Electrooxidative Double C-H/C-H Coupling of Phenols with 3-Phenylbenzo thiophenes: Facile Access to Benzothiophene Derivatives

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1. General information

All the solvents and other reagents were purchased from commercial suppliers without the purification. All reactions were performed in N₂ atmosphere unless otherwise. \(^1\)H and \(^{13}\)C NMR data were recorded with Bruker Advance III (400 MHz) or (600 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) of the products were obtained using a Bruker Daltonics micro TOF-Q spectrometer. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All reactions were monitored by thin-layer chromatography (TLC) through GF254 silica gel-coated plates. Flash chromatography was carried out on SiO₂ (silica gel 200-300 mesh). 3-Phenylbenzothiophenes were prepared by the reported literatures.\(^1\)
2. Experimental procedure for the electrochemical oxidative C-H/C-H coupling of 3-phenylbenzothiophenes and \( p \)-methoxyphenol

a) In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 3-phenylbenzothiophene (158 mg, 0.75 mmol), \( p \)-methoxyphenol (62 mg, 0.5 mmol), and \( n \)-Bu4NPF\(_6\) (290 mg, 0.75 mmol) were combined and added. The bottle was equipped with RVC anode (15 mm×15 mm×0.3 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with nitrogen. Then HFIP (6 mL) and CH\(_2\)Cl\(_2\) (4 mL) were injected into undivided three-necked bottle. The reaction mixture was stirred and electrolyzed at constant current of 10 mA under room temperature for 5 h. Upon the reaction completed, the reaction mixture was washed with water and extracted with CH\(_2\)Cl\(_2\) (10 mL×3). The organic layers were combined, dried over Na\(_2\)SO\(_4\), and concentrated under vacuum. The pure product was obtained by flash column chromatography on silica gel by petroleum ether and EtOAc (30:1) in 80% yield.

b) In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 3-phenylbenzothiophene (63 mg, 0.3 mmol), \( p \)-methoxyphenol (124 mg, 1 mmol), and \( n \)-Bu4NPF\(_6\) (387 mg, 1 mmol) were combined and added. The bottle was equipped RVC anode (15 mm×15 mm×0.3 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with nitrogen. Then HFIP (6 mL) and CH\(_2\)Cl\(_2\) (4 mL) were injected into undivided three-necked bottle. The reaction mixture was stirred and electrolyzed at constant current of 10 mA under room temperature for 3 h. Upon the reaction completed, the reaction mixture was washed with water and extracted with CH\(_2\)Cl\(_2\) (10 mL×3). The organic layers were combined, dried over Na\(_2\)SO\(_4\), and concentrated. The pure product was obtained by flash column chromatography on silica gel by petroleum ether and EtOAc (30:1) in 66% yield.

c) In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 3-phenylbenzothiophene (95 mg, 0.45 mmol), 4-methoxy-2-(3-(\( p \)-tolyl)benzo[\( b \)]thiophen-2-yl)phenol (104 mg, 0.3 mmol), and \( n \)-Bu4NPF\(_6\) (387 mg, 1 mmol) were combined and added. The bottle was equipped
RVC anode (15 mm×15 mm×0.3 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with nitrogen. Then HFIP (6 mL) and CH$_2$Cl$_2$ (4 mL) were injected into undivided three-necked bottle. The reaction mixture was stirred and electrolyzed at constant current of 10 mA under room temperature for 3 h. Upon the reaction completed, the reaction mixture was washed with water and extracted with CH$_2$Cl$_2$ (10 mL×3). The organic layers were combined, dried over Na$_2$SO$_4$, and concentrated. The pure product was obtained by flash column chromatography on silica gel by petroleum ether and EtOAc (30:1) in 70% yield.
3. Experiments on investigation of mechanism

a) In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 3-phenylbenzothiophene (158 mg, 0.75 mmol), p-methoxyphenol (62 mg, 0.5 mmol), TEMPO (156 mg, 1 mmol) and n-Bu₄NPF₆ (290 mg, 0.75 mmol) were combined and added. The bottle was equipped RVC anode (15 mm×15 mm×0.3 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with nitrogen. Then HFIP (6 mL) and CH₂Cl₂ (4 mL) were injected into undivided three-necked bottle. Upon the reaction completed, the reaction mixture was stirred and electrolyzed at constant current of 10 mA under room temperature for 5 h. The reaction mixture was washed with water and extracted with CH₂Cl₂ (10 mL×3). The organic layers were combined, dried over Na₂SO₄, and concentrated. No desired product was observed in the reaction mixture (Scheme 1).

![Scheme 1](image)

b) In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 3-phenylbenzothiophene (63 mg, 0.3 mmol), 2,5-methoxyphenol (154 mg, 1 mmol), and n-Bu₄NPF₆ (387 mg, 1 mmol) were combined and added. The bottle was equipped RVC anode (15 mm×15 mm×0.3 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with nitrogen. Then HFIP (6 mL) and CH₂Cl₂ (4 mL) were injected into undivided three-necked bottle. The reaction mixture was stirred and electrolyzed at constant current of 10 mA under room temperature for 3 h. Upon the reaction completed, the reaction mixture was washed with water and extracted with CH₂Cl₂ (10 mL×3). The organic layers were combined, dried over Na₂SO₄, and concentrated. No desired product was observed (Scheme 2).
Scheme 2

1a + 2h → 3o

RVC(+)/Pt(-): I = 10 mA
HFIP (6 mL): CH₂Cl₂ (4 mL)
Undivided cell

Not detected
4. Characterization data for the products

4-Methoxy-2,6-bis(3-phenylbenzo[b]thiophen-2-yl)phenol (3a)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 80% yield; m.p. 159-161 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87-7.85 (m, 2H), 7.72-7.70 (m, 2H), 7.39-7.33 (m, 10H), 7.27-7.24 (m, 4H), 6.72 (d, $J = 1.2$ Hz, 2H), 5.03 (br, 1H), 3.50 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 152.3, 145.4, 139.9, 139.5, 135.8, 134.7, 134.4, 129.9, 128.6, 127.6, 124.9, 124.6, 123.4, 122.3, 121.8, 118.2, 55.6. HRMS, calculated for C$_{35}$H$_{24}$NaO$_2$S$_2$ (M+Na$^+$): 563.1110, found 563.1110.

