Supporting Information

**K₂CO₃ catalyzed regioselective synthesis of thieno[2,3-b]thiochromen-4-one oximes: Access to the corresponding Amine and Nitroso derivatives**

Karuna Mahato,ᵃ Prasanta Ray Bagdi,ᵃ and Abu T Khan,ᵇ⁺⁺

ᵃDepartment of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India
Tel.: +91 361 2582305; fax: +91 361 2582349.
E-mail address: atk@iitg.ernet.in (A.T. Khan).

ᵇPresent address: Vice-Chancellor, Aliah University, IIA/27, New Town, Kolkata-700 156, West Bengal, India.

<table>
<thead>
<tr>
<th>Content</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Title Page</td>
<td>S1</td>
</tr>
<tr>
<td>2. General Information and Methods</td>
<td>S2</td>
</tr>
<tr>
<td>3. X-ray Structure of Compounds 3c, 4f and 5a</td>
<td>S3</td>
</tr>
<tr>
<td>4. Crystal Data and Structure Refinement for Compounds 3c, 4f and 5a</td>
<td>S4-S5</td>
</tr>
<tr>
<td>5. Copies of ¹H NMR, ¹³C NMR and HRMS spectra of all Compounds</td>
<td>S6-S126</td>
</tr>
</tbody>
</table>
1. General Information and Methods

$^1$H and $^{13}$C NMR spectra were recorded on 400 MHz, 600 MHz and 100 MHz, 150 MHz spectrometer TMS as internal reference; chemical shifts ($\delta$ scale) are reported in parts per million (ppm). $^1$H NMR Spectra are reported in the order: multiplicity, coupling constant (J value) in hertz (Hz) and no of protons; signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet) and b s (broad singlet). IR spectra were recorded in KBr. HRMS spectra were recorded using ESI and APCI (TOF) mode. The X-ray crystal structures were determined with a diffractometer. Complete crystallographic data of 3c (CCDC no.1454211), 4f (CCDC no.1454212) and 5a (CCDC no.1454213) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).
2. X-ray Structure of Compounds 3c, 4f and 5a

Figure 1. 30% probability of ORTEP ellipsoids of compounds 3c, 4f and 5a
3. Crystal Data and Structure Refinement for Compound 3c, 4f and 5a

