

Selected Paper

Synthesis of Biaryls and Oligoarenes Using Aryl[2-(hydroxymethyl)phenyl]dimethylsilanes

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Through intramolecular activation, highly stable aryl[2-(hydroxymethyl)phenyl]dimethylsilanes can selectively transfer their aryl groups to effect a cross-coupling reaction with various aryl bromides and chlorides in the presence of a weak non-fluoride base and a palladium/copper catalyst. This reaction tolerates a wide range of functional groups, producing the corresponding functionalized biaryls in high yields with excellent chemoselectivity. Newly disclosed reaction conditions allow the recovery of a cyclic silyl ether in modest-to-good yields and reuse for the synthesis of the arylsilanes. The introduction of two isopropyl groups on the silicon center instead of methyl groups improves the stability and allows quantitative recovery of the silicon residue. Finally, aryl halides having an *O*-protected [2-(hydroxymethyl)phenyl]dimethylsilyl group cross-couple with the arylsilane reagents to give silyl-functionalized biaryls. Upon deprotection, the biaryls further react with the silylated electrophiles. The iterative cross-coupling–deprotection sequences allow rapid assembly of silylated oligoarenes. Syntheses of di- and trisilyloligoarenes are also achieved by use of orthogonal *O*-protecting groups.

Biaryls are ubiquitous in natural products, pharmaceuticals, and materials. Metal-catalyzed cross-coupling reactions[1] of arylmetals with aryl halides or pseudo halides have been established as a standard protocol to access the biaryl structure in a regiochemically well-defined manner.[2] Significant efforts have been made to improve the efficiency of the catalysis by thoroughly investigating late-transition metal catalysts and ligands over the last forty years. Consequently, a number of reliable methods based on the development of catalyst systems with high turnover numbers are now available. Some such protocols have been commercialized successfully even on an industrial scale.[3]

Various arylmetals have also been examined to establish a highly chemoselective protocol for biaryl synthesis. Of various types of arylmetal reagents, arylsilanes have many advantages over other aryl nucleophiles such as ready availability based on the rich abundance of silicon, inherent stability derived from less polarized C–Si bonds, and non-toxicity of organosilicon compounds. Initial studies on the cross-coupling reaction using arylsilane reagents involved aryl(halo)silanes that are activated by strong nucleophiles such as fluoride[4] and hydroxide[5] to form pentacoordinate arylsilicates to undergo transmetalation with palladium(II) species generated upon the oxidative addition of aryl electrophiles to palladium(0). More recently, aryl(trialkoxy)silanes have been frequently employed in the presence of the fluoride and alkoxide activators.[6] However, these conventional arylsilane reagents suffer from the kinetic instability of heteroatom–Si bonds toward moisture, bases, and/or acids and poor chemoselectivity of the reaction conditions caused by the strong nucleophilic activators. Arylsilanolates have emerged as a convenient and mild arylating agent for silicon-based biaryl synthesis with high chemoselectivity.[7] While the use of arylsilanols first allowed the use of Cs_2CO_3 as a mild base activator,[8] silanolates have further eliminated the need for the external base, thus suppressing both the undesirable dehydration of silanols to form siloxanes and protodesilylation caused possibly by the conjugate acid derived from the base. It has also been suggested that the transmetalation of silanolates to palladium(II) proceeds through palladium silanolates as a key intermediate, which undergoes intramolecular transmetalation in a manner similar to and/or different from the pentacoordinate silicates.[9]

The use of aryl(triorgano)silanes is another promising strategy to establish a practically useful silicon-based protocol for biaryl synthesis. We initially developed aryl(triallyl)silanes as a stable tetraorganosilane reagent for the cross-coupling reaction.[10] The reagents serve as "masked aryl(fluoro)silanes or arylsilanols" to form aryl(fluoro)silanes or arylsilanols in situ through deallylation upon a treatment with fluoride and react with a range of aryl bromides or chlorides in the presence of a palladium catalyst. To further establish fluoride-free silicon-based cross-coupling reactions using tetraorganosilanes, we have developed alkenyl- and aryl[2-(hydroxymethyl)phenyl]-dimethylsilanes **1** designed on the basis of the related allyl- and benzylsilane reagents for carbonyl addition[11] and the seminal

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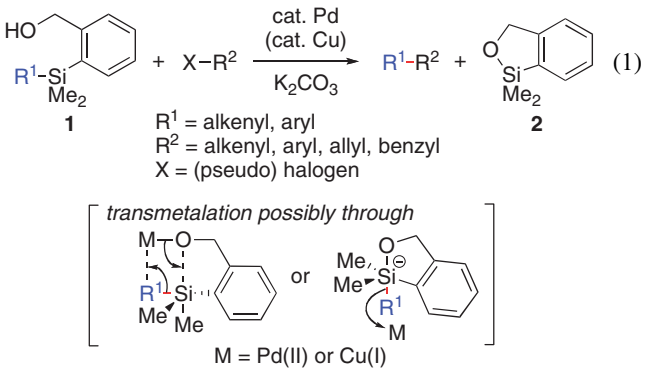
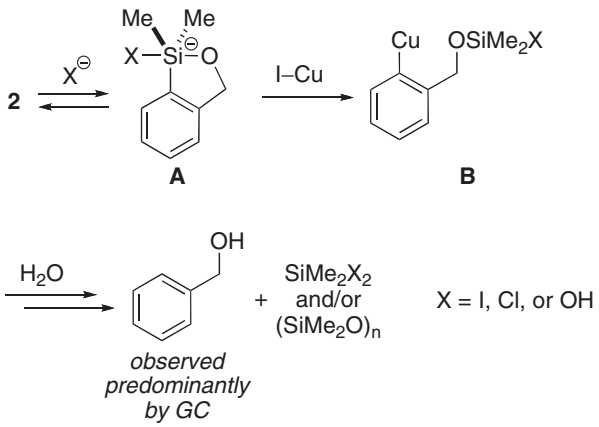
observations that proximal hydroxy groups promote the transmetalation of tetraorganosilicon compounds to copper(I)[12] and palladium(II) (eq 1).[13] The tetraorganosilicon reagents participate in the palladium-catalyzed cross-coupling reaction in the presence of K_2CO_3 as a mild and inexpensive base promoter to allow high chemoselectivity.[14] Transmetalation of **1** is supposed to proceed through pentacoordinate silicates[15] that deliver an axial or equatorial organic group on silicon to the transition metal center intramolecularly. Resulting cyclic silyl ether **2** can be readily recovered by distillation and reused for the synthesis of the silicon reagent. The ready reusability of the metal residue in such transition metal-catalyzed reactions of main group organometallic reagents has never been addressed and should be an important and advantageous feature of this protocol, especially when it is applied to an industrial-scale synthesis.

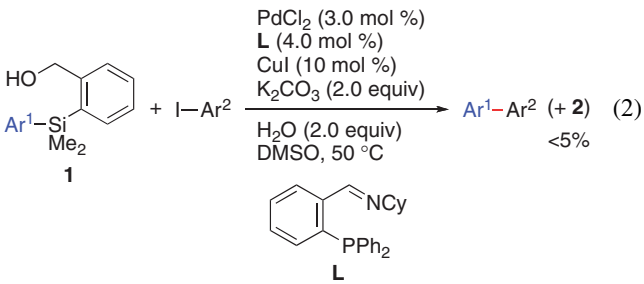


Aryl[2-(hydroxymethyl)phenyl]dimethylsilanes cross-couple with aryl iodides in the presence of palladium and copper catalysts (eq 2).[14a,14b] However, the initial conditions led to poor recovery of **2**, and benzyl alcohol was detected as a plausible fate of **2**. It seems that cyclic silyl ether **2** is further coordinated by a hydroxide, iodide, or chloride ion under the reaction conditions to form pentacoordinate silicate **A**. Formation of 2-(siloxymethyl)phenylcopper species **B** is evident through transmetalation of **A** with copper, and protonolysis of **B** finally produces benzyl alcohol (Scheme 1). We disclose herein modified reaction conditions and reagent design for the cross-coupling reaction of the 2-(hydroxymethyl)phenyl-substituted arylsilanes with aryl bromides and chlorides to give both biaryls and reusable silicon residue **2** in high yields. In



Scheme 1. Possible fate of **2** under the reaction conditions.

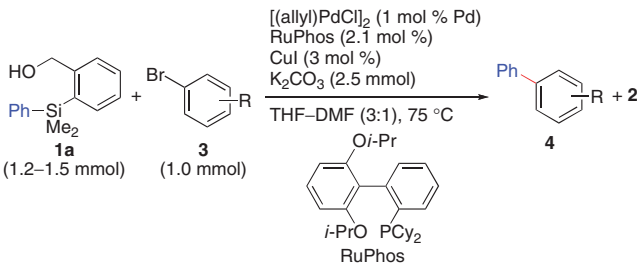
addition, we demonstrate that the reactivity of the C–Si bond of the arylsilane reagents can be switched off simply by protecting the hydroxy group and that aryl halides having the "off-positioned" silyl group serve as an electrophile for the biaryl synthesis. Deprotection then turns the switch "on" to allow the second cross-coupling reaction, and iterative operations of cross-coupling and deprotection allow silicon-based rapid assembly of oligoarenes with a silyl terminus.[16] Such reagent designs with a reversible switch of reactivity have only been available recently with organoborane reagents[17] and have never been demonstrated with other metal reagents.

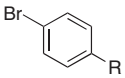
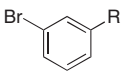
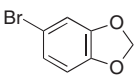
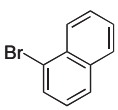
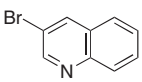
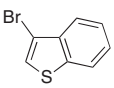


Results and Discussion

Biaryl Synthesis through Cross-Coupling Reaction of 1 with Aryl Bromides and Chlorides. The main objective of our research plan is to optimize the reaction conditions for the cross-coupling of arylsilanes **1** with aryl halides under fluoride-free conditions and to recover cyclic silyl ether **2** in good yield. Furthermore, reuse of **2** in the synthesis of starting arylsilanes would testify the atom-economical cross-coupling process. At the onset, the cross-coupling reaction of [2-(hydroxymethyl)-phenyl](dimethyl)phenylsilane (**1a**) with unactivated 4-bromoanisole (**3a**) with a catalyst system including $PdCl_2$ (5.0 mol %), the iminophosphine ligand (**L**, 5.0 mol %), CuI (10 mol %), K_2CO_3 (2.0 equiv), and H_2O (2.0 equiv) in DMSO at 80 °C for 22 h was examined to provide desired 4-methoxybiphenyl (**4aa**) in 21% yield as estimated by GC analysis; the presence of unreacted **3a** and formation of benzyl alcohol from **1a** were also observed. These observations clearly reveal that cyclic silyl ether **2** is not stable under the above conditions. We speculated that the nature and the amount of copper salts, bases, solvents, water, and reaction temperature determined the stability of the cyclic silyl ether **2** under the reaction conditions. With these factors in mind, an extensive survey of the reaction parameters in the cross-coupling of **1a** (1.5 mmol) with **3a** (1.0 mmol) has led to an optimum set of conditions including $[(allyl)PdCl]_2$ (1 mol % Pd), RuPhos[18] (2.1 mol %), CuI (3.0 mol %), and K_2CO_3 (2.5 mmol) in THF–DMF (3:1) at 75 °C, giving 4-methoxybiphenyl (**4aa**) in 91% yield after 23 h (Entry 1 of Table 1). It is worth noting that cyclic silyl ether **2** mostly tolerates these reaction conditions; the yield was estimated to be 72% on the basis of GC analysis. Among palladium catalysts including $PdCl_2$, $PdBr_2$, $Pd(OAc)_2$, $[(allyl)PdCl]_2$, and $Pd_2(dba)_3$ screened under the above conditions, $[(allyl)PdCl]_2$ turned out to be superior. Exploration of various electron-donating and bulky phosphine ligands such as RuPhos, related dialkyl(biaryl)phosphines, and PCy_3 revealed that RuPhos in combination with $[(allyl)PdCl]_2$ and K_2CO_3 was found to be effective. With the optimized palladium catalyst set

Table 1. Phenylation of Aryl Bromides with **1a**



Entry	3	Time /h	Yield of **4**/%[a]	Yield of **2**/%[b]
				
1	R = OMe (**3a**)	23	91 (**4aa**)	72
2	Me (**3b**)	19	86 (**4ab**)	71
3	$SnBu_3$ (**3c**)	10	88 (**4ac**)	>95
4[c]	B(pin) (**3d**)[d]	11	81 (**4ad**)	66
5	F (**3e**)	25	85 (**4ae**)	76
6	Cl (**3f**)	21	85 (**4af**)	76
7	CO_2Et (**3g**)	10	81 (**4ag**)	79
8	CHO (**3h**)	9	91 (**4ah**)	82
9	Ac (**3i**)	21	87 (**4ai**)	88
10	CN (**3j**)	9	92 (**4aj**)	81
11	NO_2 (**3k**)	21	97 (**4ak**)	70
12	CF_3 (**3l**)	12	91 (**4al**)	84
				
13	R = NH_2 (**3m**)	22	95 (**4am**)	77
14	CH_2OH (**3n**)	22	92 (**4an**)	68
15	CH_2OSiMe_2t-Bu (**3o**)	26	75 (**4ao**)	75
16[e]	Me (**3p**)	14	87 (**4ap**)	91[f]
17	 **3q**	21	88 (**4aq**)	91
18	 **3r**	22	88 (**4ar**)	>95
19	 **3s**	22	65 (**4as**)	53
20	 **3t**	21	97 (**4at**)	92
21	 **3u**	11	88 (**4au**)	90
22	 **3v**	22	83 (**4av**)	70

a) Isolated yields based on **3**. b) Estimated by GC based on **1a** using nonane as an internal standard. c) Treatment of **1a** with *n*-BuLi (both 1.5 mmol) at −78 °C to rt was followed by the reaction with **3d** in the absence of K_2CO_3. d) B(pin) = 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl). e) Run on a 20-mmol scale. f) Isolated yield based on **1a** (ca. 90% purity).

