Supplementary material

Benzenesulfonyl chlorides: New reagents for access to alternative regioisomers in palladium-catalysed direct arylations of thiophenes

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General:

All reactions were carried out under an inert atmosphere with standard Schlenk techniques. HPLC grade solvents (acetonitrile, dimethylsulfoxide, 1,4-dioxane and N-methyl-2-pyrrolidone) were used and stored under argon without further purification. Toluene was dried and purified by solvent purification system equipped with a series of activated filter columns. 1H NMR spectra were recorded on Bruker GPX (300 MHz, 400 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.26 ppm for 1H; 77.0 ppm for 13C), constants were reported in Hertz. 1H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). 13C NMR spectra were recorded at 75 MHz, 100 MHz on the same spectrometer and reported in ppm. All reagents were weighed and handled in air, and refilled with an inert atmosphere of argon at room temperature.
General procedure:

To a 25 mL oven dried Schlenk tube, arylsulfonyl chloride (1 mmol), thiophene derivative (1.5 mmol), Li$_2$CO$_3$ (6 mmol, 0.444 g), 1,4-dioxane (2 mL) and bis(acetonitrile)dichloropalladium(II) (0.05 mmol, 12.9 mg) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 140 °C (oil bath temperature) for 40 hours. After cooling the reaction at room temperature, the crude mixture was filtrated with a short column, the filtrate was analysed by GC and GC-MS to determine the regioselectivity, and purified by silica column chromatography (Et$_2$O/PE) to afford the corresponding C3 or C4 arylated products.

2-Methyl-4-$p$-tolylthiophene (1b)$^{[1]}$

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 1b in 75% (0.141 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.15 (s, 1H), 7.04 (s, 1H), 2.52 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.0, 140.3, 136.6, 133.3, 129.4, 126.1, 124.6, 117.3, 21.1, 15.4.

2-Methyl-4-(4-nitrophenyl)-thiophene (2)

The reaction of 4-nitrobenzenesulfonyl chloride (0.222 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 2 in 78% (0.171 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 8.8$ Hz, 2H), 7.38 (s, 1H), 7.10 (s, 1H), 2.55 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.5, 142.2, 141.7, 139.6, 126.5, 124.3, 124.2, 121.1, 15.4. Elemental analysis: calcd (%) for C$_{11}$H$_9$NO$_2$S (219.26): C 60.26, H 4.14; found: C 60.04, H 4.17.

2-Methyl-4-(4-cyanophenyl)-thiophene (3)

The reaction of 4-cyanobenzenesulfonyl chloride (0.202 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 3 in 71% (0.141 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68-7.60 (m, 4H), 7.32 (s, 1H), 7.06 (s, 1H), 2.54 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.5, 140.2, 140.0, 132.6, 126.6, 124.0, 120.4, 119.0, 110.2, 15.4. Elemental analysis: calcd (%) for C$_{12}$H$_9$NS (199.27): C 72.33, H 4.55; found: C 72.19, H 4.48.
2-Methyl-4-(4-trifluoromethylphenyl)-thiophene (4)

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 4 in 80% (0.194 g) yield as a white solid (regioselectivity 92%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.65\) (d, \(J = 8.0\) Hz, 2H), 7.62 (d, \(J = 8.0\) Hz, 2H), 7.28 (s, 1H), 7.07 (s, 1H), 2.54 (s, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta 62.42\) (s). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 141.2, 140.5, 139.4, 128.6\) (q, \(J = 32.6\) Hz), 126.5, 125.7 (q, \(J = 3.2\) Hz), 124.3, 124.0 (q, \(J = 271.8\) Hz), 119.6, 15.4. Elemental analysis: calcd (%) for C\(_{12}\)H\(_9\)F\(_3\)S (242.26): C 59.49, H 3.74; found: C 59.34, H 3.79.