4-Methoxy-2,6-bis(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (3b)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 47% yield; m.p. 181-183 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88-7.86 (m, 2H), 7.75-7.72 (m, 2H), 7.38-7.36 (m, 4H), 7.21-7.16 (m, 8H), 6.74 (s, 2H), 5.04 (br, 1H), 3.53 (s, 3H), 2.41 (s, 6H); $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$) $\delta$ 152.3, 145.5, 139.9, 139.5, 137.2, 135.6, 134.2, 131.7, 129.7, 129.3, 124.8, 124.5, 123.4, 122.3, 122.0, 118.1, 55.6, 21.4. HRMS, calculated for C$_{37}$H$_{28}$NaO$_2$S$_2$ (M+Na$^+$): 591.1423, found 591.1426.

2,6-Bis(3-(4-chlorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3c)

The title compound was prepared according to the general procedure and purified by
flash column chromatography to give the white solid, mg, 60% yield; m.p. 120-121 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90-7.87 (m, 2H), 7.68-7.65 (m, 2H), 7.41-7.36 (m, 8H), 7.20 (d, \(J = 8.0\) Hz, 4H), 6.77 (s, 2H), 4.98 (br, 1H), 3.61 (s, 3H); \(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.5, 145.3, 139.9, 139.2, 134.7, 134.5, 133.6, 133.2, 131.1, 128.8, 125.1, 124.8, 123.2, 122.4, 121.5, 118.2, 55.7. HRMS, calculated for C\(_{35}\)H\(_{22}\)Cl\(_2\)NaO\(_2\)S\(_2\) (M+Na\(^+\)): 631.0330, found 631.0334.

2,6-Bis(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3d)

![2,6-Bis(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3d)](image)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 62% yield; m.p. 141-143 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 6.0\) Hz, 2H), 7.69 (d, \(J = 6.0\) Hz, 2H), 7.42-7.38 (m, 4H), 7.27-7.24 (m, 4H), 7.08 (t, \(J = 6.0\) Hz, 4H), 6.80 (s, 2H), 4.99 (br, 1H), 3.62 (s, 3H); \(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.2 (d, \(J = 247.0\) Hz), 152.5, 145.3, 139.8, 139.4, 134.8, 134.4, 131.5 (d, \(J = 10.1\) Hz), 130.7 (d, \(J = 10.1\) Hz), 125.0, 124.8, 123.2, 122.4, 121.6, 118.2, 115.6 (d, \(J = 20.2\) Hz), 55.7. HRMS, calculated for C\(_{36}\)H\(_{24}\)F\(_2\)NaO\(_2\)S\(_2\) (M+Na\(^+\)): 613.1078, found 613.1062.

4-Methoxy-2,6-bis(3-(m-tolyl)benzo[b]thiophen-2-yl)phenol (3e)

![4-Methoxy-2,6-bis(3-(m-tolyl)benzo[b]thiophen-2-yl)phenol (3e)](image)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 36% yield. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 6.0\) Hz, 2H), 7.73 (d, \(J = 6.0\) Hz, 2H), 7.39-7.35 (m, 4H), 7.24 (t, \(J = 6.0\) Hz, 2H), 7.20 (s, 2H), 7.16 (d, \(J = 6.0\) Hz, 2H), 7.04 (d, \(J = 12.0\) Hz, 2H), 6.76 (d, \(J = 1.2\) Hz, 2H), 5.07 (br, 1H), 3.51 (s, 3H), 2.36 (s, 6H); \(^{13}\)C\(^{1}\)H NMR (151 MHz, CDCl\(_3\)) \(\delta\) 152.3, 145.4, 139.9, 139.6, 138.2, 135.7, 134.6, 134.4, 130.4, 128.6,
128.5, 127.0, 124.8, 124.5, 123.5, 122.2, 122.0, 118.2, 55.6, 21.6. HRMS, calculated for C$_{37}$H$_{29}$O$_2$S$_2$ (M+H$^+$): 569.1603, found 569.1603.

2,6-Bis(3-(3-chlorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3f)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 36% yield; m.p. 74-76 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.79-7.77 (m, 2H), 7.64-7.63 (m, 2H), 7.34-7.29 (m, 6H), 7.26 (d, $J = 6.0$ Hz, 2H), 7.23-7.20 (m, 2H), 7.07-7.05 (m, 2H), 6.73 (d, $J = 4.8$ Hz, 2H), 5.07 (br, 1H), 3.49 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 152.6, 145.4, 139.9, 139.2, 136.7, 136.7, 135.0, 135.0, 134.4, 134.4, 130.0, 129.7, 128.2, 127.9, 125.2, 124.9, 123.2, 122.4, 121.6, 121.5, 118.4, 66.0, 55.8. HRMS, calculated for C$_{35}$H$_{22}$Cl$_2$NaO$_2$S$_2$ (M+Na$^+$): 631.0330, found 631.0335.

