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An Efficient Convergent Synthesis of Novel Anisotropic Adsorbates Based on Nanometer-Sized and Tripod-Shaped Oligophenylenes End-Capped with Triallylsilyl Groups

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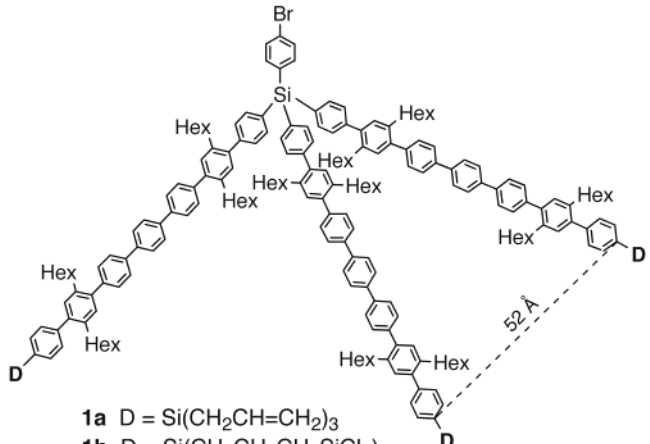
This article describes an efficient and convergent synthesis of a novel tripod-shaped oligophenylene compound. The compound consists of three oligophenylene heptamers as the tripod legs and one bromophenyl group as the functional arm, joining at a tetrahedron silicon atom. Each tripod leg is end-capped with a triallylsilyl group for covalently anchoring the molecules on hydrogen-terminated silicon surfaces via hydrosilylation. The compound may represent a new type of anisotropic adsorbates for controlling the orientation of and spacing between functional groups in organic thin films and nanostructures grown on silicon surfaces. An oligophenylene hexamer end-capped with a triallylsilyl group and a pinacol arylboronate group was readily derived from diiodoterphenyl with a bromophenyl boronic acid by selective Suzuki coupling. Reaction conditions for highly selective Suzuki coupling of sterically hindered pinacol boronate with aryl iodide in the presence of multiple ethenyl groups for the competing Heck reaction were developed. Under the optimal conditions (Pd-(PPh_3)$_4$/KOH/Bu_4NBr/toluene/H_2O, 85 °C, overnight), *p*-bromophenyl-tris(*p*-iodo-phenyl)silane reacted with 3 equiv of the hexaphenylene boronate to provide the tripod-shaped oligophenylene, composed of 22 phenylene and 9 allyl groups, in 78% yield.

Introduction

The orientation of and spacing between functional groups in organic thin films are critical for many applications. For example, alignment of molecules is necessary for eliciting nonlinear optical phenomena and orientation-dependent electronic and optical properties of conjugated molecules.[1] For biosensor applications, it is highly desirable to precisely control the spacing between the adjacent probe molecules in order to achieve maximum loading and yet not to hinder the interaction between the probe and target molecules.[2] Currently, many functional thin films are derived from self-assembled monolayers of long chain alkylsiloxane on polar surfaces or alkylthiolate on gold surfaces.[3] The orientation of the flexible molecules in these films is maintained by the close packing of the adjacent molecules. Although the average density of the functional groups on the monolayer surface can be adjusted by co-deposition with inert analogous adsorbates, it is difficult to avoid phase separation that prevents the control of spacing between surface functional groups at molecular level.[4]

In connection to our current research in novel organic thin films and nanostructures where the orientation and spacing of functional groups may be precisely controlled and single molecule AFM tips, we have designed a new type of adsorbates **1**. These compounds feature a rigid, oligophenylene-based tetrahedral framework that is multinanometric in dimension. For example, the distance between the bases of the tripod **1a**−**c** is about 52 Å according to geometry optimization with MM2.[5] The large size may allow direct observation of the individual molecules absorbed at surfaces by scanning probe microscopy. Although a wide variety of shape-persistent giant molecules have been constructed from rigid rod



1a D = $Si(CH_2CH{=}CH_2)_3$
1b D = $Si(CH_2CH_2CH_2SiCl_3)_3$
1c D = $Si(CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3)_3$

