A New Convenient Liquid- and Solid-Phase Synthesis of Quinoxalines from (*E*)-3-Diazenylbut-2-enes

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3-{[(*tert*-Butoxy)carbonyl]diazenyl}but-2-enoates react in tetrahydrofuran at room temperature with aromatic 1,2-diamines to give 3-methylquinoxaline-2-carboxylates. These products were also obtained in solid-phase synthesis, by using polymer-bound 3-diazenylbut-2-enes.

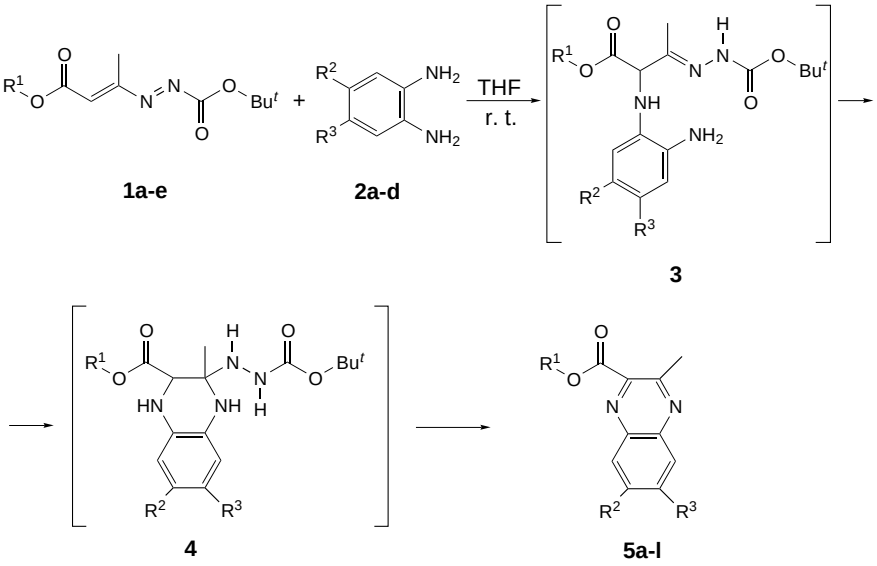
Introduction. – In recent years, quinoxalines have received much attention owing to their biological activities [1]. The often diffused methods reported for their synthesis, in general, involve the condensation of aromatic 1,2-diamines with α-diketones [2]. Based on our previous experience on the chemistry of 3-diazenylbut-2-enes [3–5], we considered a retrosynthetic route to readily obtain quinoxalines from these starting materials in one pot and under very mild conditions. In fact, we previously reported the easy nucleophilic attack of amino groups at the terminal C-atom of the heterodiene system to give the corresponding α-aminohydrazones by 1,4-addition [5]. In the case of further internal attack of a second amino group at the $\rangle$C=N– hydrazone C-atom, followed by loss of the hydrazino residue, quinoxalines could be obtained.

Our initial hypothesis was successfully verified, thus, we now report a new and convenient access to quinoxalines, not easily accessible by the classical methods, by reaction of 3-diazenylbut-2-enes with aromatic 1,2-diamines both *via* liquid- and solid-phase procedure.

Results and Discussion. – 3-{[(*tert*-butoxy)carbonyl]diazenyl}but-2-enes **1a–e** easily react in THF at room temperature with benzene-1,2-diamine (**2a**), 4,5-dimethylbenzene-1,2-diamine (**2b**), naphthalene-2,3-diamine (**2c**) and 4,5-dichlorobenzene-1,2-diamine (**2d**) to give 2,3-disubstituted quinoxalines **5a–l** in good-to-excellent yields (see *Scheme 1* and *Table 1*). The reaction takes place by the nucleophilic attack of an NH_2 group of compounds **2** on the terminal C-atom of the azo-ene system of **1** with the formation of 1,4-adducts **3** as intermediates. Compounds **3** instantaneously give rise to the ring closure due to a further nucleophilic attack of the second NH_2 group at the $\rangle$C=N– hydrazone C-atom to afford intermediates **4** with formal [4 + 2] annulation. These latter compounds lead finally quinoxalines **5a–l** by loss of *tert*-butyl hydrazine carboxylate and subsequent aromatization.

