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# Synthesis of Amino- and Bis(bromomethyl)-Substitued Bi- and Tetradentate N-Heteroaromatic Ligands: Building Blocks for Pyrazino-Functionalized Fullerene Dyads

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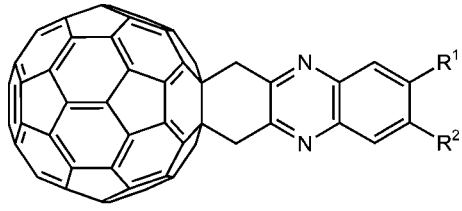
**Keywords:** Nitrogen heterocycles / Schiff bases / Amines

In this paper we describe the synthesis of amino- and bis(bromomethyl)-substituted derivatives of phenanthroline (phen), pyrazino[2,3-*f*]-phenanthroline (pphen), dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), pyrazino[2,3-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine, 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq) and 7,8-bis(2-pyridyl)pyrazino[2,3-*g*]quinoxaline. These substituted bi- and tetradentate N-heteroaromatic ligands are potential synthons for the preparation of the fullerene ligands **4**–**9**. The diketones, 1,10-phenanthroline-5,6-dione **11a** (phendione), 2,2-pyridyl **11b** and 1,4-dibromo-2,3-butanedione **33** were used as starting materials. Phendione was converted into the phendiamine **13** by a two-step synthesis via the dioxime of the diketone **11a**. Amino-substituted dppz and dpq derivatives were obtained by the reduction of the corresponding nitro compounds that were obtained by the Schiff base condensation of the diketones **11a** and **11b** and the appropriate *o*-phenylenediamine derivatives. An alternative synthetic route to the diamines **20a** and **20b** by detosylation of the diamino-substituted dppz and dpq ligands is also presented. Synthesis of the bis(bromomethyl)-substituted pphen, dpp, dppz and dpq derivatives was performed by the photochemical addition of bromine. Alternatively, synthesis of the bis(bromomethyl)-substituted pphen, pdppz and pdpq is also possible by the condensation of 1,4-dibromo-2,3-butanedione **33** and phendiamine or the diamino-substituted dppz and dpq derivatives. The latter two compounds can be also prepared by the condensation of diketones **11a** and **11b** with 6,7-diamino-2,3-bis(bromomethyl)-quinoxaline. Although the synthesis of some dppz and dpq ligands is already published, we herein present improved or alternative synthetic strategies leading to higher yields and/or higher purity of these N-heteroaromatic ligands.


## Introduction

Due to its unusual electronic and electrochemical properties,[1] the fullerene $C_{60}$ is an attractive functional group for molecular electronics[2] and light-harvesting devices.[3] Initial work was focused on charge-transfer complexes based on $C_{60}$ itself.[4] Developments in the exohedral functionalization of fullerenes[5] led to the synthesis of $C_{60}$ derivatives bearing electro- and/or photo-active substituents. These systems facilitate the study of intramolecular processes between $C_{60}$ and its substituents including energy- and electron-transfer interactions. For example, the design of pyrazino-functionalized fullerene dyads has been shown to be a versatile approach to improving the light-harvesting efficiency of fullerenes.[6] Photoexcitation of the pyrazine moiety of dyads **1**, **2** and **3** (Figure 1) is followed by rapid intramolecular deactivation by energy transfer to the fullerene ground state. In turn, the pyrazine singlet excited state, initially formed after photoexcitation, is transformed into the highly reactive fullerene triplet excited state.




**1** : $R^1 = R^2 = H$

**2** : $R^1 = H$, $R^2 = OCH_3$

**3** : $R^1 + R^2 =$ 

Figure 1. Pyrazino-functionalized fullerene dyads **1**–**3**.

Attachment of metal-binding domains that can coordinate to transition metal fragments is of particular interest from both an electrochemical and photophysical point of view as such compounds combine the properties of both the $C_{60}$ and the metal fragment. In particular, the synthesis of pyrazino-functionalized fullerene dyads containing the 2,2′-bipyridine (bpy) moiety is of great interest in the design of donor-bridge-acceptor systems in which the fullerene fragment can be coordinated to transition metal fragments

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such as $[Ru(bpy)_2]^{2+}$, $Re(CO)_3Cl$ or $[Cu(PPh_3)_2]^+$, where $PPh_3$ = triphenylphosphane. Some examples of fullerene ligands in which the pyrazine and the bpy fragment are incorporated are shown in Figure 2. As bipyridine and pyridyl-like compounds are known to form monolayers on gold surfaces[7] these dyads can also be used to prepare monolayers of fullerene derivatives.[8] For example, Echegoyen et al. reported the synthesis of a phenanthrolyl-[60]fullerene and described its self-assembly to form monolayers on a Au surface.[8a]

Synthesis of pyrazino-functionalized fullerene dyads can either be achieved by the Diels–Alder reaction of $C_{60}$ with *o*-quinodimethanes, generated in situ from the corresponding bis(bromomethyl)-substituted (hetero)aromatics first reported by Martin et al.,[9] or by the condensation of aromatic diamines with fullerocyclohexane-1,2-dione **10**, as shown by our research group.[10] In Scheme 1 both synthetic strategies are depicted. In this paper we report on the preparation of amino- or bis(bromomethyl)-substituted derivatives of 1,10-phenanthroline (phen), pyrazino[2,3-*f*]phenanthroline (pphen), dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), pyrazino[2,3-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine, 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq) and 7,8-bis(2-pyridyl)pyrazino[2,3-*g*]quinoxaline.

All bis(bromomethyl)-substituted N-heteroaromatics presented in this paper, as well as the dppz derivative **25a** and the dpq derivatives **20b**, **23b** and **25b**, are new compounds and their synthesis has not been reported elsewhere.

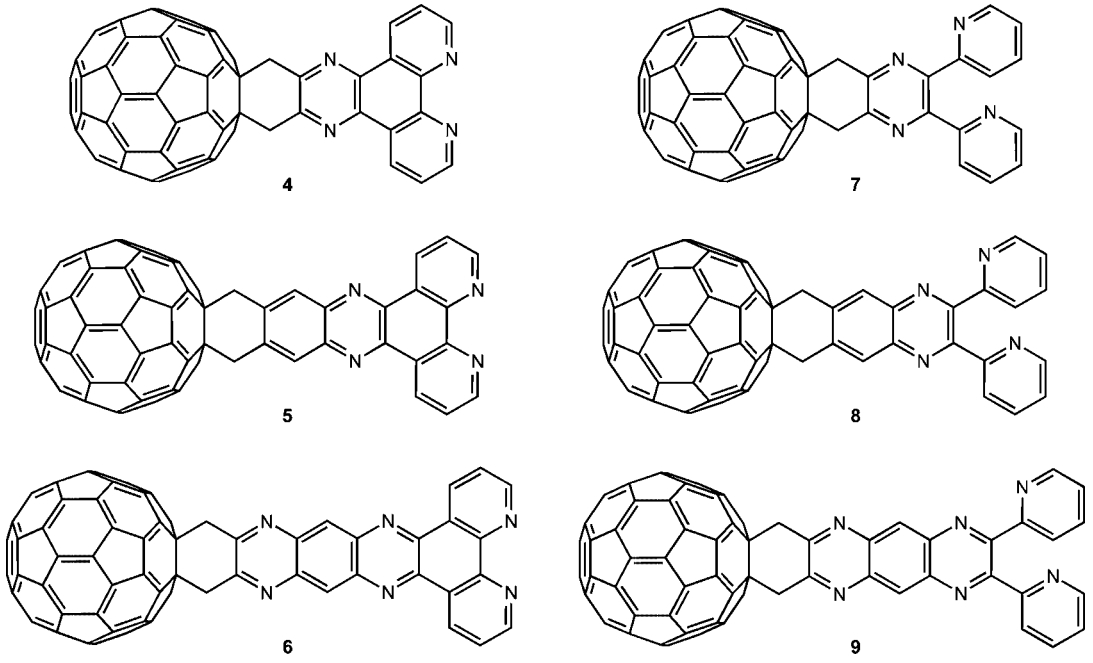
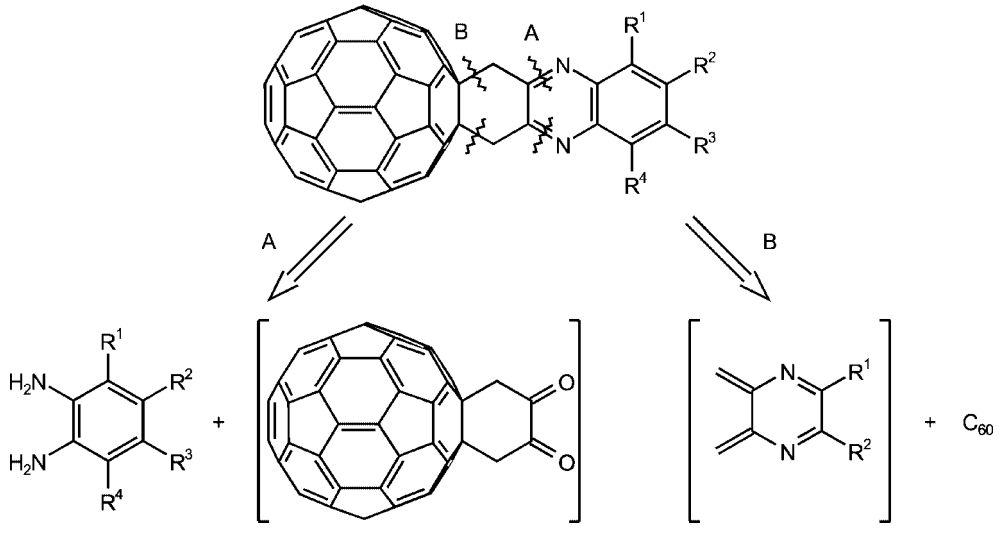



Figure 2. Pyrazino-functionalized bucky ligands containing the 2,2′-bipyridine fragment.



