JOC The Journal of Organic Chemistry

Article

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Synthesis of Benzo[c]thiophenes by Rhodium(III)-Catalyzed Dehydrogenative Annulation

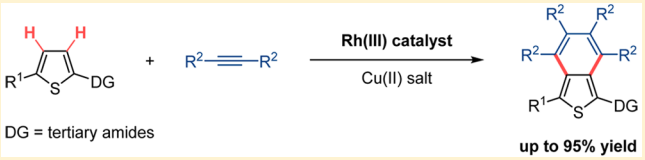
Keita Fukuzumi,[†] Yuto Unoh,[†] Yuji Nishii,[‡] Tetsuya Satoh,[§] Koji Hirano,[†] and Masahiro Miura*[,†]

[†]Department of Applied Chemistry and [‡]Frontier Research Base for Global Young Researchers, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

[§]Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Supporting Information

ABSTRACT: The dehydrogenative annulation of thiophen-2-carboxamides with 2 equiv of alkynes proceeds efficiently in the presence of a rhodium catalyst and a copper oxidant to furnish multiply substituted benzo[c]thiophenes. Some of the synthesized benzo[c]thiophenes exhibited strong solid-state fluorescence.

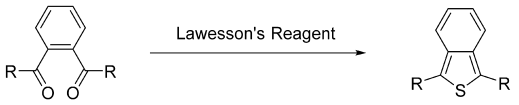


INTRODUCTION

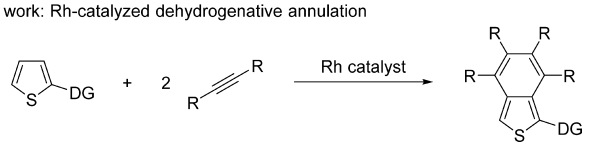
Transition-metal-catalyzed direct C−H functionalization reaction has recently emerged as a useful synthetic tool for the step- and atom-economical construction of complex molecules.[1] In particular, the dehydrogenative cyclization of heteroaromatic compounds with alkynes[2] has been utilized as one of the most effective and straightforward methods for the synthesis of benzo-fused heteroarenes, whose skeletons are of substantial importance in the area of pharmaceutical chemistry as well as materials chemistry.[3,4] Among these, thiophene-based polycyclic molecules have attracted much interest because of their potential use in various electronic devices including organic field effect transistors (OFETs) and organic light-emitting diodes (OLEDs).[5] Our continuous research interest in the rhodium-catalyzed direct C−H functionalization reaction of thiophenes[6] prompted us to develop a new synthetic protocol of benzo[c]thiophenes, which are generally called isothianaphthenes.[7] It has been revealed that polybenzo[c]thiophenes possess unique optical properties originating from their narrow HOMO−LUMO energy gaps over the past few decades.[8] More recently, functionalized benzo[c]thiophene monomers were also synthesized aiming to their use in solar cells,[9] electroluminescence devices,[10] and so on.[11] A general method for benzo[c]thiophene synthesis is the ring closure of the corresponding *ortho*-dicarbonyl benzene derivatives by treating with Lawesson's reagent (Scheme 1a).[7,12,13] In this protocol, the structural versatility of benzo[c]thiophenes is highly dependent upon the availability of the dicarbonyl compounds, and furthermore, daunting and time-consuming processes are required to obtain asymmetrically substituted benzo[c]thiophenes. For the purpose of structural modification and fine-tuning of optical properties, new synthetic approaches toward benzo[c]thiophenes are in high demand. We herein report a synthesis of benzo[c]thiophenes by Rh(III)-catalyzed dehydrogenative annulation of thiophen-2-carboxamides **1** with 2 equiv of alkynes **2** (Scheme 1b). In this system, the amide directing group plays a crucial role for the expeditious construction of various 4,5,6,7-substituted benzo[c]thiophenes **3** from the simple thiophene derivatives. In expectation,[10] some of the isothianaphthene products showed strong fluorescence in the solid state.

Scheme 1. Synthesis of Benzo[c]thiophenes

(a) Traditional synthesis of benzo[c]thiophenes



(b) This work: Rh-catalyzed dehydrogenative annulation



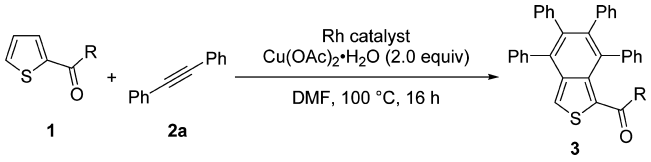
RESULTS AND DISCUSSION

On the basis of our previous study on the amide-directed dehydrogenative cyclization with alkynes,[14] we initially examined the reaction of pyrrolidin-1-yl(thiophen-2-yl)-methanone (**1a**) with diphenylacetylene (**2a**) as the representative substrates in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (2.5 mol %, Cp* = pentamethylcyclopentadienyl) and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) as catalyst and oxidant, respectively, in DMF. As expected, the desired benzo[c]thiophene **3aa** was obtained in 77% isolated yield (Table 1, entry 1), and the product structure was confirmed by X-ray crystallography (see the Supporting Information). A neutral Rh(III) complex $[Cp^*RhCl_2]_2$ showed inferior catalytic activity to afford the comparable yield only with a higher catalyst loading (10 mol %

Received: January 6, 2016
Published: February 19, 2016

DOI: 10.1021/acs.joc.6b00030
J. Org. Chem. 2016, 81, 2474−2481

Table 1. Optimization of Reaction Conditions[a]



