

# Convenient Synthesis of Benzo[*b*]thiophene-5,6-dicarboximide Derivatives and Their Photophysical Properties

Naoki Kobayashi<sup>1</sup>, Shinya Yamamoto<sup>1</sup>, Haruki Shimosasa<sup>1</sup>, Mitsunori Oda<sup>1,\*</sup>, Ryuta Miyatake<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Shinshu University, Nagano, Japan

<sup>2</sup>Centre for Environmental Conservation and Research Safety, University of Toyama, Toyama, Japan

## Email address:

mituoda@shinshu-u.ac.jp (M. Oda)

\*Corresponding author

## To cite this article:

Naoki Kobayashi, Shinya Yamamoto, Haruki Shimosasa, Mitsunori Oda, Ryuta Miyatake. Convenient Synthesis of Benzo[*b*]thiophene-5,6-dicarboximide Derivatives and Their Photophysical Properties. *Modern Chemistry*. Vol. 4, No. 5, 2016, pp. 45-51. doi: 10.11648/j.mc.20160405.11

Received: October 5, 2016; Accepted: October 18, 2016; Published: November 10, 2016

**Abstract:** Phosphine-assisted annulation of thiophene-2,3-dicarbaldehyde with *N*-substituted maleimides provided the *N*-substituted benzo[*b*]thiophene-5,6-dicarboximides in good to high yields. Introduction of cyano and aryl groups to the thiophene moiety of the *N*-cyclohexyl product was achieved by metal-catalyzed coupling reactions via its bromo derivative. Photophysical properties of the products were also reported.

**Keywords:** Annulation, Phosphine, Copper-Mediated Cyanation, Mizoroki-Heck Reaction, Emission

## 1. Introduction

Arene-dicarboximides display unique photophysical and electrochemical properties and have been attractive to be used as organic electronic materials, such as light-emitting diodes, [1] semiconductors, [2] bio-sensors, [3-4] and electron acceptors in solar cells. [5-6] Thus, synthetic improvements to access to these imides have continuously made. [7-8]

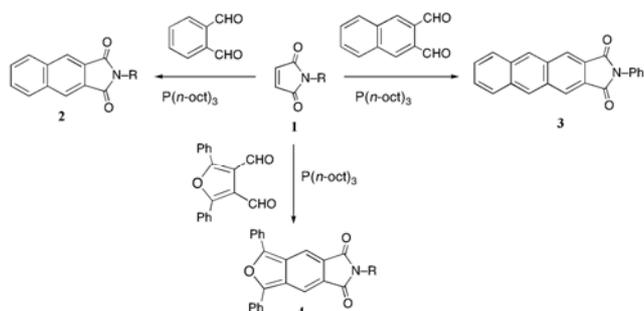


Figure 1. Previously reported annulations by us.

We recently developed an efficient method of annulation between arene-1,2-dicarbaldehydes and maleimides [9-11] by

improving the previously reported Haddadin's result. [12] various naphthalene-, anthracene-, and isobenzofuran-dicarboximides 2–4 can be obtained in one-pot from the corresponding arene-1,2-dicarbaldehydes and maleimides in good to high yields (Fig. 1). These reactions proceed efficiently with the aid of trialkylphosphine in refluxing dioxane. It is worthy to note that the reaction procedure of this method is very simple, because the products were obtained directly from the reaction mixtures just by filtration.

In this paper, we present the synthesis of the benzo[*b*]thiophene-5,6-dicarboximides by applying this method to annulation of thiophene-2,3-dicarbaldehyde with *N*-substituted maleimides (Fig. 2), derivatization of the *N*-cyclohexyl product, and also photophysical properties of the products.

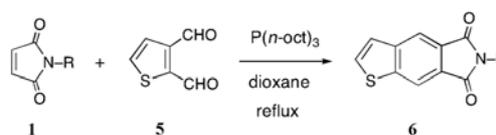


Figure 2. A synthetic route to *N*-substituted benzo[*b*]thiophene-5,6-dicarboximides described in this paper.

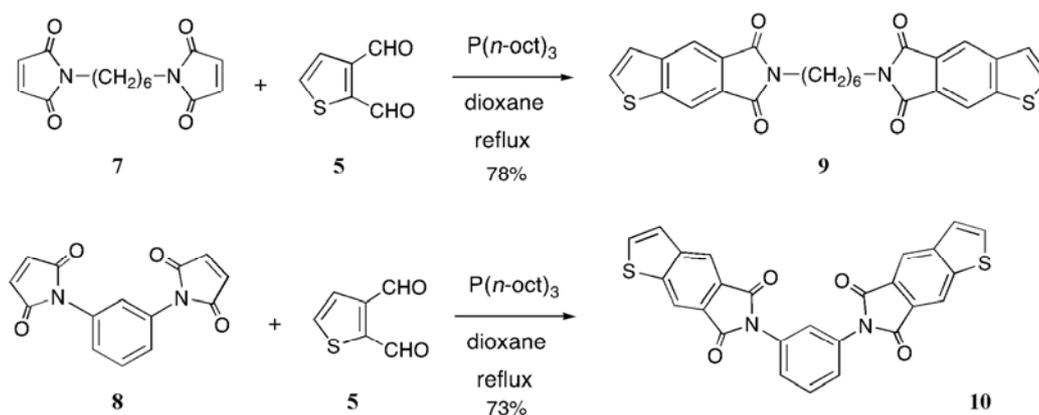
## 2. Results and Discussion

Commercially available thiophene-2,3-dicarbaldehyde (**5**) was subjected to the annulation reaction with various *N*-substituted maleimides in the presence of tri-*n*-octylphosphine in refluxing dioxane. Various *N*-substituted benzo[*b*]thiophene-5,6-dicarboximides (**6a–i**) were obtained in good to high yields. The results are shown in Table 1, indicating that both *N*-alkyl- and *N*-aryl-maleimides serve as a reactant for the annulation. Also, annulation of dialdehyde **5** with bismaleimides **7** and **8** provided bis(benzo[*b*]thiophene-5,6-dicarboximide)s **9** and **10** in good yields (Figure 3). It should be noted that most of all reactions completed for a short reaction time and the products were isolated directly from the reaction mixtures just by filtration. In literature there is only one reference, which described synthesis of benzo[*b*]thiophene-5,6-dicarboximides (Fig. 4). [13] Although this method seems to be useful for preparing the 9-substituted compound, it requires an expensive samarium reagent and the yield of the two-pot procedures is moderate. Our method described in this paper is superior to the reported one in points of simplicity and efficiency of the reaction. Optical properties of some products are shown in

