1,3-Dipolar Cycloaddition Reactions with 1,2,3-Triazinium Ylides

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Dedicated to Professor Oleg N. Chupakhin on the occasion of his 70th birthday

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1,3-Dipolar cycloadditions were carried out with 1,2,3-triazinium 2-dicyanomethylylides **4** and deprotonated 2-ethyl-1,2,3-triazinium salts **2**. Pyrazolo[2,1-*a*]- and pyrazolo[1,2-*b*][1,2,3]triazines **5** and **9** were synthesized, representing new heterocyclic systems.

Introduction

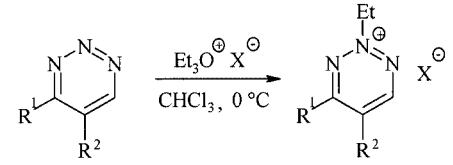
Since the 1960s 1,3-dipolar cycloadditions have often been used to synthesize heterocyclic ring systems.[1] In particular, the synthesis of nitrogen-bridged heterocycles such as indolizines through 1,3-dipolar cycloadditions with corresponding *N*-ylides is possible.[2,3] Electron-deficient dipolarophiles are normally used, initiating a dipole-*HO*-controlled reaction.[4] Recently, Miyakoshi published a reaction in which cyclooctyne was used as the dipolarophile, resulting in a dipole-*LO*-controlled 1,3-dipolar cycloaddition.[5]

In continuation of our work on the reactivity of 1,2,3-triazinium salts[6] we investigated the possibility of 1,3-dipolar cycloadditions with appropriate *N*-ylides. Ohsawa reported a reaction between 1,2,3-triazinium-*N*-imines and dimethyl acetylenedicarboxylate (DMAD) to provide products that were interpreted in terms of an intramolecular rearrangement of the primarily formed cycloaddition product.[7] With the use of less reactive ylides, however, it should be possible to isolate the expected cycloaddition product.

In this work we would like to publish the first 1,3-dipolar cycloaddition reaction with 1,2,3-triazinium *N*-ylides, affording new classes of bicyclic heterocycles.

Results and Discussion

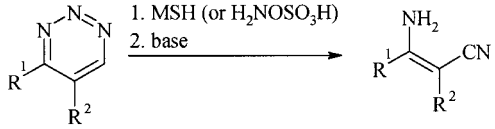
We concentrated in our work on monosubstituted 1,2,3-triazines **1**.[8] The 1,2,3-triazinium ylides used were synthesized by an electrophilic attack at the ring nitrogen atoms. As published, treatment with triethyloxonium salts provides 2-ethyl-1,2,3-triazinium salts **2** (Scheme 1).[6]



1a R^1 = Ph, R^2 = H — **2a** X = BF_4
1b R^1 = H, R^2 = Ph — **2b** X = BF_4
1c R^1 = CH_3, R^2 = H — **2c** X = PF_6
1d R^1 = H, R^2 = CH_3 — **2d** X = PF_6

Scheme 1. Ethylation of 1,2,3-triazines **1a**−**d** with triethyloxonium salts

In contrast with the known reactions of 4,6-disubstituted 1,2,3-triazines,[9] we were not able to aminate (and deprotonate) the monosubstituted 1,2,3-triazines **1**. Both *O*-(mesitylenesulfonyl)hydroxylamine (MSH) and hydroxylamine-*O*-sulfonic acid gave only 3-amino-2(3)-phenylacrylonitriles **3** (Scheme 2).



