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π-Allyl palladium methodology for selective deprotection of allylamines. Practical synthesis of secondary amines

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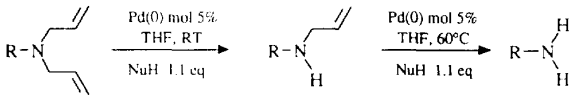
Summary – The palladium-promoted deallylation of allylamines derived from primary and secondary amines is achieved with high to quantitative yield in the presence of 2-mercaptobenzoic acid as an allyl scavenger. This method was used for the sequential cleavage of diallylamines. A synthetic application of this procedure is presented in the preparation of secondary amines from diallylamines.

allylamine / deallylation / sequential deprotection / π-allyl palladium complexes / 2-mercaptobenzoic acid / substitution of amines

Introduction

In the literature, most methods for the deallylation of allylamines involve a preliminary step of isomerization of the double bond [1a] in the presence of transition metals, particularly Rh [1b], Pd [1c], Ir [1d] and Zr [1e], followed by cleavage of the enamine [2]. In our continuing interest in the area of palladium-promoted reactions [3], we previously reported that allylcarboxylates, allylcarbonates and carbamates are cleaved using Pd(0) catalysts and nitrogen or sulfur nucleophiles as allyl trapping agents in anhydrous [4a] and aqueous [4b] media. In preliminary work we also discovered that selective deallylation of allylamines could be achieved in the presence of 2-mercaptobenzoic acid as allyl scavenger and $Pd(dba)_2$/DPPB catalyst under anhydrous conditions [5] (scheme 1).



Pd(0): $Pd(dba)_2$/DPPB (1/1); NuH: 2-mercaptobenzoic acid.

Scheme 1

Recently, Guibé proposed a Pd(0) catalyzed deprotective procedure for the cleavage of mono- and diallylamines with *N*,*N*-dimethyl barbituric acid as a carbon nucleophile [6]. Our sequential method allows the differentiation of the two hydrogen atoms on the nitrogen of primary amines that can be independently substituted. In this paper, we wish to present some additional examples of deprotection of allylamines as well as a practical synthesis of secondary amines using this technology.

Results and discussion

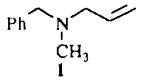
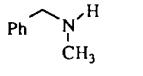
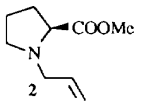
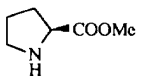
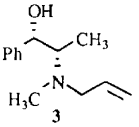
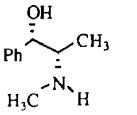
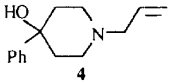
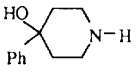
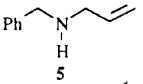
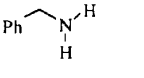
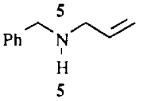
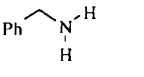
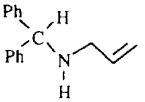
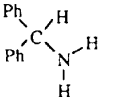
Deallylation of mono and diallylamines

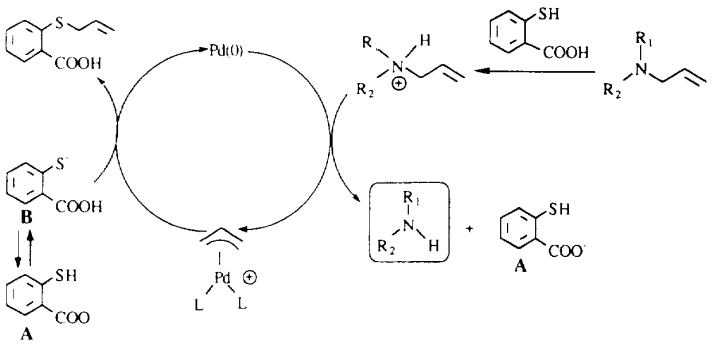
When allylamines derived from secondary amines are treated in THF with 2-mercaptobenzoic acid in the presence of 0.05 molar equivalents of the preformed catalyst $Pd(dba)_2$/DPPB (1:1), smooth deallylation occurs at room temperature (table I, entries 1 to 4). Within 25 min *N*-benzyl-*N*-methylallylamine **1** was cleaved with quantitative yield (entry 1). These conditions were also applied with success to the deallylation of aminoesters such as methyl prolinate (entry 2). Moreover, the allyl group was removed from (1*R*,2*S*)-*N*-allylephedrine **3** and 1-allyl-4-phenylpiperidin-4-ol **4** within 15 to 30 min (entries 3 and 4), proving that the procedure is compatible with polyfunctionalized substrates. Nevertheless, under the above conditions, allylamines derived from primary amines remained unreacted, even after 3 d at room temperature (entry 5). In fact, we found that the cleavage of secondary allylamines requires a higher temperature. At 60°C, it was thus possible to recover the free primary amines from *N*-allylbenzylamine **5** and the rather hindered *N*-(diphenylmethyl)allylamine **6** in excellent yield (entries 6 and 7).

At this stage of our study, the difference in reactivity between secondary and tertiary allylamines towards

* Correspondence and reprints

Table I. Deallylation of tertiary and secondary allylamines using $Pd(dba)_2$/DPPB (1:1) catalyst.

Entry	Substrates	Temp. (°C)	Time	Products	Yield (%)
1	 **1**	20	25 min		100
2	 **2**	20	15 min		100
3	 **3**	20	15 min		100
4	 **4**	20	30 min		100
5	 **5**	20	3 d		0
6	 **5**	60	30 min		100
7	 **6**	60	20 min		100



Scheme 2

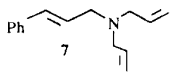
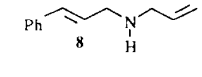
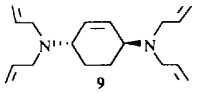
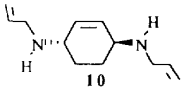
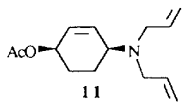
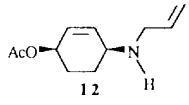
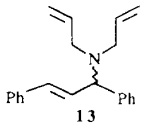
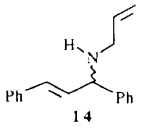
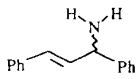
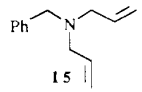
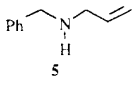
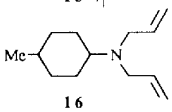
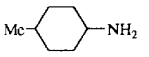
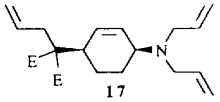
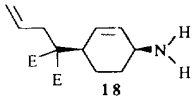
our deprotective system seemed difficult to explain. Nevertheless, we can propose the following mechanism for the deallylation reaction (scheme 2).

The success of the deallylation process involves a preliminary step of protonation of the allylamine by 2-mercaptobenzoic acid, followed by oxidative addition of zerovalent palladium catalyst on the allyl moiety to give a π-allyl palladium complex and the deprotected amine. Thiolate **B** stemming from rapid equilibrium with 2-mercaptobenzoate **A** then traps the π-allyl complex to regenerate the Pd(0) species, with formation of 2-(allylthio)benzoic acid as a by-product.

In view of this difference in reactivity, our catalytic system allowed us to achieve sequential cleavage of diallylamines. In the first step, one allyl moiety is selectively removed at room temperature, using 1.1 equiv of nucleophile, to give the corresponding monoallylamines which are fully deallylated in a second step at higher temperature. As shown in table II, diallylamine derivative **7** underwent selective monodeallylation in the presence of 1.1 equiv of 2-mercaptobenzoic acid at 20°C, with 79% yield (entry 1). In the same way, a disubstituted cyclohexene derivative **9** was symmetrically cleaved to give *N*,*N*′-diallylcyclohex-2-ene-1,4-diamine **10** within 90 min in excellent yield (entry 2).

Such selectivity was also achieved on *cis*-4-(diallylamino)cyclohex-2-enyl acetate **11** [7] which was smoothly monodeallylated in 80% yield (entry 3). Using

Table II. Selective deprotection of diallylamines using Pd(0) catalyst and 2-mercaptobenzoic acid as nucleophile.

