

Simple synthesis of 2-alkylidene- and 2-keto-7-triazolylquinoxaline systems from 2-nitrosodiarylamines

Zbigniew Wróbel,^{*} Robert Bujok, Michał Tryniszewski, and Andrzej Kwast

Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warsaw, Poland Email: <u>zbigniew.wrobel@icho.edu.pl</u>

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Abstract

A synthesis of triazole-substituted 1-arylquinoxaline derivatives from halogenated 2-nitrosodiarylamines by two routes is presented. Regioselective substitution of fluorine or chlorine in the starting compounds by sodium azide followed by double cyclocondensation of both the azide substituent and the nitrosoamine group leads to functionalized 2-methylenequinoxaline derivatives. The alternative route separates the two cyclocondensation reactions, allowing obtention of triazole-substituted quinoxalin-2-one derivatives by using two different dicarbonyl reagents.



Keywords: Triazoles, cyclocondensation, heterocycles, nucleophilic aromatic substitution, nitroso group

Introduction

Triazoles are compounds of great importance particularly in medicinal chemistry.¹⁻⁴ Nitrogen polycyclic heterocycles possessing triazole ring as a substituent attract continuous attention. Synthesis of triazoles is accomplished most frequently using the azido group as a three-nitrogen atom donor. Thus, heteroaromatic azides become crucial starting materials in the synthesis of such polyheterocyclic systems.



Figure 1. Examples of important structures of polyheterocyclic compounds A^5 and B^6 bearing triazole ring.

In 2007, we discovered the reaction of nitroarenes with aromatic amines in the presence of a strong base leading to 2-nitrosodiarylamines^{-7,8} These compounds turned out to be versatile starting materials for synthesis of a number of two-nitrogen-containing heterocycles such as phenazines,^{9,10} benzimidazoles¹¹ and quinoxalinones.¹² On the other hand, when the leaving group was present in the ring containing the nitroso group, the latter acted as a strong electron-withdrawing group activating the leaving group for aromatic nucleophilic substitution. The reaction was found efficient for alkoxy or alkylamine nucleophiles. However, due to high reactivity of the nitroso group towards various nucleophiles as well as its susceptibility to redox processes, the choice of potential nucleophiles has been limited.¹³

Recently we found that the range of suitable nucleophiles can be extended to azide anions. In this report, we present a simple synthesis of 5-azido-2-nitrosodiarylamines which can be further transformed into 2-alkylidenequinoxalines bearing triazole group in position 7, via the cascade reaction with β -dicarbonyl compounds. This method allows for obtaining complex structures starting from simple substrates under mild, heavy-metal-free conditions. Furthermore, a complementary approach which make use of 2-nitrosodiarylamines in the synthesis of triazole-substituted quinoxalin-2-one derivatives is presented.

Results and Discussion

Substitution of halogens (F, Cl) at the para position to the nitroso group with sodium azide proceeded smoothly with very good to excellent yields at room temperature in the systems: water-alcohol, dipolar aprotic solvents or catalytic two-phase solid-liquid system (PTC). PTC was chosen for a standard procedure (Table 1). The obtained crude products were pure enough for further use, thus, as they are not stable under column chromatographic conditions, they were used without purification.

The reaction was highly regioselective. Azide ions exclusively substituted the *para*-chloro position in 3,5dichloro-2-nitrosodiarylamine (Table 1, entry 7). This is in accordance with the results of the previously examined reactions of halogenated nitrosodiarylamines with alkyl amines or alcohols.¹³ The regioselectivity





Entry	Nitrosodiarylamine		1	D ²	ъ ³	Azide 2			
	Х	Y	1	- K	К	К	2	Conditions ^a	Yield ^b %
1	F	Н	1a	Ι	Н	Cl	2 a	А	71 ^c
2	F	Н	1b	Me	Me	Н	2b	А	99
3	Cl	Н	1c	I	Н	Me	2c	В	98
4	Cl	Н	1d	<i>t</i> -Bu	Н	Н	2d	В	96
5	Cl	Н	1e	Me	Me	Me	2e	В	97
6	Cl	Н	1f	Et	Me	Н	2f	В	89
7	Cl	Cl	1g	Me	Me	н	2g	В	98/63 ^c

^a Conditions A: MeCN 5% mol Bu₄NBr; B: MeCN, 10% mol Bu₄NHSO₄.

^b Crude products, pure enough for further transformations.

^c Isolated and purified by column chromatography.

Substitution of *ortho*-chloride, when it is the only leaving group in the molecule, occurs very slowly and is followed by intramolecular condensation of the azido and nitroso groups resulted in formation of a benzofurazan system **4a** (Scheme 2). The *ortho* azido nitroso compounds **3** were not isolated nor observed, but it seems reasonable to assume them as intermediates leading to **4**. Surprisingly, the methoxy group at *para* position resists of substitution by azide ions in **1i**, while it was preferentially substituted with pyrrolidine in 3-chloro-5-methoxy-2-nitrosodiarylamines.¹³





The substitution of *ortho* halogens by azide ions forming benzofurazan derivatives was observed and described earlier for a few 2,6-dihalonitrosobenzenes in their reaction with sodium azide in DMSO at elevated

temperature.^{14,15} Since the cyclization seems to be much faster than the substitution, obtaining *o*-azidonitrosoarenes this way was not possible.

Functionalization of 2-nitrosodiarylamines with an azido group opened up a new perspective for building complex heterocyclic systems containing multiple rings. Initially we tried to build a triazole ring by coppercatalyzed cycloaddition¹⁶ of the azido group with propargyl alcohol derivatives but the results were disappointing, probably because of reactivity of the nitroso group under the reaction conditions. Thus, we turned out to the most straightforward and reasonable idea to build two different heterocyclic rings on the two reactive centers, the *ortho*-nitrosoaniline and the azido functions, in the reaction with the same shared reagent. While double condensation reactions of **2** with benzyl cyanide, cyanoacetic acid esters and malonates were unsuccessful, with 1,3-diketones or β -ketoesters gave positive results. The reaction worked satisfactorily in MeCN with various β -diketones, provided that they possessed at least one terminal methyl group. *tert*-Butylamine was chosen as a catalyst since it had been found to be the best catalyst for the previously developed reaction of 2-nitrosodiarylamines with β -diketones leading to the condensed pyrazine ring.^{17,18}

Table 2. Double cyclization of 2 with 1,3-dicarbonyl compounds



Entry	Aziue							
	2	Z	5	Yield ^b (%)				
2	2a	Me	5a	49				
3	2b	Me	5b	82				
4	2b	OEt	5c	22				
5	2b	<i>i</i> -Pr	5d	54				
6	2c	Me	5e	56				
7	2d	Me	5f	51				
8	2e	Me	5g	65				
9	2e	iPr	5h	40				
10	2f	Me	5i	71				
11	2f	<i>i</i> -Pr	5j	46				

^a Substituents as shown in Table 1.

