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Reaction of 3-chloroquinoline-2,4-diones with ethanolamine and rearrangement of the reaction products

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ABSTRACT

The reaction of tertiary α-chloroketones with ethanolamine has not been hitherto described in the literature. Herein, we describe the reaction of tertiary 3-chloroquinoline-2,4-diones with ethanolamine to give novel 3-(2-hydroxyethylamino)quinoline-2,4-diones. These compounds provide 3-(2-oxooxazolidin-3-yl)quinoline-2,4(1*H*,3*H*)-diones and new compounds with dimeric character after reaction with triphosgene. Molecular rearrangement proceeds during the reaction of 3-(2-hydroxyethylamino)quinoline-2,4-diones with isocyanic acid. Three types of reaction products arise: 2-(2-hydroxyethyl)imidazo[1,5-*c*]quinazoline-3,5-diones, 3-(2-hydroxyethyl)-3,3a-dihydro-2*H*-imidazo[4,5-]quinoline-4(5*H*)diones and primarily 5-hydroxy-1-(hydroxyethyl)-1′*H*-spiro[imidazolidine-5,3′-indole]-2,2′-diones. The reaction mechanism and product stereochemistry are discussed. The ^{1}H, ^{13}C and ^{15}N NMR spectra of the prepared compounds were measured, and all resonances were assigned from appropriate two-dimensional experiments.

1. Introduction

In our previous paper we studied the reaction of 3-chloroquinoline-2,4-diones **2** with ammonia and primary amines.[1] The reaction proceeded smoothly and 3-amino or 3-alkylaminoquinoline-2,4-diones were prepared in good yields. These compounds rearrange during reaction with urea,[2,3] nitrourea,[4,5] isocyanates,[6] isothiocyanates,[7–9] and isocyanic and isothiocyanic acids[10,11] to give a broad palette of new heterocyclic compounds: imidazo[1,5-*c*]quinazoline-3,5-diones, 3-(3-acylureido)-2,3-dihydro-1*H*-indol-2-ones, 4-alkylidene-1′*H*-spiro[imidazolidine-5,3′-indole]-2,2′-diones and spiro-linked imidazoline-2-thiones. 3-Aminoquinoline-2,4-quinolinediones were also reduced[12] by $NaBH_4$ and the reaction products were converted to 3-alkyl/aryl-2,3-dihydro-1*H*-indol-2-ones. With regard to the interesting results described above, we carried out some of the aforementioned reactions using an amine containing yet another functional group, potentially capable to participate during the molecular rearrangement.

In this paper, we describe the reactions of 3-chloroquinoline-2,4-diones **2** with easily accessible and inexpensive ethanolamine. We presumed that the reaction would proceed through the formation of 3-(3-hydroxyethyl)amino derivatives **3**, whose reactions with isocyanic acid can lead, according to our experiences, to more complex products of the molecular rearrangements than as with simple 3-alkylaminoquinolinediones.

2. Results and discussion

The reaction of **2** with ethanolamine (Scheme 1) proceeded easily and in good yields (Table 1). In all cases, 3-(3- hydroxyethyl) amino derivatives **3** were obtained, and their NMR spectra are given in Table 2. When substituent R^2 was a benzyl group, 3-hydroxyderivatives **4b**, **e**, **h** and minor compounds **5e**, **h** were also obtained.

The formation of compounds **4** was the result of the hydrolysis of **3**. The structure of the condensation products **5** was established by the analysis of very complicated NMR spectra (Table 3), in which the chemical shifts of −OH groups were absent. These compounds arose from the reaction of 3-chloroderivatives **2** with 4-hydroxyquinolin-2-one **1**, stemming from the reductive hydrolysis of **2** in alkaline medium. The conversion of **2** to **1** in alkaline medium is known.[13] The structures of **5e** and **5h** were confirmed by their synthesis from **1** and **2**, though in very small yields. The main

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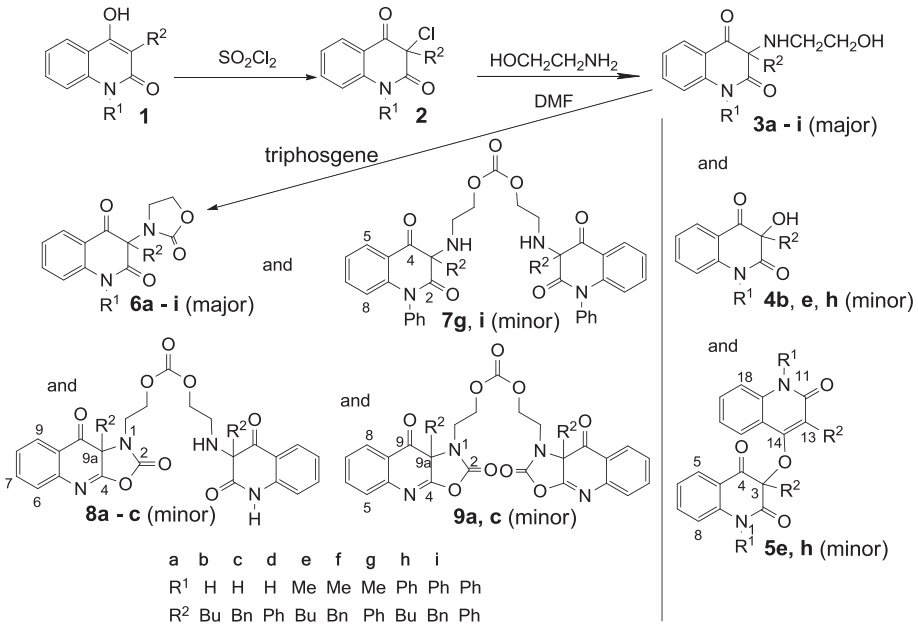

Scheme 1.

Table 1
Reaction of 3-chloroquinolinediones **2** with ethanolamine.

Starting compound	Product(s), (yield, %)
2a	**3a** (51)
2b	**3b** (24), **2b** (3), **4b** (11)
2c	**3c** (69)
2d	**3d** (68)
2e	**3e** (31), **4e** (15), **5e** (4)
2f	**3f** (88)
2g	**3g** (65)
2h	**3h** (17), **4h** (9), **5h** (5)
2i	**3i** (56)

product was starting compound **1**, arising from the reductive hydrolysis of **2**.

After obtaining compounds **3**, we studied their reaction with triphosgene in order to install an additional ring on the molecule. We obtained compounds **6** in all cases (Table 4), and their NMR spectra are given in Table 5. The structure of compounds **6** were also proposed according to the results obtained from ESI-MS experiments. In the first-order mass spectra of compounds **6** the sodium adduct of the molecule $[M+Na]^+$ represents the most abundant ion (except for compound **6a**). This signal was usually accompanied by a singly charged signal that was twice as high, which we assigned to the sodium adduct of the dimer $[2\cdot M + Na]^+$. Furthermore, we studied the gas-phase behavior of compounds **6** in detail using ESI-MS/MS experiments under collision-induced dissociation (CID). In the ESI-MS/MS spectra of compounds **6a**, **6d** and **6g**, three independent neutral losses were observed. These neutral losses were assigned as a water molecule (18 *m/z*), carbon dioxide (44 *m/z*) and C_4H_8 from the butyl chain (56 *m/z*). Only one neutral loss at *m/z* 87 was observed in the case of compounds **6b**, **6e** and **6h**. According to the structures of these compounds, we propose that the covalent bond between C(3) and the nitrogen atom was cleaved and the neutral loss of oxazolidin-2-one (87 *m/z*) occurred. In the case of compounds **6b**, **6e** and **6h**, the $[M+H]^+$ ion was not successfully isolated, and tandem mass spectra were not recorded.

In several cases, minor compounds were also obtained from the reaction of **3** with triphosgene, identified as dimeric compounds **7**, **8**, and **9** (Scheme 1, Tables 6 and 7). Compounds **7** were symmetric dimers created from two molecules of compound **3** and triphosgene and signals corresponding to one carbon possessed half the intensity of the other signals in their ^{13}C NMR spectra. Moreover, these signals showed the appropriate cross-peaks in the 2D $^1H-^{13}C$ HMBC spectrum due to existence of $^3J(^{13}C, OCH_2)$, providing clear evidence for the existence of an OC(=O)O fragment in compounds **7**. Proton signals from NH groups were not detected probably due to rapid exchange with water protons, but their presence follows from MS data.

The precursors of compounds **9** contained NH protons in position 1; however, no acidic protons were detected in the ^1H NMR spectra of **9** (Table 6). Two types of C=O groups in a ratio of 2:1 were found in the NMR spectra of compounds **9**. The correlation between the protons in the OCH_2 group and the carbonyl group of relative intensity one and correlation of protons of NCH_2 group and the carbonyl group with a two-fold intensity through $^3J(\mathbf{C}{=}O, CH_2)$ in HMBC spectra help correct the structure of **9**. The 2D $^1H-^{15}N$ in the HMBC spectra of compounds **9** were of key importance in the correct determination of their constitution because the ^{15}N chemical shifts resonating at ca. −145 ppm clearly indicate the presence of a so-called "pyridine" type of nitrogen in the molecule. The alternative possibility corresponding to the existence of a N–C(=O)–N fragment instead of O–C(=O)–N can thus be excluded. Compounds **8** are unsymmetric and likely arise from the reaction of **7** with an additional molecule of triphosgene. The ^1H and ^{13}C NMR spectra of compounds **8** (Table 7) are rather complicated, but the typical chemical shifts observed in symmetrical compounds **7** and **9** were relatively easily detected in these spectra. Thus, compounds **8** contain - in one molecule - structural motifs from both compounds **7** and **9**. Analogously, the ^{15}N chemical shifts resonating at ca. −144 ppm and (−285 ± 5) ppm belong to a structural motif that is similar to that from compound **7**, and those observed at ca. −241 ppm and (−341 ± 3) ppm belong to a structural motif that is similar to that from compound **9.**

The formation of compounds **7**, **8**, and **9** is rather surprising and shows that, in the presence of catalytic *N,N*-dimethylaminopyridine, triphosgene can react with not only the amino group, but also

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Table 2
^{1}H and ^{13}C chemical shifts of compounds **3** in DMSO-d_6.