4-(4-Chlorophenyl)-2-methylthiophene (5)

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 5 in 67% (0.139 g) yield as a white solid (regioselectivity 98%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.48\) (d, \(J = 8.0\) Hz, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 7.18 (s, 1H), 7.02 (s, 1H), 2.53 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta 140.8, 140.7, 134.6, 132.6, 128.8, 127.4, 124.3, 118.3, 15.4\). Elemental analysis: calcd (%) for C\(_{11}\)H\(_9\)ClS (208.71): C 63.30, H 4.35; found: C 63.18, H 4.17.

4-(4-Bromophenyl)-2-methylthiophene (6)

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 6 in 88% (0.223 g) yield as a white solid (regioselectivity 98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.49\) (d, \(J = 8.2\) Hz, 2H), 7.41 (d, \(J = 8.2\) Hz, 2H), 7.18 (s, 1H), 7.02 (s, 1H), 2.53 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 140.9, 140.8, 135.0, 131.8, 127.7, 124.3, 120.7, 118.4, 15.4\). Elemental analysis: calcd (%) for C\(_{11}\)H\(_9\)BrS (253.16): C 52.19, H 3.58; found: C 52.27, H 3.44.

4-(4-Fluorophenyl)-2-methylthiophene (7)[1]

The reaction of 4-fluorobenzenesulfonyl chloride (0.195 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 7 in 88% (0.169 g) yield as a white solid (regioselectivity 98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.57-7.48\) (m, 2H), 7.13 (d, \(J = 1.4\) Hz, 1H), 7.11-7.03 (m, 2H), 7.02 (m, 1H), 2.54 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 162.0\) (d, \(J = 245.4\) Hz), 141.0, 140.7, 132.3 (d, \(J = 3.3\) Hz), 127.6 (d, \(J = 8.1\) Hz), 124.5, 117.7, 115.5 (d, \(J = 21.3\) Hz), 15.3.

Electronic Supplementary Material (ESI) for Chemical Science

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2-Methyl-4-phenylthiophene (8)

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 8 in 81% (0.141 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.30 (t, $J = 8.0$ Hz, 2H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.0, 140.5, 136.1, 128.7, 126.9, 126.2, 124.6, 118.0, 15.5.

2-Methyl-4-naphthalen-1-ylthiophene (9)

The reaction of naphthalene-1-sulfonyl chloride (0.227 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 9 in 31% (0.069 g) yield as a white solid (regioselectivity 98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.49-7.47 (m, 4H), 7.13 (s, 1H), 6.97 (s, 1H), 2.59 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 140.9, 139.5, 135.3, 133.8, 131.7, 128.2, 127.9, 127.5, 126.7, 126.0, 125.9, 125.7, 125.4, 121.2, 15.3. Elemental analysis: calcd (%) for C$_{15}$H$_{12}$S (224.32): C 80.31, H 5.39; found: C 80.47, H 5.28.

4-(4-Methoxyphenyl)-2-methylthiophene (10)

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords 10 in 41% (0.086 g) yield as a white solid (regioselectivity 96%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.08 (s, 1H), 7.01 (s, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 3.82 (s, 3H), 2.52 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.7, 141.7, 140.3, 129.1, 127.3, 124.6, 116.6, 114.1, 55.3, 15.4. Elemental analysis: calcd (%) for C$_{12}$H$_{12}$OS (204.29): C 70.55, H 5.92; found: C 70.59, H 6.02.

2-n-Butyl-4-(4-chlorophenyl)-thiophene (11)

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-n-butylthiophene (0.210 g, 1.5 mmol), affords 11 in 62% (0.155 g) yield as a white solid (regioselectivity 98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.20 (s, 1H), 7.03 (s, 1H), 2.84 (t, $J = 7.6$ Hz, 2H), 1.72 (quint., $J = 7.6$ Hz, 2H), 1.43 (sext., $J = 7.6$ Hz, 2H), 0.96 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.0, 140.5, 134.7, 132.6, 128.8, 127.4, 123.1, 118.0, 33.7, 29.8, 22.2, 13.8. Elemental analysis: calcd (%) for C$_{12}$H$_{13}$ClS (250.79): C 70.55, H 6.03; found: C 67.19, H 6.00.

