

# Electron transfer induced ring opening of 2-(bromomethyl)aziridines by magnesium in methanol

Kourosch Abbaspour Tehrani,<sup>†</sup> Tuyen NguyenVan, Michinori Karikomi, Mario Rottiers and Norbert De Kimpe<sup>\*</sup>

Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

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**Abstract**—Magnesium metal in methanol was used as a simple electron transfer induced ring-opening reagent of 2-(bromomethyl)aziridines to afford allylamines derivatives in 70–90% yield. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

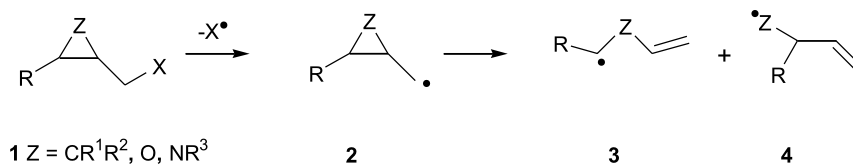
Three-membered heterocycles, including epoxides, oxaziridines and aziridines are prone to ring opening because of the high ring strain present in these small molecules. As a consequence, ring-opening reactions of small rings by radical rearrangement have received much attention recently (Scheme 1).<sup>1</sup> Ring opening of cyclopropanes **1** ( $Z=CR^1R^2$ ) and oxiranes ( $Z=O$ ) via cyclopropylmethyl radicals **2** and 2-oxiranylmethyl radicals **2** ( $Z=O$ ), respectively, have been regularly reported in the literature.<sup>1</sup> Such radical-induced ring cleavages have been utilized in a variety of useful synthetic transformations.<sup>2–5</sup> For example, this ring opening constitutes a useful strategy for the synthesis of allylic compounds. Analogously, also the rearrangement of 2-aziridinylmethyl radicals **2** ( $Z=NR^3$ ) holds some synthetic potential in organic synthesis. However, very few such reactions have been reported so far.<sup>6,7</sup>

Recently, we have shown that 2-(halomethyl)aziridines are easily accessible starting materials for the generation of 2-aziridinylmethyl radicals by two alternative methods. The

first procedure used a zinc–copper couple<sup>8</sup> under sonochemical conditions, and the second procedure used tributyltinhydride and AIBN for the radical initiation.<sup>9</sup> Both methods constitute a synthetic method for *N*-allylamines. However, the former method uses an ultrasonic generator and the latter method utilized substantial amounts of toxic tin reagent, in addition requiring elaborate purification of the final reaction products.

The synthetic utility of magnesium in methanol as electron transfer agent is being used more and more.<sup>10–12</sup> The major advantage of the Mg–MeOH method is the low cost and easy handling, contrary to other methods. For example, the reduction of alkyl halides to alkanes was executed with magnesium in methanol.<sup>13</sup> Another example is the reductive cleavage of 2-(halomethyl)oxiranes with magnesium in methanol, which provided a facile method for the synthesis of allylic alcohols.<sup>14</sup>

In this article, the use of magnesium in methanol as a simple electron transfer reagent for the ring opening of 2-(bromomethyl)aziridines towards allylamine derivatives is reported.



Scheme 1.

**Keywords:** aziridines.

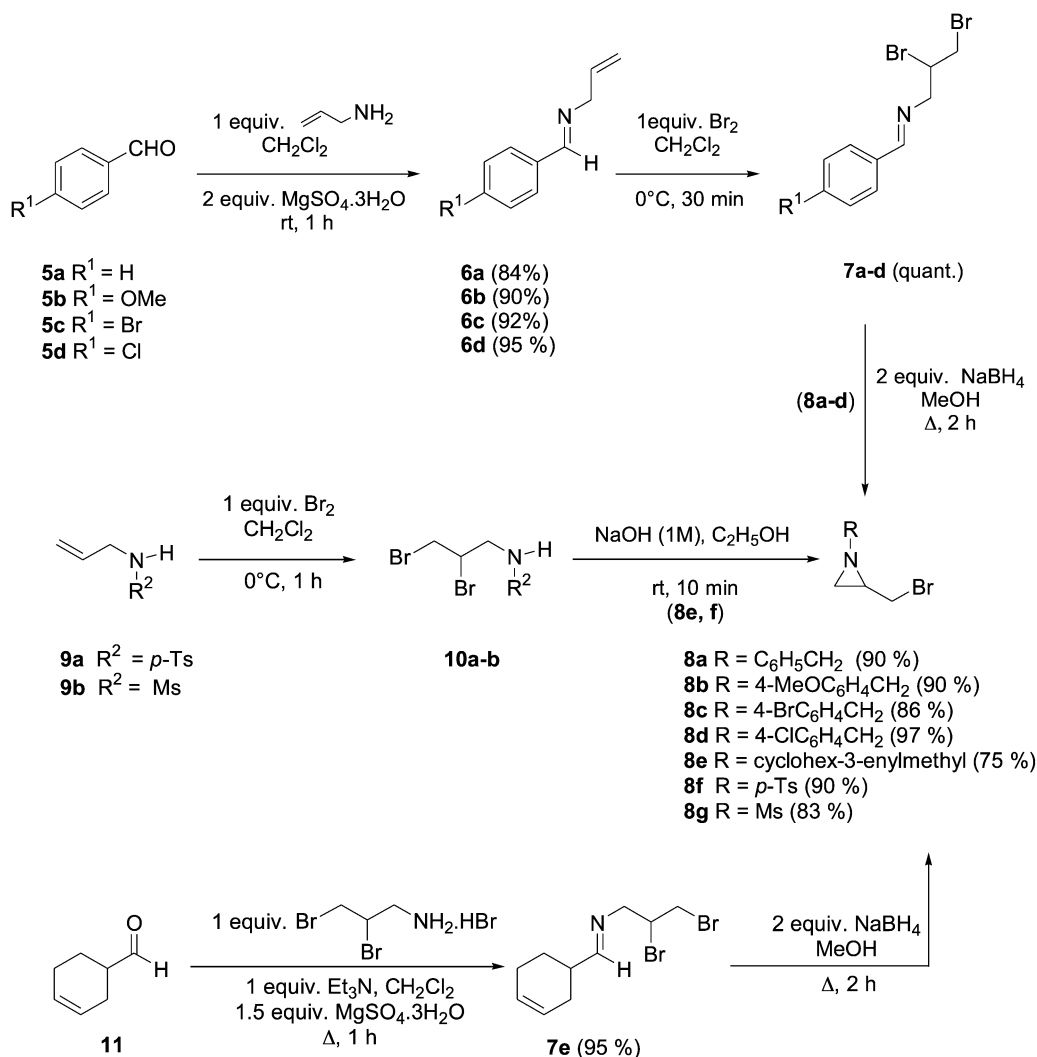
<sup>\*</sup> Corresponding author. Tel.: +32-9-264-59-51; fax: +32-9-264-62-43; e-mail: norbert.dekimpe@rug.ac.be

<sup>†</sup> Post-doctoral Fellow of the F.W.O.-Flanders (Belgium).

