Efficient Synthesis of 1-Arylquinoxalin-2(1*H*)-ones *via* Cyclocondensation of *N*-Aryl-Substituted 2-Nitrosoanilines with Functionalized Alkyl Acetates

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N-Aryl-substituted 2-nitrosoanilines (=2-nitrosobenzenamines) **1**, readily available by nucleophilic substitution of the *ortho*-H-atom in nitroarenes with arenamines, react with 2-substituted acetic acid esters in the presence of a weak base giving 1-arylquinoxalin-2(1*H*)-ones (*Scheme 2*). This cyclocondensation allows for the synthesis of compounds **2**–**4**, unsubstituted at C(3) or substituted by alkyl, aryl, ester, amide, and keto groups, in good to excellent yields (*Tables 1–4*).

Introduction. – Nucleophilic substitution of a H-atom in aromatic nitro compounds is a reaction of great value in organic synthesis because it allows to introduce a variety of substituents into electron-deficient aromatic rings without the requirement for the presence of a leaving group [1]. As the most versatile leaving groups in the classical S_NAr processes are halogen atoms, the alternative substitution of a H-atom (S_N^HAr) provides a shorter, halogen-free, thus more environmentally friendly synthetic approach. A few years ago, we described a synthesis of a wide range of *N*-aryl-substituted 2-nitrosoarenamines *via* nucleophilic substitution of a H-atom in the reaction of nitroarenes with anilines (= benzenamines) in the presence of a strong base [2]. The reaction belongs to a narrow, but interesting group of S_N^HAr processes, in which σ^H-adducts are converted into substituted nitrosoarenes according to an intramolecular redox stoichiometry [3]. It should be stressed that such reactions proceed also with *o*- and *p*-halonitrobenzenes; thus a general rule that nucleophilic substitution of H-atom proceeds faster than conventional substitution (S_NAr) of halogen atoms is confirmed [1c][4]. The reaction is so far the only useful method for the preparation of *N*-aryl-substituted 2-nitrosoanilines (=2-nitrosobenzenamines) and now, a variety of them become readily available.

N-Aryl-substituted 2-nitrosoanilines are ideal starting materials for the regioselective synthesis of many polycyclic compounds because they provide an aromatic ring having two N-containing groups of opposite reactivity, a nucleophilic amino group and a strongly electrophilic nitroso group. In our preceding papers, we reported simple and efficient synthesis of substituted phenazines [5] and benzimidazoles [6], which benefit

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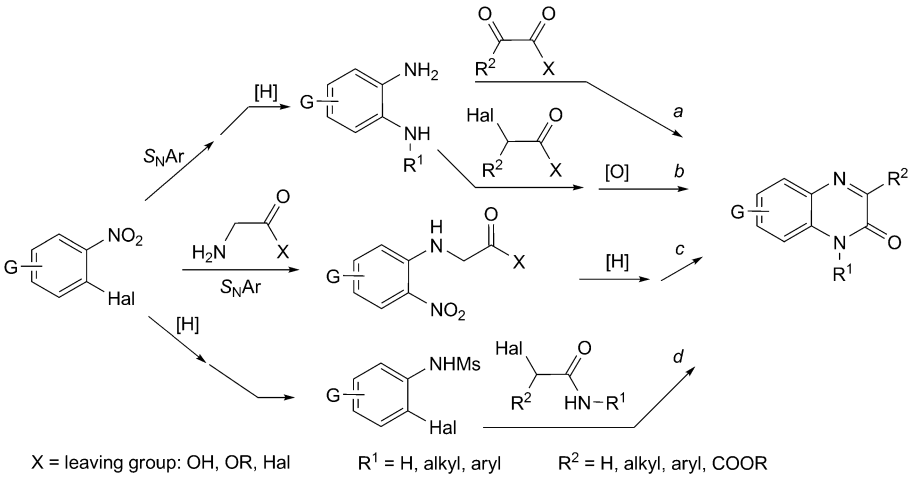
from that feature. Here, we report the synthesis of 1-arylquinoxalin-2(1*H*)-ones in the reaction between *N*-aryl-substituted 2-nitrosoanilines and 2-substituted acetic acid esters.

The quinoxalin-2(1*H*)-one scaffold is a core of an important class of heterocyclic molecules, which has shown a variety of biological activities such as antithrombotic, antitumor, antimicrobial, and many other activities [7–11]. The 1-arylquinoxalin-2(1*H*)-ones, although less common than their 1-alkyl and unsubstituted analogues, draw also notable attention as interesting biologically active compounds [12].

Almost all known synthetic ways to quinoxalinones can be derived from *ortho*-halonitroarenes as a source of the carbocyclic ring of the quinoxalin-2(1*H*)-ones and of at least one of its N-atoms (*Scheme 1*). The classical and most common approach consists in the coupling of substituted *ortho*-arenediamines with appropriate α-keto acid derivatives (*Scheme 1*, *Path a*). This method is widely applied for unsubstituted, 1-alkyl or 1-aryl derivatives and is quite practical in numerous instances [7][10][13]. However, it reveals some limitations concerning location of substituents which led to mixtures of isomers [7c]. Differentiation of the two *ortho* N-containing groups with respect to their reactivity could solve the regioselectivity issues but is usually much more laborious (*Scheme 1*, *Path c*) [11b][14].

Scheme 1. *Common Existing Synthetic Ways to Substituted Quinoxalin-2(1*H*)-ones*



Aromatic *ortho*-diamines require often multistep synthesis *via* substitution of the halogen atom in *ortho*-halonitrobenzene derivatives with an appropriate amine, followed by reduction of the nitro group. The synthesis of the suitable dicarbonyl or an equivalent partner can also be challenging (*Scheme 1*, *Path b*) [10b].

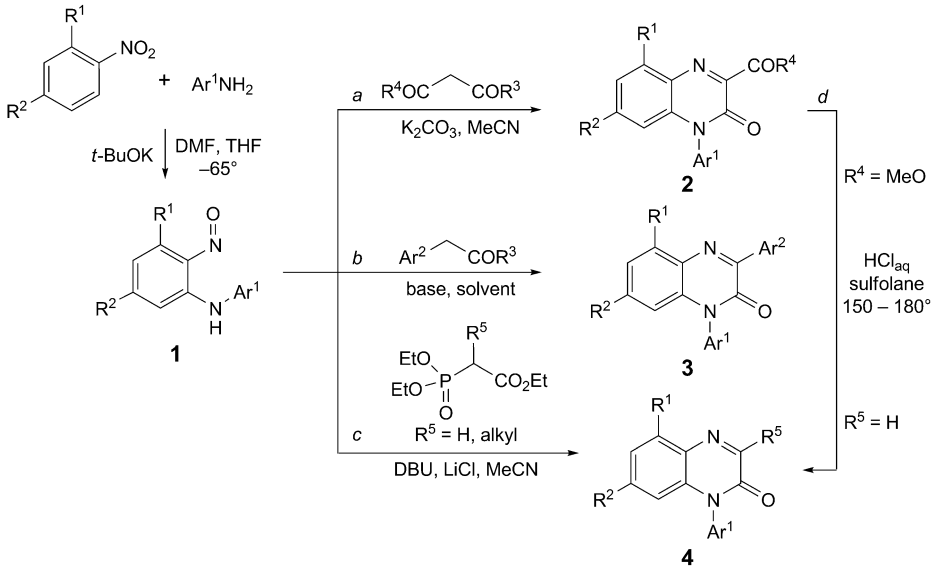
Usually, 1-aryl-substituted quinoxalin-2(1*H*)-ones were obtained by standard condensations of *N*-arylarenamines [15] (*Scheme 1*, *Path a* and *b*); thus, preceding synthesis of the latter from the appropriate 2-fluoronitroarenes was often required. Sporadically, other reactions leading to 1-arylquinoxalin-2(1*H*)-ones were also reported [16]. Recently, *Chen* and *Bao* developed a regioselective, one-pot, Cu^I catalyzed reaction of *N*-(2-iodophenyl)methanesulfonamides with *N*-aryl-2-haloacet-

amides, leading directly to quinoxalin-2(1*H*)-ones with 1-aryl and 1-alkyl substituents in good yields (*Scheme 1*, *Path d*) [17].