2-nButyl-4-p-tolyli thiophene (12)
The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-n-butylthiophene (0.210 g, 1.5 mmol), affords 12 in 63% (0.145 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.46 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.18 (s, 1H), 7.06 (s, 3H), 2.84 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.72 (quint., J = 7.6 Hz, 2H), 1.43 (sext., J = 7.6 Hz, 2H), 0.96 (t, J = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.5, 141.7, 136.6, 133.4, 129.4, 126.1, 123.4, 117.1, 33.7, 29.9, 22.2, 21.1, 13.8. Elemental analysis: calcd (%) for C$_{15}$H$_{18}$S (230.37): C 78.21, H 7.88; found: C 78.02, H 7.67.

**2-nButyl-4-(4-methoxyphenyl)-thiophene (13)**

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and 2-n-butylthiophene (0.210 g, 1.5 mmol), affords 13 in 43% (0.106 g) yield as a white solid (regioselectivity 98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, J = 8.0 Hz, 2H), 7.11 (s, 1H), 7.03 (s, 1H), 6.91 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 2.84 (t, J = 7.6 Hz, 2H), 1.72 (quint., J = 7.6 Hz, 2H), 1.43 (sext., J = 7.6 Hz, 2H), 0.96 (t, J = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.7, 146.5, 141.4, 129.1, 127.3, 123.3, 116.3, 114.1, 55.3, 33.7, 29.9, 22.2, 13.8. Elemental analysis: calcd (%) for C$_{15}$H$_{18}$OS (246.37): C 73.13, H 7.36; found: C 73.24, H 7.38.

**3-p-Tolylthiophene (14)**

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and thiophene (0.504 g, 6 mmol), affords 14 in 48% (0.084 g) yield as a white solid (regioselectivity 98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, J = 7.9 Hz, 2H), 7.41 (s, 1H), 7.37 (s, 1H), 7.20 (d, J = 7.9 Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.3, 136.8, 133.1, 129.5, 129.4, 126.3, 126.0, 119.6, 21.1. The formation of 3,4-di-p-tolylthiophene in low yield was also observed. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.29 (s, 2H), 7.09 (d, J = 7.9 Hz, 4H), 7.06 (d, J = 7.9 Hz, 4H), 2.33 (s, 6H).

**3-(4-Methoxyphenyl)-thiophene (15)**

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and thiophene (0.504 g, 6 mmol), affords 15 in 34% (0.065 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52 (d, J = 8.3 Hz, 2H), 7.41-7.35 (m, 3H), 6.95 (d, J = 8.3 Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.8, 142.0, 128.7, 127.5, 126.2, 126.0, 118.9, 114.2, 55.3.
2-Chloro-4-(4-trifluoromethylphenyl)-thiophene (16)\(^6\)

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.490 g, 2 mmol) and 2-chlorothiophene (0.119 g, 1 mmol), affords 16 in 41% (0.108 g) yield as a white solid (regioselectivity 98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.65 (d, \(J = 8.0\) Hz, 2H), 7.62 (d, \(J = 8.0\) Hz, 2H), 7.28 (d, \(J = 1.8\) Hz, 1H), 7.23 (d, \(J = 1.8\) Hz, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.2, 138.4, 131.5, 129.5 (q, \(J = 33.0\) Hz), 126.3, 126.0 (q, \(J = 3.6\) Hz), 125.2, 124.1 (q, \(J = 273.0\) Hz), 120.0.

2-Chloro-4-phenylthiophene (17)\(^2\)

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-chlorothiophene (0.178 g, 1.5 mmol), affords 17 in 69% (0.134 g) yield as a white solid (regioselectivity >98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.53 (d, \(J = 7.8\) Hz, 2H), 7.39 (t, \(J = 7.8\) Hz, 2H), 7.31 (t, \(J = 7.3\) Hz, 1H), 7.22 (s, 1H), 7.19 (d, \(J = 1.5\) Hz, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.6, 135.1, 130.7, 128.7, 127.6, 126.1, 125.5, 118.4.

