JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

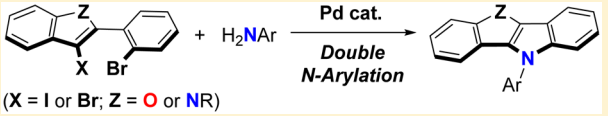
Synthesis of Benzofuro- and Indolo[3,2-*b*]indoles via Palladium-Catalyzed Double *N*-Arylation and Their Physical Properties

Minh Anh Truong and Koji Nakano*

Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

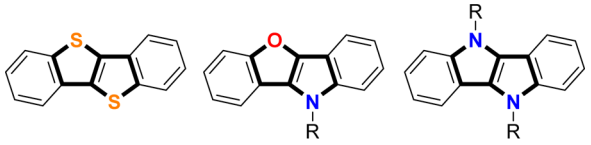
Supporting Information

ABSTRACT: Two kinds of ladder-type π-conjugated compounds, benzofuro[3,2-*b*]indoles (BFIs) and indolo[3,2-*b*]indoles (IIs), were successfully synthesized using palladium-catalyzed double *N*-arylation of anilines with the corresponding dihalobiaryls. Photophysical properties were evaluated by UV−vis and photoluminescence spectroscopies and theoretical calculations. BFI derivatives showed higher quantum yields (33−39%) than the II derivative (29%). The absorption bands of the II derivative were more red-shifted compared to BFI derivatives.



Ladder-type π-conjugated compounds fused with heterocycle(s) have attracted much interest owing to their potential application as organic semiconductors for organic field-effect transistors (OFETs).[1] A huge range of ladder-type π-conjugated compounds have been synthesized and characterized in the last few decades. In particular, thiophene-fused compounds have been widely studied,[2] leading to the development of high-performance organic semiconductors, such as benzothieno[3,2-*b*]benzothiophenes (BTBTs) (Chart 1).[3] Pyrrole- or furan-fused compounds, such as indolo[3,2-*b*]carbazoles (ICs) and naphtho[2,3-*b*:6,7-*b*′]difurans, were also reported to demonstrate high semiconducting properties.[4−6]

Chart 1. Molecular Structures of BTBT, BFI, and II



Benzofuro[3,2-*b*]carbazoles (BFIs) and indolo[3,2-*b*]indoles (IIs) are oxygen/nitrogen and nitrogen homologues of BTBTs, respectively (Chart 1). Recently, these compounds have emerged as new families of organic semiconductors for OFETs.[7] However, their physical properties have been less thoroughly investigated despite the fact that the parent BFI and II have been known for a relatively long time.[8] This should partially be attributed to the limitation in their synthesis until recently. BFIs have been synthesized using a conventional approach including Fischer indole synthesis.[8a,b,9] Recently, more facile approaches were reported in which Cadogan cyclization[10] or intramolecular electrophilic amination of an arene C−H bond[11] was used as a key reaction. The metal-catalyzed intramolecular C−N bond formation[12] and the metal-catalyzed C−H/C−H coupling reaction[13] were also applied to the synthesis of BFI derivatives. Synthesis of II has been achieved via reductive cyclization of dinitrobenzils[14] or 2-(2-nitrophenyl)indoles,[15] thermal cyclization of diazidostilbenes,[16] and Fischer indole synthesis with phenylhydrazines and indolin-3-ones.[17] These methods generally result in low yield and/or require multistep synthesis of the starting materials. Very recently, more convenient methods have been reported that utilize reductive cyclization of 6,12-dibenzo[*b*,*f*][1,5]-diazocines,[7a,18] intramolecular C−H/C−H coupling reaction of 2-(aminophenyl)indoles,[13] or double *N*-arylation of primary amines with 3-bromo-2-(2-bromophenyl)-1-methylindole (the same approach reported in this work, see below).[19] In this context, for further development of organic semiconductors containing the BFI or II moiety, it is highly desirable to investigate both efficient synthetic routes and structure−property relationships.

We have previously reported palladium-catalyzed double *N*-arylation of primary amines with dihalobiaryls to construct the carbazole skeleton.[20] This synthetic method is an important extension of the Buchwald−Hartwig *N*-arylation and has been applied to the synthesis of a variety of carbazole-based natural products and π-conjugated compounds.[21] Indeed, we successfully synthesized ladder-type π-conjugated compounds, such as benzofuro[3,2-*b*]carbazoles and ICs.[22] As part of our ongoing efforts in the application of this synthetic method, we herein report double *N*-arylation of anilines with the corresponding dihalobiaryls to synthesize BFIs and IIs. To the best of our knowledge, there has been no report of the application of the double *N*-arylation strategy to BFI synthesis. The same approach was reported for the synthesis of IIs very recently, although the investigation was limited to 5-methyl-IIs.[19] We have expanded the scope of this approach and successfully synthesized 5,10-diaryl-IIs. Photophysical and electrochemical

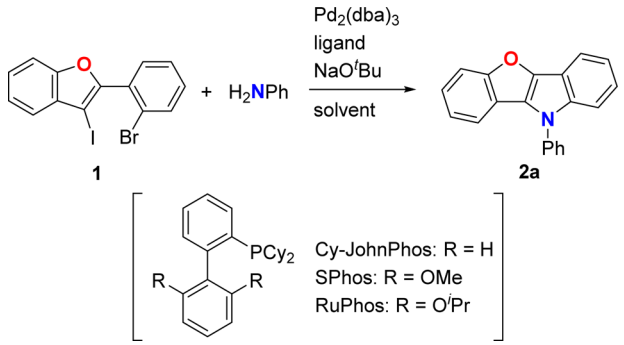
Received: September 6, 2015
Published: October 27, 2015

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566−11572

properties are also discussed in conjugation with theoretical studies.

