Stereoselective Synthesis of Novel 2-Alkenyl-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepines and 2-Alkenyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ols

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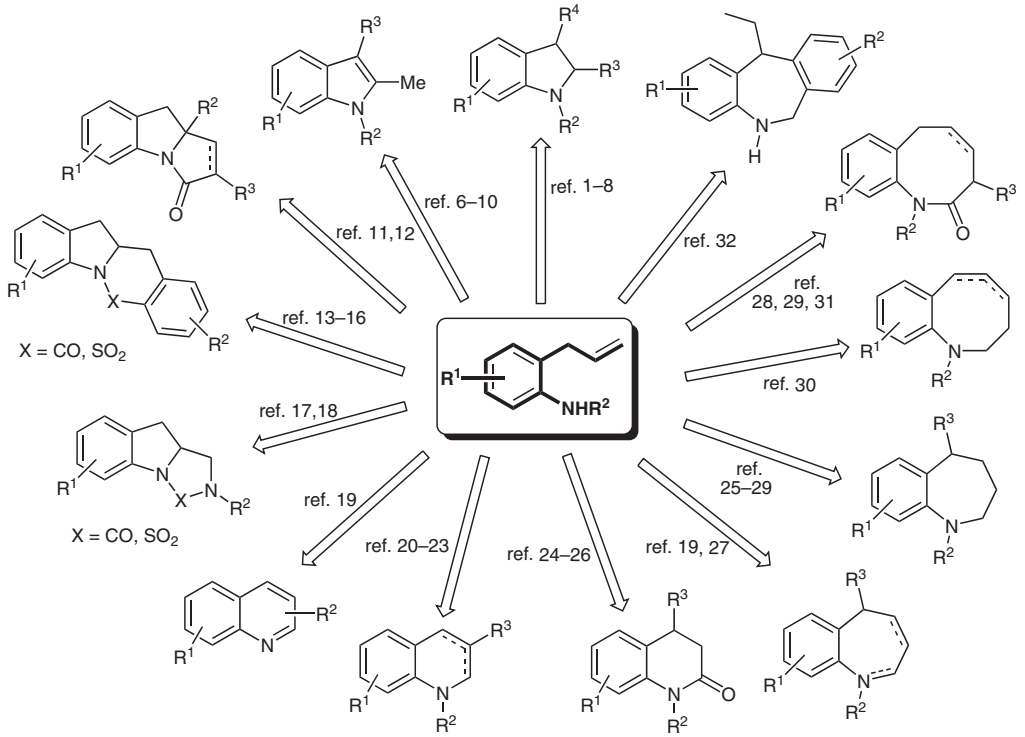
Abstract: New series of polyfunctionalized 2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepines and 2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ols substituted at C2 with 2-methylprop-1-enyl, (*E*)-styryl, and (*E*)-pent-1-enyl were synthesized starting from the corresponding *N*-alkenyl-substituted [prenyl, *trans*-cinnamyl, (*E*)-hex-2-enyl] 2-allylanilines by a three-step sequence consisting of selective oxidation of aromatic secondary amines, intramolecular nitrone–olefin 1,3-dipolar cycloaddition, and reductive cleavage. The intramolecular 1,3-dipolar cycloaddition is stereoselective favoring the *exo*-cycloadducts (ratio *exo*/*endo* 2–3:1). The stereochemistry was determined by exhaustive NMR analysis and X-ray diffraction.

Key words: 1,3-dipolar cycloaddition, 2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepines, 2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ols, reductive cleavage, nitrogen heterocycles

It is well-documented that substituted *o*-allylanilines are useful precursors for the synthesis of diverse classes of nitrogen-containing heterocycles, for example they are known to lead to indolines,[1–8] indoles,[6–10] pyrrolo[1,2-*a*]indolones,[11,12] indolo[1,2-*b*]isoquinolinones and benzo[5,6][1,2]thiazino[2,3-*a*]indole 5,5-dioxides,[13–16] imidazo[1,5-*a*]indolones and [1,2,5]thiadiazolo[2,3-*a*]indole 1,1-dioxides,[17,18] quinolines,[19] dihydroquinolines,[20–23] tetrahydroquinolin-2-ones,[24–26] 4,5-dihydro-3*H*-1-benzazepines,[19] 2,5-dihydro-1*H*-1-benzazepines,[27] tetrahydro-1-benzazepines,[25–29] tetrahydro-1-benzazocines,[30] 3,4,5,6-tetrahydro-1-benzazocin-2-ones,[28,29] 3,6-dihydro-1-benzazocin-2-ones,[31] or dihydrodibenzo[*b*,*e*]azepines,[32] among other aza-heterocycles (Scheme 1).



Scheme 1 *o*-Allylanilines as versatile precursors for the construction of several classes of nitrogen-containing heterocycles

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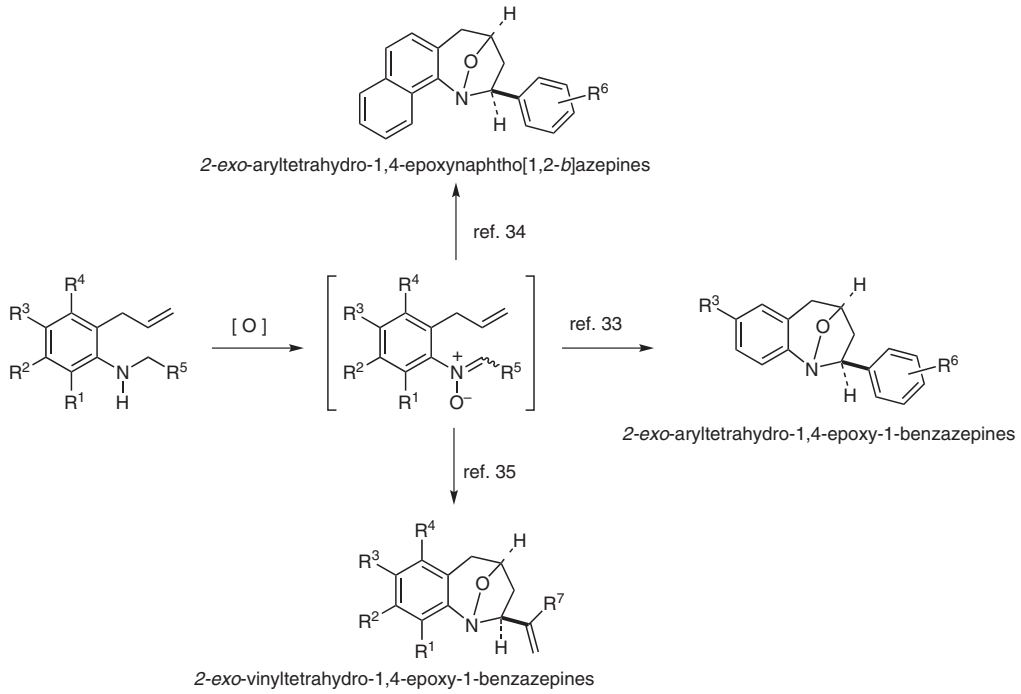
As part of our search program for bioactive aza-heterocyclic compounds, we have previously reported the use of nitrones derived from *o*-allyl-*N*-(arylmethyl)anilines, 2-allyl-*N*-(arylmethyl)-1-naphthylamines, and *N*,2-diallylanilines as versatile templates to furnish 2,4-disubtituted tetrahydro-1-benzazepine and tetrahydronaphtho[1,2-*b*]azepine nuclei via intramolecular nitrone–olefin 1,3-dipolar cycloaddition;[33–35] we have established that the internal cycloaddition of this type of nitrone proceeds with a high level of stereoselectivity towards the formation of 2-*exo*-1,4-epoxycycloadducts as unique stereoisomers (Scheme 2). Many of the synthesized tetrahydro-1-benzazepines and tetrahydronaphtho[1,2-*b*]azepines have shown remarkable in vitro activity against epimastigote and promastigote forms of *Trypanosoma cruzi* and *Leishmania chagasi* parasites,[36,37] most of them bearing an aryl group at C2.

Accordingly, we planned examine the influence of an alkenyl substituent at C2 in the azepine ring on the bioactivity of benzazepines. We report herein the details of the synthesis and stereochemistry of six novel series of tetrahydro-1,4-epoxy-1-benzazepines and their reduction products, tetrahydro-1-benzazepin-4-ols, bearing at C2 2-methylprop-1-enyl, (*E*)-styryl, and (*E*)-pent-1-enyl moieties, with the aim of evaluating their antiparasitic activity. To the best of our knowledge, these types of substituted tetrahydro-1-benzazepines have not yet been described in the literature.

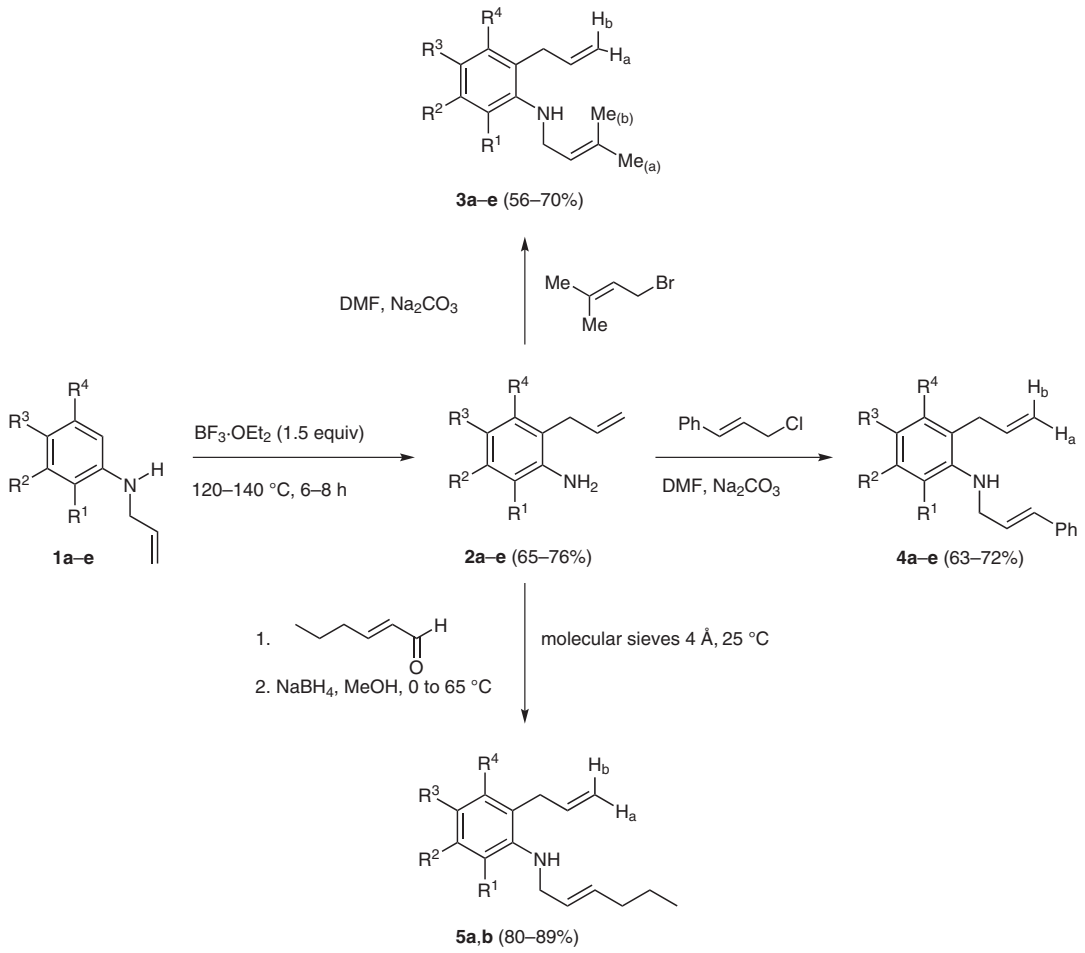
To prepare the key intermediates that will afford the target 1,4-epoxy cycloadducts bearing 2-(2-methylprop-1-enyl) **6**, **7**, 2-[(*E*)-styryl] **8**, **9**, and 2-[(*E*)-pent-1-enyl] moieties **10**, **11**, we synthesized the corresponding *N*-prenyl- **3**, *N*-(*trans*-cinnamyl)- **4**, and *N*-[(*E*)-hex-2-enyl]-substituted *o*-allylanilines by an efficient two-step sequence from the corresponding mono-*N*-allylanilines **1** (Scheme 3).

First, *N*-allylanilines **1a**–**e** were heated with excess boron trifluoride–diethyl ether complex to give the aza-Claisen rearrangement products **2a**–**e** in good yields.[35] To prepare the *N*-prenyl- and *N*-*trans*-cinnamyl-substituted anilines **3a**–**e** and **4a**–**e**, nucleophilic substitution of prenyl bromide or *trans*-cinnamyl chloride with *o*-allylanilines **2a**–**e** was used. These intermediates **3**, **4** were isolated, after chromatographic purification, in good yields as oily residues. To introduce the *N*-[(*E*)-hex-2-enyl] moiety, nucleophilic substitution was not efficient and the reductive amination methodology was used instead to give *o*-allyl-*N*-[(*E*)-hex-2-enyl]anilines **5a**,**b** from the anilines **2b**,**d**. To perform this reaction, solvent-free condensation of *o*-allylaniline **2b** or **2d** with (*E*)-hex-2-enal was carried out at room temperature in the presence of molecular sieves (4 Å) to yield the corresponding imine intermediate which was reduced in situ with sodium borohydride in methanol to afford **5a** or **5b**, respectively, in good overall yields. The assignment of all signals to individual H and C atoms in compounds **3**–**5** (see experimental section) were made from their chemical shift values and coupling constants, and confirmed on the basis of COSY, HSQC, and HMBC spectra.

In the next step of our approach, we focused our attention on the transformation of the key intermediates **3**–**5** into 2-alkenyltetrahydro-1,4-epoxy-1-benzazepines by employing the tandem selective oxidation of secondary aromatic



Scheme 2 *o*-Allylanilines as versatile templates for the construction of 2-*exo*-substituted tetrahydro-1,4-epoxy-1-benzazepine and tetrahydro-1,4-epoxynaphtho[1,2-*b*]azepine nuclei



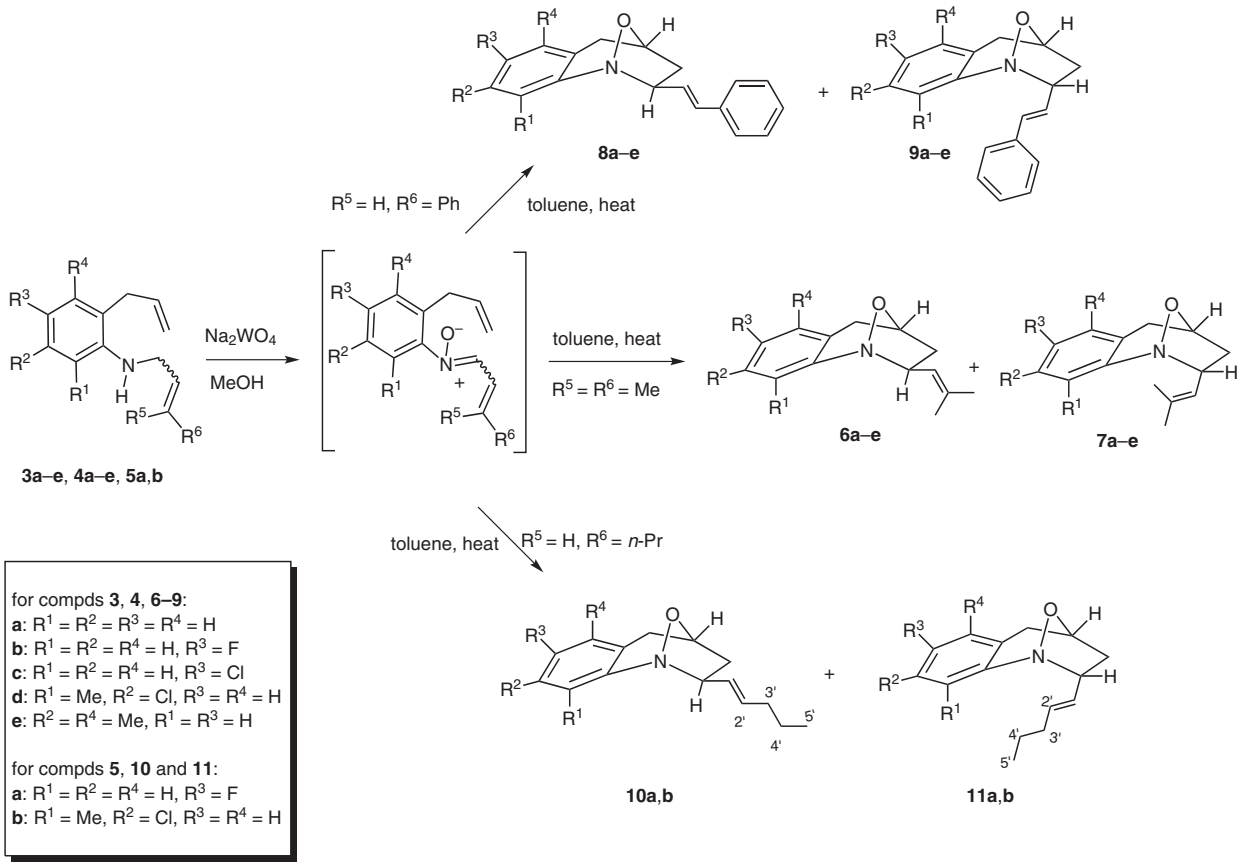
Scheme 3 Synthesis of *N*-alkenyl-substituted *o*-allylanilines **3a**–**e**, **4a**–**e**, and **5a**,**b**

amines (Murahashi methodology)[38] and thermal intramolecular 1,3-dipolar cycloaddition (Scheme 4). Thus, the preparation of the target 1,4-epoxy cycloadducts was carried out by first reacting compounds **3a**–**e**, **4a**–**e**, and **5a**,**b** in methanol with excess hydrogen peroxide solution in the presence of catalytic amounts of sodium tungstate at a temperature rising from 0 °C to 25 °C. The organic residues (nitrones), obtained after easy work-up and without further purification, were heated in toluene and underwent intramolecular 1,3-dipolar cycloaddition across the terminal C=C bond of the pendant allylic fragment (dipolarophile) in the *ortho* position to give 1,4-epoxy cycloadducts in reasonable times and with moderate-to-good yields (Table 1). The intramolecular 1,3-dipolar cycloaddition of nitrones from **3** proceeds within six hours, while that derived from **4** and **5** require more time, up to 12 hours; this could be due to steric hindrance.

This thermal 1,3-dipolar cycloaddition accomplished the formation of both 2-*exo*- and 2-*endo*-1,4-epoxy cycloadducts along with a considerable amounts of byproduct, indicative of decomposition. The *exo*- and *endo*-cycloadducts were successfully separated by silica gel column chromatography as high-viscosity maroon oils or as crystalline substances (see experimental section), and their structures as well as stereochemistry deduced from NMR spectroscopic analysis, both 1D and 2D, specially using the coupling constant values of the tertiary H2 and H4 azepinic protons, together with spatial correlations observed in the NOESY spectra. The major products were assigned as 2-*exo*-1,4-epoxy cycloadducts **6**, **8**, and **10**, and the minor products as 2-*endo*-1,4-epoxy cycloadducts **7**, **9**, and **11** in a ratio of 2–3:1.

For *endo*-cycloadducts **7**, **9**, and **11** the NOESY shows an NOE cross-peak between H2 and H4, this shows that the tetrahydro-1,4-epoxy-1-benzazepine ring contains these two hydrogens in the *cis* orientation, while for the *exo*-cycloadducts **6**, **8** and **10** this NOE cross-peak does not appear.

To confirm the assigned stereochemistry of both *exo*- and *endo*-1,4-epoxy cycloadducts, single crystal X-ray analysis of derivatives both with pendant 2-prenyl **6c**, **6d**, **7d**, and 2-styryl **8b**, **8c**, **9b**, and **9c** substituents was also performed.[39–41] The molecular structures of isomeric *exo*-cycloadducts **6d** and **8c**, and *endo*-cycloadducts **7d** and **9c**, with numbering scheme, are shown in Figure 1 and Figure 2, and agree with the stereochemistry deduced from NMR analysis.



