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Synthesis of Ladder-Type π-Conjugated Heteroacenes via Palladium-Catalyzed Double N-Arylation and Intramolecular O-Arylation

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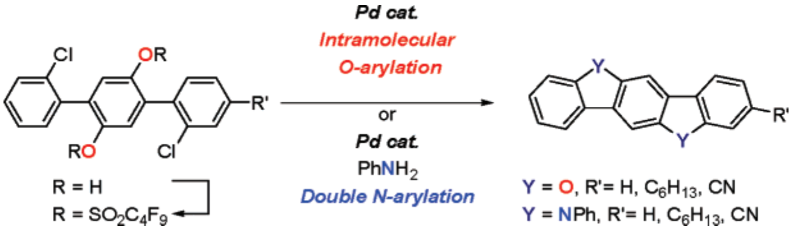

Ladder-type heteroacenes containing pyrrole or furan rings, indolo[3,2-*b*]carbazoles and dibenzo[*d*,*d*′]benzo[1,2-*b*:4,5-*b*′]difurans, were effectively synthesized from the common intermediates, 2,5-bis(*o*-chloroaryl)hydroquinones. The key reactions are palladium-catalyzed double N-arylation of aniline and intramolecular O-arylation, which enable regioselective ring closure. In addition to the parent indolo[3,2-*b*]carbazole and dibenzo[*d*,*d*′]benzo[1,2-*b*:4,5-*b*′]difuran, their derivatives with an alkyl or cyano group were first synthesized. Photophysical and electrochemical studies showed that the obtained heteroacenes have lower HOMO energy levels and larger band gaps than the corresponding hydrocarbon acene, pentacene. An X-ray analysis of dibenzo[*d*,*d*′]benzo[1,2-*b*:4,5-*b*′]difuran revealed that it was packed in herringbone fashion.

Introduction

Organic field-effect transistors (OFETs) are of great interest in recent years because of their potential applications for low-cost, flexible, and large-area electronic devices.[1,2] For the practical use of OFETs, organic semiconducting materials should combine high charge carrier mobility with remarkable stability when processed or operated under ambient conditions. In the field of organic semiconductors, a lot of research efforts have been devoted to acenes which typically showed high carrier mobilities. Among the ladder-type acene molecules ever reported, pentacene has recorded the highest level of mobility (5 $\mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$), comparable to that of amorphous silicon.[3,4] Such high mobilities of acenes should originate from the highly ordered and close molecular packing which increase the $\pi-\pi$ interaction between the adjacent molecules.[5−8] However, acene-type molecules have some drawbacks for a practical application to organic devices. For example, their high-lying HOMOs and narrow band gaps leave them sensitive to photooxidation, resulting in the deterioration of semiconductor performance under ambient conditions.[9] Therefore, it is important to develop new organic semiconducting materials which achieve both high charge carrier mobility and high stability under ambient conditions.

Introduction of heteroatoms in the fused-ring system has been one of the major approaches to modify physical and chemical properties of ladder-type acene molecules. Anthradithiophene

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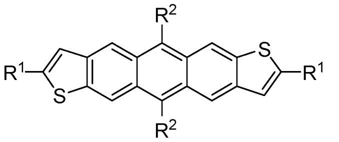
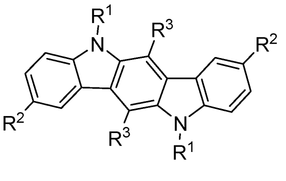
10.1021/jo070427p CCC: $37.00

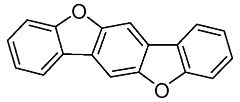
1[10] and indolo[3,2-*b*]carbazole **2a**[11] and **2b**[12] have oxidative stability higher than that of pentacene because of their lower-lying HOMOs and larger band gaps. These heteroacene molecules form π-stacking arrangement in the solid states and show relatively high charge carrier mobility (0.14−1 $\mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$). These properties would allow heteroacene molecules to be promising candidates for OFET materials. Thus, facile and diverse synthetic approaches should be necessary for the fast improvement of heteroacene-based OFET materials.[13−26]



1a:$R^1 = C_6H_{13}$, $R^2 = H$
1b:$R^1 = H$, $R^2 = C{\equiv}C\text{-}SiEt_3$



2a:$R^1 = C_{12}H_{25}$, $R^2 = Cl$, $R^3 = H$
2b:$R^1 = C_8H_{17}$, $R^2 = H$, $R^3 = Me$
2c:$R^1 = Ph$, $R^2 = H$, $R^3 = H$



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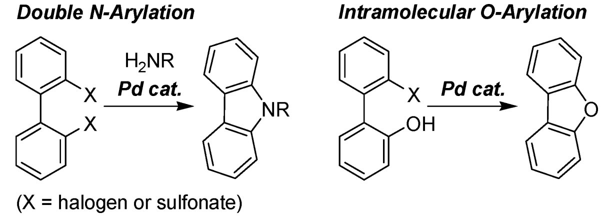
We now report effective syntheses of ladder-type heteroacenes **2c** and **3** containing pyrrole and furan rings, respectively. We have recently developed new methodologies for the syntheses of carbazole and dibenzofuran derivatives by using the palladium-catalyzed double N-arylation of primary amines with biphenyl dihalide or biphenylylene disulfonate and the intramolecular O-arylation of hydroxybiphenyl sulfonate, respectively, as key reactions (Scheme 1).[27−29] These reactions effectively give carbazoles and dibenzofurans with a variety of functional groups through the regioselective ring closure at the carbon(s) attached to the leaving group X (X = halogen or sulfonate).[30] Furthermore, the substrates for these key reactions are easily available by the transition-metal-catalyzed cross-coupling reactions. Thus, these reactions enable us to design an efficient synthetic route to various ladder-type heteroacenes that contain pyrrole or furan rings in the fused-ring framework. In addition to **2c** and **3**, their derivatives with an alkyl or cyano substituent were designed and synthesized in this report. Structural and physical properties of the synthesized heteroacenes are also discussed.

SCHEME 1. Key Reactions for Syntheses of Ladder-Type Heteroacenes



Results and Discussion

Synthetic Strategy of Ladder-Type π-Conjugated Heteroacene. The syntheses of heteroacene compounds generally require multiple steps, and a limited number of synthetic routes to them have been reported. Bergman et al. synthesized indolo-[3,2-*b*]carbazoles via double Fischer cyclization (Scheme 2).[24] However, the lack of regioselectivity in the ring closure steps often produced the undesirable regioisomers as side products. Leclerc et al. reported the selective synthesis of 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole **2b** in a nine-step synthetic sequence where the indolo[3,2-*b*]carbazole framework was formed by Cadogan reductive cyclization of a *N*-alkyl-substituted carbazole precursor.[12] Since Cadogan ring closure is generally not regioselective, the use of a carbazole precursor with two methyl protecting groups is essential to obtain the desired isomer selectively. Heteroacene **3** with two furan rings was obtained via cyclodehydrogenation of 1,4-diphenoxybenzene with $Pd(OAc)_2$ in AcOH, along with byproducts.[31]

In order to achieve efficient syntheses of the furan- or pyrrole-containing heteroacenes, we designed the synthetic route to **2c** and **3** from common intermediate **4**: heteroacene **3** should be obtained by the intramolecular O-arylation of hydroquinone **4** bearing two *ortho*-chlorophenyl groups, and heteroacene **2c** should be obtained by the double N-arylation of aniline with dinonaflate **5**, which is easily prepared from **4** (Scheme 3).[32] Terphenyl skeleton **4** is easily prepared by a Suzuki−Miyaura cross-coupling reaction of the corresponding aryl diiodide with the arylboronic acid.

