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# An efficient method for the synthesis of imidazo[1,5-*a*]quinoxalines from 3-acylquinoxalinones and benzylamines via a novel imidazoannulation

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ABSTRACT

The reaction of 3-aroylquinoxalin-2(1*H*)-ones and their *N*-alkyl analogues with benzylamines in DMSO proceeds through an intermediate formation of *N*-(α-quinoxalinylbenzylydene)benzylamine, which when subjected to oxidative cyclocondensation gives imidazo[1,5-*a*]quinoxalines. Applying this new approach of imidazoannullation to the bis-3-aroylquinoxalines makes it possible to develop fundamentally new methods of the synthesis of bis-imidazo[1,5-*a*]quinoxalines with the use of different benzylamines and heteromacrocycles with the 1,3-bis(3-arylimidazo[1,5-*a*]quinoxalin-1-yl)benzene structural fragment when *m*-xylylenediamine is used.

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## 1. Introduction

Imidazoquinoxalines are one of the important classes of heterocycles that are often found in biologically active and pharmacologically useful agents such as Dazoquinast (antiallergic), LU 73068 (anticonvulsant (glycine/NMDA) but not the NMDA receptor antagonist), FG 10571 NNC 14-0571, Panadiplon, U-78875 anxiolytic (benzodiazepine receptor partial agonist), U-8044 (antidepressant, anxiolytic), U-97775 (anxiolytic ($GABA_A$ receptor ligand)).[1,2] Synthetic sequences have attracted considerable attention in recent years.[3,4]

Four methods have been previously developed for the preparation of imidazo[1,5-*a*]quinoxalines based quinoxaline derivatives. The first method involved intramolecular cyclization of functionalized quinoxaline derivatives.[2–8] Of the four sub-variants for the construction of the tricyclic system three **a**[2–6], **b**[7] and **c**[8] have been implemented (Chart 1). The second approach involved the reaction of quinoxaline derivatives with the sources of monoatomic synthons. Of the three possible sub-variants for the construction of the tricyclic system only one **d**[7,9,10] has been developed. The third approach involves the cyclization of quinoxaline and quinoxalin-2(1*H*)-one derivatives proceeding with the formation of N(10)–C(1) and C(3)–C(3a) bonds on exposure to a source of the C–N–C fragment (sub-variant **f**[11–22]) (Chart 1).

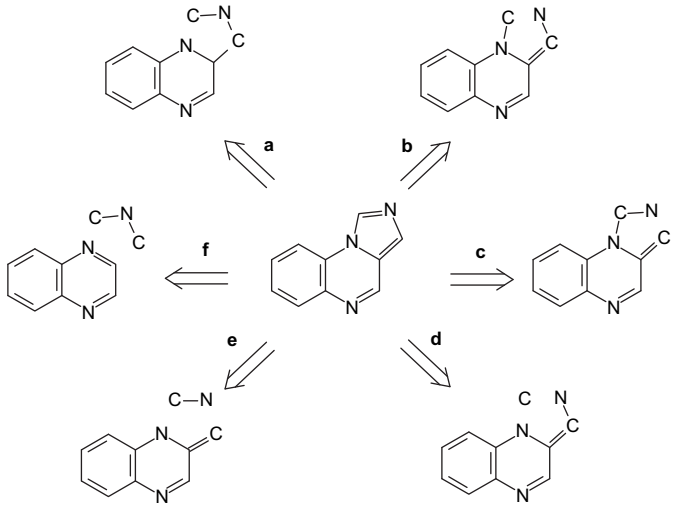


**Chart 1.** Implemented methods for the construction of imidazo[1,5-*a*]quinoxalines based on quinoxaline derivatives.

Recently, we have developed a fourth variant for the construction of imidazo[1,5-*a*]quinoxalin-2(1*H*)-ones, proceeding with the

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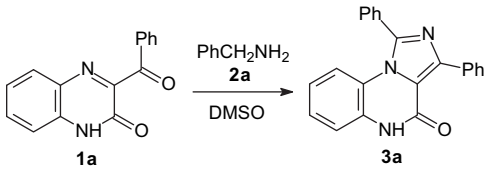
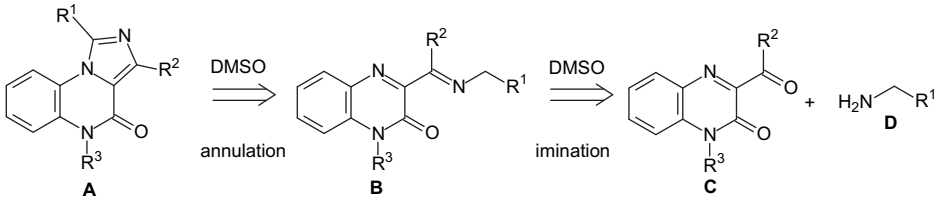
formation of N(10)–C(1) and N(2)–C(3) bonds (sub-variant **e**), i.e., the closure of the imidazole ring with the parting of compounds, which provide the C–N fragment into the newly formed imidazo[1,5-*a*]quinoxalin-2(1*H*)-one system. The reactions of 3-α-chlorobenzyl quinoxalin-2(1*H*)-ones with potassium thiocyanate and potassium isocyanate, as synthetic equivalents of C–N synthons led to the formation of 1-mercaptane and 1-hydroxy-derivatives of imidazo[1,5-*a*]quinoxalin-4(5*H*)-ones[6,10] correspondingly. In addition to inorganic reagents, benzylamine and *m*-xylylenediamine provide a useful source of the C–N fragment. Previously, we found that 3-benzoylquinoxalin-2(*1H*)-one (**1a**) when heated in DMSO at the temperature of 150 °C for 2 h undergoes condensation with the formation of 1,3-diphenylimidazo[1,5-*a*]quinoxalin-4(5*H*)-one (**3a**) (Scheme 1).[23]




**Scheme 1.** Oxidative imidazoannulation of 3-benzoylquinoxalin-2-one (**1a**) with benzylamine.

## 2. Results and discussion

The paper is devoted to the development of a new approach to the design of imidazo[1,5-*a*]quinoxalines through the introduction of the C–N fragment into quinoxaline derivatives, based on the above-mentioned reaction (Scheme 1). In this case, both various types of 3-aroyl(alkanoyl)quinoxalin-2-ones and benzyl-, α(β)-picolylamines were used and bis-analogues of the reagent were used as well. The approach towards the construction of the imidazo[1,5-*a*]quinoxaline system could be represented in the following retrosynthetic scheme (Scheme 2), which implies that the interaction of 3-aroyl(alkanoyl)quinoxalin-2-ones of type **C** with the compound **D** containing aminomethyl fragment at the first stage of the reaction proceeds with the formation of Schiff bases **B**. Under the reaction conditions in DMSO the latter are subjected to intramolecular cyclization with the imidazoannulation to the quinoxaline system and the desired tricycle **A** is directly formed (Scheme 2).



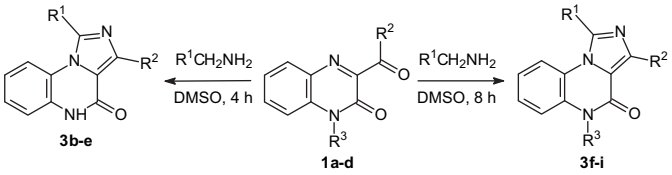

**Scheme 2.** Retrosynthetic representation of the implementation of the variant **e**.

The ready availability of the starting reagents—3-aroyl(alkanoyl)quinoxalin-2-ones[24–30] and appropriate amines and the simplicity of the experimental procedure make this method widely applicably.

### 2.1. Synthesis of imidazo[1,5-*a*]quinoxalin-4(5*H*)-ones 3b–i

The use of 3-acetylquinoxalin-2(1*H*)-one **1b** and *N*-alkyl derivatives **1c**,**d**,**e** instead of 3-benzoylquinoxalin-2(1*H*)-one **1a** as well as aminomethylpyridines instead of benzylamine do not preclude the reaction of imidazoannulation and lead to 1-pyridyl-3-phenylimidazo[1,5-*a*]quinoxalin-4(5*H*)-ones **3b**,**c**, 1-phenyl-3-methylimidazo[1,5-*a*]quinoxalin-4(5*H*)-one **3d**, 1-pyridyl-3-methylimidazo[1,5-*a*]quinoxalin-4(5*H*)-one **3e** and their *N*-alkylated derivatives **3f**–**i** (Table 1).