The simplest approach to substituted quinoxalinones appears to be the use of 2-nitrosoanilines which seem to be supreme substrates for the formation of the fused pyrazinone moiety. Since the N-containing groups in the substrate are of opposite reactivity, formation of the new C–N bonds in the reaction with suitable bifunctional reagents should occur regiospecifically. For instance, formation of the pyrazinone ring in the reaction of enolates of malonates and β-keto acetates, *etc.*, with nitroso derivatives of pyrimidinamines [18] or aminouracils [19] was used for the synthesis of some substituted pteridinones.

Results and Discussion. – In this study, we show that *N*-aryl-substituted 2-nitrosoanilines **1** undergo base-promoted cyclocondensation with esters of acetic acid activated by carbanion-stabilizing substituents, providing a variety of 1-arylquinoxalin-2(1*H*)-ones in good to excellent yields (*Scheme 2*). The reaction occurs under very mild conditions and, when combined with the earlier described general procedure for the preparation of substituted *N*-aryl-substituted 2-nitrosoanilines **1**, provides the shortest, two-step method for the synthesis of compounds **2**–**4** from simple, easily available nitroarenes (*Scheme 2*).

Scheme 2. *Synthesis of Substituted 1-Arylquinoxalin-2(1*H*)-ones* **2**–**4** *from Nitroarenes.* For R^1 to R^5, Ar^1 and Ar^2, see *Tables 1* (**2**), *2* (**3**), and *3* and *4* (**4**)



N-Aryl-substituted 2-nitrosoanilines are highly N–H acidic compounds and, to behave as electrophilic reagents in the condensation with enolates, they should remain neutral, at least partially, while the nucleophile precursor is, at least partially, deprotonated. Thus, only such alkyl acetates that contain an additional electron-withdrawing group meet this requirement. The reaction of **1** with esters of acetic acid

substituted by carbonyl groups occurred by simple mixing of both reactants in the presence of an excess of a weak base at room temperature. Suitable selection of the esters allowed for synthesis of 1-arylquinoxalin-2(1*H*)-ones **2**–**4** with a number of substituents at C(3) including alkoxycarbonyl, benzoyl, amido or aryl substituents. For strongly C–H acidic esters, such as alkyl malonates, the heterogeneous system K_2CO_3 in MeCN worked well (→**2**; *Table 1*). Less acidic 2-arylacetates required more basic conditions, thus Cs_2CO_3 in MeCN or DBU in DMF (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) were effective for the synthesis of quinoxalin-2(1*H*)-ones containing a wide range of carbo- and heterocyclic substituents at C(3) (→**3**; *Table 2*).

Table 1. *Cyclocondensation of* N-*Aryl-Substituted 2-Nitrosoanilines* **1** *with Carbonyl-substituted Acetic Acid Esters*[a]). See *Scheme 2*, *Path a.*

Entry	R^1	R^2	Ar^1	R^3	R^4	Time [h]	Product **2**	Yield[b]) [%]
1	H	Cl	2,6-$Me_2C_6H_3$	MeO	MeO	1	**a**	93
2	Cl	Cl	4-$EtOC_6H_4$	MeO	MeO	2.5	**b**	82
3	MeO	Cl	4-$EtOC_6H_4$	MeO	MeO	0.5	**c**	68
4	H	MeO	4-MeC_6H_4	MeO	MeO	1[c])	**d**	91
5	H	Ph	2,6-$Me_2C_6H_3$	MeO	MeO	1	**e**	88
6	H	Cl	4-$EtOC_6H_4$	MeO	MeO	2	**f**	76
7	H	Cl	pyridin-4-yl	MeO	MeO	24	**g**	93
8	H	Cl	Ph	MeO	MeO	1.5	**h**	93
9	Cl	Cl	4-ClC_6H_4	EtO	Ph	1	**i**	93
10	H	MeO	4-MeC_6H_4	EtO	$N(C_2H_4)_2O$	72	**j**	83

[a]) Conditions: K_2CO_3 in MeCN, r.t. [b]) Yield of isolated product. [c]) Reaction carried out in DMF.

Table 2. *Synthesis of 3-Arylquinoxalin-2(1*H*)-ones* **3** *from* N-*Aryl-Substituted 2-Nitrosoanilines* **1** *and 2-Arylacetic Acid Esters.* See *Scheme 2*, *Path b.*

Entry	R^1	R^2	Ar^1	Ar^2	R^3	Condition[a]), Time [h]	Product **3**	Yield[b]) [%]
1	H	Cl	2,6-$Me_2C_6H_3$	Ph	MeO	*A*, 1	**a**	74
2	H	Cl	2,6-$Me_2C_6H_3$	Ph	$(i\text{-}Pr)_2N$	*A*, 96	**a**	54
3	MeO	Cl	4-$EtOC_6H_4$	Ph	MeO	*B*, 2	**b**	75
4	H	MeO	4-MeC_6H_4	Ph	MeO	*C*, 24	**c**	80
5	H	MeO	4-MeC_6H_4	2-thienyl	EtO	*C*, 0.2	**d**	98
6	H	MeO	4-MeC_6H_4	pyridin-4-yl	EtO	*C*, 0.02	**e**	97
7	H	Cl	2,6-$Me_2C_6H_3$	6-MeO(3-NO_2)pyridin-2-yl	EtO	*A*, 1	**f**	78
8	H	MeO	4-MeC_6H_4	6-MeO(3-NO_2)pyridin-2-yl	EtO	*A*, 24	**g**	64
9	H	MeO	4-MeC_6H_4	1-nitronaphthalen-2-yl	EtO	*A*, 20	**h**	82
10	MeO	Cl	4-$EtOC_6H_4$	5-Cl(2-NO_2)C_6H_3	EtO	*A*, 20	**i**	62
11	H	MeO	4-MeC_6H_4	5-Cl(2-NO_2)C_6H_3	EtO	*A*, 20	**j**	67

[a]) Base and solvent: *A* = DBU in MeCN, *B* = Cs_2CO_3 in DMF and, *C* = DBU in DMF. [b]) Yield of isolated product.

Attempts to obtain 3-alkyl-substituted quinoxalinones in the reaction of **1** with esters of alkanoic acids failed, apparently due to the unfavorable relation of the acidity of the reagents. More basic alkanolates or other stronger bases in protic solvents had to

be excluded owing to a predisposition of *N*-aryl-substituted 2-nitrosoanilines to intramolecular cyclization leading to phenazines under such conditions [5].

To overcome this limitation, we tried to use acetic acid derivatives activated by substituents capable to depart in the course of the condensation. Since the initial attempts with the *Wittig* reagents were unsuccessful, we switched to the more reactive carbanions of ethyl 2-(diethoxyphosphoryl)acetate, -propanonate and -butanoate. The reactions of **1** with these reagents, carried out in the presence of LiCl/DBU in MeCN, gave 3-alkyl- or 3-unsubstituted quinoxalin-2(1*H*)-ones **4** in moderate to good yields, with a few exceptions in which the yield was rather low (*Table 3*). For the synthesis of 3-unsubstituted 1-arylquinoxalin-2(1*H*)-ones **4a**–**4c**, an alternative two-step procedure was carried out (*Scheme 2*, *Path a* + *d*). It consisted of the reaction of **1** with dimethyl malonate resulting in **2** (*Table 1*), followed by hydrolysis/decarboxylation of the 3-methoxycarbonyl group (*Table 4*). The latter reaction proceeded relatively easily, did not require copper or other catalysts, and occurred efficiently at 150–180° in sulfolane (= tetrahydrothiophene 1,1-dioxide). As a result, the sequence was more effective than

Table 3. *Cyclocondensation of* N-*Aryl-Substituted 2-Nitrosoanilines* **1** *with Ethyl 2-(Diethoxyphosphoryl)acetates*[a]). See *Scheme 2*, *Path c.*

