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New α-Amido-α-aminonitrones As Building-blocks for Constructing Heterocyclic Systems.

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Abstract: New stable α-amido-α-aminonitrones were obtained in good yields from 3-oxobutyric acid *N*-pyridin-2-ylamides and nitrosobenzene. The α-amido-α-aminonitrones were then used as new versatile building-blocks in obtaining various heterocycles with both bielectrophilic and binucleophilic reagents. With diiodomethane as reagent 1,2,5-oxadiazine derivatives were formed, whereas reactions with aromatic 1,2-, 1,3- and 1,4-diamines yielded quinoxaline, quinazoline, perimidine, and dibenzo[*d*,*f*][1,3]diazepine derivatives.

Key words: building-blocks, nitrones, heterocycles, alkylations, cyclisations

Nitrones are widely used in organic synthesis.[1a–c] They mainly serve as electrophiles and 1,3-dipoles,[1d-f] also in a stereospecific manner,[1d–h] and spin traps.[1a–c, i-k] They have also been used as active equivalents of the carbonyl group.[1c, l-m, 2a] However, there have only been several reports regarding α-aminonitrones.[2] They can be derived from nitriles and hydroxylamines,[2a] from imidoformic acid esters or α-chloroimines,[2g] from hydroxylamines and methylene amines, [2g,3d] from secondary amines[2f] and nitroso compounds, and from other nitrones.[2b] The tautomerism[2a,3d] and the crystal structure[2a,3d] of α-aminonitrones have been studied. The only report about using α-aminonitrones in synthesis was the one provided by Prabhakar and co-workers,[2a] who exploited nucleophilic centers in α-aminonitrones in monoalkylation and diacylation reactions. The authors reported only one reaction of an α-aminonitrone as bielectrophilic reagent. α-Amido-α-aminonitrones had not been reported before.

The results presented below are an elaboration of the study conducted by Zaleska and co-workers[4a,b,d, 5] upon building-blocks derived from amides of 3-oxoacids **1**. In the past years they have reported syntheses of various heterocyclic rings of 1,3- and 1,4-diazines[4] from thioanilides **1**, whereas anilides **2** turned out to be unreactive.[5] In an attempt to modify the reactivity of **1** we decided to introduce pyridin-2-yls instead of aryl substituents in the amide moieties in **1**, along with replacing the sulphur atom with an oxygen atom, to obtain pyridilides **3** (Figure 1).

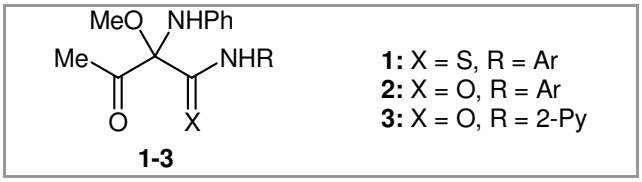
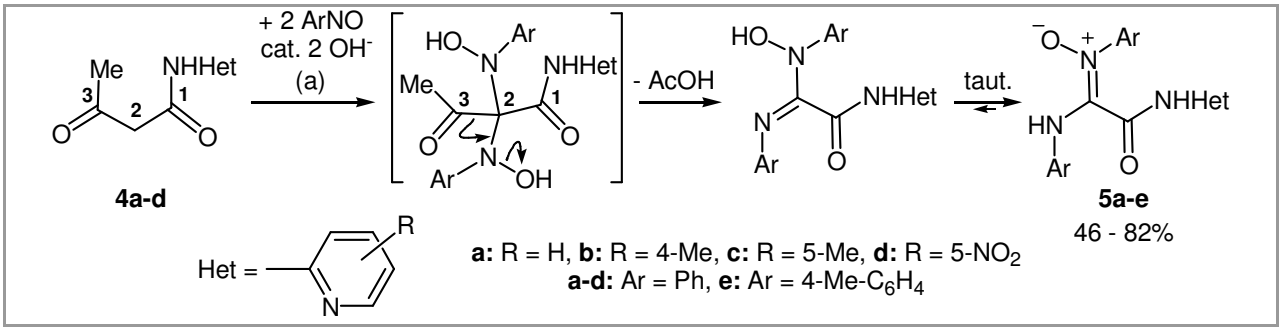


Figure 1

In the reactions of ethyl acetoacetate and variously substituted 2-aminopyridines we obtained corresponding pyridilides **4a-d** (**4d** had not been reported before), which were then treated with nitrosobenzene in methanol in an attempt to obtain C-2 disubstituted products of type **3**.[6] Using two equivalents of nitrosobenzene yielded unexpected products. The spectra and elemental analyses encouraged the conclusion that the actual products were nitrones **5a-e** (Scheme 1).



Scheme 1 Conditions: (a) MeOH, r.t., 12 h.

The structure of **5a** was confirmed by an X-ray structure analysis.[3a] The experiment showed that the compound crystallized from methanol with about one molecule of CH_3OH per two molecules of **5a**, which coincided with the result of the elemental analysis of **5a**. Two symmetrically independent molecules of **5a** found in the crystalline state are shown in Figure 2 (an *ORTEP* drawing).[3b] The N–C=N$^+$–O$^-$ moiety is planar with *Z* configuration in respect to the C10–N12 double bond, which is slightly elongated, while the C10–N11 single bond is shortened,[3c] both deviations due to π-delocalisation. The values of bond lengths led us to the conclusion that only

one mesomeric structure of **5a** prevailed, contrary to (*Z*)-*N*-[(phenylamino)methylene]aniline oxide.[3d] All functional groups in **5a** are involved in intermolecular hydrogen N–H···O and N–H···N type bonds, which stabilise the molecular structure of **5a**.

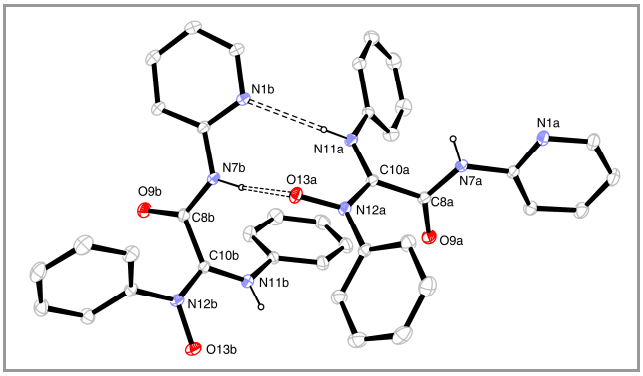


Figure 2 The mutual arrangements of two symmetrically independent molecules of **5a** (aromatic hydrogen atoms were removed for clarity; non-hydrogen atom displacement ellipsoids were set at 10 % probability level). The values of C8–C10, C10–N11, and C10-N12 bond lengths are 151.1(3), 134.7(3), and 131.5(3) pm for (a) and 151.6(4), 134.3(3), and 131.1(3) pm for (b). The sum of valence angles at C10 is 359.9(6)° for both (a) and (b). The N11–C10–N12–O13 torsion angles are: 2.6(3)° for (a) and –4.1(3)° for (b).

MS(EI) spectra of **5a-e** show very small peaks of molecular ions and distinctive M^+–16 peaks, corresponding with the loss of the oxygen atom from **5** during fragmentation. In MS(ESI) spectra M^++H peaks of **5** are the base (or even the only) peaks.

We proposed a mechanism for the formation of **5a-e** (Scheme 1). After a base-catalyzed attack of two molecules of nitrosobenzene on C2 of **4a-d**, a splitting of C2–C3 bonds takook place (acidic cleavage). The loss of a molecule of acetic acid followed by a proton shift resulted in obtaining nitrones **5a-e**. We thus transformed 3-oxobutanoic acid derivatives into oxalic acid derivatives.

It should be noted that the introduction of a phenyl group in place of the methyl group at C3 of **4a** totally changes the reactivity of the corresponding pyridylide against nitrosobenzenes.[6]

The presence of several nucleophilic centers in α-amido-α-aminonitrones **5** allowed their use in dialkylation reactions with alkyl dihalides. First we examined the reaction with diiodomethane in anhydrous DMF. After adding 2 equiv of NaH to the reaction mixture, TLC indicated completion of the reaction in 1.5 h.

