Preparation of 4,7-Dibromobenzo[*b*]thiophene as a Versatile Building Block and Synthetic Application to a Bis(ethynylthienyl)oligoarene System

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Benzo[*b*]thiophene, 4,7-dibromobenzo[*b*]thiophene, thieno[3,2-*b*]thiophene, and 3-bromothieno[3,2-*b*]thiophene were prepared by AuCl-catalyzed cyclization of (*t*-butylsulfanyl)(ethynyl)benzenes or (*t*-butylsulfanyl)(ethynyl)thiophenes. Several reactions of 4,7-dibromobenzo[*b*]thiophene were investigated, including metallation and cross coupling reactions.

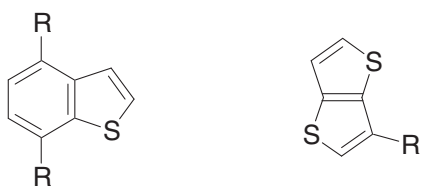
Ring-fused thiophenes, such as benzo[*b*]thiophenes and thieno[3,2-*b*]thiophenes, have attracted much interest in the fields of physical organic chemistry, materials science, and synthetic organic chemistry.[1] Brominated benzo[*b*]thiophenes and thieno[3,2-*b*]thiophenes are often used for introduction of substituents and functional groups to the fused rings. Consequently, preparations of various bromobenzo[*b*]thiophenes[2] and bromothieno[3,2-*b*]thiophenes[3] have been reported. However, direct and selective introduction of bromine atom to the 4- and 7-positions of benzo[*b*]thiophene is difficult: Electrophilic substitution reactions of parent benzo[*b*]thiophene proceed normally at the 3-, 5-, or 6-positions. In fact, 4,7-dibromobenzo[*b*]thiophene (**1a**, Chart 1), without substituents at the other positions, remained unexplored. Nevertheless, development of a new synthetic method for ring-fused thiophenes may find a route to the missing bromobenzothiophene derivatives: We report here a preparation and reactions of hitherto unknown compound **1a**. Preparations of parent benzo[*b*]thiophene (**1b**) and thieno[3,2-*b*]thiophene derivatives **2a** and **2b** as well as some oligoarenes containing the ring-fused thiophene moieties are also described.

Results and Discussion

In a synthetic plan of **1a**, bromine atoms should be introduced before construction of the benzothiophene skeleton, because the straightforward bromination of parent benzo[*b*]-thiophene (**1b**) at the 4- and/or 7-positions is difficult as mentioned above. Among some possible routes to benzo[*b*]-thiophenes,[4] a cyclization of ethynyl(sulfanyl)benzene derivative seemed to be promising. Nakamura and co-workers reported Au-catalyzed cyclization of **3** (Scheme 1, $R^2 \neq H$).[4a,4b] In this reaction, a substituent R^2 on the sulfur atom rearranges to the 3-position of the cyclized product to give **4**. However, if we use a *t*-butylsulfanyl group as a substituent, the *t*-butyl group may be removed by appropriate reagent under acidic conditions, before or after cyclization. Based on this plan, preparation of parent **1b** was investigated as follows. 2-*t*-Butylsulfanylbenzaldehyde (**6b**)[5] was prepared by the reaction of 2-bromobenzaldehyde (**5b**) with *t*-BuSNa (Scheme 2). Reaction of **6b** with dimethyl 1-diazo-2-oxo-2-phenylethylphosphonate (**7**)[6] gave 2-(*t*-butylsulfanyl)(ethynyl)benzene (**8b**). When **8b** was treated with AuCl in 1,4-dioxane and water (6:1) for 10 min, **1b** was obtained in 56% yield.

For preparation of the desired congener **1a**, we chose commercially available 3,6-dibromo-2-fluorobenzaldehyde (**5a**) as a starting material. Reaction of **5a** with *t*-BuSNa gave **6a**, which was converted to **8a**, by reaction with **7**. Treatment of **8a** with AuCl in 1,4-dioxane and water afforded **1a** in 97% yield.

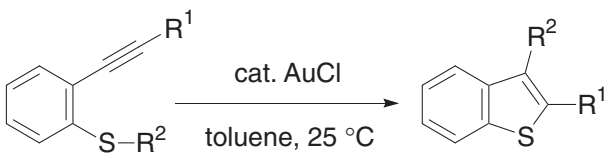
3-Bromothieno[3,2-*b*]thiophene (**2a**)[3a] was also prepared (Scheme 3) by the (*t*-butylsulfanyl)(ethynyl)arene/AuCl method as follows. A reaction of 3,4-dibromothiophene-2-carbaldehyde (**9a**) with *t*-BuSNa formed **10a**, which was converted to **11a** by reaction with **7**. When **11a** was treated with



1a: R=Br
b: R=H

2a: R=Br
b: R=H

Chart 1.



3 **4**

Scheme 1. AuCl-catalyzed synthesis of benzo[*b*]thiophenes.[4a,4b]

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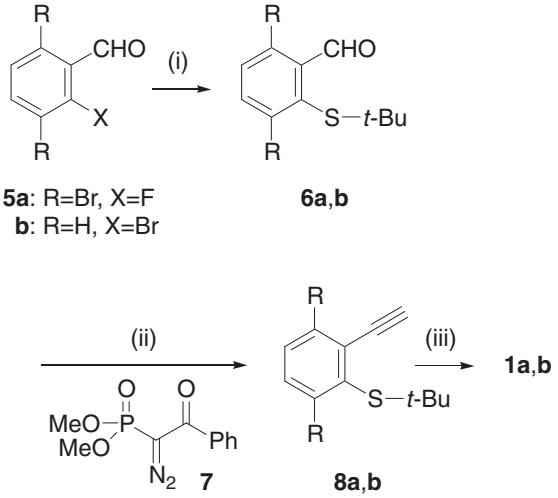
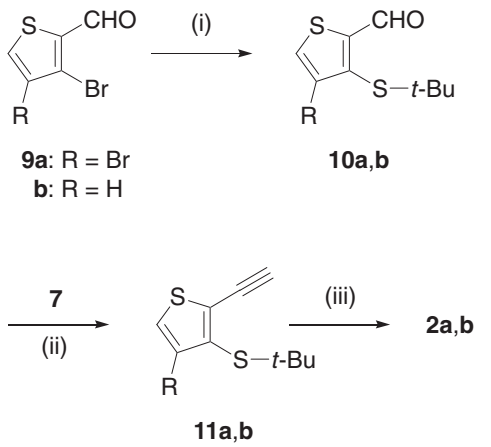


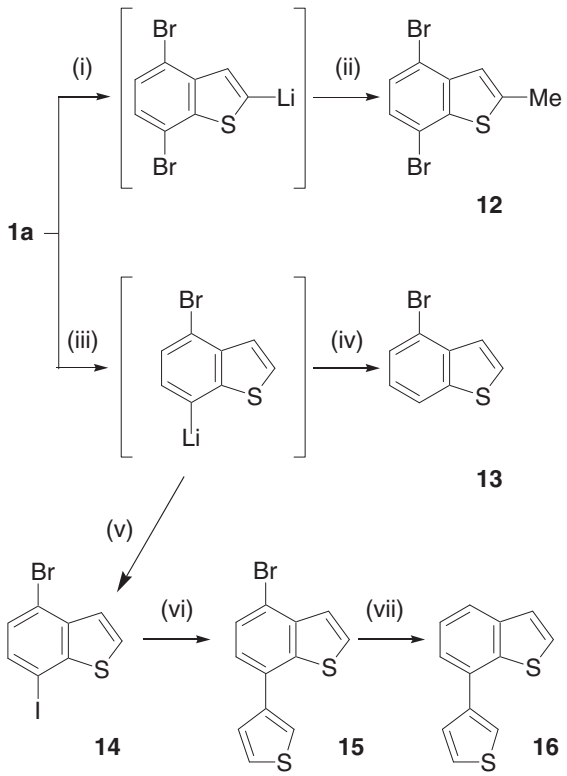
Scheme 2. Reagents and conditions: (i) *t*-BuSNa, *N*,*N*-dimethylformamide (DMF), −30 °C, 7 h; (ii) K_2CO_3, MeOH, 0 °C to r.t.; (iii) AuCl (5 mol %), 1,4-dioxane, H_2O, r.t., 10 min.



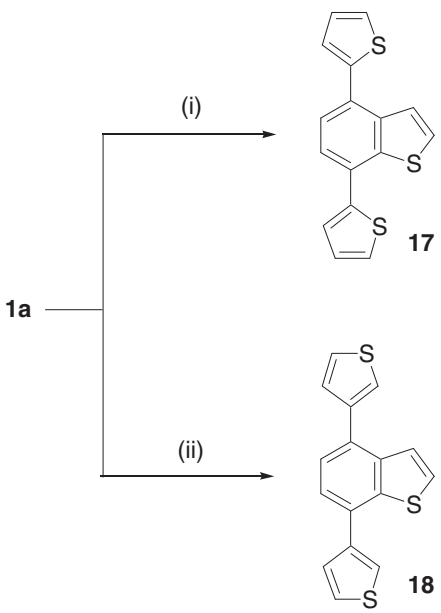
Scheme 3. Reagents and conditions: (i) *t*-BuSNa, DMF, −30 °C, 4 h (for **10a**) or r.t., 12 h (for **10b**); (ii) K_2CO_3, MeOH, 0 °C to r.t., 12 h; (iii) AuCl (2–8 mol %), 1,4-dioxane, H_2O, r.t., 3 h.