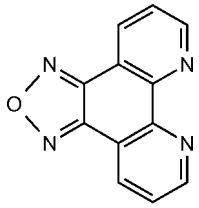

Scheme 1. Synthesis of pyrazino-functionalized fullerene dyads by condensation of fullerocyclohexane-1,2-dione with aromatic diamines (path A) or by Diels–Alder addition of *o*-quinodimethanes (path B).

## Results and Discussion

**Synthesis of Amino-Substituted N-Heteroaromatic Ligands:** In Figure 2 some examples of pyrazino-functionalized fullerene dyads containing the bpy fragment are shown. Of these dyads, only dyads **4**, **6**, **7** and **9** can be synthesized by the condensation reaction of the fullerocyclohexane-1,2-dione **10** with the corresponding amine. In addition, the synthesis of fullerene triads containing the cyclohexandiimine substructure, with an additional chelating coordination site, may be possible by using monoamines. Therefore, we will now describe the synthesis of suitable mono- and di-amines.

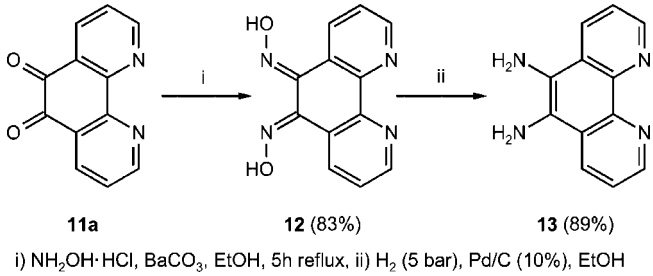
MacDonnell et al. described the preparation of 5,6-diamino-1,10-phenanthroline **13** (phendiamine) by a two-step synthesis starting from phendione **11a** in 79% overall yield.[11] Phendione was prepared by the bromine-catalyzed oxidation of 1,10-phenanthroline with a mixture of concentrated sulfuric and nitric acid.[12] Quinone **11a** is known to lose carbon monooxide under basic conditions to give 4,5-diazafluoren-9-one.[13] Thus, after oxidation of 1,10-phenanthroline to the diketone the reaction mixture must be very carefully neutralized to avoid this side reaction. Treatment of **11a** with hydroxylamine-hydrochloride and barium carbonate led to the dioxime derivative **12** (phendioxime) which, after reduction with hydrazine hydrate (80%) and Pd/C (10%), was transformed into the phendiamine **13**. Following this reaction procedure we obtained the desired diamine in only ca. 45% overall yield. We noticed a loss of product in the synthesis of dioxime **12** using the work-up procedure described by MacDonnell et al. which requires washing the crude product with ethanol and ether as well as treatment with 0.1 N hydrochloric acid. This may be due to the solubility of the by-product 1,2,5-oxadiazolo[3,4-*f*]-1,10-phenanthroline **14** (Figure 3)[14] or the solubility of the phendioxime in ethanol, ether and in diluted mineral acids as reported by Smith et al.[15]



**14**

Figure 3. 1,2,5-Oxadiazolo[3,4-*f*]-1,10-phenanthroline **14**.

The dioxime **12** can react either under acidic or basic conditions to form the 1,2,5-oxadiazole **14**. The reaction of phendione with hydroxylamine hydrochloride, without addition of barium carbonate, led exclusively to the formation of the 1,2,5-oxadiazole. It is therefore necessary to minimize the concentration of the free base hydroxylamine by addition of hydroxylamine hydrochloride to an ethanol solution of the phendione and to neutralize the hydrogen chloride, generated by the condensation reaction, by addition of a weak base. As prolonged heating also favors the successive formation of the 1,2,5-oxadiazole the reaction time was reduced to five hours. In further reactions the dioxime was purified by washing it with a small amount of ether and water only. Therefore, sodium carbonate was used to neutralize the hydrogen chloride generated during the formation of the dioxime in order to avoid problems in removing any unreacted reagent. Finally, the phendioxime was transformed into the diamino derivative **13** by palladium-catalyzed hydrogenation. Hydrogen reduction was preferred because use of the toxic hydrazine hydrate could be avoided. The diamine was obtained in higher yield and no further work-up was necessary (Scheme 2).

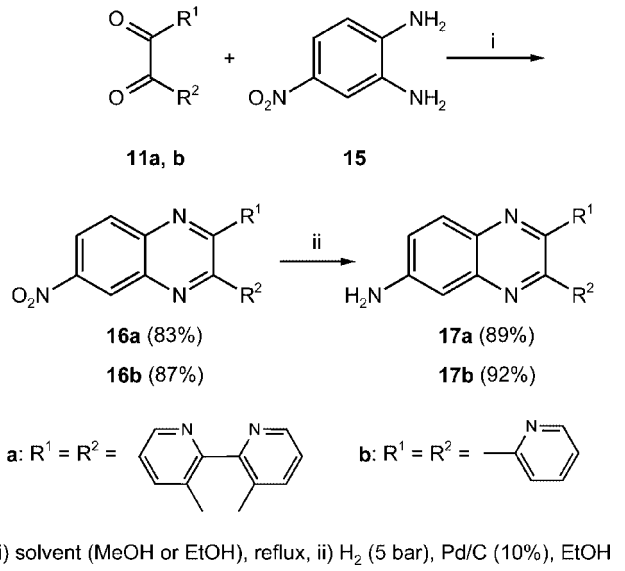



Scheme 2. Synthesis of phendiamine **14** starting from phendione **11a**.

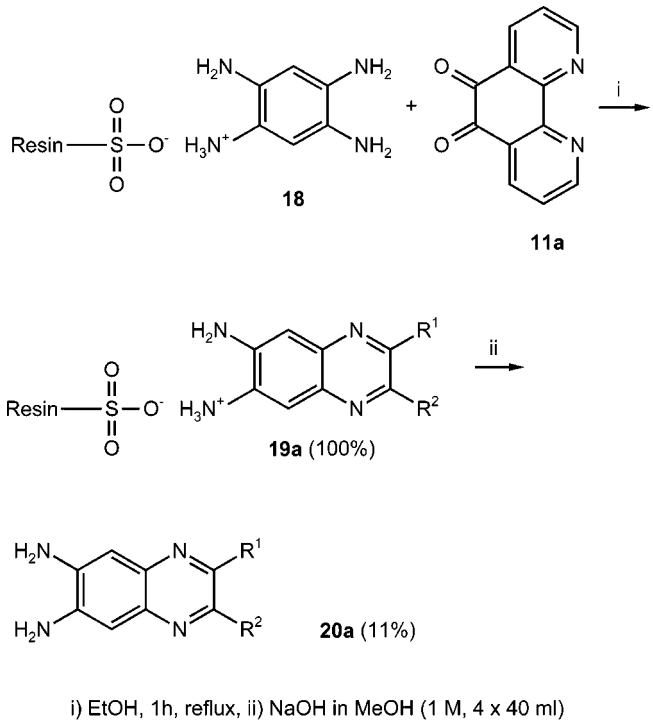
Synthesis of the amino-substituted dppz and dpq derivatives **17a** and **17b** is already published in the literature.[16,17] These derivatives were obtained by the reduction of the corresponding nitro compounds **16a** and **16b** which were prepared by the Schiff base condensation of the diketones phendione **11a** and 2,2′-pyridyl **11b** with an excess of the 4-nitro-substituted *o*-phenylenediamine **15** under reflux conditions. Palladium-catalyzed reduction of the nitro groups with hydrogen (5 bar) in a Parr apparatus gave the desired amino derivatives in higher yields and higher purity compared to the reduction with $NaBH_4$ in the case of the dppz derivative or with $SnCl_2$ in the case of the dpq derivative. The compounds were identical in all aspects to that reported in ref.[16] and ref.[17] (Scheme 3).

