REACTION OF 5-AMINOBENZOTRIAZOLES WITH METHYL PROPIOLATE. FORMATION OF TRIAZOLO[4,5-*f*]QUINOLINES AND RELATED COMPOUNDS. UNUSUAL PRODUCTS IN THE MICHAEL ADDITION REACTION OF 2-METHYL-2*H*-5-AMINOBENZOTRIAZOLE

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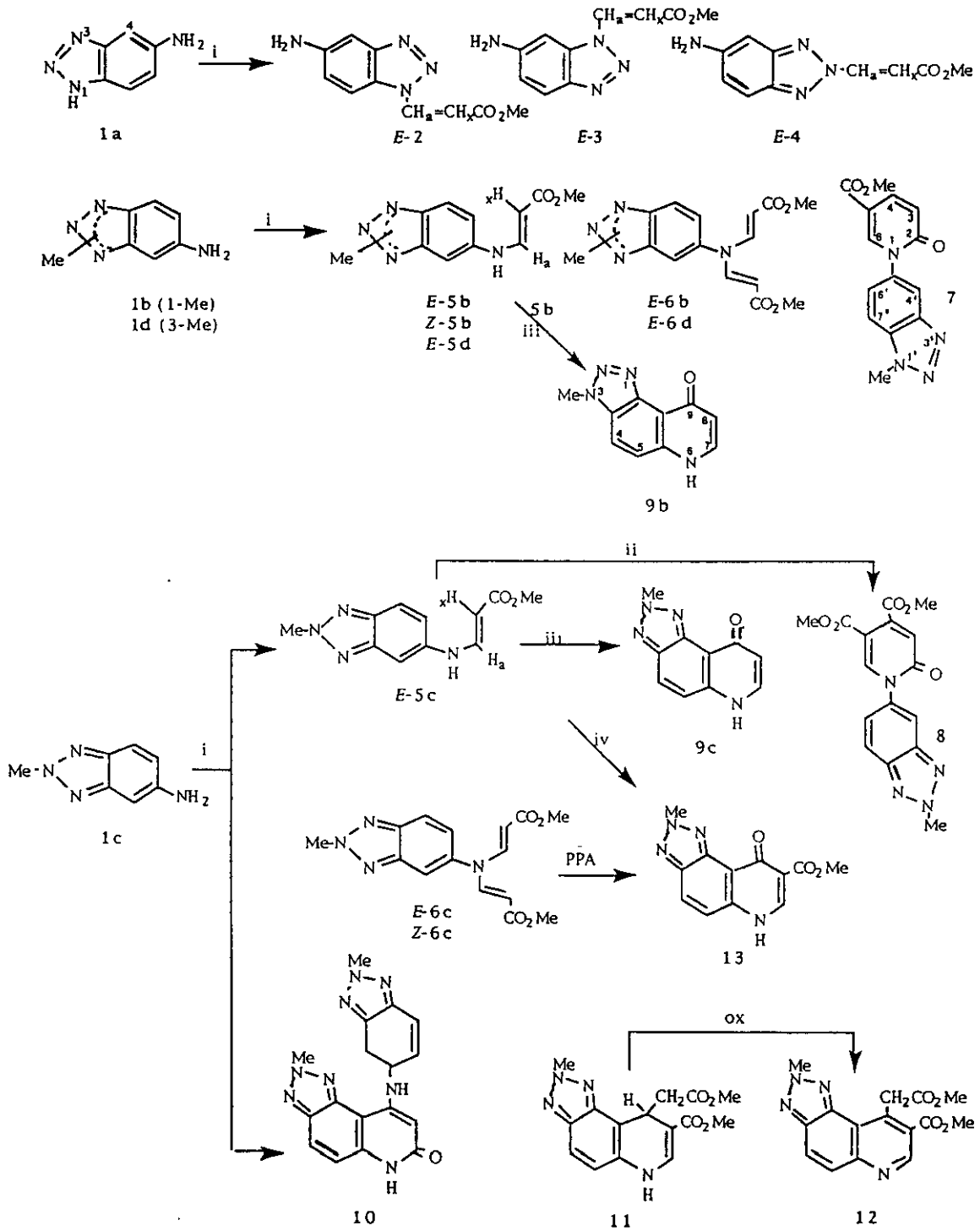
Abstract- Reaction of 5-aminobenzotriazoles (**1b-d**) with methyl propiolate gives (*Z/E*)-3-[1(2)(3)-methyl(benzotriazol-5-yl)]aminomonopropenoates (**5b-d**) and (*E*)-3-[1(2)(3)-methyl(benzotriazol-5-yl)]aminobispropenoates (**6b-d**), while in the case of **1a** addition took place on the nitrogen of the triazole ring to give mixtures of (*E*)-3-(5-aminobenzotriazol-1(2)(3)-yl)propenoates (**2,3,4**). Mono- (**5b-d**) and bis-adducts (**6b-d**) underwent further reaction which also led to the isolation of triazolo[4,5-*f*]quinolines, of a triazolo[4,5-*f*]carbostyril and 1-[benzotriazol-5-yl]-2-pyridones. Formation of these compounds depends on the reaction conditions: the solvent employed and the temperature. Thermal cyclization of Michael adduct (*Z/E*)-(**5c**) gave triazoloquinolinone (**9c**) and the rearranged product (**13**) in various ratio depending on the concentration of Dowtherm used.

The development in the chemistry of triazolo[4,5-*f*]-, [4,5-*g*]-, [4,5-*h*]quinoline from our laboratory is closely related to the synthesis of new compounds designed for a medicinal chemistry project.[1-3] In particular, we have been investigating the reaction of 5-aminobenzotriazoles (**1a-d**) with acetylenic esters with the aim of obtaining 9-hydroxytriazolo[4,5-*f*]quinoline, necessary for building up 9-aminoalkyl(aryl)aminotriazolo[4,5-*f*]quinolines as potential anticancer compounds.[4] In the above context, we have recently reported that 5-aminobenzotriazoles (**1a-d**), when treated with dimethyl acetylenedicarboxylate (**DMAD**), give rise to Michael adducts accompanied by *benzotriazol-5-yl-2-pyridones,* a *9,10-dihydrotriazolo[4,5-g]-1H-benzoazepine* and a *triazolo-2-oxoindole*.[5] However, from



Scheme 1

i, according to the conditions of Table 1; ii, only *E*-5c with DMAD in refluxing acetonitrile; iii, on heating in Dowtherm at 250°C in a ratio of 1:20 with the solvent; iv, in Dowtherm at 250°C in a ratio of 1:10 with the solvent

these results it appeared evident that the triazole moiety acts as "sleeping partner", since it is not involved in either cycloaddition across the positions 2 and 3 of the heterocycle or ring expansion and rearrangement to quinoxaline as reported by Acheson *et al.*[6] in the case of the reaction of 1-methylbenzotriazole with **DMAD.**