No reaction intermediates have been isolated, probably because of the ready cyclization and aromatization processes. Therefore, the final products **5a–l** have been obtained directly. Yields, reaction times, and melting points of **5a–l** are listed in *Table 1*.

Scheme 1



1a R^1 = Me
1b R^1 = Et
1c R^1 = Bz
1d R^1 = i-Pr
1e R^1 = $(CH_2)_2OMe$

2a $R^2 = R^3$ = H
2b $R^2 = R^3$ = Me
2c $R^2 – R^3$ =
2d $R^2 = R^3$ = Cl

5a R^1 = Me; $R^2 = R^3$ = H
5b R^1 = Et; $R^2 = R^3$ = H
5c R^1 = Bz; $R^2 = R^3$ = H
5d R^1 = i-Pr; $R^2 = R^3$ = H
5e R^1 = Et; $R^2 = R^3$ = Me
5f R^1 = i-Pr; $R^2 = R^3$ = Me
5d R^1 = $(CH_2)_2OMe$; $R^2 = R^3$= Me

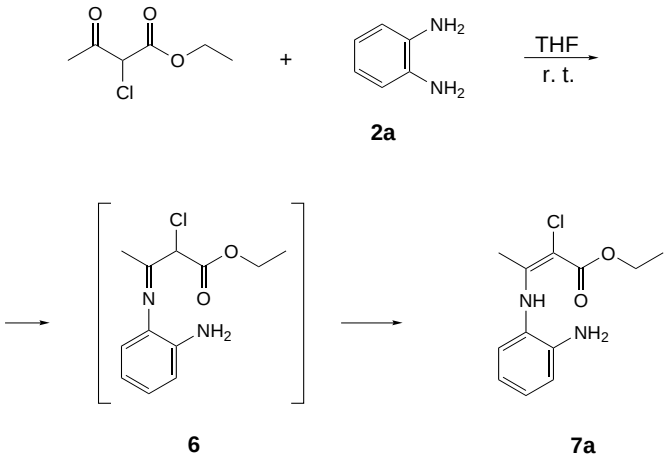
5h R^1 = Me; $R^2 – R^3$ =
5i R^1 = Bz; $R^2 – R^3$ =
5j R^1 = $(CH_2)_2OMe$; $R^2 – R^3$ =
5k R^1 = Me; $R^2 = R^3$ = Cl
5l R^1 = Et; $R^2 = R^3$ = Cl

The same quinoxalines cannot be prepared from 2-acetyl-2-chloroacetate and aromatic 1,2-diamines. In fact, we carried out the reaction of benzene-1,2-diamine **2a** with ethyl 2-acetyl-2-chloroacetate, and we achieved ethyl 3-[(2-aminophenyl)imino]-2-chlorobutanoate (**6**) that spontaneously tautomerize to the alkene form **7a**. In this case, the reaction occurred by the attack of the NH_2 group of **2a** to the ketone function of 2-acetyl-2-chloroacetate with formation of **6**, but its rapid tautomerization to ethyl 3-(2-aminoanilino)-2-chlorobut-2-enoate **7a** hindered the ring closure to quinoxaline (*Scheme 2*).

Table 1. *Yields, Reaction Times, and Melting Points of 3-Methylquinoxaline-2-carboxylates* **5a**–**k** *from 3-[[(*tert*-Butoxy)carbonyl]diazenyl]but-2-enoates* **1a**–**e**

5	R^1	R^2	R^3	Yield [%]	Reaction time [h]	M.p. [°C]
a	Me	H	H	79	5.5	58–60
b	Et	H	H	75	5.5	63–65
c	Bz	H	H	95	5.0	76–78
d	i-Pr	H	H	89	5.0	69–71
e	Me	Me	Me	84	0.5	82–85
f	i-Pr	Me	Me	92	1.5	87–90
g	$(CH_2)_2OMe$	Me	Me	81	3.0	78–80
h	Me			73	5.0	178–179
i	Bz			86	6.0	145–147
j	$(CH_2)_2OMe$			87	9.0	107–109
k	Me	Cl	Cl	87	24.0	92–94

