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Reactivity of [1,2,3]Triazolo[1,5-*a*]pyridines as 1,3-dipoles

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ABSTRACT

We have studied the reactions between [1,2,3]Triazolo[1,5-*a*]pyridines **1a,b,c** and electron-deficient ethylenes in different conditions. Compounds **1a** and **1b** react with ethyl propiolate, and dimethyl acetylene dicarboxylate giving a new class of biaryl compounds pyridyl pyrazoles, and with ethyl acrylate giving pyridyl cyclopropanes. Compound **1c** did not give any product in the studied conditions. A proposal of mechanism of these reactions is done in which the triazolopyridines act as 1,3-dipoles giving 1,3-dipolar cycloadditions.

1. Introduction

1,3-Dipolar cycloaddition between diazo compounds and electron-deficient (ED) ethylenes constitutes still nowadays an attractive approach for acceding to the interesting pyrazole motif.[1] Pyrazoles are considered privileged scaffolds due to their presence in many drugs and phytosanitary. The description of novel ED ethylenes which can become to more substituted pyrazoles by a 1,3-dipolar cycloaddition, or Lewis acid catalyzed cycloadditions, have been key discoveries in the field. However, one of the major drawbacks of this reaction is still the use of diazo compounds, due to their toxicity and potentially explosive nature.

[1,2,3]Triazolo[1,5-*a*]pyridines **1** have shown to present an equilibrium in solution with its corresponding 2-pyridyl diazo-compound **2**.[2,3] Few examples of triazolopyridines reactivity as diazo compounds, that involve the loss of nitrogen, can be found (Scheme 1). Quinolizin-2,4-dione, ylides or cyclopropanes can be obtained from triazolopyridines by flash vacuum thermolysis **(a)**,[4] photolysis **(b)**,[5] or thermic treatment **(c)**,[2a,6] respectively, through the formation of a carbene. More recently Gevorgyan et al. **(d)** have shown that cyclopropanes and indolizines can be obtained from triazolopyridines through the formation of a rhodium or copper carbene.[7] Only one mechanistic proposal of a 1,3-dipolar cycloaddition of the diazo compound derived from triazolopyridine can be found in literature. In this case, a cyclopropane is obtained by thermal treatment of a triazolopyridine in the presence of fumaronitrile **(e)**, and the authors propose that this occurs through the formation of a pyrazoline intermediate.[2a] However, there is no any example in literature in which triazolopyridine in its open form of diazo compound is able to react with an ED ethylene to form the interesting pyridine pyrazole structure.

In this work we intend to explore the behavior of stable [1,2,3]triazolo[1,5-*a*]pyridines **1a** (R = H), **1b** (R = CH_3) and **1c** (R = Ph) as 1,3-dipoles using as (ED) ethylenes ethyl propiolate (EP), dimethyl acetylene dicarboxylate (DMAD), and ethyl acrylate (EA). This reaction would afford the interesting pyridine pyrazoles, a new class of biaryl compounds. Moreover, the use of triazolopyridines as 1,3-dipoles would imply an advance in its chemistry since they should act as stable diazo compounds.

2. Results and discussion

Firstly, the reaction of [1,2,3]triazolo[1,5-*a*]pyridine **1a** in presence of 3 equivalents of EP was performed at 150 °C, using dimethylformamide (DMF) as solvent and reaction time of 24 h (Scheme 2). To our delight, in these conditions the pyridyl pyrazole **3** was obtained as major product with 44% of yield, together with minor regioisomer **4** (Table 1, entry 1). Compound **3** was obtained as a