**Table 1**
The synthesis of 1-phenyl- and hetarylimidazo[1,5-*a*]quinoxalin-4(5*H*)-ones **3b–i**




| Entry | Substrates | | Product (yield, %) |
|---|---|---|---|
| | Ketone ($R^2$, $R^3$) | Amine ($R^1$) | |
| 1 | **1a** (Ph, H) | **2b** (α-Py) | **3b** (66) |
| 2 | **1a** (Ph, H) | **2c** (β-Py) | **3c** (63) |
| 3 | **1b** (Me, H) | **2a** (Ph) | **3d** (40) |
| 4 | **1b** (Me, H) | **2c** (β-Py) | **3e** (51) |
| 5 | **1c** (Ph, Me) | **2c** (β-Py) | **3f** (65) |
| 6 | **1d** (Ph, Et) | **2a** (Ph) | **3g** (76) |
| 7 | **1d** (Ph, Et) | **2c** (β-Py) | **3h** (66) |
| 8 | **1e** (Ph, Pr) | **2a** (Ph) | **3i** (75) |

In the IR spectra of imidazo[1,5-*a*]quinoxalin-4-ones **3** there are no absorption bands of $\nu_{COket}$ in the area of 1675–1714 $cm^{-1}$ characteristic of the initial 3-acylquinoxalin-2(1*H*)-one **1**. The mass spectra of these compounds display molecular ion peaks at appropriate *m*/*z* values. Variety of NMR correlation methods[31,32] were used to establish structures of these compounds. For example, combination of 2D COSY and 1D TOCSY spectra allowed straightforward separation of three aromatic systems. $^1H$–$^{13}C$ HSQC and particularly $^1H$–$^{15}N$/$^{13}C$ HMBC correlations enable to assign these aromatic spin systems to corresponding moieties (quinoxaline, Py/Ph and Ph) and to prove the overall structure (e.g., on Fig. 1 some experimental NMR connectivities are schematically shown for **3c**). A number of NOEs strongly support these structural hypotheses (see Supplementary data).

Good correlation ($R^2$=0.97) of calculated (GIAO DFT)[33–36] versus experimental $^{13}C$ chemical shifts additionally proves the above conclusions on the structures of **3c**.

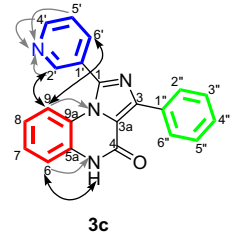


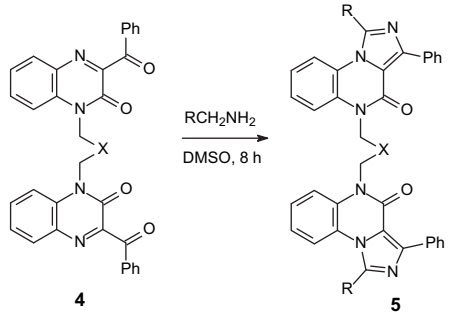

**Figure 1.** The principal HMBC $^1H$–$^{15}N$ (grey arrows, from protons to nitrogens) and NOE correlations (black arrows) for **3c**.

It is noteworthy that when compared with nonsubstituted 3-phenylimidazo[1,5-*a*]quinoxalin-4-one[6,10] the introduction of aryl substituent in the first position significantly shifts the signal H(9) to high field (by ca. 1.3 ppm) due to the selective and strong anisotropic effect of the aryl system.[37–39]

### 2.2. Synthesis of α,ω-bis(1,3-diphenylimidazo[1,5-*a*]quinoxalin-4-on-5-yl)alkanes 5a–g

This reaction has also been advantageously employed with compounds containing two benzoylquinoxalin-2-one fragments, which makes it possible to obtain podands with the terminal imidazo[1,5-*a*]quinoxalin-4-one systems connected by a spacer with the atoms N(5) of the imidazo[1,5-*a*]quinoxalin-4-one system. The interaction of α,ω-bis(3-benzoylquinoxalin-2-on-1-yl)alkanes **4**, easily available due to the reaction of 3-benzoylquinoxalin-2(1*H*)-ones with various dibromoalakanes with the benzyl-, α(β)-picolylamines in the solution of DMSO at 150 °C results in the formation of α,ω-bis(1,3-diphenylimidazo[1,5-*a*]quinoxalin-4-on-5-yl)alkanes **5** (Table 2).

**Table 2**
The synthesis of α,ω-bis(1,3-diphenylimidazo[1,5-*a*]quinoxalin-4-on-5-yl)alkanes **5a–g**




| Entry | Substrates | | Product (yield, %) |
|---|---|---|---|
| | Diketone (X) | Amine (R) | |
| 1 | **4a** ($CH_2OCH_2$) | **2a** (Ph) | **5a** (48) |
| 2 | **4b** ($(CH_2)_4$) | **2a** (Ph) | **5b** (77) |
| 3 | **4b** ($(CH_2)_4$) | **2c** (β-Py) | **5c** (65) |
| 4 | **4c** ($(CH_2OCH_2)_2$) | **2a** (Ph) | **5d** (60) |
| 5 | **4e** ($(CH_2OCH_2)_3$) | **2a** (Ph) | **5e** (79) |
| 6 | **4e** ($(CH_2OCH_2)_3$) | **2c** (β-Py) | **5f** (65) |

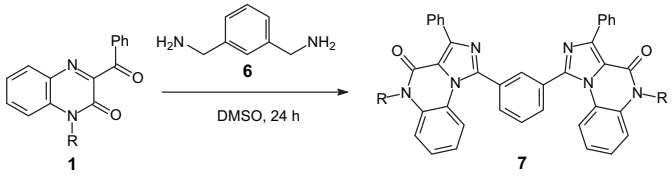
There are no absorption bands of ketone carbonyl groups in the IR spectra of compounds **5**. There are molecular ion peaks of compound **5** in the mass spectra of electron ionization. In $^1$H NMR spectra of **5** there are several lines at 2.5–5 ppm corresponding to spacer protons. In general, the aromatic fragments of $^1$H NMR spectra are similar to those for tricycles **3** although signals due to different aromatic systems are partly superimposed (e.g., for **5f** Fig. 2a). However, each spin system can be easily discerned and assigned to corresponding moieties in 1D TOCSY experiments (e.g., Fig. 2b–d). These fragments can be linked into a whole molecule by $^1$H–$^{15}$N/$^{13}$C HMBC correlations (Fig. 2e). Finally the combination of inter moiety NOEs additionally supports the above derived structures.

### 2.3. Synthesis of 1,3-bis(imidazo[1,5-*a*]quinoxalin-4-on-1-yl)benzenes 7a–d

Another approach to the synthesis of bis-1,3-diphenylimidazo[1,5-*a*]quinoxalin-4-ones includes *m*-xylylenediamine, containing two aminomethyl-groups with the reaction of 3-benzoylquinoxalin-2-ones instead of that of benzylamine with the latter. The presence of heterocyclic fragments rigidly oriented relative to each other at the *meta*-positions in the benzene ring makes 1,3-dihetarylbenzenes very interesting both as bidentate chelating agents and precursors of macrocycles. Lately bis-hetarylbenzenes,[40–43] their heteroanalogues[44,45] and macrocycles,[46–50] with the above fragments attracted considerable attention both due to their ability to act as new receptors for different substrates[48,49] and as blocks in optical materials,[42–44] and due to their biological activity[40,41] as well. Bis(imidazo[1,5-*a*]quinoxalin-4-onyl)benzenes, as well as macrocycles, containing two imidazo[1,5-*a*]quinoxaline systems have not as yet been obtained.

The interaction of *m*-xylylenediamine (**6**) with various 3-benzoylquinoxalin-2-ones **1** results in bisheteroarylbenzenes **7** (Table 3).

**Table 3**
The synthesis of 1,3-bis-imidazo[1,5-*a*]quinoxalin-4-on-1-ylbenzenes **7a–d**[a]




| Entry | Ketone (R) | Product (yield, %) |
|---|---|---|
| 1 | **1c** (Me) | **7a** (31) |
| 2 | **1d** (Et) | **7b** (43) |
| 3 | **1e** (Pr) | **7c** (39) |
| 4 | **1f** (Bn) | **7d** (32) |

[a] After solvent evaporation, the residue was purified by a short gel plug using $CH_2Cl_2$.

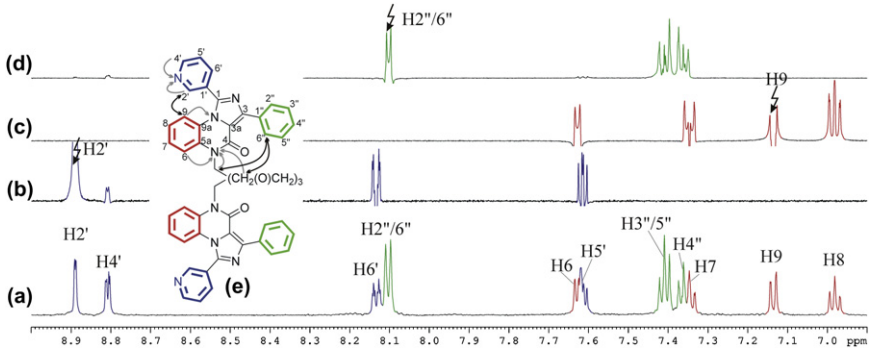



**Figure 2.** Low field fragments of $^1$H NMR spectra of **5f** in DMSO-$d_6$ (600.1 MHz) at 303 K: (a) $^1$H spectrum; (b–d) 1D TOCSY spectra (excited protons are marked by an arrow); (e) the principal HMBC $^1$H–$^{15}$N (grey arrows, from protons to nitrogens) and the NOE correlations (black arrows) for **5f**.

