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Synthesis of 4-(2-hydroxy-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene)-5-oxo-1-aryl-4,5-dihydro-1*H*-pyrrole-3-carboxylates, a new triazafulvalene system

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Dedicated to Professor Saverio Florio, University of Bari, on the occasion of his 70th birthday

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ABSTRACT

(2*E*,3*Z*)-2-(1-Methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(arylamino- or heteroarylamino)methylene] succinate **5** obtained by [2+2] cycloaddition of (5*Z*)-5-[(dimethylamino)methylene]-3-methylimidazolidine-2,4-dione (**1**) and dimethyl acetylenedicarboxylate (**2**) followed by substitution of the dimethylamino group with aromatic or heteroaromatic amines, afforded by heating in ethanol in the presence of potassium hydroxide, potassium salts **6**. Acidification of **6** with hydrochloric acid afforded mixtures of (*E*)- and (*Z*)-isomers of methyl 4-(2-hydroxy-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene)-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylates. On the other hand, alkylation of compounds **6** with methyl iodide or benzyl bromide produced the corresponding methyl (*E*)-4-(2-methoxy- or 2-benzyloxy-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene)-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylates **9**, derivatives of a new triazafulvalene system.

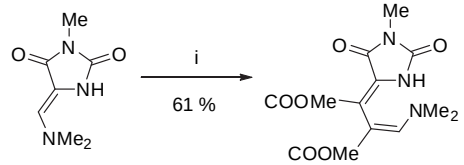
1. Introduction

The 3-(dimethylamino)propenoates and related enaminones have been demonstrated to be versatile building blocks in the synthesis of many heterocyclic systems,[1a–d] including the preparation of natural products and their analogs, such as aplysinopsins,[2a,b] meridianines,[3a,b] dipodazines,[4a–c] and triprostatins.[5] We have also reported an efficient method for preparation and functionalization of highly substituted 1-amino-2,3-dihydro-1*H*-pyrroles, 1-amino-1*H*-pyrroles, and fused pyrrolo[3,2-*d*]oxazole system from 1,2-diazabuta-1,3-dienes and 3-(dimethylamino) prop-2-enoates,[6] and the *regio*- and *stereoselective* one-pot synthesis of oxazolo fused pyridazines.[7] Recently, we reported on microwave assisted regiospecific [2+2] cycloadditions of electron poor acetylenes to 2-(acylamino)-3-(dimethylamino)prop-2-enoates, which resulted in the formation of (1*E*,3*E*)-1-(acylamino)-4-(dimethylamino)buta-1,3-dienes,[8a–c] and some of their transformations.[9]

As an extension of this research, we report here on the synthesis of triazafulvalenes. The aza- and thiafulvalenes have received considerable attention in synthetic chemistry and material sciences. Among the azafulvalenes, those possessing three nitrogen atoms in the cross-conjugated systems are the smallest group. There are a number of aza-analogs of sesquifulvalenes derived from azolyl-substituted 1,4-dihydropyridines by deprotonation of the 1-alkyl-4-azolylpyridinium salts using an anionic ion-exchange resin, such as Amberlit IRA-401.[10a–c] Some triazafulvalenes have been prepared from the 2-(4-pyridyl)substituted intermediates[11] and 4*H*-imidazole derivatives.[12]

2. Results and discussion

When 2(1′*E*),3(4″*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**3**), obtained from (5*Z*)-5-[(dimethylamino)methylene]-3-methylimidazolidine-2,4-dione (**1**) and dimethyl acetylenedicarboxylate (Scheme 1)[8c] by heating in acetonitrile under reflux for several hours, was heated in ethanol



1 **3**

Scheme 1. Reagents and conditions: (i) dimethyl acetylenedicarboxylate **2**, acetonitrile, reflux.

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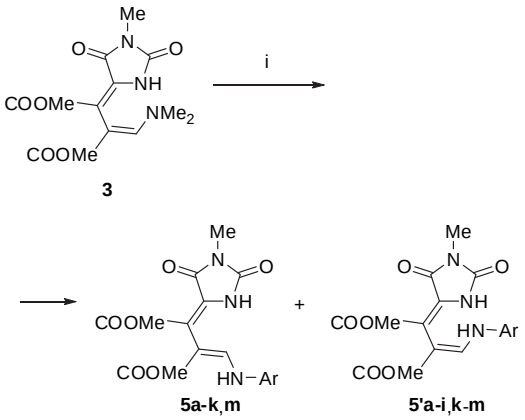


Amine	5, 5'	Ar	5 and 5', yield (%)	5 : 5'	Time (h)
4a	**a**	phenyl	64	94 : 6	5
4b	**b**	4-methylphenyl	61	95 : 5	5
4c	**c**	2-methylphenyl	53	66 : 34	5
4d	**d**	4-fluorophenyl	71	38 : 62	5
4e	**e**	4-bromophenyl	87	12 : 88	6.5
4f	**f**	2-iodophenyl	97	87 : 13	6.5
4g	**g**	3-methoxyphenyl	53	78 : 22	6.5
4h	**h**	3-nitrophenyl	96	30 : 70	6.5
4i	**i**	4-hydroxyphenyl	67	44 : 56	5
4j	**j**	4-hydroxy-2-chlorophenyl	68	100 : 0	5
4k	**k**	1-naphthyl	83	95 : 5	6.5
4l	**l**	5-chloropyridin-2-yl	38	0 : 100	5.5
4m	**m**	pyrazin-2-yl	49	8 : 92	5.5

Scheme 2. Reagents and conditions: (i) $ArNH_2 \cdot HCl$ **4a**–**d**,**g**,**i**,**j** or $ArNH_2$ **4e**,**f**,**h**,**k**–**m** and 37% HCl, EtOH, reflux.

with aromatic or heteroaromatic amines **4a**–**m** as hydrochlorides or in the presence of hydrochloric acid for 5–6.5 h mixtures of the corresponding dimethyl (2*E*,3*Z*)-2-[(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(arylamino- or heteroarylamino)methylene]succinates **5a**–**k**,**m** and (2*E*,3*E*)-isomers **5′a**–**k**, **m** were obtained in 49–97% yield (Scheme 2).

These compounds were heated in ethanol in the presence of potassium hydroxide for 1 to 3.5 h. The precipitated products were separated by filtration and washed with ethanol to give products **6a**–**e**,**g**,**h**,**m** in the form of potassium salts as dark red powders (Scheme 3). By dissolving compounds **6a**–**d**,**g**,**h**,**m** in water, and **6k** in ethanol, and adding concentrated aqueous hydrochloric acid, mixtures of (*E*)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene)-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylates **7a**–**d**,**g**,**h**,**k**,**m** and (*Z*)-isomers **7′a**–**d**,**g**,**h**,**k**,**m** were formed as yellow crystals (Scheme 4). Alkylation of potassium salts **6e**,**g**,**k** with methyl iodide (**8a**) or benzyl bromide (**8b**) in DMF at room temperature for 20–90 min produced the corresponding dark red methyl (*E*)-4-[2-(alkoxy)-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene]-1-aryl-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylates **9a**–**c** (Scheme 5).

3. Structure determination

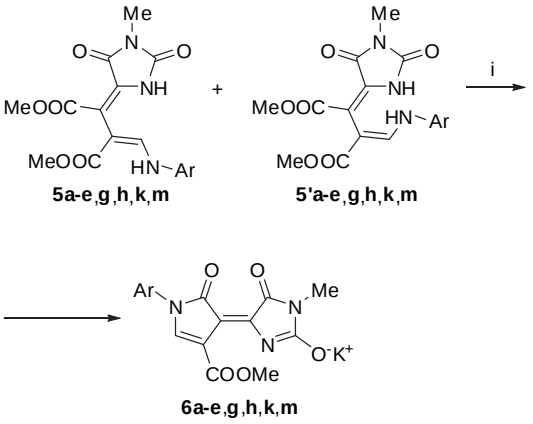
The structure of **5**-(*Z*)- and **5′**-(*E*) isomers was determined on the basis of differences in chemical shifts for N*H*–Ar protons. Namely, the N*H* protons of **5**-(*Z*) isomers appear at δ_{NH}=10.09–11.73 ppm due to the hydrogen bond formation with the ester carbonyl group in comparison to δ_{NH}=8.26–9.66 ppm in **5′**-(*E*) isomers (Fig. 1).

Orientation around the C=C double bond was confirmed by HMBC for compounds **5i**, **5′i**, and **5j**. Namely, in compounds **5i** and **5j** the heterocoupling constants $^3J_{13C,H}$=10.7 Hz and 10.4 Hz, respectively, indicate the *trans* orientation of ester carbonyl group and proton attached to the double bond, while in compound **5′i** the coupling constant $^3J_{13C,H}$=4.3 Hz, indicates the *cis* orientation between the ester carbonyl group and proton attached to the double bond (Fig. 2).

On the basis of ^{1}H NMR spectra one can conclude that compounds **6a**–**c**,**g**,**h**,**k**,**m** exist exclusively in one form, i.e., as (*E*)-4-[(1*H*)-pyrrol-3(2*H*)-ylidene]-1*H*-imidazol-2-olates, while after acidification with hydrochloric acid isomerization around the C=C double bond took place to form also the corresponding (*Z*)-isomers (Scheme 6).

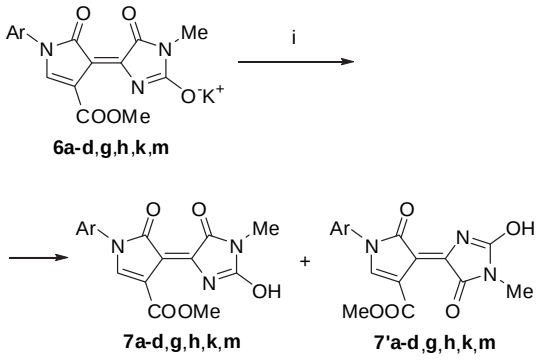
By alkylation of compound **6k** three products can be formed in principle: **9k**, **9′k**, and **9″k**, since O-alkylation can take place either to the hydroxy group attached to the pyrrole or the imidazole ring, or N-alkylation on the imidazole ring nitrogen atom can take place (Fig. 3, Table 1).