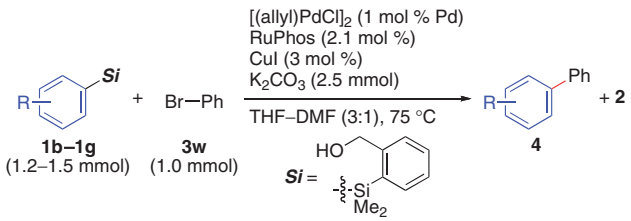
and the base in hand, effects of copper salts and solvents were surveyed. Of various copper salts used, CuI was found to be the best. The absence of the copper co-catalyst gave lower yield of the biaryl, suggesting an arylcopper species seems to be a major arylating agent under the modified reaction conditions.[14] The yield of **2** was improved when a small amount of CuI and less polar solvents such as THF and 1,4-dioxane in the absence of water were utilized in the reaction. Although the absence of water in the reaction suppresses the decomposition of **2** to benzyl alcohol, the yield of **4aa** dropped drastically. To avoid the use of water, solvents consisting of a mixture of highly polar aprotic and less polar aprotic solvents were investigated. Various combinations of mixed solvents from DMSO, DMF, THF, and 1,4-dioxane in different ratios showed that THF–DMF (3:1) was highly effective.

Bromobenzenes with a variety of substituents underwent the cross-coupling reaction with **1a** (Entries 2–18). It is worth noting that the C–Si bond in **1a** is exclusively activated over the C–Sn bond in **3c** (Entry 3), which has been believed to be considerably more reactive than C–Si bonds, although the *para*-bromo group may reduce the reactivity of the particular C–Sn bond. The C–B bond in **3d** also remained intact when the silicon reagent was pretreated with BuLi as a base to form lithium alkoxide, and the coupling reaction was performed in the absence of K_2CO_3 (Entry 4). The original conditions using K_2CO_3 as a base gave fair amounts of a polymeric insoluble material, which might be derived from competitive reactions of the C–B bond. Various electron-withdrawing functional groups including carbonyls, cyano, and nitro were also tolerated (Entries 5–12). K_2CO_3 as a mild base activator allows the use of aryl bromides having not only free amino and hydroxy groups but also a silyl protecting group, which does not survive under the conventional fluoride activation (Entries 13–15). The reaction can be performed on a gram-scale; the reusable silicon residue was isolated in good yields by the simple distillation of the crude products (ex. Entry 16). Several heteroaryl bromides also participated in the phenylation reaction in good yields (Entries 19–22).

In a manner similar to the reaction of phenylsilane **1a**, arylsilanes **1b**–**1g** underwent the cross-coupling reaction with bromobenzene (**3w**) in good to excellent yields (Table 2), regardless of the electronic nature of their substituents (Entries 1–3). Highly sterically demanding mesitylsilane **1f** gave the coupling product **4fw** in good yield (Entry 5). The cross-coupling of 2-thienylsilane **1g** proceeded successfully in the presence of $PdCl_2(dppf)\cdot CH_2Cl_2$ as a catalyst instead of the [(allyl)PdCl]$_2$/RuPhos system (Entry 6). The use of the Pd/RuPhos system gave **4au** in a lower yield with complete conversion of **1g**. The less electron-donating nature of DPPF might be beneficial for transmetalation with this particular silicon reagent that would be rather labile under the reaction conditions compared with substituted phenylsilanes.

Although we have established highly general reaction conditions to obtain biaryls in high yields, the recovery of cyclic silyl ether **2** is not always satisfactory. Indeed, we observed benzyl alcohol in significant amounts as detected by GC and ^{1}H NMR when the yield of **2** was modest (ex. Entries 14 and 19 of Table 1). In order to improve the stability of **2** under the reaction conditions, we designed a silicon reagent **1′a**

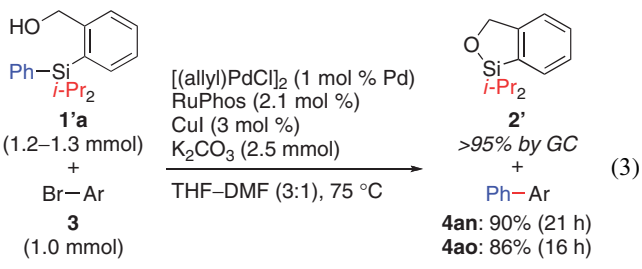
Table 2. Arylation of Bromobenzene (**3w**)

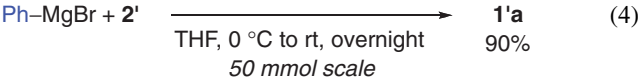


Entry	1	Time /h	Yield of **4**/%[a]	Yield of **2**/%[b]
1	R = Me (**1b**)	22	88 (**4ab**)	76
2	F (**1c**)	25	95 (**4ae**)	54
3	CN (**1d**)	22	97 (**4aj**)	46
4	**1e**	14	85 (**4ew**)	82
5[c),d)]	**1f**	7	85 (**4fw**)	94
6[d),e)]	**1g**	4	91 (**4au**)	92

a) Isolated yields based on **3w**. b) Estimated by GC based on **1** using nonane as an internal standard. c) Run with 1 mol % of CuI. d) Run with K_2CO_3 ground and dried at 120 °C overnight. e) $PdCl_2(dppf)\cdot CH_2Cl_2$ (1 mol %) as a catalyst.

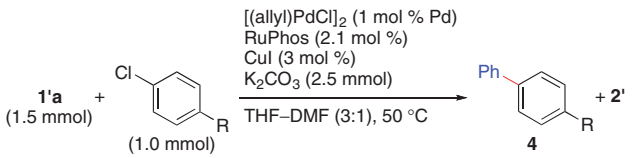
having two bulkier *i*-Pr groups in place of two Me groups on silicon to suppress the decomposition of the silicon residue by steric hindrance (eq 3). As demonstrated in eq 3, the reactions of **1′a** with several aryl bromides proceeded equally well, and both cyclic silyl ether **2′** and biaryls **4** were obtained in good to excellent yields. Treatment of **2′** with phenylmagnesium bromide gave **1′a** in 90% yield, demonstrating that the modified silicon residue is also reusable for regeneration of the arylsilane reagents (eq 4).





Having had the silicon reagents cross-couple with aryl bromides giving both biaryls and reusable silicon residue **2′** in good yields, we briefly examined the cross-coupling reaction with aryl chlorides, which are less expensive and more easily

Table 3. Phenylation of Aryl Chlorides with **1′a**



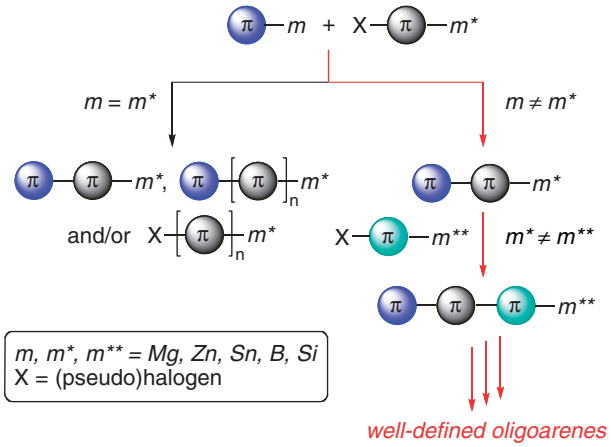
Entry	R in Cl–Ar	Time /h	Yield of **4**/%[a]	Yield of **2′**/%[b]
1	OMe	23	41 (**4aa**)[c]	>95
2	Me	48	70 (**4ab**)[c]	>95
3	CO_2Et	15	96 (**4ag**)	>95
4	CHO	42	94 (**4ah**)	86[d]
5	Ac	29	95 (**4ai**)	>95
6	NO_2	18	90 (**4ak**)	>95

a) Isolated yields based on the aryl chloride. b) Estimated by GC based on **1′a** using nonane as an internal standard. c) Estimated by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. d) Isolated yield based on **1′a**.

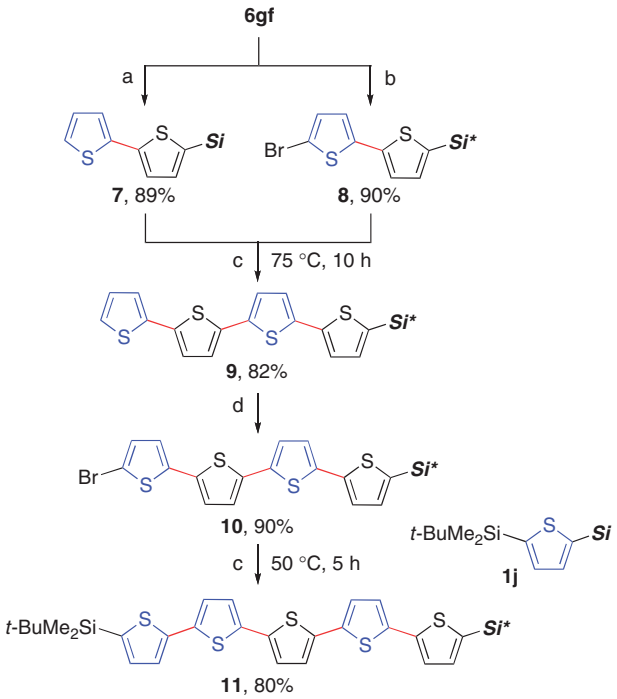
available aryl electrophiles (Table 3). While the reactions of **1′a** with electron-rich aryl chlorides under conditions similar to those for aryl bromides produced the biaryls less efficiently (Entries 1 and 2), electron-deficient substrates successfully cross-coupled with **1′a** to afford the corresponding biaryls and **2′** in good to excellent yields (Entries 3–6). The reactions performed at 75 °C showed some decomposition of cyclic silyl ether **2′**.

Oligoarene Synthesis through Iterative Cross-Coupling Reaction of 1 with Silylated Aryl Bromides. We next turned our attention to applications of the present biaryl synthesis to the efficient synthesis of oligoarenes. As briefly mentioned in the introduction, biaryls constitute an important structural element in photonic and optoelectronic materials such as organic light-emitting diodes, field-effect transistors, semiconductors, and fluorescent sensors. However, extension of biaryls to oligoarenes is essential in order to understand electronic properties of functional π-materials and assemble organic electronic materials which absorb and emit visible light at longer wavelengths.[19] Unlike simple biaryl synthesis, the assembly of oligoarenes requires the installation of a leaving group or a metallic center at terminal arenes to further extend the oligoarene structures. These additional operations make the entire sequence leading to the desired oligoarenes tedious multi-step procedures. An iterative cross-coupling strategy using metalated organic halides would streamline the synthesis of oligoarenes with well-defined structures (Scheme 2). Nevertheless, it is difficult to control their reaction modes (cross-coupling vs. homo-coupling, etc.) without the precise discrimination between the metallic moieties.[20,21]

We envisaged that our arylsilane reagents could serve as a useful building block for the iterative cross-coupling scheme. Because the enhanced reactivity of the silicon reagents is "turned off" simply upon the protection of the hydroxy group, reactive and unreactive silyl groups can be readily discriminated. Moreover, use of various types of *O*-protecting groups allows differentiation of several types of unreactive silyl groups by the independent deprotection of carefully chosen orthogonal protecting groups.

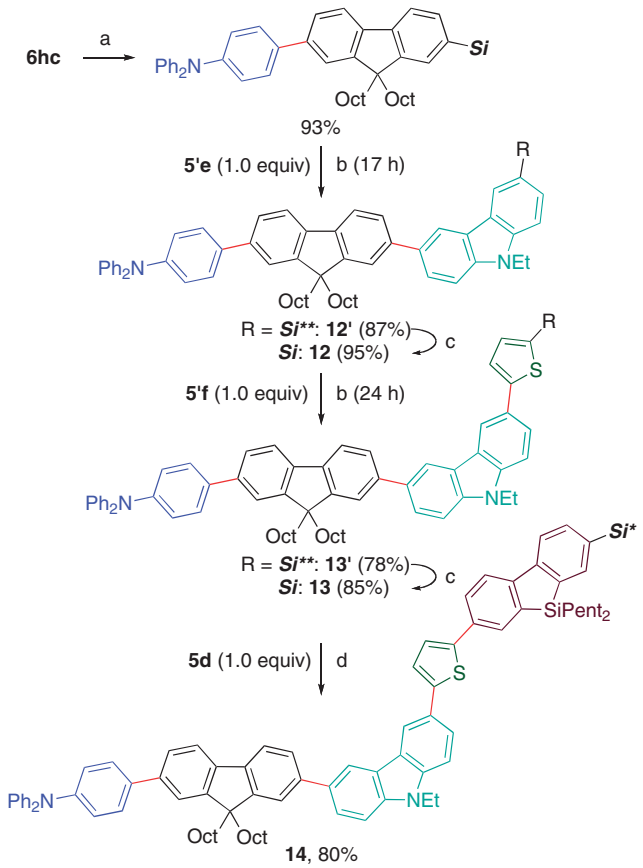


Scheme 2. Cross-coupling with metalated electrophiles.



