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2*H*-bis-1,2,3-triazolo-isoquinoline. Design, synthesis and photophysical study

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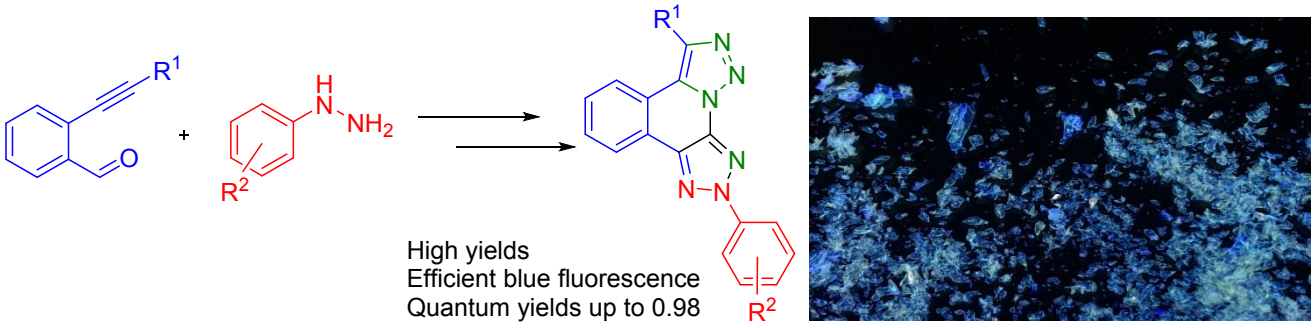


ABSTRACT

An efficient three-step synthesis of a new heterocyclic system is described wherein the - 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline ring system was elaborated using a simple synthetic strategy. The approach permits the preparation of target compounds in high yields using readily available aryl hydrazines and *o*-alkynylbenzaldehydes as starting materials. Photophysical properties of the prepared heterocycles were studied to demonstrate that the prepared compounds are attractive blue emitting fluorophores exhibiting quantum yields up to 98 % and Stokes shifts up to 67 nm. A strong effect of the steric hindrance on the absorption and emission spectra was revealed.

INTRODUCTION

Nowadays chemical space of known compounds reached significant milestone. Currently more than 100 million of chemical compounds have been described in the literature. Among this space, much more than 99% of known compounds are organic molecules. On the other hand, various heterocycles can be found most frequently as a fragment creating structural diversity. For example, combining two or more heterocycles in a molecule one can expect formation of endless structural space of molecular architectures. Both medicinal chemistry and chemistry of materials demand novel structural types of heterocycles to make them as a most attractive compounds for practical use. For example, nitrogen heterocycles are among the most significant

structural components of pharmaceuticals. More than 59% of unique small-molecule drugs contain a nitrogen heterocycle[1]. Another significant field of application of heterocycles and especially condensed heterocycles is development of various fluorescent-active dyes, effective photosensors and novel OLED materials[2]. Nowadays, there are a great number of papers devoted to the synthesis and investigation of various fluorophores, but among them there are a very small number which actually managed to reach a decent level and began to use them in industry[3]. Among other heterocycles, triazoles are one of the most attractive and popular objects of research. This heterocyclic core is one of the most common pharmacophore[4]. For example, triazoles exhibit insecticidal, herbicidal activities and they are known as fungicides, plant growth regulators in agrochemistry[5]. Recently it was demonstrated[6] that N-2-aryl-1,2,3-triazoles are unique class of effective UV/blue-light-emitting dyes (**Fig. 1**). As a result, 2-substituted 1,2,3-triazole became more and more popular for optical study[7].

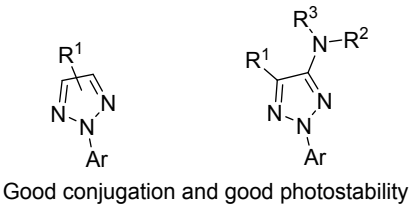


Figure 1. Generalized structures of N-2-aryl-1,2,3-triazoles

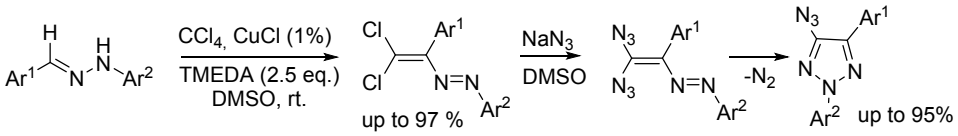
This manuscript is devoted to the synthesis of new heterocyclic system 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline. This unique heterocyclic system contains two triazole rings condensed to isoquinoline fragment. Short and highly efficient route based on intramolecular [2+3] cycloaddition to form triazole fragment was elaborated. Structural and optical properties of prepared condensed heterocycles were examined.

RESULTS AND DISCUSSION

Recently we have demonstrated efficient synthesis of 2,5-diaryl-4-azido-1,2,3-triazoles by the reaction of 1,1-dichlorodiazenes with sodium azide[8]. 1,1-Dichlorodiazadienes are known as an important class of electrophiles[9] and diazodyes[10]. Using 4,4-dichloro-1,2-diazabuta-1,3-dienes as a starting materials we have been able to synthesize very rare 1,1-bis-azides by the reaction with sodium azide (**Scheme 1**). These extremely

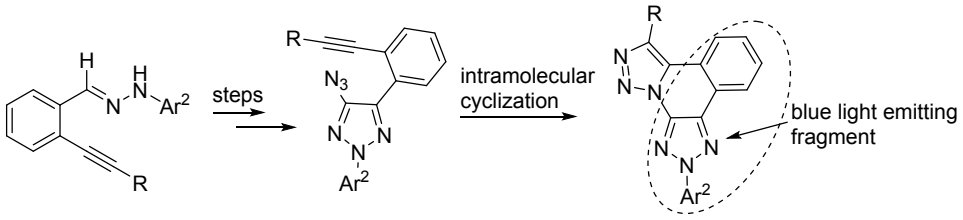
labile compounds have a tendency to cyclize into 4-azido-1,2,3-triazoles containing two aryl (heteroaryl) groups at positions 2 and 5. The reaction turned out to be very common for the high-yield synthesis of diverse 4-azidotriazoles.

Scheme 1. The formation of 4-azido-1,2,3-triazoles



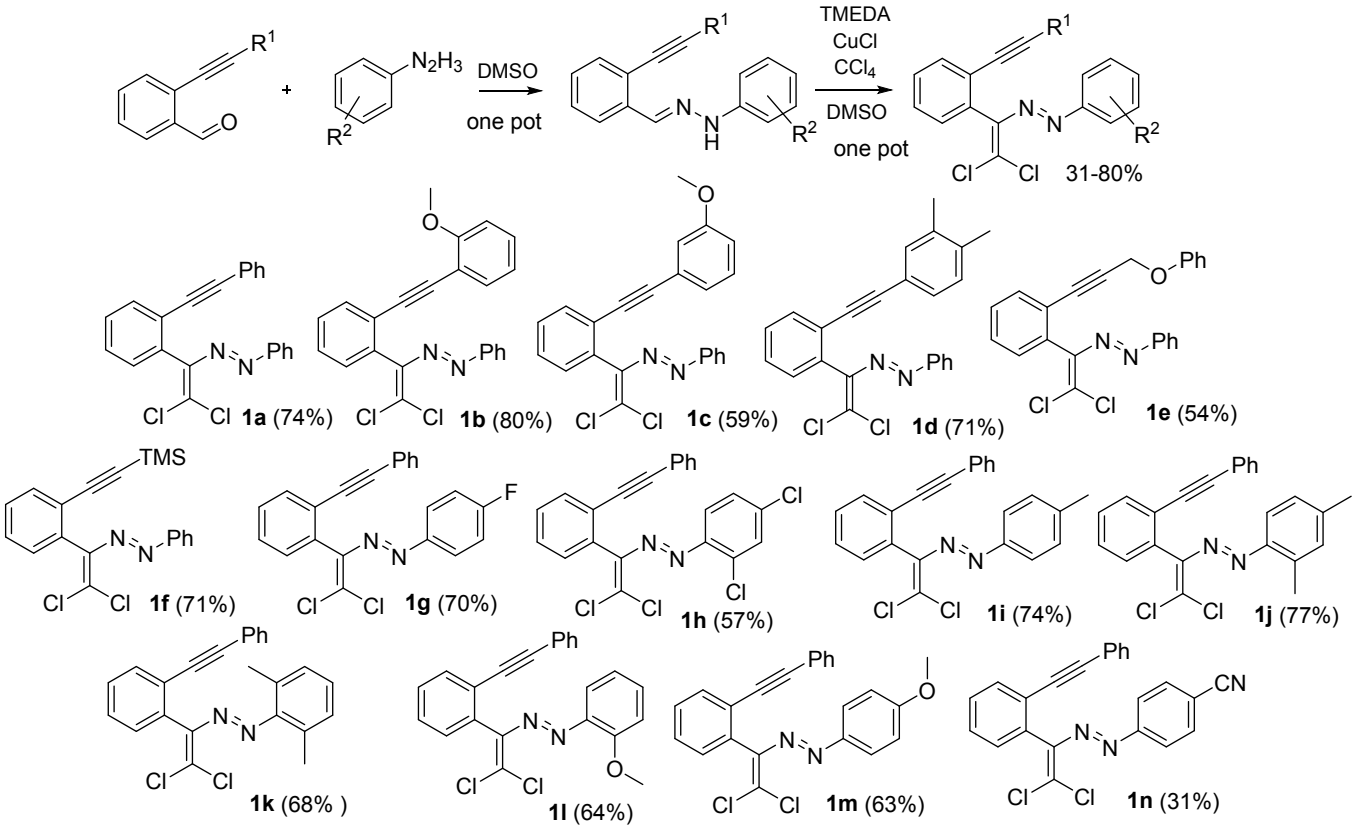
The prepared 2-arylsubstituted azidotriazoles[11] demonstrated fluorescence in 347-419 nm region, however very low quantum yields were observed (up to 0.02). Therefore, we decided to perform modification of these derivatives to improve their optical properties. We decided to study synthesis of derivatives having additional acetylenic fragment in *ortho*-position of Ar^1 group (**Scheme 2**). Subsequent intramolecular cyclization to form another 1,2,3-triazole ring can open direct access to new type of heterocycles - 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinolines. This heterocyclic system is unknown in literature; however, its flat π-conjugated system is very attractive for design of new dye compounds containing extended blue light emitting fragment.