2,6-Bis(3-(3-fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3g)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 43% yield; m.p. 127-128 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91-7.88 (m, 2H), 7.74-7.72 (m, 2H), 7.43-7.39 (m, 4H), 7.38-7.32 (m, 2H), 7.08-7.02 (m, 6H), 6.78 (s, 2H), 5.04 (br, 1H), 3.58 (s, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 162.8 (d, $J = 247.0$ Hz), 152.5, 145.3, 139.9, 139.1, 136.9 (d, $J = 10.1$ Hz), 134.9, 134.5, 130.2 (d, $J = 10.1$ Hz), 125.7, 125.0 (d, $J = 30.3$ Hz), 123.2, 122.4, 121.5, 118.3, 116.7 (d, $J = 22.2$ Hz), 114.7 (d, $J = 21.2$ Hz), 55.7. HRMS, calculated for C$_{35}$H$_{22}$F$_2$NaO$_2$S$_2$ (M+Na$^+$): 599.0921, found 599.0925.

2,6-Bis(3-(3,4-dichlorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3h)
The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 33% yield; m.p. 86-87 °C. \( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.90-7.89 (m, 2H), 7.67-7.66 (m, 2H), 7.48 (d, \( J = 6.0 \) Hz, 2H), 7.44-7.40 (m, 6H), 7.05 (dd, \( J = 8.4, 2.4 \) Hz, 2H), 6.76 (s, 2H), 5.02 (br, 1H), 3.62 (s, 3H); \( ^{13} \)C\{\( ^1 \)H\} NMR (151 MHz, CDCl\(_3\)) \( \delta \) 152.6, 145.2, 139.8, 138.9, 135.0, 134.8, 133.5, 132.7, 131.8, 131.4, 130.7, 129.1, 125.3, 125.0, 123.0, 122.5, 121.2, 118.3, 55.7. HRMS, calculated for C\(_{35}\)H\(_{20}\)Cl\(_4\)NaO\(_2\)S\(_2\) (M+Na\(^+\)): 698.9551, found 698.9553.

2,6-Bis(3-(3,4-difluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (3i)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 33% yield; m.p. 125-127 °C. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.92-7.88 (m, 2H), 7.71-7.67 (m, 2H), 7.45-7.40 (m, 4H), 7.22-7.12 (m, 4H), 7.03-6.99 (m, 2H), 6.82 (s, 2H), 5.00 (br, 1H), 3.66 (s, 3H); \( ^{13} \)C\{\( ^1 \)H\} NMR (101 MHz, CDCl\(_3\)) \( \delta \) 152.7, 150.3 (dd, \( J = 252.5, 10.1 \) Hz), 149.9 (dd, \( J = 252.5, 10.1 \) Hz), 145.2, 139.8, 139.1, 134.8, 133.8, 131.7 (d, \( J = 5.1 \) Hz), 126.0 (q, \( J = 3.0 \) Hz), 125.1 (d, \( J = 20.2 \) Hz), 123.0, 122.4, 121.4, 118.7 (d, \( J = 20.2 \) Hz), 118.3, 117.6 (d, \( J = 10.1 \) Hz), 55.7. HRMS, calculated for C\(_{35}\)H\(_{20}\)F\(_4\)NaO\(_2\)S\(_2\) (M+Na\(^+\)): 635.0733, found 635.0736.

4-Ethoxy-2,6-bis(3-phenylbenzo[b]thiophen-2-yl)phenol (3j)
The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 50% yield; m.p. 82-83 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87-7.85 (m, 2H), 7.72-7.69 (m, 2H), 7.38-7.32 (m, 10H), 7.26-7.23 (m, 4H), 6.73 (s, 2H), 5.01 (br, 1H), 3.69 (q, $J$ = 6.7 Hz, 2H), 1.21 (t, $J$ = 8.0 Hz, 3H); $^{13}$C{${^1}$H} NMR (101 MHz, CDCl$_3$) $\delta$ 151.6, 145.4, 139.9, 139.5, 135.7, 134.7, 134.5, 129.8, 128.6, 127.6, 124.8, 124.5, 123.4, 122.3, 121.8, 119.0, 64.0, 14.7. HRMS, calculated for C$_{36}$H$_{26}$NaO$_2$S$_2$ (M+Na$^+$): 577.1226, found 577.1230.

4-Ethoxy-2,6-bis(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (3k)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 41% yield; m.p. 213-215 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90-7.88 (m, 2H), 7.77-7.75 (m, 2H), 7.40-7.37 (m, 4H), 7.23-7.19 (m, 8H), 7.78 (t, $J$ = 2.0 Hz, 2H), 5.06 (br, 1H), 3.75 (q, $J$ = 8.0 Hz, 2H), 2.43 (s, 6H), 1.28-1.24 (t, $J$ = 8.0 Hz, 3H); $^{13}$C{${^1}$H} NMR (101 MHz, CDCl$_3$) $\delta$ 151.6, 145.4, 140.0, 139.6, 137.2, 135.6, 134.3, 131.7, 129.7, 129.4, 124.8, 124.5, 123.4, 122.3, 122.0, 119.0, 64.0, 21.4, 14.7. HRMS, calculated for C$_{38}$H$_{30}$NaO$_2$S$_2$ (M+Na$^+$): 605.1579, found 605.1585.

