

# Direct construction of quaternary carbon center utilizing an allylsamarium bromide reagent

Zhifang Li<sup>a</sup> and Yongmin Zhang<sup>a,b,\*</sup>

<sup>a</sup>Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou 310028, People's Republic of China

<sup>b</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, People's Republic of China

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**Abstract**—Direct geminal diallylation of lactones, lactams and acyclic amides containing a N–H bond has been achieved in the presence of allylsamarium bromide. By applying this method, quaternary carbons have been constructed, and 2,2-diallylated cyclic ethers, 2,2-diallylated nitrogen heterocycles and diallylated amides were synthesized in moderate to good yields under mild conditions. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The addition reaction of organometallics to carbonyl compounds provides a fundamental methodology in synthetic organic chemistry.<sup>1</sup> Many metals have been used in this type of reaction, such as Mg,<sup>2</sup> Zn,<sup>3</sup> Sn,<sup>4</sup> Bi<sup>5</sup> and Cd.<sup>1</sup> Significant advance in this type reaction has been achieved. However, when using these metals long reaction times are required and only reactive halides are effective. Indium in aqueous medium has shown remarkable facilities in the allylation of carbonyl groups.<sup>6</sup> Samarium diiodide, as a powerful, versatile, and ether-soluble one-electron donor, has been widely applied in Barbier–Grignard type reactions,<sup>7</sup> and the application of samarium metal has also stimulated great interest in recent years.<sup>8</sup> Aldehydes, ketones, acid halides and carboxylic acid anhydrides are widely used as simple starting materials for such transformations. Usually, homoallylic alcohols were obtained utilizing these methods, but little attention has been paid to the geminal diallylation of carbonyl compounds.<sup>9</sup> We have shown that nitriles undergo diallylation on treatment with allylsamarium bromide to give the corresponding diallylamides.<sup>10</sup> However, to the best of our knowledge, transformations of lactones, lactams and acyclic amides containing a N–H bond under the action of allylsamarium bromide has not been investigated.

We report herein the geminal diallylation of lactones, lactams and acyclic amides with allylsamarium bromide to construct quaternary carbons directly.

**Keywords:** allylsamarium bromide; lactones; lactams; 2,2-diallylated cyclic ethers.

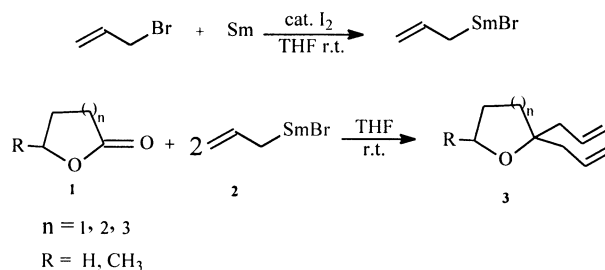
\* Corresponding author. Tel.: +86-571-5178611; fax: +86-571-8807077; e-mail: yminzhang@mail.hz.zj.cn

## 2. Results and discussion

### 2.1. The reaction of lactones and phthalic anhydride with allylic bromide

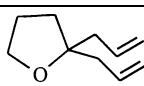
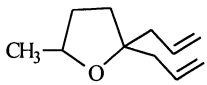
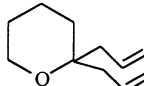
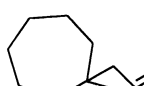
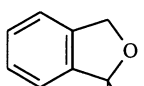
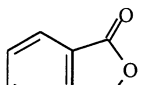
The reaction of Grignard reagents with lactones was first investigated by Houben.<sup>11</sup> He found that simple aliphatic  $\gamma$ -lactones might be expected to yield glycols, but cyclic etherification of the primary reaction products of lactones of this type is apparently relatively rare. Harrowven reported the addition of allylmagnesium chloride to tetrahydrofuranones to give diallylated products under a cooled ( $-90^{\circ}\text{C}$ ) solution.<sup>12</sup> We found that when lactones (**1**) were treated with allylsamarium bromide (**2**) in THF at room temperature, 2,2-diallylated cyclic ethers (**3**) were obtained in good yields (Scheme 1). The lactones and allylsamarium bromide were used in a ratio of 1:2.2.

