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

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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]

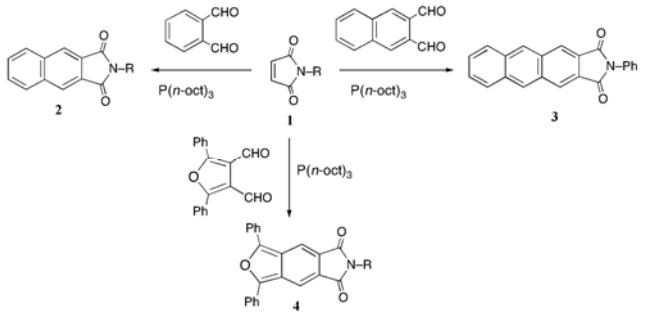

Figure 1. *Previously reported annulations by us.*

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.

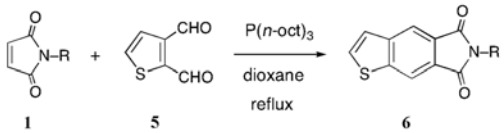

Figure 2. *A synthetic route to N-substituted benzo[b]thiophene-5,6-dicarboximides described in this paper.*

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 is 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-dicarboxyimides 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	6a	86
2	Et	1	6b	86
3	*c*-hexyl	3	6c	78
4	Ph	1	6d	83
5	4-Br-C_6H_4-	3	6e	93
6	4-I-C_6H_4-	4	6f	71
7	4-MeO-C_6H_4-	2	6g	90
8	4-NO_2-C_6H_4-	2	6h	89
9	4-Ph-C_6H_4-	2	6i	88
10	3-pyridyl	2	6j	75

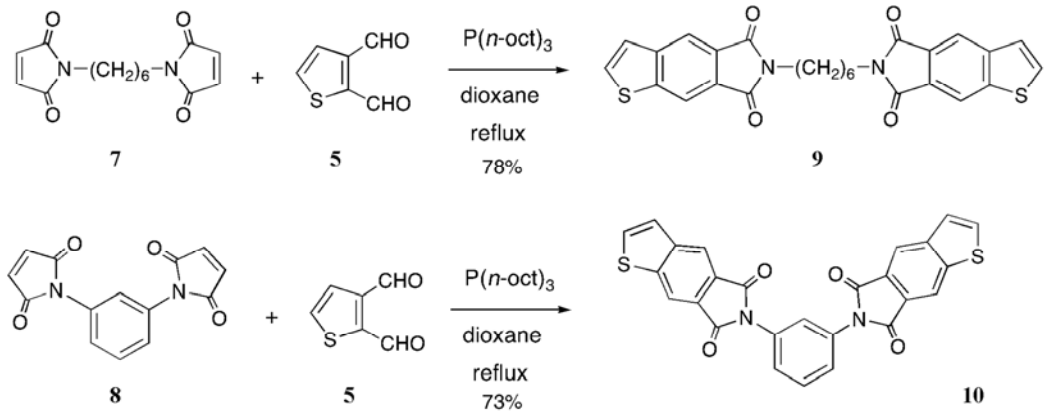

Figure 3. *Synthesis of bis(benzo[b]thiophene-5,6-dicarboximide)s 9 and 10.*

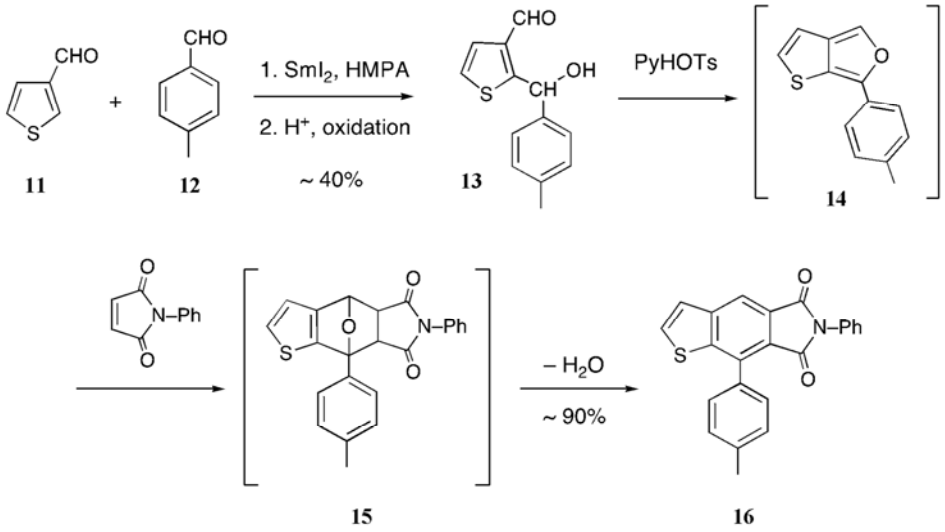

Figure 4. *A previously reported synthetic route to benzo[b]thiophene-5,6-dicarboximide derivatives.*

