Copper Catalyzed Aerobic Oxidative Alkynylation of 3,4-Dihydroquinoxalin-2-ones

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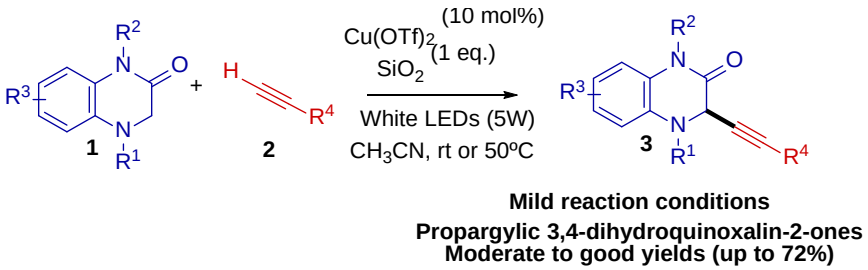

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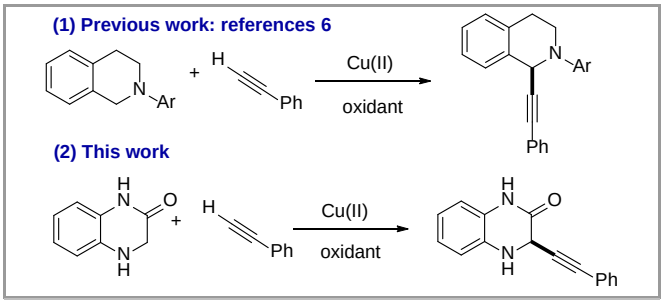
Abstract Herein, we described a ligand-free copper catalyzed aerobic oxidative functionalization of 3,4-dihydroquinoxalin-2-ones with terminal alkynes using visible-light and oxygen as terminal oxidant. The corresponding products are obtained with moderate to good yields. Moreover, we demonstrate the versatility of the propargylic 3,4-dihydroquinoxalin-2-ones obtained, preparing several 3,4-dihydroquinoxalin-2-one derivatives.

Key words dihydroquinoxalinones, alkynes, copper, cross-dehydrogenative coupling, oxidation, nitrogen heterocycles

The creation of carbon-carbon (C-C) bonds is a fundamental transformation in organic synthesis, therefore the development of methodologies for C-C bond formation plays a central role in organic chemistry. In this context, the construction of C-C bonds through cross-dehydrogenative coupling (CDC) of two accessible C-H bonds, under oxidative conditions, has emerged as one of the most straightforward approach for increasing molecular complexity from an economical point of view with the minimal waste generation.[1] In this regard, the oxidative dehydrogenative sp^3-C-H functionalization of tertiary amines have become a hot topic in organic synthesis in the last years.[2] From all CDC of tertiary amines, the oxidative alkynylation represents a powerful transformation because this methodology affords propargylic amines,[3] which are versatile building blocks for the synthesis of fine chemicals, pharmaceuticals, agrochemicals or natural products.[4] Several copper catalyzed oxidative alkynylation of amines have been described in the literature using acyclic[5] and cyclic[6] tertiary amines. For example, Li described the alkynylation of *N*,*N*-dimethylanilines[5a] as well as *N*-aril tetrahydroisoquinolines[6a-b] using CuBr as catalyst and stoichiometric tBuOOH as oxidant. Fu[5b] described the copper catalyzed alkynylation of acyclic tertiary amines using *N*-bromosuccinimide (NBS) as oxidant, while Li[5f] described the use of diethyl azodicarboxylate (DEAD) as oxidant. Concerning cyclic amines, Rueping[6c] and Khan[6e] described the copper catalyzed oxidative alkynylation of *N*-aril tetrahydroisoquinolines using visible-light and O_2 as oxidant. However, the corresponding oxidative alkynylation of dihydroquinoxalin-2-ones has not been described despite the importance of such scaffold in medicinal chemistry (Scheme 1).



Scheme 1 Oxidative cross-dehydrogenative coupling of cyclic amines with terminal alkynes

Quinoxaline derivatives are an important class of nitrogen heterocyclic compounds present in numerous pharmaceuticals and biologically active compounds.[7] Consequently, many of them serve as key building blocks in synthesis of pharmaceutical products. In this context, 3,4-dihydroquinoxalin-2-ones and their derivatives display a wide spectrum of biological activities such as antiviral,[8] antidepressant,[9] antitumoral,[10] anxiolytic[11] among others (Figure 1). Therefore, the functionalization of dihydroquinoxalin-2-one derivatives is significant for pharmaceutical industry. In this context, several oxidative functionalization of dihydroquinoxalinones have been described recently.[12] For example, in 2016 Xiao reported the photocatalytic functionalization with benzophenone,[12a] while Hong, in 2018,

reported the Friedel-Crafts alkylation of dihydroquinoxalines under visible-light irradiation.[12b]

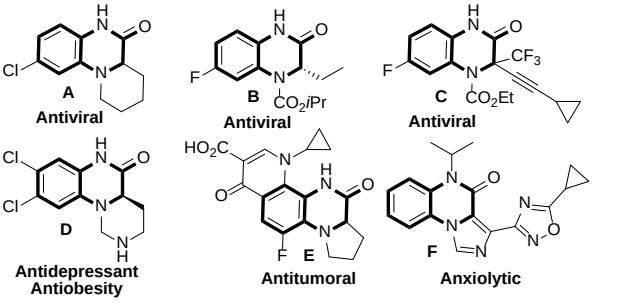
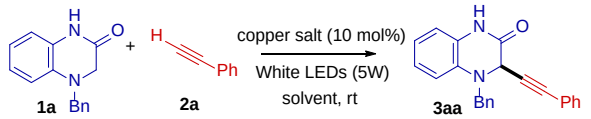


Figure 1 Biologically active 3,4-dihydroquinoxalin-2-one derivatives

Continuing with our efforts for the synthesis of propargylic amines[13] and the oxidative sp^3-C-H functionalization of amines,[14] in this communication, we report the oxidative alkynylation of 3,4-dihydroquinoxalin-2-ones with terminal alkynes using simple $Cu(OTf)_2$ as catalyst and oxygen as terminal oxidant under visible light irradiation.[15]

Table 1 Optimization of reaction conditions for the oxidative alkynylation.[a]



