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Multicomponent reaction of conjugated enynones with malononitrile and sodium alkoxides: complex reaction mechanism of the formation of pyridine derivatives

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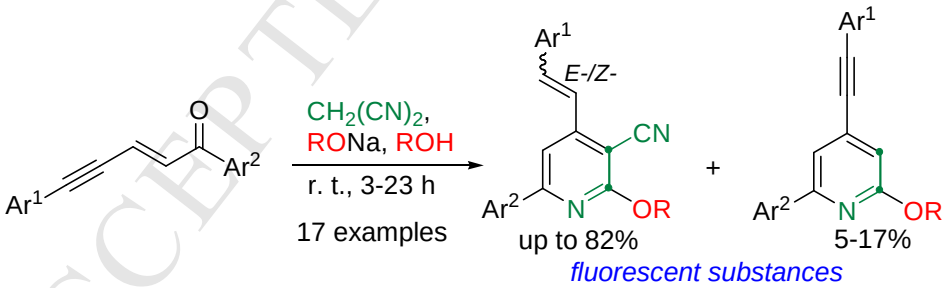
Keywords: conjugated enynones; pyridines; nicotinonitriles; reaction mechanism, fluorescence

Graphical abstract



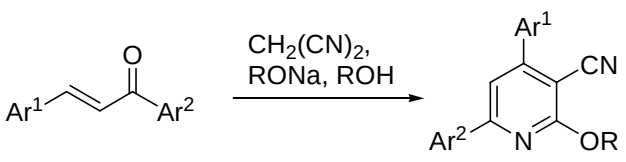
Abstract

Reaction of conjugated enynones,1,5-diarylpent-2-en-4-yn-1-ones, with malononitrile and sodium alkoxides in the corresponding alcohols at room temperature for 3-23 h results in the formation of two types of compounds *(E)-/(Z)*-6-aryl-4-(2-arylethenyl)-2-alkoxypyridine-3-carbonitriles (substituted nicotinonitriles), as the major reaction products in yields up to ca. 40-80%, and 6-aryl-4-arylethynyl-2-alkoxypyridines, as the minor reaction products in yields of 5-17%. Plausible mechanism of this complex and multistep reaction is discussed. The obtained pyridines possess fluorescent properties.

Introduction

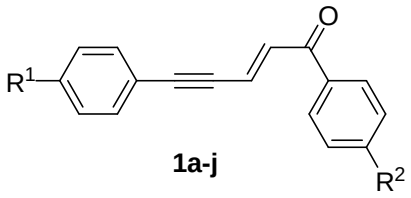
Conjugated enynones, pent-2-en-4-yn-1-ones, represent an important class of multifunctional organic compounds due to the presence of three important functional groups in their structures: double and triple carbon-carbon bonds, and carbonyl group. Chemistry of these compounds has been recently reviewed [1]. The conjugated enynone system is a versatile building block for synthesis of various substances. Reactivity of unsaturated carbon-carbon bonds towards nucleophilic reagents in these compounds is enhanced by the conjugation with electron withdrawing carbonyl group. Thus, reactions of conjugated enynones with N- and S-nucleophiles proceed very easily, forming products of addition to both double or triple carbon-carbon bonds, depending on reaction conditions [2-5]. There are many examples of preparation of heterocycles by reactions of enynones under nucleophilic conditions, namely, furans [6-15], aziridines (followed by their conversion into pyrroles) [16], pyrazols [17,18], triazoles [18], and pyridines [19]. Apart from that, these conjugated enynones may be transformed into various indane derivatives under supereletrophilic activation conditions [20,21].

In 1989, a study on the synthesis of 3-cyanopyridines (nicotinonitriles) by the reaction of 1,3-diarylprop-2-en-1-ones (chalcones) with malononitrile and sodium alkoxides in alcohols was reported (Scheme 1) [22]. It should be mentioned that such nicotinonitriles have been obtained even earlier in 1922 [23]. Thereafter, this reaction [24-26] and similar transformations [27-29] were used to obtain various nicotinonitriles. It should be specially emphasized that substituted nicotinonitriles have been used in agriculture as antidotes and plant growth regulators [30]. Furthermore, nicotinonitriles possess cytotoxity to cancer cell line [31], and antioxidant [32], antiviral [33] and antibacterial [34, 35] activities. Many nicotinonitriles are characterized by a complex of valuable photophysical [36] and photochemical [37] properties. Due to that, nicotinonitriles are promising as liquid crystals [24], fluorescent [26, 38-40] and nonlinear optical materials [36]. Thus, the synthesis of these very important compounds is an actual goal of organic chemistry.



Scheme 1. The reaction of chalcones with malononitrile and sodium alkoxides in alcohols leading to substituted pyridines (nicotinonitriles) (data from ref. [22]).

Based on our studies on the chemistry of conjugated enynones [1], and data from the prior work [22], we undertook a special investigation on transformations of 1,5-diarylpent-2-en-4-yn-1-ones (see starting enynones in Figure 1) in multicomponent reaction with malononitrile and sodium alkoxides. The main goals of this study were to find out a regioselectivity of this reaction, which carbon-carbon bond, double or triple one, takes part in an interaction with nucleophilic species, and to propose a plausible mechanism for this complex reaction.



1a-j

$R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = Me$ (**b**);
$R^1 = H$, $R^2 = Cl$ (**c**); $R^1 = H$, $R^2 = OMe$ (**d**);
$R^1 = Me$, $R^2 = H$ (**e**); $R^1 = Cl$, $R^2 = H$ (**f**);
$R^1 = OMe$, $R^2 = H$ (**g**); $R^1 = Me$, $R^2 = Cl$ (**h**);
$R^1 = Me$, $R^2 = Br$ (**i**); $R^1 = H$, $R^2 = NO_2$ (**j**)

Figure 1. Starting 1,5-diarylpent-2-en-4-yn-1-ones used in this study.

Results and discussion

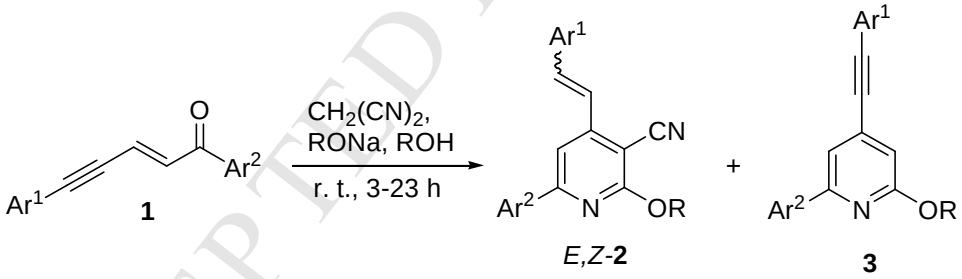
The multicomponent reaction of malononitrile and alkoxides with enynones **1a-j** was found to be much more complicated than the same reaction of chalcones [22-26] (see Scheme 1). Transformations of enynones **1a-j** with malononitrile and sodium alkoxides in the corresponding alcohols gave mixtures of two types of the reaction products, *(E)-/(Z)*-isomers of 4-arylethenyl (styryl) pyridines **2** and 4-arylethynyl (arylacetylene) pyridines **3** (Table 1). Both of the reaction products **2** and **3** contain an alkoxy group in the position 2 of the pyridine system. Pyridines **2** bear 3-cyano group, however, pyridines **3** do not contain this substituent, which is contrary to data from the prior work [22] (see Scheme 1). Compounds *(E)-/(Z)*-**2** (yields of 15-82 %) are the major reaction products, the *E- : Z*- ratios for them is roughly 1 : 1, with rare exceptions (see Table 1). Compounds **3** (yields of 5-17%) are the minor reaction products. Structures of pyridines *E*-**2a**, *Z*-**2c**, **3c** and **3p** were additionally confirmed by X-ray data (see Table 1). It should be specially noted that such 6-aryl-4-arylethynyl-2-alkoxypyridines **3** have been obtained for the first time, previously they were unknown compounds

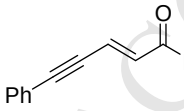
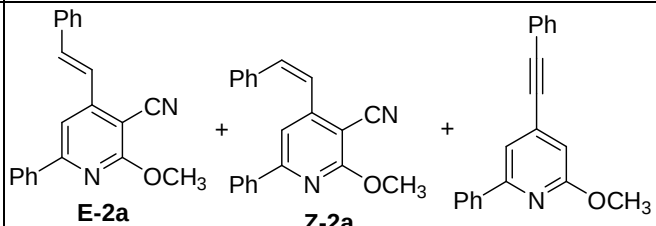
Various sodium alkoxides may be involved in this reaction. Apart from methoxide, the use of other sodium alkoxides, generated from ethanol (entries 4, 8, 11, 13, 18), propan-1-ol (entry 5), and butan-1-ol (entry 6), resulted in the formation of the corresponding 2-alkoxysubstituted pyridines **2** and **3**. However, when using alcohols, other than methanol, the combined yields of compounds **2** and **3** were decreased. It was found that electron-donating substituents in aromatic ring at the carbonyl groups of enynones **1b,d** led to the increase of yields of reaction products (entries 7, 8, 10, 11). On the other hand, enynone **1j** beraing acceptor nitro group gave rise a complex mixture of reaction products (entry 19).

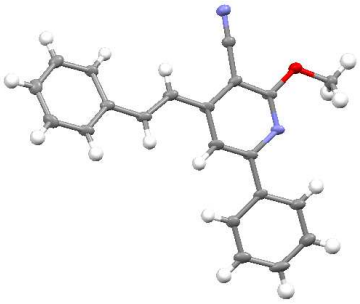
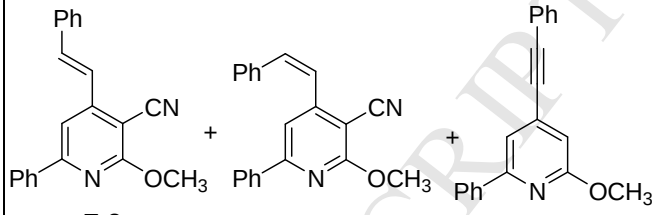
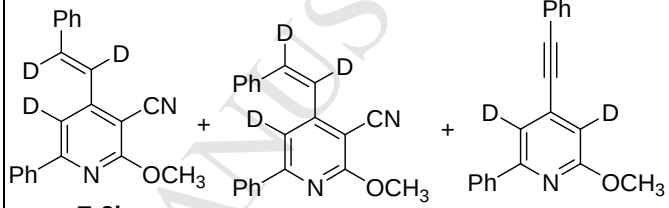
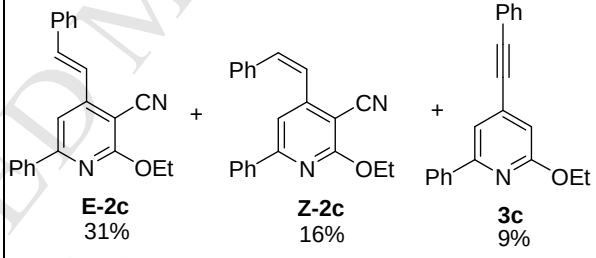
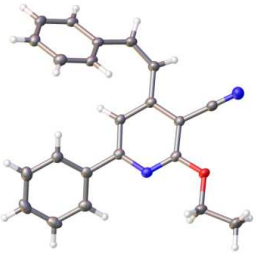
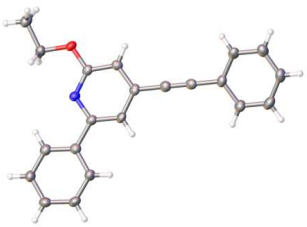
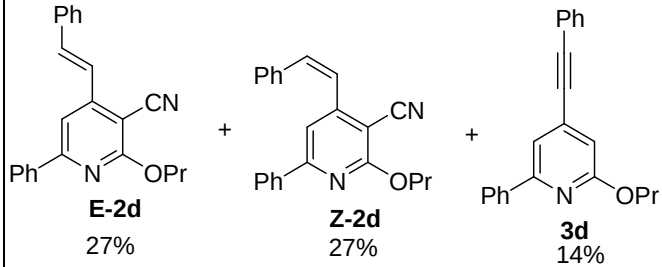
(E)-/(Z)-Isomers of styryl pyridines **2** have very close chromatographic retention parameters. Thus, in most cases, we were not able to isolate individually each isomer by usual column chromatography on silica gel. However, preparative HPLC separation of (*E*)- and (*Z*)-isomers of **2f** was carried out, as an example of possibility of individual isolation of these isomers. Mixtures of *E,Z*-isomers of **2** were analyzed by means of NMR and HRMS. *(E)-/(Z)*-Configuration of compounds **2** was determined on the basis of values of spin-spin interaction constants of vinyl protons at the double C=C bond in ^{1}H NMR and (see Experimental Part and Supporting Information).