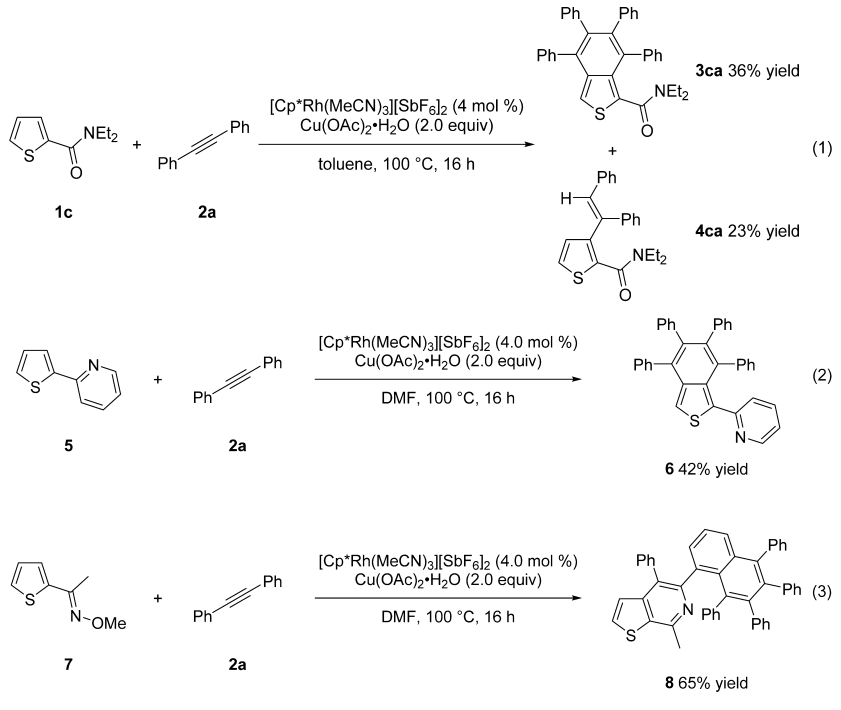
entry	R	catalyst	yield[b]
1	1-pyrrolidyl (**1a**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (2.5 mol %)	77% (**3aa**)
2	1-pyrrolidyl (**1a**)	$[Cp^*RhCl_2]_2$ (5.0 mol %)	80% (**3aa**)
3[c]	1-pyrrolidyl (**1a**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (2.5 mol %)	83% (**3aa**)
4[c]	1-pyrrolidyl (**1a**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	95% (**3aa**)
5[c]	$NiPr_2$ (**1b**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	95% (**3ba**)
6[c]	NEt_2 (**1c**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	95% (**3ca**)
7[c]	NMe_2 (**1d**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	94% (**3da**)
8[c,d]	NEt_2 (**1c**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	36% (**3ca**)
9[c]	Me (**1e**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	n.d.[e]
10[c]	OMe (**1f**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	n.d.[e]
11[c]	NMeOMe (**1g**)	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %)	n.d.[e]

[a]Reaction conditions: A mixture of **1** (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol), and Rh catalyst in DMF (2 mL) was heated for 16 h under N_2. [b]Isolated yield. [c]0.5 mmol of **2a** was used. [d]Toluene (2.0 mL) was used as solvent. [e]n.d. = Not detected.

Rh, entry 2). A significant increase of the yield was obtained by increasing the amount of alkyne **2a** (2.5 equiv) as well as that of the Rh catalyst (4.0 mol %) (entries 3 and 4). Under the optimized reaction conditions (entry 4), we investigated with respect to the directing groups on thiophene. *N*,*N*-Diisopropylamide **1b**, *N*,*N*-diethylamide **1c**, and *N*,*N*-dimethylamide **1d** were all applicable to this reaction system to give the corresponding benzo[*c*]thiophenes in excellent yields (entries 5−7). When the reaction of amide **1c** was conducted in toluene solvent, a 1:1 coupling product **4ca** was obtained in 23% yield along with the formation of **3ca** in 36% yield (entry 8 and Scheme 2, eq 1). This result clearly indicates that the first C−H cleavage occurred at C3 of the thiophene, and additionally, DMF solvent would prevent protonation to give **4ca** before the second C−H scission at C4 in a catalytic cycle (*vide infra*). In sharp contrast, use of methyl ketone **1e**, methyl ester **1f**, and *N*,*O*-dimethylhydroxyamide **1g** (Weinreb amide) as directing groups, instead of the tertiary amides, did not trigger any C−C bond forming reactions (entries 9−11). 2-(Thiophen-2-yl)-pyridine (**5**) underwent cyclization to form the corresponding benzo[*c*]thiophenes **6** in 42% yield under the present reaction conditions (Scheme 2, eq 2). *O*-Methyloxime **7** was converted into thieno[2,3-*c*]pyridine **8** incorporating three alkyne molecules as reported previously (Scheme 2, eq 3).[15]

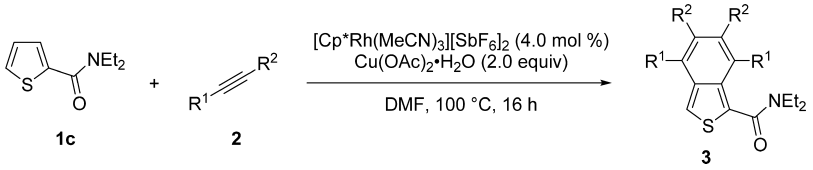
Next, we evaluated the scope and limitations of the present reaction with *N*,*N*-diethylamide **1c** and various alkynes (Table 2). Substituents on the phenyl rings of diphenylacetylene, including electron-donating groups (**2b**, **2c**, **2g**, **2h**) and electron-withdrawing groups (**2d**, **2e**, **2f**), did not significantly affect the reaction, and the corresponding benzo[*c*]thiophenes **3** were obtained in high to excellent yields (entries 1−7). While a limitation was encountered with aliphatic alkyne **2i** to afford the corresponding product **3ci** in a low yield (entry 8), it was found that $[Cp^*RhCl_2]_2$ gave a better result (entry 9). No reaction proceeded with diethyl acetylenedicarboxylate (**2j**, entry **10**). A terminal alkyne **2k** dimerized under the catalytic condition to produce 1,4-bis(4-methoxyphenyl)buta-1,3-diyne, and the desired product was not detected (entry 11). An asymmetric alkyne **2l** gave an inseparable mixture of regioisomers in 37% yield (entry 12).