2-Chloro-4-\(p\)-tolylthiophene (18)\(^6\)

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-chlorothiophene (0.178 g, 1.5 mmol), affords 18 in 56% (0.117 g) yield as a white solid (regioselectivity >98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.41 (d, \(J = 8.0\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 7.19 (s, 1H), 7.14 (d, \(J = 1.5\) Hz, 1H), 2.37 (s, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.6, 137.4, 132.4, 130.5, 129.5, 125.9, 125.5, 117.8, 21.3.

2-Bromo-4-\(p\)-tolylthiophene (19)

The reaction of 4-methylbenzenesulfonyl chloride (0.382 g, 2 mmol) and 2-bromothiophene (0.163 g, 1 mmol), affords 19 in 53% (0.134 g) yield as a white solid (regioselectivity >98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.34 (d, \(J = 8.0\) Hz, 2H), 7.19 (s, 1H), 7.18 (s, 1H), 7.12 (d, \(J = 8.0\) Hz, 2H), 2.37 (s, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.7, 137.4, 132.2, 129.5, 129.1, 126.0, 120.7, 112.7, 21.1.

Elemental analysis: calcd (%) for C\(_{11}\)H\(_9\)BrS (253.16): C 52.19, H 3.58; found: C 52.04, H 3.77.

2-Bromo-4-(4-chlorophenyl)-3-methylthiophene (20)
The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-bromo-3-methylthiophene (0.266 g, 1.5 mmol), affords 20 in 80% (0.230 g) yield as a colorless oil (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.13 (s, 1H), 2.16 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.8, 135.5, 135.3, 133.5, 129.8, 128.6, 122.5, 110.8, 14.8.

Elemental analysis: calcd (%) for C$_{11}$H$_8$BrClS (287.60): C 45.94, H 2.80; found: C 46.08, H 3.04.

2-Bromo-3-methyl-4-phenylthiophene (21)$^7$

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-bromo-3-methylthiophene (0.266 g, 1.5 mmol), affords 21 in 67% (0.170 g) yield as a colourless oil (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (t, $J = 7.4$ Hz, 2H), 7.40-7.30 (m, 3H), 7.15 (s, 1H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.1, 136.9, 135.7, 128.5, 128.4, 127.4, 122.2, 110.5, 14.8.

2-Bromo-3-methyl-4-p-tolylthiophene (22)

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-bromo-3-methylthiophene (0.266 g, 1.5 mmol), affords 22 in 71% (0.190 g) yield as a colourless oil (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24 (s, 4H), 7.11 (s, 1H), 2.40 (s, 3H), 2.18 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.1, 137.2, 135.7, 134.0, 129.1, 128.4, 121.9, 110.3, 21.1, 14.8. Elemental analysis: calcd (%) for C$_{12}$H$_{11}$BrS (267.19): C 53.94, H 4.15; found: C 53.99, H 4.31.

1-(4-Phenylthiophen-2-yl)-ethanone (23)$^8$

The reaction of benzenesulfonyl chloride (0.354 g, 2 mmol) and 2-methyl-2-(thiophen-2-yl)-1,3-dioxolane (0.170 g, 1 mmol), affords 23 in 61% (0.123 g) yield as a yellow oil (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (s, 1H), 7.73 (s, 1H), 7.58 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 1H), 2.61 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.7, 144.9, 143.4, 134.8, 131.1, 129.0, 128.3, 127.8, 126.3, 26.9.

1-[4-(4-Bromophenyl)-thiophen-2-yl]-ethanone (24)

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and 2-methyl-2-(thiophen-2-yl)-1,3-dioxolane (0.255 g, 1.5 mmol), affords 24 in 29% (0.082 g) yield as a white solid (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (s, 1H), 7.64 (s, 1H), 7.48 (d, $J = 7.4$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 1H), 2.61 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.7, 144.9, 143.4, 134.8, 131.1, 129.0, 128.3, 127.8, 126.3, 26.9.
\( J = 8.0 \text{ Hz, 2H}, 7.37 (d, J = 8.0 \text{ Hz, 2H}), 2.53 (s, 3H). \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3): \delta 190.5, 145.2, 142.1, 133.7, 132.1, 130.6, 128.4, 127.8, 121.8, 26.9. \)

Elemental analysis: calcd (%) for C\(_{13}\)H\(_9\)BrOS (281.17): C 51.26, H 3.23; found: C 51.21, H 3.08.