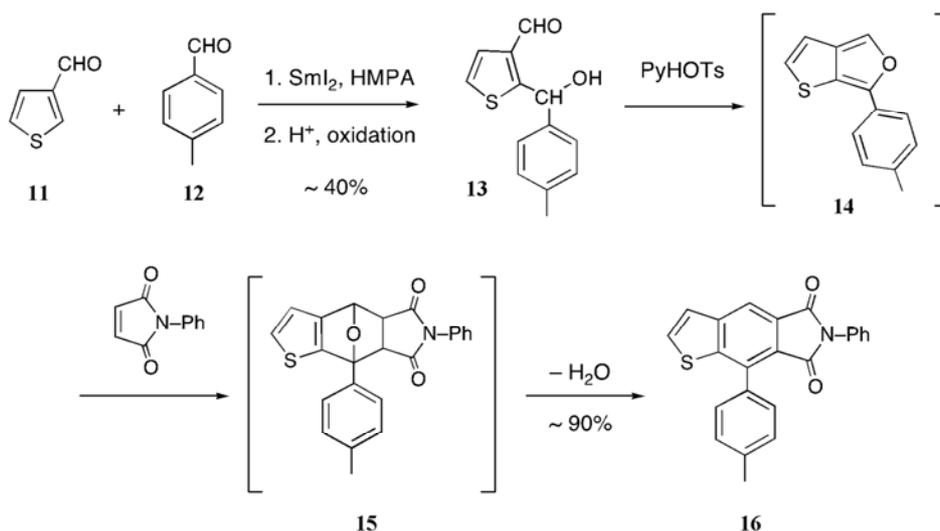
Table 2. The *N*-4-methoxyphenyl derivative **6g** shows clear dual emission in acetonitrile as seen in the spectra of *N*-arylnaphthalene-2,3-dicarboximides. [14] Emission quantum yields of **6** are smaller than those of the corresponding naphthalene-2,3-dicarboximides **2**, [15] probably because of a heavy atom effect of the sulfur atom. [16]

**Table 1.** Reaction time and yields of *N*-substituted benzo[*b*]thiophene-5,6-dicarboximides (**6a–j**).

entry	R	reaction time	product	yield (%)
1	Me	1	<b>6a</b>	86
2	Et	1	<b>6b</b>	86
3	<i>c</i> -hexyl	3	<b>6c</b>	78
4	Ph	1	<b>6d</b>	83
5	4-Br-C <sub>6</sub> H <sub>4</sub> -	3	<b>6e</b>	93
6	4-I-C <sub>6</sub> H <sub>4</sub> -	4	<b>6f</b>	71
7	4-MeO-C <sub>6</sub> H <sub>4</sub> -	2	<b>6g</b>	90
8	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -	2	<b>6h</b>	89
9	4-Ph-C <sub>6</sub> H <sub>4</sub> -	2	<b>6i</b>	88
10	3-pyridyl	2	<b>6j</b>	75



**Figure 3.** Synthesis of bis(benzo[*b*]thiophene-5,6-dicarboximide)s **9** and **10**.



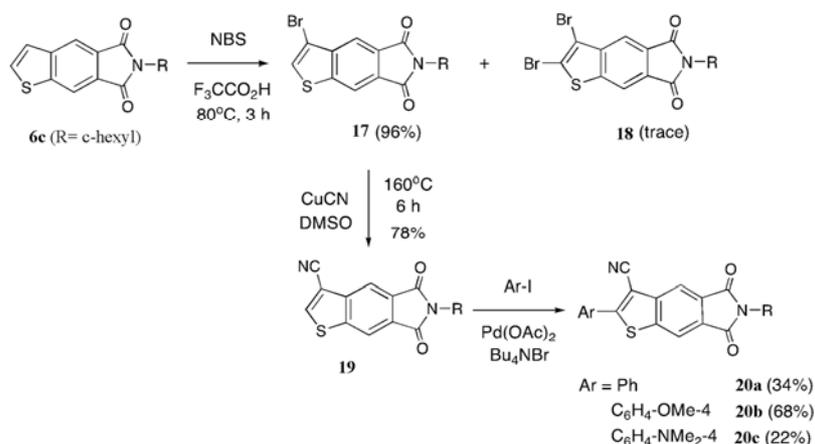
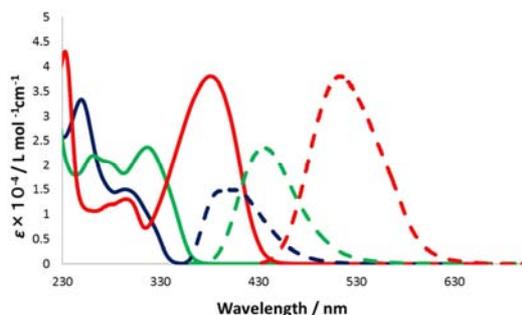
**Figure 4.** A previously reported synthetic route to benzo[*b*]thiophene-5,6-dicarboximide derivatives.

**Table 2.** Optical properties of selected benzo[*b*]thiophene-5,6-dicarboximides 6.

Imides	solvent	$\lambda_{\text{abs}} / \text{nm}$	$\log \epsilon$	$\lambda_{\text{emi}} / \text{nm}$	Stokes shift / nm	$\Phi / \%$
6a	CH <sub>3</sub> OH	344	3.77	461	117	4
6b	CHCl <sub>3</sub>	348	3.79	379	31	3
6c	CHCl <sub>3</sub>	348	3.78	413sh	65	2
				380	32	
6d	CH <sub>3</sub> CN	347	3.50	409sh	61	0.3
				461	114	
6d	CHCl <sub>3</sub>	350	3.83	477	127	0.6
6e	CH <sub>3</sub> CN	347	3.86	485	138	0.2
6f	CH <sub>3</sub> CN	347	3.81	415	68	0.3
				513	166	
6g	CH <sub>3</sub> CN	348	3.80	415	67	0.3
				513	165	
6g	CHCl <sub>3</sub>	349	3.85	514	165	0.03

Next, we turned our attention to derivatization of the product in order to increase the quantum yield and to gain an insight to possibility for tuning absorption and emission wavelengths. Introduction of cyano and aryl groups to the thiophene moiety of 6c was examined via its bromo derivative. Since Lemaire *et al.* reported an efficient access to 2-aryl derivatives from benzo[*b*]thiophene itself, we applied their methodology to chemical modification in our work. [17] At first, 3-bromo compound 17 was synthesized from 6c. Bromination of 6c with *N*-bromosuccinimide (NBS) in trifluoroacetic acid at 80°C for a short reaction time yielded 3-bromo derivative 7 in 96% yield, accompanied with a trace amount of 2,3-dibromo derivative 18. (Fig. 5) Although

Lemaire *et al.* found that benzo[*b*]thiophene can be brominated by NBS in refluxing acetic acid, the reaction of 6c under the same conditions in refluxing acetic acid required a longer reaction time and the yield of 17 was found to be moderate. It is stressed that using trifluoroacetic acid as a solvent in the reaction of 6c improved both the reaction time and the yield. Introduction of a cyano group was achieved by heating 17 with CuCN in dimethylsulfoxide (DMSO). [18] While reaction of 17 with an excess of CuCN in DMSO at 125°C for 12 h resulted in formation of 19 in 17% yield, accompanied with 53% of recovery, the reaction of 17 at 160°C for a shorter reaction time of 6 h provided 19 in 78% yield.

