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Preparation of functionalized aryl(diallyl)ethoxysilanes and their palladium-catalyzed coupling reactions giving sol–gel precursors

Yoshifumi Maegawa,[a] Toyohiro Nagano,[a] Tatsuya Yabuno,[a] Hiroki Nakagawa[a] and Toyoshi Shimada[a,b,*]

[a]*Department of Chemical Engineering, Nara National College of Technology, 22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan*
[b]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

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Abstract—A series of molecular building blocks containing allylsilyl groups, which can be incorporated into the appropriate sol–gel precursors as fragments, were prepared. The allylsilyl group is retained unchanged over the course of all reactions giving sol–gel precursors and behave as the synthetic equivalent of alkoxysilyl groups toward sol–gel polymerization, but are stable enough to allow purification by silica gel chromatography. These allylsilanes were successfully used as building blocks to construct functional sol–gel precursors via palladium-catalyzed coupling reactions.

1. Introduction

Organic–inorganic hybrid materials integrate the intrinsic characteristics of organic and inorganic materials. The usual method of preparation to date has been polymerization of organotrialkoxysilanes under sol–gel conditions.[1] Materials which incorporate functional organomoieties in a silica matrix have been prepared by Shea and Loy,[2a–c] Schubert,[2d] Corriu and Cerveau,[2e–g] Inagaki,[2h] Ozin,[1d] Moreau and Dautel,[2i] and our group.[2j] In the pioneer work in this area, Shea and Loy reported the preparation and sol–gel polymerization of a variety of bridged trialkoxyarylenesilanes.[2a] However, the development of appropriate sol–gel precursors for organic–inorganic hybrid materials has been rather slow compared to the progress in the synthesis of chemicals and medicines, because trialkoxysilyl groups are so reactive toward hydrolysis that their compounds cannot be handled under hydrolytic conditions and cannot be purified by silica gel chromatography.

We recently found that allylsilyl groups behave as the synthetic equivalent of alkoxysilyl groups, but are stable enough to allow purification by silica gel chromatography.[3] For example, the use of 1,4-bis(triallylsilyl)benzene or 1,4-bis(diallylethoxysilyl)benzene in the place of 1,4-bis(triethoxysilyl)benzene gave the same organic–inorganic hybrid materials containing periodic mesostructures with crystal-like pore walls.[3c]

* Corresponding author. Tel./fax: +81 743 55 6154; e-mail: shimada@chem.nara-k.ac.jp

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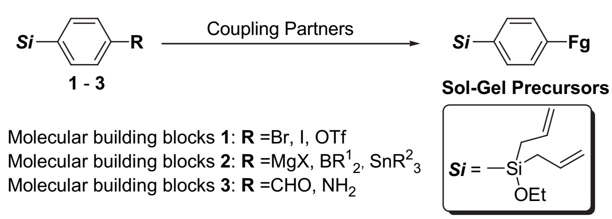
Herein we disclose a novel preparation method for a series of molecular building blocks containing allylsilyl groups, which can be incorporated into the appropriate sol–gel precursors as fragments, and their palladium-catalyzed coupling reactions giving sol–gel precursors (Scheme 1).

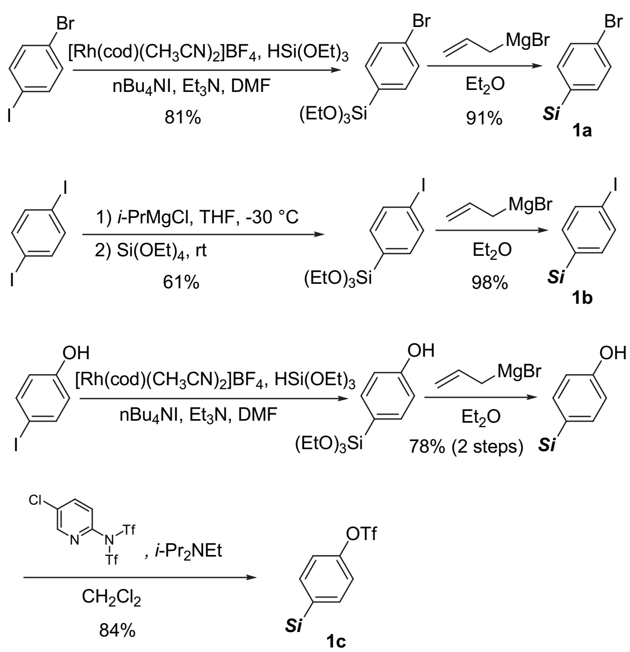


Scheme 1. Coupling reactions with allylsilane building blocks.

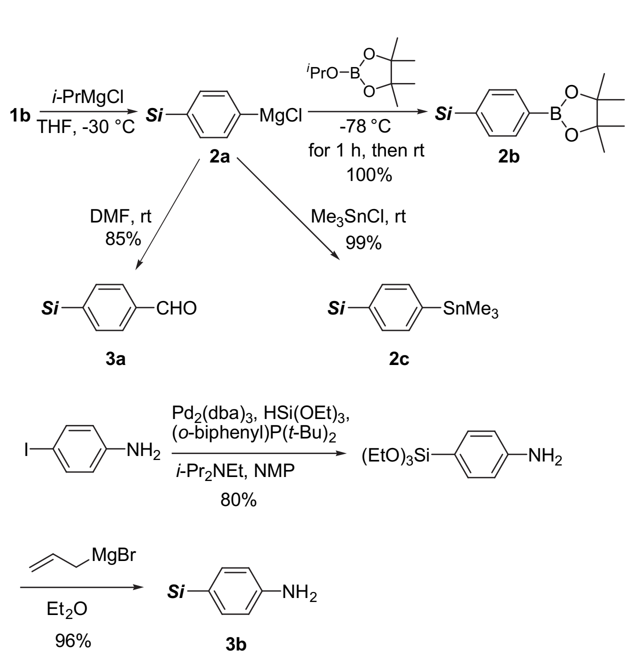
2. Results and discussion

2.1. Preparation of molecular building blocks for allylsilane sol–gel precursors

The use of a diallylethoxysilyl group as a polymerizable moiety in allylsilyl sol–gel precursors is not only more effective for sol–gel polymerization, but also confers stability under general hydrolysis conditions. We focused on diallylethoxysilyl sol–gel precursors as promising precursors of organic–inorganic hybrid materials. Molecular building blocks for allylsilane sol–gel precursors (MBAS) **1**, **2**, and **3** contain both a diallylethoxysilyl group to form Si–O–Si bonds by polymerization under sol–gel conditions, and a functional group which is active toward cross-coupling reactions to give the desired sol–gel precursors. Bromide **1a** was prepared by rhodium-catalyzed triethoxysilylation[4] of 1-bromo-4-iodobenzene with triethoxysilane followed by the addition of allylmagnesium bromide, with a total yield of 74%.[5] A Grignard-exchange reaction of 1,4-diiodobenzene with isopropylmagnesium chloride[6] followed by the addition of tetraethoxysilane and subsequent treatment with allylmagnesium bromide gave iodide **1b** in a total yield of 60%. Trifluoromethanesulfonylation of 4-(diallylethoxysilyl)phenol, prepared from 4-iodophenol, was achieved by treatment with Comins' reagent[7] to give the triflate **1c** in 84% yield (Scheme 2).



