Isocyanide-Based Three-Component Synthesis of Highly Substituted 1,6-Dihydro-6,6-dimethylpyrazine-2,3-dicarbonitrile, 3,4-Dihydrobenzo[*g*]quinoxalin-2-amine, and 3,4-Dihydro-3,3-dimethylquinoxalin-2-amine Derivatives

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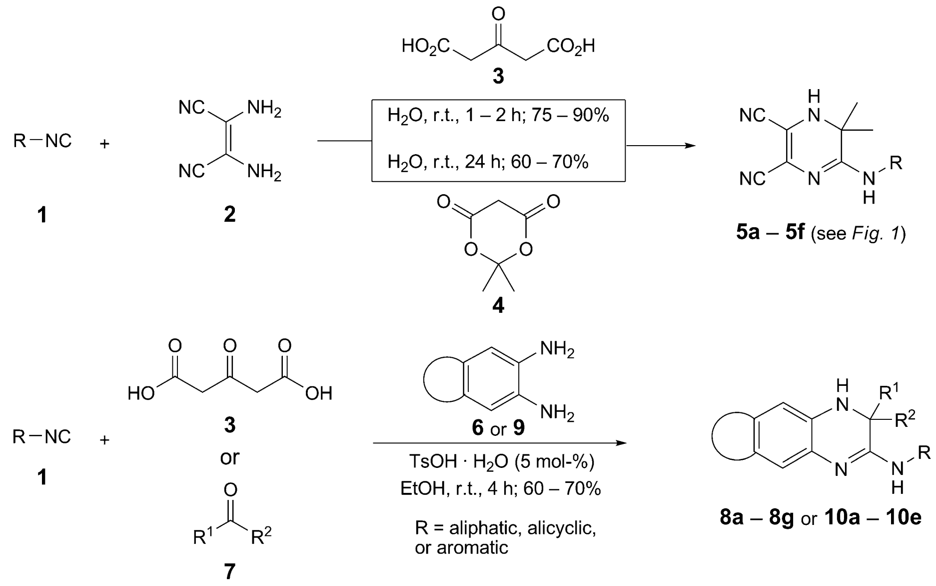
A novel and efficient isocyanide-based multicomponent reaction between alkyl or aryl isocyanides **1**, 2,3-diaminomaleonitrile (**2**), naphthalene-2,3-diamines (**6**) or benzene-1,2-diamine (**9**), and 3-oxopentanedioic acid (**3**) or *Meldrum*'s acid (**4**) or ketones **7** was developed for the ecologic synthesis, at room temperature under mild conditions, of 1,6-dihydropyrazine-2,3-dicarbonitriles **5a**–**5f** in H_2O without using any catalyst, and of 3,4-dihydrobenzo[*g*]quinoxalin-2-amine and 3,4-dihydro-3,3-dimethylquinoxalin-2-amine derivatives **8a**–**8g** and **10a**–**10e**, respectively, in the presence of a catalytic amount of *p*-toluenesulfonic acid (TsOH) in EtOH, in good to excellent yields (*Scheme 1*).

Introduction. – Quinoxalines and their derivatives are an important class of benzoheterocycles [1–3] displaying a broad spectrum of biological activities [4–7], including antidiabetic [8] and antiviral effects, in particular against retroviruses such as HIV [9]. They also are inhibitors of aldose reductase [10][11], partial agonists of the γ-aminobutyric acid (GABA)/benzodiazepine receptor complex [12], and antagonists of the AMPA and angiotensin II receptors [13]. They have found applications as dyes [14–16] and also as building blocks in the synthesis of organic semiconductors [17][18]. They also serve as useful rigid subunits in macrocyclic receptors for molecular recognition [19][20] and chemically controllable switches [21][22].

Multicomponent reactions (MCRs), especially isocyanide-based MCRs (IMCRs), are used extensively in medicinal chemistry as fast and selective methods for the synthesis of large libraries of organic molecules by simply varying each component through a chain of consecutive elementary transformations [23–25]. The great potential of isocyanides for the development of multicomponent reactions lies in their functional-group tolerance, diversity of bond-forming processes, and high levels of chemo-, regio-, and stereoselectivity [24][25].

Results and Discussion. – In view of our current studies on isocyanide-based multicomponent reactions (IMCRs) and a full account of our previous works [26][27], we disclose herein a novel ecologic IMCR for the synthesis of 1,6-dihydro-6,6-dimethylpyrazine-2,3-dicarbonitriles **5a**–**5f** *via* a condensation reaction between an isocyanide **1**, 2,3-diaminomaleonitrile (=(2*E*)-2,3-diaminobut-2-enedinitrile; **2**), and 3-oxopentanedioic acid (**3**) or *Meldrum*'s acid (=2,2-dimethyl-1,3-dioxane-4,6-dione; **4**) in H_2O at room temperature without using a catalyst, and of 3,4-dihydrobenzo[*g*]quinoxalin-2-amines **8a**–**8g** and 3,4-dihydro-3,3-dimethyl-quinoxalin-2-amines and **10a**–**10e** *via* a condensation reaction between diamines **6** or **9**, ketones **7** or 3-oxopentanedioic acid (**3**), and an isocyanide **1** in the presence of a catalytic amount of *p*-toluenesulfonic acid (TsOH · H_2O) in EtOH at room temperature in good to excellent yields (*Scheme 1*).

