A Convenient Synthesis of 1,2,4-Triazino[2,3-b]indazol-3-amine Derivatives via Tandem Abnormal-Staudinger/Aza-Wittig/Isomerization Reaction

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**Table 1.** Crystal data and structure refinement for \textit{7a}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>\textit{7a}</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C17 H15 N5</td>
</tr>
<tr>
<td>Formula weight</td>
<td>289.34</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(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)/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>\begin{align*} a &amp;= 9.2337(11) \text{ Å} \ b &amp;= 11.0390(13) \text{ Å} \ c &amp;= 15.7307(16) \text{ Å} \end{align*}</td>
</tr>
<tr>
<td>Volume</td>
<td>1594.1(3) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.206 M/g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.076 mm⁻¹</td>
</tr>
<tr>
<td>\textit{F}(000)</td>
<td>608</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.14 x 0.06 x 0.05 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.22 to 25.02 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-10 ≤ h ≤ 10, 0 ≤ k ≤ 13, 0 ≤ l ≤ 18</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>2789 / 2789 [R(int) = 0.0000]</td>
</tr>
<tr>
<td>Completeness to theta = 25.02</td>
<td>99.3 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9962 and 0.9894</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on \textit{F}²</td>
</tr>
</tbody>
</table>
Data / restraints / parameters 2789 / 0 / 201

Goodness-of-fit on F^2 1.024

Final R indices [I>2sigma(I)]  R1 = 0.0945, wR2 = 0.1382

R indices (all data)  R1 = 0.2931, wR2 = 0.1754

Largest diff. peak and hole 0.260 and -0.199 e.A^-3

Figure 1 X-ray structures of 7a CCDC 2281905
$^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 3a:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3a:

IR(3a):
HRMS(3a):

\[ \text{Elemental Composition Report} \]

**Single Mass Analysis**
- Tolerance = 20.0 PPM
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
385 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
- C: 17-17
- H: 16-16
- N: 0-100
- O: 0-100
- Na: 0-1
- 9

230810-1-3a 9 (0.118)

\[ \text{H NMR (500 MHz, CDCl}_3\text{)} \text{ spectra of compound 3b:} \]

\[ \text{\includegraphics{hrms.png}} \]

\[ \text{\includegraphics{nmr.png}} \]
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3b:

IR(3b):
HRMS(3b):

Elemental Composition Report
Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
422 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18  H: 18-18  N: 0-100  O: 0-100  Na: 0-1
9
320810-1-3b 8 (0.102)

1H NMR (500 MHz, CDCl3) spectra of compound 3c:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3c:

IR(3c):
HRMS(3c):

Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
459 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 19-19 H: 20-20 N: 0-100 O: 0-100 Na: 0-1

9
230810-1-3c 8 (0.102)

\[
\begin{array}{cccccc}
\text{Mass} & \text{Calc. Mass} & \delta \text{a} & \text{Ppm} & \text{DBE} & \text{i-FIT} \\
334.1669 & 334.1668 & 0.1 & 0.3 & 12.3 & 14.3 \\
\end{array}
\]

\[
\text{Conf (c)} \quad \text{Formula}
\]

\[
\text{C19 H20 N5 O}
\]

\[^1\text{H NMR (500 MHz, CDCl}_3\text{) spectra of compound 3d:}
\]
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3d:

IR(3d):
HRMS(3d):

Elemental Composition Report
Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18  H: 18-18  N: 0-100  O: 0-100  Na: 0-1

320.1506 320.1511 315.1277 315.1301 321.1533 322.1580 342.1321 343.1355

Minimum: 5.0  Maximum: 50.0

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>m/z</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>320.1506</td>
<td>320.1511</td>
<td>-0.5</td>
<td>-1.6</td>
<td>12.3</td>
<td>44.1</td>
<td>n/a</td>
<td>n/a</td>
<td>C18 H18 N5 O</td>
</tr>
</tbody>
</table>

$^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 3e:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3e:

IR of compound 3e:
HRMS(3e):

Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
718 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17  H: 15-15  N: 0-100  O: 0-100  Na: 0-1  Br: 1-3

1H NMR (500 MHz, CDCl₃) spectra of compound 3f:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3f:

IR of compound 3f:
HRMS(3f):

Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
384 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17  H: 15-15  N: 0-100  O: 0-100  Na: 0-1  F: 1-1

\[
\text{3g}
\]

\[
324.1269  \text{ (0.102)}
\]

\[
301.1591  \quad 307.1836  \quad 314.2772  \quad 318.1650  \quad 325.1320  \quad 337.7981  \quad 346.1112
\]

Minima:
5.0  20.0  50.0

Mass  Calc. Mass  abs  ppm  DBE  i-FIT  Norm  Conf(%)  Formula
324.1269  324.1261  0.8  2.5  12.5  43.7  n/a  n/a  Cl7 H15 N5 O F

\[1^1\text{H NMR (500 MHz, CDCl}_3\text{)}\text{ spectra of compound 3g:}\]
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 3g:

IR of compound 3g:
HRMS(3g):

Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1129 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 Na: 0-1 Cl: 1-4

1H NMR (500 MHz, CDCl₃) spectra of compound 7a:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7a:

IR(7a):

HRMS(7a):
$^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 7b:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7b:

IR of compound 7b:
HRMS(7b):

Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
205 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18  H: 18-18  N: 0-100  O: 0-100
12
230707-14-2b 10 (0.127)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>m/z</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Novm</th>
<th>Con (%)</th>
<th>Formula</th>
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<tbody>
<tr>
<td>304.1664</td>
<td>304.1662</td>
<td>0.4</td>
<td>1.3</td>
<td>12.5</td>
<td>n/a</td>
<td>n/a</td>
<td>C18 H18 N5</td>
</tr>
</tbody>
</table>

$^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 7c:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7c:

IR of compound 7c:
HRMS(7c):

Elemental Mass Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
225 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 19-19  H: 20-20  N: 0-100  O: 0-100

1H NMR (500 MHz, CDCl₃) spectra of compound 7d:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7d:

IR of compound 7d:
HRMS(7d):

1H NMR (500 MHz, CDCl₃) spectra of compound 7e:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7e:

IR(7e):
HRMS(7e):

Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron ions
300 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17  H: 15-15  N: 0-100  O: 0-100  Br: 1-2

Minimum: -1.5
Maximum: 5.0  20.0  50.0

Mass  Calc. Mass  exp.  ppm  DBE  i-FIT  Norm  Conf(%)  Formula
368.0068  368.0051  -0.3  -0.8  12.5  433.3  0/0  0/0  C17 H13 N5 Br

$^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 7f:
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7f:

IR of compound 7f:
HRMS(7f):

**Elemental Mass Composition Report**

**Single Mass Analysis**

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

187 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 17-17  H: 15-15  N: 0-100  O: 0-100  F: 1-1

\[ \text{1H NMR (500 MHz, CDCl}_3\text{)} \text{ spectra of compound 7g:} \]
$^{13}$C NMR (126 MHz, CDCl$_3$) spectra of compound 7g:

![NMR spectrum image]

IR (7g):

![IR spectrum image]
### Elemental Composition Report

**Single Mass Analysis**
- Tolerance: 20.0 PPM
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
187 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

**Elements Used:**
- C: 17-17
- H: 15-15
- N: 0-100
- O: 0-100
- Cl: 1-1

**Diagram:**
- 230707-14-2g
- 1: TCF MS ES+
- 3.62e+006

**Table:**

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>nDa</th>
<th>ppm</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
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<tbody>
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<td>324.1016</td>
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<td>n/a</td>
<td>C17 H16 N3 S Cl</td>
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