4-Ethoxy-2,6-bis(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)phenol (3l)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the white solid, 40% yield; m.p. 171-173 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90-7.88 (m, 2H), 7.68-7.66 (m, 2H), 7.42-7.37 (m, 4H), 7.26-7.22 (m, 4H), 7.10-7.04 (m, 4H), 6.79 (s, 2H), 4.96 (br, 1H), 3.81 (q, $J$ = 8.0 Hz, 2H), 1.31 (t, $J$ = 8.0 Hz, 3H); $^{13}$C{${^1}$H} NMR (101 MHz, CDCl$_3$) $\delta$ 162.2 (d, $J$ = 248.0 Hz, 6H), 151.6, 145.4, 140.0, 139.6, 137.2, 135.6, 134.3, 131.7, 129.7, 129.4, 124.8, 124.5, 123.4, 122.3, 122.0, 119.0, 64.0, 21.4, 14.7. HRMS, calculated for C$_{38}$H$_{30}$NaO$_2$S$_2$ (M+Na$^+$): 605.1579, found 605.1585.
Hz), 151.7, 145.2, 139.8, 139.4, 134.8, 134.4, 131.5 (d, J = 10.1 Hz), 130.7 (d, J = 10.1 Hz), 124.9 (d, J = 30.3 Hz), 123.2, 122.4, 121.6, 118.9, 115.7, 115.6 (d, J = 20.2 Hz), 64.1, 14.7. HRMS, calculated for C₃₆H₂₄F₂NaO₂S₂ (M+Na⁺): 613.1078, found 613.1082.

4-Methoxy-2-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (4a)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 72% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.87 (m, 1H), 7.77-7.75 (m, 1H), 7.39-7.37 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 4.0 Hz, 1H), 6.82-6.75 (m, 2H), 4.90 (br, 1H), 3.71 (s, 3H), 2.36 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 153.3, 147.1, 139.9, 139.7, 137.8, 135.3, 134.1, 131.2, 129.7, 129.5, 125.0, 124.8, 123.5, 122.3, 120.8, 117.2, 116.4, 116.4, 55.8, 21.4. HRMS, calculated for C₂₂H₁₈NaO₂S (M+Na⁺): 369.0920, found 369.0911.

4-Methoxy-2-(3-phenylbenzo[b]thiophen-2-yl)phenol (4b)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.90 (m, 1H), 7.79-7.77 (m, 1H), 7.43-7.36 (m, 7H), 6.87-6.84 (m, 1H), 6.81-6.77 (m, 2H), 4.89 (br, 1H), 3.71 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 153.2, 147.1, 139.9, 139.6, 135.5, 134.4, 134.3, 129.7, 128.9, 128.0, 125.0, 124.8, 123.5, 122.3, 120.6, 117.1, 116.5, 116.4, 55.8. HRMS, calculated forC₂₁H₁₆NaO₂S (M+Na⁺): 355.0763, found 355.0769.

2-(3-(4-Fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (4c)
The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 64% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.92-7.90\) (m, 1H), 7.73-7.71 (m, 1H), 7.43-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.08 (td, \(J = 8.0, 4.0\) Hz, 2H), 6.84-6.77 (m, 3H), 4.82 (br, 1H), 3.72 (s, 3H); \(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)) \(\delta 162.4\) (d, \(J = 248\) Hz), 153.3, 147.1, 139.9, 139.5, 134.5, 134.4, 131.4 (d, \(J = 10.1\) Hz), 130.3 (d, \(J = 10.1\) Hz), 125.0 (d, \(J = 20.2\) Hz), 123.2, 122.4, 120.3, 117.0, 116.5 (d, \(J = 10.1\) Hz), 115.9 (d, \(J = 20.2\) Hz), 55.8. HRMS, calculated for C\(_{21}\)H\(_{15}\)FNaO\(_2\)S (M+Na\(^+\)): 373.0670, found 373.0674.

**2-(3-(4-Chlorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (4d)**

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 50% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.91-7.88\) (m, 1H), 7.72-7.69 (m, 1H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 2H), 7.29-7.25 (m, 2H), 6.83-6.76 (m, 3H), 4.83 (br, 1H), 3.70 (s, 3H); \(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \(\delta 153.3, 147.1, 139.9, 139.3, 134.6, 134.4, 133.8, 132.8, 131.0, 129.1, 125.2, 125.0, 123.2, 122.4, 120.2, 117.0, 116.5, 116.4, 55.8. HRMS, calculated for C\(_{21}\)H\(_{15}\)ClNaO\(_2\)S (M+Na\(^+\)): 389.0373, found 389.0375.

**2-(3-(3-Fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (4e)**

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 62% yield. \(^1\)H NMR (400 MHz,
CDCl$_3$ $\delta$ 7.92-7.90 (m, 1H), 7.76-7.74 (m, 1H), 7.44-7.41 (m, 2H), 7.37-7.32 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.09-7.02 (m, 2H), 6.84-6.78 (m, 3H), 4.85 (br, 1H), 3.71 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 162.9 (d, $J = 246.0$ Hz), 153.3, 147.2, 139.8, 139.2, 136.5 (d, $J = 7.6$ Hz), 134.9, 134.3, 130.3 (d, $J = 9.1$ Hz), 125.5 (d, $J = 3.0$ Hz), 125.2, 125.0, 123.2, 122.4, 120.2, 117.0, 116.7 (d, $J = 10.6$ Hz), 116.5, 116.3, 114.9 (d, $J = 15.1$ Hz), 55.8. HRMS, calculated for C$_{21}$H$_{15}$FNaO$_2$S (M+Na$^+$): 373.0670, found 373.0675.

2-(3-(3,4-Difluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (4f)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 33% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.90 (m, 1H), 7.72-7.70 (m, 1H), 7.44-7.42 (m, 2H), 7.20-7.13 (m, 2H), 7.09-7.05 (m, 1H), 6.86-6.78 (m, 3H), 4.84 (br, 1H), 3.72 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 153.3, 150.4 (dd, $J = 241.6$, 15.1 Hz), 150.0 (dd, $J = 241.6$, 15.1 Hz), 147.1, 139.8, 139.1, 135.0, 133.5, 131.3 (d, $J = 4.5$ Hz), 126.0 (d, $J = 3.0$ Hz), 125.2 (d, $J = 30.2$ Hz), 123.0, 122.5, 120.0, 118.7 (d, $J = 15.1$ Hz), 117.6 (d, $J = 15.1$ Hz), 117.0, 116.5 (d, $J = 28.7$ Hz), 55.8. HRMS, calculated for C$_{21}$H$_{14}$F$_2$NaO$_2$S (M+Na$^+$): 391.0575, found 391.0578.

