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Pd-mediated C–H arylation of EDOT and synthesis of push–pull systems incorporating EDOT

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Abstract—The direct C–H arylation of 3,4-ethylenedioxythiophene (EDOT) is described under Heck-type experimental conditions. This methodology has been used to synthesize a series of push–pull systems containing EDOT units.

1. Introduction

Organic electro-optical materials due to their intriguing photophysical properties have received prominent attention in molecular electronic and optical devices.[1] Over the years, oligothiophenes are established as the most important electro-optical materials, which are used in the fabrication of electroluminescent and semi-conducting devices. The required oligothiophenes are mostly prepared via palladium/nickel mediated cross-coupling of either heteroaryl halides with aryl metals or aryl halides with heteroaryl metals.[2] However, the direct arylation of thiophene bearing electron-withdrawing groups was reported by Lemaire and co-workers.[3] It is also known that aryl halides/heteroaryl halides can couple directly with thiophene bearing electron-releasing groups at the reactive 2- and/or 5-position.[4] The regioselective arylation of methylthiophene-3-carboxylate by an aryl bromide, catalyzed by $Pd(PPh_3)_4$ has been reported.[5] The synthesis of 2-arylthiophene via CuI or $MnBr_2$ catalyzed cross-coupling of 2-thienyltributylstannane with aryl halides has also been reported.[6] Yokooji et al. reported a straightforward synthesis of 5,5′-diarylated-2,2′-bithiophene via a palladium catalyzed arylation.[7] Mori and co-workers recently reported the synthesis of donor–acceptor type 2,5-diarylthiophenes via palladium mediated sequential arylation reaction.[8] The 3,4-ethylenedioxythiophene (EDOT) has been used as a building block in several conjugated systems that incorporate unique properties such as electrochromic behavior[9] and in low band gap polymers.[10]

Our preliminary work on arylation of 3,4-ethylenedioxythiophene under Heck-type conditions has been recently published.[11] This simple and new method afforded various arylated products in reasonable yields in contrast with the usual arylation methods involving a metal-catalyzed cross-coupling reaction of EDOT-metals and organic halides (Kumada,[12] Negishi,[13] Stille,[14] Suzuki[15]). Borghese and co-workers also simultaneously reported similar arylation of EDOT under Heck-type conditions.[16]

Roncali and co-workers reported the synthesis of stable and soluble oligo(3,4-ethylenedioxythiophenes),[17] and also the synthesis of thienylvinylenes incorporating EDOT units.[18] Very recently, a direct arylation of heteroarenes including 3-methoxythiophene was reported with aryl iodides using rhodium catalyst.[19] Roncali and co-workers reported the synthesis of 3,4-ethylenedioxythiophene (EDOT) tethered symmetrical benzo[*c*]thiophene derivative,[20] and also reported the synthesis of push–pull chromophores.[21] Since a large number of thiophene oligomers have recently been explored as push–pull type systems,[21,22] we decided to explore our synthetic design of the NLO materials exploiting high electron-rich system of the EDOT. The low yield obtained during cross-coupling of EDOT-metals[15] with aryl halides also encouraged us to undertake the present investigation. Hence, the coupling reaction of EDOT was carried out with a variety of aryl/heteroaryl halides. The resulting arylated EDOTs are converted into the respective push–pull systems and the detailed results have been described.

2. Results and discussions

As mentioned in Section 1, there is only one report on EDOT incorporated benzo[*c*]thiophene derivative.[20] In

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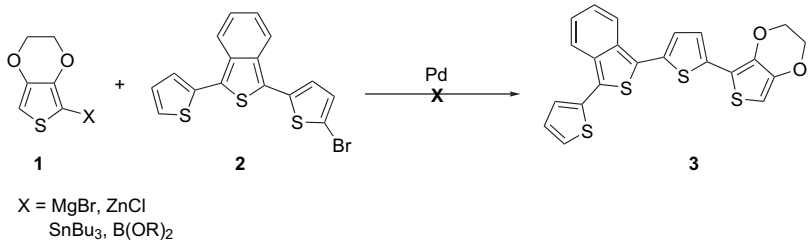
continuation of our interest on benzannelated thienyl oligomers,[23] initially, an attempt was made to incorporate EDOT unit on the benzo[*c*]thiophene skeleton using either 3,4-ethylenedioxy thiophenyl-2-magnesium bromide (Kumada) or 3,4-ethylenedioxythiopheneyl-2-zinc bromide (Negishi) or using stable 2-tributylstannyl-3,4-ethylenedioxythiophene (Stille) or pinacolboronic ester of 3,4-ethylenedioxythiophene (Suzuki) and known bromo compound **2** in the presence of various catalysts [$Pd(PPh_3)_4$, $Pd(PPh_3)Cl_2$, and $Pd(dba)_3$] without any success, Scheme 1.

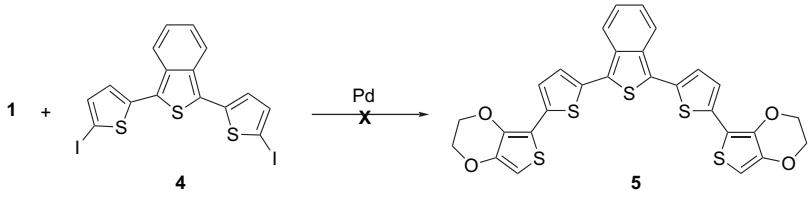
Kisselev and Thelakkat recently reported Pd-catalyzed ($Pd(dppf)Cl_2$ or $Pd_2(dba)_3$) coupling of 1,2-bis(5-iodo-2-thienyl)isothianaphthene **4** with secondary amines.[24] However, all our attempts to incorporate EDOT unit on the benzo[*c*]-thiophene skeleton using pinacolboranate ester of EDOT and iodo compound **4** in the presence of $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ were unsuccessful, Scheme 2.