^b Isolated yields.

Formation of the triazole ring proceeds most likely via the dipolar cycloaddition of the enolate form of β dicarbonyl compound and aryl azide,¹⁹⁻²¹ for which detailed mechanistic studies and explanation of the observed regioselectivity have been reported.¹⁹ The reactions **2** -> **5** are also regioselective. The expected structure of the regioisomer formed was confirmed for selected triazoles (**5a**, **d** and **f**) by NMR techniques HMBC and NOESY. The latter proved proximity of the triazole methyl group and appropriate protons of the dihydroquinoxaline aromatic ring.

Our efforts to perform consecutively both cyclizations failed, i.e. by using different dicarbonyl reagents with NO and N₃ groups. This was probably because of a multistep character of both cyclizations, and because they take place in distant regions of the starting molecule. Hence, they may occur independently of each other at the same time. Consecutive, controlled formation of both heterocyclic rings, using different dicarbonyl reagents dedicated for particular cyclization, required a different approach. Thus, we tried to introduce the azido function into bicyclic systems obtained by condensation of 2-nitrosodiarylamines with dicarbonyl compounds. This condensation, which has been described previously,^{11,12} allows for the formation of quinoxalin-2-one derivatives possessing alkoxycarbonyl substituent at C3. Carbocyclic rings of these compounds seem to be electrophilic enough for the nucleophilic substitution of halogens, placed in the activated positions 5 or 7, with azide ions. Thus, further condensation of the bicyclic azides could be carried out with another carbonyl reagent. As an illustration of this approach, the three-step synthetic sequence starting from representative 2-nitrosodiarylamines was accomplished (Table 3).



	R ² Y - R ³	O O OM		6 a-c	MaN ₃ → → →		⁰ R ² R 7a-c	3 base	e, MeCN		Y R ² R ¹ 8a - c
Entry	Х	R^1	R ²	R ³	Y	6 Yie	eld ^a (%)	7 Yie	eld ^a (%)	8 Yie	eld ^a (%)
1	F	Me	Me	Н	MeO	6a	81	7a	70	8a	46
2	F	Н	Н	Cl	Ph	6b	60	7b	80	8b	81
3	Cl	Н	Н	Me	MeO	6c	64	7c	37	8c	81
а											

^a Isolated yields.

While fluorine was substituted by sodium azide in quinoxalin-2-ones **6a** and **6b** efficiently at room temperature, the reaction of chloro derivative **6c** required elevated temperature (80 °C) and gave much lower yield of **7c**. On the other hand, relatively low yield of the cyclization of **7a** is difficult to explain. Nevertheless, the approach can be useful for the synthesis of complex nitrogen heterocyclic compounds of a specific structure.

Conclusions

It was demonstrated that halogenated 2-nitrosodiarylamines can be useful starting materials in the synthesis of triazole-substituted 1-arylquinoxaline systems by two routes. The two-step method benefits from the

efficient and regioselective nucleophilic substitution of 5-fluorine or 5-chlorine in 2-nitrosodiarylamines by sodium azide and is followed by double condensation with acetylketones. Some limitations of the method can be circumvented by separation of the two cyclization reactions. Thus, in the alternative approach, 7-halogenoquinoxalinones are prepared first, followed by substitution of halogens to form the intermediate azidoquinoxalinones. This allows to use two different dicarbonyl compounds for both cyclization processes, and therefore extends the scope of tricyclic systems obtained from 2-nitrosodiarylamines.

Experimental Section

General. ¹H and ¹³C NMR spectra were recorded on a Varian-NMR-vnmrs600 and a Varian Mercury 500 instruments at 298 K. Chemical shifts are expressed in ppm referred to TMS (¹H NMR) or to the solvent used (¹³C NMR), with coupling constants in Hertz. Mass spectra were obtained on an AutoSpec Premier (Waters) spectrometer (EI, 70 eV) and an API 365i spectrometer (ESI in MeOH). Silica gel Merck 60 (230-400 mesh) was used for column chromatography. THF was distilled from sodium/benzophenone ketyl prior to use. DMF was dried over CaH₂, distilled and stored over molecular sieves. Common reagents and materials were purchased from commercial sources and used as received. Preparation and characterization of 2-nitrosodiarylamines **1**, except **1a**, **1e** and **1f**, have been described in our previous papers.^{8,17,18} Quinoxalinones **6a-c** were prepared following the procedure published earlier.¹²

N-(5-Fluoro-2-nitrosophenyl)-*N*-(4-chloro-2-iodophenyl)amine (1a). To a solution of *t*-BuOK (3.4 g, 30 mmol) in dry THF (50 mL) cooled to -74 °C was added 4-chloro-2-iodoaniline (7.6 g, 30 mmol) in THF (5 mL) then a solution of 4-fluoronitrobenzene (4.23 g, 30 mmol) in THF (5 mL) was added dropwise. The mixture was stirred at ca -70 °C for 60 min then the mixture was alowed to warm up slowly to -30 °C, then poured into conc. HCl_{aq} (20 mL) in water (400 mL) and extracted with EtOAc. The extract was washed with water and dried (Na₂SO₄). After evaporation the product was isolated by column chromatography (SiO₂, hexane/toluene 2:1). Pure **1a** (5.75 g, 51%) was obtained as a brown solid. mp 148 °C (dec.). ¹H NMR (500 MHz, CDCl₃): δ 6.45-6.49 (m, 1H), 7.75-6.81 (m, 1H), 7.31 (d, *J* 8.5 Hz, 1H), 7.40 (dd, *J* 8.5, 2.2 Hz, 1H), 7.94 (d, *J* 2.2 Hz, 1H), 8.76 (br s, 1H), 11.58 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 96.4, 99.8 (d, *J*_{CF} 25 Hz), 107.9 (d, *J*_{CF} 27 Hz), 126.6, 129.6, 132.9, 137.8, 139.5, 154.8, 168.0 (d, *J*_{CF} 262 Hz) (two signal missing);²² HRMS (ESI): *m/z* calcd for C₁₂H₇³⁵CIFIN₂ONa: 398.9173, found: 398.9167

