



# Diallylaluminium-*N,N*-dimethylaminoethanolate, the first stable allyl-alane suitable for additions to aldehydes, ketones and imines

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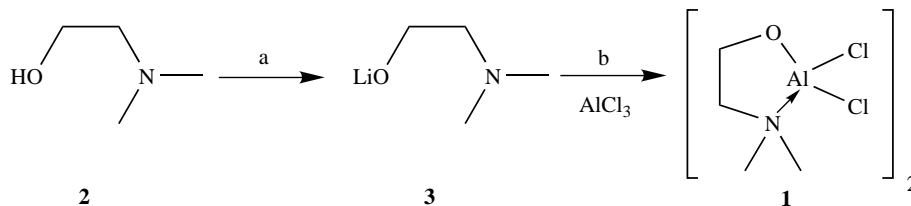
**Abstract**—The reaction of AlCl<sub>3</sub> with lithium-*N,N*-dimethylaminoethanolate (**3**) in a 1:1 ratio yields the corresponding organo-aluminium chloride [Cl<sub>2</sub>Al(μ-OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>] (**1**) from which the diallyl derivative [(CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Al(μ-OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>] (**4**) was synthesized by treatment with 2 equiv. of allyl magnesium bromide. The structures of **1** and **4** were deduced from the <sup>1</sup>H, <sup>13</sup>C, <sup>27</sup>Al NMR spectra and confirmed by X-ray structural determination. The allyl aluminium complex **4** was found to be a useful reagent for the transfer of one allyl group to aldehydes, imines and enones. The 1,2-addition products are formed in high yields. © 2002 Elsevier Science Ltd. All rights reserved.

Although organo-aluminium compounds have found a wide-spread use in organic synthesis,<sup>1</sup> only a few allyl derivatives have been investigated and found application.<sup>2</sup> The etherates of allyl-, methallyl-, and crotyl-aluminium compounds seem to be stable at room temperature,<sup>3</sup> but owing to the high auto reactivity of such allylic alanes so far only one pure compound has been isolated and characterized by <sup>1</sup>H NMR spectroscopy.<sup>4</sup>

In the framework of our studies on intramolecularly stabilized organo-aluminium compounds, we recently reported the synthesis of a vinyl-aluminium compound

and its application in organic synthesis.<sup>5</sup> In this paper the synthesis, spectroscopic investigation and characterization of the allyl analogue and its use in organic synthesis will be reported.

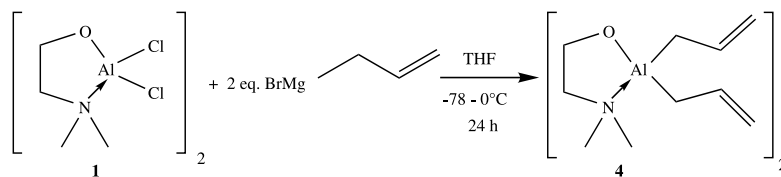
Previously we reported the synthesis of the dimeric dichloroaluminium alkoxide [Cl<sub>2</sub>Al(μ-OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>] (**1**) via abstraction of HCl by reacting equivalent amounts of AlCl<sub>3</sub> with Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (**2**).<sup>5</sup> Via an alternative route pure **1**<sup>6</sup> can be isolated by reacting the lithium-alcoholate (**3**) with equimolar amounts of AlCl<sub>3</sub> (Scheme 1).<sup>7</sup> Recrystallization of the crude product from THF yielded colorless crystals of **1**.