On the basis of chemical shifts for the methyl groups at δ_{OMe}=3.64 ppm for **9g** and δ_{OMe}=3.65 ppm for **9k**, which are characteristic for the methyl groups attached to oxygen, one can conclude that O-alkylation took place. Namely, the *N*-methyl groups in imidazolidine-2,4-diones with the exocyclic double bond



Comp.	Ar	Yield (%)	Time (h)
6a	phenyl	85	3.5
6b	4-methylphenyl	53	2
6c	2-methylphenyl	57	2
6d	4-fluorophenyl	94	2
6e	4-bromophenyl	79	1
6g	3-methoxyphenyl	94	1
6h	3-nitrophenyl	85	1
6k	1-naphthyl	79	1
6m	pyrazin-2-yl	87	1

Scheme 3. Reagents and conditions: (i) KOH (~0.19 M), EtOH, reflux.



	Ar	**7** and **7'**, yield (%)	**7** : **7'**
a	phenyl	92	84 : 16
b	4-methylphenyl	95	87 : 13
c	2-methylphenyl	92	82 : 18
d	4-fluorophenyl	94	85 : 15
g	3-methoxyphenyl	93	87 : 13
h	3-nitrophenyl	88	87 : 13
k	1-naphthyl	99	87 : 13
m	pyrazin-2-yl	85	86 : 14

Scheme 4. Reagents and conditions: (i) 37% HCl, H_2O (**6a**–**d**,**g**,**h**,**m**) or EtOH (**6k**), rt.

at position-5 appear in a very narrow range of δ=3.00–3.25 ppm regardless of (*Z*)- or (*E*)-orientation.[13] Proton at 2-position, H_2, was determined by the HMBC spectrum with the ^{13}C of the ester carbonyl group attached to C_3 (Fig. 4). The *N*-methyl group attached to imidazole ring appears at δ_{NMe}=3.17 ppm. The protons of these methyl groups are coupled in HMBC spectrum to $C_{2'}$ and $C_{5'}$ atoms. The coupling of methoxy protons with $C_{2'}$ confirms that methoxy group is attached to $C_{2'}$ atom (Fig. 5). The methylation therefore took place on the hydroxy group attached to the imidazole ring to give compound **9k**.

4. Conclusion

The synthesis of a new triazafulvalene system was developed starting from (dimethylamino)methyleneimidazolidine-2,4-dione **1**, which was transformed into the corresponding succinate **3** by [2+2] cycloaddition to dimethyl acetylenedicarboxylate. Treatment of **3** with aromatic or heteroaromatic amines produced [(aryl-amino- or heteroarylamino)methylene]succinates **5**. These were cyclized in the presence of potassium hydroxide into potassium salts of triazafulvalne system **6**. Alkylaton of **6** gave *O*-alkylated derivatives **9**.

5. Experimental

5.1. General

Melting points were determined on a Kofler micro hot stage. NMR spectra were obtained on a Bruker Avance DPX 300 at 300 MHz for ^1H, and 75.5 MHz for ^{13}C, using DMSO-d_6 and $CDCl_3$ as solvents and TMS as the internal standard. Mass spectra were recorded on an AutoSpecQ and Qtof-premier spectrometers, IR spectra on a Perkin–Elmer Spectrum BX FTIR spectrophotometer. Microanalyses were performed on a Perkin–Elmer CHN Analyser 2400 II. Column chromatography was performed on silica gel (Fluka, silica gel 60, 0.04–0.06 mm).

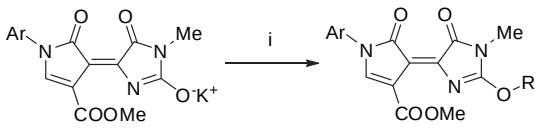
Amines **4a**–**m**, methyl iodide (**8a**), benzyl bromide (**8b**), and KOH (85%) are commercially available (Sigma–Aldrich).

5.2. Dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (3)

Dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**3**) was prepared according to a modified literature procedure.[8c] A mixture of dimethyl acetylenedicarboxylate (**2**) (7.5 mL, 60 mmol) and (*Z*)-5-[(dimethylamino)methylene]-3-methylimidazolidin-2,4-dione (**1**) (5.07 g, 30 mmol) in acetonitrile (100 mL) was heated to reflux for 3 h. Volatile components were evaporated in vacuo and the residue was crystallized from a mixture toluene (25 mL) and *n*-heptane (2 mL). Yield: 5.71 g (61%) of yellow plates; mp 165–167 °C, lit. 165–167 °C.[8c] ^1H NMR ($CDCl_3$): δ 2.99 (6H, br s, N*Me*$_2$); 3.07 (3H, s, N*Me*); 3.66 (3H, s, COO*Me*); 3.86 (3H, s, COO*Me*); 6.94 (1H, br s, N*H*); 7.65 (1H, s, 1′-*H*).

5.3. General procedure for the synthesis of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(arylamino) methylene]succinates 5a–f,m and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(arylamino) methylene]succinates 5a–i,k–m

Amine hydrochlorides **4a**–**d**,**g**,**i**,**j** (1.2–2.2 mmol) or amines **4e**,**f**,**h**,**k**–**m** (0.36–2.2 mmol) and 37% HCl (1–5 drops) were added to a solution of dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**3**) (0.33–2 mmol) in ethanol (1.5–6 mL). The reaction mixture was heated to



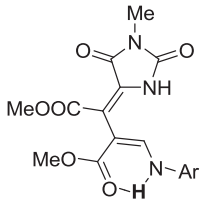
6e,**g**,**k** **9e,g,k**

Alkylhalide	Compound	Ar	R	X	Yield (%)	Time (min)
8a	**9g**	3-methoxyphenyl	methyl	I	92	40
8a	**9k**	1-naphthyl	methyl	I	91	20
8b	**9e**	4-bromophenyl	benzyl	Br	41	90

Scheme 5. Reagents and conditions: (i) RX (**8a**,**b**), DMF, rt.

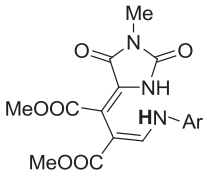
reflux. The precipitated products were filtered under reduced pressure.

*5.3.1. (2E,3Z)-Dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(phenylamino)methylene]succinate (**5a**) and (2E,3E)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(phenylamino)methylene] succinate (**5′a**).* Prepared from **3** (0.311 g, 1 mmol) and aniline hydrochloride (**4a**) (0.156 g, 1.2 mmol) in ethanol (4 mL), 5 h. Yield: 0.229 g (64%) of yellow needles; mp 207–210 °C. Ratio of isomers: **5a**/**5′a**=94:6. ^{1}H NMR ($CDCl_3$): (2*E*,3*Z*)-isomer: δ 3.00 (3H, s, N*Me*); 3.80 (3H, s, COO*Me*); 3.88 (3H, s, COO*Me*); 7.00–7.07 (2H, m, 2H of *Ph*); 7.08–7.15 (1H, m, 1H of *Ph*); 7.31–7.38 (2H, m, 2H of *Ph*); 7.56 (1H, br s, N*H*); 7.69 (1H, d, *J*=13.2 Hz, C*H*NH); 10.55 (1H, br d, *J*=13.5 Hz, CHN*H*); (2*E*,3*E*)-isomer: δ 3.05 (3H, s, N*Me*); 3.78 (3H, s, COO*Me*); 3.89 (3H, s, COO*Me*); 8.22 (1H, d, *J*=14.2 Hz, C*H*NH); 8.49 (1H, br d, *J*=13.9 Hz, CHN*H*). (Found: C, 56.94; H, 4.84; N, 11.82. $C_{17}H_{17}N_3O_6$ requires: C, 56.82; H, 4.77; N, 11.69.) ν_{max} (KBr) 3280, 3185, 3113, 2950, 1777, 1724, 1683, 1638, 1627, 1601, 1588, 1458, 1439, 1395, 1312, 1196, 1163, 752 cm^{-1}.



5a-k,**m**

δ_{NH} = 10.09-11.73 ppm
(hydrogen bond)



5'a-i,**k-m**

δ_{NH} = 8.26-9.66 ppm
(no hydrogen bond)

Comp.	δ (ppm), N*H*Ar	Comp.	δ (ppm), N*H*Ar
5a	10.55	**5'a**	8.49
5b	10.53	**5'b**	8.37
5c	10.56	**5'c**	8.26
5d	10.32	**5'd**	8.87
5e	10.09	**5'e**	8.90
5f	10.65	**5'f**	[a]
5g	10.30	**5'g**	8.83
5h	10.44	**5'h**	9.18
5i	10.30	**5'i**	8.72
5j	10.73	**5'j**	/
5k	11.34	**5'k**	9.05
5l	/	**5'l**	9.47
5m	[a]	**5'm**	9.66

[a] Overlapped by other protons .

Figure 1. Structure determination of isomers **5** and **5′** with ^{1}H NMR spectroscopy.

*5.3.2. (2E,3Z)-Dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(p-tolylamino)methylene]succinate (**5b**) and (2E,3E)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(p-tolylamino)methylene] succinate (**5′b**).* Prepared from **3** (0.623 g, 2 mmol) and 4-methylaniline hydrochloride (**4b**) (0.316 g, 2.2 mmol) in ethanol (6 mL), 5 h. Yield: 0.452 g (61%) of yellow needles; mp 189–193 °C. Ratio of isomers: **5b**/**5′b**=95:5. ^{1}H NMR ($CDCl_3$): (2*E*,3*Z*)-isomer: δ 2.32 (3H, s, Ph–*Me*); 2.95 (3H, s, N*Me*); 3.78 (3H, s, COO*Me*); 3.87 (3H, s, COO*Me*); 6.89–6.95 (2H, m, 2H of *Ph*); 7.10–7.16 (2H, m, 2H of *Ph*); 7.65 (1H, d, *J*=13.3 Hz, C*H*NH); 7.86 (1H, br s, N*H*); 10.53 (1H, br d, *J*=13.3 Hz, CHN*H*); (2*E*,3*E*)-isomer: δ 2.29 (3H, s, Ph-*Me*); 3.02 (3H, s, N*Me*); 3.77 (3H, s, COO*Me*); 3.88 (3H, s, COO*Me*); 7.50 (1H, br s, N*H*); 8.18 (1H, d, *J*=14.2 Hz, C*H*NH); 8.37 (1H, br d, *J*=14.5 Hz, CHN*H*). (Found: C, 57.98; H, 5.17; N, 11.16. $C_{18}H_{19}N_3O_6$ requires: C, 57.90; H, 5.13; N, 11.25.) ν_{max} (KBr) 3189, 3149, 2949, 1776, 1724, 1686, 1674, 1641, 1627, 1584, 1436, 1394, 1340, 1311, 1194, 1159, 783 cm^{-1}.

