Synthesis of imines, diimines and macrocyclic diimines as possible ligands, in aqueous solution

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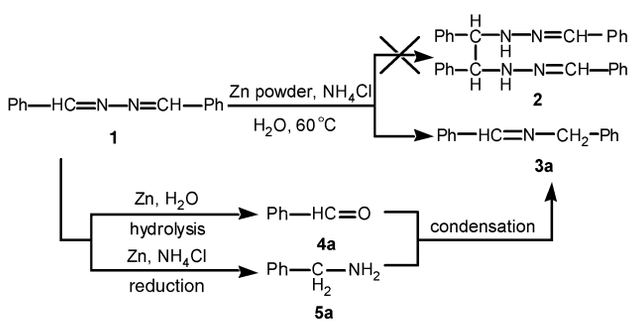
Although it is recognized that the presence of water is disadvantageous for imine synthesis, we demonstrate that such synthesis can be effective in completely aqueous media, without any catalyst and under mild conditions. Thus, aryl-aryl, aryl-alkyl, alkyl-aryl and alkyl-alkyl monoimines as well as a large variety of diimines are obtained by direct condensation of the corresponding carbonyl compounds and amines, in water. The same process is used to synthesize macrocyclic diimines starting from methylene, ethylene, trimethylene and tetramethylene glycol bis(2-formylphenyl ether) and ethylene-, trimethylene- and tetramethylene-diamine, some of these macrocycles being known for their chelating properties.

Introduction

Nowadays, regarding the new concept of Green Chemistry,[1] water tends to replace more and more organic solvents (*e.g.*, in chemical processes such as Diels–Alder[2] or aldol addition reactions[3]) taking into account environmental concerns and the aspects of cost, safety or simple operations. Following this direction, the research program of our laboratory has been devoted for some time to the study of organic reactions in water. Thus, we have been dealing for a while with reduction, reductive coupling or condensation reactions in aqueous media.[4] While studying the reductive coupling of benzaldehyde azine **1** and related compounds, instead of the desired product **2** we obtained mainly benzylidenebenzylamine **3a**. This surprising result could be explained following the pathway presented in Scheme 1.



Scheme 1

Benzaldehyde azine suffered both hydrolysis and reduction and the resulting benzaldehyde and benzylamine condensed yielding benzylidenebenzylamine. This pathway was confirmed by mixing directly in water stoichiometric amounts of benzaldehyde and benzylamine, which yielded almost quantitatively benzylidenebenzylamine. Thus, it appeared to us that imine synthesis could take place in aqueous conditions. Since its discovery in 1864 by H. Schiff,[5] the condensation reaction between aldehydes and amines was normally carried out by heating the reagents alone or in an anhydrous organic solvent, the presence of water usually being regarded as disadvantageous. However, on scrutinizing the chemical literature, we found out that in the mid-50s, based on earlier works,[6–9] the idea of 'cell-possible' reactions, which are those organic reactions that could proceed under physiological conditions, including aqueous media, had appeared. The earliest ideas regarding such non-enzymatic reactions were connected with alkaloid syntheses.[10–12] Later, Haley and Maitland[13] reported the formation of a few aromatic Schiff bases in saturated aqueous solutions and in the presence of various catalysts, performing the reactions at different pH values, from 2.5 up to 13.0. In addition, in the early 60s, Jencks and Cordes[14] studied the formation of semicarbazones,[15] oximes[15b] and the kinetics of formation of *N*-(*p*-chlorobenzylidene)aniline[14a] and hydrolysis of *N*-benzylidenebutylamine[14b] in aqueous solutions.

Our aim was to determine the scope and the limitations of the imine synthesis in aqueous media, under mild conditions, without using any buffered system or catalyst. At the same time, our purpose was to find out if these unusual, but simple and economically practical, reaction conditions are of wide application and of preparative value in the field of imine synthesis. A recent report, in which a condensation reaction between benzaldehyde and aniline occurred as a side-reaction in a Mannich-type reaction catalyzed by In,[16] in water, prompted us to report our results in this field. Our final target was to apply the same process to the synthesis of diimines (open-chain or macrocyclic) that could be used as possible chelating agents for metallic cations.

The reactions were carried out in the simplest manner, by mixing directly the amines and the carbonyl compounds in water, without adding any other solvent or catalyst, at room temperature. When the imines did not separate directly from the aqueous solution, extraction was used.

This work is described below in two sections: first, the general experiments which show the scope and limitations of the imine synthesis in aqueous media and, second, the synthesis of open-chain and macrocyclic diimines that are possible chelating agents for metallic cations.

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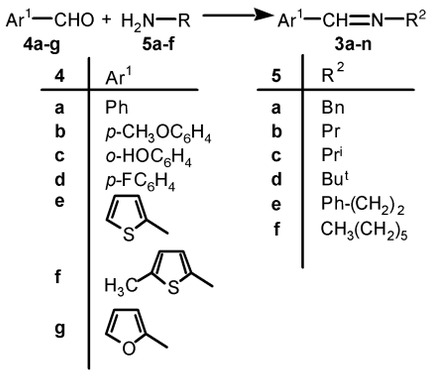
Table 1 Reaction of aromatic aldehydes with aliphatic amines



Run	4	5	3 (Yield, %)
1	**a**	**a**	**a** (85)
2	**a**	**b**	**b** (90)
3	**a**	**c**	**c** (74)
4	**a**	**d**	**d** (65)
5	**a**	**e**	**e** (76)
6	**b**	**b**	**f** (76)
7	**c**	**a**	**g** (85)
8	**b**	**e**	**h** (67)
9	**d**	**e**	**i** (86)
10	**d**	**b**	**j** (81)
11	**e**	**c**	**k** (78)
12	**e**	**e**	**l** (97)
13	**f**	**f**	**m** (79)
14	**g**	**a**	**n** (93)

Results and discussions

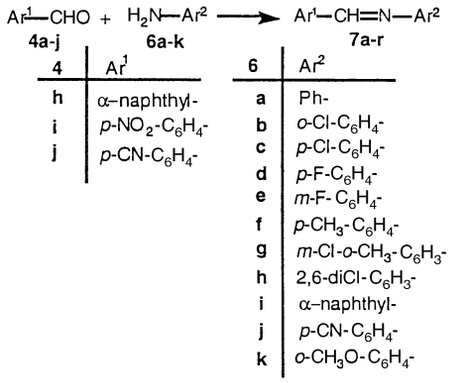
A. Synthesis of monoimines

Schiff bases of benzaldehyde and its derivatives are usually easy to obtain, under mild conditions and at relatively low temperatures, by a condensation reaction with amines.[17] General chemistry of this process showed a two-step reaction, with intermediate formation of an amino alcohol and final elimination of water.[18] Thus, in order to obtain the desired anil, excess of a suitable anhydrous organic solvent is generally used for azeotropic elimination of water from the system,[17] usually through a Dean–Stark device. In a completely different approach, we attempted the synthesis of a wide range of imine derivatives, in water and in the absence of any catalyst or buffering mixture. As starting materials we used aromatic, heteroaromatic and aliphatic aldehydes together with aliphatic and aromatic amines (the ketone series and other pseudo-keto compounds will undergo further investigations in the following step of our research).

In the first series of experiments, we studied the occurrence of aryl-aryl-and aryl-alkyl-imines (Tables 1 and 2). The crude reaction products were submitted to GC-MS and NMR analyses. Both analysis methods showed a high purity (with few exceptions) for the reaction product. Therefore, we used the same experimental procedure for all the experiments yielding monoimines. The yields are quite acceptable for a condensation process that occurs in aqueous conditions, exception being made for some halogeno-substituted anilines, especially in the *ortho*-position. On the other hand, the formation of the -CH=N- double bond decreased when using aliphatic amines > aromatic amines > substituted aromatic amines (especially *ortho*—see entries 2, 7 and 8 in Table 2). Good yields of imine formation, even at shorter reaction times, were observed in the case of heteroaryl carbaldehydes, either with aromatic or aliphatic amines.

