Supporting Information

Palladium-Catalyzed Reduction of Acid Chlorides to Aldehydes with Hydrosilanes

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Contents

1. Instrumentation and Chemicals S2
2. Preparation of Acid Chlorides S3
3. Experimental Procedures S4
4. Characterization of the Compounds S5
5. NMR Charts S8
6. References S10
1. Instrumentation and Chemicals

All solvents such as toluene were dried and purified by usual procedures. The materials which obtained from commercial suppliers were used without further purification. \(^1\) \(^\text{H}\) and \(^{13}\text{C}\) NMR spectra were measured with a JEOL ECX-400P spectrometer. The \(^1\text{H}\) NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The \(^{13}\text{C}\) NMR chemical shifts are reported relative to CDCl\(_3\) (77.0 ppm). GC analysis was carried out using a Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-1, 0.25 mm i.d. \(\times\) 25 m). Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63-210 \(\mu\)m). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Silica gel 60F254. Pd(dba)\(_2\) was prepared according to the literature. \(^2\) Triethylsilane was purchased from Shin-Etsu Chemical Co., Ltd. Others hydrosilanes were provided by Tokyo Chemical Industry Co., Ltd. (TCI). Phosphines including P(Mes)\(_3\) were purchased from Sigma-Aldrich. Acid chlorides 1a, 1q, 1r and 1u were purchased from Sigma-Aldrich, and 1c, 1d, 1f, 1g, 1o, 1s and 1t were purchased from TCI.

2. Preparation of Acid Chlorides

Acid chlorides 1b, 1c, 1h, 1i, 1j, 1k, 1l, 1p, 1v and 1w were prepared according to the following method: In a two-necked flask, carboxylic acid (5.0 mmol), SOCl\(_2\) (5.0 mL) and diethyl ether were added. The reaction mixture was stirred at room temperature overnight. After the reaction, an excess amount of SOCl\(_2\) and diethyl ether was carefully removed under vacuum. The desired acid chloride was obtained by vacuum distillation. 1m and 1n were also prepared by the reaction of the corresponding carboxylic acid with oxalyl chloride as a chlorination reagent.

**n-Docosanoyl chloride (1b):**

\[
\begin{align*}
\text{C}_{21}\text{H}_{43} & \quad \text{Cl} \\
\end{align*}
\]

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.88 (t, \(J = 7.40\) Hz, 2H), 1.74-1.67(m, 2H), 1.25 (s, 36H), 0.88 (t, \(J = 6.80\) Hz, 3H).

**3-(4-Methylphenyl)propionyl chloride (1h):**

\[
\begin{align*}
\text{Me} & \quad \text{Cl} \\
\end{align*}
\]

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.09 (d, \(J = 7.60\) Hz, 2H), 7.049 (d, \(J = 8.00\) Hz, 2H), 3.13 (t, \(J = 7.60\) Hz, 2H), 2.93 (t, \(J = 7.60\) Hz, 2H), 2.30 (s, 3H).

**3-(4-Methoxyphenyl)propionyl chloride (1i):**

\[
\begin{align*}
\text{MeO} & \quad \text{Cl} \\
\end{align*}
\]

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.08 (d, \(J = 6.80\) Hz, 2H), 6.82 (dt, \(J = 8.80, 1.60\) Hz, 2H), 3.74 (s, 3H), 3.12 (t, \(J = 7.60\) Hz, 2H), 2.90 (t, \(J = 7.60\) Hz, 2H).
3-(4-Methoxyphenyl)propionyl chloride (1k):\(^8\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.57 (d, J = 8.00 Hz, 2H), 7.03 (d, J = 8.00 Hz, 2H), 3.23 (t, J = 7.20 Hz, 2H), 3.06 (t, J = 7.20 Hz, 2H).

3-(3-Fluorophenyl)propionyl chloride (1l):\(^8\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.29-7.23 (m, 1H), 6.97 (d, J = 7.60 Hz, 1H), 6.94-6.88 (m, 2H), 3.19 (t, J = 7.60 Hz, 2H), 2.99 (t, J = 7.60 Hz, 2H).

