

# One-Pot Synthesis of Pharmacologically Active Diamines via Rhodium-Catalysed Carbonylative Hydroaminomethylation of Heterocyclic Allylic Amines

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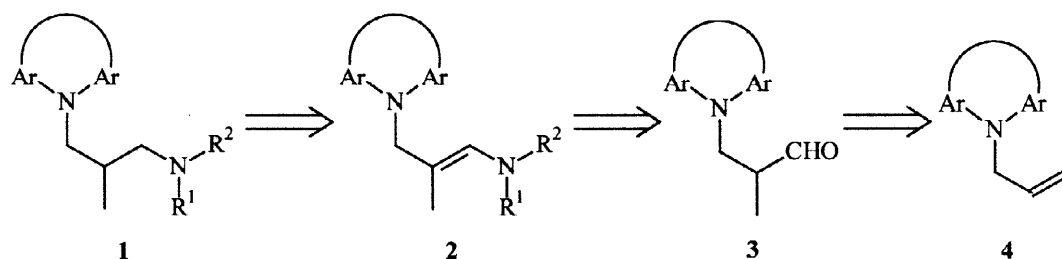
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## Abstract

Pharmacologically active derivatives of phenothiazine, iminodibenzyl, carbazole and pyrazole are prepared with high yields and chemoselectivity by the reaction of the corresponding *N*-allylic or *N*-methallylic compounds, primary or secondary amines, carbon monoxide and hydrogen in the presence of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  as catalyst via a one pot hydroformylation - amine condensation - reduction sequence. © 1999 Elsevier Science Ltd. All rights reserved.

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Due to their pharmacological activity numerous  $\gamma$ - and  $\delta$ -aminofunctionalised phenothiazine [1-14], iminodibenzyl [15-29], carbazole [30-33] and pyrazole [34-37] derivatives are commercially obtainable therapeutic agents. Although well established, these pharmaceuticals are conventionally prepared via two or more step procedures not involving transition metal catalysis. According to a retrosynthetic analysis these substrates should be more easily accessible via a hydroformylation - amine condensation - reduction sequence leading to an overall hydroaminomethylation of the starting alkene **4** (Scheme 1). Compared to the conventional methodologies this procedure should be more flexible concerning to the introduction of the amine in the final step.

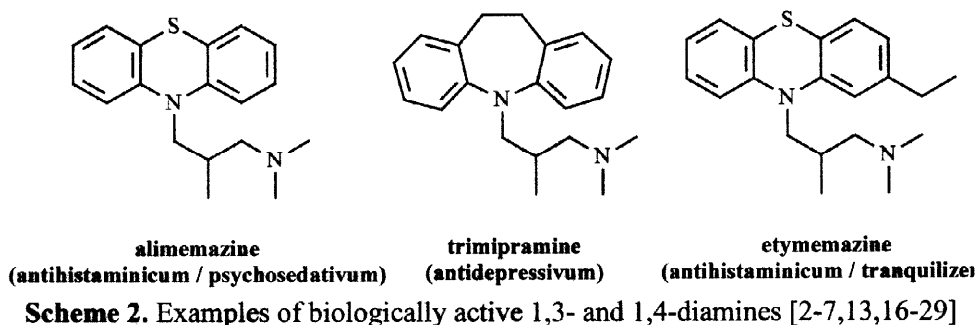


**Scheme 1.** Retrosynthetic analysis of the pharmacologically active substrates **1**

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Following our interest in rhodium catalysed hydroaminomethylation [38], which combines the three reaction steps described above in a efficient one-pot procedure, we here present use of this

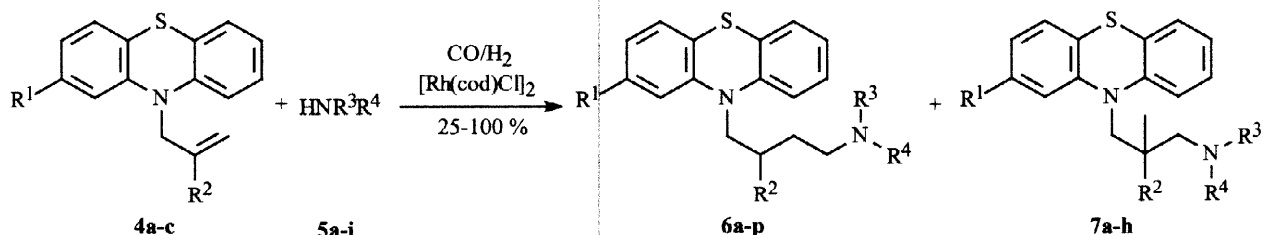
methodology for the synthesis of pharmacologically active  $\gamma$ - and  $\delta$ -aminofunctionalised phenothiazine, iminodibenzyl, carbazole and pyrazole derivatives starting from simple *N*-allylic amines **4**. Representative examples of pharmacologically active compounds of these types are shown in scheme 2.



### Synthesis of phenothiazine derivatives

As summarised in table 1 *N*-allylphenothiazine (**4a**) in the presence of primary or secondary amines under typical hydroformylation conditions undergoes selective hydroaminomethylation to form the corresponding secondary or tertiary diamines **6** and **7** in good to excellent yields (scheme 3). Aromatic, as well as aliphatic amines can satisfactorily be employed (entries 1-8, table 1). In the case of cyclic and acyclic aliphatic *N*-nucleophiles **5a-e** the generation of the *iso*-isomers **7** is slightly preferred (entries 1-5, table 1). This can be explained by a pre-coordinating effect of the nitrogen atom influencing the formation of alkyl- and acylrhodium intermediates.[39] Due to sterical hindrance hydroaminomethylation of **4a** with more bulky amines predominantly leads to the corresponding *n*-isomers. If, however, *N*-methylaniline or benzylamine, respectively, are used in the reaction sequence exclusively, the 1,4-diamines **6g** and **6h** are obtained resulting from selective *n*-hydroaminomethylation.

The conversion of the substituted *N*-allylphenothiazine **4b** with dimethylamine proceeds in comparably good yields to the corresponding pharmacologically active 1,3- and 1,4-diamines **7h/6h** (entry 8, table 1). Again the generation of the *iso*-isomers is slightly preferred due to the reasons given above.



**Scheme 3.** Hydroaminomethylation of *N*-allylic and *N*-methallylic phenothiazine derivatives **4**

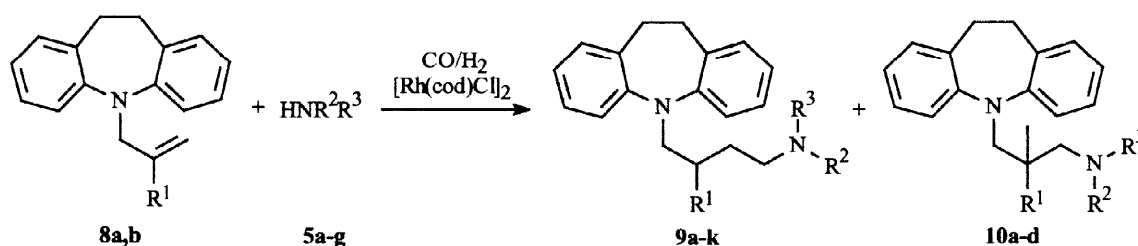
Under similar reaction conditions the hydroaminomethylation of *N*-methallylphenothiazine (**4c**) proceeds with exclusive *n*-selectivity to the corresponding secondary and tertiary amines **6i-p** in good yields (entries 9-16, table 1). Again various aliphatic as well as aromatic primary or secondary amines are tolerated in the reaction sequence. The exclusive formation of the *n*-isomers in this case may be explained by the steric hindrance of the  $\alpha$ -C-carbonylation.

**Table 1.** Hydroaminomethylation of *N*-allylic and *N*-methallylic phenothiazine derivatives

entry	olefin	R <sup>1</sup>	R <sup>2</sup>	HNR <sup>3</sup> R <sup>4</sup>	amine	product	total yield [%]	selectivity	
								[%] <b>6</b> ( <i>n</i> )	[%] <b>7</b> ( <i>iso</i> )
1	<b>4a</b>	H	H	dimethylamine	<b>5a</b>	<b>6a/7a</b>	98	19	81
2	<b>4a</b>	H	H	diethylamine	<b>5b</b>	<b>6b/7b</b>	78	42	58
3	<b>4a</b>	H	H	morpholine	<b>5c</b>	<b>6c/7c</b>	80	45	55
4	<b>4a</b>	H	H	piperidine	<b>5d</b>	<b>6d/7d</b>	95	26	74
5	<b>4a</b>	H	H	hexamethylenimine	<b>5e</b>	<b>6e/7e</b>	92	10	90
6	<b>4a</b>	H	H	<i>N</i> -methylaniline	<b>5f</b>	<b>6f</b>	92	-	-
7	<b>4a</b>	H	H	benzylamine	<b>5g</b>	<b>6g</b>	64	-	-
8	<b>4b</b>	Et	H	dimethylamine	<b>5a</b>	<b>6h/7h</b>	97	29	71
9	<b>4c</b>	H	CH <sub>3</sub>	diethylamine	<b>5b</b>	<b>6i</b>	98	-	-
10	<b>4c</b>	H	CH <sub>3</sub>	diisopropylamine	<b>5h</b>	<b>6j</b>	25	-	-
11	<b>4c</b>	H	CH <sub>3</sub>	morpholine	<b>5c</b>	<b>6k</b>	100	-	-
12	<b>4c</b>	H	CH <sub>3</sub>	pyrrolidine	<b>5i</b>	<b>6l</b>	78	-	-
13	<b>4c</b>	H	CH <sub>3</sub>	piperidine	<b>5d</b>	<b>6m</b>	97	-	-
14	<b>4c</b>	H	CH <sub>3</sub>	hexamethylenimine	<b>5e</b>	<b>6n</b>	92	-	-
15	<b>4c</b>	H	CH <sub>3</sub>	<i>N</i> -methylaniline	<b>5f</b>	<b>6o</b>	89	-	-
16	<b>4c</b>	H	CH <sub>3</sub>	benzylamine	<b>5g</b>	<b>6p</b>	89	-	-

### Synthesis of iminodibenzyl derivatives

$\gamma$ - and  $\delta$ -aminofunctionalised iminodibenzyl derivatives **9**, **10** are obtained if *N*-allyliminodibenzyls **8** are employed in the reaction sequence (scheme 4). Under typical hydroaminomethylation conditions *N*-allyliminodibenzyl (**8a**) reacts with various aliphatic and aromatic primary and secondary amines leading to the corresponding 1,3- and 1,4-diamines **9**, **10** in good to excellent yields (entries 1-6, table 2). In comparison to the conversion of **4a** generally the generation of the *n*-isomer is slightly preferred due to steric reasons.



**Scheme 4.** Hydroaminomethylation of the *N*-allylic and *N*-methallylic iminodibenzyl derivatives **8**

In case of the  $\alpha$ -substituted *N*-allyliminodibenzyl (**8b**) however hydroaminomethylation proceeds with exclusive *n*-selectivity to the corresponding 1,4-diamines **9g-k** in comparable

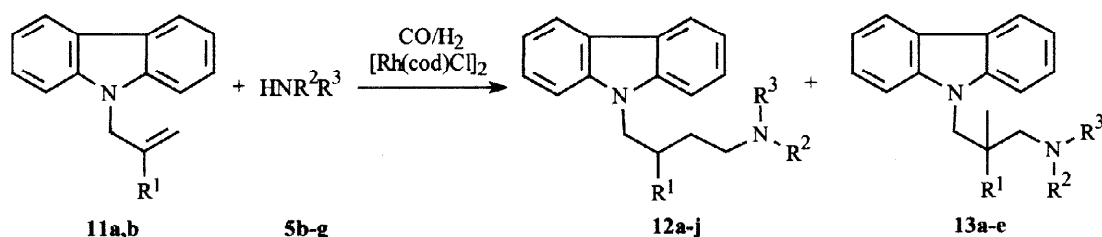
good to excellent yields (entries 7-11, table 2). Various amines of different types are tested. The results are summarised in table 2.

**Table 2.** Hydroaminomethylation of the *N*-allylic and methallylic iminodibenzyl derivatives **8**

entry	olefin	R <sup>1</sup>	HNR <sup>2</sup> R <sup>3</sup>	amine	product	total yield [%]	selectivity	
							[%] <b>9</b> ( <i>n</i> )	[%] <b>10</b> ( <i>iso</i> )
1	<b>8a</b>	H	dimethylamine	<b>5a</b>	<b>9a/10a</b>	91	80	20
2	<b>8a</b>	H	morpholine	<b>5c</b>	<b>9b/10b</b>	79	86	14
3	<b>8a</b>	H	piperidine	<b>5d</b>	<b>9c/10c</b>	86	52	48
4	<b>8a</b>	H	hexamethylenimine	<b>5e</b>	<b>9d/10d</b>	97	50	50
5	<b>8a</b>	H	<i>N</i> -methylaniline	<b>5f</b>	<b>9e</b>	90	-	-
6	<b>8a</b>	H	benzylamine	<b>5g</b>	<b>9f</b>	93	-	-
7	<b>8b</b>	CH <sub>3</sub>	diethylamine	<b>5b</b>	<b>9g</b>	93	-	-
8	<b>8b</b>	CH <sub>3</sub>	morpholine	<b>5c</b>	<b>9h</b>	94	-	-
9	<b>8b</b>	CH <sub>3</sub>	hexamethylenimine	<b>5e</b>	<b>9i</b>	86	-	-
10	<b>8b</b>	CH <sub>3</sub>	<i>N</i> -methylaniline	<b>5f</b>	<b>9j</b>	93	-	-
11	<b>8b</b>	CH <sub>3</sub>	benzylamine	<b>5g</b>	<b>9k</b>	75	-	-

### Synthesis of carbazole derivatives

If *N*-allyl-carbazoles **11** are employed in the hydroaminomethylation the corresponding  $\gamma$ - and  $\delta$ -functionalised carbazoles **12** and **13** are obtained (scheme 5). Thus, *N*-allyl carbazole (**11a**) undergoes hydroaminomethylation with various aliphatic and aromatic primary and secondary amines to give 1,3- and 1,4-diamines in good to excellent yields (entries 1-3, table 3). In almost all cases the generation of the *iso*-isomer (**13**) is slightly preferred. Even the conversion with *N*-methylaniline and benzylamine leads to a mixture of the corresponding 1,3- and 1,4-diamines (entries 4,5, table 3).