Synthesis of the diamino-substituted dppz derivative **20a** was originally reported by Lehn et al. in a Short Communication.[18] Reaction of phendione with freshly prepared 1,2,4,5-tetraaminobenzene in refluxing THF gave the desired diamine, but also the dicondensation product 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′,3′-*c*:3′′,2′′-*l*:2′′′,3′′′-*n*]-pentacene that could not be separated from the diamino-substituted dppz derivative. A good idea suggested by Torres-Garcia[19] was that the tetraaminobenzene could be neutralized using a strongly acidic cation exchange resin (Amberlyst 15®). In this way, the tetraaminobenzene derivative is protonated avoiding oxidations and is highly dispersed on the resin's surface avoiding autocondensation yielding tetraaminophenazine. Besides, the resin is not able to protonate all the amino groups of the molecule because of the great distance between two different sulfonic acids. Synthesis of 11,12-diaminodibenzo[2,3-*a*:2′,3′-*c*]phenazine and 6,7-diamino-2,3-diphenylquinoxaline was successfully performed by this method.[19] Indeed, reaction of the immo-



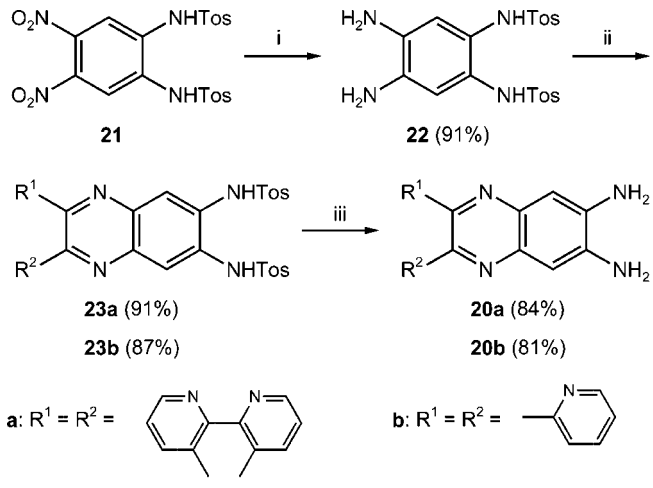

Scheme 3. Synthesis of amino-substituted dppz and dpq derivatives **17a** and **17b**.




Scheme 4. Reaction of phendione **11a** with tetraaminobenzene immobilized on amberlyst 15.

bilized tetraaminobenzene with phendione **11a** also resulted in the formation of the diamino-substituted dppz derivative (Scheme 4). Treatment of the resin with a solution of sodium hydroxide in methanol (1 M), followed by column chromatography using neutral alumina and methanol/dimethylformamide (4:1, v/v) as the eluent gave the free diamino compound in ca. 10% yield. The low yield, in contrast to that observed for the synthesis of 11,12-diaminodibenzo[2,3-*a*:2′,3′-*c*]phenazine and 6,7-diamino-2,3-diphenylquinoxaline, may be due to the strong interactions between the additional chelating coordination site of the phenanthroline fragment of the dppz derivative and the resin as well as the stationary phase.

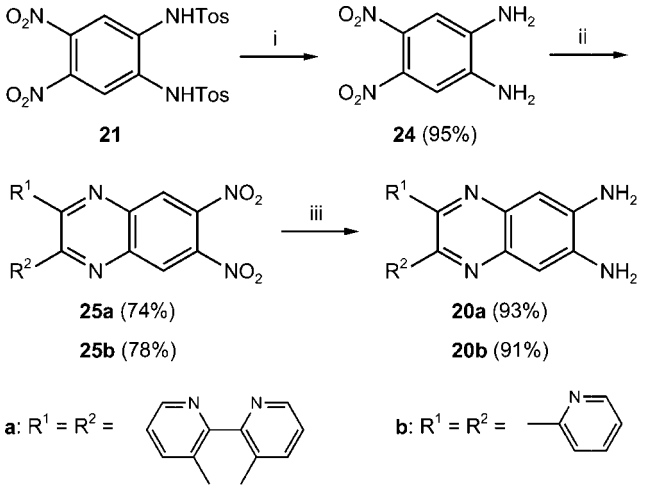
Synthesis of the diamino-substituted dibenzo[2,3-*a*;2′,3′-*c*]phenazine by detosylation of the corresponding tosylated derivative was reported by Arnold.[20] The tosylated diamine was obtained by condensation of phenanthrenequinone with 4,5-diamino-$N^1$,$N^2$-ditosyl-*o*-phenylenediamine **22**. The latter compound was prepared by palladium-catalyzed hydrogenation (5 bar) of the dinitro-substituted $N^1$,$N^2$-ditosyl-*o*-phenylenediamine derivative **21**. By analogy, the synthesis of the tosylated diamines **23a** and **23b** was performed by the condensation of the *o*-phenylenediamine derivative **22** with the diketones **11a** and **11b** (Scheme 5). Detosylation with concd. sulfuric acid gave the free diamines in nearly quantitative yields. As the diamines are sensitive to oxidation by air, the synthesis of the tosylated diamines is a good way to obtain stable precursors of the diamines that can be stored over long periods of time. These derivatives can be converted into the diamines prior to use.




Scheme 5. Synthesis of diamines **20a** and **20b** starting from 4,5-dinitro-*N*,*N*′-ditosyl-*o*-phenylenediamine **21** (method A).

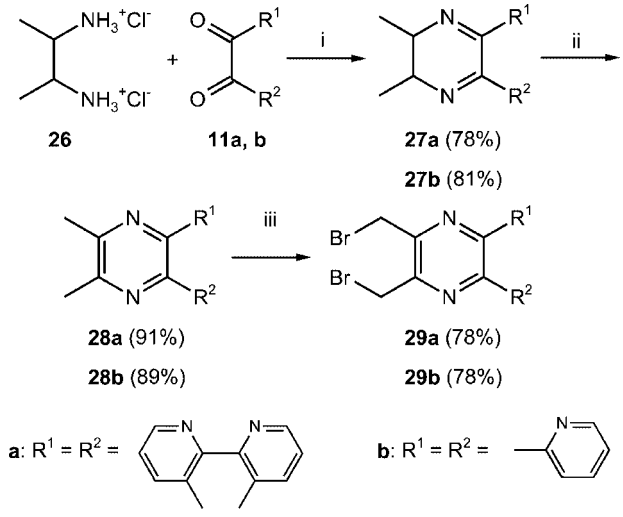
An alternative synthetic strategy, starting from 4,5-dinitro-$N^1$,$N^2$-ditosyl-*o*-phenylenediamine **21**, also resulting in the formation of diamines **20a** and **20b** is depicted in Scheme 6. Detosylation of **21** with concd. sulfuric acid led to the formation of 4,5-dinitro-*o*-phenylenediamine **24**[21] which was then reacted with the diketones **11a** and **11b** to give the dinitro-substituted dppz and dpq derivatives **25a** and **25b** in ca. 75% yield. Again, the palladium-catalyzed hydrogen reduction of the nitro compounds resulted in the formation of the diamines **20a** and **20b**.




Scheme 6. Synthesis of diamines **20a** and **20b** starting from 4,5-dinitro-*N*,*N*′-ditosyl-*o*-phenylenediamine **21** (method B).

**Synthesis of Bis(bromomethyl)-Substituted N-Heteroaromatic Ligands:** Preparation of the dyads **4**–**9** can alternatively be obtained by the Diels–Alder cycloaddition between $C_{60}$ and the appropriate *o*-quinodimethanes generated in situ from the corresponding bis(bromomethyl)-substituted derivatives. Synthesis of 2,3-dimethylpyrazino[2,3-*f*]-1,10-phenanthroline **28a**[22] and 2,3-dimethyl-5,6-bis(2-pyridyl)pyrazine **28b**[23] is already published in the literature. These compounds were obtained by the condensation of 2,3-diaminobutane with phendione **11a** or 2,2′-pyridyl **11b**. As the diamine is sensitive to oxidation by air, we decided to use the 2,3-diaminobutane dihydrochloride **26** in the condensation reaction. Use of the dihydrochloride is also advantageous because decomposition of diketone **11a** can be avoided. The free base 2,3-diaminobutane may induce loss of carbon monooxide resulting in the formation of 4,5-diazafluoren-9-one (see above). The 2,3-diaminobutane dihydrochloride was obtained by the palladium-catalyzed hydrogen reduction of dimethyldiglyoxime, as reported by Cooley et al.[24] The dihydrochloride was converted into the free diamine by addition of potassium carbonate to an ethanol solution of compound **26**. This solution was then added dropwise to an ethanolic solution of the appropriate diketone **11a** or **11b** to give the dihydropyrazine derivatives **27a** and **27b** in 78% and 81% yield, respectively. Formation of these compounds was confirmed by $^1$H NMR spectroscopy. The spectra of both compounds show the characteristic signal for the methine protons at $\delta$ = 3.73 ppm. The dimethyl-substituted pphen and dpp derivatives **28a** and **28b** were prepared by the palladium-catalyzed dehydrogenation of the dihydro derivatives **27a** and **27b**. Compounds **28a** and **28b** were characterized by $^1$H NMR spectroscopy. No signals for the methine protons were detected indicating the successful formation of the desired dimethyl-substituted pphen and dpp derivatives. In addition, the signal of the methyl groups is shifted down-field due to the aromatization of the pyrazine ring. Bromination of these methyl groups leading to the bis(bromomethyl)-substituted pphen and dpp derivatives **29a** and **29b** can be obtained by either the thermal or photochemical reaction of *N*-bromosuccinimide (NBS) and azobisisobutyronitrile (AIBN) with the dimethyl-substituted pphen and dpp derivative **28a** and **28b**. These compounds were characterized by $^1$H NMR and mass spectrometry. Addition of bromine led to a down-field shift of the methylene protons relative to the methyl protons in compounds **28a** and **28b**. This is due to the deshielding effect of the bromine atoms. In the mass spectra, signals that can be assigned to fragment ions arising from the consecutive loss of bromine atoms can be observed. For example, signals at $m/z$ = 337 $(M - Br)^+$ and $m/z$ = 259 $(M - 2Br)^+$ were detected in the mass spectrum of 2,3-bis(bromomethyl)pyrazino[2,3-*f*][1,10]phenanthroline **29a** (Scheme 7).