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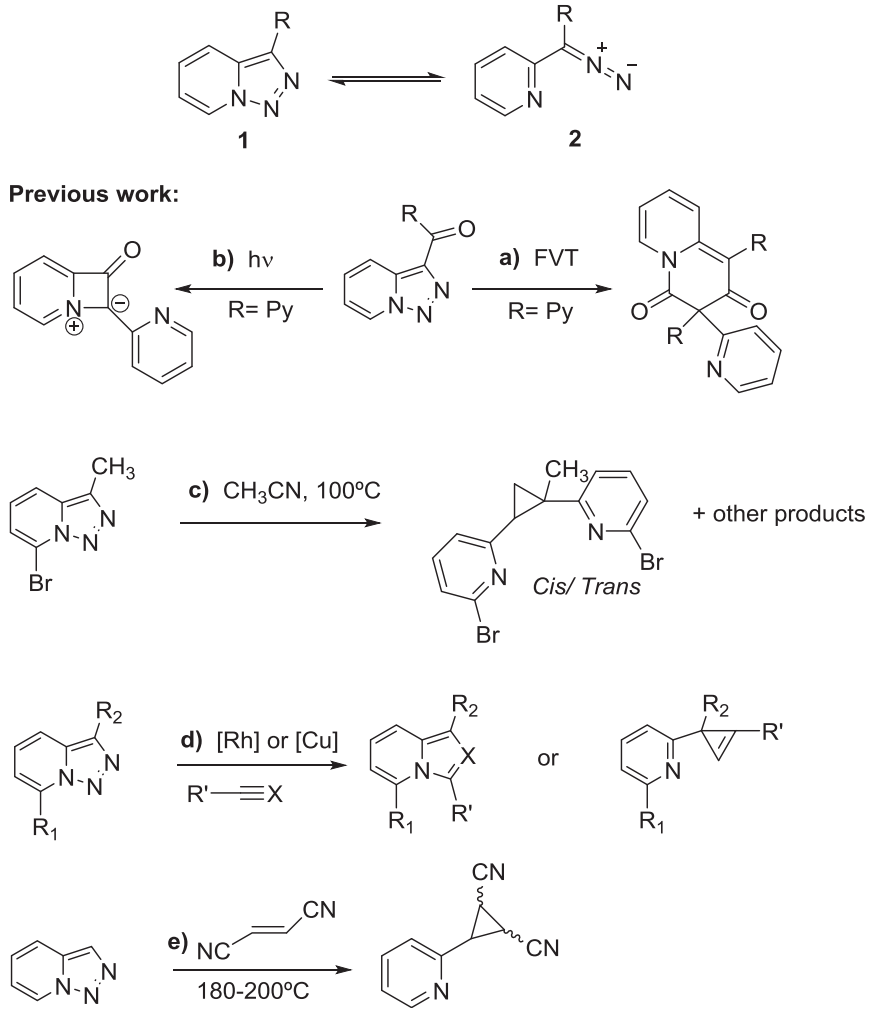
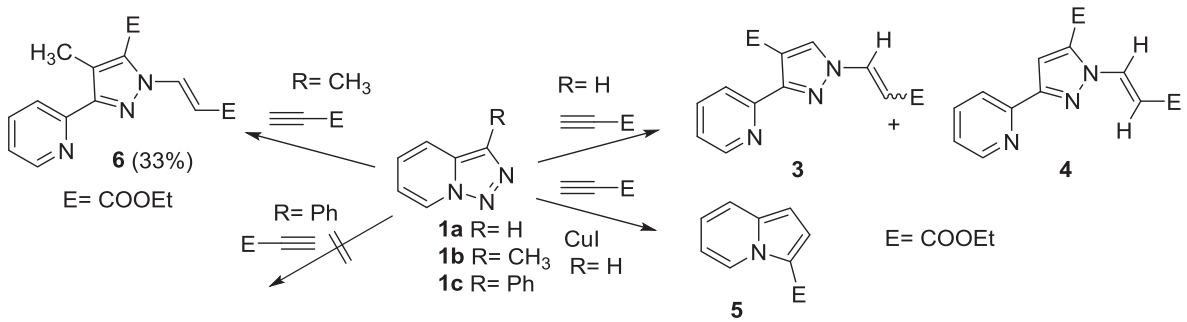


Scheme 1. Ring chain isomerization and reactions known as diazo compounds of [1,2,3]Triazolo[1,5-*a*]pyridines.



Scheme 2. Reaction of triazolopyridines **1a-c** with ethyl propiolate, toluene, 150 °C, 24 h.

mixture of E and Z isomers. The most significate NMR characteristic of these compounds are the coupling constant of the alkene hydrogens, 9.9 Hz for *Z* and 13.8 Hz for *E* isomers, and the pyrazole proton in both compounds that appears at 7.6 ppm as a singlet. The pyrazole **4** (10%) has a singlet at 7.19 ppm more shielded than pyrazole proton in compound **3** due to the anisotropic effect of 2-pyridyl substituent, and only the *E* isomer was detected.

The effect of different solvents in the reaction, dichloromethane (DCM), acetonitrile (AcN) and toluene, was explored (Table 1, entries 2–4), concluding that the best yield for pyridyl pyrazole **3** (65%) was obtained with toluene. Then, the reaction was performed with different amounts of EP (Table 1, entries 5 and 6) demonstrating that a minimum amount of 3 equivalents of ED ethylene was required for obtaining good yields of **3**. Different reaction temperatures were also tested (Table 1, entries 7 and 8), concluding that at 150 °C the best results were obtained. In addition, at a prolonged reaction time of 72 h better yields of **3** were obtained (Table 1, entry 10).