4-Methoxy-2-methyl-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (4g)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 87% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76-7.74 (m, 1H), 7.66-7.64 (m, 1H), 7.27-7.25 (m, 2H), 7.15-7.04 (m, 4H), 6.59 (s, 2H), 4.82 (br, 1H), 3.56 (s, 3H), 2.24 (s, 3H), 2.03 (s, 3H); $^{13}$C{$^1$H} NMR
(151 MHz, CDCl$_3$) $\delta$ 152.6, 145.5, 139.9, 139.8, 137.7, 135.4, 134.5, 131.2, 129.7, 129.5, 126.4, 125.0, 124.7, 123.6, 122.3, 120.0, 118.0, 113.7, 55.7, 21.4, 16.6. HRMS, calculated for C$_{23}$H$_{20}$NaO$_2$S (M+Na$^+$): 383.1076, found 383.1082.

2-(3-(4-Fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxy-6-methylphenol (4h)

![Chemical Structure](image)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 41% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.92-7.90 (m, 1H), 7.74 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.45-7.41 (m, 2H), 7.35-7.33 (m, 2H), 7.09-7.06 (m, 2H), 6.73 (d, $J = 3.0$ Hz, 1H), 6.67 (d, $J = 3.0$ Hz, 1H), 4.90 (br, 1H), 3.70 (s, 3H), 2.18 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 162.3 (d, $J = 248.0$ Hz), 152.6, 145.5, 139.9, 139.5, 134.8, 134.5, 131.4 (d, $J = 9.1$ Hz), 130.3 (d, $J = 3.0$ Hz), 126.3, 125.0 (d, $J = 30.2$ Hz), 123.3, 122.4, 119.5, 118.1, 115.9, 115.8, 113.6, 55.7, 16.5. HRMS, calculated for C$_{22}$H$_{17}$FNaO$_2$S (M+Na$^+$): 387.0826, found 387.0830.

2-(tert-Butyl)-4-methoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (4i)

![Chemical Structure](image)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 89% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.90 (m, 1H), 7.84 (t, $J = 4.0$ Hz, 1H), 7.42-7.40 (m, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 4.0$ Hz, 1H), 6.78 (dd, $J = 2.0$, 1.0 Hz, 1H), 5.08 (br, 1H), 3.75 (s, 3H), 2.37 (s, 3H), 1.29 (s, 9H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 152.5, 145.9, 140.1, 139.5, 138.3, 137.7, 135.5, 134.8, 131.1, 129.5, 129.3, 125.0, 124.8, 123.5, 122.4, 120.8, 115.3, 112.6, 55.7, 35.0, 29.2, 21.3. HRMS, calculated for C$_{26}$H$_{26}$NaO$_2$S (M+Na$^+$): 425.1546, found 425.1543.  

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2-\textit{tert-Butyl}-6-(3-(4-fluorophenyl)benzo[\textit{b}]thiophen-2-yl)-4-methoxyphenol (4j)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 79\% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.93-7.92 (m, 1H), 7.77-7.76 (m, 1H), 7.44-7.42 (m, 2H), 7.32-7.30 (m, 2H), 7.06 (t, $J$ = 6.0 Hz, 2H), 6.91 (d, $J$ = 6.0 Hz, 1H), 6.73 (d, $J$ = 3.0 Hz, 1H), 5.04 (br, 1H), 3.75 (s, 3H), 1.28 (s, 9H); $^{13}$C\{$^1$H\} NMR (151 MHz, CDCl$_3$) $\delta$ 162.4 (d, $J$ = 248.0 Hz), 152.5, 145.8, 140.0, 139.3, 138.3, 135.1, 134.6, 131.2 (d, $J$ = 7.6 Hz), 130.1 (d, $J$ = 4.5 Hz), 125.1, 124.9, 123.2, 122.5, 120.2, 115.8 (d, $J$ = 21.1 Hz), 115.4, 112.5, 55.7, 35.0, 29.2. HRMS, calculated for C$_{25}$H$_{23}$FNaO$_2$S (M+Na$^+$): 429.1295, found 429.1298.

2-Chloro-4-methoxy-6-(3-(p-tolyl)benzo[\textit{b}]thiophen-2-yl)phenol (4k)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 56\% yield. $^1$H NMR (400 MHz, DMSO-\textit{d$_6$}) $\delta$ 9.06 (br, 1H), 8.03 (d, $J$ = 8.0 Hz, 1H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.45-7.37 (m, 2H), 7.21 (s, 4H), 6.97 (d, $J$ = 4.0 Hz, 1H), 6.59 (d, $J$ = 4.0 Hz, 1H), 3.54 (s, 3H), 2.32 (s, 3H); $^{13}$C\{$^1$H\} NMR (151 MHz, DMSO-\textit{d$_6$}) $\delta$ 152.1, 145.4, 139.6, 139.5, 137.1, 132.2, 130.1, 129.6, 125.3, 125.0, 124.5, 123.3, 122.8, 122.6, 117.0, 115.8, 56.0, 21.3. HRMS, calculated for C$_{22}$H$_{17}$ClNaO$_2$S (M+Na$^+$): 403.0530, found 403.0524.

