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Rhodium-Catalyzed Dehydrogenative Coupling of Phenylheteroarenes with Alkynes or Alkenes

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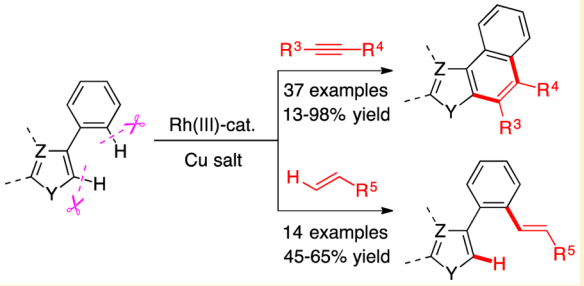
Supporting Information

ABSTRACT: Benzo-fused tri- to heptacyclic heteroarenes were effectively constructed by the rhodium-catalyzed dehydrogenative coupling of phenylheteroarenes with alkynes. Using alkenes as coupling partners, dehydrogenative alkenylation took place selectively on the phenyl moiety of phenylheteroarenes. Several experiments with deuterium-labeled substrates indicated that double C−H bond cleavages take place even in the reaction with alkenes.



INTRODUCTION

Benzo-fused heteroarene frameworks can be seen in various fine chemicals including organic materials[1] and pharmaceuticals.[2] Therefore, the development of simple and straightforward synthetic methods for constructing the fused compounds has attracted much attention. One of the most promising procedures is the transition-metal-catalyzed dehydrogenative coupling of aromatic substrates possessing a heteroatom-containing directing group with internal alkynes involving regioselective C−H bond cleavage at the ortho-position of the directing group.[3] So far, numerous reports for constructing benzo-fused oxygen-, nitrogen-, phosphorus-, and sulfur-containing heterocycles have been disclosed (Scheme 1a). Besides such σ-coordinating directing groups, π-electron units such as alkenyl, alkynyl, aryl, and cyano functions have been found to act as directing groups for ortho C−H functionalization.[4] We conceived that more highly fused polycyclic heteroarenes can be easily prepared if heteroaryl groups can be employed as directing groups in the dehydrogenative coupling with alkynes.[5] Indeed, tricyclic naphthothiophene structures could be constructed by a single treatment of 3-phenylthiophenes with alkynes under rhodium catalysis.[6,7] This reaction seems to proceed via π-electron-directed C−H bond cleavage to form a rhodacycle intermediate, alkyne insertion, and reductive elimination (Scheme 1b, Y = S, Z = CH). We succeeded in applying this procedure to constructing tri- to heptacyclic benzo-fused heteroarene derivatives **3** and **4** from readily available phenyl- or diphenylheteroarenes **1** and alkynes **2**. The oxidative coupling of 3-phenylthiophene with alkenes **5** also proceeded smoothly in the presence of a same catalyst system to form the corresponding 2′-alkenylated product **6** (Scheme 1c). New mechanistic insights were obtained for the latter reaction by some deuterium-labeling experiments. The detailed results obtained for these reactions are described herein.

RESULTS AND DISCUSSION

The reaction of 3-phenylthiophene (**1a**) with diphenylacetylene (**2a**) was explored to screen the reaction conditions, as shown in Table S1 (see Supporting Information). The desired dehydrogenative coupling product, 4,5-diphenylnaphtho[2,1-*b*]thiophene (**3aa**), was obtained in 84% yield by treatment of **1a** (0.2 mmol) with **2a** (0.1 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.2 mmol), and Cs_2CO_3 (0.03 mmol), as catalyst, oxidant, and additive, respectively, in toluene (1 mL) at 125 °C for 7 h under N_2 (entry 1 in Table 1). Doubling of the reaction scale did not affect the reaction efficiency (entry 2). Under the optimized conditions, bis(4-substituted phenyl)acetylenes possessing electron-donating (**2b**−**e**) and -withdrawing (**2f**−**h**) groups also underwent coupling with **1a** to give the corresponding naphthothiophenes **3ab**−**ah** in 54−86% yields (entries 3−9). The reaction of **1a** with di(2-naphthyl)acetylene (**2i**) proceeded efficiently to produce 4,5-di(2-naphthyl)naphtho-[2,1-*b*]thiophene (**3ai**) in 75% yield (entry 10). Besides diarylacetylenes, dialkylacetylenes such as 4-octyne (**2j**) and 8-hexadecyne (**2k**) also coupled with **1a** smoothly to afford dialkylnaphthothiophenes **3aj** and **3ak** (entries 11 and 12). The latter reaction could be readily scaled up to a gram scale. Thus, from **1a** (10 mmol) and **2k** (5 mmol), **3ak** was obtained in 56% yield (1.07 g, entry 13). Contrastingly, more functionalized alkynes, such as 2,5-dimethyl-3-hexyne-2,5-diol (**2l**) and dimethyl acetylenedicarboxylate (**2m**), did not react with **1a** at all (entries 14 and 15). It is possible that these alkynes

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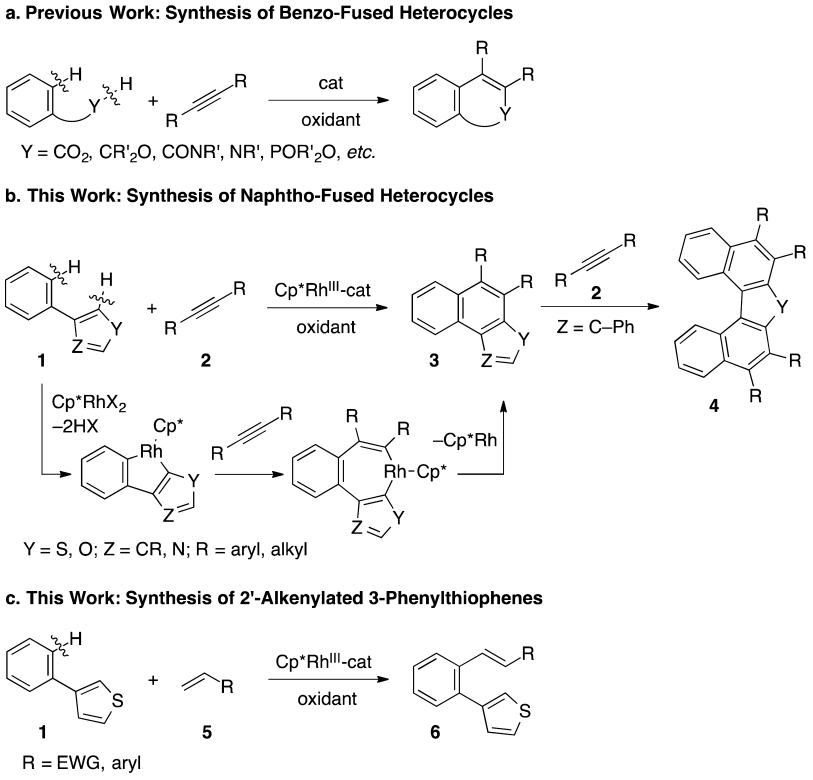
Scheme 1. Dehydrogenative Coupling of Arenes Possessing a Directing Group



deactivate the catalyst. The reaction of **1a** with an unsymmetrical alkyne, 1-phenyl-1-propyne (**2n**), produced 5-methyl-4-phenylnaphthothiophene derivative **3an** predominantly, along with a minor amount of its 4-methyl-5-phenyl derivative **3an′** (entry 16).

Next, we examined the reactions of variously substituted 3-phenylthiophenes **1b–i** with alkyne **2a** or **2j** (Scheme 2). Methyl, methoxy, chloro, phenyl, fluoro, and methoxycarbonyl substituents on either the phenyl ring or the thiophene ring were tolerated under standard conditions to furnish **3ba–3da**, **3ej**, and **3fa–3ia**. It is noted that the reaction of 3-[(1,1′-biphenyl)-4-yl]thiophene (**1e**) was conducted using **2j**, because the coupling product of **1e** with **2a** was less soluble in usual organic solvents to make its isolation difficult. Tetracyclic anthrathiophene **3ja** and benzonaphthothiophene **3ka** frameworks could be readily constructed in the annulations of 3-(2-naphthyl)thiophene (**1j**) and 3-phenylbenzothiophene (**1k**), respectively. In the latter case, a better product yield was obtained at 120 °C rather than that at 125 °C. In contrast to **1k**, its regioisomer, 2-phenylbenzothiophene (**1l**), did not show any reactivity toward **2a**, resulting in no formation of **3la**. Treatment of *p*-di(thiophen-3-yl)benzene (**1m**) with **2j** in a 2:1 ratio gave 1:1 coupling product **3mj** in 57% yield, along with a minor amount of 1:2 coupling product **4mj**. The use of **1m** and **2j** in a 1:2 ratio afforded **4mj** exclusively, albeit with a moderate yield. The reactions of meta-isomer **1n** with **2j** gave similar results, providing **3nj** and **4nj**. A mixture of regioisomers **3oa** and **3oa′** was formed in the reaction of 3,3′-bithiophene with **2a**. 3,4-Diphenylthiophene (**1p**) reacted with **2a** in a 1:1 manner under standard conditions to produce **3pa** quantitatively. Even under conditions using excess **2a**, **3pa** was formed predominantly, along with a minor amount of 1:2 coupling product **4pa**. The reaction using **1p** and **2j** in a 2:1 ratio similarly gave **3pj** almost quantitatively. In contrast, 3,6-diphenylthieno[3,2-*b*]thiophene (**3q**) reacted with **2k** efficiently in a 1:2 manner to selectively form hexacyclic **4qk**. 3-Phenylbenzofuran (**1r**) coupled with **2a** efficiently to form **3ra** in 90% yield, while the reaction of 2-phenyl isomer **1s** did not give **3sa** at all. The reactions of 2- (**1t**), 3- (**1u**), and 4- (**1v**) (thiophen-3-yl)pyridines were next examined. Although **1t** did not react with **2a**, **1u**, and **1v** underwent the annulation. In the case with **1u**, a mixture of regioisomers **3ua** and **3ua′** was formed. 6-(Thiophen-3-yl)quinoline (**1w**) could also be employed for the annulation with **2a** to selectively form tetracyclic product **3wa**. 4-Phenylthiazoles **1x** and **1y** coupled with **2a** smoothly, in contrast to 5-phenyl isomers **1z** and **1aa**. Similar results were obtained in the reactions of phenyloxazoles **1bb–ee**.