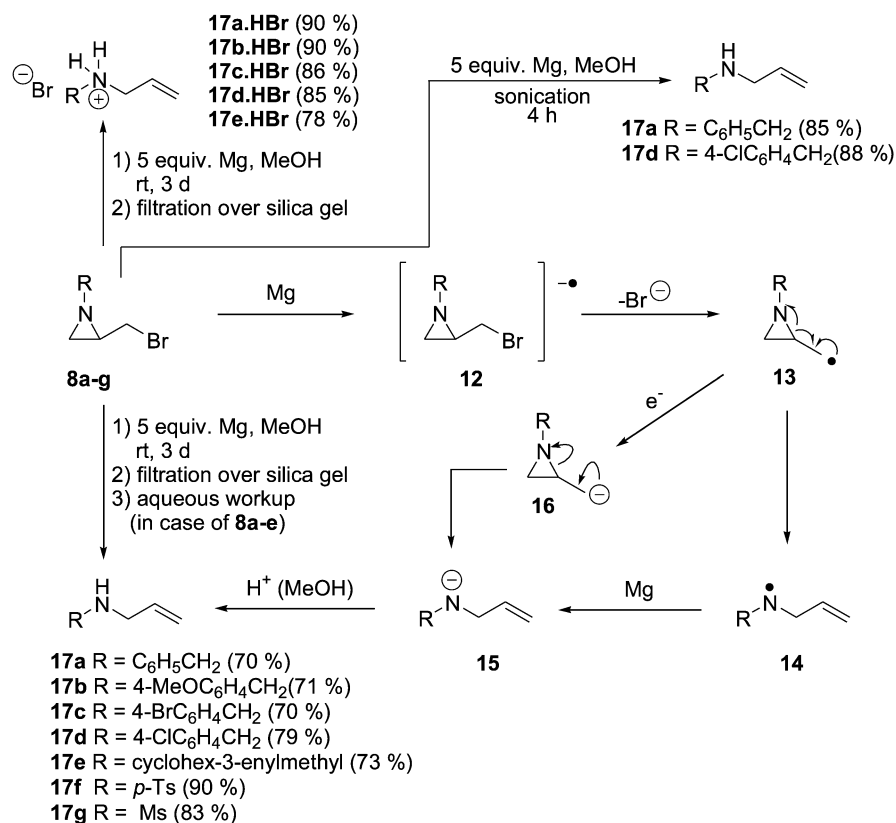
## 2. Results and discussion

2-(Bromomethyl)aziridines **8a–d** are accessible from aldehydes **5a–d** by a three-step synthetic sequence (Scheme 2). Condensation of aldehydes **5a–d** with allylamine in dichloromethane in the presence of magnesium sulfate afforded the corresponding *N*-allylimines **6a–d** (Scheme 2), which were subsequently brominated by bromine in dichloromethane to give *N*-(arylidene)-2,3-dibromopropylamines **7a–d**. The latter dibromoimines **7a–d** were not further purified because of their instability and hence reacted with sodium borohydride in methanol under reflux to produce 2-(bromomethyl)aziridines **8a–d** in 86–90% yield.<sup>15</sup> In the case of the synthesis of **8e**, 3-cyclohexene-1-carboxaldehyde **11** was condensed with 2,3-dibromo-1-propylammonium bromide in the presence of 1 equiv. triethylamine and magnesium sulfate as drying agent. Reduction of **7e** by means of sodium borohydride in methanol afforded a 1/1 mixture of diastereoisomeric aziridines **8e**, which could not be separated by column chromatography or by preparative gas chromatography. Because of the unrelevance for the next reaction, no further efforts were undertaken to separate these isomers.

*N*-Methanesulfonyl- and *N*-*p*-toluenesulfonyl-2-(bromomethyl)aziridines **8f,g** were synthesized via an alternative method (Scheme 2).<sup>16</sup> *N*-allyl-*p*-toluenesulfonamide **9a** and *N*-allylmethanesulfonamide **9b** were brominated by bromine in dichloromethane at 0°C to give *N*-tosyl and *N*-mesyl-2,3-dibromopropylamines **10a,b**, which were subsequently treated with aqueous sodium hydroxide (1 M) in ethanol at room temperature to afford the corresponding *N*-tosyl- and *N*-mesyl-2-(bromomethyl)aziridines **8f,g** in 83–90% yield (Scheme 2). 2-Bromomethyl-*N*-(*p*-toluenesulfonyl)aziridine **8e** has been prepared very recently by another group by aziridination of allylbromide with chloramine-T and pyridinium hydrobromide perbromide.<sup>17</sup> Surprisingly, the spectral data (<sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, IR) reported in this reference were different from our data and even not correct. In the <sup>1</sup>H NMR spectrum, the typical coupling between NC(H)*H*<sub>trans</sub>, NC(H)<sub>cis</sub>H and the NCH was not visible. Moreover, integrations in the region 3.50–5.25 ppm were not correct and in a very bad ratio with the aromatic signals. In addition, in the literature, a melting point was reported at 76–77°C, while our product never solidified, even not after distillation (boiling point 146°C/0.1 mmHg).



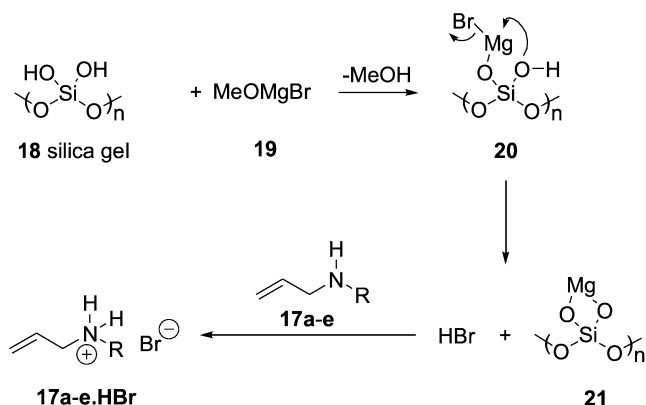
Scheme 2.



Scheme 3.

Ring opening of 2-(bromomethyl)aziridines **8a–e** in dry methanol at room temperature in the presence of 5 equiv. of magnesium metal was first executed at room temperature during 3 days. In the case of aziridines **8f,g** with a strong electron-withdrawing group the corresponding ring-opening product was isolated in excellent yield, after non-aqueous workup by filtration over silica gel. The same workup procedure, performed on the aziridines **8a–e**, however, furnished the corresponding hydrobromide salts **17a–e**. This reductive cleavage of *N*-benzyl- and *N-p*-chlorobenzylaziridine **8a,d** with magnesium in methanol has been recently reported by Pak et al.<sup>12</sup> By using the same workup procedure these authors identified the reaction products as *N*-allyl-*N*-benzylamine **17a** and *N*-allyl-(4-chlorobenzyl)amine **17d**, respectively. Since the reported spectrometric data were identical with our own results, it was concluded that also in this reference the hydrobromide salts had been isolated and as such mistakenly assigned to the free amines. To prove unequivocally that the hydrobromide salts were isolated, the free amines were treated with hydrogen bromide gas in diethyl ether at room temperature. The question remaining is why hydrobromide salts persist in a basic medium such as magnesium methoxide in methanol. The conversion of 2-(bromomethyl)aziridines **8a–g** can be interpreted as occurring via single electron transfer from magnesium metal to the substrate, followed by loss of bromide from the radical anion **12** to form the radical **13**. The latter radical **13** could rearrange to the aminyl radical **14**, which further gives the final allylamine derivatives **17a–e.HBr** (Scheme 3). A second electron transfer to the carbon-centered radical **13** might intervene, resulting in a carbanionic species **16**, which

undergoes ring opening to give the corresponding *N*-allylamine anion **15**. Protonation of the latter amide by the solvent affords allylamines **17**. From this hypothesis it was thought that after reaction the mixture contains 1 equiv. of a free allylamine **17**, 4.5 equiv. of magnesium methoxide and 0.5 equiv. of magnesium dibromide. To explain the origin of the hydrogen bromide a mixture, consisting of 4.5 equiv. of magnesium methoxide, 1 equiv. of *N*-allyl-*N*-benzylamine and 0.5 equiv. of commercial anhydrous magnesium bromide in dry methanol, was filtered over a silica gel column and eluted with methanol. In this case the hydrobromide salt of *N*-allyl-*N*-benzylamine **17a** was isolated after evaporation of methanol in vacuo. An analogous mixture without magnesium methoxide, furnished the free amine after filtration over silica gel. Alternatively it is possible and probably more likely that instead of 0.5 equiv. magnesium dibromide, 1 equiv. of methoxymagnesium bromide is formed. An indication for the presence of the latter species is found by mixing clear solutions of magnesium dibromide and magnesium methoxide in dry methanol (exothermic reaction!). A grey colloidal suspension was formed, very similar to the reaction mixture obtained by reaction of 2-(bromomethyl)aziridines **8a–g** with magnesium. The addition of 1 equiv. of *N*-allyl-*N*-benzylamine **17a** to the latter mixture, and filtration over silica gel also afforded *N*-allyl-*N*-benzylammonium bromide **17a.HBr**. It is known that the magnesium ion has a strong affinity for oxygen; therefore methoxymagnesium bromide will bind to the silica gel, releasing 1 equiv. of methanol. The presence of a strong base-like methoxide or hydroxide is required to deprotonate the weakly acidic silanol groups (pK<sub>a</sub>=5.5–7.5) and thus



