Silver-Mediated Oxidative Annulation of N-Arylthio Succinimides with Alkynes: Direct Access to Benzo[b]thiophenes

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SUPPORTING INFORMATION

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General Experimental

All the reactions were performed in an oven-dried Schlenk flask / pressure tubes under an argon atmosphere. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 Mesh or 230-400 Mesh silica gel eluting with hexane and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber.

Proton, carbon, and fluorine nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR and ¹⁹F NMR) were recorded based on the resonating frequencies as follows: (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz; ¹⁹F NMR, 376 MHz) and (¹H NMR, 500 MHz; ¹³C NMR, 126 MHz; ¹⁹F NMR, 470 MHz) having the solvent resonance as internal standard (¹H NMR, CHCl₃ at 7.26 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m =multiplet), coupling constants, J, in (Hz), and integration. Data for ¹³C NMR, ¹⁹F NMR were reported in terms of chemical shift (ppm). IR spectra were reported in cm⁻¹. High resolution mass spectra were obtained in ESI mode. LC-MS spectra were obtained with ionization voltage of 70ev; data was reported in theform of m/z (intensity relative to base peak = 100). Elemental (C, H, N) analysis were carried out using FLASH EA 1112 analyzer. Melting points were determined by electro-thermal heating and are uncorrected.

Materials: Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Following the standerd procedures, the solvents were dried and stored over molecular sieves under inert gas (nitrogen, argon) atmosphere.¹ Diphenyl acetylene (2a), 1-phenyl-1-propyne (2h), 1-phenyl-1-hexyne (2i), AgSbF₆, AgBF₄, AgoTf, and KPF₆ were purchased from Sigma Aldrich Ltd, and used as received. Analytical and spectral data of all the known compounds are exactly matching with the reported values.
**Experimental Procedures:**

**Preparation of symmetrical diaryl alkynes (2b–g); General Procedure (GP–1):**

To a mixture of PdCl₂(PPh₃)₂ (6.0 mol %), CuI (10 mol %) and aryl iodide (1.0 mmol) in benzene (5.0 mL) was added DBU (6.0 mmol) followed by trimethylsilyl acetylene (0.5 mmol) and de-ionized water (40 mol %) under an argon atmosphere at rt. The resulting mixture was heated at 80 °C for 18 h in the absence of light. Upon completion, the reaction mixture was cooled to rt and diluted with diethyl ether. The organic layer was washed with water, 10% HCl (2 × 5.0 mL), and brine and dried over Na₂SO₄. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate.

Following this procedure, compounds 2b–g were prepared.² Analytical and spectral data of these compounds are exactly matching with the reported values.

**Preparation of unsymmetrical alkynes (2j–n); General Procedure (GP–2):**

To a mixture of PdCl₂(PPh₃)₂ (2.0 mol %), CuI (4.0 mol %) and aryl iodide (1.0 mmol) in THF (5.0 mL) was added Et₃N (3.0 mmol) followed by aryl/alkyl bearing acetylenes (1.0 mmol) under an argon atmosphere at rt. The resulting mixture was heated at 60 °C for 16 h in the absence of light. Upon completion, the reaction mixture was cooled to rt and diluted with diethyl ether. The organic layer was washed with water, 10% HCl (2 × 5.0 mL), and brine.
and dried over Na₂SO₄. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane /ethyl acetate.

Following this procedure, compounds 2j-n were prepared.³ Analytical and spectral data of these compounds are exactly matching with the reported values.

Preparation of N-arylthio succinimide (1): General Procedure (GP–3):⁴

To a solution of N-chlorosuccinimide (NCS) (1.0 equiv) in CH₂Cl₂ (5.0 mL for 2.0 mmol) was added thiophenols (1’, 1.0 equiv) and Et₃N (1.0 equiv) drop wise under an argon atmosphere at 0 °C. The resulting mixture was stirred for 12 h at rt. After completion, the reaction mixture was quenched with saturated aqueous NH₄Cl solution. The organic layer was separated; the aqueous layer was extracted with CH₂Cl₂ (2 times). The combined extracts were washed with brine. The organic layer was dried over Na₂SO₄. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane /ethyl acetate (4:1).

Following this procedure, the N–arylthio succinamides 1a, 1b, 1f, 1g and 1i were prepared.⁴ Analytical and spectral data of these compounds are exactly matching with the reported values.
1-(4-tert-Butylphenylthio) pyrrolidine-2,5-dione (1c):

1c colorless solid (765 mg, 48%); mp = 138–139 °C; Rf = 0.38 (7:3 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) δ 7.59 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.77 (s, 4H), 1.27 (s, 9H); 13C NMR (101 MHz, CDCl3) δ 176.4, 153.7, 133.2, 130.3, 126.3, 34.7, 31.0, 28.5; IR (KBr) νmax 2958, 1736, 1435, 1298, 1139, 816 cm⁻¹; HRMS (ESI) for C14H18NO2S (M+H)+: calcd. 264.1058, found 264.1058.

1-(4-iso-Propylphenylthio) pyrrolidine-2,5-dione (1d):

1d colorless solid (812 mg, 51%); mp = 86–87 °C; Rf = 0.43 (7:3 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) δ 7.59 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 2.92–2.81 (m, 1H), 2.76 (s, 4H), 1.19 (d, J = 6.8 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 176.5, 151.5, 133.6, 130.5, 127.4, 33.9, 28.5, 23.6; IR (KBr) νmax 2958, 1720, 1599, 1353, 1139, 816 cm⁻¹; HRMS (ESI) for C13H16NO2S (M+H)+: calcd. 250.0902, found 250.0900.

1-(4-Fluorophenylthio) pyrrolidine-2,5-dione (1e):

1e colorless solid (1.9 g, 54%); mp = 162–164 °C; Rf = 0.26 (7:3 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) δ 7.74–7.68 (m, 2H), 7.04–6.97 (m, 2H), 2.77 (s, 4H); 13C NMR (101 MHz, CDCl3) δ 176.2, 163.9 (d, J = 252 Hz), 136.5 (d, J = 9 Hz), 129.0 (d, J = 3 Hz), 116.4 (d, J = 22 Hz), 28.5; 19F NMR (470 MHz, CDCl3) δ –108.60; IR (KBr) νmax 3090, 1709, 1479, 1216, 1139 cm⁻¹; HRMS (ESI) for C10H9FNO2S (M+H)+: calcd. 226.0338, found 226.0337.

1-(o-Tolylthio) pyrrolidine-2,5-dione (1h):

1h colorless solid (2.2 g, 61%); mp = 99–100 °C; Rf = 0.33 (7:3 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 8.0 Hz, 1H), 7.23–7.16 (m, 2H), 7.15–7.08 (m, 1H), 2.79 (s, 4H), 2.56 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 176.4, 139.2, 133.0, 131.7, 130.6, 129.4, 126.7, 28.5, 20.2; IR (KBr) νmax 3073, 1726, 1293, 1134, 745 cm⁻¹; HRMS (ESI) for C11H12NO2S (M+H)+: calcd. 222.0589, found 222.0582.
Reaction optimization.