2-Methoxy-4-methyl-6-(3-(p-tolyl)benzo[\textit{b}]thiophen-2-yl)phenol (4l)

S16
The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 63% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85-7.83 (m, 1H), 7.71-7.69 (m, 1H), 7.33-7.30 (m, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.62 (d, $J = 12$ Hz, 2H), 5.50 (br, 1H), 3.79 (s, 3H), 2.33 (s, 3H), 2.18 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 146.6, 141.5, 140.0, 139.9, 136.7, 135.1, 134.8, 132.6, 129.8, 129.1, 128.8, 124.4, 124.4, 124.2, 123.4, 122.1, 120.1, 111.8, 56.0, 21.4, 21.1. HRMS, calculated for C$_{23}$H$_{20}$NaO$_2$S (M+Na$^+$): 383.1076, found 383.1067.

5-Fluoro-4-methoxy-2-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (4m)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 74% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.90 (dd, $J = 6.0$, 3.0 Hz, 1H), 7.77 (d, $J = 6.0$, 3.0 Hz, 1H), 7.43-7.40 (m, 2H), 7.26-7.21 (m, 4H), 6.91 (d, $J = 6.0$ Hz, 1H), 6.64 (d, $J = 12.0$ Hz, 1H), 5.08 (br, 1H), 3.77 (s, 3H), 2.39 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 153.3 (d, $J = 248.0$ Hz), 147.4 (d, $J = 15.1$ Hz), 141.6 (d, $J = 15.1$ Hz), 139.7 (d, $J = 30.2$ Hz), 138.0, 135.7, 133.0, 131.0, 129.8, 129.4, 125.1, 124.9, 123.6, 122.3, 116.8, 115.3 (d, $J = 4.5$ Hz), 105.2 (d, $J = 15.1$ Hz), 57.0, 21.4. HRMS, calculated for C$_{22}$H$_{17}$FNaO$_2$S (M+Na$^+$): 387.0826, found 387.0832.

5-Fluoro-2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxyphenol (4n)
The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 71% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93-7.89 (m, 1H), 7.73-7.71 (m, 1H), 7.44-7.41 (m, 2H), 7.33-7.29 (m, 2H), 7.09 (t, $J = 10.0$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.66 (d, $J = 12.0$ Hz, 1H), 5.17 (br, 1H), 3.76 (s, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 162.4 (d, $J = 247.0$ Hz), 153.5 (d, $J = 248.0$ Hz), 147.6 (d, $J = 10.1$ Hz), 141.7 (d, $J = 10.1$ Hz), 139.6 (d, $J = 20.2$ Hz), 134.9, 134.3, 131.4 (d, $J = 10.1$ Hz), 130.2 (d, $J = 10.1$ Hz), 125.3, 125.0, 123.3, 122.4, 116.9 (d, $J = 3.0$ Hz), 116.0 (d, $J = 20.2$ Hz), 115.0 (d, $J = 10.1$ Hz), 105.1 (d, $J = 20.2$ Hz), 57.1. HRMS, calculated for C$_{21}$H$_{14}$F$_2$NaO$_2$S (M+Na$^+$): 391.0575, found 391.0580.

4-Ethoxy-2-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (4o)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 51% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89-7.86 (m, 1H), 7.77-7.75 (m, 1H), 7.39-7.37 (m, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 4.0$ Hz, 1H), 6.82-6.73 (m, 2H), 4.89 (br, 1H), 3.92 (q, $J = 8.0$ Hz, 2H), 2.36 (s, 3H), 1.36 (t, $J = 4.0$ Hz, 3H); $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 152.6, 147.1, 140.0, 139.7, 137.8, 135.3, 134.2, 131.2, 129.7, 129.5, 124.9, 124.7, 123.5, 122.3, 120.8, 117.3, 117.2, 117.1, 64.1, 21.4, 14.9. HRMS, calculated for C$_{23}$H$_{20}$NaO$_2$S (M+Na$^+$): 383.1076, found 383.1079.

4-Ethoxy-2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)phenol (4p)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 65% yield. $^1$H NMR (400 MHz,
CDCl₃ δ 7.93-7.89 (m, 1H), 7.74-7.71 (m, 1H), 7.43-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.09-7.05 (m, 2H), 6.83-6.76 (m, 3H), 4.86 (br, 1H), 3.93 (q, J = 6.7 Hz, 2H), 1.37 (t, J = 8.0 Hz, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.4 (d, J = 246.0 Hz), 152.6, 147.1, 139.9, 139.5, 134.5, 131.4, 131.3, 130.3, 125.1, 124.9, 123.2, 122.4, 120.3, 117.3 (d, J = 10.1 Hz), 117.0, 115.9 (d, J = 20.2 Hz), 64.1, 14.8. HRMS, calculated for C₂₂H₁₇FNaO₂S (M+Na⁺): 387.0826, found 387.0831.

4-Methoxy-2-(3-phenylbenzo[b]thiophen-2-yl)-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5a)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 70% yield; m.p. 147-148 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.85-7.83 (m, 2H), 7.72-7.70 (m, 2H), 7.36-7.32 (m, 8H), 7.20-7.15 (m, 5H), 6.75-6.70 (m, 2H), 5.03 (br, 1H), 3.49 (s, 3H), 2.38 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 152.4, 145.5, 140.0, 139.6, 139.5, 137.3, 135.8, 135.7, 134.8, 134.7, 134.1, 131.6, 129.9, 129.7, 129.5, 129.6, 127.6, 124.9, 124.6, 123.5, 123.4, 122.3, 122.0, 121.9, 118.2, 118.2, 55.6, 21.4. HRMS, calculated for C₃₆H₂₆NaO₂S₂ (M+Na⁺): 577.1266, found 577.1257.