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

Imides	solvent	λ_{abs} / nm	log ε	λ_{emi} / nm	Stokes shift / nm	Φ / %
6a	CH_3OH	344	3.77	461	117	4
6b	$CHCl_3$	348	3.79	379 413sh	31 65	3
6c	$CHCl_3$	348	3.78	380 409sh	32 61	2
6d	CH_3CN	347	3.50	461	114	0.3
6d	$CHCl_3$	350	3.83	477	127	0.6
6e	CH_3CN	347	3.86	485	138	0.2
6f	CH_3CN	347	3.81	415 513	68 166	0.3
6g	CH_3CN	348	3.80	415 513	67 165	0.3
6g	$CHCl_3$	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*-bromosuccimide (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.

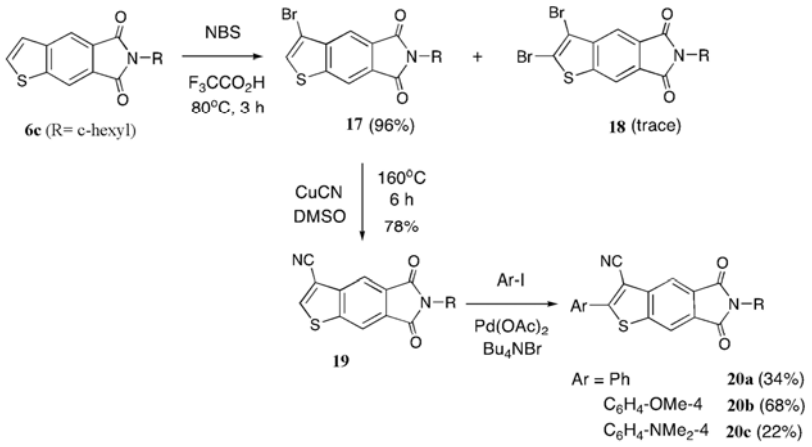

Figure 5. *Derivatization of N-cyclohexyl derivative 6c.*

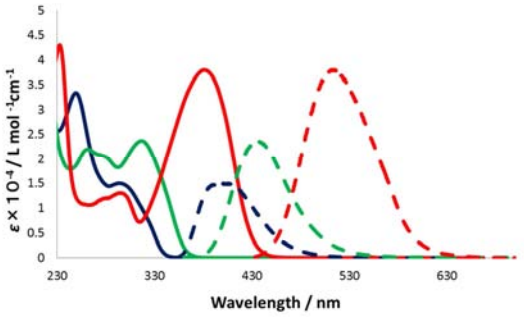

Figure 6. *UV-vis absorption (solid line) and emission (broken line) spectra of 2-aryl-3-cyano-N-cyclohexylbenzo[b]thiophene-5,6-dicarboximides 20a (blue), 20b (green) and 20c (red) in chloroform.*

Finally, the Mizoroki-Heck reactions of 19 with various aryliodides in the presence of $Pd(OAc)_2$, 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	λ_{abs} / nm	log ε	λ_{emi}/ nm	Stokes shift / nm	Φ/ %
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 (Φ = 27% in ethanol). ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL λ400 and ECA500 spectrometers. A chemical shift value of tetramethylsilane (δ = 0 ppm) for both ^{1}H-NMR ^{13}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 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*-bromosuccimide (NBS), *N*-iodosuccimide (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*-biphenylyl)-, and *N*-3-pyridyl-maleimides 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 crystalized 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}HNMR ($CDCl_3$, 400 MHz) δ = 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}CNMR ($CDCl_3$, 100 MHz) δ = 168.5, 168.3, 144.4, 143.1, 131.5, 128.4, 127.5, 125.0, 119.0, 118.4, 24.1ppm; IR (KBr) ν = 1764 (m), 1692 (vs) cm^{-1}; UV-vis (CH_3OH) λ_{max} = 215 (logε = 4.11), 235 (4.35), 256 (4.62), 328 (3.64), 344 (3.77) nm; MS (70 eV) *m/z* (%) 218 (30), 217 (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 $C_{11}H_7NO_2S$ (M^+) 217.0198, found 217.0198.