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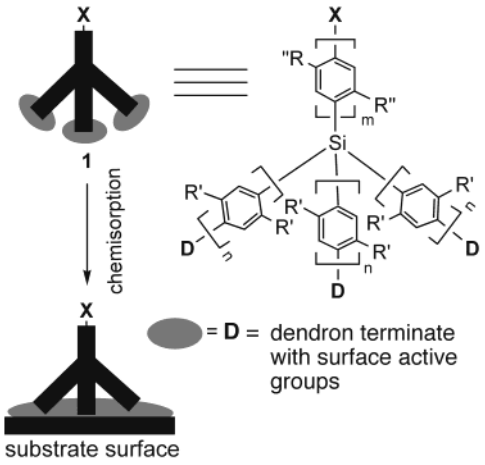
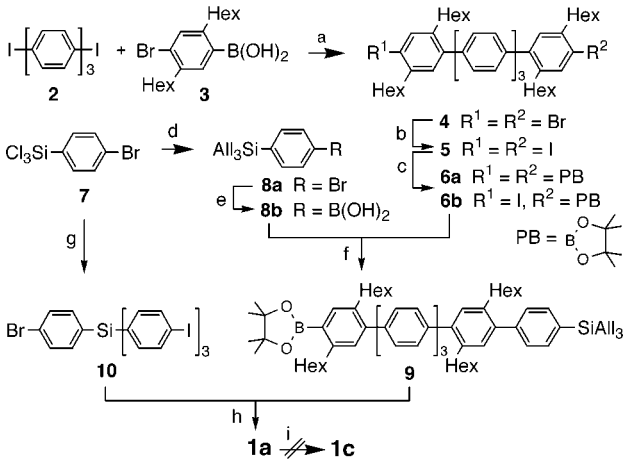
oligomers,[6] few tripod-shaped, nanometer-sized molecules have been reported.[6h−j] Tour[6i] and Shea[6j] proposed the use of such moleucles for modification of scanning probe microscopy tips. In particular, Yao and Tour described the design and synthesis of "molecular caltrops" whose core is based on a tetrahedral silicon atom, permitting the simple distinguishing of the four phenylacetylene arms.[6i] This strategy is adopted here for the designed of **1**. As compared to the monodentate adsorbates, tripodal rigid adsorbates have proven a better means to control the orientation of conjugated moiety attached at the focal point of the tripod in thin films.[7] Three of the four arms in the molecules of **1**, functioning as supporting arms, are each capped with a dendron, such as a carbosilane dendron,[8] that are terminated with multiple surface-active groups, such as alkenyl in **1a** and **1c** or $SiCl_3$ in **1b**, for covalently anchoring the molecules onto hydrogen-terminated silicon surfaces or hydroxylated surfaces, respectively.[3,9,10] Compared to the reported tripod-shaped



adsorbates that were designed for chemisorption on gold or metal surfaces through the relatively weak S-metal bonds,[6i,j,7] **1a**−**c** is larger and a multidentate base is attached to each of the tripod leg, leading to multiple strong Si−O or Si−C bonds between the base and a substrate surface, which should greatly enhance the stability against desorption of the molecules from the surface.[9] The remaining arm (functional arm) at the focal point of the molecular tripod is appointed orthogonal to the surface for derivatization. For example, the bromophenyl group in **1a** can be modified with a wide variety of moieties through palladium-catalyzed coupling reactions.[11] Precise control of surface properties of the films is possible by adjusting the four parameters: (1) the size (number of generation, *D*) of the dendrons; (2) the length of the arms (*m* and *n*); (3) the functional group (X) located at the functional arm; and (4) the side chains (R′, R″). Herein, we report an efficient synthesis of **1a**.

SCHEME 1. Divergent Synthesis of 1a−c[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_4$, aqueous Na_2CO_3, toluene, rt, 83%. (b) *t*-BuLi, THF, −78 °C; then I_2, 92%. (c) Bis(pinacolato)diboron, $PdCl_2$(dppf), KOAc, DMSO, 90 °C, 36% for **6a** and 25% for **6b**. (d) AllylMgBr, ether, reflux, 79%. (e) *n*-BuLi, ether, −78 °C; then triisopropylborate, 67%. (f) $Pd(PPh_3)_4$, aqueous Na_2CO_3, toluene, 80 °C, 98%. (g) *p*-IPhLi, ether, rt, 32%. (h) $Pd(PPh_3)_4$, aqueous KOH, Bu_4NBr, toluene, 85 °C, 78%. (i) $HSiCl_3$, H_2PtCl_6, THF, rt; AllylMgBr, ether, reflux.