We expected the dialkylation to start on the nitrone oxygen atom.[2a] The proximity of the oxygen atom and the amine NH group[2a,3d] suggested a possibility of 1,2,4-oxadiazole ring closure. However, the IR spectra of products **6a-c** no longer exhibited NH amide bands above 3100 cm^{-1}. That observation suggested that the methylene fragment linked the nitrone oxygen atom and the amide nitrogen atom; hence 1,2,5-oxadiazin-4-ones **6a-c** were formed (Scheme 2). The structure of 1,2,5-oxadiazin-4-one **6a** was confirmed by a single crystal X-ray diffraction experiment. An *ORTEP* view of a molecule of **6a** is shown in Figure 3.

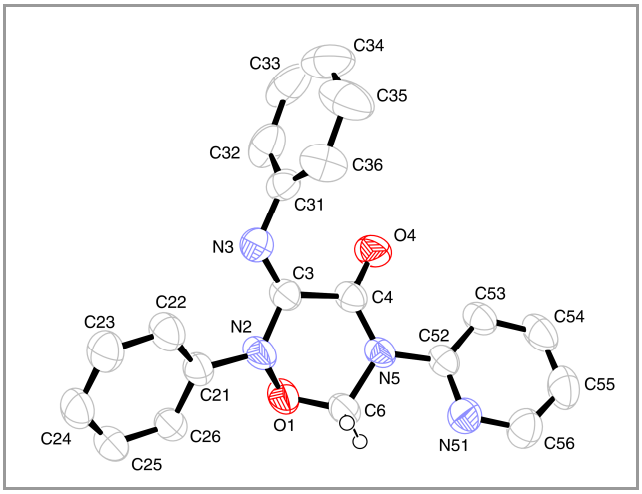
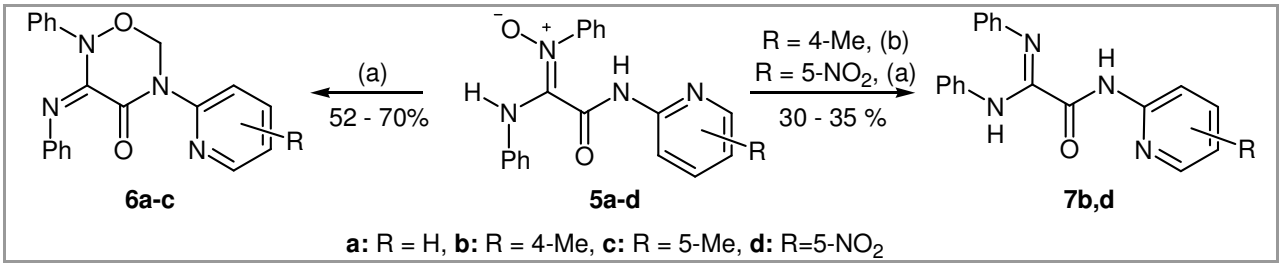


Figure 3 An *ORTEP* view of a molecule of **6a** with the crystallographic atom numbering scheme (aromatic hydrogen atoms were removed for clarity; non-hydrogen atom displacement ellipsoids were drawn at 50 % probability level). The values of the selected geometric parameters are as follows: (a) bond lenghts (pm): O1–N2 = 141.6(2), N2–C3 = 138.7(2), C3–C4 = 153.5(2), C4–N5 = 136.9(2), N5–C6 = 147.0(2), C6–O1 = 140.0(2), and C3–N3 = 126.3(2); (b) valence angles (°): C6–O1–N2 = 106.5(1), O1–N2–C3 = 110.9(1), C4–N5–C6 = 119.3(1), and C3–N3–C31 = 124.6(1); (c) torsion angles (°): O1–N2–C3–C4 = –30.4(2), N2–C3–C4–N5 = –13.0(2), C3–C4–N5–C6 = 16.8(2), C4–N5–C6–O1 = 22.7(2), N5–C6–O1–N2 = –67.1(2), and C6–O1–N2–C3 = 73.1(2).

The molecule of **6a** adopts a boat conformation with a pseudo mirror-plane cutting through O1, C4, and O4 atoms.



Scheme 2 Conditions: (a) CH_2I_2, NaH (2 equiv), anhyd DMF, –10 °C → r.t, 1.5 h; (b) $I(CH_2)_2I$, NaH (2 equiv), anhyd DMF, –10 °C → r.t, 1.5 h.

The first synthesis of the 1,2,5-oxadiazine system was reported in 1905,[7a] but it was then proved that the structure of the products had been assigned incorrectly,[7b] so the ring was probably obtained for the first time in 1930 by Busch and Kaemmerer[8a] from *Z*-α-aminooximes and aldehydes.[8b–e] Diketones[8f,g] or acetals[8h] can be used instead of aldehydes, and α-aminohydroxylamines can replace α-aminooximes.[8i] There also are other[8j–q] methods, including those basing on reactions between: α-halooximes and imines,[8j] nitrosoalkenes and imines,[8k,l] nitrones and allylamines,[8m] also in the stereoselective manner.[8n] The system can also be obtained by ring expansions.[8r-x] Diacylations of both α-aminooximes[9a–c] and α-aminohydroxylamines[9d,e] lead to 6-oxo derivatives. 1,2,5-Oxadiazines have been used for obtaining imidazole derivatives.[9d,f] The N–O bond in 1,2,5-oxadiazines can be easily broken, which leads to various products,[8e,o, 9d,f,g] for example vicinal diamines (an example of indirect amination of alkenes).[8m,n]

The reaction of **5b** with 1,2-diiodoethane did not yield the expected 1,2,5-oxadiazepan-4-one, but amidine **7b**, i.e. deoxygenation took place. The IR spectra of **7a** showed two strong NH bands between 3400 and 3200 cm^{-1} and a C=O band at about 1700 cm^{-1}. The NMR spectra did not exhibit the presence of an ethylene group. The MS spectrum of **7b** showed a molecular peak at *m/z* lowered by 16 comparing with **5b**. The result of the elemental analysis was in agreement with the proposed structure of **7b**. It should be noted that **5d**, possessing a strong electron withdrawing nitro group in the pyridine ring, gave **7d** instead of **6d** in the reaction with methylene diiodide. Examples of deoxygenation of nitrones are relatively rare.[10]

Amidines[11a] of **7b,d** type are interesting as building-blocks because their molecules contain both amidine and amide moieties.[11b] Therefore they allow many electro- and nucleophilic reaction centres. The number of methods for preparing such componds is limited;[11] derivatives of oxalic[11c,i–l] or acetic[11b,g,h,j–l] acids have mostly been used as starting materials. We proposed a method for preparing such compounds from 3-oxobutanoic acid derivatives.

α-Amido-α-aminonitrones **5a-d** were then used as bielectrophilic reagents in heterocyclisation reactions with aromatic 1,2-, 1,3-, and 1,4-diamines. In these reactions the nitrone moieties acted as active equivalents of carbonyl groups.[1c, l-n, 2a] The reaction of **5a** with *o*-phenylenediamine yielded the already known[12a-c] 3-(phenylamino)-quinoxalin-2(1*H*)-one **8a** (mp = 253.0–254.0 °C). One *o*-phenylenediamine amine group replaces the nitrone moiety of **5a** and the other one transaminates the amide moiety; this results in the formation of **8a**.[2a] This compound has been reported in two different tautomeric forms,[12a–c] with the mps 252[12a] and 247–248 °C,[12b,c] respectively. Small differences between their mps suggested that their structures may be the same, at least in the solid state. An X-ray diffraction analysis confirmed the structure of the obtained quinoxaline derivative as **8a**. Determining its structure may prove useful, since its derivatives have recently been investigated as potential glycogen phosphorylase inhibitors.[12d] An *ORTEP* view of **8a** molecule with crystallographic atom numbering scheme is shown in Figure 4.