We also examined the construction of a molecule possessing a further expanded π-conjugated system. Thus, benzonaphthothiophene **3ko**, prepared by the annulative coupling of **1k** with bis(3,4-dimethoxyphenyl)acetylene (**2o**), was treated in the presence of an excess amount of $FeCl_3$ in CH_2Cl_2/CH_3NO_2 (2:1) at room temperature for 24 h (Scheme 3).[8] As a result, dehydrogenative cyclization took place to produce heptacyclic **7**.

Under similar catalytic conditions, **1a** also underwent the dehydrogenative coupling with alkenes in place of alkynes. As shown in Table 2, treatment of **1a** (0.4 mmol) with various acrylates **5a–e** (0.2 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol), and Cs_2CO_3 (0.06 mmol) in toluene (2 mL) at 125 °C for 7 h under N_2 gave the corresponding (*E*)-3-[2-(thiophen-3-yl)phenyl]acrylates **6aa–6ae** in 47–64% yields (entries 1–5). While *N*,*N*-dimethylacrylamide (**5f**) did not react at all (entry 6), diethyl vinylphosphonate (**5g**) coupled with **1a** to give **6ag** in a moderate yield (entry 7). Not only these electron-deficient alkenes but also variously substituted styrenes **5h–n** underwent the

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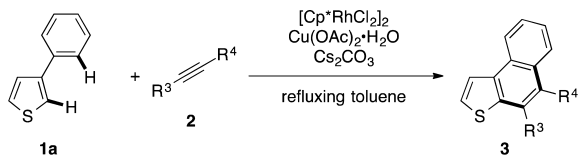
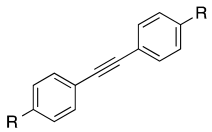
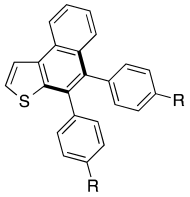
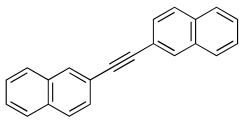
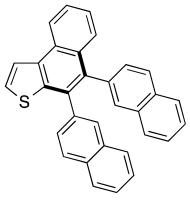
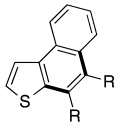
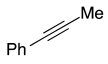
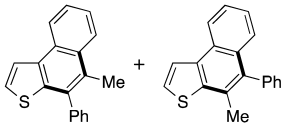
Table 1. Reaction of 3-Phenylthiophene (1a) with Alkynes 2[a]



entry	2	time (h)	product(s), % yield
			
1[b]	**2a**: R = H	7	**3aa**: R = H, 84 (90)[c]
2	**2a**: R = H	10	**3aa**: R = H, (90)[c]
3	**2b**: R = Me	10	**3ab**: R = Me, 86
4	**2c**: R = Bu^t	24	**3ac**: R = Bu^t, 65
5	**2d**: R = OMe	7	**3ad**: R = OMe, 76
6	**2e**: R = NMe_2	7	**3ae**: R = NMe_2, 71
7	**2f**: R = Br	7	**3af**: R = Br, 54
8	**2g**: R = Ac	7	**3ag**: R = Ac, 62
9	**2h**: R = CF_3	7	**3ah**: R = CF_3, 76
			
10	**2i**	7	**3ai**, 75
			
11[b]	**2j**: R = Pr^n	7	**3aj**: R = Pr^n, 79
12[b]	**2k**: R = n-C_7H_{15}	7	**3ak**: R = n-C_7H_{15}, 85
13[d]	**2k**: R = n-C_7H_{15}	24	**3ak**: R = n-C_7H_{15}, 56
14	**2l**: R = $C(OH)Me_2$	7	**3al**: R = $C(OH)Me_2$, 0
15	**2m**: R = CO_2Me	7	**3am**: R = CO_2Me, 0
			
16[b]	**2n**	7	**3an**, 50 **3an'**, 12

[a]Reaction conditions: **1a** (0.4 mmol), **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2·H_2O$ (0.4 mmol), Cs_2CO_3 (0.06 mmol) in toluene (2 mL) at 125 °C under N_2, unless otherwise noted. [b]Using **1a** (0.2 mmol), **2** (0.1 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), $Cu(OAc)_2·H_2O$ (0.2 mmol), Cs_2CO_3 (0.03 mmol) in toluene (1 mL). [c]Determined by GC. [d]Using **1a** (10 mmol), **2** (5 mmol), $[Cp^*RhCl_2]_2$ (0.25 mmol), $Cu(OAc)_2·H_2O$ (10 mmol), Cs_2CO_3 (1.5 mmol) in toluene (30 mL).

dehydrogenative coupling to form 2′-styrylated products **6ah**–**6an** (entries 8–14). In addition to styrenes, 2-vinylnaphthalene (**5o**) could also be employed for this reaction (entry 15).

The fact that the alkenylation took place selectively at the 2′-position on the phenyl ring of **1a** rather than on the thienyl moiety seems to support a reaction mechanism proposed in our preliminary communication,[6] involving thiophene π-unit directed C–H bond cleavage at the 2′-position, alkene insertion, and β-hydrogen elimination to form **6** (Scheme 4).

However, we obtained a contradicting result in our subsequent study. Thus, in the treatment of C2-deuterated **1a** (**1a**-d_1) with **5h** under standard conditions for 2 h, the 2′-styrylation proceeded accompanied by the loss of C2 deuterium to form **6ah**-d_0 (Scheme 5). In addition, no significant D/H exchange was observed in the recovered **1a**-d_1. These results indicate that the coupling reaction involves C–H(D) bond cleavages not only on the phenyl group but also on the thiophene ring.

Next, we investigated the source of the hydrogen introduced at the C2 position of coupling product **6ah** in Scheme 5. Treatment of **1a**-d_0 with D_2O or CD_3CO_2D in the presence and absence of **5h** resulted in no incorporation of deuterium in recovered **1a** as well as produced **6ah** (Schemes 6a–d). Finally, the C2-deuterium incorporation in **6ah** was observed, when deuterated styrene **5h**-d_8 was employed. Thus, C2-deuterated 2′-styrylated product **6ah**-d_8 was obtained upon treatment of **1a** with **5h**-d_8 (Scheme 6e). In this case, deuterium was not incorporated in the recovered **1a** at all.

Based on these experimental results, a revised mechanism for the reaction of **1a** with alkene **5** can be proposed (Scheme 7). Coordination of the thienyl moiety of **1a** to a Cp^*Rh^{III} center and subsequent double C–H bond cleavages would occur to form a five-membered rhodacycle intermediate **A**, as in the reaction with alkynes (Scheme 1b). Then alkene insertion into the resulting Rh–C bond to form **B**, β-hydrogen elimination, and reductive elimination of **6** from **C** may take place to release a Cp^*Rh^{I} species, which is oxidized by Cu^{II} to regenerate the Cp^*Rh^{III}. As in the reaction with alkyne **2a** (see Table S1, Supporting Information), the efficiency of the reaction of **1a** with **5h** was slightly enhanced by the addition of Cs_2CO_3. Indeed, the yield of **6ah** decreased to 40% in the absence of Cs_2CO_3. One of the possible roles of Cs_2CO_3 seems to be trapping HX formed during the coupling reaction.

In addition, two parallel reactions of **1a**-d_0 and **1a**-d_1 with **5h** were conducted separately under standard conditions (Scheme 8). The observed KIE value 2.3:1 (k_H/k_D) in the early stage suggests that the rate-determining step involves the C–H(D) bond cleavage at the C2-position of **1a**.

CONCLUSIONS

We have demonstrated that the dehydrogenative annulation of phenylheteroarenes with alkynes can be performed efficiently under rhodium catalysis. The procedure allows the ready construction of various benzo-fused heterocyclic frameworks by a single treatment. The rhodium catalyst system is also applicable to the dehydrogenative coupling with alkenes on the phenyl ring. Work is underway toward further development of this procedure utilizing other π-electron systems.

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS data were obtained by EI using a double focusing mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC-MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Phenylheteroarenes **1b–j**,[9] **1k,l**,[10] **1m,n**,[11] **1p,q**,[9] **1r**,[12] **1s**,[10] **1t–w**,[9] **1x,y**,[13] **1z,aa**,[14] **1cc**,[15] and **1ee**,[16] and alkynes **2b–d**,[17] **2e**,[18] **2f**,[19] **2g,h**,[17] **2i**,[20] and **2o**[17] were prepared according to published

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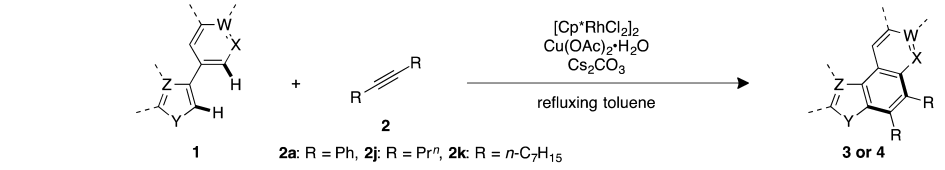
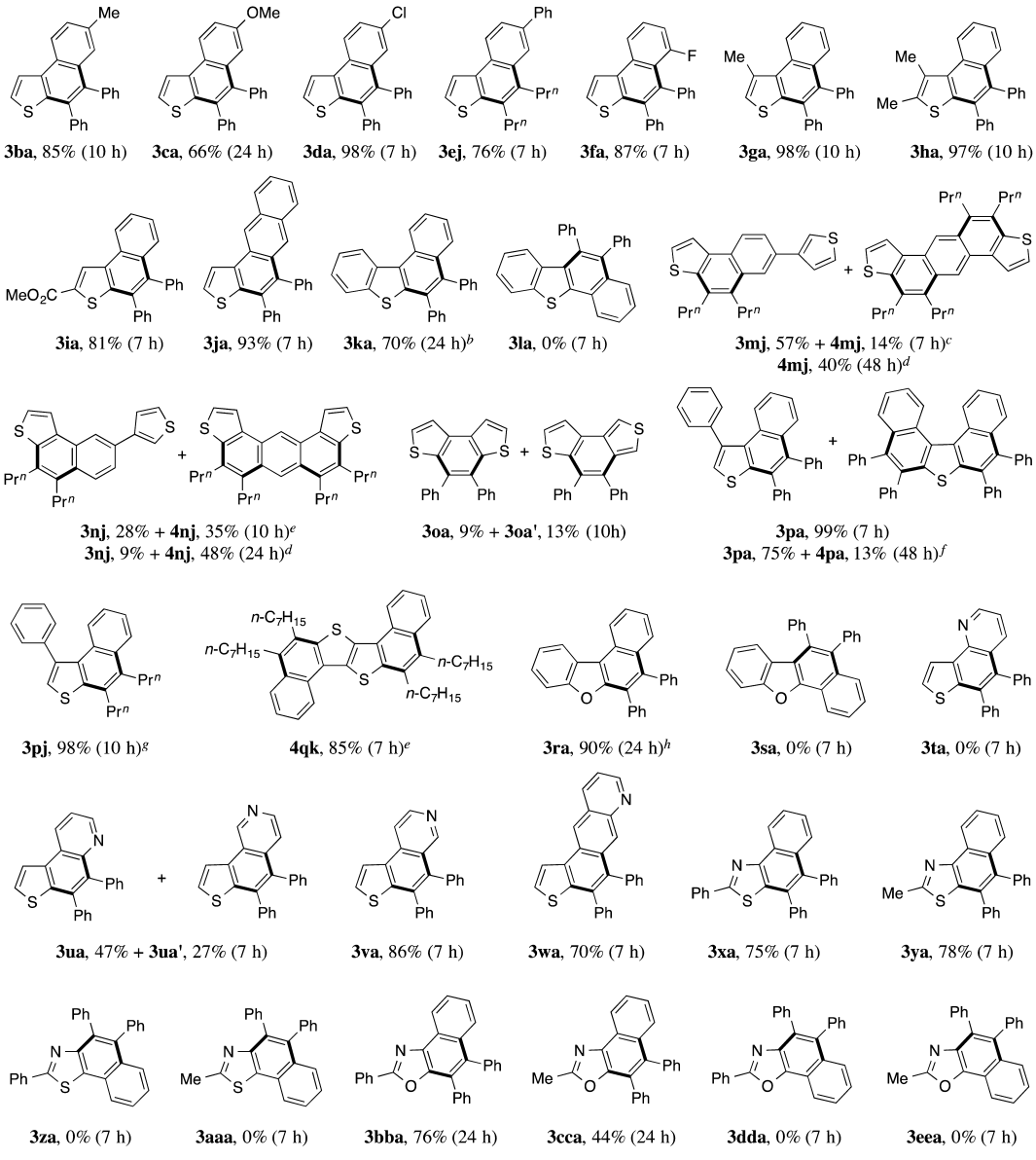
Scheme 2. Reaction of (Hetero)arylheteroarenes 1 with Alkyne 2a, 2j, or 2k[a]