The double *N*-arylation of aniline with 2-(2-bromophenyl)-3-iodobenzo[*b*]furan (**1**) was first investigated in the presence of $Pd_2(dba)_3$ (10 mol %, dba = dibenzylideneacetone), ligand (30 mol %), and NaO^{t}Bu as a base (3.0 equiv) (Table 1). The use

Table 1. Optimization for Double *N*-Arylation of Aniline with 1[a]

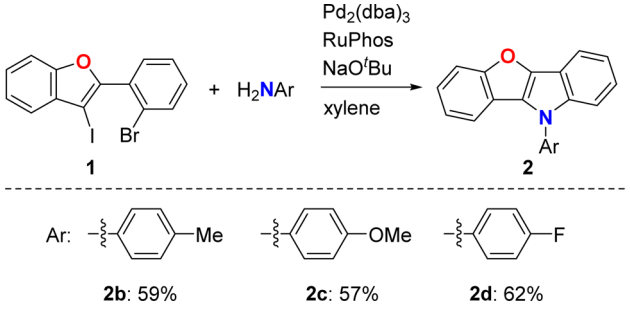


entry	ligand	solvent	T (°C)	isolated yield of **2a** (%)
1	P^{t}Bu$_3$HBF	toluene	85	19
2	Cy-JohnPhos	toluene	95	35
3	Cy-JohnPhos	xylene	120	46
4	SPhos	xylene	120	56
5	RuPhos	xylene	120	80

[a]Reaction conditions: **1** (1.0 equiv), aniline (0.90 equiv), $Pd_2(dba)_3$ (10 mol %), ligand (30 mol %), NaO^{t}Bu (3.0 equiv), solvent, T (°C), 20 h.

of P^{t}Bu$_3$HBF$_4$ in toluene (85 °C), which has been reported as an effective ligand for double *N*-arylation of aniline with dihalobiphenyl in previous work,[20a] provided desired BFI **2a** in only 19% yield (entry 1). After screening biphenylphosphine ligands,[23] solvent, and reaction temperature (entries 2−5), it was found that the double *N*-arylation with RuPhos as a ligand in xylene at 120 °C gave **2a** in high yield (80%, entry 5). With the optimized conditions in hand, other para-substituted anilines were employed for the synthesis of BFI derivatives (Scheme 1). Electron-donating substituents, such as methyl and methoxy groups, were tolerant to the reaction conditions, and anilines containing these moieties could be converted to the corresponding BFIs **2b** and **2c** in moderate yields. Compounds containing the slightly electron-withdrawing fluoro substituent

Scheme 1. Double *N*-Arylation of Anilines with 1[a]

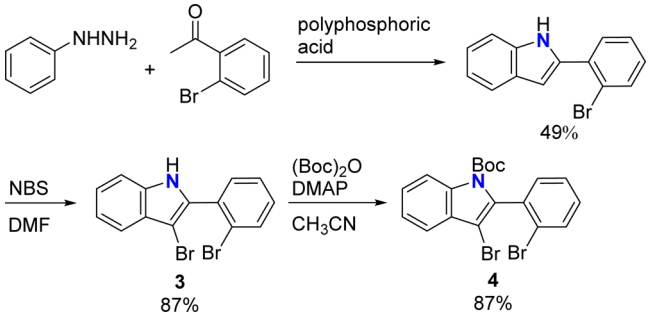


[a]Reaction conditions: **1** (1.0 equiv), aniline (0.90 equiv), $Pd_2(dba)_3$ (10 mol %), RuPhos (30 mol %), NaO^{t}Bu (3.0 equiv), xylene, 120 °C, 20 h.

could be used, but the desired compounds were not obtained from aniline derivatives bearing a more electron-withdrawing trifluoromethyl or acyl group.

The synthesis of indolo[3,2-*b*]indoles (IIs) using the double *N*-arylation strategy was investigated next. In a previous report in which the double *N*-arylation strategy was applied to the synthesis of II, 3-bromo-2-(2-bromophenyl)-1-methylindole was used as the starting material.[19] In the present work, 3-bromo-2-(2-bromophenyl)indole (**3**) was initially designed as the starting material because the free NH group allows the postfunctionalization of the double *N*-arylation product. Compound **3** was successfully synthesized via Fischer indole synthesis from commercially available 2-bromoacetophenone and phenylhydrazine[24] followed by bromination with *N*-bromosuccinimide (NBS) (Scheme 2). However, preliminary

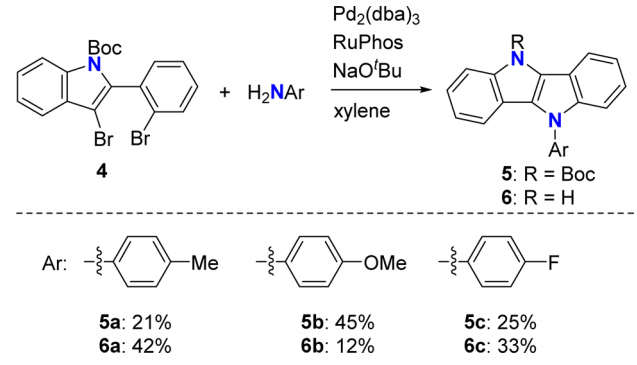
Scheme 2. Synthesis of the Starting Materials



experiments demonstrated that double *N*-arylation of 4-methylaniline with **3** did not give the desired product. Accordingly, *N*-protected compound **4** was used as the starting material. The *tert*-butoxycarbonyl (Boc) group was chosen as a protecting group because it can be cleaved easily after double *N*-arylation and allows postfunctionalization.

The double *N*-arylation of aniline derivatives with **4** was found to proceed under the optimized conditions for BFI synthesis (Scheme 3). The reaction between 4-methylaniline and **4** gave desired product **5a** in 21% yield along with deprotected compound **6a** in higher yield (42%). A decrease in reaction temperature resulted in higher **5a**/**6a** ratio (Table S1 in the Supporting Information). However, the total yield was lower. The use of weaker base (K_3PO_4) also resulted in lower total yield of **5a** and **6a**. Accordingly, the initial conditions for

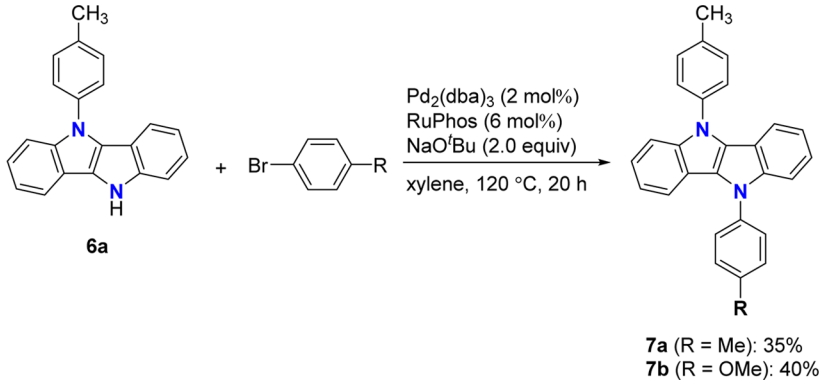
Scheme 3. Double *N*-Arylation of Anilines with 4[a]



[a]Reaction conditions: **4** (1.0 equiv), aniline (1.1 equiv), $Pd_2(dba)_3$ (10 mol %), RuPhos (30 mol %), NaO^{t}Bu (3.0 equiv), xylene, 120 °C, 20 h.

