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C–H Activation

SPECIAL ISSUE

Disilylation of Palladacycles that were Generated through the C–H Activation of Aryl Halides

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Abstract: The reactions of various C,C-palladacycles that were generated through the C–H activation of aryl halides with disilanes have been studied. The reaction of arylnorbornyl palladacycles, which were generated through a Catellani reaction, with hexamethyldisilane proceeded very efficiently to afford disilylated products. Palladacycles that were obtained through the remote C–H activation of aryl halides that contained a styrene moiety with an ether linkage also underwent a disilylation reaction with hexamethyldisilane. Furthermore, the reactions of dibenzopalladacyclopentadienes, which were generated from 2-iodobiphenyls, with diphenyltetramethyldisilane were also investigated and a range of 2-iodobiphenyls were disilylated in moderate yields.

Introduction

Owing to their unique structures, palladacycles that contain a C–Pd–C bonding motif hold great promise for exhibiting new reactivities.[1] For example, C,C-palladacycles that contain a $C(sp^2)$–Pd–$C(sp^2)$ or $C(sp^2)$–Pd–$C(sp^3)$ bonding motif have exhibited distinct reactivities to common acyclic Pd^{II} species and, in particular, high reactivities towards alkyl halides.[2] Furthermore, C,C-palladacycles contain two Pd–C bonds that can be functionalized, which offers opportunities for application in synthetically useful organic reactions, in particular the synthesis of cyclic compounds. Recently, a series of synthetically useful intermolecular reactions have been developed by taking advantage of the unique structures and reactivities of C,C-palladacycles. These palladacycles can react with a range of nucleophiles, such as carbenes, alkynes, benzynes, and dibromomethane, to form the corresponding cyclic compounds.[3] These reactions provide innovative methods for the synthesis of these compounds.

Organosilicon compounds have found extensive application in materials science[4] and organic synthesis,[5] and the development of new reactions for the synthesis of organosilicon compounds has been a topic of intensive research. The introduction of silyl groups into organic molecules through direct C–H silylation reactions for the synthesis of organosilicon compounds is highly desirable. Although this type of reaction has been studied previously, it remains relatively underdeveloped compared with other C–H functionalization reactions.[6] Notably, C–H silylation reactions that utilize palladium catalysis are particularly rare, although several excellent Pd-catalyzed C–H silylation reactions have recently been developed, primarily by using bidentate directing groups.[7]

We previously reported that C,C-palladacycles exhibited extremely high reactivity towards hexamethyldisilane.[8] Palladacycles that were obtained through three different types of C–H activation, that is, $C(sp^2)$–H, $C(sp^3)$–H, and remote C–H activation, reacted with hexamethyldisilane in a highly efficient manner and the yields were essentially quantitative, even in the presence of <1 mol% of the catalyst and one equivalent of hexamethyldisilane. Notably, both of the silyl groups of hexamethyldisilane were incorporated into the palladacycles, thereby affording disilylated products. This outcome is in contrast to other transition-metal-catalyzed C–H silylation reactions, in which only one of the silyl groups is typically incorporated into the products.

Inspired by these exciting results, we continued our investigation into the reactions of other C,C-palladacycles with hexamethyldisilane and the reactivity of other disilanes. Herein, we report that arylnorbornyl palladacycles that were obtained from a Catellani reaction and palladacycles that were obtained from the remote C–H activation of aryl halides that contained a styrene moiety through an ether linkage could react with hexamethyldisilane to form disilylated products. Diphenyltetramethyldisilane was also an effective disilylating reagent in the reaction of 2-iodobiphenyl compounds.

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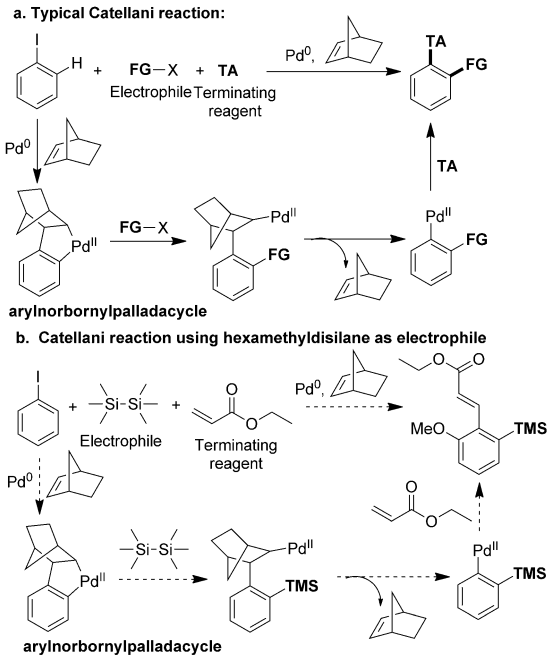
Results and Discussion

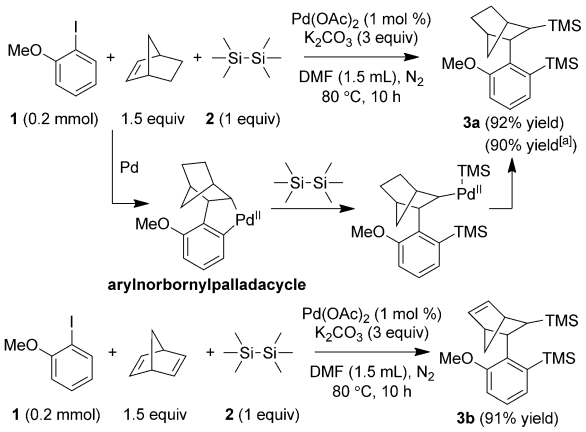
The Catellani reaction involves a palladium-catalyzed C–H functionalization of aryl halides.[9] The appealing feature of this reaction is that both the *ortho* and *ipso* positions of an aryl halide can be functionalized in a well-defined sequence in the presence of norbornene (Scheme 1 a). Over the past 20 years,