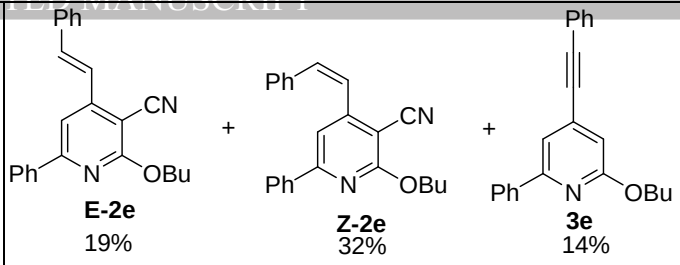
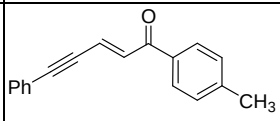
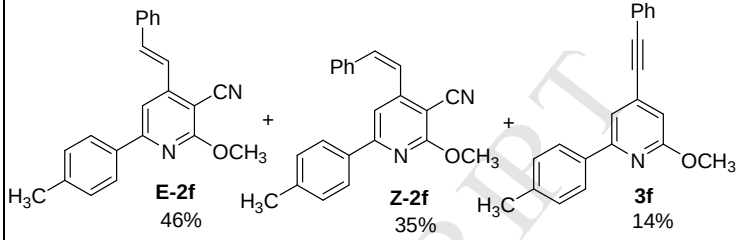
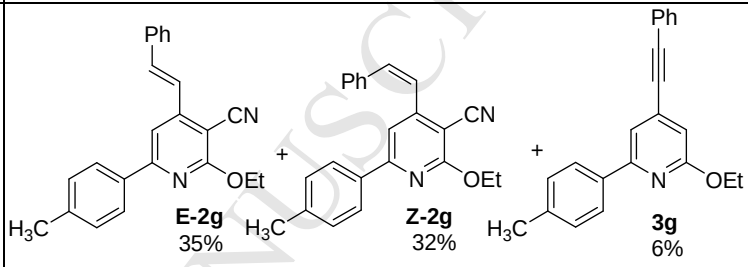
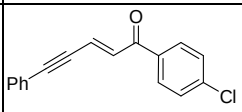
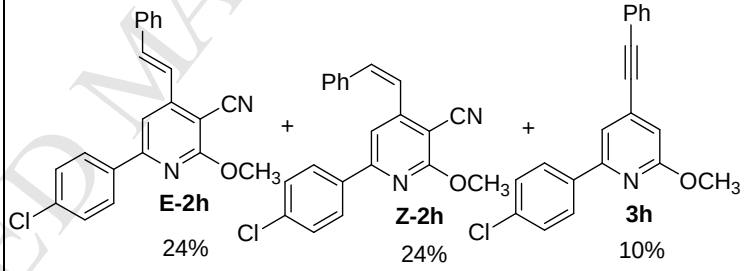
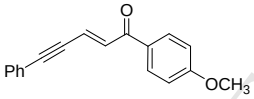
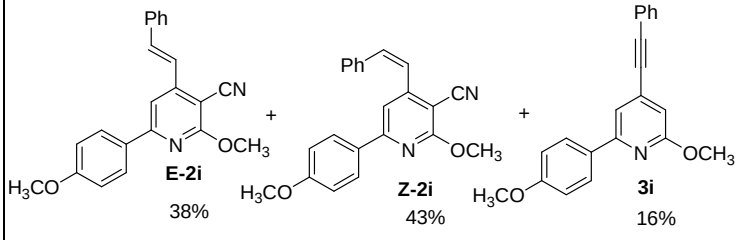
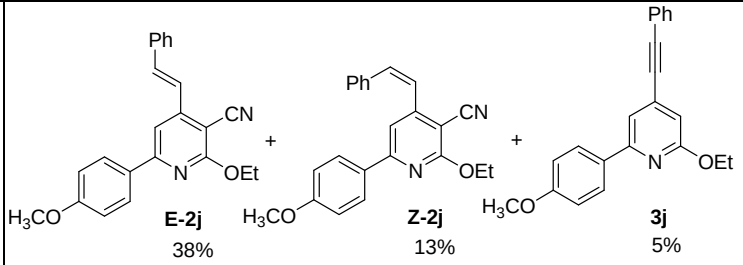
It should be specially emphasized that pyridines **2** and **3** are decomposed on silica gel, and purification by preparative TLC leads to dramatic decrease of their yields. Table 1 contains the yields of compounds **2** and **3** before chromatographic separation. These yields were determined for mixtures of pure compounds **2** and **3** precipitated from the reaction solutions in the corresponding alcohol. However, in the cases of PrOH and BuOH no precipitation of **2** and **3** was observed, and these reaction products were isolated by extraction of reaction mixtures (see Experimental Part).

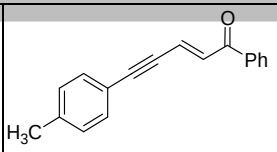
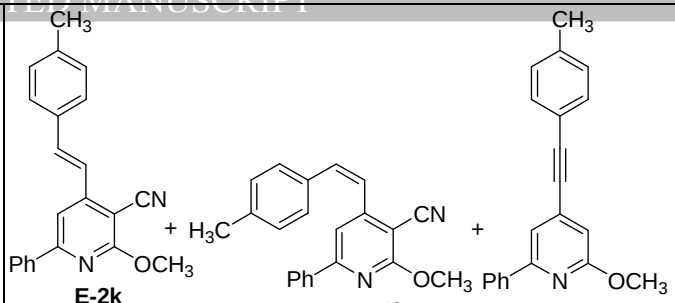
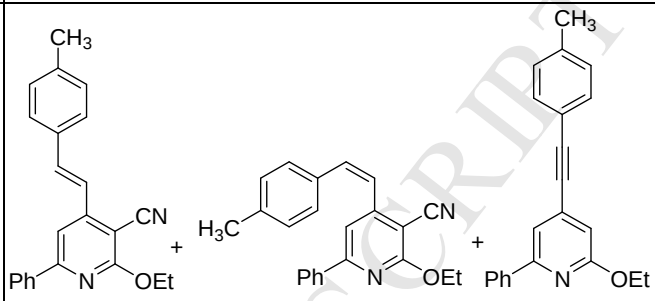
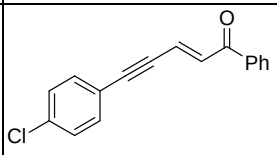
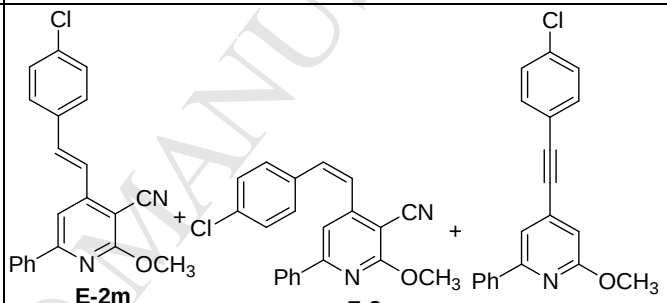
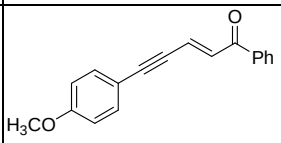
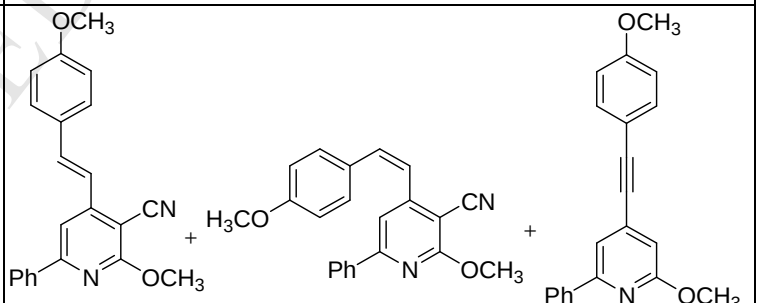
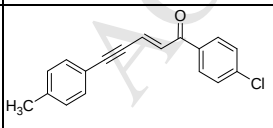
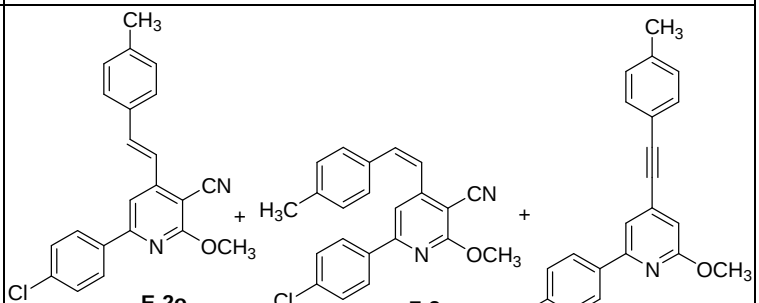
Table 1. Reactions of 1,5-diarylpent-2-en-4-yn-1-ones **1** with malononitrile and sodium alkoxides in the corresponding alcohols leading to pyridines **2** and **3** (for X-ray structures ellipsoid contours of probability levels are 50%).

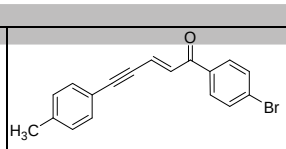
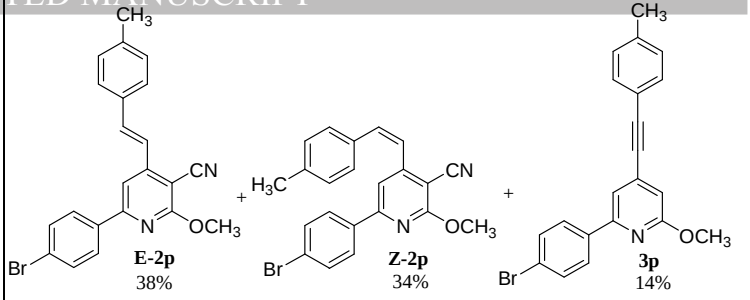
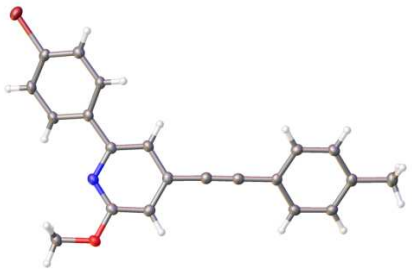
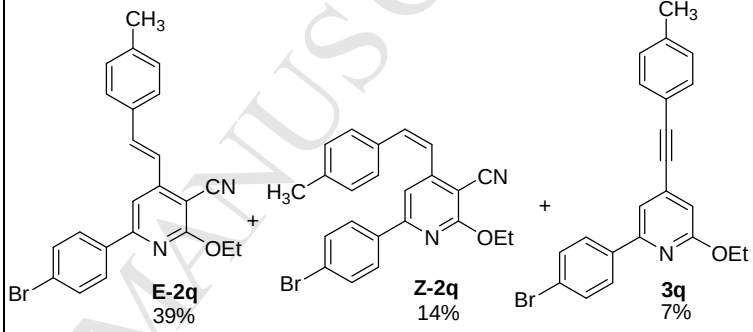
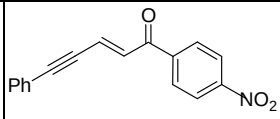


Entry	Starting enynone	Reaction conditions	Reaction products
1	 **1a**	MeONa, MeOH, r.t., 4 h	 **E-2a** 39% + **Z-2a** 35% + **3a** 13%

			 X-ray of *E*-**2a** (CCDC 1910130)
2	**1a**	MeONa, MeOH, argon, r.t., 3h	 **E-2a** 49% **Z-2a** 31% **3a** 13%
3	**1a**	MeONa, MeOD, r.t., 4 h	 **E-2b** 36% **Z-2b** 25% **3b** 12%
4	**1a**	EtONa, EtOH, r.t., 23 h	 **E-2c** 31% **Z-2c** 16% **3c** 9%  X-ray of *Z*-**2c** (CCDC 1910133)  X-ray of **3c** (CCDC 1910109)
5	**1a**	PrONa, PrOH, r.t., 17 h	 **E-2d** 27% **Z-2d** 27% **3d** 14%

