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# Concurrent pathway and unexpected products in the CuAAC reaction of ethyl prop-2-ynyl methylphosphonate with aromatic azides

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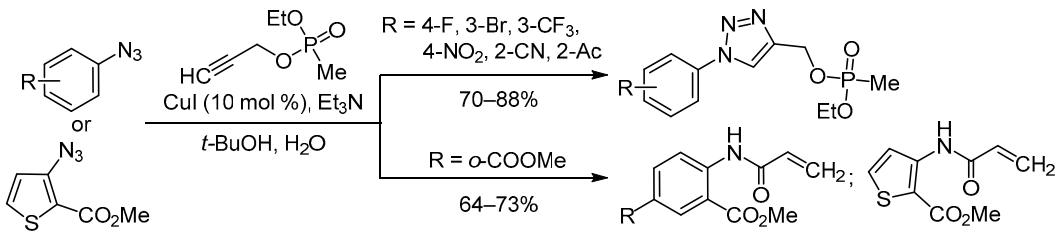



The CuI-mediated click reaction of aromatic azides, containing the carboxyl moiety in the *ortho* position to the azido group, with ethyl prop-2-ynyl methylphosphonate proceeded *via* a concurrent pathway whereby the formation of acrylamides predominated over "classical" cycloaddition products 1,2,3-triazoles. The reaction appears to be specific toward the *ortho*-carboxyl-substituted aromatic azides, while aryl azides with other substituents do not give the "reduction" products, but form the expected click products: (1-aryl-1*H*-1,2,3-triazol-4-yl)methyl ethyl methylphosphonates. The reaction mechanism is discussed.

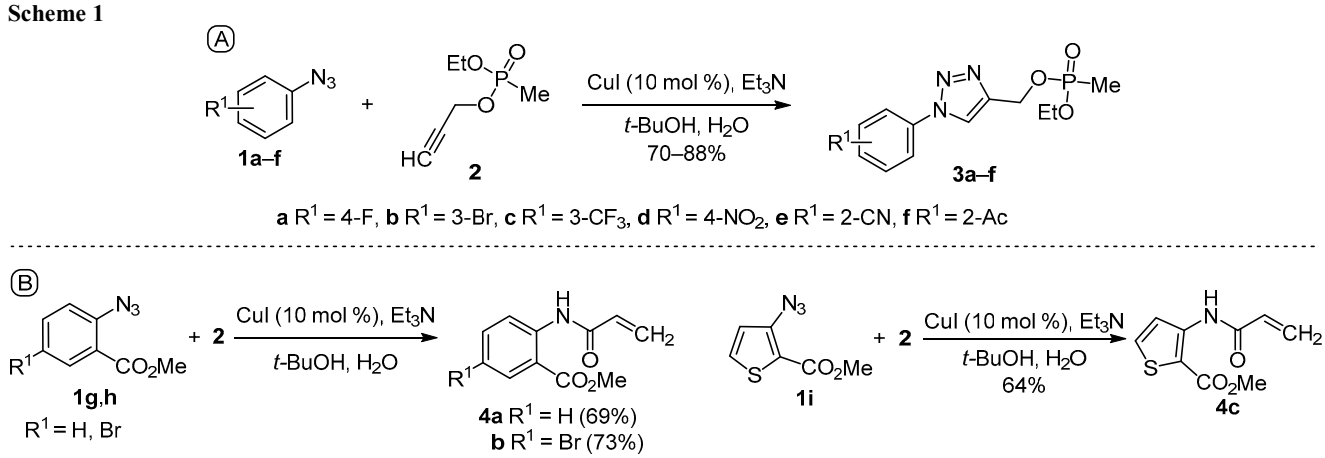
**Keywords**: azides, phosphonates, 1,2,3-triazoles, click reaction, unexpected product.