Results and Discussion

An efficient synthesis of **1a** based on a convergent approach is summarized in Scheme 1. For rapid access to the oligo(phenylene) arms in **1a**, the diiodoterphenyl **2**,[12] obtained in one step from terphenyl, was employed as a building block. Another building block, the bromophenyl boronic acid **3**[13] with a hexyl side chain for increasing the solubility of the oligo(phenylene)s, was

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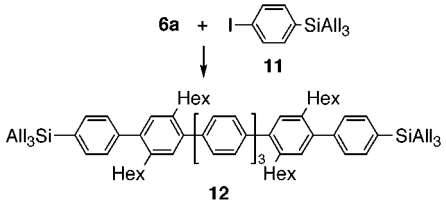
prepared in three steps from dichlorobenzene. The Suzuki coupling[11d,e] of the diiodide **2** with 2 equiv of the boronic acid **3** proceeded smoothly in toluene/H_2O at room temperature, providing the dibromo pentamer **4** in 83% yield. Despite the low solubility of **2** in the reaction mixture, no polymerization of the bifunctional **3** was observed. The high regioselectivity of coupling reaction is attributed to the much higher reactivity of the iodide **2** compared to that of the hindered bromide **3**. To facilitate the subsequent coupling reactions, the dibromide **4** was subjected to Br−I exchange by lithiation with 2 equiv of *t*-BuLi in THF at −78 °C followed by quenching with I_2 to give the diiode **5** in 92% yield. Pd-catalyzed Ishiyama−Miyaura reaction[14] of **5** with 1.5 equiv of bis(pinacolato)diboron produced the monosubstituted product **6b** in 25% yield, together with the disubstituted **6a** in 36% yield, which is a useful building block for the synthesis of oligo- and poly(phenylene) derivatives.[15]

Both ends of the supporting arms in **1a** were derived from bromophenyltrichlorosilane[16] (**7**, Scheme 1). Thus, treatment of **7** with allyl Grignard reagent led to the bromide **8a** in 79% yield, which was lithiated with *n*-BuLi and then quenched with triisopropylborate to provide the boronic acid **8b** in 67% yield. A key step in Scheme 1 is the incorporation of the triallylsilyl group to the supporting arm of **1a** via Suzuki coupling of **8b** and **6b**. It was envisioned that the boronic acid in **8b** is more reactive than the hindered pinacol borate in **6b** in the Suzuki coupling with the phenyliodide in **6b**, leading to the hexaphenylene **9** rather than the polymers of **6b**. However, it was not clear the extent of the interference of the three allyl groups in **8b** that could react with the iodide **6b** through Heck reaction[11a−c] under the Suzuki coupling conditions. Fortunately, the hexaphenylene **9** was obtained in excellent yield (98%). The ^{1}H NMR spectra of **9** exhibits a singlet (12 H) at 1.37 ppm, assigned to the four CH_3 of the pinacolato group, and a doublet at 2.88 ppm and two multiplets at 4.91−5.00 and 5.79−5.90 ppm corresponding to the three allyl groups.

For constructing the tripod framework, (4-bromophenyl)-tris(4-iodophenyl)silane (**10**) was prepared in 32% yield by treatment of **7** with 3 equiv of (*p*-iodophenyl)-lithium,[17,6i] obtained in situ by lithiation of *p*-diiodobenzene with 1 equiv of *n*-BuLi. The coupling of the triiodo derivative **10** with 3 equiv of the boronate **9** using common Suzuki coupling conditions for the synthesis of oligo- or poly(phenylene)s[15] ($Pd(PPh_3)_4$, toluene/H_2O, Na_2CO_3, 85 °C, 12 h) was unsatisfactory. The reaction was much slower than the coupling of the boronic acid **8b** with the iodide **6b** to **9**, and many unidentified byproducts with a close R_f were formed. This is likely due to the lower reactivity of the hindered boronate **9**, requiring harsh conditions to complete the Suzuki coupling with the triiodide **10**, which led to side reactions possibly including the Heck reaction between the allyl groups and the phenyliodo groups in the starting materials, the intermediates, and the product. Optimization studies on Suzuki coupling of a boronate derivative and a phenyliodide derivative in the presence of allyl groups were then performed using the diboron **6a** and 4-iodophenytriallylsilane (**11**) leading to **12** (Scheme 2); compound **11** was prepared in 64% yield by treatment of chlorotriallylsilane[17] with 4-iodophenyllithium. Many conditions were examined, including organic solvents and their mixture with H_2O (toluene, DMAc, THF, DMPU), base ($NaHCO_3$, $CsHCO_3$, Na_2CO_3, NaOH, KOH, $Ba(OH)_2$). and phase transfer catalyst (Bu_4NCl, Bu_4NBr, Bu_4NI, 18-crown-6). Among them, toluene/H_2O was the best solvent system. No reaction occurred in the absence of H_2O. In DMAc and DMPU, compound **6a** has a limited solubility, and the reaction was sluggish. In agreement with the previous observations,[18] a strong base, such as NaOH or KOH, greatly promoted the Suzuki coupling with the sterically hindered boronate **6a**. This was attributed to the formation of an "ate" complex of the boronate and OH^-, making the aryl group more nucleophilic for the transmetalation with the intermediate $Ar-Pd^{II}-I$ in the catalytic cycle.[11d,e] To further increase the effective concentration of OH^-, phase transfer catalyst was employed, and indeed, the coupling reaction was greatly facilitated. Under the optimized coupling conditions ($Pd(PPh_3)_4$/KOH/Bu_4NBr/toluene/H_2O, 90 °C, overnight), **12** was obtained in 88% yield.