Scheme 4 Synthesis of 2-*exo*- and 2-*endo*-1,4-epoxy cycloadducts **6**–**11**

Table 1 Preparation and Yields of *exo*- and *endo*-1,4-Epoxy Cycloadducts **6a**–**e**/**7a**–**e**, **8a**–**e**/**9a**–**e**, and **10a**,**b**/**11a**,**b** from *o*-Allylanilines **3a**–**e**, **4a**–**e**, and **5a**,**b**

Entry	*o*-Allylaniline	Temp (°C), time (h)		*exo*-Cycloadduct		*endo*-Cycloadduct	
	3–**5**	Oxidation	1,3-Dipolar cycloaddition	**6**, **8**, **10**	Yield[a] (%)	**7**, **9**, **11**	Yield[a] (%)
1	**3a**	0–25, 12	100, 6	**6a**	38	**7a**	16
2	**3b**	0–25, 8	100, 6	**6b**	35	**7b**	14
3	**3c**	0–25, 8	100, 6	**6c**	40	**7c**	19
4	**3d**	0–25, 72	100, 6	**6d**	40	**7d**	15
5	**3e**	0–25, 8	100, 6	**6e**	35	**7e**	11
6	**4a**	0–25, 36	100, 12	**8a**	48	**9a**	14
7	**4b**	0–25, 36	100, 12	**8b**	52	**9b**	20
8	**4c**	0–25, 32	100, 12	**8c**	54	**9c**	25
9	**4d**	0–25, 72	100, 12	**8d**	46	**9d**	19
10	**4e**	0–25, 24	100, 12	**8e**	45	**9e**	18
11	**5a**	0–25, 8	80, 12	**10a**	30	**11a**	10
12	**5b**	0–25, 32	70, 12	**10b**	28	**11b**	13

[a] Yields refer to isolated and pure compounds after column chromatography.

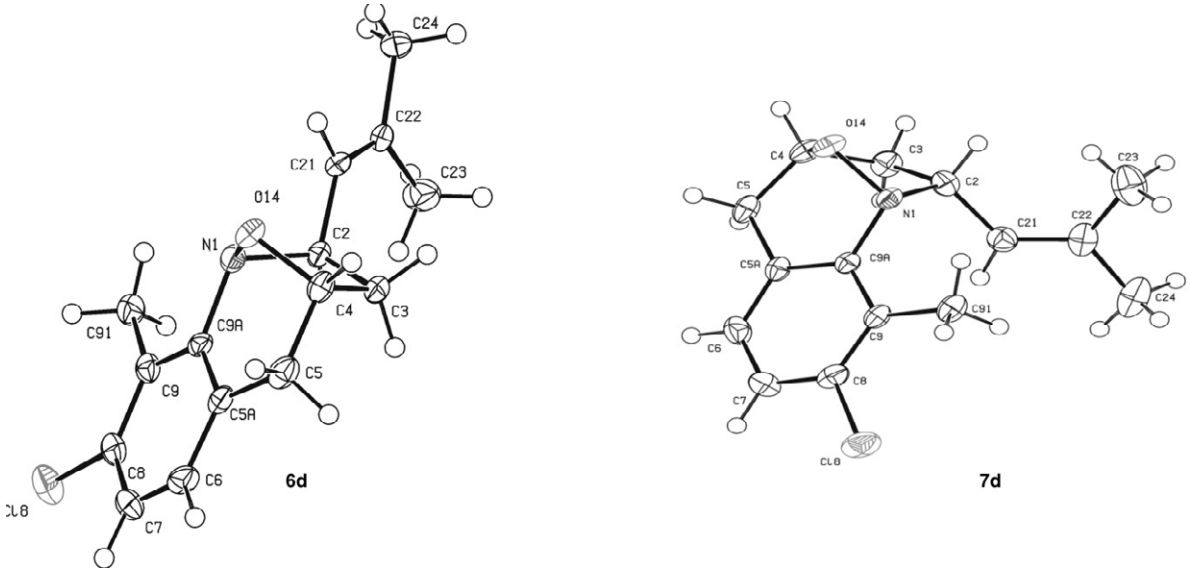


Figure 1 ORTEP drawing of molecular structures of the isomeric *exo*- and *endo*-cycloadducts **6d** and **7d**, showing the atom-labeling scheme

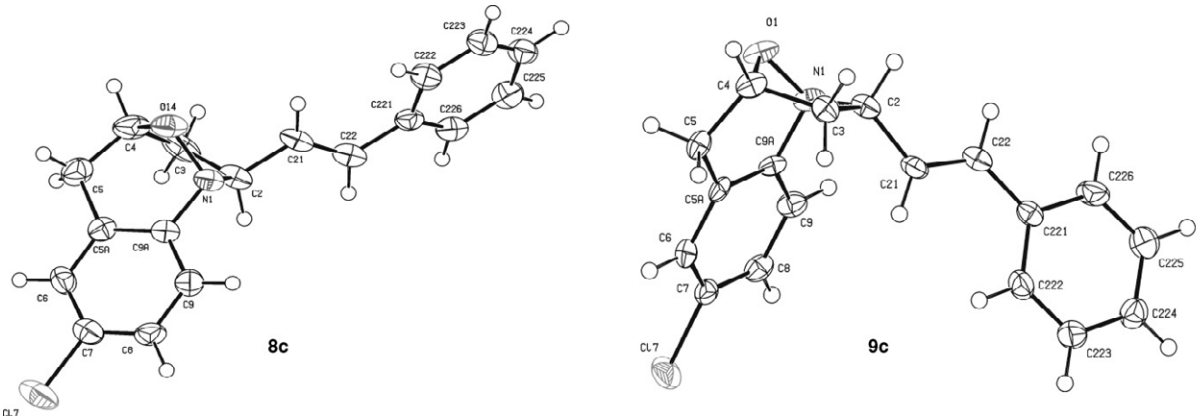
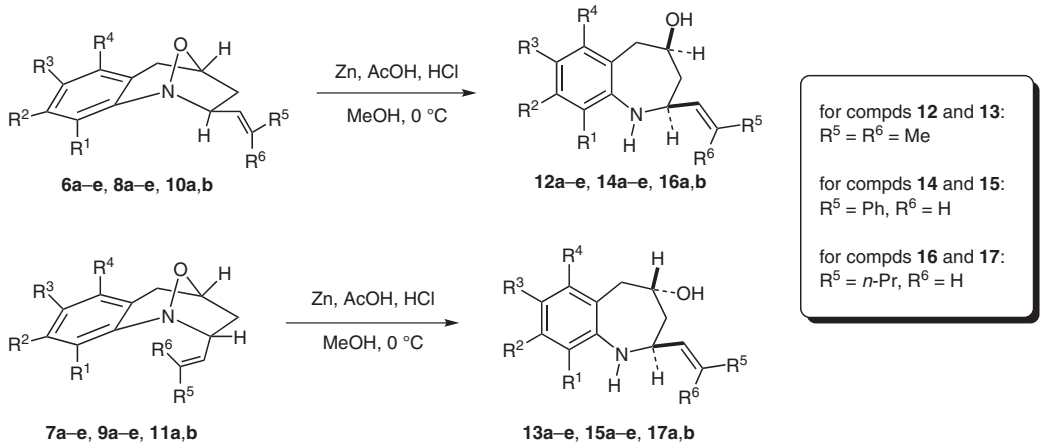


Figure 2 ORTEP drawing of molecular structures of the isomeric *exo*- and *endo*-cycloadducts **8c** and **9c**, showing the atom-labeling scheme

The last step of our approach is the reductive cleavage of the N–O bond of the obtained stereoisomeric *exo*- and *endo*-1,4-epoxy cycloadducts.[35] Thus, *exo*- and *endo*-cycloadducts were separately treated with excess zinc powder in a mixture of glacial acetic acid and concentrated hydrochloric acid at 0 °C, for 0.5–2.0 hours (Scheme 5) to afford the expected *cis*- and *trans*-2-alkenyltetrahydro-1-benzazepin-4-ols, respectively. These novel cyclic γ-amino alcohols were isolated after chromatographic purification in excellent yields (Table 2).

The structures and stereochemistry of these novel compounds were determined mainly by 1D and 2D NMR spectroscopy. As in the case of their precursors the *cis* or *trans* stereochemistry at the stereogenic C2 and C4 of the tetrahydroazepine ring was established on the basis of coupling constant values of the tertiary H2 and H4 protons and on the spatial interactions observed in 2D-NOESY spectra for the *cis* compounds **12**, **14**, and **16** but not for the *trans* derivatives. Both the 2-(2-methylprop-1-enyl), 2-styryl, and 2-pent-1-enyl moieties and 4-hydroxy group are oriented equatorially for the *cis* isomers **12**, **14**, and **16** with the tetrahydroazepine ring in the chair conformation, and in the case of the *trans* isomers **13**, **15**, and **17** the substituents at C2 are oriented equatorially but the 4-hydroxy group is now in the axial position.

We are now developing preliminary biological assays to evaluate the antiparasitic activity of these compounds. We have found that both isomeric 1,4-epoxy cycloadducts and tetrahydro-1-benzazepin-4-ols possess promising activity against the epimastigote and amastigote forms of *T. cruzi* as well as against promastigote form of *L. chagasi* parasites, the 7-chloro-substituted 2-*endo*-(2-methylprop-1-enyl)tetrahydro-1,4-epoxy-1-benzazepine **7c**, and the 7-chloro-substituted *cis*-2-(2-methylprop-1-enyl)tetrahydro-1-benzazepin-4-ol **12c** are the most active compounds, with $IC_{50} = 10.4$ and 5.8 μM, respectively. Detailed results from this biological study will be reported in the near future elsewhere.



Scheme 5 Synthesis of *cis*- and *trans*-2-alkenyltetrahydro-1*H*-1-benzazepin-4-ols **12**–**17**

Table 2 Preparation and Yields of 2-Alkenyl-Substituted *cis*- and *trans*-Tetrahydro-1*H*-1-benzazepin-4-ols **12a–e**/**13a–e**, **14a–e**/**15a–e**, and **16a**,**b**/**17a**,**b** from *exo*- and *endo*-1,4-Epoxy Cycloadducts **6a–e**/**7a–e**, **8a–e**/**9a–e**, and **10a**,**b**/**11a**,**b**

Entry	*exo*/*endo*-Cycloadducts	Time (min)	*cis*-Product	Yield[a] (%)	*trans*-Product	Yield[a] (%)
1	**6a**	30	**12a**	96	–	–
2	**6b**	30	**12b**	94	–	–
3	**6c**	30	**12c**	94	–	–
4	**6d**	120	**12d**	96	–	–
5	**6e**	60	**12e**	94	–	–
6	**7a**	30	–	–	**13a**	90
7	**7b**	30	–	–	**13b**	92
8	**7c**	30	–	–	**13c**	91
9	**7d**	120	–	–	**13d**	90
10	**7e**	60	–	–	**13e**	92
11	**8a**	30	**14a**	92	–	–
12	**8b**	30	**14b**	93	–	–
13	**8c**	30	**14c**	95	–	–
14	**8d**	120	**14d**	85	–	–
15	**8e**	60	**14e**	93	–	–
16	**9a**	30	–	–	**15a**	91
17	**9b**	30	–	–	**15b**	91
18	**9c**	30	–	–	**15c**	92
19	**9d**	120	–	–	**15d**	82
20	**9e**	60	–	–	**15e**	91
21	**10a**	30	**16a**	95	–	–
22	**10b**	45	**16b**	94	–	–
23	**11a**	30	–	–	**17a**	90
24	**11b**	45	–	–	**17b**	86

[a] Yields refer to isolated and pure compounds after column chromatography.

We have provided a convenient and simple synthetic methodology to achieve both isomeric 2-*exo*- and 2-*endo*-alkenyltetrahydro-1,4-epoxy-1-benzazepines and *cis*- and *trans*-2-alkenyltetrahydro-1-benzazepin-4-ols, compounds with potential antiparasitic activity that are not otherwise readily accessible. This work represents an interesting extension of our studies dealing with the synthesis of compounds having in their structure the tetrahydro-1-benzazepine core in order to develop novel molecules with potent antiparasitic activity.

All reagents and solvents were purchased from Sigma-Aldrich or Merck and used without further purification. Monitoring of the reactions was performed using silica gel TLC plates (silica Merck 60 F254, visualization UV light at 254 and 365 nm). Column chromatography was performed on Merck Kieselgel 60–230 mesh (ASTM). Melting points were measured with a MEL-TEMP 1201D capillary apparatus and were not corrected. IR spectra were recorded on a Nicolet Avatar 360-FTIR spectrophotometer referenced to polystyrene standard, using cells equipped with KBr windows. ^{1}H and ^{13}C NMR spectra were measured at 25 °C on a Bruker Avance III-400 spectrometer operating at 400 MHz and 100 MHz respectively, using $CDCl_3$ as the solvent. Chemical shifts are relative to the solvent peaks used as reference [$CDCl_3$: $\delta_H = 7.26$, and $\delta_C = 77.0$]. A Hewlett Packard HP 5890 A series II Gas chromatograph interfaced to a Hewlett Packard 5972 Mass Selective Detector with a HP MS ChemStation Data system, and HRMS Waters Micromass AutoSpect NT (equipped with a direct inlet probe) operating at 70 eV were used for MS identification.

2-Allyl-*N*-(3-methylbut-2-enyl)anilines 3a–e; General Procedure

1-Bromo-3-methylbut-2-ene (10 mmol) was very slowly added to a stirred and cooled (ice bath) mixture of 2-allylaniline **2a–e** (10 mmol) and Na_2CO_3 (10 mmol) in anhyd DMF (25 mL). The mixture was stirred at 0 °C for 2–6 h (TLC monitoring), it was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic extracts were washed with sufficient H_2O to remove the DMF. The soln was dried (anhyd Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, heptane–EtOAc, 90:1 to 60:1) to give **3a–e** as low-viscosity maroon oils.

2-Allyl-*N*-(3-methylbut-2-enyl)aniline (3a)

Time: 3 h; yield: 0.98 g (65%).

IR (liquid film): 3420 (N–H), 1639 (C=C allyl), 914 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 7.19 (td, *J* = 7.4, 1.3 Hz, 1 H, H5), 7.07 (dd, *J* = 7.4, 1.3 Hz, 1 H, H3), 6.72 (td, *J* = 7.4, 1.2 Hz, 1 H, H4), 6.67 (dd, *J* = 7.4, 1.2 Hz, 1 H, H6), 5.96 (ddt, *J* = 16.5, 10.2, 6.2 Hz, 1 H, CH= allyl), 5.39–5.33 (m, 1 H, =CH prenyl), 5.14 (dq, *J* = 10.2, 1.7 Hz, 1 H, =C*H*$_a$H$_b$), 5.10 (dq, *J* = 16.5, 1.7 Hz, 1 H, =CH$_a$*H*$_b$), 3.71 (d, *J* = 6.7 Hz, 2 H, NCH_2), 3.30 (dt, *J* = 6.2, 1.7 Hz, 2 H, CH_2 allyl), 1.77 (br s, 3 H, $CH_{3(a)}$ prenyl), 1.72 (br s, 3 H, $CH_{3(b)}$ prenyl).

^{13}C NMR: δ = 146.5 (C1), 136.1 (=CH allyl), 135.7 (C= prenyl), 129.7 (C3), 127.7 (C5), 123.6 (C2), 121.7 (CH= prenyl), 117.1 (C4), 116.2 (=CH_2 allyl), 110.6 (C6), 42.0 (NCH_2), 36.4 (CH_2 allyl), 25.8 ($CH_{3(a)}$ prenyl), 18.1 ($CH_{3(b)}$ prenyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 201 (M$^{+\bullet}$, 48), 133 (41), 132 (90), 131 (32), 130 (69), 118 (100), 117 (35), 69 (48).

2-Allyl-4-fluoro-*N*-(3-methylbut-2-enyl)aniline (3b)

Time: 3 h; yield: 0.90 g (62%).

IR (liquid film): 3417 (N–H), 1637 (C=C allyl), 916 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 6.88 (dd, *J* = 8.6, 3.0 Hz, 1 H, H3), 6.83 (td, *J* = 8.6, 3.0 Hz, 1 H, H5), 6.59 (dd, *J* = 8.6, 4.8 Hz, 1 H, H6), 5.93 (ddt, *J* = 17.1, 10.2, 6.2 Hz, 1 H, CH= allyl), 5.38–5.36 (m, 1 H, =CH prenyl), 5.16 (dq, *J* = 10.1, 1.6 Hz, 1 H, =C*H*$_a$H$_b$), 5.11 (dq, *J* = 17.1, 1.6 Hz, 1 H, =CH$_a$*H*$_b$), 3.67 (d, *J* = 6.7 Hz, 2 H, NCH_2), 3.26 (br d, *J* = 6.2 Hz, 2 H, CH_2 allyl), 1.77 (br s, 3 H, $CH_{3(a)}$ prenyl), 1.71 (br s, 3 H, $CH_{3(b)}$ prenyl).

^{13}C NMR: δ = 155.9 (d, *J* = 233.6 Hz, C4), 142.6 (C1), 136.0 (C= prenyl), 135.3 (=CH allyl), 125.7 (d, *J* = 6.7 Hz, C2), 121.6 (CH= prenyl), 116.9 (=CH_2 allyl), 116.5 (d, *J* = 22.5 Hz, C3), 113.5 (d, *J* = 21.4 Hz, C5), 111.7 (d, *J* = 7.1 Hz, C6), 42.8 (NCH_2), 36.1 (CH_2 allyl), 25.8 ($CH_{3(a)}$ prenyl), 18.1 ($CH_{3(b)}$ prenyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 219 (M$^{+\bullet}$, 52), 151 (59), 150 (55), 149 (23), 148 (38), 136 (100), 69 (63).

2-Allyl-4-chloro-*N*-(3-methylbut-2-enyl)aniline (3c)

Time: 3 h; yield: 0.79 g (56%).

IR (liquid film): 3425 (N–H), 1639 (C=C allyl), 919 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 7.10 (dd, *J* = 8.6, 2.4 Hz, 1 H, H5), 7.02 (d, *J* = 2.4 Hz, 1 H, H3), 6.58 (d, *J* = 8.6 Hz, 1 H, H6), 5.90 (ddt, *J* = 17.1, 10.2, 6.2 Hz, 1 H, CH= allyl), 5.33–5.29 (m, 1 H, =CH prenyl), 5.15 (dq, *J* = 10.2, 1.6 Hz, 1 H, =C*H*$_a$H$_b$), 5.11 (dq, *J* = 17.1, 1.6 Hz, 1 H, =CH$_a$*H*$_b$), 3.68 (d, *J* = 7.3 Hz, 2 H, NCH_2), 3.24 (br d, *J* = 6.2 Hz, 2 H, CH_2 allyl), 1.74 (br s, 3 H, $CH_{3(a)}$ prenyl), 1.68 (br s, 3 H, $CH_{3(b)}$ prenyl).

^{13}C NMR: δ = 144.8 (C1), 136.3 (C= prenyl), 135.2 (=CH allyl), 129.5 (C3), 127.4 (C5), 126.7 (C2), 125.6 (C4), 121.3 (CH= prenyl), 117.0 (=CH_2 allyl), 112.1 (C6), 42.4 (NCH_2), 36.1 (CH_2 allyl), 25.8 ($CH_{3(a)}$ prenyl), 18.2 ($CH_{3(b)}$ prenyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 235 (M$^{+\bullet}$, ^{35}Cl, 67), 167 (58), 166 (46), 165 (26), 164 (47), 152 (87), 151 (19), 69 (100).

6-Allyl-3-chloro-2-methyl-*N*-(3-methylbut-2-enyl)aniline (3d)

Time: 6 h; yield: 0.87 g (70%).

IR (liquid film): 3375 (N–H), 1637 (C=C allyl), 915 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 7.00 (d, *J* = 8.2 Hz, 1 H, H4), 6.91 (d, *J* = 8.2 Hz, 1 H, H5), 5.94 (ddt, *J* = 17.1, 10.1, 6.1 Hz, 1 H, CH= allyl), 5.37–5.33 (m, 1 H, =CH prenyl), 5.11 (dq, *J* = 10.1, 1.7 Hz, 1 H, =C*H*$_a$H$_b$), 5.02 (dq, *J* = 17.1, 1.7 Hz, 1 H, =CH$_a$*H*$_b$), 3.47 (d, *J* = 7.1 Hz, 2 H, NCH_2), 3.36 (dt, *J* = 6.1, 1.7 Hz, 2 H, CH_2 allyl), 2.37 (s, 3 H, 2-CH_3), 1.74 (br s, 3 H, $CH_{3(a)}$ prenyl), 1.65 (br s, 3 H, $CH_{3(b)}$ prenyl).