The intensive application in synthetic, biological chemistry and materials science of the Huisgen dipolar azide/alkyne cycloaddition catalyzed by Cu(I) salts (CuAAC) as one of the most convenient click reactions is overviewed in numerous publications and summarized in several recent reviews.[1] Moreover, a separate issue in the *Chemical Society Reviews*, edited by M. G. Finn, is devoted to this topic.[2] The CuAAC reaction is applicable for the large range of azides and terminal alkynes,[1] occurs under mild conditions, and may be used in biological objects.[3]

The diversity of Cu(I)-based catalytic systems used in the CuAAC reactions allows to find the required conditions depending on the reactants.[1] One of the most effective and currently one of the most commonly used catalyst in such reactions is CuI due to its high catalytic activity, as well as moderate solubility in many organic solvents.[4] In our recent work on new 1,2,3-triazole synthesis, we showed the high efficiency of CuI in the reaction of norbornyl azide with phenylacetylene, as well as in the one-pot three-component reaction of alkyl 3-aryl-2-bromopropanoates with sodium azide and phenylacetylene.[5] At the same time, this catalytic system is not universal and there are some examples where the reaction did not occur or side products formed.[6]

Our ongoing research in the area of CuAAC involves the construction of small molecules for anticancer studies.[7] For this purpose, the phosphonate moiety was proposed to be added to the triazole scaffold. It should be mentioned that examples of the application of alkynes with phosphonate moiety in the CuAAC are limited. For instance, the cycloaddition of fluoroalkyl propargyl methylphosphonates to various azidopeptides was demonstrated by obtaining the corresponding triazoles which were screened for the inhibitory activity toward acetylcholinesterase, butyrylcholinesterase, and carboxylesterase.[8] In another example, cycloaddition of azidoalkylphosphonates to the propargylated nucleotides affords several nucleoside phosphonates and their antiviral properties were studied.[9] Finally, a series of bis- and tris[3- and 24-(5β-cholanetriazolyl)] derivatives of phosphorus acids containing anion-binding triazolium sites and hydrophobic cholane residues were synthesized and the binding properties of such ligands for inorganic and organic anions were studied.[10] The limited use of phosphorus-containing compounds in CuAAC may be due to the

**Scheme 1**




complexation of phosphorus moiety with copper(I), thereby affecting the cyclization process.

Taking into account the lack of such studies, in our present work we have synthesized ethyl prop-2-ynyl methylphosphonate (**2**) and studied its reaction with a number of aromatic azides. In our first attempts, the CuAAC of aryl azides **1a**–**f** with ethyl prop-2-ynyl methylphosphonate (**2**) in the presence of CuI–$Et_3N$ catalytic system proceeded with the formation of triazoles **3a**–**f** in good to excellent yields (Scheme 1, A). Such a result was expected and is fully consistent with "classical" mechanism of this reaction (Scheme 2, path *a*). However, when, in order to explore the scope of the reaction, a set of azides **1g**–**i** containing the ester group in the *ortho* position was used, the cycloaddition to ethyl prop-2-ynyl methylphosphonate (**2**) did not give the expected 1,2,3-triazole, but instead acrylamides **4a**–**c** were isolated in 64–73% yields (Scheme 1, B). Such an outcome can be formally considered as the reduction of the azido group to amino. The electrons in redox process are balanced by the elimination of the nitrogen molecule and addition of water.

The structures of the synthesized products were confirmed by NMR spectra, mass spectra, and single crystal X-ray diffraction. The latter experiment revealed a similar geometry of compounds **3a**,**b** (Fig. 1). The plane of the aryl ring in crystal structures **3a,b** is slightly rotated relatively to 1*H*-1,2,3-triazole plane by 15.7(3)° and 22.9(5)°, respectively. The distorted tetrahedral surrounding of phosphorus atom ($\tau_4$ 0.91 for compound **3a** and 0.92 for compound **3b**, $\tau_4$ – four-coordinated geometry index) includes two bridging O atoms, one terminal O atom, and carbon atom of the methyl group. Phosphorus polyhedron is raised relative to the triazole ring planes (torsion angle P–O(1)–C(6)–C(4) in structures **3a** and **3b** equal to 155.5(2)° and 156.6(4)°, respectively).

