Supporting Information

for

Palladium-catalysed 2,5-diheteroarylation of 2,5-dibromothiophene derivatives

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Experimental procedures and characterization data

General information

All reactions were run under argon in Schlenk tubes using vacuum lines. DMA analytical grade was not distilled before use. KOAc (99%) was used. Commercial dibromothiophenes and heteroarenes were used without purification. The reactions were followed by GC and NMR. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (7.25 for ^{1}H NMR and 77.0 for ^{13}C NMR). Flash chromatography was performed on silica gel (230–400 mesh).

General procedure

In a typical experiment, the 2,5-dibromothiophene (1 mmol), heteroarene derivative (3 mmol), KOAc (0.294 g, 3 mmol) and $PdCl(C_3H_5)(dppb)$ (12.1 mg, 0.02 mmol), were dissolved in DMA (5 mL) under an argon atmosphere. The reaction mixture was stirred at 140 °C for 20h. After evaporation of the solvent, the product was purified by silica gel column chromatography.

Preparation of the $PdCl(C_3H_5)(dppb)$ catalyst [1]: An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ = 19.3 (s).

5-(5-Bromothiophen-2-yl)-2-ethyl-4-methylthiazole (1a)

From 2,5-dibromothiophene (0.968 g, 4 mmol) and 2-ethyl-4-methylthiazole (0.127 g, 1 mmol) product **1a** was obtained in 52% (0.150 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 3.8 Hz, 1H), 6.80 (d, J = 3.8 Hz, 1H), 2.95 (q, J = 7.6 Hz, 2H), 2.47 (s, 3H), 1.36 (t, J = 7.6 Hz, 3H).

δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.1, 135.3, 130.2, 126.6, 123.4, 112.1, 26.8, 16.3, 14.0.

$C_{10}H_{10}BrNS_2$ (288.23): Calcd C 41.67, H 3.50; Found C 41.80, H 3.38.

2,5-Bis(2-ethyl-4-methylthiazol-5-yl)thiophene (1b)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.381 g, 3 mmol) product **1b** was obtained in 81% (0.270 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (m, 2H), 2.94 (q, J = 7.6 Hz, 4H), 2.51 (s, 6H), 1.35 (t, J = 7.6 Hz, 6H).

δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 147.7, 133.9, 126.6, 123.9, 26.8, 16.5, 14.0.

$C_{16}H_{18}N_2S_3$ (334.52): Calcd C 57.45, H 5.42; Found C 57.30, H 5.28.

2,5-Bis(4-methylthiazol-5-yl)thiophene (2)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 4-methylthiazole (0.297 g, 3 mmol) product **2** was obtained in 82% (0.228 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 2H), 7.10 (s, 2H), 2.64 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.6, 134.1, 127.5, 125.0, 16.6.

$C_{12}H_{10}N_2S_3$ (278.42): Calcd C 51.77, H 3.62; Found C 51.89, H 3.49.

5,5''-Dimethyl-2,2':5',2''-terthiophene (3) [2]

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 2-methylthiophene (0.294 g, 3 mmol) product **3** was obtained in 74% (0.204 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (s, 2H), 6.21 (d, J = 3.6 Hz, 2H), 5.92 (d, J = 3.6 Hz, 2H), 1.62 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 137.7, 136.4, 128.2, 125.5, 125.4, 16.2.

5,5''-Dichloro-2,2':5',2''-terthiophene (4) [3]

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 2-chlorothiophene (0.356 g, 3 mmol) product **3** was obtained in 77% (0.244 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.91 (d, J = 3.8 Hz, 2H), 6.83 (d, J = 3.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 135.4, 129.0, 126.9, 124.4, 122.9.

5,5''-Dicarbonitrile-2,2':5',2''-terthiophene (5) [4]

From 2,5-dibromothiophene (0.242 g, 1 mmol) and thiophene-2-carbonitrile (0.327 g, 3 mmol) product **3** was obtained in 62% (0.185 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 3.6 Hz, 2H), 7.24 (s, 2H), 7.17 (d, J = 3.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.3, 135.9, 126.9, 124.1, 113.8, 108.5.