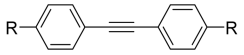
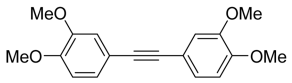
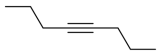
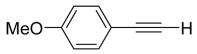
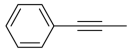
Scheme 2



DOI: 10.1021/acs.joc.6b00030
J. Org. Chem. 2016, 81, 2474−2481

Table 2. Substrate Scope for Alkynes[a]

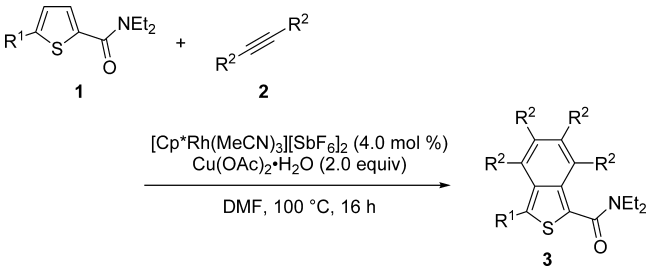


entry	alkyne		yield[b]
1		R = Me (**2b**)	88% (**3cb**)
2		R = *t*Bu (**2c**)	79% (**3cc**)
3		R = F (**2d**)	90% (**3cd**)
4		R = CF_3 (**2e**)	96% (**3ce**)
5		R = COOEt (**2f**)	84% (**3cf**)
6		R = OMe (**2g**)	89% (**3cg**)
7		**2h**	83% (**3ch**)
8		**2i**	16%[c] (**3ci**)
9		**2i**	33%[d] (**3ci**)
10		**2j**	n.d.[e]
11		**2k**	n.d.[e]
12		**2l**	37%[f]

[a]Reaction conditions: A mixture of **1c** (0.2 mmol), **2** (0.5 mmol), $Cu(OAc)_2·H_2O$ (0.4 mmol), and $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %) in DMF (2.0 mL) was heated for 16 h under N_2. [b]Isolated yield. [c]Determined by GC analysis. [d]$[Cp^*RhCl_2]_2$ (5.0 mol %) was used as catalyst. [e]n.d. = Not detected. [f]A mixture of isomers was formed and not fully characterized.

Substrate scope for C5-substituted thiophenes was also examined (Table 3). Both methyl- and phenyl-substituted thiophenes, **1h** and **1i**, smoothly underwent annulation to give the desired benzo[*c*]thiophenes **3ha** and **3ia** in 90% and 72% yields, respectively (entries 1 and 2). Reaction of **1i** with an electron-deficient alkyne **2e** afforded compound **3ie** as expected (entry 3). It was noteworthy that the C−Cl bond of **1g** remained intact during the reaction (entry 4); however, the entire hydrodebromination proceeded with 5-bromothiophene **1h** to give **3ca** as the major product (entry 5). Instead of using C5-substituted thiophenes as substrates, the postfunctionalization of the thiophene C5 position was also possible; an aryl group was installed in **3ca** via direct cross-coupling reaction with a simple $Pd(OAc)_2/PPh_3$ catalyst system (Scheme 3, eq 4).[16] On the other hand, no cyclization product was detected from furan-2-carboxamide or pyrrole-2-carboxamides (Scheme 3, eq 5).

Table 3. Substrate Scope for Thiophenes[a]



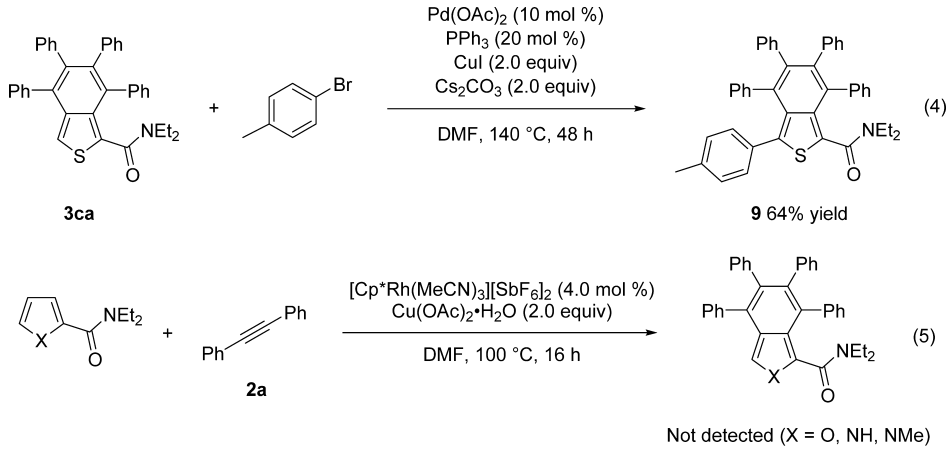
entry	substrates	yield[b]
1	R^1 = Me (**1h**), R^2 = Ph (**2a**)	90% (**3ha**)
2	R^1 = Ph (**1i**), R^2 = Ph (**2a**)	72% (**3ia**)
3	R^1 = Ph (**1i**), R^2 = 4-$CF_3C_6H_4$ (**2e**)	69% (**3ie**)
4	R^1 = Cl (**1j**), R^2 = Ph (**2a**)	77% (**3ja**)
5	R^1 = Br (**1k**), R^2 = Ph (**2a**)	[c]

[a]Reaction conditions: A mixture of **1c** (0.2 mmol), **2** (0.5 mmol), $Cu(OAc)_2·H_2O$ (0.4 mmol), and $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %) in DMF (2.0 mL) was heated for 16 h under N_2. [b]Isolated yield. [c]The corresponding annulation product **3ka** was not detected, and **3ca** was obtained as a major product.