2-(3-(4-Fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5b)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 74% yield; m.p. 127-129 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.90-7.87 (m, 2H), 7.76-7.75 (m, 1H), 7.71-7.69 (m, 1H), 7.41-7.37 (m, 4H), 7.26-7.20 (m, 6H), 7.07 (t, J = 9.0 Hz, 2H), 6.85 (d, J = 3.6 Hz, 1H), 6.76 (d, J = 3.6 Hz, 1H), 5.07 (br, 1H), 3.59 (s, 3H), 2.44 (s, 3H); ¹³C{¹H} NMR
(151 MHz, CDCl$_3$) δ 162.1 (d, $J = 248.0$ Hz), 152.4, 145.5, 139.9 (d, $J = 4.5$ Hz), 139.7, 139.4, 137.5, 135.9, 134.9, 134.6, 133.8, 131.6, 131.5, 130.9 (d, $J = 3.0$ Hz), 129.7, 129.5, 125.0, 124.9, 124.7, 123.6, 123.2, 122.4, 122.3, 121.9, 121.8, 118.3, 118.2, 115.6 (d, $J = 15.1$ Hz), 55.7, 21.4.

HRMS, calculated for C$_{36}$H$_{25}$FNaO$_2$S$_2$ (M+Na$^+$): 595.1172, found 595.1172.

2-(3-(4-Chlorophenyl)benzo[b]thiophen-2-yl)-4-methoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5c)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 33% yield; m.p. 162-165 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83-7.79 (m, 2H), 7.69-7.67 (m, 1H), 7.63-7.60 (m, 1H), 7.33-7.26 (m, 6H), 7.17-7.11 (m, 6H), 6.77 (d, $J = 4.0$ Hz, 1H), 6.66 (d, $J = 4.0$ Hz, 1H), 4.99 (br, 1H), 3.51 (s, 3H), 2.37 (s, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) δ 152.5, 145.5, 139.9, 139.7, 139.2, 137.5, 136.0, 135.2, 134.5, 133.7, 133.5, 133.4, 131.5, 131.2, 129.7, 129.5, 128.8, 125.0, 124.9, 124.7, 123.6, 123.1, 122.4, 122.3, 121.9, 121.7, 118.3, 118.2, 55.7, 21.4. HRMS, calculated for C$_{36}$H$_{25}$ClNaO$_2$S$_2$ (M+Na$^+$): 611.0877, found 611.0872.

2-(3-(3-Fluorophenyl)benzo[b]thiophen-2-yl)-4-methoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5d)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 67% yield; m.p. 122-123 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83-7.80 (m, 2H), 7.73 (t, $J = 4.0$ Hz, 1H), 7.69-7.66 (m, 1H), 7.34-7.27 (m, 5H), 7.20-7.15 (m, 4H), 7.05-6.95 (m, 3H), 6.79 (d, $J = 4.0$ Hz, 1H), 6.69 (d, $J = 3.2$ Hz, 1H), 5.06 (br, 1H), 3.49 (s, 3H), 2.36 (s, 3H); $^{13}$C{$^1$H} NMR

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(101 MHz, CDCl₃) δ 162.9 (d, J = 247.0 Hz), 152.6, 145.5, 140.0 (d, J = 5.1 Hz), 139.6, 139.2, 137.6, 137.3, 137.3, 136.0, 135.6, 134.4, 134.3, 133.8, 131.5, 130.1 (d, J = 9.1 Hz), 129.7, 129.6, 125.8, 125.8, 125.0, 125.0, 124.7, 124.7, 123.6, 123.2, 122.4, 122.1, 121.7, 118.3 (d, J = 4.0 Hz), 116.9 (d, J = 22.2 Hz), 114.5 (d, J = 20.2 Hz), 55.7, 21.4. HRMS, calculated for C₃₆H₂₅F₇NaO₂S₂ (M+Na⁺): 595.1172, found 595.1165.

2-(3-(3-Chlorophenyl)benzo[b]thiophen-2-yl)-4-methoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5e)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 28% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.80 (m, 2H), 7.73-7.70 (m, 1H), 7.67-7.65 (m, 1H), 7.33-7.26 (m, 5H), 7.18-7.16 (m, 4H), 7.04-6.95 (m, 3H), 6.78 (d, J = 4.0 Hz, 1H), 6.99 (d, J = 4.0 Hz, 1H), 5.04 (br, 1H), 3.48 (s, 3H), 2.36 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 164.1, 161.7, 152.6, 145.5, 140.0, 139.7, 139.2, 137.6, 137.3, 136.0, 135.6, 134.4, 134.3, 133.8, 131.5, 130.1, 130.0, 129.7, 129.6, 125.8, 125.0, 124.7, 123.6, 123.2, 122.4, 122.1, 121.7, 118.3, 117.0, 116.8, 114.6, 114.4, 55.7, 21.4. HRMS, calculated for C₃₆H₂₅ClNaO₂S₂ (M+Na⁺): 611.0877, found 611.0878.

2-(3-(3,4-Difluorophenyl)benzo[b]thiophen-2-yl)-4-methoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5f)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.87 (m, 2H), 7.79-7.76 (m, 1H), 7.70-7.67 (m, 1H), 7.43-7.39 (m, 4H), 7.26-7.21 (m, 4H), 7.17-7.09 (m, 2H), 7.03-7.00 (m, 1H), 6.89 (d, J = 4.0 Hz, 1H),
6.76 (d, J = 4.0 Hz, 1H), 5.07 (br, 1H), 3.63 (s, 3H), 2.44 (s, 3H); $^{13}$C-$^1$H NMR (101 MHz, CDCl$_3$) δ 152.5, 150.3 (dd, J = 252.2, 10.1 Hz), 149.8 (dd, J = 242.2, 10.1 Hz), 145.4, 139.9 (d, J = 9.1 Hz), 139.7, 139.1, 137.7, 136.0, 135.7, 133.5, 133.4, 132.0 (q, J = 3.4 Hz), 131.3, 129.6 (d, J = 3.0 Hz), 126.1 (d, J = 3.4 Hz), 125.0 (d, J = 7.1 Hz), 124.7 (d, J = 3.0 Hz), 123.6, 122.9, 122.4 (d, J = 5.1 Hz), 122.0, 121.5, 118.7 (d, J = 17.2 Hz), 118.3 (d, J = 16.2 Hz), 117.3 (d, J = 17.2 Hz), 55.7, 21.3. HRMS, calculated for C$_{36}$H$_{24}$F$_2$NaO$_2$S$_2$ (M+Na$^+$): 613.1078, found 613.1067.

