

# Synthesis and structural characterization of imines from 2,3-diphenylbutane-1,4-diamine and their ruthenium catalyzed transformation to bis-(1,3-dihydropyrrolone) derivatives

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**Dedicated to Prof. Rainer Beckert on the occasion of his 60<sup>th</sup> birthday**

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## Abstract

2,3-Diphenylbutane-1,4-diamine is prepared from 2,3-diphenylsuccinonitrile *via* the corresponding bis-acetamide. High level DFT-calculations show that the *meso* form of the diamine is stabilized by intramolecular hydrogen bonds compared to the chiral stereoisomers. Imines are obtained in high yields by condensation of the diamine with the corresponding aldehydes. Two of the imines have been characterized by X-ray diffraction. In both structures the *meso* form is observed. Imines derived from cinnamaldehyde derivatives are transformed to bis- $\gamma$ -lactams by the ruthenium catalyzed reaction with CO and ethylene.

**Keywords:** Imines, ruthenium, C-H activation,  $\gamma$ -lactams, X-ray

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## Introduction

Catalytic C-H activation reactions are in the focus of interest since the pioneering work of Murai *et al.* who were able to perform formal alkylation and acylation reactions by reacting acetophenone derivatives with either alkenes or mixtures of carbon monoxide and alkenes.<sup>1</sup> Transformations including C-H activation steps are highly attractive synthetic goals due to the inherent atom economy and the possibility to avoid the use of reactive organic intermediates as e.g. halogenated compounds that are potentially environmentally unfriendly. In the last years number of catalytic C-H activation reactions have been published and summarized in review

articles.<sup>2</sup> Most of them work *via* the precoordination of a catalytically active transition metal species. The latter are mostly composed of typical 4<sup>th</sup> and 5<sup>th</sup> row transition metals like ruthenium, rhodium or platinum. Quite recently, also copper catalyzed C-H activation reactions in combination with oxidation elementary steps attracted increasing interest.<sup>3</sup>

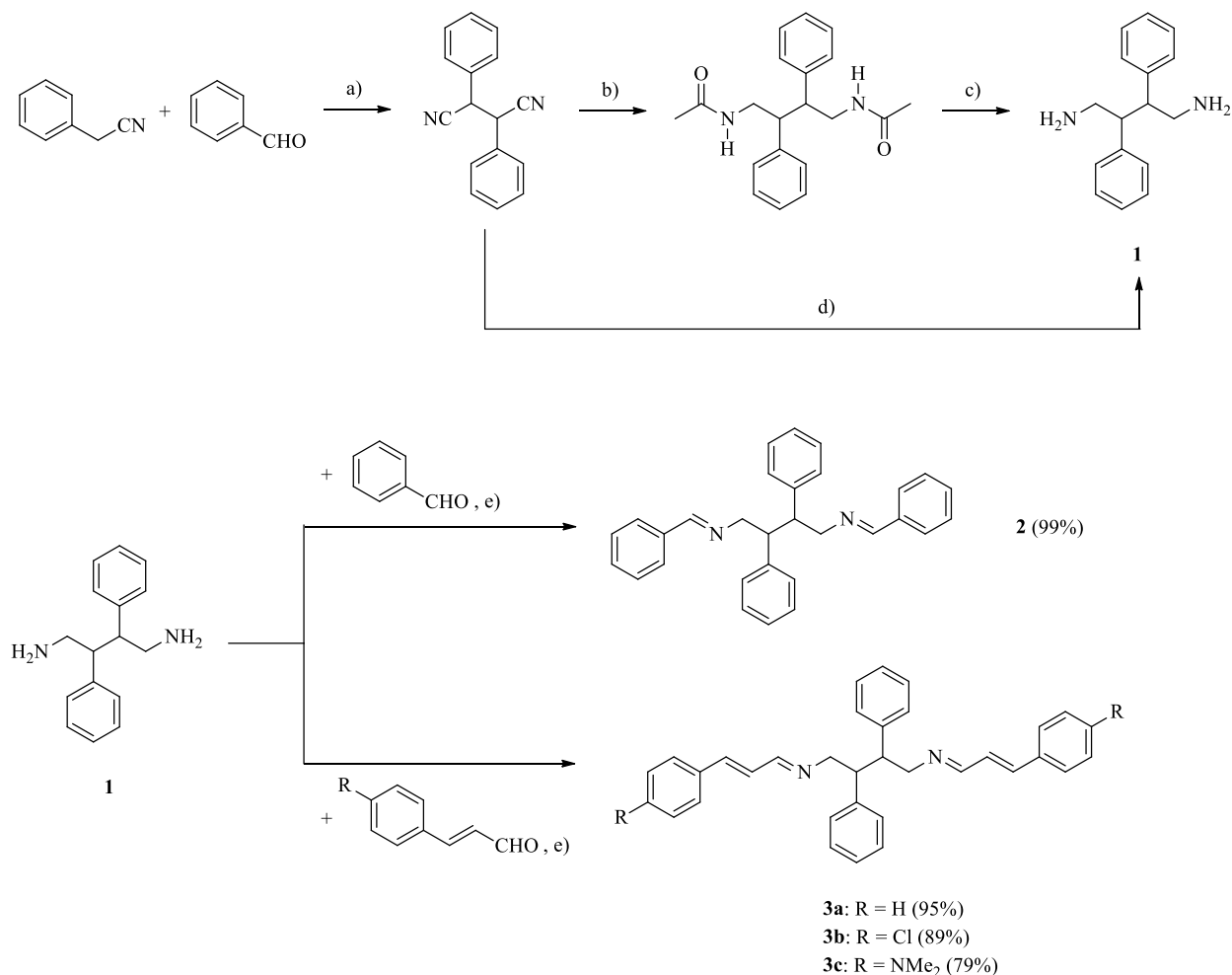
In the last years we published a number of papers concerning ruthenium catalyzed C-H activation reactions of imines derived from  $\alpha,\beta$ -unsaturated aldehydes like cinnamaldehyde or crotonic aldehyde. The reaction proceeds regioselectively at the  $\beta$ -position with respect to the imine double bond. Insertion of carbon monoxide and a 1-alkene in combination with a ring closing reaction leads to the formation of chiral  $\gamma$ -lactams as racemic mixtures. In addition, 2,3-disubstituted pyrrole derivatives are produced as side-products if the reaction is carried out in toluene. The ratio of the heterocyclic products is strongly affected by the relative permittivity of the solvent and the combination of organic residues at C $_{\beta}$  of the imine chain and at nitrogen. The reaction might also be carried out as a four component reaction without isolating the imine. This means that the corresponding primary amine and the  $\alpha,\beta$ -unsaturated aldehyde are treated with moderate pressures of carbon monoxide and ethylene in the presence of Ru<sub>3</sub>(CO)<sub>12</sub> as a precatalyst. The presence of water from the condensation of the amine and the aldehyde leads to a more polar reaction environment therefore enhancing the yield of the pyrrole derivative as it was observed for more polar solvents if the pure imine was introduced to the reaction.<sup>4</sup>