Scheme 1. a) Standard Catellani reaction; and b) proposed Catellani reaction with hexamethyldisilane as an electrophile. FG = functional group, TMS = trimethylsilyl.

the Catellani reaction has been extensively studied, and it has been utilized in a number of syntheses.[10] In a typical Catellani reaction, an arylnorbornyl palladacycle (Scheme 1 a), which is formed from an aryl halide and norbornene, functions as a key intermediate in the catalytic cycle. The palladacycle is typically captured by an electrophile, which is incorporated at the *ortho* position of the aryl halide. Because the arylnorbornyl palladacycle also contains a C–Pd–C bonding motif and is similar to the C,C-palladacycles from our previous work, we envisioned that the palladacycle in the Catellani reaction would also react with hexamethyldisilane, which would function as an electrophile (Scheme 1 b).

Therefore, we reacted 1-iodo-2-methoxybenzene (**1**) with hexamethyldisilane (**2**) and ethyl acrylate, which is a typical terminating reagent and is incorporated at the *ipso* position of the aryl halide in the Catellani reaction. This reaction was performed under similar conditions to our previously reported disilylation reaction;[8] however, disilylated product **3a** was formed as the major product (Scheme 2). In a typical Catellani reaction, the reaction of an arylnorbornyl palladacycle with an electrophile releases a norbornyl–Pd^{II} species, which then undergoes the de-insertion of norbornene to afford an aryl–Pd^{II}

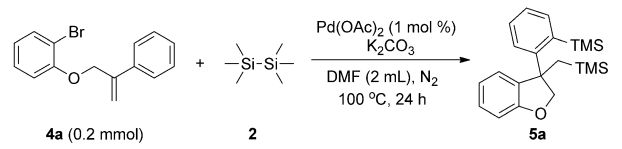


Scheme 2. Disilylation of arylnorbornyl palladacycles with hexamethyldisilane. Yields are of the isolated products. [a] Ethyl acrylate (2 equiv) was added.

intermediate that is captured by a terminating reagent (Scheme 1 a). In our reaction, the norbornylsilyl–Pd^{II} species underwent reductive elimination to form C(sp^3)–Si bonds, rather than the de-insertion of norborbene. Reductive elimination from the alkyl–Pd^{II} species is typically challenging. The high efficiency of C(sp^3)–Si bond formation in this reaction indicated that the reductive elimination from the alkylsilyl–Pd^{II} complex was rapid, which could also account for the high efficiency of our disilylation reactions. The disilylated product was also formed in similar yield in the absence of ethyl acrylate. Norbornadiene was also reactive under the same conditions, and the corresponding disilylated product was formed in high yield (Scheme 2).

Remote C–H activation through an intramolecular Heck-type cyclization reaction represents a new strategy for the functionalization of C–H bonds that are not on the same aryl ring as the directing group(s).[11] This type of reaction is initiated by the oxidative addition of an aryl halide to a Pd^0 center. Subsequent Heck reaction delivers a Pd^{II} species to remote C–H bonds, which are cleaved to form spiropalladacycles. In most of the remote C–H functionalization reactions reported to date, the haloaryl moiety and the double bond are linked through an amide group.[12] Substrates with an ether linkage can also undergo remote C–H functionalization reactions, although examples are rare.[12g,l,m,13] We had found that palladacycles that were formed from 2-phenylacrylamide derivatives reacted with hexamethyldisilane in almost-quantitative yield in the presence of $Pd(OAc)_2$ (1 mol%) and hexamethyldisilane (1 equiv).[8] Therefore, we also investigated the reaction of palladacycles that were formed through the remote C–H activation of substrates that contained an ether linkage (**4a**) with hexamethyldisilane (**2**; Table 1). Disappointingly, although the desired disilylated product (**5a**) was formed, the reaction was much less efficient than the other disilylation reactions. In the presence of compound **2** (1 equiv) and $Pd(OAc)_2$ (1 mol%), the product was formed in 63% yield (Table 1, entry 1). The yield improved to 74% by adding K_2CO_3 (2.5 equiv), and was further

Table 1. Optimization of reaction conditions for the disilylation of the ether-tethered aryl bromide with hexamethyldisilane.



