Nickel-Catalyzed syn-Stereocontrolled Ring-Opening of Oxa- and Azabicyclic Alkenes with Dialkylzinc Reagents

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Supporting Information

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1. General information

Unless otherwise indicated, all reagents were purchased from commercial suppliers and used without further purification. Toluene and pentane was distilled from sodium benzophenone ketyl and CH$_2$Cl$_2$ was distilled from calcium hydride. Super dry solvent THF, DMF, 1,4-dioxane, i-PrOH and CH$_3$CN were used without any pretreatment. All flasks were flame-dried under a stream of nitrogen and cooled to room temperature before use. Flash column chromatography was performed using the indicated solvent system on Qingdao-Haiyang silica gel (200–300 mesh). Peaks recorded are relative to the internal standards: TMS (δ = 0.00) for $^1$H NMR and CDCl$_3$ (δ = 77.00) for $^{13}$C NMR spectra. $^1$H and $^{13}$C NMR spectra were recorded at 400/500/600 MHz and 101/126/151 MHz at 25 °C in CDCl$_3$/d$_6$-DMSO/CD$_3$OD, respectively. $^{19}$F NMR spectra was recorded at 376/470/565 MHz at 25 °C in CDCl$_3$. Spectral data are reported as follows: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quadruplet, m-multiplet); coupling constants (J, Hz) and number of protons. HRMS (ion trap) were obtained from mass spectrometer (ESI) and MS were recorded using EI at 70 eV. Melting points were uncorrected.
2. Copies of $^1$H, $^{13}$C and $^{19}$F NMR spectra

3aa

400 MHz, CDCl$_3$

3aa

100 MHz, CDCl$_3$
400 MHz, $d_6$-DMSO

100 MHz, $d_6$-DMSO
3da
400 MHz, $d_6$-DMSO

3da
100 MHz, $d_6$-DMSO
3ea
376 MHz, CDCl₃

3fa
400 MHz, CDCl₃
3fa
100 MHz, CDCl₃

3ga
400 MHz, CDCl₃
3ia
150 MHz, CDCl₃

3ja
400 MHz, CDCl₃
OH

$\text{3ab}$

100 MHz, CDCl$_3$

OCH$_3$OH

$\text{3bb}$

600 MHz, CDCl$_3$
$\text{OCH}_3\text{OH}$

$\text{CH}_3$

$3\text{bb}$

150 MHz, CDCl$_3$

$\text{Br}$

$\text{OH}$

$\text{CH}_3$

$3\text{cb}$

400 MHz, CDCl$_3$
$\textbf{3cb}$

100 MHz, CDCl$_3$

$\textbf{3db}$

600 MHz, CD$_3$OD
17

$\text{F} \quad \text{CH}_3$

$\text{OH}

F\quad \text{CH}_3$

$\text{3eb}

100 \text{ MHz, CDCl}_3$

$\text{F} \quad \text{CH}_3$

$\text{OH}$

$\text{3eb}$

$376 \text{ MHz, CDCl}_3$
$\text{Br}_2\text{OHCH}_{3}$

$\text{3fb}$

$400 \text{ MHz, CDCl}_3$

$\text{Br}_2\text{OHCH}_{3}$

$\text{3fb}$

$100 \text{ MHz, CDCl}_3$
3ib
600 MHz, CDCl₃

3ib
150 MHz, CDCl₃
$3ib'$ OH
600 MHz, CDCl$_3$

$3ib'$ OH
150 MHz, CDCl$_3$
$\text{3ad}$

600 MHz, CD$_3$OD

---

$\text{3ad}$

150 MHz, CD$_3$OD
4aa
500 MHz, CDCl₃

4aa
125 MHz, CDCl₃
3. HPLC chromatograms for compounds

**Figure 1:** HPLC trace of racemic-3aa (2.5 mol% Ni(dppe)Cl₂). HPLC analysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 17.8 min and 19.8 min.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Time (min)</th>
<th>Area (mV*s)</th>
<th>Area (%)</th>
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<tbody>
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Figure 2: HPLC trace of enantioenriched-3aa (2.5 mol% Ni(dppe)Cl₂ and 2.5 mol% (S)-BINAP). The ee of 0% was determined by HPLC analysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 18.1 min and 20.2 min.

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<th>Area (%)</th>
</tr>
</thead>
<tbody>
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<td>20.178</td>
<td>454502.6</td>
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Figure 3: HPLC trace of enantioenriched-3aa (2.5 mol% Ni(dppe)Cl₂ and 2.5 mol% L1). The ee of 0% was determined by HPLC analysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH 99/1, flow: 1 mL/min, λ = 254), retention times were 18.2 min and 20.2 min.

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<td>2</td>
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<td>284821.2</td>
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**Figure 4:** HPLC trace of enantioenriched-3aa (2.5 mol% Ni(dppe)Cl₂ and 2.5 mol% L2). The ee of 0% was determined by HPLC analysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 17.9 min and 20.0 min.

<table>
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Figure 5: HPLC trace of racemic-3aa (2.5 mol% Ni(COD)$_2$ and 2.5 mol% dppe).
HPLC anlaysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, $\lambda = 254$), retention times were 18.9 min and 21.0 min.

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Figure 6: HPLC trace of enantioenriched-3aa (2.5 mol% Ni(COD)$_2$ and 2.5 mol% L1). The ee of 1% was determined by HPLC analysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, $\lambda$ = 254), retention times were 18.8 min and 20.9 min.

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Figure 7: HPLC trace of trace of enantioenriched-3aa (2.5 mol% Ni(COD)$_2$ and 2.5 mol% L2). The $ee$ of 1% was determined by HPLC analysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, $\lambda = 254$), retention times were 18.9 min and 21.1 min.

<table>
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