Entry	R^1	R^2	Ar^1	R^5	Product **4**	Time [h]	Yield[b]) [%]
1	H	Cl	2,6-$Me_2C_6H_3$	H	**a**	2	43
2	Cl	Cl	4-$EtOC_6H_4$	H	**b**	24	25
3	H	Cl	4-ClC_6H_4	H	**c**	24	24
4	MeO	Cl	4-$EtOC_6H_4$	H	**d**	2.5	83
5	MeO	Cl	4-$EtOC_6H_4$	Et	**e**	20	51
6	H	Cl	2,6-$Me_2C_6H_3$	Et	**f**	16	42
7	H	MeO	4-MeC_6H_4	Et	**g**	20	77
8	H	Ph	2,6-$Me_2C_6H_3$	Et	**h**	5	38
9	H	Ph	2,6-$Me_2C_6H_3$	H	**i**	6	54 [c])
10	MeO	Cl	4-$EtOC_6H_4$	Me	**j**	3	49
11	H	MeO	4-MeC_6H_4	H	**k**	20	54
12	H	MeO	4-MeC_6H_4	Me	**l**	3	58

[a]) Conditions: DBU/LiCl in DMF, r.t. [b]) Yield of isolated product. [c]) Accompanied by 20% of N^3-(2,6-dimethylphenyl)[1,1′-biphenyl]-3,4-diamine (**5**).

Table 4. *Hydrolysis/Decarboxylation of Methyl 3,4-Dihydro-3-oxoquinoxaline-2-carboxylates* **2** (R^4 = MeO)[a]). See *Scheme 2*, *Path d.*

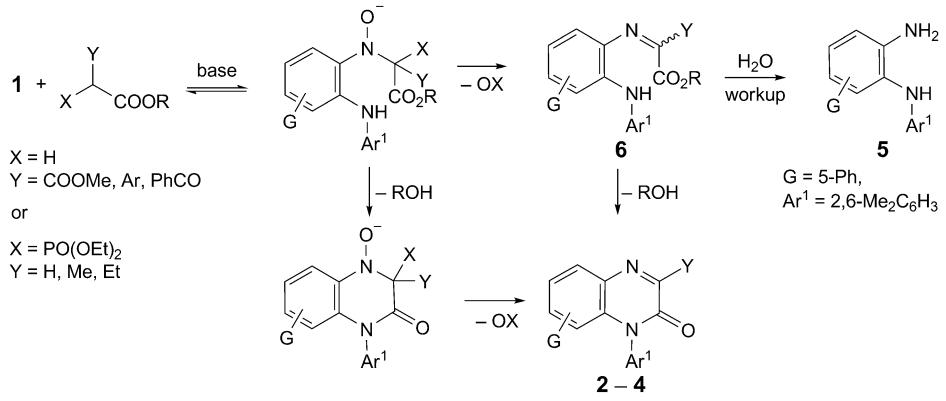
Entry	R^1	R^2	Ar^1	R^5	Product **4**	Yield[b]) [%] of **2** → **4**	Combined yield[b]) [%] of **1** → **2** → **4**
1	H	Cl	2,6-$Me_2C_6H_3$	H	**a**	79	73
2	Cl	Cl	4-$EtOC_6H_4$	H	**b**	66	54
3	H	Cl	4-ClC_6H_4	H	**c**	80	72[c])
4	H	Cl	pyridin-4-yl	H	**m**	72	51
5	H	Cl	Ph	H	**n**	80	74

[a]) Conditions: conc. HCl soln., sulfolane, 150–180°. [b]) Yield of isolated product. [c]) For the preparation of starting methyl 6-chloro-4-(4-chlorophenyl)-3,4-dihydro-3-oxoquinoxaline-2-carboxylate, see [2a].

the one-step reaction of **1** with ethyl 2-(diethoxyphosphoryl)acetate (*cf. Table 3*, *Entries* 1–3).

All presented cyclocondensations of **1** involve both condensation of the anion of the ester with the nitroso group and acylation of the N-atom of the arylamino function. The order of these events has not been considered in the literature dealing with similar cyclization processes. Our initial belief was priority of the *Ehrlich–Sachs* or aza-*Horner–Wadsworth–Emmons* condensation followed by the intramolecular acylation, but this sequence is not obvious. Since the acidity of the 2-nitrosoanilines **1** is not known and rather difficult to estimate, deprotonation of the amino group and its acylation with the neutral ester in the first step of the reaction could not be excluded. However, attempts to acylate **1** with diethyl 2,2-dimethylmalonate, which is unable to form a carbanion and, therefore, to react with the nitroso group, were unsuccessful. Under typical reaction conditions, the only process was slow decomposition, no traces of the acylation product were detected. Furthermore, formation of N^3-(2,6-dimethylphenyl)[1,1′-biphenyl]-3,4-diamine (**5**), besides the expected 1-arylquinoxalin-2(1*H*)-one **4i**, in one of the reactions (*Table 3*, *Entry* 9) is also informative. Compound **5** was apparently formed by hydrolysis of the primary product of the condensation, imine **6**, during the aqueous workup of the reaction mixture (*Scheme 3*). The above observations corroborate the priority of the enolate reaction with the nitroso group, although attempts to observe intermediate imines **6** in other reactions failed, which means that the intramolecular acylation is relatively fast, even when the *N*,*N*-diisopropylamide function is involved (*Table 2*, *Entry* 2). Thus, addition of the anionic nucleophile to the nitroso group seems to be the first step of the reaction. Whether the condensation is finalized with formation of the C=N bond prior to the cyclization, or elimination of the leaving group occurs as a final step of the quinoxalinone formation, can not be easily determined.

Scheme 3. *Possible Ways of the Formation of Quinoxalinones* **2**, **3**, **4**, *and Diamine* **5**



Conclusions. – The presented reaction allows for the synthesis of numerous 1-arylquinoxalin-2(1*H*)-ones with various substituents at C(3). Starting 2-nitrosoanilines have become easily available *via* a one-step nucleophilic substitution of H-atom in

nitroarenes with arenamines, hence overcoming the classical halogen-substitution/reduction sequence. The presented method is superior to the known ones also because of its simple procedure, mild conditions and environmentally friendly character. Combining the synthesis of *N*-aryl-substituted 2-nitrosoarenamines with their reaction with active methylene groups of acetic ester derivatives, we have developed a short, convenient way to interesting heterocyclic compounds of potential value.

Experimental Part

General. Known *N*-aryl-2-nitrosobenzenamines **1** were obtained following procedures published previously [2]. Ethyl (5-chloro-2-nitrophenyl)acetate [20], methyl (6-methoxy-3-nitropyridin-2-yl)acetate [21], and methyl (1-nitronaphthalen-2-yl)acetate [20] were obtained according to the literature. All remaining reagents were commercially available. DMF and MeCN were dried (CaH_2), distilled, and stored over molecular sieves. Column chromatography (CC): silica gel (SiO_2 *60*, 230–400 mesh; *Merck*). M.p.: uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-Avance-500* (500 (^{1}H) and 125 MHz (^{13}C)) or *Varian-NMR-vnmrs600* (600 (^{1}H) and 150 MHz (^{13}C)) instrument at 298 K; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS (70 eV): *AMD-604* spectrometer; in *m*/*z* (rel. %).

New N-*Aryl-2-nitrosobenzamines* **1**. *General Procedure.* To a cooled soln. of *t*-BuOK (6 mmol, 672 mg) in DMF (12 ml) were added dropwise at $-60°$ the appropriate benzenamine (2 mmol) in DMF (2 ml) and then the nitroarene (2 mmol) in DMF (2 ml). The mixture was stirred at $-60°$ for 30 min, then poured into conc. NH_4Cl soln. (*ca.* 50 ml), and extracted with AcOEt. The extract was washed thoroughly with H_2O and brine, dried (Na_2SO_4) and concentrated and the crude product subjected to CC (SiO_2, hexane/AcOEt or hexane/toluene).

