Supporting Information for

Pd-Catalyzed Oxidative Cross-Coupling Between Two Electron-Rich Heteroarenes

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**General information:** $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM300 and AM400 spectrometer. $^{19}$F NMR was recorded on a Bruker AM300 spectrometer (CFCl$_3$ as outside standard and low field is positive). Chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by $^{19}$F NMR using fluorobenzene as an internal standard before working up the reaction.

**Materials:** All reagents were used as received from commercial sources. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N$_2$ at room temperature. DMF and DMSO were distilled under reduced pressure from CaH$_2$. Toluene and 1,4-Dioxane was distilled from sodium and benzophenone immediately before use.

**Screens for Pd-Catalyzed Oxidative Cross-Coupling of $N,N$-Dimethylthiophene-2-carboxamide 1a with 2-Bromo-3-hexylthiophene 2a (Table S1).** To a 25 mL of Schlenck tube were added Pd(OAc)$_2$ (2.5 - 10 mol%), oxidant (1.5 - 3.0 equiv), $N,N$-dimethylthiophene-2-carboxamide 1a (1.0 - 3.0 equiv) under N$_2$. Solvent (2 mL), additive (0-4.0 equiv), and 2-bromo-3-hexylthiophene 2a (0.3 mmol-0.45 mmol, 1.0 – 1.5 equiv) were then added sequentially with stirring. The reaction mixture was stirred at 80 °C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1) to give pure product.
Table S1. Pd-Catalyzed Oxidative Cross-Coupling of \(N,N\)-Dimethylthiophene-2-carboxamide 1a with 2-Bromo-3-hexylthiophene 2a.\(^a\)

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*a*Reaction conditions (unless otherwise specified): 0.3 mmol scale, Solvent (2 mL). *b*Isolated yield. *c*Reaction run at 90 °C.

Figure S1. Structures of Thiophenes and Furans

Typical Procedure for Pd-Catalyzed Oxidative Cross-Coupling between Two Thiophenes. To a 25 mL of Schlenck tube were added Pd(OAc)₂ (2.5 mol %), Ag₂O (208 mg 3.0 equiv) and [1,1'-biphenyl]-2-carboxylic acid (119 mg, 2.0 equiv) under N₂, followed by DMSO (2 mL) with stirring. Thiophene 1a (0.9 mmol, 3 equiv) and thiophene 2a (0.3 mmol, 1 equiv) were then added subsequently. The reaction mixture was stirred at 80 °C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with 1 N HCl and brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.
Note: For compounds 3a, 3m, 3o-q, the reaction was extracted with ethyl acetate, washed with 1 N NaOH, 1 N HCl and brine, dried over Na₂SO₄, filtered and concentrated.

5'-Bromo-4'-hexyl-N,N-dimethyl-[2,2'-bithiophene]-5-carboxamide (3a). The product (85 mg, 71% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether / Ethyl Acetate = 2:1). m.p. 54 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, J = 3.9 Hz, 1H), 7.00 (d, J = 3.9 Hz, 1H), 6.92 (s, 1H), 3.19 (s, 6H), 2.53 (t, J = 7.8 Hz, 2H), 1.57 (m, 2H), 1.32 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H). ¹³C NMR (75.4 MHz, CDCl₃) δ 163.7, 143.1, 140.2, 136.4, 135.7, 130.0, 125.4, 122.9, 108.8, 31.5, 29.5, 29.4, 28.8, 22.5, 14.0. IR (thin film): νₘₐₓ 3068, 1610 cm⁻¹. MS (EI): m/z (%) 401 (M⁺), 399 (M⁺), 274 (100), 243, 171. HRMS: Calculated for C₁₇H₂₂NOS₂Br: 399.0326; Found: 399.0331.

Methyl 5'-bromo-4'-hexyl-[2,2'-bithiophene]-5-carboxylate (3b). The product (81 mg, 70% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether / Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1b. ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, J = 3.9 Hz, 1H), 7.03 (d, J = 3.9 Hz, 1H), 6.95 (s, 1H), 3.88 (s, 3H), 2.53 (t, J = 7.6 Hz, 2H), 1.57 (m, 2H), 1.32 (m, 6H), 0.89 (t, J = 6.4 Hz, 3H). ¹³C NMR (75.4 MHz, CDCl₃) δ 162.3, 143.4, 143.3, 135.6, 134.1, 131.3, 125.8, 123.6, 109.7, 52.2, 31.5, 29.51, 29.47, 28.8, 22.5, 14.0. IR (thin film): νₘₐₓ 2952, 2927, 1716 cm⁻¹. MS (EI): m/z (%) 388 (M⁺), 386 (M⁺), 237 (100). HRMS: Calculated for C₁₆H₁₉O₂S₂Br: 386.0010; Found: 386.0008.
Methyl 5'-bromo-4'-hexyl-4-methyl-[2,2'-bithiophene]-5-carboxylate (3c). The product (77 mg, 64% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1c. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.92 (s, 1H), 6.87 (s, 1H), 3.85 (s, 3H), 2.52 (t, $J = 8.1$ Hz, 2H), 2.51(s, 3H), 1.57 (m, 2H), 1.31 (m, 6H), 0.89 (t, $J = 6.4$ Hz, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 162.9, 147.1, 143.2, 140.5, 135.7, 127.5, 125.6, 124.4, 109.4, 51.7, 31.5, 29.44, 29.40, 28.8, 22.5, 16.0, 14.0. IR (thin film): $\nu_{\text{max}}$ 2953, 1713, 1466 cm$^{-1}$. MS (EI): $m/z$ (%) 402 (M$^+$), 400 (M$^+$), 251, 43(100). HRMS: Calculated for C$_{17}$H$_{21}$O$_2$S$_2$Br: 400.0166; Found: 400.0161.