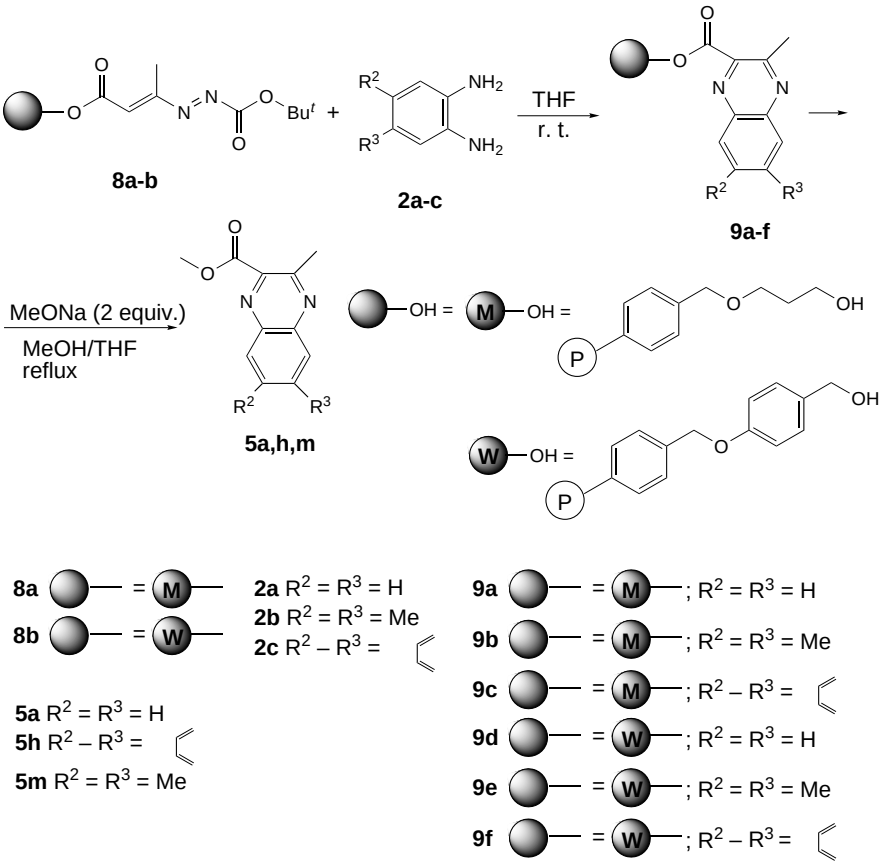
Scheme 2



Since, in the last years, combinatorial synthesis of small organic molecules has received much attention [6], we have reported in previous papers [7] the construction of 3-diazenylbut-2-enes bound to *Wang* or modified *Merrifield* resins.

In this work, we also report the use of polymer-bound 3-diazenylbut-2-enes as building blocks for the facile solid-phase preparation of quinoxaline derivatives. In particular, polymer-bound 3-diazenylbut-2-enoates **8a**–**b** easily react with benzene-1,2-diamine (**2a**), 4,5-dimethylbenzene-1,2-diamine (**2b**), and naphtalene-2,3-diamine (**2c**) in THF at room temperature to give polymer-bound quinoxalines **9a**–**f**. Final products **5a**,**h**,**m** are cleaved in MeOH/THF 1:4 under reflux, in the presence of MeONa (2 equiv.) (*Scheme 3*).

Scheme 3



The overall yields of these solid-phase reactions are comparable with the corresponding reactions in solution. Commercial *Wang* and modified *Merrifield* resins can be used with similar efficiency and yields (*Table 2*).

Conclusions. – In conclusion, the procedure described here represents a convenient entry to interesting quinoxaline-2-carboxylates, not easily accessible by other methods. This one-pot procedure proceeds under very mild reaction conditions and requires easily available starting materials.