Position	**3a**		**3b**		**3c**		**3d**		**3e**		**3f**		**3g**		**3h**		**3i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ (C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	172.6	–	172.1	–	171.7	–	172.4	–	171.7	–	171.2	–	172.5	–	171.8	–	171.3
3	–	72.6	–	73.1	–	76.1	–	73.1	–	73.9	–	76.7	–	73.5	–	73.8	–	76.9
4	–	196.5	–	196.3	–	194.1	–	195.3	–	195.2	–	193.2	–	195.1	–	195.4	–	193.9
4a	–	119.2	–	119.4	–	118.5	–	120.5	–	120.9	–	120.8	–	120.1	–	120.6	–	120.5
5	7.76	126.7	7.68	126.4	7.70	127.2	7.85	127.0	7.77	127.0	7.81	127.4	7.90	127.1	7.85	126.9	7.81	127.5
6	7.12	122.8	7.03	122.6	7.08	123.0	7.22	123.0	7.14	122.9	7.21	123.3	7.19	123.1	7.12	123.1	7.13	123.3
7	7.60	136.4	7.48	136.4	7.59	136.5	7.37	136.4	7.58	136.4	7.73	136.4	7.51	135.9	7.38	136.1	7.45	135.8
8	7.09	116.4	6.89	116.2	7.10	114.9	7.42	115.8	7.11	115.5	7.42	116.0	6.33	116.5	6.11	116.4	6.33	116.6
8a	–	141.7	–	141.5	–	141.2	–	142.6	–	142.4	–	142.3	–	143.5		143.4	–	143.0
NH	2.60	–	2.66	–	3.02	–	2.55	–	2.72	–	3.05	–	2.71	–	2.85	–	3.10	–
$NHCH_2$	2.41	46.7	2.34	46.6	2.50	47.1	2.39	46.6	2.38	46.7	2.61	47.1	2.51	46.6	2.56	46.7	2.61	47.0
	2.35		2.42						2.33		2.51				2.49		2.51	
CH_2O	3.34	60.8	3.36	60.8	3.47	60.8	3.39	60.9	3.39	60.8	3.53	61.0	3.42	60.9	3.40	60.8	3.48	60.9
	3.38										3.48							
OH	4.52	–	4.50	–	4.57	–	4.48	–	4.49	–	4.58	–	4.51	–	4.52	–	4.57	–
1′(R^1)	10.98	–	10.94	–	11.26	–	3.41	29.7	3.28	29.5	3.55	30.0	–	137.4	–	137.3	–	137.4
2′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.61	130.3	7.60	130.3	7.63	130.3
3′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.33	129.2	7.19	129.0	7.37	129.1
4′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.35	128.9	7.56	128.9	7.34	128.8
1′(R^2)	1.69	39.3	3.10	45.5	–	137.8	1.72	39.6	3.06	47.0	–	137.9	1.86	39.4	3.22,	46.7	–	137.4
			3.06				1.69		3.02						3.15			
2′(R^2)	1.12	25.1	–	134.0	7.36	126.6	1.10	25.1	–	133.6	7.32	126.8	1.20	25.2	–	133.6	7.48	126.9
							1.02											
3′(R^2)	1.12	22.3	6.96	130.0	7.33	128.8	1.10	22.2	6.85	129.7	7.32	128.9	1.20	22.2	7.00	130.2	7.35	129.1
4′(R^2)	0.74	13.8	7.10	127.8	7.30	128.6	0.73	13.7	7.06	127.6	7.32	128.7	0.77	13.8	7.16	127.9	7.35	129.1
5′(R^2)			7.10	126.9					7.06	126.7					7.16	127.2		

Table 3
^{1}H, ^{13}C and ^{15}N chemical shifts of compounds **5** in DMSO-d_6.

Position	**5e**		**5h**		Position	**5e**		**5h**	
	δ(H)	δ(C)	δ(H)	δ(C)		δ(H)	δ(C)	δ(H)	δ(C)
1	–	−248.5[a]	–		11	–	−241.9[a]	–	
2	–	167.4	–	167.0	12	–	162.5	–	162.3
3	–	89.5	–	88.5	13	–	119.2	–	119.6
4	–	190.2	–	190.4	14	–	157.9	–	157.4
4a	–	120.9	–	121.0	14a	–	119.0	–	118.1
5	7.60	126.6	[b]	[c]	15	7.94	123.9	[b]	[c]
6	7.05	123.3	[b]	[c]	16	7.26	122.8	[b]	122.0
7	7.44	136.9	7.41	137.4	17	7.62	135.2	[b]	137.4
8	6.79	115.6	5.99	116.6	18	7.56	114.6	6.55	115.6
8a	–	141.6	–	142.7	18a	–	138.1	–	139.1
1′(R^1)	3.02	29.4	–	139.1	1′(R^{11})	3.63	29.7	–	137.7
2′(R^1)	–	–	[b]	[c]	2′(R^{11})	–	–	[b]	[c]
3′(R^1)	–	–	[b]	[c]	3′(R^{11})	–	–	[b]	[c]
4′(R^1)	–	–	[b]	[c]	4′(R^{11})	–	–	[b]	[c]
1′(R^2)	3.69	49.4	3.88	48.5	1′(R^{12})	3.93	30.8	3.88	31.2
	3.62					3.74			
2′(R^2)	–	131.2	–	131.1	2′(R^{12})	–	137.3	–	136.1
3′(R^2)	6.83	127.9	[b]	[c]	3′(R^{12})	6.86	129.9	[b]	[c]
4′(R^2)	6.93	127.5	[b]	[c]	4′(R^{12})	7.03	127.7	[b]	[c]
5′(R^2)	6.80	125.6	[b]	[c]	5′(R^{12})	7.03	127.6	[b]	[c]

[a] δ(^{15}N).
[b] ^{1}H chemical shits: 6.90–7.77, overlapped signals.
[c] ^{13}C chemical shits: 127.3–130.7.

the hydroxyl group in the tautomeric form of the lactam.

Interesting results were obtained from the reaction of compounds **3** with isocyanic acid, which was generated from potassium cyanate in a solution of acetic acid (Table 4). According to the literature, the reaction of α-aminoketones with isocyanic acid was frequently used for the preparation of imidazolin-2-ones. However, only primary[15,16] or secondary[17–19] amino groups were present in the starting compounds. Compounds bearing the tertiary amino group were used only in our earlier papers.[10] Three different types of products were isolated from the reactions of .3-(3-hydroxyethyl) quinoline-2,4-diones. In consilience with the described results of the analogous reaction of 3-butylaminoquinolinediones,[10] imidazoquinazoline **10a** arose from starting compound **3a**, which was unsubstituted at N(1) (Scheme 2). 1-Substituted compounds **3** changed to **11** through intermediate **B** and primarily to **12** through intermediate **C** (Scheme 2). The NMR spectra of compounds **10** and

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Table 4
Results of the reaction of 3-chloroquinolinediones **3** with triphosgene (TP) and KOCN.

Starting compound	Reagent	Product(s), (yield, %)	Starting compound	Reagent	Product(s), (yield, %)
3a	TP	**6a** (42), **8a** (19), **9a** (3)	**3a**	KOCN	**10a** (42)
3b	TP	**6b** (17), **8b** (22), **3b** (26)	**3b**	KOCN	**12b** (34)
3c	TP	**6c** (23), **8c** (34), **9c** (8)	**3c**	KOCN	**12c** (42)
3d	TP	**6d** (31), **3d** (9)	**3d**	KOCN	**11d** (30)
3e	TP	**6e** (37), **3e** (15)	**3e**	KOCN	**11e** (3), **12e** (30)
3f	TP	**6f** (28)	**3f**	KOCN	**12f** (76)
3g	TP	**6g** (23), **7g** (6), **3g** (20)	**3g**	KOCN	**12g** (33)
3h	TP	**6h** (44), **3h** (8)	**3h**	KOCN	**12h** (45)
3i	TP	**6i** (25), **7i** (11), **3i** (4)	**3i**	KOCN	**12i** (36)

Table 5
^{1}H, ^{13}C and ^{15}N chemical shifts and $^{1}J(^{15}N, H)$ (Hz, ± 0.3 Hz) of compounds **6** in DMSO-d_6.

Position	**6a**		**6b**		**6c**		**6d**		**6e**		**6f**		**6g**		**6h**		**6i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(H)
1	–	244.9[a]	–	–	–	–	–	–	–	–	–	251.5[a]	–	–	–	–	–	–
2	–	171.2	–	170.8	–	169.3	–	170.7	–	170.4	–	168.8	–	170.7	–	170.4	–	168.3
3	–	69.1	–	68.7	–	74.2	–	69.6	–	69.2	–	74.5	–	69.8	–	68.9	–	74.8
4	–	193.6	–	194.6	–	190.5	–	192.4	–	193.5	–	189.4	–	192.6	–	194.2	–	189.3
4a	–	118.9	–	119.7	–	118.8	–	120.1	–	120.9	–	120.0	–	119.7	–	120.7	–	119.8
5	7.78	126.8	7.59	126.0	7.76	127.6	7.89	127.2	7.71	126.4	7.84	127.8	7.94	127.4	7.79	126.6	7.90	128.1
6	7.14	122.9	6.93	122.4	7.10	123.2	7.27	122.4	7.06	122.9	7.20	123.7	7.24	123.6	7.06	122.2	7.19	124.0
7	7.64	136.6	7.35	136.1	7.58	136.6	7.78	136.8	7.47	136.4	7.70	136.8	7.54	136.6	7.29	136.2	7.59	136.5
8	7.12	116.6	6.68	116.0	7.07	116.5	7.42	116.1	6.91	115.3	7.38	116.2	6.39	116.9	6.94	116.3	6.37	117.0
8a	–	141.5	–	141.1	–	140.6	–	142.4	–	142.0	–	141.6	–	143.3	–	143.0	–	142.4
NCH_2	–	286.5[a]	–	–	–	–	–	–	–	–	–	287.4[b]	–	–	–			
NCH_2	3.97	44.0	4.13	44.1	3.38	45.8	3.99	44.0	4.17	44.1	3.39	45.8	3.95	44.0	4.15	44.0	3.33	45.7
	3.91				3.23		3.89		4.11		3.20						3.24	
CH_2O	4.48	64.1	4.52	64.3	4.41	63.8	4.48	64.1	4.56	64.4	4.43	63.8	4.48	64.2	4.54	64.6	4.39	63.9
	4.44				4.38		4.44		4.51		4.38							
C=O	–	158.1	–	157.8	–	158.2	–	158.2	–	157.8	–	158.2	–	158.4	–	158.1	–	158.3
1′(R^1)	11.15	90.3[b]	10.96	–	11.44	–	3.41	29.8	3.19	29.4	3.53	30.3	–	137.0	–	136.9	–	136.9
2′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.42	129.1	7.03	129.1	7.50	129.1
													7.12	128.8	6.98	128.4	7.18	128.7
3′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.64	130.6	7.63	130.6	7.60	130.7
													7.61	130.4	7.56	130.2		130.5
4′(R^1)	–	–			–	–			–	–	–	–	7.59	129.2	7.52	129.1	7.50	129.4
1′(R^2)	1.95	35.8	3.40	43.4	–	130.7	1.95	36.0	3.38	43.9	–	130.9	2.11	35.8	3.49	43.5	–	130.4
			3.33						3.31						3.45			
2′(R^2)	1.20	25.0	–	131.0	7.42	129.6	1.12	25.2	–	131.0	7.44	129.7	1.29	25.3	–	131.0	7.50	130.0
	1.10																	
3′(R^2)	1.20	22.0	6.94	130.0	7.45	128.4	1.20	21.9	6.80	129.6	7.32	128.2	1.29	22.0	7.03	130.3	7.41	128.3
4′(R^2)	0.76	13.5	7.03	127.7	7.45	130.2	0.74	13.5	6.99	127.5	7.44	130.9	0.76	13.6	7.14	128.0	7.41	130.5
5′(R^2)	–	–	7.03	127.6	–	–	–	–	6.99	127.6	–	–	–	–	7.14	127.9	–	–

[a] $\delta(^{15}N)$.
[b] $^{1}J(^{15}N, H)$.

11 are given in Table 8. The formation of compounds analogous to **11** was previously observed in the reaction of 3-alkylaminoquinoline-2,4-diones with nitrourea.[5]

Additional compounds unsubstituted at N(1) (**3b**, **c**) reacted dissimilarly to **3a**. From these compounds and **3e**, **f**, **h**, **i**, novel spiro-compounds **12** were obtained (Scheme 2). We determined analogous structures, but otherwise substituted, for the products of the reaction of compound **3** with isocyanates.[14] These results show that transformation of intermediate **B** to **C** is preferred over **B** to **D** and also over deprotonation to **11**.

In the NMR spectra of compounds **12**, signals corresponding to two aliphatic quaternary carbons δ 69.5–75.5 ((C(4)) and 83.7–85.1 ((C(5)) ppm and two unambiguously distinguishable hydroxyl groups were detected (Table 9). The hydroxyl group proton in the hydroxyethyl fragment exists, as expected, as a triplet. Singlets corresponding to two additional acidic protons were undoubtedly differentiated using a 1D ^{1}H–^{15}N HSQC doublets due to the existence of doublets due to the existence of $^{1}J(^{15}N, H)$ were observed for protons from NH groups (Table 9). Such an unwanted reaction course must have been caused by the presence of the hydroxyethyl group as a substituent at the nitrogen atom at position 3. A hydrogen bond can be created between the two hydroxyl groups in compounds **12** stabilizing these groups against deprotonation to **11**.