4-(4-Trifluoromethylphenyl)-[2,2']bithiophenyl (25)

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and [2,2']bithiophenyl (0.249 g, 1.5 mmol), affords 25 in 78% (0.242 g) yield as a white solid (regioselectivity 92%).

\(^1\text{H NMR (400 MHz, CDCl}_3): \delta 7.68 (d, J = 8.0 \text{ Hz, 2H}), 7.64 (d, J = 8.0 \text{ Hz, 2H}), 7.44 (s, 1H), 7.39 (s, 1H), 7.26 (d, J = 3.6 \text{ Hz, 1H}), 7.22 (d, J = 2.7 \text{ Hz, 1H}), 7.07 (dd, J = 3.6, 2.7 \text{ Hz, 1H}). \)

\(^{19}\text{F NMR (376 MHz, CDCl}_3): \delta 62.4 (s). \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3): \delta 141.3, 138.8, 138.7, 136.8, 129.2 (q, J = 32.3 \text{ Hz}), 127.9, 126.4, 125.8 (q, J = 3.6 \text{ Hz}), 124.9, 124.2, 124.1 (q, J = 272.0 \text{ Hz}), 122.5, 120.5. \)

Elemental analysis: calcd (%) for C\(_{15}\)H\(_9\)F\(_3\)S\(_2\) (310.36): C 58.05, H 2.92; found: C 58.04, H 3.00.

4-(4-Bromophenyl)-[2,2']bithiophenyl (26)

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and [2,2']bithiophenyl (0.249 g, 1.5 mmol), affords 26 in 60% (0.193 g) yield as a white solid (regioselectivity >98%).

\(^1\text{H NMR (400 MHz, CDCl}_3): \delta 7.52 (d, J = 8.6 \text{ Hz, 2H}), 7.46 (d, J = 8.6 \text{ Hz, 2H}), 7.39 (d, J = 1.2 \text{ Hz, 1H}, 1H), 7.30 (d, J = 1.2 \text{ Hz, 1H}), 7.25-7.20 (m, 2H), 7.0 (dd, J = 5.2, 3.7 \text{ Hz, 1H}). \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3): \delta 141.6, 138.4, 137.0, 134.4, 131.9, 127.9, 127.8, 124.7, 124.0, 122.5, 121.2, 119.4. \)

Elemental analysis: calcd (%) for C\(_{14}\)H\(_9\)BrS\(_2\) (321.26): C 52.34, H 2.82; found: C 52.17, H 3.01.

3-Methyl-4-phenylthiophene (27)[1]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 3-methylthiophene (0.147 g, 1.5 mmol), affords 27 in 86% (0.150 g) yield as a colorless oil (regioselectivity >98%).

\(^1\text{H NMR (400 MHz, CDCl}_3): \delta 7.45-7.30 (m, 5H), 7.20 (d, J = 3.2 \text{ Hz, 1H}), 7.03 (m, 1H), 2.28 (s, 3H). \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3): \delta 143.1, 137.1, 136.1, 128.6, 128.3, 126.9, 122.9, 121.9, 15.5. \)

3-Methyl-4-\(p\)-tolylthiophene (28)[9]

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 3-methylthiophene (0.147 g, 1.5 mmol), affords 28 in 55% (0.103 g) yield as a colorless oil (regioselectivity >98%).
MHz, CDCl₃): δ 7.30 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 3.3 Hz, 1H), 7.03 (dq, J = 3.3 and 0.7 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 143.1, 136.6, 136.2, 134.2, 129.0, 128.5, 122.6, 121.8, 21.1, 15.5.

3-Chloro-4-phenylthiophene (29)[5]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 3-chlorothiophene (0.178 g, 1.5 mmol), affords 29 in 62% (0.121 g) yield as a white solid (regioselectivity >98%). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 2.2 Hz, 1H), 7.24 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 140.3, 134.4, 128.8, 128.3, 127.7, 124.5, 123.3, 121.2.