*5.3.3. (2E,3Z)-Dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(o-tolylamino)methylene]succinate (**5c**) and (2E,3E)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(o-tolylamino)methylene] succinate (**5′c**).* Prepared from **3** (0.623 g, 2 mmol) and 2-methylaniline hydrochloride (**4c**) (0.316 g, 2.2 mmol) in ethanol (6 mL), 5 h. Yield: 0.393 g (53%) of yellow needles; mp 214–218 °C. Ratio of isomers: **5c**/**5′c**=66:34. ^{1}H NMR (DMSO-d_6): (2*E*,3*Z*)-isomer: δ 2.30 (3H, s, Ph-*Me*); 2.91 (3H, s, N*Me*); 3.65 (3H, s, COO*Me*); 3.68 (3H, s, COO*Me*); 7.01 (1H, dt, *J*=7.4, 1.1 Hz, 1H of *Ph*); 7.17–7.29 (2H, m, 2H of *Ph*); 7.40 (1H, d, *J*=7.7 Hz, 1H of *Ph*); 7.96 (1H, d, *J*=12.9 Hz, C*H*NH); 10.56 (1H, br d, *J*=13.0 Hz, CHN*H*); 10.70 (1H, br s, N*H*); (2*E*,3*E*)-isomer: δ 2.28 (3H, s, Ph–*Me*); 2.90 (3H, s, N*Me*); 3.59 (3H, s, COO*Me*); 3.68 (3H, s, COO*Me*); 7.06–7.12 (1H, m, 1H of *Ph*); 7.70 (1H, d, *J*=14.0 Hz, C*H*NH); 8.26 (1H, br d, *J*=13.8 Hz, CHN*H*); 10.11 (1H, br s, N*H*). (Found: C, 57.73; H, 4.95; N, 11.21. $C_{18}H_{19}N_3O_6$ requires: C, 57.90; H, 5.13; N, 11.25.) ν_{max} (KBr) 3191, 3142, 1779, 1723, 1684, 1636, 1625, 1598, 1437, 1337, 1314, 1198, 1159, 754 cm^{-1}.

*5.3.4. (2Z,3E)-Dimethyl 2-[(4-fluorophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5d**) and (2E,3E)-*

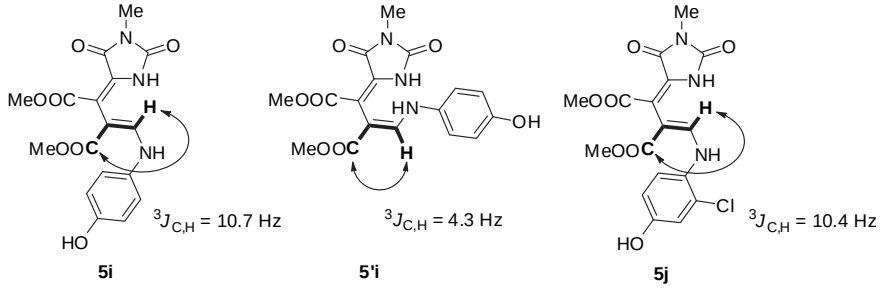
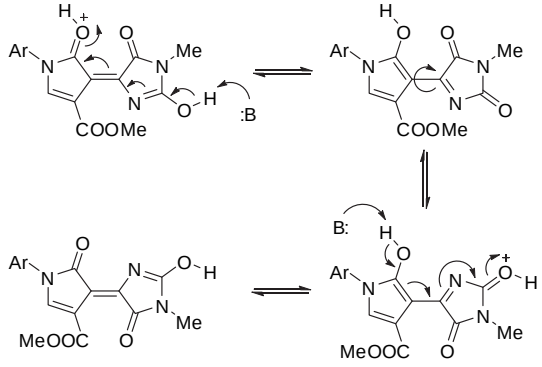


Figure 2. Determination of the configuration around the C=C double bond by HMBC.



Scheme 6. Isomerization around the C=C double bond.

*dimethyl 2-[(4-fluorophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′d**).* Prepared from **3** (0.623 g, 2 mmol) and 4-fluoroaniline hydrochloride (**4d**) (0.325 g, 2.2 mmol) in ethanol (6 mL), 5 h. Yield: 0.537 g (71%) of yellow needles; mp 207–214 °C. Ratio of isomers: **5d**/**5′d**=38:62. ^{1}H NMR (DMSO-d_6): (2*Z*,3*E*)-isomer: *δ* 2.90 (3H, s, NM*e*); 3.66 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 7.33–7.40 (4H, m, 4H of *Ph*); 7.79 (1H, d, *J*=13.4 Hz, C*H*NH); 10.32 (1H, br d, *J*=13.3 Hz, CHN*H*); 10.68 (1H, br s, N*H*); (2*E*,3*E*)-isomer: *δ* 2.91 (3H, s, NM*e*); 3.59 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 7.15–7.27 (4H, m, 4H of *Ph*); 7.84 (1H, d, *J*=14.1 Hz, C*H*NH); 8.87 (1H, br d, *J*=14.1 Hz, CHN*H*); 10.07 (1H, br s, N*H*). (Found: C, 54.00; H, 4.26; N, 11.16. $C_{17}H_{16}FN_3O_6$ requires: C, 54.11; H, 4.27; N, 11.14.) ν_{max} (KBr) 3192, 3149, 2951, 1777, 1722, 1683, 1642, 1627, 1601, 1517, 1436, 1396, 1335, 1308, 1207, 1192, 1158, 829 cm^{-1}.

*5.3.5. (2Z,3E)-Dimethyl 2-[(4-bromophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5e**) and (2E,3E)-dimethyl 2-[(4-bromophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′e**).* Prepared from **3** (0.623 g, 2 mmol), 4-bromoaniline (**4e**) (0.378 g, 2.2 mmol), and 37% HCl (5 drops) in ethanol (6 mL), 6.5 h. Yield: 0.760 g (87%) of orange and yellow needles; mp 195–198 °C and 230–233 °C. Ratio of isomers: **5e**/**5′e**=12:88. ^{1}H NMR (DMSO-d_6): (2*Z*,3*E*)-isomer: *δ* 2.91 (3H, s, NM*e*); 3.59 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 7.16–7.24 (2H, m, 2H of *Ph*); 7.46–7.53 (2H, m, 2H of *Ph*); 7.72 (1H, d, *J*=13.0 Hz, C*H*NH); 10.09 (1H, br d, *J*=13.1 Hz, CHN*H*); 10.12 (1H, br s, N*H*); (2*E*,3*E*)-isomer: *δ* 2.89 (3H, s, NM*e*); 3.56 (3H, s, COO*Me*); 3.70 (3H, s, COO*Me*); 7.02–7.10 (2H, m, 2H of *Ph*); 7.40–7.46 (2H, m, 2H of *Ph*); 7.90 (1H, d, *J*=13.4 Hz, C*H*NH); 8.90 (1H, br d, *J*=13.4 Hz, CHN*H*); 10.61 (1H, br s, N*H*). (Found: C, 46.82; H, 3.71; N, 9.54. $C_{17}H_{16}BrN_3O_6$ requires: C, 46.59; H, 3.68; N, 9.59.) ν_{max} (KBr) 3335, 2950, 1781, 1734, 1693, 1681, 1630, 1591, 1581, 1487, 1453, 1431, 1321, 1243, 1209, 1148, 824, 620 cm^{-1}.

Table 1
Chemical shifts

Comp.	*δ* (ppm), O*Me*		*δ* (ppm), OC*H*$_2$Ph
	$CDCl_3$	DMSO-d_6	$CDCl_3$
9g	3.64	3.48	—
9k	3.65	3.49	—
9e	—	—	5.65

*5.3.6. (2Z,3E)-Dimethyl 2-[(2-iodophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5f**) and (2E,3E)-dimethyl 2-[(2-iodophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′f**).* Prepared from **3** (0.623 g, 2 mmol), 2-iodoaniline (**4f**) (0.482 g, 2.2 mmol), and 37% HCl (5 drops) in ethanol (6 mL), 6.5 h. Yield: 0.943 g (97%) of yellow needles; mp 216–221 °C. Ratio of isomers: **5f**/**5′f**=87:13. EIMS: *m*/*z*=485 (M^+). ^{1}H NMR (DMSO-d_6): (2*Z*,3*E*)-isomer: *δ* 2.92 (3H, s, NM*e*); 3.67 (3H, s, COO*Me*); 3.69 (3H, s, COO*Me*); 6.82–6.89 (1H, m, 1H of *Ph*); 7.33–7.49 (2H, m, 2H of *Ph*); 7.87 (1H, dd, *J*=7.9, 1.3 Hz, 1H of *Ph*); 7.95 (1H, d, *J*=12.7 Hz, C*H*NH); 10.65 (1H, br d, *J*=12.8 Hz, CHN*H*); 10.74 (1H, br s, N*H*); (2*E*,3*E*)-isomer: *δ* 2.90 (3H, s, NM*e*); 3.62 (3H, s, COO*Me*); 3.73 (3H, s, COO*Me*); 6.76–6.82 (1H, m, 1H of *Ph*); 7.85 (1H, d, *J*=12.4 Hz, C*H*NH); 10.46 (1H, br s, N*H*). (Found: C, 42.35; H, 3.33; N, 8.62. $C_{17}H_{16}IN_3O_6$ requires: C, 42.08; H, 3.32; N, 8.62.) EI-HRMS: *m*/*z*=485.0096 (M^+); $C_{17}H_{16}IN_3O_6$ requires: *m*/*z*=485.0084 (M^+). ν_{max} (KBr) 3188, 3149, 2947, 1777, 1723, 1686, 1678, 1641, 1613, 1436, 1359, 1334, 1307, 1292, 1193, 1158, 762, 615 cm^{-1}.

*5.3.7. (2Z,3E)-Dimethyl 2-[(3-methoxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5g**) and (2E,3E)-dimethyl 2-[(3-methoxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′g**).* Prepared from **3** (0.623 g, 2 mmol) and 3-methoxyaniline hydrochloride (**4g**) (0.351 g,

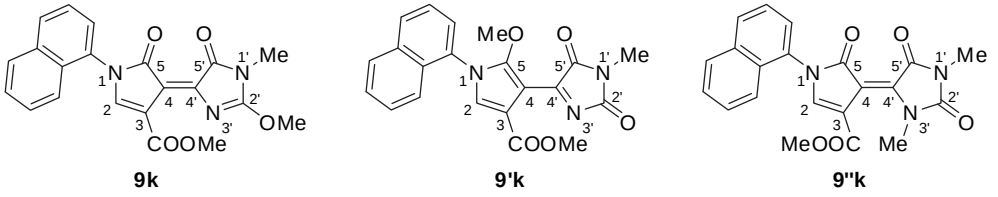


Figure 3. Possible products of alkylation of potassium 1*H*-imidazol-2-olate **6k**.

