Phenacyl Esters of Acetic Acid Derivatives and Their Application for the Synthesis of 2-Oxo-4-phenyl-5-(phenylhydrazono)-2,5-dihydro-furan-3-derivatives.

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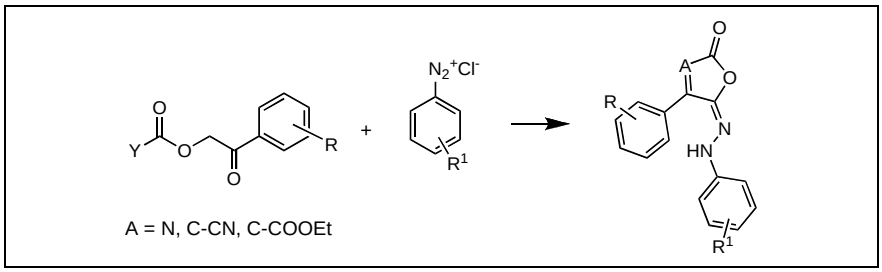

Coupling of various substituted phenacyl acetates **1** and diazonium salts **3** was studied. If the phenacyl acetates were substituted by an electronaceptor group such as CN or COOEt 3-substituted phenyl-5-(phenyl-hydrazono)-5*H*-furan-2-ones **4** were formed. Also synthesis of aza and diaza analogs is described. The compounds were characterized using MS and NMR spectroscopy.

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INTRODUCTION

Previously studied phenacyl esters of anthranilic acids have several reactive positions – ester part, amino and carbonyl group. These compounds and their derivatives are very useful starting material for the preparation of various heterocyclic compounds, for example oxazoles [1,2], quinolinones [3,4] *etc*. *N*-Substituted amino group in phenacyl esters of anthranilic acid could be isosteric with nitrogen substituted with phenyl group in azo compound **7**, which have not been studied yet. We supposed that these compounds could be prepared by coupling of diazonium salt with phenacyl ester **1a** simply. Surprisingly, the coupling of diazonium salts with phenacyl esters led to the formation of compounds **4**. During this work new compounds were prepared, new procedures for older compounds were described and mistakes from the literature were corrected.

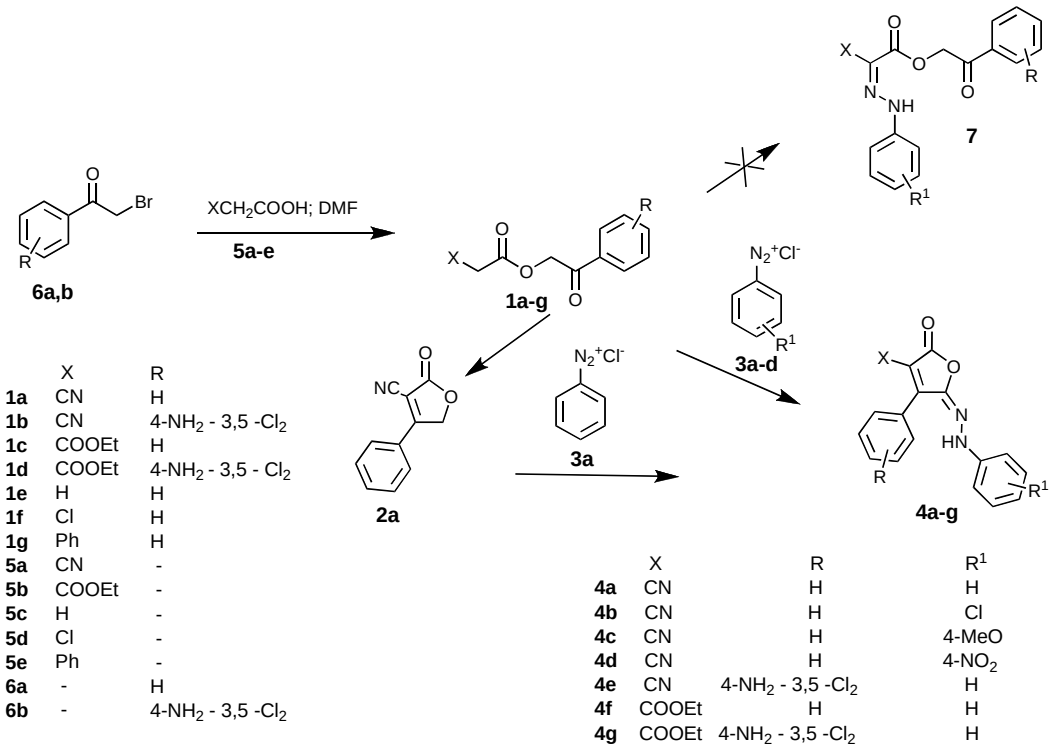
RESULTS AND DISCUSSION

Only some of the compounds **4** are described in the literature as a very intensive dyestuff [5-8]. These compounds were prepared by reaction of diazonium salt **3** with furanone **2** (Scheme 1) [5-8]. Since the compounds **2** have only one place for coupling with diazonium salt, the result is not surprising. Compounds **2** were prepared by reflux of haloketones with salt of cyanoacetic aid in ethanol, or heating of phenacyl esters of cyanoacetic acid **1** with diluted sulfuric acid for 8 hours. [5]. These phenacyl esters were mentioned as a starting material but their preparation has not been described in this work. These compounds have not been studied intensively yet. Only compound **1c** was described formerly as colorless oil prepared by esterification of 2-hydroxyacetophenone [9].