^{13}C NMR: δ = 148.0 (C1), 136.7 (=CH allyl), 135.4 (C= prenyl), 133.8 (C3), 130.1 (C6), 129.2 (C2), 128.3 (C5), 123.2 (C4), 122.4 (CH= prenyl), 116.4 (=CH_2 allyl), 47.3 (NCH_2), 36.6 (CH_2 allyl), 25.9 ($CH_{3(a)}$ prenyl), 18.0 ($CH_{3(b)}$ prenyl), 15.9 (2-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 249 (M$^{+\bullet}$, ^{35}Cl, 39), 181 (36), 180 (38), 178 (43), 166 (72), 145 (41), 144 (38), 130 (30), 69 (100).

2-Allyl-3,5-dimethyl-*N*-(3-methylbut-2-enyl)aniline (3e)

Time: 2 h; yield: 0.85 g (60%).

IR (liquid film): 3419 (N–H), 1634 (C=C allyl), 912 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 6.47 (s, 1 H, H4), 6.39 (s, 1 H, H6), 5.89 (ddt, *J* = 17.0, 10.2, 5.7 Hz, 1 H, CH= allyl), 5.38–5.33 (m, 1 H, =CH prenyl), 5.04 (dq, *J* = 10.2, 1.7 Hz, 1 H, =C*H*$_a$H$_b$), 5.00 (dq, *J* = 17.0, 1.7 Hz, 1 H, =CH$_a$*H*$_b$), 3.67 (d, *J* = 6.7 Hz, 2 H, NCH_2), 3.30 (dt, *J* = 5.7, 1.7 Hz, 2 H, CH_2 allyl), 2.29 (s, 3 H, 5-CH_3), 2.25 (s, 3 H, 3-CH_3), 1.77 (br s, 3 H, $CH_{3(a)}$ prenyl), 1.71 (br s, 3 H, $CH_{3(b)}$ prenyl).

^{13}C NMR: δ = 146.7 (C1), 136.6 (C3, C5), 135.5 (C= prenyl), 135.3 (=CH allyl), 121.9 (CH= prenyl), 120.4 (C4), 118.9 (C2), 109.8 (C6), 115.1 (=CH_2 allyl), 42.3 (NCH_2), 31.3 (CH_2 allyl), 25.7 ($CH_{3(a)}$ prenyl), 21.5 (5-CH_3), 20.0 (3-CH_3), 18.1 ($CH_{3(b)}$ prenyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 229 ($M^{+\bullet}$, 57), 161 (15), 160 (56), 159 (26), 158 (57), 146 (100), 145 (54), 69 (18).

2-Allyl-*N*-(*trans*-cinnamyl)anilines 4a–e; General Procedure
To a stirred mixture of 2-allylaniline **2a–e** (10 mmol), Na_2CO_3 (10 mmol), and KI (5 mol%) in anhyd DMF (30 mL), *trans*-cinnamyl chloride (10 mmol) was slowly added at r.t. The mixture was stirred for 22–32 h (TLC control), then extracted with CH_2Cl_2 (2 × 100 mL) and washed with H_2O to remove the DMF. The combined organic layers were dried (anhyd Na_2SO_4), and the solvent removed under reduced pressure. The crude products were purified by column chromatography (silica gel, heptane–EtOAc; 80:1 to 50:1) to give **4a–e** as viscous yellow oils.

2-Allyl-*N*-(*trans*-cinnamyl)aniline (4a)
Time: 24 h; yield: 1.37 g (65%).

IR (liquid film): 3432 (N–H), 1638 (C=C allyl), 967 (C=C *trans*-cinnamyl), 915 cm^{-1} (=C–H allyl).

^1H NMR: δ = 7.40 (dd, *J* = 7.6, 1.6 Hz, 2 H, H2′/H6′), 7.33 (td, *J* = 7.6, 1.6 Hz, 2 H, H3′/H5′), 7.27–7.23 (m, 1 H, H4′), 7.18 (td, *J* = 7.8, 1.5 Hz, 1 H, H5), 7.09 (dd, *J* = 7.8, 1.2 Hz, 1 H, H3), 6.74 (td, *J* = 7.8, 1.5 Hz, 1 H, H4), 6.73 (d, *J* = 7.8 Hz, 1 H, H6), 6.63 (d, *J* = 15.8 Hz, 1 H, =CH cinnamyl), 6.36 (dt, *J* = 15.8, 5.7 Hz, 1 H, CH= cinnamyl), 5.99 (ddt, *J* = 16.5, 10.4, 6.1 Hz, 1 H, CH= allyl), 5.16 (dq, *J* = 10.4, 1.7 Hz, 1 H, =C$H_a$$H_b$), 5.13 (dq, *J* = 16.5, 1.7 Hz, 1 H, =C$H_a$$H_b$), 3.98 (dd, *J* = 5.7, 1.4 Hz, 2 H, NCH_2), 3.35 (br d, *J* = 6.1 Hz, 2 H, CH_2 allyl).

^{13}C NMR: δ = 146.1 (C1), 136.9 (C1′), 136.1 (=CH allyl), 131.5 (=CH cinnamyl), 129.9 (C3), 128.6 (C3′/C5′), 127.8 (C5), 127.5 (C4′), 127.1 (CH= cinnamyl), 126.4 (C2′/C6′), 123.8 (C2), 117.5 (C4), 116.3 (=CH_2 allyl), 110.9 (C6), 46.1 (NCH_2), 36.5 (CH_2 allyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 249 ($M^{+\bullet}$, 18), 130 (36), 118 (33), 117 (100), 115 (61), 91 (39).

2-Allyl-*N*-(*trans*-cinnamyl)-4-fluoroaniline (4b)
Time: 24 h; yield: 1.20 g (68%).

IR (liquid film): 3428 (N–H), 1636 (C=C allyl), 966 (C=C *trans*-cinnamyl), 917 cm^{-1} (=C–H allyl).

^1H NMR: δ = 7.41–7.37 (m, 2 H, H2′/H6′), 7.33 (t, *J* = 7.6 Hz, 2 H, H3′/H5′), 7.27–7.21 (m, 1 H, H4′), 6.89 (dd, *J* = 8.4, 3.0 Hz, 1 H, H3), 6.85 (td, *J* = 8.8, 3.0 Hz, 1 H, H5), 6.65 (dd, *J* = 8.8, 4.8 Hz, 1 H, H6), 6.62 (d, *J* = 16.0 Hz, 1 H, =CH cinnamyl), 6.34 (dt, *J* = 16.0, 5.7 Hz, 1 H, CH= cinnamyl), 5.96 (ddt, *J* = 16.3, 10.2, 6.1, 1 H, CH= allyl), 5.18 (dq, *J* = 10.2, 1.7 Hz, 1 H, =C$H_a$$H_b$), 5.14 (dq, *J* = 16.3, 1.7 Hz, 1 H, =C$H_a$$H_b$), 3.93 (dd, *J* = 5.7, 1.4 Hz, 2 H, NCH_2), 3.31 (br d, *J* = 6.1 Hz, 2 H, CH_2 allyl).

^{13}C NMR: δ = 156.0 (d, *J* = 232.5 Hz, C4), 142.4 (C1), 137.0 (C1′), 135.3 (=CH allyl), 131.8 (=CH cinnamyl), 128.7 (C3′/C5′), 127.7 (C4′), 127.0 (CH= cinnamyl), 126.5 (C2′/C6′), 125.8 (C2), 117.0 (=CH_2 allyl), 116.7 (d, *J* = 22.0 Hz, C3), 113.6 (d, *J* = 21.8 Hz, C5), 112.0 (d, *J* = 8.8 Hz, C6), 46.8 (NCH_2), 36.3 (CH_2 allyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 267 ($M^{+\bullet}$, 20), 148 (18), 117 (100), 115 (43), 91 (19).

2-Allyl-4-chloro-*N*-(*trans*-cinnamyl)aniline (4c)
Time: 21 h; yield: 1.07 g (63%).

IR (liquid film): 3434 (N–H), 1637 (C=C allyl), 967 (C=C *trans*-cinnamyl), 920 cm^{-1} (=C–H allyl).

^1H NMR: δ = 7.39 (dd, *J* = 7.2, 1.6 Hz, 2 H, H2′/H6′), 7.36 (td, *J* = 7.6, 1.6 Hz, 2 H, H3′/H5′), 7.27–7.22 (m, 1 H, H4′), 7.12 (dd, *J* = 8.6, 2.4 Hz, 1 H, H5), 7.06 (d, *J* = 2.4 Hz, 1 H, H3), 6.64 (d, *J* = 8.6 Hz, 1 H, H6), 6.61 (d, *J* = 16.0 Hz, 1 H, =CH cinnamyl), 6.32 (dt, *J* = 16.0, 5.7 Hz, 1 H, CH= cinnamyl), 5.95 (ddt, *J* = 16.6, 10.2, 6.1 Hz, 1 H, CH= allyl), 5.18 (dq, *J* = 10.2, 1.7 Hz, 1 H, =C$H_a$$H_b$), 5.14 (dq, *J* = 16.6, 1.7 Hz, 1 H, =C$H_a$$H_b$), 3.94 (dd, *J* = 5.7, 1.4 Hz, 2 H, NCH_2), 3.30 (br d, *J* = 6.1 Hz, 2 H, CH_2 allyl).

^{13}C NMR: δ = 144.4 (C1), 136.7 (C1′), 135.0 (=CH allyl), 131.8 (=CH cinnamyl), 129.5 (C3), 128.6 (C3′/C5′), 127.6 (C4′), 127.3 (C5), 126.3 (C2′/C6′), 126.3 (CH= cinnamyl), 125.5 (C2), 122.1 (C4), 116.9 (=CH_2 allyl), 112.1 (C6), 46.2 (NCH_2), 36.0 (CH_2 allyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 283 ($M^{+\bullet}$, ^{35}Cl, 22), 166 (7), 117 (100), 115 (46), 91 (27).

6-Allyl-3-chloro-*N*-(*trans*-cinnamyl)-2-methylaniline (4d)
Time: 32 h; yield: 1.18 g (72%).

IR (liquid film): 3375 (N–H), 1637 (C=C allyl), 967 (C=C *trans*-cinnamyl), 916 cm^{-1} (=C–H allyl).

^1H NMR: δ = 7.41–7.38 (m, 2 H, H2′/H6′), 7.34 (td, *J* = 7.2, 1.6 Hz, 2 H, H3′/H5′), 7.28–7.24 (m, 1 H, H4′), 7.04 (d, *J* = 8.2 Hz, 1 H, H4), 6.95 (d, *J* = 8.2 Hz, 1 H, H5), 6.62 (d, *J* = 15.8 Hz, 1 H, =CH cinnamyl), 6.35 (dt, *J* = 15.8, 6.3 Hz, 1 H, CH= cinnamyl), 5.97 (ddt, *J* = 17.1, 10.2, 6.1 Hz, 1 H, CH= allyl), 5.13 (dq, *J* = 10.2, 1.6 Hz, 1 H, =C$H_a$$H_b$), 5.04 (dq, *J* = 17.2, 1.6 Hz, 1 H, =C$H_a$$H_b$), 3.70 (dd, *J* = 6.3, 1.6 Hz, 2 H, NCH_2), 3.40 (dt, *J* = 6.1, 1.6 Hz, 2 H, CH_2 allyl), 2.41 (s, 3 H, 2-CH_3).

^{13}C NMR: δ = 147.4 (C1), 136.9 (C1′), 136.6 (=CH allyl), 133.8 (C3), 131.5 (=CH cinnamyl), 130.1 (C6), 129.3 (C2), 128.6 (C3′/C5′), 128.3 (C5), 127.6 (CH= cinnamyl), 127.5 (C4′), 126.4 (C2′/C6′), 123.4 (C4), 116.4 (=CH_2 allyl), 51.5 (NCH_2), 36.5 (CH_2 allyl), 15.8 (2-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 297 ($M^{+\bullet}$, ^{35}Cl, 9), 178 (12), 166 (15), 117 (100), 115 (43), 91 (28).

2-Allyl-*N*-(*trans*-cinnamyl)-3,5-dimethylaniline (4e)
Time: 22 h; yield: 1.14 g (66%).

IR (liquid film): 3429 (N–H), 1634 (C=C allyl), 967 (C=C *trans*-cinnamyl), 913 cm^{-1} (=C–H allyl).

^1H NMR: δ = 7.40 (br d, *J* = 7.3 Hz, 2 H, H2′/H6′), 7.33 (br t, *J* = 7.3 Hz, 2 H, H3′/H5′), 7.27–7.23 (m, 1 H, H4′), 6.63 (d, *J* = 15.8 Hz, 1 H, =CH cinnamyl), 6.50 (s, 1 H, H4), 6.45 (s, 1 H, H6), 6.37 (dt, *J* = 15.8, 5.7 Hz, 1 H, CH= cinnamyl), 5.93 (ddt, *J* = 17.0, 10.3, 5.6 Hz, 1 H, CH= allyl), 5.07 (dq, *J* = 10.3, 1.8 Hz, 1 H, =C$H_a$$H_b$), 5.04 (dq, *J* = 17.0, 1.8 Hz, 1 H, =C$H_a$$H_b$), 3.95 (dd, *J* = 5.7, 1.4 Hz, 2 H, NCH_2), 3.35 (dt, *J* = 5.6, 1.8 Hz, 2 H, CH_2 allyl), 2.29 (s, 3 H, 5-CH_3), 2.27 (s, 3 H, 3-CH_3).

^{13}C NMR: δ = 146.4 (C1), 137.1 (C5), 136.9 (C3), 136.7 (C1′), 135.4 (=CH allyl), 131.4 (=CH cinnamyl), 128.7 (C3′/C5′), 127.6 (C4′), 127.5 (CH= cinnamyl), 126.5 (C2′/C6′), 120.9 (C4), 119.2 (C2), 115.4 (=CH_2 allyl), 110.1 (C6), 46.5 (NCH_2), 31.4 (CH_2 allyl), 21.7 (5-CH_3), 20.1 (3-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 277 ($M^{+\bullet}$, 58), 160 (44), 159 (32), 158 (61), 146 (68), 145 (44), 117 (100), 115 (73).

2-Allyl-*N*-[(*E*)-hex-2-enyl]anilines 5a,b; General Procedure
A mixture of *o*-allylaniline **2b**,**d** (10 mmol) and (*E*)-hex-2-enal (10 mmol) was stirred in the presence of molecular sieves (4 Å; 100 mg) at r.t. Once the imines had formed (TLC monitoring), MeOH (70 mL) was added, and to this soln $NaBH_4$ (40 mmol) was added in small portions at 0 °C. When the addition was complete, the mixture was stirred at r.t. for a further 5 h. Finally, H_2O (60 mL) was added and the mixture was heated to 65 °C for 4 h. The mixture was extracted with $CHCl_3$ (2 × 100 mL), the combined organic extracts were dried (anhyd Na_2SO_4), and solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, heptane–EtOAc, 80:1 to 50:1) to give products **5a**,**b** as low-viscosity yellow oils.

2-Allyl-4-fluoro-*N*-[(*E*)-hex-2-enyl]aniline (5a)
Time: 10 h; yield: 1.37 g (89%).

IR (liquid film): 3420 (N–H), 1637 (C=C allyl), 917 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 6.84 (td, *J* = 8.4, 2.8 Hz, 1 H, H5), 6.80 (dd, *J* = 8.4, 4.8 Hz, 1 H, H6), 6.56 (dd, *J* = 8.6, 2.8 Hz, 1 H, H3), 5.92 (ddt, *J* = 17.2, 10.2, 6.0 Hz, 1 H, CH= allyl), 5.68 (dt, *J* = 15.2, 6.6 Hz, 1 H, =CH hexenyl), 5.57 (dt, *J* = 15.2, 5.6 Hz, 1 H, CH= hexenyl), 5.18 (dq, *J* = 10.2, 1.6 Hz, 1 H, =C*H*$_a$H$_b$), 5.10 (dq, *J* = 17.2, 1.6 Hz, 1 H, =CH$_a$*H*$_b$), 3.67 (br d, *J* = 5.6 Hz, 2 H, NCH$_2$), 3.26 (d, *J* = 6.0 Hz, 2 H, CH$_2$ allyl), 2.02 (dd, *J* = 14.7, 6.6 Hz, 2 H, 4′-CH$_2$ hexenyl), 1.40 (dq, *J* = 14.7, 7.3 Hz, 2 H, 5′-CH$_2$ hexenyl), 0.90 (t, *J* = 7.3 Hz, 3 H, 6′-CH$_3$ hexenyl).

^{13}C NMR: δ = 155.7 (d, *J* = 237.0 Hz, C4), 142.5 (C1), 135.2 (=CH allyl), 133.3 (=CH hexenyl), 126.8 (CH= hexenyl), 125.4 (d, *J* = 7.0 Hz, C2), 116.8 (=CH$_2$ allyl), 116.4 (d, *J* = 22.4 Hz, C3), 111.6 (d, *J* = 7.7 Hz, C6), 113.3 (d, *J* = 21.5 Hz, C5), 46.5 (NCH$_2$), 36.1 (CH$_2$ allyl), 34.4 (4′-CH$_2$ hexenyl), 22.4 (5′-CH$_2$ hexenyl), 13.6 (6′-CH$_3$ hexenyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 233 (M$^{+\bullet}$, 41), 150 (91), 148 (100), 136 (71), 135 (43), 55 (43).

6-Allyl-3-chloro-*N*-[(*E*)-hex-2-enyl]-2-methylaniline (5b)
Time: 12 h; yield: 1.15 g (80%).

IR (liquid film): 3379 (N–H), 1637 (C=C allyl), 915 cm^{-1} (=C–H allyl).

^{1}H NMR: δ = 7.00 (d, *J* = 8.2 Hz, 1 H, H4), 6.91 (d, *J* = 8.2 Hz, 1 H, H5), 5.92 (ddt, *J* = 17.2, 10.1, 6.0 Hz, 1 H, CH= allyl), 5.62 (dt, *J* = 15.6, 6.6 Hz, 1 H, =CH hexenyl), 5.57 (dt, *J* = 15.6, 6.0 Hz, 1 H, CH= hexenyl), 5.12 (dq, *J* = 10.1, 1.6 Hz, 1 H, =C*H*$_a$H$_b$), 5.03 (dq, *J* = 17.1, 1.6 Hz, 1 H, =CH$_a$*H*$_b$), 3.46 (br d, *J* = 6.0 Hz, 2 H, NCH$_2$), 3.36 (br d, *J* = 6.0 Hz, 2 H, CH$_2$ allyl), 2.36 (s, 3 H, 2-CH$_3$), 2.02 (dd, *J* = 13.9, 6.7 Hz, 2 H, 4′-CH$_2$ hexenyl), 1.40 (dq, *J* = 14.6, 7.1 Hz, 2 H, 5′-CH$_2$ hexenyl), 0.91 (t, *J* = 7.1 Hz, 3 H, 6′-CH$_3$ hexenyl).

^{13}C NMR: δ = 147.7 (C1), 136.6 (=CH allyl), 133.7 (C3), 133.2 (=CH hexenyl), 129.9 (C6), 129.1 (C2), 128.2 (C5), 127.8 (CH= hexenyl), 123.1 (C4), 116.3 (=CH$_2$ allyl), 51.5 (NCH$_2$), 36.6 (CH$_2$ allyl), 34.4 (4′-CH$_2$ hexenyl), 22.4 (5′-CH$_2$ hexenyl), 15.8 (2-CH$_3$), 13.7 (6′-CH$_3$ hexenyl).

GC-MS (EI, 70 eV): *m*/*z* (%) = 263 (M$^{+\bullet}$, ^{35}Cl, 35), 180 (72), 178 (97), 166 (67), 145 (100), 144 (66), 130 (53).

(2*SR*,4*RS*)- and (2*RS*,4*RS*)-2-Alk-1-enyl-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepines 6–11; General Procedure
$Na_2WO_4{\cdot}2\,H_2O$ (10 mol%), and 30% aq H_2O_2 soln (30 mmol) were added to a stirred and cooled (ice bath) soln of the appropriately substituted *N*-alk-2-enyl-2-allylaniline **3a**–**e**, **4a**–**e**, and **5a**,**b** (10 mmol) in MeOH (30 mL). The resulting mixture was stirred at 0 °C for 2 h and then at r.t. for an additional 4–14 h. The solid was removed by filtration and the product was extracted with EtOAc. The combined organic extracts were dried (anhyd Na_2SO_4) and the solvent was removed under reduced pressure. Toluene (30 mL) was added to the organic black residue, and the resulting soln was heated at 70–100 °C for 6–72 h. After cooling the soln to r.t., the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, heptane–EtOAc, 60:1 to 5:1) to give 1,4-epoxycycloadducts **6a**–**e**, **7a**–**e**, **8a**–**e**, **9a**–**e**, **10a**,**b**, and **11a**,**b** as individual diastereomers.

