HETEROCYCLES, Vol. 87, No. 11, 2013, pp. 2395 - 2402. © 2013 The Japan Institute of Heterocyclic Chemistry
Received, 17th September, 2013, Accepted, 4th October, 2013, Published online, 16th October, 2013
DOI: 10.3987/COM-13-12845

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*

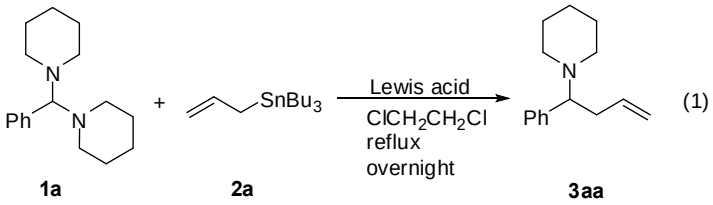
Department of Biochemical Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan
E-mail: hatano@yz.yamagata-u.ac.jp

Abstract – Allylation of *N*,*N*-acetal derivatives proceeded efficiently using allyl tin regent 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.[1] 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.[2–5] 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.[6] Especially, our developed method has some advantages in the synthesis of antispasmodic agent bearing heterocyclic system such as butaverine.[7] 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 $AlCl_3$.[8]

At first, we examined the allylation of *N*,*N*-acetal bearing heterocyclic piperidine (**1a**) with allyltributyltin (**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 $AlCl_3$ led to the formation of **3aa**, and the best result was achieved using 0.5 equivalents of $AlCl_3$ 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).[9] Other Lewis acids, such as $TiCl_4$, $ZnCl_2$, and TMSCl, were also employed in this allylation, giving **3aa** in moderate to good yields (entries 7–9).



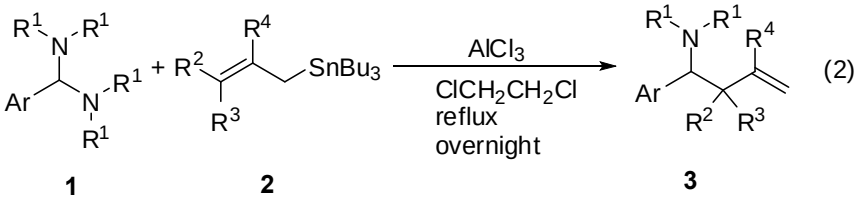
Equation 1

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

entry	Lewis acid		yield of **3aa**[b]
1	—		0
2	$AlCl_3$	(3.0 eq)	7
3	$AlCl_3$	(1.5 eq)	64
4	$AlCl_3$	(1.0 eq)	56
5	$AlCl_3$	(0.5 eq)	77
6	$AlCl_3$	(0.5 eq)	0[c]
7	$TiCl_4$	(0.5 eq)	68
8	$ZnCl_2$	(0.5 eq)	65
9	TMSCl	(0.5 eq)	76

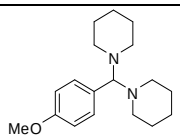
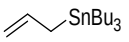
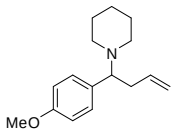
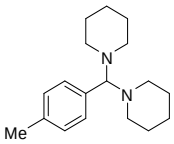
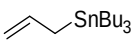
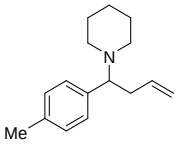
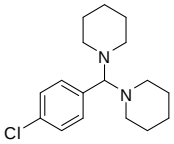
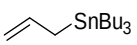
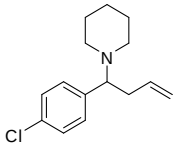
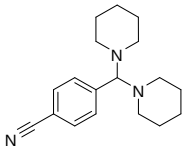
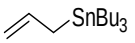
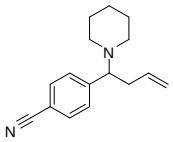
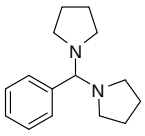
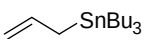
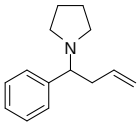
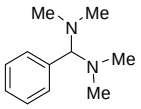
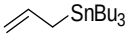
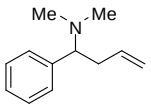
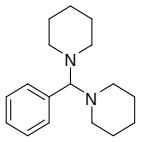
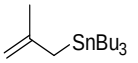
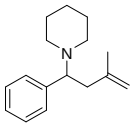
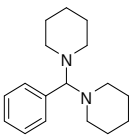
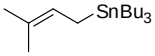
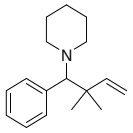
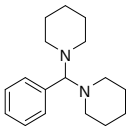
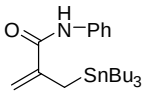
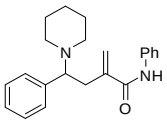
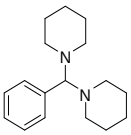
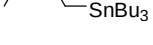
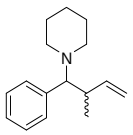
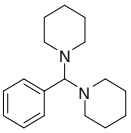
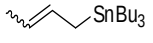
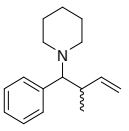
[a] Reaction conditions: **1a** (2.0 mmol), **2a** (2.2 mmol), CH_2ClCH_2Cl (5 mL), reflux, overnight, under N_2. [b] Isolated yield. [c] Allylsilane was used instead of **2a.**