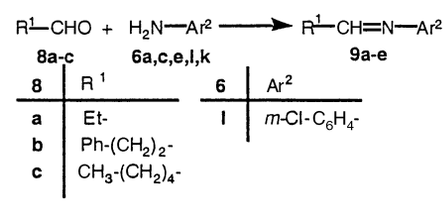
When solid imines formed in some of the reactions mentioned in Table 2 (for example entries 3, 10, 11, 13, 17, 18) the

Table 2 Reaction of aromatic aldehydes with aromatic amines



Run	4	6	7 (Yield, %)
1	**a**	**a**	**a** (97)
2	**a**	**b**	**b** (21)
3	**a**	**c**	**c** (48)
4	**a**	**d**	**d** (58)
5	**a**	**e**	**e** (32)
6	**a**	**f**	**f** (80)
7	**a**	**g**	**g** (63)
8	**a**	**h**	**h** (16)
9	**a**	**i**	**i** (80)
10	**a**	**j**	**j** (94)
11	**b**	**a**	**k** (72)
12	**c**	**a**	**l** (87)
13	**d**	**a**	**m** (78)
14	**f**	**a**	**n** (80)
15	**g**	**k**	**o** (58)
16	**h**	**a**	**p** (69)
17	**i**	**a**	**q** (94)
18	**j**	**a**	**r** (95)

Table 3 Reaction of aliphatic aldehydes with aromatic amines

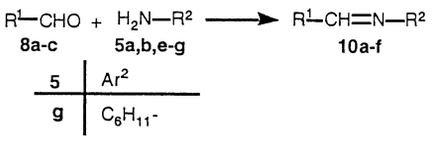


Run	8	6	9 (Yield, %)
1	**a**	**a**	**a** (45)
2	**a**	**c**	**b** (38)
3	**a**	**k**	**c** (33)
4	**b**	**l**	**d** (61)
5	**c**	**e**	**e** (36)
6	**c**	**j**	**f** (44)

imines precipitated directly from the aqueous solution. Thus, the extraction step used for the separation of the imine from the aqueous media can be avoided and the synthesis can be regarded as one 'completely performed in aqueous media' (see also part B). The second step of our investigation was the study of alkyl-alkyl- and alkyl-aryl imines (Tables 3 and 4). In this case, although the corresponding imines are formed in reasonable proportions, the yields are lower, even if reaction times are longer. This is probably because of the volatility of the starting materials and the formation of side-products such as dimers or polymers, as a result of an aldol-type condensation or of a polycondensation reaction.[19]

In order to study the influence of a modified emulsion system, some binary systems water—organic solvent (1 : 1) were used. As solvents we chose ethanol, dichloromethane or benzene (mixed in different proportions with water) and for the

Table 4 Reaction of aliphatic aldehydes with aliphatic amines



Run	8	5	10 (Yield, %)
1	**a**	**e**	**a** (72)
2	**a**	**g**	**b** (45)
3	**b**	**g**	**c** (71)
4	**b**	**f**	**d** (65)
5	**c**	**b**	**e** (53)
6	**c**	**a**	**f** (51)

sake of comparison we also performed the same reactions in pure benzene. In all these experiments, the stoichiometry was 10 mmol aldehyde : 10 mmol amine : 7.5 mL water : 7.5 mL organic solvent. Reactions in pure water or in pure benzene were carried out in 15 mL of solvent. All reactions were performed at room temperature. Solvent-modified emulsions didn't seem to be more effective than simple water. On the other hand, except for the cases when yields are comparatively the same, the addition of an organic solvent to the starting reaction mixture lowered the yields. Marvel and co-workers revealed a similar result for a polycondensation reaction involving the formation of a poly-Schiff base from *o*-phenylenediamine or hydrazine and 5,5′-methylenedisalicylaldehyde or disalicylaldehyde-5,5′-sulfone.[20] The compounds synthesized by Marvel and co-workers were used as chelating agents for nickel and cadmium salts. Thus, our attention was very soon attracted toward synthesis of such diimines that could function as possible chelating reagents for metallic cations.

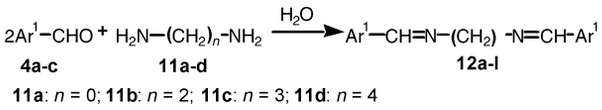
B. Open-chain and macrocyclic diimines

Most of the examples of diimines encountered in the literature were considered as chelating compounds. For example, Horrocks and co-workers prepared ethylene and trimethylene diimines of tolualdehydes and the corresponding Ni^{II} complexes in a boiling *n*-butyl alcohol solution.[21] Salicylaldehyde diimines with ethylene-, hexamethylene- or *o*-phenylene-diamine were used for complexation of Ir or Rh salts.[22] In this case, the diimines were obtained by boiling stoichiometric amounts of aldehydes and diamines in methanol. Ethylene and trimethylene diimines of salicylaldehyde, obtained by condensation in boiling absolute benzene or absolute methanol, were used in the formation of some Ge derivatives.[23] A report from 1975 presented the synthesis of some Zn complexes of salicylaldehyde and ethylenenediamine or 1,3-diaminopropane in an aqueous solution.[24]

Surprisingly, all the papers dealing with the formation of such diimines treated them especially as complexing reagents, with no physical description of the diimine molecule itself (mp, NMR or MS data). Moreover, even if these diimines were used as chelating reagents, only one attempt[24] has been made to obtain the complex diimine–metal cation directly in aqueous solution. In this case, the Zn ion in the buffered reaction mixture is considered to function by effectively reducing the condensation reaction from a second-order to a first-order process. The term *promnastic* (matchmaker) was applied to this effect.[25]

In our work, we performed the condensation reaction of benzaldehyde **4a**, anisaldehyde **4b** and salicylaldehyde **4c** with hydrazine, ethylene-, trimethylene- and tetramethylenediamine, in water, at room temperature and without any catalyst (Scheme 2).

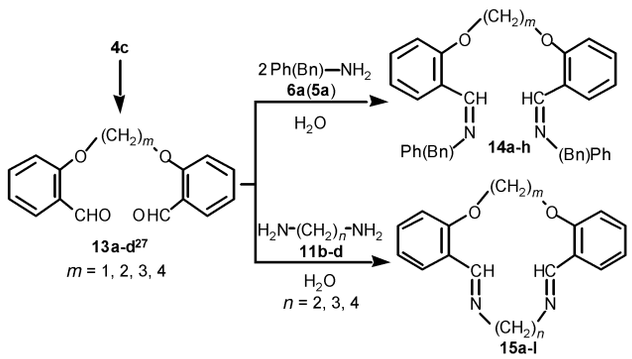
The diimines were very soon formed and readily precipitated in the reaction flask, after a few minutes of stirring. Direct



Scheme 2

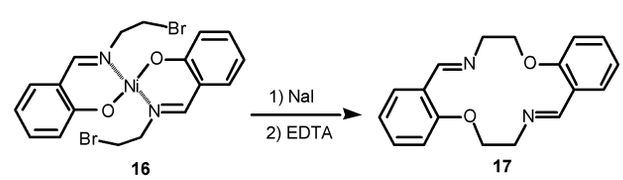
filtration and drying permitted the isolation of the pure diimine, in very good yields. For example, on comparing the yield of the benzaldehyde azine synthesis by the classical method as described in *Organic Synthesis*[26] and the yield of the same azine formation by direct condensation, in water, the difference is quite small (91–94%[26] compared with 89% – see Experimental section).

