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Synthesis of mono- and bis-arylated 3,4-(ethylenedioxythiophenes) via direct palladium catalyzed arylation reactions

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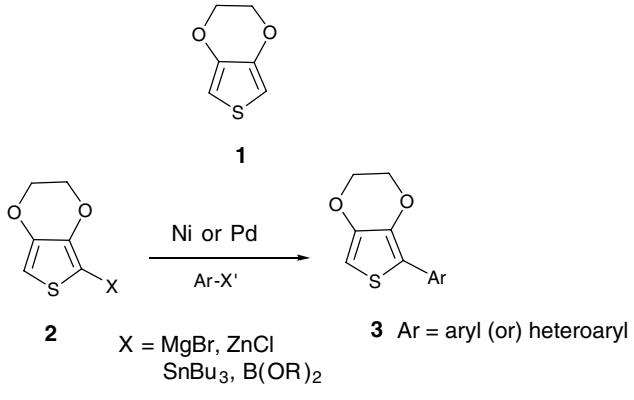
Abstract—The synthesis of arylated/heteroarylated 3,4-ethylenedioxythiophene derivatives is reported using a straightforward palladium mediated Heck coupling of 3,4-ethylenedioxythiophene with various aryl/heteroaryl halides.

In recent years, oligothiophenes, due to their physical properties have received widespread attention as components of molecular electronic and optical devices.[1] Five-membered heteroaromatics bearing substituents at the 2- and 5-positions have been explored as light emitting and liquid crystalline materials.[2] Oligothiophenes are mostly prepared via palladium/nickel mediated cross-coupling of either heteroaryl halides with arylmetals or aryl halides with heteroaryl metals.[3] However, it is known that aryl halides/heteroaryl halides can couple directly with thiophene at the reactive 2- and/or 5-positions.[4] The latter is more advantageous since it does not require the stoichiometric metallation of heterocycles. The synthesis of 2-arylthiophenes via CuI or $MnBr_2$ catalyzed cross-coupling of 2-thienyltributylstannane with aryl halides has been reported.[5] Yokkoji et al. reported a straightforward synthesis of 5,5′-diarylated 2,2′-bithiophene via a palladium catalyzed arylation.[6] In addition, Mori and co-workers recently reported the synthesis of donor–acceptor type 2,5-diarylthiophenes via a palladium mediated sequential arylation reaction.[7]

The syntheses of EDOT incorporated oligothiophenes are well known.[8] 3,4-Ethylenedioxythiophene (EDOT) has been used as a building block in several conjugated systems that incorporate unique properties such as electro chromic behaviour[9] and in low band gap polymers.[10] Judicious choice of the number and position of EDOT units in extended conjugated systems allows for the fine tuning of electronic properties. Roncali and co-workers reported, the synthesis of stable and soluble, end capped oligo(3,4-ethylenedioxy)thiophenes[11a] and also the synthesis of oligothienylenevinylenes incorporating EDOT units.[11b]

The EDOT based thienyl oligomers **3** are mostly prepared using either in situ prepared 3,4-ethylenedioxythiophenyl-2-magnesium bromide[12] (Kumada) or 3,4-ethylenedioxythiophenyl-2-zinc bromide[12] (Negishi). Additionally, the synthesis of EDOT based thienyl oligomers was also achieved using stable 2-tributylstannyl-3,4-ethylenedioxythiophene[13] (Stille) and the 2-pinacolboronate ester of 3,4-ethylenedioxythiophene[14] (Suzuki), Scheme 1. Very recently, a direct C–H arylation of heteroarenes was reported with aryl iodides using a rhodium catalyst where the arylation of various heterocycles such as thiophene, furan, pyrrole and indole was



Scheme 1.