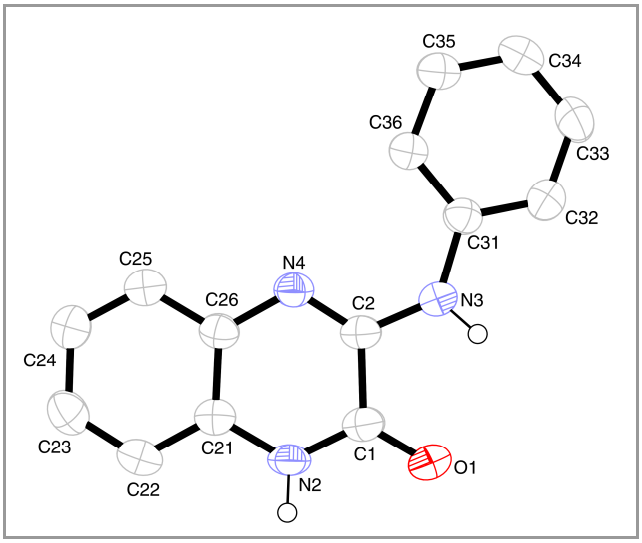
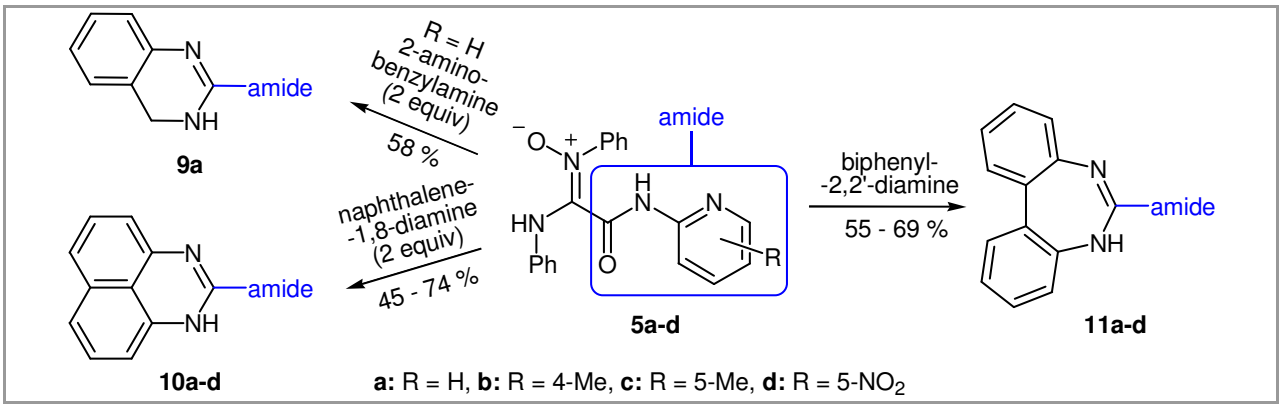


Figure 4 An *ORTEP* view of **8a** molecule with the crystalographic atom numbering scheme (aromatic hydrogen atoms were removed for clarity; non-hydrogen atom displacement ellipsoids were drawn at 50 % probability level). The values of the selected geometric parameters are as follows: (a) bond lenghts (pm): N2–C1 = 134.0(2), C1–O1 = 124.1(2), C1–C2 = 149.4(2), C2–N4 = 129.0(2), and C2–N3 = 136.4(2); (b) valence angles (°): C21–N2–C1 = 123.9(1), C2–N3–C31 = 130.2(1), and C26–N4–C2 = 118.2(1); (c) torsion angles(°): C32–C31–N3–C2 = –171.3(2) and C31–N3–C2–N4 = –3.0(2).

The whole molecule of **8a** is essentially planar. The positions of the hydrogen atoms at N2 and N3 were found basing on Fourier difference maps and confirmed by the values of the corresponding valence angles at the nitrogen atoms. The hydrogen atoms are invoved in hydrogen bonds: a linear intermolecular one (N2–H2···O1; –x, –y, –z) and an intramolecular one (N3–H3···O1).

In reactions with 2-aminobenzylamine, naphthalene-1,3-diamine, and biphenyl-2,2'-diamine the amide moieties of nitrones **5a-d** were left unaffected; the processes consist in binucleohilic attacts on C-2 carbon atoms of nitrones **5a-d**, leading to derivatives of quinazoline **9a**, perimidine **10a-d**, and dibenzo[*d,f*][1,3]diazepine **11a-d** (Scheme 3).

The ^{1}H NMR spectra of all compounds depicted in Scheme 3 contain singlets from the NH groups of the amide moieties in the range 10.89 – 9.84 ppm. Both MS (EI) spectra and elemental analyses supported the proposed structures. The structure of **11b** was unambiguously determined by single crystal structure analysis.[16]



Scheme 3 Conditions: MeCN, reflux, 2 h, TsOH (cat).

The first synthesis of 5*H*-dibenzo[*d*,*f*][1,3]diazepine was reported in 1932 by Sako.[13a,b] The vast majority of other methods consists in reactions of biphenyl-2,2'-diamine with 1,1-bielectrophilic reagents like BrCN,[13c] ethyl benzimidate hydrochloride,[13d,e] benzonitrile,[13f] or methyl arylcarbimidothioates.[13g] A review of the methods of preparing diazepines was made by Herr.[13h]

The 1*H*-perimidine system has been known since 1874, when it was obtained by de Aguiar.[14a] Transformations leading to perimidines start with 1,8-naphthalenediamine (NDA) as substrate and mostly consist in reactions with bielectrophilic reagents, e.g.: aldehydes,[14b-e] acyl chlorides,[14f] di- or tetracyanoethylene derivatives,[14g] aryl anhydrides,[14h] cyanamide,[14i] isothiocyanates,[14h] or orthoformates.[14j] 2,3-Dihydro-1*H*-perimidines can be obtained from NDA and aldehydes[14k] or by oxidation of NDA by MnO_2.[14l] Perimidines can act as substrates in reactions leading to more condensed systems,[14f,g,m] e.g. 1,3-diazapyrenes[14m] or pyrido[1,2,3-*cd*]perimidines.[14f]

Recent syntheses of quinazolines were based either on the addition of Grignard reagents to dicyjanoanilines,[15a] or the Biginelli reactions.[15b] Quinazolines can also be obtained from dimethoxybenzenes[15c] or cyanoaromatic compounds,[15d] and various aldehydes.[15e,f]

It should be stressed that compounds **11a-d** are, to the best of our knowledge, the first examples of 5*H*-dibenzo[*d*,*f*][1,3]diazepine-6-carboxylic acid derivatives.

In conclusion, reaction *N*-pyridin-2-ylamides of 3-oxobutyric acid and nitrosobenzene provided α-amido-α-aminonitrones **5a-e** in good yields; they were used as diverse building-blocks for constructing heterocyclic rings. In dialkylation reactions the relatively rare 1,2,5-oxadiazinan-4-one derivatives **6a-d** were obtained. In some cases amidines **7** were formed. Reactions of **5a-d** with aromatic 1,2-, 1,3-, and 1,4-diamines yielded derivatives of 3,4-dihydroquinoxalin-2(1*H*)-one **8a**, 3,4-dihydroquina-zoline **9a**, 1*H*-perimidine **10a-d**, and 5*H*-di-benzo[*d*,*f*][1,3]diazepine **11a-d**. All the products, with the exception of **8a**, contain *N*-pyridin-2-ylocarboxamide substituents, which may prove valuable for pharmacological uses.

Mps were determined on an Electrothermal IA9000 digital mp apparatus and are uncorrected. IR spectra were obtained on a Bruker IFS 48 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance II 300 spectrometer at 300.18 and 75.48 MHz, respectively, at 300 K. MS (EI) mass spectra were recorded by a Finnigan MAT 95S apparatus at the ionisation potential of 70 eV. MS (ESI) spectra were recorded by an Esquire 3000 mass spectrometer. The samples were solved in a MeOH/$CHCl_3$ mixture and analysed in the positive-ion mode. Elemental analyses (C, H, N) were carried out using Euro-EA 3018 analyzer. X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using MoKα radiation (λ = 0.71073 Å)[17a,b] at T = 293(2) K. The structures were solved by *SIR92*[17c] and refined by SHELXL97[17d] programs.

