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Synthesis of functionalized benzothiophenes and dibenzothiophenes by twofold Heck and subsequent 6π-electrocyclization reactions of 2,3-dibromothiophenes and 2,3-dibromobenzothiophenes

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ABSTRACT

Benzothiophenes and dibenzothiophenes were prepared by twofold Heck reactions of 2,3-dibromothiophene and 2,3-dibromobenzothiophene, respectively, and subsequent thermal 6π-electrocyclization. The Heck reaction of 2,3-dibromothiophene and 2,3-dibromobenzothiophene with 1 equiv of alkenes proceeded with different regioselectivities and afforded 2-alkenylthiophenes and 3-alkenylbenzothiophenes.

1. Introduction

The benzothiophene skeleton occurs in the structure of many natural, synthetic, and biologically active molecules, including bryoanthrathiophene,[1] mobam (4-(*N*-methyl carbamoyl)benzo[*b*]-thiophene)[2] and 3-(2-aminoethyl) benzo[*b*]thiophene.[3] Parent benzothiophene has been found in the coal tar.[4] Raloxifene, zileuton, and sertaconazole represent important drugs containing a benzothiophene unit.[5] Benzothiophene derivatives have been reported as antiangiogenics,[1] anti-inflammatories,[6] analgesics,[7] enzyme inhibitors,[6] antiestrogen,[8] antitumor,[9] and pesticides.[10] Due to their significant pharmacological properties, many methodologies for the synthesis of benzothiophenes have been reported in recent years (Fig. 1).[11]

We have reported preliminary results related to the synthesis of benzothiophenes and dibenzothiophenes by twofold Heck reactions of 2,3-dibromothiophene[12] and 2,3-dibromobenzothiophene,[13] respectively, and subsequent 6π-electrocyclization/dehydrogenation reactions. Herein, we report full details of these studies and

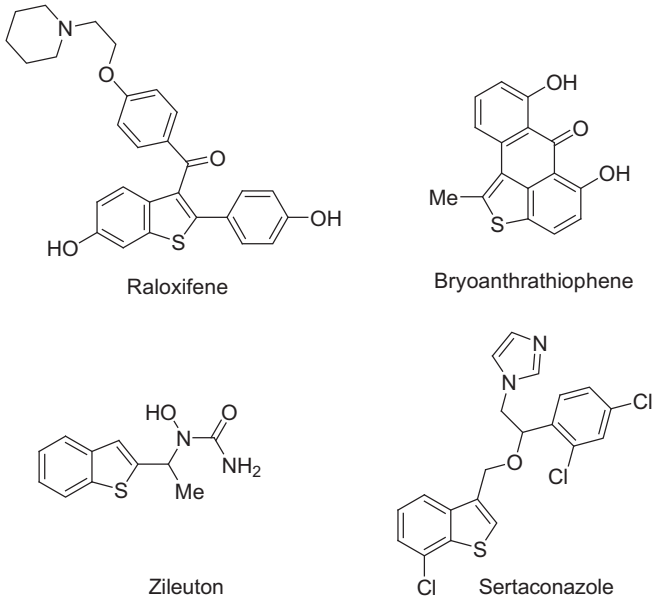

Fig. 1. Structure of raloxifene, bryoanthrathiophene, zileuton and sertaconazole.

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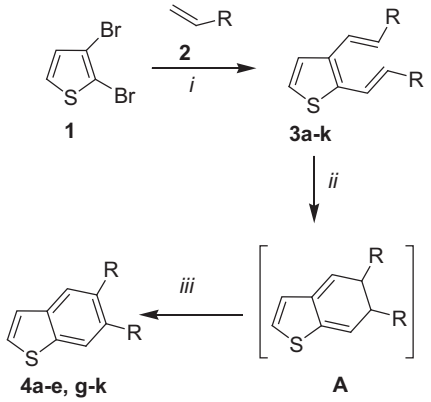
extension of the scope to 4,5-dibromothiophene-2-carbaldehyde and 5-aryl-2,3-dibromothiophenes, which are readily available by Suzuki–Miyaura reactions of 2,3,5-tribromothiophene.

2. Results and discussion

2.1. 2,3-Dibromothiophene

The Heck reaction of 2,3-dibromothiophene (**1**) with alkenes **2** (2.5 equiv) afforded the 2,3-di(alkenyl)benzothiophenes **3a**–**k** in good yields (Scheme 1, Table 1). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol %) using SPhos or XPhos (10 mol %). These biaryl monophosphine ligands were recently developed by Buchwald and co-workers (Fig. 2).[14] The reactions were carried out in DMF at 120 °C for 48 h. The employment of $Pd(PPh_3)_4$ resulted in lower yields. Heating of a xylene solution of **3a**–**e** and **3g**–**k** in the presence of Pd/C resulted in the formation of benzothiophenes **4a**–**e** and **4g**–**k** in quantitative yields. The products are formed by thermal 6π-electrocyclization and subsequent dehydrogenation. The reaction had to be carried out at 200 °C as no conversion was observed at lower temperatures.



Scheme 1. Synthesis of **3a**–**k** and **4a**–**e**,**g**–**k**. Conditions: (i), **2** (2.5 equiv), $Pd(OAc)_2$ (5 mol %), SPhos or XPhos (10 mol %), NEt_3, DMF, 120 °C, 48 h; (ii), xylene, 200 °C, 24 h; (iii), Pd/C (10 mol %), xylene, 200 °C, 48 h.

Table 1
Synthesis of **3a**–**k** and **4a**–**e**,**g**–**k**

2, 3, 4	R	% (**3**)[a]	% (**4**)[a]
a	CO_2Me	81[b]	98
b	CO_2Et	90[c]	99
c	CO_2^iBu	86[b]	98
d	CO_2^nBu	93[c]	98
e	CO_2^nHex	92[c]	97
f	CO_2^tBu	89[b]	—[d]
g	$CO_2[CH_2CH(Et)(CH_2)_3CH_3]$	85[c]	97
h	4-$^tBuC_6H_4$	94[c]	98
i	4-$(MeO)C_6H_4$	83[c]	97
j	4-MeC_6H_4	88[b]	95
k	4-ClC_6H_4	82[c]	—[d]

[a] Yields of isolated products.
[b] XPhos was used.
[c] SPhos was used.
[d] Experiment was not carried out.

The structure of **3i** was independently confirmed by X-ray crystal structure analysis (Fig. 3). In both structures, the two alkenyl groups are in the same plane and almost in the plane of the thiophene ring (torsion angle 0.8 (2)°).

The Heck reaction of **1** with only 1 equiv of alkenes **2** resulted in the formation of 2-alkenylthiophenes **5a**–**e** by regioselective coupling and subsequent Pd(0)-catalyzed reduction (Scheme 2, Table 2).

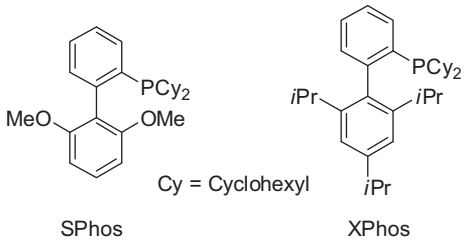


Fig. 2. Biaryl monophosphine ligands developed by Buchwald and co-workers.

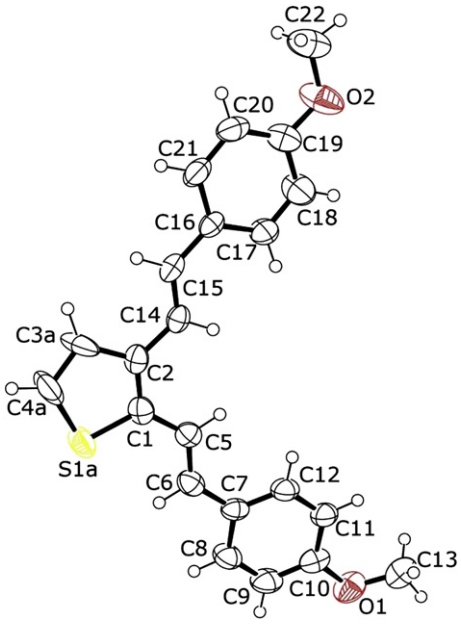
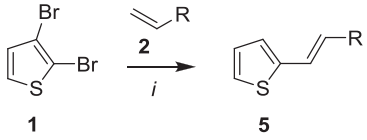


Fig. 3. Crystal structure of **3i**.



Scheme 2. Synthesis of **5a**–**e**. Conditions: (i), **2** (1.0 equiv), $Pd(OAc)_2$ (2.5–5 mol %), SPhos or XPhos (5–10 mol %), NEt_3, DMF, 120 °C, 24 h.

Table 2
Synthesis of **5a**–**e**

2	5	R	% (**5**)[a]
a	**a**	CO_2Me	75[b]
b	**b**	CO_2Et	78[c]
c	**c**	CO_2^iBu	74[b]
f	**d**	CO_2^tBu	87[b]
e	**e**	CO_2^nHex	76[c]

[a] Yields of isolated products.
[b] XPhos was used.
[c] SPhos was used.

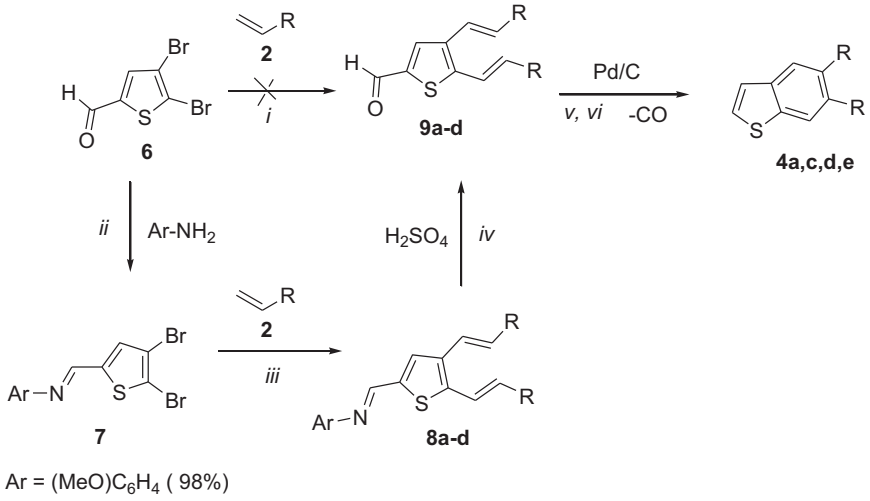
2.2. 4,5-Dibromothiophene-2-carbaldhyde

The Heck reaction of commercially available 4,5-dibromothiophene-2-carbaldehyde (**6**) with 2.5 equiv of alkenes **2** did not give the expected products **9**, but 5-alkenylthiophene-2-carbaldehyde. The formation of these products can be explained by regioselective coupling of carbon atom C-5 of **6** with the alkenes **2** and subsequent Pd(0)-catalyzed reduction of one C–Br bond. The

reduction can be due to the presence of the aldehyde, an electron withdrawing group, which makes the molecule more prone to reduction. To solve the problem, we have protected the aldehyde as a Schiff base. The reaction of **6** with 1.5 equiv of 4-methoxyaniline in glacial acetic acid gave the (*E*)-4-aryl-*N*-((4,5-dibromothiophen-2-yl) methylene) **7** (Scheme 3). The Heck reaction of **7** with alkenes **2** (2.5 equiv) afforded the desired compounds **8a**–**d** in 55–76% yield (Scheme 3, Table 3). The reactions were carried out using $Pd(OAc)_2$ (5 mol %) as the catalyst in the presence of SPhos or $P(Cy)_3$ (10 mol %). The 1-formyl-4,5-dialkenylthiophenes **9a**–**d** were obtained by hydrolysis of the imino group of **8a**–**d** (deprotection) (Scheme 3, Table 4).

11a–**d** with alkenes **2** afforded the 2-aryl-4,5-di(alkenyl) thiophenes **12a**–**d** in 75–89% yield (Scheme 4, Table 5). The reactions were carried out using $P(Cy)_3$ (10 mol %) as ligand. Products **12a**–**d** were transformed to benzothiophenes **13a**–**d** in 82–93% yield.

The structure of **13d** was independently confirmed by X-ray crystal structure analysis (Fig. 5). The phenyl ring located at carbon C1a and the benzothiophene moiety are in plane. The torsion angles between the benzothiophene and alkenyl groups are 19.7 (8) and 66.1 (3)° for O5a–C21a–C7a–C8 and O3a–C16a–C6a–C7a, respectively.



Scheme 3. Synthesis of **7**, **8a**–**d**, **9a**–**d** and **4a**,**c**,**d**,**e**. Conditions: (i), **2** (2.5 equiv), $Pd(OAc)_2$ (5 mol %), SPhos, XPhos or $P(Cy)_3$ (10 mol %), NEt_3 (8.0 equiv), DMF, 90 °C, 12 h; (ii), 30 (1.0 equiv), 4-methoxyaniline (1.5 equiv), glacial acetic acid, 20 °C, 15 min; (iii), **2** (2.5 equiv), $Pd(OAc)_2$ (5 mol %), SPhos or $P(Cy)_3$ (10 mol %), NEt_3 (8.0 equiv), DMF, 90 °C, 12 h; (iv), **8a**–**d**, dichloromethane, (H_2SO_4, 2.5 M), 20 °C, 20 h; (v), **9a**–**d**, xylene, 200 °C, 24 h; (vi), Pd/C (10 mol %), xylene, 200 °C, 48 h.

Table 3
Synthesis of **8a**–**d**

2	8	R	% (**8**)[a]
a	**a**	CO_2Me	62[b]
c	**b**	CO_2^iBu	76[c]
d	**c**	CO_2^nBu	55[c]
e	**d**	CO_2^nHex	67[c]

[a] Yields of isolated products.
[b] SPhos was used.
[c] $P(Cy)_3$ was used.

Table 4
Synthesis of **9a**–**d**

8, 9	R	% (**9**)[a]
a	CO_2Me	98
b	CO_2^iBu	95
c	CO_2^nBu	92
d	CO_2^nHex	96

[a] Yields of isolated products.

Compounds **4a**,**c**,**d**,**e** were formed after thermal 6π-electrocyclization and aromatization of **9a**–**d**. The formation of **4a**,**c**,**d**,**e** can be explained by thermal extrusion of CO. The structures of **7** were independently confirmed by X-ray crystal structure analysis (Fig. 4). The phenyl ring at C6 is twisted from the plane of the thiophene by −2.9 (9)°. The N–C5–C4 bond angle is 121.5 (3)°.

2.3. 5-Aryl-2,3-dibromothiophenes

2,3,5-Tribromothiophene (**10**) was prepared by reaction of thiophene with bromine (3.1 equiv) in 81% yield.[15] The Suzuki–Miyaura reaction of **10** with aryl boronic acids (1.1 equiv) afforded the 5-aryl-2,3-dibromothiophenes **11a**–**d**[16] (Scheme 4). The Heck reaction of

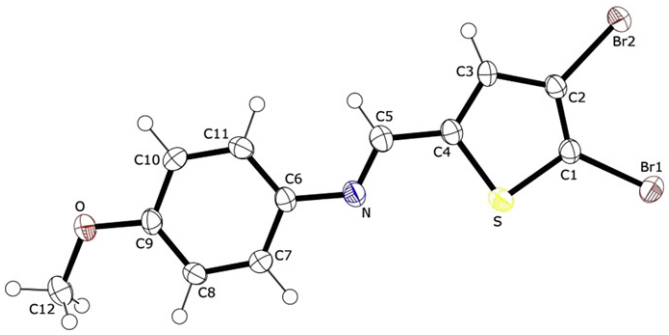
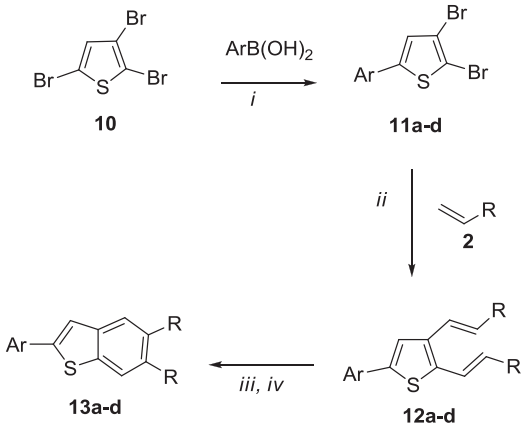


Fig. 4. Molecular structure of **7**.