As we have planned to prepare compound **7**, we have to develop a new way for the preparation of these compounds. When we used various inorganic or organic salts of cyanoacetic acid, a mixture of compounds was received. Situation changed, when we used as a base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). In this way, we received quite good yields of compounds **1a**. Surprisingly, reaction between phenacyl ester **1a** and phenyl diazonium salt formed a red dyestuff which was identified as **4a**. This reaction was observed at 0 to 5 °C with relatively long reaction time of 4 hours. Faster course was observed at temperature 50 °C and the reaction was completed during 5 minutes. We also verified stability of phenacyl ester **1a**. It was found that the formation of furanone **2a** was not observed if phenacyl ester **1a** was kept in boiling solution of sodium acetate in ethanol for 3 hours. In spite of this result, since the formation of azo derivative **4a** was observed, it is clear that formation of furanone **2** must be finished at first.

Based on this result we tested the behavior of various substituted phenacyl acetates **1b** to **1g** under similar conditions. The same reaction was observed if the acid part was substituted with an electron acceptor group such

Scheme 1



as cyano or carbethoxy group. If the electron acceptor group was changed to hydrogen, chlorine or phenyl, formation of furanone derivatives **2** or compounds **4** was not observed.

Table 1

Characteristic Data of Phenacylesters **1a-g**

Compd. No.	React. Time React. Temp	Yield (%) Base	Mp (°C)
1a	2 h 0°C	50 DBU	70-72
1b	5 h 0 °C	51 DBU	134-137
1c	2 h 0 °C	63 Na^+ salt	30-32[a]
1d	1 h 0 °C	43 Na^+ salt	104-106
1e	2 h 20 °C	83 Et_3N	45-47[b]
1f	3.5 h 20 °C	97 Et_3N	95-96[c]
1g	1.5 h 20 °C	78 Et_3N	47-49[d]

[a] Lit [9] colorless oil; [b]lit [23] mp 48-49 °C; [c] lit [24] mp 99-100 °C; [d] lit [25] mp 48-50 °C, lit [26] mp 43-46 °C

Since we were surprised by furanone cycle formation in the course of coupling of phenacylesters **1** with diazonium salt **3**, we were interested in reactivity of analogs **9** and **13** with diazonium salt **3** under similar conditions.

Compounds **9** and **13** have not been described. Oxazolone **14** and imidazolone **10** have been known from the literature. In case of oxazolone **14** the synthesis by two step reaction of hydroxy acetophenone with phosgene at first and followed by reaction with ammonium was described recently [10] but this compound was used for the next reaction without isolation, and its properties were not described [10]. Synthesis of compound **10** was mentioned several times. The most common is melting of bromoacetophenone with urea [11,12], or reaction of 2-aminoacetophenone with potassium cyanate [13].

From the literature [14] is known also synthesis of compound **11**. This compound **11** was prepared by reaction of *N*-hydroxy-3-oxo-3-phenyl-2-(phenylhydrazono)-propionamidine with thionylchloride.

At first we tried to prepare compound **14** by melting 2-hydroxyacetophenone with urea. This experiment was not successful and surprisingly imidazolinone **10** was prepared in this case (Scheme 2). Therefore we slightly modified described synthesis of chloroformate **12** by using triphosgene instead of phosgene. The reaction ran smoothly but after the reaction with ammonium instead of described compound **14** we isolated a compound that was later identified as carbamate **13**. This compound also has not been described in the literature. Then we tried the reactions conditions previously tested for coupling of phenacyl esters of cyanoacetic acid with diazonium salt,

