Supporting Information

Enantioselective Mukaiyama-Michael with 2-Enoyl Pyridine N-Oxides Catalyzed by PYBOX-DIPH-Zn(II)-Complexes at Ambient Temperature

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Figure 3. ORTEP diagrams of 4n with thermal ellipsoids at the 50% probability limit (other H-atoms are deleted for clarity).

Table 1. Crystal data and structure refinement parameters of compound 4n.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Compound 4n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C20 H17 N O3 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>351.41</td>
</tr>
<tr>
<td>Temperature</td>
<td>273(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2₁</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 11.7359(8) Å</td>
</tr>
<tr>
<td></td>
<td>b = 5.5595(4) Å</td>
</tr>
<tr>
<td></td>
<td>c = 12.5993(9) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90.000°</td>
</tr>
<tr>
<td></td>
<td>β = 90.641(2)°</td>
</tr>
<tr>
<td></td>
<td>γ = 90.000°</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Volume</td>
<td>822.00(10) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.420 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.216 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>368</td>
</tr>
<tr>
<td>Colour, Shape</td>
<td>Colourless, Block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.22 x 0.18 x 0.16 mm³</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>2.36 to 25.50°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-13≤h≤14, -6≤k≤6, -15≤l≤14</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>5875 / 3009</td>
</tr>
<tr>
<td>Reflections used</td>
<td>4834</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3009 / 1 / 226</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.075</td>
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<tr>
<td>Final R indices [I &gt;2σ(I)]</td>
<td>R₁ = 0.0296, wR₂ = 0.0708</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0323, wR₂ = 0.0726</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>-0.05(7)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.207 and -0.167 e Å⁻³</td>
</tr>
</tbody>
</table>
500 MHz $^1$H NMR spectra of compound 4a in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4a in CDCl$_3$
HPLC chromatogram of compound 4a (racemic)

HPLC chromatogram of compound 4a (Chiral)
500 MHz $^1$H NMR spectra of compound 4b in CDCl$_3$.

125 MHz $^{13}$C NMR spectra of compound 4b in CDCl$_3$. 

S6
HPLC chromatogram of compound 4b (racemic)

HPLC chromatogram of compound 4b (chiral)
500 MHz $^1$H NMR spectra of compound 4c in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4c in CDCl$_3$
HPLC chromatogram of compound 4c (racemic)

HPLC chromatogram of compound 4c (Chiral)

S9
500 MHz $^1$H NMR spectra of compound 4d in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4d in CDCl$_3$
HPLC chromatogram of compound 4d (racemic)

HPLC chromatogram of compound 4d (chiral)

S11
500 MHz $^1$H NMR spectra of compound 4e in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4e in CDCl$_3$
HPLC chromatogram of compound 4e (racemic)

HPLC chromatogram of compound 4e (chiral)
500 MHz $^1$H NMR spectra of compound 4f in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4f in CDCl$_3$
HPLC chromatogram of compound 4f (racemic)

HPLC chromatogram of compound 4f (chiral)

S15
500 MHz $^1$H NMR spectra of compound 4g in CDCl$_3$ 

125 MHz $^{13}$C NMR spectra of compound 4g in CDCl$_3$
HPLC chromatogram of compound 4g (racemic)

HPLC chromatogram of compound 4g (chiral)
500 MHz $^1$H NMR spectra of compound 4h in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4h in CDCl$_3$
HPLC chromatogram of compound 4h (racemic)

HPLC chromatogram of compound 4h (chiral)
500 MHz $^1$H NMR spectra of compound 4i in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4i in CDCl$_3$
HPLC chromatogram of compound 4i (racemic)

HPLC chromatogram of compound 4i (chiral)
500 MHz $^1$H NMR spectra of compound 4j in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4j in CDCl$_3$
HPLC chromatogram of compound 4j (racemic)

HPLC chromatogram of compound 4j (chiral)
500 MHz $^1$H NMR spectra of compound 4k in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4k in CDCl$_3$
HPLC chromatogram of compound 4k (racemic)

HPLC chromatogram of compound 4k (chiral)
500 MHz $^1$H NMR spectra of compound 4l in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4l in CDCl$_3$
HPLC chromatogram of compound 4l (racemic)

HPLC chromatogram of compound 4l (chiral)
500 MHz $^1$H NMR spectra of compound 4m in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 4m in CDCl$_3$
HPLC chromatogram of compound **4m** (racemic)

HPLC chromatogram of compound **4m** (chiral)
500 MHz $^1$H NMR spectra of compound 4n in CDCl$_3$
125 MHz $^{13}$C NMR spectra of compound 4n in CDCl$_3$

HPLC chromatogram of compound 4n (racemic)
HPLC chromatogram of compound 4n (chiral)

500 MHz $^1$H NMR spectra of compound 4o in CDCl$_3$
125 MHz $^{13}$C NMR spectra of compound 4o in CDCl$_3$.

HPLC chromatogram of compound 4o (racemic)

HPLC chromatogram of compound 4o (chiral)
500 MHz $^1$H NMR spectra of compound 6a in CDCl$_3$
125 MHz $^{13}$C NMR spectra of compound 6a in CDCl$_3$

HPLC chromatogram of compound 6a (racemic)
HPLC chromatogram of compound 6a (chiral)

500 MHz $^1$H NMR spectra of compound 6b in CDCl$_3$
125 MHz $^{13}$C NMR spectra of compound 6b in CDCl$_3$

HPLC chromatogram of compound 6b (racemic)
HPLC chromatogram of compound 6b (Chiral)

500 MHz $^1$H NMR spectra of compound 6c in CDCl$_3$
$125\,\text{MHz}$ $^{13}\text{C}$ NMR spectra of compound $6c$ in CDCl$_3$

HPLC chromatogram of compound $6c$ (racemic)
HPLC chromatogram of compound 6c (Chiral)

500 MHz $^1$H NMR spectra of compound 7 in CDCl$_3$
500 MHz $^1$H NMR spectra of compound 8 in CDCl$_3$

125 MHz $^{13}$C NMR spectra of compound 8 in CDCl$_3$
HPLC chromatogram of compound 8 (racemic)
HPLC chromatogram of compound 8 (Chiral)
Mass spectrum of compound 4a

Mass spectrum of compound 4b

Mass spectrum of compound 4c
Mass spectrum of compound 4d

Mass spectrum of compound 4e
Mass spectrum of compound $4f$

Mass spectrum of compound $4g$
Mass spectrum of compound 4h

Mass spectrum of compound 4i
Mass spectrum of compound 4j

Mass spectrum of compound 4k
Mass spectrum of compound 4l

Mass spectrum of compound 4m

S49
Mass spectrum of compound 4n
Mass spectrum of compound 4o

Mass spectrum of compound 6a

S51
Mass spectrum of compound 6b

Mass spectrum of compound 6c
Mass spectrum of compound 7

Mass spectrum of compound 8