AuCl in 1,4-dioxane and water, **2a** was obtained in 88% yield. Similarly, parent thieno[3,2-*b*]thiophene (**2b**) was prepared, from 3-bromothiophene-2-carbaldehyde (**9b**), via **10b** and **11b**. It should be mentioned that conventional preparative routes to **2a**[3b] and **2b**[3c] include high-temperature decarboxylation (Cu/quinoline/260 °C). Thus, the present Au-catalyzed method has several advantages from viewpoints of the numbers of reaction steps, yield, and reaction temperature.

As we could obtain a novel dibromobenzo[*b*]thiophene **1a**, we then investigated reactions of **1a** (Schemes 4 and 5). In the first place, metallation reactions of **1a** (Scheme 4) were investigated and reactivities at the 2-, 4-, and 7-positions were evaluated: Lithiation of **1a** with 1 molar equivalent of lithium *N*,*N*-diisopropylamide (LDA) occurred at the 2-position of **1a**. When the reaction mixture was quenched with iodomethane, 4,7-dibromo-2-methylbenzo[*b*]thiophene (**12**) was obtained in 74% yield. On the other hand, a reaction of **1a** with butyllithium (1 molar equivalent) followed by treatment with MeOH



Scheme 4. Reagents and conditions: (i) LDA, THF, −78 °C, then 0 °C, 30 min; (ii) MeI, −78 °C, then r.t., 15 h; (iii) *n*-BuLi, THF, −78 °C, 30 min; (iv) MeOH, −78 °C; (v) 1,2-diiodoethane, Et_2O, −78 °C, then r.t., 2 h; (vi) 3-thienylboronic acid, $[Pd(PPh_3)_4]$, K_2CO_3, THF, H_2O, 45 °C, 12 h; (vii) *n*-BuLi, THF, Et_2O, −78 °C, 30 min, then aq. NH_4Cl.



Scheme 5. Reagents and conditions: (i) 2-(2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 molar equivalents), $[Pd(PPh_3)_4]$, K_2CO_3, 1,4-dioxane, H_2O, 80 °C, 16 h; (ii) 3-thienylboronic acid (2.4 molar equivalents), $[Pd(PPh_3)_4]$, K_2CO_3, 1,4-dioxane, H_2O, 80 °C, 15 h.

gave **13**,[2c] via lithium–bromine exchange. When the metallation reaction was quenched by 1,2-diiodoethane, 4-bromo-7-iodo derivative **14** was obtained in 83% yield. These results show that the metallations at the 2-, 4-, and 7-positions are well controlled by choosing the lithium reagent. This selectivity helps sophisticated constructions of oligoarenes containing the benzo[*b*]thiophene-4,7-diyl moiety (see below).

In the second place, cross coupling reactions of above compounds were investigated (Schemes 4 and 5). Suzuki–Miyaura coupling of **14** with 3-thienylboronic acid afforded **15**, which was converted to **16** (Scheme 4). The spectral data of **16** obtained in this experiment matched with the reported data of **16**,[7] confirming the structures of **14** and **15**. Similarly, Suzuki–Miyaura coupling of **1a** with 2-(2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 molar equivalents) or 3-thienylboronic acid (2.4 molar equivalents) afforded **17** or **18** in 80 and 94% yield, respectively (Scheme 5). It should be mentioned that formation of **17** has been supposed in the literature of Curtis and co-workers[8] in the dehydrogenation reaction of 4,7-di(2-thienyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene with tetrachloro-*p*-benzoquinone. However, the structure could not be experimentally determined, because an attempted alternative synthesis was unsuccessful by their hands. Comparison of the physical data of **17** supported the assignment of Curtis et al. and the problem was solved.

Based on the results described above, applications of compounds **1a** and **2a** to preparations of peptide-inspired bis(2-ethynyl-3-thienyl)oligoarenes[9] **19a**, **19b**, and **20** (Chart 2) were planned in the third place (Schemes 6–9). Preparations of the terminal units of **19** and **20** are shown in Scheme 6: boronates **25** and **26** were prepared from **21**[9d] via **22**–**24**. Preparation of oligoarene **19a** with three side chains [one methyl and two (triisopropylsilyl)ethynyl groups] was carried out by a cross coupling of **12** with 2.3 molar equivalents of **25** to give **19a** in 58% yield (Scheme 7).

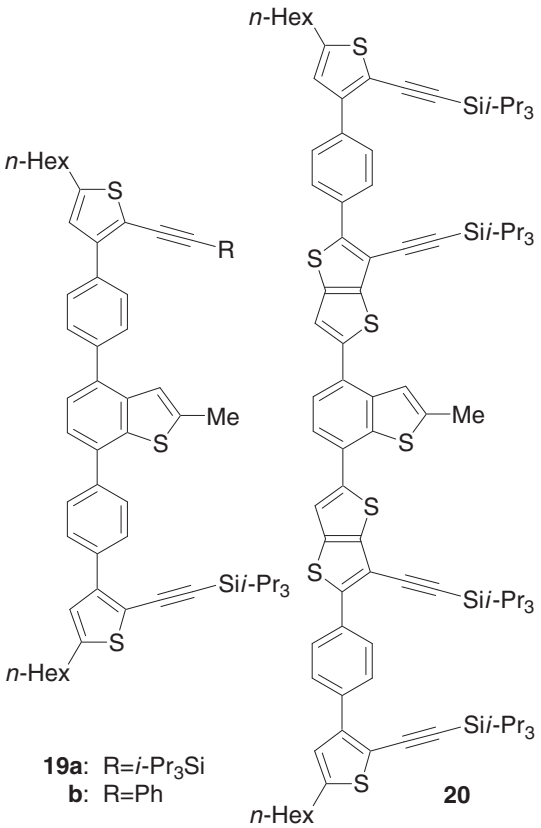
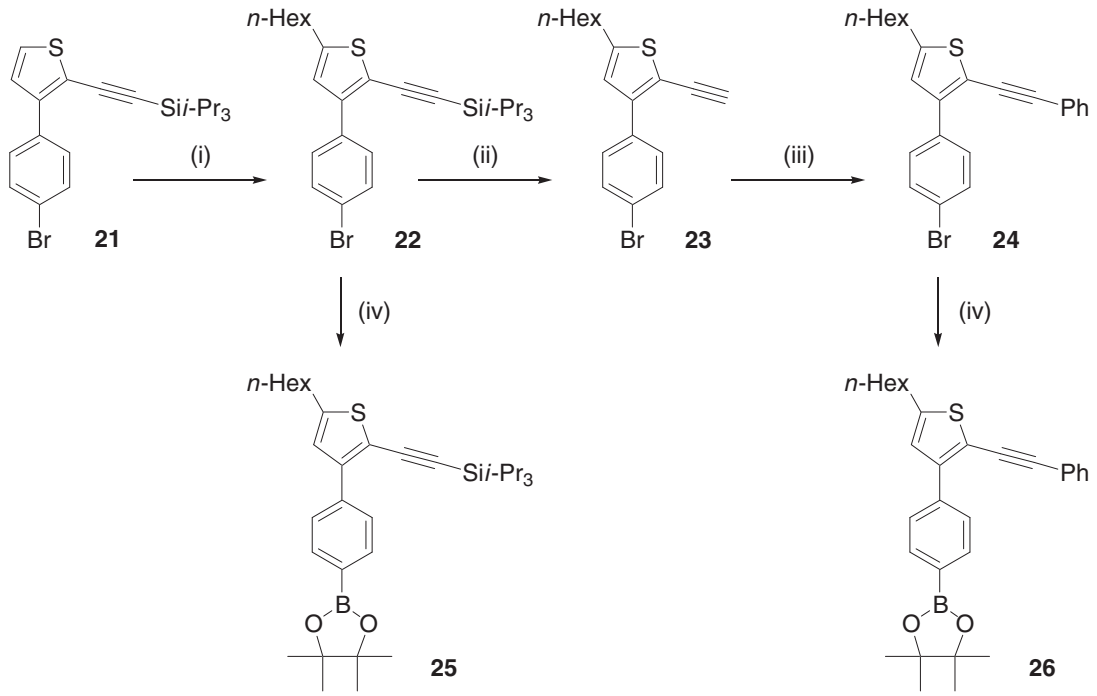
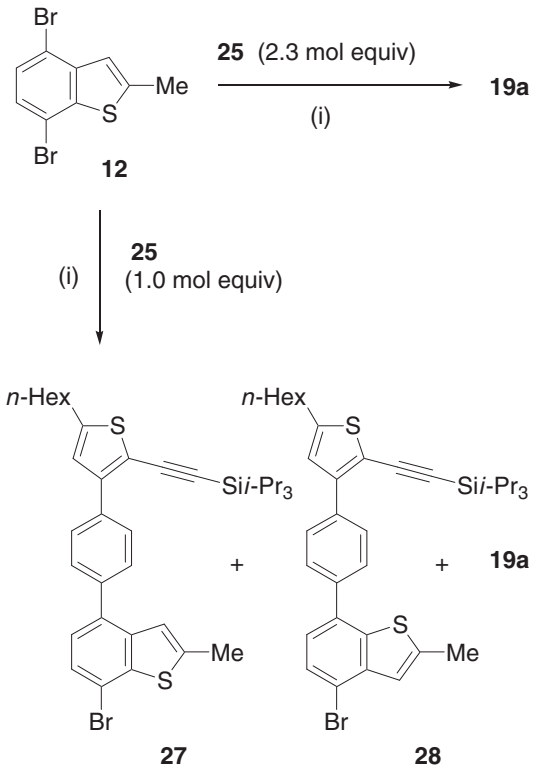


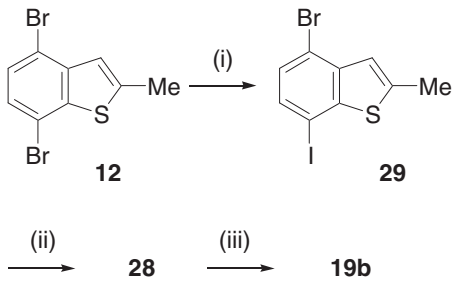
Chart 2.