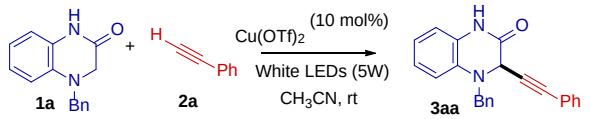
Entry	Cu salt (10 mol%)	solvent	t (h)	**3aa** (%)[b]
1	CuCl	CH_3CN	1.5	44
2	CuI	CH_3CN	48	-
3	$CuCl_2$	CH_3CN	1.5	27
4	$CuBr_2$	CH_3CN	24	32
5	$Cu(OAc)_2{\cdot}H_2O$	CH_3CN	96	21
6	$Cu(OTf)_2$	CH_3CN	20	54
7	-	CH_3CN	48	-
8	$Cu(OTf)_2$	CH_3OH	19	33
9	$Cu(OTf)_2$	toluene	120	50
10	$Cu(OTf)_2$	$CHCl_3$	216	29
11	$Cu(OTf)_2$	THF	216	30
12	$Cu(OTf)_2$	DMF	216	23
13	$Cu(OTf)_2$	DMSO	216	33
14[c]	$Cu(OTf)_2$	CH_3CN	24	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), copper salt (10 mol%) in 1mL of solvent under open air atmosphere. [b] Yields after column chromatography. [c] The reaction was runned under Ar atmosphere.

Our investigation was started by examining the model reaction of 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one **1a** with phenylacetylene (**2a**) using copper salts as catalysts under visible-light irradiation and open air atmosphere. As shown in Table 1, we started the optimization process with the screening of several copper salts (10 mol%, entries 1-6) at room temperature in CH_3CN, obtaining the best yield of the alkynylated product **3aa** when $Cu(OTf)_2$ was used (54% yield). If the reaction was runned in the absence of copper salt, product **3aa** was not observed (entry 7). Next, different solvents including CH_3OH, toluene, $CHCl_3$, THF, DMF and DMSO were further screened (entries 8-13). The yield of **3aa** did not improve in any case compared to that obtained when acetonitrile was used as a solvent (entry 6). If the reaction was runned under argon atmosphere the conversion to product **3aa** was very low (entry 14) indicating that O_2 is necessary in the reaction.

To further improve the efficiency of the oxidative alkynylation reaction, several additives were tested (Table 2, entries 1-9). From all the additives evaluated, CH_3CO_2H and SiO_2 improved the yield of the functionalized dihydroquinoxaline **3aa** to 66% and 68%, respectively. Next, using these additives different sources of light were evaluated (11 W white bulb and Blue LEDs, entries 9-12), observing a slightly decrease on the efficiency of the alkynylation reaction. After, the effect of the visible-light was evaluated by performing the reaction under darkness (entries 13-14). The corresponding product **3aa** was also obtained, however with a diminished yield (48% and 51%). Finally, we tried to decrease the equivalents of alkyne to 2.5 (entry 15) and reduce the catalyst loading to 5 mol% (entry 16), but the dihydroquinoxalinone **3aa** was obtained with lower yield.

Table 2 Optimization of reaction conditions for the oxidative alkynylation.[a]

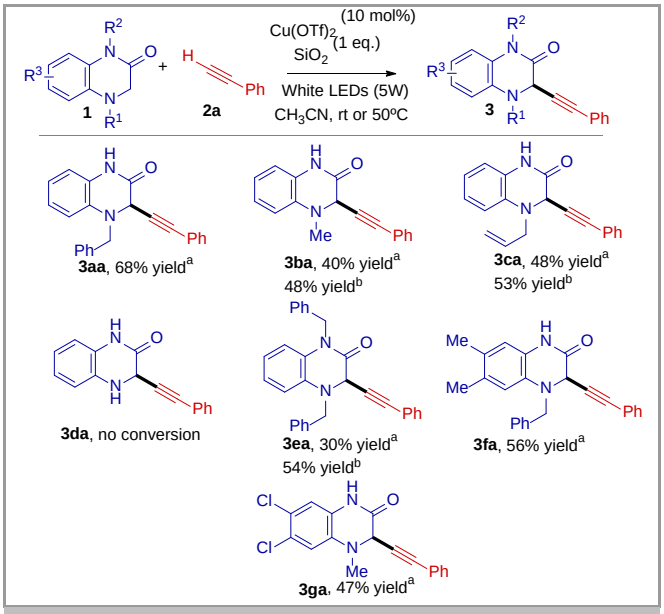


Entry	Source of light	Additive (1 eq.)	t (h)	**3aa** (%)[b]
1	White LEDs (5W)	$PhCO_2H$	48	47
2	White LEDs (5W)	CH_3CO_2H	26	66
3	White LEDs (5W)	CF_3CO_2H	3	20
4	White LEDs (5W)	*p*TsOH	27	24
5	White LEDs (5W)	*i*Pr$_2$NEt	72	-
6	White LEDs (5W)	$(PhO)_2PO_2H$	35	44
7	White LEDs (5W)	3Å MS	29	38
8	White LEDs (5W)	SiO_2	27	68
9	11 W white bulb	CH_3CO_2H	6	59
10	11 W white bulb	SiO_2	6	60
11	Blue LEDs	CH_3CO_2H	6	56
12	Blue LEDs	SiO_2	6	60
13	In the darkness	CH_3CO_2H	25	48
14	In the darkness	SiO_2	25	51
15[c]	White LEDs (5W)	SiO_2	25	53
16[c,d]	White LEDs (5W)	SiO_2	25	22

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of solvent under open air atmosphere. [b] Yields after column chromatography. [c] 2.5 eq. of **2a**. [d] $Cu(OTf)_2$ (5 mol%)

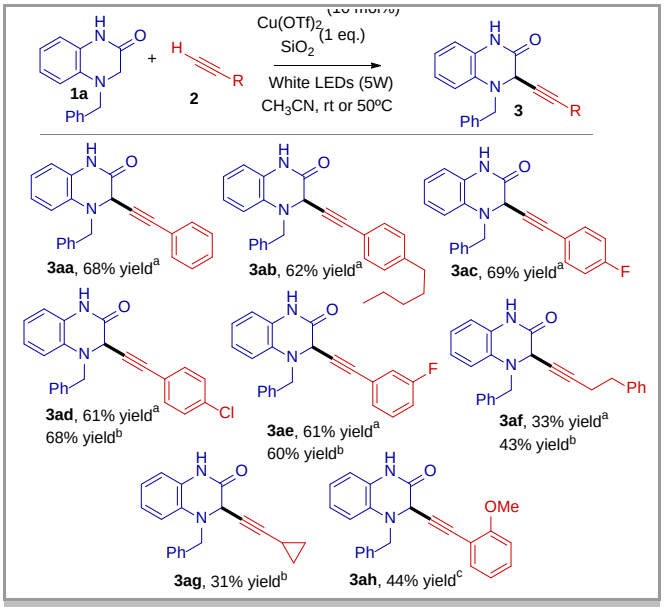
With the optimal conditions established for **3aa** (Table 2, entry 8), the substrate scope of the alkynylation reaction was studied.

