Supplementary Information

Diversity-Oriented and Diastereoselective Synthesis of Diverse Polycyclic Thieno(2,3-b)-quinolines Derivatives Using a Synergistic Strategy

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1. \(^1\)H NMR and \(^{13}\)C NMR spectra ..................................................................................................................S2

2. X-ray data of compounds 3fa, 3ia, 3ka, 5ca, 5'ce .................................................................................S56
1. $^1$H, $^{13}$C NMR

![NMR Spectra](image)

**3aa**
3ac
3ae
3ba

![Chemical Structure](image)

![NMR Spectrum](image)
3ca
3cd
3ce
3fd
3ja
3jd
3je

[Chemical structure and spectra images]
3jf
3ka
5'ac

\[
\text{NO}_2 \quad \text{S} \quad \text{O} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{N} \quad \text{O}
\]

\[
\text{NO}_2 \quad \text{S} \quad \text{O} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{N} \quad \text{O}
\]
5'ad

[Chemical structures and spectra images]

S31
$5'af$

![Chemical Structure](image1)

![Chemical Structure](image2)
5'ca
$5'_{cc}$
5cd
5'cd
5cf
5ag
5aj

\[ \text{Structure Image} \]

\[ \text{Chart Image} \]
5ak

![Chemical Structure](image)

![NMR Spectrum](image)

![NMR Spectrum](image)

S53
6'ca
7'ca

[Chemical structure images and spectra]

S55
2. X-ray data of enantiopure of 3fa, 3ia, 3ka and 5ca

Single crystals (3fa, 3ia, 3ka and 5ca) were crystallized by the slow solvent (ethyl acetate/petroleum ether) evaporation method. The crystals were characterized using single crystal X-ray diffraction.

Figure S1. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for 3fa (CCDC 2013515) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

**XRD Data for Compound 3fa**

**Crystal data and structure refinement for 3fa.**

<table>
<thead>
<tr>
<th>Identification code</th>
<th>3fa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C4.60H3.20Cl0N0.40O0.50S0.20</td>
</tr>
<tr>
<td>Formula weight</td>
<td>78.49</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 16.2300(9) Å alpha = 90 °.</td>
</tr>
<tr>
<td></td>
<td>b = 6.6999(4) Å beta = 98.587(3) °.</td>
</tr>
<tr>
<td></td>
<td>c = 19.3383(11) Å gamma = 90 °.</td>
</tr>
<tr>
<td>Volume</td>
<td>2079.3(2) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>20, 1.254 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.178 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>816</td>
</tr>
<tr>
<td>Crystal size</td>
<td>.36 x .27 x .18 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.53 to 27.56 °.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-21&lt;=h&lt;=21, -8&lt;=k&lt;=8, -25&lt;=l&lt;=25</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>67116 / 4800 [R(int) = 0.0524]</td>
</tr>
<tr>
<td>Completeness to theta = 27.56</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4800 / 0 / 263</td>
</tr>
<tr>
<td>Goodness-of-fit on F²(^2)</td>
<td>1.169</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0779, wR2 = 0.2424</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0936, wR2 = 0.2634</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.010(3)</td>
</tr>
</tbody>
</table>
Largest diff. peak and hole 1.407 and -0.282eÅ⁻³

Figure S2. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for 3ia (CCDC 2013516) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound 3ia

Identification code 3ia
Empirical formula C18H14N2O2S
Formula weight 322.08
Temperature 296(2) K
Wavelength 0.71073 Å
Crystal system, space group Orthorhombic, Pccn
Unit cell dimensions
a = 26.8368(6) Å  alpha = 90°.
b = 8.8018(2) Å  beta = 90°.
c = 12.9450(3) Å  gamma = 90°.
Volume 3057.77(12) Å³
Z, Calculated density 40, 1.401 Mg/m³
Absorption coefficient 0.223 mm⁻¹
F(000) 1344
Crystal size .36 x .23 x .11 mm
Theta range for data collection 1.52 to 27.43°.
Limiting indices 34<=h<=34, -11<=k<=11, -16<=l<=16
Reflections collected / unique 94617 / 3494 [R(int) = 0.1036]
Completeness to theta = 27.43 99.6%
Absorption correction None
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 3494 / 0 / 209
Goodness-of-fit on F² 1.104
Final R indices [I>2sigma(I)] R1 = 0.0414, wR2 = 0.0959
R indices (all data) R1 = 0.0535, wR2 = 0.1079
Extinction coefficient 0.0060(5)
Largest diff. peak and hole 0.243 and -0.209 e. Å$^{-3}$

Figure S3. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for 3ka (CCDC 2013517) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound 3ka

Crystal data and structure refinement for 3ka.