## Results and Discussion

The synthesis of 2,3-diphenylbutane-1,4-diamine is easily achieved starting from benzyl cyanide and benzaldehyde which in the presence of sodium cyanide are converted to 2,3-diphenylsuccinonitrile.<sup>5</sup> The nitrile then is reacted with acetic anhydride in the presence of Raney-nickel in an autoclave pressurized with H<sub>2</sub> to give N,N'-(2,3-diphenylbutane-1,4-diyl)diacetamide which upon hydrolysis under basic conditions is transferred to 2,3-diphenylbutane-1,4-diamine, **1**.<sup>6</sup> An alternative pathway is described by Aizencang et al. who directly convert the succinonitrile to the diamine by the reaction with BF<sub>3</sub> × THF.<sup>7</sup> The yields of both procedures are comparable. Nevertheless, the latter is less time consuming. The diamine has then been reacted with benzaldehyde and three cinnamaldehyde derivatives to produce the corresponding imines **2** and **3a-c** in excellent yields. The complete reaction sequence is summarized in Scheme 1.

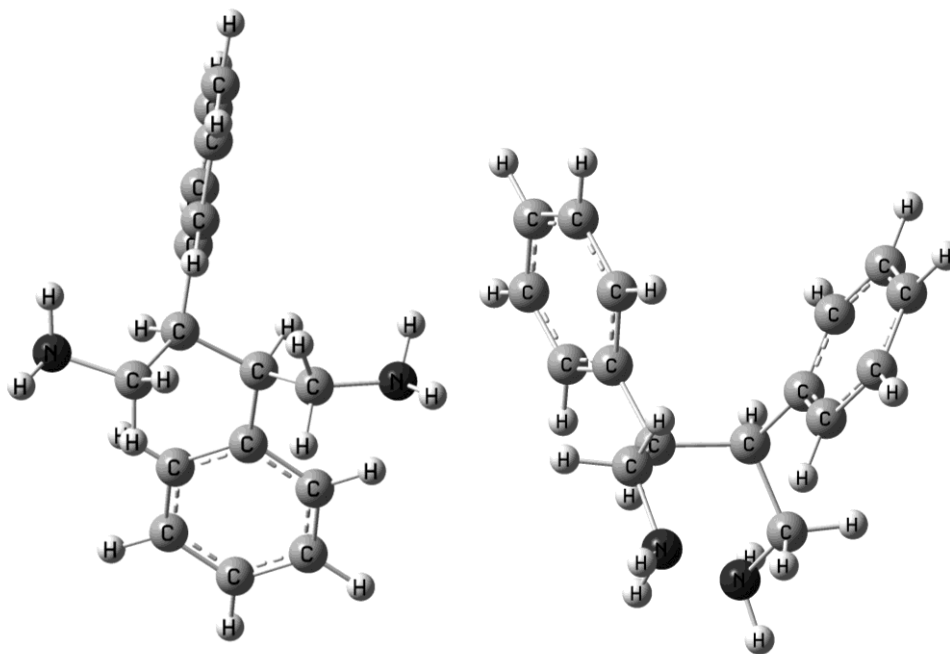
The central carbon atoms of **1** are stereogenic centers. This means that **1** might exist in two diastereomeric forms which are the *RR* and *SS* enantiomers as well as the *RS meso* form. Since the NMR spectra of **1** show only one set of signals only one of the diastereomers was formed during the synthetic procedure. DFT calculations were used to elucidate if one of the diastereomers is significantly more stable than the other. Full geometry optimizations (i. e. without symmetry constraints) were carried out with the GAUSSIAN03 program package using throughout the hybrid Hartree-Fock-DFT approach (B3LYP/6-311\*\*G(d,p)).<sup>8,9</sup> The resulting structures were rigorously characterized as minima according to the number of imaginary modes

by applying a second-order derivative calculation (vibrational analysis). Zero point energy (ZPE) corrections have been applied. Figure 1 shows both minimum structures. According to our calculations the *meso* form is 18.2 kJ mol<sup>-1</sup> more stable than the corresponding *RR* diastereomer. This may be due to the fact that there are different C—H---N interactions in the molecular structure of the *meso* form than in the structure of the *RR* configured compound. Intramolecular C—H---N interactions are attributed as weak hydrogen bonds that nevertheless contribute significantly to the conformation of molecules.<sup>10</sup> Caused by the different stereochemistry at C2 and C3 of the different diastereomers of **1** the amino nitrogen gets into close proximity to different neighboring C-H functions. In the *meso* form three close C—H---N interactions of 241.5, 245.9 and 257.2 pm are observed. On the other hand, the *RR* diastereomer only shows one such interaction of 231.9 pm. The calculations thus give a hint that the experimentally observed only diastereomer might be the *meso* form of **1**.



**Scheme 1.** Synthetic procedure for **1**, **2** and **3a-c**. a) NaCN, H<sub>2</sub>O/MeOH, reflux, 1h; b) acetic anhydride, toluene, Raney-Ni, 14 bar H<sub>2</sub>, 130 °C, 72 h; c) 5 M NaOH, 200 °C, 72 h; d) BH<sub>3</sub> × THF, THF, 20 °C, 18 h; e) EtOH, 20 °C, 3h.