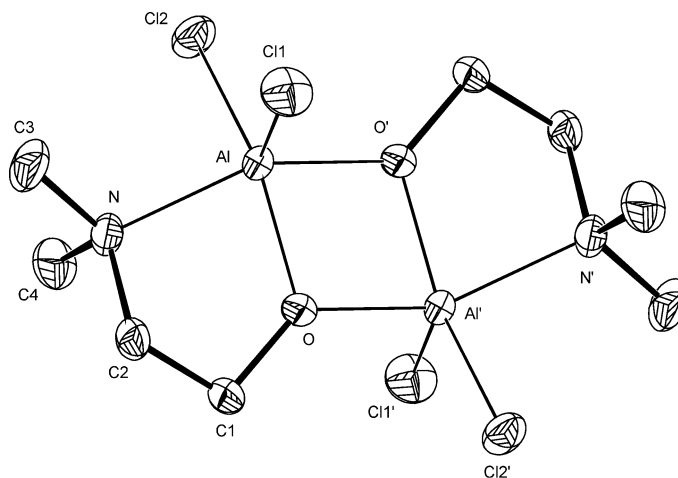
**Scheme 1.** (a) To a solution of Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (**2**) (6.24 g, 70.11 mmol) in *n*-hexane (50 mL) was added *n*-BuLi (44 mL, 70.11 mmol, 1.6 M) in *n*-hexane at 0°C. The mixture was stirred for 12 h at room temperature and the solvent was removed under reduced pressure. The crude product was recrystallized from hexane. Yield: 5.5 g (84%) of **3**. (b) To a solution of AlCl<sub>3</sub> (3.99 g, 29.9 mmol) in diethyl ether (50 mL) at 0°C was added **3** (2.84 g, 29.9 mmol) in diethyl ether (50 mL) at -78°C. The mixture was stirred for 12 h at 20°C, the solvent was decanted, and the crude product was recrystallized from THF. Yield: 4.00 g (74%) of pure **1**.

**Keywords:** addition reaction; aldehydes; allyl complexes; aluminium; imines.

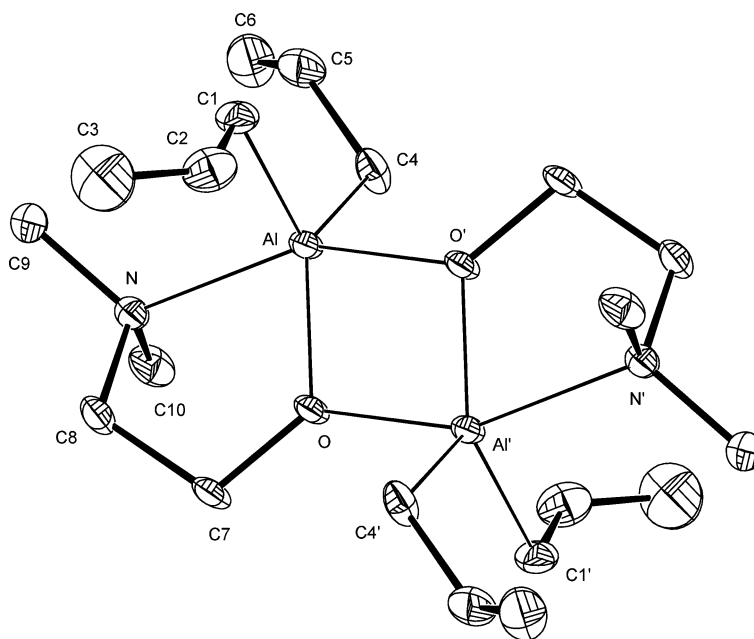
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**Scheme 2.**  $\text{CH}_2=\text{CHCH}_2\text{MgCl}$  (12.7 mL, 1.63 M) in THF was added to **1** (1.91 g, 10.32 mmol) in THF (60 mL) at  $-78^\circ\text{C}$ . The solution was stirred for 12 h at  $0^\circ\text{C}$ , the solvent was removed under vacuum, and the residue was washed with *n*-hexane (70 mL). Filtration and concentration of the organic phase yielded, after recrystallization from hexane, pure **4** (1.44 g, 71%).