Scheme 1. *Synthesis of 1,6-Dihydro-6,6-dimethylpyrazine-2,3-dicarbonitriles* **5a**–**5f**, *3,4-Dihydrobenzo[*g*]quinoxalin-2-amines* **8a**–**8g**, *and 3,4-Dihydro-3,3-dimethylquinoxalin-2-amines* **10a**–**10e**



In an exploratory experiment, **2**, **3**, and cyclohexyl isocyanide were stirred in H_2O at room temperature. After completion of the reaction (1 h), workup afforded 5-(cyclohexylamino)-1,6-dihydro-6,6-dimethylpyrazine-2,3-dicarbonitrile (**5a**; *Fig. 1*) in 90% yield (*Table*). To investigate the scope and limitations of this reaction, we replaced **3** by *Meldrum*'s acid (**4**) and conducted the reaction under the same conditions but for 24 h, when the transformation was complete: **5a** was obtained in 70% yield (*Table*). Then, a variety of aliphatic, alicyclic, and aromatic isocyanides were treated under similar conditions with **3** or **4**, yielding the dicarbonitriles **5b**–**5f** (*Fig. 1*). The results are listed in the *Table*, showing clearly the scope of these reactions. The reactions proceeded very cleanly under mild conditions at room temperature, and no undesirable side reactions were observed. The transformations not only were faster with **3** relative to **4**, but also the yields were higher with **3**. It should be mentioned that the formation of the intermediate imine derivative **12** from **3** is faster than from **4** (see below; *Scheme 4*).

Next, we extended the reaction to naphthalene-2,3-diamine (**6**) instead of **2**. In pilot experiments, **6**, ketones **7**, and isocyanides **1** in EtOH were stirred at room temperature in the presence of a catalytic amount of *p*-toluenesulfonic acid hydrate (TsOH · H_2O) to yield, after aqueous workup, 3,4-dihydrobenzo[*g*]quinoxalin-2-amine derivatives **8a**–**8g** in 60–70% yield (*Scheme 2* and *Fig. 2*). These reactions proceeded very cleanly

Table. *Synthesis of 1,6-Dihydro-6,6-dimethylpyrazine-2,3-dicarbonitriles* **5a**–**5f** (*Fig. 1*) *by Using 3-Oxopentanedioic Acid* (**3**) *or* Meldrum*'s Acid* (**4**)

R	Product	With **3**		With **4**		M.p. [°]	
		time [h]	yield [%][a])	time [h]	yield [%][a])	found	reported [27]
Cyclohexyl	**5a**	1	90	24	70	252–255	255–258
tert-Butyl	**5b**	1	85	24	65	220–223	225–228
1,1,3,3-Tetramethylbutyl	**5c**	2	80	24	60	149–151	150–151
$EtOC(=O)CH_2$	**5d**	2	78	24	60	190–192	189–191
Benzyl	**5e**	2	80	24	65	151–153	152–154
2,6-Dimethylphenyl	**5f**	2	75	24	60	260–262	–

[a]) Yield of isolated product.

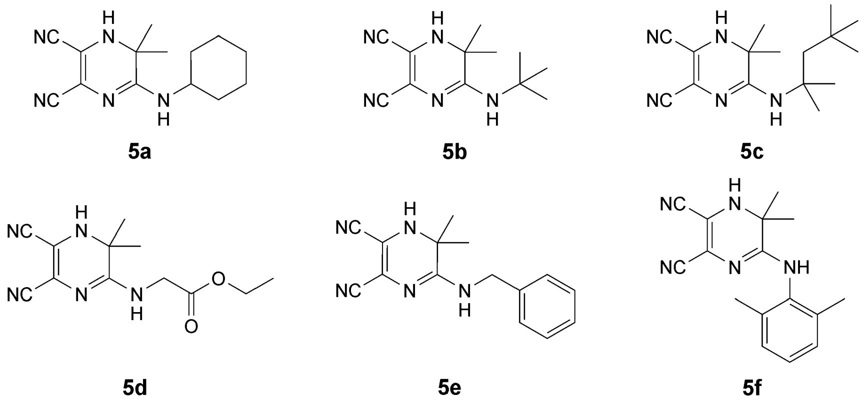
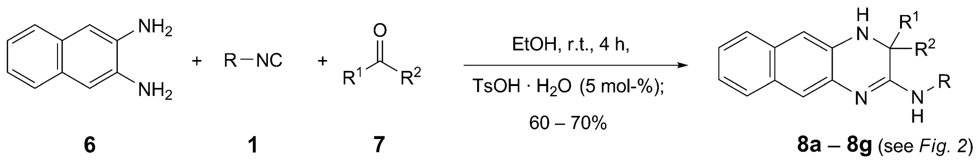


Fig. 1. *Synthesized 1,6-dihydro-6,6-dimethylpyrazine-2,3-dicarbonitriles* **5a**–**5f**

Scheme 2. *Synthesis of 3,4-Dihydrobenzo[g]quinoxalin-2-amines* **8a**–**8g**



under mild reaction conditions, and no undesirable side reactions were observed. It is important to note that the reaction did not occur in H_2O in the absence or presence of catalyst.