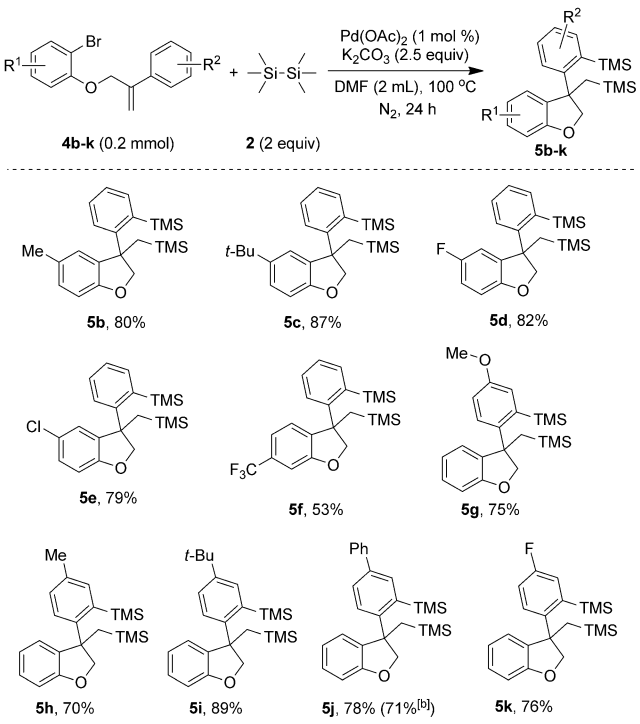
4a (0.2 mmol) **2** **5a**

Entry	Compound **2** [equiv]	K_2CO_3 [equiv]	Yield [%][a]
1	1.0	1.5	63
2	1.0	2.5	74
3	2.0	2.5	84 (81[b])

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture; [b] yield of the isolated product.

enhanced to 84% by adding an extra equivalent of compound **2** (Table 1, entries 2 and 3).

Subsequently, we examined the performance of various derivatives of compound **4a** under our optimized conditions. Electron-donating groups, such as methyl and *tert*-butyl groups, on the benzene ring that contained the bromo group had little influence on the reactivity, and the corresponding disilylated products (**5b** and **5c**, respectively) were formed in high yields (Scheme 3). Fluoro and chloro groups were well-tolerated, and similar yields were obtained. However, the presence of an electron-withdrawing trifluoromethyl group led to a lower yield of the corresponding product. The scope of substituents on the benzene ring that was linked to the double bond was also investigated and a range of groups, including

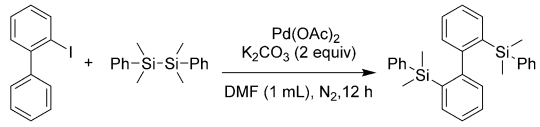


Scheme 3. Disilylation of ether-tethered aryl bromides. Yields are of the isolated products. [a] Compound **2** (1 equiv) was used.

methoxy, methyl, *tert*-butyl, phenyl, and fluoro groups (**5g**–**5k**), were well-tolerated. Notably, the yield of compound **5j** decreased slightly when one equivalent of compound **2** was used.

Hexamethyldisilane is the predominant silylating reagent for Pd-catalyzed C–H silylation reactions. Reactions with other disilanes are rare, and the yields are typically low.[7d–g] Considering the high reactivity of C,C-palladacycles towards hexamethyldisilane, we also studied the disilylation of palladacycles with other disilanes. Therefore, the reaction of 2-iodobiphenyl **6a** and diphenyltetramethyldisilane **7** was investigated. Only a trace amount of the disilylated product was obtained when one equivalent of compound **7** and 1 mol% $Pd(OAc)_2$ were used (Table 2, entry 1). Gratifyingly, increasing the catalyst loading to 5 mol% $Pd(OAc)_2$ afforded product **8a** in 55% yield (Table 2, entry 2). Further increasing the catalyst loading to 10 mol% $Pd(OAc)_2$ enhanced the yield to 67% (Table 2, entry 3), whilst using two equivalents of the disilylating reagent only slightly increased the yield further (Table 2, entry 4). Performing the reaction at a higher temperature led to a lower yield (Table 2, entry 5).

Table 2. Optimization of reaction conditions for the disilylation of 2-iodobiphenyl with diphenyltetrasilyldisilane.



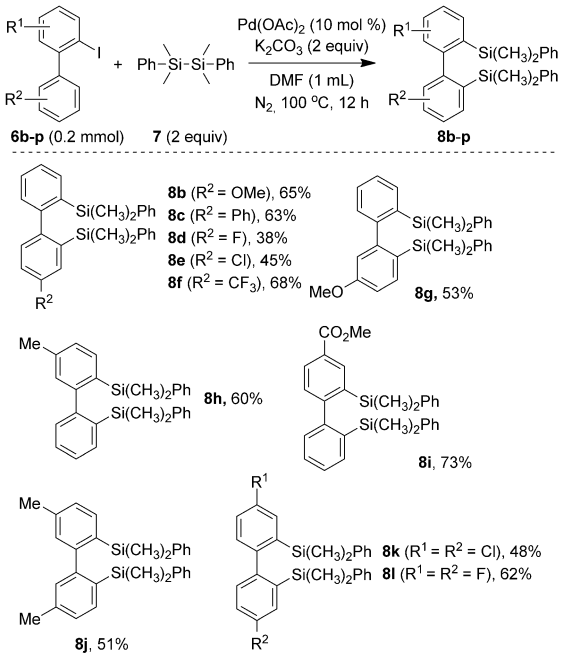
6a (0.2 mmol) **7** **8a**

Entry	$Pd(OAc)_2$ [mol%]	Compound **7** [equiv]	*T* [°C]	Yield [%][a]
1	1	1.0	100	trace
2	5	1.0	100	55
3	10	1.0	100	67
4	10	2.0	100	73 (68[b])
5	10	2.0	120	64

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture; [b] yield of the isolated product.