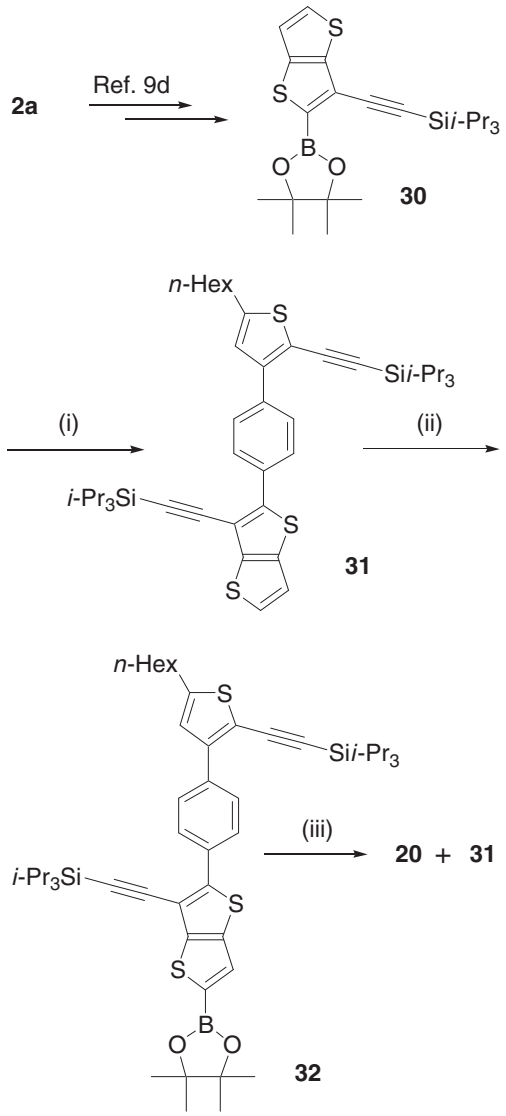
Scheme 6. Reagents and conditions: (i) LDA, THF, −78 °C, 70 min, then 1-iodohexane, −78 °C, then 50 °C, 3 h; (ii) tetrabutylammonium fluoride, THF, r.t., 70 min; (iii) iodobenzene, $[PdCl_2(PPh_3)_2]$, CuI, *N*,*N*-diisopropylamine, THF, 50 °C, 15 h; (iv) *n*-BuLi, THF, −78 °C then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C, then r.t.



Scheme 7. Reagents and conditions: (i) $[Pd(PPh_3)_4]$, K_2CO_3, 1,4-dioxane, H_2O, 90 °C, 13 h.



Scheme 8. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 30 min, then 1,2-diiodoethane, −78 °C, then r.t., 2 h; (ii) **25** (1.0 molar equivalent), $[Pd(PPh_3)_4]$, K_2CO_3, 1,4-dioxane, H_2O, 80 °C, 46 h; (iii) **26** (1.0 molar equivalent), $[Pd(PPh_3)_4]$, K_2CO_3, 1,4-dioxane, H_2O, 90 °C, 13 h.



Scheme 9. Reagents and conditions: (i) **22**, $[Pd(PPh_3)_4]$, K_2CO_3, THF, toluene, H_2O, 80 °C, 14 h; (ii) *n*-BuLi, THF, −78 °C, 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C, then r.t., 3 h; (iii) **29** (0.35 molar equivalent), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, $Pd(OAc)_2$, K_2CO_3, THF, 50 °C, 2 d.

It should be mentioned that a reaction of **12** with 1 molar equivalent of **25** under similar conditions was not regioselective: The reaction gave a mixture of **27** and **28** (ca. 1:0.4 ratio) as well as **19a**. An attempted separation of **27** and **28** by column chromatography was unsuccessful. However, when the mixture of **27** and **28** was subjected to a further cross coupling reaction with **25**, compound **19a** was obtained in 66% yield.

Confirmation of the structure of **28** and preparation of **19b** was carried out as follows (Scheme 8). Compound **12** was converted to **29**, which was then reacted with **25** under the cross coupling conditions to give an authentic **28** in 80% yield. A cross coupling of **28** with **26** afforded **19b**, which contains three different side chains [i.e., phenylethynyl, methyl, and (triisopropylsilyl)ethynyl side chains] with a *controlled sequence* (89% yield).

Thus, for the purpose of preparation of peptide-inspired systems,[9,10] utilization of the 4-bromo-7-iodobenzo[*b*]thiophene derivatives is a promising method. Sequences of side chains are regarded as important in such systems.

For further elongation of the (pseudo)axes of the oligoarenes, the benzothiophene spacer and the thienothiophene spacer were combined as follows (Scheme 9). Compound **2a** was converted to (triisopropylsilyl)ethynyl-substituted compound **30**.[9d] Suzuki–Miyaura cross coupling of **30** with **22** afforded **31** in 84% yield. The thienothiophene moiety of **31** was again converted to a dioxaborolane derivative **32** (97% yield) and subjected to Suzuki coupling with **29** (0.35 molar equivalent) to give the extended compound **20** along with the

thienothiophene **31**. Although the yield of **20** in this step is low (5% yield after repetitive purification), the major product **31** (65% yield) can be reused as a starting material of the reaction described above.

In summary, we prepared parent benzo[*b*]thiophene, 4,7-dibromobenzo[*b*]thiophene, parent thieno[3,2-*b*]thiophene, and 3-bromothieno[3,2-*b*]thiophene. Several oligoarenes such as **19a** were prepared from 4,7-dibromobenzo[*b*]thiophene (**1a**). 4-Bromo-7-iodobenzo[*b*]thiophene (**29**) was also prepared and utilized to construct oligoarene **20**. A sequence of three different side chains was controlled, in the preparation of **19b**, by utilization of **29**. Thus, 4-bromo-7-halogenobenzo[*b*]thiophenes as well as 3-bromothieno[3,2-*b*]thiophene are promising starting materials for construction of sophisticated oligoarene systems.

Experimental

Apparatus. Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and are not corrected. NMR spectra were recorded on a Bruker Avance-400 or a JEOL ECA-600 spectrometer. UV spectra were measured on a JASCO V-660 spectrometer. IR spectra were obtained on a Shimadzu FTIR-8100M spectrometer or a JASCO FT/IR-4100 spectrometer. MS (EI, 70 eV) spectra were taken on a Hitachi M-2500S spectrometer. FT-ICR-MS (ESI) spectra were measured on a Bruker APEX III spectrometer. Elemental analyses were performed at Analytical Research Center for Giant Molecules, Graduate School of Science, Tohoku University.

3,6-Dibromo-2-(*t*-butylsulfanyl)benzaldehyde (6a). To a solution of NaH (187 mg, 7.80 mmol) in *N*,*N*-dimethylformamide (DMF, 3.6 mL) was added *t*-BuSH (0.88 mL, 7.8 mmol) in DMF (3.0 mL) at 0 °C over 15 min under N_2. The reaction mixture was stirred at 0 °C for 30 min, and then 3,6-dibromo-2-fluorobenzaldehyde (**5a**, 2.00 g, 7.09 mmol) in DMF (1.0 mL) was added at −30 °C. The reaction mixture was stirred at −30 °C for 7 h. Upon completion, the mixture was poured into saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 2.33 g (6.65 mmol, 94% yield) of **6a**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (9H, s, *t*-Bu), 7.55 (1H, d, $^3J = 8.6$ Hz, phenyl), 7.71 (1H, d, $^3J = 8.6$ Hz, phenyl), and 10.4 (1H, s, CHO); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.4 (Me), 52.4 (*C*Me$_3$), 119.6, 134.4, 136.1, 136.6, 137.3, 143.3, and 192.1 (CHO); IR (neat): 3101, 2977, 2872, 1696, 1545, 1472, 1460, 1418, 1395, 1366, 1335, 1250, 1202, 1157, 1121, 1069, 968, 835, 762, and 743 cm^{-1}. HRMS (ESI): Found: *m*/*z* 372.8869. Calcd for $C_{11}H_{12}Br_2NaOS$: $(M + Na)^+$, 372.8868.

3,6-Dibromo-2-(*t*-butylsulfanyl)(ethynyl)benzene (8a). To a mixture of dimethyl 1-diazo-2-oxo-2-phenylethylphosphonate (**7**) (270 mg, 1.06 mmol) and K_2CO_3 (367 mg, 2.66 mmol) in MeOH (6.5 mL) was added a solution of **6a** (312 mg, 0.886 mmol) in MeOH (3.0 mL) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 2 h. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 217 mg (0.623 mmol, 70% yield) of **8a**: Colorless crystals, mp 56–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (9H, s, *t*-Bu), 3.66 (1H, s, C≡CH), 7.45 (1H, d, $^3J = 8.7$ Hz, phenyl), and 7.54 (1H, d, $^3J = 8.7$ Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.8 (Me), 52.9 (*C*Me$_3$), 82.5 (C≡C), 87.1 (C≡C), 126.0, 133.4, 133.7, 133.8, 133.9, and 138.8; IR (KBr): 3250 (C≡CH), 2957, 2106 (C≡C), 1470, 1456, 1414, 1366, 1348, 1161, 1117, 1073, 824, 774, and 737 cm^{-1}. HRMS (EI): Found: *m*/*z* 345.9026. Calcd for $C_{12}H_{12}Br_2S$: 345.9026. Anal. Found: C, 41.32; H, 3.55%. Calcd for $C_{12}H_{12}Br_2S$: C, 41.40; H, 3.47%.