Table 1: Screening of Catalyst, Oxidant and Solvents.

<table>
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<tr>
<th>Entry</th>
<th>Catalyst (30 mol %)</th>
<th>Oxidant (50 mol %)</th>
<th>Solvent (0.5 mL)</th>
<th>yield (%)$^b$</th>
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<tr>
<td>1</td>
<td>AgCl</td>
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<td>DCE</td>
<td>NR</td>
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<tr>
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<td>DCE</td>
<td>56</td>
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<tr>
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</tr>
<tr>
<td>7</td>
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<td>K$_2$S$_2$O$_8$</td>
<td>THF</td>
<td>NR</td>
</tr>
<tr>
<td>8</td>
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<td>K$_2$S$_2$O$_8$</td>
<td>Ph–Cl</td>
<td>NR</td>
</tr>
<tr>
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<td>AgSbF$_6$</td>
<td>K$_2$S$_2$O$_8$</td>
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<tr>
<td>10</td>
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<tr>
<td>11</td>
<td>AgSbF6</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$NO$_2$</td>
<td>24</td>
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$^a$Reaction conditions: 1a (0.1 mmol), 2a (0.1 mmol). $^b$Conversion based on crude $^1$H NMR of starting material. NR = no reaction
Comparison of structures 3a, X, and 3i.

Table 2: The H\textsuperscript{a/b/c} labeled \textsuperscript{1}H-NMR data for compound 3a, Y, and 3i.

<table>
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<th>S.No</th>
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<th>H\textsuperscript{\textit{i}}</th>
<th>ppm</th>
<th>Splitting</th>
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<td>3a</td>
<td>H\textsuperscript{a}</td>
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<td>singlet</td>
</tr>
<tr>
<td>2</td>
<td>X</td>
<td>H\textsuperscript{b}</td>
<td>7.65</td>
<td>singlet</td>
</tr>
<tr>
<td>3</td>
<td>3i</td>
<td>H\textsuperscript{c}</td>
<td>7.37-7.44</td>
<td>multiplet</td>
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</table>

The reaction of N-arylthio succinimide (1) with unactivated alkynes (2); General Procedure (GP–4):

The N-arylthio succinimide (1, 0.5 mmol), diphenylacetylene (2a, 89 mg, 0.5 mmol) and K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (68 mg, 0.25 mmol) were taken in a Schlenk tube. Subsequently, AgSbF\textsubscript{6} (52 mg, 30 mol %) was introduced into the flask in a glove box. Solvent 1,2-dichloroethane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 80 °C for 6–8 h. Upon completion, the mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2} (10 mL) and filtered over a small pad of Celite. Solvent was evaporated under the reduced pressure and the crude residue was purified through silica gel column chromatography using n-hexane eluent to give the desired product.

6-Methyl-2,3-diphenylbenzo[b]thiophene (3a):

3a colorless solid (96 mg, 64%); mp = 165–167 °C; R\textsubscript{f} = 0.46 (hexane); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.67 (s, 1H), 7.47 (d, \(J = 8.4\) Hz, 1H), 7.42–7.35 (m, 3H), 7.35–7.28 (m, 4H), 7.25–7.20 (m, 3H), 7.15 (dd, \(J = 8.4\) & 1.2 Hz, 1H), 2.48 (s, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 139.1, 138.8, 138.3, 135.7, 134.5, 134.4, 133.0, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 126.1, 123.0, 121.9, 21.5; IR (KBr) \(\nu_{\text{max}}\) 2915, 1589, 1534, 812, 684 cm\textsuperscript{-1}; HRMS (ESI) for C\textsubscript{2}H\textsubscript{16}NaS (M+Na\textsuperscript{+}): calcd. 323.0870, found 323.0876.
6-Methoxy-2,3-diphenylbenzo[b]thiophene (3b):

3b Pale yellow solid (79 mg, 50%); mp = 149–150 °C; Rf = 0.16 (hexane);

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.45 (d, \( J = 8.8 \) Hz, 1H), 7.40–7.28 (m, 8H), 7.23–7.17 (m, 3H), 6.94 (dd, \( J = 9.0 \) & 2.2 Hz, 1H), 3.84 (s, 3H); \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.6, 140.1, 136.8, 135.7, 135.0, 134.4, 132.8, 130.3, 129.4, 128.6, 128.3, 127.4, 127.3, 124.0, 114.4, 104.5, 55.6; IR (KBr) \( \nu_{\text{max}} \) 3019, 1589, 1457, 1276, 1068, 739 cm\(^{-1}\); HRMS (ESI) for C\(_{22}\)H\(_{18}\)NaOS (M+Na): calcd. 339.0820, found 339.0822.

6-tert-Butyl-2,3-diphenylbenzo[b]thiophene (3c):

3c Colorless solid (131 mg, 76%); mp = 145–146 °C; Rf = 0.5 (hexane); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.87 (s, 1H), 7.53 (d, \( J = 8.4 \) Hz, 1H), 7.42–7.29 (m, 8H), 7.25–7.20 (m, 3H), 1.40 (s, 9H); \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.0, 139.0, 138.8, 138.7, 135.7, 134.4, 132.9, 130.4, 129.6, 128.6, 128.3, 127.5, 127.3, 122.8, 122.7, 118.2, 34.9, 31.5; IR (KBr) \( \nu_{\text{max}} \) 2953, 1594, 1441, 1260, 816 cm\(^{-1}\); HRMS (ESI) for C\(_{24}\)H\(_{22}\)NaS (M+Na): calcd. 365.1340, found 365.1340.

6-iso-Propyl-2,3-diphenylbenzo[b]thiophene (3d):

3d Colorless solid (118 mg, 72%); mp = 123–124 °C; Rf = 0.4 (hexane); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.72 (d, \( J = 0.4 \) Hz, 1H), 7.51 (d, \( J = 8.4 \) Hz, 1H), 7.43–7.35 (m, 3H), 7.34–7.29 (m, 4H), 7.24–7.19 (m, 4H), 3.10–2.98 (m, 1H), 1.32 (d, \( J = 6.8 \) Hz, 6H); \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 145.7, 139.1, 138.6, 135.7, 134.4, 133.0, 130.4, 129.6, 128.6, 128.3, 127.5, 127.3, 123.8, 123.1, 119.2, 34.3, 24.2; IR (KBr) \( \nu_{\text{max}} \) 2958, 1594, 1430, 1024, 827 cm\(^{-1}\); HRMS (ESI) for C\(_{23}\)H\(_{21}\)S (M+H): calcd. 329.1364, found 329.1366.