Scheme 2. Design of new family of UV/blue-light-emitting dyes



According to scheme of assembly of azidotriazoles (**Scheme 2**), *ortho*-alkynyl substituted aldehydes can be used as a key building blocks for subsequent intramolecular cyclization. Sonogashira coupling was used to prepare a set of acetylene derived benzaldehydes starting from 2-brombenzaldehyde[12]. Next, the corresponding N-substituted hydrazones were prepared using the reaction with arylhydrazines. These starting materials were transformed *in situ* into the corresponding 1,1-dichlorodiazenes using our previously elaborated approach. Application of catalytic system CuCl (1%) - tetramethylethylenediamine CCl_4 resulted in formation of the corresponding acetylene derived diazadienes **1a-n** in up to 80% yield[8].

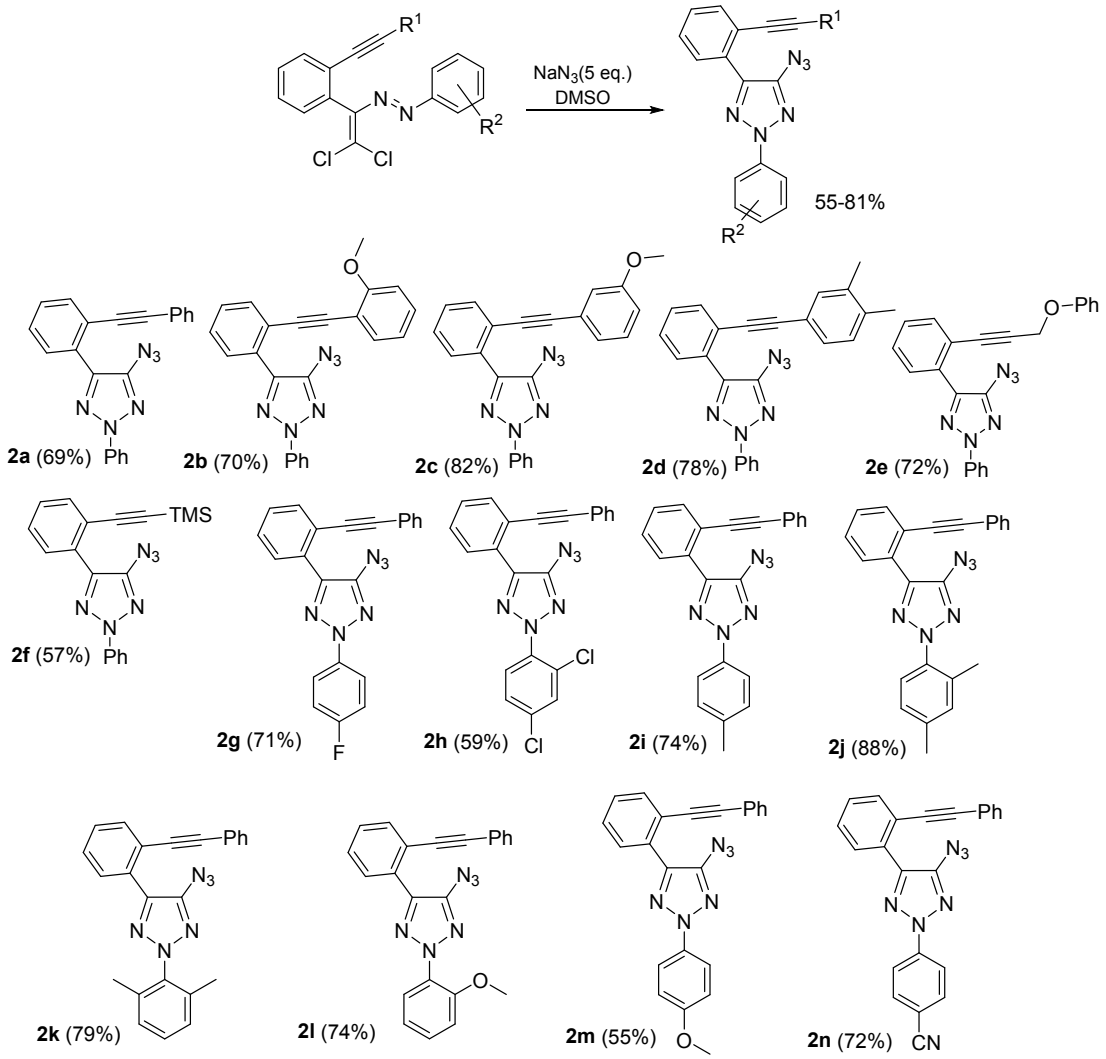
Scheme 3. The scope of 1,1-dichlorodiazenes



Only in the case of synthesis of cyano derivative **1n** decreasing yield (31%) was noticed. The proposed approach permits variation of substituents of aryl R^1 group having different acetylene fragments and R^2 substituents of hydrazine moiety (**Scheme 3**). The reaction has broad scope and we found no limitations to prepare target derivatives **1**.

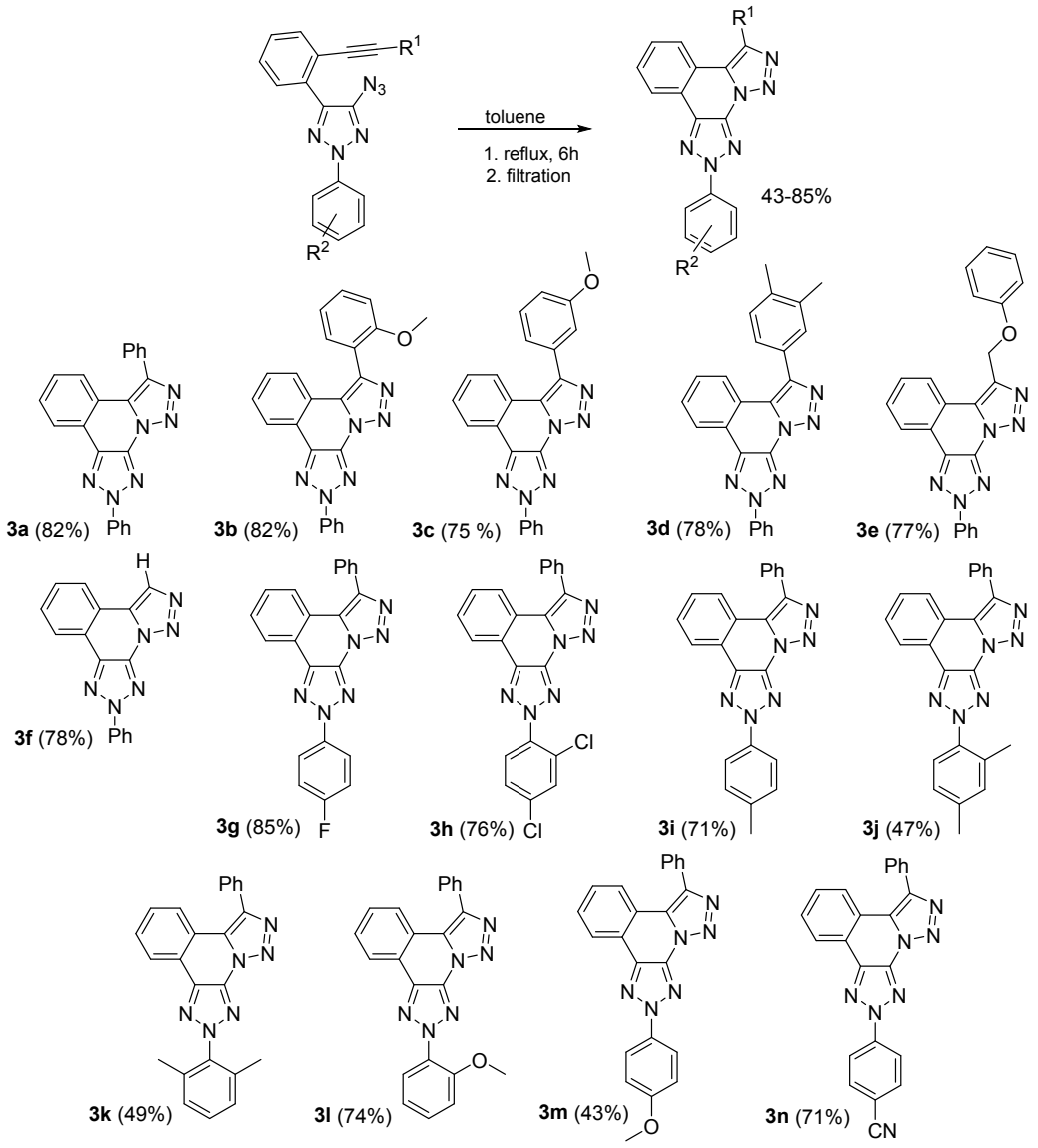
Next, the transformation of prepared diazadienes **1** into 4-azido-1,2,3-triazoles **2** was studied (**Scheme 4**). To our delight, the reaction is very general in the case of alkynyl derived diazodienes **1a-n** to give target products **2a-n** in up to 82% yield. Again, broad scope was demonstrated. Both substituents at the nitrogen and at the triple bond can be varied to open access to azidotriazoles having acetylenic fragment in the structure. It should be pointed out that due to the presence of two reactive fragments in the structure of **2a-n** these compounds have tendency to spontaneous cyclization even during storage at room temperature.

Scheme 4. The scope of 4-azido-1,2,3-triazoles



We studied intramolecular cyclization to form 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline system. It was found that reflux in toluene permits to perform such transformation very efficiently. As a result, unique condensed heterocycles **3a-n** containing two triazole rings were prepared in up to 85% yield (**Scheme 5**). Moreover, target products **3a-n** can be isolated in pure form by simple filtration of the reaction mixture after cooling to room temperature which is significant advantage of the synthetic procedure.

