielding six-, seven-, and eight-membered silacycles using Si–O bond formation and intramolecular transmetalation as driving forces (Scheme 18).[37] The activation of four- and five-membered silacycles by a nucleophile to form a pentacoordinate silicate is facilitated by their enhanced Lewis acidity, derived from ring strain release. In contrast, substrate **35** having a six-membered silacycle did not undergo the corresponding ring-expansion reaction, highlighting the role of ring strain release in this transformation. A control experiment without a catalyst indicated that free pentacoordinated silicon does not form prior to transmetalation. Instead, it suggested the concerted formation of the silicate and transmetalation pathway might be more preferred.

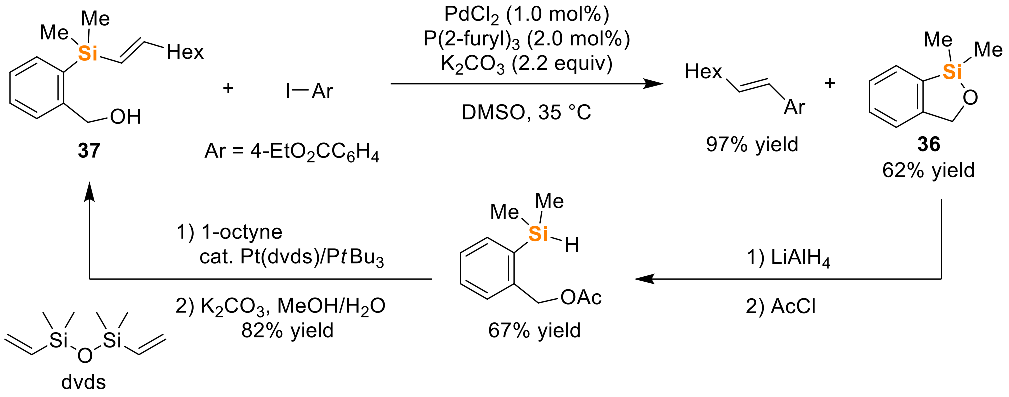


Scheme 18. Palladium-catalyzed ring-expansion to 6-, 7-, and 8-membered silacycles.

1.1.3 Synthesis of silacycles by transition-metal-catalyzed activation of unstrained Si–C bonds

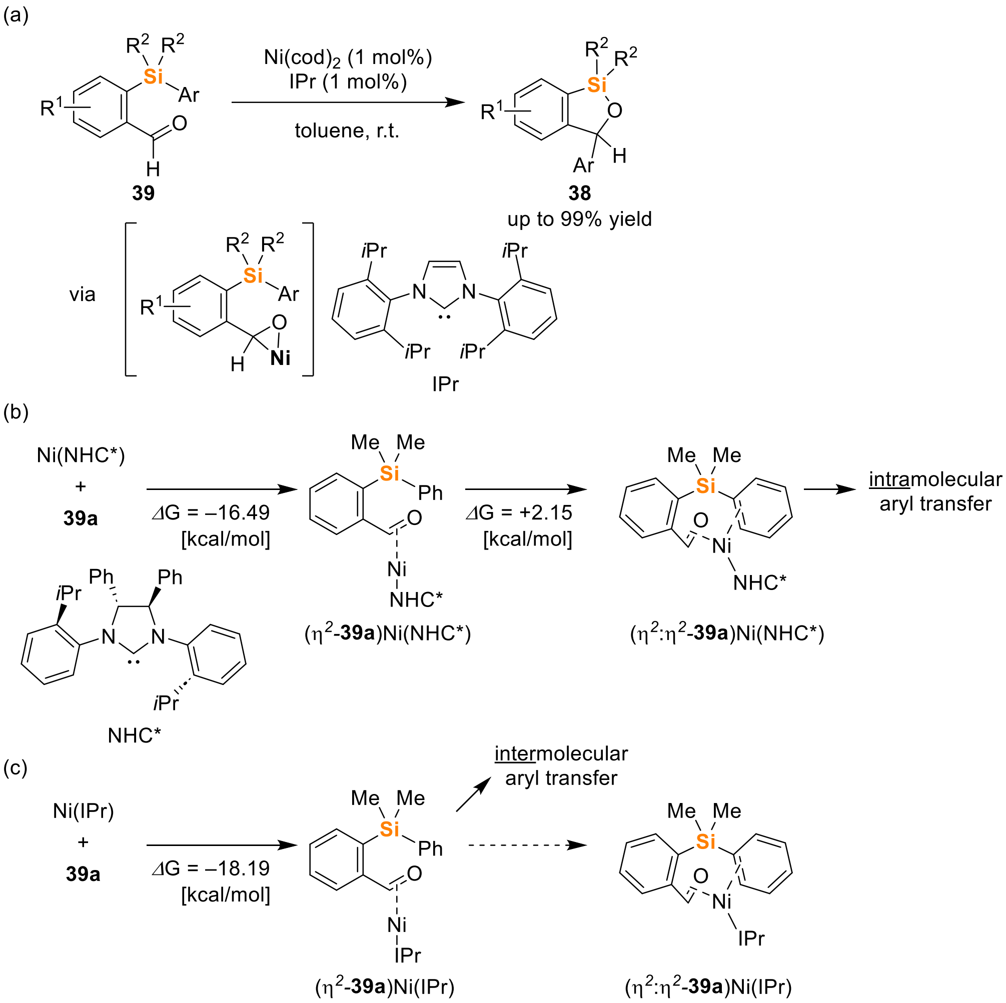
Compared to the Si–C bonds in strained organosilanes, the activation of unstrained Si–C σ-bonds is significantly more challenging due to their higher thermodynamic stability. Activation of inert Si–C bonds has been achieved using organomagnesium and organolithium reagents, but these approaches often require limited and harsh reaction conditions (see **1.1.1**). On the other hand, transition-metal catalysis provides a milder and more versatile alternative for Si–C σ-bond activation.

One of the most well-known applications of organosilicon compounds involving Si–C bond activation is the Hiyama–Denmark cross-coupling.[38] In this reaction, tetra-coordinated organosilicon compounds are activated by strong activators such as fluoride ions to form penta-coordinated silicates, which then undergo transmetalation with transition-metal catalysts. In 2005, Nakao, Hiyama, and coworkers developed alkenyl- and aryl[2-(hydroxymethyl)phenyl]dimethylsilanes, which were later named as HOMSi reagents. These reagents utilize a pendant alkoxide to activate the Si–C bond by forming five-membered silacycles, enabling efficient transmetalation of the alkenyl or aryl group to a palladium catalyst (Scheme 19).[39] Notably, this reaction proceeds without fluoride ions, and a weak base (potassium carbonate) is sufficient to form the activated silicate. Additionally, the resulting dihydrobenzoxasilole **36** can be recovered and reactivated to give alcohol **37**, representing the first example of a reusable metal residue in the cross-coupling reactions.



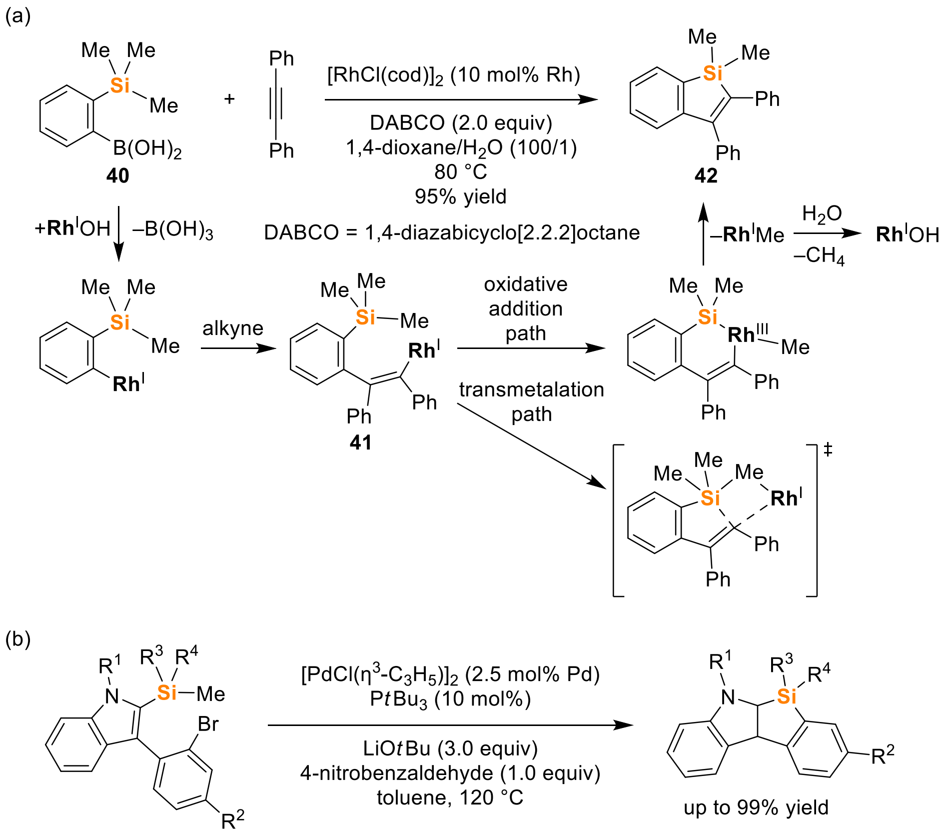
Scheme 19. Palladium-catalyzed cyclic silyl ether formation by intramolecular Si–C bond activation and its use as reusable silicon nucleophiles.

In 2014, Hoshimoto, Ogoshi, and coworkers reported Si–C bond activation with η^2-aldehyde nickel complexes and aryl transfer as a synthetic method for benzoxasiloles **38** from benzaldehydes **39** with 100% atom efficiency under mild conditions without the need for external bases (Scheme 20a).[40] This reaction proceeds through the activation of the aldehyde via back-donation from an electron-rich Ni(0)/NHC complex, enabling the generation of a hypervalent silicate as the key intermediate. Subsequent aryl transfer leads to the formation of benzoxasilole moiety. During the development of its enantioselective variant,[41] they observed a switch of the reaction mechanism for the aryl transfer step, modulated by the choice of NHC ligand. This was supported by crossover experiments and further elucidated by DFT calculations. Using the Ni(0)/NHC* catalyst, intramolecular aryl transfer proceeds due to the η^2:η^2-coordination of the substrate to the nickel complex, which facilitates the intramolecular aryl transfer (Scheme 20b). In contrast, with the Ni(0)/IPr catalyst, steric hindrance by the two isopropyl groups restricts the coordination to an η^2-mode rather than η^2:η^2-coordination, favoring an intermolecular aryl transfer (Scheme 20c).



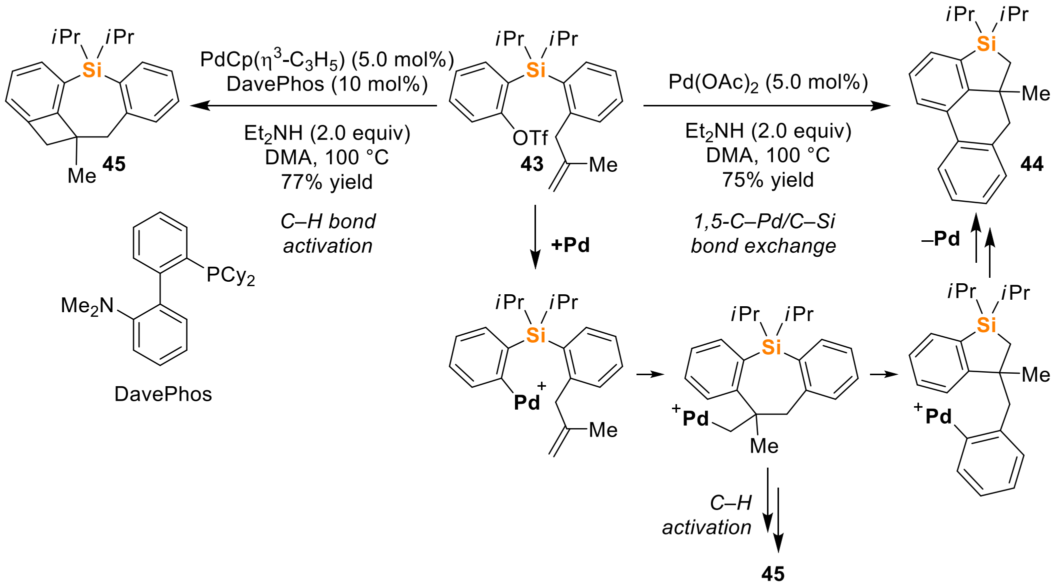
Scheme 20. (a) Nickel-catalyzed synthesis of benzooxasiloles via silicon to carbon aryl migration. (b) and (c) Plausible rationale for switching of aryl transfer process.

In addition to Si–C bond cleavage by the formation of a stronger Si–O bond, reactions involving new Si–C bond formation have also been reported. In 2009, Tobisu, Chatani, and coworkers reported a rhodium-catalyzed synthesis of benzosiloles which involves catalytic cleavage of a Si–Me bond as the key step (Scheme 21a).[42] The proposed mechanism involves the transmetalation of **40** to a rhodium hydroxide, followed by alkyne insertion to form alkenylrhodium intermediate **41**, which undergoes formal substitution at the trimethylsilyl group to afford benzosilole **42** and a methylrhodium(I) species through the cleavage of a Si–C bond. Finally, protonolysis of the methylrhodium(I) regenerates the active catalyst. The detailed reaction mechanism was elucidated by themselves[43] and Yu's group[44] through experimental studies supported by DFT calculations. It was proposed that the Si–C bond activation via oxidative addition/reductive elimination path is more plausible than the σ-bond metathesis path or a pentacoordinated silicate mechanism.[45] Later, Xi and coworkers reported a similar palladium-catalyzed synthesis of benzosilole and benzosilolo[2,3-*b*]indoles via Si–C bond activation.[46] DFT calculations for this reaction also supported an oxidative addition/reductive elimination pathway (Scheme 21b).[47]



Scheme 21. (a) Rhodium-catalyzed synthesis of benzosiloles via Si–C bond activation. (b) Palladium-catalyzed synthesis of benzosilolo[2,3-*b*]indoles via Si–C bond activation.

Recently, our group developed a palladium-catalyzed skeletal rearrangement of 2-(2-allylarylsilyl)aryl triflate **43** to give highly fused tetrahydrophenanthrosilole **44** via a 1,5-Pd–C/Si–C bond exchange (Scheme 22).[48] Additionally, tuning the palladium precatalyst and phosphine ligand enabled a four-membered ring-forming C–H bond activation rather than Si–C bond activation, yielding fused dihydrodibenzosilepin **45** from the same starting material. The key step in this transformation is the palladium-catalyzed Si–C bond activation, featuring a rare 1,5-palladium migration via a Si–C bond activation. This step is distinct from Si–Me activation, which expels active metal species from the organic molecule, and resembles the 1,4-Rh–C/Si–C bond exchange reported by Cramer and coworkers.[49] Control experiments and DFT calculations revealed that carboxylates play a crucial role in determining the product selectivity. In the absence of carboxylates, dihydrodibenzosilepin **45** is favored as the major product over tetrahydrophenanthrosilole **44**.

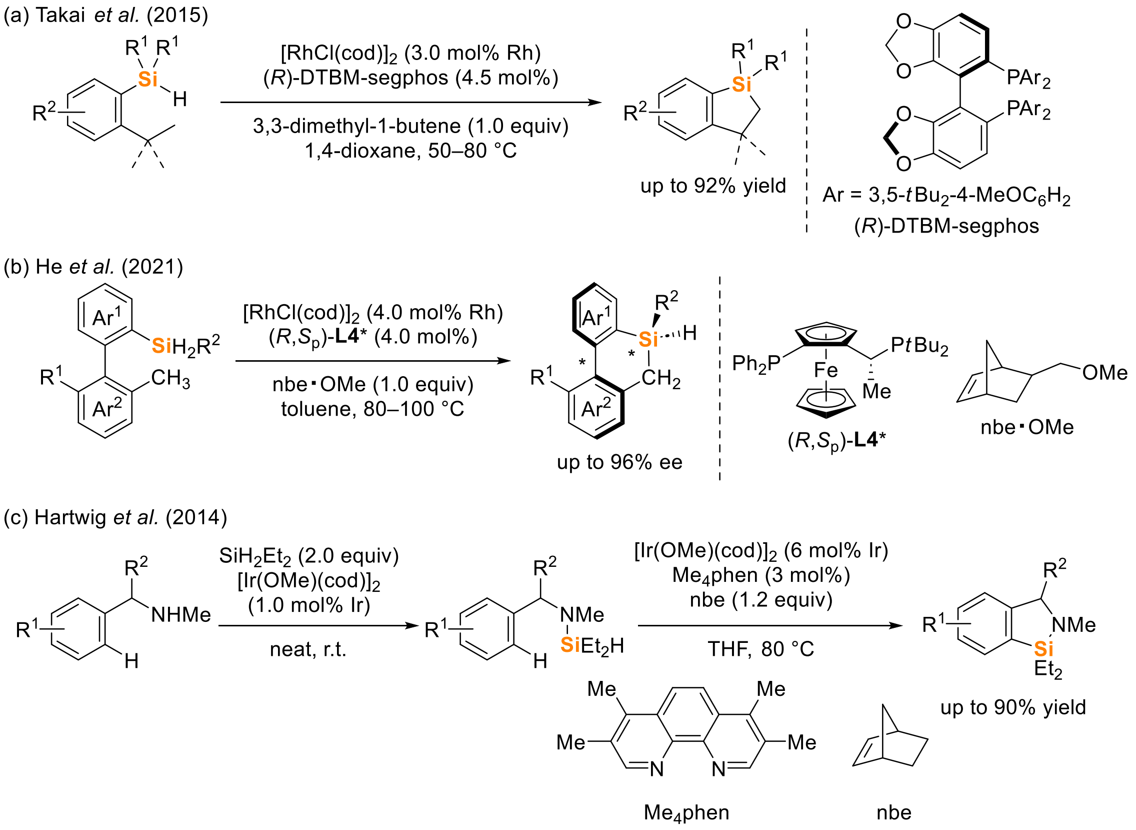


Scheme 22. Palladium-catalyzed reactions of 2-(2-allylarylsilyl)aryl triflate **43**.

1.1.4 Other catalytic approach in the synthesis of silacycles

In addition to Si–C bond activation, silacycles can also be synthesized through catalytic Si–H bond activation and cyclization at a distal position. This section highlights selected examples of this category.

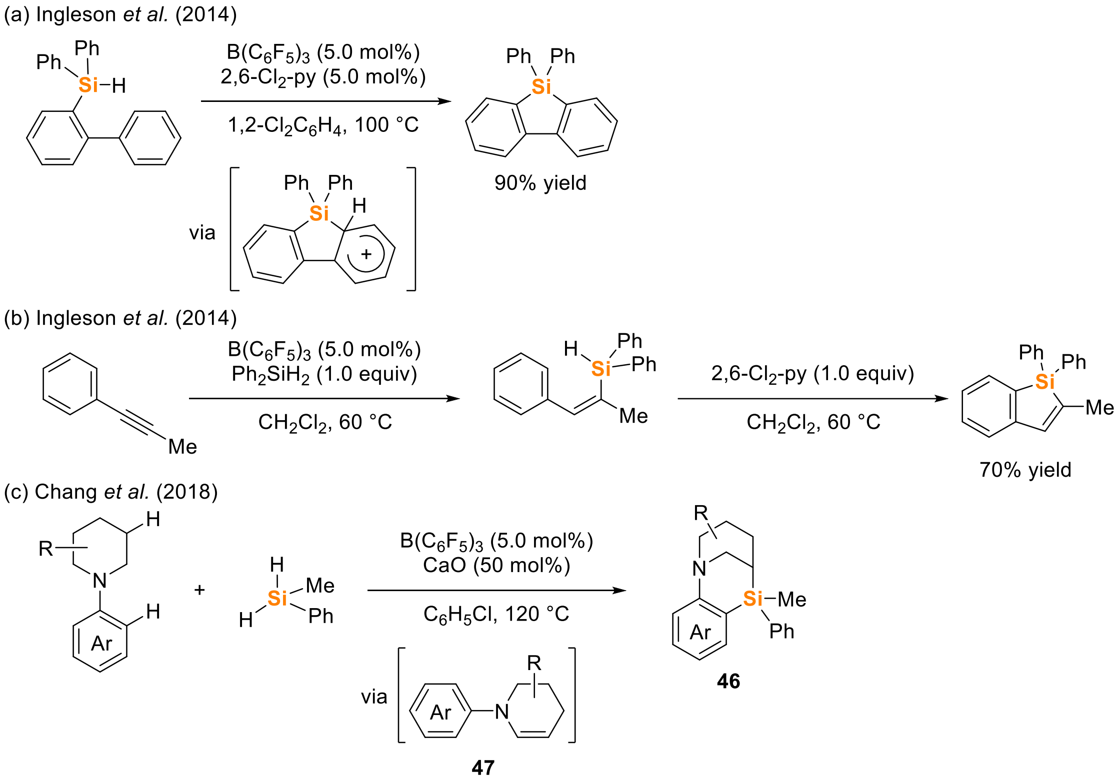
Transition-metal-catalyzed cyclization via C–H/Si–H bond coupling was pioneered by Hartwig's group. However, these transformations typically required high temperatures (135–200 °C), limiting their practical application.[50] In 2015, Takai and coworkers addressed this limitation and reported a rhodium-catalyzed intramolecular dehydrogenative Si–H/C–H coupling. By optimizing the phosphine ligand and utilizing 3,3-dimethyl-1-butene as an additive, they succeeded in lowering the reaction temperature from 180 °C to 50 °C (Scheme 23a).[51] In 2021, He and coworkers reported the first example of enantioselective C(sp^3)–H silylation by developing a catalytic asymmetric Si–H/C–H coupling, simultaneously constructing a silicon stereocenter and axial chirality in the presence of a Rh/Josiphos catalyst to afford dihydrodibenzosilines with high enantioselectivity (Scheme 23b). C(sp^2)–H/Si–H coupling reactions have also been explored.[52] For example, Hartwig and coworkers reported an iridium-catalyzed silylation of an aromatic C(sp^2)–H bond to yield 2,3-dihydro-1*H*-benzo[*c*][1,2]azasiloles, a sila-heterocycles with a Si–N bond, in good yields (Scheme 23c).[53]



Scheme 23. Transition-metal-catalyzed intramolecular Si–H/C–H coupling to give (a) tetrahydrobenzosiloles, (b) dihydrodibenzosilines, and (c) dihydrobenzoazasiloles.

Recently, pioneered by Oestreich's group, the reactivity of cationic silicon and its applications in catalysis have been extensively investigated including C–H silylation.[54] Ingleson and coworkers reported Si–H bond activation with $B(C_6F_5)_3$ as Lewis acid and its ring-closing reaction to form dibenzosiloles through an intramolecular sila-Friedel–Crafts process (Scheme 24a).[55] Control experiments revealed that the weak base facilitates the reaction, presumably by deprotonating the relatively stable arenium cation intermediate.[56] Additionally, the formation of benzosiloles was achieved under similar conditions using an alkyne and dihydrodiphenylsilane by sequential *trans*-selective hydrosilylation of the C≡C triple bond and base-assisted intramolecular C–H silylation (Scheme 24b). Using a related approach, Zhang, Park, and Chang developed cascade sp^3

and sp^2 C–H bond activations to yield bridged sila-*N*-heterocycles **46** via *in-situ* dehydrogenative generation of enamine intermediate **47** mediated by $B(C_6F_5)_3$ (Scheme 24c).[57]

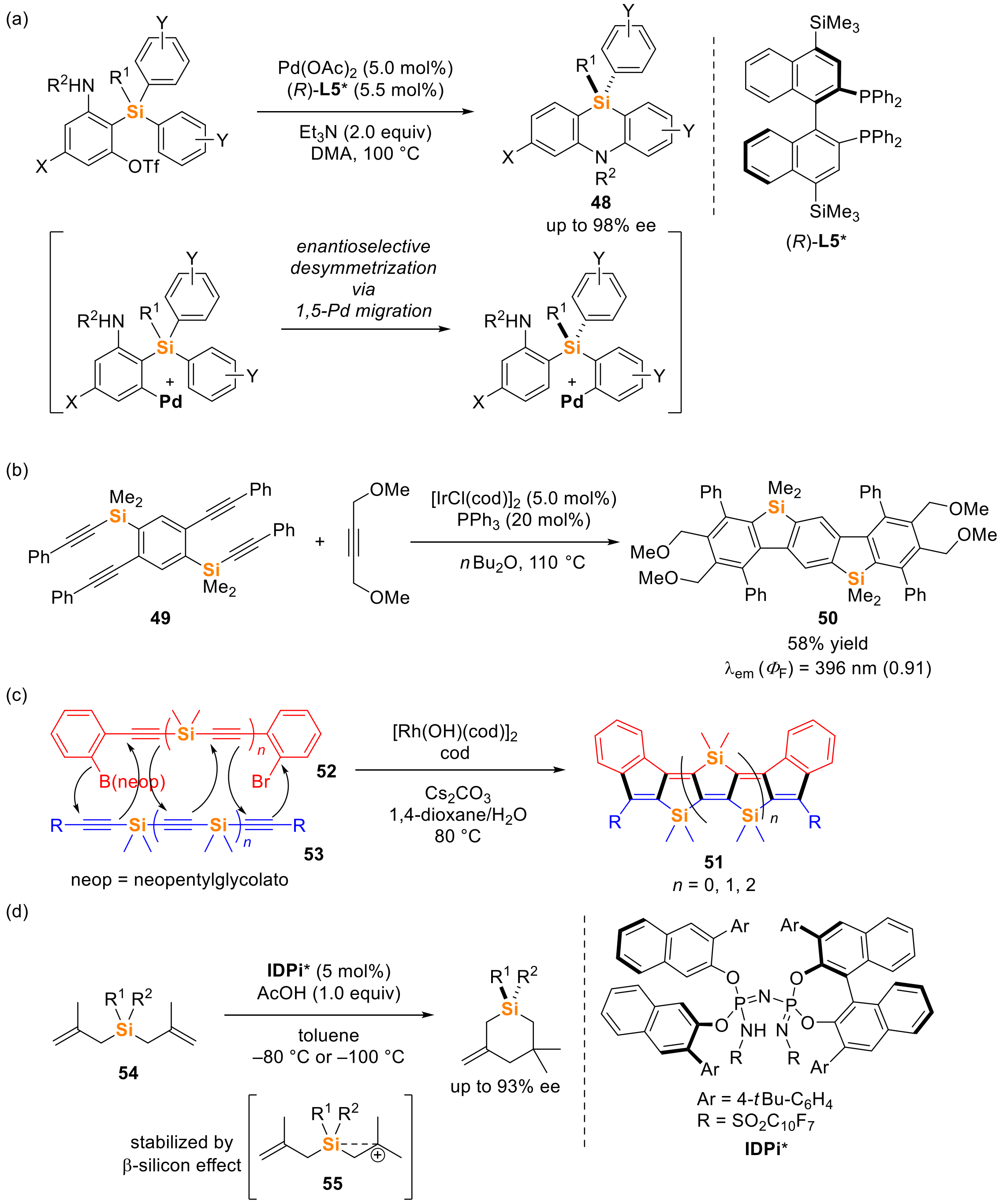


Scheme 24. Lewis acid-catalyzed intramolecular dehydrogenative Si–H/C–H coupling to give (a) dibenzosiloles, (b) benzosiloles, and (c) bridged sila-*N*-heterocycles.

Cyclization at a distal position provides an alternative strategy for the synthesis of silacycles without direct activation of Si–X bonds. Shintani, Nozaki, and coworkers developed a palladium-catalyzed asymmetric synthesis of 5,10-dihydrophenazasilines **48** via 1,5-palladium migration and C–N bond formation (Scheme 25a).[58] The 1,5-palladium migration proceeds enantioselectively, determining the chirality of the silicon stereogenic center, as one of the rare examples involving enantioselective 1,5- migration. Furthermore, by employing relevant substrates, the synthesis of six- and seven-membered π-conjugated silacarbocycles has also been realized.[59]

In 2006, Murakami and coworkers developed an iridium-catalyzed [2+2+2] cycloaddition to synthesize dibenzosilole derivatives (Scheme 25b).[60] Tetrayne substrate **49** gave ladder-type π-conjugated compound **50**, which exhibited a longer emission wavelength (λ_{em} = 396 nm) with exceptionally high fluorescence efficiency ($\Phi_F = 0.91$) compared to compounds containing a single silole unit ($\Phi_F < 0.3$). In 2016, Shintani, Nozaki, and coworkers reported the synthesis of silicon-bridged polyenes **51** by developing a rhodium-catalyzed stitching reaction. The reaction proceeds between two oligo(silylene ethynylene)s **52** and **53**, one of which contains an arylboron group on one end and a haloarene group on the other end (Scheme 25c). These substrates reacted in the presence of a rhodium catalyst to stitch them together as illustrated in Scheme 23c. Electrochemical studies of compounds **51** revealed the higher HOMO level for the longer π-conjugation system. Interestingly, the LUMO level also increased for the longer π-conjugation.[61] A similar stitching strategy has been successfully applied in the synthesis of new π-conjugated polymers with ladder-type silicon-bridged repeating units.[62]

For an example of organocatalytic cyclization, List and coworkers recently developed an asymmetric synthesis of silicon-stereogenic silacyclohexane derivatives from achiral substrates in the presence of a strongly acidic and confined imidodiphosphorimidate organocatalyst (Scheme 25d).[63] DFT calculations suggested that the protonation of **54** to form β-silicon-stabilized **55** is the enantiodetermining step. Additionally, the addition of acetic acid was found to facilitate the catalyst turnover by reactivating the resting covalent adduct which was revealed by the NMR and ESI-MS studies.



Scheme 25. Synthesis of silacycles via cyclization at a distal position. Synthesis of (a) dihydrophenazasilines, (b) dibenzosiloles, (c) silicon-bridged polyenes, and (d) silacyclohexanes.

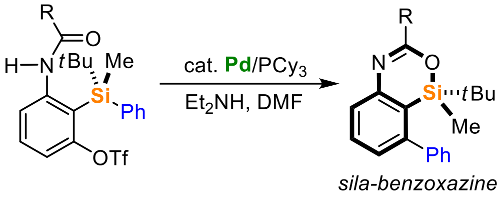
1.2 Overview of this dissertation

As described above, significant attention has been paid to developing synthetic methodologies for silacycles using transition-metal catalysts. However, several challenges still remain. For instance, the synthesis of silacycles containing multiple heteroatoms is currently limited, despite their carbon analogs being widely found as privileged structures in medicinal chemistry. This limitation likely arises from the presence of multiple reactive modes inherent to such sila-heterocycles and their potential precursors, requiring precise activation and bond formation strategies. Furthermore, while ring-expansion strategies have been extensively explored in silacycle synthesis, ring-contraction strategies remain underdeveloped, which could provide unique opportunities for editing silacycle scaffolds and deepen our understanding of the nature and activation of Si–C bonds.

To address these shortcomings, the author explored the use of intramolecular processes, which often enable unique transformations that are difficult to achieve through intermolecular processes. Specifically, the author considered that intramolecular Si–C bond activation coupled with intramolecular Si–X bond formation facilitated by transition-metal catalysts could serve as an effective strategy.

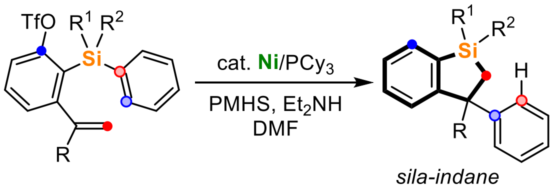
In this dissertation, the author designed substrates based on 2-silylaryl triflates, which not only serve as useful aryne precursors but also enable the precise synthesis of organosilicon compounds. By carefully constraining the relative distance and orientation between the metal center and active site within a molecule, these substrates promote selective reactions at desired positions. Using this molecular design, the author successfully developed a palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, representing a novel *N*,*O*-containing six-membered silacycles, and a nickel-catalyzed synthesis of 3,3-disubstituted 1-silaindanes via a six-to-five silacycle contraction mediated by 1,4-nickel migration.

Chapter 2 describes the synthesis of novel 4-sila-4*H*-benzo[*d*][1,3]oxazine derivatives from 3-amido-2-(arylsilyl)aryl triflates under a Pd/PCy3 complex as the catalyst. Mechanistic investigations revealed the intramolecular nature of the transmetalation with inversion of stereochemistry at the silicon center. Additionally, an asymmetric variant of this reaction was achieved by using a Josiphos-type chiral ligand. (Scheme 26).



Scheme 26. Palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazine derivatives described in Chapter 2.

Chapter 3 describes the synthesis of 3,3-disubstituted 1-silaindane derivatives from 3-alkenyl-2-(arylsilyl)aryl triflates using a Ni/PCy3 complex as the catalyst. A catalytic cycle involving a novel 1,5-nickel migration via activation of a C–H bond and a 1,4-nickel migration via activation of a Si–C bond is supported by mechanistic investigations and DFT calculations (Scheme 27).



Scheme 27. Nickel-catalyzed synthesis of 1-silaindane derivatives described in Chapter 3.

This dissertation expands the methodologies for constructing silacycles, advancing our understanding of Si–C bond activation and provides a foundation for future applications in the design of silicon-containing functional molecules. The work highlights the potential of transition-metal-catalyzed synthesis and transformations of silacycles through Si–C bond activation to address challenges in organosilicon chemistry.

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Chapter 2

Palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines by intramolecular Hiyama coupling

2.1 Introduction

Replacement of a carbon atom of functional organic molecules by a silicon atom (known as “silicon switch”) represents one of the effective ways of improving/modifying their biological activities or physical properties by taking advantage of the difference between carbon and silicon such as in the covalent radius, lipophilicity, and electronegativity, while keeping the similarity as congeners.[1] In particular, because nitrogen- and/or oxygen-containing heterocycles often appear as structural motifs for pharmaceuticals and optoelectronic materials, introduction of a silicon atom to these heterocycles would be highly attractive. Although such a strategy had been implemented for the past decades, available synthetic methods and accessible structures of silicon-containing heterocycles are currently still limited.[2,3]

Among the nitrogen- and oxygen-containing heterocycles, 4*H*-benzo[*d*][1,3]oxazines and their derivatives constitute a useful class[4] and are often found as core structures of pharmaceuticals such as etifoxine (anxiolytic and anticonvulsant drug),[5] efavirenz (antiretroviral medicine),[6] and tanaproget (nonsteroidal progestin)[7] (Figure 1a). However, their silicon-switched analogs, sila-4*H*-benzo[*d*][1,3]oxazines, have never been reported to date presumably due to the lack of their synthetic methods. To remedy this methodological deficiency, herein the author describes a palladium-catalyzed efficient synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines (Figure 1b) from 3-

amido-2-(arylsilyl)aryl triflates by the use of intramolecular Hiyama coupling, including its asymmetric variant via enantioselective transmetalation.[8]

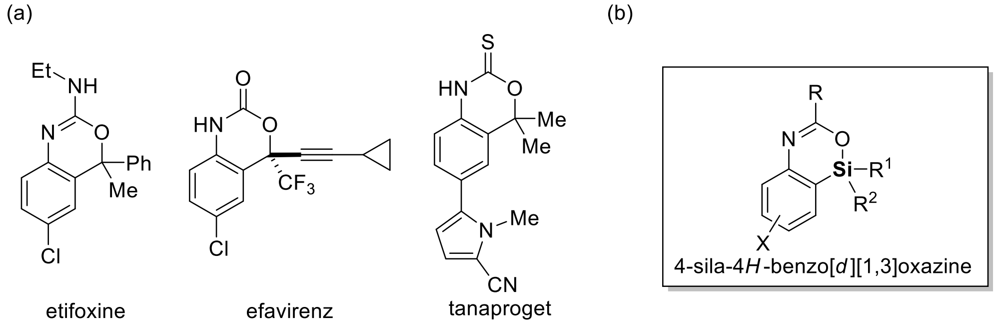
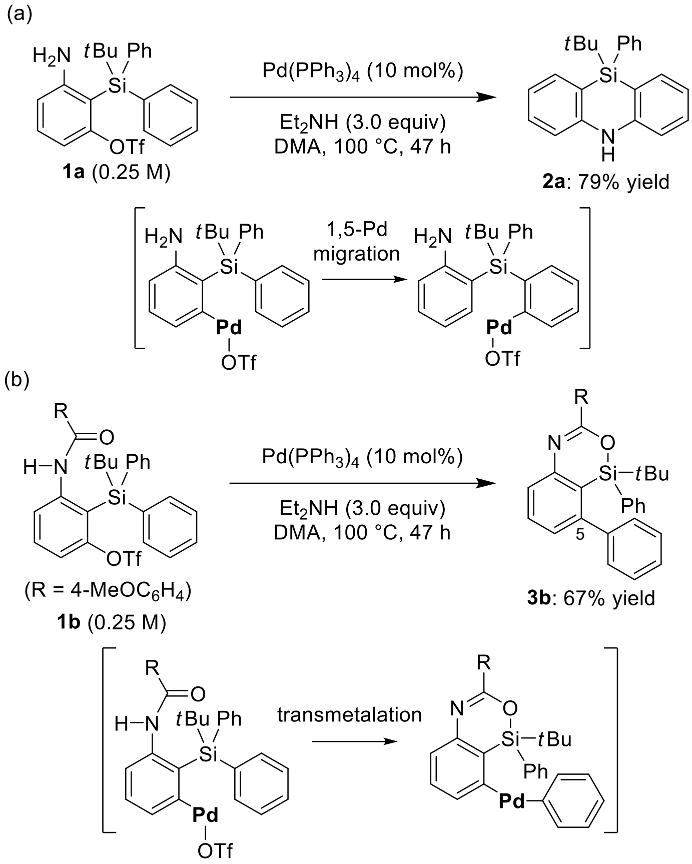


Figure 1. (a) Examples of biologically active 4*H*-benzo[*d*][1,3]oxazine derivatives. (b) The structure of 4-sila-4*H*-benzo[*d*][1,3]oxazine.

2.2 Results and discussion

2.2.1 Reaction development and scope

Recently, it was reported that the reaction of 3-amino-2-(arylsilyl)aryl triflates such as **1a** in the presence of a palladium catalyst selectively gave 5,10-dihydrophenazasilines such as **2a** via 1,5-palladium migration followed by an intramolecular C–N bond formation (Scheme 1a).[9] In stark contrast, the author newly found that, when *N*-acylated variant **1b** was employed as the substrate under the same reaction conditions, 5-phenylated 4-sila-4*H*-benzo[*d*][1,3]oxazine **3b** was selectively obtained without forming the corresponding 5,10-dihydrophenazasiline (Scheme 1b). This reaction presumably took place through intramolecular transmetalation of a phenyl group from silicon to palladium with the aid of the acyl group on nitrogen instead of 1,5-palladium migration.[10] The overall process here can therefore be described as an intramolecular Hiyama coupling reaction, but it is quite different from the typical Hiyama coupling, where a carbon–carbon bond formation between organic (pseudo)halides and organosilanes is the primary process, and the resulting silicon moiety after the reaction is considered as a low-value byproduct and usually treated as waste.[11] On the other hand, the present reaction of **1b** to give **3b** is a rare example in that the Hiyama coupling provides a silicon-containing heterocycle as the value-added main product.[12]

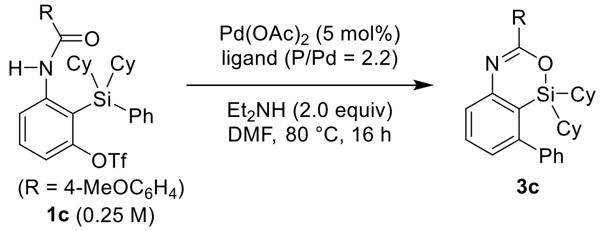


Scheme 1 (a) Synthesis of 5,10-dihydrophenazasiline from 3-amino-2-(arylsilyl)aryl triflate (previous work). (b) Initial finding for the synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazine from 3-amido-2-(arylsilyl)aryl triflate (this work).

Based on this finding, the author initiated the studies for the palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines by the intramolecular Hiyama coupling of 3-amido-2-(arylsilyl)aryl triflates. As a starting point, the author employed **1c** as the model substrate and examined the reaction conditions toward 4-sila-4*H*-

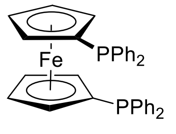
benzo[*d*][1,3]oxazine **3c** (Table 1). When the reaction was conducted in the presence of $Pd(OAc)_2$ (5 mol%) and Et_2NH (2.0 equiv) in DMF at 80 °C for 16 h, product **3c** was obtained in a moderate yield of 46% (entry 1). The use of PPh_3 (11 mol%) as the ligand for palladium did not change the reaction outcome (47% yield; entry 2). In contrast, a significantly higher yield of **3c** was achieved by using PCy_3 as the ligand (94% yield; entry 3), although the use of bulkier $P(tBu)_3$ resulted in the decrease of the yield (31% yield; entry 4). It was also found that the use of bisphosphine ligands such as dppf and binap could promote this reaction effectively as well (86–93% yield; entries 5 and 6).

Table 1. Palladium-catalyzed reaction of **1c** to give **3c**.

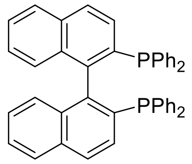


entry	ligand	conversion[a]	yield[b]
1	none	50	46
2	PPh_3	58	47
3[c]	PCy_3	100	94
4[c]	$P(tBu)_3$	31	31
5	dppf	100	93
6	binap	100	86

[a] Determined by ^1H NMR against internal standard ($MeNO_2$).
[b] Isolated yield. [c] $PR_3 \cdot HBF_4/Et_2NH$ was used.