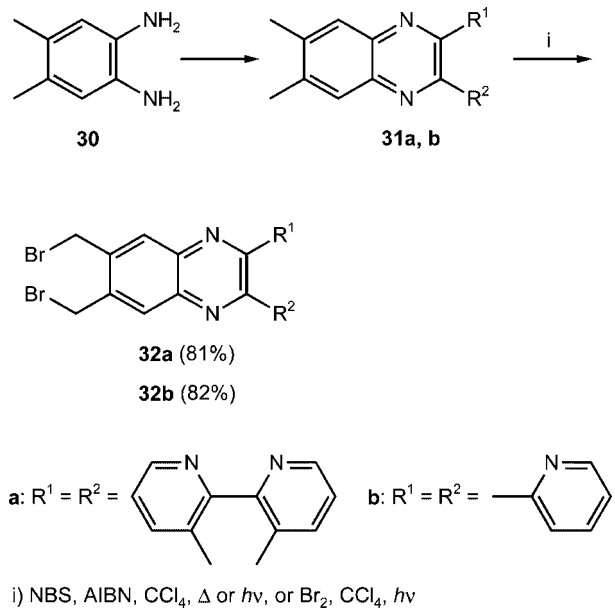



Scheme 7. Synthesis of the bis(bromomethyl)-substituted pphen and dpp derivatives **29a** and **29b**.

Alternatively, these compounds were also obtained by the irradiation of a $CCl_4$ solution of the dimethyl-substituted pphen or dpp derivative **28a** and **28b** and bromine with a 400 W tungsten lamp, affording the bis(bromomethyl)-substituted compounds **29a** and **29b** in 78% and 76% yield, respectively. Thus, the bis(bromomethyl) derivatives **29a** and **29b** were synthesized in higher yields than by bromination with NBS and AIBN. Once we knew that the photochemical addition of bromine led to higher yields we applied this method to preparing the bis(bromomethyl)-substituted derivatives of 11,12-dimethyldipyrido[3,2-*a*:2′,3′-*c*]-phenazine **31a**, obtained by the condensation of 4,5-dimethyl-*o*-phenylenediamine **30** and diketone **11a**, and commercially available 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline **31b**. Irradiation of a $CCl_4$ solution of the dimethyl-substituted dppz or dpq derivative and bromine resulted in the formation of the bis(bromomethyl) derivatives **32a** and

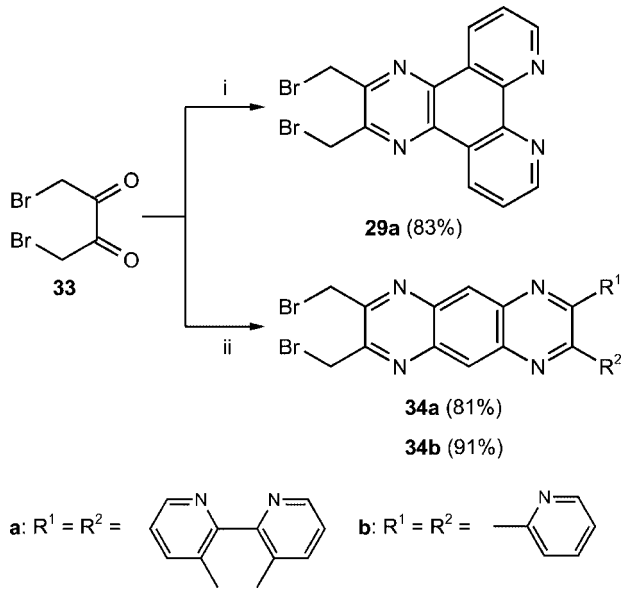
**32b** in good yields (>80%). These compounds show the expected down-field shift of the methylene protons in the $^1$H NMR spectra. Again, signals arising from the fragmentation process typical for bis(bromomethyl)-substituted compounds were observed in the mass spectra (Scheme 8).




Scheme 8. Synthesis of the bis(bromomethyl)-substituted dppz and dpq derivatives **32a** and **32b**.

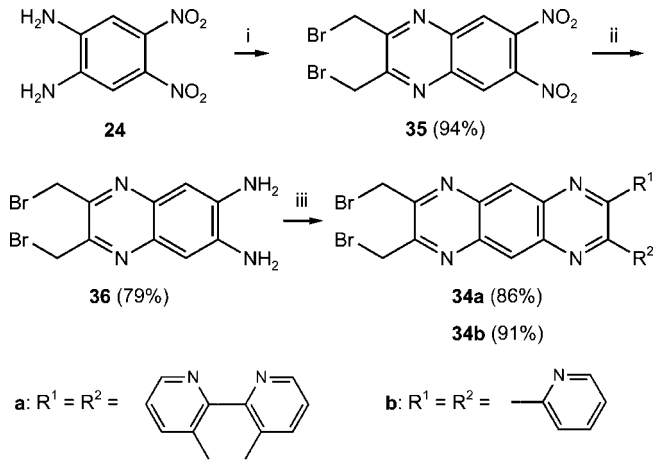
The synthesis of bis(bromomethyl)-substituted quinoxaline derivatives by the condensation of 1,4-dibromo-2,3-butanedione **33**, that can be easily prepared according to a literature procedure,[25] with appropriate diamines in ethanol at 0 °C was reported by Roland et al.[26] By analogy, the diketone **33** was reacted with an excess of phendiamine **13** affording the bis(bromomethyl)-substituted pphen derivative **29a** in 83% yield. In contrast to the published procedure refluxing of the reaction mixture was required. Furthermore, the bis(bromomethyl)-substituted pdppz and pdpq derivatives **34a** and **34b** were obtained by the condensation of the diketone **33** and the diamines **20a** and **20b** in 81% and 91% yield, respectively. Observation of the typical down-field shift of the methylene protons in the NMR spectra and the typical mass fragmentation process in the mass spectra confirmed the successful preparation of the bis(bromomethyl)-substituted compounds **34a** and **34b** (Scheme 9).

Alternatively, the synthesis of the compounds **34a** and **34b** can also be performed by the condensation of 6,7-diamino-2,3-bis(bromomethyl)quinoxaline **36** with diketones **11a** and **11b** (Scheme 10). Compound **36** was obtained by a two-step synthesis starting from 4,5-dinitro-*o*-phenylenediamine **24**. Condensation of this diamine with 1,4-dibromo-2,3-butanedione **33** resulted in the formation of the 6,7-dinitro-substituted quinoxaline derivative **35** in quantitative yield. Finally, the nitro compound was transformed into the corresponding diamino-substituted quinoxaline derivative **36** by palladium-catalyzed hydrogen reduction. Formation of 6,7-diamino-2,3-dimethylquinoxaline was




Scheme 9. Synthesis of the bis(bromomethyl)-substituted pphen, pdppz and pdpq derivatives by condensation of 1,4-dibromo-2,3-butanedione **33** with the appropriate diamine **13**, **34a** or **34b**.

also observed as a by-product. Unfortunately, this compound could not be separated from the desired diamine by column chromatography on $SiO_2$ using hexane/chloroform (1:1, v/v) as eluent. This mixture was then reacted with the diketones **11a** and **11b** affording the pdppz derivative **34a** and the pdpq derivative **34b**. Synthesis of these compounds was accompanied by the formation of the dimethyl-substituted pdppz and pdpq, respectively. Although purification of the bis(bromomethyl)-substituted derivatives **34a** and




Scheme 10. Synthesis of the bis(bromomethyl)-substituted pdppz and pdpq derivatives **34a** and **34b** by condensation of diketones **11a** and **11b** with 6,7-diamino-2,3-bis(bromomethyl)quinoxaline **36**.

**34b** failed, these mixtures can be used as synthons for the corresponding pyrazino-functionalized fullerene dyads **6** and **9**, because generation of the corresponding *o*-quinodimethanes is only possible by reductive elimination of the bis(bromomethyl)-substituted derivatives. The presence of the dimethyl-substituted pdppz or pdpq derivatives may cause trouble with the isolation or purification of the resulting dyads. Condensation of diamines **20a** and **20b** with the diketone **33** gave the pure bis(bromomethyl)-substituted derivatives. Synthesis of these compounds should be carried out using this synthetic strategy in order to avoid any possible complications in the synthesis of dyads **6** and **9**.

## Conclusion

A number of bi- and tetradentate N-heteroaromatic ligands containing the pyrazine moiety were synthesized bearing either amino or bromomethyl substituents starting from the phendione **11a** or 2,2′-pyridyl **11b**. Generally, the synthesis of the ligands was achieved by condensation of 1,2-diketones with suitable diamines followed by further transformations to the derivatives with the functionalization needed for the preparation of fullerene ligands **4**–**9** using Mattay's or Martin's synthetic pathways. Amino-substituted dppz and dpq derivatives were prepared by the reduction of the corresponding nitro compounds. In the case of the diamino derivatives **20a** and **20b**, detosylation of the corresponding tosylates **23a** and **23b** is a good alternative to obtain these diamines. Bis(bromomethyl)-substituted derivatives **29a** and **29b** and **31a** and **31b** are useful as starting materials for the pyrazino-functionalized dyads and were obtained by bromination of the methyl groups. Alternatively, compounds **29a**, **34a** and **34b** were prepared using a synthetic strategy starting from the bis(bromomethyl)-substituted diketone **33**.