2-(*t*-Butylsulfanyl)(ethynyl)benzene (8b). To a mixture of **7** (737 mg, 2.90 mmol) and K_2CO_3 (983 mg, 7.11 mmol) in MeOH (6.5 mL) was added a solution of **6b**[5] (461 mg, 2.37 mmol) in MeOH (3.0 mL) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 1 h. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and separated by silica gel column chromatography to give 324 mg (1.70 mmol, 72% yield) of **8b**: Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (9H, s, *t*-Bu), 3.30 (1H, s, C≡CH), 7.30–7.33 (2H, m, phenyl), and 7.58–7.61 (2H, m, phenyl). This compound was used in succeeding reactions without further purification.

4,7-Dibromobenzo[*b*]thiophene (1a). To a solution of compound **8a** (50.4 mg, 0.145 mmol) in 1,4-dioxane (0.5 mL) and water (0.1 mL) was added AuCl (1.7 mg, 0.0072 mmol) in 1,4-dioxane (0.1 mL) under N_2. The reaction mixture was stirred at room temperature for 10 min. Upon completion, the solvent was removed and the residue was purified by silica gel column chromatography to give 41.0 mg (0.140 mmol, 97% yield) of **1a**: Colorless needles, mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (1H, d, $^3J = 8.0$ Hz), 7.41 (1H, d, $^3J = 8.0$ Hz), 7.55 (1H, d, $^3J = 5.6$ Hz), and 7.57 (1H, d, $^3J = 5.6$ Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 114.9, 116.4, 125.4, 127.9, 128.2, 128.6, 140.0, and 142.2; IR (KBr): 3083, 1487, 1437, 1354, 1314, 1302, 1182, 1111, 1094, 1069, 905, 831, 806, and 754 cm^{-1}. HRMS (EI): Found: *m*/*z* 289.8399. Calcd for $C_8H_4Br_2S$: 289.8400. Anal. Found: C, 33.10; H, 1.53%. Calcd for $C_8H_4Br_2S$: C, 32.91; H, 1.38%.

Benzo[*b*]thiophene (1b). To a solution of **8b** (27.6 mg, 0.145 mmol) in 1,4-dioxane (0.5 mL) and water (0.1 mL) was added AuCl (1.7 mg, 0.0073 mmol) in 1,4-dioxane (0.1 mL) under N_2. The reaction mixture was stirred at room temperature for 10 min. Upon completion, the solvent was removed and the residue was purified by silica gel column chromatography to give 10.8 mg (0.0805 mmol, 56% yield) of **1b**.

4-Bromo-3-(*t*-butylsulfanyl)thiophene-2-carbaldehyde (10a). To a solution of NaH (17.8 mg, 0.741 mmol) in THF (1.0 mL) was added *t*-BuSH (0.084 mL, 0.74 mmol) in DMF (1.0 mL) at 0 °C under N_2. The resulting mixture was stirred at 0 °C for 5 min, and then **9a** (100 g, 0.370 mmol) in DMF (1.0 mL) was added at −30 °C. The reaction mixture was stirred for 4 h at −30 °C, and then allowed to warm to room temperature and stirred for 12 h. Upon completion, the mixture was poured into saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine and dried over

$MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 80.0 mg (0.287 mmol, 78% yield) of **10a**: Yellow crystals, mp 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (9H, s, *t*-Bu), 7.78 (1H, d, $^5J = 1.2$ Hz, 5-thienyl), and 10.1 (1H, d, $^5J = 1.2$ Hz, CHO); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.2 (C*Me*$_3$), 50.5 (*C*Me$_3$), 122.2, 131.2, 139.8, 147.5, and 185.3 (CHO); IR (KBr): 3106, 2975, 2957, 2865, 2847, 1653, 1472, 1458, 1399, 1362, 1335, 1308, 1208, 1163, 1138, 932, 860, 799, 758, and 671 cm^{-1}. HRMS (EI): Found: *m*/*z* 277.9433. Calcd for $C_9H_{11}BrOS_2$: 277.9435. Anal. Found: C, 38.77; H, 4.03%. Calcd for $C_9H_{11}BrOS_2$: C, 38.71; H, 3.97%.

3-(*t*-Butylsulfanyl)thiophene-2-carbaldehyde (10b). To a solution of NaH (252 mg, 10.5 mmol) in DMF (9.0 mL) was added *t*-BuSH (1.2 mL, 11 mmol) in DMF (3.0 mL) at 0 °C under N_2. The resulting mixture was stirred at 0 °C for 15 min, and then **9b** (1.00 g, 5.23 mmol) in DMF (3 mL) was added at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. Upon completion, the mixture was poured into saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 686 mg (3.43 mmol, 66% yield) of **10b**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (9H, s, *t*-Bu), 7.19 (1H, d, $^3J = 5.0$ Hz, 4-thienyl), 7.73 (1H, dd, $J = 5.0$ and 1.2 Hz, 5-thienyl), and 10.2 (1H, d, $^5J = 1.2$ Hz, CHO); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.0 (C*Me*$_3$), 47.8 (*C*Me$_3$), 133.0, 136.3, 139.3, 145.8, and 184.7 (CHO); IR (neat): 2965, 1665, 1456, 1412, 1364, 1339, 1215, 1167, 1156, 911, 826, 745, 687, 666, and 648 cm^{-1}. HRMS (ESI): Found: *m*/*z* 223.0221. Calcd for $C_9H_{12}NaOS_2$: $(M + Na)^+$, 223.0222.

4-Bromo-3-(*t*-butylsulfanyl)-2-ethynylthiophene (11a). To a mixture of **10a** (138 mg, 0.493 mmol) and K_2CO_3 (205 mg, 1.48 mmol) in MeOH (3.0 mL) was added a solution of **7** (251 mg, 0.986 mmol) in MeOH (2.0 mL) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 77.9 mg (0.283 mmol, 57% yield) of **11a**: Yellow crystals, mp 47–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (9H, s, *t*-Bu), 3.55 (1H, s, C≡CH), and 7.28 (1H, s, 5-thienyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.5 (C*Me*$_3$), 51.7 (*C*Me$_3$), 76.7 (C≡C), 85.4 (C≡C), 120.0, 123.8, 129.5, and 135.8; IR (KBr): 3306 (C≡CH), 3254 (C≡CH), 3114, 3077, 2959, 2896, 2851, 1466, 1455, 1397, 1366, 1300, 1163, 905, 770, 735, and 685 cm^{-1}. HRMS (EI): Found: *m*/*z* 273.9483. Calcd for $C_{10}H_{11}BrS_2$: 273.9486.

3-(*t*-Butylsulfanyl)-2-ethynylthiophene (11b). To a mixture of **10b** (533 mg, 2.66 mmol) and K_2CO_3 (1.10 g, 7.98 mmol) in MeOH (6.0 mL) was added a solution of **7** (879 mg, 3.46 mmol) in MeOH (3.0 mL) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 470.4 mg (2.40 mmol, 90% yield) of **11b**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (9H, s, *t*-Bu), 3.52 (1H, s, C≡CH), 7.03 (1H, d, $^3J = 5.1$ Hz, thienyl), and 7.25 (d, $^3J = 5.1$ Hz, thienyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.1 (C*Me*$_3$), 48.6 (*C*Me$_3$), 76.6 (C≡C), 84.5 (C≡C), 125.7, 127.8, 134.7, and 134.9; IR (neat): 3293 (C≡CH), 2961, 2107 (C≡C), 1719, 1470, 1456, 1402, 1364, 1279, 1169, 1076, 884, 725, 644, and 596 cm^{-1}. HRMS (EI): Found: *m*/*z* 196.0376. Calcd for $C_{10}H_{12}S_2$: 196.0380.

3-Bromothieno[3,2-*b*]thiophene (2a). A mixture of **11a** (54.4 mg, 0.197 mmol) and AuCl (2.3 mg, 0.016 mmol) in 1,4-dioxane (1.7 mL) and water (0.30 mL) was stirred at room temperature for 3 h under N_2. Upon completion, the mixture was poured into water, and extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 40.6 mg (0.173 mmol, 88% yield) of **2a**.

Thieno[3,2-*b*]thiophene (2b). To a solution of **11b** (100 mg, 0.510 mmol) in 1,4-dioxane (3.4 mL) and water (0.73 mL) was added AuCl (2.4 mg, 0.010 mmol) in 1,4-dioxane (1.0 mL) under N_2. The reaction mixture was stirred at room temperature for 3 h. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 58.0 mg (0.414 mmol, 81% yield) of **2b**.

4,7-Dibromo-2-methylbenzo[*b*]thiophene (12). To a solution of **1a** (100 mg, 0.342 mmol) in 3.0 mL of tetrahydrofuran (THF) was added 0.374 mmol of lithium *N*,*N*-diisopropylamide (LDA, 0.567 M solution in THF, 0.66 mL; M = mol dm^{-3}) at −78 °C under N_2. The reaction mixture was stirred at 0 °C for 30 min, and then iodomethane (0.026 mL, 0.41 mmol) was added at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Upon completion, the mixture was poured into saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 77.1 mg (0.252 mmol, 74% yield) of **12**: Colorless needles, mp 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (3H, d, $^4J = 1.2$ Hz, benzothienyl-*Me*), 7.21 (1H, q, $^4J = 1.2$ Hz, 3-benzothienyl), 7.24 (1H, d, $^3J = 8.1$ Hz, benzothienyl), and 7.34 (1H, d, $^3J = 8.1$ Hz, benzothienyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.3 (benzothienyl-*Me*), 114.2, 115.0, 123.0, 126.9, 128.5, 140.6, 141.6, and 143.2; IR (KBr): 1846, 1522, 1433, 1358, 1348, 1202, 1186, 1121, 1109, 1084, 912, 814, and 797 cm^{-1}. HRMS (EI): Found: *m*/*z* 303.8557. Calcd for $C_9H_6Br_2S$: 303.8554. Anal. Found: C, 35.57; H, 1.99%. Calcd for $C_9H_6Br_2S$: C, 35.32; H, 1.98%.