The mechanism of the alternative reaction pathway is not obvious and requires a detailed study as no similar results for aromatic azides were mentioned in the literature. As an example of anomalous CuAAC, some recent results could be mentioned whereby azido compound gave the corresponding amine rather than the desired cycloaddition product.[6,11] In these examples, solvent plays the role of hydrogen donor (reduction agent). Additionally, in the

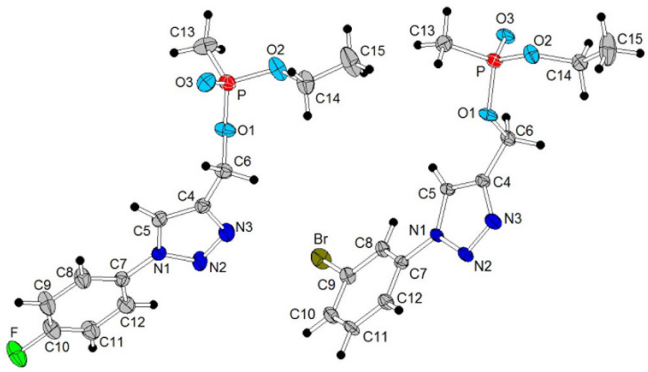
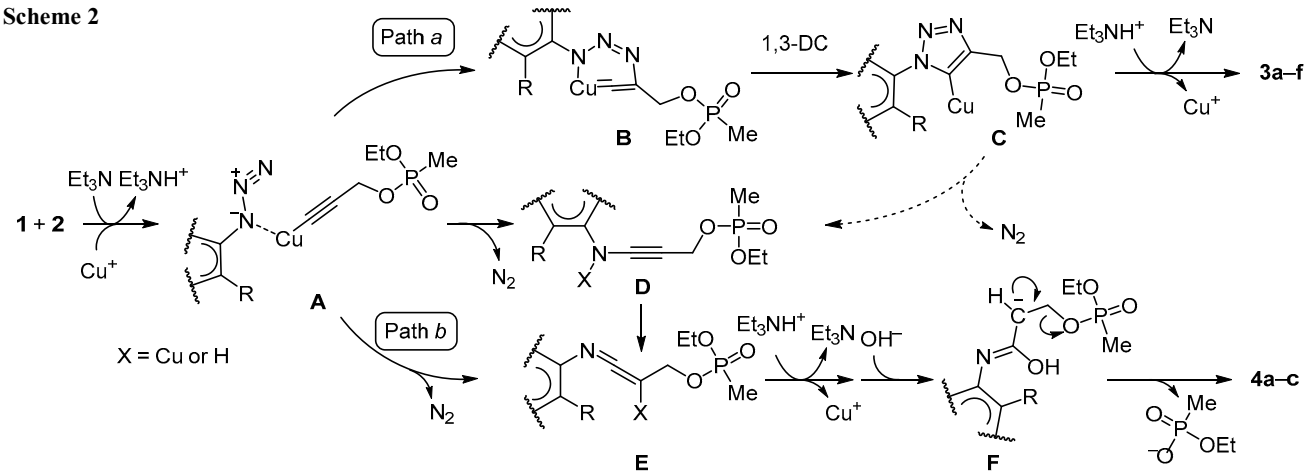



**Figure 1**. The structures of ethyl (1-aryl-1*H*-1,2,3-triazol-4-yl)-methyl methylphosphonates **3a** (left) and **3b** (right) with atoms represented by thermal vibration ellipsoids of 50% probability.

cited works,[6,11] as well as in our case (compounds **4**), azides bearing in the *ortho* position fragments suitable for Cu(I) complexation were used.

It is most likely that in our case the concurrent reaction occurred in a similar way as previously reported for sulfonyl azides *via* the formation of ketenimine intermediates.[12,13] Reaction started from "classical" intermediate complexes **A**, generated by the action of copper acetylide (from alkyne **2** and CuI) on azide **1**. According to the CuAAC mechanism[1g] (Scheme 2, path *a*), the complex **A** undergoes cycloaddition likely through intermediate **B**, and the resulting triazolyl-cuprate **C** upon protonation yields triazoles **3a**–**f**. Probably, in case of azides **1g**–**i** bearing carboxyl moiety in the *ortho* position to the azido group the formation of transitional state **B** is unfavorable due to steric effects or additional bidental bonding of a copper atom in complexes **A**. In such case, upon elimination of $N_2$ ynamide **D** or it isomeric ketenimine **E** or their copper complexes were formed (Scheme 2, path *b*). Alternatively, the formation of the ketenimine intermediate **E** may be presumed *via* 1,2,3-triazole ring cleavage of triazolyl cuprate **C** and $N_2$ elimination. Nucleophilic addition to a highly reactive ketenimine would lead to the formation of carbanion **F** which is stabilized by phosphonate elimination and after rearrangement gives acrylates **4a**–**c**. The possibility that both pathways *a* and *b* are realised at the same time, as well

**Scheme 2**




as other mechanisms that lead to the formation of acrylates **4**, cannot be completely excluded at present.