Besides, the preparation of the same products in solid-phase requires very simple workup procedures. In fact, with the exception of the cleavage steps, the reactions proceed at room temperature, with formation of by-products in traces, and the reaction mixtures were manipulated solely by filtration. The mild conditions of this reaction sequence makes it well amenable for automation.

Furthermore, the present investigation demonstrates once again the usefulness of 3-diazenylbut-2-enoates as building blocks in organic chemistry.

Table 2. *Yields, Reaction Times, and Melting Points of 3-Methylquinoxaline-2-carboxylates* **5a**,**h**,**m** *from Polymer-Bound 3-Diazenylbut-2-enoates* **8a**–**b**

5		R^2	R^3	Reaction time [h]	Yield [%][a])	M.p. [°C]
a		H	H	15.0	> 47	58–60
h				3.5	> 58	178–179
m		Me	Me	18.0	> 45	109–110
a		H	H	15.0	> 53	58–60
h				3.5	> 51	178–179
m		Me	Me	18.0	> 51	109–110

[a]) Yield of isolated **5a**,**h**,**m** with respect to the starting *tert*-butyl acetoacetate.

Experimental Part

General. 3-{[(*tert*-Butoxy)carbonyl]diazenyl}but-2-enoates (**1a**–**e**) were prepared as described in [8]. Benzene-1,2-diamine (**2a**), 4,5-dimethylbenzene-1,2-diamine (**2b**), naphthalene-2,3-diamine (**2c**), 4,5-dichlorobenzene-1,2-diamine (**2d**), MeONa, and *Amberlyst 15 H* were commercial materials and used without further purification. Solvents were purchased and used without further purification with the exception of THF, which was distilled over NaOH. Anal. TLC: precoated silica-gel plates (0.25 mm). Column chromatography (CC): silica gel, 35–70 μ. M.p.: in open capillary tubes; uncorrected. FT-IR Spectra: Nujol mulls. ^{1}H- and ^{13}C-NMR spectra: at 200 and 50.32 MHz, resp.; chemical shifts are reported relative to TMS (δ(H)) and (D_6)DMSO or $CDCl_3$ (δ(C)); coupling constants (J) values are given in Hz; broad-band-decoupled mode; the multiplicities were obtained by using 135° and 90° DEPT experiments. MS: at 70 eV.

General Procedure for the Synthesis of 3-Methylquinoxaline-2-carboxylates **5a**–**l** *in Liquid Phase.* A soln. of **1a**–**e** (2 mmol) and **2a**–**d** (1 mmol) was allowed to stand at r.t. in THF under magnetic stirring until the complete disappearance of **2a**–**d** (monitored by TLC, 0.5–24.0 h). The solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica-gel column (cyclohexane/AcOEt) to give **5a**–**l**, which were crystallized from Et_2O/petroleum ether (40–60°). For yields, see *Table 1*.

General Procedure for the Synthesis of 3-Methylquinoxaline-2-carboxylates **5a**,**h**,**m** *in Solid Phase.* To polymer-bound **8a**–**b** in THF (5 ml) under magnetic stirring diamines **2a**–**c** (10 equiv.) were added. The reaction was allowed to stand at r.t. for 3.5–18.0 h, leading to the polymer-bound 3-methylquinoxaline-2-carboxylates **9a**–**f**, which were washed with MeOH, THF, and CH_2Cl_2 (3 × 10 ml). In the presence of MeONa (2 equiv.) in MeOH/THF 2:8 [9], **9a**–**f** were refluxed, under magnetic stirring, for 2 h, which led, by filtration, to 3-methylquinoxaline-2-carboxylates **5a**,**h**,**m** in solution. The residue was washed with MeOH, THF, and CH_2Cl_2 (3 × 10 ml), and the resulting mixture was treated with *Amberlyst 15 H* under magnetic stirring at r.t. for 1 h. After evaporation of the solvents under reduced pressure, products **5a**,**h**,**m** were crystallized from Et_2O/petroleum ether (40–60°). For yields, see *Table 2*.