Keywords: EDOT; Pd-catalyzed; Arylation; Heteroarylation.
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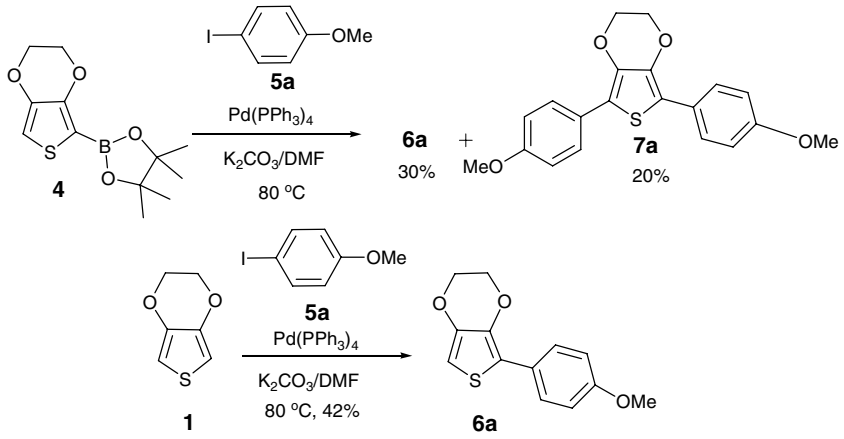


Scheme 2.

achieved. In fact, mono- and bis-arylation of 3-methoxythiophene was smoothly carried out in good yields.[15] Nevertheless, to date, straightforward coupling reactions with 3,4-ethylenedioxythiophene **1** are yet to be explored.

In continuation of our work on thienyl oligomers,[16] we wanted to prepare 2-anisyl-3,4-ethylenedioxythiophene **6a** via a palladium mediated Suzuki cross-coupling, Scheme 2. However, workup of the reaction followed by column chromatographic purification led to the isolation of mono- and bis-anisyl EDOTs **6a** and **7a** in 30% and 20% yields, respectively. Surprised by the formation of bis-anisyl product **7a**, we carried out a direct anisylation of EDOT **1** with 4-iodoanisole **5a** in the presence of $Pd(PPh_3)_4$ and K_2CO_3 in DMF at 80 °C. Workup led to the isolation of **6a** in 42% yield.

Since thiophene oligomers have recently been explored as push–pull type systems,[17] we wanted to exploit the high electron donating character of EDOT for such purpose. Thus, we decided to explore the palladium mediated coupling reaction of EDOT. The low yield obtained during cross-coupling of EDOT–metals[14] also encouraged us to undertake the present investigation. Hence, the coupling reaction of EDOT was carried out with a variety of aryl/heteroaryl halides, **5a**–**m** (1 equiv), and the results are presented in Table 1.

Table 1. Mono-arylation of 3,4-ethylenedioxythiophene

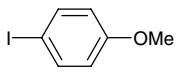
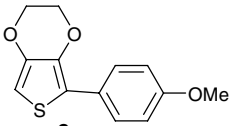
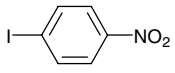
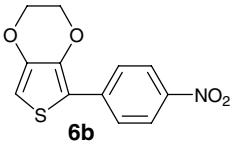
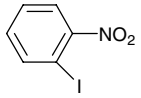
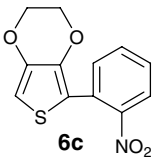
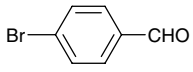
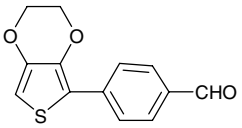
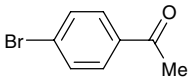
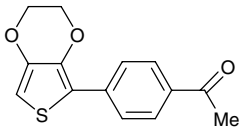
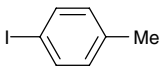
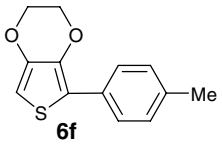
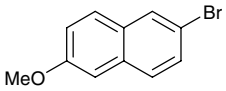
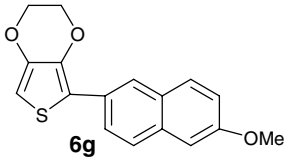
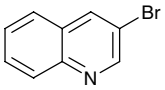
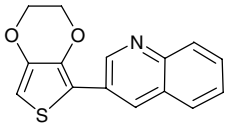
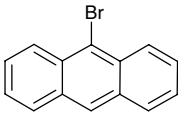
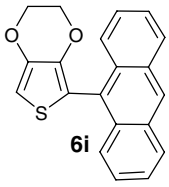
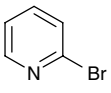
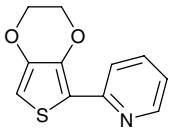
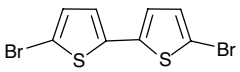
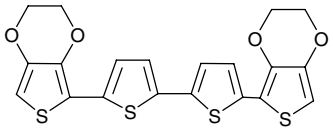
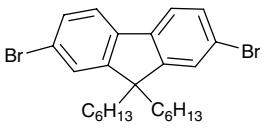
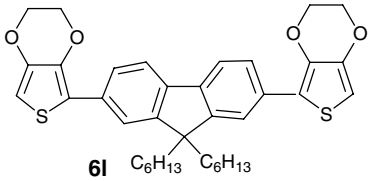
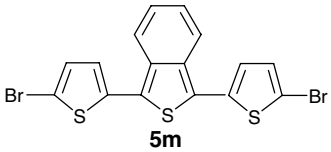
Entry	Ar–X[18]	Temperature (°C); time (h)	Product[19]	Yield[a] (%); mp (°C)
1	 **5a**	80; 14	 **6a**	42; 75
2	 **5b**	65; 8	 **6b**	55; 158
3	 **5c**	60; 8	 **6c**	50; 92
4	 **5d**	60; 10	 **6d**	50; 122