**Scheme 5.** Hydroaminomethylation of *N*-allylic and *N*-methallylic carbazole derivatives **11**

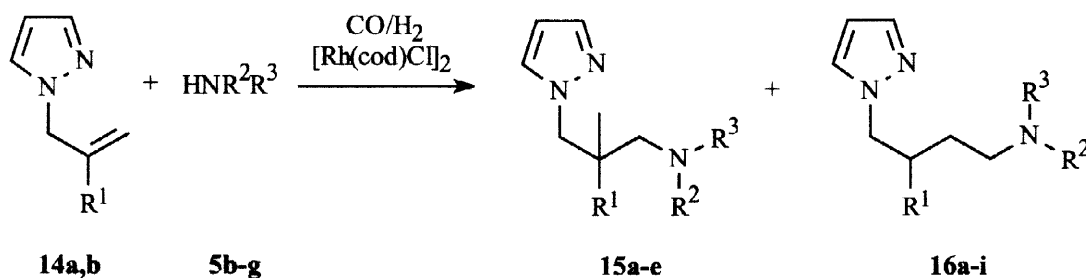
Similar to methallylic compounds **4c** and **8b** *N*-methallylcarbazole (**11b**) undergoes hydroaminomethylation *n*-selectively in presence of various amines forming the 1,4-diamines **12** in good yields (entries 6-10, table 3, scheme 5).

**Table 3.** Hydroaminomethylation of *N*-allylic and methallylic carbazole derivatives **11**

entry	olefin	R <sup>1</sup>	HNR <sup>2</sup> R <sup>3</sup>	amine	product	total yield [%]	selectivity	
							[%] <b>12</b> ( <i>n</i> )	[%] <b>13</b> ( <i>iso</i> )
1	<b>11a</b>	H	diethylamine	<b>5b</b>	<b>12a/13a</b>	70	42	58
2	<b>11a</b>	H	morpholine	<b>5c</b>	<b>12b/13b</b>	92	33	67
3	<b>11a</b>	H	hexamethylenimine	<b>5e</b>	<b>12c/13c</b>	91	34	66
4	<b>11a</b>	H	<i>N</i> -methylaniline	<b>5f</b>	<b>12d/13d</b>	69	57	43
5	<b>11a</b>	H	benzylamine	<b>5g</b>	<b>12e/13e</b>	88	34	66
6	<b>11b</b>	CH <sub>3</sub>	diethylamine	<b>5b</b>	<b>12f</b>	79	-	-
7	<b>11b</b>	CH <sub>3</sub>	morpholine	<b>5c</b>	<b>12g</b>	86	-	-
8	<b>11b</b>	CH <sub>3</sub>	hexamethylenimine	<b>5e</b>	<b>12h</b>	93	-	-
9	<b>11b</b>	CH <sub>3</sub>	<i>N</i> -methylaniline	<b>5f</b>	<b>12i</b>	78	-	-
10	<b>11b</b>	CH <sub>3</sub>	benzylamine	<b>5g</b>	<b>12j</b>	83	-	-

### Synthesis of pyrazole derivatives

Similar to the *N*-allylic compounds **4a**, **8a** and **11a** *N*-allylpyrazole (**14a**) reacts with various primary and secondary amines to give the 1,3 and 1,4- diamines **15** and **16**, in comparable good to excellent yields (scheme 6, entries 1-5, table 4). In comparison to the conversions of **4a**, **8a** and **11a** the generation of the *iso*-isomer is preferred. An explanation for this is on one hand a pre-coordinating effect of the nitrogen atom influencing the formation of the acylrhodium species[39] and on the other hand the lower sterical hindrance of the *N*-allylic amine **14a**.

**Scheme 6.** Hydroaminomethylation of *N*-allylic and *N*-methallylic pyrazole derivatives **14****Table 4.** Hydroaminomethylation of *N*-allylic and methallylic pyrazole derivatives **14**

entry	olefin	R <sup>1</sup>	HNR <sup>2</sup> R <sup>3</sup>	amine	product	total yield [%]	selectivity	
							[%] <b>15</b> ( <i>iso</i> )	[%] <b>16</b> ( <i>n</i> )
1	<b>14a</b>	H	diethylamine	<b>5b</b>	<b>15a/16a</b>	98	71	29
2	<b>14a</b>	H	morpholine	<b>5c</b>	<b>15b/16b</b>	84	71	29
3	<b>14a</b>	H	hexamethylenimine	<b>5e</b>	<b>15c/16c</b>	93	72	28
4	<b>14a</b>	H	<i>N</i> -methylaniline	<b>5f</b>	<b>15d/16d</b>	100	70	30
5	<b>14a</b>	H	benzylamine	<b>5g</b>	<b>15e/16e</b>	81	72	29
6	<b>14b</b>	CH <sub>3</sub>	diethylamine	<b>5b</b>	<b>16f</b>	78	-	-
7	<b>14b</b>	CH <sub>3</sub>	morpholine	<b>5c</b>	<b>16g</b>	85	-	-
8	<b>14b</b>	CH <sub>3</sub>	hexamethylenimine	<b>5e</b>	<b>16h</b>	83	-	-
9	<b>14b</b>	CH <sub>3</sub>	<i>N</i> -methylaniline	<b>5f</b>	<b>16i</b>	71	-	-

As summarized in table 4 1,4-diamines are exclusively obtained if the  $\alpha$ -substituted *N*-allylic pyrazole **14b** is the starting olefin (scheme 6). Aromatic as well as aliphatic amines are satisfactorily employed to form selectively the corresponding secondary or tertiary amines **16f-i** in good yields (entries 6-9, table 4).

In conclusion we have shown that the hydroaminomethylation with  $[\text{Rh}(\text{cod})\text{Cl}]_2$  as catalyst is an efficient method to transform *N*-allylic or *N*-methallylic phenothiazine, iminodibenzyl, carbazole and pyrazole derivatives directly into the corresponding diamines. All olefins employed in the reaction undergo selective one-pot hydroaminomethylation in high yield. Further investigations towards an extension of the synthetic potential of the reaction are in current progress.

## EXPERIMENTAL

NMR spectra were recorded on Bruker Spectrometers DPX 300 and DRX 400 using TMS as internal standard. IR spectra were obtained with a Nicolet Impact 400D, mass spectra on a Finnigan CA 5 and elementary analysis with a Leco CHNS-932. Column chromatography was carried out with aluminum oxide N (act. I) from ICN Biomedicals, Eschwege, by using MTBE (methyl *tert*-butyl ether) / PE (petroleum ether, bp 30–60 °C) mixtures as eluent. Gas chromatography was carried out on a Carlo Erba GC-4160 with 25 m or on a Fisons GC-8130 with 30 m CP sil-5 capillaries. GC-MS and GC-IR spectra were obtained by using comparable capillaries and a Finnigan MAT 8320 (MS) and a Bruker IFS 48 (IR). The  $[\text{Rh}(\text{cod})\text{Cl}]_2$  catalyst was prepared according to literature procedures.[40] Pressure reactions have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof, Eningen, Germany.

### General procedure

A mixture of the olefin (3.6 mmol), the corresponding amine (3.6 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (1 mol % Rh) was heated for 2 d, at 120 °C in an autoclave under 90 bar carbon monoxide and 20 bar hydrogen ( $p_{\text{total}} = 110$  bar) pressure. The residue was dissolved in  $\text{Et}_2\text{O}$  and filtered through neutral alumina. Product mixtures were separated by column chromatography on neutral alumina using a mixture of MTBE/PE as eluent or by Kugelrohr distillation.

**10-Allyl-10H-phenothiazine (4a)** [41,42] was prepared from phenothiazine and allyl bromide according to a general literature procedure [42] in 87 % yield.

**10-Allyl-2-ethyl-10H-phenothiazine (4b)** [43] was prepared from 2-ethyl-10H-phenothiazine and allyl bromide according to a general literature procedure [42] in 91 % yield.

**10-(2-Methylallyl)-10H-phenothiazine (4c)** [44–46] was prepared from phenothiazine and methallyl chloride according to a general literature procedure [42] in 91 % yield.

***N,N*-Dimethyl-*N*-[4-(10H-10-phenothiazinyl)butyl]amine (6a)**. Obtained from 10-allyl-10H-phenothiazine (**4a**) and dimethylamine (**5a**) as a colourless oil in 18 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.58 (m, 2 H), 1.82 (m, 2 H), 2.16 (s, 6 H), 2.25 (t,  $^3J = 7.3$  Hz, 2 H), 3.87 (t,  $^3J = 7.0$  Hz, 2 H), 6.88 (m, 4 H), 7.12 (m, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 24.6 ( $\text{CH}_2$ ), 24.9 ( $\text{CH}_2$ ), 45.3 (2 x  $\text{NCH}_3$ ), 47.0 ( $\text{NCH}_2$ ), 59.1 ( $\text{NCH}_2$ ), 115.4 (2 x PhH), 122.3 (2 x PhH), 125.0 (2 x SCq), 127.1 (2 x PhH), 127.3 (2 x PhH), 145.3 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 298 ( $\text{M}^+$ , 9), 100 (62), 58 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3062 w, 2939 s, 1460 vs, 1443 s, 1284 s, 1253 s, 749 vs.

***N,N*-Dimethyl-*N*-[2-methyl-3-(10H-10-phenothiazinyl)propyl]amine (7a)** [2-7]. Obtained from 10-allyl-10H-phenothiazine (**4a**) and dimethylamine (**5a**) as a colourless oil in 80 % yield.

***N,N*-Diethyl-*N*-[4-[10H-10-phenothiazinyl)butyl]amine (6b)**. Obtained from 10-allyl-10H-phenothiazine (**4a**) and diethylamine (**5b**) as a colourless oil in 33 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.95 (t,  $^3J = 7.3$  Hz, 6 H), 1.56 (m, 2 H), 1.78 (m, 2 H), 2.39 (t,  $^3J = 7.4$  Hz, 2 H), 2.45 (q,  $^3J = 7.3$  Hz, 4 H), 3.83 (t,  $^3J = 7.3$  Hz, 2 H), 6.86 (m, 4 H), 7.09 (m, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 11.5 (2 x  $\text{CH}_3$ ), 24.1 ( $\text{CH}_2$ ), 24.6 ( $\text{CH}_2$ ), 46.5 (2 x  $\text{NCH}_2$ ), 47.0 ( $\text{NCH}_2$ ), 52.1 ( $\text{NCH}_2$ ), 115.3 (2 x PhH), 122.2 (2 x PhH), 124.8 (2 x SCq), 127.0 (2 x PhH), 127.2 (2 x PhH), 145.1 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 326 ( $\text{M}^+$ , 24), 128 (91), 86 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3062 w, 2966 s, 1460 vs, 1443 s, 748 vs.

***N,N*-Diethyl-*N*-[2-methyl-3-(10*H*-10-phenothiazinyl)propyl]amine (7b)** [1e]. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and diethylamine (**5b**) as a colourless oil in 45 % yield.

**4-[4-(10*H*-10-Phenothiazinyl)butyl]morpholine (6c)**. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and morpholine (**5c**) as a colourless oil in 44 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.60 (m, 2 H), 1.86 (m, 2 H), 2.32 (m, 6 H), 3.66 (m, 4 H), 3.86 (t, <sup>3</sup>J = 6.9 Hz, 2 H), 6.88 (m, 4 H), 7.12 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 23.4 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 46.8 (NCH<sub>2</sub>), 53.5 (2 x NCH<sub>2</sub>), 58.1 (NCH<sub>2</sub>), 66.9 (2 x OCH<sub>2</sub>), 115.4 (2 x PhH), 122.3 (2 x PhH), 125.0 (2 x SCq), 127.0 (2 x PhH), 127.3 (2 x PhH), 145.1 (2 x NCq). GC-MS (EI, 70 eV): m/z (%) = 340 (M<sup>+</sup>, 17), 142 (100), 100 (33). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3054 w, 2952 m, 1467 s, 744 m. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>OS (340.5): Calc. C, 70.6 %; H, 7.1 %; N, 8.2 %. Found C, 70.6 %; H, 7.3 %; N, 8.4 %.

**4-[2-methyl-3-(10*H*-10-Phenothiazinyl)propyl]morpholine (7c)**. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and morpholine (**5c**) as a colourless oil in 36 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.95 (d, <sup>3</sup>J = 6.2 Hz, 3 H), 2.19 (m, 2 H), 2.35 (m, 5 H), 3.54 (dd, <sup>2</sup>J = 13.3 Hz, <sup>3</sup>J = 7.7 Hz, 1 H), 3.68 (t, <sup>3</sup>J = 4.5 Hz, 4 H), 4.03 (dd, <sup>2</sup>J = 13.3 Hz, <sup>3</sup>J = 4.2 Hz, 1 H), 6.91 (m, 4 H), 7.12 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.2 (CH<sub>3</sub>), 28.3 (CH), 52.0 (NCH<sub>2</sub>), 54.4 (2 x NCH<sub>2</sub>), 63.6 (NCH<sub>2</sub>), 67.0 (2 x OCH<sub>2</sub>), 115.8 (2 x PhH), 122.3 (2 x PhH), 125.7 (2 x SCq), 127.0 (2 x PhH), 127.5 (2 x PhH), 145.7 (2 x NCq). GC-MS (EI, 70 eV): m/z (%) = 340 (M<sup>+</sup>, 29), 142 (15), 100 (100), 70 (10), 56 (15). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3052 vw, 2957 vs, 1484 s, 1471 vs, 1457 vs, 1344 s, 1321 s, 1286 s, 1253 vs, 1115 vs, 1034 s, 861 vs, 760 vs, 735 vs. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>OS (340.5): Calc. C, 70.6 %; H, 7.1 %; N, 8.2 %. Found C, 70.7 %; H, 6.6 %; N, 7.9 %.