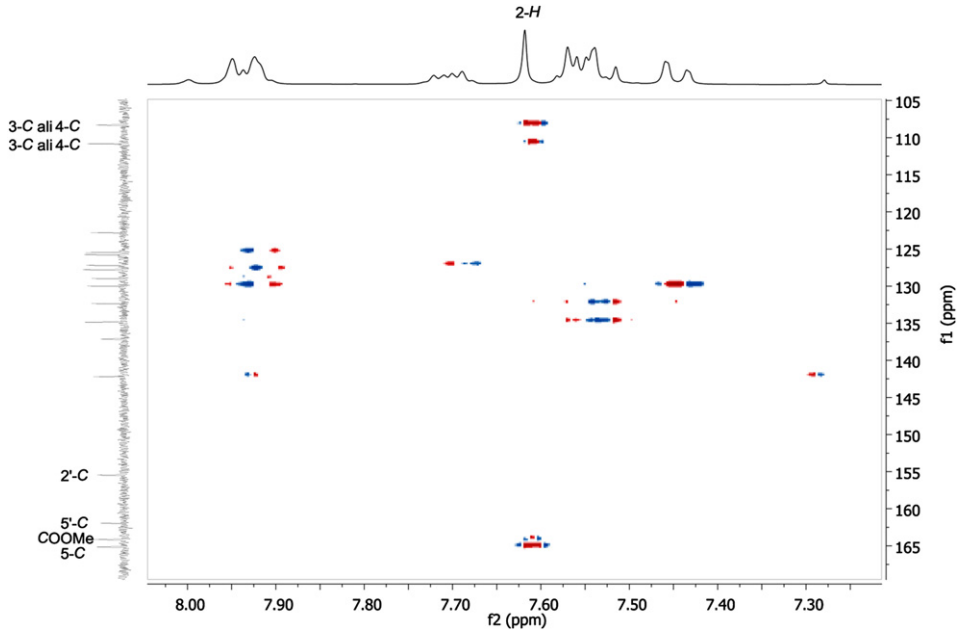


Figure 4. Aromatic part of 2D HMBC spectrum of compound **9b**.

2.2 mmol) in ethanol (6 mL), 6.5 h. The product did not precipitate from ethanol, so water was added (3 mL) and cooled to −18 °C, which resulted in the precipitation of the product. Yield: 0.410 g (53%) of yellow needles; mp 188–203 °C. Ratio of isomers: **5g**/**5′g**=78:22. ^{1}H NMR (DMSO-d_6): (2*Z*,3*E*)-isomer: δ 2.91 (3H, s, N*Me*); 3.64 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 3.76 (3H, s, O*Me*); 6.65 (1H, dd, *J*=8.2, 2.2 Hz, 4′-*H* or 6′-*H*); 6.87 (1H, dd, *J*=8.0, 2.0 Hz, 4′-*H* or 6′-*H*); 6.95 (1H, t, *J*=2.2 Hz, 2′-*H*); 7.24 (1H, t, *J*=8.1 Hz, 5′-*H*); 7.87 (1H, d, *J*=13.3 Hz, *CH*NH); 10.30 (1H, d, *J*=13.3 Hz, CHN*H*); 10.70 (1H, s, N*H*); (2*E*,3*E*)-isomer: δ 2.93 (3H, s, N*Me*); 3.60 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 3.75 (3H, s, O*Me*); 6.76 (1H, t, *J*=2.2 Hz, 2′-*H*); 6.77–6.82 (1H, m, 4′-*H* or 6′-*H*); 7.25 (1H, t, *J*=8.1 Hz, 5′-*H*); 7.89 (1H, d, *J*=14.0 Hz, *CH*NH); 8.83 (1H, br d, *J*=14.1 Hz, CHN*H*); 10.08 (1H, s, N*H*). (Found: C, 55.64; H, 5.02; N, 10.74. $C_{18}H_{19}N_3O_7$ requires: C, 55.53; H, 4.92; N, 10.79.) ν_{max} (KBr) 3191, 3149, 2951, 1780, 1726, 1683, 1644, 1623, 1607, 1584, 1495, 1455, 1436, 1279, 1191, 1152, 1043, 775 cm^{-1}.

*5.3.8. (2E,3Z)-Dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-yliden)-3-[(3-nitrophenylamino)methylene]succinate (**5h**) and (2E,3E)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(3-nitrophenylamino)methylene]succinate (**5′h**).* Prepared from **3** (0.623 g, 2 mmol), 3-nitroaniline (**4h**) (0.304 g, 2.2 mmol), and 37% HCl (5 drops) in ethanol (6 mL), 6.5 h. Yield: 0.778 g (96%) of yellow

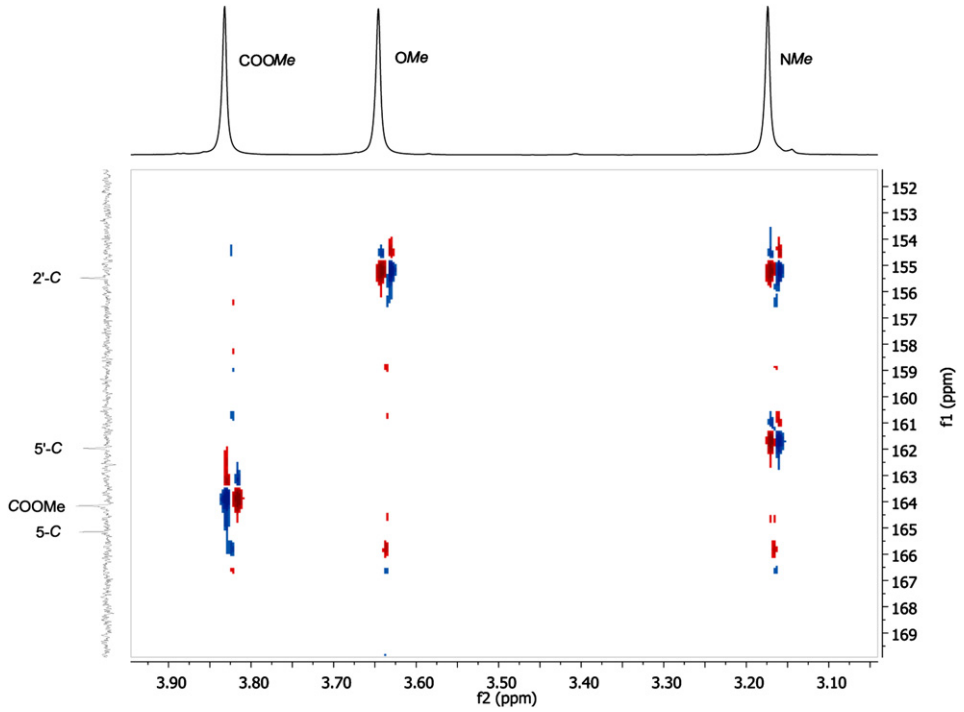


Figure 5. Carbonyl part of 2D HMBC spectrum of compound **9k**.

needles; mp 168–177 °C. Ratio of isomers: **5h**/**5′h**=30:70. ^{1}H NMR (DMSO-d_6): (2*E*,3*Z*)-isomer: δ 2.92 (3H, s, N*Me*); 3.67 (3H, s, COO*Me*); 3.68 (3H, s, COO*Me*); 7.77–7.82 (1H, m, 1H of *Ph*); 7.96 (1H, d, *J*=13.0 Hz, C*H*NH); 8.28 (1H, t, *J*=2.1 Hz, 2′-*H*); 10.44 (1H, d, *J*=13.1 Hz, CHN*H*); 10.75 (1H, s, N*H*); (2*E*,3*E*)-isomer: δ 2.93 (3H, s, N*Me*); 3.63 (3H, s, COO*Me*); 3.68 (3H, s, COO*Me*); 7.58–7.70 (2H, m, 2H of *Ph*); 7.84–7.90 (1H, m, 1H of *Ph*); 7.94 (1H, d, *J*=13.6 Hz, C*H*NH); 8.05 (1H, t, *J*=2.0 Hz, 2′-*H*); 9.18 (1H, d, *J*=13.6 Hz, CHN*H*); 10.15 (1H, s, N*H*). (Found: C, 50.57; H, 4.08; N, 13.78. $C_{17}H_{16}N_4O_8$ requires: C, 50.50; H, 3.99; N, 13.86.) ν_{max} (KBr) 3301, 3225, 2957, 1781, 1764, 1731, 1701, 1636,m 1615, 1585, 1531, 1471, 1433, 1351, 1277, 1255, 1130, 737 cm^{-1}.

*5.3.9. (2Z,3E)-Dimethyl 2-[(4-hydroxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5i**) and (2E,3E)-dimethyl 2-[(4-hydroxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′i**).* Prepared from **3** (0.623 g, 2 mmol) and 4-hydroxyaniline hydrochloride (**4i**) (0.320 g, 2.2 mmol) in ethanol (6 mL), 5 h. Yield: 0.503 g (67%) of yellow needles; mp 187–192 °C. Ratio of isomers: **5i**/**5′i**=44:56. ^{1}H NMR (DMSO-d_6): (2*Z*,3*E*)-isomer: δ 2.91 (3H, s, N*Me*); 3.62 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 6.70–6.76 (2H, m, 2H of *Ph*); 7.09–7.14 (2H, m, 2H of *Ph*); 7.70 (1H, d, *J*=13.5 Hz, C*H*NH); 9.32 (1H, s, O*H*); 10.30 (1H, d, *J*=13.5 Hz, CHN*H*); 10.63 (1H, s, N*H*); (2*E*,3*E*)-isomer: δ 2.91 (3H, s, N*Me*); 3.58 (3H, s, COO*Me*); 3.67 (3H, s, COO*Me*); 6.70–6.76 (2H, m, 2H of *Ph*); 6.99–7.05 (2H, m, 2H of *Ph*); 7.79 (1H, d, *J*=14.3 Hz, C*H*NH); 8.72 (1H, d, *J*=14.4 Hz, CHN*H*); 9.26 (1H, s, O*H*); 10.00 (1H, s, N*H*). ^{13}C NMR (DMSO-d_6): δ 24.1, 50.8, 50.9, 51.8, 52.0, 91.5, 93.0, 110.6, 115.8, 115.9, 118.4, 118.7, 127.5, 128.9, 132.0, 133.2, 142.7, 153.8, 154.0, 154.1, 154.2, 161.7, 161.9, 167.1, 167.4, 167.5, 167.8. (Found: C, 54.11; H, 4.78; N, 10.99. $C_{17}H_{17}N_3O_7$ requires: C, 54.40; H, 4.57; N, 11.20.) ν_{max} (KBr) 3191, 3137, 2952, 1775, 1706, 1683, 1637, 1617, 1520, 1457, 1438, 1355, 1335, 1313, 1212, 1194, 1162, 828 cm^{-1}.