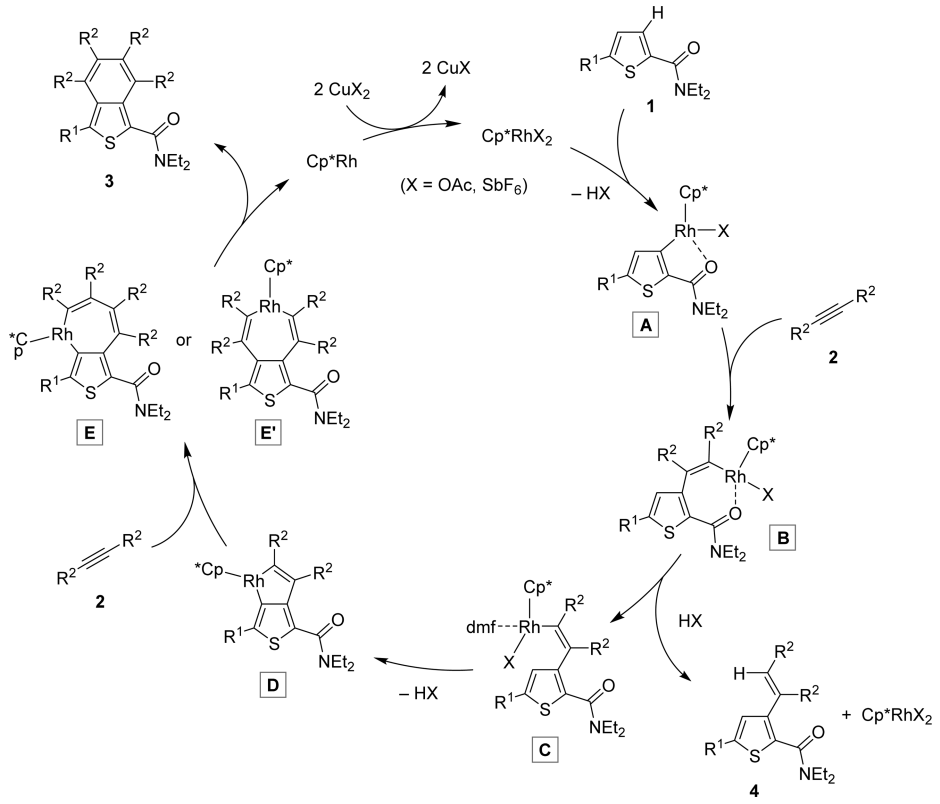
A plausible mechanism for the dehydrogenative annulation is illustrated in Scheme 4. The first amide-directed C−H cleavage appears to occur at the C3 position of thiophene **1** to generate the intermediate **A**, and the subsequent insertion of alkyne **2** gives the seven-membered Rh(III) complex **B**. In advance of the second C−H scission event, the amide-dissociated Rh(III) species **C** may be stabilized by DMF solvation to prevent undesired protonation that leads to the hydroarylation product **4** (Scheme 2, eq 1). Accordingly, the five-membered rhodacycle complex **D** undergoes sequential alkyne insertion into one of the Rh−C bonds and reductive elimination to afford the annulated product **3**. The oxidation of thus formed Cp*Rh(I)

DOI: 10.1021/acs.joc.6b00030
J. Org. Chem. 2016, 81, 2474−2481

Scheme 3



Scheme 4. Plausible Mechanism for the Dehydrogenative Annulation



species by Cu(II) to regenerate the catalytically active Cp*Rh(III) species closes the catalytic cycle.

Finally, a preliminary study on the optical properties of the synthesized benzo[*c*]thiophenes was carried out (Figure 1). It was found that a benzo[*c*]thiophene **3ia**, which has an additional phenyl group at its C5 position, exhibited a relatively strong solid-state photoluminescence (λ_{em} 491 nm) in comparison to a typical emitter, tris(8-hydroxyquinolino)-aluminum (Alq_3), probably because the perpendicularly substituted phenyl groups to the benzo[*c*]thiophene core provided steric bulkiness to minimize an intermolecular quenching.[17] A further investigation revealed that **3ie** (R^2 = 4-$CF_3C_6H_4$) was highly luminescent (λ_{em} 461 nm) with an absolute quantum yield of 0.53.

CONCLUSION

We have demonstrated that the rhodium-catalyzed dehydrogenative annulation of thiophen-2-carboxamides with 2 equiv of alkynes can afford the corresponding multiply substituted benzo[*c*]thiophenes in high yields. This simple and straightforward synthesis would ensure a rapid access to certain organic optical devices based on the benzo[*c*]thiophene framework. Thus, the preliminary survey on the luminescent properties of the products indicated that they, especially fully substituted compounds, may act as effective emitters in their solid state.

EXPERIMENTAL SECTION

General. Nuclear magnetic resonance spectra were measured at 400 MHz (^{1}H NMR), at 100 MHz (^{13}C NMR), and at 376 MHz (^{19}F NMR) in 5 mm NMR tubes. All ^{1}H NMR chemical shifts were

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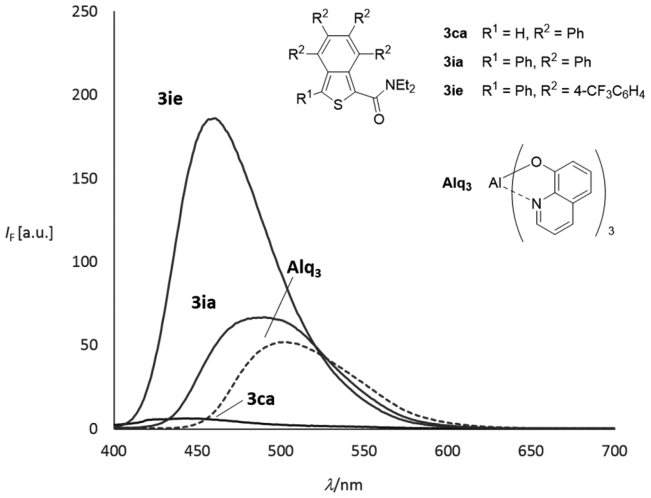

Figure 1. Fluorescence spectra of **3ca**, **3ia**, **3ie**, and **Alq$_3$** in solid state excited at 380 nm.

reported in ppm relative to the resonance in TMS at δ 0.00. All ^{13}C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform-d_1 at δ 77.16 as appeared in the spectra. High-resolution mass spectra (HRMS) were measured by APCI-TOF. Photoluminescence spectra and absolute quantum yields were measured as reported previously.[18] Thiophene-2-carboxamides (**1a**–**1k**) were synthesized by standard condensation reaction of the corresponding thiophene-2-carboxlic acids and amines by treating with 1-(3-(dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and *N*,*N*-dimethyl-4-aminopyridine (DMAP). Alkynes **2b**–**2h** were prepared as reported previously.[6b] Rhodium complexes $[Cp^*Rh(MeCN)_3][SbF_6]_2$ and $[Cp^*RhCl_2]_2$ were prepared according to the literature procedures.[19] All other reagents were purchased from commercial resources and used without further purification.

General Procedure for Rh-Catalyzed Dehydrogenative Cyclization (Tables 1–3, Scheme 2, eq 1). Thiophene **1** (0.2 mmol), alkyne **2**, rhodium catalyst, and $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol) were placed in a 20 mL two-neck flask equipped with a reflux condenser, a N_2 balloon, and a rubber cup. DMF (2.0 mL) was added via syringe, and the resulting mixture was stirred at 100 °C for 16 h. After cooling to room temperature, the reaction mixture was extracted with EtOAc (10 mL × 3) containing ethylenediamine (ca. 1 mL). The organic layer was washed with H_2O and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was subjected to silica gel column chromatography to give **3**.