4-Ethoxy-2-(3-phenylbenzo[b]thiophen-2-yl)-6-(3-(p-tolyl)benzo[b]thiophen-2-yl) phenol (5g)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 54% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82-7.80 (m, 2H), 7.72-7.69 (m, 2H), 7.36-7.30 (m, 7H), 7.25 (dd, J = 8.0, 4.0 Hz, 2H), 7.15-7.13 (m, 4H), 6.76 (d, J = 4.0 Hz, 1H), 6.71 (d, J = 3.2 Hz, 1H), 5.02 (br, 1H), 3.67 (q, J = 6.7 Hz, 2H), 2.36 (s, 3H), 1.19 (t, J = 8.0 Hz, 3H); $^{13}$C-$^1$H NMR (101 MHz, CDCl$_3$) δ 151.7, 145.5, 140.0, 139.7, 139.6, 137.3, 135.7, 135.7, 134.9, 134.8, 134.2, 131.7, 130.0, 129.8, 129.5, 128.6, 127.6, 124.9, 124.6, 123.5, 123.4, 122.3, 122.0, 122.0, 119.1, 119.1, 119.1, 64.1, 21.5, 14.8. HRMS, calculated for C$_{37}$H$_{28}$NaO$_2$S$_2$ (M+Na$^+$): 591.1423, found 591.1419.

4-Ethoxy-2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5h)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red liquid, 63% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.90-7.87 (m, 2H), 7.75 (dd, J = 7.2, 1.8 Hz, 1H), 7.70 -7.68 (m, 1H),
7.42-7.37 (m, 4H), 7.24-7.19 (m, 6H), 7.06 (t, J = 6.0 Hz, 2H), 6.84 (d, J = 3.0 Hz, 1H), 6.74 (d, J = 3.0 Hz, 1H), 5.02 (br, 1H), 3.79 (q, J = 6.0 Hz, 2H), 2.43 (s, 3H), 1.29 (t, J = 6.0 Hz, 3H); $^{13}$C{$^{1}$H} NMR (151 MHz, CDCl$_3$) $\delta$ 162.1 (d, J = 248.0 Hz), 151.7, 145.4, 139.9 (d, J = 6.0 Hz), 139.6, 139.4, 137.4, 135.8, 134.9, 134.5, 133.8, 131.5, 131.5, 130.8 (d, J = 4.5 Hz), 129.7, 129.4, 124.9, 124.8, 124.6, 123.5, 123.1, 122.3, 122.3, 121.9, 121.7, 119.0, 118.9, 115.5 (d, J = 21.1Hz), 64.0, 21.4, 14.7. HRMS, calculated for C$_{37}$H$_{27}$ClNaO$_2$S$_2$ (M+Na$^+$): 609.1329, found 609.1330.

2-(3-(4-Chlorophenyl)benzo[b]thiophen-2-yl)-4-ethoxy-6-(3-(p-tolyl)benzo[b]thiophen-2-yl)phenol (5i)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the red solid, 39% yield; m.p. 174-175 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (t, J = 6.0 Hz, 2H), 7.75-7.67 (m, 2H), 7.41-7.32 (m, 6H), 7.23-7.17 (m, 6H), 6.83 (d, J = 2.8 Hz, 1H), 6.72 (d, J = 4.0 Hz, 1H), 5.02 (br, 1H), 3.78 (q, J = 6.7 Hz, 2H), 2.43 (s, 3H), 1.30-1.27 (t, J = 6.0 Hz, 3H); $^{13}$C{$^{1}$H} NMR (151 MHz, CDCl$_3$) $\delta$ 151.7, 145.3, 139.9, 139.6, 139.1, 137.5, 135.9, 135.2, 134.3, 133.7, 133.4, 133.3, 131.4, 131.2, 129.6, 129.4, 128.7, 124.9, 124.9, 124.6, 123.5, 123.0, 122.3, 122.3, 121.8, 121.6, 119.0, 118.9, 64.0, 21.4, 14.7. HRMS, calculated for C$_{37}$H$_{27}$ClNaO$_2$S$_2$ (M+Na$^+$): 625.1033, found 625.1026.

3,3'-Diphenyl-2,2'-bibenzo[b]thiophene

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.81 (d, J = 12.0 Hz, 2H), 7.56 (d, J = 6.0 Hz, 2H), 7.35 (td, J = 7.5, 1.2 Hz, 2H), 7.30 (td, J = 7.5, 1.2 Hz, 2H), 7.25-7.20 (m, 6H), 7.04-7.02 (m, 4H); $^{13}$C{$^{1}$H} NMR (151 MHz, CDCl$_3$) $\delta$ 140.3, 139.6, 136.7, 134.7,
131.7, 129.9, 128.4, 127.1, 124.9, 124.5, 123.6, 122.1. C$_{28}$H$_{18}$Na$_2$ (M+Na$^+$):
441.0742, found 441.0732.

References:
5. $^1$H NMR and $^{13}$C NMR copies of products
$^1$H NMR (400 MHz, CDCl$_3$)

19F NMR (376 MHz, CDCl$_3$)