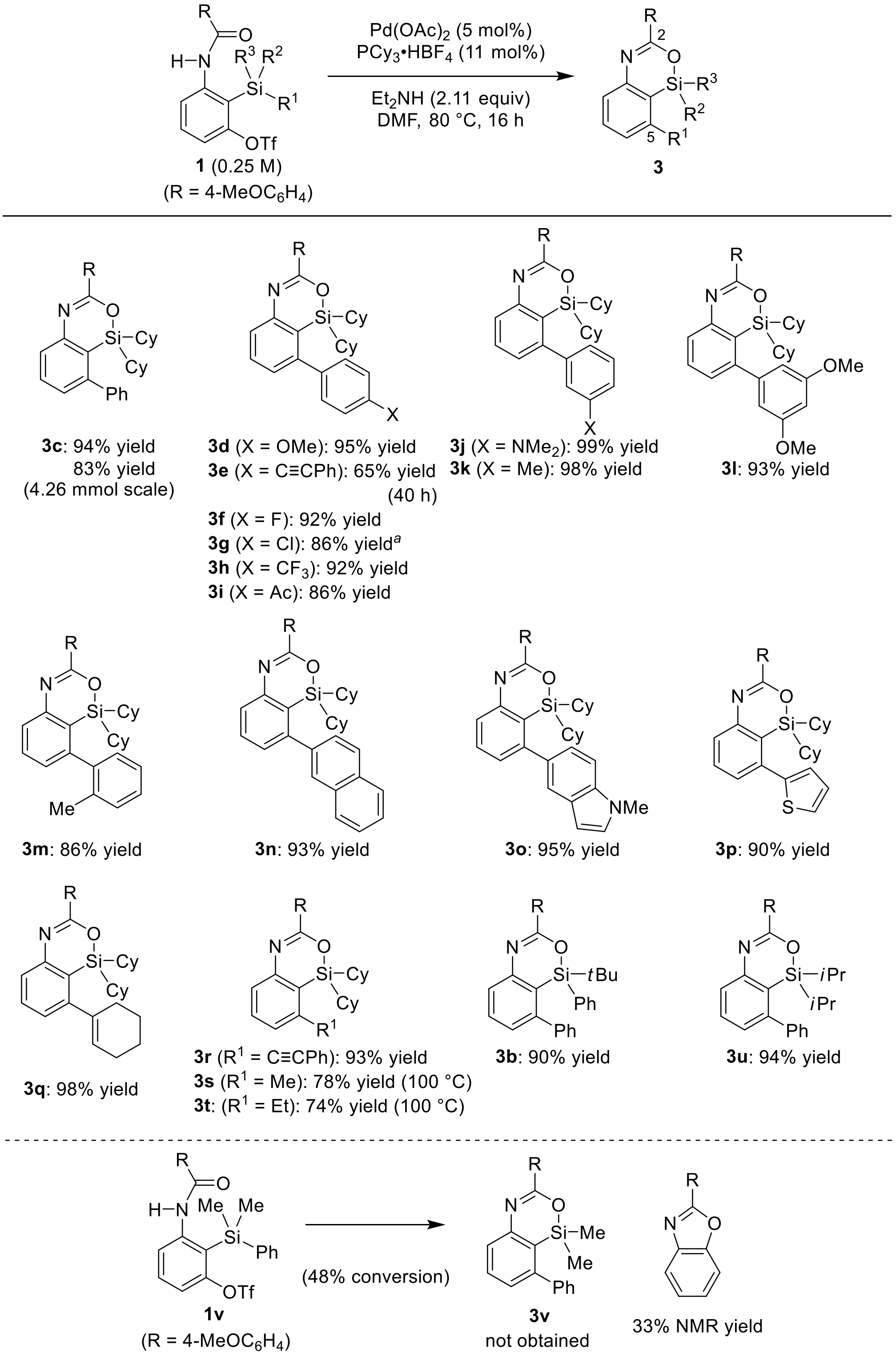


dppf

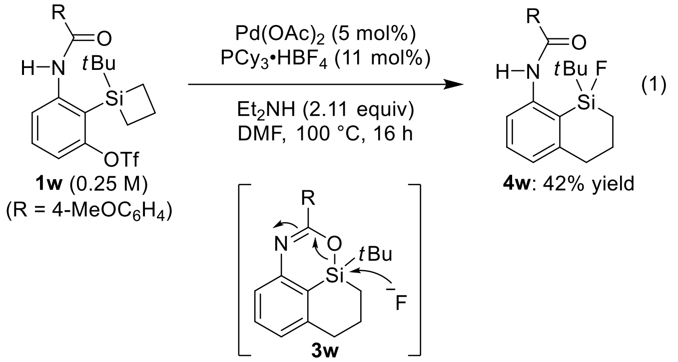


binap

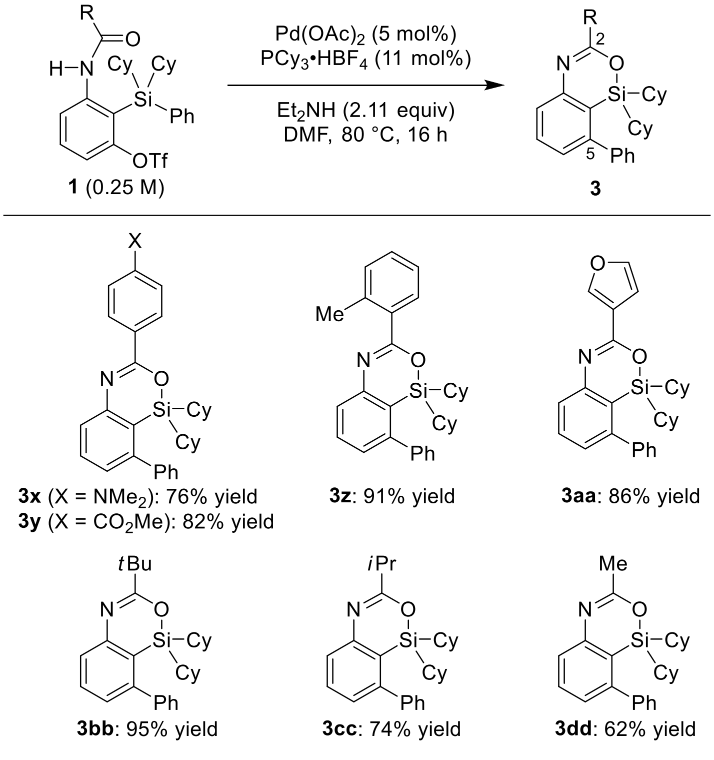
Under the conditions in Table 1, entry 3, various substituted aryl groups on the silicon atom could be transferred to the 5-position to give corresponding 4-sila-4*H*-benzo[*d*][1,3]oxazines **3d–m** in good to high yields irrespective of the electronic and steric nature of the aryl groups as summarized in Scheme 2 (65–99% yield). 2-Naphthyl, 5-indolyl, 2-thienyl, 1-cyclohexenyl, and phenylethynyl groups were also applicable as the migrating group from silicon to carbon, giving products **3n–r** in similarly high yields (90–98% yield). In addition to these (hetero)aryl, alkenyl, and alkynyl groups, methyl and ethyl groups were successfully transferred as well to give compounds **3s–t** in 74–78% yield by conducting the reaction at an elevated temperature (100 °C).[13] Regarding the 'spectator' substituents on the silicon atom, relatively bulky groups were found to be suitable such as *tert*-butyl and phenyl (**3b**) as well as diisopropyl (**3u**) other than dicyclohexyl. Substrate **1v** having sterically less hindered methyl groups on silicon gave 2-(4-methoxyphenyl)benzo[*d*]oxazole as the major product instead of corresponding **3v**, presumably through the formation of benzyne. On the other hand, substrate **1w** having a silacyclobutane as the silicon moiety underwent a ring-expansion reaction with concomitant cleavage of the initially formed silicon–oxygen bond by the fluoride, which is most likely derived from BF_4^- of the phosphine ligand salt, to give compound **4w** as the major product in 42% yield (eq 1).[12a, 14]



Scheme 2. Palladium-catalyzed synthesis of **3**: Scope of R^1–R^3 on silicon. 0.15 mmol of **1** was used unless otherwise noted. [a] 5.5 mol% of binap was used as the ligand instead of PCy$_3$•HBF$_4$/Et$_2$NH.

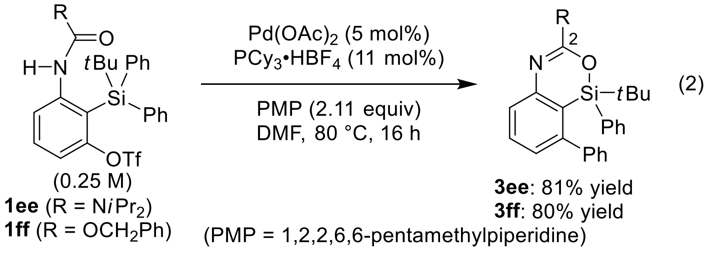


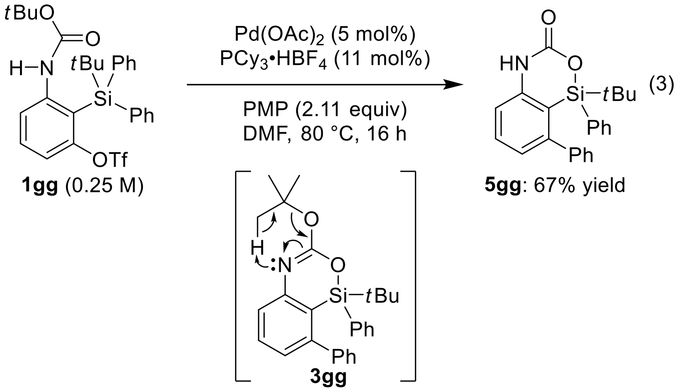
With regard to the substituent of the carbonyl group on nitrogen, various electronically and sterically different (hetero)aryl groups and alkyl groups could be tolerated, and the corresponding 2-substituted 4-sila-4*H*-benzo[*d*][1,3]oxazines **3x–dd** were obtained in 62–95% yield (Scheme 3).



Scheme 3. Palladium-catalyzed synthesis of **3**: Scope of R on carbonyl.

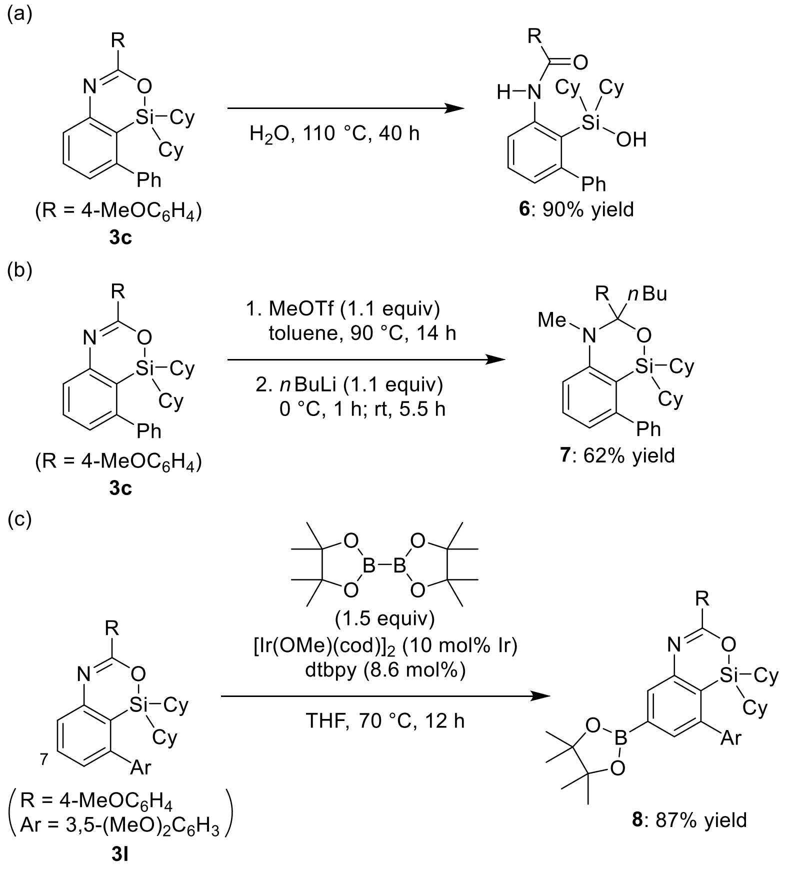
In addition, diisopropyl urea **1ee** and benzyl carbamate **1ff** could also be employed in the present catalysis to give 2-heteroatom-substituted 4-sila-4*H*-benzo[*d*][1,3]oxazines **3ee** and **3ff** under the slightly modified reaction conditions (eq 2). It is worth noting that *tert*-butyl carbamate **1gg** gave 4-sila-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **5gg** as the major product, presumably through intramolecular elimination of the *tert*-butyl group of initially formed 4-sila-4*H*-benzo[*d*][1,3]oxazine **3gg** under the reaction conditions (eq 3).





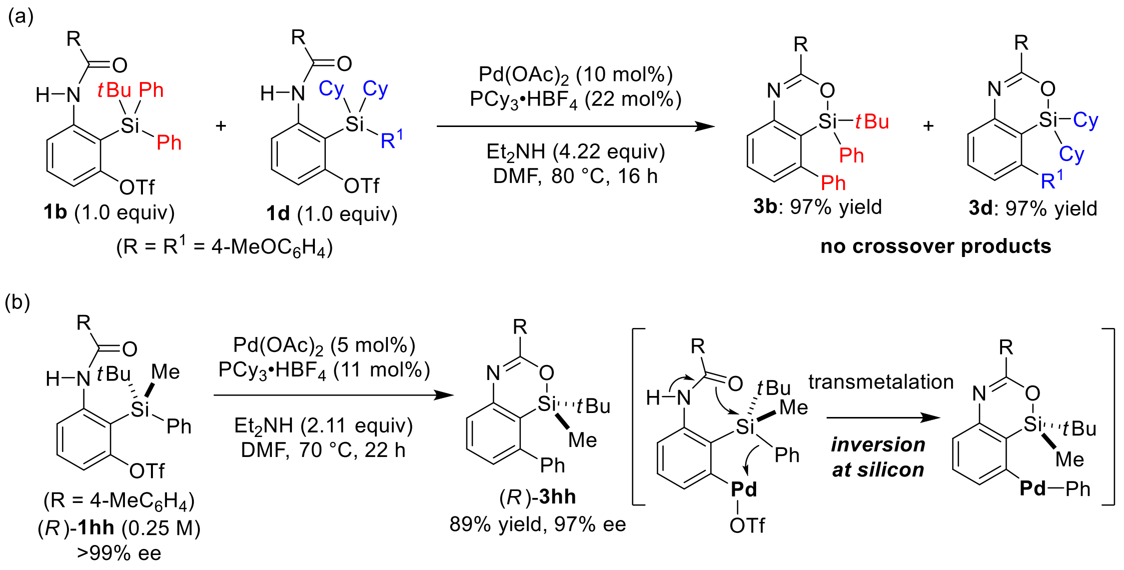
2.2.2 Diversification and mechanistic investigation

The obtained 4-sila-4*H*-benzo[*d*][1,3]oxazines **3** were found to be reasonably stable against H_2O under neutral conditions, and complete hydrolytic ring-opening of **3c** required a prolonged heating in H_2O at 110 °C for 40 h, giving corresponding silanol **6** in 90% yield (Scheme 4a). In addition, in analogy to the derivatization of 4*H*-benzo[*d*][1,3]oxazines,[15] the C–N double bond of **3c** could be dialkylated by sequential treatment with methyl triflate and *n*-butyllithium to give compound **7** in 62% yield with retaining the silacyclic structure (Scheme 4b). Furthermore, selective C–H borylation at the least hindered 7-position of **3l** was achieved under iridium catalysis to give compound **8** in 87% yield (Scheme 4c).[16]



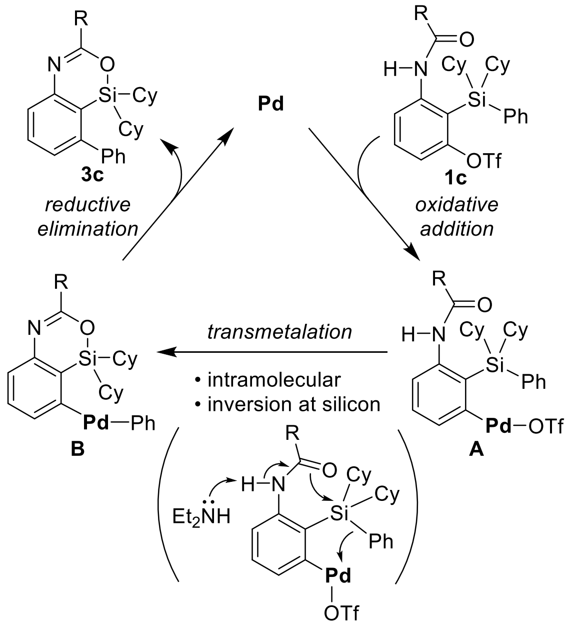
Scheme 4. (a) Hydrolysis, (b) dialkylation, and (c) C–H borylation of 4-sila-4*H*-benzo[*d*][1,3]oxazines **3**.

To gain insights into the reaction mechanism of the present catalysis, the author conducted a control experiment. When the 1:1 mixture of substrates **1b** and **1d** was subjected to the present reaction conditions, products **3b** and **3d** were obtained in nearly quantitative yields without forming any crossover products (Scheme 5a). This result indicates that the transmetalation of an aryl group from silicon to palladium takes place intramolecularly once the arylpalladium species is generated by oxidative addition of an aryl triflate to the palladium catalyst.[17] The author also prepared silicon-stereogenic enantiopure substrate (*R*)-**1hh**[14] and conducted the present reaction to probe the stereochemical outcome at the silicon atom (Scheme 5b). As a result, 4-sila-4*H*-benzo[*d*][1,3]oxazine **3hh** was obtained in 89% yield with 97% ee (*R*),[14] confirming that the transmetalation of the phenyl group from silicon to palladium takes place with inversion of configuration at the silicon stereocenter in a stereospecific manner. This represents the first example of the stereochemical investigation at silicon during transmetalation in the Hiyama coupling reaction as far as the author is aware,[18,19] although the present result may not be directly generalized due to its intramolecular nature.



Scheme 5. Mechanistic insights of the present catalysis. (a) A crossover experiment and (b) the stereochemical investigation at silicon.

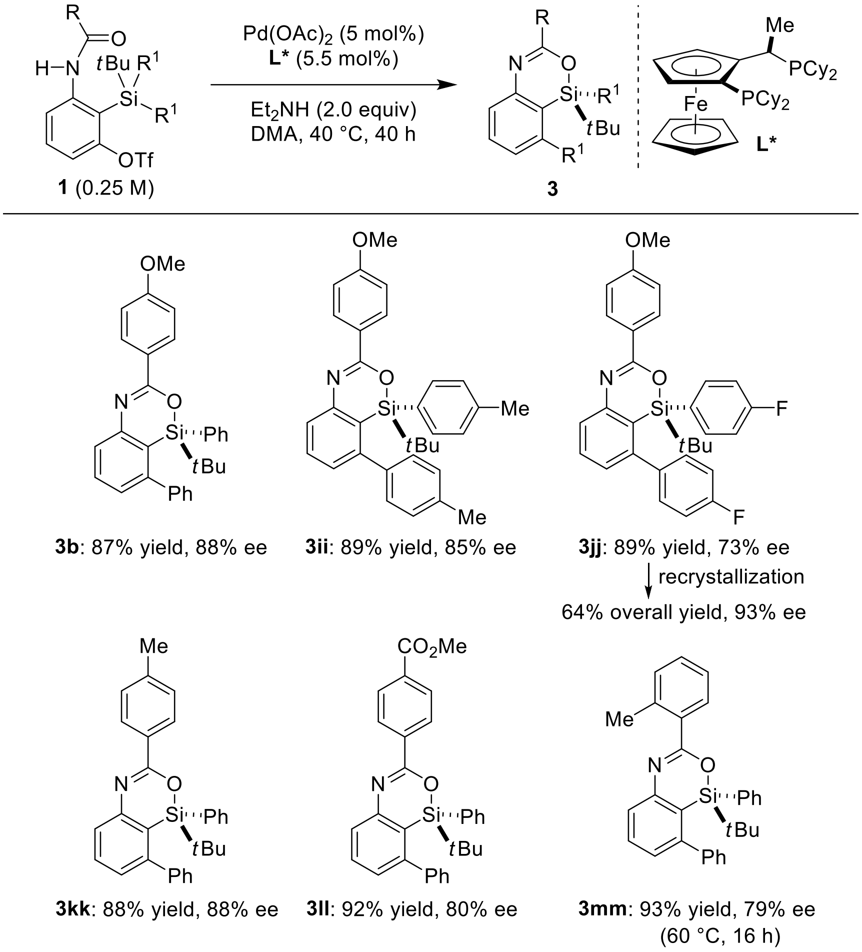
Based on the above consideration, a proposed catalytic cycle for the synthesis of **3c** from **1c** in the present catalysis is shown in Scheme 6. Oxidative addition of aryl triflate of **1c** to palladium(0) gives arylpalladium(II) species **A**. This then undergoes intramolecular transmetalation via inversion at silicon to give diarylpalladium(II) species **B**. Subsequent carbon–carbon bond-forming reductive elimination gives 4-sila-4*H*-benzo[*d*][1,3]oxazine **3c** along with regeneration of palladium(0).



Scheme 6. A proposed catalytic cycle for the palladium-catalyzed synthesis of **3c** from **1c**.

2.2.3 Development of an enantioselective variant and scope

The author found that the present catalysis could also be applied to enantioselective synthesis of silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines by using prochiral substrates in the presence of an appropriate chiral ligand.[20] In particular, Josiphos-type ligand **L*** was found to be promising in inducing relatively high enantioselectivity. Thus, the reaction of **1b** having two phenyl groups on the silicon atom led to the formation of compound **3b** in 87% yield with 88% ee (*R*) by selective transmetalation of one phenyl group over the other in the presence of a Pd/**L*** catalyst (Scheme 7).[14] Other aryl groups could also be accommodated on the silicon atom for this desymmetrization with moderate to good efficiency (**3ii** and **3jj**). Electronically or sterically different benzoyl groups on nitrogen were tolerated as well to give corresponding silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines **3kk–mm** with up to 88% ee. Although further improvement on the enantioselectivity is desirable, the result obtained here is a rare example of asymmetric catalysis involving an enantioselective transmetalation to give silicon-stereogenic compounds.[8]



Scheme 7. Palladium-catalyzed asymmetric synthesis of silicon-stereogenic **3** via enantioselective transmetalation.

2.3 Conclusion

The author developed a palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, silicon-switched analogs of biologically relevant 4*H*-benzo[*d*][1,3]oxazines, by the intramolecular Hiyama coupling of 3-amido-2-(arylsilyl)aryl triflates. The present reaction represents an unusual way of utilizing the Hiyama coupling toward the synthesis of functional organosilanes as the main products and it proceeds through intramolecular transmetalation with inversion of the stereochemistry at the silicon center. An asymmetric variant of this process was also demonstrated by employing prochiral substrates in the presence of a Josiphos-type chiral ligand to give silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines with relatively high enantioselectivity. The results obtained here will open the door for future expansion toward the synthesis of various functional organosilicon compounds.

2.4 Experimental section

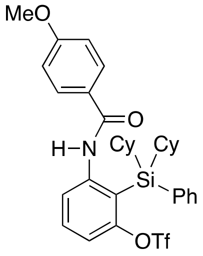
General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 spectrometer. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200 system with graphite-monochromated Mo-Kα (0.71075 Å) radiation. Preparative GPC was performed with JAI LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent.

Et_3N (Wako Chemicals), *i*Pr_2NH (Wako Chemicals), Et_2NH (Wako Chemicals), and 1,2,2,6,6-pentamethylpiperidine (Wako Chemicals) were distilled over KOH under vacuum. THF (Kanto Chemical; dehydrated), 1,2-dichloroethane (Kanto Chemical; dehydrated), CH_2Cl_2 (Kanto Chemical; dehydrated), DMA (Wako Chemicals; dehydrated), DMF (Wako Chemicals; dehydrated), and toluene (Kanto Chemical; dehydrated) were degassed by purging nitrogen. Bromobenzene (Wako Chemicals), 4-methoxybenzoyl chloride (TCI), 4-methylbenzoyl chloride (TCI), bis(trichloromethyl) carbonate (TCI), benzyl alcohol (Nacalai Tesque), *tert*-butyl alcohol (Wako Chemicals), methyl trifluoromethanesulfonate (Wako Chemicals), *N*-phenylbis(trifluoromethanesulfonimide) (Kanto Chemical), imidazole (Nacalai Tesque), dicyclohexyldichlorosilane (Gelest), *tert*-butyldichloro(phenyl)silane (TCI), bis(pinacolato)diboron (Combi-Blocks), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (TCI), PPh_3 (Wako Chemicals), PCy_3•HBF_4 (TCI), P(*t*Bu)$_3$•HBF_4 (TCI), dppf (Wako Chemicals), binap (Wako Chemicals), **L*** (Aldrich), MeLi (Kanto Chemical; 1.37 M solution in cyclopentyl methyl ether), *n*BuLi (Kanto Chemical; 1.57 M solution in hexane), *t*BuLi (Kanto Chemical; 1.60 M solution in pentane), NaH (Kishida Chemical; 60 wt% in mineral oil), Na_2SO_4 (Wako Chemicals), $MgSO_4$ (Wako Chemicals), $Pd(OAc)_2$ (Wako Chemicals), and $[Ir(OMe)(cod)]_2$ (TCI) were used as received. 3-Amino-2-bromophenol,[21] 3-amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate,[22] and $Pd(PPh_3)_4$[23] were synthesized following the literature procedures.

Representative procedures for substrates:

2-(Dicyclohexyl(phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1c)



*t*BuLi (18.9 mL, 30.2 mmol; 1.60 M solution in pentane) was added dropwise over 10 min to a solution of bromobenzene (1.60 mL, 15.1 mmol) in THF (30 mL) at –78 °C and the mixture was stirred for 1.5 h at –78 °C. Dicyclohexyldichlorosilane (3.46 mL, 14.4 mmol) was added to it and the mixture was stirred for 2 h at room temperature. 3-Amino-2-bromophenol (2.26 g, 12.0 mmol) and imidazole (2.04 g, 30.0 mmol) were then added it and the resulting mixture was stirred for 1.5 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 hexane/CH_2Cl_2 = 2/1 to afford 2-bromo-3-(dicyclohexyl(phenyl)silyloxy)aniline as a colorless oil (5.35 g, 11.7 mmol; 98% yield).

^{1}H NMR ($CDCl_3$): δ 7.68-7.58 (m, 2H), 7.45-7.32 (m, 3H), 6.84 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 6.37 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.21 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.13 (bs, 2H), 2.01-1.85 (m, 2H), 1.84-1.58 (m, 8H), 1.39-1.08 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.6, 145.8, 134.8, 134.3, 129.6. 127.8, 109.3, 108.3, 102.6, 28.23, 28.18, 27.4, 27.2, 26.9, 25.3.

*t*BuLi (22.7 mL, 36.3 mmol; 1.60 M solution in pentane) was added dropwise over 10 min to a solution of 2-bromo-3-(dicyclohexyl(phenyl)silyloxy)aniline (5.35 g, 11.7 mmol) in THF (59 mL) at –78 °C, and the mixture was stirred for 30 min at −78 °C and for 40 min at room temperature. The reaction was quenched with H_2O at 0 °C (under nitrogen) 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 resulting solid was washed with hexane to afford 3-amino-2-(dicyclohexyl(phenyl)silyl)phenol as a white solid (3.51 g, 9.24 mmol; 79% yield).

^{1}H NMR ($CDCl_3$): δ 7.67-7.54 (m, 2H), 7.46-7.33 (m, 3H), 7.03 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.15 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.12 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.81 (s, 1H), 3.65 (bs, 2H), 1.97-1.81 (m, 2H), 1.80-1.46 (m, 10H), 1.35-1.01 (m, 8H), 0.99-0.80 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.0, 154.8, 135.8, 134.4, 131.7, 129.6, 128.2, 108.9, 105.3, 102.0, 28.5, 28.3, 27.9, 27.5, 27.0, 23.8.

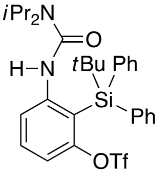
NaH (739 mg, 18.5 mmol; 60 wt% in mineral oil) was added to a solution of 3-amino-2-(dicyclohexyl(phenyl)silyl)phenol (3.51 g, 9.24 mmol) in THF (46 mL) at 0 °C, and the mixture was stirred for 10 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (3.96 g, 11.1 mmol) was added to it and the mixture was stirred 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/EtOAc = 20/1 → 5/1 and then with hexane/CH_2Cl_2 = 10/1 → 3/1 to afford 3-amino-2-(dicyclohexyl(phenyl)silyl)phenyl trifluoromethanesulfonate as a white solid (3.86 g, 7.54 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.58-7.48 (m, 2H), 7.46-7.33 (m, 3H), 7.20 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 6.77 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.45 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 3.76 (bs, 2H), 1.95-1.52 (m, 12H), 1.40-1.20 (m, 4H), 1.20-0.99 (m, 4H), 0.99-0.80 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.2, 155.3, 135.6, 133.0, 131.9, 129.8, 128.2, 118.8 (q, $^1J_{CF}$ = 321 Hz), 115.0, 107.6 (q, $^5J_{CF}$ = 2.6 Hz), 107.1, 28.2, 28.03, 27.96, 27.5, 26.9, 23.1.

Et_3N (258 μL, 1.85 mmol) and 4-methoxybenzoyl chloride (250 μL, 1.85 mmol) were added to a solution of 3-amino-2-(dicyclohexyl(phenyl)silyl)phenyl trifluoromethanesulfonate (902 mg, 1.76 mmol) in 1,2-dichloroethane (3.5 mL) at room temperature, and the mixture was stirred for 17 h at 60 °C. The reaction was quenched with saturated $NaHCO_3$aq 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/EtOAc = 5/1 to afford compound **1c** as a white solid (826 mg, 1.28 mmol; 88% yield).

^{1}H NMR ($CDCl_3$): δ 7.97 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.93 (s, 1H), 7.57-7.45 (m, 6H), 7.28-7.23 (m, 1H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.63 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.82 (s, 3H), 1.89-1.80 (m, 2H), 1.72-1.52 (m, 10H), 1.35-1.16 (m, 4H), 1.10-0.96 (m, 4H), 0.85-0.73 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.0, 162.3, 157.0, 145.6, 135.6, 132.8, 131.8, 130.4, 129.2, 128.6, 126.2, 124.1, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.2, 115.0 (q, $^5J_{CF}$ = 2.9 Hz), 113.6, 55.4, 28.0, 27.7, 27.4, 27.2, 26.6, 22.6. HRMS (FAB) calcd for $C_{33}H_{39}F_3NO_5SSi$ (M+H$^+$) 646.2265, found 646.2271.

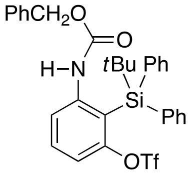
2-(*tert*-Butyldiphenylsilyl)-3-(3,3-diisopropylureido)phenyl trifluoromethanesulfonate (1ee)



3-Amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (528 mg, 1.10 mmol) was added dropwise over 2.5 h to a solution of bis(trichloromethyl) carbonate (163 mg, 0.550 mmol) and Et_3N (15.3 μL, 0.110 mmol) in 1,2-dichloroethane (3.0 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and for 4 h at 85 °C. The volatiles were removed under vacuum and the residue was dissolved in 1,2-dichloroethane (5.5 mL). *i*Pr_2NH (233 μL, 1.65 mmol) was added to the solution and the mixture was stirred for 18 h at 85 °C, and this was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 → 4/1 to afford compound **1dd** as a yellow solid (415 mg, 0.680 mmol; 62% yield).

^1H NMR ($CDCl_3$): δ 7.68-7.62 (m, 5H), 7.44 (t, $^3J_{HH} = 8.4$ Hz, 1H), 7.42-7.34 (m, 6H), 7.10 (d, $^3J_{HH} = 8.5$ Hz, 1H), 6.39 (s, 1H), 2.84 (sept, $^3J_{HH} = 6.6$ Hz, 2H), 1.25 (s, 9H), 0.99 (d, $^3J_{HH} = 6.5$ Hz, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.5, 153.5, 147.5, 135.9, 134.9, 131.3, 129.8, 128.5, 124.2, 118.5 (q, $^1J_{CF} = 322$ Hz), 117.3, 114.1 (q, $^5J_{CF} = 1.9$ Hz), 46.5, 29.6, 21.2, 20.3. HRMS (FAB) calcd for $C_{30}H_{38}F_3N_2O_4SSi$ (M+H$^+$) 607.2268, found 607.2275.

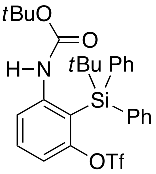
3-(Benzyloxycarbonylamino)-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (1ff)



3-Amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (528 mg, 1.10 mmol) was added dropwise over 2.5 h to a solution of bis(trichloromethyl) carbonate (163 mg, 0.550 mmol) and Et_3N (15.3 μL, 0.110 mmol) in 1,2-dichloroethane (3.0 mL) at 0 °C . The mixture was stirred for 2.5 h at room temperature and for 4.5 h at 85 °C. The volatiles were removed under vacuum and the residue was dissolved in 1,2-dichloroethane (5.5 mL). Et_3N (30.7 μL, 0.220 mmol) and benzyl alcohol (140 μL, 1.32 mmol) were added to the solution and the mixture was stirred for 17 h at 85 °C, and this was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 20/1 → 10/1 to afford compound **1ee** as a yellow viscous oil (576 mg, 0.940 mmol; 85% yield).

^{1}H NMR (CDCl$_3$): δ 7.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.68-7.62 (m, 4H), 7.50 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.40-7.29 (m, 9H), 7.23-7.16 (m, 3H), 6.83 (s, 1H), 4.90 (s, 2H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 156.4, 153.3, 145.8, 136.0, 135.6, 134.4, 132.3, 130.0, 128.7, 128.5, 128.3, 128.2, 121.3, 118.4 (q, $^1J_{CF}$ = 321 Hz), 117.0, 114.5 (q, $^5J_{CF}$ = 2.9 Hz), 66.8, 29.5, 20.1. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_5SSi$ (M+H$^+$) 614.1639, found 614.1651.

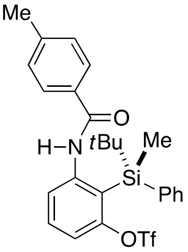
3-(*tert*-Butoxycarbonylamino)-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (1gg)



3-Amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (528 mg, 1.10 mmol) was added dropwise over 2.5 h to a solution of bis(trichloromethyl) carbonate (163 mg, 0.550 mmol) and Et$_3$N (15.3 μL, 0.110 mmol) in 1,2-dichloroethane (3.0 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and for 4 h at 85 °C. The volatiles were removed under vacuum and the residue was dissolved in *tert*-butyl alcohol (3.00 g, 40.5 mmol). The solution was stirred for 18 h at 85 °C and this was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 20/1 to afford compound **1ff** as a white solid (320 mg, 0.551 mmol; 50% yield).

^{1}H NMR (CDCl$_3$): δ 7.90 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.71-7.64 (m, 4H), 7.46 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 7.44-7.34 (m, 6H), 7.13 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.64 (s, 1H), 1.31 (s, 9H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 156.5, 152.5, 146.4, 135.7, 134.5, 132.1, 130.0, 128.6, 121.0, 118.4 (q, ${}^{1}J_{CF}$ = 321 Hz), 116.3, 114.0 (q, ${}^{5}J_{CF}$ = 2.6 Hz), 80.4, 29.5, 28.2, 20.2. HRMS (FAB) calcd for $C_{28}H_{32}F_3NO_5SSi$ (M^+) 579.1717, found 579.1718.

(*R*)-2-(*tert*-Butyl(methyl)(phenyl)silyl)-3-(4-methylbenzamido)phenyl trifluoromethanesulfonate (1hh)



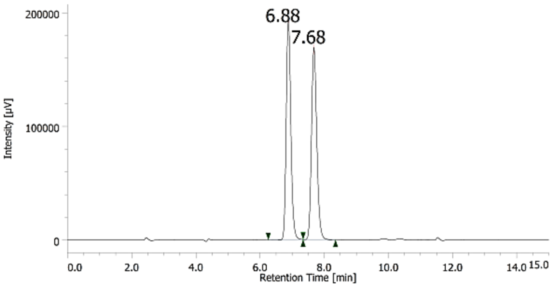
MeLi (6.26 mL, 8.57 mmol; 1.37 M solution in cyclopentyl methyl ether) was added dropwise over 15 min to a solution of *tert*-butyldichloro(phenyl)silane (1.80 mL, 8.57 mmol) in THF (34 mL) at –78 °C, and the mixture was stirred for 1.5 h at room temperature. 3-Amino-2-bromophenol (1.46 g, 7.79 mmol) and imidazole (1.35 g, 19.5 mmol) were added to it and the mixture was stirred for 2.5 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 hexane/EtOAc = 5/1 to afford 2-bromo-3-(*tert*-butyl(methyl)(phenyl)silyloxy)aniline as a colorless oil (1.93 g, 5.31 mmol; 68% yield).

${}^{1}H$ NMR ($CDCl_3$): δ 7.63-7.57 (m, 2H), 7.44-7.33 (m, 3H), 6.78 (t, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 6.34 (dd, ${}^{3}J_{HH}$ = 8.2 Hz and ${}^{4}J_{HH}$ = 1.4 Hz, 1H), 6.06 (dd, ${}^{3}J_{HH}$ = 8.2 Hz and ${}^{4}J_{HH}$ = 1.4 Hz, 1H), 4.13 (bs, 2H), 1.05 (s, 9H), 0.53 (s, 3H). ${}^{13}C\{{}^{1}H\}$ NMR ($CDCl_3$): δ 153.3, 145.9, 134.8, 134.6, 129.9, 127.9, 127.8, 109.1, 108.4, 102.6, 25.9, 18.9, –6.4.

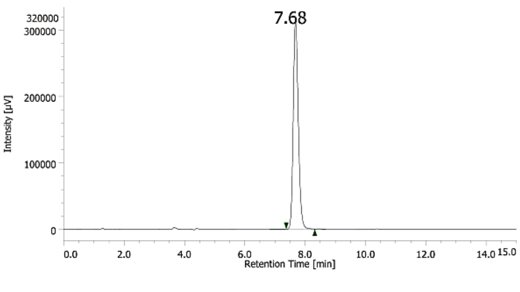
*t*BuLi (10.3 mL, 16.5 mmol; 1.60 M solution in pentane) was added dropwise over 10 min to a solution of 2-bromo-3-(*tert*-butyl(methyl)(phenyl)silyloxy)aniline (1.93 g, 5.31 mmol) in THF (27 mL) at –78 °C, and the mixture was stirred for 1 h at −78 °C and for 2 h at 0 °C. The reaction was quenched with H_2O at 0 °C (under nitrogen) 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/EtOAc = 5/1 to afford 3-amino-2-(*tert*-butyl(methyl)(phenyl)silyl)phenol (compound **S1**) as a colorless oil (1.34 g, 4.71 mmol; 89% yield). The enantiomers were separated by preparative HPLC using Daicel Chiralpak IBN-5 column (2 cm Ø x 25 cm) with hexane/2-propanol = 90/10, flow = 10.0 mL/min. Retention times: 9.8–10.3 min [(*S*)-**S1**], 10.7–11.3 min [(*R*)-**S1**]. The ee of (*R*)-**S1** was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.7 mL/min. Retention times: 6.9 min [(*S*)-enantiomer], 7.7 min [(*R*)-enantiomer]. >99% ee. $[\alpha]^{23}_{D}$ −87.9 (*c* 0.31, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.78-7.72 (m, 2H), 7.42-7.34 (m, 3H), 7.01 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.14-6.08 (m, 2H), 4.78 (s, 1H), 3.64 (bs, 2H), 1.20 (s, 9H), 0.62 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.6, 154.2, 138.9, 134.9, 131.8, 129.4, 128.6, 108.9, 105.5, 104.6, 27.9, 19.9, –0.6.

racemate



>99% ee (*R*)



Et_3N (104 µL, 0.750 mmol) and 4-methylbenzoyl chloride (89.8 µL, 0.680 mmol) were added to a solution of (*R*)-**S1** (194 mg, 0.680 mmol) in 1,2-dichloroethane (1.5 mL) at room temperature, and the mixture was stirred for 14 h at 60 °C. The reaction was quenched with saturated $NaHCO_3$aq 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/EtOAc = 3/1 to afford (*R*)-*N*-(2-(*tert*-butyl(methyl)(phenyl)silyl)-3-hydroxyphenyl)-4-methylbenzamide (compound (*R*)-**S2**) as a white solid (237 mg, 0.587 mmol; 86% yield). The absolute configuration was determined by X-ray crystallographic analysis after recrystallization from EtOAc/hexane. $[\alpha]^{25}_{D}$ +2.1 (*c* 0.54, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.77 (bs, 1H), 7.68-7.63 (m, 2H), 7.52-7.43 (m, 2H), 7.38 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.30 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 5.04 (s, 1H), 2.36 (s, 3H), 1.08 (s, 9H), 0.57 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8, 162.6, 143.9, 141.9, 138.8, 134.8, 131.6, 131.5, 129.6, 129.3, 129.1, 127.0, 117.4, 113.3, 112.2, 27.6, 21.6, 19.5, 0.0.

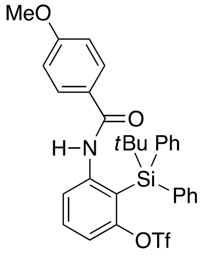
NaH (28.2 mg, 0.705 mmol; 60 wt% in mineral oil) was added to a solution of (*R*)-**S2** (237 mg, 0.587 mmol) in THF (3.0 mL) at 0 °C, and the mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (241 mg, 0.675 mmol) was added to it and the mixture was stirred for 2 h at 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 hexane/EtOAc = 8/1 to afford compound (*R*)-**1gg** as a yellow oil (267 mg, 0.499 mmol; 85% yield). $[\alpha]^{24}_{D}$ +25.3 (*c* 0.58, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.94-7.87 (m, 2H), 7.66-7.60 (m, 2H), 7.56-7.50 (m, 2H), 7.43 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.29 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.76 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 2.37 (s, 3H), 1.06 (s, 9H), 0.65 (s. 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.4, 156.9, 144.7, 142.4, 136.9, 134.4, 131.8, 130.9, 130.1, 129.7, 129.1, 127.0, 124.3, 119.6, 118.7 (q, $^1J_{CF}$ = 320 Hz), 115.4, 27.5, 21.5, 19.5, 0.2. HRMS (FAB) calcd for

$C_{26}H_{29}F_3NO_4SSi$ (M+H$^+$) 536.1533, found 536.1535.

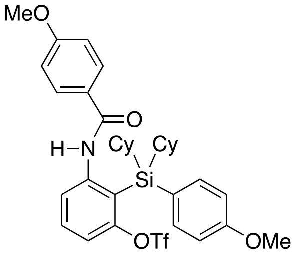
Analytical Data for Other Substrates:

2-(*tert*-Butyldiphenylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1b)



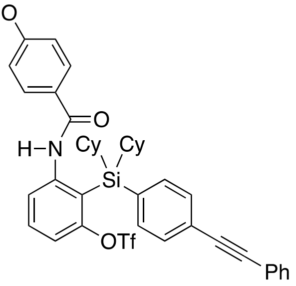
^{1}H NMR ($CDCl_3$): δ 8.04 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 8.01 (bs, 1H), 7.70-7.66 (m, 4H), 7.56 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.44-7.39 (m, 2H), 7.39-7.34 (m, 4H), 7.25 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 6.83-6.79 (m, 2H), 6.69-6.64 (m, 2H), 3.82 (s, 3H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.9, 162.5, 156.7, 145.4, 135.8, 134.5, 132.0, 130.0, 128.8, 126.1, 124.0, 118.7, 118.5 (q, $^1J_{CF}$ = 321 Hz), 115.6 (q, $^5J_{CF}$ = 1.9 Hz), 113.6, 55.4, 29.4, 20.4. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_5SSi$ (M+H$^+$) 614.1639, found 614.1643.

2-(Dicyclohexyl(4-methoxyphenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1d)



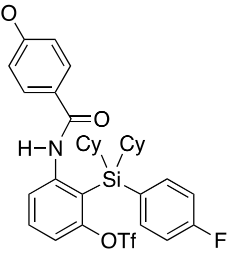
^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 8.00 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.52 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.42 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.23 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.98 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.80 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.65 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 1.88-1.77 (m, 2H), 1.74-1.50 (m, 10H), 1.36-1.15 (m, 4H), 1.11-0.96 (m, 4H), 0.86-0.71 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.1, 162.3, 161.6, 157.0, 145.8, 137.1, 131.8, 128.7, 126.5, 123.5, 122.9, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.9, 115.0, 114.8 (q, $^5J_{CF}$ = 2.6 Hz), 113.5, 55.4, 55.2, 28.0, 27.8, 27.4, 27.3, 26.6, 22.9. HRMS (FAB) calcd for $C_{34}H_{41}F_3NO_6SSi$ ($M+H^+$) 676.2370, found 676.2367.

2-(Dicyclohexyl(4-(phenylethynyl)phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1e)



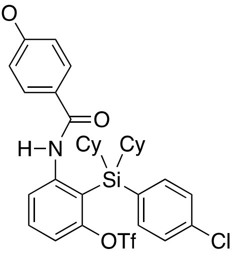
^1H NMR ($CDCl_3$): δ 7.95 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.79 (s, 1H), 7.62-7.53 (m, 5H), 7.48 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.43-7.35 (m, 3H), 7.26 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.82 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.74 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.77 (s, 3H), 1.91-1.79 (m, 2H), 1.75-1.55 (m, 10H), 1.36-1.16 (m, 4H), 1.13-0.98 (m, 4H), 0.88-0.74 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.2, 162.5, 157.0, 145.5, 135.4, 133.2, 132.02, 132.00, 131.8, 128.8, 128.6, 128.5, 126.3, 125.5, 124.0, 122.9, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.7, 115.0 (q, $^5J_{CF}$ = 2.9 Hz), 113.8, 91.6, 88.8, 55.4, 28.0, 27.7, 27.4, 27.2, 26.6, 22.7. HRMS (FAB) calcd for $C_{41}H_{43}F_3NO_5SSi$ ($M+H^+$) 746.2578, found 746.2579.

2-(Dicyclohexyl(4-fluorophenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1f)



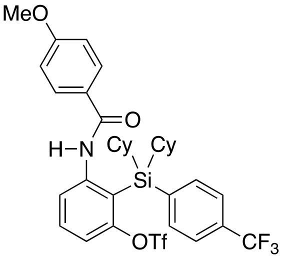
^{1}H NMR (CDCl$_3$): δ 7.95 (d, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 1H), 7.77 (s, 1H), 7.55 (t, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz, 1H), 7.46 (dd, $^{3}J_{\mathrm{HH}}$ = 8.5 Hz and $^{4}J_{\mathrm{HF}}$ = 6.1 Hz, 2H), 7.27-7.23 (m, 1H), 7.14 (t, ^{3}J = 8.8 Hz, 2H), 6.84 (d, $^{3}J_{\mathrm{HH}}$ = 8.8 Hz, 2H), 6.70 (d, $^{3}J_{\mathrm{HH}}$ = 9.0 Hz, 2H), 3.83 (s, 3H), 1.87-1.78 (m, 2H), 1.75-1.49 (m, 10H), 1.35-1.17 (m, 4H), 1.09-0.97 (m, 4H), 0.85-0.72 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.2, 164.5 (d, $^{1}J_{\mathrm{CF}}$ = 252 Hz), 162.5, 156.9, 145.5, 137.5 (d, $^{3}J_{\mathrm{CF}}$ = 6.7 Hz), 132.0, 128.4, 128.3 (d, $^{4}J_{\mathrm{CF}}$ = 3.8 Hz), 126.4, 124.0, 118.7 (q, $^{1}J_{\mathrm{CF}}$ = 320 Hz), 116.7, 116.4 (d, $^{2}J_{\mathrm{CF}}$ = 20.1 Hz), 115.1 (q, $^{5}J_{\mathrm{CF}}$ = 1.9 Hz), 113.7, 55.5, 28.0, 27.7, 27.4, 27.2, 26.6, 22.7. HRMS (FAB) calcd for $C_{33}H_{38}F_4NO_5SSi$ (M+H^{+}) 664.2171, found 664.2181.

