Simple Synthesis of Quinoxalin-2(1*H*)-one *N*-Oxides from *N*-Aryl-2-nitrosoanilines and Alkylated Cyanoacetic Esters

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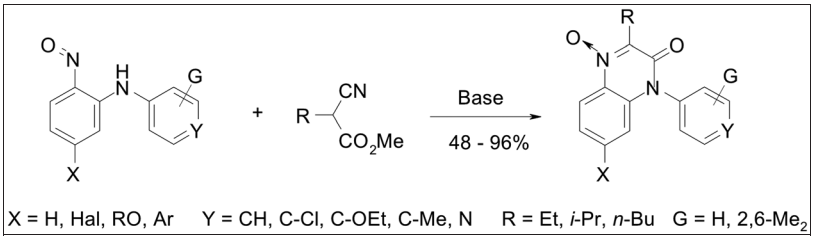

N-Aryl-2-nitrosoanilines, available from the reaction of *N*-arylamines with nitroarenes, condense under alkaline conditions with alkylated derivatives of cyanoacetic esters furnishing quinoxalin-2(1*H*)-one *N*-oxides in good to excellent yields. The reaction involves the condensation of the carbanion with the nitroso group leading to the nitrone intermediate, followed by intramolecular acylation of the amine function.

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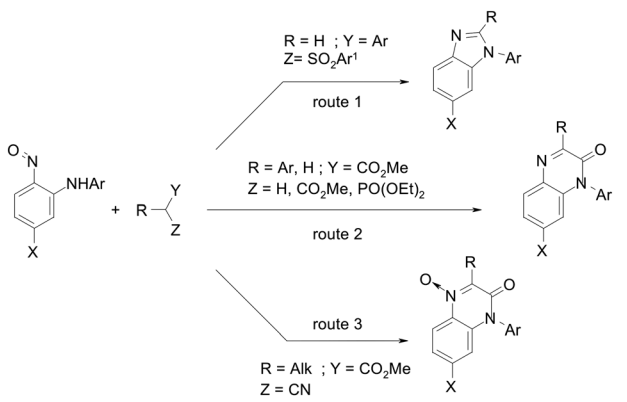
INTRODUCTION

In 2007, we published a simple method of synthesis of a variety of *N*-aryl-2-nitrosoanilines via nucleophilic substitution of hydrogen in nitroarenes with anilines that proceeded in the presence of potassium *t*-butoxide [1,2]. The vicinal position of nucleophilic amino—and strongly electrophilic nitroso—groups makes these compounds very interesting starting materials for domino reactions with properly equipped dipolar partners, leading to a variety of heterocyclic systems. It was already shown that reactions of title compounds with comparatively acidic sulfones (Scheme 1, route 1) or acetates and phosphonoacetates (Scheme 1, route 2) are efficient ways of synthesis of benzimidazoles [3] and quinoxalin-2(1*H*)-ones [4]. Here, we would like to report a new reaction of *N*-aryl-2-nitrosoanilines with alkylated derivatives of cyanoacetic esters furnishing quinoxalin-2(1*H*)-one-4 *N*-oxides in moderate to excellent yields.

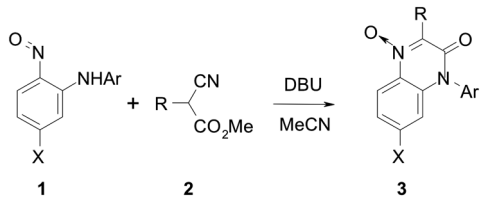
Reactions of 2-nitrosoarylamines with carbon nucleophiles leading to quinoxalin-2(1*H*)-one *N*-oxides are mentioned in the literature, but the reported examples are limited to a few intramolecular reactions of pyrimidine derivatives, easy to synthesize via direct nitrosation of appropriate aminopyrimidines [5]. Because carbocyclic *ortho*-nitrosoanilines were not so easily available, the common synthesis of carbocyclic quinoxalin-2(1*H*)-one *N*-oxides were based on the Tennant intramolecular condensation of substituted *ortho*-nitroanilines with carbanions, in which nitrone intermediate was formed [6]. Other synthetic approaches applied furoxanes [7] or dioximes [8] as starting materials. Simple oxidation of quinoxalin-2(1*H*)-ones was also frequently used [9] in the synthesis of their *N*-oxides. A variety of these compounds were synthesized via an interesting reaction of anilines with 1,2,2-trichloronitroethene [10]. The later approach introduces the nitrone group together with two lacking carbon atoms in the ring-forming process.

