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Introduction of ethynylene and thienylene spacers into 2,5-diarylthiazole and 2,5-diarylthiophene

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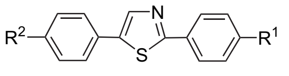
Abstract—Syntheses of 2,5-diarylthiazole and 2,5-diarylthiophene derivatives bearing ethynylene and thienylene spacers are performed. With the methods for coupling reactions of terminal alkynes and at the CH bond of heteroaromatic compounds, which we have developed, five kinds of thiazole and thiophene derivatives **3**–**7** are prepared. Spectroscopic characteristics of **3**–**7** are also measured.

1. Introduction

We have recently shown syntheses and properties of 2,5-diarylthiazoles **1** and 2,5-diarylthiophenes **2**. These molecules bearing donor–acceptor-type substituents showed intense photoluminescent properties and liquid crystalline characteristics based on the difference of the heteroaromatic ring structure.[1] Preparations of **1** and **2** were carried out by utilizing palladium-catalyzed C–H substitution reactions of 5-membered heteroaromatic compounds with various aryl halides, which we developed recently.[1–3] Introduction of conjugative spacer molecules into thiazole and thiophene derivatives is of considerable interest in the studies on the relationship of the structure and physical properties.[4] We envisaged that synthetic strategies utilizing transition metal-catalyzed coupling reactions show great advantage in the facile preparation of such compounds.[5] In particular, Sonogashira coupling is a powerful tool for the introduction of carbon–carbon triple bond.[6,7] Hence, the reaction using aqueous ammonia or 2-ethanolamine as an additive, which we have recently shown, play a significant role for the efficient synthesis of such derivatives.[8] Herein, we report synthesis of the derivatives of **1** and **2** bearing ethynylene spacers. Synthesis of 2,5-diarylthiophene bearing thienylene spacer is also described. Effect of the introduction of such spacers to spectroscopic characteristics is studied.[9]



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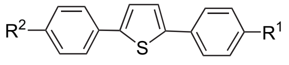

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2. Results and discussion

2.1. Syntheses of 2,5-diarylthiazole 3 and 2,5-diarylthiophenes 4–7 bearing ethynylene and thienylene spacers

We have designed several 2,5-diarylated thiazole and thiophene derivatives bearing ethynylene and thienylene spacers **3**–**7** as summarized in Chart 1. Preparation of these compounds were carried out as shown in Schemes 1–5.

Introduction of the arylethynyl group into the 2-position of a thiazole ring was performed by utilizing the coupling reaction of terminal alkynes, which we developed recently.[7] The reaction of the terminal alkyne **8** with 2-bromothiazole in the presence of a palladium catalyst/CuI (3 mol %/2 mol %) using 2-ethanolamine as an activator afforded 2-arylethynylthiazole **9** in 77% yield after stirring at 60 °C for 5 h. Arylation of **9** at the 5-position was carried out with the palladium-catalyzed C–H substitution reaction using silver(I) fluoride as an activator.[1] Treatment of **9** with ethyl 4-iodobenzoate (**10**) in the presence of $PdCl_2(PPh_3)_2$ (3 mol %) and AgF (2 equiv) furnished the 2,5-diarylthiazole derivative bearing ethynylene spacer at the 2-position of thiazole **3** in 46% yield as shown in Scheme 1.

Scheme 2 shows synthesis of the thiophene derivative bearing the spacer. The arylethynyl group was introduced in a similar manner as in the case of the thiazole **9** with

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Keywords: Sonogashira coupling; 2-Ethanolamine; Palladium catalyst; CH arylation.