**10-(4-Piperidinobutyl)-10*H*-phenothiazine (6d)**. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and piperidine (**5d**) as a colourless oil in 25 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.39 (m, 2 H), 1.52 (m, 4 H), 1.60 (m, 2 H), 1.79 (m, 2 H), 2.27 (m, 6 H), 3.84 (t, <sup>3</sup>J = 7.1 Hz, 2 H), 6.86 (m, 4 H), 7.09 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 24.1 (CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 24.6 (CH<sub>2</sub>), 25.9 (2 x CH<sub>2</sub>), 47.0 (NCH<sub>2</sub>), 54.4 (2 x NCH<sub>2</sub>), 58.5 (NCH<sub>2</sub>), 115.3 (2 x PhH), 122.2 (2 x PhH), 124.7 (2 x SCq), 127.0 (2 x PhH), 127.4 (2 x PhH), 145.1 (2 x NCq). GC-MS (EI, 70 eV): m/z (%) = 338 (M<sup>+</sup>, 12), 140 (100), 98 (47). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3061 vw, 2932 vs, 1460 vs, 1443 s, 748 s.

**10-(2-Methyl-3-piperidinopropyl)-10*H*-phenothiazine (7d)** [1e]. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and piperidine (**5d**) as a colourless oil in 70 % yield.

**10-[4-(1-Azepanyl)butyl]-10*H*-phenothiazine (6e)** [1c]. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and hexamethylenimine (**5e**) as a colourless oil in 9 % yield.

**10-[3-(1-Azepanyl)-2-methylpropyl]-10*H*-phenothiazine (7e)** [1c]. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and hexamethylenimine (**5e**) as a colourless oil in 83 % yield.

***N*-Methyl-*N*-[4-(10*H*-10-phenothiazinyl)butyl]-*N*-phenylamine (6f)**. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and *N*-methylaniline (**5f**) as a yellow oil in 92 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.57 (m, 2 H), 1.67 (m, 2 H), 2.71 (s, 3 H), 3.15 (t, <sup>3</sup>J = 7.3 Hz, 2 H), 3.73 (t, <sup>3</sup>J = 6.7 Hz, 2 H), 6.52 (m, 3 H), 6.77 (m, 4 H), 7.07 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 23.4 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 38.1 (NCH<sub>3</sub>), 46.8 (NCH<sub>2</sub>), 52.2 (NCH<sub>2</sub>), 112.2 (2 x PhH), 115.5 (2 x PhH), 115.9 (PhH), 122.4 (2 x PhH), 125.2 (2 x SCq), 127.2 (2 x PhH), 127.5 (2 x PhH), 129.1 (2 x PhH), 145.1 (2 x NCq), 149.2 (NCq). MS (EI, 70 eV): m/z (%) = 360 (M<sup>+</sup>, 31), 289 (26), 198 (100), 180 (10), 162 (53), 120 (93), 77 (14). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3060 w, 3024 w, 2926 m, 1506 vs, 1459 vs, 1443 s.

***N*-Benzyl-*N*-[4-(10*H*-10-phenothiazinyl)butyl]amine (6g)**. Obtained from 10-allyl-10*H*-phenothiazine (**4a**) and benzylamine (**5g**) as a yellow oil in 64 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.62 (m, 2 H), 1.82 (m, 2 H), 2.61 (t, <sup>3</sup>J = 7.0 Hz, 2 H), 3.71 (s, 2 H), 3.83 (t, <sup>3</sup>J = 7.0 Hz, 2 H), 6.88 (m, 5 H), 7.11 (m, 4 H), 7.25 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 24.5 (CH<sub>2</sub>), 27.2 (CH<sub>2</sub>), 47.0 (NCH<sub>2</sub>), 48.7 (NCH<sub>2</sub>), 53.8 (NCH<sub>2</sub>Ph), 115.4 (2 x PhH), 122.3 (2 x PhH), 122.3 (2 x SCq), 126.8 (PhH), 127.1 (2 x PhH), 127.3 (2 x PhH), 128.0 (2 x PhH), 128.3 (2 x PhH), 140.3 (Cq), 145.1 (2 x NCq). GC-MS (EI, 70 eV): m/z (%) = 360 (M<sup>+</sup>, 67), 257 (38), 212 (12), 199 (28), 180 (14), 162 (100), 120 (26), 106 (10), 91 (94), 70 (16). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3061 w, 3026 w, 2930 w, 1460 vs, 1456 vs, 1443 s, 748 s.

***N*-[4-(2-Ethyl-10*H*-10-phenothiazinyl)butyl]-*N,N*-dimethylamine (6h)**. Obtained from 10-allyl-2-ethyl-10*H*-phenothiazine (**4b**) and dimethylamine (**5a**) as a colourless oil in 29 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.21 (t, <sup>3</sup>J = 7.6 Hz, 3 H), 1.59 (m, 2 H), 1.83 (m, 2 H), 2.20 (s, 6 H), 2.26 (t, <sup>3</sup>J = 7.3 Hz, 2 H), 2.58 (q, <sup>3</sup>J = 7.6 Hz, 2 H), 3.88 (t, <sup>3</sup>J = 7.0 Hz, 2 H), 7.03 (m, 7 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 15.7 (CH<sub>3</sub>), 24.7 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 28.8 (PhCH<sub>2</sub>), 45.3 (2 x NCH<sub>3</sub>), 47.0 (NCH<sub>2</sub>), 59.1 (NCH<sub>2</sub>), 115.3 (PhH), 115.4 (PhH), 121.9 (PhH), 121.9 (SCq), 122.2 (PhH), 125.4 (SCq), 127.0 (PhH), 127.2 (PhH), 127.3 (PhH), 143.6 (Cq), 145.3 (NCq), 145.3 (NCq). GC-MS (EI, 70 eV): m/z (%) = 326 (M<sup>+</sup>, 19), 58 (100). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3063 m, 2940 m, 1460 s, 1443 s, 748 s.

***N*-[3-(2-Ethyl-10*H*-10-phenothiazinyl)-2-methylpropyl]-*N,N*-dimethylamine (7*h*)** [13]. Obtained from 10-allyl-2-ethyl-10*H*-phenothiazine (4*b*) and dimethylamine (5*a*) as a colourless oil in 68 % yield.

***N,N*-Diethyl-*N*-[3-methyl-4-(10*H*-10-phenothiazinyl)butyl]amine (6*i*)**. Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4*c*) and diethylamine (5*b*) as a colourless oil in 98 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.93 (t, <sup>3</sup>*J* = 7.1 Hz, 6 H), 0.97 (d, <sup>3</sup>*J* = 7.5 Hz, 3 H), 1.29 (m, 1 H), 1.71 (m, 1 H), 2.12 (m, 1 H), 2.45 (m, 6 H), 3.61 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 7.5 Hz, 1 H), 3.76 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 6.8 Hz, 1 H), 6.88 (m, 4 H), 7.12 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 11.6 (2 x CH<sub>3</sub>), 17.8 (CH<sub>3</sub>), 28.6 (CH), 31.4 (CH<sub>2</sub>), 46.5 (2 x NCH<sub>2</sub>), 50.2 (NCH<sub>2</sub>), 53.6 (NCH<sub>2</sub>), 115.9 (2 x PhH), 122.3 (2 x PhH), 125.8 (2 x SCq), 127.0 (2 x PhH), 127.4 (2 x PhH), 145.6 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 340 (M<sup>+</sup>, 13), 142 (44), 86 (100), 58 (11). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3064 w, 2966 vs, 2929 s, 1459 vs, 1444 vs, 1342 s, 1285 s, 1250 s, 750 vs. C<sub>21</sub>H<sub>28</sub>N<sub>2</sub>S (340.5): Calc. C, 74.1 %; H, 8.3 %; N, 8.2 %. Found C, 74.1 %; H, 8.2 %; N, 8.4 %.

***N,N*-Diisopropyl-*N*-[3-methyl-4-(10*H*-10-phenothiazinyl)butyl]amine (6*j*)**. Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4*c*) and diisopropylamine (5*h*) as a yellow oil in 25 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.90 (d, <sup>3</sup>*J* = 6.6 Hz, 6 H), 0.92 (d, <sup>3</sup>*J* = 6.6 Hz, 6 H), 0.97 (d, <sup>3</sup>*J* = 6.6 Hz, 3 H), 1.21 (m, 1 H), 1.69 (m, 1 H), 2.11 (m, 1 H), 2.42 (m, 2 H), 2.94 (septet, <sup>3</sup>*J* = 6.6 Hz, 2 H), 3.60 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 7.2 Hz, 1 H), 3.73 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 7.0 Hz, 1 H), 6.87 (m, 4 H), 7.12 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.7 (CH<sub>3</sub>), 20.1 (2 x CH<sub>3</sub>), 21.0 (2 x CH<sub>3</sub>), 28.2 (CH), 35.8 (CH<sub>2</sub>), 42.4 (NCH<sub>2</sub>), 47.9 (2 x NCH), 53.7 (NCH<sub>2</sub>), 115.8 (2 x PhH), 122.3 (2 x PhH), 125.7 (2 x SCq), 127.0 (2 x PhH), 127.4 (2 x PhH), 145.7 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 368 (M<sup>+</sup>, 21), 353 (13), 285 (4), 268 (15), 212 (21), 170 (21), 154 (13), 114 (100), 72 (23), 56 (17). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3064 w, 3031 vw, 2963 s, 1457 s, 750 s. C<sub>23</sub>H<sub>32</sub>N<sub>2</sub>S (368.6): Calc. C, 75.0 %; H, 8.8 %; N, 7.6 %. Found C, 75.3 %; H, 8.2 %; N, 7.6 %.

**4-[3-Methyl-4-(10*H*-10-phenothiazinyl)butyl]morpholine (6*k*)**. Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4*c*) and morpholine (5*e*) as a colourless oil in 100 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.97 (d, <sup>3</sup>*J* = 6.6 Hz, 3 H), 1.27 (m, 1 H), 1.80 (m, 1 H), 2.21 (m, 1 H), 2.32 (m, 6 H), 3.59 (m, 5 H), 3.77 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 7.5 Hz, 1 H), 6.87 (m, 4 H), 7.11 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.7 (CH<sub>3</sub>), 27.7 (CH), 30.7 (CH<sub>2</sub>), 53.5 (NCH<sub>2</sub>), 53.4 (2 x NCH<sub>2</sub>), 55.8 (NCH<sub>2</sub>), 66.8 (2 x OCH<sub>2</sub>), 115.8 (2 x PhH), 122.3 (2 x PhH), 125.6 (2 x SCq), 126.9 (2 x PhH), 127.4 (2 x PhH), 145.5 (2 x NCq). MS (EI, 70 eV): *m/z* (%) = 354 (M<sup>+</sup>, 17), 253 (34), 212 (18), 198 (34), 180 (17), 156 (100), 100 (87), 56 (14), 40 (11). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3062 m, 3004 w, 2955 vs, 1454 vs, 1120 vs, 750 vs, 728 s. C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>OS (354.5): Calc. C, 71.2 %; H, 7.4 %; N, 7.9 %. Found C, 70.9 %; H, 7.4 %; N, 7.5 %.

**10-(2-Methyl-4-pyrrolidin-1-yl-butyl)-10*H*-phenothiazine (6*l*)**. Obtained from 10-(2-methyl-allyl)-10*H*-phenothiazine (4*c*) and pyrrolidine (5*i*) as a colourless oil in 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.97 (d, <sup>3</sup>*J* = 6.8 Hz, 3 H), 1.36 (m, 1 H), 1.53 (m, 1 H), 1.72 (m, 4 H), 2.15 (m, 1 H), 2.44 (m, 6 H), 3.58 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 7.5 Hz, 1 H), 3.76 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 6.5 Hz, 1 H), 6.86 (m, 4 H), 7.10 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.8 (CH<sub>3</sub>), 23.2 (2 x CH<sub>2</sub>), 28.5 (CH), 33.5 (CH<sub>2</sub>), 53.5 (NCH<sub>2</sub>), 53.7 (NCH<sub>2</sub>), 53.9 (2 x NCH<sub>2</sub>), 115.8 (2 x PhH), 122.2 (2 x PhH), 125.6 (2 x SCq), 126.9 (2 x PhH), 127.3 (2 x PhH), 145.5 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 338 (M<sup>+</sup>, 8), 140 (100), 84 (85). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3062 w, 3030 w, 3003 w, 2960 s, 1486 s, 1456 vs, 1443 s, 1343 s, 1285 s, 1250 s, 749 s. C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>S (338.5): Calc. C, 74.5 %; H, 7.8 %; N, 8.3 %. Found C, 74.4 %; H, 7.7 %; N, 8.4 %.

**10-(2-Methyl-4-piperidinobutyl)-10*H*-phenothiazine (6*m*)**. Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4*c*) and piperidine (5*d*) as a colourless oil in 97 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.97 (d, <sup>3</sup>*J* = 6.8 Hz, 3 H), 1.37 (m, 3 H), 1.53 (m, 4 H), 1.72 (m, 1 H), 2.14 (m, 1 H), 2.33 (m, 6 H), 3.58 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 8.0 Hz, 1 H), 3.80 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 6.5 Hz, 1 H), 6.90 (m, 4 H), 7.18 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.9 (CH<sub>3</sub>), 24.5 (CH<sub>2</sub>), 26.0 (2 x CH<sub>2</sub>), 28.5 (CH), 31.6 (CH<sub>2</sub>), 53.5 (NCH<sub>2</sub>), 54.5 (2 x NCH<sub>2</sub>), 56.7 (NCH<sub>2</sub>), 115.9 (2 x PhH), 122.3 (2 x PhH), 125.7 (2 x SCq), 127.0 (2 x PhH), 127.5 (2 x PhH), 145.6 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 352 (M<sup>+</sup>, 11), 180 (11), 154 (89), 98 (100), 70 (11). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3063 w, 3032 vw, 3006 vw, 2932 s, 1463 s, 1456 s, 1444 s, 1050 s, 750 s. C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>S (352.5): Calc. C, 75.0 %; H, 8.0 %; N, 8.0 %. Found C, 74.9 %; H, 8.0 %; N, 7.7 %.