Table S2 Data collection and refinement statistics for the compounds 3c, 4f and 5a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Identification code</th>
<th>Compound 3c</th>
<th>Compound 4f</th>
<th>Compound 5a</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Empirical formula</td>
<td>C18 H13 N O2 S2</td>
<td>C17 H10 Br N O S2</td>
<td>C17 H9 N O2 S2</td>
</tr>
<tr>
<td>02</td>
<td>Formula weight</td>
<td>339.41</td>
<td>388.28</td>
<td>323.37</td>
</tr>
<tr>
<td>03</td>
<td>Temperature</td>
<td>296(2) K</td>
<td>296(2) K</td>
<td>296(2) K</td>
</tr>
<tr>
<td>04</td>
<td>Wavelength</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>05</td>
<td>Radiation type</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>06</td>
<td>Radiation source</td>
<td>Fine-focus sealed tube</td>
<td>Fine-focus sealed tube</td>
<td>Fine-focus sealed tube</td>
</tr>
<tr>
<td>07</td>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>08</td>
<td>Space group</td>
<td>P21/c</td>
<td>P21/c</td>
<td>P21/c</td>
</tr>
<tr>
<td>09</td>
<td>Cell length</td>
<td>a 8.1398(3) b 12.3213(4) c 16.5028(5)</td>
<td>a 18.1202(5) b 12.7017(3) c 14.3420(4)</td>
<td>a 6.3128(3) b 18.0467(9) c 12.6157(5)</td>
</tr>
<tr>
<td>10</td>
<td>Cell Angle</td>
<td>α 90 β 102.686(2) δ 90</td>
<td>α 90 β 113.1330(10) δ 90</td>
<td>α 90.00 β 96.132(4) δ 90.00</td>
</tr>
<tr>
<td>11</td>
<td>Cell Volume</td>
<td>1614.71(9)</td>
<td>3035.51(14)</td>
<td>1429.03(11)</td>
</tr>
<tr>
<td>12</td>
<td>Density</td>
<td>1.387</td>
<td>1.686</td>
<td>1.495</td>
</tr>
<tr>
<td>13</td>
<td>Completeness to theta</td>
<td>28.56° / 99.8%</td>
<td>28.42° / 100%</td>
<td>28.70° / 99.9%</td>
</tr>
<tr>
<td>14</td>
<td>Absorption correction</td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
</tr>
<tr>
<td>15</td>
<td>Refinement method</td>
<td>Full-matrix least-squares on F2</td>
<td>Full-matrix least-squares on F2</td>
<td>Full-matrix least-squares on F2</td>
</tr>
<tr>
<td>16</td>
<td>Index ranges</td>
<td>-10 &lt;= h &lt;= 10, -16 &lt;= k &lt;= 16, -22 &lt;= l &lt;= 22</td>
<td>-24 &lt;= h &lt;= 24, -17 &lt;= k &lt;= 17, -19 &lt;= l &lt;= 19</td>
<td>-5 &lt;= h &lt;= 8, -24 &lt;= k &lt;= 19, -16 &lt;= l &lt;= 17</td>
</tr>
<tr>
<td>17</td>
<td>Reflection number</td>
<td>4102</td>
<td>7634</td>
<td>3698</td>
</tr>
<tr>
<td>19</td>
<td>Cell formula units Z</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>20</td>
<td>CCDC no</td>
<td>1454211</td>
<td>1454212</td>
<td>1454213</td>
</tr>
</tbody>
</table>
4. Copies of $^1$H NMR, $^{13}$C NMR and HRMS spectra of all Compounds

$^1$HNMR spectra of compound: 3a
$^{13}$CNMR spectra of compound: 3a
HRMS spectra of compound: 3a

Sample Name | Position | Instrument Name | User Name | IRM Calibration Status | Acquired Time
--- | --- | --- | --- | --- | ---
| | | | | | 

$^{+}$Mixed Scan (19.5 sec) Frag=70.0V KM-NS-PI-4Cl.d

359.9916
$^1$HNMR spectra of compound: 3b
$^{13}$CNMR spectra of compound: 3b
HRMS spectra of compound: 3b

+ESI Scan (13.0 sec) Frag=135.0V KM-NS-PI-BEN.d

Counts vs. Mass-to-Charge (m/z)
$^1$HNMR spectra of compound: 3c
$^{13}$CNMR spectra of compound: 3c
HRMS spectra of compound: 3c
$^1$HNMR spectra of compound: 3d

![HNMR spectrum of compound 3d](image)
$^{13}$CNMR spectra of compound: 3d
HRMS spectra of compound: 3d

Object: Mixed Scan (15.8 sec) Frag=70.0V KM-NS-PI-4NO2.d

```
371.0146
```

Chemical structure:

![Chemical structure of compound 3d]
$^1$HNMR spectra of compound: 3e
$^{13}$CNMR spectra of compound: 3e
HRMS spectra of compound: 3e
$^1$HNMR spectra of compound: 3f
$^{13}$CNMR spectra of compound: 3f
HRMS spectra of compound: 3f

Sample Name
Inj Vol
Data Filename

Position
InjPosition
ACQ Method

Instrument Name
SampleType
Comment

User Name
IRM Calibration Status
Acquired Time

+ESI Scan (23.8 sec) Frag=135.0V KM-NS-P1-4F.d

344.0222
$^1$HNMR spectra of compound: 3g
$^{13}$CNMR spectra of compound: 3g
HRMS spectra of compound: 3g