Model Studies on Key Reactions. In preliminary studies, we investigated the two key reactions, the double N-arylation

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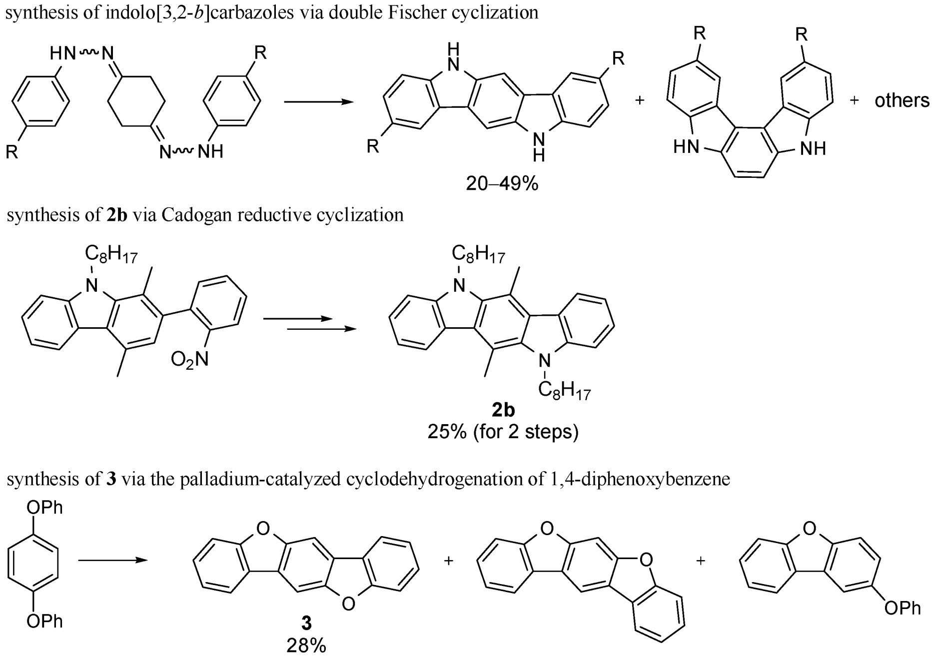
[32] For the intramolecular copper-catalyzed Ullmann reaction for the synthesis of diindolocarbazoles, see ref 18.

SCHEME 2. Examples for Syntheses of 2 and 3



SCHEME 3. Synthetic Strategy for Heteroacenes 2c and 3

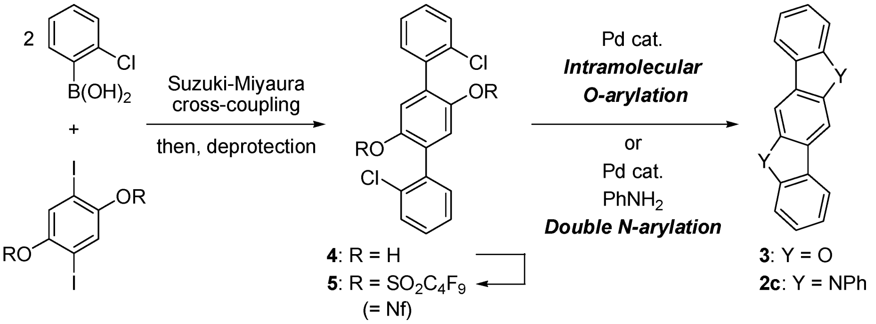
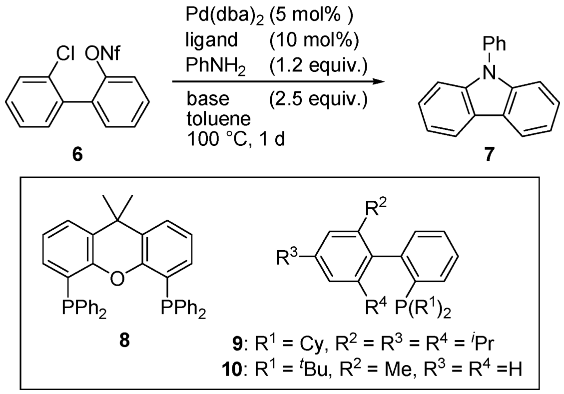
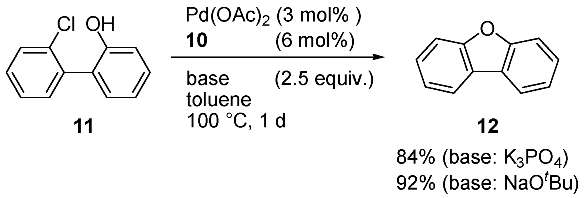


TABLE 1. Optimization for the Double N-Arylation of Aniline with 6



entry	ligand	base	yield of **7** (%)
1	**8**	K_3PO_4	trace
2	**9**	K_3PO_4	trace
3	**10**	K_3PO_4	86
4	**10**	NaO^{t}Bu	76

SCHEME 4. Optimization for the Intramolecular O-Arylation of 11



and the intramolecular O-arylation, on the level of a model system because our previous reports for the carbazole and dibenzofuran syntheses have not employed chloride as a leaving group.[27–29] For the optimization of the double N-arylation condition, 2-chloro-2′-nonafluorobutanesulfonyloxybiphenyl (**6**) and aniline were employed as substrates (Table 1). The reactions were initially carried out in presence of $Pd(dba)_2$ and K_3PO_4 as a base in toluene at 100 °C. The use of Xantphos (**8**) or biphenylphosphine **9**[33,34] as a ligand, which were effective for the reaction of aniline with 2,2′-biphenylylene ditriflate,[28] resulted in a low conversion after 1 day (entries 1 and 2). In contrast, the use of 2-di-*tert*-butylphosphino-2′-methylbiphenyl (**10**)[35] resulted in 86% isolated yield of *N*-phenylcarbazole (**7**)

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SCHEME 5. Syntheses of 4 and 5

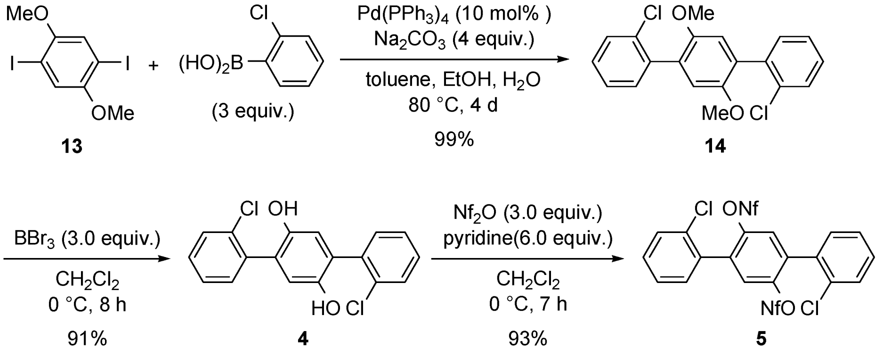
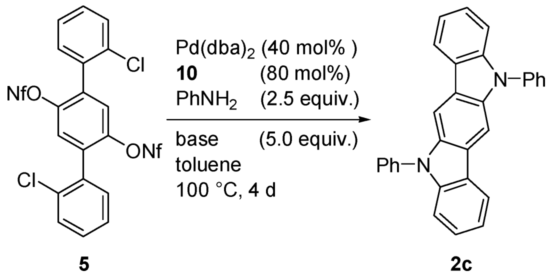


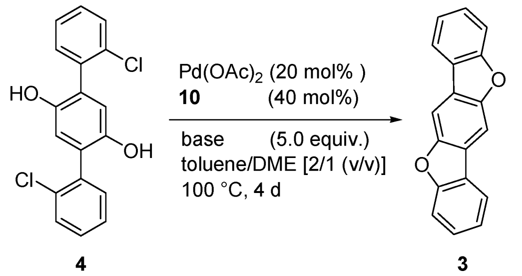
TABLE 2. Double N-Arylation of Aniline with 5[a]



entry	base	additive	yield of **2c**[b] (%)
1	NaO^{t}Bu		0
2	K_3PO_4		<5
3	KBHT		51
4	K_3PO_4	BHT[c]	86
5	KOAc	BHT[c]	23
6[d]	K_3PO_4	BHT[c]	18

[a] Reaction conditions: **5** (0.20 mmol), aniline (46 μL, 0.50 mmol), base (1.0 mmol), toluene (0.60 mL), 100 °C, 4 days. Concentration of **5** was 0.33 M. Reaction time was not optimized. [b] Isolated yield. [c] Used 3 equiv of BHT (0.60 mmol). [d] Concentration of **5** was 0.60 M [**5**: 0.30 mmol, toluene (0.50 mL)].

TABLE 3. Intramolecular O-Arylation of 4[a]



entry	base	additive	yield of **3**[b] (%)
1	NaO^{t}Bu		0
2	K_3PO_4		<10
3	KBHT		43
4	K_3PO_4	BHT[c]	61
5[d]	K_3PO_4	BHT[c]	13
6	KOAc	BHT[c]	70

[a] Reaction conditions: **4** (0.20 mmol), base (1.0 mmol), toluene (0.40 mL), DME (0.20 mL), 100 °C, 4 days. Concentration of **4** was 0.33 M. Reaction times were not optimized. [b] Isolated yield. [c] Used 3 equiv of BHT (0.60 mmol). [d] Concentration of **4** was 0.60 M [**4**: 0.30 mmol, toluene (0.35 mL), DME (0.15 mL)].