Two stereogenic centers at C(4) and C(5) are present in compounds **12**. However, in contrast to the results in our preceding paper,[14] we never obtained two racemates. In all cases, only one pure racemate arose. Therefore, the addition of water to intermediate **C** (Scheme 2) is probably stereoselective. However, this reaction course could also be caused by the instability of one of the incipient racemates. A previous paper[14] described that (*4R*,5R**) racemates are unstable and converts to (*4R*,5S**) racemates, even while standing in a DMSO solution.

If we assume the presence of a hydrogen bond between the two hydroxyl groups in **12**, than a relative configuration of (*4R*,5R**) is feasible, as well as (*4R*,5S**). According to the NMR spectra, the signals corresponding to hydrogens at C(4′) and C(5′) lies in narrow

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Table 6
Characteristic ^{1}H, ^{13}C and ^{15}N chemical shifts of compounds **7** and **9** in DMSO-d_6.[a]

Position	**7g**		**7i**		**9a**		**9c**	
	δ(H)	δ(C	δ(H)	δ(C)	δ(H	δ(C)	δ(H)	δ(C)
1	–	231.5[b]	–	231.0[b]	–	145.7[b]	–	144.6[b]
2	–	172.2	–	171.0	–	167.5	–	165.9
3	–	74.0	–	77.1	–	69.7	–	71.4
4	–	194.9	–	192.8	–	192.7	–	191.5
4a	–	120.2	–	120.7	–	121.9	–	123.2
5	7.88	127.1	7.77	127.5	7.77	126.6	7.79	126.5
6	7.17	123.1	7.08	123.3	7.37	127.2	7.33	127.4
7	7.49	135.8	7.38	135.7	7.74	136.6	7.64	136.6
8	6.31	116.4	6.28	116.6	7.39	127.1	7.29	127.1
8a	–	143.5	–	143.5	–	145.8	–	145.1
N(C=O)	–	–	–	–	–	152.5 [c]	–	152.1[d]
NCH_2	2.73	42.9	2.76	43.3	3.97,	40.3	3.73	40.7
		343.9[b]	2.70	339.5[b]	3.73	291.7[b]	3.47	282.7[b]
CH_2O	4.07	67.9	4.11	67.8	4.40	65.2	4.17	64.4
	4.02		4.07				4.11	
OC(=O)O	–	154.5	–	154.5	–	154.2[c]	–	153.8[d]
1′(R^1)	–	137.5	–	137.5	–	–	–	–
2′(R^1)	7.34	130.2	7.54	130.5	–	–	–	–
			7.65	130.2				
3′(R^1)	7.59	129.2	[e]	129.1	–	–	–	–
4′(R^1)	7.54	128.9	[e]	128.8	–	–	–	–
1′(R^2)	1.84	39.1	–	135.7	2.00	34.1	–	132.2
					1.93		–	
2′(R^2)	1.18	25.2	[e]	126.9	1.19	25.8	7.36	126.7
					1.08			
3′(R^2)	1.18	22.1	[e]	129.1	1.16	21.4	7.43	130.2
4′(R^2)	0.76	13.8	[e]	129.0	0.77	13.6	7.43	130.8

[a] The numbering of compounds **7** and **9** for NMR-purpose in Table 6 starts from N(1) and continues to C(8a).
[b] δ(^{15}N).
[c] Intensity ratio of signals at 152.5 and 154.2 ppm was 2:1.
[d] Intensity ratio of signals at 152.1 and 153.8 ppm was 2:1.
[e] ^{1}H chemical shits: 7.30–7.60 ppm, overlapped signals.

interval of δ 7.46–7.82 and 6.83–7.08 ppm. This is in conformity with appearance of signals at δ 7.71–7.82 for C(4′) and 7.14–7.24 (C-5′) in the NMR spectra of analogous compounds bearing substituents at N(1) and N(3) and having a relative configuration of (*4R*,5S**), confirmed by X-ray crystallography.[14] On the other hand, these signals for compounds possessing a relative configuration (*4R*,5R**) lies at δ 5.63–5.67 and 6.46–6.57 ppm.[14] This comparison show that compounds **12** are (*4R*,5S**) racemic diastereoisomers.

3. Conclusions

In conclusion, the 3-chloroquinoline-2,4-diones react with ethanolamine to give their 3-(3-hydroxyethyl)amino derivatives **3** in good yields. The reaction of these compounds with triphosgene provide 3(2-oxooxazolidin-3-yl)quinoline-2,4(1*H*,3*H*)-diones **6** and minor compounds with dimeric character. The most remarkable result of this paper is the rearrangement of compounds **3** into imidazoquinazolines **10**, imidazoquinolones **11** and spiro-compounds **12**. The formation of novel spiro-diols **12** is especially interesting from a theoretical viewpoint and also, owing to the simple reaction protocol, opens a path to further transformations of these compounds. Due to the significant biological activity of a number of indole derivatives, compounds **12** may also be interesting structures for study in this research area.

4. Experimental section

4.1. General

Melting points were determined on a Kofler block. IR (KBr) spectra were recorded on a Smart OMNI-Transmission Nicolet iS10 spectrophotometer. The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance 500 spectrometer (500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C and 50.68 MHz for ^{15}N) in DMSO-d_6. ^{1}H and ^{13}C chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS (δ = 0.0). ^{15}N Chemical shifts were referenced to an external neat nitromethane in a capillary (δ = 0.0). All 2D experiments (gradient-selected (gs)—COSY, gs-NOESY, gs-HMQC, gs-HMBC) were performed using manufacturer's software (TOPSPIN 3.2). The positive-ion EI mass spectra were measured on a Shimadzu QP-2010 instrument within the mass range *m/z* = 50–600 using direct inlet probe (DI). Samples were dissolved in dichloromethane (30 μg mL^{-1}) and 10 μL of the solution was evaporated in DI cuvette at 50 °C. The ion source temperature was 200 °C; the energy of electrons was 70 eV. Only signals exceeding relative abundance of 5% are listed. The electrospray mass spectra (ESI-MS) were recorded using an amaZon X ion-trap mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an electrospray ion source. All experiments were conducted in both positive and negative polarity mode. Individual samples (with a

Table 7
Characteristic ^{1}H, ^{13}C and ^{15}N chemical shifts and $^{1}J(^{15}N, H)$ (Hz, ± 0.3 Hz) of compounds **8** in DMSO-d_6.[a]

Position	**8a**		**8b**		**8c**		Position	**8a**		**8b**		**8c**	
	δ(H)	δ C)	δ(H)	δ(C)	δ(H)	δ(C)		δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	−145.3[b]	–	−145.1[b]	–	−144.3[b]	1′	–	−245.5[b]	–	−243.7[b]	–	−244.5[b]
2	–	167.6	–	166.6	–	166.9	2′	–	172.5	–	171.7	–	171.4
3	–	69.7	–	71.1	–	71.4	3′	–	73.0	–	73.5	–	76.3
4	–	192.7	–	192.0	–	191.5	4′	–	196.0	–	195.8	–	193.7
4a	–	121.9	–	121.9	–	123.2	4a'	–	119.1	–	119.4	–	119.3
5	7.76	126.7	7.86	126.7	7.78	126.5	5′	7.73	126.6	7.66	126.3	7.69	127.0
6	7.39	127.0	7.42	127.1	7.38	127.2	6	7.10	122.7	7.04	122.6	7.06	122.9
7	7.74	136.6	7.79	136.8	7.63	136.5	7′′	7.59	136.3	7.49	136.3	7.56	136.4
8	7.39	127.2	7.47	127.4	7.39	127.3	8′	7.08	116.3	6.90	116.2	7.08	116.4
8a	–	141.6	–	141.4	–	141.1	8a'	–	145.8	–	145.9	–	145.1
NCH_2	–	−291.6[b]	–	−292.5[b]	–	−280.9[b]	NH	n.o.	−343.1[b]	n.o.	−338.5[b]	n.o.	−339.4[b]
NCH_2	3.91	40.0	4.01	40.4	3.72	43.3	NCH_2	2.63	42.9	2.68	42.8	2.64	40.8
	3.72		3.86		3.47			2.59		2.58			
CH_2O	4.35	65.0	4.40	65.2	4.30	64.3	CH_2O	4.08	67.9	4.08	67.7	4.11	67.9
			4.31		4.24								
C=O	–	152.5	–	151.8	–	152.1	C=O	–	154.3	–	154.3	–	154.2
1′(R^1)	–	–	–	–	–	–	1′(R^1)	10.96	92.3[c]	10.96	91.3[c]	11.26	91.8[c]

[a] The numbering of compounds **8** for NMR-purpose in Table 7 starts from N(1) and continues to C(8a).
[b] δ (^{15}N).
[c] $^{1}J(^{15}N, H)$.

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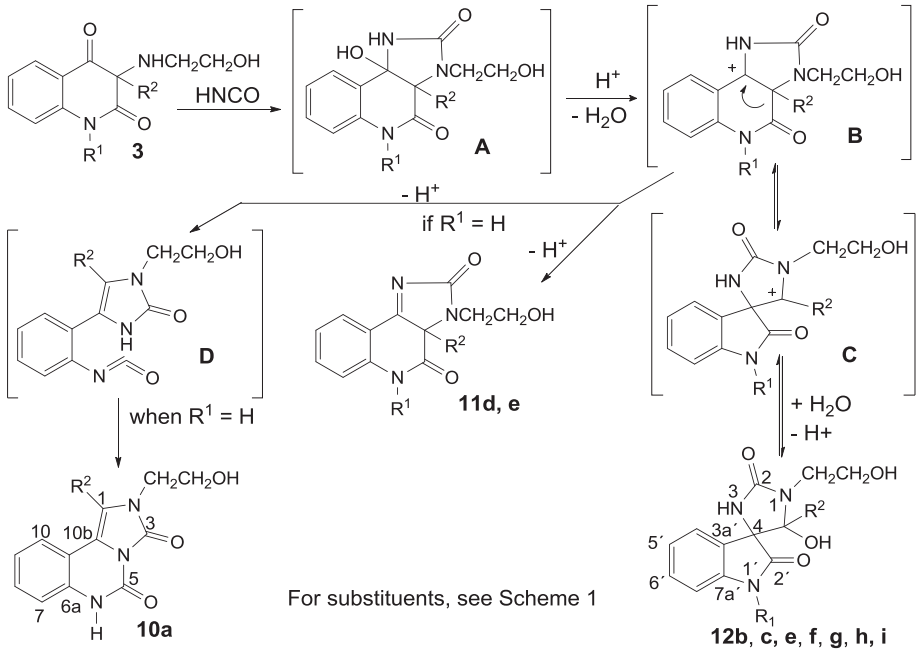

Scheme 2.

Tables 8
^{1}H and ^{13}C chemical shifts of compounds **10** and **11** in DMSO-d_6.