6-Fluoro-2,3-diphenylbenzo[b]thiophene (3e):

3e Colorless solid (92 mg, 60%); mp = 162–163 °C; Rf = 0.44 (hexane); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57–7.49 (m, 2H), 7.43–7.35 (m, 3H), 7.33–7.27 (m, 4H), 7.26–7.22 (m, 3H), 7.07 (td, \( J = 9.0 \) & 2.4 Hz, 1H); \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 160.6 (d, \( J = 245 \) Hz), 139.6 (d, \( J = 10 \) Hz), 139.0 (d, \( J = 4 \) Hz), 137.4, 135.3, 134.0, 132.7, 130.3, 129.5, 128.7, 128.4, 127.8, 127.5, 124.4 (d, \( J = 9 \) Hz), 113.3 (d, \( J = 24 \) Hz), 108.1 (d, \( J = 25 \) Hz); \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) –117.28; IR (KBr) \( \nu_{\text{max}} \) 1589, 1479, 1232, 909, 695 cm\(^{-1}\). HRMS (ESI) for C\(_{26}\)H\(_{17}\)FNaS (M+Na): calcd. 327.0620, found 327.0620.
6-Chloro-2,3-diphenylbenzo[b]thiophene (3f):

3f colorless crystalline solid (63 mg, 39%); mp = 188–189 °C; Rf = 0.56 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.42–7.36 (m, 3H), 7.33–7.28 (m, 6H), 7.27–7.23 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.0, 139.8, 139.4, 135.1, 133.8, 132.9, 130.6, 130.3, 129.5, 128.8, 128.4, 127.9, 127.6, 125.3, 124.2, 121.6; IR (KBr) νmax 1484, 1441, 1101, 789, 690 cm⁻¹; HRMS (ESI) for C₂₀H₁₄ClS (M+H)+: calcd. 321.0505, found 321.0505.

2,3-Diphenylbenzo[b]thiophene (3g):

3g colorless crystalline solid (52 mg, 36%); mp = 127–128 °C; Rf = 0.5 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.89–7.84 (m, 1H), 7.61–7.56 (m, 1H), 7.41–7.29 (m, 9H), 7.26–7.21 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 139.5, 138.8, 135.5, 134.2, 133.2, 130.4, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.3, 122.0; IR (KBr) νmax 1435, 1063, 750, 695 cm⁻¹; HRMS (ESI) for C₂₀H₁₅S (M+H)+: calcd. 287.0894, found 287.0887.

7-Methyl-2,3-diphenylbenzo[b]thiophene (3h) and 4-Methyl-2,3-diphenylbenzo[b]thiophene (3h′):

Inseparable mixture of 3h/3h′ colorless crystalline solid (70:30) (69 mg, 46%); mp = 134–135 °C; Rf = 0.48 (hexane); Peaks for major isomer 3h: ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.0 Hz, 1H), 7.38–7.29 (m, 6H), 7.26–7.21 (m, 3H), 7.20–7.15 (m, 2H), 7.04 (d, J = 7.2 Hz, 1H), 1.96 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.7, 139.6, 139.2, 138.5, 138.2, 134.4, 131.1, 129.6, 128.6, 128.3, 128.1, 127.9, 127.3, 127.1, 124.1, 120.0, 21.54; Representative peaks for minor isomer 3h′: ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.4 Hz, 0.4H), 7.38–7.29 (m, 2H), 7.26–7.21 (m, 1H), 7.20–7.15 (m, 0.6H), 2.59 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 135.8, 134.52, 134.47, 134.4, 133.9, 131.6, 130.4, 127.6, 127.4, 127.3, 124.9, 124.8, 121.0, 20.2; IR (KBr) νmax 3051, 1599, 1440, 766, 695 cm⁻¹; MS (EI) m/z (%) 301 (M⁺ + 1, 100); Anal. Calcd. for C₂₁H₁₄S: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.85; H, 5.41; S, 10.56.

Ratio of the both regioisomers 3h:3h′ was determined based on the characteristic Me-H¹ proton integration. ¹H NMR (400 MHz, CDCl₃) H¹ for 3h/3h′: δ = 1.96 (s, 3H, 70%, major)/2.59 (s, 3H, 30%, minor).
6-Methyl-2,3-diphenylbenzo[b]thiophene (3a), 5-Methyl-2,3-diphenylbenzo[b]thiophene (3i) and 7-Methyl-2,3-diphenylbenzo[b]thiophene (3h):

The reaction between 1-(m-tolylthio)pyrrolidine-2,5-dione 1i and 2a under the optimization conditions provided inseparable mixture of 3a, 3i and 3h colorless crystalline solid (50:18:32) (61 mg, 41%); mp = 132–135 °C; Rf = 0.38 (hexane); 1H NMR (400 MHz, CDCl₃) δ 7.72 (dd, J = 8.0, 4.0 Hz, 1H), 7.64 (bs, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.42–7.28 (m, 16H), 7.26–7.11 (m, 10H), 7.04 (d, J = 7.2 Hz, 1H), [2.46 (s, 3H), 2.39 (s, 1H), 1.96 (s, 2H)]; 13C NMR (101 MHz, CDCl₃) δ 141.1, 139.7, 139.6, 139.2, 139.1, 138.7, 138.5, 138.3, 138.2, 136.0, 135.7, 134.51, 134.47, 134.45, 134.37, 134.2, 133.0, 132.9, 131.1, 130.44, 130.38, 129.6, 129.55, 129.52, 128.62, 128.59, 128.3, 128.1, 127.9, 127.6, 127.5, 127.4, 127.35, 127.27, 127.1, 126.2, 126.1, 124.1, 123.2, 123.0, 121.9, 121.7, 121.1, 120.0, 21.54 (3h), 21.5 (3a); IR (KBr) νmax 3052, 1600, 1446, 812, 690 cm⁻¹; HRMS (ESI) for C₃₂H₂₉NaS (M+Na)⁺: calcd. 323.0870, found 323.0876.

Ratio of the three regioisomers 3a:3i:3h was determined based on the characteristic Me-H¹ proton integration. H¹ NMR (400 MHz, CDCl₃) H¹ for 3a/3i/3h: δ = 2.46 (s, 3H, 50%, major)/ 2.39 (s, 3H, 18%, minor)/ 1.96 (s, 3H, 32%, minor). The Me peak appeared at 2.46 and 1.96 is matching with the previously observed compound 3a and 3h, respectively.

