[2+2] Cycloadditions of Electron-Poor Acetylenes to (5Z)-5-[(Dimethylamino)methylene]imidazolidine-2,4-diones

by Uroš Uršič, Uroš Grošelj, Anton Meden, Jurij Svete, and Branko Stanovnik*

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, P.O. Box 537, 1000 Ljubljana, Slovenia

(e-mail: branko.stanovnik@fkkt.uni-lj.si)

Microwave-assisted [2+2] cycloadditions of acetylene mono- and acetylenedicarboxylates 2 to (5Z)-5-[(dimethylamino)methylene]imidazolidine-2,4-dione 4a or to the corresponding thioxo derivative 4b in MeCN furnished the highly functionalized imidazolidine-2,4-dione derivatives 5 and 6 or the corresponding thioxo derivatives 5–7 as single isomers or mixtures of two isomers (*Schemes 2* and 3, *Table 1*). When the reaction of (5Z)-5-[(dimethylamino)methylene]imidazolidine-2,4-dione (4c) with acetylenedicarboxylate 2a was performed in DMF, hydrolysis of the (dimethylamino)methylene group took place to give (2E)-2-(2,5-dioxoimidazolidin-4-ylidene)butanedioate 11 (*Scheme 5*).

Introduction. – In the last few decades, there have been some reports of reactions of simple tertiary enamines with electron-poor acetylenes, such as alkyl propiolates (=alkyl prop-2-ynoates) and dialkyl acetylenedicarboxylates (=dialkyl but-2-ynedioates) [1]. It has been generally accepted that these reactions initially proceed by a [2+2] cycloaddition. However, the structure of the final product is strongly dependent on the structure of the starting compound and reaction conditions [1d]. The geometry of the obtained products was, in some cases, unambiguously determined by *Reinhoudt* and co-workers in the early eighties [1d]. When these reactions were extended to other functionalized enamines and enaminones, in some cases, a *Michael*-type addition took place preferentially over the [2+2] cycloaddition [2].

The 3-(dimethylamino)propenoates and related enaminones have been demonstrated to be useful building blocks in the synthesis of many heterocyclic systems [3], including the preparation of natural products and their analogs, such as aplysinopsins [4], meridianines [5], dipodazines [6], and tryprostatins [7]. We have also reported an efficient method for the preparation and functionalization of highly substituted 1amino-2,3-dihydro-1*H*-pyrrole, 1-amino-1*H*-pyrrole, and fused pyrrolo[3,2-*d*]oxazole systems from '1,2-diazabuta-1,3-dienes' and 3-(dimethylamino)prop-2-enoates [8] and the regio- and stereoselective one-pot synthesis of oxazolo-fused pyridazines *via* a '*Michael*-addition – pyridazine-cyclization – oxazoline cyclization' cascade reaction [9].

As an extension of our research, we recently reported on microwave assisted regiospecific [2+2] cycloadditions of electron-poor acetylenes **2** to (2Z)-2-(acylamino)-3-(dimethylamino)prop-2-enoates **1**, which resulted in the formation of (1E,3E)-1-(acylamino)-4-(dimethylamino)buta-1,3-dienes **3** (*Scheme 1*) [10].

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Results and Discussion. – Since (5Z)-5-[(dimethylamino)methylene]imidazolidine-2,4-diones **4a**,**c** and the corresponding thioxo derivative **4b** have already been established as very useful intermediates in the synthesis of natural products such a aplysinopsins [4], we report in this article on [2+2] cycloadditions of electron-poor acetylenes **2a**-**2d** to these compounds, which are cyclic analogues of (2Z)-2-(acylamino)-3-(dimethylamino)prop-2-enoates **1** [10].

When (5Z)-5-[(dimethylamino)methylene]-3-methylimidazolidine-2,4-dione (4a) and acetylenedicarboxylates (= but-2-ynedioates) **2a,b** were heated in MeCN under microwave (MW) irradiation, (2(1')E,3(4'')E)-2-[(dimethylamino)methylene]-3-(1methyl-2,5-dioxoimidazolidin-4-ylidene)butanedioates **5a,b** were formed as the only isomers. On the other hand, the reactions of imidazolidine-2,4-dione **4a** with electronpoor but-2-ynoate **2c** and of (5Z)-5-[(dimethylamino)methylene]-3-phenyl-2-thioxoimidazolidin-4-one (**4b**) with acetylene derivatives **2a,c** produced mixtures of two isomers. In these cases, the major (2(1')E,3(4'')E)-isomers **5c** – **5d** were accompanied by (2(1')E,3(4'')Z)-isomers **6c** – **6d** (*Scheme 2, Table 1*).