Scheme 4.

enhance the affinity of oxygen for magnesium.<sup>18</sup> Next, bromide will be expelled by another silanol group, thus giving rise to hydrogen bromide, which will be trapped by the free allylamines **17a–e** (Scheme 4).

It is worth mentioning that in the case of the reaction of *N*-tosylated aziridine **8f** with magnesium in methanol only ring-opened product was isolated, and no trace of *N*-detosylated compounds have been found. In the literature, a similar reaction between 2-phenyl-*N*-tosylaziridine and magnesium gave rise to the ring-opened products and 2-phenylaziridine.<sup>19</sup> Sonication of 2-(bromomethyl)aziridines **8a,d** in methanol in the presence of 5 equiv. of magnesium turnings during 4 h at room temperature resulted in clean ring opening of the aziridine, leading to allylamines **17a,d** after filtration of the reaction mixture over silica gel. Because of the fact that in these cases the reaction time could be drastically reduced (from 3 days to 4 h) also the less reactive 1-(*p*-chlorobenzyl)-2-(chloromethyl)aziridine was treated with magnesium in methanol under sonochemical conditions. In this case, however, even after 4 h sonication only traces (<5%, <sup>1</sup>H NMR) of ring-opened product was observed.

In conclusion, magnesium in methanol showed to be a suitable and simple electron transfer reagent in the ring opening of 2-(bromomethyl)aziridines to obtain allylamine derivatives in 70–90% yield. It was possible to isolate the reaction products as free amines or as their hydrobromide salts, depending on the workup procedure. Erroneous data from the literature have been corrected.

### 3. Experimental

<sup>1</sup>H NMR spectra were recorded at 60 MHz (JEOL PMX 60 SI) or 270 MHz (JEOL JNM-EX 270) with CCl<sub>4</sub>, CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane as an internal standard. <sup>13</sup>C NMR spectra were recorded at 20 or 68 MHz (JEOL JNM-EX 270) with CDCl<sub>3</sub>, CCl<sub>4</sub> or DMSO-*d*<sub>6</sub> as solvent. Mass spectra were obtained with a mass spectrometer (VARIAN MAT 112, 70 eV) using a GC–MS coupling (RSL 200, 20 m glass capillary column, 0.53 mm i.d., He carrier gas). IR spectra were measured with a Perkin Elmer 1310 spectrophotometer or a Spectrum One FT-IR. Melting points were determined on a Büchi 540 apparatus. Sonication experiments were performed with a Transsonic

660/H ultrason bath (35 kHz). Dichloromethane was dried over calcium hydride. Methanol was dried by distillation over magnesium and diethyl ether by distillation over sodium benzophenone ketyl. Other solvents were used as received from the supplier. Silica gel had a pore diameter of ca. 6 nm, and 0.035–0.070 mm size. The synthesis and spectral data of 1-benzyl-2-(bromomethyl)aziridine **8a** and 2-(bromomethyl)-1-(4-chlorobenzyl)aziridine **8d** is reported elsewhere.<sup>15</sup> Compounds **9a** and **9b** were prepared in quantitative yield through reaction of allylamine with *p*-toluenesulfonyl chloride and methanesulfonyl chloride, respectively.<sup>20</sup> 2,3-Dibromo-1-propylammonium bromide was prepared by a literature method.<sup>21</sup>

### 3.1. *N*-Arylidene-2-propenylamines **6a–c**<sup>15</sup>

A mixture of 0.1 mol of the appropriate aromatic aldehyde **5a–c** in 100 mL of dichloromethane was treated with 0.11 mol of allylamine and 13 g of magnesium sulfate. The mixture was stirred at room temperature for 1 h, and then filtered. The filter cake was washed with dichloromethane. The combined filtrates were evaporated, after which the *N*-allylaldimines **6** were distilled in vacuo. Despite the fact that these compounds are known, spectrometric data have never been published, therefore they are reported here.

#### 3.1.1. *N*-(Phenylmethylidene)-*N*-(2-propenyl)amine **6a**.

Yield 94%; bp 58°C/0.05 mmHg. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 4.19–4.20 (2H, m, NCH<sub>2</sub>); 5.08–5.20 (2H, m, CH=CH<sub>2</sub>); 5.97–6.13 (1H, m, CH=CH<sub>2</sub>); 7.30–7.40 (3H, m, HC<sub>meta</sub> and HC<sub>para</sub>); 7.67–7.79 (2H, m, HC<sub>ortho</sub>); 8.18 (1H, s, CH=N). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 63.41 (NCH<sub>2</sub>CH); 115.88 (CH=CH<sub>2</sub>); 128.08 and 128.5 (HC<sub>ortho</sub> and HC<sub>meta</sub> or vice versa); 130.58 (HC<sub>para</sub>); 135.90 (CH=CH<sub>2</sub>); 136.19 (C–CH=N); 167.72 (C=N). IR (NaCl, cm<sup>-1</sup>): ν=1643 (C=N). MS (70 eV) *m/z* (%): 145 (M<sup>+</sup>; 61); 144 (100); 130 (4); 118 (13); 117 (39); 115 (5); 104 (38); 92 (6); 91 (31); 90 (32); 89 (16); 78 (6); 77 (19); 68 (10); 65 (7); 63 (8); 58 (7); 54 (10); 51 (18); 50 (6).

#### 3.1.2. *N*-((4-Methoxyphenyl)methylidene)-*N*-(2-propenyl)amine **6b**.

Yield 93%; bp 78°C/0.05 mmHg. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 3.83 (3H, s, OCH<sub>3</sub>); 4.22 (2H, d, *J*=5.6 Hz, NCH<sub>2</sub>); 5.11–5.25 (2H, m, CH=CH<sub>2</sub>); 5.98–6.10 (1H, m, CH=CH<sub>2</sub>); 6.89 and 7.68 (each 2H, each d, *J*=8.9 Hz, HC<sub>ortho</sub> and HC<sub>para</sub>); 8.21 (1H, s, CH=N). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 55.24 (OCH<sub>3</sub>); 63.40 (CH<sub>2</sub>N); 113.92 (2×HC<sub>meta</sub>); 115.79 (=CH<sub>2</sub>); 129.14 (C–CH=N); 129.65 (2×HC<sub>ortho</sub>); 136.21 (CH=CH<sub>2</sub>); 161.20 (CH=N); 161.63 (C–OCH<sub>3</sub>). IR (NaCl, cm<sup>-1</sup>): ν=1689 (C=N); 1648; 1606; 1578; 1512. MS (70 eV) *m/z* (%): 175 (M<sup>+</sup>; 36); 174 (M<sup>+</sup>–1, 74); 171 (14); 160 (10); 157 (72); 149 (12); 148 (15); 134 (23); 130 (58); 121 (28); 117 (100); 104 (62); 103 (39); 91 (48); 86 (27); 77 (54); 67 (16); 63 (15); 57 (28); 54 (12); 51 (52); 43 (40).