Scheme 5. The scope of isoquinoline derivatives



All prepared compounds **3** were characterized by NMR and other methods of analysis. In addition, the structure of compound **3c** was unambiguously established by X-ray diffraction study[13] (**Fig. 2**). The central fragment containing the four fused rings (two triazole, tetrahydropyridine and benzene) in **3c** are practically planar (rms deviation is 0.059 Å). The two aryl substituents are twisted relative to the parent triazole rings by 11.56(9) (C11-C16, at the N5 atom) and 54.10(7)° (C17-C22, at the C1 atom). Methoxy group is coplanar to the parent phenyl ring (the C23─O1─C19─C18 torsion angle is equal to 3.1(3)°). Crystal packing of **3c** is stacked along the crystallographic ***a*** axis. The molecules between the stacks are bound by the weak π···π stacking interactions (**Fig. 2**).

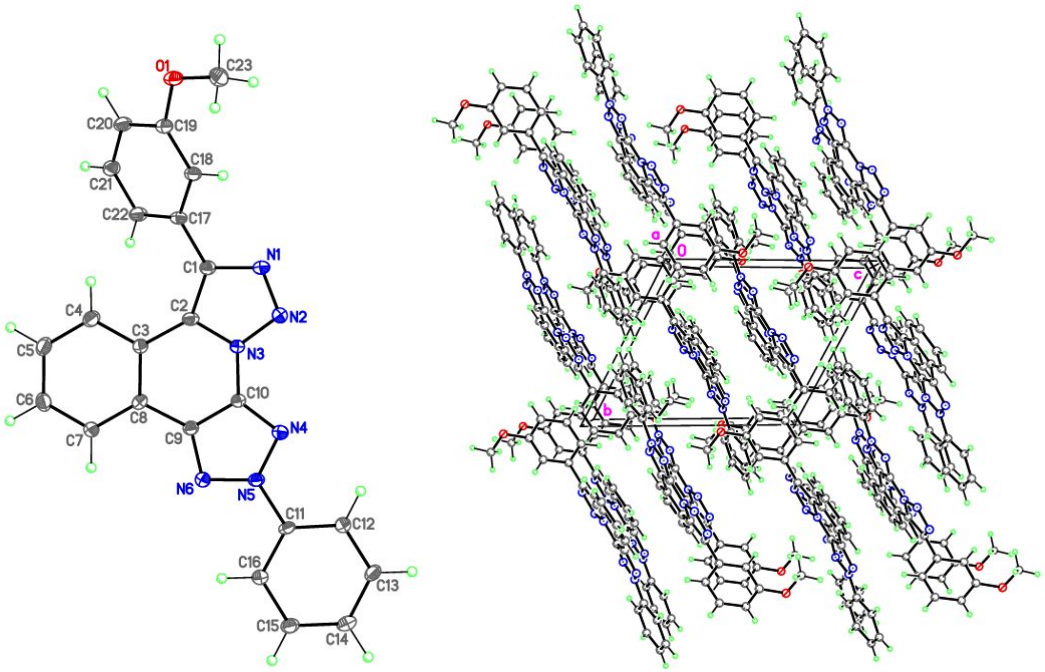
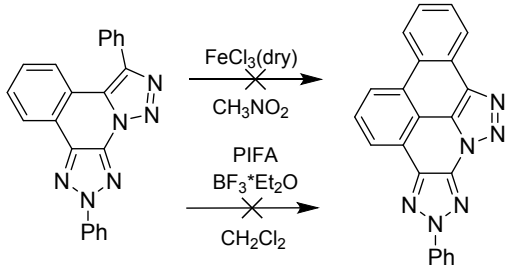


Figure 2. Molecular structure of **3c** (50% ellipsoids) and its **c**rystal structure along the crystallographic ***a*** axis

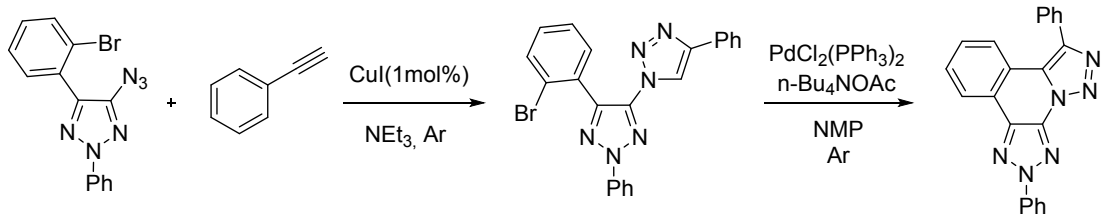
We decided also to study possibility to made additional cycle and to convert compounds **3** into totally planar conjugated system. For this aim oxidative aromatization of compound **3a** was studied (**Scheme 6**)[14]. However, our attempts of oxidative cyclization using both $FeCl_3$ and PIFA (bis(trifluoroacetoxy)iodo)benzene) were unsuccessful.

Scheme 6. Oxidative aromatization of **3a**.



We suggested also alternative approach to prepare **3a** starting from bromo-substituted azidotriazole **2a'** (**Scheme 7**). To our surprise, model Sonogashira reaction resulted in the corresponding product **2a''** having additional triazole ring. That means that copper catalyzed azide-alkyne cycloaddition[15] proceeded more quickly in this particular case. Nevertheless, the target 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline system can be synthesized using subsequent palladium catalyzed cyclization[16].

Scheme 7. Extra method of isoquinoline derivative synthesis



2a' (33%) **2a"** (82%) **3a** (78%)

The structure of compound **2a''** was established by X-ray diffraction study (**Figure 3**). The two triazole rings in **2a''** are twisted relative to each other by 45.16(13)°. Moreover, the three aryl substituents are also twisted relative to the parent triazole rings by 23.83(15) (C3-C8, at the N2 atom), 50.44(9) (C17-C22, at the C2 atom) and 24.24(12)° (C11-C16, at the C9 atom). Interestingly, the two unsubstituted phenyl substituents are turned out to be almost coplanar to each other (the corresponding interplane angle is 5.93(16)°). In the crystal of **2a''**, molecules are packed in stacks along the crystallographic ***b*** axis. The molecules within the stacks are linked by the weak C10─H10···N6 hydrogen bonds (C···N 3.374(4) Å, H···N 2.44 Å, ∠C─H···N 166°) (**Fig. 3**).

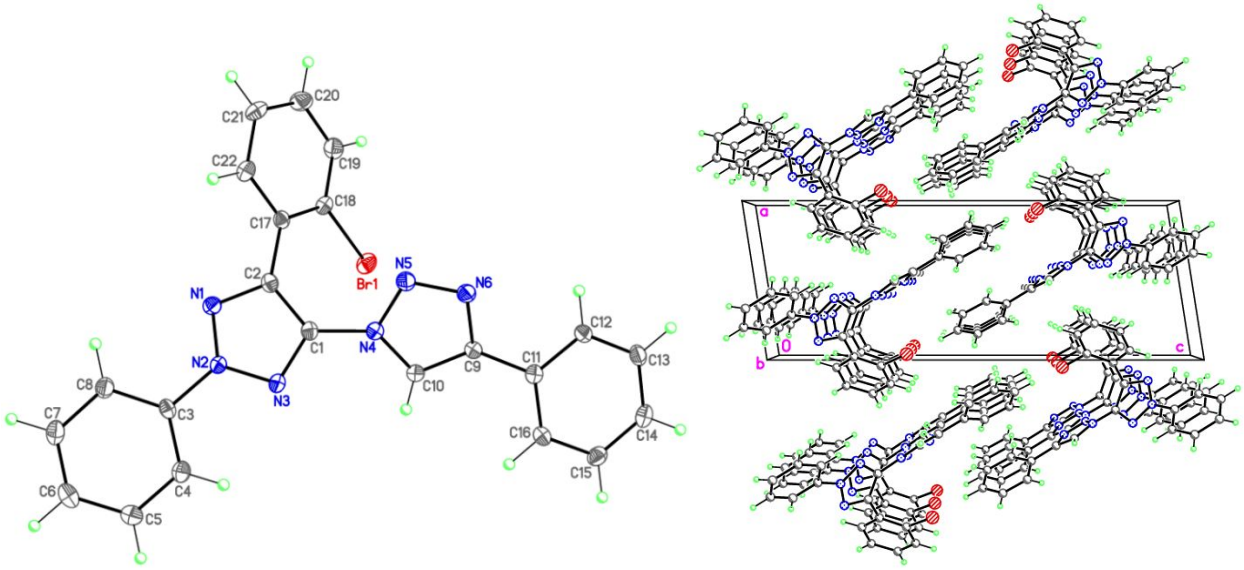


Figure 3. Molecular structure of **2a''** (50% ellipsoids) and its crystal structure along the crystallographic ***b*** axis

Having in hand new heterocyclic system of 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline, we started study of their optical properties. UV-Vis absorption and fluorescence spectra were obtained for compounds **3** using CH_2Cl_2 as a solvent (c = 10^{-6} M) at room temperature (Table 1**)**. Similar photophysical behavior was

found for all set of compounds **3** having absorption maxima in 312–349 nm range (**Fig. 4**). No significant effects of substituent R_1 on absorption spectra were observed. Compounds **3a-e** have absorption maxima in 338-340 nm region. Slight hypsochromic shift was observed for compound **3f** having unsubstituted upper triazole ring. More pronounced is the influence of the substituents in aryl group at N(2) of lower triazole.

