Supporting Information

One-step synthesis of benzo[b]thiophenes by aryne reaction with alkynyl sulfides

Tsubasa Matsuzawa, Takamitsu Hosoya, and Suguru Yoshida

Laboratory of Chemical Bioscience, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University (TMDU), 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

Contents

General Information S1
Structures of Aryne precursors 1 and Alkynyl sulfides 2 S2
Optimization of Reaction Conditions S3
Experimental Procedures S7
Deuteration Experiments S15
Characterization Data of New Compounds S17
References for Supporting Information S31

1H and 13C NMR Spectra of Compounds S32

General Information

All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 105715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60, spherical, particle size 40–50 μm, Cat. No. 37562-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel® B-5F, Cat. No. 230-00043). Recycling preparative HPLC was conducted using a YMC-GPC T2000 (600 mm × 20 φ) column (YMC Co., Ltd.) with a recycling preparative HPLC system (SHIMADZU, eluent: CHCl3). Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. 1H NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 MHz, or a Bruker AVANCE 400 spectrometer at 400 MHz. 13C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 126 MHz, or a Bruker AVANCE 400 spectrometer at 101 MHz. 19F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 °C. CDCl3 (Kanto Chemical Co. Inc., Cat. No. 07663-23) and DMSO-d6 (Kanto Chemical Co. Inc., Cat. No. 11560-43) were used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from the solvent peak (δ 7.26 for 1H NMR and δ 77.2 for 13C NMR in CDCl3, and δ 2.50 for 1H NMR in DMSO-d6) as an internal reference or α,α,α-trifluorotoluene (δ −63.0 ppm for 19F NMR in CDCl3) as an external standard with coupling constants (J) in hertz (Hz). The abbreviations s, d, t, q, m, signify singlet, doublet, triplet, quartet, septet, and multiplet, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm⁻¹. High-resolution mass spectra (HRMS) were measured on a Bruker microTOF mass spectrometer under positive electrospray ionization (ESI⁺) conditions.

S-Methyl 4-tolueneethyl sulfonate,S¹ S-ethyl 4-tolueneethyl sulfonate,S² S-isopropyl 4-tolueneethyl sulfonate,S¹ S-benzyl 4-tolueneethyl sulfonate,S¹ S-(4-tolyl) 4-tolueneethyl sulfonate,S¹ 3,17-di-O-methylenelethynestriadiol,S⁴ 2-fluoro-6-(trimethylsilyl)phenyl triflate (1e),S⁵ 3-(diethylamino)-2-(trimethylsilyl)phenyl triflate (1f),S⁶ 4-bromo-2-chloro-6-(trimethylsilyl)phenyl triflate (1h),S⁷ and 2,3-dibutyl-6-triflyloxy-7-(trimethylsilyl)benzol[b]thiophene (1i)S⁸ were prepared according to the reported methods. n-BuLi (1.65 M, in n-hexane), and LDA (1.0 M, in THF) were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.S⁹ All other chemical reagents used were commercial grade and used as received.
Structures of Aryne precursors 1 and Alkynyl sulfides 2
Optimization of Reaction Conditions

Table S1. Reactions of aryne precursor 1a with various alkynyl sulfides

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>3a : yield[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>65%</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>70%</td>
</tr>
<tr>
<td>3</td>
<td>i-Pr</td>
<td>48%</td>
</tr>
<tr>
<td>4</td>
<td>Bn</td>
<td>33%</td>
</tr>
<tr>
<td>5</td>
<td>p-Tol</td>
<td>0%</td>
</tr>
</tbody>
</table>

[a] Yields based on 1H NMR analyses.

Table S2. Optimization of activator

<table>
<thead>
<tr>
<th>entry</th>
<th>activator</th>
<th>3a : yield[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CsF</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td>KF, 18-crown-6</td>
<td>61%</td>
</tr>
<tr>
<td>3</td>
<td>n-Bu₄NF</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>n-Bu₄NF·3H₂O</td>
<td>18%</td>
</tr>
<tr>
<td>5</td>
<td>n-Bu₄NF[Ph₃SiF₃]</td>
<td>28%</td>
</tr>
<tr>
<td>6</td>
<td>Cs₂CO₃, 18-crown-6</td>
<td>32%</td>
</tr>
<tr>
<td>7</td>
<td>K₂CO₃, 18-crown-6</td>
<td>38%</td>
</tr>
</tbody>
</table>

[a] Yields based on 1H NMR analyses.
Table S3. Optimization of solvent

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>3a : yield\textsuperscript{[a]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>40%</td>
</tr>
<tr>
<td>3</td>
<td>DME</td>
<td>57%</td>
</tr>
<tr>
<td>4</td>
<td>acetone</td>
<td>38%</td>
</tr>
<tr>
<td>5</td>
<td>MeNO\textsubscript{2}</td>
<td>31%</td>
</tr>
<tr>
<td>6</td>
<td>PhCN</td>
<td>32%</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Yields based on $^1$H NMR analyses.

Table S4. Optimization of concentration

<table>
<thead>
<tr>
<th>entry</th>
<th>conc.</th>
<th>3a : yield\textsuperscript{[a]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 M</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td>0.025 M</td>
<td>68%</td>
</tr>
<tr>
<td>3</td>
<td>0.1 M</td>
<td>64%</td>
</tr>
<tr>
<td>4</td>
<td>0.2 M</td>
<td>64%</td>
</tr>
<tr>
<td>5</td>
<td>0.5 M</td>
<td>52%</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Yields based on $^1$H NMR analyses.
Table S5. Optimization of temperature

\[
\text{Cl} \quad \text{OTf} + \text{Et} \quad \text{S} \quad \text{p-Tol} \quad \text{CsF} \quad \text{MeCN (0.05 M)} \quad \text{temp., 24 h}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>temp.</th>
<th>3a : yield[^a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rt</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td>80 °C</td>
<td>72%</td>
</tr>
<tr>
<td>3</td>
<td>100 °C</td>
<td>62%</td>
</tr>
</tbody>
</table>

[^a] Yields based on \(^1\)H NMR analyses.

Table S6. Optimization of the amount of aryne precursor 1a and cesium fluoride

\[
\text{Cl} \quad \text{OTf} + \text{Et} \quad \text{S} \quad \text{p-Tol} \quad \text{CsF} \quad \text{MeCN (0.05 M)} \quad \text{80 °C, 24 h}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>x</th>
<th>y</th>
<th>3a : yield[^a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>4.0</td>
<td>72%</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>3.0</td>
<td>59%</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>2.4</td>
<td>45%</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>6.0</td>
<td>77%</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>9.0</td>
<td>79%(75%)[^b]</td>
</tr>
</tbody>
</table>

[^a] Yields based on \(^1\)H NMR analyses, unless otherwise noted.
[^b] Isolated yield.
Table S7. Optimization of quencher

\[
\begin{align*}
\text{Cl} & \quad \text{OTf} \\
\text{SiMe}_3 & \\
1a & \quad \text{(3.0 equiv)} \\
\end{align*}
\]  
\[
\begin{align*}
\text{Et} & \quad \text{S} \\
\text{p-Tol} & \\
2a & \\
\end{align*}
\]  
\[
\begin{align*}
\text{CsF} & \quad \text{(9.0 equiv)} \\
\text{MeCN (0.05 M)} & \\
80 \degree \text{C, 24 h; then, quencher} & \\
\text{rt, 5 min} & \\
3a & \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>quencher</th>
<th>3a : yield$^{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$O</td>
<td>79%</td>
</tr>
<tr>
<td>2</td>
<td>Et$_3$N</td>
<td>80%</td>
</tr>
<tr>
<td>3</td>
<td>none</td>
<td>80%</td>
</tr>
</tbody>
</table>

$^{[a]}$ Yields based on $^1$H NMR analyses.
Experimental Procedures

A typical procedure for the preparation of alkynyl sulfides:

A mixture of 4-ethynyltoluene (581 mg, 5.00 mmol), S-methyl 4-toluenethiosulfonate (1.52 g, 7.50 mmol, 1.5 equiv), CuI (47.6 mg, 0.250 mmol, 5.0 mol%), Xantphos (173.6 mg, 0.300 mmol, 6.0 mol%), and K$_2$CO$_3$ (1.04 g, 7.50 mmol, 1.5 equiv) suspended in DMSO (30 mL) was stirred at room temperature. After stirring for 24 h at the same temperature, to the mixture was added an aqueous saturated potassium carbonate solution (30 mL). The mixture was extracted with EtOAc (30 mL × 3), and the combined organic extract was washed with aqueous saturated potassium carbonate solution (20 mL × 3) and brine (20 mL), dried (Na$_2$SO$_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 20 g, n-hexane) to give methyl (4-tolyl)ethynyl sulfide (752 mg, 4.64 mmol, 93%) as a colorless oil.

According to the procedure for preparing methyl (4-tolyl)ethynyl sulfide, ethyl (4-tolyl)ethynyl sulfide (2a), isopropyl (4-tolyl)ethynyl sulfide, ethyl (4-methoxyphenyl)ethynyl sulfide (2b), (4-chlorophenyl)ethynyl ethyl sulfide (2e), ethyl (4-methoxycarbonylphenyl)ethynyl sulfide (2d), (2-bromophenyl)ethynyl ethyl sulfide (2e), ethyl (2-naphthyl)ethynyl sulfide (2f), ethyl (3-thienyl)ethynyl sulfide (2h), and 2-((3-(ethylthio)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyranyl (2l) were prepared from the corresponding thiosulfonates and terminal alkynes.

Preparation of benzyl (4-tolyl)ethynyl sulfide

To a solution of 4-ethynyltoluene (232 mg, 2.00 mmol) dissolved in THF (5.0 mL) was slowly added n-BuLi (1.65 M, hexane solution, 1.33 mL, 2.20 mmol, 1.1 equiv) at −78 °C. After stirring for 15 minutes at the same temperature, the mixture was slowly added a solution of S-benzyl 4-toluenethiosulfonate (668 mg, 2.40 mmol, 1.2 equiv) dissolved in THF (5.0 mL) at −78 °C. After stirring for 2 h at the same temperature, the mixture was allowed to warm to room temperature, and to this was added an aqueous saturated ammonium chloride solution (10 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na$_2$SO$_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 10 g, n-hexane/CH$_2$Cl$_2$ = 10/1) to give benzyl (4-tolyl)ethynyl sulfide (418 mg, 1.75 mmol, 87.7%) as a pale red oil.

According to the procedure for preparing benzyl (4-tolyl)ethynyl sulfide, 4-tolyl (4-tolyl)ethynyl sulfide, ethyl (2-phenethyl)ethynyl sulfide (2i), cyclohexylethynyl ethyl sulfide (2j), and 3,17-di-O-methyl-17-(ethylthioethynyl)estradiol (2k) were prepared from the corresponding thiosulfonates and terminal alkynes.
A typical procedure for the synthesis of benzo thiophenes by reaction of arynes with alkynyl sulfides

To a mixture of 2-chloro-6-(trimethylsilyl) phenyl triflate (1a) (99.8 mg, 0.300 mmol, 3.0 equiv) and ethyl (4-toly) ethynyl sulfide (2a) (19.2 mg, 0.100 mmol) dissolved in MeCN (2.0 mL) were added cesium fluoride (137 mg, 0.900 mmol, 9.0 equiv) at room temperature. After stirring for 24 h at 80 °C, the mixture was cooled to room temperature, and to this was added water (3 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give 4-chloro-3-(4-toly)benzo[b]thiophene (3a) (20.6 mg, 74.9 µmol, 75%) as a colorless oil.