Having failed to incorporate the EDOT unit into the benzo-[*c*]thiophene skeleton, we have turned our focus on the coupling of EDOT with simple aryl halides. As a model reaction, we have carried out coupling reaction of pinacol boronate ester of EDOT **1** with 4-iodoanisole in the presence of $Pd(PPh_3)_4$. Usual workup and purification of the crude product led to the isolation of mono- and bis-arylated products **8a** and **9a** in 30 and 20% yields, respectively. The isolation of compound **9a** prompted us to explore the direct arylation of EDOT. Thus, the direct arylation of EDOT with 4-iodoanisole in the presence of $Pd(PPh_3)_4$ and K_2CO_3 in DMF at 80 °C for 14 h afforded the corresponding mono-arylated product **8a** in reasonable yield, Scheme 3.

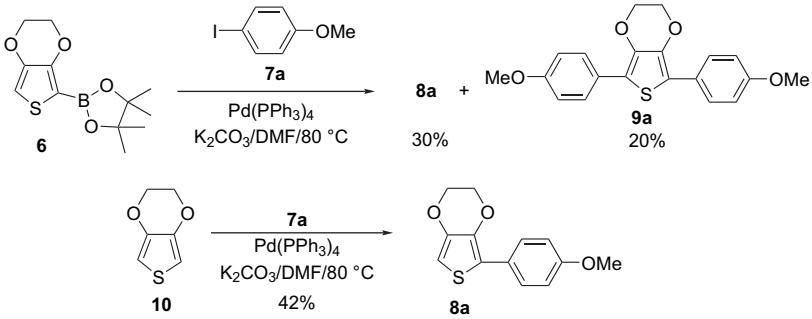
However, all attempts to couple either 1-(5-bromothiophen-2-yl)-3-(thiophen-2-yl)benzo[*c*]thiophene **2** or 1,3-bis(5-iodothiophen-2-yl)benzo[*c*]thiophene **4** with EDOT were unsuccessful. The arylation reactions of EDOT were performed in dry DMF in the presence of K_2CO_3 and catalytic amounts of $Pd(PPh_3)_4$ at 80 °C using either aryl iodide or bromide. The use of acetonitrile or THF as a solvent in place of DMF did not afford any arylated products. The selectivity observed in the polar solvent (DMF) for the arylation could be due to the ionization of the Ar–Pd–X into the $Ar–Pd^+ X^-$. The electrophilic $Ar–Pd^+ X^-$ species would react at the electron-rich 2-position of the 3,4-ethylenedioxythiophene, affording the cationic intermediate **10b**, which on proton abstraction followed by subsequent reductive elimination would afford the arylated product **10d**, Scheme 4.



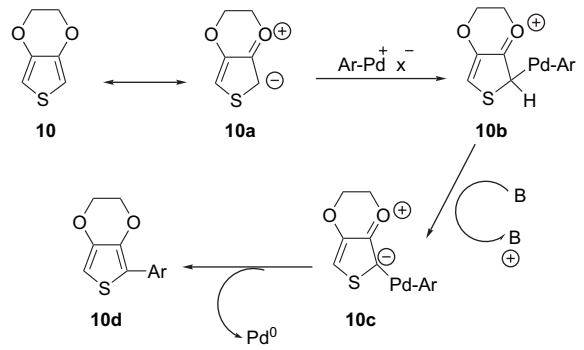
Scheme 1.



Scheme 2.



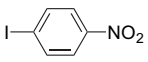
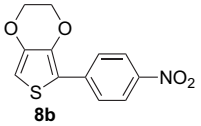
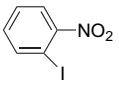
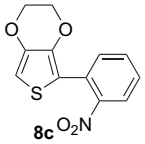
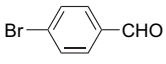
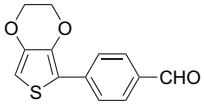
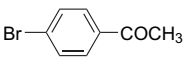
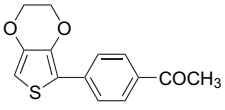
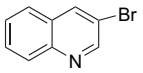
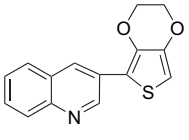
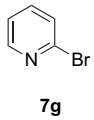
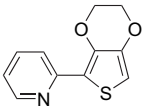
Scheme 3.



Scheme 4. Mechanistic pathway for EDOT arylation.

Among the three palladium catalysts [$Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd_2(dba)_3$] employed for arylation of EDOT, $Pd(PPh_3)_4$ was found to be the most suitable one. We also observed that aryl halides bearing electron-withdrawing groups react faster than aryl halides containing electron-donating groups. The results of coupling reaction of EDOT with aryl halides bearing electron-withdrawing groups are presented in Table 1.

Table 1. Mono-arylation of 3,4-EDOT with aryl halides bearing electron-withdrawing groups

Entry	Ar–X	Product	Temp (°C); time (h)	Yield[a] (%); mp (°C)
1	 **7b**	 **8b**	65; 8	55; 158
2	 **7c**	 **8c**	60; 8	50; 92
3	 **7d**	 **8d**	60; 10	50; 122
4	 **7e**	 **8e**	65; 8	52; 118
5	 **7f**	 **8f**	80; 10	35; 125
6	 **7g**	 **8g**	80; 10	34; 70

[a] Isolated yield after column chromatography.

The yield of the arylated products was not significantly changed by using different bases such as Cs_2CO_3 or K_3PO_4 in the place of K_2CO_3. The use of bromoaryl or iodoaryl compounds did not have much effect on the yield of the arylated products. A minor amount (5–10%) of the starting material (EDOT) was always recovered even on an extended reaction time without any appreciable change in the yield of the arylated products. The 5,5′-dibromo-2,2′-bithiophene **7h** underwent a smooth bis-arylation with EDOT to afford the coupled product **8h** in 40% yield. It should be noted that the same product was obtained in relatively very low yield (20%) involving a cross-coupling between pinacol boronate ester of EDOT **7** and 2,5-dibromothiophene.[21] The fluorenyl dibromo compound **7i** afforded the respective coupled product **8i** in 45% yield, Table 2.