#### 3.1.3. *N*-((4-Bromophenyl)methylidene)-*N*-(2-propenyl)-amine **6c**.

Yield 90%; bp 91°C/1 mmHg. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 4.22 (2H, d, *J*=5.6 Hz, NCH<sub>2</sub>); 5.13–5.25 (2H, m, CH=CH<sub>2</sub>); 5.97–6.12 (1H, m, CH=CH<sub>2</sub>); 7.51 and 7.61 (each 2H, each d, *J*=8.2 Hz, HC<sub>ortho</sub> and HC<sub>para</sub>); 8.20 (1H, s, CH=N). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 63.39 (CH<sub>2</sub>N); 116.15 (=CH<sub>2</sub>);

125.11 (=C–Br); 129.49 and 131.73 ( $HC_{ortho}$  and  $HC_{meta}$  or vice versa); 135.00 (C–CH=N); 135.58 (CH=CH<sub>2</sub>); 160.46 (CH=N). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1649 (C=N); 1589; 1487. MS (70 eV) *m/z* (%): 224/6 (M<sup>+</sup>; 100); 223 (54); 222 (98); 197 (14); 184 (23); 183 (9); 169 (19); 144 (32); 117 (16); 116 (43); 115 (12); 98 (9); 90 (16); 89 (16); 77 (9); 68 (15); 63 (16); 50 (20); 54 (33); 43 (7).

**3.1.4. *N*-((4-Chlorophenyl)methylidene)-*N*-(2-propenyl)amine 6d.** Yield 94%; bp 61–63°C/0.05 mmHg. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  4.19 (2H, d, *J*=5.48 Hz, NCH<sub>2</sub>); 5.08–5.25 (2H, m, CH=CH<sub>2</sub>); 5.94–6.09 (1H, m, CH=CH<sub>2</sub>); 7.31 and 7.60 (each 2H, each d, *J*=8.44 Hz,  $HC_{ortho}$  and  $HC_{para}$ ); 8.17 (1H, s, CH=N). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>):  $\delta$  63.07 (CH<sub>2</sub>N); 115.81 (=CH<sub>2</sub>); 128.50 and 129.00 ( $HC_{ortho}$  and  $HC_{meta}$  or vice versa); 134.41 (C–CH=N); 135.42 (CH=CH<sub>2</sub>); 136.21 (=C–Cl); 159.96 (CH=N). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1646 (C=N). MS (70 eV) *m/z* (%): 179/81 (M<sup>+</sup>; 52); 178 (100); 152 (27); 151 (27); 144 (15); 138 (24); 124 (15); 117 (9); 111 (9); 95 (13); 89 (26); 75 (12); 63 (9); 54 (14); 51 (17); 49 (42).

### 3.2. *N*-Arylidene-2,3-dibromopropylamines 7a–d<sup>15</sup>

A stirred and cooled (0°C) solution of 0.1 mol of *N*-(arylidene)allylamines **6** in 150 mL of dry dichloromethane was treated dropwise with a solution of 0.1 mol of bromine in 30 mL of dichloromethane. After complete addition, stirring was continued at 0°C for 30 min and the solvent was removed in vacuo to afford the *N*-arylidene-2,3-dibromopropylamines **7a–d** in quantitative yield (purity >97%). These labile dibromoaldimines **7** were used as such for the next step.

**3.2.1. *N*-(Benzylidene)-2,3-dibromopropylamine 7a.** Crude yield 100%, yellow oil. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>):  $\delta$  3.88 (2H, d, *J*=6.8 Hz, CH<sub>2</sub>N); 4.0–4.2 (2H, m, CH<sub>2</sub>Br); 4.2–4.7 (1H, m, CHBr); 7.3–7.6 (3H, m, =CH<sub>para, meta</sub>); 7.6–7.9 (2H, m, =CH<sub>ortho</sub>); 8.33 (1H, broad s, CH=N). <sup>13</sup>C NMR (20 MHz, CDCl<sub>3</sub>):  $\delta$  34.00 (t, CH<sub>2</sub>Br); 51.10 (d, CHBr); 64.00 (t, CH<sub>2</sub>N); 128.30 and 128.50 (each d, =C<sub>meta</sub> and =C<sub>para</sub>); 130.96 (d, =C<sub>ortho</sub>); 135.63 (s, C<sub>quat</sub>); 163.59 (d, CH=N). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1645 (C=N). MS (70 eV) *m/z* (%): 303/5/7 (M<sup>+</sup>; 1); 224/6 (24); 169/71 (2); 149 (9); 145 (7); 144 (12); 121 (5); 118 (100); 117 (10); 106 (5); 105 (7); 104 (15); 92 (7); 91 (86); 90 (12); 89 (12); 77 (19); 76 (5); 65 (7); 63 (5); 58 (5); 57 (5); 51 (14); 50 (7); 44 (3); 43 (5); 41 (33).

**3.2.2. *N*-(4-Chlorobenzylidene)-2,3-dibromopropylamine 7d.** Crude yield 100%, yellow oil. <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>):  $\delta$  3.93 (2H, d, *J*=7.2 Hz, CH<sub>2</sub>N); 4.1–4.3 (2H, m, CH<sub>2</sub>Br); 4.3–4.8 (1H, m, CHBr); 7.52 and 7.84 (each 2H, each d, *J*=8.8 Hz, =CH<sub>para, meta</sub>); 8.40 (1H, broad s, CH=N). <sup>13</sup>C NMR (20 MHz, CDCl<sub>3</sub>):  $\delta$  33.89 (t, CH<sub>2</sub>Br); 50.61 (d, CHBr); 63.34 (t, CH<sub>2</sub>N); 129.06 and 130.09 (each d, =C<sub>meta</sub> and =C<sub>para</sub>); 130.84 and 137.92 (s, C<sub>quat</sub>); 163.31 (d, CH=N). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1648 (C=N). MS (70 eV) *m/z* (%): 337/39/41/43 (M<sup>+</sup>; 10); 263 (21); 262 (21); 259/61 (12); 258/60 (42); 179 (12); 155 (15); 154 (49); 153 (30); 152 (100); 140 (12); 138 (21); 128 (12); 127 (45); 126 (22); 125 (84); 124 (15); 121 (15); 117/9 (14);

116 (12); 111 (17); 102 (14); 90 (18); 89 (34); 76 (15); 75 (21); 63 (17); 51 (15); 50 (14); 41 (36).

**3.2.3. 2,3-Dibromo-*N*-(3-cyclohexen-1-yl-methylidene)-1-propanamine 7e.** Crude yield 95%, yellow oil. Attempted distillation under vacuum (0.5 mmHg, oil bath 100°C) resulted in a very exothermic decomposition of the crude product. Therefore, the product was used as such in the next step (purity >96%). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  1.4–2.6 (8H, m, CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>CH); 3.7–4.0 (4H, m, CH<sub>2</sub>N and CH<sub>2</sub>Br); 4.35–4.48 (1H, m, CHBr); 6.69 (2H, broad s, CH=CH); 7.67 (1H, d, *J*=4.6 Hz, NCH=). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>):  $\delta$  24.08 (CH<sub>2</sub>); 25.52 (CH); 27.78 (CH<sub>2</sub>CH=); 33.82 (CH<sub>2</sub>CH=); 39.35 (CHBr); 51.12 (CH<sub>2</sub>Br); 64.08 (CH<sub>2</sub>N); 125.26 (CH=CH); 126.97 and 127.02 (CH=CH); 171.91 and 172.00 (C=N). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1670 (C=N); 1652 (C=C). It was not possible to obtain a correct mass spectrum of this compound due to its lability.