2-((4-Chlorophenyl)dicyclohexylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1g)



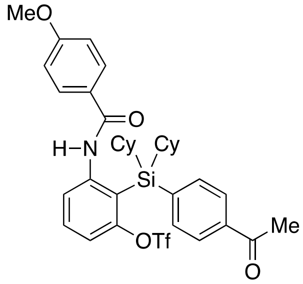
^{1}H NMR (CDCl$_3$): δ 7.93 (d, $^{3}J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 7.68 (s, 1H), 7.55 (t, $^{3}J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 7.45-7.37 (m, 4H), 7.25 (d, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 1H), 6.83 (d, $^{3}J_{\mathrm{HH}}$ = 9.2 Hz, 2H), 6.73 (d, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 3.85 (s, 3H), 1.89-1.78 (m, 2H), 1.75-1.53 (m, 10H), 1.36-1.15 (m, 4H), 1.12-0.97 (m, 4H), 0.86-0.71 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.2, 162.5, 156.9, 145.4, 136.9, 136.7, 132.1, 131.3, 129.4, 128.4, 126.3, 124.1, 118.6 (q, $^1J_{CF}$ = 320 Hz), 116.5, 115.1 (q, $^5J_{CF}$ = 2.6 Hz), 113.7, 55.5, 28.0, 27.7, 27.4, 27.2, 26.5, 22.7. HRMS (FAB) calcd for $C_{33}H_{38}ClF_3NO_5SSi$ (M+H$^+$) 680.1875, found 680.1883.

2-(Dicyclohexyl(4-(trifluoromethyl)phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1h)



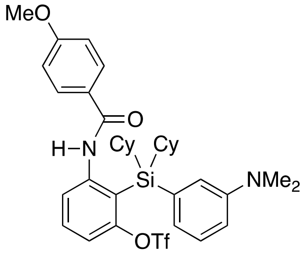
^1H NMR ($CDCl_3$): δ 7.89 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.64 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.62-7.53 (m, 3H), 7.45 (s, 1H), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.80 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.66 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.81 (s, 3H), 1.92-1.80 (m, 2H), 1.76-1.53 (m, 10H), 1.38-1.19 (m, 4H), 1.13-0.97 (m, 4H), 0.86-0.72 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.1, 162.6, 156.9, 145.3, 138.3, 135.6, 132.3, 132.1 (q, $^2J_{CF}$ = 31.6 Hz), 128.3, 126.1, 125.4 (q, $^3J_{CF}$ = 3.5 Hz), 124.6, 124.0 (q, $^1J_{CF}$ = 272 Hz), 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.7, 115.4 (q, $^5J_{CF}$ = 2.6 Hz), 113.7, 55.4, 28.0, 27.7, 27.5, 27.2, 26.5, 22.6. HRMS (FAB) calcd for $C_{34}H_{38}F_6NO_5SSi$ (M+H$^+$) 714.2139, found 714.2139.

2-((4-Acetylphenyl)dicyclohexylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1i)



^{1}H NMR (CDCl$_3$): δ 7.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.62-7.53 (m, 3H), 7.47 (s, 1H), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.81 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.59 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.80 (s, 3H), 2.58 (s, 3H), 1.92-1.79 (m, 2H), 1.76-1.54 (m, 10H), 1.38-1.19 (m, 4H), 1.14-0.97 (m, 4H), 0.89-0.72 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 197.8, 165.0, 162.4, 156.9, 145.3, 139.5, 138.1, 135.5, 132.1, 128.4, 128.1, 126.1, 124.3, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.5, 115.2 (q, $^5J_{CF}$ = 1.9 Hz), 113.6, 55.4, 27.9, 27.63, 27.55, 27.2, 26.6, 26.5, 22.7. HRMS (FAB) calcd for $C_{35}H_{41}F_3NO_6SSi$ (M+H$^+$) 688.2370, found 688.2379.

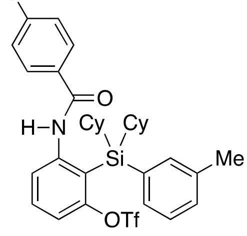
2-(Dicyclohexyl(3-dimethylaminophenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1j)



^{1}H NMR (CDCl$_3$): δ 8.19 (s, 1H), 7.94 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.52 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.24 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.89-6.81 (m, 2H), 6.81-6.75 (m, 3H), 6.64 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.82 (s, 3H), 2.91 (s, 6H), 1.88-1.79 (m, 2H), 1.75-1.50 (m, 10H), 1.37-0.99 (m, 8H), 0.91-0.76 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ

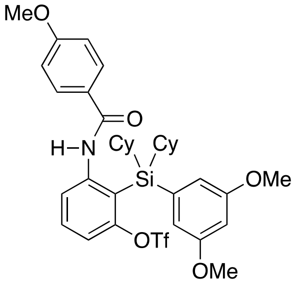
165.1, 162.2, 157.0, 150.7, 145.7, 132.9, 131.6, 130.0, 128.8, 126.3, 124.1, 123.0, 118.71 (q, $^1J_{\mathrm{CF}}$ = 320 Hz), 118.69, 117.8, 114.9 (q, $^5J_{\mathrm{CF}}$ = 1.9 Hz), 114.1, 113.5, 55.4, 40.5, 28.1, 27.8, 27.44, 27.36, 26.6, 22.9. HRMS (FAB) calcd for $C_{35}H_{44}F_3N_2O_5SSi$ (M+H$^+$) 689.2687, found 689.2694.

2-(Dicyclohexyl(3-tolyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1k)



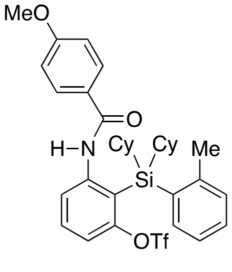
^{1}H NMR (CDCl$_3$): δ 7.98 (s, 1H), 7.95 (d, $^3J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 7.53 (t, $^3J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 7.40-7.22 (m, 5H), 6.71 (d, $^3J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 6.64 (d, $^3J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 2.36 (s, 3H), 1.90-1.78 (m, 2H), 1.74-1.50 (m, 10H), 1.37-1.14 (m, 4H), 1.12-0.97 (m, 4H), 0.86-0.71 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.0, 162.3, 157.0, 145.6, 138.7, 135.9, 132.6, 132.5, 131.7, 131.2, 129.1, 128.6, 126.2, 124.0, 118.7 (q, $^1J_{\mathrm{CF}}$ = 320 Hz), 117.3, 114.9 (q, $^5J_{\mathrm{CF}}$ = 2.9 Hz), 113.5, 55.4, 28.0, 27.7, 27.33, 27.26, 26.6, 22.6, 21.8. HRMS (FAB) calcd for $C_{34}H_{41}F_3NO_5SSi$ (M+H$^+$) 660.2421, found 660.2435.

2-(Dicyclohexyl(3,5-dimethoxyphenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1l)



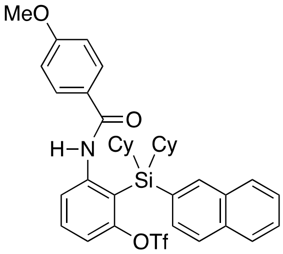
^{1}H NMR (CDCl$_3$): δ 7.920 (s, 1H), 7.916 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.53 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.25 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.91 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.57 (d, $^4J_{HH}$ = 2.3 Hz, 2H), 6.48 (t, $^4J_{HH}$ = 2.3 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 6H), 1.89-1.78 (m, 2H), 1.75-1.53 (m, 10H), 1.36-0.99 (m, 8H), 0.93-0.76 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.1, 162.3, 161.3, 156.8, 145.5, 134.8, 131.7, 128.5, 126.2, 124.2, 118.6 (q, $^1J_{CF}$ = 320 Hz), 117.2, 114.9 (q, $^5J_{CF}$ = 1.9 Hz), 113.4, 112.6, 101.6, 55.29, 55.26, 27.9, 27.7, 27.4, 27.3, 26.5, 22.7. HRMS (FAB) calcd for $C_{35}H_{43}F_3NO_7SSi$ (M+H$^+$) 706.2476, found 706.2482.

2-(Dicyclohexyl(2-tolyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1m)



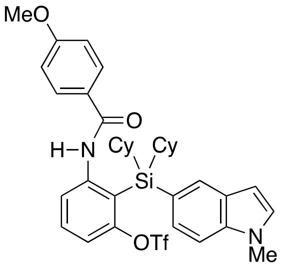
^{1}H NMR (CDCl$_3$): δ 8.18 (s, 1H), 8.05 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.52 (t, $^3J_{HH}$ = 8.5 Hz, 1H), 7.49-7.41 (m, 2H), 7.36-7.20 (m, 3H), 6.71 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.62 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.81 (s, 3H), 2.22 (s, 3H), 1.99-1.86 (m, 2H), 1.80-1.50 (m, 10H), 1.38-1.14 (m, 4H), 1.14-0.94 (m, 4H), 0.94-0.70 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.0, 162.3, 155.9, 145.7, 145.2, 136.6, 132.0, 131.6, 131.1, 130.5, 128.5, 126.1, 123.1, 118.7 (q, ${}^{1}J_{\mathrm{CF}}$ = 321 Hz), 118.4, 114.9 (q, ${}^{5}J_{\mathrm{CF}}$ = 2.9 Hz), 113.6, 55.4, 28.1, 27.8, 27.4, 26.5, 24.0, 23.8. HRMS (FAB) calcd for $C_{34}H_{41}F_{3}NO_{5}SSi$ (M+H^{+}) 660.2421, found 660.2425.

2-(Dicyclohexyl(2-naphthyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1n)



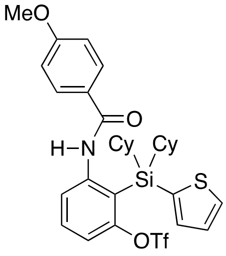
^{1}H NMR (CDCl$_3$): δ 8.01 (s, 1H), 7.98 (d, ${}^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 1H), 7.96-7.88 (m, 2H), 7.88-7.80 (m, 2H), 7.67-7.57 (m, 2H), 7.56 (t, ${}^{3}J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 7.52 (d, ${}^{3}J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 7.29 (d, ${}^{3}J_{\mathrm{HH}}$ = 8.2 Hz, 1H), 6.38 (d, ${}^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 5.97 (d, ${}^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 3.60 (s, 3H), 1.99-1.86 (m, 2H), 1.86-1.52 (m, 10H), 1.40-0.94 (m, 8H), 0.91-0.76 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.1, 162.0, 157.0, 145.7, 136.6, 134.2, 133.4, 131.9, 131.1, 130.1, 128.72, 128.68, 128.1, 128.0, 127.4, 126.7, 125.9, 123.7, 118.7 (q, ${}^{1}J_{\mathrm{CF}}$ = 320 Hz), 116.8, 114.9 (q, ${}^{5}J_{\mathrm{CF}}$ = 2.6 Hz), 113.1, 55.1, 28.0, 27.8, 27.4, 26.5, 22.8. HRMS (FAB) calcd for $C_{37}H_{41}F_{3}NO_{5}SSi$ (M+H^{+}) 696.2421, found 696.2422.

2-(Dicyclohexyl(1-methyl-1*H*-5-indolyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1o)



^{1}H NMR (CDCl$_3$): δ 8.29 (s, 1H), 8.05 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.82 (s, 1H), 7.52 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 7.38 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.29 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.28-7.22 (m, 1H), 7.16 (d, $^3J_{HH}$ = 3.1 Hz, 1H), 6.57 (d, $^3J_{HH}$ = 3.1 Hz, 1H), 6.42 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.18 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 1.94-1.84 (m, 2H), 1.75-1.50 (m, 10H), 1.38-1.19 (m, 4H), 1.18-0.96 (m, 4H), 0.87-0.75 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.1, 161.9, 157.1, 146.0, 138.0, 131.6, 129.44, 129.36, 129.2, 128.5, 128.0, 126.2, 123.2, 120.4, 118.7 (q, $^1J_{CF}$ = 321 Hz), 117.3, 114.5 (q, $^5J_{CF}$ = 2.9 Hz), 113.0, 110.5, 102.0, 55.2, 32.9, 28.1, 27.8, 27.42, 27.39, 26.6, 23.0. HRMS (FAB) calcd for $C_{36}H_{41}F_3N_2O_5SSi$ (M$^+$) 698.2452, found 698.2438.

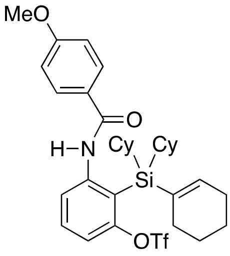
2-(Dicyclohexyl(2-thienyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1p)



^{1}H NMR (CDCl$_3$): δ 8.27 (s, 1H), 7.96 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.78 (d, $^3J_{HH}$ = 5.0 Hz, 1H), 7.53 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.40 (d, $^3J_{HH}$ = 3.6 Hz, 1H), 7.33 (dd, $^3J_{HH}$ = 5.0 and 3.6 Hz, 1H), 7.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.89 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.71 (d, $^3J_{HH}$ = 9.2

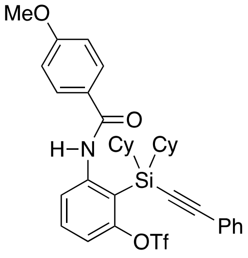
Hz, 2H), 3.84 (s, 3H), 1.87-1.77 (m, 2H), 1.75-1.49 (m, 10H), 1.35-0.99 (m, 8H), 0.90-0.74 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.2, 162.4, 156.3, 145.9, 137.6, 133.1, 132.0, 131.5, 129.5, 128.7, 126.4, 124.1, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.0, 114.9 (q, $^5J_{CF}$ = 2.2 Hz), 113.6, 55.5, 27.9, 27.70, 27.67, 27.3, 26.6, 23.9. HRMS (FAB) calcd for $C_{31}H_{37}F_3NO_5S_2Si$ (M+H$^+$) 652.1829, found 652.1839.

2-(1-Cyclohexenyldicyclohexylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1q)



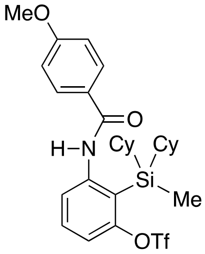
^1H NMR ($CDCl_3$): δ 8.84 (s, 1H), 8.09 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.73 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.48 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.16 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.26 (s, 1H), 3.88 (s, 3H), 2.12-1.96 (m, 4H), 1.79-1.56 (m, 10H), 1.56-1.36 (m, 6H), 1.33-1.00 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.8, 162.7, 156.6, 145.9, 142.8, 134.4, 131.5, 129.3, 127.4, 122.9, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.4, 114.8 (q, $^5J_{CF}$ = 2.9 Hz), 114.0, 55.6, 28.7, 28.24, 28.23, 28.0, 27.2, 26.9, 23.6, 22.3, 22.0. HRMS (FAB) calcd for $C_{33}H_{43}F_3NO_5SSi$ (M+H$^+$) 650.2578, found 650.2581.

2-(Dicyclohexyl(phenylethynyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1r)



^{1}H NMR (CDCl$_3$): δ 9.93 (s, 1H), 8.21 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.76 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.50 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.37 (tt, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.9 Hz, 1H), 7.30-7.24 (m, 2H), 7.23-7.19 (m, 2H), 7.17 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.55 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.67 (s, 3H), 1.91-1.81 (m, 2H), 1.77-1.56 (m, 8H), 1.46-1.14 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 166.4, 162.4, 155.6, 146.3, 132.4, 131.9, 129.5, 128.4, 127.2, 122.7, 121.9, 118.6 (q, $^1J_{CF}$ = 320 Hz), 115.5, 114.1 (q, $^5J_{CF}$ = 1.9 Hz), 113.8, 113.4, 88.5, 55.3, 28.3, 28.1, 27.9, 27.8, 26.7, 24.7. HRMS (FAB) calcd for $C_{35}H_{39}F_3NO_5SSi$ (M+H$^+$) 670.2265, found 670.2278.

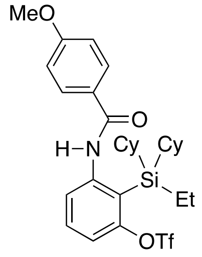
2-(Dicyclohexyl(methyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1s)



^{1}H NMR (CDCl$_3$): δ 7.87-7.84 (m, 2H), 7.82 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.47 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 7.20 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.02 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.90 (s, 3H), 1.80-1.61 (m, 8H), 1.51-1.43 (m, 2H), 1.24-1.01 (m, 12H), 0.39 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.4, 162.9, 155.9, 144.7, 131.3, 129.1, 126.7, 124.9, 122.4, 118.6 (q, $^1J_{CF}$ =

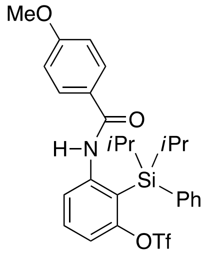
320 Hz), 116.5 (q, ${}^{5}J_{CF}$ = 1.9 Hz), 114.3, 55.6, 28.6, 28.3, 28.2, 28.1, 26.8, 25.4, −6.5. HRMS (FAB) calcd for $C_{28}H_{37}F_3NO_5SSi$ (M+H$^+$) 584.2108, found 584.2116.

2-(Dicyclohexyl(ethyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1t)



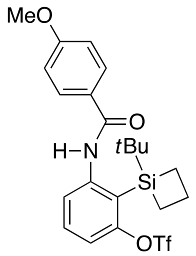
^{1}H NMR (CDCl$_3$): δ 7.97 (s, 1H), 7.92 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 1H), 7.82 (d, ${}^{3}J_{HH}$ = 8.7 Hz, 2H), 7.49 (t, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 7.19 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 7.01 (d, ${}^{3}J_{HH}$ = 9.2 Hz, 2H), 3.90 (s, 3H), 1.84-1.54 (m, 10H), 1.31-0.95 (m, 17H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.3, 162.9, 156.0, 145.0, 131.5, 129.0, 126.9, 124.4, 120.7, 118.6 (q, ${}^{1}J_{CF}$ = 320 Hz), 116.4 (q, ${}^{5}J_{CF}$ = 1.9 Hz), 114.3, 55.6, 28.9, 28.8, 28.3, 26.9, 26.0, 8.4, 3.0. HRMS (FAB) calcd for $C_{29}H_{39}F_3NO_5SSi$ (M+H$^+$) 598.2265, found 598.2266.

2-(Diisopropyl(phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1u)



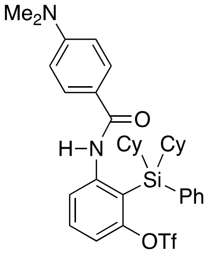
^{1}H NMR (CDCl$_3$): δ 8.01 (s, 1H), 7.97 (dd, ${}^{3}J_{HH}$ = 8.2 Hz and ${}^{4}J_{HH}$ = 0.9 Hz, 1H), 7.59-7.45 (m, 6H), 7.28 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 6.71 (d, ${}^{3}J_{HH}$ = 9.2 Hz, 2H), 6.64 (d, ${}^{3}J_{HH}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 1.81 (sept, ${}^{3}J_{HH}$ = 7.3 Hz, 2H), 1.03 (d, ${}^{3}J_{HH}$ = 7.4 Hz, 6H), 0.82 (d, $^3J_{HH}$ = 7.3 Hz, 6H). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 164.9, 162.4, 157.1, 145.6, 135.6, 132.3, 132.0, 130.5, 129.3, 128.7, 126.1, 124.2, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.7, 114.9 (q, $^5J_{CF}$ = 2.6 Hz), 113.6, 55.5, 17.7, 17.6, 11.2. HRMS (FAB) calcd for $C_{27}H_{31}F_3NO_5SSi$ (M+H$^+$) 566.1639, found 566.1627.

2-(1-(*tert*-Butyl)siletan-1-yl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1w)



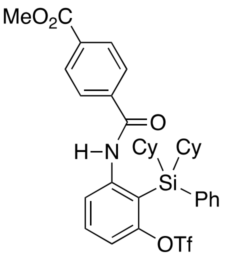
^1H NMR (CDCl$_3$): δ 8.16 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.97 (s, 1H), 7.76 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.52 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.20 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 6.98 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 2.50-2.35 (m, 1H), 2.21-2.04 (m, 1H), 1.62-1.40 (m, 4H), 1.03 (s, 9H). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 165.1, 162.9, 155.0, 144.7, 132.4, 128.9, 126.5, 122.3, 120.1, 118.5 (q, $^1J_{CF}$ = 320 Hz), 114.8 (q, $^5J_{CF}$ = 1.9 Hz), 114.3, 55.6, 26.3, 20.0, 19.3, 13.7, 13.2. HRMS (FAB) calcd for $C_{22}H_{27}F_3NO_5SSi$ (M+H$^+$) 502.1326, found 502.1330.

2-(Dicyclohexyl(phenyl)silyl)-3-(4-(dimethylamino)benzamido)phenyl trifluoromethanesulfonate (1x)



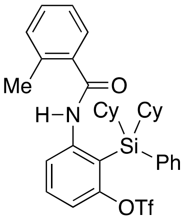
^1H NMR (CDCl$_3$): δ 7.97 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.86 (s, 1H), 7.60-7.45 (m, 6H), 7.22 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 6.62 (d, ${}^{3}J_{HH}$ = 9.2 Hz, 2H), 6.36 (d, ${}^{3}J_{HH}$ = 9.2 Hz, 2H), 2.99 (s, 6H), 1.90-1.79 (m, 2H), 1.74-1.50 (m, 10H), 1.37-1.14 (m, 4H), 1.12-0.95 (m, 4H), 0.88-0.73 (m, 2H). ${}^{13}C\{{}^{1}H\}$ NMR ($CDCl_3$): δ 165.4, 157.0, 152.5, 146.0, 135.6, 132.9, 131.7, 130.3, 129.2, 128.3, 124.1, 120.5, 118.7 (q, ${}^{1}J_{CF}$ = 321 Hz), 116.9, 114.6 (q, ${}^{5}J_{CF}$ = 2.9 Hz), 110.7, 40.1, 28.1, 27.8, 27.33, 27.27, 26.6, 22.6. HRMS (FAB) calcd for $C_{34}H_{42}F_3N_2O_4SSi$ (M+H$^+$) 659.2581, found 659.2589.

Methyl 4-((2-(dicyclohexyl(phenyl)silyl)-3-(trifluoromethylsulfonyloxy)phenyl)carbamoyl)benzoate (1y)



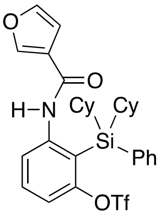
${}^{1}H$ NMR ($CDCl_3$): δ 8.09 (s, 1H), 7.99 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 7.82 (d, ${}^{3}J_{HH}$ = 8.7 Hz, 2H), 7.61-7.53 (m, 2H), 7.51-7.44 (m, 4H), 7.29 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 1H), 6.82 (d, ${}^{3}J_{HH}$ = 8.7 Hz, 2H), 3.94 (s, 3H), 1.90-1.78 (m, 2H), 1.74-1.48 (m, 10H), 1.37-1.13 (m, 4H), 1.10-0.96 (m, 4H), 0.85-0.70 (m, 2H). ${}^{13}C\{{}^{1}H\}$ NMR ($CDCl_3$): δ 166.3, 164.5, 156.9, 144.9, 137.8, 135.5, 132.9, 132.6, 132.0, 130.6, 129.7, 129.3, 126.6, 124.0, 118.7 (q, ${}^{1}J_{CF}$ = 320 Hz), 117.5, 115.6 (q, ${}^{5}J_{CF}$ = 1.9 Hz), 52.5, 27.9, 27.7, 27.4, 27.2, 26.5, 22.6. HRMS (FAB) calcd for $C_{34}H_{39}F_3NO_6SSi$ (M+H$^+$) 674.2214, found 674.2220.

2-(Dicyclohexyl(phenyl)silyl)-3-(2-methylbenzamido)phenyl trifluoromethanesulfonate (1z)



^{1}H NMR (CDCl$_3$): δ 8.11 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.71 (s, 1H), 7.55 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 7.40-7.33 (m, 3H), 7.30-7.23 (m, 3H), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.84 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.26 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 2.27 (s, 3H), 1.88-1.78 (m, 2H), 1.75-1.48 (m, 10H), 1.36-1.17 (m, 4H), 1.14-0.98 (m, 4H), 0.86-0.73 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 167.6, 156.9, 145.5, 136.9, 135.0, 134.9, 132.04, 131.98, 131.1, 130.3, 130.0, 128.8, 125.8, 125.7, 122.6, 118.7 (q, $^1J_{CF}$ = 321 Hz), 116.7, 114.9 (q, $^5J_{CF}$ = 2.9 Hz), 27.9, 27.7, 27.5, 27.3, 26.6, 22.7, 19.9. HRMS (FAB) calcd for $C_{33}H_{39}F_3NO_4SSi$ (M+H$^+$) 630.2316, found 630.2325.

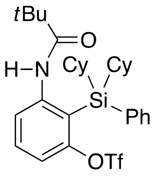
2-(Dicyclohexyl(phenyl)silyl)-3-(3-furancarboxamido)phenyl trifluoromethanesulfonate (1aa)



^{1}H NMR (CDCl$_3$): δ 7.99 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.72 (s, 1H), 7.60-7.47 (m, 6H), 7.26 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.20 (t, J_{HH} = 1.6 Hz, 1H), 6.77 (d, J_{HH} = 0.9 Hz, 1H), 5.67 (s, 1H), 1.88-1.78 (m, 2H), 1.74-1.50 (m, 10H), 1.37-1.18 (m, 4H), 1.10-0.95 (m, 4H), 0.87-0.73 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 160.6, 157.0, 144.9, 144.6, 143.6, 135.6, 132.9, 132.0, 130.7, 129.2, 123.8, 122.5, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.8, 115.3 (q, $^5J_{CF}$ =

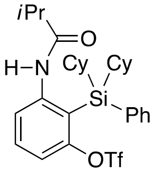
2.6 Hz), 108.0, 28.0, 27.7, 27.4, 27.2, 26.6, 22.6. HRMS (FAB) calcd for $C_{30}H_{35}F_3NO_5SSi$ ($M+H^+$) 606.1952, found 606.1949.

2-(Dicyclohexyl(phenyl)silyl)-3-pivalamidophenyl trifluoromethanesulfonate (1bb)



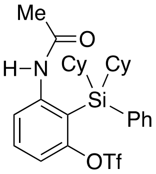
^{1}H NMR ($CDCl_3$): δ 7.80 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.54-7.39 (m, 6H), 7.33 (s, 1H), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 1.87-1.56 (m, 12H), 1.38-1.20 (m, 4H), 1.12-0.95 (m, 4H), 0.91-0.75 (m, 2H), 0.69 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 177.1, 157.0, 145.8, 135.4, 133.3, 131.5, 130.4, 128.9, 124.9, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.6, 115.1 (q, $^5J_{CF}$ = 2.6 Hz), 39.3, 28.0, 27.7, 27.4, 26.64, 26.60, 22.9. HRMS (FAB) calcd for $C_{30}H_{41}F_3NO_4SSi$ ($M+H^+$) 596.2472, found 596.2473.

2-(Dicyclohexyl(phenyl)silyl)-3-isobutyramidophenyl trifluoromethanesulfonate (1cc)



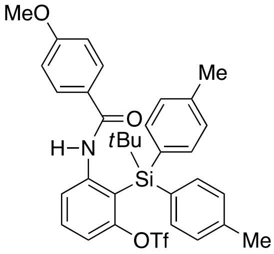
^{1}H NMR ($CDCl_3$): δ 8.10 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.58-7.52 (m, 2H), 7.52-7.43 (m, 4H), 7.29 (s, 1H), 7.19 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 1.90-1.79 (m, 2H), 1.78-1.60 (m, 10H), 1.39-1.24 (m, 4H), 1.17-0.98 (m, 5H), 0.90-0.77 (m, 2H), 0.76 (d, $^3J_{HH}$ = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 175.0, 156.9, 145.8, 135.4, 132.9, 132.0, 130.5, 128.9, 122.0, 118.7 (q, $^1J_{CF}$ = 321 Hz), 115.4, 114.4 (q, $^5J_{CF}$ = 2.6 Hz), 36.4, 28.0, 27.73, 27.70, 27.3, 26.6, 22.8, 19.0. HRMS (FAB) calcd for $C_{29}H_{39}F_3NO_4SSi$ ($M+H^+$) 582.2316, found 582.2329.

3-Acetamido-2-(dicyclohexyl(phenyl)silyl)phenyl trifluoromethanesulfonate (1dd)



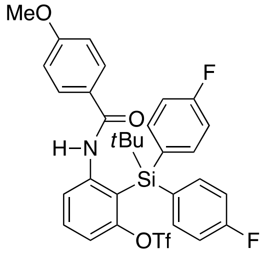
^{1}H NMR (CDCl$_3$): δ 8.02 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.58-7.44 (m, 6H), 7.23 (s, 1H), 7.21 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.90-1.80 (m, 2H), 1.78-1.61 (m, 10H), 1.39-1.26 (m, 4H), 1.22 (s, 3H), 1.18-0.98 (m, 4H), 0.90-0.76 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 167.9, 156.8, 145.4, 135.3, 132.9, 132.1, 130.4, 129.0, 122.1, 118.7 (q, $^1J_{CF}$ = 321 Hz), 115.4, 114.6 (q, $^5J_{CF}$ = 1.9 Hz), 28.0, 27.8, 27.7, 27.3, 26.6, 23.6, 22.8. HRMS (FAB) calcd for $C_{27}H_{35}F_3NO_4SSi$ (M+H$^+$) 554.2003, found 554.2015.

2-(tert-Butyldi-4-tolylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1ii)



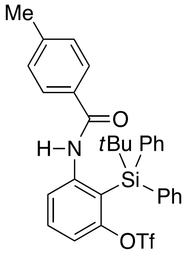
^{1}H NMR (CDCl$_3$): δ 8.10 (s, 1H), 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 7.8 Hz, 4H), 7.53 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.23 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 7.8 Hz, 4H), 6.84 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.66 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.83 (s, 3H), 2.34 (s, 6H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.1, 162.4, 156.7, 145.5, 140.0, 135.8, 131.9, 131.0, 129.6, 128.9, 126.4, 123.7, 118.9, 118.5 (q, $^1J_{CF}$ = 321 Hz), 115.5 (q, $^5J_{CF}$ = 1.9 Hz), 113.5, 55.5, 29.4, 21.6, 20.4. HRMS (FAB) calcd for $C_{33}H_{35}F_3NO_5SSi$ (M+H$^+$) 642.1952, found 642.1952.

2-(*tert*-Butylbis(4-fluorophenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1jj)



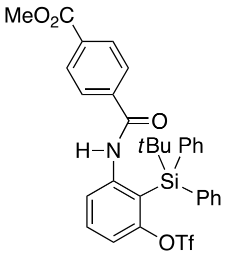
^{1}H NMR (CDCl$_3$): δ 8.01 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.81 (s, 1H), 7.58 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HF}$ = 6.0 Hz, 4H), 7.55 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.02 (t, ^3J = 8.7 Hz, 4H), 6.91 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 1.18 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.0, 164.2 (d, $^1J_{CF}$ = 252 Hz), 162.6, 156.4, 145.4, 137.8 (d, $^3J_{CF}$ = 7.7 Hz), 132.3, 129.9 (d, $^4J_{CF}$ = 3.8 Hz), 128.6, 126.2, 124.0, 118.4 (q, $^1J_{CF}$ = 322 Hz), 117.9, 116.1 (d, $^2J_{CF}$ = 20.1 Hz), 115.7 (q, $^5J_{CF}$ = 2.9 Hz), 113.7, 55.4, 29.3, 20.2. HRMS (FAB) calcd for $C_{31}H_{29}F_5NO_5SSi$ (M+H$^+$) 650.1450, found 650.1469.

2-(*tert*-Butyldiphenylsilyl)-3-(4-methylbenzamido)phenyl trifluoromethanesulfonate (1kk)



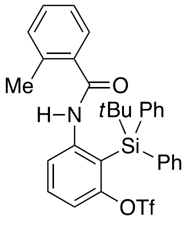
^{1}H NMR (CDCl$_3$): δ 8.07 (s, 1H), 8.05 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.70-7.63 (m, 4H), 7.56 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.28-7.32 (m, 4H), 7.26 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.74 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 2.35 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.3, 156.7, 145.3, 142.3, 135.8, 134.5, 132.1, 131.0, 130.0, 129.1, 128.8, 126.9, 124.0, 118.8, 118.5 (q, $^1J_{CF}$ = 321 Hz), 115.6, 29.4, 21.5, 20.4. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_4SSi$ ($M+H^+$) 598.1690, found 598.1699.

Methyl 4-((2-(*tert*-butyldiphenylsilyl)-3-(trifluoromethylsulfonyloxy)phenyl)carbamoyl)benzoate (1ll)



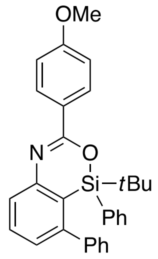
^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.84 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.68-7.62 (m, 4H), 7.59 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.37-7.28 (m, 5H), 6.92 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.95 (s, 3H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.2, 164.4, 156.6, 144.8, 137.7, 135.6, 134.3, 132.9, 132.2, 130.1, 129.6, 128.8, 126.8, 123.9, 119.0, 118.4 (q, $^1J_{CF}$ = 321 Hz), 115.9 (q, $^5J_{CF}$ = 1.9 Hz), 52.4, 29.2, 20.3. HRMS (FAB) calcd for $C_{32}H_{31}F_3NO_6SSi$ ($M+H^+$) 642.1588, found 642.1590.

2-(*tert*-Butyldiphenylsilyl)-3-(2-methylbenzamido)phenyl trifluoromethanesulfonate (1mm)



^{1}H NMR ($CDCl_3$): δ 8.15 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.70 (s, 1H), 7.60-7.53 (m, 5H), 7.31-7.17 (m, 8H), 7.09 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.92 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.49 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 2.21 (s, 3H), 1.27 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.8, 156.6, 145.6, 136.7, 135.4, 135.2, 134.1, 132.3, 131.2, 130.2, 129.9, 128.6, 126.4, 125.8, 122.8, 118.5 (q, $^1J_{CF}$ = 321 Hz), 117.8, 115.2 (q, $^5J_{CF}$ = 2.9 Hz), 29.3, 20.3, 19.8. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_4SSi$ (M+H$^+$) 598.1690, found 598.1690.

Procedure for scheme 1b.

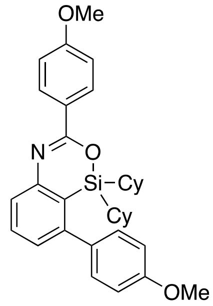


Et_2NH (46.6 µL, 0.450 mmol) and DMA (0.6 mL) were added to a mixture of compound **1b** (92.1 mg, 0.150 mmol) and $Pd(PPh_3)_4$ (17.3 mg, 15.0 µmol), and the resulting solution was stirred for 47 h at 100 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 (containing 2 vol% of Et_3N) to afford compound **3b** as a white amorphous (46.5 mg, 0.100 mmol; 67% yield).

^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.53-7.45 (m, 4H), 7.44-7.38 (m, 1H), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.25 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.12 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.09-7.04 (m, 1H), 7.00 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 6.93 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.85 (s, 3H), 0.82 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.1, 154.2, 151.3, 148.7, 143.7, 136.1, 135.2, 131.3, 130.24, 130.20, 130.17, 128.1, 127.97, 127.95, 127.50, 127.47, 127.3, 119.8, 113.6, 55.5, 26.6, 21.1. HRMS (FAB) calcd for $C_{30}H_{30}NO_2Si$ (M+H$^+$) 464.2040, found 464.2042.

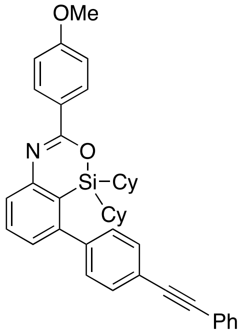
General procedure for schemes 2 and 3.

Et_2NH (33.0 µL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound **1** (0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 µmol), and PCy_3•HBF_4 (6.1 mg, 17 µmol), and the resulting solution was stirred for 16 h at 80 °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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc (containing 2 vol% of Et_3N) to afford compound **3**.



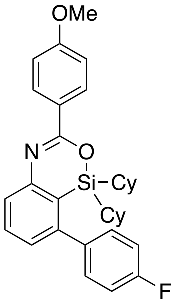
Scheme 2, compound 3d. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 95% yield (74.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.44 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.36 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.24 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.06 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.00-6.93 (m, 4H), 3.89 (s, 3H), 3.88 (s, 3H), 1.70-1.44 (m, 10H), 1.35-1.21 (m, 2H), 1.15-0.99 (m, 6H), 0.91-0.79 (m, 2H), 0.65 (tt, $^3J_{HH}$ = 12.8 and 2.8 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.0, 159.5, 154.5, 151.0, 147.6, 136.6, 130.8, 130.1, 127.5, 127.0, 126.6, 120.7, 113.8, 113.6, 55.6, 55.5, 27.91, 27.89, 27.03, 26.99, 26.7. HRMS (FAB) calcd for $C_{33}H_{40}NO_3Si$ (M+H$^+$) 526.2772, found 526.2784.



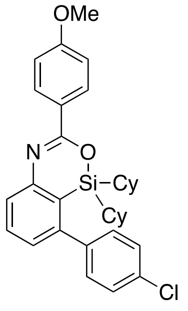
Scheme 2, compound 3e. The reaction was conducted for 40 h. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 65% yield (58.0 mg).

^{1}H NMR (CDCl$_3$): δ 8.19 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.67-7.54 (m, 4H), 7.47 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.44-7.28 (m, 6H), 7.09 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.76-1.43 (m, 10H), 1.38-1.21 (m, 2H), 1.21-0.99 (m, 6H), 0.96-0.79 (m, 2H), 0.66 (t, $^3J_{HH}$ = 12.6 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.1, 154.7, 151.1, 147.2, 144.1, 131.8, 131.6, 131.0, 130.2, 129.1, 128.6, 127.4, 127.1, 126.7, 123.3, 122.9, 120.4, 113.7, 90.3, 89.3, 55.5, 27.9, 27.1, 27.0, 26.6. HRMS (FAB) calcd for $C_{40}H_{42}NO_2Si$ (M+H$^+$) 596.2979, found 596.2985.



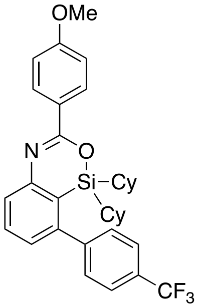
Scheme 2, compound 3f. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 92% yield (71.1 mg).

^{1}H NMR (CDCl$_3$): δ 8.18 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.45 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.39 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.29 (dd, $^3J_{HH}$ = 8.8 Hz and $^4J_{HF}$ = 5.4 Hz, 2H), 7.13 (t, ^3J = 8.6 Hz, 2H), 7.05 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 3.88 (s, 3H), 1.70-1.43 (m, 10H), 1.34-1.22 (m, 2H), 1.16-0.99 (m, 6H), 0.91-0.80 (m, 2H), 0.62 (tt, $^3J_{HH}$ = 12.7 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.7 (d, $^1J_{CF}$ = 247 Hz), 162.1, 154.6, 151.1, 146.7, 140.2 (d, $^4J_{CF}$ = 2.9 Hz), 130.9, 130.6 (d, $^3J_{CF}$ = 8.6 Hz), 130.1, 127.3, 127.0, 126.9, 120.6, 115.2 (d, $^2J_{CF}$ = 21.1 Hz), 113.6, 55.5, 27.9, 27.04, 26.97, 26.6. HRMS (FAB) calcd for $C_{32}H_{37}FNO_2Si$ (M+H$^+$) 514.2572, found 514.2579.



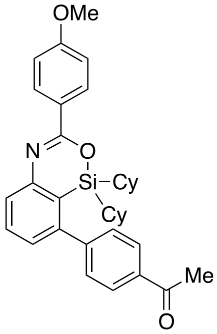
Scheme 2, compound 3g. The reaction was conducted using binap (5.5 mol%) as the ligand. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 86% yield (68.3 mg).

^{1}H NMR (CDCl$_3$): δ 8.17 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.48-7.36 (m, 4H), 7.26 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.04 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.73-1.41 (m, 10H), 1.34-1.20 (m, 2H), 1.18-0.97 (m, 6H), 0.91-0.77 (m, 2H), 0.62 (tt, $^3J_{HH}$ = 12.4 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.1, 154.6, 151.1, 146.5, 142.6, 134.0, 131.0, 130.4, 130.2, 128.5, 127.3, 127.2, 126.7, 120.5, 113.7, 55.5, 27.9, 27.1, 27.04, 26.98, 26.6. HRMS (FAB) calcd for $C_{32}H_{37}ClNO_2Si$ (M+H$^+$) 530.2277, found 530.2277.



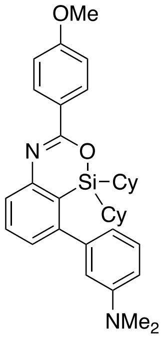
Scheme 2, compound 3h. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 92% yield (78.2 mg).

^{1}H NMR (CDCl$_3$): δ 8.18 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.72 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.52-7.40 (m, 4H), 7.08 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.88 (s, 3H), 1.71-1.41 (m, 10H), 1.33-1.18 (m, 2H), 1.15-0.96 (m, 6H), 0.88-0.73 (m, 2H), 0.59 (tt, ${}^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ${}^{13}C\{{}^1H\}$ NMR (CDCl$_3$): δ 162.2, 154.7, 151.2, 147.9, 146.3, 131.1, 130.22 (q, ${}^2J_{CF}$ = 32.6 Hz), 130.19, 129.4, 127.5, 127.2, 126.5, 125.4 (q, ${}^3J_{CF}$ = 3.5 Hz), 124.3 (q, ${}^1J_{CF}$ = 272 Hz), 120.5, 113.7, 55.5, 27.9, 27.8, 27.1, 27.0, 26.9, 26.6. HRMS (FAB) calcd for $C_{33}H_{37}F_3NO_2Si$ (M+H$^+$) 564.2540, found 564.2550.



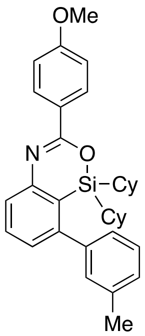
Scheme 2, compound 3i. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 86% yield (69.2 mg).

${}^1H$ NMR (CDCl$_3$): δ 8.18 (d, ${}^3J_{HH}$ = 9.2 Hz, 2H), 8.04 (d, ${}^3J_{HH}$ = 8.2 Hz, 2H), 7.52-7.38 (m, 4H), 7.07 (dd, ${}^3J_{HH}$ = 7.3 Hz and ${}^4J_{HH}$ = 0.9 Hz, 1H), 6.97 (d, ${}^3J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 2.69 (s, 3H), 1.70-1.40 (m, 10H), 1.35-1.18 (m, 2H), 1.15-0.95 (m, 6H), 0.91-0.77 (m, 2H), 0.60 (tt, ${}^3J_{HH}$ = 12.8 and 2.8 Hz, 2H). ${}^{13}C\{{}^1H\}$ NMR (CDCl$_3$): δ 197.8, 162.1, 154.6, 151.2, 149.1, 146.6, 136.4, 131.0, 130.1, 129.3, 128.4, 127.4, 127.2, 126.5, 120.3, 113.6, 55.5, 27.83, 27.80, 27.1, 27.04, 26.95, 26.9, 26.5. HRMS (FAB) calcd for $C_{34}H_{40}NO_3Si$ (M+H$^+$) 538.2772, found 538.2775.



Scheme 2, compound 3j. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 99% yield (79.7 mg).

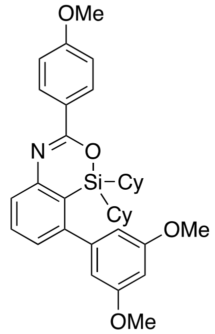
^{1}H NMR (CDCl$_3$): δ 8.19 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.44 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.37 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.27 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.12 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.80-6.74 (m, 1H), 6.68-6.63 (m, 2H), 3.88 (s, 3H), 3.00 (s, 6H), 1.69-1.48 (m, 10H), 1.35-1.21 (m, 2H), 1.14-0.97 (m, 6H), 0.93-0.78 (m, 2H), 0.71 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.0, 154.7, 150.9, 150.6, 148.9, 144.9, 130.7, 130.1, 129.1, 127.6, 126.6, 126.5, 120.5, 117.4, 113.6, 113.2, 112.0, 55.5, 40.8, 28.0, 27.9, 27.03, 26.97, 26.8, 26.7. HRMS (FAB) calcd for $C_{34}H_{43}N_2O_2Si$ (M+H$^+$) 539.3088, found 539.3102.



Scheme 2, compound 3k. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 98% yield (74.6 mg).

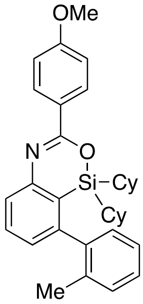
^{1}H NMR (CDCl$_3$): δ 8.18 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.45 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.38 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.22 (d, $^3J_{HH}$ = 7.6

Hz, 1H), 7.15-7.11 (m, 2H), 7.09 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H), 1.70-1.45 (m, 10H), 1.33-1.20 (m, 2H), 1.15-0.98 (m, 6H), 0.87-0.75 (m, 2H), 0.63 (tt, $^3J_{HH}$ = 12.8 and 2.8 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.0, 154.6, 151.0, 148.1, 144.0, 137.9, 130.8, 130.1, 129.9, 128.39, 128.37, 127.5, 126.7, 126.6, 126.1, 120.5, 113.6, 55.5, 27.99, 27.97, 27.1, 27.0, 26.9, 26.7, 21.6. HRMS (FAB) calcd for $C_{33}H_{40}NO_2Si$ (M+H$^+$) 510.2823, found 510.2831.