2,3-bis(4-Fluorophenyl)-6-methylbenzo[b]thiophene (4a):

4a colorless crystalline solid (116 mg, 69%); mp = 176–177 °C; Rf = 0.46 (hexane); 1H NMR (500 MHz, CDCl₃) δ 7.67 (bs, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.30–7.24 (m, 4H), 7.17 (dd, J = 8.0 & 1.0 Hz, 1H), 7.13–7.08 (m, 2H), 6.98–6.93 (m, 2H), 2.50 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 162.3 (d, J = 250 Hz), 162.2 (d, J = 248 Hz), 139.0, 138.5, 137.4, 134.8, 132.0 (d, J = 8 Hz), 131.3 (d, J = 3 Hz), 131.2 (d, J = 8 Hz), 130.3 (d, J = 3 Hz), 126.3, 122.8, 121.9, 115.8 (d, J = 22 Hz), 115.5 (d, J = 23 Hz), 21.5; 19F NMR (376 MHz, CDCl₃) δ –113.79, −114.43; IR (KBr) νmax 2909, 1604, 1500, 1226, 1018, 837 cm⁻¹; HRMS (ESI) for C₂₁H₁₄F₂NaS (M+Na)⁺: calcd. 359.0682, found 359.0679.
2,3-bis(4-Chlorophenyl)-6-methylbenzo[b]thiophene (4b):

4b colorless crystalline solid (138 mg, 75%); mp = 228–229 °C; Rf = 0.56 (hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.67 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 2H), 7.26–7.20 (m, 6H), 7.17 (dd, J = 8.5 & 1.0 Hz, 1H), 2.49 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 138.3, 137.3, 135.0, 133.8, 133.5, 132.6, 132.1, 131.6, 130.7, 129.1, 128.7, 126.5, 122.8, 122.0, 21.5; IR (KBr) v max 2920, 1533, 1495, 1084, 1013, 804 cm⁻¹; HRMS (ESI) for C₂₃H₁₅Cl₁S (M+H)⁺: calcd. 369.0272, found 369.0269.

2,3-bis(4-Bromophenyl)-6-methylbenzo[b]thiophene (4c):

4c colorless crystalline solid (170 mg, 74%); mp = 235–236 °C; Rf = 0.53 (hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.67 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.20–7.13 (m, 5H), 2.49 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 138.2, 137.3, 135.1, 134.3, 133.0, 132.1, 132.0, 131.9, 131.7, 131.0, 126.5, 122.8, 122.03, 122.00, 121.7, 21.5; IR (KBr) v max 2920, 1522, 1462, 1232, 1007, 826 cm⁻¹; HRMS (ESI) for C₂₃H₁₄Br₂SNa (M+Na)⁺: calcd. 478.9081, found 478.9079.

6-tert-Butyl-2,3-bis(4-fluorophenyl)benzo[b]thiophene (4d):

4d colorless crystalline solid (157 mg, 83%); mp = 168–169 °C; Rf = 0.51 (hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.88 (bd, J = 1.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.43 (dd, J = 8.5 & 2.0 Hz, 1H), 7.31–7.24 (m, 4H), 7.13–7.08 (m, 2H), 6.99–6.94 (m, 2H), 1.41 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 162.3 (d, J = 250 Hz), 162.2 (d, J = 248 Hz), 148.3, 138.9, 138.4, 137.9, 132.0 (d, J = 8 Hz), 131.3 (d, J = 4 Hz), 131.2 (d, J = 8 Hz), 130.3 (d, J = 3 Hz), 122.9, 122.6, 118.2, 115.8 (d, J = 22 Hz), 115.5 (d, J = 22 Hz), 35.0, 31.5; ¹⁹F NMR (376 MHz, CDCl₃) δ −113.77, −114.45; IR (KBr) v max 2958, 1605, 1512, 1221, 816 cm⁻¹; HRMS (ESI) for C₂₃H₁₃F₂S (M+H)⁺: calcd. 379.1332, found 379.1329.

6-tert-Butyl-2,3-bis(4-chlorophenyl)benzo[b]thiophene (4e):

4e colorless crystalline solid (161 mg, 78%); mp = 233–234 °C; Rf = 0.6 (hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.87 (bs, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.43 (dd, J = 8.5 & 1.5 Hz, 1H), 7.40–7.37 (m, 2H), 7.26–7.21 (m, 6H), 1.41 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 148.5, 139.0, 138.1, 137.8, 133.8, 133.5, 132.6, 132.0, 131.6,
130.7, 129.0, 128.7, 123.0, 122.6, 118.3, 35.0, 31.5; IR (KBr) \( \nu_{\text{max}} \) 2958, 1489, 1259, 1095, 897 cm\(^{-1}\); HRMS (ESI) for \( \text{C}_{23}\text{H}_{20}\text{Cl}_{2}\text{NaS} \) (M+Na\(^+\)): calcd. 433.0560, found 433.0553.

**6-tert-Butyl-2,3-bis(4-bromophenyl)benzo[\text{b}]thiophene (4f):**

4f colorless crystalline solid (198 mg, 79\%); mp = 233–234 °C; \( R_f = 0.58 \) (hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.87 (s, 1H), 7.54 (d, \( J = 8.0 \) Hz, 2H), 7.49 (d, \( J = 8.4 \) Hz, 1H), 7.45–7.36 (m, 3H), 7.22–7.12 (m, 4H), 1.41 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.5, 139.0, 138.1, 137.8, 134.3, 133.8, 133.1, 132.0, 131.9, 131.7, 131.0, 123.1, 122.6, 122.0, 121.7, 118.3, 35.0, 31.5; IR (KBr) \( \nu_{\text{max}} \) 2958, 1489, 1259, 1095, 897 cm\(^{-1}\); HRMS (ESI) for \( \text{C}_{24}\text{H}_{20}\text{Br}_{2}\text{Cl}_{2}\text{NaS} \) (M+Na\(^+\)): calcd. 498.9731, found 498.9736.

**6-Methyl-2,3-di-p-tolylbenzo[\text{b}]thiophene (4g):**

4g colorless crystalline solid (80 mg, 48\%); mp = 148–150 °C; \( R_f = 0.34 \) (hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.66 (d, \( J = 0.4 \) Hz, 1H), 7.47 (d, \( J = 8.4 \) Hz, 1H), 7.25–7.20 (m, 6H), 7.15 (d, \( J = 8.4 \) Hz, 1H), 7.06 (d, \( J = 8.0 \) Hz, 2H), 2.49 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 139.0, 138.96, 138.2, 137.3, 136.8, 134.3, 133.8, 133.1, 132.0, 131.6, 130.2, 129.35, 129.33, 129.0, 126.0, 122.9, 121.8, 21.5, 21.3, 21.2; IR (KBr) \( \nu_{\text{max}} \) 2914, 1561, 1445, 1226, 815 cm\(^{-1}\); MS (EI) \( m/z \) (%) 329 (M\(^+\) + 1, 100); Anal. Calcd. for \( \text{C}_{23}\text{H}_{21}\text{S} \): C, 84.10; H, 6.14; S, 9.76. Found: C, 84.17; H, 6.18; S, 9.69.