Entry	Substrate	Product	Time (min)	Yield[a] (%)	Product	Time (min)	Yield (%)
1	 **7**	 **8**	60	79			
2	 **9**	 **10**	90	98[b]			
3	 **11**	 **12**	60	80			
4	 **13**	 **14**	30	70		120	61
5	 **15**	 **5**	60	85		30	100
6	 **16**					30	97
7	 **17**				 **18**	240	76

a) isolated yield; b) 2-mercaptobenzoic acid 2.1 equiv.

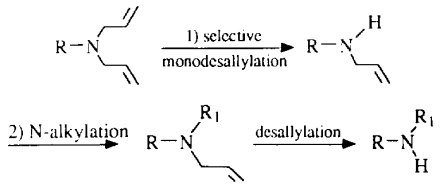
another equivalent of sulfur nucleophile at 60°C, it was then possible to remove the second allyl group.

This sequential deprotection was performed on diallylamine derivative **13** and *N,N*-diallyl benzylamine **15** with good to quantitative yield at each step (entries 4 and 5). Finally, primary amines such as 4-methylcyclohexylamine and the highly sensitive *cis*-cyclohex-2-enylamine **18** could also be obtained from direct bisdeallylation of the corresponding diallylamines, using 2.1 equiv of allyl scavenger at 60°C (entries 6 and 7).

In this way, the versatility of our deprotective system allows selective and sequential deallylation of diallylamines, and we propose a synthetic application of this methodology in the preparation of secondary amines.

Practical synthesis of secondary amines from N,N-*diallylamines*

The synthesis of functionalized amines represents an important challenge in organic chemistry since nitrogen derivatives are widely present in nature. In the literature, various methods have been developed for the preparation of substituted amines. They can be obtained by reductive amination of aldehydes and ketones [8]. Another general pathway, starting from primary amines, involves a first step of activation by a labile group (trifluoroacetyl or sulfonyl) that increases the acidity of N-H. Deprotonation is then achieved with a strong base followed by *N*-alkylation and removal of the activating moiety [9]. The use of solvents such as HMPA [10] and more recently DMPU [11] has also been described for the direct alkylation of amines since they enhance the nucleophilicity of carbanions. Our sequential method for the selective deprotection of diallylamines was used for the stepwise synthesis of secondary amines (scheme 3). Starting from diallylamines, the first step consists of the selective removal of one allyl group in the presence of $Pd(dba)_2$/DPPB catalyst and 1.1 equiv of 2-mercaptobenzoic acid at room temperature, allowing the resulting monoallylamines to be alkylated with alkyl bromides. Smooth deallylation then leads to the secondary amines.

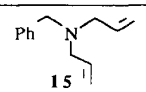
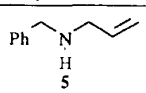
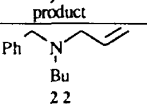
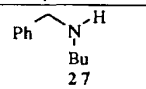
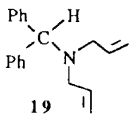
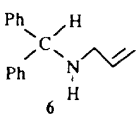
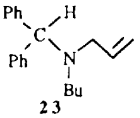
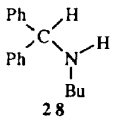
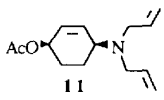
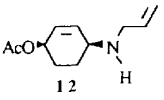
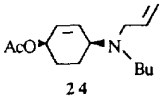
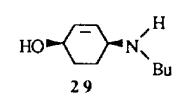
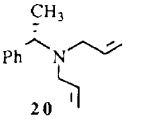
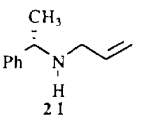
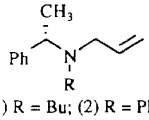
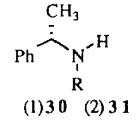


1) cat $Pd(dba)_2$/DPPB (1:1); 2-mercaptobenzoic acid 1.1 equiv; RT; 2) R_1Br 2-4 equiv; NaI cat; $NaHCO_3$ 2 equiv; THF/DMSO reflux.

Scheme 3

This synthetic route was applied to the preparation of various secondary amines, with *n*-butyl bromide as

Table III. Preparation of secondary amines from *N*,*N*-diallylamines.

Entry	Substrate	Monodeallylation product	Yield (%)	Alkylation product	Yield (%)	Deallylation product	Yield (%)
1	 **15**	 **5**	85	 **22**	72	 **27**	78
2	 **19**	 **6**	82	 **23**	85	 **28**	100
3	 **11**	 **12**	80	 **24**	93	 **29**	99[b]
4	 **20**	 **21**	88	 (1) R = Bu; (2) R = $PhCH_2$ **25** **26**	(1) 96 (2) 89[a]	 (1)**30** (2)**31**	(1) 93 (2) 85

a) Alkylating reagent : $PhCH_2Br$ 1.2 eq.; b) T = 40°C

the alkylating reagent (table III). After efficient monodeallylation, N-benzylallylamine **5** underwent alkylation with *n*-butyl bromide with 72% yield (entry 1). The reaction was carried out in a (4:1) THF/DMSO mixture at reflux, in the presence of $NaHCO_3$ and a catalytic amount of sodium iodide, which ensures the success of the alkylation since the alkyl bromides alone gave the *N*-substituted amines in very poor yields. Different solvents such as toluene and ethanol were tested but they resulted in very low conversion rates. The (4:1) THF/DMSO mixture proved to be the more favorable medium for the alkylative step, and it avoids the use of carcinogenic HMPA. The rather hindered *N*-(diphenylmethyl)allylamine **6** was treated under the same conditions to give the alkylated product in 85% yield (entry 2), proving that the method remains very efficient for bulky substrates. These conditions are also compatible with functionalized molecules as shown in entry 3, where *cis*-4-[allyl(butyl)amino]cyclohex-2-enyl acetate **24** was obtained in 93% yield.

The *N*-butylallylamines were further deallylated affording the secondary amines in good to quantitative yields. All the deprotections take place within a short reaction time ranging from 15 to 60 min.

Secondary chiral amines derived from (*S*)-(−)-1-phenylethylamine were prepared through this sequence (entry 4). In particular, (*S*)-(−)-*N*-benzyl-1-phenylethylamine **31**, which was obtained in its optically pure form [12], is a very useful synthon in asymmetric synthesis. In fact, after conversion to the corresponding chiral lithium amide base, various reactions can be performed such as enantioselective deprotonation of symmetric ketones [13] and enantiocontrolled protonation of achiral enolates [14]. 1,4-Diastereoselective addition to α,β-unsaturated esters using chiral lithium amides has also been largely developed over the past 10 years [15].

Conclusion

In summary, a practical and efficient Pd(0)-promoted procedure was developed for the cleavage of secondary and tertiary allylamines. The high yields of deprotection as well as the easy elimination of both palladium catalyst and the 2-(allylthio)benzoic acid by-product through acido-basic treatment constitute attractive assets. In fact, the crude products are generally pure enough to be directly engaged in further reactions. Moreover, the first example of sequential deallylation of diallylamines was performed using this methodology, allowing selective substitution of primary amines. Further synthetic applications of this selective deprotection technology are currently under investigation in our laboratory, especially in the area of polyamine synthesis.

Experimental section

General methods

Infrared spectra were recorded on a Perkin-Elmer 983G spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC 200 instrument at 200 MHz; chemical shifts (δ) are reported in ppm units, by reference to Me_4Si, and coupling constants (J) are reported in hertz and refer to apparent peak multiplicities. Abbrevations used are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^{13}C NMR spectra were recorded on a Bruker AC 200 instrument at 50 MHz. Mass spectra were performed on a Ribermag Instrument. Elementary analysis were done at the Regional Service of Microanalysis (université Pierre-et-Marie-Curie, Paris).

Thin-layer chromatography was carried out on silica-gel plates (Merck F_{254}) and spots were detected by UV and Kagi-Mösher or $KMnO_4$ revelators. Tetrahydrofuran and diethyl ether were distilled on sodium/benzophenone. The other commercial solvents were used without any further

purification. Unless otherwise stated, all reactions were run under an atmosphere of argon.