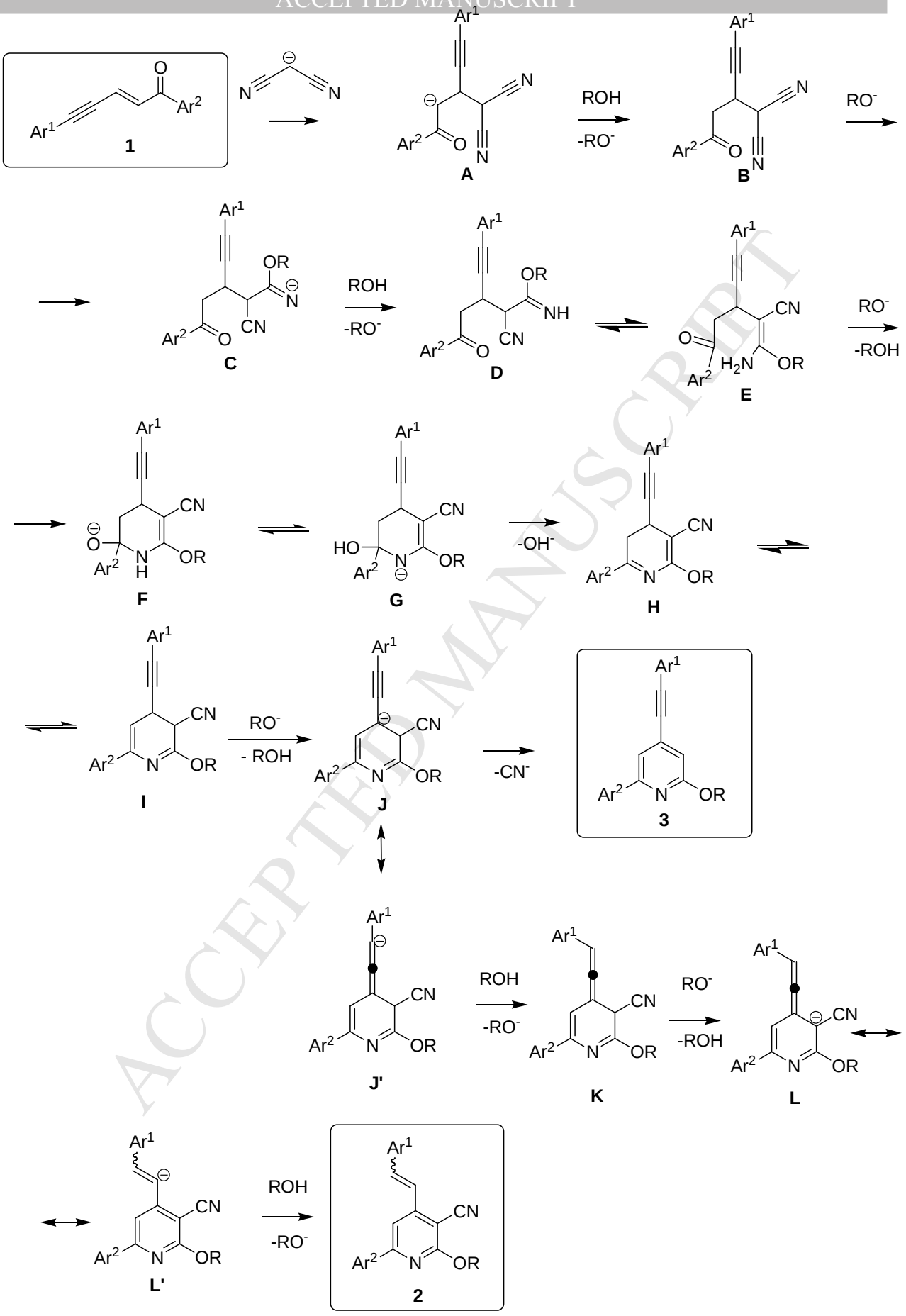
6	**1a**	BuONa, BuOH, r.t., 17 h	 **E-2e** 19% **Z-2e** 32% **3e** 14%
7	 **1b**	MeONa, MeOH, r.t., 3 h	 **E-2f** 46% **Z-2f** 35% **3f** 14%
8	**1b**	EtONa, EtOH, r.t., 17 h	 **E-2g** 35% **Z-2g** 32% **3g** 6%
9	 **1c**	MeONa, MeOH, r.t., 3 h	 **E-2h** 24% **Z-2h** 24% **3h** 10%
10	 **1d**	MeONa, MeOH, r.t., 3 h	 **E-2i** 38% **Z-2i** 43% **3i** 16%
11	**1d**	EtONa, EtOH, r.t., 17 h	 **E-2j** 38% **Z-2j** 13% **3j** 5%

12	 **1e**	MeONa, MeOH, r.t., 3 h	 **E-2k** 34% **Z-2k** 6% **3k** 5%
13	**1e**	EtONa, EtOH, r.t., 17 h	 **E-2l** 10% **Z-2l** 5% **3l** 5%
14	 **1f**	MeONa, MeOH, r.t., 3 h	 **E-2m** 18% **Z-2m** 26% **3m** 5%
15	 **1g**	MeONa, MeOH, r.t., 4 h	 **E-2n** 45% **Z-2n** 41% **3n** 12%
16	 **1h**	MeONa, MeOH, r.t., 3 h	 **E-2o** 26% **Z-2o** 32% **3o** 17%

17	 **1i**	MeONa, MeOH, r.t., 4 h	 **E-2p** 38% **Z-2p** 34% **3p** 14%  X-ray of **3p** (CCDC 1910112)
18	**1i**	EtONa, EtOH, r.t., 17 ч	 **E-2q** 39% **Z-2q** 14% **3q** 7%
19	 **1j**	MeONa, MeOH, r.t., 18 h	Complex mixture of reaction products.

To elucidate the reaction mechanism additional experiments were carried out. Reaction of enynone **1a** in inert atmosphere of argon (entry 2) afforded the same pyridines *(E)-/(Z)*-**2a** and **3a** in similar yields, as experiments in air (entry 1). This means that the use of an inert atmosphere is not crucial for this reaction and atmosphere oxygen does not participate in any steps of the process. Then, we carried out the reaction of enynone **1a** in deuterated methanol (CH_3OD). Incorporation of deuterium atoms was found in the structures of pyridines *(E)-/(Z)*-**2b** and **3b** (entry 3). The formation of deuterated double bonds in *(E)-/(Z)*-**2b** reveals that deuterium came from solvent. That means that, at the formation of compounds **2**, triple bond is transformed into double one as a result of intermolecular process of deuterium (or hydrogen) transfer, rather than intramolecular hydrogen transfer. Apart from that, incorporation of deuterium atoms in pyridine ring reveals H-D exchange in intermediate species of this reaction.

The author of the prior work [22] proposed reaction mechanism for similar transformation of chalcones (see Scheme 1). One of the key step in this mechanism is Dimroth like rearrangement of pyran ring into tetrahydropyridinone one. However, we propose an alternative way for this complex and intriguing reaction (Scheme 2).

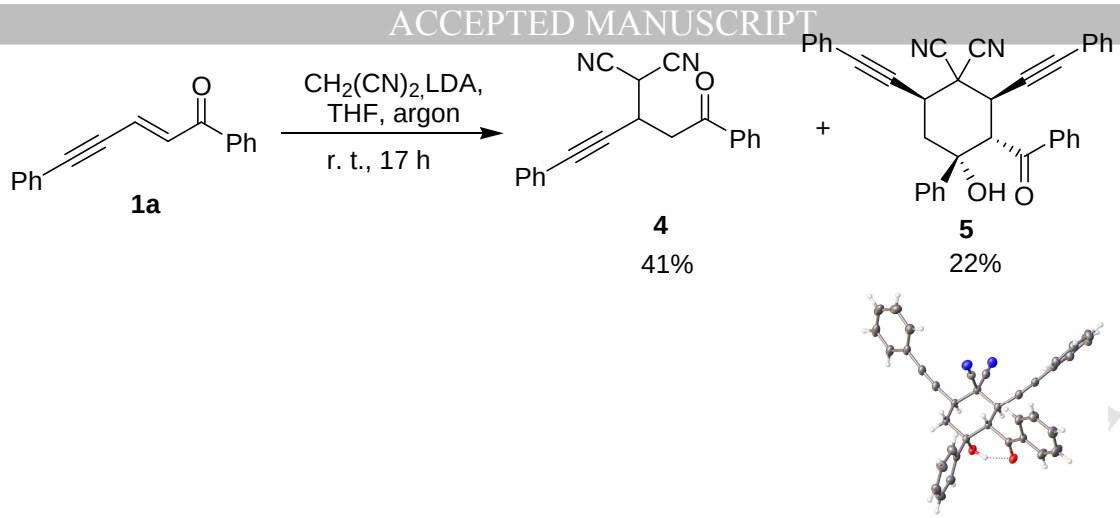


Scheme 2. Plausible mechanism of the reaction of enynones **1** with malononitrile and sodium alkoxides leading to pyridines **2** and **3**.

The reaction starts form Michael type addition of malononitrile anion to the carbon-carbon double bond of starting enynone **1**, that gives anion **A**. The latter withdraws proton from an alcohol molecule and gives compound **B**, which is undergone nucleophilic attack of alkoxide anion onto cyano group affording species **C**, then **D**, and enamine **E**. The latter is cyclized into anion **F** as a result of interaction of amino group with carbonyl carbon. Proton transfer in species **F** leads to N-centered anion **G**, which eliminates hydroxide and gives structure **H**. Isomerization of double bonds in **H** may lead to structure **I**. Deprotonation of the latter results in the formation of propargy-allyl anion **J**, which is one of the key intermediates in the reaction. There are two possibilities for further transformation of this species. First one is an elimination of the cyanide furnishing heteroaromatic pyridine system of compounds **3**. Another pathway is protonation of allenyl mesomeric form **J′** of anion **J**, which leads to allene **K**. Deprotonation of the latter in α-position to cyano group gives rise to anion **L**. Protonation of vinyl mesomeric form of **L′** results finally *(E)-/(Z)*-isomers of 4-styryl substituted pyridines **2**, as the main reaction products. Of course, this mechanism has speculative character, since it is very complex and multistep reaction.

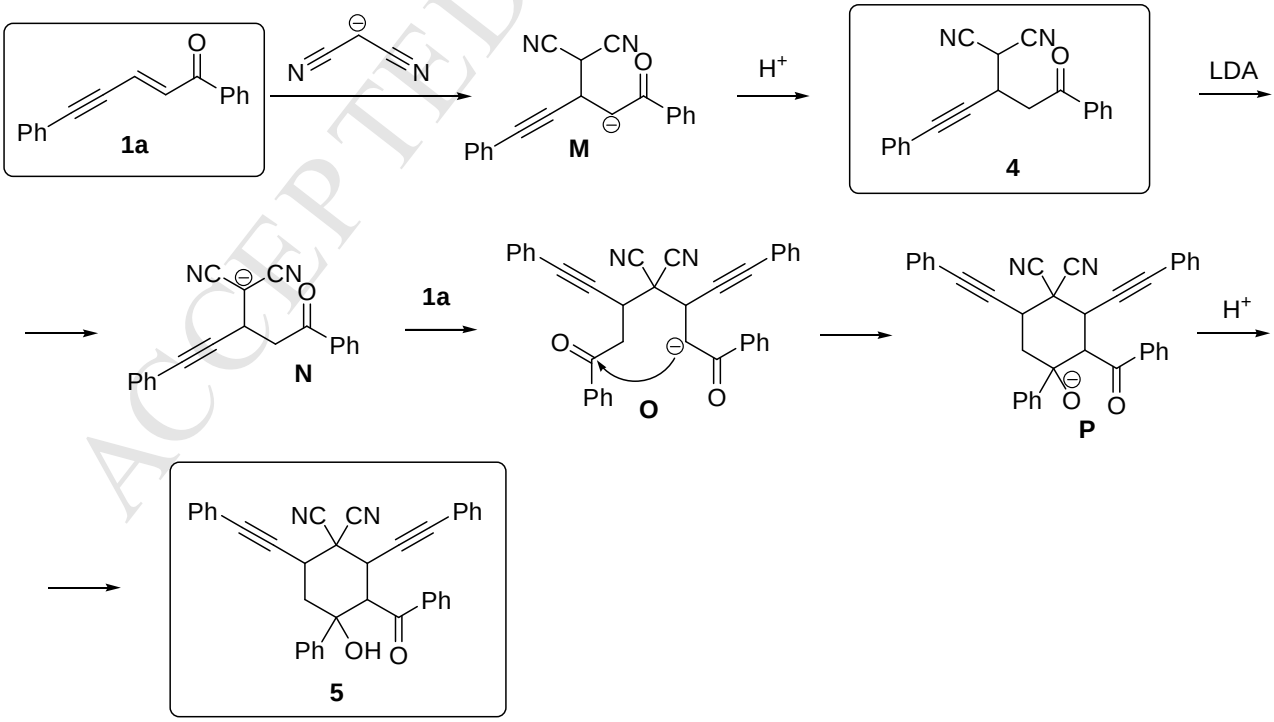
The formation of cyanide ion CN^- for the reaction of enynone **1a** (entry 1, Table) was additionally proved by gas chromatographic analysis of the vapor phase (headspace GC-analysis). The analysis over the acidified (H_2SO_4) reaction solution confirmed the presence of hydrogen cyanide (see the literature procedure [41] for the determination of HCN). At the same time, the vapor phase above the solution of malononitrile and MeONa in MeOH in a blank experiment without **1a**, after acidification with H_2SO_4, did not contain traces of HCN (see details of the experiments and chromatograms in Supporting Information). The data obtained confirm the formation of the cyanide ion in reactions of enynones and our assumptions on the reaction mechanism (Scheme 2).

To investigate the reaction mechanism deeper we carried out the reaction of enynone **1a** with such low nucleophilic base as lithium diisopropylamide (LDA) instead of sodium alkoxides. Compound **4** was obtained as the main reaction product of Michael type addition to the double C=C bond of **1a** (Scheme 3). Apart from that, compound **5** of the cyclohexane series was isolated, exact structure of **5** was determined by X-ray analysis (Scheme 3). No formation of pyridine derivatives was observed. One may propose that low nucleophilic diisopropylamide anion does not attack cyano group in **4**, contrary to alkoxides, which give rise to anions **C** in Scheme 2. That means that nucleophilc addition to cyano group is necessary for the pyridine ring formation, that does not take place in the case of lithium diisopropylamide.



Scheme 3. Reaction of enynone **1a** with malononitrile and lithium diisopropylamide (LDA) leading to compounds **4** and **5**, X-ray structure of **5** (ellipsoid contours of probability levels are 50%, CCDC 1910129).

A plausible reaction mechanism is presented in Scheme 4. Michael addition of malononitrile anion to the double carbon-carbon bond of enynone **1a** gives rise to anion **M**, the protonation of which affords compound **4**. The reaction may stop at this stage or go further leading to anion **N**. The latter reacts with one more molecule of **1a** affording anion **O**, which is cyclized into species **P** forming cyclohexane ring. Finally, protonation of anion **P** results in the stereoselective formation of compound **5**.



Scheme 4. Plausible mechanism of the reaction of enynone **1a** with malononitrile and LDA leading to compounds **4** and **5**.