**Figure 1.** ORTEP<sup>8</sup> diagram of the structure of  $[\text{Cl}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$  (**1**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Al–O 1.8403(19), Al–O' 1.8632(19), Al–N 2.066(2), Al–Cl(1) 2.1661(10), Al–Cl(2) 2.1833(10); N–Al–O' 152.94(9), O–Al–O' 75.39(9), O–Al–N 81.43(9), O–Al–Cl(1) 111.31(7), O–Al–Cl(2) 138.58(7), O'–Al–Cl(1) 100.72(7), O'–Al–Cl(2) 95.17(7), Cl(1)–Al–Cl(2) 110.06(4), Cl(1)–Al–N 100.58(7), Cl(2)–Al–N 93.02(7). Symmetry transformation used to generate equivalent atoms: (')  $-x+1, -y+1, -z+1$ .



**Figure 2.** ORTEP<sup>8</sup> diagram of the structure of  $[(\text{CH}_2=\text{CHCH}_2)_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$  (**4**). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Al–O 1.8390(16), Al–O' 1.9426(15), Al–N 2.2026(18), Al–C(1) 2.010(2), Al–C(4) 2.014(2), C(1)–C(2) 1.471(4), C(2)–C(3) 1.303(4), C(4)–C(5) 1.462(3), C(5)–C(6) 1.327(4); N–Al–O' 153.85(8), O–Al–O' 74.24(7), O–Al–N 79.72(7), O–Al–C(1) 118.69(9), O–Al–C(4) 127.28(10), O'–Al–C(1) 95.74(9), O'–Al–C(4) 97.31(8), C(1)–Al–C(4) 113.87(11), C(1)–Al–N 98.80(9), C(4)–Al–N 96.50(8). Symmetry transformation used to generate equivalent atoms: (')  $-x+1, -y+1, -z+1$ .

**Table 1.** Allyltransfer studies on 1,2- and 1,4-addition of  $[(\text{CH}_2=\text{CHCH}_2)_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2]$  (**4**) to various enones, aldehydes and imines

Entry	Starting material	Conditions	Product	Yield (%) <sup>a</sup>
	<b>5a</b>		<b>9a</b>	
1 <sup>b</sup>				93
2 <sup>b</sup>				95
3 <sup>d</sup>		T = 100°C		90
4 <sup>e</sup>				87
				(ratio 1:3)
5 <sup>f</sup>	<b>8</b>	T = 22°C, 10 mol% Ni(acac) <sub>2</sub>	<b>11b</b>	91

<sup>a</sup> Isolated yields.<sup>b</sup> 0.45 g (2.69 mmol) of **4** is solved in toluene (5 mL), added drop-wise to a solution of 0.29 g (2.96 mmol) in **5a** in toluene (5 mL) heated to 100°C for 12 h, and quenched with aqueous NaCl (20 mL) and HCl (10%, 2 mL). Extraction with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated, followed by purification by column chromatography (hexane/ethyl acetate 20/1). Yield: 0.37 g (93%) of **9a**.<sup>c</sup> 0.2 g (1.01 mmol) of **4**, 0.19 g (1.01 mmol) of **6b**. Yield: 0.22 g (95%) of **9b**.<sup>d</sup> 0.94 g (4.76 mmol) of **4**, 0.89 g (4.76 mmol) of **7**. Yield: 0.98 g (90%) of **10**.<sup>e</sup> 0.18 g (1.0 mmol) of **4**, 0.21 g (1.0 mmol) of **8**. Yield: 0.07 g of **11a** and 0.15 g of **11b** (87%).<sup>f</sup> 0.11 g (0.65 mmol) of **4** is solved in toluene (5 mL). 0.14 g (0.65 mmol) of *trans*-chalcone **8** in toluene (5 mL) and 10 mol% of Ni(acac)<sub>2</sub> are added, stirring for 12 h at 22°C. Yield: 0.15 g (91%) of **11b**.

