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Synthesis of Hexa(furan-2-yl)benzenes and Their π-Extended Derivatives

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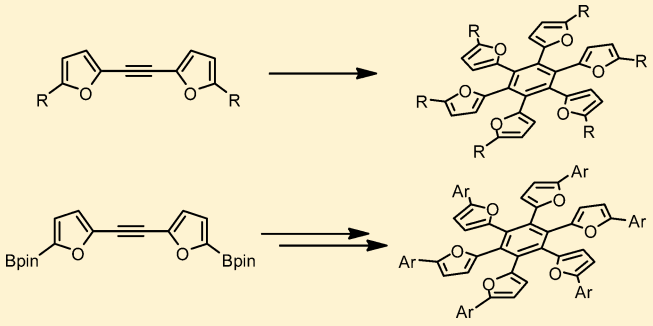
Supporting Information

ABSTRACT: The first synthesis of hexa(furan-2-yl)benzene derivatives is described. The $RhCl_3$/*i*-Pr_2NEt-catalyzed cyclotrimerization of di(furan-2-yl)acetylenes was an effective method for constructing hexa(furan-2-yl)benzene derivatives in good yields. Their π-extended derivatives were also synthesized by Suzuki−Miyaura coupling between hexakis(5-Bpinfuran-2-yl)benzene (Bpin = (pinacolato)boryl) and several aryl iodides.



Furan is an important skeleton that is commonly observed in nature.[1] Over the past decade, furan has also attracted attention as a key building block for π-conjugated compounds that have the potential for application in organic materials such as semiconductors[2] and photovoltaics.[3] Therefore, a facile access to a variety of π-conjugated furans is an important research field in organic chemistry. In addition, two-dimensional aromatic cores, such as starburst hexaarylbenzene derivatives,[4] have been synthesized, and their electrochemical and optical properties have been intensively studied.[5] In particular, Müllen and co-workers have reported several studies on this topic.[6] However, there have been a few reports on the synthesis of hexaheteroarylbenzenes. For instance, there have been few reports on the preparation of hexathienylbenzene,[7] hexapyridylbenzene,[8] and hexapyrrolylbenzene[9] derivatives and no report on hexafurylbenzenes, although they should serve as novel fascinating building blocks (Scheme 1). Additionally, to the best of our knowledge, the crystal structures of these heteroarylbenzenes have not yet been reported, except for that of hexa(1-pyrrolyl)benzene,[9c] and there is no information available on the conformations of other hexaheteroarylbenzenes, which should be important from the perspective of material science.

While one of the most straightforward ways for constructing hexaarylbenzenes is the transition-metal-catalyzed cyclotrimerization of diarylacetylenes,[10] this method is usually not suitable for use with hexaheteroarylbenzenes. The difficulty of the synthesis of hexaheteroarylbenzenes is caused by the competitive dimerization of the internal alkynes (Scheme 2). Weber reported that the reaction of di(thiophene-2-yl)-acetylene catalyzed by $RuH_2(CO)(PPh_3)_3$ gave a dimerized product, a benzothiophene derivative, as the major product, and hexa(thiophene-2-yl)benzene was obtained in only 5% yield.[7a] To avoid this problem, several methods have been reported. Müllen reported that the Co-catalyzed cyclotrimerization of di(thiophene-2-yl)acetylene bearing a long alkyl chain at the α-position of thiophenes proceeded to give hexa(thiophene-2-yl)benzene in good yield.[7b] Lin and Tao reported a tandem Kosugi−Migita−Stille coupling between tributyl(thiophene-2-yl)stannane and hexabromobenzene.[7c] For the synthesis of hexapyrrolylbenzene, Meijer reported an elimination−addition-type reaction using 1-pyrrolylsodium and hexafluorobenzene.[9c] Breslow reported another type of transformation of hexa-(pyridin-4-yl)benzene, which was synthesized by the reductive dimerization of a cyclopentene intermediate.[8a]

We recently reported an efficient method for the synthesis of hexa(thienyl)benzene derivatives by $RhCl_3$/*i*-Pr_2NEt-catalyzed cyclotrimerization of dithienylacetylenes and found that they are potent candidates for capacitor materials.[7d,e,11] In the present study, we turned our attention to the synthesis of hexa(furan-2-yl)benzenes, and we report here the first synthesis and X-ray single-crystal analyses of hexa(furan-2-yl)benzene derivatives.