The reaction between triazolopyridine **1a** and EP was also performed in presence of 7 mol % of several Lewis acids (CuI,

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Table 1
- Reaction of triazolopyridine **1a** with ethyl propiolate in different conditions.[a]

Entry	Solvent	EP (eq)	t (h)	Temperature (°C)	Yield (%)		**3**
					3	**4**	*Z*: *E*
1	DMF	3	24	150	44	10	0.36: 1
2	Toluene	3	24	150	65	10	0.63: 1
3	DCM	3	24	150	60	19	0.72: 1
4	AcN	3	24	150	64	20	0.58: 1
5	Toluene	5	24	150	61	24	0.66: 1
6	Toluene	2	24	150	46	15	0.49: 1
7	Toluene	3	24	130	34	13	0.56: 1
8	Toluene	3	24	180	57	26	0.43: 1
9	Toluene	3	15	150	41	20	0.51: 1
10	Toluene	3	72	150	70	23	0.49: 1

[a] Standard reaction conditions: triazolopyridine (0.85 mmol, 100 mg), 24 h, solvent (6 ml) in autoclave.

$Rh_2(OAc)_4$, $NiCl_2$,$FeCl_3$ and $AuCl_3$) with the aim to check whether these species could act as catalysts. Unfortunately, none of them afforded better yields of the desired pyridyl pyrazoles. However, it is interesting to note that when CuI was used with 1.1 equivalents of EP, the substituted indolizine **5** (Scheme 2) was obtained selectively with 22% yield. A high selectivity to indolizines from triazolopyridines in the presence of alkynes, catalyzed by copper species, has been recently reported by Gevorgyan et al.[7c]

Next, the reactivity of 3-methyl and 3-phenyl triazolopyridines **1b** and **1c** in presence of EP was investigated (Scheme 2). In the case of 3-methyl triazolopyridine **1b**, pyridyl pyrazole **6** was obtained in moderate yields. In the studied conditions, 3-phenyl triazolopyridine **1c** did not give any product.

With the aim of enlarging the structural diversity of pyridyl pyrazole biaryls, reactions between DMAD and triazolopyridines **1a** and **1b** were performed in DMF at 150 °C during 24 h (Scheme 3). In the case of triazolopyridine **1a**, trisubstituted and tetrasubstituted pyrazoles **7** and **8** were formed in 27% and 19% yield respectively. Triazolopyridine **1b** in the same reaction conditions gave place to *3H*-pyrazole **9** in 63% of yield as unique product.

At this point it was interesting to check the reactivity of [1,2,3] triazolo[1,5-*a*]pyridines with EA (Scheme 4). Triazolopyridine **1a** gave rice to cyclopropane **10a** in high yields (88%, obtained as a mixture of *Z*/*E* isomers) at 150 °C, using DMF as solvent and 3 equivalents of the ED ethylene (Table 2, entry 1). Both isomers could be isolated by chromatotron.

Further mitigation of reaction temperature or ED ethylene amount (Table 2, entries 3 and 4) afforded the pyridyl cyclopropanes **10a** in lower yields. In addition, triazolopyridine **1b** also underwent this reaction forming the corresponding pyridyl cyclopropanes **10b**, in 61% of isolated yield, with a better selectivity to the *E* isomer, using toluene as solvent (Table 2, entry 7). The structures of the isomers have been elucidated by NOE-dif and NOESY experiment (see Supporting Information).

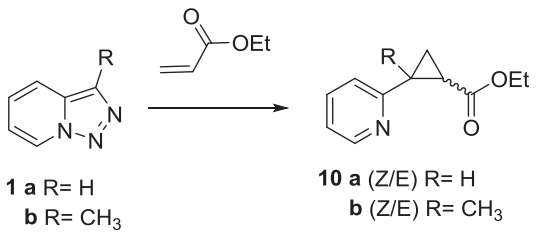
To explain all these results a mechanism based in the tautomeric equilibrium triazolopyridine **1**-diazocompound **2** is proposed (Scheme 5). The diazocompound forms, as 1,3-dipoles, react non-regioselectively with ED ethylenes, EP, DMAD or EA to give the intermediates **A** or **B**. These intermediates are unstable and therefore are able to react with another molecule of EP or DMAD in an *aza ene* reaction[8] to afford compounds **3**, **4** and **8**. From intermediate **A** when R = Me and R' = H a 1,2-shift of methyl group could give a new intermediate **C** that by reaction with another molecule of EP, in an *aza ene* reaction, explain the formation of compound **6**. Compound **7** can be explained by a 1,2-shift of hydrogen atom from the intermediate **B**. When R' = E and R = CH_3, intermediate **B** is stable as *3H*-pyrazol **9**.