Table 1. Synthesis of Compounds 5a – 5e and 6c –
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\mathbf{R}^1	Х	\mathbb{R}^2	\mathbb{R}^3	Yield [%]	5/6	Time [min]
Me	0	COOMe	COOMe	84	100:0	120
Me	Ο	COOEt	COOEt	62	100:0	120
Ph	S	COOMe	COOMe	89	54:46	120
Me	Ο	CF ₃	COOEt	97	65:35	120
Ph	S	CF ₃	COOEt	95	54:46	60
	R ¹ Me Ph Me Ph	R1XMeOMeOPhSMeOPhS	$\begin{tabular}{ c c c c c } \hline R^1 & X & R^2 \\ \hline Me & O & COOMe \\ Me & O & COOEt \\ Ph & S & COOMe \\ Me & O & CF_3 \\ Ph & S & CF_3 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c } \hline R^1 & X & R^2 & R^3 \\ \hline Me & O & COOMe & COOMe \\ Me & O & COOEt & COOEt \\ Ph & S & COOMe & COOMe \\ Me & O & CF_3 & COOEt \\ Ph & S & CF_3 & COOEt \\ \hline \end{tabular}$	R^1 X R^2 R^3 Yield [%]MeOCOOMeCOOMe84MeOCOOEtCOOEt62PhSCOOMeCOOMe89MeOCF_3COOEt97PhSCF_3COOEt95	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

The structures of products **5** and **6** were determined by elemental analysis, IR, ¹Hand ¹³C-NMR, HMBC technique, HR-MS, and X-ray analysis. The configurations of the C(2)=C(1') bond of compounds **5a**,**d** and **6d** were established by the 2D-HMBC NMR technique. The magnitude of the heteronuclear coupling constant, ${}^{3}J(C,H)$, for nuclei O=C-C=C-H with *cis* configuration of the C=C bond are smaller (2-6 Hz) than those for the *trans*-oriented ones (8-12 Hz) [3b,d][11]. Accordingly, the heteronuclear coupling constant of compounds **5a,d** and **6d** indicate the (2*E*)-configuration (*Fig. 1*). The same (2*E*)-configurations of the C(2)=C(1') bonds indicate that isomers **5** and **6** differ in the configuration of the C(3)=C(4'') bonds. Additionally, the structures of both isomers **5d** (*Fig. 2*) and **6d** (*Fig. 3*) were confirmed by X-ray analysis.



Fig. 1. Coupling constant ${}^{3}J(C,H)$ of the O=C-C=C-H moiety of **5a,d** and **6d**



Fig. 2. ORTEP View of compound **5d** at the 50% probability level. H-Atoms are drawn as spheres of arbitrary radii. The molecule of the co-crystallized solvent (CHCl₃) is omitted for clarity. Very large displacement parameters of C(223) indicate disorder of the Me group and a somewhat lower quality of the crystals; the molecular geometry is, however, unambiguous.

The reaction of **4b** with ethyl propiolate (= ethyl prop-2-ynoate; **2d**) also furnished a mixture of two isomers **5f** and **7f** (*Scheme 3*). However, in this case, the major (2(4')E,3Z)-isomer **5f** was accompanied by the minor (2(4')E,3E)-isomer **7f**, which is



Fig. 3. ORTEP View of compound 6d at the 50% probability level. H-Atoms are drawn as spheres of arbitrary radii.



structurally different from the minor isomers 6c-6e mentioned previously. The structures of isomers 5f and 7f were determined by ¹H-NMR spectroscopy, where characteristic coupling constants for *cis*-oriented (³*J*(H,H)=10.1 Hz) and *trans*-oriented protons (³*J*(H,H)=15.9 Hz) were observed (*Fig. 4*).