(2*SR*,4*RS*)-2-(2-Methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (6a)
White crystals; yield: 0.41 g (38%); mp 78 °C (heptane); R_f = 0.54 (7% EtOAc–heptane).

IR (KBr): 1263 (C–N), 1051 (C–O), 984 cm^{-1} (N–O).

^{1}H NMR: δ = 7.08 (dd, *J* = 7.6, 1.3 Hz, 1 H, H6), 7.15 (td, *J* = 7.6, 1.3 Hz, 1 H, H8), 7.11 (td, *J* = 7.6, 1.3 Hz, 1 H, H7), 7.04 (dd, *J* = 7.6, 1.3 Hz, 1 H, H9), 5.43 (ddt, *J* = 8.8, 2.6, 1.4 Hz, 1 H, CH= prenyl), 4.87 (ddd, *J* = 7.6, 5.2, 2.0 Hz, 1 H, H4), 4.22 (td, *J* = 8.6, 2.4 Hz, 1 H, H2), 3.35 (dd, *J* = 16.6, 5.2 Hz, 1 H, H5$_B$), 2.46 (d, *J* = 16.6 Hz, 1 H, H5$_A$), 2.31 (ddd, *J* = 12.4, 8.1, 2.0 Hz, 1 H, H3$_A$), 2.21 (dddd, *J* = 12.4, 7.6, 2.4, 1.2 Hz, 1 H, H3$_B$), 1.74 (d, *J* = 1.2 Hz, 3 H, CH$_{3(a)}$), 1.67 (d, *J* = 1.2 Hz, 3 H, CH$_{3(b)}$).

^{13}C NMR: δ = 150.3 (C9a), 132.8 (=C prenyl), 129.8 (C6), 127.9 (CH= prenyl), 126.5 (C8), 125.8 (C7), 125.2 (C5a), 121.8 (C9), 74.7 (C4), 70.8 (C2), 41.3 (C3), 34.8 (C5), 25.6 (CH$_{3(a)}$), 18.3 (CH$_{3(b)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 215 (M$^{+\bullet}$, 38), 198 (27), 185 (1), 130 (24), 105 (43), 104 (100).

HRMS: *m*/*z* [M]$^+$ calcd for $C_{14}H_{17}NO$: 215.1310; found: 215.1316.

(2*RS*,4*RS*)-2-(2-Methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (7a)
White crystals; yield: 0.17 g (16%); mp 41 °C (heptane); R_f = 0.43 (7% EtOAc–heptane).

IR (KBr): 1250 (C–N), 1052 (C–O), 981 cm^{-1} (N–O).

^{1}H NMR: δ = 7.13–7.06 (m, 3 H, H6, H7, H8), 6.78 (dd, *J* = 7.8, 1.3 Hz, 1 H, H9), 4.85 (ddd, *J* = 8.0, 5.2, 2.4 Hz, 1 H, H4), 4.48 (ddt, *J* = 9.0, 2.6, 1.2 Hz, 1 H, CH= prenyl), 4.43 (q, *J* = 8.2 Hz, 1 H, H2), 3.39 (dd, *J* = 16.6, 5.2 Hz, 1 H, H5$_B$), 2.67 (dtd, *J* = 12.2, 8.0, 1.0 Hz, 1 H, H3$_B$), 2.47 (d, *J* = 16.6 Hz, 1 H, H5$_A$), 1.82 (d, *J* = 1.2 Hz, 3 H, CH$_{3(a)}$), 1.65 (d, *J* = 1.2 Hz, 3 H, CH$_{3(b)}$), 1.57 (ddd, *J* = 12.2, 7.6, 2.4 Hz, 1 H, H3$_A$).

^{13}C NMR: δ = 146.2 (C9a), 138.9 (=C prenyl), 129.7 (C6), 125.7 (C5a), 125.7 (C8), 125.3 (C7), 124.5 (C9), 120.7 (CH= prenyl), 75.7 (C4), 68.8 (C2), 40.6 (C3), 35.8 (C5), 25.8 (CH$_{3(a)}$), 18.8 (CH$_{3(b)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 215 (M$^{+\bullet}$, 42), 198 (27), 185 (1), 130 (21), 105 (43), 104 (100).

HRMS: *m*/*z* [M]$^+$ calcd for $C_{14}H_{17}NO$: 215.1310; found: 215.1314.

(2*SR*,4*RS*)-7-Fluoro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (6b)
White crystals; yield: 0.37 g (35%); mp 72 °C (heptane); R_f = 0.50 (7% EtOAc–heptane).

IR (KBr): 1250 (C–N), 1051 (C–O), 983 cm^{-1} (N–O).

^{1}H NMR: δ = 7.00 (dd, *J* = 8.6, 5.4 Hz, 1 H, H9), 6.83 (td, *J* = 8.6, 2.8 Hz, 1 H, H8), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1 H, H6), 5.40 (br d, *J* = 8.8 Hz, 1 H, CH= prenyl), 4.84 (ddd, *J* = 7.6, 5.2, 2.0 Hz, 1 H, H4), 4.16 (td, *J* = 8.6, 2.2 Hz, 1 H, H2), 3.33 (dd, *J* = 16.8, 5.2 Hz, 1 H, H5$_B$), 2.44 (d, *J* = 16.8 Hz, 1 H, H5$_A$), 2.30 (ddd, *J* = 12.4, 8.0, 2.0 Hz, 1 H, H3$_A$), 2.22 (dddd, *J* = 12.4, 7.6, 2.2, 1.2 Hz, 1 H, H3$_B$), 1.73 (br s, 3 H, CH$_{3(a)}$), 1.66 (br s, 3 H, CH$_{3(b)}$).

^{13}C NMR: δ = 160.9 (d, *J* = 243.9 Hz, C7), 146.7 (d, *J* = 2.6 Hz, C9a), 133.3 (=C prenyl), 128.2 (CH= prenyl), 127.6 (d, *J* = 8.2 Hz, C5a), 123.6 (d, *J* = 8.5 Hz, C9), 116.5 (d, *J* = 22.4 Hz, C6), 113.8 (d, *J* = 22.5 Hz, C8), 74.5 (C4), 71.2 (C2), 41.7 (C3), 35.3 (d, *J* = 1.3 Hz, C5), 25.9 (CH$_{3(a)}$), 18.6 (CH$_{3(b)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 233 (M$^{+\bullet}$, 27), 216 (15), 203 (1), 148 (19), 123 (46), 122 (100).

HRMS: *m*/*z* [M]$^+$ calcd for $C_{14}H_{16}FNO$: 233.1216; found: 233.1219.

(2*RS*,4*RS*)-7-Fluoro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (7b)
White crystals; yield: 0.15 g (14%); mp 66 °C (heptane); R_f = 0.46 (7% EtOAc–heptane).

IR (KBr): 1245 (C–N), 1052 (C–O), 987 cm^{-1} (N–O).

^{1}H NMR: δ = 6.78–6.72 (m, 3 H, H6, H8, H9), 4.82 (ddd, *J* = 8.0, 5.2, 2.2 Hz, 1 H, H4), 4.45 (ddt, *J* = 8.8, 2.4, 1.2 Hz, 1 H, CH= prenyl), 4.41 (q, *J* = 8.0 Hz, 1 H, H2), 3.36 (dd, *J* = 16.6, 5.2 Hz, 1 H, H5$_B$), 2.67 (dtd, *J* = 12.8, 8.0, 0.8 Hz, 1 H, H3$_B$), 2.46 (d, *J* = 16.6 Hz, 1 H, H5$_A$), 1.81 (d, *J* = 1.2 Hz, 3 H, CH$_{3(a)}$), 1.65 (d, *J* = 0.8 Hz, 3 H, CH$_{3(b)}$), 1.55 (ddd, *J* = 12.8, 7.6, 2.2 Hz, 1 H, H3$_A$).

^{13}C NMR: δ = 160.6 (d, *J* = 243.6 Hz, C7), 142.0 (d, *J* = 2.5 Hz, C9a), 139.3 (=C prenyl), 127.7 (d, *J* = 8.1 Hz, C5a), 125.9 (d,

J = 8.4 Hz, C9), 120.5 (CH= prenyl), 116.0 (d, J = 22.3 Hz, C6), 112.4 (d, J = 22.4 Hz, C8), 75.1 (C4), 68.7 (C2), 40.6 (C3), 35.9 (d, J = 1.2 Hz, C5), 25.8 ($CH_{3(a)}$), 18.8 ($CH_{3(b)}$).

GC-MS (EI, 70 eV): m/z (%) = 233 ($M^{+\bullet}$, 24), 216 (15), 203 (1), 148 (21), 123 (45), 122 (100).

HRMS: m/z $[M]^+$ calcd for $C_{14}H_{16}FNO$: 233.1216; found: 233.1218.

(2*SR*,4*RS*)-7-Chloro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (6c)
White crystals; yield: 0.42 g (40%); mp 94 °C (heptane); R_f = 0.57 (7% EtOAc–heptane).

IR (KBr): 1255 (C–N), 1052 (C–O), 979 cm^{-1} (N–O).

^{1}H NMR: δ = 7.11 (dd, J = 8.4, 2.3 Hz, 1 H, H8), 7.07 (d, J = 2.3 Hz, 1 H, H6), 6.98 (d, J = 8.4 Hz, 1 H, H9), 5.40 (ddt, J = 8.8, 2.6, 1.2 Hz, 1 H, CH= prenyl), 4.85 (ddd, J = 7.6, 5.2, 2.2 Hz, 1 H, H4), 4.18 (td, J = 8.4, 2.4 Hz, 1 H, H2), 3.32 (dd, J = 16.7, 5.2 Hz, 1 H, $H5_B$), 2.44 (d, J = 16.7 Hz, 1 H, $H5_A$), 2.29 (ddd, J = 12.4, 8.0, 2.2 Hz, 1 H, $H3_A$), 2.24 (dddd, J = 12.4, 7.6, 2.4, 1.1 Hz, 1 H, $H3_B$), 1.73 (d, J = 0.9 Hz, 3 H, $CH_{3(a)}$), 1.66 (d, J = 1.1 Hz, 3 H, $CH_{3(b)}$).

^{13}C NMR: δ = 149.0 (C9a), 133.3 (=C prenyl), 131.1 (C7), 129.7 (C6), 127.6 (C8), 127.2 (C5a), 126.8 (CH= prenyl), 123.2 (C9), 74.3 (C4), 71.0 (C2), 41.4 (C3), 34.8 (C5), 25.7 ($CH_{3(a)}$), 18.4 ($CH_{3(b)}$).

GC-MS (EI, 70 eV): m/z (%) = 249 ($M^{+\bullet}$, ^{35}Cl, 41), 232 (18), 219 (1), 164 (15), 139 (58), 138 (100).

HRMS: m/z $[M]^+$ calcd for $C_{14}H_{16}ClNO$: 249.0920; found: 249.0932.

(2*SR*,4*RS*)-7-Chloro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (7c)
White crystals; yield: 0.20 g (19%); mp 110 °C (heptane); R_f = 0.50 (7% EtOAc–heptane).

IR (KBr): 1260 (C–N), 1051 (C–O), 983 cm^{-1} (N–O).

^{1}H NMR: δ = 7.09 (br s, 1 H, H6), 7.05 (dd, J = 8.4, 2.1 Hz, 1 H, H8), 6.73 (d, J = 8.4 Hz, 1 H, H9), 4.84 (ddd, J = 7.6, 5.2, 2.2 Hz, 1 H, H4), 4.46 (ddt, J = 8.8, 2.4, 1.2 Hz, 1 H, CH= prenyl), 4.44 (q, J = 7.6 Hz, 1 H, H2), 3.36 (dd, J = 16.6, 5.2 Hz, 1 H, $H5_B$), 2.69 (dtd, J = 12.8, 7.6, 1.0 Hz, 1 H, $H3_B$), 2.49 (d, J = 16.6 Hz, 1 H, $H5_A$), 1.82 (br s, 3 H, $CH_{3(a)}$), 1.65 (br s, 3 H, $CH_{3(b)}$), 1.57 (ddd, J = 12.8, 7.6, 2.2 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 144.6 (C9a), 140.0 (=C prenyl), 131.2 (C7), 129.7 (C6), 127.8 (C5a), 125.9 (C8), 125.7 (C9), 120.3 (CH= prenyl), 75.1 (C4), 68.7 (C2), 40.6 (C3), 35.9 (C5), 25.8 ($CH_{3(a)}$), 18.8 ($CH_{3(b)}$).

GC-MS (EI, 70 eV): m/z (%) = 249 ($M^{+\bullet}$, ^{35}Cl, 40), 232 (21), 219 (1), 164 (15), 139 (57), 138 (100).

HRMS: m/z $[M]^+$ calcd for $C_{14}H_{16}ClNO$: 249.0920; found: 249.0929.

(2*SR*,4*RS*)-8-Chloro-9-methyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (6d)
White crystals; yield: 0.42 g (40%); mp 94 °C (heptane); R_f = 0.61 (7% EtOAc–heptane).

IR (KBr): 1274 (C–N), 1051 (C–O), 976 cm^{-1} (N–O).

^{1}H NMR: δ = 7.10 (d, J = 8.0 Hz, 1 H, H7), 6.86 (d, J = 8.0 Hz, 1 H, H6), 5.45 (br d, J = 8.8 Hz, 1 H, CH= prenyl), 4.86 (ddd, J = 7.6, 5.2, 2.0 Hz, 1 H, H4), 4.11 (td, J = 8.4, 2.4 Hz, 1 H, H2), 3.31 (dd, J = 16.4, 5.2 Hz, 1 H, $H5_B$), 2.40 (d, J = 16.4 Hz, 1 H, $H5_A$), 2.34 (s, 3 H, 9-CH_3), 2.25 (ddd, J = 12.4, 8.0, 2.0 Hz, 1 H, $H3_A$), 2.19 (dddd, J = 12.4, 7.6, 2.4, 1.2 Hz, 1 H, $H3_B$), 1.75 (br s, 3 H, $CH_{3(a)}$), 1.64 (br s, 3 H, $CH_{3(b)}$).

^{13}C NMR: δ = 150.0 (C9a), 132.7 (=C prenyl), 132.3 (C8), 129.2 (C9), 128.2 (C6), 127.9 (CH= prenyl), 126.2 (C7), 123.8 (C5a), 74.8 (C4), 69.7 (C2), 41.8 (C3), 35.0 (C5), 26.0 ($CH_{3(a)}$), 18.5 ($CH_{3(b)}$), 14.1 (9-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 263 ($M^{+\bullet}$, ^{35}Cl, 46), 246 (24), 233 (1), 178 (15), 153 (100), 152 (62).

HRMS: m/z $[M]^+$ calcd for $C_{15}H_{18}ClNO$: 263.1077; found: 263.1080.

(2*RS*,4*RS*)-8-Chloro-9-methyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (7d)
White crystals; yield: 0.16 g (15%); mp 107 °C (heptane); R_f = 0.47 (7% EtOAc–heptane).

IR (KBr): 1276 (C–N), 1051 (C–O), 977 cm^{-1} (N–O).

^{1}H NMR: δ = 7.12 (d, J = 8.0 Hz, 1 H, H7), 6.87 (d, J = 8.0 Hz, 1 H, H6), 4.80 (ddd, J = 7.6, 5.2, 2.4 Hz, 1 H, H4), 4.52–4.43 (m, 2 H, CH= prenyl, H2), 3.32 (dd, J = 16.4, 5.2 Hz, 1 H, $H5_B$), 2.66 (dt, J = 12.4, 8.0 Hz, 1 H, $H3_B$), 2.46 (d, J = 16.4 Hz, 1 H, $H5_A$), 2.18 (s, 3 H, 9-CH_3), 1.81 (br s, 3 H, $CH_{3(a)}$), 1.62 (br s, 3 H, $CH_{3(b)}$), 1.58 (ddd, J = 12.4, 7.4, 2.4 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 146.4 (C9a), 139.6 (=C prenyl), 132.6 (C8), 131.9 (C9), 128.1 (C6), 126.5 (C7), 124.8 (C5a), 120.6 (CH= prenyl), 75.4 (C4), 69.0 (C2), 41.7 (C3), 36.2 (C5), 26.2 ($CH_{3(a)}$), 18.9 ($CH_{3(b)}$), 15.1 (9-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 263 ($M^{+\bullet}$, ^{35}Cl, 47), 246 (30), 233 (1), 178 (18), 153 (100), 152 (61).

HRMS: m/z $[M]^+$ calcd for $C_{15}H_{18}ClNO$: 263.1077; found: 263.1073.

(2*SR*,4*RS*)-6,8-Dimethyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (6e)
White crystals; yield: 0.37 g (35%); mp 87 °C (heptane); R_f = 0.57 (7% EtOAc–heptane).

IR (KBr): 1276 (C–N), 1055 (C–O), 971 cm^{-1} (N–O).

^{1}H NMR: δ = 6.82 (s, 1 H, H7), 6.73 (s, 1 H, H9), 5.43 (ddt, J = 8.8, 2.8, 1.4 Hz, 1 H, CH= prenyl), 4.91 (ddd, J = 7.6, 5.6, 2.0 Hz, 1 H, H4), 4.22 (td, J = 8.4, 2.4 Hz, 1 H, H2), 3.12 (dd, J = 16.8, 5.6 Hz, 1 H, $H5_B$), 2.29 (ddd, J = 12.4, 8.4, 2.0 Hz, 1 H, $H3_A$), 2.28 (s, 3 H, 8-CH_3), 2.27 (d, J = 16.8 Hz, 1 H, $H5_A$), 2.21 (dddd, J = 12.4, 7.6, 2.4, 1.2 Hz, 1 H, $H3_B$), 2.14 (s, 3 H, 6-CH_3), 1.74 (d, J = 1.2 Hz, 3 H, $CH_{3(a)}$), 1.67 (d, J = 1.2 Hz, 3 H, $CH_{3(b)}$).

^{13}C NMR: δ = 150.1 (C9a), 137.5 (C6), 136.0 (C8), 132.6 (=C prenyl), 128.1 (CH= prenyl), 128.0 (C7), 120.3 (C5a), 119.9 (C9), 74.8 (C4), 70.7 (C2), 41.9 (C3), 33.1 (C5), 25.6 ($CH_{3(a)}$), 21.1 (8-CH_3), 18.5 ($CH_{3(b)}$), 18.3 (6-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 243 ($M^{+\bullet}$, 56), 226 (27), 213 (1), 158 (12), 133 (100), 132 (50).

HRMS: m/z $[M]^+$ calcd for $C_{16}H_{21}NO$: 243.1623; found: 243.1618.

(2*RS*,4*RS*)-6,8-Dimethyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (7e)
White crystals; yield: 0.12 g (11%); mp 76 °C (heptane); R_f = 0.50 (7% EtOAc–heptane).

IR (KBr): 1277 (C–N), 1053 (C–O), 972 cm^{-1} (N–O).

^{1}H NMR: δ = 6.81 (s, 1 H, H7), 6.47 (s, 1 H, H9), 4.89 (ddd, J = 8.0, 5.2, 2.2 Hz, 1 H, H4), 4.53 (dt, J = 8.8, 1.2 Hz, 1 H, CH= prenyl), 4.42 (q, J = 8.6 Hz, 1 H, H2), 3.14 (dd, J = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.66 (dt, J = 12.0, 8.4 Hz, 1 H, $H3_B$), 2.29 (d, J = 16.8 Hz, 1 H, $H5_A$), 2.25 (s, 3 H, 8-CH_3), 2.15 (s, 3 H, 6-CH_3), 1.82 (br s, 3 H, $CH_{3(a)}$), 1.66 (br s, 3 H, $CH_{3(b)}$), 1.53 (ddd, J = 12.0, 8.4, 2.4 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 145.8 (C9a), 138.5 (=C prenyl), 137.2 (C6), 134.7 (C8), 128.0 (C7), 122.7 (C9), 120.9 (C5a), 120.9 (CH= prenyl), 75.7 (C4), 68.6 (C2), 41.1 (C3), 34.1 (C5), 25.7 ($CH_{3(a)}$), 21.0 (8-CH_3), 18.8 ($CH_{3(b)}$), 18.5 (6-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 243 ($M^{+\bullet}$, 45), 226 (24), 213 (1), 158 (15), 133 (100), 132 (53).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NO$: 243.1623; found: 243.1620.

(2*SR*,4*RS*)-2-[(*E*)-Styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (8a)
White crystals; yield: 0.51 g (48%); mp 92 °C (heptane); R_f = 0.44 (7% EtOAc–heptane).

IR (KBr): 1271 (C–N), 1072 (C–O), 976 (N–O), 952 cm^{-1} (CH=CH *E*-styryl).