We first carried out the synthesis of hexa(furan-2-yl)benzene (**2a**) by cyclotrimerization of di(furan-2-yl)acetylene (**1a**) (Table 1). Optimization of the catalyst revealed that the combination of $RhCl_3 \cdot 3H_2O$ and *i*-Pr_2NEt was essential for the reaction. In the presence of a catalytic amount of $RhCl_3 \cdot 3H_2O$ (8 mol %) and *i*-Pr_2NEt (30 mol %), the cyclotrimerization of

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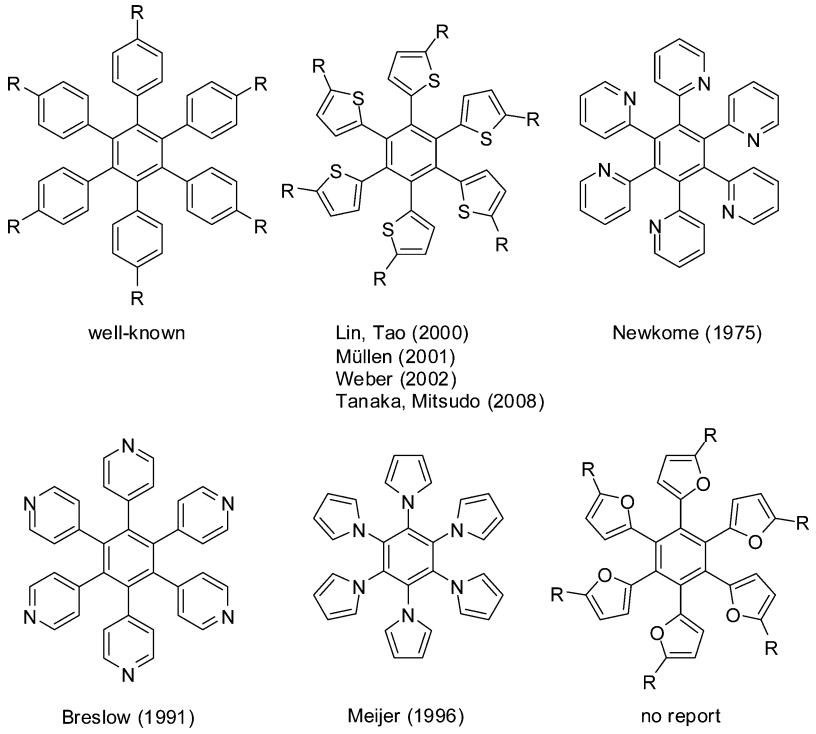
Scheme 1. Hexaarylbenzenes and Hexaheteroarylbenzenes



Scheme 2. Competition between the Trimerization and Dimerization of Diheteroarylacetylenes

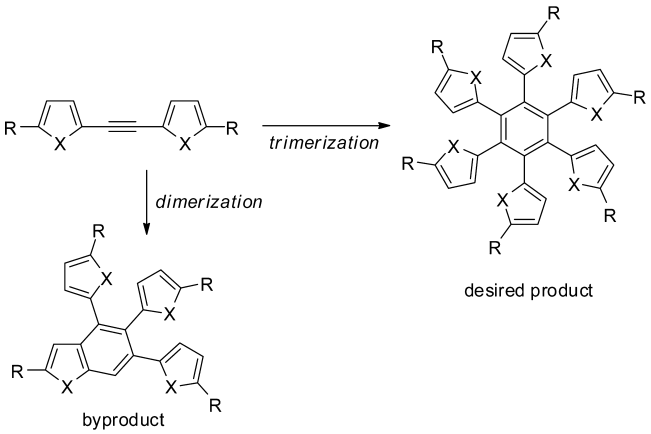
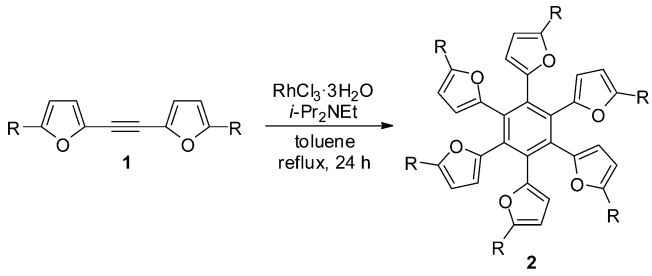


Table 1. Rh-Catalyzed [2 + 2 + 2] Cyclization of Difurylalkyne 1[a]



entry	R (**1**)	**2**	yield[b] (%)
1	H (**1a**)	**2a**	50
2	Me (**1b**)	**2b**	81
3	Bpin (**1c**)	**2c**	80 (55)[c]

[a]Reaction conditions: **1** (0.5 mmol), $RhCl_3·3H_2O$ (8 mol %), *i*-Pr_2NEt (30 mol %), toluene (2 mL), reflux, 24 h. [b]Isolated yield. [c]Performed with 2.5 mmol of **1c**.