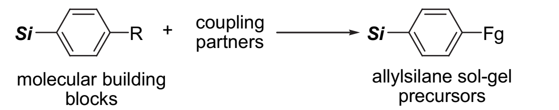
Scheme 2. Preparation of molecular building blocks **1a**–**1c**.



Scheme 3. Preparation of molecular building blocks **2** and **3**.

Our attempts to transform **1a** and **1b** to **2** via lithiation with butyllithium, and the preparation of Grignard reagent **2a** using magnesium metal, were unsuccessful. However, isopropylmagnesium chloride was successfully used for a Grignard-exchange reaction of **1b** to give key compound **2a**, leading to **2b**, **2c**, and **3a** in 100%, 99%, and 85% yields for two steps, respectively (Scheme 3). Surprisingly, diallylethoxysilyl group is compatible with Grignard moiety in **2a** derived from **1b**. It is noteworthy that easily prepared arylhalides are coupling partners of **2** in palladium-catalyzed cross-coupling reactions.

Table 1. Reactions of molecular building blocks with coupling partners[a]



Entry	Building block	Coupling partner	Product	Yield[b] (%)
1		H–C≡C–SiMe$_3$	Si–C$_6$H$_4$–C≡C–SiMe$_3$	87
2	**1a**	C$_6$H$_5$–B(OH)$_2$	Si–C$_6$H$_4$–C$_6$H$_5$	61
3		Ph$_2$NH	Si–C$_6$H$_4$–NPh$_2$	62
4		H–C≡C–C(CH$_3$)$_2$–OH	Si–C$_6$H$_4$–C≡C–C(CH$_3$)$_2$–OH	100
	1b			
5		MeO–C$_6$H$_4$–B(OH)$_2$	Si–C$_6$H$_4$–C$_6$H$_4$–OMe	89
6	**1c**	MeO–C$_6$H$_4$–B(OH)$_2$	Si–C$_6$H$_4$–C$_6$H$_4$–OMe	76
7	**2a**	2-bromopyridine (Br, N)	Si–C$_6$H$_4$–(2-pyridyl)	91
8	**2b**	I–C$_6$H$_4$–OMe	Si–C$_6$H$_4$–C$_6$H$_4$–OMe	89
9	**2c**	2-bromopyridine (Br, N)	Si–C$_6$H$_4$–(2-pyridyl)	50
10	**3a**	PPh$_3$Me$^+$I$^-$	Si–C$_6$H$_4$–CH=CH$_2$	94
11	**3b**	I–C$_6$H$_4$–Me	Si–C$_6$H$_4$–NH–C$_6$H$_4$–Me	77

[a] All the reaction conditions are shown in Section 4.
[b] Isolated yield.

Meanwhile, **3b**, obtained by palladium-catalyzed silylation[8] of 4-iodoaniline followed by allylation with allylmagnesium bromide, may be used in transition metal-catalyzed amination (Scheme 3).[9]

2.2. Cross-coupling reactions of molecular building blocks with various coupling partners

Cross-coupling reactions of MBAS were carried out with various substrates, and the results are summarized in Table 1. The diallylethoxysilyl group was retained unchanged over the course of all reactions. The molecular building block **1** smoothly underwent palladium-catalyzed Suzuki–Miyaura[10] and Sonogashira coupling reactions,[11] and Buchwald–Hartwig amination[9] to afford the corresponding coupling products containing an allylsilyl group (entries 1–6, Table 1).

Grignard cross-coupling[12] and Stille coupling reaction[13] of **2a** and **2c** with 2-bromopyridine gave 2-(4-diallylethoxysilylphenyl)pyridine in 91% and 50% yields, respectively, and Suzuki coupling reaction of **2b** with 4-iodoanisole gave the corresponding product in 89% yield (entries 7–9). Furthermore, Wittig olefination of **3a** with methyltriphenylphosphonium iodide gave a styrene MBAS, which is useful for the Mizoroki–Heck reaction, in 94% yield, and amination[9] of 4-iodotoluene with **3b** proceeded smoothly to give the corresponding product in 77% yield (entries 10 and 11).

The reactions of MBAS with various coupling partners also resulted in the development of a broadly applicable synthesis for bridged sol–gel precursors. We prepared novel sol–gel precursors such as BINAP derivative **4a** in 71% yield from the reaction of 5,5′-diethynyl-BINAP dioxide[14] with **1b**, biphenylene amine **4b** in 72% yield from the reaction of 4,4′-diiodobiphenyl with **3b**, and oligophenylene-ethynylene **4c** in 94% yield from the reaction of 4,4′-diethynyltolan[15] with **1b** (Scheme 4). We are convinced that a synthetic method using MBAS would, in addition to its wide application to easy preparation of functionally bridged sol–gel precursors, open the door to a new branch of materials chemistry.

3. Conclusions

In summary, we have demonstrated a new method of preparing many types of sol–gel precursors containing various MBAS. This method overcomes the limitations associated with the conventional method using alkoxysilanes, and thus can be applied as a general synthesis for organic–inorganic functional hybrid precursors.