^1H NMR: δ = 7.43–7.40 (m, 2 H, H2′/H6′), 7.34–7.30 (m, 2 H, H3′/H5′), 7.26–7.21 (m, 1 H, H4′), 7.18 (td, *J* = 7.4, 2.4 Hz, 1 H, H8), 7.14 (dd, *J* = 7.4, 2.4 Hz, 1 H, H6), 7.13 (td, *J* = 7.4, 1.6 Hz, 1 H, H7), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1 H, H9), 6.57 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.38 (dd, *J* = 16.0, 7.2 Hz, 1 H, CH= styryl), 4.95–4.91 (m, 1 H, H4), 4.20 (td, *J* = 7.2, 3.0 Hz, 1 H, H2), 3.40 (dd, *J* = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.51 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.45–2.35 (m, 2 H, $H3_AH_B$).

^{13}C NMR: δ = 150.1 (C9a), 136.8 (C1′), 131.5 (CH= styryl), 129.8 (=CH styryl), 129.8 (C6), 128.5 (C3′/C5′), 127.5 (C8), 126.6 (C4′), 126.5 (C2′/C6′), 126.0 (C7), 125.2 (C5a), 122.0 (C9), 74.9 (C4), 74.5 (C2), 40.8 (C3), 34.7 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 263 ($M^{+\bullet}$, 45), 246 (48), 233 (12), 130 (74), 129 (53), 128 (30), 105 (61), 104 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{17}NO$: 263.1310; found: 263.1310.

(2*RS*,4*RS*)-2-[(*E*)-Styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (9a)
White crystals; yield: 0.15 g (14%); mp 115 °C (heptane); R_f = 0.29 (7% EtOAc–heptane).

IR (KBr): 1246 (C–N), 1073 (C–O), 1010 (N–O), 968 cm^{-1} (CH=CH *E*-styryl).

^1H NMR: δ = 7.32–7.22 (m, 5 H, H2′/H6′, H3′/H5′, H4′), 7.18–7.11 (m, 3 H, H6, H7, H8), 6.92 (dd, *J* = 7.2, 1.2 Hz, 1 H, H9), 6.69 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 5.54 (dd, *J* = 16.0, 8.8 Hz, 1 H, CH= styryl), 4.96 (ddd, *J* = 7.8, 5.2, 2.4 Hz, 1 H, H4), 4.41 (q, *J* = 8.4 Hz, 1 H, H2), 3.46 (dd, *J* = 16.6, 5.2, Hz, 1 H, $H5_B$), 2.77 (ddd, *J* = 12.4, 8.2, 0.8 Hz, 1 H, $H3_B$), 2.56 (d, *J* = 16.6 Hz, 1 H, $H5_A$), 1.82 (ddd, *J* = 12.4, 8.0, 2.4 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 145.9 (C9a), 136.5 (C1′), 134.8 (=CH styryl), 130.0 (C6), 128.6 (C3′/C5′), 127.9 (C4′), 126.5 (C2′/C6′), 126.2 (C8), 125.8 (C7), 125.8 (C5a), 125.3 (CH= styryl), 124.2 (C9), 76.0 (C4), 73.6 (C2), 40.1 (C3), 35.7 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 263 ($M^{+\bullet}$, 45), 246 (49), 233 (11), 130 (75), 129 (55), 128 (33), 105 (62), 104 (100).

(2*SR*,4*RS*)-7-Fluoro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (8b)
White crystals; yield: 0.55 g (52%); mp 146 °C (heptane); R_f = 0.44 (7% EtOAc–heptane).

IR (KBr): 1244 (C–N), 1132 (C–O), 985 (N–O), 970 cm^{-1} (C=C *E*-styryl).

^1H NMR: δ = 7.43–7.40 (m, 2 H, H2′/H6′), 7.34–7.30 (m, 2 H, H3′/H5′), 7.25–7.21 (m, 1 H, H4′), 7.06 (dd, *J* = 8.6, 5.2 Hz, 1 H, H9), 6.88 (dd, *J* = 8.5, 2.8 Hz, 1 H, H6), 6.83 (td, *J* = 8.6, 2.8 Hz, 1 H, H8), 6.56 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.35 (dd, *J* = 16.0, 7.6 Hz, 1 H, CH= styryl), 4.91 (ddd, *J* = 7.2, 5.2, 2.2 Hz, 1 H, H4), 4.15 (td, *J* = 7.6, 3.0 Hz, 1 H, H2), 3.37 (dd, *J* = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.49 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.42–2.34 (m, 2 H, $H3_AH_B$).

^{13}C NMR: δ = 160.6 (d, *J* = 242.7 Hz, C7), 145.9 (C9a), 136.7 (C1′), 131.1 (CH= styryl), 129.9 (=CH styryl), 128.5 (C3′/C5′), 127.5 (C4′), 127.2 (d, *J* = 8.1 Hz, C5a), 126.4 (C2′/C6′), 123.4 (d, *J* = 8.4 Hz, C9), 116.2 (d, *J* = 22.3 Hz, C6), 113.5 (d, *J* = 22.4 Hz, C8), 74.5 (C2), 74.2 (C4), 40.7 (C3), 34.8 (d, *J* = 1.3 Hz, C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 281 ($M^{+\bullet}$, 67), 280 (31), 264 (33), 251 (21), 148 (41), 130 (61), 129 (58), 128 (37), 123 (57), 122 (100), 96 (33).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{16}FNO$: 281.1216; found: 281.1225.

(2*RS*,4*RS*)-7-Fluoro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (9b)
Pale red crystals; yield: 0.21 g (20%); mp 135 °C (heptane); R_f = 0.25 (7% EtOAc–heptane).

IR (KBr): 1247 (C–N), 1129 (C–O), 980 (N–O), 964 cm^{-1} (C=C *E*-styryl).

^1H NMR: δ = 7.31–7.24 (m, 5 H, H2′/H6′, H3′/H5′, H4′), 6.90 (dd, *J* = 8.4, 5.4 Hz, 1 H, H9), 6.85 (dd, *J* = 8.8, 2.6 Hz, 1 H, H6), 6.82 (td, *J* = 8.4, 2.6 Hz, 1 H, H8), 6.67 (d, *J* = 15.8 Hz, 1 H, =CH styryl), 5.50 (dd, *J* = 15.8, 8.8 Hz, 1 H, CH= styryl), 4.89 (ddd, *J* = 7.8, 5.2, 2.2 Hz, 1 H, H4), 4.38 (q, *J* = 8.4 Hz, 1 H, H2), 3.42 (dd, *J* = 16.7, 5.2 Hz, 1 H, $H5_B$), 2.76 (dt, *J* = 12.4, 8.4, Hz, 1 H, $H3_B$), 2.54 (d, *J* = 16.7 Hz, 1 H, $H5_A$), 1.79 (ddd, *J* = 12.4, 8.0, 2.2 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 160.7 (d, *J* = 242.8 Hz, C7), 141.6 (C9a), 136.3 (C1′), 135.2 (=CH styryl), 128.6 (C3′/C5′), 128.0 (C4′), 127.7 (d, *J* = 8.2 Hz, C5a), 126.5 (C2′/C6′), 125.6 (d, *J* = 8.4 Hz, C9), 124.8 (CH= styryl), 116.3 (d, *J* = 22.3 Hz, C6), 112.8 (d, *J* = 22.3 Hz, C8), 75.4 (C4), 73.3 (C2), 39.9 (C3), 35.8 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 281 ($M^{+\bullet}$, 64), 280 (41), 264 (33), 251 (12), 148 (29), 130 (62), 129 (58), 128 (33), 123 (56), 122 (100), 96 (30).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{16}FNO$: 281.1216; found: 281.1214.

(2*SR*,4*RS*)-7-Chloro-2-[(*E*)-styryl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (8c)
White crystals; yield: 0.57 g (54%); mp 142 °C (heptane); R_f = 0.46 (7% EtOAc–heptane).

IR (KBr): 1247 (C–N), 1177 (C–O), 980 (N–O), 964 cm^{-1} (C=C *E*-styryl).

^1H NMR: δ = 7.41 (d, *J* = 7.3 Hz, 2 H, H2′/H6′), 7.32 (t, *J* = 7.3 Hz, 2 H, H3′/H5′), 7.25–7.23 (m, 1 H, H4′), 7.14 (dd, *J* = 8.4, 2.2 Hz, 1 H, H8), 7.11 (br s, 1 H, H6), 7.03 (d, *J* = 8.4 Hz, 1 H, H9), 6.56 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.34 (dd, *J* = 16.0, 7.4 Hz, 1 H, CH= styryl), 4.91 (ddd, *J* = 7.6, 5.3, 2.0 Hz, 1 H, H4), 4.15 (td, *J* = 7.8, 2.4 Hz, 1 H, H2), 3.35 (dd, *J* = 16.7, 5.3 Hz, 1 H, $H5_B$), 2.48 (br d, *J* = 16.7 Hz, 1 H, $H5_A$), 2.42 (dddd, *J* = 12.6, 7.6, 2.4, 1.0 Hz, 1 H, $H3_B$), 2.35 (ddd, *J* = 12.6, 7.8, 2.0 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 148.5 (C9a), 136.6 (C1′), 131.1 (C7), 131.0 (CH= styryl), 129.9 (=CH styryl), 129.6 (C6), 128.5 (C3′/C5′), 127.5 (C4′), 127.1 (C5a), 126.7 (C8), 126.4 (C2′/C6′), 123.3 (C9), 74.4 (C2), 74.3 (C4), 40.6 (C3), 34.5 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 297 ($M^{+\bullet}$, ^{35}Cl, 75), 296 (7), 280 (36), 267 (11), 164 (32), 139 (71), 138 (100), 130 (96), 129 (77), 128 (41), 112 (25).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{16}ClNO$: 297.0920; found: 297.0929.

(2*RS*,4*RS*)-7-Chloro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (9c)
White crystals; yield: 0.26 g (25%); mp 130 °C (heptane); R_f = 0.33 (7% EtOAc–heptane).

IR (KBr): 1253 (C–N), 1179 (C–O), 980 (N–O), 964 cm^{-1} (C=C *E*-styryl).

^1H NMR: δ = 7.32–7.24 (m, 5 H, H2′/H6′, H3′/H5′, H4′), 7.15 (d, *J* = 2.2 Hz, 1 H, H6), 7.09 (dd, *J* = 8.4, 2.2 Hz, 1 H, H8), 6.84 (d, *J* = 8.4 Hz, 1 H, H9), 6.68 (d, *J* = 15.8 Hz, 1 H, =CH styryl), 5.51 (dd, *J* = 15.8, 8.8 Hz, 1 H, CH= styryl), 4.92 (ddd, *J* = 7.8, 5.2, 2.2 Hz, 1 H, H4), 4.38 (q, *J* = 8.4 Hz, 1 H, H2), 3.41 (dd, *J* = 16.6, 5.2 Hz, 1 H, $H5_B$), 2.76 (dt, *J* = 12.3, 8.4 Hz, 1 H, $H3_B$), 2.53 (br d, *J* = 16.6 Hz, 1 H, $H5_A$), 1.79 (ddd, *J* = 12.3, 8.1, 2.2 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 144.4 (C9a), 136.2 (C1′), 135.3 (=CH styryl), 131.3 (C7), 129.8 (C6), 128.6 (C3′/C5′), 128.0 (C4′), 127.7 (C5a), 126.5 (C2′/C6′), 125.9 (C8), 125.4 (CH= styryl), 124.6 (C9), 75.4 (C4), 73.3 (C2), 39.9 (C3), 35.5 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 297 ($M^{+\bullet}$, ^{35}Cl, 67), 296 (76), 280 (36), 267 (11), 164 (27), 139 (72), 138 (100), 130 (95), 129 (76), 128 (44), 112 (23).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{16}ClNO$: 297.0920; found: 297.0920.

(2*SR*,4*RS*)-8-Chloro-9-methyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (8d)
White crystals; yield: 0.48 g (46%); mp 161 °C (heptane); R_f = 0.47 (7% EtOAc–heptane).

IR (KBr): 1275 (C–N), 1074 (C–O), 983 (N–O), 977 cm^{-1} (CH=CH *E*-styryl).

^{1}H NMR: δ = 7.44–7.41 (m, 2 H, H2′/H6′), 7.35–7.31 (m, 2 H, H3′/H5′), 7.27–7.22 (m, 1 H, H4′), 7.13 (d, *J* = 8.2 Hz, 1 H, H7), 6.88 (d, *J* = 8.2 Hz, 1 H, H6), 6.60 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.36 (dd, *J* = 16.0, 7.6 Hz, 1 H, CH= styryl), 4.92 (ddd, *J* = 7.6, 5.2, 2.0 Hz, 1 H, H4), 4.08 (td, *J* = 7.8, 2.4 Hz, 1 H, H2), 3.35 (dd, *J* = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.45 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.41 (dddd, *J* = 12.6, 7.6, 2.4, 1.0 Hz, 1 H, $H3_B$), 2.39 (s, 3 H, 9-CH_3), 2.33 (ddd, *J* = 12.6, 8.0, 2.0 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 149.5 (C9a), 136.7 (C1′), 132.4 (C8), 130.9 (CH= styryl), 129.8 (=CH styryl), 129.0 (C9), 128.6 (C3′/C5′), 127.8 (C6), 127.5 (C4′), 126.5 (C2′/C6′), 126.0 (C7), 123.4 (C5a), 74.7 (C4), 72.9 (C2), 40.8 (C3), 34.5 (C5), 13.8 (9-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 311 ($M^{+\bullet}$, ^{35}Cl, 23), 294 (18), 281 (16), 178 (24), 153 (72), 152 (48), 130 (100), 129 (73), 128 (45).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{19}H_{18}ClNO$: 311.1077; found: 311.1076.

(2*RS*,4*RS*)-8-Chloro-9-methyl-2-[(*E*)-styryl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (9d)
White crystals; yield: 0.20 g (19%); mp 142 °C (heptane); R_f = 0.32 (7% EtOAc–heptane).

IR (KBr): 1268 (C–N), 1056 (C–O), 990 (N–O), 968 cm^{-1} (CH=CH *E*-styryl).

^{1}H NMR: δ = 7.31–7.28 (m, 2 H, H3′/H5′), 7.27–7.23 (m, 1 H, H4′), 7.22–7.19 (m, 2 H, H2′/H6′), 7.18 (d, *J* = 8.0 Hz, 1 H, H7), 6.93 (d, *J* = 8.0 Hz, 1 H, H6), 6.70 (d, *J* = 15.6 Hz, 1 H, =CH styryl), 5.46 (dd, *J* = 15.6, 9.2 Hz, 1 H, CH= styryl), 4.87 (ddd, *J* = 8.0, 5.2, 2.0 Hz, 1 H, H4), 4.41 (q, *J* = 8.4 Hz, 1 H, H2), 3.38 (dd, *J* = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.75 (dtd, *J* = 12.4, 8.4, 0.8 Hz, 1 H, $H3_B$), 2.53 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.25 (s, 3 H, 9-CH_3), 1.78 (ddd, *J* = 12.4, 8.0, 2.0 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 145.7 (C9a), 136.3 (C1′), 135.4 (=CH styryl), 132.5 (C8), 131.0 (C9), 128.7 (C3′/C5′), 128.1 (C6), 128.0 (C7), 126.5 (C4′), 126.4 (C2′/C6′), 124.6 (CH= styryl), 124.4 (C5a), 75.2 (C4), 73.6 (C2), 41.1 (C3), 35.6 (C5), 15.0 (9-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 311 ($M^{+\bullet}$, ^{35}Cl, 21), 294 (20), 281 (18), 178 (12), 153 (69), 152 (42), 130 (100), 129 (74), 128 (54).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{19}H_{18}ClNO$: 311.1077; found: 311.1072.

(2*SR*,4*RS*)-6,8-Dimethyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (8e)
White crystals; yield: 0.47 g (45%); mp 123 °C (heptane); R_f = 0.37 (7% EtOAc–heptane).

IR (KBr): 1263 (C–N), 1070 (C–O), 1000 (N–O), 966 cm^{-1} (CH=CH *E*-styryl).

^{1}H NMR: δ = 7.43–7.41 (m, 2 H, H2′/H6′), 7.34–7.30 (m, 2 H, H3′/H5′), 7.25–7.21 (m, 1 H, H4′), 6.84 (s, 1 H, H7), 6.79 (s, 1 H, H9), 6.56 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.38 (dd, *J* = 16.0, 7.6 Hz, 1 H, CH= styryl), 4.97 (ddd, *J* = 7.2, 5.2, 2.0 Hz, 1 H, H4), 4.19 (td, *J* = 7.6, 2.8 Hz, 1 H, H2), 3.15 (dd, *J* = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.40 (dddd, *J* = 12.4, 7.2, 2.8, 1.0 Hz, 1 H, $H3_B$), 2.35 (ddd, *J* = 12.4, 7.6, 2.0 Hz, 1 H, $H3_A$), 2.31 (d, *J* = 16.4 Hz, 1 H, $H5_A$), 2.30 (s, 3 H, 8-CH_3), 2.17 (s, 3 H, 6-CH_3).

^{13}C NMR: δ = 150.0 (C9a), 137.6 (C6), 137.0 (C1′), 136.2 (C8), 131.8 (CH= styryl), 129.8 (=CH styryl), 128.6 (C3′/C5′), 128.3 (C7), 127.6 (C4′), 126.6 (C2′/C6′), 120.4 (C5a), 120.2 (C9), 75.0 (C4), 74.6 (C2), 41.4 (C3), 33.1 (C5), 21.1 (8-CH_3), 18.5 (6-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 291 ($M^{+\cdot}$, 39), 172 (80), 158 (100), 145 (38), 91 (41).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{20}H_{21}NO$: 291.1623; found: 291.1622.

(2*RS*,4*RS*)-6,8-Dimethyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepines (9e)
White crystals; yield: 0.19 g (18%); mp 136 °C (heptane); R_f = 0.29 (7% EtOAc–heptane).

IR (KBr): 1267 (C–N), 1050 (C–O), 978 (N–O), 988 cm^{-1} (CH=CH *E*-styryl).

^{1}H NMR: δ = 7.31–7.21 (m, 5 H, H2′/H6′, H3′/H5′, H4′), 6.86 (s, 1 H, H9), 6.66 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.60 (s, 1 H, H7), 5.57 (dd, *J* = 16.0, 8.8 Hz, 1 H, CH= styryl), 4.97 (ddd, *J* = 7.8, 5.2, 2.2 Hz, 1 H, H4), 4.37 (q, *J* = 8.4 Hz, 1 H, H2), 3.19 (dd, *J* = 16.4, 5.2 Hz, 1 H, $H5_B$), 2.74 (dtd, *J* = 12.0, 8.2, 0.8 Hz, 1 H, $H3_B$), 2.36 (d, *J* = 16.4 Hz, 1 H, $H5_A$), 2.30 (s, 3 H, 8-CH_3), 2.17 (s, 3 H, 6-CH_3), 1.76 (ddd, *J* = 12.0, 8.0, 2.2 Hz, 1 H, $H3_A$).

^{13}C NMR: δ = 145.6 (C9a), 137.5 (C6), 136.7 (C1′), 135.2 (C8), 134.5 (=CH styryl), 128.6 (C3′/C5′), 128.4 (C7), 127.8 (C4′), 126.5 (C2′/C6′), 125.9 (CH= styryl), 122.3 (C9), 121.0 (C5a), 76.0 (C4), 73.3 (C2), 40.6 (C3), 34.1 (C5), 21.0 (8-CH_3), 18.5 (6-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 291 ($M^{+\cdot}$, 3), 272 (100), 129 (16), 128 (36), 115 (15).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{20}H_{21}NO$: 291.1623; found: 291.1623.

(2*SR*,4*RS*)-7-Fluoro-2-[(*E*)-pent-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (10a)
Viscous maroon oil; yield: 0.32 g (30%); R_f = 0.35 (7% EtOAc–heptane).

IR (liquid film): 1271 (C–N), 1035 (C–O), 990 (N–O), 970 cm^{-1} (CH=CH *E*-pentenyl).