Two major pathways can be envisioned for the cycloadditions of acetylenes 2 to 4, a concerted and a stepwise one. In the case of a concerted cycloaddition, the reaction should proceed as a $[2_s + 2_a]$ cycloaddition resulting in cyclobutene intermediate 9', which would undergo a conrotatory *retro*-electrocyclization to afford the (2(1')E,3(4'')Z)-isomer 6 ($\mathbb{R}^3 \pm \mathbb{H}$) and/or (2(1')Z,3(4'')E)-isomer 7 ($\mathbb{R}^3 \pm \mathbb{H}$), or (2(4')Z,3Z)-isomer 6 ($\mathbb{R}^3 = \mathbb{H}$) and/or (2(4')E,3E)-isomer 7 ($\mathbb{R}^3 = \mathbb{H}$). In the two-step mechanism, the initially formed intermediate 8 can cyclize to cyclobutene 9' or it may be transformed into intermediate 8', which cyclizes to cyclobutene intermediate 9. From the latter, two different products can be formed by conrotatory *retro*-electrocyclization, *i.e.*, (2(1')E,3(4'')E)-isomer 5 ($\mathbb{R}^3 \pm \mathbb{H}$) and/or (2(1')Z,3(4'')Z)-isomer 10



Fig. 4. Coupling constant ${}^{3}J(H,H)$ of the H-C=C-H moiety of **5f** and **7f**

 $(R^3 \neq H)$, or (2(4')E,3Z)-isomer 5 $(R^3 = H)$ and/or (2(4')Z,3E)-isomer 10 $(R^3 = H)$ (*Scheme 4*). The obtained results indicate that these cycloadditions proceed by a



stepwise mechanism. In the cases, where the single products 5a,b were formed, the intermediate 8 is completely transformed into intermediate 8', while in the cases where mixtures of two isomers were obtained, this transformation from 8 to 8' is not complete, and some cyclobutene intermediate 9' is formed as well.

Contrary to 4a,b, (5Z)-5-[(dimethylamino)methylene]imidazolidine-2,4-dione (4c) did not react with dimethyl acetylenedicarboxylate (2a) in MeCN, probably due to its insolubility. When 4c was treated with 2a in DMF at 80°, dimethyl (2E)-2-(2,5-dioxoimidazolidin-4-ylidene)butanedioate (11) was obtained (*Scheme 5*). This can easily be explained by the initial formation of dimethyl (2E,3E)-2-[(dimethylamino)-methylene]-3-(2,5-dioxoimidazolidin-4-ylidene)butanedioate (5g) which, under the experimental conditions, was hydrolyzed to 11 and DMF. The structure of 11 was confirmed by X-ray-analysis (*Fig. 5*). The configuration of the C(2)=C(4') bond in compound 11 confirms the proposed structure and consequently the mechanism of these cycloadditions.



Fig. 5. ORTEP View of compound 11 at the 50% probability level. H-Atoms are drawn as spheres of arbitrary radii.

Conclusions. – The [2+2] cycloaddition of electron-poor acetylenes **2** with (5*Z*)-5-[(dimethylamino)methylene]imidazolidine-2,4-diones **4a,c** or the corresponding thioxo derivative **4b** was established as an easy and efficient synthetic route to highly functionalized imidazolidine-2,4-diones, which offer wide possibilities for further transformations.

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Experimental Part

General. The acetylene derivatives 2a - 2d are commercially available (*Sigma-Aldrich*). (5*Z*)-5-[(Dimethylamino)methylene]-3-methylimidazolidine-2,4-dione (4a) [4a], (5*Z*)-5-[(dimethylamino)methylene]-3-phenyl-2-thioxoimidazolidin-4-one (4b) [12], and (5*Z*)-5-[(dimethylamino)methylene]imidazolidine-2,4-dione (4c) [4a] were prepared according to literature procedures. Microwave irradiations were performed in a *CEM-Corporation-Discover* microwave unit. Column chromatography (CC): silica gel 60 (0.04–0.06 mm; *Fluka*). Medium-pressure liquid chromatography (MPLC): silica gel 40 (0.015–0.035 mm; *Merck*), column size 15 × 460 mm; *Büchi* isocratic system with UV detection (UV detector *K-2001*; *Knauer*) at 254 nm. Melting points: *Kofler* micro hot stage. IR Spectra: *Perkin-Elmer-Spectrum-BX-FTIR* spectrophotometer; $\tilde{\nu}$ in cm⁻¹. NMR Spectra: *Bruker-Avance-DPX-300* spectrometer; at 300 MHz for ¹H and 75.5 MHz for ¹³C, (D₆)DMSO and CDCl₃ as solvents and Me₄Si as the internal standard; δ in ppm, *J* in Hz. MS: *AutoSpecQ* and *Qtof-premier* spectrometers; in *m/z*. Microanalyses: *Perkin-Elmer-CHN* analyser 2400 II.