Position	**10a**		Position	**11d**		**11e**		**11g**	
	δ(H)	δ(C)		δ(H))	δ_C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	119.8	1	–	–	–	–	–	–
2	–	254.6[a]	2	–	166.3	–	165.5	–	166.5
3	–	148.2	3	–	–	–	–	–	–
4	–	232.0[a]	3a	–	74.6	–	75.4	–	75.0
5	–	145.0	4	–	168.2	–	167.5	–	168.5
6	–	−64.6[a]	5	–	–	–	–	–	–
6a	–	145.0	5a	–	141.4	–	141.4	–	142.6
7	6.97	116.0	6	7.43	116.6	7.40	116.7	6.39	117.2
8	7.17	127.3	7	7.76	135.5	7.75	135.4	7.55	135.1
9	7.07	123.1	8	7.37	124.0	7.36	124.1	7.29	124.0
10	7.50	121.8	9	7.92	126.0	7.87	126.0	7.92	126.2
10a	–	113.7	9a	–	116.2	–	116.8	–	115.9
10b	–	111.5	9b	–	184.6	–	183.8	–	184.8
NCH_2	3.68	43.0	NCH_2	3.61	43.6	3.66	44.0	3.62	43.7
				3.44		3.55		3.42	
CH_2O	3.58	58.9	CH_2O	3.70	58.7	3.75	58.9	3.68	58.7
OH	4.95	–	OH	4.48	–	4.81	–	4.79	–
1′(R^1)	10.58	92.3[b]	1′(R^1)	3.31	29.7	3.34	29.8	–	136.9
2′(R^1)	–	–	2′(R^1)	–	–	–	–	7.48	129.5
								7.27	129.0
3′(R^1)	–	–	3′(R^1)	–	–	–	–	7.55	130.3
									130.0
4′(R^1)	–	–	4′(R^1)	–	–	–	–	7.63	129.1
1′(R^2)	2.83	23.1	1′(R^2)	2.35	35.3	3.47	41.7	3.62	35.3
				2.10		3.14		3.42	
2′(R^2)	1.52	29.1	2′(R^2)	1.18	24.2	–	131.9	1.97	24.4
3′(R^2)	1.44	21.9	3′(R^2)	0.86	21.2	6.78	129.7	0.86	21.3
				0.75				0.75	
4′(R^2)	0.93	13.8	4′(R^2)	0.75	13.6	7.18	128.0	0.75	13.7
5′(R^2)			5′(R^2)	–	–	7.56	127.7	–	–

[a] δ (^{15}N), [b] ^{1}J(^{15}N, H).

concentration of 500 ng mL^{-1}) were infused into the ESI source as methanol:water (1:1, v:v) solutions via a syringe pump with a constant flow rate of 3 μL min^{-1}. The other instrumental conditions were as follows: electrospray voltage of ±4.2 kV, capillary exit voltage of ±140 V, drying gas temperature of 220 °C, drying gas flow of 6.0 dm^3 min^{-1}, nebulizer pressure of 8.0 psi. Nitrogen was used as the nebulizing and drying gas for all experiments. Tandem mass spectra were collected using collision-induced dissociation (CID) with He as the collision gas after isolating the required ions. Column chromatography was carried out on silica gel (Merck, grade 60, 70–230 mesh) using successive mixtures of chloroform/ethanol (in ratios from 99:1 to 8:2) (S1) or benzene/ethyl acetate (in ratios from 99:1 to 8:2) (S2). Reactions as well as the course of separation and also the purity of substances were monitored by TLC (elution systems benzene/ethyl acetate (4:1) (S3), chloroform/ethanol (9:1 and 1:1) (S4 and S5), hexane/ethyl acetate (4:1) (S6), and chloroform/ethyl acetate (7:3) (S7) on Alugram® SIL G/UV$_{254}$ foils (Macherey-Nagel). Elemental analyses (C, H, N) were performed with a EA Flash EA 1112 Elemental Analyzer (Thermo Fisher Scientific).

4.2. General procedure for the reaction of 3-chloroquinolin-2-ones 2 with ethanolamine

To the solution of compound **1** (2 mmol) in DMF (10 mL), pulverized potassium carbonate (552 mg, 4 mmol) and ethanolamine (0.13 mL, 2.1 mmol) were added and the mixture was stirred at room temperature. The course of the reaction was monitored with TLC. On completion, the reaction mixture was diluted with water (20 mL). The product was filtered with suction, dried and crystallized from an appropriate solvent. In cases where the crude product was oily or waxy, the solution was extracted with chloroform (3 × 20 mL). The collected extracts were dried with anhydrous sodium sulfate, evaporated to dryness and the residue was separated by column chromatography on silica gel.

4.2.1. Major products

*4.2.1.1. 3-(Hydroxyethylamino)-3-butylquinolin-2,4(1H,3H)-dione (**3a**).* Compound was prepared from **2a** in 51% yield (282 mg; elution system S2). Colorless solid, mp 62–68 °C (ethyl acetate/hexane). IR: 3425, 3235, 2958, 2927, 2860, 1702, 1667, 1612, 1597, 1485, 1361, 1313, 1251, 1063, 757, 665, 527 cm^{-1}. ESI-MS (pos.) *m/z* (%): 277.1 [M+H]$^+$ (100). ESI-MS (neg.) *m/z* (%): 573.1 [2M-

Table 9
^{1}H, ^{13}C and ^{15}N chemical shifts and $^{1}J(^{15}N, H)$ (Hz, ± 0.3 Hz) of compounds **12** in DMSO-d_6.

Position	**12b**		**12c**		**12e**		**12f**		**12h**		**12i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	−287.3[a]	–	−288.7[a]	–	−286.6 [a]	–	−286.6[a]	–	−286.5 [a]	–	−287.3[a]
2	–	159.0	–	161.0	–	159.2	–	161.1	–	159.0	–	161.1
3	7.45	−266.5 [a]	7.67	−268.0 [a]	7.67	−266.6 [a]	7.70	−268.1 [a]	7.67	−265.8[a]	7.89	−268.2 [a]
	–	91.2[b]	–	92.1[b]	–	92.3 [b]	–	92.1[b]	–	92.2[b]	–	91.2 [b]
4	–	69.5	–	74.8	–	69.6	–	75.1	–	70.0	–	75.5
5	–	83.7	–	85.1	–	82.7	–	84.1	–	83.1	–	84.5
OH	6.85	–	6.46	–	7.00	–	6.57	–	7.00	–	6.74	–
1′	–	−244.2 [a]	–	−243.7 [a]	–	−251.4 [a]	–	−250.8 [a]	–	−231.0[b]	–	−229.2 [a]
2′	–	170.5	–	170.5	–	170.2	–	170.0	–	170.0	–	170.2
3a'	–	123.4	–	122.5	–	124.5	–	123.6	–	124.5	–	123.4
4′	7.52	125.6	7.46	127.4	7.63	125.8	7.56	127.3	7.74	126.1	7.62	127.7
5′	6.83	122.0	6.97	122.7	6.95	122.5	7.08	123.1	6.98	122.8	7.07	123.3
6′	6.87	128.7	7.28	129.8	7.04	128.9	7.41	130.0	6.89	128.8	7.22	129.8
7′	6.34	114.2	6.99	115.3	6.50	113.6	7.28	115.1	5.57	115.2	6.31	116.3
7a'	–	134.1	–	134.9	–	135.8	–	136.8	–	137.7	–	137.8
NCH_2	3.67	43.8	3.39	46.5	3.75	44.0	3.11	46.5	3.69	43.9	3.34	46.4
	3.45	–	3.13	–	3.51	–	3.06	–	3.43	–	3.04	–
CH_2O	3.60	60.2	3.75	59.4	3.62	60.2	3.73	59.4	3.59	60.2	3.72	59.3
	3.45	–	3.71	–	3.51	–	3.70	–	3.52	–	–	–
OH	4.69	–	4.71	–	4.72	–	4.71	–	4.67	–	4.71	–
1′(R^1)	10.17	90.1[b]	10.95	90.0[b]		28.9		29.8	–	137.0	–	137.8
2′(R^1)	–	–	–	–	–	–	–	–	6.80	130.5	6.80	130.8
3′(R^1)	–	–	–	–	–	–	–	–	7.48	130.0	7.48	127.2
4′(R^1)	–	–	–	–	–	–	–	–	7.43	128.5	7.43	128.8
1′(R^2)	3.26	36.3	–	133.0	3.25	36.5	–	132.9	3.42	36.5	–	132.9
	3.04	–	–	–	3.04	–	–	–	3.13	–	–	–
2′(R^2)	–	133.0	6.99	128.1	–	132.9	7.21	128.4	–	133.0	7.08	130.8
3′(R^2)	7.04	130.5	7.30	128.2	6.87	130.0	7.29	128.0	7.08	130.8	6.98	130.0
4′(R^2)	6.85	126.8	7.30	128.3	6.83	126.8	7.29	128.3	6.98	127.2	6.98	128.3
5′(R^2)	6.85	126.5	–	–	6.80	126.5	–	–	6.98	126.9	–	–

[a] $\delta(^{15}N)$.
[b] $^{1}J(^{15}N, H)$.

2H + Na]$^-$ (6), 274.9 [M-H]$^-$ (100). For $C_{15}H_{20}N_2O_3$ (276.33) calcd. C 65.20, H 7.30, N 10.14; found: C 65.28, H 7.38, N 9.99.

*4.2.1.2. 3-(Hydroxyethylamino)-3-benzylquinolin-2,4(1H,3H)-dione (**3b**).* Compound was prepared from **2b** in 24% yield (149 mg, elution system S2). Colorless solid, mp 164–170 °C (ethyl acetate/hexane). IR: 3327, 3187, 3062, 2928, 2851, 1703, 1683, 1665 1612, 1595, 1486, 1457, 1436, 1373, 1297, 1235, 1158, 1047, 945, 912, 879, 851, 765, 726, 697, 666, 588, 504 cm^{-1}. ESI-MS (pos.) *m/z* (%): 311.1 [M+H]$^+$ (100). ESI-MS (neg.) *m/z* (%): 308.9 [M-H]$^-$ (100). For $C_{18}H_{18}N_2O_3$ (310.35) calcd. C 69.66, H 5.85, N 9.03, found C 69.62, H 5.96, N 8.93.

*4.2.1.3. 3-(Hydroxyethylamino)-3-phenylquinolin-2,4(1H,3H)-dione (**3c**).* Compound was prepared from **2c** in 69% yield (409 mg). Colorless solid, mp 148–150 °C (hexane). IR: 3061, 2982, 2921, 1704, 1672, 1615, 1596, 1485, 1449, 1437, 1355, 1321, 1254, 1232, 1199,1165, 1124, 1107, 1066, 1043, 1028, 944, 906, 833, 763, 749, 698, 668, 604, 544 cm^{-1}. ESI-MS (pos.) *m/z* (%): 297.1 [M+H]$^+$ (100). ESI-MS (neg.) *m/z* (%): 613.1 [2M-2H + Na]$^-$ (6), 294.9 [M-H]$^-$ (100). For $C_{17}H_{16}N_2O_3$ (296.32) calcd. C 68.91, H 5.44, N 9.45, found: C 68.95, H 5.68, N 9.48.

*4.2.1.4. 3-(Hydroxyethylamino)-1-methyl-3-butylquinolin-2,4(1H,3H)-dione (**3d**).* Compound was prepared from **2d** in 68% yield (395 mg). Colourless solid, mp 113–118 °C (ethyl acetate). IR: 3304, 2965, 2876, 2855, 1663, 1608, 1506, 1473, 1421, 1378, 1356, 1304, 1270, 1249, 1206, 1118, 1100, 1084, 1042, 1030, 978, 943, 823, 881, 847, 827, 771, 752, 666, 643, 610, 587, 531 cm^{-1}. ESI-MS (pos.) *m/z* (%): 291.1 [M+H]$^+$ (100). For $C_{16}H_{22}N_2O_3$ (290.36) calcd. C 66.18, H 7.64, N 9.65, found: C 66.12, H 7.71, N 9.45.