### 3.3. 2-(Bromomethyl)aziridines 8a–c<sup>15</sup>

A stirred solution of 0.1 mol of *N*-arylidene-2,3-dibromopropylamine **7a–c** in 150 mL of absolute methanol was treated portionwise with 0.2 mol of sodium borohydride. The reaction was refluxed for 2 h, then cooled to room temperature. The solution was poured into water, and extraction was performed with dichloromethane (three times 100 mL). The combined extracts were dried (MgSO<sub>4</sub>) and evaporated in vacuo to give the crude aziridines, which were purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate: 8/2) affording pure compounds **8a–d**. Spectral data of compounds **8a** and **8d** have been reported elsewhere.<sup>15</sup>

**3.3.1. 2-Bromomethyl-1-(4-methoxybenzyl)aziridine 8b.** Yield 86%; colorless oil. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  1.62 (1H, d, *J*=6.3 Hz, NC(H)*H*<sub>cis</sub>); 1.78 (1H, d, *J*=3.3 Hz, NC(H)*H*<sub>trans</sub>); 1.91–1.95 (1H, m, NCH); 3.30 (1H, d×d, *J*=6.3, 2.7 Hz, CH<sub>2</sub>Br); 3.34 and 3.51 (each 1H, each d, *J*=12.9 Hz, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 3.80 (3H, s, OCH<sub>3</sub>); 6.87 and 7.25 (each 2H, each d, *J*=8.6 Hz, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>):  $\delta$  35.11 and 35.26 (CH<sub>2</sub>N and CH<sub>2</sub>Br or vice versa); 39.84 (NCH); 54.97 (OCH<sub>3</sub>); 63.40 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 113.51 and 129.18 ( $HC_{ortho+meta}$ ); 130.39 (C–CH<sub>2</sub>); 158.60 (C–OMe). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1613; 1514; 1274; 1026. MS (70 eV) *m/z* (%): 255/257 (M<sup>+</sup>; 1); 176 (11); 121 (100); 91 (96); 70 (84); 65 (7). Anal. calcd for C<sub>11</sub>H<sub>14</sub>BrNO: C 51.58%; H 5.51%; N 5.47%. Found: C 51.76%; H 5.62%; N 5.33%.

**3.3.2. 1-(4-Bromobenzyl)-2-bromomethylaziridine 8c.** Yield 90%; colorless oil. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  1.79 (1H, d, *J*=6.3 Hz, NC(H)*H*<sub>cis</sub>); 1.82 (1H, d, *J*=3.3 Hz, N(H)*H*<sub>trans</sub>); 1.89–1.96 (1H, m, NCH); 3.28 (1H, d×d, *J*=10.1, 6.9 Hz, C(H)HBr); 3.33 (1H, d×d, *J*=10.1, 6.1 Hz, C(H)HBr); 3.36 and 3.50 (each 1H, each d, *J*=13.5 Hz, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 7.23 and 7.46 (each 2H, each d, *J*=8.6 Hz, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>):  $\delta$  34.95 and 35.60 (CH<sub>2</sub>N and CH<sub>2</sub>Br); 40.20 (NCH); 63.38 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 120.94 (=C–CH<sub>2</sub>); 129.69 and 131.30 ( $HC_{ortho+meta}$ ); 137.41 (=C–Br). IR (NaCl, cm<sup>-1</sup>):  $\nu$ =1592; 1487; 1404; 1222; 1070; 1010; 801. MS (70 eV) *m/z* (%): no M<sup>+</sup>;

224/226 (M<sup>+</sup>–Br, 6); 212/214 (2); 188/190 (3); 170/172 (13); 84 (13); 51 (28); 49 (100). Anal. calcd for C<sub>10</sub>H<sub>11</sub>Br<sub>2</sub>N: C 39.38%; H 3.64%; N 4.59%. Found: C 39.49%; H 3.52%; N 4.49%.

**3.3.3. 2-(Bromomethyl)-1-(3-cyclohexen-1-yl-methyl)-aziridine 8e.** Yield 75%; light yellow oil. An inseparable mixture of two diastereomers was obtained as observed in the <sup>13</sup>C NMR spectrum. Capillary GC analysis however showed only one peak, though broadened. Spectra were recorded on the purified mixture of two diastereomers. Eluent EtOAc/*n*-hexane 40/60, R<sub>f</sub>=0.41. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.2–1.4 and 1.7–1.8 (2×1H, 2×m, CH<sub>2</sub>); 1.2–1.4 and 1.9–2.1 (2×1H, 2×m, CH<sub>2</sub>, other diastereomer); 1.7–2.2 (2H, m, CH<sub>2</sub>); 2.0–2.3 (2×1H, 2×m, CH overlap); 1.7–2.0 (1H, m, CH overlap); 1.47–1.51 and 1.7–1.8 (2×1H, m, CH<sub>2</sub>); 6.67 (2H, broad s, CH=CH). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 24.69 and 24.74 (CH<sub>2</sub>); 26.75 and 27.04 (CH<sub>2</sub>); 29.97 and 30.08 (CH); 34.27 (2×CH); 35.76 and 35.83 (CH<sub>2</sub>Br); 36.08 (2×CH<sub>2</sub>); 39.98 (2×CH<sub>2</sub>); 66.76 and 67.12 (CH<sub>2</sub>N); 125.91; 126.13; 126.83 and 127.19 (CH=CH). IR (NaCl, cm<sup>-1</sup>): ν=1651 (C=C); 3020; 2913; 2835; 1450; 1435; 1220. MS (70 eV) *m/z* (%): 230/32 (M<sup>+</sup>; 11); 187/9 (4); 151 (70); 149 (11); 110 (3); 96 (7); 95 (11); 94 (18); 81 (6); 80 (18); 71 (100); 69 (7); 68 (13); 56 (5); 55 (6); 53 (6). Anal. calcd for C<sub>10</sub>H<sub>16</sub>BrN: C 52.19%; H 7.01%; N 6.09%. Found: C 52.02%; H 7.12%; N 6.20%.

### 3.4. 1-Mesyl- and 1-tosyl-2-(bromomethyl)aziridines 8d,e

A stirred and cooled (0°C) solution of 150 mmol of *N*-allyl-*p*-toluenesulfonamide **9a** or *N*-allylmethanesulfonamide **9b** in 150 mL of dry dichloromethane was treated dropwise with a solution of 150 mmol of bromine in 50 mL of dichloromethane. After complete addition, stirring was continued at 0°C for 1 h and the solvent was removed in vacuo. Then the reaction mixture was dissolved in 100 mL of ethanol and this solution was added to 1 M aqueous sodium hydroxide solution (750 mL). The reaction mixture was stirred for 10 min at room temperature and extracted with ether. The organic solution was dried (MgSO<sub>4</sub>) and concentrated in vacuo to give the crude products.

