Supplementary Information for:

Cascade oxime formation, cyclization to a nitrone, and intermolecular dipolar cycloaddition

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1. Molecular structure data for compounds 9, 12, 16a, 17, 22, 24, 27, 28

Data for compound 9:

Empirical formula: C_{15}H_{16}N_{2}O_{3}

Formula weight: 272.30

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group: P2_1/n

Unit cell dimensions:
- a = 12.9691(19) Å, a = 90°
- b = 6.6225(11) Å, b = 104.005(11)°
- c = 15.583(3) Å, g = 90°

Volume: 1298.6(4) Å³

Z: 4

Density (calculated): 1.393 Mg/m³

Absorption coefficient: 0.098 mm⁻¹

F(000): 576

Crystal size: 0.17 x 0.13 x 0.05 mm³

 Theta range for data collection: 3.24 to 27.54°.

Index ranges: -16<=h<=16, -8<=k<=6, -20<=l<=20

Reflections collected: 11569

Independent reflections: 2984 [R(int) = 0.0846]

Completeness to theta = 27.54°: 99.6 %

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.9951 and 0.9835

Refinement method: Full-matrix least-squares on F²

Data / restraints / parameters: 2984 / 0 / 181

Goodness-of-fit on F²: 1.052

Final R indices [I>2sigma(I)]: R1 = 0.0715, wR2 = 0.1899

R indices (all data): R1 = 0.1214, wR2 = 0.2195

Largest diff. peak and hole: 0.760 and -0.475 e.Å⁻³

Crystal data deposited at CCDC 1006040
Data for compound 12:

Empirical formula: C17 H19 Br N O5.50
Formula weight: 405.24
Temperature: 100(2) K
Wavelength: 1.54178 Å
Crystal system: Monoclinic
Space group: P2_1/c
Unit cell dimensions:
- a = 11.0353(7) Å, a = 90°.
- b = 21.5973(13) Å, b = 101.886(3)°.
- c = 15.0726(9) Å, g = 90°.
Volume: 3515.3(4) Å³
Z: 8
Density (calculated): 1.531 Mg/m³
Absorption coefficient: 3.456 mm⁻¹
F(000): 1656
Crystal size: 0.380 x 0.210 x 0.180 mm³
Theta range for data collection: 3.629 to 66.827°.
Index ranges: -13<=h<=13, -25<=k<=25, -17<=l<=17
Reflections collected: 46269
Independent reflections: 6216 [R(int) = 0.0530]
Completeness to theta = 67.679°: 97.8 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.59 and 0.28
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 6216 / 0 / 444
Goodness-of-fit on F²: 1.043
Final R indices [I>2sigma(I)]: R1 = 0.0351, wR2 = 0.0794
R indices (all data): R1 = 0.0443, wR2 = 0.0835
Extinction coefficient: n/a
Largest diff. peak and hole: 0.356 and -0.614 e.Å⁻³
Crystal data deposited at CCDC 1022997
Data for compound 16a:

Empirical formula: C9 H12 N2 O3
Formula weight: 196.21
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: Pna2₁
Unit cell dimensions:
\[ a = 7.9208(3) \text{ Å} \quad \text{a} = 90^\circ \]
\[ b = 16.5681(9) \text{ Å} \quad \text{b} = 90^\circ \]
\[ c = 6.7713(3) \text{ Å} \quad \text{g} = 90^\circ \]
Volume: 888.62(7) Å³
Z: 4
Density (calculated): 1.467 Mg/m³
Absorption coefficient: 0.111 mm⁻¹
F(000): 416
Crystal size: 0.35 x 0.12 x 0.10 mm³
Theta range for data collection: 2.46 to 27.63°
Index ranges: -9<=h<=10, -19<=k<=21, -8<=l<=8
Reflections collected: 4579
Independent reflections: 2018 [R(int) = 0.0210]
Completeness to theta = 27.63°: 100.0 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.9889 and 0.9620
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 2018 / 1 / 128
Goodness-of-fit on F²: 1.279
Final R indices [I>2sigma(I)]: R1 = 0.0338, wR2 = 0.0847
R indices (all data): R1 = 0.0363, wR2 = 0.0873
Largest diff. peak and hole: 0.214 and -0.187 e.Å⁻³
Crystal data deposited at CCDC 1051097
Data for compound 17:

Empirical formula: C12 H14 N2 O3

Formula weight: 234.25

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group: P2(1)/c

Unit cell dimensions:
\[ \begin{align*}
a &= 9.0398(3) \text{ Å} \\
b &= 7.2748(3) \text{ Å} \\
c &= 17.0449(6) \text{ Å} \\
a &= 90^\circ. \\
b &= 98.643(2)^\circ. \\
g &= 90^\circ.
\end{align*} \]

Volume: 1108.19(7) Å³

Z: 4

Density (calculated): 1.404 Mg/m³

Absorption coefficient: 0.102 mm⁻¹

F(000): 496

Crystal size: 0.45 x 0.32 x 0.18 mm³

Theta range for data collection: 2.28 to 27.54°.