*N,N*-Dimethylaminoethanolatoaluminium dichloride (**1**) reacts with 2 equiv. of allyl magnesium bromide to form the new diallyl-aluminum complex  $[(\text{CH}_2=\text{CHCH}_2)_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2]$  (**4**)<sup>9</sup> via salt elimination (Scheme 2). Compound **4** could be isolated as colorless crystals from its *n*-hexane solution. The compound proved to be stable at room temperature. Even

after a couple of days storage under nitrogen no decomposition was observed.

Crystals of **1** (Fig. 1) and **4** (Fig. 2) suitable for single-crystal X-ray analysis<sup>10</sup> were obtained from THF and *n*-hexane solution at -28°C. Compounds **1** and **4** are oxygen-bridged dimeric molecules with inversion

symmetry in the solid state. In both compounds, the aluminium atoms are five-coordinated with a distorted trigonal bipyramidal geometry. The nitrogen and one oxygen atom are in the axial positions, whereas the bridging oxygen and two chlorine atoms (**1**) or the bridging oxygen and two carbon atoms of the allylic groups (**4**) occupy the equatorial positions. The Al–O<sub>axial</sub> (1.94 Å), Al–O<sub>equat.</sub> (1.84 Å) and Al–N bond lengths (2.20 Å) and the N–Al–O' angle (153.9°) in **4** are in close accordance with the values recently reported for the analogous vinylalane (Al–O<sub>axial</sub> 1.92 Å; Al–O<sub>equat.</sub> 1.84 Å; N–Al–O' 153.1°).<sup>5</sup> The electron-withdrawing effect of the chlorine is responsible for the decrease of the Al–N (2.07 Å) and Al–O<sub>axial</sub> (1.86 Å) distances in **1**, but does not affect the Al–O<sub>equat.</sub> (1.84 Å) distance, which is similar to that in **4** and close to values found for other dimethylaminoalkoxides.<sup>11</sup>

In order to test the use of compound **4** in organic synthesis, a variety of aldehydes, imines, and enones were reacted with the allyl-alane (Table 1).<sup>12</sup> In a standard procedure, a solution of the substrate in toluene was treated with **4**. The mixture was stirred for 12 h at 100°C, and after a standard workup in the case of benzaldehyde **5a**, *para*-bromo-benzaldehyde **6b** (entries 1 and 2) and benzylidene-cyclohexyl-amine **7** (entry 3), the 1,2-addition products **9a**,<sup>13</sup> **9b**<sup>14</sup> and **10**<sup>15</sup> were isolated in high yields. Treatment of 1,3-diphenyl-2-propene-1-one PhCH=CHCOPh (*trans*-chalcone) (**8**) with alane **4** at 100°C yields a mixture of 1,4- (**11a**)<sup>16</sup> and 1,2-adduct (**11b**)<sup>17</sup> in a 1:3 ratio (entry 4). The regioselectivity of the transfer improved under milder conditions upon addition of 10 mol% Ni(acac)<sub>2</sub>-catalyst. The reaction was stirred at room temperature for 12 h and solely 1,2-adduct isolated (entry 5).

In summary, *N,N*-dimethylaminoethanolatoaluminium dichloride (**1**) is an excellent starting material for the synthesis of intramolecularly stabilized organo-aluminium compounds with allylic ligands. It enables the synthesis of the first stable allyl-aluminium compound **4**, which has been characterized by X-ray structure analysis, via salt elimination. This new type of aluminium reagent shows high potentials in organic synthesis, as demonstrated in the transfer of the allyl group to a selection of aldehydes, carbonyles, and imines via a 1,2-addition.