Recently, we focused our research on the intramolecular reductive coupling reaction of some aromatic dialdehydes **13**.[27] Such dialdehydes seemed to be suitable starting materials for the synthesis of open-chain or macrocyclic diimines (Scheme 3).



Scheme 3

Scrutinizing the chemical literature, we found out that a small number of such cyclic diimines had already been obtained by the usual method of boiling stoichiometric amounts of diamine and dialdehyde in methanol.[28,29] Thus, compounds with *m*, *n* = 2, 3 were directly submitted to reduction with $NaBH_4$, generally without isolation or characterization of the diimines, and the diamine was used as a nitrogen–oxygen donor macrocyclic ligand.[28,29] There are many more examples of diamines than diimines that are used as macrocyclic donor ligands. Nevertheless, macrocyclic diimines of type **15**, with *m* = 2 and instead of $(CH_2)_n$ having the moiety $-(CH_2)_2N(CH_3)(CH_2)_2-$ proved to be effective in complexation of the Mo cation.[30] The complex was formed directly by mixing the dialdehyde, the diamine and a Mo salt in refluxing toluene. Beside the macrocyclic diimines obtained by Lindoy and co-workers,[28,29] only one other diimine macrocylic ligand, **17**, with similar structure, was previously reported[31] (see Scheme 4).



Scheme 4

Starting from bridged dialdehydes **13a**–**d**, in a series of preliminary experiments, we attempted the synthesis of some open-chain diimines, in aqueous solution. We selected aniline and benzylamine as amine partners in the condensation process. The reactions were carried out under the same protocol: mixing both reagents in water and stirring for 4 h at room temperature. After filtration and drying, the crude material was submitted to NMR analysis.

The NMR spectra of crude reaction products showed, with few exceptions, a high purity of the target molecule, confirming

that the 1 : 2 dialdehyde : amine stoichiometry and the simple reaction conditions are very effective for diimines synthesis. The exceptions mentioned presented small supplementary signals in the C*H* = N region (δ 8.70–8.90), generally at lower values of δ, which we presumed to belong to the monoimine compounds. In order to clear the affiliation of the small supplementary signals, we tried the same reactions with a 1 : 1 stoichiometry of dialdehyde : amines. For example, in the case of *o*,*o*′-tetramethylenebis(salicylideneaniline) **14g**, there are in the crude reaction product NMR spectrum two signals in the CH=N area, one at δ 8.90 and the second at δ 8.88, in the ratio 1.00 : 0.04; when performing the same reaction with 1 : 1 stoichiometry, the signal at δ 8.88 is highly increased. Nevertheless, the ratio between the main CH = N signal (of the diimine) and the secondary signal (for monoimine) never exceeded 1.00 : 0.05. Incidentally, we also found that the reaction time can be shortened to 2 h if the reaction is carried out in boiling water.

The reactions leading to the macrocyclic diimines occurred under almost the same conditions, although in this case better yields were obtained if working in boiling water. As previously mentioned, some of these diimines were prepared *in situ* and submitted directly to further reduction, by Lindoy and co-workers, to the diamine structures as macrocyclic ligands (*m*, *n* = 2, 3).[28,29] Therefore we used the abbreviations proposed by Lindoy, which seemed very clear and convenient, and can be adapted to the other compounds that we synthesized.

Along with the main reaction products, the diimines, one or two secondary reaction products were sometimes formed in this process, as a result of a polycondensation reaction. Thus, the NMR spectra of some crude reaction products presented in the region δ 8.60–8.80 two or three signals, which we assumed to come either from the monoimine (since there still is a carbaldehyde signal around δ 10.50) or from an oligomeric structure (in spite of the fact that we worked at high dilution, we couldn't eliminate the possibility of a polycondensation reaction). Indeed, according to Krassig and Greber[32] the *para*-isomer of **13a** in reaction with **11b**, **11c** or **11d** in anhydrous diethyl ether, for at least two days, yielded several open-chain oligomers with a degree of polymerization up to 10.

Although for the single imine that is described by NMR[28a] (O-tn-N-tn, **15h**) there were two distinct signals reported for the two CH=N groups (Lindoy and co-workers[28a] reported for **15h** two singlets: δ 8.66 and 8.70), our recrystallized **15h** showed only one singlet, at δ 8.66. In fact, samples taken from the crude reaction mixtures and purified by recrystallization or by Kugelrohr distillation, presented in their NMR spectra only one signal for the CH=N protons, in the diimine compounds. GC-MS and MS analyses eliminated the possibility of monoimine formation. Thus, secondary products were oligomers. There are two possibilities for the structure of oligomeric products: open-chain or macrocyclic. Analysis by mass spectra of the mixtures presenting at least two NMR signals in the area δ 8.60–8.80 showed mostly cyclic dimers as secondary reaction products (the third NMR signal, according also to MS, could be attributed to an open-chain dimer). It is interesting to note that almost all dimeric structures (open-chain or cyclic) showed higher chemical shifts for CH=N protons and for some aliphatic protons (especially protons from the C directly connected to the hetero-atom – O or N); similarly, aromatic signals for the proton in *ortho*-positions from the CH=N bond are deshielded. For example, if the signal for the CH=N protons of the cyclic diimine usually appear around δ 8.66 (see Experimental section), the dimers present a δ-value >8.70 ppm (δ 8.82 for O-tn-N-en **15g**, δ 8.74 for O-tn-N-bn **15i**, δ 8.70 for O-tn-N-tn **15h**, δ 8.84 for O-en-N-bn **15f**, δ 8.68 for O-en-N-en **15d** or 8.73 for O-bn-N-bn **15l**).5

Unfortunately, in some cases, the macrocyclic diimines couldn't be completely separated from oligomeric compounds, either by recrystallization or by column chromatography (when hydrolysis of imine compound occurred). Even small amounts of oligomer accompanying the diimine prevented it from crystallizing. Nevertheless, in these cases, the NMR spectra of the crude reaction products and GC-MS or MS analyses were a thorough confirmation of the diimine structure. For a complete proof of the cyclic structure, we performed the reduction of some cyclic diimines with $NaBH_4$,[28,29] the cyclic diamines that were formed presenting spectral and physical data identical with those collected from the literature.[28]

Table 5 Abbreviations used

m	*n*	Abbreviation	Cmpd
1	2	O-mn-N-en	**15a**
1	3	O-mn-N-tn	**15b**
1	4	O-mn-N-bn	**15c**
2	2	O-en-N-en[28,29]	**15d**
2	3	O-en-N-tn[28,29]	**15e**
2	4	O-en-N-bn	**15f**
3	2	O-tn-N-en[28,29]	**15g**
3	3	O-tn-N-tn[28,29]	**15h**
3	4	O-tn-N-bn	**15i**
4	2	O-bn-N-en	**15j**
4	3	O-bn-N-tn	**15k**
4	4	O-bn-N-bn	**15l**

Conclusions

Synthesis of imines in completely aqueous media is effective without using any catalyst or buffered solution for a wide range of aromatic, aliphatic or heteroaromatic aldehydes in reaction with aromatic or aliphatic amines. The best results were obtained in the case of monoimines coming from aromatic – including also heteroaromatic – aldehydes and aliphatic and aromatic amines (when unsubstituted in the *ortho*-position). Room temperature proved to be convenient enough for the condensation process to take place. This condensation process can be applied to the synthesis of diimines, both open-chain and macrocyclic. Both diamines (in reaction with monoaldehydes) and dialdehydes (reacting with monoamines) afforded good yields in the condensation reactions, even at room temperature. Only in the last case, and occasionally, were small amounts of monoimines recorded as side products. Macrocyclic diimines, compounds that can be used as ligands as previously mentioned in the chemical literature, were obtained in good yields, in some cases the presence of dimers (but no monoimine) being detected. So, in our view, when imine compounds (especially common ones) are desired, before using classical methods (such as azeotropic distillation, molecular sieves, *etc.*) the convenient method that requires only water and room temperature is worth trying.