Table 2

Analytical results of compound **1a-g**

Compd No.	Formula M.W.	**Full MS and MS^2 *m/z* (relative intensity)**	**Elemental analysis Calcd/found**		
			%C	**%H**	**%N**
1a	$C_{11}H_9NO_3$	MS *m/z* 204 (35) $[M+H]^+$; MS^2(204,w3,EV1), *m/z* 158, 137(100) $[C_6H_5COCH_2OH_2]^+$, 119	65.04	4.43	6.9
	203.2	$[C_6H_5COCH_2]^+$, 105, 91.	64.84	4.47	6.53
1b	$C_{11}H_8N_2O_3Cl_2$	MS *m/z* 287,289,291 (90,60,10) $[M(^{35}Cl),M(^{37}Cl)+H]^+$, 315,317,319 $[M(^{35}Cl),M(^{37}Cl)+C_2H_5]^+$;	46.03	2.79	9.76
	287.04	MS^2(289,w7,EV1), *m/z* 224, 222, 220 (100) $[M(^{35}Cl)+H\text{-}CNCH_2CO]^+$, 204, 202, 190, 188, 176, 174, 169, 167, 164, 162, 126.	45.83	2.92	10.01
1c	$C_{13}H_{14}O_5$	MS *m/z* (251 (20) $[M+H]^+$, 279 $[M+C_2H_5]^+$, 291 $[M+C_3H_5]^+$; MS^2(251,w3,EV1),	62.42	5.60	
	250.14	*m/z* 235, 137(100) $[C_6H_5COCH_2OH_2]^+$, 119 $[C_6H_5COCH_2]^+$, 91.	62.02	5.64	
1d	$C_{13}H_{13}NO_5Cl_2$	MS *m/z* 334,336,338 (18,12,2) $[M(^{35}Cl),M(^{37}Cl)+H]^+$, 262,264,266 $[M(^{35}Cl),M(^{37}Cl)+C_2H_5]^+$;	46.74	3.89	4.19
	334.06	MS^2(336,w7,EV1.5), *m/z* 224, 222, 220 (100) $[M(^{35}Cl)+H\text{-}CH_3CH_2OCOCH_2CO]^+$, 204, 202, 190, 188, 176, 174, 169, 167, 164, 162.	46.66	3.89	4.23
1e	$C_{10}H_{10}O_3$	MS *m/z* 179 (5) $[M+H]^+$; MS^2(179,w3,EV1), *m/z* 160, 137(100) $[C_6H_5COCH_2OH_2]^+$, 119	67.44	5.61	
	178.11	$[C_6H_5COCH_2]^+$, 91.	67.15	5.60	
1f	$C_{10}H_9O_3Cl$	MS *m/z* 213,215 (21,7) $[M(^{35}Cl),M(^{37}Cl)+H]^+$, 241,243 $[M(^{35}Cl),M(^{37}Cl)+C_2H_5]^+$;	56.51	4.23	
	212.56	MS^2(214,w5,EV1.5), *m/z* 137(100) $[C_6H_5COCH_2OH_2]^+$, 119 $[C_6H_5COCH_2]^+$, 91.	56.25	4.26	
1g	$C_{16}H_{14}O_3$	MS *m/z* 255 (5) $[M+H]^+$, 283 $[M+C_2H_5]^+$; MS^2(255,w3,EV1), *m/z* 168, 137(100)	75.61	5.51	
	254.18	$[C_6H_5COCH_2OH_2]^+$, 119 $[C_6H_5COCH_2]^+$, 91.	75.46	5.63	

and compound **15** was prepared in high yield. The same compounds were also prepared if the oxazolon **14** was prepared at first, followed by coupling with diazonium salt (Scheme 2).

Because of unexpectedly prepared imidazolinone **10**, we also tried its coupling with diazonium salt and compound **11** was prepared. Coupling of compound **10** with diazonium salt was carried out smoothly. We proved by NMR that compound **11** exists as 4-phenyl-5-phenylazo-1,3-dihydro-imidazol-2-one. Similar compound with similar mp was described in the literature as 4-phenyl-5-phenylazo-1,5-dihydro-imidazol-2-one [14], we reproduced described procedure and we proved by