1a proceeded smoothly to give **2a** in 50% yield (entry 1). In a similar manner, the cyclotrimerization of bis(5-methylfuran-2-yl)acetylene (**1b**) afforded hexakis(5-methylfuran-2-yl)benzene (**2b**) in 81% yield (entry 2). Compound **2c** bearing six (pinacolato)boryl (Bpin) moieties could also be obtained in 80% yield from a di(furan-2-yl)acetylene bearing two Bpin moieties (**1c**) (entry 3). Increasing the amount of **1c** to 2.5 mmol, the yield of **2c** decreased to 55%. The structures of **2a**–**c** were confirmed by X-ray single crystal analyses (Figure 1). To the best of our knowledge, **2a**–**c** are the first hexafurylbenzene derivatives to be synthesized, and this is the first report on the crystal structures of hexa(2-heteroaryl)benzenes.

NMR analyses of **2a**–**c** exhibited that their six furan rings, and the six substituents at the 5-position of the furan rings were equivalent on the NMR time scale. In contrast, X-ray analyses revealed that their crystal structures were different. For instance, X-ray analysis of **2b** revealed that it has a C_2-symmetric structure in the crystal, and there are two kinds of nonequivalent furan rings. The two furan rings associated with the *p*-position were nearly perpendicular to the benzene ring, and the dihedral angles were 82°. The four other furan rings leaned toward the benzene ring with a dihedral angle of 42°. The optimized structures calculated by density functional theory (DFT) at the B3LYP/6-31G(d) level were similar to the X-ray structures (Figure 2). At the HOMO-level, π–π conjugation was observed between the four leaning furan rings and the benzene. These results suggest that the six furan rings of **2** freely rotated in solution and were fixed in a conjugated structure in crystal form.

To expand the synthetic utility of the reaction, we next converted hexakis(5-Bpinfuran-2-yl)benzene (**2c**) to hexakis(5-arylfuran-2-yl)benzenes by Suzuki–Miyaura coupling (Table

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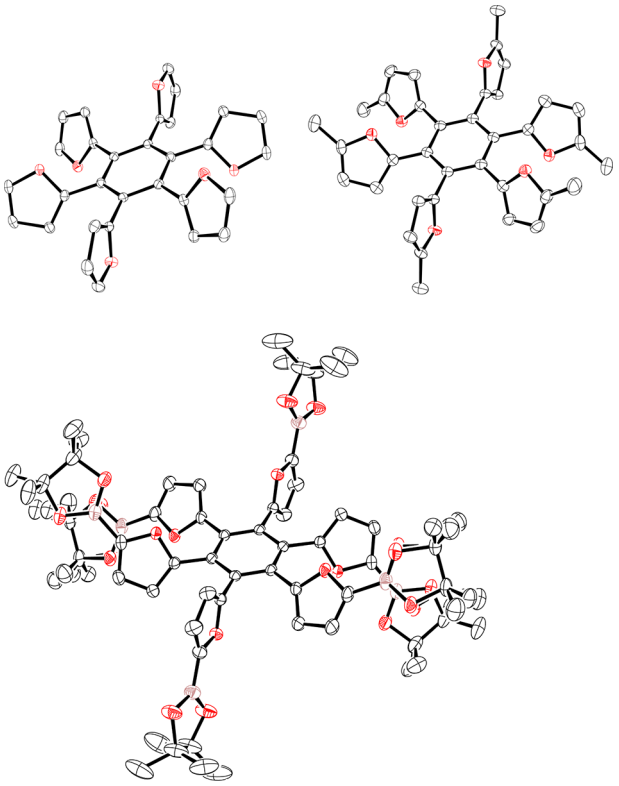


Figure 1. ORTEP drawings of **2a** (left top), **2b** (right top), and **2c** (bottom) (50% probability ellipsoids; hydrogen atoms omitted for clarity).