5,5''-Diethyl [2,2':5',2''-Terthiophene]-5,5''-dicarboxylate (6)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and ethyl thiophene-2-carboxylate (0.468 g, 3 mmol) product **6** was obtained in 58% (0.227 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 3.9 Hz, 2H), 7.18 (s, 2H), 7.13 (d, J = 3.9 Hz, 2H), 4.35 (q, J = 7.6 Hz, 4H), 1.38 (t, J = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 143.0, 136.6, 134.0, 132.3, 125.9, 124.2, 61.3, 14.3.

$C_{18}H_{16}O_4S_3$ (392.51): Calcd C 55.08, H 4.11; Found C 55.01, H 4.24.

2,5-Di(2-thienyl)thiophene (7) [5]

From 2,5-dibromothiophene (0.242 g, 1 mmol) and thiophene (0.504 g, 6 mmol) product **7** was obtained in 85% (0.211 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 5.1 Hz, 2H), 7.18 (d, *J* = 3.8 Hz, 2H), 7.09 (s, 2H), 7.03 (dd, *J* = 5.1, 3.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.2, 127.8, 124.4, 124.3, 123.7.

2,5-Bis(5-butylfuran-2-yl)thiophene (8)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 2-*n*-butylfuran (0.372 g, 3 mmol) product **8** was obtained in 79% (0.259 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 6.39 (d, *J* = 3.1 Hz, 2H), 6.04 (d, *J* = 3.1 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 4H), 1.68 (quint., *J* = 7.6 Hz, 4H), 1.43 (sext., *J* = 7.6 Hz, 4H), 0.97 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 147.5, 132.0, 122.0, 106.9, 105.7, 30.2, 27.8, 22.2, 13.8.

$C_{20}H_{24}O_2S$ (328.47): Calcd C 73.13, H 7.36; Found C 73.21, H 7.24.

1,1'-(5,5'-(Thiophene-2,5-diyl)bis(furan-5,2-diyl))diethanone (9)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 2-acetylfuran (0.330 g, 3 mmol) product **9** was obtained in 60% (0.180 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 7.24 (d, *J* = 3.6 Hz, 2H), 6.67 (d, *J* = 3.6 Hz, 2H), 2.52 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 152.1, 151.7, 132.8, 126.1, 119.4, 108.2, 26.0.

$C_{16}H_{12}O_4S$ (300.33): Calcd C 63.99, H 4.03; Found C 63.87, H 4.00.

Dimethyl 5,5'-(thiophene-2,5-diyl)bis(2-methylfuran-3-carboxylate) (10)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate (0.420 g, 3 mmol) product **10** was obtained in 63% (0.227 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 2H), 6.72 (s, 2H), 3.84 (s, 6H), 2.63 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.6, 146.8, 131.5, 123.3, 115.2, 105.6, 51.4, 13.8.

$C_{18}H_{16}O_6S$ (360.38): Calcd C 59.99, H 4.47; Found C 60.20, H 4.21.

2,5-Bis(1-methylpyrrol-2-yl)thiophene (11) [6]

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 1-methylpyrrole (0.405 g, 5 mmol) product **11** was obtained in 78% (0.189 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.72 (m, 2H), 6.36 (dd, *J* = 3.0, 1.4 Hz, 2H), 6.19 (t, *J* = 3.0 Hz, 2H), 3.77 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 126.9, 124.9, 124.1, 109.8, 107.9, 35.2.

2,5-Bis(3,5-dimethylisoxazol-4-yl)thiophene (12)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 3,5-dimethylisoxazole (0.291 g, 3 mmol) product **12** was obtained in 80% (0.219 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 2.51 (s, 6H), 2.36 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 158.3, 131.3, 126.4, 110.2, 12.0, 11.1.

$C_{14}H_{14}N_2O_2S$ (274.34): Calcd C 61.29, H 5.14; Found C 61.17, H 5.05.

2,5-Bis(5-chloro-1,3-dimethylpyrazole-4-yl) thiophene (13)

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 5-chloro-1,3-dimethylpyrazole (0.392 g, 3 mmol) product **13** was obtained in 83% (0.283 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 3.77 (s, 6H), 2.36 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 131.8, 125.0, 111.1, 36.0, 13.9.

