Decarbonylation through Aldehydic C–H Bond Cleavage by Cationic Iridium Catalyst

(Supplementary Information)

Contents

1. General information
2. Representative procedure for the cationic Ir-catalyzed decarbonylation
3. Analytical data of 2
4. General procedure and data for the cationic Ir-catalyzed asymmetric hydroacylation
1. General information

$^1$H-NMR spectra were recorded on a JEOL ECX-400II (400 MHz for $^1$H) spectrometer. Chemical shifts are reported in part per million (ppm) relative to TMS internal standard (for $^1$H, $\delta$ 0.00). $^1$H-NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. GC analysis was directly performed with chiral column (Column: RESTEK Rt- $\beta$ DEXsa) on a Shimadzu GC-2014. Flash column chromatography for Ir-catalyzed reaction was performed with Kanto Chemical silica gel 60N (spherical, neutral, particle size 60-210 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F254).

Materials.

Unless otherwise noted, materials were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dehydrated solvents (Tetrahydrofuran, Dioxane and toluene) were purchased from Kanto Chemical Co., Inc. and used under nitrogen atmosphere. IrCl$_3$·xH$_2$O was purchased from Furuya Metal Co., Ltd. [Ir(cod)$_2$](BArF$_4$)$_3$[1] was prepared by the literature procedure.

2. Representative procedure for the cationic Ir-catalyzed decarbonylation

![Chemical Structure](image)

To an oven-dried sealed tube, [Ir(cod)$_2$](BArF$_4$) (0.0125 mmol, 5 mol%) and (R)-Xyl-BINAP (0.0138 mmol, 5.5 mol%) and dry THF (1.0 mL) were added under N$_2$ atmosphere. The mixture was stirred at room temperature for 30 min, followed by the addition of benzaldehyde $1a$ (0.25 mmol). The reaction mixture was then heated at 135 °C. After being stirred for 24 h, the mixture was analyzed by GC with methyl 3-nitrobenzoate as internal standard (78% yield).

![Chemical Structure](image)

To an oven-dried sealed tube, [Ir(cod)$_2$](BArF$_4$) (0.0125 mmol, 5 mol%) and (R)-Xyl-BINAP (0.0138 mmol, 5.5 mol%) and dry THF (1.0 mL) were added under N$_2$ atmosphere. The mixture was stirred at room temperature for 30 min, followed by the addition of benzaldehyde $1b$ (0.25 mmol). The reaction mixture was then heated at 135 °C. After being stirred for 24 h, the mixture was purified with silica gel column chromatography (eluent: Hexane only) to afford pure decarbonylation product $2b$ (35% yield).
3. Analytical data of 2

Ethoxybenzene (2a): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (t, $J = 7.2$ Hz, 2H), 6.88–6.95 (m, 3H), 4.03 (q, $J = 7.2$ Hz, 2H), 1.41 (t, $J = 7.2$ Hz, 3H)

Benzyl phenyl ether (2b): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27–7.45 (m, 7H), 6.96–7.00 (m, 3H), 5.07 (s, 3H)
Phenol (2d): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (t, $J = 8.4$ Hz, 2H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 2H), 4.73 (s, 1H)

Aniline (2e): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (t, $J = 7.6$ Hz, 2H), 6.76 (t, $J = 7.6$ Hz, 1H), 6.69 (d, $J = 7.6$ Hz, 2H), 3.63 (br s, 1H)
**Methyl benzoate (2f):** $^1$H NMR (400 MHz, CDCl₃) δ 8.04 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 2H), 3.92 (s, 3H)

**Acetanilide (2g):** $^1$H NMR (400 MHz, CDCl₃) δ 7.50 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 2.17 (s, 3H)
N,N’-dimethylbenzamide (2h): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39–7.42 (m, 5H), 3.12 (s, 3H), 2.98 (s, 3H)

N,N’-diethylbenzamide (2i): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36–7.40 (m, 5H), 3.55 (br s, 2H), 3.26 (br s, 2H), 1.25 (br s, 3H), 1.11 (br s, 3H)
Acetophenone (2j): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (dd, $J$=8.4, 1.6 Hz, 2H), 7.58 (tt, $J$=7.6, 1.6 Hz, 1H), 7.47 (t, $J$=7.6 Hz, 2H), 2.62 (s, 3H)

2,3,5-Trimethylanisole (2n): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.61 (s, 1H), 6.54 (s, 1H), 3.80 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H), 2.10 (s, 3H)
Ethylbenzene (2o): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16–7.30 (m, 5H), 2.65 (q, $J$ = 7.2 Hz, 2H), 1.24 (t, $J$ = 7.6 Hz, 3H)

Nonane (2p): $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 1.24–1.33 (m, 14H), 0.88 (t, $J$ = 6.9 Hz, 6H)
4. General procedure and data for the cationic Ir-catalyzed asymmetric hydroacylation

To an oven-dried 2-neck flask with condenser, [Ir(cod)]_2(BArF_4) (0.0125 mmol, 5 mol%) and \((R)-xyl-BINAP\) (0.0138 mmol, 5.5 mol%) and dry THF (1.0 mL) were added under N_2 atmosphere. The solution was stirred at room temperature for 30 min, followed by the addition of benzaldehyde 1a (0.25 mmol). The reaction mixture was then heated at 90 °C. After being stirred for 48 h, lactone (3) was confirmed by \(^1\)H-NMR\(^{[2]}\) and conversion was determined by \(^1\)H-NMR integration comparing to substrate peak.

3-methylisobenzofuran-1(3H)-one (3): \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 7.91 (d, \(J = 7.6\) Hz, 1H), 7.68 (td, \(J = 7.6, 1.2\) Hz, 1H), 7.53 (t, \(J = 7.6\) Hz, 1H), 7.44 (dd, \(J = 8.0, 1.2\) Hz, 1H), 5.57 (q, \(J = 6.8\) Hz, 1H), 1.65 (d, \(J = 6.4\) Hz, 1H)

NMR spectrum of the compound 3 showed good agreement with the literature data.\(^{[2]}\)


\(^1\)H-NMR spectra of 3
Chiral GC analysis of 3: 70% ee, column; RESTEK Rt- β DEXsa, injector temp.; 220 °C, detector temp.; 220 °C, column temp.; 80-220 °C (10 °C/min)

<table>
<thead>
<tr>
<th>Peak #</th>
<th>tR [min]</th>
<th>Area [μV·sec]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.126</td>
<td>1862598</td>
<td>49.80</td>
</tr>
<tr>
<td>2</td>
<td>18.468</td>
<td>1878253</td>
<td>50.20</td>
</tr>
</tbody>
</table>

Peak #1 peak#2

<table>
<thead>
<tr>
<th>Peak #</th>
<th>tR [min]</th>
<th>Area [μV·sec]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.091</td>
<td>157325</td>
<td>14.99</td>
</tr>
<tr>
<td>2</td>
<td>18.474</td>
<td>891898</td>
<td>85.01</td>
</tr>
</tbody>
</table>

Peak #1 peak#2