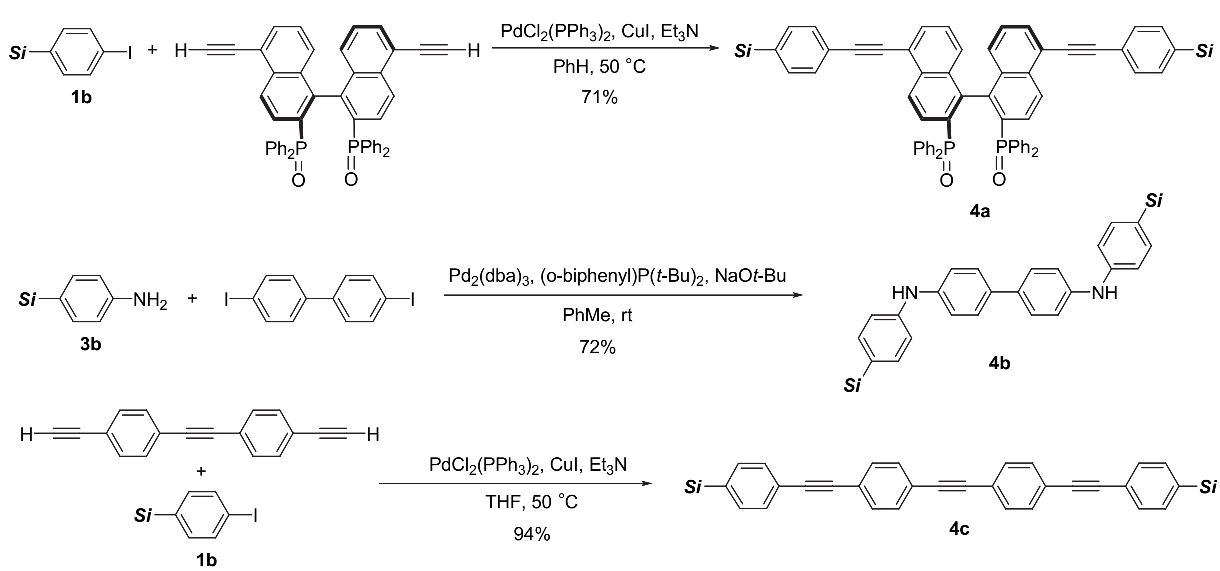
4. Experimental section

4.1. General procedures

All moisture sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Optical rotations were recorded with a JASCO DIP-370 polarimeter. NMR spectra were recorded on JEOL JNM LA500 spectrometer (270 MHz for ^{1}H, 67.5 MHz for ^{13}C, and 109 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR, chloroform-*d* (δ 77.0) for ^{13}C NMR, and an external 85% H_3PO_4 standard for ^{31}P NMR. High resolution mass spectra (HRMS) were recorded with JEOL JMS-700 spectrometer.

4.2. Preparation of molecular building blocks

4.2.1. 1-Bromo-4-(diallylethoxysilyl)benzene 1a. To a solution of 1-bromo-4-iodobenzene (2.60 g, 9.19 mmol), tetrabutylammonium iodide (3.39 g, 9.18 mmol), triethylamine (2.56 mL, 18.4 mmol), and $[Rh(cod)(CH_3CN)_2]BF_4$ (105 mg, 0.277 mmol) in DMF (26 mL) was added dropwise triethoxysilane (1.87 mL, 10.1 mmol) at 0 °C. The mixture was stirred at 80 °C for 1 h. The mixture was concentrated under reduced pressure, treated with Et_2O, and filtered



Scheme 4. Preparation of functional sol–gel precursors with molecular building blocks.

through a short Celite plug. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure to give 2.38 g (81% yield) of *1-bromo-4-(triethoxysilyl)benzene*. To the resulting ethoxysilane (4.74 g, 14.8 mmol) was added allylmagnesium bromide (59.4 mL, 1 M in ether, 59.4 mmol) in Et_2O. The reaction mixture was stirred at room temperature for 10 h and quenched with 10% HCl. It was then diluted with Et_2O and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure to give 4.20 g (91% yield) of *1-bromo-4-(diallylethoxysilyl)benzene* (**1a**): ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J=6.8 Hz, 3H), 1.91 (ddd, J=7.8 Hz, 1.4 Hz, 1.1 Hz, 4H), 3.76 (q, J=6.8 Hz, 2H), 4.92 (ddt, J=9.7 Hz, 1.6 Hz, 1.1 Hz, 2H), 4.95 (ddt, J=15.7 Hz, 1.6 Hz, 1.4 Hz, 2H), 5.79 (ddt, J=15.7 Hz, 9.7 Hz, 7.8 Hz, 2H), 7.43 (d, J=8.4 Hz, 2H), 7.52 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.32, 21.08, 59.27, 114.96, 124.68, 130.90, 132.63, 133.88, 135.50. HRMS (FAB$^+$) $[M-H]^+$ calcd for $C_{14}H_{18}OBrSi$ 309.0310, found 309.0321. Anal. Calcd for $C_{14}H_{19}OBrSi$: C, 54.02; H, 6.15. found: C, 53.93; H, 6.23.

4.2.2. 1-Iodo-4-(diallylethoxysilyl)benzene 1b. To a solution of 1,4-diiodobenzene (15 g, 45.6 mmol) in THF (114 mL) was added dropwise a solution of *i*-PrMgCl (24 mL, 2 M in THF, 48 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 5.5 h to give 4-iodophenylmagnesium chloride solution. The resulting solution of 4-iodophenylmagnesium chloride was added dropwise (three drops per second) via cannula at −30 °C to tetraethyl orthosilicate (60.6 mL, 272 mmol) in THF (90 mL), which was cooled to −30 °C. The reaction mixture was stirred at −30 °C for 1 h and then at room temperature for 44 h. To the reaction mixture was added Et_2O (100 mL) and then washed with H_2O. The mixture was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure (1.5 mmHg, 120 °C) to give *1-iodo-4-(triethoxysilyl)benzene* (10.2 g, 61%): ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J=7.3 Hz, 9H), 3.88 (q, J=7.3 Hz, 6H), 7.39 (dd, J=7.8 Hz, 1.4 Hz, 2H), 7.73 (dd, J=7.8 Hz, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.36, 21.08, 59.35, 97.08, 115.04, 132.69, 134.49, 135.59, 136.87. HRMS (EI$^+$) M$^+$ calcd for $C_{12}H_{19}O_3ISi$ 358.0250, found 358.0243. To *1-iodo-4-(triethoxysilyl)benzene* (9.4 g, 25.7 mmol) was added dropwise a solution of allylmagnesium bromide (77 mL, 1 M in Et_2O, 77 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 10 h and quenched with 10% HCl. It was then diluted with Et_2O and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=20:1 as eluent) to give *1-iodo-4-(diallylethoxysilyl)benzene* (9.0 g, 98%): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J=6.8 Hz, 3H), 1.91 (d, J=8.1 Hz, 4H), 3.75 (q, J=6.8 Hz, 2H), 4.98–4.89 (m, 4H), 5.87–5.71 (m, 2H), 7.29 (d, J=8.1 Hz, 2H), 7.72 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.34, 21.08, 59.35, 97.08, 115.04, 132.69, 134.49, 135.59, 136.87. HRMS (EI$^+$) M$^+$ calcd for $C_{14}H_{19}OISi$ 358.0250, found 358.0243. Anal. Calcd for $C_{14}H_{19}OISi$: C, 46.93; H, 5.35. Found: C, 46.80; H, 5.46.