The allylation using $AlCl_3$ 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 $AlCl_3$ 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).[10]



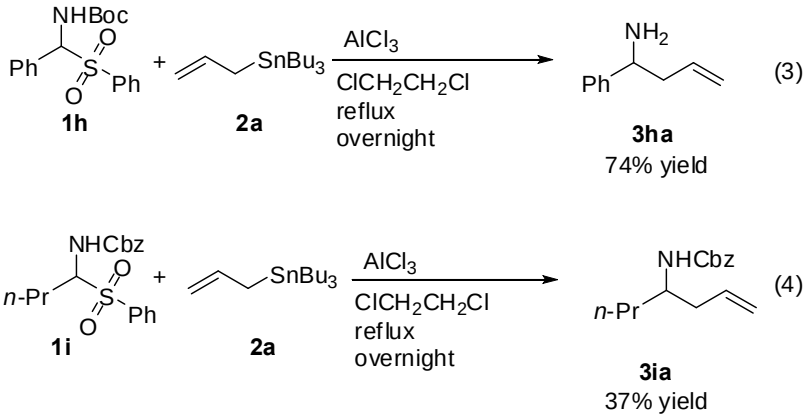
Equation 2

Table 2 The allylation of *N,N*-acetal **1** with allyl tin **2** in the presence of aluminum chloride [a]

entry	1		2		3		yield of **3** [b]
1		**1b**		**2a**		**3ba**	80
2		**1c**		**2a**		**3ca**	84
3		**1d**		**2a**		**3da**	71
4		**1e**		**2a**		**3ea**	82
5		**1f**		**2a**		**3fa**	70
6		**1g**		**2a**		**3ga**	75 [c]
7		**1a**		**2b**		**3ab**	75
8		**1a**		**2c**		**3ac**	0
9		**1a**		**2d**		**3ad**	0
10		**1a**	 *Z* / *E* = 95:5	**2e**		**3ae**	63 *syn* / *anti* = 65:35[d]
11		**1a**	 *Z* / *E* = 1:1	**2e**		**3ae**	51 *syn* / *anti* = 57:43[d]

[a] Reaction conditions: **1** (2.0 mmol), **2** (2.2 mmol), $AlCl_3$ (1.0 mmol), $ClCH_2CH_2Cl$ (5 mL), reflux, overnight, under N_2. [b] Isolated yield. [c] The product (**3ga**) was purified by Kugelrohr distillation. [d] Determined by ^1H 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).[11,12] In the case of aliphatic *N*,*S*-acetal **1i**, the allylation product **3ia** was obtained in low yield (37% yield) (Equation 4).



Equation 3 and 4

A plausible reaction pathway for allylation of **1** with allyl tin reagents **2** is illustrated in Figure 1. At first, *N,N*-acetal **1** might be activated with $AlCl_3$, generating an iminium intermediate **4**. Then, the iminium intermediate **4** reacted with allyltributyltin reagents **2** to give the homoallylamines **3**.[13]

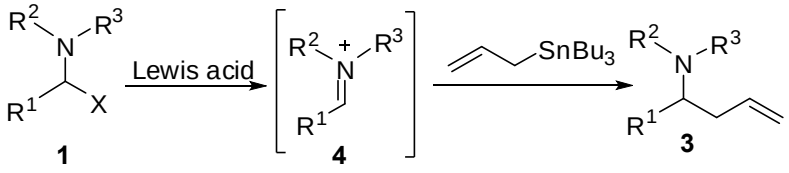


Figure 1

In summary, the allylation of *N,N*- and *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

