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

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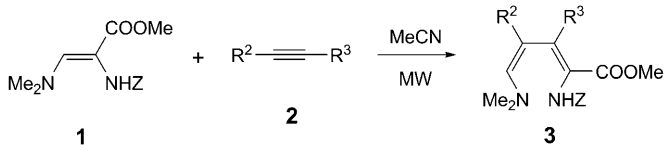
Microwave-assisted [2 + 2] cycloadditions of acetylene mono- and acetylenedicarboxylates **2** to (5*Z*)-5-[(dimethylamino)methylene]imidazolidine-2,4-dione **4a** or to the corresponding thioxo derivative **4b** in MeCN furnished the highly functionalized imidazolidine-2,4-dione derivatives **5** and **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 (5*Z*)-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 (2*E*)-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 1-amino-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 (2*Z*)-2-(acylamino)-3-(dimethylamino)prop-2-enoates **1**, which resulted in the formation of (1*E*,3*E*)-1-(acylamino)-4-(dimethylamino)buta-1,3-dienes **3** (*Scheme 1*) [10].

Scheme 1



Results and Discussion. – Since (5*Z*)-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 (2*Z*)-2-(acylamino)-3-(dimethylamino)prop-2-enoates **1** [10].

When (5*Z*)-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-(1-methyl-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 electron-poor but-2-ynoate **2c** and of (5*Z*)-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*).

Scheme 2

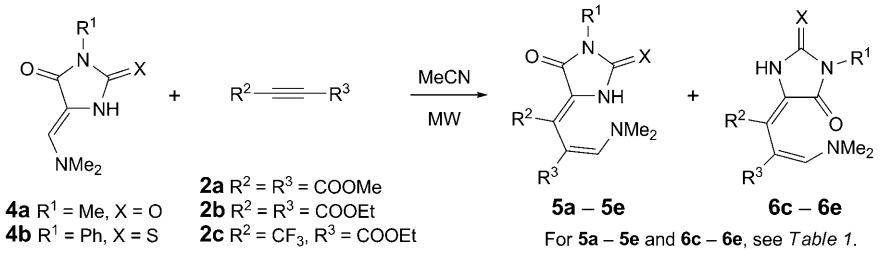


Table 1. *Synthesis of Compounds* **5a** – **5e** *and* **6c** – **6e**

5, **6**	R^1	X	R^2	R^3	Yield [%]	**5**/**6**	Time [min]
a	Me	O	COOMe	COOMe	84	100 : 0	120
b	Me	O	COOEt	COOEt	62	100 : 0	120
c	Ph	S	COOMe	COOMe	89	54 : 46	120
d	Me	O	CF_3	COOEt	97	65 : 35	120
e	Ph	S	CF_3	COOEt	95	54 : 46	60

The structures of products **5** and **6** were determined by elemental analysis, IR, ^{1}H- and ^{13}C-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, ^3J(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.

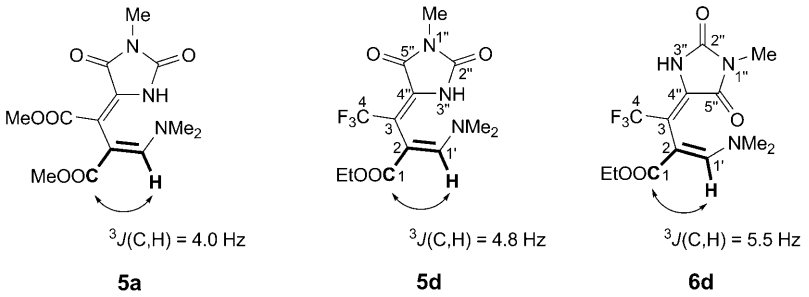


Fig. 1. *Coupling constant* ^{3}J*(C,H) of the O*=C–*C*=*C*–H *moiety of* **5a**,**d** *and* **6d**