The electron-rich aromatic halides **7a** and **7j–l** afforded the corresponding arylated products **8a** and **8j–l** in relatively less yields. Moreover, the reaction temperature and the reaction time are high compared to electron-deficient aromatic halides. The results of coupling reaction of EDOT with aryl halides bearing electron-donating groups are presented in Table 3.

The bis-arylation of EDOT was carried out with 2 equiv of aryl halides **7a–m** and the results are summarized in Table 4.

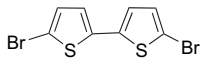
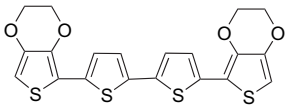
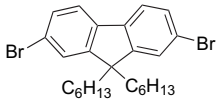
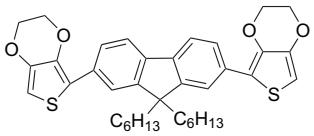
The electron-deficient aromatic halides **7b** and **7c** afforded the corresponding bis-arylated products **9b** and **9c** in 40 and 35% yields, respectively. Similar to mono-arylation, the reaction temperature and the reaction time are also less compared to electron-rich aromatic halides **7a** and **7m**. The structure of 2,5-bis(benzo[*b*]-2-thienyl)EDOT **9m** was confirmed by X-ray analysis[25] (Fig. 1).

Finally, arylation of 2,2′-bis(EDOT) **11** with 4-methoxyiodobenzene **7a** in dry DMF at 80 °C for 14 h led to the isolation of mono-arylated product **12** in 30% yield, Scheme 5. All attempts to couple bis(EDOT) **11** with other aryl/heteroaryl halo compounds are found to be unsuccessful, Scheme 5.

The push–pull system containing EDOT as a conjugated system is regarded as potential non-linear optical material. Hence, the synthesis of 3,4-ethylenedioxythiophene analogs having an electron acceptor group at one end and a donor group at the opposite end is planned. To realize the above-mentioned objective, the mono-arylated products **8a**, **8j**, and **8k** were formylated under the Vilsmeier–Haack condition to afford the corresponding mono-aldehydes **13–15** in 60–80% yields, Scheme 6. Condensation of these aldehydes with malononitrile/thiopheneacetonitrile led to the formation of corresponding cyano derivatives **16–20** in 40–65% yields, Scheme 7.

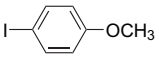
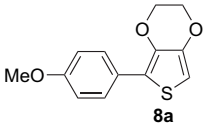
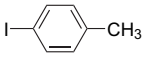
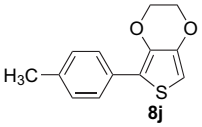
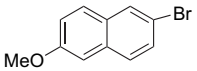
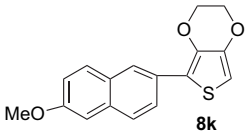
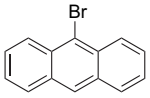
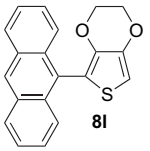
Finally, olefin tethered extended system of **16** was prepared. The Wittig reaction of 4-methoxybenzylphosphonium salt with known 3,4-ethylenedioxythiophene aldehyde afforded the corresponding vinylene **21**. The Vilsmeier–Haack formylation of the latter afforded aldehyde **22** in 55% yield. Condensation of aldehyde **22** with thiophene-2-acetonitrile using *t*-BuOK in ethanol led to the push–pull system **23** in 51% yield, Scheme 8.

Table 2. Synthesis of EDOT-based oligothiophenes

Entry	Ar–X	Product	Temp (°C); time (h)	Yield[a] (%); mp (°C)
1	 **7h**	 **8h**	80; 10	40; 190
2	 **7i**	 **8i**	80; 12	45; 105

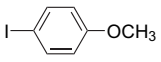
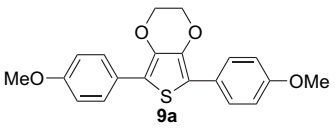
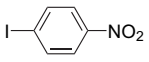
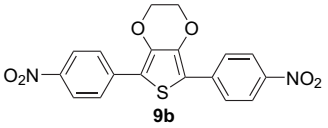
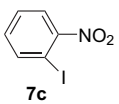
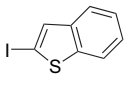
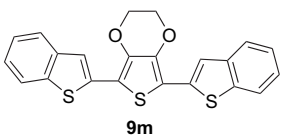
[a] Isolated yield after column chromatography.

Table 3. Mono-arylation of EDOT using aryl halides bearing electron-releasing groups

Entry	Ar–X	Product	Temp (°C); time (h)	Yield[a] (%); mp (°C)
1	 **7a**	 **8a**	80; 14	42; 75
2	 **7j**	 **8j**	80; 12	45; Liquid
3	 **7k**	 **8k**	80; 12	40; 120
4	 **7l**	 **8l**	60; 12	40; 192

[a] Isolated yield after column chromatography.

Table 4. Bis-arylation of EDOT

Entry	Ar–X	Product	Temp (°C); time (h)	Yield[a] (%); mp (°C)
1	 **7a**	 **9a**	80; 13	35; 160
2	 **7b**	 **9b**	80; 10	40; 155
3	 **7c**	 **9c**	80; 10	35; 166
4	 **7m**	 **9m**	70; 8	50; 165

[a] Isolated yield after column chromatography.