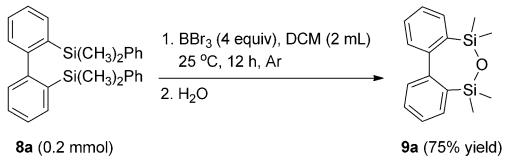
Next, we investigated the reactions of various 2-iodobiphenyl derivatives with compound **7**. First, we studied the reactions of 4′-substituted 2-iodobiphenyls and, as shown in Scheme 4, various substituents, including electron-donating methoxy and electron-withdrawing trifluoromethyl groups, were well-tolerated and the corresponding disilylated products (**8b**–**8f**) were obtained in moderate yields. Even 2′-substituted compound **7g** also underwent the disilylation reaction (**8g**). The performance of 2-iodobiphenyls that contained substituents on the iodo-substituted benzene ring was also investigated. Electron-donating methoxy and electron-withdrawing ester groups were disilylated under the standard conditions (**8h** and **8i**, respectively). Finally, disubstituted 2-iodobiphenyls also reacted with compound **2**, thereby providing tetrasubstituted biphenyl products **8j**–**8l**.

Notably, the disilylated biphenyl products could also be transformed into disiloxanes, which have been studied as ma-



Scheme 4. Disilylation of 2-iodobiphenyl derivatives with diphenyltetrasilyldisilane. Yields are of the isolated products.

terials for organic light-emitting diodes (OLEDs).[14] Thus, the treatment of compound **8a** with BBr_3 afforded disiloxane-bridged biphenyl compound **9a** in 75% yield (Scheme 5). In this reaction, the phenyl groups were cleaved selectively. This reaction provides a facile method for the synthesis of disiloxanes.



Scheme 5. Synthesis of a disiloxane-bridged biphenyl compound (**9a**) from the disilylated biphenyl product (**8a**).

Conclusion

In conclusion, a variety of C,C-palladacycles were obtained through C–H activation reactions and subsequently reacted with disilanes to form disilylated products. Arylnorbornyl palladacycles that were obtained through a Catellani reaction were disilylated with hexamethyldisilane in a highly efficient manner to form the corresponding disilylated products. Palladacycles that were obtained through the remote C–H activation of aryl halides that contained a styrene moiety with an ether linkage were also disilylated with hexamethyldisilane. Diphenyltetramethyldisilane was also an effective disilylating reagent, and a range of dibenzopalladacyclopentadienes that were generated from 2-iodobiphenyls were disilylated in moderate yields. These reactions further demonstrate the unique reactivity of C,C-palladacycles towards disilanes.

Experimental Section

General

$Pd(OAc)_2$ was purchased from Strem Chemicals. Solvents were purified by distillation prior to use. Unless otherwise noted, all other chemicals were purchased from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker ARX400 (400 MHz) or Bruker DRX-600 instruments (600 MHz) in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ ($\delta = 7.26$ ppm); ^{13}C NMR spectra were referenced to the central peak of residual $CDCl_3$ ($\delta = 77.0$ ppm). Chemical shifts (δ) are reported in ppm; coupling constants (J) are reported in Hertz (Hz). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS was performed on a Bruker MicroTOF ESI-TOF mass spectrometer.

General Procedures for the Synthesis of Compound 3

A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) was equipped with a magnetic stirrer bar and charged with $Pd(OAc)_2$ (0.45 mg, 0.002 mmol), K_2CO_3 (82.8 mg, 0.6 mmol), TMS–TMS (**2**; 29.3 mg, 0.2 mmol), 1-iodo-2-methoxybenzene (**1**; 46.8 mg, 0.2 mmol), the corresponding norbornene or norbornadiene (0.3 mmol), and DMF (1.5 mL). The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen gas 10 times. Then, the mixture was stirred at 80 °C for 10 h and, after cooling to RT, the mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC on silica gel (petroleum ether/EtOAc) to give the pure product.

General Procedures for the Synthesis of Compound 5

A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) was equipped with a magnetic stirrer bar and charged with $Pd(OAc)_2$ (0.45 mg, 0.002 mmol), K_2CO_3 (69.0 mg, 0.5 mmol), TMS–TMS (**2**; 58.6 mg, 0.4 mmol), ether-tethered aryl bromide **4** (0.2 mmol), and DMF (2 mL). The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen gas 10 times. The mixture was stirred at 100 °C for 24 h and, after cooling to RT, the mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC on silica gel (petroleum ether/EtOAc) to give the pure product.

General Procedures for the Synthesis of Compound 8

A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) was equipped with a magnetic stirrer bar and charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), compound **7** (108.2 mg, 0.4 mmol), 2-iodobiphenyl derivative **6** (0.2 mmol), and DMF (1 mL). The mixture was frozen with liquid nitrogen and the tube was evacuated and backfilled with nitrogen gas 10 times. Then, the mixture was stirred at 100 °C for 12 h and, after cooling to RT, the mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC on silica gel (petroleum ether/EtOAc) to give the pure product.

Synthesis of Compound 9a

BBr_3 (77 μL, 0.8 mmol) was added to a solution of disilylated compound **8a** (84.4 mg, 0.2 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C under an Ar atmosphere. After stirring at 25 °C for 12 h, the reaction was

quenched with water and extracted with EtOAc (15 mL). The combined organic layer was washed with brine (3 times), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC to afford compound **9a** as a white solid (75% yield, 42.6 mg).