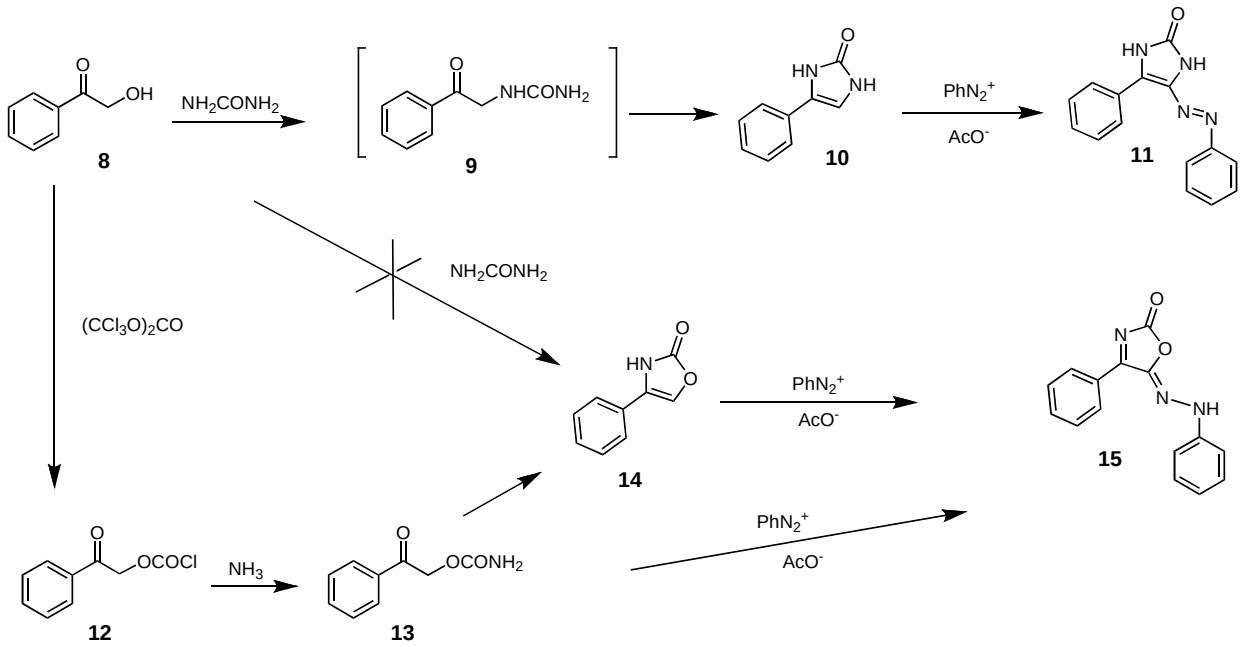
Table 3

Characteristic Data of 2,5-dihydro-furane derivatives **4a-g**

Compd. No.	Reaction time (min)	Yield (%)	Mp (°C)	λ_{max} (nm)	ε_{max} ($l.mol^{-1}.cm^{-1}$)
4a	5	66	268-271[a]	467.7	16160
4b	5	41	298-301[b]	467.5	16790
4c	5	55	253-254[c]	498.6	22840
4d	5	58	250-256	340.2	19013
4e	5	36	285-295	467.7	19680
4f	5	74	182-185	446.6	30270
4g	10	79	225-228	438.1	28280

[a] Lit. [7] mp 256-257.5 °C, Lit. [8] mp 248 °C; [b] Lit. [8] mp 290 °C; [c]Lit. [8] mp 240 °C.

Scheme 2



HPLC and MS that both compounds are identical.

We also tried to prepare compound **9** as we can test its reactivity. Unfortunately we were not able to prepare this compound, probably due to its low stability.

Color of compounds **4**, **11** and **15** is changed in dependence on pH from red to yellow in alkaline solution mostly.

Since these prepared azo-compounds could be applicable as a potential dyestuff, or as indicator, we measure the coloring of the solutions of hydrazo compounds **4**, **15** and azo compound **11** in methanolic solution. This information is in an experimental part, or is summarized in Table 3.

Identification of compounds

Mass spectra of all prepared compounds were measured giving appropriate m/z values and fragments. The detailed ^{1}H and ^{13}C NMR study was performed using both one- and two-dimensional spectra. The ^{1}H chemical shifts were assigned using gs (gradient selected) H,H-COSY, and ^{13}C chemical shifts were assigned having applied gs ^{1}H-^{13}C - HSQC and gs ^{1}H and ^{13}C HMBC (optimised for $^{1}J(^{13}C, H)$ *ca* 150 Hz and $^{3}J(^{13}C, H)$ *ca* 8 Hz, respectively).

Compounds **4** contain several quaternary carbons side-by-side. To assign quaternary carbon resonances correctly we measured two-dimensional INADEQUATE [15] (Figure 1) of compound **4g** showing clearly and undoubtedly the connectivity of directly bonded carbon atoms and, hence, tracing out the C-C framework of the molecule.

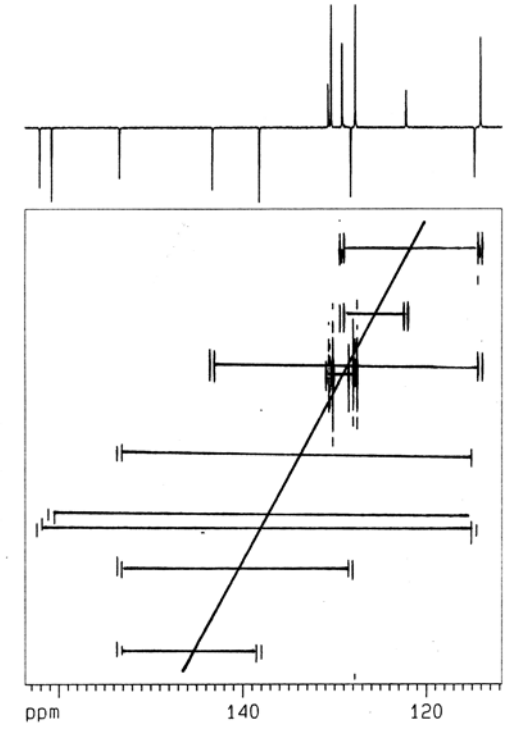


Figure. 1: 2D-INADEQUATE spectrum of compound **4g**. The connections of appropriate carbons are marked with horizontal lines for the clarity.

We also measured ^{15}N chemical shifts in compound **4g**: $\delta(^{15}N(=N-)) = -94.8$ and $\delta(^{15}N(-NH-)) = -226.4$, $^{1}J(^{15}N, ^{1}H) = 98.0$ Hz.

The ^{1}H and ^{13}C chemical shifts are collated in Tables 5-7. All diazonium salt coupling products except for compound **11** exist almost exclusively in the hydrazone forms as is clear from a comparison of ^{13}C chemical shifts of the $=NNHC_6H_5$ fragment with those in model compounds [16-18].

The ^{13}C chemical shifts of $N\text{-}C_6H_5$ fragment (carbons C(1´´) – C(4´´)) in compound **11** differ considerably from analogous carbon resonances in compound **15** (see Table 7) and are typical of the phenyl azo group [16-18]. This observation is in line with the fact that the azo tautomeric form strongly prevails in cases when NH group (and not OH group) is a partner participating in the azo/hydrazone equilibrium [17-19].

