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Transition Metal-Catalyzed Cascade Cyclization of Aryldiynes to Halogenated Benzo[*b*]naphtho[2,1-*d*]thiophene Derivatives

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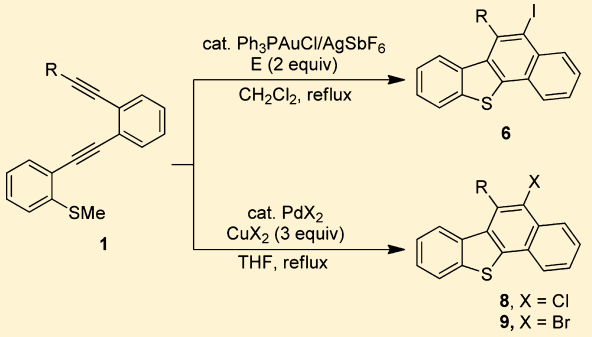
Supporting Information

ABSTRACT: Treatment of 2-(2-(2-(2-substituted ethynyl)phenyl)-ethynyl)thioanisoles (**1**) with 5 mol % of $Ph_3PAuCl/AgSbF_6$ and 2 equiv of NIS at refluxing CH_2Cl_2 gave iodo-substituted benzo[*b*]-naphtho[2,1-*d*]thiophene (**6**) in good yields. Chloro- and bromo-substituted benzo[*b*]naphtho[2,1-*d*]thiophene derivatives (**8** and **9**) were also generated by treating compound **1** with 5 mol % of PdX_2 and 3 equiv of CuX_2 at refluxing THF.

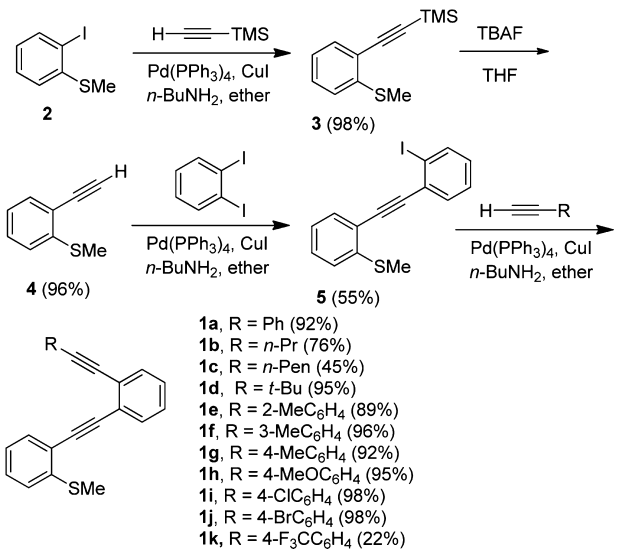


Dibenzothiophene derivatives are important molecules in materials science[1] and pharmaceutical industry.[2] However, the synthetic methods to these molecules are very limited.[3] Recently, we reported the transition metal-catalyzed cyclization of enediynes or aryldiynes to halo-substituted dibenzo[*b*,*d*]pyran-6-ones[4] and benzo[*a*]carbazoles.[5] We also found iodine can mediate the cascade cyclization of aryldiynes to iodo-substituted benzo[*a*]carbazoles without transition metal.[6] In continuation of our investigation of these types of cascade cyclization reactions, we anticipated that halo-substitutedbenzo[*b*]naphtho[2,1-*d*]thiophenes could be obtained by transition metal-catalyzed or iodine-mediated cyclization of thioanisole-substituted aryldiynes.

During our investigation, Jin and Yamamoto reported iodine-mediated cascade cyclization of thioanisole-substituted aryldiynes to give iodo-substituted benzo[*b*]naphtho[2,1-*d*]-thiophenes.[7] However, under their described reaction conditions, the aryldiyne with alkyl substituent at the 6-position gave only trace amount of the desired product. Herein, we wish to report the transition metal-catalyzed cascade halocyclization of aryldiynes to benzo[*b*]naphtho[2,1-*d*]thiophenes. With this method, both alkyl- and aryl-substituted aryldiynes can cyclize to produce the desired products. It also works well for bromo- and chloro-substituted benzo[*b*]naphtho[2,1-*d*]thiophenes.

The synthesis of 2-(2-(2-(2-substituted ethynyl)phenyl)-ethynyl)thioanisoles (**1a**–**k**) starting from 2-iodothioanisole (**2**) is outlined in Scheme 1. Compound **2** was coupled with trimethylsilylacetylene using $Pd(PPh_3)_4$ as the catalyst under Sonogashira reaction conditions to give **3** in 98% yield. Desilylation of **3** using TBAF in THF gave **4** in 96% yield. Compound **4** was then coupled with 1,2-diiodobenzene using $Pd(PPh_3)_4$ as the catalyst to give **5** in 55% yield. Finally,

Scheme 1



Sonogashira coupling reaction of **5** with various terminal alkynes to give **1a**–**k** was achieved.

First of all, compound **1a** was treated with 2 equiv of iodine in CH_2Cl_2 at room temperature for 1 h to give compound **6a** in 90% yield (Table 1, entry 1). This result is similar to the report by Jin and Yamamoto.[6] However, under the same reaction conditions, compound **1b** gave exclusively **7b** in 85% yield (Table 1, entry 2). When the reaction was carried out in refluxing CH_2Cl_2 for 72 h, compound **6b** was obtained in 15%

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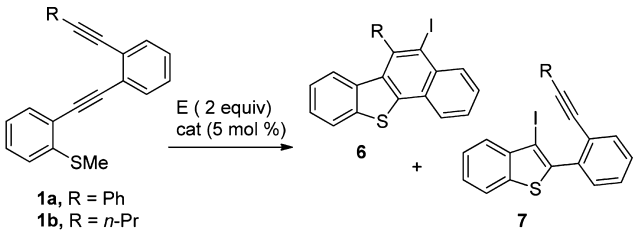
Table 1. Optimization of Reaction Conditions for Iodocyclization Reaction

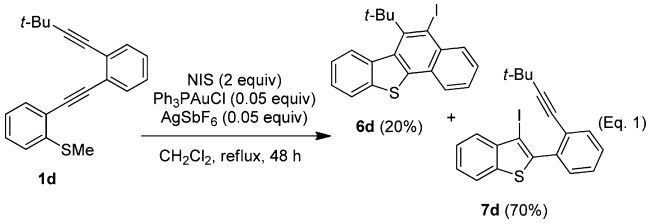


1a, R = Ph
1b, R = *n*-Pr

entry	cpd	E	catalyst	solvent	temp (°C)	time (h)	products/yields (%)
1	**1a**	I_2	–	CH_2Cl_2	rt	24	**6a**/90
2	**1b**	I_2	–	CH_2Cl_2	rt	24	**7b**/85
3	**1b**	I_2	–	CH_2Cl_2	reflux	72	**6b**/15; **7b**/58
4	**1b**	I_2	$Pd(OAc)_2$	CH_2Cl_2	reflux	72	**6b**/61; **7b**/10
5	**1b**	I_2	$Ph_3PAuCl/AgSbF_6$	CH_2Cl_2	reflux	72	**6b**/90
6	**1b**	NIS	$Ph_3PAuCl/AgSbF_6$	CH_2Cl_2	reflux	5	**6b**/92
7	**1b**	NIS	$Ph_3PAuCl/AgSbF_6$	THF	reflux	48	**6b**/82
8	**1b**	NIS	$Ph_3PAuCl/AgSbF_6$	toluene	reflux	10	**6b**/70

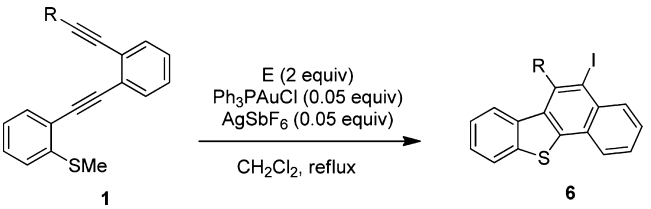
yield along with **7b** in 58% yield (Table 1, entry 3). Introducing 5 mol % of $Pd(OAc)_2$ into the reaction mixture, the yield of **6b** was increased to 61%, and the yield of **7b** was reduced to 10% (Table 1, entry 4). Using the gold catalyst (Ph_3PAuCl, 5 mol %)[8] combined with silver salt ($AgSbF_6$, 5 mol %) to carry out this iodocyclization reaction, the desired iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophene **6b** was obtained in 90% yield as the only product (Table 1, entry 5). *N*-Iodosuccinimide (NIS) was also introduced as the iodonating agent and was found to be more efficient than iodine. Thus, treatment of 2 equiv of NIS with **1b** in the presence of 5 mol % of Ph_3PAuCl and 5 mol % of $AgSbF_6$ in CH_2Cl_2 at reflux for 5 h gave **6b** in 92% yield. (Table 1, entry 6) Other solvents, such as THF, toluene, and 1,4-dioxane, were not as efficient as CH_2Cl_2.