All reactions were complete within 5 min with high yields of diallylated cyclic ethers being isolated. The product formation was ascertained by TLC monitoring and the product isolation was achieved by quenching the reaction with dilute hydrochloric acid followed by extraction. The



**Scheme 1.**

**Table 1.** The reaction of lactones and phthalic anhydride with allylic bromide

Entry	Product	Time (min)	Yields <sup>a</sup> (%)
a	 <b>3a</b>	4	95
b	 <b>3b</b>	5	90
c	 <b>3c</b>	4	95
d	 <b>3d</b>	5	85
e	 <b>3e</b>	4	85
f	 <b>3f</b>	3	95

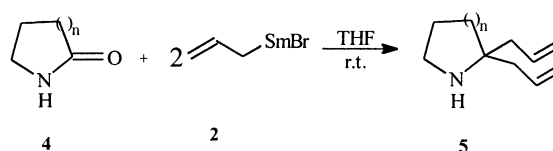
<sup>a</sup> Isolated yields based on lactones or phthalic anhydride.

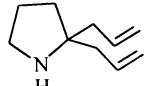
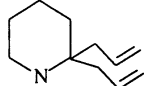
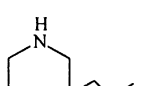
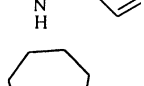
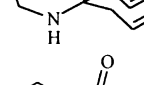
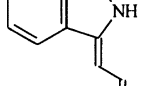
reactions were generally clean and no trace of homoallylated product could be detected in the <sup>1</sup>H NMR spectra of the crude products. However, purification wherever necessary was performed by flash chromatography. On the basis of the good results obtained with simple lactones, it seemed logical to investigate the possibility of extending this methodology to phthalic anhydride afforded the diallylated product in good yield (*entry f*). The results and the scope of this reaction are summarized in Table 1, which clearly indicates that the present strategy may afford a general diallylation protocol for the synthesis of 2,2-diallylated cyclic ethers from simple lactones.

## 2.2. The reaction of lactams with allylsamarium bromide

Lukeš reported that the reaction of RMgX with 5–8-membered lactams led to a mixture of 1-alkyl-1-aza-2-cyclenes and 2,2-dialkylated (arylated) heterocycles,<sup>13</sup> and the reaction of 2-piperidone with allylmagnesium bromide led to a compound with unknown structure (C<sub>14</sub>H<sub>23</sub>N).<sup>14</sup> Recently, Bubnov described the synthesis of 2,2-diallylated nitrogen heterocycles by the reaction of allylic boranes with lactams under harsh conditions.<sup>15</sup> We found that when lactams (**4**) were treated with allylsamarium bromide (**2**) in THF at room temperature, 2,2-diallylated nitrogen heterocycles (**5**) were obtained in good yields<sup>16</sup> (Scheme 2). All reactions were complete within 5 min. The lactams and allylsamarium bromide were used in a ratio of 1:2.2.

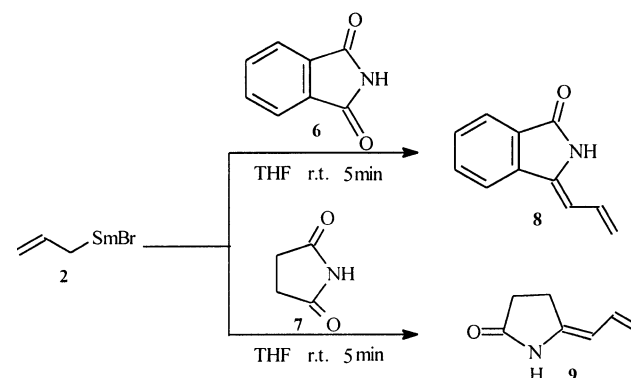
It should be noted that, when lactams, such as, 2-pyrrolidi-