EXPERIMENTAL

General procedure for preparation of phenacyl ester (1a-g). Acids 5 (58.8 mmol) were dissolved in DMF (20 mL) and suitable base (58.8 mmol) was added. The solution was cooled down from 40°C to appropriate temperature and a solution of phenacyl bromides **6** (55 mmol) in DMF (30 mL) were added over 30 minutes. The reaction mixture was stirred for given time. Completion of the reaction monitored checked by TLC. Then the mixture was poured into ice and a gummy product was extracted by diethyl ether. After washing with water and drying with sodium sulfate, an ether layer was filtrated with charcoal and diethylether was removed by vacuum evaporator. Dark oil slowly crystallized from ethanol. The results are summarized in Tables 1 and 2.

General procedure for preparation of 2-Oxo-4-phenyl-5-(subst.phenyl-hydrazono)-2,5-dihydro-furan-3-derivative (4a-g). Phenacyl esters **1** (16.2 mmol) were dissolved in ethanol (50 mL), sodium acetate (48.8 mmol) was added and solution of diazonium salts **3** (16.2 mmol) in water were slowly added at temperature 40°C. After 5 minutes no starting phenacyl ester **1** was observed on TLC. The reaction mixture was diluted by water (100 mL) and after 30 minutes stirring the precipitated solid product was collected by filtration and washed with water. The isolated product was recrystallized from ethanol. The results are summarized in Tables 3 and 4.

4-Phenyl-4-imidazolin-2-one (10). Urea (1 g, 21.7 mmol) was melted at 160°C and 2-hydroxyacetophenone (100 mg, 0.735 mmol) was added. Reaction mixture was stirred at this temperature for 10 minutes, a suspension was formed immediately after addition of 2-hydroxyacetopheneone. Then water was added and precipitated compound was collected by filtration, washed with water and recrystallized from acetone. The yield of the product **10** was 86 mg, (73 %), mp 320-323 °C (lit. [20] mp 340-343 °C); ms: m/z (relative intensity) 161 (100) $[M+H]^+$, 189 $[M+C_2H_5]^+$, 201 $[M+C_3H_5]^+$; $ms^2(161,w3,EV1)$, m/z 144, 132, 118 (100) $[M+H\text{-}CONH]^+$, 104, 91. *Anal.* Calcd.

Table 4

Analytical results of compound **4a-g**

Compd No.	Formula M.W.	**Full MS and MS^2 *m/z* (relative intensity)**	**Elemental analysis Calcd/found**		
			%C	**%H**	**%N**
4a	$C_{17}H_{11}N_3O_2$ 289.21	MS *m/z* 290 (60) $[M+H]^+$, 318 $[M+C_2H_5]^+$, 330 $[M+C_3H_5]^+$; MS^2(290,w3,EV1), *m/z* 288 $[M-H]^+$, 272 (100) $[M-OH]^+$, 262[M+H-CO]$^+$, 260 $[M-H-CO]^+$, 246 $[M+H-COO]^+$, 244 $[M-H-COO]^+$, 232, 223, 216, 206, 184, 155, 128, 127.	70.60 70.42	3.80 3.89	14.53 14.44
4b	$C_{17}H_{10}N_3O_2Cl$ 323.66	MS *m/z* 324,326 (30,10) $[M(^{35}Cl),M(^{37}Cl)+H]^+$, 352,354 $[M(^{35}Cl),M(^{37}Cl)+C_2H_5]^+$, 364,366 $[M(^{35}Cl),M(^{37}Cl)+C_3H_5]^+$; MS^2(325,w5,EV1.5), *m/z* 306, 294, 288 $[M+H-HCl]^+$, 278, 266, 260, 243, 231, 216, 184, 168, 155, 139, 128(33) $[C_6H_5N(^{37}Cl)]^+$, 126(100) $[C_6H_5N(^{35}Cl)]^+$.	63.09 63.17	3.09 3.07	12.98 13.37
4c	$C_{18}H_{13}N_3O_3$ 319.22	MS *m/z* 320 (20) $[M+H]^+$, 348 $[M+C_2H_5]^+$, 360 $[M+C_3H_5]^+$; MS^2(320,w3,EV1), *m/z* 304, 292, 276 $[M+H-COO]^+$, 260, 236, 210, 184, 156, 127, 122(100).	67.73 67.43	4.07 3.99	13.16 13.55
4d	$C_{17}H_{10}N_4O_4$ 334.21	MS *m/z* 335 (100) $[M+H]^+$, 363 $[M+C_2H_5]^+$, 375 $[M+C_3H_5]^+$; MS^2(335,w3,EV1.5), *m/z* 318 (100) $[M+H-OH]^+$, 288 $[M-NO_2]^+$, 261, 244, 233, 205.	61.09 61.29	2.99 3.04	16.76 16.70
4e	$C_{17}H_{10}N_4O_2Cl_2$ 373.12	MS *m/z* 373,375,377 (27,18,3) $[M(^{35}Cl),M(^{37}Cl)+H]^+$, 401,403,405 $[M(^{35}Cl),M(^{37}Cl)+C_2H_5]^+$; MS^2(375,w7,EV1.5), *m/z* 355, 337 $[M(^{35}Cl)+H-HCl]^+$, 329, 320, 302, 293, 281, 266, 258, 239, 229, 212, 210.	54.72 54.65	2.68 2.68	15.02 14.62
4f	$C_{19}H_{16}N_2O_4$ 336.22	MS *m/z* 337 (50) $[M+H]^+$, 365 $[M+C_2H_5]^+$, 377 $[M+C_3H_5]^+$; MS^2(337,w3,EV1.5), *m/z* 319, 309, 291 $[M+H-CH_3CH_2OH]^+$, 290 (100), 280, 263, 247, 230, 223, 201, 185, 174, 158, 146, 129	67.87 67.53	4.76 4.79	8.33 8.64
4g	$C_{19}H_{15}N_3O_4Cl_2$ 420.14	MS *m/z* 420,422,424 (27,18,3) $[M(^{35}Cl),M(^{37}Cl)+H]^+$, 448,450,452 $[M(^{35}Cl),M(^{37}Cl)+C_2H_5]^+$; MS^2(422,w7,EV1.5), *m/z* 378, 376, 374 $[M(^{35}Cl)+H-C_2H_5OH]^+$, 350, 348, 346 $[M(^{35}Cl)+H-COC_2H_5OH]^+$, 321, 315, 313, 295, 286, 284, 267, 258, 214, 212.	54.32 53.97	3.57 3.50	10.00 10.22