Scheme 3. Convergent synthesis of disilylated quinquethiophene. Reagents and conditions: (a) PPTS (20 mol %), MeOH, 40 °C, 2 h; (b) *n*-BuLi, TMEDA, THF, −40 °C to rt, 1 h, then $BrCF_2CF_2Br$, −40 °C, 1 h; (c) $PdCl_2$(dppf)·CH_2Cl_2 (3 or 5 mol %), CuI (9 or 5 mol %), K_2CO_3 (2.5 equiv), THF–DMF; (d) *n*-BuLi, TMEDA, THF, −78 °C, 5 min, then $BrCF_2CF_2Br$, −40 °C, 1 h.

Therefore, we prepared aryl bromides bearing an *O*-protected silyl group **5a**–**5f** starting simply from the corresponding dibromides and examined their coupling reaction with the arylsilanes (Table 4). The reaction conditions developed for the biaryl synthesis worked perfectly well to give a wide variety of π-conjugated molecules having phenyl, phenylethenyl, fluorenyl, sila-fluorenyl, carbazolyl, and thienyl motifs with the silyl group at their terminal arenes in good yields (Entries 1–11). Both THP and acetyl protections tolerated these reaction conditions. Gram-scale synthesis (Entries 1, 4, and 11) is used to allow an easy isolation of

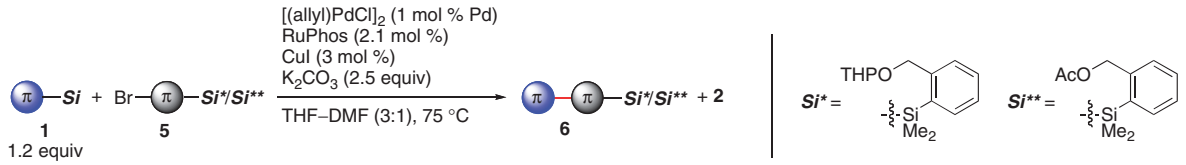


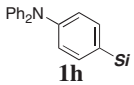
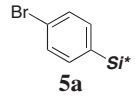
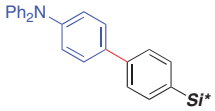
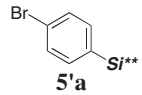
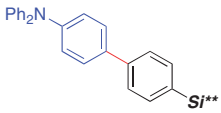
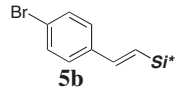
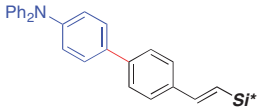
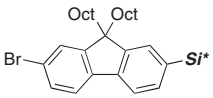
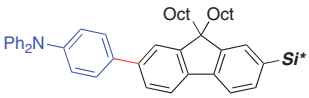
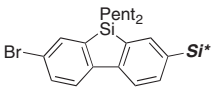
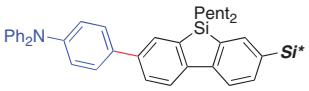
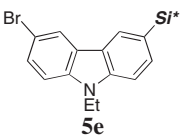
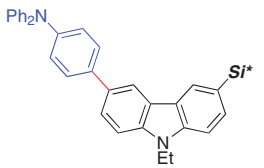
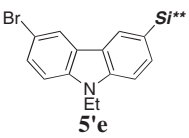
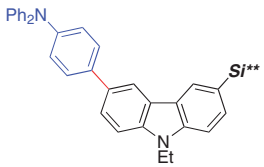
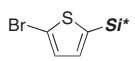
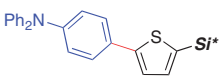
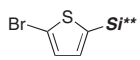
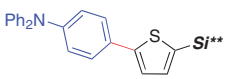
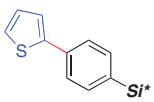
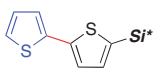
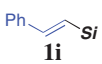
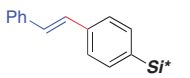
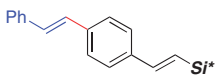
Scheme 4. Linear synthesis of oligoarenylsilane. Reagents and conditions: (a) TsOH·H_2O (2 mol %), MeOH–CH_2Cl_2 (1:1), rt, overnight; (b) [(allyl)PdCl]$_2$ (1 or 5 mol % Pd), RuPhos (2 or 11 mol %), CuI (3 or 5 mol %), K_2CO_3 (2.5 equiv), THF–DMF, 75 °C; (c) DIBAL–H (1.1 equiv), CH_2Cl_2, −78 °C, 2 h; (d) $PdCl_2$(dppf)·CH_2Cl_2 (5 mol %), CuI (5 mol %), K_2CO_3 (2.5 equiv), THF–DMF, 75 °C, 24 h.

silicon residue **2** in good yield (Entry 1). (*E*)-Styrylsilane **1i** participates in the coupling reaction in the absence of CuI to give (*E*)-phenylenevinylene substructures (Entries 12 and 13).

The deprotection and subsequent cross-coupling reaction of the silylated biaryls thus obtained proceeded successfully (Schemes 3 and 4). For example, the deprotection of **6gf** under acidic conditions gave silylbithiophene **7** with a free hydroxy group in 89% yield, whereas lithiation of **6gf** with *n*-BuLi followed by bromination with 1,2-dibromo-1,1,2,2-tetrafluoroethane gave 5-bromo-5′-silyl-2,2′-bithiophene **8** in 90% yield (Scheme 3). The observed high stability of silylated bithiophenes **7** and **8** under the acidic and basic transformations is remarkable. The coupling reaction of **7** and **8** proceeds successfully to give silylated quaterthiophene **9** that was subjected to bromination leading to **10** followed by a subsequent cross-coupling with 2,5-disilyl-substituted thiophene **1j** to give unsymmetrically disilylated quinquethiophene **11**, which would enjoy potential application to two-photon absorption materials.[22] In addition, silylated biaryls could be transformed to linear silylated oligoarenes. Thus, three deprotection–cross-coupling sequences starting with **6hc** led to π-conjugated protected oligoarenylsilane **14** in an efficient manner (Scheme 4).

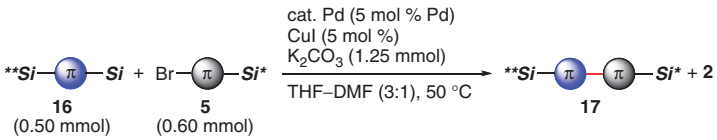
Table 4. Synthesis of Silylated Arenes[a)]

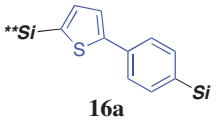
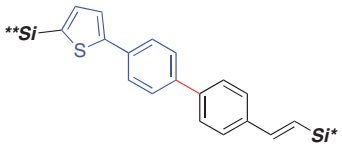
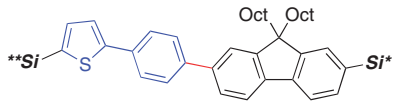
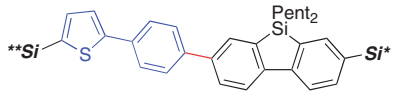
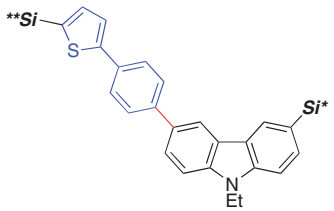
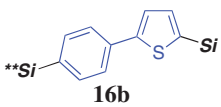
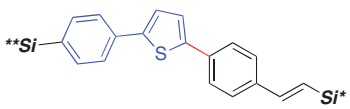
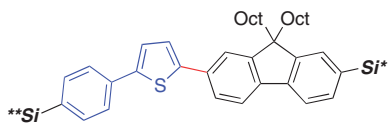
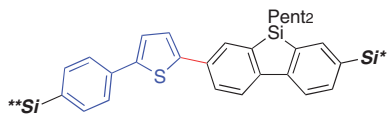
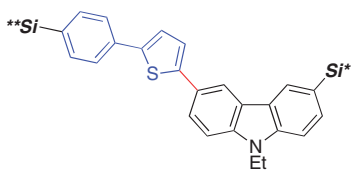


Entry	1	5	Time/h	Product	Yield of **6**/%[b)]
1[c)]	 **1h**	 **5a**	7		88 (**6ha**)[d)]
2	**1h**	 **5'a**	22		93 (**6'ha**)
3	**1h**	 **5b**	17		93 (**6hb**)
4[e)]	**1h** (1.5 equiv)	 **5c**	30		93 (**6hc**)
5[f),g)]	**1h** (1.5 equiv)	 **5d**	24		82 (**6hd**)
6	**1h**	 **5e**	22		85 (**6he**)
7	**1h** (1.5 equiv)	 **5'e**	18		94 (**6'he**)
8[h)]	**1h**	 **5f**	8		81 (**6hf**)
9[h)]	**1h**	 **5'f**	7		81 (**6'hf**)
10[h),i),j)]	**1g**	**5a**	6		96 (**6ga**)
11[e),i)]	**1g**	**5f**	6		96 (**6gf**)
12[k)]	 **1i**	**5a**	7		90 (**6ia**)
13[k)]	**1i**	**5b**	22		90 (**6ib**)

a) Reactions were performed on a 1.0-mmol scale unless otherwise noted. b) Isolated yields based on **5**. c) Run on a 10-mmol scale. d) **2** was isolated in 86% based on conversion of **1h** (88%). e) Run on a 20-mmol scale. f) Run on a 0.10-mmol scale. g) Run with 5 mol % Pd. h) Run with 3 mol % Pd. i) Run with $PdCl_2(dppf)\cdot CH_2Cl_2$ as a catalyst. j) Run at 50 °C. k) Run without CuI.

Table 5. Synthesis of Disilylated Arenes



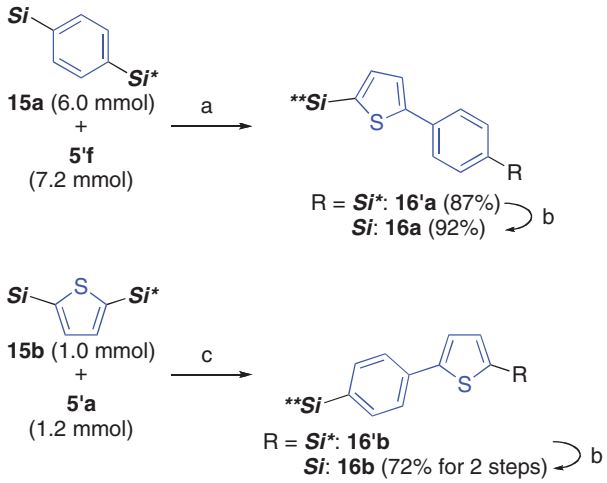
Entry	16	5	Pd cat.	Time/h	Product	Yield of 17/%[a]
1	 **16a**	**5b**	[(allyl)PdCl]$_2$/ RuPhos (10.5 mol %)	7		87 (**17ab**)
2	**16a**	**5c**	[(allyl)PdCl]$_2$/ RuPhos (10.5 mol %)	6		84 (**17ac**)
3	**16a**	**5d**	[(allyl)PdCl]$_2$/ RuPhos (10.5 mol %)	6		86 (**17ad**)
4	**16a**	**5e**	[(allyl)PdCl]$_2$/ RuPhos (10.5 mol %)	6		86 (**17ae**)
5[b]	 **16b**	**5b**	$PdCl_2(dppf)\cdot CH_2Cl_2$	6		82 (**17bb**)
6	**16b**	**5c**	$PdCl_2(dppf)\cdot CH_2Cl_2$	9		80 (**17bc**)
7	**16b**	**5d**	$PdCl_2(dppf)\cdot CH_2Cl_2$	6		82 (**17bd**)
8[b]	**16b**	**5e**	$PdCl_2(dppf)\cdot CH_2Cl_2$	8		81 (**17be**)

a) Isolated yields based on **7**. b) Run with 1 mol % CuI.

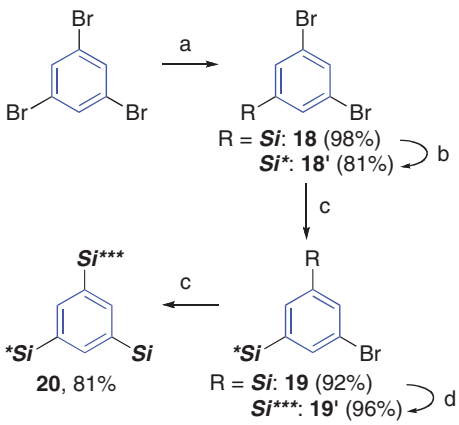
We next targeted oligoarenes bearing two silyl groups with orthogonally *O*-protecting groups (Table 5). This was initiated by the synthesis of disilylated biaryls **16a** and **16b**, which were readily obtained by the cross-coupling reactions of 1,4-disilylated benzene **15a** and 2,5-disilylated thiophene **15b** with **5′f** and **5′a** followed by deprotection, respectively (Scheme 5). Both **16a** and **16b** cross-coupled with silylated aryl bromides **5b**–**5e** in good yields to give a variety of oligoarenes **17** having two differently *O*-protected silyl groups at their terminal arene rings. Furthermore, cross-coupling of oligoarenes having three silyl groups was envisioned by employing a silyl ether as the third type of protection. Trisilylbenzene **20** was prepared first through a sequential silylation of 1,3,5-tribromobenzene followed by *O*-protection (Scheme 6). The cross-coupling of **20** with **5′a** gave **21′** in 70% yield (Scheme 7). The *t*-BuPh_2Si protection in **21′** was exclusively removed by TBAF to give **21** with other silyl and *O*-protecting groups intact, and the subsequent cross-coupling with 2-bromo-5-silylthiophene **5″f** afforded **22′**. Finally, upon treatment of **22′** with an acid catalyst to remove the THP group, resultant **22** underwent the cross-coupling with **5c** to give trisilylated oligoarene **23** with three orthogonal *O*-protecting groups at the respective arene terminus.