^{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 $CDCl_3$. ^{13}C NMR spectra were obtained at 125 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). TLC was performed on aluminum sheets coated with silica gel 60 F_{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 P_2O_5 before use. The substrates, *N*,*N*-acetal derivatives (**1a**–**1g**), were prepared according to our previous report.[6] The substrates, *N*,*S*-acetal derivatives (**1h** and **1i**), were prepared according to the literature.[14] The allyl tin reagents (**2a**－**2c**, and **2e** (*E*/*Z* = 1/1)) were prepared by the reaction of *n*-Bu_3SnCl with the corresponding Grignard reagents in usual procedure. The allyl tin reagent bearing amide group (**2d**) was prepared according to the literature.[15] Crotyl tin (**2e**, *E*/*Z* = 95/5) was prepared by the stereoselective hydrostannylation of 1,3-butadiene in the presence of a catalytic amount of $Pd(PPh_3)_4$.[16] All allyl tin compounds (**2**) were purified by column chromatography on the 10% w/w anhydrous K_2CO_3－silica to remove byproduct such as unreacted *n*-Bu_3SnCl (eluent, hexane).[17] 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 $AlCl_3$. To a solution of $AlCl_3$ (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 Et_2O (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 Et_2O (30 mL × 3). The combined ethereal solution was washed with brine (30 mL) and dried over Na_2SO_4. After evaporation, the almost pure homoallylamine **3** was obtained, and the purification of **3** was carried out by column chromatography on silica gel (eluent, CH_2Cl_2/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; ^{1}H 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 (ddd, 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); ^{13}C 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; ^{1}H 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: δ 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-(4-Methylphenyl)-4-piperidino-1-butene (3ca): (Reg. No. = 35278-89-8); light yellow oil; ^{1}H NMR: δ 7.13 (d, 2H, *J* = 8.5 Hz), 7.10 (d, 2H, *J* = 8.5 Hz), 5.61 (dddd, 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 (ddd, 1H, *J* = 14.0, 6.6, 5.1 Hz), 2.60 (ddd, 1H, *J* = 14.0, 9.6, 7.3Hz), 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: δ 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-(4-Chlorophenyl)-4-piperidino-1-butene (3da): (Reg. No. = 1082512-34-2); light yellow oil; ^{1}H NMR: δ 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: δ 138.6, 135.5, 132.6, 130.1, 128.0, 116.6, 69.6, 51.2, 36.9, 26.1, 24.5.

4-(4-Cyanophenyl)-4-piperidino-1-butene (3ea): (Reg. No. = 1082512-35-3); light yellow oil; ^{1}H NMR: δ 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: δ 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: δ 7.30 (d, 4H, *J* = 5.2 Hz), 7.25 – 7.21 (m, 1H), 5.53 (dddd, 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: δ 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: δ 7.31 (dd, 2H, *J* = 7.5, 7.5 Hz), 7.26–7.23 (m, 1H), 7.22 (d, 2H, *J* = 7.5 Hz), 5.61 (dddd, 1H, *J* = 17.1, 10.1, 7.4, 6.5 Hz), 4.95 (dd, 1H, *J* = 17.1, 2.3 Hz), 4.89 (dd, 1H, *J* = 10.1, 2.3 Hz), 3.43 (dd, 1H, *J* = 8.8, 5.4 Hz), 2.65 (ddd, 1H, *J* = 14.0, 6.5, 5.4 Hz), 2.53 (ddd, 1H, *J* = 14.0, 8.8, 7.4 Hz), 2.19 (s, 6H); ^{13}C NMR: δ 137.0, 135.7, 128.6, 127.9, 127.0, 116.4, 70.5, 42.7, 37.8.

4-Amino-4-phenyl-1-butene (3ha): (Reg. No. = 4383-23-7); colorless oil; ^{1}H NMR: δ 7.34–7.31 (m, 4H), 7.26–7.22 (m, 1H), 5.75 (dddd, 1H, *J* = 17.0, 10.3, 7.9, 6.2 Hz), 5.11 (dd, 1H, *J* = 17.0, 2.3 Hz), 5.09–5.06 (m, 1H), 3.98 (dd, 1H, *J* = 8.2, 5.4 Hz), 2.47 (ddd, 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: δ 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: δ

7.37–7.30 (m, 5H), 5.77 (dddd, 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, 1H), 2.27 (ddd, 1H, *J* = 14.0, 6.4, 5.1 Hz), 2.19 (ddd, 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); ^{13}C NMR: δ 156.0, 136.7, 134.2, 128.5, 128.0, 121.3, 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; ^{1}H 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 (ddd, 2H, *J* = 12.0, 6.0, 6.0 Hz); ^{13}C NMR: δ 143.2, 139.1, 128.9, 127.6, 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; ^{1}H 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, 2H), 3.21–3.18 (m, 1H), 2.93–2.81 (m, 1H), 2.43–2.16 (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); ^{13}C NMR: δ 145.4, 141.8, 137.6, 137.5, 129.4, 129.2, 127.5, 127.3, 126.7, 127.6 , 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)