6b: Colorless plates, m.p. 171–172 °C. ^{1}HNMR ($CDCl_3$, 400 MHz) δ = 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}CNMR ($CDCl_3$, 100 MHz) δ = 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) ν = 1761 (s), 1746 (s), 1695 (vs) cm^{-1}; MS (70 eV) *m/z* (%) 231 (M^+, 56), 216 (100), 203 (8), 189 (9), 161 (12), 132 (17). HRMS Calcd for $C_{12}H_9NO_2S$ (M^+) 231.0354, found 231.0354.

6c: Colorless microcrystals, m.p. 232–233°C. ^{1}HNMR ($CDCl_3$, 500 MHz) δ = 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}CNMR ($CDCl_3$, 126 MHz) δ = 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) ν = 1715 (s), 1700 (vs), 1684 (s) cm^{-1}; UV-vis ($CHCl_3$) λ_{max} = 260 (logε = 4.70), 333 (3.70), 348 (3.78) nm; MS (70 eV) *m/z* (%) 285 (M^+, 61), 242 (38), 204 (100), 186 (25), 161 (10), 132 (14). HRMS Calcd for $C_{16}H_{15}NO_2S$ (M^+) 285.08235, found 285.0828.

6d: Creamy white microcrystals, m.p. 250–251°C. ^{1}HNMR ($CDCl_3$, 500 MHz) δ = 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}CNMR ($CDCl_3$, 126 MHz) δ = 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) ν = 1774 (s), 1707 (vs) cm^{-1}; UV-vis (CH_3OH) λ_{max} = 234 (logε = 4.26), 260 (4.61), 345 (3.66) nm; MS (70 eV) *m/z* (%) 280 (18), 279 (M^+, 100), 236 (10), 235 (57), 132 (25). HRMS Calcd for $C_{16}H_9NO_2S$ (M^+) 279.0354, found 279.0354.

6e: Colorless microcrystals, m.p. > 300 °C. ^{1}HNMR (DMSO-d_6 at 130°C, 500 MHz) δ = 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}CNMR (DMSO-d_6 at 130°C, 126 MHz) δ = 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) ν = 1784 (m), 1717 (vs) cm^{-1}; UV-vis (CH_3CN) λ_{max} = 228 (logε = 4.43), 262 (4.81), 334sh (3.78), 347 (3.86) nm; MS (70 eV) *m/z* (%) 359 (M^+, 100), 357 (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. ^{1}HNMR (DMSO-d_6 at 130˚C, 400 MHz) δ= 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}CNMR (DMSO-d_6 at 130˚C, 126 MHz) δ= 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) ν = 1718 (vs), 1709 (vs), 1679 (s) cm^{-1}; UV-vis (CH_3CN) λ_{max} = 231 (logε = 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. ^{1}HNMR ($CDCl_3$, 500 MHz) δ= 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}CNMR ($CDCl_3$, 126 MHz) δ= 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) ν = 1769 (s), 1714 (vs) cm^{-1}; UV-vis (CH_3CN) λ_{max} = 228 (logε = 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. ^{1}HNMR (DMSO-d_6 at 130˚C, 500 MHz) δ= 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}CNMR (DMSO-d_6 at 130˚C, 126 MHz) δ= 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) ν = 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. ^{1}HNMR (DMSO-d_6 at 130˚C, 500 MHz) δ= 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}CNMR (DMSO-d_6 at 130˚C, 126 MHz) δ = 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) ν = 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. ^{1}HNMR (DMSO-d_6 at 130˚C, 400 MHz) δ= 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}CNMR (DMSO-d_6 at 130˚C, 100 MHz) δ = 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) ν = 1783 (m), 1708 (vs) cm^{-1}; UV-vis (CH_3CN) λ_{max} = 230 (logε = 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. ^{1}HNMR ($CDCl_3$, 500 MHz) δ = 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}CNMR ($CDCl_3$, 126 MHz) δ = 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) ν = 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. ^{1}HNMR (DMSO-d_6 at 100˚C, 500 MHz) δ = 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}CNMR (DMSO-d_6 at 100˚C, 126 MHz) δ = 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) ν = 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-Di-carboximide (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 $NaHCO_3$ aqueous solution and brine. After dryness over Na_2SO_4, the solvent was evaporated and the residue was purified by silica gel chromatography ($CHCl_3$/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. ^{1}HNMR ($CDCl_3$, 500 MHz) δ = 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}CNMR ($CDCl_3$, 126 MHz) δ = 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) ν = 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. ^{1}HNMR ($CDCl_3$, 400 MHz) δ= 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}CNMR ($CDCl_3$, 100 MHz) δ= 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) ν = 1765 (s), 1705 (vs) cm^{-1}; MS (70 eV) *m/z* (%) 445 (M^+, 31), 443 (M^+, 59), 441 (M^+, 29), 402 (16), 400 (29), 398 (15), 364 (53), 363 (26), 362 (100), 344 (20), 342 (20), 319 (10), 290 (13). HRMS Calcd for $C_{16}H_{13}{}^{79}Br_2NO_2S$ (M^+), 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 $NaHCO_3$ aqueous solution and brine. After dryness over Na_2SO_4, the solvent was evaporated and the residue was purified by silica gel chromatography ($CHCl_3$) 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}HNMR ($CDCl_3$, 500 MHz) δ= 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}CNMR ($CDCl_3$, 126 MHz) δ= 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) ν = 2230 (w), 1766 (s), 1702 (vs) cm^{-1}; UV-vis ($CHCl_3$) λ_{max} = 252sh (logε = 4.70), 258 (4.77), 281sh (3.83), 324 (3.60), 338 (3.67) nm; MS (70 eV) *m/z* (%) 310 (M^+, 40), 267 (31), 230 (15), 229 (100), 211 (21). HRMS Calcd for $C_{17}H_{14}N_2O_2S$ (M^+), 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_2CO_3 (2.50 mnol), and $Pd(OAc)_2$ (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 $NaHCO_3$ aqueous solution and brine. After dryness over Na_2SO_4, the solvent was evaporated and the residue was purified by silica gel chromatography with $CHCl_3$ as eluant to give the pure product.