*4.2.1.5. 3-(Hydroxyethylamino)-1-methyl-3-benzylquinolin-2,4(1H,3H)-dione (**3e**).* Compound was prepared from **2e** in 31% yield besides **4e** and **5e** (201 mg, elution system S2). Colorless solid, mp 154–156 °C (ethyl acetate). IR: 3426, 3026, 2909, 1694, 1634, 1598, 1476, 1417, 1375, 1317, 1250, 1212, 1176, 1126, 1099, 1071, 1021, 1003, 952, 914, 873, 843, 818, 769, 737, 705, 661, 643, 583, 518 cm^{-1}. ESI-MS (pos.) *m/z* (%): 325.1 [M+H]$^+$ (100). For $C_{19}H_{20}N_2O_3$ (324.37) calcd. C 70.35, H 6.21, N 8.64; found C 70.19, H 6.20, N 8.63.

*4.2.1.6. 3-(Hydroxyethylamino)-1-methyl-3-phenylquinolin-2,4(1H,3H)-dione (**3f**).* Compound was prepared from **2f** in 88% yield (546 mg). Colorless solid, mp 130–133 °C (hexane). IR: 3299, 3057, 2934, 2857, 1705, 1671, 1603, 1491, 1471, 1443, 1417, 1349, 1305, 1256, 1195, 1183, 1109, 1076, 1054, 1039, 899, 853, 800, 764, 724, 708, 656, 597, 525, 512 cm^{-1}. ESI-MS (pos.) *m/z* (%): 311.1 [M+H]$^+$ (100). For $C_{18}H_{18}N_2O_3$ (310.35) calcd. C 69.66, H 5.85, N 9.03; found C 69.63, H 5.93, N 8.96.

*4.2.1.7. 3-(Hydroxyethylamino)-3-butyl-1-phenylquinolin-2,4(1H,3H)-dione (**3g**).* Compound was prepared from **2g** in 65% yield (458 mg, elution system S2). Yellowish solid, mp 75–78 °C (hexane). IR: 3307, 2958, 1679, 1606, 1496, 1462, 1340, 1301, 1249, 1209, 1156, 1124, 1084, 1047, 941, 833, 764, 750, 703, 652 cm^{-1}. ESI-MS (pos.) *m/z* (%): 727.3 [2M + Na]$^+$ (11), 705.2 [2M + H]$^+$ (8), 375.1 [M+Na]$^+$ (9), 353.1 [M+H]$^+$ (100). For $C_{21}H_{24}N_2O_3$ (352.43) calcd. C 71.57, H 6.86, N 7.95, found C 71.31, H 6.99, N 7.78.

*4.2.1.8. 3-Benzyl-3-(hydroxyethylamino)-1-phenylquinolin-2,4(1H,3H)-dione (**3h**).* Compound was prepared from **2h** in 17% yield (131 mg, elution system S2) besides **4h** and **5h**. Colourless solid, mp 115–118 °C (hexane). IR: 3440, 3306, 3062, 2980, 2887,

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1687, 1602, 1495, 1462, 1351, 1335, 1304, 1262, 1248, 1207, 1179, 1164, 1138, 1113, 1074, 1039, 1018, 988, 965, 953, 812, 756, 729, 701, 682, 650, 596, 577, 513 cm^{-1}. ESI-MS (pos.) *m/z* (%): 795.2 $[2M + Na]^+$ (12), 599.2 $[3M + Ca]^{2+}$ (5), 425.1 $[M+K]^+$ (6), 409.1 $[M+Na]^+$ (78), 406.1 $[2M + Ca]^{2+}$ (16), 387.1 $[M+H]^+$ (100). ESI-MS (neg.) *m/z* (%): 385.0 $[M-H]^-$ (100). For $C_{24}H_{22}N_2O_3$ (386.44) calcd. C 74.59, H 5.74, N 7.25, found C 74.44, H 5.98, N 6.98.

*4.2.1.9. 3-(Hydroxyethylamino)-1,3-diphenylquinolin-2,4(1H,3H)-dione (**3i**).* Compound was prepared from **2i** in 56% yield (81 mg, elution system S2). Yellowish solid, mp 153–156 °C (benzene). IR: 3464, 3326, 3061, 2920, 2851, 1702, 1665, 1598, 1493, 1460, 1338, 1299, 1246, 1190, 1163, 1148, 1074, 926, 870, 766, 705, 575 cm^{-1}. ESI-MS (pos.) *m/z* (%): 373.1 $[M+H]^+$ (100). For $C_{23}H_{20}N_2O_3$ (372.42) calcd. C 74.18, H 5.41, N 7.52, found C 73.99, H 5.51, N 7.35.

4.2.2. Minor products

*4.2.2.1. 3-Benzyl-3-(13-benzyl-12-oxo-11-methyl-11,12-dihydroquinolin-14-yl)oxy)-1-methylquinoline-2,4(1H,3H)-dione (**5e**).* Compound was prepared from **2e** in 4% yield (21 mg, elution system S2). besides **3e** and **4e**. Colorless solid, mp 183–189 (benzene/cyclohexane). IR: 3084, 3055, 3027, 3001, 2936, 1698, 1667, 1633, 1596, 1494, 1472, 1415, 1362, 1325, 1307, 1228, 1152, 1109, 1074, 1041, 1014, 992, 932, 762, 752, 725, 699, 665, 545, 528, 504 cm^{-1}. ESI-MS (pos.) *m/z* (%): 551.2 $[M+Na]^+$ (13), 529.2 $[M+H]^+$ (100). For $C_{34}H_{28}N_2O_4$ (528.60) calcd. C 77.25, H 5.34, N 5.30, found C 77.27, H 5.29, N 5.25. The structure was confirmed by the synthesis from **1e** and **2e**.

*4.2.2.2. 3-Benzyl-3-(13-benzyl-12-oxo-11-phenyl-11,12-dihydroquinolin-14-yl)oxy)-1-phenylquinoline-2,4(1H,3H)-dione (**5h**).* Compound was prepared from **2h** in 5% yield (33 mg, elution system S2) besides **3h** and **4h**. Colorless solid, mp 111–119 °C (benzene). IR: 3062, 3030, 2925, 2850, 1742, 1704, 1673, 1648, 1599, 1493, 1464, 1351, 1299, 1270, 1220, 1155, 1098, 933, 877, 761, 700, 660, 595, 555 cm^{-1}. ESI-MS (pos.) *m/z* (%): 1327.5 $[2M + Na]^+$ (8), 691.2 $[M+K]^+$ (18), 675.3 $[M+Na]^+$ (100), 672.2 $[2M + Ca]^{2+}$ (19), 653.3 $[M+H]^+$ (19). EA: For $C_{44}H_{32}N_2O_4$ (652.74) calcd. C 80.96, H 4.94, N 4.29, found C 80.89, H 5.04, N 4.15. The structure was confirmed by the synthesis from **1h** and **2h**.

4.3. General procedure for the reaction of 3 with triphosgene

The solution of **3** (2 mmol) in benzene (50 mL) was cooled to 0 °C, triethylamine (0.6 mL, 4.2 mmol) and 4-dimethylaminopyridine (0.11 g, 0.9 mmol) were added and then triphosgene (0.215 g, 0.75 mmol) was added in small portions during 10 min. The suspension was stirred at room temperature for 5 h and evaporated to dryness. To the residue, water (20 mL) and chloroform (15 mL) were added. The mixture was shaken, then separated and the water portion was extracted with chloroform (3 × 15 mL). The combined chloroform extracts were washed with hydrochloric acid (2.5%, 15 mL), dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel.

*4.3.1. 3-Butyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6a**)*

Compound was prepared from **3a** in 42% yield (254 mg, elution system S2) besides **8a** and **9a**. Colorless solid, mp 103–108 C (benzene/hexane). IR: 3188, 3087, 2960, 2929, 2870, 1738, 1707, 1671, 1612, 1485, 1413, 1386, 1364, 1302, 1255, 1229, 1158, 1127, 1039, 976, 846, 769, 735, 682, 667, 603, 567, 526 cm^{-1}. ESI-MS (pos.) *m/z* (%): 627.2 $[2M + Na]^+$ (14), 605.2 $[2M + H]^+$ (16), 473.1 $[3M + Ca]^{2+}$ (7), 341.0 $[M+K]^+$ (16), 325.1 $[M+Na]^+$ (58), 303.1 $[M+H]^+$ (100). ESI-MS (neg.) *m/z* (%): 625.1 $[2M-2H + Na]^-$ (7), 603.1 $[2M-H]^-$ (14), 300.9 $[M-H]^-$ (100). EI-MS: 302 (M^+, 2), 260 (9), 259 (57), 218 (7), 217 (50), 215 (8), 218 (7), 217 (50), 215 (8), 200 (18), 188 (15), 187 (6), 186 (7), 176 (11), 175 (100), 174 (15), 172 (6), 161 (7), 146 (37), 130 (11), 128 (7), 120 (9), 119 (10), 92 (13), 90 (8), 77 (8), 68 (33), 65 (6), 55 (9), 54 (6), 42 (9), 41 (22). For $C_{16}H_{18}N_2O_4$ (302.33) calcd. C 63.56, H 6.00, N 9.27, found C 63.54, H 5.81, N 8.99.

*4.3.2. 3-Benzyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6b**)*

Compound was prepared from **3b** in 17% yield (114 mg, elution system S2) besides **3b** and **8b**. Colorless solid, mp 272–277 °C (benzene). IR: 3228, 3194, 3087, 2996, 2927, 1745, 1703, 1673, 1614, 1597, 1486, 1417, 1387, 1303, 1259, 1230, 1158, 1129, 1089, 1066, 1040, 979, 877, 766, 703, 686, 667, 604, 542, 525 cm^{-1}. ESI-MS (pos.) *m/z* (%): 695.2 $[2M + Na]^+$ (13), 359.0 $[M+Na]^+$ (100), 356.1 $[2M + Ca]^{2+}$ (16). ESI-MS (neg.) *m/z* (%): 334.9 $[M-H]^-$ (100). EI-MS: *m/z* (%): 336 (M^+, 3), 252 (4), 251 (24), 250 (36), 249 (100), 248 (77), 245 (10), 220 (5), 201 (12), 183 (7), 146 (12), 128 (5), 120 (5), 119 (7), 117 (8), 116 (7), 103 (6), 92 (17), 91 (93), 90 (13), 89 (6), 77 (10), 65 (11). For $C_{19}H_{16}N_2O_4$ (336.34) calcd. C 67.85, H 4.79, N 8.33, found: C 67.72, H 4.83, N 8.18.

*4.3.3. 3-Phenyl-3-(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6c**)*

Compound was prepared from **3c** in 23% yield (148 mg, elution system S2) besides **8c** and **9c**. Colorless solid, mp 158–164 C (benzene/hexane). IR: 3255, 3062, 2989, 2905, 1747, 1706 besides 1684, 1613, 1596, 1486, 1449, 1419, 1354, 1322, 1254, 1225, 1160, 1121, 1035, 993, 969, 961, 878, 852, 782, 768, 747, 732, 689, 666, 592, 540, 526 cm^{-1}. ESI-MS (pos.) *m/z* (%): 683.1 $[2M + K]^+$ (6), 667.1 $[2M + Na]^+$ (36), 645.2 $[2M + H]^+$ (15), 361.0 $[M+K]^+$ (17), 345.1 $[M+Na]^+$ (100), 323.1 $[M+H]^+$ (31). ESI-MS (neg.) *m/z* (%): 665.0 $[2M-2H + Na]^-$ (26), 643.0 $[2M-H]^-$ (23), 320.9 $[M-H]^-$ (100). EI-MS: *m/z* (%): 323 (4), 322 (21), 238 (16), 237 (100), 236 (40), 229 (11), 221 (10), 146 (11), 132 (7), 131 (9), 130 (8), 120 (11), 119 (26), 117 (13), 105 (7), 104 (27), 103 (30), 92 (14), 91 (6), 90 (9), 77 (17), 76 (9), 64 (6), 63 (5). For $C_{18}H_{14}N_2O_4$ (322.31) calcd. C 67.07, H 4.38, N 8.69, found C 66.94, H 4.49, N 8.56.