First, we studied the reaction of several 3,4-dihydroquinoxalin-2-ones **1** with phenyl acetylene (**2a**) (Scheme 2). The reaction tolerates different protecting groups (Bn, Me, allyl) at the amine group of the quinoxalin-2-ones. Nevertheles, when the protecting groups are methyl or allyl, the yields are moderate. However, if the reaction is run at 50 °C, the yields could be increased. The unprotected 3,4-dihydroquinoxalin-2-one **1d**, was completely oxidized to quinoxalin-2(1*H*)-one, which did not react with **2a**. 1,4-Dibenzyl-3,4-dihydroquinoxalin-2(1*H*)-one could be used in the alkynylation reaction, and the product **3ea** was gained in 54% yield when the reaction is performed at 50 °C. Moreover, 4-alkyl-3,4-dihydroquinoxalin-2-one (**1**) bearing electron-donating (Me) or electron-withdrawing (Cl) groups on the aromatic ring furnished the corresponding propargylic cyclic amines **3** in moderate yields (47–56%).



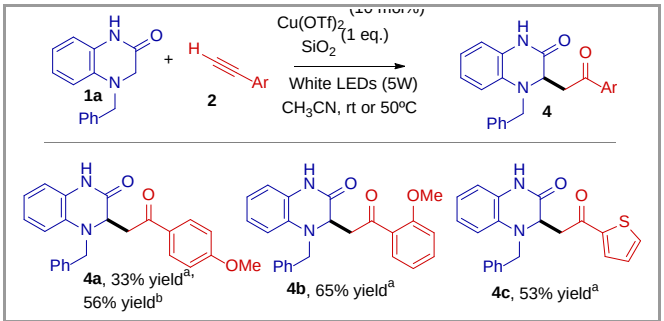
Scheme 2 Scope of the oxidative alkynylation reaction of 3,4-dihydroquinoxalin-2-ones **1** with phenylacetylene **2a**. [a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of CH_3CN under 5W White LEDs irradiation and open air atmosphere at rt. [b] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of CH_3CN under open air atmosphere at 50 °C without white LEDs irradiation. Yields after column chromatography.

After studying the reaction with different 3,4-dihydroquinoxalin-2-ones, we focused our attention in the use of various terminal alkynes **2** (Scheme 3). First, we explored the reaction with several terminal alkynes bearing different electronic and steric demands. The presence of an alkyl group (pentyl) in the *para* position resulted in the formation of **3ab** with good yield (62%). The use of *para*-fluoro-ethynylbenzene (**2c**) or *para*-chloro-ethynylbenzene (**2 d**) gave the corresponding product **3ac** and **3ad** with 72% and 61% yield respectively. An alkyne bearing a substituent (F) in *meta* gave **3ae** in good yield (63%). Finally, in order to fully study the scope of the reaction, aliphatic alkynes were evaluated. The reactions were performed at 50 °C since this allowed to obtain better conversions. When but-3-yn-1-ylbenzene (**2f**) or ethynylcyclopropane (**2g**) were used, the corresponding products were obtained with moderate yields (43% and 31%, respectively).



Scheme 3 Scope of the oxidative alkynylation reaction of 4-benzyl-3,4-dihydroquinoxalin-2-one **1a** with terminal alkynes **2.** [a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of CH_3CN under 5W White LEDs irradiation and open air atmosphere at rt. [b] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of CH_3CN under open air atmosphere at 50 °C without white LEDs irradiation. [c] Dry CH_3CN and oxygen atmosphere was used. Yields after column chromatography.

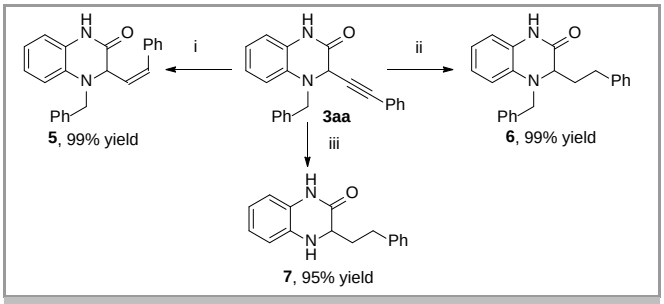
Interestingly, when the reaction is performed with terminal alkynes bearing strong electron-donating groups such as methoxy group in *para* or *ortho* positions or with 2-ethynylthiophene, the triple bond of product **3** is regioselectively hydratated[16] under the reaction conditions obtaining the corresponding aryl ketone **4** bearing a quinoxalin-2-one moiety in moderate to good yields (Scheme 4). We could avoid the hydratation product **4** performing the reaction using dry CH_3CN and oxygen atmosphere. For example, when **1a** was reacted with *ortho*-metoxyphenylacetylene under dry conditions the corresponding alkynylated product **3ai** was obtained with 44% yield (Scheme 3, bottom).



Scheme 4 S Scope of the oxidative alkynylation reaction of 3,4-dihydroquinoxalin-2-one **1a** with aromatic terminal alkynes bearing electron-donating groups**.** [a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of CH_3CN under 5W White LEDs irradiation and open air atmosphere at rt. [b] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Cu(OTf)_2$ (10 mol%) in 1mL of CH_3CN under open air atmosphere at 50 °C without white LEDs irradiation. Yields after column chromatography.

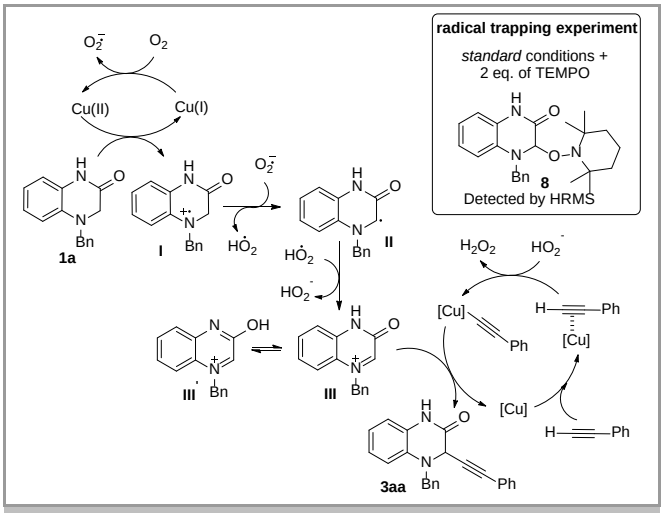
To showcase the synthetic utility of the present methodology, we have applied several chemical transformations for the synthesis of interesting dihydroquinoxalin-2-one derivatives by selective chemical reduction of the C≡C triple bond (Scheme 5). For example, the reaction of **3aa** with H_2 in the presence of Lindlar

catalyst gave the corresponding product **5** where the triple bond had been reduced stereoselectively to the *cis* C=C double bond, with an excellent 99% yield. On the other hand, a complete hydrogenation of the triple bond in the presence of $Pd/CaCO_3$(5 %) gave compound **6** with an almost quantitative yield. While the reaction of **3aa** with Pd/C (5%) under H_2 atmosphere, affords the corresponding dihydroquinoxalin-2-one **7** in 95% yield, where a complete hydrogenation of the triple bond and deprotection of the benzyl group was achieved.