In summary, an unusual pathway in the CuAAC reaction was observed and unexpected noncyclic products were isolated. The concurrent pathway is strictly controlled by the presence in the *ortho* position to azide a substituent having the tendency to coordinate the copper(I) atom. Such exceptions allow understanding the reaction mechanism and nature of copper(I) coordination in the catalytic cycle and to make prospects for controlling the reaction products formation.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on Varian Mercury 400 (400 and 101 MHz, respectively) and Bruker Avance 500 (500 and 126 MHz, respectively) spectrometers in DMSO-$d_6$ using TMS or the deuterated solvent (δ 2.50 and 39.5 ppm, for $^1$H and $^{13}$C nuclei, respectively) as internal reference. Mass spectral analyses were performed using an Agilent 1100 series LC/MSD instrument in API-ES/APCI mode (200 eV). Elemental analyses were carried out using a Carlo Erba 1106 instrument. Melting points were determined on a Boetius melting point apparatus. Progress of reactions and purity of the synthesized compounds were examined by TLC on Silufol UV-254 plates, and visualization was performed using UV lamp (254 nm) or $I_2$ vapor.

**Ethyl prop-2-ynyl methylphosphonate (2)** was synthesized according to a procedure reported previously.[14] $^1$H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 4.63 (2H, dd, *J* = 10.3, *J* = 2.4, ≡CCH$_2$); 4.05–3.97 (2H, m, CH$_3$C<u>H</u>$_2$); 3.63 (1H, t, *J* = 2.4, ≡CH); 1.49 (3H, d, $J_{PH}$ = 17.5, CH$_3$P); 1.25 (3H, t, *J* = 7.0, C<u>H</u>$_3$CH$_2$).

**Synthesis of triazoles 3a–f and acrylates 4a–c** (General method). An appropriate azide **1a**–**f** (1.0 mmol) and ethyl prop-2-ynyl methylphosphonate (**2**) (162 mg, 1.0 mmol) were dissolved in *t*-BuOH (5 ml). Water (approx. 0.4 ml) was added dropwise to the solution until an emulsion formed. After that, Et$_3$N (0.4 ml, 2.8 mmol) and CuI (19 mg, 0.1 mmol) were added. The reaction mixture was stirred at room temperature until TLC (eluent hexane–EtOAc, 5:1) indicated that all starting material had disappeared (approximately 12 h). $H_2O$ (15 ml) and concentrated aqueous $NH_3$ solution (5 ml) were added to the mixture. The product was extracted with $CH_2Cl_2$ (3×10 ml), the extract was dried with $Na_2SO_4$ and evaporated. The solid products were recrystallized from hexane.

**Ethyl [1-(4-fluorophenyl)-1*H*-1,2,3-triazol-4-yl]methyl methylphosphonate (3a)**. Yield 254 mg (85%), white solid, mp 95–97°C. $^1$H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 8.89 (1H, s, H triazole); 7.95 (2H, dd, *J* = 8.6, *J* = 4.4, H-2,6 Ar); 7.47 (2H, t, *J* = 8.6, H-3,5 Ar); 5.12 (2H, d, $J_{PH}$ = 7.9, CH$_2$); 4.09–3.91 (2H, m, CH$_3$C<u>H</u>$_2$); 1.50 (3H, d, $J_{PH}$ = 17.3, CH$_3$P); 1.23 (3H, t, *J* = 6.8, C<u>H</u>$_3$CH$_2$). $^{13}$C NMR spectrum (101 MHz), δ, ppm (*J*, Hz): 162.2 (d, $^1J_{CF}$ = 245.7, C-4 Ar); 144.4 (d, $^3J_{CP}$ = 7.0, C-4 triazole); 133.6 (d, $^4J_{CF}$ = 2.6, C-1 Ar); 123.6 (C-5 triazole); 123.1 (d, $^3J_{CF}$ = 8.9, C-2,6 Ar); 117.3 (d, $^2J_{CF}$ = 23.3, C-3,5 Ar); 61.5 (d, $^2J_{CP}$ = 6.0, CH$_2$O); 58.1 (d, $^2J_{CP}$ = 5.3, CH$_2$O); 16.6 (d, $^3J_{CP}$ = 6.2, CH$_3$); 11.1 (d, $^1J_{CP}$ = 140.0, CH$_3$P). Mass spectrum *m/z* ($I_{rel}$, %): 300 [M+H]$^+$ (100). Found, %: C 48.05; H 5.11; N 14.23. $C_{12}H_{15}FN_3O_3P$. Calculated, %: C 48.17; H 5.05; N 14.04.