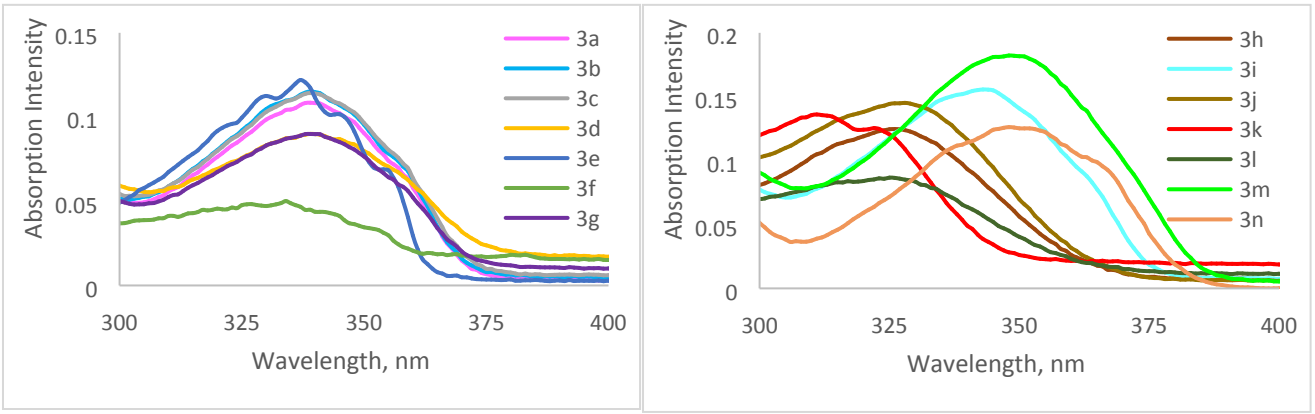


Figure 4. Absorption spectra of **3a-3n** in dichloromethane at room temperature.

Bathochromic shifts were observed for compounds **3m**,**n** containing MeO or CN group in para-position of aryl at N(2). On the contrary, hypsochromic shifts were observed for compounds **3k**, **3l**, **3j** and **3h** containing substituents in the *ortho*-position of aryl fragment at N(2) of lower triazole. The largest hypsochromic shift was observed for 2,6-disubstituted derivative **3k** having both *ortho*-positions occupied by methyl groups.

Table 1. Photophysical data for a series of isoquinoline derivatives **3a-n**

№	R^1	R^2	λ_{abs}, nm	λ_{em}, nm	lgε	Φ_F	Stokes shift, nm
3a	**Ph**	**H**	340	389	4.49	0.18	49
3b	**2-MeO-Ph**	**H**	339	396	4.55	0.36	55
3c	**3-MeO-Ph**	**H**	340	396	4.51	0.16	56
3d	**3,4-diMeC$_6$H$_4$**	**H**	340	407	4.49	0.23	67
3e	**PhOCH$_2$**	**H**	338	376	4.52	0.71	40
3f	**H**	**H**	335	362	4.09	0.90	29
3g	**Ph**	**4-F**	340	371	4.28	0.17	31
3h	**Ph**	**2,4-2Cl**	326	375	4.32	0.18	47
3i	**Ph**	**4-Me**	343	373	4.55	0.31	28
3j	**Ph**	**2,4-diMe**	328	371	4.40	0.12	43
3k	**Ph**	**2,6-diMe**	312	364	4.36	0.01	52
3l	**Ph**	**2-MeO**	326	373	4.39	0.25	49
3m	**Ph**	**4-MeO**	349	383	4.59	0.98	34
3n	**Ph**	**4-CN**	348	387	4.68	0.71	39

*Fluorescence quantum yields are measured relative to 0.1 M H_2SO_4 solution of quinine (Φ_f=0.55)[17].

Fluorescence spectra of solutions **3a-3n** were measured at an excitation wavelength corresponding to the maximum in the absorption spectra (**Fig. 5**). To our delight, all new heterocycles demonstrated high quantum yields (up to 98%). Looking at the spectra, one can immediately note almost complete quenching of fluorescence was observed for compound **3k** having two methyl-groups in the *ortho*-positions of aryl group at N(2) of triazole (**Table 1**). Partial quenching can also be detected for sterically hindered compound **3j**. These data demonstrated importance of conjugation of aryl ring at N(2) of triazole.

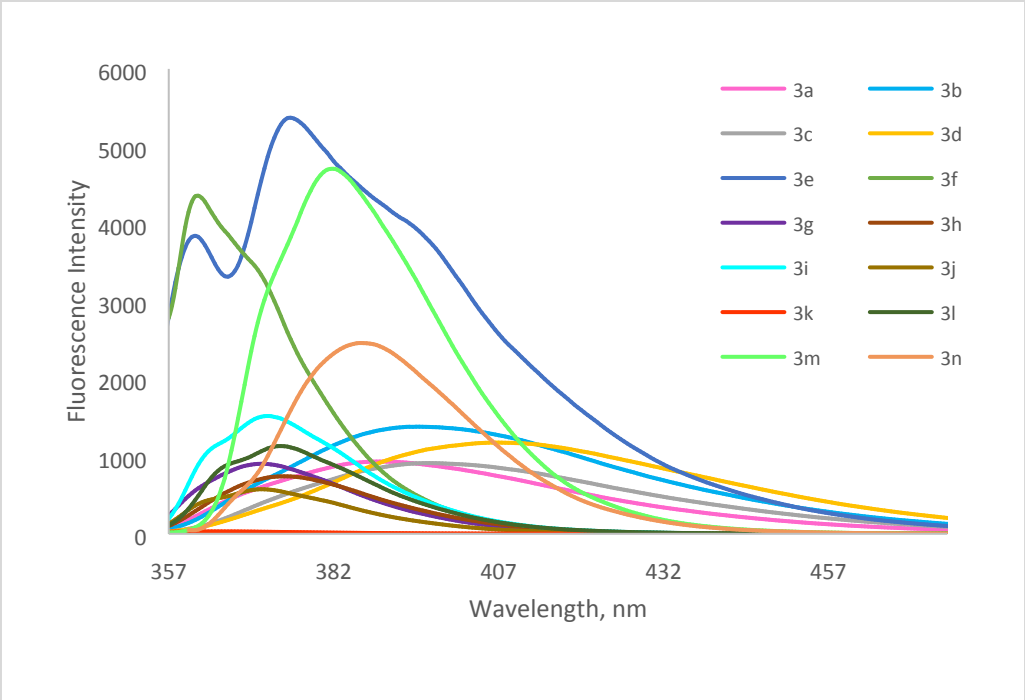


Figure 5. Emission spectra of **3a-3n** in dichloromethane at room temperature

Bulky *ortho*-substituents are not desirable in this position. On the other hand quantum yield of fluorescence was reasonably high for compound **3h** having chlorine in *ortho*-position. Most probably this difference can be explained by longer C-Cl bond. The strong electron-donor MeO-group in aryl at N(2)-triazole especially in the para-position gives powerful growth of emission (Φ_F up to 0.980, compound **3m**). The highest quantum yield was observed also for compound **3n** having a strong electron-withdrawing CN-group (Φ_F up to 0.708). Possible explanation for this behavior is the internal charge transfer from the electron-donating (electron-withdrawing) group to the part of the molecule with a deficit (surplus) of electrons, so the most effective conjugation is achieved. An interesting observation is the strong increase in fluorescence for compounds **3e**, **3f** having no aryl

substituent in upper triazole ring (Φ_F 0.708, 0.896 respectively). It makes perspective subsequent structural modification in this field.

CONCLUSIONS

Efficient approach to new type of heterocycles - differently substituted 2*H*-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinolines **3** was elaborated. The corresponding dichlorodiazenes containing phenylacetylene fragment **1** acted as building blocks for their synthesis. Subsequent reaction with sodium azide gives the corresponding 1,2,3-triazoles **2** having in the structure both azido group and acetylene fragment. The final stage was thermal cyclization of the last products which leads to unique heterocyclic compounds having in the structure two triazole rings. Target compounds **3** were prepared in high yield. These products revealed excellent photophysical properties and quantum yields of fluorescence.

EXPERIMENTAL SECTION

Materials and methods. All fine chemicals had a reagent purity and were used directly without purification unless otherwise noted. ^{1}H and ^{13}C{^{1}H} nuclear magnetic resonance (NMR) spectra were acquired at various field strengths as indicated, and were referenced to chloroform-d (7.25 and 77.00 ppm for ^{1}H and ^{13}C, respectively). ^{1}H NMR coupling constants are reported in Hertz. HRMS spectra were recorded at MicroTof Bruker Daltonics and Orbitrap Elite instrument. All IR spectra were obtained on a Nicolet iS5 (Thermo Scientific) One FT-IR spectrometer using consoles of internal reflection iS3 with ATR element from ZnSe, dip angle 45 °C. All UV data was obtained on a UV-Visible spectrophotometer Varian Cary 60 within 250-800 nm spectral range. The UV spectra were registered in cuvettes with an optical path length of 1 cm at room temperature using dichloromethane as a solvent. Emission spectra were recorded with Hitachi F2700 spectrofluorometer in 1cm quartz cells. Analytical TLC: aluminium-backed plates precoated (0.25 mm) with Merck silica sel 60 F254 and Macherey-Nagel (0.20 mm) ALUGRAM®Xtra SIL G/UV$_{254}$. Macherey-Nagel silica gel 60 (70-230 mesh) was used for flash and column chromatography. All mixed solvent eluents are

reported as v/v solutions. Solvents were purified by standard methods. DMSO was distilled over CaH_2. Tetrachloromethane was distilled over P_2O_5.

Single crystals of compounds **3c** and **2a''** were prepared using methanol as a solvent by slow evaporation method. X-ray diffraction data for **3c** and **2a''** were collected on a three-circle Bruker D8 QUEST PHOTON-III CCD diffractometer (λ(MoK$_\alpha$)-radiation, T = 100 K, graphite monochromator, φ and ω scan mode) and corrected for absorption using the SADABS program[18a]. The data were indexed and integrated using the SAINT program.[18b] For details, see ESI. The structures were solved by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups]. The absolute structure of **1** was objectively determined by the refinement of Flack parameter which has been equal to 0.007(8). All calculations were carried out using the SHELXTL[18c] program suite. Crystallographic data for **3c** and **2a''** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1973844 and CCDC 1973845, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK(Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow, Russia.