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566−11572

Scheme 4. Post-functionalization of II 6a



the reaction with 4-methoxy- and 4-fluoroanilines were employed to obtain the corresponding protected and deprotected products in moderate total yields (Scheme 3).

Postfunctionalization was demonstrated by using the deprotected compound **6a** (Scheme 4). A Buchwald–Hartwig coupling reaction between **6a** and *p*-bromotoluene gave symmetric II **7a** in 35% yield. In addition, the reaction with 4-bromoanisole afforded dissymmetric II **7b** in 40% yield.

The photophysical properties of BFIs **2** and II **7a** were evaluated using ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectroscopies. The spectra are shown in Figure 1, and photophysical data are summarized in

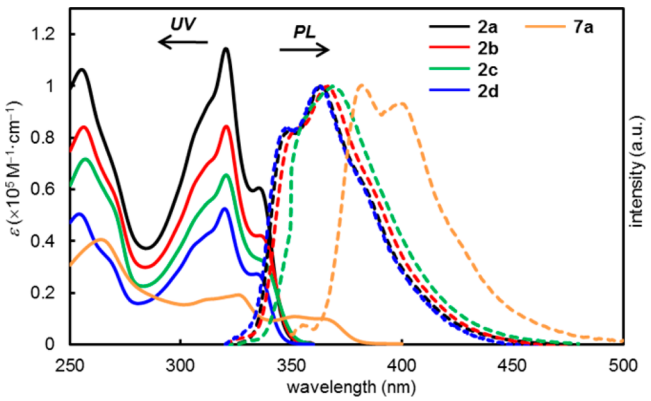


Figure 1. UV–vis absorption and photoluminescence spectra of BFIs **2** and II **7a**.

Table 2. All of the benzofuro[3,2-*b*]indoles **2** exihibited almost identical spectra with two absorption bands around 321 and 260 nm. However, the molar absorption coefficients of the compounds are different. These results indicate that the para substituent of the *N*-phenyl group has little influence on the electronic structure of the BFI core. In the PL spectra, each BFI **2** exhibited an emission maximum in the 360–370 nm region with a shoulder around 350 nm. The quantum yields in solution were relatively high (33–39%). Absorption spectrum of II **7a** showed the longest absorption maximum at 365 nm, which was red-shifted compared to those of BFIs **2**. Pyrrole is known to possess higher aromatic character than furan.[25] Therefore, the II skeleton affords more effective π-electron delocalization over the entire 18π electron system, leading to the red-shifted absorption. The PL spectrum of **7a** was also red-shifted to show violet emission (two maxima of 382 and 400 nm), whereas the quantum yield was lower than those of the

Table 2. Photophysical and Electrochemical Data of BFIs 2 and II 7a

	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	Φ (%)[c]	E_g (eV)[d]	E_{ox}^{onset} (V)[e]	E_{HOMO} (eV)[f]	calcd E_{HOMO} (eV)[g]
2a	321	363	39	3.58	0.59	−5.39	−5.15
2b	321	366	36	3.54	0.57	−5.37	−5.11
2c	321	369	33	3.54	0.56	−5.36	−5.06
2d	320	363	38	3.59	0.60	−5.40	−5.22
7a	365	382/400	29	3.26	0.25	−5.05	−4.71

[a]In CH_2Cl_2 (1.0×10^{-5} M). [b]In CH_2Cl_2 (1.0×10^{-7} M); excitation at 300 nm for BFI **2** and 320 nm for II **7a**. [c]Absolute quantum yield determined by a calibrated integrating sphere system; excitation at 260 nm for BFIs **2** and 310 nm for II **7a**. [d]Optical band gaps estimated from the onset position of the UV–vis absorption spectra in solution. [e]Onset potentials (vs Fc/Fc^+) of the first oxidation wave determined by cyclic voltammetry: 1 mM in CH_2Cl_2 with 0.1 M Bu_4NClO_4, Pt as working and counter electrodes, scan rate = 50 mV s^{-1}. [f]Calculated according to $E_{HOMO} = -(E_{ox} + 4.80)$ eV (Fc/Fc^+ redox couple: 4.8 eV below the vacuum level). [g]DFT calculation at the B3LYP/6-31G(d) level of theory.

BFIs. Absorption and emission bands of II **7a** are almost identical to those recently reported for *N*-methyl-IIs.[19] Accordingly, the substituent on the pyrrole rings has little influence on these photophysical properties.

The cyclic voltammograms of BFIs **2** and II **7a** are shown in Figure 2 and Figure S32. All of BFIs **2** showed similar voltammograms with one irreversible oxidation wave (see Figure S32 for **2b–2d**). Their oxidation onsets (E_{ox}^{onset}) were around 0.60 eV (vs Fc/Fc^+), and the HOMO energy levels were estimated to be around −5.40 eV under the premise that

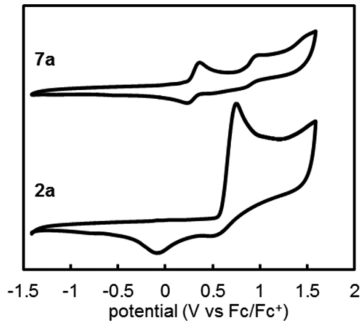


Figure 2. Cyclic voltammograms of **2a** and **7a** [measurement conditions: 1 mM in CH_2Cl_2 with Bu_4NClO_4 (0.10 M); scan rate = 50 mV s^{-1}].

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566–11572

the energy level of Fc/Fc^+ is 4.8 eV below the vacuum level.[26] Conversely, the voltammmogram of II **7a** contains two reversible oxidation waves with the first oxidation onset of 0.25 eV. Accordingly, the estimated HOMO energy level of II **7a** (−5.05 eV) was higher than those of BFIs **2**.

Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d) level of theory to obtain better understanding of the physical properties of BFIs and IIs. The calculated $S_0 \rightarrow S_1$ transition energy of BFIs **2** are 3.88−3.91 eV (319−317 nm) (see Table S7 for the selected absorption peaks) and agrees well with the experimental values (λ_{abs}) in UV−vis spectra (Table 2). The $S_0 \rightarrow S_1$ transitions are dominated by the HOMO−LUMO ($\pi-\pi^*$) transitions. The longest absorption bands in UV−vis spectra of **2a**−**2c** are derived from the $S_0 \rightarrow S_1$ transitions whereas that of **2d** involves both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions with similar oscillator strengths. The red-shifted longest absorption band of II **7a** in UV−vis spectrum (365 nm) was also predicted by calculation (344 nm). The calculated HOMO energy levels of BFIs **2** and II **7a** are slightly higher than those estimated from CV analysis (Table 2), whereas calculation supports the suggestion that BFIs **2** possess lower HOMO energy levels than those of II **7a**.

In conclusion, the synthesis of benzofuro[3,2-*b*]indoles (BFIs) and indolo[3,2-*b*]indoles (IIs) are reported here. A double *N*-arylation strategy was found to be effective for the synthesis of these compounds. The para substituent on the aryl moiety of BFIs has little effect on their physical properties. The II derivative displayed more red-shifted absorption and emission bands and a higher HOMO energy level than BFIs, which could be caused by more effective π-electron delocalization over the π-conjugated framework. These results should be useful in the development of BFI- and II-based organic functional materials.

EXPERIMENTAL SECTION

General Procedures. NMR spectra were recorded in $CDCl_3$, C_6D_6, or acetone-d_6 on a 500 MHz spectrometer (^1H 500 MHz; ^{13}C 126 MHz; ^{19}F 470 MHz) or a 400 MHz spectrometer (^1H 400 MHz; ^{13}C 101 MHz). Chemical shifts are reported in ppm relative to the internal standard signal (0 ppm for Me_4Si in $CDCl_3$) or the solvent residual signal (7.16 ppm in C_6D_6; 2.05 ppm in acetone-d_6) for ^1H and the deuterated solvent signal (77.16 ppm for $CDCl_3$; 128.06 ppm for C_6D_6; 206.26 ppm for acetone-d_6) for ^{13}C. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, and/or multiple resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on a melting point apparatus. High resolution mass spectra are taken by the atmospheric pressure chemical ionization-time-of-flight (APCI−TOF) method. UV−vis absorption spectra were recorded on a UV−vis scanning spectrophotometer. Photoluminescence spectra were recorded on a spectrofluorometer. Absolute quantum yields were determined by a calibrated integrating sphere system.

All manipulations involving air- and/or moisture-sensitive compounds were carried out with the standard Schlenk technique under argon. Most of reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25 mm of 230−400 mesh silica gel containing a fluorescent indicator. Column chromatography was performed using silica gel (spherical neutral, particle size 63−210 μm). 2-(2-Bromophenyl)-3-iodobenzo[*b*]furan (**1**)[27] and 2-(2-bromophenyl)indole[24] were synthesized according to the literature.

Computational Studies. The DFT and TD-DFT calculations were performed using the Gaussian 09 program[28] at the B3LYP/6-31G(d) level.

*General Procedure for the Double N-Arylation of Anilines with 2-(2-Bbromophenyl)-3-iodobenzo[b]furan (**1**).* A Schlenk tube was charged with **1**, aniline, $Pd_2(dba)_3$ (10 mol %), RuPhos (30 mol %), and NaO^tBu (3.0 equiv) in anhydrous xylene. After being degassed by three freeze-thaw pump cycles, the resulting mixture was stirred at 120 °C for 20 h under an argon atmosphere. Then, the reaction mixture was cooled to room temperature, diluted with $CHCl_3$ or CH_2Cl_2, and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography.

*10-Phenylbenzofuro[3,2-b]indole (**2a**).* The crude residue was obtained using **1** (459 mg, 1.2 mmol), aniline (95 μL, 1.0 mmol), $Pd_2(dba)_3$ (105 mg, 0.11 mmol), RuPhos (161 mg, 0.33 mmol), NaO^tBu (301 mg, 3.1 mmol), and anhydrous xylene (7.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/$CHCl_3$ = 9:1 as an eluent) to afford the title compound as a pale yellow solid (261 mg, 80% yield): mp 134−136 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87−7.83 (m, 1H), 7.63−7.58 (m, 4H), 7.54 (t, J = 7.8 Hz, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.28−7.14 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 143.8, 139.6, 138.4, 129.8, 126.8, 126.5, 125.1, 124.0, 123.3, 122.6, 120.8, 118.7, 118.5, 117.5, 114.7, 112.8, 111.4; HRMS-APCI$^+$ (m/z) calcd for $C_{20}H_{14}NO$ ($[M + H]^+$) 284.1070, found 284.1052.

*10-(4-Methylphenyl)benzofuro[3,2-b]indole (**2b**).* The crude residue was obtained using **1** (241 mg, 0.60 mmol), 4-methylaniline (59 mg, 0.54 mmol), $Pd_2(dba)_3$ (55 mg, 0.060 mmol), RuPhos (84 mg, 0.18 mmol), NaO^tBu (174 mg, 1.8 mmol), and anhydrous xylene (8.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/$CHCl_3$ = 9:1 as an eluent) to afford the title compound as a yellow solid (107 mg, 59% yield): mp 132−137 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.83 (m, 1H), 7.60−7.55 (m, 2H), 7.51−7.45 (m, 3H), 7.34 (d, J = 7.8 Hz, 2H), 7.28−7.14 (m, 4H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 143.6, 139.7, 136.7, 135.8, 130.4, 126.7, 125.0, 124.0, 123.1, 122.5, 120.6, 118.8, 118.5, 117.4, 114.5, 112.8, 111.4, 21.2; HRMS-APCI$^+$ (m/z) calcd for $C_{21}H_{16}NO$ ($[M + H]^+$) 298.1227, found 298.1243.

*10-(4-Methoxyphenyl)benzofuro[3,2-b]indole (**2c**).* The crude residue was obtained using **1** (228 mg, 0.57 mmol), 4-methoxyaniline (64 mg, 0.52 mmol), $Pd_2(dba)_3$ (52 mg, 0.056 mmol), RuPhos (80 mg, 0.17 mmol), NaO^tBu (165 mg, 1.7 mmol), and anhydrous xylene (8.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/$CHCl_3$ = 3:1 as an eluent) to afford the title compound as a yellow solid (101 mg, 57% yield): mp 137−140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.84 (m, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.52−7.49 (m, 3H), 7.42 (d, J = 7.3 Hz, 1H), 7.28−7.21 (m, 3H), 7.17 (t, J = 7.3 Hz, 1H), 7.07−7.04 (m, 2H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 158.5, 143.3, 140.0, 131.2, 126.9, 126.6, 124.0, 123.0, 122.6, 120.5, 118.7, 118.3, 117.4, 115.0, 114.3, 112.8, 111.2, 55.7; HRMS-APCI$^+$ (m/z) calcd for $C_{21}H_{16}NO_2$ ($[M + H]^+$) 314.1176, found 314.1197.