Now, we investigated the reaction of **1a-d** with methyl propiolate (**MP**), which is considered to be less reactive than **DMAD** because the electro-attracting group facilitates loss of the acetylenic proton to yield carbanions which can complicate the reaction.[7] Products formed during these reactions (Scheme 1) are similar, in some respects, to those in the reaction with **DMAD,** but were accompanied by a few interesting exceptions. In general, their formation was highly dependent on the reaction conditions, purity of the reactants and solvents as shown in Table 1. The aminobenzotriazoles (**1a-d**) are weaker bases than aniline derivatives, though Michael additions occur in a low or moderate yield. Formations of propenoates (*E*)-(**2**, **3**, **4**), (*E*) or (*Z*) mono-enaminoesters (**5b-d**), bis-enaminoesters (*E*),(*E*)-(**6b-d**) largely depend on both the starting amine and the reaction condition used. Thus, the amine (**1a**) did not react with **MP** at room temperature in acetonitrile, but led to the propenoates (*E*)-(**2**), (*E*)-(**3**), (*E*)-(**4**) in various proportions at forced conditions shown in Table 1, indicating that an *E*- Michael addition took place on an triazole nitrogen. The amines (**1b** and **1d**) did not react with **MP** at room temperature in acetonitrile, but under the other conditions (Table 1) gave in lesser yields the analogous Michael adducts on the amino group (*Z*)- and (*E*)-(**5b** and **5d**), the bis-adducts (*E*),(*E*)-(**6b** and **6d**) accompanied by a 2-pyridone (**7**) in the case of **1b.** The proportions of products were dependent on the solvent and the temperature.

The reaction of the amine (**1c**) upon **MP** gave different results. Compounds (**10**), (**11**) and (**12**) were produced togheter with the Michael adducts (*E* and *Z*-**5c**) depending on conditions employed. In contrast to cases of **1a** and **1b**, the bis-adduct (*E*)-(**6c**) was the major product (33% yield), while the reaction in DMSO or that with catalytic amounts of TEA, the product was accompanied by the quinolinone (**13**) in a low yield (5%), formation and structure elucidation of which being discussed below.

The formation mechanism of **7** is consistent with that described for the analogous cases of **1b-d** with **DMAD**,[5] where we postulated an *E*-addition of this ester to the initially formed enamino ester. A support for such an addition came from the observation that when pure (*E*)-**5c** was treated with **DMAD** in refluxing acetonitrile to give rise to both pyridone (**8**) (62% yield) and (*Z*)-**5c** (18% yield). Isolation of (*Z*)-**5c** accounts for an interconversion of (*E*)-**5c** into (*Z*)-**5c** that is independent of the presence of

DMAD. In fact, we could observe that when a mixture of these isomers in a 1:1 ratio was left standing in $CDCl_3$, (*E*)-**5c** was completely converted into (*Z*)-**5c** within six days. Analogous interconversion of anilinoacrylates has been reported to take place either spontaneously [8] or by acid catalysis in non polar solvents.[9]

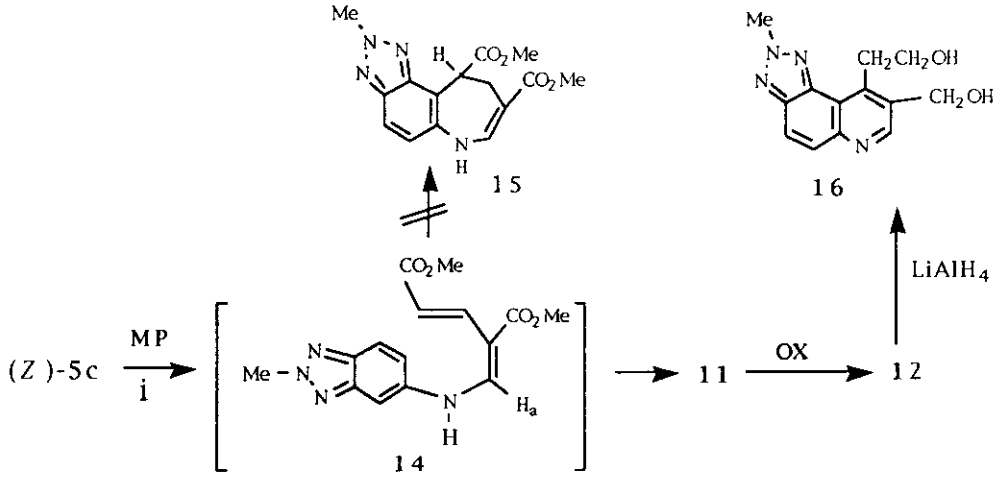
Table 1. - Reaction conditions and products isolated from the reaction of **1a-d** with **MP**

Compd [mmol]	MP [mmol]	Molar ratio	Solvent	Reaction time (h)	Temperature °C	Method	Products isolated (%Yield)
1a [8.50]	[17.0]	1:2	MeCN	72	room temperature	A	**1a** (98)
[11.2]	[22.4]	1:2	MeCN	72	reflux	A	*E*-**2** (41), *E*-**3** (22), *E*-**4** (9), **1a** (29)
[11.2]	[22.4]	1:2	n.s.	90	room temperature	B	*E*-**2**(3),*E*-**3** (1.2), *E*-**2**+*E*-**3** (ratio 1:2, 3.3), **1a** (82)
[11.2]	[22.4]	1:2	DMSO	20	70	C	*E*-**2** (35), *E*-**3** (23), *E*-**4** (3.7), **1a** (10)
1b [8.50]	[17.0]	1:2	MeCN	72	room temperature	A	**1b** (98)
[9.50]	[19.0]	1:2	MeCN	72	reflux	A	*E*-**6b** (27), **7** (1.5), **1b** (21), *E*-**5b** (trace*)
[10.1]	[50.5]	1:5	n.s.	90	room temperature	B	*E*-**6b** (7), *E*-**5b** (3.4), **1b** (87)
[11.2]	[22.4]	1:2	DMSO	20	70	C	*E*-**6b** (19), *E*-**5b** (5), *Z*-**5b** (2), **1b** (27)
1c [13.5]	[27.0]	1:2	MeCN	72	room temperature	A	*E*- **5c** (5), *Z*- **5c** (10), **10** (1), **1c** (50)
[16.7]	[33.4]	1:2	MeCN	72	reflux	A	*E*- **5c** (16), *Z*- **5c** (37), **1c** (28)
[16.2]	[40.5]	1:2.5	n.s.	90	room temperature	B	*E*- **5c** (34), *Z*- **5c** (33), **1c** (16)
[17.5]	[70.2]	1:4	n.s.	90	room temperature	B	**11** (61), **12** (12)
[13.5]	[27.0]	1:2	DMSO	20	70	C	*E*- **6c** (33), **13** (5), **1c** (21)
1d [3.37)	[6.75]	1:2	MeCN	72	room temperature	A	**1d** (100)
[7.76]	[15.5]	1:2	MeCN	72	reflux	A	*E*-**6d** (36), *E*-**5d** (trace*), **1d** (37)
[7.83]	[31.3]	1:4	n.s.	90	room temperature	B	**1d** (96)
[11.3]	[22.6]	1:2	DMSO	20	70	C	*E*-**6d** (16), **1d** (32)

* identified by its ^{1}H-nmr spectrum; â, ratio deduced by the integral proportion of protons H_a and H_x in the ^{1}H-nmr spectrum of the mixture; n.s.=no solvent.