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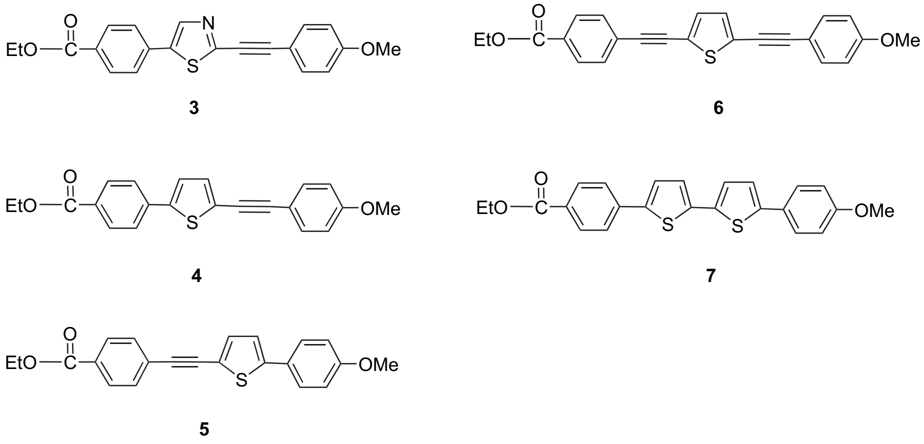
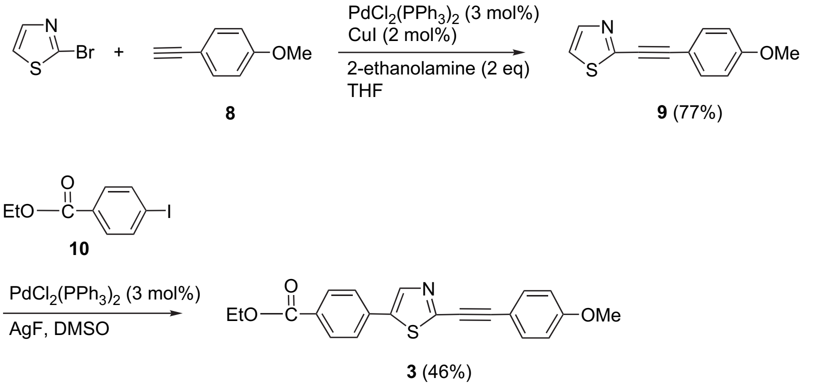
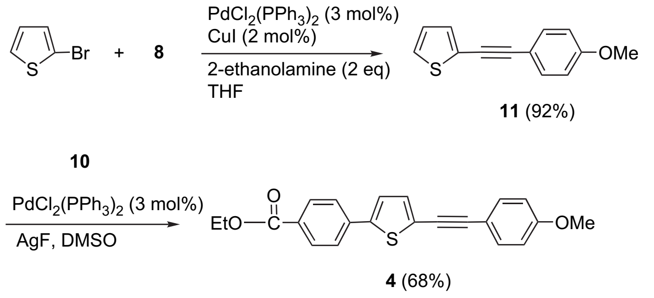


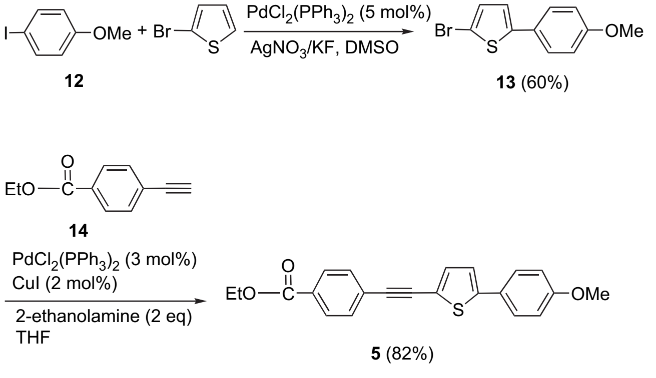
Chart 1.



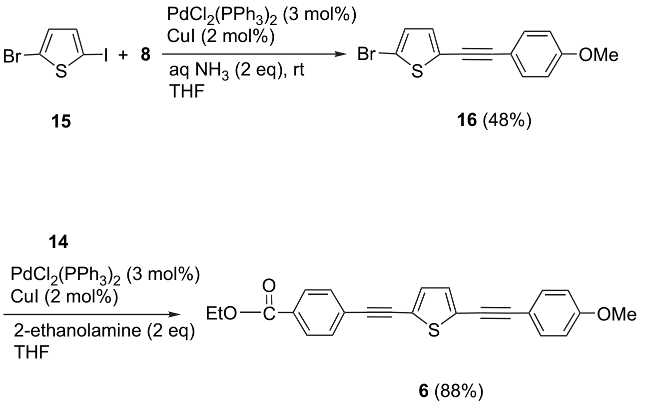
Scheme 1.