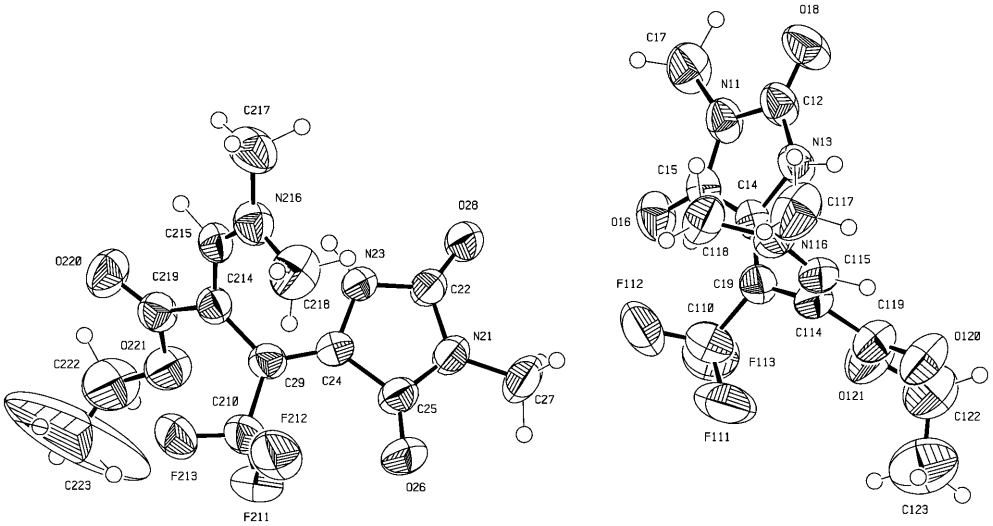


Fig. 2. *ORTEP View of compound* **5d** *at the 50% probability level.* H-Atoms are drawn as spheres of arbitrary radii. The molecule of the co-crystallized solvent ($CHCl_3$) is omitted for clarity. Very large displacement parameters of C(223) indicate disorder of the Me group and a somewhat lower quality 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*,3*Z*)-isomer **5f** was accompanied by the minor (2(4′)*E*,3*E*)-isomer **7f**, which is

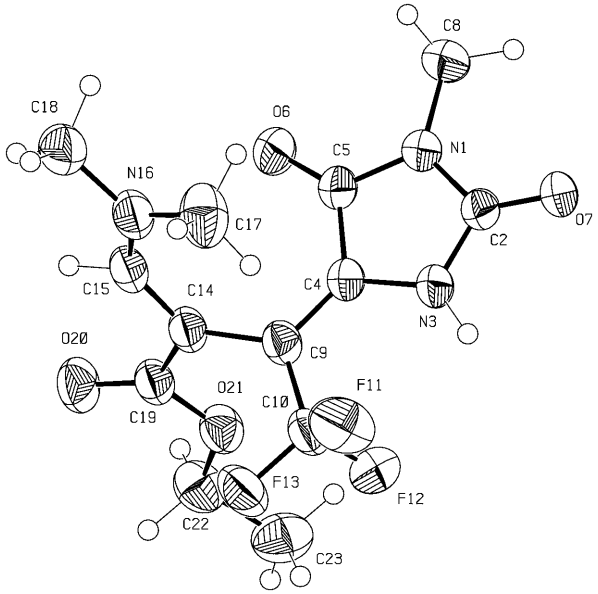
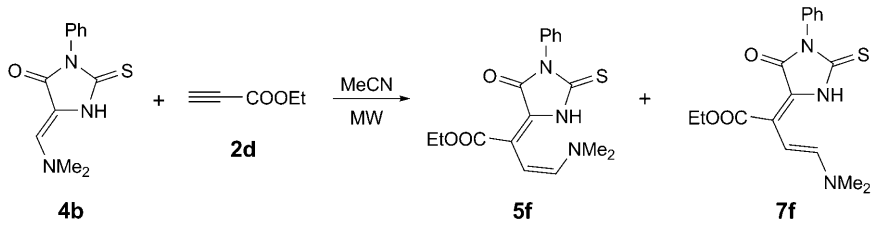


Fig. 3. *ORTEP View of compound* **6d** *at the 50% probability level.* H-Atoms are drawn as spheres of arbitrary radii.

Scheme 3



structurally different from the minor isomers **6c**–**6e** mentioned previously. The structures of isomers **5f** and **7f** were determined by ^{1}H-NMR spectroscopy, where characteristic coupling constants for *cis*-oriented (^3J(H,H) = 10.1 Hz) and *trans*-oriented protons (^3J(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** ($R^3 \neq H$) and/or (2(1′)*Z*,3(4″)*E*)-isomer **7** ($R^3 \neq H$), or (2(4′)*Z*,3*Z*)-isomer **6** ($R^3 = H$) and/or (2(4′)*E*,3*E*)-isomer **7** ($R^3 = H$). 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** ($R^3 \neq H$) and/or (2(1′)*Z*,3(4″)*Z*)-isomer **10**