Table 1 (*continued*)

Entry	Ar–X[18]	Temperature (°C); time (h)	Product[19]	Yield[a] (%); mp (°C)
5	 **5e**	65; 8	 **6e**	52; 118
6	 **5f**	80; 12	 **6f**	45; liquid
7	 **5g**	80; 12	 **6g**	40; 120
8	 **5h**	80; 10	 **6h**	35; 125
9	 **5i**	60; 12	 **6i**	40; 192
10	 **5j**	80; 10	 **6j**	34; 70
11	 **5k**	80; 10	 **6k**	40; 190
12	 **5l**	80; 12	 **6l**	45; 105
13	 **5m**	60; 24	No reaction	

[a] Isolated yield after column chromatography.

In general, the isolated yields of the mono-arylated products **6a**–**l** were low (34–55%; entries 1–12). A small amount (~10%) of the starting material (EDOT) was always recovered even on an extended reaction (more than 24 h for entries 1 and 2) without any appreciable change in the yield of arylated products **6a** or **6b**. The

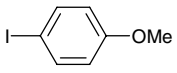
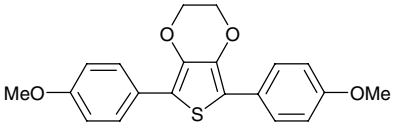
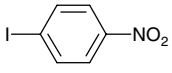
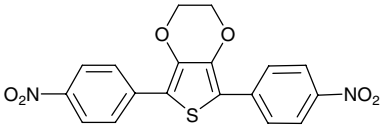
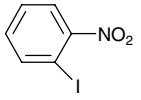
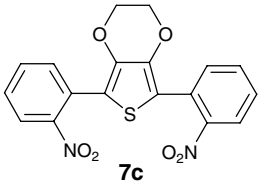
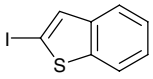
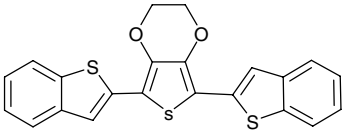
electron deficient aromatic halides (entries 2–5) afforded the corresponding mono-arylated products **6b–e** in relatively better yields than the electron rich aromatic halides (entries 1, 6 and 7). The use of bromo aryl or iodo aryl compounds did not have much effect on the yield of the arylated products. The 5,5′-dibromo-2,2′-bithiophene **5k** underwent a smooth bis-Heck arylation with excess EDOT to afford the coupled product **6k** in 40% yield (entry 11). It should be mentioned that the same product was obtained in a relatively low yield (20%), via cross-coupling between EDOT boronate ester **4** and 2,5-dibromothiophene.[14] The fluorenyl dibromo compound **5l** afforded coupled product **6l** in 45% yield (entry 12). All attempts to couple dibromo benzo[*c*]thiophene **5m** (entry 13) were unsuccessful.

The use of acetonitrile as a solvent in place of DMF did not give any product. Among the three palladium catalysts [$Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pd(dba)_3$] employed for the arylation of EDOT, $Pd(PPh_3)_4$ was found to be the best. The yield of the coupling products was not significantly altered by the use of different bases such as Cs_2CO_3 or K_3PO_4 in place of K_2CO_3.