In the mass spectra of electron ionization of compounds **7** there appear peaks of corresponding molecular ions. Similar to the above cases the structures of compounds **7** are directly established by NMR correlation methods (see Supplementary data). In Figure 3 the low field fragments of $^1$H NMR spectra of **7b** are shown and for comparison the data for **5d** are also given. In general, in **7** the phenyl group protons in position 3 (Ph″) undergo only small changes as compared with compounds without such a xylylene-linkage. At the same time there are significant low field shifts of quinoxaline protons in **7b** versus **5b** that are probably due to the mutual deshielding effect[37–39] of 'edge-to-edge' orientated quinoxaline fragments in this strained system.

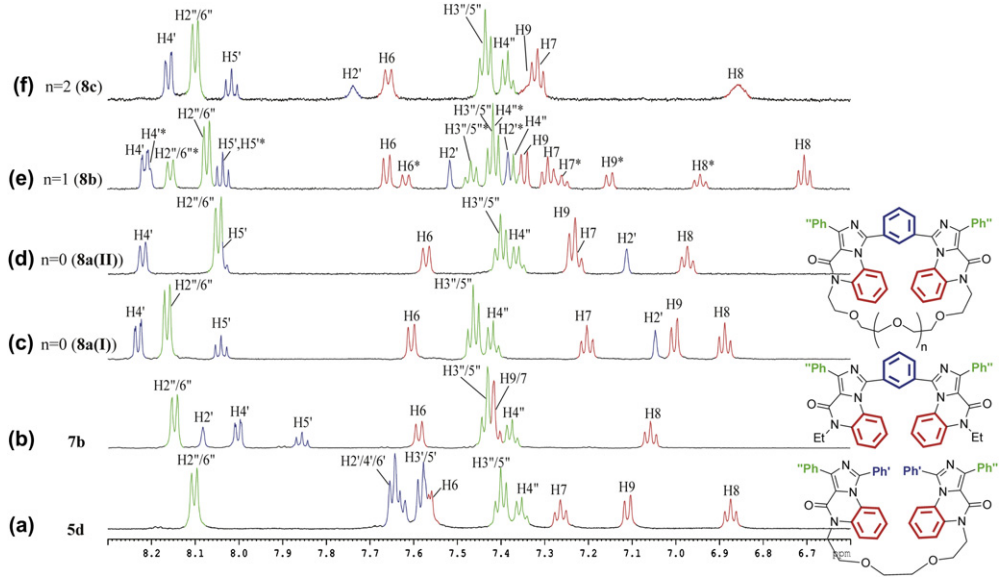


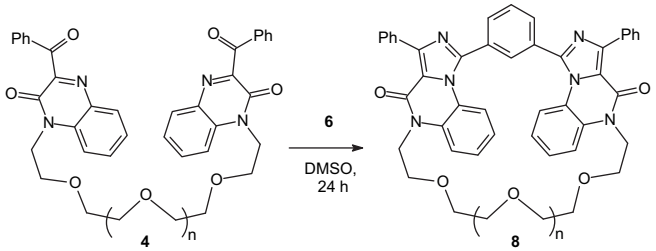

**Figure 3.** Low field fragments of $^1$H NMR spectra of **5d**, **7b** and **8a–c** in DMSO-$d_6$ (600.1 MHz) at 303 K.

## 2.4. Synthesis of diimidazoquinoxalinabenzene-cyclophanes 8a–c

The combination of the above approaches to the synthesis of bis-imidazo[1,5-*a*]quinoxalin-4-onylbenzenes with the interaction of compounds **4** and *m*-xylylenediamine **6** makes it possible to synthesize macrocyclic compounds—diimidazoquinoxalinabenzene-cyclophanes **8** in an 8–10% yields (Table 4). The use of $LiClO_4$, NaCl, KI as templates affects the yield of macrocycles in the interactions of diketones **4e** with diamino **6** in a different way. If the presence of $Li^+$ has virtually no effect on the yields of the formation of macrocycle **8b**, which in this case is 8%, in the presence of $Na^+$ the yields increase by two times and become 14%. Further increase of the cation size leads to the reduction of the yields by 11%. The reaction under high dilution does not increase the yields of the macrocycles **8**. The use of AcOH instead of DMSO leads to the formation of compound **8b** with a 7% yield. The purification of compounds **8** was performed by column chromatography with subsequent recrystallization. When pre-processed the reaction mixture was treated with the hydrochloride of semicarbazone for 3 h in boiling AcOH, which greatly facilitated the separation of the desired products.

Compound **8a** was obtained as a mixture of two diastereomers (ca. 1:1), which were separated and characterized separately (Fig. 3c and d). Presumably these diastereomers (conformers) are due to the different (*syn* and *anti*) mutual orientation of tricyclic systems. In fact, in these heteroaromatic systems there are a number of anisotropic fragments that can produce shielding/deshielding effects and therefore there are no straightforward relationships between 3D structure and low/high field shifts in $^1$H spectra. Therefore accurate high level non empirical calculations and extensive NMR investigations must be performed to establish finally the conformational structures.[51] In the case of **8b** $^1$H NMR spectra most likely correspond to the equilibrium of conformations with the population of ca. 1.0:2.0 in DMSO. In the case of macrocycle **8c** there is no atropizomerism in $^1$H NMR spectra probably because the size of the spacer is longer and the equilibrium is fast in the NMR time scale. Conformational rigidity/flexibility is also manifested in $^1$H NMR spectra of spacer protons. The geminal protons of spacers are nonequivalent ($\Delta\delta$) in **8a** and **b** while in **8c** they are essentially broadened. Large values of $\Delta\delta$ are in particularly vicinal to quinoxaline moiety in **8a**/**b** (0.7 ppm) for the spacer protons (N–$CH_2$–$CH_2$–O). In **8c** these protons are almost not observed in $^1$H NMR spectra at room temperature due to the strong collapse of signals.

**Table 4**
The synthesis of diimidazoquinoxalinabenzenecyclophanes **8a–c**[a]




| Entry | Diketone (*n*) | Product (yield, %) |
|---|---|---|
| 1 | **4c** (0) | **8a**(**I**) (5,[b] 8[c]), **8a**(**II**) (4,[b] 6[c]) |
| 2 | **4e** (1) | **8b**(**I**)+**8b**(**II**) (8,[b,c] 14,[d] 11[e]) |
| 3 | **4f** (2) | **8c** (8[b]) |

[a] After solvent evaporation, the residue was purified by a short gel plug using $CH_2Cl_2$ as eluent and recrystallized from corresponding solvent.
[b] Without template.
[c] In the presence of $Li^+$ as template.
[d] In the presence of $Na^+$ as template.
[e] In the presence of $K^+$ as template.

Mass spectra of these compounds displayed molecular ion peaks at appropriate $m/z$ values.

## 3. Conclusions

In conclusion, we have shown that the reaction of 3-aroyl- and alkanoylbenzoylquinoxalin-2-ones **1** with benzyl- and picolylamines in DMSO at the temperature of 150 °C provides a simple one-pot procedure for the synthesis of imidazo[1,5-*a*]quinoxalin-4-one derivatives **3b–i**. Moreover, the combination of the above mentioned reagents with their bis-analogues makes it possible to synthesize not only bis-analogues **5a–g**, **7b–e** of imidazo[1,5-*a*]quinoxalin-4-ones but also macrocyclic compounds with the diimidazoquinoxalinabenzene fragments **8a–c**.

## 4. Experimental section

### 4.1. General

The melting points were determined on a Boetius hot-stage apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. NMR experiments were carried out with Bruker spectrometers AVANCE-400 (400.1 MHz ($^1$H), 100.6 MHz ($^{13}$C)) and AVANCE-600 (600.1 MHz ($^1$H), 150.9 MHz ($^{13}$C), 60.8 MHz ($^{15}$N)) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the $z$-direction of 53.5 G cm$^{-1}$. All spectra were acquired in a 5-mm gradient inverse broad band probehead. Chemical shifts are reported on the $\delta$ (ppm) scale and are relative to the residual $^1$H and $^{13}$C signal of DMSO-$d_6$ and $CDCl_3$. Chemical shifts of **3c** were determined within the DFT framework using a hybrid exchange-correlation functional, B3LYP, at the 6-31G(d) level as implemented in Gaussian 98.[52] Full geometry optimizations were performed at the ab initio RHF/6-31G level. All data were referred to TMS ($^1$H and $^{13}$C) chemical shifts that were calculated in the same conditions. The MALDI mass spectra were obtained on a Bruker UltraFlex III MALDI TOF/TOF instrument with 2,5-dihydroxybenzoic acid (2,5-DHB) as a matrix. Mass spectra electronic ionization (EI) was measured on a TRACE MS spectrometer. The elemental analyses were carried out at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences.