SCHEME 2. Optimization of Suzuki Coupling Reaction between a Boronate and a Phenyliodide Derivative in the Presence of Allyl Groups



The above conditions were successfully applied to the coupling of **9** and **10** (Scheme 1) to afford the tripod-shaped oligophenylene **1a** in 78% yield. The separation of **1a** from the minor byproducts was difficult but could be achieved by preparative TLC, repeatedly eluted with hexane/toluene 3:1. The MALDI-TOF mass spectra of **1a** displayed a major peak at m/z = 3387, corresponding to **1a** complexed with a matrix molecule (dithranol) and with a loss of the bromine atom. Attempts to suppress the cleavage of the C−Br bond in **1a** during the MALDI process using a variety of conditions failed. The presence of the bromophenyl group in **1a** was indicated by the ^{13}C NMR signal at 124.9 ppm, assigned to the C-Br, based on the similar chemical shift observed in the bromides **4** (123.3 ppm), **8a** (124.3 ppm), and **10** (125.5 ppm). The ^{1}H NMR spectra of the compound show the presence of 9 allyl groups and 12 hexyl groups. Gel permeation chromatography of **1a** displayed only a single peak corresponding to the molecular weight of 6700 Dalton

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based on polystyrene standards. This high apparent molecular weight compared to the real molecular weight (3246 Dalton) of **1a** indicates a large hydrodynamic volume of the tripod structure.

Unfortunately, attempts to synthesize the carbosilane dendron **1c** through hydrosilylation of **1a** to **1b** with $HSiCl_3$ in the presence of H_2PtCl_6/*i*-PrOH (Speier's catalyst),[8,19] followed by treatment with CH_2=$CHCH_2$-MgBr, failed. The expected weak C-Br signal at 124.9 ppm in **1c** was absent in the ^{13}C NMR spectrum of the product, indicating that the Br-atom in **1a** was completely removed during the hydrosilylation possibly via reductive debromination in the presence of Pt catalyst and $HSiCl_3$. Lowering the amounts of $HSiCl_3$ and catalyst did not improve the reaction. This result was surprising in light of the reported compatibility of bromophenyl groups with hydrosilylation under similar conditions.[20]

In conclusion, we have developed an efficient convergent synthesis of novel nanometer-sized and tripod-shaped oligophenylenes designed as a new type of anisotropic adsorbates. The methodology developed in this work can be applied to the synthesis of analogous tripod-shaped oligophenylenes. The problem encountered in the synthesis of **1b** and **1c** from **1a** has promoted us to explore a more general and convergent approach to introduce dendrons to the base of the tripod legs, e.g., via amide formation between a oligophenylene tripod end-capped with a carboxy group and an allyl-terminated dendron with a NH_2 group located at the focal point. Nevertheless, the present work has provided the prototypic tripod adsorbate **1a**, which is the largest tripod-shaped adsorbate reported so far and contains nine surface-active allyl groups. The deposition of submonolayer and monolayer films of **1a** on hydrogen-terminated silicon surfaces and the characterization of the films are in progress and will be reported elsewhere.

Experimental Section

General. All of the reactions were carried out under a nitrogen atmosphere using Schlenk technique. Anhydrous diethyl ether and tetrahydrofuran (THF) were obtained by distillation under nitrogen from sodium/benzophenone ketyl. Flash chromatography was carried out on silica gel (200−400 mesh). All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using residual $CHCl_3$ as internal standard. Mass spectroscopy (MS) measurement was carried out using electron impact (EI), fast atom bombardment (FAB) or matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) technique. Samples for MALDI-TOF MS were prepared in a dithranol matrix, and the instrument was calibrated against bovine insulin standards. Compounds **2**,[12] **3**,[13] **7**,[14] and triallylchlorosilane[17] were prepared according to literature procedures.