The formation of compound **5** can be explained by the formation of a carbene intermediate **D** in a similar way as Gevorgian described.[7]

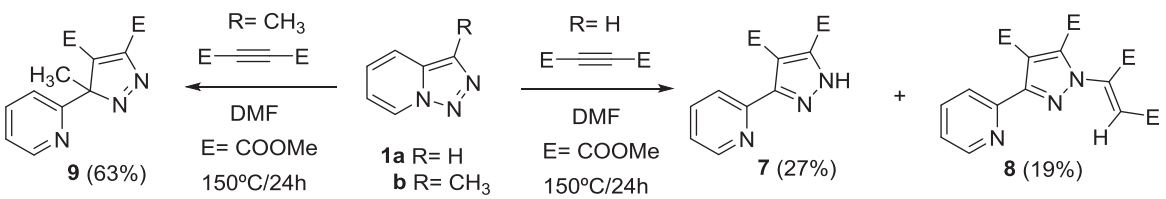
The intermediates derived from the reactions with EA cannot give an aromatic system, therefore they undergo loss of nitrogen, as has been described, to afford a diradical **E**.[9] This diradical collapses to give cyclopropanes **10a**,**b** as Wentrup reported for the thermal decomposition of triazolopyridine in presence of fumaronitrile.[2a]

3. Conclusion

The triazolopyridines **1a** and **1b** act as 1,3-dipoles through its tautomeric form of diazocompounds. New biaryl compounds pyridyl pyrazoles **3, 4, 6, 7, 8** and **9** are obtained by reaction with EP and DMAD. Reaction with EA gives pyridyl cyclopropanes **10a, b** in good



Scheme 4. Reaction of triazolopyridines **1a** and **1b** with ethyl acrylate.



Scheme 3. Reactions of triazolopyridines **1a,b** with dimethyl acetylenedicarboxylate.

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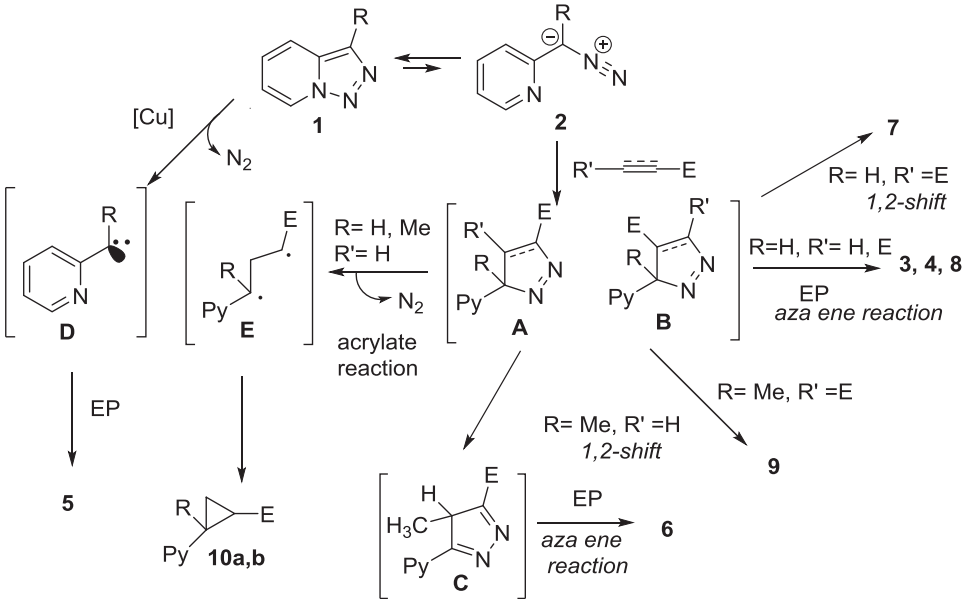
Table 2
- Reaction of triazolopyridines **1a** and **1b** with ethyl acrylate.[a]

Entry	Starting material	Solvent	Temp. (°C)	EA (eq)	Yield (%) **10**	**10** ratio *Z: E*
1	**1a**	DMF	150	3	88	0.66: 1
2	**1a**	Toluene	150	3	67	0.66: 1
3	**1a**	DMF	100	3	45	0.64: 1
4	**1a**	DMF	150	1.1	70	0.66: 1
5[b]	**1b**	DMF	150	3	41	0.47:1
6[b,c]	**1b**	DMF	150	3	55	0.45:1
7[b]	**1b**	Toluene	150	3	61	0.22: 1

[a] Standard reaction conditions: triazolopyridine (0.85 mmol, 100 mg), 24 h, solvent (6 ml) in autoclave.
[b] (E)-ethyl 4-(pyridin-2-yl)-but-3-enoate was formed as by-product in 7% (entry 5), 10% (entry 6) and 1% (entry 7).
[c] The reaction was run during 72 h.