Dehydrogenative Cyclization with 2-(Thiophen-2-yl)-pyridine (5) (Scheme 2, eq 2). 2-(Thiophen-2-yl)pyridine (**5**) (0.2 mmol), diphenylacetylene **2a** (0.5 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol) were placed in a 20 mL two-neck flask equipped with a reflux condenser, a N_2 balloon, and a rubber cup. DMF (2.0 mL) was added via syringe, and the resulting mixture was stirred at 100 °C for 16 h. After cooling to room temperature, the reaction mixture was extracted with EtOAc (10 mL × 3) containing ethylenediamine (ca. 1 mL). The organic layer was washed with H_2O and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was subjected to silica gel column chromatography (eluent: hexane/EtOAc = 3/1) to give **6** in 42% yield.

Dehydrogenative Cyclization with *O*-Methyl Oxime 7 (Scheme 2, eq 3). 1-(Thiophen-2-yl)ethan-1-one *O*-methyl oxime (**7**) (0.2 mmol), diphenylacetylene **2a** (0.5 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol) were placed in a 20 mL two-neck flask equipped with a reflux condenser, a N_2 balloon, and a rubber cup. DMF (2.0 mL) was added via syringe, and the resulting mixture was stirred at 100 °C for 16 h. After cooling to room temperature, the reaction mixture was extracted with EtOAc (10 mL × 3) containing ethylenediamine (ca. 1 mL). The organic layer was washed with H_2O and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was subjected to silica gel column chromatography (eluent: hexane/EtOAc = 3/1) to give **8** in 65% yield.

Pd-Catalyzed Arylation of 3ca with Aryl Bromide (Scheme 3, eq 4). Benzo[*c*]thiophene **3ca** (0.1 mmol), 4-bromotoluene (0.2 mmol), $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), CuI (0.2 mmol), and Cs_2CO_3 (0.2 mmol) were placed in a 20 mL two-neck flask equipped with a reflux condenser, a N_2 balloon, and a rubber cup. DMF (1.0 mL) was added via syringe, and the resulting mixture was stirred at 140 °C for 48 h. After cooling to room temperature, the reaction mixture was extracted with EtOAc (10 mL × 3) containing ethylenediamine (ca. 1 mL). The organic layer was washed with H_2O and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was subjected to silica gel column chromatography (eluent: hexane/EtOAc = 3/1) to give **9** in 64% yield.

Product Characterization Data. *Pyrrolidin-1-yl(4,5,6,7-tetraphenylbenzo[c]thiophen-1-yl)methanone (**3aa**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), 102 mg (95% yield), yellow solid; mp 235–236 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (br), 2.59 (br), 3.05 (br), 6.77–7.45 (m) with rotamers; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.40–1.70 (br, 4.2H), 2.96 (br, 2.40H), 6.72–6.94 (m, 10H), 6.98–7.38 (m, 10H), 7.50 (s, 1H) with rotamers; ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 25.6, 45.7, 48.8, 118.2, 125.5, 125.6, 126.7, 126.8, 126.8, 127.9, 129.8, 130.7, 131.5, 131.5, 132.5, 133.0, 133.4, 136.7, 138.4, 139.1, 139.5, 139.7, 140.0, 140.1, 163.3; ^{13}C NMR (100 MHz, DMSO-d_6) δ 23.7, 25.0, 45.2, 48.1, 118.2, 125.4, 125.5, 126.4, 126.6, 126.8, 127.8, 130.2, 130.4, 131.0, 131.9, 132.1, 132.7, 136.2, 137.6, 138.4, 138.5, 138.8, 139.6, 139.6, 161.6 with rotamers; HRMS (APCI) *m*/*z* calcd for $C_{37}H_{30}NOS$ ($[M + H]^+$) 536.2043, found 536.2052.

*N,N-Diisopropyl-4,5,6,7-tetraphenylbenzo[c]thiophene-1-carboxamide (**3ba**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 107 mg (95% yield), yellow solid; mp 252–253 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, *J* = 3.4 Hz, 3H), 1.01 (d, *J* = 3.3 Hz, 3H), 1.11 (d, *J* = 3.3 Hz, 3H), 1.33 (d, *J* = 3.4 Hz, 3H), 3.15–3.22 (m, 1H), 3.96–4.02 (m, 1H), 3.37–3.46 (m, 1H), 6.72–7.40 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.0, 20.8, 21.3, 45.9, 51.3, 117.0, 125.3, 125.5, 126.4, 126.7, 126.8, 127.0, 127.6, 127.8, 128.0, 130.4, 130.5, 130.9, 131.1, 131.3, 131.4, 131.6, 132.8, 133.2, 133.3, 133.9, 136.8, 138.8, 139.2, 139.6, 140.0, 140.1, 140.3, 163.4; HRMS (APCI) *m*/*z* calcd for $C_{39}H_{36}NOS$ ($[M + H]^+$) 566.2512, found 566.2517.

*N,N-Diethyl-4,5,6,7-tetraphenylbenzo[c]thiophene-1-carboxamide (**3ca**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 2/1), 102 mg (95% yield), yellow solid; mp 222–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H), 2.67–2.75 (m, 1H), 2.85–3.00 (m, 2H), 3.37–3.46 (m, 1H), 6.74–7.43 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.4, 40.3, 44.6, 117.9, 125.4, 125.6, 126.5, 126.7, 126.8, 126.8, 126.9, 127.6, 127.8, 128.0, 129.3, 130.1, 130.5, 130.9, 131.3, 131.4, 131.5, 131.5, 132.0, 132.8, 133.3, 133.6, 136.7, 138.6, 139.2, 139.5, 139.6, 140.0, 140.1, 164.4; HRMS (APCI) *m*/*z* calcd for $C_{37}H_{32}NOS$ ($[M + H]^+$) 538.2199, found 538.2207.

*N,N-Dimethyl-4,5,6,7-tetraphenylbenzo[c]thiophene-1-carboxamide (**3da**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), 96 mg (94% yield), yellow solid; mp 275–276 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.63 (s, 3H), 6.72–7.47 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.9, 39.5, 118.49, 125.5, 125.6, 126.6, 126.8, 126.9, 126.9, 127.7, 128.1, 128.6, 130.0, 130.5, 130.8, 131.5, 131.8, 132.6, 133.4, 133.6, 136.6, 138.3, 139.2, 139.4, 139.6, 140.0, 140.0, 165.0; HRMS (APCI) *m*/*z* calcd for $C_{35}H_{28}NOS$ ($[M + H]^+$) 510.1886, found 510.1866.