[Image of HRMS spectrum with molecular structure and peaks marked]
$^1$HNMR spectra of compound: 3h
$^{13}$CNMR spectra of compound: 3h
HRMS spectra of compound: 3h
$^1$HNMR spectra of compound: 3i
$^{13}$CNMR spectra of compound: 3i
HRMS spectra of compound: 3i

Sample Name
Inj Vol
Data Filename

Position
InjPosition
ACQ Method

Instrument Name
SampleType
Comment

UserName
IRM Calibration Status
Acquired Time

+ESI Scan (20.9 sec) Frag=135.0V KM-NS-P1-VER-1.d

386.0514

3i

Counts vs. Mass-to-Charge (m/z)

325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440
\(^1\text{HNMR spectra of compound: 3j}\)
$^{13}$CNMR spectra of compound: 3j
HRMS spectra of compound: 3j
$^1$HNMR spectra of compound: 3k
$^{13}$CNMR spectra of compound: 3k
HRMS spectra of compound: 3k

Sample Name | Position | Instrument Name | User Name | IRM Calibration Status | Acquired Time
---|---|---|---|---|---

Inj Vol | Inj Position | ACQ Method | Sample Type | Comment |  

+ESI Scan (16.1 sec) Frag=135.0V KM-TH-BEN.d

3k

Counts vs. Mass-to-Charge (m/z)
$^1$HNMR spectra of compound: 3l
\^{13}CNMR spectra of compound: 3l
HRMS spectra of compound: 3l

3l

Sample Name | Position | Instrument Name | User Name | IRM Calibration Status | Acquired Time
---|---|---|---|---|---
Inj Vol | InjPosition | SampleType | Comment | ACQ Method | Data Filename

x10^3

+ESI Scan (20.0 sec) Frag=135.0V KM-TH-ME-1.d

374.0060

Counts vs. Mass-to-Charge (m/z)

0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2 2.2 2.4 2.6 2.8 3 3.2 3.4 3.6 3.8 4 4.2 4.4 4.6 4.8 5 5.2 5.4 5.6 5.8 6 6.2 6.4 6.6

363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382
$^1$HNMR spectra of compound: 3m
$^{13}$CNMR spectra of compound: 3m
HRMS spectra of compound: 3m

Sample Name  Position  Instrument Name  User Name  IRM Calibration Status
Inj Vol  InjPosition  SampleType  Comment  Acquired Time
Data Filename  ACQ Method

+ESI Scan (20.9 sec) Frag=135.0V KM-TH-4CL.d

Counts vs. Mass-to-Charge (m/z)
$^1$HNMR spectra of compound: 3n
$^{13}$CNMR spectra of compound: 3n

![CNMR Spectra Image]
HRMS spectra of compound: 3n
$^1$HNMR spectra of compound: 3o
$^{13}$CNMR spectra of compound: 3o
HRMS spectra of compound: 3o

Sample Name | Position | Instrument Name | User Name | IRM Calibration Status | Acquired Time
---|---|---|---|---|---
Inj Vol | InjPosition | ACQ Method | SampleType | Comment | 
Data Filename

+ESI Scan (25.8 sec) Frag=135.0V KM-TH-3BR.d

Counts vs. Mass-to-Charge (m/z)

437.9026
439.9014
438.9097
440.8942
441.8942
442.8942
443.8942
444.8942
445.8942
446.8942

x10^4

1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0

435 436 437 438 439 440 441 442 443 444 445 446
$^1$HNMR spectra of compound: 3p
$^{13}$CNMR spectra of compound: 3p
HRMS spectra of compound: 3p

+ESI Scan (20.9 sec) Frag=135.0V KM-TH-VER.d

Counts vs. Mass-to-Charge (m/z)
$^1$HNMR spectra of compound: 3q
$^{13}$CNMR spectra of compound: 3q
HRMS spectra of compound: 3q
NOESY and COSY spectra of compound: 3q

NOESY spectra

COSY spectra
$^1$HNMR spectra of compound: 3r
$^{13}$CNMR spectra of compound: 3r
HRMS spectra of compound: 3r