Yields are given for pure products. Silica gel for column chromatography was purchased from Fluka (Silica gel 60, 70 – 230 mesh ASTM, activity 2 – 3 acc. to Brockmann, Schodder). TLC plates were purchased from Fluka (thickness 0.2 mm, pore diameter 60Å, with 254 nm fluorescent indicator). NaH was used as 55% – 60% suspension in mineral oil.

4-Methylnitrosobenzene was prepared according to the already known procedure.[18]

(*N*-pyridyn-2-yl)acetoacetamides (4a-d); General Procedure

A solution of ethyl acetylacetate (17.3 mL, 0.1 mol) in xylene (70 mL) was warmed up to boil. To the boiling mixture corresponding aminopyridine (0.1 mol) was added in portions during 1 h, and the liberated EtOH was distilled. The remaining traces of ethanol were co-distilled with 20 mL of xylene. Cooling the mixture to 0 °C yielded the products, which were then separated under reduced pressure, in pure form.

3-Oxo-*N*-pyridyn-2-ylbutanamide (4a)

Yield 14.2 g (80%): colorless needles; mp 113.0 – 114.0 °C.[3]

***N*-(4-Methylpyridin-2-yl)-3-oxobutanamide (4b)**

Yield 14.2 g (74%): colorless needles; mp 122.0 – 123.0 °C. (Lit. yield 75 %, mp 122 – 123 °C).[19]

***N*-(5-Methylpyridin-2-yl)-3-oxobutanamide (4c)**

Yield 10.9 g (57%): colorless needles; mp 162.0 – 163.0 °C. (Lit. yield 78 %, mp 152 – 153°C).[19]

***N*-(5-Nitropyridin-2-yl)-3-oxobutanamide (4d)**

Yield 16.0 g (72%): light yellow powder; mp 173.0 – 174.0 °C.

IR (KBr): 3248, 3206, 3148, 1714, 1692, 1674, 1347, 1315 cm^{-1}.

^1H NMR ($CDCl_3$): *keto* form (82%): δ = 9.91 (s, 1 H, NH), 9.17 (dd, *J* = 2.7, 0.6 Hz, 1 H, H6), 8.49 (ddd, *J* = 9.0, 2.7, 0.6 Hz, 1 H, H-4), 8.35 (dd, *J* = 9.0, 0.6 Hz, 1 H, H3) (3 H ar), 3.67 (s, 2 H, CH_2), 2.36 (s, 3 H, CH_3); *enol* form (18%): δ = 13.20 (s, 1 H, OH), 9.12 (dd, *J* = 2.7, 0.6 Hz, 1 H, H6), 8.47 (ddd, *J* = 9.0, 2.7, 0.6 Hz, 1 H, H4), 8.38 (dd, *J* = 9.0, 0.6 Hz, 1 H, H3) (3 H ar), 7.91 (s, 1 H, CH), 5.08 (d, *J* = 0.3 Hz, 1 H, NH), 2.03 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): *keto* form (82%): δ = 203.5 (**C**OCH_3), 164.4 (CONH), 154.8 (C5), 144.8 (C6), 140.8 (C2), 134.0 (C4), 113.3 (C3) (5 C ar), 49.8 (CH_2), 31.3 (CH_3); *enol* form (18%): δ = 91.3 (CH), 21.8 (CH_3).

MS (EI): *m/z* (%) = 223 (23, M^+), 208 (23, $M^+ - CH_3$), 180 (13, $M^+ - CH_3CO$), 166 (19, O_2N-C_5H_3N-$NHCO^+$), 139 (100, O_2N-C_5H_3N-NH_2^+), 123 (8, O_2N-$C_5H_3N^+$), 109 (21).

Anal. Calcd for $C_9H_9N_3O_4$: C, 48.43; H, 4.06; N, 18.83. Found: C, 48.42; H, 3.88; N, 18.86.

2-Anilino-2-[oxido(phenyl)imino]-*N*-pyridin-2-ylacetamides (5a-e); General Procedure

The suspension of corresponding 3-oxo-(*N*-pyridyn-2-yl)butanamide **4a-d** (0.01 mol), corresponding nitrosobenzene (0.02 mol) and NaOH (0.02 g) in MeOH (15 mL) was stirred at r.t. The mixtures turned brown, clarified and warmed up to 40 °C after several minutes. After 30 min white (in the case of **5d** – yellow) powders of the products started to precipitate. The suspensions were stirred overnight and the products collected under reduced pressure and washed with small amount of cold methanol.

(*Z*)-2-Anilino-2-[oxido(phenyl)imino]-*N*-pyridin-2-ylacetamide (5a)

Yield 2.70 g (81%): white powder; mp 152.0 – 153.0 °C.

IR (KBr): 3363, 3108, 1683 cm^{-1}.

^1H NMR (CD_3OD): δ = 8.19 (d, *J* = 4.2 Hz, 1 H, C-6), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.65 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.58 (d, *J* = 7.5 Hz, 2 H), 7.44 – 7.27 (m, 7 H), 7.13 (tt, *J* = 6.4, 2.4 Hz, 1 H), 7.06 (t, *J* = 5.8 Hz, 1 H).

^{13}C NMR (CD_3OD): δ = 158.5 (N-C-N), 151.5 (CONH), 149.4, 143.8, 139.5, 130.3, 130.3, 126.9, 125.8, 123.8, 122.1, 115.5.

MS (EI): *m/z* (%) = 332 (3, M^+), 316 (29, $M^+ - O$), 241 (10, $M^+ - PhN$), 225 (33, $M^+ - O - PhN$), 195 (35, $PhN{=}C\text{-}NHPh^+$), 121 (96, C_5H_4N-$NHCO^+$), 107 (34, $PhNO^+$).

MS (ESi): *m/z* = 333.2 ($M^+ + H$).

Anal. Calcd for 2 $C_{19}H_{16}N_4O_2 \cdot CH_3OH$: C, 67.23; H, 5.21; N, 16.08. Found: C, 67.65; H, 5.03; N, 16.40

(*Z*)-2-Anilino-2-[oxido(phenyl)imino]-*N*-(4-methylpyridin-2-yl)acetamide (5b)

Yield 2.85 g (82%): white powder; mp 148.0 – 149.0 °C.

IR (KBr): 3207, 3064, 1680, 1419 cm^{-1}.

^1H NMR (CD_3OD): δ = 8.03 (d, *J* = 4.8 Hz, 1 H, C-6), 7.58 (d, *J* = 7.8 Hz, 2 H), 7.56 (s, 1 H, C-3), 7.44 – 7.27 (m, 7 H), 7.14 (tt, *J* = 6.6, 1.8 Hz, 1 H), 6.29 (d, *J* = 4.8 Hz, 1 H, C-5), 2.25 (s, 3 H, CH_3). .

^{13}C NMR (CD_3OD): δ = 158.4 (N-C-N), 151.5 (CONH), 148.9, 148.4, 143.8, 130.3, 126.9, 125.8, 123.8, 123.1, 116.0, 21.2 (CH_3).

MS (EI): *m/z* (%) = 346 (1.5, M^+), 330 (23, $M^+ - O$), 238 (8, $M^+ - PhNOH$), 211 (6, $M^+ - H_3C$-C_6H_3N-NHCO), 135 (100, H_3C-C_6H_3N-$NHCO^+$), 108 (41, $PhNOH^+$).

MS (ESi): *m/z* = 347.2 ($M^+ + H$), 239.1, 213.0 ($M^+ + H - CH_3$-C_5H_3N-NHCO), 195 (diphenylcarbodiimide moiety), 135 (CH_3-C_5H_3N-$NHCO^+$).

Anal. Calcd for 2 $C_{20}H_{18}N_4O_2 \cdot CH_3OH$: C, 67.94; H, 5.56; N, 15.46. Found: C, 67.79; H, 5.41; N, 15.64.

(*Z*)-2-Anilino-2-[oxido(phenyl)imino]-*N*-(5-methylpyridin-2-yl)acetamide (5c)

Yield 1.97 g (57%): white powder; mp 136.0 – 137.0 °C.

IR (KBr): 3165, 1694, 1383, 1306 cm^{-1}.

^1H NMR (CD_3OD): δ = 8.03 (dd, *J* = 1.5, 0.8 Hz, 1 H, C-6), 7.60 – 7.56 (m, 2 H), 7.49 – 7.24 (m, 9 H), 7.14 (tt, *J* = 6.6, 1.8 Hz, 1 H), 2.22 (s, 3 H, CH_3).

