ALLYLATION OF N,N-ACETAL DERIVATIVES USING ALLYL TIN REAGENT IN THE PRESENCE OF ALUMINUM CHLORIDE

Xiaonan Sun, Takanori Obu, Tatsuro Kijima, Satoshi Murakami, Shigeru Matsuba, Miho Kusakari, and Bunpei Hatano*

Department of Biochemical Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan
E-mail: hatano@yz.yamagata-u.ac.jp

Abstract – Allylation of N,N-acetal derivatives proceeded efficiently using allyl tin reagent in the presence of aluminum chloride, giving homoallylamines in good yields. This allylation was applied for N,S-acetals to give the corresponding homoallylamines.

The addition of carbonyl compound using organometallic reagents is one of the fundamental reactions for carbon–carbon bond formation, and a large number of organometallic reagents have been developed. Among them, tin reagent has some advantages in the stability on handling and storage as well as in its preparation. Especially, allyl tin reagents are useful for the formation of homoallyl compounds, which are frequently transformed to the functionalized organic compounds such as β-hydroxyl carbonyl compounds and β-amino acids, because they have moderate reactivity with carbonyl compounds than other allyl reagents in the presence of Lewis acid. In our previous reports, we revealed that Barbier- and Reformatsky-type reaction of N,N-acetal derivatives with allyl bromides and α-bromoacetates proceeded smoothly in the presence of zinc metal and trimethylsilyl chloride, giving the corresponding homoallylamines and β-amino esteres in good yields. Especially, our developed method has some advantages in the synthesis of antispasmodic agent bearing heterocyclic system such as butaverine. During the course of our study, we found that allyl tin reagents are effective for the allylation of N,N-acetal derivatives in the presence of AlCl₃.

At first, we examined the allylation of N,N-acetal bearing heterocyclic piperidine (1a) with allylttributyltin (2a) in presence or absence of Lewis acid, as shown in Equation 1 and Table 1. When the reaction of 1a with 1.1 equivalents of 2a in refluxing 1,2-dichloroethane was conducted overnight, the desired homoallylamine 3aa was not observed at all (entry 1). The use of AlCl₃ led to the formation of 3aa, and the best result was achieved using 0.5 equivalents of AlCl₃ against the amount of 1a to give the corresponding homoallylamine 3aa in 77% yield (entries 2–5). While any attempts using the
allyltrimethylsilane only led to disappointing results (entry 6). Other Lewis acids, such as TiCl₄, ZnCl₂, and TMSCl, were also employed in this allylation, giving 3aa in moderate to good yields (entries 7–9).

\[
\begin{align*}
\text{Ph} & \quad \text{N} \\
\text{N} & \quad \text{ClCH}_2\text{CH}_2\text{Cl} \\
\text{reflux} & \quad \text{overnight} \\
\text{Ph} & \quad \text{N}
\end{align*}
\]

Equation 1

**Table 1.** Influence of Lewis acid on the allylation of 1a

<table>
<thead>
<tr>
<th>entry</th>
<th>Lewis acid</th>
<th>yield of 3aa⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>AlCl₃ (3.0 eq)</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>AlCl₃ (1.5 eq)</td>
<td>64</td>
</tr>
<tr>
<td>4</td>
<td>AlCl₃ (1.0 eq)</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>AlCl₃ (0.5 eq)</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>AlCl₃ (0.5 eq)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>TiCl₄ (0.5 eq)</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>ZnCl₂ (0.5 eq)</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>TMSCl (0.5 eq)</td>
<td>76</td>
</tr>
</tbody>
</table>

⁹ Reaction conditions: 1a (2.0 mmol), 2a (2.2 mmol), CH₂ClCH₂Cl (5 mL), reflux, overnight, under N₂.  
⁹⁹ Isolated yield.  ⁹ Allylsilane was used instead of 2a.