With the optimized reaction conditions in hand, other 2-(2-(2-(2-substituted ethynyl)phenyl)ethynyl)thioanisoles were subjected to the cyclization reaction by treating with 2 equiv NIS in the presence of 5 mol % of Ph_3PAuCl and 5 mol % of $AgSbF_6$ at reflux CH_2Cl_2, respectively. The results are summarized in Table 2. These reactions gave iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophenes in good to excellent yields. However, under the optimized reaction conditions, cyclization of **1d** even for a prolongation time of 48 h gave the monocyclization product **7d** in 70% yield, and the double-cyclization adduct **6d** was obtained in only 20% yield (eq 1).



After the successive development of iodocyclization of aryldiynes to benzo[*b*]naphtho[2,1-*d*]thiophenes, we then turn our attention to chloro- and bromocyclization reactions. In our previous studies, $CuCl_2$ and $CuBr_2$ are good halocyclization agents to give various chloro- and bromo-substituted carbocycles.[9] We examined the chloro- and bromocyclization reactions with different transition metal complexes as the catalyst and found that palladium halides are the best catalysts for these cyclization reactions (Table 3).

Table 2. Iodocyclization of 1 to Iodo-Substituted Benzo[*b*]naphtha[2,1-*d*]thiophenes



entry	E	compounds	time (h)	products/yield (%)
1	NIS	**1c**, R = *n*-pentyl	2	**6c**/82
2	NIS	**1e**, R = 2-MeC_6H_4	4	**6e**/92
3	NIS	**1f**, R = 3-MeC_6H_4	4	**6f**/73
4	NIS	**1g**, R = 4-MeC_6H_4	4	**6g**/80
5	NIS	**1h**, R = 4-$MeOC_6H_4$	1	**6h**/67
6	NIS	**1a**, R = C_6H_5	1	**6a**/80
7	NIS	**1i**, R = 4-ClC_6H_4	2	**6i**/76
8	NIS	**1j**, R = 4-BrC_6H_4	2	**6j**/67
9	NIS	**1k**, R = 4-$F_3CC_6H_4$	2	**6k**/86
10	I_2	**1h**, R = 4-$MeOC_6H_4$	12	**6h**/63
11	I_2	**1k**, R = 4-$F_3CC_6H_4$	12	**6k**/64

For instance, treatment of **1b** with 3 equiv of $CuCl_2$ and 5 mol % of $PdCl_2$ at reflux THF for 24 h gave **8a** in 88% yield (Table 3, entry 1). Similar result was observed for bromocyclization of **1b** to give **9b** using $CuBr_2$ (Table 3, entry 2). Gold catalyst was found to be less efficient in these cyclization reactions (Table 3, entries 3 and 4). Other 2-(2-(2-substituted ethynyl)phenyl)-ethynyl)thioanisoles **1a**, **1c**, and **1e**–**k** were subjected to the chlorocyclization reaction under the optimized reaction conditions. The results are summarized in Table 4. Compounds **1a**, **1h**, and **1k** were also subjected to the optimized bromocyclization reaction conditions to afford bromo-substituted benzo[*b*]naphtho[2,1-*d*]thiophenes **9a**, **9h**, and **9k** in 78, 89, and 84% yields, respectively.

Cyclization of the *tert*-butyl substituted aryldiyne **1d** with 2 equiv of CuX_2 and 10 mol % of PdX_2 in refluxing acetonitrile afford the monocyclization products **10d** and **11d** in 95 and 98% yields, respectively (eq 2).

To investigate the substituent and catalyst effects on the cyclization reaction, the following reactions have been carried out. Compound **7b** with propyl group at the terminal alkyne

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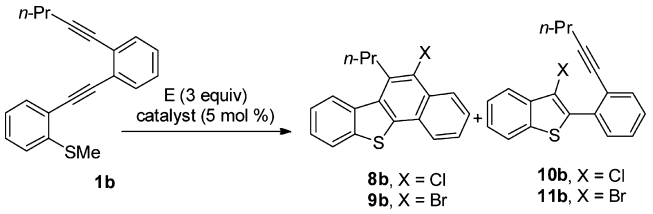
Table 3. Optimization of Chloro- and Bromocyclization of 1b

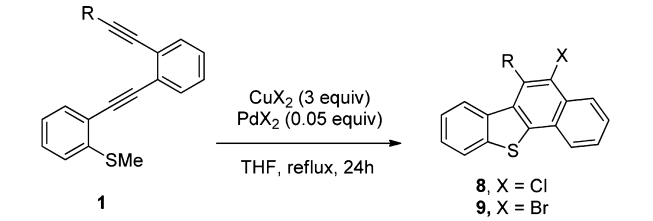


1b — **8b**, X = Cl; **9b**, X = Br — **10b**, X = Cl; **11b**, X = Br

entry	E (equiv)	catalyst	solvent	temp	time (h)	yield (%)
1	$CuCl_2$ (3)	$PdCl_2$	THF	reflux	24	**8b**/88
2	$CuBr_2$ (3)	$PdBr_2$	THF	reflux	24	**9b**/88
3	$CuCl_2$ (2)	Ph_3PAuCl/$AgSbF_6$[a]	CH_2Cl_2	reflux	48	**10b**/85
4	$CuBr_2$ (2)	Ph_3PAuCl/$AgSbF_6$[a]	CH_3CN	reflux	48	**9b**/33, **11b**/51
5	$CuCl_2$ (2)	$PdCl_2$	CH_3CN	reflux	72	**8b**/62, **10b**/20
6	$CuCl_2$ (2)	$PdCl_2$	THF	reflux	72	**8b**/56, **10b**/30

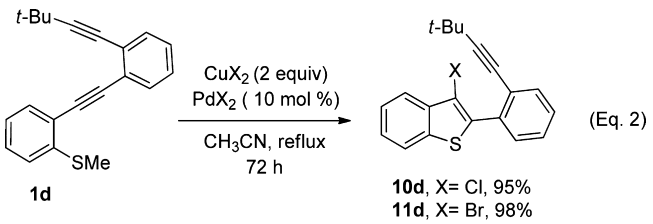
[a]0.05 equiv of $AgSbF_6$ was added.