Scheme 2.



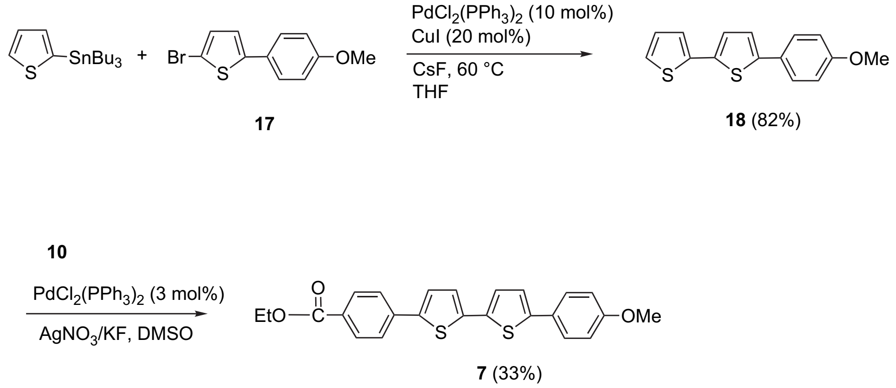
Scheme 3.



Scheme 4.

2-bromothiophene to afford 2-(arylethynyl)thiophene **11** in 92% yield.[8c] Following introduction of the aryl group bearing an electron-withdrawing substituent with **8** was also performed similarly to the manner of the thiazole case[1] to afford **4** in 68% yield.

Synthesis of the thiophene derivative bearing ethynylene spacer between the electron-deficient aryl group and thiophene was performed as shown in Scheme 3. As we reported that CH coupling occurred in the reaction of bromothiophenes



Scheme 5.

with the bromo group intact even in the presence of a palladium catalyst,[2c] synthesis of the 5-aryl-2-bromothiophene was performed by utilizing the CH coupling reaction with aryl iodide. Treatment of 2-bromothiophene with 1-iodo-4-methoxybenzene **12** in the presence of $PdCl_2(PPh_3)_2$ (5 mol %) and KF/$AgNO_3$ as an activator furnished 2-aryl-5-bromothiophene **13** in 60% yield. The reaction of the ethyl 4-ethynylbenzoate **14** with **13** in the presence of a palladium catalyst/CuI using 2-ethanolamine as an activator[8c] afforded **5** in 82% yield.

Preparation of the 2,5-diarylthiophene derivative bearing ethynyl groups at the both positions was carried out as shown in Scheme 4. The reaction of 2-iodo-5-bromothiophene **15** with a terminal alkyne using Sonogashira coupling with aqueous ammonia at room temperature[8a] selectively took place at the carbon–iodine bond to afford **16** in 48% yield. Introduction of the second arylethynyl group was performed with the Sonogashira coupling reaction of **16** with **14** in the presence of aqueous 2-ethanolamine at 60 °C to afford **6** in 88% yield.[8c]

Bithiophene **7** was also synthesized as shown in Scheme 5. Palladium-catalyzed cross-coupling of bromothiophene **17** with thienyl(tributyl)tin was effected to afford **18**.[10] CH substitution reaction of **18** with aryl iodide **10** in the presence of $AgNO_3$/KF afforded **7**.[2c]

For the coupling reactions of a (hetero)aryl bromide with terminal alkynes, for which higher reaction temperature was necessary to proceed, the method using 2-ethanolamine as an additive[8c] was found to be highly effective, while the reaction with aryl iodide at room temperature was carried out with aqueous ammonia.[8a] The reaction with ammonia at room temperature was found to proceed selectively at the carbon–iodine bond of 2-bromo-5-iodo-thiophene **15**.

CH arylation reactions of thiazole and thiophene derivatives were shown to proceed with AgF[1] or $AgNO_3$/KF.[2c] Both protocols were similarly effective for the reaction with aryl halides. Introduction of aryl group by the reaction at the CH bonds of heteroaromatic groups proceeds with a palladium or palladium/copper catalyst system in the presence of an activator. As shown in Scheme 2, the method was found to be effective for the substrate bearing a carbon–carbon triple bond.