**Figure 5.** Derivatization of *N*-cyclohexyl derivative 6c.**Figure 6.** UV-vis absorption (solid line) and emission (broken line) spectra of 2-aryl-3-cyano-*N*-cyclohexylbenzo[*b*]thiophene-5,6-dicarboximides 20a (blue), 20b (green) and 20c (red) in chloroform.

Finally, the Mizoroki-Heck reactions of 19 with various aryl iodides in the presence of Pd(OAc)<sub>2</sub>, potassium carbonate and tetra-*n*-butylammonium bromide produced 2-aryl derivatives 20a-c. Optical properties of 19 and 20a-c are summarized in Table 3. The UV-vis and emission spectra of 20a-c are shown in Fig. 6.

Although 19 shows weaker emission quantum yield (1%) than 6c does, 2-aryl derivatives 20a-c indicate the enhanced quantum yields up to 27% in spite of existence of a heavy atom of sulfur. The absorptions shift with a hyperchromic effect depending on the substituents at the para position of the phenyl group and similarly emission wavelength shifts, clearly indicating that it is possible to tune both absorption and emission wavelengths of the title compounds by

introduction of aryl groups with an electron-donating substituent at the 2 position.

**Table 3.** Optical properties of some *N*-cyclohexylbenzo[*b*]thiophene-5,6-dicarboximides 19 and 20a–c in chloroform.

Imides	$\lambda_{\text{abs}} / \text{nm}$	$\log \epsilon$	$\lambda_{\text{emi}} / \text{nm}$	Stokes shift / nm	$\Phi / \%$
19	338	3.67	368	30	1
20a	327sh	4.18	405	78	6
20b	350sh	4.37	436	86	17
20c	414	4.58	511	97	27

### 3. Experimental

#### 3.1. General Remarks

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer and relative intensity is indicated with letters, vs, v, m, and w. as very strong, strong, medium, and weak, respectively. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Emission spectra were recorded on a Shimadzu RF5300-PC spectrometer. Emission quantum yields were obtained by comparison with that of anthracene ( $\Phi = 27\%$  in ethanol).  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on JEOL  $\lambda 400$  and ECA500 spectrometers. A chemical shift value of tetramethylsilane ( $\delta = 0$  ppm) for both  $^1\text{H}$ -NMR  $^{13}\text{C}$ -NMR spectra was used as internal standard. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was performed with Silica gel 60N from Kanto Chem. DMSO, *N,N*-dimethylformamide (DMF), and 1,4-dioxane were purchased from Kanto Chem. and were distilled over  $\text{CaH}_2$ . Dichloromethane, chloroform, trifluoroacetic acid, and acetonitrile were also purchased from Kanto Chem. Tri-*n*-octylphosphine, *N*-methylmaleimide, *N*-ethylmaleimide, *N*-cyclohexylmaleimide, *N*-phenylmaleimide, *N,N'*-(*m*-phenylene)bismaleimide, *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), 4-iodoanisole, iodobenzene, and thiophene-2,3-dicarbaldehyde were purchased from Tokyo Chemical Industry, Inc. Copper(I) cyanide, palladium acetate, and tetra-*n*-butylammonium bromide were purchased from Wako Chem. *N*-(4-Methoxyphenyl)-, *N*-(4-bromophenyl)-, *N*-(4-iodophenyl)-, *N*-(*p*-biphenyl)-, and *N*-3-pyridylmaleimides were prepared according to a two-step procedure from maleic anhydride and corresponding amines reported by Cava *et al.* [19] *N,N'*-Hexamethylenedimaleimide was prepared by the method of Tona *et al.* [20] 4-Iodo-*N,N*-dimethylaniline was prepared by NIS iodination of *N,N*-dimethylaniline. [21]

#### 3.2. General Procedure for Synthesis of Benzo[*b*]Thiophene-5,6-Dicarboximides 6

To a solution of the thiophene-2,3-dicarbaldehyde (1.0 mmol) and *N*-substituted maleimide (1.1 mmol) in 2 ml of dry dioxane was added tri-*n*-octylphosphine (1.2 mmol). The mixture was refluxed on a preheated oil bath under nitrogen atmosphere for 1–4 h, and was cooled to room temperature. To the reaction mixture was added 2 ml of hexane and the

annulation product crystallized at ice-bath temperature. The crystals were collected by suction filtration and washed well with cold ether/hexane (1/1) to give a pure product.

6a: Colorless prisms, m.p. 224–226 °C.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta = 8.33$  (d,  $J = 0.8$  Hz, 1H), 8.26 (s, 1H), 7.76 (dd,  $J = 6.4, 0.8$  Hz, 1H) 7.55 (d,  $J = 8.0$  Hz, 1H), 3.22 (s, 3H) ppm;  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 168.5, 168.3, 144.4, 143.1, 131.5, 128.4, 127.5, 125.0, 119.0, 118.4, 24.1$  ppm; IR (KBr)  $\nu = 1764$  (m), 1692 (vs)  $\text{cm}^{-1}$ ; UV-vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}} = 215$  ( $\log \epsilon = 4.11$ ), 235 (4.35), 256 (4.62), 328 (3.64), 344 (3.77) nm; MS (70 eV)  $m/z$  (%) 218 (30), 217 ( $\text{M}^+$ , 100), 216 (15), 189 (33), 188 (17), 173 (76), 161 (19), 160 (28), 133 (25), 132 (60), 94 (19), 66 (11). HRMS Calcd for  $\text{C}_{11}\text{H}_7\text{NO}_2\text{S}$  ( $\text{M}^+$ ) 217.0198, found 217.0198.