4,4‴′-Dibromo-2,5,2‴,5‴′-tetrahexyl-[1,1′;4′,1″;4″,1‴;4‴,1‴′]quinquephenyl (4). A flask was charged with **3** (1.84 g, 4.98 mmol), **2** (1.20 g, 2.49 mmol), and $Pd(PPh_3)_4$ (57.8 mg, 1.0 mol %). A degassed solution of toluene (36 mL) and aqueous Na_2CO_3 (1 M, 15 mL, 15.0 mmol) was then added. The reaction mixture was vigorously stirred for 2 days at room temperature. The organic layer was separated, extracted with toluene, washed with water, and dried over anhydrous $MgSO_4$. Flash chromatography (hexane/toluene 200:1) gave **4** as a colorless solid (1.82 g, 83% yield). Mp < 30 °C. ^1H NMR ($CDCl_3$, 300 MHz): 0.82 (t, 6H, J = 6.8 Hz), 0.89 (t, 6H, J = 6.8 Hz), 1.17−1.69 (m, 32H), 2.56 (t, 4H, J = 7.5 Hz), 2.72 (t, 4H, J = 7.5 Hz), 7.10 (s, 2 H), 7.37 (d, 4H, J = 8.2 Hz), 7.46 (s, 2H), 7.70 (d, 4H, J = 8.2 Hz), 7.76 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 140.6 (broad), 140.2, 139.8, 139.7, 139.2 (broad), 133.1, 131.6, 129.6, 127.4, 126.7, 123.3, 35.8, 32.4, 31.7, 31.5, 31.2, 30.0, 29.1, 29.0, 22.6, 22.5, 14.1, 14.0. MS (FAB, *m*/*z*): calcd for $C_{54}H_{68}Br_2$ (M^+) 876.4, found 876.5. Anal. Calcd: C, 73.96; H, 7.82; Br, 18.22. Found: C, 74.15; H, 7.91; Br, 17.90.

4,4‴′-Diiodo-2,5,2‴,5‴′-tetrahexyl-[1,1′;4′,1″;4″,1‴;4‴,1‴′]quinquephenyl (5). To a solution of *t*-BuLi (1.65 M in pentane, 30.3 mL, 50.0 mmol) in dry THF (50 mL) at −78 °C was added **4** (10.96 g, 12.5 mmol) in THF (50 mL). After the addition, the reaction mixture was stirred for 50 min, treated with a solution of I_2 (13.19 g) in THF (170 mL), and then warmed to room temperature. The reaction mixture was extracted with toluene and washed with aqueous $Na_2S_2O_3$ and then water. The combined organic fractions were dried over $MgSO_4$. Flash chromatography (silica gel, hexanes/toluene 20:1) gave **5** as a white solid (11.1 g, 92%). Mp = 69−72 °C. ^1H NMR ($CDCl_3$, 300 MHz): 0.84 (t, 6H, J = 6.6 Hz), 0.91 (t, 6H, J = 6.6 Hz), 1.17−1.69 (m, 32H), 2.55 (t, 4H, J = 8.1 Hz), 2.71 (t, 4H, J = 8.4 Hz), 7.10 (s, 2H), 7.39 (d, 4H, J = 8.4 Hz), 7.72 (d, 4H, J = 8.4 Hz), 7.76 (s, 2H), 7.78 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 142.6, 141.5, 140.3, 140.0, 139.9, 139.7, 139.2, 130.6, 129.6, 127.4, 126.7, 99.5, 40.4, 32.3, 31.7, 31.5, 31.2, 30.4, 29.17, 29.12, 22.6, 22.5, 14.1, 14.0. MS (EI, *m*/*z*): calcd for $C_{54}H_{68}I_2$ (M^+) 970.3, found 970.3. Anal. Calcd: C, 66.80; H, 7.06. Found: C, 66.44; H, 7.28.