4.2.3. 4-(Diallylethoxysilyl)phenyl triflate 1c. To a mixture of 4-iodophenol (6 g, 27.3 mmol), $[Rh(cod)(CH_3CN)_2]BF_4$ (104 mg, 0.27 mmol), and *n*-Bu_4NI (10.0 g, 27.3 mmol) were added DMF (180 mL), Et_3N (11.4 mL, 81.8 mmol), and $(EtO)_3SiH$ (15.1 mL, 81.8 mmol). The reaction mixture was stirred at 80 °C for 3 h. The mixture was concentrated under reduced pressure, treated with Et_2O, and filtered through a short Celite plug. The filtrates were concentrated under reduced pressure. To the residue was added dropwise a solution of allylmagnesium bromide (1.0 M in Et_2O, 136 mL, 136 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 19 h and quenched with 10% HCl. It was then diluted with Et_2O and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=5:1 as eluent) to give 4-(diallylethoxysilyl)phenol (5.30 g, 78%, in two steps): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J=6.8 Hz, 3H), 1.92 (d, J=7.8 Hz, 4H), 3.75 (q, J=6.8 Hz, 2H), 4.92 (ddt, J=10.3 Hz, 1.4 Hz, 0.8 Hz, 2H), 4.96 (ddt, J=15.9 Hz, 1.4 Hz, 1.1 Hz, 2H), 5.57 (br, 1H), 5.82 (ddt, J=15.9 Hz, 10.3 Hz, 7.8 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 7.46 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.30, 21.24, 59.29, 114.72, 115.04, 125.85, 133.19, 135.82, 157.18. To a mixture of 4-(diallylethoxysilyl)phenol (197 mg, 0.79 mmol) and 2-[*N*,*N*-bis(trifluoromethylsulfonyl)amino]-5-chloropyridine (343 mg, 0.87 mmol) were added CH_2Cl_2 (5 mL) and *i*-Pr_2NEt (553 µL, 3.17 mmol). The reaction mixture was stirred at room temperature for 19 h. The reaction mixture was then concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=10:1 as eluent) to give 4-(diallylethoxysilyl)phenyl triflate (253 mg, 84%): ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J=7.0 Hz, 3H), 1.93 (d, J=7.8 Hz, 4H), 3.79 (q, J=7.0 Hz, 2H), 4.91–4.99 (m, 4H), 5.79 (ddt, J=16.2 Hz, 10.3 Hz, 7.8 Hz, 2H), 7.28 (d, J=8.1 Hz, 2H), 7.67 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.28, 21.13, 59.43, 115.21, 120.55, 132.40, 136.05, 136.46, 150.87. Anal. Calcd for $C_{15}H_{19}O_4F_3SSi$: C, 47.35; H, 5.03. Found: C, 47.47; H, 5.05.

4.2.4. 4-(Diallylethoxysilyl)phenylmagnesium chloride 2a. To a solution of 4-(diallylethoxysilyl)iodobenzene (255 mg, 0.71 mmol) in THF (2 mL) was added a solution of *i*-PrMgCl (0.71 mL, 2 M in THF, 1.42 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 1.5 h to give 4-(diallylethoxysilyl)phenylmagnesium chloride.

4.2.5. Diallyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethoxysilane 2b. To a solution of 4-(diallylethoxysilyl)iodobenzene (2.02 g, 5.64 mmol) in THF (15 mL) was added a solution of *i*-PrMgCl (5.9 mL, 2 M in THF, 11.8 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 4 h to give 4-(diallylethoxysilyl)phenylmagnesium chloride. To the Grignard reagent solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[16] (2.3 mL, 11.3 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and then at room temperature for 19 h. The reaction mixture was quenched with 10% HCl. It was then diluted with Et_2O and the organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give 1-(diallylethoxysilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2.02 g, 100%): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J=7.0 Hz, 3H), 1.34 (s, 12H), 1.94 (d, J=7.8 Hz, 4H), 3.75 (q, J=7.0 Hz, 2H), 4.89 (ddt, J=10.3 Hz, 1.6 Hz, 1.1 Hz, 2H), 4.94 (ddt, J=15.9 Hz, 1.6 Hz, 1.4 Hz, 2H), 5.81 (ddt, J=15.9 Hz, 10.3 Hz, 7.8 Hz, 2H), 7.58 (d, J=8.4 Hz, 2H), 7.81 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.33, 21.05, 24.81, 59.28, 83.76, 114.77, 127.74, 132.94, 133.22, 133.80, 138.49. HRMS (FAB$^+$) $[M-H]^+$ calcd for $C_{20}H_{30}O_3BSi$ 357.2057, found 357.2070.

4.2.6. Diallyl[4-(trimethylstannyl)phenyl]ethoxysilane 2c. To a solution of 4-(diallylethoxysilyl)iodobenzene (2.02 g, 5.64 mmol) in THF (15 mL) was added a solution of *i*-PrMgCl (5.9 mL, 2 M in THF, 11.8 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 4 h. To the resulting Grignard solution was added a solution of Me_3SnCl (11.2 mL, 1 M in THF, 11.2 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 1 h, and at room temperature for 19 h. The reaction mixture was then quenched with H_2O and extracted with Et_2O. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give 4-(diallylethoxysilyl)phenyltrimethyltin (2.20 g, 99%): ^{1}H NMR ($CDCl_3$) δ 0.29 (t, J (Sn–CH_3)=54.5 Hz, 9H), 1.21 (t, J=6.8 Hz, 3H), 1.93 (d, J=8.1 Hz, 4H), 3.76 (q, J=6.8 Hz, 2H), 4.92 (ddt, J=16.2 Hz, 1.6 Hz, 1.1 Hz, 2H), 4.96 (ddt, J=10.3 Hz, 1.6 Hz, 0.5 Hz, 2H), 5.84 (ddt, J=16.2 Hz, 10.3 Hz, 8.1 Hz, 2H), 7.52 (d, J=1.62 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ −9.63 (J (^{119}Sn–CH_3)=348.6 Hz, J (^{117}Sn–CH_3)=333.0 Hz), 18.40, 21.21, 59.29, 114.72, 133.20, 133.40, 134.76, 135.27, 144.58. HRMS (FAB$^+$) $[M-H]^+$ calcd for $C_{17}H_{27}OSiSn$ 395.0853, found 395.0850.