$C_{14}H_{14}Cl_2N_4S$ (341.26): Calcd C 49.27, H 4.14; Found C 49.40, H 4.27.

5,5'-(3-Methylthiophene-2,5-diyl)bis(2-ethyl-4-methylthiazole) (14)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.381 g, 3 mmol) product **14** was obtained in 83% (0.289 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 2.84-2.74 (m, 4H), 2.32 (s, 3H), 2.14 (s, 3H), 2.00 (s, 3H), 1.23-1.13 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 170.6, 152.0, 149.3, 139.3, 135.2, 131.0, 128.4, 125.5, 123.0, 28.1, 28.0, 17.7, 17.1, 15.6, 15.0, 14.9.

$C_{17}H_{20}N_2S_3$ (348.55): Calcd C 58.58, H 5.78; Found C 58.41, H 5.58.

5,5'-(3-Methylthiophene-2,5-diyl)bis(4-methylthiazole) (15)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and 4-methylthiazole (0.297 g, 3 mmol) product **15** was obtained in 80% (0.234 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.60 (s, 1H), 6.97 (s, 1H), 2.61 (s, 3H), 2.43 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 151.2, 149.9, 149.1, 138.0, 133.4, 129.8, 126.8, 125.1, 122.8, 16.6, 15.9, 14.6.

$C_{13}H_{12}N_2S_3$ (292.44): Calcd C 53.39, H 4.14; Found C 53.29, H 4.27.

3',5,5''-Trimethyl-2,2':5',2''-terthiophene (16) [7]

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and 2-methylthiophene (0.294 g, 3 mmol) product **16** was obtained in 73% (0.212 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95-6.80 (m, 3H), 6.75 (s, 1H), 6.70 (s, 1H), 2.53 (s, 6H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, AcetoneD$_6$) δ 141.3, 140.7, 136.1, 136.0, 135.6, 135.3, 131.1, 128.8, 127.9, 127.6, 127.0, 125.1, 16.2, 15.9, 15.8.

5,5''-Dichloro-3'-methyl-2,2':5',2''-terthiophene (17)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and 2-chlorothiophene (0.356 g, 3 mmol) product **17** was obtained in 74% (0.245 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 3.8 Hz, 1H), 7.07 (s, 1H), 7.03 (s, 2H), 6.98 (d, *J* = 3.8 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, AcetoneD$_6$) δ 137.3, 137.1, 136.2, 135.5, 130.7, 130.5, 130.1, 129.7, 129.4, 129.0, 127.1, 125.1, 16.2.

$C_{13}H_8Cl_2S_3$ (331.30): Calcd C 47.13, H 2.43; Found C 47.11, H 2.34.

5,5''-Diethyl [3'-methyl-2,2':5',2''-terthiophene]-5,5''-dicarboxylate (18)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and ethyl thiophene-2-carboxylate (0.468 g, 3 mmol) product **18** was obtained in 60% (0.244 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 3.9 Hz, 1H), 7.81 (d, *J* = 3.9 Hz, 1H), 7.30-7.25 (m, 2H), 7.21 (s, 1H), 4.55-4.45 (m, 4H), 2.55 (s, 3H), 1.55-1.40 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 161.9, 143.1, 142.6, 136.4, 134.7, 134.0, 133.6, 132.9, 132.2, 130.9, 129.5, 125.6, 124.0, 61.2, 15.8, 14.4, 14.3.

$C_{19}H_{18}O_4S_3$ (406.54): Calcd C 56.13, H 4.46; Found C 55.98, H 4.57.

3'-Methyl-2,2':5',2''-terthiophene (19) [8]

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and thiophene (0.504 g, 6 mmol) product **19** was obtained in 78% (0.204 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 4.8 Hz, 1H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.25-7.20 (m, 2H), 7.10-7.02 (m, 3H), 2.33 (s, 3H).

Dimethyl 5,5'-(3-methylthiophene-2,5-diyl)bis(2-methylfuran-3-carboxylate) (20)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate (0.420 g, 3 mmol) product **20** was obtained in 51% (0.191 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.70 (s, 1H), 6.65 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.63 (s, 3H), 2.62 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.1, 156.5, 156.1, 147.0, 146.9, 134.4, 130.0, 126.7, 125.7, 115.2, 115.1, 106.8, 105.5, 54.0, 51.4, 15.6, 13.8, 13.7.