4-Bromobenzo[*b*]thiophene (13). To a solution of **1a** (59.0 mg, 0.202 mmol) in THF (2 mL) was added 0.23 mmol of *n*-BuLi (1.65 M solution in hexane, 0.14 mL) at −78 °C under N_2. The resulting mixture was stirred at −78 °C for 30 min, and then quenched with 1 mL of MeOH. To the mixture was added EtOAc and water, the organic phase was separated, washed with brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure and the residue was treated with

silica gel column chromatography (hexane) to give 22.8 mg (0.107 mmol, 53% yield) of **13**.[2c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (1H, t, $^3J = 8.0$ Hz), 7.48–7.55 (3H, m), and 7.81 (1H, d, $^3J = 8.0$ Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 117.4, 121.6, 124.2, 125.1, 127.2, 127.4, 139.4, and 140.5.

4-Bromo-7-iodobenzo[*b*]thiophene (14). To a solution of **1a** (100 mg, 0.342 mmol) in Et_2O (2.0 mL) was added 0.36 mmol of *n*-BuLi (1.57 M solution in hexane, 0.23 mL) at −78 °C under N_2. The reaction mixture was stirred at −78 °C for 30 min, and then 1,2-diiodoethane (96.4 mg, 0.376 mmol) in Et_2O (1.0 mL) was added at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Upon completion, the mixture was poured into saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and the residue was treated with silica gel column chromatography to give 96.2 mg (0.284 mmol, 83% yield) of **14**: Colorless needles, mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (1H, d, $^3J = 8.0$ Hz), 7.53 (1H, d, $^3J = 8.0$ Hz), 7.59 (1H, d, $^3J = 5.5$ Hz), and 7.72 (1H, d, $^3J = 5.5$ Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 85.8, 117.8, 125.8, 127.6, 128.7, 134.4, 138.8, and 147.0; IR (KBr): 1431, 1347, 1312, 1183, 1103, 1088, 1065, 891, 826, 806, 797, 754, and 687 cm^{-1}. HRMS (EI): Found: m/z 337.8257. Calcd for C_8H_4BrIS: 337.8262. Anal. Found: C, 28.57; H, 1.23%. Calcd for C_8H_4BrIS: C, 28.34; H, 1.19%.

4-Bromo-7-(3-thienyl)benzo[*b*]thiophene (15). Compound **14** (155 mg, 0.456 mmol), 3-thienylboronic acid (64.2 mg, 0.502 mmol), K_2CO_3 (315 mg, 2.28 mmol) and tetrakis(triphenylphosphine)palladium (10.5 mg, 9.12 μmol) in THF (3.8 mL) and water (0.8 mL) was stirred at 45 °C for 12 h under N_2. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 63.4 mg (0.215 mmol, 47% yield) of **15**: Colorless needles, mp 98–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (1H, d, $^3J = 7.9$ Hz, benzothienyl), 7.46–7.50 (2H, m, 4- and 5-thienyl), 7.55 (1H, d, $^3J = 5.8$ Hz, benzothienyl), 7.56 (1H, d, $^3J = 5.8$ Hz, benzothienyl), 7.60 (1H, d, $^3J = 7.9$ Hz, benzothienyl), and 7.71 (1H, dd, $J = 2.8$ and 1.5 Hz, 2-thienyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 116.3, 122.8, 124.6, 124.9, 126.3, 127.3, 127.5, 128.0, 130.7, 139.0, 139.9, and 140.2; IR (KBr): 2361, 1449, 1335, 1200, 1096, 1082, 858, 826, 776, 758, 691, and 652 cm^{-1}. HRMS (EI): Found: m/z 293.9167. Calcd for $C_{12}H_7BrS_2$: 293.9173.

7-(3-Thienyl)benzo[*b*]thiophene (16). To a solution of **15** (35.5 mg, 0.120 mmol) in THF (1.2 mL) was added *n*-BuLi (0.0815 mL, 1.26 mmol) in Et_2O (0.5 mL) at −78 °C under N_2. The reaction mixture was stirred at −78 °C for 30 min, and then the mixture was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 19.8 mg (0.0915 mmol, 76% yield) of **16**: Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (1H, d, $^3J = 5.4$ Hz, 3-benzothienyl), 7.45 (1H, t, $^3J = 7.8$ Hz, 5-benzothienyl), 7.48 (1H, dd, $J = 4.8$ and 3.0 Hz, 5-thienyl), 7.49 (1H, d, $^3J = 5.4$ Hz, 2-benzothienyl), 7.49–7.51 (1H, m, 6-benzothienyl), 7.56 (1H, dd, $J = 4.8$ and 1.2 Hz, 4-thienyl), 7.75 (1H, dd, $J = 3.0$ and 1.2 Hz, 2-thienyl), and 7.80 (1H, dd, $J = 7.8$ and 1.2 Hz, 4-benzothienyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 122.5 (2-thienyl), 122.6 (4-benzothienyl), 123.7 (6-benzothienyl), 124.4 (3-benzothienyl), 124.7 (5-benzothienyl), 126.0 (5-thienyl), 126.5 (2-benzothienyl), 127.4 (4-thienyl), 131.4 (7-benzothienyl), 138.2 (3a-benzothienyl), 140.5 (7a-benzothienyl), and 141.1 (3-thienyl); IR (neat): 3102, 1578, 1458 (Lit.[7] 1460), 1389, 1339, 1221, 1204, 1098, 1048, 857 (Lit. 860), 803, 777 (Lit. 775), 700, and 652 cm^{-1}.

4,7-Di(2-thienyl)benzo[*b*]thiophene (17). A mixture of **1a** (86.0 mg, 0.295 mmol), 2-(2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (166 mg, 0.719 mmol), K_2CO_3 (204 mg, 1.48 mmol) and tetrakis(triphenylphosphine)palladium (17.0 mg, 0.015 mmol) in 1,4-dioxane (3.4 mL) and water (0.7 mL) was stirred at 80 °C for 16 h under N_2. Upon completion, the mixture was poured into water, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 70.6 mg (0.237 mmol, 80% yield) of **17**: Pale yellow solid, mp 71–73 °C (Lit.[8] 73 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.22 (3H, m), 7.33 (1H, dd, $J = 3.6$ and 1.1 Hz, thienyl), 7.38 (1H, dd, $J = 5.1$ and 1.0 Hz, thienyl), 7.50 (1H, d, $^3J = 5.6$ Hz, benzothienyl), 7.51 (1H, d, $^3J = 7.7$ Hz, benzothienyl), 7.56 (1H, d, $^3J = 7.7$ Hz, benzothienyl), 7.62 (1H, dd, $J = 3.6$ and 1.1 Hz, thienyl), and 7.80 (1H, d, $^3J = 5.6$ Hz, benzothienyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 123.9, 124.1, 125.47, 125.50, 125.6, 125.7, 126.1, 127.1, 127.6, 127.8, 129.0, 129.6, 138.3, 138.6, 142.3, and 142.4; IR (neat): 3104, 1460, 1426, 1370, 1354, 1346, 1331, 1269, 1213, 1183, 1103, 1080, 1048, 990, 889, 882, 847, 814 (br), 779, and 690 cm^{-1}. (Lit.[8] 1458, 850, 825, 810, 690 cm^{-1}). HRMS (EI): Found: m/z 297.9942. Calcd for $C_{16}H_{10}S_3$: 297.9945.

4,7-Di(3-thienyl)benzo[*b*]thiophene (18). A mixture of **1a** (150 mg, 0.524 mmol), 3-thienylboronic acid (161 mg, 1.26 mmol), K_2CO_3 (355 mg, 2.43 mmol), and tetrakis(triphenylphosphine)palladium (29.7 mg, 0.0262 mmol) in 1,4-dioxane (7 mL) and water (1.4 mL) was stirred at 80 °C for 15 h under N_2. Upon completion, the mixture was poured into water, and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography to give 147 mg (0.492 mmol, 94% yield) of **18**: Colorless powder, mp 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (1H, dd, $J = 5.0$ and 1.4 Hz, thienyl), 7.46–7.50 (4H, m, thienyl + benzothienyl), 7.50 (1H, d, $^3J = 7.0$ Hz, benzothienyl), 7.52 (1H, d, $^3J = 7.0$ Hz, benzothienyl), 7.56 (1H, dd, $J = 5.0$ and 1.4 Hz, thienyl), 7.64 (1H, d, $^3J = 5.6$ Hz, benzothienyl), and 7.76 (1H, dd, $J = 3.0$ and 1.4 Hz, thienyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.6, 122.7, 123.8, 123.9, 125.1, 125.7, 126.0, 126.6, 127.5, 128.5, 130.4, 131.4, 138.5, 139.0, 140.9, and 141.4; IR (KBr): 3098, 1456, 1362, 1335, 1293, 1202, 1186, 1150, 1103, 1080, 1051, 912, 855, 785, 770, 704, and 664 cm^{-1}. HRMS (EI): Found: m/z 297.9940. Calcd for $C_{16}H_{10}S_3$: 297.9945. Anal. Found: C, 64.15; H, 3.57%. Calcd for $C_{16}H_{10}S_3$: C, 64.39; H, 3.38%.