Typical procedure for the preparation of diallylamines (A)

The primary amine (10 mmol) was dissolved in 10 mL of a (4:1) THF/DMSO mixture, under an argon atmosphere. Sodium hydrogenocarbonate (20 mmol) was poured into the solution, followed by dropwise addition of allyl bromide (20–40 mmol). Finally, a catalytic amount of sodium iodide (0.3–0.5 equiv) was introduced and the mixture was heated to reflux. After complete consumption of the amine (the reaction was monitored by TLC and gas chromatography), the solution was concentrated *in vacuo*. The residue is treated with water and extracted with AcOEt. The organic layer was washed with water, dried over $MgSO_4$ and concentrated *in vacuo*. If necessary, purification was achieved by flash chromatography on silica gel.

Typical procedure for allylation of secondary amines (B)

The amine (10 mmol) was dissolved in acetonitrile (10 mL) and the solution was cooled to 0°C. Allyl bromide (5 mmol) was added dropwise; after 15 min the reaction medium was allowed to warm to room temperature and was monitored by TLC and gas chromatography. The solution was then treated according to the procedure described above.

Typical procedure for alkylation of monoallylamines (C)

The monoallylamine (x mmol) was dissolved in 6 mL of a (4:1) THF/DMSO mixture and 2 equiv of $NaHCO_3$ were poured into the solution. Butyl bromide (2–4 equiv) or benzyl bromide (1.2 equiv) were added, followed by sodium iodide (0.3 equiv). The reaction medium was heated to reflux until complete transformation of the allylamine. The resulting solution was then treated as described above.

Typical procedure for deallylation (D)

A mixture of $Pd(dba)_2$ (mol 5%) and DPPB (mol 5%) in THF (0.5 mL) was stirred at room temperature, under an argon atmosphere, for 15 min. The preformed catalyst and 2-mercaptobenzoic acid (1.1–2.1 equiv) were added to a solution of mono- or diallylamine in THF and the reaction mixture was stirred under an argon atmosphere at 20 or 60°C. After completion (the reaction was monitored by TLC and gas chromatography), the mixture was treated with a solution of HCl 10% and extracted by AcOEt to eliminate the by-product and the catalyst in organic layer. The aqueous layer containing the protonated amine was basified with a solution of 1 M NaOH and extracted by AcOEt. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*, affording clean crude products. If necessary, further purification was performed by flash chromatography.

N-*Benzyl*-N-*methylallylamine* **1**

Pale yellow oil (82% yield).

TLC: R_f = 0.65 (CH_2Cl_2/MeOH 10:1).

IR (ν cm^{-1}): 3 061, 3 025, 2 974, 2 931, 2 837, 1 638, 1 609, 1 491, 1 449.

^1H NMR ($CDCl_3$, 200 MHz, δ): 7.36 (3H, m, ArH), 7.29 (2H, m, ArH), 5.95 (1H, m, HC=), 5.24 (1H, dm, $^3J_{trans}$ = 12.0 Hz, HC=), 5.18 (1H, dm, $^3J_{cis}$ = 6.3 Hz, HC=), 3.53 (2H, s, $ArCH_2$), 3.06 (2H, d, ^3J = 6.4 Hz, CH_2 allyl), 2.22 (3H, s, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 138.91 (Ar), 135.84 (C=), 128.98 (Ar), 128.11 (Ar), 126.85 (Ar), 117.38 (C=), 61.58 ($ArCH_2$), 60.45 (CH_2 allyl), 41.98 (CH_3).

GC/MS (m/z): 161 $(M)^{+\cdot}$, 118 $(M - CH_2CH{=}CH_2 - 2)^+$, 91 $(PhCH_2)^+$, 42 $(CH_2CH{=}CH_2 + 1)^+$.

Methyl N-*allyl*-L-*prolinate* **2**

Yellow oil (55% yield).

TLC: R_f = 0.26 (AcOEt/cyclohexane 1:1).

^1H NMR ($CDCl_3$, 200 MHz, δ): 5.91 (1H, m, HC=), 5.17 (1H, dm, HC=), 5.08 (1H, dm, HC=), 3.70 (3H, s, OCH_3), 3.30 (1H, ddm, CH_2 allyl), 3.12 (3H, m, 1H CH_2 allyl and 2H NCH_2), 2.37 (1H, m, $HC(CO_2Me)$), 2.14 (1H, m, CH_2), 1.88 (3H, m, CH_2).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 174.54 (CO), 135.11 (C=), 117.40 (C=), 65.15 ($C(CO_2Me)$), 57.69 (CH_2 allyl), 53.40 (NCH_2), 51.70 (OCH_3), 29.42 (CH_2), 22.97 (CH_2).

MS (DCI/NH_3; m/z): 170 $(M + H)^+$.

Rotation: $[\alpha]_D^{20}$ = –69.2 (c = 2 5, EtOH).

(1R,2S)-N-*Allylephedrine* **3**

Pale yellow oil (60% yield).

TLC: R_f = 0.49 (AcOEt/MeOH 1:2).

IR (ν cm^{-1}): 3 422, 3 062, 3 026, 2 976, 2 934, 2 874, 1 638, 1 600, 1 490, 1 448, 1 341, 1 194.

^1H NMR ($CDCl_3$, 200 MHz, δ): 7.32 (5H, m, ArH), 5.85 (1H, m, HC=), 5.20 (1H, dm, ^3J = 8.7 Hz, HC=), 5.15 (1H, m, HC=), 5.85 (1H, d, ^3J = 4.2 Hz, HC(OH)), 3.14 (2H, d, ^3J = 6.3 Hz, CH_2 allyl), 2.88 (1H, m, HC(β-OH)), 2.28 (3H, s, NCH_3), 0.89 (3H, d, ^3J = 6.9 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 142.16 (Ar), 135.60 (C=), 127.85 (Ar), 126.77 (Ar), 125.96 (Ar), 117.18 (C=), 72.75 (C(OH)), 62.69 (CH_2 allyl), 57.60 (C(β-OH)), 38.99 (NCH_3), 9.90 (CH_3).

GC/MS (m/z): 206 $(M + 1)^+$, 188 $(M - OH)^+$, 98 $(M - PhCH(OH))^+$, 77 $(Ph)^+$, 56 $(HNCH_2CH{=}CH_2)^+$, 41 $(CH_2CH{=}CH_2)^+$.

Rotation: $[\alpha]_D^{20}$ = 9.3 (c = 0.905, $CHCl_3$).

1-Allyl-4-phenylpiperidin-4-ol **4**

Orange oil (76% yield).

TLC: R_f = 0.59 (AcOEt/MeOH 2:8).

^1H NMR ($CDCl_3$, 200 MHz, δ): 7.52 (2H, m, ArH), 7.36 (3H, m, ArH), 6.04 (1H, m, HC=), 5.39 (1H, d, $^3J_{trans}$ = 5.4 Hz, HC=), 5.32 (1H, m, HC=), 3.32 (2H, d, ^3J = 6.8 Hz, CH_2 allyl), 3.13 (1H, br s, NCH_2), 3.06 (1H, br s, NCH_2), 2.84 (2H, t, ^3J = 11.0 Hz, NCH_2), 2.42 (2H, m, CH_2 Cy), 1.92 (1H, m, CH_2 Cy), 1.83 (1H, m, CH_2 Cy).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 147.16 (Ar), 131.13 (C=), 128.36 (Ar), 127.19 (C=), 124.44 (Ar), 121.43 (C=), 70.26 (C(OH)), 60.76 (CH_2 allyl), 48.89 (NCH_2), 36.91 (CH_2 Cy).

GC/MS (m/z): 217 $(M)^{+\cdot}$, 199 $(M - H_2O)^+$, 158 $(M - CH_2CH{=}CH_2 - H_2O)^+$, 122 $(M - Ph - H_2O)^+$, 42 $(CH_2CH{=}CH_2 + 1)^+$.

N-*Benzylallylamine* **5**

Colorless oil (85% yield).

TLC: R_f = 0.49 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 313, 3 061, 3 024, 2 913, 1 638, 1 602, 1 491, 1 449.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.36 (3H, m, ArH), 7.29 (2H, m, ArH), 5.94 (1H, m, HC=), 5.22 (1H, dm, $^3J_{trans}$ = 18.5 Hz, HC=), 5.12 (1H, dm, $^3J_{cis}$ = 11.6 Hz, HC=), 3.81 (2H, s, $ArCH_2$), 3.30 (2H, dt, ^3J = 5.9 Hz and ^4J = 1.4 Hz, CH_2 allyl).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.18 (Ar), 136.71 (C=), 128.32 (Ar), 128.10 (Ar), 126.87 (Ar), 115.93 (C=), 53.18 ($ArCH_2$), 51.69 (CH_2 allyl).