According to the procedure for preparing 4-chloro-3-(4-toly)benzo[b]thiophene (3a), 4-chloro-3-(4-methoxyphenyl) benzo[b]thiophene (3b), 4-chloro-3-(4-chlorophenyl) benzo[b]thiophene (3c), 4-chloro-3-(4-methoxycarbonylphenyl)benzo[b]thiophene (3d), 3-(2-bromophenyl)-4-chlorobenz[b]thiophene (3e), 4-chloro-3-(2-naphthyl)benzo[b]thiophene (3f), 4-chloro-3-(9-phenanthryl)benzo[b]thiophene (3g), 4-chloro-3-(3-thienyl)benzo[b]thiophene (3h), 4-chloro-3-(2-phenylethyl)benzo[b]thiophene (3i), 4-chloro-3-(2-cyclohexyl)benzo[b]thiophene (3j), 4-chloro-3-(3,17-di-O-methylestradiol-17-yl)benzo[b]thiophene (3k), 3-(4-tolyl)benzo[b]thiophene (3l), 4-flouro-3-(4-toly)benzo[b]thiophene (3m), 4-bromo-3-(4-tolyl)benzo[b]thiophene (3n), 4-methoxy-3-(4-toly)benzo[b]thiophene (3o), 4-diethylaminomethyl-3-(4-tolyl)benzo[b]thiophene (3p), 5-methyl-3-(4-toly)benzo[b]thiophene (3q), 6-methyl-3-(4-tolyl) benzo[b]thiophene (3r), 5-methoxy-3-(4-toly)benzo[b]thiophene (3r'), 6-methoxy-3-(4-tolyl) benzo[b]thiophene (3w), 5,6-(methylenedioxy)-3-(4-toly)benzo[b]thiophene (3s), 6-bromo-4-chloro-3-(4-tolyl)benzo[b]thiophene (3t), 2,3-dibutyl-8-(4-tolyl)benzo[1,2-b:3,4-b']dithiophene (3u), 1-(4-tolyl)phenanthro[3,4-b']thiophene (3v), and 8-(2-bromophenyl)-2,3-(dibutyl)benzo[1,2-b:3,4-b']dithiophene (3x) were prepared from the corresponding aryne precursors and alkynyl sulfides.

Procedure for the synthesis of benzo thiophene 3a using 2.0 mmol of alkynyl sulfide 2a

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (2.00 g, 6.00 mmol, 3.0 equiv) and ethyl (4-tolyl) ethynyl sulfide (2a) (353 mg, 2.00 mmol) dissolved in MeCN (20 mL) were added cesium fluoride (2.73 g, 18.0 mmol, 9.0 equiv) at room temperature. After stirring for 24 h at 80 °C, the mixture was cooled to room temperature, and to this was added water (30 mL). The mixture was extracted with EtOAc (30 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 26 g, n-hexane) to give 4-chloro-3-(4-toly)benzo[b]thiophene (3a) (292 mg, 1.13 mmol, 56%) as a colorless oil.
A typical procedure for the functionalization of benzothiophene 3a via deprotonation at the C2 position

To a solution of 4-chloro-3-(4-tolyl)benzo[b]thiophene (3a) (25.4 mg, 98.2 µmol) dissolved in THF (500 µL) was slowly added LDA (1.00 M, THF/n-hexane solution, 150 µL, 0.150 mmol, 1.5 equiv) at −20 °C. After stirring for 15 min at the same temperature, to the mixture was slowly added a solution of S-(4-tolyl)4-toluenethiosulfonate (55.7 mg, 0.200 mmol, 2.0 equiv) dissolved in THF (500 µL) at −20 °C. After stirring for 1 h at the same temperature, the mixture was allowed to warm to room temperature, and to this was added an aqueous saturated ammonium chloride solution (5 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/EtOAc = 5/1) to give 4-chloro-3-(4-tolyl)-2-(4-tolylthio)benzo[b]thiophene (5a) (30.8 mg, 80.9 µmol, 82%) as a colorless oil.

Similarly, 4-chloro-2-iodo-3-(4-tolyl)benzo[b]thiophene (5b) and 4-chloro-2-ethoxycarbonyl-3-(4-tolyl)benzo[b]thiophene (5c) were prepared.

1. LDA (1.5 equiv)
   THF, n-hexane
   −20 °C, 15 min

2. S
   (2.0 equiv)
   −20 °C, 1 h

82%

Procedure for the synthesis of 4-chloro-3-(4-tolyl)benzo[b]thiophene S-oxide (6)\textsuperscript{S11}

To a solution of 4-chloro-3-(4-tolyl)benzo[b]thiophene (3a) (38.8 mg, 0.150 mmol) dissolved in CH2Cl2 (1.0 mL) was added BF3·OEt2 (151 µL, 1.20 mmol, 8.0 equiv) at −20 °C. To the mixture was slowly added mCPBA (ca. 65%, 39.8 mg, ca. 0.15 mmol, ca. 1.0 equiv) over 1.5 h at the same temperature. After stirring for 4 h at the same temperature, to this were added an aqueous saturated solution of sodium bicarbonate (5 mL) and an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with CH2Cl2 (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/CH2Cl2 = 1/1) to give 4-chloro-3-(4-tolyl)benzo[b]thiophene S-oxide (6) (34.1 mg, 0.124 mmol, 83%) as a colorless solid.
Procedure for the synthesis of benzothiophene 7 by C2–H arylation of benzothiophene S-oxide 6

To a mixture of 4-chloro-3-(4-tolyl)benzo[b]thiophene S-oxide (6) (10.7 mg, 38.9 µmol) and phenol (5.50 mg, 58.4 µmol, 1.5 equiv) dissolved in CH2Cl2 (500 µL) was added trifluoroacetic anhydride (8.23 µL, 58.4 µmol, 1.5 equiv) at –40 °C. After 15 min at the same temperature, the mixture was warmed to room temperature. After stirring for 12 h at room temperature, to this were added BF3·OEt2 (0.98 µL, 7.8 µmol, 20 mol %) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added water (3 mL). The mixture was extracted with CH2Cl2 (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/EtOAc = 9/1) to give 4-chloro-2-(2-hydroxyphenyl)-3-(4-tolyl)benzo[b]thiophene (7) (11 mg, 30 µmol, 78%) as a pale yellow oil.

Procedure for the synthesis of benzothiophene 5c by the reaction of aryne precursor 1a with alkynyl sulfide 2a under CO2 atmosphere

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (49.9 mg, 0.150 mmol, 3.0 equiv) and ethyl (4-tolyl)ethynyl sulfide (2a) (8.81 mg, 50.0 µmol) dissolved in MeCN (1.0 mL) was added cesium fluoride (68.4 mg, 0.450 mmol, 9.0 equiv) at room temperature. The reaction mixture was evacuated and backfilled with CO2 (1 atm) for three times. After stirring for 24 h at the same temperature, to the mixture was added water (3 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/CH2Cl2 = 3/1) to give 4-chloro-2-ethoxycarbonyl-3-(4-tolyl)benzo[b]thiophene (5c) (3.30 mg, 9.97 µmol, 20%) as a colorless solid.
Procedure for the synthesis of 4-chloro-3-(hydroxymethyl)benzo[b]thiophene (3w)

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (2.00 g, 6.00 mmol, 3.0 equiv) and 2-((3-ethylthio)prop-2-yn-1-yl)oxytetrahydro-2H-pyran (2l) (401 mg, 2.00 mmol) dissolved in MeCN (40 mL) were added cesium fluoride (2.73 g, 18.0 mmol, 9.0 equiv) at room temperature. After stirring for 24 h at room temperature, the mixture was added an aqueous saturated solution of sodium bicarbonate (30 mL). The mixture was extracted with EtOAc (30 mL × 3), and the combined organic extract was washed with brine (10 mL), and after filtration, the filtrate was concentrated under reduced pressure. All the resulting mixture was used for the following procedure.

To a solution of the residue dissolved in MeOH (20 mL) was added p-toluenesulfonic acid monohydrate (38.0 mg, 0.200 mmol, 10 mol %) at room temperature. After stirring for 2 h at room temperature, the mixture was added an aqueous saturated solution of sodium bicarbonate (30 mL). The mixture was extracted with CH₂Cl₂ (30 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 16 g, n-hexane/EtOAc = 4/1) to give 4-chloro-3-(hydroxymethyl)benzo[b]thiophene (3w) (223 mg, 1.12 mmol, 56%) as a colorless solid.

Procedure for the synthesis of 4-chlorobenzo[b]thiophene-3-carboxylic acid (9)

To a mixture of 4-chloro-3-(hydroxymethyl)benzo[b]thiophene (3w) (99.3 mg, 0.500 mmol) and CuBr₂ (11.2 mg, 50.0 µmol, 10 mol %) dissolved in MeCN (3.0 mL) was slowly added t-BuOOH (70% water solution, 640 µL, 5.00 mmol, 10 equiv) at room temperature. After stirring for 24 h at room temperature, the mixture was added an aqueous saturated solution of sodium bicarbonate (10 mL). The mixture was extracted with EtOAc (10 mL), and the aqueous layer was acidified using 1 M HCl. The aqueous layer was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 1.8 g, EtOAc) to give 4-chlorobenzo[b]thiophene-3-carboxylic acid (9) (88.9 mg, 0.418 mmol, 84%) as a colorless solid.
Procedure for the synthesis of 4-chloro-3-iodobenzo[h]thiophene (10)\textsuperscript{213}

To a mixture of 4-chlorobenzo[h]thiophene-3-carboxylic acid (9) (21.3 mg, 0.100 mmol) and I\textsubscript{2} (102 mg, 0.400 mmol, 4.0 equiv) dissolved in MeCN (500 µL) was added tripotassium phosphate (21.2 mg, 0.100 mmol, 1.0 equiv) at room temperature. After stirring for 4 h at 100 °C, the mixture was cooled to room temperature, and to this was added an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na\textsubscript{2}SO\textsubscript{4}), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give 4-chloro-3-iodobenzo[h]thiophene (10) (24.8 mg, 84.2 µmol, 84%) as a colorless solid.