**[1-(3-Bromophenyl)-1*H*-1,2,3-triazol-4-yl]methyl ethyl methylphosphonate (3b)**. Yield 285 mg (79%), white solid, mp 81–82°C. $^1$H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 8.98 (1H, s, H triazole); 8.18 (1H, s, H-2 Ar); 7.97 (1H, d, *J* = 8.0, H Ar); 7.71 (1H, d, *J* = 7.9, H Ar); 7.56 (1H, t, *J* = 8.1, H-5 Ar); 5.21–5.05 (2H, m, CH$_2$); 4.07–3.93 (2H, m, CH$_3$C<u>H</u>$_2$); 1.50 (3H, d, $J_{PH}$ = 17.4, CH$_3$P); 1.22 (3H, t, *J* = 7.0, C<u>H</u>$_3$CH$_2$). $^{13}$C NMR spectrum (126 MHz), δ, ppm (*J*, Hz): 144.5 (d, $^3J_{CP}$ = 7.1, C-4 triazole); 138.1; 132.3; 132.0; 123.4; 123.2; 122.9; 119.6; 61.5 (d, $^2J_{CP}$ = 6.1, CH$_2$O); 58.1 (d, $^2J_{CP}$ = 5.0, CH$_2$O); 16.6 (d, $^3J_{CP}$ = 5.9, CH$_3$); 11.1 (d, $^1J_{CP}$ = 139.9, CH$_3$P). Mass spectrum, *m/z* ($I_{rel}$, %): 360 [M($^{79}$Br)+H]$^+$ (100), 362 [M($^{81}$Br)+H]$^+$ (97). Found, %: C 40.11; H 4.34; N 11.73. $C_{12}H_{15}BrN_3O_3P$. Calculated, %: C 40.02; H 4.20; N 11.67.

**Ethyl {1-[3-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazol-4-yl}methyl methylphosphonate (3c)**. Yield 304 mg (87%), yellow oil. $^1$H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 9.09 (1H, s, H triazole); 8.30 (1H, s, H-3 Ar); 8.27 (1H, d, *J* = 7.7, H-6 Ar); 7.90–7.83 (2H m, H-4,5 Ar); 5.19–5.09 (2H, m, CH$_2$); 4.07–3.94 (2H, m, CH$_3$C<u>H</u>$_2$); 1.50 (3H, d, $J_{PH}$ = 17.4, CH$_3$P); 1.22 (3H, t, *J* = 7.0, C<u>H</u>$_3$CH$_2$). $^{13}$C NMR spectrum (126 MHz), δ, ppm (*J*, Hz): 144.6 (d, $^3J_{CP}$ = 7.2, C-4 triazole); 137.4; 131.8; 131.0 (q, $^2J_{CF}$ = 32.6, C-3 Ar);

125.8 (q, $^3J_{CF}$ = 3.7, C-2 Ar); 124.5; 124.0 (q, $^1J_{CF}$ = 272.2, $CF_3$); 123.6 (C-5 triazole); 117.3 (q, $^3J_{CF}$ = 3.9, C-4 Ar); 61.5 (d, $^2J_{CP}$ = 6.1, $CH_2O$); 58.1 (d, $^2J_{CP}$ = 5.2, $CH_2O$); 16.6 (d, $^3J_{CP}$ = 6.2, $CH_3$); 11.1 (d, $^1J_{CP}$ = 140.0, $CH_3P$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 350 $[M+H]^+$ (100). Found, %: C 44.77; H 4.30; N 11.92. $C_{13}H_{15}F_3N_3O_3P$. Calculated, %: C 44.71; H 4.33; N 12.03.