### Acknowledgements

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- Spectral data for **1**: <sup>1</sup>H NMR (d-pyridin): δ 2.47 (s, 6H, NCH<sub>3</sub>), 2.83 (t, 1H, *J*=6.06 Hz, NCH<sub>2</sub>), 4.05 (t, 2H, *J*=6.06 Hz, OCH<sub>2</sub>). <sup>13</sup>C NMR (d-pyridin): δ 33.12, 52.12, 58.77. <sup>27</sup>Al NMR: 58.20 Hz. Mp 248.5–249.0°C (dec.). Anal. calcd for C<sub>8</sub>H<sub>20</sub>Al<sub>2</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C, 25.83; H, 5.42. Found C, 25.61; H, 6.11%. MS: *m/z* (%): 371.9 (1) [M]<sup>+</sup>, 337.1 (11), 72.1 (18), 77.2 (23), 58.1 (100).
- All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen using Schlenk techniques. Solvents were dried over sodium, purified and saturated with nitrogen prior to use. Elemental analyses were performed on a Perkin–Elmer 240 C elemental analyser. Mass spectra (electron impact ionisation) were obtained on a Varian MAT 311 A instrument (70 eV). NMR spectra were recorded on a Bruker ARX 200 spectrometer (<sup>1</sup>H NMR at 200 MHz; <sup>13</sup>C{<sup>1</sup>H} NMR at 50.32 MHz) unless stated otherwise.
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- Spectral data for **4**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.19 (d, 8H, *J*=8.67 Hz, AlCH<sub>2</sub>), 1.87 (s, 6H, NCH<sub>3</sub>), 1.95 (t, 2H, *J*=5.88 Hz, NCH<sub>2</sub>), 3.48 (t, 2H, *J*=5.88 Hz, OCH<sub>2</sub>), 4.75–4.82 (m, 1H, CH=CHH'), 4.89–4.91 (m, 1H, CH=CHH'), 6.22–6.35 (m, 1H, CH=CHH'). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 20.18, 44.77, 56.96, 59.01, 105.34, 143.93. <sup>27</sup>Al NMR: 89.23 Hz. Mp 100.2–101.6°C. Anal. calcd for C<sub>20</sub>H<sub>40</sub>Al<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 60.89; H, 10.22. Found C, 60.12; H, 10.36%. MS: *m/z* (%): 353.1 (14) [M–C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>, 156.0 (28), 72.1 (100), 42.0 (32).
- X-Ray structure determination.** Data were collected on a Siemens SMART CCD diffractometer (graphite monochromated Mo K $\alpha$  radiation,  $\lambda$ =0.71073 Å) with area-detector at 173 K. The structures were solved by direct methods and refined on *F*<sup>2</sup> using all reflections with the SHELX-97 software package [Sheldrick, G. M. SHELX-97 Program for Crystal Structure Determination, Universität Göttingen, Göttingen, Germany, 1997]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned an isotropic displacement parameter of 0.08 Å<sup>2</sup>. SADABS [Sheldrick, G. M. SADABS Empirical Absorp-