Scheme 5 Synthetic transformations of product **3aa**. i) Lindlar catalyst (5%), H_2, benzene. ii) $Pd/CaCO_3$ (5%), H_2, EtOH. iii) Pd/C (10%), H_2, EtOH.

Based on previous literature reports[5,6] and control experiments[17] a possible mechanism for the reaction is proposed in Scheme 6. Initially, $Cu(OTf)_2$ transforms 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one **1a** into a nitrogen radical cation **I**, with the consequent reduction of the Cu(II) to Cu(I), which can be oxidized by molecular oxygen (O_2) regenerating the copper catalyst.[17] On the other hand, deprotonation of the nitrogen radical cation **I** can generate the α-amino radical **II**, which can be further oxidized to the iminium ion **III**. In parallel, the alkyne is activated by copper, generating the corresponding copper alkynylide. A further addition of the in situ generated copper alkynylide to the iminium ion **III** gives the desired product **3aa** and liberates the copper catalyst to complete the catalytic cycle. The radical mechanism was confirmed by an experiment control using a radical scavenger (TEMPO). Under these conditions, no conversion to **3aa** was observed by HRMS of the crude reaction mixture and the corresponding adduct **8** formed from radical **II** and TEMPO was detected. In this mechanism, the O_2 is the terminal oxidant which is reduced to H_2O_2. The role of molecular oxygen was also studied in a control experiment (entry 14, Table 1). When we performed the oxidative alkynylation reaction under argon atmosphere, the conversion of **1a** to product **3aa** was very low. We also confirm the presence of H_2O_2 in the reaction mixture.[18] Although, the role of irradiation is not clear, we think that the visible-light accelerates the oxidation of **1a** to the iminium ion **III** (or its tautomeric form **III'**). Regarding obtaining better yields in the final alkynylated products **3** when acetic acid or SiO_2 are used as additives, we assumed that the presence of a weak acid facilitates the regeneration of the iminium ion **III**, if **III** suffers the nucleophilic attack of H_2O or H_2O_2.



Scheme 6 Tentative mechanism for the oxidative alkynylation of dihydroquinoxalin-2-ones with terminal alkynes.

In summary, we have developed the oxidative ligand-free alkynylation of 3,4-dhydroquinoxalin-2-ones with terminal alkynes using $Cu(OTf)_2$ as catalyst under visible-light irradiation and open air atmosphere. The reaction conditions are mild, obtaining the corresponding products with moderate to good yields. Moreover, when electron-rich aromatic alkynes are used the regioselective hydratation of the triple bond is observed obtaining the corresponding aroyl ketones bearing a quinoxalin-2-one moiety. This methodology provides a straightforward procedure for the synthesis of a variety of pharmacologically and synthetically useful quinoxaline derivatives.

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Reactions were carried out in test tubes or round bottom flasks ovendried overnight at 120 °C. Commercial reagents and solvents were used as purchased. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm.

NMR spectra were run at 300 MHz for ^1H and at 75 MHz for ^{13}C NMR using residual non-deuterated solvent as internal standard ($CDCl_3$: 7.26 and 77.00 ppm respectively; Acetone-d_6: 2.05 and 29.84 ppm respectively; DMSO-d_6: 2.50 and 39.52 ppm respectively) and at 282 MHz for ^{19}F NMR using $CFCl_3$ as internal standard. Also, some NMR spectra were run at 400 MHz for ^1H and at 101 for ^{13}C. Chemical shifts are given in ppm. The carbon type was determined by DEPT experiments.

High resolution mass spectra (ESI) were recorded on a AB SCIEX Triple TOFTM spectrometer equipped with an electrospray source with a capillary voltage of 4.5 kV (ESI). Infrared (IR) spectra were recorded on a Agilent Cary 630 FTIR spectrometer.

All copper salts and terminal alkynes were commercially available Dihydroquinoxalinones **1a** and **1f** was prepared according to a reported procedure.[12b] Dihydroquinoxalinone **1e** was prepared following the same reported procedure[12b] but using 2 equivalents of BnBr instead of BnCl. Dihydroquinoxalinone **1c** was obtained as reported,[12b] but using allyl bromide as alkylating agent instead of BnCl. Dihydroquinoxalinone **1b** and **1g** were synthetized as described in the literature.[19]

Procedure A: oxidative alkynylation reaction under white LEDs irradiation:

In a 5 mL vial were placed $Cu(OTf)_2$ (3.6 mg, 10 mol %, 0.01 mmol), SiO_2 (6 mg, 1 eq., 0.1 mmol) and MeCN (1 mL). Then, the proper terminal alkyne was added (**2**, 0.5 mmol, 5 eq.) and the resulting solution was stirred for 10 minutes. After this time, the proper dihydroquinoxalinone (**1**, 0.1 mmol) was added and the resulting mixture was stirred under the

irradiation of White LEDs (5 W) until the starting material disappeared (as showed by TLC).[20] Then, the solvent was removed under reduced pressure and the residue was purified by FCC to afford product **3**.

Procedure B: oxidative alkynylation reaction at 50 °C:

In a 10 mL round bottomed flask were placed $Cu(OTf)_2$ (3.6 mg, 10 mol %, 0.01 mmol), SiO_2 (6 mg, 1 eq., 0.1 mmol) and MeCN (1 mL). Then, the proper terminal alkyne was added (**2**, 0.5 mmol, 5 eq.) and the resulting solution was stirred for 10 minutes. After this time, the proper dihydroquinoxalinone (**1**, 0.1 mmol) was added and the resulting mixture was stirred at 50 °C in an oil bath until the starting material disappeared (as showed by TLC). Then, the solvent was removed under reduced pressure and the residue was purified by FCC to afford product **3**.