Methyl 3-Methylquinoxaline-2-carboxylate (**5a**): white powder. IR (nujol): 1729, 1549, 1383. ^{1}H-NMR ($CDCl_3$): 2.99 (*s*, Me); 4.09 (*s*, MeO); 7.77–7.90 (*m*, 2 arom. H); 8.07 (*d*, J = 7.6, 1 arom. H); 8.20 (*d*, J = 7.9, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 23.8 (*q*); 53.2 (*q*); 128.5 (*d*); 129.8 (*d*); 130.9 (*d*); 132.0 (*d*); 139.9 (*s*); 142.7 (*s*); 143.7 (*s*); 153.2 (*s*); 165.9 (*s*). MS: 202 (19, M^+), 172 (10), 143 (100). Anal. calc. for $C_{11}H_{10}N_2O_2$: C 65.34, H 4.98, N 13.85; found: C 65.44, H 5.01, N 13.71.

Ethyl 3-Methylquinoxaline-2-carboxylate (**5b**): white powder. IR (nujol): 1720, 1557, 1365. ^{1}H-NMR ($CDCl_3$): 1.39 (*t*, J = 7.1, *Me*CH_2); 2.86 (*s*, Me); 4.46 (*q*, J = 7.1, MeCH_2O); 7.62–7.74 (*m*, 2 arom. H); 7.92 (*dd*, J = 7.9, 1.8, 1 arom. H); 8.06 (*dd*, J = 7.7, 2.1, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.0 (*q*); 23.5 (*q*); 62.2 (*t*);

126.2 (*d*); 129.5 (*d*); 129.6 (*d*); 131.5 (*d*); 139.6 (*s*); 142.3 (*s*); 144.2 (*s*); 152.6 (*s*); 165.4 (*s*). MS: 216 (15, M^+), 187 (17), 172 (100). Anal. calc. for $C_{12}H_{12}N_2O_2$: C 66.65, H 5.59, N 12.95; found: C 66.54, H 5.61, N 12.74.

Benzyl 3-Methylquinoxaline-2-carboxylate (**5c**): pale yellow powder. IR (nujol): 1716, 1547, 1379. ^{1}H-NMR ($CDCl_3$): 2.92 (*s*, Me); 5.53 (*s*, PhCH_2); 7.37–7.81 (*m*, 7 arom. H); 8.02 (*d*, J = 7.8, 1 arom. H); 8.17 (*d*, J = 7.6, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 23.7 (*q*); 67.9 (*t*); 128.5 (*d*); 128.6 (*d*); 128.7 (*d*); 129.7 (*d*); 129.9 (*d*); 131.8 (*d*); 135.3 (*s*); 139.9 (*s*); 142.3 (*s*); 152.8 (*s*); 165.5 (*s*). MS: 278 (6, M^+), 200 (51), 173 (100). Anal. calc. for $C_{17}H_{14}N_2O_2$: C 73.37; H 5.07; N 10.07; found: C 73.34; H 5.11; N 10.14.

Isopropyl 3-Methylquinoxaline-2-carboxylate (**5d**): white powder. IR (nujol): 1725, 1548, 1380. ^{1}H-NMR ((D_6)DMSO): 1.39 (*d*, J = 6.2, *Me*$_2$CH); 2.83 (*s*, Me); 5.30 (*sept.*, J = 6.2, Me$_2$C*H*); 7.84–8.17 (*m*, 4 arom. H). ^{13}C-NMR ((D_6)DMSO): 21.5 (*q*); 22.9 (*q*); 69.9 (*d*); 128.2 (*d*); 129.1 (*d*); 130.2 (*d*); 131.9 (*d*); 139.0 (*s*); 141.6 (*s*); 145.1 (*s*); 151.9 (*s*); 164.7 (*s*). MS: 230 (6, M^+), 186 (10), 172 (24), 144 (100). Anal. calc. for $C_{13}H_{14}N_2O_2$: C 67.81, H 6.13, N 12.17; found: C 67.24, H 6.21, N 12.04.