^{13}C NMR (CD_3OD): δ = 158.2 (N-C-N), 149.3 (CONH), 143.8, 139.9, 132.1, 130.4, 130.3, 126.9, 125.9, 123.8, 115.1, 17.8 (CH_3).

MS (EI): *m/z* (%) = 192 (26, $M^+ - 2$ Ph), 177 (17, $M^+ - 2$ Ph – CH_3), 135 (11, H_3C-C_6H_3N-$NHCO^+$), 108 (100, $PhNOH^+$), 107 (17, H_3C-C_6H_3N-NH^+, $PhNO^+$).

MS (ESi): *m/z* = 347 ($M^+ + H$).

Anal. Calcd for 2 $C_{20}H_{18}N_4O_2 \cdot CH_3OH$: C, 67.94; H, 5.56; N, 15.46. Found: C, 68.10; H, 5.86; N, 15.94.

(*Z*)-2-Anilino-2-[oxido(phenyl)imino]-*N*-(4-nitropyridin-2-yl)acetamide (5d)

Yield 2.20 g (58%): light yellow powder; mp 140.0 – 141.0 °C.

IR (KBr): 3495, 3367, 1696, 1417, 1396, 1347 cm^{-1}.

^1H NMR (CD_3OD): δ = 9.04 (d, *J* = 1.8 Hz, 1 H, C-6), 8.46 (dd, *J* = 9.3, 3.0 Hz, 1 H, C-4), 8.00 (d, *J* = 8.7, 1 H, C-3), 7.58 (d, *J* = 7.2 Hz, 2 H), 7.43 – 7.20 (m, 7 H), 7.14 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (CD_3OD): δ = 155.7 (N-C-N), 147.6, 145.8, 143.8, 142.6, 135.1, 134.0, 130.3, 126.8, 125.5, 123.9, 114.3, 108.6.

MS (EI): *m/z* (%) = 377 (3, M^+), 361 (18, M^+ – O), 211 (19, PhN(OH)-C=NPh^+), 195 (35, PhNH-C=NPh^+), 166 (86, O_2N-C_6H_3N-$NHCO^+$), 139 (22, O_2N-C_6H_3N-NH_2^+), 120 (30, C_5H_3N-$NHCO^+$).

MS (ESi): *m/z* = 378 (M^+ + H).

Anal. Calcd for 2 $C_{19}H_{15}N_5O_4 \cdot CH_3OH$: C, 59.54; H, 4.36; N, 18.30. Found: C, 59.40; H, 4.04; N, 18.80.

(*Z*)-2-Anilino-2-[oxido(4-methylphenyl)imino]-*N*-(4-methylpyridin-2-yl)acetamide (5e)

Yield 1.04 g (46 %): white powder; mp 123.0 – 124.0 °C.

IR (KBr): 3132, 1686 cm^{-1}.

^1H NMR (CD_3OD): δ =8.04 (d, *J* = 4.8 Hz, 1 H, C-6), 7.56 (s, 1 H, C-3), 7.44 (d, *J* = 7.8 Hz, 2 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 6.91 (d, *J* = 4.8 Hz, 1 H), 2.31 (s, 3 H, CH_3), 2.26 (br s, 6 H, 2 CH_3).

^{13}C NMR (CD_3OD): δ = 158.1 (N-C-N), 151.5 (CONH), 148.9, 141.2, 137.3, 136.1, 130.9, 125.9, 124.1, 123.1, 116.0, 21.2 (CH_3), 20.9 (CH_3).

MS (EI): *m/z* (%) = 374 (0.6, M^+), 358 (8, M^+ – O), 269 (7, M^+ – H_3C-C_6H_4-N), 135 (100, H_3C-C_6H_3N-$NHCO^+$), 107 (45, H_3C-C_6H_3N-NH^+).

MS (ESi): *m/z* = 375 (M^+ + H).

Anal. Calcd for 2 $C_{22}H_{22}N_4O_2 \cdot CH_3OH$: C, 69.21; H, 6.20; N, 14.35. Found: C, 69.56; H, 6.26; N, 14.73.

(*E*)-2-Phenyl-3-(phenylimino)-5-pyridin-2-yl-1,2,5-oxadiazinan-4-ones (6a-c); General Procedure

A solution of the corresponding (*Z*)-2-[oxido(phenyl) imino]-2-(phenylamino)-(*N*-pyridin-2-yl)ethanamide **5a-d** (1.5 mmol) in anhydrous DMF (10mL) was cooled in an ice-bath to –10 °C. CH_2I_2 (0.40 g, 0.12mL, 1.5 mmol) was added with stirring and the flask was closed with a tube filled with $CaCl_2$. NaH (0.063 g, 1.5 mmol as for pure NaH) was added in two portions to the stirred mixture over 30 mins. The next portion of NaH (0.063 g, 1.5 mmol as for pure NaH) was then added and the ice-bath removed. The reaction was controlled by TLC. After the next 1 h the reaction mixture was evaporated to dryness under reduced pressure (10 mm Hg) to remove DMF completely. The brown residue was chromatographed immediately with $CDCl_3$ – MeOH mixture (40:1) and the second fraction yielded the product as yellow prisms. The product was recrystallised from MeOH.

(*E*)-2-Phenyl-3-(phenylimino)-5-(pyridin-2-yl)-1,2,5-oxa-diazinan-4-one (6a)

Yield 0,36 g (70 %): yellow prisms; mp 122.5 – 123.5 °C.

IR (KBr) = 2925 (CH_2), 2855 (CH_2), 1697 (CO) cm^{-1}.

^1H NMR ($CDCl_3$): 8.37 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1 H), 7.78 (td, *J* = 8.0, 2.0 Hz, 1 H), 7.69 (m, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.21 (tt, *J* = 7.5, 1.2 Hz, 1 H), 7.15 – 7.09 (m, 3 H), 6.96 (t, *J* = 7.5 Hz, 2 H), 6.94 – 6.86 (m, 1 H), 6.81 (d, *J* = 7.5 Hz, 2 H), 6.67 (d, *J* = 7.5 Hz, 1 H), 6.07 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 158.7, 157.4, 151.4, 149.0, 148.1, 139.0, 138.8, 129.3, 129.3, 128.7, 123.4, 120.5, 119.1, 117.9, 114.4, 81.2 (CH_2).

MS (ESI): *m/z* = 345.2 (M^+ + H).

Anal. Calcd for $C_{20}H_{16}N_4O_2$: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.81; H, 4.84; N, 16.58.

(*E*)-5-(4-Methylpyridin-2-yl)-2-phenyl-3-(phenyl-imino)-1,2,5-oxadiazinan-4-one (6b)

Yield 0,28 g (52 %): yellow prisms; mp 141.0 – 143.0 °C.

IR (KBr) = 2941, 2921, 1698 (CO) cm^{-1}.

^1H NMR ($CDCl_3$): 8.22 (dd, *J* = 5.1, 0.5 Hz, 1 H), 8.03 (br s, 1 H), 7.69 (br s, 1 H), 7.39 (br s, 1 H), 7.22 (br s, 4 H), 7.03 – 6.99 (m, 1 H), 6.95 (d, *J* = 4.8 Hz, 2 H), 6.82 (dd, *J* = 8.4, 1.2 Hz, 2 H), 6.05 (s, 2 H, CH_2), 2.35 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 150.8, 149.6, 147.0, 128.6, 128.4, 128.0, 126.0, 122.7, 122.2, 121.4, 120.9, 118.4, 117.7, 80.6 (CH_2), 21.3 (CH_3).

MS (ESI): *m/z* = 359.2 (M^+ + H), 135 (H_3C-C_5H_3N-$NHCO^+$).

Anal. Calcd for $C_{21}H_{18}N_4O_2$: C, 70.38; H, 5.06; N, 15.63. Found: C, 70.62; H, 4.92; N, 15.85.

(*E*)-5-(5-Methylpyridin-2-yl)-2-phenyl-3-(phenyl-imino)-1,2,5-oxadiazinan-4-one (6c)

Yield 0,30 g (56 %): yellow prisms; mp 136.0 – 138.0 °C.