Since, it is known that many pyridine derivatives are fluorescent compounds [26, 38-40, 42-46], we investigated qualitatively fluorescent properties for pyridines **2** and **3**. Indeed, it was found that, at the excitation at 320 nm, the fluorescence peaks were observed at 365-370 nm for arylethynyl pyridines **3a**,**f**,**h**, and at 390-410 nm for styryl pyridines *E*-**2a**, *Z*-**2a**, and for mixture of isomers *E,Z*-**2f** (see details in Supporting Information).

Conclusion

We have developed a synthesis of 4-styryl- and 4-arylethynyl- substituted pyridines, bearing aryl, alkoxy, and cyano groups, on the basis of an interaction of conjugated enynones, 1,5-diarylpent-2-en-4-yn-1-ones, with malononitrile and sodium alkoxides in alcohols. Apart from that, it was found that 1,5-diphenylpent-2-en-4-yn-1-ones in reaction with malononitrile and lithium diisopropylamide gives product of Michael addition of malononitrile to the double bond and "dimeric" compound of the cyclohexane series. Intriguing mechanisms of these reactions are discussed. The obtained arylethynyl- and styryl- substituted pyridines are fluorescent compounds.

Experimental Section

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 spectrometer [at 400, 100 and 61 MHz for ^{1}H, ^{13}C, and $^{2}H(D)$ NMR spectra respectively] at 25 °C. The solvent residual signals $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR spectra, the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra, and C_6H_6 (δ 7.15 ppm) for $^{2}H(D)$ NMR spectra were used as references. IR spectra of compounds were taken with Bruker spectrometer. HRMS was carried out at instrument Bruker maXis HRMS-ESI-QTOF. Fluorescent spectra for solution of compounds in CH_2Cl_2 with concentration of 10^{-5} mol/L were taken with Fluorimax 4P Horiba machine. Analysis of the vapor phase by the Headspace GC method was performed on a Crystallux-4000M chromatograph with thermal conductivity detector and a packed column containing HayeSep Q (60/80 mesh) as a stationary phase. Column length 2 m, diameter 3 mm, temperature 120 ºC, carrier gas – He. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative TLC was performed on silica gel Chemapol L 5/40respectively. HPLC was done on a Waters machine using gradient eluation with acetonitrile-water mixtures.

X-ray Diffraction Study. Single crystal X-ray analysis was performed at single crystal diffractometer Agilent Technologies (Oxford Diffraction) «Supernova». The crystal was kept at 100(2) K during data collection. Using Olex2 [47], the structure was solved with the ShelXS [48] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. CCDC 1910130 – (*E*-**2a**), CCDC 1910133 - (*Z*-**2c**), CCDC

1910109 – (**3c**), CCDC 1910112 – (**3p**), CCDC 1910129 – (**5**) contain the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

Preparation and characterization of starting enynones **1** was previously described [21, 22, 49].

General Procedure for the Synthesis of (*E*)- and (*Z*)-2-alkoxy-6-aryl-4-(2-arylethenyl)pyridine-3-carbonitriles (*E,Z*-2a-q) and 2-alkoxy-6-aryl-4-(arylethynyl)pyridines (3a-q) from 1,5-diarylpent-2-en-4yn-1-ones (1a-i). Malononitrile (2.5 equiv.) was added to sodium alcoxide (2.5 equiv.) solution (1.08 mmol/mL) in alcohol with stirring. The solution of enynone **1** (1 equiv.) in 1-6 mL of absolute alcohol was heated (~50°C) till enynone dissolution, then the obtained solution was added to malononitrile solution and mixture was stirring at room temperature for 3-23 h. The precipitate was filtered off to give mixture of pure compounds **2** and **3** (in the case of PrOH and BuOH no precipitation). The mother solution was poured into water (30 mL), and was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried with Na_2SO_4. Solvent was evaporated under the reduced pressure. The obtained residue was subjected to preparative TCL on silica gel with eluation by petroleum ether−ethyl acetate mixtures to get additional amounts of **2** and **3**.

(E)-2-Methoxy-6-phenyl-4-(2-phenylethenyl)pyridine-3-carbonitrile (*E*-**2a**) [50, 51]. Obtained from **1a** (50 mg, 0.22 mmol) and sodium methoxide (0.55 mmol) in a yield of 27 mg (39%). Obtained from **1a** (100 mg, 0.44 mmol) and sodium methoxide (1.1 mmol) under argon in a yield of 67 mg (49%). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15. Colorless solid. ^{1}H NMR, δ, ppm: 4.19 s (3H, OCH_3), 7.39-7.47 m (6H), 7.51-7.58 m (2H), 7.65 d (2H, H^{Ph}, *J* 6.9 Hz), 7.71 s (1H, H^{Py}), 8.13 dd (2H, H^{Ph}, *J* 7.9, 1.6 Hz).^{13}C NMR, δ, ppm: 54.5 (OCH_3), 92.9 (C^{Py}-CN), 108.4 (C^{Py}-H), 115.1 (CN), 122.6, 127.3, 127.7, 128.9, 129.0, 129.7, 130.3, 135.4, 137.1, 137.7, 151.5 (C^{Py}-C=C), 157.8 (C^{Py}-Ph), 164.9 (C^{Py}-O). IR (KBr): 2217 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O$ 313.1341; Found 313.1335.

(Z)-2-Methoxy-6-phenyl-4-(2-phenylethenyl)pyridine-3-carbonitrile (*Z*-**2a**). Obtained from **1a** (50 mg, 0.22 mmol) and sodium methoxide (0.55 mmol) in a yield of 24 mg (35%). Obtained from **1a** (100 mg, 0.44 mmol) and sodium methoxide (1.1 mmol) under argon in a yield of 43 mg (31%). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15. Colorless solid. ^{1}H NMR, δ, ppm: 4.18 s (3H, OCH_3), 6.76 d (1H, =CH-, *J* 12.2 Hz), 7.07 d (1H, =CH-, *J* 12.2 Hz), 7.24 s (1H, H^{Py}), 7.29-7.33 m (4H), 7.40-7.42 m (4H), 7.75 dd (2H, H^{Ph}, *J* 7.5, 2.0 Hz).^{13}C NMR, δ, ppm: 54.4 (OCH_3), 94.0 (C^{Py}-CN), 113.1 (C^{Py}-H), 114.8 (CN), 124.5, 127.1, 128.5, 128.7, 128.7,

128.9, 130.2, 132.5, 136.7, 137.4, 152.6 (C^{Py}-C=C), 157.2 (C^{Py}-Ph), 164.7 (C^{Py}-O). IR (KBr): 2222 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O$ 313.1341; Found 313.1335.

2-Methoxy-6-phenyl-4-phenylethynylpyridine (**3a**). Obtained from **1a** (50 mg, 0.22 mmol) and sodium methoxide (0.55 mmol) in a yield of 8 mg (13%). Obtained from **1a** (100 mg, 0.44 mmol) and sodium methoxide (1.1 mmol) under argon in a yield of 16 mg (13%). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15. Colorless solid. ^{1}H NMR, δ, ppm: 4.08 s (3H, OCH_3), 6.83 s (1H, H^{Py}), 7.40-7.52 m (7H), 7.60 dd (2H, H^{Ph}, *J* 6.6, 3.1 Hz), 8.09 d (2H, H^{Ph}, *J* 7.0 Hz).^{13}C NMR, δ, ppm: 53.5 (OCH_3), 87.2 (C≡), 92.7 (C≡), 111.1 (C^{Py}-H), 115.2 (C^{Py}-H), 122.3, 126.8, 128.5, 128.6, 129.0, 129.1, 131.9, 134.2, 138.5, 154.9 (C^{Py}-Ph), 163.9 (C^{Py}-O). IR (KBr): 2219 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}NONa$ 308.1051; Found 308.1046.

(E)-5-Deutero-2-methoxy-6-phenyl-4-(1,2-dideutero-2-phenylethenyl)pyridine-3-carbonitrile (*E*-**2b**). Obtained from **1a** (100 mg, 0.44 mmol) and sodium methoxide (1.1 mmol) in MeOD. Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 50 mg (36%). Colorless solid. ^{1}H NMR, δ, ppm: 4.20 s (3H, OCH_3), 7.38-7.48 m (3H), 7.52-7.55 m (2H), 7.63-7.67 m (2H), 8.13 dd (2H, H^{Ph}, *J* 7.9, 1.7 Hz). ^{2}H NMR δ, ppm: 6.13. ^{13}C NMR, δ, ppm: 54.4 (OCH_3), 85.5 (C^{Py}-CN), 99.2 (C^{Py}-D), 114.9 (CN), 127.1, 127.3, 127.7, 128.4, 128.5, 128.6, 128.69, 128.7, 128.87, 128.96, 129.01, 130.2, 130.3, 152.3 (C^{Py}-C=), 157.1 (C^{Py}-Ph), 164.7 (C^{Py}-O). IR (KBr): 2220 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{14}D_3N_2O$ 316.1529; Found 316.1524.

(Z)-5-Deutero-2-methoxy-6-phenyl-4-(1,2-dideutero-2-phenylethenyl)pyridine-3-carbonitrile (*Z*-**2b**). Obtained from **1a** (100 mg, 0.44mmol) and sodium methoxide (1.1 mmol) in MeOD. Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 44 mg (32%). Colorless solid. ^{1}H NMR, δ, ppm: 4.18 s (3H, OCH_3), 7.29-7.34 m (4H), 7.39-7.42 m (4H), 7.73-7.76 m (2H) .^{2}H NMR δ, ppm: 6.17, 6.65, 7.09. ^{13}C NMR, δ, ppm: 54.4 (OCH_3), 94.0 (C^{Py}-CN), 112.8 t (C^{Py}-D, *J* 30.0 Hz), 114.8 (CN), 124.4 t (=CD, *J* 6.0 Hz), 127.10, 128.5, 128.69, 128.7, 128.9, 130.2, 132.5, 136.6, 137.3, 152.4 (C^{Py}-C=C), 157.1 (C^{Py}-Ph), 164.7 (C^{Py}-O). IR (KBr): 2220 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}D_3N_2ONa$ 338.1349; Found 338.1343.

3,5-Dideutero-2-methoxy-6-phenyl-4-phenylethynylpyridine (**3b**). Obtained from **1a** (100 mg, 0.44mmol) and sodium methoxide (1.1 mmol) in MeOD in a yield of 14 mg (12%). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15. Colorless solid. ^{1}H NMR, δ, ppm: 4.09 s (3H, OCH_3), 7.40-7.52 m (6H), 7.61 dd (2H, H^{Ph}, *J* 6.6, 3.0 Hz), 8.10 d (2H, H^{Ph}, *J* 7.2 Hz). ^{2}H NMR δ, ppm: 6.13, 6.94, 7.46. ^{13}C NMR, δ, ppm: 53.5 (OCH_3), 87.2 (C≡), 92.8 (C≡), 111.0 t (C^{Py}-D, *J* 25.4 Hz), 115.1 t (C^{Py}-D, *J* 25.4 Hz), 122.3(C^{Ph}-C≡), 126.8, 128.5, 129.1, 129.2, 131.9,

134.1, 138.5, 154.8 (C^{Py}-Ph), 163.9 (C^{Py}-O). IR (KBr): 2216 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}D_2N_2O$ 288.1357; Found 288.1352.

(E)-,(Z)-2-Ethoxy-6-phenyl-4-(2-phenylethenyl)pyridine-3-carbonitrile (*(E)-/(Z)*-**2c**). *Mixture of isomers.* Obtained from **1a** (100 mg, 0.44mmol) and sodium ethoxide(1.1 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 9:1 in a yield of *E*-**2c** 44 mg (31%), yield of *Z*-**2c** 22 mg (16%). Colorless solid [51]. ^{1}H NMR, *E*-**2c** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm:1.54 t (3H, CH_3, *J* 7.0 Hz), 4.67 q (2H, OCH_2, *J* 7.2 Hz), 7.65 d (2H, H^{Ph}, *J* 7.0 Hz), 7.69 s (1H, H^{Py}), 8.12 d (2H, H^{Ph}, *J* 7.6 Hz).^{1}H NMR, *Z*-**2c** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.53 t (3H, CH_3, *J* 7.0 Hz), 4.65 q (2H, OCH_2, *J* 7.0 Hz), 6.77 d (1H, HC=, *J* 12.2 Hz), 7.07 d (1H, HC=, *J* 12.2 Hz), 7.72 s (1H, H^{Py}).^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.27-7.33 m, 7.37-7.47 m, 7.51-7.58 m, 7.71-7.74 m.^{13}C NMR, *E*-**2c** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 63.4 (CH_2, OEt), 108.2 (C^{Py}-H), 114.6 (CN), 122.8, 158.1, 163.9. ^{13}C NMR, *Z*-**2c** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 63.2 (CH_2, OEt), 94.1, 112.8 (C^{Py}-H), 114.9 (CN), 152.5, 157.1, 164.4. ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 124.7, 127.1, 127.3, 127.7, 128.4,128.58, 128.66, 128.69, 128.8, 128.9, 129.0, 129.7, 130.0, 130.1, 130.3, 130.6, 132.5, 136.7, 137.5. IR (KBr): 2222 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}N_2ONa$ 349.1317; Found 349.1311. GC-MS, m/z, Irel. (%): 326 M^+ (70), 311 (20), 297 (8), 281 (15), 272 (75), 254 (30), 249 (100), 77 (32).