Ethyl 3,6,7-Trimethylquinoxaline-2-carboxylate (**5e**): white powder. IR (nujol): 1730, 1553, 1372. ^{1}H-NMR ($CDCl_3$): 1.45 (*t*, J = 7.2, *Me*CH$_2$O); 2.44 (*s*, Me); 2.46 (*s*, Me), 2.90 (*s*, Me); 4.51 (*q*, J = 7.2, MeCH_2O); 7.75 (*s*, 1 arom. H); 7.88 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.2 (*q*); 20.2 (*q*); 20.5 (*q*); 23.6 (*q*); 62.2 (*t*); 127.3 (*d*); 128.7 (*d*); 138.7 (*s*); 140.4 (*s*); 141.3 (*s*); 142.9 (*s*); 143.2 (*s*); 151.7 (*s*); 165.8 (*s*). MS: 244 (24, M^+), 215 (11), 200 (18), 172 (100). Anal. calc. for $C_{14}H_{16}N_2O_2$: C 68.83, H 6.60, N 11.47; found: C 68.72, H 6.79, N 11.35.

Isopropyl 3,6,7-Trimethylquinoxaline-2-carboxylate (**5f**): pale yellow powder. IR (nujol): 1725, 1553, 1386. ^{1}H-NMR ($CDCl_3$): 1.45 (*d*, J = 6.2, *Me*$_2$CH); 2.45 (*s*, Me); 2.47 (*s*, Me); 2.87 (*s*, Me); 5.36 (*sept.*, J = 6.2, Me$_2$C*H*); 7.74 (*s*, 1 arom. H); 7.87 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 20.2 (*q*); 20.5 (*q*); 21.8 (*q*); 23.5 (*q*); 70.1 (*d*); 127.4 (*d*); 128.7 (*d*); 136.9 (*s*); 140.2 (*s*); 141.4 (*s*); 142.4 (*s*); 144.2 (*s*); 151.3 (*s*); 165.8 (*s*). MS: 258 (9, M^+), 215 (2), 200 (33), 172 (100). Anal. calc. for $C_{15}H_{18}N_2O_2$: C 69.74, H 7.02, N 10.84; found: C 69.66, H 7.11, N 10.91.

2-Methoxyethyl 3,6,7-Trimethylquinoxaline-2-carboxylate (**5g**): white powder. IR (nujol): 1725, 1544, 1381. ^{1}H-NMR ($CDCl_3$): 2.46 (*s*, Me); 2.48 (*s*, Me), 2.91 (*s*, Me); 3.43 (*s*, MeO); 3.78 (*t*, J = 4.8, $CO_2CH_2CH_2O$); 4.60 (*t*, J = 4.8, $CO_2CH_2CH_2O$); 7.76 (*s*, 1 arom. H); 7.89 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 20.2 (*q*); 20.6 (*q*); 23.6 (*q*); 59.0 (*q*); 64.8 (*t*); 70.2 (*t*); 127.4 (*d*); 128.6 (*d*); 138.8 (*s*); 140.5 (*s*); 141.6 (*s*); 143.0 (*s*); 143.2 (*s*); 152.0 (*s*); 165.7 (*s*). MS: 274 (6, M^+), 230 (61), 215 (8), 200 (70), 172 (100). Anal. calc. for $C_{15}H_{18}N_2O_3$: C 65.68, H 6.61, N 10.21; found: C 65.81, H 6.52, N 10.32.