Wide range of biological activity of quinoxalinones and their corresponding *N*-oxides have been reported [11]. They are known as antibacterial, antiviral, anticancer, antifungal, antihelmintic, and insecticidal as well as potential antiallergic agents [12]. Additionally, a number of quinoxalinone derivatives are pharmacological agents exhibiting antimalarial activity [13]. Therefore, new methods of synthesis of this type of compounds, providing collections of different entities for biological screening purposes, are of serious interest.

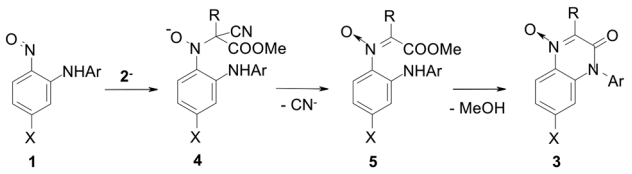
Scheme 1



Scheme 2



Scheme 3



RESULTS AND DISCUSSION

Our attempts to synthesize 3-cyanoquinoxalin-2(1*H*)-ones by the reaction of *N*-aryl-2-nitrosoaniline with methyl cyanoacetate, following route 2 in Scheme 1(R = H, Y = COOMe, Z = CN) [4], failed. It led to multicomponent intractable mixture. Unexpectedly, the situation changed radically after the alkyl substituent was introduced into cyanoacetic ester moiety. *N*-(2,6-Dimethylphenyl)-5-chloro-2-nitrosoaniline (**1a**) reacted smoothly with diethyl *n*-butylcyanoacetate in the presence of DBU in acetonitrile at RT furnishing 3-butyl-7-chloro-1-(2,6-dimethylphenyl) quinoxalin-2(1*H*)one 4-oxide (**3a**) (Scheme 2, Table 1) in 94% yield. The reaction was complete within 15 min. The structure of the product was confirmed by ^{1}H and ^{13}C-NMR as well as mass spectrum and combustion analysis.

Numerous nitrosoanilines substituted in *para*-position to the nitroso group with Cl, F, Ph, and MeO reacted the same way (Scheme 2, Table 1). Changes in *N*-aryl substituent in 2-nitroso-*N*-arylamine seems to have only small or no impact on the reaction course. The aryl group Ar can be both carbocyclic ring with various substituents such as alkyl, alkoxyl, halogen, as well as heterocyclic system. Bulky alkyl group in cyanoacetic ester moiety (*i*-Pr versus Et or *n*-Bu) only slightly lowered the reaction rate. DBU/MeCN was the system of choice, but in some cases, K_2CO_3/DMF system, despite a longer reaction time, gave better yields of the products.

We suppose that the reaction proceeds via initial addition of the carbanion to the nitrogen of the nitroso group followed by elimination of the cyanide anion from the adduct **4** to form nitrone (**5**) (Scheme 3). Subsequent intramolecular acylation of the amine function, probably in deprotonated form of **5**, provides quinoxalinone (**3**).

Formation of the nitrone moiety is probably analogous to the known reactions of carbanions-bearing leaving groups such as diazo [14], sulfonium [15], pyridinium [16], sulfonyl [17], or nitro [18] with nitrosoarenes. To our knowledge, cyano group has been reported to act in this manner only in a few cases [19], and no one was engaged in intramolecular formation of a heterocyclic ring.

In summary, a new simple, convenient, and general method of synthesis of various quinoxalin-2-one *N*-oxides was presented. The synthesis started from easily accessible substrates, that is, alkyl cyanoacetic esters and 2-nitroso-*N*-arylanilines that can be prepared from appropriate nitroarenes and anilines. Diversity of the title compounds can be achieved by simply varying the substituents in each reagent.

Table 1

Synthesis of quinoxalin-2(1*H*)-one *N*-oxides (**3**) from *N*-aryl-2-nitrosoanilines (**1**).