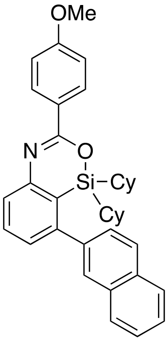
Scheme 2, compound 3l. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 93% yield (77.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.45 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.39 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.10 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.52 (t, $^4J_{HH}$ = 2.3 Hz, 1H), 6.48 (d, $^4J_{HH}$ = 2.3 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 6H), 1.74-1.48 (m, 10H), 1.38-1.24 (m, 2H), 1.18-0.98 (m, 6H), 0.95-0.81 (m, 2H), 0.74 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.0, 160.8, 154.7, 151.0, 147.9, 146.0, 130.8, 130.1, 127.4, 126.9, 126.3, 120.3, 113.6, 107.2, 100.2, 55.6, 55.5, 28.0, 27.1, 27.0, 26.9, 26.7. HRMS (FAB) calcd for $C_{34}H_{42}NO_4Si$ (M+H$^+$) 556.2878, found 556.2879.



Scheme 2, compound 3m. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 86% yield (65.5 mg).

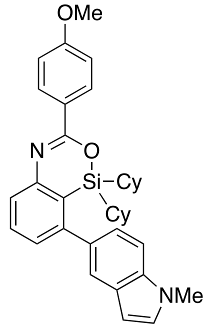
^{1}H NMR (CDCl$_3$): δ 8.18 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.44 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.38 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.35-7.20 (m, 3H), 7.15 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 3.88 (s, 3H), 2.19 (s, 3H), 1.78-1.46 (m, 8H), 1.42-0.79 (m, 12H), 0.79-0.64 (m, 1H), 0.35 (tt, $^3J_{HH}$ = 12.6 and 2.7 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.0, 154.6, 151.3, 146.7, 142.9, 136.5, 130.53, 130.51, 130.1, 129.4, 128.1, 127.5, 127.3, 126.7, 125.7, 121.0, 113.6, 55.5, 28.0, 27.9, 27.8, 27.7, 27.3, 26.9, 26.8, 26.7, 25.8, 20.4. HRMS (FAB) calcd for $C_{33}H_{40}NO_2Si$ (M+H$^+$) 510.2823, found 510.2827.



Scheme 2, compound 3n. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 93% yield (76.2 mg).

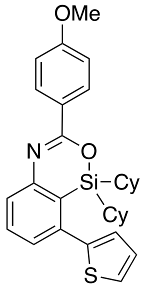
^{1}H NMR (CDCl$_3$): δ 8.19 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.97-7.80 (m, 3H), 7.76 (s, 1H), 7.60-7.45 (m, 4H), 7.43 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.18 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.97 (d, $^3J_{HH}$

= 8.7 Hz, 2H), 3.88 (s, 3H), 1.63-1.43 (m, 10H), 1.31-1.16 (m, 2H), 1.12-0.90 (m, 6H), 0.87-0.71 (m, 2H), 0.61 (t, $^3J_{HH}$ = 12.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 162.0, 154.6, 151.1, 147.9, 141.5, 133.1, 132.8, 130.9, 130.1, 128.1, 128.0, 127.9, 127.7, 127.4, 126.9, 126.8, 126.3, 120.8, 113.6, 55.5, 27.9, 27.8, 27.04, 27.03, 26.9, 26.6. HRMS (FAB) calcd for $C_{36}H_{40}NO_2Si$ (M+H$^+$) 546.2823, found 546.2823.



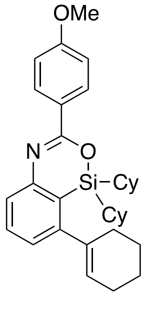
Scheme 2, compound 3o. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 95% yield (78.5 mg).

^{1}H NMR (CDCl$_3$): δ 8.19 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.53 (s, 1H), 7.45 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.37 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.36 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.19 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.15 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.13 (d, $^3J_{HH}$ = 3.2 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.51 (d, $^3J_{HH}$ = 3.2 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 1.63-1.45 (m, 10H), 1.32-1.17 (m, 2H), 1.13-0.93 (m, 6H), 0.87-0.73 (m, 2H), 0.62 (t, $^3J_{HH}$ = 12.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 161.9, 154.5, 150.9, 149.3, 136.4, 135.3, 130.6, 130.1, 129.8, 128.5, 127.7, 127.3, 126.2, 122.9, 121.2, 121.1, 113.6, 108.9, 101.2, 55.5, 33.1, 27.94, 27.88, 27.04, 26.96, 26.7. HRMS (FAB) calcd for $C_{35}H_{41}N_2O_2Si$ (M+H$^+$) 549.2932, found 549.2934.



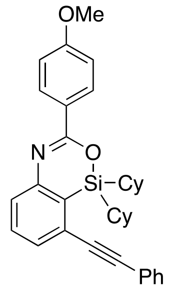
Scheme 2, compound 3p. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 90% yield (68.1 mg).

^{1}H NMR (CDCl$_3$): δ 8.18 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.44 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.37 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.20 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.09 (dd, $^3J_{HH}$ = 5.0 and 3.2 Hz, 1H), 7.02-6.88 (m, 3H), 3.88 (s, 3H), 1.78-1.47 (m, 10H), 1.40-1.25 (m, 2H), 1.21-1.01 (m, 6H), 0.98-0.85 (m, 2H), 0.77 (tt, $^3J_{HH}$ = 12.4 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.1, 154.8, 151.2, 145.2, 139.7, 130.8, 130.2, 128.1, 127.7, 127.32, 127.26, 126.4, 126.0, 121.8, 113.6, 55.5, 27.9, 27.8, 27.3, 27.1, 27.0, 26.6. HRMS (FAB) calcd for $C_{30}H_{36}NO_2SSi$ (M+H$^+$) 502.2231, found 502.2234.



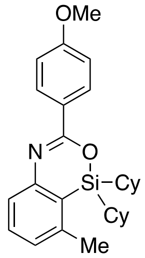
Scheme 2, compound 3q. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 98% yield (73.4 mg).

^{1}H NMR (CDCl$_3$): δ 8.18 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.37 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.26 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.00 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 5.62-5.57 (m, 1H), 3.88 (s, 3H), 2.39-2.31 (m, 2H), 2.24-2.15 (m, 2H), 2.00-1.90 (m, 2H), 1.86-1.51 (m, 12H), 1.51-1.38 (m, 2H), 1.32-1.00 (m, 10H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 161.9, 154.5, 151.4, 150.2, 141.4, 130.7, 130.1, 127.6, 126.4, 124.6, 119.2, 113.6, 55.5, 30.5, 28.2, 28.0, 27.7, 27.6, 27.5, 26.8, 25.5, 23.2, 22.0. HRMS (FAB) calcd for $C_{32}H_{42}NO_2Si$ ($M+H^+$) 500.2979, found 500.2981.



Scheme 2, compound 3r. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 93% yield (72.7 mg).

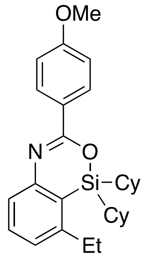
^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.57-7.51 (m, 2H), 7.46-7.34 (m, 6H), 6.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.97-1.84 (m, 2H), 1.80-1.57 (m, 8H), 1.50-1.10 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 162.2, 154.9, 151.1, 131.5, 131.2, 130.2, 129.5, 128.7, 128.6, 128.2, 127.5, 127.2, 123.4, 123.3, 113.7, 91.0, 90.8, 55.5, 27.9, 27.2, 26.72, 26.65, 25.6. HRMS (FAB) calcd for $C_{34}H_{38}NO_2Si$ ($M+H^+$) 520.2666, found 520.2670.



Scheme 2, compound 3s. The reaction was conducted at 100 °C. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 78% yield (50.5 mg).

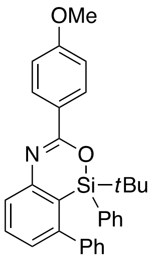
^{1}H NMR ($CDCl_3$): δ 8.16 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.34 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.22

(d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.00 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.87 (s, 3H), 2.39 (s, 3H), 1.94-1.85 (m, 2H), 1.79-1.52 (m, 8H), 1.47-1.33 (m, 2H), 1.33-1.10 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.0, 153.8, 151.1, 142.0, 131.2, 130.0, 127.6, 127.0, 125.7, 119.9, 113.6, 55.5, 27.93, 27.88, 27.3, 26.8, 26.7, 26.3, 23.5. HRMS (FAB) calcd for $C_{27}H_{36}NO_2Si$ (M+H$^+$) 434.2510, found 434.2517.

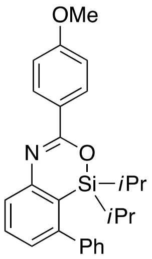


Scheme 2, compound 3t. The reaction was conducted at 100 °C. Hexane/EtOAc = 11/1 was used for silica gel chromatography. White amorphous. 74% yield (49.9 mg).

^1H NMR ($CDCl_3$): δ 8.16 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.40 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.23 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.09 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.87 (s, 3H), 2.61 (q, $^3J_{HH}$ = 7.5 Hz, 2H), 1.95-1.85 (m, 2H), 1.79-1.53 (m, 8H), 1.46-1.34 (m, 2H), 1.31 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 1.34-1.09 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.9, 153.7, 151.0, 148.5, 131.4, 130.0, 127.7, 126.0, 124.9, 119.4, 113.6, 55.5, 30.4, 27.93, 27.89, 27.4, 26.9, 26.7, 15.7. HRMS (FAB) calcd for $C_{28}H_{38}NO_2Si$ (M+H$^+$) 448.2666, found 448.2667.



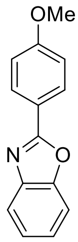
Scheme 2, compound 3b. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 90% yield (62.5 mg).



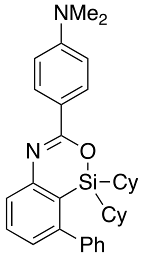
Scheme 2, compound 3u. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 94% yield (58.3 mg).

^{1}H NMR (CDCl$_3$): δ 8.17 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.47 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.44-7.32 (m, 6H), 7.11 (dd, $^3J_{HH}$ = 7.3 and $^4J_{HH}$ = 1.2 Hz, 1H), 6.95 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 3.87 (s, 3H), 0.97 (d, $^3J_{HH}$ = 7.1 Hz, 6H), 0.95-0.83 (m, 2H), 0.74 (d, J = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.1, 154.7, 151.1, 148.1, 144.2, 131.0, 130.1, 129.0, 128.5, 127.9, 127.4, 126.92, 126.87, 120.7, 113.6, 55.5, 17.4, 16.9, 15.3. HRMS (FAB) calcd for $C_{26}H_{30}NO_2Si$ (M+H$^+$) 416.2040, found 416.2037.

Scheme 2, 2-(4-methoxyphenyl)benzo[*d*]oxazole (CAS 838-34-6).

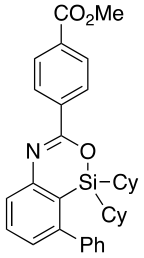


^{1}H NMR (CDCl$_3$): δ 8.20 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.77-7.72 (m, 1H), 7.58-7.53 (m, 1H), 7.37-7.28 (m, 2H), 7.04 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 163.3, 162.5, 150.8, 142.4, 129.5, 124.7, 124.6, 119.9, 119.8, 114.5, 110.5, 55.6.



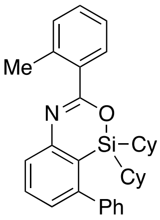
Scheme 3, compound 3x. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 76% yield (58.2 mg).

^{1}H NMR (CDCl$_3$): δ 8.11 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.47-7.29 (m, 7H), 7.05 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.74 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.05 (s, 6H), 1.69-1.45 (m, 10H), 1.34-1.21 (m, 2H), 1.15-0.96 (m, 6H), 0.90-0.76 (m, 2H), 0.60 (tt, $^3J_{HH}$ = 12.8 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.4, 152.3, 151.5, 147.9, 144.3, 130.7, 129.9, 129.0, 128.4, 127.7, 126.5, 126.1, 122.2, 120.4, 111.3, 40.3, 28.0, 27.9, 27.02, 27.00, 26.96, 26.6. HRMS (FAB) calcd for $C_{33}H_{41}N_2OSi$ (M+H$^+$) 509.2983, found 509.2989.



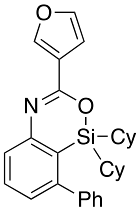
Scheme 3, compound 3y. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 82% yield (64.4 mg).

^{1}H NMR (CDCl$_3$): δ 8.30 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 8.12 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.53-7.40 (m, 5H), 7.35-7.29 (m, 2H), 7.15 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 3.95 (s, 3H), 1.70-1.43 (m, 10H), 1.31-1.19 (m, 2H), 1.14-0.99 (m, 6H), 0.85-0.74 (m, 2H), 0.65 (tt, $^3J_{HH}$ = 12.7 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 166.9, 153.7, 150.2, 148.1, 143.9, 139.0, 132.1, 131.0, 129.6, 129.0, 128.5, 128.3, 128.0, 127.7, 127.2, 120.8, 52.4, 27.84, 27.82, 27.0, 26.9, 26.6. HRMS (FAB) calcd for $C_{33}H_{38}NO_3Si$ (M+H$^+$) 524.2615, found 524.2625.



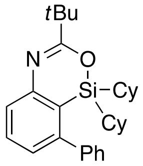
Scheme 3, compound 3z. Hexane/EtOAc = 11/1 was used for silica gel chromatography. White amorphous. 91% yield (65.2 mg).

^{1}H NMR (CDCl$_3$): δ 7.94-7.88 (m, 1H), 7.50-7.37 (m, 5H), 7.36-7.23 (m, 5H), 7.13 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.68 (s, 3H), 1.69-1.45 (m, 10H), 1.30-0.98 (m, 8H), 0.94-0.80 (m, 2H), 0.63 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 156.5, 150.7, 148.0, 144.0, 138.2, 135.2, 131.6, 130.9, 129.8, 129.6, 129.1, 128.4, 127.9, 127.3, 127.0, 125.8, 120.2, 27.90, 27.88, 27.0, 26.9, 26.7, 22.3. HRMS (FAB) calcd for $C_{32}H_{38}NOSi$ (M+H$^+$) 480.2717, found 480.2724.



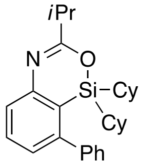
Scheme 3, compound 3aa. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 86% yield (59.2 mg).

^{1}H NMR (CDCl$_3$): δ 7.98 (s, 1H), 7.48-7.38 (m, 5H), 7.36-7.28 (m, 3H), 7.10 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.92 (d, J_{HH} = 1.8 Hz, 1H), 1.68-1.42 (m, 10H), 1.28-1.15 (m, 2H), 1.14-0.96 (m, 6H), 0.88-0.74 (m, 2H), 0.59 (tt, $^3J_{HH}$ = 12.6 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 151.3, 150.6, 148.0, 145.3, 144.0, 143.6, 130.9, 129.0, 128.4, 127.9, 127.0, 126.6, 124.2, 120.7, 109.9, 27.9, 27.8, 26.93, 26.87, 26.6. HRMS (FAB) calcd for $C_{29}H_{34}NO_2Si$ (M+H$^+$) 456.2353, found 456.2360.



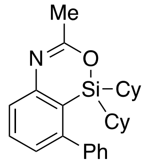
Scheme 2, compound 3bb. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 95% yield (63.5 mg).

^{1}H NMR (CDCl$_3$): δ 7.45-7.36 (m, 4H), 7.32-7.23 (m, 3H), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 1.70-1.39 (m, 10H), 1.36-0.97 (m, 8H), 1.31 (s, 9H), 0.87-0.71 (m, 2H), 0.58 (tt, $^3J_{HH}$ = 12.8 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.8, 150.9, 147.8, 144.2, 130.7, 129.1, 128.3, 127.7, 126.9, 126.8, 120.1, 39.0, 28.3, 27.93, 27.91, 27.2, 26.81, 26.79, 26.77. HRMS (FAB) calcd for $C_{29}H_{40}NOSi$ (M+H$^+$) 446.2874, found 446.2876.



Scheme 3, compound 3cc. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 74% yield (47.8 mg).

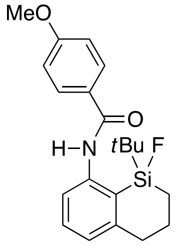
^{1}H NMR (CDCl$_3$): δ 7.44-7.35 (m, 4H), 7.31-7.21 (m, 3H), 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.70 (sept, $^3J_{HH}$ = 6.8 Hz, 1H), 1.68-1.39 (m, 10H), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.25-0.97 (m, 8H), 0.85-0.70 (m, 2H), 0.58 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 164.7, 150.7, 147.9, 144.1, 130.8, 129.1, 128.4, 127.8, 126.9, 126.4, 120.2, 36.6, 27.90, 27.88, 27.1, 26.8, 26.7, 20.3. HRMS (FAB) calcd for $C_{28}H_{38}NOSi$ (M+H$^+$) 432.2717, found 432.2719.



Scheme 3, compound 3dd. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 62% yield (37.7 mg).

^{1}H NMR (CDCl$_3$): δ 7.45-7.36 (m, 4H), 7.31-7.26 (m, 2H), 7.22 (dd, $^3J_{\mathrm{HH}}$ = 8.2 Hz and $^4J_{\mathrm{HH}}$ = 0.9 Hz, 1H), 7.08 (dd, $^3J_{\mathrm{HH}}$ = 7.3 Hz and $^4J_{\mathrm{HH}}$ = 0.9 Hz, 1H), 2.22 (s, 3H), 1.69-1.38 (m, 10H), 1.24-0.96 (m, 8H), 0.83-0.68 (m, 2H), 0.62-0.50 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 158.9, 150.5, 147.9, 144.1, 130.9, 129.0, 128.4, 127.8, 126.9, 125.9, 120.1, 27.89, 27.86, 26.9, 26.8, 26.72, 26.70, 24.1. HRMS (FAB) calcd for $C_{26}H_{34}NOSi$ (M+H$^+$) 404.2404, found 404.2401.

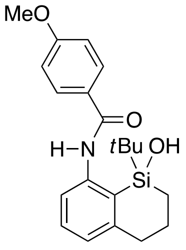
Procedure for equation 1.



Et_2NH (33.0 µL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound **1w** (75.2 mg, 0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 µmol), and PCy_3•HBF_4 (6.1 mg, 17 µmol), and the resulting solution was stirred for 16 h at 100 °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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1→6/1 and the resulting solid was washed with hexane to afford compound **4w** as a white solid (23.2 mg, 62.4 µmol; 42% yield). The structure was confirmed by X-ray crystallographic analysis after recrystallization from CH_2Cl_2/hexane.

^{1}H NMR ($CDCl_3$): δ 8.68-8.57 (m, 1H), 8.16-8.08 (m, 1H), 7.91 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.39 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.03-6.94 (m, 3H), 3.88 (s, 3H), 2.86-2.76 (m, 1H), 2.57-2.46 (m, 1H), 2.21-2.09 (m, 1H), 1.68-1.52 (m, 1H), 1.20-1.09 (m, 2H), 0.90 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.6, 162.6, 151.2 (d, $^3J_{CF}$ = 3.8 Hz), 144.2 (d, $^3J_{CF}$ = 2.9 Hz), 131.4, 129.0, 126.9, 125.2 (d, $^4J_{CF}$ = 1.9 Hz), 120.8, 119.9 (d, $^2J_{CF}$ = 13.4 Hz), 114.1, 55.6, 35.8, 25.5, 21.8 (d, $^3J_{CF}$ = 1.9 Hz), 19.6 (d, $^2J_{CF}$ = 14.4 Hz), 9.6 (d, $^2J_{CF}$ = 10.5 Hz). ^{19}F NMR ($CDCl_3$): δ –165.9 (s). HRMS (FAB) calcd for $C_{21}H_{27}FNO_2Si$ (M+H$^+$) 372.1790, found 372.1793.

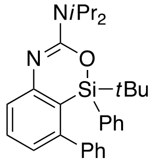
To elucidate the origin of the fluoride on silicon, the reaction of **1w** was also conducted by using free PCy_3 without HBF_4 as the ligand, which gave compound **S3** as the major product in 32% yield with no formation of compound **4w**. This result indicates that the fluoride of compound **4wv** comes from BF_4^- of the phosphine ligand salt, although the exact reaction mechanism is unclear at this stage.



S3

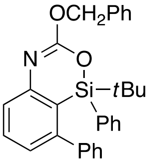
General procedure for equations 2 and 3.

1,2,2,6,6-Pentamethylpiperidine (57.0 μL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound **1** (0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), and PCy_3•HBF_4 (6.1 mg, 17 μmol), and the resulting solution was stirred for 16 h at 80 °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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc (containing 2 vol% of Et_3N) to afford compound **3** or **5**.



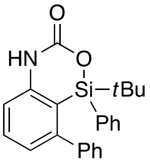
Equation 2, compound 3ee. Hexane/EtOAc = 10/1 was used for silica gel chromatography. Yellow amorphous. 81% yield (55.5 mg).

^{1}H NMR ($CDCl_3$): δ 7.54-7.46 (m, 2H), 7.43-7.37 (m, 1H), 7.37-7.28 (m, 3H), 7.18 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.11-7.02 (m, 3H), 6.99 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 6.77 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.42-3.96 (m, 2H), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 0.79 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.8, 151.4, 148.5, 144.6, 136.5, 135.0, 131.2, 130.04, 129.97, 128.0, 127.9, 127.1, 124.4, 123.3, 115.9, 46.0, 27.1, 21.5, 21.4, 20.6. HRMS (FAB) calcd for $C_{29}H_{37}N_2OSi$ (M+H$^+$) 457.2670, found 457.2673.



Equation 2, compound 3ff. Hexane/EtOAc = 10/1 was used for silica gel chromatography. Yellow viscous oil. 80% yield (55.3 mg).

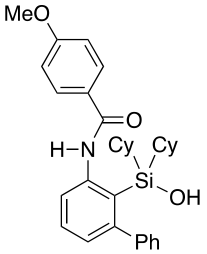
^{1}H NMR ($CDCl_3$): δ 7.49-7.27 (m, 12H), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.01-6.94 (m, 3H), 5.41 (d, $^2J_{HH}$ = 12.4 Hz, 1H), 5.37 (d, $^2J_{HH}$ = 12.4 Hz, 1H), 0.78 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.4, 151.8, 148.8, 143.8, 136.6, 135.4, 135.14, 135.05, 131.4, 130.4, 130.1, 128.5, 128.4, 128.1, 128.0, 127.5, 126.5, 125.5, 117.9, 69.9, 26.6, 20.9. HRMS (FAB) calcd for $C_{30}H_{29}NO_2Si$ (M$^+$) 463.1968, found 463.1987.



Equation 3, compound 5gg. Hexane/EtOAc = 4/1 → 1/1 was used for silica gel chromatography. White solid. 67% yield (37.8 mg).

^{1}H NMR ($CDCl_3$): δ 8.46 (s, 1H), 7.49-7.36 (m, 4H), 7.33 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.28-7.20 (m, 1H), 7.10 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 6.99-6.86 (m, 4H), 0.84 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.1, 149.5, 145.2, 143.0, 135.1, 134.1, 131.8, 130.7, 130.0, 128.2, 128.1, 127.8, 125.6, 115.7, 113.3, 26.6, 20.8. HRMS (FAB) calcd for $C_{23}H_{23}NO_2Si$ (M$^+$) 373.1498, found 373.1512.

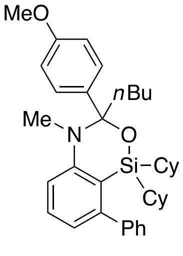
Procedure for scheme 4a.



H_2O (2 mL) was added to compound **3c** (74.4 mg, 0.150 mmol) and the mixture was stirred for 40 h at 110 °C. After cooled to room temperature, this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 → 2/1 to afford compound **6** as a white solid (69.5 mg, 0.135 mmol; 90% yield).

^{1}H NMR ($CDCl_3$): δ 10.84 (s, 1H), 8.36 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 8.00 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.45-7.35 (m, 4H), 7.29-7.21 (m, 2H), 7.01-6.91 (m, 3H), 3.88 (s, 3H), 2.31 (bs, 1H), 1.68-1.48 (m, 10H), 1.18-0.91 (m, 10H), 0.17 (t, $^3J_{HH}$ = 12.4 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.5, 162.2, 149.3, 145.8, 144.5, 129.6, 129.4, 129.3, 128.10, 128.07, 127.6, 126.1, 123.6, 121.8, 113.8, 55.5, 28.0, 27.9, 27.8, 27.6, 27.0, 26.8. HRMS (FAB) calcd for $C_{32}H_{40}NO_3Si$ (M+H$^+$) 514.2772, found 514.2770.

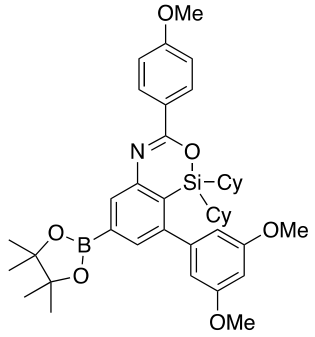
Procedure for scheme 4b.



Methyl trifluoromethanesulfonate (18.0 μL, 0.165 mmol) was added dropwise to a solution of compound **3c** (74.4 mg, 0.150 mmol) in toluene (1 mL) at room temperature, and the mixture was stirred for 14 h at 90 °C. This was cooled to –78 °C, and *n*BuLi (105 μL, 0.165 mmol; 1.57 M solution in hexane) was added dropwise to it. The resulting mixture was stirred for 1 h at 0 °C and for 5.5 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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **7** as a colorless oil (53.2 mg, 93.7 μmol; 62% yield).

^{1}H NMR ($CDCl_3$): δ 7.43-7.34 (m, 5H), 7.33-7.26 (m, 3H), 6.88-6.81 (m, 4H), 3.81 (s, 3H), 2.70 (s, 3H), 2.12 (ddd, $^3J_{HH}$ = 13.3, 12.4, and 4.1 Hz, 1H), 1.82 (ddd, $^3J_{HH}$ = 13.3, 12.4, and 4.1 Hz, 1H), 1.76-1.44 (m, 8H), 1.44-0.86 (m, 16H), 0.80 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.58 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 1H), 0.26 (tt, $^3J_{HH}$ = 12.4 and 2.3 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.5, 157.0, 147.9, 144.6, 136.0, 129.8, 129.2, 128.4, 128.0, 127.9, 127.3, 123.2, 119.8, 112.9, 91.6, 55.3, 40.6, 38.3, 28.51, 28.49, 28.4, 28.1, 27.9, 27.8, 27.5, 27.1, 27.03, 27.00, 23.0, 14.3. HRMS (FAB) calcd for $C_{37}H_{50}NO_2Si$ ($M+H^+$) 568.3605, found 568.3608.

Procedure for scheme 4c.[24]



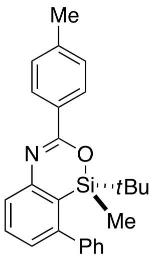
A solution of $[Ir(OMe)(cod)]_2$ (6.2 mg, 19 μmol Ir), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (4.2 mg, 16 μmol), and bis(pinacolato)diboron (70.8 mg, 0.279 mmol) in THF (0.6 mL) was stirred for 10 min at room temperature. Compound **3l** (104 mg, 0.186 mmol) and THF (1.3 mL) were added to it, and this was stirred for 12 h at 70 °C. The reaction mixture was filtered through a pad of silica gel with EtOAc and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **8** as a pale orange amorphous (111 mg, 0.162 mmol; 87% yield).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.85 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 7.53 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.53-6.47 (m, 3H), 3.87 (s, 3H), 3.83 (s, 6H), 1.76-1.47 (m, 10H), 1.44-1.18 (m, 2H), 1.35 (s, 12H), 1.18-0.97 (m, 6H), 0.95-0.81 (m, 2H), 0.74 (tt, $^3J_{HH}$ = 12.6 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 160.7, 154.4, 150.4, 147.2, 146.0, 133.2, 131.9, 130.1, 127.5, 123.6, 113.6, 107.2, 100.3, 84.0, 55.6, 55.5, 27.9, 27.03, 26.96, 26.8, 26.6, 25.0. HRMS (FAB) calcd for $C_{40}H_{53}BNO_6Si$ (M+H$^+$) 682.3730, found 682.3754.

Procedure for scheme 5a.

Et_2NH (31.0 μL, 0.300 mmol) and DMF (0.6 mL) were added to a mixture of compound **1b** (46.0 mg, 75.0 μmol), compound **1d** (50.7 mg, 75.0 μmol), $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), and PCy_3•HBF_4 (6.1 mg, 17 μmol), and the mixture was stirred for 16 h at 80 °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 Na_2SO_4, filtered, and concentrated under vacuum. The yield of compounds **3b** and **3d** were determined to be 97% yield for both by ^{1}H NMR against an internal standard ($MeNO_2$), and no crossover products were obtained.

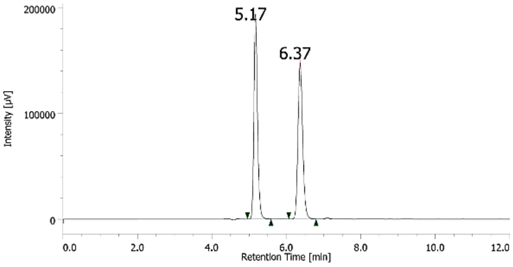
Procedure for scheme 5b.



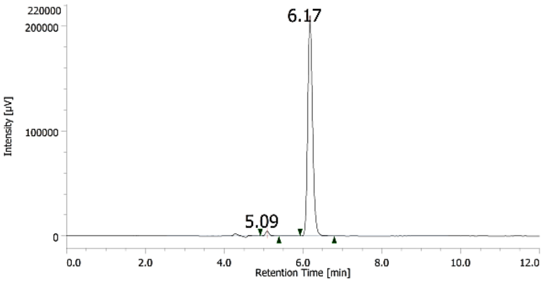
Et_2NH (33.0 μL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound (*R*)-**1gg** (80.3 mg, 0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), and PCy_3•HBF_4 (6.1 mg, 17 μmol), and the resulting solution was stirred for 22 h at 70 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 (containing 2 vol% of Et_3N) to afford compound **3gg** as a white amorphous (51.6 mg, 0.134 mmol; 89% yield). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 5.1 min [minor enantiomer], 6.2 min [major enantiomer]. 97% ee. $[\alpha]^{24}_{D}$ +38.0 (*c* 0.62, $CHCl_3$). The absolute configuration was determined to be *R* by X-ray crystallographic analysis after treatment with TfOH and recrystallization from $CHCl_3$/pentane.

^1H NMR ($CDCl_3$): δ 8.10 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.48 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.44 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.41-7.32 (m, 5H), 7.24 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.10 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 2.41 (s, 3H), 0.62 (s, 9H), 0.40 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.6, 150.9, 148.5, 144.0, 141.3, 132.1, 131.0, 130.1, 129.1, 128.4, 128.0, 127.84, 127.75, 127.4, 121.0, 25.8, 21.7, 20.7, –0.5. HRMS (FAB) calcd for $C_{25}H_{28}NOSi$ (M+H$^+$) 386.1935, found 386.1938.

racemate

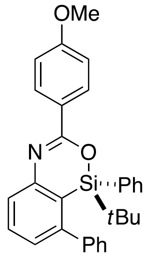


96.5% ee (*R*)



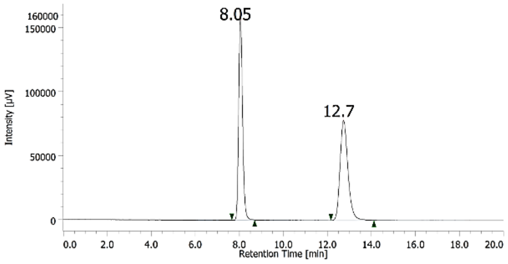
General procedure for scheme 7.

Et_2NH (31.0 µL, 0.300 mmol) and DMA (0.6 mL) were added to a mixture of compound **1** (0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 µmol), and **L*** (5.0 mg, 8.3 µmol), and the resulting solution was stirred for 40 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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc (containing 2 vol% of Et_3N) to afford compound **3**.

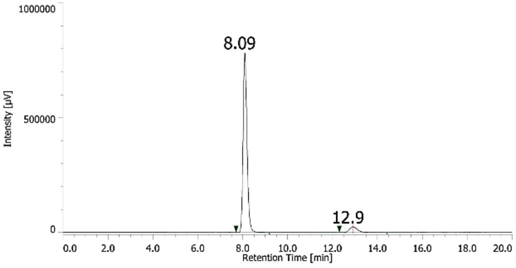


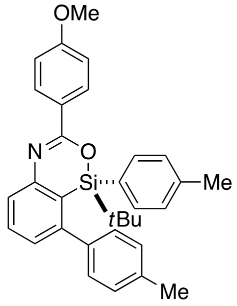
Scheme 7, compound 3b. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 87% yield (60.6 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 8.1 min [major enantiomer], 12.9 min [minor enantiomer]. 88% ee. $[\alpha]^{17}_{D}$ −70.2 (*c* 0.53, $CHCl_3$). The absolute configuration was determined to be *R* by X-ray crystallographic analysis after recrystallization from CH_2Cl_2/hexane.

racemate



87.6% ee (*R*)

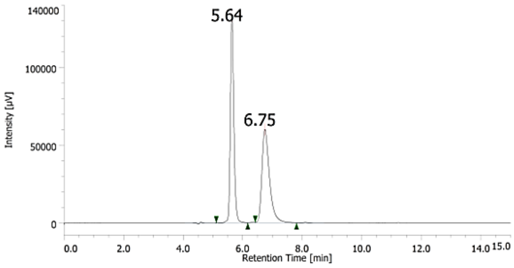




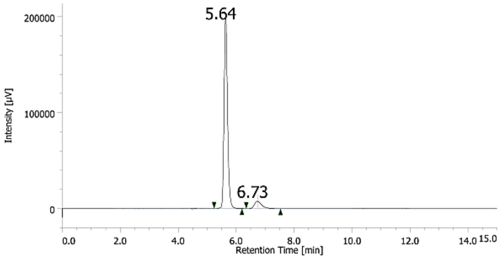
Scheme 7, compound 3ii. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 89% yield (65.6 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 5.6 min [major enantiomer], 6.7 min [minor enantiomer]. 85% ee. $[\alpha]^{22}_{D}$ −19.4 (*c* 0.54, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

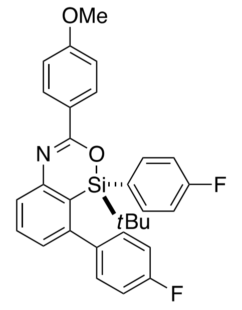
^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.54-7.47 (m, 2H), 7.41 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.16 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.12-7.05 (m, 1H), 7.01-6.90 (m, 6H), 3.86 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 0.83 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.1, 154.2, 151.3, 148.7, 141.0, 140.2, 137.2, 135.2, 132.7, 131.2, 130.2, 130.0, 128.7, 127.9, 127.4, 127.2, 120.2, 113.6, 55.5, 26.7, 21.7, 21.3, 21.0. HRMS (FAB) calcd for $C_{32}H_{34}NO_2Si$ (M+H$^+$) 492.2353, found 492.2358.

racemate



85.2% ee

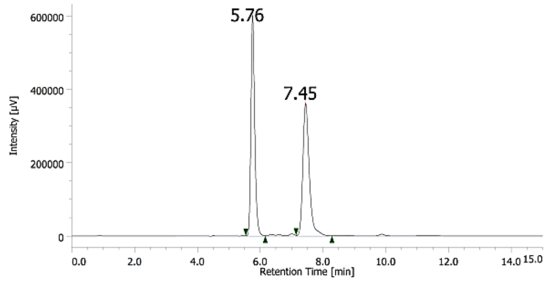




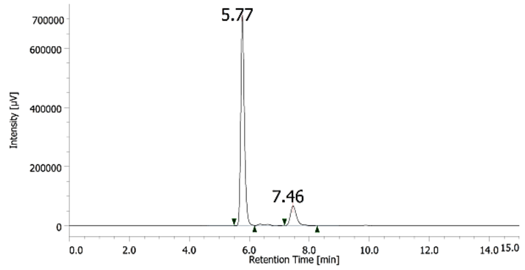
Scheme 7, compound 3jj Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 89% yield (66.8 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 5.8 min [major enantiomer], 7.5 min [minor enantiomer]. 73% ee. $[\alpha]^{19}_{\mathrm{D}}$ −78.9 (*c* 0.50, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

^{1}H NMR ($CDCl_3$): δ 8.15 (d, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 7.53-7.48 (m, 2H), 7.44 (dd, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz and $^{4}J_{\mathrm{HF}}$ = 6.0 Hz, 2H), 7.07-6.99 (m, 3H), 6.97-6.88 (m, 4H), 6.81 (t, $^{3}J_{\mathrm{HH}}$ = 8.9 Hz, 2H), 3.86 (s, 3H), 0.85 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.4 (d, $^{1}J_{\mathrm{CF}}$ = 251 Hz), 162.5 (d, $^{1}J_{\mathrm{CF}}$ = 247 Hz), 162.3, 154.2, 151.3, 147.5, 139.6 (d, $^{4}J_{\mathrm{CF}}$ = 2.9 Hz), 137.3 (d, $^{3}J_{\mathrm{CF}}$ = 8.6 Hz), 131.8 (d, $^{3}J_{\mathrm{CF}}$ = 8.6 Hz), 131.4, 131.3 (d, $^{4}J_{\mathrm{CF}}$ = 3.8 Hz), 130.2, 128.1, 127.7, 127.1, 119.7, 115.4 (d, $^{2}J_{\mathrm{CF}}$ = 19.2 Hz), 114.8 (d, $^{2}J_{\mathrm{CF}}$ = 21.1 Hz), 113.8, 55.5, 26.6, 21.2. HRMS (FAB) calcd for $C_{30}H_{28}F_2NO_2Si$ (M+H^{+}) 500.1852, found 500.1868.

racemate

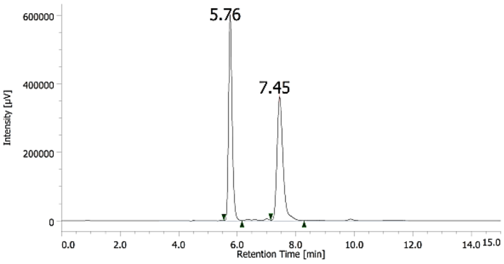


72.9% ee

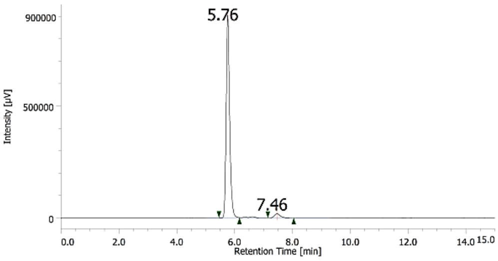


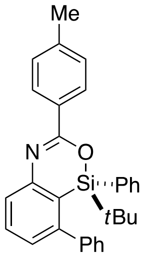
The ee of compound **3ii** could be improved by recrystallisation. Compound **3ii** (40.0 mg, 80.1 µmol; 73% ee) was dissolved in hexane (6.0 mL) at 60 °C, and the solution was slowly cooled to –35 °C to give colorless crystals (28.9 mg, 57.7 µmol; 72% yield, 93% ee).

racemate



93.3% ee

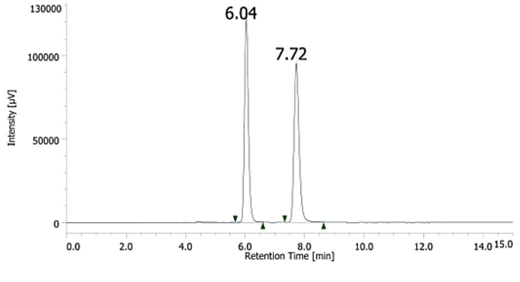




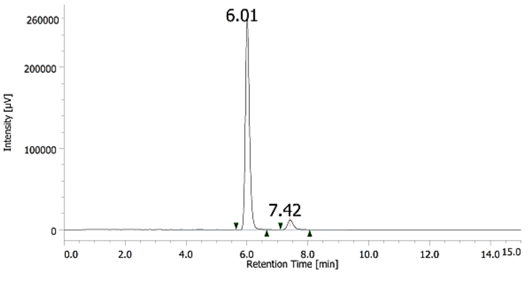
Scheme 7, compound 3kk. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 88% yield (59.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 6.0 min [major enantiomer], 7.4 min [minor enantiomer]. 88% ee. $[\alpha]^{23}_{D}$ −66.2 (*c* 0.52, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

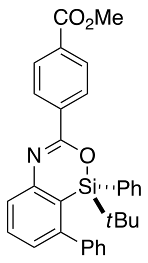
^{1}H NMR ($CDCl_3$): δ 8.11 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.55-7.46 (m, 4H), 7.41 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 2.1 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.28-7.20 (m, 3H), 7.17-7.06 (m, 3H), 7.00 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 2.41 (s, 3H), 0.82 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.4, 151.1, 148.7, 143.6, 141.4, 136.0, 135.2, 132.0, 131.3, 130.3, 130.2, 129.1, 128.5, 128.2, 128.1, 128.0, 127.6, 127.5, 120.0, 26.6, 21.7, 21.2. HRMS (FAB) calcd for $C_{30}H_{30}NOSi$ (M+H$^+$) 448.2091, found 448.2098.

racemate



88.1% ee

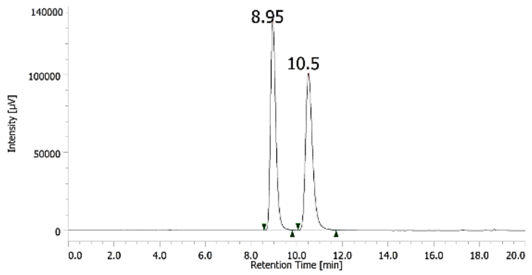




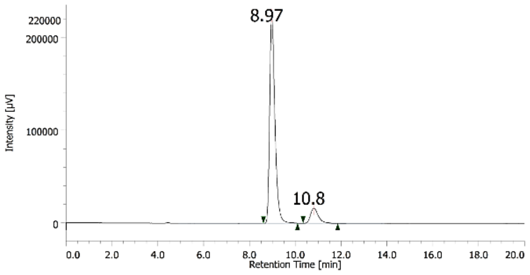
Scheme 7, compound 3ll. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 92% yield (67.5 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 9.0 min [major enantiomer], 10.8 min [minor enantiomer]. 80% ee. $[\alpha]^{19}_{\mathrm{D}}$ −48.1 (*c* 0.54, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

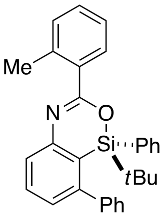
^{1}H NMR ($CDCl_3$): δ 8.27 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 8.08 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.57-7.51 (m, 2H), 7.50-7.45 (m, 2H), 7.43 (tt, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.28-7.22 (m, 1H), 7.21-7.08 (m, 3H), 6.99 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 3.94 (s, 3H), 0.81 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.9, 153.2, 150.6, 148.9, 143.4, 138.9, 135.8, 135.2, 132.1, 131.4, 130.4, 130.2, 129.6, 128.9, 128.3, 128.2, 128.1, 128.0, 127.7, 120.2, 52.4, 26.6, 21.1. HRMS (FAB) calcd for $C_{31}H_{30}NO_3Si$ ($M+H^+$) 492.1989, found 492.1987.

racemate



79.9% ee

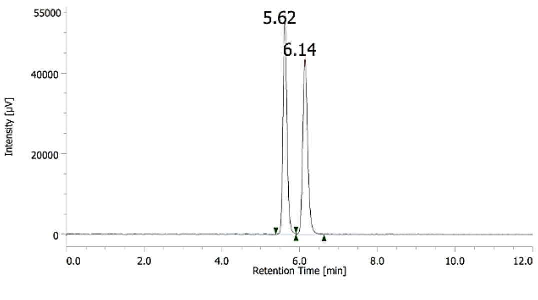




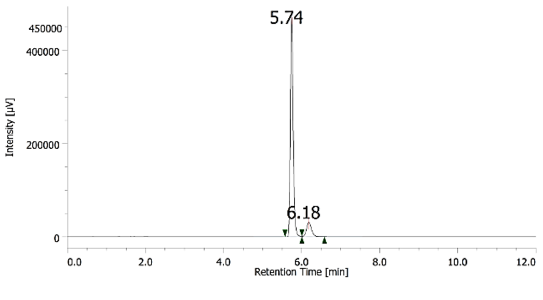
Scheme 7, compound 3mm. The reaction was conducted for 16 h at 60 °C. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 93% yield (62.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 5.7 min [major enantiomer], 6.2 min [minor enantiomer]. 79% ee. $[\alpha]^{23}_{D}$ +10.0 (*c* 0.55, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

^{1}H NMR ($CDCl_3$): δ 7.85 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.56-7.48 (m, 4H), 7.43 (t, $^3J_{HH}$ = 6.8 Hz, 1H), 7.34 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.31-7.18 (m, 4H), 7.15-7.08 (m, 3H), 7.01 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 2.61 (s, 3H), 0.80 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.9, 151.1, 148.7, 143.7, 138.4, 136.2, 135.1, 134.7, 131.6, 131.3, 130.3, 130.1, 130.0, 129.9, 128.4, 128.2, 128.1, 127.63, 127.59, 125.8, 119.7, 26.7, 22.3, 20.9. HRMS (FAB) calcd for $C_{30}H_{30}NOSi$ (M+H$^+$) 448.2091, found 448.2093.

racemate

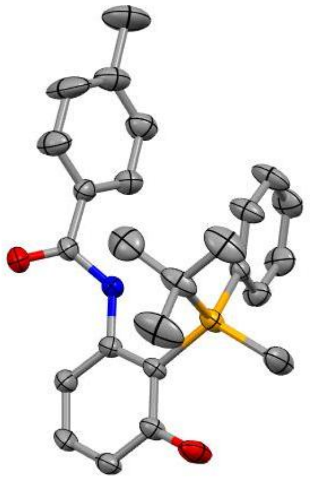


78.8% ee



X-ray crystal structures

Compound (*R*)-S2



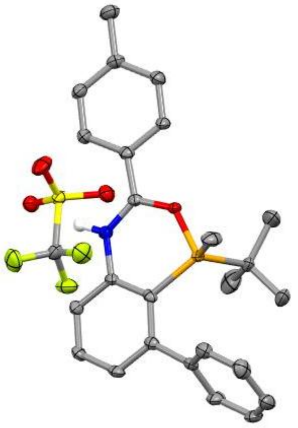
A colorless ethyl acetate solution of compound (*R*)-**S2** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature under hexane atmosphere. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2194996). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{27.5}H_{32}NO_2Si$	
Formula Weight	439.65	
Temperature	293 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Orthorhombic	
Space Group	$P2_12_12$	
Unit Cell Dimensions	a = 14.2116(14) Å	α = 90°
	b = 19.3311(19) Å	β = 90°
	c = 9.9202(9) Å	γ = 90°

Volume	2725.3(5) $Å^3$
Z Value	4
Calculated Density	1.072 g/cm^3
Absorption coefficient	0.108 mm^{-1}
F(000)	948
Crystal size	0.500 x 0.500 x 0.300 mm
Theta Range for Data Collection	3.054–27.546°
Index Ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 25$, $-12 \leq l \leq 11$
Reflections Collected	15527
Independent Reflections	6127 [R(int) = 0.0204]
Completeness to Theta = 25.242°	99.4%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.948 and 0.968
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6127 / 0 / 279
Goodness-of-Fit on F^2	1.025
Final R Indices [I>2sigma(I)]	$R1$ = 0.0542, $wR2$ = 0.1488
R Indices (All Data)	$R1$ = 0.0722, $wR2$ = 0.1614
Absolute Structure Parameter	0.07(3)
Largest Diff. Peak and Hole	0.437 and –0.175 $e^-/Å^3$

Compound (*R*)-3hh•HOTf



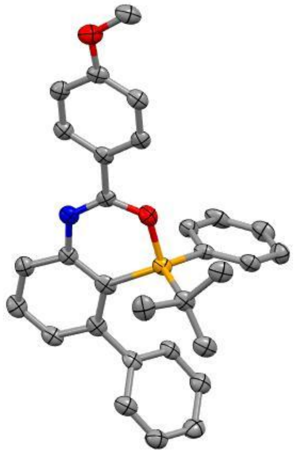
TfOH (6.9 µL, 77.8 µmol) was added to a solution of compound (*R*)-**3hh** (15.0 mg, 38.9 µmol) in 1,2-dichloroethane (0.5 mL) at room temperature. The mixture was concentrated under vacuum and the resulting solid was washed with Et_2O. A colorless $CHCl_3$ solution of this compound was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature under pentane atmosphere. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2194997). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal data and structure refinement.