**1** is easily converted to the corresponding imines **2** and **3a-c** by reaction with benzaldehyde or the corresponding cinnamaldehyde derivative, respectively. (*E*)-3-(4-Chlorophenyl)-prop-2-enal and (*E*)-3-(4-dimethylamino-phenyl)-prop-2-enal were synthesized by an aldol condensation from the corresponding substituted benzaldehyde and acetic aldehyde following literature procedures.<sup>11</sup> The imines show typical bands in the IR spectra as well as resonances for the imine function in the NMR spectra. Imines **2** and **3a** upon recrystallization gave crystals suitable for X-ray diffraction. The molecular structures are depicted in Figures 2 (**2**) and 3 (**3a**), most important bond lengths and angles are summarized in Table 1. Bond lengths angles are of typical values.<sup>11</sup> The most important fact is that the center of the C1-C1a bond represents a crystallographic center of inversion in both structures. Both molecules therefore are observed in their *meso* form which was found to be energetically slightly more stable compared to the *RR* form for the diamine **1**.

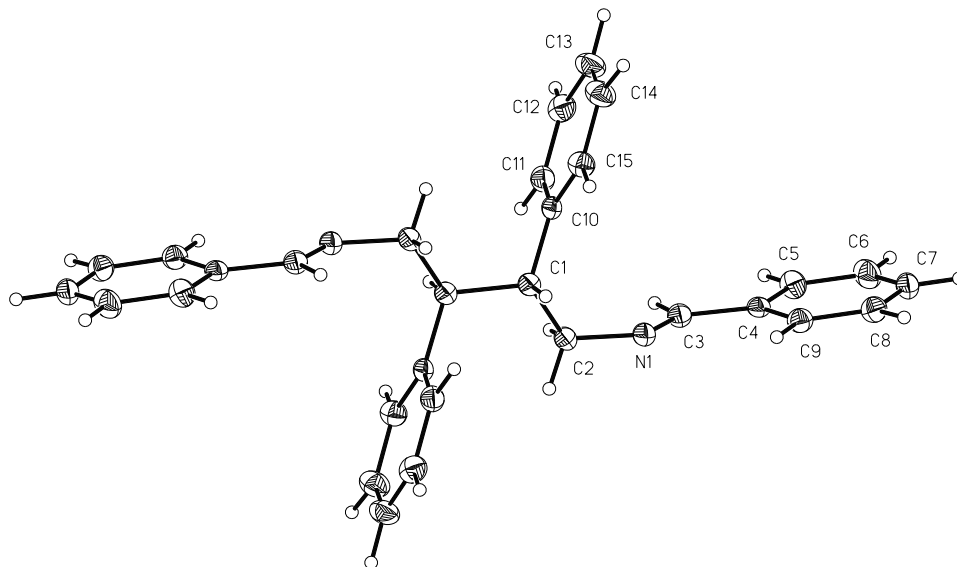


**Figure 1.** Calculated minimum structures of **1** as the *meso* form (left) and the *RR* diastereomer (right).

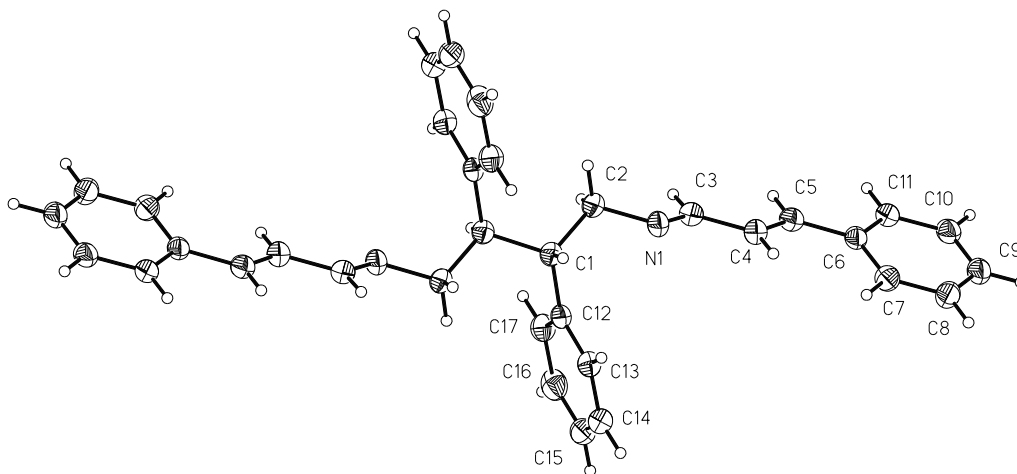
**Table 1.** Selected bond lengths [pm] and angles [°] of **2** and **3a**

<b>2</b>					
C1-C1a	1.559(3)	C1-C2	1.534(3)	C2-N1	1.466(2)
N1-C3	1.268(2)				
C1a-C1-C2	110.5(2)	C1a-C1-C10	111.4(2)	C2-C1-C10	111.8(2)
C1-C2-N1	110.05(2)	C2-N1-C3	116.9(2)	N1-C3-C4	122.8(2)

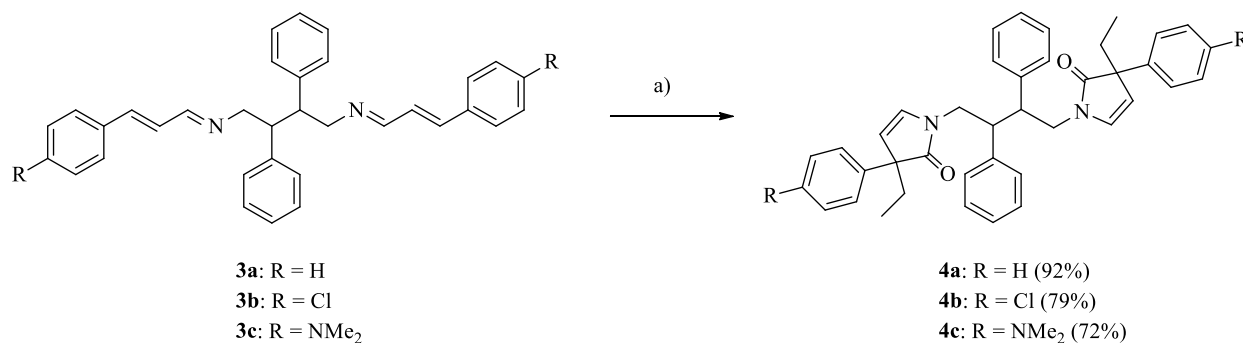
<b>3a</b>					
C1-C1a	1.551(3)	C1-C2	1.530(2)	C2-N1	1.460(2)
N1-C3	1.272(2)	C3-C4	1.447(2)	C4-C5	1.332(2)
C5-C6	1.464(3)				
C1a-C1-C2	109.7(2)	C1a-C1-C12	113.0(2)	C2-C1-C12	110.7(2)
C1-C2-N1	111.0(2)	C2-N1-C3	117.1(2)	N1-C3-C4	122.7(2)
C3-C4-C5	123.0(2)	C4-C5-C6	128.0(2)		



**Figure 2.** Molecular structure of **2**. Displacement ellipsoids are depicted on the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.