IR (KBr) = 2947, 2923, 1693 (CO) cm^{-1}. cm^{-1}.

^1H NMR ($CDCl_3$): 8.18 (dd, *J* = 1.6, 0.8 Hz, 1 H), 7.68 (dd, *J* = 8.7, 1.2 Hz, 1 H), 7.62 (ddd, *J* = 16.5, 2.2, 0.8 Hz, 1 H), 7.46 – 7.36 (m, 2 H), 7.24 – 7.18 (m, 2 H), 7.13 – 7.06 (m, 2 H), 6.99 – 6.91 (m, 2 H), 6.80 (d, *J* = 7.4 Hz, 2 H), 6.04 (s, 2 H, CH_2), 2.32 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 148.5, 147.9, 147.4, 138.7, 129.2, 128.7, 128.6, 128.3, 126.1, 124.2, 119.8, 116.7, 113.3, 78.7 (CH_2), 17.8 (CH_3).

MS (ESI): *m/z* = 359.2 (M^+ + H), 343.3 (M^+ + H – O).

Anal. Calcd for $C_{21}H_{18}N_4O_2$: C, 70.38; H, 5.06; N, 15.63. Found: C, 69.91; H, 5.00; N, 15.88.

2-(Phenylamino)-2-(phenylimino)-*N*-(pyridin-2-yl)ethanamides (7b,d); General Procedure

In the case of **7d** the procedure was analogous as for **6a-c**. In the case of **7b** 1,2-diiodoethane (0.42 g, 1.5 mmol) was used in place of diiodomethane.

***N*-(4-Methylpyridin-2-yl)-2-(phenylamino)-2-(phenylimino)ethanamide (7b)**

Yield 0.17 g (35 %): light yellow needles; mp 163.5 – 164.5 °C.

IR (KBr): 3330 (NH), 3158 (NH), 2925 (CH_3), 1702 (CONH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 10.54 (s, 1 H, CONH), 8.42 (br s, 1 H, NH), 8.23 (d, *J* = 5.1 Hz, 1 H), 8.14 – 8.13 (m, 1 H), 6.98 – 6.92 (m, 5 H), 6.88 (t, *J* = 7.2 Hz, 1 H), 6.78 (t, *J* = 7.4 Hz, 1 H), 6.68 – 6.65 (m, 4 H), 2.42 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 161.5, 151.2, 150.5, 148.6, 146.7, 141.1, 137.3, 128.6, 128.6, 125.1, 123.8, 123.4, 122.0, 115.0, 22.1 (CH_3).

MS (ESI): *m/z* = 331.2 (M^+ + H), 330.2, 316.3 (M^+ + H – CH_3), 135.0 (CH_3-C_5H_3N-$NHCO^+$).

Anal. Calcd for $C_{20}H_{18}N_4O_0$ (%): C, 72.71; H, 5.49; N, 16.96. Found: C, 72.80; H, 5.46; N, 16.86.

***N*-(5-Nitropyridin-2-yl)-2-(phenylamino)-2-(phenylimino)ethanamide (7d)**

Yield 0.16 g (30%): yellow needles; mp 176.0 – 178.0 °C.

IR (KBr): 3312 (NH), 3271 (NH), 1704 (CONH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 10.98 (s, 1 H, CONH), 9.24 (dd, *J* = 2.7, 0.6 Hz, 1 H, C6), 8.57 (dd, *J* = 9.0, 2.7 Hz, 1 H, C4), 8.50 (dd, *J* = 9.0, 0.6 Hz, 1 H, C3) (pyridine ring), 8.34 (s, 1 H, NH), 7.00 – 6.95 (m, 4 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 6.81 (t, *J* = 7.2 Hz, 1 H), 6.67 (d, *J* = 7.8 Hz, 2 H), 6.66 (d, *J* = 7.8 Hz, 1 H) (phenyl rings).

^{13}C NMR ($CDCl_3$): δ = 162.2, 155.1, 146.2, 145.7, 141.5, 140.4, 136.8, 134.7, 128.8, 128.7, 125.5, 124.3, 123.5, 122.0, 113.4.

MS (ESI): *m/z* = 362.2 (M^+ + H), 330.2 (M^+ + H – 2 O), 316.3 (M^+ + H – NO_2).

Anal. Calcd for $C_{19}H_{15}N_5O_3$ (%): C, 63.15; H, 4.18; N, 19.38. Found: C, 62.76; H, 3.91; N, 19.76.

Reactions of nitrones (5a-d) with aromatic and aliphatic-aromatic diamines; General Procedure

A solution of the corresponding 2-[oxido(phenyl)imino]-2-(phenylamino)-*N*-(pyridin-2-yl)ethanamide **5a-d** (1 mmol), corresponding diamine (2 mmol) (in the case of biphenyl-2.2'-diamine – 1 mmol, 0.18 g), and TsOH (0.01 g, cat.) in MeCN (10 mL) was heated under reflux (2 h). After cooling the mixture the product was separated under reduced pressure.

3-(Phenylamino)quinoxalin-2(1*H*)-one (8a)

Yield 0.18 g (75 %): yellow needles; mp 253.0 – 254.0 °C.

IR (KBr): 3371 (NH), 1671 (CONH) cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 12.44 (s, 1 H, NH), 9.36 (s, 1 H, CONH), 8.15 (d, *J* = 8.1 Hz, 2 H), 7.52 – 7.49 (m, 1 H); 7.36 (t, *J* = 8.1 Hz, 2 H), 7.23 – 7.17 (m, 3 H), 7.05 (t, *J* = 7.3, 1 H).

^{13}C NMR (DMSO-d_6): δ = 151.4 (CONH), 147.1 (C=N), 139.4, 132.2, 128.4, 128.4, 125.3, 124.7, 123.4, 122.5, 119.6, 114.9.

MS (EI): *m/z* (%) = 237 (96, M^+), 236 (100, M^+ – H), 208 (31, M^+ – CHO), 134 [10, $C_6H_4(NH)NHCO^+$].

***N*-(pyridin-2-yl)-3,4-dihydroquinazoline-2-carboxamide (9a)**

Yield 0.15 g (58 %): yellow needles; mp 129.0 – 131.0 °C.

IR (KBr): 3335 (br) (NH), 2998 (CH_2), 2845 (CH_2), 1691 (CONH) cm^{-1}.

^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ = 9.84 (s, 1 H, CONH), 8.91 (t, *J* = 6.3 Hz, 1 H, NH), 7.66 (d, *J* = 1.2 Hz, 1 H), 7.63 (d, *J* = 0.9 Hz, 1 H), 7.26 (dt, *J* = 7.5, 1.8 Hz, 1 H), 7.24 (dt, *J* = 8.4, 1.8 Hz, 1 H), 7.11 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.05 (tt, *J* = 7.5, 1.2 Hz, 1 H), 6.97 (td, *J* = 7.5, 1.5 Hz, 1 H), 6.62 (dd, *J* = 8.2, 0.9 Hz, 1 H), 6.56 (td, *J* = 7.4, 1.2 Hz, 1 H), 4.32 (d, *J* = 6.3 Hz, 2 H, CH_2).

^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ = 159.7, 157.2, 144.9, 136.4, 130.3, 128.2, 128.2, 124.2, 120.8, 119.5, 119.5, 116.9, 115.2.

MS (EI): *m/z* (%) = 252 (100, M^+), 251 (75, M^+ – H), 132 (72, 3,4-dihydroquinazoline moiety + H), 131 (44, 3,4-dihydroquinazoline moiety), 121 (44, C_5H_4N-$NHCO^+$), 104 (18), 95 (10), 78 (35), 77 (13).

Anal. Calcd for $C_{14}H_{12}N_4O$ (%): C, 66.65; H, 4.79; N, 22.21. Found: C, 66.10; H, 4.68; N, 22.22.

***N*-Pyridin-2-yl-1*H*-perimidine-2-carboxamide (10a)**

Yield 0.18 g (61 %): dark-red needles; mp 222.0 – 225.0 °C.