GC/MS (m/z): 146 (M - H)$^+$, 104 ($PhCH_2N$ - 1)$^+$, 91 $(PhCH_2)^+$, 56 $(HNCH_2CH{=}CH_2)^+$.

N-*(Diphenylmethyl)allylamine* **6**

Pale yellow oil (82% yield).

TLC: R_f = 0.71 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 322, 3 059, 3 023, 1 638, 1 594, 1 489, 1 449.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.42 (4H, dm, ArH), 7.36-7.19 (6H, m, ArH), 5.96 (1H, m, HC=), 5.19 (1H, dm, $^3J_{trans}$ = 17.1 Hz, HC=), 5.12 (1H, dm, $^3J_{cis}$ = 10.1 Hz, HC=), 4.89 (1H, s, HC), 3.23 (2H, dt, ^3J = 5.9 Hz and ^4J = 1.4 Hz, CH_2 allyl), 1.76 (1H, br s, NH).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 143.79 (Ar), 136.62 (C=), 128.38 (Ar), 127.23 (Ar), 126.91 (Ar), 115.84 (C=), 66.34 (CH), 50.29 (CH_2 allyl).

GC/MS (m/z): 222 (M - 1)$^+$, 167 (M - HN(allyl))$^+$, 146 (M - Ph)$^+$, 104 (M - Ph - $CH_2CH{=}CH_2$ - 1)$^+$, 77 $(Ph)^+$, 41 $(CH_2CH{=}CH_2)^+$.

N,N-*Diallyl-3-phenylallylamine* **7**

Pale yellow oil (90% yield).

TLC: R_f = 0.66 (AcOEt/cyclohexane 1:2).

IR (ν cm^{-1}): 3 077, 3 023, 2 878, 1 638, 1 596.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.39 (3H, m, ArH), 7.28 (2H, m, ArH), 6.53 (1H, d, $^3J_{trans}$ = 15.9 Hz, HC=), 6.28 (1H, dt, $^3J_{trans}$ = 15.9 and 6.6 Hz, HC=), 5.91 (2H, m, HC= allyl), 5.23 (2H, dm, ^3J = 9.4 Hz, HC= allyl), 5.16 (2H, m, HC= allyl), 3.26 (2H, dd, ^3J = 6.5 Hz and ^4J = 1.2 Hz, NCH_2), 3.15 (4H, d, ^3J = 6.6 Hz, CH_2 allyl).

^{13}C NMR (δ, ppm): 137.03 (Ar), 135.47 (C=), 132.58 (C=), 128.45 (Ar), 127.26 (Ar and C=), 126.17 (Ar), 117.64 (C=), 56.45 (CH_2 allyl), 55.67 (NCH_2).

GC/MS (m/z): 213 $(M)^{+\cdot}$, 172 (M - $CH_2CH{=}CH_2)^+$, 117 (M - N(allyl)$_2)^+$, 91 $(PhCH_2)^+$, 68 (CH_2N(allyl) - 1)$^-$, 41 $(CH_2CH{=}CH_2)^+$.

Anal calc for $C_{15}H_{19}N$: C, 84.51; H, 8.92; N, 6.57. Found: C, 84.16; H, 8.70; N, 6.42.

N-*Allyl-3-phenylallylamine* **8**

Colorless oil (93% yield).

TLC: R_f = 0.39 (CH_2Cl_2/MeOH 7:1).

IR (ν cm^{-1}): 3 312, 3 077, 3 057, 3 022, 2 914, 2 811, 1 638, 1 595, 1 489, 1 445.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.38 (3H, m, ArH), 7.27 (2H, m, ArH), 6.55 (1H, d, $^3J_{trans}$ = 15.9 Hz, HC=), 6.31 (1H, dt, $^3J_{trans}$ = 15.9 Hz and ^3J = 6.1 Hz, HC=), 5.95 (1H, m, HC= allyl), 5.21 (1H, dm, $^3J_{trans}$ = 18 Hz, HC= allyl), 5.13 (1H, dm, $^3J_{cis}$ = 10.6 Hz, HC= allyl), 3.44 (2H, dd, ^3J = 6.1 Hz and ^4J = 1.2 Hz, NCH_2), 3.32 (2H, dt, ^3J = 6 Hz and ^4J = 1.4 Hz, CH_2 allyl), 1.38 (1H, br s, NH).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 136.99 (Ar), 136.95 (C= allyl), 131.33 (C=), 128.45 (Ar), 128.19 (C=), 127.27 (Ar), 126.17 (Ar), 116.02 (C= allyl), 51.70 and 51.09 (NCH_2).

GC/MS (m/z): 173 $(M)^{+\cdot}$; 132 (M - $CH_2CH{=}CH_2)^+$, 91 $(PhCH_2)^+$, 41 $(CH_2CH{=}CH_2)^+$.

trans-N,N,N′,N′-*Tetraallylcyclohex-2-ene-1,4-diamine* **9**

This compound was obtained from *trans*-3,6-dibromocyclohexene upon reaction with diallylamine (2.5 equiv) in the presence of $Pd(OAc)_2$ (mol 2.5%), PPh_3 (mol 5%) and diisopropylamine (2.5 equiv) in THF. After 4 h at 60°C, a saturated aqueous solution of Na_2SO_3 was added and the mixture was extracted with 3 portions of ether. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford a colorless oil (80% yield).

TLC: R_f = 0.29 (AcOEt/cyclohexane 1:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.93-5.73 (6H, m, 4H HC= allyl and 2H HC= Cy), 5.17 (4H, d, $^3J_{trans}$ = 18.8 Hz, HC= allyl), 5.09 (4H, d, $^3J_{cis}$ = 12.5 Hz, HC= allyl), 3.45 (2H, m, HC Cy), 3.21 (4H, dd, ^2J = 14.2 Hz and ^3J = 5.5 Hz, CH_2 allyl), 2.97 (4H, dm, ^2J = 14.2 Hz, CH_2 allyl), 1.87 (2H, m, CH_2 Cy), 1.39 (2H, m, CH_2 Cy).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 137.20 (C= allyl), 133.09 (C= Cy), 116.35 (C= allyl), 56.37 (CH Cy), 52.90 (CH_2 allyl), 22.88 (CH_2 Cy).

GC/MS (m/z): 272 $(M)^{+\cdot}$, 245 (M - $HC{=}CH_2)^+$, 231 (M - $CH_2CH{=}CH_2)^+$, 190 (M - $2CH_2CH{=}CH_2)^+$, 176 (M - N(allyl)$_2)^+$, 149 (M - $3CH_2CH{=}CH_2)^+$, 108 (M - $4CH_2CH{=}CH_2)^+$, 79 (M - 2N(allyl)$_2$ - 1)$^+$, 41 $(CH_2CH{=}CH_2)^+$.

trans-N,N′-*Diallylcyclohex-2-ene-1,4-diamine* **10**

Pale orange oil (98% yield).

TLC: R_f = 0.28 (AcOEt/MeOH 1:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.90 (2H, m, HC= allyl), 5.72 (2H, m, HC= Cy), 5.20 (2H, dm, $^3J_{trans}$ = 16.8 Hz, HC= allyl), 5.09 (2H, dm, $^3J_{cis}$ = 9.6 Hz, HC= allyl), 3.39 (2H, dm, ^2J = 15.6 Hz, CH_2 allyl), 3.22 (2H, dm, ^2J = 15.6 Hz, CH_2 allyl), 3.01 (2H, d, ^3J = 8 Hz, HC Cy), 2.26 (2H, br s, NH), 2.08 (2H, m, CH_2 Cy), 1.54 (2H, m, CH_2 Cy).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 138.07 (C= allyl), 128.30 (C= Cy), 115.80 (C= allyl), 57.5 (CH Cy), 49.34 (CH_2 allyl), 26.03 (CH_2 Cy).

GC/MS (m/z): 191 (M - 1)$^+$, 163 (M - $HC{=}CH_2)^+$, 109 (M - $2CH_2CH{=}CH_2$ + 1)$^+$, 41 $(CH_2CH{=}CH_2)^+$.

cis-*4-(Diallylamino)cyclohex-2-enyl acetate* **11**

Colorless oil (71% yield).

