Rhodium(III)-Catalyzed Diastereoselective Ring-Opening of 7-Azabenzonorbornadienes with Aromatic Ketoximes: Synthesis of Benzophenanthridine Derivatives

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Supporting Information (SI)

Table of Contents

S2 – S3 X-Ray analysis Data
S4 – S5 Mechanistic Investigation
S6 – S75 Copies of $^1$H and $^{13}$C NMR Spectra of All Compounds.
Crystallographic Data of Compound 3ba:

Suitable single crystals for X-ray diffraction studies were obtained from the compound synthesized in this study. Single crystals were grown in a NMR tube at room temperature using CDCl₃ over a period of 3-4 weeks by slow evaporation of solvent.

X-ray data was collected with a Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromatic Mo (Kα) (λ = 0.7107 Å) radiation source. The data were collected with 100% completeness for Θ up to 25°. ω and φ scans were employed to collect the data. The frame width for ω for was fixed to 0.5° for data collection. The crystal was solved by direct methods using Bruker SHELXS (Sheldrick, 1997). The Structure was refined using the Bruker SHELXTL (Version 6.12) software package. These data were deposited with Cambridge Crystallographic Data Center with the following numbers: CCDC 1950036.

Figure S1: ORTEP representation of compound 3ba displaying thermal ellipsoid at 50% probability.
X-Ray Analysis of Compounds 3ba (the crystal is having dimeric compound).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>3ba</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{50} H_{61} N_{4} O_{8}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>846.02</td>
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<tr>
<td>Temperature</td>
<td>296(2) K</td>
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<tr>
<td>Wavelength</td>
<td>71.073 pm</td>
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<tr>
<td>Crystal system</td>
<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>P - 1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 1114.05(16) pm, ( \alpha = 89.864(5)^\circ )</td>
</tr>
<tr>
<td></td>
<td>b = 1469.54(16) pm, ( \beta = 79.407(4)^\circ )</td>
</tr>
<tr>
<td></td>
<td>c = 1523.2(2) pm, ( \gamma = 75.874(4)^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>2.3756(6) nm^3</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.183 Mg/m^3</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.080 mm(^1)</td>
</tr>
<tr>
<td>F(000)</td>
<td>906</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.250 x 0.220 x 0.150 mm^3</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.361 to 24.292°.</td>
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<tr>
<td>Index ranges</td>
<td>-12&lt;=h&lt;=12, -16&lt;=k&lt;=16, -17&lt;=l&lt;=17</td>
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<tr>
<td>Reflections collected</td>
<td>28630</td>
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<tr>
<td>Independent reflections</td>
<td>7586 [R(int) = 0.0592]</td>
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<tr>
<td>Completeness to theta = 24.292°</td>
<td>98.3 %</td>
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<tr>
<td>Absorption correction</td>
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</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>7586 / 0 / 580</td>
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<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.062</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0609, wR2 = 0.1617</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1138, wR2 = 0.1996</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0043(11)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.214 and -0.591 e.Å(^3)</td>
</tr>
</tbody>
</table>
$^1$H Spectra of Compound D-1c (CDCl$_3$ was used).

$^1$H Spectra of Compound D-3ca (CDCl$_3$ was used).
Isolation of intermediate B.

$^1$H and $^{13}$C NMR Spectra of Compound B
$^1$H and $^{13}$C NMR Spectra of Compound 3aa.
DEPT (135) NMR Spectrum of Compound 3aa.
$^1$H and $^{13}$C NMR Spectra of Compound 3ba.
$^1$H and $^{13}$C NMR Spectra of Compound 3ca.

The NMR was taken at 50 °C. The bumps range 4.6 ppm and 4.2 ppm were disappeared.
$^1$H and $^{13}$C NMR Spectra of Compound 3da.

Fine shimming NMR: expended Chemical shift 7.60 ppm to 3.8 ppm for better splitting
$^1$H and $^{13}$C NMR Spectra of Compound 3ea.
$^1$H and $^{13}$C NMR Spectra of Compound 3fa.
$^1$H and $^{13}$C NMR Spectra of Compound 3ga.
$^1$H and $^{13}$C NMR Spectra of Compound 3ha.
$^1$H and $^{13}$C NMR Spectra of Compound 3ia.

The NMR was taken at 50 °C. The bumps range 5.2 ppm and 4.5 ppm were disappeared.
$^1$H and $^{13}$C NMR Spectra of Compound 3ja.