The 3-acylquinoxalin-2-ones were synthesized according to the reported methods.[27–30]

### 4.2. General procedure for the synthesis of imidazo-[1,5-*a*]quinoxalin-4(5*H*)-ones 3 and 1,3-bis(imidazo-[1,5-*a*]quinoxalin-4-on-5-yl)alkanes 5

A solution of benzylamine or appropriate picolylamine (3.9 mmol) in DMSO (1 mL) was added to a solution of 3-acylquinoxalin-2-one **1a**,**b** (2.0–3.3 mmol), **1c–e** (2.8 mmol), **4a–e** (1.3 mmol) in DMSO (5 mL). The reaction mixture was stirred for 4–8 h at ~150 °C (Tables 1 and 2). When synthesizing **3b**,**c**,**f** and **5b** the reaction mixture was left overnight at room temperature, while the crystals of the product were precipitated, collected by suction filtration, washed with EtOH (2×5 mL) and dried in air. When synthesizing **3d**,**e**,**g**,**h**,**i** and **5a**,**c–g** after cooling to room temperature and standing overnight, the reaction mixture was poured into water (20 mL). After collection by suction filtration the crude product was washed with water (2×5 mL), dried in air and purified by recrystallization from the appropriate solvent (Tables 1 and 2).

*4.2.1. 3-Phenyl-1-(pyridin-2-yl)imidazo[1,5-a]quinoxalin-4(5H)-one (**3b**).* White powder, mp 349–351 °C. Found: C, 74.65; H, 4.21; N, 16.42. $C_{21}H_{14}N_4O$ requires: C, 74.54; H, 4.17; N, 16.56%. IR ($\nu_{max}$, cm$^{-1}$, Nujol mull): 3220–2500, 1671, 1615, 1586, 1558, 1487, 1428, 1405, 1338, 1248, 842, 748; $^1$H NMR (400.1 MHz, DMSO-$d_6$): $\delta$=6.94 (2H, m, H8, H9), 7.28–7.42 (3H, m, H6, H7, H4″), 7.45 (2H, dd, *J* 7.7, 7.4 Hz, H3″/5″), 7.67 (1H, dd, *J* 6.2, 5.3 Hz, H5′), 7.98 (1H, d, *J* 7.5 Hz, H6′), 8.12 (1H, ddd, *J* 7.7, 7.7, 1.5 Hz, H5′), 8.20 (2H, d, *J* 7.3 Hz, H2″/6″), 8.76 (1H, d, *J* 4.7 Hz, H3′), 11.48 (1H, s, NH). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=116.2, 117.6, 118.6, 120.8, 121.4, 124.9, 125.3, 126.8, 127.3, 127.8, 129.28, 129.33, 132.7, 137.5, 143.1, 143.3, 149.2, 150.2, 154.8. MS (EI, 70 eV): $m/z$ (%)=339 ($M^+$+1, 34), 338 ($M^+$, 84), 337 (100), 206 (22), 205 (60), 168 (42), 89 (11).

*4.2.2. 3-Phenyl-1-(pyridin-3-yl)imidazo[1,5-a]quinoxalin-4(5H)-one (**3c**).* White powder, mp 339–341 °C. Found: C, 74.63; H, 4.09; N, 16.48. $C_{21}H_{14}N_4O$ requires: C, 74.54; H, 4.17; N, 16.56%. IR ($\nu_{max}$, cm$^{-1}$, Nujol mull): 3220–2500 (br), 1662, 1612, 1595, 1566, 1331, 1302, 1273, 749, 722; $^1$H NMR (600.1 MHz, DMSO-$d_6$): $\delta$=6.94 (1H, ddd, *J* 8.4, 7.0, 1.5 Hz, H8), 7.04 (1H, d, *J* 8.4 Hz, H9), 7.31 (1H, dd, *J* 7.7, 7.6 Hz, H7), 7.34–7.41 (2H, m, H6, H4″), 7.45 (2H, dd, *J* 7.7, 7.0 Hz, H3″/5″), 7.66 (1H, dd, *J* 6.2, 4.8 Hz, H4′), 8.16–8.22 (3H, m, H6′, H2″/6″), 8.83 (1H, dd, *J* 4.8, 1.5 Hz, H4′), 8.93 (1H, d, *J* 1.8 Hz, H2′). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=116.6 (C6), 116.7 (C9), 118.9 (C3a), 121.2 (C9a), 121.9 (C8), 123.7 (C5′), 127.1 (C7), 127.6 (C3″/5″), 128.1 (C4″), 128.2 (C1′), 129.4 (C2″/6″), 129.7 (C5a), 132.7 (C1″), 137.2 (C6′), 141.6 (C1), 143.5 (C3), 149.7 (C2′), 150.8 (C4′), 155.1 (C4). $^{15}$N NMR (60.8 MHz, $CD_3CN$ (external)): $\delta$=131.1 (N5), 172.4 (N10), 312.7 (N3′). MS (EI, 70 eV): $m/z$ (%)=339 ($M^+$+1, 56), 338 ($M^+$, 100), 337 (89), 236 (22), 235 (62), 205 (94), 179 (16).

*4.2.3. 3-Methyl-1-phenylimidazo[1,5-a]quinoxalin-4(5H)-one (**3d**).* White powder, mp 290–292 °C. Found: C, 74.25; H, 4.82; N, 15.15. $C_{17}H_{13}N_3O$ requires: C, 74.17; H, 4.76; N, 15.26%. IR ($\nu_{max}$, cm$^{-1}$, Nujol mull): 3220–2500 (br), 1673, 1618, 1573, 1504, 1409, 1332, 1253, 1122, 838, 697, 670, 584, 469; $^1$H NMR (400.1 MHz, DMSO-$d_6$): $\delta$=2.63 (3H, c, Me), 6.87 (1H, ddd, *J* 8.5, 7.3, 1.6 Hz, H8), 7.01 (1H, d, *J* 8.5 Hz, H9), 7.26 (1H, ddd, *J* 8.1, 7.3, 1.2 Hz, H7), 7.29 (1H, dd, *J* 8.1, 1.6 Hz, H9), 7.58–7.67 (5H, m, Ph). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=13.8, 116.2, 116.6, 118.4, 121.3, 121.4, 126.3, 128.6, 129.2, 129.68, 129.7, 131.9, 141.5, 143.1, 155.7. MS (EI, 70 eV): $m/z$ (%)=276 ($M^+$+1, 26), 275 ($M^+$, 100), 274 (28), 234 (26), 206 (6), 172 (36), 144 (42), 143 (39), 118.1 (22), 104 (8), 90 (14), 81 (32), 69 (40).

*4.2.4. 3-Methyl-1-(pyridin-3-yl)imidazo[1,5-a]quinoxalin-4(5H)-one (**3e**).* White powder, mp >200 °C (dec) (EtOH). Found: C, 69.48; H, 4.29; N, 20.32. $C_{16}H_{12}N_4O$ requires: C, 69.55; H, 4.38; N, 20.28%. IR ($\nu_{max}$, cm$^{-1}$, Nujol mull): 3200–2500 (br), 1671, 1618, 1573, 1507, 1492, 1412, 1331, 1253, 1193, 1124, 1024, 811, 764, 711; $^1$H NMR (600.1 MHz, DMSO-$d_6$): $\delta$=2.64 (1H, s, $CH_3$), 6.93 (1H, ddd, *J* 8.5, 7.2, 1.3 Hz, H8), 7.01 (1H, d, *J* 8.1 Hz, H9), 7.28 (1H, ddd, *J* 8.1, 7.2, 0.9 Hz, H7), 7.32 (1H, dd, *J* 8.1, 1.3 Hz, H6), 7.63 (1H, dd, *J* 7.6, 5.0 Hz, H5′), 8.11 (1H, ddd, *J* 7.7, 1.8, 1.8 Hz, H6′), 8.81 (1H, dd, *J* 5.0, 1.8 Hz, H4′), 8.85 (1H, d, *J* 1.4 Hz, H2′), 11.31 (1H, s, NH). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=13.8, 116.1, 116.8, 119.0, 121.3, 121.6, 123.4, 126.5, 128.1, 129.7, 136.8, 140.3, 141.8, 149.5, 150.5, 155.5. MS (MALDI TOF)=277 ($M+H^+$), 299 ($M+Na^+$).