1-Bromo-4-{5-hexyl-2-[2-(triisopropylsilyl)ethynyl]-3-thienyl}benzene (22). To a solution of **21**[9d] (1.25 g, 2.98

mmol) in THF (30 mL) was added 3.7 mmol of LDA (6.3 mL of a 0.58 M solution in THF) at −78 °C under N_2. The resulting mixture was stirred at −78 °C for 70 min. To the reaction mixture was added 1-iodohexane (0.58 mL, 3.9 mmol) at −78 °C. The reaction mixture was allowed to warm to 50 °C and stirred for 3 h. After cooling to room temperature, EtOAc (ca. 200 mL) and water (ca. 200 mL) were added, the organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a silica gel column chromatography (hexane) to give 1.27 g (2.52 mmol, 85% yield) of **22**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, $^3J = 6.9$ Hz, *Me*CH_2), 1.10 (18H, br s, *Me*$_2$C), 1.31 (4H, m, $CH_2 + CH_2$), 1.38 (3H, m, Me_2CH), 1.67 (2H, quin, $^3J = 7.4$ Hz, thienyl-CH_2CH_2), 2.77 (2H, t, $^3J = 7.4$ Hz, thienyl-CH_2), 6.83 (1H, s, 4-thienyl), 7.47 (2H, m, 3- and 5-phenyl), and 7.71 (2H, m, 2- and 6-phenyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 11.3 (Me_2C), 14.1 (*Me*CH_2), 18.6 (*Me*$_2$C), 22.5 (CH_2), 28.7 (CH_2), 30.2 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 98.0 (C≡C), 99.8 (C≡C), 116.1 (2-thienyl), 121.3 (1-Ph), 124.3 (4-thienyl), 129.4 (3- and 5-Ph), 131.3 (2- and 6-Ph), 134.3 (4-Ph), 143.2 (3-thienyl), and 147.2 (5-thienyl); IR (neat): 2945, 2865, 2137 (C≡C), 1495, 1464, 1071, 1011, 997, 884, 822, 772, and 677 cm^{-1}; MS (EI): *m*/*z* (rel intensity) 504 ($M^+ + 2$; 65), 502 (M^+; 58), 461 ($M^+ - i$-Pr + 2; 100), and 459 ($M^+ - i$-Pr; 90). HRMS (EI): Found: *m*/*z* 502.1723. Calcd for $C_{27}H_{39}BrSSi$: M, 502.1725.

1-Bromo-4-(5-hexyl-2-ethynyl-3-thienyl)benzene (23). To a solution of **22** (403 mg, 0.801 mmol) in THF (8 mL) was added 0.88 mmol of tetrabutylammonium fluoride (1.0 M solution in THF, 0.88 mL) at room temperature and the reaction mixture was stirred at that temperature for 70 min under N_2. To the reaction mixture were added EtOAc (ca. 30 mL) and water (ca. 30 mL). The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was treated with silica gel column chromatography (hexane) to give 241 mg (0.694 mmol, 87% yield) of **23**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, $^3J = 6.9$ Hz, *Me*CH_2), 1.31–1.38 (6H, m, CH_2), 1.64–1.70 (2H, m, thienyl-CH_2CH_2), 2.78 (2H, t, $^3J = 7.4$ Hz, thienyl-CH_2), 3.39 (1H, S, C≡CH), 6.82 (1H, s, 4-thienyl), 7.52 (2H, d, $^3J = 8.6$ Hz, 3- and 5-phenyl), and 7.61 (2H, d, $^3J = 8.6$ Hz, 2- and 6-phenyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 14.1 (Me), 22.5 (CH_2), 28.7 (CH_2), 30.1 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 77.4 (C≡C), 83.1 (C≡C), 114.3 (2-thienyl), 121.6 (1-phenyl), 124.6 (4-thienyl), 129.3 (3- and 5-phenyl), 131.5 (2- and 6-phenyl), 134.1 (4-phenyl), 144.3 (3-thienyl), and 147.7 (5-thienyl); IR (neat): 3301 (C≡CH), 2955, 2928, 2855, 2097 (C≡C), 1495, 1466, 1456, 1402, 1069, 1066, 864, 822, 658, 583, and 500 cm^{-1}; MS (EI): *m*/*z* (rel intensity) 348 ($M^+ + 2$; 100), 346 (M^+; 97), 277 ($M^+ - n$-Pen + 2; 99), 275 ($M^+ - n$-Pen; 96), and 195 ($M^+ - n$-Pen − Br − 1; 23). HRMS (EI): Found: *m*/*z* 346.0381. Calcd for $C_{18}H_{19}BrS$: M, 346.0391.

1-Bromo-4-[5-hexyl-2-(2-phenylethynyl)-3-thienyl]benzene (24). A mixture of **23** (241 mg, 0.694 mmol), iodobenzene (0.090 mL, 0.81 mmol), dichlorobis(triphenylphosphine)palladium(II) (9.9 mg, 0.014 mmol), CuI (8.1 mg, 0.042 mmol), and *N*,*N*-diisopropylamine (1 mL) in THF (7 mL) was stirred at 50 °C for 15 h under N_2. After cooling to room temperature, EtOAc (ca. 30 mL) and water (ca. 30 mL) were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with silica gel column chromatography (hexane) to give 226 mg (0.533 mmol, 77% yield) of **24**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, $^3J = 7.0$ Hz, Me), 1.31–1.40 (6H, m, CH_2), 1.66–1.74 (2H, m, CH_2), 2.78 (2H, t, $^3J = 7.4$ Hz, theinyl-CH_2), 6.88 (1H, s, thienyl), 7.31–7.35 (3H, m, Ph), 7.43–7.45 (2H, m, Ph), 7.55 (2H, d, $^3J = 8.6$ Hz, phenyl), and 7.69 (2H, d, $^3J = 8.6$ Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.1 (Me), 22.5 (CH_2), 28.7 (CH_2), 30.2 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 83.4 (C≡C), 94.9 (C≡C), 115.6, 121.4, 123.0, 124.6, 128.2, 129.3, 131.1, 131.4, 134.5, 143.1, and 147.4; IR (neat): 2955, 2928, 2855, 2201 (C≡C), 1597, 1493, 1456, 1443, 1402, 1377, 1102, 1069, 1011, 912, 860, 824, 754, 689, and 515 cm^{-1}; MS (EI): *m*/*z* (rel intensity) 424 ($M^+ + 2$; 100), 422 (M^+; 94), 353 ($M^+ - n$-Pen + 2; 64), 351 ($M^+ - n$-Pen; 62), and 271 ($M^+ - n$-Pen − Br − 1; 25). HRMS (EI): Found: *m*/*z* 422.0703. Calcd for $C_{24}H_{23}BrS$: M, 422.0704.

2-(4-{5-Hexyl-2-[2-(triisopropylsilyl)ethynyl]-3-thienyl}-phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25). To a solution of **22** (176 mg, 0.349 mmol) in THF (3.5 mL) was added 0.393 mmol of *n*-BuLi (1.57 M solution in hexane, 0.250 mL) at −78 °C under N_2. To the resulting mixture was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.090 mL, 0.44 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, and stirred for 90 min. To the resulting mixture were added water (ca. 50 mL) and EtOAc (ca. 50 mL). The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with silica gel column chromatography (hexane–EtOAc 1:0 to 1:0.1) to give 80.9 mg (0.147 mmol, 42% yield) of **25**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, $^3J = 6.8$ Hz, *Me*CH_2), 1.10 (21H, br s, *i*-Pr), 1.26–1.36 (18H, m, CH_2 + $OCMe_2$), 1.67 (2H, m, CH_2), 2.77 (2H, t, $^3J = 7.4$ Hz, thienyl-CH_2), 6.90 (1H, s, 4-thienyl), 7.80 (2H, d, $^3J = 8.0$ Hz, phenyl), and 7.86 (2H, d, $^3J = 8.0$ Hz, phenyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 11.3 (Me_2C), 14.1 (*Me*CH_2), 18.7 (*Me*$_2$C), 22.5 (CH_2), 24.8 ($OCMe_2$), 28.7 (CH_2), 30.2 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 83.7 ($OCMe_2$), 97.9 (C≡C), 100.1 (C≡C), 116.3, 124.7, 126.9, 134.8, 138.0, 144.0, and 146.8; IR (neat): 2957, 2865, 2137 (C≡C), 1611, 1559, 1541, 1271, 1213, 1146, 1075, 1021, 997, 963, 920, 884, 860, 830, 772, 747, 675, and 579 cm^{-1}. HRMS (ESI): Found: *m*/*z* 573.3360. Calcd for $C_{33}H_{51}BNaO_2SSi$: $(M + Na)^+$, 573.3364.

2-{4-[5-Hexyl-2-(2-phenylethynyl)-3-thienyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26). To a solution of **24** (190 mg, 0.448 mmol) in THF (4.5 mL) was added 0.468 mmol of *n*-BuLi (1.67 M solution in hexane, 0.280 mL) at −78 °C under N_2. The resulting mixture was stirred for 35 min. To the solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.10 mL, 0.49 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, and stirred for 10 h. EtOAc (ca. 50 mL) and water (ca. 50 mL) were added to the mixture. The organic phase was separated, washed

with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give 203 mg (0.432 mmol, 96% yield) of **26**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, $^3J = 6.9$ Hz, $MeCH_2$), 1.32–1.42 (18H, m, CH_2 + $OCMe_2$), 1.67–1.75 (2H, m, CH_2), 2.81 (2H, t, $^3J = 7.6$ Hz, thienyl-CH_2), 6.95 (1H, s, thienyl), 7.31–7.34 (3H, m, Ph), 7.45–7.47 (2H, m, Ph), 7.85 (2H, d, $^3J = 8.3$ Hz, phenyl), and 7.88 (2H, d, $^3J = 8.3$ Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.0 ($MeCH_2$), 22.5 (CH_2), 24.8 ($OCMe_2$), 28.7 (CH_2), 30.2 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 83.7 (C≡C), 83.7 ($OCMe_2$), 94.7 (C≡C), 115.8, 123.2, 125.0, 127.0, 128.1, 131.1, 134.8, 138.3, 144.2, and 147.1; IR (neat): 2930, 2857, 2201 (C≡C), 1609, 1559, 1541, 1495, 1456, 1399, 1362, 1323, 1271, 1213, 1144, 1096, 1071, 1021, 963, 858, 830, 754, 691, 662, 652, and 521 cm^{-1}. HRMS (ESI): Found: m/z 493.2391. Calcd for $C_{30}H_{35}BNaO_2S$: $(M + Na)^+$, 493.2343.