The reaction of benzothiophene (**14**) with bromine (2.0 equiv) and KOAc (2.0 equiv) in CH_2Cl_2 (reflux, 18 h) resulted in formation of (commercially available) 2,3-dibromobenzothiophene (**15a**) in 84% yield (Scheme 5).[17,18] During our experiments related to the scale-up of this reaction we have found that more vigorous conditions (reflux, 18 h) were required to avoid the formation of monobrominated byproducts. We have also prepared known[19] 2,3,6-tribromobenzothiophene (**15b**) in 70% yield by using an excess of bromine.

The Heck reaction of **15a** with acrylates **2d**,**l** (2.5 equiv) afforded the 2,3-di(alkenyl)benzothiophenes **16b**,**e** in good yields (Scheme 6, Table 6). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol %) and the biaryl monophosphine ligand SPhos (10 mol %). The reactions were carried out in DMF at 100 °C for 12 h. Heating of a xylene solution of **16b**,**e** in the presence of Pd/C resulted in the formation of dibenzothiophene **18b**,**e** in 79–81% yield. The employment of $Pd(PPh_3)_4$ and other catalysts and ligands proved to be less successful in terms of yield.



Scheme 4. Synthesis of **12a**–**d** and **13a**–**d**. Conditions: (i), **1** (1.0 equiv), $ArB(OH)_2$ (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (2 M), 1,4-dioxane/toluene=1:1, 100 °C, 12 h; (ii), **11a**–**d**(1 equiv), **2** (2.5 equiv), $Pd(OAc)_2$ (5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (8.0 equiv), DMF, 100 °C, 24 h; (iii), **12a**–**d**, diphenylether, 200 °C, 24 h; (iv), Pd/C (10 mol %), diphenylether, 200 °C, 48 h.

Table 5
Synthesis of **12a**–**d** and **13a**–**d**

2	11, 12, 13	Ar	R	% (**12**)[a]	% (**13**)[a]
c	**a**	4-EtC_6H_4	CO_2^iBu	89	93
d	**b**	4-$^tBuC_6H_4$	CO_2^nBu	75	82
c	**c**	3,5-$Me_2C_6H_3$	CO_2^iBu	78	85
c	**d**	2-(MeO)C_6H_4	CO_2^iBu	76	88

[a] Yields of isolated products.

was established by X-ray crystal structure analysis.[13] The best yield (81%) was obtained when **15a** was treated with ethyl acrylate (**2b**) using $Pd(OAc)_2$ (5 mol %) in combination with biaryl monophosphine ligand SPhos (10 mol %). The yields dropped when $Pd(PPh_3)_4$ was used. The formation of products **19** can be explained by Heck reaction, which occurs at carbon atom C-3, and reduction of the bromide function located at carbon C-2. This result is surprising because the Heck reaction of 2,3-dibromothiophene with 1 equiv of alkenes results in the formation of 2-alkenylthiophenes **5** (vide supra).

The Heck reaction of styrene (**2l**) with 2,3,6-tribromobenzothiophene (**15b**) gave the 2,3,6-tri(alkenyl)benzothiophenes **20** (Scheme 8). The reaction was carried out in DMF at 100 °C for 12 h; $Pd(OAc)_2$ in the presence of SPhos was used as the catalyst. Product **21** was isolated (mixture of two isomers) when the reaction was carried out at 130 °C. Reflux of a xylene solution of crude **20** or **21**, in the presence of Pd/C, afforded the 2,3-diphenyl-7-styryldibenzothiophene **22**.

3. Conclusion

2,3-Dialkenylthiophenes, 4,5-dialkenylthiophene-2-carbaldehydes, 2,3-dialkenyl-5-aryl thiophenes, and 2,3-dialkenylbenzothiophenes were prepared by the first Heck reactions of 2,3-dibromo thiophenes, 4,5-dibromothiophene-2-carbaldehydes, 5-aryl-2,3-dibromothiophenes, and 2,3-dibromobenzothiophene, respectively. Functionalized benzothiophenes and dibenzothiophenes were prepared by Pd/C-catalyzed domino '6π-electrocyclization/dehydrogenation' reactions of the 2,3-dialkenylthiophenes and 2,3-

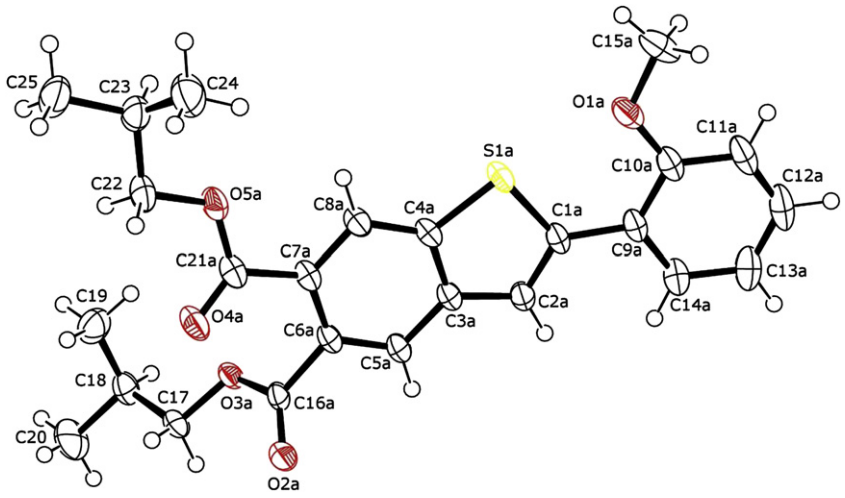


Fig. 5. Crystal structure of **13d**.

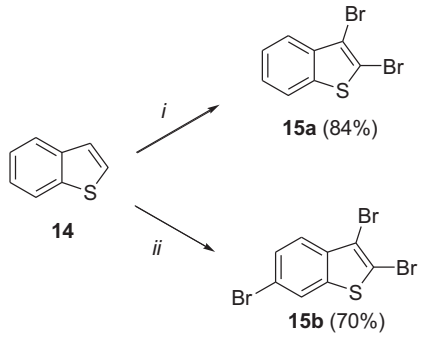
The $Pd(OAc)_2$-catalyzed reaction of **15a** with acrylates **2b**,**c**,**e** carried out at 130 °C and using biaryl monophosphine ligand SPhos, afforded the 1,2-dihydrodibenzothiophenes **17a**,**c**,**d** as a mixture of two isomers. Their formation can be explained by a domino 'two-fold Heck/thermal 6π-electrocyclization' cyclization and subsequent double bond migration. Heating of a xylene solution of crude **17a**,**c**,**d** in the presence of Pd/C resulted in the formation of dibenzothiophenes **18a**,**c**,**d** in 74–77% overall yields. The reaction of **15a** with styrene **2k** directly afforded dibenzothiophene **18f** (83%) in only one step.

Suzuki–Miyaura and Stille reactions of **15a** regioselectively occur at carbon atom C-2. Therefore, it was surprising that the Heck reaction of **15a** with 1 equiv of alkenes **2b**,**d**,**j**,**m**,**l** afforded the 3-(alkenyl)benzothiophenes **19a**–**e** (Scheme 7, Table 7). The structure dialkenylbenzothiophenes. The reaction of 2,3-dibromothiophene with 1 equiv of alkenes resulted in the formation of 2-alkenylthiophenes, while the corresponding reaction of 2,3-dibromobenzothiophene proceeded with different regioselectivity and gave 3-alkenylbenzothiophenes.

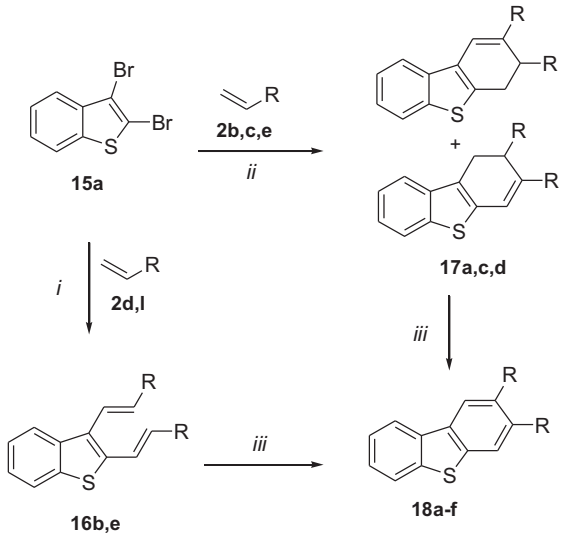
4. Experimental section

4.1. General

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI,



Scheme 5. Bromination of benzothiophene (**14**). Reagents and conditions: (i) Br_2 (2.0 equiv), KOAc (2.0 equiv), CH_2Cl_2, reflux, 18 h; (ii) Br_2 (4.5 equiv), KOAc (4.5 equiv), CH_2Cl_2, reflux, 24 h.



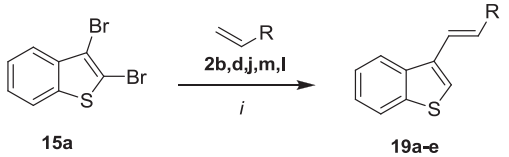
Scheme 6. Synthesis of **16b**,**e** and **18a**–**f**. Reagents and conditions: (i) $Pd(OAc)_2$ (5 mol %), XPhos (10 mol %), **2** (2.5 equiv), Et_3N (8.0 equiv), DMF, 100 °C, 12 h; (ii) $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), **2** (2.5 equiv), Et_3N, DMF, 130 °C, 48 h; (iii) Pd/C (10 mol %), xylene, reflux, 48 h.

Table 6
Synthesis of **16b**,**e** and **18a**–**f**

2	16, 18	R	% (**16**)[a]	% (**18**)[a]
b	**a**	CO_2Et	—[b]	76
d	**b**	CO_2^nBu	71	81
c	**c**	CO_2^tBu	—[b]	74
e	**d**	CO_2^nHex	—[b]	77
l	**e**	Ph	85	79
k	**f**	4-ClC_6H_4	—[b]	83[c]

[a] Yields of isolated products based on **15a**.
[b] Experiment was not carried out.
[c] Product was directly formed from **15a** in one step.

70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used. Details of the crystal structure analyses are given in Ref. 20.



Scheme 7. Synthesis of **19a**–**e**. Reagents and conditions: (i), $Pd(OAc)_2$ (2.5–5 mol %), SPhos (for **19a**,**b**,**d**) or XPhos (for **19c**,**e**) 5–10 mol %, **2** (1.25 equiv), Et_3N, DMF, 130 °C, 24 h.

Table 7
Synthesis of **19a**–**e**

2	19	R	% (**19**)[a]
b	**a**	CO_2Et	81
d	**b**	CO_2^nBu	65
m	**c**	CN	51
l	**d**	Ph	74
j	**e**	4-MeC_6H_4	76

[a] Yields of isolated products.

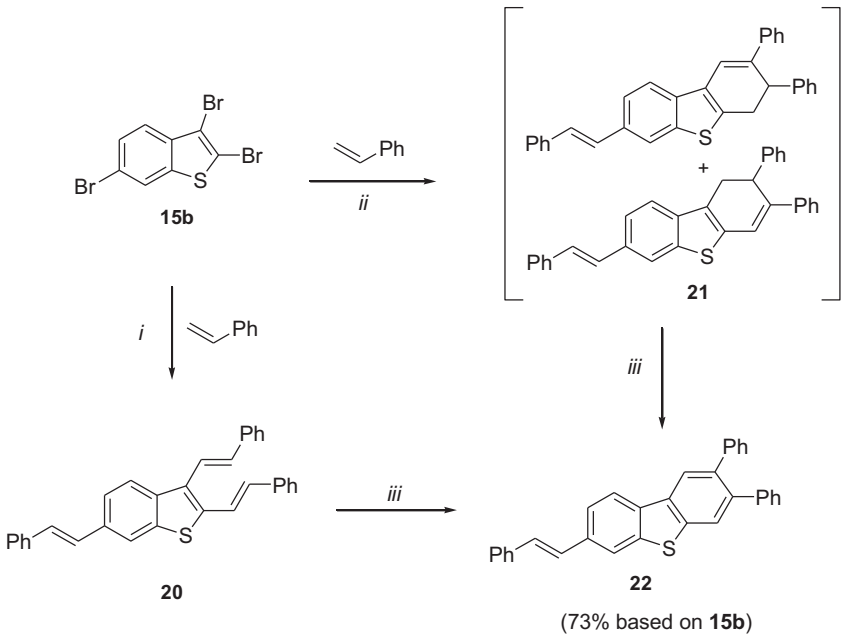
4.2. General procedure A for the synthesis of di(alkenyl) thiophenes (3), (8), (9) and (12)

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol %) and L [XPhos, SPhos or $P(Cy)_3$] (10 mol %) in DMF (5 mL) was purged with argon and stirred at 20 °C to give a yellowish or brownish clear solution. To the stirred solution were added 2,3-dibromothiophene (**1**), **7a**,**b** or **11a**–**d** (1.0 mmol), NEt_3 (1.1 mL, 8.0 mmol) and an alkene (1.25 equiv per Br). The reaction mixture was stirred at 100–120 °C for 24–48 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

*4.2.1. (2E,2′E)-Dimethyl 3,3′-(thiophene-2,3-diyl)diacrylate (**3a**).* Product **3a** was prepared starting with **1** (242 mg, 1.0 mmol), methyl acrylate (0.23 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (204 mg, 81%). ^1H NMR (300 MHz, $CDCl_3$): δ=3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.22 (d, 1H, J=15.5 Hz, CH), 6.24 (d, 1H, J=15.8 Hz, CH), 7.18 (d, 1H, J=5.5 Hz, ArH), 7.25 (d, 1H, J=5.3 Hz, ArH), 7.79 (d, 1H, J=15.8 Hz, CH), 7.94 (d, 1H, J=15.6 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=51.8, 51.9 (OCH_3), 118.8, 120.0, 126.4, 127.8, 133.7, 134.7 (CH), 138.2, 139.8 (C), 166.7, 167.1 (CO). IR (KBr, cm^{-1}): ν=3110, 2950, 2923 (w), 1705 (s), 1631 (m), 1513 (w), 1427, 1308, 1270 (m), 1190, 1170, 1159 (s), 1110, 1009 (m), 972, 805 (s), 724, 709, 612, 575, 535 (m). GC–MS (EI, 70 eV): m/z (%)= 252 (30) $[M]^+$, 221 (13), 193 (45), 192 (22), 177 (22), 161 (58), 149 (26), 135 (13), 134 (100), 133 (18), 89 (19), 67 (13). HRMS (EI, 70 eV): calcd for $C_{12}H_{12}O_4S$ $[M]^+$: 252.04508; found: 252.04533.