Initial investigations showed that, in principle, fullerene dyads **4**, **6** and **9** can be successfully obtained in moderate yields by condensation of the diamino-substituted N-heteroaromatics with fullerocyclohexane-1,2-dione **10**. In contrast, the synthesis of pyrazino-functionalized fullerene dyads **4**–**9** can be obtained by the [4+2] cycloaddition of $C_{60}$ and the corresponding *o*-quinodimethanes which are generated in situ from the bis(bromomethyl)-substituted N-heteroaromatics by reductive 1,4-elimination. Conventional heating as well as microwave-assisted reactions were applied. To date, all attempts to isolate the pure fullerene dyads have failed. Further investigations will focus on the purification of these dyads as well as on the improvement of the synthetic pathways to these fullerene ligands.

## Experimental Section

NMR spectra were recorded using a Bruker DRX 500 spectrometer at 293 K using solvent peaks as internal references if not otherwise noted. IR Spectra were recorded using the IR spectronmeter 841 (Perkin–Elmer, Überlingen, Germany). EI and CI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (vacuum Generators, Manchester, UK) equipped with a standard EI or CI source. Samples were introduced by push rod in aluminium crucibles if not otherwise noted. Ions were accelerated by 8 kV in EI mode and 6 kV in CI mode. ESI spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltronic GmbH, Bremen, Germany) equipped with a standard ESI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Nitrogen was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap. Melting points were determined using a Büchi melting point apparatus and are uncorrected.

1,10-Phenanthroline, 4-nitro-*o*-phenylenediamine, 4,5-dimethyl-*o*-phenylenediamine, 2,2′-pyridyl, 6,7-dimethyl-2,3-bis(2-pyridyl)-quinoxaline were commercially available and were used without further purification.

1,10-Phenanthroline-5,6-dione (phendione, **11a**),[11] 4,5-dinitro-$N^1$,$N^2$-ditosyl-*o*-phenylen-diamine (**21**),[21] 4,5-dinitro-*o*-phenylenediamine (**24**),[21] *rac*-2,3-diaminobutane dihydrochloride (**26**)[24] and 1,4-dibromo-2,2-butanedione (**32**)[25] were prepared according to literature procedures. Hydrogenations were performed using a Parr apparatus HyP Serie 77 (Gerhardt, Bonn, Germany). Palladium charcoal (Pd/C 10%, Aldrich) was used as the catalyst in the hydrogenation reactions.

**1,10-Phenanthroline-5,6-dioxime (12):** A mixture of 1,10-phenanthroline-5,6-dione (210 mg, 1.00 mmol) and $Na_2CO_3$ (296 mg, 1.50 mmol) were dissolved in ethanol (15 mL) and heated to reflux. To this solution hydroxylamine hydrochloride (243 mg, 3.50 mmol) in ethanol (5 mL) was added dropwise and the reaction mixture was then refluxed for 5 h. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was washed successively with water and ether and dried under vacuum at 80 °C affording **12** (199 mg, 83%) as a light yellow solid. The compound is identical in all aspects to that reported in ref. 12.

**5,6-Diamino-1,10-phenanthroline (13): 12** (100 mg, 0.48 mmol) and Pd/C (15 mg, 10%) were suspended in ethanol (100 mL). The resulting mixture was carried out at room temperature for 24 h in a hydrogen atmosphere (5 bar) in a Parr apparatus. After completion of the reaction, the catalyst was filtered off and the residue washed with boiling ethanol. The solvent was evaporated under reduced pressure. The solid obtained was dried in vacuo affording **13** in 89% yield (187 mg). $^1$H NMR ($CDCl_3$: $CD_3COOD$, 500.1 MHz): $\delta$ = 5.22 (s, 4 H, -N$H_2$), 7.60 (dd, $J$ = 8.5 Hz/4.3 Hz, 2 H, $H^3$ and $H^8$), 8.47 (dd, $J$ = 8.5 Hz/1.6 Hz, 2 H, $H^2$ and $H^9$), 8.76 (dd, $J$ = 4.3 Hz/1.6 Hz, 2 H, $H^4$ and $H^7$) ppm. IR (KBr): $\tilde{\nu}$ = 3372, 3325, 3267, 3209, 3036, 2924, 2855, 1655, 1605, 1589, 1567 cm$^{-1}$. MS (CI, $NH_3$): $m/z$ = 210 $[M]^+$.

**General Procedure for the Synthesis of dppz Derivatives by Schiff Base Condensation:** Phendione **11a** (3.00 mmol) and the appropriate *o*-phenylenediamine derivative (3.60 mmol) were dissolved in methanol (100 mL) and heated to reflux for several hours. After a short period of time the product began to precipitate from the solution. After completion of the reaction the solids were filtered off and washed with cold methanol. The crude product was then recrystallized from methanol.

**11-Nitrodipyrido[3,2-*a*:2′,3′-*c*]phenazine (16a):** Light yellow needles, 83%. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 7.83 (dd, 1 H, $J$ = 8.2 Hz/4.5 Hz, $H^2$), 7.88 (dd, 1 H, $J$ = 8.2 Hz/4.5 Hz, $H^7$), 8.52 (d, 1 H, $J$ = 9.4 Hz, $H^{13}$), 8.69 (dd, 1 H, $J$ = 9.4 Hz/2.5 Hz, $H^{12}$), 9.30 (d, 1

H, $J$ = 2.5 Hz, $H^{10}$), 9.33 (d, 1 H, $J$ = 2.5 Hz/1.8 Hz, $H^6$), 9.35 (dd, 1 H, $J$ = 4.5 Hz/1.8 Hz, $H^3$), 9.63 (dd, 1 H, $J$ = 8.2 Hz/1.8 Hz, $H^1$), 9.67 (dd, 1 H, $J$ = 8.2 Hz/1.8 Hz, $H^8$) ppm. MS (CI, $NH_3$): $m/z$ = 327 $[M]^+$.

**11,12-Dinitrodipyrido[3,2-*a*:2′,3′-*c*]phenazine (25a):** Tan solid, 74%. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 7.89 (dd, 2 H, $J$ = 8.2 Hz/4.4 Hz, $H^2$ and $H^7$), 8.95 (s, 2 H, $H^{10}$ and $H^{13}$), 9.38 (d, 2 H, $J$ = 4.4 Hz, $H^3$ and $H^6$), 9.63 (dd, 2 H, $J$ = 8.2 Hz/1.9 Hz, $H^1$ and $H^8$) ppm. MS (CI, $NH_3$): $m/z$ = 372 $[M]^+$.

**11,12-Dimethyldipyrido[3,2-*a*:2′,3′-*c*]phenazine (30a):** Light yellow needles, 95%. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 2.46 (s, 6 H, -C$H_3$), 7.73 (dd, 2 H, $J$ = 8.2 Hz/4.4 Hz, $H^2$ and $H^7$), 7.95 (s, 2 H, $H^{10}$ and $H^{13}$), 9.21 (dd, 2 H, $J$ = 4.4 Hz/1.9 Hz, $H^3$ and $H^6$), 9.52 (dd, 2 H, $J$ = 8.2 Hz/1.9 Hz, $H^1$ and $H^8$) ppm. $^{13}$C NMR ($CDCl_3$, 125.8 MHz): $\delta$ = 20.6 (p, 2C, -$CH_3$), 123.9 (q, 2C), 127.7 (t, 2C), 128.1 (q, 2C), 133.4 (q, 2C), 140.2 (t, 2C), 141.5 (t, 2C), 141.7 (q, 2C), 148.1 (t,2C), 152.1 (q, 2C) ppm. MS (CI, $NH_3$): $m/z$ = 310 $[M]^+$.

**General Procedure for the Synthesis of dpq Derivatives by Schiff Base Condensation:** 2,2′-Pyridyl **11b** (3.00 mmol) and (3.60 mmol) of the appropriate *o*-phenylenediamine derivative were dissolved in ethanol (100 mL) and heated to reflux for 12 h. The reaction was cooled to room temperature. Work-up of the reaction mixture is as follows.

**6-Nitro-2,3-bis(2-pyridyl)quinoxaline (16b):** Upon reaction the product started to precipitate from the solution. The solid was filtered off and dried in vacuo. The product was obtained as golden crystals in 87% yield. The compound is identical in all aspects to that reported in ref.[17a].

**6,7-Dinitro-2,3-bis(2-pyridyl)quinoxaline (25b):** The reaction mixture was allowed to stand at room temperature for several days. Upon slow evaporation of the solvent the product precipitated from the solution. The product was obtained as red needles in 78% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 7.34 (ddd, 2 H, $H^{5'}$), 7.94 (td, 2 H, $H^{3'}$), 8.14 (td, 2 H, $H^{4'}$), 8.35 (ddd, 2 H, $H^{6'}$), 8.77 (s, 2 H, $H^5$ and $H^8$) ppm. $^{13}$C NMR ($CDCl_3$, 125.8 MHz): $\delta$ = 105.2 (t, 2C), 127.3 (t, 2C), 127.4 (t, 2C), 137.2 (t, 2C), 141.3 (q, 2C), 143.4 (q, 2C), 148.4 (t, 2C), 155.6 (q, 2C), 156.5 (q, 2C) ppm. MS (EI, 70 eV): $m/z$ (%) = 374 (100) $[M]^+$, 282 (61) $[M^\cdot - 2NO_2]^+$, 281 (79) $[M^\cdot - NO_2 - HNO_2]^+$, 270 (15) $[M - C_5H_4N_2]^+$, 78 (31) $[C_5H_4N]^\cdot$, 51 (10).

