Electronic Supplementary Information

Divergent synthesis of
3,4-dihydrodibenzo[b,d]furan-1(2H)-ones and isocoumarins
via additive-controlled chemoselective C-C or C-N bond cleavage

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Table of content

Optimization of the Reaction condition----------------------------------S1

Copies of $^1$H and $^{13}$C NMR Spectra for all Compounds ----------S2-S49

X-Ray Crystallography structures of Compound 3aa -------------------S50

X-Ray Crystallography structures of Compound 4ab-------------------S50

HRMS spectra for all Compounds -----------------------------------S51-S66
Table S1 Optimization of the Reaction Conditions$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>additive (mol%)</th>
<th>solvent</th>
<th>Temp ($^\circ$C)</th>
<th>Yield$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(p-cymene)RuCl$_2$]$_2$</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>Ru(PPh$_3$)Cl$_2$</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)$_2$</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>CuI</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>CsOPiv (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>AgOAc (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>CsOAc (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>AgSbF$_6$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>9$^c$</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>74</td>
</tr>
<tr>
<td>10$^d$</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>67</td>
</tr>
<tr>
<td>11$^e$</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>AgNTf$_2$ (10)</td>
<td>MeOH</td>
<td>reflux</td>
<td>53</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 2-diazocyclohexane-1,3-dione 1a (0.5 mmol), 2-hydroxy-N-methylbenzamide 2a (0.5 mmol), solvent (3 mL), and catalyst (1.0 mol%), under argon atmosphere. $^b$ Isolated yields of compound 3aa. $^c$ Reaction time was 20 h. $^d$ Reaction time was 10 h. $^e$ Reaction time was 8 h.
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3aa
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ab
$^{1}$H NMR and $^{13}$C NMR Spectra of Compound 3ac

![H NMR and C NMR Spectra of Compound 3ac](image-url)
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ad
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ae
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3af
\(^{1}\)H NMR and \(^{13}\)C NMR Spectra of Compound 3ag

\[
\begin{align*}
&\text{H}_2\text{C} - \text{C} - \text{O} - \text{F} \\
&\text{H}_2\text{C} - \text{C} - \text{O} - \text{F}
\end{align*}
\]
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ah
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ai
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3aj

![Spectrum Image]
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ak
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ba

![Diagram of Compound 3ba]

\[ \text{Chemical Shifts (ppm):} \]
- $^1$H NMR: 11.08, 12.49
- $^{13}$C NMR: 20.38, 19.12, 21.32, 21.93

S13
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3bb
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3bc
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3bd

\[
\text{H}_3\text{C} \quad \text{H}_2\text{C} \quad \text{CH}_3
\]
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3be
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3bf
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ca
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3cc
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3cd
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ce
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3cf
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3cg
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ch
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3da
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3db
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3dc
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3de
\(^1\)H NMR and \(^{13}\)C NMR Spectra of Compound 3ea
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3eb
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ec
$^1$H NMR and $^{13}$C NMR Spectra of Compound 3ed
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4aa
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ab
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ac
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ad
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ae
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ba
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4bb
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4bc
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4bd
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ca
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4cb
\( ^1\text{H NMR and } ^{13}\text{C NMR Spectra of Compound 4da} \)
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4db
$^1$H NMR and $^{13}$C NMR Spectra of Compound 4ea
X-Ray Crystallography structures of Compounds 3aa and 4ab

Crystal data for 3aa: C_{14}H_{14}O_{2}, \text{Mr} = 214.26, Monoclinic, \( a = 9.4379(9) \) Å, \( b = 12.1544(11) \) Å, \( c = 9.8277 (9) \) Å, \( \alpha = 90^\circ \), \( \beta = 96.810 (10)^\circ \), \( \gamma = 90^\circ \), \( V = 1119.28 (18) \) Å³, \( T = 293 (2) \) K, space group P2(1)/n, \( Z = 8 \), 8285 reflections collected, 2061 unique (\( R_{int} = 0.0269 \)) which were used in all calculations. The ellipsoid contour probability level in the caption of 30 %.

Crystallographic data for compound 3aa reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1554775.

Crystal data for 4ab: C_{16}H_{16}O_{4}, \text{Mr} =272.29, Monoclinic, \( a = 8.8746(6) \) Å, \( b = 15.3282(11) \) Å, \( c = 10.0135 (7) \) Å, \( \alpha = 90^\circ \), \( \beta = 95.182 (2)^\circ \), \( \gamma = 90^\circ \), \( V =1356.59 (16) \) Å³, \( T = 293 (2) \) K, space group P2(1)/c, \( Z = 4 \), 23206 reflections collected, 2484 unique (\( R_{int} = 0.0390 \)) which were used in all calculation. The ellipsoid contour probability level in the caption of 30%.

Crystallographic data for compound 4ab reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 1555510.
HRMS Spectra of Compound 3aa

HRMS Spectra of Compound 3ab

HRMS Spectra of Compound 3ac
HRMS Spectra of Compound 3ad

HRMS Spectra of Compound 3ae

HRMS Spectra of Compound 3af
HRMS Spectra of Compound 3ag

HRMS Spectra of Compound 3ah

HRMS Spectra of Compound 3ai
HRMS Spectra of Compound 3bb

HRMS Spectra of Compound 3bc

HRMS Spectra of Compound 3bd
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HRMS Spectra of Compound 3bf

HRMS Spectra of Compound 3ca
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HRMS Spectra of Compound 3cc

HRMS Spectra of Compound 3cd
HRMS Spectra of Compound 3ce

HRMS Spectra of Compound 3cf

HRMS Spectra of Compound 3cg
HRMS Spectra of Compound 3cf

HRMS Spectra of Compound 3da

HRMS Spectra of Compound 3db
HRMS Spectra of Compound 3dc

HRMS Spectra of Compound 3dd

HRMS Spectra of Compound 3de
HRMS Spectra of Compound 3ea

HRMS Spectra of Compound 3eb

HRMS Spectra of Compound 3ec
HRMS Spectra of Compound 3ed

HRMS Spectra of Compound 4aa

HRMS Spectra of Compound 4ab
HRMS Spectra of Compound 4ac

HRMS Spectra of Compound 4ad

HRMS Spectra of Compound 4ae
HRMS Spectra of Compound 4bd

HRMS Spectra of Compound 4ca

HRMS Spectra of Compound 4cb
HRMS Spectra of Compound 4da

HRMS Spectra of Compound 4db