2-Ethoxy-6-phenyl-4-phenylethynylpyridine (**3c**). Obtained from **1a** (100 mg, 0.44 mmol) and sodium ethoxide(1.1 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 9:1 in a yield of 11 mg (9%). Colorless solid. ^{1}H NMR, δ, ppm: 1.47 t (3H, CH_3, *J* 7.1 Hz), 4.53 q (2H, OCH_2, *J* 7.1 Hz), 6.81 s (1H, H^{Py}), 7.40-7.45 m (3H), 7.47 s (1H, H^{Py}), 7.48-7.51 m (3H), 7.58-7.61 m (2H), 8.07 d (2H, H^{Ph}, *J* 7.0 Hz). ^{13}C NMR, δ, ppm: 14.7 (OEt), 61.8 (OEt), 87.3 (C≡), 92.5 (C≡), 111.3 (C^{Py}-H), 115.0 (C^{Py}-H), 122.4, 126.7, 128.5, 128.6, 129.0, 129.1, 131.9, 134.1, 138.6, 154.9, 163.7. IR (KBr): 2211cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; Found 300.1383.

(E)-,(Z)-6-Phenyl-4-(2-phenylethenyl)-2-propoxypyridine-3-carbonitrile (*(E)-/(Z)*-**2d**). *Mixture of isomers.* Obtained from **1a** (50 mg, 0.22mmol) and sodium propoxide (0.55 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 9:1 in a yield of *E*-**2d** 20 mg (27%), yield of *Z*-**2d** 20 mg (27%). Colorless solid. ^{1}H NMR, *E*-**2d** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.13 t (3H, CH_3 from OPr, *J* 7.3 Hz), 1.94 sec (2H, CH_2 from OPr, *J* 7.3, 6.9 Hz), 4.56 t (2H, OCH_2 from OPr, *J* 6.7 Hz). ^{1}H NMR, *Z*-**2d** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.12 t (3H, CH_3 from OPr, *J* 7.5 Hz), 1.93 sec (2H, CH_2 from OPr, *J* 7.3, 6.7 Hz), 4.53 t (2H, OCH_2 from OPr, *J* 6.7 Hz), 6.76

d (1H, HC=, *J* 12.2 Hz), 7.06 d (1H, HC=, *J* 12.2 Hz), 7.22 s (1H, H^{Py}). ^{1}H NMR, (signals of mixture of isomers) δ, ppm:7.28-7.33 m, 7.37-7.45 m, 7.51-7.58 m, 7.66-7.73 m, 8.07-8.13 m. ^{13}C NMR, *E-2***e** (selected signals, obtained from spectrum of mixture of isomers)δ, ppm: 11.0 (CH_3, OPr), 23.0 (CH_2, OPr), 68.9 (OCH_2, OPr), 93.3 (C^{Py}, C-CN), 108.2 (C^{Py}-H), 114.6 (CN), 122.8 (C=), 151.5 (C^{Py}, C-C=), 157.8 (C^{Py}, C-Ph), 164.8 (C^{Py}, C-O). ^{13}C NMR, *Z*-**2d** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 10.5 (CH_3, OPr), 22.2 (CH_2, OPr), 68.8 (OCH_2, OPr), 94.1 (C^{Py}, C-CN), 112.8 (C^{Py}-H), 114.8 (CN), 124.6 (C=), 152.5 (C^{Py}, C-C=), 157.1 (C^{Py}, C-Ph), 164.6 (C^{Py}, C-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.1, 127.3, 127.6, 128.4, 128.6, 128.7, 128.7, 128.8, 128.9, 128.9, 129.0, 130.1, 132.5, 136.7, 136.9, 137.3, 137.5. IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O$ 341.1654; Found 341.1648.

2-Phenyl-4-phenylethynyl-6-propoxypyridine (**3d**). Obtained from **1a** (50 mg, 0.22 mmol) and sodium propoxide (0.55 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 9:1 in a yield of 10 mg (14%). Colorless solid. ^{1}H NMR, δ, ppm: 1.09 t (3H, CH_3 from OPr, *J* 7.4 Hz), 1.88 sec (2H, CH_2 from OPr, *J* 7.2, 7.0 Hz), 4.43 t (2H, OCH_2 from OPr, *J* 6.7 Hz), 6.82 s (1H, H^{Py}), 7.40-7.51 m (4H), 7.58-7.60 m (5H), 8.07 d (2H, H^{Ph}, *J* 7.1 Hz). ^{13}C NMR, δ, ppm: 10.6 (CH_3, OPr), 22.4 (CH_2, OPr), 67.7 (OCH_2, OPr), 87.3 (C≡), 92.6 (C≡), 111.3 (C^{Py}-H), 115.0 (C^{Py}-H), 122.4, 126.8, 128.5, 128.6, 129.0, 129.1, 131.9, 134.2, 138.6, 154.8 (C^{Py}, C-Ph), 163.9 (C^{Py}, C-O). IR (KBr): 2212 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO$ 314.1545; Found 314.1539.

(E)-,(Z)-2-Butoxy-6-phenyl-4-(2-phenylethenyl)pyridine-3-carbonitrile (*(E)-/(Z)*-**2e**). *Mixture of isomers.* Obtained from **1a** (50 mg, 0.22 mmol) and sodium butoxide (0.55 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 9:1 in a yield of *E-2***e** 15 mg (19%), yield of *Z-2***e** 25 mg (32%). Colorless solid. ^{1}H NMR, *E*-**2e** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.04 t (3H, CH_3 from OBu, *J* 7.3 Hz), 1.45 sec (2H, CH_2 from OBu, *J* 7.3, 6.4 Hz), 1.90 p (2H, from OBu, *J* 7.8, 6.7 Hz), 4.60 t (2H, OCH_2 from OBu, *J* 6.7 Hz). ^{1}H NMR, *Z*-**2e** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.04 t (3H, CH_3fromOBu, *J* 7.3 Hz), 1.45 sec (2H, CH_2 from OBu, *J* 7.3, 6.4 Hz), 1.89 p (2H, from OBu, *J* 7.8, 6.6 Hz), 4.58 t (2H, OCH_2 from OBu, *J* 6.6 Hz), 6.76 d (1H, HC=, *J* 12.2 Hz), 7.06 d (1H, HC=, *J* 12.2 Hz), 7.22 s (1H, H^{Py}). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.29-7.33 m, 7.37-7.47 m, 7.51-7.58 m, 7.65-7.74 m, 8.07-8.12 m.^{13}C NMR, *E*-**2e** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.0 (CH_3, OBu), 19.2 (CH_2, OBu), 30.9 (CH_2, OBu), 67.2 (OCH_2, OBu), 93.0 (C^{Py}, C-CN), 108.1 (C^{Py}-H), 114.6 (CN), 122.8 (C=), 151.5 (C^{Py}, C-C=), 157.8 (C^{Py}, C-Ph), 164.8 (C^{Py}, C-O). ^{13}C NMR, *Z*-**2e** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 13.9 (CH_3, OBu), 19.3 (CH_2, OBu), 30.9 (CH_2, OBu), 67.1 (OCH_2, OBu), 94.1 (C^{Py}, C-CN), 112.8 (C^{Py}-H), 114.9 (CN), 124.6 (C=), 152.5 (C^{Py}, C-C=), 157.1 (C^{Py}, C-

Ph), 164.6 (C^{Py}, C-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.1, 127.3, 127.7, 128.4, 128.6, 128.66, 128.69, 128.81, 128.84, 128.88, 128.90, 129.0, 130.08, 130.1, 130.2, 132.5, 136.7, 136.9, 137.3, 137.5. IR (KBr): 2222 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{22}N_2ONa$ 377.1630; Found 377.1624.

2-Butoxy-6-phenyl-4-phenylethynylpyridine (**3e**). Obtained from **1a** (50 mg, 0.22 mmol) and sodium butoxide (0.55 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 9:1 in a yield of 10 mg (14%). Colorless solid. ^{1}H NMR, δ, ppm: 1.03 t (3H, CH_3 from OBu, *J* 7.4 Hz), 1.45 sec (2H, CH_2 from OBu, *J* 7.3, 6.7 Hz), 1.84 p (2H, CH_2 from OBu, *J* 7.2, 6.7 Hz), 4.47 t (2H, OCH_2 from OBu, *J* 6.6 Hz), 6.82 s (1H, H^{Py}), 7.40-7.44 m (2H), 7.47 s (1H, H^{Py}), 7.47-7.50 m (2H), 7.54-7.60 m (2H), 7.72-7.75 m (2H), 8.07 d (2H, H^{Ph}, *J* 7.2 Hz).^{13}C NMR, δ, ppm: 13.9 (CH_3, OBu), 19.4 (CH_2, OBu), 31.2 (CH_2, OBu), 65.9 (OCH_2, OBu), 87.3 (C≡), 92.53 (C≡), 111.3 (C^{Py}-H), 115.0 (C^{Py}-H), 122.4 (C^{Ph}-C≡), 126.8, 128.5, 128.6, 129.0, 129.1, 131.9, 134.1, 138.7, 154.9 (C^{Py}, C-Ph), 163.9 (C^{Py}, C-O). IR (KBr): 2217 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{21}NONa$ 350.1521; Found 350.1515.

(E)-6-(4-Methylphenyl)-2-methoxy-4-(2-phenylethenyl)pyridine-3-carbonitrile (*E*-**2f**). Obtained from **1b** (50 mg, 0.20mmol) and sodium methoxide (0.51 mmol) in a yield of 31 mg (48%). Purification by preparative HPLC. Colorless solid. ^{1}H NMR, δ, ppm: 2.46 s (3H, CH_3), 4.19 s (3H, OCH_3), 7.34 d (2H, H^{Ar}, *J* 8.0 Hz), 3.38-7.47 m (4H), 7.55 d (1H, CH=, *J* 16.2 Hz), 7.66-7.69 m (2H), 7.68 s (1H, H^{Py}), 8.02 dd (2H, H^{Ar}, *J* 13.0, 8.2 Hz). ^{13}C NMR δ, ppm: 21.4 (CH_3), 54.4 (OCH_3), 92.5 (C^{Py}-CN), 108.0 (C^{Py}-H), 115.2 (CN), 122.7, 127.6, 128.6, 129.0, 129.6, 132.5, 134.9, 135.4, 136.9, 140.7, 151.4 (C^{Py}-C=C), 157.8 (C^{Py}-Ar), 164.9 (C^{Py}-O). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O$ 327.1497; Found 327.1492.

(Z)-6-(4-Methylphenyl)-2-methoxy-4-(2-phenylethenyl)pyridine-3-carbonitrile (*Z*-**2f**). Obtained from **1b** (50 mg, 0.20mmol) and sodium methoxide (0.51 mmol) in a yield of 24 mg (37%). Purification by preparative HPLC. Colorless solid. ^{1}H NMR δ, ppm: 2.39 s (3H, CH_3), 4.17 s (3H, OCH_3), 6.75 d (1H, CH=, *J* 12.2 Hz), 7.06 d (1H, CH=, *J* 12.2 Hz), 7.19-7.21 m (3H), 7.26-7.32 m (5H), 7.65 d (2H, H^{Ar}, *J* 8.2 Hz). ^{13}C NMR δ, ppm: 21.3 (CH_3), 54.3 (OCH_3), 93.6 (C^{Py}-CN), 112.7 (C^{Py}-H), 115.0 (CN), 124.6, 127.0, 128.4, 128.6, 128.9, 129.5, 134.6, 136.7, 137.3, 140.6, 152.4 (C^{Py}-C=C), 157.3 (C^{Py}-Ar), 164.7 (C^{Py}-O). IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O$ 327.1497; Found 327.1492.

2-(4-Methylphenyl)-6-methoxy-4-(phenylethynyl)pyridine (**3f**). Obtained from **1b** (50 mg, 0.20mmol) and sodium methoxide (0.51 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 9 mg (15%). Colorless solid. ^{1}H NMR, δ, ppm: 2.44 s (3H, CH_3), 4.07 s (3H, OCH_3), 6.80 s (1H, H^{Py}), 7.29 d (2H, H^{Ar}, *J* 8.6 Hz), 7.40-7.41 m (2H), 7.46 s (1H, H^{Py}), 7.58-7.61 m (3H), 7.99 d (2H, H^{Ar}, *J* 8.2 Hz). ^{13}C NMR, δ, ppm: 21.3 (CH_3), 53.4 (OCH_3), 87.3 (C≡), 92.5 (C≡), 110.7 (C^{Py}-H), 114.8 (C^{Py}-H), 122.4 (C^{Ph}-C≡), 126.6, 128.5,

129.0, 129.4, 131.9, 134.1, 135.8, 139.2, 154.9 (C^{Py}-C_6H_4Cl), 163.9 (C^{Py}-O). IR (KBr): 2218 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; Found 300.1383.