$C_{19}H_{18}O_6S$ (374.41): Calcd C 60.95, H 4.85; Found C 60.99, H 4.78.

2,2'-(3-Methylthiophene-2,5-diyl)bis(1-methylpyrrole) (21)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and 1-methylpyrrole (0.405 g, 5 mmol)) product **21** was obtained in 77% (0.197 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.75 (m, 1H), 6.70 (m, 1H), 6.34 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.24 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.21 (t, *J* = 3.4 Hz, 1H), 6.17 (t, *J* = 3.4 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.9, 127.4, 127.3, 127.1, 125.3, 124.1, 123.2, 111.2, 109.7, 108.0, 107.5, 35.3, 34.5, 14.9.

$C_{15}H_{16}N_2S$ (256.37): Calcd C 70.27, H 6.29; Found C 70.37, H 6.37.

2,5-Bis(3,5-dimethylisoxazol-4-yl)-3-methylthiophene (22)

From 2,5-dibromo-3-methylthiophene (0.256 g, 1 mmol) and 3,5-dimethylisoxazole (0.291 g, 3 mmol) product **22** was obtained in 75% (0.216 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 2.52 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 2.22 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.6, 159.8, 158.4, 137.2, 131.3, 128.8, 124.4, 110.3, 109.1, 14.4, 12.1, 11.7, 11.3, 10.6.

$C_{15}H_{16}N_2O_2S$ (288.36): Calcd C 62.48, H 5.59; Found C 62.19, H 5.69.

2-Ethyl-5-(5-(2-isobutylthiazol-5-yl)thiophen-2-yl)-4-methylthiazole (23)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and 2-isobutylthiazole (0.211 g, 1.5 mmol) product **23** was obtained in 89% (0.310 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.05 (d, *J* = 3.8 Hz, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 2.97 (q, *J* = 7.6 Hz, 2H), 2.85 (d, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 2.18-2.07 (m, 1H), 1.38 (t, *J* = 7.6 Hz, 3H), 1.01 (d, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.4, 147.9, 137.9, 133.5, 133.4, 131.1, 126.9, 125.5, 123.9, 42.3, 29.7, 26.8, 22.2, 16.6, 14.0.

$C_{17}H_{20}N_2S_3$ (348.55): Calcd C 58.58, H 5.78; Found C 58.40, H 5.71.

2-Ethyl-4-methyl-5-(5'-methyl-2,2'-bithiophen-5-yl)thiazole (24)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) product **24** was obtained in 70% (0.213 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 3.8 Hz, 1H), 6.96 (d, *J* = 3.8 Hz, 1H), 6.94 (d, *J* = 3.8 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H), 2.97 (q, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 2.48 (s, 3H), 1.39 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 147.6, 139.5, 138.0, 134.5, 132.0, 127.0, 126.0, 124.4, 123.7, 123.2, 26.9, 16.6, 15.3, 14.1.

$C_{15}H_{15}NS_3$ (305.48): Calcd C 58.98, H 4.95; Found C 59.04, H 5.09.

5'-(2-Ethyl-4-methylthiazol-5-yl)-2,2'-bithiophene-5-carbonitrile (25)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and thiophene-2-carbonitrile (0.164 g, 1.5 mmol) product **25** was obtained in 67% (0.212 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 3.8 Hz, 1H), 7.22 (d, J = 3.8 Hz, 1H), 7.12 (d, J = 3.8 Hz, 1H), 7.01 (d, J = 3.8 Hz, 1H), 2.99 (q, J = 7.6 Hz, 2H), 2.56 (s, 3H), 1.39 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.4, 143.9, 138.1, 135.4, 134.4, 127.2, 126.2, 123.5, 123.2, 113.9, 107.4, 26.8, 16.6, 13.9.

$C_{15}H_{12}N_2S_3$ (316.46): Calcd C 56.93, H 3.82; Found C 57.10, H 3.99.