*Methyl 3-Methylbenzo[*g*]quinoxaline-2-carboxylate* (**5h**): yellow powder. IR (nujol): 1735, 1567, 1358. ^{1}H-NMR ($CDCl_3$): 3.00 (*s*, Me); 4.11 (*s*, MeO); 7.56–7.62 (*m*, 2 arom. H); 8.05–8.13 (*m*, 2 arom. H); 8.58 (*s*, 1 arom. H); 8.79 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 24.2 (*q*); 53.3 (*q*); 126.6 (*d*); 126.9 (*d*); 127.7 (*d*); 128.4 (*d*); 128.8 (*d*); 128.9 (*d*); 133.7 (*s*); 135.1 (*s*); 136.4 (*s*); 138.5 (*s*); 144.7 (*s*); 153.0 (*s*); 165.8 (*s*). MS: 252 (65, M^+), 237 (12), 221 (4), 192 (100). Anal. calc. for $C_{15}H_{12}N_2O_2$: C 71.42, H 4.79, N 11.10; found: C 71.33, H 4.89, N 11.09.

*Benzyl 3-Methylbenzo[*g*]quinoxaline-2-carboxylate* (**5i**): yellow powder. IR (nujol): 1730, 1558, 1386. ^{1}H-NMR ($CDCl_3$): 2.94 (*s*, Me); 5.56 (*s*, PhCH_2); 7.40–7.61 (*m*, 6 arom. H); 8.06–8.12 (*m*, 3 arom. H); 8.60 (*s*, 1 arom. H); 8.78 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 24.0 (*q*); 68.0 (*t*); 126.6 (*d*); 126.8 (*d*); 127.6 (*d*); 128.5 (*d*); 128.6 (*d*); 128.7 (*d*); 128.8 (*d*); 129.0 (*d*); 133.7 (*s*); 135.0 (*s*); 135.2 (*d*); 136.5 (*s*); 138.4 (*s*); 145.1 (*s*); 145.2 (*s*); 152.7 (*s*); 165.4 (*s*). MS: 328 (1, M^+), 251 (63), 237 (38), 192 (100). Anal. calc. for $C_{21}H_{16}N_2O_2$: C 76.81, H 4.91, N 8.53; found: C 76.75, H 4.79, N 8.61.

*2-Methoxyethyl 3-Methylbenzo[*g*]quinoxaline-2-carboxylate* (**5j**): yellow powder. IR (nujol): 1730, 1562, 1381. ^{1}H-NMR ($CDCl_3$): 2.96 (*s*, Me); 3.46 (*s*, MeO); 3.62 (*t*, J = 4.8, $CO_2CH_2CH_2O$); 4.67 (*t*, J = 4.8, $CO_2CH_2CH_2O$); 7.56–7.62 (*m*, 2 arom. H); 8.07–8.12 (*m*, 2 arom. H); 8.57 (*s*, 1 arom. H); 8.76 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 23.8 (*q*); 59.0 (*q*); 65.1 (*t*); 70.1 (*t*); 126.4 (*d*); 126.8 (*d*); 127.6 (*d*); 128.4 (*d*); 128.7 (*d*); 128.9 (*d*); 133.6 (*s*); 135.0 (*s*); 136.5 (*s*); 138.1 (*s*); 145.2 (*s*); 152.6 (*s*); 165.5 (*s*). MS: 296 (15, M^+); 252 (58); 237 (13); 222 (13); 192 (100). Anal. calc. for $C_{17}H_{16}N_2O_3$: C 68.91, H 5.44, N 9.45; found: C 68.75, H 5.51, N 9.37.

Methyl 6,7-Dichloro-3-methylquinoxaline-2-carboxylate (**5k**): white powder. IR (nujol): 1745, 1567, 1380. ^{1}H-NMR ($CDCl_3$): 2.97 (*s*, Me); 4.01 (*s*, MeO); 8.11 (*s*, 1 arom. H); 8.25 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 23.1 (*q*); 53.2 (*q*); 129.3 (*d*); 130.0 (*d*); 134.1 (*s*); 136.3 (*s*); 138.5 (*s*); 141.3 (*s*); 145.3 (*s*); 154.4 (*s*); 164.8 (*s*). MS: 274 (1, $[M+4]^+$); 272 (5, $[M+2]^+$), 270 (11, M^+), 245 (1), 243 (6), 241 (9), 212 (100). Anal. calc. for $C_{11}H_8Cl_2N_2O_2$: C 48.73, H 2.97, N 10.33; found: C 48.79, H 3.02, N 10.41.