*5.3.10. (2Z,3E)-Dimethyl 2-[(2-chloro-4-hydroxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5j**).* Prepared from **3** (0.623 g, 2 mmol) and 4-hydroxy-2-chloroaniline hydrochloride (**4j**) (0.396 g, 2.2 mmol) in ethanol (6 mL), 5 h. Yield: 0.554 g (68%) of yellow needles; mp 233–235 °C. ^{1}H NMR (DMSO-d_6): δ 2.91 (3H, s, N*Me*); 3.64 (3H, s, COO*Me*); 3.68 (3H, s, COO*Me*); 6.79 (1H, dd, *J*=2.6, 8.9 Hz, 5′-*H*); 6.92 (1H, d, *J*=2.7 Hz, 3′-*H*); 7.43 (1H, d, *J*=9.1 Hz, 6′-*H*); 7.86 (1H, d, *J*=12.9 Hz, C*H*NH); 9.76 (1H, s, O*H*); 10.69 (1H, s, N*H*); 10.73 (1H, d, *J*=13.0 Hz, CHN*H*). ^{13}C NMR (DMSO-d_6): δ 24.0, 51.2, 52.0, 93.2, 114.1, 115.5, 115.8, 117.0, 121.5, 128.4, 128.5, 147.3, 153.9, 154.0, 161.7, 167.5, 167.7. (Found: C, 49.68; H, 3.96; N, 10.25. $C_{17}H_{16}ClN_3O_7$ requires: C, 49.83; H, 3.94; N, 10.25.) ν_{max} (KBr) 3309, 3191, 3124, 2953, 1775, 1702, 1684, 1632, 1608, 1513, 1440, 1337, 1297, 1206, 1162, 990, 842, 614 cm^{-1}.

*5.3.11. (2E,3Z)-Dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(naphthalen-1-ylamino)methylen]succinate (**5k**) and (2E,3E)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(naphthalen-1-ylamino)methylen]succinate (**5′k**).* Prepared from **3** (0.623 g, 2 mmol), 1-naphthylamine (**4k**) (0.304 g, 2.2 mmol), and 37% HCl (5 drops) in ethanol (6 mL), 6.5 h. Yield: 0.678 g (83%) of yellow needles; mp 216–219 °C. Ratio of isomers: **5k**/**5′k**=95:5. ^{1}H NMR (DMSO-d_6): (2*E*,3*Z*)-isomer: δ 2.92 (3H, s, N*Me*); 3.70 (3H, s, COO*Me*); 3.72 (3H, s, COO*Me*); 7.50–7.56 (2H, m, 2H of *Ar*); 7.62 (1H, ddd, *J*=1.1, 6.9, 8.0 Hz, 1H of *Ar*); 7.67–7.74 (2H, m, 2H of *Ar*); 7.95 (1H, d, *J*=8.3 Hz, 1H of *Ar*); 8.00 (1H, dd, *J*=1.2, 8.2 Hz, 1H of *Ar*); 8.11 (1H, d, *J*=12.6 Hz, C*H*NH); 10.76 (1H, s, N*H*); 11.34 (1H, d, *J*=12.7 Hz, CHN*H*); (2*E*,3*E*)-isomer: δ 9.05 (1H, d, *J*=13.4 Hz, CHN*H*); 10.30 (1H, s, N*H*). (Found: C, 61.41; H, 4.69; N, 10.28. $C_{21}H_{19}N_3O_6$ requires: C, 61.61; H, 4.68; N, 10.26.) ν_{max} (KBr) 3189, 3149, 2947, 1779, 1723, 1685, 1674, 1636, 1611, 1594, 1437, 1329, 1307, 1267, 1190, 1156, 768 cm^{-1}.

*5.3.12. (2E,3E)-Dimethyl 2-[(5-chloropyridin-2-ylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′l**).* Prepared from **3** (0.104 g, 0.33 mmol), 5-chloropyridine-2-amine (**4l**) (0.047 g, 0.36 mmol), and 37% HCl (1 drop) in ethanol (1.5 mL), 5.5 h. Yield: 0.050 g (38%) of yellow needles; mp 220–223 °C. ^{1}H NMR (DMSO-d_6): δ 2.89 (3H, s, N*Me*); 3.58 (3H, s, COO*Me*); 3.70 (3H, s, COO*Me*); 6.63 (1H, d, *J*=8.8 Hz, 3′-*H*); 7.73 (1H, dd, *J*=8.8, 2.7 Hz, 4′-*H*); 8.28 (1H, d, *J*=2.6 Hz, 6′-*H*); 8.56 (1H, d, *J*=12.6 Hz, C*H*NH); 9.47 (1H, br d, *J*=12.6 Hz, CHN*H*); 10.68 (1H, s, N*H*). (Found: C, 48.53; H, 3.81; N, 14.11. $C_{16}H_{15}ClN_4O_6$ requires: C, 48.68; H, 3.83; N, 14.19.) ν_{max} (KBr) 3328, 2957, 1777, 1734, 1705, 1698, 1676, 1653, 1632, 1593, 1482, 1473, 1432, 1365, 1236, 1152, 1135, 832 cm^{-1}.

*5.3.13. (2E,3Z)-Dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(pyrazin-2-ylamino)methylene]succinate (**5m**) and (2E,3E)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(pyrazin-2-ylamino)methylene]succinate (**5′m**).* Prepared from **3** (0.467 g, 1.5 mmol), pyrazine-2-amine (**4m**) (0.157 g, 1.65 mmol), and 37% HCl (5 drops) in ethanol (3 mL), 5.5 h. Yield: 0.263 g (49%) of yellow needles; mp 211–214 °C. Ratio of isomers: **5m**/**5′m**=8:92. EIMS: *m*/*z*=361 (M^+). ^{1}H NMR (DMSO-d_6): (2*E*,3*Z*)-isomer: δ 2.93 (3H, s, N*Me*); 3.76 (3H, s, COO*Me*); (2*E*,3*E*)-isomer: δ 2.90 (3H, s, N*Me*); 3.60 (3H, s, COO*Me*); 3.72 (3H, s, COO*Me*); 8.14 (1H, d, *J*=2.5 Hz, 1H of *Ar*); 8.24–8.28 (2H, m, 2H of *Ar*); 8.53 (1H, d, *J*=12.5 Hz, C*H*NH); 9.66 (1H, br d, *J*=12.5 Hz, CHN*H*); 10.74 (1H, s, N*H*). ^{13}C NMR ($CDCl_3$): δ 24.2, 51.1, 52.1, 100.2, 103.8, 134.5, 136.0, 137.1, 137.3, 141.8, 149.0, 153.9, 161.8, 166.0, 167.1. (Found: C, 49.41; H, 4.25; N, 18.98. $C_{15}H_{15}N_5O_6$ requires: C, 49.86; H, 4.18; N, 19.38.) EI-HRMS: *m*/*z*=361.1033 (M^+); $C_{15}H_{15}N_5O_6$ requires: *m*/*z*=361.1022 (M^+). ν_{max} (KBr) 3325, 2954, 1776, 1731, 1705, 1653, 1636, 1540, 1502, 1455, 1434, 1393, 1294, 1247, 1188, 1155, 1077, 836, 618 cm^{-1}.

5.4. General procedure for the synthesis of potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-aryl-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olates 6a–e,g,h,k,m

Potassium hydroxide (0.028–0.099 g) was added to a solution of a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(arylamino)methylene]succinate **5a**–**e**,**g**,**h**,**k**,**m** and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(arylamino)methylene]succinate **5′a**–**e**,**g**,**h**,**k**,**m** (0.5–1.5 mmol) in ethanol (2.5–8 mL). The reaction mixture was heated to reflux. The precipitated product was filtered under reduced pressure.

*5.4.1. Potassium (E)-4-[4-(methoxycarbonyl)-2-oxo-1-phenyl-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6a**).* Prepared from a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(phenylamino)methylene]succinate (**5a**) and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(phenylamino)methylene]succinate (**5′a**) (0.180 g, 0.5 mmol) and KOH (0.028 g, 0.42 mmol) in ethanol (3 mL), 3.5 h. Yield: 0.155 g (85%) of fine dark red powder; mp decomposition above 250 °C. EIMS: *m*/*z*=327 ($(M-K)H^+$). ^{1}H NMR (DMSO-d_6): δ 2.83 (3H, s, N*Me*); 3.58 (3H, s, COO*Me*); 7.17–7.23 (1H, m, 1H of *Ph*); 7.30 (1H, s, 5′-*H*); 7.37–7.44 (2H, m, 2H of *Ph*); 7.58–7.63 (2H, m, 2H of *Ph*). (Found: C, 52.58; H, 3.46; N, 11.21. $C_{16}H_{12}KN_3O_5$ requires: C, 52.59; H, 3.31; N, 11.50.) EI-HRMS: *m*/*z*=327.0862 ($(M-K)H^+$); $C_{16}H_{13}N_3O_5$ requires: *m*/*z*=327.0855 ($(M-K)H^+$). ν_{max} (KBr) 2952, 1738, 1712, 1691, 1659, 1571, 1503, 1448, 1389, 1224, 1199, 1120, 1034, 767, 621 cm^{-1}.

5.4.2. Potassium (E)-4-[4-(methoxycarbonyl)-2-oxo-1-p-tolyl-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate

(**6b**). Prepared from a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(*p*-tolylamino)methylene] succinate (**5b**) and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(*p*-tolylamino)methylene]succinate (**5′b**) (0.187 g, 0.5 mmol) and KOH (0.028 g, 0.42 mmol) in ethanol (3 mL), 2 h. Yield: 0.101 g (53%) of fine dark red powder; mp 280–282 °C with decomposition. ^{1}H NMR (DMSO-d_6): δ 2.31 (3H, s, Ph–*Me*); 2.83 (3H, s, N*Me*); 3.58 (3H, s, COO*Me*); 7.17–7.23 (2H, m, 2H of *Ph*); 7.25 (1H, s, 5′-*H*); 7.44–7.50 (2H, m, 2H of *Ph*). ^{13}C NMR (DMSO-d_6): δ 20.5, 24.3, 50.7, 98.7, 111.9, 122.0, 127.0, 129.2, 134.3, 135.2, 156.6, 164.2, 165.4, 166.8, 168.4. (Found: C, 53.61; H, 3.85; N, 10.88. $C_{17}H_{14}KN_3O_5$ requires: C, 53.82; H, 3.72; N, 11.08.) ν_{max} (KBr) 2955, 1739, 1709, 1691, 1656, 1571, 1516, 1447, 1389, 1220, 1207, 1115, 1029, 610 cm^{-1}.