*4.2.2. (2E,2′E)-Diethyl 3,3′-(thiophene-2,3-diyl)diacrylate (**3b**).* Product **3b** was prepared starting with **1** (242 mg, 1.0 mmol), ethyl acrylate (0.27 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown semisolid (252 mg, 90%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.26 (t, 3H, J=7.1 Hz, CH_3), 1.27 (t, 3H, J=7.1 Hz, CH_3), 4.20 (q, 2H, J=7.1 Hz, CH_2O), 4.21 (q, 2H, J=7.1 Hz, CH_2O), 6.23 (d, 1H, J=15.5 Hz, CH), 6.24 (d, 1H, J=15.8 Hz, CH), 7.18 (d, 1H, J=5.6 Hz, ArH), 7.24 (d, 1H, J=5.3 Hz, ArH), 7.79 (d, 1H, J=15.8 Hz, CH), 7.93 (d, 1H, J=15.5 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.3 ($2CH_3$), 60.6, 60.7 (CH_2O), 119.2, 120.4, 126.4, 127.7, 133.5, 134.5 (CH), 138.2, 139.8 (C), 166.3, 166.7 (CO). IR (KBr, cm^{-1}): ν=3095, 2985, 2939, 2872 (w), 1697 (s), 1621 (m), 1505, 1471, 1443, 1394 (w), 1369, 1315, 1298, 1278, 1254, 1212 (m), 1176 (s), 1110, 1028, 976, 956, 868, 851 (m), 831, 808 (w), 771, 764, 718, 701, 664, 627, 582 (m). GC–MS (EI, 70 eV): m/z (%)=280 (24) $[M]^+$, 235 (11), 207 (31), 206 (15), 179 (21), 178 (08), 163 (45), 162 (07), 161 (34), 136 (12), 135 (100), 134 (44), 91 (16), 89 (13), 29 (19). HRMS (EI, 70 eV): calcd for $C_{14}H_{16}O_4S$ $[M]^+$: 280.07638; found: 280.07680.

*4.2.3. (2E,2′E)-Diisobutyl 3,3′-(thiophene-2,3-diyl)diacrylate (**3c**).* Product **3c** was prepared starting with **1** (242 mg, 1.0 mmol), *iso*-butyl



Scheme 8. Synthesis of **22**. Conditions: (i) $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), **2** (3.75 equiv), NEt_3 (8.0 equiv), DMF, 100 °C, 12 h; (ii) $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), **2** (3.75 equiv), NEt_3, DMF, 130 °C, 48 h; (iii) Pd/C (10 mol %), xylene, reflux, 48 h.

acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (288 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.92 (d, 12H, J=6.7 Hz, $4CH_3$), 1.89–1.98 (m, 2H, CH), 3.92 (d, 2H, J=6.7 Hz, CH_2O), 3.93 (d, 2H, J=6.7 Hz, CH_2O), 6.23 (d, 1H, J=15.5 Hz, CH), 6.25 (d, 1H, J=15.7 Hz, CH), 7.19 (d, 1H, J=5.4 Hz, ArH), 7.25 (d, 1H, J=5.4 Hz, ArH), 7.79 (d, 1H, J=15.8 Hz, CH), 7.93 (d, 1H, J=15.6 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.1 ($4CH_3$), 27.8 (2CH), 70.8, 70.9 (CH_2O), 119.2, 120.4, 126.4, 127.7, 133.5, 134.5 (CH), 138.2, 139.8 (C), 166.4, 166.8 (CO). IR (KBr, cm^{-1}): ν=3106, 2959, 2873 (w), 1704, 1619 (s), 1508, 1468, 1393, 1375, 1342 (w), 1311, 1266, 1237, 1201 (m), 1154 (s), 1018, 967, 852 (m), 832, 750 (w), 709 (m), 665, 620, 586, 533 (w). GC–MS (EI, 70 eV): m/z (%)=336 (25) $[M]^+$, 263 (19), 180 (15), 179 (100), 178 (36), 163 (82), 162 (12), 161 (42), 135 (83), 134 (59), 91 (13), 57 (80), 41 (34). HRMS (EI, 70 eV): calcd for $C_{18}H_{24}O_4S$ $[M]^+$: 336.13898; found: 336.13894.

*4.2.4. (2E,2′E)-Dibutyl 3,3′-(thiophene-2,3-diyl)diacrylate (**3d**).* Product **3d** was prepared starting with **1** (242 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (312 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, 6H, J=7.4 Hz, $2CH_3$), 1.32–1.40 (m, 4H, $2CH_2$), 1.59–1.64 (m, 4H, $2CH_2$), 4.14 (t, 2H, J=6.7 Hz, CH_2O), 4.15 (t, 2H, J=6.7 Hz, CH_2O), 6.21 (d, 1H, J=15.5 Hz, CH), 6.24 (d, 1H, J=15.8 Hz, CH), 7.18 (d, 1H, J=5.3 Hz, ArH), 7.24 (d, 1H, J=5.4 Hz, ArH), 7.78 (d, 1H, J=15.8 Hz, CH), 7.93 (d, 1H, J=15.6 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.7 ($2CH_2$), 64.5, 64.6 (CH_2O), 119.3, 120.4, 126.4, 127.7, 133.5, 134.4 (CH), 138.2, 139.8 (C), 166.4, 166.8 (CO). IR (KBr, cm^{-1}): ν=2957, 2931, 2872 (w), 1704 (s), 1619 (m), 1509, 1463, 1433, 1383, 1354 (w), 1309, 1276, 1238, 1202 (m), 1159 (s), 1061, 1024, 968, 853, 751, 710 (m), 665, 619, 584 (w). GC–MS (EI, 70 eV): m/z (%)=336 (26) $[M]^+$, 263 (11), 235 (15), 234 (10), 180 (12), 179 (94), 178 (32), 163 (62), 162 (11), 161 (45), 135 (100), 134 (50), 91 (14), 57 (56), 41 (33), 29 (21). HRMS (EI, 70 eV): calcd for $C_{18}H_{24}O_4S$ $[M]^+$: 336.13898; found: 336.13896.

*4.2.5. (2E,2′E)-Dihexyl 3,3′-(thiophene-2,3-diyl)diacrylate (**3e**).* Product **3e** was prepared starting with **1** (242 mg, 1.0 mmol), hexyl acrylate (2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (360 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, 6H, J=6.9 Hz, $2CH_3$), 1.22–1.37 (m, 12H, $6CH_2$), 1.58–1.68 (m, 4H, $2CH_2$), 4.13 (t, 2H, J=6.8 Hz, CH_2O), 4.14 (t, 2H, J=6.8 Hz, CH_2O), 6.22 (d, 1H, J=15.5 Hz, CH), 6.24 (d, 1H, J=15.8 Hz, CH), 7.18 (d, 1H, J=5.3 Hz, ArH), 7.24 (d, 1H, J=5.4 Hz, ArH), 7.78 (d, 1H, J=15.8 Hz, CH), 7.93 (d, 1H, J=15.5 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.7 ($2CH_2$), 31.4 ($2CH_2$), 64.9, 65.0 (CH_2O), 119.3, 120.4, 126.4, 127.6, 133.5, 134.4 (CH), 138.2, 139.8 (C), 166.4, 166.8 (CO). IR (KBr, cm^{-1}): ν=2954, 2927, 2857 (w), 1707 (s), 1620 (m), 1510, 1465, 1434, 1379 (w), 1309, 1267, 1240, 1201 (m), 1160 (s), 1058, 1013, 970 (m), 906 (w), 854 (m), 834, 750 (w), 710 (m), 665, 620, 586 (w). GC–MS (EI, 70 eV): m/z (%)=392 (07) $[M]^+$, 263 (32), 262 (18), 205 (16), 180 (14), 179 (100), 178 (29), 161 (44), 135 (35), 134 (16), 91 (07), 57 (07), 41 (46). HRMS (EI, 70 eV): calcd for $C_{22}H_{32}O_4S$ $[M]^+$: 392.20158; found: 392.20182.

*4.2.6. (2E,2′E)-Bis(tert-butyl) 3,3′-(thiophene-2,3-diyl) diacrylate (**3f**).* Product **3f** was prepared starting with **1** (242 mg, 1.0 mmol), *tert*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as yellowish solid (299 mg, 89%), mp=85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.45 (s, 9H, $3CH_3$), 1.46 (s, 9H, $3CH_3$), 6.13 (d, 1H, J=15.5 Hz, CH), 6.16 (d, 1H, J=15.7 Hz, CH), 7.15 (d, 1H, J=5.3 Hz, ArH), 7.20 (d, 1H, J=5.4 Hz, ArH), 7.68 (d, 1H, J=15.7 Hz, CH), 7.84 (d, 1H, J=15.6 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.2 ($6CH_3$), 80.1, 80.7 (C–O), 121.1, 122.2, 126.4, 127.3, 132.7, 133.6 (CH), 138.0, 139.6 (C), 165.6, 166.1 (CO). IR (KBr, cm^{-1}): ν=2976, 2932, 2872 (w), 1700 (s), 1617 (m), 1506, 1474, 1456, 1432, 1390 (w), 1364, 1313, 1275, 1249, 1199 (m), 1137 (s), 1039 (m), 999 (w), 971, 960, 911, 849 (m), 787 (w), 754, 727, 712, 694, 662, 621, 582 (m). GC–MS (EI, 70 eV): m/z (%)=336 (05) $[M]^+$, 263 (04), 224 (41), 180 (14), 179 (50), 178 (30), 163 (19), 162 (10), 161 (34), 136 (10), 135 (100), 134 (42), 91 (23), 57 (64), 41 (72), 29 (21). HRMS (ESI): calcd for $C_{18}H_{24}NaO_4S$ $[M+Na]^+$: 359.12875; found: 359.12877.

*4.2.7. (2E,2′E)-Bis(2-ethylhexyl) 3,3′-(thiophene-2,3-diyl)diacrylate (**3g**).* Product **3g** was prepared starting with **1** (242 mg, 1.0 mmol),

2-ethylhexyl acrylate (0.52 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (380 mg, 85%). ^1H NMR (300 MHz, $CDCl_3$): δ=0.85 (t, 12H, J=7.1 Hz, $4CH_3$), 1.17–1.38 (m, 16H, CH-Aliphatic), 1.55–1.61 (m, 2H, CH), 4.02–4.07 (m, 4H, $2CH_2O$), 6.22 (d, 1H, J=15.5 Hz, CH), 6.24 (d, 1H, J=15.8 Hz, CH), 7.19 (d, 1H, J=5.4 Hz, ArH), 7.24 (d, 1H, J=5.3 Hz, ArH), 7.78 (d, 1H, J=15.8 Hz, CH), 7.93 (d, 1H, J=15.5 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.0 ($2CH_3$), 14.0 ($2CH_3$), 23.0 ($2CH_2$), 23.8, 23.9 (CH_2), 28.9 ($2CH_2$), 30.4, 30.5 (CH_2), 38.8 (2CH), 67.2 ($2CH_2O$), 119.3, 120.5, 126.4, 127.6, 133.5, 134.4 (CH), 138.2, 139.8 (C), 166.5, 166.9 (CO). IR (KBr, cm^{-1}): ν=2957, 2927, 2858 (w), 1708 (s), 1621 (m), 1510, 1461, 1379 (w), 1308, 1267, 1241 (m), 1161 (s), 1028, 970 (m), 854, 833, 750, 710, 665, 620, 586 (w). GC–MS (EI, 70 eV): m/z (%)=448 (04) $[M]^+$, 207 (24), 180 (17), 179 (100), 178 (31), 161 (30), 135 (19), 134 (11), 71 (23), 57 (31), 43 (20). HRMS (EI, 70 eV): calcd for $C_{26}H_{40}O_4S$ $[M]^+$: 448.26418; found: 448.26485.

*4.2.8. 2,3-Bis(4-tert-butylstyryl)thiophene (**3h**).* Product **3h** was prepared starting with **1** (242 mg, 1.0 mmol), 4-*tert*-butylstyrene (0.45 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown solid (376 mg, 94%), mp=171–174 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.25 (s, 9H, $3CH_3$), 1.26 (s, 9H, $3CH_3$), 6.83 (d, 1H, J=15.9 Hz, CH), 6.88 (d, 1H, J=16.1 Hz, CH), 7.04 (d, 1H, J=5.3 Hz, ArH), 7.15–7.22 (m, 3H, ArH), 7.28–7.32 (m, 4H, ArH), 7.35–7.39 (m, 4H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=31.3 ($6CH_3$), 34.6, 34.7 (C), 119.0, 120.3, 123.6 (CH), 125.7 (4CH), 126.0 (CH), 126.2 (4CH), 129.0, 129.5 (CH), 134.4, 134.8, 136.8, 138.4, 150.8, 150.9 (C). IR (KBr, cm^{-1}): ν=3028 (w), 2957 (m), 2864, 1903, 1605, 1515, 1504, 1462, 1409, 1391 (w), 1361, 1268 (m), 1246, 1199, 1107, 1015 (w), 953, 940, 852, 827, 809 (m), 741 (w), 714 (m), 665 (w), 635 (m), 610 (w), 558 (s). GC–MS (EI, 70 eV): m/z (%)=400 (100) $[M]^+$, 385 (27), 343 (15), 287 (10), 254 (11), 253 (42), 209 (14), 185 (36), 157 (20), 147 (20), 91 (12), 57 (47). HRMS (EI, 70 eV): calcd for $C_{28}H_{32}S$ $[M]^+$: 400.22192; found: 400.22190.

*4.2.9. 2,3-Bis(4-methoxystyryl)thiophene (**3i**).* Product **3i** was prepared starting with **1** (242 mg, 1.0 mmol), 4-methoxystyrene (0.33 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (289 mg, 83%). ^1H NMR (300 MHz, $CDCl_3$): δ=3.69 (s, 6H, $2OCH_3$), 6.74–6.80 (m, 6H, 4ArH and 2CH), 6.97 (d, 1H, J=5.3 Hz, ArH), 7.06 (d, 1H, J=16.1 Hz, CH), 7.12 (d, 1H, J=5.4 Hz, ArH), 7.21 (d, 1H, J=15.9 Hz, CH), 7.33 (dd, 4H, J=2.8, 8.8 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=55.3 ($2OCH_3$), 114.2 (2CH), 114.3 (2CH), 117.7, 119.0, 123.3, 125.9 (CH), 127.6 (2CH), 127.7 (2CH), 128.6, 129.0 (CH), 130.0, 130.3, 136.5, 138.2, 159.3, 159.4 (C). IR (KBr, cm^{-1}): ν=3030, 2963, 2834 (w), 1597 (m), 1573 (w), 1510, 1505 (m), 1462, 1455, 1440, 1435, 1410, 1303, 1283 (w), 1246, 1172 (s), 1107, 1093 (w), 1024, 967, 957, 946, 931, 849, 812, 804, 778, 765, 726, 704, 631 (m). GC–MS (EI, 70 eV): m/z (%)=348 (100) $[M]^+$, 347 (10), 240 (10), 227 (39), 225 (10), 121 (51). HRMS (EI, 70 eV): calcd for $C_{22}H_{20}O_2S$ $[M]^+$: 348.11785; found: 348.11778.