4-Bromo-7-{4-[5-hexyl-2-(triisopropylsilylethynyl)-3-thienyl]phenyl}-2-methylbenzo[*b*]thiophene (28). A mixture of **25** (343 mg, 0.622 mmol), **29** (222 mg, 0.628 mmol), tetrakis(triphenylphosphine)palladium (29.1 mg, 0.0252 mmol), K_2CO_3 (435 mg, 3.15 mmol), 1,4-dioxane (5 mL), and water (2 mL) was heated under nitrogen at 80 °C for 46 h under N_2. After cooling to room temperature, EtOAc and water were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, the residue was treated with silica gel column chromatography (hexane) to give 322 mg (0.496 mmol, 80% yield) of **28**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, $^3J = 6.9$ Hz, $MeCH_2$), 1.11 (21H, s, *i*-Pr), 1.32–1.40 (6H, m, CH_2), 1.66–1.73 (2H, m, CH_2), 2.60 (3H, d, $^4J = 1.2$ Hz, benzothienyl-*Me*), 2.80 (2H, t, $^3J = 7.5$ Hz, thienyl-CH_2), 6.93 (1H, s, 4-thienyl), 7.16 (1H, d, $^4J = 7.9$ Hz, benzothienyl), 7.22 (1H, q, $^4J = 1.2$ Hz, 3-benzothienyl), 7.57 (1H, d, $^4J = 7.9$ Hz, benzothienyl), 7.66 (2H, d, $^4J = 8.5$ Hz, phenyl), and 7.94 (2H, d, $^4J = 8.5$ Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.4 (Me_2C), 14.1 ($MeCH_2$), 16.0 (benzothienyl-*Me*), 18.7 (Me_2C), 22.6 (CH_2), 28.7 (CH_2), 30.2 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 97.6 (C≡C), 100.3 (C≡C), 115.2, 116.0, 122.4, 124.2, 124.5, 127.8, 127.9, 128.0, 128.2, 135.2, 138.7, 139.0, 140.4, 142.4, 144.0, and 146.9; IR (neat): 2928, 2863, 2135 (C≡C), 1512, 1460, 1346, 1203, 1118, 1081, 1017, 995, 919, 882, 811, 771, 677, 577, and 505 cm^{-1}. HRMS (ESI): Found: m/z 671.1804. Calcd for $C_{36}H_{45}BrNaS_2Si$: $(M + Na)^+$, 671.1808.

4-Bromo-7-iodo-2-methylbenzo[*b*]thiophene (29). To a solution of **12** (219 mg, 0.716 mmol) in THF (5 mL) was added 0.75 mmol of *n*-BuLi (1.67 M solution in hexane, 0.45 mL) at −78 °C under N_2. The resulting mixture was stirred at −78 °C for 30 min and 1,2-diiodoethane (243 mg, 0.862 mmol) in THF (2 mL) was added at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. To the reaction mixture were added EtOAc and saturated aqueous NH_4Cl and the resulting mixture was treated with saturated aqueous $Na_2S_2O_3$ solution. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure, and purified by silica gel column chromatography (hexane) to give 234 mg (0.663 mmol, 93% yield) of **29**: Colorless powder, mp 113–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (3H, d, $^4J = 1.2$ Hz, benzothienyl-*Me*), 7.21 (1H, d, $^4J = 8.1$ Hz, benzothienyl), 7.38 (1H, q, $^4J = 1.2$ Hz, 3-benzothienyl), and 7.43 (1H, d, $^4J = 8.1$ Hz, benzothienyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.3 (benzothienyl-*Me*), 85.3, 116.4, 123.4, 128.5, 133.3, 139.4, 142.6, and 146.4; IR (KBr): 3064, 2970, 2949, 2912, 2844, 1847, 1598, 1556, 1513, 1431, 1352, 1342, 1309, 1200, 1183, 1117, 1102, 1077, 896, 813, 795, 762, 716, 674, 646, 525, and 506 cm^{-1}. HRMS (EI): Found: m/z 351.8415. Calcd for C_9H_6BrIS: M, 351.8418.

Cross Coupling Reaction of 12 with 25 (1 molar equivalent). A mixture of **12** (79.4 mg, 0.259 mmol), **25** (141 mg, 0.256 mmol), tetrakis(triphenylphosphine)palladium (9.2 mg, 0.0079 mmol), K_2CO_3 (179 mg, 1.30 mmol), 1,4-dioxane (2.3 mL), and water (1.2 mL) was heated at 90 °C for 13 h under N_2. After cooling to room temperature, $CHCl_3$ and water were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, the residue was treated with silica gel column chromatography (hexane to hexane–EtOAc 30:1) to give 43.2 mg (0.0435 mmol, 17% yield) of **19a** and 87.1 mg (0.134 mmol, 52% yield) of an isomeric mixture of **27** and **28** (1.0:0.43). **27** (major signals in the mixture): ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, $^3J = 6.9$ Hz, $MeCH_2$), 1.12 (21H, s, *i*-Pr), 1.32–1.43 (6H, m, CH_2), 1.66–1.74 (2H, m, CH_2), 2.58 (3H, d, $^4J = 1.2$ Hz, benzothienyl-*Me*), 2.80 (2H, t, $^3J = 7.5$ Hz, thienyl-CH_2), 6.93 (1H, s, 4-thienyl), 7.20 (1H, d, $^4J = 7.8$ Hz, benzothienyl), 7.21 (1H, br s, 3-benzothienyl), 7.48 (1H, d, $^4J = 7.8$ Hz, benzothienyl), 7.51 (2H, d, $^4J = 8.3$ Hz, phenyl), and 7.93 (2H, d, $^4J = 8.3$ Hz, phenyl). The isomeric mixture was subjected to a further cross coupling reaction: To the mixture of **27** and **28** (80.7 mg, 0.124 mmol) were added **25** (68.3 mg, 0.124 mmol), tetrakis(triphenylphosphine)palladium (4.0 mg, 0.0037 mmol), K_2CO_3 (92.4 mg, 0.669 mmol), 1,4-dioxane (1.8 mL), and water (0.8 mL). The resulting mixture was heated at 90 °C for 40 h under N_2. After cooling to room temperature, $CHCl_3$ and water were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was successively treated with silica gel column chromatography (hexane–EtOAc 30:1) and gel permeation chromatography to give 81.0 mg of **19a** (0.0815 mmol, 66% yield).

4,7-Bis{4-[5-hexyl-2-(triisopropylsilylethynyl)-3-thienyl]-phenyl}-2-methylbenzo[*b*]thiophene (19a). A mixture of **12** (19.3 mg, 0.0631 mmol), **25** (81.4 mg, 0.148 mmol), tetrakis(triphenylphosphine)palladium (3.5 mg, 3.0 μmol), and K_2CO_3 (82.7 mg, 0.598 mmol) in 1,4-dioxane (1.8 mL) and water (1.0 mL) was stirred at 90 °C for 13 h under N_2. After cooling to room temperature, $CHCl_3$ and water were added to the reaction mixture. The organic layer was separated, washed with brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure and the residue was treated with silica gel column chromatography (hexane–EtOAc 40:1) to give a crude product, which was purified by successive silica gel column chromatography (hexane–EtOAc 100:1) to give 36.5 mg (0.0367 mmol, 58% yield) of **19a**: Colorless solid, mp 46–48 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (6H, t, $^3J = 6.9$ Hz, $MeCH_2$), 1.13 (42H, s, *i*-Pr), 1.32–1.41 (12H, m, CH_2), 1.67–1.74 (4H, m, CH_2), 2.57 (3H, d, $^4J = 1.2$ Hz, benzothienyl-*Me*),

2.81 (4H, t, $^3J = 7.6$ Hz, thienyl-CH_2), 6.96 (2H, s, 4-thienyl), 7.21 (1H, q, $^4J = 1.2$ Hz, 3-benzothienyl), 7.39 (1H, d, $^3J = 7.6$ Hz, benzothienyl), 7.43 (1H, d, $^3J = 7.6$ Hz, benzothienyl), 7.60 (2H, d, $^3J = 8.3$ Hz, phenyl), 7.76 (2H, d, $J = 8.3$ Hz, phenyl), 7.96 (2H, d, $^3J = 8.3$ Hz, phenyl), and 7.98 (2H, d, $^3J = 8.3$ Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.4 (Me_2C), 14.1 ($MeCH_2$), 16.1 (benzothienyl-*Me*), 18.7 (Me_2C), 22.6 (CH_2), 28.7 (CH_2), 30.3 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 97.4 (C≡C), 97.6 (C≡C), 100.3 (C≡C), 100.4 (C≡C), 115.9, 116.0, 121.4, 123.7, 124.7, 125.4, 127.9, 128.0, 128.2, 129.0, 134.5, 135.0, 135.1, 135.6, 139.2, 139.3, 139.6, 140.0, 141.3, 144.2, 144.3, 146.8, and 146.9; UV–vis (CH_2Cl_2): 264 (log ε 4.65), 316 (4.63), and 340 nm (sh, 4.60); IR (neat): 2928, 2863, 2135 (C≡C), 1519, 1463, 1380, 1260, 1173, 1116, 1073, 1044, 1016, 995, 919, 882, 818, 771, 676, 578, 520, and 503 cm^{-1}. HRMS (ESI): Found: *m/z* 1015.5156. Calcd for $C_{63}H_{84}NaS_3Si_2$: $(M + Na)^+$, 1015.5166.