**10-[4-(1-Azepanyl)-2-methylbutyl]-10*H*-phenothiazine (6*n*)**. Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4*c*) and hexamethylenimine (5*e*) as a colourless oil in 92 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.95 (d, <sup>3</sup>*J* = 6.8 Hz, 3 H), 1.30 (m, 1 H), 1.53 (m, 8 H), 1.67 (m, 1 H), 2.15 (m, 1 H), 2.48 (m, 6 H), 3.57 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 8.0 Hz, 1 H), 3.77 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 6.5 Hz, 1 H), 6.87 (m, 4 H), 7.11 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.8 (CH<sub>3</sub>), 26.8 (2 x CH<sub>2</sub>), 28.1 (2 x CH<sub>2</sub>), 28.2 (CH), 32.2 (CH<sub>2</sub>), 53.5 (NCH<sub>2</sub>), 55.4 (2 x NCH<sub>2</sub>), 55.6 (NCH<sub>2</sub>), 115.84 (2 x PhH), 122.2 (2 x PhH), 125.6 (2 x SCq), 126.9 (2 x PhH), 127.4 (2 x PhH), 145.6 (2 x NCq). MS (EI, 70 eV): *m/z* (%) = 366 (M<sup>+</sup>, 1), 253 (24), 199 (33), 167 (37), 163 (16), 148 (60), 112 (60), 106 (13), 91 (100), 86 (13), 58 (13), 43 (12). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3062 w, 3031 vw, 3005 vw, 2924 s, 1460 s, 1456 s, 1443 s, 749 s. C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>S (366.6): Calc. C, 75.4 %; H, 8.3 %; N, 7.7 %. Found C, 75.2 %; H, 8.1 %; N, 7.9 %.



***N*-Methyl-*N*-[3-methyl-4-(10*H*-10-phenothiazinyl)butyl]-*N*-phenylamine (6o).** Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4c) and *N*-methylaniline (5f) as a yellow oil in 89 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.04 (d, <sup>3</sup>*J* = 6.8 Hz, 3 H), 1.40 (m, 1 H), 1.86 (m, 1 H), 2.11 (m, 1 H), 2.79 (s, 3 H), 3.30 (m, 2 H), 3.68 (m, 2 H), 6.60 (d, <sup>3</sup>*J* = 8.0 Hz, 2 H), 6.65 (t, <sup>3</sup>*J* = 7.2 Hz, 1 H), 6.82 (d, <sup>3</sup>*J* = 8.0 Hz, 2 H), 6.91 (t, <sup>3</sup>*J* = 7.5 Hz, 2 H), 7.16 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.8 (CH<sub>3</sub>), 28.2 (CH), 30.7 (CH<sub>2</sub>), 37.7 (NCH<sub>3</sub>), 50.1 (NCH<sub>2</sub>), 53.5 (NCH<sub>2</sub>), 112.2 (2 x PhH), 115.8 (2 x PhH), 115.9 (PhH), 122.5 (2 x PhH), 125.9 (2 x SCq), 127.1 (2 x PhH), 127.5 (2 x PhH), 129.0 (2 x PhH), 145.5 (2 x NCq), 149.2 (NCq). MS (EI, 70 eV): *m/z* (%) = 374 (M<sup>+</sup>, 71), 212 (42), 198 (23), 180 (19), 176 (100), 120 (78), 114 (17). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3090 w, 3060 m, 3024 m, 2959 s, 2926 s, 2867 s, 1599 vs, 1571 s, 1505 vs, 1485 s, 1454 vs, 1443 vs, 747 vs. HR-MS(C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>S): Calc. 374.1817. Found 374.1816.

***N*-Benzyl-*N*-[3-methyl-4-(10*H*-10-phenothiazinyl)butyl]amine (6p).** Obtained from 10-(2-methylallyl)-10*H*-phenothiazine (4c) and benzylamine (5g) as a colourless oil in 89 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.84 (d, <sup>3</sup>*J* = 6.6 Hz, 3 H), 1.24 (m, 1 H), 1.76 (m, 1 H), 2.07 (m, 1 H), 2.36 (m, 2 H), 3.41 (m, 2 H), 3.53 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 6.5 Hz, 1 H), 3.65 (dd, <sup>2</sup>*J* = 13.3 Hz, <sup>3</sup>*J* = 1.8 Hz, 1 H), 6.80 (d, <sup>3</sup>*J* = 8.1 Hz, 2 H), 6.87 (t, <sup>3</sup>*J* = 7.5 Hz, 2 H), 7.14 (m, 9 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.6 (CH<sub>3</sub>), 28.3 (CH), 31.1 (CH<sub>2</sub>), 50.7 (NCH<sub>2</sub>Ph), 53.6 (NCH<sub>2</sub>), 57.8 (NCH<sub>2</sub>), 115.9 (2 x PhH), 122.3 (2 x PhH), 125.6 (2 x SCq), 126.5 (PhH), 127.1 (2 x PhH), 127.5 (2 x PhH), 127.9 (2 x PhH), 129.0 (2 x PhH), 139.5 (Cq), 145.6 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 374 (M<sup>+</sup>, 100), 199 (57), 176 (100), 152 (32), 120 (14), 107 (14), 91 (50). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3308 w, 3062 s, 3027 s, 3005 s, 2953 s, 1495 s, 1488 s, 1471 s, 1464 s, 1456 s, 1373 s, 1328 s, 725 s.

**5-Allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a)** [47] was prepared from iminodibenzyl and allyl bromide according to a general literature procedure [42] in 68 % yield.

**5-(2-Methylallyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8b)** was prepared from iminodibenzyl and methallyl chloride according to a general literature procedure [42] in 62 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.65 (s, 3 H), 3.18 (s, 4 H), 4.30 (s, 2 H), 4.88 (s, 1 H), 5.02 (s, 1 H), 6.90 (m, 2 H), 7.03-7.20 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 20.5 (CH<sub>3</sub>), 32.4 (2 x CH<sub>2</sub>), 57.8 (NCH<sub>2</sub>), 114.0 (CH<sub>2</sub>), 120.1 (2 x PhH), 122.4 (2 x PhH), 126.1 (2 x PhH), 129.7 (2 x PhH), 133.8 (Cq), 141.9 (2 x Cq), 148.1 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 249 (M<sup>+</sup>, 48), 194 (100), 180 (22), 89 (13), 63 (16). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3101 w, 3068 w, 3024 w, 1495 s, 1486 vs, 772 vs, 750 vs. C<sub>18</sub>H<sub>19</sub>N (249.4): Calc. C, 86.7 %; H, 7.7 %; N, 5.6 %. Found C, 86.6 %; H, 7.8 %; N, 5.5 %.

***N*-[4-(10,11-Dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)butyl]-*N,N*-dimethylamine (9a)** [15b,c]. Obtained from 5-allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a) and dimethylamine (5a) as a colourless oil in 72 % yield.

***N*-[3-(10,11-Dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)-2-methylpropyl]-*N,N*-dimethylamine (10a)** [16-29]. Obtained from 5-allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a) and dimethylamine (5a) as a colourless oil in 19 % yield.

**4-[4-(10,11-Dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)butyl]morpholine (9b).** Obtained from 5-allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a) and morpholine (5c) as a colourless oil in 79 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.48 (m, 2 H), 1.56 (m, 2 H), 2.23 (t, <sup>3</sup>*J* = 7.0 Hz, 2 H), 2.29 (m, 4 H), 3.14 (s, 4 H), 3.62 (m, 4 H), 3.71 (m, 2 H), 6.89 (m, 2 H), 7.06 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 23.8 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 32.1 (2 x CH<sub>2</sub>), 50.3 (NCH<sub>2</sub>), 53.5 (2 x NCH<sub>2</sub>), 58.4 (NCH<sub>2</sub>), 66.8 (2 x OCH<sub>2</sub>), 119.8 (2 x PhH), 122.2 (2 x PhH), 126.2 (2 x PhH), 129.7 (2 x PhH), 134.1 (2 x Cq), 148.2 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 336 (M<sup>+</sup>, 16), 208 (19), 194 (16), 142 (100), 100 (47). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3026 w, 3021 w, 2944 s, 1456 s, 1447 s, 1117 s, 910 s, 763 s, 733 s.

**5-(4-Piperidinobutyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (9c).** Obtained from 5-allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a) and piperidine (5d) as a colourless oil in 45 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.33 (m, 2 H), 1.46 (m, 8 H), 2.13 (t, <sup>3</sup>*J* = 7.3 Hz, 2 H), 2.20 (m, 4 H), 3.07 (s, 4 H), 3.64 (t, <sup>3</sup>*J* = 6.6 Hz, 2 H), 6.81 (m, 2 H), 7.00 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 24.43 (CH<sub>2</sub>), 24.44 (CH<sub>2</sub>), 25.9 (2 x CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 32.2 (2 x CH<sub>2</sub>), 50.6 (NCH<sub>2</sub>), 54.4 (2 x NCH<sub>2</sub>), 59.1 (NCH<sub>2</sub>), 119.9 (2 x PhH), 122.2 (2 x PhH), 126.2 (2 x PhH), 129.7 (2 x PhH), 134.1 (2 x Cq), 148.3 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 334 (M<sup>+</sup>, 14), 140 (84), 98 (100), 85 (11), 70 (17), 55 (13). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3063 w, 3022 w, 2932 s, 1487 s.

**5-(2-Methyl-3-piperidinopropyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (10c)** [15i]. Obtained from 5-allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a) and piperidine (5d) as a colourless oil in 41 % yield.

**5-[4-(1-Azepanyl)butyl]-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (9d).** Obtained from 5-allyl-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8a) and hexamethylenimine (5e) as a colourless oil in 48 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 1.49 (m, 12 H), 2.38 (t, <sup>3</sup>*J* = 7.2 Hz, 2 H), 2.53 (m, 4 H), 3.15 (s, 4 H), 3.73 (t, <sup>3</sup>*J* = 6.7 Hz, 2 H), 6.89 (m, 2 H), 7.08 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 25.1 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 26.9 (2 x CH<sub>2</sub>), 27.9 (2 x CH<sub>2</sub>), 32.2 (2 x CH<sub>2</sub>), 50.6 (NCH<sub>2</sub>), 55.4 (2 x NCH<sub>2</sub>), 57.8 (NCH<sub>2</sub>), 120.0 (2 x PhH), 122.2 (2 x PhH), 126.2 (2 x PhH), 129.7 (2 x PhH), 134.2 (2 x Cq), 148.4 (2 x NCq). GC-MS (EI, 70 eV): *m/z* (%) = 348 (M<sup>+</sup>, 14), 154 (54), 112 (100), 58 (34). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3061 w, 3023 w, 2923 s, 1487 s. C<sub>24</sub>H<sub>32</sub>N<sub>2</sub> (348.5): Calc. C, 82.7 %; H, 9.3 %; N, 8.0 %. Found C, 82.2 %; H, 9.1 %; N, 8.1 %.

**5-[3-(1-Azepanyl)-2-methylpropyl]-10,11-dihydro-5H-dibenzo[b,f]azepine (10d).** Obtained from 5-allyl-10,11-dihydro-5H-dibenzo[b,f]azepine (**8a**) and hexamethylenimine (**5e**) as a colourless oil in 48 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.88 (d,  $^3J = 6.8$  Hz, 3 H), 1.59 (br s, 8 H), 1.90 (m, 1 H), 2.23 (dd,  $^2J = 12.6$  Hz,  $^3J = 6.3$  Hz, 1 H), 2.37 (dd,  $^2J = 12.6$  Hz,  $^3J = 7.8$  Hz, 1 H), 2.54 (m, 4 H), 3.18 (m, 5 H, 2 x  $\text{CH}_2$ ), 4.06 (dd,  $^2J = 12.7$  Hz,  $^3J = 4.7$  Hz, 1 H), 6.89 (m, 2 H), 7.14 (m, 6 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 17.6 ( $\text{CH}_3$ ), 27.1 (2 x  $\text{CH}_2$ ), 28.4 (2 x  $\text{CH}_2$ ), 29.9 (CH), 32.3 (2 x  $\text{CH}_2$ ), 56.2 ( $\text{NCH}_2$ ), 56.4 (2 x  $\text{NCH}_2$ ), 63.5 ( $\text{NCH}_2$ ), 120.1 (2 x PhH), 122.1 (2 x PhH), 126.2 (2 x PhH), 129.7 (2 x PhH), 134.0 (2 x Cq), 148.7 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 348 ( $\text{M}^+$ , 13), 249 (30), 234 (11), 153 (20), 112 (100), 58 (75). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3062 w, 3022 w, 2922 s, 1487 s.  $\text{C}_{24}\text{H}_{32}\text{N}_2$  (348.5): Calc. C, 82.7 %; H, 9.3 %; N, 8.0 %. Found C, 82.7 %; H, 9.3 %; N, 8.3 %.

**N-[4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)butyl]-N-methyl-N-phenylamine (9e).** Obtained from 5-allyl-10,11-dihydro-5H-dibenzo[b,f]azepine (**8a**) and *N*-methylaniline (**5f**) as a colourless oil in 90 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.57 (m, 4 H), 2.80 (s, 3 H), 3.10 (t,  $^3J = 6.4$  Hz, 2 H), 3.11 (s, 4 H), 3.73 (t,  $^3J = 6.0$  Hz, 2 H), 6.60 (m, 3 H), 6.90 (m, 2 H), 7.09 (m, 8 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 24.1 ( $\text{CH}_2$ ), 25.4 ( $\text{CH}_2$ ), 32.2 (2 x  $\text{CH}_2$ ), 38.1 ( $\text{NCH}_3$ ), 50.3 ( $\text{NCH}_2$ ), 52.4 ( $\text{NCH}_2$ ), 112.1 (2 x PhH), 115.9 (PhH), 119.9 (2 x PhH), 122.3 (2 x PhH), 126.3 (2 x PhH), 129.0 (2 x PhH), 129.8 (2 x PhH), 134.2 (2 x Cq), 148.2 (2 x NCq), 149.2 (NCq). MS (EI, 70 eV):  $m/z$  (%) = 356 ( $\text{M}^+$ , 5), 249 (59), 234 (24), 220 (10), 195 (100), 180 (28), 158 (14), 120 (36), 97 (20). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3061 w, 3024 w, 2919 m, 1599 s, 1506 s, 1487 s, 748 s, 733 s.  $\text{C}_{25}\text{H}_{28}\text{N}_2$  (356.5): Calc. C, 84.2 %; H, 7.9 %; N, 7.8 %. Found C, 84.4 %; H, 7.7 %; N, 7.5 %.