IR (KBr): 3307 (N–H); 1688 (C=O), 1631, 1575, 1539 (C=N), 1435, 1370, 1306 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 11.14 (s, 1 H, NH), 10.01 (s, 1 H, CONH), 8.41 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1 H), 8.15 (d, *J* = 8.5 Hz, 1 H), 7.92 (td, *J* = 7.9, 1.8 Hz, 1 H), 7.24 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.76 (d, *J* = 7.0 Hz, 1 H), 6.66 (d, *J*

= 7.0 Hz, 1 H).

^{13}C NMR (DMSO-d_6): δ = 157.6 (CONH), 149.7, 148.4, 146.3, 143.1, 138.7, 137.4, 135.1, 128.7, 128.1, 122.9, 121.0, 120.5, 118.4, 114.6, 113.1, 104.0.

MS (EI): *m/z* (%) = 288 (100, M^+), 168 (21, M^+ – 2-Py-NCO – H), 166 [82, $C_{11}H_6N_2$ (1*H*-perimidine moiety)], 140 (28, $C_{10}H_6N^+$, benzoazepinium), 121 (12, 2-Py-NHCO$^+$); 78 ($C_5H_4N^+$).

Anal. Calcd for $C_{17}H_{12}N_4O$ (%): C, 70.82; H, 4.20; N, 19.43. Found: C, 70.55; H, 4.21; N, 19.83.

N-(4-Methylpyridin-2-yl)-1*H*-perimidine-2-carboxamide (10b)

Yield 0.17 g (55 %); dark-red plates: mp 206.0 – 208.0 °C.

IR (KBr): 3329 (N–H), 1704 (C=O), 1631, 1593, 1540 (C=N), 1469, 1447, 1370, 1302 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 11.12 (s, 1 H, NH), 9.95 (s, 1 H, CONH), 8.26 (dd, *J* = 5.1, 0.3 Hz, 1 H), 7.99 (t, *J* = 0.8 Hz, 1 H), 7.22 – 7.06 (m, 5 H), 6.77 (d, *J* = 7.0 Hz, 1 H), 6.68 (d, *J* = 7.0 Hz, 1 H), 2.38 (s, 3 H, CH_3).

^{13}C NMR (DMSO-d_6): δ = 157.5 (CONH), 149.8, 149.5, 148.0, 146.3, 137.5, 135.1, 128.7, 128.1, 122.9, 121.5, 121.0, 118.5, 118.4, 114.6, 113.4, 104.0, 20.9 (CH_3).

MS (EI): *m/z* (%) = 302 (100, M^+), 168 (57, M^+ – 4-Me-2'-Py-NCO – H), 166 (72, $C_{11}H_6N_2^+$, perimidinium), 140 (23, $C_{10}H_6N^+$, benzoazepinium), 135 (36, 4-Me-2'-Py-NHCO$^+$), 92 (18, 4-Me-$C_5H_3N^+$).

Anal. Calcd for $C_{18}H_{14}N_4O$ (%): C, 71.51; H, 4.67; N, 18.53. Found: C, 71.40; H, 4.75; N, 18.42.

N-(5-Methylpyridin-2-yl)-1*H*-perimidine-2-carboxamide (10c)

Yield 0.14 g (45 %): dark-red needles; mp 244.0 – 245.0 °C.

IR (KBr): 3318 (N–H), 1689 (C=O), 1631, 1594, 1544 (C=N), 1481, 1448, 1371, 1311 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 11.12 (s, 1 H, NH), 9.94 (s, 1 H, CONH), 8.22 (dd, *J* = 1.6, 0.8 Hz, 1 H), 8.04 (d, *J* = 8.4 Hz, 1 H), 7.72 (ddd, *J* = 8.4, 1.2, 0.6 Hz, 1 H), 7.21 – 7.02 (m, 4 H), 6.74 (d, *J* = 6.9 Hz, 1 H), 6.66 (d, *J* = 6.9 Hz, 1 H), 2.27 (s, 3 H, CH_3).

^{13}C NMR (DMSO-d_6): δ = 157.4 (CONH), 148.2, 147.5, 146.3, 143.1, 138.9, 137.5, 135.1, 129.7, 128.7, 128.1, 122.9, 120.9, 118.4, 114.5, 112.6, 104.0, 17.2 (CH_3).

MS (EI): *m/z* (%) = 302 (100, M^+), 168 (37, M^+ – 5-Me-2'-Py-NCO – H), 166 (59, $C_{11}H_6N_2^+$, perimidinium), 140 (15, $C_{10}H_6N^+$, benzoazepinium), 135 (10, 5-Me-2'-Py-NHCO$^+$).

Anal. Calcd for $C_{18}H_{14}N_4O$ (%): C, 71.51; H, 4.67; N, 18.53. Found: C, 71.46; H, 4.61; N, 18.18.

N-(5-Nitropyridin-2-yl)-1*H*-perimidine-2-carboxamide (10d)

Yield 0.26 g (74 %): dark-red needles; mp 243.0 – 244.0 °C.

IR (KBr): 3386 (N–H), 3318 (NH), 1704 (C=O), 1632, 1580, 1542 (C=N), 1478, 1448, 1374, 1342, 1296 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 10.98 (s, 1 H, NH), 10.89 (s, 1 H, CONH), 9.24 (td, *J* = 2.2, 0.6 Hz, 1 H), 8.73 (dt, *J* = 9.3, 2.7 Hz, 1 H), 8.32 (tt, *J* = 9.9, 0.6 Hz, 1 H), 7.83 (dt, *J* = 8.7, 1.6 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 7.20 – 7.08 (m, 3 H), 6.72 (td, *J* = 3.0, 0.6 Hz, 1 H).

^{13}C NMR (DMSO-d_6): δ = 159.5 (CONH), 157.1, 153.8, 151.3, 146.2, 144.9, 141.7, 138.2, 137.3, 135.1, 134.8, 134.5, 128.7, 124.8, 120.5, 113.4, 112.6.

MS (EI): *m/z* (%) = 333 (54, M^+), 168 (12, M^+ – 5-NO_2-2'-Py-NCO – H), 166 (100, $C_{11}H_6N_2^+$, perimidinium), 140 (19, $C_{10}H_6N^+$, benzoazepinium).

Anal. Calcd for $C_{18}H_{14}N_4O$ (%): C, 61.26; H, 3.33; N, 21.01. Found: C, 61.30; H, 3.38; N, 20.97.

Anal. Calcd for $C_{14}H_{11}N_3O$ (%): C, 70,87; H, 4.67; N, 17.71. Found: C, 70.52; H, 4.68; N, 17.71.

N-Pyridin-2-yl-5*H*-dibenzo[*d*,*f*][1,3]diazepine-6-carboxamide (11a)

Yield 0.21 g (65 %): orange needles; mp 180.0 – 182.0 °C.

IR (KBr): 3273, 1687, 1489, 1433 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 10.25 (s, 1 H, CONH), 8.37 (ddd, 1 H, *J* = 4.8, 1.8, 0.9 Hz), 8.23 (dt, 1 H, *J* = 8.4, 0.9), 7.75 (td, 1 H, *J* = 7.8, 1.6 Hz), 7.61 (s, 1 H, NH), 7.29 – 7.02 (m, 8 H), 6.65 (dd, 1 H, *J* = 7.8, 1.2 Hz).

^{13}C NMR ($CDCl_3$): δ = 158.9 (CONH), 150.8, 150.3 (2 N–C=N), 148.3, 146.8, 146.3, 138.4, 134.9, 130.3, 130.0, 129.9, 129.6, 129.2, 128.8, 127.7, 125.2, 120.3, 119.9, 113.7.

MS (EI): *m/z* (%) = 314 (72, M^+), 194 (100, M^+ – 2-Py-NCO), 167 [10, $C_{12}H_9N$ (carbazole moiety)], 121 (24, 2-PyNHCO$^+$), 78 (9, $C_5H_4N^+$).

Anal. Calcd for $C_{19}H_{14}N_4O$ (%): C, 72.60; H, 4.49; N, 17.82. Found: C, 72.75; H, 4.42; N, 18.05.