1a, b — **3a, b**

Scheme 2. Reaction of 1,2,3-triazines **1a** and **1b** with aminating reagents

We suggest that the reason for this unexpected result is the proton in the C-6 position in the 1,2,3-triazine **1**. After amination at N-2, ring opening occurs, resulting in the ob-

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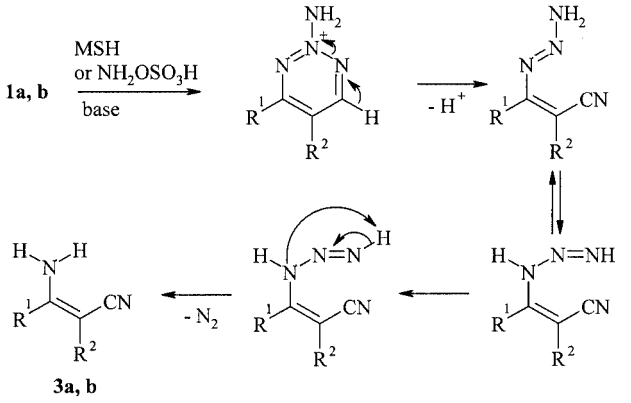
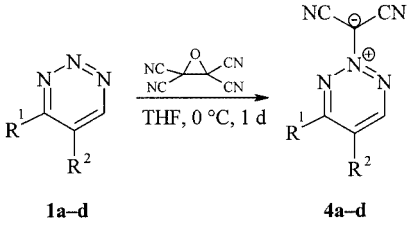


Scheme 3. Suggested reaction mechanism for the formation of **3**

served products (Scheme 3). 4,6-Disubstituted 1,2,3-triazines do not face this problem, and the isolation of 1,2,3-triazinium-*N*-imines is possible.[9]

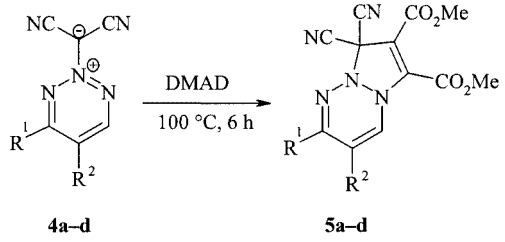
Since it was not possible to synthesize the desired 1,2,3-triazinium-*N*-imines, we looked for other ylide options. In our first approach to 1,3-dipolar cycloadditions we used 1,2,3-triazinium 2-dicyanomethylylides **4**, which are known to be very stable compounds.[10,11] By using tetracyanoethylene oxide (TCEO) and the known method we were able to isolate and completely characterise four new derivatives of 1,2,3-triazinium 2-dicyanomethylylides **4** (Scheme 4).



Scheme 4. Synthesis of 1,2,3-triazinium 2-dicyanomethylylides **4a**−**d**.

The isolated 2-dicyanomethylylides **4** are similar to the known pyridine[12] or pyrimidine[13] *N*-dicyanomethylylides and their reactivity towards dipolarophiles is also similar. These compounds react easily with activated dipolarophiles in dipole-*HO*-controlled cycloadditions, and so we used DMAD as an electron-deficient dipolarophile. Our experiments showed that the reaction proceeded best when no additional solvent was used.

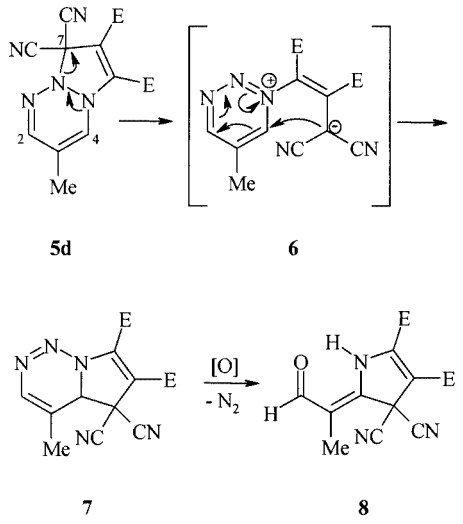
In a typical procedure, the 1,2,3-triazinium 2-dicyanomethylylide **4** was dissolved in DMAD and stirred at 100 °C (oil bath) for 6 h (Scheme 5). The formed products



Scheme 5. Synthesis of the pyrazolo[2,1-*a*][1,2,3]triazines **5a**−**d**

5 were isolated by liquid chromatography and completely characterised (see Exp. Sect. for details).