1-(5'-Bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)ethanone (3d). 5% of Pd(OAc)$_2$ was used. The product (85 mg, 76%) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1d. m.p. 69 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 3.9$ Hz, 1H), $\delta$ 7.06 (d, $J = 3.9$ Hz, 1H), 6.99 (s, 1H), 2.54 (t, $J = 7.6$ Hz, 2H), 2.53 (s, 3H), 1.57 (m, 2H), 1.32 (m, 6H), 0.92 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 190.3, 145.0, 143.5, 142.4, 135.6, 133.2, 126.2, 123.9, 110.2, 31.5, 29.6, 29.5, 28.4, 26.5, 22.6, 14.1. IR (thin film): $\nu_{\text{max}}$ 2923, 1652 cm$^{-1}$. MS (EI): $m/z$ (%) 372 (M$^+$), 370 (M$^+$), 221, 43(100). HRMS: Calculated for C$_{16}$H$_{19}$OS$_2$Br: 370.0061; Found: 370.0065.

5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3e). 5% of Pd(OAc)$_2$ was used. This compound is known. The product (77 mg, 72% yield) as a yellow liquid was purified by silica chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1e. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.85 (s, 1H), 7.64 (d, $J = 4.0$ Hz, 1H), $\delta$ 7.14
(d, *J* = 4.0 Hz, 1H), 7.03 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.58 (m, 2H) , 1.32 (m, 6H), 0.89 (t, *J* = 6.2 Hz, 3H). 13C NMR (75.4 MHz, CDCl3) δ 182.4, 146.2, 143.6, 141.6, 137.2, 135.3, 126.7, 124.0, 110.9, 31.5, 29.5, 29.4, 28.8, 22.5, 14.0. IR (thin film): νmax 2954, 1664, 1460 cm⁻¹. MS (EI): m/z (%) 358 (M⁺), 356 (M⁺), 207 (100), 43. HRMS: Calculated for C15H17OBrS2: 355.9904; Found: 355.9901.

5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbonitrile (3f). The product (56 mg, 53%) as a yellow solid was purified by silica chromatography (Petroleum ether /Ethyl Acetate = 50:1). m.p. 49 ºC. 1H NMR (300 MHz, CDCl3) δ 7.50 (d, *J* = 4.0 Hz, 1H), δ 7.03 (d, *J* = 4.0 Hz, 1H), 6.96 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.58 (m, 2H) , 1.32 (m, 6H), 0.90 (t, *J* = 6.0 Hz, 3H). 13C NMR (75.4 MHz, CDCl3) δ 143.8, 143.6, 138.2, 134.1, 126.6, 123.2, 114.0, 110.7, 107.5, 31.5, 29.52, 29.46, 28.8, 22.5, 14.0. IR (thin film): νmax 2922, 2852, 2222, 1580, 1457 cm⁻¹. MS (EI): m/z (%) 355 (M⁺), 353 (M⁺), 204, 86, 84 (100). HRMS: Calculated for C15H16NS2Br: 352.9908; Found: 352.9906

Methyl 5'-bromo-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3g). The product (67 mg, 71% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1b. m.p. 90 ºC. 1H NMR (300 MHz, CDCl3) δ 7.65 (d, *J* = 3.8 Hz, 1H), 7.02 (d, *J* = 3.8 Hz, 1H), 6.95 (s, 1H), 3.88 (s, 3H), 2.18 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 162.3, 143.2, 138.4, 135.4, 134.2, 131.3, 126.8, 123.7, 110.1, 52.2, 15.2. IR (thin film): νmax 2921, 2850, 1717, 1470 cm⁻¹. MS (EI): m/z (%) 318 (M⁺), 316 (M⁺,100), 287, 285, 213. HRMS: Calculated for C11H9O2S2Br: 315.9227; Found: 315.9226.
Methyl 5'-bromo-[2,2'-bithiophene]-5-carboxylate (3h). The product (55 mg, 62% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1b. This compound is known.3 m.p. 108 °C. 1H NMR (300 MHz, CDCl3) δ 7.68 (d, J = 3.9 Hz, 1H), 7.08 (d, J = 3.9 Hz, 1H), 7.02 (d, J = 3.9 Hz, 1H), 7.01 (d, J = 3.9 Hz, 1H), 3.89 (s, 3H).

Methyl 5'-chloro-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3i). The product (57 mg, 70% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1b. m.p. 86 °C. 1H NMR (400 MHz, CDCl3) δ 7.64 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 4.0 Hz, 1H), 6.92 (s, 3H), 3.87 (s, 3H), 2.16 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 162.3, 143.3, 135.5, 134.1, 132.2, 131.3, 126.5, 125.5, 123.6, 52.2, 13.5. IR (thin film): νmax 2924, 1708 cm⁻¹. MS (EI): m/z (%) 274 (M⁺), 272 (M⁺,100), 243, 241, 169. HRMS: Calculated for C11H9O2S2Cl: 271.9733; Found: 271.9738.