N-(5-Chloro-2-nitrosophenyl)-*N*-mesitylamine (1e). To a cooled to -74 °C solution of *t*-BuOK (3.4 g, 30 mmol) in dry THF (50 mL) was added mesitylamine (1.3 g, 9.6 mmol) in THF (5 mL) then a solution of 4-chloronitrobenzene (1.51 g, 9.6 mmol) in THF (5 mL) was added dropwise. The mixture was stirred at ca -70 °C for 40 min then poured into saturated NH₄Cl and extracted with EtOAc. The extract was washed with water and dried (Na₂SO₄). After evaporation the product was isolated by column chromatography (SiO₂, hexane/toluene 5:1 – 1:1. Pure **1e** (2.08 g, 78%) was obtained as a dark solid. mp 64-69 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.05 (s, 6H), 2.32 (s, 3H), 6.32 (d, *J* 1.7 Hz, 1H), 6.90 (br d, *J* 8.2 Hz, 1H), 6.97 (s, 2H), 8.75 (br s, 1H), 11.71 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 18.0, 21.0, 114.2, 118.1, 129.5, 130.5, 135.5, 137.9, 142.1, 144.8, 155.1 (one signal missing);²² MS (EI): *m/z* (%) 274 (M⁺, 1), 261 (46), 259 (100), 242 (21); HRMS (EI): *m/z* calcd for C₁₅H₁₅³⁵Cl N₂O: 274.0873, found: 274.0872.

N-(5-Chloro-2-nitrosophenyl)-*N*-(2-ethyl-6-methylphenyl)amine (1f). Obtained according to the procedure described for 1e from 2-ethyl-6-methylaniline (1.30 g, 9.6 mmol) and 4-chloronitrobenzene (1.51 g, 9.6 mmol)

as dark oil (2.03 g, 77%). ¹H NMR (600 MHz, CDCl₃): δ 1.09 (t, *J* 7.5 Hz, 3H), 2.08 (s, 3H), 2.43 (q, *J* 7.5 Hz, 2H), 6.30 (d, *J*1.1 Hz, 1H), 6.91 (d, *J* 7.3 Hz, 1H), 7.16 (d, *J* 7.6 Hz, 1H), 7.18 (d, *J* 7.6 Hz, 1H), 7.25 (t, *J* 7.6 Hz, 1H), 8.78 (br s, 1H), 11.81 (br s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 14.7, 18.1, 24.8, 114.2, 118.2, 127.1, 128.4, 128.8, 132.5, 136.0, 141.7, 142.2, 144.8, 155.0 (one signal missing);²² MS (EI): *m/z* (%) 274 (M⁺, 2), 259 (36), 245 (100); HRMS (ESI): *m/z* calcd for C₁₅H₁₆³⁵ClN₂O [M+H]⁺: 275.0951, found: 275.0947.

General procedure for the reactions of 2-nitrosodiarylamines 1a-g with sodium azide. A mixture of 2-nitrosodiarylamine 1 (0.5 mmol), sodium azide (129 mg, 2.0 mmol) and NBu₄HSO₄ (69 mg, 0.2 mmol) in CH₃CN (4 mL) was stirred at room temperature for 2-5 h (tlc controlled). When the reaction was complete CH₃CN was evaporated at room temperature. To the residue Et₂O (40 mL) and water (5 mL) were added and the layers were separated. The organic layer was dried (Na₂SO₄) and the solvent was evaporated to obtain products pure enough for further reactions. When it was necessary, the Et₂O solution was poured through a small SiO₂ pad before evaporation to remove tars. Additional purification for analytical purposes was performed by column chromatography (SiO₂, hexane/ethyl acetate, 9:1 to 2:1). and/or recrystallization from hexane/ethyl acetate mixture.

5-Azido-4'-chloro-2'-iodo-2-nitrosodiphenylamine (2a). Brown powder (142 mg, 71%). mp 127-129 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.35 (s, 1H), 6.75 (br d, *J* 8.3 Hz, 1 H), 7.29 (d, *J* 8.3 Hz, 1H), 7.39 (dd, *J* 8.3, 2.2 Hz, 1H), 7.93 (d, *J* 2.2 Hz, 1H), 8.67 (br s, 1H), 11.65 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 96.4, 102.8, 110.1, 126.6, 129.5, 132.8, 137.9, 139.6, 149.7, 154.6 (two signals invisible);²² MS (EI): m/z (%) 399 (4), 246 (100), 227 (76). HRMS (EI): m/z calcd for $C_{12}H_7N_5^{35}$ ClIO: 398.9384, found: 398.9391.

5-Azido-2',6'-dimethyl-2-nitrosodiphenylamine (2b). Dark crystals (133 mg, 71%). mp 98-102 °C (dec.); ¹H NMR (500 MHz, CDCl₃): δ 2.10 (s, 6H), 5.80 (s, 1H), 6.67 (br s, 1 H), 7.12-7.17 (m, 2H), 7.18-7.22 (m, 1H), 8.80 (br s, 1H), 11.99 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 18.1, 102.6, 109.1, 121.0, 128.1, 128.8, 135.8, 143.4, 149.5, 154.7, (one signal invisible);²² MS (EI): m/z (%) 267 (19), 252 (100), 224 (92), 207 (86), 144 (66); HRMS (EI): m/z calcd for C₁₄H₁₃N₅O: 267.1120, found: 267.1112.

5-Azido-2'-iodo-4'-methyl-2-nitrosodiphenylamine (2c). Dark red oil (185 mg, 98%); ¹H NMR (500 MHz, CDCl₃): δ 2.35 (s, 3H), 6.32 (s, 1H), 6.66-6.73 (m, 1 H), 7.15-7.26 (m, 2H), 7.78 (s, 1H), 8.76 (br s, 1H), 11.87 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 20.5, 96.4, 109.8, 114.4, 118.9, 126.3, 130.1, 136.1, 139.1, 140.6, 144.6, 154.6, 155.0; MS (ESI): m/z (%) 402 [M+Na]⁺, HRMS (ESI): m/z calcd for C₁₃H₁₀N₅IONa: 401.9228, found: 401.9217.