*N,N-Diethyl-4,5,6,7-tetra-p-tolylbenzo[c]thiophene-1-carboxamide (**3cb**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 2/1), 104 mg (88% yield), yellow solid; mp 251–252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.22 (s, 3H), 2.30 (s, 3H), 2.64–2.71 (m, 1H), 2.91–2.97 (m, 2H), 3.34–3.41 (m, 1H), 6.61–7.41 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 14.3, 21.2, 21.3, 21.4, 40.1, 44.5, 117.6, 127.2, 127.4, 127.4, 128.3, 128.4, 128.5, 128.7, 128.9, 129.9, 130.3, 130.7, 131.1, 131.3, 131.7, 132.6, 133.1,

DOI: 10.1021/acs.joc.6b00030
J. Org. Chem. 2016, 81, 2474–2481

134.0, 134.4, 134.6, 135.9, 136.0, 136.1, 136.8, 136.9, 137.2, 137.3, 139.4, 139.9, 164.6; HRMS (APCI) m/z calcd for $C_{41}H_{40}NOS$ ($[M + H]^+$) 594.2825, found 594.2807.

*4,5,6,7-Tetrakis(4-tert-butylphenyl)-N,N-diethylbenzo[c]thiophene-1-carboxamide (**3cc**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 5/1), 120 mg (79% yield), yellow solid; 241−242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H), 1.07 (s, 9H), 1.08 (s, 9H), 1.19 (s, 9H), 1.27 (s, 9H), 2.60−2.69 (m, 1H), 2.83−2.97 (m, 2H), 3.37−3.46 (m, 1H), 6.52−7.28 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.4, 31.3, 31.4, 31.4, 34.1, 34.2, 34.5, 34.6, 40.3, 44.5, 117.7, 122.9, 123.2, 123.3, 123.6, 124.0, 124.3, 124.7, 128.8, 130.1, 130.6, 131.0, 131.0, 131.1, 131.2, 131.4, 132.6, 133.0, 133.5, 135.8, 136.7, 137.1, 137.3, 137,3, 139.6, 140.0, 147.6, 147.9, 149.1, 149.3, 164.7; HRMS (APCI) m/z calcd for $C_{53}H_{64}NOS$ ($[M + H]^+$) 762.4703, found 762.4704.

*N,N-Diethyl-4,5,6,7-tetrakis(4-fluorophenyl)benzo[c]thiophene-1-carboxamide (**3cd**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 2/1), 109 mg (90% yield), yellow solid; mp 212−213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H), 2.71−2.77 (br, 1H), 2.99−3.04 (m, 2H), 3.35−3.40 (br, 1H), 6.56−7.43 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 14.3, 40.3, 44.5, 113.9, 114.1, 114.3, 114.4, 114.8, 115.0, 115.2, 115.4, 118.1, 129.7, 131.3, 131.4, 131.8, 131.9, 132.3, 132.3, 132.3, 132.4, 132.6, 132.7, 132.7, 132.8, 132.9, 133.6, 133.6, 133.7, 134.2 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 135.0 (d, $^3J_{C\text{-}F}$ = 3.7 Hz), 135.6 (d, $^3J_{C\text{-}F}$ = 3.3 Hz), 135.7 (d, $^3J_{C\text{-}F}$ = 3.7 Hz), 135.9, 138.4, 139.4, 160.9 (d, $^1J_{C\text{-}F}$ = 244.3 Hz), 161.0 (d, $^1J_{C\text{-}F}$ = 244.3 Hz), 161.8 (d, $^1J_{C\text{-}F}$ = 245.2 Hz), 162.0 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 164.1; ^{13}C {^{1}H, ^{19}F} NMR (400 MHz, $CDCl_3$) δ 13.1, 14.3, 40.2, 44.5, 114.0, 114.0, 114.1, 114.2, 114.3, 114.9, 115.0, 115.3, 118.1, 129.6, 131.3, 131.9, 132.3, 132.3, 132.5, 132.6, 132.7, 132.8, 132.9, 133.5, 133.6, 134.2, 135.0, 135.6, 135.6, 135.9, 138.3, 139.4, 160.8, 161.0, 161.8, 161.9, 164.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −116.31, −116.19, −115.08, −114.83; HRMS (APCI) m/z calcd for $C_{37}H_{28}F_4NOS$ ($[M + H]^+$) 610.1822, found 610.1814.

*N,N-Diethyl-4,5,6,7-tetrakis[4-(trifluoromethyl)phenyl]benzo[c]thiophene-1-carboxamide (**3ce**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 156 mg (96% yield), yellow solid; mp 225−226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H), 2.78 (br, 1H), 2.91−2.96 (m, 2H), 3.37 (br, 1H), 6.84−7.52 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 14.4, 40.3, 44.6, 118.7, 119.8, 120.0, 122.5, 122.6, 122.7, 124.2, 124.4, 125.0, 125.3, 125.3, 125.4, 128.0, 128.1, 128.3, 128.5, 128.6, 128.8, 128.9, 129.1, 129.2, 129.3, 129.5, 129.6, 129.9, 130.0, 130.2, 130.5, 130.6, 131.0, 131.5, 132.4, 132.6, 133.0, 133.1, 135.0, 137.3, 138.8, 141.4, 142.2, 142.7, 142.7, 163.5; ^{13}C {^{1}H, ^{19}F} NMR (400 MHz, $CDCl_3$) δ13.0, 14.4, 40.3, 44.6, 93.8, 118.7, 124.1, 124.4, 128.6, 128.7, 129.7, 129.8, 130.5, 131.4, 131.5, 132.6, 133.0, 133.1, 135.0, 137.3, 138.8, 141.4, 142.0, 142.2, 142.6, 142.7, 163.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.86, −62.81, −62.76, −62.64; HRMS (APCI) m/z calcd for $C_{41}H_{28}F_{12}NOS$ ($[M + H]^+$) 810.1695, found 810.1692.