**General Procedure for the Synthesis of Amino-Substituted dppz (17a, 20a) and dpq Derivatives (17b, 20b) by Reduction of the Corresponding Nitro-Substituted Derivatives:** The nitro-substituted heterocycle **16a** or **16b** or dinitro-substituted heterocycle **25a** or **25b** (150 mg) and Pd/C (15 mg, 10%) were suspended in ethanol (100 mL). The resulting mixture was carried out at room temperature for 24 h in a hydrogen atmosphere (5 bar) in a Parr apparatus. After completion of the reaction, the catalyst was filtered off and the residue washed with boiling ethanol. The solvent was evaporated under reduced pressure.

**11-Aminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (17a):** Orange-red solid, 89%. $^1$H NMR [D$_6$]DMSO, 500.1 MHz): $\delta$ = 7.24 (d, 1 H, $J$ = 9.2 Hz, $H^{10}$), 7.95 (dd, 1 H, $J$ = 8.0 Hz/4.3 Hz, $H^7$), 8.01 (dd, 1 H, $J$ = 8.0 Hz/4.3 Hz, $H^2$), 8.14 (d, 1 H, $J$ = 2.1 Hz, $H^{13}$), 9.18 (dd, 1 H, $J$ = 4.3 Hz/1.4 Hz, $H^3$), 9.25 (dd, 1 H, $J$ = 4.3 Hz/1.4 Hz, $H^6$), 9.51 (dd, 1 H, $J$ = 8.0 Hz/1.3 Hz, $H^1$), 9.57 (dd, 1 H, $J$ = 8.0 Hz/1.3 Hz, $H^8$) ppm. MS (CI, $NH_3$): $m/z$ = 297 $[M]^+$.

**11,12-Diaminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (20a):** Brown solid, 93%. $^1$H NMR [D$_6$]DMSO, 500.1 MHz): $\delta$ = 6.27 (s, 4 H, N$H_2$), 7.15 (s, 2 H, $H^{10}$ and $H^{13}$), 7.84 (dd, 2 H, $J$ = 8.1 Hz/4.5 Hz, $H^2$ and $H^7$), 9.08 (dd, 2 H, $J$ = 4.5 Hz/1.8 Hz, $H^3$ and $H^6$), 9.44 (dd, 2 H, $J$ = 8.1 Hz/1.8 Hz, $H^1$ and $H^8$) ppm. MS (ESI): $m/z$ = 312 $[M^+]$.

**6-Amino-2,3-bis(2-pyridyl)quinoxaline (17b):** Brownish solid, 92%. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.53 (s, 2 H, -N$H_2$), 7.03 (dd, 1 H, $J$ = 9.1 Hz/2.2 Hz, $H^7$), 7.07 (d, 1 H, $J$ = 2.2 Hz, $H^5$), 7.13 (m, 2 H, $H^{5'}$), 7.71 (m, 2 H, $H^{3'}$), 7.80 (dd, 2 H, $H^{4'}$), 7.86 (d, 1 H, $J$ = 9.1 Hz, $H^8$), 8.37 (dd, 2 H, $J$ = 4.8 Hz/1.8 Hz, $H^{6'}$) ppm. $^{13}$C NMR ($CDCl_3$, 125.8 MHz): $\delta$ = 107.3 (t, 1C), 122.3 (t, 2C), 122.6 (t, 1C), 123.9 (t, 1C), 124.1 (t, 1C), 129.9 (q, 1C), 135.8 (q, 1C), 136.2 (t, 1C), 136.3 (t, 1C), 142.9 (t, 1C), 148.3 (t, 1C), 148.9 (q, 1C), 151.9 (q, 2C), 157.5 (q, 1C), 157.6 (q, 1C) ppm. MS (CI, $NH_3$): $m/z$ = 299 $[M]^+$.

**6,7-Diamino-2,3-bis(2-pyridyl)quinoxaline (20b):** Brownish solid, 91%. $^1$H NMR [D$_6$]DMSO, 500.1 MHz): $\delta$ = 5.89 (s, 4 H, -N$H_2$), 6.99 (s, 2 H, $H^5$ and $H^8$), 7.24–7.22 (m, 2 H, $J$ = 6.9 Hz/5.0 Hz/1.9 Hz, $H^{5'}$), 7.80 (d, 2 H, $J$ = 7.5 Hz, $H^{3'}$), 7.85–7.79 (m, 2 H, $H^{4'}$), 8.20 (d, 2 H, $J$ = 5.0 Hz, $H^{6'}$) ppm. $^{13}$C NMR [D$_6$]DMSO, 125.8 MHz): $\delta$ = 104.9 (t, 2C), 121.9 (t, 2C), 123.4 (t, 2C), 136.1 (t, 2C), 137.3 (q, 2C), 142.0 (q, 2C), 146.5 (q, 2C), 147.6 (t, 2C), 158.5 (q, 2C) ppm. MS (CI, $NH_3$): $m/z$ = 314 $[M^{+]}$.

**Synthesis of Compound 20a by Reaction of Immobilized Tetraaminobenzene with Phendione 11a:** To a degassed solution of tetraaminobenzene tetrahydrochloride (284 mg, 1.0 mmol) in water (5 mL) in an argon atmosphere a solution of potassium hydroxide (224 mg, 4.0 mmol) in water (5 mL) was added. The red solution rapidly turned yellow, and then the cation exchange resin amberlyst 15 was added (5 g). The solution rapidly became colorless as the amine joined to the resin. The resin was filtered off, washed with acetonitrile (4 × 50 mL), ether (4 × 50 mL) and dried under vacuum. This resin was added to a solution of phendione **11a** (210 mg, 1.0 mmol) in ethanol (20 mL) and was then refluxed for 1 h. The ethanol was filtered off and the resin treated with a NaOH in methanol solution (1 M, 4 × 40 mL). The solvent was evaporated under reduced pressure and the product **20a** was obtained in ca. 10% yield after column chromatography on neutral alumina using methanol/dimethylformamide (4:1, v/v) as the eluent.

**Synthesis of Diamines 20a and 20b by Detosylation of the Corresponding Tosylated dppz and dpq Derivatives 23a and 23b**

**4,5-Diamino-$N^1$,$N^2$-ditosyl-*o*-phenylenediamine (22):** 4,5-Dinitro-$N^1$,$N^2$-ditosyl-*o*-phenylenediamine (**21**) (200 mg, 0.39 mmol) and Pd/C (30 mg, 10%) were suspended in ethanol (100 mL). The resulting mixture was carried out at room temperature for 24 h in a hydrogen atmosphere (5 bar) in a Parr apparatus. After completion of the reaction, the catalyst was filtered off and the residue washed with boiling ethanol. The solvent was evaporated under reduced pressure. After recrystallization from methanol, product **22** was obtained as a white solid in 91% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 2.43 (s, 6 H, -C$H_3$), 6.52 (s, 2 H, $H^3$ and $H^6$), 7.27 (m, 2 H, $H^{2'}$ and $H^{6'}$), 7.72 (m, 2 H, $H^{3'}$ and $H^{5'}$) ppm. MS (EI): $m/z$ (%) = 446 (17) $[M]^+$, 276 (100) $[M^\cdot - C_7H_7SO_2]^+$.

**General Procedure for the Synthesis of the Tosylated Diamines 23a and 23b by Condensation of Compound 22 with the Diketones 11a and 11b:** 4,5-Diamino-$N^1$,$N^2$-ditosyl-*o*-phenylenediamine (**22**) (1.34 g, 3.00 mmol) and the corresponding diketone **11a** or **11b** (2.50 mmol) were suspended in methanol (30 mL) and heated to reflux resulting in a clear solution. To complete the reaction, heating of the reaction mixture was continued for further 60 min. In the case of the dppz derivative the product started to precipitate after a short period of time. The hot solution was filtered and the crude

product was washed thoroughly with methanol. In the case of the dpq derivative the solvent was evaporated under reduced pressure. The crude products were dried in vacuo.

**Tosylated dppz Derivative 23a:** Brown solid, 91%. $^1$H NMR ([D$_6$]-DMSO, 500.1 MHz): $\delta$ = 9.48 (d, 2 H, $J$ = 8.2 Hz, H$^1$ and H$^8$), 9.16 (d, 2 H, $J$ = 4.6 Hz, H$^3$ and H$^6$), 7.93 (dd, 2 H, $J$ = 8.2 Hz/4.6 Hz, H$^2$ and H$^7$), 7.86 (s, 2 H, H$^{10}$ and H$^{13}$), 7.78 (d, 2 H, $J$ = 8.1 Hz, H$^{2'}$ and H$^{6'}$), 7.36 (d, 2 H, $J$ = 8.1 Hz, H$^{3'}$ and H$^{5'}$), 2.28 (s, 6 H, -C$H_3$) ppm. MS (EI): $m/z$ (%) = 620 [M]$^+$, 464 (100) [M$^\cdot$ – $C_7H_7SO_2$].