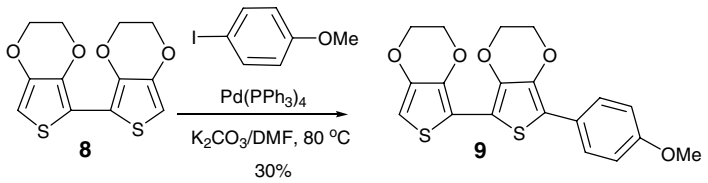
The bis-arylation of EDOT **1** was carried out with various aryl iodides and the results are described in Table 2. 4-Iodoanisole **5a** (2 equiv) afforded the expected product **7a** (entry 1) in a low yield (35%). The 4-iodo and 2-iodo nitrobenzenes **5b** and **5c** afforded the corresponding bis-arylated products **7b** and **7c** in 40% and 35% yields (entries 2 and 3), respectively. 2-Iodobenzo[*b*]thiophene **5n** underwent a smooth cross-coupling with EDOT to afford the respective coupled product **7d** in 50% isolated yield (entry 4).

Finally, the attempted bis-arylation of 2,2′-bis(EDOT) **8** with 4-methoxyiodobenzene in dry DMF at 80 °C for 14 h led to the isolation of mono-anisylated product **9** in 30% yield, Scheme 3. All attempts to couple bis-(EDOT) **8** with other aryl/heteroaryl halo compounds proved to be unsuccessful.

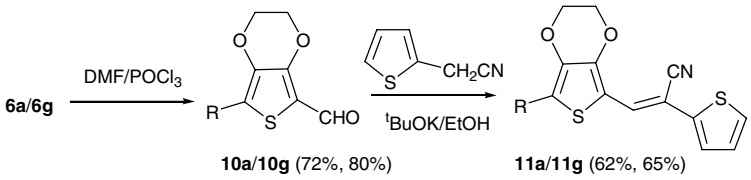
Table 2. Bis-arylation of 3,4-ethylenedioxythiophene

Entry	Ar–X[18]	Temperature (°C); time (h)	Product[19]	Yield[a] (%); mp (°C)
1	 **5a**	80; 13	 **7a**	35; 160
2	 **5b**	80; 10	 **7b**	40; 155
3	 **5c**	80; 10	 **7c**	35; 166
4	 **5n**	70; 8	 **7d**	50; 165

[a] Isolated yield after column chromatography.



Scheme 3.



Scheme 4.

As a model study, the formylation of mono-arylated EDOTs **6a/6g** was carried out under Vilsmeier formylation conditions to give mono aldehydes **10a/10g**. The latter on condensation with thiophene-2-acetonitrile afforded the respective push-pull systems **11a/11g** (Scheme 4).

In summary, the synthesis of a variety of mono- and bis-arylated EDOT analogs has been achieved in moderate yields, involving direct Heck arylation of EDOT with various aryl and heteroaryl halides. Extension of this coupling procedure for other heteroaryl halides is in progress and hopefully this new method will be applicable to the synthesis of different types of EDOT analogs. Investigations are underway to synthesize different types of push-pull systems using mono-arylated EDOT derivatives.

Acknowledgements

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18. Aryl halides are either commercially available or else were prepared using known procedures.
19. All compounds gave satisfactory spectral and analytical data.

A representative procedure for mono-arylation:

A solution of 4-bromo acetophenone **5e** (1 g, 5 mmol), 3,4-ethylenedioxythiophene **1** (0.717 g, 5 mmol), $Pd(PPh_3)_4$ (583 mg, 0.5 mmol) and dry K_2CO_3 (0.83 g, 6.05 mmol) in DMF (10 mL) was heated for 8 h at 65 °C under an N_2 atmosphere. The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed several times with brine, water and then dried (Na_2SO_4). Removal of the solvent followed by a column chromatography of the residue (silica gel, hexane:EtOAc; 9:1) afforded **6e** as a colourless solid (0.682 g, 52%); mp 118 °C.

A representative procedure for diarylation:

A solution of 4-iodoanisole **5a** (1 g, 4.27 mmol), 3,4-ethylenedioxythiophene **1** (0.30 g, 2.11 mmol), $Pd(PPh_3)_4$ (493 mg, 0.426 mmol) and dry K_2CO_3 (0.67 g, 4.85 mmol) in DMF (10 mL) was heated for 13 h at 80 °C under an N_2 atmosphere. The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed several times with brine, water and then dried (Na_2SO_4). Removal of the solvent followed by column chromatography of the residue (silica gel, hexane:EtOAc; 9:1) afforded **7a** as a colourless solid (0.53 g, 35%); mp 160 °C.