**6-tert-Butyl-2,3-di-p-tolylbenzo[\text{b}]thiophene (4h):**

4h colorless crystalline solid (97 mg, 52\%); mp = 160–162 °C; \( R_f = 0.36 \) (hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.89 (d, \( J = 1.6 \) Hz, 1H), 7.55 (d, \( J = 8.4 \) Hz 1H), 7.41 (dd, \( J = 8.8 \) & 1.8 Hz, 1H), 7.25–7.20 (m, 6H), 7.08 (d, \( J = 7.6 \) Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H) 1.43 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 147.7, 138.84, 138.82, 138.6, 137.3, 136.8, 132.8, 132.4, 131.7, 130.2, 129.4, 129.3, 129.0, 122.8, 122.5, 118.1, 34.9, 31.5, 21.3, 21.2; IR (KBr) \( \nu_{\text{max}} \) 2964, 2915, 1517, 1463, 1254, 816 cm\(^{-1}\); HRMS (ESI) for \( \text{C}_{26}\text{H}_{27}\text{S} \) (M+H\(^+\)): calcd. 371.1833, found 371.1835.
6-Fluoro-2,3-bis(4-fluorophenyl)benzo[\textit{b}]thiophene (4i): 

4i colorless crystalline solid (106 mg, 62%); mp = 138–140 °C; \( R_f = 0.46 \) (hexane); \(^1\text{H NMR} \) (500 MHz, CDCl\(_3\) \( \delta \) 7.55 (dd, \( J = 8.5 \& 2.5 \) Hz, 1H), 7.48 (dd, \( J = 9.0 \& 5.0 \) Hz 1H), 7.29–7.22 (m, 4H), 7.14–7.08 (m, 3H), 6.99–6.94 (m, 2H); \(^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\) \( \delta \) 162.4 (d, \( J = 250 \) Hz), 162.3(d, \( J = 248 \) Hz), 160.7 (d, \( J = 247 \) Hz), 139.5 (d, \( J = 10 \) Hz), 138.1 (d, \( J = 4 \) Hz), 137.1, 131.9 (d, \( J = 8 \) Hz), 131.7, 131.2 (d, \( J = 8 \) Hz), 130.9 (d, \( J = 4 \) Hz), 129.8 (d, \( J = 3 \) Hz), 124.2 (d, \( J = 9 \) Hz), 115.9 (d, \( J = 22 \) Hz), 115.6 (d, \( J = 23 \) Hz), 113.6 (d, \( J = 24 \) Hz), 108.2 (d, \( J = 25 \) Hz); \(^{19}\text{F NMR} \) (470 MHz, CDCl\(_3\) \( \delta \) –113.26, –113.64, –113.89, –116.84; IR (KBr) \( \nu_{\text{max}} \) 1600, 1506, 1221, 1156, 838 cm\(^{-1}\); HRMS (ESI) for C\(_{20}\)H\(_{16}\)F\(_2\)NaS (M+Na\(^{+}\)): calcd. 363.0431, found 363.0432.

6-Fluoro-2,3-bis(4-bromophenyl)benzo[\textit{b}]thiophene (4j):

4j light yellow solid (149 mg, 64%); mp = 176–177 °C; \( R_f = 0.53 \) (hexane); \(^1\text{H NMR} \) (500 MHz, CDCl\(_3\) \( \delta \) 7.57–7.53 (m, 3H), 7.49 (dd, \( J = 9.0 \& 5.0 \) Hz 1H), 7.42–7.39 (m, 2H), 7.19–7.13 (m, 4H), 7.10 (td, \( J = 8.9 \& 2.3 \) Hz, 1H); \(^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\) \( \delta \) 160.8 (d, \( J = 245 \) Hz), 139.7 (d, \( J = 10 \) Hz), 138.1 (d, \( J = 4 \) Hz), 136.9, 133.8, 132.6, 132.2, 131.9, 131.8, 130.9, 124.3 (d, \( J = 9 \) Hz), 122.3, 122.0, 113.7 (d, \( J = 24 \) Hz), 108.3 (d, \( J = 25 \) Hz); \(^{19}\text{F NMR} \) (470 MHz, CDCl\(_3\) \( \delta \) –116.26; IR (KBr) \( \nu_{\text{max}} \) 1534, 1457, 1249, 1068, 1002, 805 cm\(^{-1}\); HRMS (ESI) for C\(_{20}\)H\(_{16}\)Br\(_2\)FS (M+H\(^{+}\)): calcd. 460.9010, found 460.9010.

6-\textit{tert}-Butyl-2,3-bis(3-(trifluoromethyl)phenyl)benzo[\textit{b}]thiophene (4k):

4k colorless crystalline solid (120 mg, 50%); mp = 141–142 °C; \( R_f = 0.55 \) (hexane); \(^1\text{H NMR} \) (500 MHz, CDCl\(_3\) \( \delta \) 7.97 (s, 1H), 7.73–7.68 (m, 2H), 7.62–7.49 (m, 7H), 7.41 (t, \( J = 7.75 \) Hz, 1H), 1.48 (s, 9H); \(^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\) \( \delta \) 148.9, 139.2, 137.9, 137.8, 136.0, 134.7, 133.6, 132.7, 132.4, 131.3 (q, \( J = 32 \) Hz), 131.0 (q, \( J = 32 \) Hz), 129.4, 129.0, 127.1 (q, \( J = 3.0 \) Hz), 126.3 (q, \( J = 3.0 \) Hz), 125.2 (d, \( J = 22 \) Hz), 124.47 (q, \( J = 4.0 \) Hz), 123.4, 122.6, 118.4, 35.0, 31.4; \(^{19}\text{F NMR} \) (470 MHz, CDCl\(_3\) \( \delta \) –62.78, –63.06; IR (KBr) \( \nu_{\text{max}} \) 2969, 1605, 1358, 1326, 1117, 673 cm\(^{-1}\); HRMS (ESI) for C\(_{26}\)H\(_{20}\)F\(_3\)NaS (M+Na\(^{+}\)): calcd. 501.1088, found 501.1087.
6-tert-Butyl-2,3-bis(3,4-dichlorophenyl)benzo[b]thiophene (4l):

4l pale yellow solid (178 mg, 74%); mp = 144–145 °C; Rf = 0.63 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.88 (bs, 1H), 7.51–7.44 (m, 5H), 7.33 (d, J = 8.4 Hz, 1H), 7.10 (dd, J = 8.4 & 2.0 Hz, 1H), 7.04 (dd, J = 8.4 & 2.0 Hz, 1H), 1.41 (s, 9H); 13C NMR (101 MHz, CDCl3) δ 149.0, 139.1, 137.7, 136.9, 135.0, 133.8, 133.0, 132.8, 132.2, 132.0, 131.8, 131.4, 131.1, 130.9, 130.5, 129.7, 128.6, 123.4, 122.6, 118.4, 35.1, 31.4; IR (KBr) νmax 2964, 1583, 1463, 1134, 1030, 810 cm⁻¹; HRMS (ESI) for C26H19Cl3S (M+H)⁺: calcd. 478.9962, found 478.9961.

6-Methyl-2,3-bis(3,4-dichlorophenyl)benzo[b]thiophene (4m):

4m colorless crystalline solid (83 mg, 38%); mp = 147–148 °C; Rf = 0.56 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.67 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.47–7.45 (m, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 8.4 & 0.8 Hz, 1H), 7.10 (dd, J = 8.0 & 2.0 Hz, 1H), 7.03 (dd, J = 8.4 & 2.0 Hz, 1H), 2.50 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 139.1, 137.8, 136.4, 135.6, 135.0, 133.8, 133.0, 132.8, 132.2, 132.0, 131.9, 131.4, 131.1, 130.9, 130.5, 129.7, 128.6, 126.8, 122.7, 122.1, 21.5; IR (KBr) νmax 2915, 1457, 1123, 1035, 816 cm⁻¹; HRMS (ESI) for C21H15Cl3S (M+H)⁺: calcd. 436.9492, found 436.9499.