Synthesis and characterization. *General procedure for preparation of dichlorodiazabutadienes* ***1.*** Dichlorodiazabutadienes containing phenylacetylene were synthesized based on previous work[8]. The corresponding 2-(phenylethynyl)benzaldehyde (1.5 mmol) and phenyl hydrazine (1.5 mmol) were stirring in DMSO (5 ml) for 2 hours. Further tetramethylethylenediamine (TMEDA) (3.75 mmol, 2.5 eq.), CuCl (0.015 mmol, 0.01 eq.) and carbon tetrachloride (15 mmol, 10 eq.) were put into the reaction mixture during 5 min under cooling with water bath. After TLC analysis revealed complete removal of intermediate product (hydrazone), the reaction mixture was transferred to water (200 mL), and extracted with CH_2Cl_2 (3 x 20 mL). The collected organic phase was washed with water (3 x 50 mL), brine (1 x 30 mL) and dried over anhydrous

sodium sulfate. Volatiles were removed in vacuo of the rotary evaporator, the residue was purified by column chromatography on silica gel using a mixture of n-hexane and CH_2Cl_2 (3/1).

(E)-1-(2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-phenyldiazene (**1a**): Yield 558 mg (74 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1576, 1598, 2218. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.26 (m, 1H), 7.32-7.34 (m, 3H), 7.42-7.49 (m, 7H), 7.67-7.71 (m, 1H), 7.83-7.87 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 87.5, 92.7, 122.9, 123.2, 123.6, 128.0, 128.2, 128.3, 128.7, 128.9, 130.1, 131.4, 131.5, 131.7, 136.2, 136.3, 151.6, 153.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{15}Cl_2N_2$ 377.0607; Found 377.0615.

(E)-1-(2,2-Dichloro-1-(2-((2-methoxyphenyl)ethynyl)phenyl)vinyl)-2-phenyldiazene (**1b**): Yield 651 mg (80 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1575, 1595, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.83 (d, 1H, J=8.3 Hz), 6.89 (td, 1H, J=7.5, 0.9 Hz), 7.20-7.22 (m, 1H), 7.25-7.29 (m, 1H), 7.39 (dd, 1H, J=7.6, 1.7 Hz), 7.41-7.46 (m, 5H), 7.69-7.71 (m, 1H), 7.80-7.83 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.5, 89.0, 91.3, 110.5, 112.2, 120.2, 123.1, 124.0, 127.8, 128.6, 128.8, 129.7, 129.9, 131.2, 131.7, 133.3, 136.0, 136.4, 151.6, 152.9, 160.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}Cl_2N_2O$ 407.0712; Found 407.0705.

(E)-1-(2,2-Dichloro-1-(2-((3-methoxyphenyl)ethynyl)phenyl)vinyl)-2-phenyldiazene (**1c**): Yield 360 mg (59 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange-red oil. IR (ν, cm^{-1}): 1575, 1598, 2249. ^1H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 6.88-6.91 (m, 1H), 6.95-6.96 (m, 1H), 7.05 (dt, 1H, J=7.6, 1.1 Hz), 7.22-7.26 (m, 2H), 7.43-7.48 (m, 5H), 7.67-7.71 (m, 1H), 7.83-7.88 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.1, 87.3, 92.6, 115.1, 116.0, 123.1, 123.5, 123.9, 124.0, 128.0, 128.7, 128.9, 129.3, 130.1, 131.4, 131.7, 136.2, 136.4, 151.6, 152.9, 159.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}Cl_2N_2O$ 407.0712; Found 407.0717.

(E)-1-(2,2-Dichloro-1-(2-((3,4-dimethylphenyl)ethynyl)phenyl)vinyl)-2-phenyldiazene (**1d**): Yield 288 mg (71 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1577, 1598, 2209. ^1H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.25 (s, 3H), 7.06 (d, 1H, J=7.7 Hz), 7.14-7.16 (m, 2H), 7.20-7.22 (m, 1H), 7.40-7.45 (m, 5H), 7.62-7.65 (m, 1H), 7.80-7.82 (m, 2H). $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$): δ 19.5, 19.7, 86.6, 93.1, 120.2, 123.2, 123.9, 127.7, 128.7, 128.9, 128.9, 129.5, 130.0, 131.3, 131.6, 132.6, 136.0, 136.3, 136.5, 137.3, 151.7, 153.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}Cl_2N_2$ 405.0920; Found 405.0926.

(E)-1-(2,2-Dichloro-1-(2-(3-phenoxyprop-1-yn-1-yl)phenyl)vinyl)-2-phenyldiazene (**1e**): Yield 440 mg (54 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1587, 1598, 2237. ^1H NMR (400 MHz, $CDCl_3$): δ 4.79 (s, 2H), 6.91-6.95 (m, 3H), 7.14-7.16 (m, 1H), 7.21-7.26 (m, 2H), 7.36-7.41 (m, 2H), 7.43-7.46 (m, 3H), 7.54-7.57 (m, 1H), 7.71-7.75 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 56.2, 85.0, 87.0, 114.8, 121.2, 122.7, 123.2, 128.5, 128.6, 129.3, 130.0, 131.4, 132.4, 136.3, 136.4, 151.3, 152.9, 157.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}Cl_2N_2O$ 407.0712; Found 407.0708.

(E)-1-(2,2-Dichloro-1-(2-((trimethylsilyl)ethynyl)phenyl)vinyl)-2-phenyldiazene (**1f**): Yield 264 mg (71 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange-red oil. IR (ν, cm^{-1}): 1599, 1578, 2159. ^1H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 9H), 7.18-7.20 (m, 1H), 7.36-7.41 (m, 2H), 7.45-7.47 (m, 3H), 7.57-7.59 (m, 1H), 7.79-7.82 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (-0.3), 98.1, 103.1, 123.1, 123.5, 128.2, 128.6, 128.9, 129.9, 131.3, 131.7, 136.3, 136.9, 151.5, 152.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{19}Cl_2N_2Si$ 373.0689; Found 373.0683.

(E)-1-(2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(4-fluorophenyl)diazene (**1g**): Yield 415 mg (70 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1578, 1592, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 7.11-7.17 (m, 2H), 7.21-7.25 (m, 1H), 7.31-7.34 (m, 3H), 7.41-7.48 (m, 4H), 7.66-7.71 (m, 1H), 7.82-7.87 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 87.4, 92.7, 115.8, 116.0, 122.9, 123.6, 125.2, 125.3, 128.0, 128.2, 128.3, 128.8, 130.0, 131.5, 131.7, 136.1, 136.3, 149.5, 149.5, 151.5, 163.3, 165.8. ^{19}F (376.3 MHz, CDCl3): -109.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{14}Cl_2FN_2$ 395.0513; Found 395.0502.

(E)-1-(2,2-dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(2,4-dichlorophenyl)diazene (**1h**): Yield 382 mg (57 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1561, 1575, 1597, 2218. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21-7.28 (m, 2H), 7.31-7.33 (m, 3H), 7.40-7.46 (m, 5H), 7.61-7.66 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 87.4, 92.7, 118.4, 123.0, 123.5, 127.6, 128.0,

128.3, 128.3, 128.9, 130.0, 130.4, 131.5, 131.7, 135.6, 136.6, 137.5, 138.2, 147.6, 152.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{13}Cl_4N_2$ 446.9798; Found 446.9793.

(E)-1-(2,2-dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(p-tolyl)diazene (**1i**): Yield 434 mg (74 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1574, 1582, 1600, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.21-7.26 (m, 3H), 7.30-7.33 (m, 3H), 7.41-7.46 (m, 4H), 7.65-7.69 (m, 1H), 7.74 (d, 2H, J=8.3 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.5, 87.5, 92.6, 123.0, 123.2, 123.6, 128.0, 128.2, 128.2, 128.6, 129.6, 130.1, 131.5, 131.7, 135.4, 136.4, 142.1, 151.1, 151.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}Cl_2N_2$ 391.0763; Found 391.0757.

(E)-1-(2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(2,4-dimethylphenyl)diazene (**1j**): Yield 468 mg (77 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange-red oil. IR (ν, cm^{-1}): 1575, 1599, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.37 (s, 3H), 7.07-7.08 (m, 2H), 7.23-7.26 (m, 1H), 7.32-7.35 (m, 3H), 7.42-7.48 (m, 4H), 7.66-7.71 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 16.9, 21.4, 87.6, 92.4, 115.2, 123.0, 123.5, 127.1, 127.8, 128.2, 128.2, 128.5, 129.9, 131.5, 131.5, 131.7, 134.5, 136.8, 139.1, 142.0, 148.9, 152.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}Cl_2N_2$ 405.0920; Found 405.0911.

(E)-1-(2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(2,6-dimethylphenyl)diazene (**1k**): Yield 413 mg (68 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1582, 1598, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 6H), 7.05 (d, 2H, J=7.7 Hz), 7.10 -7.14 (m, 1H), 7.20-7.23 (m, 1H), 7.31-7.33 (m, 3H), 7.41-7.44 (m, 4H), 7.62-7.67 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.3, 87.4, 92.5, 123.0, 123.6, 128.0, 128.3, 128.3, 128.7, 129.1, 129.7, 131.6, 131.7, 132.0, 136.1, 136.6, 150.6, 152.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}Cl_2N_2$ 405.0920; Found 405.0912.

(E)-1-(2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(2-methoxyphenyl)diazene (**1l**): Yield 391 mg (64 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1574, 1592, 2216. ^1H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 6.97 (t, 2H, J=7.8 Hz), 7.23-7.25 (m, 1H), 7.30-7.31 (m, 3H), 7.34-7.38 (m, 1H), 7.40-7.42 (m, 4H), 7.61-7.63 (m, 1H), 7.65 (d, 1H, J=8.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 57.6, 87.6, 92.6, 114.9, 117.2, 120.9, 123.1, 123.5, 128.0, 128.2, 128.3, 128.6, 130.1,

131.5, 131.7, 132.8, 135.5, 136.4, 143.1, 152.0, 157.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}Cl_2N_2O$ 407.0712; Found 407.0707.