(entry 3). Change of a base to NaO^{t}Bu led to the slightly reduced yield (entry 4). Next, the intramolecular O-arylation was examined by using 2-chlorobiphenyl-2′-ol (**11**) as a substrate in the presence of Pd(OAc)$_2$, phosphine ligand **10**, and a base in toluene at 100 °C (Scheme 4). Consequently, we found that the use of NaO^{t}Bu led to higher yield of dibenzofuran (**12**) than that of K_3PO_4 after 1 day.

Syntheses of Ladder-Type π-Conjugated Heteroacenes Containing Pyrrole or Furan Rings. Syntheses of the starting materials for heteroacenes **2c** and **3** are described in Scheme 5. Diiodobenzene **13** was obtained in 82% yield by the reaction of commercially available 1,4-dimethoxybenzene with ICl in methanol according to the literature.[36] Suzuki−Miyaura cross-coupling reaction of **13** with 2-chlorophenylboronic acid (99% yield)[37] and the following demethylation of **14** by using boron tribromide at low temperature (91% yield) gave terphenyl **4**, a common intermediate for heteroacenes **2c** and **3**. Subsequently, treatment of **4** with nonafluorobutanesulfonic anhydride in cold pyridine/CH_2Cl_2 gave dinonaflate **5** in 93% isolated yield after recrystallization from $CHCl_3$/hexane [1/10 (v/v)].

Based on the result of the model system, we examined the double N-arylation of aniline with **5** in the presence of Pd(dba)$_2$ (40 mol % of **5**, 10 mol % of total C−N bond formation), ligand **10** (80 mol %), and NaO^{t}Bu or K_3PO_4 as a base (5.0 equiv) (Table 2). The desired **2c** was not obtained when using NaO^{t}Bu (Table 2, entry 1). The ^{1}H NMR spectrum of the crude residue showed broad and complex peaks, indicating the production of polymeric materials.[38] The use of K_3PO_4 provided a small amount of **2c**, although major products were polymeric materials (entry 2). In order to optimize the reaction conditions, we examined the effect of the base. Employment of potassium 2,6-di-*tert*-butyl-4-methylphenoxide (KBHT) achieved 51% yield of **2c** (entry 3). A small amount of **3** was obtained as a byproduct, which would result from the hydrolysis of dinonaflate and the subsequent intramolecular O-arylation. Optimally, the combination of 2,6-di-*tert*-butyl-4-methylphenol (BHT) with K_3PO_4 improved the yield of **2c** up to 86% (entry 4).[39] The concentration of **5** was also an important factor for the predominant

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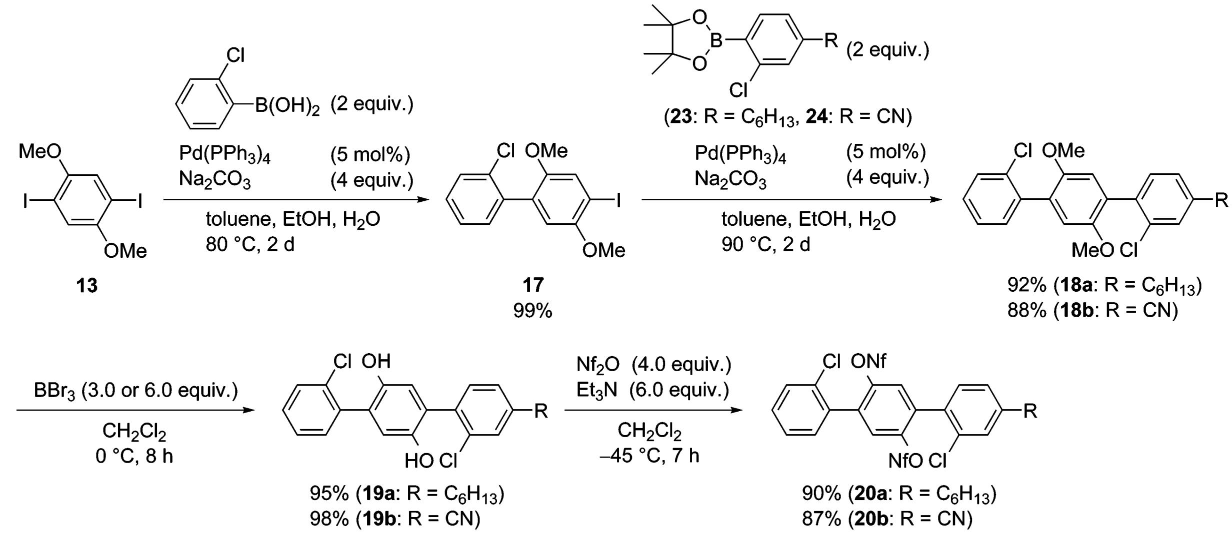
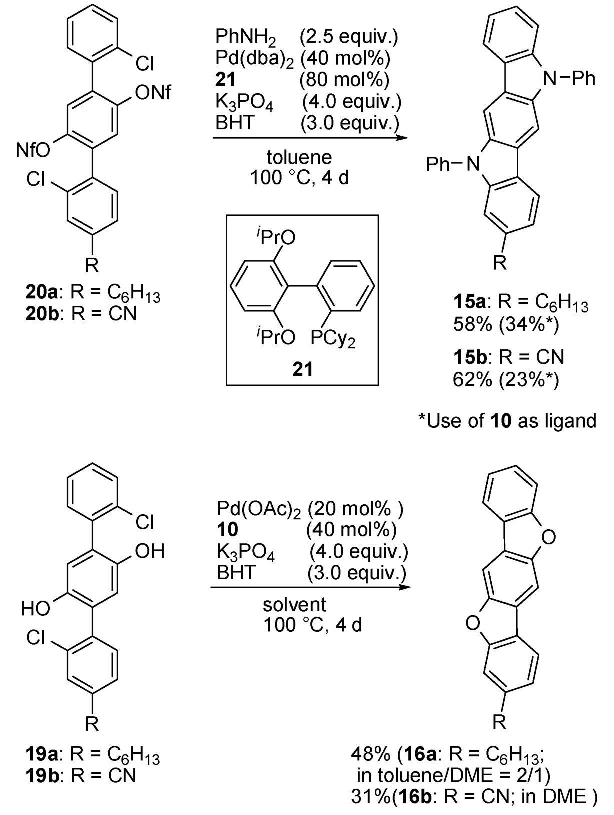
[37] We monitored the reaction by TLC analysis and found that the complete consumption of the iodobiphenyl intermediate generally required 3−4 days.

[38] As described in the literature (Hennings, D. D.; Iwama, T.; Rawal, V. H. *Org. Lett.* **1999**, *1*, 1205), hydroquinone is proposed to work as reductant in the palladium-catalyzed homocoupling reaction of haloarenes. When the N-arylation of aniline with **5** proceeds at the two carbons bearing a nonaflate group, the resulting *p*-phenylenediamine is capable of working as reductant in a manner similar to that of hydroquinone, resulting in the oligomerization of **5**.

SCHEME 6. Syntheses of Terphenyls 19 and 20



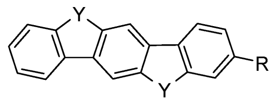
SCHEME 7. Syntheses of Dissymmetric Heteroacenes



formation of **2c**. The reaction proceeded smoothly at the concentration of 0.33 M (entry 4), while side reactions predominantly occurred at concentrations higher than >0.33 M (entry 6). Accordingly, the reaction was conducted in low concentration.

Next, we investigated the intramolecular O-arylation of **4** to synthesize heteroacene **3** (Table 3). Because of low solubility of the reaction mixture in toluene, DME was used as cosolvent [toluene/DME = 2/1 (v/v)]. The use of NaO^{t}Bu or K_3PO_4 as a base resulted in the formation of a substantial amount of polymeric products (entries 1 and 2). Similar to the case of double N-arylation of aniline with **5**, the use of KBHT or a combination of BHT with K_3PO_4 was found to be effective, resulting in the production of **3** in moderate yields (entries 3 and 4). The concentration of **4** also remarkably was related to the yield of **3**. The desired reaction proceeded smoothly at the concentration of 0.33 M (entry 4), preventing the side reactions which became dominant at higher concentration of 0.60 M (entry 5). The use of KOAc slightly improved the yield to 70% (entry 6).