Conclusion

In summary, we have demonstrated that 2-(hydroxymethyl)-phenyl-substituted arylsilanes serve as efficient reagents for



Scheme 5. Synthesis of disilylated biaryls **16a** and **16b**. Reagents and conditions: (a) $[(allyl)PdCl]_2$ (3 mol % Pd), RuPhos (6.3 mol %), CuI (9 mol %), K_2CO_3 (2.5 equiv), THF–DMF, 75 °C, 8 h; (b) PPTS (20 mol %), MeOH, 40 °C, 3 or 6 h; (c) $PdCl_2(dppf)\cdot CH_2Cl_2$ (3 mol %), CuI (9 mol %), K_2CO_3 (2.5 equiv), THF–DMF, 75 °C, 6 h.

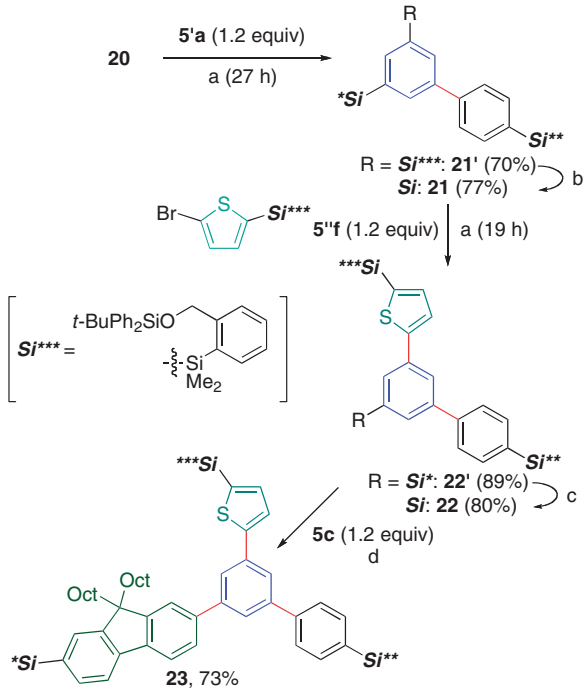


Scheme 6. Synthesis of trisilylated benzene **20**. Reagents and conditions: (a) *n*-BuLi, Et_2O, −78 °C, 2 h, then **2**, −78 °C to rt; (b) 3,4-dihydro-2*H*-pyran, PPTS (10 mol %), CH_2Cl_2, rt, 5 h; (c) **2**, *t*-BuLi, Et_2O, −78 °C to rt, overnight; (d) *t*-$BuPh_2Si$–Cl, imidazole, DMF, rt, 3 h.

palladium/copper-catalyzed biaryl synthesis. Newly developed reaction conditions as well as arylsilane reagents allow a general substrate scope for a silicon-based approach to producing biaryls with excellent chemoselectivity and higher yields of recoverable and reusable cyclic silyl ether. A simple switch of the arylsilane reactivity by *O*-protection is demonstrated to be highly useful and efficient to access a wide variety of silylated oligoarenes. Future studies will focus on the development of more practical protocols for the iterative cross-coupling sequence involving a one-pot deprotection–cross-coupling system as well as applications to solid-phase synthesis.

Experimental

General. All manipulations of oxygen- and moisture-sensitive materials were conducted with Schlenk techniques



Scheme 7. Linear synthesis of trisilylated oligoarene. Reagents and conditions: (a) $[(allyl)PdCl]_2$ (5 mol % Pd), RuPhos (11 mol %), CuI (5 mol %), K_2CO_3 (2.5 equiv), THF–DMF, 50 °C; (b) TBAF (2.0 equiv), THF, rt, 1 h; (c) PPTS (20 mol %), MeOH–THF, rt, overnight; (d) $[(allyl)PdCl]_2$ (10 mol % Pd), RuPhos (10 mol %), CuI (5 mol %), K_2CO_3 (2.5 equiv), THF–DMF, 50 °C, 24 h.

under a nitrogen or argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Varian Mercury 400 (^1H NMR, 400 MHz; ^{13}C NMR 101 MHz) spectrometer with solvent resonance as the internal standard (^1H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. Melting points were determined using a YANAKO MP-500D. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer and are reported in cm^{-1}. Elemental analyses were performed by the Elementary Analysis Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI), JEOL JMS-HX110A (FAB), or Bruker Daltonics Autoflex III (MALDI) spectrometer. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H using chloroform as an eluent. GC analysis was performed on a Shimadzu GC 2014 equipped with an ENV-1 column (Kanto Chemical, 30 m × 0.25 mm, pressure = 31.7 kPa, detector =

FID, 290 °C) with helium gas as a carrier.

Chemicals. Unless otherwise noted, commercially available liquid chemicals were distilled and degassed before use. Solid chemicals were used without purification. Anhydrous THF was purchased from Kanto Chemical and degassed by purging vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[23] Anhydrous DMF was purchased from Nacalai Tesque and used as received. RuPhos was prepared according to the Buchwald protocol.[18] Aryl[2-(hydroxymethyl)phenyl]dimethylsilanes **1**[14] and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bromobenzene (**3d**)[24] were prepared following a reported procedure. All the spectral data of biaryls shown in Tables 1–3 and eq 3 agreed perfectly with those reported previously by ourselves, unless otherwise described below.[10] Data for silylated oligoarenes shown in Table 4, Schemes 3 and 4 have been reported in a previous communication.[16]

Preparation of (4-Bromophenyl)tributylstannane (3c).[25] To a solution of 1,4-dibromobenzene (3.5 g, 15 mmol) in THF (30 mL) was added a 1.6 M solution of *n*-BuLi in hexane (9.4 mL, 15 mmol) over 1 h at −78 °C, and the resulting mixture was stirred at −78 °C for an additional 1 h. Tributylchlorostannane (4.9 g, 15 mmol) was added at −78 °C, and then the resulting mixture was stirred at −78 °C for 1 h. The reaction was quenched with a saturated NH_4Cl aqueous solution, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and then brine, and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (5.6 g, 83%) as a colorless oil, $R_f = 0.69$ (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.42 (m, 2H), 7.38–7.24 (m, 2H), 1.63–1.41 (m, 6H), 1.33 (sext, $J = 7.3$ Hz, 6H), 1.15–0.95 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.6, 137.9, 131.0, 122.7, 29.0, 27.3, 13.7, 9.6.

Preparation of [2-(Hydroxymethyl)phenyl]dimethyl(4-methylphenyl)silane (1b). To a solution of 1,1-dimethyl-2-oxa-1-silaindan (**2**,[14a] 7.5 g, 46 mmol) in THF (180 mL) was added a 0.5 M solution of *p*-tolylmagnesium bromide in diethyl ether (100 mL, 50 mmol) over 30 min at 0 °C. The resulting mixture was stirred at rt overnight. The reaction was quenched with a saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and then brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (9.7 g, 83%) as a colorless solid (mp 55.6–56.5 °C) $R_f = 0.19$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.37 (m, 4H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.32 (td, $J = 7.0$, 2.0 Hz, 1H), 7.18 (dd, $J = 8.1$, 0.5 Hz, 2H), 4.54 (d, $J = 6.0$ Hz, 2H), 2.36 (s, 3H), 1.28 (t, $J = 6.0$ Hz, 1H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 139.0, 136.0, 135.3, 135.1, 133.7, 129.8, 128.8, 128.1, 126.9, 65.3, 21.6, −0.9; IR (KBr): 3285, 3059, 3030, 3009, 2951, 2920, 1599, 1460, 1435, 1408, 1391, 1258, 1248, 1200, 1128, 1105, 1078, 1038, 1018, 826, 797, 775, 756, 745, 716, 689, 660, 602, 500, 490, 430, 407 cm^{-1}; Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86%. Found: C, 75.00; H, 7.93%.

Preparation of 1,1-Diisopropyl-2-oxa-1-silaindan (2′). A 1.6 M *n*-BuLi solution in hexane (12.7 mL, 20 mmol) was added to a solution of 2-(tetrahydro-2*H*-pyran-2-yloxymethyl)-bromobenzene (5.0 g, 18.4 mmol) in THF (3.8 mL) over 5 min at −78 °C, and the resulting solution was stirred for 2 h before the addition of chlorodiisopropylsilane (3.3 g, 22 mmol) at −78 °C. The mixture was allowed to warm to rt overnight before dilution with diethyl ether. The whole was washed with a saturated $NaHCO_3$ aqueous solution, water, and then brine, and the organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was dissolved in MeOH (74 mL), and *p*-toluenesulfonic acid monohydrate (175 mg, 0.92 mmol) was added portionwise at rt. The mixture was stirred overnight before concentration in vacuo. The residue was distilled to give the title compound (4.1 g, 82%) as a colorless oil (bp 75 °C at 3.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, $J = 7.3$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.31–7.21 (m, 2H), 5.15 (s, 2H), 1.25 (sept, $J = 7.3$ Hz, 2H), 1.04 (d, $J = 7.3$ Hz, 6H), 1.01 (d, $J = 7.3$ Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.5, 132.0, 131.6, 129.3, 126.4, 121.4, 72.5, 17.1, 13.2; IR (neat): 2941, 2864, 1464, 1443, 1067, 1049, 880, 781, 746, 716, 667, 642 cm^{-1}; Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%. Found: C, 70.75; H, 8.92%.

Preparation of [2-(Hydroxymethyl)phenyl](diisopropyl)-phenylsilane (1′a). To a solution of **2′** (11.0 g, 50 mmol) in THF (125 mL) was added a 1.07 M solution of phenylmagnesium bromide in THF (51 mL, 55 mmol) over 30 min at 0 °C, and the resulting mixture was stirred at rt overnight. The reaction was quenched with a saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and then brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (13.5 g, 90%) as a colorless solid (mp 119.0–119.6 °C), $R_f = 0.69$ (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.55 (m, 2H), 7.52–7.29 (m, 7H), 4.40 (d, $J = 5.6$ Hz, 2H), 1.67 (sept, $J = 7.2$ Hz, 2H), 1.38 (t, $J = 5.8$ Hz, 1H), 1.00 (d, $J = 7.2$ Hz, 6H), 0.98 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 136.7, 134.9, 134.8, 130.9, 129.6, 129.1, 128.6, 127.7, 126.5, 65.6, 18.0, 17.9, 10.7; IR (KBr): 3364, 2953, 2924, 2889, 2862, 1636, 1462, 1427, 1381, 1364, 1313, 1277, 1234, 1198, 1123, 1105, 1078, 1015, 995, 918, 878, 816, 758, 745, 708, 687, 656, 615, 517, 488, 459 cm^{-1}; Anal. Calcd for $C_{19}H_{26}OSi$: C, 76.45; H, 8.78%. Found: C, 76.24; H, 8.96%.

Cross-Coupling Reaction of 1 with Aryl Bromides. A General Procedure: To a mixture of **1** (1.2–1.5 mmol), K_2CO_3 (0.35 g, 2.5 mmol), $[(allyl)PdCl]_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added an aryl bromide (1.0 mmol), and the resulting mixture was stirred at 75 °C. After the time specified in Tables 1 and 2, the mixture was filtered through a Florisil pad, diluted with diethyl ether, washed with water and then brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding biaryl in a yield listed in Tables 1 and 2. The yield of cyclic silyl ether **2** was determined by GC analysis using nonane as an internal standard.

(Biphenyl-4-yl)tributylstannane (4ac, Entry 3 of Table 1);[26] A colorless oil, $R_f = 0.35$ (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.47 (m, 6H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 1.68–1.46 (m, 6H), 1.35 (sext, $J = 7.3$ Hz, 6H), 1.18–1.00 (m, 6H), 0.91 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.3, 140.9, 140.7, 136.9, 128.7, 127.15, 127.09, 126.6, 29.1, 27.4, 13.7, 9.6.

3-Aminobiphenyl (4am, Entry 13 of Table 1);[27] An off-white solid (mp 29.5–30.6 °C), $R_f = 0.19$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.54 (m, 2H), 7.45–7.39 (m, 2H), 7.33 (tt, $J = 6.6$, 1.4 Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 7.00 (ddd, $J = 4.5$, 1.6, 0.9 Hz, 1H), 6.92 (t, $J = 2.0$ Hz, 1H), 6.69 (ddd, $J = 7.9$, 2.4, 0.9 Hz, 1H), 3.75 (br, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 142.2, 141.2, 129.5, 128.5, 127.1, 127.0, 117.6, 114.0, 113.8.

3-Hydroxymethylbiphenyl (4an, Entry 14 of Table 1);[28] A colorless solid (mp 49.1–49.9 °C), $R_f = 0.23$ (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.57 (m, 3H), 7.54 (dt, $J = 7.7$, 1.5 Hz, 1H), 7.48–7.42 (m, 3H), 7.39–7.33 (m, 2H), 4.78 (s, 2H), 1.77 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.4, 141.2, 140.8, 128.9, 128.6, 127.2, 127.0, 126.4, 125.72, 125.66, 65.4.