(E)-,(Z)-2-Ethoxy-6-(4-methylphenyl)-4-(2-phenylethenyl)pyridine-3-carbonitrile (*(E)-/(Z)-***2g**). Obtained from **1b** (50 mg, 0.20mmol) and sodium ethoxide (0.51 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2g** 24 mg (35%), yield of *Z*-**2g** 22 mg (32%). Colorless solid. ^{1}H NMR, *E*-**2g** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm:1.53 t (2H, OEt, *J* 7.0 Hz), 2.46 s (3H, Me), 4.65 q (3H, OEt, *J* 7.2 Hz), 7.54 d (1H, HC=, *J* 17.1 Hz), 7.69 s (1H, H^{Py}). ^{1}H NMR, *Z*-**2g** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.52 t (2H, OEt, *J* 7.0 Hz), 2.39 s (3H, Me), 4.64 q (3H, OEt, *J* 7.2 Hz), 6.75 d (1H, HC=, *J* 12.2 Hz), 7.05 d (1H, HC=, *J* 12.2 Hz), 7.62 d (2H, H^{Ar}, *J* 8.2 Hz). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.19-7.21 m, 7.31-7.34 m, 7.39-7.47 m, 7.66-7.69 m, 7.97-8.03 m. ^{13}C NMR, *E*-**2g** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 21.4 (Me), 63.2 (CH_2, OEt), 92.6 (C^{Py}-CN), 107.8 (C^{Py}-H), 114.3 (CN), 122.9 (C=), 135.0, 135.5, 136.7, 140.6, 151.4, 157.8, 164.6 (C^{Py}-O). ^{13}C NMR, Z-**2g** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 21.3 (Me), 63.1 (CH_2, OEt), 93.6 (C^{Py}-CN), 112.4 (C^{Py}-H), 115.0 (CN), 124.7 (C=), 134.7, 136.8, 137.1, 140.5, 152.4, 157.2, 164.4 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.0, 127.2, 127.6, 128.4, 128.6, 128.9, 129.0, 129.4, 129.57, 129.63, 132.4. IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}N_2O$ 341.1654; Found 341.1678. GC-MS, m/z, Irel. (%): 340 M^+ (70), 325 (20), 311 (10), 295 (12), 286 (70), 263 (100), 91 (20), 77 (15).

2-Ethoxy-6-(4-methylphenyl)-4-phenylethynylpyridine (**3g**). Obtained from **1b** (50 mg, 0.20mmol) and sodium ethoxide (0.51 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 4 mg (6%). Colorless solid. ^{1}H NMR, δ, ppm: 1.47 t (3H, OEt, *J* 7.0 Hz), 2.43 s (3H, Me), 4.52 q (2H, OEt, *J* 7.1 Hz), 6.78 s (1H, H^{Py}), 7.28-7.30 m (3H), 7.40-7.41 m (2H), 7.44 s (1H, H^{Py}), 7.54-7.60 m (2H), 7.97 d (2H, H^{Ar}, *J* 8.1 Hz).^{13}C NMR, δ, ppm: 14.7 (CH_3, OEt), 21.3 (Me), 61.8 (CH_2, OEt), 87.4 (C≡), 92.4 (C≡), 110.8 (C^{Py}-H), 114.6 (C^{Py}-H), 122.4,128.5, 129.0, 129.3, 130.90, 134.0, 135.9, 139.1, 154.9, 163.6 (C^{Py}-O). IR (KBr): 2219 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd fo $rC_{22}H_{20}NO$ 314.1545; Found 314.1539.

(E)-,(Z)-6-(4-Chlorophenyl)-2-methoxy-4-(2-phenylethenyl)pyridine-3-carbonitrile (*(E)-/(Z)-***2h**). *Mixture of isomers.* Obtained from **1c** (50 mg, 0.19 mmol) and sodium methoxide (0.48 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 8:2 in a yield of *E*-**2h** 16 mg (24%), yield of *Z*-**2h** 16 mg (24%). Colorless solid. ^{1}H NMR, *E*-**2h** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 4.18 s (3H, OCH_3), 7.56 d (1H, CH=, *J* 16.2 Hz), 8.08 d (2H, H^{Ar}, *J* 8.6 Hz). ^{1}H NMR, *Z*-**2h** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 4.16 s (3H, OCH_3), 6.76 d (1H, CH=, *J* 12.2 Hz), 7.09 d (1H, CH=, *J* 12.2 Hz), 7.18 s (1H, H^{Py}). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.32-7.52 m, 7.65-7.67

m. ^{13}C NMR, *E*-**2h** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.5 (OCH_3), 93.2 (C^{Py}-CN), 108.2 (C^{Py}-H), 114.9 (CN), 122.5, 136.3, 136.1, 136.5, 137.3, 151.7 (C^{Py}-C=C), 156.5 (C^{Py}-Ar), 164.9 (C^{Py}-O). ^{13}C NMR, *Z*-**2h** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.4 (OCH_3), 94.4 (C^{Py}-CN), 112.9 (C^{Py}-H), 114.7 (CN), 124.4, 135.7, 135.8, 136.4, 137.7, 152.7 (C^{Py}-C=C), 155.8 (C^{Py}-Ar), 164.7 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.7, 128.3, 128.5, 128.6, 128.7, 128.8, 128.96, 129.02, 129.1, 129.9. IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}ClNONa$ 369.0771; Found 369.0765.

2-(4-chlorophenyl)-6-methoxy-4-phenylethynyl–pyridine (**3h**). Obtained from **1c** (50 mg, 0.19 mmol) and sodium methoxide (0.48 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 8:2 in a yield of 6 mg (10%). Colorless solid. ^{1}H NMR, δ, ppm: 4.07 s (3H, OCH_3), 6.84 s (1H, H^{Py}), 7.40-7.42 m (2H), 7.45-7.47 m (2H), 7.54-7.60 m (2H), 7.72-7.74 m (2H), 8.03 d (2H, H^{Ar}, *J* 8.6 Hz). ^{13}C NMR, δ, ppm: 53.5 (OCH_3), 87.0 (C≡), 92.9 (C≡), 111.5 (C^{Py}-H), 115.0 (C^{Py}-H), 122.2, 128.01, 128.5, 128.8, 129.1, 131.9, 134.3, 136.2, 137.0, 153.6 (C^{Py}-Ph), 167.7 (C^{Py}-O). IR (KBr): 2220 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{20}H_{14}ClNO$ 320.0842; Found 320.0837.

(E)-,(Z)-2-Methoxy-6-(4-methoxyphenyl)-4-(2-phenylethenyl)pyridine-3-carbonitrile (*(E)-/(Z)*-**2i**). *Mixture of isomers.* Obtained from **1d** (50 mg, 0.19 mmol) and sodium methoxide (0.47 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2i** 25 mg (38%), yield of *Z*-**2i** 28 mg (43%). Colorless solid. ^{1}H NMR, *E*-**2i** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 23.92 s (3H, OCH_3), 4.18 s (3H, OCH_3), 7.54 d (1H, CH=, *J* 16.2 Hz), 7.63 s (1H, H^{Py}), 8.09 dd (2H, H^{Ar}, *J* 14.4, 8.9 Hz). ^{1}H NMR, **Z-2i** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 3.86 s (3H, OCH_3), 4.16 s (3H, OCH_3), 6.74 d (1H, CH=, *J* 12.2 Hz), 6.91 d (2H, H^{Ar}, *J* 8.9 Hz), 7.05 d (1H, CH=, *J* 12.1 Hz) 7.17 s (1H, H^{Py}), 7.71 d (2H, H^{Ar}, *J* 8.9 Hz).^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.27-7.33 m, 7.37-7.49 m, 7.66-.7.73 m. ^{13}C NMR, *E*-**2i** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.4 (OCH_3), 55.5 (OCH_3), 91.9 (C^{Py}-CN), 107.5 (C^{Py}-H), 114.2 (C^{ap}, o-OCH_3), 115.3 (CN), 122.8, 128.6, 128.8, 129.0, 129.7, 132.4, 135.4, 136.8, 151.3 (C^{Py}-C=C), 157.5 (C^{Py}-Ar), 161.6 (C^{Ar}-O), 164.9 (C^{Py}-O). ^{13}C NMR, *Z*-**2i** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.3 (OCH_3), 55.4 (OCH_3), 93.0 (C^{Py}-CN), 112.1 (C^{Py}-H), 114.1 (C^{ap}, o-OCH_3), 115.1 (CN), 124.7, 127.6, 128.4, 128.6, 128.9, 129.9, 135.8, 137.2, 152.3 (C^{Py}-C=C), 156.9 (C^{Py}-Ar), 161.5 (C^{Ar}-O), 164.6 (C^{Py}-O). IR (KBr): 2219 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O$ 343.1447; Found 343.1441.

2-Methoxy-6-(4-methoxyphenyl)-4-(phenylethynyl)pyridine (**3i**). Obtained from **1d** (50 mg, 0.19 mmol) and sodium methoxide (0.47 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 10 mg (16%). Colorless solid. ^{1}H NMR, δ, ppm:

3.90 s (3H, OCH_3), 4.06 s (3H, OCH_3), 6.77 s (1H, H^{Py}), 7.01 d (2H, H^{Ar}, *J* 8.9 Hz), 7.28-7.33 m (2H), 7.40-7.42 m (2H), 7.58-7.61 m (2H), 8.05 d (2H, H^{Ar}, *J* 9.0 Hz). ^{13}C NMR, δ, ppm: 55.4 (OCH_3), 87.4 (C≡), 92.5 (C≡), 114.0 (o-OCH^3-C^{Ar}), 114.1 (C^{Py}-H), 114.4 (C^{Py}-H), 122.4, 128.2. 128.5. 128.9. 129.0, 131.9. 154.6 (C^{Py}-Ar), 160.6 (C^{Py}-O), 163.9 (C^{Ar}-O). IR (KBr): 2219 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO_2$ 316.1338; Found 316.1332.

(E)-,(Z)-2-Ethoxy-6-(4-methoxyphenyl)-4-(2-phenylethenyl)pyridine-3-carbonitrile (*(E)-/(Z)-***2j**). *Mixture of isomers.* Obtained from **1d** (50 mg, 0.19 mmol) and sodium ethoxide (0.48 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 8:2 in a yield of *E*-**2j** 27 mg (38%), yield of *Z*-**2j** 9 mg (13%). Colorless solid. ^{1}H NMR, *E*-**2j** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.52 t (2H, OEt, *J* 7.0 Hz), 3.91 s (3H, OMe), 4.65 q (3H, OEt, *J* 7.0 Hz), 7.53 d (1H, HC=, *J* 16.2 Hz), 7.61 s (1H, H^{Py}).^{1}H NMR, *Z*-**2j** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.51 t (2H, OEt, *J* 7.0 Hz), 3.86 s (3H, OMe), 4.63 q (3H, OEt, *J* 7.2 Hz), 6.74 d (1H, HC=, *J* 12.2 Hz), 6.90 d (2H, H^{Ar}, *J* 8.9 Hz), 7.14 s (1H, H^{Py}). ^{1}H NMR, (signals of mixture of isomers) δ, ppm:7.02-7.06 m, 7.29-7.32 m, 7.38-7.51 m, 7.64-7.70 m, 8.04-8.10 m. ^{13}C NMR, *E*-**2j** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 55.4 (OMe), 63.3 (CH_2, OEt), 96.2 (C^{Py}-CN), 107.2 (C^{Py}-H), 114.1, 114.3, 114.3 (CN), 122.9 (C=), 136.6, 137.0, 151.3, 157.8, 161.8, 163.9 (C^{Py}-O). ^{13}C NMR, *Z*-**2j** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 55.4 (OMe), 63.1 (CH_2, OEt), 92.1 (C^{Py}-CN), 111.9 (C^{Py}-H), 113.7, 114.2, 115.4 (CN), 121.4 (C=), 136.5, 138.2, 152.3, 157.4, 161.5, 164.6 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 124.8, 127.6, 128.3, 128.6, 128.58, 128.62, 128.76, 128.82, 128.9, 129.0, 129.56, 129.61, 129.9, 130.0, 130.3, 132.4. IR (KBr): 2220 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}N_2O_2Na$ 379.1422; Found 379.1417. GC-MS, m/z, Irel. (%): 356 M^+ (100), 341 (22), 327 (8), 311 (10), 302 (75), 279 (85), 77 (18).

2-Ethoxy-6-(4-methoxyphenyl)-4-phenylethynylpyridine (**3j**). Obtained from **1d** (50 mg, 0.19 mmol) and sodium ethoxide (0.48 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 8:2 in a yield of 3 mg (5%). Colorless solid. 1H NMR, δ, ppm:1.47 t (3H, OEt, *J* 7.1 Hz), 3.89 s (3H, OMe), 4.51 q (2H, OEt, *J* 7.0 Hz), 6.75 s (1H, H^{Py}), 7.01 d (2H, H^{Ar}, *J*8.9 Hz), 7.40-7.41 m (4H), 7.58-7.60 m (2H), 8.03 d (2H, H^{Ar}, *J* 8.8 Hz).^{13}C NMR, δ, ppm:14.7 (CH_3, OEt), 55.4 (Me), 61.7 (CH_2, OEt), 87.4 (C≡), 92.4 (C≡), 110.3 (C^{Py}-H), 114.0 (C^{Ar}), 114.2 (C^{Py}-H), 128.1, 128.5, 129.0, 131.3, 131.9, 134.0, 154.6, 160.6, 163.6 (C^{Py}-O). IR (KBr): 2218 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_2$ 330.1494; Found 330.1489.