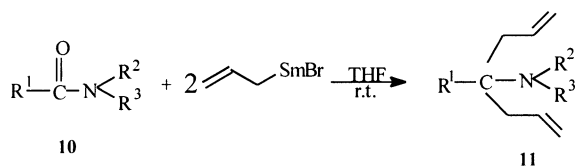
**Scheme 2.****Table 2.** The reaction of lactams with allylsamarium bromide

Entry	Product	Time (min)	Yields <sup>a</sup> (%)
a		5	95
b		5	90
c		4	95
d		5	85
e		4	85
f		5	75

<sup>a</sup> Isolated yields based on lactams.

none, 2-piperidone, piperazinone and caprolactam were used in this reaction, the corresponding diallylated nitrogen heterocycles were obtained in excellent yields (Table 2). But when *o*-phthalimide (**6**) and succinimide (**7**) were treated with allylsamarium bromide under the same conditions, the diallylated compounds were not detected at all, with 3-[(*Z*)-2-propenylidene]-1-isoindolinone (**8**) and 5-[(*Z*)-2-propenylidene]-2-pyrrolidinone (**9**) being obtained, respectively (Scheme 3).

**Scheme 3.**



Scheme 4.

Table 3. The reaction of acyclic amides with allylsamarium bromide

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time (h)	Yield <sup>a</sup> (%)
a	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	2	75
b	CH <sub>3</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	H	3	75
c	CH <sub>3</sub> CH <sub>2</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	4	75
d	CH <sub>3</sub> CH <sub>2</sub>	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	3	70
e	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	3	65
f	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	4	50
g	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	4	50
h	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	10	0 <sup>b</sup>
i	C <sub>6</sub> H <sub>5</sub>	H	H	3	60 <sup>c</sup>

<sup>a</sup> Isolated yields based on acyclic amides.

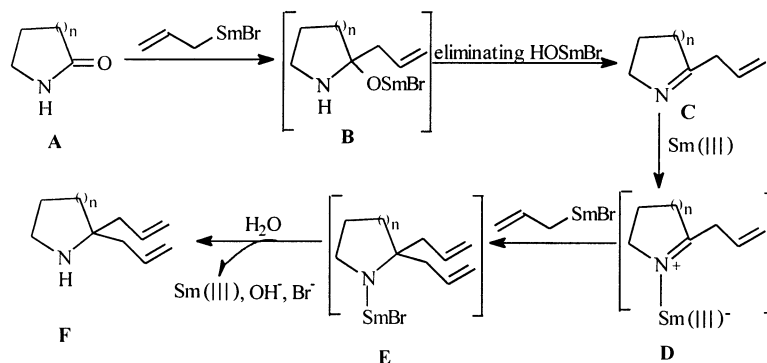
<sup>b</sup> The expected compound **9h** could not be detected.

<sup>c</sup> Diallyl carbinol was isolated in moderate yield.

It is interesting that acyclic amides (**10**) containing a N–H bond also can react with allylsamarium bromide to give the analogous diallylated amines (**11**) in moderate to good yields (Scheme 4). The reaction conditions and scope of this reaction are shown in Table 3.

As shown in Table 3, acyclic amides (**10**) containing a N–H bond undergo the diallylation reaction smoothly, and the diallylated amides (**11**) were obtained in moderate to good yields. But when *N,N*-diethylbenzamide was treated with allylsamarium bromide for 10 h under the same conditions, the expected compound (**11h**) could not be detected.

A possible mechanism of the diallylation of lactams and acyclic amides containing a N–H bond is shown in Scheme 5. Firstly, lactams (**A**) undergo allylation leading to intermediates (**B**), which eliminate the HOSmBr fragment to produce imines (**C**). Then, Sm(III) will work as a Lewis acid to form iminium ions (**D**), which would, in turn, undergo allylation with allylsamarium bromide leading to the intermediates (**E**), which was decomposed by water to produce the desired diallylation products (**F**).



Scheme 5.