6b: Colorless plates, m.p. 171–172 °C.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta = 8.33$  (t,  $J = 0.7$  Hz, 1H), 8.26 (d,  $J = 0.7$  Hz, 1H), 7.75 (d,  $J = 5.5$  Hz, 1H), 7.55 (dd,  $J = 5.5, 0.7$  Hz, 1H), 3.79 (q,  $J = 7.3$  Hz, 2H), 1.31 (t,  $J = 7.3$  Hz, 3H) ppm;  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 168.2, 168.1, 144.4, 143.1, 131.4, 128.4, 127.6, 125.0, 119.0, 118.4, 33.1, 14.0$  ppm; IR (KBr)  $\nu = 1761$  (s), 1746 (s), 1695 (vs)  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (%) 231 ( $\text{M}^+$ , 56), 216 (100), 203 (8), 189 (9), 161 (12), 132 (17). HRMS Calcd for  $\text{C}_{12}\text{H}_9\text{NO}_2\text{S}$  ( $\text{M}^+$ ) 231.0354, found 231.0354.

6c: Colorless microcrystals, m.p. 232–233 °C.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 8.30$  (t,  $J = 0.9$  Hz, 1H), 8.23 (d,  $J = 0.9$  Hz, 1H), 7.73 (d,  $J = 5.5$  Hz, 1H), 7.54 (dd,  $J = 5.5, 0.9$  Hz, 1H), 4.15 (tt,  $J = 12.8, 3.7$  Hz, 1H), 2.25 (qd,  $J = 12.8, 3.7$  Hz, 2H), 1.88 (dm,  $J = 12.8$  Hz, 2H), 1.76 (dm,  $J = 12.8$  Hz, 2H), 1.70 (dm,  $J = 12.8$  Hz, 1H), 1.39 (qt,  $J = 12.8, 3.7$  Hz, 2H), 1.29 (qt,  $J = 12.8, 3.7$  Hz, 1H) ppm;  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta = 168.4, 168.3, 144.3, 143.1, 131.2, 128.3, 127.5, 125.0, 118.8, 118.2, 51.1, 29.9, 26.1, 25.1$  ppm; IR (KBr)  $\nu = 1715$  (s), 1700 (vs), 1684 (s)  $\text{cm}^{-1}$ ; UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}} = 260$  ( $\log \epsilon = 4.70$ ), 333 (3.70), 348 (3.78) nm; MS (70 eV)  $m/z$  (%) 285 ( $\text{M}^+$ , 61), 242 (38), 204 (100), 186 (25), 161 (10), 132 (14). HRMS Calcd for  $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{S}$  ( $\text{M}^+$ ) 285.08235, found 285.0828.

6d: Creamy white microcrystals, m.p. 250–251 °C.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta = 8.46$  (t,  $J = 0.9$  Hz, 1H), 8.38 (d,  $J = 0.9$  Hz, 1H), 7.80 (d,  $J = 5.5$  Hz, 1H), 7.60 (dd,  $J = 5.5, 0.6$  Hz, 1H) 7.50 (m, 4H), 7.42 (tm,  $J = 6.5$  Hz, 1H) ppm;  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta = 167.4, 167.3, 145.0, 143.6, 132.02, 131.98, 129.2, 128.2, 128.0, 127.1, 126.7, 125.2, 119.7, 119.2$  ppm; IR (KBr)  $\nu = 1774$  (s), 1707 (vs)  $\text{cm}^{-1}$ ; UV-vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}} = 234$  ( $\log \epsilon = 4.26$ ), 260 (4.61), 345 (3.66) nm; MS (70 eV)  $m/z$  (%) 280 (18), 279 ( $\text{M}^+$ , 100), 236 (10), 235 (57), 132 (25). HRMS Calcd for  $\text{C}_{16}\text{H}_9\text{NO}_2\text{S}$  ( $\text{M}^+$ ) 279.0354, found 279.0354.

6e: Colorless microcrystals, m.p. > 300 °C.  $^1\text{H}$ NMR ( $\text{DMSO}-d_6$  at 130 °C, 500 MHz)  $\delta = 8.62$  (s, 1H), 8.44 (s, 1H), 8.12 (d,  $J = 5.5$  Hz, 1H), 7.75 (d,  $J = 5.5$  Hz, 1H), 7.70 (d,  $J = 8.0$  Hz, 1H), 7.46 (d,  $J = 8.0$  Hz, 1H) ppm;  $^{13}\text{C}$ NMR ( $\text{DMSO}-d_6$  at 130 °C, 126 MHz)  $\delta = 165.9, 165.8, 144.1, 143.1, 132.7, 131.2, 131.2, 128.4, 127.1, 126.1, 124.6, 120.2, 118.8, 118.6$  ppm; IR (KBr)  $\nu = 1784$  (m), 1717 (vs)  $\text{cm}^{-1}$ ; UV-vis ( $\text{CH}_3\text{CN}$ )  $\lambda_{\text{max}} = 228$  ( $\log \epsilon = 4.43$ ), 262 (4.81), 334sh (3.78), 347 (3.86) nm; MS (70 eV)  $m/z$  (%) 359 ( $\text{M}^+$ , 100), 357 ( $\text{M}^+$ , 97), 315 (33), 160 (10), 139 (15), 132 (15). HRMS Calcd for

$C_{16}H_8^{79}BrNO_2S$  ( $M^+$ ), 356.9459, found 356.9458.

6f: Creamy white microcrystals, m.p. > 300 °C.  $^1H$ NMR (DMSO- $d_6$  at 130°C, 400 MHz)  $\delta$  = 8.28 (s, 1H), 8.04 (s, 1H), 7.74 (d,  $J$  = 5.6 Hz, 1H), 7.46 (dm,  $J$  = 8.4 Hz, 2H), 7.34 (d,  $J$  = 5.2 Hz, 1H), 6.86 (dm,  $J$  = 8.4 Hz, 2H) ppm;  $^{13}C$ NMR (DMSO- $d_6$  at 130°C, 126 MHz)  $\delta$  = 165.8, 165.7, 144.1, 143.0, 137.1, 132.5, 131.7, 128.4, 127.1, 126.1, 124.6, 118.7, 118.5, 116.1 ppm; IR (KBr)  $\nu$  = 1718 (vs), 1709 (vs), 1679 (s)  $cm^{-1}$ ; UV-vis (CH<sub>3</sub>CN)  $\lambda_{max}$  = 231 (log  $\epsilon$  = 4.39), 263 (4.76), 334 (3.74), 347 (3.81) nm; MS (70 eV)  $m/z$  (%) 406 (19), 405 ( $M^+$ , 100), 361 (23), 234 (23), 132 (45). HRMS Calcd for  $C_{16}H_{15}NIO_2S$  ( $M^+$ ) 404.9320, found 404.9321.