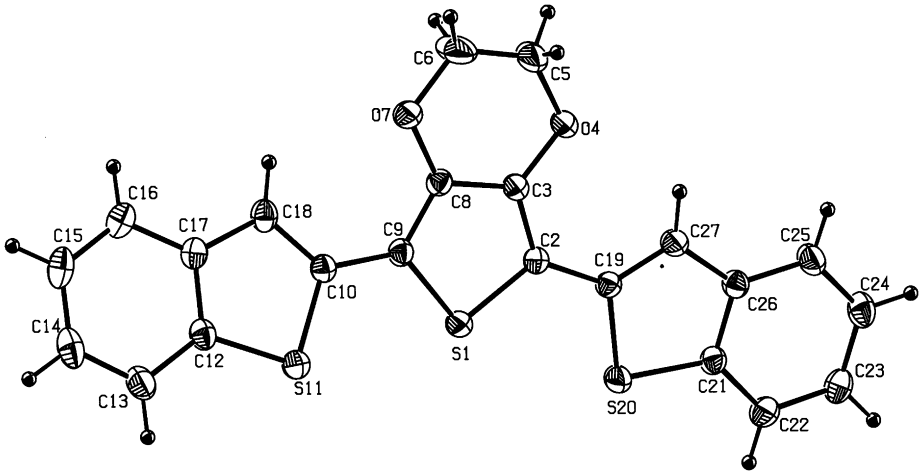
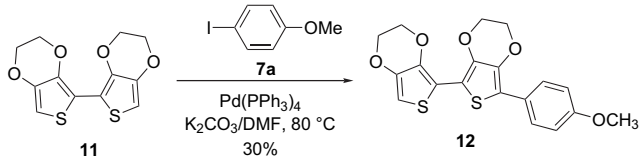
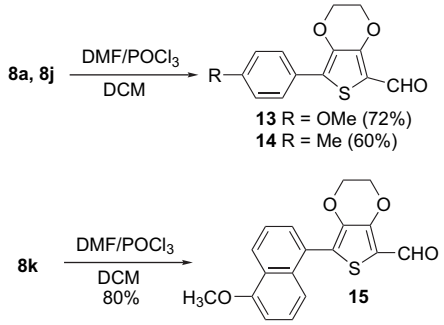


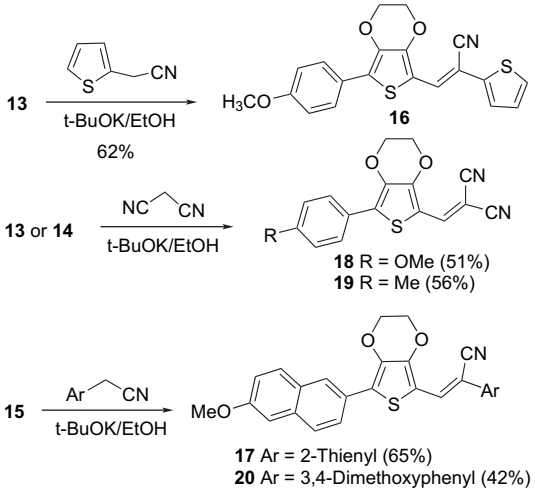
Figure 1. ORTEP style plot of compound **9m** in thermal ellipsoids drawn at the 50% probability level.



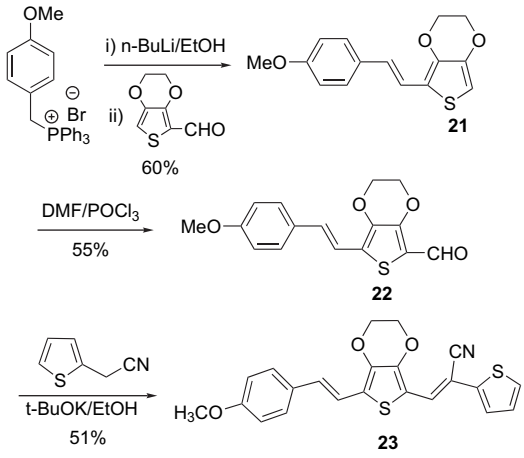
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

3. UV–vis spectroscopy

The electronic absorption data of the arylated products and cyanovinylenes are listed in Table 5.

The UV–vis spectra are characterized by a well-resolved fine structure with EDOT median core. The arylated products of

Table 5. Electronic absorption data (DCM)

Compound	λ_{max} (DCM)
8a	301
8b	376
8c	345
8d	445
8e	335
8k	318
8l	370
9b	374
9m	395
16	435
17	377
18	379
20	365
23	460

EDOT containing electron-withdrawing group produce a slight bathochromic shift of the absorption bands compared to EDOT containing electron-releasing group. On the other hand, comparison of these data shows that replacement of electron-withdrawing group by electron-releasing group in arylated products produces a >30–60 nm shift of the absorption bands. The UV–vis spectra of thienylvinylene incorporating EDOT units show λ_{max} value greater than 400 nm, which indicates the bathochromic shift of the absorption bands.

4. Conclusions

The syntheses of a variety of mono- and bis-arylated EDOT analogs have been achieved in moderate yields, involving direct Heck arylation of EDOT with various aryl and heteroaryl halides. The synthesis of push–pull systems containing 3,4-ethylenedioxythiophenes has been achieved in good yield.

5. Experimental

5.1. General

All melting points are uncorrected. IR spectra were recorded on a Shimadzu FT-IR 8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Jeol 400 spectrometer at 400 and 100 MHz and Bruker spectrometer at 300 and 75 MHz, respectively. Mass spectra were recorded on a Jeol DX 303 HF spectrometer. Elemental analyses were carried out on a Perkin–Elmer 240 B instrument.

5.2. A representative procedure for mono-arylation

5.2.1. 2,3-Dihydro-5-(4-methoxyphenyl)thieno[3,4-*b*][1,4]dioxine (8a). A two-necked flask containing 4-iodoanisole **8a** (0.5 g, 2.13 mmol), EDOT (0.3 g, 2.11 mmol), $Pd(PPh_3)_4$ (246 mg, 0.21 mmol), and K_2CO_3 (0.34 g, 2.52 mmol) was evacuated. To this, dry DMF (10 mL) was added via syringe. The reaction mixture was allowed to stir at 80 °C for 14 h. Then, the mixture was cooled to room temperature and passed through a Celite pad, which was successively washed with chloroform. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layer was extracted with anhydrous sodium sulfate and concentrated under pressure to leave a crude residue. Purification by chromatography on silica gel (hexane–EtOAc 9:1) afforded 0.22 g of **8a** as a colorless solid (42%); mp 75 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 3.71 (3H, s, OCH_3), 4.22–4.31 (4H, m, OCH_2), 6.33 (1H, s, EDOT), 6.61 (2H, d, J=8.8 Hz, CH_APh), 7.61 (2H, d, J=8.8 Hz, CH_BPh); mass m/z: 248 (M^+); ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ_C 55.35, 64.50, 64.73, 96.45, 114.10, 114.21, 125.98, 127.44, 127.74, 158.44, 158.75. Anal. Calcd for $C_{13}H_{12}SO_3$: C, 62.88; H, 4.87; S, 12.91. Found: C, 62.66; H, 4.96; S, 12.79.