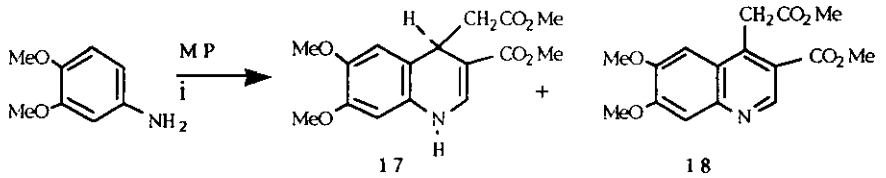
In contrast with this, compound (**1c**) when heated with an excess of **MP**, in the absence of solvent, did

not produce the corresponding pyridone but led to the isolation of the dihydrotriazoloquinoline (**11**) (61%) and the triazoloquinoline ester (**12**) (12%). This result would suggest that addition of one further mole of **MP** on (*E*)-**5c** took place leading to the intermediate (**14**) which cyclized *via* **11** to **12** (Scheme 2). Isolation of **11** and **12** clearly confirms that ring closure to quinoline is favored rather than that into the dihydrotriazolobenzoazepine (**15**), as postulated in the analogous case of (*Z*)-(*2-methylbenzotriazol-5-yl)aminobutenedioate* with **DMAD**.[5] Conversion of the dihydroquinoline (**11**) into **12** was easily accomplished on standing in the air. The ^{1}H-nmr spectrum of the oxidized compound (**12**) showed the collapse of the ABX system due to the non equivalent CH_2 in **11** into a singlet. Compound (**12**) was reduced to **16** with $LiAlH_4$. The structure of **16** was supported by its ^{1}H-nmr spectrum.



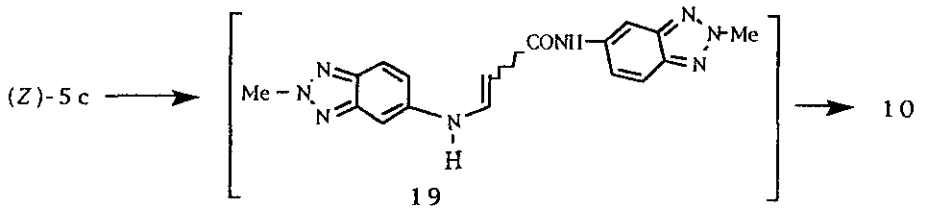
Scheme 2

An analogous cyclization was observed by Harris in the reaction of 3,4-dimethoxyaniline with ethyl propiolate.[10] Re-examination of his experiment using **MP** instead of the ethyl ester gave compounds (**17**) (29% yield) and (**18**) (1.1% yield) (Scheme 3).



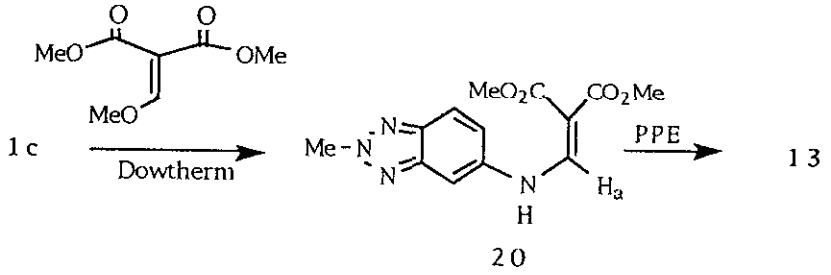
Scheme 3

Another side reaction is the formation of **10** (1% yield), which could be produced from the intermediate amide (**19**) formed from (*Z/E*)-**5c** and an excess of the amine (**1c**) (Scheme 4).



Scheme 4

Heating of (*Z*)- and (*E*)-adducts (**5b-c**) in refluxing Dowtherm gave the expected cyclization products **9b-c**. However, in the case of (*E*)-**5c**, **13** was also formed in 23% yield when the reaction was carried out with a 1:10 ratio of the compound and solvent. (*Z*)-**5c** afforded compound (**9c**) in 76% yield along with **13** (3%). In the case of a mixture of (*Z/E*)-**5c** and of (*Z*)-**5c** alone, when their ratio with Dowtherm was of 1:20, only **9c** was obtained in high yield. Compound (**13**) was obtained in 68% yield on heating (*E*)-**6c** in polyphosphoric acid (**PPA**) at 160 °C, while the attempted cyclization of (*E*)-**6c** in Dowtherm failed. These results suggest that the yields of **13** are dependent not only upon the stereochemistry of the adducts but also upon the concentration of both (*Z*)- and (*E*) -**5c** in Dowtherm and, for the case of (*E*)-**6c**, upon the solvent (**PPA**). The structure of **13** was elucidated on the basis of its analytical and spectroscopic data. In particular, its uv spectrum in EtOH was superimposable with that of *2-methyl-8-ethoxycarbonyl-6,9-dihydro-9-oxo-triazolo*[4,5-*f*]*quinoline*.[1] The structure was proved by an alternative synthesis (Scheme 5).

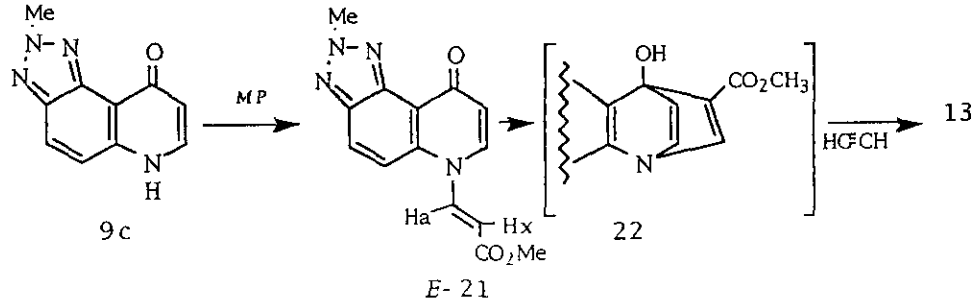


Scheme 5

In the light of the above demonstration and on the basis of the conditions employed to obtain **13**, it is our opinion that its formation follows the mechanism shown in Scheme 6.

The isolation of **1c** (29% yield) during the cyclization of (*E*)-**5c** which led to **9c** and **13** was of particular significance, since it would confirm that a retro Michael addition partly occurred and the freed **MP** was in part undergoing Michael *NH*- addition to the formed **9c** to give compound (**21**) followed by

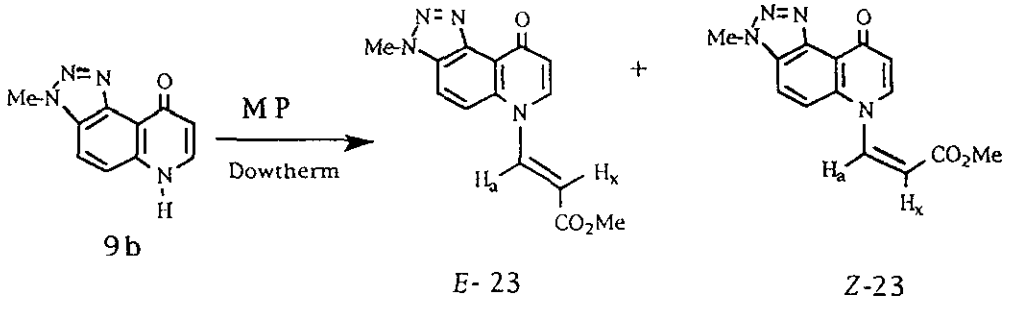
intramolecular aldol-type cyclization onto carbonyl group of the quinolone to give an unstable cycloadduct (**22**). Following retro Diels-Alder elimination of acetylene would lead to **13** (Scheme 6).