Palladium-catalyzed direct C2 C–H arylation for the synthesis of benzo[h]thiophene 11\textsuperscript{214}

To a mixture of 6-bromo-4-chloro-3-(4-tolyl)benzo[h]thiophene (3t) (68.0 mg, 0.180 mmol, 1.5 equiv) and 4-idoanisole (28.0 mg, 0.120 mmol) dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (3.0 mL) were added Pd(OAc)\textsubscript{2} (1.35 mg, 6.00 µmol, 5.0 mol %), Ag\textsubscript{2}O (27.8 mg, 0.120 mmol, 1.0 equiv), and AcONa (4.92 mg, 60.0 µmol, 0.50 equiv) at 30 °C. After stirring for 17 h at the same temperature, the resultant mixture was diluted with EtOAc (5 mL) and filtered through a plug of silica. The silica plug was flushed with EtOAc (30 mL), and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/CH\textsubscript{2}Cl\textsubscript{2} = 9/1) to give 6-bromo-4-chloro-2-(4-methoxyphenyl)-3-(4-tolyl)benzo[h]thiophene (11) (25.6 mg, 57.7 µmol, 48%) as a colorless oil.
Consecutive Suzuki–Miyaura cross-coupling for the synthesis of benzo[b]thiophene 12

![Chemical structure](image)

To a mixture of 6-bromo-4-chloro-2-(4-methoxyphenyl)-3-(4-toly)benzo[b]thiophene (11) (17.8 mg, 40.0 µmol) and 4-(trifluoromethyl)phenylboronic acid (11.4 mg, 60.0 µmol, 1.5 equiv) dissolved in 1,4-dioxane (720 µL) and water (80 µL) were added (amphos)PdCl₂ (2.83 mg, 4.00 µmol, 10 mol%), K₂CO₃ (16.6 mg, 0.120 mmol, 3.0 equiv) at room temperature. After stirring for 24 h at 90 °C, the mixture was cooled to room temperature, and to this was added water (5 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. All the resulting mixture was used for the following procedure.

To a mixture of the residue prepared above and phenylboronic acid (14.6 mg, 0.120 mmol, 3.0 equiv) dissolved in toluene (800 µL) were added Pd(OAc)₂ (0.45 mg, 2.0 µmol, 5.0 mol%), SPhos (1.64 mg, 4.0 µmol, 10 mol%), and K₃PO₄ (42.5 mg, 0.200 mmol, 5.0 equiv) at room temperature. After stirring for 24 h at 110 °C, the mixture was cooled to room temperature, and to this was added water (5 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/CH₂Cl₂ = 3/1) to give 2-(4-methoxyphenyl)-4-phenyl-3-(4-toly)-6-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (12) (5.3 mg, 9.6 µmol, 24%) as a colorless solid.

Procedure for the iodination of benzo[b]thiophene 3x via deprotlithilation at the C2 position

![Chemical structure](image)

To a solution of 8-(2-bromophenyl)-2,3-(dibutyl)benzo[1,2-b:3,4-b']dithiophene (3x) (24.2 mg, 52.8 µmol) dissolved in THF (500 µL) was slowly added LDA (1.00 M, THF/n-hexane solution, 75.0 µL, 75.0 µmol, 1.4 equiv) at −20 °C. After stirring for 15 min at the same temperature, to this was added an aqueous saturated solution of sodium bicarbonate (5 mL) and an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/CH₂Cl₂ = 5/1) to give 8-(2-bromophenyl)-2,3-dibutyl-7-iodobenzo[1,2-b:3,4-b']dithiophene (13) (19.8 mg, 33.9 µmol, 64%) as a pale yellow oil.
Procedure for the synthesis of benzothiophene 14 by palladium-catalyzed N-arylation

To a mixture of 8-(2-bromophenyl)-2,3-dibutyl-7-iodobenzo[1,2-b;3,4-b']dithiophene (13) (33.7 mg, 57.8 µmol) and p-toluidine (9.29 mg, 86.7 µmol, 1.5 equiv) dissolved in toluene (1.0 mL) were added RuPhos Pd G1 (4.20 mg, 5.78 µmol, 10 mol %), RuPhos (2.70 mg, 5.78 µmol, 10 mol %), and t-BuONa (16.6 mg, 0.173 mmol, 3.0 equiv) at room temperature. After stirring for 21 h at 110 °C, the mixture was cooled to room temperature, and to this was added water (5 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/CH2Cl2 = 6/1) to give 2,3-dibutyl-7-(4-tolyl)-7H-thieno[3''2'':5',6']benzo[1'2':4,5]thieno[2,3-b]indole (14) (17.5 mg, 36.3 µmol, 63%) as a colorless solid.
Deuteration Experiments

**Deuteration experiment using CD$_3$CN**

![Chemical Reaction Diagram](image)

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (49.9 mg, 0.150 mmol, 3.0 equiv) and ethyl (4-tolyl)ethynyl sulfide (2a) (8.81 mg, 50.0 µmol) dissolved in CD$_3$CN (1.0 mL) was added cesium fluoride (68.4 mg, 0.450 mmol, 9.0 equiv) at room temperature. After stirring for 24 h at 80 °C, the mixture was cooled to room temperature, and to this was added water (3 mL). The mixture was extracted with EtOAc (10 mL x 3), and the combined organic extract was washed with brine (5 mL), dried (Na$_2$SO$_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give mixture of 3a and d-3a (9.0 mg, 35 µmol, 70%, 23 atom %D) (determined by comparing the relative values of integration for the peaks observed at 7.70 ppm (1H for 3a) in DMSO-d$_6$) was obtained as a colorless oil.

**Deuteration experiment using deuterated ethyl-substituted alkynyl sulfide 2a-d**

![Chemical Reaction Diagram](image)

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (49.9 mg, 0.150 mmol, 3.0 equiv) and pentadeuteroethyl (4-tolyl)ethynyl sulfide (2a-d) (11.1 mg, 50.0 µmol) dissolved in MeCN (1.0 mL) was added cesium fluoride (68.4 mg, 0.450 mmol, 9.0 equiv) at room temperature. After stirring for 24 h at 80 °C, the mixture was cooled to room temperature, and to this was added water (3 mL). The mixture was extracted with EtOAc (10 mL x 3), and the combined organic extract was washed with brine (5 mL), dried (Na$_2$SO$_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give mixture of 3a and 3a-d (9.20 mg, 35.5 µmol, 71%, 29 atom %D) (determined by comparing the relative values of integration for the peaks observed at 7.70 ppm (1H for 3a) in DMSO-d$_6$) was obtained as a colorless oil.
**Benzothiophene synthesis in the presence of D$_2$O**

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (49.9 mg, 0.150 mmol, 3.0 equiv) and ethyl (4-toly)ethynyl sulfide (2a) (8.81 mg, 50.0 µmol) dissolved in MeCN (1.0 mL) was added cesium fluoride (68.4 mg, 0.450 mmol, 9.0 equiv) and deuterium oxide (0.91 µL, 50 µmol, 1.0 equiv) at room temperature. After stirring for 24 h at 80 °C, the mixture was cooled to room temperature, and to this was added water (3 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na$_2$SO$_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give mixture of 3a and d-3a (4.5 mg, 17 µmol, 35%, 36 atom %D) (determined by comparing the relative values of integration for the peaks observed at 7.70 ppm (1H for 3a) in DMSO-d$_6$) was obtained as a colorless oil.

**Benzothiophene synthesis using D$_2$O in work-up**

To a mixture of 2-chloro-6-(trimethylsilyl)phenyl triflate (1a) (49.9 mg, 0.150 mmol, 3.0 equiv) and ethyl (4-toly)ethynyl sulfide (2a) (8.81 mg, 50.0 µmol) dissolved in MeCN (1.0 mL) was added cesium fluoride (68.4 mg, 0.450 mmol, 9.0 equiv) at room temperature. After stirring for 24 h at 80 °C, the mixture was cooled to room temperature, and to this was added deuterium oxide (2 mL). After stirring for 5 min at the same temperature, the mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na$_2$SO$_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give 4-chloro-3-(4-toly)benzo[b]thiophene (3a) (9.1 mg, 35 µmol, 70%) as a colorless oil, in which no incorporation of deuterium was observed.
Characterization Data of New Compounds

Methyl (4-toly1)ethynyl sulfide\(^{15}\), ethyl (4-toly1)ethynyl sulfide (2a),\(^{15}\) 4-toly1 (4-toly1)ethynyl sulfide,\(^{16}\) ethyl (4-methoxyphenyl)ethynyl sulfide (2b),\(^{17}\) (4-chlorophenyl)ethyl ethynyl sulfide (2c),\(^{18}\) ethyl (2-naphtyl)ethyl ethynyl sulfide (2f),\(^{19}\) 3-(4-toly1)benzol[b]thiophene (3i),\(^{20}\) 5-methyl-3-(4-toly1)benzol[b]thiophene (3q),\(^{21}\) 6-methyl-3-(4-toly1)benzol[b]thiophene (3q'),\(^{22}\) 5-methoxy-3-(4-toly1)benzol[b]thiophene (3r),\(^{22}\) and 6-methoxy-3-(4-toly1)benzol[b]thiophene (3r')\(^{24}\) were identical in spectra data with those reported in the literature.

Isopropyl (4-toly1)ethynyl sulfide

Colorless oil; TLC \( R_t \) 0.32 (n-hexane); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 1.42 (d, 6H, \( J = 6.7 \) Hz), 2.34 (s, 3H), 3.24 (sept, 1H, \( J = 6.7 \) H), 7.08–7.12 (AA’BB’, 2H), 7.30–7.34 (AA’BB’, 2H); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \( \delta \) 21.4 (1C), 22.9 (2C), 39.8 (1C), 77.5 (1C), 94.8 (1C), 120.5 (1C), 129.0 (2C), 131.4 (2C), 138.1 (1C); IR (KBr, \( \text{cm}^{-1} \)) 814, 1051, 1236, 1248, 1450, 1506, 2864, 2922, 2963; HRMS (ESI\(^+\)) \( m/z \) 191.0890 ([M+H]\(^+\), \( \text{C}_8\text{H}_18\text{S}^+ \) requires 191.0889).

Benzyl (4-toly1)ethynyl sulfide

Pale red oil; TLC \( R_t \) 0.14 (n-hexane); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 2.33 (s, 3H), 4.00 (s, 2H), 7.06–7.11 (AA’BB’, 2H), 7.22–7.26 (AA’BB’, 2H), 7.27–7.40 (m, 5H); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \( \delta \) 21.5 (1C), 40.5 (1C), 78.1 (1C), 94.6 (1C), 120.2 (1C), 127.7 (1C), 128.5 (2C), 129.0 (2C), 129.1 (2C), 131.4 (2C), 136.6 (1C), 138.3 (1C); IR (KBr, \( \text{cm}^{-1} \)) 530, 696, 764, 816, 1454, 1495, 1506, 3028; HRMS (ESI\(^+\)) \( m/z \) 239.0887 ([M+H]\(^+\), \( \text{C}_{16}\text{H}_{18}\text{S}^+ \) requires 239.0889).

Ethyl (4-methoxy carbonyl phenyl)ethynyl sulfide (2d)

Pale yellow solid; Mp 37–39 \(^\circ\)C; TLC \( R_t \) 0.30 (n-hexane/CH\(_2\)Cl\(_2\) = 1/1); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 1.47 (t, 3H, \( J = 7.3 \) Hz), 2.85 (q, 2H, \( J = 7.3 \) Hz), 3.91 (s, 3H), 7.41–7.47 (AA’BB’, 2H), 7.94–7.99 (AA’BB’, 2H); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \( \delta \) 14.7 (1C), 30.0 (1C), 52.2 (1C), 83.4 (1C), 93.2 (1C), 128.2 (1C), 128.9 (1C), 129.4 (2C), 130.8 (2C), 166.5 (1C); IR (KBr, \( \text{cm}^{-1} \)) 768, 1107, 1175, 1275, 1308, 1435, 1603, 1722, 2162, 2949; HRMS (ESI\(^+\)) \( m/z \) 243.0449 ([M+Na]\(^+\), \( \text{C}_8\text{H}_{18}\text{O}_2\text{S}^+ \) requires 243.0450).