In summary, quaternary carbons are constructed efficiently from lactones, lactams and acyclic amides containing a N–H bond utilizing allylsamarium bromide. By applying this method, 2,2-diallylated cyclic ethers, 2,2-diallylated nitrogen heterocycles and analogous diallylated amides are obtained under mild conditions, which contain two double bonds and can be used for the preparation of various derivatives such as bicyclic compounds and spiro-compounds.

### 3. Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-400 instrument as CDCl<sub>3</sub> solutions using TMS as an internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* are given in Hz. IR spectra were taken as thin films with a Bruker Vector-22 infrared spectrometer. Elemental analyses were performed on an EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources and were used without further purification. The starting material *N*-benzanilide was prepared by published method.<sup>17</sup>

#### 3.1. General procedure for the synthesis of 2,2-diallylated cyclic ethers (3)

Allyl bromide (2.2 mmol) and samarium (2 mmol) with a catalytic amount of iodine (0.01 mmol) in dry THF (10 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 5 min, and a purple color was formed. Lactones (1 mmol) was added, the purple color of the mixture disappeared immediately. The reaction mixture was stirred for 1–5 min and then was quenched with 0.1 M hydrochloric acid. The resulting mixture was extracted with diethyl ether (3×10 mL), the diethyl ether solution was washed with saturated NaCl (2×10 mL) and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded 2,2-diallylated cyclic ethers.

**3.1.1. 2,2-Diallyltetrahydrofuran (3a).** Colorless oil; yield: 144 mg (95%); IR: ν<sub>max</sub> (liquid film) 1639, 998; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.79–5.89 (2H, m, 2×CH),

5.08–5.13 (4H, m,  $2\times\text{CH}_2=$ ), 3.60 (2H, t,  $J=5.9$  Hz,  $\text{CH}_2\text{O}$ ), 2.21–2.25 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.51–1.66 (4H, m,  $2\times\text{CH}_2$ ); MS:  $m/z$  (%) 153 ( $\text{M}^+ + 1$ ), 135 (15.97), 119 (1.56), 111 (100). Anal. calcd.  $\text{C}_{10}\text{H}_{16}\text{O}$ : C, 78.95; H, 10.53. Found: C, 78.89; H, 10.47%.

**3.1.2. 2,2-Diallyl-5-methyltetrahydrofuran (3b).** Colorless oil; yield: 149 mg (90%); IR:  $\nu_{\text{max}}$  (liquid film) 1639, 998;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.79–5.88 (2H, m,  $2\times\text{CH}$ ), 5.08–5.13 (4H, m,  $2\times\text{CH}_2=$ ), 3.74–3.78 (1H, m,  $\text{CHCH}_3$ ), 2.21–2.25 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.25–1.51 (4H, m,  $2\times\text{CH}_2$ ), 1.18 (3H, d,  $J=6.2$  Hz,  $\text{CH}_3$ ); MS:  $m/z$  (%) 167 ( $\text{M}^+ + 1$ ), 149 (29.11), 125 (100). Anal. calcd.  $\text{C}_{11}\text{H}_{18}\text{O}$ : C, 79.52; H, 10.84. Found: C, 79.48; H, 10.80%.

**3.1.3. 2,2-Diallyltetrahydro-2H-pyran (3c).** Colorless oil; yield: 158 mg (95%); IR:  $\nu_{\text{max}}$  (liquid film) 1639, 998;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.79–5.89 (2H, m,  $2\times\text{CH}$ ), 5.08–5.13 (4H, m,  $2\times\text{CH}_2=$ ), 3.62 (2H, t,  $J=5.9$  Hz,  $\text{CH}_2\text{O}$ ), 2.21–2.25 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.51–1.66 (6H, m,  $3\times\text{CH}_2$ ); MS:  $m/z$  (%) 167 ( $\text{M}^+ + 1$ ), 149 (15.97), 133 (1.56), 125 (100). Anal. calcd.  $\text{C}_{11}\text{H}_{18}\text{O}$ : C, 79.52; H, 10.84. Found: C, 79.35; H, 10.57%.