Procedure C: oxidative alkynylation under O_2 atmosphere using dry MeCN:

In a 10 mL round bottomed flask were placed $Cu(OTf)_2$ (3.6 mg, 10 mol %, 0.01 mmol) and SiO_2 (6 mg, 1 eq., 0.1 mmol). The flask was purged with O2 and afterward dry MeCN (1 m) was added. Then, the proper terminal alkyne was added (**2**, 0.5 mmol, 5 eq.) and the resulting solution was stirred for 10 minutes. After this time, the proper dihydroquinoxalinone (**1**, 0.1 mmol) was added and the resulting mixture was stirred under the irradiation of White LEDs (5 W) until the starting material disappeared (as showed by TLC). Then, the solvent was removed under reduced pressure and the residue was purified by FCC to afford product **3**.

4-Benzyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3aa)

Yield: 23.4 mg (68%); yellow solid, m. p.: 174-180 °C.

IR (neat): 1694, 1655, 1504, 1377, 977, 747, 690 cm^{-1}.

^1H NMR (300 MHz, DMSO) δ 10.81 (bs, 1H), 7.62 – 7.12 (m, 10H), 6.98 – 6.87 (m, 2H), 6.87 – 6.78 (m, 2H), 4.75 (s, 1H), 4.68 (d, *J* = 14.6 Hz, 1H), 4.30 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 162.66 (C), 136.80 (C), 133.55 (C), 131.58 (CH), 129.08 (CH), 128.70 (CH), 128.66 (CH), 128.03 (CH), 127.50 (CH), 127.44 (C), 123.23 (CH), 121.10 (C), 120.04 (CH), 115.36 (CH), 114.20 (CH), 85.46 (C), 82.78 (C), 53.81 (CH), 51.59 (CH_2).

HRMS (ESI^+): *m/z* 339.1489 $[M + H]^+$, $C_{23}H_{19}N_2O$ requires 339.1492.

4-Methyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ba)

Yield: following Procedure A, 10.5 mg (40%), following Procedure B, 12.6 mg (48%); yellow solid, m. p.: 172-176 °C.

IR (neat): 1687, 1508, 1388, 744, 684 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 8.80 (bs, 1H), 7.24 – 7.10 (m, 5H), 7.04 – 6.94 (m, 1H), 6.79 (dd, *J* = 4.9, 0.8 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.74 (s, 1H), 2.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.94 (C), 134.51 (C), 131.95 (CH), 128.62 (CH), 128.12 (CH), 126.17 (C), 124.39 (CH), 121.85 (C), 120.09 (CH), 115.52 (CH), 113.41 (CH), 86.84 (C), 80.91 (C), 56.86 (CH), 35.98 (CH_3).

HRMS (ESI^+): *m/z* 263.1180 $[M + H]^+$, $C_{17}H_{15}N_2O$ requires 263.1184.

4-Allyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ca)

Yield: following Procedure A, 13.9 mg (48%), following Procedure B, 15.3 mg (53%); brown oil.

IR (neat): 1685, 1500, 1217, 923, 751, 686 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (bs, 1H), 7.33 – 7.16 (m, 5H), 7.12 – 6.98 (m, 1H), 6.93 – 6.82 (m, 3H), 5.96 (dddd, *J* = 17.5, 10.1, 7.5, 4.9 Hz, 1H), 5.47 (ddd, *J* = 17.2, 2.9, 1.5 Hz, 1H), 5.35 (ddd, *J* = 10.2, 2.6, 1.3 Hz, 1H), 4.92 (s, 1H), 4.14 (ddd, *J* = 14.4, 3.4, 1.5 Hz, 1H), 3.75 (dd, *J* = 14.4, 7.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.13 (C), 133.91 (C), 132.78 (CH), 131.93 (CH), 128.59 (CH), 128.12 (CH), 126.44 (C), 124.23 (CH), 121.94 (C), 120.20 (CH), 119.68 (CH_2), 115.74 (CH), 113.94 (CH), 86.50 (C), 81.40 (C), 53.59 (CH), 50.86 (CH_2).

HRMS (ESI^+): *m/z* 289.1336 $[M + H]^+$, $C_{19}H_{17}N_2O$ requires 289.1341.

1,4-Dibenzyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ea)

Yield: following Procedure A, 12.8 mg (30%), following Procedure B, 23.1 mg (54%); yellow solid, m. p.: 110-115 °C.

IR (neat): 1679, 1502, 1396, 1027, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.21 (m, 15H), 7.07 – 6.97 (m, 1H), 6.96 – 6.87 (m, 2H), 6.87 – 6.78 (m, 1H), 5.63 (d, *J* = 16.3 Hz, 1H), 4.85 (d, *J* = 16.4 Hz, 1H), 4.81 (s, 1H), 4.73 (d, *J* = 13.6 Hz, 1H), 4.20 (d, *J* = 13.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.31 (C), 136.41 (C), 135.94 (C), 135.77 (C), 131.95 (CH), 129.50 (C), 128.93 (CH), 128.82 (CH), 128.66 (CH), 128.60 (CH), 128.21 (CH), 127.99 (CH), 127.15 (CH), 126.07 (CH), 124.00 (CH), 121.97 (C), 120.58 (CH), 115.62 (CH), 114.25 (CH), 86.84 (C), 81.52 (C), 53.84 (CH), 52.33 (CH_2), 45.92 (CH_2).

HRMS (ESI^+): *m/z* 429.1665 $[M + H]^+$, $C_{30}H_{25}N_2O$ requires 429.1967.

4-Benzyl-6,7-dimethyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3fa)

Yield: following Procedure A, 20.5 mg (56%); yellow oil.

IR (neat): 1683, 1519, 1396, 1221, 865, 751 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (bs, 1H), 7.45 – 7.26 (m, 8H), 7.25 – 7.18 (m, 2H), 6.68 (s, 1H), 6.65 (s, 1H), 4.70 (d, *J* = 13.5 Hz, 1H), 4.64 (s, 1H), 4.13 (d, *J* = 13.4 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.22 (C), 135.93 (C), 132.14 (C), 132.02 (CH), 131.97 (C), 128.83 (CH), 128.74 (CH), 128.54 (CH), 128.40 (C), 128.11 (CH), 127.91 (CH), 124.17 (C), 122.09 (C), 116.97 (CH), 115.44 (CH), 86.52 (C), 81.38 (C), 53.20 (CH), 51.73 (CH_2), 19.77 (CH_3), 18.82 (CH_3).