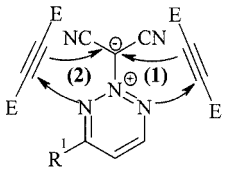
The isolated bicyclic compounds **5** are stable under inert gas at 0 °C. In solution ($CDCl_3$) we observed slow rearrangement to the bicyclic system **7**, which is oxidized during the workup procedure to form the aldehyde **8**. We suggest that this mechanism is initiated by the cleavage of the N-7a/C-7a bond and followed by a Claisen-type rearrangement/(1,5)-sigmatropic carbon shift (see Scheme 6). However, we did not observe any solvent effects.



Scheme 6. Suggested Claisen-type rearrangement of **5d** in $CDCl_3$ (E = CO_2CH_3)

Two recorded ^{1}H NMR spectra of **5d** showed characteristic differences. The first spectrum was recorded immediately after isolation of **5d** and showed the expected data (see Exp. Sect.). The second ^{1}H NMR spectrum was recorded after 24 h in solution and shows that the signal for the 2-H proton has shifted from δ = 8.83 ppm (**5d**) to δ = 8.23 ppm (**7**) and the proton signal at δ = 5.67 ppm (4-H) has disappeared. Correlated spectra showed a long-range coupling of the new proton (δ = 2.23 ppm) with the dicyano-substituted C-7 (^{13}C, δ = 6.66 ppm). These results are best explained by the mechanism suggested (Scheme 6). Product **7** could not be isolated in a pure state. Instead we observed the aldehyde **8**, which showed the typical ^{1}H NMR signal δ = 9.27 ppm (CHO) and the quaternary ^{13}C NMR signal at δ = 194.42 ppm. This product can be easily explained by nitrogen elimination and oxidation during the workup procedure.

In the case of the 4-substituted 1,2,3-triazinium 2-dicyano methylylides **4a** and **4c**, two orientations of the dipolarophile are possible (Figure 1). Path (1) leads to the isolated pyrazolo[2,1-*a*][1,2,3]triazines **5a** and **5c**, while path (2) would afford pyrazolo[1,2-*b*][1,2,3]triazines **9**.



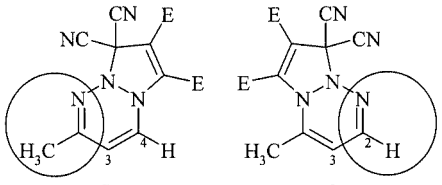
4a, c

Figure 1. The two possible orientations for the 1,3-dipolar cycloaddition reactions with compounds **4a** and **4c** (E = CO_2CH_3)

2a, b 10a, b

Scheme 7. 1,3-Dipolar cycloadditions with 2-ethyl-1,2,3-triazinium salts **2a** and **2b** (E = CO_2CH_3)

Only the reaction of 4-methyl-1,2,3-triazinium 2-dicyanomethylylide (**4c**) gave both products (Figure 2). The two structures can be distinguished by their mass spectra, in which the pyrazolo[2,1-*a*][1,2,3]triazine **5c** eliminates acetonitrile (*m*/*z* = 41) and pyrazolo[1,2-*b*][1,2,3]triazine **9** eliminates HCN (*m*/*z* = 27).



5c 9

Figure 2. 1,3-Dipolar cycloaddition products of 4-methyl-1,2,3-triazinium 2-dicyanomethylylide (**4c**) and DMAD (E = CO_2CH_3); characteristic mass losses are highlighted

In addition, the proton shifts of the 1,2,3-triazine ring protons are different (Table 1). The bicyclic system **9** has an imine function, in which the corresponding proton 2-H is shifted to lower field than the olefin function in **5c**. This structural difference can be observed in the ^{1}H NMR spectra by a proton shift of 0.31 (4-H/2-H).