(3-Methoxy-2-((3R)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-phenyl)trimethylsilane (3a)

Colorless oil (63.7 mg, 92% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.17 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.75 (s, 3H), 3.23 (d, J = 10.8 Hz, 1H), 2.46 (s, 1H), 2.34 (d, J = 2.8 Hz, 1H), 2.27 (d, J = 9.0 Hz, 1H), 1.83–1.79 (m, 1H), 1.57–1.54 (m, 1H), 1.43 (t, J = 10.1 Hz, 1H), 1.35–1.32 (m, 1H), 1.29 (d, J = 11.2 Hz, 1H), 1.19 (d, J = 9.1 Hz, 1H), 0.36 (s, 9H), −0.38 ppm (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.8, 142.3, 138.4, 126.8, 126.5, 112.2, 53.9, 51.6, 43.9, 42.5, 39.2, 38.7, 33.1, 32.7, 1.5, −1.0 ppm; MS (EI): m/z: 346.20 $[M]^+$.

(3-Methoxy-2-((3R)-3-(trimethylsilyl)bicyclo[2.2.1]hept-5-en-2-yl)phenyl)trimethylsilane (3b)

Colorless oil (62.6 mg, 91% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.18 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 1.6 Hz, 1H), 6.09 (s, 1H), 3.71 (s, 3H), 3.04 (d, J = 10.5 Hz, 1H), 2.98 (s, 1H), 2.91 (s, 1H), 2.29 (d, J = 7.9 Hz, 1H), 1.36 (d, J = 7.8 Hz, 1H), 0.98 (d, J = 10.4 Hz, 1H), 0.26 (s, 9H), −0.34 ppm (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.1, 143.4, 138.8, 137.4, 136.5, 127.0, 126.6, 112.1, 53.9, 49.8, 48.0, 47.7, 44.8, 32.6, 1.2, −1.0 ppm; MS (EI): m/z: 344.19 $[M]^+$.

Trimethyl(2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (5a)

Colorless oil (57.4 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.74 (m, 1H), 7.24–7.19 (m, 1H), 7.18–7.13 (m, 3H), 7.04–7.01 (m, 1H), 6.97 (t, J = 7.3 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 4.78 (d, J = 8.8 Hz, 1H), 4.61 (d, J = 8.8 Hz, 1H), 1.98 (d, J = 15.0 Hz, 1H), 1.49 (d, J = 15.0 Hz, 1H), 0.44 (s, 9H), −0.16 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.9, 155.2, 137.5, 137.2, 133.9, 128.6, 128.5, 127.1, 127.0, 125.3, 120.3, 110.0, 84.5, 54.8, 31.9, 3.2, 0.1 ppm; HRMS (ESI-TOF): m/z calcd for $C_{21}H_{30}NaOSi_2$: 377.1727 $[M+Na]^+$; found: 377.1745.

Trimethyl(2-(5-methyl-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (5b)

White solid (58.9 mg, 80%)* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 1H), 7.21–7.14 (m, 2H), 7.09–7.06 (m, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.94 (s, 1H), 6.76 (d, J = 8.1 Hz, 1H), 4.76 (d, J = 8.7 Hz, 1H), 4.61 (d, J = 8.7 Hz, 1H), 2.36 (s, 3H), 1.97 (d, J = 14.9 Hz, 1H), 1.49 (d, J = 14.9 Hz, 1H), 0.44 (s, 9H), −0.14 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.8, 155.2, 137.4, 137.2, 133.9, 129.4, 128.9, 128.4, 127.4, 127.2, 125.3, 109.5, 84.6, 54.8, 31.9, 20.9, 3.23, 0.1 ppm; HRMS (ESI-TOF): m/z calcd for $C_{22}H_{32}NaOSi_2$: 391.1884 $[M+Na]^+$; found: 391.1874.

(2-(5-(tertButyl)-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (5c)

White solid (71.4 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.81 (m, 1H), 7.31–7.28 (m, 1H), 7.24–7.19 (m, 3H), 7.10–7.08 (m, 1H), 6.84 (d, J = 8.4 Hz, 1H), 4.83 (d, J = 8.8 Hz, 1H), 4.64 (d, J = 8.7 Hz, 1H), 2.04 (d, J = 14.9 Hz, 1H), 1.57 (d, J = 14.9 Hz, 1H), 1.39 (s, 9H), 0.49 (s, 9H), −0.10 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.7, 155.3, 143.1, 137.5, 137.3, 133.3, 128.5, 127.2, 125.4, 125.3, 123.8, 109.1, 84.7, 55.0, 34.4, 31.9, 31.7, 3.3, 0.1 ppm; HRMS (ESI-TOF): m/z calcd for $C_{25}H_{38}NaOSi_2$: 433.2353 $[M+Na]^+$; found: 433.2345.

(2-(5-Fluoro-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (5d)

White solid (61.0 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 1H), 7.21–7.15 (m, 2H), 7.02 (d, J = 7.0 Hz, 1H), 6.94–6.90 (m, 1H), 6.85–6.83 (m, 1H), 6.79–6.76 (m, 1H), 4.80 (d, J = 8.8 Hz, 1H), 4.63 (d, J = 8.8 Hz, 1H), 1.98 (d, J = 15.0 Hz, 1H), 1.43 (d, J = 15.0 Hz, 1H), 0.43 (s, 9H), −0.12 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.5 (d, J = 237.3 Hz), 155.8 (d, J = 1.0 Hz), 154.4, 137.6, 137.2, 135.6 (d, J = 7.7 Hz), 128.6, 126.9, 125.5, 115.0 (d, J = 25.4 Hz), 113.7 (d, J = 23.9 Hz), 110.2 (d, J = 7.9 Hz), 85.0, 55.2, 31.8, 3.2, 0.0 ppm; HRMS (ESI-TOF): m/z calcd for $C_{21}H_{29}FNaOSi_2$: 395.1633 $[M+Na]^+$; found: 395.1631.