5-Azido-2'-t-butyl-2-nitrosodiphenylamine (2d). Brown solid (150 mg, 96%). mp 96 °C (dec.); ¹H NMR (500 MHz, CDCl₃): δ 1.37 (s, 9H), 6.24 (br s, 1H), 6.67 (br s, 1H), 7.14-7.18 (m, 1H), 7.23-7.27 (m, 1H), 7.29 (ddd, *J* 7.7, 7.4, 1.5 Hz, 1H), 7.52 (dd *J* 7.7, 1.5 Hz, 1H), 8.76 (br s, 1H), 12.58 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 30.6, 35.0, 103.3, 109.4, 114.2, 127.1, 127.6, 127.7, 127.8, 129.3, 134.6, 136.3, 143.1, 146.3, 149.5, 154.9; MS (EI): *m/z* (%) 295 (2), 250 (92), 238 (74), 210 (100), 194 (74); MS (ESI): *m/z* 318 [M+Na]⁺; HRMS (ESI): *m/z* calcd for C₁₆H₁₇N₅ONa: 318.1331, found: 318.1315.

5-Azido-2-nitroso-2',4',6'-trimethyldiphenylamine (2e). Dark oil (136 mg, 97%). mp 93-96 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.05 (s, 6H), 2.32 (s, 3H), 5.81 (s, 1H), 6.66 (br s, 1H), 6.95 (s, 2H), 8.78 (br s, 1H), 11.97 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 18.0, 21.0, 102.6, 109.1, 129.4, 130.6, 135.3, 136.7, 137.8, 140.2, 149.5, 154.7; MS (ESI): m/z (%) 304 [M+Na]⁺, HRMS (ESI): m/z calcd for C₁₅H₁₅N₅ONa: 304.1174, found: 304.1167.

5-Azido-2'-ethyl-6'-methyl-2-nitrosodiphenylamine (2f). Brown solid (125 mg, 89%); mp 130-132 °C (dec.); ¹H NMR (500 MHz, CDCl₃): δ 1.10 (t, *J* 7.5 Hz, 3H), 2.08 (s, 3H), 2.40-2.46(m, 2H), 5.80 (s, 1H), 6.67 (br s, 1H), 7.14-7.19 (m, 2 H), 7.23-7.25 (m, 1H), 8.80 (br s, 1H), 12.06 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 14.8, 18.1, 24.8,

102.6, 109.1, 127.1, 128.3, 128.8, 132.7, 135.9, 136.6, 141.6, 143.2, 149.6, 154.6; MS (ESI): *m/z* 280 [M-H]⁺, HRMS (ESI): *m/z* calcd for C₁₅H₁₄N₅O: 280.1998, found: 280.1998.

5-Azido-3-chloro-2', 6'-dimethyl-2-nitrosodiphenylamine (2g). Brown crystals, crude yield 148 mg, 98%), after column chromatography (hexane/EtOAc) 95 mg, 63%). mp 128-130 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.08 (s, 6H), 5.73 (d, *J* 2.2 Hz, 1H), 6.74 (d, *J* 2.2 Hz, 1H), 7.13-7.16 (m, 2 H), 7.19-7.23 (m, 1H), 12.62 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 18.0, 101.9, 110.1, 128.4, 128.9, 132.9, 135.5, 137.6, 147.6, 150.1, 150.5; MS (EI): *m/z* (%) 301 (73), 258 (74), 207 (82), 193 (100), 144 (95), HRMS (EI): *m/z* calcd for $C_{14}H_{12}^{35}CIN_5O$: 301.0730, found: 301.0723.

General procedure for the reactions of 3-chloro-2-nitrosodiarylamines 1h and 1i with sodium azide. A mixture of 2-nitrosodiarylamine 1 (0.5 mmol) and sodium azide (129 mg, 2.0 mmol) in DMF (5 mL) was stirred at room temperature for 10 days or for 24 h at 80 °C with comparable results. When the reaction was complete the mixture was diluted with water (70 mL) and extracted with EtOAc (30 mL). The extract was washed with water (3 x 50 mL), brine and dried (Na₂SO₄). The solvent was evaporated to obtain crude products which were purified by column chromatography (SiO₂, hexane/ethyl acetate, 9:1 to 1:1) then recrystallized from *i*-PrOH for analytical purposes.

N-(2,6-Dimethylphenyl)-2,1,3-benzoxadiazol-4-amine (4a). Yellow crystals, 92 mg, 77% yield. mp 116-117 °C (*i*-PrOH); ¹H NMR (500 MHz, CDCl₃): δ 2.26 (s, 6H), 5.72 (d, *J* 7.1 Hz, 1H), 6.28 (br s, 1H), 7.09 (d, *J* 8.9 Hz, 1H), 7.14 (dd, *J* 8.9, 7.1 Hz, 1H), 7.17-7.21 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 18.0,102.9, 103.1, 127.4, 128.8, 133.9, 134.5, 135.5, 136.4, 144.7, 150.2. MS (EI): *m/z* (%) 239 (87), 224 (47), 194 (100). HRMS (EI): *m/z* calcd for C₁₄H₁₃N₃O: 239.1059, found: 239.1065.

N-(2,6-Dimethylphenyl)-6-methoxy-2,1,3-benzoxadiazol-4-amine (4b). Yellow crystals, 103 mg, 76% yield. mp 126-128 °C (*i*-PrOH); ¹H NMR (500 MHz, CDCl₃): δ 2.55 (s, 6H), 3.81 (s, 3H), 5.43 (d, *J* 1.9 Hz, 1H), 6.23 (br s, 1H), 6.26 (d, *J* 1.9 Hz, 1H), 7.15-7.18 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 18.0, 55.6, 78.8, 99.3, 127.5, 128.8, 134.9, 135.2, 136.3, 143.3, 151.0, 164.6. MS (EI): *m/z* (%) 269 (100), 254 (41), 224 (90). HRMS (EI): *m/z* calcd for C₁₅H₁₅N₃O: 269.1164, found: 269.1173.

General procedure for the double condensation of 5-azido-2-nitrosodiarylamines 2 with dicarbonyl compounds. A solution of 2 (0.5 mmol), the dicarbonyl compound (1.1 mmol) and *t*-BuNH₂ (175 mg, 2.4 mmol) in CH₃CN (5.0 mL) was stirred at room temperature for 24 h. When the reaction was complete CH₃CN was evaporated. Water (4 mL) was added to the residue and the mixture was extracted with EtOAc (10 mL). The extract was dried (Na₂SO₄) and the solvent was evaporated. The crude product was purified by column chromatography (SiO₂, hexane/ethyl acetate, 9:1 to 2:1) to obtain pure product **5**.