Spectral data of various mono- and bis-arylated 3,4-ethylenedioxythiophenes:

Compound **6a**: mp 75 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ 3.71 (s, 3H), 4.22–4.31 (m, 4H), 6.33 (s, 1H), 6.61 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 8.8$ Hz, 2H). MS (EI) *m*/*z* (%): 248 (M^+, 87%), 15 (100), 81 (10), 69 (11). Anal. Calcd for $C_{13}H_{12}SO_3$: C, 62.88; H, 4.87; S, 12.90. Found: C, 62.66; H, 4.96; S, 12.79.

Compound **6c**: mp 92 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ 4.13–4.18 (m, 4H), 6.59 (s, 1H), 7.53 (m, 2H), 7.67–7.69 (m, 1H), 7.89 (d, $J = 8.28$ Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 65.21, 65.31, 100.89, 111.84, 125.48, 127.03, 129.26, 132.71, 133.57, 140.22. 142.59, 149.98. MS (EI) *m*/*z* (%): 263 (M^+, 100%), 145 (66), 103 (22), 102 (19). 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.

Compound **6e**: mp 118 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ 2.53 (s, 3H), 4.27–4.35 (m, 4H), 6.54 (s, 1H), 7.79 (d, $J = 8.32$ Hz, 2H), 7.95 (d, $J = 8.32$ Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 26.52, 65.13, 65.85, 100.32, 116.24, 125.92, 129.54, 135.65, 138.58, 141.0, 143.61, 197.16. MS (EI) *m*/*z* (%): 260 (M^+, 100%), 245 (91), 120 (49), 82 (29). 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.

Compound **6h**: mp 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20 (d, $J = 4$ Hz, 2H), 4.28 (d, $J = 3.6$ Hz, 2H), 6.33 (s, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 8$ Hz, 1H), 8.05 (d, $J = 8.40$ Hz, 1H) 8.32 (s, 1H), 9.2 (d, $J = 2$ Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 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. MS (EI) *m*/*z* (%): 269 (M^+, 100%), 210 (80), 191 (26), 113 (47). 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.

Compound **6l**: mp 105 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ 0.72 (t, $J = 6.84$ Hz, 6H), 1.02–1.20 (m, 16H), 2.90–2.93 (m, 4H), 4.26–4.37 (m, 8H), 6.43 (s, 2H), 7.71–7.80 (m, 6H). ^{13}C NMR (100.6 MHz, CD_3COCD_3): δ 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. MS (EI) *m*/*z* (%): 614 (M^+, 100%), 500 (39), 499 (100), 344 (19). 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.

Compound **7a**: mp 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 6H), 4.38 (s, 4H), 6.95 (d, $J = 8.82$ Hz, 4H), 7.65 (d, $J = 8.82$ Hz, 4H), MS (EI) *m*/*z* (%): 354 (M^+, 100%), 151 (99), 119 (29), 108 (21) Anal. Calcd for $C_{20}H_{18}O_4S$: C, 66.78; H, 5.12; S, 9.05. Found: C, 66.57; H, 4.98; S, 9.16.

Compound **9**: mp 135 °C; ^{1}H NMR (400 MHz, CD_3COCD_3): δ 3.81 (s, 3H), 4.26–4.37 (m, 8H), 6.31 (s, 1H), 6.90 (d, $J = 9.28$ Hz, 2H), 7.60 (d, $J = 8.82$ Hz, 2H), MS (EI) *m*/*z* (%): 388 (M^+, 10%), 213 (24), 150 (20), 116 (12). 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.

Compound **10a**: mp 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.29–4.36 (m, 4H), 6.93 (d, $J = 8.28$ Hz, 2H), 7.73 (d, $J = 8.38$ Hz, 2H), 9.92 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 55.3, 64.4, 65.1, 110.6, 114.8, 124.4, 128.4, 136.8, 141.7, 149.1, 160.1, 180.1. 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, 16.67.

Compound **11a**: mp 165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 4.28–4.35 (m, 4H), 6.92 (d, $J = 8.00$ Hz, 2H), 7.02 (m, 2H), 7.21 (m, 1H), 7.54 (s, 1H), 7.74 (d, $J = 7.96$ Hz, 2H), ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 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. 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.