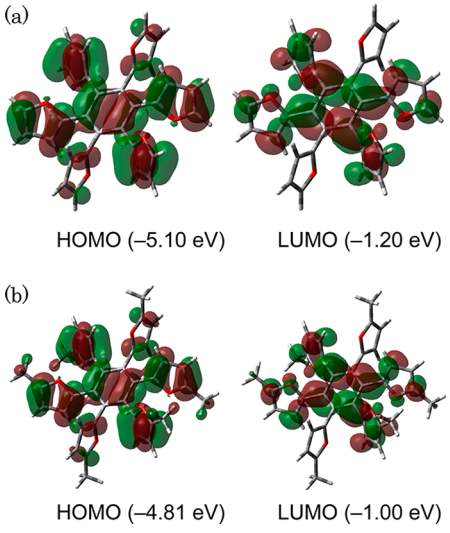
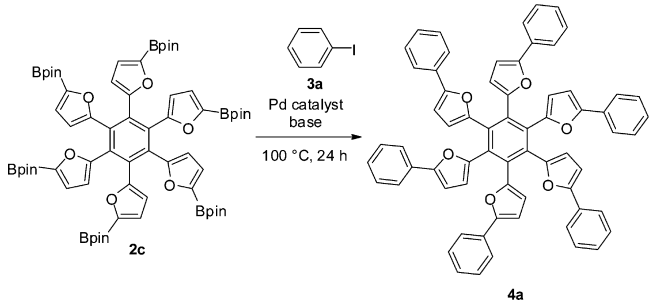


Figure 2. Kohn–Sham HOMO and LUMO of **2a** (a) and **2b** (b) calculated at the B3LYP/6-31G(d) level of theory.

2). In the presence of $Pd(PPh_3)_4$ (10 mol %) and base (0.6 mmol), **2c** (0.05 mmol) was treated with iodobenzene **3a** (0.35 mmol) in 0.5 mL of DME at 100 °C. When NaOAc or Na_2CO_3 was used as a base, the desired coupling product was not obtained at all (entries 1 and 2). Screening of the base revealed that Cs_2CO_3 was an effective base for the reaction, and hexaphenyl-substituted hexa(furan-2-yl)benzene (**4a**) was obtained in 48% yield (entry 3). In the next step, we evaluated different Pd(0) complexes as catalysts and found that the use of $Pd[P(t\text{-}Bu)_3]_2$ slightly increased the yield of **4a** (50% yield,

Table 2. Suzuki–Miyaura Coupling of 2c and Iodobenzene (3a)[a]



entry	Pd catalyst	base	solvent	yield[b] (%)
1	$Pd(PPh_3)_4$	NaOAc	DME	nd[c]
2	$Pd(PPh_3)_4$	Na_2CO_3	DME	nd
3	$Pd(PPh_3)_4$	Cs_2CO_3	DME	48
4	$Pd[P(t\text{-}Bu)_3]_2$	Cs_2CO_3	DME	50 (70)[d]
5	$Pd[P(t\text{-}Bu)_3]_2$	Cs_2CO_3	DME/H_2O (4/1)	38
6	$Pd[P(t\text{-}Bu)_3]_2$	Cs_2CO_3	DMF	56
7	$Pd[P(t\text{-}Bu)_3]_2$	Cs_2CO_3	toluene	26
8	$Pd[P(t\text{-}Bu)_3]_2$	Cs_2CO_3	1,4-dioxane	6

[a]Reaction conditions: **2c** (0.05 mmol), iodobenzene **3a** (0.35 mmol), Pd catalyst (10 mol %), base (0.6 mmol), solvent (0.5 mL), 100 °C, 24 h. [b]Isolated yield. [c]Not detected. [d]Performed in 1.0 mL of solvent.

entry 4). The concentration of the reaction mixture also highly influenced the reaction. With 1.0 mL of DME, the yield of **4a** dramatically increased to 70%. Screening of the solvent was examined next (entries 5–8). In the presence of water, protonated byproducts were observed and the yield of **4a** decreased (entry 5). DMF was similarly an effective solvent, and **4a** was obtained in 56% yield (entry 6). In contrast, toluene and 1,4-dioxane were ineffective solvents in the reaction (entries 7 and 8).

Finally, under the optimized conditions, several aryl iodides were applied to the sequential Suzuki–Miyaura coupling (Table 3). With *p*-iodotoluene (**3b**) or *p*-iodoanisole (**3c**), the corresponding coupling products **4b** and **4c** were obtained in 60% and 76% yields, respectively (entries 2 and 3). We next performed the coupling reaction using iodoarenes bearing electron-withdrawing groups. With *p*-chloroiodobenzene (**3d**), **4d** was obtained in 62% yield (entry 4). *p*-Fluoroiodobenzene (**3e**) and *p*-trifluoromethyliodobenzene (**3f**) could also be applied to the reaction, and the corresponding hexafurylbenzene derivatives were both obtained in 60% yield (entries 5 and 6). We next sought to construct molecules with a further π-extended system. With the use of *p*-cyanoiodobenzene (**3g**) or 1-iodonaphthalene (1-NpI, **3h**), coupling adducts **4g** and **4h** were obtained (92% and 88%, entries 7 and 8).