TLC: R_f = 0.33 (Et_2O/pentane 1:3).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.96 (1H, d, ^3J = 11.2 Hz, HC= Cy), 5.88 (1H, dm, ^3J = 11.2 Hz, HC= Cy), 5.82 (2H, m, HC= allyl), 5.17 (2H, dm, $^3J_{trans}$ = 17.2 Hz, HC= allyl), 5.11 (1H, m, HC(OAc)), 5.08 (2H, dm, $^3J_{cis}$ = 9 Hz, HC= allyl), 3.37 (1H, m, HCN(allyl)$_2$), 3.21 (2H, ddt, ^2J = 14 Hz, ^3J = 4.8 Hz and ^4J = 2.0 Hz, NCH_2), 3.00 (2H, dd, ^2J = 14 Hz and ^3J = 7.6 Hz, NCH_2), 2.03 (3H, s, $COCH_3$), 1.91 (1H, m, HCy), 1.72 (1H, m, HCy), 1.66 (2H, m, HCy).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 170.53 (C=O), 137.01 (C= allyl), 130.17 (C= Cy), 126.70 (C= Cy), 116.54 (C= allyl), 66.16 (C(OAc)), 55.71 (CN(allyl)$_2$), 53.08 (NCH_2), 27.16 (CH_2 Cy), 24.71 (CH_2 Cy), 21.22 ($COCH_3$).

GC/MS (m/z): 235 $(M)^{+\cdot}$, 207 (M − $HC{=}CH_2$ − 1)$^+$, 192 (M − Ac)$^+$, 180 (M − N(allyl)$_2$ − 1)$^+$, 79 (M − OAc − N(allyl)$_2$ − 1)$^+$, 41 $(CH_2CH{=}CH_2)^+$.

cis-*4-(Allylamino)cyclohex-2-enyl acetate* **12**

Pale orange oil (80% yield).

TLC: R_f = 0.23 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 317, 3 075, 3 030, 2 944, 2 859, 1 726, 1 638, 1 447, 1 368, 1 242.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.98 (1H, dd, ^3J = 10.1 Hz and ^3J = 2.6 Hz, HC= Cy), 5.92 (1H, m, HC= allyl), 5.79 (1H, ddd, ^3J = 10.1 Hz, ^3J = 3.9 Hz and ^4J = 1.9 Hz, HC= Cy), 5.20 (1H, dm, $^3J_{trans}$ = 17.2 Hz, HC= allyl), 5.18 (1H, m, HC(OAc)), 5.07 (1H, dm, $^3J_{cis}$ = 10.2 Hz, HC= allyl), 3.33 (2H, d, ^3J = 6.2 Hz, NCH_2), 3.16 (1H, dm, ^3J = 3.9 Hz, HCN(allyl)$_2$), 2.04 (3H, s, $COCH_3$), 1.84 (2H, m, H Cy), 1.60 (2H, m, H Cy), 1.57 (1H, br s, NH).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 170.59 (C=O), 136.66 (C= allyl), 135.24 (C= Cy), 126.27 (C= Cy), 115.96 (C= allyl), 67.05 (C(OAc)), 52.17 (NCH_2), 49.45 (CN(allyl)$_2$), 26.00 (CH_2 Cy), 25.16 (CH_2 Cy), 21.21 ($COCH_3$).

GC/MS (m/z): 194 (M − 1)$^+$, 167 (M − $HC{=}CH_2$ − 1)$^+$, 137 (M − OAc + 1)$^+$, 125 (HNCH(allyl))$^+$, 109 (M − OAc − $HC{=}CH_2$)$^+$, 41 $(CH_2CH{=}CH_2)^+$.

N,N-*Diallyl-1,3-diphenylallylamine* **13**

Colorless oil (85% yield).

TLC: R_f = 0.82 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 079, 3 059, 3 024, 2 923, 2 848, 1 638, 1 596, 1 489, 1 445.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.50–7.21 (10H, m, ArH), 6.56 (1H, d, ^3J = 13.8 Hz, HC=), 6.35 (1H, dd, ^3J = 13.8 Hz and ^3J = 8.4 Hz, HC=), 5.89 (2H, m, HC= allyl), 5.21 (2H, dm, $^3J_{trans}$ = 9.0 Hz, HC= allyl), 5.17 (2H, m, HC= allyl), 4.44 (1H, d, ^3J = 8.4 Hz, HCN(allyl)$_2$), 3.26 (2H, dd, ^2J = 10.3 Hz, ^3J = 5.6 Hz, CH_2 allyl), 3.14 (2H, dd, ^2J = 10.3 Hz, ^3J = 5.6 Hz, CH_2 allyl).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 142.12 (Ar), 136.33 (Ar), 135.98 (C= allyl), 132.33 (C=), 129.68 (C=), 128.46 (Ar), 128.25 (Ar), 127.88 (Ar), 127.39 (Ar), 126.89 (Ar), 126.30 (Ar), 117.01 (C= allyl), 66.96 (CN(allyl)$_2$), 52.57 (CH_2 allyl).

GC/MS (m/z): 289 $(M)^{+\cdot}$, 248 (M − $CH_2CH{=}CH_2$)$^+$, 193 (M − N(allyl)$_2$)$^+$, 115 (M − Ph − N(allyl)$_2$ − 1)$^+$, 91 $(PhCH_2)^+$, 41 $(CH_2CH{=}CH_2)^+$.

N-*Allyl-1,3-diphenylallylamine* **14**

Yellow oil (70% yield).

TLC: R_f = 0.30 (AcOEt/cyclohexane 1:2).

IR (ν cm^{-1}): 3 319, 3 079, 3 058, 3 023, 2 922, 1 638, 1 596, 1 489, 1 446.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.45–7.21 (10H, m, ArH), 6.61 (1H, d, ^3J = 16 Hz, HC=), 6.32 (1H, dd, ^3J = 16 Hz and ^3J = 7.4 Hz, HC=), 5.92 (1H, m, HC= allyl), 5.21 (1H, dm, $^3J_{trans}$ = 17.3 Hz, HC= allyl), 5.15 (1H, dm, $^3J_{cis}$ = 8.0 Hz, HC= allyl), 4.43 (1H, d, ^3J = 7.4 Hz, HC(NH allyl)), 3.27 (1H, m, CH_2 allyl), 3.11 (1H, d, ^3J = 4.7 Hz, CH_2 allyl).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 142.8 (Ar), 136.66 (1C Ar and 1C= allyl), 132.44 (C=), 130.23 (C=), 128.52 (Ar), 128.41 (Ar), 127.22 (Ar), 126.31 (Ar), 115.89 (C= allyl), 64.63 (CH), 49.93 (CH_2 allyl).

GC/MS (m/z): 249 $(M)^{+\cdot}$, 220 (M − $HC{=}CH_2$ − 1)$^+$, 208 (M − $CH_2CH{=}CH_2$)$^+$, 172 (M − Ph)$^+$, 158 (M − $PhCH_2$)$^+$, 144 (M − Ph − $HC{=}CH_2$ − 1)$^+$, 115 (PhCH=CHCH$_2$ − 1)$^+$, 91 $(PhCH_2)^+$, 41 $(CH_2CH{=}CH_2)^+$.

N-*Allyl*-N-*benzylallylamine* **15**

Pale yellow oil (92% yield).

TLC: R_f = 0.80 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 075, 3 025, 2 919, 2 878, 1 638, 1 583, 1 490, 1 449.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.37 (5H, m, ArH), 5.96 (2H, m, HC=), 5.27 (2H, dm, ^3J = 14 Hz, HC=), 5.19 (2H, dm, ^3J = 8 Hz, HC=), 3.65 (2H, s, $ArCH_2$), 3.16 (4H, dt, ^3J = 6.3 Hz and ^4J = 1.2 Hz, CH_2 allyl).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 139.20 (Ar), 135.68 (C=), 128.27 (Ar), 128.15 (Ar), 126.83 (Ar), 117.45 (C=), 57.50 ($ArCH_2$), 56.34 (CH_2 allyl).

GC/MS (m/z): 187 $(M)^{+\cdot}$, 160 (M − $HC{=}CH_2$)$^+$, 146 (M − $CH_2CH{=}CH_2$)$^+$, 110 (M − Ph)$^+$, 91 $(PhCH_2)^+$, 41 $(CH_2CH{=}CH_2)^+$.