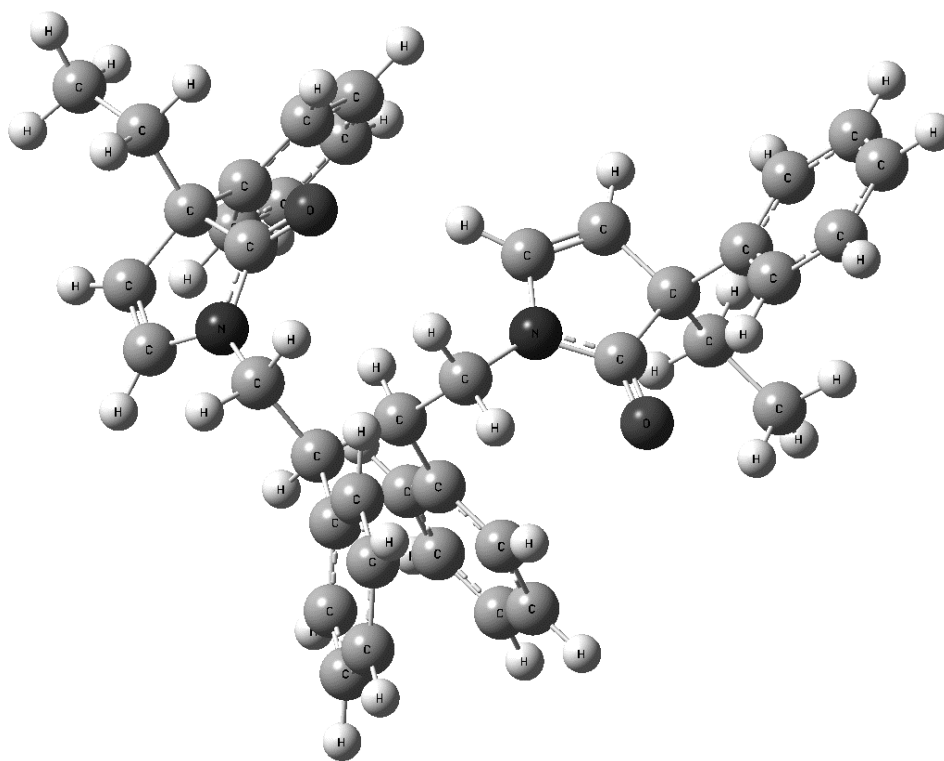
**Figure 3.** Molecular structure of **3a**. Displacement ellipsoids are depicted on the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.



**Scheme 2.** Synthetic procedure for **4a-c**. a) 3 mol% Ru<sub>3</sub>(CO)<sub>12</sub>, 12 bar CO, 8 bar C<sub>2</sub>H<sub>4</sub>, toluene, 145°C, 16h.

Scheme 2 shows the synthesis of bis-dihydropyrrolone derivatives **4a-c** starting from diimines **3a-c**. We reported earlier that reactions of this kind might produce two different classes of heterocyclic compounds, namely dihydropyrrolones as shown in Scheme 2 and 2,3-disubstituted pyrroles.<sup>4</sup> Both compounds exhibit two protons at the respective heterocyclic system that give rise to two doublets in the <sup>1</sup>H NMR spectrum at very characteristic chemical shifts. From NMR spectra of the crude reaction mixtures we saw that there were no signals representing unreacted imine functions and there were no signals that might be attributed to pyrroles. The reaction of **3a-c** therefore proceeds with high chemoselectivity to products **4a-c** in which both imine groups are transformed to pyrrolone systems.

Compounds **4a-c** were purified by column chromatography. The formation of each pyrrolone system is accompanied by the formation of an additional stereogenic center at C3 of the heterocyclic moiety. If we assume that the *meso* stereochemistry of the central chiral carbon atoms is retained, the formation of two diastereomeric pairs of enantiomers either with *RR* and *SS* or with *RS* and *SR* configuration at the new stereogenic centers is envisaged. From NMR spectra it became obvious that indeed different diastereomers are formed since part of the spectra show multiple sets of signals. Apparently, one of the diastereomers is formed predominantly. Nevertheless, since we were not able to isolate crystalline material of a quality suitable for X-ray diffraction we cannot reliably conclude which diastereomer is formed preferably. Therefore, we calculated the minimum structures of the *SS* and *RS* (absolute configuration of the chiral carbon atoms of the pyrrolone moiety) diastereomer of **4a**. The calculations showed that both diastereomers represent minima on the hypersurface. Nevertheless, the *RS* diastereomer is just 4,3 kJ mol<sup>-1</sup> more stable with respect to the *SS* diastereomer. This means that also according to our calculations it is not possible to make a statement which diastereomer is more likely to be the one that is obtained with higher yield. The calculated structure of the *RS* diastereomer is presented in Figure 4.



**Figure 4.** Calculated minimum structure of the *RS* diastereomer of **4a**.

## Conclusions

We have shown that 2,3-diphenylbutane-1,4-diamine is obtained in its *meso* form exclusively when prepared following literature synthetic procedures and that it is a highly suitable substrate for the synthesis of bis-imines with both aromatic or  $\alpha,\beta$ -unsaturated aldehydes. The corresponding bis-imines from 2,3-diphenylbutane-1,4-diamine and cinnamaldehyde have been catalytically reacted with CO and ethylene to produce a mixture of diastereomeric bis- $\gamma$ -lactams. The reaction proceeds highly chemoselective in a sense that always both imine subunits of the substrate reacted and that both imine functions give rise to the same heterocyclic system whereas no formation of pyrroles is observed, although this side reaction is commonly observed if mono-imines are introduced to the same reaction scheme.