2.2. Properties of thiazole and thiophene derivatives bearing ethynylene spacers

Measurements of UV–vis absorption and photoluminescent spectra were carried out and the results were summarized in Table 1. The λ_{max} value of thiazole **3** was slightly red-shifted compared with **1** by the introduction of ethynylene group at the 2-position compared with the corresponding 2,5-diarylthiazole, while the λ_{max} value of **4** was observed at the slightly smaller wavelength than that of **2**.[1] Properties of **5**, which possessed ethynylene spacer into the opposite position, were also found to show similar values. The λ_{max} value of thiophene **6**, which possessed two ethynylene groups at the 2- and 5-positions was observed at 364 nm, which red-shifted ca. 5–10 nm. On the other hand, the λ_{max} value of the corresponding bithiophene derivative was observed at 395 nm suggesting that the introduction of the thiophene ring showed more remarkable than ethynylene. Concerning photoluminescent spectra of thiophene and thiazole derivatives, quantum yields were found to decrease by the introduction of spacers compared with the corresponding 2,5-diarylthiazole **1** (Φ=0.24) and 2,5-diarylthiophene **2** (Φ=0.79).[1]

Table 1. Spectroscopic characteristics of 2,5-diarylthiazole and 2,5-thiophenes bearing ethynylene and thienylene spacers[a]

Compound	UV–vis absorption spectrum		Photoluminescent spectrum	
	λ_{max}, nm	ε	E_m	Φ
3	354	26 500	429	0.20
4	350	24 013	438	0.40
5	358	29 875	445	0.11
6	364	69 565	437	0.03
7	395	31 655	485	0.10
1[b]	347	26 800	424	0.24
2[b]	357	32 200	441	0.79

[a] See Section 4. E_m: wavelength maximum of the photoluminescent spectrum. Φ: quantum yield of the photoluminescence.

[b] Data from Ref. 1 (R^1=OMe, R^2=COOEt).

3. Conclusion

In summary, several thiazole and thiophene derivatives, which possessed ethynylene and thiophene spacers were synthesized and UV–vis absorption and photoluminescent properties were examined. These thiazole and thiophene derivatives, which had not been synthesized previously, were prepared in a facile manner by employing coupling methodologies at the CH bond of heteroaromatic compounds and coupling of terminal alkynes using 2-ethanolamine as an activator that underwent the reaction smoothly and efficiently. Although remarkable spectroscopic characteristics were not observed in these thiazole and thiophene derivatives bearing a spacer molecule, the synthesis demonstrated that coupling methodologies with a transition metal catalyst were highly effective for the synthesis of compounds bearing heteroaromatic and/or alkyne moieties.

4. Experimental

4.1. General

DMSO was distilled from CaH_2 and stored over MS 4A under an argon atmosphere. THF (anhydrous grade) was purchased from Kanto Chemicals Co. Ltd and used without further purification. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on Varian Mercury 300 NMR spectrometer. Infrared spectra were measured with Shimadzu FTIR-8000A. High-resolution mass spectra (EI) were obtained by JEOL MStation. Elemental analyses were carried out at Elemental Analysis Center of Chemical Resources Laboratory, Tokyo Institute of Technology using Yanako MT2 CHN CORDER. UV–vis spectra were measured as a 1×10^{-5} M chloroform solution with JASCO Ubest V-550. Photoluminescent spectra were measured as a 1×10^{-6} M chloroform solution with JASCO FP-6300. Quantum yields (Φ) were estimated with an aqueous solution of quinine sulfate (Φ=0.59) as a reference.