Experimental

Distilled water was used in all experiments. Aldehydes (with the exception of dialdehydes **13a**–**d**) and amines used as starting materials were purchased from chemical companies and were purified before use (when needed). Mps were determined on a Yanaco Micro Melting-Point Apparatus and are uncorrected. All NMR spectra were recorded on a JEOL JNM-LA 300, 300 MHz, for samples in $CDCl_3$ with Me_4Si as internal standard. Coupling constants (*J*-values) are given in Hz. Identification of monoimines was made by GC (Shimadzu GC-17A GC instrument, carrier gas N_2, pressure 135 kgf cm^{-2}, † flow 55 mL min^{-1} on a J&W Scientific DB-1 fused silica capillary column, length 30 m, I.D. 0.32 mm with film thickness of 0.25 mm) and GC-MS (Hewlett-Packard HP6890 GC, carrier gas He, flow 1.5 mL min^{-1}, velocity 48 cm s^{-1} and pressure 10.3 psi, J&W Scientific DB-1 fused silica capillary column and JEOL – Automass

† 1kgf = 9.806 N.

system II MS). Mass spectra and high-resolution mass spectra were recorded on a JEOL JMS-700T, with 45 eV ionization energy and 600 μA current.

General procedure for the synthesis of monoimines 3, 7, 9, 10

In a standard procedure, in a three-necked round-bottom flask equipped with a mechanical stirrer and, optionally, with a reflux condenser, were introduced 10 mmol of carbonyl compound and 15 mL of water. The amine (10.0 mmol) was added in one portion and the flask was kept at room temperature under vigorous mechanical stirring for 2 h for aryl-aryl and aryl-alkyl imines, and for 3 h for alkyl-aryl and alkyl-alkyl imines. If no precipitation occurred, the aqueous mixture was extracted twice with dichloromethane. The crude precipitate (when formed) was analyzed by GC-MS and NMR. In case of extraction, combined organic layers were dried over $MgSO_4$. The organic solvent was evaporated off and the residue was analyzed by GC-MS and NMR. All synthesized imines presented the same retention times, corresponding mps or bps, and identical NMR spectra as authentic samples (Aldrich or Sigma – when available – or obtained by the classic method of Dean–Stark azeotropic distillation).

***N*-Salicylideneaniline 7.** (1.72 g, 87%): yellow needles (from hexane), mp 50–51 °C (lit.,[33] 51 °C); δ_H 6.92–7.09 (2H, m, ArH), 7.25–7.45 (m, 7H, ArH), 8.62 (1H, s, CH=N), 13.27 (1H, s, OH); δ_C 117.2, 119.0, 119.2, 121.1, 126.9, 129.4, 132.3, 133.1, 148.5 (C^{ar}-N), 161.1 (C^{ar}-OH), 162.7 (CH=N); *m*/*z* 197 (100, M^+), 180 (17, $M^+ - HO$), 120 (22, $M^+ - Ph$), 77 (66).

***N*-Salicylidenebenzylamine 3g.** (1.79 g, 85%) lemon yellow plates (from hexane), mp 29–30 °C; δ_H 4.77 (2H, s, CH_2), 6.83–6.97 (2H, m, ArH), 7.21–7.36 (7H, m, ArH), 8.39 (1H, s, CH=N), 13.41 (1H, s, OH); δ_C 63.2 (CH_2), 117.0, 118.6, 118.8, 127.3, 127.8, 127.9, 128.7, 131.4, 132.4, 138.2 (C^{ar}-CH_2-N), 161.1 (C^{ar}-OH), 165.6 (CH=N); *m*/*z* 211 (29, M^+), 194 (4, $M^+ - HO$), 120 (7, $M^+ - PhCH_2$), 91 (100).

General procedure for the synthesis of dialdehydes 13

In a 500 mL 3-necked round-bottom flask provided with reflux condenser were introduced 12.2 g (0.1 mol) salicylaldehyde in 10 mL of EtOH and 200 mL of 2% aq. NaOH (0.1 mol NaOH). After 15 min of stirring, a solution of 0.05 mol of the corresponding dibrominated compound dissolved in 150 mL of EtOH was added in one portion. The mixture was magnetically stirred, under reflux, for 72 h. The reaction mixture was cooled and kept for 24 h on ice. The dialdehyde slowly precipitated. After filtration and drying *in vacuo* the crude dialdehydes were recrystallized from EtOH or P^irOH. All these compounds have been described elsewhere.[27]

General procedure for the synthesis of open-chain diimines 12, 14

In a standard procedure, in a 100 mL round-bottom flask equipped with a reflux condenser were introduced 20 mmol of dialdehyde or 0.1 mol of aldehyde and 30 mL of water. The amine (40 mmol) or diamine (0.05 mol) was added in one portion and the flask was kept at room temperature under vigorous magnetic stirring for 2 h in the case of diimines **12** and at room temperature for 4 h or under reflux for 2 h for diimines **14**. Diimines **12** were separated by direct filtration while most of the diimines **14** needed extraction. The crude reaction products were analyzed by NMR and GC-MS, MS and high-resolution MS. When needed, further purification by recrystallization was performed.

***N,N′*-Ethylenebis[benzylidenealdimine] 12b.** (1.93 g, 82%): very light yellow prisms (from hexane), mp 52–53 °C (lit.,[34] 52–53 °C); δ_H 3.96 [4H, s, $=N(CH_2)_2N=$], 7.33–7.39 (6H, m, ArH), 7.62–7.70 (4H, m, ArH), 8.26 (2H, s, 2 × CH=N); δ_C 61.6 (N-C-C-N), 128.1, 128.5, 130.5, 136.1 (C^{ar}-CH=), 162.6 (CH=N); *m*/*z* 236 (1, M^+), 132 (63, $M^+ - PhCH=N$), 118 (28, $M^+ - PhCH=NCH_2$), 104 [70, $M^+ - Ph\text{-}CH=N\ (CH_2)_2$], 91 (100).

***N,N′*-Trimethylenebis[benzylidenealdimine] 12c.** (2.22 g, 89%) white prisms (from hexane), mp 82–83 °C; δ_H 2.15 (2H, quintet, *J* 6.9, $=NCH_2CH_2CH_2N=$), 3.72 (4H, t, *J* 6.9, $=NCH_2CH_2CH_2N=$), 7.39–7.42 (6H, m, ArH), 7.71–7.74 (4H, m, ArH), 8.30 (2H, s, 2 × CH=N); δ_C 31.9 (N-C-*C*-C-N), 59.2 (N-*C*-C-*C*-N), 127.8, 128.5, 129.4, 130.5, 136.2 (C^{ar}-CH=), 161.3 (CH=N); *m*/*z* 250 (1, M^+), 146 (35, $M^+ - PhCH=N$), 132 (56, $M^+ - PhCH=NCH_2$), 118 [100, $M^+ - PhCH=N(CH_2)_2$], 91 (42).

***N,N′*-Tetramethylenebis[benzylidenealdimine] 12d.** (2.11 g, 80%) white prisms (from hexane), mp 41 °C (lit.,[33] 41–42 °C); δ_H 1.76–1.80 (4H, m, $=NCH_2CH_2CH_2CH_2N=$), 3.61–3.65 (4H, m, $=NCH_2CH_2CH_2CH_2N=$), 7.34–7.37 (6H, m, ArH), 7.68–7.71 (4H, m, ArH), 8.23 (2H, s, 2 × CH=N); δ_C 28.5 (N-C-*C*-*C*-C-N), 61.3 (N-*C*-C-C-*C*-N), 127.8, 128.1, 128.6, 129.0, 130.3, 136.0 (C^{ar}-CH=), 160.7 (CH=N); *m*/*z* 264 (1, M^+), 159 (100, $M^+ - PhCH=N$), 132 [13, $M^+ - PhCH=N(CH_2)_2$], 91 (93).