**N-[4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)butyl]-N-phenylamine (9f).** Obtained from 5-allyl-10,11-dihydro-5H-dibenzo[b,f]azepine (**8a**) and benzylamine (**5g**) as a colourless oil in 93 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.55 (m, 4 H), 2.55 (t,  $^3J = 6.7$  Hz, 2 H), 3.14 (s, 4 H), 3.69 (br s, 4 H), 6.89 (m, 2 H), 7.09 (m, 6 H), 7.25 (m, 5 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 25.7 ( $\text{CH}_2$ ), 27.5 ( $\text{CH}_2$ ), 32.2 (2 x  $\text{CH}_2$ ), 49.0 ( $\text{NCH}_2$ ), 50.5 ( $\text{NCH}_2$ ), 53.8 ( $\text{NCH}_2$ ), 119.9 (2 x PhH), 122.3 (2 x PhH), 126.3 (2 x PhH), 126.8 (PhH), 128.0 (2 x PhH), 128.3 (2 x PhH), 129.7 (2 x PhH), 134.2 (2 x Cq), 140.4 (Cq), 148.3 (2 x NCq). MS (EI, 70 eV):  $m/z$  (%) = 356 ( $\text{M}^+$ , 64), 248 (15), 220 (17), 208 (100), 193 (50), 162 (65), 133 (12), 120 (19), 106 (10), 91 (83), 70 (34). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3061 w, 3025 w, 2918 s, 1487 vs, 1471 s, 1456 s, 1447 s, 1436 s, 763 s, 741 s, 698 s, 620 s.  $\text{C}_{25}\text{H}_{28}\text{N}_2$  (356.5): Calc. C, 84.2 %; H, 7.9 %; N, 7.9 %. Found C, 83.9 %; H, 8.1 %; N, 7.5 %.

**N-[4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)-3-methylbutyl]-N,N-diethylamine (9g).** Obtained from 5-(2-methylallyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (**8b**) and diethylamine (**5b**) as a colourless oil in 93 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.91 (d,  $^3J = 6.6$  Hz, 3 H), 0.96 (t,  $^3J = 7.1$  Hz, 6 H), 1.22 (m, 1 H), 1.61 (m, 1 H), 1.77 (m, 1 H), 2.41 (m, 6 H), 3.17 (s, 4 H), 3.41 (dd,  $^2J = 12.6$  Hz,  $^3J = 7.8$  Hz, 1 H), 3.64 (dd,  $^2J = 12.6$  Hz,  $^3J = 6.4$  Hz, 1 H), 6.88 (m, 2 H), 7.08 (m, 6 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 11.6 (2 x  $\text{CH}_3$ ), 18.2 ( $\text{CH}_3$ ), 29.3 (CH), 31.6 ( $\text{CH}_2$ ), 32.3 (2 x  $\text{CH}_2$ ), 46.6 (2 x  $\text{NCH}_2$ ), 50.3 ( $\text{NCH}_2$ ), 57.5 ( $\text{NCH}_2$ ), 119.8 (2 x PhH), 122.2 (2 x PhH), 126.2 (2 x PhH), 129.7 (2 x PhH), 134.0 (2 x Cq), 148.5 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 336 ( $\text{M}^+$ , 24), 208 (18), 142 (24), 86 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3062 w, 3021 w, 2966 s, 2923 s, 1488 s, 1468 s, 763 s, 743 s.

**4-[4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)-3-methylbutyl]morpholine (9h).** Obtained from 5-(2-methylallyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (**8b**) and morpholine (**5c**) as a colourless oil in 94 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.91 (d,  $^3J = 6.5$  Hz, 3 H), 1.23 (m, 1 H), 1.68 (m, 1 H), 1.87 (m, 1 H), 2.28 (m, 6 H), 3.15 (s, 4 H), 3.42 (dd,  $^2J = 12.8$  Hz,  $^3J = 7.5$  Hz, 1 H), 3.62 (m, 5 H), 6.87 (m, 2 H), 7.07 (m, 6 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 18.1 ( $\text{CH}_3$ ), 28.6 (CH), 31.2 ( $\text{CH}_2$ ), 32.1 (2 x  $\text{CH}_2$ ), 53.5 (2 x  $\text{NCH}_2$ ), 56.2 ( $\text{NCH}_2$ ), 57.2 ( $\text{NCH}_2$ ), 66.8 (2 x  $\text{OCH}_2$ ), 119.7 (2 x PhH), 122.2 (2 x PhH), 126.1 (2 x PhH), 129.7 (2 x PhH), 133.8 (2 x Cq), 148.3 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 350 ( $\text{M}^+$ , 52), 208 (100), 194 (16), 100 (55), 70 (16), 56 (26). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3062 w, 3020 w, 2952 s, 2919 s, 2852 s, 1486 s, 1468 s, 1118 s, 764 s, 751 m.  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}$  (350.5): Calc. C, 78.8 %; H, 8.6 %; N, 8.0 %. Found C, 79.0 %; H, 8.7 %; N, 8.2 %.

**5-[4-(1-Azepanyl)-2-methylbutyl]-10,11-dihydro-5H-dibenzo[b,f]azepine (9i).** Obtained from 5-(2-methylallyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (**8b**) and hexamethylenimine (**5e**) as a colourless oil in 86 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.90 (d,  $^3J = 6.8$  Hz, 3 H), 1.25 (m, 1 H), 1.56 (m, 8 H), 1.66 (m, 1 H), 1.81 (m, 1 H), 2.43 (m, 2 H), 2.54 (m, 4 H), 3.18 (s, 4 H), 3.36 (dd,  $^2J = 12.6$  Hz,  $^3J = 8.0$  Hz, 1 H), 3.71 (dd,  $^2J = 12.6$  Hz,  $^3J = 6.0$  Hz, 1 H), 6.89 (m, 2 H), 7.14 (m, 6 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 18.3 ( $\text{CH}_3$ ), 26.9 (2 x  $\text{CH}_2$ ), 28.1 (2 x  $\text{CH}_2$ ), 29.2 (CH), 32.2 (2 x  $\text{CH}_2$ ), 32.6 ( $\text{CH}_2$ ), 55.5 (2 x  $\text{NCH}_2$ ), 56.0 ( $\text{NCH}_2$ ), 57.5 ( $\text{NCH}_2$ ), 119.9 (2 x PhH), 122.2 (2 x PhH), 126.2 (2 x PhH), 129.8 (2 x PhH), 134.0 (2 x Cq), 148.6 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 362 ( $\text{M}^+$ , 26), 208 (23), 168 (35), 112 (35), 58 (48). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3063 w, 3021 w, 2921 s, 1489 s, 1487 s, 1456 s.  $\text{C}_{25}\text{H}_{34}\text{N}_2$  (362.6): Calc. C, 82.8 %; H, 9.5 %; N, 7.7 %. Found C, 83.0 %; H, 9.3 %; N, 8.2 %.

**N-[4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)-3-methylbutyl]-N-methyl-N-phenylamine (9j).** Obtained from 5-(2-methylallyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (**8b**) and *N*-methylaniline (**5f**) as a yellow oil in 93 % yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.96 (d,  $^3J = 6.6$  Hz, 3 H), 1.28 (m, 1 H), 1.81 (m, 2 H), 2.78 (s, 3 H), 3.09 (s, 4 H), 3.18 (dd,  $^2J = 10.0$  Hz,  $^3J = 5.5$  Hz, 1 H), 3.34 (dd,  $^2J = 10.0$  Hz,  $^3J = 4.9$  Hz, 1 H), 3.52 (m, 2 H), 6.74 (m, 3 H), 7.10 (m, 10 H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 20 °C):

$\delta$  [ppm] = 18.1 (CH<sub>3</sub>), 29.0 (CH), 31.0 (CH<sub>2</sub>), 32.1 (2 x CH<sub>2</sub>), 38.0 (NCH<sub>3</sub>), 50.4 (NCH<sub>2</sub>), 57.3 (NCH<sub>2</sub>), 112.2 (2 x PhH), 115.9 (PhH), 119.7 (2 x PhH), 122.3 (2 x PhH), 126.2 (2 x PhH), 129.1 (2 x PhH), 129.9 (2 x PhH), 134.1 (2 x Cq), 148.3 (2 x NCq), 149.0 (NCq). MS (EI, 70 eV):  $m/z$  (%) = 370 (M<sup>+</sup>, 36), 208 (100), 193 (23), 120 (24). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3091 w, 3060 w, 3024 w, 2951 s, 1495 s, 1489 s, 1456 s, 762 s, 746 s. C<sub>26</sub>H<sub>30</sub>N<sub>2</sub> (370.5): Calc. C, 84.3 %; H, 8.2 %; N, 7.6 %. Found C, 84.6 %; H, 8.1 %; N, 7.9 %.

***N*-Benzyl-*N*-[4-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)-3-methylbutyl]amine (9k).** Obtained from 5-(2-methylallyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (8b) and benzylamine (5g) as a yellow oil in 75 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 0.90 (d, <sup>3</sup>*J* = 6.6 Hz, 3 H), 1.27 (m, 1 H), 1.70 (m, 1 H), 1.85 (m, 1 H), 2.62 (m, 2 H), 3.16 (s, 4 H), 3.39 (dd, <sup>2</sup>*J* = 12.6 Hz, <sup>3</sup>*J* = 7.9 Hz, 1 H), 3.67 (dd, <sup>2</sup>*J* = 12.6 Hz, <sup>3</sup>*J* = 6.2 Hz, 1 H), 3.71 (s, 2 H), 6.89 (m, 2 H), 7.08 (m, 6 H), 7.24 (m, 5 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 18.2 (CH<sub>3</sub>), 28.8 (CH), 32.1 (2 x CH<sub>2</sub>), 34.9 (CH<sub>2</sub>), 46.9 (NCH<sub>2</sub>), 53.8 (NCH<sub>2</sub>), 57.4 (NCH<sub>2</sub>), 119.7 (2 x PhH), 122.2 (2 x PhH), 126.1 (2 x PhH), 126.7 (PhH), 127.9 (2 x PhH), 128.2 (2 x PhH), 129.7 (2 x PhH), 133.9 (2 x Cq), 140.3 (Cq), 148.4 (2 x NCq). MS (EI, 70 eV):  $m/z$  (%) = 370 (M<sup>+</sup>, 27), 208 (100), 194 (24), 176 (10), 91 (33). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3062 m, 3025 m, 2949 s, 1495 s, 1489 s, 1475 s, 1471 s, 1468 s, 1464 s, 1456 s, 1447 s, 1438 s, 1110 s, 762 s, 742 s, 698 s. C<sub>26</sub>H<sub>30</sub>N<sub>2</sub> (370.5): Calc. C, 84.3 %; H, 8.2 %; N, 7.6 %. Found C, 84.1 %; H, 8.3 %; N, 7.8 %.

**9-Allyl-9*H*-carbazole (11a)** [42,48-50] was prepared from carbazole and allyl bromide according to a general literature procedure [42] in 73 % yield.

**9-(2-Methylallyl)-9*H*-carbazole (11b)** [42,52] was prepared from carbazole and methallyl chloride according to a general literature procedure in 65 % yield.

***N*-[4-(9*H*-9-Carbazolyl)butyl]-*N,N*-diethylamine (12a).** Obtained from 9-allyl-9*H*-carbazole (11a) and diethylamine (5b) as a colourless oil in 29 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 0.96 (t, <sup>3</sup>*J* = 7.1 Hz, 6 H), 1.52 (m, 2 H), 1.84 (m, 2 H), 2.38 (t, <sup>3</sup>*J* = 7.5 Hz, 2 H), 2.44 (q, <sup>3</sup>*J* = 7.1 Hz, 4 H), 4.27 (t, <sup>3</sup>*J* = 7.3 Hz, 2 H), 7.12 (m, 2 H), 7.20 (t, <sup>3</sup>*J* = 6.8 Hz, 2 H), 7.43 (m, 2 H), 8.07 (d, <sup>2</sup>*J* = 7.8 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 12.1 (2 x CH<sub>3</sub>), 25.5 (CH<sub>2</sub>), 27.5 (CH<sub>2</sub>), 43.4 (NCH<sub>2</sub>), 47.2 (2 x NCH<sub>2</sub>), 53.1 (NCH<sub>2</sub>), 109.1 (2 x PhH), 119.2 (2 x PhH), 120.8 (2 x PhH), 123.3 (2 x Cq), 126.0 (2 x PhH), 140.8 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 295 (M<sup>+</sup>, 15), 86 (100). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3051 m, 2967 vs, 1484 vs, 1464 vs, 1453 vs, 750 vs, 724 vs.

***N*-[3-(9*H*-9-Carbazolyl)-2-methylpropyl]-*N,N*-diethylamine (13a).** Obtained from 9-allyl-9*H*-carbazole (11a) and diethylamine (5b) as a colourless oil in 41 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 0.83 (d, <sup>3</sup>*J* = 6.0 Hz, 3 H), 1.04 (t, <sup>3</sup>*J* = 7.0 Hz, 6 H), 2.31 (m, 3 H), 2.52 (m, 4 H), 3.90 (dd, <sup>2</sup>*J* = 14.6 Hz, <sup>3</sup>*J* = 9.0 Hz, 1 H), 4.51 (dd, <sup>2</sup>*J* = 14.6 Hz, <sup>3</sup>*J* = 3.5 Hz, 1 H), 7.20 (m, 2 H), 7.42 (d, <sup>3</sup>*J* = 3.8 Hz, 4 H), 8.07 (d, <sup>3</sup>*J* = 7.8 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 12.0 (2 x CH<sub>3</sub>), 17.6 (CH<sub>3</sub>), 32.9 (CH), 47.6 (2 x NCH<sub>2</sub>), 48.0 (NCH<sub>2</sub>), 58.5 (NCH<sub>2</sub>), 109.0 (2 x PhH), 118.6 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.4 (2 x PhH), 140.9 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 295 (M<sup>+</sup>+1, 7), 86 (100). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3053 w, 3022 w, 2931 s, 1484 s, 1453 s, 749 s.

**4-[4-(9*H*-9-Carbazolyl)butyl]morpholine (12b).** Obtained from 9-allyl-9*H*-carbazole (11a) and morpholine (5c) as a colourless oil in 31 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 1.48 (quintet, *J* = 7.3 Hz, 2 H), 1.84 (quintet, *J* = 7.3 Hz, 2 H), 2.26 (m, 6 H), 3.62 (t, <sup>3</sup>*J* = 4.6 Hz, 4 H), 4.23 (t, <sup>3</sup>*J* = 7.3 Hz, 2 H), 7.21 (m, 2 H), 7.39 (m, 4 H), 8.06 (d, <sup>3</sup>*J* = 7.8 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 24.0 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 42.6 (NCH<sub>2</sub>), 53.5 (2 x NCH<sub>2</sub>), 58.2 (NCH<sub>2</sub>), 66.8 (2 x OCH<sub>2</sub>), 108.5 (2 x PhH), 118.6 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.4 (2 x PhH), 140.2 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 308 (M<sup>+</sup>, 14), 142 (17), 100 (100), 56 (12). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3051 w, 3039 w, 2958 m, 1484 s, 1451 s, 1118 vs, 1000 s, 747 vs, 720 vs. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O (308.4): Calc. C, 77.9 %; H, 7.9 %; N, 9.1 %. Found C, 77.4 %; H, 7.7 %; N, 9.0 %.