(2-Bromophenyl)ethyl ethynyl sulfide (2e)

Colorless oil; TLC \( R_t \) 0.22 (n-hexane); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 1.51 (t, 3H, \( J = 7.3 \) Hz), 2.86 (q, 2H, \( J = 7.3 \) Hz), 7.12 (ddd, 1H, \( J = 7.7, 7.7, 1.7 \) Hz), 7.23 (ddd, 1H, \( J = 7.7, 7.7, 1.2 \) Hz), 7.41 (dd, 1H, \( J = 7.7, 1.7 \) Hz), 7.55 (dd, 1H, \( J = 7.7, 1.2 \) Hz); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \( \delta \) 14.9 (1C), 30.1 (1C), 84.8 (1C), 92.2 (1C), 124.8 (1C), 125.6 (1C), 126.9 (1C), 128.8 (1C), 132.3 (1C), 132.6 (1C); IR (KBr, \( \text{cm}^{-1} \)) 679, 750, 1024, 1045, 1258, 1431, 1464, 2170, 2926, 2965; HRMS (ESI\(^+\)) \( m/z \) 262.9496 ([M+Na]\(^+\), \( \text{C}_8\text{H}_{18}\text{BrNaS}^+ \) requires 262.9501).
Ethyl (9-phenanthrenyl)ethynyl sulfide (2g)

Yellow solid; Mp 56–57 °C; TLC Rf 0.63 (n-hexane/CHCl₃ = 1/1); ¹H NMR (CDCl₃, 500 MHz) δ 1.55 (t, 3H, J = 7.3 Hz), 2.93 (q, 2H, J = 7.3 Hz), 7.57 (ddd, 1H, J = 7.9, 7.9, 1.0 Hz), 7.60–7.71 (m, 3H), 7.82 (d, 1H, J = 8.0 Hz), 7.95 (s, 1H), 8.37–8.43 (m, 1H), 8.62 (d, 1H, J = 8.0 Hz), 8.64–8.69 (m, 1H); ¹³C NMR (CDCl₃, 126 MHz) δ 14.9 (1C), 30.2 (1C), 83.8 (1C), 91.8 (1C), 119.9 (1C), 122.6 (1C), 122.7 (1C), 126.85 (1C), 126.91 (1C), 127.0 (1C+1C, two signals overlapped), 127.3 (1C), 128.4 (1C), 130.0 (1C), 130.1 (1C), 131.16 (1C), 131.19 (1C), 131.2 (1C); IR (KBr, cm⁻¹) 723, 748, 764, 891, 1256, 1377, 1450, 1491, 2924; HRMS (ESI⁺) m/z 285.0700 ([M+Na]⁺, C₁₂H₁₄NaS⁺ requires 285.0708).

Ethyl (3-thienyl)ethynyl sulfide (2h)

Colorless oil; TLC Rf 0.19 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 1.44 (t, 3H, J = 7.3 Hz), 2.80 (q, 2H, J = 7.3 Hz), 7.10 (dd, 1H, J = 5.0, 1.2 Hz), 7.24 (dd, 1H, J = 5.0, 3.0 Hz), 7.43 (dd, 1H, J = 3.0, 1.2 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 14.7 (1C), 29.9 (1C), 78.5 (1C), 88.2 (1C), 122.5 (1C), 125.1 (1C), 128.9 (1C), 130.0 (1C); IR (KBr, cm⁻¹) 625, 779, 837, 872, 957, 1260, 1354, 1447, 2924, 2965; HRMS (ESI⁺) m/z 169.0144 ([M+H]⁺, C₉H₁₀NaS⁺ requires 169.0140).

Ethyl (2-phenethyl)ethynyl sulfide (2i)

Pale yellow oil; TLC Rf 0.22 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 1.32 (t, 3H, J = 7.3 Hz), 2.60 (t, 2H, J = 7.5 Hz), 2.65 (q, 2H, J = 7.3 Hz), 2.84 (t, 2H, J = 7.3 Hz), 7.18–7.24 (m, 3H), 7.26–7.32 (AA′BB′C, 2H); ¹³C NMR (CDCl₃, 126 MHz) δ 14.6 (1C), 22.3 (1C), 29.5 (1C), 35.2 (1C), 69.0 (1C), 93.9 (1C), 126.3 (1C), 128.3 (2C), 128.4 (2C), 140.6 (1C); IR (KBr, cm⁻¹) 698, 748, 1260, 1452, 1495, 2926, 2965, 3026; HRMS (ESI⁺) m/z 213.0708 ([M+Na]⁺, C₁₀H₁₃S⁺ requires 213.0708).

Cyclohexylethynyl ethyl sulfide (2j)

Colorless oil; TLC Rf 0.30 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 1.25–1.35 (m, 3H), 1.38 (t, 3H, J = 7.3 Hz), 1.40–1.54 (m, 3H), 1.65–1.74 (m, 2H), 1.75–1.84 (m, 2H), 2.44–2.53 (m, 1H), 2.68 (q, 2H, J = 7.3 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 14.5 (1C), 24.8 (1C), 25.8 (2C), 29.6 (2C), 30.4 (1C), 32.7 (1C), 67.8 (1C), 98.9 (1C); IR (KBr, cm⁻¹) 970, 1032, 1055, 1072, 1258, 1447, 2853, 2928; HRMS (ESI⁺) m/z 169.1040 ([M+H]⁺, C₁₀H₁₃S⁺ requires 169.1045).
3,17-Di-O-methyl-17-(ethylthioethynyl)estradiol (2k)

Colorless oil; TLC Rf 0.25 (n-hexane/CH2Cl2 = 1/1); 1H NMR (CDCl3, 500 MHz) δ 0.87 (s, 3H), 1.31–1.53 (m, 7H), 1.72–2.04 (m, 6H), 2.16–2.27 (m, 2H), 2.28–2.36 (m, 1H), 2.69–2.79 (m, 2H), 2.80–2.94 (m, 2H), 3.40 (s, 3H), 3.77 (s, 3H), 6.62 (d, 1H, J = 2.7 Hz), 6.71 (dd, 1H, J = 8.6, 2.7 Hz), 7.20 (d, 1H, J = 8.6 Hz); 13C NMR (CDCl3, 126 MHz) δ 12.9 (1C), 14.9 (1C), 22.8 (1C), 26.6 (1C), 27.3 (1C), 29.8 (1C), 29.9 (1C), 34.4 (1C), 36.8 (1C), 39.2 (1C), 43.5 (1C), 47.9 (1C), 49.7 (1C), 53.3 (1C), 55.2 (1C), 77.2 (1C), 86.7 (1C), 95.2 (1C), 111.5 (1C), 113.8 (1C), 126.3 (1C), 132.6 (1C), 137.9 (1C), 157.4 (1C); IR (KBr, cm−1) 1047, 1082, 1098, 1238, 1256, 1452, 1499, 2870, 2930; HRMS (ESI+) m/z 407.2014 ([M+Na]+, C24H32NaO2S+ requires 407.2015).

2-((3-(Ethylthio)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran (2l)

Colorless oil; TLC Rf 0.34 (n-hexane/EtOAc = 10/1); 1H NMR (CDCl3, 500 MHz) δ 1.30 (t, 3H, J = 7.3 Hz), 1.60–1.88 (m, 4H), 2.73 (q, 2H, J = 7.3 Hz), 3.49–3.56 (m, 1H), 3.80–3.88 (m, 1H), 4.31–4.44 (m, 2H), 4.80–4.85 (m, 1H); 13C NMR (CDCl3, 126 MHz) δ 14.6 (1C), 19.0 (1C), 25.3 (1C), 29.5 (1C), 30.2 (1C), 55.0 (1C), 62.0 (1C), 76.3 (1C), 90.6 (1C), 96.5 (1C); IR (KBr, cm−1) 903, 1015, 1038, 1061, 1076, 1119, 2928, 2941; HRMS (ESI+) m/z 223.0764 ([M+Na]+, C10H16NaO2S+ requires 223.0763).

4-Chloro-3-(4-toly)benzo[4]thiophene (3a)

Colorless oil; TLC Rf 0.33 (n-hexane); 1H NMR (DMSO-d6, 500 MHz) δ 2.37 (s, 3H), 7.19–7.24 (AA′BB′, 2H), 7.27–7.30 (AA′BB′, 2H), 7.36–7.44 (m, 2H), 7.70 (s, 1H), 8.07 (dd, 1H, J = 7.6, 1.3 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.3 (1C), 121.6 (1C), 124.8 (1C), 126.2 (1C), 126.3 (1C), 128.0 (2C), 129.4 (1C), 130.1 (2C), 134.28 (1C), 134.33 (1C), 137.1 (1C), 138.4 (1C), 142.4 (1C); IR (KBr, cm−1) 745, 770, 814, 829, 1092, 1198, 1395, 1443, 1526; HRMS (ESI+) m/z 281.0166 ([M+Na]+, C13H10ClNaO2S+ requires 281.0162).

The regiochemistry of 3a was determined by the HMBC experiment.
4-Chloro-3-(4-methoxyphenyl)benzo[b]thiophene (3b)

Pale yellow solid; Mp 94–96 °C; TLC Rf 0.55 (n-hexane/CH₂Cl₂ = 1/1); ¹H NMR (CDCl₃, 500 MHz) δ 3.87 (s, 3H), 6.91–6.96 (AA’BB’, 2H), 7.24–7.30 (m, 2H), 7.31–7.36 (m, 3H), 7.80 (dd, 1H, J = 8.0, 1.0 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 55.3 (1C), 112.8 (2C), 121.6 (1C), 124.8 (1C), 126.2 (1C), 126.3 (1C), 129.5 (1C), 129.6 (1C), 131.4 (2C), 134.4 (1C), 138.1 (1C), 142.4 (1C), 159.1 (1C); IR (KBr, cm⁻¹) 746, 772, 833, 1034, 1175, 1246, 1287, 1491, 1526; HRMS (ESI⁺) m/z 297.0111 ([M+Na]⁺, C₁₅H₁₁₃ClNaOS⁺ requires 297.0111).

4-Chloro-3-(4-chlorophenyl)benzo[b]thiophene (3c)

Colorless oil; TLC Rf 0.32 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 7.29 (dd, 1H, J = 7.9, 7.9 Hz), 7.32 (s, 1H), 7.33–7.39 (m, 5H), 7.82 (dd, 1H, J = 7.9, 1.1 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 121.7 (1C), 125.1 (1C), 126.4 (1C), 126.7 (1C), 127.6 (2C), 129.3 (1C), 131.6 (2C), 133.5 (1C), 134.4 (1C), 135.7 (1C), 137.1 (1C), 142.4 (1C); IR (KBr, cm⁻¹) 743, 772, 833, 1016, 1092, 1198, 1327, 1395, 1479, 1516; HRMS (ESI⁺) m/z 278.9799 ([M+H]⁺, C₁₄H₉₃Cl₂S⁺ requires 278.9797).