Table 1. Proton shifts (CD_3CN) of the characteristic ring protons in compounds **5c** and **9**

Proton	**5c**	**9**
3-H	δ_H = 5.92	δ_H = 6.31
4-H (**5c**) / 2-H (**9**)	δ_H = 7.28	δ_H = 7.59

The recently synthesized 2-ethyl-1,2,3-triazinium salts **2a**–**d** were treated with weak bases in order to create triazinium ylides in situ. After several tests we finally succeeded in using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a non-nucleophilic base at room temperature. Treatment of **2a** and **2b** with DMAD gave two new pyrazolo[2,1-*a*]-[1,2,3]triazines (Scheme 7). The yields were poor, however, with many side reactions occurring, and the synthesized methyl-substituted 1,2,3-triazinium salts **2c** and **2d** decomposed quickly under similar reaction conditions.

Conclusion

We were able to complete 1,3-dipolar cycloaddition reactions with 1,2,3-triazinium ylides through the use of DMAD as dipolarophile. Those reactions gave fused ring systems, bridged over two nitrogen atoms. Those bicyclic systems were to the best of our knowledge previously unknown and represent two new classes of heterocycles. However, the reaction is very limited in terms of the use of dipolarophiles and substrates. Only reactions with highly electron-deficient dipolarophiles are possible, and only the reactions with DMAD afforded the expected pyrazolo-[1,2,3]triazines **5** and **9**. We tried to use several other dipolarophiles (such as malonate esters or malononitriles), but were not able to isolate the expected products. Problems occur due to the poor solubility of the starting materials **2** and **4**. If the 1,2,3-triazinium salts **4** did not dissolve in the dipolarophile used, no reaction was observed. In the case of the ethylated salts **2** it is not even possible to heat the reaction mixture without fast decomposition of the starting material. Additionally, no dipolarophiles with possible nucleophilic, acidic, or base character are possible without side reactions dominating.

Experimental Section

All reactions were carried out under Ar with purified solvents (p.a. from Merck, VWR International Inc., Darmstadt; dried with molecular sieves). IR spectra were obtained with a Nicolet impact 400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 300, ARX 300 and DRX 500 spectrometers with tetramethylsilane as internal standard. MS were determined with a Varian 212 instrument at 70 eV. Elemental analysis were obtained with Perkin–Elmer CHN 240 A or 240 B machines. Silica gel 60 (0.063–0.2 mm, 70–230 mesh ASTM) from FLUKA was used for column chromatography.

1,2,3-Triazinium *N*-Ylides 4. General Procedure: Tetracyanoethylene oxide (575 mg, 4.00 mmol) in THF (3 mL) was added dropwise to a cooled (0 °C) solution of the corresponding 1,2,3-triazine **1** (2.00 mmol) in THF (5 mL). The reaction was followed by TLC and stopped when no further changes were observed. The solvent was removed under reduced pressure, and the crude residue was purified by column chromatography (CH_2Cl_2/EtOAc, 5:1).

4-Phenyl-1,2,3-triazinium 2-Dicyanomethylylide (4a): Yield: 306 mg (69%) as yellow crystals, m.p. 196 °C (THF). IR (KBr): $\tilde{\nu}$ = 3118,

3048, 2967, 2209, 1533, 1436, 1328, 949, 771, 690 cm^{-1}. ^1H NMR (300 MHz, [D$_6$]acetone): δ = 8.88 (d, $^3J_{5,6}$ = 6.2 Hz, 1 H, 6-H), 8.18−8.15 (m, 2 H, Ph), 7.75−7.68 (m, 3 H, Ph), 7.55 (d, $^3J_{5,6}$ = 6.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75.7 MHz, [D$_6$]acetone): δ = 163.24 (C-4), 156.55 (C-6), 134.24, 132.13, 130.33, 128.27 (Ph), 113.63, 113.53 (CN), 105.75 (C-5) ppm. MS (EI, 70 eV): *m*/*z* (%) = 222 (13) [M$^+$ + 1], 221(100) [M$^+$], 195 (7), 167 (9), 142 (11), 129 (21), 116 (6), 103 (52), 89 (11), 77 (68), 63 (16), 51 (27), 39 (15). $C_{12}H_7N_5$ (221.22): calcd. C 65.15, H 3.19, N 31.66; found C 65.34, H 3.26, N 31.40. HRMS: calcd. for $C_{12}H_7N_5$ 221.0702; found 221.0704.