To further investigate this IMCR, we extended it to 3-oxopentanedioic acid (**3**) instead of ketones **7**. Thus, naphthalene-2,3-diamine (**6**) or benzene-1,2-diamine (**9**), **3**, and an isocyanide **1** in EtOH were stirred at room temperature in the presence of a catalytic amount of $TsOH \cdot H_2O$ to give, after aqueous workup, 3,4-dihydro-3,3-dimethylbenzo[*g*]quinoxalin-2-amines **8a**–**8c** or 3,4-dihydro-3,3-dimethylquinoxaline-

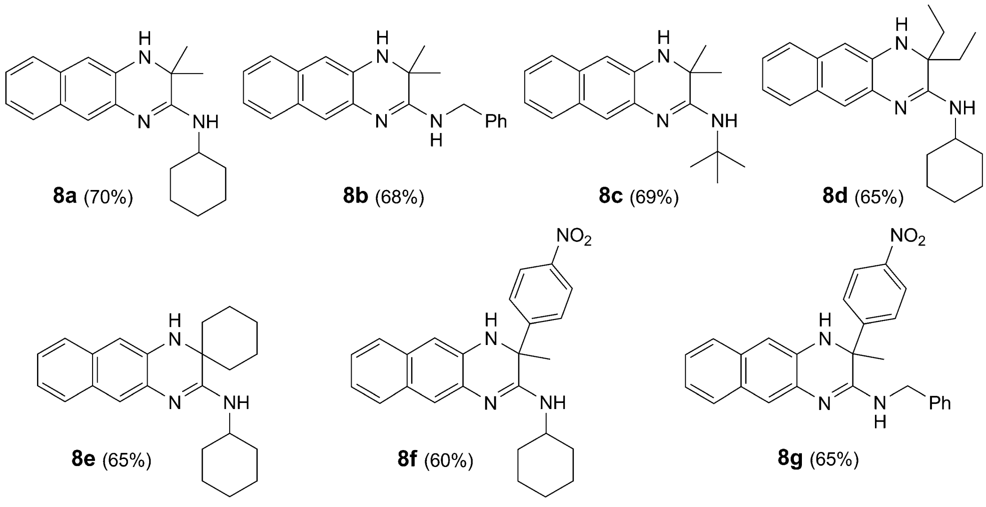
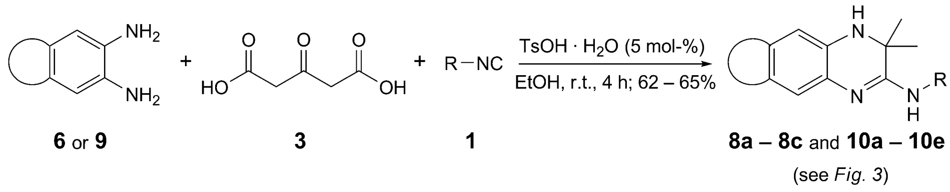


Fig. 2. *Synthesized 3,4-dihydrobenzo[*g*]quinoxalin-2-amines* **8a**–**8g**. Yields in parentheses.

2-amines, **10a**–**10e** respectively, in 62–65% yield (*Scheme 3* and *Fig. 3*). Again the reaction did not work in H_2O in the absence of or in the presence of catalyst.

Scheme 3. *Synthesis of 3,4-Dihydro-3,3-dimethylbenzo[*g*]quinoxalin-2-amines* **8a**–**8c** *and 3,4-Dihydro-3,3-dimethylquinoxalin-2-amines* **10a**–**10e**



A possible mechanism for the formation of products **5a**–**5f** is shown in *Scheme 4*. It is conceivable that the initial event is the formation of imine derivative **11** by a condensation of **2** and **3** [28–33]. In the case of *Meldrum*'s acid (**4**), the reaction may be rationalized by initial formation of malonic acid (**15**) and acetone (**16**) by the well-known hydrolysis of **4** in H_2O [34]. In the next step, imine derivative **12** is obtained by decarboxylation of **11** [35] or by condensation of **2** and **16**. On the basis of the well-established chemistry of the reaction of isocyanides with imines [24][25][36][37], intermediate **13** is produced by a nucleophilic attack of isocyanide **1** on **12**, followed by an intramolecular nucleophilic attack by the NH_2 group at the activated nitrile moiety to give intermediate **14**. Finally, imine-enamine tautomerization of intermediate **14** produces the 1,6-dihydropyrazine-2,3-dicarbonitrile derivatives **5a**–**5f**.