5-Chloro-2-nitroso-N-*phenylbenzenamine* (**1**; R^1 = H, R^2 = Cl, Ar^1 = Ph): Yield 68%. Dark solid. M.p. 100–102°. ^{1}H-NMR (500 MHz, (D_6)DMSO): 6.88 (*dd*, *J* = 8.8, 1.8, 1 H); 7.17 (*d*, *J* = 1.8, 1 H); 7.28–7.33 (*m*, 1 H); 7.43–7.51 (*m*, 4 H); 7.68 (br. *s*, 1 H); 11.49 (br. *s*, 1 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 115.1; 117.7; 124.5; 125.9; 126.9; 129.6; 137.6; 140.8; 143.9; 155.5. EI-MS: 231 ([*M* − 1]$^+$, 13), 215 (100), 201 (23), 166 (16). HR-MS: 232.0392 ([*M* − 1]$^+$, $C_{12}H_8{}^{35}ClN_2O^+$; calc. 232.0403).

N-*(5-Chloro-2-nitrosophenyl)pyridin-4-amine* (**1**; R^1 = H, R^2 = Cl, Ar^1 = pyridin-4-yl): Yield 85%. Orange solid. M.p. 128–132°. ^{1}H-NMR (500 MHz, (D_6)DMSO): 6.80 (*d*, *J* = 8.9, 1 H); 6.99 (*dd*, *J* = 8.9, 2.0, 1 H); 7.43–7.46 (*m*, 2 H); 7.77 (*d*, *J* = 2.0, 1 H); 8.48–8.51 (*m*, 2 H); 11.11 (br. *s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$)[4]): 115.1; 116.2; 120.6; 145.0; 145.4; 151.4; 155.2. EI-MS: 233 (6, *M*$^+$), 216 (100), 202 (11), 168 (17). HR-MS (ESI) 234.0438 ([*M* + H]$^+$, $C_{11}H_9{}^{35}Cl^+N_3O$; calc. 234.0429).

N-*(2,6-Dimethylphenyl)-4-nitroso[1,1′-biphenyl]-3-amine* (**1**; R^1 = H, R^2 = Ph, Ar^1 = 2,6-$Me_2C_6H_3$). Yield 33%. Dark solid. M.p. 117–120°. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.15 (*s*, 6 H); 6.48 (*d*, *J* = 1.6, 1 H); 7.14–7.24 (*m*, 4 H); 7.38–7.41 (*m*, 3 H); 7.46–7.49 (*m*, 2 H); 8.87 (br. *s*, 1 H); 12.05 (br. *s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$)[4]): 18.2; 112.5; 117.0; 127.4; 127.8; 128.7; 128.9; 129.2; 133.7; 135.9; 139.4; 140.9; 150.4; 155.6. EI-MS: 302 (3, *M*$^+$), 287 (100), 270 (8). HR-MS: 302.1424 ($C_{20}H_{18}N_2O^+$; calc. 302.1420).

Reaction of N-*Aryl-2-nitrosobenzenamines* **1** *with Esters of Carbonyl- or Aryl-Activated Acetic Acid to Quinoxalinones* **2** *and* **3**: *General Procedure.* To a soln. of **1** (0.5 mmol) and an appropriate ester (0.7 mmol) in dry MeCN or DMF (6 ml) was added K_2CO_3 (552 mg, 4 mmol), or Cs_2CO_3 (1300 mg, 4 mmol), or DBU ((0.3 ml, 2.0 mmol). The mixture was stirred at r.t. for the time specified in *Tables 1* and *2*. Then, the mixture was poured into NH_4Cl soln. and extracted with AcOEt, the combined extract washed with H_2O and brine, dried (Na_2SO_4), and concentrated, and product **2** or **3** isolated by CC (SiO_2).

Reaction of N-*Aryl-2-nitrosobenzenamines* **1** *with Esters of 2-(Diethoxyphosphoryl)acetic Acid* to *Quinoxalinones* **4**: *General Procedure.* To a soln. of **1** (0.4 mmol) and an appropriate 2-(diethoxyphosphoryl)acetic acid ester (=2-(diethoxyphosphinyl)acetic acid ester; 0.44 mmol) in dry MeCN (5 ml) were added LiCl (20 mg, 0.48 mmol) and DBU (0.3 ml, 2.0 mmol). The mixture was stirred at r.t. for the time specified in *Table 3.* Then, the mixture was poured into NH_4Cl soln. and extracted with AcOEt, the

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[4]) One or more signals are not visible.

combined extract washed with H_2O and brine, dried (Na_2SO_4), and concentrated, and the product **4** isolated by CC (SiO_2).

Hydrolysis/Decarboxylation of Methyl 3,4-Dihydro-3-oxoquinoxaline-3-carboxylates **2** (R^4 = MeO): *General Procedure*. To a soln. of **2** (R^4 = MeO; 0.3 mmol) in sulfolane (3 ml) at r.t. was added conc. HCl soln. (0.1 ml), and the soln. was warmed to 80° and kept at 80° until the substrate disappeared (TLC monitoring). Then, the temp. was raised slowly to 150–180°, depending on the particular substrate. After the evolution of CO_2 ceased, the mixture was cooled, poured onto ice/H_2O containing sat. aq. NaCl soln. (10 ml), and extracted with AcOEt (3 × 20 ml). The combined extract was washed twice with dil. NaCl soln., dried (Na_2SO_4), and concentrated, the residue subjected to CC (SiO_2), and the product **4** recrystallized.

Methyl 6-Chloro-4-(2,6-dimethylphenyl)-3,4-dihydro-3-oxoquinoxaline-2-carboxylate (**2a**): White crystals. M.p. 173–176° (AcOEt). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.99 (*s*, 6 H); 4.03 (*s*, 3 H); 6.54 (*d*, *J* = 2.1, 1 H); 9.26–7.29 (*m*, 2 H); 7.35 (*dd*, *J* = 8.7, 2.1, 1 H); 7.35–7.39 (*m*, 1 H); 7.94 (*d*, *J* = 8.7, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 17.6; 53.3; 114.3; 125.2; 129.4; 130.0; 130.5; 132.2; 132.6; 134.7; 135.3; 139.2; 149.2; 150.9; 163.6. EI-MS: 342 (94, M^+), 282 (100), 255 (61), 219 (87). HR-MS: 342.0777 ($C_{18}H_{15}{}^{35}ClN_2O_3^+$; calc. 342.0771).

Methyl 6,8-Dichloro-4-(4-ethoxyphenyl)-3,4-dihydro-3-oxoquinoxaline-2-carboxylate (**2b**): Yellow crystals. M.p. 203–205° (hexane/AcOEt). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.48 (*t*, *J* = 7.0, 3 H); 4.02 (*s*, 3 H); 4.12 (*q*, *J* = 7.0, 2 H); 6.67 (*d*, *J* = 2.2, 1 H); 7.08–7.12 (*m*, 2 H); 7.13–7.16 (*m*, 2 H); 7.43 (*d*, *J* = 2.2, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 14.7; 53.3; 63.9; 114.6; 116.2; 125.4; 126.4; 127.4; 128.9; 136.6; 137.4; 138.0; 149.5; 152.0; 150.0; 163.4. EI-MS: 394 (81), 392 (100, M^+), 305 (33), 278 (64). HR-MS: 392.0323 ($C_{18}H_{14}{}^{35}Cl_2N_2O_4^+$; calc. 392.0331).

Methyl 6-Chloro-4-(4-ethoxyphenyl)-3,4-dihydro-8-methoxy-3-oxoquinoxaline-2-carboxylate (**2c**). Pale yellow crystals. M.p. 258–260° (AcOEt). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.47 (*t*, *J* = 7.0, 3 H); 3.99 (*s*, 3 H); 4.04 (*s*, 3 H); 4.11 (*q*, *J* = 7.0, 2 H); 6.33 (*d*, *J* = 2.0, 1 H); 6.78 (*d*, *J* = 2.0, 1 H); 7.07–7.11 (*m*, 2 H); 7.14–7.18 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.7; 53.1; 56.9; 63.9; 106.6; 107.9; 116.1; 121.3; 127.0; 129.0; 137.5; 139.6; 146.4; 152.5; 157.2; 159.8; 163.5. EI-MS: 388 (100, M^+), 356 (42), 328 (29), 300 (92), 272 (49). HR-MS: 388.0834 ($C_{19}H_{17}{}^{35}ClN_2O_5^+$; calc. 388.0826).