Empirical formula C24H16N2O3S
Formula weight 412.09
Temperature 296(2) K
Wavelength 0.71073 Å
Crystal system, space group Monoclinic, P2(1)/n
Unit cell dimensions $a = 8.2185(6)$ Å, alpha = 90 °.
$b = 15.6692(11)$ Å, beta = 92.798(4) °.
$c = 16.9546(13)$ Å, gamma = 90 °.
Volume 2180.8(3) Å$^3$
Z, Calculated density 28, 1.354 Mg/m$^3$
Absorption coefficient 0.187 mm$^{-1}$
F(000) 920
Crystal size .38 x .26 x .18 mm
Theta range for data collection 1.77 to 27.45 °.
Limiting indices -10<=h<=10, -20<=k<=20, -21<=l<=21
Reflections collected / unique 71857 / 4967 [R(int) = 0.0468]
Completeness to theta = 27.45 99.9 %
Absorption correction None

Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4967 / 0 / 290
Goodness-of-fit on F² 1.129
Final R indices [I>2sigma(I)] R1 = 0.0899, wR2 = 0.2813
R indices (all data) \( R1 = 0.1065, wR2 = 0.3095 \)
Extinction coefficient \( 0.018(4) \)
Largest diff. peak and hole \( 1.950 \) and \( -0.625 \) e.Å\(^{-3}\)

**Figure S4. Displacement Ellipsoids Are Drawn at the 30% Probability Level.**

Crystal data for **5ca** (CCDC 2013518) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]
Final R indices [I>2\textsigma(I)] \quad R1 = 0.0479, \, wR2 = 0.1027
R indices (all data) \quad R1 = 0.0619, \, wR2 = 0.1113
Extinction coefficient \quad 0.0206(17)
Largest diff. peak and hole \quad 0.211 and -0.216 e. Å^{-3}

5c‘e

Figure S5. Displacement Ellipsoids Are Drawn at the 30\% Probability Level.

Crystal data for 5c‘e (CCDC 2013519) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

XRD Data for Compound 5c‘e

Crystal data and structure refinement for 5c‘e.

Empirical formula \quad C_{17}H_{17}NO_{2}S
Formula weight \quad 299.10
Temperature \quad 296(2) K
Wavelength \quad 0.71073 Å
Crystal system, space group \quad Monoclinic, P2(1)/c
Unit cell dimensions \quad a = 12.5624(3) Å \quad \alpha = 90 \degree
\quad b = 11.3761(2) Å \quad \beta = 99.5230(10) \degree
\quad c = 10.3690(2) Å \quad \gamma = 90 \degree
Volume \quad 1461.42(5) Å^3
Z, Calculated density \quad 19, 1.361 Mg/m^3
Absorption coefficient \quad 0.225 mm^{-1}
F(000) \quad 632
Crystal size \quad 0.42 x 32 x 22 mm
Theta range for data collection \quad 1.64 to 27.51 \degree
Limiting indices \quad -16<=h<=16, -14<=k<=14, -13<=l<=13
Reflections collected / unique \quad 51602 / 3356 [R(int) = 0.0488]
Completeness to theta = 27.28 \degree \quad 99.7 \%
Absorption correction \quad None
Refinement method \quad Full-matrix least-squares on F^2
Data / restraints / parameters \quad 3356 / 0 / 191
Goodness-of-fit on F^2 \quad 1.067
Final R indices [I>2\textsigma(I)] \quad R1 = 0.0457, \, wR2 = 0.1209
R indices (all data)                    \( R_1 = 0.0569, \ wR_2 = 0.1356 \)
Extinction coefficient                    \( 0.010(2) \)
Largest diff. peak and hole              \( 0.651 \) and \(-0.496\) e. Å\(^{-3}\)