1. For review, see: J. A. Marshall, 'in *Organometallics in Synthesis. A Manual*, 2nd ed.,' ed. by M. Schlosser, Wiley, Chichester, 2002, pp. 353–464.
2. For reviews for allylation to carbonyl compounds, see: (a) Y. Yamamoto, *Acc. Chem., Res.*, 1987, **20**, 243; (b) W. R. Roush, 'in *Comprehensive Organic Synthesis*,' ed. by B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, Vol. 2, pp. 1–53; (c) Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.
3. Recently review for allyl tin reagent, see: (a) I. Fleming, 'in *Comprehensive Organic Synthesis*,' ed. by B. M. Trost and I. Fleming, Pergamon: Oxford, 1991, Vol. 2, pp. 563–593; (b) B. W. Gung, *Org. React.*, 2004, **64**, 1; (c) S. Pratihar and S. Roy, *Organometallics*, 2011, **30**, 3257; (d) See also ref. 1.
4. Recent advancements in the homoallylamine chemistry, see: C. O. Puentes and V. J. Kouznetsov, *J. Heterocycl. Chem.*, 2002, **39**, 595.

5. Review for addition of organometallic reagents to imine, see: R. Bloch, *Chem. Rev.*, 1998, **98**, 1407.
6. B. Hatano, K. Nagahashi, and T. Kijima, *J. Org. Chem.*, 2008, **73**, 9188.
7. (a) C. B. Pollard and G. C. Mattson, *J. Am. Chem. Soc.*, 1956, **78**, 4089; (b) H. Pacheco, M. Dreux, and A. Beauvillain, *Bull. Soc. Chim. Fr.*, 1962, 1379; (c) G. Cerbai and G. F. Di Paco, *Boll. Chim. Farm.*, 1966, **105**, 45.
8. Selected references for nucleophilic addition to *N,N*-acetals, see: (a) R. Tanigaki, N. Konya, and A. Kaji, *Chem. Lett.*, 1985, 1583; (b) E. G. Nolen, A. Allocco, M. Broody, and A. Zuppa, *Tetrahedron Lett.*, 1991, **32**, 73; (c) A. R. Katritzky, N. Shobana, and P. A. Harris, *Tetrahedron Lett.*, 1991, **32**, 4247; (d) X. Wang, J. Li, and Y. Zhang, *Synth. Commun.*, 2003, **33**, 3575; (e) C. Y. K. Tan, D. Wainman, and D. F. Weaver, *Bioorg. Med. Chem.*, 2003, **11**, 113; (f) A. R. Katritzky, K. Manju, S. K. Singh, and N. K. Meher, *Tetrahedron*, 2005, **61**, 2555.
9. Dolbier and coworkers reported that *N,N*-acetals bearing CF_3 group at α-position reacted with allyltrimethylsilane in the presence of ZnI_2, see: Y. Xu and W. R. Dolbier, Jr., *J. Org. Chem.*, 2000, **65**, 2134.
10. The any other regioisomers were not obtained along with homoallylamine **3ae**.
11. Preparation of *N,S*-acetal (**1h** and **1i**), see; A. M. Kanazawa, J.-N. Denis, and A. E. Greene, *J. Org. Chem.*, 1994, **59**, 1238.
12. Review for nucleophilic addition to *N,S*-acetals, see: M. Petrini, *Chem. Rev.*, 2005, **105**, 3949.
13. (a) B. Hatano, K. Nagahashi, and S. Habaue, *Chem. Lett.*, 2007, **36**, 1418; (b) B. Hatano, T. Tachikawa, T. Mori, K. Nagahashi, and T. Kijima, *Tetrahedron Lett.*, 2011, **52**, 3467; (c) See also ref. 4.
14. T. Mecozzi and M. Petrini, *J. Org. Chem.*, 1999, **64**, 8970.
15. K. Tanaka, H. Yoda, Y. Isobe, and A. Kaji, *J. Org. Chem.*, 1986, **51**, 1856.
16. H. Miyake and K. Yamamura, *Chem. Lett.*, 1992, 507.
17. D. C. Harrowven, D. P. Curran, S. L. Kostiuk, I. L. Wallis-Guy, S. Whiting, K. J. Stenning, B. Tang, E. Packard, and L. Nanson, *Chem. Commun.*, 2010, **46**, 6335.