3-Chloro-4-p-tolylthiophene (30)

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 3-chlorothiophene (0.178 g, 1.5 mmol), affords 30 in 43% (0.089 g) yield as a white solid (regioselectivity >98%). ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, J = 8.0 Hz, 2H), 7.28-7.22 (m, 4H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 140.3, 137.6, 131.8, 129.0, 128.6, 124.8, 122.9, 121.1, 21.2. Elemental analysis: calcd (%) for C₁₁H₉ClS (208.71): C 63.30, H 4.35; found: C 63.17, H 4.20.

3-Chloro-4-(4-methoxyphenyl)-thiophene (31)

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and 3-chlorothiophene (0.178 g, 1.5 mmol), affords 31 in 61% (0.137 g) yield as a white solid (regioselectivity 98%). ¹H NMR (400 MHz, CDCl₃): δ 7.45 (d, J = 8.0 Hz, 2H), 7.22 (s, 2H), 6.96 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.3, 140.0, 129.9, 127.0, 124.8, 122.5, 121.1, 113.7, 55.3. Elemental analysis: calcd (%) for C₁₁H₉ClOS (224.71): C 58.80, H 4.04; found: C 58.64, H 4.19.

3-Phenylbenzo[b]thiophene (32)[2]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 32 in 83% (0.174 g) yield as a colorless oil (regioselectivity >98%). ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.93 (m, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.45-7.38 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 140.7, 138.1, 137.9, 136.0, 128.7, 128.5, 127.5, 124.4, 124.3, 123.4, 122.9.
3-p-Tolylbenzob[b]thiophene (33)\textsuperscript{[10]}

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 33 in 50\% (0.112 g) yield as a colorless oil (regioselectivity >98\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.94-7.90\) (m, 2H), 7.49 (d, \(J = 8.0\) Hz, 2H), 7.42-7.38 (m, 2H), 7.37 (s, 1H), 7.30 (d, \(J = 8.0\) Hz, 2H), 2.44 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 140.7, 138.1, 138.0, 137.3, 133.1, 129.4, 128.6, 124.3, 124.2, 123.1, 123.0, 122.9, 21.2.

3-(4-Methoxyphenyl)-benzob[b]thiophene (34)\textsuperscript{[10]}

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 34 in 62\% (0.149 g) yield as a colorless oil (regioselectivity 96\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.93-7.88\) (m, 2H), 7.52 (d, \(J = 8.0\) Hz, 2H), 7.42-7.38 (m, 2H), 7.34 (s, 1H), 7.03 (d, \(J = 8.0\) Hz, 2H), 3.89 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 159.1, 140.6, 138.1, 137.7, 129.8, 128.5, 124.3, 124.2, 122.9, 122.8, 122.5, 114.1, 55.3.

3-(4-Chlorophenyl)-benzob[b]thiophene (35)\textsuperscript{[1]}

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 35 in 88\% (0.215 g) yield as a colorless oil (regioselectivity 97\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.94-7.84\) (m, 2H), 7.53 (d, \(J = 8.0\) Hz, 2H), 7.46 (d, \(J = 8.0\) Hz, 2H), 7.42-7.39 (m, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 140.7, 137.6, 136.8, 134.4, 133.5, 129.9, 128.9, 124.5, 124.4, 123.7, 123.0.

3-(4-Bromophenyl)-benzob[b]thiophene (36)\textsuperscript{[1]}

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 36 in 83\% (0.240 g) yield as a white solid (regioselectivity 95\%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.96-7.84\) (m, 2H), 7.62 (d, \(J = 8.0\) Hz, 2H), 7.46 (d, \(J = 8.0\) Hz, 2H), 7.42-7.39 (m, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 140.7, 137.5, 136.8, 134.4, 133.5, 129.9, 130.2, 124.6, 124.5, 123.7, 123.0, 122.6, 121.6.