^{1}H NMR: δ = 7.01 (dd, *J* = 8.6, 5.4 Hz, 1 H, H9), 6.83 (td, *J* = 8.8, 2.8 Hz, 1 H, H8), 6.78 (dd, *J* = 9.2, 2.8 Hz, 1 H, H6), 5.63 (dd, *J* = 15.2, 6.4 Hz, 1 H, CH= pentenyl), 5.58 (dd, *J* = 15.2, 5.6 Hz, 1 H, =CH pentenyl), 4.83 (ddd, *J* = 7.6, 5.4, 2.4 Hz, 1 H, H4), 3.92 (td, *J* = 6.4, 2.8 Hz, 1 H, H2), 3.32 (dd, *J* = 16.8, 5.4 Hz, 1 H, $H5_B$), 2.44 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.29 (dddd, *J* = 12.4, 7.6, 2.8, 1.0 Hz, 1 H, $H3_B$), 2.24 (ddd, *J* = 12.4, 7.6, 2.4 Hz, 1 H, $H3_A$), 2.06–1.99 (m, 2 H, 3′-CH_2), 1.42 (dtd, *J* = 15.0, 7.2, 1.6 Hz, 2 H, 4′-CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 160.5 (d, *J* = 242.4 Hz, C7), 146.2 (d, *J* = 2.3 Hz, C9a), 131.8 (CH= pentenyl), 131.3 (=CH pentenyl), 127.2 (d, *J* = 8.2 Hz, C5a), 123.4 (d, *J* = 8.4 Hz, C9), 116.1 (d, *J* = 22.2 Hz, C6), 113.4 (d, *J* = 22.3 Hz, C8), 74.6 (C4), 74.2 (C2), 40.5 (C3), 34.9 (C5), 34.3 (3′-CH_2), 22.2 (4′-CH_2), 13.8 (5′-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 247 ($M^{+\bullet}$, 15), 230 (9), 217 (1), 148 (24), 123 (49), 122 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{15}H_{18}FNO$: 247.1372; found: 247.1376.

(2*RS*,4*RS*)-7-Fluoro-2-[(*E*)-pent-1-enyl)-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (11a)
Viscous maroon oil; yield: 0.11 g (10%); R_f = 0.26 (7% EtOAc–heptane).

IR (liquid film): 1250 (C–N), 1049 (C–O), 969 (N–O), 942 cm^{-1} (CH=CH *E*-pentenyl).

^{1}H NMR: δ = 6.85–6.78 (m, 3 H, H6, H8, H9), 5.75 (dtd, *J* = 15.2, 7.0, 0.6 Hz, 1 H, =CH pentenyl), 4.84 (ddd, *J* = 8.0, 5.2, 2.0 Hz, 1 H, H4), 4.79 (ddt, *J* = 15.2, 8.4, 1.2 Hz, 1 H, CH= pentenyl), 4.17 (q, *J* = 8.4 Hz, 1 H, H2), 3.36 (dd, *J* = 16.4, 5.2 Hz, 1 H, $H5_B$), 2.64 (dtd, *J* = 12.4, 8.4, 0.8 Hz, 1 H, $H3_B$), 2.46 (br d, *J* = 16.4 Hz, 1 H, $H5_A$), 1.92 (ddd, *J* = 14.8, 8.2, 1.4 Hz, 2 H, 3′-CH_2), 1.63 (ddd, *J* = 12.4, 8.0, 2.0 Hz, 1 H, $H3_A$), 1.32 (dt, *J* = 14.8, 7.4 Hz, 2 H, 4′-CH_2), 0.84 (t, *J* = 7.4 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 160.7 (d, *J* = 242.4 Hz, C7), 141.7 (d, *J* = 2.7 Hz, C9a), 137.0 (=CH pentenyl), 127.7 (d, *J* = 8.1 Hz, C5a), 125.8 (d, *J* = 8.4 Hz, C9), 125.5 (CH= pentenyl), 116.2 (d, *J* = 22.2 Hz, C6), 112.5 (d, *J* = 22.3 Hz, C8), 75.2 (C4), 73.2 (C2), 39.7 (C3), 35.9 (d, *J* = 1.2 Hz, C5), 34.5 (3′-CH_2), 22.1 (4′-CH_2), 13.6 (5′-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 247 ($M^{+\bullet}$, 27), 230 (15), 217 (1), 148 (22), 123 (61), 122 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{15}H_{18}FNO$: 247.1372; found: 247.1375.

(2*SR*,4*RS*)-8-Chloro-9-methyl-2-[(*E*)-pent-1-enyl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (10b)
Viscous maroon oil; yield: 0.29 g (28%); R_f = 0.38 (7% EtOAc–heptane).

IR (liquid film): 1255 (C–N), 1053 (C–O), 972 (N–O), 945 cm^{-1} (CH=CH *E*-pentenyl).

^{1}H NMR: δ = 7.09 (d, *J* = 8.0 Hz, 1 H, H7), 6.85 (d, *J* = 8.0 Hz, 1 H, H6), 5.62 (dd, *J* = 15.2, 6.4 Hz, 1 H, CH= pentenyl), 5.60 (dd, *J* = 15.2, 5.4 Hz, 1 H, =CH pentenyl), 4.85 (ddd, *J* = 7.6, 5.6, 2.0 Hz, 1 H, H4), 3.85 (td, *J* = 6.4, 2.8 Hz, 1 H, H2), 3.30 (dd, *J* = 16.8, 5.6 Hz, 1 H, $H5_B$), 2.39 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.35 (s, 3 H, 9-CH_3), 2.28 (dddd, *J* = 12.6, 7.6, 2.8, 1.0 Hz, 1 H, $H3_B$), 2.20 (ddd, *J* = 12.6, 7.8, 2.0 Hz, 1 H, $H3_A$), 2.06–2.00 (m, 2 H, 3′-CH_2), 1.45–1.40 (m, 2 H, 4′-CH_2), 0.91 (t, *J* = 7.4 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 149.7 (C9a), 132.3 (C8), 131.5 (CH= pentenyl), 131.3 (=CH pentenyl), 128.9 (C9), 127.2 (C6), 125.8 (C7), 123.4 (C5a), 74.6 (C4), 73.2 (C2), 40.5 (C3), 34.4 (C5), 34.2 (3′-CH_2), 22.3 (4′-CH_2), 13.8 (9-CH_3), 13.7 (5′-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 277 ($M^{+\bullet}$, ^{35}Cl, 33), 260 (21), 247 (1), 178 (9), 153 (100), 152 (50).

(2*RS*,4*RS*)-8-Chloro-9-methyl-2-[(*E*)-pent-1-enyl]-2,3,4,5-tetrahydro-1,4-epoxy-1-benzazepine (11b)
Viscous maroon oil; yield: 0.14 g (13%); R_f = 0.33 (7% EtOAc–heptane).

IR (liquid film): 1269 (C–N), 1045 (C–O), 979 (N–O), 946 cm^{-1} (CH=CH *E*-pentenyl).

^{1}H NMR: δ = 7.13 (d, *J* = 8.0 Hz, 1 H, H7), 6.88 (d, *J* = 8.0 Hz, 1 H, H6), 5.79 (dt, *J* = 15.2, 6.8 Hz, 1 H, =CH pentenyl), 4.80 (ddd, *J* = 8.0, 5.2, 2.0 Hz, 1 H, H4), 4.78 (ddt, *J* = 15.2, 8.6, 1.2 Hz, 1 H, CH= pentenyl), 4.21 (q, *J* = 8.4 Hz, 1 H, H2), 3.32 (dd, *J* = 16.8, 5.2 Hz, 1 H, $H5_B$), 2.64 (dtd, *J* = 12.4, 8.2, 1.0 Hz, 1 H, $H3_B$), 2.46 (d, *J* = 16.8 Hz, 1 H, $H5_A$), 2.26 (s, 3 H, 9-CH_3), 1.98–1.82 (m, 2 H, 3′-CH_2), 1.65 (ddd, *J* = 12.4, 8.0, 2.0 Hz, 1 H, $H3_A$), 1.36–1.26 (m, 2 H, 4′-CH_2), 0.84 (t, *J* = 7.4 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 145.8 (C9a), 137.2 (=CH pentenyl), 132.3 (C8), 131.1 (C9), 127.8 (C6), 126.3 (C7), 125.0 (CH= pentenyl), 124.4 (C5a), 74.9 (C4), 73.6 (C2), 40.9 (C3), 35.6 (C5), 34.4 (3′-CH_2), 22.1 (4′-CH_2), 15.3 (9-CH_3), 13.7 (5′-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 277 ($M^{+\bullet}$, ^{35}Cl, 30), 260 (21), 247 (1), 178 (15), 153 (100), 152 (54).

***cis*- and *trans*-2-Alkenyl-4-hydroxy-2,3,4,5-tetrahydro-1*H*-1-benzazepines 12a–e, 13a–e, 14a–e, 15a–e, 16a,b, and 17a,b; General Procedure**
Zn powder (6.54 g, 100 mmol), glacial AcOH (4 mL, 70 mmol), and 37% HCl soln (6.81 mL, 70 mmol) were added to a stirred and cooled (ice bath) soln of 2-*exo*- and 2-*endo*-1,4-epoxy cycloadducts **6**, **8**, **10** and **7**, **9**, **11** (10 mmol) in MeOH (25 mL). The resulting mixture was stirred at 0 °C for an additional 0.5–2 h (TLC monitoring). Solid was removed from the mixture by filtration and the filtrate was neutralized with 25% aq NH_4OH to pH 8, extracted with EtOAc (3 × 50 mL), and dried (anhyd Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, heptane–EtOAc, 10:1 to 1:1) to give **12**, **14**, **16** and **13**, **15**, **17**.

***cis*-2-(2-Methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (12a)**
White crystals; yield: 0.97 g (96%); mp 86 °C (heptane); R_f = 0.31 (33% EtOAc–heptane).

IR (KBr): 3347 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 7.13 (dd, *J* = 7.6, 1.2 Hz, 1 H, H6), 7.08 (td, *J* = 7.6, 1.2 Hz, 1 H, H8), 6.88 (td, *J* = 7.6, 1.2 Hz, 1 H, H7), 6.71 (dd, *J* = 7.8, 1.2 Hz, 1 H, H9), 5.31 (ddt, *J* = 8.4, 2.8, 1.4 Hz, 1 H, CH= prenyl), 3.80 (tt, *J* = 9.8, 3.6 Hz, 1 H, $H4_{ax}$), 3.61 (ddd, *J* = 11.2, 8.4, 2.0 Hz, 1 H, $H2_{ax}$), 3.31 (br s, 1 H, NH), 3.00 (dd, *J* = 13.6, 9.8 Hz, 1 H, $H5_{ax}$), 2.94 (dt, *J* = 13.6, 2.0 Hz, 1 H, $H5_{eq}$), 2.12 (br s, 1 H, OH), 2.03 (ddt, *J* = 12.8, 3.6, 2.0 Hz, 1 H, $H3_{eq}$), 1.77 (ddd, *J* = 12.8, 11.2, 10.0 Hz, 1 H, $H3_{ax}$), 1.74 (d, *J* = 1.3 Hz, 3 H, $CH_{3(A)}$), 1.66 (d, *J* = 1.3 Hz, 3 H, $CH_{3(B)}$).

^{13}C NMR: δ = 149.4 (C9a), 134.6 (=C prenyl), 131.7 (C6), 128.3 (C5a), 128.0 (CH= prenyl), 127.5 (C8), 121.7 (C7), 120.1 (C9), 70.0 (C4), 54.5 (C2), 46.8 (C3), 44.6 (C5), 25.7 ($CH_{3(A)}$), 18.5 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 217 ($M^{+\bullet}$, 74), 173 (21), 172 (42), 162 (2), 158 (100), 144 (15), 130 (43), 118 (42), 111 (18), 107 (53), 106 (78).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{19}NO$: 217.1467; found: 217.1466.

***cis*-7-Fluoro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (12b)**
White crystals; yield: 0.95 g (94%); mp 71 °C (heptane); R_f = 0.38 (33% EtOAc–heptane).

IR (KBr): 3347 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.83 (dd, *J* = 9.2, 2.8 Hz, 1 H, H6), 6.74 (td, *J* = 8.4, 2.8 Hz, 1 H, H8), 6.63 (dd, *J* = 8.4, 5.2 Hz, 1 H, H9), 5.27 (ddt, *J* = 8.4, 2.8, 1.4 Hz, 1 H, CH= prenyl), 3.74 (tdd, *J* = 10.0, 3.6, 2.4 Hz, 1 H, $H4_{ax}$), 3.52 (ddd, *J* = 11.2, 8.4, 2.0 Hz, 1 H, $H2_{ax}$), 3.20 (br s, 1 H, NH), 2.98 (dd, *J* = 13.4, 10.0 Hz, 1 H, $H5_{ax}$), 2.85 (dt, *J* = 13.4, 1.6 Hz, 1 H, $H5_{eq}$), 2.23 (br s, 1 H, OH), 2.00 (ddt, *J* = 12.8, 3.6, 2.0 Hz, 1 H, $H3_{eq}$), 1.75 (ddd, *J* = 12.8, 11.2, 10.0 Hz, 1 H, $H3_{ax}$), 1.73 (d, *J* = 1.3 Hz, 3 H, $CH_{3(A)}$), 1.65 (d, *J* = 1.3 Hz, 3 H, $CH_{3(B)}$).

^{13}C NMR: δ = 157.6 (d, *J* = 237.9 Hz, C7), 145.5 (d, *J* = 2.3 Hz, C9a), 134.7 (=C prenyl), 130.3 (d, *J* = 7.4 Hz, C5a), 127.8 (CH= prenyl), 121.0 (d, *J* = 8.0 Hz, C9), 117.9 (d, *J* = 21.9 Hz, C6), 113.6 (d, *J* = 22.0 Hz, C8), 69.8 (C4), 54.8 (C2), 46.8 (C3), 44.3 (d, *J* = 0.6 Hz, C5), 25.7 ($CH_{3(A)}$), 18.5 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 235 ($M^{+\bullet}$, 67), 191 (27), 190 (36), 180 (2), 176 (100), 162 (3), 148 (45), 136 (48), 125 (64), 124 (80), 111 (47).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}FNO$: 235.1372; found: 235.1372.

***cis*-7-Chloro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (12c)**
White crystals; yield: 0.95 g (94%); mp 95 °C (heptane); R_f = 0.41 (33% EtOAc–heptane).

IR (KBr): 3355 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 7.10 (d, *J* = 2.4 Hz, 1 H, H6), 7.01 (dd, *J* = 8.2, 2.4 Hz, 1 H, H8), 6.62 (d, *J* = 8.2 Hz, 1 H, H9), 5.28 (ddt, *J* = 8.8, 2.6, 1.4 Hz, 1 H, CH= prenyl), 3.77 (tt, *J* = 9.6, 3.6 Hz, 1 H, $H4_{ax}$), 3.57 (ddd, *J* = 11.2, 8.8, 2.0 Hz, 1 H, $H2_{ax}$), 3.29 (br s, 1 H, NH), 2.95 (dd, *J* = 13.6, 9.6 Hz, 1 H, $H5_{ax}$), 2.88 (dt, *J* = 13.6, 2.0 Hz, 1 H,

$H5_{eq}$), 2.01 (ddt, J = 12.8, 3.6, 2.0 Hz, 1 H, $H3_{eq}$), 1.76 (ddd, J = 12.8, 11.2, 10.0 Hz, 1 H, $H3_{ax}$), 1.74 (d, J = 1.4 Hz, 3 H, $CH_{3(A)}$), 1.66 (d, J = 1.4 Hz, 3 H, $CH_{3(B)}$).

^{13}C NMR: δ = 147.9 (C9a), 134.8 (=C prenyl), 131.1 (C6), 129.8 (C5a), 127.6 (CH= prenyl), 127.1 (C8), 126.1 (C7), 121.1 (C9), 69.6 (C4), 54.4 (C2), 46.4 (C3), 44.0 (C5), 25.6 ($CH_{3(A)}$), 18.4 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 251 ($M^{+\bullet}$, ^{35}Cl, 72), 207 (27), 206 (36), 196 (3), 192 (97), 178 (6), 164 (42), 152 (39), 141 (84), 140 (98), 111 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}ClNO$: 251.1077; found: 251.1075.

cis-8-Chloro-9-methyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (12d)

White crystals; yield: 0.97 g (96%); mp 105 °C (heptane); R_f = 0.45 (33% EtOAc–heptane).

IR (KBr): 3405 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.92 (d, J = 8.4 Hz, 1 H, H6), 6.89 (d, J = 8.4 Hz, 1 H, H7), 5.33 (ddt, J = 8.8, 2.8, 1.4 Hz, 1 H, CH= prenyl), 3.81–3.74 (m, 1 H, $H4_{ax}$), 3.55 (ddd, J = 11.2, 8.8, 2.2 Hz, 1 H, $H2_{ax}$), 3.43 (br s, 1 H, NH), 2.95 (dd, J = 13.6, 7.6 Hz, 1 H, $H5_{ax}$), 2.91 (dd, J = 13.6, 1.2 Hz, 1 H, $H5_{eq}$), 2.24 (s, 3 H, 9-CH_3), 2.01 (ddt, J = 12.8, 3.6, 2.2 Hz, 1 H, $H3_{eq}$), 1.88 (br s, 1 H, OH), 1.77 (d, J = 1.4 Hz, 3 H, $CH_{3(A)}$), 1.74 (ddd, J = 12.8, 11.2, 9.6 Hz, 1 H, $H3_{ax}$), 1.67 (d, J = 1.4 Hz, 3 H, $CH_{3(B)}$).

^{13}C NMR: δ = 148.8 (C9a), 134.7 (=C prenyl), 132.8 (C8), 129.5 (C6), 127.6 (CH= prenyl), 127.0 (C5a), 124.2 (C9), 121.8 (C7), 69.7 (C4), 54.0 (C2), 46.3 (C3), 44.1 (C5), 25.7 ($CH_{3(A)}$), 18.4 ($CH_{3(B)}$), 14.3 (9-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 265 ($M^{+\bullet}$, ^{35}Cl, 50), 221 (15), 220 (24), 210 (4), 206 (57), 192 (6), 178 (30), 166 (30), 155 (58), 154 (100), 111 (45).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{15}H_{20}ClNO$: 265.1233; found: 265.1231.

cis-6,8-Dimethyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (12e)

White crystals; yield: 0.95 g (94%); mp 116 °C (heptane); R_f = 0.38 (33% EtOAc–heptane).

IR (KBr): 3355 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.64 (s, 1 H, H7), 6.42 (s, 1 H, H9), 5.29 (ddt, J = 8.8, 2.6, 1.4 Hz, 1 H, CH= prenyl), 3.78 (tdd, J = 9.6, 4.2, 2.0 Hz, 1 H, $H4_{ax}$), 3.63 (ddd, J = 11.2, 8.8, 2.4 Hz, 1 H, $H2_{ax}$), 3.16 (br s, 1 H, NH), 3.09 (dt, J = 14.0, 1.6 Hz, 1 H, $H5_{eq}$), 2.84 (dd, J = 14.0, 9.6 Hz, 1 H, $H5_{ax}$), 2.31 (s, 3 H, 6-CH_3), 2.22 (s, 3 H, 8-CH_3), 2.18 (br s, 1 H, OH), 2.01 (dddd, J = 12.8, 4.2, 2.4, 1.4 Hz, 1 H, $H3_{eq}$), 1.77 (ddd, J = 12.8, 11.2, 9.6 Hz, 1 H, $H3_{ax}$), 1.75 (d, J = 1.2 Hz, 3 H, $CH_{3(A)}$), 1.67 (d, J = 1.2 Hz, 3 H, $CH_{3(B)}$).

^{13}C NMR: δ = 149.5 (C9a), 137.7 (C6), 136.3 (C8), 134.4 (=C prenyl), 128.1 (CH= prenyl), 124.9 (C7), 124.0 (C5a), 118.9 (C9), 69.7 (C4), 54.7 (C2), 46.2 (C3), 37.9 (C5), 25.6 ($CH_{3(A)}$), 20.8 (6-CH_3), 20.8 (8-CH_3), 18.5 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 245 ($M^{+\bullet}$, 65), 201 (24), 200 (40), 190 (2), 186 (58), 172 (9), 158 (30), 146 (32), 135 (33), 134 (100), 111 (3).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}NO$: 245.1780; found: 245.1785.

trans-2-(2-Methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (13a)

Colorless viscous oil; yield: 0.91 g (90%); R_f = 0.39 (33% EtOAc–heptane).

IR (liquid film): 3348 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 7.11 (dd, J = 7.6, 1.4 Hz, 1 H, H6), 7.09 (td, J = 7.6, 1.4 Hz, 1 H, H8), 6.88 (td, J = 7.6, 1.0 Hz, 1 H, H7), 6.75 (dd, J = 7.8, 1.0 Hz, 1 H, H9), 5.27 (ddt, J = 8.4, 2.8, 1.4 Hz, 1 H, CH= prenyl), 4.23–4.18 (m, 1 H, $H4_{eq}$), 3.84 (ddd, J = 10.8, 8.4, 2.4 Hz, 1 H, $H2_{ax}$), 3.38 (br s, 1 H, NH), 3.06 (dd, J = 14.0, 2.4 Hz, 1 H, $H5_{eq}$), 3.02 (dd, J = 14.0, 6.0 Hz, 1 H, $H5_{ax}$), 1.91 (ddt, J = 14.0, 3.6, 2.4 Hz, 1 H, $H3_{eq}$), 1.81 (ddd, J = 14.0, 10.8, 2.8 Hz, 1 H, $H3_{ax}$), 1.74 (d, J = 1.0 Hz, 3 H, $CH_{3(A)}$), 1.68 (d, J = 1.2 Hz, 3 H, $CH_{3(B)}$), 1.52 (br s, 1 H, OH).