4.2.7. Diallyl(4-formylphenyl)ethoxysilane 3a. To a solution of 4-(diallylethoxysilyl)iodobenzene (255 mg, 0.71 mmol) in THF (2 mL) was added a solution of *i*-PrMgCl (0.71 mL, 2 M in THF, 1.42 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 1.5 h to give 4-(diallylethoxysilyl)phenylmagnesium chloride. To the Grignard reagent solution was added DMF (110 μL, 1.42 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 13 h. The reaction mixture was quenched with 10% HCl and extracted with Et_2O. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=20:1 as eluent) to give diallyl(4-formylphenyl)ethoxysilane (158 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J=6.8 Hz, 3H), 1.96 (ddd, J=8.1 Hz, 1.4 Hz, 0.8 Hz, 4H), 3.81 (q, J=6.8 Hz, 2H), 4.91–4.99 (m, 4H), 5.80 (ddt, J=16.2 Hz, 10.3 Hz, 8.1 Hz, 2H), 7.75 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.4 Hz, 2H), 10.0 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.35, 21.06, 59.50, 115.24, 128.58, 132.43, 134.53, 137.07, 143.53, 192.55. HRMS (EI$^+$) M$^+$ calcd for $C_{15}H_{20}O_2Si$ 260.1233, found 260.1236.

4.2.8. Diallyl(4-aminophenyl)ethoxysilane 3b. To a mixture of 4-iodoaniline (1316 mg, 6.0 mmol), $Pd_2(dba)_3$ (82.4 mg, 0.090 mmol), and (*o*-biphenyl)P(*t*-Bu)$_2$ (107.6 mg, 0.36 mmol) were added NMP (24 mL), *i*-Pr_2NEt (3.13 mL, 18 mmol), and $(EtO)_3SiH$ (1.66 mL, 9.0 mmol). The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was then concentrated to remove excess of amine and triethoxysilane. The residue was diluted with Et_2O, the organic layer was washed with H_2O, dried over $MgSO_4$, and concentrated. The residue was distilled under reduced pressure (0.1 mmHg, 110 °C) to give 4-(triethoxysilyl)aniline (1.23 g, 80%). To 4-(triethoxysilyl)aniline (1.15 g, 4.5 mmol) was added dropwise a solution of allylmagnesium bromide (1.0 M in Et_2O, 22.5 mL, 22.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 13 h. The reaction was quenched with H_2O and the mixture was extracted with Et_2O. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give 4-(diallylethoxysilyl)aniline (1.08 g, 96%): ^{1}H NMR ($CDCl_3$) δ 1.48 (t, J=7.0 Hz, 3H), 1.90 (d, J=8.4 Hz, 4H), 3.73 (q, J=7.0 Hz, 4H containing NH_2), 4.86–4.98 (m, 4H), 5.79 (ddt, J=16.2 Hz, 9.5 Hz, 8.1 Hz, 2H), 6.68 (d, J=8.1 Hz, 2H), 7.36 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.36, 21.36, 59.04, 114.37, 122.82, 133.55, 135.42, 136.00, 147.90. HRMS (FAB$^+$) $[M+H]^+$ calcd for $C_{14}H_{22}ONSi$ 248.1471, found 248.1471.

4.3. Coupling reaction of molecular building blocks with coupling partners

4.3.1. Sonogashira coupling reaction of 1a with trimethylsilylacetylene giving 1-diallylethoxysilyl-4-(trimethylsilylethynyl)benzene (Table 1, entry 1). To a mixture of $Pd_2(dba)_3$ (82 mg, 0.14 mmol), PPh_3 (152 mg, 0.58 mmol), and CuI (50 mg, 0.26 mmol) were added a solution of trimethylsilylacetylene (545 μL, 3.86 mmol) and **1a** (1000 mg, 3.21 mmol) in Et_3N (50 mL). The reaction mixture was stirred at 75 °C for 24 h. The reaction mixture was then diluted with Et_2O, washed with H_2O and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=5:1 as eluent) to give 1-diallylethoxysilyl-4-(trimethylsilylethynyl)benzene (920 mg, 87%): ^{1}H NMR ($CDCl_3$) δ 0.249 (s, 9H), 1.20 (t, J=6.8 Hz, 3H), 1.92 (d, J=8.1 Hz, 4H), 3.78 (q, J=6.8 Hz, 2H), 4.88–4.99 (m, 4H), 5.79 (ddt, J=16.2 Hz, 9.5 Hz, 8.1 Hz, 2H), 7.45 (d, J=8.1 Hz, 2H), 7.51 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.074, 18.36, 21.10, 59.34, 95.21, 104.97, 114.92, 124.39, 131.05, 132.81, 133.77, 135.78. HRMS (FAB$^+$) $[M-H]^+$ calcd for $C_{19}H_{27}OSi_2$ 327.1600, found 327.1606.

4.3.2. Suzuki coupling reaction of 1a with phenylboronic acid giving 4-(diallylethoxysilyl)biphenyl (Table 1, entry 2). To a mixture of **1a** (152 mg, 0.49 mmol), $Pd(PPh_3)_4$ (16.9 mg, 0.015 mmol), K_2CO_3 (101 mg, 0.73 mmol), and phenylboronic acid (71.4 mg, 0.59 mmol) was added toluene (5 mL). The reaction mixture was stirred at 80 °C for 13 h. The reaction mixture was then diluted with Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=10:1 as eluent) to give 4-(diallylethoxysilyl)biphenyl (91.2 mg, 61%): ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J=6.8 Hz, 3H), 1.97 (d, J=7.8 Hz, 4H), 3.80 (q, J=6.8 Hz, 2H), 4.93 (ddt, J=9.7 Hz, 1.4 Hz, 1.1 Hz, 2H), 4.99 (ddt, J=15.9 Hz, 1.4 Hz, 0.5 Hz, 2H), 5.86 (ddt, J=15.9 Hz, 9.7 Hz, 7.8 Hz, 2H), 7.36 (t, J=7.0 Hz, 1H), 7.45 (t, J=7.0 Hz, 2H), 7.60–7.68 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 18.38, 21.24, 59.29, 114.78, 126.46, 127.10, 127.45, 128.73, 133.09, 133.75, 134.49, 140.83, 142.43. HRMS (FAB$^+$) $[M-H]^+$ calcd for $C_{20}H_{23}OSi$ 307.1518, found 307.1526. Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.87; H, 7.84. Found: C, 77.62; H, 8.03.