*4.2.5. 5-Methyl-3-phenyl-1-(pyridin-3-yl)imidazo[1,5-a]quinoxalin-4-one (**3f**).* White powder, mp 234–236 °C (DMSO). Found: C, 74.88; H, 4.49; N, 15.82. $C_{22}H_{16}N_4O$ requires: C, 74.98; H, 4.58; N, 15.90%. IR ($\nu_{max}$, cm$^{-1}$, Nujol mull): 1660, 1610, 1591, 1567, 1542, 1483, 1420, 1391, 1362, 1334, 1301, 1281, 1252, 1187, 1101, 970, 819, 754, 722, 695, 671; $^1$H NMR (600.1 MHz, $CDCl_3$): $\delta$=3.67 (3H, s, $CH_3$), 6.97 (1H, ddd, *J* 8.1, 6.8, 1.4 Hz, H8), 7.29 (1H, d, *J* 8.5 Hz, H9), 7.33–7.42 (3H, m, H6, H7, H4″), 7.47 (2H, dd, *J* 7.7, 7.6 Hz, H3″/5″), 7.52 (1H, dd, *J* 7.7, 4.9 Hz, H5′), 8.07 (1H, d, *J* 8.1 Hz, H6′), 8.13 (2H, d, *J* 7.4 Hz, H2″/6″), 8.82 (1H, d, *J* 4.9 Hz, H4′), 8.98 (1H, s, H2′). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=28.5, 116.3, 116.9, 118.3, 121.8, 122.0,

123.5, 127.1, 127.3, 127.8, 127.9, 129.4, 130.8, 132.6, 136.8, 141.2, 143.8, 149.5, 150.6, 154.6. MS (MALDI TOF)=353 ($M+H^+$), 375 ($M+Na^+$).

*4.2.6. 1,3-Diphenyl-5-ethylimidazo[1,5-a]quinoxalin-4-one (**3g**).* White powder, mp 175–177 °C (EtOH). Found: C, 78.97; H, 5.29; N, 11.41. $C_{24}H_{19}N_3O$ requires: C, 78.88; H, 5.24, N, 11.50%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1655, 1610, 1588, 1540, 1487, 1325, 1394, 1300, 1267, 1248, 1181, 1109, 858, 780, 744; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=1.27 (3H, t, *J* 7.1 Hz, $CH_3$), 4.27 (2H, q, *J* 7.1 Hz, $CH_2$), 6.97 (1H, dd, *J* 8.8, 7.8 Hz, H8), 7.18 (1H, d, *J* 8.8 Hz, H9), 7.36–7.41 (2H, m, H7, H4″), 7.44 (2H, dd, *J* 8.1, 7.6 Hz, H3″/5″), 7.56–7.66 (4H, m, H6, H3′/5′, H4′), 7.71 (2H, d, *J* 8.0 Hz, H2′/6′), 8.14 (2H, d, *J* 7.6 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=12.3 ($CH_3$), 36.1 ($CH_2$), 116.1 (C6), 117.4 (C9), 117.7 (C3a), 121.8 (C8), 122.2 (C9a), 127.1 (C7), 127.4 (C3″/5″), 127.9 (C4″), 128.9 (C3′/5′), 129.4 (C2′/6′), 129.6 (C5a), 129.5 (C2″/6″), 130.1 (C4′), 131.8 (C1′), 132.9 (C1″), 143.4 (C3), 144.0 (C1), 154.3 (C4). MS (MALDI TOF)=366 ($M+H^+$), 388 ($M+Na^+$), 404 ($M+K^+$).

*4.2.7. 5-Ethyl-3-phenyl-1-(pyridin-3-yl)imidazo[1,5-a]quinoxalin-4(5H)-one (**3h**).* White powder, mp 208–210 °C. Found: C, 75.28; H, 5.03; N, 15.32. $C_{23}H_{18}N_4O$ requires: C, 75.39; H, 4.95; N, 15.29%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1651, 1594, 1500, 1484, 1396, 1325, 1300, 1252, 1181, 1111, 754, 695; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=1.28 (3H, t, *J* 7.2 Hz, $CH_3$), 4.28 (2H, q, *J* 7.2 Hz, $CH_2$), 7.04 (1H, ddd, *J* 8.5, 7.8, 1.1 Hz, H8), 7.19 (1H, dd, *J* 8.5, 1.2 Hz, H9), 7.37–7.47 (4H, m, H7, H3″/5″, H4″), 7.62 (1H, d, *J* 8.5 Hz, H6), 7.65 (1H, ddd, *J* 7.7, 4.8, 0.7 Hz, H5′), 8.14 (2H, d, *J* 7.2 Hz, H2″/6″), 8.18 (1H, ddd, *J* 7.9, 1.8, 1.8 Hz, H6′), 8.82 (1H, dd, *J* 4.9, 1.5 Hz, H4′), 8.93 (1H, d, *J* 1.5 Hz, H2′). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=12.3 ($CH_3$), 36.1 ($CH_2$), 116.3 (C6), 117.4 (C9), 118.2 (C3a), 122.0 (C8, C9a), 123.7 (C5′), 127.3 (C7), 127.5 (C3″/5″), 128.1 (C4″), 128.1 (C1′), 129.5 (C5a, C2″/6″), 132.7 (C1″), 137.1 (C6′), 141.2 (C1), 143.7 (C3), 149.7 (C2′), 150.8 (C4′), 154.2 (C4). $^{15}N$ NMR (60.8 MHz, $CD_3CN$-$d_3$ (external)): $\delta$=137.5 (N5), 170.5 (N10), 312.7 (N3′). MS (MALDI TOF)=367 ($M+H^+$), 389 ($M+Na^+$), 405 ($M+K^+$).

*4.2.8. 1,3-Diphenyl-5-propylimidazo[1,5-a]quinoxalin-4-one (**3i**).* White powder, mp 198–200 °C (EtOH). Found: C, 75.69; H, 5.21; N, 14.62. $C_{24}H_{20}N_4O$ requires: C, 75.77; H, 5.30; N, 14.73%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1647, 1607, 1589, 1546, 1484, 1334, 1324, 1297, 1247, 1182, 1116, 786, 746, 708, 693; $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$=1.07 (3H, t, *J* 7.4 Hz, $CH_3$), 1.83 (2H, m, $CH_2$), 4.20 (2H, dd, *J* 9.7, 8.0 Hz, $CH_2N$), 6.89 (1H, m, H8), 7.27–7.40 (4H, m, H6, H7, H9, H4″), 7.46 (2H, dd, *J* 7.6, 7.1 Hz, H3″/5″), 7.51–7.60 (3H, m, H3′/5′, H4′), 7.70 (2H, m, H2′/6′), 8.16 (2H, d, *J* 7.0 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=10.7, 19.9, 42.3, 116.0, 117.2, 117.5, 121.6, 122.0, 126.9, 127.2, 127.7, 128.7, 129.2, 129.4, 129.7, 129.9, 131.7, 132.8, 143.4, 143.8, 154.5. MS (MALDI TOF)=380 ($M+H^+$), 402 ($M+Na^+$).

*4.2.9. 1,5-Bis(1,3-diphenylimidazo[1,5-a]quinoxalin-4-on-1-yl)-3-oxapentane (**5a**).* White powder, mp 174–176 °C (DMCO). Found: C, 77.32; H, 4.95; N, 11.36. $C_{48}H_{36}N_6O_3$ requires: C, 77.40; H, 4.87; N, 11.28%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1655, 1610, 1503, 1485, 1447, 1337, 1324, 1300, 1255, 1180, 1108, 1053, 781, 750, 694; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=3.85 (4H, t, *J* 5.5 Hz, $OCH_2$), 4.39 (4H, t, *J* 5.5 Hz, $NCH_2$), 6.87 (2H, dd, *J* 8.1, 7.6 Hz, H8), 7.10 (2H, d, *J* 8.3 Hz, H9), 7.15 (2H, dd, *J* 7.9, 7.3 Hz, H7), 7.37 (2H, dd, *J* 7.3, 6.5 Hz, H4″), 7.41 (4H, dd, *J* 7.3, 7.1 Hz, H3″/5″), 7.57 (2H, d, *J* 8.9 Hz, H6), 7.60 (4H, d, *J* 7.1 Hz, H2′/6′), 7.64 (2H, dd, *J* 7.6, 6.8 Hz, H4′), 7.65 (4H, d, *J* 7.6 Hz, H3′/5′), 8.12 (4H, d, *J* 7.6 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=41.0, 67.5, 116.5, 117.0, 117.5, 121.7, 121.9, 126.6, 127.3, 127.8, 128.8, 129.2, 129.4, 129.9, 130.0, 131.8, 132.8, 143.6, 143.9, 154.8. MS (EI, 70 eV): *m*/*z* (%)=746 ($M^+$+2, 2), 745 ($M^+$+1, 6), 744 ($M^+$, 11), 746 (2), 745 (6), 744 $[M]^+$ (11), 757 (8), 407 (8), 381 (28), 363 (44), 337 (100), 260 (10), 234 (18), 219 (24), 205 (32), 102 (38).