5.4.3. Potassium (E)-4-[4-(methoxycarbonyl)-2-oxo-1-o-tolyl-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6c**). Prepared from a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(*o*-tolylamino)methylene]succinate (**5c**) and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(*o*-tolylamino)methylene]succinate (**5′c**) (0.187 g, 0.5 mmol) and KOH (0.028 g, 0.42 mmol) in ethanol (2.5 mL), 2 h. Yield: 0.108 g (57%) of fine dark red powder; mp 285–287 °C with decomposition. ^{1}H NMR (DMSO-d_6): δ 2.14 (3H, s, Ph-*Me*); 2.84 (3H, s, N*Me*); 3.57 (3H, s, COO*Me*); 7.00 (1H, s, 5′-*H*); 7.12–7.18 (1H, m, 1H of *Ph*); 7.22–7.34 (3H, m, 3H of *Ph*). (Found: C, 53.74; H, 3.83; N, 10.99. $C_{17}H_{14}KN_3O_5$ requires: C, 53.82; H, 3.73; N, 11.08.) ν_{max} (KBr) 3150, 1742, 1717, 1695, 1648, 1569, 1543, 1496, 1440, 1389, 1224, 1196, 1114, 1028, 750, 623 cm^{-1}.

5.4.4. Potassium (E)-4-[1-(4-fluorophenyl)-4-(methoxycarbonyl)-2-oxo-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6d**). Prepared from a mixture of (2*Z*,3*E*)-dimethyl 2-[(4-fluorophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5d**) and (2*E*,3*E*)-dimethyl 2-[(4-fluorophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′d**) (0.189 g, 0.5 mmol) and KOH (0.035 g, 0.5 mmol) in ethanol (2.5 mL), 2 h. Yield: 0.180 g (94%) of fine dark red powder; mp 276–278 °C with decomposition. ^{1}H NMR (DMSO-d_6): δ 2.83 (3H, s, N*Me*); 3.58 (3H, s, COO*Me*); 7.19–7.28 (2H, m, 2H of *Ph*); 7.29 (1H, s, 5′-*H*); 7.58–7.67 (2H, m, 2H of *Ph*). (Found: C, 49.94; H, 3.05; N, 10.71. $C_{16}H_{11}FKN_3O_5$ requires: C, 50.13; H, 2.89; N, 10.96.) ν_{max} (KBr) 2953, 1737, 1713, 1698, 1656, 1571, 1513, 1449, 1392, 1225, 1200, 1118, 1029, 847, 609 cm^{-1}.

5.4.5. Potassium (E)-4-[1-(4-bromophenyl)-4-(methoxycarbonyl)-2-oxo-1H-pyrrol-3(2H)-yliden]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6e**). Prepared from a mixture of (2*Z*,3*E*)-dimethyl 2-[(4-bromophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5e**) and (2*E*,3*E*)-dimethyl 2-[(4-bromophenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′e**) (0.219 g, 0.5 mmol) and KOH (0.035 g, 0.5 mmol) in ethanol (2.5 mL), 1 h. Yield: 0.175 g (79%) of fine dark red powder; mp decomposition above 255 °C. ^{1}H NMR (DMSO-d_6): δ 2.84 (3H, s, N*Me*); 3.59 (3H, s, COO*Me*); 7.33 (1H, s, 5′-*H*); 7.55–7.60 (2H, m, 2H of *Ph*); 7.61–7.66 (2H, m, 2H of *Ph*). ^{13}C NMR (DMSO-d_6): δ 24.3, 50.8, 98.3, 112.7, 117.2, 123.6, 125.9, 131.6, 136.9, 157.0, 164.1, 165.4, 166.9, 168.3. (Found: C, 43.10; H, 2.64; N, 9.14. $C_{16}H_{11}BrKN_3O_5$ requires: C, 43.29; H, 2.50; N, 9.46.) ν_{max} (KBr) 2953, 1740, 1713, 1693, 1658, 1570, 1493, 1444, 1390, 1254, 1227, 1199, 1119, 1029, 835 cm^{-1}.

5.4.6. Potassium (E)-4-[4-(methoxycarbonyl)-1-(3-methoxyphenyl)-2-oxo-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6g**). Prepared from a mixture of (2*Z*,3*E*)-dimethyl 2-[(3-methoxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5g**) and (2*E*,3*E*)-dimethyl 2-[(3-methoxyphenylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**5′g**) (0.506 g, 1.3 mmol) and KOH (0.086 g, 1.3 mmol) in ethanol (6 mL), 1 h. Yield: 0.482 g (94%) of fine dark red powder; mp 240–242 °C with decomposition. ESI-MS: m/z=396.1 (MH^+). ^{1}H NMR (DMSO-d_6): δ 2.84 (3H, s, N*Me*); 3.59 (3H, s, COO*Me*); 3.78 (3H, s, O*Me*); 6.77 (1H, ddd, J=8.2, 2.6, 1.0 Hz, 4″-*H* or 6″-*H*); 7.18 (1H, ddd, J=8.0, 2.0, 1.0 Hz, 4″-*H* or 6″-*H*); 7.25 (1H, t, J=2.2 Hz, 2″-*H*); 7.30 (1H, t, J=8.1 Hz, 5″-*H*); 7.32 (1H, s, 5′-*H*). ^{13}C NMR (DMSO-d_6): δ 24.2, 50.7, 55.1, 98.6, 107.7, 110.6, 112.2, 113.9, 126.6, 129.5, 138.6, 156.7, 159.5, 164.2, 165.3, 166.8, 168.3. EI-HRMS m/z=396.0585 (MH^+); $C_{17}H_{15}KN_3O_5$ requires: m/z=396.0598 (MH^+). ν_{max} (KBr) 2965, 1739, 1710, 1690, 1655, 1605, 1573, 1560, 1495, 1448, 1389, 1260, 1211, 1121, 1031, 802, 632 cm^{-1}.

5.4.7. Potassium (E)-4-[4-(methoxycarbonyl)-1-(3-nitrophenyl)-2-oxo-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6h**). Prepared from a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(3-nitrophenylamino)methylene] succinate (**5h**) and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(3-nitrophenylamino)methylene]succinate (**5′h**) (0.202 g, 0.5 mmol) and KOH (0.035 g, 0.5 mmol) in ethanol (2.5 mL), 1 h. Yield: 0.175 g (85%) of fine dark red powder; mp decomposition above 267 °C. ESI-MS: m/z=373.1 ($(M-K)H_2^+$), 411.0 (MH^+). ^{1}H NMR (DMSO-d_6): δ 2.85 (3H, s, N*Me*); 3.61 (3H, s, COO*Me*); 7.51 (1H, s, 5′-*H*); 7.69 (1H, t, J=8.2 Hz, 5″-*H*); 8.02 (1H, ddd, J=8.3, 2.3, 0.9 Hz, 4″-*H* or 6″-*H*); 8.08 (1H, ddd, J=8.2, 2.1, 0.9 Hz, 4″-*H* or 6″-*H*); 8.70 (1H, t, J=2.2 Hz, 2″-*H*). ^{13}C NMR (DMSO-d_6): δ 24.3, 50.8, 97.9, 113.3, 115.8, 119.2, 125.3, 127.2, 130.2, 138.4, 147.9, 156.9, 164.1, 165.2, 166.7, 168.0. EI-HRMS: m/z=373.0777 ($(M-K)H_2^+$); $C_{16}H_{13}N_4O_7$ requires: m/z=373.0784 ($(M-K)H_2^+$). ν_{max} (KBr) 2954, 1734, 1694, 1667, 1572, 1531, 1487, 1442, 1388, 1351, 1256, 1203, 1120, 1034, 735, 625 cm^{-1}.

5.4.8. Potassium (E)-4-[4-(methoxycarbonyl)-1-(naphthalen-1-yl)-2-oxo-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6k**). Prepared from a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(naphthalen-1-ylamino)methylene]succinate (**5k**) and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(naphthalen-1-ylamino)methylene]succinate (**5′k**) (0.623 g, 1.5 mmol) and KOH (0.099 g, 1.5 mmol) in ethanol (8 mL), 1 h. Yield: 0.490 g (79%) of fine dark red powder; mp 288–290 °C with decomposition. ESI-MS: m/z=416 (MH^+). ^{1}H NMR (DMSO-d_6): δ 2.86 (3H, s, N*Me*); 3.60 (3H, s, COO*Me*); 7.13 (1H, s, 5′-*H*); 7.44 (1H, dd, J=7.3, 1.0 Hz, 1H of *Ar*); 7.63–7.51 (4H, m, 4H of *Ar*); 7.95–8.04 (2H, m, 2H of *Ar*). ^{13}C NMR (DMSO-d_6): δ 24.2, 50.7, 98.1, 111.3, 123.2, 125.2, 125.5, 126.3, 126.6, 127.9, 128.1, 129.8, 133.8, 134.2, 156.4, 165.3, 165.4, 166.6, 168.2. EI-HRMS: m/z=416.0636 (MH^+); $C_{20}H_{15}KN_3O_5$ requires: m/z=416.0649 (MH^+). ν_{max} (KBr) 3167, 1748, 1716, 1695, 1645, 1597, 1567, 1542, 1445, 1408, 1395, 1202, 1183, 1122, 1042, 774, 622 cm^{-1}.