Syntheses of Substituted Ladder-Type π-Conjugated Heteroacenes. Successful syntheses of heteroacene **2c** and **3** prompted us to synthesize the substituted heteroacenes. Since substituents are expected to vary electronic properties of the molecules as well as the molecular orientation in solid-state structures, a synthetic route with structural diversity is desirable. As shown in the following, we selected alkyl or cyano groups as substituents and demonstrated the syntheses of dissymmetric heteroacenes **15** and **16** containing pyrrole and furan rings, respectively.



15a: Y = NPh, R = C_6H_{13}
15b: Y = NPh, R = CN
16a: Y = O, R = C_6H_{13}
16b: Y = O,R = CN

Dissymmetrically substituted terphenyls **19** were obtained in high yields through (1) monoarylation of diiodobenzene **13** with 2-chlorophenylboronic acid, (2) the second arylation of the resulting iodobiphenyl **17** with the boronic acid pinacolate **23** or **24**, and (3) the following demethylation (Scheme 6). The resulting terphenyls **19** were transformed into dinonaflates **20** in good yields.

The double N-arylation of dinonaflate **20** and the intramolecular O-arylation of hydroquinone **19** were conducted under the optimized conditions for the syntheses of symmetric compounds **2c** and **3**, respectively (Scheme 7). Although the desired **15a** and **15b** were obtained, the yields were low. Further optimization of the reaction conditions revealed that the use of ligand **21**[40,41] gave better results. Furan-based heteroacenes **16a** and **16b** were obtained in moderate yields when using ligand

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(39) When the reaction was carried out at the reduced catalyst loading (5−20 mol %), the yield of **2c** decreased and the amount of polymeric byproducts was increased.

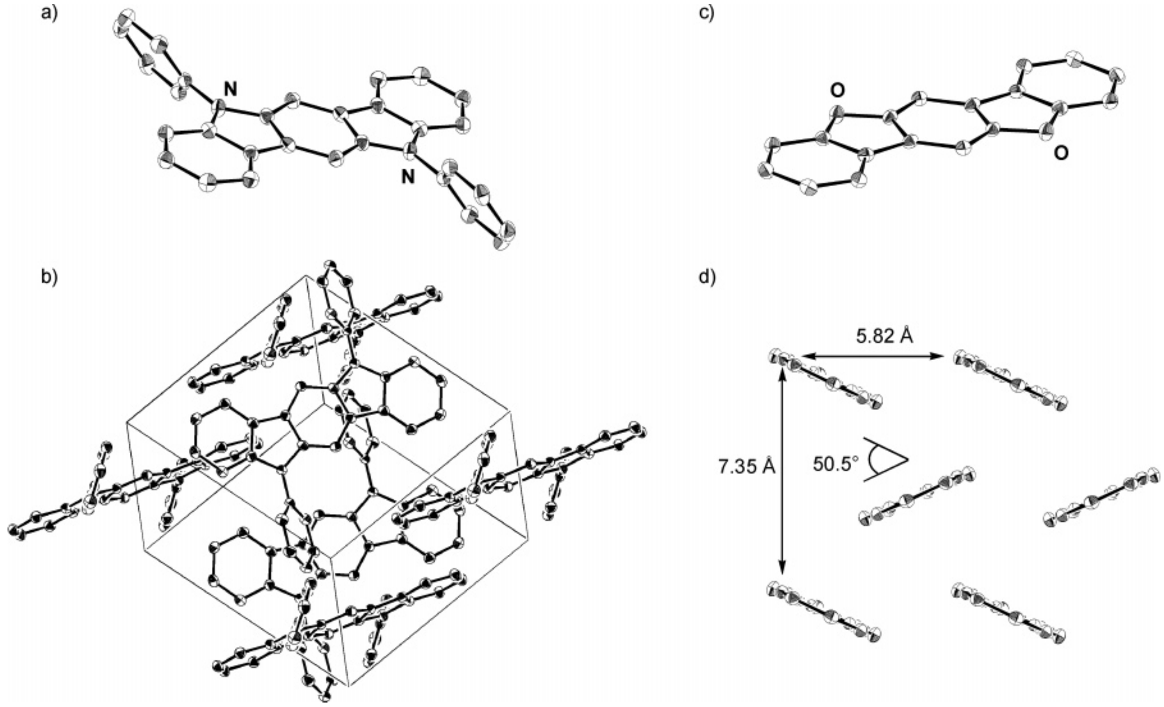

FIGURE 1. ORTEP drawings (50% probability) of **2c** (a, single molecule; b, packing structure) and **3** (c, single molecule; d, packing structure). Disorder in the structure of **3** is omitted for clarity.

TABLE 4. Photophysical and Electrochemical Data of Heteroacenes

compound	λ_{max} (nm)	E_g (eV)[a]	E_{ox}^{peak} (V)	E_{ox}^{onset} (V)[b]	E_{HOMO} (eV)[c]	E_{LUMO} (eV)[d]
2c	422	2.95	0.67 1.24	0.46	−5.08	−2.13
15a	434	2.86	0.67 1.27	0.45	−5.07	−2.21
15b	453	2.74	0.80 1.26	0.55	−5.17	−2.43
3	354	3.50	1.59	1.16	−5.78	−2.28
16a	356	3.48	1.39 1.62	1.18	−5.80	−2.32
16b	381	3.26	1.64	1.42	−6.04	−2.78
pentacene[e]	−	2.21	−	−	−4.60	−

[a] Optical band gaps estimated from the onset position of the UV−vis absorption spectra in solution. [b] Onset potentials (vs Ag/Ag$^+$) of the first oxidation wave determined by cyclic voltammetry: 0.1 M Bu_4NClO_4 in CH_2Cl_2, Pt as working and counter electrodes, scan rate = 100 mV·s^{-1}. [c] Calculated according to $E_{HOMO} = -e(E_{ox}^{onset} + 4.62)$. [d] All values were estimated from the optical band gaps and E_{HO}. [e] See ref 44.

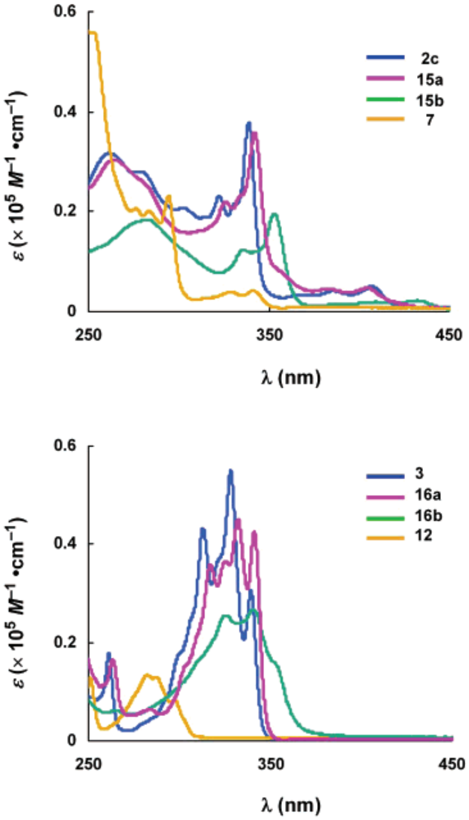

FIGURE 2. Absorption spectra of heteroacenes containing pyrrole rings (tops) and furan rings (bottom) in $CHCl_3$ (1 × 10^{-5} M).

10. All of the heteroacenes were obtained in pure form after purification by silica gel column chromatography.

Solid-State Structures of 2c and 3. Heteroacenes **2c** and **15** were obtained as pale yellow solids, and **3** and **16** were obtained as colorless solids. Each of them was soluble in most common organic solvents, such as CH_2Cl_2, THF, and AcOEt, and was stable under ambient conditions. Solid-state structures of heteroacenes **2c** and **3** were determined by X-ray crystallography (Figure 1). In the crystal packing, **2c** has little overlap between π-planes of the fused-ring framework. Such molecular orientation should be attributed to steric effect of two phenyl groups. On the other hand, **3** is packed in a herringbone arrangement, similar to pentacene. The herringbone angle is smaller (50.5°), and the intramolecular distances (5.82, 7.35 Å)

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(40) Charles, M. D.; Schultz, P.; Buchwald, S. L. *Org. Lett.* **2005**, *7*, 3965.

(41) Fang, Y. Q.; Lautens, M. *Org. Lett.* **2005**, *7*, 3549.