6g: Yellowish microcrystals, m.p. 228–229 °C.  $^1H$ NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  = 8.45 (s, 1H), 8.36 (s, 1H), 7.79 (d,  $J$  = 5.2 Hz, 1H), 7.59 (d,  $J$  = 5.2 Hz, 1H), 7.38 (d,  $J$  = 9.0 Hz, 2H), 7.03 (d,  $J$  = 9.0 Hz, 2H), 3.86 (s, 3H) ppm;  $^{13}C$ NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta$  = 167.5, 167.4, 159.2, 144.7, 143.4, 131.7, 127.92, 127.89, 127.1, 125.0, 124.5, 119.5, 118.9, 114.4, 55.5 ppm; IR (KBr)  $\nu$  = 1769 (s), 1714 (vs)  $cm^{-1}$ ; UV-vis (CH<sub>3</sub>CN)  $\lambda_{max}$  = 228 (log  $\epsilon$  = 4.46), 260 (4.66), 334 (3.74), 345 (3.80) nm; MS (70 eV)  $m/z$  (%) 310 (20), 309 ( $M^+$ , 100), 294 (40), 265 (9), 186 (9), 132 (11). HRMS Calcd for  $C_{17}H_{11}NO_3S$  ( $M^+$ ) 309.0460, found 309.0461.

6h: Colorless microcrystals, m.p. >300 °C.  $^1H$ NMR (DMSO- $d_6$  at 130°C, 500 MHz)  $\delta$  = 8.67 (s, 1H), 8.49 (s, 1H), 8.36 (d,  $J$  = 8.4 Hz, 2H), 8.15 (d,  $J$  = 5.2 Hz, 1H), 7.86 (d,  $J$  = 8.4 Hz, 2H), 7.78 (d,  $J$  = 5.2 Hz, 1H) ppm;  $^{13}C$ NMR (DMSO- $d_6$  at 130°C, 126 MHz)  $\delta$  = 165.5, 165.4, 146.0, 144.3, 143.2, 137.5, 132.8, 126.9, 126.7, 125.9, 124.6, 123.3, 118.9, 118.7 ppm; IR (KBr)  $\nu$  = 1765 (s), 1729 (vs)  $cm^{-1}$ ; MS (70 eV)  $m/z$  (%) 324 ( $M^+$ , 100), 294 (25), 280 (24), 234 (22), 222 (10), 160 (14), 132 (45). HRMS Calcd for  $C_{16}H_8N_2O_4S$  ( $M^+$ ) 324.0205, found 324.0207.

6i: Yellowish leaflets, m.p. >300 °C.  $^1H$ NMR (DMSO- $d_6$  at 130°C, 500 MHz)  $\delta$  = 8.63 (s, 1H), 8.46 (s, 1H), 8.12 (d,  $J$  = 5.6 Hz, 1H), 7.78 (m, 3H), 7.71 (d,  $J$  = 8.4 Hz, 2H), 7.58 (d,  $J$  = 8.4 Hz, 2H), 7.49 (t,  $J$  = 7.3 Hz, 2H), 7.39 (t,  $J$  = 7.3 Hz, 1H) ppm;  $^{13}C$ NMR (DMSO- $d_6$  at 130°C, 126 MHz)  $\delta$  = 166.2, 166.1, 144.1, 143.1, 139.5, 139.1, 132.5, 131.1, 128.3, 127.2, 127.0, 126.7, 126.5, 126.3, 126.2, 124.6, 118.7, 118.4 ppm; IR (KBr)  $\nu$  = 1774 (m), 1703 (vs)  $cm^{-1}$ ; MS (70 eV)  $m/z$  (%) 356 (25), 355 ( $M^+$ , 100), 311 (20), 152 (13), 132 (22). HRMS Calcd for  $C_{22}H_{13}NO_2S$  ( $M^+$ ) 355.0667, found 355.0670.

6j: Yellowish microcrystals, m.p. >300 °C.  $^1H$ NMR (DMSO- $d_6$  at 130°C, 400 MHz)  $\delta$  = 8.76 (d,  $J$  = 0.7 Hz, 1H), 8.72 (d,  $J$  = 2.0 Hz, 1H), 8.63 (dm,  $J$  = 4.8 Hz, 1H), 8.52 (d,  $J$  = 0.7 Hz, 1H), 8.20 (d,  $J$  = 5.5 Hz, 1H), 7.96 (ddm,  $J$  = 8.1, 2.0 Hz, 1H), 7.80 (d,  $J$  = 5.5 Hz, 1H), 7.60 (dd,  $J$  = 8.1, 4.8 Hz, 1H) ppm;  $^{13}C$ NMR (DMSO- $d_6$  at 130°C, 100 MHz)  $\delta$  = 165.9, 165.8, 148.0, 147.0, 144.1, 143.1, 133.7, 132.7, 128.7, 127.1, 126.1, 124.6, 123.0, 118.8, 118.6 ppm; IR (KBr)  $\nu$  = 1783 (m), 1708 (vs)  $cm^{-1}$ ; UV-vis (CH<sub>3</sub>CN)  $\lambda_{max}$  = 230 (log  $\epsilon$  = 4.28), 261 (4.71), 334 (3.70), 347 (3.79) nm; MS (70 eV)  $m/z$  (%) 281 (18), 280 ( $M^+$ , 100), 236 (53), 235 (44), 210 (11), 159 (11), 132 (61). HRMS Calcd for  $C_{15}H_8N_2O_2S$  ( $M^+$ ) 280.0307, found 280.0309.

### 3.3. General Procedure for Synthesis of Bis(Benzo[b]Thiophene-5,6-Dicarboximide)s 9 and 10

To a solution of thiophene-2,3-dicarbaldehyde (1.0 mmol) and *N*-substituted maleimide (0.55 mmol) in 2 ml of dry dioxane was added tri-*n*-octylphosphine (1.2 mmol). The mixture was refluxed on a preheated oil bath under nitrogen atmosphere for 4 h, and was cooled to ice-bath temperature. The crystals formed were collected by suction filtration and washed well with cold ether/hexane (1/1) to give a product.

9: Brownish solids, m.p. 257–258 °C.  $^1H$ NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  = 8.31 (t,  $J$  = 0.8 Hz, 2H), 8.24 (d,  $J$  = 0.8 Hz, 2H), 7.74 (d,  $J$  = 5.5 Hz, 2H), 7.54 (dd,  $J$  = 5.5, 0.8 Hz, 2H), 3.71 (t,  $J$  = 7.3 Hz, 4H), 1.71 (quin,  $J$  = 7.3 Hz, 4H), 1.41 (quin,  $J$  = 7.3 Hz, 4H) ppm;  $^{13}C$ NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta$  = 168.3, 168.2, 144.3, 143.0, 131.3, 128.3, 127.5, 125.0, 119.0, 118.4, 38.0, 28.5, 26.5 ppm; IR (KBr)  $\nu$  = 1758 (s), 1699 (vs)  $cm^{-1}$ ; MS  $m/z$  (%) = 488 ( $M^+$ , 48), 272 (22), 230 (10), 216 (100), 204 (10), 186 (10), 161 (10). HRMS Calcd for  $C_{26}H_{20}N_2O_4S_2$  ( $M^+$ ) 488.0865, found 488.0860.