***N,N′*-Ethylenebis[*p*-methoxybenzylidenealdimine] 12f.** (2.54 g, 86%) light yellow pellets (from hexane–EtOH), mp 112–113 °C; δ_H 3.81 (6H, s, 2 × OCH_3), 3.91 [4H, s, $=N(CH_2)_2N=$], 7.26 (8H, dd, J_{AB} 23.0 and 8.7, 2 × ArH), 8.16 (2H, s, 2 × CH=N); δ_C 55.3 (N-C-C-N), 61.7 (2 × OCH_3), 113.8, 129.1, 129.6, 161.5 (C^{ar}-O), 161.9 (CH=N); *m*/*z* 296 (1, M^+), 163 (95, $M^+ - CH_3OC_6H_4CH=N$), 135 [76, $M^+ - CH_3OC_6H_4CH=N\text{-}(CH_2)_2$], 121 [100, $M^+ - CH_3OC_6H_4CH=N\ (CH_2)_2N=$].

***N,N′*-Trimethylenebis[*p*-methoxybenzylidenealdimine] 12g.** (2.57 g, 83%) colorless pellets (from hexane–EtOH), mp 74–76 °C; δ_H 2.09 (2H, quintet, *J* 6.8, $=NCH_2CH_2CH_2N=$), 3.69 (4H, t, *J* 6.8, $=NCH_2\text{-}CH_2CH_2N=$), 3.83 (6H, s, 2 × OCH_3), 7.26 (8H, dd, J_{AB} 24.6 and 8.7, 2 × ArH), 8.21 (2H, s, 2 × CH=N); δ_C 32.0 (N-C-*C*-C-N), 55.3 (N-*C*-C-*C*-N), 59.1 (OCH_3), 113.8, 129.2, 129.5, 160.5 (C^{ar}-O), 161.4 (CH=N); *m*/*z* 310 (2, M^+), 176 (48, $M^+ - CH_3OC_6H_4CH=N$), 162 (61, $M^+ - CH_3OC_6H_4CH=NCH_2$), 148 [100, $M^+ - CH_3OC_6H_4\text{-}CH=N(CH_2)_2$], 134 [23, $M^+ - CH_3OC_6H_4CH=N(CH_2)_3$], 120 [26, $M^+ - CH_3OC_6H_4CH=N(CH_2)_3N=$].

***N,N′*-Tetramethylenebis[*p*-methoxybenzylidenaldimine] 12h.** (2.43 g, 75%): white prisms (hexane–EtOH), mp 116–117 °C; δ_H 1.73–1.78 (4H, m, $=NCH_2CH_2CH_2CH_2N=$), 3.71–3.75 (4H, m, $=NCH_2CH_2CH_2CH_2N=$), 3.83 (6H, s, 2 × OCH_3), 7.26 (8H, dd, J_{AB} 8.7 and 23.2, ArH), 8.15 (2H, s, 2 × CH=N); δ_C 28.8 (N-C-*C*-*C*-C-N), 55.3 (N-*C*-C-C-*C*-N), 61.4 (OCH_3), 113.9, 114.2, 129.2, 129.5, 131.9, 160.2 (CH=N), 161.4 (C^{ar}-O); *m*/*z* 324 (1, M^+), 189 (100, $M^+ - CH_3OC_6H_4CH=N$), 162 [15, $M^+ - CH_3OC_6H_4CH=N(CH_2)_2$], 134 [36, $M^+ - CH_3OC_6H_4\text{-}CH=N(CH_2)_4$], 91 (21).

***N,N′*-Ethylenebis[salicyldinealdimine] 12j.** (2.17 g, 81%): lemon yellow plates (from hexane–MeOH), mp 130–131 °C (lit.,[22] 139 °C); δ_H 3.92 [4H, s, $=N(CH_2)_2N=$], 6.82–6.94 (4H, m, ArH), 7.20–7.29 (4H, m, ArH), 8.34 (2H, s, 2 × CH=N), 13.21 (2H, s, 2 × OH); δ_C 59.8 (CH_2), 117.0, 118.6, 118.7, 131.5, 132.4, 161.0 (C^{ar}-OH), 166.6 (CH=N); *m*/*z* 268 (35, M^+), 147 (52, $M^+ - HOC_6H_4CH=N$), 107 (100).

***N,N′*-1,3-Trimethylenebis[salicylidenealdimine] 12k.** (2.37 g, 84%): lemon yellow plates (from hexane), mp 52–53 °C (lit.,[23] 52 °C); δ_H 2.11 (2H, quintet, *J* 6.6, $=NCH_2CH_2CH_2N=$), 3.71 (4H, t, $=NCH_2CH_2CH_2N=$), 6.85–6.97 (4H, m, ArH), 7.22–7.34 (4H, m, ArH), 8.37 (2H, s, 2 × CH=N), 13.44 (2H, s, OH);

δ_C 31.6 (C-*C*-C), 56.8 (*C*-C-*C*), 116.9, 118.6, 118.7, 131.2, 132.2, 161.0 (C^{ar}-OH), 165.4 (CH=N); *m*/*z* 282 (16, M^+), 148 (100, $M^+ - HOC_6H_4CH{=}NCH_2$), 134 [86, $M^+ - HOC_6H_4CH{=}N(CH_2)_2$)].

***N,N′*-1,4-Tetramethylenebis[salicylidenealdimine] 12l.** (2.37 g, 80%): lemon yellow plates (from hexane), mp 89–90 °C; δ_H 1.79 (4H, s, $=NCH_2CH_2CH_2CH_2N=$), 3.64 (4H, s, $=NCH_2CH_2CH_2CH_2N=$), 6.84–6.96 (4H, m, ArH), 7.22–7.32 (4H, m, ArH), 8.35 (2H, s, 2 × CH=N), 13.52 (2H, s, OH); δ_C 28.5 (C-*C*-*C*-C), 59.2 (*C*-C-C-*C*), 116.9, 118.5, 118.7, 131.1, 132.1, 161.1 (C^{ar}-OH), 164.8 (CH=N); *m*/*z* 296 (34, M^+), 175 (100, $M^+ - HOC_6H_4CH{=}N$).

***O,O′*-Methylenebis(salicylideneaniline) 14a.** (0.7 g, 87%): white prisms (from hexane), mp 89–91 °C (lit.,[35] 88.5–90 °C); δ_H 5.91 (2H, s, OCH_2O), 7.10–7.48 (16H, m, ArH), 8.15–8.18 (2H, dd, *J* 7.8 and 1.6, ArH), 8.81 (2H, s, 2 × CH=N); δ_C 91.7 (O-C-O), 115.1, 120.9, 123.1, 125.8, 126.0, 127.9, 129.1, 132.7, 152.4 (C^{ar}-N=), 155.8 (CH=N), 156.8 (C^{ar}-O); *m*/*z* 406 (5, M^+), 376 (57), 210 (100, $M^+ - PhN{=}CHC_6H_4O$), 196 (89, $M^+ - PhN{=}CHC_6H_4OCH_2$).