Methyl 3,4-Dihydro-6-methoxy-4-(4-methylphenyl)-3-oxoquinoxaline-2-carboxylate (**2d**). Pale green crystals. M.p. 157° (hexane/AcOEt). ^{1}H-NMR (500 MHz, (D_6)DMSO): 2.44 (*s*, 3 H); 3.69 (*s*, 3 H); 3.89 (*s*, 3 H); 5.95 (*d*, *J* = 2.6, 1 H); 7.07 (*dd*, *J* = 9.0, 2.6, 1 H); 7.30–7.34 (*m*, 2 H); 7.43 (*m*, 2 H); 7.87 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 21.3; 53.0; 56.2; 99.7; 112.2; 126.6; 128.4; 131.1; 132.2; 133.0; 137.4; 139.6; 146.0; 152.4; 162.7; 164.4. EI-MS: 324 (100, M^+), 293 (10), 281 (16), 237 (47). HR-MS: 324.1117 ($C_{18}H_{16}N_2O_4^+$; calc. 324.1110).

Methyl 4-(2,6-Dimethylphenyl)-3,4-dihydro-3-oxo-6-phenylquinoxaline-2-carboxylate (**2e**): Yellow crystals. M.p. 158° (hexane/ AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.02 (*s*, 6 H); 4.04 (*s*, 3 H); 6.13 (*d*, *J* = 2.0, 1 H); 7.26–7.28 (*m*, 2 H); 7.34–7.44 (*m*, 6 H); 7.62 (*dd*, *J* = 8.4, 2.0, 1 H); 8.09 (*d*, *J* = 8.4, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.7; 53.2; 112.4; 123.8; 127.4; 128.7; 129.0; 129.3; 129.8; 131.4; 131.5; 133.0; 134.2; 135.4; 139.2; 146.0; 148.7; 151.4; 163.9. EI-MS: 384 (100, M^+), 324 (62), 297 (60). HR-MS: 384.1484 ($C_{24}H_{20}N_2O_3^+$; calc. 384.1474).

Methyl 6-Chloro-4-(4-ethoxyphenyl)-3,4-dihydro-3-oxoquinoxaline-2-carboxylate (**2f**): Yellow solid. M.p. 181–182°. ^{1}H-NMR (600 MHz, $CDCl_3$): 1.48 (*t*, *J* = 7.0, 3 H); 4.02 (*s*, 3 H); 4.13 (*q*, *J* = 7.0, 2 H); 6.76 (d, *J* = 2.1, 1 H); 7.09–7.12 (*m*, 2 H); 7.16–7.19 (*m*, 2 H); 7.31 (*dd*, *J* = 8.6, 2.1, 1 H); 7.89 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 14.7; 53.2; 63.9; 115.6; 116.2; 124.9; 126.6; 129.0; 130.3; 131.9; 136.3; 138.6; 149.1; 152.3; 159.9; 163.7. EI-MS: 358 (100, M^+), 271 (22), 243 (32). HR-MS: 358.0730 ($C_{18}H_{15}{}^{35}ClN_2O_4^+$; calc. 358.0720).

Methyl 6-Chloro-3,4-dihydro-3-oxo-4-(pyridin-4-yl)quinoxaline-2-carboxylate (**2g**): Yellow solid. M.p. 186–189°. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.03 (*s*, 3 H); 6.68 (*d*, *J* = 2.0, 1 H); 7.31–7.33 (*m*, 2 H); 7.38 (*dd*, *J* = 8.6, 2.0, 1 H); 7.94 (*d*, *J* = 8.6, 1 H); 8.94–8.97 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 53.4; 114.8; 123.1; 125.5; 130.1; 132.3; 134.4; 139.1; 142.4; 148.7; 151.1; 152.4; 163.1. EI-MS: 315 (91, M^+), 256 (23), 228 (100). HR-MS: 315.0408 ($C_{15}H_{10}{}^{35}ClN_3O_3^+$; calc. 315.0411).

Methyl 6-Chloro-3,4-dihydro-3-oxo-4-phenylquinoxaline-2-carboxylate (**2h**): Pale yellow solid. M.p. 184–186°. ^{1}H-NMR (500 MHz, (D_6)DMSO): 3.92 (*s*, 3 H); 6.49 (*d*, *J* = 2.3, 1 H); 7.46–7.51 (*m*, 3 H);

7.60–7.64 (*m*, 1 H); 7.65–7.69 (*m*, 2 H); 7.96 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 53.3; 115.2; 124.7; 128.8; 130.3; 130.4; 130.8; 132.1; 135.2; 136.6; 137.0; 150.2; 151.9; 164.0. EI-MS: 314 (71, M^+), 227 (100). HR-MS: 314.0447 ($C_{16}H_{11}{}^{35}ClN_2O_3^+$; calc. 314.0458).

*3-Benzoyl-5,7-dichloro-1-(4-chlorophenyl)quinoxalin-2(1*H*)-one* (**2i**): Yellow crystals. M.p. 223–225° (MeOH). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.65 (*d*, *J* = 2.1, 1 H); 7.25–7.28 (*m*, 2 H); 7.47 (*d*, *J* = 2.1, 1 H); 7.49–7.53 (*m*, 2 H); 7.59–7.62 (*m*, 2 H); 7.62–7.67 (*m*, 1 H); 8.04–8.07 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 114.1; 125.6; 127.5; 128.7; 129.5; 130.2; 130.9; 132.7; 134.4; 134.5; 136.4; 136.5; 136.8; 137.7; 152.2; 154.7; 190.2. EI-MS: 430 (18, $[M+2]^+$), 428 (19, M^+), 373 (5), 105 (100), 77 (43). HR-MS: 427.9885 ($C_{21}H_{11}{}^{35}Cl_3N_2O_2^+$; calc. 427.9886).

*7-Methoxy-1-(4-methylphenyl)-3-(morpholin-4-ylcarbonyl)quinoxalin-2(1*H*)-one* (**2j**): White crystals. M.p. 199–202° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.46 (*s*, 3 H); 3.44–3.48 (*m*, 2 H); 3.72 (*s*, 3 H); 3.73–3.75 (*m*, 2 H); 3.78–3.85 (*m*, 4 H); 6.17 (*d*, *J* = 2.6, 1 H); 6.92 (*dd*, *J* = 9.0, 2.6, 1 H); 7.15–7.18 (*m*, 2 H); 7.39–7.42 (*m*, 2 H); 7.83 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.3; 42.1; 47.0; 55.7; 66.6; 66.7; 99.6; 111.8; 127.3; 127.6; 131.0; 131.7; 132.3; 136.3; 139.9; 149.9; 152.9; 162.0; 164.1. EI-MS: 379 (100, M^+), 321 (18), 294 (54), 266 (76), 237 (98). HR-MS: 379.1521 ($C_{21}H_{21}N_3O_4^+$; calc. 379.1532).

*7-Chloro-1-(2,6-dimethylphenyl)-3-phenylquinoxalin-2(1*H*)-one* (**3a**): Beige crystals. M.p. 175–178° (hexane). ^{1}H-NMR (600 MHz, $CDCl_3$): 2.02 (*s*, 6 H); 6.52 (*d*, *J* = 2.2, 1 H); 7.29–7.31 (*m*, 2 H); 7.32 (*dd*, *J* = 8.6, 2.2, 1 H); 7.36–7.39 (*m*, 1 H); 7.47–7.51 (*m*, 3 H); 7.93 (*d*, *J* = 8.6, 1 H); 8.42–8.45 (*m*, 2 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 17.7; 113.8; 124.6; 128.1; 129.4; 129.6; 129.7; 130.8; 131.3; 131.8; 133.6; 133.6; 135.3; 135.5; 136.4; 153.2; 154.5. EI-MS: 360 (100, M^+), 331 (14), 317 (29), 255 (25). HR-MS: 360.1021 ($C_{22}H_{17}{}^{35}ClN_2O^+$; calc. 360.1029).