*Tetraethyl 4,4′,4″,4‴-(1-(diethylcarbamoyl)benzo[c]thiophene-4,5,6,7-tetrayl)tetrabenzoate (**3cf**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), 139 mg (84% yield), yellow solid; mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.0 Hz, 3H), 1.32 (t, J = 7.1 Hz, 6H), 1.36 (t, J = 7.1 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H), 2.79 (br, 1H), 2.89−2.94 (m, 2H), 3.38 (br, 1H), 4.23−4.39 (m, 8H), 6.82−7.93 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 14.4, 14.4, 14.4, 14.5, 40.3, 44.6, 61.0, 61.1, 61.2, 118.4, 128.1, 128.3, 128.4, 128.6, 129.2, 129.4, 129.5, 129.5, 129.7,131.1, 131.2, 131.9, 132.6, 133.1, 133.2, 135.4, 137.6, 138.8, 142.7, 143.4, 144.0, 144.1, 163.7, 166.4; HRMS (APCI) m/z calcd for $C_{49}H_{48}NO_9S$ ($[M + H]^+$) 826.3044, found 826.3040.

*N,N-Diethyl-4,5,6,7-tetrakis(4-methoxyphenyl)benzo[c]thiophene-1-carboxamide (**3cg**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), 120 mg (89% yield), yellow solid; mp 143−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.1 Hz, 3H), 2.63−2.72 (m, 1H), 2.96−3.02 (m, 2H), 3.34−3.43 (m, 1H), 3.61 (s, 3H), 3.62 (s, 3H), 3.73, (s, 3H), 3.78 (s, 3H), 6.38−7.43 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.3, 40.2, 44.5, 55.0, 55.2, 55.3, 112.2, 112.3, 112.4, 113.2, 113.4, 117.6, 129.0, 131.2, 131.3, 131.5, 131.6, 132.0, 132.2, 132.3, 132.4, 132.5, 132.5, 132.5, 132.8, 132.9, 132.9, 133.0, 134.1, 136.8, 139.4, 140.0, 157.0, 157.1, 158.2, 158.3, 164.6; HRMS (APCI) m/z calcd for $C_{41}H_{40}NO_5S$ ($[M + H]^+$) 658.2622, found 658.2633.

*4,5,6,7-Tetrakis(3,4-dimethoxyphenyl)-N,N-diethylbenzo[c]thiophene-1-carboxamide (**3ch**).* Purified by silica gel column chromatography (eluent: EtOAc), 128 mg (83% yield), yellow solid; mp 127−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (br, 3H), 0.92 (br, 3H), 2.57 (br, 1H), 3.01 (br, 2H), 3.33 (br, 1H), 3.43−3.88 (m, 24H), 6.30−7.59 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 13.2, 14.2, 29.8, 40.1, 40.2, 44.0, 44.4, 55.6, 55.7, 55.8, 55.9, 109.8, 110.3, 111.0, 114.1, 114.4, 115.1, 115.3, 115.4, 115.7, 117.9, 118.2, 122.6, 122.7, 123.2, 124.0, 124.3, 124.6, 124.8, 129.5, 131.4, 132.4, 133.1, 138.8, 139.4, 139.5, 146.7, 146.8, 147.6, 147.7, 147.8, 148.0, 148.3, 148.5, 164.6; HRMS (APCI) m/z calcd for $C_{45}H_{47}NO_9S$ ($[M + H]^+$) 778.3044, found 778.3062.

*N,N-Diethyl-4,5,6,7-tetrapropylbenzo[c]thiophene-1-carboxamide (**3ci**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 26 mg (33% yield), pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97−1.71 (m, 26H), 2.55−2.84 (m, 8H), 3,14 (br, 1H), 3.41 (br, 1H), 3.80 (br, 1H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 14.0, 14.9, 15.0, 15.1, 15.2, 23.8, 24.3, 25.0, 25.1, 31.9, 32.0, 32.0, 32.8, 39.7, 43.9, 113.5, 125.3, 129.7, 130.1, 134.5, 134.7, 136.8, 139.7, 166.7; HRMS (APCI) m/z calcd for $C_{25}H_{40}NOS$ ($[M + H]^+$) 402.2825, found 402.2851

*N,N-Diethyl-3-methyl-4,5,6,7-tetraphenylbenzo[c]thiophene-1-carboxamide (**3ha**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 99 mg (90% yield), yellow solid; mp 226−227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 7.0 Hz, 3H), 1.03 (t, J = 6.9 Hz, 3H), 1.95 (s, 3H), 2.70−2.76 (m, 1H), 2.85−2.95 (m, 2H), 3.47−3.52 (m, 1H), 6.72−7.15 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.5, 15.7, 40.2, 44.6, 123.4, 125.2, 125.3, 126.4, 126.6, 126.7, 126.8, 127.2, 127.5, 127.5, 130.0, 131.0, 131.2, 131.4, 131.4, 132.1, 132.2, 133.1, 133.3, 133.8, 135.3, 137.4, 138.7, 138.7, 139.8, 140.0, 140.2, 164.6; HRMS (APCI) m/z calcd for $C_{38}H_{34}NOS$ ($[M + H]^+$) 552.2356, found 552.2343.

*N,N-Diethyl-3,4,5,6,7-pentaphenylbenzo[c]thiophene-1-carboxamide (**3ia**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 89 mg (72% yield), yellow solid; mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H), 2.81−3.02 (m, 3H), 3.58−3.66 (m, 1H), 6.62−7.33 (m, 25H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.5, 40.2, 44.8, 125.2, 125.3, 125.9, 126.4, 126.4, 126.6, 126.7, 126.9, 127.0, 127.1, 127.2, 127.6, 127.7, 127.8, 129.8, 130.1, 130.5, 131.2, 131.2, 131.4, 131.4, 131.5, 131.6, 131.7, 132.3, 132.7, 133.2, 133.6, 134.3, 135.6, 136.6, 138.1, 138.5, 138.6, 139.1, 140.2, 140.2, 164.3; HRMS (APCI) m/z calcd for $C_{43}H_{36}NOS$ ($[M + H]^+$) 614.2544, found 614.2530.