Empirical Formula	$C_{26}H_{28}F_3NO_4SSi$	
Formula Weight	535.64	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Monoclinic	
Space Group	$P2_1$	
Unit Cell Dimensions	a = 9.145(2) Å	α = 90°

	b = 19.109(5) Å	β = 98.006(6)°
	c = 15.052(4) Å	γ = 90°
Volume	2604.7(11) Å^3	
Z Value	4	
Calculated Density	1.366 g/cm^3	
Absorption coefficient	0.225 mm^{-1}	
F(000)	1120	
Crystal size	0.500 x 0.100 x 0.100 mm	
Theta Range for Data Collection	3.099–27.567°	
Index Ranges	$-11 \le h \le 11$, $-24 \le k \le 24$, $-19 \le l \le 19$	
Reflections Collected	49778	
Independent Reflections	11925 [R(int) = 0.0758]	
Completeness to Theta = 25.242°	99.7%	
Absorption Correction	Semi-empirical from equivalents	
Max. and Min. Transmission	0.896 and 0.978	
Refinement Method	Full-matrix least-squares on F^2	
Data / Restraints / Parameters	11925 / 1 / 659	
Goodness-of-Fit on F^2	0.989	
Final R Indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1167	
R Indices (All Data)	R1 = 0.0645, wR2 = 0.1225	
Absolute Structure Parameter	–0.02(4)	
Largest Diff. Peak and Hole	1.055 and –0.435 e$^-$/Å^3	

Compound (*R*)-3b



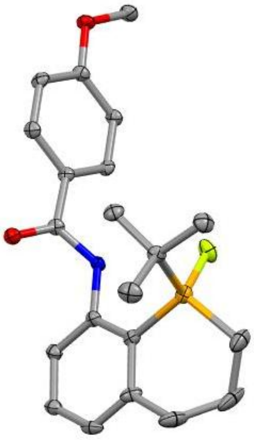
A colorless dichloromethane solution of compound (*R*)-**3b** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature under hexane atmosphere. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2194998). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal data and structure refinement.

Empirical Formula	$C_{30}H_{29}NO_2Si$	
Formula Weight	463.63	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Monoclinic	
Space Group	$P2_1$	
Unit Cell Dimensions	a = 9.521(3) Å	α = 90°
	b = 12.367(3) Å	β = 112.719(6)°
	c = 11.509(3) Å	γ = 90°
Volume	1250.0(6) $Å^3$	

Z Value	2
Calculated Density	1.232 g/cm^3
Absorption coefficient	0.121 mm^{-1}
F(000)	492
Crystal size	0.200 x 0.200 x 0.100 mm
Theta Range for Data Collection	3.536–27.480°
Index Ranges	$-12 \leq h \leq 11$, $-16 \leq k \leq 15$, $-14 \leq l \leq 14$
Reflections Collected	22935
Independent Reflections	5645 [*R*(int) = 0.1207]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.976 and 0.988
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5645 / 1 / 311
Goodness-of-Fit on F^2	0.908
Final *R* Indices [I>2sigma(I)]	$R1$ = 0.0598, $wR2$ = 0.1253
R Indices (All Data)	$R1$ = 0.0820, $wR2$ = 0.1305
Absolute Structure Parameter	0.02(12)
Largest Diff. Peak and Hole	0.665 and –0.395 e$^-$/Å^3

Compound 4w



A colorless CH_2Cl_2 solution of compound **4v** was prepared. Crystals suitable for X-ray analysis were obtained by layering hexane and slow diffusion of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2247904). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal data and structure refinement.

Empirical Formula	$C_{21}H_{26}FNO_2Si$	
Formula Weight	371.52	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Triclinic	
Space Group	*P*–1	
Unit Cell Dimensions	a = 9.572(3) Å	α = 108.6130(10)°
	b = 12.507(5) Å	β = 90.260(7)°
	c = 17.419(6) Å	γ = 92.4160(10)°
Volume	1974.2(12) $Å^3$	

Z Value	4
Calculated Density	1.250 g/cm^3
Absorption coefficient	0.143 mm^{-1}
F(000)	792
Crystal size	0.200 x 0.200 x 0.050 mm
Theta Range for Data Collection	3.153–27.344°
Index Ranges	$-11 \le h \le 12$, $-16 \le k \le 15$, $-22 \le l \le 22$
Reflections Collected	35709
Independent Reflections	8865 [R(int) = 0.1274]
Completeness to Theta = 25.242°	99.8%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.993 and 0.972
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	8865 / 0 / 485
Goodness-of-Fit on F^2	1.045
Final R Indices [I>2sigma(I)]	$R1$ = 0.0828, $wR2$ = 0.2023
R Indices (All Data)	$R1$ = 0.1466, $wR2$ = 0.2222
Largest Diff. Peak and Hole	0.901 and –0.466 e$^-$/Å^3

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Chapter 3

Nickel-catalyzed synthesis of silaindanes via sequential C–H activating 1,5-nickel migration and C–Si activating 1,4-nickel migration

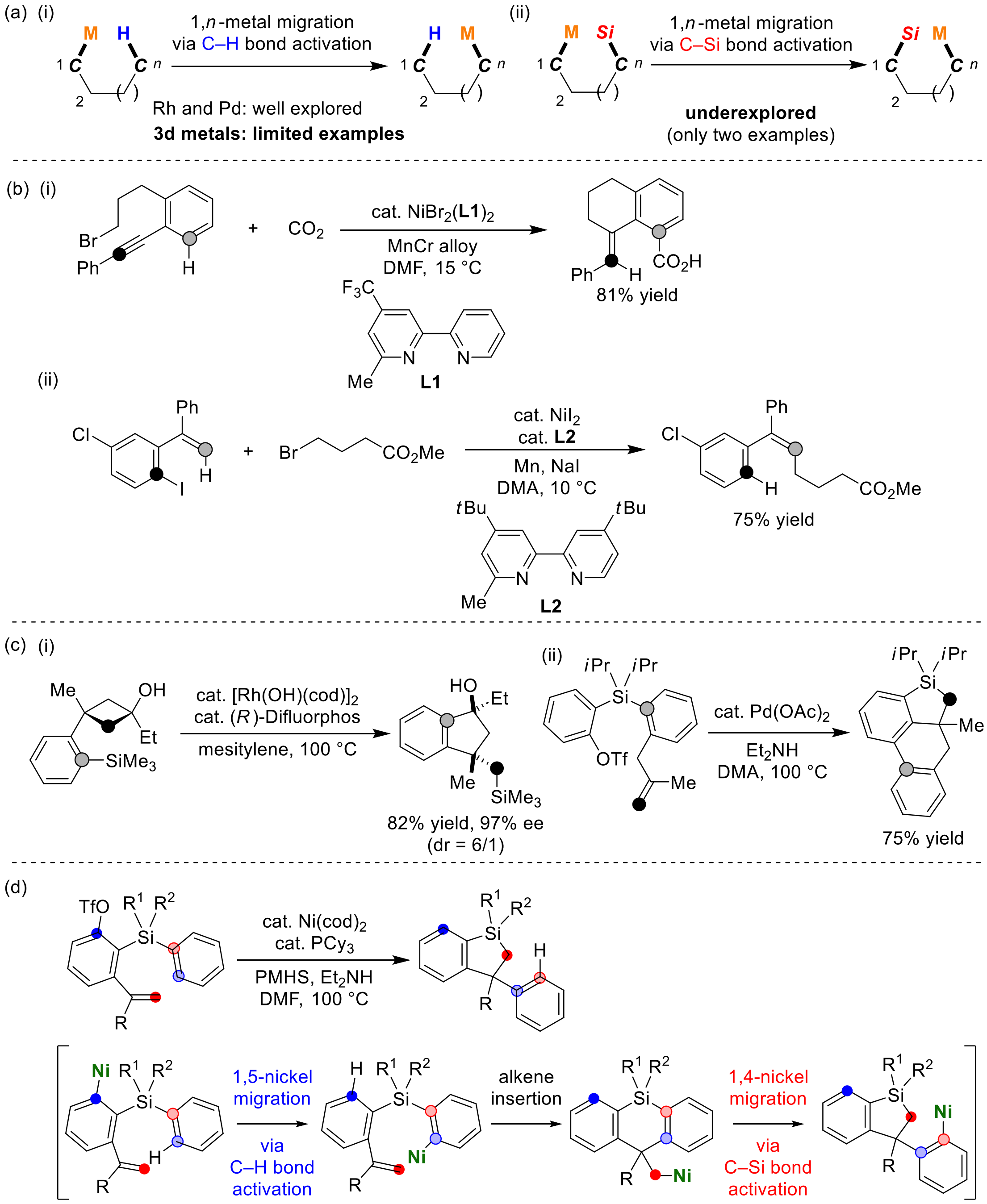
3.1 Introduction

Development of a new method of carbon–carbon or carbon–heteroatom bond formation is of high importance in advancement of organic synthesis because it not only enables an access to new molecular skeletons but also allows an alternative synthetic strategy for existing molecules. In particular, the reactions involving activation of unreactive bonds under transition-metal catalysis are attractive in view of efficiency of the overall synthetic process.

Among them, 1,*n*-metal migration from carbon to carbon within organic compounds through the exchange of a carbon–metal bond and a C–H bond is highly effective for functionalization at a remote unreactive C–H bond (Scheme 1a(i)).[1] The metals of choice in the literature are typically rhodium[2] and palladium,[3] and their 1,4-migration processes are most widely known to date along with some examples involving 1,5-migration of these metals.[4,5] In contrast, the use of less precious and more abundant 3d transition metals has been much less explored,[6] and regarding the use of nickel as the migrating metal catalyst, several examples of 1,4-nickel migration started to appear only recently (Scheme 1b).[7,8] Considering the wide utility of nickel-catalyzed reactions in organic synthesis,[9] expanding the scope of 1,*n*-nickel migration processes would be desirable for developing new and more sustainable methods of synthesizing various useful organic compounds that are currently difficult to prepare.

In addition to 1,*n*-metal migration via activation of a C–H bond, analogous processes involving the activation of a C–Si bond would be synthetically attractive particularly in the context of preparation of complex organosilicon compounds (Scheme 1a(ii)), because intramolecular silylation of an originally formed carbon–metal bond can take place along with simultaneous formation of a new carbon–metal bond for further transformation. Although various reactions involving the cleavage of an unactivated C–Si bond have been reported to date,[10] such 1,*n*-metal migration processes are significantly much less explored. In fact, a report by Cramer and coworkers involving a 1,4-C–Rh/C–Si bond exchange for the synthesis of silicon-substituted indanols[11] and a recent report by our group involving a 1,5-C–Pd/C–Si bond exchange for the synthesis of highly fused tetrahydrophenanthrosiloles[12] are the only examples that can be categorized in this reaction pattern (Scheme 1c).

Regarding the utility of organosilanes, they are becoming indispensable not only as synthetic intermediates[13] but also as functional molecules for bioactive substances[14] or optoelectronic materials.[15] In particular, silicon-containing cyclic compounds are attracting increasing attention in the fields of pharmaceutical and materials science, which makes it even more important to develop new and efficient synthetic methods of various silacyclic compounds. In this context, herein the author devised a new way of synthesizing 3,3-disubstituted 1-silaindanes,[16] silicon-switched analogs of biologically relevant indanes,[17] from 3-alkenyl-2-(arylsilyl)aryl triflates under nickel catalysis, highlighting the involvement of unprecedented 1,5-nickel migration via activation of a C–H bond and 1,4-nickel migration via activation of a C–Si bond in a single catalytic process (Scheme 1d).

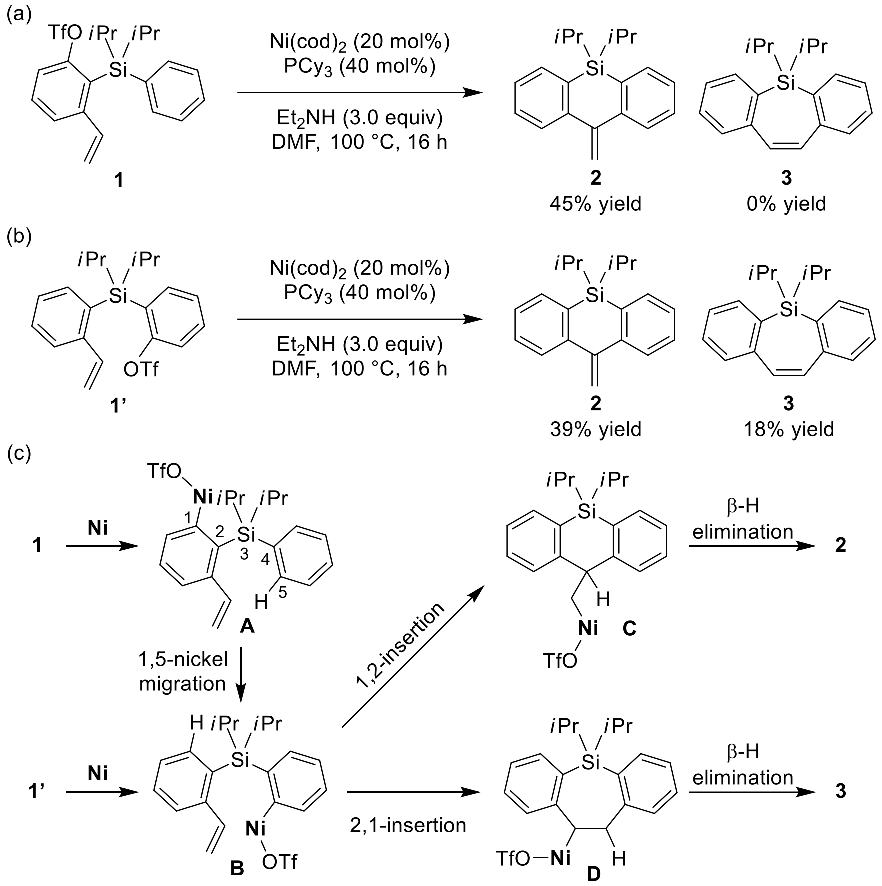


Scheme 1. (a) 1,*n*-Metal migration via (i) C–H bond activation and (ii) C–Si bond activation. (b) Examples of reactions involving 1,4-nickel migration via C–H bond activation. (c) Examples of reactions involving 1,*n*-metal migration via C–Si bond activation. (d) This work: nickel-catalyzed synthesis of 1-silaindanes through 1,5-nickel migration via C–H bond activation and 1,4-nickel migration via C–Si bond activation.

3.2 Results and discussion

3.2.1 Reaction development and scope

In an initial investigation, the author explored the feasibility of 1,5-nickel migration and its utility by employing 3-vinyl-2-(diisopropylphenylsilyl)phenyl triflate (**1**) as a model substrate (Scheme 2a). In the presence of a catalytic amount of Ni(cod)$_2$ and PCy$_3$ with Et$_2$NH in DMF at 100 °C, product **2** with a 6-membered silacycle was obtained in 45% yield with no formation of its isomer **3** with a 7-membered ring. The reaction pathway from **1** to **2** is explained as follows (Scheme 2c).[18] Oxidative addition of aryl triflate of **1** to nickel(0) gives arylnickel species **A**. This then undergoes 1,5-nickel migration via activation of a C–H bond of the phenyl group to give another arylnickel species **B**. From this intermediate, intramolecular 1,2-insertion of the pendant vinyl group followed by β-hydrogen elimination leads to product **2** via intermediate **C**. On the other hand, if the alkene insertion proceeds in a 2,1-fashion, isomeric compound **3** would be obtained after β-hydrogen elimination of intermediate **D**. In comparison, the reaction was also conducted using substrate **1'**, which should directly generate intermediate **B** without going through the 1,5-nickel migration (Scheme 2b). As a result, both compounds **2** and **3** were obtained in the ratio of 68/32. These results indicate that 1,5-nickel migration is indeed a viable process and that the presence or absence of this migration can significantly influence the product selectivity despite the involvement of seemingly the same reaction intermediate, which has not been well appreciated in the reported 1,*n*-metal migration reactions.[5d]

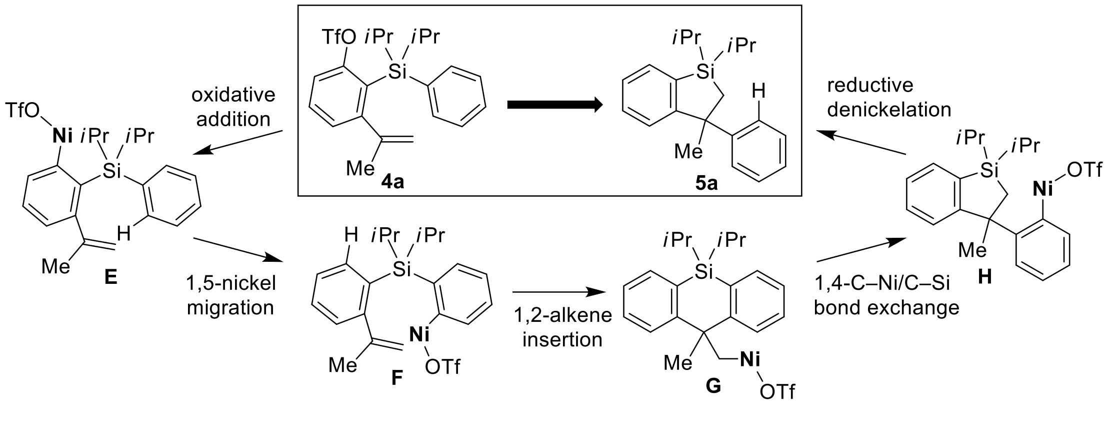


Scheme 2. Nickel-catalyzed reactions of (a) **1** and (b) **1'** to give **2** and/or **3**. (c) Proposed reaction pathways from **1** and **1'** to **2** and **3**.

Based on this initial assessment, the author designed 2-(arylsilyl)aryl triflate **4a** having propen-2-yl group at the 3-position as a substrate for a nickel-catalyzed reaction to promote further transformation of the initially formed 6-membered silacycle by suppressing the subsequent β-hydrogen elimination. After some investigation, the author found that 5-membered silaindane **5a** could be obtained as the major product under reductive conditions in the presence of poly(methylhydrosiloxane) (PMHS) along with minor amounts of 7-membered **6a** and **6a'** (Table 1, entry 1). A proposed reaction pathway from **4a** to **5a** is illustrated in Scheme 3. As was the case for the reaction of **1**, oxidative addition of aryl triflate **4a** to nickel(0) gives arylnickel species **E**, which undergoes 1,5-

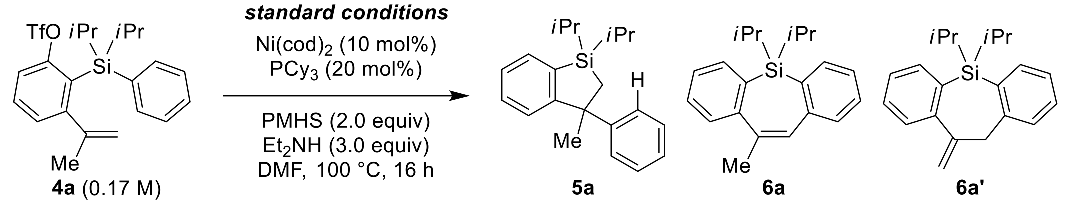
nickel migration to give another arylnickel species **F**. Subsequent intramolecular 1,2-insertion of the alkene gives alkylnickel intermediate **G** having a 6-membered silacycle. Since this has no β-hydrogen to eliminate, a new elemental step "1,4-C–Ni/C–Si bond exchange" takes place to give arylnickel species **H** with a 5-membered silaindane structure. Finally, reductive cleavage of the C–Ni bond leads to product **5a**.

As is discussed later, the use of isomeric compound **4a'** as the substrate resulted in a lower selectivity of **5a**/(**6a**+**6a'**) under the same conditions (entry 2), which is consistent with the trend observed for the reaction of **1'** in place of **1** (Scheme 2). Regarding the effect of the reaction conditions, PCy_3 was found to be a superior ligand compared to some other ligands such as PPh_3, IPr, and dtpby (entries 3–5). In addition to PMHS, other reducing agents such as Et_3SiH and Zn powder were also effective (entries 6 and 7). The yield of **5a** became much lower in the absence of Et_2NH or PMHS (entries 8 and 9), but the reaction with 10 equiv of Et_2NH showed a decent yield of **5a** even in the absence of PMHS, suggesting that the amine alone can serve as a hydrogen donor (vide infra). Furthermore, the use of a palladium catalyst did not provide silaindane **5a** and preferentially led to the formation of **6a'** along with dibenzosilole **7a**[19] (entry 11).



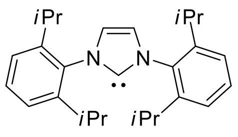
Scheme 3. Proposed reaction pathway from **4a** to **5a**.

Table 1. Nickel-catalyzed reaction of **4a**: Effect of reaction conditions.

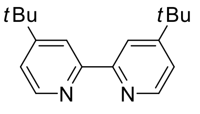


entry	deviation from the standard conditions	yield of **5a** (%)[a]	yield of **6a**+**6a'** (%)[a]
1	none	82	6
2	**4a'** instead of **4a**	22	16
3	PPh$_3$ instead of PCy$_3$	20	2
4	IPr instead of PCy$_3$	4	0
5	dtbpy (10 mol%) instead of PCy$_3$	24	0
6	Et$_3$SiH instead of PMHS	82	6
7	Zn instead of PMHS	64	2
8	no Et$_2$NH	30	0
9	no PMHS	22	0
10	no PMHS, 10 equiv of Et$_2$NH	61	5
11[b]	Pd(OAc)$_2$ instead of Ni(cod)$_2$	0	39

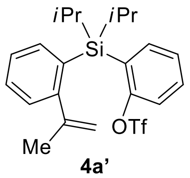
[a] Determined by ^{1}H NMR against internal standard (MeNO$_2$). [b] Compound **7a** was obtained in 26% yield.



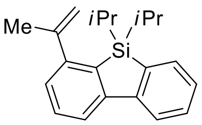
IPr



dtbpy

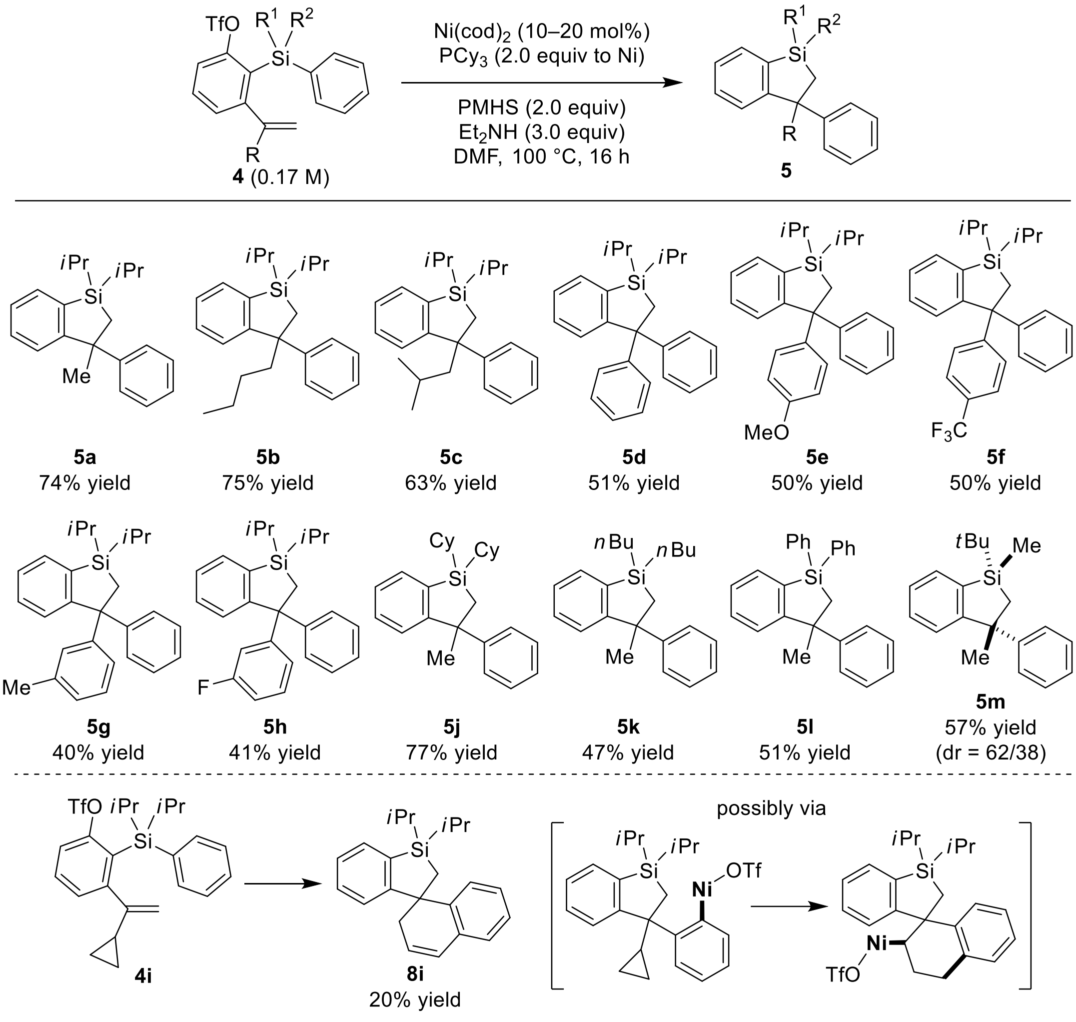


4a'



7a

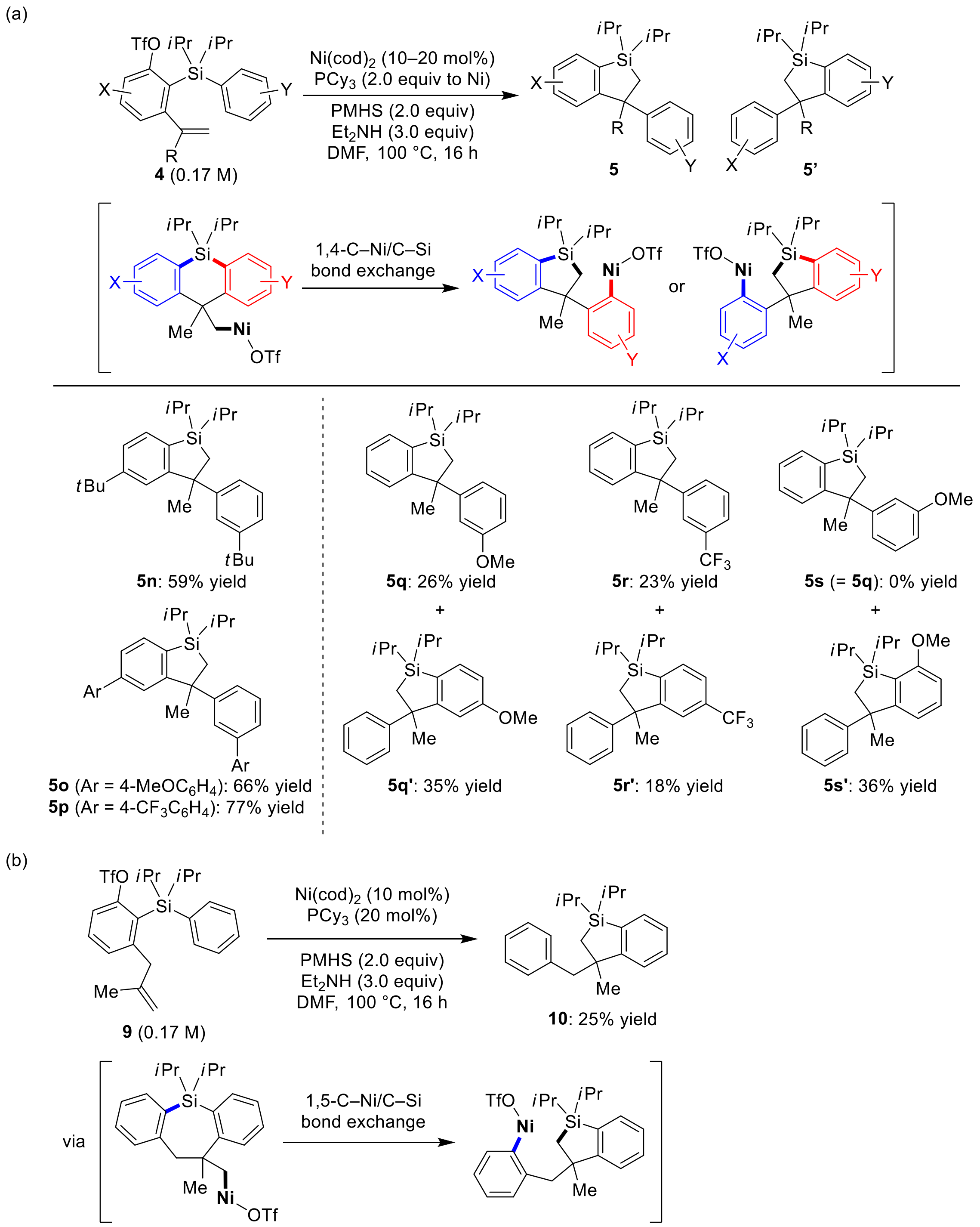
Under the conditions in Table 1, entry 1, several R groups on the alkene were tolerated including both alkyl and aryl groups to give corresponding silaindanes **5b–h** as summarized in Scheme 4. The structure of **5d** was unambiguously established by X-ray crystallographic analysis.[20] On the other hand, cyclopropyl substituted compound **4i** gave spirocyclic silaindane **8i** via ring-opening of the cyclopropane, albeit in a modest yield. Regarding the substituents R^1 and R^2 on silicon, both alkyl and aryl groups can be incorporated to give products **5j–m** in moderate to good yields with diastereoselectivity of 62/38 for unsymmetric **5m**.



Scheme 4. Nickel-catalyzed reactions of **4** to give **5**: Scope 1.

For the substrates having substituents on the benzene rings on silicon, two different products could potentially be obtained depending on the position selectivity for the C–Si bond cleavage (**G** → **H** in Scheme 3). When substrates that lead to a symmetric intermediate are employed, corresponding **5n–p** were obtained as the only silaindane products due to the nonexistence of this selectivity issue (Scheme 5a). On the other hand, substrates with X ≠ Y actually gave a mixture of two isomeric products. For example, substrate **4q** with X = H and Y = 4-OMe gave products **5q** and **5q'** in the ratio of 43/57, slightly favoring the C–Si bond cleavage of the benzene ring without the methoxy group. In the case of substrate **4r** with X = H and Y = 4-CF_3, products **5r** and **5r'** were obtained in the ratio of 56/44, slightly favoring the C–Si bond cleavage of the trifluoromethylated benzene ring. It is worth noting that the use of substrate **4s** with 2-methoxyphenyl group on silicon (X = H, Y = 2-OMe) gave **5s'** as the only silaindane product with no formation of **5s** although the yield was moderate. These results indicate that the electronic nature does not significantly affect the position of C–Si bond cleavage and the steric environment seems to be more influential.

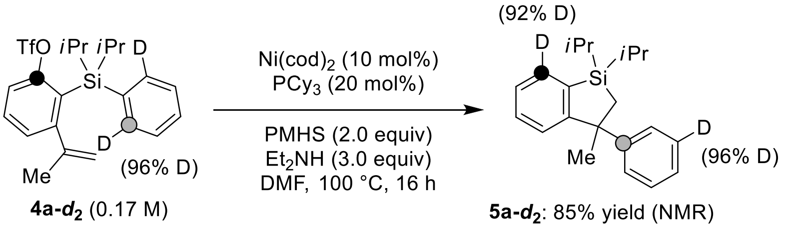
In addition to 2-(arylsilyl)aryl triflates **4** having a 2-substituted alkenyl group at the 3-position, compound **9** having a methallyl group at the 3-position was also examined as a substrate for the present catalysis (Scheme 5b). Although the reaction efficiency became lower, silaindane **10** with a benzyl group was obtained, indicating the involvement of a new 1,5-nickel migration via a C–Si bond activation to form a 5-membered silacycle from a 7-membered intermediate.[12]



Scheme 5. (a) Nickel-catalyzed reactions of **4** to give **5** and/or **5'**: Scope 2. (b) Nickel-catalyzed reaction of **9** to give **10** via 1,5-C–Ni/C–Si bond exchange.

3.2.2 Mechanistic investigation

To gain insights into the reaction mechanism of the present catalysis, the author conducted some deuterium labeling experiments. At first, to probe the involvement of 1,5-nickel migration via a C–H bond activation of the phenyl group on silicon (**E** → **F** in Scheme 3), substrate **4a-*d*₂** having 2,6-bisdeuteriophenyl group was employed (eq 1). Product **5a-*d*₂** thus obtained showed high deuterium contents at the 7-position of the silaindane framework and the 3-position of the phenyl group, indicating that the exchange between nickel and deuterium did take place in a 1,5-fashion as expected.

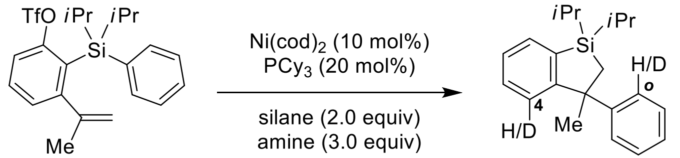


(1)

The author also explored to identify the hydrogen donor at the reductive cleavage of the C–Ni bond of intermediate **H** in Scheme 3. Considering the easier access to a deuterated variant, the author employed Et_3SiH instead of PMHS for the reaction of **4a** in this study (Table 2, entry 1). When Et_3SiD was used under otherwise the same conditions, product **5a** was obtained with 20% deuterium incorporation at the *ortho*-position of the phenyl group (C_o) along with 19% deuterium incorporation at the 4-position of the silaindane (C_4) (entry 2). In addition, when $(CD_3CD_2)_2NH$ was used instead of Et_2NH in the presence of Et_3SiH, obtained product **5a** showed 20% deuterium incorporation at C_o and 41% deuterium incorporation at C_4 (entry 3). These results indicate that both Et_3SiH and Et_2NH act as a hydrogen donor presumably through the formation of nickel hydride **I** as shown in Scheme 6a.[21] Furthermore, arylnickel species

H partially undergoes another 1,5-nickel migration to form intermediate **J** through the activation of a C–H bond at C_4 prior to the hydride reduction (Scheme 6b). When the reaction of **4a** was conducted using Et_3SiD and $(CD_3CD_2)_2NH$ at the same time, the deuterium incorporation in **5a** was increased both at C_o (26%) and C_4 (60%) (entry 4). In comparison, the use of $(n\mathrm{Bu})_2ND$ in the presence of Et_3SiH led to no incorporation of deuterium in **5a** (entry 5), confirming that the hydrogen atom is installed as hydride, not as proton.

Table 2. Nickel-catalyzed reaction of **4a**: Effect of deuterated reagents.

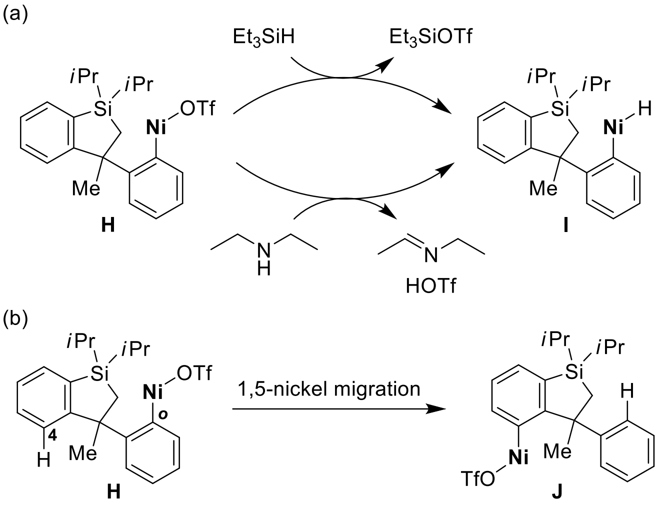


4a (0.17 M)

5a: 81–85% (NMR)

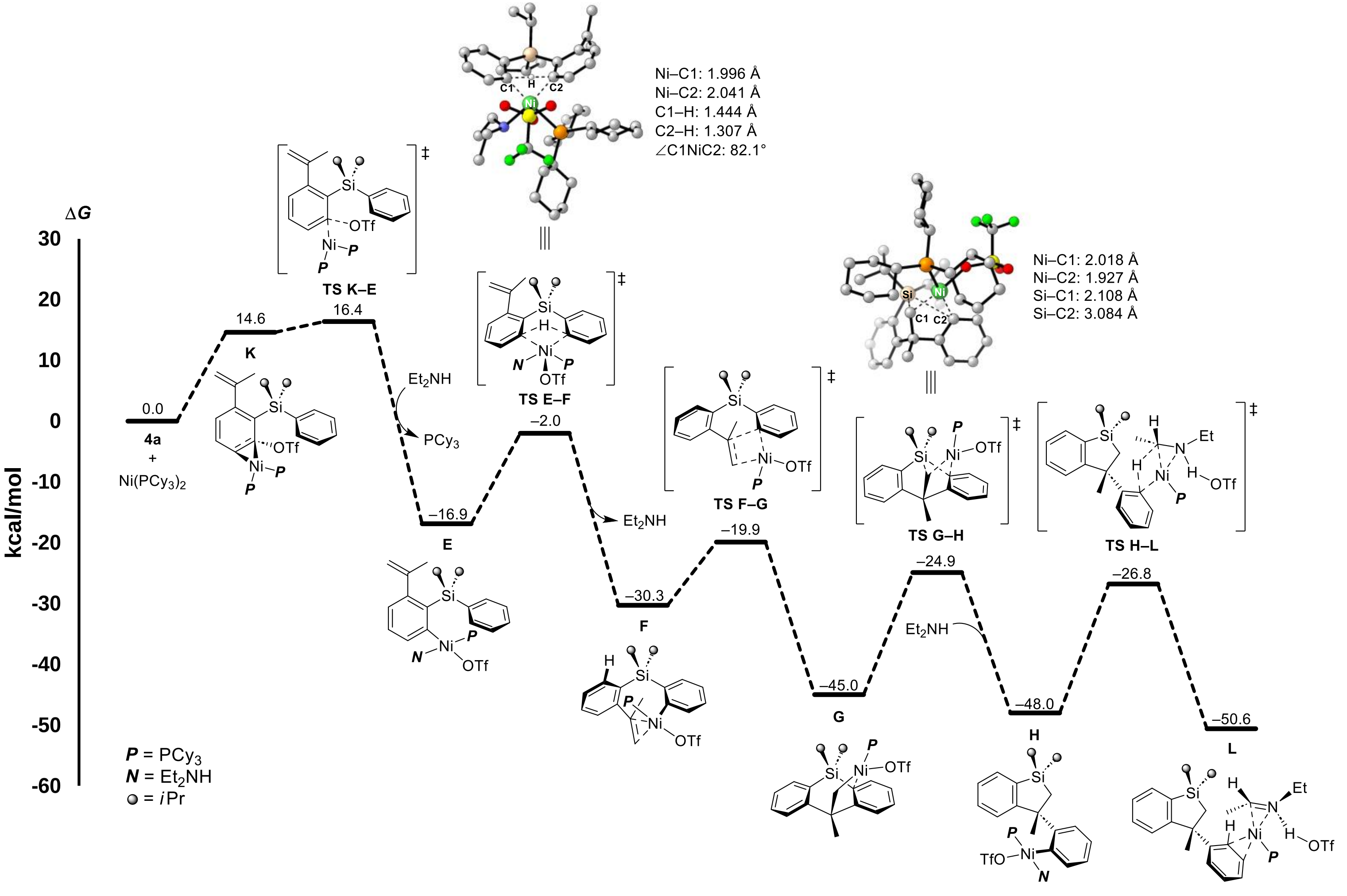
entry	silane	amine	deuterium content (%)[a]	
			C_o	C_4
1	Et_3SiH	Et_2NH	—	—
2	Et_3SiD	Et_2NH	20	19
3	Et_3SiH	$(CD_3CD_2)_2NH$	20	41
4	Et_3SiD	$(CD_3CD_2)_2NH$	26	60
5	Et_3SiH	$(n\mathrm{Bu})_2ND$	0	0

[a] Determined by ^1H NMR.



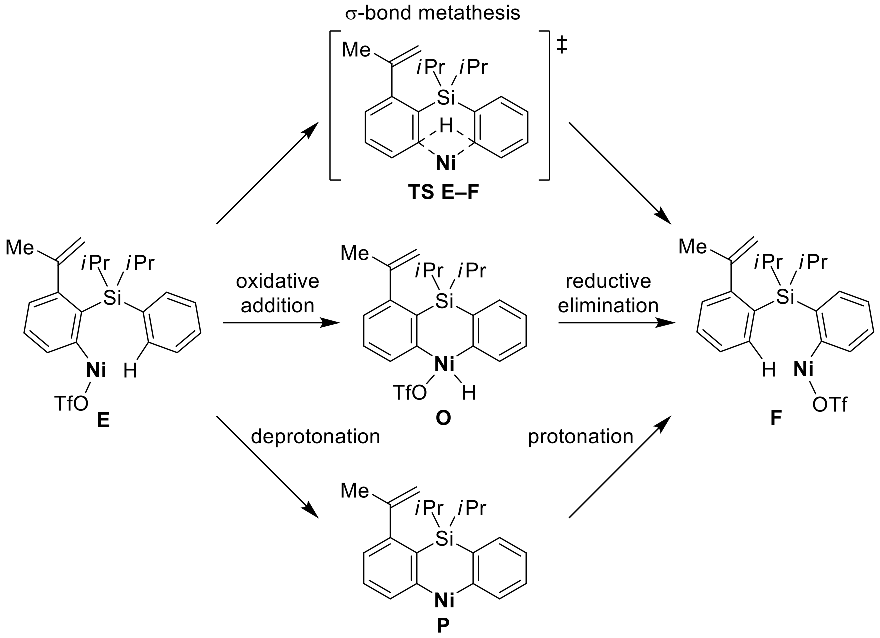
Scheme 6. (a) Proposed pathways for the formation of nickel hydride **I** from **H**. (b) 1,5-nickel migration from C_o to C_4 in **H** to give **J**.