(E)-,(Z)-2-Methoxy-4-(2-(4-methylphenyl)ethenyl)-6-phenylpyridine-3-carbonitrile (*(E)-/(Z)-***2k**). *Mixture of isomers.* Obtained from **1e** (50 mg, 0.20 mmol) and sodium methoxide (0.50 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2k** 22 mg (34%), yield of *Z*-**2k** 4 mg (6%). Colorless solid. ^{1}H NMR, *E*-**2k** (selected signals,

obtained from spectrum of mixture of isomers) δ, ppm: 2.42 s (3H, CH_3), 4.19 s (3H, OCH_3), 7.37 d (1H, CH=, *J* 16.2 Hz), 7.70 s (1H, H^{Py}), 8.13 dd (2H, H^{Ar}, *J* 7.9, 1.6 Hz). ^{1}H NMR, *Z*-**2**l (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 2.37 s (3H, CH_3), 4.18 s (3H, OCH_3), 6.70 d (1H, CH=, *J* 12.2 Hz), 7.02 d (1H, CH=, *J* 12.2 Hz), 7.12 d (2H, H^{Ar}, *J* 8.1 Hz), 7.17 d (2H, H^{Ar}, *J* 8.1 Hz). ^{13}C NMR, *E*-**2k** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 21.5 (CH_3), 54.4 (OCH_3), 92.7 (C^{Py}-CN), 108.3 (C^{Py}-H), 115.2 (CN), 121.6, 137.0, 137.7, 140.1, 151.7 (C^{Py}-C=C), 157.7 (C^{Py}-Ar), 164.9 (C^{Py}-O). ^{13}C NMR, *Z*-**2k** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 21.3 (CH_3), 54.4 (OCH_3), 113.1 (C^{Py}-H), 114.8 (CN), 123.8, 137.4, 138.5, 140.6, 153.0 (C^{Py}-C=C), 157.1 (C^{Py}-Ar), 164.7 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.1, 127.3, 127.6, 128.7, 128.8, 129.3, 129.7, 130.2, 130.3, 132.4, 132.6. IR (KBr): 2219 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O$ 327.1497; Found 327.1492.

2-Methoxy-4-(4-methylphenyl)ethynyl-6-phenylpyridine (**3k**). Obtained from **1e** (50 mg, 0.20mmol) and sodium methoxide (0.50 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 3 mg (5%). Colorless solid. ^{1}H NMR, δ, ppm: 2.41 s (3H, OCH_3), 4.07 s (3H, OCH_3), 6.82 s (1H, H^{Py}), 7.12-7.56 m (5H), 8.09 d (2H, H^{Ar}, *J* 8.5 Hz). ^{13}C NMR (selected signals – low concentration), δ, ppm: 23.0 (CH_3), 54.4 (OCH_3), 86.7 (C≡), 93.0 (C≡), 111.0 (C^{Py}-H), 115.3 (C^{Py}-H), 128.7, 128.8, 129.1, 129.3, 131.8, 138.6, 139.4, 154.8 (C^{Py}-Ph), 164.0 (C^{Py}-O). IR (KBr): 2221 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; Found 300.1383.

(E)-,(Z)-2-Ethoxy-4-(2-(4-methylphenyl)ethenyl)-6-phenylpyridine-3-carbonitrile (*(E)-/(Z)*-**2l**). *Mixture of isomers.* Obtained from **1e** (50 mg, 0.20 mmol) and sodium ethoxide (0.50 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2l** 17 mg (10%), yield of *Z*-**2l** 8 mg (5%). Colorless solid. ^{1}H NMR, *E*-**2l** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.53 t (2H, OEt, *J* 7.2 Hz), 2.42 s (3H, Me), 4.66 q (3H, OEt, *J* 7.0 Hz), 7.68 s (1H, H^{Py}), 8.11 d (2H, H^{Ar}, *J*8.2 Hz). ^{1}H NMR, *Z*-**2l** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.52 t (2H, OEt, *J* 7.0 Hz), 2.37 s (3H, Me), 4.65 q (3H, OEt, *J* 7.0 Hz), 6.70 d (1H, HC=, *J* 12.1 Hz), 7.01 d (1H, HC=, *J* 12.2 Hz), 7.12 d (2H, H^{Ar}, *J* 8.1 Hz), 7.18 d (2H, H^{Ar}, *J* 8.1 Hz), 7.36 s (1H, H^{Py}). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.22-7.26 m, 7.39-7.42 m, 7.50-7.59 m, 7.24-7.77 m. ^{13}C NMR, *E*-**2l** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 21.4 (Me), 63.2 (CH_2, OEt), 92.9 (C^{Py}-CN), 108.0 (C^{Py}-H), 114.6 (CN), 121.7 (HC=), 140.1, 151.7, 157.7, 164.7 (C^{Py}-O). ^{13}C NMR, *Z*-**2l** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 21.3 (Me), 63.1 (CH_2, OEt), 94.1 (C^{Py}-CN), 112.8 (C^{Py}-H), 115.2 (CN), 123.9 (HC=), 140.6, 152.9, 158.0, 164.4 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.1, 124.2, 127.6, 128.7, 128.8, 128.86, 128.88, 129.3, 129.4, 129.7, 130.1, 130.2, 130.5, 130.9,

132.4, 132.7, 132.8, 136.9, 137.1, 137.2, 137.5, 137.8. IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}N_2ONa$ 363.1473; Found 363.1468.

2-Ethoxy-4-(4-methylphenyl)ethynyl-6-phenylpyridine (**3l**). Obtained from **1e** (50 mg, 0.20mmol) and sodium ethoxide (0.50 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 6 mg (5%). Colorless solid. ^{1}H NMR, δ, ppm:1.47 t (3H, OEt, *J* 7.1 Hz), 2.41 s (3H, Me), 4.53 q (2H, OEt, *J* 7.1 Hz), 6.79 s (1H, H^{Py}), 7.21 d (2H, H^{Ar}, *J* 7.9 Hz), 7.40-7.44 m (2H), 7.46 s (1H, H^{Py}), 7.47-7.49 m (3H), 8.07 d (2H, H^{Ar}, *J* 7.1 Hz). ^{13}C NMR, δ, ppm: 13.7 (CH_3, OEt), 19.2 (Me), 65.6 (CH_2, OEt), 86.8 (C≡), 93.0 (C≡), 111.2 (C^{Py}-H), 115.1 (C^{Py}-H), 119.3, 126.6, 128.6, 128.9, 129.1, 129.5, 130.9, 131.8, 132.4, 134.4, 138.6, 139.3, 154.8, 163.7, 137.7 (C^{Py}-O). IR (KBr): 2212 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO$ 314.1545; Found 314.1539.

(E-),(Z)- 4-(2-(4-chlorophenyl)ethenyl)-2-methoxy-6-phenylpyridine-3-carbonitrile (*(E)-/(Z)*-**2m**). *Mixture of isomers.* Obtained from **1f** (50 mg, 0.19 mmol) and sodium methoxide (0.48 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2m** 12 mg (18%), yield of *Z*-**2m** 18 mg (26%). Colorless solid. ^{1}H NMR, *E*-**2m** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 4.20 s (3H, OCH_3), 7.69 s (1H, H^{Py}), 8.13 dd (2H, H^{Ar}, *J* 7.7, 1.8 Hz).^{1}H NMR, Z-**2m** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 4.19 s (3H, OCH_3), 6.77 d (1H, CH=, *J* 12.2 Hz), 6.99 d (1H, CH=, *J* 12.2 Hz), 7.80 dt (2H, H^{Ar}, *J* 7.5, 3.6 Hz). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.19-7.59 m. ^{13}C NMR, *E*-**2m** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.5 (OCH_3), 97.3 (C^{Py}-CN), 108.4 (C^{Py}-H), 151.2 (C^{Py}-C=C), 155.9 (C^{Py}-Ar). ^{13}C NMR, *Z*-**2m** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.5 (OCH_3), 94.0 (C^{Py}-CN), 112.9 (C^{Py}-H), 114.7 (CN), 151.2 (C^{Py}-C=C), 157.5 (C^{Py}-Ar), 164.7 (C^{Py}-O). ^{13}C NMR,(signals of mixture of isomers) δ, ppm: 125.2, 127.1, 127.3, 128.2, 128.7, 128.8, 128.85, 128.88, 128.92, 129.3, 129.6, 130.2, 130.4, 132.6, 134.0, 134.4, 135.8, 137.2. IR (KBr): 2222 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}ClNONa$ 369.0771; Found 369.0765.

4-(4-Chlorophenyl)ethynyl-2-methoxy-6-phenylpyridine (**3m**). Obtained from **1f** (50 mg, 0.19mmol) and sodium methoxide (0.48 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 3 mg (5%). Colorless solid. ^{1}H NMR, δ, ppm: 4.08 s (3H, OCH_3), 6.82 s (1H, H^{Py}), 7.39 d (2H, H^{Ar}, *J* 8.5 Hz), 7.44-7.56 m (4H), 7.73 dd (2H, H^{Ar}, *J* 5.6, 3.4 Hz), 8.08 d (2H, H^{Ar}, *J* 7.0 Hz).^{13}C NMR (selected signals – low concentration), δ, ppm: 53.4 (OCH_3), 111.2 (C^{Py}-H), 115.1 (C^{Py}-H), 126.8, 128.7, 128.8, 128.9, 130.9, 130.1. IR (KBr): 2223 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}ClNO$ 320.0842; Found 320.0837.

(E)-,(Z)-2-Methoxy-4-(2-(4-methoxyphenyl)ethenyl)-6-phenylpyridine-3-carbonitrile (*(E)-/(Z)*-**2n**). *Mixture of isomers.* Obtained from **1g** (50 mg, 0.16mmol) and sodium methoxide (0.40

mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2n** 25 mg (45%), yield of *Z*-**2n** 23 mg (41%). Colorless solid. 1H NMR, *E*-**2n** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 3.89 s (3H, OCH_3), 4.19 s (3H, OCH_3), 6.83 d (2H, H^{Ar}, *J* 8.8 Hz), 7.68 s (1H, H^{Py}), 7.83 dd (2H, H^{Ar}, *J* 6.5, 3.2 Hz), 8.13 dd (2H, H^{Ar}, *J* 8.0, 1.6 Hz). ^{1}H NMR, *Z*-**2n** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 3.82 s (3H, OCH_3), 4.18 s (3H, OCH_3^Z), 6.64 d (1H, =CH, *J* 12.1 Hz), 6.78 d (2H, H^{Ar}, *J* 8.7 Hz), 7.35 s (1H, H^{Py}), 7.97 dd (2H, H^{Ar}, *J* 7.3, 2.3 Hz), 8.10 dd (2H, H^{Ar}, *J* 7.4, 2.3 Hz). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 6.93-6.98 m, 7.22-7.30 m, 7.41-7.43 m, 7.50-7.54 m, 7.59-7.64 m. ^{13}C NMR, *E*-**2n** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.4 (OCH_3), 55.3 (OCH_3), 94.0 (CN). ^{13}C NMR, *Z*-**2n** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 54.4 (OCH_3), 55.4 (OCH_3), 92.5 (CN). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 108.1, 112.9, 114.1, 114.5, 114.3, 114.6, 114.9, 115.3, 120.3, 122.7, 127.1, 127.3, 127.4, 128.0, 128.1, 128.7, 129.2, 128.8, 128.9, 130.17, 130.21, 130.5, 130.6, 134.2, 136.7, 136.8, 137.4, 137.8, 138.8, 151.9, 153.2, 157.2, 157.6, 159.8, 161.0, 161.1, 164.7, 165.0. IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O_2$ 343.1447; Found 343.1441.

2-Methoxy-4-(2-(4-methoxyphenyl)ethynyl)–6-phenylpyridine (**3n**). Obtained from **1g** (50 mg, 0.16mmol) and sodium methoxide (0.40mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 6 mg (12%). Colorless solid. ^{1}H NMR, δ, ppm: 3.87 s (3H, OCH_3), 4.07 s (3H, OCH_3), 6.81 s (1H, H^{Py}), 6.93 d (2H, H^{Ar}, *J* 8.8 Hz), 7.41-7.55 m (6H), 8.09 d (2H, H^{Ar}, *J* 8.5 Hz).^{13}C NMR, δ, ppm: 53.4 (OCH_3), 55.3 (OCH_3), 86.2, 92.9, 110.8, 114.1, 115.1, 126.7, 128.6, 129.1, 133.5, 134.5, 138.6, 154.7, 160.2, 163.9. IR (KBr): 2219cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{21}H_{18}NO_2$316.1338; Found 316.1392.

(E),(Z)-6-(4-chlorophenyl)-2-methoxy-4-(2-(4-methylphenyl)ethenyl)pyridine-3-carbonitrile (*(E)-/(Z)*-**2o**). *Mixture of isomers.* Obtained from **1h** (50 mg, 0.18 mmol) and sodium methoxide (0.45 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2o** 17 mg (26%), yield of *Z*-**2o** 21 mg (32%). Colorless solid. 1H NMR, *E*-**2o** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 2.43 s (3H, CH_3), 4.18 s (3H, OCH_3), 7.66 s (1H, H^{Py}), 8.04 d (2H, H^{Ar}, *J* 8.7 Hz), 8.07 d (2H, H^{Ar}, *J* 8.7 Hz) .^{1}H NMR, *Z*-**2o** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 2.37 s (3H, CH_3), 4.16 s (3H, OCH_3), 6.69 d (1H, CH=, *J* 12.1 Hz), 7.04 d (1H, CH=, *J* 12.2 Hz), 7.12 d (2H, H^{Ar}, *J* 8.1 Hz), 7.17 d (2H, H^{Ar}, *J* 8.2 Hz), 7.23 s (1H, H^{Py}), 7.37 d (2H, H^{Ar}, *J* 8.7 Hz), 7.69 d (2H, H^{Ar}, *J* 8.7 Hz). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.34-7.39 m, 7.48-7.58 m, 7.67-7.71 m. ^{13}C NMR, *E*-**2o** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 21.5 (CH_3), 54.5 (OCH_3), 93.0 (C^{Py}-CN), 108.1 (C^{Py}-H), 115.0 (CN), 121.4, 132.5, 135.4, 137.3, 138.9, 140.3, 151.9 (C^{Py}-C=C), 156.4 (C^{Py}-Ar), 164.9 (C^{Py}-O). ^{13}C NMR, *Z*-**2o** (selected signals, obtained from

spectrum of mixture of isomers) δ, ppm: 21.3 (CH_3), 54.4 (OCH_3), 94.4 (C^{Py}-CN), 112.9 (C^{Py}-H), 114.7 (CN), 123.6, 132.4, 132.7, 135.9, 136.4, 138.6, 153.0 (C^{Py}-C=C), 155.8 (C^{Py}-Ar), 164.7 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 27.7, 128.4, 128.5, 128.8, 128.9, 129.0, 129.4, 129.8. IR (KBr): 2222 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N_2O$ 361.1108; Found 361.1102.