5-Phenyl-1,2,3-triazinium 2-Dicyanomethylylide (4b): Yield: 301 mg (68%) as light brown crystals; dec. 280 °C (THF). IR (KBr): ṽ = 3110, 3086, 2928, 2201, 1598, 1424, 972, 775, 686 cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 9.53 (s, 2 H, 4-H, 6-H), 7.95 (m$_c$, 2 H, Ph), 7.57 (m$_c$, 3 H, Ph) ppm. ^{13}C NMR (75.7 MHz, [D$_6$]DMSO): δ = 152.52 (C-4, C-6), 130.53, 129.87, 129.51, 126.23 (Ph), 120.79 (C-5), 113.75 (CN) ppm. MS (EI, 70 eV): *m*/*z* (%) = 222 (12) [M$^+$ + 1], 221 (100) [M$^+$], 195 (2), 167 (4), 142 (26), 129 (7), 115 (24), 102 (65), 89 (9), 76 (20), 63 (17), 51 (15), 39 (11). $C_{12}H_7N_5$ (221.22): calcd. C 65.15, H 3.19, N 31.66; found C 65.24, H 3.21, N 31.55. HRMS: calcd. for $C_{12}H_7N_5$ 221.0702; found 221.0715.

4-Methyl-1,2,3-triazinium 2-Dicyanomethylylide (4c): Yield: 134 mg (42%) as yellow crystals; m.p. 183 °C (THF). IR (KBr): ṽ = 3118, 3056, 2967, 2213, 1560, 1540, 1424, 1324, 941 cm^{-1}. ^1H NMR (300 MHz, [D$_6$]acetone): δ = 8.69 (d, $^3J_{5,6}$ = 2.0 Hz, 1 H, 6-H), 6.94 (d, $^3J_{5,6}$ = 2.0 Hz, 1 H, 5-H), 2.52 (s, 3 H, 4-CH$_3$) ppm. ^{13}C NMR (75.7 MHz, [D$_6$]acetone): δ = 167.83 (C-4), 155.40 (C-6), 113.59 (CN), 109.95 (C-5), 21.56 (4-CH$_3$) ppm. MS (EI, 70 eV): 160 (11) [M$^+$ + 1], 159 (100) [M$^+$], 120 (9), 105 (33), 91 (23), 80 (8), 66 (24), 53 (22), 40 (29). $C_7H_5N_5$ (159.15): calcd. C 52.83, H 3.17, N 44.00; found C 52.94, H 3.14, N 43.89 HRMS: calcd. for $C_7H_5N_5$ 159.0545; found 159.0528.

5-Methyl-1,2,3-triazinium 2-Dicyanomethylylide (4d): Yield: 232 mg (73%) as yellow crystals; dec. 206 °C (THF). IR (KBr): ṽ = 3099, 3056, 2979, 2209, 2194, 1598, 1440, 1007, 774 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]acetone): δ = 8.69 (s, 2 H, 4-H, 6-H), 2.22 (s, 3 H, 5-CH$_3$) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 156.91 (C-4, C-6), 130.66 (C-5), 118.91, 114.01 (CN), 74.82 (C-1),[14] 15.30 (5-CH$_3$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 159 (100) [M$^+$], 106 (4), 91 (20), 78 (13), 64 (37), 52 (33), 39 (61). $C_7H_5N_5$ (159.15): calcd. C 52.83, H 3.17, N 44.00; found C 52.98, H 3.20, N 43.81. HRMS: calcd. for $C_7H_5N_5$: 159.0545; found 159.0570.

Pyrazolo[2,1-*a*]- and [1,2-*b*][1,2,3]triazines 5 and 9. General Procedure: The 1,2,3-triazinium 2-dicyanomethylylide (0.32 mmol) was dissolved in dimethyl acetylenedicarboxylate (1.5 mL, 12.2 mmol), and the mixture was heated at 100 °C for 6 h (oil bath temperature). The reaction was followed by TLC and stopped when no further changes were observed. The reaction mixture was purified by column chromatography (cyclohexane/EtOAc, 1:1).