Scheme 6

Under the conditions examined (Dowtherm 250°C) detection of acetylene is hard to be evidentiated. A support of the suggested mechanism came from the observation that, when **9c** was treated with **MP** in dry DMSO at 70 °C, we isolated the compound (*E*)-(**21**) in 42% yield and **13** (4% yield). This result would exclude the assumption of Proctor *et al.*[11] that whenever a possible mesoionic equilibrium exists in quinolinone of this type an exclusive *O*-addition occurs in the reaction with DMAD.

In contrast to the behaviour of (*Z*)-**5c** and (*E*)-**6c**, the mono-adduct (*E*)-(**5b**) and the bis-adduct (*E*)-(**6b**), when submitted to cyclization in PPA or PPE under the above-mentioned conditions for (Z)-**5c**, respectively, gave no tractable material,whereas the treatment of compound (**9b**) with **MP** in refluxing Dowtherm gave a mixture of (*Z/E*)-isomers of **23** from which only the isomer (*E*)-(**23**) was isolated pure (Scheme 7). This fact further confirms that a Michael addition upon the *NH* group of the quinolinone form is preferred. Assignment of this structure instead of a possible *O*-alkylated isomer was deduced from ^{13}C-nmr spectrum of (*E*)-**23** which showed an unambiguous C=O resonance at δ 175.87 for the quinolinone form, similarly to that observed for (*E*)-**21** at δ 175.93.



Scheme 7

EXPERIMENTAL

Melting points are uncorrected and were taken on a Kofler apparatus. Uv spectra were recorded in nm (log ε) for ethanolic solutions with a Perkin-Elmer Lambda 5 spectrophotometer. Ir spectra are for nujol mulls and were made by a Perkin-Elmer 781 infrared spectrophotometer. ^{1}H-Nmr spectral data were obtained by a Varian XL-200 (200 MHz) instrument using TMS as internal standard. ^{13}C-Nmr spectral data were measured with a Varian XL-200 spectrometer at 50 MHz. Elemental analyses were performed at the Laboratorio di Microanalisi, Dipartimento di Scienze Farmaceutiche, University of Padua-Italy.

Materials - Acetonitrile used in the reactions was dried over basic alumina Woelm. The silica gel used for chromatography was Merck 60 (0.050-0.200) and Merck 60 (0.040-0.063 mm) in the case of flash chromatography. Amines (**1a-d**) were prepared according to the procedures previously described.[1]

General procedures for the reactions of amines (1a-d) with methyl propiolate (MP).

Method A- A mixture of the appropriate amine (**1a-d**) and **MP** (Aldrich) in the molar ratio and for the time indicated in Table 1, in dry acetonitrile (25-50 ml), was stirred at room temperature or refluxed. After evaporation of the solvent, the separation of the reaction products was accomplished by fractional crystallization or by chromatography followed, in some case, by further purification of the residue obtained from the evaporation of the eluates by trituration with ether. Physical and analytical data of the products thus obtained and listed in Table 1 are reported below.

Method B- A mixture of the appropriate amine (**1a-d**) and **MP**, in the molar ratio and for the time reported in Table 1, was stirred at room temperature. After distillation *in vacuo* of the excess of **MP**, the residue was chromatographed through silica gel column eluting with ether. On evaporation of the eluates, the residue was purified by trituration with ether to yield the products reported in Table 1. Mp's, ir, uv, ^{1}H and ^{13}C-nmr spectra of all the products listed in Table 1 and depicted in Scheme 1 are reported below.

Method C- A solution of **1a-d** and **MP**, in the ratio indicated in Table 1, and five drops of triethylamine in dry dimethyl sulfoxide (30 ml), was heated at 70°C for 20 h. After evaporation of the solvent under reduced pressure, the residue was taken up with water and extracted with ether. The combined extracts, dried over anhydrous sodium sulfate, on evaporation yielded an oily residue which was purified by column chromatography on neutral alumina, using ether as eluent, to give compounds listed in Table 1 and depicted in Scheme 1 whose physical and spectroscopic data are reported below .

(*E*)-**2**; mp 162-164 °C (from chloroform). Anal. Calcd for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 54.98; H, 4.55; N, 25.49. Ir: 3390, 3320, 1710, 1660 cm^{-1}; uv: λ_{max} 346 infl, 286, 242, 212 nm; ^{1}H-nmr ($CDCl_3$): δ 8.46 (1H, d, J=14.5 Hz, H_a), 7.52 (1H, d, J=8.8 Hz, H-7), 7.27 (1H, d, J=2 Hz, H-4), 7.02 (1H, dd, J=8.8 and 2 Hz, H-6), 6.62 (1H, d, J=14.5 Hz, H_X), 3.97 (2H, s, NH_2), 3.86 (3H, s, CO_2Me); ^{13}C-nmr (DMSO-d_6): δ 166.06 (s, CO), 147.95 (s, C-3a), 147.53 (s, C-5), 135.98 (d, C-H_a), 124.09 (s, C-7a), 120.24 (d, C-6), 111.76 (d, C-7), 105.7 (d, C-H_X), 98.56 (d, C-4), 51.78 (q, *O*-Me).

(*E*)-**3**; mp 130-132 °C (from ether). Anal. Calcd for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 55.36; H, 4.71; N, 25.43. Ir: 3420, 3360, 3250, 1710, 1650, 1620 cm^{-1}; uv: λ_{max} 398, 317, 267 infl, 240, 211 nm; ^{1}H-nmr ($CDCl_3$): δ 8.32 (1H, d, J=13.6 Hz, H_a), 7.65 (1H, d, J=9.2 Hz, H-7), 6.92 (1H, d, J=9.2 Hz, H-6), 6.86 (1H, d, J=13.6, H_X), 6.79 (1H, s, H-4), 4.10 (2H, s, NH_2), 3.85 (3H, s, CO_2Me). ^{13}C-nmr (DMSO-d_6): δ 165.62 (s, CO), 149.55 (s, C-5), 147.80 (s, C-3a), 141.13 (s, C-7a), 140.05 (d, C-H_a), 125.15 (d, C-7), 118.69 (d, C-6), 108.80 (d, C-H_X), 90.55 (d, C-4), 51.95 (q, *O*-Me).