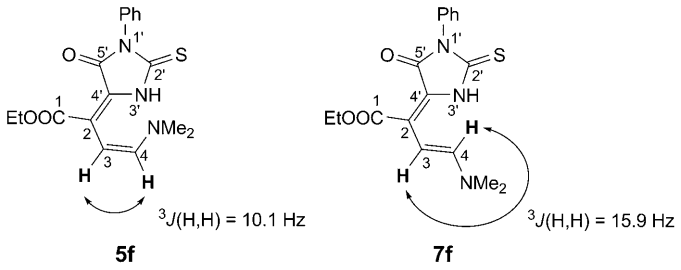
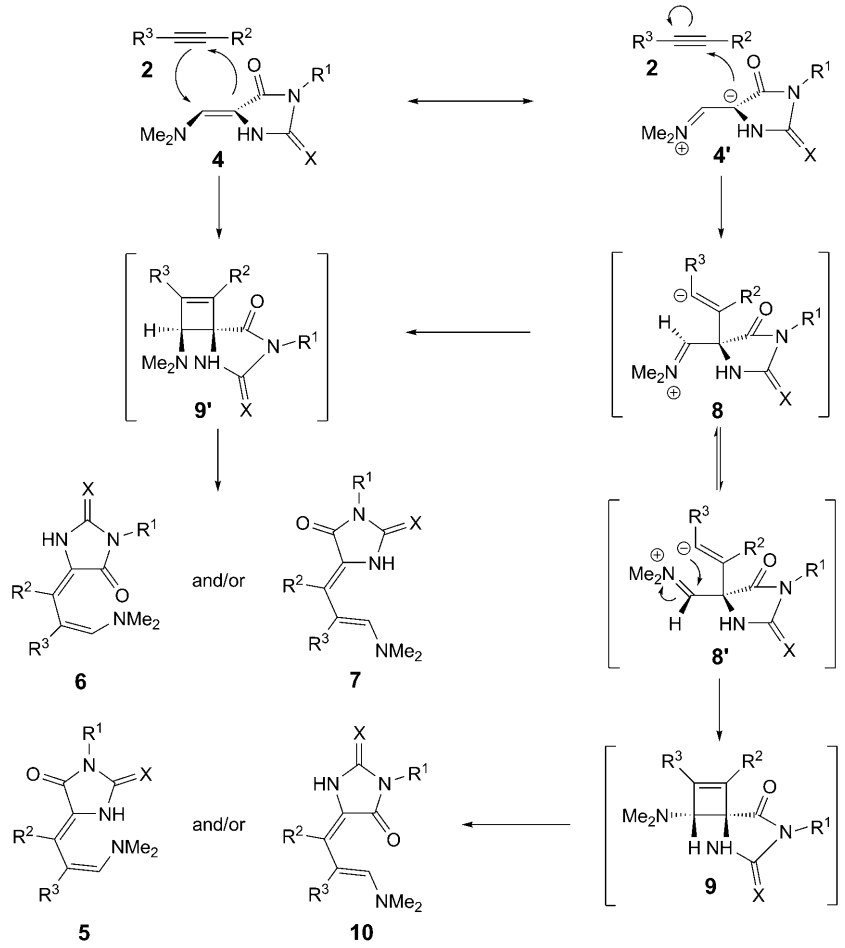


Fig. 4. *Coupling constant* $^3J(H,H)$ *of the* $H-C=C-H$ *moiety of* **5f** *and* **7f**

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

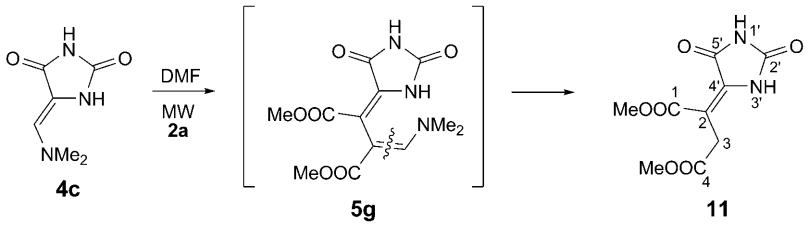
Scheme 4



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**, (5*Z*)-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 (2*E*)-2-(2,5-dioxoimidazolidin-4-ylidene)butanedioate (**11**) was obtained (*Scheme 5*). This can easily be explained by the initial formation of dimethyl (2*E*,3*E*)-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.