*10-(4-Fluorophenyl)benzofuro[3,2-b]indole (**2d**).* The crude residue was obtained using **1** (219 mg, 0.55 mmol), 4-fluoroaniline (50 μL, 0.50 mmol), $Pd_2(dba)_3$ (50 mg, 0.055 mmol), RuPhos (77 mg, 0.16 mmol), NaO^tBu (158 mg, 1.7 mmol), and anhydrous xylene (8.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/$CHCl_3$ = 5:1 to 9:1 as eluents) to afford the title compound as a yellow solid (102 mg, 62% yield): mp 158−162 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87−7.84 (m, 1H), 7.62−7.57 (m, 3H), 7.53−7.51 (m, 1H), 7.40 (d, J = 7.3 Hz, 1H), 7.31−7.18 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J_{CF} = 247 Hz), 159.4, 143.7, 139.9, 134.5 (d, J_{CF} = 3 Hz), 126.9 (d, J_{CF} = 9 Hz), 126.7, 124.2, 123.4, 122.7, 120.9, 118.5, 118.2, 117.6, 116.8 (d, J_{CF} = 23 Hz), 114.6, 112.9, 111.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −114.4; HRMS-APCI$^+$ (m/z) calcd for $C_{20}H_{13}FNO$ ($[M + H]^+$) 302.0976, found 302.0996.

*3-Bromo-2-(2-bromophenyl)indole (**3**).* A Schlenk tube was charged with 2-(2-bromophenyl)indole (923 mg, 3.4 mmol) and anhydrous DMF (15 mL). To the mixture was added a solution of *N*-bromosuccinimide (604 mg, 3.4 mmol) in anhydrous DMF (15 mL) dropwise at room temperature. After stirring at room temperature for

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566−11572

14 h, the reaction mixture was diluted with Et_2O and then washed with water. The organic layer was dried over Na_sSO_4 and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 as an eluent) to afford the title compound as a yellow oil (958 mg, 81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (brs, 1H), 7.72 (dd, J = 7.9, 1.0 Hz, 1H), 7.62 (dt, J = 7.7, 1.4 Hz, 2H), 7.46−7.39 (m, 2H), 7.32−7.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 133.8, 133.4, 133.1, 132.2, 130.6, 127.5, 127.4, 123.7, 123.4, 120.9, 119.6, 111.4, 92.1; HRMS-APCI$^+$ (m/z) calcd for $C_{14}H_{10}Br_2N$ ([M + H]$^+$) 351.9155 (100%), 349.9175 (51%), and 353.9134 (49%), found 351.9174, 349.9193, and 353.9156.

*1-(tert-Butoxycarbonyl)-3-bromo-2-(2-bromophenyl)indole (**4**).* A Schlenk tube was charged with **3** (387 mg, 1.1 mmol), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (4 mg, 0.033 mmol), and anhydrous acetonitrile (5.0 mL). To the mixture was added $(Boc)_2O$ (0.28 mL, 1.2 mmol) at room temperature. After stirring at room temperature for 23 h, the reaction mixture was evaporated under reduced pressure. Then, the reaction mixture was diluted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 as an eluent) to afford the the title compound as a colorless solid (431 mg, 87% yield): mp 98−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.2 Hz, 1H), 7.68−7.68 (m, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.45−7.28 (m, 5H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 135.7, 135.3, 135.2, 132.5, 132.1, 130.2, 128.4, 127.2, 126.0, 125.0, 123.6, 119.7, 115.9, 101.4, 83.9, 27.6; HRMS-APCI$^+$ (m/z) calcd for $C_{15}H_{10}Br_2NO_2$ ([M − ^{t}Bu + 2H]$^+$) 395.9052 (100%), 393.9073 (51%), and 397.9032 (49%), found 395.9063, 393.9084, and 397.9035.

*General Procedure for the Double N-Arylation of Anilines with **4**.* A Schlenk tube was charged with **4**, aniline, $Pd_2(dba)_3$ (10 mol %), RuPhos (30 mol %), and NaO^{t}Bu (3.0 equiv) in anhydrous xylene. After being degassed by three freeze-thaw pump cycles, the resulting mixture was stirred at 120 °C for 20 h under an argon atmosphere. Then, the reaction mixture was cooled to room temperature, diluted with $CHCl_3$, and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography.

*5-(tert-Butoxycarbonyl)-10-(4-methylphenyl)indolo[3,2-b]indole (**5a**) and 5-(4-Methylphenyl)indolo[3,2-b]indole (**6a**).* The crude residue was obtained using **4** (303 mg, 0.67 mmol), 4-methylaniline (72 mg, 0.67 mmol), $Pd_2(dba)_3$ (62 mg, 0.067 mmol), RuPhos (94 mg, 0.20 mmol), NaO^{t}Bu (194 mg, 2.0 mmol), and anhydrous xylene (6.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 as an eluent) to afford **5a** as a yellow solid (52 mg, 21%) and **6a** as a yellow solid (81 mg, 42% yield). **5a**: mp 152−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56−8.54 (m, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.48−7.39 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.36−7.29 (m, 2H), 7.27−7.22 (m, 2H), 7.16 (d, J = 7.1 Hz, 1H), 2.50 (s, 3H), 1.82 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.9, 141.3, 139.7, 137.5, 135.5, 130.4, 128.5, 126.5, 124.3, 123.9, 123.0, 122.5, 121.8, 120.2, 118.9, 118.2, 117.1, 116.9, 110.6, 84.2, 28.7, 21.4; HRMS-APCI$^+$ (m/z) calcd for $C_{22}H_{17}N_2O_2$ ([M − ^{t}Bu + 2H]$^+$) 341.1285, found 341.1288. **6a**: mp 147−151 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.77 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.38−7.32 (m, 3H), 7.30−7.25 (m, 2H), 7.20−7.18 (m, 1H), 7.14−7.10 (m, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.82 (brs, 1H), 2.12 (s, 3H); ^{13}C{^{1}H} (126 MHz, acetone-d_6) δ 141.9, 141.6, 137.5, 137.0, 131.1, 129.8, 127.0, 126.9, 126.0, 123.3, 122.8, 120.3, 119.3, 118.9, 118.7, 116.9, 115.8, 113.2, 111.4, 21.1; HRMS-APCI$^+$ (m/z) calcd for $C_{21}H_{17}N_2$ ([M + H]$^+$) 297.1387, found 297.1401.