*4.2.10. 1,6-Bis(1,3-diphenylimidazo[1,5-a]quinoxalin-4-on-1-yl)hexane (**5b**).* White powder, mp 271–273 °C (DMCO). Found: C, 79.46; H, 5.28; N, 11.21. $C_{50}H_{40}N_6O_2$ requires: C, 79.34; H, 5.33; N, 11.10%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1655, 1611, 1503, 1485, 1447, 1395, 1335, 1300, 1250, 1121, 1050, 781, 747, 704, 694; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=1.45–1.55 (4H, m, $(CH_2)_2(CH_2)_2(CH_2)_2$), 1.65–1.75 (4H, m, $(CH_2CH_2(CH_2)_2CH_2CH_2)$), 4.24 (4H, t, *J* 7.5 Hz, $NCH_2$), 6.97 (2H, dd, *J* 8.3, 8.1 Hz, H8), 7.19 (2H, dd, *J* 8.4, 1.3 Hz, H9), 7.43–7.47 (4H, m, H7, H4″), 7.44 (4H, dd, *J* 7.6, 7.3 Hz, H3″/5″), 7.57 (2H, d, *J* 8.1 Hz, H6), 7.60–7.68 (6H, m, H3′/5′, H4′), 7.72 (2H, dd, *J* 7.6, 1.6 Hz, H2′/6′), 8.14 (4H, dd, *J* 7.7, 1.3 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=25.8, 26.5, 40.8, 116.1, 117.3, 117.6, 121.7, 122.1, 127.0, 127.4, 127.8, 128.8, 129.3, 129.5, 129.7, 130.0, 131.8, 132.9, 143.5, 144.0, 154.5. MS (EI, 70 eV): *m*/*z* (%)=757 ($M^+$+1, 7), 756 ($M^+$, 11), 420 (32), 406 (44), 378 (50), 364 (57), 337 (70), 322 (16), 205 (16).

*4.2.11. 1,6-Bis{3-phenyl-1-(pyridin-3-yl)imidazo[1,5-a]quinoxalin-4-on-1-yl}hexane (**5c**).* White powder, mp 278–280 °C (DMCO). Found: C, 75.86; H, 5.08; N, 14.71. $C_{48}H_{38}N_8O_2$ requires: C, 75.97; H, 5.05; N, 14.77%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1649, 1592, 1501, 1485, 1411, 1396, 1301, 1254, 1112, 1053, 1025, 752, 698, 421; $^1H$ NMR (400.1 MHz, DMSO-$d_6$): $\delta$=3.30 ($CH_2$), 4.24 (4H, m, $CH_2N$), 7.01 (2H, ddd, *J* 8.4, 7.7, 1.1 Hz, H8), 7.17 (2H, dd, *J* 8.4, 1.1 Hz, H9), 7.35–7.47 (8H, m, H7, H3″/5″, H4″), 7.58 (2H, d, *J* 8.4 Hz, H6), 7.64 (2H, ddd, *J* 7.7, 4.8, 0.8 Hz, H5′), 8.12 (4H, ddd, *J* 7.0, 2.4, 1.5 Hz, H2″/6″), 8.17 (2H, ddd, *J* 7.9, 2.3, 2.0 Hz, H6′), 8.82 (2H, dd, *J* 4.9, 1.5 Hz, H4′), 8.92 (2H, d, *J* 2.3 Hz, H2′). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=25.8, 26.5, 40.9, 116.3, 117.3, 118.1, 121.9, 122.0, 123.6, 127.3, 127.4, 128.0, 128.1, 129.5, 129.7, 132.7, 137.0, 141.2, 143.8, 149.6, 150.7, 154.4. MS (EI, 70 eV): *m*/*z* (%)=758 ($M^+$, 6), 421 (20), 420 (34), 407 (40), 365 (46), 352 (46), 338 (100), 337 (36), 223 (24), 219 (20), 205 (30), 18 (58).

*4.2.12. 1,8-Bis(1,3-diphenylimidazo[1,5-a]quinoxalin-4-on-1-yl)-3,5-dioxaoctane (**5d**).* White powder, mp 216–218 °C (DMCO). Found: C, 76.27; H, 5.23; N, 10.56. $C_{50}H_{40}N_6O_4$ requires: C, 76.12; H, 5.11; N, 10.65%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1645, 1609, 1591, 1504, 1485, 1445, 1393, 1352, 1326, 1300, 1257, 1246, 1178, 1124, 1101, 1033, 1005, 777, 744, 695, 670; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=3.57 (4H, s, $CH_2$-3), 3.71 (4H, dd, *J* 7.3, 6.2 Hz, $CH_2$-2), 4.32 (4H, dd, *J* 7.9, 6.2 Hz, $CH_2$-1($CH_2N$)), 6.88 (2H, dd, *J* 8.3, 7.7 Hz, H8), 7.11 (2H, d, *J* 8.3 Hz, H9), 7.26 (2H, dd, *J* 8.3, 7.7 Hz, H7), 7.35 (2H, dd, *J* 7.7, 7.4 Hz, H4″), 7.40 (4H, dd, *J* 8.3, 7.4 Hz, H3″/5″), 7.54–7.6 (6H, m, H6, H3′/5′), 7.61–7.67 (6H, m, H2′/6′, H4′), 8.10 (4H, d, *J* 7.7 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=40.9 ($CH_2$-1($CH_2N$)), 67.4 ($CH_2$-2), 70.0 ($CH_2$-3), 116.7 (C6), 117.1 (C9), 117.6 (C3a), 121.8 (C8), 122.0 (C9a), 126.8 (C7), 127.4 (C3″/5″), 128.0 (C4″), 128.9 (C3′/5′), 129.3 (C2′/6′), 129.5 (C2″/6″), 130.1 (C5a, C4′), 131.7 (C1′), 132.8 (C1″), 143.6 (C3), 144.0 (C1), 154.7 (C4). MS (EI, 70 eV): *m*/*z* (%)=788 ($M^+$, 5), 452 (5), 425 (7), 394 (7), 364 (37), 337 (100), 322 (5), 234 (11), 219 (25), 205 (15).

*4.2.13. 1,11-Bis(1,3-diphenylimidazo[1,5-a]quinoxalin-4-on-1-yl)-3,5,8-trioxaundecane (**5e**).* White powder, mp 168–170 °C ($CH_3CN$). Found: C, 74.89; H, 5.36, N, 10.00. $C_{52}H_{44}N_6O_5$ requires: C, 74.98; H, 5.32, N, 10.09%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1655, 1609, 1552, 1502, 1485, 1444, 1395, 1363, 1331, 1289, 1251, 1178, 1102, 991, 750, 727, 689, 669; $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$=3.53–3.59 (4H, m, $OCH_2$), 3.59–3.63 (4H, m, $OCH_2$), 3.85 (4H, t, *J* 6.0 Hz, $OCH_2$), 4.42 (4H, t, *J* 6.0 Hz, $NCH_2$), 6.86 (2H, ddd, *J* 8.2, 7.3, 1.0 Hz, H8), 7.22–7.30 (4H, m, Ar), 7.34–7.40 (2H, m, Ar), 7.44 (4H, dd, *J* 7.6, 7.3 Hz, H3″/5″), 7.50–7.59 (8H, m, Ar), 7.66–7.72 (4H, m, H2′/6′), 8.14 (4H, dd, *J* 7.6, 1.3 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=67.3, 69.7, 69.8, 116.6, 117.1, 117.6, 121.8, 122.0, 126.7, 127.3, 127.9, 128.8, 129.2, 129.4, 130.0,

130.1, 131.7, 132.8, 143.6, 143.9, 154.7. MS (MALDI TOF)=833 ($M+H^+$), 855 ($M+Na^+$), 871 ($M+K^+$).

*4.2.14. 1,11-Bis(1-pyrydinyl-3-phenylimidazo[1,5-a]quinoxalin-4-on-1-yl)-3,5,8-trioxaundecane (**5f**).* White powder, mp 202–204 °C ($CH_3CN$). Found: C, 71.87; H, 5.03, N, 13.36. $C_{50}H_{42}N_8O_5$ requires: C, 71.93; H, 5.07, N, 13.42%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1649, 1611, 1595, 1539, 1483, 1445, 1395, 1335, 1299, 1254, 1120, 1054, 1024, 750, 716, 693, 669; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=3.45 (4H, m, $CH_2$-4), 3.51 (4H, m, $CH_2$-3), 3.72 (4H, dd, *J* 6.7, 6.0 Hz, $CH_2$-2), 4.36 (4H, dd, *J* 6.7, 6.0 Hz, $CH_2$-1($CH_2N$)), 6.98 (2H, dd, *J* 8.5, 7.5 Hz, H8), 7.14 (2H, d, *J* 8.5 Hz, H9), 7.33–7.38 (4H, m, H7, H4″), 7.41 (4H, dd, *J* 7.7, 7.5 Hz, H3″/5″), 7.62 (4H, m, H6, H5′), 8.10 (4H, d, *J* 7.7 Hz, H2″/6″), 8.13 (2H, ddd, *J* 7.9, 1.9, 1.7 Hz, H6′), 8.81 (2H, dd, *J* 5.0, 1.4 Hz, H4′), 8.89 (2H, d, *J* 1.4 Hz, H2′). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=40.9 ($CH_2$-1($CH_2N$)), 67.3 ($CH_2$-2), 69.7 ($CH_2$-4), 69.9 ($CH_2$-3), 116.9 (C6), 117.1 (C9), 118.1 (C3a), 121.8 (C9a), 122.1 (C8), 123.7 (C5′), 127.1 (C7), 127.5 (C3″/5″), 128.1 (C1′, C4″), 129.5 (C2″/6″), 130.1 (C5a), 132.6 (C1″), 137.0 (C6′), 141.3 (C1), 144.0 (C3), 149.6 (C2′), 150.8 (C4′), 154.7 (C4). $^{15}N$ NMR (60.8 MHz, $CD_3CN$ (external)): $\delta$=131.1 (N5), 170.6 (N10), 312.5 (N3′). MS (MALDI TOF)=835 ($M+H^+$).