**3.4.1. 1-(Bromomethyl)-1-(*p*-toluenesulfonyl)aziridine 8e.** Yield 90%; colorless oil; bp 146°C/0.1 mmHg. Flash chromatography on silica gel: EtOAc/*n*-hexane: 1/4, R<sub>f</sub>=0.24. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 2.21 (1H, d, J=4.0 Hz, NC(H)*H*<sub>trans</sub>); 2.43 (3H, s, CH<sub>3</sub>); 2.82 (1H, d, J=6.6 Hz, NC(H)*H*<sub>cis</sub>); 3.05–3.10 (1H, m, NCH); 3.25 (2H, d, J=6.3 Hz, CH<sub>2</sub>Br); 7.36 and 7.82 (2H, d, J=8.3 Hz, HC<sub>meta</sub> and HC<sub>ortho</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.61 (CH<sub>3</sub>); 30.73 (CH<sub>2</sub>N); 34.20 (CH<sub>2</sub>Br); 39.83 (NCH); 128.24 (2×HC<sub>arom</sub>); 129.72 (2×HC<sub>arom</sub>); 134.30 (C<sub>quat</sub>); 144.89 (C<sub>quat</sub>). IR (KBr, cm<sup>-1</sup>): ν=1647; 1596; 1425; 1162; 1093. MS (70 eV) *m/z* (%): 289/291 (M<sup>+</sup>, 1); 210 (M<sup>+</sup>–Br, 35); 155 (49); 134 (63); 91 (100); 55 (71). Anal. calcd for C<sub>10</sub>H<sub>12</sub>BrSO<sub>2</sub>N: C 41.39%; H 4.17%; N 4.83%. Found: C 41.25%; H 4.27%; N 4.76%.

**3.4.2. 2-(Bromomethyl)-1-(methanesulfonyl)aziridine 8f.** Yield 83%; colorless oil. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ

2.67 (1H, d, J=4.0 Hz, NC(H)*H*<sub>trans</sub>); 2.79 (1H, d, J=6.9 Hz, NC(H)*H*<sub>cis</sub>); 3.05–3.18 (1H, m, NCH); 3.14 (3H, s, CH<sub>3</sub>); 3.20 (1H, d, J=10.5, 8.2 Hz, C(H)HBr); 3.51 (1H, d, J=10.5, 4.6 Hz, C(H)HBr). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.25 (CH<sub>3</sub>); 33.49 (CH<sub>2</sub>N); 39.70 (CH<sub>2</sub>Br); 40.00 (NCH). IR (NaCl, cm<sup>-1</sup>): ν=3028; 1648; 1428; 1314. MS (70 eV) *m/z* (%): 215/213 (M<sup>+</sup>, 1); 134 (87); 55 (100). Anal. calcd for C<sub>4</sub>H<sub>8</sub>BrSO<sub>2</sub>N: C 22.44%; H 3.77%; N 6.54%. Found: C 22.38%; H 3.86%; N 6.69%.

### 3.5. Reaction of 2-(bromomethyl)aziridines with magnesium in methanol

**Method 1.** To a stirred solution of 3 mmol of 2-(bromomethyl)aziridine **8** in 10 mL of dry methanol was added 0.36 g (15 mmol) of magnesium metal (turnings). The reaction mixture was stirred at room temperature for 3 days under nitrogen atmosphere. Afterwards the reaction mixture was passed through a silica gel column (diameter 2 cm, 20 cm length) and the column was eluted with 50 mL of methanol. The elutes were concentrated in vacuo to give the pure ammonium bromide **17a–e.HBr** or *N*-allylamide **17f,g**. Compounds **17f,g** could be purified by high vacuum distillation. Basic workup of the hydrobromides **17a–e.HBr** with 2 M aqueous sodium hydroxide solution and extraction with dichloromethane furnished the free amines **17a–e** as colorless to light yellow oils after drying (MgSO<sub>4</sub>) and evaporation of the solvent in vacuo.

**Method 2.** To a solution of 3 mmol of 2-(bromomethyl)aziridine **8** in 10 mL of dry methanol was added 0.36 g (15 mmol) of magnesium metal (turnings). The reaction mixture was sonicated for 4 hours under nitrogen atmosphere. The reaction was started at room temperature and gradually the temperature rose to 50–60°C after 4 h. The workup procedure is identical to method 1.

**3.5.1. *N*-Allyl-*N*-benzylamine hydrobromide 17a.HBr.** Yield 90%; white crystals; mp 139.5–140.1°C. The <sup>1</sup>H NMR and <sup>13</sup>C NMR are in agreement between certain limits with the literature data published for the so-called free amine **17a** (see text).<sup>12</sup> <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 3.48 (2H, d, J=6.9 Hz, CH<sub>2</sub>NH); 4.08 (2H, s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N); 5.41–5.49 (2H, m, CH<sub>2</sub>=CH); 6.04–6.19 (1H, m, CH<sub>2</sub>=CH); 7.36–7.44 (3H, m, HC<sub>meta</sub> and HC<sub>para</sub>); 7.59–7.63 (2H, m, HC<sub>ortho</sub>); 9.5 (2H, broad s, +NH<sub>2</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 48.16 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>); 49.40 (CH<sub>2</sub>NH); 124.49 (CH<sub>2</sub>=CH); 127.46; 129.09 (2×=CH<sub>arom</sub>); 129.54; 129.77; 130.65 (2×=CH<sub>arom</sub>). IR (KBr pellet, cm<sup>-1</sup>): ν=3130–2551; 2399; 1646; 1612; 1572; 1501; 1455; 1424; 1213; 989; 942. Anal. calcd for C<sub>10</sub>H<sub>14</sub>BrN: C 52.65%; H 6.19%; N 6.14%. Found: C 52.55%; H 6.26%; N 6.22%.

**3.5.2. *N*-Allyl-*N*-benzylamine 17a.** Yield 70%; colorless oil. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.44 (1H, broad s, NH); 3.25 (2H, d, J=5.9, 1.3 Hz, NHCH<sub>2</sub>); 3.76 (2H, s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>); 5.07–5.21 (2H, m, CH=CH<sub>2</sub>); 5.84–5.99 (1H, m, CH=CH<sub>2</sub>); 7.19–7.31 (5H, m, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 51.75 (NHCH<sub>2</sub>); 53.24 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 115.94 (CH<sub>2</sub>=CH); 126.92 (HC<sub>para</sub>); 128.16 and 128.37 (HC<sub>ortho+meta</sub>); 136.80 (CH<sub>2</sub>=CH); 140.27 (C<sub>arom, quat</sub>). IR (NaCl, cm<sup>-1</sup>): ν=3314 (NH); 1643; 1604; 1495; 1454

(C=C). MS (70 eV)  $m/z$  (%): 148 ( $M^+$ ; 31); 91 (100); 57 (31). These spectra are in accordance with the literature data.<sup>22</sup>

### 3.5.3. *N*-Allyl-*N*-(4-methoxybenzyl)amine hydrobromide

**17b.HBr.** Yield 90%; white crystals; mp 136.7–137.6°C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 3.43 (2H, txd,  $J=5.9$ , 5.1 Hz, =CH<sub>2</sub>CH<sub>2</sub>N); 3.72 (3H, s, OCH<sub>3</sub>); 3.98 (2H, t,  $J=5.4$  Hz, CH<sub>2</sub>NH<sub>2</sub>); 5.38–5.45 (2H, m, CH<sub>2</sub>=CH); 5.99–6.15 (1H, m, CH<sub>2</sub>=CH); 6.86 (2H, d,  $J=8.6$  Hz, 2×HC<sub>arom</sub>); 7.49 (2H, d,  $J=8.6$  Hz, 2×HC<sub>arom</sub>); 9.3 (2H, broad s, +NH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 48.00 and 48.98 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and CH<sub>2</sub>NH); 55.20 (OCH<sub>3</sub>); 114.37 (2×HC<sub>arom</sub>); 121.62 and 124.35 (CH<sub>2</sub>=CH and C–CH<sub>2</sub>); 127.56 (CH<sub>2</sub>=CH); 132.22 (2×HC<sub>arom</sub>); 160.37 (C–OMe). IR (KBr pellet, cm<sup>-1</sup>): ν=3130–2300; 1614; 1584; 1568; 1516; 1455; 1431; 1299; 1250; 1180; 1036. Anal. calcd for C<sub>11</sub>H<sub>16</sub>BrNO: C 51.18%; H 6.25%; N 5.43%. Found: C 51.30%; H 6.31%; N 5.31%.