1-{1-[2-Acetyl-4-(4-chloro-2-iodophenyl)-3-methylene-3,4-dihydroquinoxalin-6-yl]-5-methyl-1*H***-1,2,3-triazol-4-yl}ethanone (5a**). Dark solid (135 mg, 49%). mp 93-96 °C (dec.); ¹H NMR (500 MHz, CDCl₃): δ 2.51 (s, 3H), 2.64 (s, 3H), 2.69 (s, 3H), 3.68 (d, *J* 2.6 Hz, 1H), 4.99 (d, *J* 2.6 Hz, 1H), 5.92 (d, *J* 2.1 Hz, 1H), 6.93 (dd, *J* 8.2, 2.1 Hz, 1H), 7.27 (d, *J* 8.2 Hz, 1H), 7.57 (d, *J* 2.3 Hz, 1H), 7.56-7.63 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 10.2, 27.7, 27.8, 92.8, 99.6, 108.8, 117.3, 131.1, 131.4, 132.0, 132.9, 134.5, 136.1, 136.4, 137.1, 137.3, 138.3, 141.5, 143.7, 156.6, 194.2, 198.7; MS (EI): m/z (%) 545 (21), 390 (17), 43 (100); HRMS (EI): m/z calcd for $C_{22}H_{17}^{35}$ ClIN₅O₂: 545.0116, found: 545.0125.

1-{1-[2-Acetyl-4-(2,6-dimethylphenyl)-3-methylene-3,4-dihydroquinoxalin-6-yl]-5-methyl-1*H***-1,2,3-triazol-4-yl}ethanone** (**5b**). Dark red solid (170 mg, 82%). mp 128-133 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.13 (s, 6H), 2.43 (s, 3H), 2.64 (s, 3H), 2.68 (s, 3H), 3.65 (d, *J* 1.9 Hz, 1H), 4.87 (d, *J* 1.9 Hz, 1H), 5.86 (d, *J* 2.0 Hz, 1H), 6.89 (dd, *J*

8.2, 2.0 Hz, 1H), 7.22-7.27 (m, 3H), 7.56 (d, *J* 8.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.1, 17.7, 27.7, 27.8, 90.3, 107.7, 116.6, 129.5, 130.1, 131.0, 132.8, 133.8, 134.0, 136.4, 136.6, 137.1, 137.5, 143.7, 157.0, 194.2, 199.0; MS (EI): *m/z* (%) 413 (53), 370 (96), 342 (100); HRMS (EI): *m/z* calcd for C₂₄H₂₃N₅O₂: 413.1852, found: 413.1847.

Ethyl 6-[4-(ethoxycarbonyl)-5-methyl-1*H*-1,2,3-triazol-1-yl]-4-(2,6-dimethylphenyl)-3-methylene-3,4dihydroquinoxaline-2-carboxylate (5c). Brown solid (52 mg, 22%). mp 93-96 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.40 (t, *J* 7.2 Hz, 3H), 1.44 (t, *J* 7.2 Hz, 3H), 2.14 (s, 6H), 2.42 (s, 3H), 3.64 (d, *J* 2.4 Hz, 1H), 4.39-4.48 (m, 5H), 5.88 (d, *J* 2.2 Hz, 1H), 6.91 (dd, *J* 8.3, 2.2 Hz, 1H), 7.23-7.28 (m, 3H), 7.60 (d, *J* 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 9.9, 14.1, 14.3, 17.7, 61.1, 62.4, 89.1, 107.9, 117.1, 129.6, 130.1, 130.8, 132.9, 133.9, 134.8, 136.0, 136.4, 136.8, 137.2, 138.6, 155.3, 161.6, 164.1; MS (EI): *m/z* (%) 473 (70), 430 (100), 372 (74), 356 (57); HRMS (EI): *m/z* calcd for C₂₆H₂₇N₅O₄: 473.2063, found: 473.2061.

1-{1-[4-(2,6-Dimethylphenyl)-2-isobutyryl-3-methylene-3,4-dihydroquinoxalin-6-yl]-5-methyl-1H-1,2,3triazol-4-yl}-2-methylpropan-1-one (5d). Red solid (130 mg, 54%). mp 143-144 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.22 (d, *J* 6.9 Hz, 6H), 1.24 (d, *J* 6.9 Hz, 6H), 2.14 (s, 6H), 2.44 (s, 3H), 3.61 (d, *J* 2.2 Hz, 1H), 3.64 (q, *J* 6.9 Hz, 1H), 3.85 (q, *J* 6.9 Hz, 1H), 4.67 (d, *J* 2.2 Hz, 1H), 5.91 (d, *J* 2.0 Hz, 1H), 6.90 (dd, *J* 8.2, 2.0 Hz, 1H), 7.22-7.90 (m, 3H), 7.54 (d, *J* 8.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.1, 17.6, 17.7, 18.6, 37.1, 37.4, 89.6, 107.8, 116.8, 129.5, 130.1, 130.6, 133.0, 134.1, 134.7, 136.2, 136.5, 137.2, 137.7, 142.5, 159.6, 200.7, 204.6; MS (EI): *m/z* (%) 469 (100), 440 (55), 370 (56), 300 (38); HRMS (EI): *m/z* calcd for C₂₈H₃₁N₅O₂: 469.2478, found: 469.2483.

1-{1-[2-Acetyl-4-(2-iodo-4-methylphenyl)-3-methylene-3,4-dihydroquinoxalin-6-yl]-5-methyl-1H-1,2,3-

triazol-4-yl}ethanone (**5e**). Brown solid (147 mg, 56%). mp 67-71 °C. ¹H NMR (600 MHz, CDCl₃): δ 2.39 (s, 3H), 2.49 (s, 3H), 2.63 (s, 3H), 2.69 (s, 3H), 3.68 (d, *J* 2.4 Hz, 1H), 4.93 (d, *J* 2.4 Hz, 1H), 5.88 (d, *J* 2.2 Hz, 1H), 6.91 (dd, *J* 8.3, 2.2 Hz, 1H), 7.16 (d, *J* 8.0 Hz, 1H), 7.36 (ddd, *J* 8.0, 2.0, 0.7 Hz, 1H), 7.56 (d, *J* 8.3 Hz, 1H), 7.89 (dd, *J* 2.0, 0.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 10.2, 20.7, 26.9, 27.7, 92.3, 98.6, 109.0, 116.9, 130.0, 130.9, 132.4, 132.9, 134.8, 136.8, 136.9, 137.0, 137.3, 141.6, 142.3, 143.7, 157.0, 194.3, 198.9; MS (EI): *m/z* (%) 525 (39), 370 (48), 302 (40), 43 (100); HRMS (EI): *m/z* calcd for C₂₃H₂₀N₅IO₂: 525.0662, found: 525.0671.