Table 4. Synthesis of Chloro- and Bromo-Substituted Benzo[*b*]naphtha[2,1-*d*]thiophenes



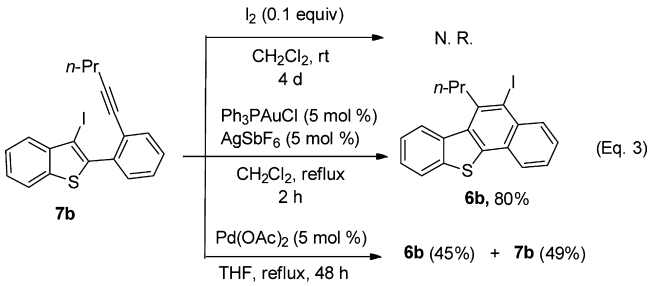
1 — **8**, X = Cl; **9**, X = Br

entry	X	compounds	products/yield (%)
1	Cl	**1c**, R = *n*-Pentyl	**8c**/83
2	Cl	**1e**, R = 2-MeC_6H_4	**8e**/83
3	Cl	**1f**, R = 3-MeC_6H_4	**8f**/68
4	Cl	**1g**, R = 4-MeC_6H_4	**8g**/75
5	Cl	**1h**, R = 4-$MeOC_6H_4$	**8h**/78
6	Cl	**1a**, R = C_6H_5	**8a**/76
7	Cl	**1i**, R = 4-ClC_6H_4	**8i**/88
8	Cl	**1j**, R = 4-BrC_6H_4	**8j**/85
9	Cl	**1k**, R = 4-$F_3CC_6H_4$	**8k**/80
10	Br	**1h**, R = 4-$MeOC_6H_4$	**9h**/89
11	Br	**1a**, R = C_6H_5	**9a**/78
12	Br	**1k**, R = 4-$F_3CC_6H_4$	**9k**/84

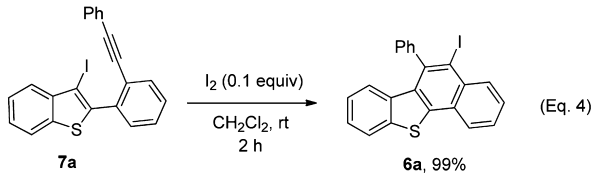


1d — **10d**, X= Cl, 95%; **11d**, X= Br, 98% (Eq. 2)

was treated with 0.1 equiv of iodine (I_2) in CH_2Cl_2 at room temperature, and no reaction took place even after stirring the reaction mixture for 4 days. However, treatment of **7b** with 5 mol % of Ph_3PAuCl and 5 mol % of $AgSbF_6$ at reflux CH_2Cl_2 gave iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophene **6b** in 80% yield. Palladium acetate was also employed as the catalyst in this study. Thus, treatment of **7b** with 5 mol % of $Pd(OAc)_2$ at reflux THF for 48 h gave iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophene **6b** in only 45% yield and recovered 49% of starting material (eq 3). On the other hand, compound **7a** with



7b (Eq. 3)



7a — **6a**, 99% (Eq. 4)

phenyl group at the terminal alkyne reacted very fast with catalytic amount of iodine to give the benzo[*b*]naphtho[2,1-*d*]thiophene **6a** in almost quantitative yield (eq 4). With these data we can conclude that iodonium ion is electrophilic enough to promote the atom-transfer cyclization with more electron rich alkyne, such as compound **7a**. However, iodonium ion was found to be not electrophilic enough to promote the cyclization of the electron poor alkyne, such as compound **7b**; a highly eletrophilic transition metal, such as the gold or palladium catalyst, is needed. The gold catalyst with silver salt is more efficient to promote the iodo-transfer cyclization reaction than palladium catalyst.

In conclusion, we have developed an efficient cascade cyclization reaction of aryldiynes to provide halogenated benzo[*b*]naphtho[2,1-*d*]thiophene derivatives. With the described reaction conditions, we are able to synthesize the chlori-, bromi-, and iodinated benzo[*b*]naphtho[2,1-*d*]-thiophenes with either alkyl or aryl substituent at 7-position. Since benzo[*b*]naphtho[2,1-*d*]thiophenes are important molecules in material science, we believe that the chemistry described here will have a strong impact on the development of new materials.

EXPERIMENTAL SECTION

General Procedure of Sonogashira Coupling Reaction to Compound 1a. To a stirred solution of compound **5** (200.0 mg, 0.57 mmol) in Et_2O (15 mL) containing $Pd(PPh_3)_4$ (33.0 mg, 0.03 mmol) was added 1-pentyne (42.8 mg, 0.62 mmol), CuI (10.9 mg, 0.06 mmol) and *n*-$BuNH_2$ (50.2 mg, 0.68 mmol). The resulting solution was stirred at room temperature for 6 h. A saturated aqueous NH_4Cl solution was then added. The reaction mixture was extracted with EtOAc (20 mL × 2). The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography in silica gel (*n*-hexane as eluent) to give the products.

General Procedure of Sonogashira Coupling Reaction to Compound 3. To a stirred solution of 2-iodothioanisole (**2**) (2.57 g, 10.3 mmol) in Et_2O (30 mL) containing $Pd(PPh_3)_4$ (0.59 g, 0.51 mmol) was added trimethylsilylacetylene (1.11 g, 11.3 mmol), CuI (0.19 g, 1.0 mmol) and *n*-$BuNH_2$ (0.90 g, 12.3 mmol). The resulting solution was stirred at room temperature for 6 h. A saturated aqueous NH_4Cl solution was then added. The reaction mixture was extracted

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with EtOAc (50 mL × 2). The combined organic extracts were dried over anhydrous $MgSO_4$.

General Procedure of Desililation Reaction to Compound 4. A solution of compound **3** (1.0 g, 4.0 mmol) in the presence of TBAF (1.43 g, 5.45 mmol) in THF (20.0 mL) was stirred at room temperature for 30 min. The saturated aqueous solutions of NaCl were added subsequently into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

General Procedure of Sonogashira Coupling Reaction to Compound 5. To a stirred solution of compound **4** (1.53 g, 10.3 mmol) in Et_2O (20 mL) containing $Pd(PPh_3)_4$ (0.59 g, 0.51 mmol) was added 1,2-diiodobenzene (3.75 g, 11.4 mmol), CuI (0.19 g, 1.0 mmol) and *n*-$BuNH_2$ (0.90 g, 12.3 mmol). The resulting solution was stirred at room temperature for 6 h. A saturated aqueous NH_4Cl solution was then added. The reaction mixture was extracted with EtOAc (50 mL × 2). The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography in silica gel (*n*-hexane as eluent) to give the products.

General Procedure of Compound 6b. To a solution of copound **1b** (50 mg, 0.17 mmol) in the presence of NIS (77.5 mg, 0.34 mmol), Ph_3PAuCl (4.27 mg, 0.008 mmol) and $AgSbF_6$ (2.96 mg, 0.0086 mmol) was stirred in refluxing CH_2Cl_2 for 5 h. The saturated aqueous solutions of $Na_2S_2O_3$ were added subsequently into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_{4(S)}$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

General Procedure of Compound 7b. To a solution of compound **1b** (50 mg, 0.17 mmol) in the presence of I_2 (86.3 mg, 0.34 mmol) was stirred in CH_2Cl_2 at room temperature for 24 h. The saturated aqueous solution of NaCl was added subsequently into the reaction mixture and extracted by EtOAc. The combined organic extracts were dried over anhydrous $MgSO_{4(S)}$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

General Procedure of Compound 8a. To a solution of compound **1a** (50 mg, 0.15 mmol) in the presence of $CuCl_2$ (60.5 mg, 0.45 mmol), $PdCl_2$ (1.3 mg, 0.008 mmol) was stirred in refluxing THF for 24 h. The saturated aqueous solutions of $Na_2S_2O_3$ were added subsequently into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

General Procedure of Compound 10b. To a solution of copound **1b** (50 mg, 0.17 mmol) in the presence of $CuCl_2$ (40.3 mg, 0.30 mmol), Ph_3PAuCl (4.27 mg, 0.008 mmol) and $AgSbF_6$ (2.96 mg, 0.0086 mmol) was stirred in refluxing CH_2Cl_2 for 48 h. The saturated aqueous solutions of $Na_2S_2O_3$ were added subsequently into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

General Procedure of Compound 11b. To a solution of copound **1b** (50 mg, 0.17 mmol) in the presence of $CuBr_2$ (67.0 mg, 0.30 mmol), Ph_3PAuCl (4.27 mg, 0.008 mmol) and $AgSbF_6$ (2.96 mg, 0.0086 mmol) were stirred in refluxing CH_3CN for 48 h. The saturated aqueous solutions of $Na_2S_2O_3$ were added subsequently into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

Methyl(2-((2-(phenylethynyl)phenyl)ethynyl)phenyl)sulfane (1a). Yield 170.0 mg, 92%; A yellow solid: R_f = 0.34 (30:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.08−7.18 (m, 2H), 7.28−7.35 (m, 7H), 7.52−7.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 88.3, 90.8, 93.5, 94.6, 121.3, 123.5, 124.1, 124.1, 125.5, 125.7, 127.9, 128.1, 128.2, 128.3, 128.8, 131.9, 132.0, 132.2, 132.6, 141.9; mp 71−73 °C; MS (70 eV) *m*/*z* (%) 324 (21) [M^+], 309 (91), 308 (100); HRMS (ESI-TOF) Calcd for $C_{23}H_{16}S$, 324.0973, found 324.0972.