Table 5

^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds 1a-g in DMSO-d_6

Position	**1a**		**1b**		**1c**		**1d**		**1e**		**1f**		**1g**	
	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
1	-	164.1	-	165.8	-	166.2	-	166.2	-	170.0	-	167.1	-	170.8
2	4.31	24.3	4.26	24.3	3.72	40.9	3.68	40.9	2.20	20.4	4.64	40.9	3.91	40.1
X	-	114.9	-	115.0	-	166.2	-	166.1	-	-	-	-	-	134.3
	-	-	-	-	4.19	61.1	-	61.1	-	-	-	-	7.41	129.5
	-	-	-	-	1.26	14.0	-	14.0	-	-	-	-	7.41	128.5
	-	-	-	-	-	-	-	-	-	-	-	-	7.34	127.0
1′	5.71	68.1	5.57	67.6	5.62	67.3	5.49	66.7	5.52	66.5	5.67	67.8	5.59	66.9
2′	-	191.9	-	188.1	-	192.3	-	188.5	-	192.9	-	192.1	-	192.7
3′	-	133.7	-	122.0	-	133.9	-	122.2	-	133.9	-	133.7	-	133.9
4′	8.02	127.9	7.88	127.8	8.02	127.9	7.88	128.3	8.01	127.8	8.02	127.9	8.03	127.9
5′	7.62	129.0	-	117.6	7.61	129.0	-	117.5	7.62	129.0	7.62	129.0	7.60	129.0
6′	7.76	134-2	6.59[a]	146.3	7.74	134.1	6.60[a]	146.2	7.72	134-0	7.75	134.2	7.73	134.0

[a] **δ**(NH_2).

Table 6

^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds **4a-h** in DMSO-d_6

Position	**4a**		**4b**		**4c**		**4d**		**4e**		**4f**		**4g**	
	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	-	162.3	-	162.0	-	162.8	-	161.7	-	162.6	-	162.1	-	162.2
3	-	95.9	-	96.5	-	93.8	-	99.3	-	91.1	-	114.9	-	115.7
4	-	155.2	-	155.3	-	156.2	-	156.3	-	151.1	-	153.4	-	150.7
5	-	137.3	-	137.6	-	136.9	-	139.8	-	137.1	-	138.3	-	138.1
X	-	113.2	-	112.9	-	113.7	-	112.7	-	113.8	-	160.8	-	161.0
	-	-	-	-	-	-	-	-	-	-	4.20	60.9	4.26	60.9
	-	-	-	-	-	-	-	-	-	-	1.15	13.8	1.26	13.9
1′	-	127.1	-	126.9	-	127.6	-	126.9	-	114.5	-	128.5	-	112.7
2′	8.04	129.9	8.03	129.9	8.03	130.1	8.07	130.2	8.14	130.1	7.66	130.4	7.74	131.1
3′	7.75	129.3	7.73	129.2	7.73	129.4	7.73	129.6	-	117.9	7.58	127.9	-	116.9
4′	7.75	132.8	7.76	132.8	7.73	132.8	7.77	133.4	[b]	145.9	7.68	130.8	[c]	144.0
NH	11.78	-	11.77	-	11.83	-	11.98	-	11.58	-	11.40	-	11.32	-
1′′	-	142.9	-	141.8	-	137.1	-	142.0	-	143.0	-	142.3	-	143.5
2′′	7.39	114.7	7.38	116.0	7.37	116.5	7.47	114.5	7.38	114.3	7.28	114.1	7.29	113.9
3′′	7.39	129.6	7.42	129.3	7.01	115.2	8.23	126.6	7.38	129.5	7.32	129.3	7.34	129.4
4′′	7.08	123.3	-	126.7	-[a]	137.1[a]	-	148.8	7.05	123.0	6.98	122.3	6.98	122.2

[a] δ(OCH_3) = ′3.78 / 55.6 [b] δ(NH_2) = 6.94 [c] δ(NH_2) = 6.41.