(E)-1-(2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)-2-(4-methoxyphenyl)diazene (**1m**): Yield 385 mg (63 %), reaction was carried out at 70^0C on a heating mantle, purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1592, 1600, 2215. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.92 (d, 2H, J=9.0 Hz), 7.18-7.20 (m, 1H), 7.28-7.29 (m, 3H), 7.37-7.42 (m, 4H), 7.62-7.64 (m, 1H), 7.78 (d, 2H, J=9.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.5, 87.6, 92.5, 114.1, 123.0, 123.6, 125.2, 127.9, 128.2, 128.2, 128.6, 130.1, 131.6, 131.7, 134.2, 134.6, 136.6, 147.4, 151.4, 162.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}Cl_2N_2O$ 407.0712; Found 407.0524.

(E)-4-((2,2-Dichloro-1-(2-(phenylethynyl)phenyl)vinyl)diazenyl)benzonitrile (**1n**): Yield 187 mg (31 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), orange oil. IR (ν, cm^{-1}): 1576, 1598, 2227. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.20 (m, 1H), 7.29-7.36 (m, 5H), 7.40-7.47 (m, 2H), 7.63-7.65 (m, 1H), 7.70-7.73 (m, 2H), 7.82-7.85 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 87.2, 92.9, 114.2, 118.4, 122.7, 123.6, 128.1, 128.3, 128.5, 129.1, 130.0, 131.5, 131.9, 133.0, 135.4, 139.7, 152.1, 154.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{14}Cl_2N_3$ 402.0559; Found 402.0547.

General procedure for preparation of 4-azido-1,2,3-triazoles ***2.*** 4-Azido-2,5-diaryl-1,2,3-triazoles bearing phenylacetylene were obtained according to the procedure described[11]. To sodium azide (5 eq.) in DMSO (10 mL) corresponding dichlorodiazene (1 mmol, 1 eq.) was added dropwise over 15 min and stirred at room temperature for 2 h. The resulting mixture was transferred to water (100 mL) and extracted with DCM (3 x 20 mL). The combined extract was washed with water (3 x 50 mL), brine (1 x 30 ml) and dried over sodium sulfate. Volatiles were removed in vacuum of the rotary evaporator, the residue was purified by column chromatography on silica gel using a mixture of n-hexane and CH_2Cl_2 (3/1).

4-Azido-2-phenyl-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2a**): Yield 250 mg (69 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellowish oil. IR (ν, cm^{-1}): 2132, 2217. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.38 (m, 4H), 7.41-7.51 (m, 6H), 7.65-7.75 (m, 2H), 8.08-8.13 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)(some signals are duplicated due to the phenomenon of atropisomerism): δ 88.3, 93.3,

118.2, 118.5, 122.6, 123.2, 127.4, 127.8, 128.3, 128.3, 128.3, 128.9, 129.3, 129.3, 129.7, 130.1, 130.2, 131.6, 133.1, 137.7, 139.4, 144.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{15}N_6$ 363.1353; Found 363.1345.

4-Azido-5-(2-((2-methoxyphenyl)ethynyl)phenyl)-2-phenyl-2H-1,2,3-triazole (**2b**): Yield 439 mg (70 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2133, 2216. ^1H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 3H), 6.84-6.92 (m, 2H), 7.29-7.32 (m, 2H), 7.43-7.49 (m, 5H), 7.63-7.66 (m, 1H), 7.73-7.75 (m, 1H), 8.12 (d, 2H, J=8.2 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)(some signals are duplicated due to the atropisomerism): δ 55.5, 89.9, 92.0, 110.4, 110.6, 112.2, 118.1, 118.4, 120.3, 120.4, 123.2, 127.2, 128.1, 128.9, 129.2, 129.2, 129.2, 129.7, 129.8, 130.2, 130.5, 132.9, 133.5, 134.3, 138.0, 139.4, 144.4, 160.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1457.

4-Azido-5-(2-((3-methoxyphenyl)ethynyl)phenyl)-2-phenyl-2H-1,2,3-triazole (**2c**): Yield 285 mg (82 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2134, 2247. ^1H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 6.88-6.91 (m, 1H), 6.97 (m, 1H), 7.08 (dt, 1H, J=7.6, 1.1 Hz), 7.23 (t, 1H, J=8.0 Hz), 7.34-7.37 (m, 1H), 7.42-7.50 (m, 4H), 7.67-7.75 (m, 2H), 8.11-8.13 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.0, 88.1, 93.2, 115.3, 115.9, 118.2, 122.4, 124.1, 124.1, 127.3, 128.3, 128.8, 129.2, 129.3, 129.6, 130.2, 133.1, 137.7, 139.4, 144.2, 159.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1453.

4-Azido-5-(2-((3,4-dimethylphenyl)ethynyl)phenyl)-2-phenyl-2H-1,2,3-triazole (**2d**):Yield 217 mg (78 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2136, 2198. ^1H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.27 (s, 3H), 7.08 (d, 1H, J=7.6 Hz), 7.21-7.23 (m, 2H), 7.37 (t, 1H, J=7.3 Hz), 7.41-7.51 (m, 4H), 7.66-7.72 (m, 2H), 8.13 (d, 2H, J=8.1 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.5, 19.7, 87.4, 93.7, 118.2, 120.4, 122.8, 127.3, 128.0, 128.8, 129.0, 129.2, 129.6, 129.6, 130.0, 132.7, 133.0, 136.6, 137.3, 137.8, 139.4, 144.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_6$ 391.1666; Found 391.1655.

4-Azido-5-(2-(3-phenoxyprop-1-yn-1-yl)phenyl)-2-phenyl-2H-1,2,3-triazole (**2e**): Yield 305 mg (72 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellowish oil. IR (ν, cm^{-1}): 2134, 2230. ^1H NMR (400 MHz, $CDCl_3$): δ 4.92 (s, 2H), 6.93-7.00 (m, 3H), 7.23-7.27 (m, 2H), 7.35-7.52 (m, 5H),

7.62-7.65 (m, 2H), 8.11 (d, 2H, J=8.2 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 56.4, 85.7, 87.8, 114.6, 118.0, 121.2, 121.6, 127.3, 128.6, 128.7, 129.2, 129.3, 129.6, 130.5, 133.3, 137.3, 139.3, 144.0, 157.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1454.

4-Azido-2-phenyl-5-(2-((trimethylsilyl)ethynyl)phenyl)-2H-1,2,3-triazole (**2f**): Yield 102 mg (57 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2132, 2159. ^1H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 9H), 7.39 (t, 1H, J=7.4 Hz), 7.43-7.46 (m, 2H), 7.49-7.53 (m, 2H), 7.47-7.60 (m, 1H), 7.64-7.67 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (-0.3), 98.9, 103.0, 118.5, 123.2, 127.8, 128.5, 129.1, 129.3, 129.9, 130.6, 133.3, 137.3, 139.4, 144.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{19}N_6Si$ 359.1435; Found 359.1436.

4-Azido-2-(4-fluorophenyl)-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2g**): Yield 283 mg (71 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellowish oil. IR (ν, cm^{-1}): 2133, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 7.13-7.20 (m, 2H), 7.30-7.36 (m, 3H), 7.42-7.49 (m, 4H), 7.65-7.74 (m, 2H), 8.04-8.09 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 88.3, 93.3, 116.0, 116.2, 119.9, 120.0, 122.5, 123.1, 128.3, 128.4, 128.9, 129.6, 130.0, 131.5, 133.1, 135.7, 137.7, 144.3, 160.4, 162.9. ^{19}F (376.3 MHz, CDCl3): -114.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{14}FN_6$ 381.1258; Found 381.1252.

4-Azido-2-(2,4-dichlorophenyl)-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2h**): Yield 217 mg (59 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellowish solid, m.p. 95^0C. IR (ν, cm^{-1}): 2128, 2214. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.37 (m, 4H), 7.43-7.47 (m, 4H), 7.59 (d, 1H, J=2.2 Hz), 7.63-7.68 (m, 2H), 7.69-7.74 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 88.0, 93.3, 122.8, 123.0, 127.6, 127.9, 128.3, 128.4, 129.1, 129.6, 129.8, 129.8, 130.9, 131.4, 133.0, 135.2, 136.2, 138.4, 144.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{13}N_6Cl_2$ 431.0573; Found 431.0560.

4-Azido-5-(2-(phenylethynyl)phenyl)-2-(p-tolyl)-2H-1,2,3-triazole (**2i**): Yield 279 mg (74 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2133, 2218. ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.28 (d, 2H, J=8.1 Hz), 7.30-7.35 (m, 4H), 7.41-7.51 (m, 4H), 7.67-7.76 (m, 2H), 7.99-8.03 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the

phenomenon of atropisomerism): δ 21.0, 88.0, 88.3, 93.2, 118.1, 118.3, 122.5, 123.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.7, 129.2, 129.7, 129.7, 129.8, 130.0, 130.2, 131.5, 132.9, 133.1, 136.8, 137.2, 137.3, 137.3, 137.8, 143.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6$ 377.1509; Found 377.1505.

4-Azido-2-(2,4-dimethylphenyl)-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2j**): Yield 343 mg (88 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2132, 2218. ^1H NMR (400 MHz, $CDCl_3$): δ 2.40-2.43 (m, 6H), 7.10 (d, 1H, J=8.0 Hz), 7.14 (s, 1H), 7.27-7.32 (m, 3H), 7.41-7.50 (m, 4H), 7.53 (t, 1H, J=8.6 Hz), 7.62-7.73 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 18.8, 19.1, 21.1, 21.1, 88.0, 88.3, 93.1, 122.7, 123.1, 123.2, 123.4, 124.7, 124.9, 127.2, 127.2, 128.2, 128.3, 128.3, 128.3, 128.8, 129.1, 129.8, 130.1, 130.4, 130.5, 131.5, 131.5, 132.1, 132.2, 132.3, 132.8, 133.0, 136.3, 137.0, 137.1, 138.7, 139.1, 143.5, 144.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_6$ 391.1666; Found 391.1658.