## Experimental Section

**General.** Benzaldehyde, 4-chloro-benzaldehyde, 4-dimethylamino-benzaldehyde and cinnamaldehyde were purchased from Sigma Aldrich and were used without further purification. (E)-3-(4-Chlorophenyl)-prop-2-enal and (E)-3-(4-dimethylamino-phenyl)-prop-2-enal were synthesized by an aldol condensation from the corresponding substituted benzaldehyde and acetic aldehyde following literature procedures.<sup>11</sup> 2,3-Diphenylbutane-1,4-diamine, **1**, has been prepared starting from benzaldehyde and benzyl cyanide.<sup>5-7</sup> All catalytical reaction procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents.<sup>12</sup> NMR spectra were recorded on a Bruker AC 200 spectrometer (<sup>1</sup>H: 200 MHz, <sup>13</sup>C: 50.32 MHz, CDCl<sub>3</sub> as internal standard) or a Bruker DRX 400 spectrometer (<sup>1</sup>H: 400.13 MHz; <sup>13</sup>C: 100.62 MHz; CDCl<sub>3</sub> as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. High-resolution mass spectra were recorded on a Finnigan MAT 95 XL using EI techniques. IR spectra were recorded on a Shimadzu IRAffinity-1 (FTIR) at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry of Friedrich-Schiller-University Jena.

**Computational methods.** Full geometry optimizations (i. e. without symmetry constraints) were carried out with the GAUSSIAN03 program package using throughout the hybrid Hartree-Fock-DFT approach (B3LYP/6-311\*\*G(d,p)).<sup>8,9,13</sup> The stationary point of the geometry optimization was characterized to be a minimum structure according to the absence of any imaginary modes by applying a second-order derivative calculation.

**Structure determinations.** Intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K<sub>α</sub> radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects<sup>14,15</sup>. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares techniques against Fo<sup>2</sup> (SHELXL-97).<sup>16</sup> All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. Crystallographic data as well as structure solution and refinement details are summarized in Table 2. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC- 842334 for **2**, and CCDC- 842335 for **3a**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].



**Table 2.** Crystal data and refinement details for the X-ray structure determinations of the compounds **2** and **3a**

Compound	<b>2</b>	<b>3a</b>
formula	C <sub>30</sub> H <sub>28</sub> N <sub>2</sub>	C <sub>34</sub> H <sub>32</sub> N <sub>2</sub>
fw (g·mol <sup>-1</sup> )	416.54	468.62
<i>T</i> /K	-140(2)	-140(2)
crystal system	monoclinic	monoclinic
space group	P 21/n	P 21/n
<i>a</i> /Å	10.7489(8)	11.5824(9)
<i>b</i> /Å	6.0524(4)	5.4881(4)
<i>c</i> /Å	18.3725(15)	21.5178(19)
$\alpha$ /°	90	90
$\beta$ /°	99.295(3)	99.555(4)
$\gamma$ /°	90	90.00
<i>V</i> /Å <sup>3</sup>	1179.56(15)	1348.81(19)
<i>Z</i>	2	2
$\rho$ (g·cm <sup>-3</sup> )	1.173	1.154
$\mu$ (mm <sup>-1</sup> )	.68	.67
measured data	7612	7852
data with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	1419	1512
unique data ( <i>R</i> <sub>int</sub> )	2676/0.0948	3011/0.0857
<i>wR</i> <sub>2</sub> (all data, on <i>F</i> <sup>2</sup> ) <sup>a)</sup>	0.1127	0.1274
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a)</sup>	0.0509	0.0564
<i>S</i> <sup>b)</sup>	0.931	0.964
Res. dens./e·Å <sup>-3</sup>	0.183/-0.233	0.193/-0.225
absorpt method	NONE	NONE
CCDC No.	842334	842335

<sup>a)</sup> Definition of the *R* indices:  $R_1 (\sum ||F_o| - |F_c||) / \sum |F_o|$ ;

$wR_2 \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$  with  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ ;  $P [2F_c^2 + \text{Max}(F_o^2)]/3$ ;

<sup>b)</sup>  $S \{ \sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$ .

**General synthetic procedure for the preparation of imines **2** and **3a-c**.** In a 25 ml Schlenk tube 135 mg (0.6 mmol) 1,4-diamino-2,3-diphenylbutane dissolved in 10 ml ethanol were mixed with 1.2 mmol of the corresponding aldehyde (120 mg benzaldehyde, 160 mg cinnamaldehyde, 200 mg 3-(4-chlorophenyl)-prop-2-enal or 210 mg 3-(4-dimethylamino-phenyl)-prop-2-enal, respectively) under an argon atmosphere. During the reaction a white precipitate was formed. After stirring the reaction mixture for 3 h, the solvent was evaporated *in vacuo*. The remaining

solid residue was washed two times with 10 ml n-heptane and after decanting the solvent the solid residue was dried.

***N,N*-Dibenzyliden-2,3-diphenylbutan-1,4-diamin (2).** White powder, yield: 247 mg, 99%; <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 3.49-3.51 (m, 4H, CH<sub>2</sub>), 3.75-3.79 (m, 2H, CH), 7.11-7.35 (m, 16H, CH<sub>ar</sub>), 7.45-7.52 (m, 4H, CH<sub>ar</sub>), 7.69 (s, 2H, N=CH); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 50.1 (CH), 65.3 (CH<sub>2</sub>), 126.4 (CH<sub>ar</sub>), 127.9 (CH<sub>ar</sub>), 128.2 (CH<sub>ar</sub>), 128.3 (CH<sub>ar</sub>), 129.0 (CH<sub>ar</sub>), 130.2 (CH<sub>ar</sub>), 136.4 (C<sub>ar</sub>), 142.3 (C<sub>ar</sub>), 161.4 (N=CH); MS (EI) m/z (%): 417 (10) [MH<sup>+</sup>], 311 (50) [M<sup>+</sup>-C<sub>7</sub>H<sub>6</sub>NH], 296 (30), [M<sup>+</sup>-C<sub>8</sub>H<sub>10</sub>N], 207 (65), [C<sub>16</sub>H<sub>15</sub><sup>+</sup>], 179 (15) [C<sub>14</sub>H<sub>11</sub><sup>+</sup>], 118 (90) [C<sub>8</sub>H<sub>8</sub>N<sup>+</sup>], 104 (20) [C<sub>7</sub>H<sub>6</sub>N<sup>+</sup>], 91 (100) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 83 (35) [C<sub>5</sub>H<sub>9</sub>N<sup>+</sup>], 69 (20) [C<sub>4</sub>H<sub>7</sub>N<sup>+</sup>], 57 (25) [C<sub>3</sub>H<sub>7</sub>N<sup>+</sup>], 42 (20) [C<sub>2</sub>H<sub>4</sub>N<sup>+</sup>]; HRMS C<sub>30</sub>H<sub>28</sub>N<sub>2</sub> (416.22525): 416.22154, Δ 3.71 mmu. IR (KBr): ν [cm<sup>-1</sup>] 3048, 3066, 3027, 3004, 2930, 2909, 2874, 2839 (CH), 1644 (C=N), 1601, 1580, 1493 (C<sub>ar</sub>), 1449 (C<sub>al</sub>).