4.1.1. 2-(4-Methoxyphenylethynyl)thiazole (9). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (10.5 mg, 0.015 mmol), CuI (1.7 mg, 0.010 mmol), 2-bromothiazole (82.0 mg, 0.5 mmol), 4-(methoxyphenyl)acetylene (**8**, 79.2 mg, 0.6 mmol), and 3 mL of THF under an argon atmosphere. Then, 2 mL of aqueous 2-ethanolamine solution (0.5 M, 1.0 mmol) was added to the mixture and the Schlenk tube was heated at 60 °C for 5 h. After cooling to room temperature, the solution was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel to afford 82.9 mg of **9** as a colorless oil (77%): ^1H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.90 (d, J=9.0 Hz, 2H), 7.35 (d, J=3.3 Hz, 1H), 7.54 (d, J=9.0 Hz, 2H), 7.84 (d, J=3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.28, 81.24, 94.26, 113.33, 114.14, 120.27, 133.51, 143.38, 149.17, 160.53; IR (KBr) 2837, 2206, 1605, 1514, 1294, 1252, 1175, 1091, 1055, 831 cm^{-1}. HRMS (EIMS) m/z calcd for $C_{12}H_9NOS$; 215.0405, found; 215.0404.

4.1.2. 5-(4-Ethoxycarbonylphenyl)-2-(4-methoxyphenylethynyl)thiazole (3). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (10.5 mg, 0.015 mmol), ethyl 4-iodobenzoate (**10**, 0.101 mL, 0.6 mmol), **9** (107.6 mg, 0.5 mmol), and 3 mL of DMSO under an argon atmosphere. AgF (64 mg, 0.5 mmol) was added to the mixture and the Schlenk tube was heated at 80 °C for 24 h. After cooling to room temperature, the resulting suspension was filtered and the residue was washed with dichloromethane repeatedly. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by chromatography on silica gel to afford 83.4 mg of **3** as a yellow solid (46%): ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, J=7.2 Hz, 3H), 3.84 (s, 3H), 4.39 (q, J=7.2 Hz, 2H), 6.90 (d, J=8.7 Hz, 2H), 7.55 (d, J=8.7 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H), 8.07 (d, J=8.4 Hz, 2H), 8.08 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.28, 55.32, 61.14, 81.50, 95.67, 113.18, 114.21, 126.41, 130.25, 130.41, 133.62, 133.66, 134.97, 140.11, 141.04, 160.70, 165.86; IR (KBr) 2978, 2924, 2581, 2548, 2207, 1703, 1605, 1516, 1275, 1254, 1190, 1106, 1026, 841, 772, 695 cm^{-1}. HRMS (EIMS) m/z calcd for $C_{19}H_{22}OS$; 363.0929, found; 363.0903.

4.1.3. 2-(4-Methoxyphenylethynyl)thiophene (11). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (10.5 mg, 0.015 mmol), CuI (1.7 mg, 0.010 mmol), 2-bromothiophene (0.048 mL, 0.5 mmol), 4-(methoxyphenyl)acetylene (**8**, 79.2 mg, 0.6 mmol), and 3 mL of THF under an argon atmosphere. Then, 2 mL of 2-ethanolamine aqueous solution (0.5 M, 1.0 mmol) was added to the mixture and the Schlenk tube was heated at 60 °C for 5 h. After cooling to room temperature, the solution was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel to afford 98.6 mg of **11** as a colorless oil (92%): ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.87 (d, J=9.0 Hz, 2H), 7.00 (dd, J=2.7 Hz, 1H), 7.25 (m, 2H), 7.45 (d, J=9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.09, 81.22, 93.01, 113.93, 114.81, 123.57, 126.73, 126.96, 131.34, 132.80, 159.63; IR (KBr) 3102, 3073, 2963, 2842, 1603, 1524, 1501, 1460, 1289, 1246, 1186, 1175, 1109, 1021, 853, 700 cm^{-1}. HRMS (EIMS) m/z calcd for $C_{13}H_{10}OS$; 214.0452, found; 214.0427.