The allylation using AlCl₃ was useful for other aromatic N,N-acetal derivatives 1 and allyl tin reagents 2 as shown in Equation 2 and Table 2. The allylation of p-methoxy, p-methyl, p-chloro, and p-cyano derivatives (1b, 1c, 1d, and 1e) proceeded smoothly to give the corresponding homoallylamines (3ba, 3ca, 3da and 3ea) in moderate to good yields (entries 1–4). The substituted group of nitrogen did not affect in this allylation at all. The substituent bearing pyrrolidine also reacted with 2a, giving the corresponding homoallylamine 3fa (entry 5). Although the homoallylamine bearing N,N-dimethyl group 3ga was unstable to silica gel chromatography, the reaction proceeded smoothly to give 3ga after Kugelrohr distillation (entry 6). This allylation is also applicable to some allyl tin reagents. Allylation of 1a with 2b in the present of AlCl₃ proceeded smoothly, giving the corresponding homoallylamine 3ab in good yield (entry 7), while the allylation with 2c and 2d did not proceed at all (entries 8 and 9). Crotyl tin 2e was also used in this allylation, although the stereoselectivity of the homoallylamine (3ae) did not observed (entries 10 and 11).

\[
\begin{align*}
\text{Ar} & \quad \text{N} \\
\text{R} & \quad \text{N} \\
\text{R} & \quad \text{R} \\
\text{Ar} & \quad \text{N} \\
\text{R} & \quad \text{R} \\
\text{SnBu₃} & \quad \text{AlCl₃} \\
\text{ClCH}_2\text{CH}_2\text{Cl} & \quad \text{reflux} \\
\text{overnight} & \quad \text{overnight} \\
\text{Ar} & \quad \text{N} \\
\text{R} & \quad \text{N} \\
\text{R} & \quad \text{R}
\end{align*}
\]

Equation 2
Table 2  The allylation of $N,N$-acetal 1 with allyl tin 2 in the presence of aluminum chloride $^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>yield of 3 $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{MeO}^-$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{MeO}^-$</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Cl}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Cl}$</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>75 $^c$</td>
</tr>
<tr>
<td>7</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>63 $^{\text{syn/anti}=65:35^d}$</td>
</tr>
<tr>
<td>11</td>
<td>$\text{Me}$</td>
<td>$\text{SnBu}_3$</td>
<td>$\text{Me}$</td>
<td>51 $^{\text{syn/anti}=57:43^d}$</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 1 (2.0 mmol), 2 (2.2 mmol), AlCl$_3$ (1.0 mmol), ClCH$_2$CH$_2$Cl (5 mL), reflux, overnight, under N$_2$.  
$^b$ Isolated yield. $^c$ The product (3ga) was purified by Kugelrohr distillation. 
$^d$ Determined by $^1$H NMR of crude 3ae.
Allylation using allyl tin reagent 2a was also applied for N,S-acetal 1h derived from benzaldehyde, giving 3ha in 74% yield after work up in acidic conditions (Equation 3).\textsuperscript{11,12} In the case of aliphatic N,S-acetal 1i, the allylation product 3ia was obtained in low yield (37% yield) (Equation 4).

\begin{equation}
\text{Ph} \text{NHBoc} \begin{array}{c}
\text{SO} \\
\text{O}
\end{array} \text{Ph} + \begin{array}{c}
\text{SnBu}_3 \\
\text{ClCH}_2\text{CH}_2\text{Cl}
\end{array} \xrightarrow{\text{AlCl}_3, \text{reflux overnight}} \begin{array}{c}
\text{NH}_2 \\
\text{Ph}
\end{array} \quad (3)
\end{equation}

\text{74\% yield}

\begin{equation}
\text{n-Pr} \text{NHCbz} \begin{array}{c}
\text{SO} \\
\text{O}
\end{array} \text{Ph} + \begin{array}{c}
\text{SnBu}_3 \\
\text{ClCH}_2\text{CH}_2\text{Cl}
\end{array} \xrightarrow{\text{AlCl}_3, \text{reflux overnight}} \begin{array}{c}
\text{HCbz} \\
n-\text{Pr}
\end{array} \quad (4)
\end{equation}