***N,N*-Bis(*E*)-3-phenylallylidene)-2,3-diphenylbutane-1,4-diamine (3a).** White powder, yield 267 mg, 95%; <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 3.30-3.45 (m, 4H, CH<sub>2</sub>), 3.65-3.82 (m, 2H, CH), 6.63-6.72 (m, 4H, =CH), 7.08-7.36 (m, 20H, CH<sub>ar</sub>), 7.45 (d, *J* 6.4 Hz, 2H, CH=N); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 50.7 (CH), 65.7 (CH<sub>2</sub>), 126.6 (=CH), 127.1 (CH<sub>ar</sub>), 128.2 (CH<sub>ar</sub>), 128.4 (CH<sub>ar</sub>), 128.7 (CH<sub>ar</sub>), 128.8 (CH<sub>ar</sub>), 128.9 (CH<sub>ar</sub>), 135.7 (C<sub>ar</sub>), 140.9 (=CH), 142.1 (C<sub>ar</sub>), 163.1 (CH=N); MS (EI) m/z (%): 468 (4) [M<sup>+</sup>], 337 (60) [M<sup>+</sup>-C<sub>9</sub>H<sub>8</sub>NH], 322 (40) [M<sup>+</sup>-C<sub>10</sub>H<sub>10</sub>NH<sub>2</sub>], 232 (20) [C<sub>17</sub>H<sub>14</sub>N<sup>+</sup>], 157 (90), 144 (95) [C<sub>10</sub>H<sub>10</sub>N<sup>+</sup>], 130 (25) [C<sub>9</sub>H<sub>8</sub>N<sup>+</sup>], 115 (100) [C<sub>9</sub>H<sub>7</sub><sup>+</sup>], 104 (25) [C<sub>8</sub>H<sub>8</sub><sup>+</sup>], 91 (50) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 77 (10) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]; HRMS C<sub>34</sub>H<sub>32</sub>N<sub>2</sub> (468.25655): 468.25611, Δ 0.44 mmu. IR (KBr): ν [cm<sup>-1</sup>] 3082, 3058, 3027, 3001, 2910, 2835 (CH), 1635 (C=N), 1601, 1494 (CH<sub>ar</sub>), 1450 (C<sub>al</sub>).

***N,N*-Bis(*E*)-3-(4-chlorophenyl)allylidene)-2,3-diphenylbutane-1,4-diamine (3b).** White powder, yield 288 mg (89%); <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 3.32-3.40 (m, 4H, CH<sub>2</sub>), 3.65-3.72 (m, 2H, CH), 6.56-6.64 (m, 4H, =CH), 7.23-7.35 (m, 18H, CH<sub>ar</sub>), 7.42 (d, *J* 6.8 Hz, 2H, CH=N); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 50.6 (CH), 65.7 (CH<sub>2</sub>), 126.6 (=CH), 128.2 (CH<sub>ar</sub>), 128.4 (CH<sub>ar</sub>), 128.7 (br, CH<sub>ar</sub>), 128.9 (CH<sub>ar</sub>), 134.3 (C<sub>ar</sub>), 134.7 (C<sub>ar</sub>), 139.4 (=CH), 142.0 (C<sub>ar</sub>), 162.8 (CH=N); MS (FAB in nba) m/z (%): 537 (85) [M<sup>+</sup>], 389 (45) [M<sup>+</sup>-C<sub>9</sub>H<sub>5</sub>Cl], 372 (100) [M<sup>+</sup>-C<sub>9</sub>H<sub>8</sub>ClN], 356 (30) [M<sup>+</sup>-C<sub>10</sub>H<sub>12</sub>ClN], 268 (30) [C<sub>17</sub>H<sub>15</sub>ClN<sup>+</sup>]; HRMS C<sub>34</sub>H<sub>30</sub>N<sub>2</sub><sup>35</sup>Cl<sub>2</sub> (536.17861): 536.17698, Δ 1.63 mmu. IR (KBr): ν [cm<sup>-1</sup>] 3028, 3002, 2913, 2840 (CH), 1635 (C=N), 1590, 1490 (C<sub>ar</sub>), 1452, 1407 (C<sub>al</sub>).

***N,N*-Bis(*E*)-3-(4-dimethylaminophenyl)allylidene)-2,3-diphenylbutane-1,4-diamine (3c).** Yellow powder, yield 263 mg (79%); <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 2.94 (s, 12H, CH<sub>3</sub>), 3.29-3.35 (m, 4H, CH<sub>2</sub>), 3.61-3.69 (m, 2H, CH), 6.46-6.65 (m, 8H, =CH, CH<sub>ar</sub>), 7.13-7.32 (m, 14H, CH<sub>ar</sub>), 7.38 (d, *J* 6.4 Hz, CH=N); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 40.2 (CH<sub>3</sub>), 50.9 (CH), 65.6 (CH<sub>2</sub>), 112.0 (CH<sub>ar</sub>), 123.8 (C<sub>ar</sub>), 124.0 (=CH), 126.4 (CH<sub>ar</sub>), 128.3 (CH<sub>ar</sub>), 128.4 (CH<sub>ar</sub>), 128.8 (CH<sub>ar</sub>), 141.4 (=CH), 142.4 (C<sub>ar</sub>), 150.9 (C<sub>ar</sub>), 163.7 (CH=N); MS (FAB in nba) m/z (%): 556 (100) [MH<sub>2</sub><sup>+</sup>], 530 (10) [MH<sub>2</sub><sup>+</sup>-C<sub>2</sub>H<sub>2</sub>], 398 (10) [M<sup>+</sup>-C<sub>11</sub>H<sub>10</sub>N], 381 (60) [M<sup>+</sup>-C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>], 275 (30) [C<sub>19</sub>H<sub>19</sub>N<sub>2</sub><sup>+</sup>]; HRMS C<sub>38</sub>H<sub>42</sub>N<sub>4</sub> (554.34095): 554.33990, Δ 1.05 mmu. IR (KBr): ν [cm<sup>-1</sup>] 3027, 2906, 2851 (CH), 1635 (C=N), 1630, 1493, 1482 (C<sub>ar</sub>), 1444 (C<sub>al</sub>).