Table 7

^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds **10, 11, 14** and **15** in DMSO-d_6

Position	**10**		**11**		**14**		**15**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2	-	155.1	-	152.4	-	156.2	-	160.5
4	-	130.1	-	127.9	-	127.2	-	173.2
5	6.93	105.8	-	129.3	7.73	124.8	-	138.8
1´	-	122.1	-	135.0	-	126.9	-	128.3
2´	7.54	122.9	8.11	128.0	7.60	124.1	8.47	130.6
3´	7.37	128.8	7.56	129.0	7.47	129.0	7.71	129.3
4´	7.20	126.3	7.47	129.3	7.38	127.4	7.80	134.4
NH	10.58[a], 10.11[b]	-	11.77[c], 11.20[d]	- azo	11.42	-	11.59	- hydrazo
1´´	-	-	-	153.0	-	-	-	142.9
2´´	-	-	7.78	121.9	-	-	7.49	114.8
3´´	-	-	7.56	129.5	-	-	7.43	129.6
4´´	-	-	7.43	129.4	-	-	7.10	123.2

[a] $^1J(^{15}N, ^1H)$ = 97.1 Hz, [b] $^1J(^{15}N, ^1H)$ = 97.2 Hz, [c] $^1J(^{15}N, ^1H)$ = 97.4 Hz, [d] $^1J(^{15}N, ^1H)$ = 99.6 Hz.

for $C_9H_8N_2O$ (M= 160.06): C, 67.51; H, 5.00; N, 17.5. Found C, 67.85; H, 4.77; N, 17.15.

5-Phenyl-4-phenylazo-3-imidazolin-2-one (11). Imidazolinone **10** (2.23 g, 13.9 mmol) was suspended in ethanol (120 mL), sodium acetate (7.5 g) was added and the reaction mixture was heated to 40°C and diazonium salt (13.9 mmol) in water (12 mL) was added. Reaction was stirred at this temperature for 30 minutes. An orange suspension was formed immediately after addition of the first drop of diazonium salt solution. Then the reaction mixture was diluted by water and red product was collected by filtration and crystallized from ethanol. The yield after crystallization was 1 g, (27 %) of red product **11**, mp 208-211 °C (lit. [14] mp 200 °C); uv: λ max 419.7 nm (ε max 2.12. 10^4 l.mol^{-1}.cm^{-1}); ms: m/z (relative intensity) 265 (100) $[M+H]^+$, 293 $[M+C_2H_5]^+$, 305 $[M+C_3H_5]^+$; MS^2(265,w3,EV1), m/z 263$[M-H]^+$, 248, 236, 222 $[M+H\text{-}CONH]^+$, 220, 205, 195, 193, 187 $[M+H\text{-}C_6H_6]^+$, 180, 167, 165, 162, 145, 135, 119, 104, 93. *Anal*. Calcd. for $C_{15}H_{12}N_4O$ (M= 264.19): C, 68.2; H, 4.54; N, 21.21. Found: C, 68.44; H, 4.77; N, 20.92.

O-Phenacyl carbamate (13). 2-Hydroxyacetophenone (5.25 g, 38.6 mmol) was dissolved in toluene (54 mL) and *N,N*-dimethylaniline (11.55 mL, 91.2 mmol) was added, the mixture was cooled to -5 to 0 °C and solution of triphosgene (13.06 g, 44 mmol) in toluene (20 mL) was added. The reaction mixture was stirred for an additional 30 minutes at 0°C then concentrated ammonium hydroxide (45 mL) was added and the reaction mixture was stirred for next 30 minutes. The reaction was then quenched by the addition of sulfuric acid until a pH 3 is obtained. The reaction was diluted with water (300 mL) and ethyl acetate (100 mL). The organic layer was separated and the aqueous layer was re-extracted with ethyl acetate (2 x 100 mL). The combine organic layers were washed with brine (100 mL), dried with sodium sulfate, filtered and concentrated *in vacuo*. The product was collected by filtration, washed with ethyl acetate to give 3.6 g, (59 %), mp 145-149 °C; ms: m/z (relative intensity) 180 (10) $[M+H]^+$, 208 $[M+C_2H_5]^+$; ms^2(180,w3,EV1): m/z 163 $[M+H\text{-}NH_3]^+$, 137 (100) $[M+H\text{-}CONH]^+$, 119 $[C_6H_5COCH_3]^+$, 91. *Anal*. Calcd. for $C_9H_9NO_3$ (M= 179.11): C, 60.35; H, 5.02; N, 7.82. Found: C, 60.26; H, 5.08; N, 7.42.