*5-(tert-Butoxycarbonyl)-10-(4-methoxyphenyl)indolo[3,2-b]-indole (**5b**) and 5-(4-Methoxyphenyl)indolo[3,2-b]indole (**6b**).* The crude residue was obtained using **4** (419 mg, 0.93 mmol), 4-methylaniline (126 mg, 1.0 mmol), $Pd_2(dba)_3$ (85 mg, 0.093 mmol), RuPhos (0.13 g, 0.28 mmol), NaO^{t}Bu (268 mg, 2.8 mmol), and anhydrous xylene (8.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 as an eluent) to afford **5b** as a yellow solid (174 mg, 45% yield) and **6b** as a yellow solid (36 mg, 12% yield). **5b**: mp 170−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55−8.53 (m, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.54−7.50 (m, 2H), 7.42−7.38 (m, 1H), 7.33−7.22 (m, 4H), 7.17−7.19 (m, 3H), 3.92 (s, 3H), 1.82 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.0, 150.9, 141.6, 139.7, 130.9, 128.8, 128.1, 124.3, 123.6, 123.0, 122.5, 121.8, 120.1, 118.9, 118.1, 117.0, 116.9, 115.0, 110.5, 84.2, 55.8, 28.7; HRMS-APCI$^+$ (m/z) calcd for $C_{22}H_{17}N_2O_3$ ([M − ^{t}Bu + 2H]$^+$) 357.1234, found 357.1236. **6b**: mp 185−190 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.82 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.38−7.21 (m, 6H), 7.12−7.10 (m, 1H), 6.82 (brs, 1H), 6.77−6.73 (m, 2H), 3.31 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ 159.4, 141.94, 141.90, 132.8, 127.7, 127.4, 126.6, 123.3. 122.8, 120.2, 119.3, 118.9, 118.6, 116.7, 115.9, 115.8, 113.2, 111.4, 56.0; HRMS-APCI$^+$ (m/z) calcd for $C_{21}H_{17}N_2O$ ([M + H]$^+$) 313.1335, found 313.1364.

*5-(tert-Butoxycarbonyl)-10-(4-fluorophenyl)indolo[3,2-b]indole (**5c**) and 5-(4-Fluorophenyl)indolo[3,2-b]indole (**6c**).* The crude residue was obtained using **4** (470 mg, 1.0 mmol), 4-fluoroaniline (0.11 mL, 1.1 mmol), $Pd_2(dba)_3$ (95 mg, 0.10 mmol), RuPhos (146 mg, 0.31 mmol), NaO^{t}Bu (300 mg, 3.1 mmol), and anhydrous xylene (8.0 mL). The resulting crude residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 as an eluent) to afford **5c** as a yellow solid (90 mg, 25% yield) and **6c** as a brown solid (104 mg, 33% yield). **5c**: mp 177−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57−8.55 (m, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.60−7.56 (m, 2H), 7.41−7.38 (m, 1H), 7.34−7.23 (m, 6H), 7.16 (t, J = 7.5 Hz, 1H), 1.82 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J_{CF} = 247 Hz), 150.8, 141.3, 139.7, 134.2 (d, J_{CF} = 3 Hz), 128.5 (d, J_{CF} = 9 Hz), 124.4, 124.1, 123.3, 122.6, 122.0, 120.5, 118.6, 117.9, 117.2, 117.0, 116.8 (d, J_{CF} = 23 Hz), 110.3, 84.3, 28.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ −113.6; HRMS-APCI$^+$ (m/z) calcd for $C_{21}H_{14}FN_2O_2$ ([M − ^{t}Bu + 2H]$^+$) 345.1034, found 345.1046. **6c**: mp 201−205 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 10.55 (brs, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.80−7.77 (m, 2H), 7.57 (m, 2H), 7.49−7.45 (m, 3H), 7.28−7.19 (m, 3H), 7.05−7.02 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ 161.9 (d, J_{CF} = 245 Hz), 141.9, 141.8, 136.4 (d, J_{CF} = 2 Hz), 128.2 (d, J_{CF} = 8 Hz), 127.0, 123.6, 123.0, 120.7, 119.5, 119.0, 118.5, 117.4 (d, J_{CF} = 23 Hz), 117.1, 115.7, 113.32, 113.26, 111.3; ^{19}F NMR (470 MHz, acetone-d_6) δ −117.0; HRMS-APCI$^+$ (m/z) calcd for $C_{20}H_{14}FN_2$ ([M + H]$^+$) 301.1136, found 301.1166.

*5,10-Bis(4-methylphenyl)indolo[3,2-b]indole (**7a**).* A Schlenk tube was charged with **6a** (69 mg, 0.23 mmol), 4-bromotoluene (44 mg, 0.26 mmol), $Pd_2(dba)_3$ (4 mg, 4.6 μmol), RuPhos (7 mg, 0.014 mmol), and NaO^{t}Bu (45 mg, 0.47 mmol) in anhydrous xylene (5.0 mL). After being degassed by three freeze-thaw pump cycles, the resulting mixture was stirred at 120 °C for 20 h. Then, the reaction mixture was cooled to room temperature, diluted with $CHCl_3$, and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 to 6:1 as eluents) to afford the title compound as a yellow solid (32 mg, 35% yield): mp 218−223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 4H), 7.60−7.55 (m, 4H), 7.41 (d, J = 8.2 Hz, 4H), 7.25−7.21 (m, 2H), 7.09 (t, J = 7.3 Hz, 2H), 2.50 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.0, 136.6, 136.4, 130.3, 126.8, 125.8, 122.6, 119.4, 118.5, 115.6, 111.0, 21.3; HRMS-APCI$^+$ (m/z) calcd for $C_{28}H_{23}N_2$ ([M + H]$^+$) 387.1856, found 387.1879.