Scheme 5. Mechanistic proposal.

yields. The mechanism of formation of these compounds can be explained starting by a 1,3-dipolar cycloaddition.

4. Experimental

4.1. General methods

Melting points were determined on a Kofler heated stage and are uncorrected. NMR spectra were recorded on a Bruker AC300 MHz in $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported in δ units, parts per million (ppm) and were measured relative to the signals for residual chloroform (7.27 ppm). COSY experiments were done for all compounds. In some cases Dif-NOE or NOESY experiment was carried out. HRMS Electron Impact (EI). Quadrupole time of flight (QqTOF) 5600 system (Applied Biosystems-MDS Sciex). Positive mode. Conditions: Gas1 35 psi, GS2: 35, CUR: 25, temperature: 450 °C, ion spray voltage: 5500 V. Collision energy (CE): 25–35 V. IR spectra were recorded using a Thermo-scientific Nicolet FT IR iS10 ATR. Column chromatography was carried out on a column packed with silica-gel 60 N spherical neutral size 63–210 μm. Cromatotron were used in several cases. All starting products used are from commercial sources (Aldrich). [1,2,3]Triazolo[1,5-*a*]pyridine **1a**,[10] 3-methyl-[1,2,3]Triazolo[1,5-*a*] pyridine **1b**,[11] and 3-phenyl-[1,2,3] triazolo[1,5-*a*]pyridine **1c**,[11] are synthesized as described elsewhere.

4.2. General procedure

To a solution of the corresponding triazolopyridine (100 mg) in DMF, reagent (3 eq), with catalyst (7 mol%) o without if is the case, were added. The mixture was charged in an autoclave and was maintained at 150 °C for 24 h. After cooling to room temperature, reaction mixture was filtered and washed with dichloromethane. Then, water was added and was extracted with dichloromethane. Organic solvent was evaporated and dried giving a residue which was purified by chromatotron, eluting firstly with hexane and then with mixtures ethyl acetate/hexane at increasing polarity.

4.2.1. Reaction with ethyl propiolate

4.2.1.1. Using as substrate [1,2,3]triazolo[1,5-a]pyridine *1a*

*4.2.1.1.1. (E)-Ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(pyridin-2-yl)-1H-pyrazole-4-carboxylate **3**(E).* White solid mp. 126-127 °C: IR (ATR) (cm^{-1}) 3317, 3106, 2978, 2917, 1718, 1693, 1637, 1543, 1515, 1443, 1393, 1288, 1216, 1182, 1152, 1080, 1021, 988, 955, 852, 783, 766, 730, 694. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.99 (d, J = 13.8 Hz, 1H), 8.65 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 8.10 (ddd, J = 7.6, 1.1, 0.9 Hz, 1H), 7.78 (ddd, J = 7.6, 7.6, 1.8 Hz, 1H), 7.67 (s, 1H), 7.28 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.76 (d, J = 13.8 Hz, 1H), 4.40 (c, J = 7.1 Hz, 2H), 4.28 (c, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 4H). ^{13}C NMR (75 MHz, Cl_3CD) δ 166.5 (CO), 159.1 (CO), 153.6 (C), 150.4 (C), 149.7 (CH), 138.1 (CH), 137.0 (CH), 134.9 (C), 123.9 (CH), 120.8 (CH),

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113.1 (CH), 109.6 (CH), 61.9 (CH2), 60.7 (CH2), 14.5 (CH3), 14.3 (CH3). MS (Q-TOF) *m/z* (%):316 (27), 288 (37), 260 (100), 242 (7), 216 (4), 198 (7), 190 (3), 172 (15), 146 (5), 116 (4). HRMS (ESI-TOF) *m/z* C16H18N3O4 (M^++1): 316.1292, found 316.1293.

*4.2.1.1.2. (Z)-Ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(pyridin-2-yl)-1H-pyrazole-4-carboxylate **3**(Z).* Yellow solid mp. 89-91 °C (AcOEt): IR (ATR) (cm^{-1}) 2986, 2920, 2845, 1715, 1643, 1587, 1543, 1438, 1288, 1288, 1229, 1188, 1168, 1071, 1018, 988, 957, 860, 788, 758, 744, 727. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.63 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.98 (ddd, *J* = 7.9, 1.1 Hz, 1H), 7.90 (d, *J* = 9.9 Hz, 1H), 7.74 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.62 (s, 1H), 7.25 (m, 1H), 5.79 (d, *J* = 9.9 Hz, 1H), 4.37 (c, *J* = 7.1 Hz, 2H), 4.24 (c, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) 166.4 (CO), 159.5 (CO), 152.3 (C), 150.8 (C), 149.6 (CH), 136.9 (CH), 134.4 (C), 129.8 (CH), 123.5 (CH), 120.4 (CH), 112.0 (CH), 111.6 (CH), 61.7 (CH2), 61.2 (CH2), 14.3 (CH3), 14.2 (CH3). MS (Q-TOF) *m/z* (%):316 (3), 288 (8), 270 (81), 260 (9), 242 (100), 226 (1), 218 (8), 198 (38), 190 (11), 172 (28), 146 (19), 116 (4). HRMS (ESI-TOF) *m/z* C16H18N3O4 (M^++1): 316.1292, found 316.1290.