**4-[3-(9*H*-9-Carbazolyl)-2-methylpropyl]morpholine (13b).** Obtained from 9-allyl-9*H*-carbazole (11a) and morpholine (5c) as a colourless oil in 61 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 0.89 (d, <sup>3</sup>*J* = 6.5 Hz, 3 H), 2.19-2.45 (m, 7 H), 3.65 (m, 4 H), 4.03 (dd, <sup>2</sup>*J* = 14.8 Hz, <sup>3</sup>*J* = 8.3 Hz, 1 H), 4.43 (dd, <sup>2</sup>*J* = 14.8 Hz, <sup>3</sup>*J* = 4.8 Hz, 1 H), 7.21 (m, 2 H), 7.43 (m, 4 H), 8.08 (d, <sup>3</sup>*J* = 7.8 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 17.5 (CH<sub>3</sub>), 31.1 (CH), 47.7 (NCH<sub>2</sub>), 54.2 (2 x NCH<sub>2</sub>), 63.8 (NCH<sub>2</sub>), 66.9 (2 x OCH<sub>2</sub>), 108.9 (2 x PhH), 118.7 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.4 (2 x PhH), 140.9 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 308 (M<sup>+</sup>, 13), 100 (100), 56 (10). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3046 w, 2957 m, 1461 s, 1455 s, 1119 vs, 750 vs. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O (308.4): Calc. C, 77.9 %; H, 7.9 %; N, 9.1 %. Found C, 77.8 %; H, 8.0 %; N, 9.0 %.

**9-[4-(1-Azepanyl)butyl]-9*H*-carbazole (12c).** Obtained from 9-allyl-9*H*-carbazole (11a) and hexamethylenimine (5e) as a colourless oil in 31 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 1.45 (m, 10 H), 1.77 (quintet, *J* = 7.5 Hz, 2 H), 2.35 (t, <sup>3</sup>*J* = 7.3 Hz, 2 H), 2.45 (m, 4 H), 4.19 (t, <sup>3</sup>*J* = 7.3 Hz, 2 H), 7.12 (m, 2 H), 7.33 (m, 4 H), 7.99 (d, <sup>3</sup>*J* = 7.7 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  [ppm] = 25.3 (CH<sub>2</sub>), 26.8 (CH<sub>2</sub>), 26.9 (2 x CH<sub>2</sub>), 28.0 (2 x CH<sub>2</sub>), 42.9 (NCH<sub>2</sub>), 55.5 (2 x NCH<sub>2</sub>), 57.7 (NCH<sub>2</sub>), 108.6 (2 x PhH), 118.6 (2 x PhH), 120.3 (2 x PhH), 122.8 (2 x Cq), 125.5 (2 x PhH), 140.3 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 321

( $M^+ + 1$ , 21), 112 (100), 58 (33). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3050 vw, 2921 s, 1466 s, 1452 s, 751 vs.,  $\text{C}_{22}\text{H}_{28}\text{N}_2$  (320.5): Calc. C, 82.4 %; H, 8.8 %; N, 8.8 %. Found C, 82.1 %; H, 8.8 %; N, 8.6 %.

**9-[3-(1-Azepanyl)-2-methylpropyl]-9H-carbazole (13c).** Obtained from 9-allyl-9H-carbazole (**11a**) and hexamethylenimine (**5e**) as a colourless oil in 60 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.81 (d,  $^3J = 6.5$  Hz, 3 H), 1.63 (m, 8 H), 2.29 (m, 1 H), 2.37 (m, 2 H), 2.62 (m, 4 H), 3.96 (dd,  $^2J = 14.7$  Hz,  $^3J = 9.0$  Hz, 1 H), 4.50 (dd,  $^2J = 14.7$  Hz,  $^3J = 4.3$  Hz, 1 H), 7.20 (m, 2 H), 7.42 (m, 4 H), 8.07 (d,  $^3J = 7.8$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 17.4 ( $\text{CH}_3$ ), 26.7 (2 x  $\text{CH}_2$ ), 28.6 (2 x  $\text{CH}_2$ ), 33.0 (CH), 47.8 ( $\text{NCH}_2$ ), 56.4 (2 x  $\text{NCH}_2$ ), 63.6 ( $\text{NCH}_2$ ), 109.1 (2 x PhH), 118.5 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.4 (2 x PhH), 141.0 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 321 ( $M^+ + 1$ , 15), 112 (100), 58 (25). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3052 w, 3022 vw, 2925 s, 1484 s, 1464 s, 1452 s, 1325 s, 749 vs, 723 s.  $\text{C}_{22}\text{H}_{28}\text{N}_2$  (320.5): Calc. C, 82.4 %; H, 8.8 %; N, 8.8 %. Found C, 82.4 %; H, 8.8 %; N, 8.9 %.

**N-[4-(9H-9-Carbazolyl)butyl]-N-methyl-N-phenylamine (12d) and N-[3-(9H-9-carbazolyl)-2-methylpropyl]-N-methyl-N-phenylamine (13d).** Obtained from 9-allyl-9H-carbazole (**11a**) and *N*-methylamine (**5f**) as a yellow oil in 69 % yield (*n*-*iso*-ratio = 1.3/1).

**N-[4-(9H-9-Carbazolyl)butyl]-N-methyl-N-phenylamine (12d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.60 (m, 2 H), 1.84 (m, 2 H), 2.76 (s, 3 H), 3.20 (t,  $^3J = 5.6$  Hz, 2 H), 4.22 (t,  $^3J = 6.1$  Hz, 2 H), 6.60 (m, 2 H), 7.20 (m, 9 H), 8.07 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 24.7 ( $\text{CH}_2$ ), 26.9 ( $\text{CH}_2$ ), 38.1 ( $\text{NCH}_3$ ), 47.2 ( $\text{NCH}_2$ ), 57.6 ( $\text{NCH}_2$ ), 108.5 (2 x PhH), 112.1 (2 x PhH), 116.1 (PhH), 118.8 (2 x PhH), 120.3 (2 x PhH), 122.8 (2 x Cq), 125.6 (2 x PhH), 129.1 (2 x PhH), 140.2 (2 x NCq), 149.2 (NCq).

**N-[3-(9H-9-Carbazolyl)-2-methylpropyl]-N-methyl-N-phenylamine (13d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.90 (d,  $^3J = 6.4$  Hz, 3 H), 2.68 (m, 1 H), 2.92 (s, 3 H), 3.17 (m, 1 H), 3.25 (dd,  $^2J = 14.5$  Hz,  $^3J = 7.3$  Hz, 1 H), 4.02 (dd,  $^2J = 14.5$  Hz,  $^3J = 9.0$  Hz, 1 H), 4.26 (m, 1 H), 6.62 (m, 2 H), 7.20 (m, 9 H), 8.07 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 16.9 ( $\text{CH}_3$ ), 33.1 (CH), 39.1 ( $\text{NCH}_3$ ), 42.8 ( $\text{NCH}_2$ ), 52.3 ( $\text{NCH}$ ), 108.8 (2 x PhH), 112.2 (2 x PhH), 116.4 (PhH), 118.8 (2 x PhH), 120.3 (2 x PhH), 122.7 (2 x Cq), 125.6 (2 x PhH), 129.1 (2 x PhH), 140.6 (2 x NCq), 149.3 (NCq).

MS (EI, 70 eV, **12d/13d**):  $m/z$  (%) = 328 ( $M^+$ , 10), 295 (10), 207 (26), 180 (25), 152 (79), 120 (100), 106 (11), 98 (15), 86 (55), 73 (10), 69 (15), 56 (50), 41 (31). IR (NaCl/film, **12d/13d**):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3053 s, 3023 m, 2928 vs, 1484 vs, 1463 vs, 1452 vs, 749 vs.

**N-Benzyl-N-[4-(9H-9-carbazolyl)butyl]amine (12e).** Obtained from 9-allyl-9H-carbazole (**11a**) and benzylamine (**5g**) as a yellow oil in 30 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.39 (m, 2 H), 1.74 (m, 2 H), 2.43 (t,  $^3J = 7.0$  Hz, 2 H), 3.55 (s, 2 H), 4.11 (t,  $^3J = 7.0$  Hz, 2 H), 7.20 (m, 11 H), 7.96 (d,  $^3J = 7.8$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 26.6 ( $\text{CH}_2$ ), 27.6 ( $\text{CH}_2$ ), 42.7 ( $\text{NCH}_2$ ), 48.4 ( $\text{NCH}_2$ ), 53.9 ( $\text{NCH}_2\text{Ph}$ ), 108.5 (2 x PhH), 118.7 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.5 (2 x PhH), 126.8 (PhH), 128.0 (2 x PhH), 128.2 (2 x PhH), 140.2 (3 x NCq). MS (EI, 70 eV):  $m/z$  (%) = 328 ( $M^+$ , 53), 257 (26), 237 (42), 220 (14), 194 (11), 180 (65), 167 (14), 152 (12), 120 (68), 106 (73), 91 (100), 70 (34), 58 (18). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3052 w, 3025 w, 2931 s, 1484 s, 1463 s, 1452 s, 750 vs, 724 vs.

**N-Benzyl-N-[3-(9H-9-carbazolyl)-2-methylpropyl]amine (13e).** Obtained from 9-allyl-9H-carbazole (**11a**) and benzylamine (**5g**) as a yellow oil in 58 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.92 (d,  $^3J = 6.8$  Hz, 3 H), 2.33 (m, 1 H), 2.51 (dd,  $^2J = 11.8$  Hz,  $^3J = 5.8$  Hz, 1 H), 2.58 (dd,  $^2J = 11.8$  Hz,  $^3J = 6.6$  Hz, 1 H), 3.68 (s, 2 H), 4.03 (dd,  $^2J = 14.7$  Hz,  $^3J = 7.6$  Hz, 1 H), 4.38 (dd,  $^2J = 14.7$  Hz,  $^3J = 6.6$  Hz, 1 H), 7.26 (m, 7 H), 7.42 (d,  $^3J = 4.2$  Hz, 4 H), 8.07 (d,  $^3J = 7.7$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 16.8 ( $\text{CH}_3$ ), 34.3 (CH), 47.3 ( $\text{NCH}_2$ ), 53.3 ( $\text{NCH}_2$ ), 54.2 ( $\text{NCH}_2\text{Ph}$ ), 109.0 (2 x PhH), 118.7 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.5 (2 x PhH), 126.9 (PhH), 128.0 (2 x PhH), 128.3 (2 x PhH), 140.4 (Cq), 140.8 (2 x NCq). MS (EI, 70 eV):  $m/z$  (%) = 328 ( $M^+$ , 17), 225 (26), 194 (100), 180 (31), 167 (31), 120 (25), 112 (12), 106 (18), 91 (29), 86 (89), 58 (18). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3055 w, 2930 w, 1484 vs, 1463 vs, 1453 vs.  $\text{C}_{23}\text{H}_{24}\text{N}_2$  (328.5): Calc. C, 84.1 %; H, 7.4 %; N, 8.5 %. Found C, 83.6 %; H, 7.5 %; N, 8.4 %.

**N-[4-(9H-9-Carbazolyl)-3-methylbutyl]-N,N-diethylamine (12f).** Obtained from 9-(2-methyl-allyl)-9H-carbazole (**11b**) and diethylamine (**5b**) as a colourless oil in 79 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.73 (d,  $^3J = 6.6$  Hz, 3 H), 0.83 (t,  $^3J = 7.1$  Hz, 6 H), 1.26 (m, 1 H), 1.44 (m, 1 H), 2.15 (m, 1 H), 2.31 (m, 6 H), 3.85 (dd,  $^2J = 14.4$  Hz,  $^3J = 6.1$  Hz, 1 H), 4.03 (dd,  $^2J = 14.4$  Hz,  $^3J = 8.9$  Hz, 1 H), 7.06 (m, 2 H), 7.26 (m, 4 H), 7.93 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 11.5 (2 x  $\text{CH}_3$ ), 18.3 ( $\text{CH}_3$ ), 31.8 (CH), 32.1 ( $\text{CH}_2$ ), 46.5 (2 x  $\text{NCH}_2$ ), 49.4 ( $\text{NCH}_2$ ), 50.5 ( $\text{NCH}_2$ ), 109.0 (2 x PhH), 118.6 (2 x PhH), 120.1 (2 x PhH), 122.6 (2 x Cq), 125.4 (2 x PhH), 140.7 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 309 ( $M^+ + 1$ , 7), 142 (6), 86 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3052 m, 2967 vs, 1484 vs, 1463 vs, 1453 vs, 1326 vs, 749 vs, 723 vs.

**4-[4-(9H-9-Carbazolyl)-3-methylbutyl]morpholine (12g).** Obtained from 9-(2-methylallyl)-9H-carbazole (**11b**) and morpholine (**5e**) as a colourless oil in 86 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.92 (d,  $^3J = 6.7$  Hz, 3 H), 1.44 (m, 1 H), 1.58 (m, 1 H), 2.29 (m, 7 H), 3.64 (t,  $^3J = 4.7$  Hz, 4 H), 4.03 (dd,  $^2J = 14.6$  Hz,  $^3J = 8.5$  Hz, 1 H), 4.20 (dd,  $^2J = 14.6$  Hz,  $^3J = 6.6$  Hz, 1 H), 7.21 (m, 2 H), 7.43 (m, 4 H), 8.08 (d,  $^3J = 7.7$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 18.4 ( $\text{CH}_3$ ), 31.3 ( $\text{CH}_2$ ), 31.5 (CH), 49.3 ( $\text{NCH}_2$ ), 53.6 (2 x  $\text{NCH}_2$ ), 56.4 ( $\text{NCH}_2$ ), 66.9 (2 x  $\text{OCH}_2$ ), 108.9 (2 x PhH), 118.7 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x

Cq), 125.5 (2 x PhH), 140.7 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 323 ( $M^+ + 1$ , 3), 180 (13), 156 (16), 100 (100). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3050 w, 2964 m, 1484 s, 1465 s, 1454 s, 1114 vs, 748 vs.,  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}$  (322.5): Calc. C, 78.2 %; H, 8.1 %; N, 8.7 %. Found C, 77.6 %; H, 8.2 %; N, 8.4 %.