*5-(4-Methoxyphenyl)-10-(4-methylphenyl)indolo[3,2-b]indole (**7b**).* A Schlenk tube was charged with **6a** (74 mg, 0.25 mmol), 1-bromo-4-methoxybenzene (30 μL, 0.25 mmol), $Pd_2(dba)_3$ (4 mg, 5.0 μmol), RuPhos (7 mg, 0.015 mmol), and NaO^{t}Bu (48 mg, 0.50 mmol) in anhydrous xylene (7.0 mL). After being degassed by three freeze-thaw pump cycles, the resulting mixture was stirred at 120 °C for 20 h. Then, the reaction mixture was cooled to room temperature, diluted with $CHCl_3$, and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatog-

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566−11572

raphy (hexane/EtOAc = 5:1 as an eluent) to afford the title compound as a yellow solid (41 mg, 40% yield): mp 188−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.55 (m, 6H), 7.53−7.51 (m, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.25−7.21 (m, 2H), 7.14 (d, J = 8.7 Hz, 2H), 7.09 (t, J = 7.6 Hz, 2H), 3.93 (s, 3H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.5, 141.3, 141.0, 136.6, 136.4, 131.9, 130.3, 127.4, 127.1, 126.5, 125.7, 122.6, 122.5, 119.4, 119.3, 118.5, 118.4, 115.6, 115.5, 114.9, 111.0, 110.8, 55.8, 21.3; HRMS-APCI$^+$ (m/z) calcd for $C_{28}H_{23}N_2O$ ([M + H]$^+$) 403.1805, found 403.1826.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02086.

^{1}H, ^{13}C, and ^{19}F NMR spectra for synthesized compounds, cyclic voltammograms, DFT and TD−DFT calculation results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: k_nakano@cc.tuat.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by MEXT KAKENHI Grant Number 26104510. The computations were performed using the Research Center for Computational Science, Okazaki, Japan.

■ REFERENCES

(1) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028−5048. (b) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066−1096. (c) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2012**, *112*, 2208−2267.

(2) (a) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347−4370. (b) Cinar, M. E.; Ozturk, T. *Chem. Rev.* **2015**, *115*, 3036−3140.

(3) (a) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604−12605. (b) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem. Soc.* **2007**, *129*, 15732−15733. (c) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224−2225. (d) Niimi, K.; Kang, M. J.; Miyazaki, E.; Osaka, I.; Takimiya, K. *Org. Lett.* **2011**, *13*, 3430−3433. (e) Yamamoto, T.; Nishimura, T.; Mori, T.; Miyazaki, E.; Osaka, I.; Takimiya, K. *Org. Lett.* **2012**, *14*, 4914−4917.

(4) For ladder-type π-conjugated semiconducting compounds fused with pyrrole ring(s), see: (a) Li, Y. N.; Wu, Y. L.; Gardner, S.; Ong, B. S. *Adv. Mater.* **2005**, *17*, 849−853. (b) Wu, Y. L.; Li, Y. N.; Gardner, S.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 614−618. (c) Boudreault, P. L. T.; Wakim, S.; Blouin, N.; Simard, M.; Tessier, C.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2007**, *129*, 9125−9136. (d) Simokaitiene, J.; Stanislovaityte, E.; Grazulevicius, J. V.; Jankauskas, V.; Gu, R.; Dehaen, W.; Hung, Y.-C.; Hsu, C.-P. *J. Org. Chem.* **2012**, *77*, 4924−4931. (e) Levick, M. T.; Grace, I.; Dai, S.-Y.; Kasch, N.; Muryn, C.; Lambert, C.; Turner, M. L.; Procter, D. J. *Org. Lett.* **2014**, *16*, 2292−2295. (f) Reig, M.; Puigdollers, J.; Velasco, D. *J. Mater. Chem. C* **2015**, *3*, 506−513.

(5) For ladder-type π-conjugated semiconducting compounds fused with other nitrogen-heterocycle(s), see: (a) Wang, C.; Liang, Z.; Liu, Y.; Wang, X.; Zhao, N.; Miao, Q.; Hu, W.; Xu, J. *J. Mater. Chem.* **2011**, *21*, 15201. (b) Liang, Z.; Tang, Q.; Mao, R.; Liu, D.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 5514−5518. (c) Bunz, U. H. F.; Engelhart, J. U.; Lindner, B. D.; Schaffroth, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 3810−3821.

(6) For ladder-type π-conjugated semiconducting compounds fused with furan ring(s), see: (a) Li, H.; Jiang, P.; Yi, C.; Li, C.; Liu, S.-X.; Tan, S.; Zhao, B.; Braun, J.; Meier, W.; Wandlowski, T.; Decurtins, S. *Macromolecules* **2010**, *43*, 8058−8062. (b) Kobilka, B. M.; Dubrovskiy, A. V.; Ewan, M. D.; Tomlinson, A. L.; Larock, R. C.; Chaudhary, S.; Jeffries-El, M. *Chem. Commun.* **2012**, *48*, 8919. (c) Mitsui, C.; Soeda, J.; Miwa, K.; Tsuji, H.; Takeya, J.; Nakamura, E. *J. Am. Chem. Soc.* **2012**, *134*, 5448−5451. (d) Nakano, M.; Mori, H.; Shinamura, S.; Takimiya, K. *Chem. Mater.* **2012**, *24*, 190−198. (e) Watanabe, M.; Su, W.-T.; Chang, Y. J.; Chao, T.-H.; Wen, Y.-S.; Chow, T. J. *Chem. - Asian J.* **2013**, *8*, 60−64. (f) Mitsui, C.; Okamoto, T.; Matsui, H.; Yamagishi, M.; Matsushita, T.; Soeda, J.; Miwa, K.; Sato, H.; Yamano, A.; Uemura, T.; Takeya, J. *Chem. Mater.* **2013**, *25*, 3952−3956. (g) Shi, S.; Xie, X.; Gao, C.; Shi, K.; Chen, S.; Yu, G.; Guo, L.; Li, X.; Wang, H. *Macromolecules* **2014**, *47*, 616−625. (h) Nakahara, K.; Mitsui, C.; Okamoto, T.; Yamagishi, M.; Matsui, H.; Ueno, T.; Tanaka, Y.; Yano, M.; Matsushita, T.; Soeda, J.; Hirose, Y.; Sato, H.; Yamano, A.; Takeya, J. *Chem. Commun.* **2014**, *50*, 5342−5344. (i) Mitsui, C.; Soeda, J.; Miwa, K.; Shoyama, K.; Ota, Y.; Tsuji, H.; Takeya, J.; Nakamura, E. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 776−783.

(7) (a) Qiu, L.; Yu, C.; Zhao, N.; Chen, W.; Guo, Y.; Wan, X.; Yang, R.; Liu, Y. *Chem. Commun.* **2012**, *48*, 12225. (b) Takaku, K.; Sotoyama, W.; Koyanagi, M. JP 2014-170928A, 2014.