Based on the above experimental results, DFT calculation was carried out for the detailed reaction pathways of the present catalysis. Calculations were performed for the reaction of **4a** in the presence of $Ni(PCy_3)_2$ and Et_2NH with the Gaussian 16 package.[22] Geometry optimizations were conducted under vacuum using the DFT-M06 functional[23] with LANL2DZ basis set[24] for Ni and P, 6-31+G(d) basis set[25] for Si, and 6-31G(d) basis set[25] for other atoms. Frequency analyses were carried out to confirm that each structure is a local minimum (no imaginary frequency) or a transition state (only one imaginary frequency). The energies were further estimated by means of single-point calculations using the same level of theory as the geometry optimization, including the solvation effect with the SCF-SMD model[26] using the experimental DMF solvent. For **K** and **TS K–E**, geometry optimizations were carried out including solvation effect. The Gibbs energy changes were assessed at standard conditions (298.15 K and 1 atm), and the resulting Gibbs energy profiles are depicted in Scheme 7.



Scheme 7. Calculated reaction pathway from **4a** to give **5a**.

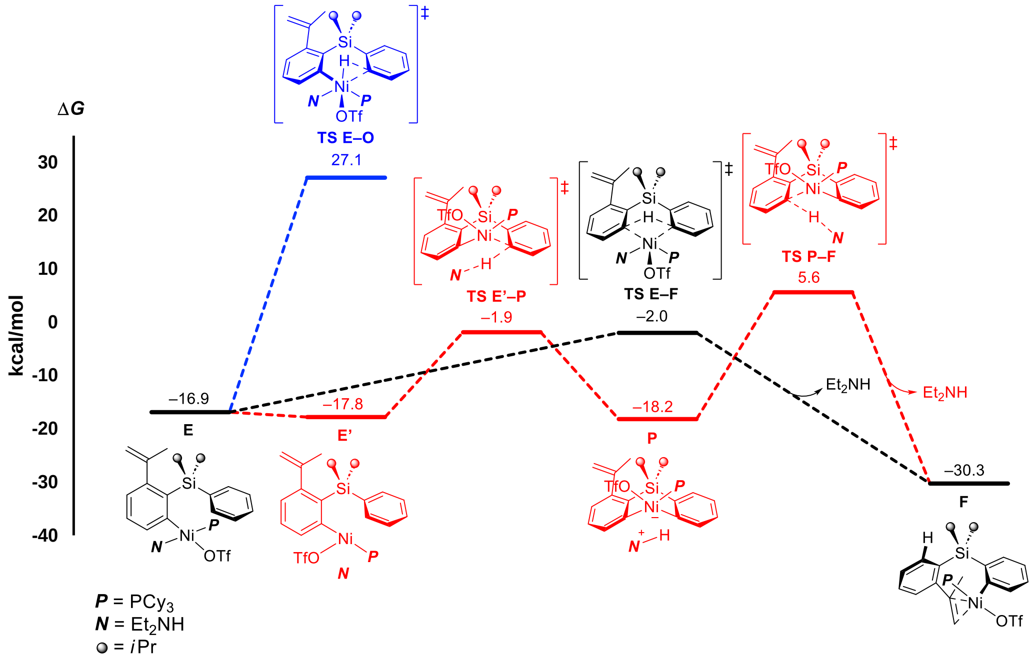
The catalytically active species Ni(PCy$_3$)$_2$, generated *in-situ* from Ni(cod)$_2$ and PCy$_3$, forms a complex with substrate **4a** to give **K** (14.6 kcal/mol). This undergoes oxidative addition of the C–O bond to the nickel center to give arylnickel complex **E** (–16.9 kcal/mol) through **TS K–E** (16.4 kcal/mol, $\Delta G^\ddagger$ = 1.8 kcal/mol).[27] Subsequent 1,5-nickel migration is exergonic by 13.4 kcal/mol due to the coordination of the alkene moiety to nickel, giving another arylnickel intermediate **F** (–30.3 kcal/mol) by σ-bond metathesis of a C–Ni bond and a C–H bond via **TS E–F** (–2.0 kcal/mol, $\Delta G^\ddagger$ = 14.9 kcal/mol). Intramolecular 1,2-insertion of the alkene to the C–Ni bond then takes place through **TS F–G** (–19.9 kcal/mol, $\Delta G^\ddagger$ = 10.4 kcal/mol) to give alkylnickel intermedaite **G** having a 6-membered silacycle (–45.0 kcal/mol). Subsequently, 1,4-C–Ni/C–Si bond exchange proceeds by σ-bond metathesis via **TS G–H** (–24.9 kcal/mol, $\Delta G^\ddagger$ = 20.1 kcal/mol) to form arylnickel complex **H** with a silaindane framework (–48.0 kcal/mol). From this intermediate, one of the possible pathways for the reductive C–Ni bond cleavage is calculated as representative. Thus, reduction of the C–Ni bond by coordinated Et$_2$NH was found to occur in a concerted manner, delivering a methylene hydrogen of the amine to the aryl carbon via **TS H–L** (–26.8 kcal/mol, $\Delta G^\ddagger$ = 21.2 kcal/mol) to give **5a**-bound nickel(0) species **L** (–50.6 kcal/mol) without forming nickel hydride intermediate **I** (see Scheme 6). In addition to this pathway, reduction by hydrosilane (PMHS or Et$_3$SiH) as well as another 1,5-nickel migration to the 4-position of the silaindane prior to the reduction would compete in the real system.



Scheme 8. Possible reaction pathways for the 1,5-nickel migration from **E** to give **F**.

In addition to the proposed 1,5-nickel migration pathway from **E** to **F** by σ-bond metathesis via **TS E–F** (Scheme 8, top), two other possible pathways (1) oxidative addition–reductive elimination via nickel(IV) (Scheme 8, middle) and (2) arylation by deprotonation–dearylation by protonation via nickel(II) (Scheme 8, bottom) were theoretically examined (Scheme 9). As a result, the reaction pathway involving oxidative addition was found to be kinetically unfavored (**TS E–O**: $\Delta G^{\ddagger}$ = 44.0 kcal/mol). This is consistent with the previous reports that the formation of nickel(IV) species usually requires strong oxidants and appropriate multidentate ligands.[28] In the case of deprotonative arylation of **E** with the aid of Et_2NH as base to give diarylnickel(II) **P**, dissociation of coordinated Et_2NH from the nickel center of **E** (–16.9 kcal/mol) gives **E'** (–17.8 kcal/mol), and Et_2NH abstracts a proton from the *ortho*-position of the neighboring phenyl group via transition state **TS E'–P** (–1.9 kcal/mol, $\Delta G^{\ddagger}$ = 15.9 kcal/mol) to give **P** (–18.2 kcal/mol). Subsequent protonation of the original aryl–nickel bond by the resulting tertiary ammonium takes place through transition state **TS P–F** (5.6 kcal/mol, $\Delta G^{\ddagger}$ = 23.8

kcal/mol) to give 1,5-migrated intermediate **F** (–30.3 kcal/mol). This pathway is slightly less favorable compared to the concerted σ-bond metathesis via **TS E–F**. Therefore, it is suggested that 1,5-nickel migration from **E** to **F** proceeds via the concerted σ-bond metathesis mechanism.

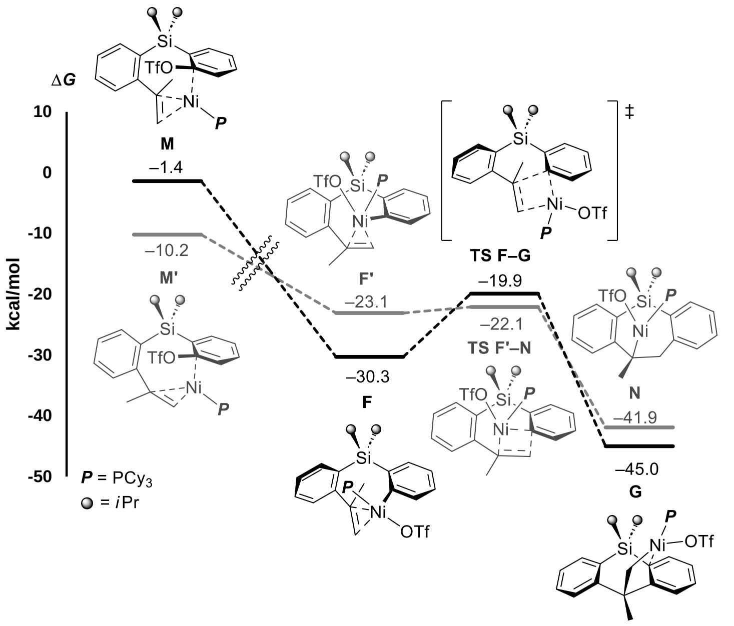


Scheme 9. Alternative calculated reaction pathways from **E** to give **F**.

As described in Table 1, the reaction of **4a** via 1,5-nickel migration showed higher selectivity toward **5a** than the reaction of isomeric **4a'** without 1,5-nickel migration, which gave a significant amount of 7-membered silacycles **6a**/**6a'**. To understand the origin of this selectivity difference, DFT calculation was conducted to probe the effect of propen-2-yl group on the oxidative addition of **4a'** and the subsequent intramolecular alkene insertion (Scheme 10).

Two possible alkene-coordinated Ni/**4a'** complexes **M** and **M'** were considered. **M** has a conformation toward intermediate **G** having a 6-membered silacycle via oxidative adduct **F**, and **M'** has a conformation toward intermediate **N** having a 7-

membered silacycle via oxidative adduct **F'**. **M'** was found to be more stable than **M**, and arylnickel intermediate **F'** generated by oxidative addition of **M'** undergoes almost barrierless 2,1-insertion of the coordinated alkene via **TS F'–N** ($\Delta G^‡$ = 1.0 kcal/mol) to give alkylnickel intermediate **N** having a 7-membered ring. Subsequent β-hydrogen elimination of **N** results in the formation of **6a** or **6a'**. On the other hand, oxidative addition of less stable **M** gives arylnickel intermediate **F**, which is more stable than intermediate **F'**. Subsequent 1,2-insertion of alkene via **TS F–G** ($\Delta G^‡$ = 10.4 kcal/mol) gives alkylnickel intermediate **G** with a 6-membered silacycle as was described in Scheme 7. For the reaction of substrate **4a**, intramolecular alkene coordination can occur only after 1,5-nickel migration from intermediate **E** (see Scheme 7), and energetically more stable intermediate **F** would be preferentially generated. This leads to the formation of 6-membered silacycle **G**, which eventually provides silaindane product **5a**. Although the calculated energy values do not directly coincide with the experimentally observed product ratios, pre-coordination of propen-2-yl group of **4a'** to nickel before the oxidative addition as opposed to post-coordination of the alkene after 1,5-nickel migration in the case of **4a** provides a plausible explanation for the observed selectivity difference and illustrates the important role of 1,5-nickel migration in the present catalytic process.



Scheme 10. Calculated reaction pathways for alkene insertion steps for the reaction of **4a'**.

3.3 Conclusion

The author developed a nickel-catalyzed synthesis of 3,3-disubstituted 1-silaindanes, silicon-switched analogs of bioactive indane skeletons, from 3-alkenyl-2-(arylsilyl)aryl triflates. The reaction involves hitherto unreported 1,5-nickel migration with a C–H bond activation followed by 1,4-nickel migration with a C–Si bond activation. It was found that 1,5-nickel migration not only enables the C–H bond activation at a remote position, but also can change the regioselectivity of subsequent alkene insertion compared to the direct nickelation of the same position. Deuterium labeling experiments revealed that both hydrosilane and secondary amine can serve as a hydride donor in the present catalysis with the involvement of additional 1,5-nickel migration prior to reductive denickelation. DFT calculations suggested that both of these 1,5-C–Ni/C–H and 1,4-C–Ni/C–Si bond exchanges proceed through a σ-bond metathesis mechanism. The results obtained here demonstrate the high potential of catalytic reactions involving nickel migrations via C–H and C–Si bond activations for the synthesis of cyclic organosilicon compounds through a new reaction pathway.

3.4 Experimental section

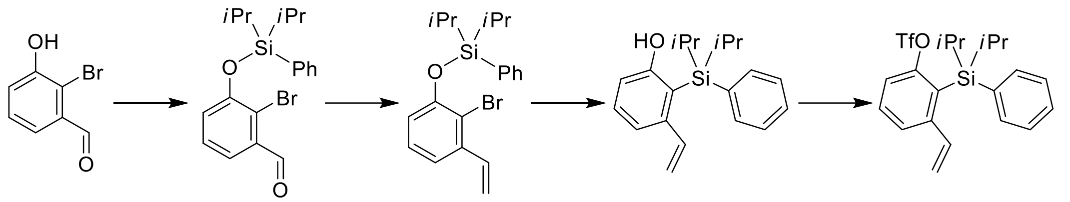
General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. Preparative GPC was performed with JAI LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent. Reversed-phase chromatography was performed with JAI LaboACE LC-5060 equipped with Mightysil RP-18GPII columns using MeCN as an eluent. NMR spectra were recorded on JEOL JNM-ECS400, JEOL JNM-ECZL400S, or Agilent UnityInova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 spectrometer. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200 system with graphite-monochromated Mo-Kα (0.71075 Å) radiation. Computations were performed using workstation at Research Center for Computational Science, National Institutes of Natural Sciences, Okazaki, Japan.

Et_2NH (FUJIFILM Wako Chemicals) was distilled over KOH under vacuum. DMF (FUJIFILM Wako Chemicals; dehydrated), acetone (FUJIFILM Wako Chemicals), EtOH (FUJIFILM Wako Chemicals), and H_2O (Kishida Chemical) were degassed by purging nitrogen prior to use for palladium- or nickel-catalyzed reactions. THF (Kanto Chemical; dehydrated), Et_2O (FUJIFILM Wako Chemicals; dehydrated), CH_2Cl_2 (Kanto Chemical; dehydrated), toluene (Kanto Chemical; dehydrated), MeCN (FUJIFILM Wako Chemicals), MeOH (FUJIFILM Wako Chemicals), AcOH (FUJIFILM Wako Chemicals), bromobenzene (FUJIFILM Wako Chemicals), 1-bromo-2-vinylbenzene (Angene Chemical), 2-bromophenol (TCI), 2-amino-3-nitrophenol (TCI), 2-bromo-3-hydroxybenzaldehyde (Angene Chemical), iodomethane (Nacalai Tesque), 1-bromobutane (FUJIFILM Wako Chemicals), chloromethyl methyl ether (Nacalai Tesque), *N*-bromosuccinimide (FUJIFILM Wako Chemicals), dichlorodiisopropylsilane (TCI), dichloro(methyl)(phenyl)silane (TCI), *tert*-butylchlorodimethylsilane (Kanto Chemical), poly(methylhydrosiloxane) (Aldrich; M_n = 1700–3200), triethylsilane (TCI), triethylsilane-*d* (Aldrich; 97% D), isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (FUJIFILM Wako Chemicals), 4-methoxyphenylboronic acid (TCI), *N*-phenylbis(trifluoromethanesulfonimide) (Angene Chemical), diethylamine-d_{10} (Aldrich; 98% D), imidazole (Nacalai Tesque), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (TCI), PPh_3 (FUJIFILM Wako Chemicals), PCy_3 (FUJIFILM Wako Chemicals), methyltriphenylphosphonium bromide (TCI), (methoxymethyl)triphenylphosphonium chloride (FUJIFILM Wako Chemicals), pyridinium chlorochromate (TCI), bromine (TCI), HCl (FUJIFILM Wako Chemicals; 36% in H_2O), HBr (FUJIFILM Wako Chemicals; 48% in H_2O), H_2SO_4 (Nacalai Tesque; concentrated), *n*BuLi (Kanto Chemical; 1.51–1.56 M solution in hexane), *t*BuLi (Kanto Chemical; 1.70 M solution in pentane), LiOAc (FUJIFILM Wako Chemicals), KO*t*Bu (TCI), NH_4Cl (Kanto Chemical), Celite (Nacalai Tesque), NaH (Kishida Chemical; 60 wt% in mineral oil), $NaNO_2$ (FUJIFILM Wako Chemicals), Na_2CO_3 (FUJIFILM Wako Chemicals), KI (FUJIFILM Wako Chemicals), K_2CO_3 (FUJIFILM Wako Chemicals), $MgSO_4$ (FUJIFILM Wako Chemicals), Mg turnings (Nacalai Tesque), Fe powder (FUJIFILM Wako Chemicals), Zn powder (FUJIFILM Wako Chemicals), $Ni(cod)_2$ (FUJIFILM Wako Chemicals), $Pd(OAc)_2$ (FUJIFILM Wako Chemicals), and CuBr (Kishida Chemical) were used as received. 2,6-Dideuterio-1-iodobenzene,[29] 2-bromo-3-(methoxymethoxy)benzaldehyde,[30] 3-bromo-5-(*tert*-butyl)phenol,[31] *N*-(2-pyridyl)triflimide,[32] $(nBu)_2ND$ (>95% D),[33] IPr,[34] and $Pd(PPh_3)_4$[35] were prepared according to the literature procedures.

Representative procedures for substrates:

2-(Diisopropyl(phenyl)silyl)-3-vinylphenyl trifluoromethanesulfonate (1)



nBuLi (7.95 mL, 12.0 mmol; 1.51 M solution in hexane) was added dropwise over 10 min to a solution of bromobenzene (1.26 mL, 12.0 mmol) in THF (24 mL) at –78 °C, and the mixture was stirred for 30 min at –78 °C. Dichlorodiisopropylsilane (2.16 mL, 12.0 mmol) was added to it and the mixture was stirred for 1.5 h at room temperature. 2-Bromo-3-hydroxybenzaldehyde (2.01 g, 10.0 mmol) and imidazole (1.70 g, 25.0 mmol) were then added it and the resulting mixture was stirred for 4 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 hexane/EtOAc = 50/1 → 30/1 to afford 2-bromo-3-((diisopropyl(phenyl)silyl)oxy)benzaldehyde as a colorless oil (3.90 g, 10.0 mmol; 100% yield).

^{1}H NMR (CDCl$_3$): δ 10.43 (s, 1H), 7.65 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 2H), 7.49 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.47-7.37 (m, 3H), 7.14 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 6.99 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 1.52 (sept, $^3J_{HH}$ = 7.6 Hz, 2H), 1.16 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.08 (d, $^3J_{HH}$ = 7.3 Hz, 6H).

KOtBu (711 mg, 6.34 mmol) was added to a suspension of methyltriphenylphosphonium bromide (2.26 g, 6.34 mmol) in THF (16 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. A solution of 2-bromo-3-((diisopropyl(phenyl)silyl)oxy)benzaldehyde (1.24 g, 3.17 mmol) in THF (16 mL) was added to it at 0 °C, and the resulting mixture was stirred for 16 h at 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 hexane to afford (2-bromo-3-vinylphenoxy)diisopropyl(phenyl)silane as a colorless oil (416 mg, 1.07 mmol; 34% yield).

^{1}H NMR ($CDCl_3$): δ 7.66 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 2H), 7.46-7.35 (m, 3H), 7.17-7.08 (m, 2H), 7.00 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 5.67 (d, $^3J_{HH}$ = 17.5 Hz, 1H), 5.34 (d, $^3J_{HH}$ = 11.2 Hz, 1H), 1.49 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.14 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 1.07 (d, $^3J_{HH}$ = 7.8 Hz, 6H).

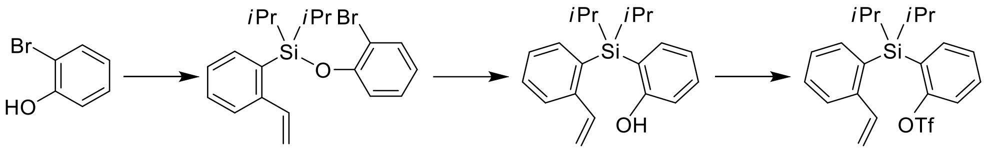
*n*BuLi (779 µL, 1.18 mmol; 1.51 M solution in hexane) was added dropwise over 5 min to a solution of (2-bromo-3-vinylphenoxy)diisopropyl(phenyl)silane (416 mg, 1.07 mmol) in THF (4.0 mL) at –78 °C, and the mixture was stirred for 30 min at −78 °C and for 1.5 h at 0 °C. The reaction was quenched with 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 hexane/EtOAc = 10/1 to afford 2-(diisopropyl(phenyl)silyl)-3-vinylphenol as a colorless oil (301 mg, 0.971 mmol; 91% yield).

^{1}H NMR ($CDCl_3$): δ 7.58 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 2H), 7.46-7.35 (m, 3H), 7.27 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.97 (dd, $^3J_{HH}$ = 17.1 and 10.7 Hz, 1H), 6.68 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 5.50 (dd, $^3J_{HH}$ = 17.1 Hz and $^2J_{HH}$ = 1.5 Hz, 1H), 5.10 (bs, 1H), 5.09 (dd, $^3J_{HH}$ = 10.7 Hz and $^2J_{HH}$ = 1.5 Hz, 1H), 1.74 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.04 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.91 (d, $^3J_{HH}$ = 7.3 Hz, 6H).

NaH (77.7 mg, 1.94 mmol; 60% in mineral oil) was added to a solution of 2-(diisopropyl(phenyl)silyl)-3-vinylphenol (301 mg, 0.971 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 20 min at room temperature. *N*-Phenylbis(trifluoromethanesulfonimide) (693 mg, 1.94 mmol) was added to it, and the resulting mixture was stirred for 10 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 to afford compound **1** as a white solid (370 mg, 836 µmol; 86% yield).

^{1}H NMR ($CDCl_3$): δ 7.51 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 7.45 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.43-7.27 (m, 6H), 6.61 (dd, $^3J_{HH}$ = 17.1 and 10.7 Hz, 1H), 5.38 (dd, $^3J_{HH}$ = 17.1 Hz and $^2J_{HH}$ = 1.0 Hz, 1H), 4.86 (dd, $^3J_{HH}$ = 10.7 Hz and $^2J_{HH}$ = 1.0 Hz, 1H), 1.82 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.05 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.95 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR ($CDCl_3$): δ 157.3, 148.9, 139.2, 135.0, 134.5, 131.3, 129.1, 127.7, 126.0, 124.7, 118.6, 117.7, 116.2, 18.5, 18.2, 11.9. ^{19}F NMR ($CDCl_3$): δ –74.2 (s). HRMS (FAB) calcd for $C_{21}H_{26}F_3O_3SSi$ (M+H$^+$) 443.1319, found 443.1330.

2-(Diisopropyl(2-vinylphenyl)silyl)phenyl trifluoromethanesulfonate (1')



*t*BuLi (3.53 mL, 6.00 mmol; 1.70 M solution in pentane) was added dropwise over 7 min to a solution of 1-bromo-2-vinylbenzene (389 µL, 3.00 mmol) in Et_2O (6.0 mL) at –78 °C, and the mixture was stirred for 2 h at –78 °C. Dichlorodiisopropylsilane (539 µL, 3.00 mmol) was added to it and the mixture was stirred for 2 h at room temperature. 2-Bromophenol (475 µL, 4.50 mmol) and imidazole (511 g, 7.50 mmol) were then added to it and the resulting mixture was stirred for 16 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 hexane → hexane/EtOAc = 30/1 to afford (2-bromophenoxy)diisopropyl(2-vinylphenyl)silane as a colorless oil (797 mg, 2.05 mmol; 69% yield).

^{1}H NMR ($CDCl_3$): δ 7.72-7.66 (m, 2H), 7.52 (dd, $^3J_{HH}$ = 7.9 and $^4J_{HH}$ = 1.6 Hz, 1H), 7.42 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.31-7.27 (m, 1H), 7.09 (dd, $^3J_{HH}$ = 17.0 and 10.8 Hz, 1H), 6.99 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.76 (td, $^3J_{HH}$ = 7.7 Hz and $^3J_{HH}$ = 1.5 Hz, 1H), 6.69 (dd, $^3J_{HH}$ = 8.3 and $^3J_{HH}$ = 1.5 Hz, 1H), 5.64 (dd, $^3J_{HH}$ = 17.0 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 5.19 (dd, $^3J_{HH}$ = 10.8 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 1.55-1.47 (m, 2H), 1.13 (d, $^3J_{HH}$ = 7.5 Hz, 6H), 1.16 (d, $^3J_{HH}$ = 7.5 Hz, 6H).

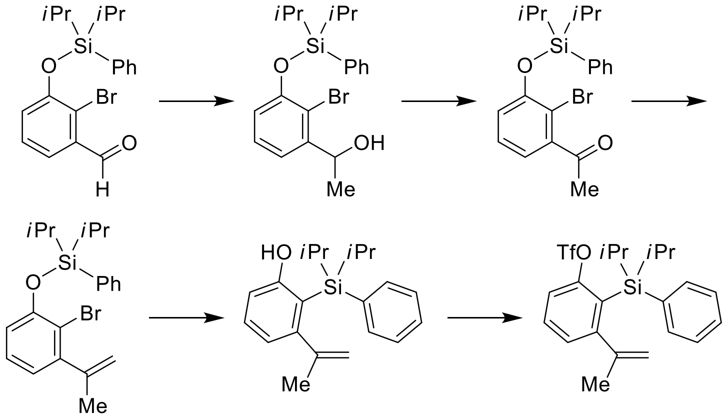
*n*BuLi (1.58 mL, 2.46 mmol; 1.56 M solution in hexane) was added dropwise over 5 min to a solution of (2-bromophenoxy)diisopropyl(2-vinylphenyl)silane (797 mg, 2.05 mmol) in THF (4.0 mL) at –78 °C, and the mixture was stirred for 40 min at −78 °C and for 40 min at room temperature. The reaction was 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 hexane/EtOAc = 50/1 → 30/1 to afford 2-(diisopropyl(2-vinylphenyl)silyl)phenol as a colorless oil (534 mg, 1.72 mmol; 83% yield).

^{1}H NMR ($CDCl_3$): δ 7.68 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.37-7.47 (m, 2H), 7.32 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 6.97 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.90 (dd, $^3J_{HH}$ = 16.9 and $^3J_{HH}$ = 11.0 Hz, 1H), 6.78 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 5.61 (d, $^3J_{HH}$ = 17.4 Hz, 1H), 5.05 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 4.82 (s, 1H), 1.70 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 0.99 (d, J = 7.3 Hz, 12H).

NaH (78.1 mg, 1.89 mmol; 60% in mineral oil) was added to a solution of 2-(diisopropyl(2-vinylphenyl)silyl)phenol (534 mg, 1.72 mmol) in THF (10 mL) at 0 °C and the mixture was stirred for 20 min at room temperature. *N*-Phenylbis(trifluoromethanesulfonimide) (675 mg, 1.89 mmol) was added to it, and the resulting mixture was stirred 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 hexane → hexane/EtOAc = 30/1 to afford compound **1'** as a colorless oil (452 mg, 1.02 mmol; 59% yield).

^{1}H NMR ($CDCl_3$): δ 7.62 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.56-7.50 (m, 2H), 7.47 (ddd, $^3J_{HH}$ = 8.2 and 7.3 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.43-7.37 (m, 2H), 7.34-7.26 (m, 2H), 6.63 (dd, $^3J_{HH}$ = 17.4 and 11.0 Hz, 1H), 5.54 (d, $^3J_{HH}$ = 17.4 Hz, 1H), 4.96 (d, $^3J_{HH}$ = 11.0 Hz, 1H), 1.78 (sept, $^3J_{HH}$ = 7.4 Hz, 1H), 1.03 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.00 (d, $^3J_{HH}$ = 7.4 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR ($CDCl_3$) : δ 155.9, 144.7, 138.9, 138.6, 136.6, 131.5, 131.2, 129.8, 127.1, 126.84, 126.82, 125.7, 118.7, 118.4, 114.7, 18.4, 18.0, 11.7. ^{19}F NMR ($CDCl_3$): δ –74.7 (s). HRMS (FAB) calcd for $C_{21}H_{26}F_3O_3SSi$ (M+H$^+$) 443.1319, found 443.1329.

2-(Diisopropyl(phenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4a)



A solution of iodomethane (933 μL, 15.0 mmol) in Et_2O (7.5 mL) was added dropwise over 10 min to Mg turnings (486 mg, 20.0 mmol) in Et_2O (7.5 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. The resulting mixture was diluted with Et_2O (5.0 mL) and this was added to a solution of 2-bromo-3-((diisopropyl(phenyl)silyl)oxy)benzaldehyde (3.91 g, 10.0 mmol) in Et_2O (15 mL) at 0 °C. This was stirred for 10 min at 0 °C and 30 min at 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 to afford 1-(2-bromo-3-((diisopropyl(phenyl)silyl)oxy)phenyl)ethanol, which was used for the next step without further purification.

^{1}H NMR ($CDCl_3$): δ 7.70-7.62 (m, 2H), 7.47-7.35 (m, 3H), 7.16 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.08 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.71 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.30 (q, $^3J_{HH}$ = 6.4 Hz, 1H), 2.02 (bs, 1H), 1.55-1.43 (m, 5H), 1.14 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 1.13 (d, $^3J_{HH}$ = 7.8 Hz, 3H), 1.07 (d, $^3J_{HH}$ = 7.8 Hz, 3H), 1.06 (d, $^3J_{HH}$ = 7.8 Hz, 3H).

1-(2-Bromo-3-((diisopropyl(phenyl)silyl)oxy)phenyl)ethanol obtained above was dissolved in CH_2Cl_2 (80 mL). A mixture of pyridinium chlorochromate (3.23 g, 15.0 mmol) and Celite (3.23 g) was added to it and the reaction mixture was stirred for 2.5 h at room temperature. This was passed through a pad of Celite with CH_2Cl_2 and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 15/1 to afford 1-(2-bromo-3-((diisopropyl(phenyl)silyl)oxy)phenyl)ethanone as a pale yellow oil (3.94 g, 9.73 mmol; 97% yield over 2 steps).

^{1}H NMR ($CDCl_3$): δ 7.64 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 2H), 7.47-7.36 (m, 3H), 7.08 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.91 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.82 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 2.62 (s, 3H), 1.50 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.15 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.07 (d, $^3J_{HH}$ = 7.3 Hz, 6H).

KO*t*Bu (1.53 g, 13.6 mmol) was added to a suspension of methyltriphenylphosphonium bromide (4.86 g, 13.6 mmol) in THF (50 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. A solution of 1-(2-bromo-3-((diisopropyl(phenyl)silyl)oxy)phenyl)ethanone (3.94 g, 9.73 mmol) in THF (47 mL) was added to it at 0 °C, and the resulting mixture was stirred for 10 h at 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 hexane to afford (2-bromo-3-(propen-2-yl)phenoxy)diisopropyl(phenyl)silane as a colorless oil (3.13 g, 7.75 mmol; 80% yield).

^{1}H NMR ($CDCl_3$): δ 7.71-7.64 (m, 2H), 7.46-7.35 (m, 3H), 6.98 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.75 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.69 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 5.19 (s, 1H), 4.92 (s, 1H), 2.10 (s, 3H), 1.49 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.14 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.07 (d, $^3J_{HH}$ = 7.8 Hz, 6H).

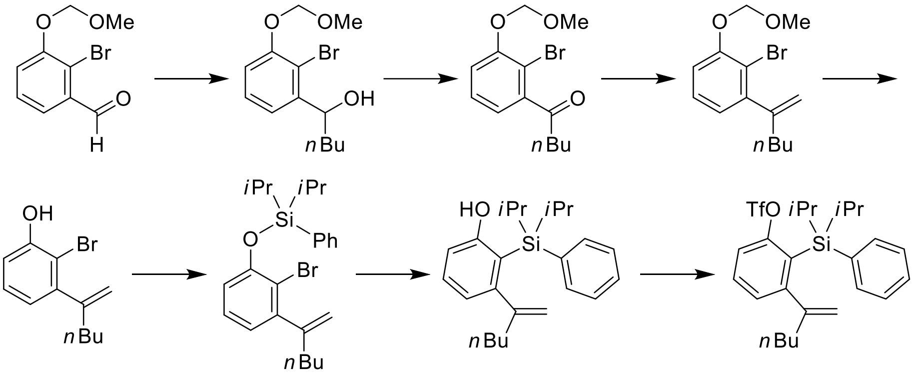
*n*BuLi (5.65 mL, 8.53 mmol; 1.51 M solution in hexane) was added dropwise over 5 min to a solution of (2-bromo-3-(propen-2-yl)phenoxy)diisopropyl(phenyl)silane (3.13 g, 7.75 mmol) in THF (31 mL) at –78 °C, and the mixture was stirred for 30 min at −78 °C and for 1.5 h at 0 °C. The reaction was quenched 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 hexane/EtOAc = 10/1 to afford 2-(diisopropyl(phenyl)silyl)-3-(propen-2-yl)phenol as a colorless oil (2.07 g, 6.39 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.58-7.51 (m, 2H), 7.42-7.30 (m, 3H), 7.22 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.77 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.65 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 5.04 (s, 1H), 4.92 (s, 1H), 4.84 (s, 1H), 1.96 (s, 3H), 1.76 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.02 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 1.00 (d, $^3J_{HH}$ = 7.3 Hz, 6H).

NaH (383 mg, 9.59 mmol; 60% in mineral oil) was added to a solution of 2-(diisopropyl(phenyl)silyl)-3-(propen-2-yl)phenol (2.07 g, 6.39 mmol) in THF (32 mL) at 0 °C and the mixture was stirred for 30 min at room temperature. *N*-Phenylbis(trifluoromethanesulfonimide) (3.43 g, 9.59 mmol) was added to it, and the resulting mixture was stirred for 11 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/EtOAc = 50/1 to afford compound **4a** as a white solid (2.23 g, 4.87 mmol; 76% yield).

^1H NMR ($CDCl_3$): δ7.43-7.35 (m, 3H), 7.35-7.24 (m, 4H), 7.09 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 4.76 (s, 1H), 4.69 (s, 1H), 1.79 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.56 (s, 3H), 1.15 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H). $^{13}C\{^1H,^{19}F\}$ NMR ($CDCl_3$): δ 157.2, 155.4, 146.3, 135.4, 130.5, 128.8, 127.5, 127.4, 125.9, 118.6, 118.3, 116.5, 24.3, 20.0, 19.3, 13.0. ^{19}F NMR ($CDCl_3$): δ –74.3 (s). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 0.1. HRMS (FAB) calcd for $C_{22}H_{27}F_3O_3SSi$ (M^+) 456.1397, found 456.1405.

2-(Diisopropyl(phenyl)silyl)-3-(hexen-2-yl)phenyl trifluoromethanesulfonate (4b)



A solution of 1-bromobutane (755 µL, 7.00 mmol) in Et_2O (6.0 mL) was added dropwise over 10 min to Mg turnings (205 mg, 8.45 mmol) in Et_2O (3.0 mL) at 0 °C, and the mixture was stirred for 30 min at room temperature. The resulting mixture was diluted with Et_2O (3.0 mL) and this was added to a solution of 2-bromo-3-(methoxymethoxy)benzaldehyde (1.22 g, 4.97 mmol) in Et_2O (6.0 mL) at 0 °C. This was stirred for 20 min at 0 °C and 40 min at 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 hexane/EtOAc = 10/1 → 5/1 to afford 1-(2-bromo-3-(methoxymethoxy)phenyl)pentanol as a colorless oil (1.18 g, 3.88 mmol; 78% yield).

^{1}H NMR ($CDCl_3$): δ 7.27 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.22 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.06 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 2.0 Hz, 1H), 5.26 (d, $^2J_{HH}$ = 6.8 Hz, 2H), 5.24 (d, $^2J_{HH}$ = 6.8 Hz, 2H), 5.13 (dd, $^3J_{HH}$ = 8.3 and 4.4 Hz, 1H), 3.52 (s, 3H), 1.98 (s, 1H) 1.85-1.74 (m, 1H), 1.72-1.61 (m, 1H), 1.56-1.33 (m, 4H), 0.91 (t, $^3J_{HH}$ = 6.6 Hz, 3H).

Pyridinium chlorochromate (1.25 g, 5.82 mmol) and Celite (1.25 g) were added to a solution of 1-(2-bromo-3-(methoxymethoxy)phenyl)pentan-1-ol (1.18 g, 3.88 mmol) in CH_2Cl_2 (31 mL), and the mixture was stirred for 16 h at room temperature. This was passed through a pad of Celite with CH_2Cl_2 and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 → 5/1 to afford 1-(2-bromo-3-(methoxymethoxy)phenyl)pentanone as a colorless oil (1.06 g, 3.52 mmol; 91% yield).

^{1}H NMR ($CDCl_3$): δ 7.29 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.19 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.92 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.27 (s, 2H), 3.52 (s, 3H), 2.88 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 1.70 (quint, $^3J_{HH}$ = 7.6 Hz, 2H), 1.40 (sext, $^3J_{HH}$ = 7.3 Hz, 2H), 0.94 (t, $^3J_{HH}$ = 7.3 Hz, 3H).

KO*t*Bu (474 mg, 4.22 mmol) was added to a suspension of methyltriphenylphosphonium bromide (1.51 g, 4.22 mmol) in THF (14 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. A solution of 1-(2-bromo-3-(methoxymethoxy)phenyl)pentanone (1.06 g, 3.52 mmol) in THF (14 mL) was added to it at 0 °C, and the resulting mixture was stirred for 14 h at 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 hexane/EtOAc = 20/1 → 10/1 to afford 2-bromo-1-(hexen-2-yl)-3-(methoxymethoxy)benzene as a colorless oil (1.03 g, 3.46 mmol; 98% yield).

^{1}H NMR ($CDCl_3$): δ 7.18 (dd, $^3J_{HH}$ = 8.3 and 7.3 Hz, 1H), 7.05 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.82 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.25 (s, 2H), 5.19 (q, J_{HH} = 1.5 Hz, 1H), 4.93 (d, $^2J_{HH}$ = 1.0 Hz, 1H), 3.54 (s, 3H), 2.41 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 1.44-1.28 (m, 4H), 0.89 (t, $^3J_{HH}$ = 7.1 Hz, 3H).

HCl (176 μL; 36% in H_2O) and MeOH (8.8 mL) were added to a solution of 2-bromo-1-(hexen-2-yl)-3-(methoxymethoxy)benzene (1.08 g, 3.52 mmol) in CH_2Cl_2 (8.8 mL), and the mixture was stirred for 40 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/EtOAc = 5/1 to afford 2-bromo-3-(hexen-2-yl)phenol as a colorless oil (601 mg, 3.29 mmol; 93% yield).

^{1}H NMR ($CDCl_3$): δ 7.15 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.93 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.72 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.71 (s, 1H), 5.20 (q, J_{HH} = 1.5 Hz, 1H), 4.95 (d, $^2J_{HH}$ = 1.0 Hz, 1H), 2.39 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 1.43-1.28 (m, 4H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H).

*n*BuLi (3.15 mL, 4.76 mmol; 1.51 M solution in hexane) was added dropwise over

5 min to a solution of bromobenzene (501 μL, 4.76 mmol) in THF (10 mL) at –78 °C, and the mixture was stirred for 30 min at –78 °C. Dichlorodiisopropylsilane (818 μL, 4.55 mmol) was added to it and the mixture was stirred for 2 h at 0 °C. 2-Bromo-3-(hexen-2-yl)phenol (1.06 g, 4.14 mmol) and imidazole (706 mg, 10.4 mmol) were then added to it and the resulting mixture was stirred for 1 h at 50 °C and for 16 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/EtOAc = 1/0 → 30/1 to afford (2-bromo-3-(hexen-2-yl)phenoxy)diisopropyl(phenyl)silane as a colorless oil (1.47 g, 3.30 mmol; 80% yield).

^{1}H NMR ($CDCl_3$): δ 7.68 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 2H), 7.46-7.34 (m, 3H), 6.98 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.71 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.17 (q, J_{HH} = 1.6 Hz, 1H), 4.93 (d, $^2J_{HH}$ = 1.9 Hz, 1H), 2.42 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 1.49 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.42-1.30 (m, 4H), 1.14 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 1.07 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H).

*n*BuLi (2.40 mL, 3.63 mmol; 1.51 M solution in hexane) was added dropwise over 5 min to a solution of (2-bromo-3-(hexen-2-yl)phenoxy)diisopropyl(phenyl)silane (1.47 g, 3.30 mmol) in THF (13 mL) at –78 °C, and the mixture was stirred for 30 min at −78 °C and for 1 h at 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 hexane/EtOAc = 100/1 → 5/1 to afford 2-(diisopropyl(phenyl)silyl)-3-(hexen-2-yl)phenol as a colorless oil (1.20 g, 3.27 mmol; 99% yield).

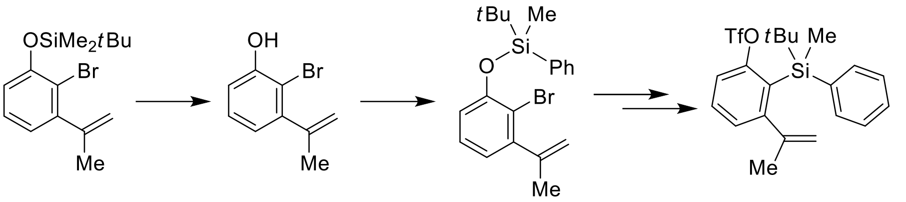
^{1}H NMR ($CDCl_3$): δ 7.58-7.52 (m, 2H), 7.41-7.29 (m, 3H), 7.21 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 6.65 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ =

1.0 Hz, 1H), 5.04 (s, 1H), 4.90-4.87 (m, 1H), 4.86 (q, J_{HH} = 1.6 Hz, 1H), 2.26-2.10 (m, 2H), 1.72 (sept, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 2H), 1.35-1.20 (m, 4H), 1.01 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H), 0.99 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H), 0.88 (t, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 3H).

NaH (262 mg, 6.54 mmol; 60% in mineral oil) was added to a solution of 2-(diisopropyl(phenyl)silyl)-3-(hexen-2-yl)phenol (1.20 g, 3.27 mmol) in THF (16 mL) at 0 °C and the mixture was stirred for 20 min at room temperature. *N*-(2-Pyridyl)triflimide (2.34 g, 6.54 mmol) was added to it, and the resulting mixture was stirred for 2 h at 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 hexane → hexane/EtOAc = 50/1 to afford compound **4b** as a colorless oil (1.26 g, 2.53 mmol; 77% yield).

^{1}H NMR ($CDCl_3$): δ 7.46-7.41 (m, 2H), 7.38 (dd, $^3J_{\mathrm{HH}}$ = 8.3 and 7.3 Hz, 1H), 7.36-7.30 (m, 2H), 7.30-7.24 (m, 2H), 7.06 (dd, $^3J_{\mathrm{HH}}$ = 7.3 Hz and $^4J_{\mathrm{HH}}$ = 1.5 Hz, 1H), 4.76 (d, $^2J_{\mathrm{HH}}$ = 1.5 Hz, 1H), 4.72 (q, J_{HH} = 1.5 Hz, 1H), 1.99-1.69 (m, 2H), 1.78 (sept, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2H), 1.23-0.87 (m, 16H), 0.82 (t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 3H). $^{13}C\{^1H,^{19}F\}$ NMR ($CDCl_3$): δ 157.2, 155.6, 150.8, 135.4, 135.2, 130.4, 128.8, 128.4, 127.3, 125.6, 118.6, 116.5, 115.6, 37.7, 29.3, 22.6, 20.0, 19.3, 14.1, 13.0. ^{19}F NMR ($CDCl_3$): δ –74.3 (s). HRMS (FAB) calcd for $C_{25}H_{33}F_3O_3SSi$ (M^+) 498.1866, found 498.1877.

2-(*tert*-Butyl(methyl)(phenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4m)



(2-Bromo-3-(propen-2-yl)phenoxy)(*tert*-butyl)dimethylsilane was prepared in the same way as (2-bromo-3-(propen-2-yl)phenoxy)diisopropyl(phenyl)silane from 2-bromo-3-hydroxybenzaldehyde as described above. LiOAc (76.5 mg, 1.16 mmol) was added to a solution of (2-bromo-3-(propen-2-yl)phenoxy)(*tert*-butyl)dimethylsilane (3.80 mg, 11.6 mmol) in DMF (50 mL) and H_2O (1 mL), and the resulting mixture was stirred for 13 h at 70 °C. 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 hexane/EtOAc = 10/1 to afford 2-bromo-3-(propen-2-yl)phenol as a white solid (1.77 mg, 8.32 mmol; 72% yield).

^{1}H NMR ($CDCl_3$): δ 7.16 (dd, $^3J_{HH}$ = 8.1 and 7.3 Hz, 1H), 6.93 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 6.76 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 5.69 (s, 1H), 5.24-5.21 (m, 1H), 4.96-4.94 (m, 1H), 2.08 (dd, $^4J_{HH}$ = 1.5 and 1.0 Hz, 3H).

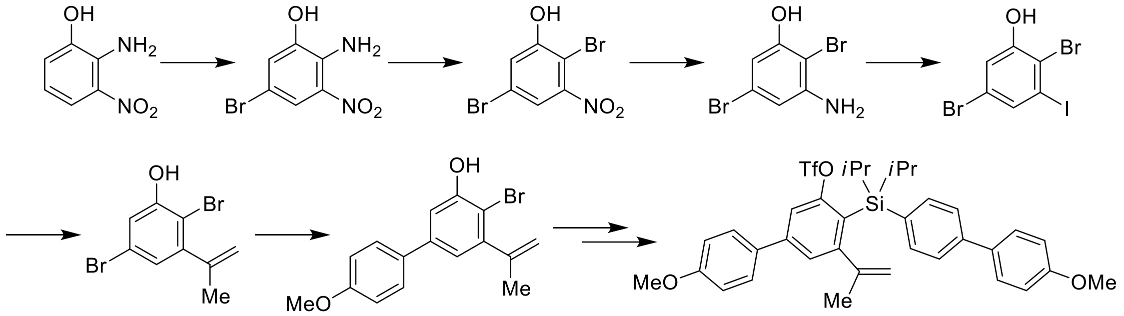
*t*BuLi (1.24 mL, 2.10 mmol; 1.70 M solution in pentane) was added dropwise over 3 h to a solution of dichloro(methyl)(phenyl)silane (401 μL, 2.10 mmol) in Et_2O (2.1 mL) at 0 °C, and the mixture was stirred for 30 min at –78 °C. A solution of 2-bromo-3-(propen-2-yl)phenol (426 mg, 2.00 mmol) and imidazole (340 mg, 5.00 mmol) in THF (4.0 mL) were then added to it and the resulting mixture was stirred for 20 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 hexane/EtOAc = 100/1 → 50/1 to afford (2-bromo-3-(propen-2-yl)phenoxy)(*tert*-butyl)(methyl)(phenyl)silane as a colorless oil (591 mg, 1.52 mmol; 76% yield).