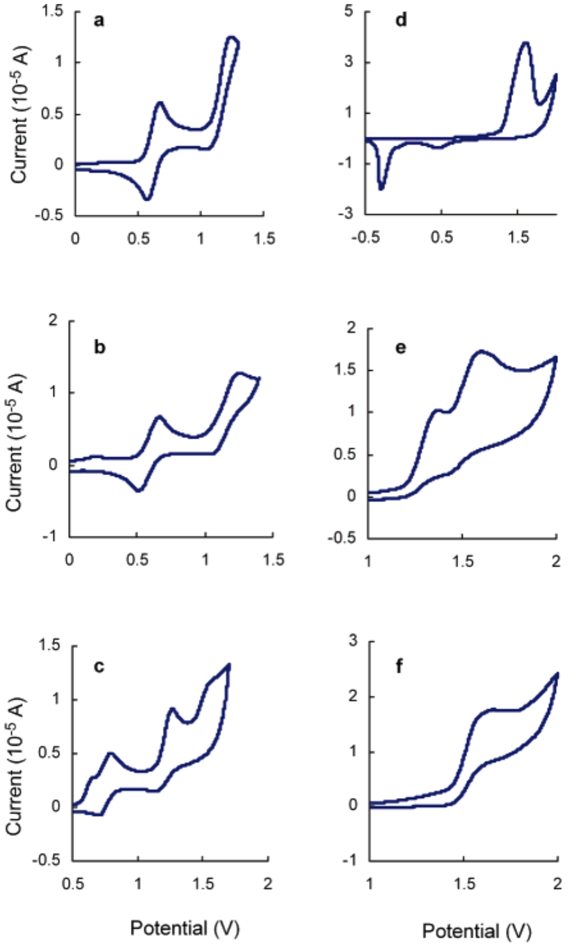

FIGURE 3. Cyclic voltammograms of heteroacenes containing pyrrole rings (a, **2c**; b, **15a**; c, **15b**) and furan rings (d, **3**; e, **16a**; f, **16b**). Measurement conditions: 1 mM in CH_2Cl_2 for all compounds with Bu_4NClO_4 (0.10 M); scan rate = 100 mV·s^{-1}.

are shorter than those of pentacene (53°, 6.27, 7.78 Å).[42] These facts show a dense packing structure of **3**, which would be advantageous to achieve high charge carrier mobility.

UV−Vis Absorption and Electrochemical Properties of Ladder-Type π-Conjugated Heteroacenes. The photophysical and electrochemical data of produced ladder-type heteroacenes are summarized in Table 4 and Figures 2 and 3. The absorption of pyrrole-based heteroacenes **2c** and **15** was significantly red-shifted compared to those of furan-based heteroacenes **3** and **16** (Figure 2). Such a trend corresponds to the relationship between 9-phenylcarbazole (**7**) and dibenzofuran (**12**). The absorption maximums of alkyl-group-substituted **15a** and **16a** were almost similar to that of parent **2c** and **3**, respectively. On the other hand, the cyano-group-substituted **15b** and **16b** showed slightly red-shifted absorption maximums because of conjugation of the parent framework with the cyano group (Figure 2).

The cyclic voltammetry (CV) analyses of pyrrole-based heteroacenes **2c** and **15** demonstrated two reversible oxidation waves [oxidation peak potential ($E_{\mathrm{ox}}^{\mathrm{peak}}$) vs Ag/Ag$^+$; 0.67, 1.24 V for **2c**, 0.67, 1.27 V for **15a**, 0.80, 1.26 V for **15b**] at the scan rate between 30 and 100 mV·s^{-1} as depicted in Figure 3a−c. The first and second oxidation peaks would be identified as consecutive electron-transfer reactions to form the dication. A similar process has been proposed for organic materials with two carbazole moieties.[43] The CV analyses of furan-based heteroacenes **3** and **16a** gave quasi-reversible wave ($E_{\mathrm{ox}}^{\mathrm{peak}}$ vs Ag/Ag$^+$; 1.59 V for **3**, 1.39 and 1.62 V for **16a**), whereas that of **16b** showed a reversible wave (1.64 V vs Ag/Ag$^+$) at the scan rate between 30 and 100 mV·s^{-1} (Figure 3d−f). Two oxidation waves of **16a** indicate the dication formation, similar to pyrrole-based heteroacenes. Although the CV curve of **3** showed one oxidation wave at +1.59 V, it should consist of a two-electron oxidation process. The CV analyses of **16b** also showed one oxidation wave. However, based on the higher oxidation onset and lower current value than those of **3**, the second oxidation wave was probably not observed in the potential window scanned (±2.0 V). The HOMO energy levels (E_{HOMO}) of heteroacenes were estimated from the first oxidation onsets ($E_{\mathrm{ox}}^{\mathrm{onset}}$) to be −5.08 eV for **2c**, −5.07 eV for **15a**, −5.17 eV for **15b**, −5.78 eV for **3**, −5.80 eV for **16a**, and −6.04 eV for **16b**.

Based on the HOMO energy levels and the optical band gaps (E_g) evaluated from the onset wavelengths of UV−vis absorption spectra, LUMO energy levels (E_{LUMO}) of heteroacenes were calculated to be −2.13 eV for **2c**, −2.21 eV for **15a**, −2.43 eV for **15b**, −2.28 eV for **3**, −2.32 eV for **16a**, and −2.78 eV for **16b**. In the produced heteroacene, the introduction of an electron-donating alkyl group in **15a** or **16a** had little influence on the HOMO and LUMO energy levels, while the introduction of the cyano group in **15b** or **16b** resulted in a significant decrease of the HOMO and LUMO energy levels, leaving the HOMO−LUMO energy gaps almost unchanged. These presented compounds practically have lower-lying HOMO energy levels and larger band gaps than pentacene ($E_{\mathrm{HOMO}} = -4.60$ eV, $E_g = -2.21$ eV),[44] which are indicative of better stabilities under ambient conditions.

Conclusion

In summary, we have described an efficient approach for the syntheses of ladder-type π-conjugated heteroacenes containing pyrrole or furan rings from a common intermediate, 2,5-bis(*o*-chloroaryl)hydroquinone **4**, easily prepared by Suzuki−Miyaura cross-coupling reaction of the corresponding aryl diiodide and arylboronic acids. By use of palladium-catalyzed double N-arylation of aniline and intramolecular O-arylation as key reactions, the heteroacenes were regioselectively generated. This synthetic approach should offer rapid preparation of a large variety of ladder-type heteroacenes containing pyrrole or furan rings because various terphenyl skeletons can be designed by appropriate choice of aryl groups. For instance, dissymmetric pyrrole- and furan-based heteroacenes substituted by an alkyl or cyano group were obtained, which have never synthesized so far. Because there has been only limited reports on electronic and structural properties of ladder-type π-conjugated heteroacenes containing furan rings, the synthesis demonstrated here should open a new field, especially in their application to organic semiconducting materials in OFETs.

Experimental Section

Cyclic Voltammetry (CV) Measurements. Cyclic voltammetric measurements were performed in CH_2Cl_2 containing 1.0 mM of

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[42] Cornil, J.; Calbert, J. P.; Brédas, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 1250.

[43] Russell, D.; Meyer, R.; Jubran, N.; Tokarski, Z.; Moudry, R.; Law, K. *J. Electroanal. Chem.* **2004**, *567*, 19.

[44] Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C. H. *Adv. Mater.* **2003**, *15*, 1090.

substrate and 0.1 M of Bu_4NClO_4 as supporting electrolyte at a scan rate between 30 and 100 mV·s^{-1}. The counter and working electrodes were Pt wires, and the reference electrode was Ag/Ag$^+$. The HOMO levels (E_{HOMO}) of all compounds were calculated by using the potential of −4.8 eV for ferrocene/ferrocenium (FOC) on the zero vacuum level scale,[45] the value of 0.18 V (versus Ag/Ag$^+$) for the potential of FOC in a CH_2Cl_2 solution, and the onset value of the first oxidation wave of the substrate (E_{ox}^{onset}), that is, $E_{HOMO} = -e(4.62 + E_{ox}^{onset})$. Accordingly, the LUMO levels were obtained by $E_{LUMO} = -[E_{HOMO} + E_g]$, where E_g was the optical band gaps estimated from the onset position of the UV−vis absorption spectra in the solution.

Representative Procedure for Optimization of the Model Double N-Arylation (Table 1). A 5 mL vial containing a magnetic stirring bar was charged with **6** (83 mg, 0.17 mmol), aniline (18 μL, 0.20 mmol), $Pd(dba)_2$ (5.0 mg, 8.5 μmol), ligand (0.017 mmol), base (0.43 mmol), and toluene (0.30 mL) in a glovebox filled with argon. The vial was taken outside the glovebox, and the resulting mixture was stirred at 100 °C for 1 day under argon. The reaction mixture was cooled to ambient temperature, filtered through a pad of Celite, and concentrated. The crude residue was purified by column chromatography (silica gel; 14% AcOEt in hexane as eluent, R_f 0.45) to provide *N*-phenylcarbazole (**9**) as a colorless solid.