2-(4-Chlorophenyl)-6-methoxy-4-(4-methylphenyl)ethynylpyridine (**3o**). Obtained from **1h** (50 mg, 0.18mmol) and sodium methoxide (0.45mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 10 mg (17%). Colorless solid. ^{1}H NMR, δ, ppm: 2.41 s (3H, CH_3), 4.06 s (3H, OCH_3), 6.83 s (1H, H^{Py}), 7,21 d (2H, H^{Ar}, *J* 7.9 Hz), 7.44-7.49 m (5H), 8.02 d (2H, H^{Ar}, *J* 8.6 Hz). ^{13}C NMR, δ, ppm: 24.6 (CH_3), 53.5 (OCH_3), 86.5 (C≡), 93.3 (C≡), 111.3 (C^{Py}-H), 115.0 (C^{Py}-H), 119.1 (C^{Ar}-C≡), 128.0, 128.8, 129.3, 131.8, 134.6, 136.1, 137.0, 139.4, 153.5 (C^{Py}-C_6H_4Cl), 164.0 (C^{Py}-O). IR (KBr): 2219 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{15}NONa$ 308.1051; Found 308.1046.

(E)-,(Z)-6-(4-Bbromphenyl)-2-methoxy-4-(2-(4-methylphenyl)ethenyl)pyridine-3-carbonitrile (*(E)-/(Z)*-**2p**). *Mixture of isomers.* Obtained from **1i** (50 mg, 0.16 mmol) and sodium methoxide (0.40 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 95:5 in a yield of *E*-**2p** 23 mg (38%), yield of *Z*-**2p** 21 mg (34%). Colorless solid. ^{1}H NMR, *E*-**2p** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 2.42 s (3H, CH_3), 4.18 s (3H, OCH_3), 7.26 d (2H, H^{Ar}, *J* 7.9 Hz), 7.36 d (1H, HC=, *J* 16.2 Hz), 8.00 d (2H, H^{Ar}, J 8.5 Hz). ^{1}H NMR, *Z*-**2p** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 2.37 s (3H, CH_3), 4.16 s (3H, OCH_3), 6.70 d (1H, HC=, *J* 12.2 Hz), 7.04 d (1H, HC=, *J* 12.2 Hz), 7.12 d (2H, H^{Ar}, *J* 8.1 Hz), 7.17 d (2H, H^{Ar}, *J* 8.1 Hz), 7.23 s (1H, H^{Py}). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.51-7.56 m, 7.61-7.67 m. ^{13}C NMR, *E*-**2p** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 21.5 (CH_3), 54.5 (OCH_3), 93.1 (C^{Py}, C-CN), 108.1 (C^{Py}-H), 115.0 (CN), 124.9, 151.9, 156.4, 164.9. ^{13}C NMR, *Z*-**2p** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 21.3 (CH_3), 54.4 (OCH_3), 94.4 (C^{Py}, C-CN), 112.9 (C^{Py}-H), 114.7 (CN), 124.8, 153.1, 155.8, 164.7. ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 121.4, 123.6, 127.7, 128.6, 128.8, 129.3, 129.7, 131.9, 132.0, 132.4, 132.5, 132.7, 136.3, 136.6, 137.3, 137.7, 138.6, 140.3. IR (KBr): 2221 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}BrN_2O$ 405.0603; Found 405.0597.

6-(4-Bromphenyl)-2-methoxy-4-(2-(4-methylphenyl)ethynyl)pyridine (**3p**). Obtained from **1i** (50 mg, 0.16 mmol) and sodium methoxide (0.40 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 95:5 in a yield of 8 mg (14%). Colorless solid. ^{1}H NMR, δ, ppm: 2.41 s (3H, CH_3), 4.06 s (3H, OCH_3), 6.83 s (1H, H^{Py}), 7.21 d (2H, H^{Ar}, *J* 7.9 Hz), 7.44 s (1H, H^{Py}), 7.48 d (2H, H^{Ar}, *J* 8.1 Hz), 7.61 d (2H, H^{Ar}, *J* 8.6 Hz), 7.96 d (2H, H^{Ar},*J* 8.7 Hz). ^{13}C NMR, δ, ppm: 21.6 (CH_3), 53.5 (OCH_3), 86.5, 93.2, 111.4, 115.0, 119.1, 123.5, 128.3, 129.3, 131.8, 134.2,

134.6, 137.5, 139.4, 153.6, 164.0. IR (KBr): 2219 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}BrNO$ 478.0494; Found 478.0511.

(E)-,(Z)-6-(4-Bromphenyl)-2-ethoxy-4-(2-(4-methylphenyl)ethenyl)pyridine-3-carbonitrile (*(E)-/(Z)*-**2q**). *Mixture of isomers.* Obtained from **1i** (50 mg, 0.16 mmol) and sodium ethoxide (0.40 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of *E*-**2q** 25 mg (39%), yield of *Z*-**2q** 9 mg (14%). Colorless solid. ^{1}H NMR, *E*-**2q** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm:1.53 t (2H, OEt, *J* 7.0 Hz), 2.43 s (3H, Me), 4.64 q (3H, OEt, *J* 7.2 Hz), 7.34 d (1H, HC=, *J* 16.2 Hz). ^{1}H NMR, *Z*-**2q** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 1.52 t (2H, OEt, *J* 7.0 Hz), 2.37 s (3H, Me), 4.62 q (3H, OEt, *J* 7.0 Hz), 6.69 d (1H, HC=, *J* 12.2 Hz), 7.03 d (1H, HC=, *J* 12.1 Hz), 7.12 d (2H, H^{Ar}, *J* 8.1 Hz), 7.17 d (2H, H^{Ar}, *J* 8.1 Hz), 7.20 s (1H, H^{Py}), 7.24 d (2H, H^{Ar}, *J* 8.0 Hz). ^{1}H NMR, (signals of mixture of isomers) δ, ppm: 7.50-7.61 m, 7.64-7.75 m, 7.73-7.75 m, 7.94-7.99 m.^{13}C NMR, *E*-**2q** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 13.7 (CH_3, OEt), 21.3 (Me), 66.6 (CH_2, OEt), 94.5 (C^{Py}-CN), 107.8 (C^{Py}-H), 114.8 (CN), 121.2 (C=), 138.6, 151.9, 156.4, 167.7 (C^{Py}-O). ^{13}C NMR, *Z*-**2q** (selected signals, obtained from spectrum of mixture of isomers) δ, ppm: 14.5 (CH_3, OEt), 19.2 (Me), 63.2 (CH_2, OEt), 94.5 (C^{Py}-CN), 112.7 (C^{Py}-H), 114.3 (CN), 123.7 (C=), 137.5, 153.0, 155.8, 164.4 (C^{Py}-O). ^{13}C NMR, (signals of mixture of isomers) δ, ppm: 127.7, 128.6, 128.7, 128.8, 128.9, 129.3, 129.4, 129.7, 130.9, 131.9, 132.0, 132.1, 132.4, 132.8. IR (KBr): 2223 cm^{-1} (CN). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}BrN_2O$ 419.0759; Found 419.0754.

2-(4-Bromphenyl)-6-ethoxy-4-(4-methylphenyl)ethynylpyridine (**3q**). Obtained from **1i** (50 mg, 0.16 mmol) and sodium ethoxide (0.40 mmol). Purification by preparative TLC with mixture petroleum ether–ethyl acetate, 85:15 in a yield of 4 mg (7%). Colorless solid. ^{1}H NMR, δ, ppm:1.46 t (3H, OEt, *J* 7.1 Hz), 2.41 s (3H, Me), 4.50 q (2H, OEt, *J* 7.0 Hz), 6.81 s (1H, H^{Py}), 7.21 d (2H, H^{Ar}, *J* 7.9 Hz), 7.42 s (1H, H^{Py}), 7.48 d (2H, H^{Ar}, *J* 8.1 Hz), 7.60 d (2H, H^{Ar}, *J* 8.6 Hz), 7.94 d (2H, H^{Ar}, *J* 8.6 Hz). ^{13}C NMR, δ, ppm: 14.1 (CH_3, OEt), 21.6 (Me), 65.6 (CH_2, OEt), 86.6 (C≡), 93.2 (C≡), 111.6 (C^{Py}-H), 114.8 (C^{Py}-H), 119.2, 128.3, 128.9, 129.3, 130.9, 131.8, 131.8, 139.4, 153.6, 163.8, 167.7 (C^{Py}-O). IR (KBr): 2214 cm^{-1} (C≡C). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}BrNO$ 392.0650; Found 392.0645.

Procedure for the Synthesis of 1-cyano-5-oxo-5-phenyl-3-phenylethynylpentannitrile (4) and 4-hydroxy-3-(oxophenylmethyl)-4-phenyl-2,6-(bis(phenyletynyl)cyclohexane-1,1-dicarbonitrile (5). Malononitrile (36.3 mg, 0.55 mmol) was added to absolute THF (1 mL), the flask was filled with argon and the solution (0.2 mL, 2 mmol/mL) of LDA (0.55 mmol) in THF was dropwise added to obtained mixture. The solution of (E)-1,5-diphenylpent-2-en-4-yn-1-one **1a** (50 mg, 0.22 mmol) in absolute THF(1 mL) was added to malononitrile solution and mixture was stirring at room temperature for 17 h. The reaction mixture was poured into water (30 mL), and

extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried with Na_2SO_4. Solvent was evaporated under the reduced pressure. The obtained residue was subjected to preparative TCL on silica gel with eluation by petroleum ether−ethyl acetate mixture (75 : 25 vol.).

1-Cyano-5-oxo-5-phenyl-3-phenylethynylpentannitrile (**4**)*, 4-hydroxy-3-(oxophenylmethyl)-4-phenyl-2,6-(bis(phenyletynyl)cyclohexane-1,1-dicarbonitrile* (**5**). Mixture of compounds in a yield of **4** 27 mg (41%), yield of **5** 13 mg (22%). Yellow crystals. ^{1}H NMR, **4** (selected signals, obtained from spectrum of mixture of compounds) δ, ppm: 3.60 d (1H, CH_2, *J* 8.8 Hz), 3.67 d (1H, CH_2, *J* 4.5 Hz), 3.98 dt (1H, CH-C≡C, *J* 9.0, 4.6 Hz), 4.61 d (1H, CH-$(CN)_2$, *J* 4.6 Hz), 7.68 t (1H, H^{Ph}, *J* 7.4 Hz), 8.02 d (2H, H^{Ph}, *J* 7.3 Hz). ^{1}H NMR, **5** (selected signals, obtained from spectrum of mixture of compounds) δ, ppm: 2.40 s (1H, OH), 3.55 d (1H, CH_2, *J* 8.8 Hz), .3.72 d (1H, CH_2, *J* 4.5 Hz), 4.06 dd (1H, CH-CH_2, *J* 9.8, 6.0 Hz), 4.15 d (1H, CH-CO, *J* 11.5 Hz), 4.60 d (1H, CH-CH-CO, *J* 10.3 Hz), 6.97 d (2H, H^{Ph}, *J* 7.2 Hz), 7.87 d (2H, H^{Ph}, *J* 7.5 Hz). ^{1}H NMR, (signals of mixture of compounds) δ, ppm: 7.13-7.26 m, 7.33-7.42 m, 7.49-7.57 m. ^{13}C NMR, **4** (selected signals, obtained from spectrum of mixture of compounds) δ, ppm: 28.0 (CH-$(CN)_2$), 30.6 (CH-C≡C), 40.3 (CH_2), 83.9 (C≡), 86.9 (C≡), 111.1 (CN), 111.6 (CN), 128.2, 128.39, 129.0, 132.0, 196.9 (CO). ^{13}C NMR, **5** (selected signals, obtained from spectrum of mixture of compounds) δ, ppm: 34.3 (CH-CH_2), 37.3 (CH_2), 41.9 (C-$(CN)_2$), 46.2 (CH-CH-CO), 49.9 (CH-CO), 73.8 (C-OH), 82.2 (C≡), 83.9 (C≡), 86.7 (C≡), 89.4 (C≡), 112.4 (CN), 113.9 (CN), 202.8 (CO). ^{13}C NMR, (signals of mixture of compounds) δ, ppm: 120.9, 121.5, 121.7, 124.4, 128.0, 128.1, 128.36, 128.66, 128.72, 128.8, 129.10, 129.14, 131.7, 132.06, 134.4, 135.5, 137.2, 142.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **4** $C_{20}H_{14}N_2ONa$ 321.1004; Found 321.0998. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **5** $C_{37}H_{26}N_2O_2Na$ 553.1892; Found 553.1886. IR (KBr): 1664 cm^{-1} (CO), 1683 cm^{-1} (CO), 2219 cm^{-1} (CN, C≡C).

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Supplementary data

The data contain ^{1}H, ^{13}C NMR, IR spectra of compounds, X-Ray data, fluorescent spectra, and HPLC data.

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