*7-Chloro-1-(4-ethoxyphenyl)-5-methoxy-3-phenylquinoxalin-2(1*H*)-one* (**3b**): Yellow crystals. M.p. 251–253° (hexane/AcOEt). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.48 (*t*, *J* = 7.0, 3 H); 4.05 (*s*, 3 H); 4.14 (*q*, *J* = 7.0, 2 H); 6.31 (*d*, *J* = 2.0, 1 H); 6.78 (*d*, *J* = 2.0, 1 H); 7.08–7.14 (*m*, 2 H); 7.18–7.23 (*m*, 2 H); 7.42–7.46 (*m*, 3 H); 8.35–8.39 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.8; 56.7; 63.9; 106.3; 107.7; 116.1; 122.4; 128.0; 128.1; 129.1; 129.7; 130.4; 135.8; 136.4; 136.5; 152.3; 154.8; 156.7; 159.6. EI-MS: 406 (100, M^+), 377 (94), 349 (36). HR-MS: 406.1092 ($C_{23}H_{19}{}^{35}ClN_2O_3^+$; calc. 406.1084).

*7-Methoxy-1-(4-methylphenyl)-3-phenylquinoxalin-2(1*H*)-one* (**3c**): Yellow crystals. M.p. 217–220° (AcOEt). ^{1}H-NMR (500 MHz, (D_6)DMSO): 2.45 (*s*, 3 H); 3.68 (*s*, 3 H); 5.96 (*d*, *J* = 2.6, 1 H); 7.04 (*dd*, *J* = 8.9, 2.6, 1 H); 7.31–7.35 (*m*, 2 H); 7.45–7.49 (*m*, 5 H); 7.88 (*d*, *J* = 8.9, 1 H); 8.21–8.25 (*m*, 2 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 20.8; 55.6; 99.0; 110.9; 127.3; 127.8; 128.1; 129.0; 129.8; 130.6; 131.1; 133.6; 135.9; 136.0; 138.7; 150.4; 154.0; 160.6. EI-MS: 342 (100, M^+), 314 (28), 299 (57). HR-MS: 342.1364 ($C_{22}H_{18}N_2O_2^+$; calc. 342.1368).

*7-Methoxy-1-(4-methylphenyl)-3-(2-thienyl)quinoxalin-2(1*H*)-one* (**3d**): Pale yellow solid. M.p. 231–234°. ^{1}H-NMR (500 MHz, (D_6)DMSO): 2.45 (*s*, 3 H); 3.67 (*s*, 3 H); 5.97 (*d*, *J* = 2.6, 1 H); 7.04 (*dd*, *J* = 8.9, 2.6, 1 H); 7.22 (*dd*, *J* = 5.1, 3.8, 1 H); 7.32–7.35 (*m*, 2 H); 7.46–7.48 (*m*, 2 H); 7.79 (*dd*, *J* = 5.1, 1.1, 1 H); 7.83 (*d*, *J* = 8.9, 1 H); 8.29 (*dd*, *J* = 3.8, 1.1, 1 H). ^{13}C-NMR (125 MHz, (D_6)DMSO)[4]): 44.5; 79.3; 122.8; 134.9; 150.8; 151.5; 151.8; 154.1; 154.2; 154.9; 157.0; 158.9; 162.5; 162.9; 169.0; 176.7; 183.9. EI-MS: 348 (100, M^+), 305 (58). HR-MS: 348.0918 ($C_{20}H_{16}N_2O_2S^+$; calc. 348.0932).

*7-Methoxy-1-(4-methylphenyl)-3-(pyridin-4-yl)quinoxalin-2(1*H*)-one* (**3e**): Yellow crystals. M.p. 220–223° (hexane/AcOEt). ^{1}H-NMR (500 MHz, (D_6)DMSO): 2.43 (*s*, 3 H); 3.67 (*s*, 3 H); 5.96 (*d*, *J* = 2.6, 1 H); 7.05 (*dd*, *J* = 2.6, 8.8, 1 H); 7.30–7.33 (*m*, 2 H); 7.42–7.46 (*m*, 2 H); 7.91 (*d*, *J* = 8.8, 1 H); 8.14–8.18 (*m*, 2 H); 8.67–8.91 (*m*, 2 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 21.3; 56.2; 99.4; 111.9; 123.3; 127.7; 128.6; 131.1; 132.1; 133.8; 136.9; 139.4; 143.3; 148.4; 150.1; 154.4; 161.9. EI-MS: 343 (100, M^+), 315 (21), 300 (37). HR-MS: 343.1335 ($C_{21}H_{17}N_3O_2^+$; calc. 343.1321).

*7-Chloro-1-(2,6-dimethylphenyl)-3-(6-methoxy-3-nitropyridin-2-yl)quinoxalin-2(1*H*)-one* (**3f**): White crystals. M.p. 247–249° (AcOEt). ^{1}H-NMR (500 MHz, (D_6)DMSO): 1.96 (*s*, 6 H); 4.04 (*s*, 3 H); 6.47 (*d*, *J* = 2.2, 1 H); 7.24 (*d*, *J* = 9.0, 1 H); 7.36–7.39 (*m*, 2 H); 7.42–7.46 (*m*, 1 H); 7.58 (*dd*, *J* = 8.6, 2.2, 1 H); 8.09 (*d*, *J* = 8.6, 1 H); 8.59 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 16.9; 55.2; 112.6; 113.5; 125.1; 129.3; 130.0; 131.0; 132.0; 132.4; 133.6; 135.1; 136.2; 136.7; 140.0; 147.5; 151.9; 155.5; 166.0. EI-MS: 436 (7, M^+), 419 (8), 390 (100). HR-MS: 436.0933 ($C_{22}H_{17}{}^{35}ClN_4O_4^+$; calc. 436.0938).

*7-Methoxy-3-(6-methoxy-3-nitropyridin-2-yl)-1-(4-methylphenyl)quinoxalin-2(1*H*)-one* (**3g**): Pale yellow crystals. M.p. 214–216° (hexane/AcOBu). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.45 (*s*, 3 H); 3.74 (*s*, 3 H); 4.09 (*s*, 3 H); 6.23 (*d*, *J* = 2.6, 1 H); 6.90 (*d*, *J* = 9.0, 1 H); 6.94 (*dd*, *J* = 8.9, 2.6, 1 H); 7.20–7.23 (*m*, 2 H); 7.37–7.40 (*m*, 2 H); 7.89 (*d*, *J* = 8.9, 1 H); 8.39 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$)[4]): 21.3; 55.0; 55.7; 99.7; 111.4; 111.9; 127.8; 130.9; 131.6; 132.7; 135.3; 136.5; 139.6; 140.1; 149.1; 152.3; 154.1; 161.7; 166.3. EI-MS: 418 (10, M^+), 386 (8), 372 (100). HR-MS: 418.1266 ($C_{22}H_{18}N_4O_5^+$; calc. 418.1277).

*7-Methoxy-1-(4-methylphenyl)-3-(1-nitronaphthalen-2-yl)quinoxalin-2(1*H*)-one* (**3h**). Yellow crystals. M.p. 173–176° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.46 (*s*, 3 H); 3.73 (*s*, 3 H); 6.19 (*d*, *J* = 2.6, 1 H); 6.93 (*dd*, *J* = 8.9, 2.6, 1 H); 7.20–7.24 (*m*, 2 H); 7.39–7.42 (*m*, 2 H); 7.61–7.69 (*m*, 2 H); 7.85 (*d*, *J* = 8.9, 1 H); 7.93–7.96 (*m*, 1 H); 8.00 (*d*, *J* = 8.6, 1 H); 8.08 (*d*, *J* = 8.6, 1 H); 8.10–8.13 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$)[4]): 21.3; 55.7; 99.5; 111.7; 122.9; 124.7; 126.9; 127.8; 127.9; 128.1; 128.9; 131.0; 131.2; 131.8; 132.9; 134.3; 136.4; 139.6; 147.4; 150.4; 154.1; 161.8. EI-MS: 437 (2, M^+), 405 (2), 391 (100). HR-MS: 437.1386 ($C_{26}H_{19}N_3O_4^+$; calc. 437.1376).