To clarify the proposed mechanism for the reaction with *Meldrum*'s acid (**4**), dinitride **2**, acetone (**16**), and cyclohexyl isocyanide in the presence of malonic acid (**15**)

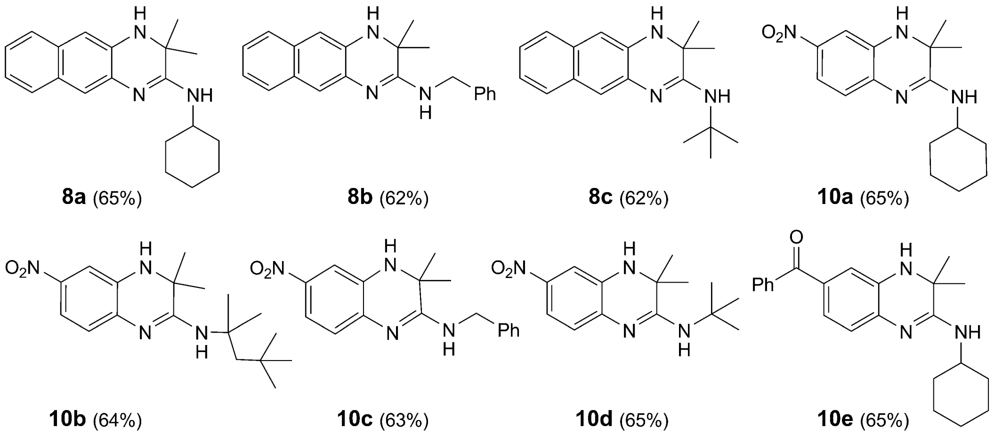
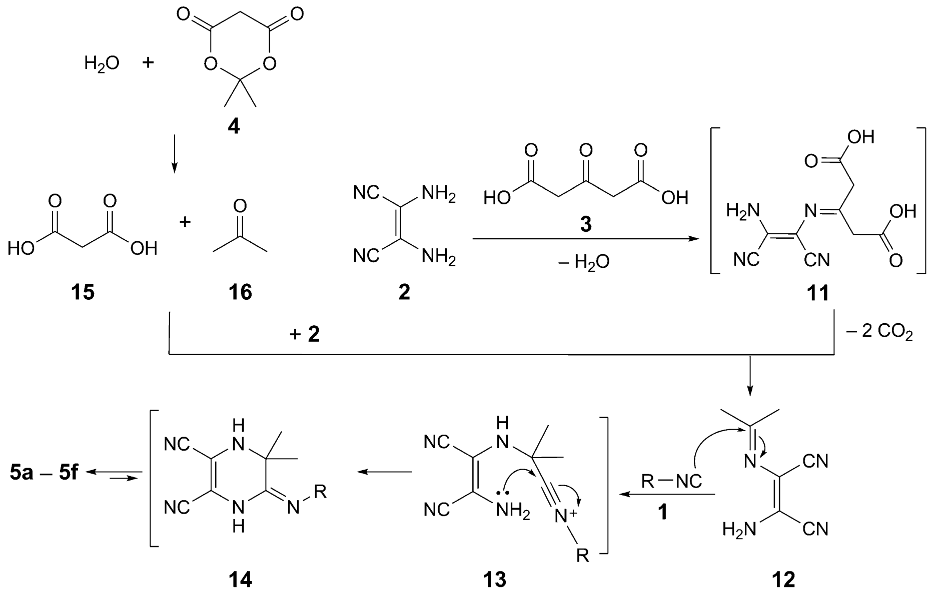


Fig. 3. *Synthesized 3,4-dihydro-3,3-dimethylbenzo[*g*]quinoxalin-2-amines* **8a**–**8c** *and 3,4-dihydro-3,3-dimethylquinoxalin-2-amines* **10a**–**10**. Yields in parentheses.

Scheme 4. *Possible Mechanism of Formation of Products* **5a**–**5f**



were subjected to the IMCR under the usual conditions (in H_2O for 1 h at r.t.), and indeed, **5a** was obtained in a yield of 90%.

To illustrate the role of malonic acid (**15**), the reaction of **2**, acetone (**16**), and cyclohexyl isocyanide was performed in the absence of **15**: reaction occured, not even after 24 h at room temperature, thus establishing that malonic acid acts as a catalyst in this reaction. Moreover, GC analysis of the reaction mixture of **4**, **2**, and cyclohexyl isocyanide revealed the formation of malonic acid (**15**) as a by-product, which supports the proposed mechanism.

Compounds **5a**–**5f**, **8a**–**8g**, and **10a**–**10e** were stable solids whose structures were identified by their IR, ^{1}H- and ^{13}C-NMR, and MS data, and by elemental analysis. Products **5a**–**5e** are known compounds, and their IR and NMR data and melting points were compared with reported values [27].

Conclusion. – We developed an IMCR for the synthesis of pharmaceutically relevant, highly substituted 1,6-dihydropyrazine-2,3-dicarbonitriles, 3,4-dihydrobenzo[*g*]quinoxalin-2-amines, especially a spiro-type compound, *i.e.* **8e**, and 3,4-dihydro-3,3-dimethylquinoxalin-2-amines in good to excellent yields. The reactions were easy to perform and allowed the introduction of at least three local sites of diversity in the final products and access to a multitude of compounds. Workup procedures were simple and free of chromatographic separations, and the obtained target materials were of high purity.

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Experimental Part

General. All chemicals were obtained from *Fluka* or *Merck* and were applied without further purification. M.p.: *Electrothermal-9100* apparatus. IR Spectra: *Bomem-MB* FT-IR spectrophotometer; in KBr; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-DRX-300-Avance* spectrometer; in (D_6)DMSO; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *Shimadzu-GCMS-QP-1100EX* mass spectrometer; at 70 eV; in *m*/*z*. Elemental analyses: *Elementaranalysensysteme GmbH VarioEL,* CHNS mode.