*4.2.10. 2,3-Bis(4-methylstyryl)thiophene (**3j**).* Product **3j** was prepared starting with **1** (242 mg, 1.0 mmol), 4-methyl styrene (2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (278 mg, 88%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.28 (s, 6H, $2CH_3$), 6.83 (d, 1H, J=15.9 Hz, CH), 6.85 (d, 1H, J=16.1 Hz, CH), 7.03 (d, 1H, J=5.4 Hz, ArH), 7.09 (d, 4H, J=7.8 Hz, ArH), 7.16–7.22 (m, 2H, ArH), 7.30–7.37 (m, 5H, 3ArH and 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.2 ($2CH_3$), 118.8, 119.9, 123.6, 125.9 (CH), 126.4 (4CH), 129.1 (CH), 129.4 (4CH), 129.6 (CH), 134.4, 134.7, 136.7, 137.6, 137.7, 138.4 (C). IR (KBr, cm^{-1}): ν=3123, 2916, 2853, 1609, 1511, 1440, 1377, 1259, 1180, 1091, 1017 (w), 957 (s), 938, 905, 850, 829 (m), 800, 729 (s), 707, 637 (m). GC–MS (EI, 70 eV): m/z (%)=316 (100) $[M]^+$, 315 (11), 301 (22), 225 (17), 224 (12), 212 (10), 211 (62), 209 (12). HRMS (EI, 70 eV): calcd for $C_{22}H_{20}S$ $[M]^+$: 316.12802; found: 316.12823.

*4.2.11. 2,3-Bis(4-chlorostyryl)thiophene (**3k**).* Product **3k** was prepared starting with **1** (242 mg, 1.0 mmol), 4-chloro styrene (0.32 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown solid (292 mg, 82%), mp=106–108 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=6.80 (d, 1H, J=15.7 Hz, CH), 6.81 (d, 1H, J=16.1 Hz, CH), 7.07 (d, 1H, J=5.2 Hz, ArH), 7.14–7.29 (m, 7H, 5ArH and 2CH), 7.33–7.36 (dd, 4H, J=3.2, 8.3 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=119.9, 121.1, 124.3, 125.9 (CH), 127.6 (4CH), 128.0, 128.6 (CH), 128.9 (2CH), 129.0 (2CH), 133.3, 133.4, 135.5, 135.9, 136.8, 138.5 (C). IR (KBr, cm^{-1}): ν=3093, 3037, 2990, 2851, 1622, 1613, 1565, 1510 (w), 1488 (m), 1439, 1401, 1328, 1255, 1245, 1178, 1103 (w), 1087, 1009, 957, 939, 852, 829 (m), 806 (s), 729, 705, 690, 636 (m), 592 (w). GC–MS (EI, 70 eV): m/z (%)=356 (70) $[M^+$ (^{37}Cl, ^{37}Cl)], 356 (100) $[M^+$ (^{35}Cl, ^{37}Cl)], 321 (15), 320 (13), 286 (12), 252 (13), 245 (24), 231 (99), 210 (27), 142 (14), 125 (19). HRMS (EI, 70 eV): calcd for $C_{20}H_{14}Cl_2S$ $[M^+$ (Cl, ^{37}Cl)]: 354.00313; found: 354.00225.

4.3. General procedure B for the synthesis of benzothiophenes (4) and (13)

A xylene or diphenylether solution (3 mL) of **3a–e**, **h–l** or **12a–d** (0.5 mmol) was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol %) was added. The solution was stirred at 200 °C for 48 h under argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

*4.3.1. Dimethyl benzo[b]thiophene-5,6-dicarboxylate (**4a**).* Compound **4a** was prepared starting with **3a** (100 mg, 0.39 mmol), following general procedure B, as a brown highly viscous oil (99 mg, 98%). ^1H NMR (300 MHz, $CDCl_3$): δ=3.86 (s, 6H, OCH_3), 7.34 (d, 1H, J=5.4 Hz, ArH), 7.59 (d, 1H, J=5.5 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=51.7, 51.7 (OCH_3), 122.9, 124.1, 123.5 (CH), 126.2, 127.4 (C), 129.8 (CH), 139.9, 140.6 (C), 167.0, 167.4 (CO). IR (KBr, cm^{-1}): ν=2950, 2925, 2852, 1840, 1780 (w), 1716 (s), 1601, 1545, 1491 (w), 1433 (m), 1400, 1356 (w), 1316, 1277, 1263, 1246, 1220, 1198, 1124, 1099, 1075 (m), 1009, 968, 893, 836, 787, 777, 759, 736, 703, 651, 628, 604, 530 (w). GC–MS (EI, 70 eV): m/z (%)=250 (40) $[M]^+$, 220 (13), 219 (100), 133 (12). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}O_4S$ $[M]^+$: 250.02943; found: 250.02983.

*4.3.2. Diethyl benzo[b]thiophene-5,6-dicarboxylate (**4b**).* Compound **4b** was prepared starting with **3b** (100 mg, 0.36 mmol), following general procedure B, as a brown highly viscous oil (99 mg, 99%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.32 (t, 6H, J=7.1 Hz, $2CH_3$), 1.32 (q, 4H, J=7.1 Hz, $2OCH_2$), 7.34 (d, 1H, J=5.4 Hz, ArH), 7.58 (d, 1H, J=5.4 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1 ($2CH_3$), 61.6, 61.7 (OCH_2), 123.8, 124.1, 124.5 (CH), 127.7, 128.8 (C), 130.6 (CH), 140.8, 141.5 (C), 167.5, 168.0 (CO). IR (KBr, cm^{-1}): ν=2979, 2933, 2903, 2871 (w), 1714 (s), 1622, 1600, 1544, 1490, 1463, 1449, 1388 (w), 1365, 1313 (m), 1273, 1241 (s), 1191, 1173, 1120, 1095, 1073, 1018 (m), 972, 907, 854, 804 (w), 774, 755, 701 (m), 649, 607, 545 (w). GC–MS (EI, 70 eV): m/z (%)=278 (30) $[M]^+$, 233 (20), 206 (15), 205 (100), 121 (12). HRMS (EI, 70 eV): calcd for $C_{14}H_{14}O_4S$ $[M]^+$: 278.06073; found: 278.06090.

*4.3.3. Diisobutyl benzo[b]thiophene-5,6-dicarboxylate (**4c**).* Compound **4c** was prepared starting with **3c** (100 mg, 0.30 mmol), following

general procedure B, as a brown oil (99 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (d, 6H, J=6.7 Hz, $2CH_3$), 0.94 (d, 6H, J=6.7 Hz, $2CH_3$), 1.91–2.06 (m, 2H, CH), 4.05 (d, 4H, J=6.8 Hz, $2CH_2O$), 7.35 (dd, 1H, J=0.7, 5.6 Hz, ArH), 7.58 (d, 1H, J=5.5 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.1 ($2CH_3$), 19.2 ($2CH_3$), 27.7, 27.8 (CH), 71.8, 71.9 (CH_2O), 123.8, 124.0, 124.4 (CH), 127.8, 128.9 (C), 130.6 (CH), 140.8, 141.5 (C), 167.6, 168.3 (CO). IR (KBr, cm^{-1}): ν=3106, 2958, 2873 (w), 1716 (s), 1626, 1601, 1545, 1490, 1468 (w), 1448, 1452, 1405, 1392, 1392, 1375, 1341 (m), 1314, 1271, 1239, 1190, 1167, 1119, 1097, 1073 (s), 1005, 982, 945, 904, 785, 775, 754, 702 (m), 682, 653, 626 (w). GC–MS (EI, 70 eV): m/z (%)=334 (8) $[M]^+$, 222 (57), 206 (17), 205 (100), 178 (15), 160 (06). HRMS (EI, 70 eV): calcd for $C_{18}H_{22}O_4S$ $[M]^+$: 334.12388; found: 334.12360.

*4.3.4. Dibutyl benzo[b]thiophene-5,6-dicarboxylate (**4d**).* Compound **4d** was prepared starting with **3d** (100 mg, 0.30 mmol), following general procedure B, as a brown oil (99 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, 6H, J=7.4 Hz, $2CH_3$), 1.32–1.42 (m, 4H, $2CH_2$), 1.62–1.71 (m, 4H, $2CH_2$), 4.26 (t, 4H, J=6.7 Hz, $2CH_2O$), 7.35 (dd, 1H, J=0.6, 5.4 Hz, ArH), 7.57 (d, 1H, J=5.4 Hz, ArH), 8.09 (s, 1H, ArH), 8.19 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.6 ($2CH_2$), 65.5, 65.6 (CH_2O), 123.8, 124.1, 124.4 (CH), 127.8, 128.8 (C), 130.6 (CH), 140.8, 141.5 (C), 167.6, 168.1 (CO). IR (KBr, cm^{-1}): ν=2957, 2930, 2871 (w), 1717 (s), 1625, 1600, 1543, 1490, 1452, 1405, 1381 (w), 1314 (m), 1273 (s), 1241, 1190, 1119, 1096, 1074 (m), 1018, 961, 942, 903, 840 (w), 775, 754, 736, 700 (m), 651, 545 (w). GC–MS (EI, 70 eV): m/z (%)=334 (11) $[M]^+$, 222 (27), 206 (13), 205 (100), 178 (11). HRMS (EI, 70 eV): calcd for $C_{18}H_{22}O_4S$ $[M]^+$: 334.12333; found: 334.12338.

*4.3.5. Dihexyl benzo[b]thiophene-5,6-dicarboxylate (**4e**).* Compound **4e** was prepared starting with **3e** (100 mg, 0.26 mmol), following general procedure B, as a brown oil (99 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.80–0.85 (m, 6H, $2CH_3$), 1.18–1.40 (m, 12H, $6CH_2$), 1.63–1.72 (m, 4H, $2CH_2$), 4.25 (q, 4H, J=6.8 Hz, $2OCH_2$), 7.35 (dd, 1H, J=0.5, 5.5 Hz, ArH), 7.58 (d, 1H, J=5.5 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.5 ($2CH_2$), 31.5 ($2CH_2$), 65.8, 65.9 (OCH_2), 123.8, 124.1, 124.4 (CH), 127.8, 128.8 (C), 130.5 (CH), 140.8, 141.5 (C), 167.6, 168.0 (CO). IR (KBr, cm^{-1}): ν=2953, 2926, 2856 (w), 1720 (s), 1624, 1601, 1544, 1490, 1465, 1455, 1378, 1314 (w), 1272, 1241, 1189, 1167, 1120, 1097, 1074 (m), 993, 904, 837, 776, 755, 724, 701, 652 (w). GC–MS (EI, 70 eV): m/z (%)=390 (7) $[M]^+$, 222 (23), 206 (13), 205 (100). HRMS (EI, 70 eV): calcd for $C_{22}H_{30}O_4S$ $[M]^+$: 390.18593; found: 390.18607.

*4.3.6. Bis(2-ethylhexyl) benzo[b]thiophene-5,6-dicarboxylate (**4g**).* Compound **4g** was prepared starting with **3g** (100 mg, 0.26 mmol), following general procedure B, as a brown oil (99 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.77–0.88 (m, 12H, $4CH_3$), 1.25–1.41 (m, 16H, CH-Aliphatic), 1.59–1.65 (m, 2H, CH), 4.15–4.18 (m, 4H, $2CH_2O$), 7.33 (d, 1H, J=5.4 Hz, ArH), 7.56 (d, 1H, J=5.4 Hz, ArH), 8.07 (s, 1H, ArH), 8.17 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=11.0 ($2CH_3$), 14.1 ($2CH_3$), 23.0 ($2CH_2$), 23.8 ($2CH_2$), 29.0 ($2CH_2$), 30.4 ($2CH_2$), 38.7, 38.8 (CH), 68.1, 68.2 (CH_2O), 123.7, 124.1, 124.4 (CH), 127.9, 129.0 (C), 130.5 (CH), 140.8, 141.5 (C), 167.7, 168.1 (CO). IR (KBr): ν=2956, 2927 (m), 2858 (w), 1720 (s), 1625, 1459, 1379, 1313 (w), 1270 (s), 1240, 1190, 1167, 1120, 1097, 1073, 774, 701 (m), 654, 544 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=446 (02) $[M]^+$, 223 (27), 222 (41), 205 (100), 57 (10). HRMS (EI, 70 eV): calcd for $C_{26}H_{38}O_4S$ $[M]^+$: 446.24853; found: 446.24915.

*4.3.7. 5,6-Bis(4-tert-butylphenyl)benzo[b]thiophene (**4h**).* Compound **4h** was prepared starting with **3h** (100 mg, 0.25 mmol), following general procedure B, as a brown highly viscous oil (99 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.21 (s, 18H, $6CH_3$), 7.01 (d, 4H, J=8.3 Hz, ArH), 7.13 (d, 4H, J=8.1 Hz, ArH), 7.26 (d, 1H, J=5.3 Hz, ArH), 7.36 (d, 1H, J=5.4 Hz, ArH), 7.77 (s, 1H, ArH), 7.83 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=31.4 ($6CH_3$), 34.4 (2C), 123.7, 123.9 (CH), 124.6 (4CH), 125.1, 126.9 (CH), 129.6 (2CH), 129.7 (2CH), 137.6, 137.7, 138.6, 138.7, 138.8, 138.9 (C), 149.2, 149.3 (C). IR (KBr, cm^{-1}): ν=3026, 2958, 2902, 2864, 2245, 1906, 1602, 1514, 1449, 1408, 1390 (w), 1361 (m), 1320, 1307 (w), 1267 (m), 1200, 1181, 1111, 1085, 1085, 1058, 1038, 1014, 960, 907, 894, 876 (w), 834 (s), 776, 762 (w), 731, 719 (m), 683, 661, 646, 633 (w), 602, 562 (m). GC–MS (EI, 70 eV): m/z (%)=398 (100) $[M]^+$, 384 (25), 383 (84), 184 (12), 156 (16), 57 (29). HRMS (EI, 70 eV): calcd for $C_{28}H_{30}S$ $[M]^+$: 398.20627; found: 398.20642.

*4.3.8. 5,6-Bis(4-methoxyphenyl)benzo[b]thiophene (**4i**).* Compound **4i** was prepared starting with **3i** (100 mg, 0.29 mmol), following general procedure B, as a brown highly viscous oil (99 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.69 (s, 6H, $2OCH_3$), 6.7 (dd, 4H, J=1.3, 8.6 Hz, ArH), 7.01 (dd, 4H, J=1.9, 8.7 Hz, ArH), 7.25 (d, 1H, J=5.4 Hz, ArH), 7.35 (d, 1H, J=5.4 Hz, ArH), 7.72 (s, 1H, ArH), 7.78 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.2 ($2OCH_3$), 113.4 (4CH), 123.7, 123.9, 125.1, 126.9 (CH), 131.0 (2CH), 131.1 (2CH), 134.1, 134.3, 137.2, 137.3, 138.8, 138.9 (C), 158.2, 158.3 (C–O). IR (KBr, cm^{-1}): ν=3132, 2952, 2929, 2833, 2540, 1712 (w), 1607 (m), 1574 (w), 1484, 1449, 1439 (m), 1415, 1390, 1319 (w), 1286 (m), 1240, 1173 (s), 1107 (m), 1087, 1085 (w), 1044, 1025 (m), 958 (w), 905 (m), 830 (s), 801, 759, 730, 716 (m), 683, 670, 657, 628, 603 (w), 585, 546, 534 (m). GC–MS (EI, 70 eV): m/z (%)=346 (100) $[M]^+$, 271 (12). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O_2S$ $[M]^+$: 346.10220; found: 346.10260.