\text{37\% yield}

Equation 3 and 4

A plausible reaction pathway for allylation of 1 with allyl tin reagents 2 is illustrated in Figure 1. At first, \textit{N,N}-acetal 1 might be activated with \textit{AlCl}_3, generating an iminium intermediate 4. Then, the iminium intermediate 4 reacted with allyltributyltin reagents 2 to give the homoallylamines 3.\textsuperscript{13}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Figure 1}
\end{figure}

In summary, the allylation of \textit{N,N}- and \textit{N,S}-acetal derivatives efficiently reacted with allyltributyltin reagents in the presence of aluminum chloride, giving the corresponding homoallylamines in moderate to good yields. Further detailed applications are now in progress.

**EXPERIMENTAL**

\textsuperscript{1}H NMR spectra were recorded on a Varian or JEOL 500 MHz spectrometers and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl\textsubscript{3}. \textsuperscript{13}C NMR spectra were obtained at 125 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl\textsubscript{3}). TLC was performed on aluminum sheets coated with silica gel 60 F\textsubscript{254} (Merck). Visualization on TLC was achieved by use of UV light (254 nm) and treatment with anisaldehyde or
phosphomolybdic acid stain followed by heating. Column chromatography was performed on silica gel (63–210 μm). 1,2-Dichloroethane was freshly distilled under nitrogen over P2O5 before use. The substrates, N,N-acetal derivatives (1a–1g), were prepared according to our previous report. The substrates, N,S-acetal derivatives (1h and 1i), were prepared according to the literature. The allyl tin reagents (2a–2c, and 2e (E/Z = 1/1)) were prepared by the reaction of n-Bu3SnCl with the corresponding Grignard reagents in usual procedure. The allyl tin reagent bearing amide group (2d) was prepared according to the literature. Crotly tin (2e, E/Z = 95/5) was prepared by the stereoselective hydrostannylation of 1,3-butadiene in the presence of a catalytic amount of Pd(PPh3)4. All allyl tin compounds (2) were purified by column chromatography on the 10% w/w anhydrous K2CO3–silica to remove byproduct such as unreacted n-Bu3SnCl (eluent, hexane). Other reagents are of commercial quality. All reactions were carried out under nitrogen atmosphere in well-dried glassware.

**Typical Procedure for the Allylation of N,N-Acetal Derivatives (1) Using Allyl Tin Reagents (2) in the Presence of AlCl3.** To a solution of AlCl3 (134 mg, 1.0 mmol) in 1,2-dichloroethane (5 mL) was added N,N-acetal derivative 1 (2.0 mmol) at 0 °C. After stirring for 30 min at 0 °C, allyl tin compound 2 (2.2 mmol) was added to mixture at the same temperature. Then, the reaction mixture was allowed to warm to room temperature, stirred for 1 h, and then heated to reflux. After stirring overnight at reflux, the mixture was cooled to room temperature. After 1N HCl (30 mL) was added to the mixture with stirring for 30 min, the resulting suspension was extracted with Et2O (50 mL) to remove tributyltin chloride. The obtained aqueous layer was basified with 3N NaOH (20 mL) until pH > 14. The aqueous layer was extracted with Et2O (30 mL × 3). The combined ethereal solution was washed with brine (30 mL) and dried over Na2SO4. After evaporation, the almost pure homoallylamine 3 was obtained, and the purification of 3 was carried out by column chromatography on silica gel (eluent, CH2Cl2/MeOH = 100:0, 98:2, 96:4, 94:6, 92:8, 90:10, 100 mL × each).