Representative Procedure for Optimization of the Model Intramolecular O-Arylation (Scheme 4). A 5 mL vial containing a magnetic stirring bar was charged with **11** (139 mg, 0.68 mmol), $Pd(OAc)_2$ (4.6 mg, 0.020 mmol), ligand (0.040 mmol), base (1.7 mmol), and toluene (0.90 mL) in a glovebox filled with argon. The vial was taken outside the glovebox, and the resulting mixture was stirred at 100 °C for 1 day under argon. The reaction mixture was cooled to ambient temperature, filtered through a pad of Celite, and concentrated. The crude residue was purified by column chromatography (silica gel; 14% AcOEt in hexane as eluent, R_f 0.50) to provide dibenzofuran (**12**) as a colorless solid.

Synthesis of 2,2′′-Dichloro-2′,5′-dimethoxy[1,1′:4′,1′′-terphenyl] (14). A flame-dried 250 mL Schlenk tube containing a magnetic stirring bar was charged with $Pd(PPh_3)_4$ (575 mg, 0.50 mmol), Na_2CO_3 (2.1 g, 20 mmol), 1,4-diiodo-2,5-dimethoxybenzene[36] (2.0 g, 5.0 mmol), and 2-chlorophenylboronic acid (2.3 g, 15 mmol). The tube was evacuated and backfilled with argon, and then toluene (10 mL), EtOH (5.0 mL), and H_2O (10 mL) were added through the septum via syringe. After the mixture was degassed by freeze−pump−thaw cycles, it was stirred at 80 °C for 4 days under argon. The reaction mixture was cooled to ambient temperature and then poured into 10 mL of water. The organic layer was separated, and the aqueous layer was extracted with AcOEt (3 × 40 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude compound was purified by column chromatography (silica gel; 10% $CHCl_3$ in hexane as an eluent, R_f 0.40) to provide 1.78 g of the title product as a colorless solid (99% yield): mp 195.2−199.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.50−7.48 (m, 2H), 7.41−7.39 (m, 2H), 7.35−7.29 (m, 4H), 6.85 (s, 2H), 3.74 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.6, 137.6, 134.0, 131.9, 129.6, 128.8, 126.6, 114.6, 56.5. Anal. Calcd for $C_{20}H_{16}Cl_2O_2$: C, 66.81; H, 4.57. Found: C, 66.87; H, 4.49.

Synthesis of 2,2′′-Dichloro[1,1′:4′,1′′-terphenyl]-2′,5′-diol (4). A flame-dried 100 mL round-bottom flask containing a magnetic stirring bar was charged with **14** (1.07 g, 3.0 mmol) and 30 mL of dichloromethane under argon. The solution was cooled to 0 °C, and boron tribromide (9.0 mL, 9.0 mmol; 1.0 M in dichloromethane) was added to the solution over 10 min. The reaction mixture was stirred under argon at 0 °C for 8 h and then quenched slowly at 0 °C with 10 mL of H_2O. The resulting mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed twice with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.30) to provide 904 mg of the title product as a colorless solid (91% yield): mp 198.2−202.3 °C; ^{1}H NMR ($CDCl_3$) δ 7.56−7.52 (m, 2H), 7.43−7.36 (m, 6H), 6.83 (s, 2H), 4.58 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 146.4, 135.5, 133.9, 132.2, 130.3, 129.9, 127.5, 127.3, 118.0. HRMS-FAB$^+$ (*m/z*) calcd for $C_{18}H_{12}Cl_2O_2$ 330.0214, found 330.0208.

Synthesis of 2′,5′-Bis(1,1,2,2,3,3,4,4,4-nonafluorobutanesulfonyloxy)-2,2′′-dichloro[1,1′:4′,1′′-terphenyl] (5). A flame-dried 100 mL round-bottom flask containing a magnetic stirring bar was charged with **4** (904 mg, 3.0 mmol), anhydrous pyridine (1.46 mL, 18.0 mmol), and 30 mL of dichloromethane under argon. After the mixture was degassed by freeze−pump−thaw cycles, the flask was filled with argon and cooled to 0 °C. Nonafluorobutanesulfonic anhydride (2.8 mL, 9.0 mmol) was slowly added to the solution. The reaction mixture was stirred under argon at 0 °C for 7 h and then quenched slowly at 0 °C with 5.0 mL of 1.0 M aqueous HCl. The resulting mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed twice with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (silica gel; 10% AcOEt in hexane as an eluent, R_f 0.50) to provide 2.5 g of the title product as a colorless solid (93% yield): mp 117.1−119.6 °C; ^{1}H NMR ($CDCl_3$) δ 7.57−7.55 (m, 2H), 7.50 (s, 2H), 7.47−7.40 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 145.6, 134.9, 133.7, 132.6, 131.9, 131.0, 130.1, 127.1, 125.7, 118.3−109.4 (m, $CF_2CF_2CF_2CF_3$). Anal. Calcd for $C_{26}H_{10}Cl_2F_{18}O_6S_2$: C, 34.88; H, 1.13. Found: C, 35.04; H, 1.37.

Synthesis of 5,11-Diphenylindolo[3,2-*b*]carbazole (2c). A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with K_3PO_4 (212 mg, 1.0 mmol), 2-di-*tert*-butylphosphino-2′-methylbiphenyl (**10**) (50 mg, 0.16 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (132 mg, 0.60 mmol), and **5** (179 mg, 0.20 mmol). The tube was evacuated and backfilled with argon, and then aniline (46 μL, 0.50 mmol) and toluene (0.60 mL) were added through the septum via syringe. After the mixture was degassed by freeze−pump−thaw cycles, $Pd(dba)_2$ (46 mg, 0.080 mmol) was added to the mixture under argon. The resulting mixture was degassed by freeze−pump−thaw cycles again and stirred at 100 °C for 4 days under argon. The reaction mixture was cooled to ambient temperature, filtered through a pad of Celite, and concentrated. The crude residue was purified by column chromatography (silica gel; 20% $CHCl_3$ in hexane as eluent, R_f 0.40) to provide 70 mg of the title product as a pale yellow solid (86% yield). Recrystallization from hexane/chloroform gave the platelet crystals suitable for crystallographic analysis: mp 180.5−182.3 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 2H), 8.08 (s, 2H), 7.71−7.67 (m, 8H), 7.55−7.51 (m, 2H), 7.44−7.38 (m, 4H), 7.26−7.22 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 142.2, 138.5, 137.2, 130.2, 127.4, 126.1, 123.6, 123.5, 120.4, 119.5, 109.6, 100.0. HRMS-FAB$^+$ (*m/z*) calcd for $C_{30}H_{20}N_2$ 408.1627, found 408.1627.

Synthesis of Dibenzo[*d*,*d*′]benzo[1,2-*b*:4,5-*b*′]difuran (3). A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with KOAc (245 mg, 1.0 mmol), 2-di-*tert*-butylphosphino-2′-methylbiphenyl (**10**) (25 mg, 0.080 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (132 mg, 0.60 mmol), and **4** (66 mg, 0.20 mmol). The tube was evacuated and backfilled with argon, and then toluene (0.40 mL) and DME (0.20 mL) were added through the septum via syringe. After the mixture was degassed by freeze−pump−thaw cycles, $Pd(OAc)_2$ (9.0 mg, 0.040 mmol) was added to the mixture under argon. The resulting mixture was degassed by freeze−pump−thaw cycles again and stirred at 100 °C for 4 days under argon. The reaction mixture was cooled to ambient temperature, filtered with a pad of Celite, and concentrated. The crude compound was purified by column chromatography (silica gel; 20% $CHCl_3$ in hexane as an eluent, R_f 0.35) to provide 37 mg of the title product as a colorless solid (71% yield). Recrystallization from hexane/THF gave the platelet crystals suitable for crystallographic analysis: ^{1}H NMR ($CDCl_3$) δ 8.07 (s, 2H), 8.03 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.50 (td, J = 7.7, 1.1 Hz,

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[45] Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

2H), 7.38 (td, J = 7.6, 0.95 Hz, 2H). These ^{1}H NMR data are identical to that in the previous literature.[31] HRMS-FAB^{+} (m/z) calcd for $C_{18}H_{10}O_2$ 258.0681, found 258.0681.