(*E*)-**4**; mp 212-214 °C (from acetone). Anal. Calcd for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 55.27 ; H, 4.59; N, 25.42. Ir: 3455, 3360, 3230, 1710, 1650, 1640, 1610, 1580 cm^{-1}; uv: λ_{max} 342, 321, 286, 250, 225, 201 nm; ^{1}H-nmr (DMSO-d_6): δ 8.40 (1H, d, J=14.2 Hz, H_a), 7.74 (1H, d, J=9 Hz, H-7), 6.94 (1H, d, J=1.8 Hz, H-4), 6.83 (1H, dd, J=9 and 1.8 Hz, H-6), 6.45 (1H, d, J=14.2 Hz, H_X), 6.03 (2H, s, NH_2), 3.75 (3H, s, CO_2Me); ^{13}C-nmr (DMSO-d_6): δ 166.14 (s, CO), 151.40 (s, C-5), 138.83 (s, C-7a), 136.15 (d, C-H_a), 133.62 (s, C-3a), 120.55 (d, C-7), 116.02 (d, C-6), 104.87 (d, C-H_X), 90.71 (d, C-4), 51.79 (q, *O*-Me).

(*E*)-**5b**; mp 228-230 °C (from acetone). Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found: C, 56.51; H, 5.14; N, 23.82. Ir: 3280, 1700, 1630, 1600 cm^{-1}; uv: λ_{max} 320 sh, 297, 265, 208 nm; ^{1}H-nmr ($CDCl_3$+DMSO-d_6): δ 9.72 (1H, d, J=12.6 Hz, NH), 7.95 (1H, dd, J=12.6 and 13 Hz, H_a), 7.71 (1H, d, J=8.4, H-7), 7.53 (1H, s, H-5), 7.30 (1H, d, J=8.4, H-6), 5.20 (1H, d, J=13 Hz, H_X), 4.27 (3H, s, *N*-Me), 3.62 (3H, s, CO_2Me).

(*Z*)-**5b**; mp 177-179 °C (from ethanol). Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found: C, 56.60; H, 5.23; N, 24.03. Ir: 3300, 1660, 1620 cm^{-1}; uv: λ_{max}: 339, 301, 267, 209 nm; ^{1}H-nmr ($CDCl_3$): δ 10.05 (1H, d, J=13 Hz, NH), 7.55 (1H, d, J=1.8 Hz, H-4), 7.45 (1H, d, J=8.8 Hz, H-7), 7.31 (1H, dd, J=13 and 8.3 Hz, H_a), 7.16 (1H, dd, J=8.8 and 1.8 Hz, H-6), 4.94 (1H, d, J=8.3 Hz, H_X), 4.28

(3H, s, *N*-Me), 3.74 (3H, s, CO_2Me).

(*E*)-**5c**; mp 162-165 °C (from ether). Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found: C, 57.12; H, 5.18; N, 24.47. Ir: 3300, 1670, 1615, 1600 cm^{-1}; uv: λ_{max} 345 (4.33), 300 sh (4.18), 280 (4.34), 239 (3.93), 205 (4.23) nm; ^{1}H-nmr ($CDCl_3$): δ 7.92 (1H, d, J =13 Hz, H_a), 7.58 (1H, d, J=9 Hz, H-7), 7.15 (1H, d, J=2 Hz, H-4), 7.12 (1H, d, J=13 Hz, NH), 6.90 (1H, dd, J=9 and 2 Hz, H-6), 5.18 (1H, d, J=13 Hz, H_X), 4.33 (3H, s, *N*-Me), 3.13 (3H, s, CO_2Me).

(*Z*)-**5c**; mp 125-127 °C (from ether). Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found: C, 56.74; H, 5.36; N, 24.11. Ir: 3300, 1660, 1650, 1620 cm^{-1}; uv: λ_{max} 344 (4.65), 300 infl (4.42), 280 (4.57), 234 sh (4.22) nm; ^{1}H-nmr ($CDCl_3$): δ 10.00 (1H, br d, J=8 Hz, NH), 7.72 (1H, d, J=9 Hz, H-7), 7.36 (1H, d, J=8 Hz, H_a), 7.21 (1H, d, J=2 Hz, H-4), 7.00 (1H, dd, J=9 and 2 Hz, H-6), 4.88 (1H, d, J=8 Hz, H_X), 4.42 (3H, s, *N*-Me), 3.70 (3H, s, CO_2Me).

(*E*)-**6b**; mp 160-162 °C (from acetone). Anal. Calcd for $C_{15}H_{16}N_4O_4$+0.75 H_2O: C, 54.62; H, 4.85; N, 16.99. Found: C, 55.05; H, 4.98; N, 16.53. Ir: 1740, 1700, 1660, 1600 cm^{-1}; uv: λ_{max} 301 (4.60), 252 (4.04), 205 (4.48) nm; ^{1}H-nmr ($CDCl_3$): δ 7.91 (1H, d, J=1.8 Hz, H-4), 7.87 (2H, d, J=13.4 Hz, H_a), 7.73 (1H, d, J=8.8 Hz, H-7), 7.29 (1H, dd, J=8.8 and 1.8 Hz, H-6), 4.73 (2H, d, J=13.4 Hz, H_X), 4.38 (3H, s, *N*-Me), 3.67 (6H, s, 2 CO_2Me).

(*E*)-**6c**; mp 162-164 °C (from ether). Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.95; H, 5.10; N, 17.71. Found: C, 56.87; H, 5.14; N, 17.57. Ir: 1715, 1690, 1600 cm^{-1}; uv: λ_{max} 301 (4.88), 246 infl (4.29), 205 (4.80) nm; ^{1}H-nmr ($CDCl_3$): δ 8.02 (1H, d, J=9 Hz, H-7), 7.84 (2H, d, J=13.4 Hz, H_a), 7.73 (1H, d, J=1.8 Hz, H-4), 7.13 (1H, dd, J=9 and 1.8 Hz, H-6), 4.80 (2H, d, J=13.4 Hz, H_X), 4.58 (3H, s, *N*-Me), 3.68 (6H, s, 2 CO_2Me).

(*E*)-**6d**; mp 158-160 °C (by trituration with ether). Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.95; H, 5.10; N, 17.71. Found: C, 56.78; H, 5.15; N, 17.40. Ir: 1700, 1650, 1600 cm^{-1}; uv: λ_{max} 301 (4.60), 250 (3.96), 204 (4.48) nm; ^{1}H-nmr ($CDCl_3$): δ 8.22 (1H, d, J=8.7 Hz, H-7), 7.84 (2H, d, J=12.4 Hz, H_a), 7.42 (1H, d, J=1 Hz, H-4), 7.17 (1H, dd, J=8.7 and 1 Hz, H-6), 4.76 (2H, d, J=12.4 Hz, H_X), 4.34 (3H, s, *N*-Me), 3.68 (6H, s, 2 CO_2Me).

7; mp 223-225 °C (from acetone). Anal. Calcd for: $C_{14}H_{12}N_4O_3$+0.5 H_2O: C, 57.33; H, 4.10; N, 19.11.