*7-Chloro-3-(5-chloro-2-nitrophenyl)-1-(4-ethoxyphenyl)-5-methoxyquinoxalin-2(1*H*)-one* (**3i**): Yellow crystals. M.p. 219–223° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.46 (*t*, *J* = 7.1, 3 H); 4.06 (*s*, 3 H); 4.10 (*t*, *J* = 7.1, 2 H); 6.38 (*d*, *J* = 1.9, 1 H); 6.83 (*d*, *J* = 1.9, 1 H); 7.05–7.09 (*m*, 2 H); 7.14–7.18 (*m*, 2 H); 7.55 (*dd*, *J* = 8.7, 2.4, 1 H); 7.78 (*d*, *J* = 2.4, 1 H); 8.07 (*d*, *J* = 8.7, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.8; 56.8; 63.9; 106.7; 108.1; 116.1; 122.2; 125.5; 127.3; 129.1; 130.3; 132.0; 133.2; 136.9; 137.7; 140.3; 147.2; 153.1; 154.0; 156.9; 159.8. EI-MS: 485 (22, M^+), 439 (100). HR-MS: 485.0537 ($C_{23}H_{17}{}^{35}Cl_2N_3O_5^+$; calc. 485.0545).

*3-(5-Chloro-2-nitrophenyl)-7-methoxy-1-(4-methylphenyl)quinoxalin-2(1*H*)-one* (**3j**): Yellowish crystals. M.p. 181–183° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.45 (*s*, 3 H); 3.74 (*s*, 3 H); 6.20 (*d*, *J* = 2.5, 1 H); 6.95 (*dd*, *J* = 8.8, 2.5, 1 H); 7.14–7.19 (*m*, 2 H); 7.37–7.40 (*m*, 2 H); 7.54 (*dd*, *J* = 8.6, 2.3, 1 H); 7.79 (*d*, *J* = 2.3, 1 H); 7.87 (*d*, *J* = 8.8, 1 H); 8.05 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.3; 55.7; 99.7; 111.6; 125.5; 127.7; 127.8; 130.0; 131.0; 131.6; 131.8; 132.7; 133.2; 136.4; 139.7; 139.9; 147.4; 151.4; 154.1; 161.8. EI-MS: 421 (19, M^+), 375 (100). HR-MS: 421.0812 ($C_{22}H_{16}{}^{35}ClN_3O_4^+$; calc. 421.0829).

*7-Chloro-1-(2,6-dimethylphenyl)quinoxalin-2(1*H*)-one* (**4a**): Gray crystals. M.p. 103–105° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.99 (*s*, 6 H); 6.53 (*d*, *J* = 2.1, 1 H); 7.27–7. 33 (*m*, 3 H); 7.36–7.40 (*m*, 1 H); 7.88 (*d*, *J* = 8.5, 1 H); 8.41 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.6; 114.2; 124.6; 129.4; 130.0; 131.4; 131.9; 132.7; 133.6; 135.4; 137.4; 151.2; 153.5. EI-MS: 284 (100, M^+), 267 (25), 281 (16), 255 (93). HR-MS: 284.0712 ($C_{16}H_{13}{}^{35}ClN_2O^+$; calc. 284.0716).

*5,7-Dichloro-1-(4-ethoxyphenyl)quinoxalin-2(1*H*)-one* (**4b**): Yellow crystals. M.p. 218–220° (hexane/AcOBu). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.48 (*t*, *J* = 6.8, 3 H); 4.12 (*q*, *J* = 6.8, 2 H); 6.67 (*d*, *J* = 2.0, 1 H); 7.10–7.13 (*m*, 2 H); 7.14–7.17 (*m*, 2 H); 7.42 (*d*, *J* = 2.0, 1 H); 8.44 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$)[4]): 14.7; 63.9; 114.6; 116.3; 124.9; 126.6; 128.6; 129.0; 135.8; 136.6; 151.0; 154.5; 160.0. EI-MS: 334 (100, M^+), 278 (94). HR-MS: 334.0270 ($C_{16}H_{12}{}^{35}Cl_2N_2O_2^+$; calc. 334.0276).

*7-Chloro-1-(4-chlorophenyl)quinoxalin-2(1*H*)-one* (**4c**): White solid. M.p. 175–180°. ^{1}H-NMR (500 MHz, $CDCl_3$): 6.69 (*d*, *J* = 2.1, 1 H); 7.22–7.25 (*m*, 2 H); 7.31 (*d*, *J* = 8.6, 2.1, 1 H); 7.61–7.65 (*m*, 2 H); 7.84 (*d*, *J* = 8.6, 1 H); 8.35 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 115.1; 124.6; 129.5; 130.9; 131.4; 131.7; 133.0; 134.6; 136.1; 137.1; 150.6; 154.2. EI-MS: 290 9 (100, M^+), 262 (96). HR-MS: 290.0001 ($C_{14}H_8{}^{35}Cl_2N_2O^+$; calc. 290.0014).

*7-Chloro-1-(4-ethoxyphenyl)-5-methoxyquinoxalin-2(1*H*)-one* (**4d**): White crystals. M.p. > 250° (AcOEt). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.48 (*t*, *J* = 7.0, 3 H); 4.05 (*s*, 3 H); 4.11 (*q*, *J* = 7.0, 2 H); 6.34 (*d*, *J* = 2.1, 1 H); 6.78 (*d*, *J* = 2.1, 1 H); 7.08–7.11 (*m*, 2 H); 7.14–7.17 (*m*, 2 H); 8.33 (*s*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 14.8; 56.7; 63.9; 106.4; 108.0; 116.1; 122.5; 127.1; 129.0; 136.4; 137.6; 148.6; 155.1; 156.7; 159.8. EI-MS: 330 (100, M^+), 301 (83), 273 (45), 245 (17). HR-MS: 330.0785 ($C_{17}H_{15}{}^{35}ClN_2O_3^+$; calc. 330.0771).

*7-Chloro-1-(4-ethoxyphenyl)-3-ethyl-5-methoxyquinoxalin-2(1*H*)-one* (**4e**): White solid. M.p. 213–217° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.36 (*t*, *J* = 7.5, 3 H); 1.47 (*t*, *J* = 7.5, 3 H); 3.01 (*q*, *J* = 7.5, 2 H); 4.04 (*s*, 3 H); 4.12 (*q*, *J* = 7.5, 2 H); 6.29 (*d*, *J* = 2.0, 1 H); 6.75 (*d*, *J* = 2.0, 1 H); 7.06–7.10 (*m*, 2 H); 7.13–7.17 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.3; 14.8; 28.0; 56.8; 63.9; 106.3; 107.9; 116.0; 121.8; 127.9; 129.1; 135.6; 136.3; 154.8; 156.2; 159.6; 161.2. EI-MS: 358 (100, M^+), 329 (96), 301 (36). HR-MS: 358.1076 ($C_{19}H_{19}{}^{35}ClN_2O_3^+$; calc. 358.1084).

*7-Chloro-1-(2,6-dimethylphenyl)-3-ethylquinoxalin-2(1*H*)-one* (**4f**): Gray solid. M.p. 79–82°. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.37 (*t*, *J* = 7.5, 3 H); 1.96 (*s*, 6 H); 3.02 (*q*, *J* = 7.5, 2 H); 6.47 (*d*, *J* = 2.1, 1 H); 7.25–7.29 (*m*, 3 H); 7.33–7.37 (*m*, 1 H); 7.83 (*d*, *J* = 8.5, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 10.5; 17.6; 27.3; 113.9; 124.3; 129.3; 129.6; 130.5; 131.3; 133.4; 134.5; 135.3; 135.5; 153.3; 163.2. EI-MS: 312 (100, M^+), 283 (37), 255 (88). HR-MS: 312.1035 ($C_{18}H_{17}{}^{35}ClN_2O^+$; calc. 312.1029).