*4.3.9. 5,6-Di-p-tolylbenzo[b]thiophene (**4j**).* Compound **4j** was prepared starting with **3j** (100 mg, 0.32 mmol), following general procedure B, as a brown highly viscous oil (99 mg, 95%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.23 (s, 6H, $2CH_3$), 6.94 (d, 4H, J=7.3 Hz, ArH), 6.99 (d, 4H, J=8.2 Hz, ArH), 7.25 (d, 1H, J=5.4 Hz, ArH), 7.35 (d, 1H, J=5.5 Hz, ArH), 7.74 (s, 1H, ArH), 7.79 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.2 ($2CH_3$), 123.7, 124.0, 125.3, 127.0 (CH), 128.6 (4CH), 129.9 (2CH), 130.0 (2CH), 135.9, 136.0, 137.5, 137.6, 138.7 (C), 138.8 (2C), 138.9 (C). IR (KBr, cm^{-1}.): ν=3020, 2916, 2848 (w), 1512 (m), 1484 (w), 1448 (m), 1409, 1319, 1181, 1110, 1087, 1057, 1036, 1018, 943, 894, 875 (m), 814 (s), 758, 724, 657, 583, 526 (w). GC–MS (EI, 70 eV): m/z (%)=314 (100) $[M]^+$, 299 (42), 298 (19), 285 (10), 284 (28). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}S$ $[M]^+$: 314.11237; found: 314.11245.

4.4. Synthesis of 2-alknylthiophenes (5)

*4.4.1. (E)-Methyl-3-(thiophen-2-yl)acrylate (**5a**).* Product **5a** was prepared starting with **1** (242 mg, 1.0 mmol), methyl acrylate (0.09 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (126 mg, 75%). ^{1}H NMR (230 MHz, $CDCl_3$): δ=3.71 (s, 3H, OCH_3), 6.18 (d, 1H, J=15.9 Hz, CH), 7.18–7.27 (m, 2H, ArH), 7.40–7.42 (m, 1H, ArH), 7.60 (d, 1H, J=15.9 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=51.6 (OCH_3), 117.4, 125.1, 126.9, 128.1 (CH), 137.5 (C), 138.3 (CH), 167.6 (CO). IR (KBr, cm^{-1}): ν=3098, 29,993, 2946, 2841 (w), 1703, 1699, 1632 (s), 1515 (w), 1435 (m), 1392, 1370 (w), 1306, 1275, 1247, 1197 (m), 1168 (s), 1054, 1043, 1012, 979, 922, 865, 842, 828 (m), 793 (s), 754, 736, 725, 666, 608, 590 (m). GC–MS (EI, 70 eV): m/z (%)=168 (62) $[M]^+$, 138 (10), 137 (100), 110 (08), 109 (42), 65 (16). HRMS (EI, 70 eV): calcd for $C_8H_8O_2S$ $[M]^+$: 168.02395; found: 168.02367.

*4.4.2. (E)-Ethyl-3-(thiophen-2-yl)acrylate (**5b**).* Product **5b** was prepared starting with **1** (242 mg, 1.0 mmol), ethyl acrylate (0.11 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (141 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.26 (t, 3H, J=7.1 Hz, CH_3), 4.18 (q, 2H,

J=7.1 Hz, CH_2O), 6.18 (d, 1H, J=15.9 Hz, CH), 7.19–7.26 (m, 2H, ArH), 7.40–7.42 (m, 1H, ArH), 7.59 (d, 1H, J=15.9 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.3 (CH_3), 60.4 (CH_2O), 117.9, 125.1, 126.9, 127.9, 138.0 (CH), 137.6 (C), 167.2 (CO). IR (KBr, cm^{-1}): ν=3098, 2978, 2927, 2853 (w), 1703 (s), 1632 (m), 1518, 1463, 1444, 1392, 1365 (w), 1302, 1276, 1244, 1204 (m), 1152 (s), 1094, 1033, 975, 863, 828, 783, 700, 666, 605, 592 (m). GC–MS (EI, 70 eV): m/z (%)=182 (46) $[M]^+$, 154 (11), 138 (12), 137 (100), 110 (20), 109 (37), 65 (16). HRMS (EI, 70 eV): calcd for $C_9H_{10}O_2S$ $[M]^+$: 182.03960; found: 182.03963.

*4.4.3. (E)-Isobutyl-3-(thiophen-2-yl)acrylate (**5c**).* Product **5c** was prepared starting with **1** (242 mg, 1.0 mmol), *iso*-butyl acrylate (0.14 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown highly viscous oil (155 mg, 74%). ^1H NMR (250 MHz, $CDCl_3$): δ=0.90 (d, 6H, J=6.7 Hz, $2CH_3$), 1.85–2.01 (m, 1H, CH), 3.91 (d, 2H, J=6.7 Hz, CH_2O), 6.20 (d, 1H, J=15.9 Hz, CH), 7.18–7.25 (m, 2H, ArH), 7.40–7.42 (m, 1H, ArH), 7.59 (d, 1H, J=15.9 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.2 ($2CH_3$), 27.9 (CH), 70.6 (CH_2O), 117.9, 125.2, 126.9, 127.9 (CH), 137.6 (C), 138.0 (CH), 167.3 (CO). IR (KBr): ν=3098, 2958, 2931, 2872 (w), 1704 (s), 1632 (m), 1518, 1468, 1426, 1394, 1375, 1342 (w), 1305, 1276, 1203 (m), 1151 (s), 1084 (w), 1013, 974 (m), 867, 859, 828 (w), 783 (m), 699, 667 (w), 605 (m), 569, 537 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=210 ($[M]^+$, 12), 154 (71), 138 (10), 137 (100), 112 (12), 109 (31), 65 (13), 39 (08). HRMS (EI, 70 eV): calcd for $C_{11}H_{14}O_2S$ $[M]^+$: 210.07090; found: 210.07110.

*4.4.4. (E)-tert-Butyl-3-(thiophen-2-yl)acrylate (**5d**).* Product **5d** was prepared starting with **1** (242 mg, 1.0 mmol), *tert*-butyl acrylate (0.14 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (182 mg, 87%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.45 (s, 9H, $3CH_3$), 6.12 (d, 1H, J=15.9 Hz, CH), 7.18–7.25 (m, 2H, ArH), 7.36–7.39 (m, 1H, ArH), 7.59 (d, 1H, J=16.0 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.2 ($3CH_3$), 80.4 (C–O), 119.9, 125.2, 126.8, 127.4, 137.1 (CH), 137.8 (C), 166.6 (CO). IR (KBr, cm^{-1}): ν=3098, 2976, 2927, 2855 (w), 1705 (s), 1633 (m), 1518, 1455, 1392 (w), 1366, 1309, 1281 (m), 1248, 1219 (w), 1148 (s), 1085, 1041, 978, 855, 829, 787, 702, 665, 606, 529 (w). GC–MS (EI, 70 eV): m/z (%)=210 (16) $[M]^+$, 154 (100), 137 (57), 126 (10), 112 (30), 109 (21), 65 (12), 57 (20), 41 (14). HRMS (EI, 70 eV): calcd for $C_{11}H_{14}O_2S$ $[M]^+$: 210.07090; found: 210.07071.

*4.4.5. (E)-Hexyl-3-(thiophen-2-yl)acrylate (**5e**).* Product **5e** was prepared starting with **1** (242 mg, 1.0 mmol), hexyl acrylate (1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (180 mg, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, 3H, J=6.8 Hz, CH_3), 1.21–1.29 (m, 6H, $3CH_2$), 1.54–1.64 (m, 2H, CH_2), 4.11 (t, 2H, J=6.8 Hz, CH_2O), 6.19 (d, 1H, J=15.9 Hz, CH), 7.18–7.25 (m, 2H, ArH), 7.40–7.42 (m, 1H, ArH), 7.59 (d, 1H, J=15.9 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.5, 25.6, 28.7, 31.4 (CH_2), 64.7 (CH_2O), 118.0, 125.1, 126.9, 127.9 (CH), 137.6 (C), 138.0 (CH), 167.3 (CO). IR (KBr, cm^{-1}): ν=3098, 2953, 2927, 2856 (w), 1707 (s), 1632 (m), 1518, 1465, 1391, 1379 (w), 1302, 1276, 1245, 1203 (m), 1162 (s), 1112, 1082, 976 (m), 908, 867, 860, 829 (w), 784, 711 (m), 668 (w), 605 (m). GC–MS (EI, 70 eV): m/z (%)=238 (12) $[M]^+$, 155 (16), 154 (100), 138 (10), 137 (81), 112 (13), 110 (12), 109 (32), 65 (14). HRMS (EI, 70 eV): calcd for $C_{13}H_{18}O_2S$ $[M]^+$: 238.10220; found: 238.10245.

4.5. Synthesis of (*E*)-*N*-[(4,5-dibromothiophen-2-yl)methylene]-4-methoxyaniline (7)

A mixture of 4,5-dibromothiophene-2-carbaldehyde (**6**) (269 mg, 1.0 mmol), 4-methoxyaniline (184 mg, 1.5 mmol) in glacial acetic acid (5 mL) was stirred at room temperature for 15 min to give a greenish precipitate. Then it was filtered and washed with ethanol to give the pure imine **7** (365 mg, 98%), mp=136–137 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.75 (s, 3H, OCH_3), 6.83 (dd, 2H, J=2.1, 6.8 Hz, ArH), 7.12 (s, 1H, ArH), 7.14 (dd, 2H, J=2.1, 6.8 Hz, ArH), 8.33 (s, 1H, N=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=55.5 (OCH_3), 114.5 (2CH), 122.5 (2CH), 132.8 (CH), 143.1 (2C–Br), 144.0 (2C), 148.2 (CH), 158.9 (C–O). IR (KBr, cm^{-1}): ν=2932, 2834 (w), 1614, 1579, 1519, 1502, 1463, 1427, 1417, 1287 (m), 1239 (s), 1200, 1183, 1159, 1118 (m), 1030 (s), 991, 950 (m), 827 (s), 770, 665, 636, 582 (m), 546 (w). GC–MS (EI, 70 eV): m/z (%)=377 (53) [M^+ (^{81}Br, ^{81}Br)], 375 (100) [M^+ (Br, ^{81}Br)], 373 (52) [M^+ (Br, Br)], 360 (93), 358 (47), 172 (19), 92 (12), 77 (12), 64 (11). HRMS (EI, 70 eV): calcd for $C_{12}H_9Br_2NOS$ [M^+ (Br, ^{81}Br)]$^+$: 374.87456; found: 374.87422.

4.6. Synthesis of 2,3-di(alkenyl)thiophenes (8)

*4.6.1. (2E,2′E)-Dimethyl 3,3′-{5-[(E)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl}diacrylate (**8a**).* Product **8a** was prepared starting with **7** (186 mg, 0.5 mmol), methyl acrylate (0.12 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), SPhos (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (119 mg, 62%). ^1H NMR (300 MHz, $CDCl_3$): δ=3.75 (s, 9H, $3OCH_3$), 6.25 (d, 1H, J=16.4 Hz, CH), 6.31 (d, 1H, J=16.4 Hz, CH), 6.85 (d, 2H, J=9.0 Hz, ArH), 7.15 (d, 2H, J=9.0 Hz, ArH), 7.46 (s, 1H, ArH), 7.76 (d, 1H, J=15.7 Hz, CH), 7.92 (d, 1H, J=15.3 Hz, CH), 8.44 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=51.9, 52.0, 55.5 (OCH_3), 114.5 (2CH), 120.2, 120.3 (CH), 122.6 (2CH), 129.1, 133.4, 134.3 (CH), 138.5 (C), 142.2 (C–N), 143.2, 144.4 (C), 149.0 (CH), 159.1 (C–O), 166.6, 167.0 (CO). IR (KBr, cm^{-1}): ν=2957, 2935, 2830 (w), 1709, 1637 (m), 1614 (s), 1574, 1508, 1453, 1440, 1386, 1367, 1304, 1291 (m), 1243, 1171, 1162 (s), 1120, 1108 (m), 1022, 970 (s), 864 (m), 832 (s), 795, 780, 732, 705, 678, 599, 554, 537 (m). GC–MS (EI, 70 eV): m/z (%)=385 (60) $[M^+]$, 383 (19), 326 (79), 327 (100), 310 (35), 294 (60), 267 (16), 252 (27), 162 (12), 147 (20), 134 (35). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}NO_5S$ $[M]^+$: 385.09784; found: 385.09850.

*4.6.2. (2E,2′E)-Diisobutyl 3,3′-{5-[(E)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl}diacrylate (**8b**).* Product **8b** was prepared starting with **7** (186 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (178 mg, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ=0.92 (dd, 12H, J=0.8, 6.7 Hz, $4CH_3$), 1.92–1.98 (m, 2H, CH), 3.76 (s, 3H, OCH_3), 3.92 (dd, 4H, J=1.9, 6.7 Hz, $2CH_2O$), 6.31 (t, 2H, J=15.8 Hz, CH), 6.85 (dd, 2H, J=2.1, 6.8 Hz, ArH), 7.18 (dd, 2H, J=2.2, 6.8 Hz, ArH), 7.49 (s, 1H, ArH), 7.76 (d, 1H, J=15.8 Hz, CH), 7.92 (d, 1H, J=15.5 Hz, CH), 8.45 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.1 ($4CH_3$), 26.8 (2CH), 54.5 (OCH_3), 69.9, 70.0 (CH_2O), 113.5 (2CH), 119.7, 119.8 (CH), 121.6 (2CH), 128.2, 132.2, 133.1 (CH), 137.4 (C), 141.2 (C–N), 142.2, 143.3 (C), 148.0 (CH), 158.0 (C–O), 165.2, 165.6 (CO). IR (KBr, cm^{-1}): ν=2960, 2873, 2835 (w), 1692 (s), 1608, 1574, 1501, 1465, 1393, 1377, 1367 (m), 1343, 1305 (w), 1282, 1268 (m), 1246, 1234 (s), 1199, 1178 (m), 1166, 1156 (s), 1109 (m), 1024, 1014 (s), 967, 951, 930, 908, 856, 843 (m), 827 (s), 779, 735, 712, 664, 636, 617, 599, 553, 535 (m). MS (EI, 70 eV): m/z (%)=469 (100) $[M^+]$, 343 (15), 312 (21), 296 (16), 294 (10), 268 (26), 252 (10), 134 (17), 78 (12), 63 (14), 57 (32). HRMS (EI, 70 eV): calcd for $C_{26}H_{31}NO_5S$ $[M]^+$: 469.19175; found: 469.19242.

*4.6.3. (2E,2′E)-Dibutyl 3,3′-{5-[(E)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl}diacrylate (**8c**).* Product **8c** was prepared starting with **7** (186 mg, 0.5 mmol), *n*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general

procedure A, as a brown oil (128 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, 6H, J=7.4 Hz, $2CH_3$), 1.30–1.43 (m, 4H, $2CH_2$), 1.57–1.68 (m, 4H, $2CH_2$), 3.76 (s, 3H, OCH_3), 4.15 (t, 2H, J=6.7 Hz, CH_2O), 4.16 (t, 2H, J=6.7 Hz, CH_2O), 6.27 (d, 1H, J=15.9 Hz, CH), 6.32 (d, 1H, J=15.6 Hz, CH), 6.85 (dd, 2H, J=2.8, 9.0 Hz, ArH), 7.14–7.20 (m, 2H, ArH), 7.51 (s, 1H, ArH), 7.76 (d, 1H, J=15.8 Hz, CH), 7.92 (d, 1H, J=15.5 Hz, CH), 8.45 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.7 ($2CH_2$), 55.5 (OCH_3), 64.7, 64.8 (CH_2O), 114.4 (2CH), 120.8, 122.4 (CH), 122.6 (2CH), 129.2, 133.2, 134.1 (CH), 138.4 (C), 142.3 (C–N), 143.3, 144.3 (C), 149.1 (CH), 159.1 (C–O), 166.3, 166.7 (CO). IR (KBr, cm^{-1}): ν=2956, 2869, 2835 (w), 1698, 1613 (s), 1557, 1529 (w), 1503, 1455, 1392 (m), 1281, 1242 (s), 1202 (m), 1164 (s), 1108, 1064, 1031 (m), 963 (s), 933, 858 (m), 833 (s), 800, 780, 739, 713, 666, 601, 555, 531 (m). MS (EI, 70 eV): m/z (%)=469 (100) [M^+], 343 (15), 312 (20), 296 (15), 294 (10), 268 (27), 252 (10), 134 (19), 78 (14), 63 (15), 57 (15). HRMS (EI, 70 eV): calcd for $C_{26}H_{31}NO_5S$ [$M]^+$: 469.19175; found: 469.19256.