HRMS (ESI^+): *m/z* 367.1813 $[M + H]^+$, $C_{25}H_{23}N_2O$ requires 367.1810.

6,7-dichloro-4-methyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ga)

Yield: following Procedure A, 15.6 mg (47%); yellow solid, m. p.: decomposes over 200 °C.

IR (neat): 1685, 1500, 870, 757 cm^{-1}.

^1H NMR (400 MHz, Acetone-d_6) δ 9.89 (bs, 1H), 7.39 – 7.29 (m, 5H), 7.16 (s, 1H), 7.02 (s, 1H), 4.94 (s, 1H), 3.06 (s, 3H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 163.01 (C), 135.89 (C), 132.61 (CH), 129.87 (CH), 129.42 (CH), 128.55 (C), 126.58 (C), 122.71 (C), 122.57 (C), 116.90 (CH), 115.65 (CH), 87.12 (C), 82.21 (C), 56.81 (CH), 36.36 (CH_3).

HRMS (ESI^+): *m/z* 330.0331 $[M + H]^+$, $C_{17}H_{12}Cl_2N_2O$ requires 330.0327.

4-Benzyl-3-((4-pentylphenyl)ethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ab)

Yield: following Procedure A, 25.3 mg (62%); yellow oil.

IR (neat): 2926, 2855, 1687, 1504, 740, 697 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 9.17 (bs, 1H), 7.46 – 7.28 (m, 5H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.10 – 6.97 (m, 3H), 6.93 – 6.85 (m, 3H), 4.71 (d, *J* = 13.8 Hz, 1H), 4.68 (s, 1H), 4.19 (d, *J* = 13.6 Hz, 1H), 2.61 – 2.50 (m, 2H), 1.62 – 1.48 (m, 2H), 1.35 – 1.21 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.58 (C), 143.86 (C), 135.76 (C), 134.25 (C), 131.89 (CH), 128.85 (CH), 128.61 (CH), 128.26 (CH), 127.93 (CH), 126.57 (C), 124.23 (CH), 120.39 (CH), 119.03 (C), 115.83 (CH), 114.01 (CH), 86.92 (C), 80.39 (C), 53.25 (CH), 51.82 (CH_2), 35.79 (CH_2), 31.32 (CH_2), 30.86 (CH_2), 22.45 (CH_2), 13.96 (CH_3).

HRMS (ESI^+): *m/z* 409.2277 $[M + H]^+$, $C_{28}H_{29}N_2O$ requires 409.2280.

4-Benzyl-3-((4-fluorophenyl)ethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ac)

Yield: following Procedure A, 24.6 mg (69%); yellow oil.

IR (neat): 1669, 1247, 727, 689 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 9.38 (bs, 1H), 7.48 – 7.22 (m, 8H), 7.09 – 7.00 (m, 1H), 7.00 – 6.88 (m, 4H), 4.74 (d, *J* = 13.8 Hz, 1H), 4.70 (s, 1H), 4.20 (d, *J* = 13.6 Hz, 1H).

^{19}F NMR (282 MHz, $CDCl_3$) δ -110.08.

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.51 (C), 162.65 (d, J_{C-F} = 250.3 Hz, C), 135.65 (C), 134.13 (C), 133.94 (d, J_{C-F} = 8.4 Hz, CH), 128.89 (CH), 128.56 (CH), 128.00 (CH), 126.52 (CH), 124.31 (CH), 120.47 (CH), 117.94 (d, J_{C-F} = 3.6 Hz, C), 115.92 (CH), 115.46 (d, J_{C-F} = 22.1 Hz, CH), 113.99 (CH), 85.63 (C), 80.93 (d, J_{C-F} = 1.5 Hz, C), 53.17 (CH), 51.86 (CH_2).

HRMS (ESI$^+$): *m/z* 357.1393 [M + H]$^+$, $C_{23}H_{18}FN_2O$ requires 357.1398.

3-((4-Chlorophenyl)ethynyl)-4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (3ad)

Yield: following Procedure A (22.8 mg, 0.061 mmol, 61% yield); following Procedure B (25.2 mg, 0.068 mmol, 68% yield); yellow solid, m. p.: 160-163 °C.

IR (neat): 1682, 1489, 1504, 822, 742, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (bs, 1H), 7.45 – 7.31 (m, 5H), 7.21 (s, 4H), 7.03 (dd, *J* = 8.1, 4.8 Hz, 1H), 6.97 – 6.85 (m, 3H), 4.72 (d, *J* = 13.8 Hz, 1H), 4.69 (s, 1H), 4.18 (d, *J* = 13.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.21 (C), 135.59 (C), 134.75 (C), 134.09 (C), 133.21 (CH), 128.91 (CH), 128.56 (CH), 128.51 (CH), 128.03 (CH), 126.47 (C), 124.35 (C), 120.52 (C), 120.33 (C), 115.85 (CH), 114.04 (CH), 85.57 (C), 82.24 (C), 53.21 (CH), 51.89 (CH_2).

HRMS (ESI$^+$): *m/z* 373.1102 [M + H]$^+$, $C_{23}H_{18}ClN_2O$ requires 373.1096.

4-Benzyl-3-((3-fluorophenyl)ethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ae)

Yield: following Procedure A, 21.8 mg (61%); following Procedure B, 21.5 mg (60%); yellow oil.

IR (neat): 1672, 1247, 727, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.42 (bs, 1H), 7.54 – 7.22 (m, 5H), 7.20 – 6.84 (m, 8H), 4.73 (d, *J* = 13.6 Hz, 1H), 4.70 (s, 1H), 4.18 (d, *J* = 13.6 Hz, 1H).

^{19}F NMR (282 MHz, $CDCl_3$) δ -109.54.

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.35 (C), 162.11 (C, d, J_{C-F} = 246.7 Hz), 135.57 (C), 134.06 (C), 129.76 (CH, d, *J* = 8.6 Hz), 128.91 (CH), 128.58 (CH), 128.03 (CH), 127.88 (CH, d, J_{C-F} =3.2 Hz), 126.49 (C), 124.37 (CH), 123.64 (C, d, J_{C-F} = 9.4 Hz), 120.56 (CH), 118.77 (CH, d, J_{C-F} = 23.0 Hz), 116.06 (CH, d, J_{C-F} = 21.2 Hz), 115.95 (CH), 114.01 (CH), 85.41 (C, d, J_{C-F} = 3.3 Hz), 82.23 (C), 53.11 (CH), 51.87 (CH_2).

HRMS (ESI$^+$): *m/z* 357.1396 [M + H]$^+$, $C_{23}H_{18}FN_2O$ requires 357.1398.