Fine shimming NMR: expended Chemical shift 7.30 ppm to 3.9 ppm for better splitting.
$^1$H and $^{13}$C NMR Spectra of Compound 3ka.

Fine shimming NMR expended: Chemical shift 7.60 ppm to 3.8 ppm for better splitting
$^1$H and $^{13}$C NMR Spectra of Compound 3la.

Fine shimming NMR expended: Chemical shift 7.30 ppm to 3.9 ppm for better splitting
$^1$H and $^{13}$C NMR Spectra of Compound 3ma.

The NMR was taken at 50 °C. The bumps range 5.9 ppm and 4.6 ppm were disappeared.
$^{1}$H and $^{13}$C NMR Spectra of Compound 3na.
$^1$H and $^{13}$C NMR Spectra of Compound 30a.
DEPT (135) NMR Spectrum of Compound 30a.

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[Chemical structure and NMR spectrum image]
$^1$H and $^{13}$C NMR Spectra of Compound 3pa.
DEPT (135) NMR Spectrum of Compound 3pa.
$^1$H and $^{13}$C NMR Spectra of Compound 3qa.

The NMR was taken at 50 °C. The bumps range 5.0 ppm and 4.4 ppm were disappeared.
$^1$H and $^{13}$C NMR Spectra of Compound 3ra.
$^1$H and $^{13}$C NMR Spectra of Compound 3sa.
DEPT (135) NMR Spectrum of Compound 3sa.
$^1$H and $^{13}$C NMR Spectra of Compound 3ta.
DEPT (135) NMR Spectrum of Compound 3ta.
$^{1}H$ and $^{13}C$ NMR Spectra of Compound 3ua.
DEPT (135) NMR Spectrum of Compound 3ua.
\(^1\)H and \(^{13}\)C NMR Spectra of Compound 3eb.
DEPT (135) NMR Spectrum of Compound 3eb.
\( ^1H \) and \( ^13C \) NMR Spectra of Compound 3cc.
DEPT (135) NMR Spectrum of Compound 3ec.
\(^1\)H and \(^{13}\)C NMR Spectra of Compound 3ec.
\(^1\)H and \(^{13}\)C NMR Spectra of Compound 3cd.
DEPT (135) NMR Spectrum of Compound 3cd.
$^1$H and $^{13}$C NMR Spectra of Compound 3ee.
$^1$H and $^{13}$C NMR Spectra of Compound 3ae.
DEPT (135) NMR Spectrum of Compound 3ae.
$^1$H and $^{13}$C NMR Spectra of Compound 3ec.
DEPT (135) NMR Spectrum of Compound 3ec.
$^1$H and $^{13}$C NMR Spectra of Compound 4a.
DEPT (135) NMR Spectrum of Compound 4a.
$^{1}\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 4b.

Fine shimming NMR expended Chemical shift 7.75 ppm to 3.0 ppm for better splitting.
DEPT (135) NMR Spectrum of Compound 4b.
$^1$H and $^{13}$C NMR Spectra of Compound 4c.
DEPT (135) NMR Spectrum of Compound 4c.
$^1$H and $^{13}$C NMR Spectra of Compound 4d.
DEPT (135) NMR Spectrum of Compound 4d.
$^1$H and $^{13}$C NMR Spectra of Compound 4e.
$^1$H and $^{13}$C NMR Spectra of Compound 4f.

\[ \text{Diagram of compound 4f} \]
DEPT (135) NMR Spectrum of Compound 4f.
$^1$H and $^{13}$C NMR Spectra of Compound 4g.

Fine shimming NMR expended Chemical shift 7.6 ppm to 3.0 ppm for better splitting
DEPT (135) NMR Spectrum of Compound 4g.
$^1$H and $^{13}$C NMR Spectra of Compound 4h.
DEPT (135) NMR Spectrum of Compound 4h.
$^1$H and $^{13}$C NMR Spectra of Compound 4i.

Fine shimming NMR expended: Chemical shift 7.54 ppm to 3.0 ppm for better splitting
DEPT (135) NMR Spectrum of Compound 4i.
$^1$H and $^{13}$C NMR Spectra of Compound 4j.
DEPT (135) NMR Spectrum of Compound 4j.
$^1$H and $^{13}$C NMR Spectra of Compound 5a.
DEPT (135) NMR Spectrum of Compound 5a.
$^1$H and $^{13}$C NMR Spectra of Compound 5b.
DEPT (135) NMR Spectrum of Compound 5b.