[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2·H_2O$ (0.4 mmol), Cs_2CO_3 (0.06 mmol) in toluene (2 mL) at 125 °C under N_2, unless otherwise noted. [b]At 120 °C. [c]Using $Cu(OAc)_2·H_2O$ (0.8 mmol). [d]Using **1** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.02 mmol), $Cu(OAc)_2·H_2O$ (0.8 mmol), and Cs_2CO_3 (0.12 mmol). [e]Using **1** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2·H_2O$ (0.8 mmol), and Cs_2CO_3 (0.12 mmol). [f]Using **1** (0.2 mmol), **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2·H_2O$ (0.8 mmol), and Cs_2CO_3 (0.06 mmol). [g]Using **1** (2 mmol), **2** (1 mmol), $[Cp^*RhCl_2]_2$ (0.05 mmol), $Cu(OAc)_2·H_2O$ (2 mmol), and Cs_2CO_3 (0.3 mmol) in toluene (10 mL). [h]Using **1** (0.2 mmol), **2** (0.1 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), $Cu(OAc)_2·H_2O$ (0.2 mmol), and Cs_2CO_3 (0.03 mmol) in toluene (1 mL).

procedures. Phenylheteroarene **1a**-d_1 was prepared as shown below. Other starting materials and reagents were commercially available.

Preparation of 1a-d_1. 2-Bromo-3-phenylthiophene was prepared according to published procedures.[21] To a solution of 2-bromo-3-phenylthiophene (3.0 mmol, 720 mg) in Et_2O (6 mL) was added a solution of ^{n}BuLi in hexane (1.63 M, 1.9 mL, 3.1 mmol) dropwise at −78 °C under N_2. The reaction mixture was stirred for 0.5 h and warmed to 0 °C, to which D_2O (5 mL) was added slowly. The mixture was warmed to room temperature and stirred overnight. Then the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, C2-deuterated 3-phenylthiophene (**1a**-d_1) was isolated (338 mg, 70%).

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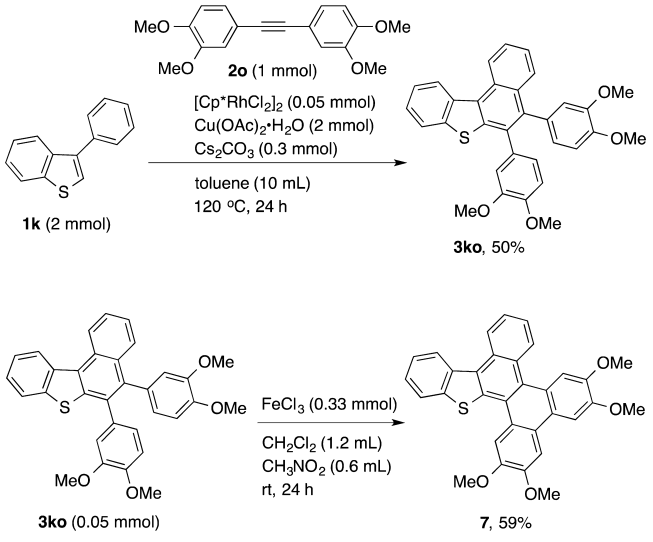
Scheme 3. Reaction of 1k with 2o and Further Cyclization



General Procedure for the Reaction of Phenylheteroarenes 1 with Alkynes 2. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added phenylheteroarene **1** (0.4 mmol), alkyne **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature). After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **3** was isolated by column chromatography on silica gel using hexane as eluant. Further purification by GPC (gel permeation chromatography) was performed, if needed.

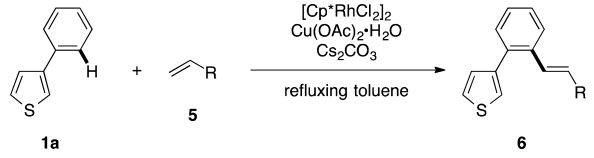
Reaction of 1a-d_1 with 5h-d_0 (Scheme 5). To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 3-phenylthiophene (**1a**-d_1) (0.4 mmol, 64 mg; 83% D), styrene (**5h**-d_0) (0.2 mmol, 21 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature) for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **6ah**-d_0 (6 mg, 12%) and **1a**-d_1 (55 mg, 86%) were isolated by column chromatography on silica gel using hexane as eluant.

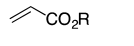
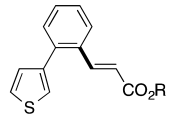
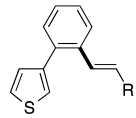
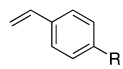
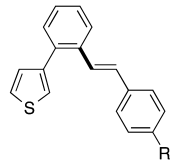
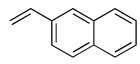
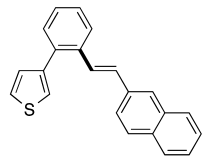
Treatment of 1a-d_0 with D_2O (Scheme 6a). To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 3-phenylthiophene (**1a**-d_0) (0.4 mmol, 64 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), D_2O (0.8 mmol, 16 mg) and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature) for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **1a**-d_0 (61 mg, 95%) was isolated by column chromatography on silica gel using hexane as eluant.

Treatment of 1a-d_0 with CD_3CO_2D (Scheme 6b). To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 3-phenylthiophene (**1a**-d_0) (0.4 mmol, 64 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), CD_3CO_2D (0.8 mmol, 51 mg) and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature) for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **1a**-d_0 (61 mg, 96%) was isolated by column chromatography on silica gel using hexane as eluant.

Reaction of 1a-d_0 with 5h-d_0 in the Presence of D_2O (Scheme 6c). To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 3-phenylthiophene (**1a**-d_0) (0.4 mmol, 64 mg), styrene (**5h**-d_0) (0.2 mmol, 21 mg), $[Cp^*RhCl_2]_2$

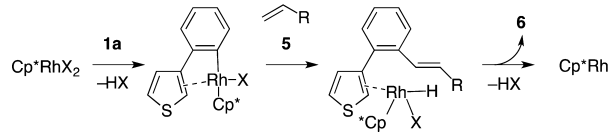
Table 2. Reaction of 3-Phenylthiophene (1a) with Alkenes 5[a]



entry	5	time (h)	product, % yield
			
1	**5a**: R = Bu^n	7	**6aa**: R = Bu^n, 60
2	**5b**: R = Bu^i	7	**6ab**: R = Bu^i, 50
3	**5c**: R = Bu^t	7	**6ac**: R = Bu^t, 52
4	**5d**: R = Et	7	**6ad**: R = Et, 47
5	**5e**: R = Cy[b]	7	**6ae**: R = Cy,[b] 64
			
6	**5f**: R = $CONMe_2$	7	**6af**: R = $CONMe_2$, 0
7	**5g**: R = $P(O)(OEt)_2$	10	**6ag**: R = $P(O)(OEt)_2$, 47
			
8	**5h**: R = H	10	**6ah**: R = H, 58
9	**5i**: R = Me	10	**6ai**: R = Me, 53
10	**5j**: R = Bu^t	10	**6aj**: R = Bu^t, 45
11	**5k**: R = OMe	10	**6ak**: R = OMe, 53
12	**5l**: R = Ph	10	**6al**: R = Ph, 65
13	**5m**: R = Cl	10	**6am**: R = Cl, 63
14	**5n**: R = CF_3	10	**6an**: R = CF_3, 63
			
15	**5o**	10	**6ao**, 50

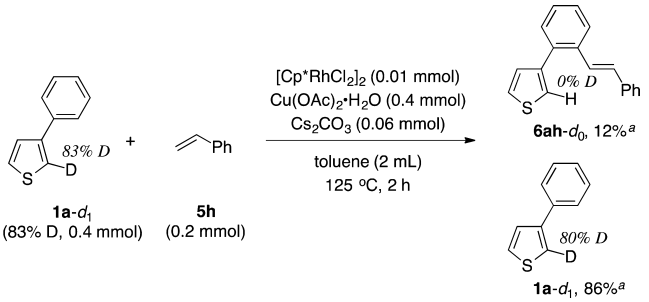
[a]Reaction conditions: **1a** (0.4 mmol), **5** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol), and Cs_2CO_3 (0.06 mmol) in toluene (2 mL) at 125 °C under N_2. [b]Cy = cyclohexyl.

Scheme 4. Previously Proposed Mechanism for the Reaction of 1a with 5



DOI: 10.1021/acs.joc.5b00155
J. Org. Chem. 2015, 80, 2804−2814

Scheme 5. Reaction of 1a-d_1 with 5h



[a]Isolated yield based on the amount of **5h** used.