**General synthetic procedure for the preparation of bis-pyrrolones 4a-c.** In a stainless steel autoclave 1 mmol of the corresponding imine **3a-c** (**3a**: 470 mg, **3b**: 540 mg, **3c**: 550 mg) and 0.03 mmol Ru<sub>3</sub>(CO)<sub>12</sub> (19 mg) are dissolved in 4 ml anhydrous toluene. The autoclave is then pressurized with 12 bar carbon monoxide and 8 bar ethylene and is afterwards heated to 145°C for 16 h. After cooling down the autoclave to room temperature and releasing the pressure the solvent is evaporated *in vacuo*. The oily residue is dissolved in a mixture of light petroleum (b.p. 40-60°C) and CH<sub>2</sub>Cl<sub>2</sub> 70:30 and is purified by column chromatography using silica as the stationary phase. Products **4a-c** are eluted using mixtures of light petroleum (b.p. 40-60°C) and CH<sub>2</sub>Cl<sub>2</sub> (**4a, 4b**: 70:30; **4c**: 50:50).

**1,1'-(2,3-Diphenylbutane-1,4-diyl)bis(3-ethyl-3-phenyl-1H-pyrrol-2(3H)-one) (4a).** Red powder, yield 533 mg (92%); <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 0.45 (t, *J* 7.4 Hz, 5.5H, CH<sub>3</sub>), 0.67 (t, *J* 7.4 Hz, 0.5H, CH<sub>3</sub>), 1.52 – 1.95 (m, 4H, CH<sub>2</sub>), 3.18 – 3.46 (m, 6H, CH<sub>2</sub>, CH), 5.18 – 5.30 (m, 2H, =CH), 5.77 – 5.96 (m, 2H, =CH), 7.02 – 7.38 (m, 20H, Ph); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 8.9 (CH<sub>3</sub>), 30.4 (CH<sub>2</sub>), 46.6 (CH), 48.3 (CH<sub>2</sub>), 58.1 (C), 112.2 (=CH), 126.6 (C<sub>ar</sub>), 126.9 (C<sub>ar</sub>H), 127.4 (C<sub>ar</sub>H), 128.3 (C<sub>ar</sub>H), 128.4 (C<sub>ar</sub>H), 128.8 (C<sub>ar</sub>H), 131.7 (=CH), 139.5 (C<sub>ar</sub>), 139.8 (C<sub>ar</sub>H), 179.4 (C=O); MS (EI) *m/z* (%): 580 (18) [M<sup>+</sup>], 551 (4) [M<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>], 466 (12) [C<sub>34</sub>H<sub>30</sub>N<sub>2</sub><sup>+</sup>], 437 (3) [C<sub>32</sub>H<sub>25</sub>N<sub>2</sub><sup>+</sup>], 381 (11) [C<sub>28</sub>H<sub>17</sub>N<sub>2</sub><sup>+</sup>], 365 (15) [C<sub>27</sub>H<sub>13</sub>N<sub>2</sub><sup>+</sup>], 291 (18) [MH<sup>2+</sup>], 262 (12) [M<sup>2+</sup> - 2 CO], 234 (16) [M<sup>2+</sup> - 2 CO - 2 C<sub>2</sub>H<sub>4</sub>], 200 (98) [C<sub>15</sub>H<sub>20</sub><sup>+</sup>], 172 (100) [C<sub>13</sub>H<sub>16</sub><sup>+</sup>], 158 (27) [C<sub>12</sub>H<sub>14</sub><sup>+</sup>], 143 (20) [C<sub>11</sub>H<sub>11</sub><sup>+</sup>], 129 (18) [C<sub>10</sub>H<sub>9</sub><sup>+</sup>], 115 (30) [C<sub>9</sub>H<sub>7</sub><sup>+</sup>], 91 (67) [C<sub>8</sub>H<sub>9</sub><sup>+</sup>], 77 (20) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>], 57 (47) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>], 44 (64) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]; IR (KBr): ν [cm<sup>-1</sup>] 3060, 3028, 2966, 2929 (CH), 1697 (C=O), 1609, 1495 (CC<sub>ar</sub>), 1453 (CC<sub>al</sub>), 1262, 1156 (CN).