1-{1-[2-Acetyl-4-(2-t-butylphenyl)-3-methylene-3,4-dihydroquinoxalin-6-yl]-5-methyl-1H-1,2,3-triazol-4-

yl}ethanone (**5f**). Brown solid (112 mg, 51%). mp 89-91 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.34 (s, 9H), 2.44 (s, 3H), 2.62 (s, 3H), 2.68 (s, 3H), 3.68 (d, *J* 1.8 Hz, 1H), 4.97 (d, *J* 1.8 Hz, 1H), 5.92 (d, *J* 2.0 Hz, 1H), 6.86 (dd, *J* 8.2, 2.0 Hz, 1H), 7.00 (d, *J* 7.6 Hz, 1H), 7.36-7.45 (m, 2H), 7.54 (d, *J* 8.2, 1H), 7.68 (d, *J* 7.6 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.1, 27.7, 27.8, 31.8, 36.1, 94.0, 110.38, 116.6, 129.6, 129.7, 130.6, 131.1, 131.7, 133.2, 134.9, 136.9, 137.1, 137.5, 139.3, 143.6, 148.1, 156.9, 194.2, 198.9; MS (EI): *m/z* (%) 541 (33), 398 (100), 370 (55), 356 (52); HRMS (EI): *m/z* calcd for C₂₆H₂₇N₅O₂: 441.2165, found: 441.2161.

1-{1-[2-Acetyl-3-methylene-4-(2,4,6-trimethylphenyl) -3,4-dihydroquinoxalin-6-yl]-5-methyl-1*H***-1,2,3-triazol-4-yl}ethanone (5g**). Dark solid (136 mg, 66%). mp 95-99 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.08 (s, 6H), 2.32 (s, 3H), 2.44 (s, 3H), 2.63 (s, 3H), 2.69 (s, 3H), 3.68 (d, *J* 1.8 Hz, 1H), 4.84 (d, *J* 1.8 Hz, 1H), 5.89 (d, *J* 2.1 Hz, 1H), 6.88 (dd, *J* 8.3, 2.1 Hz, 1H), 7.03 (s, 2H), 7.54 (d, *J* 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.1, 17.6, 21.1, 26.9, 27.7, 27.8, 90.2, 107.9, 116.5, 130.8, 130.9, 131.3, 132.9, 134.0, 135.9, 136.9, 137.1, 137.5, 139.4, 143.7, 157.1, 194.3, 199.1; MS (EI): *m/z* (%) 427 (56), 384 (83), 356 (87), 314 (37), 43 (100); HRMS (EI): *m/z* calcd for $C_{25}H_{25}N_5O_2$: 427.2010, found: 427.2008.

1-{1-[2-IsobutyryI-3-methylene-4-(2,4,6-trimethylphenyI)-3,4-dihydroquinoxalin-6-yI]-5-methyl-1H-1,2,3-triazoI-4-yI}-2-methylpropan-1-one (5h). Brown solid (97 mg, 40%). mp 166-170 °C (dec). ¹H NMR (600 MHz, CDCl₃): δ 1.23 (d, *J* 7.0 Hz, 6H), 1.24 (d, *J* 7.0 Hz, 6H), 1.25 (s, 3H), 2.09 (s, 6H), 2.32 (s, 3H), 2.45 (s, 3H), 3.62 (br s, 1H), 3.63 (sept, *J* 7.0, 1H), 3.86 (sept, *J* 7.0, 1H), 4.44 (br s, 1H), 5.94 (d, *J* 2.2 Hz, 1H), 6.89 (dd, *J* 8.2, 2.2 Hz,

1H), 7.03 (s, 2H), 7.53 (d, *J* 8.2, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 10.1, 17.5, 17.6, 18.6, 21.1, 37.1, 37.4, 89.5, 108.0, 116.6, 129.9, 130.5, 130.8, 131.4, 133.0, 136.0, 136.4, 137.1, 137.7, 139.4, 142.5, 159.6, 200.7, 204.7; MS (ESI): *m/z* (%) 484 [M]⁺, HRMS (ESI): *m/z* calcd for C₂₉H₃₄N₅O₂: 484.2713, found: 484.2709.

1-{1-[2-Acetyl-4-(2-ethyl-6-methylphenyl)-3-methylene-3,4-dihydroquinoxalin-6-yl]-5-methyl-1H-1,2,3triazol-4-yl}ethanone (5i). Dark solid (151 mg, 71%). mp 94-98 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.16 (t, *J* 7.6 Hz, 3H), 2.13 (s, 3H), 2.42 (s, 3H), 2.43-2.56 (m, 2H), 2.64 (s, 3H), 2.68 (s, 3H), 3.66 (d, *J* 2.0 Hz, 1H), 4.87 (d, *J* 2.0 Hz, 1H), 5.85 (d, *J* 2.2 Hz, 1H), 6.9 ((dd, *J* 8.3, 2.2 Hz, 1H), 7.23-7.35 (m, 3H), 7.55 (d, *J* 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.1, 13.7, 17.9, 23.6, 27.7, 27.8, 90.7, 108.1, 116.6, 128.1, 129.7, 130.1, 131.0, 132.8, 133.5, 134.3, 136.3, 137.0, 137.1, 137.4, 141.9, 143.7, 157.0, 194.2, 199.0; MS (EI): *m/z* (%) 427 (46), 384 (100), 356 (96); HRMS (EI): *m/z* calcd for C₂₅H₂₅N₅O₂: 427.2004, found: 427.2008.