N-(4-Methylpyridin-2-yl)-5*H*-dibenzo[*d*,*f*][1,3]diazepine-6-carboxamide (11b)

Yield 0.23 g (69 %): orange needles; mp 203.0 – 204.0 °C.

IR (KBr): 3335, 3303, 3289, 1694, 1488, 1432 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 10.21 (s, 1 H, CONH), 8.22 (d, *J* = 5.1 Hz, 1 H), 8.07 (t, *J* = 0.6 Hz, 1 H), 7.62 (s, 1 H, NH), 7.29 (d, *J* = 4.5 Hz, 1 H), 7.26 (dd, *J* = 5.4, 1.8 Hz, 1 H), 7.23 (dd, *J* = 3.8, 2.1 Hz, 1 H) , 7.19 (dd, *J* = 3.0, 1.5 Hz, 1 H), 7.13 (td, *J* = 8.1, 1.2 Hz, 2 H), 7.05 (td, *J* = 7.8, 1.2 Hz, 1 H), 6.92 (ddd, *J* = 5.1, 0.6, 0.3 Hz, 1 H), 6.65 (dd, *J* = 7.8, 1.2 Hz, 1 H), 2.39 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 158.9 (CONH), 150.9, 150.4,

149.9, 147.9, 146.8, 146.4, 134.9, 130.3, 130.0, 129.9, 129.6, 129.2, 128.8, 127.6, 125.2, 121.5, 119.8, 114.2, 21.4 (CH_3).

MS (EI): *m/z* (%) = 328 (26, M^+), 194 (53, M^+ – 4-Me-2'-Py-NCO), 167 (5, $C_{12}H_9N^+$, carbazolium), 135 (24, 4-Me-2'-PyNHCO$^+$), 92 (81, Me-$C_5H_4N^+$), 91 (100).

Anal. Calcd for $C_{20}H_{16}N_4O$ (%): C, 73.15; H, 4.91; N, 17.06. Found: C, 73.27; H, 4.89; N, 17.19.

N-(5-Methylpyridin-2-yl)-5*H*-dibenzo[*d*,*f*][1,3]diazepine-6-carboxamide (11c)

Yield 0.18 g (57 %): orange plates; mp 204.0 – 205.0 °C.

IR (KBr): 3303, 3267, 1681, 1487, 1435 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 10.11 (s, 1 H, CONH), 8.10 (dd, *J* = 1.5, 0.6 Hz, 1 H), 8.04 (d, *J* = 8.4 Hz, 1 H), 7.55 (s, 1 H, NH), 7.48 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.21 – 7.09 (m, 4 H), 7.05 (td, *J* = 7.8, 1.2 Hz, 2 H), 6.97 (t, *J* = 7.3 Hz, 1 H), 6.57 (d, *J* = 7.8 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 158.8 (CONH), 151.0, 148.2, 148.2, 146.8, 146.4, 138.9, 134.9, 130.2, 130.0, 129.9, 129.8, 129.6, 129.2, 128.8, 127.6, 125.2, 119.9, 113.2, 17.9 (CH_3).

MS (EI): *m/z* (%) = 328 (55, M^+), 194 (100, M^+ – 5-Me-2'-Py-NCO), 167 (6, $C_{12}H_9N^+$, carbazolium), 135 (25, 5-Me-2'-PyNHCO$^+$), 92 (6, Me-$C_5H_4N^+$).

Anal. Calcd for $C_{20}H_{16}N_4O$ (%): C, 73.15; H, 4.91; N, 17.06. Found: C, 73.16; H, 4.96; N, 17.17.

N-(5-nitropyridin-2-yl)-5*H*-dibenzo[*d*,*f*][1,3]diazepine-6-carboxamide (11d)

Yield 0.19 g (55 %): red needles; mp 207.0 – 208.0 °C.

IR (KBr): 3341, 3287, 1708, 1498, 1437 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 10.53 (s, 1 H, CONH), 9.13 (dd, *J* = 2.4, 0.6 Hz, 1 H), 8.46 (dd, *J* = 9.0, 2.7 Hz, 1 H), 8.35 (td, *J* = 9.0, 0.3 Hz, 1 H), 7.40 (s, 1 H, NH), 7.22 – 6.97 (m, 7 H), 6.57 (dd, *J* = 7.8, 1.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 159.4 (CONH), 154.2, 149.9, 146.4, 145.9, 145.0, 140.8, 134.9, 134.1, 130.4, 130.1, 129.8, 129.4, 128.9, 128.2, 125.5, 120.0, 112.7.

MS (EI): *m/z* (%) = 359 (78, M^+), 194 (100, M^+ – 5-NO_2-2'-Py-NCO), 167 (15, $C_{12}H_9N^+$, carbazolium), 166 (18, 5-NO_2-2'-PyNHCO$^+$), 139 (9, NO_2-$C_5H_5N^+$), 120 (10, C_5H_3N-NHCO$^+$), 91 (7).

Anal. Calcd for $C_{19}H_{13}N_5O_3$ (%): C, 63.51; H, 3.65; N, 19.49. Found: C, 63.38; H, 3.58; N, 19.60.

X-ray crystallographic data for compound 6a

Crystals suitable for the X-ray diffraction analysis were grown from methanol as yellow blocks; the chemical formula was $C_{20}H_{16}N_4O_2$ (*FW* = 344.37); triclinic, space group *P*–1; *a* = 7.2690(2), *b* = 10.1355(3), *c* = 12.9066(4) Å; α = 67.916(2), β = 81.547(1), γ = 80.982(1)°, *V* = 866.20(4) Å^3, *Z* = 2, D_{calcd} = 1.320 Mg·m^{-3}, F(000) = 360e; μ(MoKα) = 0.089 mm^{-1}. Reflections collected/unique/observed: 5309/3911/3165, R_1 = 0.0550 (observed reflections, $I > 2\sigma$), wR_2 = 0.1739, *S* = 0.918.[20]

X-ray crystallographic data for compound 8a

Crystals suitable for the X-ray diffraction analysis were grown from methanol as yellow plates; the chemical formula was $C_{14}H_{11}N_3O$ (*FW* = 237.26); monoclinic, space group $P2_1/c$; *a* = 14.1186(3), *b* = 5.6424(1), *c* = 15.8454(5) Å; α = 90, β = 115.342(1), γ = 90°, *V* = 1140.82(5) Å^3, *Z* = 4, D_{calcd} = 1.381 Mg·m^{-3}, *F*(000) = 496e; μ(MoKα) = 0.091 mm^{-1}. Reflections collected /unique/observed: 3700/2608/1678, R_1 = 0.0461 (observed reflections, $I > 2\sigma$), wR_2=0.1294, *S*=1.015.[20]

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(20) Details of X-ray analysis for compounds **6a** and **8a** have been deposited in the Cambridge Crystallographic Data Centre, CCDC Nos. 683408 and 644908, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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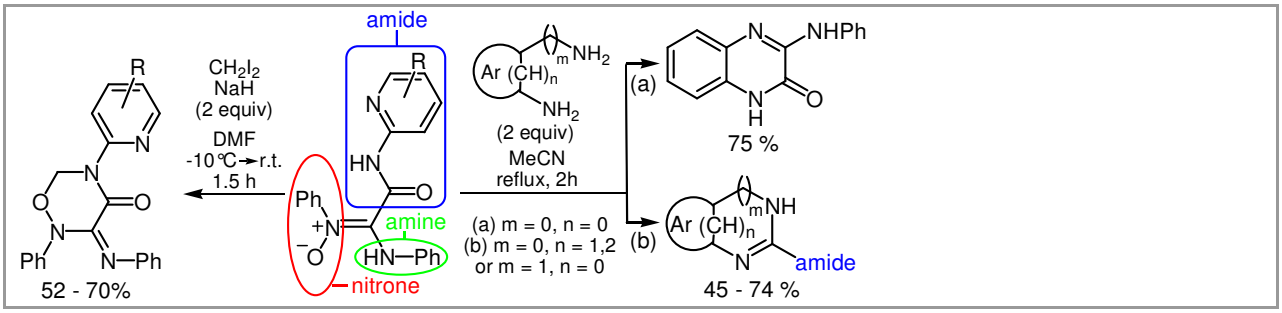

Graphical Abstract