Pyrazolo[2,1-*a*][1,2,3]triazine 5a: First fraction (R_f = 0.71): Yield: 8.00 mg (6%) **5a** as a red oil. IR (KBr): ṽ = 3068, 2959, 2256, 2232, 2128, 1737, 1451, 1307, 1223, 1069, 767, 697 cm^{-1}. ^1H NMR (500 MHz, CD$_3$CN): δ = 8.18 (d, $^3J_{2,3}$ = 16.7 Hz, 1 H, 4-H), 7.77−7.76 (m, 2 H, Ph), 7.58−7.54 (m, 3 H, Ph), 5.90 (d, $^3J_{2,3}$ = 16.7 Hz, 1 H, 3-H), 3.91, 3.90 (2 s, 6 H, OCH$_3$). ^{13}C NMR (125 MHz, CD$_3$CN): δ = 165.97 (q, C-2), 154.85, 154.17 (C=O), 143.58 (C-5), 142.13 (C-4), 133.02, 130.11, 129.25, 126.59 (Ph), 119.99, 118.28 (CN), 110.72 (C-3), 103.43 (C-6), 52.58, 52.43 (OCH$_3$), 9.59 (C-7) ppm. MS (EI, 70 eV): *m*/*z* (%) = 364 (9) [M$^+$ + 1], 363 (42) [M$^+$], 332 (8), 254 (20), 229 (60), 178 (18), 154 (100), 140 (49), 103 (38), 77 (84), 51 (28). HRMS: calcd. for $C_{18}H_{13}N_5O_4$: 363.0968; found 363.1012.

Pyrazolo[2,1-*a*][1,2,3]triazine 5b: First fraction (R_f = 0.58): Yield: 53.0 mg (46%) **5b** as a red oil. IR (KBr): ṽ = 3060, 2959, 2225, 1734, 1444, 1308, 1215, 1076, 767, 701 cm^{-1}. ^1H NMR (500 MHz, CD$_3$CN): δ = 8.57 (d, $^4J_{2,4}$ = 1.4 Hz, 1 H, 2-H), 7.44−7.38 (m, 5 H, Ph), 6.12 (d, $^4J_{2,4}$ = 1.4 Hz, 1 H, 4-H), 3.83 (s, 6 H, OCH$_3$) ppm. ^{13}C NMR (125 MHz, CD$_3$CN): δ = 158.38 (C-2), 155.45, 153.07 (C=O), 142.14 (C-5), 133.72, 132.22, 130.14, 127.65 (Ph), 111.24 (CN), 108.47 (C-6), 105.82 (C-3) 100.20 (C-4), 53.72, 53.61 (OCH$_3$), 15.80 (C-7) ppm. MS (EI, 70 eV): *m*/*z* (%) = 364 (9) [M$^+$ + 1], 363 (34) [M$^+$], 332 (13), 272 (15), 229 (14), 178 (23), 154 (100), 127 (28), 101 (10), 77 (21), 59 (10). HRMS: calcd. for $C_{18}H_{13}N_5O_4$: 363.0968; found 363.0994.

Pyrazolo[2,1-*a*][1,2,3]triazine 5c and Pyrazolo[1,2-*b*][1,2,3]triazine 9: First fraction (R_f = 0.57): Yield: 16.0 mg (16%) **9** as a red oil. IR (KBr): ṽ = 3083, 2963, 2248, 2232, 1753, 1726, 1440, 1312, 1084, 972, 775 cm^{-1}. ^1H NMR (500 MHz, CD$_3$CN): δ = 7.59 (d, $^3J_{2,3}$ = 16.6 Hz, 1 H, 2-H), 6.31 (d, $^3J_{2,3}$ = 16.6 Hz, 1 H, 3-H), 3.91, 3.90 (2 s, 6 H, OCH$_3$), 2.53 (s, 3 H, 4-CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 168.30 (C-4), 161.54, 160.77 (C=O), 142.31 (C-5), 141.34 (C-2), 111.69 (C-3), 120.84, 117.31 (CN), 108.82 (C-6), 53.64, 53.58 (OCH$_3$), 21.50 (4-CH$_3$), 16.67 (C-7) ppm. MS (EI, 70 eV): *m*/*z* (%) = 302 (7) [M$^+$ + 1], 301 (38) [M$^+$], 286 (50), 270 (48), 259 (19), 242 (12), 229 (100), 210 (39), 190 (13), 178 (55), 158 (16), 93 (59), 78 (22), 66 (39), 59 (59), 52 (74), 42 (35). HRMS: calcd. for $C_{13}H_{11}N_5O_4$: 301.0811; found 301.0860.