*4.6.4. (2E,2′E)-Dihexyl 3,3′-{5-[(E)-(4-methoxyphenylimino)methyl] thiophene-2,3-diyl}diacrylate (**8d**).* Product **8d** was prepared starting with **7** (186 mg, 0.5 mmol), *n*-hexyl acrylate (0.22 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (176 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, 6H, J=6.7 Hz, $2CH_3$), 1.23–1.35 (m, 12H, $6CH_2$), 1.59–1.67 (m, 4H, $2CH_2$), 3.76 (s, 3H, OCH_3), 4.14 (t, 2H, J=6.8 Hz, CH_2O), 4.15 (t, 2H, J=6.8 Hz, CH_2O), 6.27 (d, 1H, J=16.4 Hz, CH), 6.33 (d, 1H, J=15.7 Hz, CH), 6.85 (d, 2H, J=8.9 Hz, ArH), 7.17–7.20 (m, 2H, ArH), 7.48 (s, 1H, ArH), 7.75 (d, 1H, J=15.8 Hz, CH), 7.92 (d, 1H, J=15.5 Hz, CH), 8.45 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.6, 28.7 (CH_2), 31.4 ($2CH_2$), 55.5 (OCH_3), 65.0, 65.1 (CH_2O), 114.5 (2CH), 120.8 (2CH), 122.6 (2CH), 129.2, 133.2, 134.1 (CH), 138.4 (C), 142.3 (C–N), 143.3, 144.3 (C), 149.1 (CH), 159.0 (C–O), 166.3, 166.7 (CO). IR (KBr, cm^{-1}): ν=2954, 2927, 2857 (w), 1695, 1612 (s), 1575, 1529 (w), 1502, 1454 (m), 1268, 1237, 1165, 1158 (s), 1015, 969, 827, 779 (m), 711, 662, 601 (w), 553, 533 (m). MS (EI, 70 eV): m/z (%)=525 (100) [M^+], 312 (22), 296 (19), 294 (10), 268 (29), 252 (10), 134 (22), 43 (44), 41 (12). HRMS (EI, 70 eV): calcd for $C_{30}H_{39}NO_5S$ [$M]^+$: 525.25435; found: 525.25419.

4.7. General procedure C for the synthesis of 2,3-di(alkenyl)-5-formylthiophenes (9)

In a pressure tube (glass bomb), to a solution of compounds **8a**–**e** (0.5 mmol) in dichloromethane (1 mL) was added H_2SO_4 (4 mL, 2.5 M). The reaction mixture was stirred at room temperature for 20 h. The solution was poured into H_2O and CH_2Cl_2 (25 mL each) and the organic and the aqueous layer were separated. The latter was extracted with CH2Cl2 (3×25 mL), the organic phases were combined, dried (Na_2SO_4), filtered, and concentrated in vacuo.

*4.7.1. (2E,2′E)-Dimethyl 3,3′-(5-formylthiophene-2,3-diyl)diacrylate (**9a**).* Compound **9a** was prepared starting with **8a** (192 mg, 0.50 mmol), following general procedures C, as a brown solid (137 mg, 98%), mp=142–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 6H, $2CH_3O$), 6.32 (d, 1H, J=15.8 Hz, CH), 6.40 (d, 1H, J=15.6 Hz, CH), 7.75 (d, 1H, J=15.9 Hz, CH), 7.82 (s, 1H, ArH), 7.92 (d, 1H, J=15.7 Hz, CH), 9.85 (s, 1H, O=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=51.1, 51.2 (CH_3O), 120.4, 121.5, 131.9, 132.8, 133.1 (CH), 137.3, 142.4, 145.3 (C), 165.0, 165.6 (CO), 181.6 (O=CH). IR (KBr, cm^{-1}): ν=3084, 2958, 2922, 2850 (w), 1708, 1668, 1620 (s), 1442, 1472, 1302, 1276, 1242, 1212 (m), 1191, 1160 (s), 1031, 1015 (m), 966 (s), 915, 863, 853, 730, 685, 663, 607, 538 (m). GC–MS (EI, 70 eV): m/z (%)=280 (47) [M^+], 249 (23), 221 (100), 220 (47), 205 (47), 189 (80), 177 (46), 161 (75), 149 (23), 134 (64), 89 (39), 67 (17), 59 (41). HRMS (EI, 70 eV): calcd for $C_{13}H_{12}O_5S$ [$M]^+$: 280.04000; found: 280.04067.

*4.7.2. (2E,2′E)-Diisobutyl 3,3′-(5-formylthiophene-2,3-diyl)diacrylate (**9b**).* Compound **9c** was prepared starting with **8b** (234 mg, 0.50 mmol), following general procedures C, as a brown oil (172 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (d, 12H, J=6.7 Hz, $4CH_3$), 1.88–2.02 (m, 2H, CH), 3.95 (d, 4H, J=6.7 Hz, $2CH_2O$), 6.33 (d, 1H, J=15.8 Hz, CH), 6.41 (d, 1H, J=15.6 Hz, CH), 7.74 (d, 1H, J=15.8 Hz, CH), 7.84 (s, 1H, ArH), 7.92 (d, 1H, J=15.6 Hz, CH), 9.85 (s, 1H, O=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.1 ($4CH_3$), 27.8 (2CH), 71.1, 71.3 (CH_2O), 121.9, 122.9, 132.7, 133.6, 134.3 (CH), 138.3, 143.3, 146.3 (C), 165.6, 166.2 (CO), 182.6 (O=CH). IR (KBr, cm^{-1}): ν=2978, 2926, 2848 (w), 1708, 1671 (s), 1625, 1449, 1375, 1279, 1240 (m), 1176, 1157, 1031 (s), 968, 954, 854, 677 (m). GC–MS (EI, 70 eV): m/z (%)=364 (20) [M^+], 291 (18), 208 (22), 207 (100), 191 (72), 163 (61), 135 (33), 91 (11), 89 (15), 57 (75), 41 (37), 29 (18). HRMS (EI, 70 eV): calcd for $C_{19}H_{24}O_5S$ [$M]^+$: 364.13390; found: 364.13470.

*4.7.3. (2E,2′E)-Dibutyl 3,3′-(5-formylthiophene-2,3-diyl)diacrylate (**9c**).* Compound **9c** was prepared starting with **8c** (234 mg, 0.50 mmol), following general procedures C, as a brown oil (167 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, 6H, J=7.4 Hz, $2CH_3$), 1.33–1.40 (m, 4H, $2CH_2$), 1.59–1.66 (m, 4H, $2CH_2$), 4.15 (t, 2H, J=6.8 Hz, CH_2O), 4.17 (t, 2H, J=6.7 Hz, CH_2O), 6.32 (d, 1H, J=15.8 Hz, CH), 6.39 (d, 1H, J=15.6 Hz, CH), 7.74 (d, 1H, J=15.9 Hz, CH), 7.82 (s, 1H, ArH), 7.90 (d, 1H, J=15.6 Hz, CH), 9.84 (s, 1H, O=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7 ($2CH_3$), 19.0, 19.1 (CH_2), 30.6, 30.7 (CH_2), 64.9, 65.1 (CH_2O), 121.9, 123.0, 132.7, 133.6, 134.2 (CH), 138.3, 143.2, 146.3 (C), 165.7, 166.3 (CO), 182.5 (O=CH). IR (KBr, cm^{-1}): ν=2957, 2930, 2871 (w), 1705, 1671 (s), 1621, 1443, 1308, 1274, 1242 (m), 1162 (s), 1061, 1025, 967, 856, 661, 600 (m). GC–MS (EI, 70 eV): m/z (%)=364 (06) [M^+], 263 (35), 262 (19), 207 (100), 189 (40), 163 (15), 161 (15), 135 (28), 91 (11), 57 (23), 41 (25), 29 (21). HRMS (EI, 70 eV): calcd for $C_{19}H_{24}O_5S$ [$M]^+$: 364.13390; found: 364.13398.

*4.7.4. (2E,2′E)-Dihexyl 3,3′-(5-formylthiophene-2,3-diyl)diacrylate (**9d**).* Compound **9d** was prepared starting with **8d** (262 mg, 0.50 mmol), following general procedures C, as a brown oil (201 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.29 (t, 6H, J=6.8 Hz, $2CH_3$), 0.69–0.81 (m, 12H, $6CH_2$), 1.07–1.12 (m, 4H, $2CH_2$), 3.61 (t, 4H, J=6.8 Hz, $2CH_2O$), 5.78 (d, 1H, J=15.8 Hz, CH), 5.85 (d, 1H, J=15.6 Hz, CH), 7.20 (d, 1H, J=15.8 Hz, CH), 7.29 (s, 1H, ArH), 7.37 (d, 1H, J=15.6 Hz, CH), 9.30 (s, 1H, O=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.5 ($2CH_2$), 28.5, 28.6 (CH_2), 31 ($2CH_2$), 65.2, 65.4 (CH_2O), 121.9, 123.0, 132.7, 133.6, 134.2 (CH), 138.3, 143.2, 146.3 (C), 165.6, 166.2 (CO), 182.5 (O=CH). IR (KBr, cm^{-1}): ν=2953, 2926, 2855 (w), 1707, 1670 (s), 1622, 1443, 1305, 1271, 1243 (m), 1163 (s), 966, 857 (m), 725, 684 (w), 661 (m), 601 (w). GC–MS (EI, 70 eV): m/z (%)=420 (04) [M^+], 291 (32), 233 (20), 207 (100), 189 (37), 163 (11), 135 (18), 43 (49), 41 (16). HRMS (EI, 70 eV): calcd for $C_{23}H_{32}O_5S$ [$M]^+$: 420.19650; found: 420.19703.

4.8. Synthesis of 2,3-di(alkenyl)-5-arylthiophenes (12)

*4.8.1. (2E,2′E)-Isobutyl 3,3′-(5-(4-ethylphenyl)thiophene-2,3-diyl)diacrylate (**12a**).* Product **12a** was prepared starting with **11a** (173 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (196 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (d, 6H, J=6.7 Hz, $2CH_3$), 0.91 (d, 6H, J=6.7 Hz, $2CH_3$), 1.17 (t, 3H, J=7.6 Hz, CH_3), 1.87–2.01 (m, 2H, 2CH), 2.58 (q, 2H, J=7.6 Hz, CH_2), 3.92 (d, 2H, J=6.7 Hz, CH_2O), 3.93 (d, 2H, J=6.7 Hz, CH_2O), 6.20 (d, 1H, J=15.4 Hz, CH), 6.29 (d, 1H, J=15.7 Hz, CH), 7.15 (d, 2H, J=8.2 Hz, ArH), 7.37 (s, 1H, ArH), 7.42 (d, 2H, J=8.2 Hz, ArH), 7.76 (d,

1H, J=16.0 Hz, CH), 7.91 (d, 1H, J=15.4 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.3 (CH_3), 18.1 ($4CH_3$), 26.8 (2CH), 27.6 (CH_2), 69.8 ($2CH_2O$), 117.4, 119.4, 120.1 (CH), 125.0 (2CH), 127.6 (2CH), 129.2 (C), 132.4, 133.4 (CH), 137.5, 138.2, 144.4, 145.3 (C), 165.5, 165.8 (CO). IR (KBr, cm^{-1}): ν=2960, 2933, 2872 (w), 1702 (s), 1622 (m), 1504, 1468, 1417, 1392, 1375 (w), 1303, 1271, 1246, 1220 (m), 1156 (s), 1019, 969, 823 (m), 774, 713, 680, 614, 550 (w). MS (EI, 70 eV): m/z (%)=440 (51) [M^+], 367 (16), 283 (53), 265 (46), 239 (57), 223 (23), 221 (12), 207 (21), 169 (13), 149 (12), 133 (15), 111 (18), 97 (26), 83 (28), 69 (69), 57 (100), 44 (68). HRMS (EI, 70 eV): calcd for $C_{26}H_{32}O_4S$ [M]$^+$: 440.20158; found: 440.20124.

*4.8.2. (2E,2′E)-Dibutyl 3,3′-[5-(4-tert-butylphenyl)thiophene-2,3-diyl]diacrylate (**12b**).* Product **12b** was prepared starting with **11b** (187 mg, 0.5 mmol), *n*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (176 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, 6H, J=6.8 Hz, $2CH_3$), 1.26 (s, 9H, $3CH_3$), 1.32–1.40 (m, 4H, $2CH_2$), 1.57–1.67 (m, 4H, $2CH_2$), 4.14 (t, 2H, J=6.8 Hz, CH_2O), 4.16 (t, 2H, J=6.7 Hz, CH_2O), 6.20 (d, 1H, J=15.6 Hz, CH), 6.29 (d, 1H, J=15.8 Hz, CH), 7.33–7.36 (m, 3H, ArH), 7.45 (d, 2H, J=8.4 Hz, ArH), 7.77 (d, 1H, J=15.9 Hz, CH), 7.92 (d, 1H, J=15.3 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 ($2CH_3$), 19.2 ($2CH_2$), 30.8 ($2CH_2$), 31.2 ($3CH_3$), 34.8 (C), 64.6, 64.7 (CH_2O), 118.5, 120.5, 121.2 (CH), 125.8 (2CH), 126.1 (2CH), 130.0 (C), 133.5, 134.5 (CH), 138.6, 139.3, 146.2, 152.4 (C), 166.6, 166.9 (CO). IR (KBr, cm^{-1}): ν=2957, 2932, 2871 (w), 1714 (m), 1695 (s), 1613 (m), 1504, 1456, 1391, 1361 (w), 1271, 1251, 1228 (m), 1163 (s), 1113, 1064, 1026, 968, 823 (m), 739, 607, 529 (w). MS (EI, 70 eV): m/z (%)=468 (26) [M^+], 367 (10), 366 (18), 351 (16), 322 (12), 311 (36), 293 (23), 267 (47), 251 (22), 237 (15), 223 (12), 211 (13), 91 (27), 69 (15), 66 (12), 57 (100), 44 (48), 41 (68). HRMS (ESI): calcd for $C_{28}H_{37}O_4S$ [M+H]$^+$: 469.2407; found: 469.2405.