1-{1-[2-IsobutyryI-3-methylene-4-(2-ethyl-6-methylphenyI)-3,4-dihydroquinoxalin-6-yI]-5-methyl-1*H***-1,2,3-triazoI-4-yI}-2-methylpropan-1-one (5j). Brown solid (111 mg, 46%). mp 99-103 °C. ¹H NMR (600 MHz, CDCI₃): δ 1.16 (t,** *J* **7.6 Hz, 3H), 1.23 (d,** *J* **6.9 Hz, 6H), 1.24 (d,** *J* **6.9 Hz, 3H), 1.25 (d,** *J* **6.9 Hz, 3H), 2.13 (s, 3H), 2.43 (s, 3H), 2.44-2.57 (m, 2H), 3.61 (d,** *J* **2.0 Hz, 1H), 3.62-3.67 (m, 2H), 4.47 (d,** *J* **2.0 Hz, 1H), 5.91 (d,** *J* **2.2 Hz, 1H), 6.90 (dd,** *J* **8.2, 2.2 Hz, 1H), 7.24-7.36 (m, 3H), 7.54 (d,** *J* **8.2 Hz, 1H); ¹³C NMR (150 MHz, CDCI₃): δ 10.1, 13.7, 17.5, 17.6, 17.8, 18.6, 23.6, 26.9, 37.1, 37.4, 90.0, 108.1, 116.7, 128.1, 129.7, 130.1, 130.5, 132.9, 133.6, 135.2, 136.4, 136.6, 137.0, 137.7, 141.9, 142.5, 159.6, 200.7, 204.6; MS (ESI):** *m/z* **(%) 484 [M]⁺, HRMS (ESI):** *m/z* **calcd for C₂₉H₃₄N₅O₂: 484.2713, found: 484.2711.**

Methyl 4-(2,6-dimethylphenyl)-6-fluoro-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (6a). Beige precipitate (133 mg, 81%). mp 134-135 °C. ¹H NMR (600 MHz, CDCl₃): δ 1.99 (s, 6H), 4.03 (s, 3H), 6.25 (dd, *J* 9.7, 2.5 Hz, 1H), 7.11 (dd, *J* 8.7, 2.5 Hz, 1H), 7.26-7.29 (m, 2H), 7.35-7.39 (m, 1H), 8.02 (dd, *J* 8.7, 5.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 17.6, 53.2, 101.2 (d, *J*_{CF} 28 Hz), 112.9 (d, *J*_{CF} 24 Hz), 128.7 (d, *J*_{CF} 2 Hz), 129.4, 130.0, 132.8, 133.4 (d, *J*_{CF} 11 Hz), 135.2, 135.7 (d, *J*_{CF} 12 Hz), 148.1 (d, *J*_{CF} 4 Hz), 151.1, 163.6, 165.1 (d, *J*_{CP} 255 Hz); MS (ESI): *m/z* (%) 327 [M]⁺ HRMS (ESI): *m/z* calcd for C₁₈H₁₆FN₂O₃: 327.1145, found: 327.1140.

3-Benzoyl-1-(4-chlorophenyl)-7-fluoroquinoxalin-2(1*H***)-one (6b). Pale yellow crystals (113 mg, 60%). mp 168-169 °C. ¹H NMR (600 MHz, CDCl₃): \delta 6.47 (dd,** *J* **9.8, 2.6 Hz, 1H), 7.10 (ddd,** *J* **9.0, 8.0, 2.6 Hz, 1H), 7.28-7.31 (m, 2H), 7.48-7.52 (m, 2H), 7.59-7.66 (m, 3H), 7.94 (dd,** *J* **9.0, 5.8 Hz, 1H), 8.01-8.04 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): \delta 102.3 (d,** *J***_{CP} 28 Hz), 112.6 (d,** *J***_{CP} 24 Hz), 128.7, 128.8, 129.5, 130.0, 130.8, 132.9 (d,** *J***_{CP} 11 Hz), 133.0, 134.3, 134.7, 136.1 (d,** *J***_{CP} 12 Hz), 136.2, 152.6, 153.9 (d,** *J***_{CP} 4 Hz), 163.2, 164.2 (d,** *J***_{CP} 254 Hz), 190.9; MS (EI):** *m/z* **(%) 380 (20), 378 (41, [M]⁺), 349 (21), 105 (100); HRMS (EI):** *m/z* **calcd for C₂₁H₁₂³⁵CIFN₂O₂: 378.0571, found: 378.0572.**

Methyl 6-chloro-4-(4-methylphenyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (6c). Pale beige crystals (104 mg, 64%). mp 206-207 °C. ¹H NMR (600 MHz, CDCl₃): δ 2.48 (s, 3H), 4.02 (s, 3H), 6.74 (d, *J* 2.1 Hz, 1H), 7.14-7.17 (m, 2H), 7.31 (dd, *J* 8.6, 2.1 Hz, 1H), 7.41-7.44 (m, 2H), 7.90 (d, *J* 8.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 21.3, 53.2, 115.6, 124.9, 127.6, 130.3, 131.2, 131.7, 131.9, 136.0, 138.6, 140.3, 149.1, 152.1, 163.6; MS (EI): m/z (%) 330 (38), 238 (71), 240 (100); HRMS (EI): m/z calcd for C₁₇H₁₃³⁵ClN₂O₃: 328.0615, found: 328.0618.

Synthesis of 7-azidoquinazolinones 7a-c. General procedure. 7-Fluoro or 7-chloroquinoxalinone **6** (0.5 mmol) and sodium azide (162 mg, 2.5 mmol) were stirred in DMF (3.0 mL) at room temperature (**6a** and **6b**) or at 80 °C (**6c**) for 12 - 48 h (tlc control). After the reaction was complete the mixture was dissolved with water and extracted with EtOAc. The extract was washed thoroughly with water then with brine and dried (Na₂SO₄).

After evaporation the solid residue was recrystallized from *i*-PrOH (**7a** and **7b**) or the product was isolated by column chromatography (SiO₂, hexane/EtOAc) (**7c**).

Methyl 6-azido-4-(2,6-dimethylphenyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (7a). Yellow powder (122 mg, 70%). mp 153-155 °C (*i*-PrOH). ¹H NMR (600 MHz, CDCl₃): δ 1.98 (s, 6H), 4.03 (s, 3H), 6.09 (d, *J* 2.3 Hz, 1H), 7.10 (dd, *J* 8.7, 2.3 Hz, 1H), 7.25-7.28 (m, 2H), 7.34-7.38 (m, 1H), 8.02 (d, *J* 8.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 17.6, 53.2, 104.1, 115.5, 129.4, 130.0, 132.7, 132.8, 135.22, 135.23, 135.5, 145.1, 147.6, 151.2, 163.7; MS (EI): *m/z* (%) 349 (36), 321 (100), 306 (47), 274 (43), 234 (56); HRMS (EI): *m/z* calcd for C₁₈H₁₅N₅O₃: 349.1175, found: 349.1169.