4-{4-[5-Hexyl-2-(phenylethynyl)-3-thienyl]phenyl}-7-{4-[5-hexyl-2-(triisopropylsilylethynyl)-3-thienyl]phenyl}-2-methylbenzo[*b*]thiophene (19b). A mixture of **26** (64.1 mg, 0.136 mmol), **28** (85.6 mg, 0.132 mmol), tetrakis(triphenylphosphine)palladium (5.8 mg, 0.0050 mmol), K_2CO_3 (90.4 mg, 0.654 mmol), 1,4-dioxane (1.8 mL), and water (0.8 mL) was heated at 90 °C for 13 h under N_2. After cooling to room temperature, EtOAc and water were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with silica gel column chromatography (hexane–EtOAc, 1:0 to 30:1) to give 107.3 mg (0.118 mmol, 89% yield) of **19b**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97–0.99 (6H, m, $MeCH_2$), 1.20 (21H, s, *i*-Pr), 1.38–1.47 (12H, m, CH_2), 1.74–1.80 (4H, m, CH_2), 2.62 (3H, d, $^4J = 1.1$ Hz, benzothienyl-*Me*), 2.83–2.90 (4H, m, thienyl-CH_2), 7.00 (1H, s, 4-thienyl), 7.05 (1H, s, 4′-thienyl), 7.31 (1H, q, $^4J = 1.1$ Hz, 3-benzothienyl), 7.34–7.39 (3H, m, Ph), 7.44 (1H, d, $^3J = 7.5$ Hz, benzothienyl), 7.50–7.55 (3H, m, Ph + benzothienyl), 7.73 (2H, d, $^3J = 8.3$ Hz, phenyl), 7.82 (2H, d, $^3J = 8.3$ Hz, phenyl), and 8.02–8.05 (4H, m, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.4 (Me_2C), 14.1 ($MeCH_2$), 16.1 (benzothienyl-*Me*), 18.7 (Me_2C), 22.5 (CH_2), 22.6 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 30.2 (CH_2), 30.3 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 31.5 ($CH_2 \times 2$), 84.0 (C≡C), 94.7 (C≡C), 97.6 (C≡C), 100.3 (C≡C), 115.4, 116.0, 121.4, 123.4, 123.7, 124.7, 125.0, 125.5, 127.9, 128.0, 128.1, 128.2, 128.3, 129.1, 131.1, 134.6, 135.0, 135.1, 135.5, 139.2, 139.3, 139.6, 140.1, 141.3, 144.1, 144.2, 146.9, and 147.3; UV–vis (CH_2Cl_2): 265 (log ε 4.71) and 322 nm (4.75); IR (neat): 2927, 2862, 2198 (C≡C), 2135 (C≡C), 1597, 1518, 1468, 1378, 1200, 1119, 1071, 1044, 1016, 996, 909, 882, 819, 771, 754, 677, 538, and 503 cm^{-1}. HRMS (ESI): Found: *m/z* 935.4145. Calcd for $C_{60}H_{68}NaS_3Si$: $(M + Na)^+$, 935.4137.

Compound 31. A mixture of **22** (51.0 mg, 0.498 mmol), **30** (184 mg, 0.412 mmol), tetrakis(triphenylphosphine)palladium (11.4 mg, 0.00986 mmol), K_2CO_3 (348 mg, 2.52 mmol), toluene (4 mL), THF (4 mL), and water (3 mL) was heated at 80 °C for 14 h under N_2. After cooling to room temperature, $CHCl_3$ and water were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with silica gel column chromatography (hexane) to give 257 mg (0.0346 mmol, 84% yield) of **31**: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (3H, t, $^3J = 6.0$ Hz, CH_2Me), 1.16 (21H, s, $CHMe_2$), 1.23 (21H, s, $CHMe_2$), 1.31–1.48 (6H, m, CH_2), 1.73 (2H, quin, $^3J = 7.4$ Hz, thienylCH_2CH_2), 2.82 (2H, t, $^3J = 7.5$ Hz, thienylCH_2), 6.94 (1H, s, 4-thienyl), 7.23 (1H, d, $^3J = 5.2$ Hz, thienothienyl), 7.40 (1H, d, $^3J = 5.2$ Hz, thienothienyl), 7.91 (2H, d, $^3J = 7.9$ Hz, phenyl), and 8.07 (2H, d, $^3J = 7.9$ Hz, phenyl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.3 ($CHMe_2$), 11.4 ($CHMe_2$), 14.1 (CH_2Me), 18.68 ($CHMe_2$), 18.72 ($CHMe_2$), 22.6 (CH_2), 28.8 (CH_2), 30.3 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 97.6 (C≡C), 97.9 (C≡C), 100.2 (C≡C), 100.6 (C≡C), 110.9, 116.2, 119.6, 124.6, 127.18 (phenyl), 127.22, 128.0 (phenyl), 133.2, 135.3, 135.4, 143.8, 143.9, 147.0, and 147.5; IR (neat): 2940, 2890, 2864, 2136 (C≡C), 1520, 1462, 1382, 1357, 1242, 1175, 1062, 1016, 995, 955, 911, 882, 830, 772, 735, 711, 668, and 504 cm^{-1}. Found: *m/z* 765.3443. Calcd for $C_{44}H_{62}NaS_3Si_2$: $(M + Na)^+$, 765.3444.

Compound 20. To a solution of **31** (163.1 mg, 0.219 mmol) in THF (2 mL) was added 0.25 mmol of *n*-BuLi (1.65 M solution in hexane, 0.15 mL) at −78 °C under N_2 and the resulting mixture was stirred for 1 h. To the mixture was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.060 mL, 0.29 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, and stirred for 3 h. To the resulting mixture were added water (ca. 30 mL) and EtOAc (ca. 30 mL). The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with a short silica gel column chromatography (EtOAc) to give 184.9 mg (0.213 mmol) of **32** in 97% yield. **32**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, $^3J = 6.6$ Hz, CH_2Me), 1.10 (21H, s, $CHMe_2$), 1.18 (21H, s, $CHMe_2$), 1.27–1.34 (6H, m, CH_2), 1.38 (12H, s, CMe_2), 1.69 (2H, quin, $^3J = 7.5$ Hz, thienylCH_2CH_2), 2.79 (2H, t, $^3J = 7.5$ Hz, thienylCH_2), 6.90 (1H, s, thienyl), 7.71 (1H, s, thienothienyl), 7.85 (2H, d, $^3J = 8.6$ Hz, phenyl), and 8.02 (2H, d, $^3J = 8.6$ Hz, phenyl). This procedure was repeated, the products were combined, and used in Suzuki–Miyaura reaction: A mixture of **32** (263.5 mg, 0.303 mmol), **29** (37.3 mg, 0.106 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (10.3 mg, 0.0251 mmol), palladium(II) aceate (1.9 mg, 0.0084 mmol), K_2CO_3 (142.3 mg, 1.03 mmol), in THF (3 mL) was heated at 50 °C for 2 days under N_2. After cooling to room temperature, $CHCl_3$ and water were added to the reaction mixture. The organic phase was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure. Successive treatment of the residue with silica gel column chromatography (hexane–EtOAc) and gel permeation column chromatography gave 33.3 mg of **20** (crude) and 146.3 mg (0.197 mmol, 65% yield) of **31**. Recrystallization of the crude product **20** from hexane followed by a short silica gel column chromatographic treatment (hexane–CH_2Cl_2 15:1) gave 9.0 mg (0.0055 mmol, 5% yield) of **20**: Yellow solid, mp 242–245 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (6H, t, $^3J = 6.5$ Hz, CH_2Me), 1.12 (42H, s, $CHMe_2$), 1.20 (42H, m, $CHMe_2$), 1.33–1.41 (12H, m, CH_2), 1.66–1.74 (4H, m, CH_2), 2.66 (3H, s, benzothienyl-Me), 2.80 (4H, t, $^3J = 7.5$ Hz, thienylCH_2), 6.90 (2H, s, 4-thienyl), 7.44 (1H,

s, thienothienyl), 7.51 (1H, br s, 3-benzothienyl), 7.53–7.58 (2H, m, benzothienyl), 7.74 (1H, s, thienothienyl'), 7.87 (4H, d, $^3J = 8.1$ Hz, phenyl), and 8.04 (4H, d, $^3J = 8.1$ Hz, phenyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 11.3 ($CHMe_2$), 11.4 ($CHMe_2$), 14.1 (CH_2Me), 16.3 (benzothienyl-Me), 18.7 ($CHMe_2$), 18.8 ($CHMe_2$), 22.6 (CH_2), 28.8 (CH_2), 30.3 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 97.8 (C≡C), 98.0 (C≡C), 100.1 (C≡C), 100.4 (C≡C), 111.0, 111.1, 116.2, 118.0, 118.5, 121.5, 123.4, 124.6, 125.9, 127.2, 127.2, 128.0, 128.9, 129.0, 133.0, 133.1, 135.5, 135.5, 135.7, 135.9, 138.4, 139.2, 142.3, 143.3, 143.6, 143.9, 144.2, 144.5, 147.0, 147.1, and 147.4; UV–vis (CH_2Cl_2): 243 (log ε, 4.65), 302 (4.55), and 407 nm (4.85); IR (neat): 2940, 2890, 2863, 2134 (C≡C), 1519, 1461, 1381, 1173, 1062, 995, 956, 918, 882, 829, 771, 711, 677, 578, 503, and 459 cm^{-1}. Found: m/z 1651.7030 Calcd for $C_{97}H_{128}NaS_7Si_4$: $(M + Na)^+$, 1651.7045.

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