Methyl(2-((2-(pent-1-yn-1-yl)phenyl)ethynyl)phenyl)sulfane (1b). Yield 125.7 mg, 76%; A yellow oil: R_f = 0.43 (30:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.2 Hz, 3H), 1.64−1.69 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 7.09−7.32 (m, 5H), 7.42−7.58 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 13.6, 15.2, 21.8, 22.2, 79.5, 90.1, 94.8, 94.9, 121.6, 124.2, 125.5, 126.3, 127.2, 128.0, 128.7, 131.9, 132.1, 132.5, 141.6; MS (70 eV) *m*/*z* (%) 290 (11) [M^+], 246 (39), 247 (100); HRMS (ESI-TOF) Calcd for $C_{20}H_{18}S$, 290.1129, found 290.1126.

(2-((2-(Hept-1-yn-1-yl)phenyl)ethynyl)phenyl)(methyl)-sulfane (1c). Yield 81.8 mg, 45%; A brown oil: R_f = 0.24 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.31 (t, *J* = 8.0 Hz, 2H), 1.41−1.49 (m, 2H), 1.62−1.65 (m, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.24−7.27 (m, 2H), 7.31 (td, *J* = 8.0, 1.2 Hz, 1H), 7.43−7.45 (m, 1H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56−7.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 15.2, 19.9, 22.2, 28.5, 31.2, 79.4, 90.2, 94.8, 95.1, 121.6, 124.2, 124.2, 125.5, 126.4, 127.1, 128.0, 128.7, 131.9, 132.0, 132.6, 141.6; MS (70 eV) *m*/*z* (%) 318 (6) [M^+], 221 (72), 247 (100); HRMS (ESI-TOF) Calcd for $C_{22}H_{22}S$, 318.1442, found 318.1444.

(2-((2-(3,3-Dimethylbut-1-yn-1-yl)phenyl)ethynyl)phenyl)-(methyl)sulfane (1d). Yield 164.7 mg, 95%; A brown oil: R_f = 0.29 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.51 (s, 3H), 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.23−7.25 (m, 2H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.41−7.43 (m, 1H), 7.51 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.56−7.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 28.2, 31.0, 77.9, 90.1, 94.9, 103.0, 121.7, 124.2, 125.5, 126.3, 127.1, 128.0, 128.7, 131.9, 132.1, 132.4, 141.7; MS (70 eV) *m*/*z* (%) 304 (18) [M^+], 259 (54), 274 (100), 289 (80); HRMS (ESI-TOF) Calcd for $C_{21}H_{20}S$, 304.1286, found 304.1286.

Methyl(2-((2-(*o*-tolylethynyl)phenyl)ethynyl)phenyl)sulfane (1e). Yield 171.5 mg, 89%; A brown oil: R_f = 0.55 (50:1 Hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.51 (s, 3H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 7.13−7.16 (m, 2H), 7.19−7.25 (m, 2H), 7.29−7.33 (m, 3H), 7.48 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.55−7.64 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 20.9, 90.7, 92.1, 92.5, 94.7, 121.3, 123.2, 124.0, 124.1, 125.4, 125.4, 125.7, 127.8, 128.1, 128.3, 128.8, 129.3, 132.0, 132.2, 132.3, 132.5, 140.5, 142.0; MS (70 eV) *m*/*z* (%) 338 (17) [M^+], 321 (81), 323 (100); HRMS (ESI-TOF) Calcd for $C_{24}H_{18}S$, 338.1129, found 338.1127.

Methyl(2-((2-(*m*-tolylethynyl)phenyl)ethynyl)phenyl)sulfane (1f). Yield 185.0 mg, 96%; A brown oil: R_f = 0.30 (50:1 Hex/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.40 (s, 3H), 7.08−7.24 (m, 4H), 7.28−7.32 (m, 3H), 7.39−7.43 (m, 2H), 7.53−7.58 (m, 2H), 7.60−7.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 21.2, 88.0, 90.8, 93.8, 94.6, 121.4, 123.2, 124.0, 124.1, 125.6, 125.7, 127.8, 128.1, 128.1, 128.8, 128.9, 129.2, 131.9, 132.1, 132.6, 132.6, 137.8, 141.9; MS (70 eV) *m*/*z* (%) 338 (26) [M^+], 308 (100), 323 (73); HRMS (ESI-TOF) Calcd for $C_{24}H_{18}S$, 338.1129, found 338.1129.

Methyl(2-((2-(*p*-tolylethynyl)phenyl)ethynyl)phenyl)sulfane (1g). Yield 177.3 mg, 92%; A yellow oil: R_f = 0.30 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.41 (s, 3H), 7.09−7.19 (m, 4H), 7.29−7.33 (m, 3H), 7.49−7.64 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 21.5, 87.7, 90.8, 93.8, 94.6, 120.4, 121.4, 124.1, 124.1, 125.6, 125.7, 127.7, 128.0, 128.8, 129.0, 131.8, 131.9, 132.1, 132.6, 138.4, 141.8; MS (70 eV) *m*/*z* (%) 338 (18) [M^+], 57 (63), 308 (100), 323 (69); HRMS (ESI-TOF) Calcd for $C_{24}H_{18}S$, 338.1129, found 338.1127.

(2-((2-((4-Methoxyphenyl)ethynyl)phenyl)ethynyl)phenyl)-(methyl)sulfane (1h). Yield 191.7 mg, 95%; A brown oil: R_f = 0.26 (30:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.83 (s, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.29−7.33 (m, 3H), 7.52−7.63 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 55.3, 87.1, 90.7, 93.7, 94.7, 113.9, 115.6, 124.1, 124.2, 125.4, 125.9, 127.6, 128.1, 128.8, 131.8, 132.1, 132.6, 133.4, 141.8, 159.7; MS (70 eV) *m*/*z* (%) 354 (21) [M^+], 57

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(100), 295 (52), 339 (42); HRMS (ESI-TOF) Calcd for $C_{24}H_{18}OS$, 354.1078, found 354.1079.

(2-((2-((4-Chlorophenyl)ethynyl)phenyl)ethynyl)phenyl)-(methyl)sulfane (1i). Yield 200.0 mg, 98%; A brown oil: R_f = 0.21 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.11 (td, J = 7.6, 1.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.30−7.36 (m, 5H), 7.50−7.57 (m, 4H), 7.62−7.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 89.3, 90.9, 92.3, 94.4, 94.4, 121.2, 122.0, 124.1, 124.2, 125.2, 125.7, 128.1, 128.2, 128.5, 128.9, 131.9, 132.2, 132.5, 133.1, 134.3, 141.8; MS (70 eV) m/z (%) 360 (5) [M+2], 358 (12) [M$^+$], 308 (100); HRMS (ESI-TOF) Calcd for $C_{23}H_{15}ClS$, 358.0583, found 358.0584.

(2-((2-((4-Bromophenyl)ethynyl)phenyl)ethynyl)phenyl)-(methyl)sulfane (1j). Yield 224.6 mg, 98%; A yellow solid: R_f = 0.30 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.11 (td, J = 7.2, 1.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.30−7.35 (m, 3H), 7.47 (s, 4H), 7.51−7.53 (m, 1H), 7.62−7.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 89.5, 90.9, 92.4, 94.4, 121.1, 122.4, 122.5, 124.0, 124.1, 125.1, 125.7, 128.1, 128.2, 128.9, 131.4, 131.9, 132.2, 132.5, 133.3, 141.8; mp 105−107 °C; MS (70 eV) m/z (%) 404 (8) [M+2], 402 (8) [M$^+$], 308 (100); HRMS (ESI-TOF) Calcd for $C_{23}H_{15}BrS$, 402.0078, found 402.0080.