**4-Phenyl-4-piperidino-1-butene (3aa):** (Reg. No. = 35278-83-2); colorless oil; 1H NMR: δ 7.31 (dd, 2H, J = 6.8, 6.8 Hz), 7.26–7.24 (m, 1H), 7.23 (d, 2H, J = 6.8 Hz), 5.61 (dddd, 1H, J = 17.1, 10.1, 7.6, 6.3 Hz), 4.97 (dd, 1H, J = 17.1, 2.3 Hz), 4.89 (dd, 1H, J = 10.1, 2.3 Hz), 3.43 (dd, 1H, J = 9.4, 5.4 Hz), 2.70 (ddd, 1H, J = 13.5, 6.3, 5.4 Hz), 2.60 (dd, 1H, J = 13.5, 9.4, 7.6 Hz), 2.50–2.30 (m, 4H), 1.61–1.52 (m, 4H), 1.36 (ddd, 2H, J = 11.9, 5.8, 5.8 Hz); 13C NMR: δ 139.8, 135.9, 128.9, 127.9, 127.0, 116.2, 70.3, 51.2, 37.0, 26.1, 24.5.

**4-(4-Methoxyphenyl)-4-piperidino-1-butene (3ba):** (Reg. No. = 1082512-33-1); light yellow oil; 1H NMR: δ 7.13 (d, 2H, J = 8.5 Hz), 6.85 (d, 2H, J = 8.5 Hz), 5.61 (dddd, 1H, J = 17.1, 10.2, 7.2, 6.3 Hz), 4.96 (dd, 1H, J = 17.1, 2.5 Hz), 4.89 (dd, 1H, J = 10.2, 2.5 Hz), 3.80 (s, 3H), 3.40 (dd, 1H, J = 9.1, 5.3 Hz), 2.68 (ddd, 1H, J = 13.5, 6.3, 5.3 Hz), 2.58 (ddd, 1H, J = 13.5, 9.1, 7.2 Hz), 2.45–2.30 (m, 4H),
1.60–1.51 (m, 4H), 1.34 (ddd, 2H, $J = 12.0, 6.0, 6.0$ Hz); $^{13}$C NMR: $\delta$ 158.5, 136.1, 131.7, 129.8, 116.1, 113.1, 69.5, 55.1, 51.1, 37.0, 26.1, 24.6.

4-(Methylphenyl)-4-piperidino-1-butene (3ca): (Reg. No. = 35278-89-8); light yellow oil; $^1$H NMR: $\delta$ 7.13 (d, 2H, $J = 8.5$ Hz), 7.10 (d, 2H, $J = 8.5$ Hz), 5.61 (ddddd, 1H, $J = 17.0, 10.2, 7.3, 6.6$ Hz), 4.97 (dd, 1H, $J = 17.0, 2.3$ Hz), 4.89 (dd, 1H, $J = 10.2, 2.3$ Hz), 3.41 (dd, 1H, $J = 9.6, 5.1$ Hz), 2.69 (dd, 1H, $J = 14.0, 6.6, 5.1$ Hz), 2.60 (ddd, 1H, $J = 14.0, 9.6, 7.3$ Hz), 2.45–2.35 (m, 4H), 2.33 (s, 3H), 1.65–1.48 (m, 4H), 1.35 (ddd, 2H, $J = 12.0, 6.2, 6.2$ Hz); $^{13}$C NMR: $\delta$ 136.5, 136.3, 136.0, 128.8, 128.6, 116.1, 69.9, 51.1, 36.9, 26.1, 24.5, 21.1.

4-(Chlorophenyl)-4-piperidino-1-butene (3da): (Reg. No. = 1082512-34-2); light yellow oil; $^1$H NMR: $\delta$ 7.28 (d, 2H, $J = 8.5$ Hz), 7.16 (d, 2H, $J = 8.5$ Hz), 5.58 (dddd, 1H, $J = 17.0, 10.2, 7.6, 6.4$ Hz), 4.95 (dd, 1H, $J = 17.0, 2.3$ Hz), 4.90 (dd, 1H, $J = 10.2, 2.3$ Hz), 3.39 (dd, 1H, $J = 9.4, 5.1$ Hz), 2.66 (ddd, 1H, $J = 13.5, 6.4, 5.1$ Hz), 2.54 (ddd, 1H, $J = 13.5, 9.4, 7.6$ Hz), 2.45–2.30 (m, 4H), 1.60–1.50 (m, 4H), 1.36 (ddd, 2H, $J = 12.0, 5.8, 5.8$ Hz); $^{13}$C NMR: $\delta$ 138.6, 135.5, 132.6, 130.1, 128.0, 116.6, 69.6, 51.2, 36.9, 26.1, 24.5.