3-(4-Trifluoromethylphenyl)-benzob[b]thiophene (37)\textsuperscript{[1]}

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The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 37 in 88% (0.245 g) yield as a colorless oil (regioselectivity 92%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90-7.67 (m, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.39 (s, 1H), 7.38-7.31 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ 62.4 (s). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.7, 139.6, 137.4, 136.6, 129.5 (q, $J = 32.6$ Hz), 128.8, 125.7 (q, $J = 4.0$ Hz), 124.7, 124.6 (m), 124.1 (q, $J = 271.8$ Hz), 123.1, 122.5.

4-Benzo[b]thiophen-3-ylbenzonitrile (38)

The reaction of 4-cyanobenzenesulfonyl chloride (0.202 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 38 in 83% (0.195 g) yield as a colorless oil (regioselectivity >98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97-7.90 (m, 1H), 7.89-7.83 (m, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.50 (s, 1H), 7.46-7.39 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.7, 140.5, 137.0, 136.1, 132.5, 129.1, 125.3, 124.8, 124.7, 123.1, 122.3, 118.8, 111.1. Elemental analysis: calcd (%) for C$_{15}$H$_9$NS (235.30): C 76.56, H 3.86; found: C 76.38, H 3.70.

Methyl 3-benzo[b]thiophen-3-ylthiophene-2-carboxylate (39)

The reaction of methyl 3-chlorosulfonylthiophene-2-carboxylate (0.241 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords 39 in 51% (0.140 g) yield as a colorless oil (regioselectivity 89%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J = 8.1$ Hz, 1H), 7.59 (d, $J = 5.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.51 (s, 1H), 7.40-7.32 (m, 2H), 7.19 (d, $J = 5.0$ Hz, 1H), 3.69 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.2, 141.4, 139.5, 138.5, 131.5, 130.9, 130.4, 129.0, 125.6, 124.3, 124.2, 122.8, 122.7, 51.9. Elemental analysis: calcd (%) for C$_{14}$H$_{10}$O$_2$S$_2$ (274.36): C 61.29, H 3.67; found: C 61.09, H 3.54.


2-Methyl-4-p-tolylthiophene (1b)
2-Methyl-4-(4-nitrophenyl)-thiophene (2)

$\text{H-NMR, 1H, CDCl}_3$

$\text{C-NMR, 13C, CDCl}_3$

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2-Methyl-4-(4-cyanophenyl)-thiophene (3)

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2-Methyl-4-(4-trifluoromethylphenyl)-thiophene (4)
4-(4-Chlorophenyl)-2-methylthiophene (5)

$^1$H-NMR, 300 MHz, CDCl$_3$
4-(4-Bromophenyl)-2-methylthiophene (6)

\[
\begin{align*}
\text{H-NMR. 400 MHz, CDCl}_3
\end{align*}
\]
2-Methyl-4-naphthalen-1-ylthiophene (9)

\[^1\text{H-NMR, 400MHz, CDCl}_3\]

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4-(4-Methoxyphenyl)-2-methylthiophene (10)

$^{1}H$-NMR, 400 MHz, CDCl$_3$

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2-nButyl-4-(4-chlorophenyl)-thiophene (11)
2-n-Butyl-4-p-tolylthiophene (12)

\[ ^1H \text{NMR, } 400 \text{MHz, CDCl}_3 \]

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2-nButyl-4-(4-methoxyphenyl)-thiophene (13)

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2-Bromo-4-p-tolylthiophene (19)

\[
\begin{align*}
{\text{H-NMR, 400 MHz, CDCl}_3}
\end{align*}
\]
2-Bromo-4-(4-chlorophenyl)-3-methylthiophene (20)
2-Bromo-3-methyl-4-p-tolylthiophene (22)
1-[4-(4-Bromophenyl)-thiophen-2-yl]-ethanone (24)

£H-NMR, 400 MHz, CDCl3

13C-NMR, 100 MHz, CDCl3

Dept
4-(4-Trifluoromethylphenyl)-[2,2']bithiophenyl (25)

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3-Chloro-4-p-tolyliophene (30)
4-Benzob[thiophen-3-ylbenzonitrile (38)
Methyl 3-benzo[b]thiophen-3-ylthiophene-2-carboxylate (39)