tion Correction Program, Universität Göttingen, Göttingen, Germany, 1996.] was used to perform area-detector scaling and absorption corrections (**1**:  $T_{\max}=0.9197$ ,  $T_{\min}=0.4573$ ; **4**:  $T_{\max}=0.9640$ ,  $T_{\min}=0.4536$ ). Crystal data for  $C_8H_{20}Al_2Cl_4N_2O_2$  (**1**): fw=372.02, crystal dimensions 0.52×0.14×0.19 mm, monoclinic, space group  $P2_1/n$ ,  $a=6.9432(1)$ ,  $b=10.2031(2)$ ,  $c=11.9044(3)$  Å,  $\beta=92.822(1)^\circ$ ,  $V=842.31(3)$  Å<sup>3</sup>,  $Z=2$ ,  $\rho_{\text{calcd}}=1.467\times 10^3$  kg m<sup>-3</sup>,  $\mu=0.802$  mm<sup>-1</sup>,  $F(000)=384$ ,  $5.26^\circ\leq 2\theta\leq 55.0^\circ$ ,  $-7\leq h\leq 9$ ,  $-13\leq k\leq 11$ ,  $-14\leq l\leq 15$ , 6289 data collected, 1926 unique data ( $R_{\text{int}}=0.0824$ ), 1404 data with  $I>2\sigma(I)$ , 84 refined parameters, GOF ( $F^2$ )=1.001, final  $R$  indices ( $R_1=\Sigma\|F_o|-|F_c|\|/\Sigma|F_o|$ ,  $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ )  $R_1=0.0449$ ,  $wR_2=0.0942$ , max./min. residual electron density 0.400/−0.455 e Å<sup>-3</sup>. Crystal data for  $C_{20}H_{40}Al_2N_2O_2$  (**4**): fw=394.50, crystal dimensions 0.36×0.45×0.66 mm, triclinic, space group  $P-1$ ,  $a=7.6631(4)$ ,  $b=7.7609(4)$ ,  $c=10.7628(5)$  Å,  $\alpha=96.895(2)$ ,  $\beta=98.853(1)$ ,  $\gamma=107.717(1)^\circ$ ,  $V=592.92(5)$  Å<sup>3</sup>,  $Z=1$ ,  $\rho_{\text{calcd}}=1.105\times 10^3$  kg m<sup>-3</sup>,  $\mu=0.138$  mm<sup>-1</sup>,  $F(000)=216$ ,  $3.90^\circ\leq 2\theta\leq 55.0^\circ$ ,  $-9\leq h\leq 9$ ,  $-6\leq k\leq 10$ ,  $-13\leq l\leq 13$ , 4529 data collected, 2686 unique data ( $R_{\text{int}}=0.0489$ ), 1919 data with  $I>2\sigma(I)$ , 120 refined parameters, GOF ( $F^2$ )=1.001, final  $R$  indices ( $R_1=\Sigma\|F_o|-|F_c|\|/\Sigma|F_o|$ ,  $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ )  $R_1=0.0588$ ,  $wR_2=0.1374$ , max./min. residual electron density 0.400/−0.455 e Å<sup>-3</sup>. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no CCDC-178877 (**1**) and CCDC-178878 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