*4.2.1.1.3. (E)-Ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-(pyridin-2-yl)-1H-pyrazole-5-carboxylate **4**.* Yellow solid mp. 92-94 °C (AcOEt): IR (ATR) (cm^{-1}) 3134, 2984, 2928, 2856, 1743, 1699, 1643, 1582, 1471, 1432, 1424, 1354, 1218, 1085, 999, 857, 769, 688. ^{1}H NMR (300 MHz, Cl_3CD) δ = 9.09 (d, *J* = 13.8 Hz, 1H), 8.76 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.83 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.64 (ddd, *J* = 7.9, 1.1, 0.9 Hz, 1H), 7.35 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 7.19 (s, 1H), 6.84 (d, *J* = 13.8 Hz, 1H), 4.45 (c, *J* = 7.1 Hz, 2H), 4.25 (c, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) 166.8 (CO), 161.8 (CO), 149.9 (CH), 148.0 (C), 145.8 (C), 144.1 (C), 139.4 (CH), 137.5 (CH), 123.9 (CH), 123.8 (CH), 111.0 (CH), 110.5 (CH), 61.7 (CH2), 60.7 (CH2), 14.5 (CH3), 14.4 (CH3). MS (Q-TOF) *m/z* (%):270 (100), 242 (50), 226 (23), 218 (10), 214 (4), 198 (26), 190 (9), 172 (15), 146 (8), 129 (1), 116 (3). HRMS (ESI-TOF) *m/z* C16H18N3O4 (M^++1): 316.1292, found 316.1282.

*4.2.1.2. Using as substrate 3-Methyl-[1,2,3]triazolo[1,5-a]pyridine **1b***

*4.2.1.2.1. (E)-Ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-methyl-3-(pyridin-2-yl)-1H-pyrazole-5-carboxylate **6**.* Oil: IR (ATR) (cm^{-1}) 2981, 2934, 1718, 1654, 1596, 1449, 1388, 1365, 1282, 1260, 1163, 1093, 1030, 988, 946, 857, 783, 746, 724. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.66 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.97 (d, *J* = 13.7 Hz, 1H), 7.73 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.8, 1.1, 1.1 Hz, 1H), 7.29–7.23 (m, 1H), 6.78 (d, *J* = 13.7 Hz, 1H), 4.34–4.23 (m, 4H), 2.45 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, Cl_3CD) 166.6 (CO), 162.0 (CO), 151.0 (C), 149.4 (CH), 143.7 (C), 141.5 (C), 136.0 (CH), 135.6 (CH), 126.0 (CH), 124.3 (C), 122.4 (CH), 110.1 (CH), 61.5 (CH2), 61.0 (CH2), 14.4 (CH3), 14.2 (CH3), 10.2 (CH3). MS (Q-TOF) *m/z* (%):284 (35), 256 (100), 210 (3), 143 (1). HRMS (ESI-TOF) *m/z* C17H20N3O4 (M^++1): 330.1448, found 330.1446.

*4.2.2. Reaction with ethyl propiolate using as substrate [1,2,3] triazolo[1,5-a]pyridine **1a** and CuI as catalyst*

*4.2.2.1. Ethyl indolizine-3-carboxylate **5**.* Oil: IR (ATR) (cm^{-}) 2981, 2923, 2853, 1687, 1471, 1402, 1332, 1227, 1179, 1132, 1049, 749. ^{1}H NMR (300 MHz, Cl_3CD) δ = 9.42 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.52 (d, *J* = 4.5 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.00 (ddd, *J* = 8.9, 6.9, 1.1 Hz, 1H), 6.79 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 1H), 6.47 (d, *J* = 4.5 Hz, 1H), 4.37 (c, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) 161.6 (CO), 138.2 (C), 127.5 (CH), 121.8 (CH), 121.6 (CH), 119.0 (CH), 114.2 (C), 112.7 (CH), 101.2 (CH), 59.9 (CH2), 14.7 (CH3). MS (Q-TOF) *m/z* (%):162 (14), 144 (35), 117 (100), 91 (9). HRMS (ESI-TOF) *m/z* C11H12NO2 (M^++1): 190.0863, found 190.0863.