6-Oxo-6-phenylhexanoyl chloride (1n):\(^13\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.97-7.94 (m, 2H), 7.60-7.55 (m, 1H), 7.49-7.45 (m, 2H), 3.04-2.95 (m, 4H), 1.86-1.76 (m, 4H).

(1-Naphthyl)acetyl chloride (1p):\(^9\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.83-7.31 (m, 7H), 4.45 (s, 2H).

2-Tridecenoyl chloride (1w):\(^11\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.27-7.19 (m, 1H), 6.06 (dt, J = 15.2, 1.2 Hz, 1H), 2.29 (dq, J = 7.20, 2.00 Hz, 2H), 1.54-1.46 (m, 2H), 1.34-1.27 (m, 14H), 0.88 (t, J = 7.00 Hz, 3H).
3. Experimental Procedure

3.1. General procedure of Table 1 and Table S1

Pd precursor (0.0125 mmol) and ligand (0.025 mmol) were added to a 10 mL Schlenk flask with a magnetic stir bar. The flask was evacuated and backfilled with argon three times. Then, solvent (1.0 mL) was added to the flask and the resultant solution was stirred at room temperature for 10 min. Hydrosilane (0.55 mmol) and 3-phenylpropionyl chloride ($1a$) (74 μL, 0.50 mmol) were added to the flask in this order and the reaction mixture was stirred at 40 °C for 1.5 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with diethyl ester (5.0 mL) and tetradecane (50 μL, 0.19 mmol) as an internal standard was added. The yield of 3-phenylpropanal ($2a$) was analyzed by gas chromatography.

Table S1. Effect of Pd precursors and solvents on the palladium-catalyzed reduction of 3-phenylproponyl chloride ($1a$)

<table>
<thead>
<tr>
<th>entry</th>
<th>Pd-precursor</th>
<th>solvent</th>
<th>yield of $2a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(dba)$_2$</td>
<td>toluene</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)$_2$</td>
<td>toluene</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>PdCl$_2$(PhCN)$_2$</td>
<td>toluene</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>Pd(dba)$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>Pd(dba)$_2$</td>
<td>THF</td>
<td>62</td>
</tr>
</tbody>
</table>

"Reaction conditions: 3-Phenylpropionyl chloride ($1a$, 0.50 mmol), Pd-precursors (0.0125 mmol, 2.5 mol %), P(Mes)$_3$ (0.025 mmol, 5.0 mol %), HSIEt$_3$ (0.55 mmol), in solvent (1.0 mL), at 40 °C for 1.5 h. Analyzed by GC analysis.

3.2. General procedure of Table 2 and Table 3

Pd(dba)$_2$ (7.2 mg, 0.0125 mmol) and P(Mes)$_3$ (9.7 mg, 0.025 mmol) were added to a 10 mL Schlenk flask with a magnetic stir bar. The flask was evacuated and backfilled with argon three times. Then, toluene (1.0 mL) was added to the flask and the resultant solution was stirred at room temperature for 10 min. HSIEt$_3$ (88 μL, 0.55 mmol) and $1$ (0.50 mmol) were added to the flask in this order and the reaction mixture was stirred at 40 °C for 1.5 h under an argon atmosphere. After cooling to room temperature, all volatiles were removed in vacuo and $2$ was isolated by silica gel column chromatography (Hexane : EtOAc = 13 : 1).
4. Characterization of the Compounds

The compounds 2f, 2g, 2o, and 2r were characterized by GC analysis.