Methyl 5'-chloro-[2,2'-bithiophene]-5-carboxylate (3j). The product (48 mg, 61% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material 1b. This compound is known.4 m.p. 87 °C. 1H NMR (300 MHz, CDCl3) δ 7.67 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.9 Hz, 1H), 7.03 (d, J = 3.9 Hz, 1H), 6.86 (d, J = 3.9 Hz, 1H), 3.89 (s, 3H). 13C NMR (75.4 MHz, CDCl3) δ 162.3, 143.0, 134.2, 131.6, 130.6, 127.2, 124.3, 123.9, 52.3. IR (thin film): νmax 2919, 1717 cm⁻¹. MS (EI): m/z (%) 260 (M⁺), 258 (M⁺), 229, 227 (100), 155, 157. HRMS: Calculated for C10H7O2S2Cl: 257.9576; Found: 257.9578.
Methyl 5'-methyl-[2,2'-bithiophene]-5-carboxylate (3k). The product (38 mg, 53% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material 1b. This compound is known.\(^5\) m.p. 106 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 3.8\) Hz, 1H), 7.07 (d, \(J = 3.6\) Hz, 1H), 7.05 (d, \(J = 3.8\) Hz, 1H), 6.69 (m, 1H), 3.88 (s, 3H), 2.49 (s, 3H). \(^13\)C NMR (75.4 MHz, CDCl\(_3\)) \(\delta\) 162.6, 144.7, 141.2, 134.2, 133.9, 130.4, 126.3, 125.2, 123.1, 52.1, 15.4. IR (thin film): \(\nu_{\text{max}}\) 2917, 1708 cm\(^{-1}\). MS (EI): \(m/z\) (%) 238 (M\(^+\), 100), 207, 179, 135. HRMS: Calculated for C\(_{11}\)H\(_{10}\)O\(_2\)S\(_2\): 238.0122; Found: 238.0126.

Methyl 5-(benzo[b]thiophen-2-yl)thiophene-2-carboxylate (3l). The product (49 mg, 60% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material 1b. This compound is known.\(^4\) m.p. 139 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.76 (m, 2H), 7.72 (d, \(J = 4.0\) Hz, 1H), 7.49 (s, 1H), 7.35 (m, 2H), 7.24 (d, \(J = 4.0\) Hz, 1H), 3.90 (s, 3H). \(^13\)C NMR (75.4 MHz, CDCl\(_3\)) \(\delta\) 162.4, 144.0, 140.0, 139.5, 135.9, 134.2, 132.3, 125.2, 125.1, 124.9, 123.9, 122.2, 121.4, 52.3. IR (thin film): \(\nu_{\text{max}}\) 2918, 2849, 1716 cm\(^{-1}\). MS (EI): \(m/z\) (%) 275 (M\(^+\) + H\(^+\)), 274 (M\(^+\), 100), 243, 171, 149. HRMS: Calculated for C\(_{14}\)H\(_{10}\)O\(_2\)S\(_2\): 274.0122; Found: 274.0121.

N,N-dimethyl-5'-phenyl-[2,2'-bithiophene]-5-carboxamide (3m). The product (60 mg, 64%) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 2:1). m.p. 172 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 7.5\) Hz, 2H), 7.39 (t, \(J = 7.2\) Hz, 2H), 7.32-7.21 (m, 4H), 7.12 (d, \(J = 3.6\) Hz, 1H), 3.22(s, 6H). \(^13\)C NMR (75.4 MHz, CDCl\(_3\)) \(\delta\) 163.8,
144.2, 140.8, 136.2, 135.5, 133.7, 128.8, 127.7, 125.5, 123.8, 122.8. IR (thin film): $\nu_{\text{max}}$ 3108, 1601, 1407 cm$^{-1}$. MS (EI): $m/z$ (%) 314 (M$^{+}$ + H$^+$), 313 (M$^+$), 269 (100), 197. HRMS: Calculated for C$_{17}$H$_{15}$NOS$_2$: 313.0595; Found: 313.0590.

5'-Phenyl-[2,2'-bithiophene]-5-carbaldehyde (3n). The product (53 mg, 65%) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1). m.p. 121 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.87 (s, 1H), 7.69 (d, $J = 3.9$ Hz 1H), 7.62 (d, $J = 6.9$ Hz 2H), 7.42 (t, $J = 7.0$ Hz 2H), 7.35 (d, $J = 3.9$ Hz 2H), 7.28 (t, $J = 3.6$ Hz, 2H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 182.4, 147.2, 146.1, 141.5, 137.4, 135.0, 133.4, 129.0, 128.2, 127.1, 125.8, 124.2, 124.0. MS (EI): $m/z$ (%) 270 (M+,100 ) 241, 197 . HRMS: Calculated for C$_{15}$H$_{10}$OS$_2$: 270.0173; Found: 270.0175.

N,N-dimethyl-5'-(phenylethynyl)-[2,2'-bithiophene]-5-carboxamide (3o). The product (53 mg, 52% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 2:1). m.p. 124 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.52 (m, 2H), 7.36 (m, 3H), 7.28 (d, $J = 3.6$ Hz, 1H), 7.20 (d, $J = 3.6$ Hz, 1H), 7.15-7.10 (m, 2H), 3.21 (s, 6H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 163.6, 139.9, 137.6, 136.9, 132.8, 131.3, 130.0, 128.5, 128.3, 124.5, 123.4, 123.0, 122.5, 94.6, 82.3. IR (thin film): $\nu_{\text{max}}$ 3062, 2915, 2180, 1595 cm$^{-1}$. MS (EI): $m/z$ (%) 338 (M$^{+}$ + H$^+$), 337 (M$^+$), 293, 221, 43 (100). HRMS: Calculated for C$_{19}$H$_{15}$NOS$_2$: 337.0595; Found: 337.0592.