5-Amino-6,6-dimethyl-1,6-dihydropyrazine-2,3-dicarbonitriles (**5**): *Typical Procedure for* **5a**. A soln. of 2,3-diaminomaleonitrile (**2**; 1.0 mmol), 3-oxopentanedioic acid (**3**; 1.1 mmol) or *Meldrum*'s acid (**4**; 2.0 mmol), and cyclohexyl isocyanide (1.0 mmol) in H_2O (3 ml) was stirred for 1 h or 24 h, at r.t., resp. After completion of the reaction, (TLC (AcOEt/hexane 3:1) monitoring), the precipitate was filtered off and then crystallized from acetone: **5a**. Colorless crystals.

*3,4-Dihydrobenzo[*g*]quinoxalin-2-amines* **8a**–**8g** *and 3,4-Dihydroquinoxalin-2-amines* **10a**–**10e**: *General Procedure.* To a soln. of diamine **6** or **9** (1 mmol), 3-oxopentanedioic acid (**3**; 1.1 mmol) or ketone **7** (1.0 mmol), and isocyanide **1** (1.0 mmol) in EtOH (3 ml) was added TsOH·H_2O (5 mol-%). The resulting mixture was stirred for 4 h at r.t. After completion of the reaction (TLC (AcOEt/hexane 2:1) monitoring), the product was precipitated by addition of H_2O (10 ml). The residue was crystallized from EtOH: pure **8a**–**8g** and **10a**–**10e**.

5-(Cyclohexylamino)-1,6-dihydro-6,6-dimethylpyrazine-2,3-dicarbonitrile (**5a**): Colorless crystals. M.p. 252–255°. IR: 3342, 3080, 2933, 2850, 2217, 1578, 1538, 1456, 1391. ^{1}H-NMR: 1.00–2.00 (*m*, 5 CH_2 of chx, 2 Me); 3.68 (*m*, CH of chx); 6.87 (*d*, *J* = 7.5, NH); 7.12 (*s*, NH). ^{13}C-NMR: 24.3; 25.2; 25.7; 31.9; 49.6; 50.0; 110.2; 110.8; 114.9; 118.4; 155.8. MS: 257 (20, M^+), 242 (25), 175 (25), 160 (100), 133 (22), 57 (45), 41 (75). Anal. calc. for $C_{14}H_{19}N_5$: C 65.34, H 7.44, N 27.22; found: C 65.28, H 7.33, N 27.20.

5-[(1,1-Dimethylethyl)amino)-1,6-dihydro-6,6-dimethylpyrazine-2,3-dicarbonitrile (**5b**): Light yellow crystals. M.p. 220–223°. IR: 3412, 3323, 2976, 2929, 2861, 2212, 1564, 1540, 1497, 1461, 1367, 1309. ^{1}H-NMR: 1.18 (*s*, 2 Me); 1.32 (*s*, 3 Me); 6.18 (*s*, NH); 7.15 (*s*, NH). ^{13}C-NMR: 24.0; 28.5; 49.4; 52.5; 110.0; 110.2; 114.9; 118.4; 154.8. MS: 232 (20, $[M+1]^+$), 160 (100), 133 (26), 57 (50), 41 (75). Anal. calc. for $C_{12}H_{17}N_5$: C 62.31, H 7.41, N 30.28; found: C, 62.24, H 7.33, N 30.18.

1,6-Dihydro-6,6-dimethyl-5-[(1,1,3,3-tetramethylbutyl)amino]pyrazine-2,3-dicarbonitrile (**5c**): White powder. M.p. 149–151°. IR: 3412, 3344, 2981, 2966, 2950, 2903, 2861, 2212, 1577, 1559, 1542, 1448, 1393, 1372. ^{1}H-NMR: 0.93 (*s*, 3 Me); 1.17 (*s*, 2 Me); 1.36 (br. *s*, 2 Me); 1.82 (br. *s*, CH_2); 6.04 (*s*, NH); 7.12 (*s*, NH). ^{13}C-NMR: 23.9; 29.3; 31.6; 31.8; 49.2; 49.8; 56.4; 109.8; 110.1; 114.9; 118.4; 154.0. MS: 287 (17, M^+), 176 (48), 160 (100), 133 (15), 97 (17), 57 (60), 41 (63). Anal. calc. for $C_{16}H_{25}N_5$: C 66.86, H 8.77, N 24.37; found: C 66.75, H 8.71, N 24.27.

Ethyl 2-[(5,6-Dicyano-3,3-dimethyl-3,4-dihydropyrazin-2-yl)amino]acetate (**5d**): Colorless crystals. M.p. 190–192°. IR: 3379, 3293, 3080, 3049, 2997, 2960, 2934, 2217, 1744, 1579, 1502, 1461, 1406, 1322. ^{1}H-NMR: 1.17 (*t*, $J = 7.2$, Me); 1.24 (*s*, 2 Me); 3.90 (*d*, $J = 5.4$, CH_2); 4.09 (*q*, $J = 6.9$, CH_2); 7.37 (*s*, NH); 7.77 (br. *s*, NH). ^{13}C-NMR: 14.5; 24.4; 43.0; 50.0; 60.8; 106.5; 109.6; 111.7; 114.5; 118.2; 156.6; 169.8. MS: 262 (50, $[M+1]^+$), 246 (45), 172 (100), 133 (25), 42 (27). Anal. calc. for $C_{12}H_{15}N_5O_2$: C 55.16, H 5.79, N 26.80; found: C 55.11, H 5.72, N 26.70.