*4.8.3. (2E,2′E)-Diisobutyl 3,3′-[5-(3,5-dimethylphenyl)thiophene-2,3-diyl]diacrylate (**12c**).* Product **12c** was prepared starting with **11c** (173 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (171 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (d, 6H, J=6.7 Hz, $2CH_3$), 0.92 (d, 6H, J=6.7 Hz, $2CH_3$), 1.88–2.02 (m, 2H, 2CH), 2.28 (s, 6H, $2CH_3$), 3.93 (d, 2H, J=6.7 Hz, CH_2O), 3.94 (d, 2H, J=6.7 Hz, CH_2O), 6.22 (d, 1H, J=15.5 Hz, CH), 6.32 (d, 1H, J=15.8 Hz, CH), 6.92 (s, 1H, ArH), 7.15 (s, 2H, ArH), 7.37 (s, 1H, ArH), 7.78 (d, 1H, J=15.8 Hz, CH), 7.93 (d, 1H, J=15.5 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.2 ($4CH_3$), 21.3 ($2CH_3$), 27.9 (2CH), 70.8 (CH_2O), 70.9 (CH_2O), 118.5, 120.4, 121.5 (CH), 123.9 (2CH), 130.7 (CH), 132.6 (C), 133.5, 134.5 (CH), 138.7 (C), 138.8 (2C), 139.2, 146.5 (C), 166.5, 166.8 (CO). IR (KBr, cm^{-1}): ν=2958 (m), 2872 (w), 1705 (s), 1615, 1602 (m), 1530 (w), 1467, 1375, 1309, 1265, 1240, 1213 (m), 1155 (s), 1021, 967, 829, 687 (m), 598, 541 (w). GC–MS (EI, 70 eV): m/z (%)=440 (34) [M^+], 339 (14), 338 (16), 309 (11), 283 (65), 265 (51), 240 (18), 239 (100), 238 (30), 224 (18), 91 (16), 57 (94), 44 (63), 41 (51). HRMS (ESI): calcd for $C_{26}H_{33}O_4S$ [M+H]$^+$: 441.2094; found: 441.2090.

*4.8.4. (2E,2′E)-Diisobutyl 3,3′-[5-(2-methoxyphenyl)thiophene-2,3-diyl]diacrylate (**12d**).* Product **12d** was prepared starting with **11d** (174 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (168 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (d, 12H, J=6.8 Hz, $4CH_3$), 1.86–2.01 (m, 2H, 2CH), 3.86 (s, 3H, OCH_3), 3.92 (d, 2H, J=6.6 Hz, CH_2O), 3.93 (d, 2H, J=6.6 Hz, CH_2O), 6.23 (d, 1H, J=15.3 Hz, CH), 6.28 (d, 1H, J=15.3 Hz, CH), 6.88–6.94 (m, 2H, ArH), 7.20–7.26 (m, 1H, ArH), 7.52–7.58 (m, 2H, ArH), 7.78 (d, 1H, J=15.7 Hz, CH), 7.93 (d, 1H, J=15.6 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.2 ($4CH_3$), 26.8 (2CH), 54.6 (OCH_3), 69.7, 69.8 (CH_2O), 110.7, 117.0, 118.9, 120.0 (CH), 120.6 (C), 122.8, 127.2, 128.9, 132.7, 133.7 (CH), 136.9, 138.1, 140.6, 154.9 (C), 165.6, 165.9 (CO). IR (KBr, cm^{-1}): ν=3099, 2957, 2844 (w), 1692 (s), 1605, 1462 (m), 1441, 1393, 1375, 1342 (w), 1268, 1253, 1240, 1210 (s), 1179, 1162, 1115 (m), 1024, 970 (s), 950, 846 (m), 744 (s), 717, 683, 603 (w). MS (EI, 70 eV): m/z (%)=442 (11) [M^+], 285 (57), 269 (13), 267 (25), 243 (11), 241 (54), 57 (100), 41 (42). HRMS (ESI): calcd for $C_{25}H_{31}O_5S$ [M+H]$^+$: 443.1887; found: 443.1876.

4.9. Synthesis of benzothiophenes (13)

*4.9.1. Diisobutyl 2-(4-ethylphenyl)benzo[b]thiophene-5,6-dicarboxylate (**13a**).* Compound **13a** was prepared starting with **12a** (100 mg, 0.23 mmol), following the general procedure B, as a brown semisolid (92 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (d, 6H, J=6.8 Hz, $2CH_3$), 0.93 (d, 6H, J=6.7 Hz, $2CH_3$), 1.18 (t, 3H, J=7.6 Hz, CH_3), 1.92–2.05 (m, 2H, 2CH), 2.60 (q, 2H, J=7.6 Hz, CH_2), 4.03 (d, 2H, J=6.7 Hz, CH_2O), 4.04 (d, 2H, J=6.7 Hz, CH_2O), 7.18 (d, 2H, J=8.8 Hz, ArH), 7.47 (s, 1H, ArH), 7.54 (dd, 2H, J=1.7, 6.6 Hz, ArH), 7.98 (s, 1H, ArH), 8.13 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.4 (CH_3), 19.2 ($4CH_3$), 27.7, 27.8 (CH), 28.7 (CH_2), 71.8 ($2CH_2O$), 118.7, 123.5, 123.9 (CH), 126.6 (2CH), 127.3 (C), 128.6 (2CH), 129.4, 130.8, 140.9, 142.2, 145.6, 149.0 (C), 167.5, 168.2 (CO). IR (KBr, cm^{-1}): ν=2958, 2873 (m), 1721, 1708 (s), 1593, 1552, 1526 (w), 1495, 1469 (m), 1419, 1403, 1392 (w), 1371, 1303 (m), 1281, 1254, 1229, 1179, 1119, 1090 (s), 1013, 982, 945, 898, 888, 832 (m), 818 (s), 780, 719, 691 (m), 657, 634, 590, 549 (w). GC–MS (EI, 70 eV): m/z (%)=438 (69) [M^+], 382 (16), 326 (24), 310 (22), 309 (100), 221 (13). HRMS (EI, 70 eV): calcd for $C_{26}H_{30}O_4S$ [M]$^+$: 438.18593; found: 438.18532.

*4.9.2. Dibutyl 2-(4-tert-butylphenyl)benzo[b]thiophene-5,6-dicarboxylate (**13b**).* Compound **13b** was prepared starting with **12b** (100 mg, 0.21 mmol), following general procedure B, as a yellowish solid (81 mg, 82%), mp=56–58 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.89 (t, 6H, J=7.3 Hz, $2CH_3$), 1.28 (s, 9H, $3CH_3$), 1.34–1.43 (m, 4H, $2CH_2$), 1.61–1.72 (m, 4H, $2CH_2$), 4.25 (t, 2H, J=6.7 Hz, CH_2O), 4.26 (t, 2H, J=6.7 Hz, CH_2O), 7.39 (dd, 2H, J=1.9, 6.6 Hz ArH), 7.48 (s, 1H, ArH), 7.58 (dd, 2H, J=1.9, 6.6 Hz, ArH), 7.99 (s, 1H, ArH), 8.13 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.6, 30.7 (CH_2), 31.2 ($3CH_3$), 34.8 (C), 65.6 ($2CH_2O$), 118.7, 123.6, 123.9 (CH), 126.1 (2CH), 126.4 (2CH), 127.2, 129.3, 130.6, 140.9, 142.2, 148.9, 152.5 (C), 167.5, 168.2 (CO). IR (KBr, cm^{-1}): ν=2955, 2927, 2869 (m), 1709 (s), 1650, 1625, 1595, 1497, 1460, 1390, 1359 (w), 1330 (m), 1306, 1284, 1258, 1239 (s), 1189, 1122 (m), 1094 (s), 1060, 1017, 834, 819, 778 (m), 729, 719, 578 (w), 532 (m). GC–MS (EI, 70 eV): m/z (%)=466 (100) [M^+], 452 (20), 451 (67), 410 (11), 395 (23), 337 (62), 321 (14), 250 (13). HRMS (ESI): calcd for $C_{28}H_{35}O_4S$ [M+H]$^+$: 467.2251; found: 467.2256. Anal. Calcd for $C_{28}H_{34}O_4S$: C, 72.07; H, 7.34; S, 6.87. Found: C, 72.08; H, 7.52; S, 6.88.

*4.9.3. Diisobutyl 2-(3,5-dimethylphenyl)benzo[b]thiophene-5,6-dicarboxylate (**13c**).* Compound **13c** was prepared starting with **12c** (100 mg, 0.23 mmol), following general procedure B, as a white solid (84 mg, 85%), mp=66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (d, 6H, J=6.7 Hz, $2CH_3$), 0.94 (d, 6H, J=6.7 Hz, $2CH_3$), 1.92–2.08 (m, 2H, 2CH), 2.29 (s, 6H, $2CH_3$), 4.03 (d, 2H, J=6.7 Hz, CH_2O), 4.04 (d, 2H, J=6.7 Hz, CH_2O), 6.94 (s, 1H, ArH), 7.17 (s, 2H, ArH), 7.49 (s, 1H, ArH), 7.99 (s, 1H, ArH), 8.13 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=18.2 ($4CH_3$), 20.3 ($2CH_3$), 26.7, 26.8 (CH), 70.8 ($2CH_2O$), 118.0, 122.5, 123.0 (CH), 123.5 (2CH), 126.3, 128.3 (C), 129.8 (CH), 132.2 (C), 137.7 (2C), 140.0, 141.0, 148.2 (C), 166.5, 167.1 (CO). IR (KBr, cm^{-1}): ν=2957, 2924, 2871 (m), 1716 (s), 1600, 1514, 1487 (w), 1468 (m), 1405, 1392, 1376, 1344 (w), 1305, 1273, 1261 (m), 1236 (s), 1180, 1163, 1120, 1091, 1012, 979, 946, 899, 843, 816, 781, 748, 721,

690, 681, 603 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=438 (57) $[M]^+$, 382 (12), 326 (26), 310 (22), 309 (100), 236 (14). HRMS (ESI): calcd for $C_{26}H_{31}O_4S$ $[M+H]^+$: 439.1938; found: 439.1944. Anal. Calcd for $C_{26}H_{30}O_4S$: C, 71.20; H, 6.89; S, 7.31. Found: C, 71.08; H, 7.13; S, 7.47.

*4.9.4. Diisobutyl 2-(2-methoxyphenyl)benzo[b]thiophene-5,6-dicarboxylate (**13d**).* Compound **13d** was prepared starting with **12d** (100 mg, 0.23 mmol), following general procedure B, as yellowish solid (87 mg, 88%), mp=96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (d, 12H, *J*=6.7 Hz, $4CH_3$), 1.92–2.06 (m, 2H, 2CH), 3.89 (s, 3H, OCH_3), 4.03 (d, 2H, *J*=6.7 Hz, CH_2O), 4.04 (d, 2H, *J*=6.7 Hz, CH_2O), 6.93–6.99 (m, 2H, ArH), 7.24–7.29 (m, 1H, ArH), 7.63 (dd, 1H, *J*=1.5, 7.7 Hz, ArH), 7.73 (s, 1H, ArH), 8.02 (s, 1H, ArH), 8.14 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.2 ($4CH_3$), 27.8 (2CH), 55.6 (OCH_3), 71.8 ($2CH_2O$), 111.8, 121.1, 122.0 (CH), 122.3 (C), 123.2, 124.0 (CH), 127.2, 128.9 (C), 129.3, 130.1 (CH), 141.3, 141.5, 144.6, 156.4 (C), 167.7, 168.3 (CO). IR (KBr, cm^{-1}): ν=2955, 2928, 2872 (w), 1707 (s), 1627, 1594, 1579, 1547, 1509, 1481 (w), 1468, 1458 (m), 1435, 1408, 1376, 1341 (w), 1307, 1283, 1267 (m), 1252, 1242 (s), 1167, 1125, 1101, 1025, 982, 906, 833, 772 (m), 755 (s), 735, 690 (m), 594, 548 (w). GC–MS (EI, 70 eV): *m*/*z* (%)=440 (63) $[M]^+$, 384 (12), 328 (13), 312 (20), 311 (100). HRMS (ESI): calcd for $C_{25}H_{29}O_5S$ $[M+H]^+$: 441.1730; found: 441.1738. Anal. Calcd for $C_{25}H_{28}O_5S$: C, 68.16; H, 6.41; S, 7.28. Found: C, 68.15; H, 6.55; S, 7.48.

4.10. Synthesis of 2,3-dibromobenzothiophene (15a)

To a CH_2Cl_2 solution (50 mL) of benzo[*b*]thiophene (**14**, 5.00 g, 37.3 mmol) and KOAc (7.30 g, 74.6 mmol) was added Br_2 (3.8 mL, 74.6 mmol) at 20 °C, and the solution was heated under reflux for 24 h. To the solution was added a satd solution of $Na_2S_2O_3$ and $NaHCO_3$. The organic and the aqueous layer were separated, and the latter was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash silica column chromatography (pure heptanes) to yield **15a** as a white solid (9.1 g, 84%). The spectroscopic data were identical with those reported.[17,18]

4.11. Synthesis of 2,3,6-tribromobenzothiophene (15b)

To a CH_2Cl_2 solution (50 mL) of benzo[*b*]thiophene (**14**, 5.00 g, 37.3 mmol) and KOAc (16.5 g, 167.9 mmol) was added Br_2 (8.6 mL, 167.9 mmol) at 20 °C, and the solution was heated under reflux for 24 h. To the solution was added a satd solution of $Na_2S_2O_3$ and $NaHCO_3$. The organic and the aqueous layer were separated, and the latter was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash silica column chromatography (pure heptanes) to yield **15b** as a white solid (9.7 g, 70%). The spectroscopic data were identical with those reported.[19]

4.12. General procedure D for the synthesis of (18a–f)

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 2.5 mol % per Br atom) and dicyclohexyl-(2′,6′-dimethoxybiphenyl-2-yl) phosphine (SPhos) (41 mg, 10 mol %) in DMF (5 mL) was flushed with Ar and stirred at 20 °C to give a yellowish or brownish transparent solution. To the stirred solution were added the 2,3-dibromobenzothiophene (**15a**, 292 mg, 1.0 mmol), Et_3N (1.1 mL, 8.0 mmol), and the acrylate (1.25 equiv per Br). The reaction mixture was stirred at 100–130 °C for 12–48 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), concentrated in vacuo, and passed through a column (silica gel). To a xylene solution (3 mL) of the crude product was added Pd/C (30 mg, 10 mol %). The solution was stirred under reflux for 48 h under argon atmosphere. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes–EtOAc) to yield the product.

*4.12.1. Diethyl dibenzo[b,d]thiophene-2,3-dicarboxylate (**18a**).* Compound **18a** was prepared starting with **15a** (292 mg, 1.0 mmol) as an amorphous white solid (249 mg, 76%); mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.33 (t, 3H, *J*=7.76 Hz, CH_3), 1.35 (t, 3H, *J*=7.76 Hz, CH_3), 4.31–4.40 (m, 4H, $2CH_2O$), 7.41–7.48 (m, 2H, ArH), 7.79–7.82 (m, 1H, ArH), 8.12 (s, 1H, ArH), 8.13–8.15 (m, 1H, ArH), 8.43 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.2 ($2CH_3$), 61.7, 61.8 (CH_2O), 122.3, 122.4, 123.0, 123.6, 125.1, 128.0 (CH), 128.5, 130.4, 134.4, 137.1, 140.7, 141.9 (C), 167.5, 167.7 (CO). IR (KBr): $\tilde{\nu}$=3053 (w), 2975 (w), 2931 (w), 2896 (w), 2867 (w), 1706 (s), 1632 (w), 1603 (w), 1540 (w), 1483 (w), 1469 (w), 1440 (m), 1366 (m), 1314 (m), 1247 (s), 1229 (s), 1098 (s), 1021 (s), 913 (w), 885 (w), 873 (w), 853 (w), 765 (s), 757 (s), 708 (s), 642 (w), 583 (w), 552 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=328 (40) $[M]^+$, 284 (06), 257 (54), 229 (19), 211 (58), 185 (100); HRMS (EI, 70 eV): *m*/*z* calcd for $C_{18}H_{16}O_4S$ $[M]^+$: 328.08715; found: 328.08765.