The crystal structures of **4a** and **4f** were confirmed by X-ray crystallography (Figure 3). While the conformation of the furan rings of these compounds was different from those of **2a–c**, the six furan rings of **4a–h** were equivalent in NMR measurement, the same as those of **2a–c**. In particular, the packing structure of **4f** was quite different from those in the other compounds, probably due to the intra- and intermolecular interactions between trifluoromethyl groups. These results suggest that their furan rings would rotate freely, and their structures in the solid state highly depend on the substituents on the furan rings.

In conclusion, we have achieved the first synthesis of hexa(furan-2-yl)benzene derivatives by the $RhCl_3$/*i*-Pr_2NEt-

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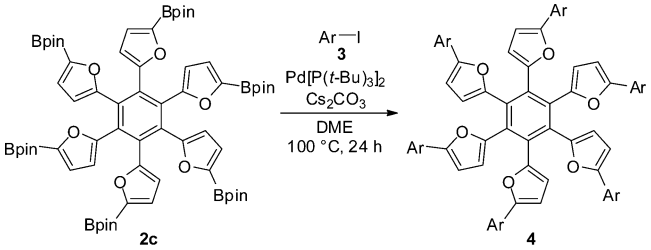
Table 3. Synthesis of Various Hexakis(5-arylfuran-2-yl)benzenes[a]



entry	Ar (3)	4	yield[b] (%)
1	C_6H_5 (**3a**)	**4a**	70
2	*p*-MeC_6H_4 (**3b**)	**4b**	60
3	*p*-$MeOC_6H_4$ (**3c**)	**4c**	76
4	*p*-ClC_6H_4 (**3d**)	**4d**	62
5	*p*-FC_6H_4 (**3e**)	**4e**	60
6[c]	*p*-$CF_3C_6H_4$ (**3f**)	**4f**	60
7	*p*-CNC_6H_4 (**3g**)	**4g**	92
8	1-Np (**3h**)	**4h**	88

[a]Reaction conditions: **2c** (0.05 mmol), iodoarene (0.35 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (10 mol %), Cs_2CO_3 (0.6 mmol), DME (1.0 mL), 100 °C, 24 h. [b]Isolated yield. [c]Performed in 0.5 mL of DME.

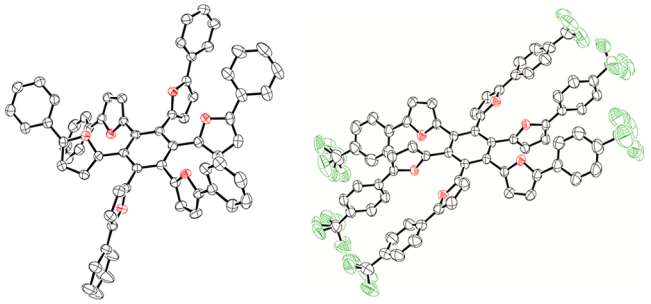


Figure 3. ORTEP drawings of **4a** (left) and **4f** (right) (50% probability ellipsoids; hydrogen atoms omitted for clarity; trifluoromethyl groups of **4f** disordered).

catalyzed cyclotrimerization of di(furan-2-yl)acetylenes. A 6-fold Bpin-substituted hexa(furan-2-yl)benzene could also be prepared by this method, and a wide variety of π-extended hexa(furan-2-yl)benzene derivatives were obtained by subsequent Suzuki–Miyaura coupling.

EXPERIMENTAL SECTION

General Methods. Nuclear magnetic resonance (NMR) spectra were recorded on 600 or 400 MHz in $CDCl_3$. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to residual $CHCl_3$ in $CDCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). All new compounds were further characterized by elemental analyses or HRMS (DART), and the mass analyzer type used for HRMS was orbitrap.

2-Iodofuran and 5-methyl-2-iodofuran were prepared according to the literature.[12] 1,2-Dimethoxyethane (DME) was dried over MS 4A prior to use. Toluene was distilled from CaH_2. Dry dimethylformamide (DMF) and dry 1,4-dioxane were purchased from commercial suppliers. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. All reactions were performed under argon.