4-Azido-2-(2,6-dimethylphenyl)-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2k**): Yield 302 mg (79 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2133, 2220. ^1H NMR (400 MHz, $CDCl_3$): δ 2.10-2.12 (m, 6H), 7.15-7.18 (m, 2H), 7.28-7.35 (m, 4H), 7.38-7.51 (m, 4H), 7.64-7.76 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 17.4, 87.9, 88.2, 93.0, 122.8, 123.0, 123.2, 123.5, 128.2, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.8, 129.1, 129.8, 129.9, 130.0, 130.1, 130.4, 130.4, 131.4, 131.4, 132.8, 133.0, 135.9, 136.0, 137.0, 139.1, 143.5, 144.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_6$ 391.1666; Found 391.1661.

4-Azido-2-(2-methoxyphenyl)-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2l**): Yield 279 mg (74 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2132, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.03-7.10 (m, 2H), 7.28-7.34 (m, 3H), 7.40-7.49 (m, 5H), 7.58-7.61 (m, 1H), 7.63-7.73 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 56.1, 88.3, 93.1, 112.6, 112.7, 120.5, 120.5, 122.8, 123.1, 123.2, 123.4, 127.0, 127.1, 128.2, 128.2, 128.8, 129.1, 129.4, 129.9, 130.1, 130.5, 130.6, 130.8, 131.5, 131.5, 132.6, 132.7, 137.5, 143.8, 153.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1454.

4-Azido-2-(4-Methoxyphenyl)-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazole (**2m**): Yield 204 mg (55 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2131, 2217. ^1H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.96-7.02 (m, 2H), 7.28-7.35 (m, 3H), 7.41-7.50 (m, 4H), 7.64-7.76 (m, 2H), 8.00-8.06 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 55.5, 88.0, 88.4, 93.2, 93.2, 114.2, 114.3, 119.7, 119.9, 122.4, 123.0, 123.2, 128.2, 128.3, 128.3, 128.3, 128.7, 129.1, 129.6, 130.0, 130.3, 130.3, 131.5, 132.9, 133.1, 133.1, 133.2, 136.6, 137.1, 143.6, 144.2, 158.9, 159.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1450.

4-(4-Azido-5-(2-(phenylethynyl)phenyl)-2H-1,2,3-triazol-2-yl)benzonitrile (**2n**): Yield 130 mg (72 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellow oil. IR (ν, cm^{-1}): 2132, 2230. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.37 (m, 3H), 7.42-7.48 (m, 4H), 7.65-7.75 (m, 4H), 8.16-8.19 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 88.1, 93.5, 110.5, 118.3, 118.4, 122.5, 123.0, 128.3, 128.3, 128.5, 129.3, 129.3, 129.5, 131.4, 133.3, 133.4, 139.2, 141.8, 145.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{14}N_7$ 388.1305; Found 388.1297.

*General procedure for preparation of 2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinolines **3.*** Method A: The corresponding 1,2,3-triazole **2** (1 mmol) was refluxed for 6 h in 3 ml of toluene. Next, the mixture was cooled to room temperature and left to stand overnight. The precipitate was filtered and dried. Method B[16]: To a solution of compound **2a''** (0.26 mmol) in NMP (5 mL) at room temperature under argon $PdCl_2(PPh_3)_2$ (0.01 mmol) and n-Bu_4NOAc (0.73 mmol) were successively added. The resulting mixture was stirred at 100^0C on a heating mantle for 10 h, then was quenched with a saturated aqueous solution of NH_4Cl (20 ml) and extracted with ethyl acetate (3 x 25 mL). The organic extracts were washed with an aqueous solution of NaCl (3 x 40 ml), dried over Na_2SO_4 and concentrated under vacuo. Purification by column chromatography was held with n-hexane/EtOAc (3/2).

2,7-Diphenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3a**): Yield 298 mg (82 %, by A), 73 mg (78 %, by B), purified by column chromatography on silica gel (n-hexane/EtOAc= 3/2), white solid, m.p. 250^0C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.52 (m,

2H), 7.57-7.63 (m, 5H), 7.67-7.71 (m, 1H), 7.76-7.80 (m, 2H), 8.17 (d, 1H, J=8.2 Hz), 8.38-8.40 (m, 2H), 8.48 (dd, 1H, J=7.9, 0.6 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 119.5, 122.5, 123.2, 123.7, 124.7, 128.7, 128.8, 128.9, 129.2, 129.5, 129.8, 129.8, 131.4, 134.8, 139.6, 143.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{15}N_6$ 363.1353; Found 363.1355.

For the remaining compounds, the synthesis was carried out according to method A.

7-(2-Methoxyphenyl)-2-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3b**): Yield 360 mg (82 %), yellow solid, m.p. 249^0C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 3H), 7.12 (d, 1H, J=8.3 Hz), 7.19 (td, 1H, J=7.5, 0.7 Hz), 7.44-7.49 (m, 2H), 7.54-7.60 (m, 3H), 7.65-7.68 (m, 2H), 7.76 (d, 1H, J=8.1 Hz), 8.37-8.39 (m, 2H), 8.46 (d, 1H, J=7.5 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 55.4, 111.1, 119.5, 120.3, 121.1, 122.4, 123.2, 123.6, 125.4, 128.6, 129.0, 129.5, 129.5, 130.0, 131.0, 132.7, 134.9, 139.5, 139.7, 139.8, 157.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1454.

7-(3-Methoxyphenyl)-2-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3c**): Yield 214 mg (75 %), yellow solid, m.p. 205^0C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 7.08-7.11 (m, 1H), 7.31-7.35 (m, 2H), 7.42-7.51 (m, 3H), 7.55 (t, 2H, J=7.8 Hz), 7.62 (t, 1H, J=7.6 Hz), 8.15 (d, 1H, J=8.2 Hz), 8.32 (d, 2H, J=8.4 Hz), 8.37 (d, 1H, J=8.0 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 55.4, 114.9, 115.3, 119.4, 122.1, 122.3, 123.0, 123.5, 124.7, 128.6, 128.7, 129.1, 129.5, 129.8, 129.9, 132.5, 134.6, 139.5, 143.0, 159.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1457.

7-(3,4-Dimethylphenyl)-2-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3d**): Yield 169 mg (78 %), white solid, m.p. 256^0C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.41 (s, 3H), 7.33 (d, 1H, J=7.7 Hz), 7.43-7.49 (m, 3H), 7.54-7.58 (m, 3H), 7.61-7.66 (m, 1H), 8.19 (d, 1H, J=8.2 Hz), 8.34 (d, 2H, J=8.4 Hz), 8.40 (d, 1H, J=7.9 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 19.8, 19.8, 119.4, 122.3, 123.3, 123.5, 124.7, 127.0, 128.6, 128.6, 128.7, 129.1, 129.5, 129.6, 130.0, 130.9, 134.7, 137.3, 137.8, 139.6, 139.6, 143.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_6$ 391.1666; Found 391.1657.

7-(Phenoxymethyl)-2-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3e**): Yield 234 mg (77 %), white solid, m.p. 246^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (s, 2H), 7.02 (t, 1H, J=7.3 Hz), 7.16 (d, 2H, J=8.3 Hz), 7.34 (t, 2H, J=7.9 Hz), 7.48 (t, 1H, J=7.5 Hz), 7.59 (t, 2H, J=7.8 Hz), 7.75 (q, 2H, J=7.6 Hz), 8.37 (d, 2H, J=8.2 Hz), 8.46 (d, 1H, J=7.8 Hz), 8.51 (d, 1H, J=7.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 62.3, 115.1, 119.5, 121.6, 122.7, 122.8, 123.6, 126.5, 128.8, 129.6, 129.6, 129.9, 130.1, 131.9, 134.8, 138.3, 139.6, 157.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1455.

To TMS-containing compound (0,31 mmol) in THF (2 ml) TBAF (1 eq.) was added. After completion of the reaction (about 2 h) the reaction mixture was concentrated under vacuo. The residue was purified by flash-chromatography using mixture of n-hexane and EtOAc (6/1) as eluent.

2-Phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3f**): Yield 64 mg (78 %), purified by column chromatography on silica gel (n-hexane/EtOAc= 6/1),white solid, m.p. 83^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (tt, 1H, J=7.4, 1.3 Hz), 7.68-7.73 (m, 2H), 7.83-7.88 (m, 2H), 8.27-8.30 (m, 2H), 8.43-8.46 (m, 1H), 8.49-8.53 (m, 1H), 8.97 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.5, 122.3, 122.5, 123.7, 125.2, 128.1, 128.1, 128.7, 129.5, 129.6, 129.6, 130.1, 134.7, 139.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{11}N_6$ 287.1040; Found 287.1041.

For the remaining compounds, the synthesis was carried out according to method A (continuation).

2-(4-Fluorophenyl)-7-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3g**): Yield 241 mg (85 %), yellow solid, m.p. 255^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.30 (m, 2H), 7.48-7.52 (m, 1H), 7.55-7.63 (m, 3H), 7.67-7.71 (m, 1H), 7.77-7.79 (m, 2H), 8.17 (d, 1H, J=8.1 Hz), 8.35-8.38 (m, 2H), 8.46 (d, 1H, J=8.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (some signals are duplicated due to the phenomenon of atropisomerism): δ 116.4, 116.6, 121.3, 121.4, 122.4, 123.3, 123.7, 124.7, 128.9, 129.0, 129.3, 129.3, 129.8, 129.9, 131.3, 134.9, 135.9, 135.9, 139.7, 143.3. ^{19}F (376.3 MHz, CDCl3): -113.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{14}FN_6$ 381.1258; Found 381.1250.

2-(2,4-Dichlorophenyl)-7-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3h**): Yield 165 mg (76 %), white solid, m.p. 273^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.49-7.55 (m, 2H), 7.57-7.63 (m, 3H), 7.68-7.72 (m, 2H), 7.76-7.79 (m, 2H), 7.83 (d, 1H, J=8.6 Hz), 8.19 (d, 1H, J=8.3 Hz), 8.47 (d, 1H, J=7.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 122.3, 123.5, 123.9, 124.8, 128.0, 128.2, 128.7, 129.0, 129.0, 129.3, 129.6, 129.8, 130.0, 130.4, 131.1, 131.3, 135.4, 136.4, 139.9, 143.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{13}N_6Cl_2$ 431.0573; Found 431.0560.