4.1.4. 5-(4-Ethoxycarbonylphenyl)-2-(4-methoxyphenylethynyl)thiophene (4). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (17.5 mg, 0.025 mmol), ethyl 4-iodobenzoate (**10**, 0.100 mL, 0.6 mmol), **11** (107.0 mg, 0.5 mmol), and 3 mL of DMSO under an argon atmosphere. AgF (64 mg, 0.5 mmol) was added to the mixture and the Schlenk tube was heated at 100 °C for 5 h. After cooling to room temperature, the resulting suspension was filtered and the residue was washed with dichloromethane repeatedly. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by chromatography on silica gel to afford 123.1 mg of **4** as a yellow solid (68%): ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, J=8.4 Hz, 3H), 3.84 (s, 3H), 4.39 (q, J=8.4 Hz, 2H), 6.89 (d, J=8.7 Hz, 2H), 7.23 (d, J=3.6 Hz, 1H), 7.31 (d, J=3.6 Hz, 1H), 7.47 (d, J=8.7 Hz, 2H), 7.64 (d, J=8.4 Hz, 2H), 8.05 (d, J=8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 14.33, 55.31, 61.02, 81.27, 94.65, 114.10, 114.77, 124.39, 125.36, 129.46, 130.28, 132.63, 132.97, 137.87, 143.78, 159.92, 166.14; IR (KBr) 2988, 2940, 2842, 1713, 1603, 1514, 1291, 1275, 1248, 1186, 1109, 1028, 851, 837, 808, 768 cm^{-1}. HRMS (EIMS) *m/z* calcd for $C_{22}H_{18}O_3S$; 363.0929, found; 363.0903.

Synthesis of *2-bromo-5-(4-methoxyphenyl)thiophene (13)* was carried out in a similar manner to that we described previously. Spectroscopic characteristics and physical properties of **13**[2c] were identical with those of the authentic sample.

4.1.5. 2-(4-Ethoxycarbonylphenylethynyl)-5-(4-methoxyphenyl)thiophene (5). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (10.5 mg, 0.015 mmol), CuI (1.7 mg, 0.010 mmol), **13** (134.6 mg, 0.5 mmol), 4-(ethoxycarbonylphenyl)acetylene (**14**, 104.5 mg, 0.6 mmol), and 3 mL of THF under an argon atmosphere. Then, 2 mL of 2-ethanolamine aqueous solution (0.5 M, 1.0 mmol) was added to the mixture and the Schlenk tube was heated at 60 °C for 5 h. After cooling to room temperature, the solution was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel to afford 147.2 mg of **5** (82%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (t, *J*=7.2 Hz, 3H), 3.84 (s, 3H), 4.39 (q, *J*=7.2 Hz, 2H), 6.93 (d, *J*=9.0 Hz, 2H), 7.11 (d, *J*=3.9 Hz, 1H), 7.26 (d, *J*=3.9 Hz, 1H), 7.53 (d, *J*=9.0 Hz, 2H), 7.55 (d, *J*=9.0 Hz, 2H), 8.03 (d, *J*=9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.26, 55.29, 61.07, 86.05, 92.90, 114.36, 120.59, 122.08, 126.37, 127.15, 127.55, 129.44, 131.01, 132.35, 133.70, 146.70, 159.68, 165.96; IR (KBr) 2965, 2936, 2840, 1723, 1605, 1514, 1497, 1306, 1291, 1252, 1181, 1105, 1028, 801, 764 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_3S$: C, 72.90; H, 5.01; S, 8.85. Found: C, 72.72; H, 4.85; S, 8.70.

4.1.6. 2-Bromo-5-(4-methoxyphenylethynyl)thiophene (16). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (10.5 mg, 0.015 mmol), CuI (1.7 mg, 0.010 mmol), 2-bromo-5-iodothiophene (**15**, 173.4 mg, 0.6 mmol), **8** (66.1 mg, 0.5 mmol), and 3 mL of THF under an argon atmosphere. Then, 2 mL of aqueous ammonia (0.5 M, 1.0 mmol) was added to the mixture and stirred at room temperature for 5 h. The solution was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel to afford 70.4 mg of **16**. The product **16**, whose yield was estimated to be 48% by ^{1}H NMR analysis, contained a trace amount of impurity, which was hardly eliminated by column chromatography on silica gel. Thus, the mixture was conducted to the following reaction without further purification.