+ESI Scan (19.0 sec) Frag=135.0V KM-TH-5-4CL.d

Counts vs. Mass-to-Charge (m/z)

393.9529
$^1$HNMR spectra of compound: 3s
$^{13}$CNMR spectra of compound: 3s
HRMS spectra of compound: 3s
$^1$HNMR spectra of compound: 3t
$^{13}$CNMR spectra of compound: 3t
HRMS spectra of compound: 3t
$^{1}$HNMR spectra of compound: 3u
$^{13}$CNMR spectra of compound: 3u

[Diagram of compound 3u with chemical structures and NMR spectrum]
HRMS spectra of compound: 3u
$^1$HNMR spectra of compound: 3v
$^{13}$CNMR spectra of compound: 3v

![CNMR Spectra Image](Image)
HRMS spectra of compound: 3v

S72
$^1$HNMR spectra of compound: 3w
$^{13}$CNMR spectra of compound: 3w
HRMS spectra of compound: 3w
$^1$HNMR spectra of compound: 4a
$^{13}$CNMR spectra of compound: 4a
HRMS spectra of compound: 4a
$^1$HNMR spectra of compound: 4b
$^{13}$CNMR spectra of compound: 4b
HRMS spectra of compound: 4b

\[ \text{ESI Scan (9.3 sec) Frag=135.0V KM-BR-ME.d} \]

Counts vs. Mass-to-Charge (m/z)

$324.0515$

$^1$HNMR spectra of compound: 4c
$^{13}$CNMR spectra of compound: 4c

HRMS spectra of compound: 4c
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>KM-BR-4CL</th>
<th>Position</th>
<th>Vial 1</th>
<th>Instrument Name</th>
<th>Instrument 1</th>
<th>User Name</th>
<th>IRM Calibration Status</th>
<th>Acquired Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inj Vol</td>
<td>0</td>
<td>InjPosition</td>
<td></td>
<td>Sample</td>
<td>Sample</td>
<td></td>
<td>All Ions Missed</td>
<td>2/3/2016 11:25:30 AM</td>
</tr>
<tr>
<td>Data Filename</td>
<td>KM-BR-4CL.d</td>
<td>ACQ Method</td>
<td></td>
<td>Comment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**+ESI Scan (38.8 sec) Frag=135.0V KM-BR-4CL.d**

![Graph of mass spectrometry data](image)

Counts vs. Mass-to-Charge (m/z)

343.9977
$^1$HNMR spectra of compound: 4d
$^{13}$CNMR spectra of compound: 4d

HRMS spectra of compound: 4d
$^1$HNMR spectra of compound: 4e

$^{13}$CNMR spectra of compound: 4e
HRMS spectra of compound: 4e
$^1$HNMR spectra of compound: 4f
$^{13}$CNMR spectra of compound: 4f
HRMS spectra of compound: 4f

[Image of HRMS spectrum with molecular structure of 4f and masses 387.9452 and 388.9639]
$^1$HNMR spectra of compound: 4g
$^{13}$CNMR spectra of compound: 4g
HRMS spectra of compound: 4g

![Graph of HRMS spectra for compound 4g]
$^1$HNMR spectra of compound: 4h
$^{13}$CNMR spectra of compound: 4h
HRMS spectra of compound: 4h

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Position</th>
<th>Instrument Name</th>
<th>User Name</th>
<th>IRM Calibration Status</th>
<th>Acquired Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inj Vol</td>
<td>InjPosition</td>
<td>ACQ Method</td>
<td>SampleType</td>
<td>Comment</td>
<td></td>
</tr>
</tbody>
</table>

+APCI Scan (30.0 sec) Frag=135.0V KM-N5-ME.d

![Spectrum Diagram](image-url)