Entry	X	Ar	R	Conditions[a]	Time (min)	**3**	Yield (%)[b]
1	Cl	2,6-$Me_2C_6H_3$	*n*-Bu	A	15	**a**	94
2	Cl	2,6-$Me_2C_6H_3$	Et	A	20	**b**	64
3	Cl	2,6-$Me_2C_6H_3$	*i*-Pr	A	30	**c**	93
4	Cl	2-MeC_6H_4	*n*-Bu	A	15	**d**	74
5	Cl	2-MeC_6H_4	*i*-Pr	A	20	**e**	89
6	Cl	4-$EtOC_6H_4$	*n*-Bu	A	5	**f**	59
7	Cl	4-$EtOC_6H_4$	*n*-Bu	B	120	**f**	74
8	Cl	4-Py	*i*-Pr	A	15	**g**	54
9	Cl	4-Py	*i*-Pr	B	60	**g**	77
10	F	Ph	Et	A	15	**h**	78
11	Ph	2,6-$Me_2C_6H_3$	Et	A	5	**i**	98
12	OMe	4-MeC_6H_4	Et	B	150	**j**	65
13	OMe	4-MeC_6H_4	*i*-Pr	B	30[c]	**k**	43
14	F	4-ClC_6H_4	Et	A	1	**l**	80

[a]A: DBU/MeCN; B: K_2CO_3/DMF.
[b]Isolated yield.
[c]Hours

EXPERIMENTAL

Melting points are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded on a Varian-NMR-vnmrs500 (Varian, Inc., presently Agilent Technologies, Colorado Springs, CO) (500 MHz for ^{1}H and 125 MHz for ^{13}C spectra) instrument at 298 K. Chemical shifts δ are expressed in parts per million referred to TMS, and coupling constants in Hertz. IR spectra were recorded on a FT-IR Jasco 6200 (Jasco Inc., Easton, MD) apparatus. Mass spectra (EI, 70 eV) were obtained on an AMD 604S (AMD Analysis & Technology AG, Germany) spectrometer. Silica gel Merck 60 (230–400 mesh) (Merck, Darmstadt, Germany) was used for column chromatography. Acetonitrile and DMF were dried over CaH_2, distilled, and stored over molecular sieves. *N*-Aryl-2-nitrosoanilines (**1**) were obtained following the procedures published previously [1,2].

General procedure for the synthesis of quinoxalin-2(1*H*)-one *N*-oxides (3)

Method A. 2-Nitroso-*N*-arylaniline (**1**) (0.5 mmol) and methyl alkylcyanoacetate (**2**) (1.0 mmol) were dissolved in acetonitrile (5 mL). DBU (2.5 mmol, 0.37 mL) was added in one portion, and the mixture was stirred at ambient temperature for the time specified in Table 1. After the reaction was complete, the reaction mixture was poured into saturated water solution of ammonium chloride (10 mL), extracted with ethyl acetate (3 × 20 mL). The extract was dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The residue was separated by column chromatography (silica gel, hexane/ethyl acetate 8:1—2:1 mixture).

Method B. 2-Nitroso-*N*-arylaniline (**1**) (0.5 mmol) and methyl alkylcyanoacetate (**2**) (1.0 mmol) were dissolved in DMF (5 mL), and potassium carbonate (5 mmol, 690 mg) was added in one portion with stirring. The reaction mixture was then stirred vigorously at ambient temperature for the time specified in Table 1. After the reaction was complete, the reaction mixture was worked up as in method A.

3-Butyl-7-chloro-1-(2,6-dimethylphenyl)quinoxalin-2(1H)-one 4-oxide (3a). This compound was obtained as yellow crystals (hexane), mp 172–176°C; IR (potassium bromide): 1647, 1614, 1586 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.42–1.51 (m, 2H), 1.69–1.73 (m, 2H), 2.01 (s, 6H), 3.13–3.16 (m, 2H), 6.58 (d, *J* = 2.1 Hz, 1H), 7.26–7.30 (m, 2H), 7.32 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.37 (dd, *J* = 8.1, 7.0 Hz, 1H), 8.44 (d, *J* = 8.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 13.8, 17.6, 22.9, 25.5, 26.7, 114.4, 122.4, 124.4, 129.4, 129.5, 130.0, 132.9, 133.0, 135.8, 138.2, 144.5, 155.5; MS (70 eV, electron impact) *m/z* 356 (2), 341 (39), 339 (100), 314 (39), 297 (64). *Anal*. Calcd for $C_{20}H_{21}N_2O_2Cl$: C, 67.32; H, 5.93; N, 7.85. Found: C, 67.71; H, 6.47; N, 8.15.