4-(Cyanophenyl)-4-piperidino-1-butene (3ea): (Reg. No. = 1082512-35-3); light yellow oil; $^1$H NMR: $\delta$ 7.61 (d, 2H, $J = 8.2$ Hz), 7.35 (d, 2H, $J = 8.2$ Hz), 5.57 (dddd, 1H, $J = 17.0, 10.3, 7.3, 6.6$ Hz), 4.95–4.91 (m, 2H), 3.43 (dd, 1H, $J = 9.1, 5.3$ Hz), 2.69 (ddd, 1H, $J = 13.6, 6.6, 5.3$ Hz), 2.60 (ddd, 1H, $J = 13.6, 9.1, 7.3$ Hz), 2.46–2.36 (m, 4H), 1.64–1.47 (m, 4H), 1.35 (ddd, 2H, $J = 12.0, 6.2, 6.2$ Hz); $^{13}$C NMR: $\delta$ 146.5, 134.6, 131.8, 129.3, 118.9, 117.1, 110.6, 69.9, 51.4, 36.7, 26.1, 24.4.

4-Phenyl-4-pyrrolidino-1-butene (3fa): (Reg. No. = 634878-72-1); light yellow oil; $^1$H NMR: $\delta$ 7.30 (d, 4H, $J = 5.2$ Hz), 7.25–7.21 (m, 1H), 5.53 (ddddd, 1H, $J = 17.1, 10.1, 7.1, 6.3$ Hz), 4.93 (dd, 1H, $J = 17.1, 2.3$ Hz), 4.88 (dd, 1H, $J = 10.1, 2.3$ Hz), 3.17 (dd, 1H, $J = 9.6, 5.0$ Hz), 2.72–2.66 (m, 1H), 2.65–2.53 (m, 3H), 2.46–2.35 (m, 2H), 1.80–1.72 (m, 4H); $^{13}$C NMR: $\delta$ 142.3, 135.3, 128.2, 128.0, 126.9, 116.4, 70.9, 52.6, 40.4, 23.2.

4-Dimethylamino-4-phenyl-1-butene (3ga): (Reg. No. = 20599-34-2); colorless oil; $^1$H NMR: $\delta$ 7.31 (d, 2H, $J = 5.2$ Hz), 7.25–7.21 (m, 1H), 5.53 (ddddd, 1H, $J = 17.1, 10.1, 7.1, 6.3$ Hz), 4.93 (dd, 1H, $J = 17.1, 2.3$ Hz), 4.88 (dd, 1H, $J = 10.1, 2.3$ Hz), 3.17 (dd, 1H, $J = 9.6, 5.0$ Hz), 2.72–2.66 (m, 1H), 2.65–2.53 (m, 3H), 2.46–2.35 (m, 2H), 1.80–1.72 (m, 4H); $^{13}$C NMR: $\delta$ 142.3, 135.3, 128.2, 128.0, 126.9, 116.4, 70.9, 52.6, 40.4, 23.2.

4-Amino-4-phenyl-1-butene (3ha): (Reg. No. = 4383-23-7); colorless oil; $^1$H NMR: $\delta$ 7.34–7.31 (m, 4H), 7.26–7.22 (m, 1H), 5.75 (ddddd, 1H, $J = 17.0, 10.3, 7.9, 6.2$ Hz), 5.11 (dd, 1H, $J = 17.0, 2.3$ Hz), 5.09–5.04 (m, 1H), 3.98 (dd, 1H, $J = 8.2, 5.4$ Hz), 2.47 (dd, 1H, $J = 13.5, 6.2, 5.4$ Hz), 2.36 (ddd, 1H, $J = 13.5, 8.2, 7.9$ Hz), 1.71 (s, 2H); $^{13}$C NMR: $\delta$ 145.7, 135.4, 128.4, 126.9, 126.3, 117.6, 55.3, 44.1.