Cross-Coupling Reaction of 1a with 3d (Entry 4 of Table 1). To a solution of **1a** (0.36 g, 1.5 mmol) in THF (1.1 mL) was added a 1.6 M solution of *n*-BuLi in hexane (0.94 mL, 1.5 mmol) at 0 °C, and the resulting mixture was stirred for 5 min. To the mixture were added sequentially DMF (0.4 mL), $[(allyl)PdCl]_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), CuI (5.7 mg, 30 μmol), and **3d** (0.28 g, 1.0 mmol) at rt. The resulting mixture was stirred at 75 °C for 11 h before filtration through a Florisil pad. The filtrate was diluted with diethyl ether, washed with water and then brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel followed by preparative GPC to give **4ad** (0.23 g, 81%) as a colorless oil, $R_f = 0.23$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, $J = 8.1$ Hz, 2H), 7.66–7.60 (m, 4H), 7.48–7.43 (m, 2H), 7.39–7.34 (m, 1H), 1.39 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.7, 140.8, 135.1, 128.6, 127.4, 127.1, 126.3, 83.8, 25.0; IR (neat): 3028, 2978, 2928, 1609, 1398, 1362, 1321, 1302, 1273, 1259, 1215, 1144, 1092, 1040, 1022, 1009, 962, 860, 841, 768, 735, 696, 658 cm^{-1}; Anal. Calcd for $C_{18}H_{21}BO_2$: C, 77.17; H, 7.55%. Found: C, 77.41; H, 7.27%.

Gram-Scale Cross-Coupling Reaction of 1a with 3p (Entry 16 of Table 1). To a mixture of **1a** (6.3 g, 26 mmol), K_2CO_3 (6.9 g, 50 mmol), $[(allyl)PdCl]_2$ (37 mg, 0.100 mmol), RuPhos (184 mg, 0.40 mmol), and CuI (114 mg, 0.60 mmol) in DMF (10 mL) and THF (20 mL) was added **3p** (3.4 g, 20 mmol), and the resulting mixture was stirred at 75 °C for 14 h before filtration through a Florisil pad. The filtrate was diluted with diethyl ether, washed with water and then brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was distilled under vacuum (45 °C at 1.0 mmHg) to give **2** [3.1 g, 91% (ca. 90% purity)]; the residue was further purified by flash chromatography on silica gel (hexane–ethyl acetate = 13:1 as an eluent) to give 3-methylbiphenyl (**4ap**, 2.9 g, 87%).

Cross-Coupling Reaction of 1′a with Aryl Chlorides. A General Procedure: To a mixture of **1′a** (0.45 g, 1.5 mmol), K_2CO_3 (0.35 g, 2.5 mmol), $[(allyl)PdCl]_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added an aryl chloride (1.0 mmol), and the resulting mixture was stirred at 50 °C. After the time specified in Table 3, the mixture was filtered through a Florisil pad, diluted with diethyl ether, washed with water and then brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding biaryl in a yield listed in Table 3. The yield of cyclic silyl ether **2′** was determined by GC analysis using tridecane as an internal standard.

Preparation of {Dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-4-{[2-(hydroxymethyl)phenyl]dimethylsilyl}benzene (15a). To a solution of **5a** (14.4 g, 36 mmol) in THF (80 mL) was added a 1.6 M solution of *n*-BuLi in hexane (24 mL, 38 mmol) at −78 °C, and the resulting mixture was stirred at −78 °C for 1 h. To this was added **2** (5.7 g, 35 mmol) at −78 °C, and the resulting mixture was stirred overnight during which time the mixture was allowed to warm to rt. The entirety was diluted with diethyl ether and to it was added water. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (14.4 g, 82%) as a colorless viscous oil, $R_f = 0.18$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, $J = 14.8$, 7.3 Hz, 2H), 7.51–7.36 (m, 8H), 7.33–7.23 (m, 2H), 4.55 (d, $J = 12.3$ Hz, 1H), 4.50 (d, $J = 5.9$ Hz, 2H), 4.40 (t, $J = 3.2$ Hz, 1H), 4.29 (d, $J = 12.3$ Hz, 1H), 3.77–3.67 (m, 1H), 3.35 (td, $J = 11.2$, 4.1 Hz, 1H), 1.90 (t, $J = 5.9$ Hz, 1H), 1.85–1.72 (br m, 1H), 1.64–1.40 (m, 5H), 0.60 (s, 6H), 0.58 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 144.0, 139.7, 139.6, 135.5, 135.2, 135.1, 133.3, 133.0, 129.7, 129.5, 127.9, 127.2, 126.61, 126.60, 97.5, 68.7, 64.9, 61.6, 30.4, 25.5, 19.1, −0.9, −1.10, −1.15, −1.2 (a signal for sp^2-carbon overlaps with others); IR (neat): 3443, 3049, 2993, 2951, 2897, 2872, 1925, 1823, 1589, 1564, 1466, 1454, 1435, 1410, 1381, 1350, 1323, 1285, 1250, 1200, 1182, 1132, 1078, 1055, 1024, 976, 907, 868, 835, 814, 773, 754, 689, 654, 606 cm^{-1}; Anal. Calcd for $C_{29}H_{38}O_3Si_2$: C, 70.97; H, 7.80%. Found: C, 70.68; H, 7.87%.

Preparation of 2-{Dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-5-{[2-(hydroxymethyl)phenyl]dimethylsilyl}thiophene (15b). To a solution of **5f** (20 g, 49 mmol) in THF (29 mL) was added a 1.6 M solution of *n*-BuLi in hexane (32 mL, 52 mmol) at −78 °C, and the resulting mixture was stirred at −40 °C for 1 h. To this was added magnesium bromide ethyl etherate (13.2 g, 52 mmol) at −40 °C, and the mixture was stirred for 0.5 h before addition of **2** (8.0 g, 49 mmol) all at the same temperature. The resulting mixture was allowed to warm to rt overnight with stirring, and diluted with diethyl ether. Water was added, and the organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the title compound (23 g, 95%) as a brown viscous oil, $R_f = 0.15$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.38 (m, 6H), 7.34–7.24 (m, 4H), 4.64 (d, $J = 12.3$ Hz, 1H), 4.61 (d, $J = 5.3$ Hz, 2H), 4.50 (t, $J = 3.3$ Hz, 1H), 4.37 (d, $J = 12.3$ Hz, 1H), 3.82–3.71 (m, 1H), 3.44–3.36 (m, 1H), 2.20 (br s, 1H), 1.87–1.73 (m, 1H), 1.69–1.43 (m, 5H), 0.66 (s, 6H), 0.64 (s, 6H); ^{13}C NMR (101 MHz,

$CDCl_3$): δ 146.8, 144.8, 144.7, 143.9, 136.4, 136.3, 135.5, 135.0, 134.9, 134.8, 129.9, 129.7, 128.1, 127.3, 126.68, 126.65, 97.6, 68.7, 64.9, 61.7, 30.5, 25.5, 19.1, 0.4, 0.2; IR (neat): 3445, 3055, 2951, 2872, 1589, 1564, 1487, 1435, 1410, 1350, 1250, 1202, 1126, 1078, 1005, 976, 907, 835, 808, 777, 754, 691, 652 cm^{-1}; Anal. Calcd for $C_{27}H_{36}O_3SSi_2$: C, 65.27; H, 7.30%. Found: C, 65.16; H, 7.50%.

Preparation of 2-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-(4-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}phenyl)thiophene (16′a). To a mixture of **15a** (2.9 g, 6.0 mmol), K_2CO_3 (2.1 g, 15.0 mmol), $[(allyl)PdCl]_2$ (32 mg, 87 μmol), RuPhos (176 mg, 0.38 μmol), and CuI (103 mg, 0.54 μmol) in DMF (4.8 mL) and THF (13 mL) was added **5′f** (2.7 g, 7.2 mmol), and the resulting mixture was stirred at 75 °C for 8 h. The mixture was filtered through a Florisil pad, and the filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the corresponding coupling product (3.2 g, 87%) as a pale yellow oil, $R_f = 0.13$ (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.24 (m, 13H), 7.20 (d, $J = 3.3$ Hz, 1H), 5.10 (s, 2H), 4.67 (d, $J = 12.1$ Hz, 1H), 4.45 (br s, 1H), 4.39 (d, $J = 12.1$ Hz, 1H), 3.82–3.69 (m, 1H), 3.45–3.37 (m, 1H), 2.00 (s, 3H), 1.85–1.71 (m, 1H), 1.67–1.39 (m, 5H), 0.69 (s, 6H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 150.3, 144.0, 141.1, 138.2, 137.8, 136.6, 136.3, 135.8, 135.43, 135.35, 134.5, 134.4, 129.9, 129.56, 129.53, 128.5, 127.6, 126.7, 125.2, 124.4, 97.8, 68.8, 66.6, 62.0, 30.6, 25.5, 21.1, 19.4, 0.2, −0.8, −0.9; IR (neat): 3055, 3013, 2951, 2899, 2870, 2851, 1738, 1697, 1593, 1566, 1543, 1524, 1466, 1454, 1433, 1379, 1360, 1319, 1234, 1202, 1182, 1153, 1117, 1078, 1026, 995, 974, 949, 907, 870, 812, 777, 756, 729, 689, 660, 638, 615, 588 cm^{-1}; Anal. Calcd for $C_{35}H_{42}O_4SSi_2$: C, 68.36; H, 6.88%. Found: C, 68.24; H, 6.99%.

Preparation of 2-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-(4-{[2-(hydroxymethyl)phenyl]dimethylsilyl}phenyl)-thiophene (16a). To a solution of **16′a** (3.2 g, 5.2 mmol) in MeOH (50 mL) was added pyridinium *p*-toluenesulfonate (PPTS, 0.30 g, 1.2 mmol), and the resulting mixture was stirred at 40 °C for 3 h. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (2.5 g, 92%) as a colorless viscous oil, $R_f = 0.08$ (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.54 (m, 4H), 7.51–7.28 (m, 9H), 7.21 (d, $J = 3.7$ Hz, 1H), 5.10 (s, 2H), 4.56 (d, $J = 6.0$ Hz, 2H), 2.00 (s, 3H), 1.33 (t, $J = 5.9$ Hz, 1H), 0.69 (s, 6H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 150.1, 146.4, 141.1, 138.1, 137.9, 136.5, 136.3, 135.40, 135.37, 134.7, 134.3, 129.91, 129.86, 129.5, 127.8, 127.6, 126.8, 125.3, 124.5, 109.6, 66.6, 65.2, 21.0, 0.2, −0.9; IR (neat): 3441, 3055, 3011, 2955, 2899, 1738, 1593, 1564, 1543, 1524, 1468, 1433, 1381, 1362, 1317, 1298, 1256, 1236, 1163, 1126, 1111, 1078, 1026, 995, 949, 924, 876, 812, 777, 756, 729, 691, 660, 638, 606, 588 cm^{-1}; Anal. Calcd for $C_{30}H_{34}O_3SSi_2$: C, 67.88; H, 6.46%. Found: C, 67.74; H, 6.48%.

Preparation of 5-(4-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}phenyl)-2-{[2-(hydroxymethyl)phenyl]dimethylsilyl}-thiophene (16b). To a mixture of **15b** (0.50 g, 1.0 mmol), K_2CO_3 (0.35 g, 2.5 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (24 mg, 30 μmol), and CuI (17.1 mg, 90 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added **5′a** (1.2 mmol), and the resulting mixture was stirred at 75 °C for 6 h. The mixture was filtered through a Florisil pad, and the filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was dissolved in MeOH (5 mL) and treated with PPTS (50 mg, 0.20 mmol) at rt for 6 h. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (0.38 g, 72%) as a colorless viscous oil, $R_f = 0.08$ (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.55 (m, 4H), 7.52–7.29 (m, 9H), 7.23 (d, $J = 3.5$ Hz, 1H), 5.00 (s, 2H), 4.69 (d, $J = 5.7$ Hz, 2H), 1.93 (s, 3H), 1.57 (br t, $J = 5.6$ Hz, 1H), 0.70 (s, 6H), 0.64 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 150.1, 146.4, 141.1, 138.5, 137.7, 136.9, 136.2, 135.6, 135.23, 135.16, 134.6, 134.4, 130.1, 129.7, 129.5, 128.0, 127.5, 127.0, 125.2, 124.6, 66.6, 65.3, 21.0, 0.3, −0.9; IR (neat): 3441, 3055, 3013, 2955, 2899, 1736, 1593, 1546, 1543, 1524, 1462, 1433, 1414, 1381, 1362, 1319, 1300, 1256, 1236, 1163, 1126, 1111, 1078, 1026, 995, 947, 924, 876, 835, 812, 777, 756, 729, 689, 660, 638 cm^{-1}; Anal. Calcd for $C_{30}H_{34}O_3SSi_2$: C, 67.88; H, 6.46%. Found: C, 68.10; H, 6.58%.

Cross-Coupling Reaction of 16a with 5b–5e. A General Procedure: To a mixture of **16a** (0.27 g, 0.50 mmol), K_2CO_3 (0.17 g, 1.25 mmol), $[(allyl)PdCl]_2$ (4.3 mg, 12 μmol), RuPhos (25 mg, 53 μmol), and CuI (4.8 mg, 25 μmol) in DMF (0.4 mL) and THF (1.1 mL) was added **5b–5e** (0.60 mmol), and the resulting mixture was stirred at 50 °C for 6–7 h before filtration through a Florisil pad. The filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **17ab–17ae** in a yield listed in Entries 1–4 of Table 5.