(0.01 mmol, 6 mg), $Cu(OAc)_2·H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), D_2O (0.8 mmol, 16 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature) for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **6ah**-d_0 (22 mg, 42%) and **1a**-d_0 (37 mg, 58%) were isolated by column chromatography on silica gel using hexane as eluant.

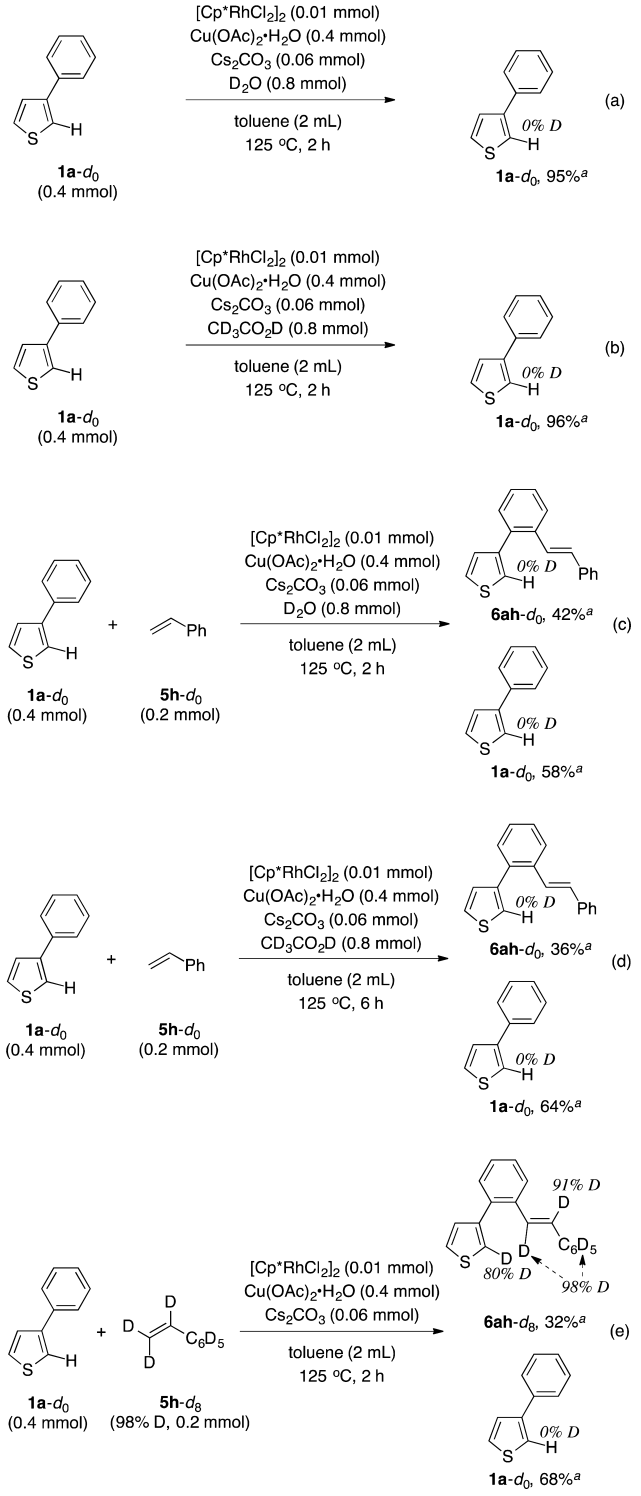
Reaction of 1a-d_0 with 5h-d_0 in the Presence of CD_3CO_2D (Scheme 6d). To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 3-phenylthiophene (**1a**-d_0) (0.4 mmol, 64 mg), styrene (**5h**-d_0) (0.2 mmol, 21 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2·H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), CD_3CO_2D (0.8 mmol, 51 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature) for 6 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **6ah**-d_0 (19 mg, 36%) and **1a**-d_0 (41 mg, 64%) were isolated by column chromatography on silica gel using hexane as eluant.

Reaction of 1a-d_0 with 5h-d_8 (Scheme 6e). To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 3-phenylthiophene (**1a**-d_0) (0.4 mmol, 64 mg), styrene (**5h**-d_8) (0.2 mmol, 22 mg; 98% D), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2·H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). Then the resulting mixture was stirred under nitrogen at 125 °C (bath temperature) for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **6ah**-d_8 (17 mg, 32%) and **1a**-d_0 (44 mg, 68%) were isolated by column chromatography on silica gel using hexane as eluant.

Parallel Reactions of 1a-d_0 and 1a-d_1 (Scheme 8). To a 20 mL two-necked flask were added 3-phenylthiophene-d_0 or $-d_1$ (**1a**-d_0 or **1a**-d_1) (0.4 mmol), styrene (**5h**) (0.2 mmol, 21 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6 mg), $Cu(OAc)_2·H_2O$ (0.4 mmol, 80 mg), Cs_2CO_3 (0.06 mmol, 20 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). The resulting mixture was stirred under N_2 at 125 °C for 0.75 h. GC and GC-MS analyses of the mixture confirmed formation of **6ah**-d_0 (14% from **1a**-d_0; 6% from **1a**-d_1): k_H/k_D = 2.3.

4,5-Diphenylnaphtho[2,1-*b*]thiophene (3aa):[6] mp 189−190 °C (pale yellow powder), 28 mg (84%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.19−7.29 (m, 10H), 7.41−7.46 (m, 1H), 7.58 (d, J = 5.5 Hz, 1H), 7.59−7.63 (m, 1H), 7.67 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 5.5 Hz, 1H), 8.43 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.3, 123.6, 125.4, 126.1, 126.6, 126.7, 127.2, 127.7, 127.8, 128.0, 128.7, 130.0, 131.3, 131.5, 133.7, 134.8, 135.3, 138.8, 139.8, 139.9; HRMS m/z Calcd for $C_{24}H_{16}S$ (M^+) 336.0973, found 336.0972.

Scheme 6. Deuterium Incorporation



[a]Isolated yield based on the amount of **5h** used.

4,5-Bis(4-methylphenyl)naphtho[2,1-*b*]thiophene (3ab):[6] mp 193−194 °C (brown powder), 63 mg (86%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.33 (s, 3H), 7.05−7.08 (m, 6H), 7.17 (d, J = 8.0 Hz, 2H), 7.38−7.42 (m, 1H), 7.54 (d, J = 5.4 Hz, 1H), 7.56−7.60 (m, 1H), 7.67 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 5.5 Hz, 1H), 8.39 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.25, 21.30, 122.2, 123.5, 125.3, 126.0, 126.4, 127.9, 128.4 (overlapped), 128.7, 129.8, 131.3, 131.6, 133.7, 134.8, 135.2, 135.9, 136.1, 136.6, 137.1, 140.2; HRMS m/z Calcd for $C_{26}H_{20}S$ (M^+) 364.1286, found 364.1291.

DOI: 10.1021/acs.joc.5b00155
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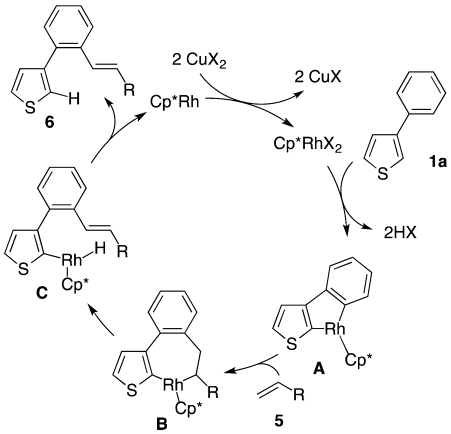
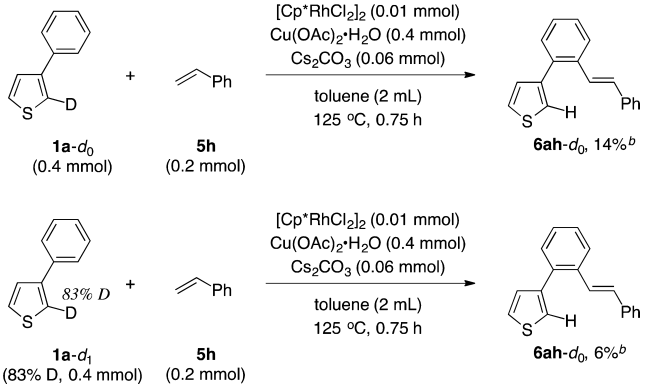
Scheme 7. Plausible Mechanism for the Reaction of 1a with 5



Scheme 8. Parallel Reactions of 1a-d_0 and 1a-d_1[a]



[a]Reaction conditions: 1a (0.4 mmol), 5h (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol), and Cs_2CO_3 (0.06 mmol) in toluene (2 mL) at 125 °C under N_2 for 0.75 h. [b]GC yield based on the amount of 5 h used.

4,5-Bis[4-(*tert*-butyl)phenyl]naphtho[2,1-*b*]thiophene (3ac):[6] mp 233−234 °C (pale yellow powder), 59 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 9H), 1.28 (s, 9H), 7.08 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 7.20−7.25 (m, 4H), 7.41−7.45 (m, 1H), 7.55 (d, J = 5.4 Hz, 1H), 7.59−7.61 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 5.6 Hz, 1H), 8.41 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.25, 31.32, 34.42, 34.44, 122.2, 123.5, 124.3, 124.5, 125.3, 125.9, 126.3, 128.0, 128.7, 129.6, 131.2, 132.3, 133.9, 135.1, 135.2, 135.8, 136.9, 139.8, 149.3, 149.7; HRMS m/z Calcd for $C_{32}H_{32}S$ (M^+) 448.2225, found 448.2227.

4,5-Bis(4-methoxyphenyl)naphtho[2,1-*b*]thiophene (3ad):[6] mp 218−220 °C (white powder), 60 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.80 (s, 3H), 6.77−6.83 (m, 4H), 7.07−7.13 (m, 2H), 7.17−7.21 (m, 2H), 7.39−7.43 (m, 1H), 7.55 (d, J = 5.4 Hz, 1H), 7.56−7.60 (m, 1H), 7.69 (d, J = 7.3 Hz, 1H), 8.06 (d, J = 5.5 Hz, 1H), 8.39 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.09, 55.14, 113.2, 113.4, 122.3, 123.5, 125.3, 126.0, 126.4, 127.8, 128.7, 131.1, 131.2, 131.7, 132.45, 132.52, 133.6, 134.56, 135.1, 140.3, 158.2, 158.5; HRMS m/z Calcd for $C_{26}H_{20}O_2S$ (M^+) 396.1184, found 396.1181.