Methyl(2-((2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-ethynyl)phenyl)sulfane (1k). Yield 49.2 mg, 22%; A white solid: R_f = 0.45 (100:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.12 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.30−7.38 (m, 3H), 7.52 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.63−7.65 (m, 1H), 7.69 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 90.7, 91.1, 91.9, 94.3, 121.1, 124.0, 124.2, 124.8, 125.0, 125.1, 125.1, 126.0, 127.3, 128.2, 128.5, 129.0, 132.1, 132.1, 132.3, 132.5, 141.8; mp 106−107 °C; MS (70 eV) m/z (%) 392 (55) [M$^+$], 308 (100), 376 (75), 377 (73); HRMS (ESI-TOF) Calcd for $C_{24}H_{15}F_3S$, 392.0847, found 392.0850.

Trimethyl((2-(methylthio)phenyl)ethynyl)silane (3). Yield 2.22 g, 98%; A yellow oil: R_f = 0.41 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.28 (s, 9H), 2.45 (s, 3H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.26−7.29 (m, 1H), 7.42 (dd, J = 7.5, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1, 14.9, 101.4, 102.1, 121.1, 123.9, 124.0, 128.9, 132.6, 142.0; MS (70 eV) m/z (%) 220.0 (11) [M$^+$], 153.0 (35), 89.0 (59), 77.0 (100); HRMS (ESI-TOF) Calcd for $C_{12}H_{16}SiS$, 220.0742, found 220.0742.

(2-Ethynylphenyl)(methyl)sulfane (4). Yield 0.56 g, 96%; A brown oil: R_f = 0.38 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.47 (s, 1H), 7.09 (td, J = 7.6, 1.2 Hz, 1H), 7.17 (d, J = 8 Hz, 1H), 7.32 (td, J = 7.6, 1.2 Hz, 1H), 7.46 (td, J = 7.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 81.0, 83.5, 120.2, 124.3, 129.3, 133.1, 141.8; MS (70 eV) m/z (%) 149 (100) [M+1], 71 (51), 57 (67); HRMS (ESI-TOF) Calcd for C_9H_8S, 148.0347, found 148.0347.

(2-((2-Iodophenyl)ethynyl)phenyl)(methyl)sulfane (5). Yield 1.98 g, 55%; A yellow oil: R_f = 0.46 (20:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.02 (td, J = 7.6, 1.6 Hz, 1H), 7.11−7.21 (m, 2H), 7.31−7.36 (m, 2H), 7.59 (d, J = 8.0, 1.2 Hz, 2H), 7.88 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 90.5, 97.4, 100.5, 121.0, 124.2, 124.3, 127.7, 129.1, 129.4, 129.8, 132.7, 132.9, 138.7, 141.8; MS (70 eV) m/z (%) 350 (92) [M$^+$], 208 (63), 221 (98), 223 (100); HRMS (ESI-TOF) Calcd for $C_{15}H_{11}IS$, 349.9626, found 349.9627.

5-Iodo-6-phenylbenzo[*b*]naphtho[2,1-*d*]thiophene (6a). Yield 59.3 mg, 80%; A yellow solid: R_f = 0.48 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (dd, J = 8.4, 0.8 Hz, 1H), 7.07 (td, J = 7.6, 1.2 Hz, 1H), 7.32−7.37 (m, 3H), 7.61−7.70 (m, 5H), 7.88 (d, J = 8.4 Hz, 1H), 8.13−8.17 (m, 1H), 8.46−8.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.6, 122.6, 124.2, 124.8, 124.9, 125.9, 127.3, 128.3, 128.4, 128.4, 129.1, 129.5, 131.6, 132.6, 134.5, 136.2, 138.8, 139.1, 142.2, 145.5; mp 140−142 °C; MS (70 eV) m/z (%) 436 (100) [M$^+$], 69 (72), 308 (76); HRMS (ESI-TOF) Calcd for $C_{22}H_{13}IS$, 435.9783, found 435.9781.

5-Iodo-6-propylbenzo[*b*]naphtho[2,1-*d*]thiophene (6b). Yield 62.9 mg, 92%; A white solid: R_f = 0.52 (Hex); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.29 (t, J = 7.8 Hz, 3H), 1.90 (h, J = 9.6 Hz, 2H), 3.66−3.72 (b, 2H), 7.49−7.65 (m, 4H), 7.98−8.00 (m, 1H), 8.09−8.10 (m, 1H), 8.29 (d, J = 7.8 Hz, 1H), 8.44−8.45 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 21.9, 43.0, 105.6, 123.1, 124.7, 124.9, 124.9, 125.8, 126.6, 127.8, 128.1, 131.3, 133.0, 134.3, 136.3, 139.0, 139.7, 141.4; mp 112−113 °C; MS (70 eV) m/z (%) 402 (35) [M$^+$], 69 (100), 81 (44); HRMS (ESI-TOF) Calcd for $C_{19}H_{15}IS$, 401.9939, found 401.9942.

5-Iodo-6-pentylbenzo[*b*]naphtho[2,1-*d*]thiophene (6c). Yield 59.9 mg, 82%; A yellow solid: R_f = 0.67 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, J = 7.6 Hz, 3H), 1.48−1.57 (m, 2H), 1.65−1.72 (m, 2H), 1.81−1.89 (m, 2H), 3.65−3.69 (brs, 2H), 7.46−7.63 (m, 4H), 7.95−7.98 (m, 1H), 8.04−8.07 (m, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.41−8.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.5, 28.1, 32.0, 41.2, 105.5, 123.1, 124.7, 124.8, 124.9, 125.7, 126.6, 127.8, 128.0, 131.3, 133.0, 134.2, 136.3, 139.0, 139.7, 141.5; mp 90−93 °C; MS (70 eV) m/z (%) 430 (26) [M$^+$], 57 (55), 69 (100), 247 (68); HRMS (ESI-TOF) Calcd for $C_{21}H_{19}IS$, 430.0252, found 430.0250.

6-(*tert*-Butyl)-5-iodobenzo[*b*]naphtho[2,1-*d*]thiophene (6d). Yield 14.1 mg, 20%; A brown oil: R_f = 0.66 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 9H), 7.48−7.70 (m, 4H), 7.94−7.96 (m, 1H), 8.74−8.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8, 40.8, 100.9, 121.7, 123.3, 124.7, 124.7, 125.8, 126.3, 127.2, 128.5, 131.3, 134.7, 135.1, 135.7, 138.8, 139.0, 145.8; MS (70 eV) m/z (%) 416 (22) [M$^+$], 61 (81), 69 (100), 70 (56); HRMS (ESI-TOF) Calcd for $C_{20}H_{17}IS$, 416.0096, found 416.0092.

5-Iodo-6-(*o*-tolyl)benzo[*b*]naphtho[2,1-*d*]thiophene (6e). Yield 72.7 mg, 92%; A brown oil: R_f = 0.50 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 6.45 (d, J = 8.8 Hz, 1H), 7.09 (td, J = 8.0, 0.8 Hz, 1H), 7.20 (dd, J = 7.2, 0.8 Hz, 1H), 7.36 (td, J = 7.2, 1.2 Hz, 1H), 7.43−7.56 (m, 3H), 7.66−7.71 (m, 2H), 7.90 (dd, J = 8.0, 0.8 Hz, 1H), 8.16−8.20 (m, 1H), 8.46−8.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 104.6, 122.6, 124.2, 124.6, 124.8, 126.0, 126.8, 127.3, 128.2, 128.4, 128.8, 129.4, 130.5, 131.4, 132.8, 134.3, 136.3, 136.3, 138.8, 139.3, 142.2, 144.6; MS (70 eV) m/z (%) 450 (37) [M$^+$], 57 (88), 69 (100), 71 (57); HRMS (ESI-TOF) Calcd for $C_{23}H_{15}IS$, 449.9939, found 449.9939.