5.2.2. 2,3-Dihydro-5-(4-nitrophenyl)thieno[3,4-*b*][1,4]-dioxine (8b). Following the general procedure, compound **8b** was obtained as a yellow solid (0.30 g, 55%); mp 158 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 4.19–4.21 (2H, m, OCH_2), 4.28–4.30 (2H, m, OCH_2), 6.38 (1H, s, EDOT), 8.09 (2H, d, J=8.8 Hz, CH_APh), 8.26 (2H, d, J=8.4 Hz, CH_BPh); ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ_C 64.28, 65.00, 100.97, 115.14, 124.03, 124.35, 125.66, 128.30, 140.61, 144.95; mass m/z: 263 (M+). Anal. Calcd for $C_{12}H_9NSO_4$: C, 54.75; H, 3.45; N, 5.32; S, 12.18. Found: C, 54.64; H, 3.52; N, 5.38; S, 12.10.

5.2.3. 2,3-Dihydro-5-(2-nitrophenyl)thieno[3,4-*b*][1,4]-dioxine (8c). Following the general procedure, compound **8c** was obtained as a yellow solid (0.23 g, 50%); mp 92 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 4.13–4.18 (4H, m, OCH_2), 6.59 (1H, s, EDOT), 7.53 (2H, m, Ph), 7.67–7.69 (1H, m, Ph), 7.89 (1H, d, J=8.28 Hz, Ph); ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ_C 65.21, 65.31, 100.89, 111.84, 125.48, 127.03, 129.26, 132.71, 133.57, 140.22, 142.59, 149.98; mass m/z: 263 (M+). Anal. Calcd for $C_{12}H_9NO_4S$: C, 54.75; H, 3.45; S, 12.18; N, 5.32. Found: C, 54.66; H, 3.30; S, 12.29; N, 5.25.

5.2.4. 4-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)benzaldehyde (8d). Following the general procedure, compound **8d** was obtained as a white solid (0.43 g, 50%); mp 122 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 4.25–4.27 (4H, m, OCH_2), 6.51 (1H, s, EDOT), 7.72 (2H, d, J=8.21 Hz, CH_APh), 8.13 (2H, d, J=8.21 Hz, CH_BPh), 9.97 (1H, s, CHO); ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ_C 64.26, 64.85, 100.13, 116.13, 125.72, 130.27, 133.93, 139.24, 140.03, 142.37; mass m/z: 246 (M+). Anal. Calcd for $C_{13}H_{10}O_3S$: C, 63.40; H, 4.09; S, 13.02. Found: C, 63.52; H, 4.02; S, 12.98.

5.2.5. 1-(4-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)-phenyl)ethanone (8e). Following the general procedure, compound **8e** was obtained as a white solid (0.68 g, 52%); mp 118 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 2.53 (3H, s, CH_3), 4.27–4.35 (4H, m, OCH_2), 6.54 (1H, s, EDOT), 7.79 (2H, d, J=8.32 Hz, CH_APh), 7.95 (2H, d, J=8.32 Hz, CH_BPh); ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ_C 26.52, 65.13, 65.85, 100.32, 116.24, 125.92, 129.54, 135.65, 138.58, 141.0, 143.61, 197.16; mass m/z: 260 (M+). Anal. Calcd for $C_{14}H_{12}SO_3$: C, 64.60; H, 4.65; S, 12.32. Found: C, 64.71; H, 4.56; S, 12.25.

5.2.6. 3-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)quinoline (8f). Following the general procedure, compound **8f** was obtained as a white solid (0.26 g, 35%); mp 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.20–4.22 (2H, m, OCH_2), 4.28–4.31 (2H, m, OCH_2), 6.33 (1H, s, EDOT), 7.41 (1H, t, J=7.4 Hz, ArH), 7.61 (1H, t, J=7.6 Hz, ArH), 7.71 (1H, d, J=8 Hz, ArH), 8.05 (1H, d, J=8.40 Hz, ArH), 8.32 (1H, s, ArH), 9.2 (1H, d, J=4.0 Hz, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 64.4, 64.9, 99.1, 113.9, 126.7, 126.9, 127.8, 127.9, 128.9, 129.2, 131.1, 139.5, 142.4, 146.5, 148.7; mass m/z: 269 (M+). Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20; S, 11.91. Found: C, 66.78; H, 4.20; N, 5.26; S, 12.01.

5.2.7. 2-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)pyridine (8g). Following the general procedure, compound **8g** was obtained as a white solid (0.52 g, 34%); mp 70 °C; ^{1}H

NMR (300 MHz, $CDCl_3$): δ_H 4.32–4.35 (4H, m, OCH_2), 6.36 (1H, s, EDOT), 7.34 (1H, d, J=5.8 Hz, ArH), 7.67 (2H, m, ArH), 7.91 (1H, d, J=5.8 Hz, ArH); mass *m/z*: 219 (M+). Anal. Calcd for $C_{11}H_9NO_2S$: C, 60.26; H, 4.14; N, 6.39; S, 14.62. Found: C, 60.15; H, 4.20; N, 6.35; S, 14.72.