^{13}C NMR: δ = 149.0 (C9a), 134.3 (=C prenyl), 132.6 (C6), 127.8 (CH= prenyl), 127.8 (C8), 127.0 (C5a), 121.5 (C7), 120.0 (C9), 65.8 (C4), 50.3 (C2), 44.5 (C3), 41.7 (C5), 25.6 ($CH_{3(A)}$), 18.4 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 217 ($M^{+\bullet}$, 75), 173 (24), 172 (42), 162 (2), 158 (100), 144 (17), 130 (44), 118 (42), 111 (18), 107 (54), 106 (81).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{19}NO$: 217.1467; found: 217.1495.

trans-7-Fluoro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (13b)

White crystals; yield: 0.93 g (92%); mp 75 °C (heptane); R_f = 0.39 (33% EtOAc–heptane).

IR (KBr): 3344 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.85 (dd, J = 9.2, 2.8 Hz, 1 H, H6), 6.78 (td, J = 8.4, 2.8 Hz, 1 H, H8), 6.68 (dd, J = 8.4, 5.0 Hz, 1 H, H9), 5.24 (ddt, J = 8.8, 2.8, 1.4 Hz, 1 H, CH= prenyl), 4.23–4.19 (m, 1 H, $H4_{eq}$), 3.78 (ddd, J = 10.8, 8.8, 2.4 Hz, 1 H, $H2_{ax}$), 3.28 (br s, 1 H, NH), 3.04 (dd, J = 14.0, 1.2 Hz, 1 H, $H5_{eq}$), 2.95 (ddd, J = 14.0, 7.0, 0.8 Hz, 1 H, $H5_{ax}$), 1.89 (dddd, J = 14.0, 4.0, 2.4, 1.2 Hz, 1 H, $H3_{eq}$), 1.79 (ddd, J = 14.0, 10.8, 2.8 Hz, 1 H, $H3_{ax}$), 1.73 (d, J = 0.8 Hz, 3 H, $CH_{3(A)}$), 1.67 (d, J = 1.2 Hz, 3 H, $CH_{3(B)}$), 1.52 (br s, 1 H, OH).

^{13}C NMR: δ = 158.0 (d, J = 239.4 Hz, C7), 145.0 (d, J = 2.3 Hz, C9a), 134.4 (=C prenyl), 129.5 (d, J = 7.3 Hz, C5a), 127.6 (CH= prenyl), 120.9 (d, J = 7.9 Hz, C9), 118.8 (d, J = 21.9 Hz, C6), 113.9 (d, J = 21.7 Hz, C8), 65.6 (C4), 50.4 (C2), 44.5 (C3), 41.5 (C5), 25.6 ($CH_{3(A)}$), 18.5 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 235 ($M^{+\bullet}$, 72), 191 (21), 190 (39), 180 (2), 176 (100), 162 (3), 148 (45), 136 (42), 125 (70), 124 (83), 111 (51).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}FNO$: 235.1372; found: 235.1374.

trans-7-Chloro-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (13c)

Colorless viscous oil; yield: 0.92 g (91%); R_f = 0.46 (33% EtOAc–heptane).

IR (liquid film): 3356 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 7.10 (d, J = 2.4 Hz, 1 H, H6), 7.03 (dd, J = 8.4, 2.4 Hz, 1 H, H8), 6.66 (d, J = 8.4 Hz, 1 H, H9), 5.24 (ddt, J = 8.8, 2.4, 1.2 Hz, 1 H, CH= prenyl), 4.23–4.19 (m, 1 H, $H4_{eq}$), 3.84 (ddd, J = 10.4, 8.8, 2.4 Hz, 1 H, $H2_{ax}$), 3.37 (br s, 1 H, NH), 3.00 (dd, J = 14.0, 2.4 Hz, 1 H, $H5_{eq}$), 2.96 (dd, J = 14.0, 6.0 Hz, 1 H, $H5_{ax}$), 1.89 (ddt, J = 14.0, 4.0, 2.4 Hz, 1 H, $H3_{eq}$), 1.82 (ddd, J = 14.0, 10.4, 2.8 Hz, 1 H, $H3_{ax}$), 1.73 (d, J = 0.8 Hz, 3 H, $CH_{3(A)}$), 1.67 (d, J = 1.0 Hz, 3 H, $CH_{3(B)}$), 1.48 (br s, 1 H, OH).

^{13}C NMR: δ = 147.5 (C9a), 134.6 (=C prenyl), 132.0 (C6), 129.1 (C5a), 127.5 (CH= prenyl), 127.4 (C8), 126.1 (C7), 121.0 (C9), 65.6 (C4), 50.2 (C2), 44.3 (C3), 41.5 (C5), 25.6 ($CH_{3(A)}$), 18.4 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 251 ($M^{+\bullet}$, ^{35}Cl, 72), 207 (24), 206 (36), 196 (3), 192 (89), 178 (6), 164 (39), 152 (39), 141 (84), 140 (90), 111 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}ClNO$: 251.1077; found: 251.1076.

***trans*-8-Chloro-9-methyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (13d)**
Colorless viscous oil; yield: 0.91 g (90%); R_f = 0.50 (33% EtOAc–heptane).

IR (liquid film): 3402 cm^{-1} (N–H, O–H).

^1H NMR: δ = 6.91 (d, *J* = 8.4 Hz, 1 H, H6), 6.89 (d, *J* = 8.4 Hz, 1 H, H7), 5.29 (ddt, *J* = 8.8, 2.8, 1.4 Hz, 1 H, CH= prenyl), 4.20–4.16 (m, 1 H, $H4_{eq}$), 3.84 (td, *J* = 9.2, 4.2 Hz, 1 H, $H2_{ax}$), 3.50 (br s, 1 H, NH), 3.00 (d, *J* = 14.0 Hz, 1 H, $H5_{eq}$), 2.97 (dd, *J* = 14.0, 4.4 Hz, 1 H, $H5_{ax}$), 2.26 (s, 3 H, 9-CH_3), 1.85 (dt, *J* = 14.0, 4.0 Hz, 1 H, $H3_{eq}$), 1.80 (ddd, *J* = 14.0, 7.6, 4.4 Hz, 1 H, $H3_{ax}$), 1.75 (d, *J* = 1.2 Hz, 3 H, $CH_{3(A)}$), 1.68 (d, *J* = 1.2 Hz, 3 H, $CH_{3(B)}$), 1.59 (br s, 1 H, OH).

^{13}C NMR: δ = 148.4 (C9a), 134.4 (=C prenyl), 133.2 (C8), 130.3 (C6), 127.6 (CH= prenyl), 125.9 (C5a), 124.2 (C9), 121.6 (C7), 65.7 (C4), 50.0 (C2), 44.2 (C3), 41.4 (C5), 25.7 ($CH_{3(A)}$), 18.3 ($CH_{3(B)}$), 14.4 (9-CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 265 ($M^{+\bullet}$, ^{35}Cl, 49), 221 (15), 220 (33), 210 (4), 206 (56), 192 (6), 178 (33), 166 (28), 155 (60), 154 (100), 111 (45).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{15}H_{20}ClNO$: 265.1233; found: 265.1223.

***trans*-6,8-Dimethyl-2-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (13e)**
Colorless viscous oil; yield: 0.93 g (92%); R_f = 0.44 (33% EtOAc–heptane).

IR (liquid film): 3354 cm^{-1} (N–H, O–H).

^1H NMR: δ = 6.63 (s, 1 H, H7), 6.44 (s, 1 H, H9), 5.26 (ddt, *J* = 8.8, 2.8, 1.4 Hz, 1 H, CH= prenyl), 4.23–4.18 (m, 1 H, $H4_{eq}$), 3.81 (td, *J* = 9.2, 4.0 Hz, 1 H, $H2_{ax}$), 3.22 (dd, *J* = 14.0, 7.6 Hz, 1 H, $H5_{ax}$), 2.84 (dd, *J* = 14.0, 1.2 Hz, 1 H, $H5_{eq}$), 2.30 (s, 3 H, 6-CH_3), 2.23 (s, 3 H, 8-CH_3), 1.84 (dt, *J* = 14.0, 4.0 Hz, 1 H, $H3_{eq}$), 1.81 (ddd, *J* = 14.0, 7.6, 4.4 Hz, 1 H, $H3_{ax}$), 1.74 (d, *J* = 1.2 Hz, 3 H, $CH_{3(A)}$), 1.68 (d, *J* = 1.2 Hz, 3 H, $CH_{3(B)}$), 1.58 (br s, 1 H, OH).

^{13}C NMR: δ = 149.3 (C9a), 138.7 (C6), 136.6 (C8), 134.0 (=C prenyl), 128.1 (CH= prenyl), 124.8 (C7), 122.4 (C5a), 118.8 (C9), 65.9 (C4), 50.6 (C2), 44.3 (C3), 35.1 (C5), 25.6 ($CH_{3(A)}$), 20.8 (8-CH_3), 20.7 (6-CH_3), 18.4 ($CH_{3(B)}$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 245 ($M^{+\bullet}$, 49), 201 (18), 200 (33), 190 (2), 186 (48), 172 (12), 158 (37), 146 (36), 135 (33), 134 (100), 111 (3).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}NO$: 245.1780; found: 245.1785.

***cis*-2-[(*E*)-Styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (14a)**
White crystals; yield: 0.93 g (92%); mp 114 °C (heptane); R_f = 0.32 (33% EtOAc–heptane).

IR (KBr): 3318 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.42–7.40 (m, 2 H, H2′/H6′), 7.37–7.33 (m, 2 H, H3′/H5′), 7.30–7.25 (m, 1 H, H4′), 7.15 (dd, *J* = 7.6, 1.2 Hz, 1 H, H6), 7.10 (td, *J* = 7.6, 1.2 Hz, 1 H, H8), 6.91 (td, *J* = 7.6, 1.2 Hz, 1 H, H7), 6.75 (dd, *J* = 8.0, 1.2 Hz, 1 H, H9), 6.63 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.36 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 3.87 (tt, *J* = 9.6, 3.6 Hz, 1 H, $H4_{ax}$), 3.65 (ddd, *J* = 11.2, 8.0, 2.0 Hz, 1 H, $H2_{ax}$), 3.57 (br s, 1 H, NH), 3.05 (dd, *J* = 14.0, 9.2 Hz, 1 H, $H5_{ax}$), 3.00 (dt, *J* = 14.0, 2.0 Hz, 1 H, $H5_{eq}$), 2.20 (ddt, *J* = 12.8, 3.6, 2.0 Hz, 1 H, $H3_{eq}$), 1.91 (ddd, *J* = 12.8, 11.2, 9.8 Hz, 1 H, $H3_{ax}$), 1.66 (br s, 1 H, OH).

^{13}C NMR: δ = 148.7 (C9a), 136.5 (C1′), 131.8 (CH= styryl), 131.6 (C6), 131.0 (=CH styryl), 128.7 (C3′/C5′), 128.0 (C5a), 127.9 (C4′), 127.5 (C8), 126.5 (C2′/C6′), 121.8 (C7), 120.2 (C9), 69.8 (C4), 58.7 (C2), 46.5 (C3), 44.4 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 265 ($M^{+\bullet}$, 48), 159 (21), 130 (54), 117 (84), 115 (39), 107 (52), 106 (100), 91 (63), 77 (42).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{19}NO$: 265.1467; found: 265.1470.

***cis*-7-Fluoro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (14b)**
White crystals; yield: 0.94 g (93%); mp 137 °C (heptane); R_f = 0.39 (33% EtOAc–heptane).

IR (KBr): 3319 (N–H), 3288 cm^{-1} (O–H).

^1H NMR: δ = 7.41–7.38 (m, 2 H, H2′/H6′), 7.37–7.32 (m, 2 H, H3′/H5′), 7.27–7.25 (m, 1 H, H4′), 6.87 (dd, *J* = 9.2, 2.8 Hz, 1 H, H6), 6.78 (td, *J* = 8.4, 2.8 Hz, 1 H, H8), 6.69 (dd, *J* = 8.4, 5.0 Hz, 1 H, H9), 6.61 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.33 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 3.82 (tdd, *J* = 10.0, 4.0, 2.4 Hz, 1 H, $H4_{ax}$), 3.56 (ddd, *J* = 11.2, 8.0, 1.6 Hz, 1 H, $H2_{ax}$), 3.48 (br s, 1 H, NH), 3.03 (dd, *J* = 13.6, 10.0 Hz, 1 H, $H5_{ax}$), 2.92 (dt, *J* = 13.6, 2.0 Hz, 1 H, $H5_{eq}$), 2.18 (ddt, *J* = 12.8, 4.0, 2.0 Hz, 1 H, $H3_{eq}$), 1.88 (ddd, *J* = 12.8, 11.2, 10.0 Hz, 1 H, $H3_{ax}$), 1.69 (br s, 1 H, OH).

^{13}C NMR: δ = 158.1 (d, *J* = 238.3 Hz, C7), 144.8 (d, *J* = 2.4 Hz, C9a), 136.3 (C1′), 131.5 (CH= styryl), 131.1 (=CH styryl), 130.2 (d, *J* = 7.4 Hz, C5a), 128.8 (C3′/C5′), 128.0 (C4′), 126.5 (C2′/C6′), 121.2 (d, *J* = 7.9 Hz, C9), 117.8 (d, *J* = 21.9 Hz, C6), 113.7 (d, *J* = 21.8 Hz, C8), 69.5 (C4), 59.0 (C2), 46.6 (C3), 44.1 (d, *J* = 0.4 Hz, C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 283 ($M^{+\bullet}$, 62), 159 (48), 130 (33), 125 (64), 124 (100), 117 (21), 115 (48), 91 (69), 77 (33).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{18}FNO$: 283.1372; found: 283.1378.

***cis*-7-Chloro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (14c)**
White crystals; yield: 0.96 g (95%); mp 123 °C (heptane); R_f = 0.43 (33% EtOAc–heptane).

IR (KBr): 3400 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.41–7.39 (m, 2 H, H2′/H6′), 7.37–7.32 (m, 2 H, H3′/H5′), 7.30–7.25 (m, 1 H, H4′), 7.13 (d, *J* = 2.4 Hz, 1 H, H6), 7.04 (dd, *J* = 8.4, 2.4 Hz, 1 H, H8), 6.67 (d, *J* = 8.4 Hz, 1 H, H9), 6.62 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.32 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 3.84 (tt, *J* = 9.6, 3.6 Hz, 1 H, $H4_{ax}$), 3.61 (ddd, *J* = 11.2, 8.0, 2.0 Hz, 1 H, $H2_{ax}$), 2.99 (dd, *J* = 14.0, 9.6 Hz, 1 H, $H5_{ax}$), 2.93 (dt, *J* = 14.0, 2.0, Hz, 1 H, $H5_{eq}$), 2.19 (ddt, *J* = 12.8, 4.0, 2.0 Hz, 1 H, $H3_{eq}$), 1.88 (ddd, *J* = 12.8, 11.2, 9.8 Hz, 1 H, $H3_{ax}$), 1.62 (br s, 1 H, OH).

^{13}C NMR: δ = 147.3 (C9a), 136.3 (C1′), 131.4 (CH= styryl), 131.2 (=CH styryl), 131.2 (C6), 129.7 (C5a), 128.7 (C3′/C5′), 128.1 (C4′), 127.2 (C8), 126.5 (C2′/C6′), 126.4 (C7), 121.4 (C9), 69.4 (C4), 58.7 (C2), 46.3 (C3), 44.0 (C5).

GC-MS (EI, 70 eV): *m*/*z* (%) = 299 ($M^{+\bullet}$, ^{35}Cl, 33), 159 (61), 141 (57), 140 (82), 130 (24), 117 (48), 115 (68), 91 (100), 77 (72).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{18}ClNO$: 299.1077; found: 299.1079.

***cis*-8-Chloro-9-methyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (14d)**
White crystals; yield: 0.86 g (85%); mp 138 °C (heptane); R_f = 0.39 (33% EtOAc–heptane).

IR (KBr): 3411 (N–H), 3238 cm^{-1} (O–H).

^1H NMR: δ = 7.43–7.41 (m, 2 H, H2′/H6′), 7.38–7.34 (m, 2 H, H3′/H5′), 7.31–7.27 (m, 1 H, H4′), 6.95 (d, *J* = 8.0 Hz, 1 H, H7), 6.92 (d, *J* = 8.0 Hz, 1 H, H6), 6.64 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.38 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 3.85 (tt, *J* = 8.8, 4.0, Hz, 1 H, $H4_{ax}$), 3.67 (br s, 1 H, NH), 3.59 (ddd, *J* = 11.2, 8.0, 1.6 Hz, 1 H, $H2_{ax}$), 3.00 (dd, *J* = 13.6, 8.0 Hz, 1 H, $H5_{ax}$), 2.97 (dd, *J* = 13.6, 1.2 Hz, 1 H, $H5_{eq}$), 2.29 (s, 3 H, 9-CH_3), 2.18 (ddt, *J* = 12.8, 3.6, 1.6 Hz, 1 H, $H3_{eq}$), 1.88 (ddd, *J* = 12.8, 11.2, 10.0 Hz, 1 H, $H3_{ax}$), 1.69 (br s, 1 H, OH).

^{13}C NMR: δ = 148.3 (C9a), 136.3 (C1′), 133.0 (C8), 131.5 (CH= styryl), 131.3 (=CH styryl), 129.4 (C6), 128.7 (C3′/C5′), 128.1

(C4′), 127.2 (C5a), 126.5 (C2′/C6′), 124.6 (C9), 122.1 (C7), 69.4 (C4), 58.4 (C2), 45.8 (C3), 43.8 (C5), 14.6 (9-CH_3).

GC-MS (EI, 70 eV): *m/z* (%) = 313 ($M^{+\bullet}$, ^{35}Cl, 36), 159 (39), 155 (41), 154 (100), 130 (38), 117 (21), 115 (44), 91 (75), 77 (36).

HRMS: *m/z* $[M]^+$ calcd for $C_{19}H_{20}ClNO$: 313.1233; found: 313.1234.

cis-6,8-Dimethyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (14e)
White crystals; yield: 0.94 g (93%); mp 124 °C (heptane); R_f = 0.36 (33% EtOAc–heptane).

IR (KBr): 3273 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.41 (dd, *J* = 7.2, 1.6 Hz, 2 H, H2′/H6′), 7.35 (td, *J* = 7.2, 1.6 Hz, 2 H, H3′/H5′), 7.30–726 (m, 1 H, H4′), 6.67 (s, 1 H, H7), 6.61 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.47 (s, 1 H, H9), 6.34 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 3.85 (tdd, *J* = 9.2, 4.2, 2.2 Hz, 1 H, $H4_{ax}$), 3.66 (ddd, *J* = 11.2, 8.0, 2.0 Hz, 1 H, $H2_{ax}$), 3.44 (br s, 1 H, NH), 3.14 (d, *J* = 14.0 Hz, 1 H, $H5_{eq}$), 2.91 (dd, *J* = 14.0, 9.2 Hz, 1 H, $H5_{ax}$), 2.34 (s, 3 H, 6-CH_3), 2.24 (s, 3 H, 8-CH_3), 2.19 (br s, 1 H, OH), 2.17 (ddt, *J* = 12.8, 4.2, 2.0 Hz, 1 H, $H3_{eq}$), 1.90 (ddd, *J* = 12.8, 11.2, 9.2 Hz, 1 H, $H3_{ax}$).

^{13}C NMR: δ = 148.8 (C9a), 137.7 (C6), 136.6 (C8), 136.4 (C1′), 131.9 (CH= styryl), 130.8 (=CH styryl), 128.7 (C3′/C5′), 127.9 (C4′), 126.5 (C2′/C6′), 125.1 (C7), 123.9 (C5a), 119.1 (C9), 69.4 (C4), 59.0 (C2), 45.7 (C3), 37.8 (C5), 20.8 (6-CH_3), 20.7 (8-CH_3).

GC-MS (EI, 70 eV): *m/z* (%) = 293 ($M^{+\bullet}$, 51), 159 (6), 135 (26), 134 (100), 130 (18), 117 (9), 115 (24), 91 (30), 77 (12).