Benzyl hept-1-en-4-ylcarbamate (3ia): (Reg. No. = 646480-70-8); colorless solid; $^1$H NMR: $\delta$
7.37–7.30 (m, 5H), 5.77 (dd, 1H, J = 17.3, 9.6, 7.4, 6.4 Hz), 5.10–5.05 (m, 4H), 4.56 (d, 1H, J = 7.4 Hz), 3.80–3.61 (m, 2H), 2.27 (dd, 1H, J = 14.0, 6.4, 5.1 Hz), 2.19 (dd, 1H, J = 14.0, 8.2, 7.4 Hz), 1.51–1.43 (m, 1H), 1.41–1.34 (m, 3H), 0.91 (t, 1H, J = 6.8 Hz); 13C NMR: δ 156.0, 136.7, 134.2, 128.5, 128.0, 117.8, 66.5, 50.4, 39.4, 36.8, 19.1, 13.9.

2-Methyl-4-phenyl-4-piperidino-1-butene (3ab): (Reg. No. = 1082512-40-0); light yellow oil; ¹H NMR: δ 7.30 (dd, 2H, J = 7.5, 7.5 Hz), 7.25–7.22 (m, 1H), 7.20 (d, 2H, J = 7.5 Hz), 4.63 (s, 1H), 4.56 (s, 1H), 3.61 (dd, 1H, J = 9.6, 5.1 Hz), 2.69 (dd, 1H, J = 13.6, 5.1 Hz), 2.56 (dd, 1H, J = 13.6, 9.6 Hz), 2.45–2.30 (m, 4H), 1.63 (s, 3H), 1.60–1.50 (m, 4H), 1.33 (dd, 2H, J = 12.0, 6.0, 6.0 Hz); 13C NMR: δ 143.2, 139.1, 128.9, 126.9, 112.4, 68.7, 51.0, 40.6, 26.2, 24.5, 22.6.

3-Methyl-4-phenyl-4-piperidino-1-butene (3ae): (Reg. No. = 1082512-41-1); light yellow oil; ¹H NMR: anti-isomer δ 7.32–7.20 (m, 3H), 7.15–7.10 (m, 1H) 5.92 (ddd, 1H, J = 17.3, 10.0, 7.5 Hz), 5.03–4.98 (m, 1H), 2.93–2.16 (m, 4H), 1.62–1.41 (m, 4H), 1.31 (ddd, 2H, J = 12.0, 6.0, 6.0 Hz), 0.80 (d, 3H, J = 6.5 Hz); syn-isomer δ 7.32–7.20 (m, 3H), 7.15–7.10 (m, 1H) 5.63 (ddd, 1H, J = 17.4, 10.4, 7.5 Hz), 4.88–4.82 (m, 2H), 3.13 (d, 1H, J = 9.1 Hz), 2.93–2.81 (m, 1H), 2.43–2.16 (m, 4H), 1.62–1.41 (m, 4H), 1.31 (dd, 2H, J = 12.0, 6.0, 6.0 Hz), 1.09 (d, 3H, J = 6.5 Hz); 13C NMR: δ 145.4, 141.8, 137.6, 137.5, 129.4, 129.2, 127.5, 127.3, 126.7, 127.5, 114.8, 112.4, 75.4, 75.1, 50.9, 38.2, 37.7, 26.4, 24.8, 24.7, 17.8, 17.2.

ACKNOWLEDGEMENTS
The authors acknowledge the financial support of a Grant-in-Aid for Scientific Research (C) (No. 23550187) from the Japan Society for the Promotion of Science (JSPS).

REFERENCES (AND NOTES)
10. The any other regioisomers were not obtained along with homoallylamine 3ae.