11. Francis, J. A.; McMahon, C. N.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 4399.
12. Reagents for addition reactions were bought from Aldrich. Imine **6** was synthesized according to the literature [Parry, K. A. W. *J. Chem. Soc. B* **1970**, 700]. The addition products were isolated as racemic mixtures. First evidence shows that the stereochemistry in the products can be controlled using chiral auxiliaries.
13. Spectral data for 1,2-addition product **9a** ( $C_{10}H_{12}O$ ): <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.59 (m, 2H, CH<sub>2</sub>), 2.79 (s, br, 1H, OH), 4.77 (t, 1H,  $J=6.4$  Hz, OCH), 5.18–5.27 (m, 2H, CH=CHH'), 5.79–5.97 (m, 1H, CH=CHH'), 7.41–7.45 (m, 4H, C<sub>arom.</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  43.5, 73.2, 117.9, 125.7, 127.3, 128.3, 134.4, 143.8. IR (cm<sup>-1</sup>): 3367 (s), 3030 (m), 1895 (s), 1494 (m), 1107 (m), 757 (s). MS:  $m/z$  (%): 148.0 (1) [M]<sup>+</sup>, 107.0 (100), 77.2 (23), 77.0 (36), 40.9 (6).
14. Spectral data for 1,2-addition product **9b** ( $C_{10}H_{11}BrO$ ): <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.23 (s, br, 1H, OH), 2.46 (m, 2H, CH<sub>2</sub>), 4.69 (dd, 1H,  $J=5.6, 7.3$  Hz, OCH), 5.11–5.13 (m, 1H, CH=CHH'), 5.18–5.20 (m, 1H, CH=CHH'), 5.67–5.84 (m, 1H, CH=CHH'), 7.19–7.25 (m, 2H, C<sub>arom.</sub>), 7.44–7.49 (m, 2H, C<sub>arom.</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  43.6, 72.5, 118.7, 121.2, 127.5, 131.4, 133.9, 142.8. IR (cm<sup>-1</sup>): 3388 (s), 2978 (m), 1895 (s), 1639 (m), 1580 (m), 1070 (s), 870 (s). MS:  $m/z$  (%): 227.0 (1) [M]<sup>+</sup>, 186.9 (72), 156.9 (26), 77.0 (100), 40.9 (12).
15. Spectral data for 1,2-addition product **10** ( $C_{16}H_{23}N$ ): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  1.15 (m, 4H, CH<sub>2</sub>), 1.58 (m, 4H, CH<sub>2</sub>), 1.98 (m, 4H, CH<sub>2</sub>), 2.27 (m, 2H, CH<sub>2</sub>), 2.37 (m, 1H, CH), 1.35 (s, 1H, NH), 3.87 (t, 1H,  $J=6.42$  Hz, NCHC<sub>6</sub>H<sub>5</sub>), 5.02–5.15 (m, 2H, CH=CHH'), 5.73 (m, 1H, CH=CHH'), 7.23–7.34 (m, 5H, C<sub>arom.</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  24.68, 25.00, 25.99, 32.77, 34.58, 43.37, 56.06, 58.81, 117.09, 126.42, 126.85, 128.14, 135.48, 144.60. IR (cm<sup>-1</sup>): 3427 (m), 2853 (s), 1451 (m), 759 (s). MS:  $m/z$  (%): 228.0 (1) [M]<sup>+</sup>, 188.0 (100), 131.0 (3), 105.9 (56), 79.0 (15), 40.9 (11).
16. Spectral data for 1,2-addition product **11b** ( $C_{18}H_{18}O$ ): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  2.33 (s, br, 1H, OH), 2.82 (m, 2H, CH<sub>2</sub>), 5.21 (m, 2H, CH=CHH'), 5.74 (m, 1H, CH=CHH'), 6.54 (d, 1H,  $J=16.0$  Hz, C<sub>6</sub>H<sub>5</sub>CH=CH), 6.67 (d, 1H,  $J=16.0$  Hz, C<sub>6</sub>H<sub>5</sub>CH=CH), 7.23–7.40 (m, 8H, C<sub>arom.</sub>), 7.52–7.54 (m, 2H, C<sub>arom.</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  47.2, 75.7, 118.7, 120.3, 125.5, 126.6, 127.1, 127.7, 128.4, 133.2, 135.3, 136.8, 145.3. IR (cm<sup>-1</sup>): 3555 (s), 3080 (m), 2978 (m), 1753 (s), 1345 (m), 1030 (m), 844 (s). MS:  $m/z$  (%): 250.0 (1) [M]<sup>+</sup>, 209.0 (100), 130.9 (53), 115 (9), 77.0 (40), 40.9 (7).
17. Spectral data for 1,4-addition product **11a** ( $C_{18}H_{18}O$ ): <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.45 (m, 2H, CH<sub>2</sub>CH=CHH'), 3.32 (m, 2H, CH<sub>2</sub>), 3.50 (m, 1H, CH), 5.00 (m, 2H, CH=CHH'), 5.71 (m, 1H, CH=CHH'), 7.19–7.30 (m, 4H, C<sub>arom.</sub>), 7.44–7.55 (m, 4H, C<sub>arom.</sub>), 7.89–7.94 (m, 2H, C<sub>arom.</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  40.6, 40.7, 44.5, 116.8, 126.3, 127.5, 128.0, 128.4, 128.5, 132.9, 136.3, 137.2, 144.3, 198.9. IR (cm<sup>-1</sup>): 3422 (w), 3062 (w), 1686 (s), 1494 (s), 1202 (m), 1002 (s), 846 (s). MS:  $m/z$  (%): 250.0 (7) [M]<sup>+</sup>, 129.0 (7), 104.9 (100), 77.0 (40).