Methyl 5'-(dimethylcarbamoyl)-[2,2'-bithiophene]-5-carboxylate (3p). 3 equiv of 1a was used. The product (61 mg, 69% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1). m.p. 163 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 3.6$ Hz, 1H), 7.66 (d, $J = 1.0$ Hz, 1H), 7.35-7.30 (m, 2H), 3.21 (s, 6H).
N,N-Dimethyl-5'-(perfluorophenyl)-[2,2'-bithiophene]-5-carboxamide (3q). 3 equiv of 1a was used. The product (72 mg, 60% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1). m.p. 185 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.44 (d, \( J = 3.8 \) Hz, 1H), 7.26 (d, \( J = 3.8 \) Hz, 1H), 7.24 (d, \( J = 3.8 \) Hz, 1H), 7.13 (d, \( J = 3.8 \) Hz, 1H), 3.18 (s, 6H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 163.6, 143.9 (dm, \( J = 251.6 \) Hz), 139.9 (dm, \( J = 257.0 \) Hz), 139.5, 139.0(t, \( J = 4.1 \) Hz), 138.0 (dm, \( J = 255.7 \) Hz), 137.5, 131.1(t, \( J = 5.4 \) Hz), 126.1 (m), 124.7, 123.9, 109.5(dt, \( J = 4.1,10.7 \) Hz ), 37.4; \(^{19}F\) NMR (282 MHz, CDCl\(_3\)) \( \delta \) -139.1 (m, 2F), -154.9 (m, 1F), -161.3 (m, 2F). IR (thin film): \( \nu_{\text{max}} \) 2920, 1602, 1539, 1526, 1499 cm\(^{-1}\). MS (EI): \( m/z \) (%) 403 (M\(^+\)), 359 (100), 287. HRMS: Calculated for C\(_{17}H_{10}NOS_2F_5\): 403.0124; Found: 403.0127.

5-Bromo-4-hexyl-5'-methoxy-2,2'-bithiophene (3r). The reaction was run in a sealed tube with 3 equiv of 2j. The product (60 mg, 56% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether(100%)). \(^1H\) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 6.72 (d, \( J = 3.9 \) Hz, 1H), 6.69 (s, 1H), 6.10 (d, \( J = 3.9 \) Hz, 1H), 3.90 (s, 3H), 2.52 (t, \( J = 7.6 \) Hz, 2H), 1.58 (m, 2H), 1.32 (m, 6H), 0.91 (t, \( J = 5.8 \) Hz, 3H). \(^{13}C\) NMR (75.4 MHz, CDCl\(_3\)) \( \delta \) 165.6, 142.6, 137.4, 132.1, 123.0, 121.4, 106.1, 104.3, 60.2, 31.6, 29.6, 29.55, 28.9, 22.6, 14.1. IR (thin film): \( \nu_{\text{max}} \) 2955, 1539, 1499 cm\(^{-1}\). MS (EI): \( m/z \) (%) 360 (M\(^+\) + H\(^+\)), 358 (M\(^+\)), 345, 343, 84 (100). HRMS: Calculated for C\(_{15}H_{19}OBrS_2\): 358.0061; Found: 358.0057.
5-Methoxy-5'-methyl-2,2'-bithiophene (3s). The reaction was run in a sealed tube with 3 equiv of 2f. The product (27 mg, 44% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether(100%)). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.80 (d, $J$ = 3.2 Hz, 1H), 6.71 (d, $J$ = 4.0 Hz, 1H), 6.62 (d, $J$ = 3.2 Hz, 1H), 6.10 (d, $J$ = 4.0 Hz, 1H), 3.90 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 165.0, 138.0, 135.6, 125.6, 124.2, 122.1, 120.5, 104.2, 60.2, 15.3. IR (thin film): $\nu$$_{max}$ 2921, 2851, 1540, 1507 cm$^{-1}$. MS (EI): m/z (%) 211 (M$^+$ + H$^+$), 210 (M$^+$), 195 (100), 167. HRMS: Calculated for C$_{10}$H$_{10}$OS$_2$: 210.0173; Found: 210.0175.

5-Bromo-4-hexyl-5'-phenyl-2,2'-bithiophene (3t). The product (80 mg, 66% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether(100%)) and then distilled under vacuum to get rid of starting material 2h. m.p. 50 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 7.6 Hz, 2H), 7.36 (t, $J$ = 7.2 Hz, 2H), 7.27 (t, $J$ = 7.2 Hz, 1H), 7.18 (d, $J$ = 3.2 Hz, 1H), 7.03 (d, $J$ = 3.2 Hz, 1H), 6.87 (s, 1H), 2.53 (t, $J$ = 7.2 Hz, 2H), 1.59 (m, 2H), 1.33 (m, 6H), 0.93 (s, 3H). $^{13}$C NMR (100.5 MHz, CDCl$_3$) $\delta$ 143.2, 142.9, 136.7, 135.9, 133.8, 128.9, 127.6, 125.6, 124.4, 124.2, 123.6, 107.6, 31.6, 29.6, 29.5, 28.9, 22.6, 14.1. MS (EI): m/z (%) 406 (M$^+$), 404 (M$^+$), 255 (100), 160. HRMS: Calculated for C$_{20}$H$_{21}$S$_2$Br: 404.0268; Found: 404.0267.