7-Chloro-1-(2,6-dimethylphenyl)-3-ethylquinoxalin-2(1H)-one 4-oxide (3b). This compound was obtained as white crystals (hexane/ethyl acetate), mp 164–167°C; IR (potassium bromide): 1650, 1615, 1587 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.29 (t, *J* = 7.4 Hz, 3H), 2.01 (s, 3H), 3.16 (q, *J* = 7.4 Hz, 4H), 6.58 (d, *J* = 2.1 Hz, 1H), 7.28–7.30 (m, 2H), 7.33 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.38 (dd, *J* = 8.1, 7.1 Hz, 1H), 8.45 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 9.0, 17.6, 19.4, 114.4, 122.4, 124.4, 129.4, 129.5, 130.0, 132.9, 133.0, 135.8, 138.3, 145.2, 155.2; MS (70 eV, electron impact) *m/z* 330 (12), 328 (32), 313 (35), 311 (100), 283 (13), 255 (11). *Anal*. Calcd for $C_{18}H_{17}N_2O_2Cl$: C, 65.75; H, 5.21; N, 8.52. Found: C, 65.43; H, 5.30; N, 8.45.

7-Chloro-1-(2,6-dimethylphenyl)-3-isopropylquinoxalin-2(1H)-one 4-oxide (3c). This compound was obtained as orange crystals (hexane/ethyl acetate), mp 170–173°C; 1653, 1615, 1584 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.46 (d, *J* = 7.0 Hz, 6H), 2.00 (s, 6H), 4.14 (sept., *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 1H), 7.26–7.30 (m, 2H), 7.31 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.37 (dd, *J* = 8.1, 6.9 Hz, 1H), 8.44 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 17,1, 17.6, 26.6, 114.3, 122.6, 124.3, 129.4, 129.7, 129.9, 132.9, 133.1, 135.8, 138.2, 147.4, 155.0; MS (70 eV, electron impact) *m/z* 342 (7), 327 (45), 325 (100). *Anal*. Calcd for $C_{19}H_{19}N_2O_2Cl$: C, 66.57; H, 5.59; N, 8.17. Found: C, 66.21; H, 5.57; N, 8.12.

3-Butyl-7-chloro-1-(2-methylphenyl)quinoxalin-2(1H)-one 4-oxide (3d). This compound was obtained as violet crystals (hexane/ethyl acetate), mp 120–122°C; IR (potassium bromide): 1653, 1614, 1585 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.43–152 (m, 2H), 1.67–177 (m, 2H), 2.06 (s, 3H), 3.13 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 2.1 Hz, 1H), 7.18–7.21 (m, 1H), 7.31 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.42–7.52 (m, 3H), 8.43 (d, *J* = 8.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 13.8, 17.4, 23.0, 25.6, 26.7, 115.2, 122.3, 124.3, 128.1, 128.4, 129.4, 130.2, 132.0, 133.8, 133.9, 136.1, 137.9, 144.3, 156.0; MS (70 eV, electron impact) *m/z* 342 (2), 327 (35), 325 (100), 300 (41), 283 (73). *Anal*. Calcd for $C_{19}H_{19}N_2O_2Cl$: C, 66.57; H, 5.59; N, 8.17. Found: C, 66.64; H, 5.60; N, 8.14.

7-Chloro-1-(2-methylphenyl)-3-isopropylquinoxalin-2(1H)-one 4-oxide (3e). This compound was obtained as white crystals (hexane/ethyl acetate); mp 135–137°C; IR (potassium bromide): 1649, 1615, 1585 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.45 (d, *J* = 7.0 Hz, 6H), 2.06 (s, 3H), 4.12 (sept., *J* = 7.0 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 7.18–7.22 (m, 1H), 7.30 (dd, *J* = 9.0, 2.0, 1H), 7.42–7.52 (m, 2H), 8.43 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 17.1, 17.1, 17.4, 26.6, 115.0, 122.5, 124.2, 128.1, 128.48, 129.6, 130.2, 132.0, 133.9, 133.9, 136.1, 137.9, 147.1, 155.6; MS (70 eV, electron impact) *m/z* 328 (4), 313 (31), 311 (100), 284 (16), 269 (12), 241 (14). *Anal*. Calcd for $C_{18}H_{17}N_2O_2Cl$: C, 65.75; H, 5.21; N, 8.52. Found: C, 65.59; H, 5.23; N, 8.39.