5-Mer Diboronate (6a) and 5-Mer Monoboronate (6b). A 200 mL round-bottom flask was charged with KOAc (3.07 g, 31.2 mmol) and dried under high vacuum at 100 °C for 1 h. After it cooled to room temperature, a solution of **5** (10.01 g, 10.3 mmol), bis(pinacolato)diboron (3.82 g, 15.0 mmol), and $PdCl_2$(dppf) (282.8 mg, 0.30 mmol) in anhydrous DMSO (60 mL) was added. The reaction mixture was vigorously stirred at 90 °C overnight. The mixture was extracted twice with toluene. The combined organic layers were washed once with H_2O and dried over $MgSO_4$. Flash chromatography (silica gel, hexane/toluene 3:1 to 2:1) gave **6a** (3.49 g, 36%) and **6b** (2.37 g, 25%) as white solids. **6a**: Mp = 128−130 °C. ^1H NMR ($CDCl_3$, 300 MHz): 0.82 (t, 6H, J = 6.7 Hz), 0.90 (t, 6H, J = 6.4 Hz), 1.16−1.64 (m, 32H), 1.37 (s, 24H), 2.61 (t, 4H, J = 8.1 Hz), 2.88 (t, 4H, J = 8.0 Hz), 7.09 (s, 2H), 7.41 (d, 4H, J = 8.1 Hz), 7.71 (d, 4H, J = 8.1 Hz), 7.71 (s, 2H), 7.77 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 147.5, 143.6, 141.3, 139.7, 139.0, 137.2, 136.8, 130.9, 129.6, 127.4, 126.5, 83.3, 35.5, 33.5, 32.6, 31.8, 31.7, 31.5, 29.5, 29.3, 24.8, 22.7, 22.5, 14.1, 14.0. MS (EI, *m*/*z*): calcd for $C_{66}H_{92}B_2O_4$ (M^+) 970.7, found 970.6. Anal. Calcd: C, 81.63; H, 9.55. Found: C, 81.62; H, 9.48. **6b**: Mp = 102−106 °C. ^1H NMR ($CDCl_3$, 300 MHz): 0.80−0.85 (m, 6H), 0.88−0.92 (m, 6H), 1.20−1.62 (m, 32H), 1.38 (s, 12H), 2.55 (t, 2H, J = 8.1 Hz), 2.62 (t, 2H, J = 8.1 Hz), 2.70 (t, 2H, J = 7.5 Hz), 2.89 (t, 2H, J = 8.0 Hz), 7.09 (s, broad, 2H), 7.38 (d, J = 7.8, 2H), 7.42 (d, J = 8.5, 2H), 7.71 (d, J = 7.5, 4H), 7.72 (s, 1H), 7.76 (s, 1H), 7.77 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 147.5, 143.7, 142.7, 141.7, 141.5, 140.3, 140.1, 140.0, 139.9, 139.7, 139.4, 139.0, 137.2, 136.8, 130.9 (broad), 130.7, 129.8, 129.7, 129.6, 127.5, 127.4, 126.7, 126.6, 99.5, 83.4, 40.4, 35.6, 33.5, 32.7, 32.3, 31.9, 31.7, 31.65, 31.60, 31.5, 31.2, 30.4, 29.5, 29.3, 29.2, 29.1, 24.9, 22.7, 22.6, 22.5, 14.13, 14.06. MS (EI, *m*/*z*): calcd for $C_{60}H_{80}BIO_2$ (M^+) 970.5, found 970.3. Anal. Calcd: C, 74.22; H, 8.30. Found: C, 74.37; H, 8.10.

4-Bromophenyltriallylsilane (8a). A solution of **7** (10.2 g, 35.0 mmol) in anhydrous ether (15 mL) was added dropwise to allylmagnesium bromide (1.0 M in ether, 105 mL, 105 mmol). The mixture was refluxed overnight and hydrolyzed with aqueous H_2SO_4 (10%, 35 mL). The organic layer was separated, and the aqueous phase was extracted twice with ether. The combined organic fractions were dried over anhydrous $MgSO_4$. The solvent was removed in a vacuum to give a pale yellow liquid. Fractional distillation at 97 °C/1 mmHg

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gave **8a** (8.5 g, 79%) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.83−1.86 (m, 6H), 4.88−4.95 (m, 6H), 5.69−5.84 (m, 3H), 7.37 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 135.8, 134.0, 133.4, 130.9, 124.3, 114.6, 19.4. MS (EI, m/z): calcd for $C_{15}H_{39}BrSi$ (M^+) 306.0, found 306.0. Anal. Calcd: C, 58.63; H, 6.23. Found: C, 58.55; H, 6.17.

4-Triallylphenylboronic Acid (8b). To a solution of **8a** (4.50 g, 14.61 mmol) in ether (50 mL) at −78 °C was added *n*-BuLi in hexane (2.45 N, 6.14 mL, 14.61 mmol). After the addition, the solution was stirred for 2 h at room temperature, transferred into an additional funnel under N_2, and added dropwise into a solution of triisopropylboronate (5.50 g, 29.2 mmol) in ether (200 mL) at −78 °C. After the addition, the white suspension was stirred overnight at room temperature and hydrolyzed with aqueous HCl (2 M, 45 mL). The organic layer was separated, and the aqueous solution was extracted twice with ether. The combined organic fractions were dried over anhydrous $MgSO_4$. Flash chromatography (silica gel, hexane/ether 1:1) gave **8b** as a white solid (2.66 g, 67% yield). Mp = 59−62 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.93 (d, 6H, J = 7.8 Hz), 4.91−4.99 (m, 6H), 5.75−5.90 (m, 3H), 7.67 (d, 2H, J = 7.8 Hz), 8.21 (d, 2H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 140.9, 134.6, 133.8, 133.6, 114.5, 19.4.