4.3.3. Buchwald–Hartwig amination of 1a with diphenylamine giving 4-diallylethoxysilyl-*N*,*N*-diphenylaniline (Table 1, entry 3). To a mixture of **1a** (486 mg, 1.56 mmol), $Pd_2(dba)_3$ (21.5 mg, 0.023 mmol), (*o*-biphenyl)P(*t*-Bu)$_2$ (42.0 mg, 0.14 mmol), NaO*t*-Bu (225 mg, 2.34 mmol), and diphenylamine (317 mg, 1.87 mmol) was added toluene (15 mL). The reaction mixture was stirred at 80 °C for 19 h. The reaction mixture was then diluted with Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=5:1 as eluent) to give 4-diallylethoxysilyl-*N*,*N*-diphenylaniline (384 mg, 62%): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J=7.0 Hz, 3H), 1.92 (d, J=8.1 Hz, 4H), 3.77 (q, J=7.0 Hz, 2H), 4.90–5.00 (m, 4H), 5.77–5.93 (m, 2H), 7.03 (d, J=8.1 Hz, 2H), 7.02–7.13 (m, 6H), 7.25 (d, J=8.1 Hz, 2H), 7.28 (d, J=8.1 Hz, 2H), 7.41 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.40, 21.34, 59.17, 114.58, 121.69, 123.28, 124.95, 127.30, 129.27, 133.37, 134.95, 147.33, 149.19. HRMS (FAB$^+$) $[M+H]^+$ calcd for $C_{26}H_{30}ONSi$ 400.2097, found 400.2093.

4.3.4. Sonogashira coupling reaction of 1b with 2-methyl-3-butyn-2-ol giving 1-diallylethoxysilyl-4-(3-hydroxy-3-methyl-1-butynyl)benzene (Table 1, entry 4). To a mixture of **1b** (130 mg, 0.36 mmol), $PdCl_2(PPh_3)_2$ (10.2 mg, 0.015 mmol), and CuI (2.8 mg, 0.015 mmol) were added THF (3 mL), Et_3N (3 mL), and 2-methyl-3-butyn-2-ol (42 μL, 0.43 mmol). The reaction mixture was stirred at 50 °C for 1.5 h. The reaction mixture was then diluted with Et_2O, washed with H_2O and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=5:1 as eluent) to give 1-diallylethoxysilyl-4-(3-hydroxy-3-methyl-1-butynyl)benzene (114 mg, 100%): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J=7.0 Hz, 3H), 1.62 (s, 6H), 1.92 (d, J=8.1 Hz, 4H), 2.09 (s, 1H), 3.76 (q, J=7.0 Hz, 2H), 4.89–4.96 (m, 4H), 5.71–5.87 (m, 2H), 7.41 (d, J=8.1 Hz, 2H), 7.51 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.33, 21.08, 31.42, 59.32, 65.57, 82.03, 94.71, 114.91, 124.02, 130.74, 132.79, 133.81, 135.44. HRMS (FAB$^+$) $[M-H]^+$ calcd for $C_{19}H_{25}O_2Si$ 313.1624, found 313.1624.

4.3.5. Suzuki coupling reaction of 1b with 4-methoxyphenylboronic acid giving 4-diallylethoxysilyl-4′-methoxybiphenyl (Table 1, entry 5). To a mixture of **1b** (187 mg, 0.52 mmol), $Pd(PPh_3)_4$ (18.1 mg, 0.016 mmol), K_2CO_3 (108 mg, 0.78 mmol), and 4-methoxyphenylboronic acid (95.2 mg, 0.63 mmol) was added toluene (5 mL). The reaction mixture was stirred at 80 °C for 13 h. The reaction mixture was then diluted with Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under vacuum to give a residue. The residue was chromatographed on silica gel (hexane/EtOAc=10:1 as eluent) to give 4-diallylethoxysilyl-4′-methoxybiphenyl (157.3 mg, 89%): ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J=6.8 Hz, 3H), 1.97 (d, J=8.1 Hz, 4H), 3.79 (q, J=6.8 Hz, 2H), 3.86 (s, 3H), 4.93 (ddt, J=9.5 Hz, 1.4 Hz, 0.8 Hz, 2H), 4.98 (ddt, J=17.3 Hz, 1.4 Hz, 1.1 Hz, 2H), 5.86 (ddt, J=17.3 Hz, 9.5 Hz, 8.1 Hz, 2H), 6.99 (d, J=8.4 Hz, 2H), 7.55 (d, J=8.4 Hz, 2H), 7.57 (d, J=7.6 Hz, 2H), 7.63 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.38, 21.24, 55.22, 59.25, 114.17, 114.73, 125.98, 128.09, 132.94, 133.14, 133.28, 134.47, 141.99, 159.27. HRMS (FAB$^+$) M$^+$ calcd for $C_{21}H_{26}O_2Si$ 338.1702, found 338.1707. Anal. Calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74. Found: C, 74.38; H, 7.87.

4.3.6. Suzuki coupling reaction of 1c with 4-methoxyphenylboronic acid giving 4-diallylethoxysilyl-4′-methoxybiphenyl (Table 1, entry 6). To a mixture of 4-(diallylethoxysilyl)phenyl triflate (150 mg, 0.39 mmol), $Pd(PPh_3)_4$ (13.6 mg, 0.012 mmol), K_2CO_3 (81.7 mg, 0.59 mmol), and 4-methoxyphenylboronic acid (71.9 mg, 0.47 mmol) was added toluene (5 mL). The reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was then diluted with Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under vacuum to give a residue. The residue was chromatographed on silica gel (hexane/EtOAc=10:1 as eluent) to give 4-diallylethoxysilyl-4′-methoxybiphenyl (101.7 mg, 76%).