Synthesis of 2′-Chloro-2,5-dimethoxy-4-iodobiphenyl (17). The crude material was obtained by using 1,4-diiodo-2,5-dimethoxybenzene[36] (2.38 g, 6.1 mmol), 2-chlorophenylboronic acid (1.9 g, 12.2 mmol), Pd(PPh$_3$)$_4$ (352 mg, 0.30 mmol), Na_2CO_3 (424 mg, 24.4 mmol) in toluene (10 mL), EtOH (5 mL), and H_2O (10 mL) (80 °C, 2 days) according to the procedure described for the synthesis of compound **14**. Purification by column chromatography (silica gel; 10% $CHCl_3$ in hexane as an eluent, R_f 0.45) provided 371 mg of the title product as a colorless solid (99% yield): mp 54.1−58.6 °C; ^{1}H NMR (CDCl$_3$) δ 7.49−7.45 (m, 1H), 7.38 (s, 1H), 7.32−7.28 (m, 3H), 6.70 (s, 1H), 3.84 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 152.5, 151.6, 137.0, 133.8, 131.6, 129.6, 129.5, 129.0, 126.6, 122.7, 113.9, 85.4, 57.2, 56.7. HRMS-FAB^{+} (m/z) calcd for $C_{14}H_{12}ClIO_2$ 373.9571, found 373.9572.

Synthesis of 2,2″-Dichloro-2′,5′-dimethoxy-4-hexyl[1,1′4′,1″-terphenyl] (18a). The crude material was obtained by using **17** (38 mg, 0.10 mmol), the crude **23** (75 mg, 0.20 mmol of **23**, see Supporting Information), Pd(PPh$_3$)$_4$ (6.0 mg, 0.0050 mmol), Na_2CO_3 (42 mg, 0.40 mmol) in toluene (0.60 mL), EtOH (0.20 mL), and H_2O (0.20 mL) (90 °C, 2 days) according to the procedure described for the synthesis of compound **14**. Purification by column chromatography (silica gel; 10% $CHCl_3$ in hexane as an eluent, R_f 0.40) provided 41 mg of the title product as a colorless solid (92% yield): mp 102.8−103.4 °C; ^{1}H NMR (CDCl$_3$) δ 7.50 (dd, J = 7.6, 1.1 Hz, 1H), 7.41 (dd, J = 6.9, 2.0 Hz, 1H), 7.36−7.30 (m, 4H), 7.15 (d, J = 7.8, 0.7 Hz, 1H), 6.86 (s, 1H), 6.85 (s, 1H), 3.751 (s, 3H), 3.747 (s, 3H), 2.65 (t, J = 7.8 Hz, 2H), 1.68 (quint, J = 7.8 Hz, 2H), 1.43−1. 30 (m, 6H), 0.92 (t, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 150.7, 150.5, 144.0, 137.7, 134.7, 134.0, 133.6, 132.0, 131.6, 129.6, 129.4, 128.9, 128.8, 128.6, 126.8, 126.6, 114.9, 114.6, 56.54, 56.52, 35.6, 31.9, 31.3, 29.2, 22.8, 14.3. Anal. Calcd for $C_{26}H_{28}Cl_2O_2$: C, 70.28; H, 6.36. Found: C, 70.43; H, 6.36.

Synthesis of 2,2″-Dichloro-2′,5′-dimethoxy[1,1′:4′,1″-terphenyl]-4-yl Cyanide (18b). The crude material was obtained by using **17** (712 g, 1.9 mmol), **24** (1.0 mg, 3.8 mmol, see Supporting Information), Pd(PPh$_3$)$_4$ (216 mg, 0.19 mmol), Na_2CO_3 (600 mg, 5.7 mmol) in toluene (5.0 mL), EtOH (2.5 mL), and H_2O (5.0 mL) (90 °C, 2 days) according to the procedure described for the synthesis of compound **14**. Purification by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.40) provided 639 mg of the title product as a colorless solid (88% yield): mp 213.1−215.7 °C; ^{1}H NMR (CDCl$_3$) δ 7.78 (d, J = 1.4 Hz, 1H), 7.62 (dd, J = 7.8, 1.6 Hz, 1H), 7.52−7.48 (m, 2H), 7.39−7.31 (m, 3H), 6.86 (s, 1H), 6.80 (s, 1H), 3.74 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 150.7, 150.2, 142.9, 137.3, 135.2, 133.9, 133.0, 132.8, 131.8, 130.1, 130.0, 129.7, 129.0, 126.8, 126.7, 117.8, 114.6, 114.0, 112.6, 56.6, 56.4. HRMS-FAB^{+} (m/z) calcd for $C_{21}H_{15}Cl_2NO_2$ 383.0480, found 383.0497.

Synthesis of 2,2″-Dichloro-4-hexyl[1,1′:4′,1″-terphenyl]-2′,5′-diol (19a). The crude material was obtained by using **18a** (275 mg, 0.62 mmol) and boron tribromide (1.9 mL, 1.9 mmol; 1.0 M in dichloromethane) in dichloromethane (6.0 mL) (0 °C, 8 h) according to the procedure described for the synthesis of compound **4**. Purification by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.30) provided 245 mg of the title product as a colorless solid (95% yield): mp 85.6−86.8 °C; ^{1}H NMR (CDCl$_3$) δ 7.53−7.51 (m, 1H), 7.41−7.34 (m, 4H), 7.29 (d, J = 7.8 Hz, 1H), 7.18 (dd, J = 7.8, 1.1 Hz, 1H), 6.815 (s, 1H), 6.810 (s, 1H), 4.71 (br s, 1H), 2.64 (t, J = 7.8 Hz, 2H), 1.66 (quint, J = 7.8 Hz, 2H), 1.41−1.31 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 146.4, 146.2, 145.3, 135.6, 133.9, 133.5, 132.4, 132.2, 131.9, 130.2, 130.0, 129.8, 127.7, 127.4, 127.2, 127.1, 118.1, 117.8, 35.6, 31.8, 31.2, 29.1, 22.7, 14.2. HRMS-FAB^{+} (m/z) calcd for $C_{24}H_{24}Cl_2O_2$ 414.1153, found 414.1160.

Synthesis of 2,2″-Dichloro-2′,5′-dihydroxy[1,1′4′,1″-terphenyl]-4-yl Cyanide (19b). The crude material was obtained by using **18b** (289 mg, 0.75 mmol) and boron tribromide (4.5 mL, 4.5 mmol; 1.0 M in dichloromethane) in dichloromethane (7 mL) (0 °C, 8 h) according to the procedure described for the synthesis of compound **4**. Purification by column chromatography (silica gel; 50% AcOEt in hexane as an eluent, R_f 0.30) provided 262 mg of the title product as a colorless solid (98% yield): decompose at 229 °C; ^{1}H NMR (CDCl$_3$) δ 7.82 (d, J = 1.6 Hz, 1H), 7.66 (dd, J = 7.8, 1.4 Hz, 1H), 7.57−7.54 (m, 2H), 7.41−7.39 (m, 3H), 6.82 (s, 1H), 6.80 (s, 1H), 4.644 (s, 1H), 4.636 (s, 1H); ^{13}C NMR (acetone-d_6) δ 148.3, 147.8, 143.9, 138.4, 135.6, 134.4, 134.1, 133.7, 133.0, 131.3, 130.4, 129.9, 129.1, 127.7, 126.4, 119.1, 118.28, 118.25, 113.4. Anal. Calcd for $C_{19}H_{11}Cl_2NO_2$: C, 64.07; H, 3.11; N, 3.93. Found: C, 63.80; H, 3.38; N, 3.88.

Synthesis of 2′,5′-Bis(1,1,2,2,3,3,4,4,4-nonafluorobutanesulfonyloxy)-2,2″-dichloro-4-hexyl[1,1′:4′,1″-terphenyl] (20a). The crude material was obtained by using **19a** (369 mg, 0.90 mmol), triethylamine (0.43 mL, 5.3 mmol), and nonafluorobutanesulfonic anhydride (1.1 mL, 3.5 mmol) in dichloromethane (10 mL) (−45 °C, 7 h) according to the procedure described for the synthesis of compound **5**. Purification by column chromatography (silica gel; 25% AcOEt in hexane as an eluent, R_f 0.50) provided 785 mg of the title product as a colorless solid (90% yield): mp 61.1−64.2 °C; ^{1}H NMR (CDCl$_3$) δ 7.56 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 6.0 Hz, 2H), 7.46−7.39 (m, 3H), 7.38 (s, 1H), 7.31 (br s, 1H), 7.22 (dd, J = 7.8, 1.1 Hz, 1H), 2.67 (t, J = 7.6 Hz, 2H), 1.66 (quint, J = 7.6 Hz, 2H), 1.40−1.27 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 146.6, 145.8, 145.6, 135.1, 134.7, 133.7, 133.3, 132.7, 132.0, 131.7, 130.9, 130.1, 129.9, 129.7, 127.3, 127.1, 125.8, 125.7, 120.8−105.8 (m, $CF_2CF_2CF_2CF_3$), 35.6, 31.8, 31.2, 29.0, 22.7, 14.2. HRMS-FAB^{+} (m/z) calcd for $C_{32}H_{22}Cl_2F_{18}O_6S_2$ 977.9947, found 977.9947.