Imidazolidine Derivatives 5a-5f, 6c-6e, and 7f: General Procedure. Acetylene 2a-2d was added to a soln. of (5Z)-5-[(dimethylamino)methylene]imidazolidine derivative 4a, b in MeCN (4 ml), and the mixture was stirred in a closed vessel under microwave irradiation at constant temp. The mixture was cooled, volatile components were evaporated, and the residue was purified by CC (silica gel).

Dimethyl (2E,3E)-2-[(*Dimethylamino*)*methylene*]-3-(1-*methyl*-2,5-dioxoimidazolidin-4-ylidene)*butanedioate* (**5a**). Prepared from **4a** (0.169 g, 1 mmol) and dimethyl but-2-ynedioate (**2a**; 0.250 ml, 2 mmol) at 80° for 120 min. CC (AcOEt/petroleum ether 4:1) and crystallization (toluene) gave 0.262 g (84%) of **5a**. M.p. 165–167°. IR (KBr): 3213, 2953, 1771, 1720, 1711, 1674, 1632, 1562, 1453, 1441, 1291, 1229, 1106, 1097, 1046, 942, 783, 756. ¹H-NMR (CDCl₃): 2.99 (br. *s*, Me₂N); 3.07 (*s*, MeN); 3.66 (*s*, COOMe); 3.86 (*s*, COOMe); 6.94 (br. *s*, NH); 7.65 (*s*, CHNMe₂). ¹³C-NMR (CDCl₃): 24.4; 51.3; 52.6; 89.1; 115.3; 127.7; 153.0; 154.1; 160.9; 167.0; 168.2. Anal. calc. for $C_{13}H_{17}N_3O_6$ (311.29): C 50.16, H 5.50, N 13.50; found: C 50.12, H 5.73, N 13.50.

Diethyl (2E,3E)-2-[(*Dimethylamino*)*methylene*]-3-(1-*methyl*-2,5-*dioxoimidazolidin*-4-ylidene)*butanedioate* (**5b**). Prepared from **4a** (0.169 g, 1 mmol) and diethyl but-2-ynedioate (**2b**; 0.325 ml, 2 mmol) at 80° for 120 min. CC (AcOEt/petroleum ether 3 :2) and crystallization (toluene/hexane) gave 0.213 g (63%) of **5b**. M.p. 140–143°. IR (KBr): 3208, 2986, 1759, 1714, 1678, 1626, 1594, 1456, 1387, 1280, 1218, 1097, 1023, 724, 618. ¹H-NMR (CDCl₃): 1.23 (t, J = 7.1, $MeCH_2O$); 1.35 (t, J = 7.1, $MeCH_2O$); 2.98 (br. s, Me₂N); 3.07 (s, MeN); 4.14–4.23 (m, 1 H, MeCH₂O); 4.27–4.36 (m, 3 H MeCH₂O); 6.76 (br. s, NH); 7.65 (s, $CHNMe_2$). Anal. calc. for C₁₅H₂₁N₃O₆ (339.34): C 53.09, H 6.24, N 12.38; found: C 53.29, H 6.47, N 12.19.

Dimethyl (2E,3E)-2-[(Dimethylamino)methylene]-3-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)butanedioate (**5c**) and Dimethyl (2E,3Z)-2-[(Dimethylamino)methylene]-3-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)butanedioate (**6c**). Prepared from **4b** (0.247 g, 1 mmol) and dimethyl but-2ynedioate (**2a**; 0.250 ml, 2 mmol) at 80° for 120 min. CC (AcOEt) and crystallization (AcOEt/heptane) gave 0.345 g (89%) of **5c/6c** 54 :46 which were not separated. M.p. 136–148°. IR (KBr): 3435, 2950, 1732, 1682, 1622, 1496, 1434, 1416, 1358, 1252, 1202, 1175, 1133, 1082, 962, 733. ¹H-NMR (CDCl₃): (2E,3E)- isomer **5c**: 3.21 (*s*, 3 H, Me₂N); 3.49 (*s*, 3 H, Me₂N); 3.72 (*s*, COOMe); 3.76 (*s*, COOMe); 6.74 (*s*, NH); 7.11 (*s*, CHNMe₂); 7.29–7.50 (*m*, Ph); (2*E*,3*Z*)-isomer **6c**: 3.25 (*s*, 3 H, Me₂N); 3.57 (*s*, 3 H, Me₂N); 3.73 (*s*, COOMe); 3.77 (*s*, COOMe); 6.28 (*s*, NH); 7.19 (*s*, CHNMe₂); 7.29–7.50 (*m*, Ph). Anal. calc. for $C_{18}H_{19}N_{3}O_{5}S$ (389.43): C 55.52, H 4.92, N 10.79; found: C 55.77, H 5.11, N 10.63.