Synthesis of Di(furan-2-yl)acetylene (1a). To a mixture of $Pd(PPh_3)_2Cl_2$ (633 mg, 0.902 mmol) and CuCl (298 mg, 3.01 mmol) in DMF (60 mL) were added DBU (26.9 mL, 180 mmol) and trimethylsilylacetylene (2.1 mL, 15 mmol). To the mixture were added 2-iodofuran (5.82 g, 30.0 mmol) and distilled water (216 μL, 12.0 mmol). The reaction vessel was covered with aluminum foil and stirred at room temperature for 22 h. The resulting mixture was extracted with diethyl ether (3 × 30 mL). The organic phase was washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to afford di(furan-2-yl)acetylene as a yellow oil (1.57 g, 9.95 mmol, 66%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.43 (dd, J = 3.4, 1.8 Hz, 2H), 6.71 (dd, J = 3.4, 0.6 Hz, 2H), 7.44 (dd, J = 1.8, 0.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.2, 111.1, 116.5, 136.4, 144.2; IR (neat) 3145, 3131, 1494, 1462 cm^{-1}. Anal. Calcd for $C_{10}H_6O_2$: C, 75.94; H, 3.82. Found: C, 76.04; H, 3.76.

Synthesis of Bis(5-methylfuran-2-yl)acetylene (1b). Similar procedure to **1a**: yellow oil (1.81 g, 9.74 mmol, 62%); ^1H NMR (600 MHz, $CDCl_3$) δ 2.32 (brs, 6H), 6.01 (dq, J = 3.2, 1.0 Hz, 2H), 6.58 (dd, J = 3.2, 0.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 83.3, 107.3, 117.4, 134.8, 154.3; IR (KBr) 2922, 2181, 1557, 1198, 1021, 948, 785 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.32; H, 5.69.

Synthesis of Bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-yl]acetylene (1c). To a solution of di(furan-2-yl)acetylene (1.541 g, 9.75 mmol) in Et_2O (100 mL) was added dropwise a solution of *n*-BuLi (1.6 M in hexane, 13.8 mL, 22.0 mmol) at −78 °C. The reaction mixture was then stirred at the same temperature for 30 min and then stirred at 0 °C for 2.5 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.2 mL, 50.0 mmol) was added to the mixture at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with aq saturated NH_4Cl (20 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc) and then recrystallized from CH_2Cl_2/hexane to afford bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-yl]acetylene (**1c**) as a yellow solid (2.83 g, 6.91 mmol, 71%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 24H), 6.67 (d, J = 3.5 Hz, 2H), 7.04 (d, J = 3.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.7, 84.3, 84.5, 116.6, 124.0, 140.5; IR (KBr) 3125, 2980, 2934, 2870, 1756 cm^{-1}; mp 214.5–217.5 °C. Anal. Calcd for $C_{22}H_{28}B_2O_6$: C, 64.44; H, 6.88. Found: C, 64.56; H, 6.84.

Hexa(furan-2-yl)benzene (2a). To a solution of $RhCl_3{\cdot}3H_2O$ (10.4 mg, 0.04 mmol) and *i*-Pr_2NEt (26.2 μL, 0.15 mmol) in toluene (2.0 mL) was added di(furan-2-yl)acetylene (79.0 mg, 0.50 mmol), and the mixture was stirred at 120 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1) to afford hexa(furan-2-yl)benzene (**2a**) as a yellow solid (39.4 mg, 0.08 mmol, 50%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.92 (dd, J = 3.3, 0.8 Hz, 6H), 6.20 (dd, J = 3.3, 1.8 Hz, 6H), 7.23 (dd, J = 1.8, 0.8 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 109.7, 110.6, 133.9, 141.9, 150.2; IR (KBr) 2363, 2341, 1507, 1002, 731 cm^{-1}; mp >280 °C. Anal. Calcd for $C_{30}H_{18}O_6$: C, 75.94; H, 3.82. Found: C, 75.85; H, 3.79.

Hexakis(5-methylfuran-2-yl)benzene (2b). To a solution of $RhCl_3{\cdot}3H_2O$ (10.6 mg, 0.04 mmol) and *i*-Pr_2NEt (26.2 μL, 0.15 mmol) in toluene (2.0 mL) was added bis(5-methylfuran-2-yl)-acetylene (93.6 mg, 0.50 mmol), and the mixture was stirred at 130 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5:1) to afford hexakis(5-methylfuran-2-yl)benzene (**2b**) as a yellow solid (75.5 mg, 0.14 mmol, 81%): ^1H NMR (600 MHz, $CDCl_3$) δ 2.13 (d, J = 0.8 Hz, 18H), 5.78 (d, J = 3.0 Hz, 6H), 5.80 (dd, J = 0.8, 3.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 106.5, 110.2, 133.2, 149.2, 150.8; IR (KBr) 3440, 3103, 2947, 2919, 2882 cm^{-1}; mp 149.8–152.5 °C. Anal. Calcd for $C_{36}H_{30}O_6$: C, 77.40; H, 5.41. Found: C, 77.36; H, 5.11.