5.4.9. Potassium (E)-4-[4-(methoxycarbonyl)-2-oxo-1-(pyrazin-2-yl)-1H-pyrrol-3(2H)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-olate (**6m**). Prepared from a mixture of (2*E*,3*Z*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(pyrazin-2-ylamino) methylene]succinate (**5m**) and (2*E*,3*E*)-dimethyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(pyrazin-2-ylamino)methylene] succinate (**5′m**) (0.307 g, 0.85 mmol) and KOH (0.056 g, 0.85 mmol) in ethanol (3.5 mL), 1 h. Yield: 0.271 g (87%) of fine dark red powder; mp 279–281 °C with decomposition. EIMS: m/z=330.1 ($(M-K)H_2^+$). ^{1}H NMR (DMSO-d_6): δ 2.85 (3H, s, N*Me*); 3.62 (3H, s, COO*Me*); 7.59 (1H, s, 5′-*H*); 8.43 (1H, d, J=2.6 Hz, 6″-*H*); 8.47 (1H, dd, J=2.6, 1.5 Hz, 5″-*H*); 9.63 (1H, d, J=1.5 Hz, 3″-*H*).

^{13}C NMR (DMSO-d_6): δ 24.3, 51.0, 97.5, 115.0, 121.8, 136.5, 140.2, 142.6, 146.3, 157.7, 163.8, 165.2, 166.8, 168.1. (Found: C, 41.24; H, 2.84; N, 16.87. $C_{14}H_{10}KN_5O_5 \cdot ½KOH$ requires: C, 42.53; H, 2.68; N, 17.71.) EI-HRMS: m/z=330.0847 ($(M-K)H_2^+$); $C_{14}H_{12}N_5O_5$ requires: m/z=330.0838 ($(M-K)H_2^+$). ν_{max} (KBr) 2952, 1718, 1696, 1656, 1568, 1530, 1481, 1446, 1429, 1395, 1254, 1232, 1208, 1127, 1049, 729 cm^{-1}.

5.5. General procedure for the synthesis of (*E*)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene)-5-oxo-1-aryl-4,5-dihydro-1*H*-pyrrole-3-carboxylates 7a–d,g,h,k,m and (*Z*)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1*H*-imidazol-4(5*H*)-ylidene)-5-oxo-1-aryl-4,5-dihydro-1*H*-pyrrole-3-carboxylates 7′a–d,g,h,k,m

HCl of 37% (2–13 drops) was added to a suspension of potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-aryl-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate **6a**-**d**,**g**,**h**,**k**,**m** (0.1–1 mmol) in water (1–8 mL) or in case of **6k** (0.5 mmol) in ethanol (2 mL). The suspension was stirred at room temperature. The precipitated product was filtered under reduced pressure and washed with water.

*5.5.1. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**7a**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′a**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-phenyl-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6a**) (0.037 g, 0.1 mmol) and 37% HCl (2 drops) in water (1 mL), 15 min. Yield: 0.030 g (92%) of yellow needles; mp 194–200 °C. Ratio of isomers: 84:16. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.96 (3H, s, N*Me*); 3.70 (3H, s, COO*Me*); 7.29–7.36 (1H, m, 1H of *Ph*); 7.44–7.52 (2H, m, 2H of *Ph*); 7.57–7.63 (2H, m, 2H of *Ph*); 8.04 (1H s, 2-*H*); 11.38 (1H, br s, O*H*); minor isomer: δ 2.97 (3H, s, N*Me*); 3.84 (3H, s, COO*Me*); 8.51 (1H, s, 2-*H*); 11.63 (1H, br s, O*H*). (Found: C, 58.74; H, 3.91; N, 12.76. $C_{16}H_{13}N_3O_5$ requires: C, 58.72; H, 4.00; N, 12.84.) ν_{max} (KBr) 3285, 3077, 2955, 1793, 1779, 1730, 1718, 1692, 1640, 1559, 1455, 1440, 1390, 1346, 1231, 1147, 1124, 1013, 929, 750, 710, 620 cm^{-1}.

*5.5.2. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-p-tolyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**7b**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-p-tolyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′b**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-*p*-tolyl-1*H*-pyrrol-3(2*H*)-yliden]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6b**) (0.190 g, 0.5 mmol) and 37% HCl (4 drops) in water (4 mL), 15 min. Yield: 0.162 g (95%) of yellow needles; mp 176–182 °C (toluene). Ratio of isomers: 87:13. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.33 (3H, s, Ph–*Me*); 2.96 (3H, s, N*Me*); 3.69 (3H, s, COO*Me*); 7.25–7.31 (2H, m, 2H of *Ph*); 7.44–7.49 (2H, m, 2H of *Ph*); 7.99 (1H, s, 2-*H*); 11.35 (1H, br s, O*H*); minor isomer: δ 2.34 (3H, s, Ph-*Me*); 2.97 (3H, s, N*Me*); 3.83 (3H, s, COO*Me*); 7.40–7.45 (2H, m, 2H of *Ph*); 8.46 (1H, s, 2-*H*); 11.62 (1H, br s, O*H*). (Found: C, 60.01; H, 4.39; N, 12.24. $C_{17}H_{15}N_3O_5$ requires: C, 59.82; H, 4.43; N, 12.31.) ν_{max} (KBr) 3274, 3155, 2954, 1789, 1735, 1719, 1707, 1691, 1637, 1559, 1517, 1449, 1388, 1346, 1239, 1122, 821, 748, 606 cm^{-1}.

*5.5.3. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-o-tolyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**7c**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-o-tolyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′c**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-*o*-tolyl-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6c**) (0.126 g, 0.33 mmol) and 37% HCl (3 drops) in water (3 mL), 15 min. Yield: 0.105 g (92%) of yellow needles; mp 164–171 °C (toluene–*n*-heptane). Ratio of isomers: 82:18. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.16 (3H, s, Ph–*Me*); 2.96 (3H, s, N*Me*); 3.68 (3H, s, COO*Me*); 7.24–7.40 (4H, m, 4H of *Ph*); 7.78 (1H, s, 2-*H*); 11.29 (1H, br s, O*H*); minor isomer: δ 2.14 (3H, s, Ph–*Me*); 2.96 (3H, s, N*Me*); 3.81 (3H, s, COO*Me*); 8.35 (1H, s, 2-*H*); 11.64 (1H, br s, O*H*). (Found: C, 60.10; H, 4.41; N, 12.18. $C_{17}H_{15}N_3O_5$ requires: C, 59.82; H, 4.43; N, 12.31.) ν_{max} (KBr) 3261, 2948, 1779, 1729, 1695, 1644, 1564, 1460, 1390, 1345, 1293, 1240, 1205, 1155, 1128, 1011, 750, 621 cm^{-1}.

*5.5.4. (E)-Methyl 1-(4-fluorophenyl)-4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7d**) and (Z)-methyl 1-(4-fluorophenyl)-4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′d**).* Prepared from potassium (*E*)-4-[1-(4-fluorophenyl)-4-(methoxycarbonyl)-2-oxo-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6d**) (0.127 g, 0.33 mmol) and 37% HCl (4 drops) in water (2.5 mL), 15 min. Yield: 0.108 g (94%) of yellow needles; mp 207–210 °C (toluene). Ratio of isomers: 85:15. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.96 (3H, s, N*Me*); 3.69 (3H, s, COO*Me*); 7.28–7.37 (2H, m, 2H of *Ph*); 7.59–7.66 (2H, m, 2H of *Ph*) of yellow crystals; 8.02 (1H, s, 2-*H*); 11.39 (1H, br s, O*H*); minor isomer: δ 2.97 (3H, s, N*Me*); 3.83 (3H, s, COO*Me*); 8.50 (1H, s, 2-*H*); 11.56 (1H, br s, O*H*). (Found: C, 55.79; H, 3.64; N, 12.02. $C_{16}H_{12}FN_3O_5$ requires: C, 55.66; H, 3.50; N, 12.17.) ν_{max} (KBr) 3274, 1792, 1780, 1731, 1721, 1690, 1639, 1513, 1455, 1440, 1390, 1235, 1123, 1012, 848, 613 cm^{-1}.

*5.5.5. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(3-methoxyphenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7g**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(3-methoxyphenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′g**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-1-(3-methoxyphenyl)-2-oxo-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6g**) (0.395 g, 1 mmol) and 37% HCl (13 drops) in water (8 mL), 15 min. Yield: 0.333 g (93%) of yellow needles; mp 210–213 °C (toluene–DMF). Ratio of isomers: 87:13. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.96 (3H, s, N*Me*); 3.70 (3H, s, COO*Me*); 3.76 (3H, s, O*Me*); 6.86–6.92 (1H, m, 1H of *Ph*); 7.13–7.22 (2H, m, 2H of *Ph*); 7.33–7.43 (1H, m, 1H of *Ph*); 8.07 (1H, s, 2-*H*); 11.40 (1H, br s, O*H*); minor isomer: δ 2.97 (3H, s, N*Me*); 3.81 (3H, s, COO*Me*); 3.84 (3H, s, O*Me*); 6.91–6.97 (1H, m, 1H of *Ph*); 8.51 (1H, s, 2-*H*); 11.62 (1H, br s, O*H*). (Found: C, 57.31; H, 4.25; N, 11.83. $C_{17}H_{15}N_3O_6$ requires: C, 57.14; H, 4.23; N, 11.76.) ν_{max} (KBr) 3285, 3075, 2954, 1784, 1728, 1688, 1637, 1599, 1557, 1495, 1440, 1393, 1264, 1218, 1124, 1013, 753, 625 cm^{-1}.

*5.5.6. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(3-nitrophenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7h**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(3-nitrophenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′h**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-1-(3-nitrophenyl)-2-oxo-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6h**) (0.328 g, 0.8 mmol) and 37% HCl (7 drops) in water (6 mL), 15 min. Yield: 0.263 g (88%) of orange needles; mp 245–254 °C (toluene–DMF). Ratio of isomers: 87:13. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.97 (3H, s, N*Me*); 3.72 (3H, s, COO*Me*); 7.77 (1H, t, J=8.2 Hz, 5″-*H*); 8.08 (1H, ddd, J=8.2, 2.1, 0.8 Hz, 4″-*H* or 6″-*H*); 8.15 (1H, ddd, J=8.2, 2.2, 0.8 Hz, 4″-*H* or 6″-*H*); 8.24 (1H, s, 2-*H*); 8.64 (1H, t, J=2.1 Hz, 2″-*H*); 11.54 (1H, br s, O*H*); minor isomer: δ 2.98 (3H, s, N*Me*); 3.86 (3H, s, COO*Me*); 7.78 (1H, t, J=8.2 Hz, 5″-*H*); 8.52 (1H, t, J=2.0 Hz, 2″-*H*); 8.69 (1H, s, 2-*H*). (Found: C, 51.69; H, 3.24; N, 15.01. $C_{16}H_{12}N_4O_7$ requires: C, 51.62; H, 3.25; N, 15.05.) ν_{max} (KBr) 3099,

2956, 1788, 1740, 1684, 1628, 1561, 1533, 1443, 1386, 1351, 1316, 1240, 1197, 1109, 1042, 737, 619 cm^{-1}.