4-Chloro-3-(4-methoxycarbonylphenyl)benzo[b]thiophene (3d)

Colorless solid; Mp 109–111 °C; TLC Rf 0.26 (n-hexane/CH₂Cl₂ = 1/1); ¹H NMR (CDCl₃, 500 MHz) δ 3.96 (s, 3H), 7.30 (dd, 1H, J = 7.8, 7.8 Hz), 7.34–7.37 (m, 2H), 7.48–7.52 (AA’BB’, 2H), 7.83 (dd, 1H, J = 7.8, 1.1 Hz), 8.05–8.09 (AA’BB’, 2H); ¹³C NMR (CDCl₃, 126 MHz) δ 52.1 (1C), 121.7 (1C), 125.1 (1C), 126.4 (1C), 126.9 (1C), 128.6 (2C), 129.1 (1C), 129.3 (1C), 130.4 (1C), 134.1 (1C), 134.4 (1C), 137.1 (1C), 142.4 (1C), 167.0 (1C); IR (KBr, cm⁻¹) 704, 766, 1101, 1113, 1177, 1198, 1275, 1308, 1435, 1717; HRMS (ESI⁺) m/z 325.0055 ([M+Na]⁺, C₁₆H₁₁₃ClNaO₂S⁺ requires 325.0060).

3-(2-Bromophenyl)-4-chlorobenzo[b]thiophene (3e)

Pale yellow oil; TLC Rf 0.21 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 7.24–7.30 (m, 2H), 7.31–7.38 (m, 4H), 7.64 (d, 1H, J = 8.0 Hz), 7.81 (dd, 1H, J = 7.9, 1.0 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 121.6 (1C), 125.1 (1C), 125.7 (1C), 126.1 (1C), 126.6 (1C), 126.7 (1C), 129.4 (1C+1C, two signals overlapped), 131.86 (1C), 131.92 (1C), 133.4 (1C), 136.8 (1C), 138.5 (1C), 141.9 (1C); IR (KBr, cm⁻¹) 743, 756, 772, 826, 1092, 1200, 1396, 1460; HRMS (ESI⁺) m/z 344.9118 ([M+Na]⁺, C₁₆H₉₇BrClNaS⁺ requires 344.9111).
4-Chloro-3-(2-naphthyl)benzo[b]thiophene (3f)

Pale yellow oil; TLC Rf 0.16 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 7.29 (dd, 1H, J = 7.7, 7.7 Hz), 7.35 (dd, 1H, J = 7.7, 1.0 Hz), 7.40 (s, 1H), 7.49–7.54 (m, 2H), 7.56 (dd, 1H, J = 8.3, 1.7 Hz), 7.82–7.92 (m, 5H); ¹³C NMR (CDCl₃, 126 MHz) δ 121.7 (1C), 125.0 (1C), 126.0 (1C), 126.2 (1C), 126.3 (1C), 126.5 (1C), 126.8 (1C), 127.7 (1C), 128.0 (1C), 128.7 (1C), 128.9 (1C), 129.5 (1C), 132.7 (1C), 132.8 (1C), 134.5 (1C), 134.9 (1C), 138.4 (1C), 142.5 (1C); IR (KBr, cm⁻¹) 743, 766, 773, 818, 827, 853, 1090, 1200; HRMS (ESI⁺) m/z 317.0159 ([M+Na]⁺, C₁₈H₁₁ClNaS⁺ requires 317.0162).

4-Chloro-3-(9-phenanthrenyl)benzo[b]thiophene (3g)

Pale yellow oil; TLC Rf 0.70 (n-hexane/CH₂Cl₂ = 1/1); ¹H NMR (CDCl₃, 500 MHz) δ 7.23–7.34 (m, 2H), 7.42–7.52 (m, 3H), 7.60–7.66 (m, 2H), 7.69 (ddd, 1H, J = 7.0, 7.0, 1.4 Hz), 7.76 (s, 1H), 7.86–7.92 (m, 2H), 8.72–8.78 (m, 2H); ¹³C NMR (CDCl₃, 126 MHz) δ 121.6 (1C), 122.60 (1C), 122.64 (1C), 125.1 (1C), 126.1 (1C), 126.4 (1C), 126.6 (1C), 126.8 (1C+1C, two signals overlapped), 126.9 (1C), 127.2 (1C), 128.5 (1C), 128.7 (1C), 129.6 (1C), 129.8 (1C), 130.4 (1C), 131.3 (1C), 133.3 (1C), 134.0 (1C), 135.7 (1C), 136.2 (1C), 142.2 (1C); IR (KBr, cm⁻¹) 725, 746, 827, 1200, 1215, 1395, 1441, 1450; HRMS (ESI⁺) m/z 367.0316 ([M+Na]⁺, C₂₂H₁₃ClNaS⁺ requires 367.0319).

4-Chloro-3-(3-thienyl)benzo[b]thiophene (3h)

Pale yellow oil; TLC Rf 0.25 (n-hexane); ¹H NMR (CDCl₃, 500 MHz) δ 7.18 (dd, 1H, J = 4.8, 1.0 Hz), 7.24–7.29 (m, 2H), 7.30–7.37 (m, 3H), 7.79 (d, 1H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 121.7 (1C), 123.8 (1C), 124.1 (1C), 124.9 (1C), 126.3 (1C), 126.8 (1C), 129.4 (1C), 130.6 (1C), 133.0 (1C), 134.5 (1C), 137.0 (1C), 142.2 (1C); IR (KBr, cm⁻¹) 652, 743, 768, 827, 1092, 1200, 1310, 1396, 1445; HRMS (ESI⁺) m/z 250.9757 ([M+H]⁺, C₁₂H₃ClS₂⁺ requires 250.9750).
4-Chloro-3-(2-phenylethyl)benzo[b]thiophene (3i)

\[
\begin{align*}
\text{Colorless oil; TLC } R_f & 0.27 \text{ (n-hexane); } ^1H \text{ NMR (CDCl}_3, 500 MHz) \delta 3.02-3.08 \text{ (m, 2H), 3.43–3.49 (m, 2H), 7.08 (s, 1H), 7.19–7.26 (m, 4H), 7.28–7.33 (AA'BB'C, 2H), 7.37 (dd, 1H, } J = 7.8, 0.9 Hz), 7.74 \text{ (dd, 1H, } J = 7.8, 0.9 Hz); ^13C \text{ NMR (CDCl}_3, 126 MHz) \delta 33.3 \text{ (1C), 37.3 (1C), 121.8 (1C), 123.9 (1C), 124.6 (1C), 126.0 (1C), 126.1 (1C), 128.4 (2C), 128.5 (2C), 129.0 (1C), 134.8 (1C), 137.1 (1C), 141.6 (1C), 143.2 (1C); IR (KBr, cm}^{-1}\text{) 698, 741, 764, 820, 1200, 1398, 1445, 1495, 1547; HRMS (ESI\(^+\)) m/z 295.0312 ([M+Na]\(^+\), C\(_{16}\)H\(_{13}\)35ClNaS\(^+\) requires 295.0319). \\
\end{align*}
\]

4-Chloro-3-cyclohexylbenzo[b]thiophene (3j)

\[
\begin{align*}
\text{Colorless oil; TLC } R_f & 0.51 \text{ (n-hexane); } ^1H \text{ NMR (CDCl}_3, 500 MHz) \delta 1.23–1.43 \text{ (m, 3H), 1.44–1.55 (m, 2H), 1.75–1.91 (m, 3H), 2.12–2.21 (m, 2H), 3.56–3.64 (m, 1H), 7.13–7.22 (m, 2H), } J = 7.8, 1.0 Hz, 7.73 \text{ (dd, 1H, } J = 7.8, 1.0 Hz); ^13C \text{ NMR (CDCl}_3, 126 MHz) \delta 26.4 \text{ (1C), 26.9 (2C), 34.9 (2C), 38.8 (1C), 120.9 (1C), 121.8 (1C), 124.2 (1C), 126.3 (1C), 128.9 (1C), 134.6 (1C), 143.2 (1C), 144.1 (1C); IR (KBr, cm}^{-1}\text{) 743, 758, 770, 822, 1200, 1443, 2849, 2926; HRMS (ESI\(^+\)) m/z 251.0660 ([M+H]\(^+\), C\(_{14}\)H\(_{16}\)35ClS\(^+\) requires 251.0656). \\
\end{align*}
\]

4-Chloro-3-(3,17-di-O-methylestradiol-17-yl)benzo[b]thiophene (3k)

\[
\begin{align*}
\text{Colorless solid; Mp 198–200 °C; TLC } R_f & 0.29 \text{ (n-hexane/CH}_2\text{Cl}_2 = 1/1); ^1H \text{ NMR (CDCl}_3, 500 MHz) \delta 0.69 \text{ (ddd, 1H, } J = 13.0, 13.0, 4.2 Hz), 1.22–1.34 \text{ (m, 3H), 1.36–1.53 (m, 3H), 1.56–1.67 (m, 1H), 1.79–1.86 (m, 1H), 1.86–1.95 (m, 2H), 1.98–2.06 (m, 1H), 2.31–2.39 (m, 1H), 2.42 \text{ (ddd, 1H, } J = 12.6, 3.5, 3.5 Hz), 2.53 \text{ (ddd, 1H, } J = 14.6, 9.8, 4.8 Hz), 2.76–2.91 \text{ (m, 2H), 3.08 \text{ (s, 3H), 3.74 \text{ (s, 3H), 6.59 \text{ (d, 1H, } J = 2.7 Hz), 6.63 \text{ (dd, 1H, } J = 8.6, 2.7 Hz), 7.03 \text{ (d, 1H, } J = 8.6 Hz), 7.22–7.27 \text{ (m, 2H), 7.53 \text{ (dd, 1H, } J = 7.6, 1.2 Hz), 7.78 \text{ (dd, 1H, } J = 7.6, 1.2 Hz); ^13C \text{ NMR (CDCl}_3, 126 MHz) \delta 14.7 \text{ (1C), 23.1 (1C), 26.4 (1C), 27.4 (1C), 29.9 (1C), 33.1 (1C), 38.1 (1C), 39.3 (1C), 43.2 (1C), 48.2 (1C), 49.3 (1C), 52.3 (1C), 55.1 (1C), 92.1 (1C), 111.3 (1C), 113.7 (1C), 121.8 (1C), 124.2 (1C), 126.2 (1C), 127.3 (1C), 128.9 (1C), 129.4 (1C), 132.7 (1C), 136.5 (1C), 137.8 (1C), 139.2 (1C), 143.3 (1C), 157.3 (1C); IR (KBr, cm}^{-1}\text{) 756, 773, 1090, 1099, 1236, 1254, 1431, 1499, 2928; HRMS (ESI\(^+\)) m/z 489.1635 ([M+Na]\(^+\), C\(_{28}\)H\(_{31}\)35ClNaO\(_2\)S\(^+\) requires 489.1625). \\
\end{align*}
\]
4-Fluoro-3-(4-tolyl)benzo[b]thiophene (3m)

Colorless oil; TLC Rf 0.21 (n-hexane); 1H NMR (CDCl3, 500 MHz) δ 2.41 (s, 3H), 7.01 (ddd, 1H, J = 11.7, 8.0, 0.7 Hz), 7.20–7.25 (m, 3H), 7.30 (ddd, 1H, J = 8.0, 8.0, 4.6 Hz), 7.40–7.44 (m, 2H), 7.65 (dd, 1H, J = 8.0, 0.7 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.2 (1C), 110.3 (d, 1C, 2JCF = 21.0 Hz), 118.8 (d, 1C, 2JCF = 4.0 Hz), 124.3 (1C), 125.2 (d, 1C, 3JCF = 7.9 Hz), 126.6 (d, 1C, 2JCF = 15.3 Hz), 128.6 (2C), 129.1 (2C), 133.5 (1C), 136.5 (d, 1C, 4JCF = 3.7 Hz), 137.2 (1C), 143.3 (d, 1C, 3JCF = 6.3 Hz), 158.5 (d, 1C, 1JCF = 253.8 Hz); 19F NMR (CDCl3, 376 MHz) δ −113.7 to −113.3 (m); IR (KBr, cm−1) 741, 772, 818, 922, 1240, 1335, 1462, 1528, 1557; HRMS (ESI+) m/z 265.0453 ([M+Na]+, C15H11FNaS+ requires 265.0458).