3-Butyl-7-chloro-1-(4-ethoxylphenyl)quinoxalin-2(1H)-one 4-oxide (3f). This compound was obtained as white crystals (hexane/ethyl acetate), mp 156°C; IR (potassium bromide): 1651, 1613, 1582, 1507 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.44–1.52 (m, 2H), 1.48 (t, *J* = 7.0 Hz, 3H), 1.68–1.73 9 (m, 2H), 3.08–3.12 (m, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 1H), 7.09–7.12 (m, 2H), 7.18–7.21 (m, 2H), 7.29 (dd, *J* = 8.9, 2.1 Hz, 1H), 8.40 (9d, *J* = 8.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 13.8, 14.7, 23.1, 25. 7, 26.7, 63.9, 115.8, 116.2, 122.1, 124.1, 127.0, 129.3, 129.5, 134.7, 137.6, 144.1, 156.8, 159.8; MS (70 eV, electron impact) *m/z* 372 (3), 357 (37), 355 (100), 330 (34), 313 (70), 257 (22). *Anal*. Calcd for $C_{20}H_{21}N_2O_3Cl$: C, 64.43; H, 5.68; N, 7.51. Found: C, 63.98; H, 5.65; N, 7.36.

7-Chloro-3-isopropyl-1-pyridin-4-ylquinoxalin-2(1H)-one 4-oxide (3g). This compound was obtained as yellow crystals (hexane/ethyl acetate), mp178–180°C; IR (potassium bromide): 1648, 1617, 1586 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.44 (d, *J* = 7.0 Hz, 3H), 4.07 (sept., *J* = 7.0 Hz, 1H), 6.69 (d, 2.0 Hz, 1H), 7.32–7.36 (m, 3H), 8.43 (d, *J* = 9.0 Hz, 1H), 8.94–8.97 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ 17.0, 26.6, 114.9, 122.7, 123.7, 124.7, 129.7, 133.1, 138.0, 142.9, 146.7.152.4, 155.5; MS (70 eV, electron impact) *m/z* 315 (3), 300 (30), 298 (100). *Anal*. Calcd for $C_{19}H_{19}N_2O_2Cl$; C, 60.86; H, 4.47; N, 13.31. Found: C, 60.85; H, 4.36; N, 13.38.

3-Ethyl-7-fluoro-1-phenylquinoxalin-2(1H)-one 4-oxide (3h). This compound was obtained as yellow crystals, mp 158-159°C; IR (potassium bromide): 1649, 1631, 1589 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.29 (t, *J* = 7.4 Hz, 3H), 3.13 (q, *J* = 7.4 Hz, 2H), 6.45

(dd, J_{HF} = 9.7 Hz, J = 2.5 Hz, 1H), 7.06 (ddd, J_{HF} = 7.5 Hz, J = 9.3, 2.5 Hz, 1H), 7.30–7.34 (m, 2H), 7.58–7.67 (m, 3H), 8.49 (dd, J_{HF} = 5.7 Hz, J = 9.3 Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 9.0, 19.3, 102.8 (d, J_{CF} = 29 Hz), 111.7 (d, J_{CF} = 24 Hz), 123.2 (d, J_{CF} = 10 Hz), 127.4, 128.4, 129.9, 130.5, 135.1 (d, J_{CF} = 9 Hz), 144.0, 156.5, 163.9 (d, J_{CF} = 251 Hz) (lack of one signal); MS (70 eV, electron impact) *m/z* 284 (24), 267 (100), 239 (27). *Anal*. Calcd for $C_{16}H_{13}N_2O_2F$: C, 67.60; H, 4.61; N, 9.85. Found: C, 67.91; H, 4.44; N, 9.88.