10: Brownish solids, m.p. >300 °C.  $^1H$ NMR (DMSO- $d_6$  at 100°C, 500 MHz)  $\delta$  = 8.67 (s, 2H), 8.47 (s, 2H), 8.14 (d,  $J$  = 5.6 Hz, 2H), 7.77 (d,  $J$  = 5.6 Hz, 2H), 7.68 (m, 2H), 7.58 (m, 2H) ppm;  $^{13}C$ NMR (DMSO- $d_6$  at 100°C, 126 MHz)  $\delta$  = 165.94, 165.85, 144.1, 143.1, 132.5, 132.3, 128.4, 127.1, 126.2, 125.8, 124.8, 124.6, 118.7, 118.5 ppm; IR (KBr)  $\nu$  = 1770 (s), 1722 (vs)  $cm^{-1}$ ; MS  $m/z$  (%) = 481 (31), 480 ( $M^+$ , 100), 240 (8), 132 (22). HRMS Calcd for  $C_{26}H_{12}N_2O_4S_2$  ( $M^+$ ) 480.0239, found 480.0242.

### 3.4. 3-Bromo-*N*-CyclohexylBenzo[b]Thiophene-5,6-Dicarboximide (17)

A mixture of 285 mg (1.00 mmol) of 6c and 890 mg (5.00 mmol) of NBS in 15 mL of trifluoroacetic acid was heated on an oil bath for 3 h. The reaction mixture was poured into water and was extracted with ether (30 ml x 3). The combined organic layer was washed with a saturated NaHCO<sub>3</sub> aqueous solution and brine. After dryness over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated and the residue was purified by silica gel chromatography (CHCl<sub>3</sub>/hexane = 3/1) to give 252 mg of 17 (96%) as colorless microcrystals, followed by a trace amount of 18. Independently, 18 was obtained as colorless microcrystals by NBS bromination for a longer reaction time (14 h) from 17 in 84% yield.

17: M.p. 221–223 °C.  $^1H$ NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  = 8.28 (d,  $J$  = 0.7 Hz, 1H), 8.27 (d,  $J$  = 0.7 Hz, 1H), 7.71 (s, 1H), 4.17 (tt,  $J$  = 12.4, 3.7 Hz, 1H), 2.25 (qd,  $J$  = 12.4, 3.7 Hz, 2H), 1.89 (dm,  $J$  = 12.4 Hz, 2H), 1.77 (dm,  $J$  = 12.4 Hz, 2H), 1.71 (dm,  $J$  = 12.4 Hz, 1H), 1.25–1.44 (m, 3H) ppm;  $^{13}C$ NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta$  = 168.03, 167.97, 143.6, 141.5, 129.1, 128.6, 128.3, 118.8, 118.5, 109.4, 51.4, 30.0, 26.2, 25.3 ppm; IR (KBr)  $\nu$  = 1766 (m), 1702 (vs)  $cm^{-1}$ ; MS (70 eV)  $m/z$  (%) 365 ( $M^+$ , 57), 363 ( $M^+$ , 55), 322 (32), 320 (30), 285 (14), 284 (100), 283 (27), 282 (98), 281 (15), 266 (23), 264 (22), 239 (12), 212 (13), 210 (13). HRMS Calcd for  $C_{16}H_{14}^{79}BrNO_2S$  ( $M^+$ ), 362.9927, found 362.9926.

18: M.p. 277–279 °C.  $^1H$ NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 8.17

(d,  $J = 0.4$  Hz, 1H), 8.13 (d,  $J = 0.4$  Hz, 1H), 4.13 (tt,  $J = 12.6$ , 3.4 Hz, 1H), 2.21 (qd,  $J = 12.6$ , 3.4 Hz, 2H), 1.86 (dm,  $J = 12.6$  Hz, 2H), 1.73 (dm,  $J = 12.6$  Hz, 2H), 1.69 (dm,  $J = 12.6$  Hz, 1H), 1.41–1.21 (m, 3H) ppm;  $^{13}\text{C}$ NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta = 167.6$ , 143.6, 141.3, 129.3, 128.6, 119.0, 118.6, 117.4, 113.3, 54.3, 51.3, 29.8, 26.0, 25.1 ppm; IR (KBr)  $\nu = 1765$  (s), 1705 (vs) cm<sup>-1</sup>; MS (70 eV)  $m/z$  (%) 445 (M<sup>+</sup>, 31), 443 (M<sup>+</sup>, 59), 441 (M<sup>+</sup>, 29), 402 (16), 400 (29), 398 (15), 364 (53), 363 (26), 362 (100), 344 (20), 342 (20), 319 (10), 290 (13). HRMS Calcd for C<sub>16</sub>H<sub>13</sub><sup>79</sup>Br<sub>2</sub>NO<sub>2</sub>S (M<sup>+</sup>), 440.9034, found 440.9036.

### 3.5. 3-Cyano-*N*-CyclohexylBenzo[*b*]Thiophene-5,6-Dicarboximide (19)

A mixture of 182 mg (0.500 mmol) of 17 and 134 mg (1.50 mmol, 3.0 eq.) of CuCN in 5 mL of dry DMSO was heated on an oil bath at 125 °C for 12 h. The reaction mixture was cooled to room temperature and was passed through a Celite® pad. The filtrate was poured into water and was extracted with ether (20 ml x 3). The combined organic layer was washed with a saturated NaHCO<sub>3</sub> aqueous solution and brine. After dryness over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated and the residue was purified by silica gel chromatography (CHCl<sub>3</sub>) to give 96 mg of 17 (53% recovery), followed by 26.0 mg of 19 (32% based on consumed 17) as colorless microcrystals. The product 19 was obtained in 78% yield under similar reaction conditions at 160 °C for 6 h. M.p. 210–211 °C.  $^1\text{H}$ NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta = 8.44$  (d,  $J = 0.8$  Hz, 1H), 8.37 (s, 1H), 8.36 (d,  $J = 0.8$  Hz, 1H), 4.18 (tt,  $J = 12.3$ , 3.7 Hz, 1H), 2.25 (qd,  $J = 12.3$ , 3.7 Hz, 2H), 1.89 (dm,  $J = 12.3$  Hz, 2H), 1.77 (dm,  $J = 12.3$  Hz, 2H), 1.72 (dm,  $J = 12.3$  Hz, 1H), 1.44–1.25 (m, 3H) ppm;  $^{13}\text{C}$ NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta = 149.4$ , 149.3, 129.9, 128.4, 128.3, 119.5, 119.1, 110.4, 109.9, 106.0, 102.5, 56.7, 39.4, 36.3, 35.6 ppm; IR (KBr)  $\nu = 2230$  (w), 1766 (s), 1702 (vs) cm<sup>-1</sup>; UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}} = 252$ sh (log  $\epsilon = 4.70$ ), 258 (4.77), 281sh (3.83), 324 (3.60), 338 (3.67) nm; MS (70 eV)  $m/z$  (%) 310 (M<sup>+</sup>, 40), 267 (31), 230 (15), 229 (100), 211 (21). HRMS Calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S (M<sup>+</sup>), 310.0776, found 310.0773.