Synthesis of Hexakis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)furan-2-yl]benzene (2c). To a solution of $RhCl_3{\cdot}3H_2O$

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(10.4 mg, 0.04 mmol) and *i*-Pr_2NEt (26.2 μL, 0.15 mmol) in toluene (2.0 mL) was added bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)furan-2-yl]acetylene (0.206 g, 0.50 mmol), and the mixture was stirred at 120 °C for 24 h. After being cooled to room temperature, the resulting mixture was filtered through a Celite pad and concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2/hexane to afford hexakis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)furan-2-yl]-benzene (**2c**) as a colorless solid (164 mg, 0.133 mmol, 80%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 72H), 6.04 (d, *J* = 3.4 Hz, 6H), 6.80 (d, *J* = 3.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.7, 83.7, 111.5, 124.4, 133.1, 154.8; IR (KBr) 3426, 2979, 2933, 1589, 1542 cm^{-1}; mp >280 °C; Anal. Calcd for $C_{66}H_{84}B_6O_{18}$: C, 64.44; H, 6.88. Found: C, 64.64; H 6.83.

Typical Procedure of Suzuki−Miyaura Coupling between 2c and Iodoarene (Table 3, Entry 1). To a solution of $Pd[P(t\text{-}Bu)_3]_2$ (2.9 mg, 0.006 mmol) and Cs_2CO_3 (198.7 mg, 0.60 mmol) in DME (1.0 mL) were added hexakis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-furan-2-yl]benzene (**2c**) (61.9 mg, 0.05 mmol) and iodobenzene (**3a**, 72.8 mg, 0.36 mmol). The mixture was stirred at 100 °C for 24 h. After being cooled to room temperature, aq saturated NH_4Cl was poured into the mixture, and the aqueous phase was extracted with $CHCl_3$ (3 × 10 mL). To the combined organic phase was added EtOH (10 mL), and the mixture was concentrated under reduced pressure. The residue was recrystallized from $CHCl_3$/hexane to afford hexakis(5-phenyfuran-2-yl)benzene (**4a**) as a yellow solid.

Hexakis(5-phenylfuran-2-yl)benzene (4a): yellow solid (32.6 mg, 0.035 mmol, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (d, *J* = 3.4 Hz, 6H), 6.46 (d, *J* = 3.4 Hz, 6H), 7.14−7.16 (m,18H), 7.44−7.47 (m,12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.5, 112.1, 123.7, 127.0, 128.4, 130.6, 133.8, 149.9, 153.3; IR (KBr) 3060.5, 1484.9, 1022.1, 757.9 cm^{-1}; mp: 246.0−246.2 °C; HRMS (DART) *m*/*z* calcd for $C_{66}H_{43}O_6$ $[M + H]^+$ 931.3054, found 931.3034.

Hexakis[5-(4-methyl-phenyl)furan-2-yl]benzene (4b): yellow solid (30.0 mg, 0.030 mmol, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 18H), 6.09 (d, *J* = 3.4 Hz, 6H), 6.38 (d, *J* = 3.4 Hz, 6H), 6.96 (d, *J* = 8.0 Hz, 12H), 7.33 (d, *J* = 8.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 105.8, 111.9, 123.7, 128.1, 129.0, 133.7, 136.7, 149.7, 153.4; IR (KBr) 3120.3, 3025.8, 2917.8, 2859.0, 1496.5, 783.9 cm^{-1}; mp >280 °C; HRMS (DART) *m*/*z* calcd for $C_{72}H_{55}O_6$ $[M + H]^+$ 1015.3993, found 1015.3969.

Hexakis[5-(4-methoxyphenyl)furan-2-yl]benzene (4c): yellow solid (42.6 mg, 0.038 mmol, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 18H), 6.08 (d, *J* = 3.4 Hz, 6H), 6.32 (d, *J* = 3.4 Hz, 6H), 6.70 (d, *J* = 8.8 Hz, 12H), 7.39 (d, *J* = 8.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 105.0, 111.9, 113.8, 123.9, 125.2, 133.6, 149.5, 153.2, 158.7; IR (KBr) 3126.0, 3001.7, 2940.0, 2834.9, 1497.5, 1251.6 cm^{-1}; mp >280 °C; HRMS (DART) *m*/*z* calcd for $C_{72}H_{55}O_{12}$ $[M + H]^+$ 1111.3688, found 1111.3664.