(*E*)-2-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-[4′-(2-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-ethenyl)biphenyl-4-yl]thiophene (17ab, Entry 1 of Table 5); A yellow viscous oil, $R_f = 0.22$ (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.69–7.56 (m, 8H), 7.55–7.48 (m, 3H), 7.47–7.27 (m, 6H), 7.23 (d, $J = 3.5$ Hz, 1H), 6.97 (d, $J = 19.0$ Hz, 1H), 6.70 (d, $J = 19.2$ Hz, 1H), 5.11 (s, 2H), 4.88 (d, $J = 11.9$ Hz, 1H), 4.67 (t, $J = 3.5$ Hz, 1H), 4.63 (d, $J = 11.9$ Hz, 1H), 3.93–3.84 (m, 1H), 3.53–3.44 (m, 1H), 2.01 (s, 3H), 1.91–1.79 (m, 1H), 1.77–1.43 (m, 5H), 0.77 (s, 6H), 0.52 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 149.9, 144.1, 143.8, 141.1, 139.8, 139.5, 137.8, 137.2, 136.5, 136.4, 135.4, 134.9, 133.1, 129.9, 129.5, 129.4, 128.4, 128.1, 127.6, 127.1, 126.84, 126.76, 126.2, 124.4, 97.9, 68.9, 66.6, 62.2, 30.7, 25.6, 21.0, 19.5, 0.2, −1.0, −1.1 (two signals for sp^2-carbons overlap with others); IR (neat): 3055, 2916, 2849, 1736, 1601, 1578, 1541, 1512, 1489, 1466, 1433, 1400, 1377, 1360, 1223, 1200, 1182, 1153, 1126, 1117, 1076, 1024, 993, 949, 905, 835, 808, 779, 752, 689 cm^{-1}; Anal. Calcd for $C_{43}H_{48}O_4SSi_2$: C, 72.02; H, 6.75%. Found: C, 71.86; H, 6.86%.

2-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-[4-(7-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-9,9-dioctyl-9*H*-fluoren-2-yl)phenyl]thiophene (17ac, Entry 2 of Table 5); A brown viscous oil, $R_f = 0.10$ (hexane–ethyl

acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.7 Hz, 1H), 7.72–7.54 (m, 6H), 7.52–7.34 (m, 9H), 7.28–7.22 (m, 4H), 5.13 (s, 2H), 4.70 (d, J = 11.9 Hz, 1H), 4.52 (t, J = 3.5 Hz, 1H), 4.44 (d, J = 12.1 Hz, 1H), 3.87–3.77 (m, 1H), 3.49–3.41 (m, 1H), 2.04–1.90 (m, 7H), 1.88–1.77 (m, 1H), 1.72–1.43 (m, 5H), 1.29–0.98 (m, 20H), 0.82 (t, J = 7.0 Hz, 6H), 0.76–0.60 (m, 4H), 0.72 (s, 6H), 0.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 151.5, 150.1, 150.0, 144.0, 141.4, 141.1, 140.6, 140.3, 139.3, 137.7, 137.2, 136.6, 136.4, 135.5, 135.4, 132.9, 132.6, 129.9, 129.5, 129.4, 128.4, 128.2, 127.6, 127.4, 126.6, 126.2, 125.6, 124.3, 121.1, 120.0, 119.1, 97.6, 68.8, 66.6, 61.9, 55.1, 40.3, 31.9, 30.6, 30.1, 29.29, 29.27, 25.6, 23.9, 22.7, 21.0, 19.4, 14.2, 0.2, −0.6, −0.7 (a signal for sp^2-carbon overlaps with others); IR (neat): 2920, 2849, 1736, 1578, 1541, 1464, 1437, 1406, 1377, 1364, 1254, 1225, 1202, 1117, 1078, 1026, 955, 951, 907, 837, 806, 777, 754 cm^{-1}; Anal. Calcd for $C_{64}H_{82}O_4SSi_2$: C, 76.60; H, 8.24%. Found: C, 76.80; H, 8.42%.

7-[4-(5-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}thiophen-2-yl)phenyl]-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)-phenyl]silyl}-5,5-dipentyl-5*H*-dibenzo[*b*,*d*]silole (17ad, Entry 3 of Table 5); A yellow viscous oil, R_f = 0.30 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 1.6 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.75 (s, 1H), 7.72–7.60 (m, 6H), 7.59–7.33 (m, 8H), 7.32–7.24 (m, 1H), 7.24 (d, J = 3.5 Hz, 1H), 5.13 (s, 2H), 4.71 (d, J = 11.9 Hz, 1H), 4.50 (t, J = 3.5 Hz, 1H), 4.45 (d, J = 11.9 Hz, 1H), 3.82–3.73 (m, 1H), 3.46–3.33 (m, 1H), 2.01 (s, 3H), 1.86–1.72 (m, 1H), 1.70–1.16 (m, 17H), 1.00–0.92 (m, 4H), 0.85–0.77 (m, 6H), 0.71 (s, 6H), 0.65 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 150.0, 148.5, 147.4, 144.0, 141.1, 140.2, 139.0, 138.8, 138.7, 137.6, 137.2, 137.0, 136.5, 136.4, 136.2, 135.9, 135.4, 132.9, 131.3, 129.9, 129.5, 129.4, 128.5, 128.4, 127.6, 127.2, 126.6, 126.2, 124.3, 121.2, 120.1, 97.6, 68.8, 66.5, 61.9, 35.6, 30.6, 25.5, 23.7, 22.2, 21.0, 19.4, 14.1, 12.3, 0.2, −0.7, −0.8 (a signal for sp^2-carbon overlaps with others); IR (neat): 2953, 2916, 2849, 1736, 1578, 1541, 1460, 1433, 1414, 1379, 1364, 1252, 1236, 1202, 1115, 1078, 1024, 997, 951, 837, 810, 777, 754 cm^{-1}; Anal. Calcd for $C_{57}H_{70}O_4SSi_3$: C, 73.18; H, 7.54%. Found: C, 73.27; H, 7.79%.

6-[4-(5-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}thiophen-2-yl)phenyl]-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-9-ethyl-9*H*-carbazole (17ae, Entry 4 of Table 5); A yellow viscous oil, R_f = 0.15 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 1.3 Hz, 1H), 8.31 (s, 1H), 7.75–7.56 (m, 8H), 7.52–7.36 (m, 8H), 7.30 (td, J = 7.3, 1.3 Hz, 1H), 7.24 (d, J = 3.3 Hz, 1H), 5.14 (s, 2H), 4.71 (d, J = 12.1 Hz, 1H), 4.45 (d, J = 11.9 Hz, 1H), 4.45–4.35 (m, 3H), 3.76–3.67 (m, 1H), 3.37–3.28 (m, 1H), 2.02 (s, 3H), 1.82–1.69 (m, 1H), 1.63–1.37 (m, 5H), 1.47 (t, J = 7.2 Hz, 3H), 0.72 (s, 6H), 0.713 (s, 3H), 0.710 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 150.3, 144.1, 141.14, 141.09, 141.0, 139.3, 137.3, 136.8, 136.7, 136.4, 135.4, 132.1, 131.5, 131.4, 129.9, 129.5, 129.4, 128.5, 127.6, 127.4, 126.6, 126.4, 126.2, 124.8, 124.1, 123.3, 122.8, 118.6, 108.6, 108.3, 97.8, 68.9, 66.6, 62.0, 37.7, 30.6, 25.5, 21.1, 19.4, 14.0, 0.3, −0.3, −0.4 (two sp^2-carbon signals overlap with others); IR (neat): 3049, 2949, 1736, 1624, 1591, 1564, 1531, 1477, 1431, 1377, 1346, 1277, 1250, 1232, 1157, 1128, 1117, 1097, 1078, 1024, 995, 974, 949, 905, 860, 835, 802, 775, 754, 689, 648, 582, 505 cm^{-1}; Anal. Calcd for $C_{49}H_{53}NO_4SSi_2$: C, 72.82; H, 6.61%. Found: C, 72.60; H, 6.62%.

Cross-Coupling Reaction of 16b with 5b–5e. A General Procedure: To a mixture of **16b** (0.27 g, 0.50 mmol), K_2CO_3 (0.17 g, 1.25 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (21 mg, 25 μmol), and CuI (4.8 mg, 25 μmol) in DMF (0.4 mL) and THF (1.1 mL) was added **5b**–**5e** (0.60 mmol), and the resulting mixture was stirred at 50 °C for 6–9 h before filtration through a Florisil pad. The filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **17bb**–**17be** in a yield listed in Entries 5–8 of Table 5.

(*E*)-2-(4-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}phenyl)-5-[4-(2-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}ethenyl)phenyl]thiophene (17bb, Entry 5 of Table 5); A yellow viscous oil, R_f = 0.25 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.56 (m, 6H), 7.53–7.23 (m, 12H), 6.93 (d, J = 19.0 Hz, 1H), 6.68 (d, J = 19.0 Hz, 1H), 5.01 (s, 2H), 4.87 (d, J = 11.9 Hz, 1H), 4.67 (t, J = 3.5 Hz, 1H), 4.62 (d, J = 11.9 Hz, 1H), 3.93–3.83 (m, 1H), 3.53–3.44 (m, 1H), 1.92 (s, 3H), 1.90–1.44 (m, 6H), 0.64 (s, 6H), 0.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 143.9, 143.8, 143.3, 141.1, 137.7, 137.3, 136.9, 136.5, 135.6, 134.9, 134.7, 134.5, 133.7, 129.7, 129.5, 129.4, 128.4, 128.0, 127.6, 126.9, 126.8, 125.5, 124.8, 124.2, 124.0, 97.9, 68.9, 66.6, 62.2, 30.7, 25.6, 21.0, 19.5, −0.9, −1.0, −1.1 (a signal for sp^2-carbon overlaps with others); IR (neat): 2916, 2849, 1738, 1595, 1578, 1539, 1493, 1470, 1454, 1435, 1412, 1391, 1377, 1360, 1248, 1225, 1200, 1113, 1076, 1024, 814, 793, 777, 754, 729, 665 cm^{-1}; HRMS (EI) Calcd for $C_{43}H_{48}O_4SSi_2$: M^+, 716.2812. Found: m/z 716.2806.

5-(4-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}phenyl)-2-(7-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-9,9-dioctyl-9*H*-fluoren-2-yl)thiophene (17bc, Entry 6 of Table 5); A yellow viscous oil, R_f = 0.13 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.65–7.58 (m, 4H), 7.57 (s, 1H), 7.53–7.32 (m, 12H), 7.29–7.22 (m, 1H), 5.02 (s, 2H), 4.70 (d, J = 12.1 Hz, 1H), 4.52 (t, J = 3.5 Hz, 1H), 4.43 (d, J = 12.1 Hz, 1H), 3.87–3.76 (m, 1H), 3.50–3.40 (m, 1H), 2.03–1.90 (m, 4H), 1.93 (s, 3H), 1.89–1.76 (m, 1H), 1.72–1.42 (m, 5H), 1.30–0.97 (m, 20H), 0.82 (t, J = 7.0 Hz, 6H), 0.73–0.59 (m, 4H), 0.66 (s, 6H), 0.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 151.6, 149.9, 144.5, 144.0, 142.9, 141.3, 141.1, 140.5, 137.5, 137.4, 137.0, 136.6, 135.6, 135.5, 134.8, 134.5, 133.1, 132.6, 129.7, 129.5, 129.4, 128.4, 128.2, 127.6, 126.6, 124.8, 124.4, 124.1, 123.7, 120.1, 119.7, 119.0, 97.6, 68.8, 66.6, 61.9, 55.1, 40.3, 31.9, 30.6, 30.1, 29.31, 29.28, 25.6, 23.9, 22.7, 21.0, 19.4, 14.2, −0.6, −0.7, −0.9; IR (neat): 2920, 2849, 1740, 1595, 1578, 1541, 1466, 1437, 1377, 1360, 1246, 1225, 1202, 1115, 1078, 1026, 976, 907, 814, 800, 775, 754, 729, 689 cm^{-1}; Anal. Calcd for $C_{64}H_{82}O_4SSi_2$: C, 76.60; H, 8.24%. Found: C, 76.59; H, 8.29%.

7-[5-(4-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}phenyl)-thiophen-2-yl]-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymeth-

yl)phenyl]silyl}-5,5-dipentyl-5*H*-dibenzo[*b*,*d*]silole (17bd, Entry 7 of Table 5); A yellow viscous oil, $R_f = 0.33$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.73 (m, 2H), 7.69 (d, $J = 8.6$ Hz, 1H), 7.64–7.58 (m, 3H), 7.58–7.24 (m, 14H), 5.02 (s, 2H), 4.71 (d, $J = 11.9$ Hz, 1H), 4.50 (t, $J = 6.2$ Hz, 1H), 4.44 (d, $J = 11.7$ Hz, 1H), 3.83–3.73 (m, 1H), 3.46–3.37 (m, 1H), 1.93 (s, 3H), 1.85–1.73 (m, 1H), 1.68–1.17 (m, 17H), 0.96 (distorted t, $J = 8.1$ Hz, 4H), 0.82 (t, $J = 6.6$ Hz, 6H), 0.65 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 148.4, 147.6, 144.0, 143.0, 141.2, 139.0, 138.8, 137.5, 137.4, 137.0, 136.3, 136.0, 135.6, 135.5, 134.8, 134.5, 132.9, 130.1, 129.8, 129.5, 129.4, 128.4, 127.6, 127.3, 126.7, 124.8, 124.2, 123.7, 121.2, 120.1, 97.7, 68.8, 66.6, 62.0, 35.6, 30.6, 25.6, 23.7, 22.2, 21.0, 19.4, 14.1, 12.4, −0.7, −0.8, −0.9 (two signals for sp^2-carbons overlap with others); IR (neat): 2953, 2918, 2849, 1738, 1593, 1578, 1539, 1466, 1439, 1392, 1377, 1366, 1250, 1225, 1200, 1113, 1076, 1026, 976, 953, 907, 824, 800, 775, 754, 729, 665 cm^{-1}; Anal. Calcd for $C_{57}H_{70}O_4SSi_3$: C, 73.18; H, 7.54%. Found: C, 72.88; H, 7.61%.