Second fraction (R_f = 0.48): Yield: 41.0 mg (42%) **5c** as a red oil. IR (KBr): ṽ = 3064, 2959, 2244, 2225, 1749, 1482, 1440, 1227, 1076, 871, 798, 786 cm^{-1}. ^1H NMR (500 MHz, CD$_3$CN): δ = 7.28 (d, $^3J_{3,4}$ = 12.5 Hz, 1 H, 4-H), 5.92 (d, $^3J_{3,4}$ = 12.5 Hz, 1 H, 3-H), 3.91, 3.90 (2 s, 6 H, OCH$_3$), 2.62 (s, 3 H, 2-CH$_3$) ppm. ^{13}C NMR (125 MHz, CD$_3$CN): δ = 168.09 (q, C-2), 161.59, 160.72 (C=O), 143.64 (C-4), 142.08 (C-5), 120.50 (CN), 108.79 (C-6), 105.73 (C-3), 53.78, 53.58 (OCH$_3$), 23.65 (2-CH$_3$), 14.53 (C-7) ppm. MS (EI, 70 eV): *m*/*z* (%) = 302 (3) [M$^+$ + 1], 301 (26) [M$^+$], 286 (12), 270 (24), 245 (10), 229 (100), 210 (16), 178 (20), 93 (52), 80 (11), 52 (38), 42 (26). HRMS: calcd. for $C_{13}H_{11}N_5O_4$: 301.0811; found 301.0837.

Pyrazolo[2,1-*a*][1,2,3]triazine 5d: First fraction (R_f = 0.56): Yield: 22.0 mg (23%) **5d** as a red oil. IR (KBr): ṽ = 2971, 2372, 1718, 1440, 1359, 1324, 1212, 1034, 806, 744, 635 cm^{-1}. ^1H NMR (500 MHz, CD$_3$CN): δ = 8.83 (s, 1 H, 2-H), 5.67 (s, 1 H, 4-H), 3.93, 3.91 (2 s, 6 H, OCH$_3$), 2.34 (s, 3 H, 3-CH$_3$) ppm. ^{13}C NMR (125 MHz, CD$_3$CN): δ = 154.41 (C-2), 151.74, 151.62 (C=O), 144.00 (C-6), 116.90 (C-3), 111.34 (CN), 109.69 (C-4), 105.92 (C-5), 52.90, 52.67 (2 OCH$_3$), 16.59 (C-7), 14.41 (3-CH$_3$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 302 (1) [M$^+$ + 1], 301 (10) [M$^+$], 274 (100), 243 (36), 215 (10), 178 (11), 158 (15), 91 (10), 78 (11), 59 (31), 42 (18), 34 (18). HRMS: calcd. for $C_{13}H_{11}N_5O_4$: 301.0811; found 301.0773.