4-(5-(benzo[b]thiophen-2-yl)thiophen-2-yl)-N,N-diphenylaniline (3u). The product (73 mg, 53% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether: Ethyl Acetate = 100:1). m.p. 196 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 7.8 Hz, 1H), 7.71 (d, $J$ = 7.8 Hz, 1H), 7.47 (d, $J$ = 8.4 Hz, 2H), 7.39 (s, 1H), 7.35-7.23 (m, 7H), 7.16-7.12 (m, 5H), 7.08-7.03
(m, 4H). $^{13}$C NMR (150.8 MHz, CDCl$_3$) $\delta$ 147.5, 147.3, 144.3, 140.4, 138.9, 137.3, 135.6, 129.3, 127.7, 126.4, 126.0, 124.7, 124.6, 124.4, 123.4, 123.3, 123.2, 122.8, 122.0, 119.2. MS (EI): $m/z$ (%) 459(M$^+$), 266, 105 (100). HRMS: Calculated for C$_{30}$H$_{21}$NS$_2$: 459.1115; Found: 459.1114

1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3v). To a 25 mL of sealed tube were added Pd(TFA)$_2$ (10 mol %), AgOAc (150 mg 3.0 equiv) and 1.10-phen (10.8 mg, 0.2 equiv) under N$_2$, followed by DMA (0.5 mL), DMSO (1.5 mL) with stirring. Thiophene 1e (0.3 mmol, 1 equiv) and furan 2k (0.9 mmol, 3 equiv) were then added subsequently. The reaction mixture was stirred at 100 $^\circ$C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered, washed with brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) to provide pure product (33 mg, 50% yield) as a pale yellow solid. m.p. 55 $^\circ$C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J$ = 3.9 Hz, 1H), 7.17 (d, $J$ = 3.9 Hz, 1H), 6.59 (d, $J$ = 3.3 Hz, 1H), 6.08 (d, $J$ = 3.3 Hz, 1H), 2.70 (q, $J$ = 7.5 Hz, 2H), 2.54 (s, 3H), 1.27 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 190.4, 159.1, 146.7, 142.2, 141.3, 133.3, 121.8, 109.0, 106.8, 26.5, 21.5, 12.0. IR (thin film): $\nu_{max}$ 1647 cm$^{-1}$. MS (EI): $m/z$ (%) 220 (M$^+$), 205 (100). HRMS: Calculated for C$_{12}$H$_{12}$O$_2$S: 220.0558; Found: 220.0560.

1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3w). To a 25 mL of sealed tube were added Pd(TFA)$_2$ (10 mol %), AgOAc (150 mg 3.0 equiv) and 1.10-phen (10.8 mg, 0.2 equiv) under N$_2$, followed by DMA (0.5 mL), DMSO (1.5 mL) with stirring. Thiophene 1b (0.3 mmol, 1 equiv) and furan 2l (0.9 mmol, 3 equiv) were then added subsequently. The reaction mixture was stirred at 100 $^\circ$C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered, washed with brine, dried over Na$_2$SO$_4$, and concentrated. The residue
was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1) to provide pure product (39 mg, 49% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 4.0 Hz, 1H), 7.13 (d, J = 4.0 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 6.06 (d, J = 3.2 Hz, 1H), 3.88 (s, 3H), 2.66 (t, J = 7.8 Hz, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 157.6, 146.7, 141.0, 134.1, 130.1, 121.5, 108.2, 107.3, 52.0, 30.0, 27.8, 22.2, 13.7. MS (EI): m/z (%) 264 (M⁺), 221 (100). HRMS: Calculated for C₁₄H₁₆O₃S: 264.0820; Found: 264.0818.

1-(5'-Ethyl-[2,2'-bifuran]-5-yl)ethanone (3x). The product (15 mg, 25% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1). m.p. 81 ºC. ¹H NMR (300 MHz, CDCl₃) δ 7.22 (d, J = 3.9 Hz, 1H), 6.75 (d, J = 3.3 Hz, 1H), 6.59 (d, J = 3.9 Hz, 1H), 6.11 (d, J = 3.9 Hz, 1H), 2.71 (q, J = 7.6 Hz, 2H), 2.48 (s, 3H), 1.27 (t, J = 7.6 Hz, 3H); ¹³C NMR (75.4 MHz, CDCl₃) δ 186.0, 159.6, 151.0, 150.4, 143.5, 119.7, 109.6, 106.6, 106.2, 25.9, 21.5, 12.0. IR (thin film): νmax 2918, 1652, 1540 cm⁻¹. MS (EI): m/z (%) 204 (M⁺), 189 (100), 133, 86, 84. HRMS: Calculated for C₁₂H₁₂O₃: 204.0786; Found: 204.0784.