5-Iodo-6-(*m*-tolyl)benzo[*b*]naphtho[2,1-*d*]thiophene (6f). Yield 55.8 mg, 73%; A brown oil: R_f = 0.49 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 6.47 (dd, J = 8.4, 0.8 Hz, 1H), 7.08 (td, J = 8.4, 0.8 Hz, 1H), 7.14−7.16 (m, 2H), 7.35 (td, J = 8.0, 0.8 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.89 (dt, J = 8.0, 0.8 Hz, 1H), 8.14−8.18 (m, 1H), 8.46−8.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 104.5, 122.6, 124.2, 124.8, 125.1, 125.9, 126.5, 127.3, 128.2, 128.4, 128.9, 129.1, 130.0, 131.7, 132.6, 134.5, 136.3, 138.8, 139.0, 143.0, 145.3; MS (70 eV) m/z (%) 450 (17) [M$^+$], 57 (100), 71 (64); HRMS (ESI-TOF) Calcd for $C_{23}H_{15}IS$, 449.9939, found 449.9940.

5-Iodo-6-(*p*-tolyl)benzo[*b*]naphtho[2,1-*d*]thiophene (6g). Yield 61.2 mg, 80%; A yellow solid: R_f = 0.48 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 6.52 (d, J = 8.0 Hz, 1H), 7.09 (td, J = 8.4, 1.2 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.35 (td, J = 8.4, 1.2 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.63−7.70 (m, 2H), 7.89 (d, J = 8.4 Hz, 1H), 8.13−8.17 (m, 1H), 8.45−8.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 105.9, 122.5, 124.2, 124.8, 125.0, 125.9, 127.3, 128.2, 128.4, 129.3, 129.8, 131.8, 132.6, 134.5, 136.4, 138.1, 138.8, 139.0, 142.5, 142.9; mp 151−153 °C; MS (70 eV) m/z (%) 450 (100) [M$^+$], 57 (82), 71 (53); HRMS (ESI-TOF) Calcd for $C_{23}H_{15}IS$, 449.9939, found 449.9941.

5-Iodo-6-(4-methoxyphenyl)benzo[*b*]naphtho[2,1-*d*]-thiophene (6h). Yield 53.1 mg, 67%; A brown solid: R_f = 0.43 (50:1 Hex/EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.99 (s, 3H), 6.57 (d, J = 8.4 Hz, 1H), 7.11 (t, J = 8.4 Hz, 1H), 7.14−7.16 (m, 2H), 7.24−7.26 (m, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.24−7.26 (m, 2H), 7.65−7.69 (m, 2H), 7.89 (d, J = 8.4 Hz, 1H), 8.14−8.17 (m, 1H), 7.46−7.48 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.4, 105.8, 114.4, 122.6, 124.3, 124.8, 125.0, 125.9, 127.3, 128.2, 128.4, 130.6, 132.1, 132.7, 134.6, 136.4, 138.0, 138.8, 139.0, 142.5, 159.6; mp 200−202 °C; MS (70 eV) m/z (%) 466 (63) [M$^+$], 85 (45), 71 (65), 57 (100); HRMS (ESI-TOF) Calcd for $C_{23}H_{15}IOS$, 465.9888, found 465.9888.

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6-(4-Chlorophenyl)-5-iodobenzo[*b*]naphtho[2,1-*d*]-thiophene (6i). Yield 60.3 mg, 76%; A yellow solid: R_f = 0.52 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, J = 8.4 Hz, 1H), 7.13 (td, J = 8.0, 1.2 Hz, 1H), 7.26−7.29 (m, 2H), 7.37 (td, J = 8.4, 1.2 Hz, 1H), 7.59−7.69 (m, 4H), 7.89 (d, J = 8.4 Hz, 1H), 8.13−8.15 (m, 1H), 8.43−8.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.7, 122.7, 124.4, 124.7, 124.8, 126.0, 127.6, 128.4, 128.5, 129.5, 131.0, 131.3, 132.5, 134.4, 134.5, 136.0, 138.8, 139.2, 141.4, 143.8; mp 163−164 °C; MS (70 eV) m/z (%) 472 (38) [M+2], 470 (100) [M$^+$], 308 (65); HRMS (ESI-TOF) Calcd for $C_{22}H_{12}ClIS$, 469.9393, found 469.9391.

6-(4-Bromophenyl)-5-iodobenzo[*b*]naphtho[2,1-*d*]-thiophene (6j). Yield 58.5 mg, 67%; A yellow solid: R_f = 0.52 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, J = 8.8 Hz, 1H), 7.14 (td, J = 8.8, 1.2 Hz, 1H), 7.20−7.24 (m, 2H), 7.37 (td, J = 8.0, 1.2 Hz, 1H), 7.65−7.70 (m, 2H), 7.74−7.78 (m, 2H), 7.89 (dd, J = 8.0, 0.8 Hz, 1H), 8.12−8.16 (m, 1H), 8.43−8.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.6, 122.6, 122.7, 124.4, 124.7, 124.8, 126.0, 127.6, 128.4, 128.5, 131.2, 131.4, 131.4, 132.5, 134.5, 136.0, 1138.8, 139.3, 141.3, 144.2; mp 175−177 °C; MS (70 eV) m/z (%) 516 (64) [M+2], 514 (60) [M$^+$], 69 (100); HRMS (ESI-TOF) Calcd for $C_{22}H_{12}BrIS$, 513.8888, found 513.8889.

5-Iodo-6-(4-(trifluoromethyl)phenyl)benzo[*b*]naphtho[2,1-*d*]thiophene (6k). Yield 73.7 mg, 86%; A yellow solid: R_f = 0.52 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 8.4 Hz, 1H), 7.09 (td, J = 8.0, 0.8 Hz, 1H), 7.37 (td, J = 8.0, 0.8 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.66−7.72 (m, 2H), 7.90 (dd, J = 8.0, 0.4 Hz, 3H), 8.14−8.18 (m, 1H), 8.43−8.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.0, 122.8, 124.4, 124.5, 124.9, 126.2, 126.2, 126.2, 127.7, 128.5, 128.6, 130.2, 132.4, 134.5, 135.8, 138.9, 139.4, 141.1, 148.9; mp 153−156 °C; MS (70 eV) m/z (%) 504 (12) [M$^+$], 77 (28), 151 (100); HRMS (ESI-TOF) Calcd for $C_{23}H_{12}F_3IS$, 503.9656, found 503.9654.

3-Iodo-2-(2-(pent-1-yn-1-yl)phenyl)benzo[*b*]thiophene (7b). Yield 58.1 mg, 85%; A yellow oil: R_f = 0.49 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, J = 7.2 Hz, 3H), 1.35−1.44 (m, 2H), 2.23 (t, J = 7.2 Hz, 2H), 7.36−7.50 (m, 5H), 7.54−7.57 (m, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 21.5, 21.8, 79.2, 95.2, 119.0, 122.1, 122.3, 124.8, 124.9, 125.3, 127.3, 128.8, 131.0, 132.6, 134.0, 135.6, 136.9, 137.7; MS (70 eV) m/z (%) 402 (41) [M$^+$], 245 (77), 247 (89), 275 (100); HRMS (ESI-TOF) Calcd for $C_{19}H_{15}IS$, 401.9939, found 401.9937.

2-(2-(3,3-Dimethylbut-1-yn-1-yl)phenyl)-3-iodobenzo[*b*]-thiophene (7d). Yield 49.5 mg, 70%; A brown oil: R_f = 0.57 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 9H), 7.36−7.53 (m, 6H), 7.81 (dd, J = 8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8, 30.4, 77.5, 82.6, 103.4, 122.0, 125.0, 125.2, 125.3, 125.8, 127.2, 128.9, 130.6, 131.8, 137.3, 139.3, 141.1, 142.0; MS (70 eV) m/z (%) 416 (28) [M$^+$], 258 (61), 259 (71), 289 (100); HRMS (ESI-TOF) Calcd for $C_{20}H_{17}IS$, 416.0096, found 416.0097.