*N,N-Diethyl-3-phenyl-4,5,6,7-tetrakis(4-(trifluoromethyl)phenyl)-benzo[c]thiophene-1-carboxamide (**3ie**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 118 mg (69% yield), yellow solid; mp 236−237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.0 Hz, 3H), 2.88−2.97 (m, 3H), 3.56−3.62 (m, 1H), 6.76−7.47 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 14.5, 40.2, 44.7, 122.5, 122.6, 122.7, 124.0, 124.2, 125.0, 125.2, 125.4, 127.6, 128.0, 128.0, 128.1, 128.2, 128.3, 128.4, 128.4, 128.6, 128.7, 129.0, 129.5, 129.8, 130.0, 130.1, 130.5, 131.1, 131.3, 131.5, 131.7, 132.2, 132.6, 132.9, 133.2, 133.3, 134.9, 136.5, 137.1, 137.6, 140.9, 141.6, 142.8, 142.9, 163.5; ^{13}C {^{1}H, ^{19}F} NMR (400 MHz, $CDCl_3$) δ13.0, 14.5, 40.2, 44.7, 122.4, 123.9, 123.9, 124.0, 124.0, 124.1, 124.2, 127.6, 127.6, 128.4, 128.5, 128.8, 129.6, 130.0, 130.5, 131.1, 131.2, 131.4, 131.6, 131.6, 132.2, 132.5, 132.9, 134.9, 136.5, 137.1, 137.6, 140.9, 141.6, 142.0, 142.8, 142.9, 163.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.94, −62.86, −62.83, −62.73; HRMS (APCI) m/z calcd for $C_{47}H_{32}F_{12}NOS$ ($[M + H]^+$) 886.2008, found 886.1993.

DOI: 10.1021/acs.joc.6b00030
J. Org. Chem. 2016, 81, 2474−2481

*3-Chloro-N,N-diethyl-4,5,6,7-tetraphenylbenzo[c]thiophene-1-carboxamide (**3ja**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 88 mg (77% yield), yellow solid; mp 237−238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H), 2.73−2.96 (m, 3H), 3.45−3.51 (m, 1H), 6.71−7.34 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.5, 40.4, 44.7, 122.3, 125.4, 125.5, 125.6, 126.5, 126.7, 126.8, 127.0, 127.1, 127.3, 127.7, 130.0, 131.0, 131.2, 131.4, 132.1, 132.5, 133.2, 134.0, 137.7, 137.9, 139.5, 139.6, 139.7, 163.2; HRMS (APCI) m/z calcd for $C_{37}H_{31}ClNOS$ ([M + H]$^+$) 572.1809, found 572.1807.

*(E)-3-(1,2-Diphenylvinyl)-N,N-diethylthiophene-2-carboxamide (**4ca**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 17 mg (23% yield), pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (br, 3H), 1.12 (br, 3H), 3.30−3.35 (m, 4H), 6.75 (d, J = 5.8 Hz, 1H), 6.87 (s, 1H), 6.94−7.27 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 14.2, 39.6, 43.5, 124.4, 127.1, 127.8, 128.1, 128.6, 128.9, 129.7, 130.2, 130.6, 133.1, 136.3, 137.0, 139.8, 142.4, 164.9; HRMS (APCI) m/z calcd for $C_{23}H_{24}NOS$ ([M + H]$^+$) 362.1573, found 362.1569.

*2-(4,5,6,7-Tetraphenylbenzo[c]thiophen-1-yl)pyridine (**6**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 43 mg (42% yield), yellow solid; mp 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (m, 1H), 6.70−6.90 (m, 16H), 7.00 (m, 1H), 7.15−7.32 (m, 6H), 8.32−8.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.8, 120.6, 125.4, 125.5, 125.6, 125.8, 126.6, 126.8, 126.9, 127.9, 130.8, 131.4, 131.5, 131.7, 132,6, 132.7, 133.7, 134.3, 136.4, 136.5, 138.8, 139.5, 139.6, 140.2, 140.3, 140.8, 148.4, 153.3; HRMS (APCI) m/z calcd for $C_{37}H_{26}NS$ ([M + H]$^+$) 516.1780, found 516.1776.

*7-Methyl-4-phenyl-5-(5,6,7,8-tetraphenylnaphthalen-1-yl)-thieno[2,3-c]pyridine (**8**).*[15] Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 86 mg (65% yield), yellow solid; mp 234−235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 6.22−6.28 (m, 1H), 6.46−6.88 (m, 14H), 6.91−6.96 (m, 1H), 7.02−7.30 (m, 12H), 7.34−7.40 (m, 1H), 7.42−7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 124.1, 124.5, 124.5, 125.0, 125.1, 125.2, 125.5, 126.2, 126.4, 126.4, 126.5, 126.6, 126.6, 127.4, 127.4, 127.5, 127.6, 128.1, 130.0, 130.3, 131.1, 131.1, 131.2, 131.3, 131.4, 131.5, 131.5, 131.9, 133.4, 133.6, 133.7, 137.5, 138.0, 138.3, 138.5, 138.6, 140.2, 140.4, 140.8, 140.9, 144.5, 150.0, 152.8; HRMS (APCI) m/z calcd for $C_{48}H_{34}NS$ ([M+H]$^+$) 656.2406, found 656.2413.

*N,N-Diethyl-4,5,6,7-tetraphenyl-3-(p-tolyl)benzo[c]thiophene-1-carboxamide (**9**).* Purified by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), 40 mg (64% yield), yellow solid; mp 227−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H), 2.20 (s, 3H), 2.80−3.01 (m, 3H), 3.57−3.66 (m, 1H), 6.55−6.90 (m, 19H), 7.02−7.22 (m, 4H), 7.27−7.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.5, 21.2, 40.2, 44.8, 125.2, 125.3, 125.6, 126.3, 126.4, 126.5, 126.6, 126.6, 126.7, 126.9, 127.1, 127.7, 127.9, 130.0, 130.3, 131.2, 131.3, 131.4, 131.4, 131.6, 131.7, 131.7, 132.2, 132.6, 133.1, 133.7, 135.5, 136.3, 136.8, 138.2, 138.3, 138.7, 139.0, 140.2, 140.3; HRMS (APCI) m/z calcd for $C_{44}H_{38}NOS$ ([M + H]$^+$) 628.2669, found 628.2680.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00030.

Detailed information for structural determination of compound **3aa** and NMR spectra for the products (PDF)

Crystallographic data for **3aa** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: miura@chem.eng.osaka-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research from the MEXT, JSPS, and JST (ACT-C) of Japan.

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