### 4.3. General procedure for the synthesis of 1,3-bis(imidazo[1,5-*a*]quinoxalin-4-on-1-yl)-benzenes 7 and cyclophanes 8

A solution of *m*-xylylenediamine (70 mg, 0.51 mmol) in DMSO (1 mL) was added to the solution of 3-acylquinoxalin-2(1*H*)-one **1** (0.72 mmol) or α,ω-bis(1,3-diphenylimidazo[1,5-*a*]quinoxalin-4-on-5-yl)alkane **4** (0.34 mmol) in DMSO (5 mL). The reaction mixture was stirred for 24 h at ~150 °C. The solvents were removed in vacuum and after allowing the reaction mixture to cool to room temperature water (5 mL) was added and the crystals of the product were precipitated, collected by suction filtration, washed with water (2×5 mL) and dried in air. The solution of semicarbazide hydrochloride (33 mg, 0.3 mmol) in AcOH (5 mL) was added to a solution of this crude product in AcOH (5 mL), and the reaction mixture was stirred for 2 h at ~120 °C. The solvent was removed in vacuum, and the crystals of the product were precipitated by addition of water (3 mL), collected by suction filtration, washed with water (2×5 mL) and dried in air. After the usual column chromatographic purification process ($CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOH=100:1) pure **7** and **8** were obtained as white solids (Tables 3 and 4).

*4.3.1. 1,3-Bis(5-methyl-3-phenylimidazo[1,5-a]quinoxalin-4-on-1-yl)benzene (**7a**).* White powder, mp 321–323 °C. $R_f$=0.36 (EtAc/hexane=3:7). Found: C, 76.85; H, 4.61; N, 13.32. $C_{40}H_{28}N_6O_2$ requires: C, 76.91; H, 4.52; N, 13.45%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1656, 1591, 1502, 1396, 1348, 1333, 1303, 1259, 1104, 750, 695; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=3.60 (6H, s, Me), 7.11 (2H, dd, *J* 8.2, 7.6 Hz, H8), 7.35–7.50 (10H, m, H7,9, H3″/5″, H4″), 7.58 (2H, d, *J* 7.8 Hz, H6), 7.89 (1H, dd, *J* 7.8, 7.6 Hz, H5′), 8.03 (2H, d, *J* 7.7 Hz, H4′/6′), 8.12 (1H, s, H2′), 8.16 (4H, d, *J* 7.1 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=28.5, 116.2, 117.1, 117.9, 121.88, 121.9, 126.9, 127.3, 127.8, 129.3, 129.6, 130.3, 130.81, 130.82, 132.5, 132.7, 142.9, 143.5, 154.6. MS (EI, 70 eV): *m*/*z* (%)=625 ($M^+$+1, 40), 624 ($M^+$, 86), 521 (30), 381 (32), 337 (62), 312 (12), 273 (18), 233 (30), 218 (100), 205 (34), 150 (24), 106 (32), 97 (42), 94 (50), 54 (56).

*4.3.2. 1,3-Bis(5-ethyl-3-phenylimidazo[1,5-a]quinoxalin-4-on-1-yl)-benzene (**7b**).* White powder, mp 322–324 °C. $R_f$=0.63 (EtAc/hexane=3:7). Found: C, 77.35; H, 4.81; N, 12.75. $C_{42}H_{32}N_6O_2$ requires: C, 77.28; H, 4.94; N, 12.87%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1653, 1609, 1588, 1500, 1446, 1400, 1301, 1253, 1184, 1111, 926, 859, 823, 728, 715, 695; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=1.25 (6H, t, *J* 7.1 Hz, $CH_3$), 4.25 (4H, q, *J* 7.1 Hz, $CH_2$), 7.05 (2H, dd, *J* 8.6, 7.7 Hz, H8), 7.35–7.45 (10H, m, H7, H9, H3″/5″, H4″), 7.58 (2H, d, *J* 8.5 Hz, H6), 7.85 (1H, dd, *J* 8.7, 7.7 Hz, H5′), 8.00 (2H, dd, *J* 7.7, 1.2 Hz, H4′/H6′), 8.08 (1H, s, H2′), 8.15 (4H, d, *J* 7.4 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=12.3 ($CH_3$), 36.1 ($CH_2$), 116.2 (C6), 117.5 (C9), 117.9 (C3a), 122.0 (C8), 122.1 (C9a), 127.3 (C7), 127.5 (C3″/5″), 128.0 (C4″), 129.5 (C2″/6″), 129.6 (C5a), 129.8 (C5′), 130.5 (C2′), 131.0 (C4′), 132.6 (C1′), 132.8 (C1″), 143.0 (C1), 143.5 (C3), 154.3 (C4). MS (EI, 70 eV): *m*/*z* (%)=653 ($M^+$+1, 28), 652 ($M^+$, 76), 549 (18), 326 (59), 312 (40), 273 (18), 261 (30), 233 (76), 205 (100), 157 (18), 105 (20), 89 (44), 44 (58), 18 (86).

*4.3.3. 1,3-Bis(5-propyl-3-phenylimidazo[1,5-a]quinoxali–4-on-1-yl)-benzene (**7c**).* White powder, mp 146–148 °C. $R_f$=0.79 (EtAc/hexane=3:7). Found: C, 77.48; H, 5.27; N, 12.46. $C_{44}H_{36}N_6O_2$ requires: C, 77.63; H, 5.33, N, 12.34%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1662, 1611, 1591, 1485, 1298, 1252, 1228, 1181, 1144, 1114, 1075, 783, 750, 694; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=0.98 (6H, t, *J* 7.4 Hz, Me), 1.65–1.72 (4H, m, $CH_2CH_3$), 4.18 (4H, t, *J* 7.4 Hz, $NCH_2$), 7.09 (2H, dd, *J* 8.2, 7.6 Hz, H8), 7.30–7.50 (10H, m, H7,9, H3″/5″, H4″), 7.59 (2H, d, *J* 8.7 Hz, H6), 7.88 (1H, dd, *J* 7.6, 7.6 Hz, H5′), 8.02 (2H, d, *J* 7.6 Hz, H4′,6′), 8.11 (1H, s, H2′), 8.14 (4H, d, *J* 7.6 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=10.1, 19.9, 42.2, 116.1, 117.3, 117.8, 121.7, 121.9, 126.9, 127.2, 127.8, 129.4, 129.6, 129.7, 130.4, 130.8, 132.6, 132.7, 142.8, 143.5, 154.4. MS (EI, 70 eV): *m*/*z* (%)=682 (M+2, 2), 681 ($M^+$+1, 10), 680 ($M^+$, 24), 638 (6), 596 (8), 375 (10), 304 (16), 298 (36), 246 (25), 233 (29), 219 (49), 205 (100), 190 (18).

*4.3.4. 1,3-Bis(5-benzyl-3-phenylimidazo[1,5-a]quinoxalin-4-on-1-yl)benzene (**7d**).* White powder, mp 143–145 °C. $R_f$=0.82 (EtAc/hexane=3:7). Found: C, 80.47; H, 4.71; N, 10.75. $C_{52}H_{36}N_6O_2$ requires: C, 80.39; H, 4.67; N, 10.82%. IR ($\nu_{max}$, $cm^{-1}$, Nujol mull): 1656, 1612, 1592, 1495, 1485, 1401, 1300, 1257, 1128, 1076, 1028, 960, 782, 670, 458; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=5.40 (4H, s, $CH_2$), 7.09 (2H, dd, *J* 8.2, 7.6 Hz, H8), 7.20–7.50 (22H, m, H 6, 7, 9, H3″/5″, H4″, $CH_2$*Ph*), 7.88 (1H, dd, *J* 7.9, 7.4 Hz, H5′), 8.05 (2H, d, *J* 7.4 Hz, H4′/6′), 8.15 (1H, s, H2′), 8.16 (4H, d, *J* 7.4 Hz, H2″/6″). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=44.1, 116.7, 117.3, 117.7, 122.1, 122.2, 126.4, 126.8, 126.9, 127.4, 127.9, 128.4, 129.5, 129.8, 129.9, 130.5, 131.0, 132.6, 132.7, 136.2, 143.0, 144.0, 154.9. MS (EI, 70 eV): *m*/*z* (%)=776 ($M^+$, 2), 685 (6), 233 (3), 205 (7).