4-Benzyl-3-(4-phenylbut-1-yn-1-yl)-3,4-dihydroquinoxalin-2(1*H*)-one (3af)

Yield: following Procedure A, 12.1 mg (33%); following Procedure B, 15.6 mg (43%); yellow oil.

IR (neat): 1685, 1504, 740, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (bs, 1H), 7.29 – 7.19 (m, 5H), 7.18 – 7.08 (m, 3H), 7.03 – 6.91 (m, 3H), 6.85 – 6.75 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.47 (d, *J* = 13.7 Hz, 1H), 4.32 (t, *J* = 2.1 Hz, 1H), 3.88 (d, *J* = 13.7 Hz, 1H), 2.62 (dd, *J* = 10.8, 4.2 Hz, 2H), 2.33 (ddd, *J* = 4.6, 3.4, 1.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.68 (C), 140.25 (C), 135.81 (C), 134.27 (C), 128.77 (CH), 128.51 (CH), 128.45 (CH), 128.33 (CH), 127.83 (CH), 126.49 (C), 126.23 (CH), 124.17 (CH), 120.21 (CH), 115.61 (CH), 114.01 (CH), 86.68 (C), 72.77 (C), 52.76 (C), 51.54 (CH_2), 34.58 (CH_2), 20.70 (CH_2).

4-Benzyl-3-(cyclopropylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (3ag)

Yield: following Procedure B, 9.4 mg (31%); colorless oil.

IR (neat): 1690, 1504, 744, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (bs, 1H), 7.41 – 7.28 (m, 5H), 7.01 (ddd, *J* = 7.9, 6.8, 2.2 Hz, 1H), 6.92 – 6.77 (m, 3H), 4.63 (d, *J* = 13.8 Hz, 1H), 4.41 (d, *J* = 1.8 Hz, 1H), 4.09 (d, *J* = 13.8 Hz, 1H), 1.19 – 1.07 (m, 1H), 0.74 – 0.64 (m, 2H), 0.60 – 0.51 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.64 (C), 135.91 (C), 134.28 (C), 128.78 (CH), 128.45 (CH), 127.83 (CH), 126.48 (C), 124.12 (CH), 120.15 (CH), 115.55 (CH), 114.00 (CH), 90.79 (C), 66.94 (C), 52.98 (CH), 51.71 (CH_2), 8.49 (CH_2), -0.55 (CH).

HRMS (ESI$^+$): *m/z* 303.1499 [M + H]$^+$, $C_{20}H_{19}N_2O$ requires 303.1497.

4-benzyl-3-((2-methoxyphenyl)ethynyl)-3,4-dihydroquinoxalin-2(1H)-one (3ah)

Yield: following Procedure C, 16.2 mg (44%); brown oil.

IR (neat): 1685, 1493, 1259, 1026, 728, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (bs, 1H), 7.46 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.25 – 7.18 (m, 2H), 7.08 – 6.97 (m, 1H), 6.94 – 6.76 (m, 5H), 4.71 (d, *J* = 14.0 Hz, 1H), 4.69 (s, 1H), 4.23 (d, *J* = 13.5 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.37 (C), 160.46 (C), 135.83 (C), 134.50 (C), 133.58 (CH), 130.02 (CH), 128.82 (CH), 128.78 (CH), 127.91 (CH), 126.66 (C), 124.13 (CH), 120.33 (CH), 120.21 (CH), 115.65 (CH), 114.17 (CH), 111.40 (C), 110.77 (CH), 85.14 (C), 83.24 (C), 55.67 (CH_3), 53.44 (CH), 51.72 (CH_2).

HRMS (ESI$^+$): *m/z* 368.1529 [M + H]$^+$, : $C_{24}H_{20}N_2O_2$ requires 368.1525.

4-Benzyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3,4-dihydroquinoxalin-2(1*H*)-one (4a)

Yield: following Procedure A, 12.8 mg (33%); following Procedure B, 21.6 mg (56%); bright yellow oil.

IR (neat): 1683, 1593, 1506, 740, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.12 (bs, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.28 – 7.21 (m, 5H), 6.86 (d, *J* = 8.9 Hz, 1H), 6.80 – 6.75 (m, 2H), 6.64 (d, *J* = 7.9 Hz, 2H), 4.69 (dd, *J* = 7.5, 4.4 Hz, 1H), 4.55 (d, *J* = 15.6 Hz, 1H), 4.42 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 3.28 (dd, *J* = 15.7, 7.5 Hz, 1H), 3.11 (dd, *J* = 15.7, 4.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.49 (C), 168.16 (C), 163.70 (C), 137.13 (C), 133.14 (C), 130.57 (CH), 129.55 (C), 128.60 (CH), 127.31 (CH), 127.29 (CH), 126.24 (C), 124.21 (CH), 119.38 (CH), 115.60 (CH), 114.63 (CH), 113.76 (CH), 59.26 (CH), 55.44 (CH_3), 53.57 (CH_2), 38.56 (CH_2).

HRMS (ESI$^+$): *m/z* 387.1697 [M + H]$^+$, $C_{24}H_{23}N_2O_3$ requires 387.1703.

4-Benzyl-3-(2-(2-methoxyphenyl)-2-oxoethyl)-3,4-dihydroquinoxalin-2(1*H*)-one (4b)

Yield: following Procedure A, 25.1 mg (65%); yellow oil.

IR (neat): 1679, 1595, 1506, 1290, 1245, 746 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (bs, 1H), 7.65 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.43 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.29 – 7.16 (m, 5H), 7.00 – 6.94 (m, 1H), 6.92 – 6.83 (m, 2H), 6.76 (dd, *J* = 5.0, 0.9 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.70 (dd, *J* = 7.8, 4.3 Hz, 1H), 4.56 (d, *J* = 15.8 Hz, 1H), 4.41 (d, *J* = 15.8 Hz, 1H), 3.73 (s, 3H), 3.41 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.20 (dd, *J* = 15.9, 4.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.89 (C), 168.00 (C), 158.57 (C), 137.36 (C), 133.94 (CH), 133.37 (C), 130.74 (CH), 128.56 (CH), 127.54 (C), 127.21 (CH), 127.15 (CH), 126.30 (C), 124.05 (CH), 120.71 (CH), 119.12 (CH), 115.31 (CH), 114.59 (CH), 111.47 (CH), 59.42 (CH), 55.34 (CH_3), 53.64 (CH_2), 43.70 (CH_2).

HRMS (ESI$^+$): *m/z* 387.1708 [M + H]$^+$, $C_{24}H_{23}N_2O_3$ requires 387.1703.