4,4′-(Naphtho[2,1-*b*]thiophene-4,5-diyl)bis(*N*,*N*-dimethylaniline) (3ae). mp 234−236 °C (brown powder), 60 mg (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (s, 6H), 2.94 (s, 6H), 6.63 (d, J = 7.4 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.8 Hz, 2H), 7.36−7.41 (m, 1H), 7.51 (d, J = 5.2 Hz, 1H), 7.52−7.57 (m, 1H), 7.76 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 5.6 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.5, 40.6, 111.9, 112.0, 122.2, 123.4, 125.0, 125.6, 126.1, 127.4, 128.1, 128.60, 128.64, 130.8, 132.2, 132.3, 134.0, 134.86, 134.89, 141.0, 149.0, 149.2; HRMS m/z Calcd for $C_{28}H_{26}N_2S$ (M^+) 422.1817, found 422.1819.

4,5-Bis(4-bromophenyl)naphtho[2,1-*b*]thiophene (3af). mp 220−222 °C (white powder), 54 mg (54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.40−7.46 (m, 5H), 7.58−7.64 (m, 3H), 8.07 (d, J = 5.5 Hz, 1H), 8.41 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2, 121.7, 122.4, 123.7, 125.7, 126.5, 126.9, 127.5, 128.8, 130.9, 131.1, 131.5, 131.6, 132.5, 133.0, 133.5, 135,7, 137.5, 138.4, 139.2; HRMS m/z Calcd for $C_{24}H_{14}Br_2S$ (M^+) 491.9183, found 491.9185.

1,1′-(Naphtho[2,1-*b*]thiophene-4,5-diylbis(4,1-phenylene))diethanone (3ag). mp 251−252 °C (white powder), 62 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 2.60 (s, 3H), 7.31 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.44−7.48 (m, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.61−7.67 (m, 2H), 7.85−7.89 (m, 4H), 8.10 (d, J = 5.6 Hz, 1H), 8.44 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6 (overlapped), 122.4, 123.8, 125.9, 126.7, 127.2, 127.4, 127.9, 128.3, 128.9, 130.3, 130.6, 131.7, 132.6, 133.7, 135.7, 135.9, 136.0, 138.8, 143.8, 144.4, 197.7, 197.8; HRMS m/z Calcd for $C_{28}H_{20}O_2S$ (M^+) 420.1184, found 420.1186.

4,5-Bis[4-(trifluoromethyl)phenyl]naphtho[2,1-*b*]thiophene (3ah):[6] mp 225−226 °C (white powder), 70 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.45−7.49 (m, 1H), 7.52−7.56 (m, 5H), 7.62 (d, J = 5.4 Hz, 1H), 7.64−7.68 (m, 1H), 8.10 (d, J = 5.5 Hz, 1H), 8.44 (d, J = 8.12 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.4, 123.8, 124.0 (q, J = 270.5 Hz), 124.1 (q, J = 270.4 Hz), 124.9 (q, J = 3.7 Hz), 125.3 (q, J = 3.6 Hz), 126.0, 126.8, 127.2, 127.3, 129.0, 129.3 (q, J = 32.2 Hz), 129.7 (q, J = 33.3 Hz), 130.3, 130.7, 131.8, 132.4, 133.5,136.1, 138.9, 142.3, 143.0; HRMS m/z Calcd for $C_{26}H_{14}F_6S$ (M^+) 472.0720, found 472.0717.

4,5-Di(naphthalen-2-yl)naphtho[2,1-*b*]thiophene (3ai). mp 215−217 °C (white powder), 65 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.41 (m, 7H), 7.56−7.72 (m, 10H), 7.92 (s, 1H), 8.10 (d, J = 5.6 Hz, 1H), 8.44 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.3, 123.6, 125.5, 125.8, 125.9 (overlapped), 126.0, 126.2, 126.8, 127.3, 127.61, 127.63, 127.7, 127.90, 127.92, 128.1 (overlapped), 128.9, 129.0, 129.6, 130.5, 131.6, 132.2, 132.4, 132.9, 133.0, 133.8, 134.8, 135.5, 136.4, 137.5, 140.1; HRMS m/z Calcd for $C_{32}H_{20}S$ (M^+) 436.1286, found 436.1283.

4,5-Dipropylnaphtho[2,1-*b*]thiophene (3aj):[6] mp 83−84 °C (white powder), 21 mg (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09−1.14 (m, 6H), 1.68−1.85 (m, 4H), 3.00−3.04 (m, 2H), 3.09−3.13 (m, 2H), 7.49 (d, J = 5.4 Hz, 1H), 7.51−7.55 (m, 2H), 7.96 (d, J = 5.4 Hz, 1H), 8.07−8.11 (m, 1H), 8.30−8.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7 (overlapped), 23.2, 24.4, 30.7, 35.4, 122.6, 124.1, 124.2, 124.9, 125.1, 125.2, 128.7, 130.7, 132.0, 132.2, 134.4, 139.7; HRMS m/z Calcd for $C_{18}H_{20}S$ (M^+) 268.1286, found 268.1288.

4,5-Diheptylnaphtho[2,1-*b*]thiophene (3ak):[6] mp 39−40 °C (yellow powder), 65 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88−0.92 (m, 6H), 1.32−1.43 (m, 12H), 1.48−1.57 (m, 4H), 1.64−1.80 (m, 4H), 3.00−3.04 (m, 2H), 3.10−3.14 (m, 2H), 7.48 (d, J = 5.4 Hz, 1H), 7.51−7.54 (m, 2H), 7.95 (d, J = 5.4 Hz, 1H), 8.08−8.11 (m, 1H), 8.29−8.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (overlapped), 22.7 (overlapped), 28.6, 29.1, 29.2, 29.8, 30.2, 30.3, 31.2, 31.8, 31.9, 33.3, 122.6, 124.1, 124.2, 124.9, 125.0, 125.2, 128.7, 130.7, 132.16, 132.23, 134.3, 139.7; HRMS m/z Calcd for $C_{26}H_{36}S$ (M^+) 380.2538, found 380.2534.

5-Methyl-4-phenylnaphtho[2,1-*b*]thiophene (3an):[6] mp 69−71 °C (white powder), 27 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H), 7.43−7.48 (m, 4H), 7.50−7.54 (m, 2H), 7.57−7.65 (m, 2H), 8.00 (d, J = 5.4 Hz, 1H), 8.14−8.17 (m, 1H), 8.37- 8.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 122.2, 124.0, 125.3, 125.5, 125.6, 125.9, 127.7, 127.8, 128.6, 128.8, 129.6, 131.3, 133.9, 134.1, 140.2, 140.6; HRMS m/z Calcd for $C_{19}H_{14}S$ (M^+) 274.0816, found 274.0815.

4-Methyl-5-phenylnaphtho[2,1-*b*]thiophene (3an′):[6] mp 114−116 °C (white powder), 7 mg (12%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.30−7.33 (m, 2H), 7.35−7.39 (m, 1H), 7.46−7.48 (m, 2H), 7.50−7.56 (m, 3H), 7.61 (d, J = 5.4 Hz, 1H), 8.07

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(d, J = 5.4 Hz, 1H), 8.36 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 122.7, 123.4, 125.1, 125.29, 125.33, 127.2, 127.3, 127.7, 128.1, 128.4, 130.6, 131.6, 134.97, 134.98, 139.5, 139.6; HRMS m/z Calcd for $C_{19}H_{14}S$ (M^+) 274.0816, found 274.0814.

5,6-Bis(3,4-dimethoxyphenyl)benzo[*b*]naphtho[1,2-*d*]-thiophene (3ko). mp 231−233 °C (pink powder), 254 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.69 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 6.67−6.98 (m, 6H), 7.43−7.50 (m, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.90 (s, 1H), 8.88 (d, J = 8.4 Hz, 1H), 9.09 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 90 °C) δ 56.61, 56.66, 56.68, 56.7, 112.9, 113.0, 115.9, 117.1, 123.2, 123.8, 123.9, 124.5, 125.5, 125.9, 126.0, 126.2, 127.8, 128.6, 128.8, 130.3, 131.9, 132.6, 133.1, 134.5, 137.1, 137.9, 140.3, 141.6, 149.0, 149.36, 149.4, 149.5; HRMS (APCI) m/z Calcd for $C_{32}H_{27}O_4S$ ([M + H]$^+$) 507.1625, found 507.1624.

7-Methyl-4,5-diphenylnaphtho[2,1-*b*]thiophene (3ba):[6] mp 162−163 °C (white powder), 60 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.18−7.29 (m, 10H), 7.43−7.46 (m, 2H), 7.55 (d, J = 5.5 Hz, 1H), 8.05 (d, J = 5.4 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 122.2, 123.5, 126.5, 126.6, 126.9, 127.0, 127.1, 127.6, 127.9, 128.1, 130.0, 131.4, 131.6, 133.8, 134.4, 135.0, 135.3, 138.95, 139.03, 140.1; HRMS m/z Calcd for $C_{25}H_{18}S$ (M^+) 350.1129, found 350.1126.

7-Methoxy-4,5-diphenylnaphtho[2,1-*b*]thiophene (3ca):[6] mp 196−197 °C (pale yellow powder), 49 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 7.03 (d, J = 2.6 Hz, 1H), 7.18−7.28 (m, 11H), 7.54 (d, J = 5.4 Hz, 1H), 7.99 (d, J = 5.5 Hz, 1H), 8.31 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 107.7, 117.2, 122.0, 123.9, 125.1, 126.69, 126.73, 127.1, 127.7, 127.9, 123.0, 131.4, 132.6, 134.1, 134.2, 135.4, 137.9, 138.9, 140.0, 157.2; HRMS m/z Calcd for $C_{25}H_{18}OS$ (M^+) 366.1078, found 366.1080.

7-Chloro-4,5-diphenylnaphtho[2,1-*b*]thiophene (3da):[6] mp 194−195 °C (pale yellow powder), 74 mg (98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06−7.09 (m, 2H), 7.13−7.21 (m, 8H), 7.44 (q, J = 2.2, 8.7 Hz, 1H), 7.49 (d, J = 5.5 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 5.5 Hz, 1H), 8.23 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.1, 125.2, 126.7 (overlapped), 126.99, 127.03, 127.3, 127.4, 127.9, 128.0, 129.8, 131.3, 131.4, 132.4, 134.0, 134.9, 135.1, 138.1, 139.5, 140.0; HRMS m/z Calcd for $C_{24}H_{15}ClS$ (M^+) 370.0583, found 370.0586.