5-Chloro-6-phenylbenzo[*b*]naphtho[2,1-*d*]thiophene (8a). Yield 39.2 mg, 76%; A yellow solid: R_f = 0.48 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ (d, J = 8.0 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.41−7.43 (m, 2H), 7.60−7.62 (m, 3H), 7.68−7.72 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 8.20−8.22 (m, 1H), 8.48−8.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.6, 124.2, 124.7, 124.7, 125.9, 126.2, 127.3, 127.6, 128.3, 128.7, 128.9, 129.1, 129.1, 129.5, 131.4, 135.3, 136.4, 136.9, 138.9, 139.1; mp 141−143 °C; MS (70 eV) m/z (%) 61 (100), 70 (55), 344 (64) [M$^+$], 346 (26) [M +2]; HRMS (ESI-TOF) Calcd for $C_{22}H_{13}ClS$, 344.0426, found 344.0428.

5-Chloro-6-propylbenzo[*b*]naphtho[2,1-*d*]thiophene (8b). Yield 40.9 mg, 88%; A white solid: R_f = 0.57 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.6 Hz, 3H), 1.86−1.96 (m, 2H), 3.58−3.63 (m, 2H), 7.48−7.56 (m, 2H), 7.60−7.69 (m, 2H), 7.99 (d, J = 7.6 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 7.6 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.9, 33.4, 123.1, 124.6, 124.6, 124.9, 125.7, 125.9, 126.6, 127.4, 127.9, 129.1, 129.3, 131.5, 135.2, 136.5, 137.4, 139.3; mp 102−104 °C; MS (70 eV) m/z (%) 245 (30), 281 (81), 310 (100) [M$^+$], 312 (34) [M+2]; HRMS (ESI-TOF) Calcd for $C_{19}H_{15}ClS$, 310.0583, found 310.0580.

5-Chloro-6-pentylbenzo[*b*]naphtho[2,1-*d*]thiophene (8c). Yield 42.1 mg, 83%; A white solid: R_f = 0.59 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 3H), 1.48 (x, J = 7.5 Hz, 2H), 1.64 (p, J = 7.5 Hz, 2H), 1.82−1.89 (m, 2H), 3.59 (t, J = 8.0 Hz, 2H), 7.47−7.54 (m, 2H), 7.58−7.67 (m, 2H), 7.97 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.43 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 28.2, 31.5, 32.0, 123.1, 124.6, 124.7, 124.8, 125.7, 125.8, 126.5, 127.4, 127.9, 129.0, 129.3, 131.4, 135.4, 136.4, 137.4, 139.2; mp 90−91 °C; MS (70 eV) m/z (%) 61 (100), 178 (98), 338 (76) [M$^+$], 340 (28) [M+2]; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}ClS$, 338.0896, found 338.0893.

5-Chloro-6-(*o*-tolyl)benzo[*b*]naphtho[2,1-*d*]thiophene (8e). Yield 44.6 mg, 83%; A yellow oil: R_f = 0.47 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 3H), 6.54 (d, J = 8.5 Hz, 1H), 7.07 (t, J = 8.0 Hz, 1H), 7.24−7.26 (m, 1H), 7.33−7.52 (m, 4H), 7.67−7.72 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 8.20−8.22 (m, 1H), 8.48−8.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.6, 124.0, 124.6, 124.8, 125.9, 126.1, 126.7, 127.3, 127.5, 128.7, 128.7, 128.7, 129.2, 129.3, 130.4, 131.2, 134.6, 136.4, 136.7, 137.0, 138.2, 139.1; mp 124−127 °C; MS (70 eV) m/z (%) 61 (100), 70 (35), 358 (24) [M$^+$], 360 (9) [M+2]; HRMS (ESI-TOF) Calcd for $C_{23}H_{15}ClS$, 358.0583, found 358.0584.

5-Chloro-6-(*m*-tolyl)benzo[*b*]naphtho[2,1-*d*]thiophene (8f). Yield 36.5 mg, 68%; A yellow oil: R_f = 0.47 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.47 (s, 3H), 6.61 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 8.5 Hz, 1H), 7.21−7.22 (m, 2H), 7.34 (t, J = 7.0 Hz, 1H), 7.39−7.41 (m, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.67−7.72 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 8.19−8.21 (m, 1H), 8.48−8.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 122.6, 124.2, 124.7, 124.8, 125.8, 126.1, 126.4, 127.3, 127.6, 128.7, 128.8, 128.9, 129.0, 129.1, 130.0, 131.5, 135.5, 136.4, 136.8, 138.8, 138.8, 139.1; MS (70 eV) m/z (%) 61 (96), 358 (100) [M$^+$], 360 (39) [M+2]; HRMS (ESI-TOF) Calcd for $C_{23}H_{15}ClS$, 358.0583, found 358.0585.

5-Chloro-6-(*p*-tolyl)benzo[*b*]naphtho[2,1-*d*]thiophene (8g). Yield 40.3 mg, 75%; A yellow oil: R_f = 0.47 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.55 (s, 3H), 6.66 (d, J = 8.5 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 7.29−7.31 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.41−7.43 (m, 2H), 7.67−7.71 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 8.19−8.21 (m, 1H), 8.47−8.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.6, 124.2, 124.7, 124.8, 125.8, 126.2, 127.3, 127.6, 128.7, 129.0, 129.1, 129.3, 129.8, 131.6, 135.4, 135.9, 136.5, 136.8, 138.0, 139.1; MS (70 eV) m/z (%) 57 (37), 358 (100) [M$^+$], 360 (40) [M+2]; HRMS (ESI-TOF) Calcd for $C_{23}H_{15}ClS$, 358.0583, found 358.0585.

5-Chloro-6-(4-methoxyphenyl)benzo[*b*]naphtho[2,1-*d*]-thiophene (8h). Yield 43.7 mg, 78%; A yellow solid: R_f = 0.19 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 6.71 (d, J = 8.5 Hz, 1H), 7.09−7.15 (m, 3H), 7.32−7.36 (m, 3H), 7.66−7.71 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 9.0 Hz, 1H), 8.48 (d, J = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 114.5, 122.6, 124.3, 124.7, 124.8, 125.8, 126.2, 127.3, 127.5, 128.7, 129.1, 129.4, 130.6, 131.2, 131.9, 135.0, 136.5, 136.8, 139.1, 159.5; mp 180−182 °C; MS (70 eV) m/z (%) 57 (100), 71 (68), 374 (84) [M$^+$], 376 (33) [M+2]; HRMS (ESI-TOF) Calcd for $C_{23}H_{15}ClOS$, 374.0532, found 374.0533.

5-Chloro-6-(4-chlorophenyl)benzo[*b*]naphtho[2,1-*d*]-thiophene (8i). Yield 49.9 mg, 88%; A yellow solid: R_f = 0.45 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (d, J = 8.5 Hz, 3H), 7.13 (t, J = 8.0 Hz, 1H), 7.35−7.39 (m, 3H), 7.59 (d, J = 8.5 Hz, 2H), 7.69−7.73 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 8.20−8.22 (m, 1H), 8.46−8.48 (m, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.8, 124.4, 124.5, 124.8, 126.0, 126.2, 127.6, 127.7, 128.8, 129.0, 129.0, 129.4, 131.0, 131.1, 133.9, 134.3, 136.1, 137.0, 137.3, 139.1; mp 156−158 °C; MS (70 eV) m/z (%) 61 (100), 378 (22) [M$^+$], 380 (16) [M+2]; HRMS (ESI-TOF) Calcd for $C_{22}H_{12}Cl_2S$, 378.0037, found 378.0038.

6-(4-Bromophenyl)-5-chlorobenzo[*b*]naphtho[2,1-*d*]-thiophene (8j). Yield 53.8 mg, 85%; A yellow solid: R_f = 0.46 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (d, J = 8.5 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 8.0 Hz, 1H), 7.68−7.75 (m, 4H), 7.90 (d, J = 8.5 Hz, 1H), 8.19−8.21 (m, 1H), 8.46−8.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.5, 122.8, 124.4, 124.5, 124.8, 126.0, 126.2, 127.6, 127.7, 128.2, 128.9, 129.0, 131.0, 131.3, 132.4, 133.9, 136.1, 137.1, 137.8, 139.1; mp 176−177 °C; MS (70 eV)

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m/*z* (%) 61 (100), 70 (52), 422 (4) [M$^+$], 424 (4) [M+2]; HRMS (ESI-TOF) Calcd for $C_{22}H_{12}BrClS$, 421.9532, found 421.9533.