Ethyl (2E,3E)-2-[(Dimethylamino)methylene]-4,4,4-trifluoro-3-(1-methyl-2,5-dioxoimidazolidin-4ylidene)butanoate (5d) and Ethyl (2E,3Z)-2-[(Dimethylamino)methylene]-4,4,4-trifluoro-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)butanoate (6d). Prepared from 4a (0.169 g, 1 mmol) and ethyl 4,4,4trifluorobut-2-ynoate (2c; 0.220 ml, 1.33 mmol) at 80° for 120 min. CC (AcOEt/petroleum ether 1:1): 0.326 g (97%) of 5d/6d 65:35. The isomers were separated by MPLC (AcOEt/petroleum ether 1:1). M.p. 145-148° (5d), 149-152° (6d). IR (KBr): (2E,3E)-isomer 5d: 3215, 2984, 1779, 1724, 1698, 1644, 1611, 1462, 1399, 1283, 1257, 1214, 1173, 1126, 1082, 991, 957, 825, 763, 711; (2E,3Z)-isomer 6d: 3237, 2983, 1767, 1725, 1699, 1648, 1614, 1457, 1398, 1329, 1271, 1245, 1215, 1193, 1109, 1048, 1027, 991, 949, 818, 764, 617. ¹H-NMR (CDCl₃): (2E,3E)-isomer **5d**: 1.22 (t, J = 7.1, MeCH₂O); 2.97 (br. s, Me₂N); 3.11 (s, MeN); 3.99-4.10 (m, 1 H, MeCH₂O); 4.16-4.28 (m, 1 H, MeCH₂O); 7.63 (s, CHNMe₂); 8.45 (br. s, NH); (2E,3Z)-isomer 6d: 1.21 $(t, J = 7.1, MeCH_2O)$; 2.92 (s, Me_2N) ; 3.08 (s, MeN); 4.01 – 4.24 $(m, MeCH_2O)$; 7.69 (s, CHNMe₂); 8.47 (br. s, NH). ¹³C-NMR (CDCl₃): (2E,3E)-isomer **5d**: 14.0; 24.4; 42.6 (br. s); 60.1; 86.4 (q, J=2.2); 112.0 (q, J=37.2); 122.0 (q, J=273); 131.4 (q, J=2.2); 152.2; 153.9; 159.3; 168.0; (2E,3Z)-isomer **6d**: 14.2; 24.5; 42.8 (br. s); 59.9; 85.0 (deg. q); 109.7 (q, J = 32.7); 123.0 (q, J = 275); 129.3 (deg. q); 109.7 (deg. q) $(\deg, q); 152.7; 153.8; 161.0; 168.5. EI-MS: 335 (M^+). EI-HR-MS: 335.110030 (M^+, C_{13}H_{16}F_3N_3O_4^+; calc.$ 335.109291). Anal. calc. for $C_{13}H_{16}F_3N_3O_4$ (335.28): C 46.57, H 4.81, N 12.53; found: C 46.48, H 4.98, N 12.27.