**3.1.4. 2,2-Dialyloxepane (3d).** Colorless oil; yield: 153 mg (85%); IR:  $\nu_{\text{max}}$  (liquid film) 1639, 998;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.79–5.89 (2H, m,  $2\times\text{CH}$ ), 5.08–5.13 (4H, m,  $2\times\text{CH}_2=$ ), 3.62 (2H, t,  $J=5.9$  Hz,  $\text{CH}_2\text{O}$ ), 2.21–2.25 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.49–1.66 (8H, m,  $4\times\text{CH}_2$ ); MS:  $m/z$  (%) 181 ( $\text{M}^+ + 1$ ), 163 (15.97), 147 (1.56), 139 (100). Anal. calcd.  $\text{C}_{12}\text{H}_{20}\text{O}$ : C, 80.00; H, 11.11. Found: C, 79.79; H, 10.87%.

**3.1.5. 1,1-Diallyl-1,3-dihydroisobenzofuran (3e).** Yellow oil; yield: 170 mg (85%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17–7.25 (4H, m, ArH), 5.62–5.69 (2H, m,  $2\times\text{CH}$ ), 5.04–5.09 (4H, m,  $2\times\text{CH}_2=$ ), 4.73 (2H, s,  $\text{CH}_2\text{O}$ ), 2.56–2.76 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ); MS:  $m/z$  (%) 201 ( $\text{M}^+ + 1$ ), 183 (3.83), 159 (98.90), 131 (100). Anal. calcd.  $\text{C}_{14}\text{H}_{16}\text{O}$ : C, 84.00; H, 8.00; found; C, 83.97; H, 8.05%.

**3.1.6. 3,3-Diallyl-1,5-dihydro-1-isobenzofuranone (3f).** Yellow oil; yield: 203 mg (95%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.91 (4H, m, ArH), 5.51–5.57 (2H, m,  $2\times\text{CH}$ ), 5.04–5.09 (4H, m,  $2\times\text{CH}_2=$ ), 2.63–2.76 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ); MS:  $m/z$  (%) 215 ( $\text{M}^+ + 1$ ), 197 (20.09), 173 (100), 133 (95.72), 117 (78.50), 105 (26.36). Anal. calcd.  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : C, 78.50; H, 6.54. Found: C, 78.45; H, 6.49%.

### 3.2. General procedure for the synthesis of 2,2-diallylated nitrogen heterocycles (5)

Samarium (0.33 g, 2.2 mmol) and allyl bromide (0.30 g, 2.5 mmol) in THF (20 mL) were added to a three-necked flask with stirring at room temperature under nitrogen. When the color of the mixture turned into purple, stirring was continued for 1 h until the samarium powder disappeared, then lactams (1 mmol) were added to the solution, and the mixture was stirred at room temperature for 5 min. Five milliliters of water was added. The reaction mixture

was extracted with diethyl ether ( $3\times 10$  mL), the diethyl ether solution was washed with saturated  $\text{NH}_4\text{Cl}$  ( $2\times 10$  mL) and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane–ethyl acetate (3:1) as eluent).

**3.2.1. 2,2-Diallylpyrrolidine (5a).** Colorless liquid; yield: 144 mg (95%); bp 86–88°C (13 Torr);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.75–5.77 (2H, m,  $2\times\text{CH}$ ), 5.17–5.20 (4H, m,  $2\times\text{CH}_2=$ ), 3.02 (2H, t,  $J=6.8$  Hz,  $\text{CH}_2\text{N}$ ), 2.38 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.45–1.70 (5H, m,  $2\times\text{CH}_2+\text{NH}$ ); MS:  $m/z$  (%): 152 ( $\text{M}^+ + 1$ ), 2.33), 151 ( $\text{M}^+$ , 4.78), 110 (100). Anal. calcd.  $\text{C}_{10}\text{H}_{17}\text{N}$ : C, 79.47; H, 11.26; N, 9.27. Found: C, 79.39; H, 11.29; N, 9.29%.