4-Phenyl-4-oxazolin-2-one (14). Compound **13** (50 mg, 0.279 mol) was heated to 350 °C without solvent for 10 minutes. Then dark solid was dissolved in ethanol, filtered with charcoal, concentrated *in vacuo* and precipitated by diethyl ether. Solid product was collected by filtration and dried. Yield of yellow solid was 31.4 mg (70 %), mp 151-154 °C (lit. [21,22] mp 151 – 153 °C); ms: m/z (relative intensity) 162 (100) $[M+H]^+$, 190 $[M+C_2H_5]^+$, 202 $[M+C_3H_5]^+$; MS^2(162,w3,EV1), m/z 134 $[M+H\text{-}CO]^+$, 118 $[M+H\text{-}COO]^+$, 116(100) $[M+H\text{-}COOH_2]^+$, 91.

4-Phenyl-5-phenylazo-3-oxazolin-2-one (15).

Method A. Oxazolon **14** (200 mg, 1.24 mmol) was dissolved in ethanol (20 mL) sodium acetate (0.31 g, 3.78 mmol) was added and the reaction mixture was heated to 20°C and diazonium salt (1.24 mmol) in water (12 mL) was added. The reaction was stirred at this temperature for 5 minutes, an orange suspension was formed immediately after addition of the first drop of diazonium salt solution. Then the reaction mixture was diluted by water and red product was collected by filtration and crystallized from ethanol. The yield after crystallization was 100 mg, (30 %) of red product, mp 232-235 °C; uv: λ max 467.6 nm (ε max 1.2 .10^3 l.mol^{-1}.cm^{-1}); ms: m/z (relative intensity) 266 (100) $[M+H]^+$, 294 $[M+C_2H_5]^+$, 306 $[M+C_3H_5]^+$; ms^2(266, w3, EV1), m/z 264 $[M-H]^+$, 238 $[M+H\text{-}CO]^+$, 223, 222 $[M+H\text{-}COO]^+$, 220, 205, 195, 193, 167, 157, 144, 135, 131, 119, 109, 104, 92. *Anal*. Calcd. for $C_{15}H_{11}N_3O_2$ (M= 265.19): C, 67.94; H, 4.15; N, 15.85. Found C, 67.6; H, 4.19; N, 15.81.

Method B. Carbamate **13** (55 mg, 0.31 mmol) were dissolved in ethanol (15 mL), sodium acetate (74 mg, 0.93 mmol) was added and solution of diazonium salts **3** (0.31 mmol) in water were slowly added at temperature 40°C. The reaction mixture was diluted by water (10 mL) after 5 minutes. The precipitated solid product was collected by filtration and washed with water after 30 minutes of stirring. The isolated product was recrystallized from ethanol. The yield was 40 mg, (49 %) of red product, mp 235-237 °C

Analytical measurement. MS characterization was carried out using the DEP-CI-MS-MS (direct exposure probe-chemical ionization-tandem mass spectrometry) technique with quadrupole ion trap mass analyzer and methane as a CI reagent gas. Results are summarized in Tables 2 and 4

The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance spectrometer (500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C

and 50.39 MHz for ^{15}N) in DMSO-d_6 at laboratory temperature in 5 mm NMR tubes. The ^{1}H and ^{13}C chemical shifts were referenced to internal TMS. The ^{15}N chemical shifts were referenced to external neat nitromethane. All 2D experiments (gradient-selected (gs)-COSY, gs-HMQC, gs-HMBC) were performed using the manufacturer's software. Numbering of molecules is given in Figure 2.

Visible spectra were recorded on a Shimadzu UV/VIS spectrometer in the range 400-800 nm, sample solution 1mg/100mL in methanol and at a temperature of 25 °C.

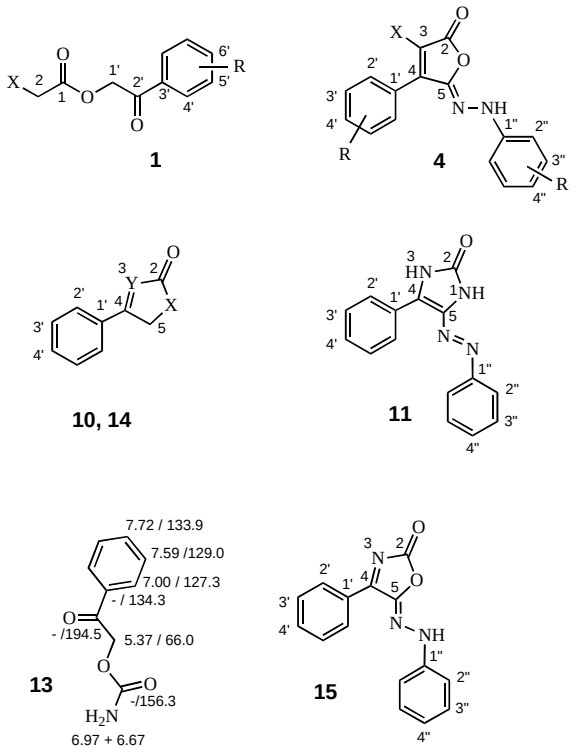


Figure. 2 NMR numbering of molecules.

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