Scheme 5



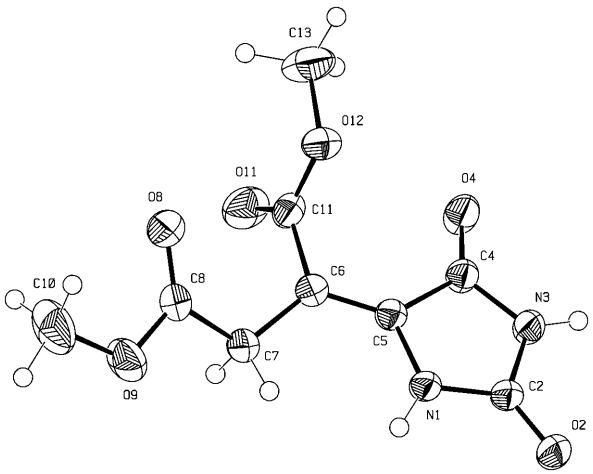


Fig. 5. *ORTEP View of compound* **11** *at the 50% probability level.* H-Atoms are drawn as spheres of arbitrary radii.

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 thio-

xo 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 ^{13}C, (D_6)DMSO and $CDCl_3$ as solvents and Me_4Si 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 (5*Z*)-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*,3*E*)-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 ($CDCl_3$): 2.99 (br. *s*, Me_2N); 3.07 (*s*, MeN); 3.66 (*s*, COOMe); 3.86 (*s*, COOMe); 6.94 (br. *s*, NH); 7.65 (*s*, C*H*NMe_2). ^{13}C-NMR ($CDCl_3$): 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*,3*E*)-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 ($CDCl_3$): 1.23 (*t*, $J = 7.1$, *Me*CH_2O); 1.35 (*t*, $J = 7.1$, *Me*CH_2O); 2.98 (br. *s*, Me_2N); 3.07 (*s*, MeN); 4.14–4.23 (*m*, 1 H, MeCH_2O); 4.27–4.36 (*m*, 3 H MeCH_2O); 6.76 (br. *s*, NH); 7.65 (*s*, C*H*NMe_2). Anal. calc. for $C_{15}H_{21}N_3O_6$ (339.34): C 53.09, H 6.24, N 12.38; found: C 53.29, H 6.47, N 12.19.

*Dimethyl (*2E*,3*E*)-2-[(Dimethylamino)methylene]-3-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)butanedioate* (**5c**) *and Dimethyl (*2E*,3*Z*)-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-2-ynedioate (**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 ($CDCl_3$): (2*E*,3*E*)-

isomer **5c**: 3.21 (*s*, 3 H, Me_2N); 3.49 (*s*, 3 H, Me_2N); 3.72 (*s*, COOMe); 3.76 (*s*, COOMe); 6.74 (*s*, NH); 7.11 (*s*, C*H*NMe_2); 7.29–7.50 (*m*, Ph); (2*E*,3*Z*)-isomer **6c**: 3.25 (*s*, 3 H, Me_2N); 3.57 (*s*, 3 H, Me_2N); 3.73 (*s*, COOMe); 3.77 (*s*, COOMe); 6.28 (*s*, NH); 7.19 (*s*, C*H*NMe_2); 7.29–7.50 (*m*, Ph). Anal. calc. for $C_{18}H_{19}N_3O_5S$ (389.43): C 55.52, H 4.92, N 10.79; found: C 55.77, H 5.11, N 10.63.