Ethyl 6,7-Dichloro-3-methylquinoxaline-2-carboxylate (**5l**): white powder. IR (nujol): 1730, 1561, 1374. ^{1}H-NMR ($CDCl_3$): 1.47 (*t*, J = 7.2, *Me*CH$_2$); 2.92 (*s*, Me); 4.54 (*q*, J = 7.2, MeCH_2); 8.14 (*s*, 1 arom. H); 8.27 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.2 (*q*); 23.7 (*q*); 62.6 (*t*); 129.2 (*d*); 130.2 (*d*); 134.5 (*s*); 136.5 (*s*); 138.5 (*s*); 141.2 (*s*); 145.4 (*s*); 154.1 (*s*); 165.1 (*s*). MS: 288 (2, $[M+4]^+$), 286 (13, $[M+2]^+$), 284 (20, M^+), 259 (11), 257

(7), 255 (10), 244 (2), 242 (11), 240 (21), 216 (10), 214 (67), 212 (100). Anal. calc. for $C_{12}H_{10}Cl_2N_2O_2$: C 50.55, H 3.54, N 9.82; found: C 50.39, H 3.48, N 9.91.

Methyl 3,6,7-Trimethylquinoxaline-2-carboxylate (**5m**): white powder. IR (nujol): 1730, 1554, 1380. ^{1}H-NMR ($CDCl_3$): 2.47 (*s*, Me); 2.50 (*s*, Me); 2.95 (*s*, Me); 4.05 (*s*, MeO); 7.79 (*s*, 1 arom. H); 7.91 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 20.3 (*q*); 20.6 (*q*); 23.7 (*q*); 53.1 (*q*); 127.3 (*d*); 128.7 (*d*); 138.9 (*s*); 140.6 (*s*); 141.4 (*s*); 142.4 (*s*); 143.3 (*s*); 152.3 (*s*); 166.0 (*s*). MS: 230 (21, M^+), 215 (7), 200 (14), 172 (100). Anal. calc. for $C_{13}H_{14}N_2O_2$: C 67.81, H 6.13, N 12.17; found: C 67.75, H 6.21, N 12.08.

Synthesis of Ethyl 3-(2-Aminoanilino)-2-chlorobut-2-enoate (**7a**). A soln. of ethyl 2-acetyl-2-chloroacetate (1 mmol) and benzene-1,2-diamine (**2a**; 1 mmol) was allowed to stand at r.t. in THF under magnetic stirring until the complete disappearance of the reagents (monitored by TLC, 3.5 h). The solvent was then evaporated under reduced pressure, and the residue was chromatographed on a silica-gel column (cyclohexane/AcOEt) to give **7a**, which was crystallized from AcOEt/petroleum ether (40–60°).

Data of **7a**: 74%. 3.5 h. White powder. M.p. 110–112°. IR (nujol): 3325, 3210, 3110, 1725, 1550. ^{1}H-NMR ($CDCl_3$): 1.36 (*t*, $J = 7.6$, *Me*CH_2); 2.05 (*s*, Me); 3.62 (br. *s*, NH_2, D_2O exchange), 4.26 (*q*, $J = 7.6$, MeCH_2); 6.70–7.26 (*m*, 4 arom. H); 10.16 (br. *s*, NH, D_2O exchange). ^{13}C-NMR ($CDCl_3$): 14.5 (*q*); 17.8 (*q*); 60.6 (*t*); 115.7 (*s*); 118.4 (*s*); 128.2 (*d*); 128.4 (*d*); 128.7 (*s*); 129.1 (*s*); 143.3 (*s*); 159.3 (*s*); 167.4 (*s*). MS: 256 (10, $[M+2]^+$); 254 (34, M^+), 218 (63), 190 (3), 173 (23), 144 (100). Anal. calc. for $C_{12}H_{15}ClN_2O_2$: C 56.59, H 5.94, N 11.00; found: C 56.64, H 5.85, N 11.18.

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