4.1.7. 5-(4-Ethoxycarbonylphenylethynyl)-2-(4-methoxyphenylethynyl)thiophene (6). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (10.5 mg, 0.015 mmol), CuI (1.7 mg, 0.010 mmol), **16** (146.6 mg, 0.5 mmol), **12** (104.5 mg, 0.6 mmol), and 3 mL of THF under an argon atmosphere. Then, 2 mL of 2-ethanolamine aqueous solution (0.5 M, 1.0 mmol) was added to the mixture and the Schlenk tube was heated at 60 °C for 5 h. After cooling to room temperature, the solution was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel to afford 70.4 mg of **6** as a yellow solid (88%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, *J*=7.2 Hz, 3H), 3.84 (s, 3H), 4.39 (q, *J*=7.2 Hz, 2H), 6.89 (d, *J*=8.7 Hz, 2H), 7.13 (d, *J*=3.9 Hz, 1H), 7.19 (d, *J*=3.9 Hz, 1H), 7.46 (d, *J*=8.7 Hz, 2H), 7.57 (d, *J*=8.4 Hz, 2H), 8.03 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.25, 55.22, 61.11, 80.85, 85.22, 93.13, 94.58, 114.03, 114.40, 123.28, 125.86, 127.10, 129.43, 131.15, 131.34, 132.25, 132.34, 132.44, 132.99, 159.93, 165.88; IR (KBr) 2979, 2842, 2197, 1715, 1605, 1528, 1512, 1308, 1287, 1281, 1173, 1107, 1028, 831, 768 cm^{-1}. HRMS (EIMS) *m/z* calcd for $C_{24}H_{18}O_3S$; 386.0977, found; 386.0988.

4.1.8. 2-(4-Methoxyphenyl)-5,5′-bithiophene (18).[2c] To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added **17** (0.135 g, 0.5 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), CuI (0.019 g, 0.10 mmol), and DMF (3 mL) under an argon atmosphere. To the mixture was added tributyl(2-thienyl)stannane (0.190 mL, 0.6 mmol) dropwise. CsF (0.151 g, 1.0 mmol) was then added in one portion. The resulting mixture was heated at 60 °C and stirring was continued for 8 h. After cooling to room temperature, the mixture was poured into 20 mL of water. The aqueous was extracted with chloroform twice (20 mL×2) and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel using hexanes–ethyl acetate (5:1) as an eluent to afford 0.111 g of 5-(4-methoxyphenyl)-2,2′-bithiophene (**18**) in 82% yield: ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3H), 6.91 (d, *J*=9.0 Hz, 2H), 7.02 (dd, *J*=4.8, 3.6 Hz, 1H), 7.12 (AB, 2H), 7.17–7.22 (m, 2H), 7.53 (d, *J*=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 57.70, 114.35, 122.64, 123.37, 124.11, 124.56, 126.92, 127.80, 135.69, 137.58, 143.14, 147.96, 159.31; IR (KBr) 3070, 2960, 2910, 2845, 1605, 1497, 1289, 1246, 1183, 1032, 797.

4.1.9. 2-(4-Ethoxycarbonylphenyl)-2′-(4-methoxyphenyl)-5,5′-bithiophene (7). To a 25-mL of Schlenk tube equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_3$ (17.5 mg, 0.025 mmol), **10** (0.100 mL, 0.6 mmol), **18** (136.2 mg, 0.5 mmol), potassium fluoride (72.6 mg, 1.25 mmol), and 5 mL of DMSO under an argon atmosphere. The mixture was heated in an oil bath at 100 °C for 8 h, during which period $AgNO_3$ (168.9 mg, 1.0 mmol) was added in 4 portions with a 2 h interval. After cooling to room temperature, the resulting suspension was filtered and the residue was washed with dichloromethane repeatedly. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by chromatography on silica gel to afford 40.9 mg of **7** as a yellow solid (33%): ^{1}H NMR ($CDCl_3$) δ 1.41 (t, *J*=7.2 Hz, 3H), 3.85 (s, 3H), 4.39 (q, *J*=7.2 Hz, 2H), 6.93 (d, *J*=8.7 Hz, 2H), 7.13 (d, *J*=3.9 Hz, 1H), 7.18

(d, J=3.3 Hz, 2H), 7.35 (d, J=3.6 Hz, 1H), 7.54 (d, J=8.7 Hz, 2H), 7.65 (d, J=8.7 Hz, 2H), 8.05 (d, J=8.7 Hz, 2H); IR (KBr) 2910, 2890, 1709, 1605, 1283, 1184, 1111, 1030, 830, 795, 770. HRMS (EIMS) m/z calcd for $C_{24}H_{20}O_3S_2$; 420.0854, found; 420.0833.

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