4.3.7. Grignard cross-coupling of 2a with 2-bromopyridine giving 2-[4-(diallylethoxysilyl)phenyl]pyridine (Table 1, entry 7). To a solution of **1b** (240 mg, 0.67 mmol) in THF (2 mL) was added a solution of *i*-PrMgCl (0.70 mL, 2 M in THF, 1.40 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 2 h to give 4-(diallylethoxysilyl)phenylmagnesium chloride. To a solution of $Pd_2(dba)_3$ (25.6 mg, 0.028 mmol), dppf (15.5 mg, 0.028 mmol), and 2-bromopyridine (54.4 μL, 0.56 mmol) in THF (3 mL) was added 4-(diallylethoxysilyl)phenylmagnesium chloride at −30 °C. The reaction mixture was stirred at −30 °C for 17 h. The reaction mixture was then quenched with saturated NH_4Cl and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give 2-[4-(diallylethoxysilyl)phenyl]pyridine (158 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J=7.0 Hz, 3H), 1.97 (d, J=8.4 Hz, 4H), 3.79 (q, J=7.0 Hz, 2H), 4.92 (ddt, J=10.0 Hz, 1.9 Hz, 0.8 Hz, 2H), 4.98 (ddt, J=16.2 Hz, 1.9 Hz, 1.4 Hz, 2H), 5.84 (ddt, J=16.2 Hz, 10.0 Hz, 8.4 Hz, 2H), 7.33 (dt, J=5.1 Hz, 0.5 Hz, 1H), 7.69 (d, J=8.4 Hz, 2H), 7.73–7.80 (m, 2H), 8.00 (d, J=8.4 Hz, 2H), 8.71 (dt, J=5.1 Hz, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.35, 21.16, 59.30, 114.95, 120.62, 122.25, 126.00, 132.96, 134.55, 135.82, 136.69, 140.55, 149.68, 157.20. HRMS (FAB$^+$) $[M+H]^+$ calcd for $C_{19}H_{24}ONSi$ 310.1627, found 310.1635. Anal. Calcd for $C_{19}H_{23}ONSi$: C, 73.74; H, 7.49; N, 4.53. Found: C, 74.19; H, 7.84; N, 4.02.

4.3.8. Suzuki coupling reaction of 2b with 4-iodoanisole giving 4-diallylethoxysilyl-4′-methoxybiphenyl (Table 1, entry 8). To a mixture of **2b** (200 mg, 0.558 mmol), 4-iodoanisole (109 mg, 0.465 mmol), silver carbonate (154 mg, 0.558 mmol), and $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) was added 5 mL of THF. The reaction mixture was stirred at 60 °C for 24 h, diluted with ether, and filtered through a Celite plug. The filter cake was rinsed with ether. The combined filtrates were concentrated in vacuo and the residue was chromatographed on silica gel (hexane/ethyl acetate=3:1) to give 4-diallylethoxysilyl-4′-methoxybiphenyl (134 mg, 89%).

4.3.9. Migita–Kosugi–Stille coupling of 2c with 2-bromopyridine giving 2-[4-(diallylethoxysilyl)phenyl]pyridine (Table 1, entry 9). A mixture of 74.8 mg (0.473 mmol) of 2-bromopyridine, 205 mg (0.521 mmol) of **2c**, 31.9 mg (0.0276 mmol) of $Pd(PPh_3)_4$, 64.6 mg (1.52 mmol) of LiCl, and toluene (3 mL) was refluxed for 1 h, diluted with diethyl ether, and treated successively with water. The reaction mixture was extracted with Et_2O, washed with water, saturated aqueous $NaHCO_3$, and aqueous sodium chloride. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give the desired 2-[4-(diallylethoxysilyl)phenyl]pyridine (73.5 mg, 50%) with (diallylethoxysilyl)benzene (7.9 mg, 7%) and 4,4′-bis(diallylethoxysilyl)biphenyl (10.9 mg, 1%) as byproducts.

4.3.10. Wittig olefination of 3a with methyltriphenylphosphonium iodide giving 4-(diallylethoxysilyl)styrene (Table 1, entry 10). To a mixture of $PPh_3Me^+I^-$ (970 mg, 2.4 mmol) and KO*t*-Bu (269 mg, 2.4 mmol) was added toluene (15 mL). The reaction mixture was stirred at 80 °C for 2 h. To the reaction mixture was added a solution of 4-(diallylethoxysilyl)benzaldehyde (250 mg, 0.96 mmol) in toluene (5 mL) at 50 °C. The reaction mixture was stirred at 50 °C for 12 h. The reaction mixture was then quenched with H_2O and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give 4-(diallylethoxysilyl)styrene (233.2 mg, 94%): ^1H NMR ($CDCl_3$) δ 1.20 (t, J=7.0 Hz, 3H), 1.93 (ddd, J=8.1 Hz, 1.4 Hz, 1.1 Hz, 4H), 3.76 (q, J=7.0 Hz, 2H), 4.90 (ddt, J=10.3 Hz, 1.6 Hz, 1.1 Hz, 2H), 4.96 (ddt, J=16.2 Hz, 1.6 Hz, 1.4 Hz, 2H), 5.27 (dd, J=11.1 Hz, 0.8 Hz, 1H), 5.79 (dd, J=17.8 Hz, 0.8 Hz, 1H), 5.82 (ddt, J=16.2 Hz, 10.3 Hz, 8.1 Hz, 2H), 6.73 (dd, J=17.8 Hz, 11.1 Hz, 1H), 7.41 (d, J=8.1 Hz, 2H), 7.54 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.36, 21.21, 59.25, 114.55, 114.75, 125.54, 133.05, 134.27, 134.62, 136.72, 138.81. HRMS (FAB$^+$) $[M+H]^+$ calcd for $C_{16}H_{23}OSi$ 259.1518, found 259.1512.

4.3.11. Buchwald–Hartwig amination of 3b with 4-iodotoluene giving *N*-[4-(diallylethoxysilyl)phenyl](4-methylphenyl)amine (Table 1, entry 11). To a mixture of 4-(diallylethoxysilyl)aniline (254 mg, 1.0 mmol), $Pd_2(dba)_3$ (4.3 mg, 0.0047 mmol), 4-iodotoluene (204 mg, 0.94 mmol), (*o*-biphenyl)P(*t*-Bu)$_2$ (8.4 mg, 0.028 mmol), and NaO*t*-Bu (135 mg, 1.4 mmol) was added toluene (7 mL). The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under vacuum to give a residue. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give *N*-[4-(diallylethoxysilyl)phenyl](4-methylphenyl)amine (242 mg, 77%): ^1H NMR ($CDCl_3$) δ 1.20 (t, J=6.8 Hz, 3H), 1.91 (d, J=8.1 Hz, 4H), 2.32 (s, 3H), 3.95 (q, J=6.8 Hz, 2H), 4.90 (dd, J=10.0 Hz, 1.1 Hz, 2H), 4.96 (dd, J=16.5 Hz, 1.1 Hz, 2H), 5.70 (br, 1H), 5.85 (ddt, J=16.5 Hz, 10.0 Hz, 8.1 Hz, 2H), 6.98 (d, J=8.4 Hz, 2H), 7.04 (d, J=8.6 Hz, 2H), 7.11 (d, J=8.6 Hz, 2H), 7.43 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.40, 20.72, 21.37, 59.11, 114.47, 115.13, 119.95, 124.58, 129.85, 131.71, 133.50, 135.37, 139.21, 145.68. HRMS (EI$^+$) M$^+$ calcd for $C_{21}H_{27}ONSi$ 337.1862, found 337.1863.