6-iso-Propyl-2-methyl-3-phenylbenzo[b]thiophene (5a):

The reaction between 1-(4-iso-propylphenylthio)pyrrolidine-2,5-dione (1d) and 1-phenyl-1-propyne under the optimized conditions provided 5a along with an unidentified product. The compounds 5a and unidentified product are inseparable, forming 4:1 ratio.

5a pale yellow viscous liquid (64 mg, 48%); Rf = 0.52 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.73 (s, 1H), 7.59–7.50 (m, 3H), 7.49–7.45 (m, 3H), 7.25–7.21 (m, 1H), 3.15–3.03 (m, 1H), 2.55 (s, 3H), 1.39 (d, J = 6.8 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 144.8, 138.53, 138.46, 135.5, 135.0, 133.5, 130.0, 128.4, 127.1, 123.4, 122.2, 119.2, 34.1, 24.2, 14.4; Representative peaks for the inseparable unidentified product: 1H NMR (400 MHz, CDCl3) δ 2.99–2.89 (m, 0.3H), 1.30 (d, J = 6.8 Hz, 2H); 13C NMR (101 MHz, CDCl3) δ 148.2, 134.3, 128.2, 127.2, 122.7, 121.7, 119.9, 33.7, 23.9; IR (KBr) IR (Neat) νmax 3052, 2958, 2915, 2865, 1600, 1479, 816 cm⁻¹; HRMS (ESI) for C18H19S (M+H)⁺: calcd. 267.1207, found 267.1209.

The ratio of 5a:unidentified product (UP) was determined based on the characteristic H¹ proton integration; δ = 3.15–3.03 (m, 1H, 78%, for 5a)/ 2.99–2.89 (m, 1H, 22%, minor).
2-Butyl-6-isopropyl-3-phenylbenzo[b]thiophene (5b):

The reaction between 1-(4-iso-Propylphenylthio)pyrrolidine-2,5-dione (1d) and 1-phenyl-1-hexyne under the optimized conditions provided 5a along with an unidentified product. The compounds 5a and unidentified product are inseparable, forming 6:1 ratio.

5b colorless viscous liquid (80 mg, 52%); R_f = 0.64 (hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.79 ( d, J = 0.8 Hz, 1H), 7.62–7.54 (m, 2H), 7.54–7.47 (m, 4H), 7.31–7.27 (m, 1H), 3.12–3.06 (m, 1H), 2.96 (t, J = 7.6 Hz, 2H), 1.83–1.74 (m, 2H), 1.43 (d, J = 6.8 Hz, 6H), 1.38–1.32 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^13C NMR (101 MHz, CDCl_3) δ 144.8, 141.5, 138.6, 138.4, 135.8, 133.2, 130.0, 128.4, 127.1, 123.3, 121.9, 119.3, 34.2, 33.9, 28.5, 24.2, 22.2, 13.8; Representative peaks for the inseparable unidentified product: ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.32 (m, 0.26H), 7.27–7.25 (m, 0.24H), 1.47 (d, J = 7.6 Hz, 1H); ^13C NMR (101 MHz, CDCl_3) δ 148.2, 134.3, 128.2, 126.1, 122.3, 33.7, 23.9; IR (KBr) ν_max 3057, 2953, 2865, 1600, 1479, 816, 701 cm⁻¹; HRMS (ESI) for C_{21}H_{25}S (M+H)^+: calcd. 309.1677, found 309.1673.

The ratio of 5b:unidentified product (UP) was determined based on the characteristic H^1 proton integration; δ = 1.43 (d, 6H, 85%, for 5b)/ 1.47 (d, 6H, 15%, minor).

2-Hexyl-6-methyl-3-phenylbenzo[b]thiophene (5c):

The reaction between 1-(4-iso-Propylphenylthio)pyrrolidine-2,5-dione (1d) and 1-phenyl-1-octyne under the optimized conditions provided 5a along with an unidentified product. The compounds 5a and unidentified product are inseparable, forming 7:1 ratio.

5c as colorless viscous thick liquid (48 mg, 30%); R_f = 0.64 (hexane); Representative peaks for major isomer 5c: ^1H NMR (400 MHz, CDCl_3) δ 7.63 (bs, 1H), 7.53–7.47 (m, 2H), 7.45–7.36 (m, 4H), 7.15–7.10 (m, 1H), 2.85 (t, J = 7.8 Hz, 2H), 2.48 (s, 3H), 1.74–1.65 (m, 2H), 1.36–1.22 (m, 6H), 0.88 (t, J = 7.0 Hz 3H); ^13C NMR (101 MHz, CDCl_3) δ 141.3, 138.4, 138.3, 135.8, 133.6, 133.2, 130.0, 128.4, 127.1, 125.7, 122.1, 121.9, 31.7, 31.5, 28.8, 28.7, 22.5, 21.4, 14.0; Representative peaks for the inseparable unidentified product: ^1H NMR (400 MHz, CDCl_3) δ 7.75–7.70 (m, 0.14H), 2.34 (s, 0.42H); ^13C NMR (101 MHz, CDCl_3) δ 137.5, 137.4, 133.9, 130.2, 130.1, 129.8, 128.5, 21.0; IR (Neat) ν_max 2953, 2849, 1468, 810, 706 cm⁻¹; HRMS (ESI) for C_{21}H_{25}S (M+H)^+: calcd. 309.1677, found 309.1679.
The ratio of 5c:unidentified product (UP) was determined based on the characteristic H¹ proton integration; \( \delta = 2.48 \) (s, 3H, 88%, for 5c)/ 2.34 (s, 3H, 12%, minor).

3-(4-Fluorophenyl)-6-methyl-2-phenylbenzo[\( b \)]thiophene (5d) and 2-(4-Fluorophenyl)-6-methyl-3-phenylbenzo[\( b \)]thiophene (5d’):

Inseparable mixture of 5d and 5d’ colorless crystalline solid (1:1, 89 mg, 56%); mp = 150–151 °C; \( R_f = 0.46 \) (hexane); ¹H NMR (400 MHz, CDCl₃) \( \delta \) 7.65 (s, 1H), 7.49–7.33 (m, 2H), 7.31–7.21 (m, 6H), 7.18–7.04 (m, 2H), 6.96–6.88 (m, 1H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) \( \delta \) 162.2 (d, \( J = 250 \) Hz), 162.1 (d, \( J = 248 \) Hz), 139.1, 139.0, 138.6, 137.1, 135.5, 134.6, 134.2, 133.1, 132.0 (d, \( J = 8 \) Hz), 131.9, 131.6, 131.2 (d, \( J = 8 \) Hz), 130.3, 129.5, 128.7, 128.4, 127.6, 127.4, 126.2, 123.0, 122.7, 122.0, 121.9, 115.6 (d, \( J = 22 \) Hz), 115.3 (d, \( J = 22 \) Hz), 21.5; ¹⁹F NMR (470 MHz, CDCl₃) \( \delta \) -114.08, -114.70 (1:1); IR (KBr) \( \nu_{\text{max}} \) 2914, 1599, 1501, 1227, 816, 690 cm⁻¹; HRMS (ESI) for C₂₂H₁₅FN₃S (M+Na)⁺: calcd. 341.0776, found 341.0776.