**3.2.2. 2,2-Diallylpiperidine (5b).** Colorless liquid; yield: 149 mg (90%); bp 66–67°C (1 Torr);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.75–5.77 (2H, m,  $2\times\text{CH}$ ), 5.17–5.20 (4H, m,  $2\times\text{CH}_2=$ ), 2.75 (2H, t,  $J=6.8$  Hz,  $\text{CH}_2\text{N}$ ), 2.34 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.40–1.55 (7H, m,  $3\times\text{CH}_2+\text{NH}$ ); MS:  $m/z$  (%): 166 ( $\text{M}^+ + 1$ ), 2.33), 165 ( $\text{M}^+$ , 4.78), 124 (100). Anal. calcd.  $\text{C}_{11}\text{H}_{19}\text{N}$ : C, 80.00; H, 11.52; N, 8.48. Found: C, 79.89; H, 11.49; N, 8.40%.

**3.2.3. 2,2-Diallylpiperazine (5c).** Colorless liquid; yield: 158 mg (95%); bp 54–57°C (0.2 Torr);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.75–5.77 (2H, m,  $2\times\text{CH}$ ), 5.17–5.20 (4H, m,  $2\times\text{CH}_2=$ ), 2.65 (4H, s,  $\text{CH}_2\text{CH}_2$ ), 2.5 (2H, s,  $\text{CH}_2\text{N}$ ), 2.28 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.50 (2H, s,  $2\times\text{NH}$ ). Anal. calcd.  $\text{C}_{10}\text{H}_{18}\text{N}_2$ : C, 72.28; H, 10.84; N, 16.87. Found: C, 72.20; H, 10.85; N, 16.79%.

**3.2.4. 2,2-Diallylazepane (5d).** Colorless liquid; yield: 152 mg (85%); bp 75–77°C (1 Torr);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.75–5.77 (2H, m,  $2\times\text{CH}$ ), 5.17–5.20 (4H, m,  $2\times\text{CH}_2=$ ), 2.65 (2H, t,  $J=6.8$  Hz,  $\text{CH}_2\text{N}$ ), 2.28 (4H, d,  $J=7.3$  Hz,  $2\times\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.45–1.70 (9H, m,  $4\times\text{CH}_2+\text{NH}$ ); MS:  $m/z$  (%): 180 ( $\text{M}^+ + 1$ ), 2.33), 179 ( $\text{M}^+$ , 4.78), 138 (100). Anal. calcd.  $\text{C}_{12}\text{H}_{21}\text{N}$ : C, 80.45; H, 11.73; N, 7.82. Found: C, 80.38; H, 11.68; N, 7.79%.

**3.2.5. 3-[(Z)-2-Propenylidene]-1-isoindolinone (5e).** White solid; yield: 145 mg (85%); mp 98–101°C; IR:  $\nu_{\text{max}}$ : 3320 (NH), 1707 (C=O), 1650, 1615 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.52 (1H, br s, NH), 7.89–7.27 (4H, m, ArH), 6.81–6.85 (1H, m, CH), 6.23 (1H, d,  $J=11.5$  Hz, CH), 4.88–5.45 (2H, m,  $\text{CH}_2=$ ); MS:  $m/z$  (%): 172 ( $\text{M}^+ + 1$ ), 2.03), 171 ( $\text{M}^+$ , 5.47), 130 (100), 102 (34.15). Anal. calcd.  $\text{C}_{11}\text{H}_9\text{NO}$ : C, 77.19; H, 5.26; N, 8.19. Found: C, 77.16; H, 5.20; N, 8.18%.

**3.2.6. 5-[(Z)-2-Propenylidene]-1-pyrrolidinone (5f).** White solid; yield: 92 mg (75%); mp 98–101°C; IR:  $\nu_{\text{max}}$ : 3320 (NH), 1700 (C=O), 1650, 1615 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.48 (1H, br s, NH), 6.25–6.34 (1H, m, CH), 5.80 (1H, d,  $J=7.0$  Hz, CH), 5.00–5.05 (2H, m,  $\text{CH}_2=$ ), 2.75–2.82 (2H, t,  $J=6.0$  Hz,  $\text{CH}_2\text{C}=\text{O}$ ), 2.53–2.57 (2H, t,  $J=6.0$  Hz,  $\text{CH}_2$ ). Anal. calcd.  $\text{C}_7\text{H}_9\text{NO}$ : C, 68.29; H, 7.31; N, 11.38. Found: C, 68.25; H, 7.28; N, 11.30%.