***O,O′*-Methylenebis(salicylidenebenzylamine) 14b.** (0.77 g, 89%): white needles (from hexane), mp 55–57 °C; δ_H 4.74 (4H, s, 2 × ArCH_2 from N=), 5.87 (2H, s, OCH_2O), 7.07–7.44 (16H, m, ArH), 8.02–8.06 (2H, dd, *J* 7.7 and 1.4, ArH), 8.74 (2H, s, 2 × CH=N); δ_C 65.4 (Ar-*C*-N=), 65.8 (Ar-*C*-N=), 91.8 (O-C-O), 115.1, 122.9, 126.0, 126.8, 127.8, 127.9, 128.4, 131.9, 139.4, 156.5 (C^{ar}-O), 157.4 (CH=N); *m*/*z* 434 (1, M^+), 404 (1), 343 (65, $M^+ - PhCH_2$), 211 (63, $M^+ - PhCH_2N{=}CHC_6H_4OCH_2$), 91 (100).

***O,O′*-Ethylenebis(salicylideaniline) 14c.** (0.6 g, 72%): white prisms (from hexane–EtOH), mp 143–145 °C (lit.,[35,36] 128–150 °C); δ_H from 4.46 (4H, s, OCH_2CH_2O), 6.99–7.45 (16H, m, ArH), 8.12–8.15 (2H, dd, *J* 7.7 and 1.7, ArH), 8.84 (2H, s, 2 × CH=N); δ_C 67.4 (O-C-C-O), 112.6, 115.2, 121.1, 121.7, 125.3, 125.8, 127.9, 129.1, 129.4, 132.8, 152.7 (C^{ar}-N=), 156.2 (CH=N), 158.6 (C^{ar}-O); *m*/*z* 420 (16, M^+), 390 (18), 343 (87, $M^+ - Ph$), 224 (31, $M^+ - PhN{=}CHC_6H_4O$), 197 (100, $M^+ - PhN{=}CHC_6H_4OCH_2$).

***O,O′*-Ethylenebis(salicylidenebenzylamine) 14d.** (0.54 g, 65%): white plates (from hexane–$CHCl_3$ 99 : 1), mp 107–108 °C; δ_H 4.44 (4H, s, OCH_2CH_2O), 4.74 (4H, s, 2 × ArCH_2N=), 6.97–7.04 (4H, m, ArH), 7.20–7.29 (10H, m, ArH), 7.37–7.42 (2H, ddd, *J* 8.8, 1.7 and 0.9, ArH), 8.03–8.06 (2H, dd, *J* 7.7 and 1.7, ArH), 8.79 (2H, s, 2 × CH=N); δ_C 65.3 (Ar-*C*-N=), 67.2 (O-C-C-O), 112.4, 121.5, 125.1, 126.8, 127.7, 127.9, 128.3, 131.9, 139.5, 157.6 (CH=N), 157.9 (C^{ar}-O-); *m*/*z* 448 (10, M^+), 357 (100, $M^+ - PhCH_2$), 211 [40, $M^+ - PhCH_2N{=}CHC_6H_4O(CH_2)_2$], 91 (54).

***O,O′*-Trimethylenebis(salicylideaniline) 14e.** (0.77 g, 89%): very light yellow prisms (from Et_2O), mp 85–87 °C (lit.,[35] 86–87 °C); δ_H 2.36 (2H, t, *J* 6.0, $CH_2CH_2CH_2$), 4.27 (4H, t, *J* 6.0, $CH_2CH_2CH_2$), 6.94–7.24 (16H, m, ArH), 8.12–8.15 (2H, dd, *J* 7.7 and 1.7, ArH), 8.88 (2H, s, 2 × CH=N); δ_C 29.1 (C-*C*-C), 64.8 (*C*-C-*C*), 112.1, 120.9, 121.1, 124.8, 125.6, 127.7, 129.1, 132.7, 152.8 (C^{ar}-N=), 156.2 (CH=N), 158.6 (C^{ar}-O); *m*/*z* 434 (38, M^+), 357 (100, $M^+ - Ph$), 237 (26, $M^+ - PhN{=}CHC_6H_4O$), 197 [24, $M^+ - PhN{=}CHC_6H_4O(CH_2)_3$), 77 (17).

***O,O′*-Trimethylenebis(salicylidenebenzylamine) 14f.** (0.76 g, 82%): white needles (from Et_2O), mp 53–55 °C; δ_H 2.18 (2H, quintet, *J* 6.0, $OCH_2CH_2CH_2O$), 4.05 (4H, t, *J* 6.0, $OCH_2CH_2CH_2CH_2O$), 4.66 (4H, s, 2 × ArCH_2N=), 6.75–6.87 (4H, m, ArH), 7.08–7.24 (12H, m, ArH), 7.90–7.93 (2H, dd, *J* 1.7 and 7.7, ArH), 8.69 (2H, s, 2 × CH=N); δ_C 29.0 (O-C-*C*-C-O), 64.8 (O-*C*-C-*C*-O), 65.2 (Ar*C*N=), 11.8, 112.2, 120.9, 124.6, 126.7, 127.4, 127.8, 127.9, 128.1, 128.2, 128.4, 130.6, 131.8, 139.4, 157.5 (CH=N), 157.8 (C^{ar}-O); *m*/*z* 462 (7, M^+), 371 (100, $M^+ - PhCH_2$), 266 (10, $M^+ - PhCH_2N{=}CHC_6H_4O$), 91 (36).

***O,O′*-Tetramethylenebis(salicylideaniline) 14g.** (0.77 g, 86%): white prisms (from MeOH–$CHCl_3$), mp 102–104 °C (lit.,[35] 103–104.5 °C); δ_H 2.05 (4H, quintet, *J* 5.3, $OCH_2CH_2CH_2CH_2O$), 4.13 (4H, t, *J* 5.3, $OCH_2CH_2CH_2CH_2O$), 6.90–7.05 (4H, m, ArH), 7.16–7.41 (12H, m, ArH), 8.12–8.15 (2H, dd, *J* 7.7 and 1.7, ArH), 8.90 (2H, s, 2 × CH=N); δ_C 26.1 (O-C-*C*-*C*-C-O), 67.9 (O-*C*-C-C-*C*-O), 111.9, 121.0, 121.1, 125.1, 125.7, 127.7, 129.1, 132.7, 152.9 (C^{ar}-N=), 156.3 (CH=N), 158.8 (C^{ar}-O); *m*/*z* 448 (52, M^+), 371 (100, $M^+ - Ph$), 252 (12, $M^+ - PhN{=}CHC_6H_4O$), 196 [28, $M^+ - PhN{=}CHC_6H_4O(CH_2)_4$].

***O,O′*-Tetramethylenebis(salicylidenebenzylamine) 14h.** (0.85 g, 89%): white prisms (from hexane–$CHCl_3$), mp 94–96 °C; δ_H 2.02 (4H, quintet, *J* 5.3, $OCH_2CH_2CH_2CH_2O$), 4.10 (4H, t, *J* 5.3, $OCH_2CH_2CH_2CH_2O$), 4.79 (4H, s, 2 × ArCH_2N=), 6.88–6.99 (4H, m, ArH), 7.21–7.37 (12H, m, ArH), 8.01–8.04 (2H, dd, *J* 7.7 and 1.7, ArH), 8.83 (2H, s, 2 × CH=N); δ_C 26.1 (O-C-*C*-*C*-C-O), 65.3 (Ar*C*N=), 67.7 (O-*C*-C-C-*C*-O), 11.8, 120.8, 124.7, 126.8, 127.5, 127.9, 128.4, 131.9, 139.5, 157.7 (CH=N), 158.1 (C^{ar}-O); *m*/*z* 476 (16, M^+), 385 (100, $M^+ - PhCH_2$), 280 (9, $M^+ - PhCH_2N{=}CHC_6H_4O$), 91 (32).