N-*Allyl*-N-*(4-methylcyclohexyl)allylamine* **16**

Yellow oil (22% yield); *cis/trans* = 38:62.

IR (ν cm^{-1}): 3 074, 3 004, 2 921, 2 850, 2 803, 1 638, 1 446.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.83 (2H, m, HC=), 5.15 (2H, dm, $^3J_{trans}$ = 16 Hz, HC=), 5.07 (2H, dm, $^3J_{cis}$ = 8 Hz, HC=), 3.13 (4H, dm, ^3J = 6 Hz, CH_2 allyl), 2.52 (1H, tt, ^3J = 12 and 3.6 Hz, NCH Cy), 1.74 (3H, m, CH and CH_2 Cy), 1.49 (4H, m, CH_2 Cy), 1.25 (2H, m, CH_2 Cy), 0.92 and 0.86 (3H, 2d, ^3J = 6 Hz, CH_3 *cis* and *trans*).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 137.43 (C= *trans*), 137.07 (C= *cis*), 116.14 (C= *cis*), 116.07 (C= *trans*), 58.80 (CH Cy *trans*), 58.21 (CH Cy *cis*), 52.93 (CH_2 allyl *trans*), 52.75 (CH_2 allyl *cis*), 34.63 (CH_2 Cy *trans*), 32.63 (CH Cy *trans*), 30.85 (CH_2 Cy *cis*), 28.50 (CH_2 Cy *trans*), 28.00 (CH Cy *cis*), 24.16 (CH_2 Cy *cis*), 22.20 (CH_3 *trans*), 18.33 (CH_3 *cis*).

GC/MS (m/z): 193 $(M)^{+\cdot}$, 166 (M − $HC{=}CH_2$)$^+$, 152 (M − $CH_2CH{=}CH_2$)$^+$, 136 (M − $CH_2CH{=}CH_2$ − CH_3 − 1)$^+$, 123 ($CH_2CHN(allyl)_2$)$^+$, 108 (CHN(allyl)$_2$)$^+$, 95 N(allyl)$_2$)$^+$, 70 $(C_5H_{10})^+$, 41 $(CH_2CH{=}CH_2)^+$.

*Dimethyl 1-[*cis*-4-(diallylamino)cyclohex-2-enyl]but-3-ene-1,1-dicarboxylate* **17**

Yellow oil (80% yield).

TLC: R_f = 0.55 (AcOEt/cyclohexane 1:2).

IR (ν cm^{-1}): 3 035, 2 949, 2 923, 2 862, 1 726, 1 640, 1 586, 1 430.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 6.00–5.60 (5H, m, 2HC= Cy and 3HC= allyl), 5.20 to 5.00 (6H, m, HC= allyl), 3.73 (3H, s, CO_2CH_3), 3.70 (3H, s, CO_2CH_3), 3.10 (4H, d, ^3J = 6.5 Hz, CH_2 diallyl), 3.40 to 2.40 (4H, m, CH_2 allyl and 2HC Cy), 1.90 to 1.20 (4H, m, CH_2 Cy).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 171.00 (CO), 136.91 (C= diallyl), 132.79 (C= Cy), 130.50 (C= Cy), 129.52 (C= allyl), 118.52 (C= allyl), 116.53 (C= diallyl), 58.03 (C(CO_2Me)), 55.93 (CH Cy), 53.17 (CH_2 allyl), 52.89 (CH_2 diallyl), 52.03 (CH Cy), 36.98 (CH_2 Cy), 26.51 (CH_2 Cy), 18.28 (CO_2CH_3).

GC/MS (m/z): 347 $(M)^{+\cdot}$, 332 (M − CH_3)$^+$, 316 (M − OCH_3)$^+$, 306 (M − $CH_2CH{=}CH_2$)$^+$, 288 (M − CO_2Me)$^+$, 176 (M − C(CO_2Me)$_2$(allyl))$^+$.

Dimethyl 1-(cis-4-aminocyclohex-2-enyl)but-3-ene-1,1-dicarboxylate **18**

Yellow oil (76% yield).

TLC: R_f = 0.35 (AcOEt/cyclohexane 1:2).

IR (ν cm^{-1}): 3 300, 3 030, 2 948, 2 860, 1 727, 1 639, 1 580, 1 432.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.90–5.60 (3H, m, 2HC= Cy and 1HC= allyl), 5.10 to 4.90 (2H, m, HC= allyl), 3.70 (3H, s, CO_2CH_3), 3.67 (3H, s, CO_2CH_3), 2.80 to 2.60 (4H, m, CH_2 allyl and 2HC Cy), 1.80 to 1.20 (6H, m, CH_2 Cy and 2H, br s, NH_2).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 170.98 (CO), 132.91 (C= Cy), 130.68 (C= Cy), 128.43 (C= allyl), 118.57 (C= allyl), 61.18 (C(CO_2Me)), 52.02 (CH Cy), 39.17 (CH_2 Cy), 37.17 (CH_2 Cy), 20.89 (CO_2CH_3), 14.05 (CH(NH_2)).

GC/MS (m/z): 266 (M – 1)$^+$, 236 (M – OMe)$^+$, 208 (M – CO_2Me)$^+$, 148 (M – CO_2Me – $CH_2CH{=}CH_2$ + 1)$^+$, 41 ($CH_2CH{=}CH_2$)$^+$.

N-*Allyl*-N-*(diphenylmethyl)allylamine* **19**

Yellow oil (98% yield).

TLC: R_f = 0.80 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 060, 3 023, 2 974, 2 923, 1 658, 1 638, 1 595, 1 488, 1 449, 1 331.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.41 (4H, m, ArH), 7.28 (6H, m, ArH), 5.91 (2H, m, HC=), 4.10 (2H, m, HC=), 5.03 (2H, m, HC=), 4.91 (1H, s, HC), 3.12 (4H, d, ^3J = 6.2 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 141.99 (Ar), 135.57 (C=), 128.36 (Ar), 128.12 (Ar), 126.73 (Ar), 117.14 (C=), 69.29 (CH), 52.39 (CH_2 allyl).

GC/MS (m/z): 263 (M)$^{+\cdot}$, 236 (M – HC=CH_2)$^+$, 222 (M – $CH_2CH{=}CH_2$)$^+$, 186 (M – Ph)$^+$, 167 (M – N(allyl)$_2$)$^+$, 96 (N(allyl)$_2$)$^+$, 77 (Ph)$^+$, 41 ($CH_2CH{=}CH_2$)$^+$.

(S)-*(–)*-N-*Allyl*-N-*(1-phenylethyl)allylamine* **20**

TLC: R_f = 0.78 (AcOEt/cyclohexane 1:2).

IR (ν cm^{-1}): 3 076, 2 972, 2 924, 2 849, 1 638, 1 599, 1 448.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.34 (3H, m, ArH), 7.28 (2H, m, ArH), 5.87 (2H, m, HC=), 5.18 (2H, dm, $^3J_{trans}$ = 16 Hz, HC=), 5.12 (2H, dm, $^3J_{cis}$ = 8 Hz, HC=), 3.92 (1H, q, ^3J = 6.7 Hz), 3.17 (2H, dd, ^2J = 14.4 Hz and ^3J = 6.2 Hz, CH_2 allyl), 3.04 (2H, ddd, ^2J = 14.4 Hz, ^3J = 6.2 Hz and ^4J = 1.2 Hz, CH_2 allyl), 1.37 (3H, d, ^3J = 6.7 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 143.89 (Ar), 136.44 (C=), 127.96 (Ar), 127.58 (Ar), 126.55 (Ar), 116.69 (C=), 58.22 (C(CH_3)), 52.44 (CH_2 allyl), 16.88 (CH_3).

GC/MS (m/z): 201 (M)$^{+\cdot}$, 186 (M – CH_3)$^+$, 144 (M – CH_3 – $CH_2CH{=}CH_2$ – 1)$^+$, 124 (M – Ph)$^+$, 105 (M – N(allyl)$_2$)$^+$, 77 (Ph)$^+$, 41 ($CH_2CH{=}CH_2$)$^+$.

Rotation: $[\alpha]_D^{20}$ = –38.8 (c = 1.4, $CHCl_3$).