### 3.3. The reaction of acyclic amides with allylsamarium bromide

Samarium (0.33 g, 2.2 mmol) and allyl bromide (0.30 g, 2.5 mmol) in THF (20 mL) were added to a three-necked flask with stirring at room temperature under nitrogen. When the color of the mixture turned into purple, stirring was continued for 1 h until the samarium powder disappeared, then acyclic amides (1 mmol) were added to the solution, and the mixture was stirred at room temperature for the appropriate times (Table 3). Five milliliters of water was added. The reaction mixture was extracted with diethyl ether (3×10 mL), the diethyl ether solution was washed with saturated NH<sub>4</sub>Cl (2×10 mL) and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane–ethyl acetate (4:1) as eluent).

**3.3.1. *N*-(1-Allyl-1-methyl-3-butenyl)-*N*-phenylamine (11a).** Yellow oil; yield: 151 mg (75%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.11–7.21 (2H, m, ArH), 6.71–6.73 (3H, m, ArH), 5.81–5.87 (2H, m, 2×CH), 5.05–5.11 (4H, m, 2×CH<sub>2</sub>=), 3.49 (1H, br, NH), 2.30–2.47 (4H, d, *J*=7.3 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 1.27 (3H, s, CH<sub>3</sub>); MS: *m/z* (%): 202 (M+1, 6.72), 201 (M<sup>+</sup>, 4.03), 160 (100), 118 (61.75), 77 (27.68). Anal. calcd. C<sub>14</sub>H<sub>19</sub>N: C, 83.58; H, 9.45; N, 6.96. Found: C, 83.50; H, 9.35; N, 6.85%.

**3.3.2. *N*-(1-Allyl-1-ethyl-3-butenyl)-*N*-phenylamine (11b).** Yellow oil; yield: 161 mg (75%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.11–7.14 (2H, m, ArH), 6.67–6.71 (3H, m, ArH), 5.78–5.85 (2H, m, 2×CH), 5.05–5.11 (4H, m, 2×CH<sub>2</sub>=), 3.45 (1H, br, NH), 2.37 (4H, d, *J*=7.3 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 1.65 (2H, q, *J*=7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.88 (3H, t, *J*=7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>); MS: *m/z* (%): 216 (M+1, 1.66), 215 (M<sup>+</sup>, 2.57), 174 (100), 132 (58.14), 77 (27.42). Anal. calcd. C<sub>15</sub>H<sub>21</sub>N: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.56; H, 9.62; N, 6.44%.

**3.3.3. *N*-(1-Allyl-1-ethyl-3-butenyl)-*N*-(4-chlorophenyl)-amine (11c).** Yellow oil; yield: 188 mg (75%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.05–7.07 (2H, d, *J*=8.9 Hz, ArH), 6.61–6.63 (2H, d, *J*=8.8 Hz, ArH), 5.75–5.82 (2H, m, 2×CH), 5.05–5.12 (4H, m, 2×CH<sub>2</sub>=), 3.45 (1H, br, NH), 2.37 (4H, d, *J*=7.3 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 1.65 (2H, q, *J*=7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.88 (3H, t, *J*=7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>); MS: *m/z* (%): 251 (3.42), 250 (12.13), 249 (4.42), 208 (100), 166 (58.14). Anal. calcd. C<sub>15</sub>H<sub>21</sub>ClN: C, 72.13; H, 8.07; N, 5.61. Found: C, 72.06; H, 7.85; N, 5.52%.