*4.3.4. 3-Butyl-1-methyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6d**)*

Compound was prepared from **3d** in 31% yield (196 mg, elution system S2). Yellowish oil. IR: 2959, 2929, 2872, 1748, 1707, 1669, 1602, 1474, 1414, 1362, 1301, 1258, 1231, 1154, 1143, 1118, 1038, 979, 931, 863, 828, 758, 730, 709, 663, 565, 532 cm^{-1}. ESI-MS (pos.) *m/z* (%): 655.2 $[2M + Na]^+$ (20), 355.0 $[M+K]^+$ (11), 339.1 $[M+Na]^+$ (100), 317.1 $[M+H]^+$ (4). EI-MS: *m/z* (%): 317 (1), 316 (M^+, 5), 273 (6), 232 (6), 231 (38), 215 (6), 214 (10), 202 (18), 201 (8), 200 (11), 190 (13), 189 (100), 188 (12), 187 (6), 186 (24), 175 (7), 160 (13), 146 (6), 134 (9), 133 (5), 132 (8), 105 (9), 104 (11), 91 (5), 85 (6), 84 (6), 83 (6), 78 (7), 77 (13), 71 (7), 68 (6), 57 (13), 55 (11), 43 (11), 41 (16). EA: For $C_{17}H_{20}N_2O_4$ (316.35) calcd. C 64.54, H 6.37, N 8.86, found: C 64.23, H 6.53, N 8.59.

*4.3.5. 3-Benzyl-1-methyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6e**)*

Compound was prepared from **3e** in 37% yield (259 mg, elution system S1). Colorless solid, mp 200–207 °C (benzene/hexane). IR: 3029, 2979, 2922, 1743, 1700, 1665, 1602, 1474, 1455, 1441, 1414, 1369, 1318, 1302, 1264, 1240, 1170, 1142, 1036, 977, 922, 911, 867, 760, 737, 704, 663, 584, 546, 508 cm^{-1}. ESI-MS (pos.) *m/z* (%): 723.2 $[2M + Na]^+$ (7), 389.0 $[M+K]^+$ (19), 373.0 $[M+Na]^+$ (100), 370.0 $[2M + Ca]^{2+}$ (9), 351.0 $[M+H]^+$ (4). For $C_{20}H_{18}N_2O_4$ (350.37) calcd. C 68.56, H 5.18, N 8.00; found C 68.51, H 5.26, N 7.82.

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*4.3.6. 1-Methyl-3-phenyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6f**)*

Compound was prepared from **3f** in 28% yield (188 mg, elution system S2). Colorless solid, mp 199–204 °C (benzene/hexane). IR: 3086, 2957, 2907, 1740, 1708, 1669, 1601, 1496, 1473, 1447, 1407, 1359, 1299, 1240, 1227, 1207, 1144, 1095, 1065, 1036, 1002, 976, 916, 871, 831, 769, 758, 713, 699, 665, 618, 571, 524 cm^{-1}. ESI-MS (pos.) *m/z* (%): 695.2 $[2M + Na]^+$ (18), 375.1 $[M+K]^+$ (47), 359.1 $[M+Na]^+$ (100), 356.1 $[2M + Ca]^{2+}$ (12), 337.1 $[M+H]^+$ (95). EI-MS: *m/z* (%): 336 (M^+, 4), 252 (17), 251 (100), 250 (56), 133 (7), 132 (6), 130 (7), 105 (17), 104 (21), 103 (16), 78 (6), 77 (12), 57 (6). For $C_{19}H_{16}N_2O_4$ (336.34) calcd. C 67.85, H 4.79, N 8.33, found:C 67.95, H 4.91, N 8.17.

*4.3.7. 3-Butyl-1-phenyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6g**)*

Compound was prepared from **3g** in 23% yield (174 mg, elution system S1) besides **7g**. Colorless solid, mp 165–175 °C (benzene/cyclohexane). IR: 3063, 2961, 2929, 2873, 1739, 1704, 1672, 1601, 1492, 1465, 1415, 1349, 1303, 1258, 1236, 1186, 1168, 1027, 1073, 1039, 978, 915, 852, 821, 756, 731, 711, 695, 662, 612, 576, 517 cm^{-1}. ESI-MS (pos.) *m/z* (%): 779.3 $[2M + Na]^+$ (30), 417.1 $[M+K]^+$ (14), 401.1 $[M+Na]^+$ (100), 379.1 $[M+H]^+$ (3). For $C_{22}H_{22}N_2O_4$ (378.42) calcd. C 69.83, H 5.86, N 7.40, found C 69.85, H 6.06, N 7.22.

*4.3.8. 3-Benzyl-1-phenyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6h**)*

Compound was prepared from **3h** in 44% yield (363 mg, elution system S2). Colorless solid, mp 226–231 °C (benzene/hexane). IR: 3075, 3029, 2970, 2914, 1752, 1695, 1663, 1603, 1489, 1463, 1410, 1365, 1301, 1257, 1238, 1223, 1180, 1162, 1120, 1091, 1071, 1043, 969, 902, 865, 817, 767, 738, 706, 691, 661, 613, 550, 507 cm^{-1}. ESI-MS (pos.) *m/z* (%): 847.2 $[2M + Na]^+$ (6), 451.0 $[M+K]^+$ (16), 435.1 $[M+Na]^+$ (100), 432.0 $[2M + Ca]^{2+}$ (14), 413.1 $[M+H]^+$ (4). For $C_{25}H_{20}N_2O_4$ (412.44) calcd. C 72.80, H 4.89, N 6.79, found C 73.01, H 4.89, N 6.56.

*4.3.9. 1,3-diphenyl-3(2-oxooxazolidin-3-yl)quinoline-2,4(1H,3H)-dione (**6i**)*

Compound was prepared from **3i** in 25% yield (199 mg, elution system S2) besides **7i**. Colorless solid, mp 261–265 °C (benzene). IR: 3504, 3065, 2971, 2917, 1761, 1716, 1685, 1601, 1491, 1462, 1452, 1409, 1341, 1302, 1285, 1237, 1167, 1119, 1041, 1002, 969, 916, 864, 762, 716, 665, 607, 517 cm^{-1}. ESI-MS (pos.) *m/z* (%): 819.2 $[2M + Na]^+$ (18), 437.0 $[M+K]^+$ (8), 421.0 $[M+Na]^+$ (100), 418.0 $[2M + Ca]^{2+}$ (7), 399.0 $[M+H]^+$ (3). For $C_{24}H_{18}N_2O_4$ (398.41) calcd. C 72.35, H 4.55, N 7.03, found:C 72.51, H 4.75, N 6.98.

*4.3.10. Bis(2-((2,4-dioxo-3-butyl-1-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)amino)ethyl carbonate (**7g**)*

Compound was prepared from **3g** in 6% yield (44 mg, elution system S2) besides **6g**. Oil, with hexane colorless solid, mp 77–93 °C (hexane). IR: 3347, 3067, 3040, 2957, 2930, 2871, 1748, 1808, 1673, 1600, 1492, 1463, 1403, 1346, 1300, 1259, 1160, 1072, 1024, 962, 759, 702, 664, 587, 515 cm^{-1}. ESI-MS (pos.) *m/z* (%): 769.3 $[M+K]^+$ (6), 753.4 $[M+Na]^+$ (100), 731.4 $[M+H]^+$ (47). EI-MS: *m/z* (%): 730 (M^+, 0.01), 429 (2), 378 (3), 334 (6), 322 (6), 321 (22), 318 (5), 294 (8), 293 (23), 292 (9), 291 (22), 278 (16), 277 (20), 276 (12), 265 (13), 264 (25), 263 (9), 262 (14), 252 (21), 251 (100), 250 (37), 249 (6), 248 (11), 238 (5), 237 (12), 236 (5), 223 (7), 222 (13), 221 (6), 210 (7), 209 (6), 208 (9), 296 (29), 295 (28), 294 (5), 180 (11), 168 (15), 167 (29), 166 (12), 140 (15), 139 (9), 128 (25), 113 (6), 112 (9), 111 (6), 110 (8), 99 (6), 98 (12), 97 (9), 92 (10), 91 (7), 85 (31), 84 (38), 83 (12), 82 (6), 77 (31), 71 (11), 70 (6), 69 (13), 68 (7), 57 (28), 56 (9), 55 (26), 54 (11), 51 (16), 45 (12), 44 (49), 43 (25), 42 (22), 41 (30). For $C_{43}H_{46}N_4O_7$ (730.85) calcd. C 70.67, H 6.34, N 7.67, found: C 70.39, H 6.54, N 7.45.

*4.3.11. Bis(2-((2,4-dioxo-1,3-diphenyl-1,2,3,4-tetrahydroquinolin-3-yl)amino)ethyl carbonate (**7i**)*

Compound was prepared from **3i** in 11% yield (85 mg, elution system S2) besides **6i**. Colorless solid, mp 131–135 °C (benzene). IR: 3462, 3064, 3035, 2957, 2857, 1747, 1710, 1676, 1601, 1492, 1462, 1402, 1337, 1256, 1161, 1072, 1024, 1003, 917, 868, 761, 699, 656, 606, 571, 515 cm^{-1}. ESI-MS (pos.) *m/z* (%): 809.2 $[M+K]^+$ (6), 793.2 $[M+Na]^+$ (100), 771.3 $[M+H]^+$ (53). For $C_{47}H_{38}N_4O_7$ (770.83) calcd. C 73.23, H 4.97, N 7.27, found C 72.99, H 5.16, N 7.12.

*4.3.12. 2-((3-Butyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)amino)ethyl (2-(9a-butyl-2,9-dioxo-9,9a-dihydrooxazolo[5,4-b]quinolin-1(2H)-yl)ethyl) carbonate (**8a**)*

Compound was prepared from **3a** in 19% yield (115 mg, elution system S1) besides **6a** and **9a. C**olorless solid, mp 68–84 °C (cyclohexane). IR: 3070, 2959, 2928, 2853, 1815, 1750, 1691, 1672, 1600, 1485, 1463, 1371, 1260, 1190, 1158, 1035, 999, 953, 884, 786, 765, 676, 651, 626, 564, 535 cm^{-1}. ESI-MS (pos.) *m/z* (%): 643.2 $[M+K]^+$ (10), 627.2 $[M+Na]^+$ (100), 624.2 $[2M + Ca]^{2+}$ (7), 605.3 $[M+H]^+$ (67). ESI-MS (neg.) *m/z* (%): 603.1 $[M-H]^-$ (100). EI-MS: *m/z* (%): 604 (M^+, 3), 548 (4), 547 (12), 390 (13), 389 (6), 388 (23), 303 (17), 302 (19), 285 (14), 260 (10), 259 (56), 258 (32), 257 (6), 245 (37), 244 (5), 243 (35), 231 (6), 230 (5), 229 (30), 227 (8), 217 (26), 216 (20), 215 (70), 214 (8), 203 (17), 202 (38), 201 (100), 200 (13), 198 (8), 189 (20), 188 (18), 187 (17), 186 (19), 185 (6), 176 (7), 175 (57), 174 (22), 173 (18), 172 (8), 161 (14), 160 (6), 148 (7), 147 (10), 146 (64), 145 (7), 144 (8), 132 (18), 131 (6), 130 (38), 128 (19), 120 (28), 119 (27), 118 (10), 117 (8), 116 (8), 104 (7), 103 (7), 102 (15), 93 (7), 92 (22), 91 (10), 90 (27), 89 (17), 84 (68), 82 (8), 77 (16), 76 (10), 68 (18), 65 (9), 64 (8), 63 (7), 55 (7), 54 (16), 51 (6), 45 (21), 44 (64), 42 (51), 41 (35). $\delta(^{13}C)$: 196.0, 192.7, 172.5, 167.6, 154.3, 152.5, 145.6, 141.6, 136.6, 136.3, 127.2, 127.0, 126.7, 126.6122.7, 121.9, 119.1, 116.3, 73.0, 69.7, 37.9, 64.9, 42.9, 40.4, 34.2, 25.8, 25.0, 22.1, 21.4. For $C_{32}H_{36}N_4O_8$ (604.65) calcd. C 63.56, H 6.00, N 9.27, found C 63.77, H 6.25, N 8.91.