3-Phenylpropanal (2a):\textsuperscript{14} Pale yellow oil (51.6 mg, 77%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.82 (s, 1H), 7.29 (t, \textit{J} = 7.60 Hz, 2H), 7.21 (t, \textit{J} = 8.00 Hz, 3H), 2.96 (t, \textit{J} = 8.00 Hz, 2H), 2.78 (t, \textit{J} = 7.60 Hz, 2H).

n-Docosanal (2b):\textsuperscript{15} Pale yellow solid (145.4 mg, 90%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.77 (t, \textit{J} = 1.80 Hz, 1H), 2.42 (t, \textit{J} = 8.00 Hz, 2H), 1.66-1.56 (m, 2H), 1.30-1.25 (m, 36H), 0.88 (t, \textit{J} = 6.80 Hz, 3H).

n-Tetradecanal (2c):\textsuperscript{16} White solid (72.6 mg, 68%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.76 (t, \textit{J} = 1.40 Hz, 1H), 2.42 (td, \textit{J} = 7.60, 2.00 Hz, 2H), 1.66-1.59 (m, 2H), 1.34-1.23 (m, 20H), 0.88 (t, \textit{J} = 6.80 Hz, 3H).

4-Phenylbutanal (2e):\textsuperscript{17} Yellow oil (55.0 mg, 74%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.75 (t, \textit{J} = 1.60 Hz, 1H), 7.28 (ddd, \textit{J} = 7.60, 2H), 7.19 (ddd, \textit{J} = 7.20, 3H), 2.66 (t, \textit{J} = 7.8 Hz, 2H), 2.44 (td, \textit{J} = 7.20, 1.20 Hz, 2H), 1.96 (t, \textit{J} = 7.20, 2H).

3-(4-Methylphenyl)propanal (2h):\textsuperscript{18} Pale yellow oil (53.6 mg, 72%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.81 (t, \textit{J} = 1.40 Hz, 1H), 7.12-7.07 (m, 4H), 2.92 (t, \textit{J} = 7.60 Hz, 2H), 2.76 (t, \textit{J} = 8.40 Hz, 2H), 2.32 (s, 3H).

3-(4-Methoxyphenyl)propanal (2i):\textsuperscript{18} Pale yellow oil (57.3 mg, 70%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.81 (t, \textit{J} = 1.60 Hz, 1H), 7.11 (dt, \textit{J} = 9.20, 2.80 Hz, 2H), 6.83 (dt, \textit{J} = 8.80, 3.20 Hz, 2H), 3.79 (s, 3H), 2.91 (t, \textit{J} = 7.60 Hz, 2H), 2.75 (t, \textit{J} = 7.80 Hz, 2H).

3-(4-Chlorophenyl)propanaldehyde (2j):\textsuperscript{18} Pale yellow oil (63.6 mg, 76%), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 9.80 (m, 1H), 7.25 (d, \textit{J} = 8.40 Hz, 2H), 7.12 (d, \textit{J} = 8.80 Hz, 2H), 2.92 (t, \textit{J} = 7.60 Hz, 2H),
2.78-2.74 (m, 2H).

3-(4-(Trifluoromethyl)phenyl)propanal (2k):\(^{19}\)

![3-(4-(Trifluoromethyl)phenyl)propanal](image)

Pale yellow oil (80.3 mg, 79%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.82-9.81 (m, 1H), 7.54 (d, \(J = 8.00\) Hz, 2H), 7.31 (d, \(J = 8.40\) Hz, 2H), 3.01 (d, \(J = 7.40\) Hz, 2H), 2.81 (d, \(J = 7.60\) Hz, 2H).

3-(3-Fluorophenyl) propanal (2l):\(^{20}\)

![3-(3-Fluorophenyl) propanal](image)

Pale yellow oil (58.4 mg, 77%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.81 (t, \(J = 1.40\) Hz, 1H), 7.27-7.22 (m, 1H), 6.97 (d, \(J = 7.60\) Hz, 1H), 6.91-6.88 (m, 2H), 2.95 (t, \(J = 7.40\) Hz, 2H), 2.80-2.76 (m, 2H).

Methyl 10-oxo-decanoate (2m):\(^{21}\)

![Methyl 10-oxo-decanoate](image)

Colorless oil (73.1 mg, 73%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.77-9.75 (m, 1H), 3.67 (d, \(J = 1.20\) Hz, 3H), 2.42 (tt, \(J = 7.20, 1.60\) Hz, 2H), 2.30 (td, \(J = 8.00, 1.60\) Hz, 2H), 1.64-1.60 (m, 4H), 1.31 (s, 8H).