(2-(5-Chloro-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (5e)

White solid (61.3 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.75 (m, 1H), 7.21–7.17 (m, 3H), 7.09 (d, J = 2.2 Hz, 1H), 7.03–7.01 (m, 1H), 6.79 (d, J = 8.5 Hz, 1H), 4.80 (d, J = 8.8 Hz, 1H), 4.64 (d, J = 8.8 Hz, 1H), 1.99 (d, J = 15.0 Hz, 1H), 1.45 (d, J = 15.0 Hz, 1H), 0.44 (s, 9H), −0.12 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.6, 154.3, 137.6, 137.2, 136.2, 128.6, 128.5, 126.9, 126.9, 125.6, 125.1, 111.0, 85.1, 55.0, 31.9, 3.2, 0.0 ppm; MS (EI): m/z: 388.14 $[M]^+$.

Trimethyl(2-(6-(trifluoromethyl)-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (5f)

White solid (44.8 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 1H), 7.24–7.12 (m, 4H), 7.09 (s, 1H), 6.92–6.90 (m, 1H), 4.84 (d, J = 8.9 Hz, 1H), 4.67 (d, J = 8.9 Hz, 1H), 2.01 (d, J = 15.0 Hz, 1H), 1.47 (d, J = 15.0 Hz, 1H), 0.43 (s, 9H), −0.17 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.1, 154.2, 138.4, 137.7, 137.3, 131.2 (q, J = 32.0 Hz), 128.6, 127.1, 126.9, 125.6, 124.1 (q, J = 270.1 Hz), 117.4 (q, J = 4.0 Hz), 107.1 (q, J = 3.9 Hz), 85.1, 54.6, 31.9, 3.2, 0.0 ppm; HRMS (ESI-TOF): m/z calcd for $C_{22}H_{29}F_3NaOSi_2$: 445.1601 $[M+Na]^+$; found: 445.1626.

(5-Methoxy-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (5g)

White solid (57.6 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 2.9 Hz, 1H), 7.23–7.19 (m, 1H), 7.13 (d, J = 7.4 Hz, 1H), 6.98–6.95 (m, 2H), 6.86 (d, J = 7.9 Hz, 1H), 6.66–6.63 (m, 1H), 4.75 (d, J = 8.7 Hz, 1H), 4.58 (d, J = 8.7 Hz, 1H), 3.77 (s, 3H), 1.96 (d, J = 14.9 Hz, 1H), 1.47 (d, J = 14.9 Hz, 1H), 0.43 (s, 9H), −0.16 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8, 156.6, 147.3, 138.9, 134.4, 128.5, 128.5, 126.7, 124.5, 120.3, 111.7, 110.0, 84.7, 55.0, 54.1, 32.1, 3.2, 0.0 ppm; HRMS (ESI-TOF): m/z calcd for $C_{22}H_{32}NaOSi_2$: 407.1833 $[M+Na]^+$; found: 407.1841.

Trimethyl(5-methyl-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (5h)

White solid (51.5 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.25–7.21 (m, 1H), 7.15 (d, J = 7.4 Hz, 1H), 7.00–6.93 (m, 3H), 6.87 (d, J = 8.0 Hz, 1H), 4.79 (d, J = 8.8 Hz, 1H), 4.61 (d, J = 8.7 Hz, 1H), 2.33 (s, 3H), 1.99 (d, J = 15.0 Hz, 1H), 1.49 (d, J =

14.9 Hz, 1H), 0.46 (s, 9H), −0.14 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.9, 152.3, 138.4, 137.0, 134.4, 134.2, 129.1, 128.5, 127.2, 126.8, 120.2, 109.9, 84.6, 54.4, 32.1, 20.9, 3.3, 0.0 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{22}H_{32}NaOSi_2$: 391.1884 $[M+Na]^+$; found: 391.1878.

(5-(tertButyl)-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (5i)

White solid (82.9 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 2.2 Hz, 1H), 7.24–7.20 (m, 1H), 7.17–7.14 (m, 2H), 6.99–6.94 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.77 (d, *J* = 8.7 Hz, 1H), 4.62 (d, *J* = 8.7 Hz, 1H), 1.99 (d, *J* = 15.0 Hz, 1H), 1.52 (d, *J* = 15.0 Hz, 1H), 1.31 (s, 9H), 0.46 (s, 9H), −0.15 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.9, 152.3, 147.2, 136.3, 134.7, 134.2, 128.5, 126.9, 126.8, 125.2, 120.2, 109.9, 84.5, 54.3, 34.3, 31.9, 31.3, 3.3, 0.1 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{25}H_{38}NaOSi_2$: 433.2353 $[M+Na]^+$; found: 433.2349.