Found: C, 57.25; H, 4.26; N, 19.06. Ir: 1715, 1670, 1610 cm^{-1}; uv: λ_{max} 308 infl, 286 sh, 262, 207 nm; ^{1}H-nmr ($CDCl_3$): δ 8.31 (1H, d, J=2.4 Hz, H-6), 8.05 (1H, d, J=1.6 Hz, H-4'), 7.97 (1H, dd, J=9.6 and 2.4 Hz, H-4), 7.66 (1H, d, J=8.6 Hz, H-7'), 7.57 (1H, dd, J=8.6 and 1.6 Hz, H-6'), 6.68 (1H, d, J=9.6 Hz, H-3), 4.37 (3H, s, *N*-Me), 3.88 (3H, s, CO_2Me).

10; 270-271 °C (from acetone). Anal. Calcd for $C_{17}H_{14}N_8O$: C, 58.95; H, 4.07; N, 32.35. Found: C, 58.66; H, 4.45; N, 32.33. Ir: 3300, 3180, 1680, 1639, 1625, 1590 cm^{-1}; uv: λ_{max} 321 (4.36), 281 (4.24), 232 (4.95) nm; ^{1}H-nmr (DMSO-d_6): δ 8.12 (1H, br s, NH-CO), 7.82 (1H, d, J=9.1 Hz, H-5), 7.62 (1H, d, J=9.1 Hz, H-4), 7.23 (1H, s, NH), 7.01 (1H, d, J=2 Hz, H-4'), 6.96 (1H, d, J=9.1 Hz, H-7'), 6.76 (1H, dd, J=9.1 and 2 Hz, H-6'), 5.47 (1H, br s, H-8), 4.46 (3H, s, *N*-Me), 4.43 (3H, s, *N*-Me).

11; mp 175-177 °C (from ether). Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.90; H, 5.09; N, 17.71. Found: C, 57.00; H, 5.25; N, 17.67. Ir: 3360, 1710, 1680, 1640, 1595, 1570 cm^{-1}; uv: λ_{max} 431, 311, 243, 202 nm; ^{1}H-nmr ($CDCl_3$): δ 8.02 (1H, s, H-7), 7.60 (1H, d, J=9 Hz, H-4), 6.69 (1H, d, J=9 Hz, H-5), 5.07 (1H, dd, J=10.6 and 1.8 Hz, H-9), 4.41 (3H, s, *N*-Me), 3.80 (3H, s, CO_2Me), 3.69 (3H, s, CO_2Me), 4.92 (1H, dd, J=16.8 and 10.6 Hz, CH_2-9), 4.76 (1H, dd, J=16.8 and 2 Hz, CH_2-9).

12; mp 148-150 °C (from ether). Anal. Calcd for $C_{15}H_{14}N_4O_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 56.95; H, 4.51; N, 17.50. Ir: 1740, 1710, 1625, 1590 cm^{-1}; uv: λ_{max} 300 (3.80), 263 (4.10), 260 sh (4.08), 224 (4.05) nm; ^{1}H-nmr ($CDC1_3$): δ 9.33 (lH, s, H-7), 8.00 (lH, d, J=9 Hz, H-4), 7.79 (lH, d, J=9 Hz, H-5), 4.60 (3H, s, *N*-Me), 4.43 (2H, s, CH_2), 3.95 (3H, s, CO_2Me), 3.70 (3H, s, CO_2Me); ^{13}C-nmr ($CDCl_3$): δ 171.21 (*s*, CO), 166.12 (*s*, CO), 134.34 (d, C-7), 154.83 (s, C-8), 149.44 (s, C-9), 123.39 (s, C-9a), 140.88 (s, C-9b), 118.54 (s, C-3a), 122.35 (d, C-4), 129.01 (d, C-5), 142.48 (s, C-5a), 43.11 (t, CH_2), 52.47 (q, *O*-Me), 52.00 (q, *O*-Me), 44.23 (q, *N*-Me).

Cyclization reactions of propenoates (*E*)-(5b) into 9b and (*Z*)/(*E*)-(5c) into 9c and 13.

9-Oxo-6,9-dihydro-1-methyl-1*H*-triazolo[4,5-*f*]quinoline (9b).- Compound (*E*)-(**5b**) (1.1 g, 4.74 mmol) was added in small portions to refluxing Dowtherm (12 ml) while stirring and heating were continued for an additional 20 min. After cooling, the suspension was filtered and the solid thoroughly washed with light petroleum (bp 60-80 °C) to yield **9b** (0.83 g, 88% yield) as brown dust, mp 328-330 °C. Anal. Calcd for $C_{10}H_8N_4O$: C, 55.04; H, 4.62; N, 25.68. Found: C, 55.50; H, 4.61; N, 25.72. Ir: 3450, 1630, 1620, 1600, 1575, 1525 cm^{-1}; uv: λ_{max} 324, 311, 284, 272, 242, 239 nm; ^{1}H-nmr (DMSO-

d_6): δ 8.13 (1H, d, J=9 Hz, H-5), 8.00 (1H, d, J=6 Hz, H-8), 7.74 (1H, d, J=9 Hz, H-4), 6.29 (1H, d, J=6 Hz, H-7), 4.36 (3H, s, *N*-Me), NH not observed due to exchange with the solvent.

9-Oxo-2-methyl-2*H* -triazolo[4,5-*f*]quinoline (9c).

i- Compound (*Z*)-(**5c**) (1.1 g, 4.74 mmol) in Dowtherm (20 g) in a ratio of 1:20, in an identical manner as for the above case of (*E*)-**5b**, gave **9c** (0.9 g, 94% yield), mp 310-312 °C (from dimethyl sulfoxide). Anal. Calcd for $C_{10}H_8N_4O$+0.5 H_2O: C, 57.41; H, 4.34; N, 26.78. Found: C, 57.57; H, 3.95; N, 27.12. Ir: 3400 br cm^{-1}; uv: λ_{max} 334 (4.09), 321 (4.16), 300 sh (4.06), 292 sh (4.10), 286 (4.11), 270 (4.44), 257 (4.46), 248 sh (4.42), 214 (4.56) nm; ^{1}H-nmr (DMSO-d_6): δ 8.10 (1H, d, J=9 Hz, H-4), 7.96 (1H, d, J=7 Hz, H-7), 7.57 (1H, d, J=9 Hz, H-5), 6.28 (1H, d, J=7 Hz, H-8), 4.48 (3H, s, *N*-Me), 3.40 (1H, br s, NH which collapses with D_2O); ^{13}C-nmr (DMSO-d_6): δ 175.08 (s, C=O), 141.12 (d, C-7), 140.20 (s, C-5a), 139.76 (s, C-9b), 136.20 (s, C-3a), 122.37 (d, C-4), 120.09 (d, C-5), 114.96 (s, C-9a), 113.07 (d, C-8), 43.06 (q, *N*-Me).

ii- In a similar run as above the isomer (*E*)-(**5c**) (1.09 g; 4.69 mmol) after reflux for 45 min gave **9c** in 92% yield.

iii- Following the above procedure, starting from a mixture of (*Z*)/(*E*)-(**5c**) (2.15 g; 23 mmol) compound (**9c**) was obtained in 83% yield.

iv- Compound (*E*)-(**5c**) (0.65 g; 2.8 mmol) in refluxing Dowtherm (6.5 g) (in a ratio 1:10) for 20 min and working-up the reaction mixture as under **i**) yielded **13** (170 mg, 23% yield), as pale yellow crystals, mp 204-205 °C (from acetone), identical to a sample isolated from the reaction in DMSO and to an authentic specimen obtained by an independent route described below. The mother liquors on evaporation gave a solid residue which after purification by silica gel column chromatography eluting with ether gave (*E*)-**5c** (0.11 g, 17% yield), and eventually with a mixture of ether-ethanol yielded the amine (**1c**) (0.12 g, 29% yield).

v- In the same manner as under **iv** compound (*Z*)-(**5c**) yielded **9c** (76% yield), identical with an authentic specimen described earlier, and **13** (3% yield).