1-(2,6-Dimethylphenyl)-3-ethyl-7-phenylquinoxalin-2(1H)-one 4-oxide (3i). This compound was obtained as yellow crystals (hexane/ethyl acetate), mp 166–169°C; IR (potassium bromide): 1649, 1610, 1594 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.32 (t, J = 7.4 Hz, 3H), 3.21 (q, J = 7.4 Hz, 2H), 6.76 (d, J = 1.8 Hz, 1H), 7.26–7.30 (m, 2H), 7.34–7.42 (m, 7H), 7.59 (dd, J = 8.7, 1.8 Hz, 1H), 8.56 (d, J = 8.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 9.1, 17.7, 19.4, 112.7, 121.3, 123.2, 127.3, 128.6, 129.0, 129.3, 129.7, 130.2, 132.5, 133.3, 135.9, 139.0, 145.0, 145.2, 155.4; MS (70 eV, electron impact) *m/z* 370 (24), 353 (100), 325 (10), 297 (12). *Anal*. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.49; H, 6.09; N, 7.67.

3-Ethyl-7-methoxy-1-(4-methylphenyl)quinoxalin-2(1H)-one 4-oxide (3j). This compound was obtained as white crystals (hexane/ethyl acetate), mp 207–209°C; IR (potassium bromide): 1651 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.28 (t, J = 7.4 Hz, 3H), 2.47 (s, 3H), 3.12 (q, J = 7.4 Hz, 2H), 3.72 (s, 3H), 6.20 (d, J = 2.5 Hz, 1H), 6.89 (dd, J = 9.3, 2.5 Hz, 1H), 7.17–7.21 (m, 2H), 7.38–7.42 (m, 2H), 8.39 (d, J = 9.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 9.1, 19.2, 21.3, 55.7, 100.2, 110.7, 122.2, 125.4, 128.2.131.0, 132.8, 135.2, 142.6, 156.9, 161.8; MS (70 eV, electron impact) *m/z* 310 (20), 293 (100). *Anal*. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.62; H, 5.86; N, 9.12.

3-Isopropyl-1-(4-methylphenyl)-7-methoxyquinoxalin-2(1H)-one 4-oxide (3k). This compound was obtained as light brown crystals (hexane/ethyl acetate), mp 164–167°C; IR (potassium bromide): 1655 (C═O) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.45 (d, J = 7.0 Hz, 6H), 2.64 (s, 3H), 3.71 (s, 3H), 4.11 (sept., J = 7.0, 1H), 6.17 (d, J = 2.5 Hz, 1H), 6.88 (dd, J = 9.3, 2.6 Hz, 1H), 7.17–7.21 (m, 2H), 7.39–7.42 (m, 2H), 8.38 (d, J = 9.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 17.2, 21.3, 26.4, 55.7, 100.0, 110.7, 122.4, 125.6, 128.2, 131.0, 132.9, 135.3, 139.6, 144.7, 156.8, 161.8; MS (70 eV, electron impact) *m/z* 324 (10), 307 (100). *Anal*. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.45; H, 6.11; N, 8.79.

1-(4-Chlorophenyl)-3-ethyl-7-fluoroquinoxalin-2(1H)-one 4-oxide (3l). This compound was obtained as white crystals (hexane/ethyl acetate), mp 21–218°C : IR (potassium bromide): 1653, 1632, 1593 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.27 (t, J = 7.4 Hz, 3H), 3.11 (q, J = 7.4 Hz, 2H), 6.46 (dd, J = 2.5 Hz, J_{CF} = 9.5 Hz, 1H), 7.07 (ddd, J = 9.6 Hz, 2.6 Hz, J_{CF} = 7.6 Hz, 1H), 7.26–7.30 (m, 2H), 7.60–7.63 (m, 2H), 8.48 (dd, J = 9.3 Hz, J_{CF} = 5.6 Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 9.0, 19.3, 102.6 (J_{CF} = 28.8 Hz), 111.9 (J_{CF} = 23.5 Hz), 123.4 (J_{CF} = 10.4 Hz), 127.5 (J_{CF} = 2.3 Hz), 129.9, 130.8, 133.5, 134.8 (J_{CF} = 11.5 Hz), 136.1, 143.9, 156.4, 163.9 (J_{CF} = 251.8 Hz). MS (70 eV, electron impact) *m/z* 318 (24), 301 (100), 273 (19). *Anal*. Calcd for $C_{16}H_{12}N_2O_2ClF$: C, 60.29; H, 3.79; N, 8.79. Found: C, 60.08; H, 3.74; N, 8.75.

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