**9-[4-(1-Azepanyl)-2-methylbutyl]-9H-carbazole (12h).** Obtained from 9-(2-methylallyl)-9H-carbazole (**11b**) and hexamethylenimine (**5e**) as a colourless oil in 93 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.87 (d,  $^3J = 6.7$  Hz, 3 H), 1.45 (m, 1 H), 1.57 (m, 9 H), 2.32 (m, 1 H), 2.44 (m, 1 H), 2.56 (m, 5 H), 3.99 (dd,  $^2J = 14.6$  Hz,  $^3J = 9.1$  Hz, 1 H), 4.22 (dd,  $^2J = 14.6$  Hz,  $^3J = 5.9$  Hz, 1 H), 7.20 (m, 2 H), 7.41 (m, 4 H), 8.07 (d,  $^3J = 7.7$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 18.5 ( $\text{CH}_3$ ), 26.9 (2 x  $\text{CH}_2$ ), 28.1 (2 x  $\text{CH}_2$ ), 31.7 (CH), 32.8 ( $\text{CH}_2$ ), 49.4 ( $\text{NCH}_2$ ), 55.6 (2 x  $\text{NCH}_2$ ), 55.9 ( $\text{NCH}_2$ ), 109.0 (2 x PhH), 118.6 (2 x PhH), 120.2 (2 x PhH), 122.7 (2 x Cq), 125.4 (2 x PhH), 140.8 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 335 ( $M^+ + 1$ , 37), 112 (100), 58 (24). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3046 w, 2919 s, 1484 s, 1463 s, 1453 s, 1327 s, 751 vs, 722 s.  $\text{C}_{23}\text{H}_{30}\text{N}_2$  (334.5): Calc. C, 82.6 %; H, 9.0 %; N, 8.4 %. Found C, 82.3 %; H, 9.0 %; N, 8.6 %.

**N-[4-(9H-9-Carbazolyl)-3-methylbutyl]-N-methyl-N-phenylamine (12i).** Obtained from 9-(2-methylallyl)-9H-carbazole (**11b**) and N-methylaniline (**5f**) as a yellow oil in 78 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.95 (d,  $^3J = 6.7$  Hz, 3 H), 1.49 (m, 1 H), 1.72 (m, 1 H), 2.26 (m, 1 H), 2.74 (s, 3 H), 3.16 (m, 1 H), 3.36 (m, 1 H), 4.02 (dd,  $^2J = 14.6$  Hz,  $^3J = 8.5$  Hz, 1 H), 4.15 (dd,  $^2J = 14.6$  Hz,  $^3J = 6.7$  Hz, 1 H), 6.65 (m, 3 H), 7.20 (m, 4 H), 7.38 (m, 4 H), 8.08 ( $^3d$ ,  $J = 7.7$  Hz, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 18.2 ( $\text{CH}_3$ ), 31.4 ( $\text{CH}_2$ ), 31.6 (CH), 37.9 ( $\text{NCH}_3$ ), 49.5 ( $\text{NCH}_2$ ), 50.5 ( $\text{NCH}_2$ ), 108.9 (2 x PhH), 112.3 (2 x PhH), 116.2 (PhH), 118.8 (2 x PhH), 120.3 (2 x PhH), 122.7 (2 x Cq), 125.6 (2 x PhH), 129.2 (2 x PhH), 140.7 (2 x NCq), 149.2 (NCq). MS (EI, 70 eV):  $m/z$  (%) = 342 ( $M^+$ , 27), 180 (22), 120 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3052 m, 3023 m, 2958 s, 1600 s, 1504 s, 1486 s, 1453 s.  $\text{C}_{24}\text{H}_{26}\text{N}_2$  (342.5): Calc. C, 84.2 %; H, 7.7 %; N, 8.2 %. Found C, 83.8 %; H, 7.7 %; N, 7.9 %.

**N-Benzyl-N-[4-(9H-9-Carbazolyl)-3-methylbutyl]amine (12j).** Obtained from 9-(2-methyl-allyl)-9H-carbazole (**11b**) and benzylamine (**5g**) as a yellow oil in 83 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.86 (d,  $^3J = 6.8$  Hz, 3 H), 1.40 (m, 1 H), 1.54 (m, 1 H), 2.19 (m, 1 H), 2.51 (m, 1 H), 2.66 (m, 1 H), 3.62 (s, 2 H), 3.97 (dd,  $^2J = 14.6$  Hz,  $^3J = 8.0$  Hz, 1 H), 4.10 (dd,  $^2J = 14.6$  Hz,  $^3J = 7.0$  Hz, 1 H), 7.16–7.42 (m, 11 H), 8.04 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 18.0 ( $\text{CH}_3$ ), 31.6 (CH), 34.9 ( $\text{CH}_2$ ), 47.0 ( $\text{NCH}_2$ ), 49.4 ( $\text{NCH}_2\text{Ph}$ ), 53.9 ( $\text{NCH}_2$ ), 108.9 (2 x PhH), 118.7 (2 x PhH), 120.2 (2 x PhH), 122.6 (2 x Cq), 125.5 (2 x PhH), 126.8 (PhH), 128.0 (2 x PhH), 128.3 (2 x PhH), 140.2 (Cq), 140.7 (2 x Cq). MS (EI, 70 eV):  $m/z$  (%) = 342 ( $M^+$ , 33), 257 (15), 251 (31), 180 (63), 120 (63), 106 (47), 100 (14), 91 (100), 84 (34). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3052 w, 3025 w, 2954 m, 1463 s, 1453 s, 1326 s, 750 vs.  $\text{C}_{24}\text{H}_{26}\text{N}_2$  (342.5): Calc. C, 84.2 %; H, 7.7 %; N, 8.2 %. Found C, 83.8 %; H, 7.6 %; N, 7.8 %.

**1-Allyl-1H-pyrazole (14a)** [42,51] was prepared from pyrazole and allyl bromide according to a general literature procedure [42] in 78 % yield.

**1-(2-Methylallyl)-1H-pyrazole (14b)** [42,52] was prepared from pyrazole and methylallyl chloride according to a general literature procedure in 72 % yield.

**N,N-Diethyl-N-[2-methyl-3-(1H-1-pyrazolyl)propyl]amine (15a).** Obtained from 1-allyl-1H-pyrazole (**14a**) and diethylamine (**5b**) as a colourless oil in 69 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.84 (d,  $^3J = 7.1$  Hz, 3 H), 0.98 (t,  $^3J = 6.3$  Hz, 6 H), 2.22 (m, 3 H), 2.49 (m, 4 H), 3.82 (dd,  $^2J = 13.5$  Hz,  $^3J = 7.7$  Hz, 1 H), 4.28 (dd,  $^2J = 13.5$  Hz,  $^3J = 4.3$  Hz, 1 H), 6.21 (t,  $J = 2.0$  Hz, 1 H), 7.36 (d,  $^3J = 2.2$  Hz, 1 H), 7.49 (d,  $^3J = 1.5$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 11.6 (2 x  $\text{CH}_3$ ), 16.4 ( $\text{CH}_3$ ), 33.2 (CH), 47.2 (2 x  $\text{NCH}_2$ ), 56.4 ( $\text{NCH}_2$ ), 57.5 ( $\text{NCH}_2$ ), 104.8 (CH), 127.5 (CH), 138.8 (CH). GC-MS (EI, 70 eV):  $m/z$  (%) = 196 ( $M^+ + 1$ , 12), 123 (15), 86 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3105 w, 2969 vs, 748 s.  $\text{C}_{11}\text{H}_{21}\text{N}_3$  (195.3): Calc. C, 67.6 %; H, 10.8 %; N, 21.5 %. Found C, 68.1 %; H, 10.3 %; N, 21.3 %.

**N,N-Diethyl-N-[4-(1H-1-pyrazolyl)butyl]amine (16a).** Obtained from 1-allyl-1H-pyrazole (**14a**) and diethylamine (**5b**) as a colourless oil in 29 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.99 (t,  $^3J = 7.2$  Hz, 6 H), 1.44 (m, 2 H), 1.87 (m, 2 H), 2.42 (t,  $^3J = 7.5$  Hz, 2 H), 2.48 (q,  $^3J = 7.2$  Hz, 4 H), 4.14 (t,  $^3J = 7.2$  Hz, 2 H), 6.23 (t,  $J = 2.1$  Hz, 1 H), 7.37 (d,  $^3J = 2.1$  Hz, 1 H), 7.49 (d,  $^3J = 1.6$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 11.5 (2 x  $\text{CH}_3$ ), 24.1 ( $\text{CH}_2$ ), 28.5 ( $\text{CH}_2$ ), 46.7 (2 x  $\text{NCH}_2$ ), 51.9 ( $\text{NCH}_2$ ), 52.2 ( $\text{NCH}_2$ ), 105.1 (CH), 128.7 (CH), 138.9 (CH). GC-MS (EI, 70 eV):  $m/z$  (%) = 196 ( $M^+ + 1$ , 8), 123 (18), 98 (12), 86 (100), 58 (17). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 2968 s, 2934 s, 751 s.  $\text{C}_{11}\text{H}_{21}\text{N}_3$  (195.3): Calc. C, 67.6 %; H, 10.8 %; N, 21.5 %. Found C, 67.7 %; H, 10.6 %; N, 20.6 %.

**4-[2-Methyl-3-(1H-1-pyrazolyl)propyl]morpholine (15b).** Obtained from 1-allyl-1H-pyrazole (**14a**) and morpholine (**5c**) as a colourless oil in 60 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.86 (d,  $^3J = 6.6$  Hz, 3 H), 2.17 (d,  $^3J = 7.8$  Hz, 2 H), 2.36 (m, 5 H), 3.70 (t,  $^3J = 4.7$  Hz, 4 H), 3.89 (dd,  $^2J = 13.6$  Hz,  $^3J = 7.8$  Hz, 1 H), 4.27 (dd,  $^2J = 13.6$  Hz,  $^3J = 4.9$  Hz, 1 H), 6.22 (t,  $J = 2.0$  Hz, 1 H), 7.37 (d,  $^3J = 2.1$  Hz, 1 H), 7.50 (d,  $^3J = 0.8$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 16.3 ( $\text{CH}_3$ ), 31.5 (CH), 53.9 (2 x  $\text{NCH}_2$ ), 56.1 ( $\text{NCH}_2$ ), 62.8 ( $\text{NCH}_2$ ), 67.0 (2 x  $\text{OCH}_2$ ), 104.9 (CH), 129.8 (CH), 139.0 (CH). GC-MS (EI, 70 eV):  $m/z$

(%) = 210 ( $M^+ + 1$ , 30), 123 (28), 100 (100), 70 (21), 56 (22). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3104 w, 2959 s, 1457 s, 1397 s, 1118 s, 751 s.  $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}$  (209.3): Calc. C, 63.1 %; H, 9.2 %; N, 20.1 %. Found C, 63.2 %; H, 9.1 %; N, 20.0 %.

**4-[4-(1H-1-Pyrazolyl)butyl]morpholine (16b).** Obtained from 1-allyl-1H-pyrazole (**14a**) and morpholine (**5c**) as a colourless oil in 24 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.47 (m, 2 H), 1.90 (m, 2 H), 2.32 (t,  $^3J = 7.5$  Hz, 2 H), 2.39 (m, 4 H), 3.68 (t,  $^3J = 4.6$  Hz, 4 H), 4.14 (t,  $^3J = 7.1$  Hz, 2 H), 6.23 (t,  $J = 2.0$  Hz, 1 H), 7.37 (d,  $^3J = 2.0$  Hz, 1 H), 7.49 (s, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 23.4 ( $\text{CH}_2$ ), 28.1 ( $\text{CH}_2$ ), 51.7 ( $\text{NCH}_2$ ), 53.5 (2 x  $\text{NCH}_2$ ), 58.1 ( $\text{NCH}_2$ ), 66.7 (2 x  $\text{OCH}_2$ ), 105.1 (CH), 128.6 (CH), 138.9 (CH). GC-MS (EI, 70 eV):  $m/z$  (%) = 210 ( $M^+ + 1$ , 16), 123 (49), 100 (100), 81 (18), 70 (28), 56 (34). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3104 w, 2950 s, 1118 s, 752 s.  $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}$  (209.3): Calc. C, 63.1 %; H, 9.2 %; N, 20.1 %. Found C, 63.0 %; H, 9.2 %; N, 19.8 %.

**1-[2-Methyl-3-(1H-1-pyrazolyl)propyl]azepane (15c).** Obtained from 1-allyl-1H-pyrazole (**14a**) and hexamethylenimine (**5e**) as a colourless oil in 67 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.84 (d,  $^3J = 6.5$  Hz, 3 H), 1.60 (m, 8 H), 2.24 (m, 3 H), 2.59 (m, 4 H), 3.90 (dd,  $^2J = 13.6$  Hz,  $^3J = 7.6$  Hz, 1 H), 4.30 (dd,  $^2J = 13.6$  Hz,  $^3J = 4.5$  Hz, 1 H), 6.22 (t,  $J = 2.0$  Hz, 1 H), 7.38 (d,  $^3J = 1.3$  Hz, 1 H), 7.49 (d,  $^3J = 0.9$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 16.4 ( $\text{CH}_3$ ), 27.1 (2 x  $\text{CH}_2$ ), 28.4 (2 x  $\text{CH}_2$ ), 33.4 (CH), 55.8 (2 x  $\text{NCH}_2$ ), 56.1 ( $\text{NCH}_2$ ), 62.1 ( $\text{NCH}_2$ ), 104.8 (CH), 129.7 (CH), 138.9 (CH). GC-MS (EI, 70 eV):  $m/z$  (%) = 222 ( $M^+ + 1$ , 39), 123 (14), 112 (100), 58 (45). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3104 w, 2925 vs, 747 s.  $\text{C}_{13}\text{H}_{23}\text{N}_3$  (221.3): Calc. C, 70.5 %; H, 10.5 %; N, 19.0 %. Found C, 70.4 %; H, 10.4 %; N, 19.2 %.