5-(2,2'-Bithiophen-5-yl)-2-ethyl-4-methylthiazole (26)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and thiophene (0.202 g, 2 mmol) product **26** was obtained in 41% (0.119 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 5.1 Hz, 1H), 7.18 (d, J = 3.8 Hz, 1H), 7.11 (d, J = 3.8 Hz, 1H), 7.03 (dd, J = 5.1, 3.8 Hz, 1H), 6.98 (d, J = 3.8 Hz, 1H), 3.01 (q, J = 7.6 Hz, 2H), 2.58 (s, 3H), 1.40 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 137.6, 136.8, 132.5, 127.9, 127.2, 124.7, 124.4, 124.0, 123.8, 26.8, 16.6, 14.2.

$C_{14}H_{13}NS_3$ (291.45): Calcd C 57.69, H 4.50; Found C 57.47, H 4.71.

2-ethyl-4-methyl-5-(5-(1-methylpyrrol-2-yl)thiophen-2-yl)thiazole (27)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and 1-methylpyrrole (0.162 g, 2 mmol) product **27** was obtained in 74% (0.213 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 3.8 Hz, 1H), 6.96 (d, J = 3.8 Hz, 1H), 6.73-6.70 (m, 1H), 6.36 (dd, J = 3.0, 1.4 Hz, 1H), 6.17 (t, J = 3.0 Hz, 1H), 3.75 (s, 3H), 2.98 (q, J = 7.6 Hz, 2H), 2.57 (s, 3H), 1.40 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 147.3, 135.1, 132.4, 126.5, 126.4, 124.8, 124.3, 124.2, 110.0, 107.9, 35.1, 26.7, 16.4, 14.0.

$C_{15}H_{16}N_2S_2$ (288.43): Calcd C 62.46, H 5.59; Found C 62.57, H 5.67.

Methyl 5-(5-(2-ethyl-4-methylthiazol-5-yl)thiophen-2-yl)-2-methylfuran-3-carboxylate (28)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate (0.210 g, 1.5 mmol) product **28** was obtained in 62% (0.215 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 3.8 Hz, 1H), 6.98 (d, J = 3.8 Hz, 1H), 6.73 (s, 1H), 3.84 (s, 3H), 2.98 (q, J = 7.6 Hz, 2H), 2.63 (s, 3H), 2.55 (s, 3H), 1.38 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 164.1, 158.6, 147.8, 146.7, 132.9, 132.6, 126.9, 124.2, 123.2, 115.2, 105.6, 51.4, 26.8, 16.6, 14.1, 13.8.

$C_{17}H_{17}NO_3S_2$ (347.45): Calcd C 58.77, H 4.93; Found C 58.97, H 4.69.

4-(5-(2-Ethyl-4-methylthiazol-5-yl)thiophen-2-yl)-3,5-dimethylisoxazole (29)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and 3,5-dimethylisoxazole (0.146 g, 1.5 mmol) product **29** was obtained in 66% (0.201 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 3.8 Hz, 1H), 6.94 (d, J = 3.8 Hz, 1H), 2.98 (q, J = 7.6 Hz, 2H), 2.55 (s, 3H), 2.52 (s, 3H), 2.37 (s, 3H), 1.39 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 165.9, 158.4, 147.9, 133.9, 131.5, 126.7, 126.5, 123.9, 110.2, 26.9, 16.6, 14.1, 12.1, 11.2.

$C_{15}H_{16}N_2OS_2$ (304.43): Calcd C 59.18, H 5.30; Found C 59.07, H 5.22.

5-(5-(5-Chloro-1,3-dimethylpyrazol-4-yl)thiophen-2-yl)-2-ethyl-4-methylthiazole (30)

From 5-(5-bromothiophen-2-yl)-2-ethyl-4-methylthiazole **1a** (0.288 g, 1 mmol) and 5-chloro-1,3-dimethylpyrazole (0.196 g, 1.5 mmol) product **30** was obtained in 72% (0.243 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 3.8 Hz, 1H), 7.04 (d, J = 3.8 Hz, 1H), 3.82 (s, 3H), 2.98 (q, J = 7.6 Hz, 2H), 2.56 (s, 3H), 2.39 (s, 3H), 1.39 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 147.5, 146.1, 133.3, 132.7, 126.5, 125.5, 125.3, 124.3, 111.0, 36.2, 26.9, 16.6, 14.2, 14.0.