**3.3.4. *N*-(1-Allyl-1-ethyl-3-butenyl)-*N*-(2-methylphenyl)-amine (11d).** Yellow oil; yield: 160 mg (70%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.01–7.03 (2H, m, ArH), 6.82–6.84 (1H, d, *J*=7.9 Hz, ArH), 6.60–6.62 (1H, m, ArH), 5.77–5.84 (2H, m, 2×CH), 5.05–5.10 (4H, m, 2×CH<sub>2</sub>=), 3.45 (1H, br, NH), 2.41–2.43 (4H, d, *J*=7.4 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 2.09 (3H, s, CH<sub>3</sub>), 1.74 (2H,

q, *J*=7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.88 (3H, t, *J*=7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>); MS: *m/z* (%): 230 (M+1, 8.52), 229 (M<sup>+</sup>, 4.20), 188 (100), 146 (59.44), 91 (17.00). Anal. calcd. C<sub>16</sub>H<sub>23</sub>N: C, 83.79; H, 10.11; N, 6.11. Found: C, 83.56; H, 10.01; N, 5.90%.

**3.3.5. *N*-(1-Allyl-1-(4-phenyl)-3-butenyl)-*N*-benzylamine (11e).** Yellow oil; yield: 180 mg (65%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.20–7.52 (10H, m, ArH), 5.77–5.84 (2H, m, 2×CH), 5.05–5.10 (4H, m, 2×CH<sub>2</sub>=), 3.50 (2H, s, CH<sub>2</sub>NH), 3.45 (1H, br, NH), 2.60–2.62 (4H, d, *J*=7.4 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>); MS: *m/z* (%): 278 (M+1, 11.99), 277 (M<sup>+</sup>, 2.99), 236 (100), 91 (73.24). Anal. calcd. C<sub>20</sub>H<sub>23</sub>N: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.45; H, 8.15; N, 5.25%.

**3.3.6. *N*-(1-Allyl-1-(4-phenyl)-3-butenyl)-*N*-(4-methylphenyl)amine (11f).** Yellow oil; yield: 139 mg (50%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.02–7.42 (9H, m, ArH), 5.77–5.84 (2H, m, 2×CH), 5.05–5.10 (4H, m, 2×CH<sub>2</sub>=), 3.45 (1H, br, NH), 2.60–2.62 (4H, d, *J*=7.4 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 2.22 (3H, s, CH<sub>3</sub>); MS: *m/z* (%): 278 (M+1, 12.27), 277 (M<sup>+</sup>, 6.32), 236 (100), 91 (73.24). Anal. calcd. C<sub>20</sub>H<sub>23</sub>N: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.40; H, 8.25; N, 5.20%.

**3.3.7. *N*-(1-Allyl-1-(4-methylphenyl)-3-butenyl)-*N*-phenylamine (11g).** Yellow oil; yield: 138 mg (50%); IR (liquid film):  $\nu_{\max}$ : 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.16–7.75 (9H, m, ArH), 6.05–6.11 (2H, m, 2×CH), 5.18–5.23 (4H, m, 2×CH<sub>2</sub>=), 3.45 (1H, br, NH), 2.75–2.82 (4H, d, *J*=7.4 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 2.40 (3H, s, CH<sub>3</sub>); MS: *m/z* (%): 278 (M+1, 2.27), 277 (M<sup>+</sup>, 6.32), 236 (7.50), 119 (100), 91 (50.22). Anal. calcd. C<sub>20</sub>H<sub>23</sub>N: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.35; H, 8.22; N, 5.16%.

**3.3.8. 4-(4-Phenyl)-1,6-heptadien-4-ol (11i).** Yellow oil; yield: 113 mg (60%); IR (liquid film):  $\nu_{\max}$ : 3330 (OH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.32–7.64 (5H, m, ArH), 6.57–5.61 (2H, m, 2×CH), 5.06–5.12 (4H, m, 2×CH<sub>2</sub>=), 2.49–2.71 (4H, d, *J*=7.4 Hz, 2×CH<sub>2</sub>CH=CH<sub>2</sub>), 2.20 (1H, br, OH). Anal. calcd. C<sub>13</sub>H<sub>16</sub>O: C, 82.94; H, 8.57. Found: C, 82.75; H, 8.41%.

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