**Ethyl [1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]methyl methylphosphonate (3d)**. Yield 287 mg (88%), white solid, mp 129–130°C. $^1$H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 9.13 (1H, s, H triazole); 8.46 (2H, d, *J* = 8.2, H-3,5 Ar); 8.24 (2H, d, *J* = 8.3, H-2,6 Ar); 5.27–5.03 (2H, m, $CH_2$); 4.09–3.90 (2H, m, $CH_3C\underline{H}_2$); 1.51 (3H, d, $J_{PH}$ = 17.3, $CH_3P$); 1.23 (3H, t, *J* = 6.8, $C\underline{H}_3CH_2$). $^{13}$C NMR spectrum (126 MHz), δ, ppm (*J*, Hz): 146.8; 144.5 (d, $^3J_{CP}$ = 7.0, C-4 triazole); 140.7; 125.6 (2C); 123.2 (C-5 triazole); 120.7 (2C); 61.1 (d, $^2J_{CP}$ = 6.1, $CH_2O$); 57.5 (d, $^2J_{CP}$ = 5.2, $CH_2O$); 16.1 (d, $^3J_{CP}$ = 6.7, $CH_3$); 10.6 (d, $^1J_{CP}$ = 139.8, $CH_3P$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 327 $[M+H]^+$ (100). Found, %: C 44.05; H 4.70; N 17.21. $C_{12}H_{15}N_4O_5P$. Calculated, %: C 44.18; H 4.63; N 17.17.

**[1-(2-Cyanophenyl)-1*H*-1,2,3-triazol-4-yl]methyl ethyl methylphosphonate (3e)**. Yield 220 mg (72%), yellow oil. $^1$H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 8.85 (1H, s, H triazole); 8.14 (1H, d, *J* = 7.6, H-6 Ar); 7.96 (1H, t, *J* = 7.7, H-4 Ar); 7.88 (1H, d, *J* = 8.0, H-3 Ar); 7.77 (1H, t, *J* = 7.6, H-5 Ar); 5.18 (2H, d, $J_{PH}$ = 8.5, $CH_2$); 4.07–3.95 (2H, m, $CH_3C\underline{H}_2$); 1.51 (3H, d, $J_{PH}$ = 17.3, $CH_3P$); 1.22 (3H, t, *J* = 7.0, $C\underline{H}_3CH_2$). $^{13}$C NMR spectrum (126 MHz, DMSO-$d_6$), δ, ppm (*J*, Hz): 144.2 (d, $^3J_{CP}$ = 6.9, C-4 triazole); 138.2; 135.3; 135.2; 130.9; 126.4; 126.1; 116.2; 107.7; 61.6 (d, $^2J_{CP}$ = 6.2, $CH_2O$); 58.0 (d, $^2J_{CP}$ = 5.2, $CH_2O$); 16.6 (d, $^2J_{CP}$ = 5.9, $CH_3$); 11.2 (d, $^1J_{CP}$ = 140.0, $CH_3P$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 307 $[M+H]^+$ (100). Found, %: C 50.90; H 4.99; N 18.21. $C_{13}H_{15}N_4O_3P$. Calculated, %: C 50.98; H 4.94; N 18.29.

**[1-(2-Acetylphenyl)-1*H*-1,2,3-triazol-4-yl]methyl ethyl methylphosphonate (3f)**. Yield 226 mg (70%), yellow oil. $^1$H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 8.69 (1H, s, H triazole); 7.84 (1H, d, *J* = 7.5, H-6 Ar); 7.74 (1H, t, *J* = 7.5, H-5 Ar); 7.71–7.63 (2H, m, H-3,4 Ar); 5.13 (2H, d, $J_{PH}$ = 8.5, $CH_2$); 4.08–3.94 (2H, m, $CH_3C\underline{H}_2$); 2.21 (3H, s, $CH_3CO$); 1.49 (3H, d, $J_{PH}$ = 17.4, $CH_3P$); 1.22 (3H, t, *J* = 6.9, $C\underline{H}_3CH_2$). $^{13}$C NMR spectrum (126 MHz), δ, ppm (*J*, Hz): 199.9; 144.0 (d, $^3J_{CP}$ = 6.7, C-4 triazole); 136.1; 134.1; 132.7; 130.4; 129.4; 126.2; 126.1; 61.5 (d, $^2J_{CP}$ = 6.1, $CH_2O$); 58.1 (d, $^2J_{CP}$ = 5.2, $CH_2O$); 29.7; 16.6 (d, $^3J_{CP}$ = 5.8, $CH_3$); 11.2 (d, $^1J_{CP}$ = 139.8, $CH_3P$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 324 $[M+H]^+$ (100). Found, %: C 52.05; H 5.57; N 13.14. $C_{14}H_{18}N_3O_4P$. Calculated, %: C 52.01; H 5.61; N 13.00.