Both the regioisomeric products 5d and 5d’ are indistinguishable by 1H NMR, however, the 13C NMR studies clearly reveals the formation of both regioisomers 5d and 5d’ as inseparable mixture.

3-(4-Chlorophenyl)-6-methyl-2-phenylbenzo[\( b \)]thiophene (5e) and 2-(4-Chlorophenyl)-6-methyl-3-phenylbenzo[\( b \)]thiophene (5e’):

Inseparable mixture of 5e and 5e’ colorless crystalline solid (1:1, 97 mg, 58%); mp = 193–195 °C; \( R_f = 0.5 \) (hexane); ¹H NMR (400 MHz, CDCl₃) \( \delta \) 7.65, (s, 1H), 7.45 (d, \( J = 8.4 \) Hz 1H), 7.42–7.33 (m, 3H), 7.31–7.22 (m, 4H), 7.19 (bd, \( J = 4.0 \) Hz, 2H), 7.17–7.12 (m, 1H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) \( \delta \) 139.2, 139.0, 138.8, 138.7, 138.4, 136.8, 135.4, 134.8, 134.7, 134.2, 134.1, 133.5, 133.50, 133.3, 132.9, 131.7, 131.6, 130.7, 130.3, 129.6, 128.9, 128.7, 128.5, 128.4, 127.7, 127.5, 126.3, 123.1, 122.7, 122.0, 121.9, 21.51, 21.50; IR (KBr) \( \nu_{\text{max}} \) 2914, 1594, 1484, 1441, 1227, 1084, 810 cm⁻¹; HRMS (ESI) for C₂₂H₁₅ClNaS (M+Na)⁺: calcd. 357.0481, found 357.0481.

Both the regioisomeric products 5e and 5e’ are indistinguishable by 1H NMR, however, the 13C NMR studies clearly reveals the formation of both regioisomers 5e and 5e’ as inseparable mixture.
3-(4-Bromophenyl)-6-methyl-2-phenylbenzo[b]thiophene (5f) and 2-(4-Bromophenyl)-6-methyl-3-phenylbenzo[b]thiophene (5f'):

Inseparable mixture of 5f and 5f' colorless crystalline solid (1:1; 112 mg, 59%); mp = 202–205 °C; Rf = 0.48 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.66 (s, 1H), 7.53–7.50 (m, 1H), 7.46 (d, J = 8.8 Hz 1H), 7.43–7.34 (m, 3H), 7.32–7.26 (m, 3H), 7.22–7.14 (m, 3H), 2.49 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 139.1, 139.0, 138.8, 138.6, 138.3, 136.8, 135.3, 134.9, 134.7, 134.6, 134.0, 133.5, 133.4, 133.0, 132.1, 131.8, 131.6, 131.5, 131.0, 129.8, 129.6, 128.8, 128.5, 127.8, 127.5, 126.3, 123.1, 122.6, 122.0, 121.9, 121.7, 121.4, 21.53, 21.51; IR (KBr) νmax 2909, 1594, 1441, 1238, 1002, 816, 690 cm⁻¹; MS (EI) m/z (%): calcd. for C21H18BrS: C, 66.50; H, 3.91; S, 8.45; found: C, 66.42; H, 3.91; S, 8.38.

Both the regioisomeric products 5f and 5f' are indistinguishable by 1H NMR, however, the 13C NMR studies clearly reveals the formation of both regioisomers 5f and 5f' as inseparable mixture.

3-(2-Bromophenyl)-6-methyl-2-phenylbenzo[b]thiophene (5g) and 2-(2-Bromophenyl)-6-methyl-3-phenylbenzo[b]thiophene (5g'):

Inseparable mixture of 5g and 5g' pale yellow solid (5:1; 119 mg, 63%); mp = 93–94 °C; Rf = 0.4 (hexane); Representative peaks for major isomer 5g: 1H NMR (400 MHz, CDCl3) δ 7.76–7.69 (m, 2H), 7.39–7.32 (m, 4H), 7.28–7.25 (m, 4H), 7.23–7.18 (m, 2H), 2.52 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 139.4, 138.6, 138.3, 137.1, 134.6, 134.2, 133.0, 132.5, 129.9, 129.3, 128.8, 128.4, 127.7, 127.6, 126.1, 125.0, 122.9, 121.9, 21.56; Representative peaks for minor isomer 5g': 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.4 Hz, 0.19H), 7.59 (dd, J = 8.0 & 1.2 Hz, 0.2H), 7.31–7.28 (m, 1H), 7.18–7.14 (m, 0.38H), 2.53 (s, 0.5H); 13C NMR (101 MHz, CDCl3) δ 140.0, 136.8, 135.4, 135.0, 134.8, 133.2, 132.8, 132.0, 129.7, 128.2, 127.1, 126.9, 123.1, 122.0, 21.52; IR (KBr) νmax 2920, 1599, 1430, 1030, 810, 684 cm⁻¹; HRMS (ESI) for C21H19BrNS (M+NH₄)⁺: calcd. 396.0422, found 396.0422.

The ratio of 5g : 5g' was determined based on the characteristic H¹ proton integration; δ = 2.52 (s, 3H, 84%, major)/ 2.53 (s, 3H, 16%, minor).
**General procedure for the Suzuki reaction of 4c; Synthesis of 6 (GP 5):**

A mixture of compound 4c (100 mg, 0.218 mmol), phenyl boronic acid (80 mg, 0.655 mmol), Pd(PPh₃)₄ (15 mg, 0.013 mmol) and Na₂CO₃ (69 mg, 0.654 mmol) in toluene and H₂O (1:1, 3.0 mL) was heated at 80 °C for 12 h. The reaction mixture was extracted with ethylacetate (3 x 15 mL), dried over Na₂SO₄ and concentrated under vacuum to give a light yellow solid. The crude material was purified by silica gel column chromatography eluting with hexane to give compound 6 as colorless crystalline solid.