### 3.6. General Procedure for Mizoroki-Heck Reactions of 19

A suspension of 19 (1.00 mmol), aryl iodide (1.25 mmol), tetra-*n*-butylammonium bromide (1.25 mmol), K<sub>2</sub>CO<sub>3</sub> (2.50 mmol), and Pd(OAc)<sub>2</sub> (0.010 mmol) in DMF (5.0 mL) was heated on an oil bath at 125 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was filtered through a Celite® pad, washed well with ether. The filtrate was poured into water and was extracted with ether (20 ml x 3). The combined organic layer was washed with a saturated NaHCO<sub>3</sub> aqueous solution and brine. After dryness over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated and the residue was purified by silica gel chromatography with CHCl<sub>3</sub> as eluant to give the pure product.

20a: Yellowish microcrystals, m.p. 245–246 °C.  $^1\text{H}$ NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta = 8.33$  (s, 1H), 8.22 (s, 1H), 7.87–7.84 (m, 2H), 7.52–7.49 (m, 3H), 4.11 (tt,  $J = 12.4$ , 3.6 Hz, 1H), 2.18 (qd,  $J = 12.4$ , 3.6 Hz, 2H), 1.83 (dm,  $J = 12.4$  Hz, 2H), 1.71 (dm,  $J = 12.4$  Hz, 2H), 1.65 (dm,  $J = 12.4$  Hz, 1H), 1.37–

1.21 (m,  $J = 12.4$ , 3.6 Hz, 3H) ppm;  $^{13}\text{C}$ NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta = 167.6$ , 167.6, 159.1, 143.1, 141.8, 131.6, 130.7, 130.1, 129.8, 129.3, 128.5, 118.1, 117.9, 114.2, 103.3, 51.6, 30.0, 26.2, 25.2 ppm; IR (KBr)  $\nu = 2224$  (m), 1769 (m), 1701 (vs) cm<sup>-1</sup>; UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}} = 259$ sh (log  $\epsilon = 4.41$ ), 282 (4.52), 327sh (4.18) nm; MS (70 eV)  $m/z$  (%) 386 (M<sup>+</sup>, 72), 343 (29), 306 (23), 305 (100), 304 (44), 287 (20). HRMS Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S (M<sup>+</sup>), 386.1089, found 386.1090.

20b: Yellowish microcrystals, m.p. 240–242 °C.  $^1\text{H}$ NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta = 8.33$  (d,  $J = 0.8$  Hz, 1H), 8.22 (d,  $J = 0.8$  Hz, 1H), 7.89 (d,  $J = 8.8$  Hz, 2H), 7.05 (d,  $J = 8.8$  Hz, 2H), 4.15 (tt,  $J = 12.4$ , 3.6 Hz, 1H), 3.89 (s, 3H), 2.23 (qd, 2H,  $J = 12.4$ , 3.6 Hz, 1H), 1.87 (d,  $J = 12.4$  Hz, 2H), 1.75 (d,  $J = 12.4$  Hz, 2H), 1.69 (d,  $J = 12.4$  Hz, 1H), 1.42–1.26 (m, 3H) ppm;  $^{13}\text{C}$ NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta = 167.756$ , 167.750, 162.4, 159.1, 143.3, 141.3, 130.0, 129.0, 123.2, 117.9, 117.5, 115.2, 114.6, 101.8, 55.7, 51.7, 30.0, 26.2, 25.2 ppm;  $^{13}\text{C}$ NMR (CD<sub>2</sub>Cl<sub>2</sub>, 126 MHz)  $\delta = 167.82$ , 167.79, 162.6, 159.3, 143.5, 141.7, 130.31, 130.05, 129.3, 123.5, 118.1, 117.4, 115.3, 114.8, 102.1, 56.0, 51.7, 30.2, 26.5, 25.6 ppm; [22] IR (KBr)  $\nu = 2211$  (w), 1765 (vs), 1706 (s) cm<sup>-1</sup>; UV-vis (CDCl<sub>3</sub>)  $\lambda_{\text{max}} = 250$  (log  $\epsilon = 4.45$ ), 257 (4.49), 294 (4.64), 313 (4.31), 350sh (4.37) nm; MS (70 eV)  $m/z$  (%) 416 (M<sup>+</sup>, 71), 336 (14), 335 (100), 317 (10), 263 (10). HRMS Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S (M<sup>+</sup>), 416.1195, found 416.1191.

20c: Orange microcrystals, m.p. 282–283 °C.  $^1\text{H}$ NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta = 8.28$  (d,  $J = 0.8$  Hz, 1H), 8.18 (d,  $J = 0.8$  Hz, 1H), 7.89 (d,  $J = 5.5$  Hz, 2H), 6.78 (d,  $J = 5.5$  Hz, 2H), 4.16 (tt,  $J = 12.3$ , 3.7 Hz, 1H), 2.25 (qd,  $J = 12.3$ , 3.7 Hz, 2H), 1.89 (dm,  $J = 12.3$  Hz, 2H), 1.77 (dm,  $J = 12.3$  Hz, 2H), 1.71 (dm,  $J = 12.3$  Hz, 1H), 1.43–1.28 (m, 3H) ppm;  $^{13}\text{C}$ NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta = 167.7$ , 167.7, 160.0, 152.2, 143.8, 140.5, 129.7, 129.4, 128.1, 117.8, 117.7, 116.7, 115.2, 111.9, 98.9, 51.2, 40.1, 29.9, 26.0, 25.1 ppm; IR (KBr)  $\nu = 2212$  (w), 1760 (s), 1704 (s), 1366 (vs) cm<sup>-1</sup>; UV-vis (CH<sub>3</sub>CN)  $\lambda_{\text{max}} = 256$ sh (log  $\epsilon = 4.57$ ), 266 (4.63), 310 (4.07), 328 (4.11), 414 (4.58) nm; MS (70 eV)  $m/z$  (%) 430 (29), 429 (M<sup>+</sup>, 100), 348 (10), 347 (33), 346 (20). HRMS Calcd for C<sub>25</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>S (M<sup>+</sup>), 429.1511, found 429.1518.