7-Phenyl-2-(p-tolyl)-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3i**): Yield 198 mg (71 %), yellowish solid, m.p. 257^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.38 (d, 2H, J=8.3 Hz), 7.46-7.50 (m, 1H), 7.56-7.62 (m, 3H), 7.66-7.70 (m, 1H), 7.77-7.80 (m, 2H), 8.16 (d, 1H, J=8.1 Hz), 8.25 (d, 2H, J=8.4 Hz), 8.46 (d, 1H, J=7.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.2, 119.4, 122.6, 123.2, 123.6, 124.7, 128.8, 128.9, 129.1, 129.2, 129.8, 129.9, 130.1, 131.4, 134.5, 137.5, 138.9, 139.5, 143.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6$ 377.1509; Found 377.1500.

2-(2,4-Dimethylphenyl)-7-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3j**): Yield 161 mg (47 %), yellowish solid, m.p. 263^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 2.54 (s, 3H), 7.20-7.24 (m, 2H), 7.46-7.50 (m, 1H), 7.54-7.62 (m, 3H), 7.65-7.69 (m, 1H), 7.71 (d, 1H, J=8.1 Hz), 7.79 (dd, 2H, J=7.8, 1.4 Hz), 8.17 (d, 1H, J=8.2 Hz), 8.44 (d, 1H, J=7.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.1, 21.2, 122.7, 123.1, 123.6, 124.6, 125.4, 127.4, 128.8, 128.9, 129.0, 129.2, 129.8, 129.8, 131.5, 132.5, 134.3, 137.1, 139.3, 139.7, 143.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_6$ 391.1666; Found 391.1665.

2-(2,6-Dimethylphenyl)-7-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3k**): Yield 145 mg (49 %), white solid, m.p. 241^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 6H), 7.26 (d, 1H, J=7.5 Hz), 7.40 (t, 1H, J=7.6 Hz), 7.49-7.53 (m, 1H), 7.54-7.63 (m, 3H), 7.67-7.71 (m, 1H), 7.78-7.81 (m, 2H), 8.22 (d, 1H, J=7.9 Hz), 8.46 (dd, 1H, J=7.9, 0.7 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 17.5, 122.7, 123.2, 123.7, 124.6, 128.4, 128.8, 128.9, 129.1, 129.1, 129.8, 130.4, 131.5, 134.3, 134.5, 135.8, 139.3, 139.3, 143.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_6$ 391.1666; Found 391.1677.

2-(2-Methoxyphenyl)-7-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3l**): Yield 206 mg (74 %), yellowish solid, m.p. 241^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz,

$CDCl_3$): δ 3.92 (s, 3H), 7.13-7.18 (m, 2H), 7.45-7.49 (m, 1H), 7.52-7.61 (m, 4H), 7.63-7.67 (m, 1H), 7.73 (dd, 1H, J=7.8, 1.7 Hz), 7.76-7.79 (m, 2H), 8.16 (d, 1H, J=8.1 Hz), 8.43 (d, 1H, J=7.4 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 56.2, 112.8, 120.6, 122.7, 123.1, 123.7, 124.5, 127.5, 128.7, 128.9, 129.0, 129.1, 129.4, 129.7, 129.8, 131.4, 131.5, 134.5, 139.5, 143.1, 153.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1464.

2-(4-Methoxyphenyl)-7-phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinoline (**3m**): Yield 88 mg (43 %), white solid, m.p. 268^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.07-7.11 (m, 2H), 7.47-7.52 (m, 1H), 7.54-7.63 (m, 3H), 7.67-7.71 (m, 1H), 7.77-7.80 (m, 2H), 8.18 (d, 1H, J=8.2 Hz), 8.29-8.33 (m, 2H), 8.48 (dd, 1H, J=7.9, 0.6 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.7, 114.6, 121.0, 122.7, 123.1, 123.6, 124.7, 128.8, 128.9, 129.0, 129.8, 129.9, 131.5, 133.3, 134.4, 139.5, 143.2, 160.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{17}N_6O$ 393.1458; Found 393.1454.

4-(7-Phenyl-2H-bis([1,2,3]triazolo)[5,1-a:4',5'-c]isoquinolin-2-yl)benzonitrile (**3n**): Yield 117 mg (71 %), white solid, m.p. 283^{0}C. IR (ν, cm^{-1}): no signals of triple bond and azido group. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53-7.64 (m, 4H), 7.73 (t, 1H, J=7.6 Hz), 7.77-7.80 (m, 2H), 7.92 (d, 2H, J=8.6 Hz), 8.19 (d, 1H, J=8.2 Hz), 8.50 (d, 1H, J=7.8 Hz), 8.54 (d, 2H, J=8.6 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 112.1, 118.0, 119.8, 122.0, 123.7, 124.1, 124.9, 129.0, 129.4, 129.8, 130.0, 130.1, 131.1, 133.8, 136.1, 140.4, 142.2, 143.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{14}N_7$ 388.1305; Found 388.1303.

Procedure for preparation of **2a'.** 2-brombenzaldehyde (5 mmol) and phenylhydrazine (5 mmol) were stirring in DMSO (15 ml) for 2 hours.. Next tetramethylethylenediamine (TMEDA) (12.5 mmol, 2.5 eq.), CuCl (0.05 mmol, 0.01 eq.) and carbon tetrachloride (50 mmol, 10 eq.) were put into the reaction mixture during 5 min under cooling with water bath. After TLC analysis showed complete removal of intermediate product (hydrazone), sodium azide (25 mmol, 5 eq.) was slowly added over 20-30 min and stirred at room temperature. Upon completion of the reaction, reaction mixture was transferred to water (350 mL), extracted with CH_2Cl_2 (50x3 mL). The collected extract was washed with water (150x3 mL), brine (100x2 ml) and dried over sodium

sulfate. Volatiles were removed in vacuo of the rotary evaporator, the residue was purified by column chromatography on silica gel using a mixture of n-hexane and CH_2Cl_2 (3/1).

4-Azido-5-(2-bromophenyl)-2-phenyl-2H-1,2,3-triazole (**2a'**): Yield 561 mg (33 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 3/1), yellowish solid, m.p. 138^{0}C. IR (ν, cm^{-1}): 2131. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.44 (m, 3H), 7.48-7.53 (m, 3H), 7.74 (dd, 1H, J=8.0, 1.1 Hz), 8.09-8.11 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 118.2, 123.3, 127.3, 127.5, 129.3, 129.5, 130.7, 131.8, 133.4, 137.9, 139.3, 144.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{10}BrN_6$ 341.0145; Found 341.0153.

*Synthesis of **2a''**.* Phenylacetylene (0.92 mmol) and CuI (1 mol %) were added to the just synthesized 4-azido-5-(2-bromophenyl)-2-phenyl-2H-1,2,3-triazole (0.54 mmol) in 3ml of NEt_3. The reaction mixture was heated at 80^{0}C on a heating mantle for 8 h under Ar. After completion of the reaction the solvent was removed in vacuo and the residue subjected to column chromatography in n-hexane/CH_2Cl_2 (1/2) to give the desired product.

5'-(2-Bromophenyl)-2',4-diphenyl-2'H-1,4'-bi(1,2,3-triazole) (**2a''**): Yield 195 mg (82 %), purified by column chromatography on silica gel (n-hexane/CH_2Cl_2= 1/2), yellowish solid, m.p. 150^{0}C. IR (ν, cm^{-1}): 664 (C-Br). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.40 (M, 2H), 7.43-7.49 (m, 4H), 7.54-7.58 (m, 2H), 7.64-7.69 (m, 2H), 7.91-7.93 (m, 2H), 8.18-8.20 (m, 2H), 8.36 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 118.8, 118.9, 123.9, 125.9, 127.5, 128.4, 128.6, 128.9, 129.5, 129.7, 129.8, 131.1, 132.2, 133.0, 139.1, 139.9, 141.7, 147.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{16}BrN_6$ 443.0614; Found 443.0607.

Compounds **1e'** and **1d'** were prepared according to the methodology presented in this article[12].

2-((3,4-Dimethylphenyl)ethynyl)benzaldehyde (**1e'**): Yield 421 mg (36 %), purified by column chromatography on silica gel (n-hexane/methyl t-butyl ether= 3/1), yellow solid, m.p. 84^{0}C. IR (ν, cm^{-1}): 1693, 2205. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29(s, 3H), 2.31 (s, 3H), 7.16 (d, 1H, J=7.7 Hz), 7.31-7.36 (m, 2H), 7.43-7.46 (m, 1H), 7.57-7.65 (m, 2H), 7.95 (d, 1H, J=7.7 Hz), 10.7 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 19.6, 19.9, 84.0, 96.9, 119.5, 127.1, 127.3, 128.3, 129.1, 129.8, 132.7, 133.1, 133.8, 135.7, 136.9, 138.2, 191.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{15}O$ 235.1117; Found 235.1126.

2-(3-Phenoxyprop-1-yn-1-yl)benzaldehyde (**1d'**): Yield 566 mg (48 %), purified by column chromatography on silica gel (n-hexane/methyl t-butyl ether= 3/1), yellowish oil. IR (ν, cm^{-1}): 1699, 2232. ^1H NMR (400 MHz, $CDCl_3$): δ 4.99 (s, 2H), 7.02-7.07 (m, 3H), 7.33-7.38 (m, 2H), 7.42-7.46 (m, 1H), 7.51-7.56 (m, 2H), 7.90-7.92 (m, 1H), 10.43 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 56.2, 82.7, 91.0, 114.8, 121.6, 125.5, 127.1, 128.9, 129.5, 133.4, 133.6, 136.0, 157.4, 191.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}O_2$ 237.0910; Found 237.0913.

ASSOCIATED CONTENT

Supporting Information

The supporting Information is available free of charge

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Notes

The authors declare no competing financial interest.

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