4.2.3. Reaction with dimethyl acetylenedicarboxylate (DMAD)

*4.2.3.1. Using as substrate [1,2,3]triazolo[1,5-a]pyridine **1a***

*4.2.3.1.1. Dimethyl (E)-1-(1,4-dimetoxy-1,4-dioxobut-2-en-2-yl)-3-(pyridin-2-yl)-1H-pyrazol-4,5-dicarboxylate **8**.* Was eluted first as a yellow solid mp. 118-119 °C (AcOEt), IR (ATR) (cm^{-}) 3106, 3039, 3000, 2961, 1737, 1715, 1585, 1460, 1374, 1310, 1218, 1143, 1074, 949, 783, 735, 710. ^{1}H NMR (300 MHz, Cl_3CD) δ 8.56 (ddd, *J* = 4.9, 1.8. 1.0 Hz, 1H), 7.88 (ddd, *J* = 7.6, 1.1, 1.1 Hz, 1H), 7.70 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.19 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 4.56 (s, 1H), 4.20 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (75 MHz, Cl_3CD) 168.2 (CO), 166.2 (CO), 165.6 (CO), 159.4 (CO), 155.3 (C), 150.3 (C), 149.6 (CH), 147.4 (C), 136.6 (CH), 131.8 (C), 123.1 (CH), 120.7 (CH), 117.7 (C), 84.5 (CH), 52.8 (CH3), 52.7 (CH3), 50.9 (CH3), 40.2 (CH3). MS (Q-TOF) *m/z* (%):276 (5), 244 (100). HRMS (ESI-TOF) *m/z* C13H14N3O4 (M^++1 - C5H4O4): 276.0979, found 276.0981.

*4.2.3.1.2. Dimethyl-3-(pyridin-2-yl)-1H-pyrazol-4,5-dicarboxylate **7**.* Oil, ^{1}H NMR (300 MHz, Cl_3CD) δ 8.60 (ddd, *J* = 4.9, 1.7, 0.9 Hz, 1H), 8.01 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 1H), 7.80 (ddd, *J* = 8.0, 7.7, 1.8 Hz, 1H), 7.32 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, Cl_3CD165.0 (CO), 161.7 (CO), 149.8 (C), 149.4 (CH), 146.5 (C), 137.7 (CH), 136.8 (C), 124.4 (CH), 122.4 (CH), 113.7 (C), 52.9 (CH3), 52.7 (CH3). MS (Q-TOF) *m/z* (%):262 (5), 230 (100), 198 (13). HRMS (ESI-TOF) *m/z* C12H12N3O4 (M^++1): 262.0822, found 262.0823.

*4.2.3.2. Using as substrate 3-methyl[1,2,3]triazolo[1,5-a]pyridine **1b***

*4.2.3.2.1. Dimethyl-3-methyl-3-(pyridin-2-yl)-3H-pyrazol-4,5-dicarboxylate **9**.* Yellow solid mp. 95-96 °C (AcOEt), IR (ATR) (cm^{-1}) 2959, 2920, 1715, 1610, 1538, 1451, 1432, 1368, 1293, 1202 1154, 1080, 1032, 841, 783, 741, 691. ^{1}H NMR (300 MHz, Cl_3CD) δ 8.48 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.89–7.80 (m, 2H), 7.34–7.28 (m, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (75 MHz, Cl_3CD 163.5 (CO), 163.0 (CO), 152.3 (C), 148.0 (CH), 145.4 (C), 144.6 (C), 138.9 (CH), 123.3 (CH), 118.3 (CH), 114.2 (C), 52.7 (CH3), 52.0 (CH3), 13.1 (CH3). MS (Q-TOF) *m/z* (%):244 (100), 214 (34). HRMS (ESI-TOF) *m/z* C13H14N3O4 (M^++1): 276.0979 found 276.0983.

4.2.4. Reaction with ethyl acrylate

*4.2.4.1. Using as substrate [1,2,3]triazolo[1,5-a]pyridine **1a***

*4.2.4.1.1. (E)-Ethyl 2-(pyridin-2-yl)cyclopropanecarboxylate **10a**(E).* Oil: IR (ATR) (cm^{-1}) 2978, 2928, 2903, 1718, 1596, 1568, 1476, 1429, 1327, 1260, 1174, 1043, 1021, 927, 846, 769, 744. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.44 (ddd, *J* = 4.9, 1.7, 0.9 Hz, 1H), 7.55 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.22 (ddd, *J* = 7.8, 1.0, 1.0 Hz, 1H), 7.08 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 4.16 (c, *J* = 7.2 Hz, 2H), 2.62–2.53 (m, 1H), 2.27–2.21 (m, 1H), 1.65–1.55 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) δ 173.6 (CO), 159.1 (C), 149.6 (CH), 136.2 (CH), 122.7 (CH), 121.4 (CH), 60.9 (CH2), 27.4 (CH), 24.5 (CH), 17.4 (CH2), 14.4 (CH3). MS (Q-TOF) *m/z* (%): 146 (6), 118 (100), 91 (13). HRMS (ESI-TOF) *m/z* C11H14NO2 (M^++1): 192.1019, found 192.1019.