The regiochemistry of 3m was determined by the HMBC experiment.

4-Bromo-3-(4-tolyl)benzo[b]thiophene (3n)

Colorless oil; TLC Rf 0.25 (n-hexane); 1H NMR (CDCl3, 500 MHz) δ 2.42 (s, 3H), 7.14–7.22 (m, 3H), 7.25–7.30 (AA’BB’, 2H), 7.31 (s, 1H), 7.55 (dd, 1H, J = 7.8, 0.8 Hz), 7.85 (dd, 1H, J = 7.8, 0.8 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.3 (1C), 117.4 (1C), 122.2 (1C), 125.0 (1C), 126.6 (1C), 128.0 (2C), 130.0 (1C), 130.5 (2C), 134.2 (1C), 135.5 (1C), 137.3 (1C), 139.1 (1C), 142.2 (1C); IR (KBr, cm−1) 745, 768, 818, 1072, 1196, 1327, 1393, 1439, 1526; HRMS (ESI+) m/z 324.9654 ([M+Na]+, C15H11BrNaS+ requires 324.9657).

The regiochemistry of 3n was determined by the HMBC experiment.
4-Methoxy-3-(4-toly)benzo[b]thiophene (3o)

Colorless oil; TLC $R_t$ 0.61 (n-hexane/CH$_2$Cl$_2$ = 1/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 2.41 (s, 3H), 3.70 (s, 3H), 6.76 (d, 1H, $J$ = 7.9 Hz), 7.13 (s, 1H), 7.16–7.21 (AA’BB’, 2H), 7.30 (dd, 1H, $J$ = 7.9, 7.9 Hz), 7.36–7.40 (AA'BB', 2H), 7.48 (d, 1H, $J$ = 7.9 Hz); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 21.2 (1C), 55.2 (1C), 105.2 (1C), 115.4 (1C), 123.2 (1C), 125.3 (1C), 127.6 (1C), 127.8 (2C), 129.5 (2C), 135.1 (1C), 136.3 (1C), 138.3 (1C), 142.6 (1C), 156.3 (1C); IR (KBr, cm$^{-1}$) 743, 772, 816, 1045, 1261, 1335, 1464, 1526, 1558; HRMS (ESI) $m/z$ 277.0648 ([M+Na]$^+$, C$_{16}$H$_{14}$NaOS$^+$ requires 277.0658).

The regiochemistry of 3o was determined by the HMBC experiment.

4-Diethylamino-3-(4-toly)benzo[b]thiophene (3p)

Pale yellow oil; TLC $R_t$ 0.45 (n-hexane/CH$_2$Cl$_2$ = 1/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.10 (t, 6H, $J$ = 7.1 Hz), 2.42 (s, 3H), 3.30 (q, 4H, $J$ = 7.1 Hz), 7.02 (d, 1H, $J$ = 7.8 Hz), 7.26–7.30 (AA’BB’, 2H), 7.31–7.36 (m, 2H), 7.46–7.50 (AA’BB’, 2H), 7.58 (d, 1H, $J$ = 7.8 Hz); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 12.6 (2C), 21.2 (1C), 46.7 (2C), 115.9 (1C), 117.7 (1C), 122.8 (1C), 125.0 (1C), 128.6 (2C), 129.3 (2C), 133.5 (1C), 137.1 (1C), 137.6 (1C), 138.6 (1C), 139.3 (1C), 145.9 (1C); IR (KBr, cm$^{-1}$) 729, 793, 820, 1252, 1468, 1497, 1562, 2928, 2970; HRMS (ESI) $m/z$ 296.1475 ([M+H]$^+$, C$_{19}$H$_{22}$NS$^+$ requires 296.1467).

The regiochemistry of 3p was determined by the HMBC experiment.
5,6-(Methylenedioxy)-3-(4-tolyl)benzo[b]thiophene (3s)

Yellow oil; TLC Rf 0.56 (n-hexane/CH2Cl2 = 1/1); 1H NMR (CDCl3, 500 MHz) δ 2.42 (s, 3H), 6.01 (s, 2H), 7.20 (s, 1H), 7.25–7.30 (m, 4H), 7.41–7.44 (AA′BB′, 2H); 13C NMR (CDCl3, 126 MHz) δ 21.2 (1C), 101.4 (1C), 101.82 (1C), 101.85 (1C), 128.4 (2C), 129.4 (2C), 132.8 (1C), 133.2 (1C), 134.2 (1C), 137.3 (1C), 137.8 (1C), 146.7 (1C), 146.9 (1C); IR (KBr, cm⁻¹) 764, 820, 945, 1040, 1105, 1249, 1439, 1462, 1499; HRMS (ESI⁺) m/z 269.0629 ([M+H]⁺, C16H13O2S requires 269.0631).

6-Bromo-4-chloro-3-(4-tolyl)benzo[b]thiophene (3t)

Colorless oil; TLC Rf 0.32 (n-hexane); 1H NMR (CDCl3, 500 MHz) δ 2.42 (s, 3H), 7.18–7.22 (AA′BB′, 2H), 7.24–7.29 (m, 3H), 7.47 (d, 1H, J = 1.5 Hz), 7.93 (d, 1H, J = 1.5 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.3 (1C), 117.5 (1C), 124.1 (1C), 126.5 (1C), 128.1 (2C), 129.0 (1C), 130.0 (1C), 130.1 (2C), 133.4 (1C), 133.6 (1C), 137.4 (1C), 138.3 (1C), 143.5 (1C); IR (KBr, cm⁻¹) 785, 799, 812, 843, 1194, 1325, 1360, 1422, 1520, 1570; HRMS (ESI⁺) m/z 358.9266 ([M+Na]⁺, C15H10Br3ClNaS requires 358.9267).

The regiochemistry of 3t was determined by the HMBC experiment.

2,3-Dibutyl-8-(4-tolyl)benzo[1,2-b:3,4-b′]dithiophene (3u)

Colorless oil; TLC Rf 0.77 (n-hexane/CH2Cl2 = 1/1); 1H NMR (CDCl3, 500 MHz) δ 0.88–1.00 (m, 6H), 1.32–1.47 (m, 4H), 1.53–1.63 (m, 4H), 2.49 (s, 3H), 2.73–2.84 (m, 4H), 7.29–7.34 (m, 3H), 7.41–7.46 (AA′BB′, 2H), 7.62 (d, 1H, J = 8.6 Hz), 7.82 (d, 1H, J = 8.6 Hz); 13C NMR (CDCl3, 126 MHz) δ 13.8 (1C), 14.0 (1C), 21.4 (1C), 22.5 (1C), 22.8 (1C), 26.4 (1C), 27.9 (1C), 32.4 (1C), 34.0 (1C), 118.4 (1C), 118.8 (1C), 124.2 (1C), 128.9 (2C), 129.9 (2C), 131.2 (1C), 132.5 (1C), 132.6 (1C), 133.3 (1C), 136.0 (1C), 137.8 (1C), 138.0 (1C), 138.2 (1C), 138.5 (1C); IR (KBr, cm⁻¹) 772, 814, 849, 1213, 1404, 1464, 2857, 2928, 2955; HRMS (ESI⁺) m/z 415.1530 ([M+Na]⁺, C25H28NaS2 requires 415.1525).
The regiochemistry of 3u was determined by the HMBC experiment.

![Chemical structure of 3u](image)

**1-(4-Toly)phenanthro[3,4-b]thiophene (3v)**

Colorless solid; Mp 174–176 °C; TLC Rf: 0.14 (n-hexane); \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 2.47 (s, 3H), 7.33–7.38 (AA'BB', 2H), 7.53–7.58 (AA'BB', 2H), 7.62 (s, 1H), 7.71 (ddd, 1H, J = 7.8, 7.8, 1.1 Hz), 7.84–7.90 (m, 2H), 7.91–7.95 (m, 2H), 8.05 (dd, 1H, J = 7.8, 1.1 Hz), 8.12 (d, 1H, J = 8.5 Hz), 9.29 (d, 1H, J = 8.5 Hz); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) δ 21.3 (1C), 122.2 (1C), 123.0 (1C), 126.0 (1C), 126.2 (1C), 126.3 (1C), 126.4 (1C), 126.8 (1C), 126.89 (1C), 127.7 (1C), 129.06 (1C), 129.11 (1C), 129.5 (2C), 129.6 (2C), 130.8 (1C), 132.9 (1C), 133.2 (1C), 135.8 (1C), 137.5 (1C), 137.7 (1C), 138.6 (1C); IR (KBr, cm\(^{-1}\)) 745, 773, 820, 835, 856, 1217, 1450, 2920; HRMS (ESI\(^+\)) m/z 347.0873 ([M+Na\(^+\)]\(^+\), \(C_{23}H_{16}NaS\) requires 347.0865).

The regiochemistry of 3v was determined by the HMBC experiment.