*Ethyl (2*E*,3*E*)-2-[(Dimethylamino)methylene]-4,4,4-trifluoro-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)butanoate* (**5d**) *and Ethyl (2*E*,3*Z*)-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 4,4,4-trifluorobut-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): (2*E*,3*E*)-isomer **5d**: 3215, 2984, 1779, 1724, 1698, 1644, 1611, 1462, 1399, 1283, 1257, 1214, 1173, 1126, 1082, 991, 957, 825, 763, 711; (2*E*,3*Z*)-isomer **6d**: 3237, 2983, 1767, 1725, 1699, 1648, 1614, 1457, 1398, 1329, 1271, 1245, 1215, 1193, 1109, 1048, 1027, 991, 949, 818, 764, 617. ^{1}H-NMR ($CDCl_3$): (2*E*,3*E*)-isomer **5d**: 1.22 (*t*, *J* = 7.1, *Me*CH_2O); 2.97 (br. *s*, Me_2N); 3.11 (*s*, MeN); 3.99–4.10 (*m*, 1 H, MeC*H*$_2$O); 4.16–4.28 (*m*, 1 H, MeC*H*$_2$O); 7.63 (*s*, C*H*NMe_2); 8.45 (br. *s*, NH); (2*E*,3*Z*)-isomer **6d**: 1.21 (*t*, *J* = 7.1, *Me*CH_2O); 2.92 (*s*, Me_2N); 3.08 (*s*, MeN); 4.01–4.24 (*m*, MeC*H*$_2$O); 7.69 (*s*, C*H*NMe_2); 8.47 (br. *s*, NH). ^{13}C-NMR ($CDCl_3$): (2*E*,3*E*)-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; (2*E*,3*Z*)-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*); 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 (2*E*,3*E*)-2-[(Dimethylamino)methylene]-4,4,4-trifluoro-3-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)butanoate* (**5e**) *and Ethyl (2*E*,3*Z*)-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. ^{1}H-NMR ($CDCl_3$): (2*E*,3*E*)-isomer **5e**: 1.27 (*t*, *J* = 7.1, *Me*CH_2O); 3.23 (*s*, 3 H, Me_2N); 3.53 (*s*, 3 H, Me_2N); 4.20 (*q*, *J* = 7.1, MeC*H*$_2$O); 6.49 (*s*, NH); 7.17 (*s*, C*H*NMe_2); 7.28–7.49 (*m*, Ph); (2*E*,3*Z*)-isomer **6e**: 1.29 (*t*, *J* = 7.1, *Me*CH_2O); 3.26 (*s*, 3 H, Me_2N); 3.59 (*s*, 3 H, Me_2N); 4.23 (*q*, *J* = 7.1, CH_2O); 6.72 (*s*, NH); 7.23 (*s*, C*H*NMe_2); 7.28–7.49 (*m*, Ph). EI-MS: 413 (M^+). EI-HR-MS: 413.103250 (M^+, $C_{18}H_{18}F_3N_3O_3S^+$; calc. 413.102098). Anal. calc. for $C_{18}H_{18}F_3N_3O_3S$ (413.41): C 52.08, H 4.55, N 9.94; found: C 52.29, H 4.39, N 10.16.

*Ethyl (2*E*,3*Z*)-4-(Dimethylamino)-2-(5-oxo-1-phenyl-2-thioxoimidazolidin-4-ylidene)but-3-enoate* (**5f**) *and Ethyl (2*E*,3*E*)-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. ^{1}H-NMR ($CDCl_3$): (2*E*,3*Z*)-isomer **5f**: 1.27 (*t*, *J* = 7.1, *Me*CH_2O); 3.24 (*s*, 3 H, Me_2N); 3.63 (*s*, 3 H, Me_2N); 4.19 (*q*, *J* = 7.1, MeC*H*$_2$O); 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, *Me*CH_2O); 3.23 (br. *s*, 3 H, Me_2N); 3.62 (br. *s*, 3 H, Me_2N); 4.20 (*q*, *J* = 7.1, MeC*H*$_2$O); 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)). ^{13}C-NMR ($CDCl_3$): 14.0; 39.5; 46.2; 46.3; 60.3; 60.4; 114.5; 114.9; 115.2; 118.6; 127.0; 127.2; 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 $C_{17}H_{19}N_3O_3S$ (345.42): C 59.11, H 5.54, N 12.17; found: C 59.27, H 5.64, N 11.99.

*Dimethyl (2*E*)-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^+). ^{1}H-NMR (D_6)(DMSO): 3.45 (*s*, CH_2); 3.62 (*s*, COOMe); 3.66 (*s*, COOMe); 10.54 (br. *s*, NH); 11.32 (br. *s*, NH). ^{13}C-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^+, $C_9H_{10}N_2O_6^+$; calc. 242.053886). Anal. calc. for $C_9H_{10}N_2O_6$ (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* **11**[1]). 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*.

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

	5d	**6d**	**11**
Formula	$(C_{13}H_{16}F_3N_3O_4)_2 \cdot CHCl_3$	$C_{13}H_{16}F_3N_3O_4$	$C_9H_{10}N_2O_6$
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)
b [Å]	12.3965(3)	12.8666(6)	12.2444(2)
c [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)
Z	2	4	4
ρ [Mg m^{-3}]	1.401	1.446	1.482
μ [mm^{-1}]	0.326	0.131	0.127
Color of crystal	yellow	yellow	colorless
Shape of crystal	block	block	block
Dimensions [mm]	$0.14 \times 0.10 \times 0.08$	$0.22 \times 0.18 \times 0.14$	$0.20 \times 0.20 \times 0.12$
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_w	0.078, 0.082	0.052, 0.053	0.044, 0.007
$(\Delta/\sigma)_{max}$	0.55	0.0002	0.0004
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	− 0.55, 0.60	− 0.31, 0.33	− 0.26, 0.30

[1]) 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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