*4.12.2. Dibutyl dibenzo[b,d]thiophene-2,3-dicarboxylate (**18b**).* Compound **18b** was prepared starting with **15a** (292 mg, 1.0 mmol) as a highly viscous oil (311 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (t, 3H, *J*=7.3 Hz, CH_3), 0.92 (t, 3H, *J*=7.4 Hz, CH_3), 1.34–1.47 (m, 4H), 1.64–1.74 (m, 4H), 4.28 (t, 2H, *J*=6.7 Hz, OCH_2), 4.30 (t, 2H, *J*=6.6 Hz, OCH_2), 7.44–7.48 (m, 2H, ArH), 7.80–7.83 (m, 1H, ArH), 8.13 (s, 1H, ArH), 8.15–8.17 (m, 1H, ArH), 8.43 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=12.7 ($2CH_3$), 18.2, 29.6, 64.7 (CH_2), 121.3, 121.4, 122.0, 122.6, 124.0, 127.0 (CH), 127.5, 129.4, 133.4, 136.1, 139.7, 140.8 (C), 166.5, 166.8 (CO). IR (KBr): $\tilde{\nu}$=2957 (m), 1717 (s), 1459 (m), 1263 (s), 1119 (m), 1092 (m), 1018 (w), 760 (m), 731 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=384 (20) $[M]^+$, 328 (06), 311 (04), 272 (31), 255 (100), 228 (10), 211 (05), 171 (12). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{22}H_{24}O_4S$ $[M]^+$: 384.13898; found: 384.139182.

*4.12.3. Diisobutyl dibenzo[b,d]thiophene-2,3-dicarboxylate (**18c**).* Com pound **18c** was prepared starting with **15a** (292 mg, 1.0 mmol) as highly viscous oil (284 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.94 (d, 6H, *J*=1.6 Hz, CH_3), 0.96 (d, 6H, *J*=1.6 Hz, CH_3), 1.94–2.06 (m, 2H), 4.06 (d, 2H, *J*=6.5 Hz, OCH_2), 4.08 (d, 2H, *J*=6.7 Hz, OCH_2), 7.44–7.47 (m, 2H), 7.80–7.83 (m, 1H), 8.13 (s, 1H, ArH), 8.15–8.16 (m, 1H), 8.43 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.2 (CH_3), 71.9 (OCH_2), 27.7, 122.3, 122.4, 123.0, 123.6, 125.0, 128.0 (CH), 128.6, 130.4, 134.4, 137.1, 140.7, 141.8 (C), 167.5, 167.8 (CO). IR (KBr): $\tilde{\nu}$=2959 (m), 2873 (w), 1717 (s), 1604 (w), 1468 (m), 1263 (s), 1120 (m), 1091 (m), 982 (m), 759 (m), 730 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=384 (20) $[M]^+$, 328 (06), 311 (02), 272 (56), 255 (100), 228 (11), 211 (05). 171 (12). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{22}H_{24}O_4S$ $[M]^+$: 384.13898; found: 384.13901.

*4.12.4. Dihexyl dibenzo[b,d]thiophene-2,3-dicarboxylate (**18d**).* Compound **18d** was prepared starting with **15a** (292 mg, 1.0 mmol) as highly viscous oil (338 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, 3H, *J*=6.1 Hz, CH_3), 0.84 (t, 3H, *J*=5.4 Hz, CH_3), 1.23–1.39 (m, 12H), 1.64–1.74 (m, 4H), 4.27 (t, 2H, *J*=6.8 Hz, OCH_2), 4.28 (t, 2H, *J*=6.9 Hz, OCH_2), 7.43–7.46 (m, 2H), 7.79–7.82 (m, 1H), 8.12 (s, 1H, ArH), 8.13–8.15 (m, 1H), 8.42 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0 ($2CH_3$), 22.5, 25.6, 28.5, 31.5 (CH_2), 66.0 (OCH_2), 122.3, 122.4, 123.0, 123.6, 125.0, 128.0 (CH), 128.6, 130.4, 134.4, 137.1, 140.7, 141.9 (C), 167.6, 167.8 (CO). IR (KBr): $\tilde{\nu}$=2953 (m), 2927 (m), 1718 (s), 1459 (w), 1263 (s), 1120 (m), 1092 (m), 760 (m), 729 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=440 (14) $[M]^+$, 356 (06), 272 (33), 255 (100), 228

(09), 182 (07). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{26}H_{32}O_4S$ $[M]^+$: 440.20158; found: 440.20186.

*4.12.5. 2,3-Diphenyldibenzo[b,d]thiophene (**18e**).* Compound **18e** was prepared starting with **15a** (292 mg, 1.0 mmol) as a brownish semisolid (265 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.11–7.34 (m, 10H), 7.44–7.50 (m, 4H), 7.70 (d, 1H, *J*=8.3 Hz, ArH), 7.89 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=120.7, 122.7, 123.6, 123.7, 126.5, 126.7, 127.6, 128.6, 128.7, 128.8 (CH), 130.3, 133.8, 137.4, 139.1, 140.4 (C). IR (KBr): $\tilde{\nu}$=2926 (w), 2850 (w), 1665 (m), 1594 (m), 1446 (m), 1246 (m), 1107 (m), 958 (w), 746 (m), 691 (s), 595 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=336 (15) $[M]^+$, 321 (06), 302 (03), 261 (32), 184 (04), 167 (05). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{24}H_{16}S$ $[M]^+$: 336.09672; found: 336.09660.

*4.12.6. 2,3-Bis(4-chlorophenyl)dibenzo[b,d]thiophene (**18f**).* Compound **18f** was prepared starting with **15a** (292 mg, 1.0 mmol) as a brown semisolid (336 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.24–7.43 (m, 10H), 7.60–7.93 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=121.3, 121.9, 122.2, 123.0, 124.4, 124.6, 124.9, 127.6, 127.7, 128.9 (CH), 133.3, 133.6, 133.8, 135.1, 135.9, 137.2, 137.7, 140.1, 140.5, 142.5 (C). IR (KBr): $\tilde{\nu}$=3058 (w), 1708 (s), 1587 (m), 1489 (m), 1421 (w), 1358 (w), 1219 (m), 1090 (m), 1012 (m), 828 (m), 756 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=404 (40) $[M]^+$, 384 (67), 368 (08), 351 (08), 334 (07), 307 (12), 266 (12), 224 (15), 202 (07), 161 (34). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{24}H_{14}Cl_2S$ $[M]^+$: 404.01878; found: 404.01880.

4.13. General procedure E for the synthesis of (19a–e)

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (06 mg, 0.025 mmol) and dicyclohexyl-(2′,6′-dimethoxybiphenyl-2-yl) phosphine (SPhos, 21 mg, 0.05 mmol) in DMF (5 mL) was flushed with Ar and stirred at 20 °C to give a yellowish or brownish transparent solution. To the stirred solution were added the 2,3-dibromobenzothiophene (**15a**, 292 mg, 1.0 mmol), Et_3N (1.1 mL, 8.0 mmol), and the acrylate (1.25 mmol). The reaction mixture was stirred at 130 °C for 24 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), concentrated in vacuo, and passed through a column (flash silica gel, heptanes–EtOAc) to yield the product.

*4.13.1. (E)-Ethyl 3-(benzo[b]thiophen-3-yl)acrylate (**19a**).* Compound **19a** was prepared starting with **15a** (292 mg, 1.0 mmol) as a colorless viscous oil (188 mg, 81%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.28 (t, 3H, *J*=7.1 Hz, CH_3), 4.21 (q, 2H, *J*=7.2, 14.3 Hz, OCH_2), 6.45 (d, 1H, *J*=16.1 Hz), 7.25–7.40 (m, 2H), 7.66 (s, 1H, ArH), 7.78–7.81 (m, 1H), 7.88 (d, 1H, *J*=16.1 Hz), 7.91–7.95 (m, 1H). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.3 (CH_3), 60.5 (OCH_2), 118.7, 122.1, 123.0, 124.9, 125.0, 128.0 (CH), 131.6 (C), 136.3 (CH), 137.1, 140.5 (C), 167.1 (CO). IR (KBr): $\tilde{\nu}$=2978 (w), 1703 (s), 1627 (s), 1503 (w), 1368 (m), 1257 (m), 1158 (s), 1093 (w), 1043 (m), 971 (m), 731 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=232 (92) $[M]^+$, 217 (02), 204 (09), 187 (100), 175 (04), 160 (29), 147 (07), 115 (67). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{13}H_{12}O_2S$ $[M]^+$: 232.05525; found: 232.05530.

*4.13.2. (E)-Butyl 3-(benzo[b]thiophen-3-yl)acrylate (**19b**).* Compound **19b** was prepared starting with **15a** (292 mg, 1.0 mmol) as a colorless viscous oil (169 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, 3H, *J*=7.4 Hz, CH_3), 1.30–1.42 (m, 2H), 1.57–1.69 (m, 2H), 4.16 (t, 2H, *J*=6.7 Hz, OCH_2), 6.45 (d, 1H, *J*=15.9 Hz), 7.25–7.41 (m, 2H), 7.66 (s, 1H, ArH), 7.77–7.81 (m, 1H), 7.88 (d, 1H, *J*=16.1 Hz), 7.91–7.95 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.7 (CH_3), 18.2, 29.7 (CH_2), 63.4 (OCH_2), 117.7, 121.1, 121.9, 123.9, 124.0, 126.9 (CH), 130.6 (C), 135.2 (CH), 136.1, 139.4 (C), 166.2 (CO). IR (KBr): $\tilde{\nu}$=2956 (m), 1719 (s), 1542 (w), 1459 (m), 1316 (m), 1262 (s), 1119 (m), 1092 (m), 1018 (w), 898 (w), 760 (m), 731 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=260 (90) $[M]^+$, 245 (14), 231 (20), 217 (40), 204 (27), 187 (100), 175 (18), 160 (29). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{15}H_{16}O_2S$ $[M]^+$: 260.09110; found: 260.09136.

*4.13.3. (E)-3-(Benzo[b]thiophen-3-yl)acrylonitrile (**19c**).* Compound **19c** was prepared starting with **15a** (292 mg, 1.0 mmol) as light brown semisolid (94 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.63 (d, 1H, *J*=16.3 Hz), 7.26–7.41 (m, 1H), 7.49 (d, 1H, *J*=16.2 Hz), 7.68–7.73 (m, 3H), 7.78–7.84 (m, 1H). ^{13}C NMR (62 MHz, $CDCl_3$): δ=96.9 (CH), 117.7 (C), 122.5, 124.8, 125.2, 127.0 (CH), 128.5 (C), 129.2 (CH), 138.1, 139.2 (C), 143.3 (CH). IR (KBr). $\tilde{\nu}$ =2921 (m), 2213 (w), 1611 (m), 1457 (m), 1365 (w), 1107 (m), 952 (m), 745 (s), 618 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=260 (90) $[M]^+$, 185 (100), 158 (09), 140 (10), 126 (01), 114 (05). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{11}H_7NS$ $[M]^+$: 185.02937; found: 185.02874.

*4.13.4. (E)-3-Styrylbenzo[b]thiophene (**19d**).* Compound **19d** was prepared starting with **15a** (292 mg, 1.0 mmol) as a colorless crystalline solid (174 mg, 76%); mp 93–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.12–7.23 (m, 2H), 7.28–7.36 (m, 5H), 7.46 (s, 1H, ArH), 7.46–7.49 (m, 2H, ArH), 7.77–7.83 (m, 1H, ArH), 7.91–7.94 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=120.7, 121.8, 122.0, 123.0, 124.33, 124.6, 126.4, 127.7, 128.8, 130.3 (CH), 134.2, 137.4, 137.8, 140.5 (C). IR (KBr): $\tilde{\nu}$=2921 (s), 2851 (s), 1667 (m), 1598 (m), 1492 (m), 1454 (m), 1446 (m), 1434 (m), 1377 (w), 1365 (w), 1346 (w), 1260 (w), 1243 (w), 1204 (w), 1176 (w), 1156 (w), 1029 (w), 1019 (w), 948 (w), 907 (w), 887 (w), 864 (w), 757 (s), 748 (s), 730 (s), 696 (s), 623 (w), 591 (w), 555 (w), 538 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=236 (100) $[M]^+$, 221 (18), 202 (16), 189 (05), 117 (08). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{16}H_{12}S$ $[M]^+$: 236.06542; found: 236.064490.

*4.13.5. (E)-3-(4-Methylstyryl)benzo[b]thiophene (**19e**).* Compound **19e** was prepared starting with **15a** (292 mg, 1.0 mmol) as a white crystalline solid (190 mg, 76%); mp 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.29 (s, 3H, CH_3), 7.11–7.38 (m, 6H), 6.88 (d, 1H, *J*=16.0 Hz), 7.79 (d, 2H, *J*=7.3 Hz), 7.92 (d, 2H, *J*=7.2 Hz). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.3 (CH_3), 119.7, 121.4, 121.9, 123.0, 124.2, 124.5, 126.3, 129.4, 130.2 (CH), 134.3, 134.6, 137.6, 137.8, 140.5 (C). IR (KBr): $\tilde{\nu}$=2919 (m), 1642 (w), 1425 (m), 1234 (m), 1109 (w), 962 (m), 805 (s), 754 (s), 730 (s), 709 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=250 (75) $[M]^+$, 235 (100), 221 (06), 202 (11), 189 (04), 158 (02), 139 (02). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{17}H_{14}S$ $[M]^+$: 250.08107; found: 250.08125.

4.14. Synthesis of (*E*)-2,3-diphenyl-7-styryldibenzo[*b*,*d*]thiophene (22)

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 1.7 mol % per Br atom) and dicyclohexyl-(2′,6′-dimethoxybiphenyl-2-yl) phosphine (SPhos, 41 mg, 0.10 mmol) in DMF (5 mL) was flushed with Ar and stirred at 20 °C to give a yellowish or brownish transparent solution. To the stirred solution were added the 2,3,6-tribromobenzothiophene (**15b**, 371 mg, 1.0 mmol), Et_3N (1.1 mL, 8.0 mmol), and styrene (1.25 equiv per Br). The reaction mixture was stirred at 130 °C for 48 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layers were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), concentrated in vacuo, and passed through a column (silica gel). To a xylene solution (3 mL) of the crude product was added Pd/C (30 mg, 10 mol %). The solution was stirred under reflux for 48 h under argon atmosphere. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes–EtOAc) to yield the product.

*4.14.1. (E)-2,3-Diphenyl-7-styryldibenzo[b,d]thiophene (**22**).* Compound **22** was prepared starting with **15b** (371 mg, 1.0 mmol) as a brownish semisolid (319 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.01–7.20 (m, 7H), 7.24–7.34 (m, 7H), 7.40–7.47 (m, 6H), 7.75–7.86 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=120.7, 121.3, 122.1, 122.3, 122.9, 125.6, 126.5, 126.6, 127.5, 128.6, 128.7, 128.8 (CH), 129.7, 130.3 (C), 130.4 (CH), 137.3, 137.4, 137.4, 137.5, 139.9, 140.5, 141.2, 142.1 (C). IR (KBr): $\tilde{\nu}$=3054 (w), 3023 (w), 291 (w), 1681 (m), 1596 (m), 1493 (m), 1445 (m), 1178 (w), 1155 (w), 1072 (w), 1026 (w), 956 (s), 908 (w), 876 (w), 812 (w), 747 (s), 733 (s), 688 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=438 (19) [M]$^+$, 368 (31), 338 (100), 259 (20), 234 (16), 202 (10), 105 (15). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{32}H_{22}S$ [M]$^+$: 438.14422; found: 438.144012.

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