Dimethyl (2-methyl-2*H*-benzotriazol-5-yl)aminomethylenemalonate (20). - A mixture of the amine (**1c**) (2.2 g, 14.8 mmol) and dimethyl methoxymethylenemalonate (2.84 g; 16.3 mmol) in Dowtherm (22 g) was heated under stirring at 150°C for 4 h. After cooling, the mixture was diluted with light petroleum

(220 ml) and stirred for an additional 30 min. Then, the precipitate was collected and washed with ether to give **20** (2.82 g, 66% yield), mp 149-150 °C (from ether). Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.70; H, 5.00; N, 19.05. Ir: 3300-2500, 1690, 1650, 1630, 1600 cm^{-1}; uv: λ_{max} 332 (4.76), 291 (4.52), 222 (4.56) nm; ^{1}H-nmr ($CDCl_3$): δ 11.15 (1H, d, J=13 Hz, collapses with D_2O, NH), 8.39 (1H, d, J=13 Hz, H_a), 7.68 (1H, d, J=9 Hz, H-7), 7.38 (1H, d, J=2 Hz, H-4), 7.05 (lH, dd, J=9 and 2 Hz, H-6), 4.38 (3H, s, *N*-Me), 3.78 (3H, s, CO_2Me), 3.70 (3H, s, CO_2Me).

2-Methyl-8-methoxycarbonyl-6,9-dihydro-9-oxo-2*H*-triazolo[4,5-*f*]quinoline (13). i- Compound (**20**) (1 g; 3.44 mmol) was added slowly to ethyl polyphosphate (**PPE**) (10 g) preheated at 150-160°C. The resulting mixture was heated and stirred for an additional 1 h. After cooling, the mixture was poured onto iced-water (100 ml) and the aqueous solution was made alkaline (pH=8-9) with conc. ammonium hydroxide solution and extracted with chloroform.The extracts, dried over anhydrous sodium sulfate, on evaporation gave a solid residue which was purified by silica gel column chromatography, eluting first with a 7:3 mixture of ether-light petroleum (bp 60-80 °C) and then with ether only, to give compound (**13**) (0.1 g; 11% yield), mp 204-205 °C (from acetone) (mixed mp with the sample obtained by an alternative route showed no depression, and ir, uv, ^{1}H- and ^{13}C-nmr spectra were coincident). Anal. Calcd for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.90; N, 21.70. Found: C, 55.52; H, 3.81; N, 21.77. Ir: 3400, 1730, 1630, 1600 cm^{-1}; uv: λ_{max} 328 infl (3.93), 300 (4.41), 263 (4.48), 256 infl (4.81), 222 (4.79) nm; ^{1}H-nmr ($CDC1_3$): δ 9.52 (lH, d, J=2.1 Hz, H-7), 9.45 (lH, d, J=2.1 Hz, NH), 8.12 (lH, d, J=9.4 Hz, H-4), 7.99 (lH, d, J=9.4 Hz, H-5), 4.59 (3H, s, *N*-Me), 4.05 (3H, s, CO_2Me);

ii- Compound (*E*)-(**6c**) (0.49 g; 1.55 mmol) was added in small portions to polyphosphoric acid (**PPA**) (4.9 g) preheated at 100 °C. The temperature was then raised to 160 °C and the stirring continued for an additional 1 h. After cooling, the mixture was poured onto crushed ice and the resulting aqueous solution was made neutral (pH=7) by addition of conc. ammonium hydroxide solution. The resulting precipitate was filtered off obtaining **13** (0.06 g; 15% yield). Further amount of **13** (0.21 g; 53% yield) was obtained by extraction with chloroform of the mother liquors.

iii- Cyclization of (*E*)-**6c** (0.49 g; 1.55 mmol), carried out in Dowtherm (5 ml) at 250°C for 1 h, failed affording 88% of unreacted (*E*)-**6c**.

Addition reactions of (Z)/(*E*)-5c with DMAD.

Dimethyl 1-(2-methyl-2*H*-benzotriazol-5-yl)-2-oxo-2*H*-pyridine-3,4-dicarboxylate (8). i- A solution

of equimolar amounts (2.93 mmol) of (*E*)-**5c** and **DMAD** in dry acetonitrile (20 ml) was refluxed for 24 h. After evaporation of the solvent, the residue was taken up with ether and thoroughly triturated affording **8** (0.31 g, 31% yield), mp 187-188 °C (from ether). Anal. Calcd for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37. Found: C, 56.18; H, 4.07; N, 16.60. Ir: 3450, 1742, 1715, 1690 cm^{-1}; uv: λ_{max} 312 (4.08), 264 (4.65), 206 (4.90) nm; ^{1}H-nmr ($CDCl_3$): δ 8.27 (lH, s, H-6), 7.99 (lH, d, J=9 Hz, H-7'), 7.87 (lH, d, J=2 Hz, H-4'), 7.37 (lH, dd, J=9 and 2 Hz, H-6'), 6.69 (lH, s, H-3), 4.57 (3H, s, *N*-Me), 3.96 (3H, s, CO_2Me), 3.84 (3H, s, CO_2Me).

The ethereal mother liquors were evaporated *in vacuo* to give an oily residue which was chromatographed through a silica gel column, using a 1:1 mixture of ether-petroleum ether (60-80 °C) as eluent. Evaporation of the first fractions gave a small amount of (*Z*)-**5c** (0.12 g; 18% yield), identical to an autentical specimen previously isolated, and successively an additional amount of **8** (0.31 g; 31% yield).

ii- Following the above described procedure, a solution of equimolar amounts (4.3 mmol) of (*Z*)-**5c** and **DMAD** in acetonitrile (30 ml), heated under reflux for 48 h, afforded **8** (0.98 g; 68% yield).