5.2.8. 2,3-Dihydro-5-(5-(5-(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-7-yl)thiophen-2-yl)thiophen-2-yl)thieno[3,4-*b*][1,4]dioxine (8h). Following the general procedure, compound **8h** was obtained as a red solid (0.11 g, 40%); mp 190 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.25–4.27 (m, 4H, OCH_2), 4.36–4.68 (m, 4H, OCH_2), 6.23 (2H, s, EDOT), 7.07 (2H, d, J=3.8 Hz, thiophene), 7.11 (2H, d, J=3.9 Hz, thiophene); mass *m/z*: 445 (M+). Anal. Calcd for $C_{20}H_{14}O_4S_4$: C, 53.79; H, 3.16; S, 28.72. Found: C, 53.93; H, 3.21; S, 27.61.

5.2.9. 5-(9,9-Dihexyl-2-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-7-yl)-9*H*-fluoren-7-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (8i). Following the general procedure, compound **8i** was obtained as a yellow solid (0.38 g, 45%); mp 105 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 0.72 (6H, t, J=6.84 Hz, CH_3), 1.02–1.20 (16H, m, CH_2), 2.90–2.93 (4H, m, CH_2), 4.26–4.37 (8H, m, OCH_2), 6.43 (2H, s, EDOT), 7.71–7.80 (6H, m, Ph); ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ_C 14.33, 23.22, 24.66, 30.74, 41.03, 56.07, 65.39, 65.92, 98.24, 118.38, 120.81, 120.93, 125.82, 133.33, 139.54, 140.34, 143.73, 152.15; mass *m/z*: 614 (M+). Anal. Calcd for $C_{37}H_{42}O_4S_2$: C, 72.28; H, 6.89; S, 10.43. Found: C, 72.15; H, 6.77; S, 10.52.

5.2.10. 2,3-Dihydro-5-(2-methoxynaphthalen-6-yl)thieno[3,4-*b*][1,4]dioxine (8k). Following the general procedure, compound **8k** was obtained as a white solid (0.41 g, 40%); mp 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.0 (3H, s, OCH_3), 3.38–3.45 (4H, m, OCH_2), 6.18–6.20 (2H, m, Ph), 6.22 (1H, s, EDOT), 6.78–6.92 (4H, m, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 54.23, 64.03, 63.85, 104.89, 112.36, 118.18, 122.56, 122.93, 124.22, 126.18, 127.03, 128.04, 128.30, 128.45, 132.29, 137.27, 137.61; mass *m/z*: 298 (M+). Anal. Calcd for $C_{17}H_{14}SO_3$: C, 68.44; H, 4.73; S, 10.75. Found: C, 68.37; H, 4.69; S, 10.82.

5.2.11. 5-(Anthracen-10-yl)-2,3-dihydrothieno[3,4-*b*]-[1,4]dioxine (8l). Following the general procedure, compound **8l** was obtained as a brown solid (0.17 g, 40%); mp 192 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.13 (2H, br s, OCH_2), 4.26 (2H, br s, OCH_2), 6.67 (1H, s, EDOT), 7.48 (4H, br s, CH_APh), 7.91–8.01 (4H, m, CH_BPh), 8.53 (1H, s, CH_CPh); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 64.80, 64.87, 100.00, 112.47, 126.21, 126.59, 128.46, 128.67, 131.52, 132.07, 139.12, 141.12; mass *m/z*: 318 (M+). Anal. Calcd for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.39; H, 4.38; S, 10.11.

5.2.12. 2,3-Dihydro-5-(2,3-dihydro-5-(4-methoxyphenyl)thieno[3,4-*b*][1,4]dioxin-7-yl)thieno[3,4-*b*][1,4]dioxine (12). A two-necked flask containing 4-iodoanisole **8a** (1.41 g, 1.77 mmol), BEDOT **11** (0.5 g, 1.77 mmol), $Pd(PPh_3)_4$ (200 mg, 0.17 mmol), and K_2CO_3 (0.3 g, 2.17 mmol) was evacuated. To this, dry DMF (10 mL) was added via syringe. The reaction mixture was allowed to stir at 80 °C for 14 h. Then, the mixture was cooled to room temperature and passed through a Celite pad, which was successively washed with chloroform. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layer was extracted with anhydrous sodium sulfate and concentrated under pressure to leave a crude residue. Purification by chromatography on silica gel (hexane–EtOAc 9:1) afforded (0.20 g, 30%) **12** as a yellow solid; mp 135 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ_H 3.81 (3H, s, OCH_3), 4.26–4.37 (8H, m, OCH_2), 6.31 (1H, s, BEDOT), 6.90 (2H, d, J=9.28 Hz, CH_APh), 7.60 (2H, d, J=8.82 Hz, CH_BPh); mass *m/z*: 388 (M+). Anal. Calcd for $C_{19}H_{16}O_5S_2$: C, 58.75; H, 4.15; S, 16.51. Found: C, 58.67; H, 4.26; S, 16.60.

5.3. A representative procedure for bis-arylation

5.3.1. 2,3-Dihydro-5,7-bis(4-nitrophenyl)thieno[3,4-*b*][1,4]dioxine (9b). A two-necked flask containing 4-iodo nitrobenzene **8b** (1.75 g, 7.04 mmol), EDOT (0.5 g, 3.52 mmol), $Pd(PPh_3)_4$ (810 mg, 0.70 mmol), and K_2CO_3 (1.06 g, 7.74 mmol) was evacuated. To this, dry DMF (10 mL) was added via syringe. The reaction mixture was allowed to stir at 80 °C for 14 h. Then, the mixture was cooled to room temperature and passed through a Celite pad, which was successively washed with chloroform. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layer was extracted with anhydrous sodium sulfate and concentrated under pressure to leave a crude residue. Purification by chromatography on silica gel (hexane–EtOAc 9:1) afforded (0.54 g, 40%) **9b** as a yellow solid; mp 155 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.45 (4H, s, OCH_2), 7.75 (4H, d, J=8.7 Hz, CH_APh), 8.30 (4H, d, J=8.4 Hz, CH_BPh); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 64.58, 115.17, 124.04, 128.31, 140.61, 145.50, 148.10; mass *m/z*: 384 (M+). Anal. Calcd for $C_{18}H_{12}N_2O_6S$: C, 56.25; H, 3.15; N, 7.29; S, 8.34. Found: C, 56.36; H, 3.22; N, 7.16; S, 8.25.