6-[5-(4-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}phenyl)-thiophen-2-yl]-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-9-ethyl-9*H*-carbazole (17be, Entry 8 of Table 5); A yellow viscous oil, $R_f = 0.18$ (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.30 (s, 1H), 7.74 (dd, $J = 8.4$, 1.1 Hz, 1H), 7.64–7.22 (m, 17H), 5.02 (s, 2H), 4.70 (d, $J = 11.9$ Hz, 1H), 4.44 (d, $J = 11.9$ Hz, 1H), 4.44–4.32 (m, 3H), 3.76–3.67 (m, 1H), 3.36–3.28 (m, 1H), 1.93 (s, 3H), 1.81–1.68 (m, 1H), 1.65–1.30 (m, 8H), 0.71 (s, 6H), 0.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 145.1, 144.0, 141.8, 141.1, 140.9, 139.3, 137.1, 137.0, 136.8, 135.6, 135.4, 135.0, 134.4, 131.5, 129.7, 129.5, 129.4, 128.5, 127.54, 127.48, 126.7, 126.4, 125.5, 124.6, 124.1, 123.8, 123.1, 122.7, 122.6, 117.5, 108.6, 108.3, 97.8, 68.8, 66.6, 61.9, 37.7, 30.5, 25.5, 21.0, 19.4, 14.0, −0.3, −0.4, −0.9; IR (neat): 3456, 3055, 3013, 2955, 2930, 2897, 2856, 1738, 1589, 1472, 1435, 1427, 1402, 1379, 1362, 1252, 1225, 1204, 1126, 1111, 1082, 1063, 1026, 1011, 978, 876, 833, 814, 802, 775, 752, 700, 648 cm^{-1}; HRMS (FAB+) Calcd for $C_{49}H_{53}NO_4SSi_2$: M^+, 807.3234. Found: m/z 807.3231.

Preparation of (3,5-Dibromophenyl)[2-(hydroxymethyl)-phenyl]dimethylsilane (18). To a solution of 1,3,5-tribromobenzene (4.7 g, 15 mmol) in diethyl ether (150 mL) was added a 1.6 M solution of *n*-BuLi in hexane (9.4 mL, 15 mmol) over 30 min at −78 °C, and the resulting mixture was stirred at −78 °C for 2 h. To this was added **2** (2.5 g, 15 mmol) at −78 °C, and the resulting mixture was allowed to warm to rt overnight with stirring before being quenched with water at 0 °C. The aqueous layer was extracted with diethyl ether three times, and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (5.9 g, 98%) as a pale brown oil, $R_f = 0.22$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (t, $J = 1.8$ Hz, 1H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.50–7.42 (m, 4H), 7.36–7.30 (m, 1H), 4.56 (d, $J = 5.9$ Hz, 2H), 1.42 (t, $J = 5.9$ Hz, 1H), 0.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 144.7, 135.6, 134.8, 134.4, 133.9, 130.3, 127.8, 127.1, 123.3, 65.4, −0.9; IR (neat): 3576, 3342, 3055, 2955, 2918, 2895, 1591, 1562, 1537, 1464, 1435, 1421, 1410, 1381, 1356, 1288, 1252, 1202, 1126, 1111, 1099, 1080, 1011, 986, 949, 854, 837, 824, 779, 754, 733, 675, 648 cm^{-1}; Anal. Calcd for $C_{15}H_{16}Br_2OSi$: C, 45.02; H, 4.03%. Found: C, 44.99; H, 3.93%.

Preparation of (3,5-Dibromophenyl)dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (18′). A solution of **18** (3.9 g, 9.8 mmol) and 3,4-dihydro-2*H*-pyran (1.81 g, 14.7 mmol) and PPTS (0.25 g, 0.98 mmol) in CH_2Cl_2 (69 mL) was stirred at rt for 5 h. The mixture was diluted with diethyl ether (50 mL) and then neutralized with a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel gave the title compound (3.8 g, 81%) as a pale brown oil, $R_f = 0.38$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, $J = 1.8$ Hz, 1H), 7.54–7.40 (m, 5H), 7.32 (t, $J = 7.3$ Hz, 1H), 4.65 (d, $J = 11.9$ Hz, 1H), 4.48 (t, $J = 6.8$ Hz, 1H), 4.33 (d, $J = 11.9$ Hz, 1H), 3.83–3.72 (m, 1H), 3.51–3.41 (m, 1H), 1.86–1.73 (m, 1H), 1.69–1.43 (m, 5H), 0.61 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 143.9, 135.4, 134.9, 134.3, 134.2, 130.0, 128.9, 127.0, 123.1, 97.8, 68.8, 62.2, 30.5, 25.5, 19.5, −0.9, −1.0; IR (neat): 3055, 2941, 2870, 2849, 1562, 1537, 1439, 1381, 1352, 1258, 1202, 1128, 1099, 1078, 1055, 1026, 974, 907, 839, 822, 779, 756, 733, 689, 675, 648 cm^{-1}; Anal. Calcd for $C_{20}H_{24}Br_2O_2Si$: C, 49.60; H, 4.99%. Found: C, 49.87; H, 4.99%.

Preparation of 1-Bromo-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-5-{[2-(hydroxymethyl)phenyl]dimethylsilyl}benzene (19). To a solution of **18′** (2.6 g, 5.3 mmol) and **2** (0.87 g, 5.3 mmol) in diethyl ether (10.6 mL) was added a 1.58 M solution of *t*-BuLi in pentane (3.3 mL, 5.3 mmol) over 1 h at −78 °C, and the resulting mixture was allowed to warm to rt overnight with stirring before being quenched with water at 0 °C. The aqueous layer was extracted with diethyl ether three times, and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (2.8 g, 92%) as a colorless viscous oil, $R_f = 0.18$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.38 (m, 9H), 7.32–7.25 (m, 2H), 4.482 (d, $J = 5.7$ Hz, 2H), 4.480 (d, $J = 12.1$ Hz, 1H), 4.36 (t, $J = 3.4$ Hz, 1H), 4.21 (d, $J = 12.3$ Hz, 1H), 3.72–3.62 (m, 1H), 3.40–3.37 (m, 1H), 2.49 (t, $J = 5.6$ Hz, 1H), 1.83–1.70 (m, 1H), 1.65–1.40 (m, 5H), 0.57 (s, 6H), 0.549 (s, 3H), 0.546 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 143.7, 141.7, 141.6, 137.4, 136.9, 136.8, 135.09, 135.06, 134.9, 134.0, 129.9, 129.8, 128.2, 126.81, 126.78, 126.6, 123.4, 97.7, 68.6, 64.8, 62.0, 30.5, 25.4, 19.3, −1.07, −1.09, −1.18, −1.21; IR (neat): 3439, 3055, 3011, 2949, 2895, 2872, 1589, 1564, 1537, 1464, 1454, 1435, 1410, 1385, 1377, 1356, 1323, 1285, 1258, 1200, 1182, 1134, 1078, 1055, 1024, 976, 907, 866, 824, 777, 748, 691, 648, 604 cm^{-1}; Anal. Calcd for $C_{29}H_{37}BrO_3Si_2$: C, 61.14; H, 6.55%. Found: C, 61.33; H, 6.56%.

Preparation of 1-Bromo-3-({2-[(*tert*-butyldiphenylsilyl-oxy)methyl]phenyl}dimethylsilyl)-5-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}benzene (19′). A solution of **19** (2.8 g, 4.9 mmol) and *tert*-butyldiphenylsilyl chloride (1.48 g, 5.4 mmol) and imidazole (0.73 g, 10.8 mmol) in DMF (4.9 mL) was stirred at rt for 3 h. The mixture was diluted with diethyl ether, and water was added. The organic layer was dried

over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (3.8 g, 96%) as a colorless viscous oil, $R_f = 0.32$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, $J = 7.1$ Hz, 1H), 7.61–7.55 (m, 4H), 7.51 (dd, $J = 2.1$, 1.0 Hz, 1H), 7.47–7.29 (m, 13H), 7.27–7.19 (m, 2H), 4.61 (s, 2H), 4.60 (d, $J = 11.9$ Hz, 1H), 4.45 (t, $J = 5.9$ Hz, 1H), 4.31 (d, $J = 11.9$ Hz, 1H), 3.81–3.72 (m, 1H), 3.46–3.38 (m, 1H), 1.85–1.71 (m, 1H), 1.67–1.40 (m, 5H), 1.06 (s, 9H), 0.50 (s, 3H), 0.49 (s, 3H), 0.36 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.6, 143.8, 141.5, 141.1, 137.4, 137.1, 136.7, 135.31, 135.26, 134.9, 133.2, 132.9, 129.8, 129.6, 129.5, 128.7, 127.6, 126.8, 126.1, 125.9, 123.3, 97.6, 68.7, 65.7, 62.0, 30.6, 27.0, 25.5, 19.4, −0.9, −1.0, −1.2 (two signals for sp^2- and sp^3-carbons overlap with others); IR (neat): 3057, 2951, 2918, 2851, 1580, 1560, 1541, 1466, 1427, 1356, 1256, 1202, 1128, 1113, 1080, 1063, 1026, 974, 907, 837, 822, 777, 743, 700 cm^{-1}; Anal. Calcd for $C_{45}H_{55}BrO_3Si_3$: C, 66.88; H, 6.86%. Found: C, 66.72; H, 6.79%.

Preparation of 1-({2-[(*tert*-Butyldiphenylsilyloxy)methyl]-phenyl}dimethylsilyl)-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-5-{[2-(hydroxymethyl)phenyl]dimethylsilyl}benzene (20). To a solution of **19′** (0.58 g, 0.70 mmol) and **2** (117 mg, 0.70 mmol) in diethyl ether (14 mL) was added a 1.58 M solution of *t*-BuLi in pentane (0.45 mL, 0.70 mmol) over 1 h at −78 °C, and the resulting mixture was allowed to warm to rt overnight with stirring before being quenched with water at 0 °C. The aqueous layer was extracted with diethyl ether three times, and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (0.52 g, 81%) as a colorless viscous oil, $R_f = 0.22$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, $J = 7.3$ Hz, 1H), 7.62–7.57 (m, 4H), 7.55 (t, $J = 1.3$ Hz, 1H), 7.51–7.14 (m, 19H), 4.67 (s, 2H), 4.47 (d, $J = 12.3$ Hz, 1H), 4.42 (d, $J = 5.7$ Hz, 2H), 4.37 (t, $J = 3.3$ Hz, 1H), 4.21 (d, $J = 12.1$ Hz, 1H), 3.74–3.65 (m, 1H), 3.39–3.31 (m, 1H), 2.14 (t, $J = 5.6$ Hz, 1H), 1.82–1.69 (m, 1H), 1.65–1.38 (m, 5H), 1.06 (s, 9H), 0.48 (s, 12H), 0.321 (s, 3H), 0.319 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 146.5, 143.7, 140.2, 140.1, 136.9, 136.8, 136.6, 135.8, 135.4, 135.14, 135.09, 135.0, 134.9, 133.9, 133.3, 129.6, 129.5, 129.4, 128.1, 127.5, 126.8, 126.6, 126.4, 126.0, 125.8, 97.6, 68.7, 65.8, 64.8, 61.8, 30.5, 27.0, 25.5, 19.5, 19.2, −0.9, −1.1 (a signal for sp^2-carbon overlaps with others); IR (neat): 3441, 3053, 3003, 2953, 2856, 1589, 1560, 1541, 1466, 1427, 1375, 1249, 1202, 1124, 1113, 1080, 1061, 1026, 841, 826, 775, 750, 702, 689, 644 cm^{-1}; Anal. Calcd for $C_{54}H_{68}O_4Si_4$: C, 72.59; H, 7.67%. Found: C, 72.66; H, 7.65%.

Preparation of (5-Bromothiophen-2-yl){2-[(*tert*-butyldiphenylsilyloxy)methyl]phenyl}dimethylsilane (5″f). A solution of 5-bromothienyl[2-(hydroxymethyl)phenyl]dimethylsilane (5.2 g, 15.9 mmol, prepared by C(5)-silylation of 2-bromothiophene through C(5)-lithiation with LDA, transmetalation with $MgBr_2 \cdot Et_2O$, and silylation with **2** in 64% yield), *t*-butyldiphenylsilyl chloride (4.9 g, 17.6 mmol) and imidazole (2.4 g, 35 mmol) in DMF (16 mL) was stirred at rt for 3 h. The mixture was diluted with diethyl ether, and water was added. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (8.8 g, 98%) as a pale yellow oil, $R_f = 0.38$ (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, $J = 8.1$, 0.9 Hz, 1H), 7.62–7.56 (m, 4H), 7.50–7.32 (m, 8H), 7.27 (t, $J = 7.3$ Hz, 1H), 6.90 (d, $J = 3.5$ Hz, 1H), 6.72 (d, $J = 3.5$ Hz, 1H), 4.68 (s, 2H), 1.09 (s, 9H), 0.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 141.0, 135.4, 134.5, 133.2, 132.5, 131.0, 130.1, 129.6, 127.6, 126.1, 125.8, 117.2, 65.5, 27.0, 19.4, −0.3 (a signal for sp^2-carbon overlaps with others); IR (neat): 3069, 3051, 3013, 2957, 2930, 2893, 2856, 1958, 1888, 1821, 1589, 1541, 1504, 1472, 1427, 1404, 1391, 1362, 1286, 1258, 1204, 1124, 1111, 1063, 999, 955, 831, 816, 777, 743, 702, 656, 617, 592 cm^{-1}. Anal. Calcd for $C_{29}H_{33}BrOSSi_2$: C, 61.57; H, 5.88%. Found: C, 61.87; H, 5.96%.