## 4. Conclusion

We have demonstrated that the novel benzo[*b*]thiophene-5,6-dicarboximides 6, 9, and 10 can be synthesized easily by phosphine-assisted annulation between thiophene-2,3-dicarbaldehydes and various *N*-substituted maleimides. Introduction of a cyano group to the thiophene moiety of the *N*-cyclohexyl product was achieved by copper-mediated coupling reaction via its bromo derivatives and Mizoroki-Heck reaction of the 3-cyano product led to 2-aryl-3-cyano derivatives. Although the emission quantum yields of 6 are low, 2-aryl-3-cyano derivatives 20 indicate the enhanced emission quantum yield up to 27%. Also, we have demonstrated that the absorption and emission wavelengths are tunable by a substituent on the aryl moiety in this structure of 2-aryl-3-cyanobenzo[*b*]thiophene-5,6-dicarboximide.

---

## References

- [1] P. Nandhikonda and M. D. Heagy, "Dual fluorescent *N*-aryl-2,3-naphthalimides: applications in ratiometric DNA detection and white organic light-emitting devices", *Org. Lett.* 2010, 12, 4796–4799.
- [2] X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, and S. R. Marde, "Rylene and diimides for organic electronics", *Adv. Mater.* 2011, 23, 268–284.
- [3] P. Nandhikonda and M. D. Heagy, "An abiotic fluorescent probe for cardiac troponin I", *J. Am. Chem. Soc.*, 2011, 133, 14972–14974.
- [4] K. Hutt, R. Hernandez, and M. D. Heagy, "Toward intrinsically fluorescent proteomimetics: Fluorescent probe response to alpha helix structure of poly-*N*-benzyl-L-glutamate", *Tetrahedron Lett.* 2006, 16, 5436–5438.
- [5] N. Sakai, J. Mareda, E. Vauthey, and S. Matile, "Core-substituted naphthalenediimides", *Chem. Commun.* 2010, 46, 4225–4237.
- [6] Y. Zhou, L. Ding, K. Shi, Y.-Z. Dai, N. Ai, J. Wang, and J. Pei, "A non-fullerene small bulk heterojunction solar cells", *Adv. Mater.* 2012, 24, 957–961.
- [7] T. V. Pho, F. M. Toma, M. L. Chabinyk, and F. Wudl, "Self-assembling decacyclene triimides prepared through a regioselective hexuple Freidel-Crafts carbamylation", *Angew. Chem. Int. Ed.* 2013, 52, 1446–1451.
- [8] Y. Zhong, B. Kumar, S. Oh, M. T. Trinh, Y. Wu, K. Elbert, P. Li, X. Zhu, S. Xiao, F. Ng, M. L. Steigerwald, and C. Nuckolls, "Helical ribbons for molecular electronics", *J. Am. Chem. Soc.* 2014, 136, 8122–8130.
- [9] M. Oda, H. Shimosasa, Y. Kumai, A. Ohta, and R. Miyatake, "An improved synthesis of arenedicarboximides by phosphine-assisted annulation of arene-1,2-dicarbaldehyde with *N*-substituted maleimide", *Modern Chem.* 2014, 2 (4), 29–35.
- [10] H. Shimosasa, R. Miyatake, N. Kobayashi, and M. Oda "Synthesis and emission behavior of 1,3-diarylisobenzofuran-5,6-dicarboximides and their transformation into naphthalene-2,3:6,7-bis(diacboximide)s", *Modern Chem.* 2016, 4 (6), 16–23.
- [11] T. Yanagisawa, N. Kobayashi, H. Shimosasa, Y. Kumai, R. Miyatake, and M. Oda, "Synthesis and fluorescence property of 2,3-naphthalimie derivateives bearing phenyl substituents on the naphthalene skeleton", *Dyes Pigments* in press, <http://dx.doi.org/10.1016/j.dyepig.2016.09.050>.
- [12] M. J. Haddadin, B. J. Agha, and R. F. Tabri, "Syntheses of some furans and naphtho[2,3-*c*] derivatives of furan, pyrrole, and thiophene", *J. Org. Chem.* 1979, 44, 494–497.
- [13] S.-M. Yang and J.-M. Fang, "Coupling reactions and coupling-alkylations of thiophenecarbaldehydes promoted by samarium diiodide", *J. Org. Chem.* 1999, 64, 394–399.
- [14] P. Valat, V. Wintgens, J. Kossanyi, L. Biczók, A. Demeter, and T. Bérces, "Influence of geometry on the emitting properties of 2,3-naphthalimides", *J. Am. Chem. Soc.* 1992, 114, 946–953.
- [15] For examples, an emission quantum yield of *N*-ethyl-naphthlene-2,3-dicarboximide, corresponding to 6b, in chloroform is 0.37 and that of *N*-phenyl-naphthalene-2,3-dicarboximide, corresponding to 6d, is 0.10.
- [16] The low quantum yields of 6e and 6f are ascribed also to a heavy atom effect of the bromine and iodine atoms.
- [17] J. F. D. Chabert, L. Joucla, E. David and M. Lemaire, "An efficient phosphine-free palladium coupling for the synthesis of new 2-arylbenzo[*b*]thiophenes", *Tetrahedron* 2004, 60, 3221–3230.
- [18] Although Lemaire *et al.* reported cyanation of 3-bromobenzo[*b*]thiophene with CuCN in *N,N*-dimethylacetamide in ref 9, cyanation of 12 under the similar conditions yielded 13 in low yield.
- [19] M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, "N-Phenylmaleimide", *Org. Synth. Coll. Vol.* 5, 1973, 944–946.
- [20] R. Tona and R. Häner, "Crosslinking of diene-modified DNA with bis-maleimides", *Mol. BioSyst.* 2005, 1, 93–98.
- [21] H. Shen, K. C. Vollhardt, and C Peter, "Remarkable switch in the regiochemistry of the iodination of anilines by *N*-iodosuccinimide: synthesis of 1,2-dichloro-3,4-diiodo-benzene", *Synlett* 2012, 23, 208–214.
- [22] Although the <sup>13</sup>C NMR spectrum of 20b in CDCl<sub>3</sub> shows only 19 signals, which are short for the structure of 20b, the spectrum in CD<sub>2</sub>Cl<sub>2</sub> indicates 20 signals enough for the structure of 20b.