Trimethyl((3-(3-(trimethylsilyl)-[1,1′-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-yl)methyl)silane (5j)

White solid (67.1 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44–7.39 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.89 (d, *J* = 8.8 Hz, 1H), 4.73 (d, *J* = 8.8 Hz, 1H), 2.09 (d, *J* = 14.9 Hz, 1H), 1.61 (d, *J* = 15.0 Hz, 1H), 0.56 (s, 9H), −0.06 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.9, 154.4, 140.9, 137.8, 137.8, 136.5, 134.0, 128.8, 128.7, 127.7, 127.1, 127.0, 126.9, 120.4, 110.1, 84.4, 54.6, 31.9, 3.3, 0.1 ppm; MS (EI): *m/z*: 430.21 $[M]^+$.

(5-Fluoro-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (5k)

White solid (56.6 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 1H), 7.24–7.20 (m, 1H), 7.12–7.11 (m, 1H), 7.00–6.95 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80–6.75 (m, 1H), 4.75 (d, *J* = 8.8 Hz, 1H), 4.56 (d, *J* = 8.8 Hz, 1H), 1.94 (d, *J* = 14.9 Hz, 1H), 1.47 (d, *J* = 14.9 Hz, 1H), 0.44 (s, 9H), −0.16 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.3 (d, *J* = 247.4 Hz), 159.8, 150.9 (d, *J* = 3.1 Hz), 140.5 (d, *J* = 3.2 Hz), 134.0, 129.1 (d, *J* = 6.7 Hz), 128.8, 126.7, 123.8 (d, *J* = 19.5 Hz), 120.4, 114.4 (d, *J* = 19.8 Hz), 110.1, 84.5, 54.3, 32.1, 3.0, 0.0 ppm; MS (EI): *m/z*: 372.17 $[M]^+$.

2,2′-Bis(dimethyl(phenyl)silyl)-1,1′-biphenyl (8a)

Colorless oil (57.4 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.4 Hz, 2H), 7.39–7.30 (m, 12H), 7.22 (t, *J* = 7.4 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 0.20 (s, 6H), 0.08 ppm (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.0, 139.8, 136.6, 135.5, 134.1, 130.3, 128.7, 128.2, 127.6, 126.4, −0.5, −2.0 ppm; MS (EI): *m/z*: 445.18 $[M]^+$.

(4-Methoxy-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8b)

Colorless oil (58.8 mg, 65% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.2 Hz, 1H), 7.26–7.17 (m, 11H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.97 (s, 1H), 6.80 (d, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.67 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), −0.03 (s, 3H), −0.07 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.9, 150.0, 142.5, 139.9, 139.5, 138.3, 137.1, 135.4, 134.1, 134.1, 131.4, 130.7, 128.7, 128.6, 128.2, 127.6, 127.6, 126.3, 121.4, 112.5, 55.1, −0.4, −0.6, −1.9, −2.1 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{29}H_{32}NaOSi_2$: 475.1884 $[M+Na]^+$; found: 475.1891.

[1,1′:4′,1″-Terphenyl]-2,2′-diylbis(dimethyl(phenyl)silane (8c)

White solid (62.7 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 1.7 Hz, 1H), 7.60 (t, *J* = 8.6 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.40–7.30 (m, 12H), 7.25–7.21 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 0.26 (s, 3H), 0.25 (s, 3H), 0.12 (s, 3H), 0.07 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.7, 149.0, 141.1, 139.6, 139.6, 138.9, 137.1, 136.8, 135.5, 134.1, 134.1, 130.7, 130.3, 128.8, 128.7, 128.6, 128.3, 127.6, 127.6, 127.2, 127.1, 126.8, 126.5, −0.4, −0.4, −1.9, −2.1 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{34}H_{34}NaSi_2$: 521.2091 $[M+Na]^+$; found: 521.2102.

(4-Fluoro-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8d)

White solid (33.5 mg, 38% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.29–7.16 (m, 13H), 6.84–6.79 (m, 3H), 0.18 (s, 3H), 0.13 (s, 3H), 0.01 (s, 3H), 0.00 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 247.5 Hz), 148.9, 145.8 (d, *J* = 3.2 Hz), 139.9 (d, *J* = 3.7 Hz), 139.5, 138.8, 137.0, 135.5, 134.0, 134.0, 131.9 (d, *J* = 6.9 Hz), 130.5, 129.0, 128.8, 128.3, 127.7,127.7, 126.6, 121.6 (d, *J* = 19.0 Hz), 114.8 (d, *J* = 21.4 Hz), −0.4, −0.8, −2.0, −2.3 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{28}H_{29}FNaSi_2$: 463.1684 $[M+Na]^+$; found: 463.1680.

(4-Chloro-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8e)

White solid (41.0 mg,45% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 6.8 Hz, 1H), 7.40 (s, 1H), 7.25–7.24 (m, 11H), 7.13–7.06 (m, 2H), 6.78–6.73 (m, 2H), 0.16 (s, 3H), 0.12 (s, 3H), 0.00 (s, 3H), −0.05 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.6, 148.2, 139.6, 139.4, 138.8, 136.7, 135.5, 134.8, 134.0 133.9, 132.9, 131.7, 130.3, 129.0, 128.8, 128.3, 128.1, 127.7, 127.6, 126.7, −0.4, −0.6, −1.9, −2.4 ppm; MS (EI): *m/z*: 456.15 $[M]^+$.