*4.3.5. 1⁴,3⁴,-Dioxa-1³,3³-diphenyl-1,3(1,5)-diimidazo[1,5-a]quinoxalina-2(1,3)benzene-6,9-dioxacycloundecane (**8a**(**I**)).* White powder, mp >360 °C. IR ($\nu_{max}$, $cm^{-1}$, KBr): 3053, 2956, 2924, 2856, 1658, 1609, 1484, 1443, 1395, 1353, 1297, 1253, 1126, 1090, 1049, 992, 744, 711, 693; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=2.78 and 3.06 (4H, m, $CH_2$-3), 3.32 and 3.71 (4H, m, $CH_2$-2), 4.11 and 4.71 (4H, m, $CH_2$-1($CH_2N$)), 6.89 (2H, dd, *J* 8.6, 7.7 Hz, H8), 7.01 (2H, d, *J* 8.6 Hz, H9), 7.05 (1H, s, H2′), 7.20 (2H, ddd, *J* 8.6, 7.8, 1.1 Hz, H7), 7.42 (2H, dd, *J* 8.3, 7.3 Hz, H4″), 7.46 (4H, dd, *J* 8.0, 7.3 Hz, H3″/5″), 7.61 (2H, d, *J* 8.5 Hz, H6), 8.04 (1H, dd, *J* 8.5, 7.7 Hz, H5′), 8.17 (4H, d, *J* 8.0 Hz, H2″/6″), 8.23 (2H, dd, *J* 7.7, 1.5 Hz, H4′). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$): $\delta$=40.1 ($CH_2$-1($CH_2N$)), 68.6 ($CH_2$-2), 69.1 ($CH_2$-3), 117.7 (C6), 118.7 (C9), 118.9 (C3a), 121.2 (C9a), 121.9 (C8), 126.9 (C7), 127.6 (C3″/5″), 128.5 (C4″), 129.5 (C2′, C2″/6″), 129.9 (C4′), 130.4 (C5a), 130.6 (C1′), 131.4 (C5′), 132.1 (C1″), 143.3 (C1), 144.8 (C3), 154.9 (C4). MS (EI, 70 eV): *m*/*z* (%) 711 ($M^+$+1, 42), 710 ($M^+$, 81), 597 (18), 596 (38), 233 (26), 219 (100), 218 (56), 190 (32), 165 (30), 91 (48), 69 (52), 43 (94).

*4.3.6. 1⁴,3⁴,-Dioxa-1³,3³-diphenyl-1,3(1,5)-diimidazo[1,5-a]quinoxalina-2(1,3)benzene-6,9-dioxacycloundecane (**8a**(**II**)).* White powder. IR ($\nu_{max}$, $cm^{-1}$, KBr): 2922, 2854, 1662, 1608, 1481, 1446, 1412, 1387, 1359, 1334, 1299, 1255, 1118, 1049, 997, 747, 694; $^1H$ NMR (600.1 MHz, DMSO-$d_6$): $\delta$=2.56 and 2.97 (4H, m, $CH_2$-3), 3.44 and 3.62 (4H, m, $CH_2$-2), 4.05 and 4.77 (4H, m, $CH_2$-1($CH_2N$)), 6.97 (2H,

dd, *J* 8.8, 7.7 Hz, H8), 7.11 (1H, s, H2′), 7.21–7.26 (4H, m, H7, H9), 7.36 (2H, dd, *J* 8.0, 7.1 Hz, H4″), 7.40 (4H, dd, *J* 8.0, 7.5 Hz, H3″/5″), 7.57 (2H, d, *J* 8.2 Hz, H6), 8.02–8.07 (5H, m, H5′, H2″/6″), 8.22 (2H, d, *J* 7.6 Hz, H4′, H6′). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=40.3 ($CH_2$-1($CH_2$N)), 68.4 ($CH_2$-2), 70.2 ($CH_2$-3), 117.9 (C6), 118.3 (C9), 118.8 (C3a), 121.8 (C9a), 123.6 (C8), 125.8 (C7), 127.6 (C3″/5″), 128.3 (C4″), 129.3 (C2″/6″), 129.4 (C4′), 129.7 (C5a), 131.2 (C5′), 131.4 (C2′), 132.1 (C1′), 132.3 (C1″), 143.4 (C1), 144.6 (C3), 155.2 (C4). MS (MALDI TOF) $[MH]^+$=712.

*4.3.7. 1⁴,3⁴,-Dioxa-1³,3³-diphenyl-1,3(1,5)-diimidazo[1,5-a]quinoxalina-2(1,3)benzene-6,9,12-trioxacyclotetradecane (**8b**(**I**)+**8b**(**II**)).* White powder, mp 322–324 °C (MeOH). IR ($\nu_{max}$, $cm^{-1}$, KBr): 2917, 2859, 1660, 1610, 1484, 1444, 1391, 1359, 1334, 1299, 1258, 1110, 1094, 1053, 996, 753, 702; $^1$H NMR (600.1 MHz, DMSO-$d_6$): $\delta$=2.86–3.03 (12H, m, $CH_2$-4, $CH_2$-4*), 3.05–3.24 (12H, m, $CH_2$-3, $CH_2$-3*), 3.52–3.71 (12H, m, $CH_2$-2, $CH_2$-2*), 4.04–4.13 and 4.77–4.86 (12H, m, $CH_2$-1, $CH_2$-1*), 6.71 (4H, dd, *J* 8.5, 7.8 Hz, H8), 6.94 (2H, dd, *J* 8.7, 7.8 Hz, H8*), 7.15 (2H, d, *J* 8.3 Hz, H9*), 7.24–7.31 (6H, m, H7, H7*), 7.33–7.39 (10H, m, H9, H4″, H2′*), 7.42 (10H, m, H3″/5″, H4″), 7.47 (4H, dd, *J* 8.4, 7.6 Hz, H3″/5″*), 7.52 (2H, s, H2′), 7.62 (2H, d, *J* 8.9 Hz, H6*), 7.66 (4H, d, *J* 8.8 Hz, H6), 8.04 (3H, dd, *J* 8.4, 7.8 Hz, H5′, H5′*), 8.07 (8H, d, *J* 7.8 Hz, H2″/6″), 8.16 (4H, d, *J* 7.6 Hz, H2″/6″*), 8.19–8.23 (6H, m, H4′, H4′*). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): $\delta$=40.0 ($CH_2$-1), 40.2 ($CH_2$-1*), 67.6 ($CH_2$-2*), 68.4 ($CH_2$-2), 69.5 ($CH_2$-4), 69.6 ($CH_2$-4*), 70.0 ($CH_2$-3*), 70.1 ($CH_2$-3), 117.4 (C6*), 117.5 (C9), 117.6 (C6), 117.8 (C9*), 118.1 (C3a), 121.5 (C9a*), 121.8 (C9a), 121.9 (C8*), 122.4 (C8), 126.4 (C7), 126.7 (C7*), 127.5 (C3″/5″), 127.6 (C3″/5″*), 128.2 (C4″), 128.3 (C2′*), 129.5 (C2″/6″), 129.6 (C2″/6″*), 130.0 (C2′), 130.1 (C5a), 130.3 (C5a*), 130.7 (C4′, C4′*), 130.8 (C5′, C5′*), 132.2 (C3′, C3′*), 132.5 (C1″*), 132.6 (C1″), 143.0 (C1, C1*), 144.0 (C3), 144.3 (C3*), 154.9 (C4, C4*). MS (EI, 70 eV): *m*/*z* (%) 755 ($M^+$+1, 6), 754 ($M^+$, 14), 596 (14), 318 (6), 202 (7), 142 (100), 100 (38), 51 (14), 44 (66).

*4.3.8. 1⁴,3⁴,-Dioxa-1³,3³-diphenyl-1,3(1,5)-diimidazo[1,5-a]quinoxalina-2(1,3)benzene-6,9,12,15-tetraoxacycloheptadecane (**8c**).* White powder, mp 293–295 °C (DMSO). IR ($\nu_{max}$, $cm^{-1}$, KBr): 2921, 2888, 2856, 1656, 1614, 1483, 1442, 1397, 1332, 1301, 1257, 1125, 1096, 1067, 751, 696; $^1$H NMR (600.1 MHz, DMSO-$d_6$): $\delta$=2.88 (4H, br, $CH_2$-5), 3.14 (4H, br, $CH_2$-4), 3.31 ($CH_2$-3), 3.67 (4H, br, $CH_2$-2), 3.9–5.0 (br, $CH_2$-1), 6.86 (2H, br, H8), 7.29–7.36 (4H, m, H7, H9), 7.38 (2H, dd, *J* 8.5, 7.4 Hz, H4″), 7.44 (4H, dd, *J* 8.5, 7.7 Hz, H3″/5″), 7.66 (2H, d, *J* 8.4 Hz, H6), 7.74 (1H, br, H2′), 8.02 (1H, dd, *J* 8.5, 7.7 Hz, H5′), 8.10 (4H, d, *J* 7.7 Hz, H2″/6″), 8.16 (2H, dd, *J* 7.7, 1.3 Hz, H4′, H6′). MS (MALDI TOF) $[MH]^+$=799.

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## Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.08.081.

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