General procedure for the synthesis of macrocyclic diimines 15

In a standard procedure, into a 100 mL round-bottom flask equipped with a reflux condenser were introduced 10 mmol of dialdehyde in 30 mL of water. The diamine (10.0 mmol) was added in one portion and the flask was kept at reflux under vigorous magnetic stirring for 2 h. The aqueous solution was extracted twice with dichloromethane. Combined organic layers were dried on $MgSO_4$ and the organic solvent was evaporated off. The crude reaction products obtained after evaporation was analyzed by NMR, MS and high-resolution MS. When possible, further purification by recrystallization was performed.

14,15-Dihydrodibenzo[*d*,*l*][1,3,7,10]dioxadiazacyclotridecine (O-mn-N-en) 15a. (0.42 g, 76%): light yellow prisms (hexane–$CHCl_3$), mp 61–63 °C; δ_H 3.88 (4H, s, $=NCH_2CH_2N=$), 5.63 (2H, s, OCH_2O), 6.98–7.32 (6H, m, ArH), 7.89–7.92 (2H, dd, *J* 1.7 and 7.7, ArH), 8.59 (2H, s, 2 × CH=N); δ_C 59.2 (N-C-C-N), 98.6 (O-C-O), 114.8, 115.7, 117.9, 123.6, 128.5, 131.5, 159.0 (C^{ar}-O), 161.4 (CH=N); *m*/*z* 280 (8, M^+), 279 (4), 162 (7), 148 (6), 135 (100), 121 (3), 91 (5).

15,16-Dihydro-6*H*,14*H*-dibenzo[*d*,*m*][1,3,7,11]dioxadiazacyclotetradecine (O-mn-N-tn) 15b. (0.51 g, 87%): light yellow plates (from MeOH), mp 63–66 °C; δ_H 2.01 (2H, t, *J* 5.8, $=NCH_2CH_2CH_2N=$), 3.60 (4H, t, *J* 5.8, $=NCH_2CH_2CH_2N=$), 5.77 (2H, s, OCH_2O), 7.02–7.39 (6H, m, ArH), 7.92–7.95 (2H, dd, *J* 1.6 and 7.7, ArH), 8.60 (2H, s, 2 × CH=N); δ_C 27.0 (N-C-*C*-C-N), 58.6 (N-*C*-C-*C*-N), 97.8 (O-C-O), 118.3, 123.1, 123.9, 127.1, 127.5, 127.8, 131.8, 157.5 (C^{ar}-O), 158.6 (CH=N); *m*/*z* 294 (78, M^+), 293 (62), 266 (60), 162 (42), 148 (46), 134 (100), 91 (47).

14,15,16,17-Tetrahydro-6*H*-dibenzo[*d*,*n*][1,3,7,12]dioxadiazacyclopentadecine (O-mn-N-bn) 15c. (0.48 g, 79%); white prisms (from MeOH), mp 64–68 °C; δ_H 1.71 (4H, br s, $=NCH_2CH_2CH_2CH_2N=$), 3.58 (4H, br s, $=NCH_2CH_2CH_2CH_2N=$), 5.80 (2H, s, OCH_2O), 6.92–7.38 (6H, m, ArH), 7.94–7.97 (2H, dd, *J* 1.0 and 7.6, ArH), 8.61 (2H, s, 2 × CH=N); δ_C 28.6 (N-C-*C*-C-C-N), 61.7 (N-*C*-C-C-*C*-N), 91.6 (O-C-O), 114.7, 122.5, 122.8, 123.6, 126.9, 127.5, 128.5, 131.6, 156.1 (C^{ar}-O), 156.4 (CH=N); *m*/*z* 308 (9, M^+), 307 (13), 279 (15), 162 (16), 148 (11), 135 (100), 91 (19).

6,7,15,16-Tetrahydrodibenzo[*e*,*m*][1,4,8,11]dioxadiazacyclotetradecine (O-en-N-en) 15d. (0.38 g, 65%); white amorphous, mp 174–176 °C; δ_H 3.98 (4H, s, =NCH$_2$CH$_2$N=), 4.38 (2H, s, OCH$_2$CH$_2$O), 6.95–7.06 (4H, m, ArH), 7.33–7.39 (2H, ddd, *J* 1.7, 7.7 and 8.3, ArH), 7.65–7.68 (2H, dd, *J* 1.7 and 7.7, ArH), 8.58 (2H, s, 2 × CH=N); δ_C 59.1 (N-C-C-N), 66.6 (O-C-C-O), 114.2 122.0, 122.7, 128.8, 131.2, 157.3 (C^{ar}-O), 161.2 (CH=N); *m*/*z* 294 (24, M$^+$), 293 (17), 265 (9), 176 (100), 148 (77), 121 (67), 91 (45).

Tetrahydro-15*H*-dibenzo[*e*,*n*][1,4,8,12]dioxadiazacyclopentadecine (O-en-N-tn) 15e. (0.44 g, 71%): white prisms (dist. Kugel rohr 250 °C/0.1 Torr), mp 149–151 °C (lit.,[28a] 164 °C); δ_H 2.29 (2H, quintet, *J* 5.3, =NCH$_2$C*H*$_2$CH$_2$N=), 3.60 (4H, t, *J* 5.3, =NC*H*$_2$CH$_2$C*H*$_2$N=), 4.39 (4H, s, OCH$_2$CH$_2$O), 6.95–6.98 (2H, dd, *J* 8.3 and 0.6, ArH), 7.02–7.07 (2H, ddd, *J* 0.6, 7.4 and 8.3, ArH), 7.37–7.43 (2H, ddd, *J* 1.7, 7.4 and 8.3, ArH), 7.94–7.97 (2H, dd, *J* 1.7 and 7.4, ArH), 8.72 (2H, s, 2 × CH=N); δ_C 28.5 (N-C-*C*-C-N), 57.9 (N-*C*-C-*C*-N), 68.0 (O-*C*-*C*-O), 113.5, 121.7, 125.6, 127.0, 128.7, 131.7, 135.9, 158.6 (C^{ar}-O), 158.8 (CH=N); *m*/*z* 308 (19, M$^+$), 307 (33), 279 (24), 190 (43), 162 (100), 148 (16), 134 (73), 107 (99), 91 (63).

6,7,15,16,17,18-Hexahydrodibenzo[*e*,*o*][1,4,8,13]dioxadiazacyclohexadecine (O-en-N-bn) 15f. (0.42 g, 66%); light yellow prisms (from MeOH–CHCl$_3$), mp 59–61 °C; δ_H 1.69–1.75 (4H, t, *J* 5.2, =NCH$_2$C*H*$_2$C*H*$_2$CH$_2$N=), 3.70–3.73 (4H, t, *J* 5.2, =NC*H*$_2$CH$_2$CH$_2$C*H*$_2$N=), 4.43 (4H, s, OCH$_2$CH$_2$O), 6.90–7.03 (4H, m, ArH), 7.31–7.39 (2H, m, ArH), 7.88–7.92 (2H, dd, *J* 1.8 and 7.7, ArH), 8.63 (2H, s, 2 × CH=N); δ_C 26.4 (N-C-*C*-*C*-C-N), 58.9 (N-*C*-C-C-*C*-N), 66.1 (O-*C*-*C*O), 113.0, 121.8, 126.0, 127.5, 127.6, 131.6, 157.0 (C^{ar}-O), 158.1 (CH=N); *m*/*z* 322 (21), 321 (32), 293 (50), 253 (100), 204 (67), 176 (21), 148 (46), 121 (87), 91 (25).