4-Benzyl-3-(2-oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydroquinoxalin-2(1*H*)-one (4c)

Yield: following Procedure A, 19.2 mg (53%); yellow solid, m. p.: 202-208 °C.

IR (neat): 1681, 1599, 1234, 1305, 623 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (bs, 1H), 7.88 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.45 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.28 (d, *J* = 2.9 Hz, 1H), 7.26 – 7.18 (m, 5H), 6.92 (ddd, *J* = 8.0, 6.7, 2.3 Hz, 1H), 6.88 – 6.73 (m, 2H), 6.66 (d, *J* = 7.9 Hz, 1H), 4.65 (dd, *J* = 7.5, 4.3 Hz, 1H), 4.55 (d, *J* = 15.6 Hz, 1H), 4.41 (d, *J* = 15.6 Hz, 1H), 3.22 (dd, *J* = 15.5, 7.6 Hz, 1H), 3.07 (dd, *J* = 15.5, 4.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.18 (C), 167.57 (C), 141.72 (C), 136.96 (C), 133.12 (C), 132.73 (CH), 128.65 (CH), 127.43 (CH), 127.35 (CH), 126.89

(CH), 126.56 (CH), 126.11 (C), 124.33 (CH), 119.52 (CH), 115.41 (CH), 114.74 (CH), 59.14 (CH), 53.63 (CH_2), 40.33 (CH_2).

HRMS (ESI$^+$): *m/z* 345.1068 [M + H]$^+$, $C_{21}H_{17}N_2OS$ requires 345.1062.

(*Z*)-4-Benzyl-3-styryl-3,4-dihydroquinoxalin-2(1*H*)-one (5)

In a 25 mL round bottomed flask was added compound **3aa** (20.6 mg, 0.061 mmol) and it was dissolved in benzene (1 mL). Then, Lindlar Catalyst (4 mg, 5 wt. % over $CaCO_3$, poisoned with lead) was added and the resulting mixture was stirred at rt for 24 h in the presence of an hydrogen-filled balloon. When the starting material disappeared (as showed by TLC) the reaction mixture was filtered through a pad of silica to afford compound **5** (20.5 mg, 0.060 mmol, 99% yield).

Yield: 20.5 mg (99%); yellow oil.

IR (neat): 1677, 1504, 1375, 740, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (bs, 1H), 7.61 – 7.53 (m, 2H), 7.41 – 7.28 (m, 4H), 7.13 – 6.92 (m, 5H), 6.89 – 6.76 (m, 3H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.57 (dd, *J* = 11.4, 10.4 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 14.3 Hz, 1H), 3.80 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.74 (C), 136.00 (C), 135.56 (CH), 133.97 (C), 128.94 (CH), 128.31 (CH), 127.88 (CH), 127.78 (CH), 127.16 (CH), 126.11 (C), 124.18 (CH), 122.63 (CH), 119.28 (CH), 115.48 (CH), 113.26 (CH), 58.23 (CH), 51.32 (CH_2).

HRMS (ESI$^+$): *m/z* 341.1647 [M + H]$^+$, $C_{23}H_{21}N_2O$ requires 341.1648.

4-Benzyl-3-phenethyl-3,4-dihydroquinoxalin-2(1*H*)-one (6)

In a 25 mL round bottomed flask was added compound **3aa** (19.4 mg, 0,057 mmol) and it was dissolved in EtOH (5 mL). Then, Pd 5% over $CaCO_3$ (7.4 mg, 0.003 mmol) was added and the resulting mixture was stirred at rt for 5 h in the presence of an hydrogen-filled balloon. When the starting material disappeared (as showed by TLC) the reaction mixture was filtered through a pad of silica to afford compound **6** (19.4 mg, 0.057 mmol, 99% yield).

Yield: 19.4 mg (99%); yellow oil.

IR (neat): 1672, 1495, 742, 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (bs, 1H), 7.35 – 7.20 (m, 7H), 7.20 – 7.08 (m, 3H), 6.98 – 6.88 (m, 1H), 6.81 – 6.76 (m, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.63 (d, *J* = 15.0 Hz, 1H), 4.21 (d, *J* = 15.0 Hz, 1H), 3.97 – 3.84 (m, 1H), 2.78 – 2.56 (m, 2H), 2.02 – 1.81 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.17 (C), 141.03 (C), 136.69 (C), 134.05 (C), 128.74 (CH), 128.38 (CH), 128.34 (CH), 127.68 (CH), 127.56 (CH), 126.27 (C), 126.00 (CH), 124.15 (CH), 119.27 (CH), 115.33 (CH), 113.99 (CH), 61.25 (CH), 53.12 (CH_2), 31.67 (CH_2), 30.73 (CH_2).

HRMS (ESI$^+$): *m/z* 343.1804 [M + H]$^+$, $C_{23}H_{23}N_2O$ requires 343.1805.

3-Phenethyl-3,4-dihydroquinoxalin-2(1*H*)-one (7)

In a 25 mL round bottomed flask was added compound **3aa** (22.4 mg, 0,066 mmol) and it was dissolved in EtOH (6 mL). Then, Pd 10% over C (8.6 mg, 0.008 mmol) was added and the resulting mixture was stirred at rt for 2.5 h in the presence of an hydrogen-filled balloon. When the starting material disappeared (as showed by TLC) the reaction mixture was filtered through a pad of silica to afford compound **7** (15.8 mg, 0.063 mmol, 95% yield).

Yield: 15.8 mg (95%); brown solid, m. p.: 195-200 °C.

IR (neat): 3058, 3027, 1664, 1603, 1504, 1370, 1303, 740, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (bs, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 6.88 (ddd, *J* = 7.8, 6.2, 2.7 Hz, 1H), 6.82 – 6.67 (m, 2H), 6.56 (d, *J* = 7.6 Hz, 1H), 3.96 (ddd, *J* = 7.6, 4.6, 2.1 Hz, 1H), 3.80 (bs, 1H), 2.81 (td, *J* = 9.2, 4.6 Hz, 2H), 2.32 – 2.14 (m, 1H), 2.05 (ddd, *J* = 15.9, 14.4, 7.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.71 (C), 140.93 (C), 132.83 (C), 128.61 (CH), 128.41 (CH), 126.22 (CH), 125.24 (C), 123.85 (CH), 119.44 (CH), 115.30 (CH), 114.21 (CH), 56.13 (CH), 33.25 (CH_2), 31.88 (CH_2).

HRMS (ESI$^+$): *m/z* 253.1334 [M + H]$^+$, $C_{16}H_{17}N_2O$ requires 253.1335.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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