3,6-bis(5'-bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3y). The reaction was run on a 0.1 mmol scale in 3 mL DMSO and 5 mol % Pd(OAc)₂ was used. The product 3y (42 mg, 41% yield) as a purple-black solid was purified with silica gel chromatography (Petroleum ether/dichloromethane = 8:1). m.p. 157 ºC. ¹H NMR (400 MHz, CDCl₃) δ 8.84 (br, 2H), 7.19 (d, J = 3.6 Hz, 2H), 6.99 (br, 2H), 4.05 (t, J = 8.0 Hz, 4H), 2.55 (t, J = 7.6 Hz, 4H), 1.73 (m, 4H), 1.60 (m, 4H), 1.43-1.25 (m, 30H), 0.92-0.85 (m, 12H). ¹³C NMR (150 MHz, CDCl₃) δ 161.0, 143.5, 141.9, 138.8, 136.3, 135.5, 128.1, 125.8, 124.6, 110.0, 108.2, 42.2, 31.8.
31.6, 30.0, 29.7, 29.6, 29.20, 29.19, 28.9, 26.9, 22.7, 22.62, 22.60, 14.1. MS (MALDI): \( m/z \) (%)
1018 (M⁺), 1017 (M⁺), 1016 (M⁺), 1014 (M⁺), 1012 (M⁺). HRMS (MALDI): Calculated for C₅₀H₆₆O₂N₂S₄Br₂: 1012.2368; Found: 1012.2362.

5''-Bromo-4''-hexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (5). 3 equiv of 2a and 5 mol% of Pd(OAc)₂ were used. The product (93 mg, 71% yield (0.3 mmol scale); 534 mg, 68% yield (1.8 mmol scale in 5 mL DMSO)) as a yellow solid was purified with silica gel chromatography (Petroleum ether/ Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material 4. This compound is known.\(^2\) ¹H NMR (300 MHz, CDCl₃) \( \delta \)
9.85 (s, 1H), 7.65 (d, \( J = 3.8 \) Hz, 1H), 7.20 (d, \( J = 3.8 \) Hz, 1H), 7.01 (d, \( J = 3.8 \) Hz, 1H), 6.89 (s, 1H), 2.53 (t, \( J = 7.6 \) Hz, 2H), 1.58 (m, 2H), 1.33 (m, 6H), 0.90 (t, \( J = 6.6 \) Hz, 3H). \(^{13}\)C NMR (75.4 MHz, CDCl₃) \( \delta \)
182.3, 146.5, 143.2, 141.6, 138.3, 137.3, 135.7, 134.5, 126.8, 125.1, 124.4, 124.0, 108.8, 31.5, 29.54, 29.50, 28.8, 22.5, 14.0. IR (thin film): \( \nu_{\max} \) 2925, 2854, 1663, 1507, 1464, 1440 cm⁻¹. MS (EI): \( m/z \) (%)
440 (M⁺), 438 (M⁺), 289, 194, 57 (100). HRMS: Calculated for C₁₉H₁₉OBrS₃: 437.9781; Found: 437.9778.

5'''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2''-quaterthiophene]-5-carbaldehyde (6). To a 25 mL of Schlenck tube were added Pd(OAc)₂ (6.0 mg, 5 mol%), PPh₃ (13.1 mg 10 mol%), K₂CO₃ (138 mg 2.0 equiv), 5 (220 mg, 1.0 equiv) and 2r (250 mg, 1.5 equiv) under N₂. DMF (2.5 mL) was then added. The reaction mixture was stirred at 80 °C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with CH₂Cl₂, filtered, washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified with silica gel
chromatography (Petroleum ether/ Ethyl Acetate = 50:1) to give pure product (253 mg, 74% yield) as a deep brown solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.83 (s, 1H), 7.63 (d, $J$ = 4.0 Hz, 1H), 7.45 (d, $J$ = 8.2 Hz, 2H), 7.28-7.23 (m, 5H), 7.19 (d, $J$ = 4.0 Hz, 1H), 7.10-7.15 (m, 5H), 7.00-7.07 (m, 7H), 2.76 (br, 2H), 1.66 (m, 2H), 1.39 (m, 2H), 1.32 (m, 4H), 0.89 (t, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 182.2, 147.34, 147.28, 146.7, 144.1, 141.4, 140.1, 138.9, 137.2, 134.1, 134.0, 133.5, 131.0, 129.2, 127.8, 127.3, 126.7, 126.3, 124.5, 124.2, 123.8, 123.4, 123.1, 122.5, 31.6, 30.4, 29.5, 29.2, 22.6, 14.1. MS (MALDI): $m/z$ (%) 685.2 (M$^+$,100), 614.1, 581.1 HRMS: Calculated for C$_{41}$H$_{35}$NOS$_4$: 685.1601; Found: 685.1585.