HRMS: *m/z* $[M]^+$ calcd for $C_{20}H_{23}NO$: 293.1780; found: 293.1779.

trans-2-[(*E*)-Styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (15a)
Colorless viscous oil; yield: 0.92 g (91%); R_f = 0.31 (33% EtOAc–heptane).

IR (liquid film): 3345 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.40–7.37 (m, 2 H, H2′/H6′), 7.35–7.31 (m, 2 H, H3′/H5′), 7.28–7.24 (m, 1 H, H4′), 7.15 (dd, *J* = 7.6, 1.6 Hz, 1 H, H6), 7.12 (td, *J* = 7.6, 1.6 Hz, 1 H, H8), 6.91 (td, *J* = 7.6, 1.2 Hz, 1 H, H7), 6.79 (dd, *J* = 7.6, 1.2 Hz, 1 H, H9), 6.62 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.32 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 4.29–4.24 (m, 1 H, $H4_{eq}$), 3.86 (ddd, *J* = 10.4, 8.0, 2.0 Hz, 1 H, $H2_{ax}$), 3.65 (br s, 1 H, NH), 3.11 (dd, *J* = 14.0, 2.0 Hz, 1 H, $H5_{eq}$), 3.05 (dd, *J* = 14.0, 6.4 Hz, 1 H, $H5_{ax}$), 2.10–2.05 (m, 1 H, $H3_{eq}$), 1.95 (ddd, *J* = 14.0, 10.4, 2.8 Hz, 1 H, $H3_{ax}$), 1.53 (br s, 1 H, OH).

^{13}C NMR: δ = 148.4 (C9a), 136.6 (C1′), 132.5 (C6), 132.0 (CH= styryl), 130.8 (=CH styryl), 128.7 (C3′/C5′), 127.9 (C4′), 127.8 (C8), 127.0 (C5a), 126.4 (C2′/C6′), 121.8 (C7), 120.2 (C9), 65.6 (C4), 54.8 (C2), 44.4 (C3), 41.8 (C5).

GC-MS (EI, 70 eV): *m/z* (%) = 265 ($M^{+\bullet}$, 48), 159 (21), 130 (54), 117 (81), 115 (45), 107 (51), 106 (100), 91 (66), 77 (39).

HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{19}NO$: 265.1467; found: 265.1457.

trans-7-Fluoro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (15b)
Colorless viscous oil; yield: 0.92 g (91%); R_f = 0.27 (33% EtOAc–heptane).

IR (liquid film): 3348 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.39–7.36 (m, 2 H, H2′/H6′), 7.35–7.31 (m, 2 H, H3′/H5′), 7.28–7.24 (m, 1 H, H4′), 6.88 (dd, *J* = 9.2, 2.8 Hz, 1 H, H6), 6.80 (td, *J* = 8.4, 2.8 Hz, 1 H, H8), 6.72 (dd, *J* = 8.4, 5.2 Hz, 1 H, H9), 6.61 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.30 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 4.27–4.24 (m, 1 H, $H4_{eq}$), 3.83 (ddd, *J* = 10.4, 8.0, 2.4 Hz, 1 H, $H2_{ax}$), 3.54 (br s, 1 H, NH), 3.09 (dd, *J* = 14.0, 1.6 Hz, 1 H, $H5_{eq}$), 2.98 (dd, *J* = 14.0, 6.8 Hz, 1 H, $H5_{ax}$), 2.09–2.03 (m, 1 H, $H3_{eq}$), 1.93 (ddd, *J* = 14.0, 10.4, 2.8 Hz, 1 H, $H3_{ax}$), 1.55 (br s, 1 H, OH).

^{13}C NMR: δ = 158.1 (d, *J* = 238.3 Hz, C7), 144.3 (d, *J* = 2.2 Hz, C9a), 136.6 (C1′), 131.8 (CH= styryl), 130.9 (=CH styryl), 129.5 (d, *J* = 7.3 Hz, C5a), 128.7 (C3′/C5′), 127.9 (C4′), 126.4 (C2′/C6′), 121.2 (d, *J* = 7.9 Hz, C9), 118.7 (d, *J* = 21.9 Hz, C6), 113.9 (d, *J* = 21.7 Hz, C8), 65.4 (C4), 54.8 (C2), 44.3 (C3), 41.6 (C5).

GC-MS (EI, 70 eV): *m/z* (%) = 283 ($M^{+\bullet}$, 60), 159 (45), 130 (15), 125 (64), 124 (100), 117 (21), 115 (48), 91 (71), 77 (36).

HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{18}FNO$: 283.1372; found: 283.1374.

trans-7-Chloro-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (15c)
Colorless viscous oil; yield: 0.93 g (92%); R_f = 0.34 (33% EtOAc–heptane).

IR (liquid film): 3407 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.39–7.37 (m, 2 H, H2′/H6′), 7.36–7.32 (m, 2 H, H3′/H5′), 7.28–7.24 (m, 1 H, H4′), 7.12 (d, *J* = 2.4 Hz, 1 H, H6), 7.06 (dd, *J* = 8.4, 2.4 Hz, 1 H, H8), 6.70 (d, *J* = 8.4 Hz, 1 H, H9), 6.62 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.29 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 4.27–4.23 (m, 1 H, $H4_{eq}$), 3.88 (ddd, *J* = 10.4, 8.0, 2.4 Hz, 1 H, $H2_{ax}$), 3.63 (br s, 1 H, NH), 3.05 (dd, *J* = 14.0, 2.4 Hz, 1 H, $H5_{eq}$), 2.99 (dd, *J* = 14.0, 6.4 Hz, 1 H, $H5_{ax}$), 2.08–2.02 (m, 1 H, $H3_{eq}$), 1.94 (ddd, *J* = 14.0, 10.4, 3.2 Hz, 1 H, $H3_{ax}$), 1.57 (br s, 1 H, OH).

^{13}C NMR: δ = 146.8 (C9a), 136.5 (C1′), 131.9 (C6), 131.6 (CH= styryl), 131.1 (=CH styryl), 129.1 (C5a), 128.7 (C3′/C5′), 127.9 (C4′), 127.5 (C8), 126.4 (C2′/C6′), 126.3 (C7), 121.3 (C9), 65.5 (C4), 54.6 (C2), 44.1 (C3), 41.6 (C5).

GC-MS (EI, 70 eV): *m/z* (%) = 299 ($M^{+\bullet}$, ^{35}Cl, 27), 159 (51), 141 (49), 140 (73), 130 (33), 117 (42), 115 (68), 91 (100), 77 (78).

HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{18}ClNO$: 299.1077; found: 299.1081.

trans-8-Chloro-9-methyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (15d)
Colorless viscous oil; yield: 0.83 g (82%); R_f = 0.34 (33% EtOAc–heptane).

IR (liquid film): 3395 cm^{-1} (N–H, O–H).

^1H NMR: δ = 7.41–7.39 (m, 2 H, H2′/H6′), 7.36–7.33 (m, 2 H, H3′/H5′), 7.29–7.25 (m, 1 H, H4′), 6.93 (s, 2 H, H6, H7), 6.64 (d, *J* = 16.0 Hz, 1 H, =CH styryl), 6.33 (dd, *J* = 16.0, 8.0 Hz, 1 H, CH= styryl), 4.26–4.22 (m, 1 H, $H4_{eq}$), 3.88 (td, *J* = 9.6, 3.6 Hz, 1 H, $H2_{ax}$), 3.74 (br s, 1 H, NH), 3.07 (dd, *J* = 14.0, 2.4 Hz, 1 H, $H5_{eq}$), 3.00 (dd, *J* = 14.0, 7.2 Hz, 1 H, $H5_{ax}$), 2.30 (s, 3 H, 9-CH_3), 2.04–1.99 (m, 1 H, $H3_{eq}$), 1.97 (ddd, *J* = 14.0, 9.6, 3.2 Hz, 1 H, $H3_{ax}$), 1.60 (br s, 1 H, OH).

^{13}C NMR: δ = 147.8 (C9a), 136.5 (C1′), 133.4 (C8), 131.7 (CH= styryl), 131.1 (=CH styryl), 130.1 (C6), 128.7 (C3′/C5′), 128.0 (C4′), 126.5 (C2′/C6′), 126.1 (C5a), 124.5 (C9), 122.0 (C7), 65.5 (C4), 54.5 (C2), 43.8 (C3), 41.3 (C5), 14.7 (9-CH_3).

GC-MS (EI, 70 eV): *m/z* (%) = 313 ($M^{+\bullet}$, ^{35}Cl, 24), 159 (9), 155 (33), 154 (100), 130 (36), 117 (24), 115 (57), 91 (85), 77 (53).

HRMS: *m/z* $[M]^+$ calcd for $C_{19}H_{20}ClNO$: 313.1233; found: 313.1231.

trans-6,8-Dimethyl-2-[(*E*)-styryl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (15e)
White crystals; yield: 0.92 g (91%); mp 105 °C (heptane); R_f = 0.38 (33% EtOAc–heptane).

IR (KBr): 3317 (N–H), 3238 cm^{-1} (O–H).

^1H NMR: δ = 7.39 (dd, *J* = 7.2, 1.2 Hz, 2 H, H2′/H6′), 7.34 (dt, *J* = 7.2, 1.4 Hz, 2 H, H3′/H5′), 7.29–7.25 (m, 1 H, H4′), 6.66 (s, 1 H, H7), 6.60 (d, *J* = 15.6 Hz, 1 H, =CH styryl), 6.49 (s, 1 H, H9), 6.30 (dd, *J* = 15.6, 8.0 Hz, 1 H, CH= styryl), 4.27–4.23 (m, 1 H, $H4_{eq}$), 3.86 (ddd, *J* = 10.4, 8.0, 3.4 Hz, 1 H, $H2_{ax}$), 3.50 (br s, 1 H, NH), 3.22 (dd, *J* = 14.0, 7.6 Hz, 1 H, $H5_{ax}$), 2.93 (dd, *J* = 14.0, 2.0

Hz, 1 H, $H5_{eq}$), 2.33 (s, 3 H, 6-CH_3), 2.25 (s, 3 H, 8-CH_3), 2.02–1.96 (m, 1 H, $H3_{eq}$), 1.94 (ddd, J = 14.0, 10.4, 3.6 Hz, 1 H, $H3_{ax}$), 1.65 (br s, 1 H, OH).

^{13}C NMR: δ = 148.5 (C9a), 138.5 (C6), 136.7 (C8), 136.7 (C1′), 132.2 (CH= styryl), 130.6 (=CH styryl), 128.7 (C3′/C5′), 127.8 (C4′), 126.4 (C2′/C6′), 124.9 (C7), 122.6 (C5a), 119.1 (C9), 65.7 (C4), 55.2 (C2), 43.8 (C3), 35.2 (C5), 20.9 (6-CH_3), 20.7 (8-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 293 ($M^{+\bullet}$, 51), 159 (6), 135 (26), 134 (100), 130 (18), 117 (9), 115 (24), 91 (32), 77 (15).

HRMS: m/z $[M]^+$ calcd for $C_{20}H_{23}NO$: 293.1780; found: 293.1778.

***cis*-7-Fluoro-2-[(*E*)-pent-1-enyl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (16a)**

White crystals; yield: 0.96 g (95%); mp 68 °C (heptane); R_f = 0.30 (33% EtOAc–heptane).

IR (KBr): 3320 (N–H), 3283 cm^{-1} (O–H).

^{1}H NMR: δ = 6.83 (dd, J = 9.2, 2.8 Hz, 1 H, H6), 6.75 (td, J = 8.4, 2.8 Hz, 1 H, H8), 6.65 (dd, J = 8.4, 5.0 Hz, 1 H, H9), 5.68 (dt, J = 15.4, 6.6 Hz, 1 H, =CH pentenyl), 5.57 (dd, J = 15.4, 7.6 Hz, 1 H, CH= pentenyl), 3.76 (tt, J = 10.0, 3.6 Hz, 1 H, $H4_{ax}$), 3.34 (ddd, J = 11.2, 7.6, 2.0 Hz, 1 H, $H2_{ax}$), 3.32 (br s, 1 H, NH), 2.97 (dd, J = 13.6, 10.0 Hz, 1 H, $H5_{ax}$), 2.86 (dt, J = 13.6, 2.0 Hz, 1 H, $H5_{eq}$), 2.08 (ddt, J = 12.8, 4.0, 2.0 Hz, 1 H, $H3_{eq}$), 2.02 (dd, J = 14.0, 7.2 Hz, 2 H, 3′-CH_2), 1.96 (br s, 1 H, OH), 1.75 (ddd, J = 12.8, 11.2, 10.4 Hz, 1 H, $H3_{ax}$), 1.42 (dq, J = 14.0, 7.6 Hz, 2 H, 4′-CH_2), 0.91 (t, J = 7.6 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 157.9 (d, J = 237.9 Hz, C7), 145.1 (d, J = 2.3 Hz, C9a), 132.6 (CH= pentenyl), 132.2 (=CH pentenyl), 130.0 (d, J = 7.3 Hz, C5a), 121.1 (d, J = 7.9 Hz, C9), 117.7 (d, J = 22.0 Hz, C6), 113.5 (d, J = 21.7 Hz, C8), 69.6 (C4), 58.7 (C2), 46.8 (C3), 44.2 (C5), 34.3 (3′-CH_2), 22.3 (4′-CH_2), 13.6 (5′-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 249 ($M^{+\bullet}$, 54), 205 (12), 204 (12), 180 (3), 162 (100), 148 (21), 136 (34), 125 (38), 124 (50).

HRMS: m/z $[M]^+$ calcd for $C_{15}H_{20}FNO$: 249.1529; found: 249.1528.

***cis*-8-Chloro-9-methyl-2-[(*E*)-pent-1-enyl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (16b)**

Colorless viscous oil; yield: 0.95 g (94%); R_f = 0.27 (33% EtOAc–heptane).

IR (liquid film): 3367 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.89 (d, J = 8.0 Hz, 1 H, H7), 6.88 (d, J = 8.0 Hz, 1 H, H6), 5.70 (dt, J = 15.4, 6.4 Hz, 1 H, =CH pentenyl), 5.62 (dd, J = 15.4, 7.2 Hz, 1 H, CH= pentenyl), 3.79–3.72 (m, 1 H, $H4_{ax}$), 3.54 (br s, 1 H, NH), 3.33 (ddd, J = 11.2, 7.2, 2.0 Hz, 1 H, $H2_{ax}$), 2.93 (dd, J = 13.6, 8.0 Hz, 1 H, $H5_{ax}$), 2.90 (dd, J = 13.6, 1.6 Hz, 1 H, $H5_{eq}$), 2.29 (br s, 1 H, OH), 2.26 (s, 3 H, 9-CH_3), 2.10–2.03 (m, 1 H, $H3_{eq}$), 2.04 (dd, J = 14.6, 6.8 Hz, 2 H, 3′-CH_2), 1.74 (ddd, J = 12.8, 11.2, 10.0 Hz, 1 H, $H3_{ax}$), 1.42 (dq, J = 14.6, 7.4 Hz, 2 H, 4′-CH_2), 0.92 (t, J = 7.4 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 148.7 (C9a), 132.8 (C8), 132.7 (CH= pentenyl), 132.6 (=CH pentenyl), 129.4 (C6), 127.1 (C5a), 124.3 (C9), 121.9 (C7), 69.5 (C4), 58.2 (C2), 46.0 (C3), 43.9 (C5), 34.3 (3′-CH_2), 22.3 (4′-CH_2), 14.4 (9-CH_3), 13.6 (5′-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 279 ($M^{+\bullet}$, ^{35}Cl, 76), 235 (12), 234 (18), 210 (2), 192 (93), 178 (36), 166 (39), 155 (43), 154 (100).

HRMS: m/z $[M]^+$ calcd for $C_{16}H_{22}ClNO$: 279.1390; found: 279.1393.

***trans*-7-Fluoro-2-[(*E*)-pent-1-enyl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (17a)**

Colorless viscous oil; yield: 0.91 g (90%); R_f = 0.35 (33% EtOAc–heptane).

IR (liquid film): 3353 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.84 (dd, J = 9.2, 2.8 Hz, 1 H, H6), 6.78 (td, J = 8.4, 2.8 Hz, 1 H, H8), 6.69 (dd, J = 8.4, 5.2 Hz, 1 H, H9), 5.66 (dt, J = 15.2, 6.8 Hz, 1 H, =CH pentenyl), 5.52 (ddt, J = 15.2, 7.6, 1.2 Hz, 1 H, CH= pentenyl), 4.19 (ddt, J = 6.8, 4.8, 2.6 Hz, 1 H, $H4_{eq}$), 3.57 (ddd, J = 10.4, 7.6, 2.4 Hz, 1 H, $H2_{ax}$), 3.02 (dd, J = 14.0, 1.6 Hz, 1 H, $H5_{eq}$), 2.93 (ddd, J = 14.0, 6.8, 0.6 Hz, 1 H, $H5_{ax}$), 2.00 (ddd, J = 14.4, 7.6, 0.8 Hz, 2 H, 3′-CH_2), 1.63 (br s, 1 H, OH), 1.93 (dddd, J = 14.0, 4.8, 2.4, 1.0 Hz, 1 H, $H3_{eq}$), 1.83 (ddd, J = 14.0, 10.4, 2.8 Hz, 1 H, $H3_{ax}$), 1.39 (dq, J = 14.4, 7.2 Hz, 2 H, 4′-CH_2), 0.90 (t, J = 7.2 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 158.0 (d, J = 237.9 Hz, C7), 144.6 (d, J = 2.2 Hz, C9a), 132.6 (CH= pentenyl), 132.1 (=CH pentenyl), 129.3 (d, J = 7.3 Hz, C5a), 121.0 (d, J = 7.9 Hz, C9), 118.7 (d, J = 21.9 Hz, C6), 113.9 (d, J = 21.7 Hz, C8), 65.5 (C4), 54.6 (C2), 44.5 (C3), 41.6 (C5), 34.4 (3′-CH_2), 22.3 (4′-CH_2), 13.7 (5′-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 249 ($M^{+\bullet}$, 44), 205 (12), 204 (12), 180 (3), 162 (100), 148 (27), 136 (34), 125 (36), 124 (50).

HRMS: m/z $[M]^+$ calcd for $C_{15}H_{20}FNO$: 249.1529; found: 249.1526.

***trans*-8-Chloro-9-methyl-2-[(*E*)-pent-1-enyl]-2,3,4,5-tetrahydro-1*H*-1-benzazepin-4-ol (17b)**

Colorless viscous oil; yield: 0.87 g (86%); R_f = 0.35 (33% EtOAc–heptane).

IR (KBr): 3400 cm^{-1} (N–H, O–H).

^{1}H NMR: δ = 6.89 (d, J = 7.5 Hz, 2 H, H6, H7), 5.69 (dt, J = 15.2, 6.6 Hz, 1 H, =CH pentenyl), 5.57 (ddt, J = 15.2, 7.6, 1.0 Hz, 1 H, CH= pentenyl), 4.18 (td, J = 7.2, 3.6 Hz, 1 H, $H4_{eq}$), 3.62 (ddd, J = 10.4, 7.6, 2.8 Hz, 1 H, $H2_{ax}$), 3.61 (br s, 1 H, NH), 2.99 (dd, J = 13.8, 2.4 Hz, 1 H, $H5_{eq}$), 2.95 (dd, J = 13.8, 5.6 Hz, 1 H, $H5_{ax}$), 2.27 (s, 3 H, 9-CH_3), 2.02 (ddd, J = 14.8, 7.6, 0.8 Hz, 2 H, 3′-CH_2), 1.93–1.88 (m, 1 H, $H3_{eq}$), 1.83 (ddd, J = 14.0, 10.4, 3.6 Hz, 1 H, $H3_{ax}$), 1.59 (br s, 1 H, OH), 1.41 (dq, J = 14.8, 7.4 Hz, 2 H, 4′-CH_2), 0.91 (t, J = 7.4 Hz, 3 H, 5′-CH_3).

^{13}C NMR: δ = 148.2 (C9a), 133.2 (C8), 132.7 (CH= pentenyl), 132.4 (=CH pentenyl), 130.1 (C6), 126.0 (C5a), 124.3 (C9), 121.7 (C7), 65.6 (C4), 54.3 (C2), 44.0 (C3), 41.3 (C5), 34.3 (3′-CH_2), 22.3 (4′-CH_2), 14.6 (9-CH_3), 13.6 (5′-CH_3).

GC-MS (EI, 70 eV): m/z (%) = 279 ($M^{+\bullet}$, ^{35}Cl, 57), 235 (10), 234 (18), 210 (9), 192 (57), 178 (33), 166 (63), 155 (39), 154 (100).

HRMS: m/z $[M]^+$ calcd for $C_{16}H_{22}ClNO$: 279.1390; found: 279.1393.

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Supporting Information

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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