**3.5.4. *N*-Allyl-*N*-(4-methoxybenzyl)amine 17b.** This compound has been reported before in the literature, spectroscopic data however are lacking.<sup>23</sup> Yield 71%, colorless oil.

<sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.5 (1H, broad s, NH); 3.26 (2H, d,  $J=5.9$  Hz, CH<sub>2</sub>NH); 3.73 (2H, s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N); 3.80 (3H, s, OCH<sub>3</sub>); 5.09–5.22 (2H, m, CH<sub>2</sub>=CH); 5.86–6.00 (1H, m, CH<sub>2</sub>=CH); 6.86 (2H, d,  $J=8.6$  Hz, 2×HC<sub>arom</sub>); 7.23 (2H, d,  $J=8.6$  Hz, 2×HC<sub>arom</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 52.0 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>); 53.0 (CH<sub>2</sub>NH); 55.7 (OCH<sub>3</sub>); 114.2 (CH<sub>2</sub>=CH); 116.6 (2×HC<sub>arom</sub>); 129.7 (2×HC<sub>arom</sub>); 130.4 (C<sub>quat</sub>); 137.0 (CH<sub>2</sub>=CH); 159.0 (C<sub>quat</sub>). IR (NaCl, cm<sup>-1</sup>): ν=3317 (NH); 1612 (C=); 1513; 1463; 1301; 1247; 1176; 1036. MS (70 eV)  $m/z$  (%): 177 ( $M^+$ , 33); 149 (10); 121 (100); 83 (58); 56 (10).

### 3.5.5. *N*-Allyl-*N*-(4-bromobenzyl)amine hydrobromide

**17c.HBr.** Yield 86%; white crystals; mp 195.8–196.2°C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 3.46 (2H, d,  $J=6.9$  Hz, CH<sub>2</sub>NH<sub>2</sub>); 4.02 (2H, s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N); 5.40–5.52 (2H, m, CH<sub>2</sub>=CH); 6.00–6.15 (1H, m, CH<sub>2</sub>=CH); 7.48 and 7.53 (each 2H, each d,  $J=8.6$  Hz, HC<sub>ortho+meta</sub>); 9.5 (2H, broad s, +NH<sub>2</sub>). <sup>1</sup>H NMR (270 MHz, DMSO): δ 3.62 (2H, d,  $J=6.6$  Hz, CH<sub>2</sub>NH<sub>2</sub>); 4.14 (2H, s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N); 5.40–5.51 (2H, m, CH<sub>2</sub>=CH); 5.88–6.03 (1H, m, CH<sub>2</sub>=CH); 7.50 and 7.65 (each 2H, each d,  $J=8.3$  Hz, HC<sub>ortho+meta</sub>); 9.2 (2H, broad s, +NH<sub>2</sub>). <sup>13</sup>C NMR (68 MHz, DMSO): δ 48.43 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and CH<sub>2</sub>NH); 122.31 (C<sub>quat</sub>); 122.32 (CH<sub>2</sub>=CH); 128.73 (CH<sub>2</sub>=CH); 131.07 (C<sub>quat</sub>); 131.39 and 132.38 (HC<sub>ortho+meta</sub>). IR (KBr pellet, cm<sup>-1</sup>): ν=3070–2500; 2411; 1576; 1492; 1432; 1074. Anal. calcd for C<sub>10</sub>H<sub>13</sub>Br<sub>2</sub>N: C 39.12%; H 4.27%; N 4.56%. Found: C 39.02%; H 4.35%; N 4.65%.

**3.5.6. *N*-Allyl-*N*-(4-bromobenzyl)amine 17c.** Yield 70%; colorless oil. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.70 (1H, broad s, NH); 3.24 (2H, dxt,  $J=5.9$ , 1.3 Hz, CH<sub>2</sub>NH); 3.73 (2H, s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N); 5.11 (1H, dxdxt,  $J=10.2$ , 1.7, 1.3 Hz, CH=C(H)H); 5.18 (1H, dxdxt,  $J=17.2$ , 1.7, 1.7 Hz, CH=C(H)H); 5.85–5.95 (1H, dxdxt,  $J=17.2$ , 10.2, 5.9 Hz, CH=CH<sub>2</sub>); 7.19 and 7.43 (each 2H, each d,  $J=8.4$  Hz, HC<sub>ortho+meta</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 51.52 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>); 52.33 (CH<sub>2</sub>NH); 116.10 (CH<sub>2</sub>=CH); 120.58 (C<sub>quat</sub>); 129.76 and 131.30 (HC<sub>ortho+meta</sub>); 136.42

(CH<sub>2</sub>=CH); 139.12 (C<sub>quat</sub>); IR (NaCl, cm<sup>-1</sup>): ν=3312 (NH); 1643 (CH=CH<sub>2</sub>); 1592; 1487; 1403; 1104; 1070; 1011; 994. MS (70 eV)  $m/z$  (%): 225/227 ( $M^+$ , 37); 214/212 (15); 172/170 (100); 122 (55); 121 (57). Anal. calcd for C<sub>10</sub>H<sub>12</sub>BrN: C 53.12%; H 5.35%; N 6.19%. Found: C 52.97%; H 5.25%; N 6.31%.

### 3.5.7. *N*-Allyl-*N*-(4-chlorobenzyl)amine hydrobromide

**17d.HBr.** Yield 85%; white crystals; mp 194.8–195.6°C. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data are in agreement between certain limits with the literature data published for the so-called free amine **17d**.<sup>16</sup> <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 3.46 (2H, d,  $J=6.9$  Hz, +NH<sub>2</sub>CH<sub>2</sub>CH=); 4.04 (2H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 5.42–5.51 (2H, m, CH=CH<sub>2</sub>); 6.08 (1H, dxdxt,  $J=17.2$ , 10.9, 6.9 Hz, CH=CH<sub>2</sub>); 7.37 and 7.56 (2×2H, 2×d,  $J=8.4$  Hz, C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR (270 MHz, DMSO): δ 3.62 (2H, d,  $J=6.3$  Hz, +NH<sub>2</sub>CH<sub>2</sub>CH=); 4.16 (2H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 5.40–5.51 (2H, m, CH=CH<sub>2</sub>); 5.88–6.03 (1H, m, CH=CH<sub>2</sub>); 7.51 and 7.59 (2×2H, 2×d,  $J=8.3$  Hz, C<sub>6</sub>H<sub>4</sub>); 9.1 (2H, broad s, +NH<sub>2</sub>). <sup>13</sup>C NMR (68 MHz, DMSO): δ 48.34 and 48.39 (NHCH<sub>2</sub> and C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 122.51 (CH<sub>2</sub>=CH); 128.46 (HC<sub>ortho</sub>); 128.84 (CH<sub>2</sub>=CH); 130.83 (C<sub>quat</sub>); 132.06 (HC<sub>ortho</sub>); 133.56 (C<sub>arom, quat</sub>). IR (KBr pellet, cm<sup>-1</sup>): ν=3170–2450; 2399; 1568; 1495; 1434; 1094; 1019. Anal. calcd for C<sub>10</sub>H<sub>13</sub>BrClN: C 45.74%; H 4.99%; N 5.33%. Found: C 45.64%; H 4.10%; N 5.24%.