Synthesis of 2′,5′-Bis(1,1,2,2,3,3,4,4,4-nonafluorobutanesulfonyloxy)-2,2″-dichloro[1,1′4′,1″-terphenyl]-4-yl Cyanide (20b). The crude material was obtained by using **19b** (160 mg, 0.45 mmol), triethylamine (0.38 mL, 2.7 mmol), and nonafluorobutanesulfonic anhydride (0.55 mL, 1.8 mmol) in dichloromethane (4.5 mL) (−45 °C, 7 h) according to the procedure described for the synthesis of compound **5**. Purification by column chromatography (silica gel; 14% AcOEt in hexane as an eluent, R_f 0.30) provided 360 mg of the title product as a colorless solid (87% yield): mp 66.2−68.4 °C; ^{1}H NMR (CDCl$_3$) δ 7.87 (d, J = 1.6 Hz, 1H), 7.72 (dd, J = 8.0, 1.6 Hz, 1H), 7.60−7.53 (m, 3H), 7.48−7.40 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 145.7, 145.0, 137.4, 136.1, 135.0, 133.6, 133.5, 133.0, 132.8, 132.2, 131.8, 131.2, 130.6, 130.2, 127.2, 126.1, 125.2, 118.4−107.8 (m, $CF_2CF_2CF_2CF_3$), 116.9, 115.1. HRMS-FAB^{+} (m/z) calcd for $C_{27}H_9Cl_2F_{18}NO_6S_2$ 918.8961, found 919.8962.

Synthesis of 5,11-Diphenyl-3-hexylindolo[3,2-*b*]carbazole (15a). The crude material was obtained using **20a** (98 mg, 0.10 mmol), Pd(dba)$_2$ (23 mg, 0.040 mmol), K_3PO_4 (85 mg, 0.40 mmol), 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (**21**) (37 mg, 0.08 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (66 mg, 0.30 mmol), and aniline (23 μL, 0.25 mmol) in toluene (0.30 mL) (100 °C, 4 days) according to the procedure described for the synthesis of compound **2c**. Purification by column chromatography (silica gel; 20% $CHCl_3$ in hexane as an eluent, R_f 0.45) provided 28 mg of the title product as a pale yellow solid (58% yield): mp 88.6−90.1 °C; ^{1}H NMR (CDCl$_3$) δ 8.11 (d, J = 7.8 Hz, 1H), 8.03 (d, J = 6.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 1H), 7.70−7.66 (m, 8H), 7.54−7.50 (m, 2H), 7.43−7.37 (m, 2H), 7.24−7.21 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 2.73 (t, J = 7.8 Hz, 2H), 1.66 (quint, J = 7.8 Hz, 2H), 1.37−1.27 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 142.6, 142.1, 141.8, 138.6, 138.5, 137.4, 137.2, 130.1, 127.5, 127.44, 127.36, 127.3, 125.9, 123.7, 123.0, 121.5, 120.4, 120.3, 120.1, 119.4, 109.6, 109.1, 99.9, 99.7, 36.9, 32.2, 31.9, 29.3, 22.8, 14.3. HRMS-FAB^{+} (m/z) calcd for $C_{36}H_{32}N_2$ 492.2565, found 492.2550.

Synthesis of 5,11-Diphenylindolo[3,2-*b*]carbazol-3-yl Cyanide (15b). The crude material was obtained using **20b** (92 mg, 0.10 mmol), Pd(dba)$_2$ (23 mg, 0.040 mmol), K_3PO_4 (85 mg, 0.40 mmol), 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (**21**) (37 mg, 0.08 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (66 mg, 0.30 mmol), and aniline (23 μL, 0.25 mmol) in toluene (0.15 mL) and DME (0.15 mL) (100 °C, 4 days) according to the procedure described for the synthesis of compound **2c**. Purification by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.40) provided 27 mg of the title product as a pale yellow solid (62% yield): mp 258.1−261.4 °C; ^{1}H NMR (CDCl$_3$) δ 8.17 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 8.08 (s, 2H), 7.74−7.64 (m, 9H), 7.59 (m, 1H), 7.55 (m, 1H), 7.49 (dd, J = 8.0, 1.0 Hz, 1H), 7.47−7.41 (m, 2H), 7.27 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 142.7, 141.1, 138.2, 138.1, 137.6, 137.3, 130.5, 130.3, 128.3, 127.8, 127.44, 127.37, 127.1, 127.0, 125.4, 123.2, 122.6, 122.0, 121.0, 120.8, 120.4, 119.8, 113.8, 109.8, 108.3, 100.7, 100.5. HRMS-FAB$^+$ (m/z) calcd for $C_{31}H_{19}N_3$ 433.1579, found 433.1571.

Synthesis of 3-Hexyldibenzo[*d*,*d*′]benzo[1,2-*b*:4,5-*b*′]difuran (16a). The crude material was obtained by using **19a** (83 mg, 0.20 mmol), Pd(OAc)$_2$ (9 mg, 0.040 mmol), K_3PO_4 (170 mg, 0.80 mmol), 2-di-*tert*-butylphosphino-2′-methylbiphenyl (**10**) (25 mg, 0.080 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (132 mg, 0.60 mmol) in toluene (0.40 mL) and DME (0.2 mL) (100 °C, 4 days) according to the procedure described for the synthesis of compound **3**. Purification by column chromatography (silica gel; 20% CHCl$_3$ in hexane as an eluent, R_f 0.50) provided 33 mg of the title product as a colorless solid (48% yield): mp 159.7−166.1 °C; ^{1}H NMR (CDCl$_3$) δ 8.03 (s, 1H), 8.02−8.00 (m, 2H), 7.90 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.49 (td, J = 7.8, 1.1 Hz, 1H), 7.41 (s, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.20 (dd, J = 7.9, 0.8 Hz, 1H), 2.80 (t, J = 7.8 Hz, 2H), 1.71 (quint, J = 7.8 Hz, 2H), 1.40−1.31 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 157.8, 157.3, 152.9, 152.8, 143.6, 127.4, 124.8, 124.5, 123.6, 123.5, 122.7, 122.2, 120.8, 120.4, 111.8, 111.5, 102.6, 102.4, 36.6, 31.9, 29.1, 22.8, 14.3. HRMS-FAB$^+$ (m/z) calcd for $C_{24}H_{22}O_2$ 342.1620, found 342.1500.

Synthesis of Dibenzo[*d*,*d*′]benzo[1,2-*b*:4,5-*b*′]difuran-3-yl Cyanide (16b). The crude material was obtained by using **19b** (71 mg, 0.20 mmol), Pd(OAc)$_2$ (9 mg, 0.040 mmol), K_3PO_4 (170 mg, 0.80 mmol), 2-di-*tert*-butylphosphino-2′-methylbiphenyl (**10**) (25 mg, 0.080 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (132 mg, 0.60 mmol) in DME (0.60 mL) (100 °C, 4 days) according to the procedure described for the synthesis of compound **3**. Purification by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.45) provided 18 mg of the title product as a colorless solid (31% yield): mp 276.5−277.8 °C; ^{1}H NMR (CDCl$_3$) δ 8.12−8.09 (m, 3H), 8.05 (d, J = 7.8 Hz, 1H), 7.90 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H); ^{13}C NMR (acetone-d_6) δ 156.8, 155.2, 152.8, 152.4, 133.0, 130.4, 130.3, 129.7, 127.5, 126.6, 123.7, 123.0, 121.3, 119.7, 117.4, 116.5, 115.0, 110.7, 108.8. HRMS-FAB$^+$ (m/z) calcd for $C_{19}H_9NO_2$ 283.0633, found 283.0635.

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Supporting Information Available: General experimental procedures, syntheses of boron reagents, ^{1}H and ^{13}C NMR spectra for synthesized compounds, and crystallographic information files (CIF) for **2c** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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