6-Mer Boronate (9). A flask was charged with **6b** (97.1 mg, 0.10 mmol), **8b** (28.0 mg, dehydrated, 0.11 mmol), and $Pd(PPh_3)_4$ (1.1 mg, 0.95 μmol). A degassed solution of toluene (0.6 mL) and aqueous Na_2CO_3 (1 M, 0.30 mL) was added. The mixture was stirred at 80 °C overnight. The mixture was diluted with toluene, washed with water, and dried over anhydrous $MgSO_4$. Flash chromatography (hexane/AcOEt 40:1) gave **9** as a colorless viscous liquid (105 mg, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80−0.84 (m, 9H), 0.87−0.92 (m, 3H), 1.19−1.33 (m, 24H), 1.37 (s, 12H), 1.48−1.56 (m, 8H), 1.93 (d, 6H, J = 8.1 Hz), 2.56−2.66 (m, 6H), 2.88 (t, 2H, J = 8.1 Hz), 4.91−5.00 (m, 6H), 5.79−5.90 (m, 3H), 7.09 (s, 1H), 7.17 (s, 1H), 7.19 (s, 1H), 7.38 (d, 2H, J = 8.4 Hz), 7.41 (d, 2H, J = 8.1 Hz), 7.47 (d, 2H, J = 7.8 Hz), 7.58 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 7.8 Hz), 7.70 (s, 1H), 7.73 (d, 2H, J = 8.1 Hz), 7.78 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 147.5, 143.6, 142.9, 141.3, 141.0, 140.6, 140.4, 139.8, 139.7, 138.9, 137.6, 137.5, 136.8, 133.9, 133.2, 130.9, 130.8, 129.8, 129.6, 128.7, 127.4, 126.6, 126.5, 114.3, 83.3, 35.5, 33.5, 32.64, 32.59, 31.8, 31.7, 31.5, 31.45, 31.38, 31.3, 29.7, 29.5, 29.3, 29.24, 29.20, 29.1, 24.9, 22.7, 22.52, 22.49, 19.7, 14.1, 14.0. MS (EI, m/z): calcd for $C_{75}H_{99}BO_2Si$ (M^+) 1070.8, found 1070.6. Anal. Calcd: C, 84.07; H, 9.31. Found: C, 83.76; H, 9.39.

(4-Bromophenyl)-tris(4-iodophenyl)silane (10). To a suspension of 1,4-diiodobenzene (1.32 g, 4.0 mmol) in anhydrous ether (25 mL) at −78 °C was added *n*-BuLi in hexane (2.45 N, 1.27 mL, 3.1 mmol). The solution was stirred for at −78 °C for 1 h and treated with **7** (0.291 g, 1.0 mmol). The white suspension was stirred overnight at room temperature and treated with water (10 mL). The organic layer was separated, and the aqueous solution was extracted twice with ether. The combined organic fractions were dried over anhydrous $MgSO_4$. The solvent was removed in a vacuum to give a crystalline white solid. Flash chromatography (silica gel, hexane/tolulene 20:1) gave **10** as a white solid (230 mg, 32%). Mp = 298−301 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.19 (d, 6H, J = 8.7 Hz), 7.33 (d, 2H, J = 8.1 Hz), 7.53 (d, 2H, J = 8.1 Hz), 7.74 (d, 6H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 137.8, 137.6, 137.5, 132.1, 131.5, 128.3, 125.5, 97.7. MS (EI, m/z): calcd for $C_{24}H_{16}BrI_3Si$ (M^+) 791.7, found 791.6. Anal. Calcd: C, 36.35; H, 2.03. Found: C, 36.29; H, 1.86.

4-Iodophenyltriallylsilane (11). To a suspension of 1,4-diiodobenzene (9.90 g, 30.0 mmol) in ether (200 mL) at −78 °C was added *n*-BuLi in hexane (2.45 N, 12.3 mL, 30.0 mmol). After the addition, the solution was stirred for 1 h and treated with chlorotriallylsilane (5.90 g, 30.0 mmol). The white suspension was stirred overnight at room temperature and quenched with H_2O (30 mL). The organic layer was separated, and the aqueous solution was extracted twice with ether. The combined organic fractions were dried over $MgSO_4$. The solvent was removed in a vacuum to give a pale yellow liquid. Flash chromatography (silica gel/hexane) gave **11** as a colorless liquid (6.85 g, 64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): 1.82−1.86 (m, 6H), 4.88−4.96 (m, 6H), 5.70−5.84 (m, 3H), 7.24 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 136.8, 135.8, 134.6, 133.4, 114.6, 96.5, 19.3. MS (EI, m/z): calcd for $C_{15}H_{39}ISi$ (M^+) 354.0, found 354.0. Anal. Calcd: C, 50.85; H, 5.41. Found: C, 50.83; H, 5.37.