^{1}H NMR ($CDCl_3$): δ 7.64-7.58 (m, 2H), 7.45-7.34 (m, 3H), 6.94 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.73 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.54 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.21-5.17 (m, 1H), 4.94-4.90 (m, 1H), 2.12-2.08 (m, 3H), 1.06 (s, 9H), 0.54 (s, 3H).

(2-Bromo-3-(propen-2-yl)phenoxy)(*tert*-butyl)(methyl)(phenyl)silane (591 mg, 1.52 mmol) was converted to compound **4m**, following the procedure for compound **4b**. White solid (492 mg, 1.11 mmol; 73% yield over 2 steps).

^{1}H NMR ($CDCl_3$): δ 7.52 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.38 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.35-7.26 (m, 4H), 7.09 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 5.07 (s, 1H), 4.93-4,89 (m, 1H), 1.86 (s, 3H), 1.18 (s, 9H), 0.61 (s, 3H). $^{13}C\{^1H,^{19}F\}$ NMR ($CDCl_3$): δ 157.1, 155.4, 147.1, 138.7, 134.8, 130.8, 128.8, 128.1, 127.9, 125.6, 118.7, 117.4, 116.7, 29.4, 26.5, 19.7, 1.0. ^{19}F NMR ($CDCl_3$): δ –73.9 (s). HRMS (FAB) calcd for $C_{21}H_{25}F_3O_3SSi$ (M^+) 442.1240, found 442.1251.

2-(Diisopropyl(4-(4-methoxyphenyl)phenyl)silyl)-5-(4-methoxyphenyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4o)



Bromine (2.81 mL, 54.9 mmol) was added dropwise over 1 h to a mixture of 2-amino-3-nitrophenol (7.71 g, 50.0 mmol) in AcOH (150 mL) at room temperature (placed in a water bath), and the resulting mixture was stirred for 18 h at room temperature. The precipitates that formed were collected by filtration with hexane, and the solid thus obtained was dissolved in a mixture of EtOAc and H_2O. This was extracted with EtOAc, and the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum to afford 2-amino-5-bromo-3-nitrophenol (CAS 867338-56-5) as a dark red solid (15.1 g), which was used without further purification.

^{1}H NMR (DMSO-d_6): δ 11.0 (bs, 1H), 7.59 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 7.02 (s, 2H), 6.96 (d, $^4J_{HH}$ = 2.3 Hz, 1H).

HBr (14 mL; 48% in H_2O) was added to a mixture of 2-amino-5-bromo-3-nitrophenol obtained above (15.1 g) and H_2O (6.0 mL) at 0 °C. A solution of $NaNO_2$ (3.76 g, 54.5 mmol) in H_2O (14 mL) was added to it over 10 min, and the mixture was stirred for 30 min at 0 °C. A suspension of CuBr (8.25 g, 57.5 mmol) in HBr (28 mL; 48% in H_2O) was then added to it over 5 min, and the resulting mixture was stirred for 30 min at 0 °C, 10 min at room temperature, and 50 min at 100 °C. After cooled to room temperature, the reaction mixture was filtered through Celite with EtOAc and H_2O. 5% $Na_2S_2O_3$aq was added to it and this was extracted with EtOAc. 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 to afford 2,5-dibromo-3-nitrophenol (CAS 2088851-12-9) as a red solid (10.2 g, 34.3 mmol; 69% yield over 2 steps).

^{1}H NMR ($CDCl_3$): δ 7.61 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.42 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 6.25 (bs, 1H).

Fe powder (9.58 g, 172 mmol) was added to a mixture of 2,5-dibromo-3-nitrophenol (10.2 g, 34.3 mmol) and NH_4Cl (7.34 g, 137 mmol) in EtOH (42 mL) and H_2O (28 mL), and the mixture was stirred for 12 h at 80 °C. After cooled to room temperature, the reaction mixture was filtered through Celite with EtOAc and H_2O. 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 hexane/CH_2Cl_2/EtOAc = 20/20/1 to afford 3-amino-2,5-dibromophenol (CAS 2092343-54-7) as a white solid (7.45 g, 27.9 mmol; 81% yield).

^{1}H NMR ($CDCl_3$): δ 6.59 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 6.51 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 5.44 (s, 1H), 4.12 (bs, 2H).

H_2SO_4 (23 mL; concentrated) and ice (23 g) were added to a suspension of 3-amino-2,5-dibromophenol (7.79 g, 29.2 mmol) in MeCN (23 mL) at 0 °C. A solution of $NaNO_2$ (3.63 g, 52.6 mmol) in H_2O (8.0 mL) was added to it over 5 min, and the mixture was stirred for 30 min at 0 °C. A solution of KI (17.0 g, 102 mmol) in H_2O (18 mL) was then added to it over 5 min, and the resulting mixture was stirred for 30 min at 0 °C. This was diluted with $CHCl_3$ and the reaction was quenched with saturated $NaHCO_3$aq. After extraction with $CHCl_3$, the organic layer was washed with 5% $Na_2S_2O_3$aq and with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/CH_2Cl_2/EtOAc = 15/15/1 →

10/10/1 to afford 2,5-dibromo-3-iodophenol (CAS 2169478-86-6) as a white solid (8.62 g, 22.8 mmol; 78% yield).

^{1}H NMR ($CDCl_3$): δ 7.57 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.16 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 5.64 (s, 1H).

2-Isopropenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.08 mL, 11.0 mmol), toluene (20 mL), EtOH (20 mL), and H_2O (20 mL) were added to a mixture of 2,5-dibromo-3-iodophenol (3.78 g, 10.0 mmol), $Pd(PPh_3)_4$ (1.16 g, 1.00 mmol), and K_2CO_3 (4.15 g, 30.0 mmol) in toluene (60 mL), and the resulting mixture was stirred for 23 h at 82–85 °C. After cooled to room temperature, 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 hexane/EtOAc = 30/1 $\rightarrow$ 10/1 (gradient) to afford 2,5-dibromo-3-(propen-2-yl)phenol as a colorless oil (1.33 g, 4.55 mmol; 46% yield) along with recovery of 2,5-dibromo-3-iodophenol as a white solid (1.51 g, 4.00 mmol; 40% recovery).

^{1}H NMR ($CDCl_3$): δ 7.10 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 6.92 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 5.74 (s, 1H), 5.26-5.22 (m, 1H), 4.97-4.94 (m, 1H), 2.07-2.03 (m, 3H).

A suspension of 2,5-dibromo-3-(propen-2-yl)phenol (876 mg, 3.00 mmol), 4-methoxyphenylboronic acid (912 mg, 6.00 mmol), $Pd(OAc)_2$ (67.4 mg, 0.300 mmol), and Na_2CO_3 (954 mg, 9.00 mmol) in acetone (30 mL) and H_2O (42 mL) was stirred for 2.5 h at 38 °C. The mixture was diluted 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/EtOAc = 10/1 to afford 2-bromo-5-(4-methoxyphenyl)-3-(propen-2-yl)phenol as a white solid (660 mg, 2.07 mmol; 69% yield).

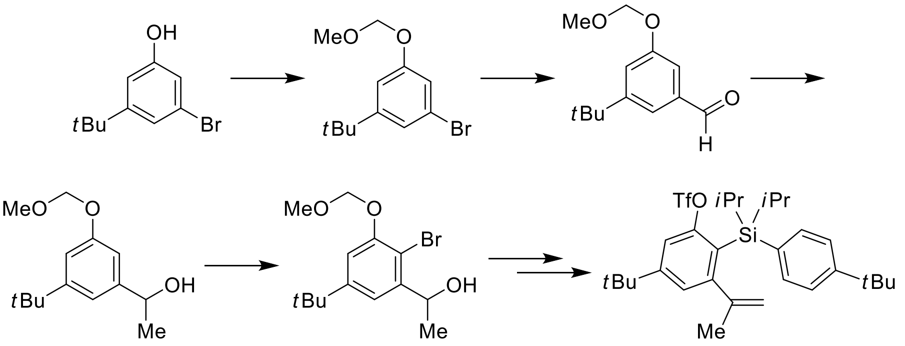
^{1}H NMR ($CDCl_3$): δ 7.51 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.13 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.00-

6.92 (m, 3H), 5.74 (s, 1H), 5.25 (s, 1H), 5.00 (s, 1H), 3.85 (s, 3H), 2.11 (s, 3H).

2-Bromo-5-(4-methoxyphenyl)-3-(propen-2-yl)phenol (687 mg, 2.15 mmol) was converted to compound **4o**, following the procedure for compound **4b**. Pale yellow amorphous (568 mg, 0.849 mmol; 39% yield over 3 steps).

^{1}H NMR (CDCl$_3$): δ 7.58 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.55-7.48 (m, 7H), 7.27 (d, $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.03-6.96 (m, 4H), 4.81 (s, 1H), 4.76 (s, 1H), 3.86 (s, 6H), 1.84 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.62 (s, 3H), 1.21 (d, $^{3}J_{HH}$ = 7.8 Hz, 6H), 1.09 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 160.1, 159.4, 157.7, 155.5, 146.4, 143.3, 140.8, 136.1, 133.7, 133.4, 131.5, 128.3, 128.2, 125.52, 125.48, 123.5, 118.7, 118.2, 114.7, 114.6, 114.3, 55.5, 24.6, 20.1, 19.4, 13.1. ^{19}F NMR (CDCl$_3$): δ –74.2 (s). HRMS (FAB) calcd for $C_{36}H_{39}F_3O_5SSi$ (M$^+$) 668.2234, found 668.2240.

5-(*tert*-Butyl)-2-((4-*tert*-butylphenyl)diisopropylsilyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4n)



A solution of 3-bromo-5-(*tert*-butyl)phenol (2.26 g, 9.47 mmol) in THF (5 mL) was added over 5 min to a suspension of NaH (456 mg, 11.4 mmol; 60% in mineral oil) in THF (20 mL) at 0 °C, and the mixture was stirred for 30 min at 0 °C. Chloromethyl methyl ether (855 μL, 11.4 mmol) was added to it, and this was stirred for 12 h at room temperature. The reaction mixture was filtered through Celite with Et$_2$O and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 20/1 to afford 1-bromo-3-(*tert*-butyl)-5-(methoxymethoxy)benzene (CAS 2918833-89-1) as a colorless oil (2.38 g, 8.71 mmol; 92% yield).

^{1}H NMR ($CDCl_3$): δ 7.16 (dd, $^4J_{HH}$ = 2.0 and 1.5 Hz, 1H), 7.05 (t, $^4J_{HH}$ = 2.0 Hz, 1H), 6.96 (t, $^4J_{HH}$ = 1.9 Hz, 1H), 5.14 (s, 2H), 3.48 (s, 3H), 1.28 (s, 9H).

*n*BuLi (6.14 mL, 9.27 mmol; 1.51 M solution in hexane) was added slowly over 10 min to a solution of 1-bromo-3-(*tert*-butyl)-5-(methoxymethoxy)benzene (2.38 g, 8.71 mmol) in THF (20 mL) at –75 °C, and the resulting mixture was stirred for 25 min at –75 °C. DMF (1.30 mL, 16.9 mmol) was added to it and the mixture was stirred for 15 min at –75 °C and for 3 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/EtOAc = 15/1 → 10/1 (gradient) to afford 3-(*tert*-butyl)-5-(methoxymethoxy)benzaldehyde (CAS 2918943-79-8) as an orange oil (1.65 g, 7.41 mmol; 85% yield).

^{1}H NMR ($CDCl_3$): δ 9.96 (s, 1H), 7.56 (t, $^4J_{HH}$ = 1.5 Hz 1H), 7.38 (dd, $^4J_{HH}$ = 2.4 and 1.0 Hz, 1H), 7.31 (dd, $^4J_{HH}$ = 2.5 and 1.9 Hz, 1H), 5.23 (s, 2H), 3.50 (s, 3H), 1.35 (s, 9H).

A solution of iodomethane (493 μL, 7.92 mmol) in Et_2O (7.0 mL) was added slowly over 20 min to a suspension of Mg turnings (206 mg, 8.47 mmol) in Et_2O (3.0 mL), and the resulting mixture was stirred for 45 min at room temperature. This was cooled to –75 °C and a solution of 3-(*tert*-butyl)-5-(methoxymethoxy)benzaldehyde (1.60 g, 7.20 mmol) in Et_2O (13 mL) was added to it over 5 min. The mixture was stirred for 2.5 h at room temperature and the reaction was quenched with saturated NH_4Claq. This was extracted with Et_2O, and the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 4/1 → 2/1 (gradient) to afford 1-(3-(*tert*-butyl)-5-(methoxymethoxy)phenyl)ethanol as a colorless oil (1.66 g, 6.96 mmol; 97% yield).

^{1}H NMR (CDCl$_3$): δ 7.05 (t, $^4J_{HH}$ = 1.5 Hz, 1H), 6.97 (t, $^4J_{HH}$ = 2.0 Hz, 1H), 6.90 (dd, $^4J_{HH}$ = 2.0 and 1.5 Hz, 1H), 5.18 (s, 2H), 4.87 (qd, $^3J_{HH}$ = 6.3 and 3.4 Hz, 1H), 3.49 (s, 3H), 1.80 (d, $^3J_{HH}$ = 3.4 Hz, 1H), 1.50 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 1.31 (s, 9H).

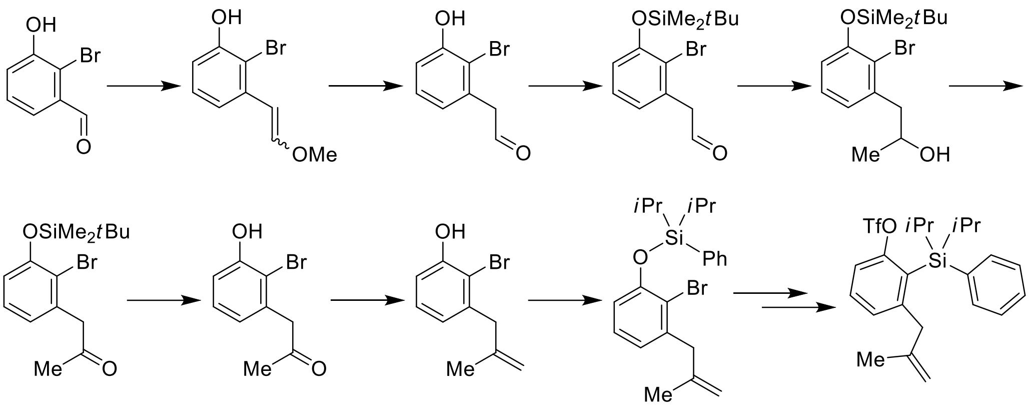
A solution of 1-(3-(*tert*-butyl)-5-(methoxymethoxy)phenyl)ethanol (1.59 g, 6.67 mmol) in THF (10 mL) was added over 5 min to a solution of *N*-bromosuccinimide (1.55 g, 8.71 mmol) in THF (15 mL) and DMF (10 mL) at 0 °C, and the mixture was stirred for 3 h at 0 °C. The reaction was poured into H_2O and this was extracted with Et_2O. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 to afford 1-(2-bromo-5-(*tert*-butyl)-3-(methoxymethoxy)phenyl)ethanol as a pale yellow solid (1.36 g, 4.29 mmol; 64% yield).

^{1}H NMR (CDCl$_3$): δ 7.32 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 7.09 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 5.29 (qd, $^3J_{HH}$ = 6.4 and 3.9 Hz, 1H), 5.25 (d, $^2J_{HH}$ = 7.3 Hz, 1H), 5.23 (d, $^2J_{HH}$ = 6.8 Hz, 1H), 3.54 (s, 3H), 2.01 (d, $^3J_{HH}$ = 3.4 Hz, 1H), 1.49 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.32 (s, 9H).

1-(2-Bromo-5-(*tert*-butyl)-3-(methoxymethoxy)phenyl)ethanol (1.36 g, 4.29 mmol) was converted to compound **4n**, following the procedure for compound **4b**. White solid (1.29 g, 2.27 mmol; 53% yield over 6 steps).

^{1}H NMR (CDCl$_3$): δ 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.31-7.23 (m, 3H), 7.02 (d, $^4J_{HH}$ = 1.5 Hz, 1H), 4.71 (s, 1H), 4.64 (s, 1H), 1.77 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.49 (s, 3H), 1.31 (s, 9H), 1.30 (s, 9H), 1.16 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.03 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.4, 154.7, 154.2, 151.6, 146.8, 135.6, 131.7, 124.4, 124.1, 122.6, 118.7, 117.7, 114.0, 35.0, 34.7, 31.4, 31.0, 24.5, 20.1, 19.4, 13.1. ^{19}F NMR (CDCl$_3$): δ –74.3 (s). HRMS (FAB) calcd for $C_{30}H_{43}F_3O_3SSi$ (M$^+$) 568.2649, found 568.2660.

2-(Diisopropyl(phenyl)silyl)-3-(2-methylallyl)phenyl trifluoromethanesulfonate (9)



KO*t*Bu (2.81 g, 25.0 mmol) was added to a suspension of (Methoxymethyl)triphenylphosphonium chloride (7.71 g, 22.5 mmol) in THF (90 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. A solution of 2-bromo-3-hydroxybenzaldehyde (2.01 g, 10.0 mmol) in THF (10 mL) was added to it at 0 °C, and the resulting mixture was stirred for 13 h at 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 hexane/EtOAc = 4/1 → 2/1 to afford 2-bromo-3-(2-methoxyvinyl)phenol as a colorless oil, which was used without further purification.

^{1}H NMR ($CDCl_3$): δ 7.60 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 0.47H), 7.18-7.08 (m, 1H), 6.99 (d, $^3J_{HH}$ = 12.7 Hz, 0.53H), 6.91 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 0.53H), 6.87-6.81 (m, 1H), 6.26 (d, $^3J_{HH}$ = 7.3 Hz, 0.47H), 6.01 (d, $^3J_{HH}$ = 13.1 Hz, 0.53H), 5.64 (s, 0.53H), 5.62 (s, 0.47H), 5.51 (d, $^3J_{HH}$ = 7.3 Hz, 0.47H), 3.79 (s, 1.41H), 3.73 (s, 1.59H).

HCl (3.3 mL; 3 M in H_2O) was added to a solution of 2-bromo-3-(2-methoxyvinyl)phenol obtained above in THF (40 mL) and the resulting mixture was stirred for 2.5 h at 0 °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/EtOAc = 5/1 → 2/1 to afford (2-bromo-3-hydroxyphenyl)acetaldehyde (CAS 2229576-67-2) as a white solid (1.64 g, 7.64 mmol; 76% yield over 2 steps).

^{1}H NMR ($CDCl_3$): δ 9.74 (t, $^3J_{HH}$ = 1.5 Hz, 1H), 7.22 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.99 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.82 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 5.81-5.60 (m, 1H), 3.86 (d, $^3J_{HH}$ = 1.5 Hz, 2H).

A solution of (2-bromo-3-hydroxyphenyl)acetaldehyde (1.64 g, 7.64 mmol) in THF (10 mL) and imidazole (1.70 g, 25.0 mmol) were added to a solution of *tert*-butylchlorodimethylsilane (1.21 g, 8.02 mmol) in THF (5 mL), and the resulting mixture was stirred for 1 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 hexane → hexane/EtOAc = 100/1 to afford (2-bromo-3-((*tert*-butyldimethylsilyl)oxy)phenyl)acetaldehyde as a colorless oil (1.32 g, 4.02 mmol; 53% yield).

^{1}H NMR ($CDCl_3$): δ 9.74 (t, $^3J_{HH}$ = 1.9 Hz, 1H), 7.16 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 6.84 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 3.86 (d, $^3J_{HH}$ = 2.0 Hz, 2H), 1.05 (s, 9H), 0.26 (s, 6H).

A solution of iodomethane (374 μL, 6.00 mmol) in Et_2O (2.0 mL) was added dropwise over 10 min to Mg turnings (166 mg, 6.83 mmol) in Et_2O (4.0 mL) at 0 °C, and the mixture was stirred for 30 min at room temperature. This was diluted with Et_2O (2.0 mL) and added to a solution of (2-bromo-3-((*tert*-butyldimethylsilyl)oxy)phenyl)acetaldehyde (1.32 g, 4.02 mmol) in Et_2O (4.0 mL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C and 1 h at room temperature, and the reaction was quenched with saturated NH_4Claq. 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 hexane → hexane/EtOAc = 4/1 to afford 1-(2-bromo-3-((*tert*-butyldimethylsilyl)oxy)phenyl)propan-2-ol as a yellow oil (1.09 g, 3.17 mmol; 79% yield).

^{1}H NMR ($CDCl_3$): δ 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.86 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.77 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.21-4.07 (m, 1H), 3.00 (dd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 4.9 Hz, 1H), 2.84 (dd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 8.3 Hz, 1H), 1.28 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 1.05 (s, 9H), 0.25 (s, 6H).

Pyridinium chlorochromate (1.03 g, 4.76 mmol) and Celite (1.03 g) were added to a solution of 1-(2-bromo-3-((*tert*-butyldimethylsilyl)oxy)phenyl)propan-2-ol (1.09 g, 3.17 mmol) in CH_2Cl_2 (25 mL), and the mixture was stirred for 2.5 h at room temperature. This was passed through a pad of Celite with CH_2Cl_2 and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane → hexane/EtOAc = 10/1 to afford 1-(2-bromo-3-((*tert*-butyldimethylsilyl)oxy)phenyl)propan-2-one as a colorless oil (906 mg, 2.64 mmol; 83% yield).

^{1}H NMR ($CDCl_3$): δ 7.13 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.86-6.77 (m, 2H), 3.87 (s, 2H), 2.19 (s, 3H), 1.04 (s, 9H), 0.25 (s, 6H).

LiOAc (17.2 mg, 0.261 mmol) was added to the solution of 1-(2-bromo-3-((*tert*-butyldimethylsilyl)oxy)phenyl)propan-2-one (906 mg, 2.64 mmol) in DMF (25 mL) and H_2O (0.5 mL), and the resulting mixture was stirred for 1.5 h at 70 °C. 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 hexane/EtOAc = 2/1 to afford 1-(2-bromo-3-hydroxyphenyl)propan-2-one (CAS 1379333-76-2) as a colorless oil (336 mg, 1.47 mmol; 56% yield).

^{1}H NMR ($CDCl_3$): δ 7.19 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 6.96 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 6.80 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 5.60 (bs, 1H), 3.86 (s, 2H), 2.21 (s, 3H).

KO*t*Bu (628 mg, 5.60 mmol) was added to a suspension of methyltriphenylphosphonium bromide (1.80 g, 5.04 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. A solution of 1-(2-bromo-3-hydroxyphenyl)propan-2-one (513 mg, 2.24 mmol) in THF (7.0 mL) was added to it at 0 °C, and the resulting mixture was stirred for 11 h at 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 hexane/EtOAc = 20/1 → 5/1 to afford 2-bromo-3-(2-methylallyl)phenol as a colorless oil (478 mg, 2.11 mmol; 94% yield).

^{1}H NMR ($CDCl_3$): δ 7.15 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.91 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.80 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 5.65 (s, 1H), 4.86 (s, 1H), 4.60 (s, 1H), 3.44 (s, 2H), 1.75 (s, 3H).

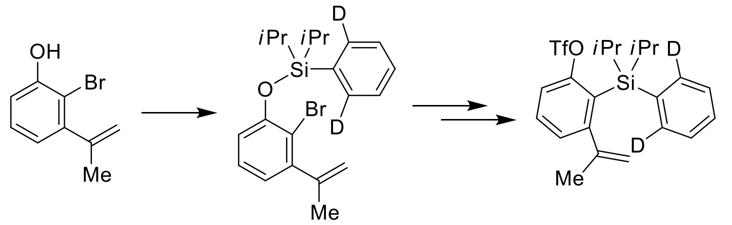
*n*BuLi (2.24 mL, 3.38 mmol; 1.51 M solution in hexane) was added dropwise over 10 min to a solution of bromobenzene (354 μL, 3.38 mmol) in THF (7.0 mL) at –78 °C, and the mixture was stirred for 30 min at –78 °C. Dichlorodiisopropylsilane (608 μL, 3.38 mmol) was added to it and the mixture was stirred for 2.5 h at room temperature. 2-Bromo-3-(2-methylallyl)phenol (641 mg, 2.82 mmol) and imidazole (480 g, 7.05 mmol) were then added it and the resulting mixture was stirred for 4 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 hexane to afford (2-bromo-3-(2-methylallyl)phenoxy)diisopropyl(phenyl)silane as a colorless oil (964 mg, 2.31 mmol; 82% yield).

^{1}H NMR (CDCl$_3$): δ 7.70-7.64 (m, 2H), 7.45-7.35 (m, 3H), 6.98 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.80 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.67 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.84 (s, 1H), 4.58 (s, 1H), 3.49 (s, 2H), 1.76 (s, 3H), 1.49 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.13 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 1.06 (d, $^3J_{HH}$ = 7.8 Hz, 6H).

(2-Bromo-3-(2-methylallyl)phenoxy)diisopropyl(phenyl)silane (964 mg, 2.31 mmol) was converted to compound **9**, following the procedure for compound **4a**. White solid (962 mg, 2.04 mmol; 88% yield over 2 steps).

^{1}H NMR (CDCl$_3$): δ 7.44-7.33 (m, 4H), 7.33-7.27 (m, 3H), 7.22 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.77 (s, 1H), 4.40 (s, 1H), 3.03 (s, 2H), 1.82 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.30 (s, 3H), 1.08 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.95 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.4, 150.1, 144.9, 134.7, 134.6, 130.8, 129.6, 129.0, 127.8, 126.0, 118.7, 116.4, 113.6, 45.6, 22.5, 18.6, 18.4, 12.0. ^{19}F NMR (CDCl$_3$): δ –74.2 (s). HRMS (FAB) calcd for $C_{23}H_{28}F_3O_3SSi$ (M–H$^-$) 469.1475, found 469.1482.

2-(Diisopropyl(2,6-dideuteriophenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4a-*d*$_2$)



*t*BuLi (2.83 mL, 4.81 mmol; 1.70 M solution in pentane) was added dropwise over 30 min to a solution of 2,6-dideuterio-1-iodobenzene (540 mg, 2.63 mmol; 96% D) in THF (7.2 mL) at –78 °C, and the mixture was stirred for 30 min at –78 °C.

Dichlorodiisopropylsilane (433 μL, 2.40 mmol) was added to it, and the mixture was stirred for 2 h at room temperature. 2-Bromo-3-(propen-2-yl)phenol (487 mg, 2.29 mmol) and imidazole (390 mg, 5.73 mmol) were then added to it and the resulting mixture was stirred for 2 h at 40 °C. The reaction mixture was filtered through Celite with Et_2O and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 100/1 → 50/1 to afford (2-bromo-3-(propen-2-yl)phenoxy)diisopropyl(2,6-dideuteriophenyl)silane as a colorless oil (823 mg, 2.03 mmol; 85% yield, 96% D).

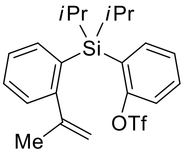
^{1}H NMR ($CDCl_3$): δ 7.69-7.65 (m, 0.08H), 7.47-7.36 (m, 3H), 6.98 (dd, $^3J_{HH}$ = 8.3 and 7.3 Hz, 1H), 6.75 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 6.69 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 5.21-5.17 (m, 1H), 4.94-4.91 (m, 1H), 2.10 (dd, $^4J_{HH}$ = 1.4 and 1.0 Hz, 3H), 1.49 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.14 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.07 (d, $^3J_{HH}$ = 7.3 Hz, 6H).

(2-Bromo-3-(propen-2-yl)phenoxy)diisopropyl(2,6-dideuteriophenyl)silane (823 mg, 2.03 mmol; 96% D) was converted to compound **4a-*d*₂**, following the procedure for compound **4b**. White solid (690 mg, 1.50 mmol; 74% yield over 2 steps, 96% D).

^{1}H NMR ($CDCl_3$): δ 7.44-7.36 (m, 1.08H), 7.36-7.26 (m, 4H), 7.09 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 4.78-4.75 (m, 1H), 4.71-4.68 (m, 1H), 1.80 (sept, $^3J_{HH}$ = 7.4Hz, 2H), 1.58-1.54 (m, 3H), 1.15 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.03 (d, $^3J_{HH}$ = 7.3 Hz, 6H). $^{13}C\{^1H,^{19}F\}$ NMR ($CDCl_3$): δ 157.2, 155.4, 146.3, 135.2, 135.1 (t, $^1J_{CD}$ = 23.9 Hz), 130.5, 128.8, 127.5, 127.3, 125.9, 118.7, 118.3, 116.6, 24.3, 20.0, 19.3, 13.0. ^{19}F NMR ($CDCl_3$): δ –74.3 (s). HRMS (FAB) calcd for $C_{22}H_{25}D_2F_3O_3SSi$ (M^+) 458.1522, found 458.1539.

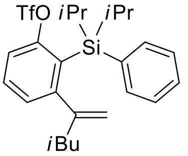
Analytical data for other substrates:

2-(Diisopropyl(2-(propen-2-yl)phenyl)silyl)phenyl trifluoromethanesulfonate (4a')



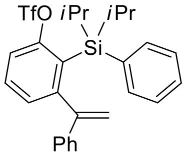
^{1}H NMR (CDCl$_3$): δ 7.64 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 7.58 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 2.0 Hz, 1H), 7.42 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 2.0 Hz, 1H), 7.36-7.28 (m, 3H), 7.25 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 7.07 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 4.87 (s, 1H), 4.58 (s, 1H), 1.89 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.55 (s, 3H) 1.20 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.12 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 156.1, 151.2, 147.4, 138.1, 136.5, 131.4, 131.1, 129.9, 129.0, 128.0, 126.9, 125.9, 118.6, 118.4, 115.9, 24.8, 19.4, 19.3, 13.1. ^{19}F NMR (CDCl$_3$): δ –74.6 (s). HRMS (FAB) calcd for $C_{22}H_{27}F_3O_3SSi$ (M$^+$) 456.1397, found 456.1418.

2-(Diisopropyl(phenyl)silyl)-3-(4-methylpenten-2-yl)phenyl trifluoromethanesulfonate (4c)



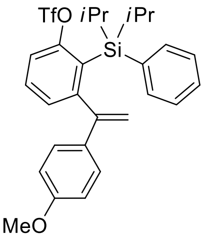
^{1}H NMR (CDCl$_3$): δ 7.46-7.41 (m, 2H), 7.40-7.29 (m, 3H), 7.29-7.23 (m, 2H), 7.04 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 4.82 (d, $^2J_{HH}$ = 1.4 Hz, 1H), 4.75-4.72 (m, 1H), 1.93-1.61 (m, 2H), 1.78 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.35 (sept, $^3J_{HH}$ = 6.6 Hz, 1H), 1.13 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.78 (d, $^3J_{HH}$ = 6.4 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.2, 155.2, 149.4, 135.7, 135.0, 130.5, 129.1, 128.9, 127.3, 125.4, 118.6, 117.1, 116.6, 48.3, 25.8, 22.4, 20.1, 19.3, 12.8. ^{19}F NMR (CDCl$_3$): δ –74.3 (s). HRMS (FAB) calcd for $C_{25}H_{33}F_3O_3SSi$ (M$^+$) 498.1866, found 498.1873.

2-(Diisopropyl(phenyl)silyl)-3-(1-phenylvinyl)phenyl trifluoromethanesulfonate (4d)



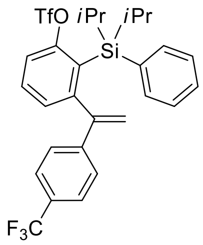
^{1}H NMR (CDCl$_3$): δ 7.49-7.40 (m, 2H), 7.25-7.11 (m, 7H), 7.05 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 6.95-6.89 (m, 2H), 5.44 (s, 1H), 4.98 (s, 1H), 1.66-1.44 (m, 2H), 0.98 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.90 (d, $^3J_{HH}$ = 6.8 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.6, 152.3, 148.5, 139.8, 135.4, 134.5, 131.1, 130.6, 128.7, 128.0, 127.8, 127.2, 127.0, 126.9, 118.7, 117.1, 116.7, 19.7, 19.2, 12.5. ^{19}F NMR (CDCl$_3$): δ –74.1 (s). HRMS (FAB) calcd for $C_{27}H_{29}F_3O_3SSi$ (M$^+$) 518.1553, found 518.1551.

2-(Diisopropyl(phenyl)silyl)-3-(1-(4-methoxyphenyl)vinyl)phenyl trifluoromethanesulfonate (4e)



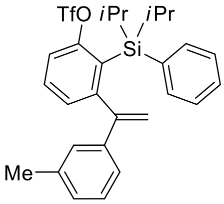
^{1}H NMR (CDCl$_3$): δ 7.48-7.40 (m, 2H), 7.28-7.23 (m, 2H), 7.19 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.13 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.07 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 6.86 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 5.32 (s, 1H), 4.88 (s, 1H), 3.80 (s, 3H), 1.79-1.42 (m, 2H), 1.01 (d, $^3J_{HH}$ = 6.0 Hz, 6H), 0.93 (d, $^3J_{HH}$ = 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 159.5, 157.5, 152.6, 147.9, 135.4, 134.6, 132.8, 131.0, 130.5, 128.7, 128.1, 127.2, 126.9, 118.7 (q, $^1J_{CF}$ = 321 Hz), 117.0 (q, $^5J_{CF}$ = 2.6 Hz), 114.7, 113.3, 55.4, 19.8, 19.2, 12.5. HRMS (FAB) calcd for $C_{28}H_{31}F_3O_4SSi$ (M$^+$) 548.1659, found 548.1671.

2-(Diisopropyl(phenyl)silyl)-3-(1-(4-trifluoromethylphenyl)vinyl)phenyl trifluoromethanesulfonate (4f)



^{1}H NMR (CDCl$_3$): δ 7.52-7.45 (m, 2H), 7.37 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.23-7.18 (m, 2H), 7.14 (tt, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.09 (dd, $^3J_{HH}$ = 6.0 Hz and $^4J_{HH}$ = 2.8 Hz, 1H), 7.02-6.96 (m, 4H), 5.53 (s, 1H), 5.09 (s, 1H), 1.75-1.50 (m, 2H), 1.06 (d, $^3J_{HH}$ = 7.8 Hz, 6H), 0.93 (d, $^3J_{HH}$ = 6.4 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.5, 151.2, 147.2, 142.8, 135.6, 134.1, 130.9, 130.8, 129.6, 129.0, 127.6, 127.0, 126.8, 124.9, 124.3, 118.8, 118.7, 117.5, 19.7, 19.2, 12.7. ^{19}F NMR (CDCl$_3$) = –62.7 (s), –74.1 (s). HRMS (FAB) calcd for $C_{28}H_{28}F_6O_3SSi$ (M$^+$) 586.1427, found 586.1443.

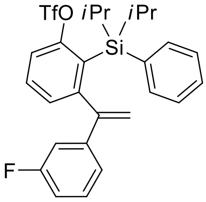
2-(Diisopropyl(phenyl)silyl)-3-(1-(3-methylphenyl)vinyl)phenyl trifluoromethanesulfonate (4g)



^{1}H NMR (CDCl$_3$): δ 7.50-7.40 (m, 2H), 7.25-7.17 (m, 3H), 7.16-7.12 (m, 1H), 7.09-6.98 (m, 4H), 6.70 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 6.65 (s, 1H), 5.42 (s, 1H), 4.96 (s, 1H), 2.24 (s, 3H), 1.69-1.40 (m, 2H), 1.00 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.91 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.5, 152.4, 148.7, 139.8, 137.4, 135.5, 134.5, 131.2, 130.6, 128.6, 128.5, 127.9, 127.5, 127.2, 126.9, 124.1, 118.7, 117.0, 116.5, 21.5, 19.7, 19.2, 12.5. ^{19}F NMR (CDCl$_3$): δ –74.1 (s). HRMS (FAB) calcd for $C_{28}H_{32}F_3O_3SSi$

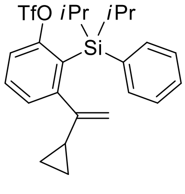
(M+H$^+$) 533.1788, found 533.1807.

2-(Diisopropyl(phenyl)silyl)-3-(1-(3-fluorophenyl)vinyl)phenyl trifluoromethanesulfonate (4h)



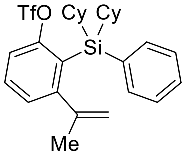
^{1}H NMR (CDCl$_3$): δ 7.51-7.41 (m, 2H), 7.25-7.14 (m, 3H), 7.09 (td, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.3 Hz, 2H), 7.03 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 6.87 (td, ^3J = 8.3 Hz and $^4J_{HH}$ = 2.4 Hz, 1H), 6.65 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.54 (d, $^3J_{HF}$ = 10.7 Hz, 1H), 5.42 (s, 1H), 5.01 (s, 1H), 1.68-1.47 (m, 2H), 1.03 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.92 (d, $^3J_{HH}$ = 6.4 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 162.7, 157.5, 151.5, 147.4, 142.0, 135.6, 134.2, 131.0, 130.7, 129.3, 128.8, 127.4, 127.0, 122.6, 118.7, 117.8, 117.3, 114.5, 113.4, 19.7, 19.2, 12.7. ^{19}F NMR (CDCl$_3$): δ –74.1 (s), –114.0 (m). HRMS (FAB) calcd for $C_{27}H_{28}F_4O_3SSi$ (M$^+$) 536.1459, found 536.1478.

3-(1-Cyclopropylvinyl)-2-(diisopropyl(phenyl)silyl)phenyl trifluoromethanesulfonate (4i)



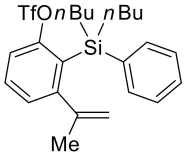
^{1}H NMR (CDCl$_3$): δ 7.43-7.36 (m, 3H), 7.35-7.29 (m, 2H), 7.29-7.22 (m, 3H), 4.58 (s, 1H), 4.46 (s, 1H), 1.82 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.13 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.11-1.03 (m, 1H), 1.03 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 0.66-0.52 (m, 2H), 0.40-0.30 (m, 2H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.4, 155.3, 152.3, 135.6, 135.5, 130.4, 128.7, 128.4, 127.4, 126.2, 118.8, 116.8, 111.5, 19.9, 19.4, 17.9, 13.1, 9.2. ^{19}F NMR (CDCl$_3$): δ –74.3 (s). HRMS (FAB) calcd for $C_{24}H_{30}F_3O_3SSi$ (M+H$^+$) 483.1632, found 483.1638.

2-(Dicyclohexyl(phenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4j)



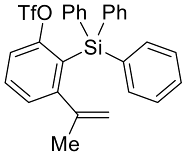
^{1}H NMR (CDCl$_3$): δ 7.43-7.30 (m, 4H), 7.30-7.24 (m, 3H), 7.09 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 4.79-4.76 (m, 1H), 4.70-4.67 (m, 1H), 1.86-1.66 (m, 10H), 1.65 (s, 3H), 1.62-1.54 (m, 2H), 1.37-1.06 (m, 10H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.3, 155.3, 146.0, 136.0, 135.4, 130.4, 128.7, 127.7, 127.4, 125.4, 118.7, 118.1, 116.6, 29.8, 29.2, 28.6, 28.5, 27.1, 25.6, 24.8. ^{19}F NMR (CDCl$_3$): δ –74.1 (s). HRMS (FAB) calcd for $C_{28}H_{35}F_3O_3SSi$ (M$^+$) 536.2023, found 536.2044.

2-(Dibutyl(phenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4k)



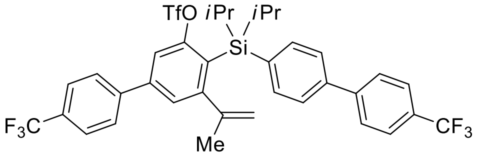
^{1}H NMR (CDCl$_3$): δ 7.42-7.34 (m, 3H), 7.34-7.20 (m, 4H), 7.10 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 4.97 (s, 1H), 4.76 (s, 1H), 1.69 (s, 3H), 1.43-1.12 (m, 12H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 156.4, 155.1, 146.3, 137.7, 134.7, 130.7, 128.8, 127.59, 127.55, 127.4, 118.6, 118.0, 117.7, 26.7, 26.3, 24.9, 14.2, 13.8. ^{19}F NMR (CDCl$_3$): δ –74.2 (s). HRMS (FAB) calcd for $C_{24}H_{31}F_3O_3SSi$ (M$^+$) 484.1710, found 484.1724.

3-(Propen-2-yl)-2-(triphenylsilyl)phenyl trifluoromethanesulfonate (4l)



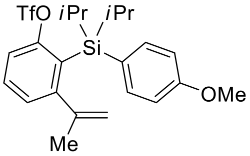
^{1}H NMR (CDCl$_3$): δ 7.62-7.55 (m, 6H), 7.50 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.41-7.28 (m, 10H), 7.17 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 4.64 (s, 1H), 4.47 (s, 1H), 1.36 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 156.19, 156.17, 145.3, 136.4, 134.8, 131.6, 129.4, 127.7, 127.5, 124.8, 119.4, 118.0 (q, $^1J_{CF}$ = 320 Hz), 117.6 (q, $^5J_{CF}$ = 1.9 Hz), 24.4. HRMS (FAB) calcd for $C_{28}H_{23}F_3O_3SSi$ (M$^+$) 524.1084, found 524.1086.

2-(Diisopropyl(4-(4-trifluoromethylphenyl)phenyl)silyl)-3-(propen-2-yl)-5-(4-trifluoromethylphenyl)phenyl trifluoromethanesulfonate (4p)



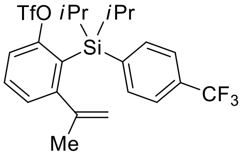
^{1}H NMR (CDCl$_3$): δ 7.78-7.67 (m, 8H), 7.62-7.54 (m, 5H), 7.35 (d, $^4J_{HH}$ = 1.5 Hz, 1H), 4.89 (s, 1H), 4.83 (s, 1H), 1.88 (sept, $^3J_{HH}$ = 7.4 Hz, 2H), 1.70 (s, 3H), 1.23 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 1.11 (d, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.7, 155.9, 146.0, 144.7, 142.5, 142.3, 140.0, 136.1, 135.4, 130.7, 129.6, 127.6, 127.5, 126.23, 126.19, 125.9, 125.4, 124.5, 124.2, 118.8, 118.7, 115.4, 24.6, 20.1, 19.3, 13.0. ^{19}F NMR (CDCl$_3$): δ –62.5 (s), –62.7 (s), –74.2 (s). HRMS (FAB) calcd for $C_{36}H_{33}F_9O_3SSi$ (M$^+$) 744.1770, found 744.1767.

2-(Diisopropyl(4-methoxyphenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4q)



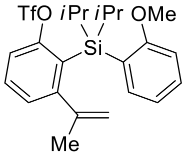
^{1}H NMR (CDCl$_3$): δ 7.40-7.32 (m, 3H), 7.29 (dd, $^3J_{\mathrm{HH}}$ = 8.2 Hz and $^4J_{\mathrm{HH}}$ = 0.9 Hz, 1H), 7.07 (dd, $^3J_{\mathrm{HH}}$ = 7.4 Hz and $^4J_{\mathrm{HH}}$ = 0.9 Hz, 1H), 6.84 (d, $^3J_{\mathrm{HH}}$ = 8.7 Hz, 2H), 4.78-4.75 (m, 1H), 4.67-4.64 (m, 1H), 3.82 (s, 3H), 1.76 (sept, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2H), 1.55 (s, 3H), 1.14 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 160.2, 157.1, 155.4, 146.4, 137.1, 130.4, 127.6, 126.3, 126.1, 118.6, 118.0, 116.5, 113.1, 55.1, 24.5, 20.0, 19.3, 13.2. ^{19}F NMR (CDCl$_3$): δ –74.3 (s). HRMS (FAB) calcd for $C_{23}H_{29}F_3O_4SSi$ (M$^+$) 486.1502, found 486.1528.

2-(Diisopropyl(4-trifluoromethylphenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4r)



^{1}H NMR (CDCl$_3$): δ 7.57-7.51 (m, 4H), 7.41 (dd, $^3J_{\mathrm{HH}}$ = 8.3 and 7.8 Hz, 1H), 7.33 (d, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 1H), 7.13 (dd, $^3J_{\mathrm{HH}}$ = 7.3 Hz and $^4J_{\mathrm{HH}}$ = 1.0 Hz, 1H), 4.81-4.78 (m, 1H), 4.74-4.71 (m, 1H), 1.82 (sept, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 2H), 1.61 (s, 3H), 1.15 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H), 1.02 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 157.1, 155.1, 146.0, 140.9, 135.4, 130.9, 130.8, 127.6, 124.8, 124.4, 123.9, 118.8, 118.6, 116.7, 24.4, 19.9, 19.2, 12.9. ^{19}F NMR (CDCl$_3$): δ –63.0 (s), –74.3 (s). HRMS (FAB) calcd for $C_{23}H_{26}F_6O_3SSi$ (M$^+$) 524.1271, found 524.1258.