Counts vs. Mass-to-Charge (m/z)
$\text{HNMR spectra of compound: 4i}$

![HNMR spectra](image)

kn-n5-4cl-1hal
kn-n5-4d-1ha
$^{13}$CNMR spectra of compound: 4i

![NMR spectrum of compound 4i](image-url)
HRMS spectra of compound: 4i

[HRMS spectrum image with molecular structure and mass-to-charge ratio (m/z) axis]
\textsuperscript{1}HNMR spectra of compound: 4j
$^{13}$CNMR spectra of compound: 4j
HRMS spectra of compound: 4j

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Position</th>
<th>Inj Vol</th>
<th>Inj Position</th>
<th>Instrument Name</th>
<th>Instrument 1</th>
<th>User Name</th>
<th>IRM Calibration Status</th>
<th>Acquired Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>KM-N53F</td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Some Ions Missed</td>
<td>2/3/2016 4:07:53 PM</td>
</tr>
</tbody>
</table>

\[ \text{+ESI Scan (43.6 sec) Frag=135.0V KM-N53F.d} \]

361.9870

![HRMS spectrum of compound 4j](image_url)
$^1$HNMR spectra of compound: 4k
$^{13}$CNMR spectra of compound: 4k
HRMS spectra of compound: 4k

Sample Name: KM-5BR-A3BR
Inj Vol: 0
Data Filename: KM-5BR-A3BR.d

+ESI Scan (20.6 sec) Frag=135.0V KM-5BR-A3BR.d

Counts vs. Mass-to-Charge (m/z)

423.9024
421.9049
425.8992
$^1$HNMR spectra of compound: 5a
$^{13}$CNMR spectra of compound: $5a$
HRMS spectra of compound: 5a
\(^1\)HNMR spectra of compound: 5b
$^{13}$CNMR spectra of compound: 5b
HRMS spectra of compound: 5b
$^1$HNMR spectra the compound: 5d
$^{13}$CNMR spectra of compound: 5c
HRMS spectra of compound: 5c

Sample Name: Unavailable
Inj Vol: Unavailable
Data Filename: KM-B-3BR.d

Position: Unavailable
InjPosition: Unavailable
ACQ Method: Unavailable

Instrument Name: Unavailable
SampleType: Unavailable
Comment: Sample information is unavailable

User Name: Unavailable
IRM Calibration Status: All Ions Missed
Acquired Time: Unavailable

+ESI Scan (21.6 sec) Frag=135.0V KM-B-3BR.d

401.9266

Counts vs. Mass-to-Charge (m/z)

401.8 402 402.2 402.4 402.6 402.8 403 403.2 403.4 403.6 403.8 404 404.2 404.4

403.9303

5c

B
$^1$HNMR spectra the compound: 5d
$^{13}$CNMR spectra of compound: 5d
HRMS spectra of compound: 5d

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>KM-4B-BEN</th>
<th>Position</th>
<th>Val 1</th>
<th>Instrument Name</th>
<th>Instrument 1</th>
<th>User Name</th>
<th>IRM Calibration Status</th>
<th>Acquired Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inj Vol</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Some Ions Missed</td>
<td>2/16/2016 11:03:29 AM</td>
</tr>
<tr>
<td>Data Filename</td>
<td>KM-4B-BEN.d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+ESI Scan (19.9 sec) Frag=100.0V KM-4B-BEN.d
$^1$HNMR spectra of compound: 5e
$^{13}$CNMR spectra of compound: 5e
HRMS spectra of compound: 5e
$^1$HNMR spectra of compound: 5f
$^{13}$CNMR spectra of compound: 5f
HRMS spectra of compound: 5f

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>KM-4B-A-38R</th>
<th>Position</th>
<th>Val 1</th>
<th>Instrument Name</th>
<th>Instrument 1</th>
<th>User Name</th>
<th>IRM Calibration Status</th>
<th>Acquired Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inj Vol</td>
<td>0</td>
<td>InjPos</td>
<td>ACQ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![HRMS spectrum of compound 5f](image)

+ESI Scan (27.4 sec) Frag=135.0V KM-4B-A-3BR.d

- **437.8856**
- **435.8840**
- **439.8914**

![Chemical structure of compound 5f](image)