20a: Yellowish microcrystals, m.p. 245–246 ˚C. ^{1}HNMR ($CDCl_3$, 400 MHz) δ= 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}CNMR ($CDCl_3$, 100 MHz) δ = 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) ν = 2224 (m), 1769 (m), 1701 (vs) cm^{-1}; UV-vis ($CHCl_3$) λ_{max} = 259sh (logε = 4.41), 282 (4.52), 327sh (4.18) nm; MS (70 eV) *m/z* (%) 386 (M^+, 72), 343 (29), 306 (23), 305 (100), 304 (44), 287 (20). HRMS Calcd for $C_{23}H_{18}N_2O_2S$ (M^+), 386.1089, found 386.1090.

20b: Yellowish microcrystals, m.p. 240–242 ˚C. ^{1}HNMR ($CDCl_3$, 500 MHz) δ= 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}CNMR ($CDCl_3$, 126 MHz) δ = 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}CNMR (CD_2Cl_2, 126 MHz) δ= 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) ν= 2211 (w), 1765 (vs), 1706 (s) cm^{-1}; UV-vis ($CDCl_3$) λ_{max} = 250 (logε = 4.45), 257 (4.49), 294 (4.64), 313 (4.31), 350sh (4.37) nm; MS (70 eV) *m/z* (%) 416 (M^+, 71), 336 (14), 335 (100), 317 (10), 263 (10). HRMS Calcd for $C_{24}H_{20}N_2O_3S$ (M^+), 416.1195, found 416.1191.

20c: Orange microcrystals, m.p. 282–283 ˚C. ^{1}HNMR ($CDCl_3$, 500 MHz) δ= 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}CNMR ($CDCl_3$, 126 MHz) δ = 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) ν= 2212 (w), 1760 (s), 1704 (s), 1366 (vs) cm^{-1}; UV-vis (CH_3CN) λ_{max} = 256sh (logε = 4.57), 266 (4.63), 310 (4.07), 328 (4.11), 414 (4.58) nm; MS (70 eV) *m/z* (%) 430 (29), 429 (M^+, 100), 348 (10), 347 (33), 346 (20). HRMS Calcd for $C_{25}H_{23}N_{23}O_2S$ (M^+), 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 Mirozoroki-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.

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