Optimized Reaction Conditions for Suzuki Coupling of 6a and 11 to 12. A flask was charged with **11** (35.4 mg, 0.10 mmol), **6a** (48.6 mg, 0.05 mmol), $Pd(PPh_3)_4$ (1.7 mg, 0.0015 mmol), KOH (28 mg, 0.50 mmol), and *n*-Bu_4NBr (2.8 mg, 0.0087 mmol). A degassed solution of toluene (0.5 mL) and water (0.2 mL) was then added. The mixture was stirred at 90 °C overnight. The organic layer was separated, extracted with toluene, washed with water, and dried over anhydrous $MgSO_4$. Flash chromatography (silica gel, hexane/EtOAc 40:1) gave **12** as a white solid (52 mg, 88%). Mp = 86−88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.85 (t, 12H, J = 6.4 Hz), 1.14−1.31 (m, 24H), 1.46−1.61 (m, 8H), 1.96 (d, 12H, J = 8.4 Hz), 2.60−2.70 (m, 8H), 4.94−5.02 (m, 12H), 5.80−5.96 (m, 6H), 7.19 (s, 2H), 7.22 (s, 2H), 7.40 (d, 4H, J = 8.1 Hz), 7.50 (d, 4H, J = 8.4 Hz), 7.61 (d, 4H, J = 8.4 Hz), 7.76 (d, 4H, J = 8.1 Hz), 7.81 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 143.0, 141.1, 140.7, 140.4, 139.8, 139.0, 137.6, 134.0, 133.3, 131.0, 130.9, 129.8, 128.7, 127.4, 126.6, 114.3, 32.7, 31.6, 31.54, 31.46, 29.3, 29.2, 22.5, 19.7, 14.0. Calcd for $C_{84}H_{106}Si_2$ (M^+) 1170.8, found 1171.0. Anal. Calcd: C, 86.09; H, 9.12. Found: C, 85.64; H, 9.03.

Tripod Compound (1a). A flask was charged with **10** (31.8 mg, 0.04 mmol), **9** (132.8 mg, 0.124 mmol), $Pd(PPh_3)_4$ (2.0 mg, 0.0018 mmol), KOH (33.6 mg, 0.60 mmol), and *n*-Bu_4NBr (3.3 mg, 0.010 mmol). A degassed solution of toluene (0.5 mL) and water (0.2 mL) was added. The mixture was stirred at 85 °C overnight. The mixture was diluted with toluene, washed with water, and dried over $MgSO_4$. Preparative TLC (silica gel, repeatedly eluted with hexane/toluene 3:1) gave **1a** as a colorless solid (101 mg, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80−0.92 (m, 36H), 1.19−1.38 (m, 72H), 1.50−1.68 (m, 24H), 1.99 (d, 18H, J = 8.1 Hz), 2.56−2.80 (m, 24H), 4.95−5.08 (m, 18H), 5.84−6.01 (m, 9H), 7.24−7.94 (m, 76H). ^{13}C NMR ($CDCl_3$, 75 MHz): 143.8, 143.2, 141.3, 140.8, 140.7, 140.5, 139.9, 139.1, 138.1, 137.9, 137.6, 136.2, 134.0, 133.5, 132.0, 131.3, 131.06, 130.99, 130.95, 129.9, 129.1, 128.8, 127.5, 126.6, 124.9, 114.4, 32.8, 31.59, 31.55, 31.46, 31.38, 29.2, 22.5, 19.9, 14.0. MALDI-TOF MS (dithranol as matrix) (m/z): calcd for $C_{245}H_{287}BrO_3Si_4$ [M + Matrix − Br]$^+$ 3389, found 3388.

Attempted Synthesis of 1b and 1c. A Schlenk flask was charged with **1a** (50 mg, 0.0154 mmol), THF (0.5 mL), $HSiCl_3$ (56 mg, 0.554 mmol), and a drop of H_2PtCl_6 in *i*-PrOH (0.1 M). The reaction mixture was stirred at room temperature overnight. The reaction was monitored by ^{1}H NMR until the disappearance of the allyl groups. The solvents were removed under high vacuum to give an oil. Dry THF (1.0 mL) was added to dissolve the residue under Ar. Allylmagnesium bromide (1.0 M in ether, 0.28 mL, 0.28 mmol) was added dropwise. The mixture was refluxed overnight, hydrolyzed with aqueous HCl (1 M), diluted with toluene, washed with water, and dried over $MgSO_4$. Preparative TLC (silica gel, repeatedly eluted with hexane/toluene 3:1) gave a white solid (28 mg). ^{13}C NMR ($CDCl_3$, 75 MHz): showed the absence of the C-Br signal at 124.9 ppm.

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Supporting Information Available: NMR spectra of **8b**, **1a**, and the products of hydrosilylation and Grignard reaction of **1a**; MALDI-TOF MS and GPC of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.
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