McLaughlin, G, Morris, N, Kavanagh, PV, Power, JD, Twamley, B, O'Brien, J, Talbot, B, Dowling, G and Brandt, SD

The synthesis and characterization of the 'research chemical' N-(1-amino-3-methyl-1-oxobutan-2-yl)-1-(cyclohexylmethyl)-3-(4-fluorophenyl)-1H-pyrazole-5-carboxamide (3,5-AB-CHMFUPPYCA) and differentiation from its 5,3-regioisomer.

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Article

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1. GC-MS data for chlorinated by-product formed during the synthesis of 3,5-AB-CHMFUPPYCA

Abundance

Time-->  
Abundance

Scan 1885 (16.063 min): RouteBRecryst.D  

m/z-->
2. LC-MS data for the chlorinated by-product formed during the synthesis of 3,5-AB-CHMFUPPYCA
3. HR-MS data for the AB-CHMFUPPYCA isomers and vendor sample
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<th>Formula</th>
<th>Relative Abundance</th>
<th>ppm</th>
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</thead>
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<td>C_{9}H_{14}ON_{2}F</td>
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<td>-3.5229</td>
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<td>341.2390</td>
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<td>356.2118</td>
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<tr>
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<td>401.2328</td>
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<tr>
<td>403.2390</td>
<td>C_{22}H_{27}O N F</td>
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<td></td>
</tr>
</tbody>
</table>
4. Proton NMR spectra for the AB-CHMFUPPYCA isomers and vendor sample

**Route A**
Synthesized standard
$^1$H-NMR, d$_6$-DMSO (600 MHz)

**Route B**
Synthesized standard
$^1$H-NMR, d$_6$-DMSO (600 MHz)

**Vendor sample**
$^1$H-NMR, d$_6$-DMSO (600 MHz)
5. Carbon$^{13}$ NMR spectra for the AB-CHMFUPPYCA isomers and vendor sample

**Route A**
Synthesized standard

$^{13}$C-NMR, d$_6$-DMSO (150 MHz)

**Route B**
Synthesized standard

$^{13}$C-NMR, d$_6$-DMSO (150 MHz)

**Vendor sample**

$^{13}$C-NMR, d$_6$-DMSO (150 MHz)
6. Fluorine\textsuperscript{19} NMR spectra for the AB-CHMFUPPYCA isomers and vendor sample

- **Route A**
  - Synthesized standard
  - \textsuperscript{19}F-NMR, d\textsubscript{6}-DMSO

- **Route B**
  - Synthesized standard
  - \textsuperscript{19}F-NMR, d\textsubscript{6}-DMSO

- **Vendor sample**
  - \textsuperscript{19}F-NMR, d\textsubscript{6}-DMSO
7. NMR nuclear Overhauser effect experiment assignments

**5,3-AB-CHMFUPPYCA**

**3,5-AB-CHMFUPPYCA**

Carbon-13 NMR 150 MHz $^{19}$F-13C coupling in Hz (black)

Proton (blue), Nitrogen-15 (red), Fluorine-19 (black) NMR

Spin coupling (Hz): 7.27ppm (d, $J_{HH}$ 8.8, d, $J_{19FH}$ 8.8), 7.83ppm (d, $J_{HH}$ 8.8, d, $J_{19FH}$ 5.0)
8. Additional x-ray crystallography data

Table 1. Hydrogen bonds for 3,5-AB-CHMFUPPYCA [Å and °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(11)-H(11)...O(27)#1</td>
<td>0.95</td>
<td>2.47</td>
<td>3.266(2)</td>
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<tr>
<td>N(28)-H(28A)...O(27)#2</td>
<td>0.88(3)</td>
<td>2.00(3)</td>
<td>2.856(2)</td>
<td>166(2)</td>
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<tr>
<td>N(28)-H(28B)...N(29)#3</td>
<td>0.90(3)</td>
<td>2.20(2)</td>
<td>3.039(2)</td>
<td>155(2)</td>
</tr>
<tr>
<td>N(21)-H(21)...O(27)#1</td>
<td>0.87(2)</td>
<td>2.11(2)</td>
<td>2.963(2)</td>
<td>167(2)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+1   #2 -x,y+1/2,-z+1   #3 x,y+1,z
Hydrogen bonding network shown in dashed lines in 3,5-AB-CHMFUPPYCA showing the connectivity of the chain that extends parallel to the b axis. Unit cell shown and hydrogen atoms omitted for clarity.
Packing diagram of 3,5-AB-CHMFUPPYCA viewed down the b-axis showing the hydrogen bonded chain network and the channel occupied with acetonitrile. Dashed lines indicate hydrogen bonding. Hydrogen atoms omitted for clarity.