*4.3.13. 2-((3-benzyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)amino)ethyl (2-(9a-benzyl-2,9-dioxo-9,9a-dihydrooxazolo[5,4-b]quinolin-1(2H)-yl)ethyl) carbonate (**8b**)*

Compound was prepared from **3b** in 22% yield (148 mg, elution system S2) besides **6b**. Colorless solid, mp106-114 °C (cyclohexane). IR: 3300, 3064, 3032, 2925, 2853, 1815, 1747, 1391, 1668, 1599, 1785, 1758, 1369, 1261, 1158, 1084, 1034, 1002, 947, 769, 749, 703, 680, 651, 576, 527, 498 cm^{-1}. ESI-MS (pos.) *m/z* (%): 711.2 $[M+K]^+$ (13), 695.2 $[M+Na]^+$ (100), 692.2 $[2M + Ca]^{2+}$ (9), 673.2 $[M+H]^+$ (47). ESI-MS (neg.) *m/z* (%): 671.1 $[M-H]^-$ (100). EI-MS *m/z* (%): 336 (2), 293 (6), 292 (20), 248 (4), 202 (5), 201 (13), 161 (5), 146 (5), 130 (6), 92 (12), 91 (100), 90 (7), 65 (11), 44 (12). $\delta(^{13}C)$: 195.8, 192.0, 171.7, 166.6, 154.3, 151.8, 145.9, 141.4, 136.7, 136.3, 133.7, 132.4, 130.0, 129.9, 128.6, 128.2, 127.8, 127.4, 127.1, 127.0, 126.7, 126.5, 122.6, 121.9, 119.4, 116.2, 73.5, 71.1, 67.7, 65.2, 45.6, 42.8, 38.9. For $C_{38}H_{32}N_4O_8$ (672.68) calcd. C 67.85, H 4.79, N 8.33, found C 67.69, H 5.01, N 8.16.

*4.3.14. 2-((3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)amino)ethyl (2-(9a-phenyl-2,9-dioxo-9,9a-dihydrooxazolo[5,4-b]quinolin-1(2H)-yl)ethyl) carbonate (**8c**)*

Compound was prepared from **3c** in 34% yield (219 mg, elution system S2) besides **6c** and **9c**. Yellowish solid, mp 110–128 °C (hexane). IR: 3063, 2961, 2924, 2859, 1815, 1747, 1693, 1600, 1486, 1449, 1357, 1263, 1192, 1158, 1115, 1033, 991, 943, 887, 764, 749, 698, 668, 628, 590 cm^{-1}. ESI-MS (pos.) *m/z* (%): 645.2 $[M+H]^+$ (100). ESI-MS (neg.) *m/z* (%): 1287.1 $[2M-H]^-$ (23), 643.0 $[M-H]^-$ (100). EI-MS: *m/z* (%): 644 (M^+, 0.46), 323 (9), 322 (43), 279 (6), 278 (30), 277 (8), 265 (10), 263 (21), 261 (8), 250 (7), 249 (15), 238 (10), 237 (61), 236

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(47), 235 (10), 222 (5), 221 (24), 220 (9), 219 (7), 218 (6), 207 (9), 180 (8), 179 (6), 175 (10), 152 (6), 148 (8), 147 (10), 146 (46), 132 (15), 131 (8), 130 (22), 120 (32), 119 (44), 118 (13), 117 (19), 105 (20), 104 (100), 103 (29), 102 (7), 92 (25), 91 (13), 90 (29), 89 (14), 77 (49), 76 (24), 64 (10), 63 (12), 51 (18), 50 (12), 45 (11), 44 (71), 42 (33). $\delta(^{13}C)$: 193.7, 191.5, 171.4, 165.9, 154.2, 152.1, 145.1, 141.1, 137.3, 136.5, 136.4, 132.3, 130.7, 130.2, 129.6, 128.9, 128.7, 127.3, 127.2, 126.7, 126.5123.2, 122.9, 119.3, 116.4, 76.3, 71.4, 64.3, 43.3, 40.8. For$C_{36}H_{28}N_4O_8$ (644.63) calcd. C 67.07, H 4.38, N 8.69, found: C 66.95, H 4.54, N 8.43.

4.3.15. Bis[(2-(2,9-dioxo-9a-butyl-9,9a-dihydrooxazolo][5,4-b] quinolin-1(2H)-yl)ethyl) carbonate (**9a**)

Compound was prepared from **3a** in 3% yield (19 mg, elution system S2) besides **6a**. Colorless solid, mp 85–98 °C (hexane). IR: 3068, 2961, 2934, 2873, 1813, 1752, 1712, 1690, 1600, 1570, 1462, 1376, 1339, 1259, 1195, 1157, 1128, 1098, 1035, 999, 955, 883, 861, 783, 768, 752, 674, 651, 625, 564, 536, 501 cm^{-1}. ESI-MS (pos.) *m/z* (%): 669.2 $[M+K]^+$ (17), 653.2 $[M+Na]^+$ (100), 650.2 $[2M + Ca]^{2+}$ (10), 631.2 $[M+H]^+$ (2). EI-MS: *m/z* (%): 631 (13), 630 (M^+, 34), 587 (9), 558 (15), 557 (44), 302 (9), 286 (8), 285 (48), 284 (6), 259 (19), 244 (16), 243 (100), 242 (10), 241 (37), 240 (8), 231 (5), 230 (9), 229 (64), 228 (9), 227 (27), 217 (7), 215 (17), 214 (55), 213 (16), 212 (9), 211 (15), 202 (6), 201 (25), 200 (7), 199 (10), 198 (24), 197 (8), 187 (8), 186 (10), 185 (18), 184 (12), 183 (8), 175 (12), 174 (6), 158 (12), 157 (6), 146 (61), 144 (10), 142 (9), 132 (13), 131 (8), 130 (75), 129 (8), 128 (8), 121 (29), 120 (8), 116 (6), 110 (8), 104 (6), 103 (6), 102 (18), 90 (17), 89 (23), 84 (8), 77 (8), 76 (7), 68 (13), 54 (14), 45 (9), 44 (25), 42 (14), 41 (24). For $C_{33}H_{34}N_4O_9$ (630.64) calcd. C 62.85, H 5.43, N 8.88, found: C 62.81, H 5.69, N 8.69.

4.3.16. Bis[(2-(2,9-dioxo-9a-phenyl-9,9a-dihydrooxazolo][5,4-b] quinolin-1(2H)-yl)ethyl) carbonate (**9c**)

Compound was prepared from **3c** in 8% yield (54 mg, elution system S2) besides **6c** and **8c**. Colorless solid, mp 227–236 °C (benzene/hexane). IR: 3254, 1746, 1706, 1613, 1596, 1486, 1449, 1419, 1354, 1254, 1225, 1121, 1035, 782, 768, 732, 689, 666, 592 cm^{-1}. ESI-MS (pos.) *m/z* (%): 709.1 $[M+K]^+$ (26), 693.2 $[M+Na]^+$ (100), 671.2 $[M+H]^+$ (93). EI-MS: *m/z* (%): 672 (10), 671 (40), 670 (M^+, 94), 322 (24), 306 (15), 305 (78), 304 (62), 278 (6), 277 (12), 275 (7), 263 (41), 262 (14), 261 (50), 250 (14), 249 (8), 248 (14), 247 (61), 237 (32), 236 (32), 235 (10), 234 (12), 233 (11), 231 (7), 221 (11), 220 (37), 219 (29), 218 (11), 208 (9), 191 (10), 190 (8), 179 (7), 153 (15), 146 (100), 132 (11), 131 (11), 130 (63), 120 (9), 119 (9), 118 (11), 117 (29), 105 (16), 104 (44), 103 (28), 102 (11), 91 (8), 90 (31), 89 (43), 77 (28), 76 (19), 63 (6), 51 (9), 50 (7), 44 (25. For $C_{37}H_{26}N_4O_9$ (670.62) calcd. C 66.27, H 3.91, N 8.35, found: C 65.99, H 4.07, N 8.07.

4.4. General procedure for the reaction of 3 with potassium cyanate

To the stirring solution of **3** (2 mmol) in acetic acid (6 mL), solid KNCO (0.2535 g, 3125 mmol) was gradually added during 5 min at room temperature. After 18 h, crushed ice was added and the mixture was extracted with chloroform (3 × 10 mL). The collected extracts were dried and evaporated to dryness. The residue was crystallized from appropriate solvent or column chromatographed.

4.4.1. 1-butyl-2-(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5(2H,6H)-dione (**10a**)

Compound was prepared from **3a** in 42% yield (263 mg). Colorless solid, mp 271–274 °C (ethanol). IR: 3423, 3207, 3097, 2959, 2926, 2875, 1754, 1672, 1631, 1609, 1586, 1488, 1468, 1435, 1380, 1340, 1311, 1288, 1259, 1058, 948, 897, 866, 802, 750, 696, 630, 586, 546 cm^{-1}. ESI-MS (pos.) *m/z* (%): 625.2 $[2M + Na]^+$ (41), 471.2 $[3M + Ca]^{2+}$ (21), 340.1 $[M+K]^+$ (22), 324.1 $[M+Na]^+$ (82), 302.1 $[M+H]^+$ (100). ESI-MS (neg.) *m/z* (%): 623.1 $[2M\text{-}2H + Na]^-$ (14), 601.0 $[2M\text{-}H]^-$ (7), 300.0 $[M\text{-}H]^-$ (100). EI-MS: *m/z* (%): 301 (M^+, 87), 259 (15), 258 (100), 228 (9), 215 (23), 214 (15), 186 (5), 173 (6), 172 (6), 171 (10), 129 (5), 118 (5), 45 (7), 44 (6). For $C_{16}H_{19}N_3O_3$ (301.34) calcd. C 63.77, H 6.36, N 13.97, found C 63.51, H 6.51, N 14.06.

4.4.2. 3a-butyl-3-(2-hydroxyethyl)-5-methyl-3,3a-dihydro-2H-imidazo[4,5-c]quinoline-2,4(5H)dione (**11d**)

Compound was prepared from **3d** in 30% yield (189 mg, elution system S2). Yellowish solid, mp 161–163 °C (benzene). IR: 3384, 2950, 2872, 1711, 1696, 1612, 1472, 1432, 1367, 1351, 1284, 1190, 1162, 1112, 1075, 1051, 1014, 989, 970, 846, 777, 766, 726, 681, 649, 569, 535 cm^{-1}. ESI-MS (pos.) *m/z* (%): 653.3 $[2M + Na]^+$ (17), 354.0 $[M+K]^+$ (9), 338.1 $[M+Na]^+$ (100), 335.1 $[2M + Ca]^{2+}$ (14), 316.1 $[M+H]^+$ (5). EI-MS: *m/z* (%): 315 (M^+, 23), 297 (26), 285 (11), 272 (25), 257 (5), 241 (14), 229 (13), 228 (31), 215 (11), 214 (17), 201 (25), 200 (15), 188 (8), 185 (9), 173 (11), 132 (5), 130 (6), 129 (14), 128 (100), 98 (11), 84 (63), 57 (15), 55 (10), 45 (15), 43 (9), 41 (17). For C $_{17}H_{21}N_3O_3$ (315.37) calcd. C 64.74, H 6.71, N 13.32, found: C 64.68, H 6.70, N 13.29.