Addition reaction of compound (9c) with MP.- A mixture of **9c** (0.55 g, 2.75 mmol) and **MP** (0.58 g, 6.9 mmol) in dry DMSO (10 ml) was heated at 70 °C for 3 h and then left standing for 65 h. After evaporation of the solvent *in vacuo*, the residue was washed with hot acetone and filtered off to give (*E*)-**21** (0.33 g, 42% yield), mp 228-230 °C from DMSO. Anal. Calcd for $C_{14}H_{12}N_4O_3$: C, 59.15; H, 4.26; N, 19.71. Found: C, 59.32; H, 4.30; N, 19.55. Ir: 1735, 1635, 1600, 1580; uv: λ_{max} 350, 338, 287, 259, 210 nm; ^{1}H-nmr ($CDCl_3$+DMSO-d_6): δ 8.44 (1H, d, J=14 Hz, H_a), 8.35 (1H, d, J=8.4 Hz, H-7), 8.24 (1H, d, J=9.2 Hz, H-4), 7.84 (1H, d, J=9.2 Hz, H-5), 6.54 (1H, d, J=14 Hz, H_X), 6.45 (1H, d, J=8.4 Hz, H-8), 4.58 (3H, s, *N*-Me), 3.81 (3H, s, CO_2Me); ^{13}C-nmr ($CDCl_3$+DMSO-d_6): δ 175.93 (s, C=O), 165.96 (s, C=O), 141.45 (s, C-3a), 140.91 (d, C-7), 140.25 (s, C-5a), 138.96 (s, C-9b), 138.39 (d, C-10), 123.54 (d, C-8), 116.81 (d, C-4), 115.62 (s, C-9a), 115.00 (d, C-5), 111.54 (d, C-11), 51.96 (q, *O*-Me), 43.42 (q, *N*-Me). The mother liquors, after evaporation of the solvent, gave a residue that on recrystallization from acetone produced **13** (4% yield) identical with an authentic sample described earlier.

Addition reaction of compound (9b) with MP.- To a solution of **9b** (0.78 g, 3.9 mmol) in boiling Dowtherm (10 ml), **MP** (5 ml, 6.25 mmol) was added and the mixture refluxed for 45 min. The work-up of the reaction mixture as described above gave a crude solid (0.88 g, 80% yield) of a mixture of (*Z*)/(*E*)

-**23** (tlc, $CHCl_3$/MeOH ratio 3:1 one spot) which was purified by silica gel column chromatography eluting with a mixture of $CHCl_3$-MeOH (ratio 3:1) and further recrystallization from methanol to give compound (*E*)-(**23**) as brownish dust, mp 270-275 °C. Anal. Calcd for $C_{14}H_{12}N_4O_3$+0.55 H_2O: C, 57.14; H, 4.42; N, 19.00. Found: C, 56.87; H, 4.44; N, 19.35. Ir: 1730, 1715, 1620, 1595 cm^{-1}; uv: λ_{max} 356, 344, 307, 295, 280 infl, 260, 205 nm; ^{1}H-nmr (d-TFA): δ 8.87 (1H, d, J=7.6 Hz, H-7), 8.76 (1H, d, J=13.7 Hz, H_a), 8.72 (1H, d, J=9.7 Hz, H-4), 8.59 (1H, d, J=9.7 Hz, H-5), 7.63 (1H, d, J=7.6 Hz, H-8), 6.93 (1H, d, J=13.7 Hz, H_X), 4.90 (3H, s, *N*-Me), 4.14 (3H, s, CO_2Me); ^{13}C-nmr (d-TFA): δ 175.87 (s, C=O), 168.39 (s, C=O), 147.06 (d, C-10), 142.24 (s, C-9b), 142.05 (d, C-7), 134.24 (s, C-5a), 133.15 (s, C-3a), 123.22 (d, C-8), 122.91 (d, C-11), 120.58 (d, C-4), 114.16 (d, C-5), 112.08 (d, C-9a), 54.63 (q, *O*-Me), 38.71 (q, *N*-Me).

8-Hydroxymethyl-9-(2-hydroxyethyl)-2-methyl-2*H*-triazolo[4,5-*f*]quinoline (16).- To a stirred suspension of lithium aluminum hydride (0.045 g; 1.15 mmol) in anhydrous ether (20 ml), a solution of **12** (0.24 g; 0.76 mmol) in the same solvent (30 ml) was slowly added. The resulting mixture was allowed to reflux for 12 h, cooled with an ice bath and the excess of lithium aluminum hydride destroyed by addition of water (3 ml) followed by 2M aqueous sodium hydroxide solution. The precipitated oxides were filtered off and thoroughly washed with ether. The organic solution was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The oily residue was purified by "flash" chromatography on silica gel column, using a mixture of ether with increasing amount of ethanol. Compound (**16**) was obtained as a solid (0.05 g; 25% yield) with mp 188-189 °C (from acetonitrile). Anal. Calcd for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.70. Found: C, 60.72; H, 5.69; N, 21.38. Ir: 3250 (strong) cm^{-1}; uv: λ_{max} 322, 307, 292 sh, 260, 217 nm; ^{1}H-nmr (DMSO-d_6): δ 8.72 (lH, s, H-7), 7.99 (lH, d, J=9 Hz, H-4), 7.81 (lH, d, J=9 Hz, H-5), 5.55 (lH, t, J=5.2 Hz, OH-12, collapses with D_2O), 4.81 (2H, d, J=5.2 Hz, CH_2-12), 4.75 (lH, t, J=4.2 Hz, OH-11, collapses with D_2O), 4.51 (3H, s, *N*-Me), 3.87 (2H, q, J=5 Hz, CH_2-11), 3.05 (2H, t, J=6.5 Hz, CH_2-10).

Reaction of 3,4-dimethoxyaniline with MP.- Following the procedure described by Harris,[10] a mixture of 3,4-dimethoxyaniline (Janssen) (4 g; 26.1 mmol) and **MP** (3.45 g; 41 mmol) was stirred at room temperature for 72 h. After dilution with chloroform (50 ml) the organic layer was washed with a 2M HCl aqueous solution, a 3% sodium hydrogencarbonate aqueous solution and eventually with water. The chloroformic phase was dried on dry sodium sulfate and evaporated *in vacuo* to give an oily residue

which after fractional recrystallization from boiling isopropanol afforded **17** (2.47 g; 29% yield), mp 128-130 °C. Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.80; H, 5.96; N, 4.36. Found: C, 59.63; H, 6.16; N, 4.15. Ir: 3380, 1735, 1680, 1630, 1570 cm-1; uv: λ_{max} 425, 309, 269, 242, 210 nm; ^{1}H-nmr ($CDCl_3$): δ 7.41 (lH, s, H-2), 6.59 (lH, s, H-8), 6.11 (lH, s, H-5), 4.86 (lH, dd, J=10.2 and 2.2 Hz, H-4), 3.84 (3H, s, CO_2Me), 3.79 (6H, s, 2 *O*-Me), 3.69 (3H, s, CO_2Me), 2.79 (1H, dd, J=10.2 and 16.7 Hz, CH_2-4), 2.35 (lH, dd, J=16.7 and 2.2 Hz, CH_2-4); and successively **18** (0.1 g; 1.1%), mp 139-140 °C. Anal. Calcd for $C_{16}H_{17}NO_6$: C, 60.18; H, 5.37; N, 4.39. Found: C, 60.01; H, 5.51; N, 4.41. Ir: 1740, 1720, 1620, 1600 cm^{-1}; uv: λ_{max} 340, 328, 305, 254 nm; ^{1}H-nmr ($CDCl_3$): δ 8.72 (lH, s, H-2), 7.40 (lH, s, H-8), 7.11 (lH, s, H-5), 4.38 (2H, s, CH_2-4), 4.04 (3H, s, *O*-Me), 4.03 (3H, s, *O*-Me), 3.94 (3H, s, CO_2Me), 3.72 (3H, s, CO_2Me).

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