Ethyl (2E,3E)-2-[(*Dimethylamino*)*methylene*]-4,4,4-*trifluoro-3*-(5-*oxo-1-phenyl-2-thioxoimidazoli-din-4-ylidene*)*butanoate* (**5e**) *and Ethyl* (2E,3Z)-2-[(*Dimethylamino*)*methylene*]-4,4,4-*trifluoro-3*-(5-*oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene*)*butanoate* (**6e**). Prepared from **4b** (0.247 g, 1 mmol) and ethyl 4,4,4-trifluorobut-2-ynoate (**2c**; 0.246 ml, 1.48 mmol) at 80° for 60 min. CC (AcOEt): 0.394 g (95%) of **5b/6e** 54:46 which were not separated. Oil. IR (KBr): 3443, 2984, 2934, 1731, 1681, 1620, 1497, 1418, 1358 1264, 1178, 1141, 1084, 1027, 962, 733. ¹H-NMR (CDCl₃): (2*E*,3*E*)-isomer **5e**: 1.27 (*t*, *J* = 7.1, *Me*CH₂O); 3.23 (*s*, 3 H, Me₂N); 3.53 (*s*, 3 H, Me₂N); 4.20 (*q*, *J* = 7.1, MeCH₂O); 6.49 (*s*, NH); 7.17 (*s*, CHNMe₂); 7.28 – 7.49 (*m*, Ph); (2*E*,3*Z*)-isomer **6e**: 1.29 (*t*, *J* = 7.1, *Me*CH₂O); 3.26 (*s*, 3 H, Me₂N); 3.59 (*s*, 3 H, Me₂N); 4.23 (*q*, *J* = 7.1, CH₂O); 6.72 (*s*, NH); 7.23 (*s*, CHNMe₂); 7.28 – 7.49 (*m*, Ph). EI-MS: 413 (*M*⁺). EI-HR-MS: 413.103250 (*M*⁺, C₁₈H₁₈F₃N₃O₃S⁺; calc. 413.102098). Anal. calc. for C₁₈H₁₈F₃N₃O₃S (413.41): C 52.08, H 4.55, N 9.94; found: C 52.29, H 4.39, N 10.16.

Ethyl (2E,3Z)-4-(*Dimethylamino*)-2-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)but-3-enoate (**5f**) and *Ethyl* (2E,3E)-4-(*Dimethylamino*)-2-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)but-3-enoate (**7f**). Prepared from **4b** (0.247 g, 1 mmol) and ethyl prop-2-ynoate (**2d**; 0.410 ml, 4 mmol) at 100° for 210 min. CC (AcOEt) and crystallization (AcOEt/petroleum ether) gave 0.326 g (94%) of **5f/7f** 61:39 which were not separated. M.p. 136–148°. IR (KBr): 3447, 3039, 2975, 2927, 1695, 1685, 1629, 1583, 1498, 1413, 1360, 1313, 1223, 1170, 1127, 1071, 1026, 963, 735. ¹H-NMR (CDCl₃): (2*E*,3*Z*)-isomer **5f**: 1.27 (*t*, *J* = 7.1, *Me*CH₂O); 3.24 (*s*, 3 H, Me₂N); 3.63 (*s*, 3 H, Me₂N); 4.19 (*q*, *J* = 7.1, MeCH₂O); 6.10 (*d*, *J* = 10.1, H–C(3)); 7.12 (*s*, NH); 7.28–7.50 (*m*, Ph); 8.29 (*d*, *J* = 10.1, H–C(4)); (2*E*,3*E*)-isomer **7f**: 1.28 (*t*, *J* = 7.1, MeCH₂O); 3.23 (br. *s*, 3 H, Me₂N); 3.62 (br. *s*, 3 H, Me₂N); 4.20 (*q*, *J* = 7.1, MeCH₂O); 6.08 (*d*, *J* = 15.9, H–C(3)); 7.14 (*s*, NH); 7.28–7.50 (*m*, Ph); 8.34 (*d*, *J* = 15.9, H–C(4)). ¹³C-NMR (CDCl₃): 140.; 39.5; 46.2; 46.3; 60.3; 60.4; 114.5; 114.9; 115.2; 118.6; 1270; 1272; 128.3; 128.4; 129.1; 129.2; 133.0; 133.1; 139.2; 139.5; 140.2; 140.7; 140.8; 143.8; 164.5; 166.3; 168.3; 168.7. Anal. calc. for C₁₇H₁₉N₃O₃S (345.42): C 59.11, H 5.54, N 12.17; found: C 59.27, H 5.64, N 11.99.

Dimethyl (2E)-2-(2,5-*Dioxoimidazolidin-4-ylidene)butanedioate* (**11**). Dimethyl but-2-ynedioate (**2a**; 0.250 ml, 2 mmol) was added to a soln. of **4c** (0.156 g, 1 mmol) in DMF (4 ml), and the mixture was stirred in a closed vessel under microwave irradiation at 80° for 180 min. The mixture was cooled, volatile components were evaporated, and the residue was purified by CC (silica gel, AcOEt/petroleum ether 1:1). The product was crystallized from AcOEt/petroleum ether: 0.112 g (46%) of **11**. M.p. 160–163°. IR (KBr): 3184, 3075, 1773, 1744, 1725, 1670, 1439, 1402, 1384, 1367, 1339, 1208, 1170, 1118, 1035, 868, 781, 757. EI-MS: 242 (M^+). ¹H-NMR (D_6)(DMSO): 3.45 (s, CH₂); 3.62 (s, COOMe); 3.66 (s, COOMe); 10.54 (br. s, NH); 11.32 (br. s, NH). ¹³C-NMR ((D_6)DMSO): 34.4; 51.9; 52.0; 108.0; 132.9; 154.2; 162.2; 166.9;