1,6-Dihydro-6,6-dimethyl-5-[(phenylmethyl)amino]pyrazine-2,3-dicarbonitrile (**5e**): Brown powder. M.p. 151–153°. IR: 3431, 3185, 3044, 2966, 2918, 2210, 1574, 1554, 1513, 1455, 1419, 1317. ^{1}H-NMR: 1.26 (*s*, 2 Me); 4.45 (*d*, $J = 5.3$, CH_2); 7.20–7.35 (*m*, 6 H, arom. H, NH); 7.88 (*t*, $J = 5.0$, NH). ^{13}C-NMR: 24.4; 44.3; 50.0; 110.4; 110.9; 114.8; 119.3; 127.2; 127.5; 128.8; 139.3 165.6. MS: 266 (3, $[M+1]^+$), 250 (4), 193 (6), 174 (9), 132 (22), 108 (45), 43 (100). Anal. calc. for $C_{15}H_{15}N_5$: C 67.90, H 5.70, N 26.40; found: C, 67.80, H 5.66, N 26.32.

5-[(2,6-Dimethylphenyl)amino]-1,6-dihydro-6,6-dimethylpyrazine-2,3-dicarbonitrile (**5f**): Colorless crystals. M.p. 260–262°. IR: 3346, 3387, 3341, 3190, 2981, 2918, 2850, 2211, 1597, 1576, 1549, 1524, 1457, 1393, 1367, 1312. ^{1}H-NMR: 1.40 (2 Me); 2.10 (2 Me); 7.10 (3 arom. H); 7.45 (*s*, NH); 8.60 (*s*, NH). ^{13}C-NMR: 18.2; 24.6; 50.3; 109.9; 111.7; 114.6; 118.2; 127.4; 128.3; 135.5; 136.0; 155.3. MS: 280 (10, $[M+1]^+$), 264 (20), 248 (4), 207 (2), 158 (6), 183 (100), 77 (15), 43 (10). Anal. calc. for $C_{16}H_{17}N_5$: C 68.79, H 6.13, N 25.07; found: C 68.69, H 6.03, N 25.00.

N-*Cyclohexyl-3,4-dihydro-3,3-dimethylbenzo[*g*]quinoxalin-2-amine* (**8a**). Green powder. M.p. 252–254°. IR: 3287, 3047, 2931, 2857, 1655, 1599, 1534, 1504, 1454. ^{1}H-NMR: 0.80–2.20 (*m*, 5 CH_2, 2 Me); 4.02 (*m*, CH–N); 6.82 (*s*, NH); 7.00–7.80 (*m*, 6 arom. H); 9.00 (*d*, $J = 7.6$, NH). ^{13}C-NMR: 21.2; 24.8; 25.1; 25.5; 32.1; 52.1; 53.4; 109.1; 115.2; 123.7; 126.0; 127.7; 127.8; 128.6; 132.5; 134.2; 138.2; 161.8. MS: 308 (65, $[M^+ + 1]$), 210 (100), 183 (90), 140 (15), 107 (25), 91 (75), 65 (45), 41 (60). Anal. calc. for $C_{20}H_{25}N_3$: C 78.14, H 8.20, N 13.67; found: C 78.10, H 8.10, N 13.57.

*3,4-Dihydro-3,3-dimethyl-*N*-(phenylmethyl)-benzo[*g*]quinoxalin-2-amine* (**8b**): Grass green powder. M.p. 248–250°. IR: 3401, 2935, 2855, 1602, 1456. ^{1}H-NMR: 1.54 (br. *s*, 2 Me); 4.86 (*m*, CH_2–N); 6.89 (*s*, NH); 7.00–7.80 (*m*, 11 arom. H); 9.98 (*s*, NH). ^{13}C-NMR: 21.2; 45.7; 53.6; 109.2; 115.4; 123.6; 126.0; 126.3; 127.7; 127.8; 128.3; 128.6; 129.2; 132.5; 134.4; 135.7; 138.4; 163.3. MS: 316 (15, $[M+1]^+$), 300 (25), 209 (25), 183 (30), 140 (15), 107 (15), 91 (100), 65 (35), 39 (20). Anal. calc. for $C_{20}H_{25}N_3$: C 78.14, H 8.20, N 13.67; found: C 78.10, H 8.10, N 13.57.