Hexakis[5-(4-chlorophenyl)furan-2-yl]benzene (4d): yellow solid (35.3 mg, 0.031 mmol, 62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.12 (d, *J* = 3.4 Hz, 6H), 6.44 (d, *J* = 3.4 Hz, 6H), 6.15 (d, *J* = 8.7 Hz, 12H), 7.32 (d, *J* = 8.7 Hz, 12H); ^{13}C NMR could not be measured due to the low solubility; IR (KBr) 3125.1, 1480.1, 1093.4, 787.8 cm^{-1}; mp >280 °C; HRMS (DART) *m*/*z* calcd for $C_{66}H_{37}O_6Cl_6$ $[M + H]^+$ 1135.0716, found 1135.0696.

Hexakis[5-(4-fluorophenyl)furan-2-yl]benzene (4e): yellow solid (31.5 mg, 0.030 mmol, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, *J* = 3.4 Hz, 6H), 6.39 (d, *J* = 3.4 Hz, 6H), 6.87 (dd, *J* = 8.8 Hz, J_{H-F} = 8.8 Hz 12H), 7.38 (dd, *J* = 8.8, 5.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.1, 115.5 (d, J_{C-F} = 22 Hz), 112.2, 125.4 (d, J_{C-F} = 8.0 Hz), 126.8 (d, J_{C-F} = 3.4 Hz), 133.6, 149.8, 152.5, 162.0 (d, J_{C-F} = 246.0 Hz); IR (KBr) 3452.0, 1495.5, 1233.6, 788.7 cm^{-1}; mp >280 °C; HRMS (DART) *m*/*z* calcd for $C_{66}H_{37}O_6F_6$ $[M + H]^+$ 1039.2489, found 1039.2464.

Hexakis[5-(4-trifluorometylphenyl)furan-2-yl]benzene (4f): yellow solid (40.8 mg, 0.030 mmol, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 3.5 Hz, 6H), 6.58 (d, *J* = 3.5 Hz, 6H), 7.40 (d, *J* = 8.3 Hz, 12H), 7.49 (d, *J* = 8.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.4, 112.8, 123.5, 124.0 (q, J_{C-F} = 270.6 Hz), 125.5 (q, J_{C-F} = 3.9 Hz), 129.1 (q, J_{C-F} = 32.5 Hz), 133.2 (d, J_{C-F} = 1.1 Hz), 133.7, 150.4, 152.1; IR (KBr) 1617.0, 1323.9, 1172.5, 1122.4, 1073.2 cm^{-1}; mp >280 °C; HRMS (DART) *m*/*z* calcd for $C_{72}H_{36}O_6F_{18}$ $[M^+]$ 1338.2219, found 1338.2198.

Hexakis[5-(4-cyanophenyl)furan-2-yl]benzene (4g): yellow solid (50.0 mg, 0.046 mmol, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, *J* = 3.5 Hz, 6H), 6.64 (d, *J* = 3.5 Hz, 6H), 7.42 (d, *J* = 8.5 Hz, 12H), 7.47 (d, *J* = 8.5 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 109.5, 110.6, 113.3, 118.6, 123.6, 132.5, 133.4, 133.7, 150.7, 151.7; mp >280 °C; HRMS (DART) *m*/*z* calcd for $C_{72}H_{36}O_6N_6$ $[M^+]$ 1080.2691, found 1080.2712.

Hexakis[5-(naphthalen-1-yl)furan-2-yl]benzene (4h): yellow solid (53.7 mg, 0.044 mmol, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, *J* = 3.2 Hz, 6H), 6.68 (d, *J* = 3.2 Hz, 6H), 7.15−7.22 (m, 12H), 7.33 (t, *J* = 8.0 Hz, 6H), 7.45 (d, *J* = 6,4 Hz, 6H), 7.68 (d, *J* = 8.0 Hz, 6H), 7.77 (d, *J* = 8.0 Hz, 6H), 8.19 (t, *J* = 8.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 110.7, 112.3, 125.2, 125.5, 125.6, 125.9, 126.4, 128.0, 128.1, 128.2, 129.8, 133.8, 134.1, 150.3, 152.9; IR (KBr) 3048.9, 1395.3, 788.7, 772.4 cm^{-1}; mp 216.3−217.0 °C; HRMS (DART) *m*/*z* calcd for $C_{90}H_{55}O_6$ $[M + H]^+$ 1231.3993, found 1231.3981.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all new compounds; X-ray data for **1c**, **2a−c**, and **4a**,**f** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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