Anal calc for $C_{14}H_{19}N$: C, 83.58; H, 9.45; N, 6.97. Found: C, 83.44; H, 9.59; N, 6.96.

(S)-*(–)*-N-*(1-phenylethyl)allylamine* **21**

Pale yellow oil (88% yield).

TLC: R_f = 0.12 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 317, 3 079, 3 023, 2 971, 2 922, 2 865, 1 638, 1 600, 1 488, 1 448, 1 367, 1 351.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.34 (3H, m, ArH), 7.28 (2H, m, ArH), 5.91 (1H, m, HC=), 5.14 (1H, dm, $^3J_{trans}$ = 15.5 Hz, HC=), 5.08 (1H, dm, $^3J_{cis}$ = 6.5 Hz, HC=), 3.82 (1H, q, ^3J = 6.6 Hz, HC(CH_3)), 3.12 (2H, d, ^3J = 6 Hz, CH_2 allyl), 1.38 (4H, d and br s, ^3J = 6.6 Hz, CH_3 and NH).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 145.42 (Ar), 136.89 (C=), 128.33 (Ar), 126.80 (Ar), 126.51 (Ar), 115.56 (C=), 57.43 (C(CH_3)), 50.14 (CH_2 allyl), 24.12 (CH_3).

GC/MS (m/z): 161 (M)$^{+\cdot}$, 146 (M – CH_3)$^+$, 105 (M – HN(allyl))$^+$, 91 ($PhCH_2$)$^+$, 84 (M – Ph)$^+$, 77 (Ph)$^+$, 41 ($CH_2CH{=}CH_2$)$^+$.

Rotation: $[\alpha]_D^{20}$ = –46 (EtOH, c = 0.66).

N-*Benzyl*-N-*butylallylamine* **22**

Pale yellow oil (72% yield).

TLC: R_f = 0.73 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 062, 3 025, 2 954, 2 929, 2 870, 1 638, 1 600, 1 490, 1 449, 1 366.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.31 (5H, m, ArH), 5.91 (1H, m, HC=), 5.21 (1H, dm, $^3J_{trans}$ = 14 Hz, HC=), 5.12 (1H, dm, $^3J_{cis}$ = 6.9 Hz, HC=), 3.58 (2H, s, $ArCH_2$), 3.08 (2H, dt, ^3J = 6.3 Hz and ^4J = 1.3 Hz, CH_2 allyl), 2.44 (2H, t, ^3J = 7.2 Hz, NCH_2), 1.49 (2H, m, CH_2), 1.31 (2H, m, CH_2), 0.89 (3H, t, ^3J = 7.1 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.00 (Ar), 136.10 (C= allyl), 128.75 (Ar), 127.99 (Ar), 126.57 (Ar), 116.86 (C= allyl), 57.88 ($ArCH_2$), 56.69 (CH_2 allyl), 53.08 (NCH_2), 29.11 (CH_2), 20.43 (CH_2), 13.94 (CH_3).

GC/MS (m/z): 203 (M)$^{+\cdot}$; 160 (M – C_3H_7)$^+$, 112 (M – $PhCH_2$)$^+$, 91 ($PhCH_2$)$^+$, 41 ($CH_2CH{=}CH_2$)$^+$.

N-*Butyl*-N-*(diphenylmethyl)allylamine* **23**

Colorless oil (85% yield).

TLC: R_f = 0.85 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 059, 3 023, 2 957, 2 926, 2 868, 1 638, 1 596, 1 487, 1 449.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.42 (4H, m, ArH), 7.28 (6H, m, ArH), 5.94 (1H, m, HC=), 5.13 (2H, m, H_2C=), 4.88 (1H, s, HC), 3.13 (2H, d, ^3J = 6.3 Hz, CH_2 allyl), 2.49 (2H, t, ^3J = 7.1 Hz, NCH_2), 1.46 (2H, m, CH_2), 1.26 (2H, m, CH_2), 0.88 (3H, t, ^3J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 142.44 (Ar), 136.02 (C=), 128.39 (Ar), 128.08 (Ar), 126.65 (Ar), 116.66 (C=), 70.24 (CH), 52.88 (NCH_2), 49.42 (CH_2 allyl), 28.56 (CH_2), 20.40 (CH_2), 14.03 (CH_3).

GC/MS (m/z): 279 (M)$^{+\cdot}$, 236 (M – C_3H_7)$^+$, 202 (M – Ph)$^+$, 167 (M – C_4H_9 – N(allyl))$^+$, 91 ($PhCH_2$)$^+$, 41 ($CH_2CH{=}CH_2$)$^+$.

cis-*4-[Allyl(butyl)amino]cyclohex-2-enyl acetate* **24**

Pale orange oil (93% yield).

TLC: R_f = 0.60 (AcOEt/cyclohexane 1:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.97 (1H, d, ^3J = 10.8 Hz, HC= Cy), 5.85 (1H, dm, ^3J = 10.8 Hz, HC= Cy), 5.82 (1H, m, HC= allyl), 5.18 (1H, dm, $^3J_{trans}$ = 17.8 Hz, HC= allyl), 5.09 (2H, dm and m, HC= allyl and HC(OAc)), 3.34 (1H, br s, $HCNR_2$), 3.21 (1H, dd, ^2J = 14.3 Hz and ^3J = 5.5 Hz, CH_2 allyl), 3.04 (1H, dd, ^2J = 14.3 Hz and ^3J = 7 Hz, CH_2 allyl), 2.45 (2H, m, NCH_2 Bu), 2.06 (3H, s, $COCH_3$), 2.03 (1H, br d, CH_2 Cy), 1.66 (3H, m, 2H CH_2 Bu and 1H CH_2 Cy), 1.5–1.22 (4H, m, CH_2 Bu and CH_2 Cy), 0.91 (3H, t, ^3J = 7 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 170.72 (CO), 137.48 (C= allyl), 126.48 (2C= Cy), 116.38 (C= allyl), 66.19 (C(OAc)),

56.44 (CH_2 Bu), 53.94 (CH_2 allyl), 49.85 (CNR_2), 30.87 (CH_2 Bu), 27.26 ($COCH_3$), 21.26 (CH_2 Cy), 20.42 (CH_2 Bu), 18.45 (CH_2 Cy), 13.95 (CH_3).

GC/MS (m/z): 251 $(M)^{+\cdot}$, 223 $(M - C_2H_5 + 1)^+$, 208 $(M - C_3H_7)^+$, 165 $(M - OAc - HC{=}CH_2)^+$, 139 (M N(Bu)allyl)$^+$, 79 $(M - OAc - N(Bu)allyl)^+$.

(S)-(−)-N-*Butyl*-N-*(1-phenylethyl)allylamine* **25**

Pale yellow oil (96% yield).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.30 (5H, m, ArH), 5.89 (1H, m, HC=), 5.19 (1H, dm, $^3J_{trans}$ = 16 Hz), 5.10 (1H, dm, $^3J_{cis}$ = 10.5 Hz), 3.88 (1H, q, ^3J = 6 Hz), 3.15 (1H, dd, ^2J = 15 Hz and ^3J = 5.5 Hz, CH_2 allyl), 3.03 (1H, dd, ^2J = 15 Hz and ^3J = 5.5 Hz, CH_2 allyl), 2.44 (2H, m, NCH_2), 1.42 (2H, m, CH_2), 1.35 (3H, d, ^3J = 6 Hz, CH_3), 1.28 (2H, m, CH_2), 0.88 (3H, t, ^3J = 7.5 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 144.40 (Ar), 137.10 (C=), 127.86 (Ar), 127.60 (Ar), 126.40 (Ar), 116.12 (C=), 58.59 (CH), 52.96 (CH_2 allyl), 49.04 (NCH_2), 29.41 (CH_2), 20.39 (CH_2), 16.71 (CH_3), 13.96 (CH_3).

GC/MS (m/z): 217 $(M)^{+\cdot}$, 202 $(M - CH_3)^+$, 176 $(M - CH_2CH{=}CH_2)^+$, 174 $(M - C_3H_7)^+$, 105 $(PhCH(CH_3))^+$, 70 $(CH_2N(allyl))^+$, 41 $(CH_2CH{=}CH_2)^+$.

(S)-(−)-N-*Benzyl*-N-*(1-phenylethyl)allylamine* **26**

Colorless oil (89% yield).