(8) There have been some reports on biological activity of BFIs, see: (a) Butera, J. A.; Antane, S. A.; Hirth, B.; Lennox, J. R.; Sheldon, J. H.; Norton, N. W.; Warga, D.; Argentieri, T. M. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2093−2097. (b) Gormemis, A. E.; Ha, T. S.; Im, I.; Jung, K.-Y.; Lee, J. Y.; Park, C.-S.; Kim, Y.-C. *ChemBioChem* **2005**, *6*, 1745−1748. (c) Ha, T. S. *Mol. Pharmacol.* **2005**. (d) dela Peña, I. C.; Yoon, S. Y.; Kim, S. M.; Lee, G. S.; Park, C.-S.; Kim, Y. C.; Cheong, J. H. *Arch. Pharmacal Res.* **2009**, *32*, 413−420. (e) dela Peña, I. C.; Yoon, S. Y.; Kim, S. M.; Lee, G. S.; Ryu, J. H.; Park, C.-S.; Kim, Y. C.; Cheong, J. H. *Pharmacology* **2009**, *83*, 367−378. (f) dela Peña, I.; Cheong, J. H. *J. Biomed. Biotechnol.* **2011**, *2011*, 1−7. (g) Ahn, H. S.; dela Peña, I.; Kim, Y. C.; Cheong, J. H. *Pharmacology* **2011**, *87*, 331−340. (h) Lee, B. C.; Lim, H. H.; Kim, S.; Youn, H. S.; Lee, Y.; Kim, Y. C.; Eom, S. H.; Lee, K. W.; Park, C. S. *Mol. Pharmacol.* **2012**, *82*, 143−155. (i) Sung, H. H.; Choo, S. H.; Han, D. H.; Chae, M. R.; Kang, S. J.; Park, C.-S.; So, I.; Park, J. K.; Lee, S. W. *J. Sex. Med.* **2015**, *12*, 29−38.

(9) (a) Cawley, S. R.; Plant, S. G. P. *J. Chem. Soc.* **1938**, 1214−1218. (b) Schroeder, D. C.; Corcoran, P. O.; Holden, C. A.; Mulligan, M. C. *J. Org. Chem.* **1962**, *27*, 586−591. (c) Karnik, A. V.; Upadhyay, S. P. *Indian J. Chem.* **2004**, *43B*, 1345−1348.

(10) Kato, S.; Furuya, T.; Nitani, M.; Hasebe, N.; Ie, Y.; Aso, Y.; Yoshihara, T.; Tobita, S.; Nakamura, Y. *Chem. - Eur. J.* **2015**, *21*, 3115−3128.

(11) Gao, H.; Xu, Q.-L.; Yousufuddin, M.; Ess, D. H.; Kürti, L. *Angew. Chem., Int. Ed.* **2014**, *53*, 2701−2705.

(12) (a) Carril, M.; SanMartin, R.; Domínguez, E.; Tellitu, I. *Green Chem.* **2007**, *9*, 219. (b) Takamatsu, K.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2014**, *16*, 2892−2895.

(13) Saito, K.; Chikkade, P. K.; Kanai, M.; Kuninobu, Y. *Chem. - Eur. J.* **2015**, *21*, 8365−8368.

(14) (a) Ruggli, P.; Zaeslin, H. *Helv. Chim. Acta* **1935**, *18*, 845−852. (b) Murray, M. M.; Kaszynski, P.; Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8152−8161.

(15) Jackson, A. H.; Johnston, D. N.; Shannon, P. V. R. *J. Chem. Soc., Chem. Commun.* **1975**, 911−912.

(16) Kaszynski, P.; Dougherty, D. A. *J. Org. Chem.* **1993**, *58*, 5209−5220.

(17) Grinyov, A. N.; Ryabova, S. Y. *Khim. Geterotsikl. Soedin.* **1982**, 199−200.

(18) Qiu, L.; Wang, X.; Zhao, N.; Xu, S.; An, Z.; Zhuang, X.; Lan, Z.; Wen, L.; Wan, X. *J. Org. Chem.* **2014**, *79*, 11339−11348.

(19) Hung, T. Q.; Hancker, S.; Villinger, A.; Lochbrunner, S.; Dang, T. T.; Friedrich, A.; Breitsprecher, W.; Langer, P. *Org. Biomol. Chem.* **2015**, *13*, 583−591.

(20) (a) Nozaki, K.; Takahashi, K.; Nakano, K.; Hiyama, T.; Tang, H. Z.; Fujiki, M.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**,

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566−11572

42, 2051−2053. (b) Kuwahara, A.; Nakano, K.; Nozaki, K. *J. Org. Chem.* **2005**, *70*, 413−419.
(21) (a) Ueno, A.; Kitawaki, T.; Chida, N. *Org. Lett.* **2008**, *10*, 1999−2002. (b) Evenson, S. J.; Pappenfus, T. M.; Delgado, M. C. R.; Radke-Wohlers, K. R.; Navarrete, J. T. L.; Rasmussen, S. C. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6101. (c) Hung, T. Q.; Thang, N. N.; Hoang, D. H.; Dang, T. T.; Ayub, K.; Villinger, A.; Lochbrunner, S.; Flechsig, G.-U.; Langer, P. *Eur. J. Org. Chem.* **2015**, *2015*, 1007−1019 and reference cited therein.
(22) (a) Kawaguchi, K.; Nakano, K.; Nozaki, K. *J. Org. Chem.* **2007**, *72*, 5119−5128. (b) Kawaguchi, K.; Nakano, K.; Nozaki, K. *Org. Lett.* **2008**, *10*, 1199−1202.
(23) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338−6361.
(24) Liu, Y.; McWhorter, W. W. *J. Am. Chem. Soc.* **2003**, *125*, 4240−4252.
(25) (a) Cordell, F. R.; Boggs, J. E. *J. Mol. Struct.: THEOCHEM* **1981**, *85*, 163−178. (b) Juric, A.; Sabljic, A.; Trinajstic, N. *J. Heterocycl. Chem.* **1984**, *21*, 273−282.
(26) (a) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551−554. (b) Johansson, T.; Mammo, W.; Svensson, M.; Andersson, M. R.; Inganäs, O. *J. Mater. Chem.* **2003**, *13*, 1316. (c) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367−2371.
(27) Iida, A.; Sekioka, A.; Yamaguchi, S. *Chem. Sci.* **2012**, *3*, 1461.
(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.

DOI: 10.1021/acs.joc.5b02086
J. Org. Chem. 2015, 80, 11566−11572