7-Phenyl-4,5-dipropylnaphtho[2,1-*b*]thiophene (3ej). mp 116−117 °C (white powder), 52 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10−1.16 (m, 6H), 1.73−1.86 (m, 4H), 3.02−3.06 (m, 2H), 3.15−3.19 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.49−7.53 (m, 3H), 7.74 (d, J = 7.2 Hz, 2H), 7.78 (dd, J = 1.6, 8.4 Hz, 1H), 7.97 (d, J = 5.6 Hz, 1H), 8.28 (d, J = 1.2 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 14.8, 23.2, 24.5, 30.7, 35.4, 122.6, 123.3, 124.4, 124.65, 124.67, 127.1, 127.5, 127.8, 128.9, 130.9, 132.3, 132.5, 134.2, 137.9, 139.8, 141.9; HRMS m/z Calcd for $C_{24}H_{24}S$ (M^+) 344.1599, found 344.1601.

6-Fluoro-4,5-diphenylnaphtho[2,1-*b*]thiophene (3fa):[6] mp 181−183 °C (white powder), 62 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (ddd, J = 1.1, 7.7, 13.2 Hz, 1H), 7.14−7.25 (m, 10H), 7.53 (td, J = 4.8, 7.9 Hz, 1H), 7.57 (d, J = 5.4 Hz, 1H), 8.03 (d, J = 5.5 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.7 (d, J = 23.2 Hz), 119.8 (d, J = 4.2 Hz), 120.8 (d, J = 8.6 Hz), 122.5, 126.2, 126.6 (d, J = 9.3 Hz), 126.8, 127.2, 127.4, 127.8, 129.9, 130.2 (d, J = 4.1 Hz), 131.0 (d, J = 3.3 Hz), 131.1 (d, J = 2.3 Hz), 135.0 (d, J = 2.9 Hz), 135.5, 139.3, 140.77, 140.81, 160.2 (d, J = 254.0 Hz); HRMS m/z Calcd for $C_{24}H_{15}FS$ (M^+) 354.0878, found 354.0876.

1-Methyl-4,5-diphenylnaphtho[2,1-*b*]thiophene (3ga). mp 182−184 °C (pale yellow powder), 69 mg (98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (d, J = 0.8 Hz, 3H), 7.17−7.27 (m, 11H), 7.42 (ddd, J = 1.2 Hz, 6.8 Hz, 8.4 Hz, 1H), 7.60 (ddd, J =1.2, 6.8, 8.4 Hz, 1H), 7.70 (dd, J = 0.8, 8.4 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 123.3, 123.7, 124.8, 125.7, 126.6, 127.2, 127.6, 127.9, 128.0, 130.1, 130.2, 131.4, 131.9, 133.1, 134.2, 134.8, 135.0, 139.0, 139.7, 141.7; HRMS m/z Calcd for $C_{25}H_{18}S$ (M^+) 350.1129, found 350.1127.

1,2-Dimethyl-4,5-diphenylnaphtho[2,1-*b*]thiophene (3ha). mp 245−247 °C (pale yellow powder), 71 mg (97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 2.81 (s, 3H), 7.17−7.27 (m, 10H), 7.39 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.57 (ddd, J = 1.2, 6.8, 8.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 8.81 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 16.7, 123.2, 124.5, 125.4, 126.5, 127.1, 127.6, 127.8, 128.0, 129.8, 129.9, 130.0, 131.5, 132.0, 133.6, 133.8, 134.3, 134.7, 137.9, 139.2, 140.0; HRMS m/z Calcd for $C_{26}H_{20}S$ (M^+) 364.1286, found 364.1287.

Methyl 4,5-diphenylnaphtho[2,1-*b*]thiophene-2-carboxy-late (3ia). mp 221−222 °C (white powder), 64 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.17−7.30 (m, 10H), 7.46 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.62−7.68 (m, 2H), 8.42 (d, J = 8.0 Hz, 1H), 8.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 123.4, 126.1, 126.90, 126.97, 127.5, 127.7, 128.10, 128.14, 128.6, 129.3, 129.9, 131.2, 131.5, 132.8, 133.6, 134.7, 137.8, 138.2, 139.0, 143.6, 163.3; HRMS m/z Calcd for $C_{26}H_{18}O_2S$ (M^+) 394.1028, found 394.1025.

4,5-Diphenylanthra[2,1-*b*]thiophene (3ja). mp 200−203 °C (white powder), 72 mg (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.33 (m, 10H), 7.42 (ddd, J = 1.2, 6.4, 8.0 Hz, 1H), 7.50 (ddd, J = 1.1, 6.4, 7.9 Hz, 1H), 7.57 (d, J = 5.2 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H), 8.21 (d, J = 5.2 Hz, 1H), 8.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.6, 122.9, 125.1, 125.9, 126.2, 126.8, 127.1, 127.2, 127.5, 127.7, 127.8, 127.9, 128.6, 130.0, 130.6, 131.2, 131.5, 131.6, 133.4, 134.7, 135.0, 138.9, 139.6, 139.8; HRMS m/z Calcd for $C_{28}H_{18}S$ (M^+) 386.1129, found 386.1128.

5,6-Diphenylbenzo[*b*]naphtho[1,2-*d*]thiophene (3ka):[6] mp 205−206 °C (white powder), 27 mg (35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.30 (m, 10H), 7.48 (t, J = 8.5 Hz, 2H), 7.61 (t, J = 7.7 Hz, 1H), 7.71−7.79 (m, 2H), 7.90 (d, J = 7.9 Hz, 1H), 8.91 (d, J = 8.4 Hz, 1H), 9.12 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.0, 123.1, 124.76, 124.82, 124.9, 125.2, 126.75, 126.83, 127.4, 127.7, 128.0, 128.57, 128.63, 130.1, 130.2, 131.3, 131.9, 134.1, 137.0, 137.4, 138.8, 139.7, 140.2, 141.1; HRMS m/z Calcd for $C_{28}H_{18}S$ (M^+) 386.1129, found 386.1125.

4,5-Dipropyl-7-(thiophen-3-yl)naphtho[2,1-*b*]thiophene (3mj). mp 165−166 °C (white powder), 40 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10−1.17 (m, 6H), 1.72−1.86 (m, 4H), 3.01−3.05 (m, 2H), 3.14−3.18 (m, 2H), 7.44−7.46 (m, 1H), 7.50 (d, J = 5.2 Hz, 1H), 7.53−7.57 (m, 2H), 7.78 (dd, J = 1.6, 8.4 Hz, 1H), 7.95 (d, J = 5.6 Hz, 1H), 8.29 (d, J = 1.6 Hz, 1H), 8.33 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 14.8, 23.2, 24.5, 30.7, 35.4, 120.3, 122.4, 122.6, 124.1, 124.5, 124.7, 126.4, 126.6, 127.8, 131.0, 132.2, 132.59, 132.61, 134.3, 139.7, 143.0; HRMS m/z Calcd for $C_{22}H_{22}S_2$ (M^+) 350.1163, found 350.1160.

4,5,10,11-Tetrapropylanthra[2,1-*b*:6,5-*b*′]dithiophene (4mj). mp 188−189 °C (pale yellow powder), 13 mg (14%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, J = 7.6 Hz, 6H), 1.22 (t, J = 7.6 Hz, 6H), 1.81−1.91 (m, 8H), 3.05−3.09 (m, 4H), 3.28−3.32 (m, 4H), 7.56 (d, J = 5.4 Hz, 2H), 8.16 (d, J = 5.4 Hz, 2H), 9.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 14.9, 23.3, 24.4, 30.9, 35.4, 119.4, 122.8, 124.0, 126.9, 128.8, 131.68, 131.71, 134.4, 139.4; HRMS m/z Calcd for $C_{30}H_{34}S_2$ (M^+) 458.2102, found 458.2098.

4,5-Dipropyl-8-(thiophen-3-yl)naphtho[2,1-*b*]thiophene (3nj). mp 91−92 °C (brown powder), 20 mg (28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10−1.16 (m, 6H), 1.69−1.86 (m, 4H), 3.00−3.06 (m, 2H), 3.10−3.14 (m, 2H), 7.45 (dd, J = 2.8, 5.2 Hz, 1H), 7.51 (d, J = 5.2 Hz, 1H), 7.57 (dd, J = 1.6, 5.2 Hz, 1H), 7.61 (dd, J = 1.2, 2.8 Hz, 1H), 7.78 (dd, J = 1.6, 8.4 Hz, 1H), 8.01 (d, J = 5.6 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 8.50 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7 (overlapped), 23.2, 24.5, 30.7, 35.3, 120.5, 121.3, 122.5, 124.1, 124.4, 125.5, 126.3, 126.6, 128.9, 129.8, 132.05, 132.07, 132.4, 134.4, 140.2, 142.5; HRMS m/z Calcd for $C_{22}H_{22}S_2$ (M^+) 350.1163, found 350.1164.

4,5,7,8-Tetrapropylanthra[2,1-*b*:7,8-*b*′]dithiophene (4nj). mp 152−153 °C (white powder), 32 mg (35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 6H), 1.23 (t, J = 7.2 Hz, 6H), 1.81−1.90 (m, 8H), 3.04−3.08 (m, 4H), 3.25−3.29 (m, 4H), 7.55 (d, J = 5.4 Hz, 2H), 8.19 (d, J = 5.4 Hz, 2H), 8.83 (s, 1H), 9.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 15.0, 23.3, 24.5, 31.2, 35.5, 118.0, 120.9,

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123.0, 123.9, 126.6, 128.8, 131.3, 132.0, 134.0, 139.7; HRMS *m*/*z* Calcd for $C_{30}H_{34}S_2$ (M^+) 458.2102, found 458.2103.

4,5-Diphenylbenzo[1,2-*b*:4,3-*b*′]dithiophene (3oa):[22] mp 184−185 °C (white powder), 12 mg (9%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.34 (m, 10H), 7.54 (d, J = 5.4 Hz, 2H), 7.78 (d, J = 5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.1, 127.2, 127.3, 128.1, 130.3, 131.4, 133.7, 139.36, 139.4; HRMS *m*/*z* Calcd for $C_{22}H_{14}S_2$ (M^+) 342.0537, found 342.0538.

4,5-Diphenylbenzo[1,2-*b*:3,4-*c*′]dithiophene (3oa′). oil, 18 mg (13%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.31 (m, 10H), 7.43 (d, J = 3.2 Hz, 1H), 7.46 (d, J = 5.3 Hz, 1H), 7.78 (d, J = 5.3 Hz, 1H), 7.91 (d, J = 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.0, 119.7, 123.1, 126.1, 126.8, 127.3, 127.9, 128.0, 130.0, 130.2, 130.8, 130.90, 130.94, 133.7, 138.7, 138.8, 139.1, 139.3; HRMS *m*/*z* Calcd for $C_{22}H_{14}S_2$ (M^+) 342.0537, found 342.0539.