Preparation of 4′-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-3-({2-[(*tert*-butyldiphenylsilyloxy)methyl]phenyl}dimethylsilyl)-5-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}biphenyl (21′). To a mixture of **20** (0.22 g, 0.25 mmol), K_2CO_3 (86 mg, 0.63 mmol), $[(allyl)PdCl]_2$ (2.2 mg, 6.0 μmol), RuPhos (12.3 mg, 27 μmol), and CuI (2.4 mg, 13 μmol) in DMF (0.2 mL) and THF (0.55 mL) was added **5′a** (109 mg, 0.30 mmol), and the resulting mixture was stirred at 50 °C for 27 h. The mixture was filtered through a Florisil pad, and the filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (0.18 g, 70%) as a colorless viscous oil, $R_f = 0.30$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $J = 7.9$ Hz, 1H), 7.63–7.18 (m, 28H), 5.02 (s, 2H), 4.69 (s, 2H), 4.65 (d, $J = 12.1$ Hz, 1H), 4.45 (t, $J = 3.5$ Hz, 1H), 4.38 (d, $J = 12.1$ Hz, 1H), 3.79–3.69 (m, 1H), 3.43–3.33 (m, 1H), 1.89 (s, 3H), 1.82–1.68 (m, 1H), 1.64–1.36 (m, 5H), 1.03 (s, 9H), 0.63 (s, 6H), 0.553 (s, 3H), 0.549 (s, 3H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 146.6, 143.9, 142.2, 141.2, 139.3, 138.4, 138.1, 137.0, 136.7, 135.9, 135.6, 135.4, 135.3, 134.9, 134.2, 133.6, 133.5, 133.2, 129.7, 129.5, 129.4, 128.5, 127.5, 126.7, 126.0, 125.7, 97.6, 68.8, 66.6, 65.8, 61.9, 30.5, 27.0, 25.5, 20.9, 19.4, −0.7, −0.8, −1.1 (five signals for sp^2-carbons and a signal for sp^3-carbon overlap with others); IR (neat): 3055, 3013, 2955, 2928, 2855, 1738, 1587, 1576, 1541, 1470, 1437, 1427, 1379, 1360, 1252, 1236, 1202, 1124, 1113, 1080, 1059, 1026, 841, 773, 754, 702 cm^{-1}; HRMS (MALDI) Calcd for $C_{62}H_{74}NaO_5Si_4$: $[M + Na]^+$, 1033.4511. Found: m/z 1033.4506.

Preparation of 4′-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-3-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-5-{[(2-hydroxymethyl)phenyl]dimethylsilyl}biphenyl (21). 21′ (2.7 g, 2.7 mmol) was treated with a 1.0 M solution of TBAF in THF (5.4 mL, 5.4 mmol) at rt for 1 h. The mixture was filtered through a Florisil pad, and the filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (1.6 g, 77%) as a colorless viscous oil, $R_f = 0.20$ (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, $J = 1.9$, 1.2 Hz, 1H), 7.63–7.24 (m, 18H), 5.00 (s, 2H), 4.53 (d, $J = 5.3$ Hz, 2H),

4.52 (d, $J = 12.4$ Hz, 1H), 4.36 (t, $J = 3.4$ Hz, 1H), 4.26 (d, $J = 12.3$ Hz, 1H), 3.70–3.60 (m, 1H), 3.36–3.27 (m, 1H), 2.49 (t, $J = 5.6$ Hz, 1H), 1.89 (s, 3H), 1.80–1.67 (m, 1H), 1.62–1.36 (m, 5H), 0.62 (s, 6H), 0.61 (s, 6H), 0.592 (s, 3H), 0.587 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 146.9, 143.7, 142.0, 141.1, 139.5, 138.6, 138.3, 137.0, 136.9, 135.6, 135.1, 135.0, 134.7, 134.2, 133.4, 133.3, 129.7, 129.54, 129.50, 128.1, 127.5, 126.74, 126.69, 126.65, 126.5, 97.7, 68.7, 66.6, 64.8, 61.8, 30.4, 25.4, 20.9, 19.2, −0.87, −0.92, −1.0, −1.05, −1.09 (three signals for sp^2-carbons overlap with others); IR (neat): 3441, 3055, 3013, 2953, 2920, 2868, 2851, 1736, 1597, 1591, 1578, 1541, 1464, 1437, 1408, 1379, 1362, 1250, 1202, 1126, 1115, 1078, 1057, 1024, 974, 841, 800, 773, 754, 687, 665, 646 cm^{-1}; HRMS (FAB−) Calcd for $C_{46}H_{55}O_5Si_3$: $[M - H]^-$, 771.3357. Found: m/z 771.3361.

Preparation of 5-(4′-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}biphenyl-3-yl)-2-({2-[(*tert*-butyldiphenylsilyloxy)methyl]phenyl}dimethylsilyl)thiophene (22′). To a mixture of **21** (1.16 g, 1.50 mmol), K_2CO_3 (0.52 g, 3.8 mmol), [(allyl)PdCl]$_2$ (13.2 mg, 36 μmol), RuPhos (74 mg, 0.160 μmol), and CuI (14.4 mg, 76 μmol) in DMF (1.2 mL) and THF (3.3 mL) was added **5″f** (1.02 g, 1.8 mmol), and the resulting mixture was stirred at 50 °C for 19 h. The mixture was filtered through a Florisil pad, and the filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (1.46 g, 89%) as a colorless viscous oil, $R_f = 0.30$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, $J = 7.7$ Hz, 1H), 7.70 (t, $J = 1.7$ Hz, 1H), 7.65 (t, $J = 1.3$ Hz, 1H), 7.62–7.23 (m, 26H), 7.17 (d, $J = 3.5$ Hz, 1H), 6.94 (d, $J = 3.5$ Hz, 1H), 5.03 (s, 2H), 4.732 (s, 2H), 4.728 (d, $J = 11.9$ Hz, 1H), 4.49 (d, $J = 11.9$ Hz, 1H), 4.47 (t, $J = 3.8$ Hz, 1H), 3.78–3.68 (m, 1H), 3.40–3.32 (m, 1H), 1.93 (s, 3H), 1.80–1.67 (m, 1H), 1.64–1.32 (m, 5H), 1.07 (s, 9H), 0.672 (s, 3H), 0.668 (s, 3H), 0.65 (s, 6H), 0.47 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 149.9, 146.8, 144.0, 141.6, 141.2, 140.8, 140.2, 137.8, 137.3, 137.0, 136.1, 135.6, 135.4, 135.3, 134.5, 134.3, 134.1, 133.2, 133.1, 131.9, 130.4, 129.8, 129.7, 129.6, 129.5, 129.4, 128.6, 127.53, 127.47, 126.8, 126.6, 126.1, 125.6, 124.5, 97.8, 68.9, 66.6, 65.5, 62.0, 30.6, 27.0, 25.5, 20.9, 19.5, 19.4, −0.2, −0.7, −0.80, −0.84 (two signals for sp^2-carbons overlap with others); IR (neat): 3049, 2955, 2918, 2851, 1736, 1578, 1560, 1541, 1466, 1435, 1427, 1377, 1364, 1250, 1225, 1202, 1126, 1113, 1080, 1061, 1026, 976, 831, 814, 775, 754, 700, 665 cm^{-1}; HRMS (FAB+) Calcd for $C_{66}H_{76}O_5SSi_4$: M^+, 1092.4491. Found: m/z 1092.4523.

Preparation of 5-(4′-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-{[2-(hydroxymethyl)phenyl]dimethylsilyl}biphenyl-3-yl)-2-({2-[(*tert*-butyldiphenylsilyloxy)methyl]phenyl}dimethylsilyl)thiophene (22). A solution of **22′** (1.46 g, 1.33 mmol) and PPTS (67 mg, 0.27 mmol) in MeOH (13 mL) and THF (6.7 mL) was stirred at rt overnight before concentration in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (1.1 g, 80%) as a colorless viscous oil, $R_f = 0.18$ (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.69 (m, 2H), 7.66–7.22 (m, 27H), 7.17 (d, $J = 3.5$ Hz, 1H), 6.94 (d, $J = 3.5$ Hz, 1H), 5.01 (s, 2H), 4.72 (s, 2H), 4.62 (d, $J = 6.0$ Hz, 2H), 1.92 (s, 3H), 1.42 (t, $J = 6.0$ Hz, 1H), 1.06 (s, 9H), 0.68 (s, 6H), 0.65 (s, 6H), 0.47 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 149.7, 146.8, 146.4, 141.4, 141.1, 140.9, 140.3, 138.0, 137.4, 137.0, 136.1, 135.6, 135.5, 135.3, 135.1, 134.5, 134.3, 134.2, 133.2, 133.1, 131.7, 130.2, 129.93, 129.89, 129.7, 129.5, 129.4, 127.8, 127.6, 127.5, 126.9, 126.6, 126.1, 125.8, 125.6, 124.6, 66.6, 65.5, 65.3, 27.0, 21.0, 19.4, −0.2, −0.8, −0.9; IR (neat): 3456, 3055, 3013, 2957, 2930, 2895, 2856, 1738, 1589, 1472, 1437, 1427, 1402, 1379, 1362, 1256, 1225, 1126, 1111, 1082, 1063, 1028, 1011, 978, 876, 833, 814, 777, 754, 702, 665, 650, 617, 592 cm^{-1}; Anal. Calcd for $C_{61}H_{68}O_4SSi_4$: C, 72.57; H, 6.79%. Found: C, 72.33; H, 6.57%.

Preparation of 5-[4′-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-(7-{dimethyl[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]silyl}-9,9-dioctyl-9*H*-fluoren-2-yl)biphenyl-3-yl]-2-({2-[(*tert*-butyldiphenylsilyloxy)methyl]phenyl}dimethylsilyl)thiophene (23). To a mixture of **22** (0.50 g, 0.50 mmol), K_2CO_3 (0.17 g, 1.25 mmol), [(allyl)PdCl]$_2$ (9.1 mg, 25 μmol), RuPhos (23 mg, 50 μmol), and CuI (4.8 mg, 25 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added **5c** (0.43 g, 0.60 mmol), and the resulting mixture was stirred at 50 °C for 24 h. The mixture was filtered through a Florisil pad, and the filtrate was diluted with diethyl ether and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the title compound (0.54 g, 73%) as a colorless viscous oil, $R_f = 0.28$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.21 (m, 36H), 7.01 (d, $J = 3.3$ Hz, 1H), 5.06 (s, 2H), 4.76 (s, 2H), 4.71 (d, $J = 12.1$ Hz, 1H), 4.53 (t, $J = 3.0$ Hz, 1H), 4.45 (d, $J = 11.9$ Hz, 1H), 3.87–3.77 (m, 1H), 3.51–3.42 (m, 1H), 2.08–1.90 (m, 4H), 1.96 (s, 3H), 1.90–1.77 (m, 1H), 1.72–1.43 (m, 5H), 1.37–0.86 (m, 20H), 1.08 (s, 9H), 0.80 (t, $J = 7.0$ Hz, 6H), 0.76–0.56 (m, 4H), 0.68 (s, 6H), 0.67 (s, 6H), 0.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 151.6, 150.0, 149.8, 146.8, 144.0, 142.7, 142.0, 141.5, 141.4, 141.2, 140.5, 139.7, 138.1, 137.6, 137.3, 136.9, 136.6, 136.1, 135.7, 135.5, 135.4, 135.2, 134.5, 134.4, 133.2, 133.1, 132.6, 129.9, 129.8, 129.50, 129.45, 129.4, 128.4, 128.2, 127.6, 127.5, 126.7, 126.6, 126.1, 126.0, 125.6, 125.2, 124.7, 124.0, 123.7, 121.4, 120.1, 119.2, 97.6, 68.8, 66.7, 65.5, 61.9, 55.2, 40.3, 31.9, 30.6, 30.1, 29.3, 27.0, 25.6, 24.0, 22.7, 21.0, 19.44, 19.41, 14.2, −0.21, −0.60, −0.69, −0.80 (a signal for sp^3-carbon overlaps with others); IR (neat): 3053, 3013, 2934, 2857, 1960, 1923, 1890, 1819, 1746, 1738, 1732, 1591, 1566, 1545, 1485, 1470, 1464, 1454, 1435, 1427, 1402, 1379, 1360, 1323, 1250, 1223, 1202, 1184, 1155, 1127, 1113, 1092, 1080, 1063, 1026, 1009, 978, 907, 876, 818, 777, 754, 702, 665, 657, 648, 623, 617, 592, 571, 554, 540 cm^{-1}; Anal. Calcd for $C_{95}H_{116}O_5SSi_4$: C, 76.97; H, 7.89%. Found: C, 76.68; H, 7.89%.

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