![Chemical structure of 3v](image)

**4-Chloro-3-(hydroxymethyl)benzo[b]thiophene (3w)**

Colorless solid; Mp 116–118 °C; TLC Rf: 0.29 (n-hexane/EtOAc = 4/1); \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 2.23 (s, 1H), 5.14 (s, 2H), 7.26 (dd, 1H, J = 7.8, 7.8 Hz), 7.38 (dd, 1H, J = 7.8, 0.9 Hz), 7.52 (s, 1H), 7.76 (dd, 1H, J = 7.8, 0.9 Hz); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) δ 61.1 (1C), 121.9 (1C), 124.9 (1C), 125.8 (1C), 126.0 (1C), 128.2 (1C), 134.2 (1C), 136.2 (1C), 143.5 (1C); IR (KBr, cm\(^{-1}\)) 758, 822, 1061, 1078, 1200, 1404, 1452, 3240, 3258; HRMS (ESI\(^+\)) m/z 198.9978 ([M+H\(^+\)], \(C_{9}H_{8}ClO_{3}\)S requires 198.9979).
8-(2-Bromophenyl)-2,3-(dibutyl)benzo[1,2-b:3,4-b']dithiophene (3x)

Yellow oil; TLC Rf 0.75 (n-hexane/CH2Cl2 = 1/1); 1H NMR (CDCl3, 500 MHz) δ 0.87–0.98 (m, 6H), 1.29–1.46 (m, 4H), 1.49–1.62 (m, 4H), 2.71–2.81 (m, 4H), 7.34–7.45 (m, 4H), 7.62 (d, 1H, J = 8.6 Hz), 7.75 (d, 1H, J = 7.8 Hz), 7.82 (d, 1H, J = 8.6 Hz); 13C NMR (CDCl3, 126 MHz) δ 13.8 (1C), 14.0 (1C), 22.5 (1C), 22.9 (1C), 26.4 (1C), 28.0 (1C), 32.4 (1C), 33.9 (1C), 118.6 (1C), 118.7 (1C), 124.8 (1C), 125.4 (1C), 127.2 (1C), 130.0 (1C), 131.3 (1C), 132.4 (1C), two signals overlapped), 132.6 (1C), 132.7 (1C), 135.5 (1C), 136.0 (1C), 137.2 (1C), 138.0 (1C), 138.9 (1C); IR (KBr, cm⁻¹) 752, 800, 1302, 1408, 1431, 1462, 2857, 2930, 2955; HRMS (ESI⁺) m/z 479.0459 ([M+Na]⁺, C29H16BrNaS⁺ requires 479.0473).

3-Chloro-2-ethoxy-1-((trifluoromethyl)sulfonyl)benzene (4)

Yellow oil; TLC Rf 0.33 (n-hexane/EtOAc = 10/1); 1H NMR (CDCl3, 500 MHz) δ 1.50 (t, 3H, J = 7.0 Hz), 4.30 (q, 2H, J = 7.0 Hz), 7.31 (dd, 1H, J = 8.1, 8.1 Hz), 7.80 (dd, 1H, J = 8.1, 1.5 Hz), 7.94 (dd, 1H, J = 8.1, 1.5 Hz); 13C NMR (CDCl3, 126 MHz) δ 14.9 (1C), 71.9 (1C), 119.8 (q, 1C, 1Jc,F = 326.6 Hz), 124.9 (1C), 128.5 (1C), 130.7 (1C), 131.3 (1C), 138.9 (1C), 156.0 (1C); 19F NMR (CDCl3, 376 MHz) δ −76.0 (s); IR (KBr, cm⁻¹) 600, 637, 1016, 1082, 1130, 1207, 1254, 1368, 1389, 1450; HRMS (ESI⁺) m/z 288.9901 ([M+H]⁺, C7H5ClF3OSS⁻ requires 288.9908).

4-Chloro-3-(4-tolyl)-2-(4-tolylthio)benzo[b]thiophene (5a)

Colorless oil; TLC Rf 0.13 (n-hexane); 1H NMR (CDCl3, 400 MHz) δ 2.32 (s, 3H), 2.42 (s, 3H), 7.08–7.12 (AA′BB′, 2H), 7.17 (dd, 1H, J = 7.8, 7.8 Hz), 7.21–7.23 (m, 4H), 7.24–7.28 (m, 3H), 7.59 (dd, 1H, J = 7.8, 1.0 Hz); 13C NMR (CDCl3, 101 MHz) δ 21.1 (1C), 21.5 (1C), 120.6 (1C), 124.7 (1C), 126.5 (1C), 128.4 (2C), 128.8 (1C), 130.0 (2C), 130.5 (2C), 131.5 (1C), 131.6 (2C), 132.9 (1C), 135.5 (1C), 137.0 (1C), 137.5 (1C), 138.1 (1C), 138.7 (1C), 142.2 (1C); IR (KBr, cm⁻¹) 762, 806, 845, 1105, 1206, 1395, 1443, 1489; HRMS (ESI⁺) m/z 403.0345 ([M+Na]⁺, C27H17Cl3S⁺ requires 403.0352).

4-Chloro-2-iodo-3-(4-tolyl)benzo[b]thiophene (5b)

Colorless oil; TLC Rf 0.29 (n-hexane); 1H NMR (CDCl3, 500 MHz) δ 2.44 (s, 3H), 7.13–7.17 (AA′BB′, 2H), 7.20 (dd, 1H, J = 7.8, 7.8 Hz), 7.23–7.27 (m, 3H), 7.68 (dd, 1H, J = 7.8, 1.1 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.6 (1C), 85.6 (1C), 120.4 (1C), 125.0 (1C), 126.5 (1C), 128.6 (2C), 128.8 (1C), 130.5 (2C), 134.4 (1C), 135.1 (1C), 137.9 (1C), 143.2 (1C), 145.8 (1C); IR (KBr, cm⁻¹) 640, 743, 770, 839, 980, 1103, 1202, 1310, 1391, 1441; HRMS (ESI⁺) m/z 406.9134 ([M+Na]⁺, C27H17ICl3S⁺ requires 406.9129).
4-Chloro-2-ethoxycarbonyl-3-(4-tolyl)benzo[b]thiophene (5c)

![Chemical Structure]

Colorless solid; Mp 84–86 ºC; TLC Rf 0.46 (n-hexane/CH2Cl2 = 1/1); 1H NMR (CDCl3, 400 MHz) δ 1.15 (t, 3H, J = 7.1 Hz), 2.43 (s, 3H), 4.17 (q, 2H, J = 7.1 Hz), 7.16–7.24 (m, 4H), 7.29–7.37 (m, 2H), 7.78 (dd, 1H, J = 7.4, 1.6 Hz); 13C NMR (CDCl3, 101 MHz) δ 13.8 (1C), 21.4 (1C), 61.2 (1C), 121.3 (1C), 127.0 (1C), 127.1 (1C), 128.0 (2C), 129.4 (2C), 130.7 (1C), 131.4 (1C), 133.1 (1C), 135.3 (1C), 137.3 (1C), 142.2 (1C), 143.6 (1C), 162.1 (1C); IR (KBr, cm⁻¹) 746, 775, 1076, 1198, 1240, 1263, 1339, 1697, 1728; HRMS (ESI⁺) m/z 353.0380 ([M+Na]⁺, C18H15ClNaO2S require 353.0373).

4-Chloro-3-(4-tolyl)benzo[b]thiophene S-oxide (6)

![Chemical Structure]

Colorless solid; Mp 117–119 ºC; TLC Rf 0.27 (n-hexane/EtOAc = 1/1); 1H NMR (CDCl3, 500 MHz) δ 2.42 (s, 3H), 6.89 (s, 1H), 7.20–7.25 (AA'BB', 2H), 7.26–7.31 (AA'BB', 2H), 7.39–7.47 (m, 2H), 7.88 (dd, 1H, J = 6.7, 1.7 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.4 (1C), 125.1 (1C), 128.3 (2C), 128.7 (2C), 129.9 (1C), 130.7 (1C), 131.2 (1C), 133.5 (1C), 134.3 (1C), 135.5 (1C), 139.1 (1C), 148.9 (1C), 149.0 (1C); IR (KBr, cm⁻¹) 592, 748, 772, 779, 827, 1043, 1084, 1142, 1441, 1504; HRMS (ESI⁺) m/z 297.0109 ([M+Na]⁺, C15H11ClNaOS requires 297.0111).

4-Chloro-2-(2-hydroxyphenyl)-3-(4-tolyl)benzo[b]thiophene (7)

![Chemical Structure]

Pale yellow oil; TLC Rf 0.31 (n-hexane/CH2Cl2 = 1/1); 1H NMR (CDCl3, 500 MHz) δ 2.32 (s, 3H), 5.06 (s, 1H), 6.80 (d, 1H, J = 7.8 Hz), 6.85 (ddd, 1H, J = 7.6, 7.6, 0.9 Hz), 7.04–7.09 (AA'BB', 2H), 7.12–7.15 (AA'BB', 2H), 7.16–7.22 (m, 2H), 7.29 (dd, 1H, J = 7.8, 7.8 Hz), 7.36 (dd, 1H, J = 7.6, 0.9 Hz), 7.80 (dd, 1H, J = 7.6, 0.9 Hz); 13C NMR (CDCl3, 126 MHz) δ 21.3 (1C), 115.9 (1C), 119.8 (1C), 120.3 (1C), 121.0 (1C), 125.1 (1C), 126.9 (1C), 128.3 (2C), 129.6 (1C), 130.4 (1C), 130.5 (2C), 132.0 (1C), 132.1 (1C), 135.3 (1C), 136.3 (1C), 136.6 (1C), 137.4 (1C), 141.8 (1C), 153.1 (1C); IR (KBr, cm⁻¹) 824, 1105, 1150, 1179, 1194, 1229, 1288, 3528; HRMS (ESI⁺) m/z 373.0422 ([M+Na]⁺, C21H15ClNaOS+ requires 373.0424).
4-Chlorobenzo[b]thiophene-3-carboxylic acid (9)

![Chemical structure of 4-Chlorobenzo[b]thiophene-3-carboxylic acid (9)](image)

Colorless solid; Mp 185–187 ºC; TLC Rf 0.37 (EtOAc); 1H NMR (CDCl₃, 500 MHz) δ 7.36 (dd, 1H, J = 7.8, 7.8 Hz), 7.50 (d, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 7.8 Hz), 8.18 (s, 1H); 13C NMR (CDCl₃, 126 MHz) δ 121.4 (1C), 125.9 (1C), 127.3 (1C), 128.4 (1C), 129.2 (1C), 133.2 (1C), 134.8 (1C), 142.1 (1C), 168.2 (1C); IR (KBr, cm⁻¹) 750, 1204, 1456, 1674, 1709, 3105; HRMS (ESI⁺) m/z 234.9597 ([M+Na]⁺, C₉H₅ClNaO₂S⁺ requires 234.9591).

4-Chloro-3-iodobenzo[b]thiophene (10)

![Chemical structure of 4-Chloro-3-iodobenzo[b]thiophene (10)](image)

Colorless solid; Mp 99–100 ºC; TLC Rf 0.47 (n-hexane); 1H NMR (CDCl₃, 500 MHz) δ 7.26 (dd, 1H, J = 7.8, 7.8 Hz), 7.39 (dd, 1H, J = 7.8, 0.9 Hz), 7.72 (s, 1H), 7.81 (dd, 1H, J = 7.8, 0.9 Hz); 13C NMR (CDCl₃, 126 MHz) δ 71.5 (1C), 121.7 (1C), 125.4 (1C), 127.0 (1C), 129.5 (1C), 132.8 (1C), 133.3 (1C), 140.5 (1C); IR (KBr, cm⁻¹) 727, 764, 835, 1094, 1198, 1273, 1391, 1435; HRMS (ESI⁺) m/z 316.8659 ([M+Na]⁺, C₈H₄ClNaO₂S⁺ requires 316.8659).