*4.2.4.1.2. (Z)-Ethyl 2-(pyridin-2-yl)cyclopropanecarboxylate **10a**(Z).* Oil: IR (ATR) (cm^{-1}) 3050, 2978, 2925, 2900, 1718, 1582, 1562, 1471, 1429, 1188, 1157, 1091, 1027, 999, 963, 849, 799, 746. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.47 (ddd, *J* = 4.8, 1.7, 0.8 Hz, 1H), 7.56 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.08 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.88 (c, *J* = 7.2 Hz, 2H), 2.70 (ddd, *J* = 16.6, 8.8, 8.8 Hz, 1H), 2.18–2.10 (m, 1H), 1.86–1.75 (m, 1H), 1.45–1.33 (m, 1H), 0.99 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) 171.1 (CO), 156.8 (C), 149.0 (CH), 135.9 (CH), 123.7 (CH), 121.7 (CH), 60.4 (CH2), 27.3 (CH), 21.7 (CH), 14.1 (CH), 11.7 (CH3). MS (Q-TOF) *m/z* (%):146 (19), 118 (100), 91 (13). HRMS (ESI-TOF) *m/z* C11H14NO2 (M^++1): 192.1019, found 192.1017.

*4.2.4.2. Using as substrate the 3-methyl-[1,2,3]triazolo[1,5-a]pyridine **1b***

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4.2.4.2.1. (E)-Ethyl 2-methyl-2-(pyridin-2-yl)cyclopropanecarboxylate ***10b****(E).* Oil: IR (ATR) (cm^{-1})3050, 2981, 2942, 2884, 1721, 1579, 1565, 1468, 1424, 1371, 1293, 1266, 1174, 1132, 1071, 1046, 1018, 977, 846, 785, 746, 666. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.48 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H), 7.61 (ddd, J = 8.0, 7.5, 1.9 Hz, 1H), 7.37 (ddd, J = 8.0, 1.0, 1.0 Hz, 1H), 7.08 (ddd, J = 7.4, 4.8, 1,1 Hz, 1H), 4.17 (cd, J = 7.2, 3.4 Hz, 2H), 2.38 (dd, J = 8.4, 6.3 Hz, 1H), 1.79 (dd, J = 8.4, 4.1 Hz, 1H), 1.64 (s, 3H), 1.48 (dd, J = 6.3, 4.0 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) δ 172.1 (CO), 162.6 (C), 149.2 (CH), 136.3 (CH), 121.1 (CH), 120.3 (CH), 60.7 (CH2), 30.0 (CH), 29.5 (C), 22.7 (CH2), 15.9 (CH3), 14.5 (CH3). MS (Q-TOF) m/z (%):160 (13), 145 (5), 132 (100), 117 (81), 90 (1). HRMS (ESI-TOF) m/z C12H16NO2 (M^++1): 206.1176, found 206.1173.

4.2.4.2.2. (Z)-Ethyl 2-methyl-2-(pyridin-2-yl)cyclopropanecarboxylate ***10b****(Z).* Oil: IR (ATR) (cm^{-1}) 2978, 2928, 2903, 1718, 1596, 1568, 1476, 1429, 1327, 1260, 1174, 1043, 1021, 927, 846, 769, 744. ^{1}H NMR (300 MHz, Cl_3CD) δ = 8.51 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.60 (ddd, J = 7.7, 7.7, 1.9 Hz, 1H), 7.27 (ddd, J = 7.9, 1.0, 1.0 Hz, 1H), 7.11 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 3.87 (c, J = 7.1 Hz, 2H), 1.96 (dd, J = 7.5, 5.5 Hz, 1H), 1.92−1.89 (m, 1H), 1.53 (s, 3H), 1.25 (dd, J = 7.5, 4.4 Hz, 1H), 1.01 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Cl_3CD) δ 171.5 (CO), 161.0 (C), 149.2 (CH), 136.4 (CH), 123.5 (CH), 121.8 (CH), 60.4 (CH2), 33.6 (C), 28.5 (CH), 26.4 (CH3), 19.8 (CH2), 14.2 (CH3). MS (Q-TOF) m/z (%):206 (1), 160 (88), 132 (100), 117 (29), 91 (1). HRMS (ESI-TOF) m/z C12H16NO2 (M^++1): 206.1176, found 206.1172.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2016.11.006.

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