Dimethyl 4,4-Dicyano-5-(1-methyl-2-oxoethylidene)-4,5-dihydro-1*H*-pyrrole-2,3-dicarboxylate (8): Pyrazolo[2,1-*a*][1,2,3]triazine (**5d**, 22 mg, 73.09 mmol) was dissolved in CD$_3$CN (0.7 mL) and allowed to stand at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (cyclohexane/EtOAc, 1:1). It was not possible to isolate either product **7** nor product **8** in a pure state. Instead we obtained a mixture with compound **8** as the main product (> 90%), which could be easily distinguished in the NMR spectra, but no appropriate mass spectra could be recorded. First fraction (R_f =

0.67): Yield: 14.0 mg. ^{1}H NMR (500 MHz, CD_3CN): δ = 9.27 (s, 1 H, CHO), 3.92, 3.89 (2 s, 6 H, OCH_3), 5.12 (br. s, 1 H, N−H), 2.28 (s, 3 H, 3-CH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 194.42 (C-2′), 152.89, 151.32 (C=O), 144.00 (C-2), 131.12 (C-5), 124.23 (C-1′), 116.90 (C-3), 112.01 (CN), 51.79, 50.98 (2 OCH_3), 18.12 (CH_3), 15.68 (C-4) ppm.

Pyrazolo[2,1-*a*][1,2,3]triazines 10. General Procedure: The 2-ethyl-1,2,3-triazinium tetrafluoroborate (**2a, 2b**, 200 mg, 0.73 mmol) was dissolved in CH_2Cl_2 (20 mL), and DBU (111 mg, 0.73 mmol) was added at room temperature. Immediately after the addition of DBU a solution of dimethyl acetylenedicarboxylate (0.1 mL, 0.81 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The reaction was followed by TLC and stopped when no further changes were observed. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography (cyclohexane/EtOAc, 1:1).

Pyrazolo[2,1-*a*][1,2,3]triazine 10a: First fraction (R_f = 0.72): Yield: 14.0 mg (6%) **10a** as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3052, 2973, 1722, 1459, 768, 696 cm^{-1}. ^{1}H NMR (500 MHz, [D_6]acetone): δ = 7.88 (d, $^3J_{3,4}$ = 7.5 Hz, 1 H, 4-H), 7.44−7.39 (m, 5 H, Ph), 5.93 (m_c, 1 H, 7-H), 5.72 (d, $^3J_{3,4}$ = 7.5 Hz, 1 H, 3-H), 3.81, 3.61 (2 s, 6 H, OCH_3), 2.24 (d, ^3J = 7.2 Hz, 3 H, 7-CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 328 (21) [M^+ + 1], 327 (96) [M^+], 268 (100), 252 (7), 236 (100), 220 (12), 209 (67), 185 (100), 152 (22), 128 (10), 77 (10), 59 (11). HRMS: calcd. for $C_{17}H_{17}N_3O_4$: 327.1212; found 327.1261.

Pyrazolo[2,1-*a*][1,2,3]triazine 10b: First fraction (R_f = 0.69): Yield: 19.0 mg (8%) as a light yellow oil. IR (KBr): $\tilde{\nu}$ = 2986, 2952, 1726, 1602, 1440, 1250, 763, 701 cm^{-1}. ^{1}H NMR (500 MHz, CD_3CN): δ = 7.33−7.12 (m, 5 H, Ph), 6.97 (s, 1 H, 2-H), 6.06 (m_c, 1 H, 7-H), 3.80, 3.67 (2 s, 6 H, OCH_3), 3.61 (s, 1 H, 4-H), 2.27 (m_c, 3 H, 7-CH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 167.98, 165.98 (C=O), 153.12 (C-5), 136.99 (C-3), 133.70 (C-2), 131.20, 129.32, 128.19, 125.48 (Ph), 110.06 (C-6), 108.20 (C-7), 54.48, 53.24 (OCH_3), 52.27 (C-4), 16.51 (7-CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 328 (10) [M^+ + 1], 327 (36) [M^+], 268 (58), 267 (60), 236 (100), 220 (10), 209 (46), 194 (23), 180 (36), 165 (11), 152 (13), 111 (10), 77 (9). HRMS: calcd. for $C_{17}H_{17}N_3O_4$: 327.1212; found 327.1219.

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[14] The ^{13}C NMR signal of the ylide atom C-1 is only observable in the 125 MHz spectrum of **4d**. In all other recorded spectra the intensity of the signal is too poor.

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