### 3.5.8. *N*-Allyl-*N*-(4-chlorobenzyl)amine 17d.

Yield 79%; colorless oil. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.5 (1H, broad s, NH); 3.25 (2H, dxt,  $J=5.9$ , 1.3 Hz, NHCH<sub>2</sub>CH=); 3.76 (2H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 5.12 (1H, dxdxt,  $J=10.9$ , 1.7, 1.3 Hz, CH=C(H)H); 5.19 (1H, dxdxt,  $J=17.2$ , 1.7, 1.7 Hz, CH=C(H)H); 5.92 (1H, dxdxt,  $J=17.2$ , 10.9, 5.9 Hz, CH=CH<sub>2</sub>); 7.18–7.30 (4H, m, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 51.66 (NHCH<sub>2</sub>); 52.43 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>); 116.19 (CH<sub>2</sub>=CH); 128.48 and 129.50 (HC<sub>ortho+meta</sub>); 132.59 (=C–Cl); 136.57 (CH<sub>2</sub>=CH); 138.74 (C<sub>arom, quat</sub>). IR (NaCl, cm<sup>-1</sup>): ν=3315 (NH); 1643; 1597; 1491; 1453 (C=C). MS (70 eV)  $m/z$  (%): 182/4 ( $M^+$ , 34); 126/8 (100); 57 (17). Anal. calcd for C<sub>10</sub>H<sub>12</sub>ClN: C 66.12%; H 6.66%; N 7.71%. Found: C 66.01%; H 6.75%; N 7.62%.

### 3.5.9. *N*-Allyl-*N*-(3-cyclohexen-1-yl-methyl)amine hydrobromide

**17e.HBr.** Flash chromatography with CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1,  $R_f=0.15$ . Yield 78%; light yellow waxy solid. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.32–1.46 and 1.81–1.99 (overlap) (2×1H, 2×m, CH(H) and CH(H)); 2.09 (2H, broad s, CH<sub>2</sub>CH=CH (overlap)); 1.81–1.99 (overlap) and 2.16–2.36 (2×1H, 2×m, CH(H) and CH(H)); 2.16–2.36 (1H, m (overlap), CHCH<sub>2</sub>N); 2.86 (2H, d,  $J=6.6$  Hz, CHCH<sub>2</sub>N); 3.68 (2H, d,  $J=6.9$  Hz, NHCH<sub>2</sub>CH=); 5.08 (1H, dxdxt,  $J=10.1$ , 2.0, 1.6 Hz, CH=C(H)H); 5.17 (1H, dxdxt,  $J=17.2$ , 1.6, 1.6 Hz, CH=C(H)H); 5.67 (2H, broad s, CH=CH); 5.91 (1H, dxdxt,  $J=17.2$ , 10.1, 5.9 Hz, CH=CH<sub>2</sub>); 6.9 (2H, broad s, NH<sub>2</sub><sup>+</sup>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 24.04 (CH<sub>2</sub>CH=CH); 26.31 (CHCH<sub>2</sub>CH<sub>2</sub>); 29.47 (CH=CHCH<sub>2</sub>); 30.93 (CHCH<sub>2</sub>); 50.48 (CH<sub>2</sub>=CHCH<sub>2</sub>NH); 51.73 (CHCH<sub>2</sub>NH); 124.04 (CH<sub>2</sub>=CH); 124.71 and 126.95 (CH=CH); 128.17 (CH<sub>2</sub>=CH). IR (NaCl, cm<sup>-1</sup>): ν=3414; 1651 (C=C). Anal. calcd for C<sub>10</sub>H<sub>18</sub>BrN: C 51.73%; H 7.81%; N 6.03%. Found: C 51.55%; H 7.92%; N 6.13%.

**3.5.10. N-Allyl-N-(3-cyclohexen-1-yl-methyl)amine 17e.**

Yield 73%. These spectra are in accordance with the literature data.<sup>24</sup> For the sake of completeness full spectroscopic data are reported here. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.15–1.35 (2H, m, CH(H) and NH); 1.65–1.81 (3H, m, 2×CH(H) and CH<sub>2</sub>CH); 2.00–2.15 (3H, m, CHCH<sub>2</sub>CH= and CH(H)); 2.53 (2H, d, *J*=6.3 Hz, CHCH<sub>2</sub>N); 3.25 (2H, d, *J*=5.9, 1.3 Hz, NHCH<sub>2</sub>CH=); 5.08 (1H, d, *J*=10.1, 2.0, 1.6 Hz, CH=C(H)H); 5.17 (1H, d, *J*=17.2, 1.6, 1.6 Hz, CH=C(H)H); 5.67 (2H, broad s, CH=CH); 5.91 (1H, d, *J*=17.2, 10.1, 5.9 Hz, CH=CH<sub>2</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 24.92 (CH<sub>2</sub>CH=CH); 27.04 (CHCH<sub>2</sub>CH<sub>2</sub>); 30.10 (CH=CHCH<sub>2</sub>); 33.96 (CHCH<sub>2</sub>); 53.72 (CH<sub>2</sub>=CHCH<sub>2</sub>NH); 55.40 (CHCH<sub>2</sub>NH); 115.85 (CH<sub>2</sub>=CH); 126.13 and 127.11 (CH=CH); 137.00 (CH<sub>2</sub>=CH). IR (NaCl, cm<sup>-1</sup>): ν=3401; 3023; 2926; 1650; 1456; 1378; 1195; 1075; 995; 940; 940; 1670 (C=N); 1652 (C=C). MS (70 eV) *m/z* (%): 151 (M<sup>+</sup>; 3); 136 (2); 122 (2); 109 (10); 108 (4); 94 (4); 79 (8); 70 (100); 68 (6); 56 (3).

**3.5.11. N-Tosylallylamine 17f.**<sup>20,25</sup>

Since no spectra have been published in the literature full spectroscopic data are given here. Crude yield 93%; white solid; mp 63–64°C. After Kugelrohr distillation the yield was 57%; bp 170–180°C/0.1 mmHg. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 2.44 (3H, s, CH<sub>3</sub>); 3.59 (2H, t, *J*=5.9 Hz, CH<sub>2</sub>NH); 4.82 (1H, broad s, NH); 5.08–5.82 (2H, m, CH<sub>2</sub>=CH); 5.66–5.80 (1H, m, CH<sub>2</sub>=CH); 7.32 (2H, d, *J*=8.0 Hz, C<sub>6</sub>H<sub>4</sub>); 7.78 (2H, d, *J*=8.0 Hz, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.50 (CH<sub>3</sub>); 45.71 (CH<sub>2</sub>NH); 117.53 (CH<sub>2</sub>=CH); 127.09 (2×HC<sub>arom</sub>); 129.72 (2×HC<sub>arom</sub>); 133.03 (CH<sub>2</sub>=CH); 136.94 (C<sub>quat</sub>); 143.42 (C<sub>quat</sub>). IR (NaCl, cm<sup>-1</sup>): ν=3283; 1601; 1415; 1153; 1091. MS (70 eV) *m/z* (%): 211 (M<sup>+</sup>, 45); 155 (81); 139 (44); 120 (46); 105 (35); 91 (100).

**3.5.12. N-Mesylallylamine 17g.**<sup>20,25</sup>

Since no spectra have been published in the literature full spectroscopic data are given here. Yield 91%; colorless oil. After Kugelrohr distillation the yield was 81%; bp 104–107°C/0.25 mmHg. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 2.98 (3H, s, CH<sub>3</sub>); 3.76 (2H, t, *J*=4.6 Hz, CH<sub>2</sub>NH); 4.95 (1H, broad s, NH); 5.19–5.35 (2H, m, CH<sub>2</sub>=CH); 5.80–5.94 (1H, m, CH<sub>2</sub>=CH). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 40.38 (CH<sub>3</sub>); 45.27 (CH<sub>2</sub>NH); 117.25 (CH<sub>2</sub>=CH); 133.35 (CH<sub>2</sub>=CH). IR (NaCl, cm<sup>-1</sup>): ν=3292; 1647; 1434; 1413; 1314.

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