5.3.2. 2,3-Dihydro-5,7-bis(2-nitrophenyl)thieno[3,4-*b*][1,4]dioxine (9c). Following the general procedure, compound **9c** was obtained as a yellow solid (0.47 g, 35%); mp 166 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.08 (4H, s, OCH_2), 7.33–7.39 (2H, m, Ph), 7.47–7.55 (4H, m, Ph), 7.79 (2H, d, J=7.8 Hz, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 64.43, 112.22, 124.90, 125.93, 128.00, 128.36, 131.76, 132.13, 132.60, 138.88, 148.95; mass *m/z*: 384 (M+). Anal. Calcd for $C_{18}H_{12}N_2O_6S$: C, 56.25; H, 3.15; N, 7.29; S, 8.34. Found: C, 56.37; H, 3.07; N, 7.38; S, 8.26.

5.3.3. 5,7-Di(benzo[*b*]thiophen-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (9m). Following the general procedure, compound **9m** was obtained as a green solid (0.71 g, 50%); mp 165 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.43 (4H, s, OCH_2), 7.25–7.35 (4H, m, Ph), 7.50 (2H, s, ArH), 7.70–7.79 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 65.01, 110.94, 119.44, 121.98, 122.18, 123.21, 124.61, 134.26, 138.81, 139.05, 139.95. mass *m/z*: 406 (M+). Anal. Calcd for $C_{22}H_{14}O_2S_3$: C, 65.00; H, 3.47; S, 23.66. Found: C, 65.20; H, 3.39; S, 23.59.

5.3.4. 2,3-Dihydro-5,7-bis(4-methoxyphenyl)thieno[3,4-*b*][1,4]dioxine (9a). Following the general procedure, compound **9a** was obtained as a colorless solid (0.53 g, 35%); mp

160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.82 (6H, s, OCH_3), 4.38 (4H, s, OCH_2), 6.95 (4H, d, J=8.82 Hz, CH_APh), 7.65 (4H, d, J=8.82 Hz, CH_BPh); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 55.33, 64.57, 97.54, 114.51, 125.87, 127.35, 137.63, 158.30; mass *m/z*: 354 (M+). Anal. Calcd for $C_{20}H_{18}O_4S$: C, 67.78; H, 5.12; S, 9.05. Found: C, 67.67; H, 4.98; S, 9.16.

5.4. A representative procedure for Vilsmeier–Haack formylation

5.4.1. 2,3-Dihydro-7-(4-methoxyphenyl)thieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (13). $POCl_3$ (0.14 mL, 1.6 mmol) was slowly added to a mixture of dry DCM (10 mL) and DMF (0.12 mL, 1.6 mmol) at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature until a pale yellow color (Vilsmeier reagent) formed. Then it was added to a solution of **9a** (0.2 g, 0.80 mmol) in dry DCM (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for additional 10 h. Then the solvent was completely removed and treated with aqueous 5% NaOH (20 mL) at room temperature for 15 min. The crude product was then extracted with DCM (30 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification of the crude product on neutral alumina (hexane–EtOAc 9:1) afforded **13** as orange solid (0.15 g, 72%); mp 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.81 (3H, s, OCH_3), 4.29–4.36 (4H, m, OCH_2), 6.93 (2H, d, J=8.28 Hz, CH_APh), 7.73 (2H, d, J=8.38 Hz, CH_BPh), 9.92 (1H, s, CHO); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 55.3, 64.4, 65.1, 110.6, 114.8, 124.4, 128.4, 136.8, 141.7, 149.1, 160.1, 180.1; mass *m/z*: 276 (M+). Anal. Calcd for $C_{14}H_{12}O_4S$: C, 60.86; H, 4.38; S, 11.60. Found: C, 60.72; H, 4.47; S, 11.67.

5.4.2. 2,3-Dihydro-7-*p*-tolylthieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (14). Following the general procedure, compound **14** was obtained as a yellow solid (0.19 g, 60%); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.83 (3H, s, CH_3), 4.40–4.43 (4H, m, OCH_2), 6.93 (2H, d, J=7.80 Hz, CH_APh), 7.53 (2H, d, J=8.1 Hz, CH_BPh), 9.89 (1H, s, CHO); mass *m/z*: 260 (M+). Anal. Calcd for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65; S, 12.32. Found: C, 64.52; H, 4.81; S, 12.25.

5.4.3. 2,3-Dihydro-7-(2-methoxynaphthalen-6-yl)thieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (15). Following the general procedure, compound **15** was obtained as a yellow solid (0.19 g, 60%); mp 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.9 (3H, s, OCH_3), 4.25–4.27 (2H, m, OCH_2), 4.34–4.36 (2H, m, OCH_2), 7.11–7.16 (2H, m, Ph), 7.71–7.79 (4H, m, Ph), 9.91 (1H, s, CHO); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 53.33, 65.15, 65.27, 105.85, 110.66, 115.46, 118.52, 119.48, 124.89, 126.95, 127.25, 128.69, 129.56, 134.51, 141.80, 158.51, 149.09; mass *m/z*: 326 (M+). Anal. Calcd for $C_{18}H_{14}O_4S$: C, 66.24; H, 4.32; S, 9.82. Found: C, 66.32; H, 4.22; S, 9.75.