2-(Diisopropyl(2-methoxyphenyl)silyl)-3-(propen-2-yl)phenyl trifluoromethanesulfonate (4s)

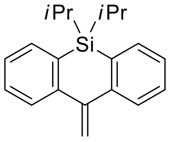


^{1}H NMR (CDCl$_3$): δ 7.39 (dd, $^3J_{\mathrm{HH}}$ = 7.3 Hz and $^4J_{\mathrm{HH}}$ = 1.9 Hz, 1H), 7.36-7.30 (m, 2H), 7.29-7.24 (m, 1H), 7.05 (dd, $^3J_{\mathrm{HH}}$ = 7.3 Hz and $^4J_{\mathrm{HH}}$ = 1.0 Hz, 1H), 6.93 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 1H), 6.72 (d, $^3J_{\mathrm{HH}}$ = 8.3 Hz, 1H), 4.76-4.72 (m, 1H), 4.67 (s, 1H), 3.54 (s, 3H), 1.80 (sept, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2H), 1.65 (s, 3H), 1.10 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H), 1.03 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 163.9, 156.8, 154.6, 145.7, 136.5, 130.6, 129.8, 127.4, 126.8, 124.1, 120.3, 118.7, 117.3, 116.3, 109.2, 54.2, 24.8, 20.1, 19.5, 13.5. ^{19}F NMR (CDCl$_3$): δ –74.2 (s). HRMS (FAB) calcd for $C_{23}H_{29}F_3O_4SSi$ (M^+) 486.1502, found 486.1498.

Catalytic reactions

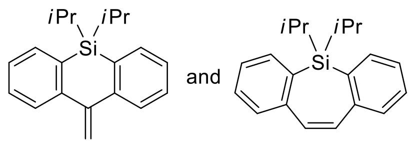
Procedure for schemes 2a and 2b.

Et_2NH (31.0 µL, 0.300 mmol) and DMF (0.6 mL) were added to a mixture of compound **1** or **1'** (44.3 mg, 0.100 mmol), $Ni(cod)_2$ (5.5 mg, 20 µmol), and PCy_3 (11.2 mg, 39.9 µmol), and the resulting solution was stirred for 16 h at 100 °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 passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The yields of **2** and **3** were determined by ^{1}H NMR against internal standard ($MeNO_2$). For analytical purpose, this was purified by reversed phase chromatography with MeCN and by GPC with $CHCl_3$.



Scheme 2a. 45% NMR yield of compound **2**.

2: ^{1}H NMR ($CDCl_3$): δ 7.69 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.62 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 7.41 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.0 Hz, 2H), 7.31 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 5.57 (s, 2H), 1.47 (sept, $^3J_{HH}$ = 7.5 Hz, 2H), 1.04 (d, $^3J_{HH}$ = 7.8 Hz, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.8, 147.3, 133.4, 131.0, 129.5, 126.4, 126.2, 117.4, 18.1, 12.3. HRMS (FAB) calcd for $C_{20}H_{25}Si$ (M+H$^+$) 293.1720, found 293.1735.

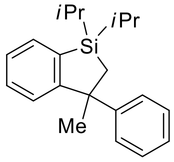


Scheme 2b. 39% NMR yield of compound **2** and 18% NMR yield of compound **3** (CAS 2577416-85-2)).

3: ^{1}H NMR ($CDCl_3$): δ 7.69 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H), 7.39-7.28 (m, 6H), 6.81 (s, 2H), 1.64 (sept, $^{3}J_{HH}$ = 7.6 Hz, 2H), 1.16 (d, $^{3}J_{HH}$ = 7.8 Hz, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 142.6, 134.5, 134.4, 133.4, 130.8, 129.0, 127.0, 18.5, 10.6.

General procedure for schemes 4–5 and equation 1.

Et_2NH (77.6 µL, 0.750 mmol), PMHS (29.9 µL, 0.500 mmol), and DMF (1.5 mL) were added to a mixture of compound **4** (0.250 mmol), $Ni(cod)_2$ (6.9 mg, 25 µmol), and PCy_3 (14.0 mg, 49.9 µmol), and the resulting solution was stirred for 16 h at 100 °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 passed through a pad of silica gel with hexane and EtOAc, and purified by reversed phase chromatography with MeCN to afford compound **5**.



Scheme 4, compound 5a. Colorless oil (57.2 mg, 0.185 mmol; 74% yield).

^{1}H NMR ($CDCl_3$): δ 7.56 (dd, $^{3}J_{HH}$ = 6.4 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.28 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.25-7.16 (m, 5H), 7.13 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H), 6.94 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 1.71 (s, 3H), 1.34 (d, $^{2}J_{HH}$ = 15.6 Hz, 1H), 1.25 (d, $^{2}J_{HH}$ = 15.6 Hz, 1H), 1.27-1.12 (m, 2H), 1.10 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H), 1.09 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H), 0.99 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H), 0.97 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 162.0, 153.7, 136.9, 132.9, 129.7, 128.0, 126.9, 126.8, 125.8, 125.4, 51.4, 32.9, 26.3, 18.9, 18.82, 18.78, 18.6, 12.4, 12.0. ^{29}Si{^{1}H} NMR (CDCl$_3$): δ 21.2. HRMS (FAB) calcd for $C_{21}H_{28}Si$ (M$^+$) 308.1955, found 308.1965.

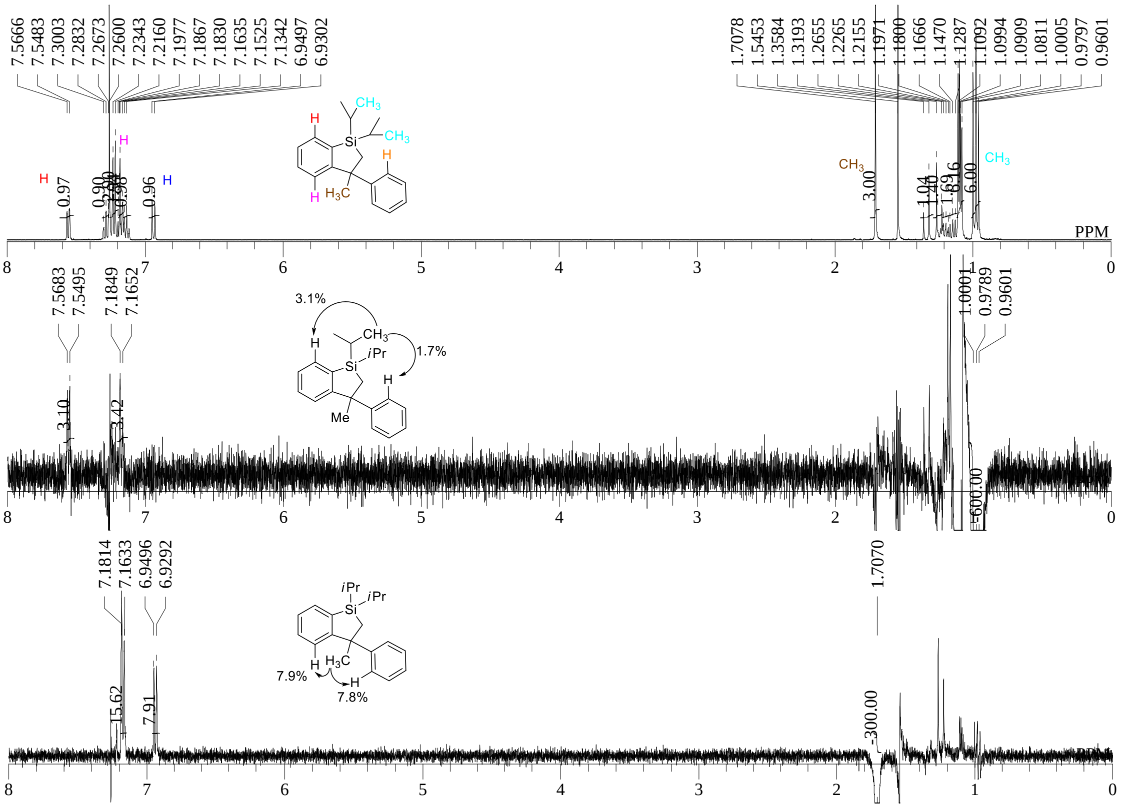


Figure S1. ^{1}H NMR spectrum and NOE spectra of **5a** in CDCl$_3$.

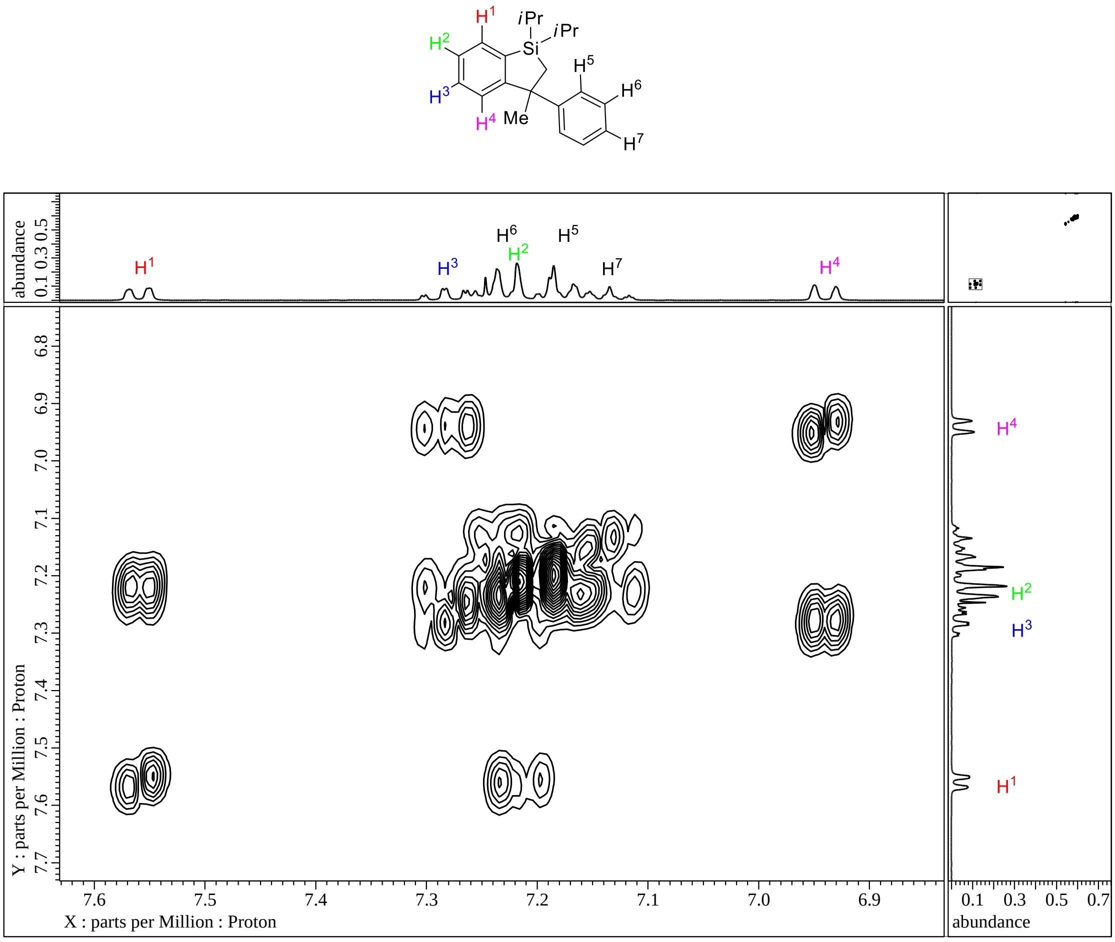


Figure S2. ^{1}H–^{1}H COSY spectrum (aromatic region) of **5a** in CDCl$_3$.

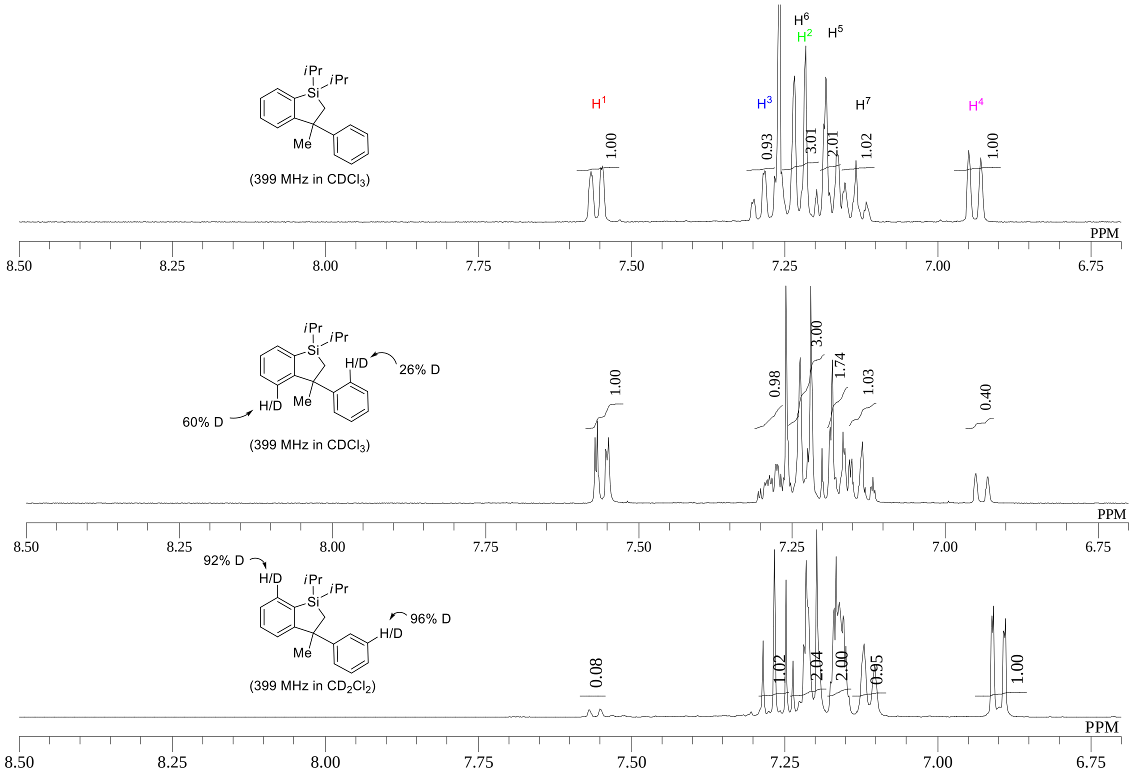
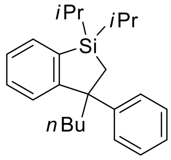
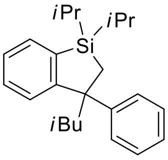


Figure S3. ^{1}H NMR spectra (aromatic region) of **5a** (Scheme 4) and **5a-*d*$_{0.86}$** (Table 2, entry 4) in $CDCl_3$ and **5a-*d*$_{1.88}$** (eq 1) in CD_2Cl_2.



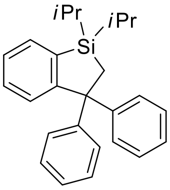
Scheme 4, compound 5b. Colorless oil (65.5 mg, 0.187 mmol; 75% yield).

^{1}H NMR ($CDCl_3$): δ 7.59 (dd, $^{3}J_{HH}$ = 6.8 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.35 (td, $^{3}J_{HH}$ = 7.5 Hz and $^{4}J_{HH}$ = 1.5 Hz, 1H), 7.26 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.0 Hz, 1H), 7.23-7.18 (m, 2H), 7.14-7.07 (m, 4H), 2.16-2.06 (m, 2H), 1.42 (d, $^{2}J_{HH}$ = 15.6 Hz, 1H), 1.37-1.17 (m, 4H), 1.26 (d, $^{2}J_{HH}$ = 15.6 Hz, 1H), 1.17-1.05 (m, 1H), 1.13 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 1.08 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H), 1.05-0.92 (m, 1H), 0.88 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H), 0.86 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H), 0.84 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 158.4, 152.9, 138.9, 133.2, 129.1, 127.9, 127.5, 127.3, 125.8, 125.3, 55.4, 43.8, 27.8, 23.5, 22.8, 19.1, 18.8, 18.5, 14.2, 12.4, 12.0. HRMS (FAB) calcd for $C_{24}H_{33}Si$ (M–H$^-$) 349.2346, found 349.2357.



Scheme 4, compound 5c. Colorless oil (50.5 mg, 0.157 mmol; 63% yield).

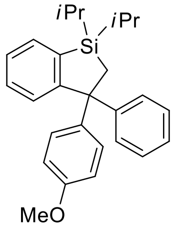
^{1}H NMR (CDCl$_3$): δ 7.58 (d, $^3J_{HH}$ = 6.3 Hz, 1H), 7.34 (td, $^3J_{HH}$ = 7.6 and $^4J_{HH}$ = 1.5 Hz, 1H), 7.25 (td, $^3J_{HH}$ = 7.2 and $^4J_{HH}$ = 1.1 Hz, 1H), 7.22-7.15 (m, 3H), 7.13-7.06 (m, 3H), 2.13 (dd, $^2J_{HH}$ = 14.1 and $^3J_{HH}$ = 4.9 Hz, 1H), 2.06 (dd, $^2J_{HH}$ = 14.1 and $^3J_{HH}$ = 4.9 Hz, 1H), 1.67-1.56 (m, 1H), 1.50-1.18 (m, 3H), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.09 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 0.96-0.86 (m, 1H), 0.86-0.79 (m, 9H), 0.70 (d, $^3J_{HH}$ = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 158.1, 153.1, 139.1, 133.3, 128.9, 128.0, 127.8, 127.4, 125.9, 125.3, 55.9, 52.4, 25.9, 25.5, 25.0, 23.0, 19.1, 18.84, 18.75, 18.5, 12.4, 12.1. HRMS (FAB) calcd for $C_{24}H_{33}Si$ (M–H$^-$) 349.2346, found 349.2348.



Scheme 4, compound 5d. White solid (47.7 mg, 0.129 mmol; 51% yield). The structure was determined by X-ray crystallographic analysis after recrystallization from hexane.

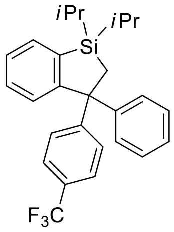
^{1}H NMR (CDCl$_3$): δ 7.64-7.58 (m, 1H), 7.30-7.19 (m, 6H), 7.18-7.13 (m, 2H), 7.06 (dd, $^3J_{HH}$ = 8.5 and $^3J_{HH}$ = 1.3 Hz, 4H), 6.80-6.73 (m, 1H), 2.03 (s, 2H), 1.06-0.97 (m, 2H), 0.96-0.89 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 159.3, 151.0, 138.2, 133.2, 129.5, 129.4, 129.1, 127.7, 126.1, 125.8, 61.5, 27.8, 18.8, 18.5, 11.9. HRMS (EI) calcd for

$C_{26}H_{30}Si$ (M^+) 370.2111, found 370.2115.



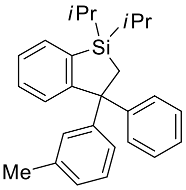
Scheme 4, compound 5e. White solid (49.8 mg, 0.124 mmol; 50% yield).

^1H NMR ($CDCl_3$): δ 7.62-7.56 (m, 1H), 7.29-7.18 (m, 4H), 7.18-7.12 (m, 1H), 7.08-7.02 (m, 2H), 6.96 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.79-6.72 (m, 3H), 3.78 (s, 3H), 1.98 (s, 2H), 1.07-0.87 (m, 14H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.6, 157.6, 151.4, 143.0, 138.1, 133.2, 130.4, 129.4, 129.3, 129.1, 127.7, 126.0, 125.7, 113.0, 60.8, 55.3, 27.7, 18.9, 18.5, 11.93, 11.88. HRMS (FAB) calcd for $C_{27}H_{32}OSi$ (M^+) 400.2217, found 400.2221.



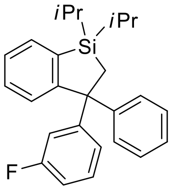
Scheme 4, compound 5f. Colorless oil (54.5 mg, 0.124 mmol; 50% yield).

^1H NMR ($CDCl_3$): δ 7.65-7.59 (m, 1H), 7.51-7.44 (m, 2H), 7.32-7.15 (m, 7H), 7.05-7.00 (m, 2H), 6.77-6.70 (m, 1H), 2.06 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.95 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.11-0.85 (m, 14H). $^{13}C\{^1H,^{19}F\}$ NMR ($CDCl_3$): δ 158.4, 155.5, 150.0, 138.2, 133.4, 129.6, 129.39, 129.37, 129.3, 128.1, 128.0, 126.4, 126.2, 124.7, 124.5, 61.6, 27.8, 18.82, 18.76, 18.5, 18.4, 11.9. ^{19}F NMR ($CDCl_3$): δ –62.4 (s). HRMS (FAB) calcd for $C_{27}H_{29}F_3Si$ (M^+) 438.1985, found 438.1990.



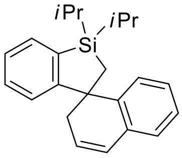
Scheme 4, compound 5g. White solid (38.9 mg, 0.101 mmol; 40% yield).

^{1}H NMR (CDCl$_3$): δ 7.62-7.56 (m, 1H), 7.29-7.18 (m, 4H), 7.18-7.12 (m, 1H), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.07-7.03 (m, 2H), 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.90 (s, 1H), 6.82 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.79-6.74 (m, 1H), 2.25 (s, 3H), 2.02 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.97 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.07-0.86 (m, 14H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 159.4, 151.0, 138.1, 137.1, 133.1, 130.1, 129.5, 129.4, 129.1, 127.7, 127.5, 126.55, 126.53, 126.0, 125.8, 61.4, 27.7, 21.8, 18.9, 18.8, 18.51, 18.47, 11.93, 11.91. HRMS (FAB) calcd for $C_{27}H_{32}Si$ (M$^+$) 384.2268, found 384.2275.



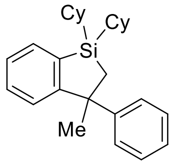
Scheme 4, compound 5h. White solid (40.3 mg, 0.104 mmol; 41% yield).

^{1}H NMR (CDCl$_3$): δ 7.63-7.58 (m, 1H), 7.31-7.13 (m, 6H), 7.06-7.00 (m, 2H), 6.90-6.83 (m, 2H), 6.78-6.72 (m, 2H), 2.03 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.95 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.09-0.87 (m, 14H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 162.6, 158.7, 153.9, 150.3, 138.1, 133.3, 129.33, 129.28, 129.23, 129.0, 127.8, 126.3, 126.1, 125.1, 116.5, 112.7, 61.4, 27.7, 18.8, 18.5, 18.4, 11.88, 11.85. ^{19}F NMR (CDCl$_3$): δ –113.8 (s). HRMS (FAB) calcd for $C_{26}H_{30}FSi$ (M+H$^+$) 389.2095, found 389.2105.



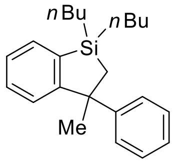
Scheme 4, compound 8i. The reaction was conducted using 20 mol% of Ni(cod)$_2$ and 40 mol% of PCy$_3$. Colorless oil (17.0 mg, 51.1 μmol; 20% yield).

^{1}H NMR (CDCl$_3$): δ 7.57 (dd, $^3J_{HH}$ = 7.8 and $^3J_{HH}$ = 1.0 Hz, 1H), 7.40-7.31 (m, 2H), 7.30-7.25 (m, 1H), 7.15-7.07 (m, 2H), 7.04-6.95 (m, 1H), 6.63-6.54 (m, 2H), 6.03-5.96 (m, 1H), 2.80 (dt, $^2J_{HH}$ = 17.6 and $^3J_{HH}$ = 2.4 Hz, 1H), 2.31 (dd, $^2J_{HH}$ = 17.6 and $^3J_{HH}$ = 6.3 Hz, 1H), 1.72 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.27-1.10 (m, 2H), 1.10-1.06 (m, 6H), 0.97-0.90 (m, 6H), 0.80 (d, $^2J_{HH}$ = 15.6 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 160.5, 146.5, 138.3, 132.9, 132.7, 129.7, 128.3, 127.5, 127.2, 126.9, 126.6, 126.23, 126.19, 126.1, 51.8, 42.5, 19.2, 18.8, 18.7, 18.6, 18.4, 12.3, 11.8. HRMS (FAB) calcd for $C_{23}H_{28}Si$ (M$^+$) 332.1955, found 332.1966.



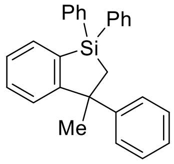
Scheme 4, compound 5j. Yellow oil (74.5 mg, 0.192 mmol; 77% yield).

^{1}H NMR (CDCl$_3$): δ 7.54 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.30-7.11 (m, 7H), 6.92 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 1.97-1.61 (m, 13H), 1.37-0.86 (m, 14H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.0, 153.7, 136.9, 133.0, 129.6, 128.0, 126.9, 126.8, 125.6, 125.3, 51.5, 32.9, 28.74, 28.68, 28.6, 28.41, 28.38, 28.34, 28.33, 28.28, 27.02, 26.95, 26.2, 24.2, 23.9. HRMS (EI) calcd for $C_{27}H_{36}Si$ (M$^+$) 388.2581, found 388.2582.



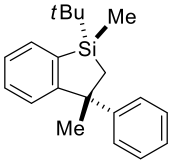
Scheme 4, compound 5k. The reaction was conducted using 20 mol% of Ni(cod)$_2$ and 40 mol% of PCy$_3$. Colorless oil (39.9 mg, 0.119 mmol; 47% yield).

^{1}H NMR (CDCl$_3$): δ 7.55 (dd, $^3J_{HH}$ = 6.6 and $^3J_{HH}$ = 1.2 Hz, 1H), 7.29 (td, $^3J_{HH}$ = 7.6 and $^3J_{HH}$ = 1.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.18-7.11 (m, 3H), 6.96 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 1.71 (s, 3H), 1.49-1.21 (m, 10H), 0.93-0.79 (m, 8H), 0.77-0.68 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 161.3, 153.1, 138.5, 132.4, 129.7, 128.0, 126.9, 126.5, 125.9, 125.4, 51.7, 32.6, 30.1, 26.7, 26.6, 26.5, 14.3, 13.92, 13.85, 13.7. HRMS (FAB) calcd for $C_{23}H_{33}Si$ (M+H$^+$) 337.2346, found 337.2352.



Scheme 4, compound 5l. The reaction was conducted using 20 mol% of Ni(cod)$_2$ and 40 mol% of PCy$_3$. Colorless oil (48.0 mg, 0.127 mmol; 51% yield).

^{1}H NMR (CDCl$_3$): δ 7.75-7.71 (m, 1H), 7.67-7.63 (m, 2H), 7.54-7.50 (m, 2H), 7.44-7.28 (m, 8H), 7.26-7.23 (m, 4H), 7.19-7.13 (m, 1H), 6.99 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 1.94 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.82 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.70 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.6, 152.4, 135.8, 135.7, 135.5, 135.4, 135.3, 133.1, 130.5, 129.72, 129.70, 128.2, 128.1, 128.0, 127.0, 126.7, 126.5, 125.7, 51.9, 32.2, 31.7. HRMS (FAB) calcd for $C_{27}H_{24}Si$ (M$^+$) 376.1642, found 376.1643.



Scheme 4, compound 5m. Colorless oil (42.0 mg, 0.143 mmol; 57% yield (dr = 62/38), containing ca. 3% impurity).

^{1}H NMR (CDCl$_3$): δ 7.58 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.31 (t, $^3J_{HH}$ = 7.6 Hz, 0.62H), 7.28-7.01 (m, 6.76H), 6.83 (d, $^3J_{HH}$ = 6.8 Hz, 0.62H), 1.79 (s, 1.14H), 1.65 (s, 1.86H), 1.43 (d, $^2J_{HH}$ = 15.1 Hz, 0.62H), 1.32 (s, 0.76H), 1.21 (d, $^2J_{HH}$ = 15.1 Hz, 0.62H), 1.01 (s, 3.42H), 0.99 (s, 5.58H), 0.35 (s, 1.86H), 0.14 (s, 1.14H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 162.4, 160.9, 153.40, 153.36, 138.2, 137.5, 132.3, 129.9, 129.8, 128.1, 128.0, 127.0, 126.8, 126.6, 126.5, 126.0, 125.9, 125.5, 125.3, 51.4, 51.0, 32.9, 32.4, 29.2, 28.34, 28.31, 27.1, 27.0, 17.4, 17.1, –4.5, –5.0. HRMS (FAB) calcd for $C_{20}H_{25}Si$ (M–H$^-$) 293.1720, found 293.1726.

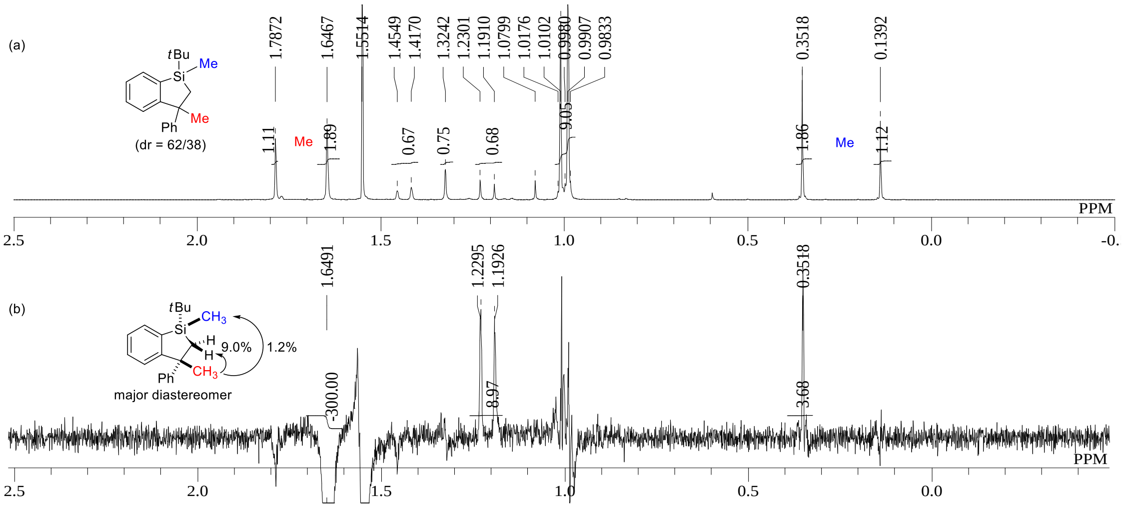
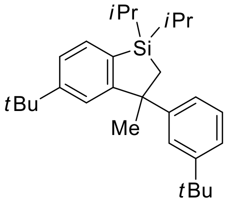
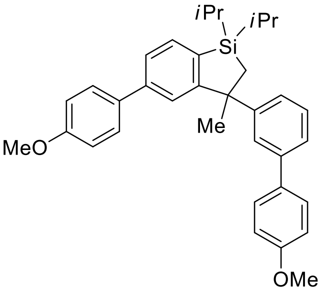


Figure S4. (a) ^{1}H NMR spectrum (aliphatic region) and (b) the NOE spectrum of compound **5m** in CDCl$_3$.



Scheme 5, compound 5n. The reaction was conducted using 20 mol% of Ni(cod)$_2$ and 40 mol% of PCy$_3$. Colorless oil (62.1 mg, 0.148 mmol; 59% yield).

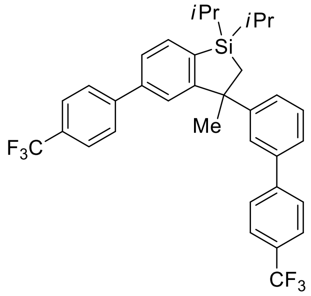
^{1}H NMR (CDCl$_3$): δ 7.48 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.26 (dd, $^3J_{HH}$ = 7.8 and $^3J_{HH}$ = 1.5 Hz, 2H), 7.24-7.12 (m, 3H), 7.02 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 6.95 (t, $^4J_{HH}$ = 1.7 Hz, 1H), 1.73 (s, 3H), 1.35-1.21 (m, 11H), 1.17 (s, 9H), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 8H), 0.92 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 0.87 (d, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 161.6, 153.5, 152.4, 150.3, 133.6, 132.4, 127.5, 125.0, 123.9, 123.5, 122.9, 121.9, 51.8, 34.9, 34.8, 33.3, 31.5, 31.4, 26.8, 18.9, 18.8, 18.6, 12.4, 11.8. HRMS (FAB) calcd for $C_{29}H_{43}Si$ (M–H$^-$) 419.3129, found 419.3135.



Scheme 5, compound 5o. The reaction was conducted using 20 mol% of Ni(cod)$_2$ and 40 mol% of PCy$_3$. White amorphous (85.3 mg, 0.164 mmol; 66% yield).

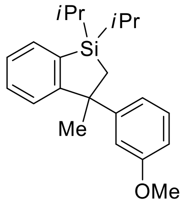
^{1}H NMR (CDCl$_3$): δ 7.62 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.51-7.41 (m, 6H), 7.35 (dt, $^3J_{HH}$ = 7.8 and $^4J_{HH}$ = 1.5 Hz, 1H), 7.29 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.16 (d, $^3J_{HH}$ = 1.5 Hz, 1H), 7.14 (dt, $^3J_{HH}$ = 7.8 and $^4J_{HH}$ = 1.5 Hz, 1H), 6.95 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.91 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 1.81 (s, 3H), 1.44 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.33 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.29-1.16 (m, 2H), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 6H), 1.05 (d, $^3J_{HH}$ =

7.3 Hz, 3H), 1.02 (d, ${}^{3}J_{HH}$ = 7.3 Hz, 3H). ${}^{13}C\{{}^{1}H\}$ NMR ($CDCl_3$): δ 162.7, 159.2, 159.1, 154.1, 142.2, 140.4, 135.0, 134.4, 134.1, 133.2, 128.42, 128.38, 128.3, 125.6, 125.3, 125.0, 124.7, 124.0, 114.25, 114.17, 55.5, 55.4, 51.6, 33.1, 26.7, 18.93, 18.90, 18.8, 18.7, 12.4, 12.1. HRMS (FAB) calcd for $C_{35}H_{40}O_2Si$ (M^+) 520.2792, found 520.2793.



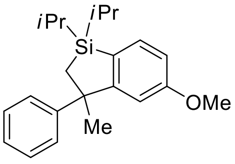
Scheme 5, compound 5p. The reaction was conducted using 20 mol% of Ni(cod)$_2$ and 40 mol% of PCy$_3$. Colorless oil (115 mg, 0.193 mmol; 77% yield).

${}^{1}H$ NMR ($CDCl_3$): δ 7.70-7.54 (m, 9H), 7.50-7.46 (m, 2H), 7.40 (d, ${}^{3}J_{HH}$ = 7.6 Hz, 1H), 7.35 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 1H), 7.23 (d, ${}^{3}J_{HH}$ = 7.6 Hz, 1H), 7.17 (s, 1H), 1.82 (s, 3H), 1.44 (d, ${}^{2}J_{HH}$ = 15.6 Hz, 1H), 1.36 (d, ${}^{2}J_{HH}$ = 15.6 Hz, 1H), 1.32-1.16 (m, 2H), 1.16-1.11 (m, 6H), 1.05 (d, ${}^{3}J_{HH}$ = 7.3 Hz, 3H), 1.02 (d, ${}^{3}J_{HH}$ = 7.3 Hz, 3H). ${}^{13}C\{{}^{1}H,{}^{19}F\}$ NMR ($CDCl_3$): δ 162.7, 154.3, 145.3, 145.1, 141.3, 139.6, 137.1, 133.6, 129.42, 129.36, 128.8, 127.7, 127.6, 126.9, 125.8, 125.7, 125.5, 125.3, 124.7, 124.5, 124.4, 51.7, 33.0, 26.7, 18.9, 18.8, 18.6, 12.4, 12.0. ${}^{19}F$ NMR ($CDCl_3$): –62.50 (s), –62.53 (s). HRMS (FAB) calcd for $C_{35}H_{34}F_6Si$ (M^+) 596.2328, found 596.2335.



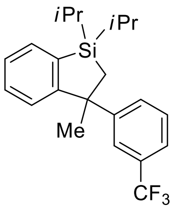
Scheme 5, compound 5q. Colorless oil (21.9 mg, 64.6 μmol; 26% yield).

^{1}H NMR (CDCl$_3$): δ 7.54 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.30-7.25 (m, 1H), 7.21 (td, $^3J_{HH}$ = 7.1 and $^4J_{HH}$ = 1.0 Hz, 1H), 7.16 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.94 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.80-6.72 (m, 2H), 6.69 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.0 Hz, 1H), 3.73 (s, 3H), 1.68 (s, 3H), 1.38-1.12 (m, 2H), 1.12-1.04 (m, 6H), 1.02-0.95 (m, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 161.9, 159.3, 155.5, 136.7, 132.8, 129.8, 128.9, 126.8, 125.8, 119.6, 113.3, 110.2, 55.2, 51.5, 32.9, 26.1, 18.9, 18.83, 18.77, 18.6, 12.4, 12.0. HRMS (FAB) calcd for $C_{22}H_{30}OSi$ (M^+) 338.2060, found 338.2071.



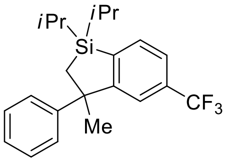
Scheme 5, compound 5q'. Colorless oil (29.8 mg, 88.0 μmol; 35% yield).

^{1}H NMR (CDCl$_3$): δ 7.47 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.28-7.16 (m, 4H), 7.13 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 6.82 (dd, $^3J_{HH}$ = 7.8 and $^4J_{HH}$ = 2.4 Hz, 1H), 6.46 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 3.70 (s, 3H), 1.71 (s, 3H), 1.34 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.25 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 1.22-1.05 (m, 8H), 1.02-0.92 (m, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 164.2, 161.4, 153.4, 133.8, 128.02, 127.98, 126.8, 125.4, 112.7, 111.8, 55.1, 51.4, 32.8, 26.8, 18.9, 18.81, 18.79, 18.6, 12.4, 12.1. HRMS (FAB) calcd for $C_{22}H_{30}OSi$ ($M+H^+$) 338.2060, found 338.2071.



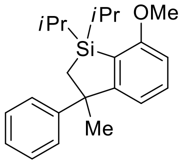
Scheme 5, compound 5r. Colorless oil (21.5 mg, 57.0 μmol; 23% yield).

^{1}H NMR (CDCl$_3$): δ 7.57 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 7.49 (s, 1H), 7.40 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.36-7.21 (m, 4H), 6.90 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 1.74 (s, 3H), 1.30-1.05 (m, 10H), 1.03-0.91 (m, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 161.0, 154.6, 136.9, 133.0, 130.6, 130.2, 130.0, 128.5, 126.6, 126.2, 124.5, 123.3, 122.3, 66.0, 51.5, 32.8, 26.2, 18.8, 18.7, 18.5, 15.4, 12.3, 11.9. ^{19}F NMR (CDCl$_3$): δ –62.6 (s). HRMS (FAB) calcd for $C_{22}H_{26}F_3Si$ (M–H$^-$) 375.1750, found 375.1761.



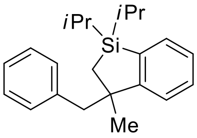
Scheme 5, compound 5r'. Colorless oil (16.6 mg, 44.1 μmol; 18% yield).

^{1}H NMR (CDCl$_3$): δ 7.67 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.47 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.29-7.23 (m, 2H), 7.21-7.09 (m, 4H), 1.72 (s, 3H), 1.44-1.05 (m, 10H), 1.02-0.91 (m, 6H). ^{13}C{^{1}H,^{19}F} NMR (CDCl$_3$): δ 162.5, 152.6, 141.9, 133.3, 131.9, 128.3, 126.7, 125.8, 124.6, 123.2, 122.5, 51.6, 32.9, 26.3, 18.8, 18.78, 18.71, 18.4, 12.1, 11.8. ^{19}F NMR (CDCl$_3$): δ –62.6 (s). HRMS (FAB) calcd for $C_{22}H_{26}F_3Si$ (M–H$^-$) 375.1750, found 375.1760.



Scheme 5, compound 5s'. White solid (30.2 mg, 89.2 µmol; 36% yield).

^{1}H NMR (CDCl$_3$): δ 7.28-7.17 (m, 5H), 7.13 (tt, $^3J_{HH}$ = 7.1 and $^3J_{HH}$ = 1.8 Hz, 1H), 6.65 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.52 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 3.82 (s, 3H), 1.69 (s, 3H), 1.33-1.16 (m, 4H), 1.10 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 1.05 (d, $^3J_{HH}$ = 7.3 Hz, 3H), 0.98-0.93 (m, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 163.9, 162.9, 153.5, 131.7, 128.0, 126.8, 125.6, 125.3, 119.5, 106.4, 55.0, 51.4, 32.5, 26.4, 19.2, 19.0, 18.9, 18.6, 12.4, 12.0. HRMS (FAB) calcd for $C_{27}H_{30}OSi$ (M^+) 338.2060, found 338.2067.

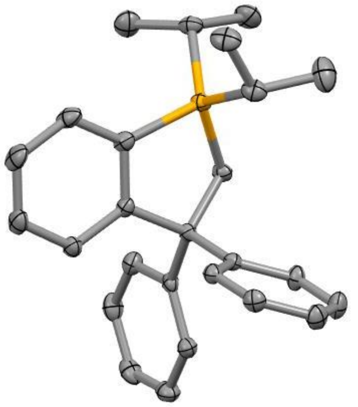


Scheme 5, compound 10. Colorless oil (19.8 mg, 61.4 µmol; 25% yield).

^{1}H NMR (CDCl$_3$): δ 7.47 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.38 (td, $^3J_{HH}$ = 7.4 and $^4J_{HH}$ = 1.1 Hz, 1H), 7.32 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.24-7.11 (m, 4H), 6.98 (dd, $^3J_{HH}$ = 7.3 Hz and $^3J_{HH}$ = 2.0 Hz, 2H), 2.99 (d, $^2J_{HH}$ = 13.2 Hz, 1H), 2.87 (d, $^2J_{HH}$ = 13.2 Hz, 1H), 1.38 (s, 3H), 1.21-1.05 (m, 2H), 1.03-0.94 (m, 6H), 0.93-0.81 (m, 7H), 0.60 (d, $^2J_{HH}$ = 15.6 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 161.1, 139.6, 137.2, 133.1, 131.0, 129.4, 127.7, 126.1, 125.7, 124.9, 51.2, 47.8, 33.1, 18.8, 18.7, 18.6, 18.4, 17.7, 12.03, 11.96. HRMS (FAB) calcd for $C_{22}H_{29}Si$ ($M{-}H^-$) 321.2033, found 321.2030.

X-ray crystal structure

Compound 5d



A colorless hexane solution of compound **5d** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2394443). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal data and structure refinement.

Empirical Formula	$C_{26}H_{30}Si$	
Formula Weight	370.59	
Temperature	113 ± 2K	
Wavelength	0.71075 Å	
Crystal System	triclinic	
Space Group	*P*−1	
Unit Cell Dimensions	a = 9.0338(19) Å	α = 76.192(8)°
	b = 10.1354(19) Å	β = 84.406(11)°
	c = 12.0954(19) Å	γ = 89.983(12)°
Volume	1070.0(3) Å	

Z Value	2
Calculated Density	1.150 g/cm^3
Absorption coefficient	0.117 mm^{-1}
F(000)	400
Crystal size	0.300 x 0.300 x 0.200 mm
Theta Range for Data Collection	3.106–27.566°
Index Ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$
Reflections Collected	19474
Independent Reflections	4898 [R(int) = 0.0416]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.977 and 0.966
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	4898 / 0 / 248
Goodness-of-Fit on F^2	1.093
Final R Indices [I>2sigma(I)]	$R1 = 0.0429$, $wR2 = 0.1317$
R Indices (All Data)	$R1 = 0.0518$, $wR2 = 0.1395$
Largest Diff. Peak and Hole	0.488 and –0.359 e$^-$/Å^3

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List of Publications

Publications

1. “Palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines by intramolecular Hiyama coupling”

   Donghyeon Lee, Ryo Shintani; *Chem. Sci.* **2023**, *14*, 4114–4119.

2. “Nickel-Catalyzed Synthesis of Silaindanes via Sequential C–H Activating 1,5-Nickel Migration and C–Si Activating 1,4-Nickel Migration”

   Donghyeon Lee, Ikuya Fujii, Ryo Shintani; *ACS Catal.* **2025**, *15*, 907–916.

Related publications

3. “Intermolecular Three-Component Synthesis of Fluorene Derivatives by a Rhodium-Catalyzed Stitching Reaction/Remote Nucleophilic Substitution Sequence”

   Masaki Nishida, Donghyeon Lee, Ryo Shintani; *J. Org. Chem.* **2020**, *85*, 8489–8500.

4. “Photoredox-Enabled Dearomative [2π+2σ] Cycloaddition of Phenols”

   Subhabrata Dutta, Donghyeon Lee, Kristers Ozols, Constantin G. Daniliuc, Ryo Shintani, Frank Glorius; *J. Am. Chem. Soc.* **2024**, *146*, 2789–2797.

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