1,4,5-Triphenylnaphtho[2,1-*b*]thiophene (3pa). mp 188−190 °C (brown powder), 62 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.33 (m, 13H), 7.49−7.58 (m, 5H), 7.65 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.9, 125.0, 125.3, 125.6, 126.7, 127.3, 127.65, 127.72, 127.9, 128.0, 128.6, 129.3, 130.0, 130.1, 131.4, 132.0, 132.3, 133.9, 135.3, 138.9, 139.2, 139.6, 140.5, 141.3; HRMS *m*/*z* Calcd for $C_{30}H_{20}S$ (M^+) 412.1286, found 412.1283.

5,6,8,9-Tetraphenyldinaphtho[2,1-*b*:1′,2′-*d*]thiophene (4pa). mp 313−314 °C (white powder), 16 mg (13%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.30 (m, 20H), 7.48 (ddd, J = 1.2, 6.8, 8.0 Hz, 2H), 7.58 (ddd, J = 1.6, 6.8, 8.4 Hz, 2H), 7.77 (dd, J = 0.8, 8.4 Hz, 2H), 9.00 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.4, 125.3, 126.0, 126.8, 127.2, 127.6, 127.8, 128.0, 129.3, 130.2, 131.1, 131.4, 132.1, 133.8, 137.0, 138.7, 139.3, 141.2; HRMS *m*/*z* Calcd for $C_{44}H_{28}S$ (M^+) 588.1912, found 588.1908.

1-Phenyl-4,5-dipropylnaphtho[2,1-*b*]thiophene (3pj). oil, 336 mg (98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13−1.17 (m, 6H), 1.70−1.89 (m, 4H), 3.04−3.08 (m, 2H), 3.11−3.15 (m, 2H), 7.16 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.25 (s, 1H), 7.41−7.51 (m, 6H), 7.83 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.78, 14.80, 23.2, 24.3, 30.9, 35.2, 123.2, 124.2, 124.5, 124.78, 124.83, 127.5, 128.5, 129.2, 129.5, 131.28, 131.34, 132.1, 132.6, 139.5, 140.8, 141.0; HRMS *m*/*z* Calcd for $C_{24}H_{24}S$ (M^+) 344.1599, found 344.1597.

5,6,12,13-Tetraheptylnaphtho[2,1-*b*]naphtho[1′,2′:4,5]-thieno[2,3-*d*]thiophene (4qk). mp 215−216 °C (pale yellow powder), 124 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90−0.95 (m, 12H), 1.32−1.52 (m, 24H), 1.54−1.65 (m, 8H), 1.70−1.78 (m, 4H), 1.82−1.90 (m, 4H), 3.10−3.19 (m, 8H), 7.62 (ddd, J = 1.2, 6.8, 8.4 Hz, 2H), 7.71 (ddd, J = 0.8, 6.8, 8.0 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 8.59 (dd, J = 1.2, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 22.7, 22.8, 28.9, 29.1, 29.2, 30.0, 30.3, 30.4, 31.3, 31.88, 31.93, 33.0, 124.9, 125.0, 125.3, 125.5, 127.3, 127.5, 131.0, 132.4, 133.0, 133.2, 142.5; HRMS *m*/*z* Calcd for $C_{50}H_{68}S_2$ (M^+) 732.4762, found 732.4764.

5,6-Diphenylnaphtho[2,1-*b*]benzofuran (3ra):[5a] mp 213- 215 °C (white powder), 33 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.33 (m, 10H), 7.43−7.49 (m, 3H), 7.62−7.65 (m, 1H), 7.72 (ddd, J = 1.2, 6.8, 8.4 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 8.44−8.49 (m, 1H), 8.72 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.2, 116.8, 122.0, 123.2, 123.4, 124.5, 125.0, 125.9, 126.5, 126.87, 126.92, 127.1, 127.69, 127.73, 128.4, 128.7, 130.2, 131.0, 131.6, 135.5, 138.5, 138.8, 152.7, 156.0; HRMS *m*/*z* Calcd for $C_{28}H_{18}O$ (M^+) 370.1358, found 370.1357.

4,5-Diphenylthieno[3,2-*f*]quinoline (3ua). mp 200−203 °C (yellow powder), 31 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.31 (m, 10H), 7.51 (dd, J = 4.4, 8.4 Hz, 1H), 7.64 (d, J = 5.6 Hz, 1H), 8.06 (d, J = 5.6 Hz, 1H), 8.69 (dd, J = 1.6, 8.4 Hz, 1H), 8.94 (dd, J = 2.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.8, 122.0, 123.8, 126.6, 127.3, 127.5, 127.7, 128.1, 129.8, 131.5, 131.9, 134.8, 135.8, 137.1, 138.1, 139.6, 140.1, 146.5, 149.2; HRMS *m*/*z* Calcd for $C_{23}H_{15}NS$ (M^+) 337.0925, found 337.0927.

5,6-Diphenylthieno[2,3-*h*]isoquinoline (3ua′). mp 201−202 °C (white powder), 19 mg (27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.19 (m, 2H), 7.26−7.30 (m, 8H), 7.50 (d, J = 5.4 Hz, 1H), 7.72 (d, J = 5.5 Hz, 1H), 8.21 (d, J = 5.5 Hz, 1H), 8.54 (d, J = 5.8 Hz, 1H), 9.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.2, 121.3, 123.6, 127.2, 127.7, 127.9, 128.1, 128.7, 129.7, 131.4, 133.2, 134.67, 134.69, 137.2, 137.9, 139.0, 141.0, 143.7, 148.0; HRMS *m*/*z* Calcd for $C_{23}H_{15}NS$ (M^+) 337.0925, found 337.0926.

4,5-Diphenylthieno[3,2-*f*]isoquinoline (3va). mp 222−223 °C (light brown powder), 58 mg (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.31 (m, 10H), 7.64 (d, J = 5.2 Hz, 1H), 8.06 (d, J = 5.6 Hz, 1H), 8.14 (dd, J = 0.8, 5.6 Hz, 1H), 8.68 (d, J = 5.6 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.4, 122.2, 126.3, 127.2, 127.60, 127.65, 127.8, 128.1, 129.8, 131.4, 131.8, 133.7, 134.3, 135.0, 136.8, 138.9, 143.6, 143.8, 152.0; HRMS *m*/*z* Calcd for $C_{23}H_{15}NS$ (M^+) 337.0925, found 337.0923.

4,5-Diphenylthieno[2′,3′:5,6]benzo[1,2-*g*]quinoline (3wa). mp 272−273 °C (pale yellow powder), 55 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.33 (m, 10H), 7.39 (dd, J = 4.0, 8.4 Hz, 1H), 7.62 (d, J = 5.2 Hz, 1H), 8.20 (d, J = 5.2 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.52 (s, 1H), 8.84 (s, 1H), 8.92 (dd, J = 1.6, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.9, 121.8, 122.9, 126.3, 126.7, 127.0, 127.4, 127.7, 127.9, 128.0, 128.4, 129.9, 131.5, 133.3, 134.4, 134.7, 134.9, 135.9, 138.3, 139.5, 140.2, 144.7, 150.9; HRMS *m*/*z* Calcd for $C_{27}H_{17}NS$ (M^+) 387.1082, found 387.1078.

2,4,5-Triphenylnaphtho[2,1-*d*]thiazole (3xa). mp 262−264 °C (white powder), 62 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.31 (m, 10H), 7.45−7.51 (m, 4H), 7.66−7.70 (m, 2H), 8.15−8.18 (m, 2H), 9.02 (dd, J =1.2, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.1, 126.3, 126.6, 126.9, 127.2, 127.3, 127.4, 127.7, 128.1 (overlapped), 129.0, 129.7, 130.5, 131.5, 132.2, 132.4, 134.0, 134.5, 135.8, 138.4, 140.5, 150.0, 167.3; HRMS *m*/*z* Calcd for $C_{29}H_{19}NS$ (M^+) 413.1238, found 413.1239.

2-Methyl-4,5-diphenylnaphtho[1,2-*d*]thiazole (3ya). mp 258−260 °C (white powder), 55 mg (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (s, 3H), 7.18−7.30 (m, 10H), 7.46 (ddd, J = 1.6, 7.2, 8.4 Hz, 1H), 7.63−7.69 (m, 2H), 8.86 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 123.8, 126.1, 126.5, 126.8, 127.2, 127.3, 127.6, 127.7, 128.0, 129.6, 131.5, 132.0, 132.3, 134.7, 135.1, 138.5, 140.6, 148.6, 166.5; HRMS *m*/*z* Calcd for $C_{24}H_{17}NS$ (M^+) 351.1082, found 351.1079.

2,4,5-Triphenylnaphtho[1,2-*d*]oxazole (3bba). mp 207−208 °C (white powder), 61 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.34 (m, 10H), 7.42−7.50 (m, 4H), 7.66 (ddd, J = 1.2, 6.8, 8.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 8.25−8.27 (m, 2H), 8.68 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.2, 124.8, 125.6, 125.9, 126.6, 127.0, 127.2, 127.38, 127.41, 127.78, 127.81, 127.9, 128.8, 130.7, 131.0, 131.1, 131.7, 135.1, 136.2, 137.1, 138.3, 146.9, 162.5; HRMS *m*/*z* Calcd for $C_{29}H_{19}NO$ (M^+) 397.1467, found 397.1466.

5,6-Diphenylnaphtho[2,1-*b*]benzofuran (3cca). mp 233−235 °C (yellow powder), 30 mg (44%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (s, 3H), 7.20−7.33 (m, 10H), 7.42 (ddd, J =1.2, 6.8, 8.4 Hz, 1H), 7.64 (ddd, J = 1.2, 6.8, 8.0 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 121.9, 124.7, 125.3, 125.6, 126.6, 127.0, 127.2, 127.74, 127.78, 127.82, 130.6, 130.8, 131.7, 135.1, 135.6, 136.0, 138.3, 147.0, 163.2; HRMS *m*/*z* Calcd for $C_{24}H_{17}NO$ (M^+) 335.1310, found 335.1313.

(*E*)-Butyl 3-[2-(thiophen-3-yl)phenyl]acrylate (6aa):[6] oil, 34 mg (60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H), 1.36−1.46 (m, 2H), 1.62−1.69 (m, 2H), 4.17 (t, J = 6.6 Hz, 2H), 6.39 (d, J = 15.9 Hz, 1H), 7.14−7.16 (m, 1H), 7.23−7.24 (m, 1H), 7.33−7.44 (m, 4H), 7.66 (d, J = 7.1 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.7, 64.3, 119.4, 124.2, 125.7, 126.9, 127.6, 129.1, 129.8, 130.2, 132.9, 137.4, 140.4, 143.7, 167.0; HRMS *m*/*z* Calcd for $C_{17}H_{18}O_2S$ (M^+) 286.1028, found 286.1027.