6-Bromo-4-chloro-2-(4-methoxyphenyl)-3-(4-tolyl)benzo[b]thiophene (11)

![Chemical structure of 6-Bromo-4-chloro-2-(4-methoxyphenyl)-3-(4-tolyl)benzo[b]thiophene (11)](image)

Colorless oil; TLC Rf 0.62 (n-hexane/CH₂Cl₂ = 1/1); 1H NMR (CDCl₃, 500 MHz) δ 2.38 (s, 3H), 3.75 (s, 3H), 6.71–6.75 (AA’BB’, 2H), 7.10–7.18 (m, 6H), 7.42 (d, 1H, J = 1.8 Hz), 7.87 (d, 1H, J = 1.8 Hz); 13C NMR (CDCl₃, 126 MHz) δ 21.4 (1C), 55.2 (1C), 113.7 (2C), 116.9 (1C), 123.2 (1C), 125.9 (1C), 128.5 (2C), 129.3 (1C), 129.9 (1C), 130.8 (2C), 131.2 (2C), 132.4 (1C), 133.0 (1C), 133.5 (1C), 137.2 (1C), 141.4 (1C), 141.8 (1C), 159.3 (1C); IR (KBr, cm⁻¹) 829, 1034, 1179, 1252, 1292, 1423, 1487, 1514, 1607; HRMS (ESI⁺) m/z 464.9676 ([M+Na]⁺, C₂₂H₁₆BrClNaO₂S⁺ requires 464.9686).
2-(4-Methoxyphenyl)-4-phenyl-3-(4-tolyl)-6-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (12)

![Chemical structure of 2-(4-Methoxyphenyl)-4-phenyl-3-(4-tolyl)-6-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (12)](image)

Colorless solid; Mp 122–124 °C; TLC R₁ 0.60 (n-hexane/CH₂Cl₂ = 1/1); ¹H NMR (CDCl₃, 500 MHz) δ 2.19 (s, 3H), 3.76 (s, 3H), 6.60–6.68 (m, 4H), 6.72–6.77 (AA'BB', 2H), 6.88–6.95 (m, 4H), 6.99–7.04 (AA'BB', 1H), 7.11–7.17 (AA'BB', 2H), 7.48 (d, 1H, J = 1.7 Hz), 7.68–7.74 (AA'BB', 2H), 7.79–7.85 (AA'BB', 2H), 8.12 (d, 1H, J = 1.7 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 21.1 (1C), 55.2 (1C), 113.6 (2C), 119.6 (1C), 124.3 (3q, 1C, J_C-F = 272.0 Hz), 125.6 (1C), 125.8 (q, 2C, J_C-F = 3.6 Hz), 126.8 (1C), 126.9 (2C), 127.1 (1C), 127.5 (2C), 128.1 (2C), 129.2 (q, 1C, J_C-F = 31.4 Hz), 129.4 (2C), 130.4 (2C), 131.0 (2C), 133.1 (1C), 133.4 (1C), 134.8 (1C), 135.6 (1C), 137.1 (1C), 139.7 (1C), 140.0 (1C), 140.7 (1C), 141.0 (1C), 144.2 (1C), 159.1 (1C); ¹⁹F NMR (CDCl₃, 376 MHz) δ −62.6 (s); IR (KBr, cm⁻¹) 835, 1072, 1113, 1125, 1165, 1179, 1252, 1325; HRMS (ESI⁺) m/z 573.1466 ([M+Na⁺], C₃₅H₂₃F₃NaOS⁺ requires 573.1470).

8-(2-Bromophenyl)-2,3-dibutyl-7-iodobenzo[1,2-b:3,4-b']dithiophene (13)

![Chemical structure of 8-(2-Bromophenyl)-2,3-dibutyl-7-iodobenzo[1,2-b:3,4-b']dithiophene (13)](image)

Pale yellow oil; TLC R₁ 0.75 (n-hexane/CH₂Cl₂ = 1/1); ¹H NMR (CDCl₃, 400 MHz) δ 0.86–0.97 (m, 6H), 1.28–1.46 (m, 4H), 1.47–1.61 (m, 4H), 2.68–2.79 (m, 4H), 7.33 (dd, 1H, J = 7.6, 1.5 Hz), 7.41–7.52 (m, 2H), 7.56 (d, 1H, J = 8.6 Hz), 7.71 (d, 1H, J = 8.6 Hz), 7.79 (dd, 1H, J = 7.6, 1.5 Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 13.8 (1C), 14.0 (1C), 22.5 (1C), 22.9 (1C), 26.4 (1C), 27.9 (1C), 32.4 (1C), 33.8 (1C), 81.9 (1C), 117.5 (1C), 118.6 (1C), 125.4 (1C), 127.7 (1C), 130.6 (1C), 131.3 (1C), 131.9 (1C), 132.3 (1C), 132.5 (1C), 133.0 (1C), 137.6 (1C), 138.2 (1C), 139.2 (1C), 139.3 (1C), 142.0 (1C); IR (KBr, cm⁻¹) 725, 756, 799, 1406, 1458, 2857, 2928, 2953; HRMS (ESI⁺) m/z 604.9442 ([M+Na⁺], C₃₆H₂₂BrNaOS⁺ requires 604.9440).

2,3-Dibutyl-7-(4-tolyl)-7H-thieno[3',2':5,6']benzo[1',2':4,5]thieno[2,3-b]indole (14)

![Chemical structure of 2,3-Dibutyl-7-(4-tolyl)-7H-thieno[3',2':5,6']benzo[1',2':4,5]thieno[2,3-b]indole (14)](image)

Colorless solid; Mp 137–139 °C; TLC R₁ 0.75 (n-hexane/CH₂Cl₂ = 1/1); ¹H NMR (CDCl₃, 500 MHz) δ 0.95–1.05 (m, 6H), 1.42–1.55 (m, 4H), 1.65 (tt, 2H, J = 7.7, 7.7 Hz), 1.83 (tt, 2H, J = 7.7, 7.7 Hz), 2.47 (s, 3H), 2.86 (t, 2H, J = 7.7 Hz), 2.99 (t, 2H, J = 7.7 Hz), 3.70 (dd, 1H, J = 8.0, 8.0 Hz), 5.35–5.42 (m, 3H), 7.52–7.61 (m, 4H), 7.70 (d, 1H, J = 8.5 Hz), 8.78 (d, 1H, J = 8.0 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 14.0 (1C), 14.1 (1C), 21.2 (1C), 22.6 (1C), 22.9 (1C), 26.6 (1C), 28.3 (1C), 32.4 (1C), 34.0 (1C), 110.4 (1C), 116.4 (1C), 118.1 (1C), 119.4 (1C), 120.6 (1C), 120.7 (1C), 122.2 (1C), 122.9 (1C), 124.3 (2C), 127.2 (1C), 130.61 (2C), 130.65 (1C), 131.18 (1C), 132.23 (1C), 135.8 (1C), 137.5 (1C), 138.35 (1C), 138.41 (1C), 141.4 (1C), 143.4 (1C); IR (KBr, cm⁻¹) 739, 756, 1404, 1450, 1481, 1514, 2857, 2928, 2953; HRMS (ESI⁺) m/z 504.1800 ([M+Na⁺], C₃₅H₂₃NNaS₂⁺ requires 504.1790).
References for Supporting Information

$^1$H and $^{13}$C NMR Spectra of Compounds

$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of isopropyl (4-tolyl)ethynyl sulfide (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of benzyl (4-tolyl)ethynyl sulfide (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of ethyl (4-methoxycarbonylphenyl)ethynyl sulfide (2d) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of (2-bromophenyl)ethynyl ethyl sulfide (2e) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of ethyl (9-phenanthrenyl)ethynyl sulfide (2g) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of ethyl (3-thienyl)ethynyl sulfide (2h) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of ethyl (2-phenethyl)ethyl sulfide (2i) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of cyclohexylethynyl ethyl sulfide (2j) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3,17-di-O-methyl-17-(ethylthioethynyl)estradiol (2k) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2-((3-(ethylthio)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran (2l) (CDCl$_3$)
\(^1\text{H} \text{NMR} \) (500 MHz, DMSO-\(d_6\)) and \(^{13}\text{C} \text{NMR} \) (126 MHz, CDCl\(3\)) spectra of 4-chloro-3-(4-tolyl)benzo[\(b\)]thiophene (3a)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(4-methoxyphenyl)benzo[b]thiophene (3b) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(4-chlorophenyl)benzo[b]thiophene (3c) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(4-methoxycarbonylphenyl)benzo[b]thiophene (3d) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-(2-bromophenyl)-4-chlorobenzo[b]thiophene (3e) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(2-naphthyl)benzo[b]thiophene (3f) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(9-phenanthrenyl)benzo[θ]thiophene (3g) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(3-thienyl)benzo[b]thiophene (3h) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(2-phenylethyl)benzo[b]thiophene (3i) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-cyclohexylbenzo[b]thiophene (3j) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(3,17-di-O-methylestradiol-17-yl)benzo[b]thiophene (3k) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-fluoro-3-(4-tolyl)benzo[b]thiophene (3m) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-bromo-3-(4-tolyl)benzo[b]thiophene (3n) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-methoxy-3-(4-tolyl)benzo[b]thiophene (3o) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-diethylamino-3-(4-tolyl)benzo[b]thiophene (3p) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 5,6-(methylenedioxy)-3-(4-tolyl)benzo[b]thiophene (3s) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 6-bromo-4-chloro-3-(4-tolyl)benzo[b]thiophene (3t) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2,3-dibutyl-8-(4-tolyl)benzo[1,2-b:3,4-b']dithiophene (3u) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(4-tolyl)phenanthro[3,4-$b$]thiophene (3v) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-(hydroxymethyl)benzo[b]thiophene (3w) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 8-(2-bromophenyl)-2,3-(dibutyl)benzo[1,2-$b$:3,4-$b'$]dithiophene (3x) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-chloro-2-ethoxy-1-((trifluoromethyl)sulfonyl)benzene (4) (CDCl$_3$)
$^1$H NMR (400 MHz) and $^{13}$C NMR (101 MHz) spectra of 4-chloro-3-(4-tolyl)-2-(4-tolylthio)benzo[\textit{b}]thiophene (5a) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-2-iodo-3-(4-tolyl)benzo[b]thiophene (5b) (CDCl$_3$)
$^1$H NMR (400 MHz) and $^{13}$C NMR (101 MHz) spectra of 4-chloro-2-ethoxycarbonyl-3-(4-tolyl)benzo[b]thiophene (5c) (CDCl$_3$)
\(^1\)H NMR (500 MHz) and \(^{13}\)C NMR (126 MHz) spectra of 4-chloro-3-(4-tolyl)benzo[b]thiophene S-oxide (6) (CDCl\(_3\))
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-2-(2-hydroxyphenyl)-3-(4-tolyl)benzo[b]thiophene (7) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chlorobenzo[b]thiophene-3-carboxylic acid (9) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-chloro-3-iodo[7]thiophene (10) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 6-bromo-4-chloro-2-(4-methoxyphenyl)-3-(4-toly)benzo[b]thiophene (11) (CDCl₃)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2-(4-methoxyphenyl)-4-phenyl-3-(4-tolyl)-6-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (12) (CDCl$_3$)
$^1$H NMR (400 MHz) and $^{13}$C NMR (101 MHz) spectra of 8-(2-bromophenyl)-2,3-dibutyl-7-iodobenzo[1,2-$b$:3,4-$b'$]dithiophene (13) (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2,3-dibutyl-7-(4-tolyl)-7$H$-thieno[3$''$,2$''$:5$'$,6$'$]benzo[1$'$,2$'':4,5]thieno[2,3-$b$]indole (14) (CDCl$_3$)