168.8. EI-MS: 242 (M^+). EI-HR-MS 242.052544 (M^+ , C₉H₁₀N₂O₆⁺; calc. 242.053886). Anal. calc. for C₉H₁₀N₂O₆ (242.19): C 44.63, H 4.16, N 11.57; found: C 44.83, H 4.27, N 11.53.

X-Ray Crystal Structures of 5d, 6d, and 11¹). Single crystal X-ray diffraction data of compounds 5d, 6d, and 11 were collected at r.t. with a Nonius-Kappa-CCD diffractometer and the Nonius Collect Software [13]. DENZO and SCALEPACK [14] were used for indexing and scaling of the data, and the structures were solved by means of SIR97 [15]. Refinement was done with the Xtal3.4 [16] program package. Crystal structures were refined on F values by the full-matrix least-squares procedure. The non-H atoms were refined anisotropically in all cases, while the positions of H-atoms were geometrically calculated, and their positional and isotropic atomic displacement parameters were not refined. Absorption correction was not necessary. Regina [17] weighting scheme was used in all cases. Difference Fourier maps for compounds 5d, 6d, and 11 do not show any significant features. The crystal data and details concerning data collection and refinement for 5d, 6d, and 11 are given in Table 2. The ORTEP III [18] drawing of the content of the asymmetric unit of 5d, 6d, and 11 showing the atom-labeling scheme are presented in Figs. 2, 3, and 5.

	5d	6d	11
Formula	$(C_{13}H_{16}F_3N_3O_4)_2 \cdot CHCl_3$	$C_{13}H_{16}F_{3}N_{3}O_{4}$	$C_9H_{10}N_2O_6$
$M_{ m r}$	721.8	335.3	242.2
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/a$
a [Å]	10.2964(2)	8.6660(3)	9.63630(10)
<i>b</i> [Å]	12.3965(3)	12.8666(6)	12.2444(2)
<i>c</i> [Å]	15.7860(3)	14.0048(5)	10.2366(2)
α [Å]	88.4712(13)	90.00000	90.00000
β [°]	71.6915(12)	99.467(2)	116.0526(9)
γ [°]	78.3911(14)	90.00000	90.00000
V [Å ³]	1872.34(7)	1540.29(11)	1085.10(3)
Ζ	2	4	4
ho [Mg m ⁻³]	1.401	1.446	1.482
$\mu \text{ [mm^{-1}]}$	0.326	0.131	0.127
Color of crystal	yellow	yellow	colorless
Shape of crystal	block	block	block
Dimensions [mm]	$0.14 \times 0.10 \times 0.08$	$0.22\times0.18\times0.14$	$0.20 \times 0.20 \times 0.12$
Temperature [K]	293(1)	293(1)	293(1)
Wavelength [Å]	0.71073	0.71073	0.71073
θ_{\max} [°]	27.49	27.46	27.44
No. of integrated refl.	32306	20278	15073
No. of independent refl.	8462	3500	2467
R _{int}	0.032	0.035	0.032
No. of observed reflections	5491	2372	2076
Threshold criterion	$I > 2.0\sigma(I)$	$I > 2.0\sigma(I)$	$I > 2.0\sigma(I)$
No. of refined parameters	479	208	154
Final R and $R_{\rm w}$	0.078, 0.082	0.052, 0.053	0.044, 0.007
$(\Delta/\sigma)_{\rm max}$	0.55	0.0002	0.0004
$\Delta ho_{\rm max}, \Delta ho_{\rm min} \ [{ m e} \ { m \AA}^{-3}]$	-0.55, 0.60	- 0.31, 0.33	-0.26, 0.30

Table 2. Crystal Data, Data Collection, and Structure Refinement for Compounds 5d, 6d, and 11

 CCDC-691932, -691933, and -695011 contain the supplementary crystallographic data for the structures 5d, 6d, and 11, resp., described in this work. These data can be obtained, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif.).

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