TLC: R_f = 0.73 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 089, 3 060, 3 025, 2 970, 2 925, 1 638, 1 599, 1 489, 1 440, 1 372.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.46 to 7.22 (10H, m, ArH), 5.90 (1H, m, HC=), 5.19 (1H, dm, $^3J_{trans}$ = 15.5 Hz, HC=), 5.13 (1H, dm, $^3J_{cis}$ = 8.2 Hz, HC=), 3.96 (1H, q, ^3J = 6.8 Hz, ArCH), 3.63 (1H, d, ^2J = 14 Hz, $ArCH_2$), 3.51 (1H, ^2J = 14 Hz, $ArCH_2$), 3.18 (1H, dd, ^2J = 14.5 Hz and ^3J = 6.5 Hz, CH_2 allyl), 3.01 (1H, dd, ^2J = 14.5 Hz and ^3J = 6.5 Hz, CH_2 allyl), 1.41 (3H, d, ^3J = 6.8 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 143.64 (Ar), 140.55 (Ar), 136.54 (C=), 128.45 (Ar), 128.04 (Ar), 127.93 (Ar), 127.69 (Ar), 126.53 (Ar), 116.75 (C=), 57.45 (ArCH), 53.52 ($ArCH_2$), 52.21 (CH_2 allyl), 15.54 (CH_3).

GC/MS (m/z): 251 $(M)^{+\cdot}$, 236 $(M - CH_3)^+$, 194 $(M - CH_3 - CH_2CH{=}CH_2 - 1)^+$, 174 $(M - Ph)^+$, 146 $(M - PhCH(CH_3))^+$, 91 $(PhCH + 1)^+$, 77 $(Ph)^+$, 41 $(CH_2CH{=}CH_2)^+$.

Rotation: $[\alpha]_D^{20} = -40.7$ (EtOH, c = 0.55).

Anal calc for $C_{18}H_{21}N$: C, 86.05; H, 8.37; N, 5.58. Found: C, 86.01; H, 8.41; N, 5.50.

N-*Benzylbutylamine* **27**

Colorless oil (78% yield)

TLC: R_f = 0.24 (Et_2O/pentane 1:1).

IR (ν cm^{-1}): 3 304, 3 060, 2 954, 2 925, 2 869, 1 600, 1 490, 1 450.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.32 (3H, m, ArH), 7.27 (2H, m, ArH), 3.80 (2H, s, $ArCH_2$), 2.64 (2H, t, ^3J = 6.9 Hz, NCH_2), 1.50 (3H, m and br s, CH_2 and NH), 1.38 (2H, m, CH_2), 0.92 (3H, t, ^3J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.48 (Ar), 128.27 (Ar), 128.01 (Ar), 126.75 (Ar), 54.02 ($ArCH_2$), 49.12 (NCH_2), 32.16 (CH_2), 20.40 (CH_2), 13.93 (CH_3).

GC/MS (m/z): 163 $(M)^{+\cdot}$, 162 $(M - H)^+$, 120 $(M - C_3H_7)^+$, 91 $(PhCH_2)^+$.

N-*(Diphenylmethyl)butylamine* **28**

Pale orange oil (100% yield).

TLC: R_f = 0.42 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 387, 3 059, 2 954, 2 923, 2 868, 1 595, 1 488, 1 449.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.46 (4H, dm, ArH), 7.29 (6H, m, ArH), 4.85 (1H, s, CH), 2.61 (2H, t, ^3J = 6.8 Hz, NCH_2), 1.75 (1H, br s, NH), 1.55 (2H, m, CH_2), 1.39 (2H, m, CH_2), 0.93 (3H, t, ^3J = 7.1 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 144.21 (Ar), 128.31 (Ar), 127.16 (Ar), 126.77 (Ar), 67.52 (CH), 47.89 (NCH_2), 32.27 (CH_2), 20.36 (CH_2), 13.91 (CH_3).

GC/MS (m/z): 239 $(M)^{+\cdot}$, 224 $(M - CH_3)^+$, 196 $(M - C_3H_7)^+$, 162 $(M - Ph)^+$, 91 $(PhCH_2)^+$.

cis-*4-(Butylamino)cyclohex-2-en-1-ol* **29**

Orange oil (99% yield).

IR (ν cm^{-1}): 3 381, 2 952, 2 928, 2 860, 1 641, 1 449, 1 242.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 5.82 (2H, s, HC=), 4.12 (1H, m, HC(OH)), 3.08 (1H, m, HCN(Bu)), 2.65 (2H, t, ^3J = 7.1 Hz, NCH_2 Bu), 1.77 (2H, m, CH_2 Bu), 1.63 (2H, m, CH_2 Cy), 1.53–1.28 (4H, m, CH_2 Bu and CH_2 Cy), 0.91 (3H, t, ^3J = 7.2 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 132.58 (HC=), 130.72 (HC=), 64.36 (C(OH)), 52.96 (CNH(allyl)), 46.63 (NCH_2), 32.21 (CH_2 Cy), 29.07 (CH_2 Cy), 24.57 (CH_2 Bu), 20.39 (CH_2 Bu), 13.86 (CH_3).

GC/MS (m/z): 169 $(M)^{+\cdot}$, 141 $(M - C_2H_5 + 1)^+$, 125 $(M - C_3H_7 - 1)^+$, 79 $(M - OH - NHBu - 1)^+$, 41 $(CH_2CH{=}CH_2)^+$.

(S)-(−)-N-*(1-Phenylethyl)butylamine* **30**

Colorless oil (93% yield).

TLC: R_f = 0.23 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 060, 2 956, 2 923, 2 869, 1 600, 1 488, 1 366.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.36 (3H, m, ArH), 7.26 (2H, m, ArH), 3.78 (1H, q, ^3J = 6.6 Hz, $HC(CH_3)$), 2.49 (2H, m, NCH_2), 1.55 to 1.23 (4H, m, CH_2 Bu and 1H, br s, NH), 1.38 (3H, d, ^3J = 6.6 Hz, CH_3), 0.90 (3H, t, ^3J = 7.0 Hz, CH_3 Bu).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 145.85 (Ar), 128.28 (Ar), 126.69 (Ar), 126.44 (Ar), 58.31 ($C(CH_3)$), 47.49 (NCH_2), 32.35 (CH_2), 24.27 (CH_2), 20.39 (CH_3), 13.90 (CH_3).

GC/MS (m/z): 177 $(M)^{+\cdot}$, 162 $(M - CH_3)^+$, 105 $(PhCH(CH_3))^+$, 53 $(C_3H_7)^+$.

Rotation: $[\alpha]_D^{20} = -59$ (c = 0.675, EtOH).

(S)-(−)-N-*Benzyl-1-phenylethylamine* **31**

Pale yellow oil (85% yield).

TLC: R_f = 0.44 (AcOEt/cyclohexane 1:1).

IR (ν cm^{-1}): 3 058, 3 326, 2 964, 2 921, 1 599, 1 489, 1 449.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.40 (6H, m, ArH), 7.32 (4H, m, ArH), 3.86 (1H, q, ^3J = 6.6 Hz, HC(Me)), 3.71 (1H, d, ^2J = 13.2 Hz, $ArCH_2$), 3.63 (1H, d, ^2J = 13.2 Hz, $ArCH_2$), 1.65 (1H, br s, NH), 1.41 (3H, ^3J = 6.6 Hz, CH_3).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 145.50 (Ar), 140.57 (Ar), 128.38 (Ar), 128.28 (Ar), 128.04 (Ar), 126.84 (Ar), 126.75 (Ar), 57.42 (C(Me)), 51.38 ($ArCH_2$), 24.42 (CH_3).

GC/MS (m/z): 211 $(M)^{+\cdot}$, 196 $(M - CH_3)^+$, 134 $(M - Ph)^+$, 120 $(M - PhCH_2)^+$, 91 $(PhCH_2)^+$.

Rotation: $[\alpha]_D^{20} = -53$ (EtOH, $c = 0.3$). Lit [13]: $[\alpha]_D^{20} = -53.6$ (EtOH, $c = 3.8$).

Anal calc for $C_{15}H_{17}N$: C, 85.31; H, 8.06; N, 6.63. Found: C, 85.24, H, 8.01; N, 6.58.

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