6-Oxo-6-phenylhexanal (2n):\(^{22}\)

![6-Oxo-6-phenylhexanal](image)

White solid (80.9 mg, 85%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.79 (t, \(J = 1.60\) Hz, 1H), 7.97-7.94 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 3.01 (t, \(J = 7.70\) Hz, 2H), 2.51 (td, \(J = 7.20, 1.20\) Hz, 2H), 1.84-1.71 (m, 4H).

1-Naphthylacetaldehyde (2p):\(^{23}\)

![1-Naphthylacetaldehyde](image)

Yellow oil (70.3 mg, 83%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 9.75 (t, \(J = 2.40\), Hz, 1H), 7.89-7.81 (m, 3H), 7.55-7.37 (m, 4H), 4.07 (d, \(J = 2.80\), Hz,2H).

2-Naphthaldehyde (2q):\(^{24}\)

![2-Naphthaldehyde](image)

White solid (65.9 mg, 84%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.17 (s, 1H), 8.35 (s, 1H), 8.03-7.91 (m, 4H), 7.67-7.58 (m, 2H).

4-Methoxybenzaldehyde (2s):\(^{24}\)

![4-Methoxybenzaldehyde](image)

Pale yellow oil (49.6 mg, 73%), \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.89 (s, 1H), 7.85-7.83 (d, \(J = 8.80\) Hz, 2H), 7.01 (d, \(J = 8.80\) Hz, 2H), 3.90 (d, \(J = 2.00\) Hz, 3H).
4-Chlorobenzaldehyde (2t):  
White solid (53.0 mg, 73%), $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.99 (s, 1H), 7.85-7.82 (m, 2H), 7.54-7.51 (m, 2H).

Cinnamaldehyde (2u):  
Pale yellow oil (56.8 mg, 86%), $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 9.71 (d, $J = 8.00$ Hz, 1H), 7.59-7.55 (m, 2H), 7.50-7.41 (m, 4H), 6.73 (dd, $J = 16.00$, 8.00 Hz, 1H).

4-Chlorocinnamaldehyde (2v):  
Pale yellow solid (63.3 mg, 76%), $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.71 (d, $J = 7.60$ Hz, 1H), 7.51 (d, $J = 8.80$ Hz, 2H), 7.46-7.41 (m, 3H), 6.69 (dd, $J = 16.04$, 7.80 Hz, 1H).

2-Tridecenal (2w):  
Pale yellow oil (69.6 mg, 71%), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.51 (d, $J = 8.40$ Hz, 1H), 6.90-6.82 (m, 1H), 6.15-6.09 (m, 1H), 2.34 (dq, $J = 8.80$, 1.60 Hz, 2H), 1.55-1.47 (m, 2H), 1.31-1.27 (m, 14H), 0.88 (t, $J = 7.2$ Hz, 3H).

$n$-Docosanal-d$_1$ (3b):  
Pale yellow solid (149.8 mg, 92%, (99% D)), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.42 (t, $J = 7.20$ Hz, 2H), 1.66-1.55 (m, 2H), 1.34-1.21 (m, 36H), 0.88 (t, $J = 6.80$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.7 ($J_{C-D} = 30.7$ Hz), 43.7, 31.9, 29.7, 29.6, 29.4, 29.2, 22.7, 22.0, 14.1. HR-MS for C$_{22}$H$_{43}$D: 325.3455. Found: 325.3466.

2-Naphthaldehyde-d$_1$ (3q):  
White solid (58.2 mg, 74%, (98% D)), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 (s, 1H), 8.03-7.91 (m, 4H), 7.68-7.57 (m, 2H).

Cinnamaldehyde-d$_1$ (3u):  
Yellow oil (53.2 mg, 80%, (97% D)), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59-7.55 (m, 2H), 7.50-7.41 (m, 4H), 6.73 (d, $J = 16.00$ Hz, 1H).
5. NMR Charts

**Figure S1.** $^1$H NMR spectrum of 3b in CDCl$_3$. 
Figure S2. $^{13}$C NMR spectrum of 3b in CDCl$_3$. 

S9
6. References