$C_{15}H_{16}ClN_3S_2$ (337.89): Calcd C 53.32, H 4.77; Found C 53.50, H 4.87.

5-Bromo-5'-methyl-2,2'-bithiophene (31) [9]

From 2,5-dibromothiophene (0.242 g, 1 mmol) and 2-methylthiophene (0.294 g, 3 mmol) product **31** was obtained in 35% (0.090 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 3.8 Hz, 1H), 6.78 (d, J = 3.8 Hz, 1H), 6.70 (d, J = 3.8 Hz, 1H), 6.54 (d, J = 3.8 Hz, 1H), 2.36 (s, 3H).

2,2'-Bithiophene (32)

From 2-bromothiophene (0.163 g, 1 mmol) and thiophene (0.504 g, 6 mmol) product **32** was obtained in 58% (0.096 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 5.1 Hz, 1H), 7.17 (d, J = 3.8 Hz, 1H),7.00 (dd, J = 5.1, 3.8 Hz, 1H).

1-Methyl-2-(thiophen-2-yl)-pyrrole (33) [10]

From 2-bromothiophene (0.163 g, 1 mmol) and 1-methylpyrrole (0.486 g, 6 mmol) product **33** was obtained in 61% (0.099 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 5.1 Hz, 1H), 7.06 (dd, J = 5.1, 3.8 Hz, 1H), 7.02 (d, J

= 3.8 Hz, 1H), 6.72-6.68 (m, 1H), 6.35-6.30 (m, 1H), 6.16 (t, J = 4.0 Hz, 1H), 3.71 (s, 3H).

4,7-Bis(2-ethyl-4-methylthiazol-5 yl)benzo[c][1,2,5]thiadiazole (34)

From 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.294 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.381 g, 3 mmol) product **34** was obtained in 92% (0.355 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 3.05 (q, J = 7.6 Hz, 4H), 2.52 (s, 6H), 1.42 (t, J = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 153.6, 150.1, 129.1, 125.3, 125.2, 26.8, 16.9, 14.0.

$C_{18}H_{18}N_4S_3$ (386.56): Calcd C 55.93, H 4.69; Found C 55.78, H 4.54.

4,7-Bis(5-methylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (35) [11]

From 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.294 g, 1 mmol) and 2-methylthiophene (0.294 g, 3 mmol) product **35** was obtained in 86% (0.282 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 3.6 Hz, 2H), 7.75 (s, 2H), 6.85 (d, J = 3.6 Hz, 2H), 2.57 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 141.5, 137.1, 127.5, 126.3, 125.7, 125.1, 15.4.

4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (36) [12]

From 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.294 g, 1 mmol) and thiophene (0.504 g, 6 mmol) product **36** was obtained in 82% (0.246 g) yield.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.12-8.07 (m, 2H), 7.88-7.79 (m, 2H), 7.47 (t, J = 4.1 Hz, 2H), 7.20 (dd, J = 7.0, 4.3 Hz, 2H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 153.1, 139.9, 128.4, 128.0, 127.4, 126.3, 126.1.

4,7-Bis(1-methylpyrrol-2-yl)benzo[c][1,2,5]thiadiazole (37) [13]

From 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.294 g, 1 mmol) and 1-methylpyrrole (0.405 g, 5 mmol)) product **37** was obtained in 78% (0.229 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 6.87 (m, 2H), 6.57 (dd, J = 3.6, 1.8 Hz, 2H), 6.33 (t, J = 3.0 Hz, 2H), 3.71 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 130.1, 128.7, 125.4, 124.9, 111.9, 108.4, 35.7.

4,7-Bis(3,5-dimethylisoxazol-4-yl)benzo[c][1,2,5]thiadiazole (38)

From 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.294 g, 1 mmol) and 3,5-dimethylisoxazole (0.291 g, 3 mmol) product **38** was obtained in 85% (0.277 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 2.43 (s, 6H), 2.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 159.1, 153.9, 129.7, 123.8, 112.8, 12.1, 11.1.

$C_{16}H_{14}N_4O_2S$ (326.37): Calcd C 58.88, H 4.32; Found C 58.97, H 4.20.

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