*3-Ethyl-7-methoxy-1-(4-methylphenyl)quinoxalin-2(1*H*)-one* (**4g**): White crystals. M.p. 152–155° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.35 (*t*, *J* = 7.4, 3 H); 2.46 (*s*, 3 H); 2.95 (*q*, *J* = 7.4, 2 H); 3.70 (*s*, 3 H); 6.12 (*d*, *J* = 2.6, 1 H); 6.86 (*dd*, *J* = 8.9, 2.6, 1 H); 7.13–7.16 (*m*, 2 H); 7.37–7.40 (*m*, 2 H); 7.76 (*d*, *J* = 8.9, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 10.9; 21.3; 27.1; 55.5; 99.7; 110.6; 127.6; 127.8; 130.4; 130.9; 133.3; 135.5; 139.3; 155.0; 159.3; 160.1. EI-MS: 294 (100, M^+), 265 (15), 251 (37). HR-MS: 294.1362 ($C_{18}H_{18}N_2O_2^+$; calc. 294.1368).

*1-(2,6-Dimethylphenyl)-3-ethyl-7-phenylquinoxalin-2(1*H*)-one* (**4h**): Beige crystals. M.p. 157° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.40 (*t*, *J* = 7.4, 3 H); 1.99 (*s*, 6 H); 3.05 (*q*, *J* = 7.4, 2 H); 6.67 (*d*, *J* = 2.0, 1 H); 7.25–7.28 (*m*, 2 H); 7.31–7.35 (*m*, 2 H); 7.37–7.43 (*m*, 4 H); 7.55 (*dd*, *J* = 8.2, 2.0, 1 H); 7.96 (*d*, *J* = 8.2, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 10.7; 17.7; 27.4; 112.3; 123.0; 127.3; 128.0; 128.9; 129.2; 129.4; 129.7; 132.2; 132.8; 133.8; 135.4; 139.9; 142.7; 153.7; 162.9. EI-MS: 354 (100, M^+), 325 (20), 297 (71). HR-MS: 354.1728 ($C_{24}H_{22}N_2O^+$; calc. 354.1732).

*1-(2,6-Dimethylphenyl)-7-phenylquinoxalin-2(1*H*)-one* (**4i**): Gray crystals. M.p. 144–147° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.02 (*s*, 6 H); 6.72 (*d*, *J* = 1.9, 1 H); 7.27–7.30 (*m*, 2 H); 7.34–7.39 (*m*, 2 H); 7.40–7.43 (*m*, 4 H); 7.58 (*dd*, *J* = 8.3, 1.9, 1 H); 8.01 (*d*, *J* = 8.3, 1 H); 8.45 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$)[4]): 17.6; 112.5; 132.3; 127.3; 128.3; 129.0; 129.3; 129.7; 130.6; 133.0; 133.1; 135.5; 139.5; 144.4; 150.9; 154.0. EI-MS: 326 (100, M^+), 297 (98). HR-MS: 326.1414 ($C_{22}H_{18}N_2O^+$; calc. 326.1419).

*7-Chloro-1-(4-ethoxyphenyl)-5-methoxy-3-methylquinoxalin-2(1*H*)-one* (**4j**): White solid. M.p. 249–254°. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.47 (*t*, *J* = 7.0, 3 H); 2.64 (*s*, 3 H); 4.04 (*s*, 3 H); 4.11 (*q*, *J* = 7.0, 2 H); 6.29 (*d*, *J* = 2.0, 1 H); 6.76 (*d*, *J* = 2.0, 1 H); 7.07–7.11 (*m*, 2 H); 7.13–7.16 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.7; 21.6; 56.7; 63.8; 106.1; 107.9; 116.0; 121.6; 127.8; 129.0; 135.6; 136.3; 155.2; 155.9; 157.4; 159.6. EI-MS: 344 (100, M^+), 329 (16), 315 (97) 287 (48). HR-MS: 344.0939 ($C_{18}H_{17}{}^{35}ClN_2O_3^+$; calc. 344.0928).

*7-Methoxy-1-(4-methylphenyl)quinoxalin-2(1*H*)-one* (**4k**): Gray crystals. M.p. 133–135° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.47 (*s*, 3 H); 3.71 (*s*, 3 H); 6.16 (*d*, *J* = 2.6, 1 H); 6.90 (*dd*, *J* = 9.1, 2.6, 1 H); 7.15–7.18 (*m*, 2 H); 7.39–7.43 (*m*, 2 H); 7.81 (*d*, *J* = 9.1, 1 H); 8.23 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.3; 55.6; 99.7; 111.1; 127.7; 128.3; 134.1; 131.4; 132.6; 135.8; 139.7; 147.5; 155.3; 161.4. EI-MS: 266 (100, M^+), 238 (22), 223 (60). HR-MS: 266.1048 ($C_{16}H_{14}N_2O_2^+$; calc. 266.1055).

*7-Methoxy-3-methyl-1-(4-methylphenyl)quinoxalin-2(1*H*)-one* (**4l**): White solid. M.p. 155–160°. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.47 (*s*, 3 H); 2.59 (*s*, 3 H); 3.70 (*s*, 3 H); 6.12 (*d*, *J* = 2.6, 1 H); 6.87 (*dd*, *J* = 8.9, 2.6, 1 H); 7.12–7.17 (*m*, 2 H); 7.38–7.42 (*m*, 2 H); 7.75 (*d*, *J* = 8.9, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.1; 21.3; 55.5; 99.7; 110.7; 127.4; 127.8; 130.1; 130.9; 133.2; 135.7; 139.4; 155.3; 155.6; 160.2. EI-MS: 280 (100, M^+), 252 (48), 237 (82). HR-MS: 280.1216 ($C_{17}H_{16}N_2O_2^+$; calc. 280.1212).

*7-Chloro-1-(pyridin-4-yl)quinoxalin-2(1*H*)-one* (**4m**): Yellow solid. M.p. 204–209°. ^{1}H-NMR (500 MHz, (D_6)DMSO): 6.60 (*d*, *J* = 2.1, 1 H); 7.46 (*dd*, *J* = 8.6, 2.1, 1 H); 7.56–7.58 (*m*, 2 H); 7.93 (*d*, *J* = 8.6,, 1 H); 8.36 (*s*, 1 H); 8.89–8.92 (*m*, 2 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 114.8; 124.2; 124.5; 131.7; 131.8; 134.5; 135.7; 143.2; 151.7; 152.6; 153.7. EI-MS: 257 (100, M^+), 229 (64). HR-MS: 257.0351 ($C_{13}H_8{}^{35}ClN_3O^+$; calc. 257.0356).

*7-Chloro-1-phenylquinoxalin-2(1*H*)-one* (**4n**): Beige powder. M.p. 189–192° (hexane/AcOEt) ([17]: 187–189°). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.69 (*d*, *J* = 2.1, 1 H); 7.27–7.31 (*m*, 3 H); 7.57–7.61 (*m*, 1 H); 7.64–7.67 (*m*, 2 H); 7.84 (*d*, *J* = 8.7, 1 H); 8.37 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 115.4; 124.4; 128.1; 130.0; 130.6; 131.2; 131.7; 134.7; 134.9; 136.9; 150.8; 154.4. EI-MS: 256 9 (100, M^+), 228 (87). HR-MS: 256.0394 ($C_{14}H_9{}^{35}ClN_2O^+$; calc. 256.0403).

N^3-*(2,6-Dimethylphenyl)[1,1′-biphenyl]-3,4-diamine* (**5**): Gray crystals. M.p. 247–249° (hexane/AcOEt). ^{1}H-NMR (500 MHz, $CDCl_3$): 2.20 (*s*, 6 H); 3.7 (br. *s*, 2 H); 4.89 (br. *s*, 1 H); 6.49 (*s*, 1 H); 6.85 (*d*, *J* = 7.9, 1 H); 7.00–7.04 (*m*, 2 H); 7.09–7.12 (*m*, 2 H); 7.18–7.22 (*m*, 1 H); 7.28–7.32 (*m*, 2 H); 7.35–7.38 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.3; 114.1; 116.4; 119.5; 124.4; 126.2; 126.6; 128.5; 128.7;

132.9; 133.2; 134.4; 135.5; 139.5; 141.5. EI-MS: 288 (100, M^+). HR-MS: 288.1631 ($C_{20}H_{20}N_2^+$; calc. 288.1626).

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Received June 14, 2012