(4-(Trifluoromethyl)-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8f)

White solid (66.7 mg, 68% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.28–7.23 (m, 11H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.3 Hz, 1H), 0.18 (s, 6H), 0.00 (s, 3H), −0.03 ppm (s, 3H);^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.5, 148.6, 139.1, 138.6, 138.3, 136.5, 135.6, 134.0 (d, *J* = 2.2 Hz), 133.0, 131.7 (q, *J* = 3.8 Hz), 130.5, 130.0, 129.0, 128.9, 128.6 (q, *J* = 32.0 Hz), 128.4, 127.8, 127.7, 127.0, 124.4 (q, *J* = 272.8 Hz), 124.9 (q, *J* = 3.2 Hz), −0.4, −0.6, −1.9, −2.4 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{29}H_{29}F_3NaSi_2$: 513.1652 $[M+Na]^+$; found: 513.1652.

(5-Methoxy-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8g)

White solid (48.0 mg, 53% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.37–7.30 (m, 11H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 3.34 (s, 3H), 0.26 (s, 3H), 0.17 (s, 3H), 0.05 (s, 3H), 0.01 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.3, 151.6, 149.9, 140.2, 140.1, 136.9, 136.1, 135.5, 134.0, 133.9, 130.1, 128.9, 128.6, 128.3, 127.7, 127.6, 127.5, 126.5, 115.1, 113.3, 54.5, −0.3, −0.4,

−1.9, −2.4 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{29}H_{32}NaOSi_2$: 475.1884 $[M+Na]^+$; found: 475.1905.

(5-Methyl-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8h)

White solid (52.3 mg, 60% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.34–7.27 (m, 10H), 7.24 (s, 1H), 7.18 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.90 (d, J = 7.4 Hz, 1H), 6.60 (s, 1H), 2.08 (s, 3H), 0.21 (s, 3H), 0.13 (s, 3H), 0.02 (s, 3H), −0.03 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.1, 149.8, 140.1, 140.0, 138.0, 136.5, 135.6, 135.4, 134.1, 133.9, 132.9, 131.5, 130.1, 128.6, 128.6, 128.2, 127.6, 127.5, 127.1, 126.3, 21.0, −0.5, −0.5 −1.9, −2.5 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{29}H_{32}NaSi_2$: 459.1935 $[M+Na]^+$; found: 459.1902.

Methyl 2,2′-bis(dimethyl(phenyl)silyl)-[1,1′-biphenyl]-4-carboxylate (8i)

White solid (70.1 mg, 73% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.4 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.37 (s, 2H), 7.13–7.08 (m, 11H), 7.02 (t, J = 7.0 Hz, 1H), 6.69 (d, J = 7.1 Hz, 1H), 3.58 (s, 3H), 0.00 (s, 6H), −0.11 (s, 3H), −0.15 ppm (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.9, 150.0, 149.0, 143.0, 139.2, 138.9, 136.8, 135.6, 135.6, 134.0, 133.9, 130.9, 130.1, 129.6, 128.9, 128.6, 128.3, 127.7, 127.6, 127.1, 126.8, 51.9, −0.6, −0.7, −1.9, −2.3 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{30}H_{32}NaO_2Si_2$: 503.1833 $[M+Na]^+$; found: 503.1823.

(5,5′-Dimethyl-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8j)

White solid (45.9 mg, 51% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.5 Hz, 2H), 7.35–7.30 (m, 10H), 7.10 (d, J = 7.5 Hz, 2H), 6.62 (s, 2H), 2.10 (s, 6H), 0.21 (s, 6H), −0.02 ppm (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.0, 140.4, 138.0, 135.5, 133.9, 132.8, 131.4, 128.5, 127.6, 127.0, 21.0, −0.4, −2.4 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{30}H_{34}NaSi_2$: 473.2091 $[M+Na]^+$; found: 473.2088.

(4,4′-Dichloro-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8k)

White solid (47.0 mg, 48% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (s, 2H), 7.33–7.24 (m, 10H), 7.11 (d, J = 8.1 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 0.23 (s, 6H), 0.03 ppm (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.9, 139.7, 138.4, 134.9, 133.9, 133.3, 131.7, 129.1, 128.2, 127.8, −0.5, −2.2 ppm; MS (EI): *m/z*: 490.10 $[M]^+$.

(4,4′-Difluoro-[1,1′-biphenyl]-2,2′-diyl)bis(dimethyl(phenyl)silane) (8l)

Colorless oil (56.8 mg, 62% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 10H), 7.17–7.15 (m, 2H), 6.80–6.77 (m, 2H), 6.75–6.73 (m, 2H), 0.17 (s, 6H), −0.00 ppm (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.7 (d, J = 247.5 Hz), 144.7 (d, J = 3.1 Hz), 140.3 (d, J = 3.6 Hz), 138.6, 134.0, 132.2 (d, J = 6.9 Hz), 129.0, 127.8, 121.7 (d, J = 19.1 Hz), 114.9 (d, J = 21.3 Hz), −0.7, −2.3 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{28}H_{28}F_2NaSi_2$: 481.1590 $[M+Na]^+$; found: 481.1590.

5,5,7,7-Tetramethyl-5,7-dihydrodibenzo[c,e][1,2,7]oxadisilepine (9a)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (d, J = 7.2 Hz, 2H), 7.50–7.48 (m, 2H), 7.40–7.36 (m, 4H), 0.51 (s, 6H), −0.33 ppm (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.5, 138.0, 133.0, 130.6, 130.0, 126.5, 0.1, −0.7 ppm; MS (EI): *m/z*: 284.09 $[M]^+$.

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Conflict of interest

The authors declare no conflict of interest.

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