Index ranges: \(-11\leq h \leq 11, -9\leq k \leq 9, -22\leq l \leq 20\)

Reflections collected: 14308

Independent reflections: 2547 [R(int) = 0.0210]

Completeness to theta = 27.54°: 99.8 %

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.9818 and 0.9554

Refinement method: Full-matrix least-squares on F²

Data / restraints / parameters: 2547 / 0 / 154

Goodness-of-fit on F²: 1.022

Final R indices [I>2sigma(I)]: R1 = 0.0375, wR2 = 0.0992

R indices (all data): R1 = 0.0395, wR2 = 0.1014

Largest diff. peak and hole: 0.343 and -0.318 e.Å⁻³

Crystal data deposited at CCDC 1006037
Data for compound 22:

![Chemical Structure of Compound 22](image)

- **Empirical formula**: C15 H17 N O5
- **Formula weight**: 291.30
- **Temperature**: 296(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Monoclinic
- **Space group**: P2(1)/c
- **Unit cell dimensions**:
  - \(a = 9.124(8)\) Å, \(a = 90.13^\circ\)
  - \(b = 32.24(3)\) Å, \(b = 90.000(6)^\circ\)
  - \(c = 9.457(9)\) Å, \(g = 90^\circ\)
- **Volume**: 2782.5(4) Å³
- **Z**: 8
- **Density (calculated)**: 1.391 Mg/m³
- **Absorption coefficient**: 0.105 mm⁻¹
- **F(000)**: 1232
- **Crystal size**: 0.32 x 0.11 x 0.11 mm³
- **Theta range for data collection**: 1.26 to 27.64°.
- **Index ranges**: -11<=h<=11, -42<=k<=40, -12<=l<=12
- **Reflections collected**: 47642
- **Independent reflections**: 6429 [R(int) = 0.0773]
- **Completeness to theta = 27.64°**: 99.4 %
- **Absorption correction**: Semi-empirical from equivalents
- **Max. and min. transmission**: 0.9885 and 0.9672
- **Refinement method**: Full-matrix least-squares on F²
- **Data / restraints / parameters**: 6429 / 0 / 384
- **Goodness-of-fit on F²**: 1.035
- **Final R indices [I>2sigma(I)]**: R1 = 0.0473, wR2 = 0.1190
- **R indices (all data)**: R1 = 0.0681, wR2 = 0.1356
- **Largest diff. peak and hole**: 0.490 and -0.320 e Å⁻³
- **Crystal data deposited at CCDC 1006038**
Data for compound 24:

Empirical formula: C14 H14 N2 O3
Formula weight: 258.27
Temperature: 296(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: P2(1)/c
Unit cell dimensions:
  a = 6.8159(2) Å  a = 90°.
  b = 26.7835(7) Å  b = 114.2140(10)°.
  c = 7.0628(2) Å  g = 90°.
Volume: 1175.90(6) Å³
Z: 4
Density (calculated): 1.459 Mg/m³
Absorption coefficient: 0.104 mm⁻¹
F(000): 544
Crystal size: 0.34 x 0.12 x 0.04 mm³
Theta range for data collection: 1.52 to 27.48°.
Index ranges: -8 <= h <= 8, -34 <= k <= 34, -9 <= l <= 9
Reflections collected: 20165
Independent reflections: 2686 [R(int) = 0.0225]
Completeness to theta = 27.48°: 99.7 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.9958 and 0.9654
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 2686 / 0 / 173
Goodness-of-fit on F²: 1.106
Final R indices [I>2sigma(I)]: R1 = 0.0362, wR2 = 0.1041
R indices (all data): R1 = 0.0400, wR2 = 0.1157
Largest diff. peak and hole: 0.377 and -0.217 e.Å⁻³

Crystal data deposited at CCDC 1006039
Data for compound 27:

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<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C21 H20 N2 O5</td>
</tr>
<tr>
<td>Formula weight</td>
<td>380.39</td>
</tr>
<tr>
<td>Temperature</td>
<td>97(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.6709(10) Å</td>
</tr>
<tr>
<td></td>
<td>b = 7.6760(7) Å</td>
</tr>
<tr>
<td></td>
<td>c = 22.1886(18) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>1801.4(3) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.403 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.101 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>800</td>
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<tr>
<td>Crystal size</td>
<td>0.43 x 0.38 x 0.35 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.85 to 27.55°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13&lt;=h&lt;=13, -9&lt;=k&lt;=9, -28&lt;=l&lt;=28</td>
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<td>Reflections collected</td>
<td>33725</td>
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<tr>
<td>Independent reflections</td>
<td>4133 [R(int) = 0.0718]</td>
</tr>
<tr>
<td>Completeness to theta = 27.55°</td>
<td>99.7 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9654 and 0.9578</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>4133 / 0 / 255</td>
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<td>Goodness-of-fit on F²</td>
<td>1.054</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0412, wR2 = 0.1086</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0488, wR2 = 0.1142</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.307 and -0.290 e.Å⁻³</td>
</tr>
</tbody>
</table>

Crystal data deposited at CCDC 1006041
Data for compound 28:

Empirical formula C16 H18 N2 O5
Formula weight 318.32
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2₁/c
Unit cell dimensions
a = 9.8243(10) Å  a = 90°.
b = 8.6128(8) Å  b = 104.843(5)°.
c = 17.8328(18) Å  g = 90°.
Volume 1458.6(2) Å³
Z 4
Density (calculated) 1.450 Mg/m³
Absorption coefficient 0.109 mm⁻¹
F(000) 672
Crystal size 0.40 x 0.38 x 0.36 mm³
Theta range for data collection 2.14 to 27.57°.
Index ranges -12<=h<=12, -11<=k<=10, -22<=l<=22
Reflections collected 13444
Independent reflections 3284 [R(int) = 0.0681]
Completeness to theta = 25.00° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9619 and 0.9578
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 3284 / 0 / 211
Goodness-of-fit on F² 1.059
Final R indices [I>2sigma(I)] R1 = 0.0499, wR2 = 0.1267
R indices (all data) R1 = 0.0731, wR2 = 0.1399
Largest diff. peak and hole 0.248 and -0.274 e.Å⁻³
Crystal data deposited at CCDC 1006042
2. NMR Spectra for compounds 8–12, 14–20, macronecine, 22–24, and 26–30
14 dr 2:1
(note: compound 18 is difficult to purify)
macronecine