**Methyl 2-acrylamidobenzoate (4a)**. Compound data was compared with reported in the literature.[15] Yield 141 mg (69%), white solid, mp 45–47°C. $^1$H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 10.80 (1H, s, NH); 8.32 (1H, d, *J* = 8.3, H Ar); 7.92 (1H, d, *J* = 7.9, H Ar); 7.61 (1H, t, *J* = 7.8, H Ar); 7.20 (1H, t, *J* = 7.6, H Ar); 6.43 (1H, dd, *J* = 17.0, *J* = 10.2, CH=); 6.28 (1H, d, *J* = 17.0) and 5.83 (1H, d, *J* = 10.2, $CH_2$=); 3.85 (3H, s, $CH_3O$). $^{13}$C NMR spectrum (126 MHz), δ, ppm (*J*, Hz): 167.5; 163.3; 139.3; 133.8; 132.2; 130.5; 127.5; 123.5; 121.3; 118.0; 52.4. Mass spectrum, *m*/*z* ($I_{rel}$, %): 206 $[M+H]^+$ (100). Found, %: C 64.48; H 5.37; N 6.94. $C_{11}H_{11}NO_3$. Calculated, %: C 64.38; H 5.40; N 6.83.

**Methyl 2-acrylamido-5-bromobenzoate (4b)**. Yield 207 mg (73%), white solid, mp 83–84°C. $^1$H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 10.71 (1H, s, NH); 8.20 (1H, d, *J* = 8.9, H-3 Ar); 7.99 (1H, d, *J* = 2.1, H-6 Ar); 7.80 (1H, dd, *J* = 8.9, *J* = 2.0, H-4 Ar); 6.43 (1H, dd, *J* = 16.8, *J* = 10.2, CH=); 6.28 (1H, d, *J* = 16.8) and 5.85 (1H, d, *J* = 10.2, $CH_2$=); 3.85 (3H, s, $CH_3O$). $^{13}$C NMR spectrum (126 MHz), δ, ppm (*J*, Hz): 166.7; 163.9; 138.7; 136.8; 133.1; 132.4; 128.4; 124.2; 121.3; 115.6; 53.2. Mass spectrum, *m*/*z* ($I_{rel}$, %): 284 $[M(^{79}Br)+H]^+$ (100), 286 $[M(^{81}Br)+H]^+$ (95). Found, %: C 46.55; H 3.49; N 4.98. $C_{11}H_{10}BrNO_3$. Calculated, %: C 46.50; H 3.55; N 4.93.

**Methyl 3-acrylamidothiophene-2-carboxylate (4c)**. Yield 139 mg (64%), white solid, mp 146–147°C. $^1$H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 10.21 (1H, s, NH); 8.00 (1H, d, *J* = 5.4, H Th); 7.93 (1H, d, *J* = 5.4, H Th); 6.60 (1H, dd, *J* = 16.9, *J* = 10.3, CH=); 6.32 (1H, d, *J* = 17.0) and 5.88 (1H, d, *J* = 10.3, $CH_2$=); 3.86 (3H, s, $CH_3O$). $^{13}$C NMR spectrum (101 MHz), δ, ppm (*J*, Hz): 163.8; 162.9; 143.9; 133.4; 131.9; 129.0; 123.0; 111.7; 52.6. Mass spectrum, *m*/*z* ($I_{rel}$, %): 212 $[M+H]^+$ (100). Found, %: C 51.11; H 4.38; N 6.71. $C_9H_9NO_3S$. Calculated, %: C 51.17; H 4.29; N 6.63.

**Single crystal X-ray diffraction study of compounds 3a,b**. Crystals were obtained by crystallization from hexane. Diffraction data for compounds **3a**,**b** were collected on a Kuma KM-4-CCD diffractometer with MoKα radiation (λ 0.71073 Å). The diffraction data were processed with the CrysAlis PRO program.[16] The structures were solved by ShelXT and refined by least-squares method on $F^2$ by ShelXL programs with the following graphical user interface of Olex.[17,18] Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The complete crystallographic datasets were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1885238 (compound **3a**) and CCDC 1885239 (compound **3b**)).

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