2-cyano-3-(5''''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2''':5'',2''''-quaterthiophen]-5-yl)acrylic (7). A solution of 6 (150 mg, 0.22 mmm), 2-cyanoacetic acid (94 mg, 5.0 equiv) and ammonium acetate (51 mg, 3.0 equiv) in acetic acid (25 mL) was refluxed for 3 h in a flask. After cooled to room temperature, the reaction was quenched with water and extracted with CH$_2$Cl$_2$. The organic layer was washed with water, dried over Na$_2$SO$_4$. After filtration, the product (161 mg, 98% yield) was obtained as a dark brown solid. $^1$H NMR (400 MHz, d$_6$-DMSO) $\delta$ 13.70 (br, 1H), 8.43 (s, 1H), 7.91 (d, $J$ = 4.4 Hz, 1H), 7.51-7.48 (m, 4H), 7.33-7.27 (m, 7H), 7.12 (d, $J$ = 3.6 Hz, 1H), 7.07 (t, $J$ = 7.4 Hz, 2H), 7.04 (d, $J$ = 8.8 Hz, 4H), 6.93 (d, $J$ = 8.8 Hz, 2H), 2.68 (t, $J$ = 7.4 Hz, 2H), 1.57 (m, 2H), 1.32-1.25 (m, 6H), 0.83 (t, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (150 MHz, d$_6$-DMSO) $\delta$ 163.6, 147.0, 146.8, 146.2, 145.2, 143.3, 141.4, 140.2, 138.0, 134.0, 133.6, 133.2, 133.0, 130.2, 129.6, 128.1, 127.2, 127.1, 126.4, 125.4, 125.0, 124.4, 123.5, 123.4, 122.9, 116.6, 98.0, 31.1, 29.7, 29.0, 28.7, 22.1, 14.0. MS (MALDI): $m/z$ (%) 752.2 (M$^+$,100),708.2, 681.1 HRMS: Calculated for C$_{44}$H$_{36}$N$_2$O$_2$S$_4$: 752.1660; Found: 752.1646.
5'-(4-Methoxyphenyl)-[2,2'-bithiophene]-5-carbaldehyde (9). 3 equiv of 1e was used. The product (65 mg, 72%, 0.3 mmol scale) as a yellow solid was purified with silica gel chromatography (Petroleum ether/Ethyl Acetate = 50:1). This compound is known.\(^6\)\(^1\)H NMR (300 MHz, \(d_6\)-DMSO) \(\delta\) 9.84 (s, 1H), 7.95 (d, \(J = 3.9\) Hz, 1H), 7.60 (d, \(J = 8.4\) Hz, 2H), 7.55 (d, \(J = 3.9\) Hz, 1H), 7.48 (d, \(J = 3.9\) Hz, 1H), 7.42 (d, \(J = 3.9\) Hz, 1H), 6.97 (d, \(J = 8.4\) Hz, 2H), 3.76 (s, 3H).

5'-(4-hydroxyphenyl)-[2,2'-bithiophene]-5-carbaldehyde (10). To a solution of compound 9 (77 mg, 0.26 mmol) in dichloromethane (10 mL) was added BBr\(_3\) (4N in dichloromethane, 73 uL, 1.1 equiv) at 0 °C. After the reaction mixture was stirred for 4 h, additional BBr\(_3\) (80 uL) was added. The reaction mixture was stirred overnight, and diluted with CH\(_2\)Cl\(_2\). The resulting mixture was washed with water and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/dichloromethane = 4:1) to give product 10 (62 mg, 84% yield) as a yellow solid. m.p. 229 °C.\(^1\)H NMR (400 MHz, \(d_6\)-DMSO) \(\delta\) 9.85 (s, 1H), 9.81 (s, 1H), 7.97 (d, \(J = 3.6\) Hz, 1H), 7.54 (d, \(J = 3.6\) Hz, 1H), 7.52-7.48 (m, 3H), 7.36 (d, \(J = 3.6\) Hz, 1H), 6.80 (d, \(J = 3.6\) Hz, 2H).\(^{13}\)C NMR (100 MHz, \(d_6\)-DMSO) \(\delta\) 183.8, 158.0, 145.9, 145.8, 140.8, 139.4, 132.6, 128.3, 127.0, 124.7, 123.9, 123.4, 116.0. MS (EI): \(m/z\) (%) 286 (M\(^+\)), 84, 66 (100). HRMS: Calculated for C\(_{15}\)H\(_{10}\)O\(_2\)S\(_2\): 286.0122; Found: 286.0119.

2-((5'-(4-hydroxyphenyl)-[2,2'-bithiophen]-5-yl)methylene)malononitrile (11). To a solution of 10 (34 mg, 0.12 mmol) in dichloromethane (10 mL) were added piperidine (1 drop) and malononitrile (20 mg, 2.4 equiv) at room temperature. After the reaction mixture was stirred for 2 h. The reaction was diluted with CH\(_2\)Cl\(_2\) and washed. The resulting mixture was concentrated and the
residue was purified with silica gel chromatography (Petroleum ether/dichloromethane = 2:1) to give product 11 (30 mg, 75% yield) as a dark-red solid. This compound is known.\textsuperscript{8} m.p. 242-246 °C (lit.\textsuperscript{8} 235-240 °C). \textsuperscript{1}H NMR (400 MHz, d\textsubscript{6}-acetone) \(\delta\) 8.78 (s, 1H), 8.38 (s, 1H), 7.92 (d, \(J = 3.4\) Hz, 1H), 7.62 (d, \(J = 3.4\) Hz, 1H), 7.61 (dm, \(J = 7.8\) Hz, 2H), 7.55 (d, \(J = 3.8\) Hz, 1H), 7.40 (d, \(J = 3.8\) Hz, 1H), 6.93 (dm, \(J = 7.8\) Hz, 2H).