**2,3-di(Biphenyl-4-yl)-6-methylbenzo[b]thiophene (6):**

6 colorless crystalline solid (73 mg, 74%); mp = 218–219 °C; Rf = 0.24 (hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.73–7.68 (m, 5H), 7.62–7.57 (m, 3H), 7.54–7.33 (m, 12H), 7.21 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 140.6, 140.3, 140.2, 140.0, 139.1, 138.8, 138.0, 134.8, 134.6, 133.4, 132.7, 130.8, 129.9, 128.81, 128.76, 127.40, 127.36, 127.3, 127.0, 126.9, 126.2, 123.0, 121.9, 21.5; IR (Neat)νmax 2920, 1643, 1523, 1008, 756, 690 cm⁻¹; HRMS (ESI) for C₃₅H₃₂S (M+H)⁺: calcd. 543.1677, found 543.1677.

**General procedure for the Sonogashira reaction of 4c; Synthesis of 7 (GP 6):**

Phenylacetylene (52 μL, 0.479 mmol) was added to a stirred suspension of compound 4c (100 mg, 0.218 mmol), PdCl₂(PPh₃)₂ (15 mg, 0.0218 mmol), CuI (4.0 mg, 0.0218 mmol) and PPh₃ (6.0 mg, 0.0218 mmol) in Et₃N (4 mL) under nitrogen atmosphere. The reaction mixture was heated at 100 °C for 48 h. After cooling to room temperature, the reaction mixture was quenched with saturated NaHCO₃ solution and extracted with CH₂Cl₂ (3 x 15 mL), dried over Na₂SO₄ and concentrated under vacuum to give a light yellow solid. The crude material was purified by silica gel column chromatography eluting with hexane/EtOAc (95:5) to give compound 7 as a pale yellow crystalline solid.

**6-Methyl-2,3-bis(4-(phenylethynyl)phenyl)benzo[b]thiophene (7):**

7 yellow solid (66 mg, 60%); mp = 213–215 °C; Rf = 0.2 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.62–7.55 (m, 4H), 7.54–7.48 (m, 3H), 7.44–7.40 (m, 2H), 7.38–7.27 (m, 10H), 7.19 (dd, J = 8.2 & 1.0 Hz, 1H), 2.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 138.3, 138.0, 135.6, 135.0, 134.1, 132.8, 132.0, 131.63, 131.61, 130.4, 129.4, 128.4, 128.3, 126.4, 123.2, 123.1, 122.9, 122.5, 122.4, 122.0, 90.5, 90.1, 89.2, 89.1, 21.5; IR (Neat)νmax 2920, 1594, 1435, 838, 750, 684 cm⁻¹; HRMS (ESI) for C₃₇H₃₄S (M+H)⁺: calcd. 501.1677, found 501.1677.
General procedure for the benzylic azidation of 3a; Synthesis of 8 (GP 7): A mixture of N-bromosuccinimide (65 mg, 0.36 mmol), AIBN (3 mg, 0.01 mmol), and 6-methyl-2,3-diphenylbenzo[b]thiophene 3a (100 mg, 0.33 mmol) in dry CCl₄ (2.0 mL) were placed in a sealed tube and stirred at room temperature for 18 h. Upon complete consumption of 3a, the solvent was evaporated and the crude material was subjected to azidation. Accordingly, sodium azide (32 mg, 0.5 mmol) and water-acetone mixture (1:4, 2 mL) was added to the crude material and the resulting mixture was stirred overnight. The solvent was evaporated and the crude mixture was purified by neutral alumina column chromatography eluting with hexane/EtOAc (97:3) mixture to provide compound 8 as colorless crystalline solid.

6-(Azidomethyl)-2,3-diphenylbenzo[b]thiophene (8): 8 colorless crystalline solid (102 mg, 90%); mp = 126–127 °C; Rᵣ = 0.12 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.60 (bd, J = 8.0 Hz, 1H), 7.45–7.22 (m, 11H), 4.46 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 140.4, 139.1, 135.2, 134.0, 133.0, 131.8, 130.4, 129.6, 128.7, 128.4, 127.8, 127.5, 124.8, 123.7, 121.8, 54.9; IR (Neat) νmax 3057, 2098, 1441, 1238, 690 cm⁻¹; MS (EI) m/z (%) 342 (M⁺ + 1, 100); Anal. Calcd. for C₂₁H₁₅N₃S: C, 73.87; H, 4.43; N, 12.31; S, 9.39. Found: C, 73.96; H, 4.38; N, 12.25; S, 9.25.

General procedure for the oxidation of benzo[b]thiophenes (GP 8): To a solution of 3 (1.0 mmol) in dry CH₂Cl₂ (10 mL) was added m-CPBA (1.2 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature overnight. Upon completion, solvent was evaporated and the crude material was purified by flash column chromatography eluting with hexane/EtOAc 95:5 to give the desired sulfones.

6-Methyl-2,3-diphenylbenzo[b]thiophene-1,1-dioxide (10): 10 colorless crystalline solid (503 mg, 91%); mp = 166–168 °C; Rᵣ = 0.44 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.36–7.26 (m, 7H), 7.20–7.15 (m, 3H), 7.10 (d, J = 8.4 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 138.7, 138.3, 135.7, 134.5, 134.3, 133.0, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 126.1, 122.9, 121.9, 21.5; IR (Neat) νmax 3250, 1600, 1446, 1238, 1024, 810, 690 cm⁻¹; HRMS (ESI) for C₂₁H₁₆NaO₂S (M+Na)⁺: calcd. 355.0769, found 355.0770.
2,3-di(Biphenyl-4-yl)-6-methylbenzo[b]thiophene-1,1-dioxide (11):

![Chemical Structure](image)

**11** yellow color solid (92 mg, 86%); mp = 270–271 °C; Rf = 0.50 (40:10 hexane/EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.72–7.69 (m, 3H), 7.67–7.64 (m, 2H), 7.61–7.53 (m, 6H), 7.50–7.43 (m, 5H), 7.43–7.39 (m, 2H), 7.38–7.33 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 2.49 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 142.2, 142.1, 141.0, 140.1, 139.9, 137.7, 136.5, 136.2, 134.0, 130.6, 130.0, 129.6, 129.5, 128.9, 128.8, 127.9, 127.8, 127.7, 127.4, 127.0, 126.1, 124.0, 122.2, 21.5; IR (Neat)υmax 2920, 1736, 1484, 1298, 1150, 860, 591 cm⁻¹; HRMS (ESI) for C₃₅H₂₅NaO₂S (M+Na)⁺: calcd. 507.1395, found 507.1388.

**References**


**X-ray crystallography:** Single crystal X-ray data for the compound 3d and 3e were collected using the detector system [\(\lambda(Mo-K\alpha) = 0.71073 \ \text{Å}\)] at 293K, graphite monochromator with a \(\omega\) scan width of 0.3\(^\circ\), crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software\(^1\) was used for the intensity data acquisition and the SAINTPLUS Software\(^1\) was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program,\(^1\) an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97,\(^2\) and full-matrix least-squares refinement against \(F^2\) was carried out using SHELXL-97.\(^2\) All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

**X-ray crystal structure and data for 3d and 3e:**

![3d](image1.png) ![3e](image2.png)

**Figure 1.** Thermal ellipsoidal plot of compound 3d and 3e with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius.

**Table 1. Crystal data for 3d and 3e**

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