**1-[4-(1H-1-Pyrazolyl)butyl]azepane (16c).** Obtained from 1-allyl-1H-pyrazole (**14a**) and hexamethylenimine (**5e**) as a colourless oil in 26 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.46 (m, 2 H), 1.58 (m, 8 H), 1.87 (m, 2 H), 2.46 (t,  $^3J = 7.2$  Hz, 2 H), 2.58 (t,  $^3J = 5.2$  Hz, 4 H), 4.14 (t,  $J = 7.2$  Hz, 2 H), 6.22 (d,  $^3J = 2.0$  Hz, 1 H), 7.37 (d,  $^3J = 2.0$  Hz, 1 H), 7.49 (s, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 24.6 ( $\text{CH}_2$ ), 26.9 (2 x  $\text{CH}_2$ ), 27.9 (2 x  $\text{CH}_2$ ), 28.4 ( $\text{CH}_2$ ), 51.9 ( $\text{NCH}_2$ ), 55.4 (2 x  $\text{NCH}_2$ ), 57.5 ( $\text{NCH}_2$ ), 105.1 (CH), 128.7 (CH), 138.9 (CH). GC-MS (EI, 70 eV):  $m/z$  (%) = 222 ( $M^+ + 1$ , 21), 112 (100), 58 (41). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3105 w, 2919 s, 1455 s, 1396 s, 1286 s, 1090 s, 747 s.  $\text{C}_{13}\text{H}_{23}\text{N}_3$  (221.3): Calc. C, 70.5 %; H, 10.5 %; N, 19.0 %. Found C, 70.5 %; H, 10.2 %; N, 19.2 %.

**N-Methyl-N-[2-methyl-3-(1H-1-pyrazolyl)propyl]-N-phenylamine (15d) and N-methyl-N-phenyl-N-[4-(1H-1-pyrazolyl)butyl]amine (16d).** Obtained from 1-allyl-1H-pyrazole (**14a**) and N-methylaniline (**5f**) as a yellow oil in 100 % yield (*iso/n*-ratio = 2.3/1).

**N-Methyl-N-[2-methyl-3-(1H-1-pyrazolyl)propyl]-N-phenylamine (15d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.88 (d,  $^3J = 6.8$  Hz, 3 H), 2.53 (m, 1 H), 2.93 (s, 3 H), 3.09 (dd,  $^2J = 14.6$  Hz,  $^3J = 7.8$  Hz, 1 H), 3.26 (dd,  $^2J = 14.6$  Hz,  $^3J = 6.8$  Hz, 1 H), 3.94 (dd,  $^2J = 13.6$  Hz,  $^3J = 7.8$  Hz, 1 H), 4.11 (m, 1 H), 6.22 (d,  $^3J = 1.8$  Hz, 1 H), 6.66 (m, 3 H), 7.20 (m, 2 H), 7.31 (d,  $^3J = 2.2$  Hz, 1 H), 7.51 (m, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 15.8 ( $\text{CH}_3$ ), 33.9 (CH), 39.2 ( $\text{NCH}_3$ ), 55.9 ( $\text{NCH}_2$ ), 56.7 ( $\text{NCH}_2$ ), 105.1 (CH), 112.0 (2 x PhH), 116.1 (PhH), 129.0 (2 x PhH), 129.5 (CH), 139.1 (CH), 149.3 (NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 230 ( $M^+ + 1$ , 27), 161 (40), 120 (100).

**N-Methyl-N-phenyl-N-[4-(1H-1-pyrazolyl)butyl]amine (16d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.54 (quintet,  $^3J = 7.5$  Hz, 2 H), 1.87 (m, 2 H), 2.86 (s, 3 H), 3.28 (t,  $^3J = 7.3$  Hz, 2 H), 4.11 (t,  $^3J = 7.5$  Hz, 2 H), 6.22 (d,  $^3J = 1.8$  Hz, 1 H), 6.66 (m, 3 H), 7.20 (m, 2 H), 7.30 (d,  $^3J = 2.5$  Hz, 1 H), 7.51 (m, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 23.7 ( $\text{CH}_2$ ), 27.9 ( $\text{CH}_2$ ), 31.8 ( $\text{NCH}_3$ ), 51.7 ( $\text{NCH}_2$ ), 52.0 ( $\text{NCH}_2$ ), 105.1 (CH), 112.0 (2 x PhH), 116.0 (PhH), 128.8 (CH), 129.0 (2 x PhH), 139.0 (CH), 149.0 (NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 230 ( $M^+ + 1$ , 27), 161 (40), 120 (100).

IR (NaCl/film, **15d/16d**):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3096 w, 3061 w, 3026 m, 2959 s, 1599 vs, 1506 vs, 748 vs.

**N-Benzyl-N-[2-methyl-3-(1H-1-pyrazolyl)propyl]amine (15e).** Obtained from 1-allyl-1H-pyrazole (**14a**) and benzylamine (**5g**) as a yellow oil in 58 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 0.89 (d,  $^3J = 6.8$  Hz, 3 H), 2.21 (m, 2 H), 2.47 (m, 1 H), 3.74 (s, 2 H), 3.99 (dd,  $^2J = 13.7$  Hz,  $^3J = 7.2$  Hz, 1 H), 4.19 (dd,  $^2J = 13.7$  Hz,  $^3J = 6.3$  Hz, 1 H), 6.20 (m, 1 H), 7.28 (m, 6 H), 7.48 (d,  $^3J = 1.8$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 16.0 ( $\text{CH}_3$ ), 34.9 (CH), 52.5 ( $\text{NCH}_3$ ), 54.0 ( $\text{NCH}_2$ ), 55.9 ( $\text{NCH}_2$ ), 105.0 (CH), 126.8 (PhH), 128.0 (2 x PhH), 128.2 (2 x PhH), 129.6 (CH), 138.9 (CH), 140.3 (Cq). GC-MS (EI, 70 eV):  $m/z$  (%) = 229 ( $M^+$ , 39), 106 (45), 92 (100), 70 (40). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3308 w, 3134 w, 3105 w, 3085 w, 3062 w, 3027 m, 3001 s, 2957 s, 1454 vs, 1396 vs, 699 vs.

**N-Benzyl-N-[4-(1H-1-pyrazolyl)butyl]amine (16e).** Obtained from 1-allyl-1H-pyrazole (**14a**) and benzylamine (**5g**) as a yellow oil in 23 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 1.41 (m, 2 H), 1.82 (m, 2 H), 2.36 (t,  $^3J = 7.0$  Hz, 2 H), 3.46 (s, 2 H), 4.04 (t,  $^3J = 7.0$  Hz, 2 H), 6.20 (m, 1 H), 7.28 (m, 6 H), 7.48 (d,  $J = 1.8$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  [ppm] = 24.0 ( $\text{CH}_2$ ), 25.3 ( $\text{CH}_2$ ), 51.7 ( $\text{NCH}_2$ ), 52.8 ( $\text{NCH}_2$ ), 58.5 ( $\text{NCH}_2$ ), 105.0 (CH), 126.7 (PhH), 128.0 (2 x PhH), 128.7 (2 x PhH), 128.8 (CH), 138.9 (CH), 140.3 (NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 230 ( $M^+ + 1$ , 44), 123 (17), 106 (33), 91 (100), 81 (19), 70 (58). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3306 w, 3086 w, 3026 m, 3001 s, 2959 s, 1492 s, 1453 s, 1047 s, 700 vs.  $\text{C}_{14}\text{H}_{19}\text{N}_3$  (229.3): Calc. C, 73.3 %; H, 8.4 %; N, 18.3 %. Found C, 72.8 %; H, 8.3 %; N, 18.2 %.

***N,N*-Diethyl-*N*-[3-methyl-4-(1*H*-1-pyrazolyl)butyl]amine (16f).** Obtained from 1-(2-methyl-allyl)-1*H*-pyrazole (14b) and diethylamine (5b) as a colourless oil in 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.88 (d, <sup>3</sup>J = 6.8 Hz, 3 H), 0.99 (t, <sup>3</sup>J = 7.3 Hz, 6 H), 1.28 (m, 1 H), 1.48 (m, 1 H), 2.10 (m, 1 H), 2.43 (m, 2 H), 2.48 (q, <sup>3</sup>J = 7.3 Hz, 4 H), 3.90 (dd, <sup>2</sup>J = 13.6 Hz, <sup>3</sup>J = 8.0 Hz, 1 H), 4.05 (dd, <sup>2</sup>J = 13.6 Hz, <sup>3</sup>J = 6.5 Hz, 1 H), 6.21 (t, <sup>3</sup>J = 2.0 Hz, 1 H), 7.35 (d, <sup>3</sup>J = 2.0 Hz, 1 H), 7.48 (d, <sup>3</sup>J = 1.5 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 11.4 (2 x CH<sub>3</sub>), 17.3 (CH<sub>3</sub>), 31.1 (CH<sub>2</sub>), 32.8 (CH), 46.5 (2 x NCH<sub>2</sub>), 50.1 (NCH<sub>2</sub>), 58.0 (NCH<sub>2</sub>), 104.8 (CH), 129.2 (CH), 138.8 (CH). GC-MS (EI, 70 eV): m/z (%) = 244 (M<sup>+</sup>, 100), 176 (29), 152 (29), 137 (35), 106 (29), 91 (86), 84 (57). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 2968 vs, 2933 s, 2873 s, 2801 s, 1122 s, 749 s.

**4-[3-Methyl-4-(1*H*-1-pyrazolyl)butyl]morpholine (16g).** Obtained from 1-(2-methylallyl)-1*H*-pyrazole (14b) and morpholine (5c) as a colourless oil in 85 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.89 (d, <sup>3</sup>J = 6.8 Hz, 3 H), 1.29 (m, 1 H), 1.52 (m, 1 H), 2.13 (m, 1 H), 2.35 (m, 6 H), 3.67 (t, <sup>3</sup>J = 4.8 Hz, 4 H), 3.91 (dd, <sup>2</sup>J = 13.6 Hz, <sup>3</sup>J = 7.8 Hz, 1 H), 4.03 (dd, <sup>2</sup>J = 13.6 Hz, <sup>3</sup>J = 6.8 Hz, 1 H), 6.21 (d, <sup>3</sup>J = 2.0 Hz, 1 H), 7.35 (d, <sup>3</sup>J = 2.0 Hz, 1 H), 7.49 (t, <sup>3</sup>J = 1.5 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.3 (CH<sub>3</sub>), 30.5 (CH<sub>2</sub>), 32.6 (CH), 53.5 (2 x NCH<sub>2</sub>), 56.2 (NCH<sub>2</sub>), 58.0 (NCH<sub>2</sub>), 66.7 (2 x OCH<sub>2</sub>), 104.9 (CH), 129.3 (CH), 138.9 (CH). GC-MS (EI, 70 eV): m/z (%) = 224 (M<sup>+</sup>, 51), 156 (11), 137 (54), 100 (100), 70 (20), 56 (20). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3106 vw, 2958 vs, 2931 vs, 2893 s, 2855 vs, 2809 s, 1457 s, 1448 s, 1396 s, 1274 s, 1117 vs, 868 s, 752 vs.

**1-[3-Methyl-4-(1*H*-1-pyrazolyl)butyl]azepane (16h).** Obtained from 1-(2-methylallyl)-1*H*-pyrazole (14b) and hexamethylenimine (5e) as a colourless oil in 83 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.78 (d, <sup>3</sup>J = 6.5 Hz, 3 H), 1.27 (m, 1 H), 1.42 (m, 1 H), 1.50 (m, 8 H), 2.03 (m, 1 H), 2.38 (m, 2 H), 2.49 (m, 4 H), 3.82 (dd, <sup>2</sup>J = 13.4 Hz, <sup>3</sup>J = 7.9 Hz, 1 H), 3.99 (dd, <sup>2</sup>J = 13.4 Hz, <sup>3</sup>J = 6.3 Hz, 1 H), 6.14 (s, 1 H), 7.27 (s, 1 H), 7.41 (s, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.5 (CH<sub>3</sub>), 26.8 (2 x CH<sub>2</sub>), 27.9 (2 x CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 32.9 (CH), 55.4 (2 x NCH<sub>2</sub>), 55.6 (NCH<sub>2</sub>), 58.3 (NCH<sub>2</sub>), 104.9 (CH), 129.3 (CH), 138.9 (CH). GC-MS (EI, 70 eV): m/z (%) = 236 (M<sup>+</sup>, 60), 137 (17), 112 (100), 58 (54). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3104 vw, 2918 vs, 2853 vs, 1455 s, 1189 s, 749 s.

***N*-Methyl-*N*-[3-methyl-4-(1*H*-1-pyrazolyl)butyl]-*N*-phenylamine (16i).** Obtained from 1-(2-methylallyl)-1*H*-pyrazole (14b) and *N*-methylamine (5f) as a yellow oil in 71 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 0.91 (d, <sup>3</sup>J = 6.8 Hz, 3 H), 1.36 (m, 1 H), 1.58 (m, 1 H), 2.10 (m, 1 H), 2.85 (s, 3 H), 3.33 (m, 2 H), 3.89 (dd, <sup>2</sup>J = 13.6 Hz, <sup>3</sup>J = 7.8 Hz, 1 H), 4.02 (dd, <sup>2</sup>J = 13.6 Hz, <sup>3</sup>J = 6.8 Hz, 1 H), 6.21 (t, <sup>3</sup>J = 2.0 Hz, 1 H), 6.66 (m, 3 H), 7.20 (m, 2 H), 7.29 (d, <sup>3</sup>J = 2.3 Hz, 1 H), 7.50 (d, <sup>3</sup>J = 1.8 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ [ppm] = 17.4 (CH<sub>3</sub>), 30.4 (CH<sub>2</sub>), 32.5 (CH), 37.9 (NCH<sub>3</sub>), 50.3 (NCH<sub>2</sub>), 58.0 (NCH<sub>2</sub>), 105.0 (CH), 112.1 (2 x PhH), 116.0 (PhH), 129.0 (2 x PhH), 129.4 (CH), 139.1 (CH), 149.0 (NCq). GC-MS (EI, 70 eV): m/z (%) = 243 (M<sup>+</sup>, 9), 137 (21), 120 (100). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3095 vs, 3061 s, 3025 s, 2962 m, 1464 s, 1118 vs, 1044 vs, 1035 s, 872 vs.

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