**Kinetic isotope effect studies**

\[
\begin{align*}
\text{2h} & \xrightarrow{n-\text{BuLi}, \text{THF}} \text{D}_2\text{O, -78 °C to rt.} \rightarrow \text{d-2h \ (>99\%)}
\end{align*}
\]

To an over-dried round bottom flask were added 2h (10 mmol, 1.0 equiv), THF (20 mL) under N\textsubscript{2}. The solution was cooled to -78 °C and \(n\)-BuLi (4.4 mL, 2.5 M in hexane, 1.1equiv) was added slowly. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and re-cool to -20 °C. D\textsubscript{2}O (0.6 mL) was added slowly and the mixture was diluted with ethyl acetate, washed with water, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. The product was purified with silica gel chromatography (100% petroleum ether) to give \textit{d-2h} in >99% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.62 (d, \(J = 6.8\) Hz, 2 H), 7.39 (t, \(J = 6.8\) Hz, 2 H), 7.32-7.28 (m, 2 H), 7.08 (d, \(J = 3.6\) Hz, 1 H).

\[
\begin{align*}
\text{1-e'} & \xrightarrow{n-\text{BuLi}, \text{THF}} \text{D}_2\text{O, -78 °C to rt.} \rightarrow \text{d-1e', > 99\%}
\end{align*}
\]

Compound 1-e\textsuperscript{'} was prepared according to the literature.\textsuperscript{7} Preparation of \textit{d-1e'} is similar with \textit{d-2h}. Compound \textit{d-1e} was prepared by deprotection of \textit{d-1e'} with p-toluenesulfonic acid (catalytic amount) in THF/water (4/1) in almost quantity yield (98%). \textit{d-1e}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.97 (s, 1 H), 7.81 (d, \(J = 3.6\) Hz, 1 H), 7.23 (d, \(J = 3.6\) Hz, 1 H).
Kinetic isotope experiments.

The initial rate measurements were carried out on a 0.3 mmol scale. The reactions were carried out according to standard procedure, stopped after the corresponding reaction time (10 min-120 min) and immediately cooled to room temperature. Then 100 µL internal standard (1,3,5-trimethoxybenzene in DMSO (0.1 mmol/mL)) was added. The yield was determined by GC. The obtained yields were plotted as concentration \([3n]\) vs. time \(t\) (Figure S1). From the diagram, the following initial rates were calculated:

\[
\begin{align*}
K_H & = 2.238 \times 10^{-4} \text{ mmol} \cdot \text{mL}^{-1} \cdot \text{min}^{-1} \\
K_D(1e-2h) & = 8.570 \times 10^{-5} \text{ mmol} \cdot \text{mL}^{-1} \cdot \text{min}^{-1} \\
K_D(1e-d-2h) & = 5.454 \times 10^{-5} \text{ mmol} \cdot \text{mL}^{-1} \cdot \text{min}^{-1}
\end{align*}
\]

Therefore, the \(k_H/k_D(1e-2h) = 2.6\); \(k_H/k_D(1e-d-2h) = 4.1\)

Figure S1. Initial rates of the standard reaction \(1e-2h\) (blue), \(1e-d-2h\) (red), and \(d1e-2h\) (green).
References:


5'-Bromo-4'-hexyl-N,N-dimethyl-[2,2'-bithiophene]-5-carboxamide (3a).
Methyl 5'-bromo-4'-hexyl-[2,2'-bithiophene]-5-carboxylate (3b).
Methyl 5'-bromo-4'-hexyl-4-methyl-[2,2'-bithiophene]-5-carboxylate (3c).
1-(5'-Bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)ethanone (3d).
5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3e).
5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbonitrile (3f).
Methyl 5'-bromo-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3g).
Methyl 5'-chloro-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3i).
Methyl 5'-chloro-[2,2'-bithiophene]-5-carboxylate (3j).
Methyl 5'-methyl-[2,2'-bithiophene]-5-carboxylate (3k).
Methyl 5-(benzo[b]thiophen-2-yl)thiophene-2-carboxylate (3l).
$N,N$-Dimethyl-5'-phenyl-[2,2'-bithiophene]-5-carboxamide (3m).
5'-Phenyl-[2,2'-bithiophene]-5-carbaldehyde (3n).
$N,N$-Dimethyl-5'-{(phenylethynyl)}-2,2'-bithiophene-5-carboxamide (3o).
Methyl 5'-([dimethylcarbamoyl]-[2,2'-bithiophene]-5-carboxylate (3p).
$N,N$-dimethyl-$5'$-(perfluorophenyl)-[2,2'-bithiophene]-5-carboxamide (3q).
5-Bromo-4-hexyl-5'-methoxy-2,2'-bithiophene (3r).
5-Methoxy-5'-methyl-2,2'-bithiophene (3s).
5-Bromo-4-hexyl-5'-phenyl-2,2'-bithiophene (3t)
4-(5-(Benzo[b]thiophen-2-yl)thiophen-2-yl)-N,N-diphenylaniline(3u).
1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3v).
1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3w).

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1-(5'-Ethyl-[2,2'-bifuran]-5-yl)ethanone (3x).
3,6-bis(5'-bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3y)
5'-Bromo-4''-hexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (5).
5''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2'';5'',2''''-quaterthiophene]-5-carbaldehyde (6).
2-Cyano-3-(5''''-(4-(diphenylamino)phenyl)-4''''-hexyl-[2,2':5',2'':5'',2''''-quaterthiophen]-5-yl)acrylic (7).
5'-{4-Methoxyphenyl}-[2,2'-bithiophene]-5-carbaldehyde (9)

5'-{4-hydroxyphenyl}-[2,2'-bithiophene]-5-carbaldehyde (10)
Compound 11
$d$-2h

$d$-1e