7,8,16,17-Tetrahydro-6*H*-dibenzo[*f*,*n*][1,5,9,12]dioxadiazacyclopentadecine (O-tn-N-en) 15g. (Literature data[28,29] gave a general experimental method for the *in situ* generation of the ligand but no physical data for this compound; only the final Ni complex is characterized.) (0.41 g, 66%): δ_H 2.16 (2H, t, *J* 6.0, OCH$_2$C*H*$_2$CH$_2$O), 3.93 (4H, s, =NCH$_2$CH$_2$-N=), 4.10 (4H, t, *J* 6.0, OC*H*$_2$CH$_2$C*H*$_2$O), 6.83–9.95 (4H, m, ArH), 7.26–7.32 (2H, m, ArH), 7.89–7.91 (2H, dd, *J* 1.1 and 7.2, ArH), 8.68 (2H, s, 2 × CH=N); δ_C 29.3 (O-C-*C*-CO), 58.6 (N-*C*-*C*-N), 68.7 (O-*C*-C-*C*O), 112.9, 120.9, 121.2, 125.6, 127.4, 128.1, 131.8, 136.0, 157.8 (C^{ar}-O), 158.9 (CH=N); *m*/*z* 308 (4, M$^+$), 307 (6), 284 (45), 162 (50), 148 (24), 135 (63), 121 (100), 91 (32).

7,8,17,18-Tetrahydro-6*H*,16*H*-dibenzo[*f*,*o*][1,5,9,13]dioxadiazacyclohexadecine (O-tn-N-tn) 15h. (0.53 g, 82%); white prisms (from hexane–CHCl$_3$), mp 128–30 °C (lit., [28a] 129 °C); δ_H 2.24–2.29 (4H, 2 superimposed quintets, *J* 5.0 and 5.3, respectively, OCH$_2$C*H*$_2$CH$_2$O and =NCH$_2$C*H*$_2$CH$_2$N=, respectively), 3.61 (4H, t, *J* 5.3, =NC*H*$_2$CH$_2$C*H*$_2$-N=), 4.32 (4H, t, *J* 5.0, OC*H*$_2$CH$_2$C*H*$_2$O), 6.97–7.04, 4H, m, ArH), 7.26 (2H, ddd, *J* 1.7, 7.3 and 8.2, ArH), 7.95–7.98 (2H, dd, *J* 1.7 and 7.6, ArH), 8.66 (2H, s, 2 × CH=N); δ_C 28.7 (N-C-*C*-C-N), 29.6 (O-C-*C*-C-O), 57.1 (N-*C*-C-*C*-N), 68.3 (O-*C*-C-*C*-O), 112.7, 121.2, 125.5, 127.5, 131.7, 158.2 (C^{ar}-O), 158.8 (CH=N); *m*/*z* 322 (51, M$^+$), 321 (100), 293 (56), 176 (32), 162 (94), 148 (61), 134 (76), 107 (64), 91 (41).

Hexahydro-6*H*-dibenzo[*f*,*p*][1,5,9,14]dioxadiazacycloheptadecine (O-tn-N-bn) 15i. (0.49 g, 72%); white solid (from MeOH), mp 99–102 °C; δ_H 1.75 (4H, br s, =NCH$_2$C*H*$_2$-C*H*$_2$CH$_2$N=), 2.32 (2H, t, *J* 6.0, OCH$_2$C*H*$_2$CH$_2$O), 3.62 (4H, br s, =NC*H*$_2$CH$_2$CH$_2$C*H*$_2$N=), 4.20 (4H, t, *J* 6.0, OC*H*$_2$CH$_2$-C*H*$_2$O), 6.88–7.00 (4H, m, ArH), 7.25–7.35 (2H, m, ArH), 7.91–7.93 (2H, dd, *J* 1.2 and 7.6, ArH), 8.68 (2H, s, 2 × CH=N); δ_C 26.7 (N-C-*C*-*C*-C-N), 29.2 (O-C-*C*-C-O), 59.9 (N-*C*-C-C-*C*-N), 68.8 (O-*C*-C-*C*-O), 112.4, 121.0, 12.8, 124.9, 125.7, 127.4, 128.6, 131.8, 156.7 (C^{ar}-O), 157.7 (CH=N); *m*/*z* 336 (8, M$^+$), 335 (14), 307 (23), 267 (100), 162 (26), 148 (28), 121 (60), 91 (26).

6,7,8,9,17,18-Hexahydrodibenzo[*g*,*o*][1,6,10,13]dioxadiazacyclohexadecine (O-bn-N-en) 15j. (0.54 g, 84%): δ_H 1.82–1.90 (4H, m, OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O), 3.94 (4H, s, =NCH$_2$CH$_2$N=), 3.95–4.12 (4H, m, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 6.83–6.98 (4H, m, ArH), 7.25–7.33 (2H, m, ArH), 7.90–7.93 (2H, dd, *J* 1.2 and 7.5 ArH), 8.69 (2H, s, 2 × CH=N); δ_C 26.2 (O-C-*C*-*C*-C-O), 62.1 (N-C-C-N), 68.1 (O-*C*-C-C-*C*-O), 112.3, 115.5, 120.7, 121.6, 124.7, 127.3, 128.8, 131.4, 158.0 (C^{ar}-O), 159.3 (CH=N); *m*/*z* 322 (35, M$^+$), 321 (29), 293 (59), 204 (49), 162 (62), 148 (55), 121 (48), 91 (100).

6,7,8,9,1B,19-Hexahydro-17*H*-dibenzo[*g*,*p*][1,6,10,14]dioxadiazacyclohexadecine (O-bn-N-tn) 15k. (0.57 g, 85%): white needles (from MeOH–CHCl$_3$), mp 194–196 °C; δ_H 2.08–2.11 (4H,m,OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O),2.20–2.27(2H,m,=NCH$_2$C*H*$_2$CH$_2$-N=), 3.55–3.59 (4H, m, =NC*H*$_2$CH$_2$C*H*$_2$N=), 4.08–4.09 (4H, m, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 6.88–7.01 (4H, m, ArH), 7.34–7.40 (2H, ddd, *J* 1.8, 7.4 and 8.2, ArH), 7.89–7.92 (2H, dd, *J* 1.8 and 7.7, ArH), 8.78 (2H, s, 2 × CH=N); δ_C 26.2 (O-C-*C*-*C*-C-O), 29.0 (N-C-*C*-C-N), 56.8 (N-*C*-C-*C*-N), 67.2 (O-*C*-C-C-*C*-O), 113.6, 120.7, 124.9, 127.2, 131.7, 158.3 (C^{ar}-O), 158.7 (CH=N); *m*/*z* 336 (8, M$^+$), 335 (12), 307 (4), 190 (26), 162 (38), 148 (32), 134 (45), 107 (100), 91 (62).

6,7,8,9,17,18,19,20-Octahydrodibenzo[*g*,*q*][1,6,10,15]dioxadiazacyclooctadecine (O-bn-N-bn) 15l. (0.49 g, 70%): white prisms (from hexane–CHCl$_3$), mp 53–56 °C; δ_H 1.66–1.68 (4H, m, OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O), 1.87–1.92 (4H, m, =NCH$_2$C*H*$_2$-C*H*$_2$CH$_2$N=), 3.55–3.62 (4H, m, =NC*H*$_2$CH$_2$CH$_2$C*H*$_2$N=), 3.98–4.05 (4H, m, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 6.76–6.89 (4H, m, ArH), 7.21–7.27 (2H, m, ArH), 7.74–7.77 (2H, dd, *J* 1.8 and 7.7, ArH), 8.70 (2H, s, 2 × CH=N); δ_C 26.1 (N-C-*C*-*C*-C-N), 28.8 (O-C-*C*-*C*-C-O), 61.8 (N-*C*-C-C-*C*-N), 67.8 (O-*C*-C-C-*C*-O), 112.3, 120.6, 120.7, 121.2, 124.7, 125.9, 127.3, 128.3, 131.5, 156.6 (C^{ar}-O), 157.9 (CH=N); *m*/*z* 350 (10, M$^+$), 349 (12), 321 (20), 281 (100), 174 (19), 162 (15), 148 (12), 134 (17), 91 (12).

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