**1,1'-(2,3-Diphenylbutane-1,4-diyl)bis[3-ethyl-3-(4'-chlorophenyl)-1H-pyrrol-2(3H)-one] (4b).** Red powder, yield 512 mg (79%); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 0.45 (t, *J* 7.4 Hz, 2H, CH<sub>3</sub>), 0.85 (t, *J* 7.4 Hz, 4H, CH<sub>3</sub>), 1.50 – 1.85 (m, 4H, CH<sub>2</sub>), 3.03 – 3.48 (m, 6H, CH<sub>2</sub>, CH), 5.15 – 5.29 (m, 2H, =CH), 5.76 – 5.94 (m, 2H, =CH), 6.95 – 7.61 (m, 18H, CH<sub>ar</sub>); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ 8.8 (CH<sub>3</sub>); 11.4 (CH<sub>3</sub>), 29.0 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 41.3 (CH<sub>2</sub>), 46.7 (CH), 48.2 (CH<sub>2</sub>), 57.5 (C), 111.6 (=CH), 127.5 (CH<sub>ar</sub>), 128.0 (CH<sub>ar</sub>), 128.3 (CH<sub>ar</sub>), 128.4 (CH<sub>ar</sub>), 128.9 (CH<sub>ar</sub>), 129.4 (=CH), 132.2 (C<sub>Cl</sub>), 132.8 (C<sub>Cl</sub>), 138.2 (C<sub>ar</sub>), 139.4 (C<sub>ar</sub>), 179.1 (C=O). MS (EI) *m/z* (%): 648 (3) [M<sup>+</sup>], 620 (1) [M<sup>+</sup> - CO], 501 (1) [C<sub>32</sub>H<sub>19</sub>N<sub>2</sub>Cl<sub>2</sub><sup>+</sup>], 429 (2) [C<sub>32</sub>H<sub>17</sub>N<sub>2</sub><sup>+</sup>], 415 (2) [C<sub>31</sub>H<sub>15</sub>N<sub>2</sub><sup>+</sup>], 279 (49) [C<sub>20</sub>H<sub>11</sub>N<sub>2</sub><sup>+</sup>], 234 (17) [C<sub>16</sub>H<sub>28</sub>N<sup>+</sup>], 221 (11) [C<sub>15</sub>H<sub>27</sub>N<sup>+</sup>], 208 (18) [C<sub>14</sub>H<sub>26</sub>N<sup>+</sup>], 194 (29) [C<sub>13</sub>H<sub>24</sub>N<sup>+</sup>], 182 (21) [C<sub>12</sub>H<sub>22</sub>N<sup>+</sup>], 167 (76) [C<sub>11</sub>H<sub>21</sub>N<sup>+</sup>], 149 (100) [C<sub>11</sub>H<sub>17</sub><sup>+</sup>], 141 (98) [C<sub>8</sub>H<sub>10</sub>Cl<sup>+</sup>], 119 (83) [C<sub>9</sub>H<sub>11</sub><sup>+</sup>], 105 (75) [C<sub>8</sub>H<sub>9</sub><sup>+</sup>], 91 (60) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 83 (56) [C<sub>6</sub>H<sub>11</sub><sup>+</sup>], 71 (39) [C<sub>5</sub>H<sub>11</sub><sup>+</sup>], 57 (88) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>], 43 (54) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]; IR (KBr): ν [cm<sup>-1</sup>] 3061, 3028, 2968, 2934, 2878 (CH), 1700 (C=O), 1490 (CC<sub>ar</sub>), 1453 (CC<sub>al</sub>), 1262, 1157, 1093 (CN).

**1,1'-(2,3-Diphenylbutane-1,4-diyl)bis[3-ethyl-3-(4'-dimethylamino-phenyl)-1H-pyrrol-2(3H)-one] (4c).** Red powder, yield 480 mg (72%); <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 0.43 (t, 2H, *J* 7.4 Hz, CH<sub>3</sub>), 0.67 (t, 1H, *J* 7.4 Hz, CH<sub>3</sub>), 0.73 – 0.98 (m, 3H, CH<sub>3</sub>), 1.58 – 1.92 (m, 4H, CH<sub>2</sub>), 2.83 (s, 3H, NCH<sub>3</sub>), 2.89 (s, 9H, NCH<sub>3</sub>), 3.20 – 3.43 (m, 6H, CH, CH<sub>2</sub>), 5.18 – 5.25 (m, 2H, =CH), 5.70 – 5.87 (m, 2H, =CH), 6.50 – 6.66 (m,

4H, CH<sub>ar</sub>); 6.90 - 7.34 (m, 14H, CH<sub>ar</sub>). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 8.9 (CH<sub>3</sub>), 9.3 (CH<sub>3</sub>), 9.4 (CH<sub>3</sub>), 29.4 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 40.7 (NCH<sub>3</sub>), 46.3 (CH), 46.5 (CH), 48.3 (CH<sub>2</sub>), 48.6 (CH<sub>2</sub>), 57.2 (C), 57.3 (C), 112.6 (=CH), 112.7 (=CH), 127.1 (CH<sub>ar</sub>), 127.3 (CH<sub>ar</sub>), 127.4 (CH<sub>ar</sub>), 127.5 (CH<sub>ar</sub>), 127.6 (CH<sub>ar</sub>), 128.1 (CH<sub>ar</sub>), 128.2 (CH<sub>ar</sub>), 128.4 (CH<sub>ar</sub>), 128.5 (CH<sub>ar</sub>), 128.7 (CH<sub>ar</sub>); 128.8 (CH<sub>ar</sub>); 129.0 (CH<sub>ar</sub>), 131.2 (=CH), 131.3 (=CH), 139.6 (C<sub>ar</sub>), 139.8 (C<sub>ar</sub>), 149.5 (C<sub>ar</sub>), 149.6 (C<sub>ar</sub>), 180.0 (C=O), 180.1 (C=O); MS (EI) m/z (%): 667 (5) [MH<sup>+</sup>], 652 (1) [MH<sup>+</sup> - Me], 638 (2) [M<sup>+</sup> - CO], 545 (2) [M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>NMe<sub>2</sub>], 509 (3) [C<sub>34</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 494 (1) [C<sub>33</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 480 (2) [C<sub>32</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 466 (1) [C<sub>31</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 452 (1) [C<sub>30</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 438 (1) [C<sub>29</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 424 (1) [C<sub>28</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>], 304 (22) [C<sub>21</sub>H<sub>36</sub>N<sub>2</sub><sup>+</sup>], 243 (31) [C<sub>16</sub>H<sub>37</sub>N<sup>+</sup>], 219 (10) [C<sub>15</sub>H<sub>35</sub>N<sup>+</sup>], 215 (44) [C<sub>14</sub>H<sub>33</sub>N<sup>+</sup>], 201 (100) [C<sub>13</sub>H<sub>31</sub>N<sup>+</sup>], 186 (29) [C<sub>12</sub>H<sub>28</sub>N<sup>+</sup>], 170 (19) [C<sub>11</sub>H<sub>23</sub>N<sup>+</sup>], 148 (29) [C<sub>11</sub>H<sub>16</sub><sup>+</sup>], 134 (33) [C<sub>10</sub>H<sub>14</sub><sup>+</sup>], 120 (18) [C<sub>9</sub>H<sub>12</sub><sup>+</sup>], 91 (10) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 77 (20) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>], 57 (30) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>], 43 (20) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]; IR (KBr): ν [cm<sup>-1</sup>] 3028, 2964, 2933 (CH), 1700 (C=O), 1610, 1497 (CC<sub>ar</sub>), 1452 (CC<sub>al</sub>), 1355, 1262, 1094 (CN).

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