N-*(1,1-Dimethylethyl)-3,4-dihydro-3,3-dimethylbenzo[*g*]quinoxalin-2-amine* (**8c**): Green powder. M.p. 142–144°. IR: 3454, 3382, 2957, 2851, 1635, 1580, 1525, 1475. ^{1}H-NMR: 1.28 (*s*, 2 Me); 1.45 (*s*, 3 Me); 6.01 (*s*, NH); 6.70–7.45 (*m*, 6 arom. H); 7.53 (*s*, NH). ^{13}C-NMR: 26.6; 29.1; 50.8; 51.7; 106.1; 118.8; 121.6; 123.7; 125.1; 126.9; 128.9; 131.6; 136.6; 137.7; 161.6. MS: 282 (10, $[M+1]^+$), 224 (100), 195 (15), 57 (52), 41 (45). Anal. calc. for $C_{22}H_{29}N_3$: C 76.83, H 8.24, N 14.93; found: C 76.78, H 8.15, N 14.90.

N-*Cyclohexyl-3,3-diethyl-3,4-dihydrobenzo[*g*]quinoxalin-2-amine* (**8d**). Grass green powder. M.p. 106–108°. IR: 3452, 3383, 2958, 2850, 1633, 1588, 1521, 1480. ^{1}H-NMR: 0.80–2.20 (*m*, 5 CH_2, 2 Me); 1.95 (*m*, 2 CH_2); 5.36 (*m*, CH–N); 5.88 (*s*, NH); 6.60–7.50 (*m*, 6 arom. H); 7.47 (*d*, $J = 7.8$, NH). ^{13}C-NMR: 8.7; 29.6; 31.8; 31.9; 33.1; 52.0; 55.8; 58.5; 100.2; 103.0; 118.8; 120.8; 123.7; 124.5; 126.7; 128.2; 132.2; 135.5; 138.5; 151.9. MS: 336 (10, $[M+1]^+$), 224 (100), 197 (10), 57 (50), 41 (55). Anal. calc. for $C_{22}H_{29}N_3$: C 78.76, H 8.71, N 12.53; found: C 78.72, H 8.69, N 12.45.

N-*Cyclohexylspiro[benzo[*g*]quinoxaline-(1*H*)2,1'-cyclohexan]-3-amine* (**8e**): Green powder. M.p. > 260°. IR: 3283, 2937, 2845, 1644, 1620, 1554, 1464, 1320. ^{1}H-NMR: 0.80–2.25 (*m*, 10 CH_2); 4.10 (*m*, CH–N); 6.85 (*s*, NH); 7.00–7.75 (*m*, 6 arom. H); 8.50 (*d*, $J = 7.6$, NH). ^{13}C-NMR: 19.6; 21.2; 24.7; 24.8; 25.2; 31.2; 52.1; 55.1; 110.0; 115.2; 123.6; 123.7; 126.0; 127.7; 127.9; 132.3; 133.6; 138.3; 161.7. MS: 361 (6, M^+), 347 (80), 290 (30), 265 (75), 222 (50), 195 (90), 140 (35), 107 (60), 91 (100), 55 (90). Anal. calc. for $C_{23}H_{29}N_3$: C 79.50, H 8.41, N 12.09; found: C 79.41, H 8.35, N 12.00.

N-*Cyclohexyl-3,4-dihydro-3-methyl-3-(4-nitrophenyl)benzo[*g*]quinoxalin-2-amine* (**8f**): Green powder. M.p. 181–182°. IR: 3287, 2931, 1655, 1454, 1183, 1121. ^{1}H-NMR: 1.00–2.20 (*m*, 5 CH_2, 1 Me); 4.00 (*m*, CH–N); 6.79 (*s*, NH); 7.00–7.70 (*m*, 10 arom. H); 8.92 (*m*, NH). ^{13}C-NMR: 21.2; 24.8; 25.5; 31.1;

52.1; 53.4; 109.1; 115.2; 123.6; 126.0; 126.2; 127.9; 128.6; 132.5; 134.2; 138.3; 161.8. MS: 308 (25, [M – 106]$^+$), 292 (42), 210 (100), 183 (90), 140 (15), 107 (20), 91 (60), 65 (40), 41 (40). Anal. calc. for $C_{25}H_{26}N_4O_2$: C 72.44, H 6.32, N 13.52; found: C 72.40, H 6.22, N 13.42.

3,4-Dihydro-3-methyl-3-(4-nitrophenyl)-N-*(phenylmethyl)benzo[*g*]quinoxalin-2-amine* (**8g**):Green powder. M.p. 154 – 156°. IR: 3361, 1603, 1522, 1478, 1346, 1261. ^{1}H-NMR: 1.93 (*s*, Me); 4.46 (*s*, CH_2–N); 6.80 (*s*, NH); 7.00 – 8.30 (*m*, 15 arom. H); 8.32 (*m*, NH). ^{13}C-NMR: 30.2; 81.6; 99.7; 122.0; 123.9; 125.5; 126.8; 130.3; 141.2; 146.9; 154.8. MS: 422 (5, M^+), 290 (65), 260 (25), 244 (65), 183 (75), 158 (40), 140 (35), 115 (100), 76 (40), 51 (35). Anal. calc. for $C_{25}H_{26}N_4O_2$: C 72.44, H 6.32, N 13.52; found: C 72.40, H 6.22, N 13.42.