*5.5.7. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(naphthalen-1-yl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7k**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(naphthalen-1-yl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′k**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-1-(naphthalen-1-yl)-2-oxo-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6k**) (0.208 g, 0.5 mmol) and 37% HCl (6 drops) in ethanol (2 mL), 10 min. Yield: 0.186 g (99%) of yellow needles; mp 192–194 °C (toluene). Ratio of isomers: 83:17. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.98 (3H, s, N*Me*); 3.71 (3H, s, COO*Me*); 7.55–7.67 (5H, m, 5H of *Ar*); 7.91 (1H, s, 2-*H*); 8.04–8.11 (2H, m, 2H of *Ar*); 11.35 (1H, br s, O*H*); minor isomer: δ 2.97 (3H, s, N*Me*); 3.82 (3H, s, COO*Me*); 8.48 (1H, s, 2-*H*); 11.71 (1H, br s, O*H*). (Found: C, 63.87; H, 4.09; N, 11.12. $C_{20}H_{15}N_3O_5$ requires: C, 63.66; H, 4.01; N, 11.14.) ν_{max} (KBr) 3262, 1782, 1729, 1695, 1642, 1441, 1395, 1198, 1126, 1004, 783, 619 cm^{-1}.

*5.5.8. (E)-Methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-(pyrazin-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**7m**) and (Z)-methyl 4-(2-hydroxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-5-oxo-1-(pyrazin-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**7′m**).* Prepared from potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-(pyrazin-2-yl)-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6m**) (0.245 g, 0.67 mmol) and 37% HCl (8 drops) in water (6 mL), 15 min. Yield: 0.186 g (85%) of yellow needles; mp 247–250 °C (toluene–DMF). Ratio of isomers: 86:14. ^{1}H NMR (DMSO-d_6): major isomer: δ 2.97 (3H, s, N*Me*); 3.73 (3H, s, COO*Me*); 8.16 (1H, s, 2-*H*); 8.54–8.61 (2H, m, 2H of *Het*); 9.39 (1H, d, *J*=0.7 Hz, 3″-*H*); 11.63 (1H, br s, O*H*); minor isomer: δ 2.99 (3H, s, N*Me*); 3.88 (3H, s, COO*Me*); 8.66 (1H, s, 2-*H*); 11.52 (1H, br s, O*H*). (Found: C, 51.33; H, 3.52; N, 21.28. $C_{14}H_{11}N_5O_5$ requires: C, 51.07; H, 3.37; N, 21.27.) ν_{max} (KBr) 3135, 2955, 1772, 1733, 1702, 1641, 1570, 1473, 1444, 1426, 1389, 1247, 1224, 1189, 1151, 1137, 1011, 761, 716 cm^{-1}.

5.6. Alkylation of potassium (*E*)-4-[4-(methoxycarbonyl)-2-oxo-1-aryl-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate

*5.6.1. (E)-Methyl 4-(2-methoxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(3-methoxyphenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**9g**).* Methyliodide (**8a**) (0.030 mL, 0.44 mmol) was added to a solution of potassium (*E*)-4-[4-(methoxycarbonyl)-1-(3-methoxyphenyl)-2-oxo-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6g**) (0.158 g, 0.4 mmol) in DMF (2 mL) while stirring. The reaction mixture was stirred at room temperature for 40 min. Water (2 mL) was added to the reaction mixture and then volatile components were evaporated in vacuo. Water (5 mL) was added to the residue and the product was extracted with chloroform (2×5 mL). The organic phase was dried with Na_2SO_4, which was then filtered off and chloroform was evaporated in vacuo. Yield: 0.137 g (92%) of red needles; mp 228–230 °C (toluene). ESI-MS: *mz*=372.1 (MH^+). ^{1}H NMR ($CDCl_3$): δ 3.16 (3H, s, N*Me*); 3.65 (3H, s, O*Me*); 3.82 (3H, s, O*Me*); 3.84 (3H, s, O*Me*); 6.84–6.89 (1H, m, 1H of *Ph*); 6.97–7.02 (2H, m, 2H of *Ph*); 7.31–7.39 (1H, m, 1H of *Ph*); 7.67 (1H, s, 2-*H*). ^{1}H NMR (DMSO-d_6): δ 2.99 (3H, s, N*Me*); 3.49 (3H, s, O*Me*); 3.66 (3H, s, COO*Me*); 3.80 (3H, s, O*Me*); 6.90 (1H, ddd, *J*=1.0, 2.4, 8.3 Hz, 1H of *Ph*); 7.13–7.19 (2H, m, 2H of *Ph*); 7.37 (1H, t, *J*=8.4 Hz, 1H of *Ph*); 8.12 (1H, s, 2-*H*). ^{13}C NMR (DMSO-d_6): δ 25.2, 32.9, 51.1, 55.3, 107.2, 108.3, 110.2, 112.3, 114.7, 129.8, 136.5, 136.7, 139.3, 155.0, 159.6, 161.4, 163.0, 163.3. (Found: C, 58.46; H, 4.66; N, 11.12. $C_{18}H_{17}N_3O_6$ requires: C, 58.22; H, 4.61; N, 11.32.) ESI-HRMS: *m*/*z*=372.1193 (MH^+); $C_{18}H_{18}N_3O_6$ requires: *m*/*z*=372.1196 (MH^+). ν_{max} (KBr) 2956, 1780, 1730, 1700, 1605, 1555, 1498, 1440, 1387, 1277, 1254, 1225, 1195, 1162, 1130, 1102, 1023, 751, 624 cm^{-1}.

*5.6.2. (E)-Methyl 4-(2-methoxy-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene)-1-(napthalen-1-yl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**9k**).* Methyliodide (**8a**) (0.038 mL, 0.6 mmol) was added to a solution of potassium (*E*)-4-[4-(methoxycarbonyl)-1-(naphthalen-1-yl)-2-oxo-1*H*-pyrrol-3(2*H*)-ylidene]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6k**) (0.208 g, 0.5 mmol) in DMF (2 mL) while stirring. The reaction mixture was stirred at room temperature for 20 min. Water (0.5 mL) was added to the reaction mixture and then volatile components were evaporated in vacuo. Water (5 mL) was added to the residue and the product was extracted with chloroform (2×5 mL). The organic phase was dried with Na_2SO_4, which was then filtered off and chloroform was evaporated in vacuo. Yield: 0.178 g (91%) of red needles; mp 174–177 °C. EIMS: *m*/*z*=391 (M^+). ^{1}H NMR (DMSO-d_6): δ 3.02 (3H, s, N*Me*); 3.48 (3H, s, O*Me*); 3.67 (3H, s, COO*Me*); 7.56–7.68 (5H, m, 5H of *Ar*); 8.01 (1H, s, 2-*H*); 8.03–8.09 (2H, m, 2H of *Ar*). ^{1}H NMR ($CDCl_3$): δ 3.17 (3H, s, N*Me*); 3.64 (3H, s, O*Me*); 3.82 (3H, s, COO*Me*); 7.44 (1H, dd, *J*=7.3, 1.1 Hz, 1H of *Ar*); 7.50–7.58 (3H, m, 3H of *Ar*); 7.61 (1H, s, 2-*H*); 7.66–7.73 (1H, m, 1H of *Ar*); 7.89–7.95 (2H, m, 2H of *Ar*). ^{13}C NMR ($CDCl_3$): δ 25.7, 33.5, 52.0, 108.0, 110.5, 122.5, 125.2, 125.5, 126.9, 127.5, 128.7, 129.7, 129.8, 132.1, 134.6, 136.9, 141.9, 155.2, 161.7, 163.9, 164.9. (Found: C, 64.57; H, 4.38; N, 10.64. $C_{21}H_{17}N_3O_5$ requires: C, 64.45; H, 4.38; N, 10.74.) EI-HRMS: *m*/*z*=391.117700 (M^+); $C_{21}H_{17}N_3O_5$ requires: *m*/*z*=391.116821 (M^+). ν_{max} (KBr) 3131, 2951, 1781, 1729, 1715, 1695, 1667, 1605, 1438, 1406, 1387, 1370, 1272, 1197, 1139, 1092, 1017, 746, 623 cm^{-1}.

*5.6.3. (E)-Methyl 4-[2-(benzyloxy)-1-methyl-5-oxo-1H-imidazol-4(5H)-ylidene]-1-(4-bromophenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (**9e**).* Benzyl bromide (**8b**) (0.060 mL, 0.5 mmol) was added to a solution of potassium (*E*)-4-[1-(4-bromophenyl)-4-(methoxycarbonyl)-2-oxo-1*H*-pyrrol-3(2*H*)-yliden]-1-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-olate (**6e**) (0.222 g, 0.5 mmol) in DMF (2 mL) while stirring. The reaction mixture was stirred at room temperature for 1.5 h. Water (0.5 mL) was added to the reaction mixture and then volatile components were evaporated in vacuo. Water (5 mL) was added to the residue and the product was extracted with chloroform (2×5 mL). The organic phase was dried with Na_2SO_4, which was then filtered off and chloroform was evaporated in vacuo and the residue was purified by column chromatography on silica gel (ethyl acetate–petroleum ether=1:3, R_f=0.3). Fractions containing the product were combined and evaporated in vacuo. Yield: 0.102 g (41%) of red oil. EIMS: *m*/*z*=495 (M^+). ^{1}H NMR ($CDCl_3$): δ 3.18 (3H, s, N*Me*); 3.75 (3H, s, COO*Me*); 5.65 (2H, s, CH_2); 7.17–7.25 (2H, m, 2H of *Ph*); 7.26–7.33 (5H, m, 5H of *Ph*); 7.55 (1H, s, 2-*H*); 7.55–7.60 (2H, m, 2H of *Ph*). ^{13}C NMR ($CDCl_3$): δ 25.7, 48.0, 51.7, 109.0, 111.5, 120.3, 124.0, 127.6, 127.9, 128.6, 132.4, 134.6, 134.7, 134.8, 138.4, 154.8, 161.5, 163.3, 163.4. EI-HRMS: *m*/*z*=495.0440 (M^+); $C_{23}H_{18}BrN_3O_5$ requires: *m*/*z*=495.0430 (M^+). ν_{max} (KBr) 3092, 2950, 1783, 1727, 1693, 1606, 1493, 1446, 1390, 1377, 1244, 1167, 1118, 1035, 1008, 923, 828, 752, 699 cm^{-1}.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.04.025.

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