5.5. A representative procedure for condensation reaction

5.5.1. 3-(2,3-Dihydro-5-(4-methoxyphenyl)thieno[3,4-*b*][1,4]dioxin-7-yl)-2-(thiophen-2-yl)acrylonitrile (16). A mixture of aldehyde **13** (0.12 g, 0.43 mmol), thiophene-2-acetonitrile (0.06 g, 0.52 mmol), and *t*-BuOK (0.06 g, 0.57 mmol) in dry ethanol was stirred for 24 h under nitrogen atmosphere. The red solid was filtered, washed with hexane, and dried (0.10 g, 62%); mp 165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.83 (3H, s, OCH_3), 4.28–4.35 (4H, m, OCH_2), 6.92 (2H, d, J=8.00 Hz, CH_APh), 7.02 (2H, m, thiophene), 7.21 (1H, m, thiophene), 7.54 (1H, s, vinyl), 7.74 (2H, d, J=7.96 Hz, CH_BPh); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 55.3, 64.4, 65.1, 98.1, 110.5, 114.1, 117.8, 122.9, 124.7, 124.9, 125.5, 127.8, 128.0, 128.1, 136.7, 139.8, 144.9, 159.4; mass *m/z*: 381 (M+). Anal. Calcd for $C_{20}H_{15}NO_3S_2$: C, 62.97; H, 3.96; N, 3.67; S, 16.81. Found: C, 62.82; H, 4.05; N, 3.77; S, 16.75.

5.5.2. 3-(2,3-Dihydro-5-(2-methoxynaphthalen-6-yl)thieno[3,4-*b*][1,4]dioxin-7-yl)-2-(thiophen-2-yl)acrylonitrile (17). Following the general procedure, compound **17** was obtained as a red solid (0.12 g, 65%); mp 240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.94 (3H, s, OCH_3), 4.41–4.43 (4H, m, OCH_2), 7.04–7.06 (1H, dd, J=3.70 Hz, J=1.15 Hz, thiophene), 7.11 (1H, d, J=2.34 Hz, thiophene), 7.15 (2H, d, J=8.85 Hz, ArH), 7.24 (1H, d, J=8.50 Hz, ArH), 7.28 (1H, d, J=3.28 Hz, ArH), 7.57 (1H, s, vinyl), 7.74 (2H, dd, J=8.68 Hz, J=9.4 Hz, ArH), 7.87 (1H, dd, J=0.94 Hz, J=1.0 Hz, thiophene); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 64.49, 65.06, 98.58, 105.87, 111.29, 117.75, 119.31, 123.22, 125.03, 125.06, 125.58, 125.68, 127.09, 127.38, 127.79, 128.03, 128.88, 129.86, 134.05, 137.60, 139.79, 144.96, 158.22; mass *m/z*: 431 (M+). Anal. Calcd for $C_{24}H_{17}NO_3S_2$: C, 66.80; H, 3.97; N, 3.25; S, 14.86. Found: C, 66.71; H, 3.86; N, 3.29; S, 14.95.

5.5.3. 2-((2,3-Dihydro-5-(4-methoxyphenyl)thieno[3,4-*b*][1,4]dioxin-7-yl)methylene)malononitrile (18). Following the general procedure, compound **18** was obtained as a red solid (0.11 g, 51%); mp 198 °C; ^{1}H NMR (400 MHz, CD_3CN): δ_H 3.26 (3H, s, OCH_3), 3.84–3.87 (4H, m, OCH_2), 6.48 (2H, d, J=8.8 Hz, CH_APh), 7.21 (2H, d, J=8.8 Hz, CH_BPh), 7.45 (1H, s, vinyl); mass *m/z*: 324 (M+). Anal. Calcd for $C_{17}H_{12}N_2O_3S$: C, 62.95; H, 3.73; N, 8.64; S, 9.89. Found: C, 62.82; H, 3.82; N, 8.57; S, 9.95.

5.5.4. 2-((2,3-Dihydro-5-*p*-tolylthieno[3,4-*b*][1,4]dioxin-7-yl)methylene)malonitrile (19). Following the general procedure, compound **19** was obtained as a red solid (0.099 g, 56%); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.53 (3H, s, CH_3), 4.49–4.51 (4H, m, OCH_2), 7.20 (2H, d, J=7.8 Hz, CH_APh), 7.59 (2H, d, J=7.8 Hz, CH_BPh), 7.98 (1H, s, vinyl); mass (EI) *m/z* (%): 308 (M+). Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.22; H, 3.92; N, 9.08; S, 10.40. Found: C, 66.42; H, 4.02; N, 9.01; S, 10.29.

5.5.5. 3-(2,3-Dihydro-5-(2-methoxynaphthalen-6-yl)-thieno[3,4-*b*][1,4]dioxin-7-yl)-2-(3,4-dimethoxyphenyl)-acrylonitrile (20). Following the general procedure, compound **20** was obtained as a red solid (0.062 g, 42%); mp 220 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.76 (3H, s, OCH_3), 3.85 (6H, s, OCH_3), 4.43–4.46 (4H, m, OCH_2), 6.95–6.98 (2H, m, ArH), 7.12–7.20 (4H, m, ArH), 7.79–7.86 (3H, m, ArH), 8.41 (1H, s, vinyl); mass *m/z*: 485 (M+). Anal. Calcd for $C_{28}H_{23}NO_5S$: C, 69.26; H, 4.77; N, 2.88; S, 6.60. Found: C, 69.35; H, 4.72; N, 2.97; S, 6.55.

5.5.6. 3-(5-(4-Methoxystyryl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)-2-(thiophen-2-yl)acrylonitrile (23). Following the general procedure, compound **23** was obtained as a red solid (0.068 g, 51%); mp 195 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.83 (3H, s, OCH_3), 4.34–4.36 (4H, m, OCH_2), 6.88 (2H, d, J=8.7 Hz, CH_APh), 7.01–7.03 (3H, m), 7.22–7.28 (2H, m), 7.41 (2H, d, J=8.7 Hz, CH_BPh), 7.51 (1H, s, vinyl); mass *m*/*z*: 407 (M+). Anal. Calcd for $C_{22}H_{17}NO_3S_2$: C, 64.84; H, 4.20; N, 3.44; S, 15.74. Found: C, 64.82; H, 4.05; N, 3.57; S, 15.85.

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25. Crystallographic data for **9m** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 652138. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223 33603 or e-mail: deposit@ccdc.cam.ac.uk).