N-*Cyclohexyl-3,4-dihydro-3,3-dimethyl-6-nitroquinoxalin-2-amine* (**10a**): Orange powder. M.p. > 250°. IR: 3263, 2934, 2851, 1651, 1604, 1530, 1458, 1339. ^{1}H-NMR: 0.80 – 2.10 (*m*, 5 CH_2, 2 Me); 3.99 (*m*, CH–N); 6.52 (*s*, NH); 7.30 – 7.80 (*m*, 3 arom. H); 9.16 (*s*, NH). ^{13}C-NMR: 25.4; 25.8; 26.2; 32.3; 49.2; 50.4; 106.9; 114.6; 121.9; 136.5; 141.6; 142.8; 161.1. MS: 302 (30, M^+), 287 (65), 205 (100), 178 (20), 159 (35), 132 (15), 107 (30), 91 (65), 65 (25), 41 (22). Anal. calc. for $C_{16}H_{22}N_4O_2$: C 63.55, H 7.33, N 18.53; found: C 63.47, H 7.23, N 18.43.

3,4-Dihydro-3,3-dimethyl-6-nitro-N-*(1,1,3,3-tetramethylbutyl)quinoxalin-2-amine* (**10b**): Yellow crystals. M.p. 190 – 192°. IR: 3234, 2971, 2850, 1645, 1602, 1532, 1498, 1429. ^{1}H-NMR: 0.98 (*s*, 3 Me); 1.43 (*s*, 2 Me); 1.58 (*s*, 2 Me); 2.07 (*s*, CH_2); 7.35 – 7.80 (*m*, 3 arom. H); 7.76 (*s*, NH); 8.39 (*s*, NH). ^{13}C-NMR: 21.2; 24.7; 28.5; 31.5; 31.9; 50.3; 52.5; 53.2; 114.2; 125.9; 128.6; 135.0; 138.2; 145.9; 160.0. MS: 332 (4, M^+), 261 (1), 205 (100), 159 (20), 91 (20), 57 (25), 41 (25). Anal. calc. for $C_{18}H_{28}N_4O_2$: C 65.03, H 8.49, N 16.85; found: C 64.93, H 8.40, N 16.78.

3,4-Dihydro-3,3-dimethyl-6-nitro-N-*(phenylmethyl)quinoxalin-2-amine* (**10c**): Green powder. M.p. 198 – 200°. IR: 3230, 1644, 1601, 1542, 1497, 1435. ^{1}H-NMR: 1.51 (*s*, 2 Me); 4.82 (*m*, CH_2 – N); 6.87 (*s*, NH); 7.00 – 7.80 (*m*, 8 arom. H); 8.15 (*s*, NH). ^{13}C-NMR: 21.2; 46.2; 53.3; 109.2; 114.4; 122.0; 125.2; 127.8; 128.4; 129.1; 129.2; 135.2; 135.3; 145.3; 162.1. MS: 310 (5, M^+), 295 (6), 249 (3), 221 (1), 204 (2), 172 (10), 107 (15), 91 (100), 65 (20), 39 (15). Anal. calc. for $C_{17}H_{18}N_4O_2$: C 65.79, H 5.85, N 18.05; found: C 65.70, H 5.75, N 18.00.

N-*(1,1-Dimethylethyl)-3,4-dihydro-3,3-dimethyl-6-nitroquinoxalin-2-amine* (**10d**): Red powder. M.p. 215 – 217°. IR: 3230, 2957, 2851, 1642, 1601, 1542, 1496, 1434. ^{1}H-NMR: 1.25 (*s*, 2 Me); 1.43 (*s*, 3 Me); 6.07 (*s*, NH); 6.33 (*s*, NH); 6.84 (*ABq*, $J = 8.3$, 1 arom. H); 7.37 (*s*, 1 arom. H); 7.45 (*ABq*, $J = 8.1$, 1 arom. H). ^{13}C-NMR: 26.1; 29.0; 50.2; 52.4; 107.1; 114.5; 122.3; 136.4; 141.8; 142.2; 162.0. Anal. calc. for $C_{14}H_{20}N_4O_2$: C 60.85, H 7.30, N 20.28; found: C 60.85, H 7.30, N 20.28.

[2-(Cyclohexylamino)-3,4-dihydro-3,3-dimethyl-quinoxalin-6-yl)](phenyl)methanone (**10e**): White crystals. M.p. 181 – 182°. IR: 3274, 2929, 2845, 1650, 1607, 1508, 1461, 1320. ^{1}H-NMR: 0.80 – 2.00 (*m*, 5 CH_2, 2 Me); 3.96 (*m*, CH–N); 6.84 (*s*, NH); 7.00 – 7.80 (*m*, 8 arom. H); 9.04 (*s*, NH). ^{13}C-NMR: 21.2; 24.7; 25.2; 32.0; 52.3; 53.1; 116.1; 117.8; 121.3; 128.9; 129.7; 132.8; 134.4; 134.6; 137.9; 145.9; 160.5; 195.3. MS: 361 (20, M^+), 346 (75), 264 (80), 237 (30), 172 (20), 105 (100), 91 (60), 77 (100), 55 (50), 41 (55). Anal. calc. for $C_{23}H_{27}N_3O$: C 76.42, H 7.53, N 11.62; found: C 76.38, H 7.43, N 11.52.

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