4.4.3. 3a-benzyl-3-(2-hydroxyethyl)-5-methyl-3,3a-dihydro-2H-imidazo[4,5-c]quinoline-2,4(5H)dione (**11e**)

Compound was prepared from **3e** in 3% yield (21 mg, elution system S2) besides **12e**. Colorless solid, mp 215–220 °C (benzene). IR: 3453, 1730, 1693, 1670, 1608, 1471, 1418, 1366, 1347, 1292, 1134, 1080, 1017, 776, 754, 705, 649, 592 cm^{-1}. ESI-MS (pos.) *m/z* (%): 721.2 $[2M + Na]^+$ (15), 388.0 $[M+K]^+$ (7), 372.1 $[M+Na]^+$ (100), 369.1 $[2M + Ca]^{2+}$ (13), 350.1 $[M+H]^+$ (12). ESI-MS (neg.) *m/z* (%): 348.0 $[M\text{-}H]^-$ (100). For $C_{20}H_{19}N_3O_3$ (349.38) calcd. C 68.75, H 5.48, N 12.03, found: C 68.62, H 5.52, N 11.93.

4.4.4. 3a-butyl-3-(2-hydroxyethyl)-5-phenyl-3,3a-dihydro-2H-imidazo[4,5-c]quinoline-2,4(5H)dione (**11g**)

Compound was prepared from **3g** in 33% yield (249 mg). Colorless solid, mp 107–113 °C (benzene/hexane). IR: 3473, 3089, 2960, 2931, 2874, 1718, 1697, 1606, 1493, 1465, 1431, 1358, 1339, 1281, 1248, 1163, 1123, 1053, 775, 756, 699, 684, 653, 601, 578, 513 cm^{-1}. ESI-MS (pos.) *m/z* (%): 777.3 $[2M + Na]^+$ (9), 416.1 $[M+K]^+$ (7), 400.1 $[M+Na]^+$ (100), 397.1 $[2M + Ca]^{2+}$ (17), 378.1 $[M+H]^+$ (5). EI-MS: *m/z* (%): 377 (M^+, 49), 359 (15), 346 (17), 334 (31), 291 (9), 290 (14), 276 (11), 263 (20), 250 (17), 194 (9), 128 (100), 84 (53), 77 (19), 57 (6), 51 (5), 45 (5), 44 (9), 41 (9). For $C_{22}H_{23}N_3O_3$ (377.43) calcd. C 70.01, H 6.14, N 11.13, found C 70.19, H 6.27, N 11.01.

4.4.5. (4R*,5S*)-5-benzyl-5-hydroxy-1-(hydroxyethyl)-1′H-spiro [imidazolidine-5,3′-indole]-2,2′-dione (**12b**)

Compound was prepared from **3b** in 34% yield (240 mg, elution system S1). Colorless solid, mp 202–211 °C (THF/cyclohexane). IR: 3382, 3065, 2992, 2931, 1712, 1678, 1603, 1496, 1452, 1409, 1314, 1295, 1238, 1185, 1160, 1136, 1096, 1072, 1036, 1015, 972, 870, 839, 802, 760, 728, 701, 685, 657, 625, 575, 550 cm^{-1}. ESI-MS (pos.) *m/z* (%): 729.2 $[2M + Na]^+$ (33), 392.0 $[M+K]^+$ (11), 376.1 $[M+Na]^+$ (100). ESI-MS (neg.) *m/z* (%): 705.1 $[2M\text{-}H]^-$ (8), 351.9 $[M\text{-}H]^-$ (100). For $C_{19}H_{19}N_3O_4$ (353.37) calcd. C 64.58, H 5.42, N 11.89, found: C 64.43, H 5.57, N 11.61.

4.4.6. (4R*,5S*)-5-hydroxy-1-(hydroxyethyl)-5-phenyl-1′H-spiro [imidazolidine-5,3′-indole]-2,2′-dione (**12c**)

Compound was prepared from **3c** in 42% yield (285 mg). Colorless solid, mp 262–268 °C (ethanol). IR: 3196, 3063, 2974, 2922, 2880, 1686, 1600, 1493, 1461, 1410, 1372, 1336, 1298, 1249, 1205, 1130, 1091, 1070, 1046, 1021, 982, 949, 900, 820, 753, 703, 659, 601, 575 cm^{-1}. ESI-MS (pos.) *m/z* (%): 701.2 $[2M + Na]^+$ (28), 528.1

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[3M + Ca]$^{2+}$ (20), 378.0 [M+K]$^{+}$ (6), 362.0 [M+Na]$^{+}$ (100), 359.0 [2M + Ca]$^{2+}$ (20). ESI-MS (neg.) *m/z* (%): 699.1 [2M-2H + Na]$^{-}$ (6), 677.0 [2M-H]$^{-}$ (13), 337.9 [M-H]$^{-}$ (100). EI-MS: *m/z* (%): 339 (M^{+}, 8), 322 (21), 321 (100), 290 (37), 278 (11), 277 (46), 265 (11), 248 (6), 247 (16), 237 (12), 236 (20), 234 (13), 219 (10), 206 (8), 205 (8), 203 (8), 148 (8), 146 (35), 130 (6), 120 (60), 118 (28), 117 (14), 104 (36), 103 (8), 65 (8), 51 (8), 45 (8), 44 (7). For $C_{18}H_{17}N_3O_4$ (339.35) calcd. C 63.71, H 5.05, N 12.38, found: C 63.62, H 4.95, N 12.27.

4.4.7. (4R,5S*)-5-benzyl-5-hydroxy-1-(hydroxyethyl)-1′-methyl-1′H-spiro[imidazolidine-5,3′-indole]-2,2′-dione (**12e**)*

Compound was prepared from **3e** in 30% yield (220 mg, elution system S2) besides **11e**. Colorless solid, mp 115–130 °C (benzene). IR: 3296, 2939, 1702, 1668, 1476, 1414, 1370, 1307, 1232, 1139, 1120, 1097, 1074, 1009, 970, 756, 701, 681, 654, 606, 564, 539 cm^{-1}. ESI-MS (pos.) *m/z* (%): 757.3 [2M + Na]$^{+}$ (14), 406.0 [M+K]$^{+}$ (17), 390.1 [M+Na]$^{+}$ (100), 387.1 [2M + Ca]$^{2+}$ (19). ESI-MS (neg.) *m/z* (%): 733.1 [2M-H]$^{-}$ (5), 365.9 [M-H]$^{-}$ (100). For $C_{20}H_{21}N_3O_4$ (367.40) calcd. C 65.38, H 5.76, N 11.44, found: C 65.41, H 5.76, N 11.24.

4.4.8. (4R,5S*)-5-hydroxy-1-(hydroxyethyl)-1′-methyl-5-phenyl-1′H-spiro[imidazolidine-5,3′-indole]-2,2′-dione (**12f**)*

Compound was prepared from **3f** in 76% yield (537 mg). Colorless solid, mp 232–239 °C (benzene). IR: 3208, 1689, 1664, 1606, 1472, 1410, 1367, 1304, 1274, 1130, 1094, 1052, 1027, 968, 948, 853, 810, 758, 703, 655, 627, 507 cm^{-1}. ESI-MS (pos.) *m/z* (%): 729.2 [2M + Na]$^{+}$ (13), 392.0 [M+K]$^{+}$ (13), 376.1 [M+Na]$^{+}$ (100), 373.1 [2M + Ca]$^{2+}$ (13). ESI-MS (neg.) *m/z* (%): 705.1 [2M-H]$^{-}$ (10), 351.9 [M-H]$^{-}$ (100). EI-MS: *m/z* (%): 335 (40), 317 (12), 305 (11), 304 (33), 292 (9), 291 (6), 279 (8), 277 (7), 276 (17), 275 (16), 261 (11), 251 (10), 250 (16), 248 (14), 222 (8), 201 (33), 188 (8), 173 (14), 160 (11), 148 (100), 131 (14), 130 (19), 118 (14), 117 (22), 105 (20), 104 (100), 77 (36), 76 (6), 51 (8), 45 (14). For $C_{19}H_{19}N_3O_4$ (353.37) calcd. C 64.58, H 5.42, N 11.89, found: C 64.30, H 5.43, N 11.68.

4.4.9. (4R,5S*)-5-benzyl-5-hydroxy-1-(hydroxyethyl)-1′-phenyl-1′H-spiro[imidazolidine-5,3′-indole]-2,2′-dione (**12h**)*

Compound was prepared from **3h** in 45% yield (387 mg, elution system S2). Colorless solid, mp 233–238 (ethyl acetate). IR: 3406, 3320, 2937, 1718, 1682, 1606, 1497, 1446, 1411, 1352, 1306, 1236, 1133, 1073, 1053, 1021, 977, 765, 701, 655, 630, 562 cm^{-1}. ESI-MS (pos.) *m/z* (%): 881.3 [2M + Na]$^{+}$ (16), 663.2 [3M + Ca]$^{2+}$ (8), 468.1 [M+K]$^{+}$ (24), 452.1 [M+Na]$^{+}$ (100), 449.1 [2M + Ca]$^{2+}$ (28). ESI-MS (neg.) *m/z* (%): 428.0 [M-H]$^{-}$ (100). For $C_{25}H_{23}N_3O_4$ (429.47) calcd. C 69.92, H 5.40, N 9.78, found: C 69.77, H 5.36, N 9.52.

4.4.10. (4R,5S*)-5,1′-diphenyl-5-hydroxy-1-(hydroxyethyl)-1′H-spiro[imidazolidine-5,3′-indole]-2,2′-dione (**12i**)*

Compound was prepared from **3i** in 36% yield (299 mg). Colorless solid, mp 214–218 °C (ethyl acetate). IR: 3461, 3284, 2923, 2889, 1715, 1664, 1604, 1490, 1464, 1406, 1353, 1301, 1266, 1229, 1130, 1099, 1072, 753, 699, 655, 610 cm^{-1}. ESI-MS (pos.) *m/z* (%): 853.3 [2M + Na]$^{+}$ (39), 642.2 [3M + Ca]$^{2+}$ (6), 454.1 [M+K]$^{+}$ (15), 438.1 [M+Na]$^{+}$ (100), 435.1 [2M + Ca]$^{2+}$ (17). ESI-MS (neg.) *m/z* (%): 414.0 [M-H]$^{-}$ (100). EI-MS: *m/z* (%): 415 (M^{+}, 8), 398 (19), 397 (70), 366 (14), 354 (6), 338 (8), 337 (11), 310 (9), 263 (22), 250 (14), 235 (9), 222 (8), 213 (7), 195 (19), 194 (14), 167 (6), 148 (100), 130 (13), 117 (14), 105 (19), 104 (95), 91 (12), 77 (40), 51 (11), 45 (16). For $C_{24}H_{21}N_3O_3$ (415.44) calcd. C 69.39, H 5.10, N 10.11, found: C 69.22, H 5.21, N 9.91.

5. Preparation of compounds 5

To the solution of compound **2** (0.5 mmol) and **1** (0.5 mmol) in DMF (4 mL), pulverized potassium carbonate (164 mg, 1 mmol) was added and the mixture was stirred at r.t. The course of the reaction was monitored with TLC. After fade away of the spot corresponding to compound **2**, the reaction mixture was diluted with water (8 ml). The deposited product was filtered with suction. The filtrate was extracted with chloroform (3 × 10 mL). The collected extracts were evaporated to dryness and separated by column chromatography on silica gel. From the reaction of **1e** with **2e**, compound **5e** (2%), identical to compound isolated from the reaction of **2e** with ethanolamine, was obtained. From the reaction of **1h** with **2h**, compound **5h** (3%), identical to compound isolated from the reaction of **2h** with ethanolamine, was obtained.

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