(*E*)-Isobutyl 3-(2-(thiophen-3-yl)phenyl)acrylate (6ab). oil, 28 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 0.96 (s, 3H), 1.97 (m, 1H), 3.96 (d, J = 6.6 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 7.15 (dd, J = 1.2, 4.8 Hz, 1H), 7.23 (dd, J = 1.2, 2.8 Hz, 1H), 7.33−7.44 (m, 4H), 7.68 (d, J = 7.4 Hz, 1H), 7.88 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 27.8, 70.5, 119.4, 124.2, 125.7, 126.9, 127.6, 129.1, 129.8, 130.1, 132.9, 137.3, 140.3, 143.7, 166.9; HRMS *m*/*z* Calcd for $C_{17}H_{18}O_2S$ (M^+) 286.1028, found 286.1026.

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(*E*)-*tert*-Butyl 3-(2-(thiophen-3-yl)phenyl)acrylate (6ac). oil, 30 mg (52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 9H), 6.34 (d, J = 16.0 Hz, 1H), 7.15 (dd, J = 1.2, 4.8 Hz, 1H), 7.23 (dd, J = 1.3, 3.0 Hz, 1H), 7.32−7.43 (m, 4H), 7.67 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2, 80.4, 121.1, 124.1, 125.6, 126.7, 127.5, 129.1, 129.6, 130.1, 132.9, 137.3, 140.4, 142.5, 166.2; HRMS m/z Calcd for $C_{17}H_{18}O_2S$ (M^+) 286.1028, found 286.1026.

(*E*)-Ethyl 3-(2-(thiophen-3-yl)phenyl)acrylate (6ad). oil, 24 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 3H), 4.23 (q, J = 7.1 Hz, 2H), 6.39 (d, J = 15.9 Hz, 1H), 7.15 (dd, J = 1.6, 5.2 Hz, 1H), 7.23 (dd, J = 1.6, 3.2 Hz, 1H), 7.33−7.44 (m, 4H), 7.66 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.4, 119.4, 124.2, 125.7, 126.9, 127.6, 129.1, 129.8, 130.2, 132.9, 137.4, 140.3, 143.8, 166.9; HRMS m/z Calcd for $C_{15}H_{14}O_2S$ (M^+) 258.0715, found 258.0714.

(*E*)-Cyclohexyl 3-(2-(thiophen-3-yl)phenyl)acrylate (6ae). oil, 40 mg (64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26−1.57 (m, 6H), 1.71−1.75 (m, 2H), 1.85−1.89 (m, 2H), 4.84−4.90 (m, 1H), 6.39 (d, J = 15.6 Hz, 1H), 7.15 (dd, J = 1.6, 5.2 Hz, 1H), 7.24 (dd, J = 1.2, 2.8 Hz, 1H), 7.33−7.44 (m, 4H), 7.67 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 25.4, 31.6, 72.5, 120.0, 124.2, 125.7, 126.9, 127.6, 129.2, 129.7, 130.1, 133.0, 137.4, 140.4, 143.5, 166.3; HRMS m/z Calcd for $C_{19}H_{20}O_2S$ (M^+) 312.1184, found 312.1182.

(*E*)-Diethyl 2-(thiophen-3-yl)styrylphosphonate (6ag). oil, 30 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (dd, J = 0.4, 6.8 Hz, 6H), 4.10 (qd, J = 7.2, 14.4 Hz, 4H), 6.23 (dd, J = 17.6, 18.8 Hz, 1H), 7.13 (dd, J = 1.6, 5.2 Hz, 1H), 7.22 (dd, J = 1.2, 2.8 Hz, 1H), 7.34−7.41 (m, 4H), 7.55−7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4 (d, J = 6.5 Hz), 61.7 (d, J = 5.6 Hz), 115.5 (d, J = 190.0 Hz), 124.1, 125.7, 126.7 (d, J = 1.24 Hz), 127.6, 129.0, 129.8, 130.2 (d, J = 1.3 Hz), 133.4 (d, J = 22.7 Hz), 137.0, 140.3, 147.2 (d, J = 7.0 Hz); HRMS m/z Calcd for $C_{16}H_{19}O_3PS$ (M^+) 322.0793, found 322.0795.

(*E*)-3-(2-Styrylphenyl)thiophene (6ah):[6] oil, 30 mg (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 16.4 Hz, 1H), 7.21−7.43 (m, 12H), 7.71 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6, 125.2, 126.1, 126.5, 127.5 (overlapped), 127.6, 127.9, 128.7, 129.4, 129.7, 129.9, 135.75, 135.77, 137.5, 141.3; HRMS m/z Calcd for $C_{18}H_{14}S$ (M^+) 262.0816, found 262.0813.

(*E*)-3-(2-(4-Methylstyryl)phenyl)thiophene (6ai). oil, 30 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (s, 3H), 7.00 (d, J = 16.4 Hz, 1H), 7.13−7.40 (m, 11H), 7.70 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 123.5, 125.1, 126.0, 126.4, 126.9, 127.3, 127.5, 129.3, 129.4, 129.7, 129.9, 134.8, 135.6, 135.9, 137.4, 141.4; HRMS m/z Calcd for $C_{19}H_{16}S$ (M^+) 276.0973, found 276.0975.

(*E*)-3-(2-(4-(*tert*-Butyl)styryl)phenyl)thiophene (6aj). oil, 29 mg (45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 7.01 (d, J = 16.4 Hz, 1H), 7.19−7.23 (m, 2H), 7.27−7.40 (m, 9H), 7.71 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.6, 123.6, 125.1, 125.6, 126.1, 126.3, 127.2, 127.4, 127.5, 129.4, 129.5, 129.9, 134.8, 135.6, 136.0, 141.4, 150.7; HRMS m/z Calcd for $C_{22}H_{22}S$ (M^+) 318.1442, found 318.1441.

(*E*)-3-(2-(4-Methoxystyryl)phenyl)thiophene (6ak). oil, 31 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.87 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 16.0 Hz, 1H), 7.10 (d, J = 16.4 Hz, 1H), 7.21 (dd, J = 1.6, 5.2 Hz, 1H), 7.27−7.39 (m, 7H), 7.69 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 114.1, 123.5, 125.1, 125.8, 125.9, 127.2, 127.5, 127.7, 129.2, 129.4, 129.9, 130.4, 135.5, 136.1, 141.5, 159.2; HRMS m/z Calcd for $C_{19}H_{16}OS$ (M^+) 292.0922, found 292.0921.

(*E*)-3-(2-(2-([1,1′-Biphenyl]-4-yl)vinyl)phenyl)thiophene (6al). oil, 44 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 16.0 Hz, 1H), 7.22−7.61 (m, 12H), 7.56−7.61 (m, 4H), 7.74 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6, 125.2, 126.1, 126.9, 127.0, 127.30, 127.34, 127.57, 127.58, 128.0, 128.8, 129.2, 129.4, 130.0, 135.8 (overlapped), 136.6, 140.3, 140.6, 141.4; HRMS m/z Calcd for $C_{24}H_{18}S$ (M^+) 338.1124, found 338.1131.

(*E*)-3-(2-(4-Chlorostyryl)phenyl)thiophene (6am). oil, 38 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 16.0 Hz, 1H), 7.18−7.41 (m, 11H), 7.69 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6, 125.3, 126.1, 127.6, 127.7, 127.8, 128.4, 128.5, 128.8, 129.4, 130.0, 133.1, 135.4, 135.8, 136.0, 141.3; HRMS m/z Calcd for $C_{18}H_{13}ClS$ (M^+) 296.0426, found 296.0426.

(*E*)-3-(2-(4-(trifluoromethyl)styryl)phenyl)thiophene (6an). oil, 41 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 16.0 Hz, 1H), 7.19 (dd, J = 1.6, 5.2 Hz, 1H), 7.27 (dd, J = 1.2, 3.2 Hz, 1H), 7.30−7.43 (m, 5H), 7.49 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 9.2 Hz, 2H), 7.71−7.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.7, 124.2 (q, J = 270.0 Hz), 125.4, 125.6 (q, J = 3.8 Hz), 126.2, 126.6, 127.7, 128.1 (overlapped), 129.2 (q, J = 32.6 Hz), 129.3, 130.1, 130.4, 135.1, 136.1, 140.9, 141.1; HRMS m/z Calcd for $C_{19}H_{13}F_3S$ (M^+) 330.0690, found 330.0692.

(*E*)-3-(2-(2-(Naphthalen-2-yl)vinyl)phenyl)thiophene (6ao). oil, 31 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 16.4 Hz, 1H), 7.24 (dd, J = 1.2, 4.8 Hz, 1H), 7.31−7.48 (m, 8H), 7.60 (dd, J = 1.6, 8.4 Hz, 1H), 7.76−7.82 (m, 5H);^{13}C NMR (100 MHz, $CDCl_3$) δ 123.5, 123.6, 125.3, 125.9, 126.1, 126.3, 126.6, 127.59, 127.60, 127.7, 128.0, 128.2, 128.3, 129.4, 129.8, 130.0, 132.9, 133.6, 135.1, 135.8 (overlapped), 141.4; HRMS m/z Calcd for $C_{22}H_{16}S$ (M^+) 312.0973, found 312.0971.

2,3,6,7-Tetramethoxybenzo[*b*]benzo[11,12]chryseno[6,5-*d*]-thiophene (7). mp 235−236 °C (yellow powder), 14 mg (59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 4.17 (s, 3H), 4.19 (s, 3H), 4.20 (s, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.59−7.64 (m, 2H), 7.73 (tdd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.86 (s, 1H), 7.91 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H), 8.71 (s, 1H), 8.83 (d, J = 8.0 Hz, 1H), 8.90 (d, J = 8.4 Hz, 1H), 9.01 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.07, 56.13, 56.2, 56.4, 104.1, 104.3, 107.7, 111.1, 122.5, 123.1, 123.3, 123.9, 124.0, 124.2, 124.5, 124.9, 125.07, 125.12, 125.14, 126.6, 127.2, 128.4, 129.1, 129.36, 129.4, 134.9, 135.9, 139.5, 148.2, 149.1, 149.2 (overlapped); HRMS (APCI) m/z Calcd for $C_{32}H_{25}O_4S$ ([M + H]$^+$) 505.1468, found 505.1467.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Results for H/D exchange experiments and copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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