**Tosylated dpq Derivative 23b:** Brown solid, 87%. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 7.28–7.24 (m, 6 H, H$^{5'}$, H$^{3''}$ and H$^{5''}$), 7.41 (s, 2 H, H$^5$ and H$^8$), 7.63–7.61 (m, 2 H, H$^{3'}$), 7.71 (d, 4 H, $J$ = 8.0 Hz, H$^{2''}$ and H$^{6''}$), 7.92 (dd, 2 H, $J$ = 8.0 Hz/7.4 Hz, H$^{4'}$),8.65–8.63 (m, 2 H, H$^{6'}$), 10.52 (s, 2 H, -N$H$–$SO_2$) ppm. MS (EI): $m/z$ (%) = 622 (18) [M]$^+$ 467 (100) [M$^\cdot$ – $C_7H_7SO_2$]$^+$.

**Detosylation of Compounds 23a and 23b:** The tosylated dppz or dpq derivative **23a** or **23b** (1.00 mmol) and concd. sulfuric acid (5 mL) were heated for 4 hours in a water bath. The dark violet solution was then added dropwise to ice water and any possible precipitates were filtered off. Treatment of the resulting solution with a saturated $Na_2CO_3$ solution led to precipitation of the free diamine. The solids were filtered off, washed with a small amount of water and dried in vacuo. The free diamines **20a** and **20b** were obtained in 84% and 81% yield, respectively.

**2,3-Dimethyl-2,3-dihydropyrazino[2,3-*f*][1,10]phenanthroline (27a):** Phendione **11a** (210 mg, 1.00 mmol) was dissolved in ethanol (30 mL) and heated to reflux. To this solution a suspension of 2,3-diaminobutane dihydrochloride (193 mg, 1.20 mmol) and potassium carbonate (331 mg, 2.40 mmol) in ethanol (10 mL) was added dropwise. After this addition the resulting solution was heated for 3 h. After a short period of time a suspension of the pale yellow product was formed. Upon prolonged heating a dark violet precipitate was observed this was separated from the desired product by careful decanting of the suspension. The solvent was evaporated under reduced pressure. The crude product was recrystallized from ethanol and dried in vacuo. The product was obtained as a pale yellow microcrystalline solid in 78% yield. M.p. 161 °C. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 1.27 (s, 6 H, -C$H_3$), 3.74 (m, 2 H, H$^2$ and H$^3$), 7.23 (dd, 2 H, $J$ = 7.9 Hz/4.7 Hz, H$^6$ and H$^{11}$), 7.94 (dd, 2 H, 7.9 Hz/2.0 Hz, H$^7$ and H$^{10}$), 8.78 (dd, 2 H, $J$ = 4.7/2.0 Hz, H$^5$ and H$^{12}$) ppm. MS (EI): $m/z$ = 262 [M]$^+$.

**2,3-Dimethyl-5,6-(2-pyridyl)-2,3-dihydropyrazine (27b):** 2,2′-Pyridyl **11b** (212 mg, 1.00 mmol) was dissolved in ethanol (30 mL) and heated to reflux. To this solution a suspension of 2,3-diaminobutane dihydrochloride (193 mg, 1.20 mmol) and potassium carbonate (331 mg, 2.40 mmol) in ethanol (10 mL) was added dropwise. After this addition the resulting solution was heated for 3 h. The reaction mixture was cooled to room temperature and was then evaporated under pressure to half of its original volume. The resulting solution was stored at 4 °C overnight to allow precipitation of the product. The crude product was filtered off, recrystallized from ethanol and dried in vacuo. The product was obtained as a colourless solid in 81% yield. M.p. 131 °C. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 1.29 (m, 6 H, -C$H_3$), 3.78 (m, 2 H, H$^5$ and H$^6$), 6.85 (ddd, 2 H, $J$ = 7.4 Hz/4.9 Hz/1.2 Hz, H$^{5'}$), 7.24 (dd, 2 H, $J$ = 7.4 Hz/1.2 Hz, H$^{3'}$), 7.87 (ddd, 2 H, $J$ = 7.7 Hz/7.4 Hz/1.8 Hz, H$^{4'}$), 8.61 (dd, 2 H, $J$ = 4.9 Hz/1.8 Hz, H$^{6'}$) ppm. MS (CI, $NH_3$): $m/z$ = 264 [M]$^+$.

**General Procedure for the Dehydrogenation of the Dihydropyrazines 27a and 27b:** The dihydropyrazine derivative **27a** or **27b** (0.76 mmol) was suspended in mesitylene (10 mL) containing Pd/C (50 mg, 10%). The resulting mixture was refluxed for 20 h in an argon atmosphere. After the reaction was completed the solution was filtered hot.

**2,3-Dimethylpyrazino[2,3-*f*][1,10]phenanthroline (28a):** The reaction mixture was cooled to room temperature and was then evaporated under pressure to half of its original volume. The resulting solution was stored at 4 °C overnight to precipitate the product. The solid was filtered off and dried in vacuo. The product was obtained as a pale-yellow solid in 91% yield. M.p. 183 °C. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 2.42 (s, 6 H, -C$H_3$), 7.76 (dd, 2 H, $J$ = 8.2 Hz/4.5 Hz, H$^6$ and H$^{11}$), 8.76 (dd, 2 H, $J$ = 8.2 Hz/1.8 Hz, H$^5$ and H$^{12}$), 9.12 (dd, 2 H, $J$ = 4.5 Hz/1.8 Hz, H$^7$ and H$^{10}$) ppm. MS (CI): $m/z$ = 260 [M$^\cdot$]$^+$.

**2,3-Dimethyl-5,6-(2-pyridyl)pyrazine (28b):** The reaction mixture was cooled to room temperature. Upon cooling the crude product began to precipitate as dark brown needles. The crude product was recrystallized from ethanol and dried in vacuo. The product was obtained as a colourless solid in 91% yield. M.p. 152 °C. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 2.42 (s, 6 H, -C$H_3$), 7.23 (ddd, 2 H, $J$ = 7.4 Hz/4.8 Hz/1.2 Hz, H$^{5'}$), 7.58 (m, 2 H, H$^{3'}$), 7.93 (ddd, 2 H, $J$ = 8.0 Hz/7.4 Hz/1.8 Hz, H$^{4'}$), 8.64 (dd, 2 H, $J$ = 4.8 Hz/1.8 Hz) ppm. MS (CI, $NH_3$): $m/z$ = 262 [M]$^+$.

**General Procedure for the Synthesis of Bis(bromomethyl)-Substituted pphen, dpp, dppz, and dpq by Bromination of the Side Chains:** The dimethyl-substituted pphen, dpp, dppz or dpq derivative (0.50 mmol) was suspended in $CCl_4$ and heated to reflux. To this suspension a solution of bromine in $CCl_4$ (1 M, 1.1 mL) was added dropwise so that the solvent that condensed on the reflux condenser remained nearly colourless. During the addition of the bromine the reaction mixture was irradiated using a 400-W tungsten lamp. Work-up of the reaction mixtures was as follows.

**2,3-Bis(bromomethyl)pyrazino[2,3-*f*][1,10]phenanthroline (29a):** After completion of the reaction the volume of the reaction mixture was reduced to half of its original volume. The resulting mixture was stored at 4 °C overnight. The precipitate was filtered off and dried in vacuo. The product was obtained as a pale-yellow solid in 78% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.75 (s, 4 H, -C$H_2$), 7.84 (dd, 2 H, $J$ = 8.2 Hz/4.5 Hz, H$^6$ and H$^{11}$), 8.92 (dd, 2 H, $J$ = 8.2 Hz/1.8 Hz, H$^5$ and H$^{12}$), 9.04 (dd, 2 H, $J$ = 4.5 Hz /1.8 Hz, H$^7$ and H$^{10}$) ppm. MS (EI): $m/z$ (%) = 416/418/422 (1/2/1) [M]$^+$, 337/339 (14/13) [M$^\cdot$ – Br]$^+$, 259 (100) [M$^\cdot$ – 2 Br]$^+$, 81 (32), 79 (31).

**2,3-Bis(bromomethyl-5,6-(2-pyridyl)pyrazine (29b):** After completion of the reaction the volume of the reaction mixture was reduced to half of its original volume. The resulting mixture was stored at 4 °C overnight. The precipitate was filtered off and dried in vacuo. The product was obtained as a pale-yellow solid in 76% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.83 (s, 4 H, -C$H_2$-), 7.26 (ddd, 2 H, $J$ = 7.4 Hz/4.8 Hz/1.2 Hz, H$^{5'}$), 7.81 (m, 2 H, H$^{3'}$), 8.01 (ddd, 2 H, $J$ = 8.0 Hz/7.4 Hz/1.8 Hz, H$^{4'}$), 8.71 (dd, 2 H, $J$ = 4.8 Hz/1.8 Hz, H$^{6'}$) ppm. MS (EI): $m/z$ (%) = 339/341 (6/5) [M$^\cdot$ – Br]$^+$, 260 (100) [M]$^+$, 81/79 (18/19) [Br]$^+$.