5-Chloro-6-(4-(trifluoromethyl)phenyl)benzo[*b*]naphtho-[2,1-*d*]thiophene (8k). Yield 49.4 mg, 80%; A yellow solid: R_f = 0.55 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.54 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.0 Hz, 1H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.70−7.72 (m, 2H), 7.87−7.91 (m, 2H), 8.20−8.21 (m, 1H), 8.46−8.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.9, 124.2, 124.4, 124.8, 126.1, 126.1, 127.7, 127.8, 128.8, 128.9, 128.9, 130.2, 130.7, 133.7, 135.9, 137.2, 139.1, 142.7, 142.7; mp 146−148 °C; MS (70 eV) *m*/*z* (%) 376 (38), 412 (100) [M$^+$], 414 (41) [M+2]; HRMS (ESI-TOF) Calcd for $C_{23}H_{12}ClF_3S$, 412.0300, found 412.0297.

5-Bromo-6-phenylbenzo[*b*]naphtho[2,1-*d*]thiophene (9a). Yield 45.4 mg, 78%; A yellow solid: R_f = 0.43 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 8.5 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.38−7.41 (m, 2H), 7.60−7.63 (m, 3H), 7.67−7.72 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.20−8.21 (m, 1H), 8.51−8.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.2, 122.6, 124.3, 124.8, 124.8, 125.9, 127.4, 127.9, 128.3, 128.8, 129.0, 129.1, 129.4, 130.3, 131.7, 136.3, 137.8, 137.8, 139.0, 141.2; mp 132−134 °C; MS (70 eV) *m*/*z* (%) 390 (87) [M+2], 388 (88) [M$^+$], 308 (100); HRMS (ESI-TOF) Calcd for $C_{22}H_{13}BrS$, 387.9921, found 387.9921.

5-Bromo-6-propylbenzo[*b*]naphtho[2,1-*d*]thiophene (9b). Yield 46.7 mg, 88%; A white solid: R_f = 0.45 (Hex); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.8 Hz, 3H), 1.88−1.94 (m, 2H), 3.63−3.66 (m, 2H), 7.49−7.56 (m, 2H), 7.59−7.67 (m, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 21.9, 36.8, 123.1, 123.1, 124.6, 124.7, 124.9, 125.7, 126.6, 127.7, 128.1, 128.8, 130.6, 131.7, 136.4, 137.4, 138.3, 139.2; mp 109−111 °C; MS (70 eV) *m*/*z* (%) 356 (100) [M+2], 354 (94) [M$^+$], 69 (99), 246 (85); HRMS (ESI-TOF) Calcd for $C_{19}H_{15}BrS$, 354.0078, found 354.0078.

5-Bromo-6-(4-methoxyphenyl)benzo[*b*]naphtho[2,1-*d*]-thiophene (9h). Yield 55.8 mg, 89%; A yellow solid: R_f = 0.19 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 6.64 (d, *J* = 7.6 Hz, 1H), 7.09−7.16 (m, 3H), 7.29−7.38 (m, 4H), 7.66−7.72 (m, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 8.19−8.21 (m, 1H), 8.50−8.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 114.4, 122.6, 123.0, 124.3, 124.7, 124.9, 125.9, 127.3, 127.8, 128.8, 129.1, 130.3, 130.5, 132.2, 133.6, 136.5, 139.0, 159.5; mp 142−144 °C; MS (70 eV) *m*/*z* (%) 57 (90), 71 (61), 418 (92) [M$^+$], 420 (100) [M+2]; HRMS (ESI-TOF) Calcd for $C_{23}H_{15}BrOS$, 418.0027, found 418.0023.

5-Bromo-6-(4-(trifluoromethyl)phenyl)benzo[*b*]naphtho-[2,1-*d*]thiophene (9k). Yield 57.5 mg, 84%; A yellow solid: R_f = 0.52 (Hex); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.48 (d, *J* = 7.8 Hz, 1H), 7.10 (td, *J* = 8.4, 1.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.71−7.74 (m, 2H), 7.88−7.93 (m, 3H), 8.22−8.23 (m, 1H), 8.50−8.52 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 122.0, 122.8, 124.3, 124.5, 124.8, 126.1, 126.1, 127.7, 128.1, 129.0, 130.1, 130.1, 130.4, 130.7, 131.0, 135.9, 136.2, 138.1, 139.0, 144.8, 144.8; mp 160−162 °C; MS (70 eV) *m*/*z* (%) 458 (100) [M+2], 456 (93) [M$^+$], 57 (81), 69 (62); HRMS (ESI-TOF) Calcd for $C_{23}H_{12}BrF_3S$, 455.9795, found 455.9792.

3-Chloro-2-(2-(pent-1-yn-1-yl)phenyl)benzo[*b*]thiophene (10b). Yield 44.8 mg, 85%; A yellow oil: R_f = 0.50 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, *J* = 7.2 Hz, 3H), 1.37−1.43 (m, 2H), 2.23 (t, *J* = 6.8 Hz, 2H), 7.36−7.50 (m, 5H), 7.55−7.57 (m, 1H), 7.81−7.84 (m, 1H), 7.87−7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 21.5, 21.8, 79.2, 95.2, 119.0, 122.1, 122.2, 124.8, 124.9, 125.3, 127.3, 128.8, 131.0, 132.6, 134.0, 135.6, 136.9, 137.7; MS (70 eV) *m*/*z* (%) 312 (31) [M+2], 310 (81) [M$^+$], 245 (92), 247 (100); HRMS (ESI-TOF) Calcd for $C_{19}H_{15}ClS$, 310.0583, found 310.0585.

3-Bromo-2-(2-(pent-1-yn-1-yl)phenyl)benzo[*b*]thiophene (11b). Yield 30.7 mg, 51%; A brown oil: R_f = 0.50 (40:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.5 Hz, 3H), 1.34−1.38 (m, 2H), 2.20 (t, *J* = 7.0 Hz, 2H), 7.34−7.49 (m, 5H), 7.53−7.55 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 21.5, 21.7, 79.1, 95.2, 107.6, 122.1, 123.4, 124.9, 125.3, 127.2, 128.8, 131.0, 132.5, 135.0, 137.6, 138.3, 138.5; MS (70 eV) *m*/*z* (%) 356 (57) [M+2], 354 (53) [M$^+$], 245 (93), 247 (100); HRMS (ESI-TOF) Calcd for $C_{19}H_{15}BrS$, 354.0078, found 354.0081.

3-Chloro-2-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)benzo[*b*]-thiophene (10d). Yield 20.3 mg, 95%; A colorless oil: R_f = 0.77 (10:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 9H), 7.34−7.53 (m, 6H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 77.6, 103.1, 122.0, 122.2, 124.8, 124.9, 125.2, 127.2, 128.7, 130.8, 132.1; MS (70 eV) *m*/*z* (%) 326 (27) [M+2], 324 (81) [M$^+$], 289 (51), 274 (100), 259 (92); HRMS (ESI-TOF) Calcd for $C_{20}H_{17}ClS$, 324.0739, found 324.0742.

3-Bromo-2-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)benzo[*b*]-thiophene (11d). Yield 23.7 mg, 98%; A pale yellow oil: R_f = 0.78 (10:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 9H), 7.35−7.53 (m. 6H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl^3$) δ 30.4, 77.5, 103.2, 107.7, 122.0, 123.3, 124.9, 125.2, 127.2, 128.8, 130.7, 132.0, 135.3, 137.6, 138.2, 138.3; MS (70 eV) *m*/*z* (%) 370 (25) [M+2], 368 (24) [M$^+$], 289 (100), 259 (75); HRMS (ESI-TOF) Calcd for $C_{20}H_{17}BrS$, 368.0234, found 368.0233.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full spectral data for all new compounds. This material is free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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