7-Azido-3-benzoyl-1-(4-chlorophenyl)quinoxalin-2(1*H***)-one (7b)**. Creamy powder (175 mg, 80%). mp 172-176 °C (dec.); ¹H NMR (600 MHz, CDCl₃): δ 6.60 (d, *J* 2.2 Hz, 1H), 7.08 (dd, *J* 8.6, 2.2 Hz, 1H), 7.25-7.29 (m, 2H), 7.48-7.52 (m, 2H), 7.59-7.66 (m, 3H), 7.93 (d, *J* 8.6 Hz, 1H), 8.01-8.04 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 105.3, 115.3, 128.7, 129.3, 129.6, 130.1, 130.8, 132.4, 132.9, 134.3, 134.8, 136.0, 136.1, 144.0, 152.7, 153.7, 191.0; MS (EI): *m/z* (%) 401 (7), 375 (28), 373 (33), 345 (33), 105 (100); HRMS (EI): *m/z* calcd for C₂₁H₁₂³⁵ClN₅O₂: 401.0680, found: 401.0682.

Methyl 6-azido-4-(4-methylphenyl)-3-oxo-3,4-dihydroquinoxaline-2-carboxylate (7c). Yellow crystals (62 mg, 37%). mp 180 °C (dec.); ¹H NMR (500 MHz, CDCl₃): δ 2.47 (s, 3H), 3.17 (s, 3H), 6.29 (d, *J* 2.3 Hz, 1H), 7.05 (dd, *J* 8.6, 2.3 Hz, 1H), 7.13-7.16 (m, 2H), 7.39-7.42 (m, 2H), 7.96 (d, *J* 8.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 21.3, 53.2, 105.5, 115.3, 127.6, 129.2, 131.1, 131.9, 132.5, 136.8, 140.2, 144.4, 147.5, 152.3, 163.7; MS (EI): m/z (%) 335 (45), 307 (100), 279 (51), 247 (59), 219 (75), 304 (71); HRMS (EI): m/z calcd for C₁₇H₁₃N₅O₃: 335.1018 , found: 335.1027

Synthesis of triazoles 8a-c from dihydroquinoxalines 7a-c. A solution of 7 (0.5 mmol), acetylacetone (1.1 mmol) and t-BuNH₂ (175 mg, 2.4 mmol) in CH₃CN (5.0 mL) was stirred for 24 h at room temperature. The volatile materials were evaporated and the residue was. The crude product was purified by column chromatography (SiO₂, hexane/ethyl acetate) (8a) or treated with MeOH and the precipitate was filtered off, washed with MeOH and dried on air (8b and 8c). Analytical samples were recrystallized from MeOH or EtOAc.

Methyl 6-(4-acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-4-(2,6-dimethylphenyl)-3-oxo-3,4-dihydroquinoxaline-2carboxylate (8a). Pale yellow powder (100 mg, 46%). mp 218-219 °C (MeOH). ¹H NMR (500 MHz, CDCl₃): δ 2.02 (s, 6H), 2.50 (s, 3H), 2.70 (s, 3H), 4.06 (s, 3H), 6.65 (d, *J* 2.0 Hz, 1H), 7.25-7.28 (m, 2H), 7.33-7.38 (m, 1H), 7.52 (dd, *J* 8.6, 1H), 8.22 (d, *J* 8.6 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.2, 17.6, 27.9, 53.4, 110.8, 120.6, 129.6, 130.4, 132.0, 132.3, 132.6, 134.7, 135.2, 137.2, 138.2, 144.0, 150.8, 151.3, 163.4, 194.1; MS (EI): *m/z* (%) 431 (94), 403 (61), 388 (56), 361 (46), 316 (59), 301 (60), 272 (68), 219 (100); HRMS (EI): *m/z* calcd for $C_{23}H_{12}N_5O_4$: 431.1594, found: 431.1602.

7-(4-Acetyl-5-methyl-1*H***-1**,2,3-triazol-1-yl)- **3-benzoyl-1-(4-chlorophenyl)quinoxalin-2(1***H***)-one (8b).** Pale yellow crystals (200 mg, 81%). mp 246-247 °C (EtOAc). ¹H NMR (500 MHz, CDCl₃): δ 2.59 (s, 3H), 2.74 (s, 3H), 6.95 (d, *J* 2.0 Hz, 1H), 7.33-7.36 (m, 2H), 7.48 (dd, *J* 8.6, 2.0 Hz, 1H), 7.55 (t, *J* 7.7 Hz, 2H), 7.59-7.63 (m, 2H), 7.67-7.71 (m, 1H), 8.06 (d, *J* 7.5 Hz, 2H), 8.17 (d, *J* 8.6 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.3, 27.9, 112.3, 120.5, 128.8, 129.5, 130.0, 131.0, 132.1, 132.2, 132.5, 134.4, 134.6, 135.4, 136.6, 137.3, 137.4, 144.0, 152.3, 156.9, 190.5, 194.1; MS (EI): *m/z* (%) 483 (3), 413 (12), 105 (100); HRMS (EI): *m/z* calcd for C₂₆H₁₈³⁵ClN₅O₃: 483.1098, found: 483.1107.

Methyl 6-(4-acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-4-(4-methylphenyl)-3-oxo-3,4-dihydroquinoxaline-2carboxylate (8c). Colorless powder (81 mg, 81%). mp 255-257 °C (*i*-PrOH/EtOAc). ¹H NMR (500 MHz, CDCl₃): δ 2.45 (s, 3H), 2.53 (s, 3H), 2.71 (s, 3H), 4.05 (s, 3H), 6.87 (d, *J* 2.1 Hz, 1H), 7.17-7.20 (m, 2H), 7.39-7.42 (, 2H), 7.45 (dd, J 8.5, 2.1 Hz, 1H), 8.17 (d, J 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 10.3, 21.3, 27.9, 53.4, 112.4, 120.3, 127.5, 131.3, 131.4, 131.8, 132.3, 136.1, 137.3, 137.6, 140.6, 143.9, 151.0, 151.9, 163.4, 194.1; MS (EI): *m/z* (%) 417 (56), 389 (70), 374 (47), 347 (100), 260 (50); HRMS (EI): *m/z* calcd for C₂₂H₁₉N₅O₄: 417.1437, found: 417.1433.

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