**11,12-Bis(bromomethyl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine (31a):** After completion of the reaction the solution was cooled to room temperature and the precipitate was filtered off. The crude product was recrystallized from chloroform and dried in vacuo. The product was obtained as pale-yellow needles in 81% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.89 (s, 4 H, -C$H_2$), 7.73 (dd, 2 H, $J$ = 8.2 Hz/4.4 Hz, H$^2$ and H$^7$), 8.23 (s, 2 H, H$^{10}$ and H$^{13}$), 9.21 (dd, 2 H, $J$ = 4.4 Hz/1.9 Hz, H$^3$ and H$^6$), 9.52 (dd, 2 H, $J$ = 8.2 Hz/1.9 Hz, H$^1$ and H$^8$) ppm. MS (EI): $m/z$ (%) = 466/468/470 (1/2/1) [M]$^+$, 387/389 (5/4) [M$^\cdot$ – Br]$^+$, 308 (100) [M$^\cdot$ – 2 Br]$^+$, 81 (25), 79 (24).

**6,7-Bis(bromomethyl)-2,3-bis(2-pyridyl)quinoxaline (31b):** After completion of the reaction the solution was allowed to cool to room temperature and the precipitate was filtered off. The crude product was flash-chromatographed on silica gel using chloroform as the eluent. The product was obtained as a pale-yellow solid in 82% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.88 (s, 4 H, -C$H_2$Br), 7.25–7.22 (m, 2 H, H$^{5'}$), 7.84–7.80 (m, 2 H, H$^{4'}$), 7.96 (d, 2 H, $J$ = 7.5 Hz, H$^{3'}$), 8.21 (s, 2 H, H$^5$ and H$^8$), 8.34 (d, 2 H, $J$ = 4.4 Hz, H$^{6'}$) ppm. $^{13}$C NMR ($CDCl_3$, 125.8 MHz): $\delta$ = 29.5 (s, 2C), 123.3 (t, 2C), 124.2 (t, 2C), 131.7 (t, 2C), 136.9 (t, 2C), 138.9 (q, 2C), 140.9 (q, 2C), 148.4 (t, 2C), 153.3 (q, 2C), 156.8 (q, 2C) ppm. MS (EI): *m*/*z* (%) = 468/470/472 (1/2/1) [M]$^+$, 389/391 (27/26) [M$^\cdot$ – Br]$^+$, 310 (100) [M$^\cdot$ – 2 Br]$^+$, 100), 155 (11), 81/79 (Br, 32/33).

**General Procedure for the Synthesis of Bis(bromomethyl)-Substituted pphen, pdppz, and pdpq by Condensation Reactions of Diamines 13, 20a and 20b:** 1,4-Dibromo-2,3-butanedione **33** (122 mg, 0.50 mmol) and the appropriate diamine (0.60 mmol) were dissolved in methanol (30 mL) and refluxed for 5 h. Work-up of the reaction mixture was as follows.

**2,3-Bis(bromomethyl)pyrazino[2,3-*f*][1,10]phenanthroline (29a):** After completion of the reaction the solution was allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography ($SiO_2$, eluent hexane:chloroform (3:1, v/v)). The pure product was obtained as a pale-yellow solid in 83% yield. For analytical data, see above.

**12,13-Bis(bromomethyl)pyrazino[2,3-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine (34a):** After completion of the reaction the solution was allowed to cool to room temperature. The precipitate was filtered off, washed with methanol and dried in vacuo. The product was obtained as a brown solid in 81% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 7.77 (dd, 2 H, $J$ = 8.2 Hz/4.5 Hz, H$^2$ and H$^7$), 8.78 (dd, 2 H, $J$ = 8.2 Hz/1.8 Hz, H$^1$ and H$^8$), 9.05 (dd, 2 H, $J$ = 4.5 Hz/1.8 Hz, H$^3$ and H$^6$), 9.48 (s, 2 H, H$^{10}$ and H$^{15}$) ppm. MS (EI): *m*/*z* (%) = 439/441 (8/7) [M$^\cdot$ – Br]$^+$, 360 (100) [M$^\cdot$ – 2 Br]$^+$, 81 (22), 79 (23).

**2,3-Bis(bromomethyl)-7,8-bis(2-pyridyl)pyrazino[2,3-*g*]quinoxaline (34b):** After completion of the reaction the solution was allowed to cool to room temperature. The precipitate was filtered off, washed with methanol and dried in vacuo. The product was obtained as a brown solid in 91% yield. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.87 (s, 4 H, -C$H_2$Br), 7.23 (dd, 2 H, $J$ = 7.4 Hz/4.8 Hz, H$^{5'}$), 7.62 (dd, 2 H, $J$ = 8.1 Hz/1.2 Hz, H$^{3'}$), 7.95 (ddd, 2 H, $J$ = 8.1 Hz/7.4 Hz/1.8 Hz, H$^{4'}$), 8.66 (dd, 2 H, $J$ = 4.8 Hz/1.8, H$^{6'}$), 8.95 (s, 2 H, H$^5$ and H$^{10}$) ppm. MS (EI): *m*/*z* (%) = 441/443 (13/12) [M]$^+$, 362 (100) [M$^\cdot$ – 2 Br]$^+$, 79/81 (27/26) [Br]$^+$.

**2,3-Bis(bromomethyl)-6,7-dinitroquinoxaline (35):** 1,4-Dibromo-2,3-butanedione **33** (244 mg, 1.00 mmol) and 4,5-dinitro-*o*-phenylenediamine (236 mg, 1.20 mmol) were dissolved in methanol (30 mL) and heated to reflux for 2 h. After completion of the reaction the solution was allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography ($SiO_2$, eluent hexane:chloroform (1:1, v/v)). The product was obtained as a red solid in 94% yield. M.p. 153 °C. $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = 4.87 (s, 4 H, -C$H_2$), 8.94 (s, 2 H, H$^5$ and H$^8$) ppm. $^{13}$C NMR ($CDCl_3$, 125.8 MHz): $\delta$ = 30.4 (s, 2C), 103.8 (t, 2C), 145.5 (q, 2C), 150.4 (q, 2C) ppm. MS (EI): *m*/*z* (%) = 404/406/408 (1/2/1) [M]$^+$, 325/327 (7/6) [M$^\cdot$ – Br]$^+$, 246 (100) [M$^\cdot$ – 2 Br]$^+$, 200 (21) [M$^\cdot$ – 2 Br – $NO_2$]$^+$, 154 (34) [M$^\cdot$ – 2 Br – 2 $NO_2$]$^+$, 81 (18), 79 (19).

**6,7-Diamino-2,3-bis(bromomethyl)quinoxaline (36):** Compound **34** (150 mg, 0.37 mmol) and Pd/C (30 mg, 10%) were suspended in ethanol (100 mL). The resulting mixture was carried out at room temperature for 24 h in a hydrogen atmosphere (5 bar) in a Parr apparatus. After completion of the reaction the catalyst was filtered off and the residue washed with boiling ethanol. The solvent was evaporated under reduced pressure. The solid obtained consisted of the desired bis(bromomethyl) derivative **35** and 6,7-diamino-2,3-dimethylquinoxaline. Attempts to separate the quinoxalines failed. The bis(bromomethyl) derivative could be enriched by column chromagraphy ($SiO_2$, eluent hexane:chloroform (1:1, v/v)). $^1$H NMR ($CDCl_3$, 500.1 MHz): $\delta$ = *2.46** (s, -C$H_3$), 4.85 (s, 4 H, -C$H_2$), 5.22 (s, 4 H, -N$H_2$), *7.33**, 7.27 (s, 2 H, H$^5$ and H$^8$) ppm. $^{13}$C NMR ($CDCl_3$, 125.8 MHz): $\delta$ = 23.3 (s, 2C), *30.4**, 87.5 (t, 2C), *90.4**, 131.92 (q, 2C), 137.35 (q, 2C), *138.3**, *150.4**, 152.7 (q, 2C) ppm. MS (EI) *m*/*z* (%) = 344/346/348 (2/4/2) [M]$^+$, 265/267 (9/8) [M$^\cdot$ – Br]$^+$, 186 (100) [M$^\cdot$ – 2 Br]$^+$, 81 (23), 79 (24) (* signals arising from 6,7-diamino-2,3-dimethylquinoxaline).

**General Procedure for the Synthesis of Bis(bromomethyl)-Substituted pdppz and pdpq by Condensation of 6,7-Diamino-2,3-bis(bromomethyl)quinoxaline with Diketones 11a and 11b:** A solution of 6,7-diamino-2,3-bis(bromomethyl)quinoxaline **36** (184 mg, 1.20 mmol) and the appropriate diketone **11a** or **11b** (1.00 mol) in methanol (100 mL) were heated to reflux for 5 h. After a short period of time the product started to precipitate. After completion of the reaction the solution was allowed to cool to room temperature. The solid was filtered off and washed with methanol. The by-products dimethyl-substituted pdppz and pdpq were formed due to the impurity of compound **35**.

**12,13-Bis(bromomethyl)pyrazino[2,3-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine (33a):** 86% yield. For analytical data, see above.

**2,3-Bis(bromomethyl)-7,8-bis(2-pyridyl)pyrazino[2,3-*g*]quinoxaline (33b):** 91% yield. For analytical data, see above.

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