4.4. Preparation of functional sol–gel precursors with molecular building blocks

4.4.1. (*S*)-5,5′-Bis[4-(diallylethoxysilyl)phenylethynyl]-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl 4a. To a solution of (*S*)-5,5′-bis(trimethylsilylethynyl)-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl (301 mg, 0.355 mmol) in dichloromethane (12 mL) was added tetrabutylammonium fluoride (0.78 mL, 0.781 mmol) and the mixture was stirred at room temperature for 2 h. Solvent was removed under reduced pressure and the residue was chromatographed on silica gel (hexane/EtOAc=1:3) to give 218.4 mg (88%) of (*S*)-5,5′-diethynyl-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl: ^1H NMR ($CDCl_3$) δ 3.46 (s, 2H), 6.74–6.66 (m, 4H), 7.43–7.21 (m, 16H), 7.60–7.49 (m, 4H), 7.74–7.66 (m, 4H), 8.43–8.39 (dd, J=8.6 Hz, 2.4 Hz, 2H); ^{31}P NMR ($CDCl_3$) δ 28.48. To a solution of 4-(diallylethoxysilyl)iodobenzene (211.1 mg, 0.589 mmol), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol), and CuI (4.8 mg, 0.025 mmol) in benzene (1 mL) was added (*S*)-5,5′-diethynyl-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl (166.8 mg, 0.237 mmol) in benzene (8 mL) and the mixture was stirred at 50 °C for 23 h. Solvent was removed under reduced pressure and the residue was chromatographed on silica gel (hexane/EtOAc=1:1) to give 201.2 mg (71%) of (*S*)-5,5′-bis[4-(diallylethoxysilyl)phenylethynyl]-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl: $[\alpha]_D^{20}$ −225 (*c* 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.24 (t, J=6.8 Hz, 6H), 1.97 (d, J=8.1 Hz, 8H), 3.80 (q, J=6.8 Hz, 4H), 4.93–5.01 (m, 8H), 5.76–5.89 (m, 4H), 6.73 (d, J=4.3 Hz, 4H), 7.25–7.45 (m, 16H), 7.52–7.62 (m, 12H), 7.70–7.78 (m, 4H), 8.53–8.49 (dd, J=8.6, 2.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.38 (OCH_2CH_3), 21.11 (CH_2–CH=CH_2), 59.37 (OCH_2CH_3), 88.25, 94.57 (ethynyl *C*); ^{31}P NMR ($CDCl_3$) δ 28.68. HRMS (FAB$^+$) $[M+H]^+$ calcd for $C_{76}H_{69}O_4Si_2P_2$ 1163.4210, found 1163.4209.

4.4.2. *N*,*N*′-Bis[4-(diallylethoxysilyl)phenyl]benzidine 4b. To a mixture of 4-(diallylethoxysilyl)aniline (505 mg, 2.0 mmol) and 4,4′-diiodobiphenyl (378 mg, 0.94 mmol), $Pd_2(dba)_3$ (25 mg, 0.027 mmol), (*o*-biphenyl)P(*t*-Bu)$_2$ (49.5 mg, 0.17 mmol), and NaO*t*-Bu (267 mg, 2.8 mmol) was added toluene (7 mL). The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=3:1 as eluent) to give *N*,*N*′-bis[4-(diallylethoxysilyl)phenyl]benzidine (430 mg, 72%): ^1H NMR ($CDCl_3$) δ 1.21 (t, J=7.0 Hz, 6H), 1.93 (d, J=8.1 Hz, 8H), 3.76 (q, J=7.0 Hz, 4H), 4.89–5.00 (m, 8H), 5.78–5.94 (m, 6H), 7.08 (d, J=8.6 Hz, 4H), 7.17 (d, J=8.6 Hz, 4H), 7.48 (d, *J*=8.6 Hz, 4H), 7.50 (d, *J*=8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 18.41, 21.37, 59.17, 114.57, 116.0, 119.11, 125.54, 127.38, 133.43, 134.16, 135.42, 140.93, 144.77. HRMS (FAB^+) M^+ calcd for $C_{40}H_{48}O_2N_2Si_2$ 644.3254, found 644.3246.

4.4.3. Bis[4-[4-(diallylethoxysilyl)phenylethynyl]phenyl]-acetylene 4c. To a mixture of **1b** (75.7 mg, 0.21 mmol), $PdCl_2(PPh_3)_2$ (2.97 mg, 0.0042 mmol), CuI (0.8 mg, 0.0042 mmol), and 4,4′-(diethynylphenyl)acetylene (34.5 mg, 0.15 mmol) were added THF (5 mL) and Et_3N (1 mL). The reaction mixture was stirred at 50 °C for 15 h. The reaction mixture was diluted with Et_2O and then the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=10:1 as eluent) to give bis[4-[4-(diallylethoxysilyl)phenylethynyl]phenyl]-acetylene (68.1 mg, 94%): ^{1}H NMR ($CDCl_3$) δ 1.23 (t, *J*=7.0 Hz, 6H), 1.95 (d, *J*=8.1 Hz, 8H), 3.79 (q, *J*=7.0 Hz, 4H), 4.91–4.99 (m, 8H), 5.82 (ddt, *J*=16.2 Hz, 9.7 Hz, 8.1 Hz, 4H), 7.52 (s, 8H), 7.53 (d, *J*=8.1 Hz, 4H), 7.58 (d, *J*=8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 18.38, 21.11, 59.37, 89.96, 90.98, 91.33, 114.96, 122.89, 123.19, 124.27, 130.72, 131.54, 131.59, 132.81, 133.94, 135.85. HRMS (FAB^+) $[M+H]^+$ calcd for $C_{46}H_{47}O_2Si_2$ 687.3115, found 687.3105. Anal. Calcd for $C_{46}H_{46}O_2Si_2$: C, 80.42; H, 6.75. Found: C, 80.02; H, 6.31.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.011.

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